SUPPORTING INFORMATION FOR

Oxidative Addition of Aryl Electrophiles to a Prototypical Nickel(0) Complex: Mechanism and Structure/Activity Relationships

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1. General Experimental Details

- Manipulations of air-sensitive nickel complexes were carried out under argon using Schlenk techniques or a glovebox (≤ 0.1 ppm O_2 and water).
- Anhydrous toluene, THF, and hexane were obtained from an Inert Atmospheres PureSolv apparatus; regular Karl-Fisher analyses ensured that water content was always below 10 ppm. Anhydrous benzene-d_6 and toluene-d_8 were obtained by drying over 4 Å molecular sieves that had been activated by heating to > 200 °C under high vacuum for at least two hours.
- [Ni(COD)$_2$] was obtained from Alfa Aesar, and stored in the glovebox freezer at -40 °C. 1,1'-Bis(diphenylphosphino)ferrocene was obtained from Fluorochem and stored in the glovebox. $NiCl_2.6H_2O$ was purchased from Strem. $NiBr_2.nH_2O$ and $NiI_2.nH_2O$ were supplied by colleagues. *Ortho*-tolylmagnesium bromide was purchased from Acros, stored in the fridge, and titrated regularly using the method of Knochel.[1] Aryl halides were obtained from commercial sources, as were all starting materials for the synthesis of reagents. Potassium phosphate (anhydrous) was purchased from Alfa Aesar and used as supplied.
- [Ni(COD)(dppf)][2] and [NiCl(*o*-tol)(dppf)][3] were prepared according to literature procedures.
- NMR spectroscopy was performed using Bruker spectrometers: an AV3-400 equipped with a liquid nitrogen cryoprobe; an AV-400 equipped with a BBFO-*z*-ATMA probe and temperature control; an AV3-500HD equipped with a smartprobe and temperature control; or an AVII-600 equipped with a BBO-*z*-ATMA probe and temperature control. All kinetic experiments were carried out on the latter instrument. ^{1}H chemical shifts are reported relative to residual solvent signals.[4] ^{13}C chemical shifts are reported relative to the deuterated solvent signal.[4] ^{19}F and ^{31}P chemical shifts are reported relative to external standards.
- X-band EPR spectra were collected on a Bruker ELEXSYS E500 spectrometer and simulations were performed using Bruker's Xsophe software package.[5]
- GC-FID experiments were performed using an Agilent 7890A gas chromatograph fitted with an Agilent HP5 column (30 m x 0.25 mm I.D. x 0.25 μm). GC-MS experiments were conducted using an Agilent 7890A gas chromatograph fitted with a RESTEK RXi-5Sil column (30 m x 0.32 mm I.D. x 0.25 μm) and an Agilent 5975C MSD running in CI (CH_4) or EI mode.

2. Synthetic Experiments

2.1 Nickel Complexes

[$NiBr_2$(dppf)]. A Schlenk flask was charged with $NiBr_2.nH_2O$ (80 mg) and acetonitrile. The solution was sparged with a stream of argon for 10 minutes, then dppf (184.52 mg, 0.33 mmol) was added. The reaction was heated to reflux for 40 min, during which time the dppf dissolved. The reaction was allowed to cool to room temperature, and was then chilled to 0 °C for 10 min. The resulting solid was collected by filtration with a cannula, washed with acetonitrile (3 x 10 mL), and dried under vacuum to yield a dark green solid. Yield: 192.5 mg (0.25 mmol, 76%). **^{1}H NMR** ($CDCl_3$, 400 MHz): 20.32 (s, 8H), 9.82 (s, 4H), 3.32 (br. s, 8H), -3.22 (s, 4H), -4.92 (br. s, 4H). **Elemental analysis** Calcd (%) for $C_{34}H_{28}FeBr_2NiP_2$: C, 52.84; H, 3.65. Found: C, 52.28; H, 3.62.

[NiI_2(dppf)]. A 25 mL two-neck round bottom flask was charged with $NiI_2.nH_2O$ (473.3 mg) and ethanol. The solution was sparged with a stream of argon for 10 minutes, then dppf (559.9 mg, 1.01 mmol) was added. The reaction was heated to reflux for 30 min, during which time the dppf dissolved. The solution was chilled in the freezer. A dark red solid was recovered by filtration, washed with ethanol (2 x 10 mL) and diethyl ether (3 x 10 mL), and dried under high vacuum. Yield: 459.9 mg (0.53 mmol, 53%). **^{1}H NMR** ($CDCl_3$, 400 MHz): 19.18 (app. d, *J* = 6.8 Hz, 8H), 8.22 (s, 4H), 4.07 (br. s, 8H), -2.79 (br. s, 4H), -2.96 (s, 4H). **Elemental analysis** Calcd (%) for $C_{34}H_{28}FeI_2NiP_2$: C, 47.11; H, 3.26. Found: C, 46.69; H, 2.91.

[Ni(μ-Br)(dppf)]$_2$. Method A: A Schlenk flask was charged with [$NiBr_2$(dppf)] (42.5 mg, 0.055 mmol), [Ni(COD)(dppf)] (40 mg, 0.055 mmol) and toluene (3 mL). The mixture was heated at 50 °C for 5 h and then cooled to room temperature. The resulting solid was collected by filtration with a cannula, washed with hexane (3 x 3 mL), and dried under vacuum yielded an orange solid. Yield: 53.0 mg (0.038 mmol, 70%). **Method B:** A Schlenk flask was charged with [Ni(COD)(dppf)] (25 mg, 0.035 mmol), *p*-$F_3CC_6H_4CBr$ (98 μL, 0.70 mmol) and toluene (3 mL). The resulting mixture was heated at 50 °C for 4 h and then cooled to room temperature. The solution was dried under vacuum and the resulting orange solid was washed with hexane (3 x 3 mL). Yield: 29 mg (0.021 mmol, 60 %). **^{1}H NMR** (C_6D_6, 400 MHz): δ_H 12.66 (br, 20H), 4.49 (br, 16H), 1.33 (br, 20H).

[Ni(μ-I)(dppf)]$_2$. Method A: A Schlenk flask was charged with [NiI$_2$(dppf)] (48.1 mg, 0.055 mmol), [Ni(COD)(dppf)] (40 mg, 0.055 mmol) and toluene (3 mL). The mixture was heated at 50 °C for 4 h and then cooled to room temperature. The resulting solid was collected by filtration with a cannula, washed with hexane (3 x 3 mL), and dried under vacuum to yield a green solid. Yield: 60.1 mg (0.041 mmol, 75%). **Method B:** A Schlenk flask was charged with [Ni(COD)(dppf)] (25 mg, 0.035 mmol), *p*-$F_3CC_6H_4I$ (102 μL, 0.70 mmol) and toluene (3 mL). The resulting mixture was heated at 50 °C for 1 h and then cooled to room temperature. The solution was dried under vacuum and the resulting green solid was washed with hexane (3 x 3 mL). Yield: 35 mg (0.024 mmol, 69 %). **^{1}H NMR** (C_6D_6, 400 MHz): δ_H 12.81 (br, 20H), 4.49 (br, 16H), 1.35 (br, 20H).

Attempted Synthesis of [Ni(2-MeC$_6$H$_4$)$_2$(dppf)]. A sample of [Ni(2-MeC$_6$H$_4$)Cl(dppf)] was dissolved in toluene-d_8 in a septum-fitted NMR tube, and a few drops of 1,5-cyclooctadiene were added. The tube was removed from the glovebox and cooled to -78 °C using a dry ice/acetone bath. A solution of *ortho*-tolylmagnesium chloride in THF was added *via* an oven-dried syringe. The sample was removed from the bath and shaken briefly, before being inserted into an NMR spectrometer pre-cooled to -50 °C. ^{31}P{^{1}H} NMR spectra were acquired over the course of *ca.* 1 h, showing smooth conversion into [Ni(COD)(dppf)]. If no COD is added, the complex simply decomposes. This procedure was repeated with a much larger volume of *ortho*-tolylmagnesium chloride, but no new species could be observed.

Attempted Synthesis of [Ni(2-MeC$_6$H$_4$)(dppf)]. A sample of [NiCl(dppf)] was dissolved in benzene-d_6 in a septum-fitted NMR tube, and a few drops of 1,5-cyclooctadiene were added. The tube was removed from the glovebox. A solution of *ortho*-tolylmagnesium chloride in THF was added dropwise *via* an oven-dried syringe. The sample was shaken briefly, and ^{31}P{^{1}H} NMR spectra were acquired over, showing conversion to [Ni(COD)(dppf)]. If no COD is added, the complex simply decomposes.

2.2 Organic Compounds

Para*-trifluoromethylphenyl tosylate**. Prepared according to a literature procedure.[6] A round-bottom flask was charged with *para*-trifluoromethylphenol (7.03 g, 43.4 mmol, 1.1 equiv.), tosyl chloride (7.51 g, 39.4 mmol), DCM (150 mL), and triethylamine (5.5 mL, 3.99 g, 39.5 mmol, 1 equiv.). The reaction was stirred at 45 °C for 6 h and cooled to room temperature. The reaction mixture was then washed with NaOH (200 mL of a 1 mol L^{-1} aqueous solution), HCl (200 mL of a 1 mol L^{-1} aqueous solution), and water (200 mL), before being dried on magnesium sulfate and evaporated to yield a pale oil. The product was recrystallised from methanol to yield a white solid (7.02 g, 22.2 mmol, 56%). **^{1}H NMR** ($CDCl_3$, 500 MHz): 7.72 (d, *J* = 8.3 Hz, 2H, Ar CH), 7.57 (d, *J* = 8.1 Hz, 2H, Ar CH), 7.33 (d, *J* = 8.1 Hz, 2H, Ar CH), 7.12 (d, *J* = 8.3 Hz, 2H, Ar CH), 2.45 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 126 MHz): 152.1 (Ar C), 146.0 (Ar C), 132.2 (Ar C), 130.1 (Ar CH), 129.4 (q, *J* = 33.3 Hz, *C*CF_3), 128.6 (Ar CH), 127.1 (q, *J* = 3.6 Hz, Ar CH), 123.7 (q, *J* = 272.6 Hz, CF_3), 123.0 (Ar CH), 21.8 (CH_3). **^{19}F NMR** ($CDCl_3$, 471 MHz): -62.4. ***m/z (GC-MS: EI): 316 $[M]^+$, 161 $[F_3CC_6H_4O]^+$, 155 $[MeC_6H_4SO_2]^+$, 133.

Para*-trifluoromethylphenyl ethyl carbonate**. Prepared using a modification of a literature procedure.[7] A round-bottom flask was charged with *para*-trifluoromethylphenol (2.84 g, 17.5 mmol, 1.4 equiv.), sodium hydroxide (0.59 g, 14.8 mmol, 1.2 equiv.), and distilled water (8 mL). The orange/yellow suspension was cooled to 0 °C in an ice bath. Ethyl chloroformate (1.5 mL, 1.32 g, 12.1 mmol) was added *via* syringe. The ice bath was removed and the reaction was stirred for 2 h, during which time the colour almost completely disappeared and an oily layer appeared at the bottom of the mixture. The reaction mixture was extracted with DCM (3 x 50 mL). The combined organic layers were washed with 2.5 M aqueous NaOH (2 x 50 mL) and then water (50 mL), dried on $MgSO_4$, and evaporated to yield a pale oil, which was purified by column chromatography on silica gel (0 – 2% EtOAc/hexane). The product was obtained as a colourless oil (2.63 g, 11.2 mmol, 93%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.66 (d, *J* = 8.5 Hz, 2H, ArCH), 7.32 (d, *J* = 8.5 Hz, 2H, ArCH), 4.34 (q, *J* = 7.0 Hz, 2H, CH_2), 1.40 (t, *J* = 7.0 Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 153.6 (Ar C-O), 153.1 (C=O), 128.4 (q, *J* = 33.3 Hz, *C*CF_3), 127.0 (q, *J* = 3.7 Hz, Ar CH), 124.0 (q, *J* = 271.7 Hz, CF_3), 121.7 (Ar CH), 65.4 (CH_2), 14.3 (CH_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -62.3. ***m/z (GC-MS: CI, CH_4): 235 $[M + H]^+$, 215 $[M – F]^+$, 207, 191, 171, 163, 143.

***Para*-trifluoromethylphenyl triflate**. Prepared using a slightly modified literature procedure.[8] A round-bottom flask was charged with *para*-trifluoromethylphenol (3.28 g, 20.2 mmol), toluene (40 mL), and 30% w/v K_3PO_4 (aq.) (40 mL). The orange/yellow biphasic mixture was cooled to 0 °C in an

ice bath, and triflic anhydride (4.2 mL, 7.04 g, 25.0 mmol, 1.2 equiv.) was added dropwise with stirring over 10 min. The reaction was stirred at 0 °C for 5 minutes then warmed to RT and stirred for a further 30 min. During this time, all colour had disappeared. The layers were separated and the toluene solution was washed with water (40 mL) and evaporated. The resulting pale oil was purified by column chromatography (0 – 1% EtOAc in hexane) to yield the product as a colourless oil (3.95 g, 13.4 mmol, 66%). Analytical data are consistent with the literature.[9] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.75 (d, *J* = 8.4 Hz, 2H, ArCH), 7.42 (d, *J* = 8.4 Hz, 2H, ArCH). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 151.7 (C-O), 131.1 (q, *J* = 33.3 Hz, *C*CF_3), 127.9 (q, *J* = 3.7 Hz, C-H), 123.4 (q, *J* = 271 Hz, C*C*F_3), 122.2 (C-H), 118.9 (q, 320.9 Hz, SO_2CF_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -62.6 (s, 3F, $ArCF_3$), -72.7 (s, 3F, SO_2CF_3). ***m/z*** (GC-MS: CI, CH_4): 295 $[M + H]^+$, 275 $[M – F]^+$, 163, 147, 127.

Para*-trifluoromethylphenyl diethylcarbamate**. A round-bottom flask was charged with *para*-trifluoromethylphenol (2.98 g, 18.4 mmol), K_2CO_3 (3.88 g, 28.1 mmol, 1.5 equiv.), and acetonitrile (35 mL). Diethylcarbamoyl chloride (2.8 mL, 3.00 g, 22.1 mmol, 1.2 equiv.) was added dropwise *via* syringe and the yellow reaction mixture was heated to reflux for 15 h. The mixture was cooled to RT, diluted with water (60 mL), and extracted with DCM (3 x 60 mL). The DCM solution was washed with 5 M NaOH (aq.) (60 mL) and water (60 mL), yielding a colourless solution which was dried on $MgSO_4$ and filtered. The solvent was removed to yield a pale yellow oil which was purified by chromatography on silica gel (0 – 10% EtOAc/hexane). The product was obtained as a colourless oil (3.38 g, 12.9 mmol, 70%). Analytical data are consistent with the literature.[10] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.62 (d, *J* = 8.7 Hz, 2H, ArCH), 7.25 (d, *J* = 8.7 Hz, 2H, ArCH), 3.53 – 3.34 (m, 4H, $N(CH_2CH_3)_2$), 1.35 – 1.15 (m, 6H, $N(CH_2CH_3)_2$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 154.3 (Ar CO), 153.6 (C=O), 127.4 (q, *J* = 32.8 Hz, *C*CF_3), 126.7 (q, *J* = 3.8 Hz, Ar CH), 124.2 (q, J = 271.2 Hz, CF_3), 122.2 (Ar CH), 42.5 (CH_2), 42.1 (CH_2), 14.4 (CH_3), 13.4 (CH_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -62.1 (CF_3). ***m/z (GC-MS: CI, CH_4): 262 $[M + H]^+$, 242 $[M – F]^+$, 100.

***Para*-trifluoromethylphenyl pivalate**. A round-bottom flask was charged with 4-trifluoromethylphenol (2.81 g, 17.3 mmol), DCM (12 mL), and trimethylamine (3.5 mL, 2.54 g, 25.1 mmol, 1.5 equiv.). The solution was cooled to 0 °C using an ice bath and pivaloyl chloride (3.0 mL, 2.94 g, 24.4 mmol, 1.4 equiv.) was added dropwise with stirring. The reaction was warmed to room temperature and stirred overnight; after 20 minutes a white precipitate had begun to form. The reaction was quenched with water (20 mL) and acidified to pH 4 using HCl (1M aqueous). The mixture was extracted with DCM (2 x 75 mL), and the combined DCM layers were washed with aqueous $NaHCO_3$ (75 mL) and brine (75 mL), before being dried on $MgSO_4$ and evaporated. The

crude product was purified by column chromatography on silica gel, eluting with hexane. A white solid was obtained after drying the resulting colourless oil under high vacuum (2.08 g, 8.45 mmol, 49%). Analytical data are consistent with the literature.[11] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.67 (d, *J* = 8.5 Hz, 2H, ArCH), 7.21 (d, *J* = 8.5 Hz, 2H, ArCH), 1.39 (s, 9H, $C(CH_3)_3$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 176.7 (C=O), 153.8 (Ar CO), 128.1 (q, J = 33.0 Hz, *C*CF_3), 126.9 (q, *J* = 3.8 Hz, Ar CH), 124.1 (q, *J* = 270.5 Hz, CF_3), 122.2 (Ar CH), 39.3 (*C*$(CH_3)_3$), 27.2 (CH_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -62.2 (CF_3). ***m/z*** (GC-MS: EI): 245 $[M - H]^+$, 162 $[F_3CC_6H_4O]^+$, 133, 85 $[^tBuCO]^+$.

Para*-trifluoromethylphenyl dimethylsulfonamide**. Prepared using a modified literature procedure.[12] A round-bottom flask was flame dried, charged with 4-trifluoromethylphenol (3.28 g, 20.2 mmol, 1.1 equiv.) and dissolved in anhydrous THF (50 mL). This was transferred dropwise by cannula to a second flame-dried flask, in an ice bath, containing sodium hydride (1.01 g of a 60% w/w dispersion in mineral oil, 25.3 mmol, 1.4 equiv.). Dimethylsulfamoyl chloride (2.0 mL, 2.67 g, 18.6 mmol) was added to this yellow solution *via* syringe. The reaction was warmed to room temperature and stirred overnight. After carefully quenching with water (10 mL), the reaction mixture was diluted with diethyl ether (30 mL) and water (20 mL) and separated. The ether solution was washed with 1M aqueous potassium hydroxide (2 x 25 mL) and water (20 mL). The combined aqueous washes were extracted with diethyl ether (3 x 30 mL). The combined diethyl ether portions were then washed with brine (30 mL), dried on magnesium sulfate, and evaporated to yield a yellow oil. Purification by column chromatography on silica gel (0 – 2% EtOAc in hexane) yielded a colourless oil which was dried under high vacuum, and solidified after storage at -35 °C in the glovebox freezer (3.75 g, 13.9 mmol, 69%). Analytical data are consistent with the literature.[12] **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.66 (d, *J* = 8.5 Hz, 2H, ArCH), 7.40 (d, *J* = 8.5 Hz, 2H, ArCH), 3.01 (s, 3H, $N(CH_3)_2$). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_H 152.9 (Ar CO), 129.0 (q, *J* = 32.7 Hz, *C*CF_3), 127.3 (q, *J* = 3.9 Hz, Ar CH), 123.8 (q, *J* = 272.3 Hz, CF_3), 122.1 (Ar CH), 38.9 (CH_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_H -62.3 (CF_3). ***m/z (GC-MS: EI): 269 $[M + H]^+$, 161 $[F_3CC_6H_4O]^+$, 108 $[SO_2NMe_2]^+$.

4,4'-Bis(trifluoromethyl)-1,1'-biphenyl. Prepared according to a modified literature procedure.[13] A 100 mL round-bottom flask was charged with 4-trifluoromethylphenyl boronic acid (1.57 g, 8.3 mmol), CuCl (0.30 g, 3.0 mmol), and methanol (20 mL). The mixture was sparged with air for *ca.* 15 minutes, before being heated to 30 °C for 6 h in the open flask. The reaction was filtered through a pad of celite, which was washed with ethyl acetate. The solvent was removed from the filtrate and the resulting pale green solid was recrystallized from methanol to yield fluffy white crystals of the product (449.6 mg, 1.5 mmol, 36%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.74 (d, *J* = 8.6 Hz, 2H, ArCH), 7.70

(d, *J* = 8.6 Hz, 2H, ArCH). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 101 MHz): δ_C 143.4 (quat. ArC), 130.5 (q, *J* = 33.3 Hz, *C*CF_3), 127.8 (Ar CH), 126.1 (q, *J* = 3.8 Hz, Ar CH), 124.3 (q, *J* = 272.0 Hz, C*C*F_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -62.6 (s, 3F, ArCF_3). Analytical data are consistent with the literature.[13]

1-Phenylnaphthalene. A 25 mL round-bottom flask fitted with a septum was flame-dried and charged with phenylboronic acid (489.3 mg, 4.01 mmol, 2.0 equiv.), [$NiCl_2$(dppf)] (69.3 mg, 0.10 mmol, 5.1 mol%), and K_3PO_4 (1269.0 mg, 5.98 mmol, 3.0 equiv.). The flask was evacuated and backfilled with argon three times, and anhydrous toluene (6 mL) and 1-bromonaphthalene (280 µL, 414.4 mg, 2.00 mmol) were added *via* syringe. The reaction was heated to 90 °C for 16 h and then allowed to cool to room temperature. GC-FID analysis confirmed that all of the aryl halide had been consumed. The reaction mixture was filtered through a pad of celite and the solvent was removed using a rotary evaporator to yield a pale oil. Chromatography on silica gel (eluting with hexane) provided the desired product as a clear oil (353.6 mg, 1.73 mmol, 87%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.93 (app. d, 2H, *J* = 8.8 Hz), 7.88 (app. d, 1H, *J* = 8.2 Hz), 7.58 – 7.41 (m, 9H). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 101 MHz): δ_C 140.9, 140.4, 134.0, 131.8, 130.2, 128.9, 128.4, 127.8, 127.4, 127.3, 127.1, 126.2, 125.9, 125.5. Analytical data are consistent with the literature.[14]

2-Phenylnaphthalene. A 25 mL round-bottom flask fitted with a septum and a stir bar was flame-dried and charged with 2-bromonaphthalene (420.7 mg, 2.03 mmol), phenylboronic acid (487.5 mg, 4.00 mmol, 2.0 equiv.), [$NiCl_2$(dppf)] (66.7 mg, 0.10 mmol, 4.8 mol%), and K_3PO_4 (1284.2 mg, 6.05 mmol, 3.0 equiv.). The flask was evacuated and backfilled with argon three times, and anhydrous toluene (6 mL) was added *via* syringe. The reaction was heated to 90 °C for 16 h and then allowed to cool to room temperature. GC-FID analysis confirmed that all of the aryl halide had been consumed. The reaction mixture was filtered through a pad of celite and the solvent was removed using a rotary evaporator to yield a pale solid. Recrystallisation from methanol and drying under high vacuum provided the product as a white powder (316.6 mg, 1.55 mmol, 76%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.06 (s, 1H), 7.97 – 7.85 (m, 3H), 7.81 – 7.70 (m, 3H), 7.57 – 7.45 (m, 4H), 7.44 – 7.36 (m, 1H). **$^{13}C\{^{1}H\}$ NMR** ($CDCl_3$, 101 MHz): δ_C 141.3, 138.7, 133.8, 132.8, 129.0, 128.6, 128.3, 127.8, 127.6, 127.5, 126.4, 126.1, 126.0, 125.7. Analytical data are consistent with the literature.[15]

2,2'-Binaphthalene. A 10 mL round-bottom flask fitted with septum and a stir bar was flame-dried and charged with 2-bromonaphthalene (205.7 mg, 0.993 mmol), 2-napthylboronic acid (336.4 mg, 1.96 mmol, 2.0 equiv.), [$NiCl_2$(dppf)] (34.3 mg, 0.05 mmol, 5.1%), and K_3PO_4 (623.4 mg, 2.94 mmol, 3.0 equiv.). The flask was evacuated and backfilled with argon three times. Anhydrous toluene (3 mL)

was added by syringe and the reaction was heated to 90 °C for 16 h. After this time, the reaction mixture was filtered through celite and the solvent was removed on a rotary evaporator. The residue was recrystallised from hot methanol to yield a flaky white solid (47.7 mg, 0.188 mmol, 19%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.19 (d, *J* = 1.1 Hz, 2H), 8.01 – 7.87 (m, 8H), 7.58 – 7.47 (m, 4H). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_C 138.6 (Ar C), 133.9 (Ar C), 132.8 (Ar C), 128.7 (Ar CH), 128.4 (Ar CH), 127.8 (Ar CH), 126.5 (Ar CH), 126.3 (Ar CH), 126.2 (Ar CH), 125.9 (Ar CH). Analytical data are consistent with the literature.[13]

1-Naphthyl tosylate. Prepared according to a literature procedure.[6] 1-Naphthol (1.84 g, 12.8 mmol) was dissolved in THF (7.5 mL). Aqueous NaOH (12.5 mL of a 15% w/w solution) was added and the reaction was cooled to 0 °C in an ice bath. A solution of TsCl (2.90 g, 15.2 mmol, 1.2 equiv.) in THF (17.5 mL) was added slowly. The reaction was warmed to room temperature and stirred for 2 h. Ethyl acetate (50 mL) was added and the mixture was separated. The organic layer was washed with water (25 mL) and dried on magnesium sulfate. The solvent was removed to yield an off-white powder (3.45 g, 11.6 mmol, 90%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.91 (d, *J* = 8.6 Hz, 1H, Ar CH), 7.83 – 7.76 (m, 3H, Ar CH), 7.74 (d, *J* = 8.4 Hz, 1H, Ar CH), 7.50 – 7.40 (m, 2H, Ar CH), 7.37 (t, *J* = 7.8 Hz, 1H, Ar CH), 7.28 (dd, *J* = 8.8, 0.6 Hz, 2H, Ar CH), 7.21 (dd, *J* = 7.8, 1.0 Hz, 1H, Ar CH), 2.42 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 145.9 (Ar C), 145.5 (Ar C), 134.9 (Ar C), 133.0 (Ar C), 129.9 (Ar CH), 128.6 (Ar CH), 127.8 (Ar CH), 127.5 (Ar C), 127.2 (Ar CH), 126.8 (Ar CH), 122.0 (Ar CH), 118.5 (Ar CH), 21.8 (CH_3). ***m/z*** (GC-MS: EI): 298 $[M]^+$, 155 $[MeC_6H_4SO_2]^+$, 143 $[NapO]^+$.

2-Naphthyl tosylate. Prepared according to a literature procedure.[6] 2-Naphthol (1.85 g, 12.8 mmol) was dissolved in THF (7.5 mL). Aqueous NaOH (12.5 mL of 15% w/w solution) was added and the reaction was cooled to 0 °C in an ice bath. A solution of TsCl (2.90 g, 15.2 mmol, 1.2 equiv.) in THF (17.5 mL) was added slowly. The reaction was warmed to room temperature and stirred for 2 h. Ethyl acetate (50 mL) was added and the mixture was separated. The organic layer was washed with water (25 mL) and dried on $MgSO_4$. The solvent was removed to yield an off-white powder (3.08 g, 10.3 mmol, 81%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.84 – 7.78 (m, 1H, Ar CH), 7.78 – 7.71 (m, 4H, Ar CH), 7.53 – 7.45 (m, 3H, Ar CH), 7.29 (dd, *J* = 8.6, 0.5 Hz, 2H, Ar CH), 7.10 (dd, *J* = 9.0, 2.4 Hz, 1H, Ar CH), 2.44 (s, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 147.3 (Ar C), 145.5 (Ar C), 133.6 (Ar C), 132.6 (Ar C), 132.0 (Ar C), 129.9 (Ar CH), 128.7 (Ar CH), 128.0 (Ar CH), 127.9 (Ar CH), 127.0 (Ar CH), 126.5 (Ar CH), 121.3 (Ar CH), 120.1 (Ar CH), 21.8 (CH_3). ***m/z*** (GC-MS: EI): 298 $[M]^+$, 155 $[MeC_6H_4SO_2]^+$, 143 $[NapO]^+$.

1-Naphthyl triflate. 1-Naphthol (2.88 g, 20.0 mmol) was dissolved in toluene (40 mL). Aqueous K_3PO_4 (40 mL of a 30% w/w solution) was added and the mixture was cooled to 0 °C in an ice bath. Triflic anhydride (4.2 mL, 7.04 g, 25.0 mmol, 1.2 equiv.) was added dropwise over 10 min. The reaction was stirred for 5 min at 0 °C and then 30 min at room temperature. The layers were separated and the toluene layer was washed with water (40 mL), dried on $MgSO_4$, and evaporated to yield an oil (2.39 g, 8.7 mmol, 43%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.09 (d, *J* = 8.2 Hz, 1H, Ar CH), 7.93 (d, *J* = 8.2 Hz, 1H, Ar CH), 7.88 (dd, *J* = 6.9, 2.0 Hz, 1H, Ar CH), 7.69 – 7.58 (m, 2H, Ar CH), 7.53 – 7.45 (m, 2H, Ar CH). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 145.8 (Ar C), 135.1 (Ar C), 128.7 (Ar CH), 128.2 (Ar CH), 128.0 (Ar CH), 127.5 (Ar CH), 126.5 (Ar C), 125.3 (Ar CH), 120.9 (Ar CH), 118.9 (q, *J* = 321.9 Hz, CF_3), 117.9 (Ar CH). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -73.3 (s, 3F, CF_3). ***m/z*** (GC-MS: EI): 276 $[M]^+$, 143 $[M - SO_2CF_3]^+$.

2-Naphthyl triflate. 2-Naphthol (2.89 g, 20.0 mmol) was dissolved in toluene (40 mL). Aqueous K_3PO_4 (40 mL of a 30% w/w solution) was added and the mixture was cooled to 0 °C in an ice bath. Triflic anhydride (4.2 mL, 7.04 g, 25.0 mmol, 1.2 equiv.) was added dropwise over 10 min. The reaction was stirred for 5 min at 0 °C and then 30 min at room temperature. The layers were separated and the toluene layer was washed with water (40 mL), dried on $MgSO_4$, and evaporated to yield an oil. This was purified by column chromatography on silica gel (EtOAc/hexane) to yield a pale solid (3.56 g, 12.9 mmol, 64%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.95 – 7.84 (m, 3H, Ar CH), 7.77 (d, *J* = 2.4 Hz, 1H, Ar CH), 7.62 – 7.54 (m, 2H, Ar CH), 7.39 (dd, *J* = 8.9, 2.5 Hz, 1H, Ar CH). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 147.2 (Ar C), 133.5 (Ar C), 132.5 (Ar C), 130.7 (Ar CH), 128.1 (Ar CH), 128.0 (Ar CH), 127.7 (Ar CH), 127.3 (Ar CH), 119.6 (Ar CH), 119.3 (Ar CH), 119.0 (q, *J* = 321.3 Hz, CF_3). **^{19}F NMR** ($CDCl_3$, 376 MHz): δ_F -72.8 (s, 3F, CF_3). ***m/z*** (GC-MS: EI): 276 $[M]^+$, 143 $[M - SO_2CF_3]^+$.

Ethyl (naphthalene-1-yl)carbonate. 1-Naphthol (2.53 g, 17.5 mmol, 1.1 equiv.) was suspended in a solution of NaOH (0.62 g, 15.5 mmol) in water (8 mL), which was cooled to 0 °C in an ice bath. Ethyl chloroformate (1.5 mL, 1.70 g, 15.6 mmol) was added *via* syringe and the ice bath was removed. The reaction was stirred for 2 h at room temperature and then extracted with DCM (3 x 50 mL). The combined organic layers were washed with aqueous NaOH (2 x 50 mL of a 2.5 mol L^{-1} solution) and water (50 mL), dried on $MgSO_4$, and evaporated to yield a dark oil. This was purified by column chromatography on silica gel (0 – 2% EtOAc/hexane) to yield a colourless oil (2.62 g, 12.1 mmol, 69%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.03 – 7.96 (m, 1H, Ar CH), 7.91 – 7.85 (m, 1H, Ar CH), 7.76 (d, *J* = 8.3 Hz, 1H, Ar CH), 7.58 – 7.50 (m, 2H, Ar CH), 7.48 (app. t, *J* = 7.6 Hz, 1H, Ar CH), 7.36 (dd, *J* = 7.6, 0.9 Hz, 1H, Ar CH), 4.39 (q, *J* = 7.3 Hz, 2H, CH_2CH_3), 1.44 (t, *J* = 7.3 Hz, 3H, CH_2CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 153.9 (CO), 147.0 (Ar C), 134.8 (Ar C), 128.1 (Ar CH), 126.8 (Ar C), 126.71 (Ar CH),

126.67 (Ar CH), 126.3 (Ar CH), 125.5 (Ar CH), 121.2 (Ar CH), 117.7 (Ar CH), 65.2 (CH_2CH_3), 14.4 (CH_2CH_3). ***m/z*** (GC-MS: EI): 216 $[M]^+$, 172 $[M - C_2H_4O]^+$, 144 $[NapOH]^+$.

Ethyl (naphthalene-2-yl)carbonate. 2-Naphthol (2.52 g, 17.5 mmol, 1.1 equiv.) was suspended in a solution of NaOH (0.64 g, 16 mmol) in water (8 mL), which was cooled to 0 °C in an ice bath. Ethyl chloroformate (1.5 mL, 1.70 g, 15.6 mmol) was added *via* syringe and the ice bath was removed. The reaction was stirred for 2 h at room temperature and then extracted with DCM (3 x 50 mL). The combined organic layers were washed with aqueous NaOH (2 x 50 mL of a 2.5 mol L-1 solution) and water (50 mL), dried on $MgSO_4$, and evaporated to yield an off-white solid (1.99 g, 9.2 mmol, 59%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.91 – 7.79 (m, 3H, Ar CH), 7.66 (d, *J* = 2.3 Hz, 1H, Ar CH), 7.53 – 7.45 (m, 2H, Ar CH), 7.33 (dd, *J* = 8.9, 2.3 Hz, 1H, Ar CH), 4.36 (q, *J* = 7.1 Hz, 2H, OCH_2CH_3), 1.42 (t, *J* = 7.1 Hz, 3H, OCH_2CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 153.9 (CO), 148.9 (Ar C), 133.8 (Ar C), 131.6 (Ar C), 129.7 (Ar CH), 127.89 (Ar CH), 127.85 (Ar CH), 126.8 (Ar CH), 126.0 (Ar CH), 120.7 (Ar CH), 118.2 (Ar CH), 65.0 (OCH_2CH_3), 14.4 (OCH_2CH_3). ***m/z*** (GC-MS: EI): 216 $[M]^+$, 172 $[M - C_2H_4O]^+$, 144 $[NapOH]^+$.

Diethyl (naphthalene-1-yl)carbamate. 1-Naphthol (2.64 g, 18.3 mmol) and K_2CO_3 (3.88 g, 28.1 mmol, 1.5 equiv.) were dissolved in acetonitrile (35 mL). Diethylcarbamoyl chloride (2.8 mL, 3.00 g, 22.1 mmol, 1.2 equiv.) was added dropwise and then the mixture was heated to reflux for 15 h. Once cooled to room temperature, the mixture was diluted with water (60 mL) and extracted with DCM (3 x 60 mL). The DCM solution was washed with aqueous NaOH (60 mL of a 5 mol L^{-1} solution) and water (60 mL), dried on $MgSO_4$, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc/hexane) to yield the product as an off-white solid (1.12 g, 4.6 mmol, 25%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.96 – 7.91 (m, 1H, Ar CH), 7.89 – 7.83 (m, 1H, Ar CH), 7.71 (d, *J* = 8.3 Hz, 1H, Ar CH), 7.54 – 7.44 (m, 3H, Ar CH), 7.30 (dd, *J* = 7.6, 1.0 Hz, 1H, Ar CH), 3.63 (q, *J* = 7.0 Hz, 2H, NCH_2CH_3), 3.46 (q, *J* = 7.0 Hz, 2H, NCH_2CH_3), 1.39 (t, *J* = 7.0 Hz, 3H, NCH_2CH_3), 1.26 (t, *J* = 7.0 Hz, 3H, NCH_2CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 154.4 (CO), 147.5 (Ar C), 134.8 (Ar C), 128.1 (Ar CH), 127.7 (Ar C), 126.3 (Ar CH), 125.6 (Ar CH), 125.4 (Ar CH), 121.5 (Ar CH), 118.2 (Ar CH), 42.5 (NCH_2CH_3), 42.2 (NCH_2CH_3), 14.6 (NCH_2CH_3), 13.6 (NCH_2CH_3). ***m/z*** (GC-MS: EI): 243 $[M]^+$, 144 $[NapOH]^+$.

Diethyl (naphthalene-2-yl)carbamate. 2-Naphthol (2.64 g, 18.3 mmol) and K_2CO_3 (3.87 g, 28.0 mmol, 1.5 equiv.) were dissolved in acetonitrile (35 mL). Diethylcarbamoyl chloride (2.8 mL, 3.00 g, 22.1 mmol, 1.2 equiv.) was added dropwise and then the mixture was heated to reflux for 15 h.

Once cooled to room temperature, the mixture was diluted with water (60 mL) and extracted with DCM (3 x 60 mL). The DCM solution was washed with aqueous NaOH (60 mL of a 5 mol L-1 solution) and water (60 mL), dried on MgSO4, and evaporated. The residue was purified by column chromatography on silica gel (EtOAc/hexane) to yield the product as an off-white solid (2.07 g, 8.5 mmol, 46%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.83 (d, *J* = 8.5 Hz, 1H, Ar CH), 7.79 (d, *J* = 8.0 Hz, 1H, Ar CH), 7.59 (d, *J* = 2.1 Hz, 1H, Ar CH), 7.50 – 7.41 (m, 2H, Ar CH), 7.30 (dd, *J* = 8.8, 2.3 Hz, 1H, Ar CH), 3.59 – 3.35 (m, 4H, CH_2CH_3), 1.37 – 1.18 (m, 6H, CH_2CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 154.5 (CO), 149.3 (Ar C), 134.0 (Ar C), 131.3 (Ar C), 129.2 (Ar CH), 127.8 (Ar CH), 127.7 (Ar CH), 126.4 (Ar CH), 125.4 (Ar CH), 121.8 (Ar CH), 118.5 (Ar CH), 42.4 (CH_2CH_3), 42.1 (CH_2CH_3), 14.4 (CH_2CH_3), 13.5 (CH_2CH_3). ***m/z*** (GC-MS: EI): 243 $[M]^+$, 144 $[NapOH]^+$.

Napthalen-1-yl pivalate. 1-Naphthol (2.42 g, 16.8 mmol) was dissolved in DCM (25 mL). NEt_3 (3.5 mL, 2.54 g, 25.1 mmol, 1.5 equiv.) was added and a homogeneous solution was formed. The reaction was cooled to 0 °C in an ice bath, and pivaloyl chloride (3.0 mL, 2.94 g, 24.4 mmol, 1.5 equiv.) was added dropwise with stirring. A precipitate formed after a few minutes. The reaction was warmed to room temperature and stirred overnight. After quenching with water (20 mL), the reaction was adjusted to pH 4 with a few drops of aqueous HCl (1 mol L^{-1} solution), and extracted with DCM (2 x 75 mL). The combined DCM portions were washed with $NaHCO_3$ (75 mL of a sat. aqueous solution) and brine (75 mL), before being dried on $MgSO_4$ and evaporated to yield an orange oil. This was purified by column chromatography on silica gel (0 – 2% EtOAc/hexane) to produce a clear oil which solidified after drying under high vacuum (3.16 g, 13.9 mmol, 82%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.96 – 7.86 (m, 2H, Ar CH), 7.76 (d, *J* = 8.3 Hz, 1H, Ar CH), 7.58 – 7.47 (m, 3H, Ar CH), 7.26 (dd, *J* = 7.6, 1.0 Hz, 1H, Ar CH), 1.54 (s, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 177.1 (CO), 147.0 (Ar C), 134.8 (Ar C), 128.1 (Ar CH), 127.2 (Ar C), 126.5 (Ar CH), 126.4 (Ar CH), 125.9 (Ar CH), 125.5 (Ar CH), 39.6 ($C(CH_3)_3$), 27.5 (CH_3). ***m/z*** (GC-MS: EI): 228 $[M]^+$.

Napthalen-2-yl pivalate. 2-Naphthol (2.49 g, 17.3 mmol) was dissolved in DCM (25 mL). NEt_3 (3.5 mL, 2.54 g, 25.1 mmol, 1.5 equiv.) was added and a homogeneous solution was formed. The reaction was cooled to 0°C in an ice bath, and pivaloyl chloride (3.0 mL, 2.94 g, 24.4 mmol, 1.5 equiv.) was added dropwise with stirring. A precipitate formed after a few minutes. The reaction was warmed to room temperature and stirred overnight. After quenching with water (20 mL), the reaction was adjusted to pH 4 with a few drops of aqueous HCl (1 mol L^{-1} solution), and extracted with DCM (2 x 75 mL). The combined DCM portions were washed with $NaHCO_3$ (75 mL of a sat. aqueous solution) and brine (75 mL), before being dried on $MgSO_4$ and evaporated to yield a beige solid. This was

purified by column chromatography on silica gel (0 – 2% EtOAc/hexane) to yield a white solid which was dried under high vacuum (3.31 g, 14.5 mmol, 84%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.89 – 7.82 (m, 2H, Ar CH), 7.82 – 7.76 (m, 1H, Ar CH), 7.53 (d, *J* = 2.2 Hz, 1H, Ar CH), 7.52 – 7.43 (m, 2H, Ar CH), 7.20 (dd, *J* = 9.0, 2.3 Hz, 1H, Ar CH), 1.41 (s, 9H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 177.4 (CO), 148.9 (Ar C), 134.0 (Ar C), 131.5 (Ar C), 129.4 (Ar CH), 127.9 (Ar CH), 127.7 (Ar CH), 126.6 (Ar CH), 125.7 (Ar CH), 121.3 (Ar CH), 118.5 (Ar CH), 39.3 ($C(CH_3)_3$), 27.3 ($C(CH_3)_3$). ***m/z*** (GC-MS: EI): 228 $[M]^+$.

Napthalen-1-yl dimethylsulfamate. 1-Naphthol (2.88 g, 20.0 mmol, 1.1 equiv.) was dissolved in anhydrous THF (50 mL) and transferred by cannula, dropwise, to a flame-dried flask containing NaH (60% dispersion in mineral oil; 1.00 g, 25 mmol, 1.3 equiv.). Me_2NSO_2Cl (2.0 mL, 2.67 g, 18.6 mmol) was added dropwise with stirring. The reaction was stirred for 19 h, and then quenched by the careful addition of water (20 mL). The mixture was diluted with diethyl ether (30 mL) and water (20 ml), and then separated. The organic layer was washed with KOH (2 x 25 mL of a 1 mol L^{-1} aqueous solution) and water (25 mL). The combined aqueous portions were extracted with diethyl ether (3 x 40 mL). The combined ether portions were washed with brine (50 mL), dried on $MgSO_4$, and evaporated to yield an off-white solid, which was recrystallised from methanol and then purified by column chromatography on silica gel (0 – 5% EtOAc/hexane) to yield the product as a white powder (2.30 g, 9.2 mmol, 46%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 8.18 (d, *J* = 8.4 Hz, 1H, Ar CH), 7.88 (d, *J* = 8.0 Hz, 1H, Ar CH), 7.77 (d, *J* = 8.4 Hz, 1H, Ar CH), 7.62 – 7.50 (m, 3H, Ar CH), 7.46 (app. t, *J* = 7.6 Hz, 1H, Ar CH), 3.07 (s, 6H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 101 MHz): δ_c 146.2 (Ar C), 135.0 (Ar C), 128.1 (Ar CH), 127.3 (Ar C), 126.9 (Ar CH), 126.8 (Ar CH), 125.5 (Ar CH), 121.6 (Ar CH), 117.9 (Ar CH), 39.1 (CH_3). ***m/z*** (GC-MS: EI): 251 $[M]^+$, 143 $[M - SO_2NMe_2]^+$.

Napthalen-2-yl dimethylsulfamate. 2-Naphthol (2.84 g, 19.7 mmol, 1.1 equiv.) was dissolved in anhydrous THF (50 mL) and transferred by cannula, dropwise, to a flame-dried flask containing NaH (60% dispersion in mineral oil; 1.03 g, 25.8 mmol, 1.4 equiv.). Me_2NSO_2Cl (2.0 mL, 2.67 g, 18.6 mmol) was added dropwise with stirring. The reaction was stirred for 19 h, and then quenched by the careful addition of water (20 mL). The mixture was diluted with diethyl ether (30 mL) and water (20 ml), and then separated. The organic layer was washed with KOH (2 x 25 mL of a 1 mol L^{-1} aqueous solution) and water (25 mL). The combined aqueous portions were extracted with diethyl ether (3 x 40 mL). The combined ether portions were washed with brine (50 mL), dried on $MgSO_4$, and evaporated to yield an off-white solid, which was recrystallised from methanol and then purified by column chromatography on silica gel (0 – 5% EtOAc/hexane) to yield the product as a white powder (3.38 g, 13.5 mmol, 68%). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ_H 7.91 – 7.81 (m, 3H, Ar CH), 7.76 (d, *J* = 2.2 Hz,

1H, Ar CH), 7.56 – 7.47 (m, 2H, Ar CH), 7.42 (dd, *J* = 8.9, 2.4 Hz, 1H, Ar CH), 3.01 (s, 6H, CH_3). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 101 MHz): δ_c 147.9 (Ar C), 133.8 (Ar C), 131.9 (Ar C), 130.1 (Ar CH), 127.9 (Ar CH), 127.0 (Ar CH), 126.3 (Ar CH), 120.9 (Ar CH), 119.2 (Ar CH), 38.9 (CH_3). ***m/z*** (GC-MS: EI): 251 $[M]^+$, 143 $[M - SO_2NMe_2]^+$.

3. Kinetic Experiments

3.1 Oxidative Addition

Oxidative addition experiments were carried out as follows, by following the decay of the starting Ni^0 complex: In an argon-filled glovebox, a septum-fitted NMR tube was charged with a solution of [Ni(COD)(dppf)] (**1**) (8 mg, 0.011 mmol) and an internal standard ($OPPh_3$ or $OPCy_3$) in dry benzene-d_6 or toluene-d_8 (0.5 mL). This sample was used to tune, match, lock and shim the spectrometer, and to set the receiver gain. A spectrum was acquired to check the integrity of the sample. The aryl halide (0.22 mmol) was added to start the reaction and ^{31}P NMR spectra (16 scans/spectrum; interpulse delay = 20 s) were acquired at intervals until >87% conversion was achieved. Rate constants were obtained by plotting the natural log of the integral of the signal for Ni^0 *versus* time.

Table S1. Rate constants from kinetic experiments.

Entry	Substrate	[Subs.] (mol L^{-1})	Solvent	Temp. (K)	k_{obs} (s^{-1})	Notes
1a	*o*-MeC_6H_4I	0.44	Benzene-d_6	303	4.97×10^{-4}	
1b	*o*-MeC_6H_4I	0.44	Benzene-d_6	303	5.10×10^{-4}	
2a	*o*-MeC_6H_4Br	0.44	Benzene-d_6	323	6.84×10^{-4}	
2b	*o*-MeC_6H_4Br	0.44	Benzene-d_6	323	6.96×10^{-4}	
3a	*o*-MeC_6H_4Cl	0.44	Benzene-d_6	323	1.64×10^{-4}	
3b	*o*-MeC_6H_4Cl	0.44	Benzene-d_6	323	2.04×10^{-4}	
4a	*p*-MeC_6H_4Cl	0.44	Benzene-d_6	323	2.28×10^{-4}	
4b	*p*-MeC_6H_4Cl	0.44	Benzene-d_6	323	2.23×10^{-4}	
5a	*p*-$F_3CC_6H_4I$	0.44	Benzene-d_6	293	7.69×10^{-4}	
5b	*p*-$F_3CC_6H_4I$	0.44	Benzene-d_6	293	7.89×10^{-4}	
6a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	293	2.34×10^{-5}	
6b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	293	2.42×10^{-5}	
7a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	1.01×10^{-3}	
7b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	1.02×10^{-3}	
8a	*p*-$F_3CC_6H_4Cl$	0.44	Benzene-d_6	323	2.36×10^{-4}	
8b	*p*-$F_3CC_6H_4Cl$	0.44	Benzene-d_6	323	2.41×10^{-4}	
9a	*p*-$F_3CC_6H_4Cl$	0.55	Benzene-d_6	323	2.90×10^{-4}	
9b	*p*-$F_3CC_6H_4Cl$	0.55	Benzene-d_6	323	2.88×10^{-4}	

10a	*p*-$F_3CC_6H_4Cl$	0.66	Benzene-d_6	323	3.36×10^{-4}	
10b	*p*-$F_3CC_6H_4Cl$	0.66	Benzene-d_6	323	3.47×10^{-4}	
11a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	4.26×10^{-4}	0.044 mol L^{-1} COD
11b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	4.19×10^{-4}	
12a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	2.84×10^{-4}	0.11 mol L^{-1} COD
12b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	2.83×10^{-4}	
13a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	2.50×10^{-4}	0.22 mol L^{-1} COD
13b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	323	2.41×10^{-4}	
14a	*p*-$(H_2C{=}CH)C_6H_4Cl$	0.44	Benzene-d_6	323	2.62×10^{-4}	Intermediate η^2-styrene complex detected
14b	*p*-$(H_2C{=}CH)C_6H_4Cl$	0.44	Benzene-d_6	323	2.63×10^{-4}	
15a	PhCl	0.44	Benzene-d_6	323	3.81×10^{-4}	
15b	PhCl	0.44	Benzene-d_6	323	3.68×10^{-4}	
16a	*p*-$MeOC_6H_4Cl$	0.44	Benzene-d_6	323	1.89×10^{-4}	
16b	*p*-$MeOC_6H_4Cl$	0.44	Benzene-d_6	323	1.81×10^{-4}	
17a	*p*-$EtO_2CC_6H_4Cl$	0.44	Benzene-d_6	323	3.31×10^{-4}	
17b	*p*-$EtO_2CC_6H_4Cl$	0.44	Benzene-d_6	323	3.33×10^{-4}	
18a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	303	6.10×10^{-5}	
18b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	303	6.49×10^{-5}	
19a	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	313	3.15×10^{-4}	
19b	*p*-$F_3CC_6H_4Br$	0.44	Benzene-d_6	313	2.95×10^{-4}	
20a	*p*-$F_3CC_6H_4OTs$	0.44	Benzene-d_6	323	8.06×10^{-5}	
20b	*p*-$F_3CC_6H_4OTs$	0.44	Benzene-d_6	323	8.32×10^{-5}	
21a	*p*-$F_3CC_6H_4OTs$	0.44	Toluene-d_8	343	1.02×10^{-3}	
21b	*p*-$F_3CC_6H_4OTs$	0.44	Toluene-d_8	343	1.09×10^{-3}	
22a	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	343	4.61×10^{-4}	
22b	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	343	4.64×10^{-4}	
23a	*p*-$F_3CC_6H_4OCO_2Et$	0.44	Toluene-d_8	343	5.13×10^{-4}	
23b	*p*-$F_3CC_6H_4OCO_2Et$	0.44	Toluene-d_8	343	4.70×10^{-4}	
24a	*p*-$F_3CC_6H_4OCONEt_2$	0.44	Toluene-d_8	343	2.86×10^{-4}	
24b	*p*-$F_3CC_6H_4OCONEt_2$	0.44	Toluene-d_8	343	2.72×10^{-4}	
25a	*p*-$F_3CC_6H_4OPiv$	0.44	Toluene-d_8	343	9.15×10^{-5}	
25b	*p*-$F_3CC_6H_4OPiv$	0.44	Toluene-d_8	343	1.08×10^{-4}	
26a	*p*-$F_3CC_6H_4OSO_2NMe_2$	0.44	Toluene-d_8	343	1.86×10^{-4}	
26b	*p*-$F_3CC_6H_4OSO_2NMe_2$	0.44	Toluene-d_8	343	1.99×10^{-4}	
27	*p*-$F_3CC_6H_4OMe$	0.44	Toluene-d_8	343	(1.41×10^{-6})	Estimated from *ca.* 25% conversion after *ca.* 48h.
28	*p*-$F_3CC_6H_4F$	0.44	Toluene-d_8	343	(1.47×10^{-6})	

29a	*p*-$F_3CC_6H_4OTs$	0.44	Toluene-d_8	333	2.99×10^{-4}	
29b	*p*-$F_3CC_6H_4OTs$	0.44	Toluene-d_8	333	3.30×10^{-4}	
30a	*p*-$F_3CC_6H_4OTs$	0.44	Toluene-d_8	338	5.66×10^{-4}	
30b	*p*-$F_3CC_6H_4OTs$	0.44	Toluene-d_8	338	6.18×10^{-4}	
31a	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	333	1.42×10^{4}	
31b	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	333	1.37×10^{-4}	
32a	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	348	9.53×10^{-4}	
32b	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	348	9.72×10^{-4}	
33a	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	353	2.04×10^{-3}	
33b	*p*-$F_3CC_6H_4OTf$	0.44	Toluene-d_8	353	2.21×10^{-3}	
34	*p*-$F_3CC_6H_4Cl$	0.44	Toluene-d_8	323	1.74×10^{-4}	
35a	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	7.12×10^{-4}	
35b	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	6.89×10^{-4}	
36a	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	1.94×10^{-4}	0.044 mol L^{-1} COD
36b	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	2.06×10^{-4}	
37a	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	1.88×10^{-4}	0.11 mol L^{-1} COD
37b	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	2.02×10^{-4}	
38a	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	1.32×10^{-4}	0.22 mol L^{-1} COD
38b	*p*-$MeOC_6H_4Br$	0.44	Benzene-d_6	323	1.46×10^{-4}	
39a	1-bromonaphthalene	0.44	Benzene-d_6	293	9.15×10^{-5}	
39b	1-bromonaphthalene	0.44	Benzene-d_6	293	1.02×10^{-4}	
40a	2-bromonaphthalene	0.44	Benzene-d_6	293	1.63×10^{-4}	
40b	2-bromonaphthalene	0.44	Benzene-d_6	293	1.55×10^{-4}	

3.2 Comproportionation

Comproportionation reactions were carried out by dissolving [NiCl(*o*-tol)(dppf)] (**3-Cl**) and [Ni(COD)(dppf)] (**1**) in a 60/40 v/v mixture of benzene-d_6 and THF and heating to 50 °C. Experiments were carried out with different ratios of Ni(0) to Ni(II).

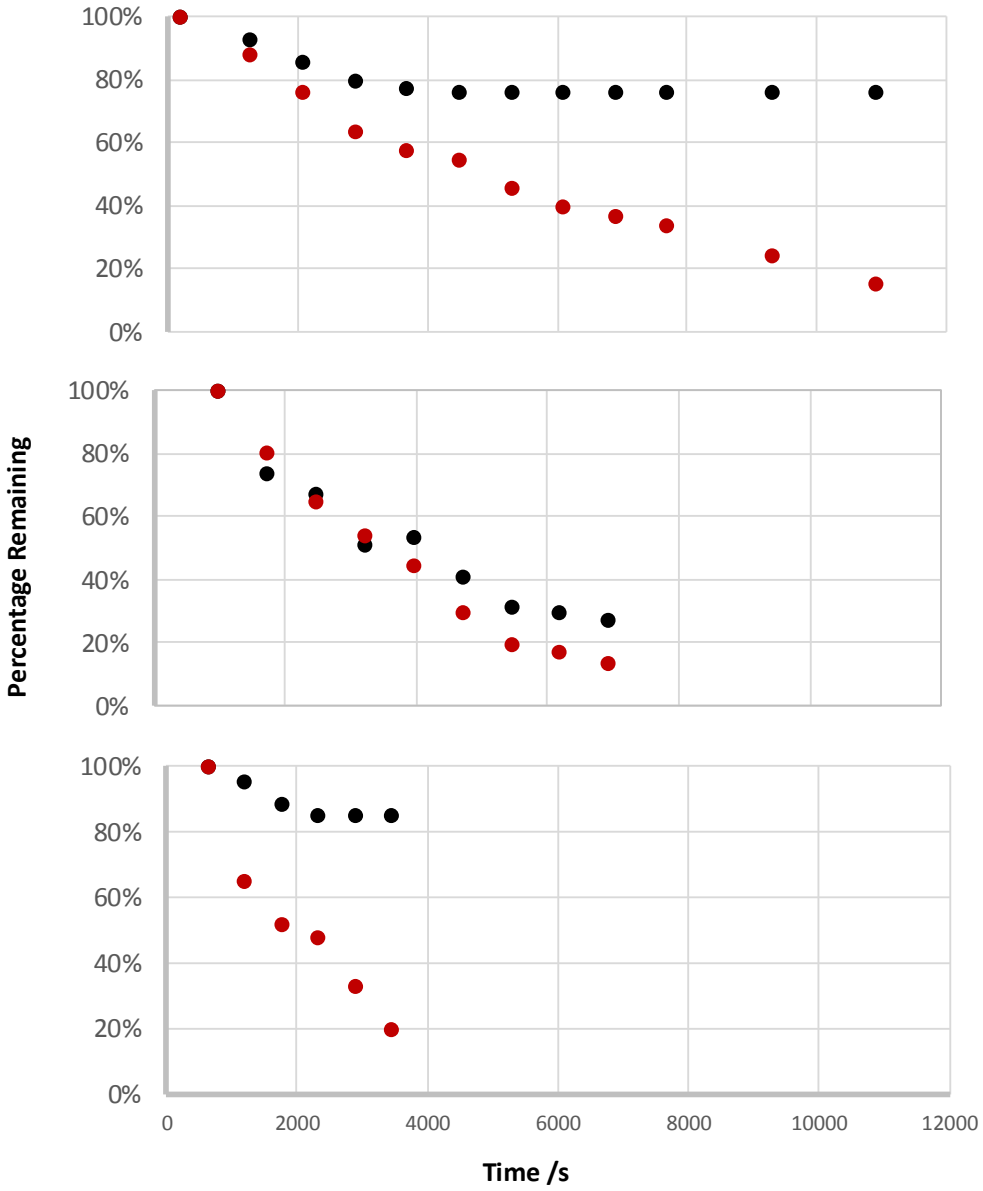

Figure S1. Concentration/time profiles for [Ni(COD)(dppf)] (**1**, black) and [NiCl(*o*-tol)(dppf)] (**3-Cl**, red) in comproportionation reactions with initial ratios of 1:1 (8 µmol **1**, 8 µmol **3-Cl**; top), 2:1 (8 µmol **1**, 4 µmol **3-Cl**; middle), and 1:2 (4 µmol **1**, 8 µmol **3-Cl**; bottom).

3.3 Data Analysis

In each plot, all experiments are displayed, not the average result from replicates. All experiments were performed in duplicate.

Order in *p*-$F_3CC_6H_4Cl$

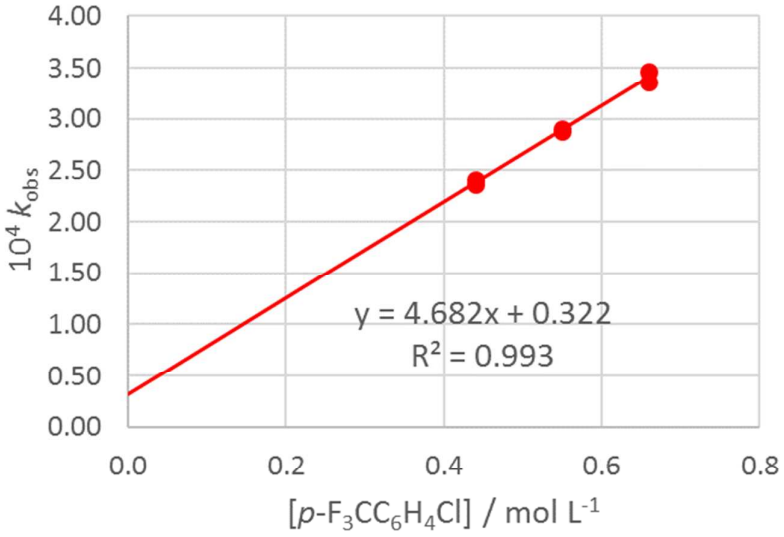

Figure S2. Plot of k_{obs} *versus* [*p*-$F_3CC_6H_4Cl$]; experiments carried out in benzene-d_6 at 50 °C.

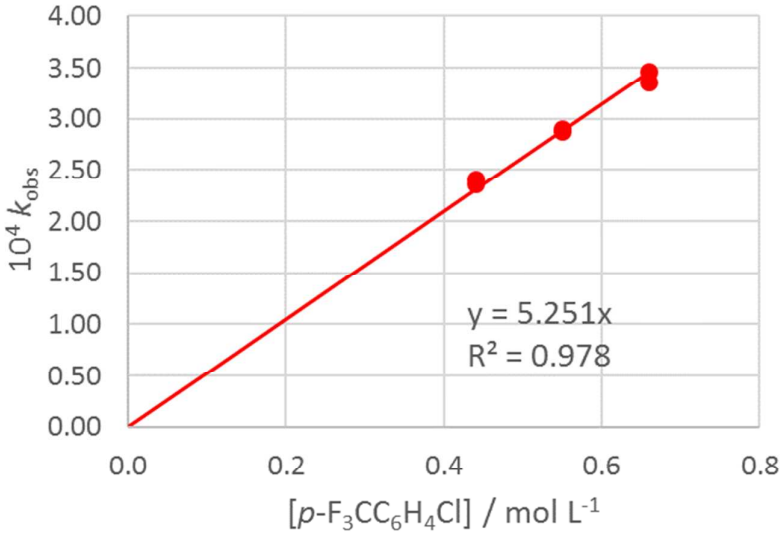

Figure S3. Plot of k_{obs} *versus* [*p*-$F_3CC_6H_4Cl$], with a forced zero intercept; experiments carried out in benzene-d_6 at 50 °C.

Order in COD

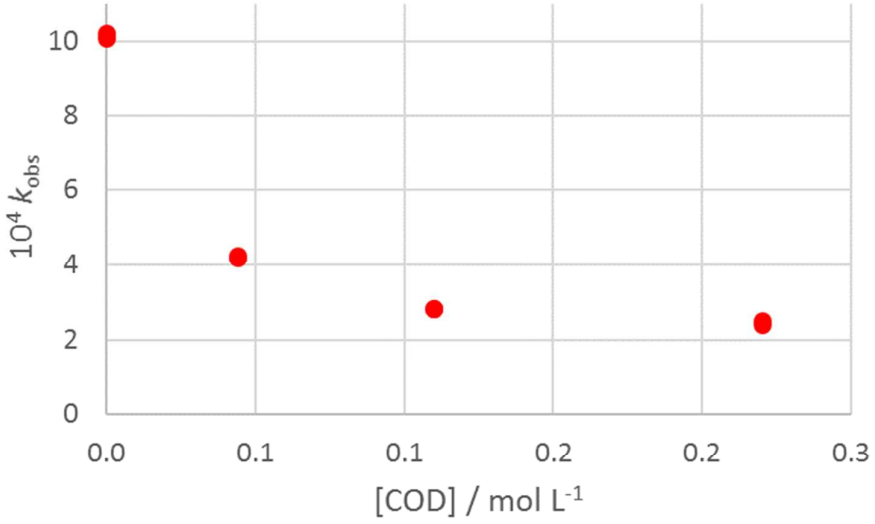

Figure S4. Plot of k_{obs} *versus* [COD]; experiments carried out with 20 equiv. *p*-$F_3CC_6H_4Br$ in benzene-d_6 at 50 °C.

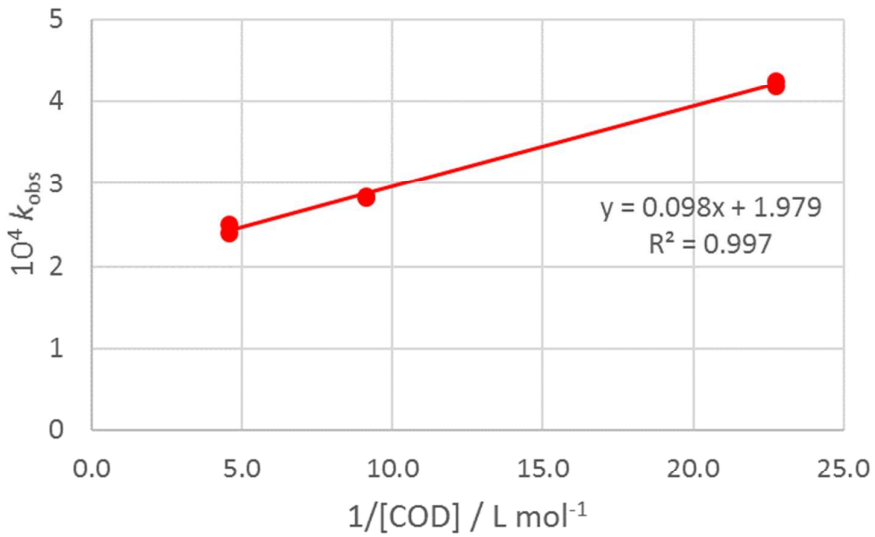

Figure S5. Plot of k_{obs} *versus* $[COD]^{-1}$; experiments carried out with 20 equiv. *p*-$F_3CC_6H_4Br$ in benzene-d_6 at 50 °C. The experiment with no added COD is not plotted.

Eyring Plot for *p*-$F_3CC_6H_4Br$

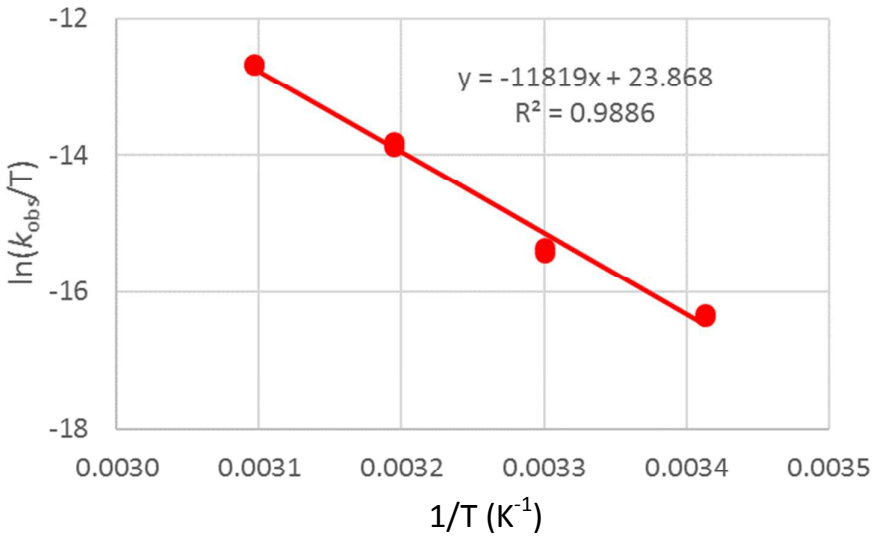

Figure S6. Eyring plot for the reaction of **1** with 20 equiv. *p*-$F_3CC_6H_4Br$ in benzene-d_6.

Errors were estimated as follows:

i. Take the difference between replicates as an estimate of the error in each point.
ii. For the leftmost and rightmost points on the plot, subtract the error from the lowest value replicate and add the error to the highest value replicate.
iii. Draw two lines that represent the 'worst case' under- and overestimates (i.e. maximum value at 1/T = 0.0031 to minimum value at 1/T = 0.0034, and *vice versa*)
iv. Use these lines to calculate $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, thereby giving an estimate of the error.

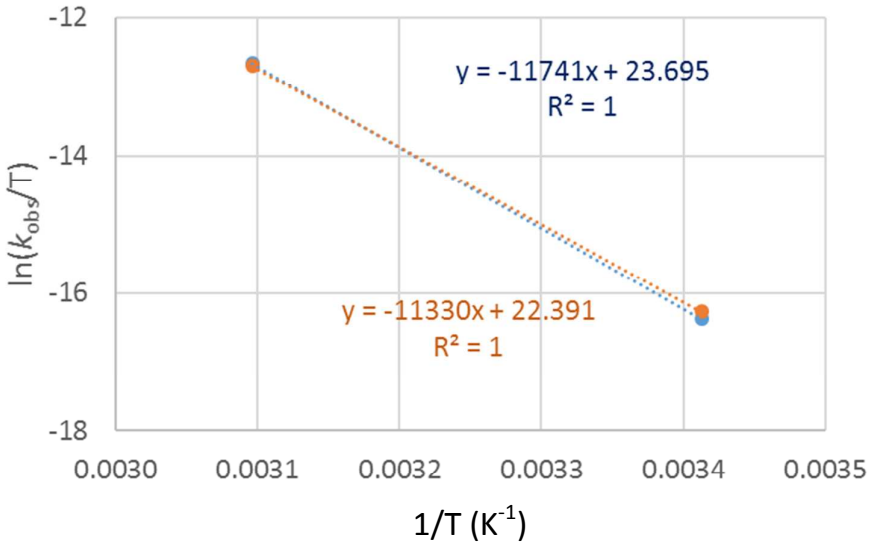

Figure S7. Estimation of errors in the Eyring plot for the reaction of **1** with 20 equiv. *p*-$F_3CC_6H_4Br$ in benzene-d_6.

Eyring Plot for *p*-$F_3CC_6H_4OTs$

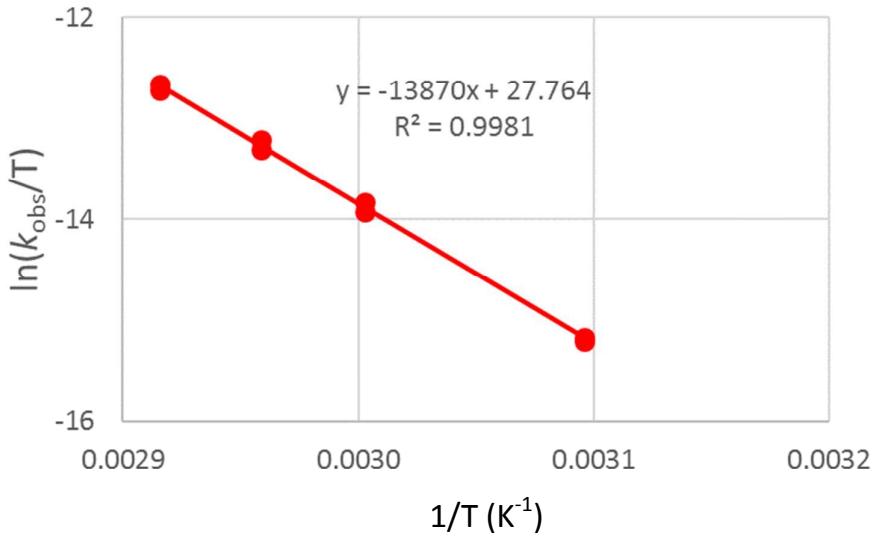

Figure S8. Eyring plot for the reaction of **1** with 20 equiv. *p*-$F_3CC_6H_4OTs$ in toluene-d_8.

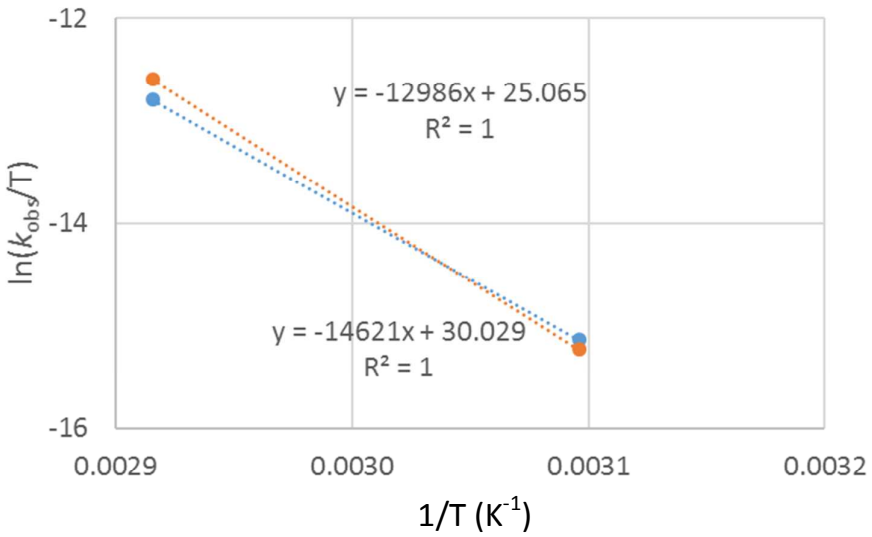

Figure S9. Estimation of errors in the Eyring plot for the reaction of **1** with 20 equiv. *p*-$F_3CC_6H_4OTs$ in toluene-d_8.

Eyring Plot for *p*-$F_3CC_6H_4OTf$

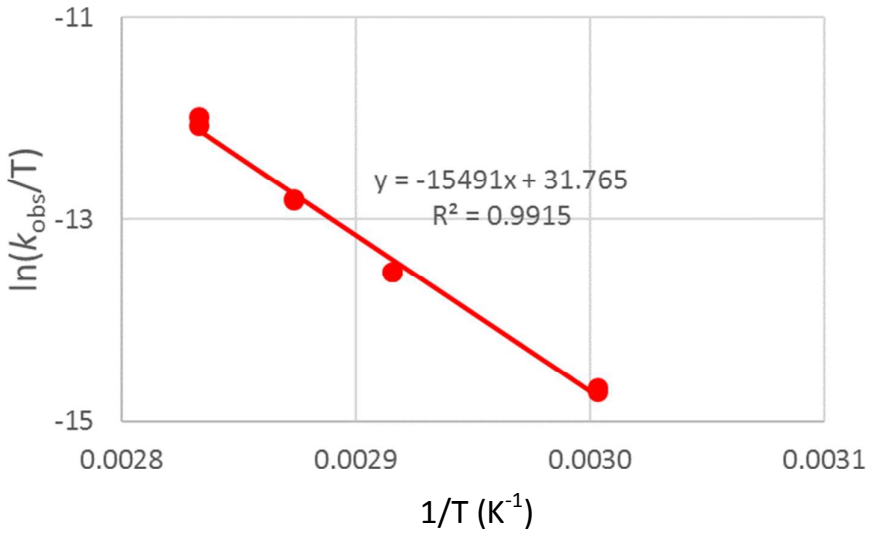

Figure S10. Eyring plot for the reaction of **1** with 20 equiv. *p*-$F_3CC_6H_4OTf$ in toluene-d_8.

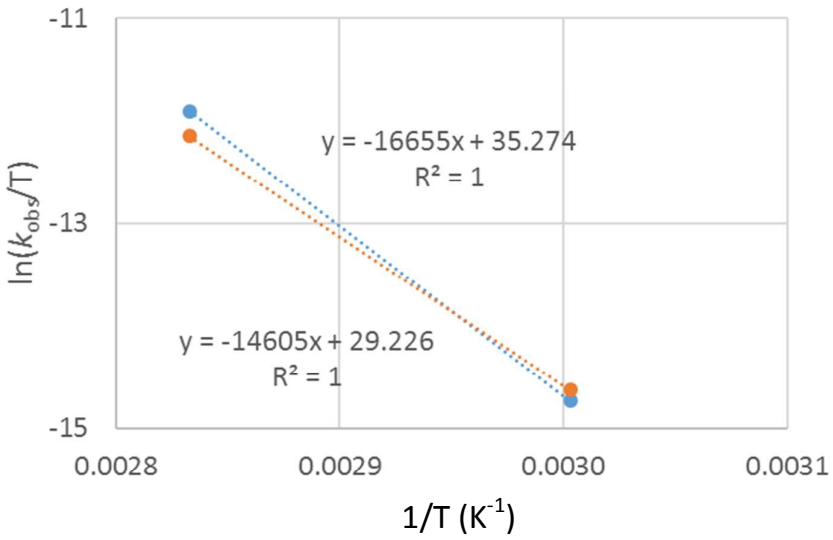

Figure S11. Estimation of errors in the Eyring plot for the reaction of **1** with 20 equiv. *p*-$F_3CC_6H_4OTf$ in toluene-d_8.

Hammett Analysis for Aryl Chlorides

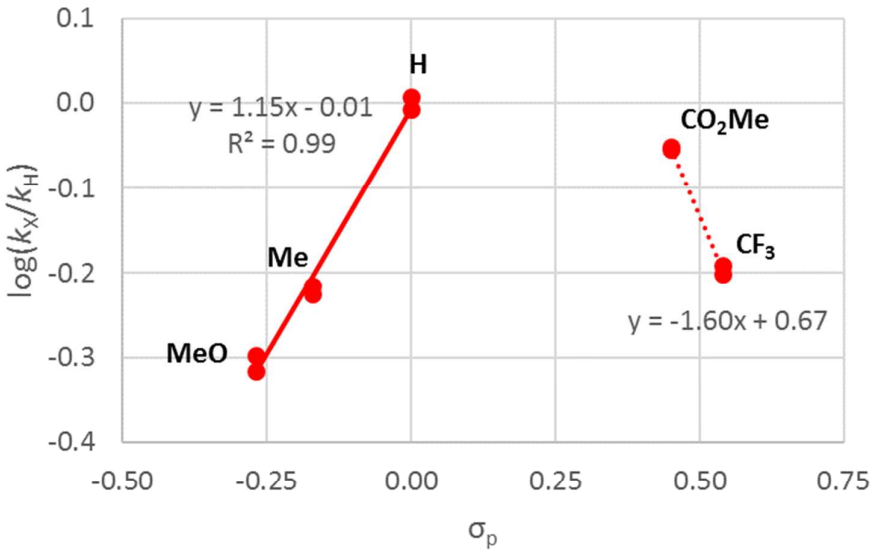

Figure S12. Hammett plot for the reaction of 20 equiv. *p*-XC_6H_4Cl with **1** in benzene-d_6 at 50 °C.

Table S2. Hammett analysis.

Substrate	σ	k_{obs}	Av. k_{obs}	k_X/k_H	Log(k_X/k_H)
p-MeO	-0.27	1.89×10^{-4}	1.85×10^{-4}	0.50	-0.30
		1.81×10^{-4}		0.48	-0.32
p-Me	-0.17	2.28×10^{-4}	2.26×10^{-4}	0.61	-0.22
		2.23×10^{-4}		0.60	-0.23
H	0.00	3.81×10^{-4}	3.75×10^{-4}	1.02	0.01
		3.68×10^{-4}		0.98	-0.01
p-MeOC(O)	0.45	3.31×10^{-4}	3.32×10^{-4}	0.88	-0.05
		3.33×10^{-4}		0.89	-0.05
p-F_3C	0.54	2.36×10^{-4}	2.39×10^{-4}	0.63	-0.20
		2.41×10^{-4}		0.64	-0.19

4. Stoichiometric Experiments

Styrene. An NMR tube was charged with **1** (8 mg, 0.011 mmol), styrene (25 µL, 0.22 mmol, 20 equiv.) and benzene-d_6 (0.5 mL).

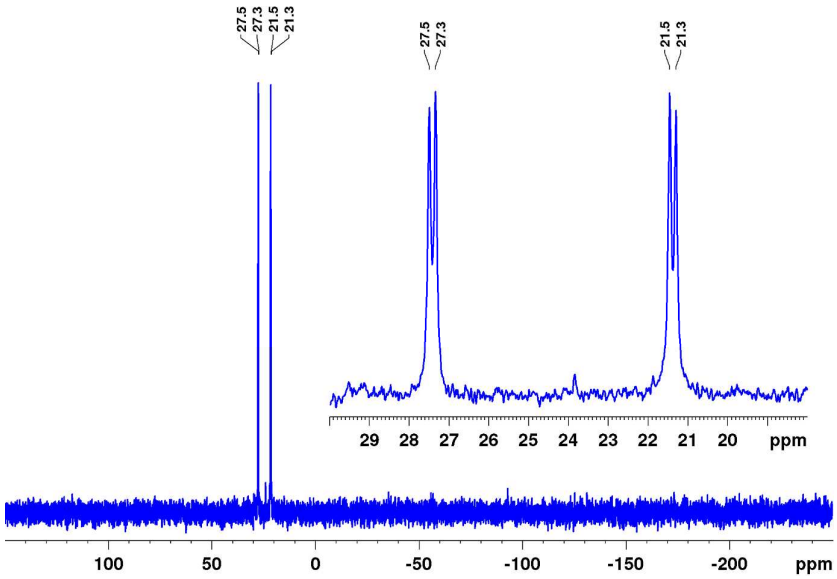

Figure S13. $^{31}P\{^1H\}$ NMR spectrum (δ_P = 27.5, 21.4 ppm; J = 31.2 Hz) for the reaction of **1** with 20 equiv. styrene.

4-Chlorostyrene. An NMR tube was charged with **1** (8 mg, 0.011 mmol), 4-chlorostyrene (28 µL, 0.22 mmol, 20 equiv.) and benzene-d_6 (0.5 mL).

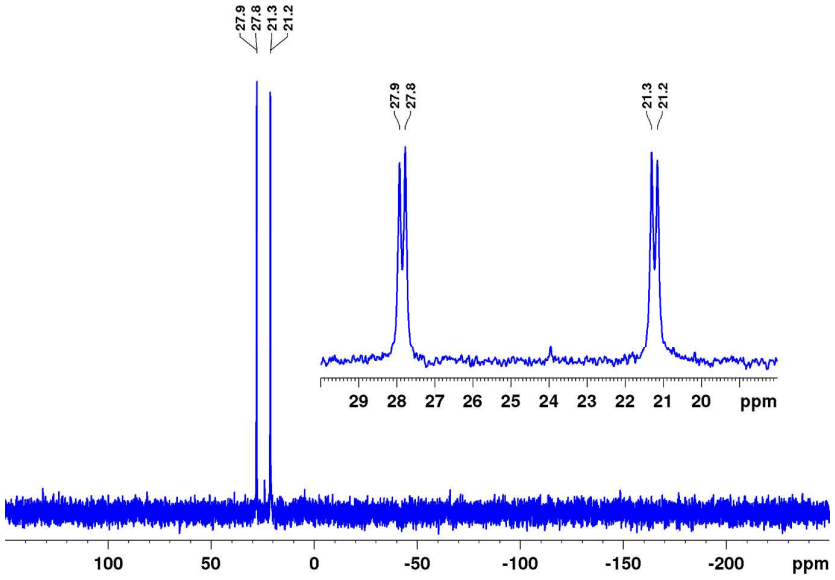

Figure S14. $^{31}P\{^1H\}$ NMR spectrum (δ_P = 27.9, 21.2 ppm; J = 30.4 Hz) for the reaction of **1** with 4-chlorostyrene.

1-naphthyl triflate. An NMR tube was charged with **1** (8 mg, 0.011 mmol) and 1-naphthyl triflate (22 µL, 0.11 mmol, 10 equiv.), and benzene-d_6 (0.5 mL).

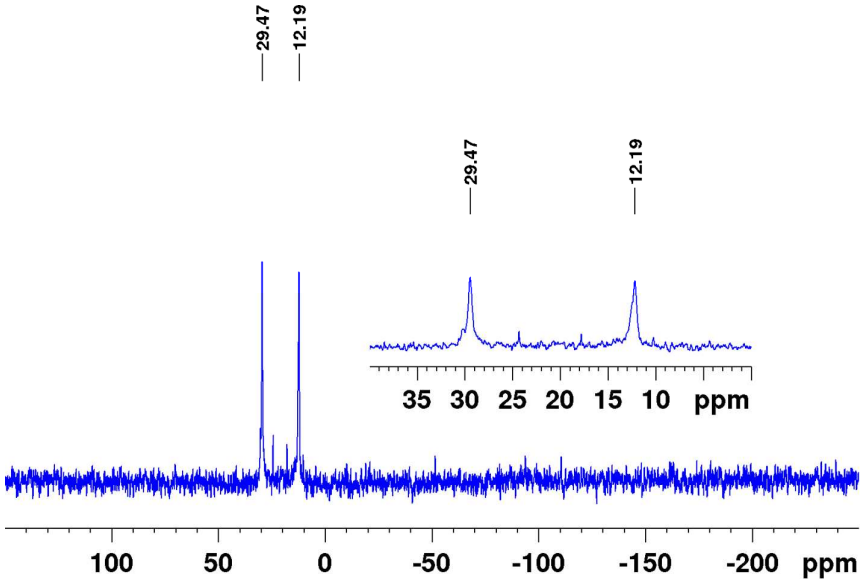

Figure S15. $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1** with 1-naphthyl triflate after 1 h at room temp. (δ_P = 29.5, 12.2 ppm).

1-naphthyl triflate/tetra(*n*-octyl)ammonium bromide. An NMR tube was charged with **1** (8 mg, 0.011 mmol) and 1-naphthyl triflate (22 µL, 0.11 mmol, 10 equiv.), (*n*-octyl)$_4$NBr (30 mg, 0.055 mmol, 5 equiv.) and benzene-d_6 (0.5 mL).

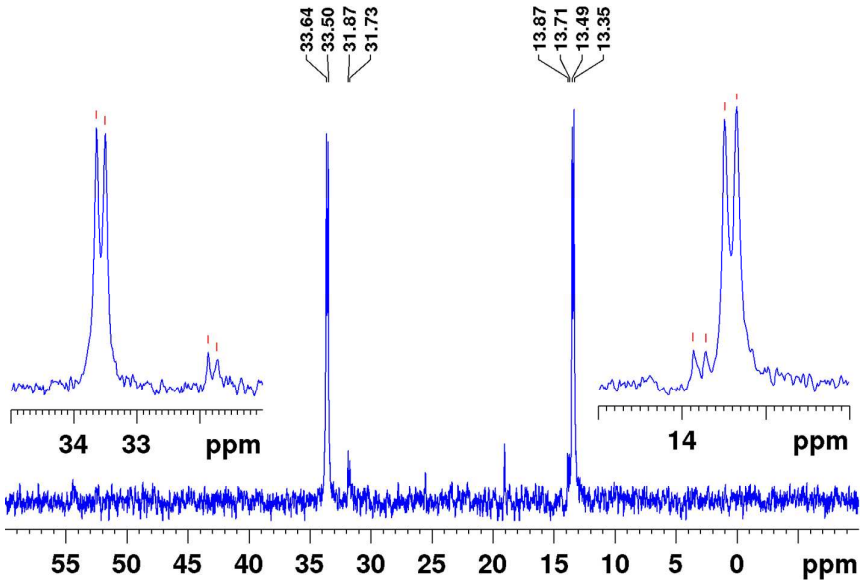

Figure S16. $^{31}P\{^1H\}$ NMR spectrum of the reaction of **1** with 1-naphthyl triflate and tetra(*n*-octyl)ammonium bromide after 3 days at room temp. (δ_P = 33.6, 13.4 ppm; J = 28.5 Hz), consistent with [NiBr(1-naphthyl)(dppf)].

Biphenylene. An NMR tube was charged with **1** (4 mg, 5.5 µmol) and biphenylene (3.4 mg, 0.022 mmol, 4 equiv.), and benzene-d_6 (0.5 mL). The ^{31}P NMR spectrum after 1 h at room temp. is below (δ_P = 13.4 ppm corresponds to the oxidative addition product; δ_P = 35.0 ppm corresponds to unreacted **1**). Attempts to drive the reaction to completion, either by heating or by leaving for extended periods at room temperature, led to decomposition.

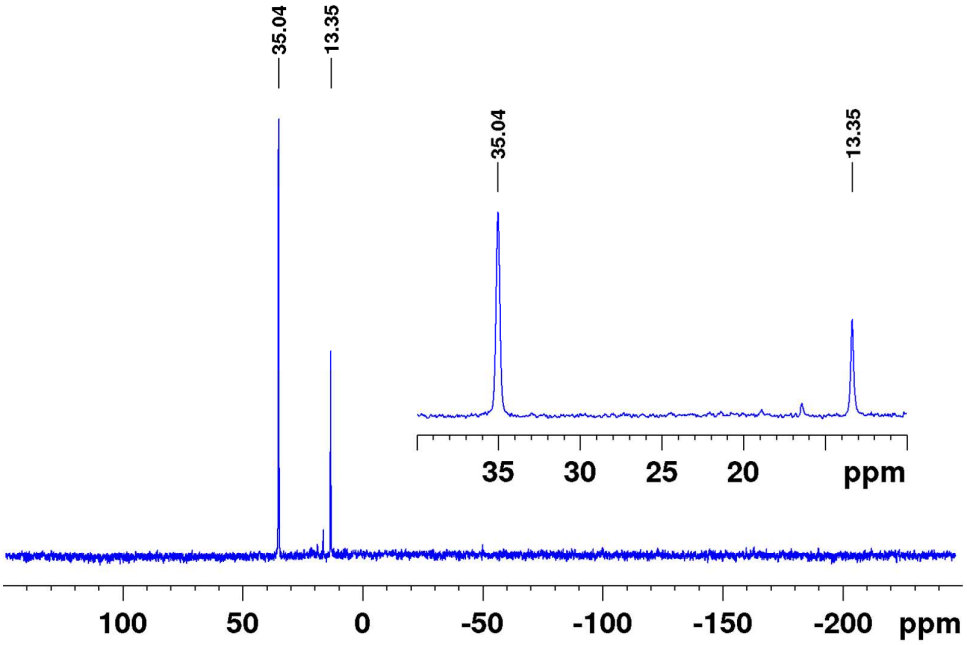

Figure S17. ^{31}P{^{1}H} NMR spectrum of the reaction of **1** with 4 equiv. biphenylene after 1 h at room temperature.

5. Catalytic Experiments

5.1 GC-FID Calibration

Calibration lines were determined from 5 – 10 samples, each weighed independently, containing known masses of the analyte of interest and tetradecane.

Table S3. Response factors for analytes detected by GC-FID analysis.

Analyte	**Response Factor**	**R^2**
naphthalene	0.6504	0.9992
1-phenylnaphthalene	0.9724	0.9998
2-phenylnaphthalene	0.9058	0.9959
1,1'-binaphthalene	1.2557	0.9997
2,2'-binaphthalene	0.5204	0.9945
1-bromonaphthalene	0.7171	0.9992
2-bromonaphthalene	0.6442	0.9988
1-tosylnapthalene	0.5729	0.9997
2-tosylnaphthalene	0.5500	0.9976
naphthalen-1-yl triflate	0.6047	0.9965
naphthalen-2-yl triflate	0.6561	0.9992
ethyl naphthalen-1-yl carbonate	0.7286	1.0000
ethyl naphthalen-1-yl carbonate	0.5953	0.9990
diethyl naphthalen-1-yl carbamate	0.9312	0.9994
diethyl naphthalen-2-yl carbamate	0.8168	0.9999
naphthalen-1-yl pivalate	0.9671	0.9963
naphthalen-2-yl pivalate	0.9185	0.9995
dimethyl naphthalen-1-yl sulfamate	0.6733	0.9998
dimethyl naphthalen-2-yl sulfamate	0.6536	0.9997

5.2 General Procedure

All reactions were set up within the glovebox to ensure a consistent, oxygen- and moisture-free atmosphere. Analysis was performed by GC-FID analysis because this allows detection and accurate quantification of reaction components that might be lost during work-up procedures or purification by column chromatography. Naphthyl substrates were used to probe the effect of steric environment on reaction outcome, and because naphthalene can be straightforwardly detected by GC-FID, whereas smaller arenes may co-elute with the solvent peak (toluene).

In the glovebox, a vial was loaded with the substrate (0.25 mmol), $PhB(OH)_2$ (0.5 mmol), K_3PO_4 (0.75 mmol), and [Ni(COD)(dppf)] (25 µmol, 10 mol% or 2.5 µmol, 1 mol%). A stirrer bar and anhydrous toluene (1 mL) were added and the vial was closed and removed from the glovebox. The reaction was inserted into a pre-heated aluminium block at 90 °C for 4 hours. The vial was then removed from the block and opened to the air, diluted with toluene, and filtered to remove solid particulates. Analysis was conducted using GC-FID instrumentation that had been calibrated for each component.

6. X-Ray Crystallography

Data were measured at low temperature with an Oxford Diffraction Xcalibur E instrument and with monochromated MoKα radiation. Both structures were refined to convergence, on F2 and against all unique reflections with SHELX-97.[16] Selected crystallographic and geometric parameters are below.

Table S4. X-ray crystallography data.

Compound	**2-Br.0.75THF**	**2-I**
Formula	$C_{71}H_{62}Br_2\ Fe_2Ni_2O_{0.75}P_4$	$C_{68}H_{56}Fe_2I_2Ni_2P_4$
Formula Weight	1440.03	1479.93
Crystal system	Monoclinic	Triclinic
Space Group	C 2/c	P -1
λ /Å	0.71073	0.71073
***a* /Å**	24.0416(4)	8.853(2)
***b* /Å**	13.7277(2)	13.508(3)
***c* /Å**	18.7831(3)	14.046(4)
α /°	90	65.71(3)
β /°	91.188(2)	73.50(3)
γ /°	90	72.75(2)
Volume /Å^3	6197.76(17)	1436.6(6)
Temp. /K	130(2)	123(2)
Z	4	1
Refls. Collected	15193	6036
2θ max °	58	44.1
Refls. Unique	7468	3515
Refls. Obs.	5781	2278
Rint	0.0288	0.0706
Goodness of Fit	1.018	1.024
R[I>2s(I)], *F*	0.0403	0.0678
Rw, *F*^{2}	0.0972	0.1357
Max/min electron density /eÅ^{-3}	0.866/-0.753	0.893/-0.734

For **2-Br**, a partially present THF solvent molecule was disordered about the crystallographically imposed 2-fold axis. After trial calculations, sof factors for THF were set such that there are 0.75 molecules of THF present per centrosymmetric dimer of **2-Br**. Restraints were placed on the displacement parameters of the THF group to approximate normal behaviour.

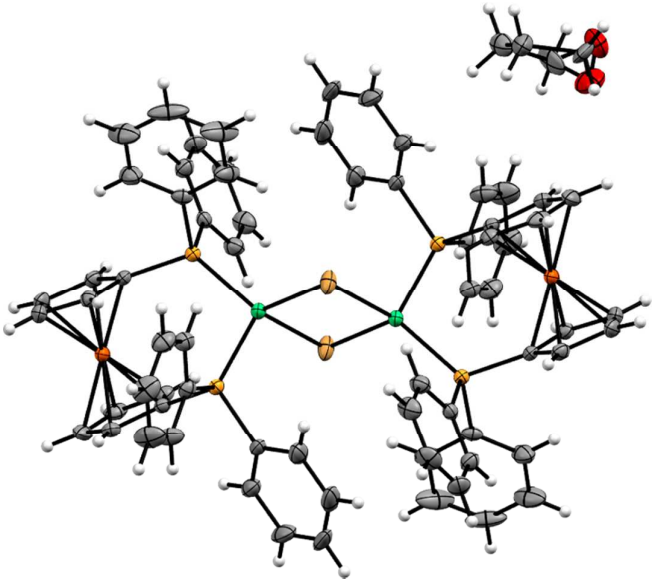

Figure S18. Molecular representation of (**2-Br**)$_2$ from X-ray crystallographic analysis, with all hydrogen atoms displayed. Thermal ellipsoids are drawn at 50% probability.

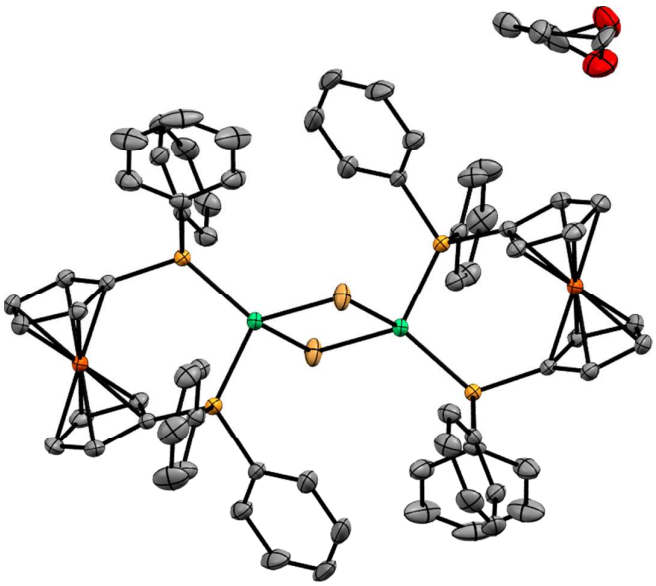

Figure S19. Molecular representation of (**2-Br**)$_2$ from X-ray crystallographic analysis, with all hydrogen atoms omitted. Thermal ellipsoids are drawn at 50% probability.

[Ni(μ-I)(dppf)]$_2$ **CCDC Reference: 1478812**

Crystals of **2-I** were found to be polycrystalline. Data for the structure presented was obtained from a small sliver cut from one such polycrystalline block. Although this sample appeared to be relatively single, it diffracted weakly and only at low angles. The structure is thus of low resolution and is used only as proof of atomic connectivity and of the dimeric nature of the compound. Given that the observed molecular structure is similar to that of the well characterised **2-Br**, the low resolution structure is sufficient for these purposes.

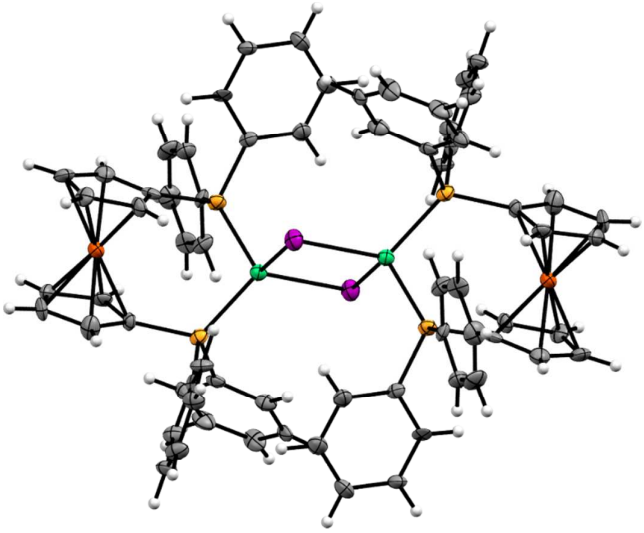

Figure S20. Molecular representation of (**2-Br**)$_2$ from X-ray crystallographic analysis, with all hydrogen atoms displayed. Thermal ellipsoids are drawn at 50% probability.

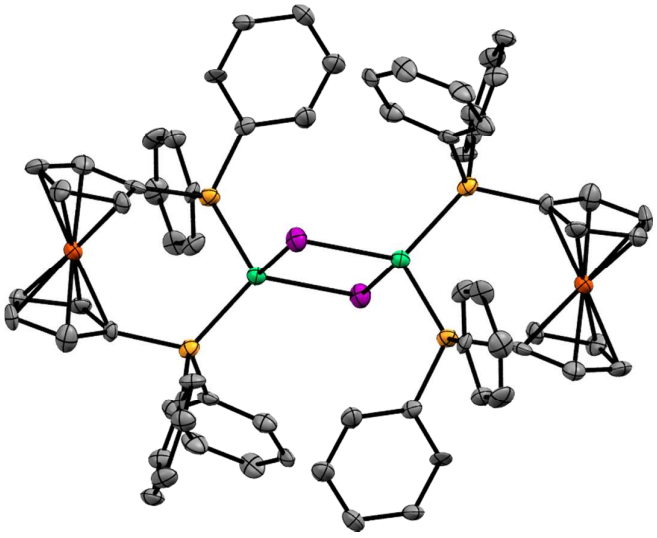

Figure S21. Molecular representation of (**2-I**)$_2$ from X-ray crystallographic analysis, with all hydrogen atoms omitted. Thermal ellipsoids are drawn at 50% probability.

7. EPR Data

Table S5. EPR Simulation Parameters

Complex	g_{iso}	A_{iso} [a]
2-Cl	2.172	66.0
2-Br[b]	2.185	62.5
2-I[b]	2.201	60.0
2-OTf	2.172	65.0
2-OTs	2.170	64.5
2-OPiv[c]	2.172	64.5
2-OCO_2Et	2.172	66.0
2-$OCONEt_2$	2.172	64.5
2-OSO_2NMe_2	2.171	65.0

[a] Hyperfine coupling of two ^{31}P nuclei of the dppf ligand in units 10^{-4} cm^{-1}. [b] Spectra recorded in THF solution. [c] Simulation includes 16% contribution of a second species: g_{iso} = 2.144; A_{iso} = 66.0 × 10^{-4} cm^{-1}.

8. NMR Spectra

[NiBr$_2$(dppf)]

^{1}H NMR

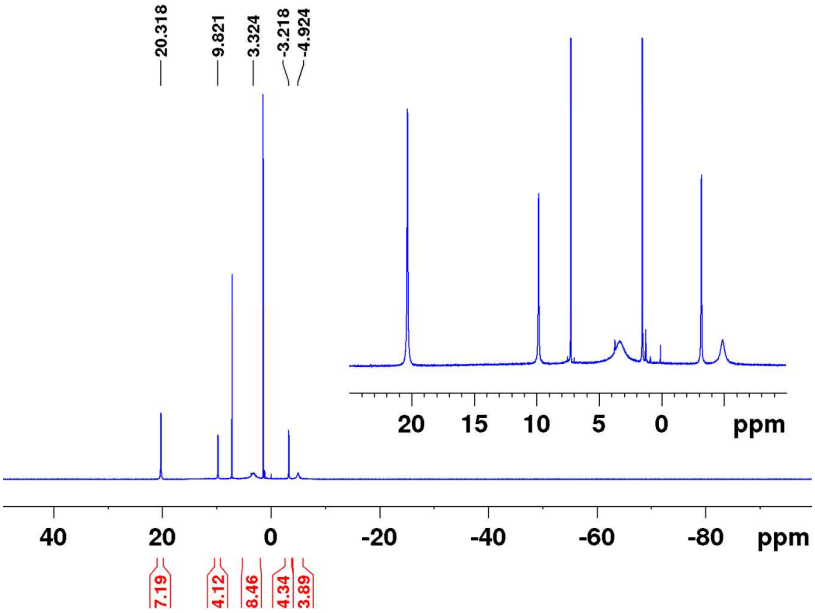

Figure S22. ^{1}H NMR spectrum of [NiBr$_2$(dppf)].

[NiI$_2$(dppf)]

^{1}H NMR

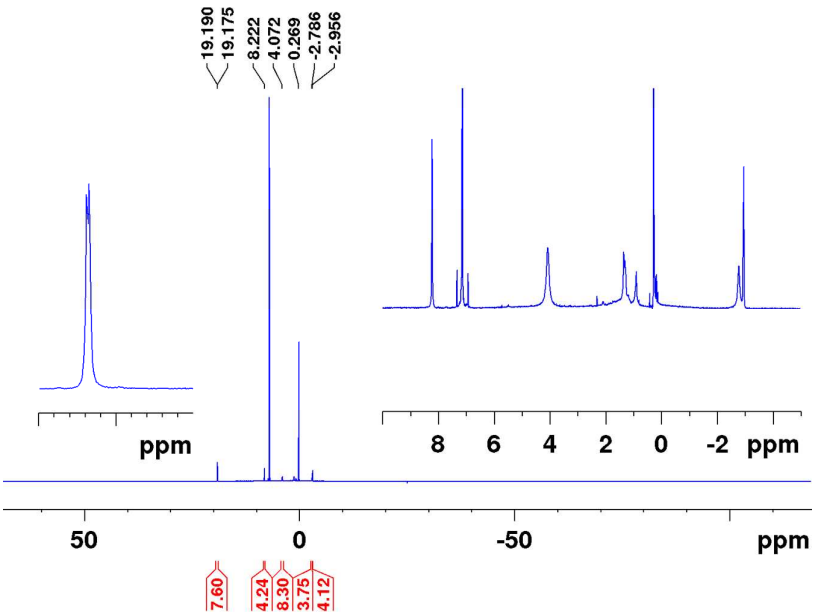

Figure S23. ^{1}H NMR spectrum of [NiI$_2$(dppf)].

[Ni(μ-Br)(dppf)]$_2$

^{1}H NMR

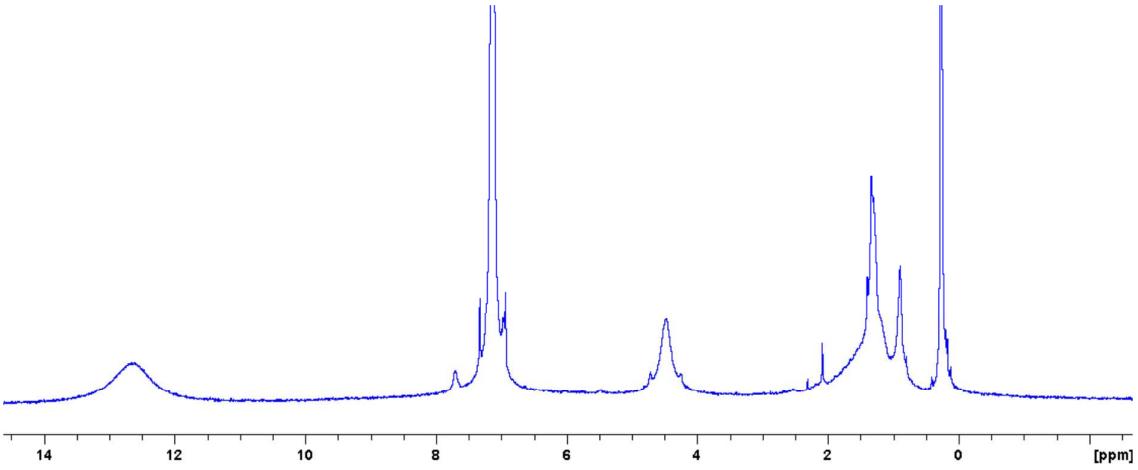

Figure S24. ^{1}H NMR spectrum of [Ni(μ-Br)(dppf)]$_2$.

[Ni(μ-I)(dppf)]$_2$

^{1}H NMR

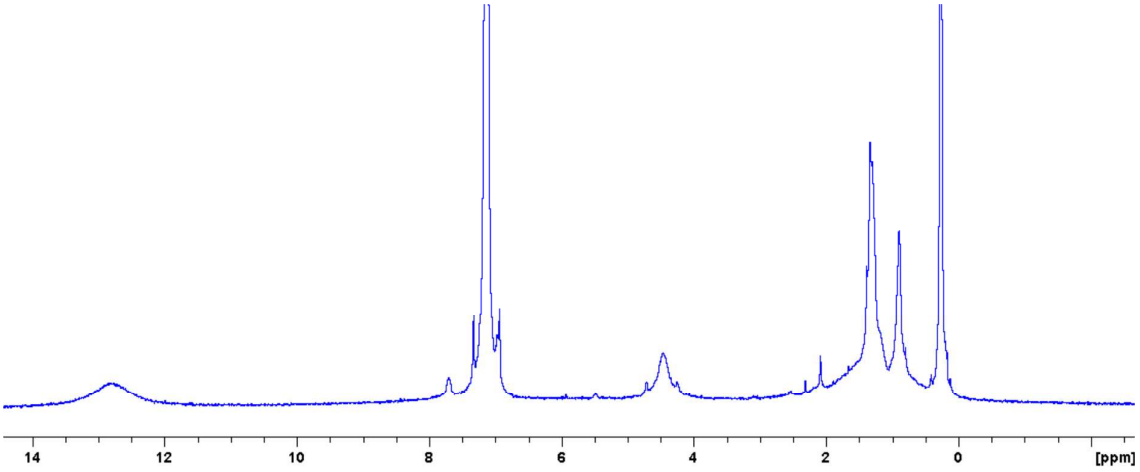

Figure S25. ^{1}H NMR spectrum of [Ni(μ-I)(dppf)]$_2$.

Para-trifluoromethylphenyl tosylate

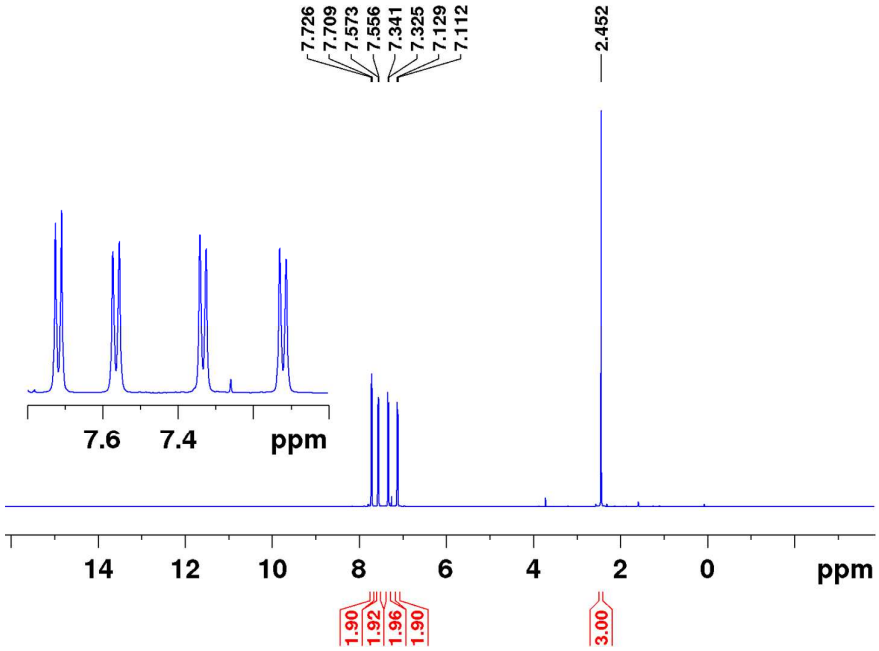

Figure S26. ^{1}H NMR spectrum of *p*-$F_3CC_6H_4OTs$.

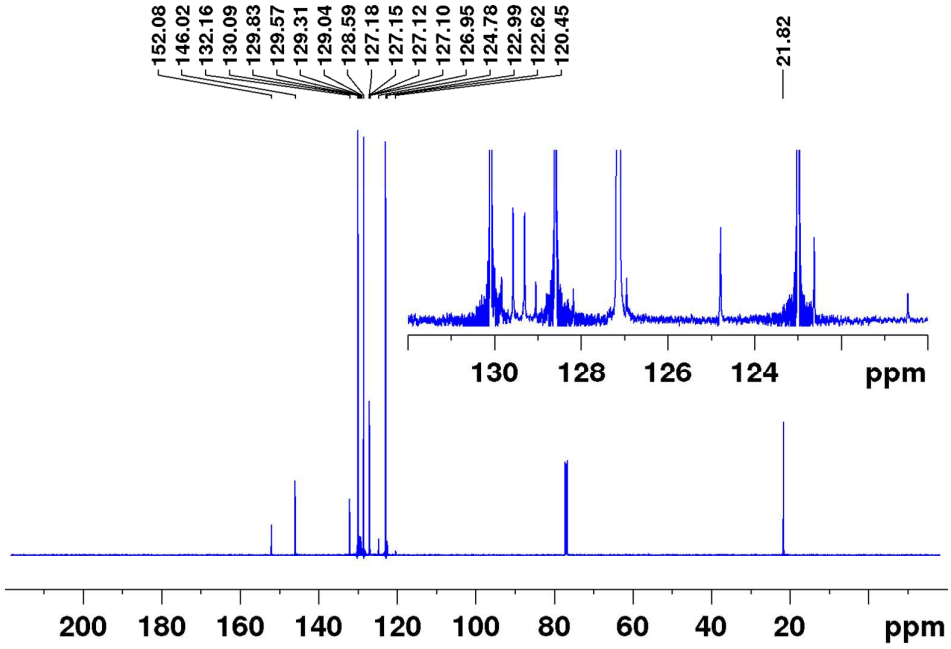

Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OTs$.

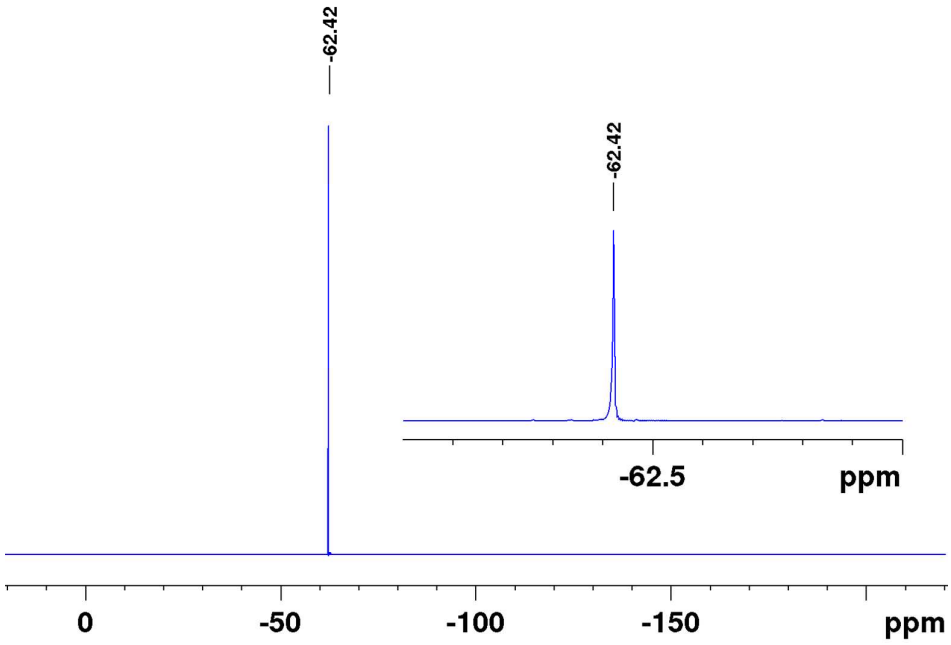

Figure S28. $^{19}F\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OTs$.

Para-trifluoromethylphenyl ethyl carbonate

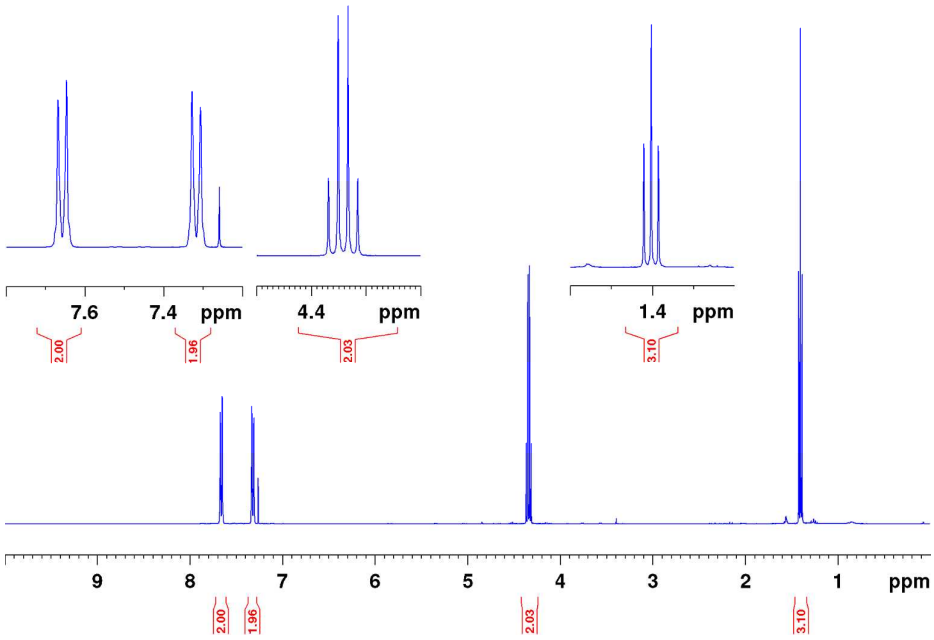

Figure S29. ^{1}H NMR spectrum of *p*-$F_3CC_6H_4OCO_2Et$.

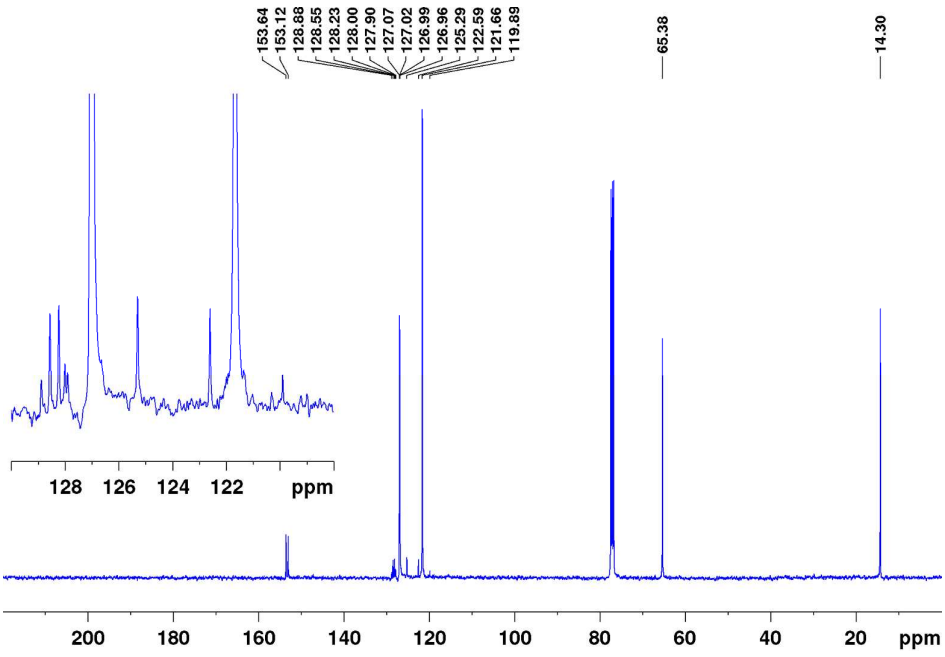

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OCO_2Et$.

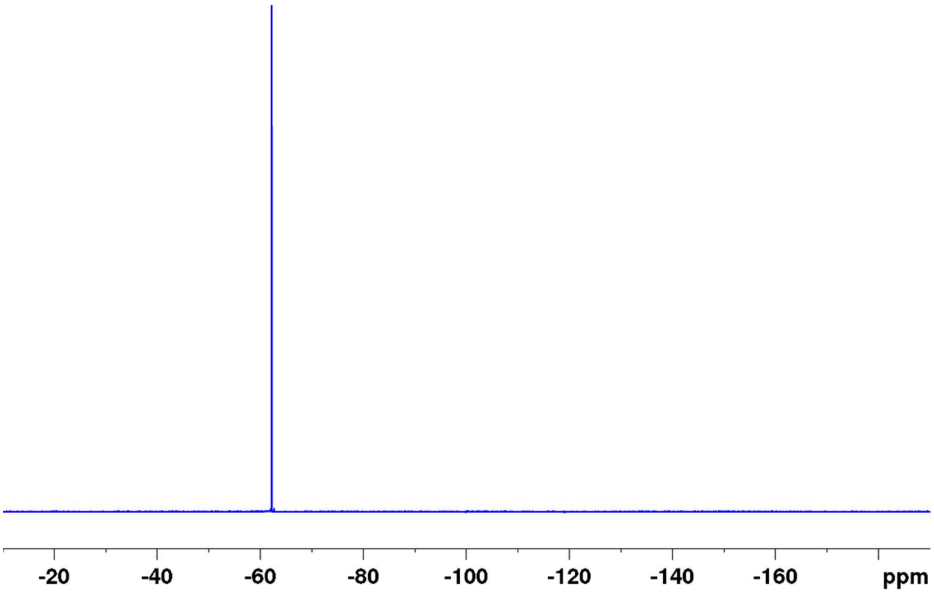

Figure S31. ^{19}F NMR spectrum of *p*-$F_3CC_6H_4OCO_2Et$.

Para-trifluoromethylphenyl triflate

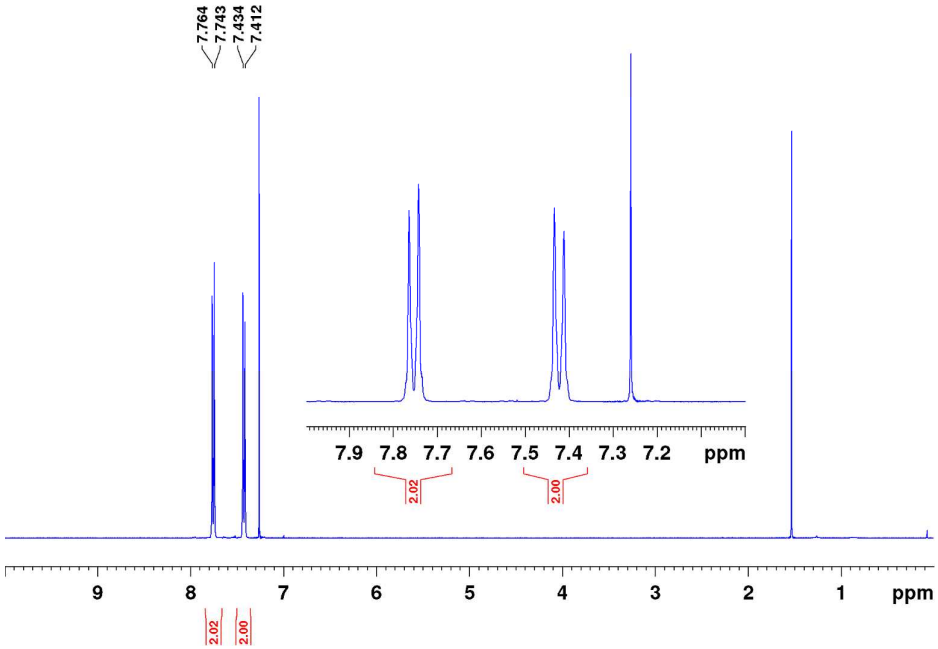

Figure S32. ^{1}H NMR spectrum of *p*-$F_3CC_6H_4OTf$.

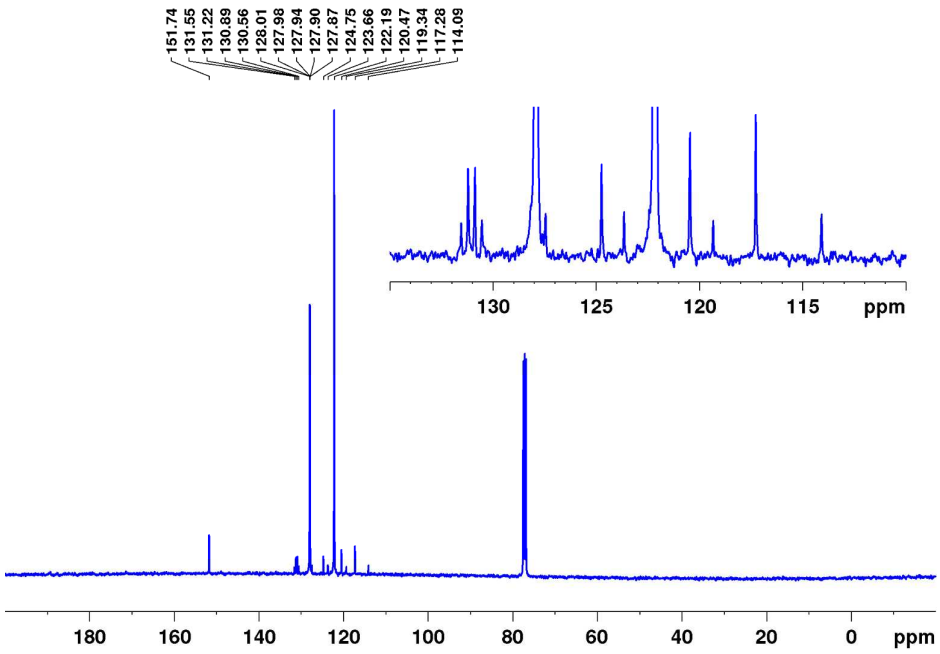

Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OTf$.

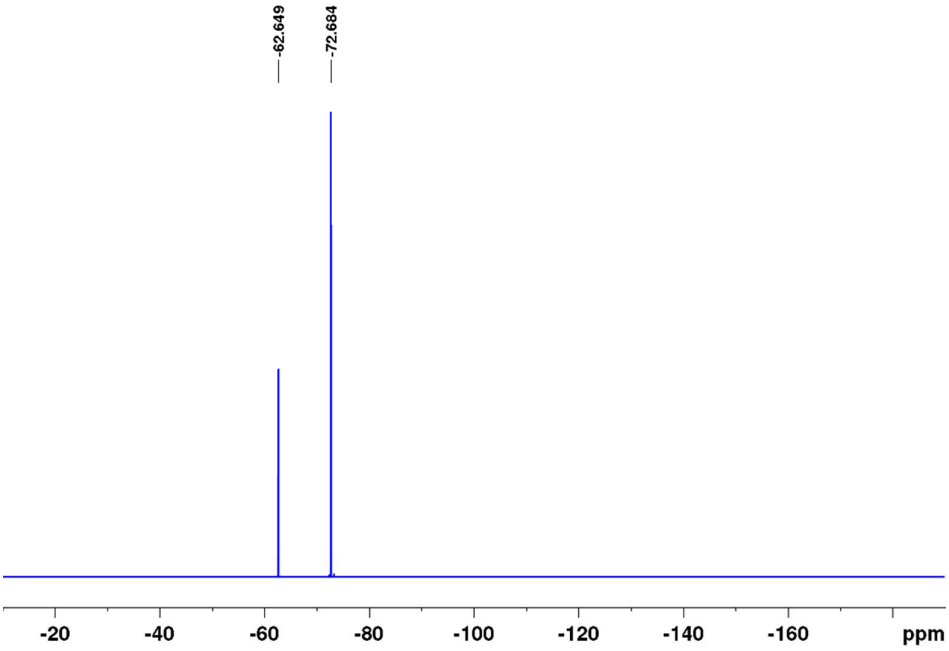

Figure S34. ^{19}F NMR spectrum of *p*-$F_3CC_6H_4OTf$.

Para-trifluoromethylphenyl diethylcarbamate

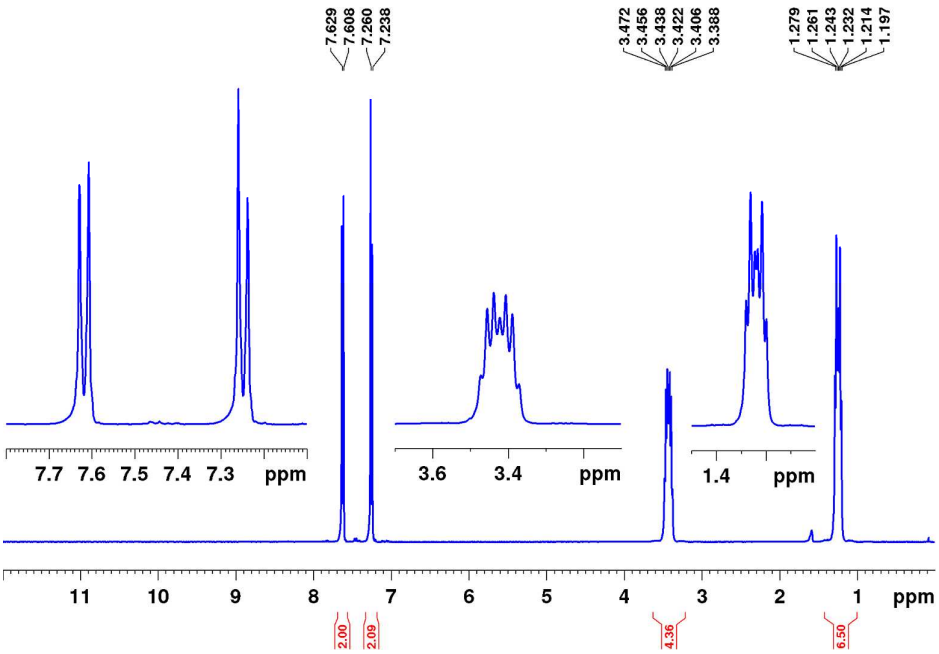

Figure S35. ^{1}H NMR spectrum of *p*-$F_3CC_6H_4OCONEt_2$.

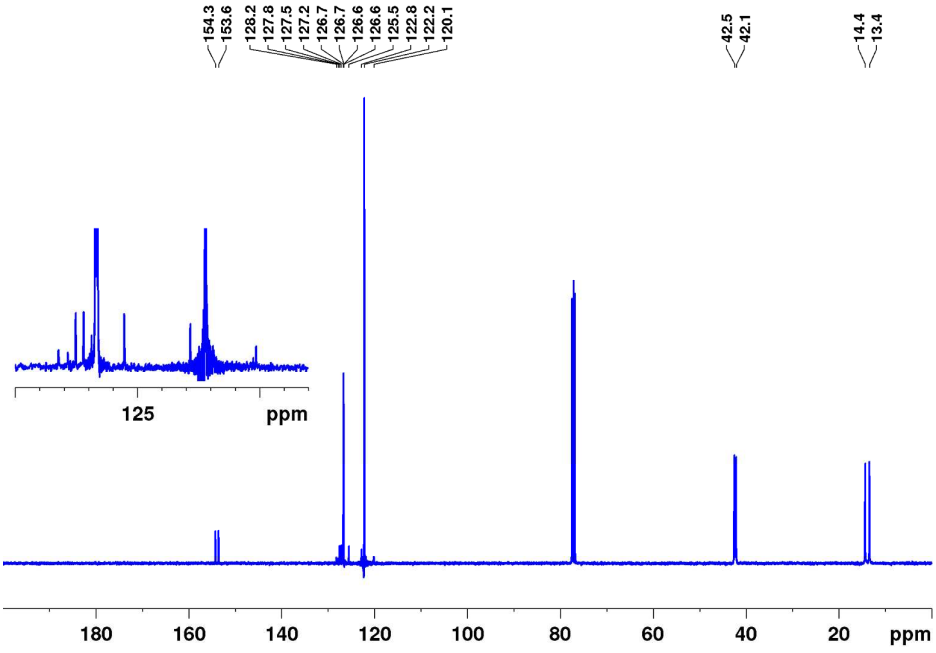

Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OCONEt_2$.

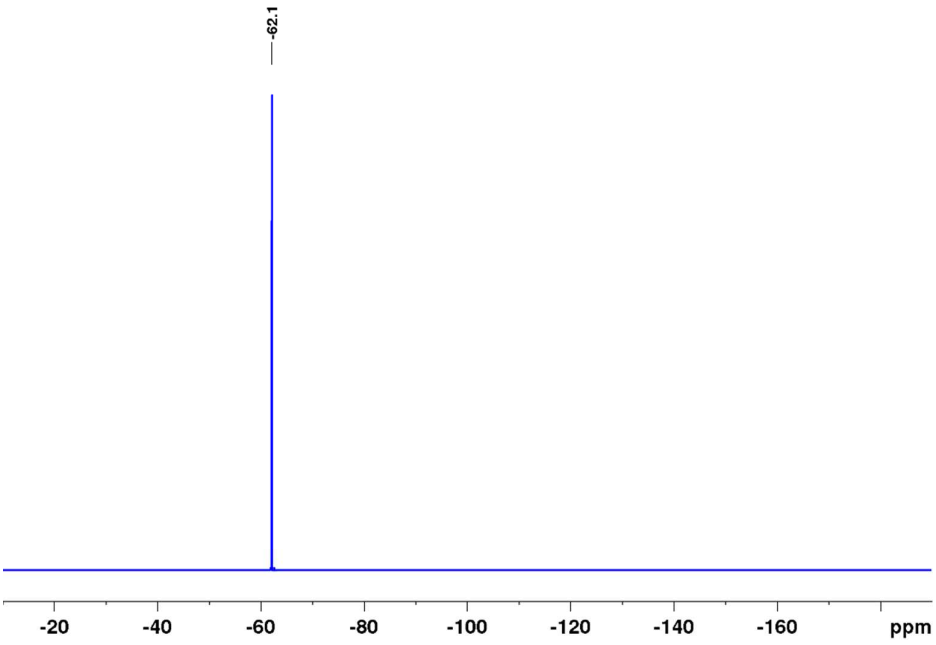

Figure S37. ^{19}F NMR spectrum of *p*-$F_3CC_6H_4OCONEt_2$.

Para-trifluoromethylphenyl pivalate

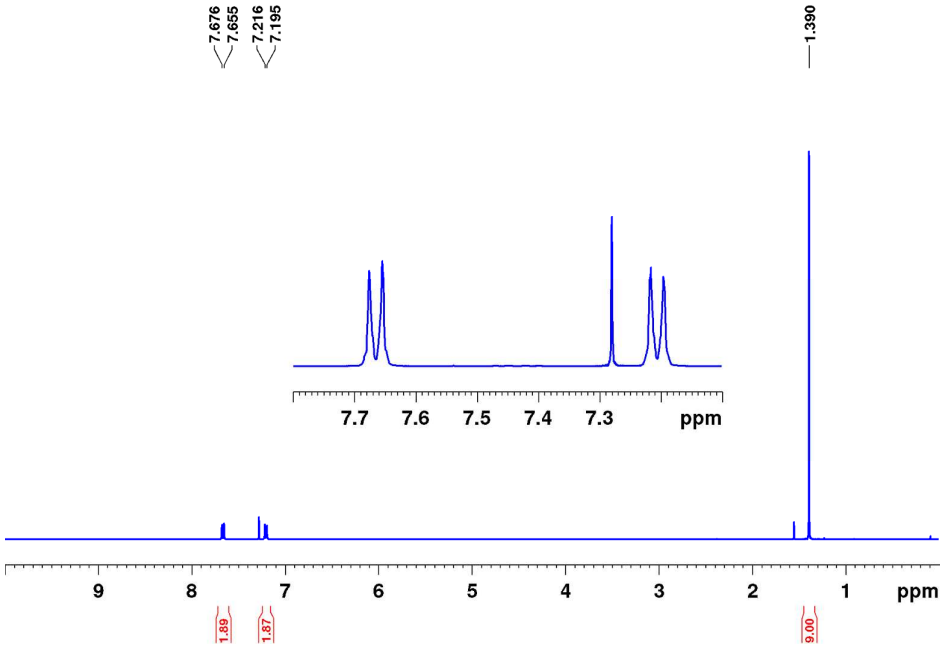

Figure S38. ^{1}H NMR spectrum of *p*-$F_3CC_6H_4OPiv$.

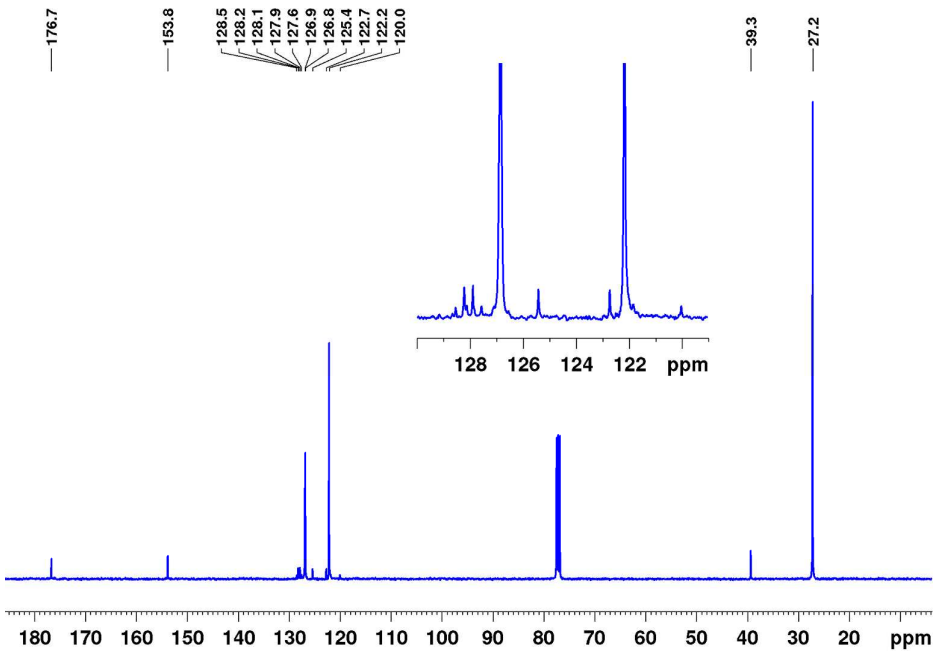

Figure S39. $^{13}C\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OPiv$.

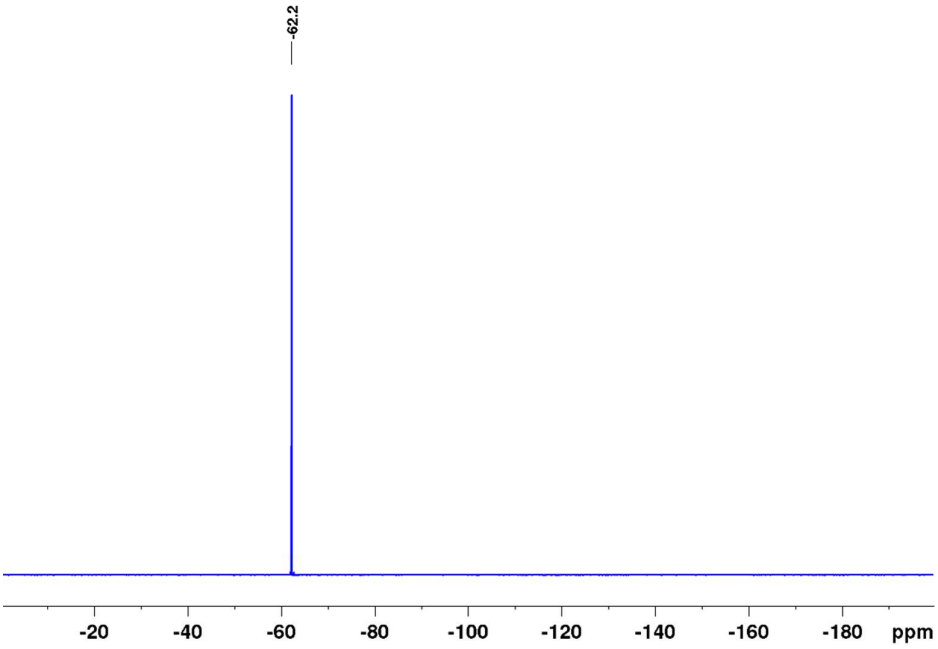

Figure S40. ^{19}F NMR spectrum of *p*-$F_3CC_6H_4OPiv$.

Para-trifluoromethylphenyl dimethylsulfonamide

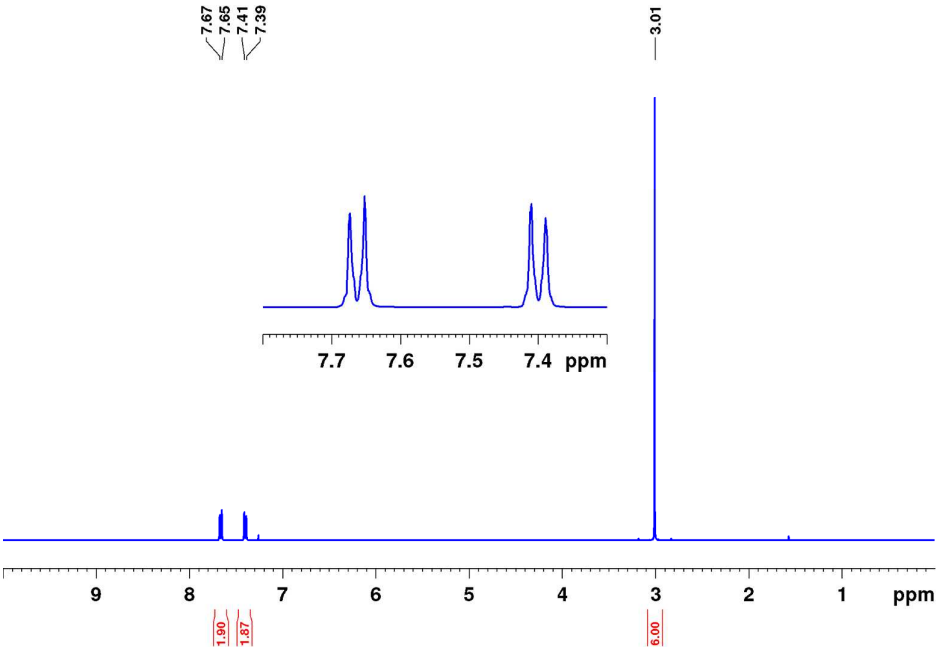

Figure S41. ^{1}H NMR spectrum of *p*-$F_3CC_6H_4OSO_2NMe_2$.

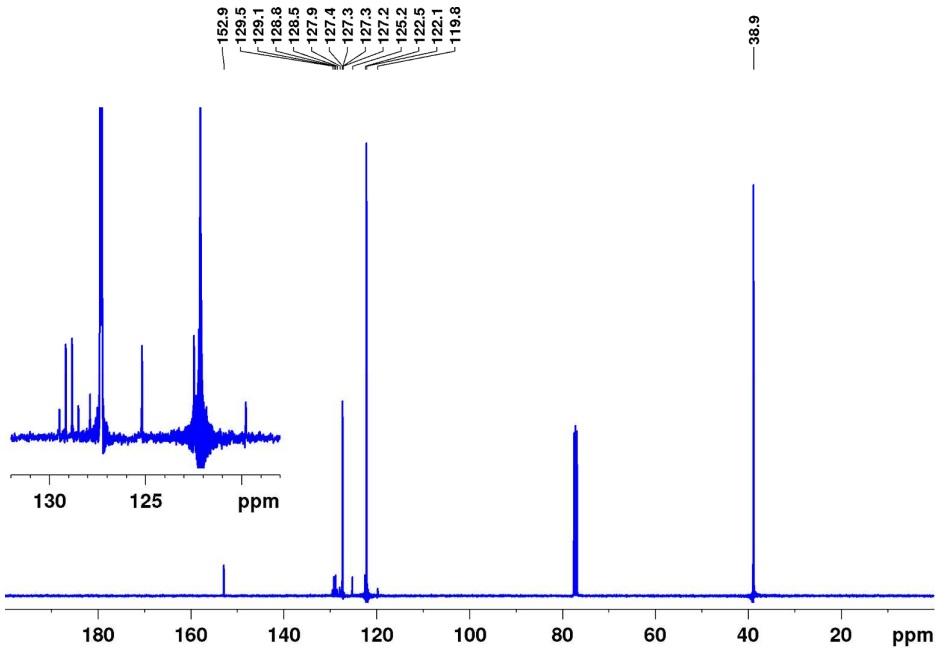

Figure S42. $^{13}C\{^{1}H\}$ NMR spectrum of *p*-$F_3CC_6H_4OSO_2NMe_2$.

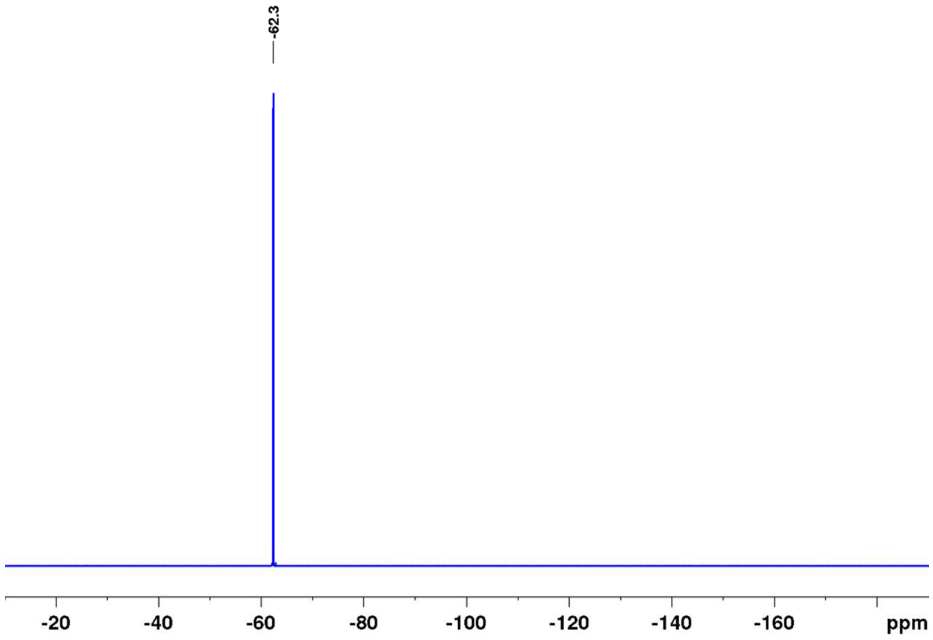

Figure S43. ^{19}F NMR spectrum of *p*-$F_3CC_6H_4OSO_2NMe_2$.

4,4'-bis(trifluoromethyl)biphenyl

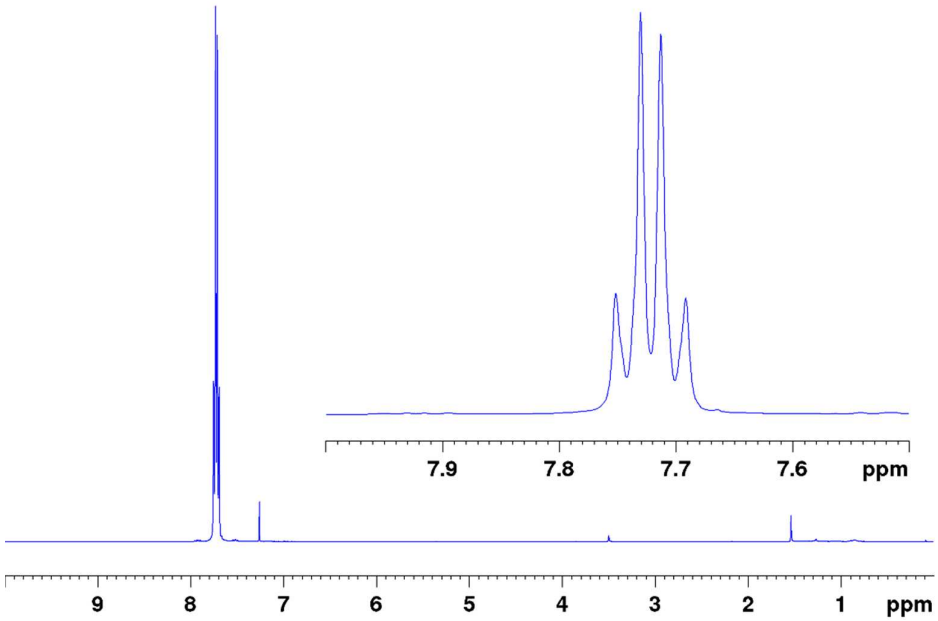

Figure S44. ^{1}H NMR spectrum of (p-$F_3CC_6H_4)_2$.

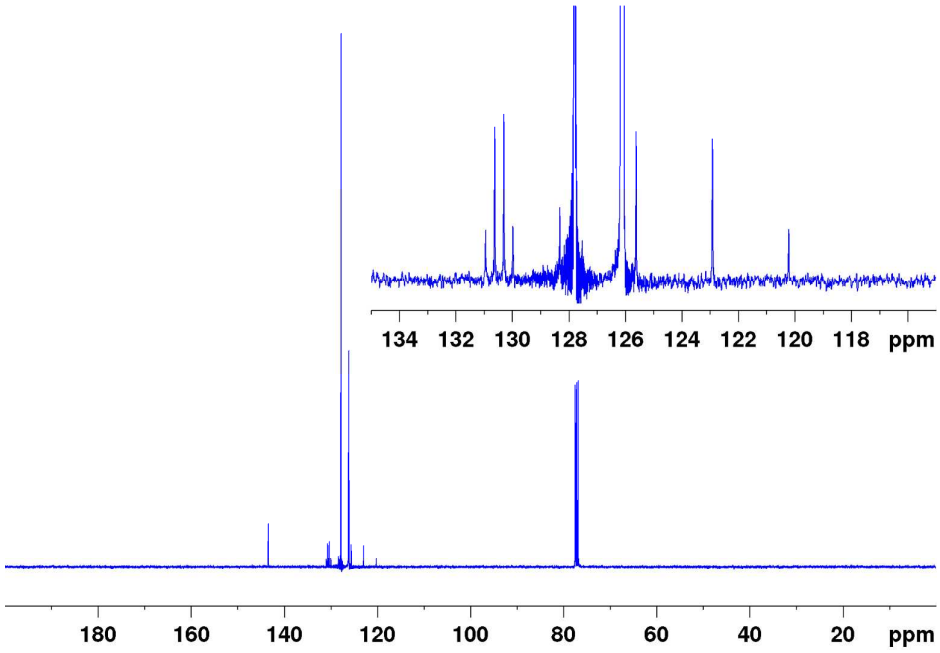

Figure S45. $^{13}C\{^{1}H\}$ NMR spectrum of (p-$F_3CC_6H_4)_2$.

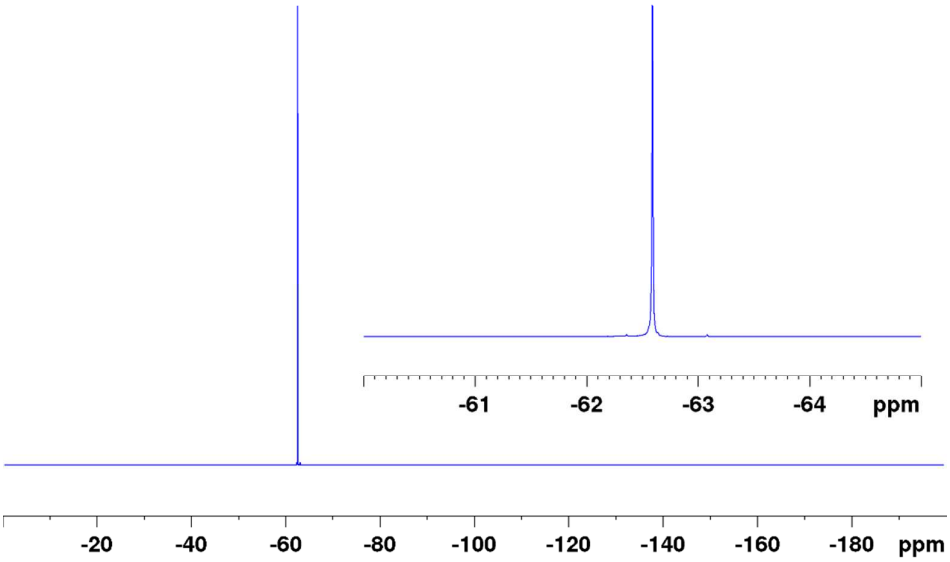

Figure S46. ^{19}F NMR spectrum of (p-$F_3CC_6H_4)_2$.

1-phenylnaphthalene

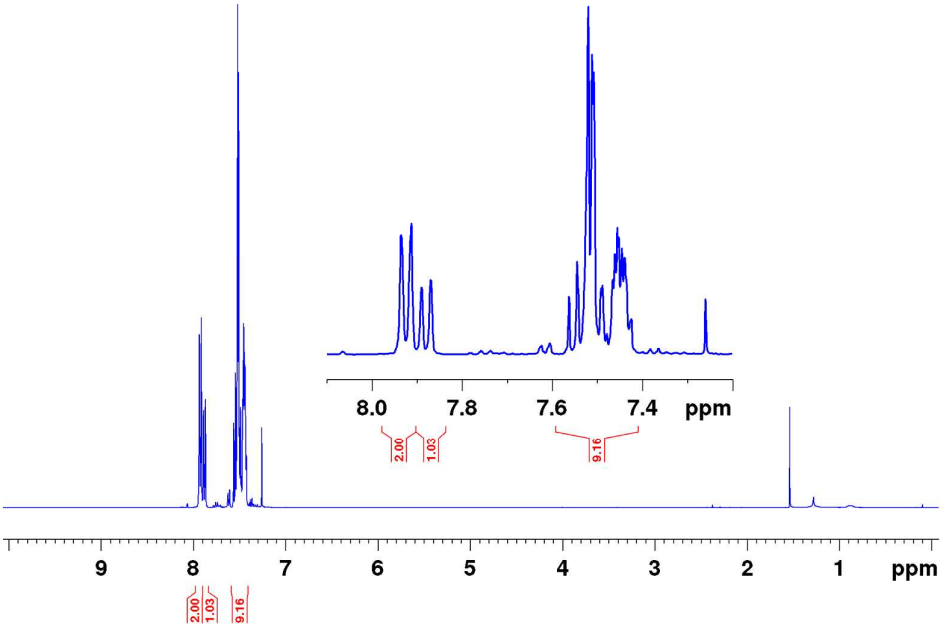

Figure S47. ^{1}H NMR spectrum of 1-phenylnaphthalene.

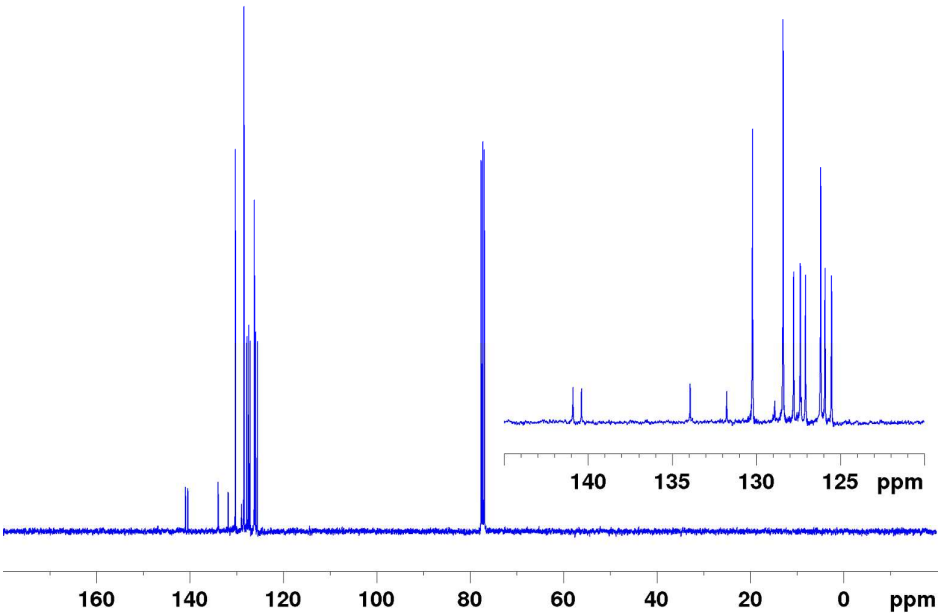

Figure S48. ^{13}C{^{1}H} NMR spectrum of 1-phenylnaphthalene

2-phenylnaphthalene

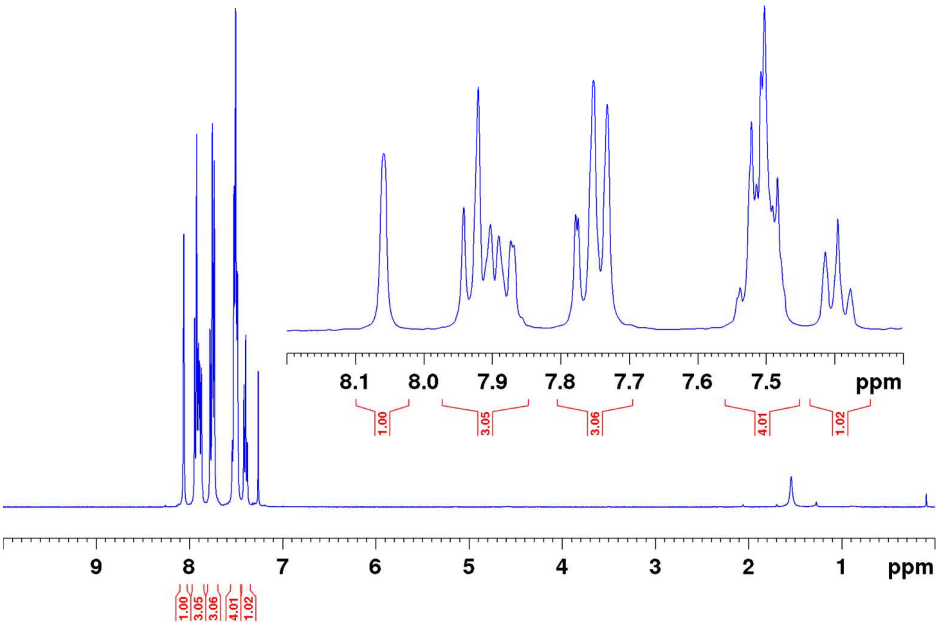

Figure S49. ^{1}H NMR spectrum of 2-phenylnaphthalene.

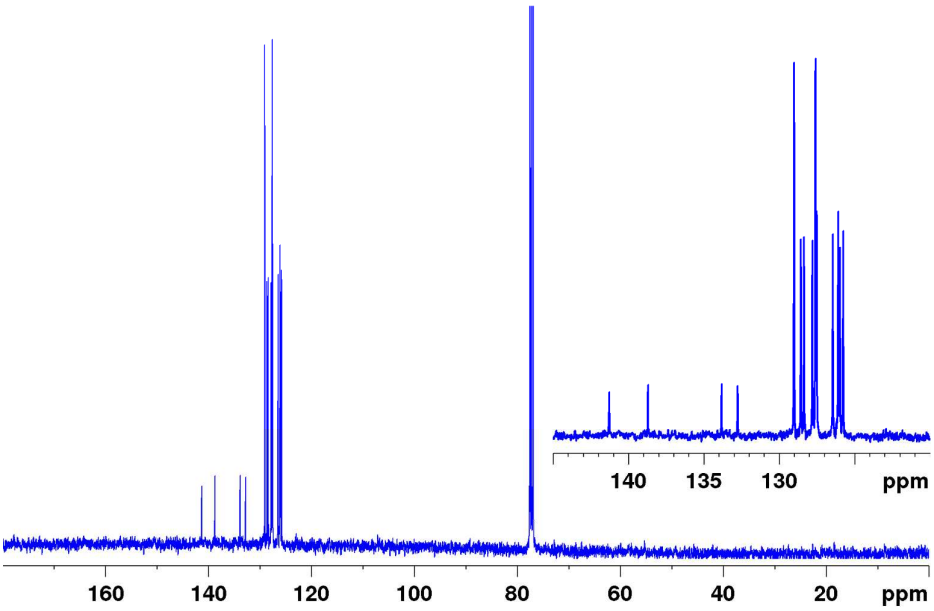

Figure S50. ^{13}C{^{1}H} NMR spectrum of 2-phenylnapthalene.

2,2'-binaphthalene

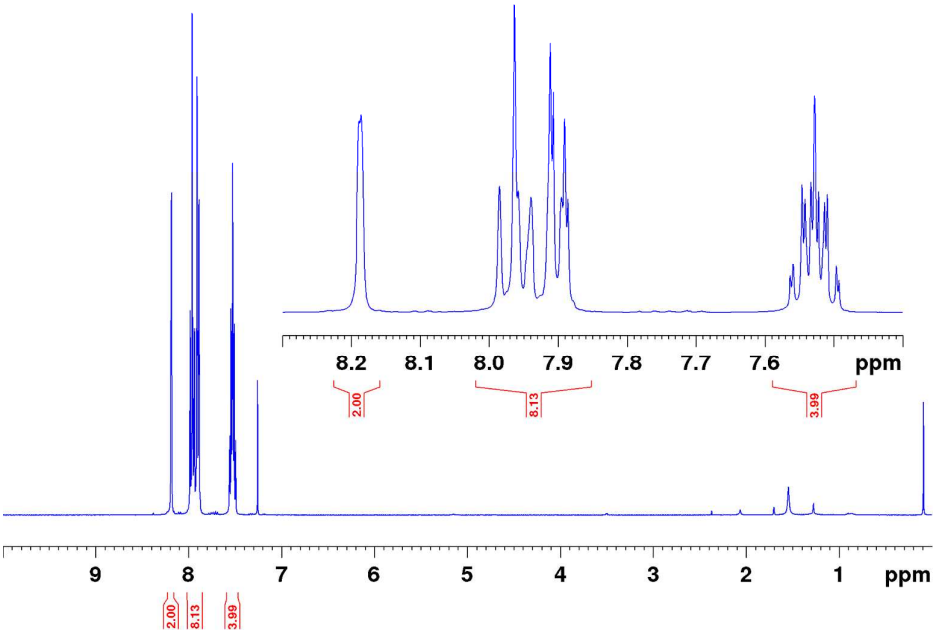

Figure S51. ^{1}H NMR spectrum of 2,2'-binaphthalene.

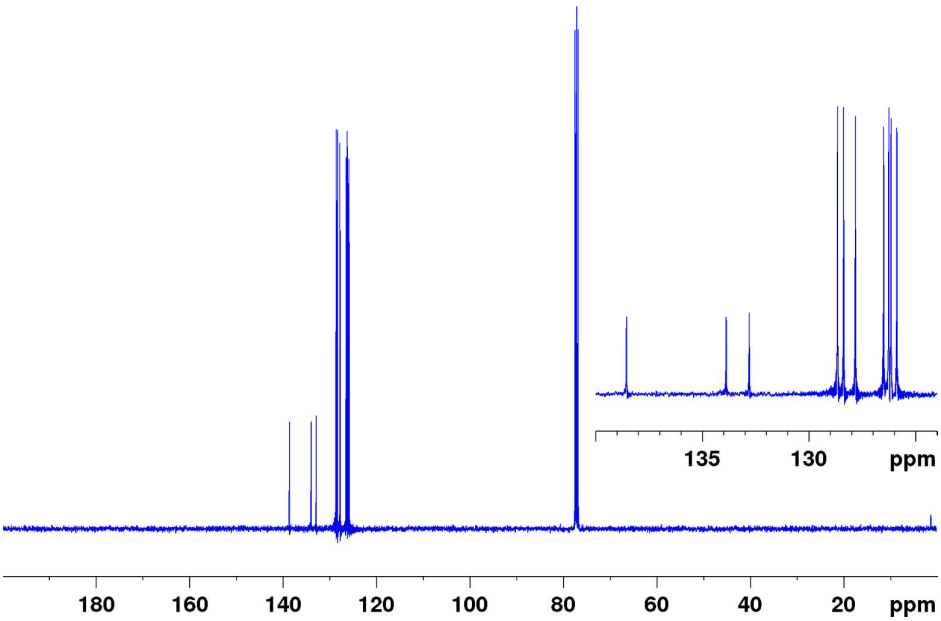

Figure S52. ^{13}C{^{1}H} NMR spectrum of 2,2'-binaphthalene.

1-naphthyl tosylate

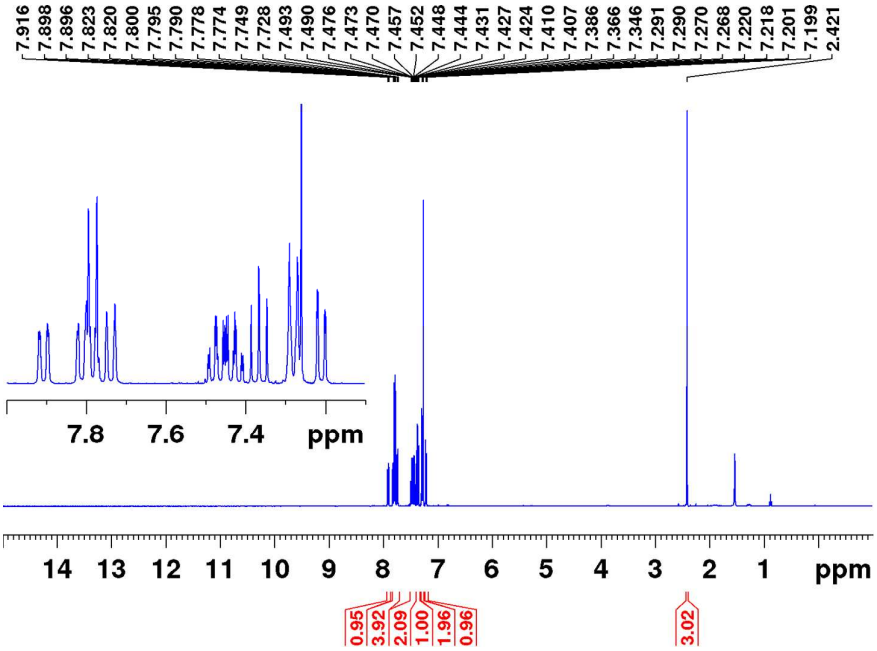

Figure S53. ^{1}H NMR spectrum of 1-naphthyl tosylate.

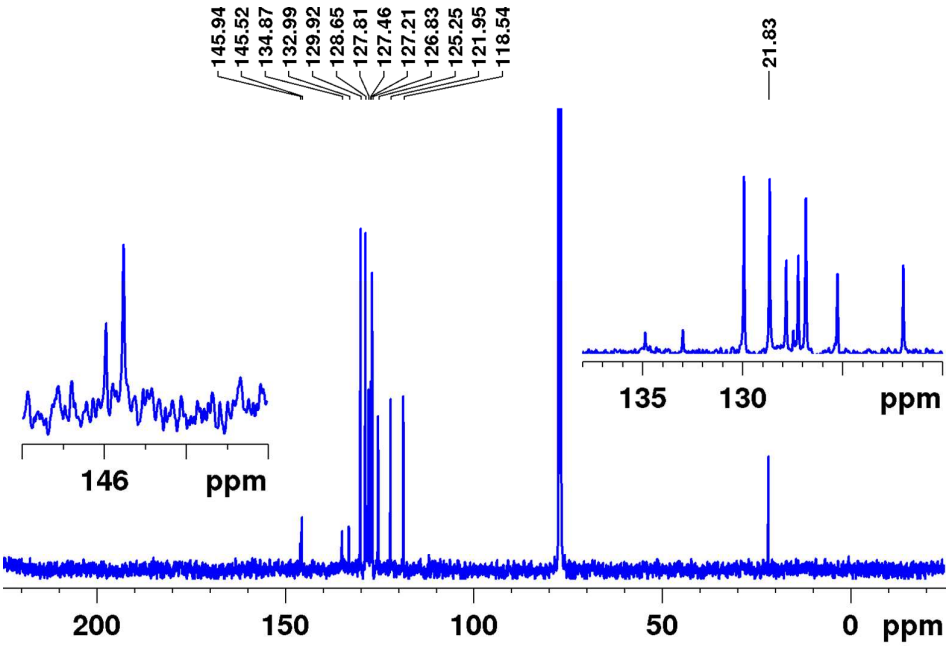

Figure S54. ^{13}C{^{1}H} NMR spectrum of 2-naphthyl tosylate.

2-naphthyl tosylate

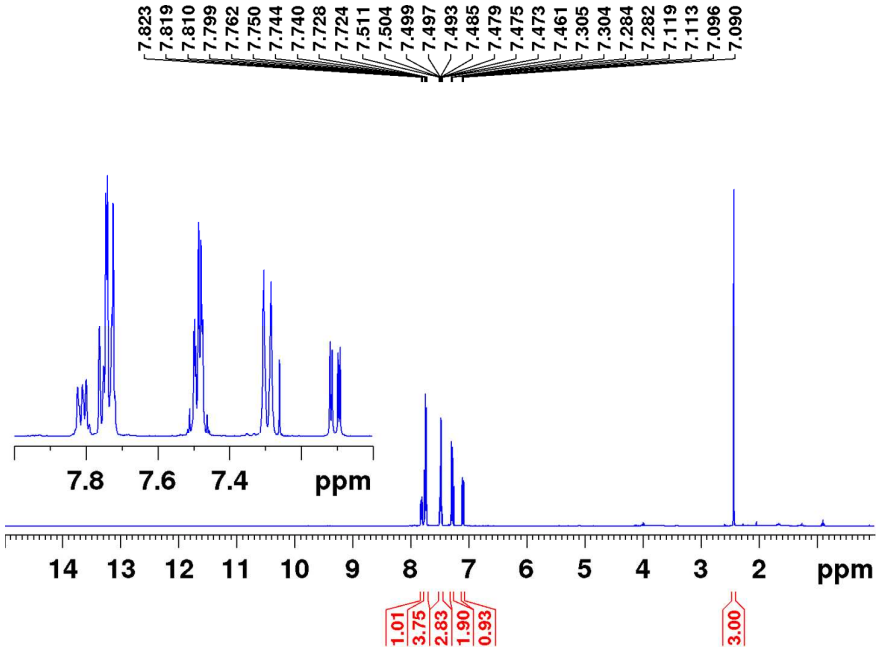

Figure S55. ^{1}H NMR spectrum of 2-naphthyl tosylate.

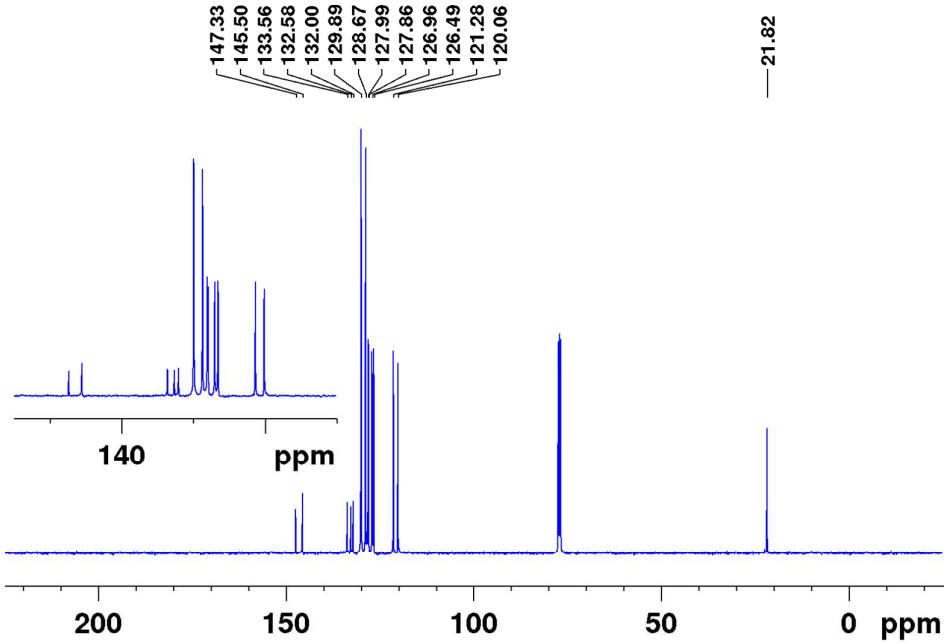

Figure S56. ^{13}C{^{1}H} NMR spectrum of 2-naphthyl tosylate.

1-naphthyl triflate

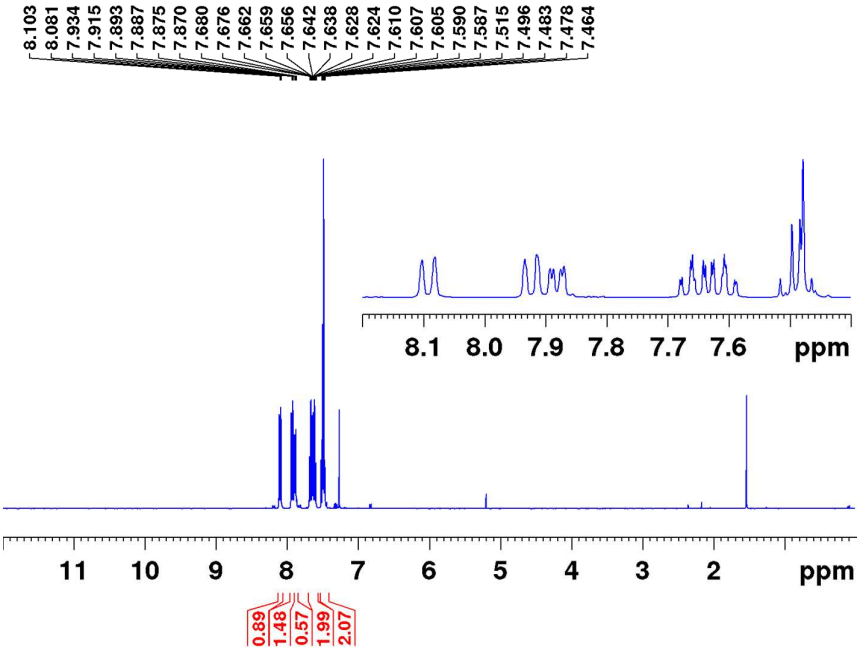

Figure S57. ^{1}H NMR spectrum of 1-naphthyl triflate.

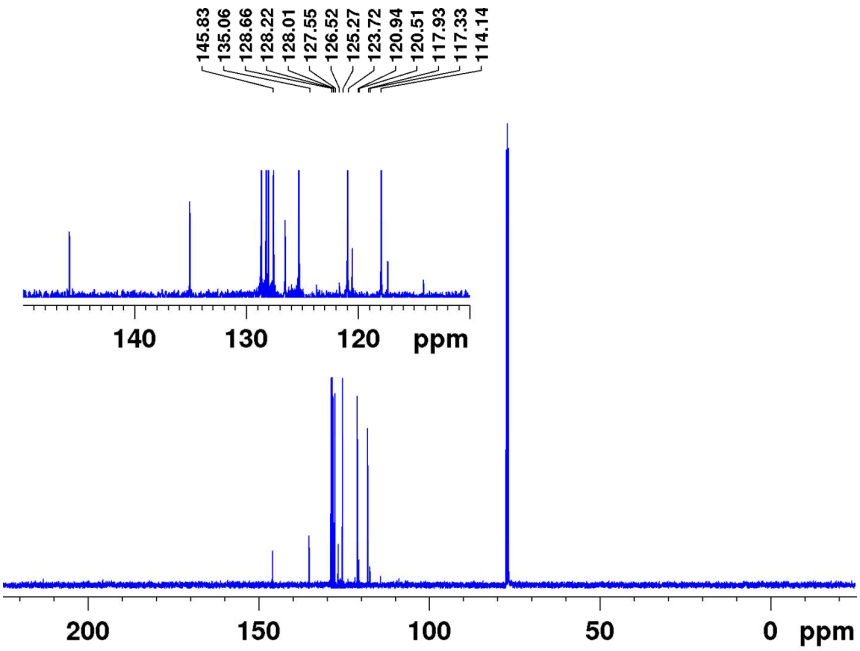

Figure S58. ^{13}C{^{1}H} NMR spectrum of 1-naphthyl triflate.

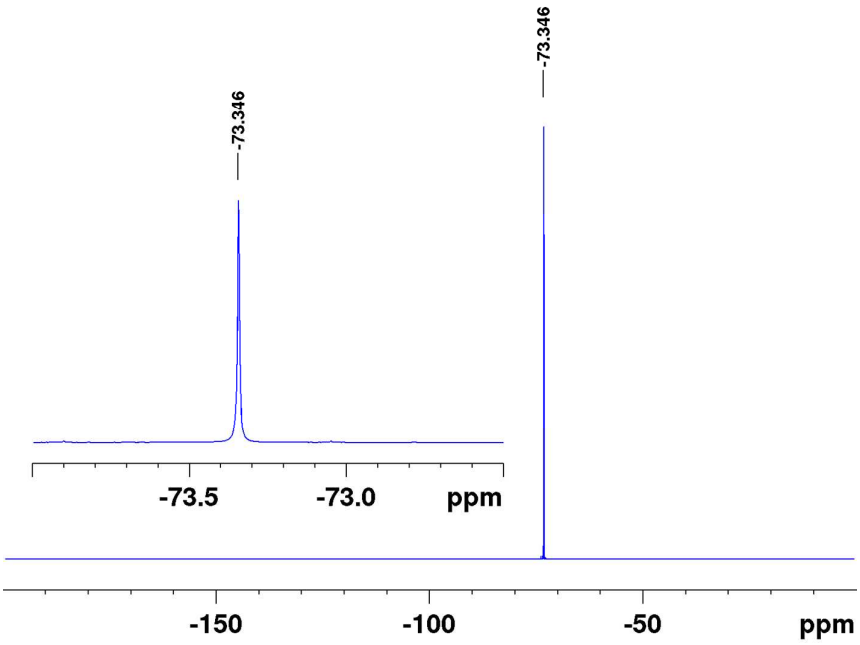

Figure S59. ^{19}F NMR spectrum of 1-naphthyl triflate.

2-naphthyl triflate

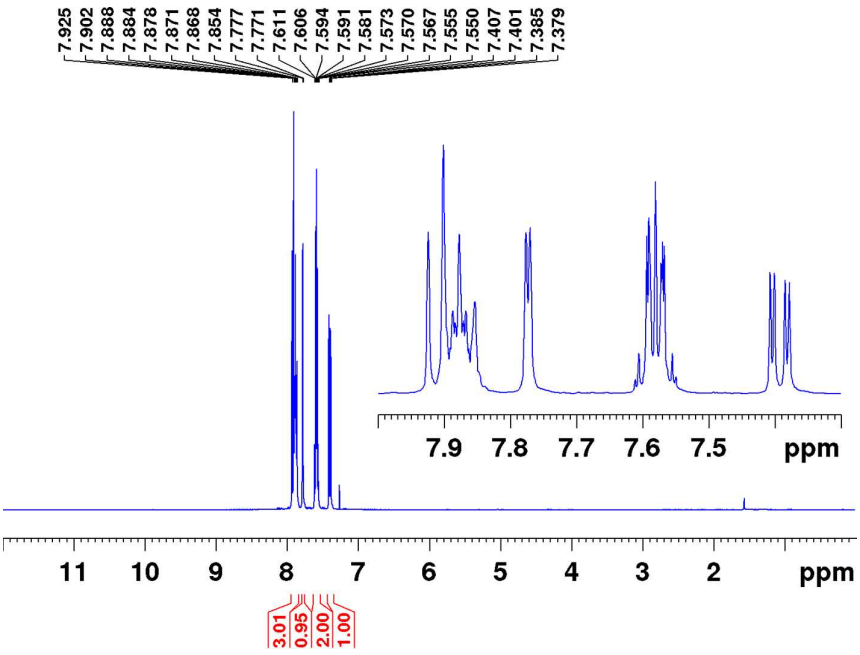

Figure S60. ^{1}H NMR spectrum of 2-naphthyl triflate.

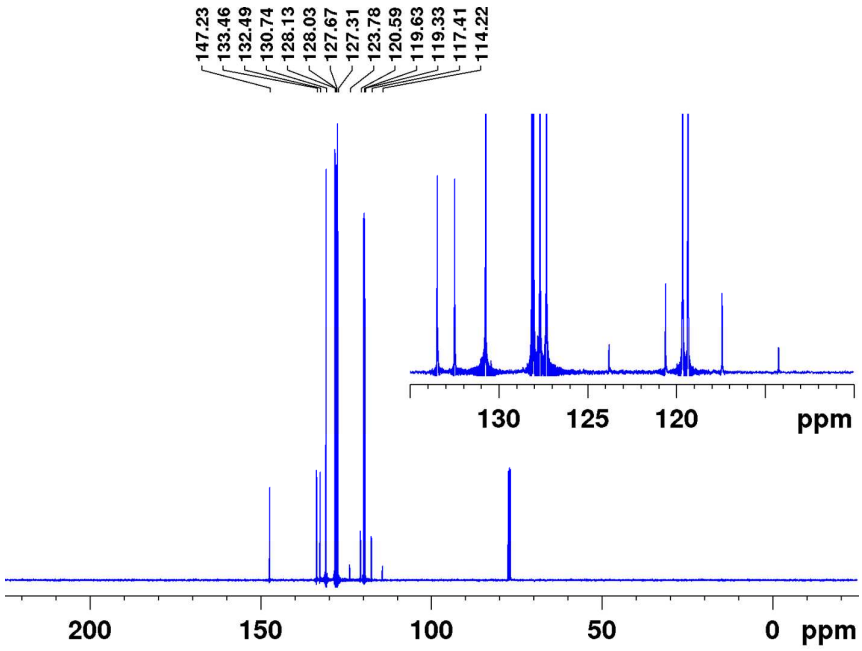

Figure S61. $^{13}C\{^{1}H\}$ NMR spectrum of 2-naphthyl triflate.

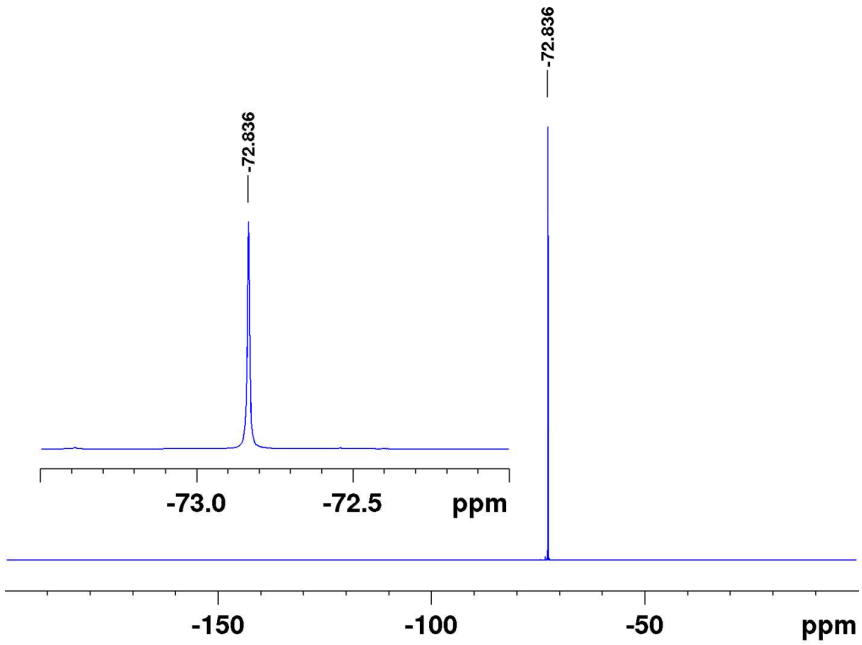

Figure S62. ^{19}F NMR spectrum of 2-naphthyl triflate.

Ethyl (naphthalen-1-yl)carbonate

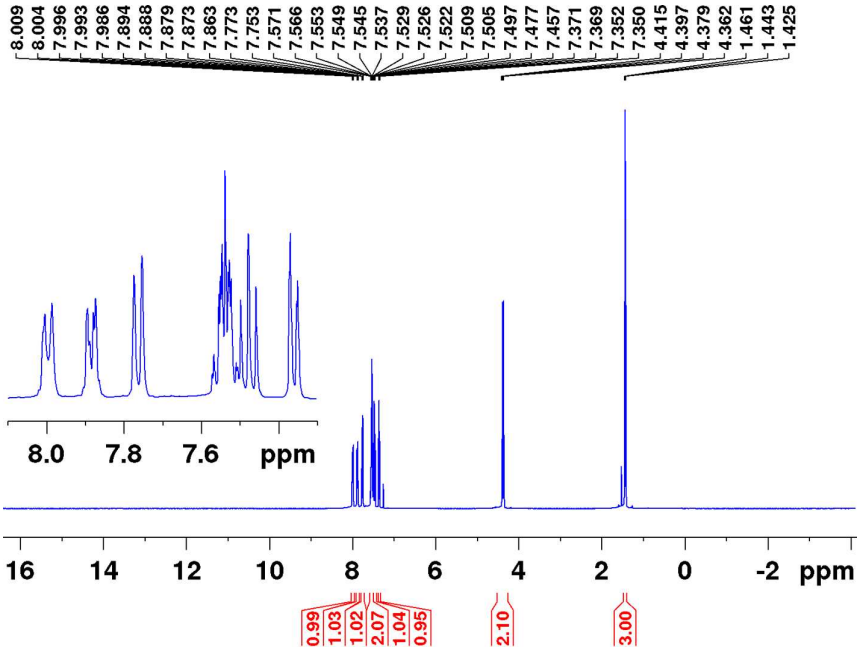

Figure S63. ^{1}H NMR spectrum of ethyl (naphthalen-1-yl)carbonate.

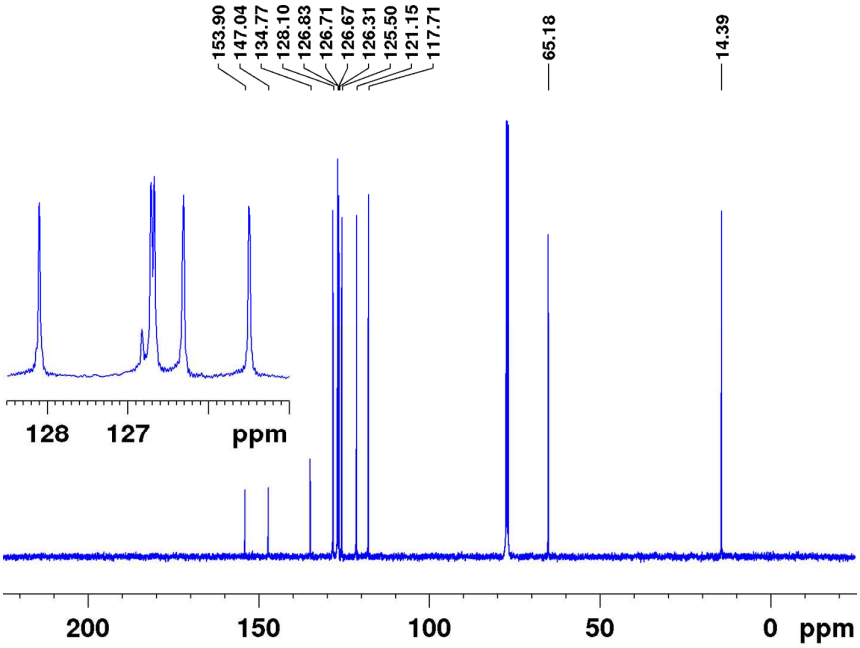

Figure S64. ^{13}C{^{1}H} NMR spectrum of ethyl (naphthalen-1-yl)carbonate.

Ethyl (naphthalen-2-yl)carbonate

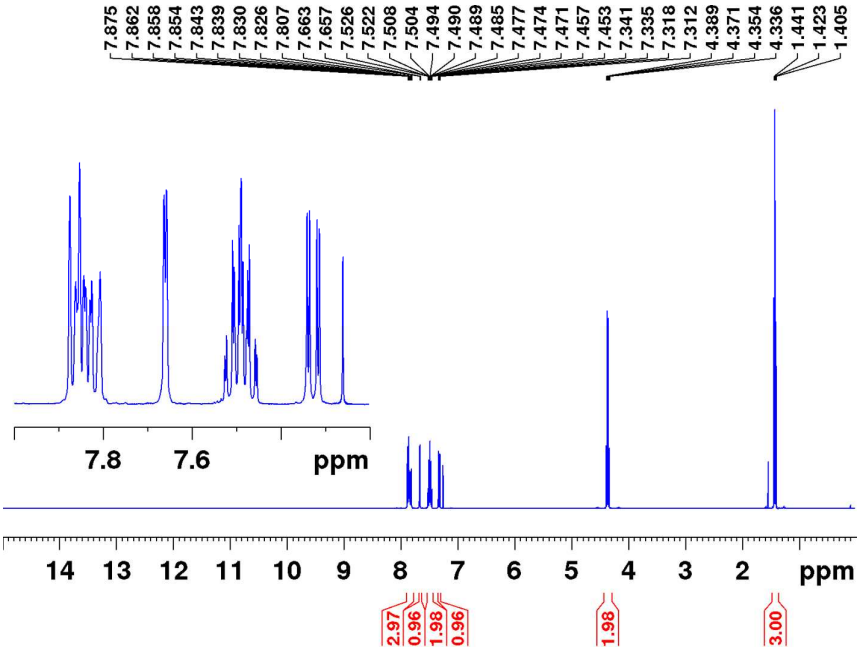

Figure S65. ^{1}H NMR spectrum of ethyl (naphthalen-2-yl)carbonate.

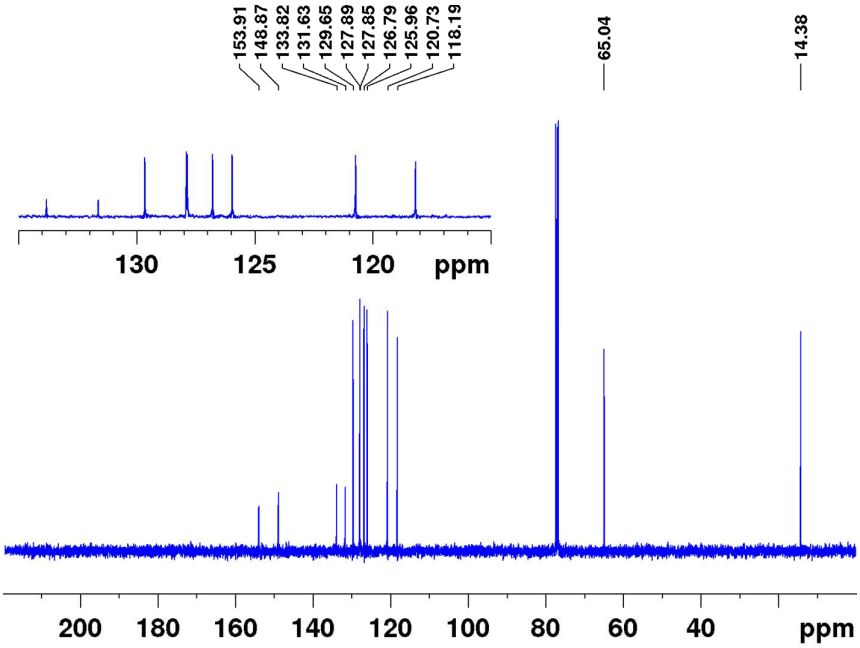

Figure S66. ^{13}C{^{1}H} NMR spectrum of ethyl (naphthalen-2-yl)carbonate.

Diethyl (naphthalen-1-yl)carbamate

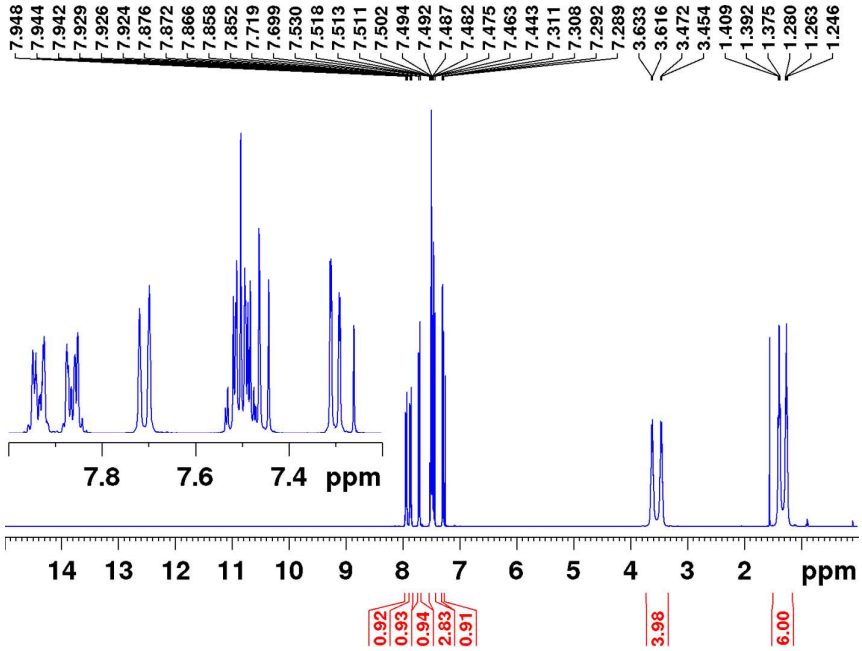

Figure S67. ^{1}H NMR spectrum of diethyl (naphthalen-1-yl)carbamate.

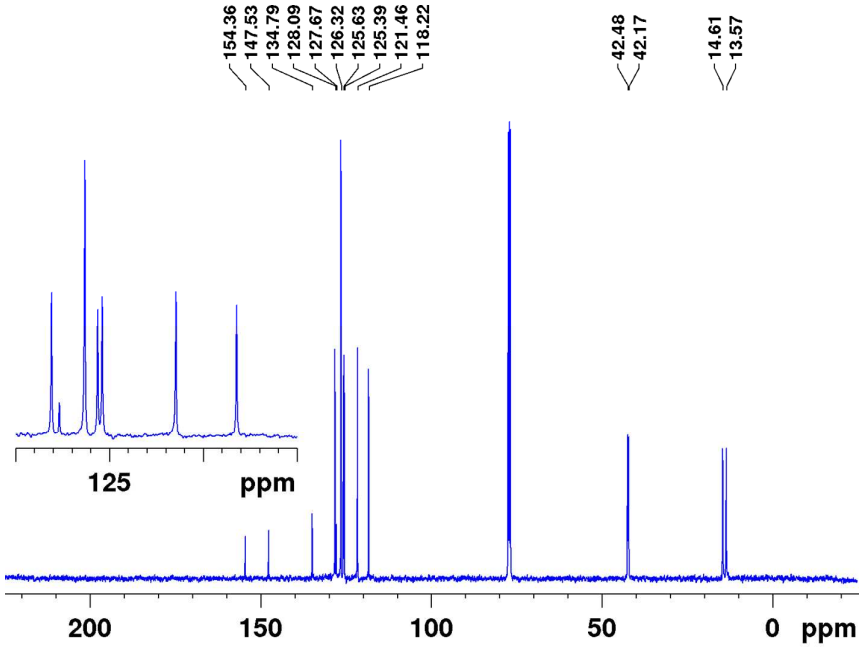

Figure S68. ^{13}C{^{1}H} NMR spectrum of diethyl (naphthalen-1-yl)carbamate.

Diethyl (naphthalen-2-yl)carbamate

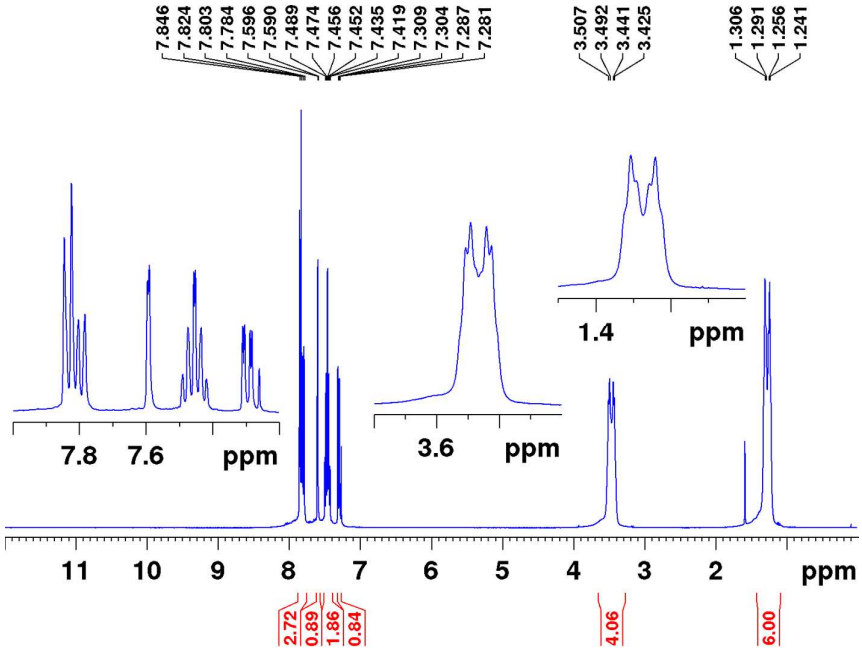

Figure S69. ^{1}H NMR spectrum of diethyl (naphthalen-2-yl)carbamate.

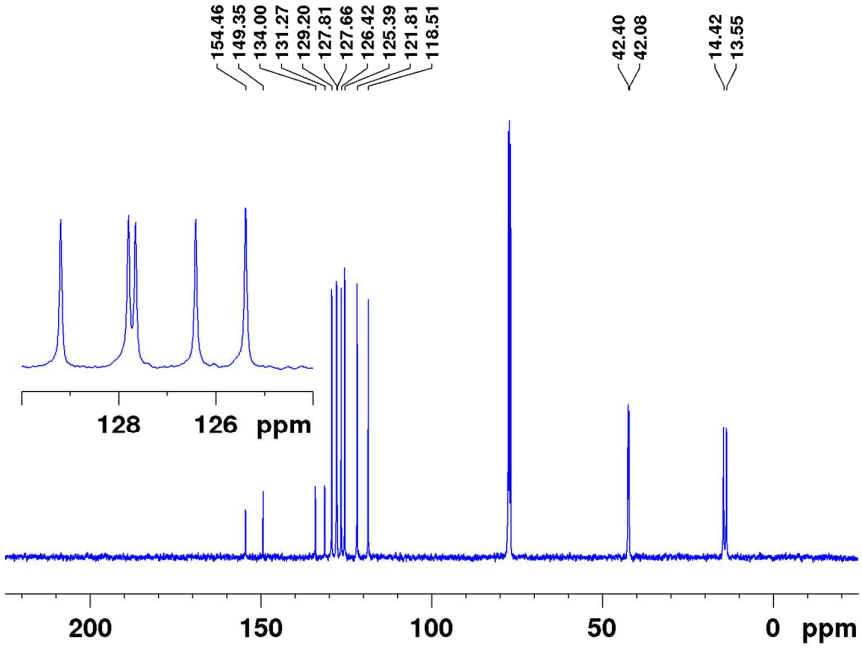

Figure S70. ^{13}C{^{1}H} NMR spectrum of diethyl (naphthalen-2-yl)carbamate.

(Naphthalen-1-yl)pivalate

^{1}H NMR

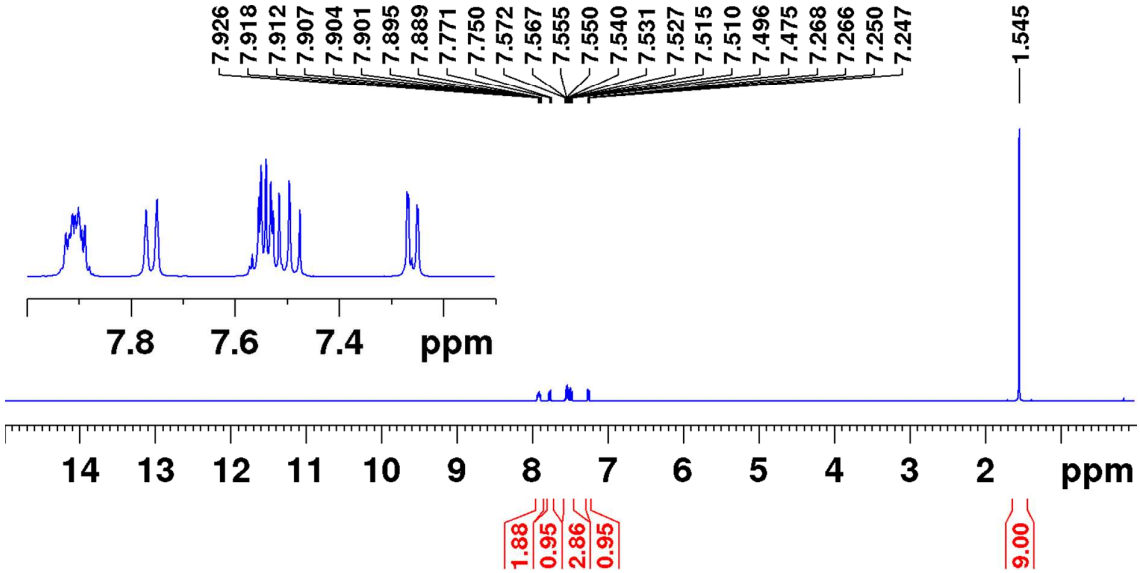

Figure S71. ^{1}H NMR spectrum of (naphthalen-1-yl)pivalate.

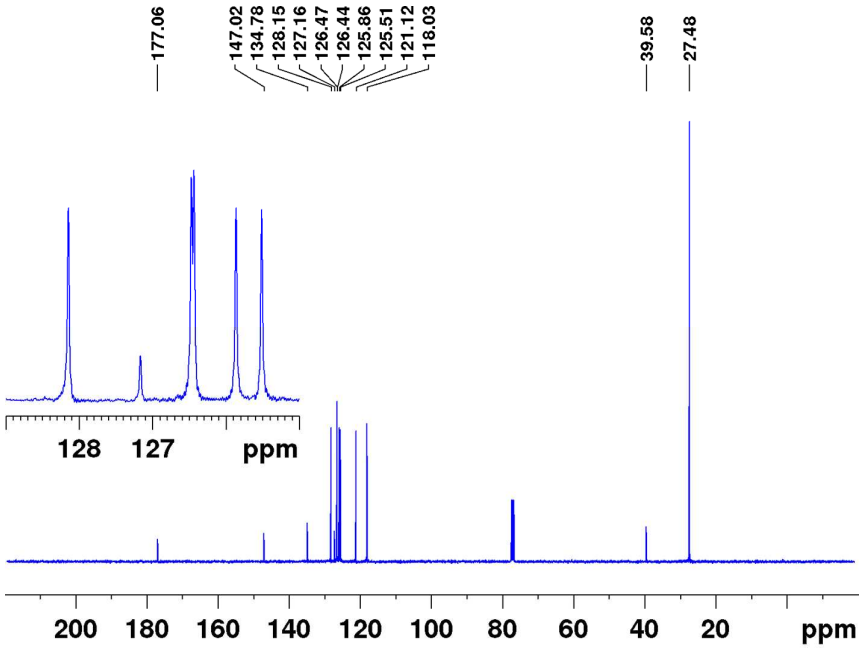

Figure S72. ^{13}C{^{1}H} NMR spectrum of naphthalen-1-yl(pivalate).

(Naphthalen-2-yl)pivalate

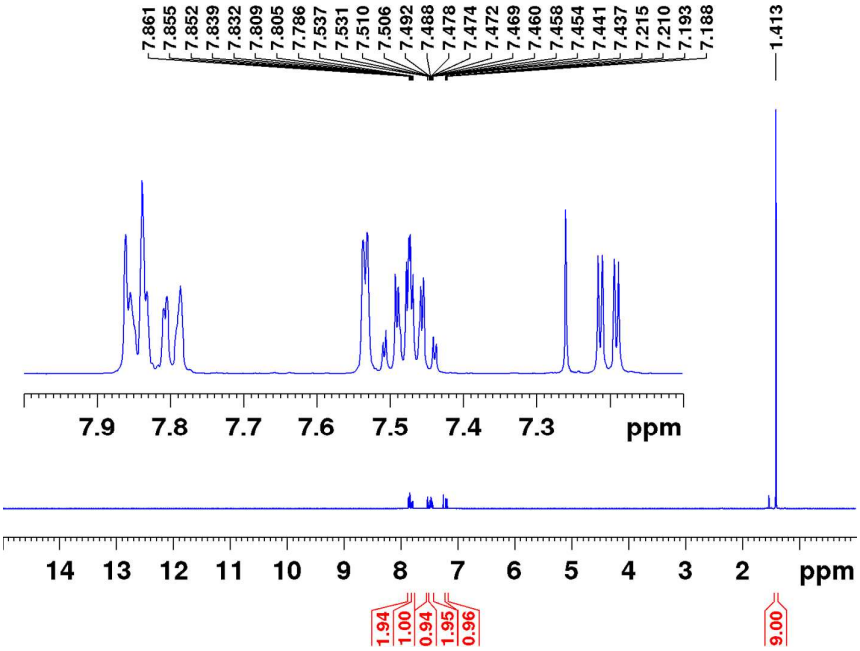

Figure S73. ^{1}H NMR spectrum of (naphthalen-2-yl)pivalate.

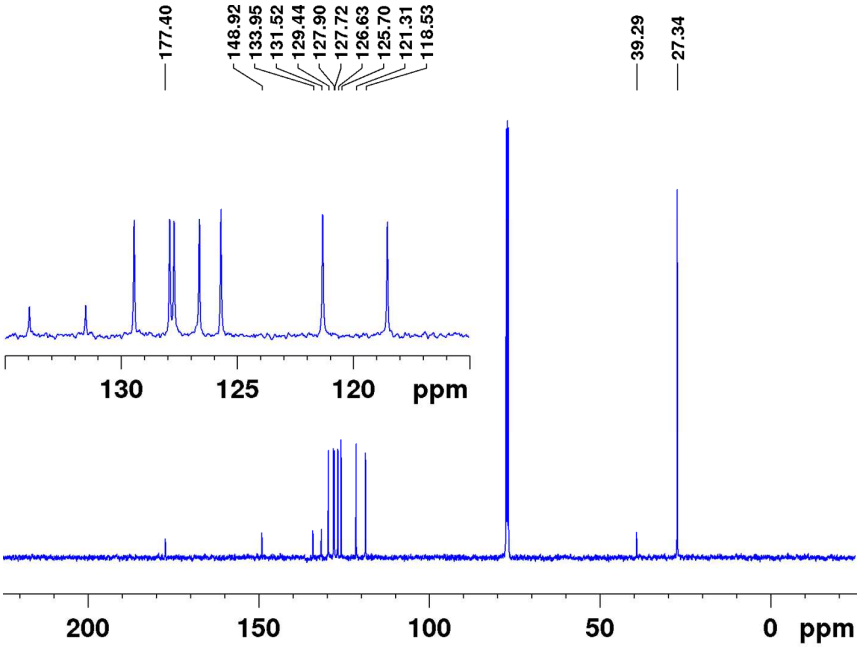

Figure S74. ^{13}C{^{1}H} NMR spectrum of naphthalen-2-yl(pivalate).

Napthalen-1-yl dimethylsulfamate

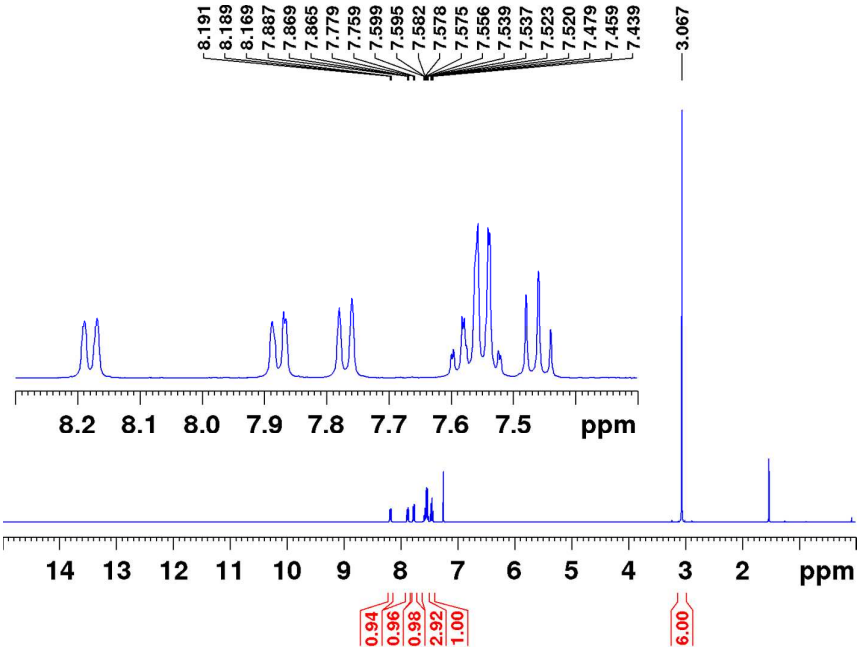

Figure S75. ^{1}H NMR spectrum of naphthalen-1-yl dimethylsulfamate.

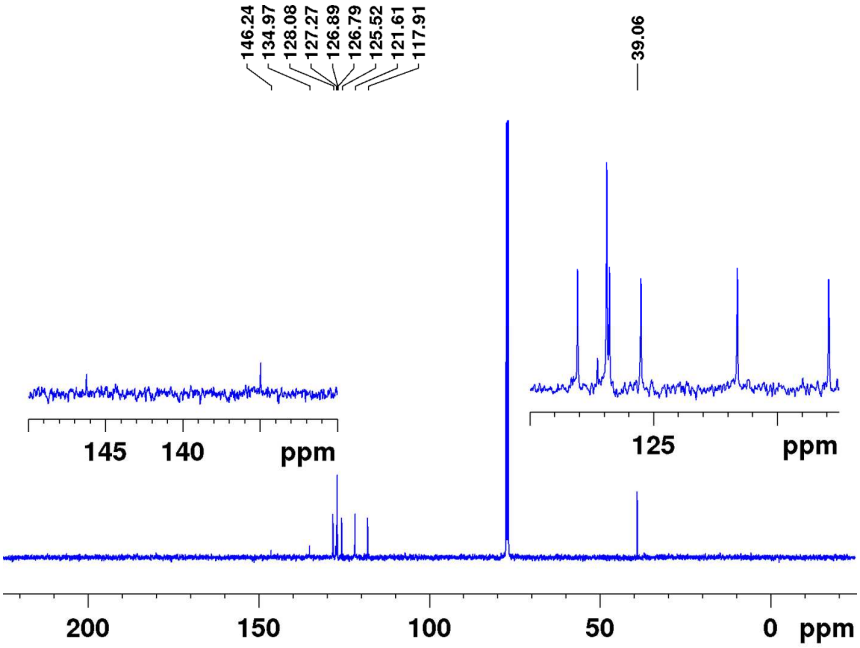

Figure S76. ^{13}C{^{1}H} NMR spectrum of naphthalen-2-yl dimethylsulfamate.

Napthalen-2-yl dimethylsulfamate

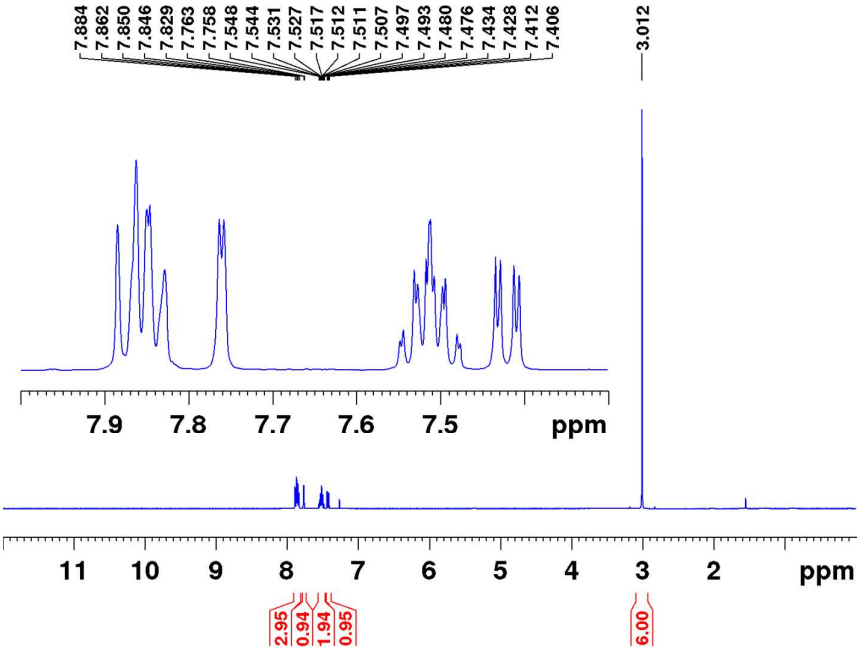

Figure S77. ^{1}H NMR spectrum of naphthalen-2-yl dimethylsulfamate.

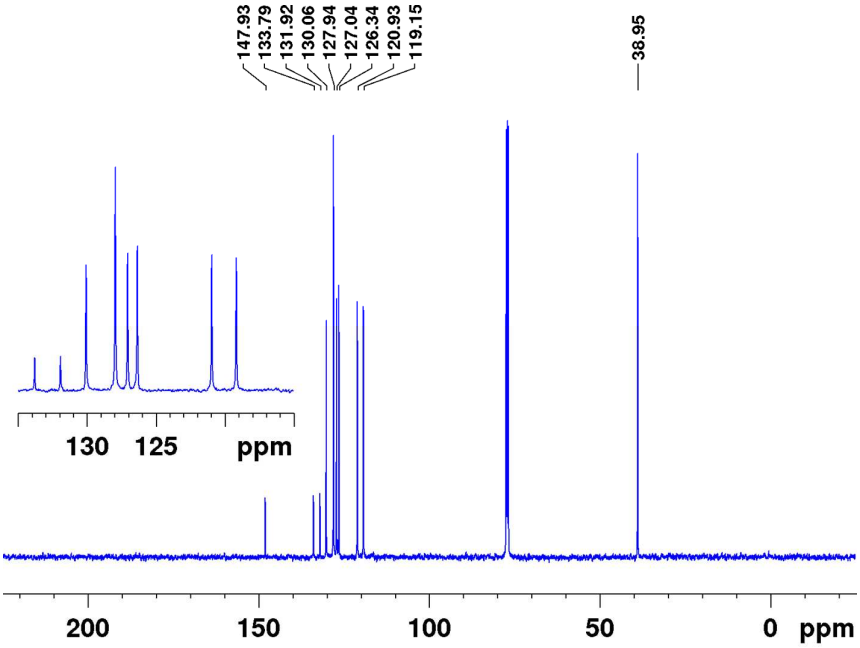

Figure S78. ^{13}C{^{1}H} NMR spectrum of naphthalen-2-yl dimethylsulfamate.

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