Supplementary information

Radical Coupling of Aryl Halides to Arenes Promoted by Ni(COD)(DQ) and other Nickel Sources

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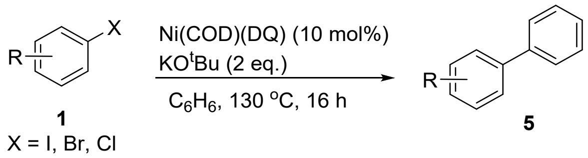
General information and procedures

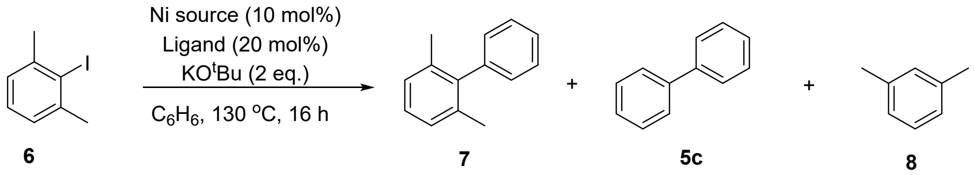
All reactions were carried out using air-free techniques under argon or prepared in a glovebox (Innovative Technology Inc., USA) under a nitrogen atmosphere and sealed, unless otherwise stated. All reagents and solvents were obtained from commercial suppliers (Fluorochem, Fisher Scientific or Sigma Aldrich) and used without further purification, unless otherwise stated. Anhydrous hexane, dichloromethane (DCM) and diethyl ether (Et_2O), where employed, were dried using a Pure-Solv 400 solvent purification system (Innovative Technology Inc., USA). Thin Layer Chromatography was performed on silica gel pre-coated aluminium plates (60 Å, F254 UV indicator) purchased from Merck. The thin layer chromatograms were analysed by UV (254 nm, UVP mineralight UVG-11 lamp) and staining either with basic $KMnO_4$ [$KMnO_4$ (6 g), K_2CO_3 (40 g), NaOH (5 mL, 10% w/w) in water (600 mL)] or an ethanolic solution of phosphomolybdic acid [phosphomolybdic acid hydrate (10 g) in ethanol (100 mL)]. Flash Column Chromatography purification was performed with 35-70 µm particle size silica gel 60 Å (200-400 mesh) purchased from Prolabo. Melting points were determined using a Gallenkamp Griffin Melting Point Apparatus. NMR spectroscopy was performed using a Bruker AV3-400 spectrometer. ^1H NMR, ^{13}C NMR, ^2H NMR and ^{19}F NMR spectra were recorded on this spectrometer operating at 400 MHz, 101 MHz, 61 MHz and 376 MHz respectively. All spectral data were acquired at 295 K. For ^1H and ^{13}C NMR spectra, chemical shifts (δ) are quoted in parts per million (ppm) relative to the following residual solvent peaks; δ_H 7.26 and δ_C 77.2 ppm for $CDCl_3$, δ_H 7.16 and δ_C 128.0 ppm for C_6D_6, δ_C 25.3, 67.5 ppm for d_8-THF. ^2H NMR spectra chemical shifts are quoted relative to the residual deuterated solvents at the same ppm as in ^1H NMR spectra. ^{19}F NMR spectra chemical shifts are quoted relative to a 2,2,2-trifluoroethanol (TFE) internal standard at δ_F -77.51 ppm in $CDCl_3$. Coupling constants (*J*) are reported in Hertz (Hz) to the nearest 0.1 Hz. The multiplicity abbreviations used are: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), br (broad), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), ddd (doublet of doublets of doublets), ddt (doublet of doublets of triplets). Infrared (IR) spectra were obtained on a Shimadzu IRAffinity-1 FTIR-ATR spectrometer instrument. GCMS spectra were obtained on an Agilent 7890A GC system coupled to a 5975C inert XL EI/CI MSD triple axis-mass detector. Electron impact (EI) ionisation was utilised, specifically the method EI320-25-1-SPLIT. The column temperature was 320 °C, and the carrier gas was helium with a flow rate of 1 mL/min. GC-FID analyses were carried out using either an Agilent 7890A gas chromatograph fitted with an Agilent HP5 column (30 m x 0.25 mm x 0.25 µm), or a Thermo Finnigan Focus gas chromatograph fitted with an Agilent HP5 column (30 m x 0.32 mm x 0.25 µm). Helium was used as the carrier gas (2.0 mL/min flow rate). The maximum column temperature was 340 °C and the instrument was operated in a splitless mode.

General procedure for coupling reaction of simple aryl halides (General procedure A)



An oven-dried 15 mL screw-top pressure flask was charged with aryl halide **1** (0.7 mmol), Ni(COD)(DQ) (23.2 mg, 0.07 mmol), KO^{t}Bu (157 mg, 1.4 mmol) and anhydrous benzene (5 mL) with a stirbar inside a glovebox. The flask was capped, removed from the glovebox and stirred in an oil bath at 130^{o}C for 16 h. The reaction mixture was then allowed to cool to room temperature, filtered through a short Celite plug, washed with hexane/EtOAc and concentrated *in vacuo*. The crude mixture was then purified *via* column chromatography with hexane/EtOAc eluent to yield to product **5**.

General procedure for coupling reaction of 2,6-dimethyliodobenzene (General procedure B)



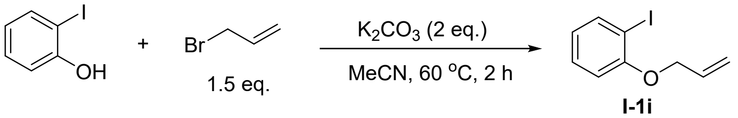
An oven-dried 15mL screw-top pressure flask was charged with **6** (101 µl, 0.7 mmol), a nickel source (0.07 mmol), a ligand if used (0.14 mmol), KO^{t}Bu (157 mg, 1.4 mmol) and anhydrous benzene (5 mL) with a stirbar inside a glovebox. The flask was capped, removed from the glovebox and stirred in an oil bath at 130^{o}C for 16 h. The reaction mixture was then allowed to cool to room temperature, *n*-dodecane was added as an internal standard (approx. 0.1 mmol) and the mixture filtered was through a short Celite plug and washed with hexane. An aliquot of the mixture was removed, diluted with CHCl$_3$ and product yields determined by GC-FID calibrated with authentic product samples (see page S24) using *n*-dodecane as an internal standard.

Reactant synthesis

Synthesis of Ni(COD)(DQ)[1]

In a glovebox, a large oven-dried screw-top pressure flask (35 mL) was charged with a stirbar, Ni(COD)$_2$ (1.68 g, 6.1 mmol), duroquinone (1.0 g, 6.1 mmol) and degassed DCM (23.5 mL). Upon the first addition of DCM, the yellow solids became a black solution. The flask was capped, removed from the glovebox and heated at 45°C in an oil bath for 17 h. The reaction mixture was then allowed to cool to room temperature, filtered through a short celite plug and washed with DCM. Volatiles were removed *in vacuo* yielding a red lumpy solid. The solid was then washed with a 40:1 mixture of hexane/DCM (69 mL x 2) to removed free COD, and then dried under high vacuum yielding Ni(COD)(DQ) as a dark red powder (1.90 g, 94%). **^{1}H NMR** (400 MHz, C_6D_6) δ 3.46 (s, 4H), 1.96 (s, 12H), 1.84 – 1.79 (m, 4H), 1.59 – 1.51 (m, 4H) **^{13}C NMR** (101 MHz, C_6D_6) δ 155.0, 112.5, 100.0, 29.3, 12.6**. IR** *v$_{max}$*/cm^{-1} (neat): 1549 (s). The data are consistent with those reported in the literature.[1]

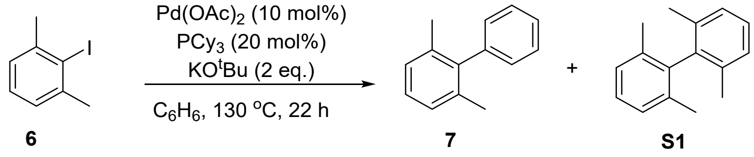
Synthesis of 1-(allyloxy)-2-iodobenzene I-1i



I-1i

A 10 ml microwave vial was charged with 2-iodophenol (550 mg, 2.5 mmol), K_2CO_3 (0.69 g, 5 mmol), then capped and evacuated. The vial was back-filled with Ar, and then allyl bromide (0.32 mL, 3.75 mmol) and degassed MeCN (5 mL) were added via syringe, giving a light brown solution with insolubles. The reaction was stirred at 60°C for 2 h, after which time the reaction was washed with H_2O (5 mL) and then extracted into Et_2O (8 mL x 3). The organic layers were then washed with brine (5 mL x 2), dried over $MgSO_4$ and concentrated giving a yellow oil **I-1i** (610 mg, 2.36 mmol, 94%) which was used in subsequent reaction without further purification. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.81 (dd, *J* = 8.2, 1.3 Hz, 1H), 6.75 – 6.70 (m, 1H), 6.07 (ddt, *J* = 17.3, 10.6, 4.8 Hz, 1H), 5.55 (dd, *J* = 17.3, 5.1 Hz, 1H), 5.33 (dq, *J* = 10.6, 1.6 Hz, 1H), 4.60 (dt, *J* = 4.8, 1.7 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.1, 139.5, 132.6, 129.4, 122.7, 117.6, 112.6, 86.7, 69.7. **IR** *v$_{max}$*/cm^{-1} (neat): 1273, 1244, 926. ***m/z*** (EI): 260.0 ([M]$^+$, 100), 219.9 (20), 190.9 (20), 133.1 (33), 119.0 (13), 105.1 (60), 92.0 (40). The data are consistent with those reported in the literature.[2]

Synthesis of 2,6-dimethylbiphenyl 7



A sample of compound **7** was prepared by combining **6** (812 mg, 3.5 mmol), $Pd(OAc)_2$ (78.6 mg, 0.35 mmol), PCy_3 (196 mg, 0.7 mmol), KO^tBu (786 mg, 7 mmol) and anhydrous benzene (15 mL) in an oven-dried pressure tube (35 mL) with a stirbar inside a glovebox. The flask was capped, removed from the glovebox and stirred in an oil bath at 130°C for 22 h, turning the solution from yellow to black. The reaction mixture was cooled, filtered through a short Celite plug and washed with hexanes. The crude mixture was concentrated and then purified by column chromatography with hexane as eluent, yielding a colourless oil (144 mg). **7** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 2H), 7.38 – 7.33 (m, 1H), 7.19 – 7.11 (m, 5H), 2.05 (s, 6H) *m/z* (EI)*:* 182.1 ($[M]^+$, 93), 167.1 (100), 152.1 (33), 139.0 (7), 128.1 (13), 115.0 (20), 89.0 (13), 77.0 (13), 63.0 (13), 51.0 (17).

Analysis by NMR and GCMS showed a 1:0.047 mixture of **7** (0.748 mmol, 21.4 %) and the homocoupled product **S1** (0.0349 mmol, 0.9 %), and thus this impurity is then corrected for in the calibration curve calculations (Page S25) using the following equation:

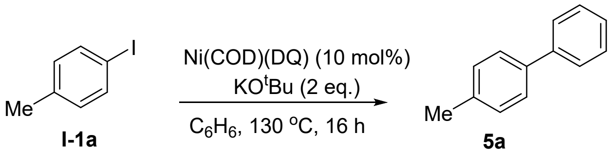
$$\text{Sample mass} = \text{mmol}(\mathbf{7})*182.27 + \text{mmol}(\mathbf{S1})*210.31$$

$$\text{Sample mass} = \text{mmol}(\mathbf{7})*182.27 + \text{mmol}(\mathbf{7})*0.0466*210.31$$

$$\text{mmol}(\mathbf{7}) = \frac{sample\ mass}{192.07}$$

Substrate scope

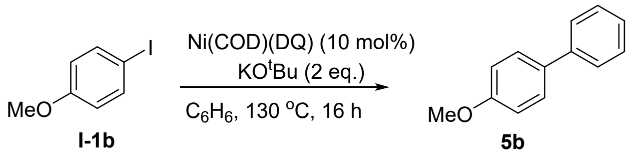
Coupling of I-1a with benzene using Ni(COD)(DQ)



This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (112 mg, 0.66 mmol, 95%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.53 – 7.50 (m, 2H), 7.47 – 7.42 (m, 2H), 7.36 – 7.32 (m, 1H), 7.29 – 7.26 (m, 2H), 2.42 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.3, 138.5, 137.1, 129.6, 128.9, 127.1, 21.2. **IR** v_{max}/cm^{-1} (neat): 3030, 2916, 1485. ***m/z*** (EI): 168.2 ($[M]^+$, 100), 152.1 (23), 139.1

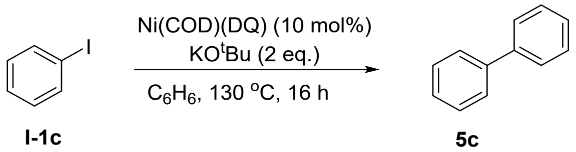
(5), 128.1 (4), 115.1 (8), 91.1 (5), 82.3 (5). The data are consistent with those reported in the literature.[2]

Coupling of I-1b with benzene using Ni(COD)(DQ)



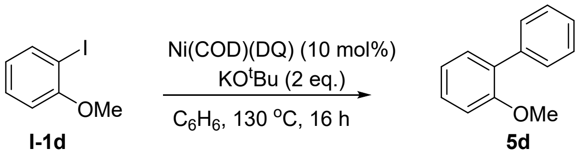
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 5% EtOAc/hexane eluent yielding **5b** as a white solid (111 mg, 0.603 mmol, 86%). **M.p.** 85-87°C (*lit*. 88-89°C)[7]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 – 7.52 (m, 4H), 7.44 – 7.39 (m, 2H), 7.33 – 7.28 (m, 1H), 7.01 – 6.96 (m, 2H), 3.86 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.3, 141.0, 134.0, 128.9, 128.3, 126.9, 126.2 114.4, 55.5. **IR** v_{max}/cm^{-1} (neat): 2835, 1483, 1246, 1034. ***m/z*** (EI): 184.1 ([M]$^+$, 100), 169.1 (47), 152.0 (7), 141.0 (53), 115.0 (40), 89.0 (7), 76.0 (5), 63.0 (8). The data are consistent with those reported in the literature.[2]

Coupling of I-1c with benzene using Ni(COD)(DQ)



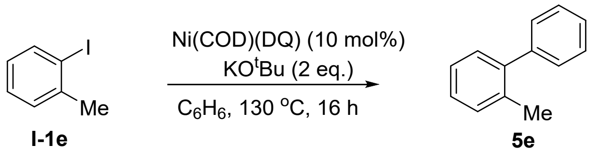
This reaction was carried out as described in General procedure A. The crude mixture was purified *via* column chromatography with hexane eluent yielding **5c** as a white solid (95.9 mg, 0.623 mmol, 89%). **M.p.** 66-68°C (*lit.* 68-70°C)[8]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 4H), 7.50 – 7.45 (m, 4H), 7.40 – 7.36 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.4, 128.9, 127.4, 127.3. **IR** v_{max}/cm^{-1} (neat): 3059, 1476, 1429. ***m/z*** (EI): 154.1 ([M]$^+$, 100), 76.0 (13), 51.0 (13). The data are consistent with those reported in the literature.[2]

Coupling of I-1d with benzene using Ni(COD)(DQ)



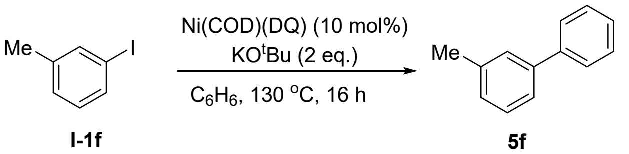
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 20% EtOAc/hexane eluent yielding **5d** as a pale-yellow oil (101 mg, 0.55 mmol, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7.54 – 7.49 (m, 2H), 7.45 – 7.39 (m, 3H), 7.15 – 7.11 (m, 1H), 7.08 (d, J = 8.0 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.6, 138.7, 131.0, 130.8, 129.7, 128.7, 128.1, 127.0, 120.9, 111.4, 55.6. **IR** ν_{max}/cm^{-1} ($CHCl_3$): 1481, 1246, 1197, 1182, 1033. ***m/z*** (EI): 184.1 ([M]$^+$, 100), 169.1 (53), 152.1 (9), 141.1 (40), 115.0 (40). The data are consistent with those reported in the literature. [3]

Coupling of I-1e with benzene using Ni(COD)(DQ)



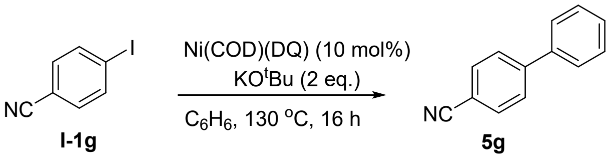
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with hexane eluent yielding **5e** as a colourless oil (77.6 mg, 0.46 mmol, 66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 – 7.42 (m, 2H), 7.39 – 7.35 (m, 3H), 7.31 – 7.27 (m, 4H), 2.31 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 135.5, 130.4, 129.9, 129.3, 128.9, 128.2, 127.4, 126.9, 125.9, 20.6. **IR** ν_{max}/cm^{-1} ($CHCl_3$): 3030, 1477. ***m/z*** (EI): 168.1 ([M]$^+$, 100), 153.1 (40), 139.1 (7), 128.1 (7), 115.1 (13). The data are consistent with those reported in the literature.[3]

Coupling of I-1f with benzene using Ni(COD)(DQ)



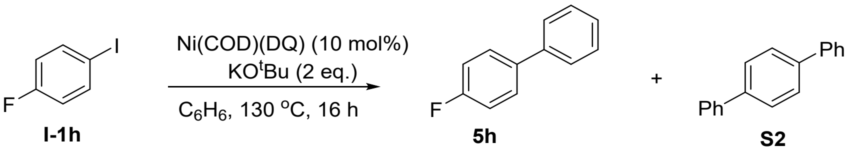
This reaction was carried out as described in General procedure A. The crude mixture was purified *via* column chromatography with hexane eluent yielding **5f** as a colourless oil (91.6 mg, 0.54 mmol, 78%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 – 7.67 (m, 2H), 7.55 – 7.49 (m, 4H), 7.46 – 7.41 (m, 2H), 7.28 – 7.25 (m, 1H), 2.52 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.5, 141.4, 138.4, 128.8, 128.1, 128.1, 127.3, 124.4, 21.7. ***m/z*** (EI): 168.2 ([M]$^+$). The data are consistent with those reported in the literature.[3]

Coupling of I-1g with benzene using Ni(COD)(DQ)



This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 20% EtOAc/hexane eluent yielding **5g** as a pale-yellow solid (88.4 mg, 0.47 mmol, 67 %). **M.p.** 82-84°C (*lit.* 85-87°C). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.61 – 7.58 (m, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 139.3, 132.8, 129.3, 128.8, 127.9, 127.4, 119.1, 111.1. **IR** v_{max}/cm^{-1} (neat): 2224, 1477. ***m/z*** (EI): 179.2 ([M]$^+$, 100), 151.1 (16), 76.1 (7). The data are consistent with those reported in the literature.[2]

Coupling of I-1h with benzene using Ni(COD)(DQ)



This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 5% EtOAc/hexane eluent yielding a mixture of **5h** and *p*-terphenyl **S6** as a yellow solid (96.5 mg). The yield of **5h** was determined to be 0.413 mmol (59 %) by ^{19}F NMR with a 2,2,2-trifluoroethanol (TFE) internal standard (55.8 mg), therefore the yield of **S2** can be determined from the total product mass as 26.0 mg (0.11 mmol, 16 %). **5h** **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.59 – 7.54 (m, 4H), 7.49 – 7.44 (m, 2H), 7.39 – 7.35 (m, 1H), 7.17 – 7.12 (m, 2H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 162.6 (d, *J* = 246.4 Hz), 140.9, 137.5 (d, *J* = 2.9 Hz), 129.0, 128.8 (d, *J* = 7.8 Hz), 127.7, 127.4, 115.8 (d, *J* = 21.6 Hz)**^{19}F NMR** (376 MHz, CDCl$_3$) δ -116.25 – -116.33 (m). **IR** v_{max}/cm^{-1} (neat): 1477, 1230. ***m/z*** (EI): 172.2 ([M]$^+$, 100), 153.1 (5), 146.1 (7), 133.1 (5), 120.1 (4), 85.1 (7). The data are consistent with those reported in the literature.[3]

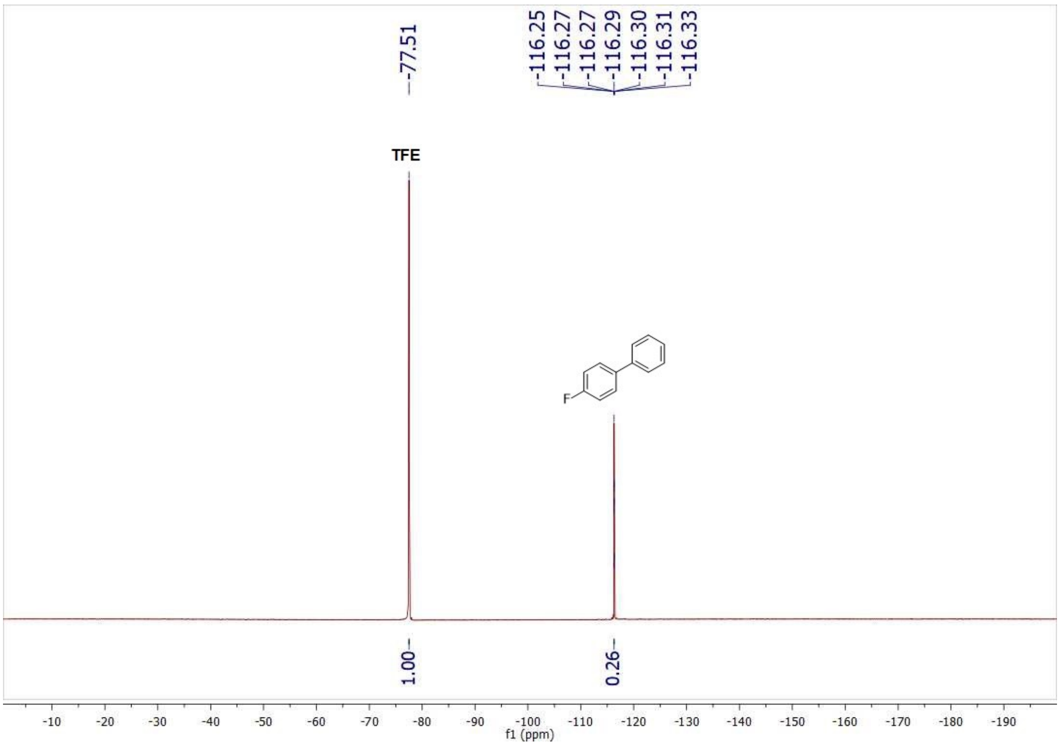
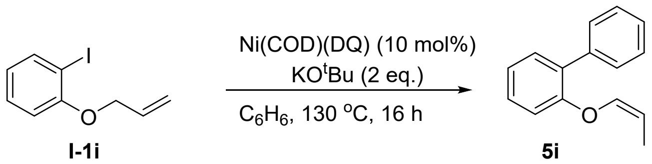


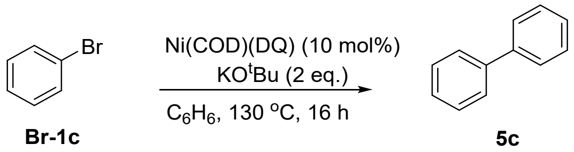
Figure S1 *– Obtaining ^{19}F NMR yield for compound **5h** with a TFE internal standard (55.8 mg).*

Coupling of I-1i with benzene using Ni(COD)(DQ)



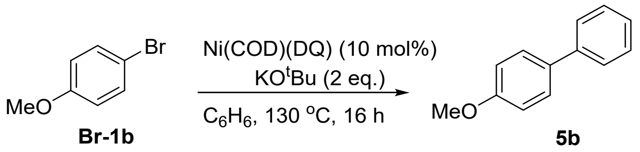
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with hexane eluent yielding **5i** as a colourless oil (90 mg, 0.43 mmol, 61%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 2H), 7.51 – 7.43 (m, 3H), 7.42 – 7.33 (m, 2H), 7.20 – 7.15 (m, 1H), 7.14 – 7.10 (m, 1H), 6.42 – 6.38 (m, 1H), 4.92 – 4.83 (m, 1H), 1.71 (dd, *J* = 6.8, 1.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 154.5, 141.5, 138.0, 131.7, 131.0, 129.6, 128.7, 128.0, 127.1, 122.9, 115.9, 107.2, 9.6. ***m/z*** (EI): 210.2 ([M]$^+$, 100), 195.1 (29), 181.1 (73), 169.1 (44), 152.1 (47), 141.1 (33), 115.1 (40). The data are consistent with those reported in the literature.[4]

Coupling of Br-1c with benzene using Ni(COD)(DQ)



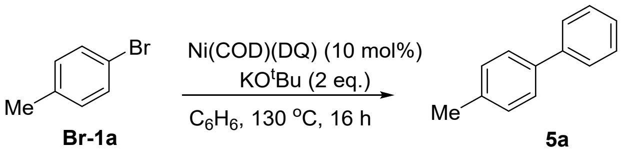
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with hexane eluent yielding **5c** as a white solid (86.2 mg, 0.56 mmol, 80%). Data are consistent with those reported above.

Coupling of Br-1b with benzene using Ni(COD)(DQ)



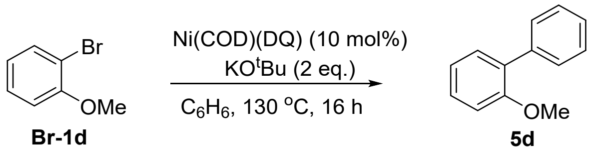
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (109 mg, 0.59 mmol, 84%). Data are consistent with those reported above.

Coupling of Br-1a with benzene using Ni(COD)(DQ)



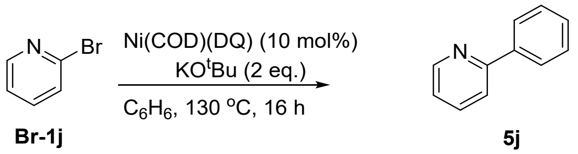
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (91.6 mg, 0.55 mmol, 78%). Data are consistent with those reported above.

Coupling of Br-1d with benzene using Ni(COD)(DQ)



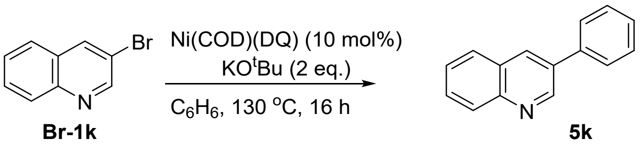
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 5% EtOAc/hexane eluent yielding **5d** as a pale-yellow oil (99.6 mg, 0.54 mmol, 77%). Data are consistent with those reported above.

Coupling of Br-1j with benzene using Ni(COD)(DQ)



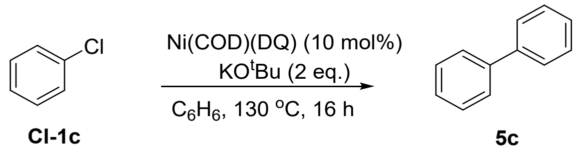
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 5% EtOAc/hexane eluent yielding **5j** as a pale-yellow oil (55.2 mg, 0.36 mmol, 51%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.71 – 8.69 (m, 1H), 8.01 – 7.98 (m, 2H), 7.77 – 7.72 (m, 2H), 7.51 – 7.46 (m, 2H), 7.44 – 7.39 (m, 1H), 7.25 – 7.21 (m, 1H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 157.6, 149.8, 139.6, 136.9, 129.1, 128.9, 127.1, 122.2, 120.7. ***m/z*** (EI): 155.1 ([M]$^+$, 100). The data are consistent with those reported in the literature.[2]

Coupling of Br-1k with benzene using Ni(COD)(DQ)



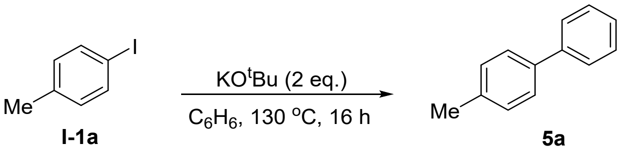
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with a 5% EtOAc/hexane eluent yielding **5k** as an orange oil (70.4 mg, 0.34 mmol, 49%). ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 9.19 (d, *J* = 2.3 Hz, 1H), 8.30 (d, *J* = 2.1 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 1H), 7.88 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.74 – 7.70 (m, 3H), 7.58 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.46 – 7.41 (m, 1H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 150.1, 147.5, 138.0, 134.0, 133.4, 129.5, 129.4, 129.3, 128.2, 128.1, 127.6, 127.1. ***m/z*** (EI): 205.1 ([M]$^+$, 100). The data are consistent with those reported in the literature.[5]

Coupling of Cl-1c with benzene using Ni(COD)(DQ)



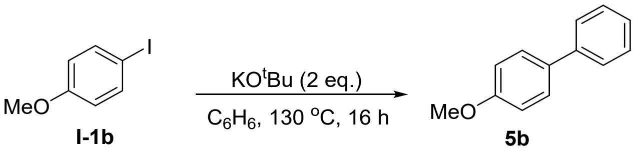
This reaction was carried out as described in General procedure A. The crude mixture was purified by column chromatography with hexane eluent yielding **5c** as a white solid (14.5 mg, 0.094 mmol, 14%). Data are consistent with those reported above.

Coupling of I-1a with benzene without a nickel source



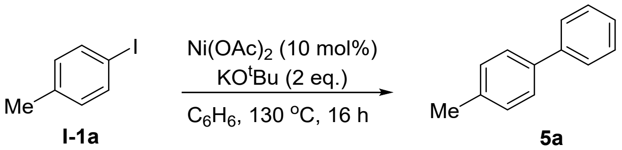
This reaction was carried out as described in General procedure A, except a Ni source was excluded. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (15.9 mg, 0.094 mmol, 13%). Data are consistent with those reported above.

Coupling of I-1b with benzene without a nickel source



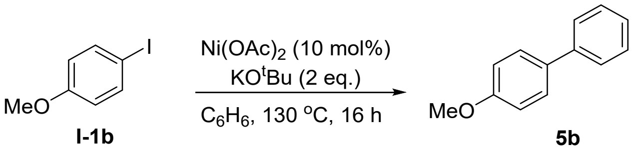
This reaction was carried out as described in General procedure A, except a Ni source was excluded. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (19.1 mg, 0.107 mmol, 15.2%). Data are consistent with those reported above.

Coupling of I-1a with benzene using Ni(OAc)$_2$



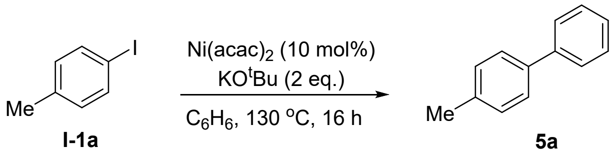
This reaction was carried out as described in General procedure A, except Ni(OAc)$_2$ (12.4 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (17.8 mg, 0.106 mmol, 15.1%). Data are consistent with those reported above.

Coupling of I-1b with benzene using Ni(OAc)$_2$



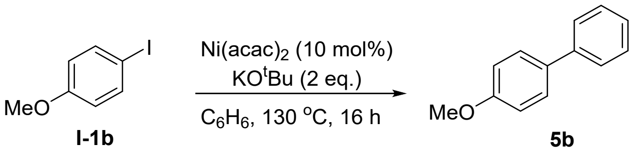
This reaction was carried out as described in General procedure A, except Ni(OAc)$_2$ (12.4 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (26.3 mg, 0.143 mmol, 20.4%). Data are consistent with those reported above.

Coupling of I-1a with benzene using Ni(acac)$_2$



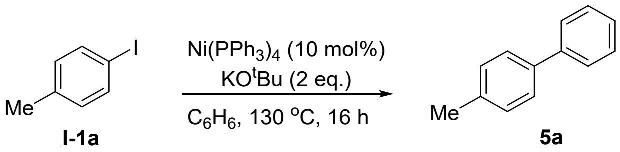
This reaction was carried out as described in General procedure A, except Ni(acac)$_2$ (18.0 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (81.4 mg, 0.484 mmol, 69.1%). Data are consistent with those reported above.

Coupling of I-1b with benzene using Ni(acac)$_2$



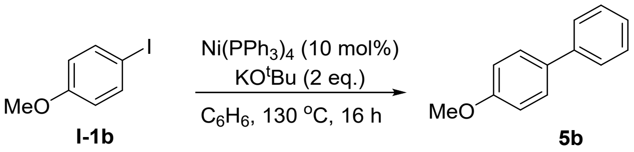
This reaction was carried out as described in General procedure A, except Ni(acac)$_2$ (18.0 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (85.2 mg, 0.463 mmol, 66.1%). Data are consistent with those reported above.

Coupling of I-1a with benzene using Ni(PPh$_3$)$_4$



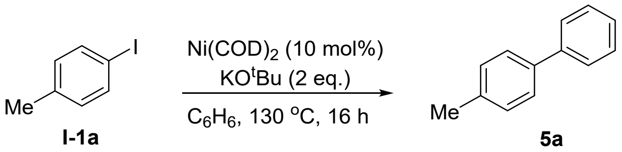
This reaction was carried out as described in General procedure A, except Ni(PPh$_3$)$_4$ (77.5 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (81.2 mg, 0.441 mmol, 63.0%). Data are consistent with those reported above.

Coupling of I-1b with benzene using $Ni(PPh_3)_4$



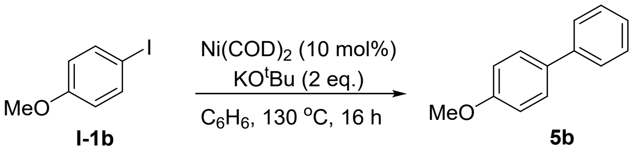
This reaction was carried out as described in General procedure A, except $Ni(PPh_3)_4$ (77.5 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (83.2 mg, 0.452 mmol, 64.6%). Data are consistent with those reported above.

Coupling of I-1a with benzene using $Ni(COD)_2$



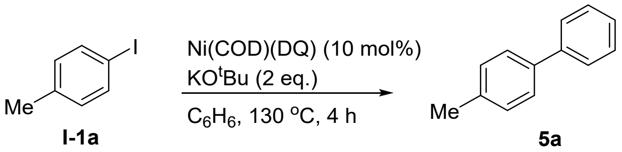
This reaction was carried out as described in General procedure A, except $Ni(COD)_2$ (19.3 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (81.3 mg, 0.484 mmol, 69.1%). Data are consistent with those reported above.

Coupling of I-1b with benzene using $Ni(COD)_2$



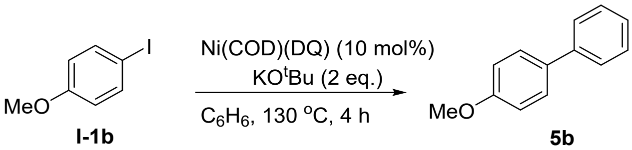
This reaction was carried out as described in General procedure A, except $Ni(COD)_2$ (19.3 mg, 0.07 mmol) was employed. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (82.5 mg, 0.448 mmol, 63.9%). Data are consistent with those reported above.

Coupling of I-1a with benzene using Ni(COD)(DQ) for 4 h



This reaction was carried out as described in General procedure A, except the reaction was run for 4 h. The crude mixture was purified by column chromatography with hexane eluent yielding **5a** as a white waxy solid (85.6 mg, 0.510 mmol, 72.8%). Data are consistent with those reported above.

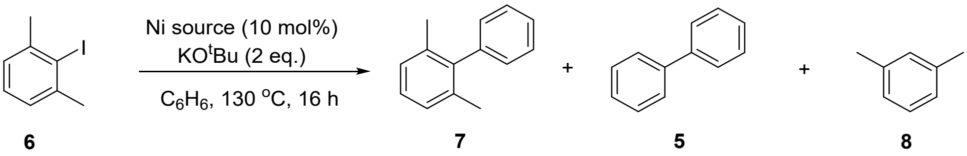
Coupling of I-1b with benzene using Ni(COD)(DQ) for 4 h



This reaction was carried out as described in General procedure A, except the reaction was run for 4 h. The crude mixture was purified by column chromatography with a 2% EtOAc/hexane eluent yielding **5b** as a white solid (104.7 mg, 0.569 mmol, 81.3%). Data are consistent with those reported above.

2,6-Dimethyliodobenzene reaction condition screen

The reactions were carried out according to General procedure B, unless stated otherwise. When the product signal is too weak to be integrated the products are labelled 'trace' and are < 0.8% yield.

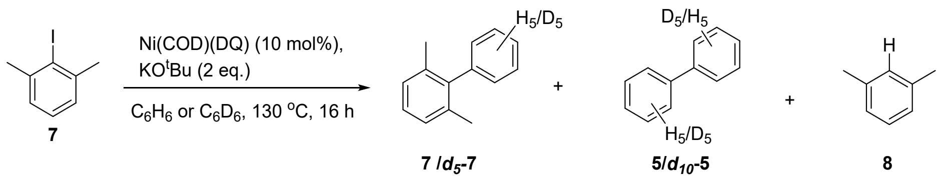


Entry	Ni source	Ligand	Dodecane added (mg)	Dodecane (peak area)	6 (peak area)	6 (% yield)	7 (peak area)	7 (% yield)	5 (peak area)	5(% yield)	8 (peak area)	8 (% yield)
1	-	-	18.5	792.0	2913.6	88.3	trace	trace	trace	trace	trace	trace
2	$NiCl_2$	-	18.6	779.6	2834.2	87.7	trace	trace	trace	trace	trace	trace
3	$Ni(OAc)_2$	-	18.3	793.4	2905.2	86.9	trace	trace	trace	trace	26.7	0.8
4	$Ni(acac)_2$	-	20.4	938.8	2361.4	66.6	79.9	1.5	235.9	4.8	511.1	13.9
5	$Ni(PPh_3)_4$	-	15.1	362.2	793.6	43.0	36.7	1.3	120.4	4.7	305.6	15.9
6	$Ni(COD)_2$	-	16.3	477.4	1124.96	49.0	41.2	1.2	114.0	3.6	667.4	31.0
7	Ni(COD)(DQ)	-	17.8	436.0	trace	trace	176.6	6.1	576.2	22.1	1485.5	75.9
8[a]	Ni(COD)(DQ)	-	18.5	386.5	554.5	34.4	117.2	4.8	324.7	14.6	886.3	53.0
9[b]	Ni(COD)(DQ)	-	16.9	600.9	2616.1	95.4	21.6	0.5	38.7	1.0	191.8	6.7
10[c]	Ni(COD)(DQ)	-	18.3	331.0	798.8	57.2	59.6	2.8	154.6	8.0	562.1	38.9
11[d]	Ni(COD)(DQ)	-	19.5	1912.2	3986.6	52.7	299.7	2.6	975.2	9.3	2676.9	34.1
12[e]	Ni(COD)(DQ)	-	19.6	2908.2	5331.5	46.6	568.6	3.3	1516.9	9.6	4311.3	36.3
13[f]	-	DQ	17.9	415.5	1411.8	78.9	56.2	1.0	90.4	1.8	391.2	21.0
14	-	PPh_3	13.0	518.9	3033.2	98.6	trace	trace	trace	trace	33.4	1.0
15	-	acac	12.9	587.5	3268.1	93.1	trace	trace	73.9	1.5	181.3	5.0
16[g]	Ni(COD)(DQ)	-	17.8	1325.3	-	-	-	-	70.3	0.9	-	-
17[h]	-	-	18.2	1190.7	-	-	-	-	0	0	-	-

Table S1– *Screen of various conditions using substrate* ***6****. [a]5 mol% of Ni(COD)(DQ). [b]1 mol% of Ni(COD)(DQ). [c]5 h reaction time. [d]Reaction at 110 °C. [e]Carried out under an atmosphere of air. [f]10 mol% DQ and excluding Ni(COD)(DQ). [g]Reaction carried out in the absence of* ***6*** *[h]Reaction carried out in absence of Ni(COD)(DQ) or* ***6****.*

Deuterated solvent experiments

These reactions were carried as outlined in General procedure B, except that d_6-benzene (5 mL) was used as solvent.



Entry	Solvent	Dodecane added (mg)	Dodecane (peak area)	6 (peak area)	6(% yield)	7 (peak area)	7 (% yield)	5 (peak area)	5 (% yield)	8 (peak area)	8 (% yield)
1	C_6H_6	17.8	436.0	trace	trace	176.6	6.1	576.2	22.1	1485.5	75.9
2	C_6D_6	20.1	575.0	672.7	30.4	140.9	4.2	44.3	1.5	1107.0	48.4

Table S2 *– GC-FID data for kinetic isotope effect experiments.*

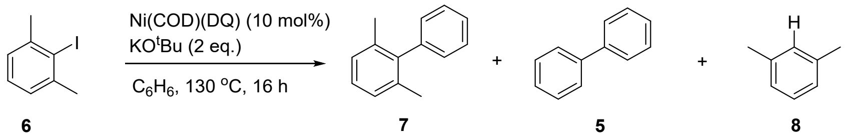
Investigating the source of hydrogen atom abstraction

In this section, the source of abstracted H in xylene product 8 was investigated. Table S3 shows the outcome of the reaction carried out without labelled components (entry 1). Entry 2 shows the effect of adding COD (20 mol%). This did not substantially increase the amount of xylene **8** and so was not a major contributor to the H of xylene.

KO^{t}Bu-d_9 was then prepared. This was used to test if D atom abstraction from KO^{t}Bu-d_9 would be observed or if using this isotopologue of KO^{t}Bu inhibited the coupling reaction. If so, this would indicate that abstraction of H from KO^{t}Bu is important. Table S3 (entry 3) shows the outcome of the coupling reaction using d_9-KO^{t}Bu + C_6D_6. This did not lead to deuteration of the xylene product.

To test if the methyl groups of iodo-*m*-xylene underwent hydrogen atom abstraction by xylyl radicals, we thought to prepare iodo-*m*-xylene-d_6, featuring deuterated methyl groups. However, the synthesis of iodomesitylene- d_9 was more convenient, and so this was prepared as a model for iodo-*m*-xylene-d_6.

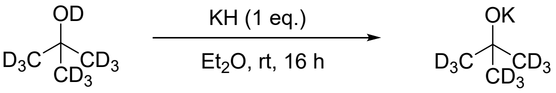
These reactions were carried out as described in General procedure B, except where stated. Yields were obtained *via* GC-FID (Table S3), while determination of deuterium incorporation was determined by GC-MS.



Entry	Conditions changed	Dodecane added (mg)	Dodecane (peak area)	6 (peak area)	6 (% yield)	7 (peak area)	7 (% yield)	5 (peak area)	5 (% yield)	8 (peak area)	8 (% yield)	Deuteration of 8 observed by GCMS?
1	-	17.8	436.0	trace	trace	176.6	6.1	576.2	22.1	1485.5	75.9	N/A
2	20 mol % COD	17.8	1321.4	222.4	3.9	383.6	4.4	1354.3	17.1	4590.7	77.3	N/A
3	*d_9-KO^{t}Bu + C_6D_6*	18.7	1056.2	551.4	12.7	339.6	5.1	164.0	2.7	2207.9	20.6	No

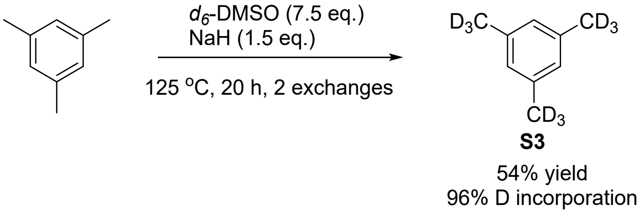
Table S3 – *GC-FID data for COD/d_9-KO^{t}Bu experiments.*

Synthesis of *d_9*-KO^{t}Bu



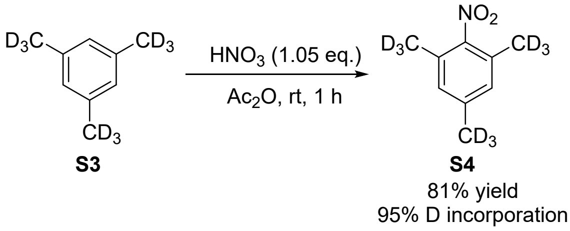
An oven-dried 3-neck round-bottom flask (100 mL) was charged with KH (205 mg, 5.11 mmol) in a glovebox. The flask was removed from the glovebox, cooled to 0 °C in an ice bath and under a flow of Ar, dry Et_2O (8 mL) was added via syringe. With stirring, dry *d_{10}*-Bu^{t}OD (0.48 mL, 5.11 mmol) was added dropwise to the stirred slurry. After the addition, the flask was left to stir at 0 °C for 20 min, and then allowed to slowly warm to room temperature and stirred for a further 16 h. The solvent was removed *in vacuo*, yielding an off-white solid. The solid was extracted into dry THF (2 x 5 mL) and concentrated *in vacuo* yielding *d_9*-Bu^{t}OK as a white solid (431 mg, 3.55 mmol, 70%). The product was characterised by comparison of its ^{13}C NMR spectrum to the spectra of *d_{10}*-Bu^{t}OD. The C-O peak shifts from δ 57.37 ppm to 66.2 ppm, and the CD_3 peak shifts from δ30.5 ppm to 33.6 ppm. **^{2}H NMR** (61 MHz, THF) δ 1.04 (br). **^{13}C NMR** (101 MHz, *d_8*-THF) δ 66.2, 34.2 – 33.0 (m).

Synthesis of *d_9*-mesitylene S3[6]



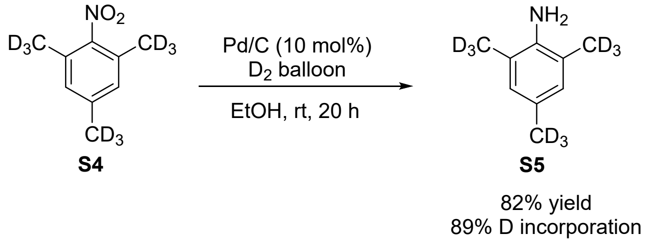
NaH (540 mg, 22.5 mmol) was added to a 3-necked round-bottomed flask (100 mL) and evacuated. The flask was placed under Ar, then mesitylene (1.80 g, 15 mmol) and d_6-DMSO (9.47 g, 113 mmol) were added *via* syringe and stirred to give a pale slurry. A condenser was fitted to the flask under Ar flow and the reaction was slowly heated to 125°C, gradually changing to a dark brown. After 20 h the reaction was allowed to cool to room temperature. The volatiles were then removed by vacuum distillation at 100 °C and collected in a trap cooled in liquid nitrogen. This distillate was washed with water (4 x 25 mL) and the upper mesitylene layer was recovered. The exchange was repeated with fresh d_6-DMSO and NaH. After vacuum distillation and washing with H_2O the product **S3** was recovered as a pale-yellow liquid (1.06 g, 8.18 mmol, 54%). Analysis by ^{1}H NMR showed a deuterium incorporation of 96%. ^{2}H NMR showed deuterium incorporation on the methyl groups only. ^{2}H NMR spectrum shows deuterium incorporation as mesitylene-d_9 (a trace of a minor peak at 2.07 ppm likely arises from mesitylene-d_8). The signals in the IR spectrum between 2060 – 2230 cm^{-1} are due to the benzylic C-D bonds, confirmed by comparison to non-deuterated mesitylene. **^{1}H NMR** (400 MHz, C_6D_6) δ 6.72 (s, 3H), 2.15 – 2.12 (m, 0.4H). **^{13}C NMR** (101 MHz, C_6D_6) δ 137.5, 127.4, 21.1 – 19.9 (m). **^{2}H NMR** (61 MHz, C_6H_6) δ 2.09 (br), 2.07 (br). **IR** ν_{max}/cm^{-1} (neat): 3013, 2924, 2230, 2203, 2127, 2064, 1603, 1443. ***m/z*** (EI): 129.1 [M]$^+$, 111.1, 96.1, 81.1.

Synthesis of d_9- nitromesitylene S4[7]



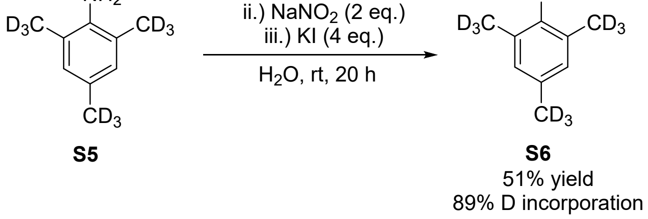
A solution of conc. HNO_3 (0.4 mL, 3.7 mmol) and acetic anhydride (2.0 mL) was cooled in an ice bath and added dropwise to a stirred solution of **S3** (426 mg, 3.3 mmol) and acetic anhydride (1.0 mL) under air, also cooled in an ice bath, quickly turning the solution from colourless to orange. After addition, the solution was allowed to warm to room temperature and stirred for a further 1 h. An aqueous K_2CO_3 solution was added until slightly basic, and then the product was precipitated in ice-water. The precipitate was vacuum filtered, washed with more ice-water and dried *in vacuo* yielding pale-yellow crystals of **S4** (465 mg, 2.67 mmol, 81%). A signal at 1724 cm^{-1} in the IR spectrum indicates traces of acetic acid are present in the product. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.91 (s, 2H), 2.28 (quin, 2.2 Hz, 0.15H), 2.25 (quin, 2.2 Hz, 0.27H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.7, 129.0, 128.9, 20.0 – 19.3 (m), 16.8 – 15.8 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 2.29 (s, 3D), 2.26 (s, 6D) **IR** v_{max}/cm^{-1} (neat): 2924, 2870, 2853, 2233, 2112, 2064, 1724, 1599, 1508, 1364. ***m/z*** (EI): 174.1 ([M]$^+$), 156.1, 144.1, 128.1, 96.1, 81.0.

Synthesis of *d*$_9$-1,3,5-trimethylaniline S5



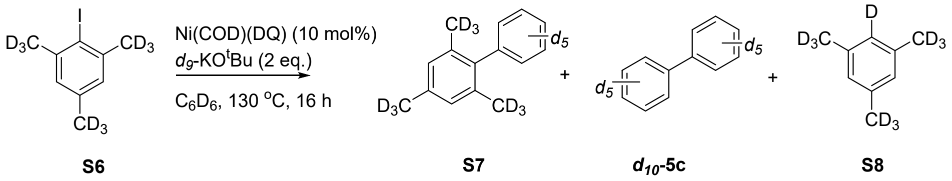
Nitroarene **S4** (465 mg, 2.67 mmol) and 20% Pd/C (188 mg, 0.267 mmol) were added to a 3-necked round-bottomed flask (250 mL) and evacuated. The flask was placed under Ar flow and degassed ethanol (20 mL) was added. With vigorous stirring, the Ar atmosphere was replaced with D_2 from a balloon. The reaction was left to stir vigorously for 20 h under an atmosphere of D_2. The reaction mixture was then filtered through a short plug of Celite, washed with EtOAc and the concentrated *in vacuo* yielding **S5** as a pale-yellow oil (301 mg, 2.19 mmol, 82 %). ^{1}H NMR showed a fall in deuterium incorporation to 89%, and also showed that the *ortho*-methyl groups are more labelled than the *para*-methyl group (93% vs 81%). Splitting of peaks in the ^{2}H NMR spectrum is due to the presence of minor isotopomers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.82 (s, 2H), 3.44 (br, 2H), 2.27 – 2.22 (m, 0.56H), 2.19 – 2.17 (m, 0.45H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.2, 128.8, 126.8, 121.6, 20.3 – 19.3 (m), 17.3 – 16.5 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 2.23 (br), 2.19 (br), 2.14 (br). ***m/z*** (EI): 144.1 ([M]$^+$), 125.1, 111.1, 95.0, 80.0, 67.0.

Synthesis of *d*$_9$- 2-iodomesitylene S6[8]



A solution of $NaNO_2$ (302 mg, 4.38 mmol) in H_2O (4 mL) was slowly added dropwise to a stirred suspension of **S5** (301 mg, 2.19 mmol) and *p*-TsOH (1.67 g, 8.76 mmol) in H_2O (6 mL) under air at 0°C, yielding a colourless solution that was left to stir for a further 10 min. A solution of KI (1.45 g, 8.76 mmol) in H_2O (4 mL) was added slowly dropwise, which upon the first addition yielded a dark purple solution that persisted once half the KI solution had been added. Once the addition was complete, the dark purple solution was allowed to slowly warm to room temperature and stirred for a further 20 h. The reaction was then extracted with EtOAc (3 x 5 mL), the combined organic fractions were then washed with sat. $Na_2S_2O_3$ (10 mL) and H_2O (5 mL) twice, then with H_2O (10 mL). The organic fractions were then dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude product was then purified by column chromatography with hexane eluent to yield **S6** as a crystalline white solid (284 mg, 1.11 mmol, 51 %). Splitting of peaks in the ^{2}H NMR spectrum is due to the presence of minor isotopomers. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.88 (s, 2H), 2.43 – 2.37 (m, 0.44H), 2.24 – 2.19 (m, 0.56H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.8, 137.4, 128.1, 104.3, 29.2 – 28.3 (m), 20.8 – 19.8 (m). **^{2}H NMR** (61 MHz, $CHCl_3$) δ 2.43 (br), 2.41 (br), 2.24 (br), 2.21 (br). **IR** ν_{max}/cm^{-1} (neat): 3026, 2922, 2228, 2204, 2106, 2062, 1572, 1410, 1271, 1001. ***m/z*** (EI): 255.1 ([M]$^+$), 127.1, 109.0, 96.1, 81.0, 68.0. HRMS Found: 255.0454. $C_9H_2D_9I^+$ (M$^+$) requires 255.0465 (deviation 4.3 ppm). (Ref 8 describes the synthesis of the corresponding non-deuterated compound. Our data are consistent with the data in that paper).

Reaction employing substrate S6



This reaction was carried out as described in General Procedure B, except substrate **S6**, *d$_6$*-benzene and *d$_9$*-KO^{t}Bu were employed. The crude reaction mixture was analysed by GC-MS, in which coupled product **S7** and **S8** were observed, along with trace amounts of ***d$_{10}$*-5c**, with the majority of the starting material **S6** remaining unconsumed (Figure S2).

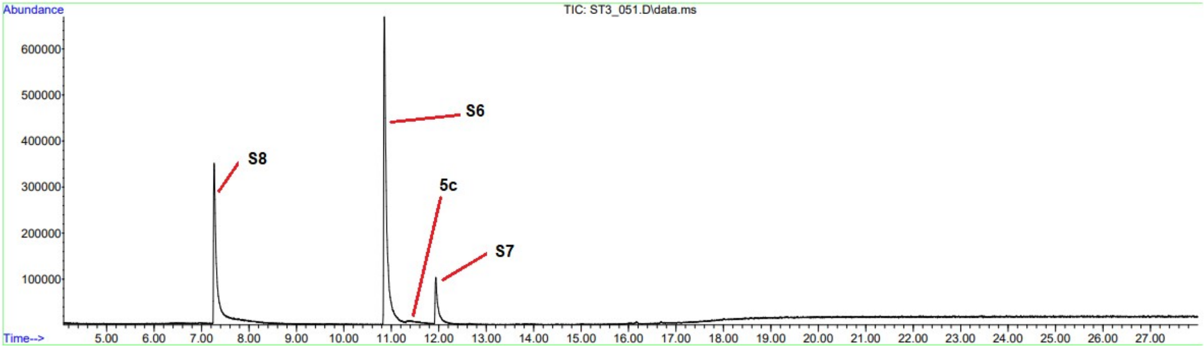


Figure S2 *– GC-MS spectrum of crude reaction mixture for coupling reaction of substrate* ***S6****.*

Due to the incomplete deuteration of substrate **S6**, determining whether deuterium atom abstraction by the mesityl radical to form **S8** had occurred was impossible by mass spectrometry, and thus ^{2}H NMR was employed. Analysis of the reaction mixture by ^{2}H NMR shows a signal at δ 6.86 ppm (Figure S3), which corresponds to Ar-D position of compound **S8**, indicating that deuterium atom abstraction has occurred, from the benzylic positions of **S6**. An analogous reaction was carried out using non-deuterated iodomesitylene (with C_6H_6 and KO^{t}Bu), giving mostly mesitylene and biphenyl as product with small quantities of heterocoupled mesitylbenzene product. The ^{1}H NMR of the crude reaction mixture shows a peak at δ 6.81 ppm corresponding to the Ar-H position of mesitylene (Figure S4), supporting the assignment of the Ar^{Mes}-D peak in Figure S3. The ^{1}H NMR spectrum of commercial non-deuterated mesitylene is provided for reference, showing a peak at δ 6.83 ppm (Figure S5), and the ^{1}H NMR for our synthesised d_9-mesitylene shows the same peak at δ 6.72 ppm (in C_6D_6). The literature value for the ^{2}H NMR spectrum of d_3-mesitylene (1,3,5-$C_6Me_3D_3$) gives a value of δ 7.02 ppm,[12] which is expected to be shifted further downfield than **S8** as the longer benzylic C-H bond length (compared to C-D) makes CH_3 a less inductively donating group. Based on these facts the signal at δ 6.86 ppm in Figure S3 corresponds to deuterated **S8**, resulting from deuterium atom abstraction by the mesityl radical from the benzylic positions of **S6**.

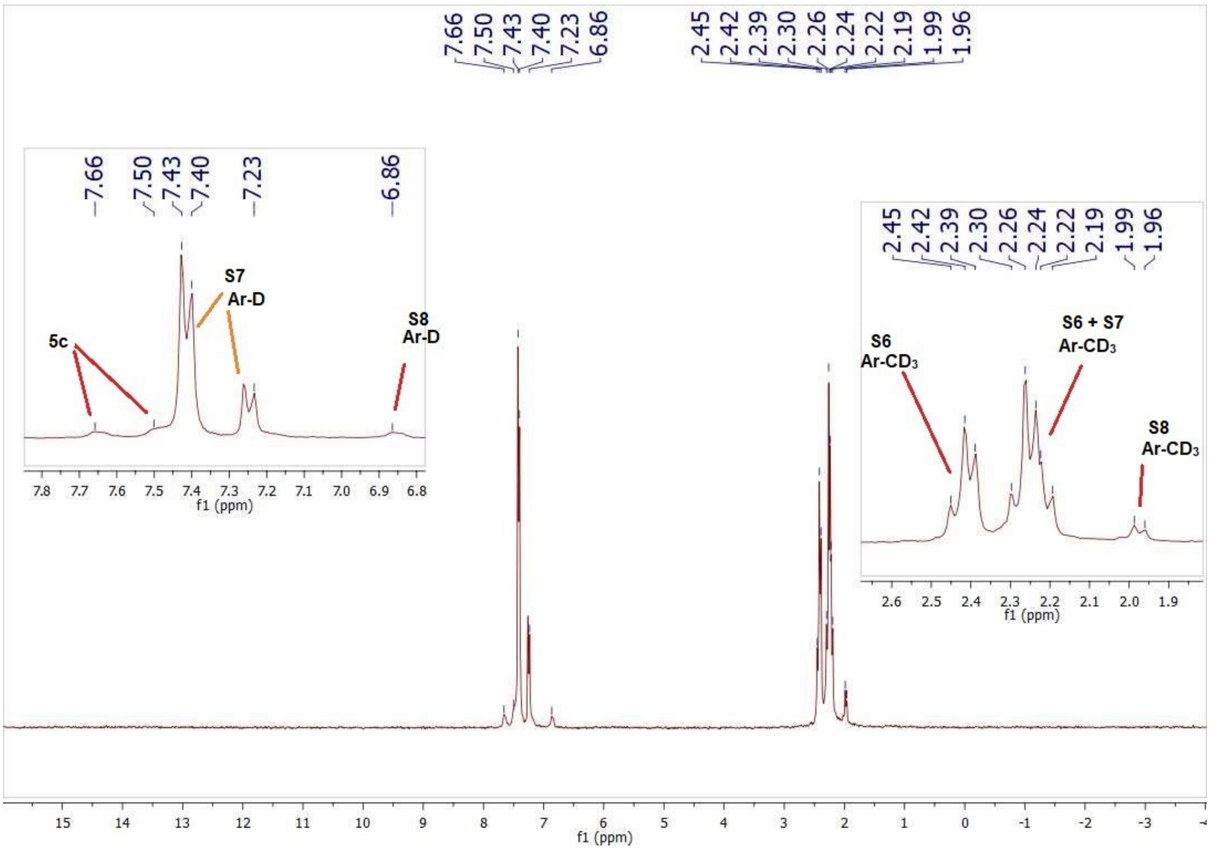


Figure S3 *– ^{2}H NMR ($CHCl_3$) spectra of crude reaction mixture for coupling reaction of substrate* ***S6*****.**

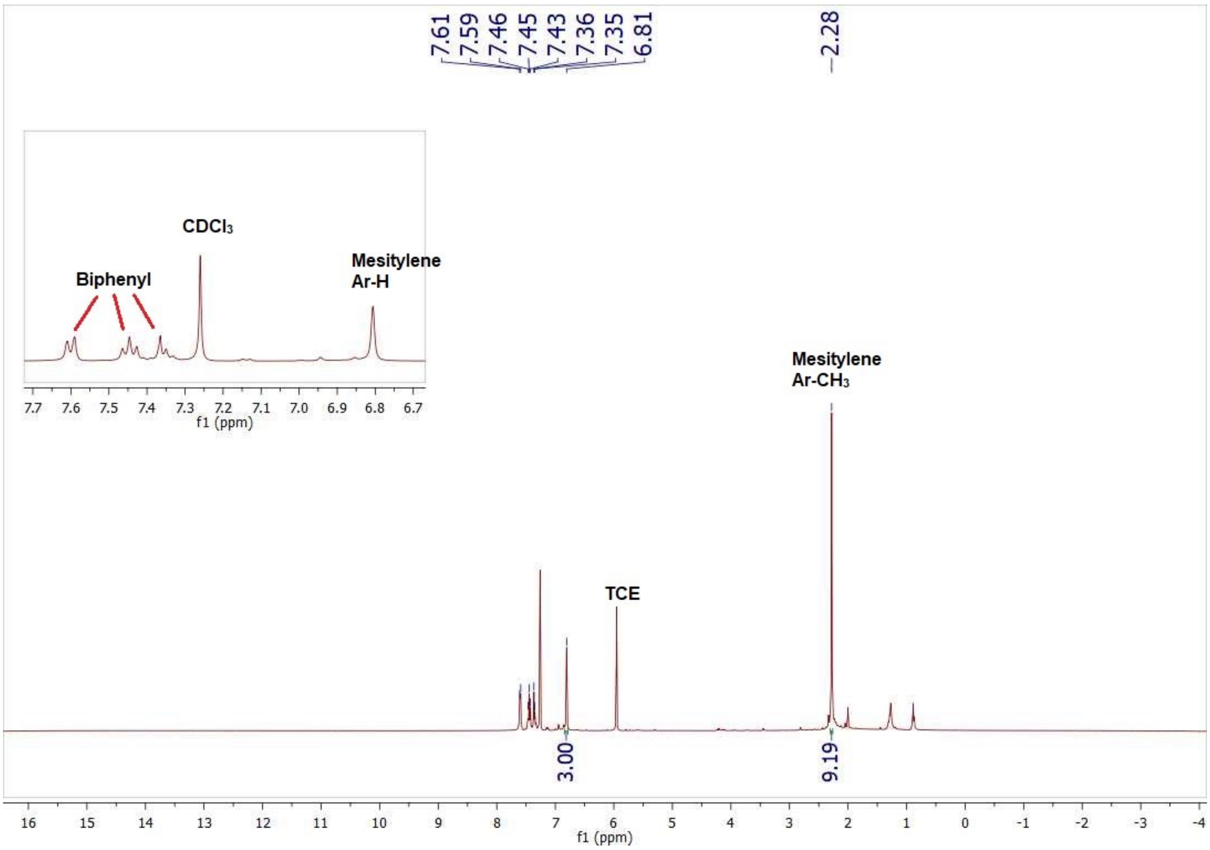


Figure S4 – *^{1}H NMR ($CDCl_3$) spectrum of crude reaction mixture for coupling reaction of non-deuterated iodomesitylene. TCE = 1,1,2,2-tetrachloroethane*

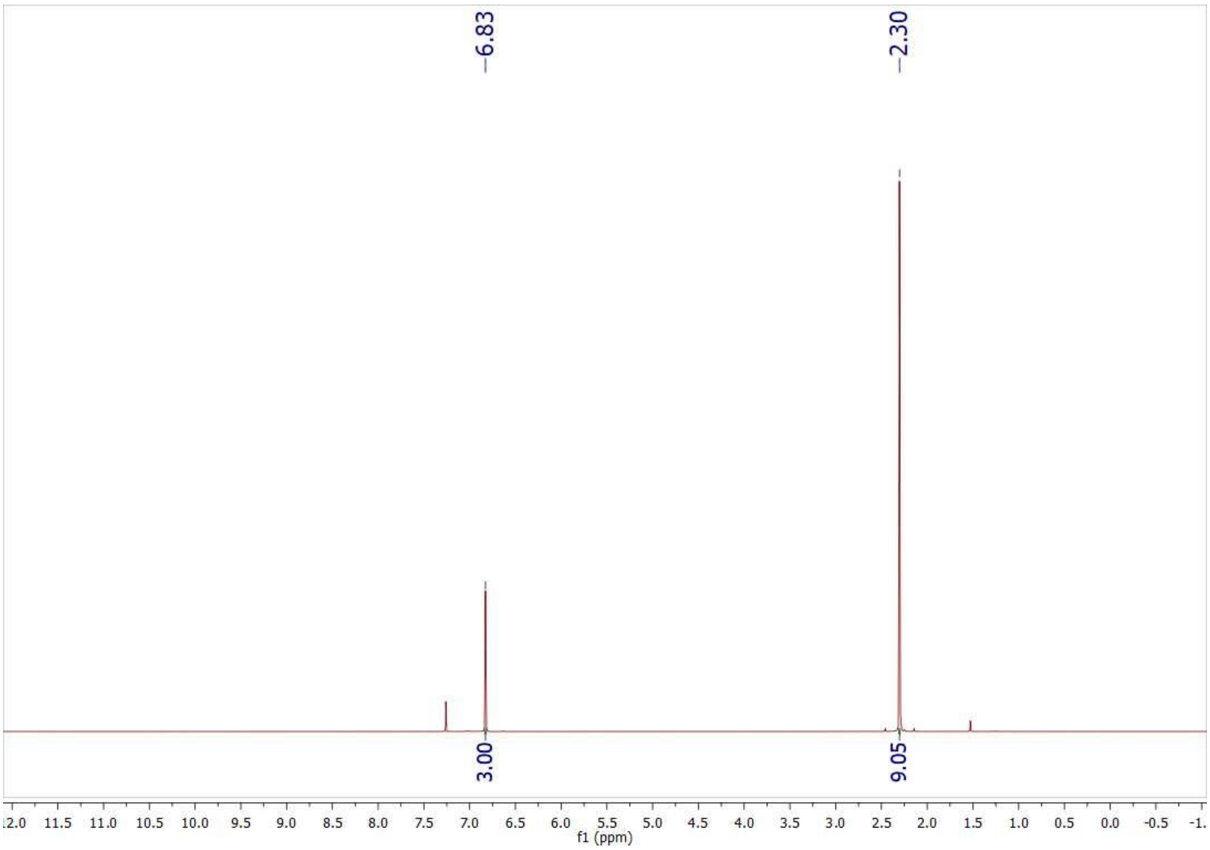
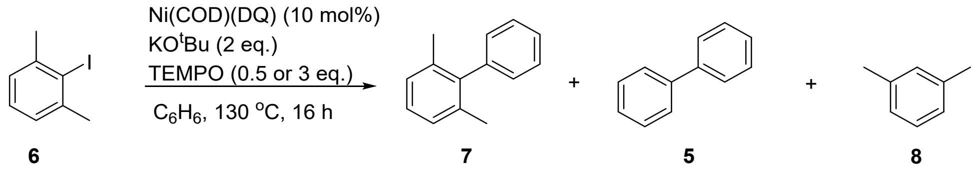


Figure S5 – *^{1}H NMR ($CDCl_3$) spectrum of non-deuterated mesitylene.*

Radical scavenging experiments with TEMPO

These reactions were carried out as outlined in General Procedure B, except radical scavenger TEMPO was added (54.7 mg, 0.35 mmol **or** 328 mg, 2.1 mmol).



Entry	TEMPO	Dodecane added (mg)	Dodecane (peak area)	6 (peak area)	6 (% yield)	7 (peak area)	7 (% yield)	5 (peak area)	5 (% yield)	8 (peak area)	8 (% yield)
1	-	17.8	436.0	trace	trace	176.6	6.1	576.2	22.1	1485.5	75.9
2	0.5 eq.	19.5	1327.1	1379.2	26.3	229.3	2.9	490.1	6.8	1634.5	30.0
3	3.0 eq.	17.9	428.7	1507.7	81.7	trace	trace	trace	trace	trace	trace

Table S4 *– GC-FID for reactions with added TEMPO.*

GC-FID calibration information

To obtain yields for inseparable mixtures of compounds **6, 7**, **5** and **8**, calibration curves were constructed for each compound using GC-FID using *n*-dodecane as an internal standard. Authentic samples of compounds **6, 5** and **8** were bought from commercial sources, while compound **7** was synthesised using the procedure outlined above and corrected for the homocoupled impurity **S1**. To construct each calibration curve, known amounts of each compound (approximately 0.01 mmol – 0.1 mmol) were mixed with a known amount of dodecane (approximately 0.1 mmol). The mixtures were then diluted with $CHCl_3$ and analysed on the GC-FID to obtain the peak area for both the sample compound (SC) and dodecane internal standard (IS). Calibration curves were constructed by plotting:

$$\frac{mmol(SC)}{mmol(IS)} \text{ vs. } \frac{area\ (SC)}{area\ (IS)}$$

The plots are forced through the origin, with the gradient representing the response factor (RF) for each compound against *n*-dodecane. To obtain the composition of relevant reaction mixtures from these curves, a known mass of dodecane was added to the reaction mixture, an aliquot of which was then removed, diluted with $CHCl_3$ and analysed by GC-FID. The peak areas for each compound were then input into the following equation to obtain the moles of **6, 7, 5** and **8**:

$$\frac{area(SC) * mmol(IS)}{area(IS) * RF} = mmol(SC)$$

Entry	Mass of **8** (mg)	mmol of **8**	Mass dodecane (mg)	mmol dodecane	mmol ratio	Area of **8**	Area Dodecane	Area ratio
1	2.1	0.0198	18.8	0.1100	0.1800	12578.9	98487.2	0.1277
2	8.6	0.0810	17.6	0.1030	0.7864	42401.7	84773.8	0.5001
3	11.0	0.1040	17.9	0.1050	0.9904	18433.6	26890.0	0.6855
4	33.2	0.3130	18.2	0.1070	2.9252	32922.7	16190.1	2.0335
5	84.6	0.7970	17.4	0.1020	7.8137	40651.0	7618.8	5.3356
6	105.8	0.9970	17.2	0.1010	9.8712	36894.7	5652.2	6.5274

***Table S5** – Calibration curve data for m-xylene **8**.*

Entry	Mass of **5** (mg)	mmol of **5**	Mass dodecane (mg)	mmol dodecane	mmol ratio	Area of **5**	Area Dodecane	Area ratio
1	2.1	0.0136	15.2	0.0892	0.1524	9428.4	68957.4	0.1367

2	7.5	0.0486	14.4	0.0845	0.5751	33761.9	65096.8	0.5186
3	16.0	0.1040	14.7	0.0863	1.2050	19101.4	18326.8	1.0422
4	47.2	0.3060	14.7	0.0863	3.5457	34515.8	11200.1	3.0817
5	109.9	0.7130	15.6	0.0916	7.7838	37752.0	5400.0	6.9911

Table S6 *– Calibration curve data for biphenyl* ***5****.*

Entry	Mass of sample (mg)	mmol of **7**	Mass dodecane (mg)	mmol dodecane	mmol ratio	Area of **7**	Area Dodecane	Area ratio
1	2.0	0.0104	18.0	0.106	0.0982	6115.4	62881.5	0.0972
2	7.8	0.0406	19.9	0.117	0.3470	12765.3	36554.7	0.3492
3	15.3	0.0796	17.5	0.103	0.7733	16138	20688.2	0.7800
4	44.1	0.2296	18.9	0.111	2.0685	22237.2	10923.1	2.0357
5	94.5	0.4920	17.9	0.105	4.6857	32072.9	6931	4.6274

Table S7 *– Calibration curve data for 2,6-dimethylbiphenyl* ***7****, with correction for impurity of* ***S1****.*

Entry	Mass of **6** (mg)	mmol of **6**	Mass dodecane (mg)	mmol dodecane	mmol ratio	Area of **6**	Area Dodecane	Area ratio
1	6.1	0.0263	16.4	0.0962	0.2734	11457.0	59542.4	0.1924
2	9.3	0.0401	17.1	0.100	0.4010	12907.3	48829.4	0.2643
3	21.7	0.0935	16.9	0.0992	0.9425	16799.3	27416.6	0.6127
4	50.8	0.219	16.4	0.0963	2.2741	27341.3	18276.5	1.4960
5	87.5	0.377	17.4	0.102	3.6961	29666.8	12433.8	2.3860
6	133.1	0.574	15.9	0.0933	6.1522	40482.1	10198.2	3.9695

Table S8 *– Calibration curve data for 2,6-dimethyliodobenzene* ***6.***

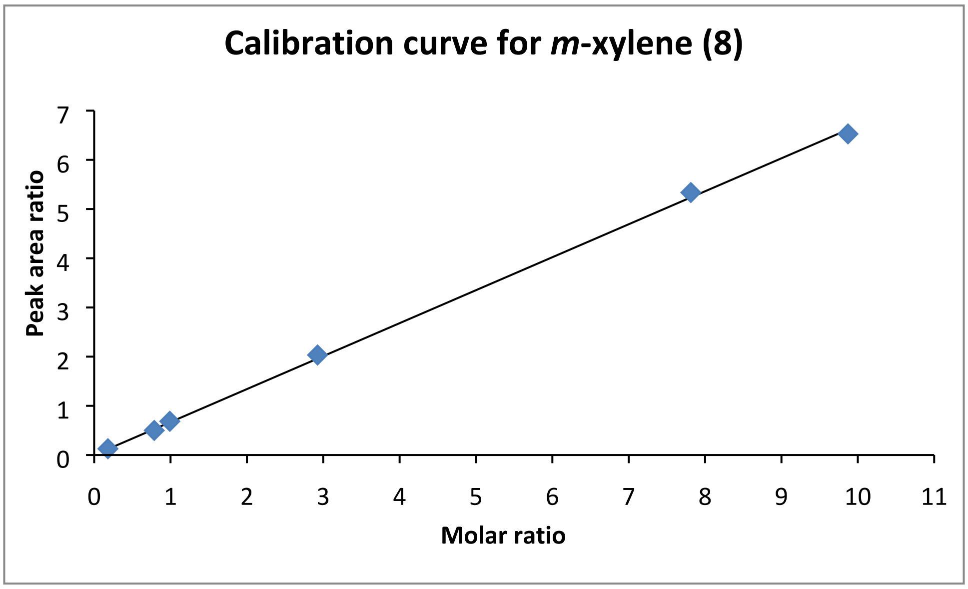


Figure S10 – *GC-FID calibration curve for m-xylene* ***8.***

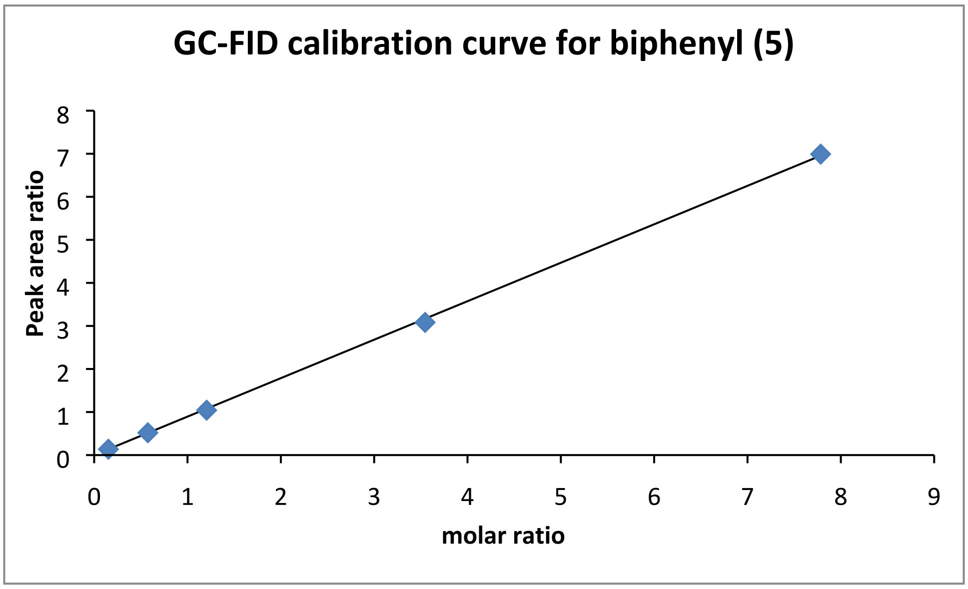


Figure S11 – *GC-FID calibration curve for biphenyl* ***5****.*

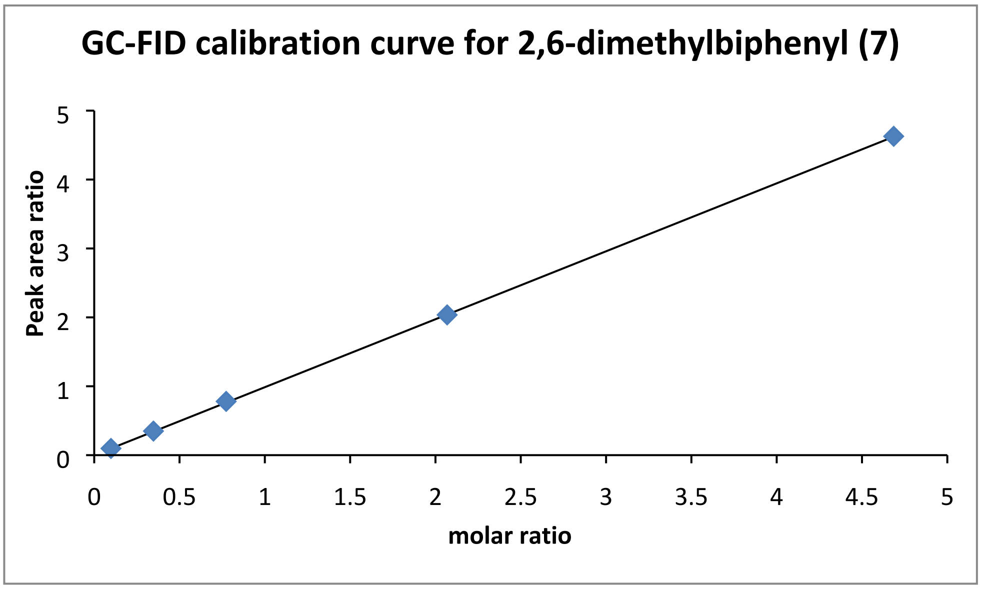


Figure S12 *– GC-FID calibration curve for 2,6-dimethylbiphenyl* ***7.***

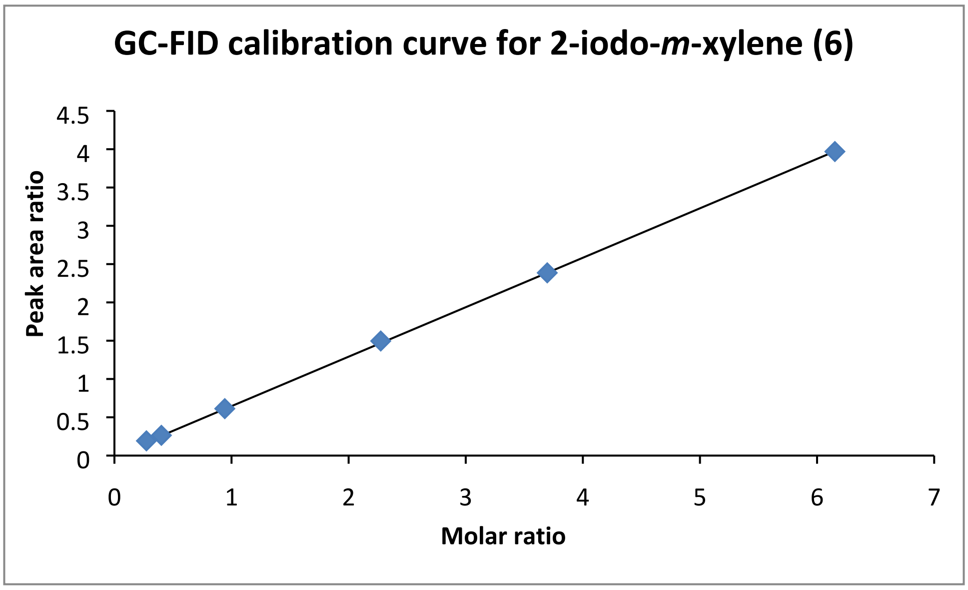
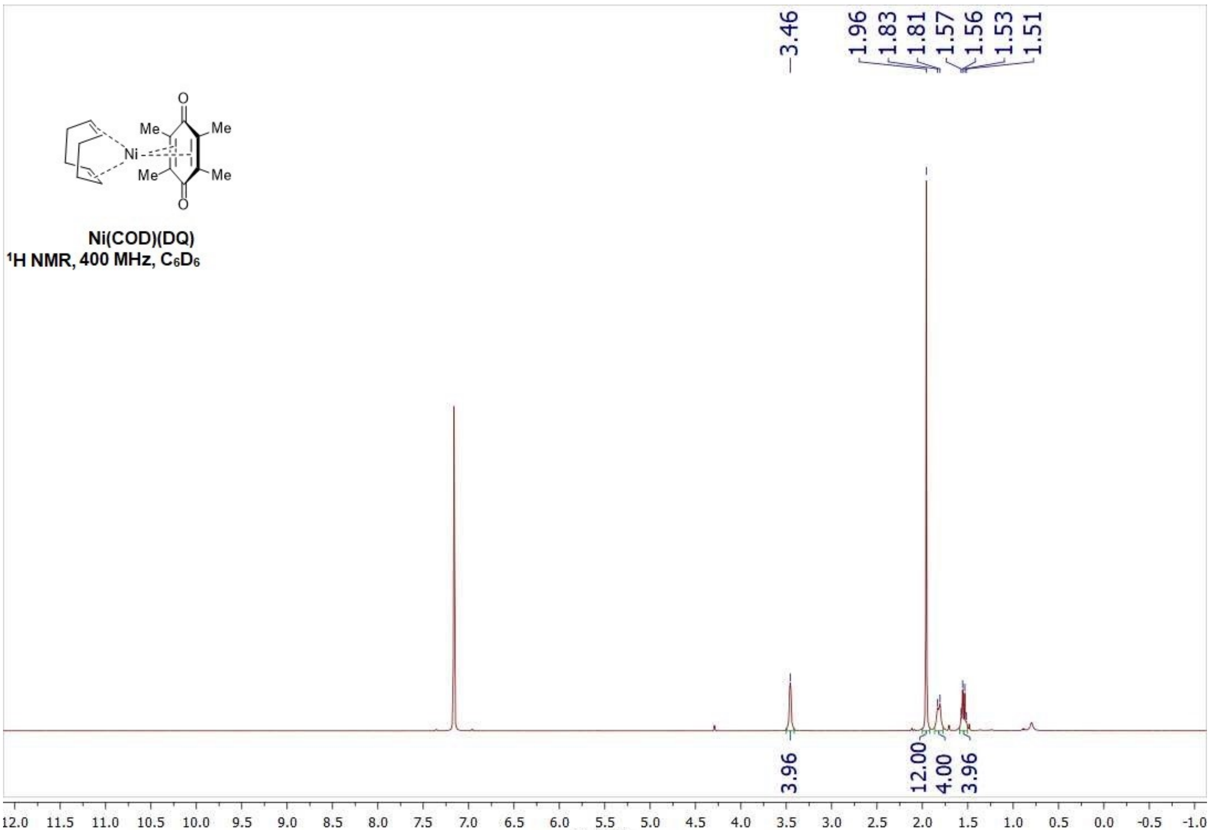
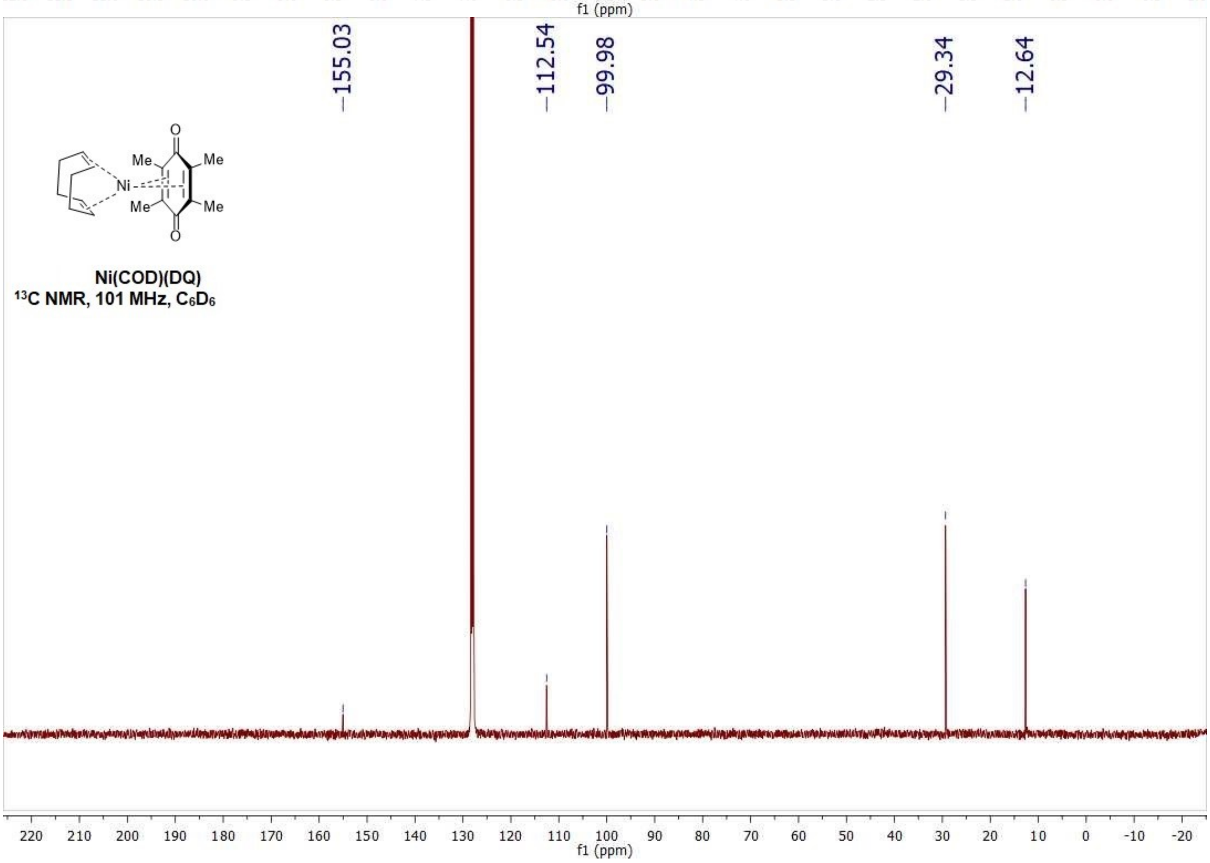
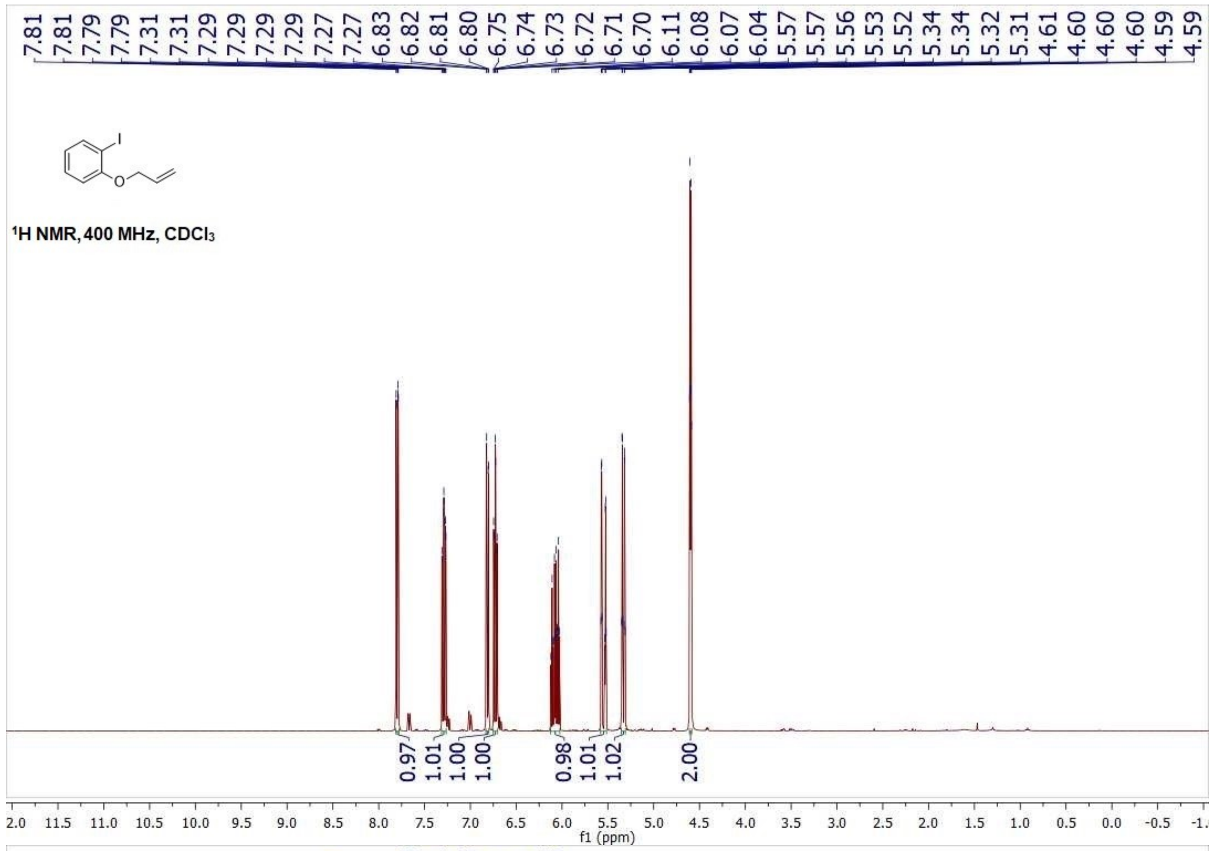


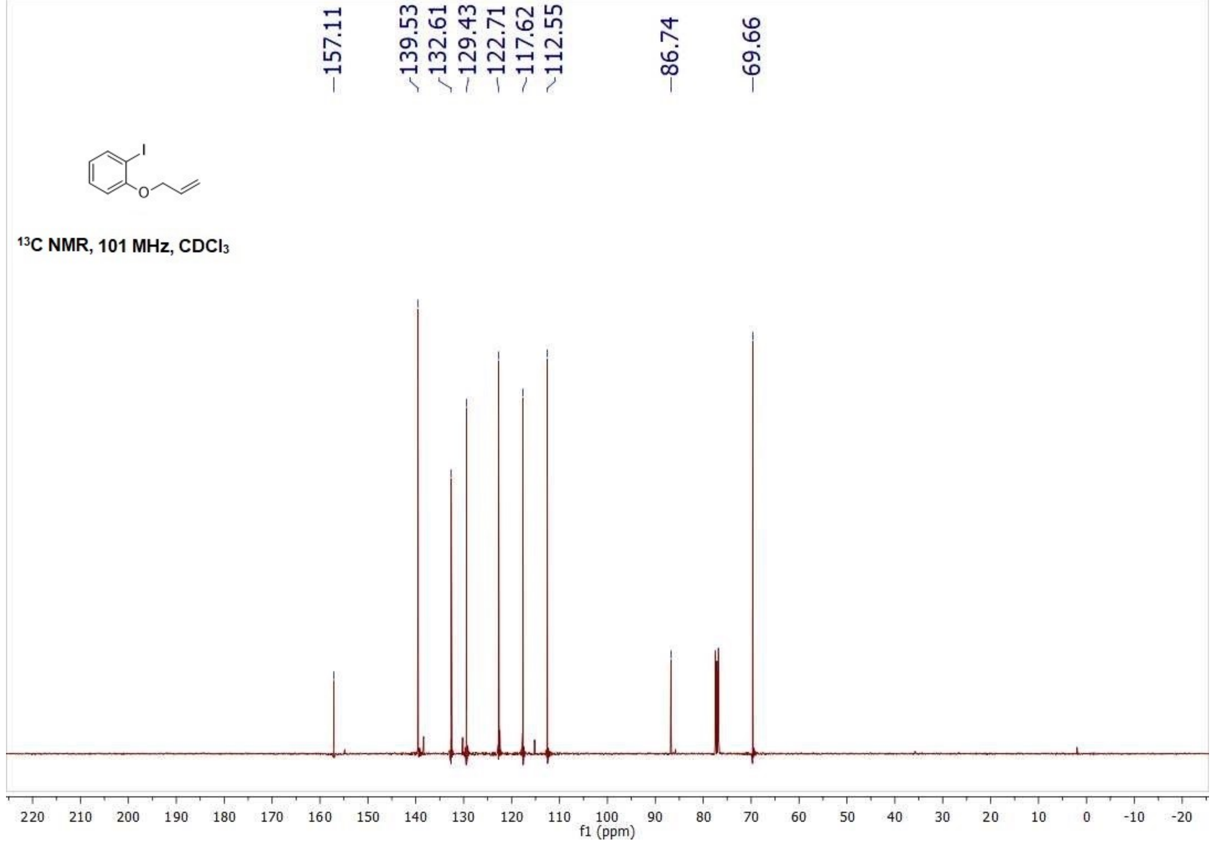
Figure S13*– GC-FID calibration curve for 2,6-dimethyliodobenzene* ***6***

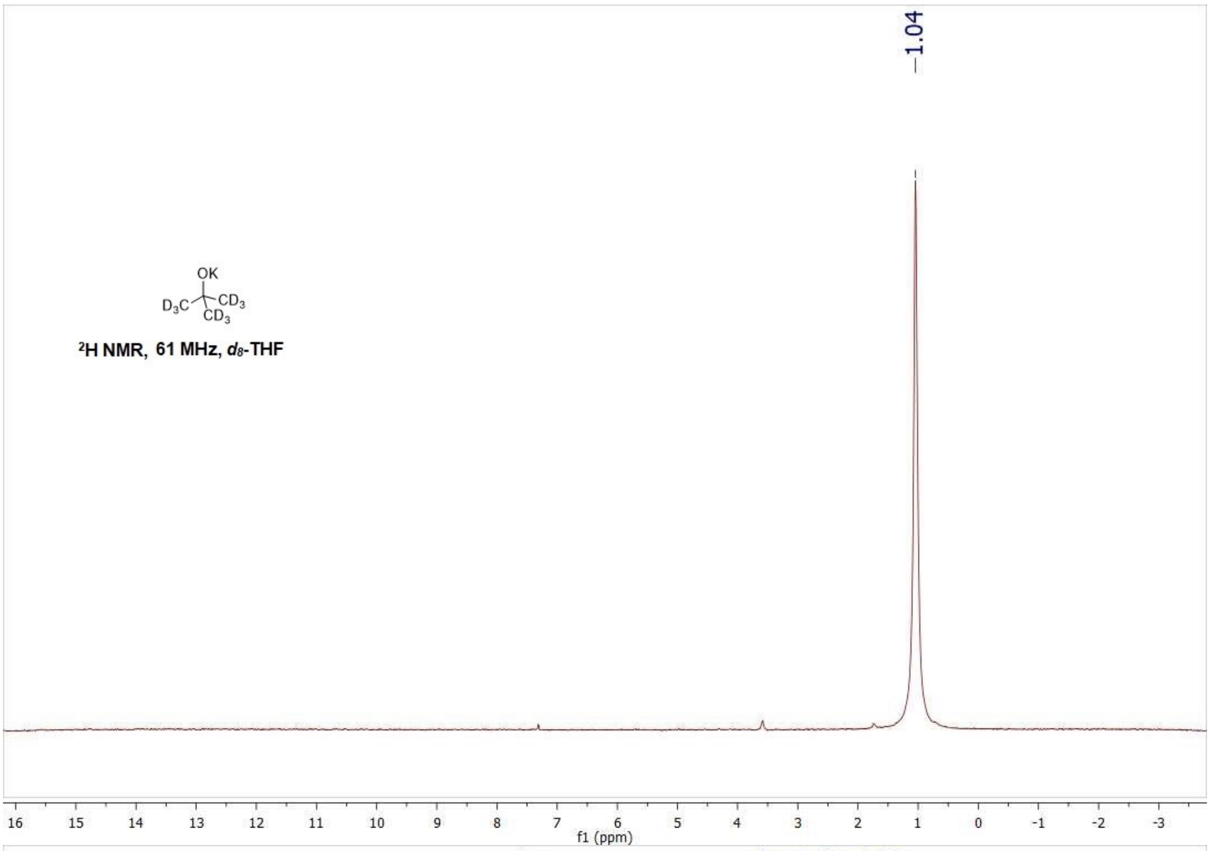
NMR spectra


Ni(COD)(DQ)
^{1}H NMR, 400 MHz, C_6D_6

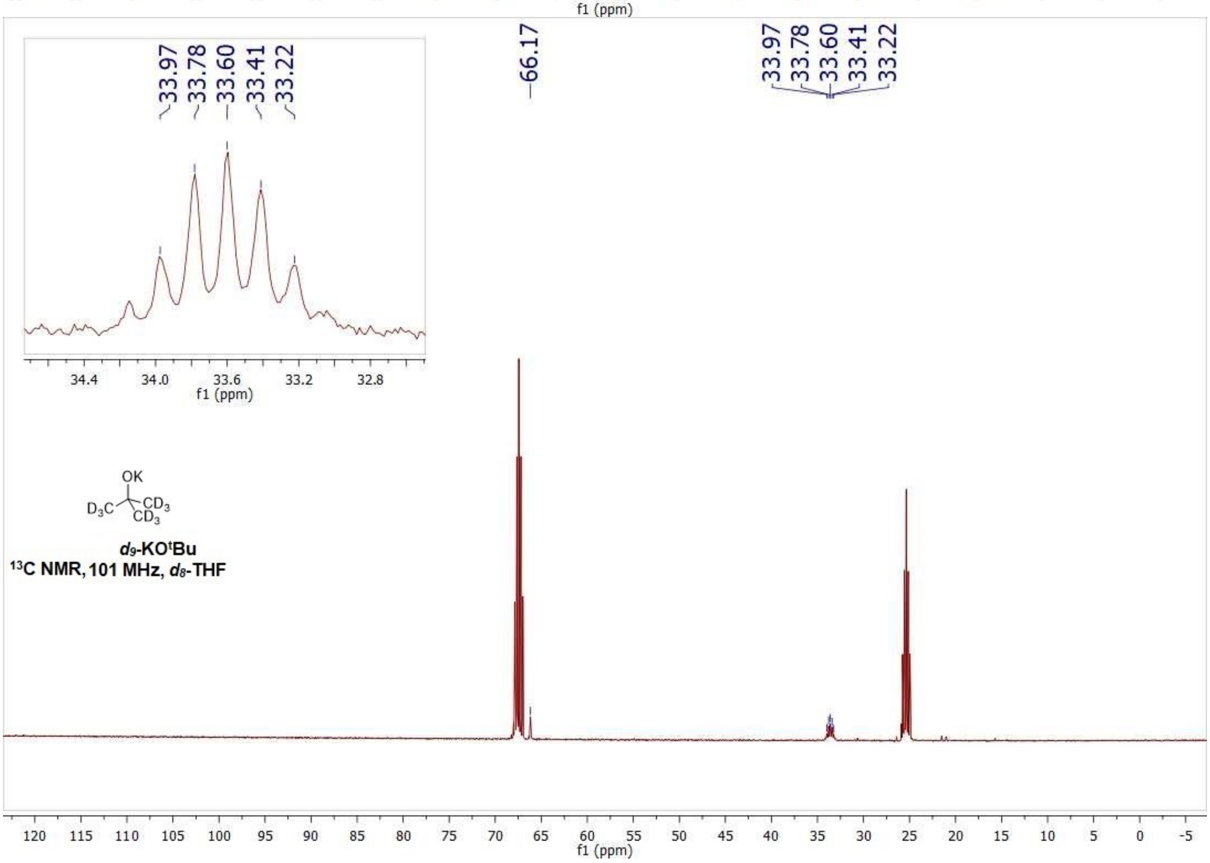

Ni(COD)(DQ)
^{13}C NMR, 101 MHz, C_6D_6


7.81
7.81
7.79
7.79
7.31
7.31
7.29
7.29
7.29
7.29
7.27
7.27
6.83
6.82
6.81
6.80
6.75
6.74
6.73
6.72
6.71
6.70
6.11
6.08
6.07
6.04
5.57
5.57
5.56
5.53
5.52
5.34
5.34
5.32
5.31
4.61
4.60
4.60
4.60
4.59
4.59
I
O
¹H NMR, 400 MHz, CDCl₃
0.97
1.01
1.00
1.00
0.98
1.01
1.02
2.00
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)

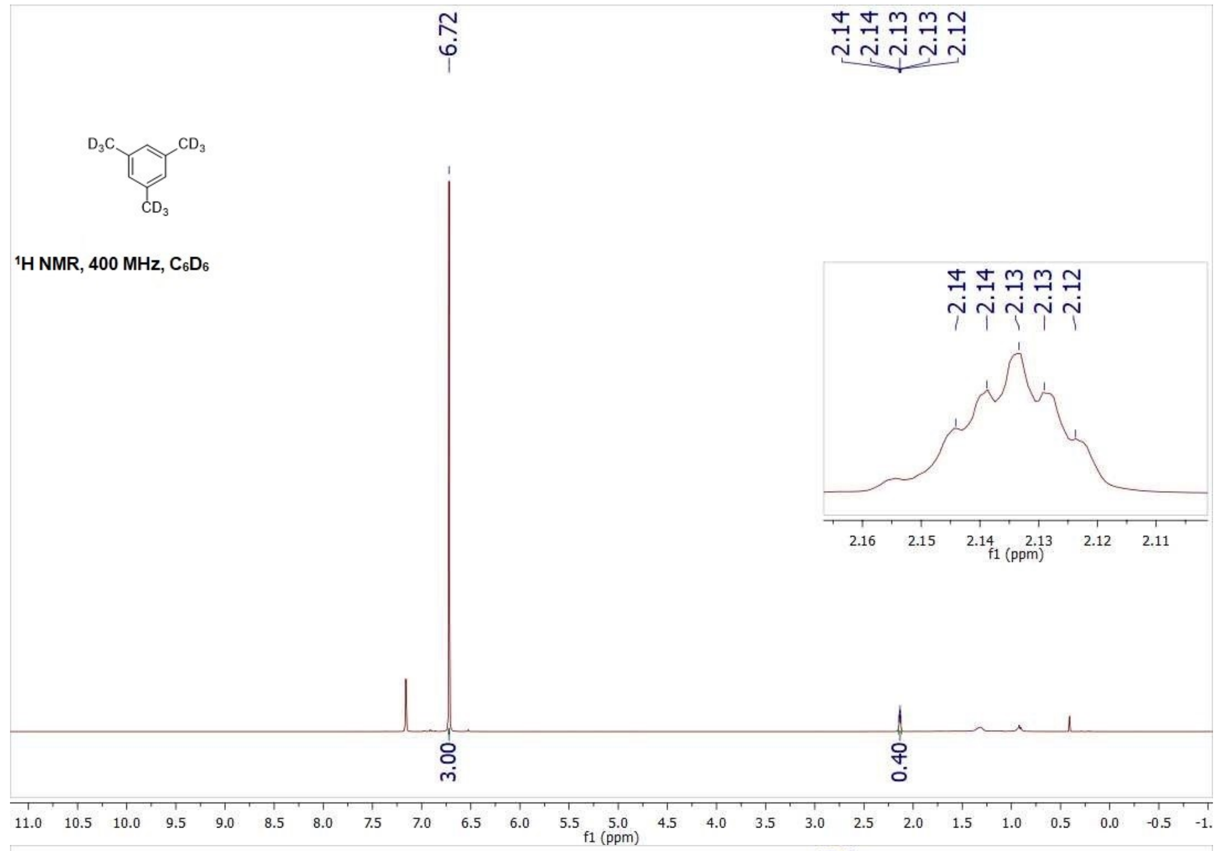

157.11
139.53
132.61
129.43
122.71
117.62
112.55
86.74
69.66
I
O
¹³C NMR, 101 MHz, CDCl₃
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)



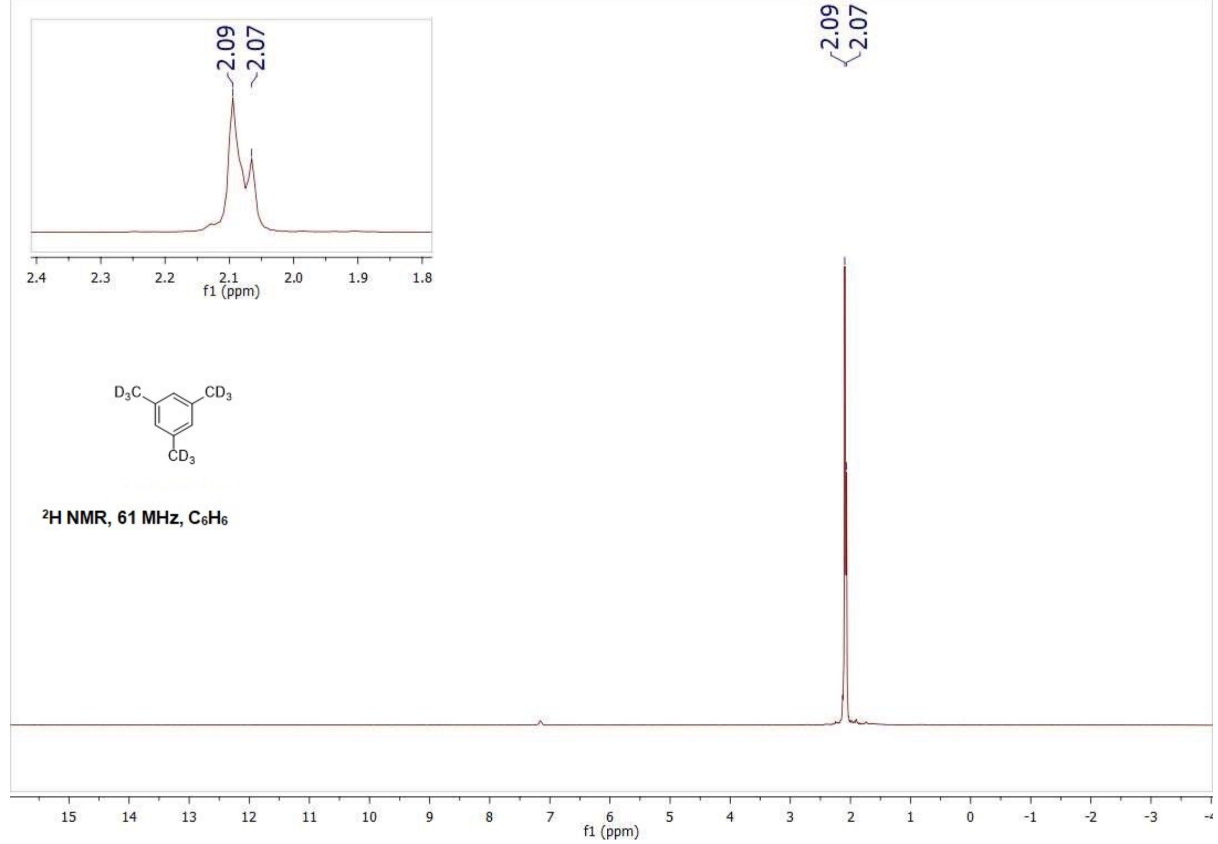
—1.04
OK
D_3C
CD_3
CD_3
²H NMR, 61 MHz, *d₈*-THF
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)



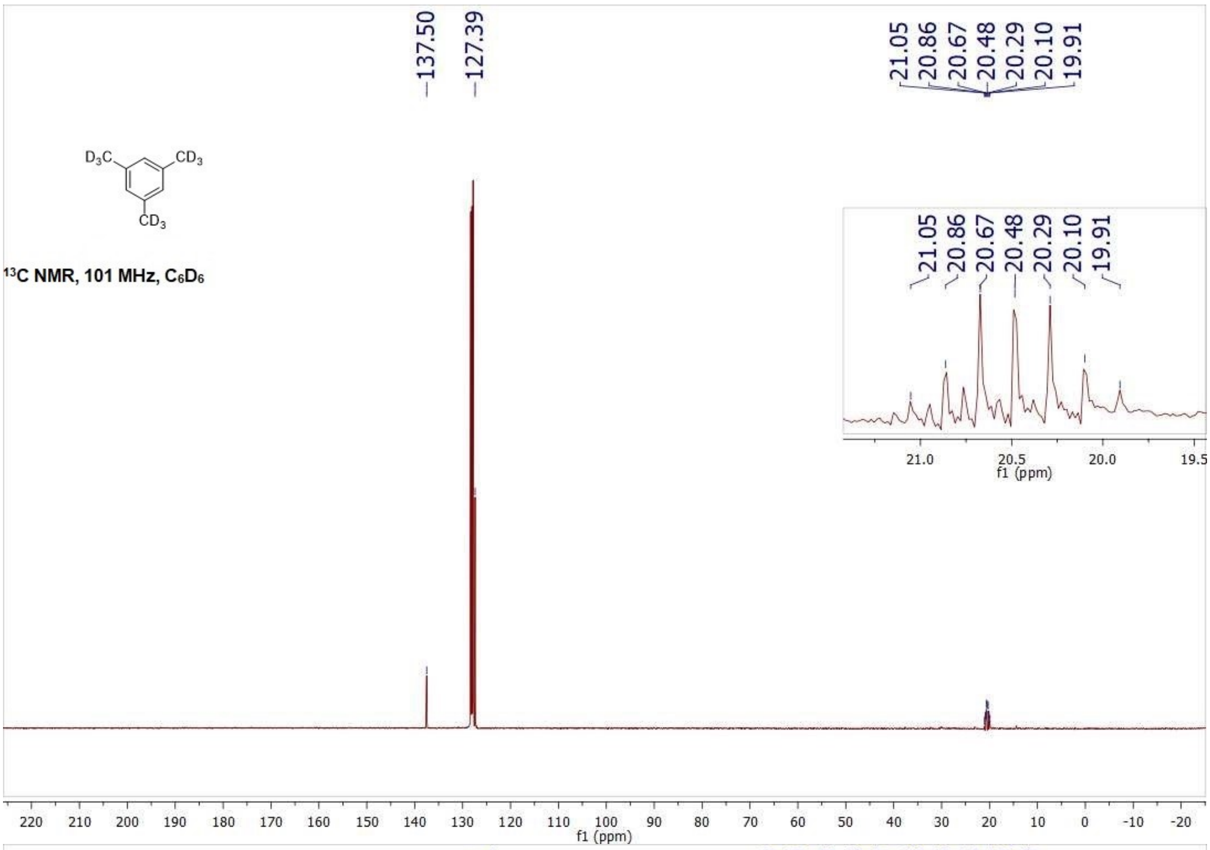
33.97
33.78
33.60
33.41
33.22
34.4 34.0 33.6 33.2 32.8
f1 (ppm)
—66.17
33.97
33.78
33.60
33.41
33.22
OK
D_3C
CD_3
CD_3
***d₉*-KOᵗBu**
¹³C NMR, 101 MHz, *d₈*-THF
120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

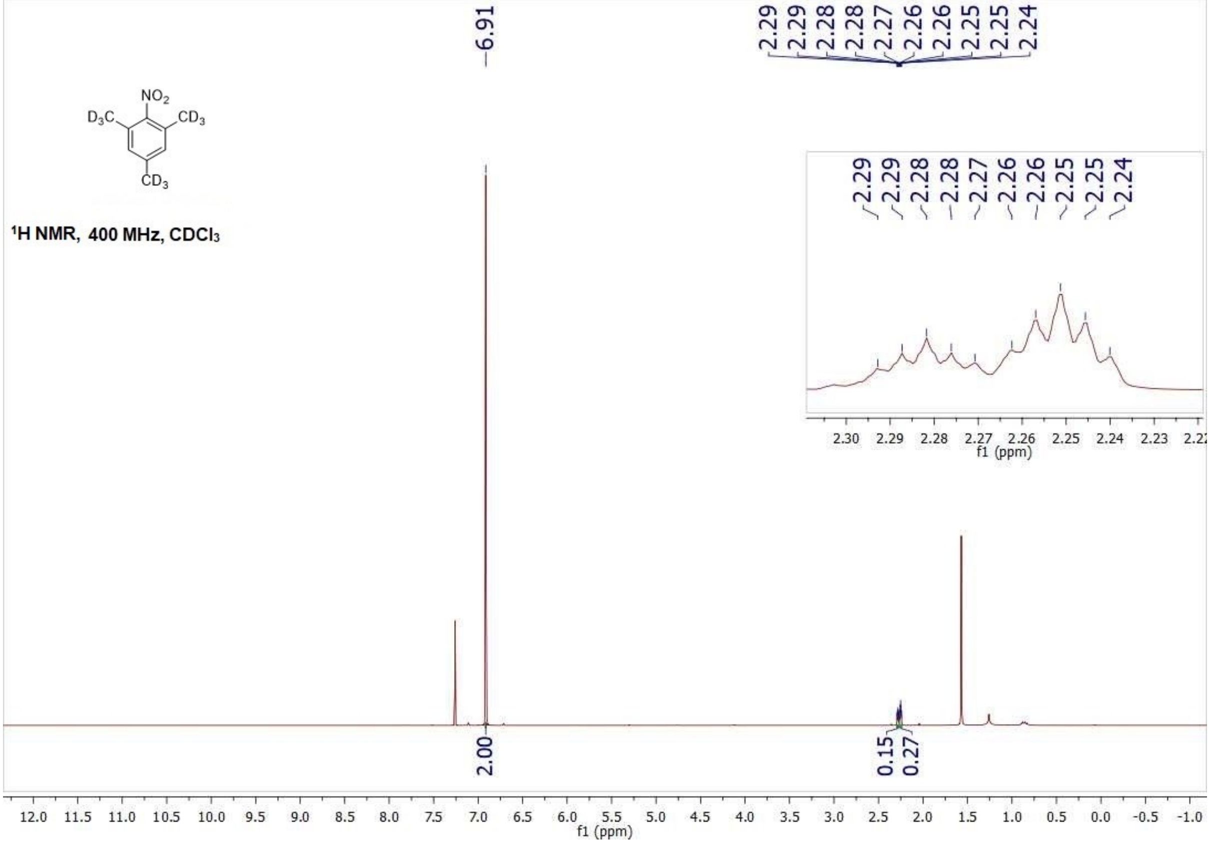


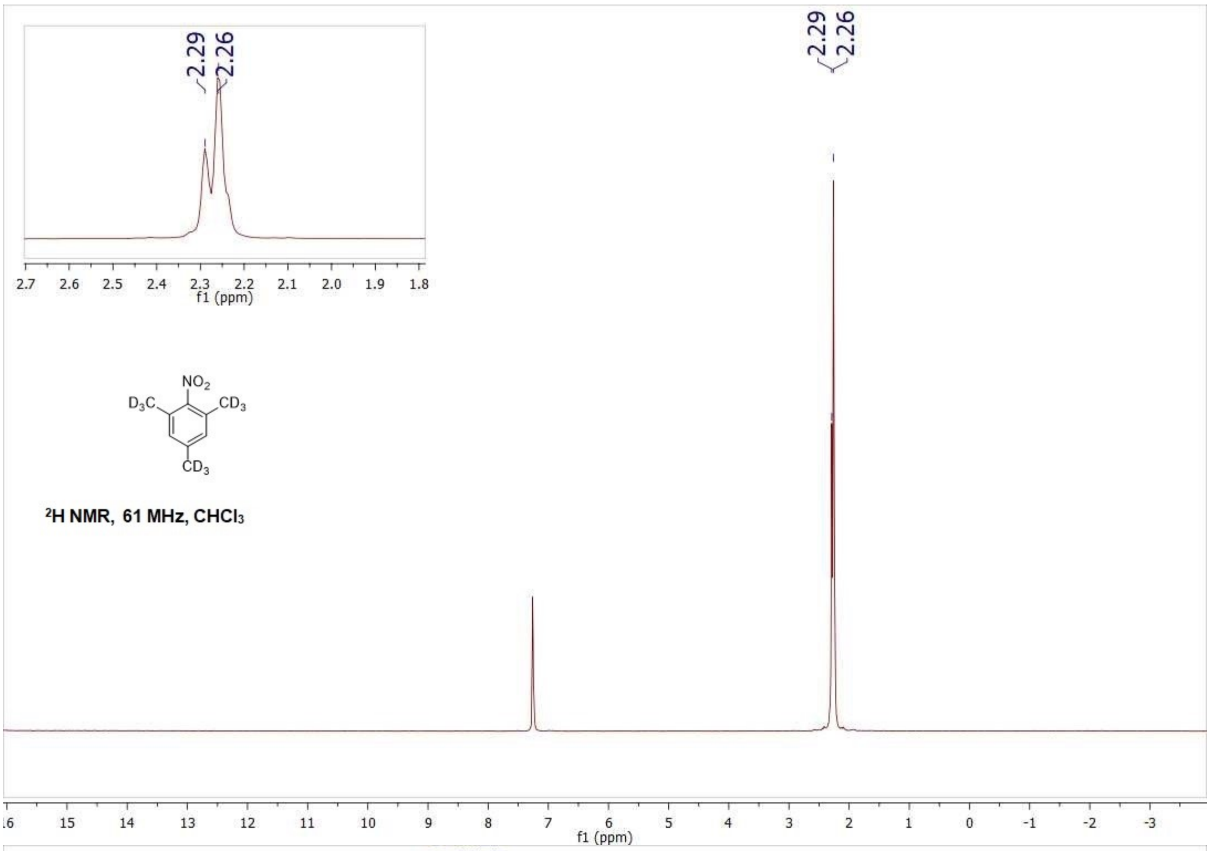
-6.72
2.14
2.14
2.13
2.13
2.12
D3C
CD3
CD3
¹H NMR, 400 MHz, C6D6
3.00
0.40
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)
2.16 2.15 2.14 2.13 2.12 2.11
f1 (ppm)

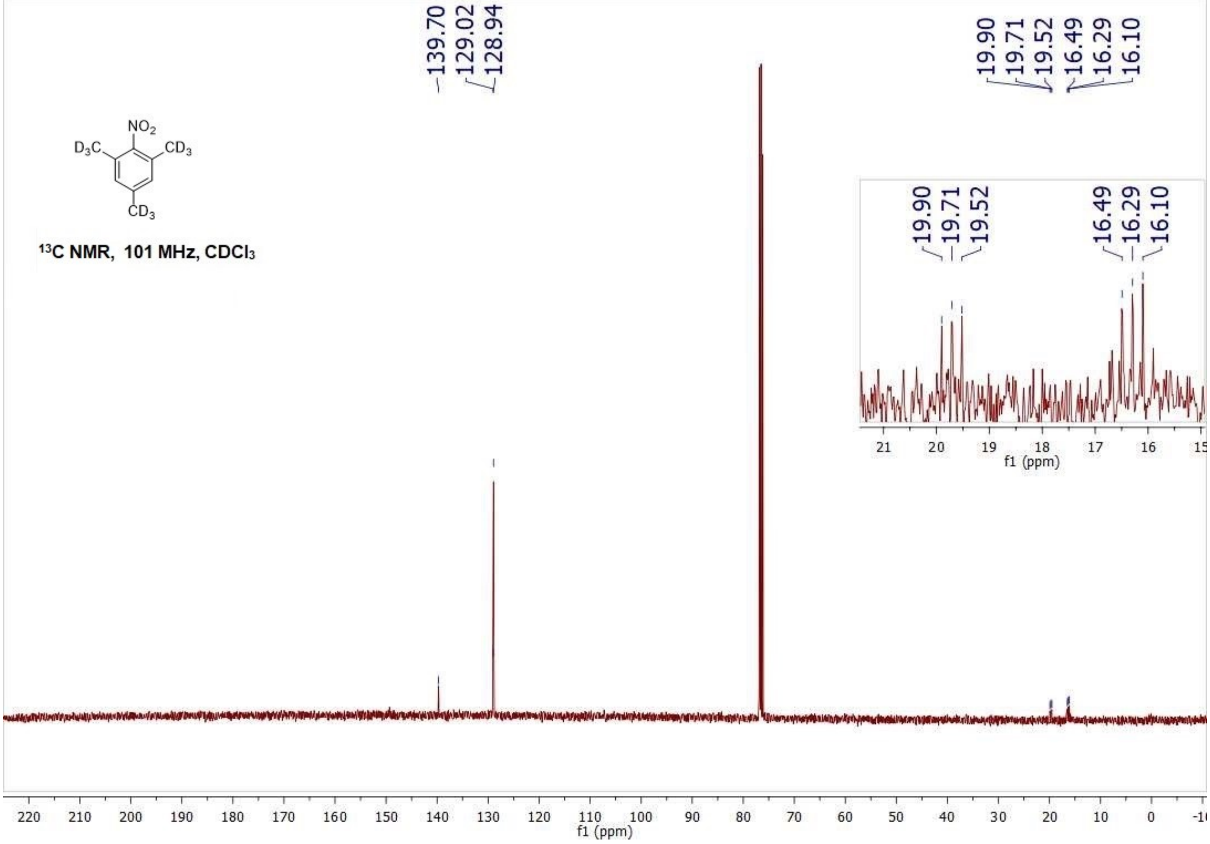


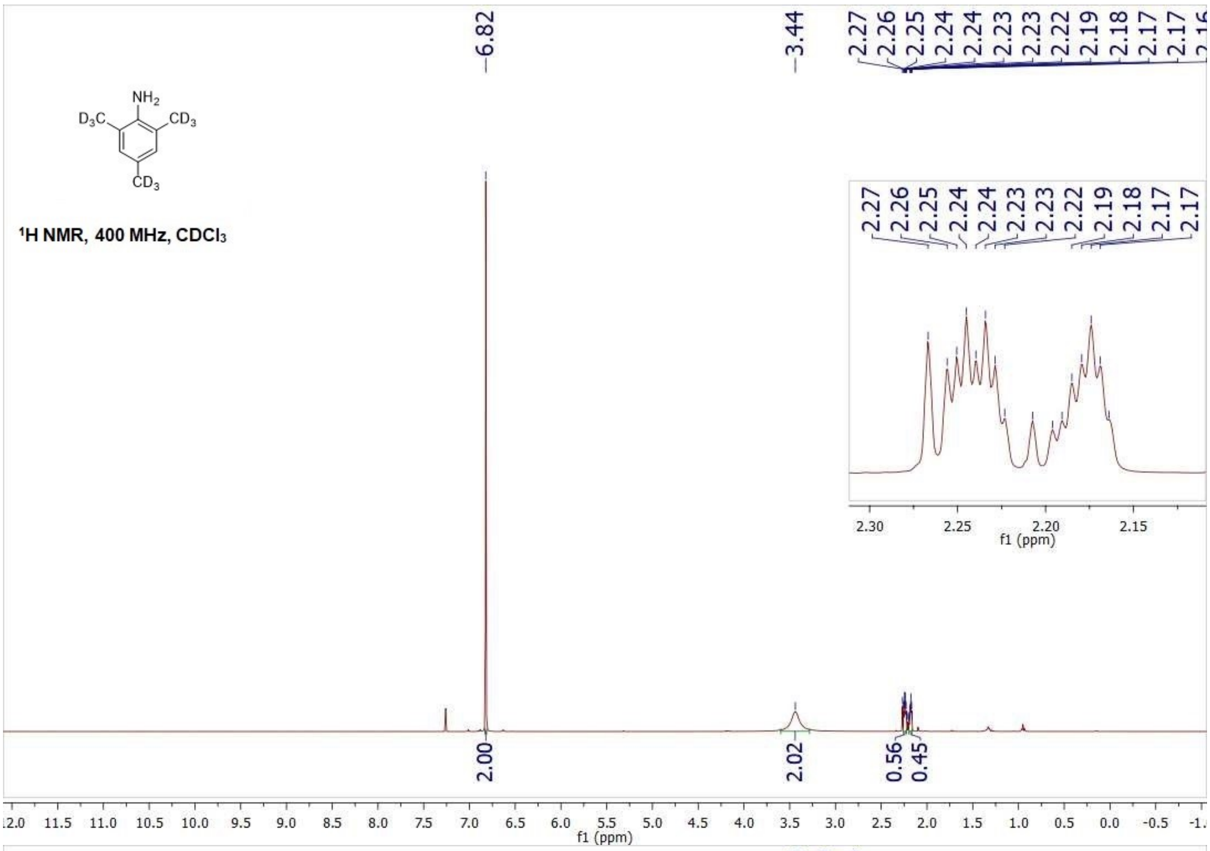
2.09
2.07
2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)
D3C
CD3
CD3
²H NMR, 61 MHz, C6H6
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


13C NMR, 101 MHz, C6D6
D3C CD3 CD3
137.50
127.39
21.05
20.86
20.67
20.48
20.29
20.10
19.91
21.0 20.5 20.0 19.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

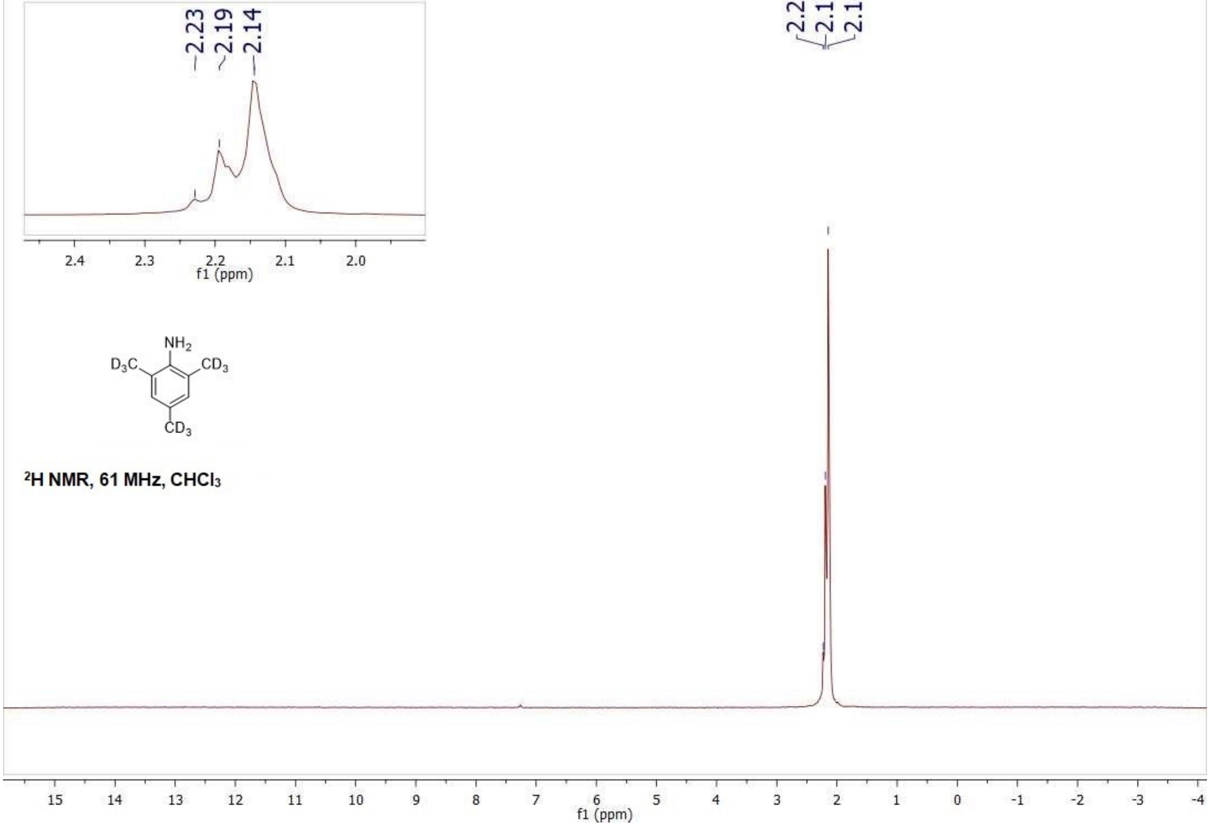

1H NMR, 400 MHz, CDCl3
NO2 D3C CD3 CD3
6.91
2.29
2.29
2.28
2.28
2.27
2.26
2.26
2.25
2.25
2.24
2.30 2.29 2.28 2.27 2.26 2.25 2.24 2.23 2.22
f1 (ppm)
2.00
0.15
0.27
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


2.29
2.26
2.7 2.6 2.5 2.4 2.3 2.2 2.1 2.0 1.9 1.8
f1 (ppm)
NO2
D3C
CD3
CD3
²H NMR, 61 MHz, CHCl₃
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3
f1 (ppm)

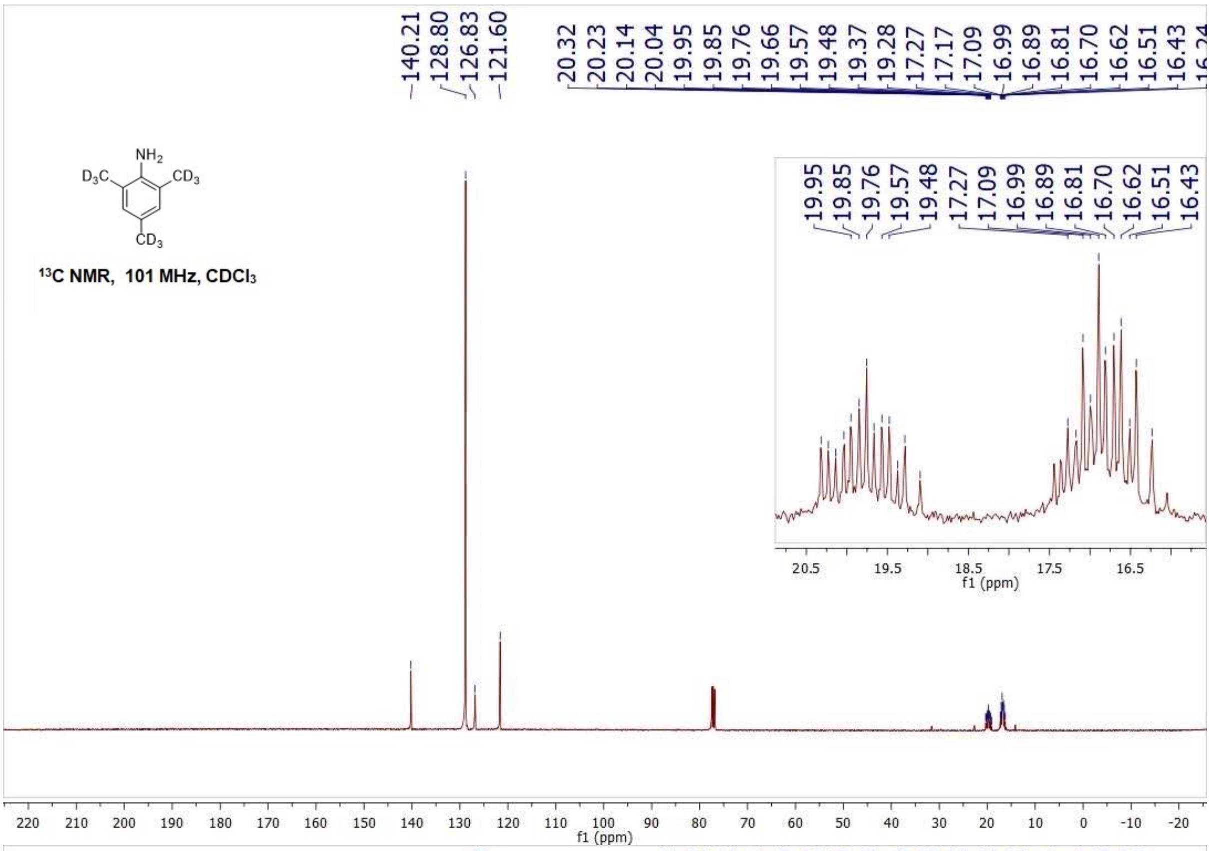

139.70
129.02
128.94
19.90
19.71
19.52
16.49
16.29
16.10
NO2
D3C
CD3
CD3
¹³C NMR, 101 MHz, CDCl₃
21 20 19 18 17 16 15
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

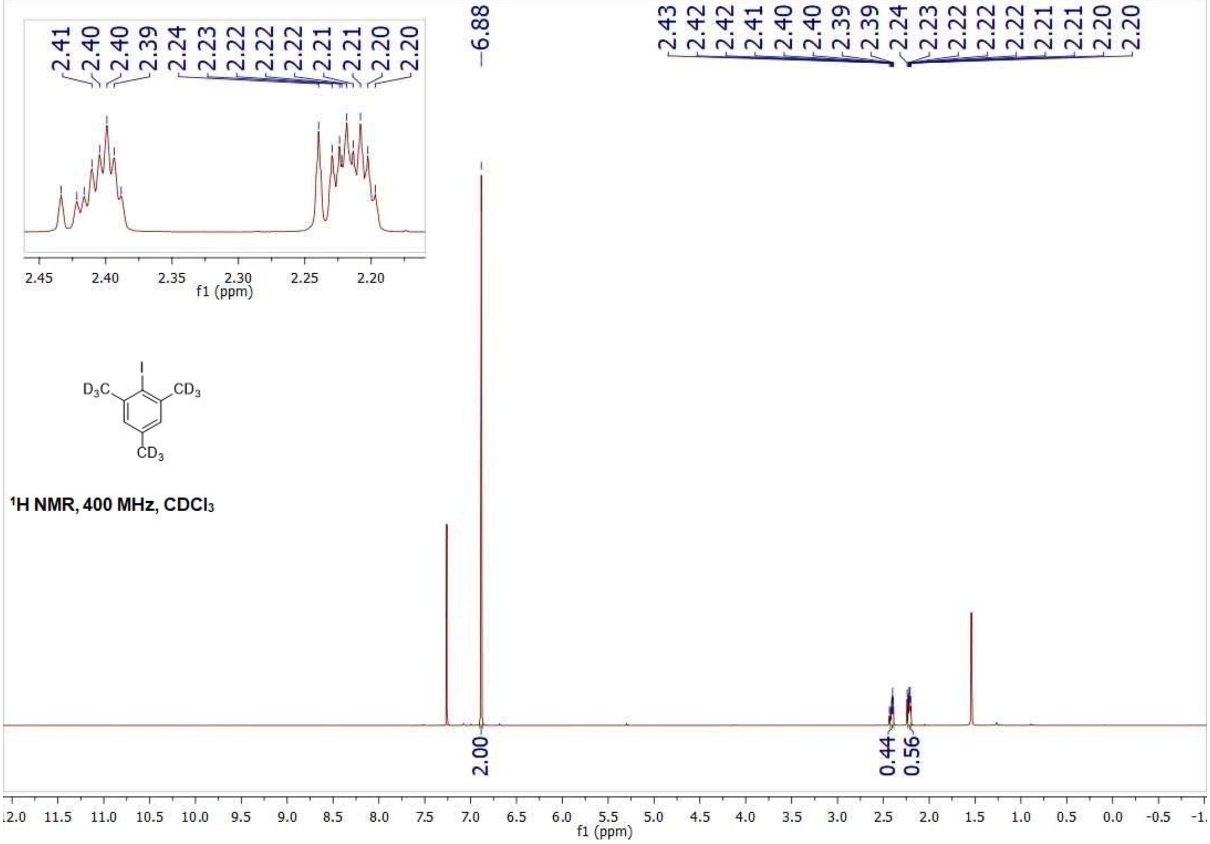


NH$_2$
D$_3$C
CD$_3$
CD$_3$
^{1}H NMR, 400 MHz, CDCl$_3$
6.82
3.44
2.27 2.26 2.25 2.24 2.24 2.23 2.23 2.22 2.19 2.18 2.17 2.17
2.00
2.02
0.56
0.45
2.30 2.25 2.20 2.15
f1 (ppm)
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



2.23 2.19 2.14
2.4 2.3 2.2 2.1 2.0
f1 (ppm)
NH$_2$
D$_3$C
CD$_3$
CD$_3$
^{2}H NMR, 61 MHz, CHCl$_3$
15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


140.21
128.80
126.83
121.60
20.32
20.23
20.14
20.04
19.95
19.85
19.76
19.66
19.57
19.48
19.37
19.28
17.27
17.17
17.09
16.99
16.89
16.81
16.70
16.62
16.51
16.43
NH2
D3C
CD3
CD3
13C NMR, 101 MHz, CDCl3
19.95
19.85
19.76
19.57
19.48
17.27
17.09
16.99
16.89
16.81
16.70
16.62
16.51
16.43
20.5
19.5
18.5
17.5
16.5
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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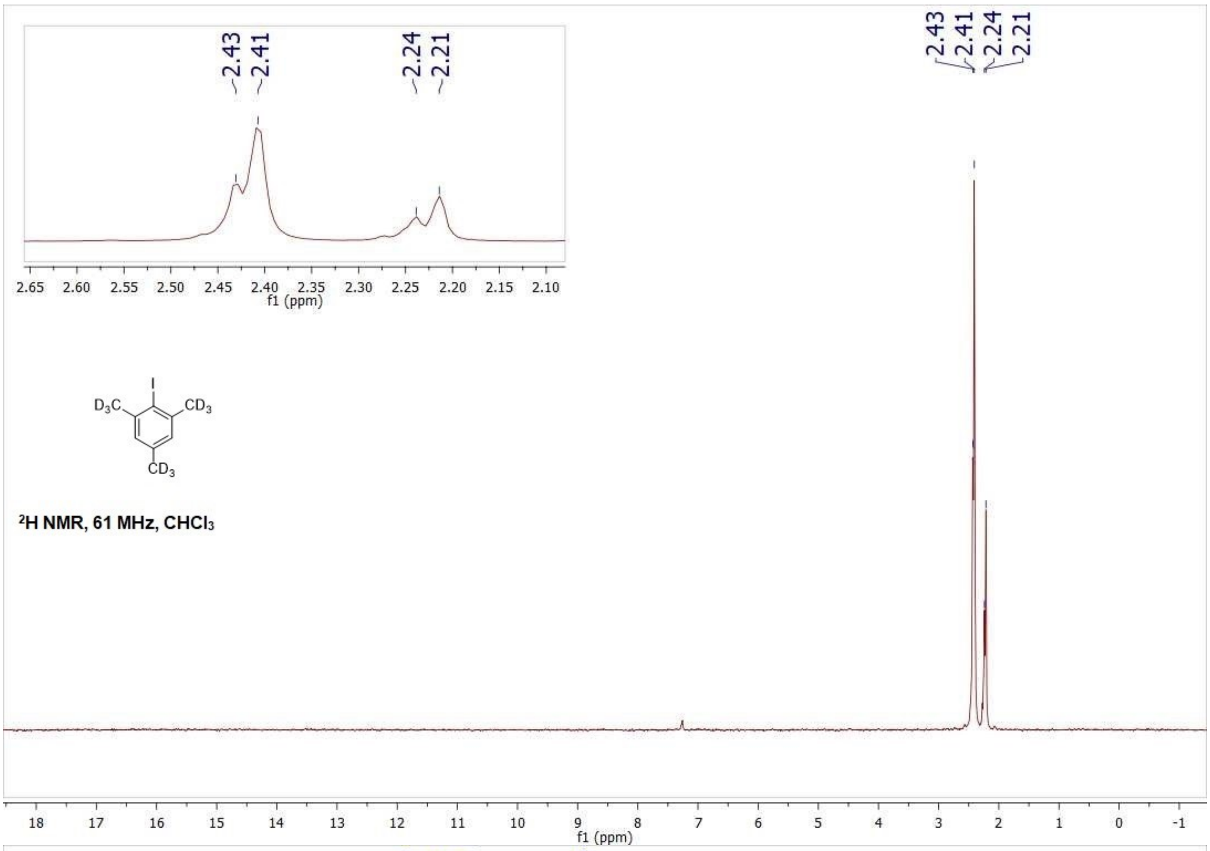
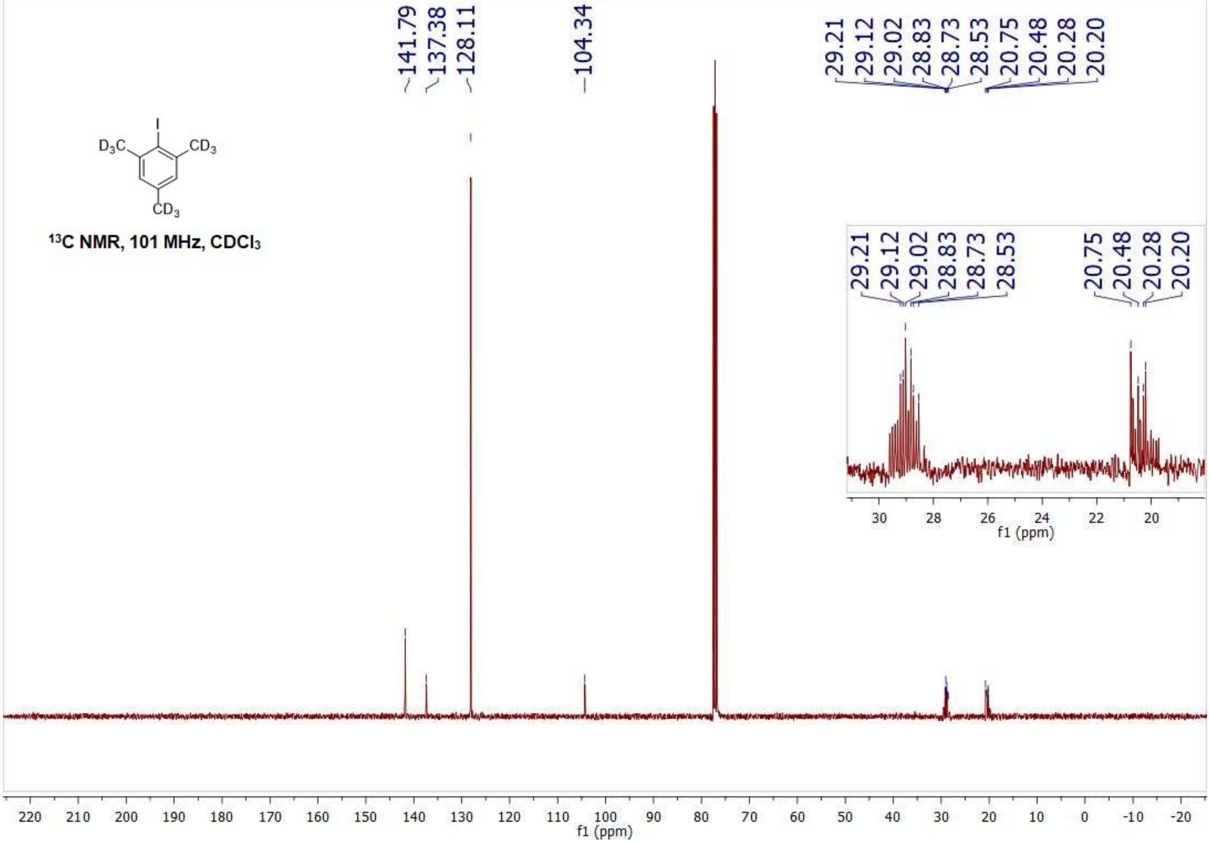
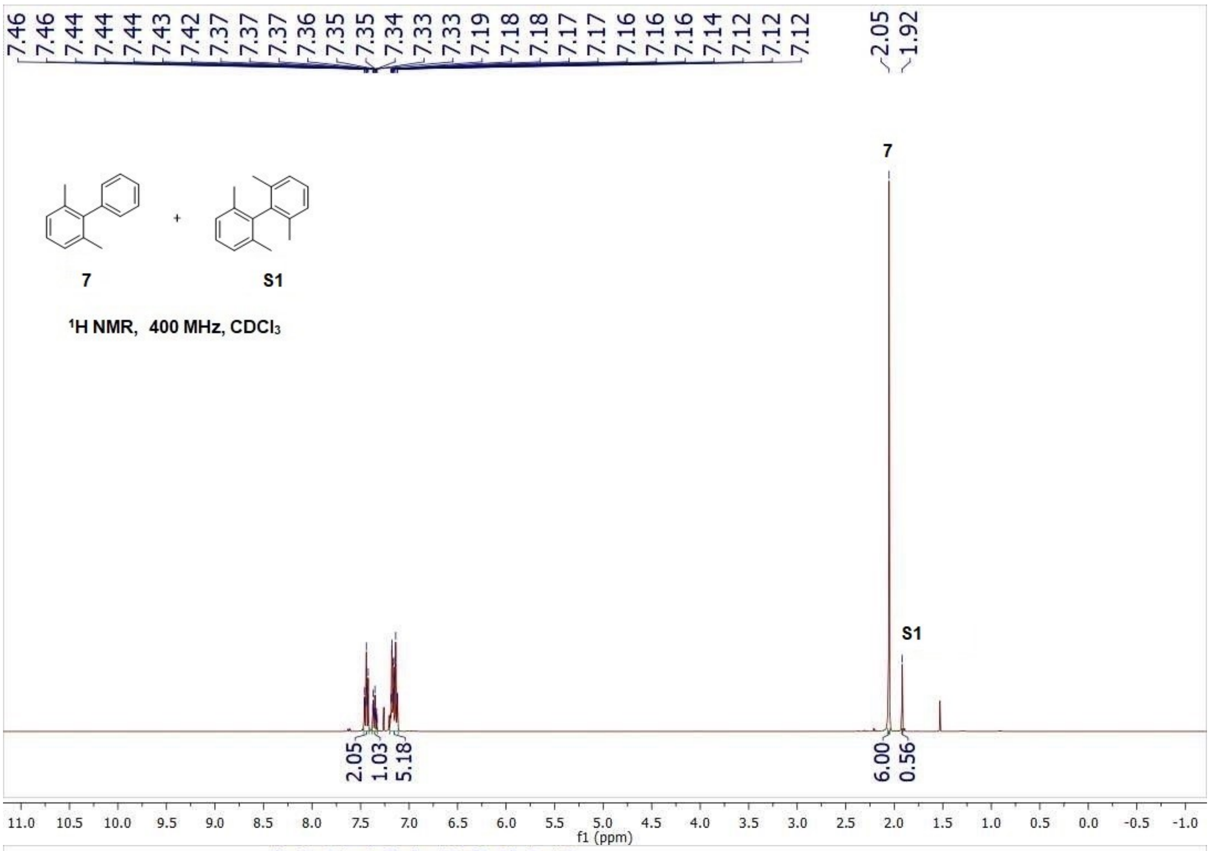
2.40
2.40
2.39
2.24
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.20
6.88
2.43
2.42
2.42
2.41
2.40
2.40
2.39
2.39
2.24
2.23
2.22
2.22
2.22
2.21
2.21
2.20
2.20
2.45
2.40
2.35
2.30
2.25
2.20
f1 (ppm)
I
D3C
CD3
CD3
1H NMR, 400 MHz, CDCl3
2.00
0.44
0.56
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)



^{2}H NMR, 61 MHz, CHCl$_3$



^{13}C NMR, 101 MHz, CDCl$_3$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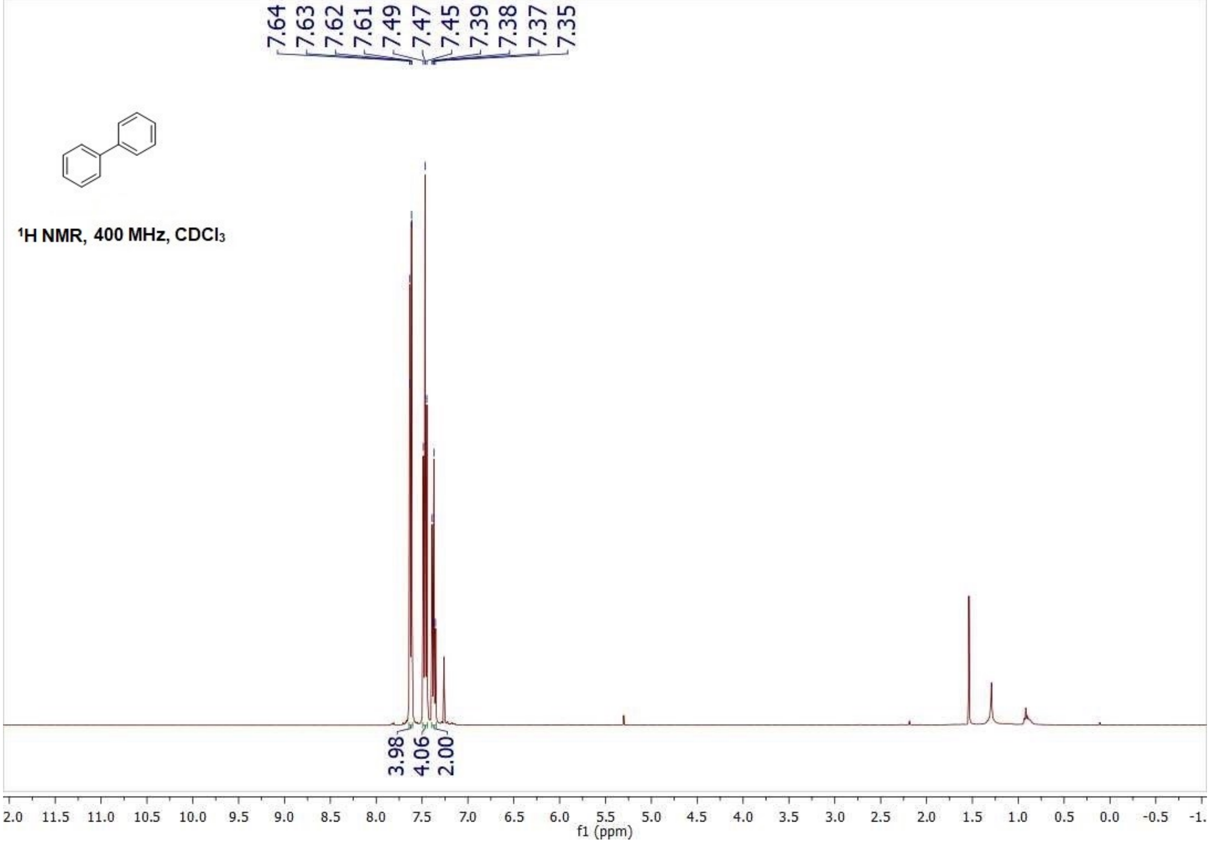
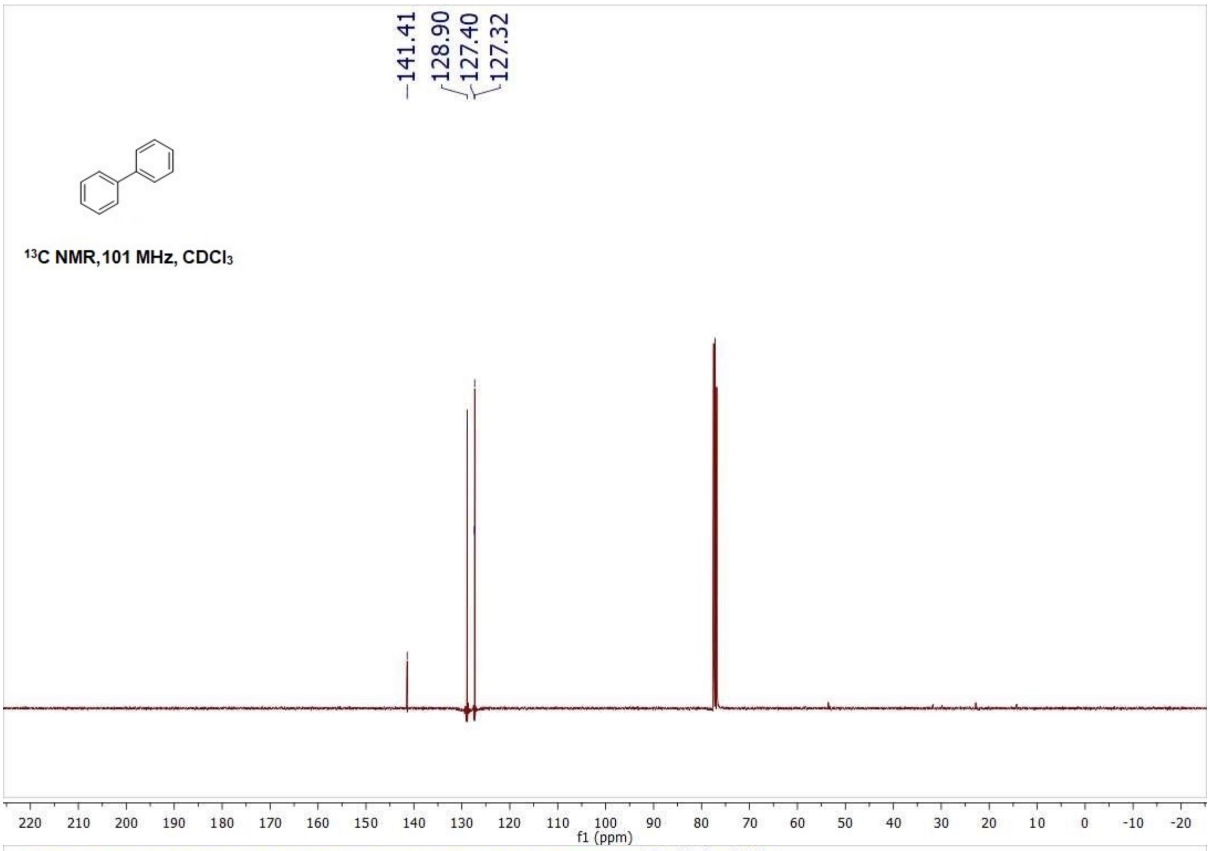
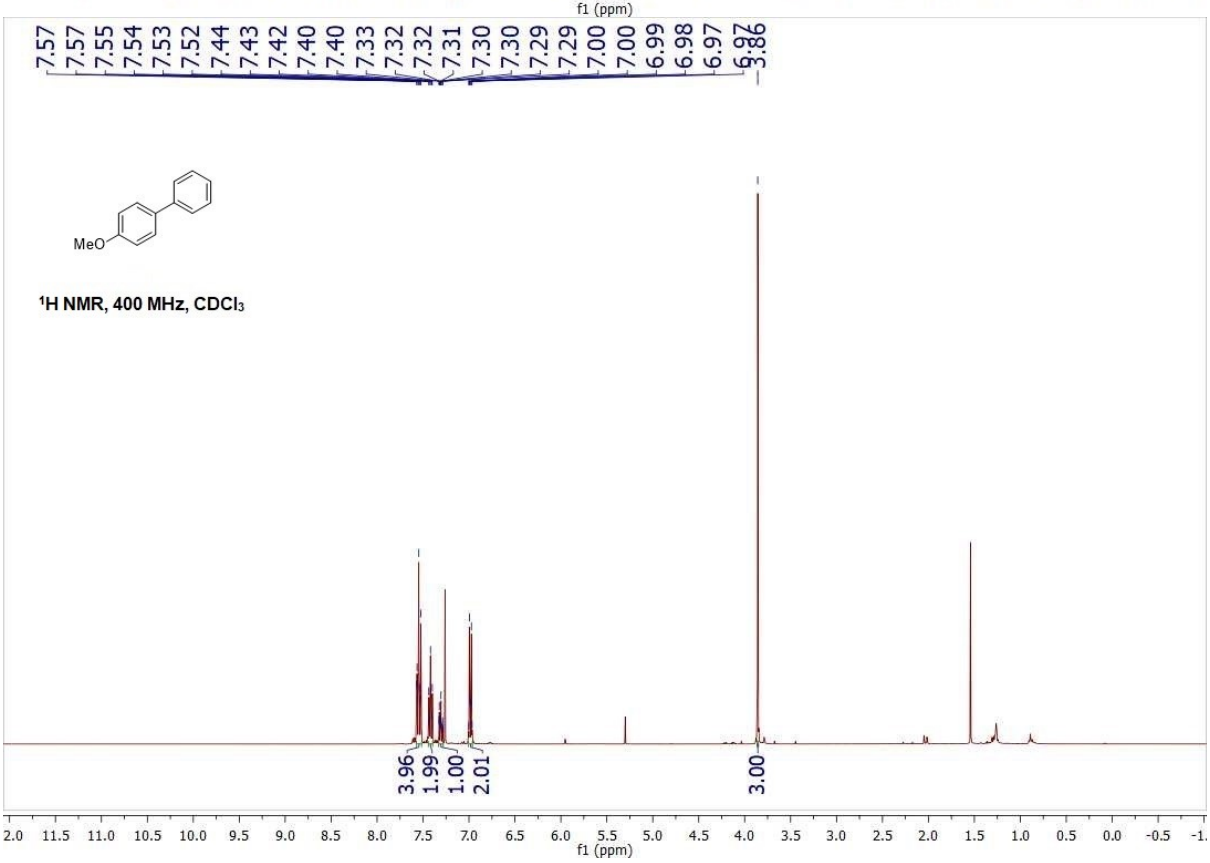
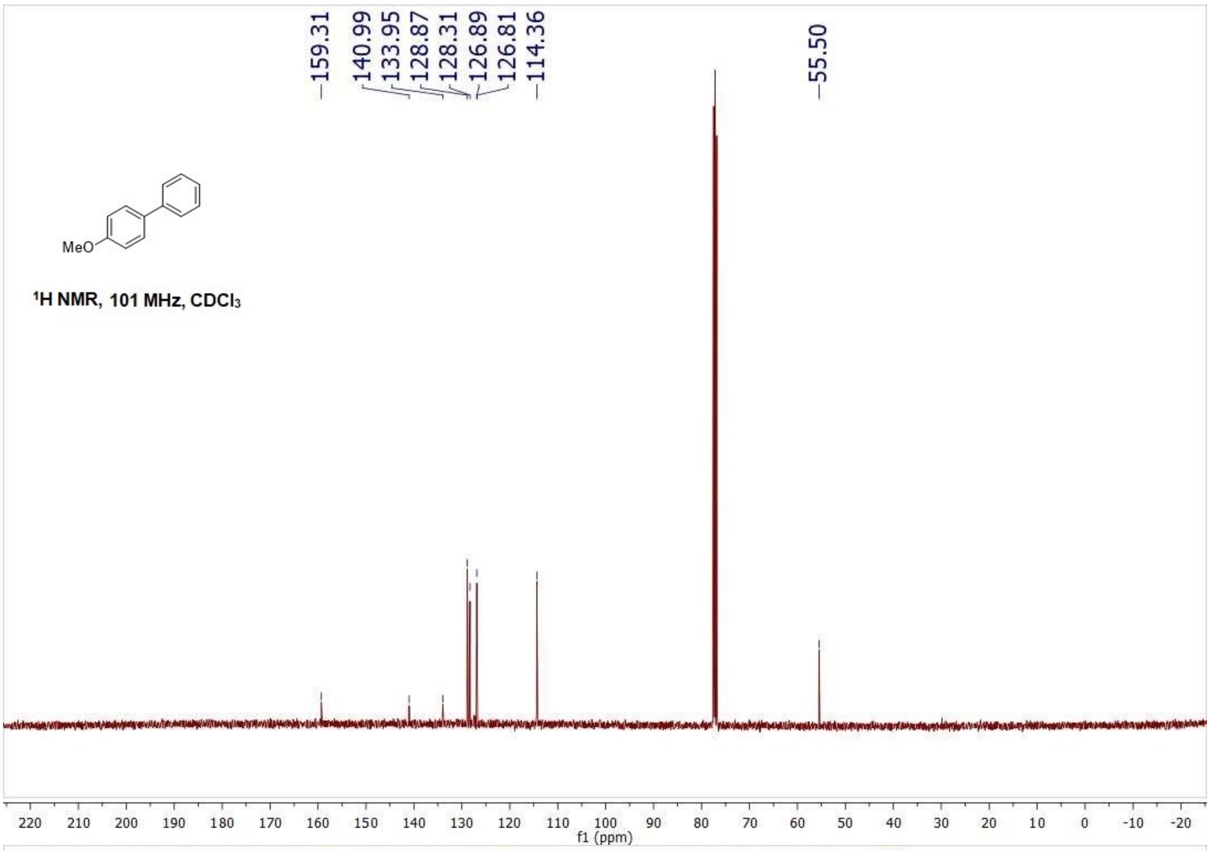
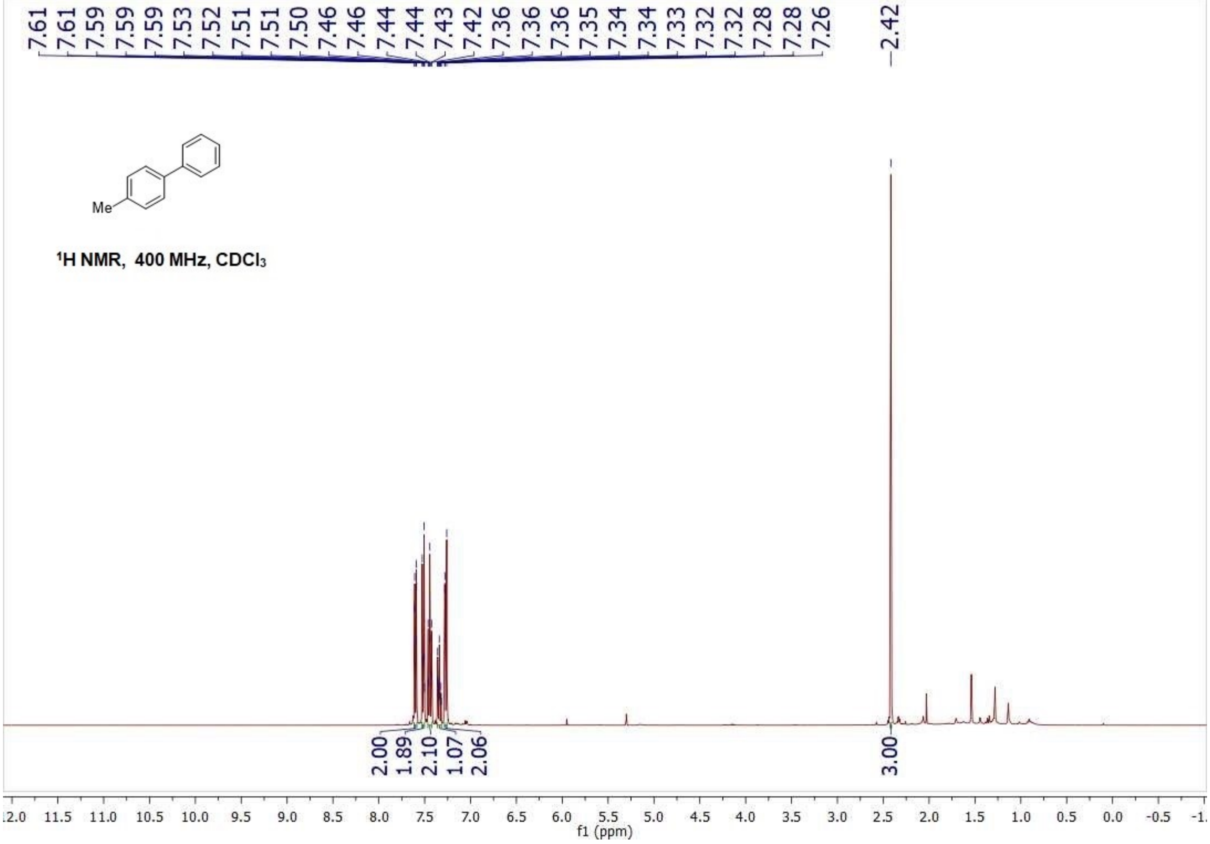
7.46
7.44
7.44
7.44
7.43
7.42
7.37
7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.16
7.14
7.12
7.12
7.12
2.05
1.92
7
S1
1H NMR, 400 MHz, CDCl3
2.05
1.03
5.18
6.00
0.56
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

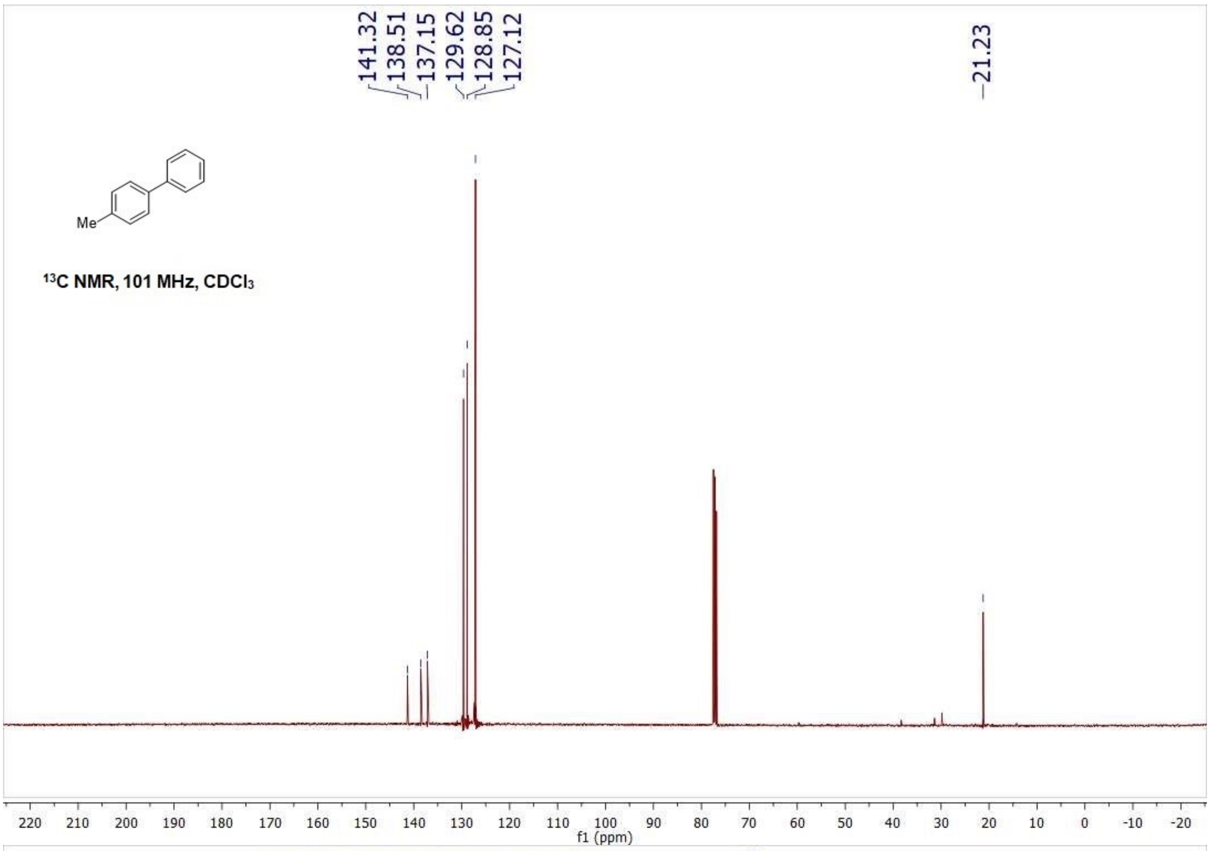

7.64
7.63
7.62
7.61
7.49
7.47
7.45
7.39
7.38
7.37
7.35
1H NMR, 400 MHz, CDCl3
3.98
4.06
2.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

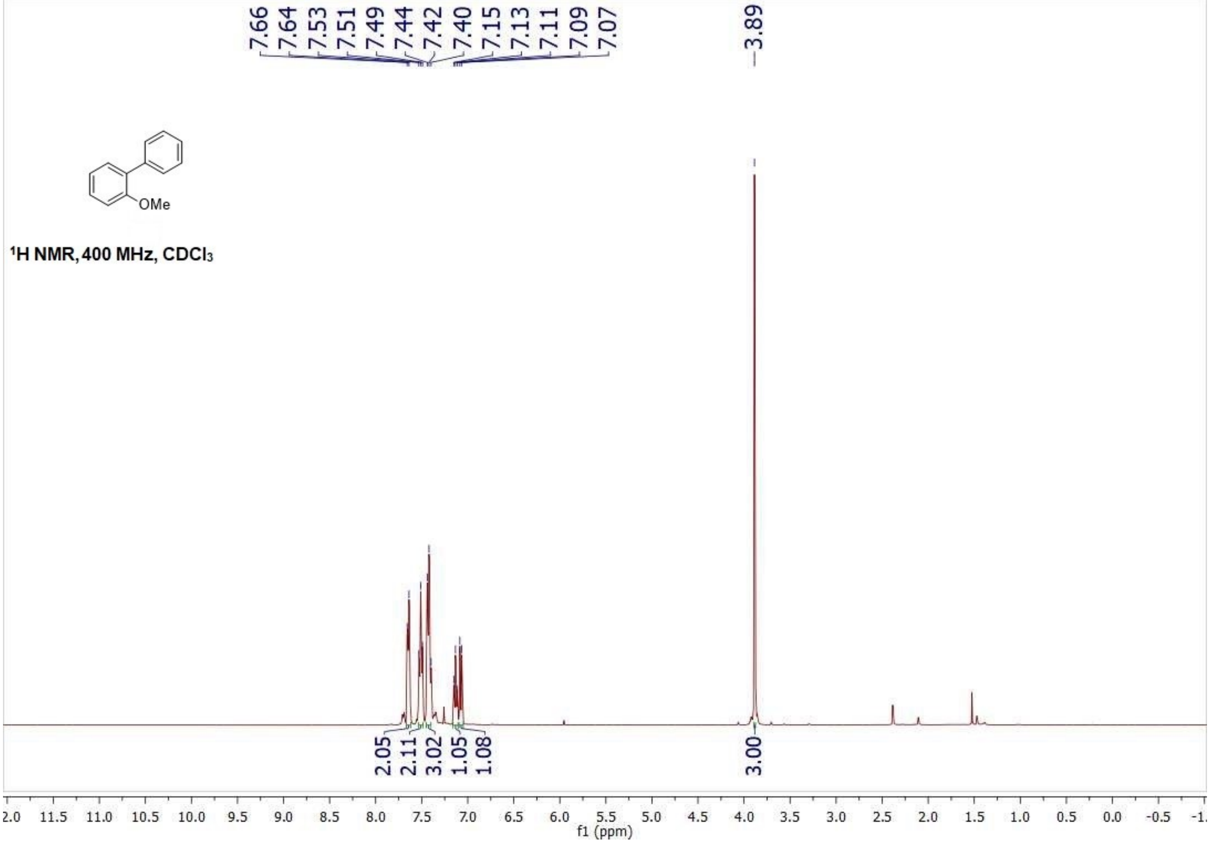

141.41
128.90
127.40
127.32
13C NMR,101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.57
7.57
7.55
7.54
7.53
7.52
7.44
7.43
7.42
7.40
7.40
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.00
7.00
6.99
6.98
6.97
6.97
3.86
MeO
1H NMR, 400 MHz, CDCl3
3.96
1.99
1.00
2.01
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


159.31
140.99
133.95
128.87
128.31
126.89
126.81
114.36
55.50
MeO
¹H NMR, 101 MHz, CDCl₃
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.61
7.61
7.59
7.59
7.59
7.53
7.52
7.51
7.51
7.50
7.46
7.46
7.44
7.44
7.43
7.42
7.36
7.36
7.36
7.35
7.34
7.34
7.33
7.32
7.32
7.28
7.28
7.26
2.42
Me
¹H NMR, 400 MHz, CDCl₃
2.00
1.89
2.10
1.07
2.06
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


141.32
138.51
137.15
129.62
128.85
127.12
21.23
Me
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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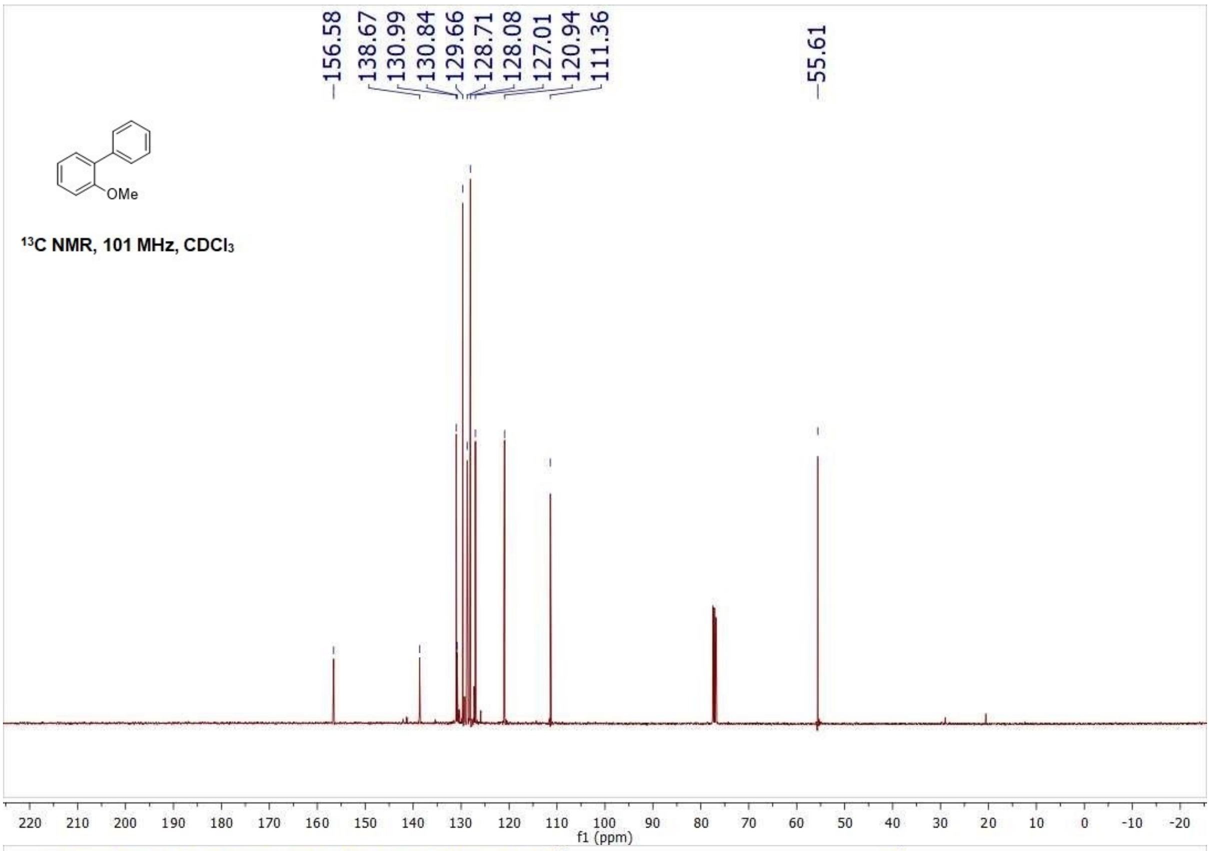
7.64
7.53
7.51
7.49
7.44
7.42
7.40
7.15
7.13
7.11
7.09
7.07
3.89
OMe
1H NMR, 400 MHz, CDCl3
2.05
2.11
3.02
1.05
1.08
3.00
2.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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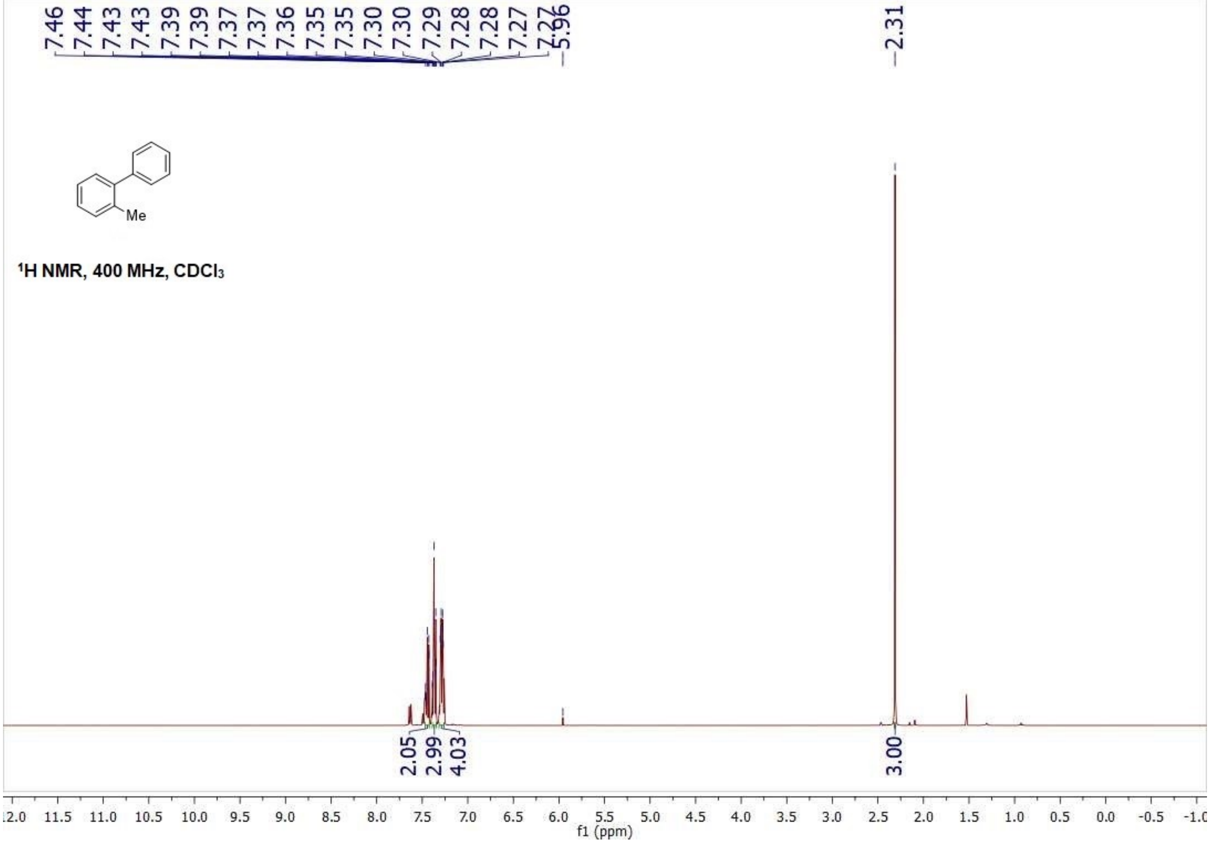
138.67
130.99
130.84
129.66
128.71
128.08
127.01
120.94
111.36
55.61
OMe
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)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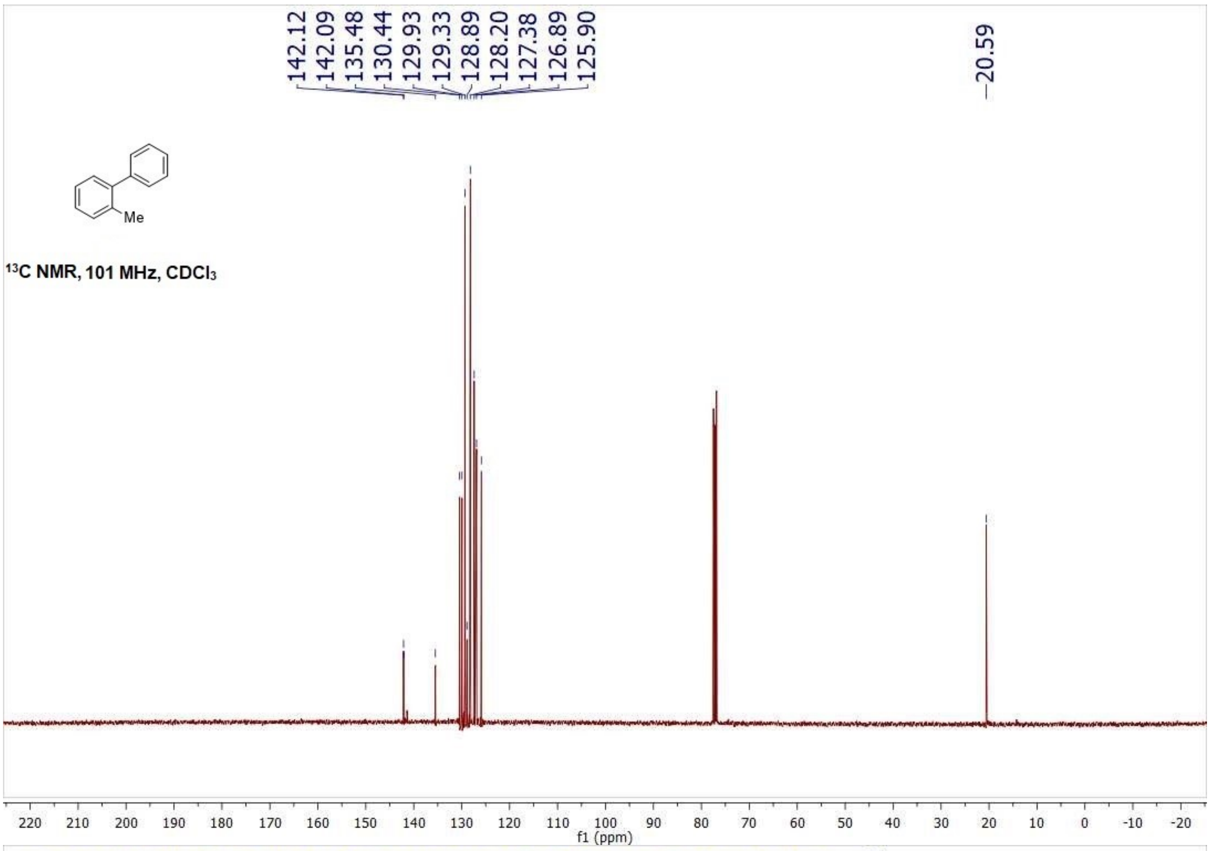
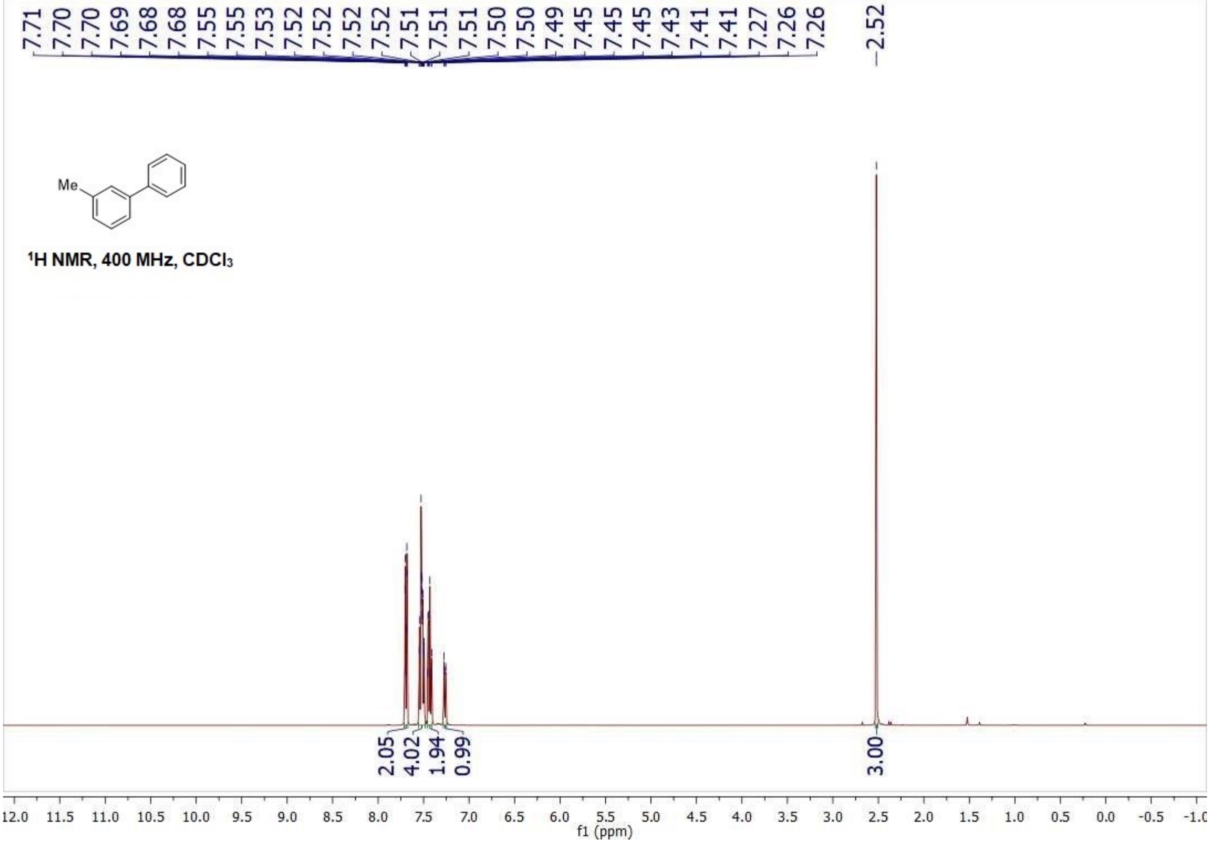
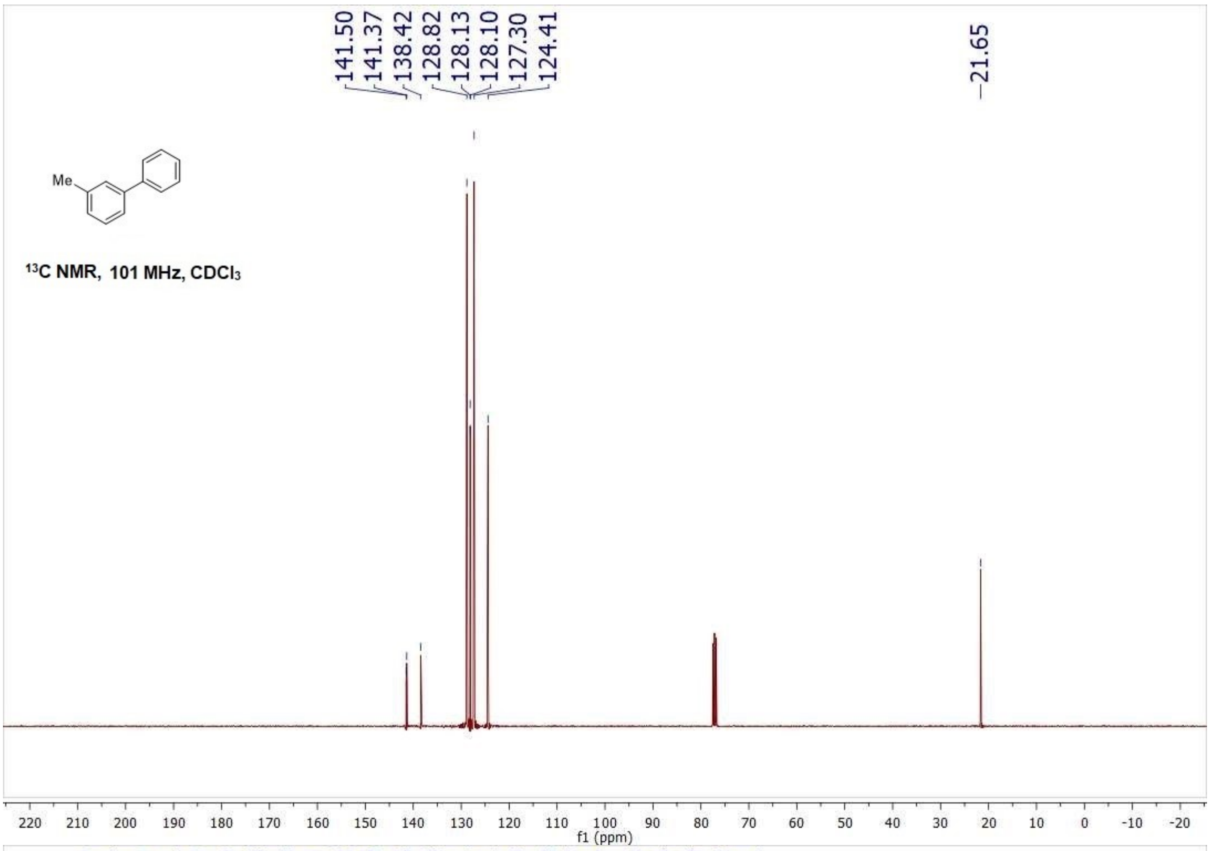
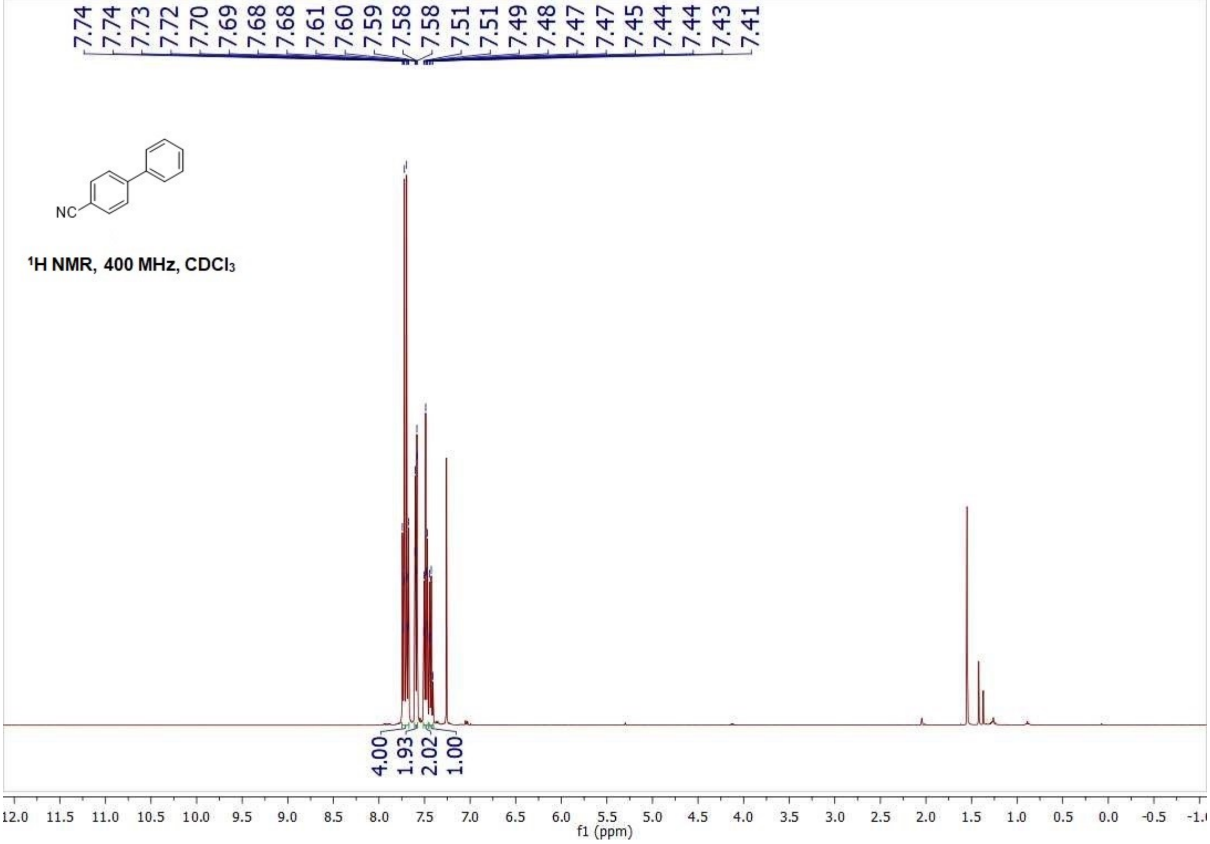
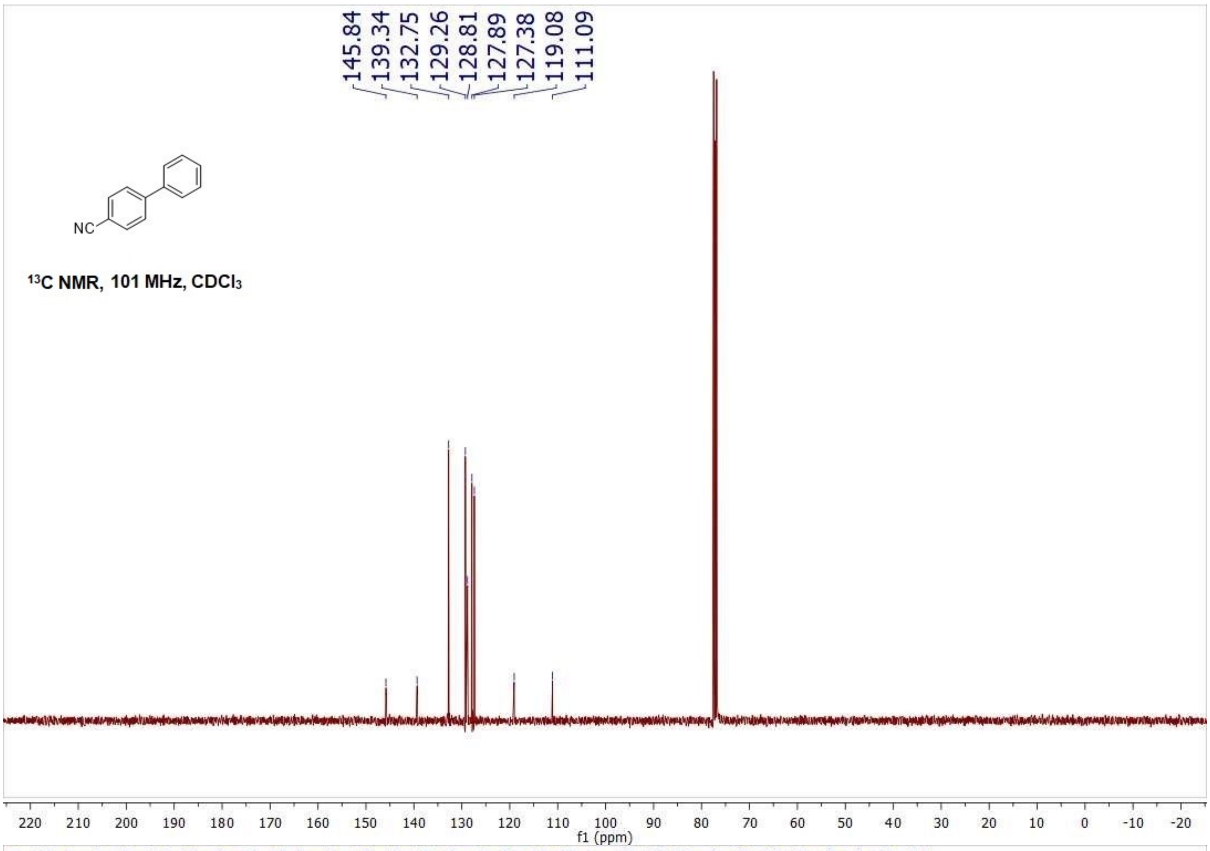
7.44
7.43
7.43
7.39
7.39
7.37
7.37
7.36
7.35
7.35
7.30
7.30
7.29
7.28
7.28
7.27
7.27
5.96
2.31
Me
1H NMR, 400 MHz, CDCl3
2.05
2.99
4.03
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


142.12
142.09
135.48
130.44
129.93
129.33
128.89
128.20
127.38
126.89
125.90
20.59
Me
13C NMR, 101 MHz, CDCl3
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

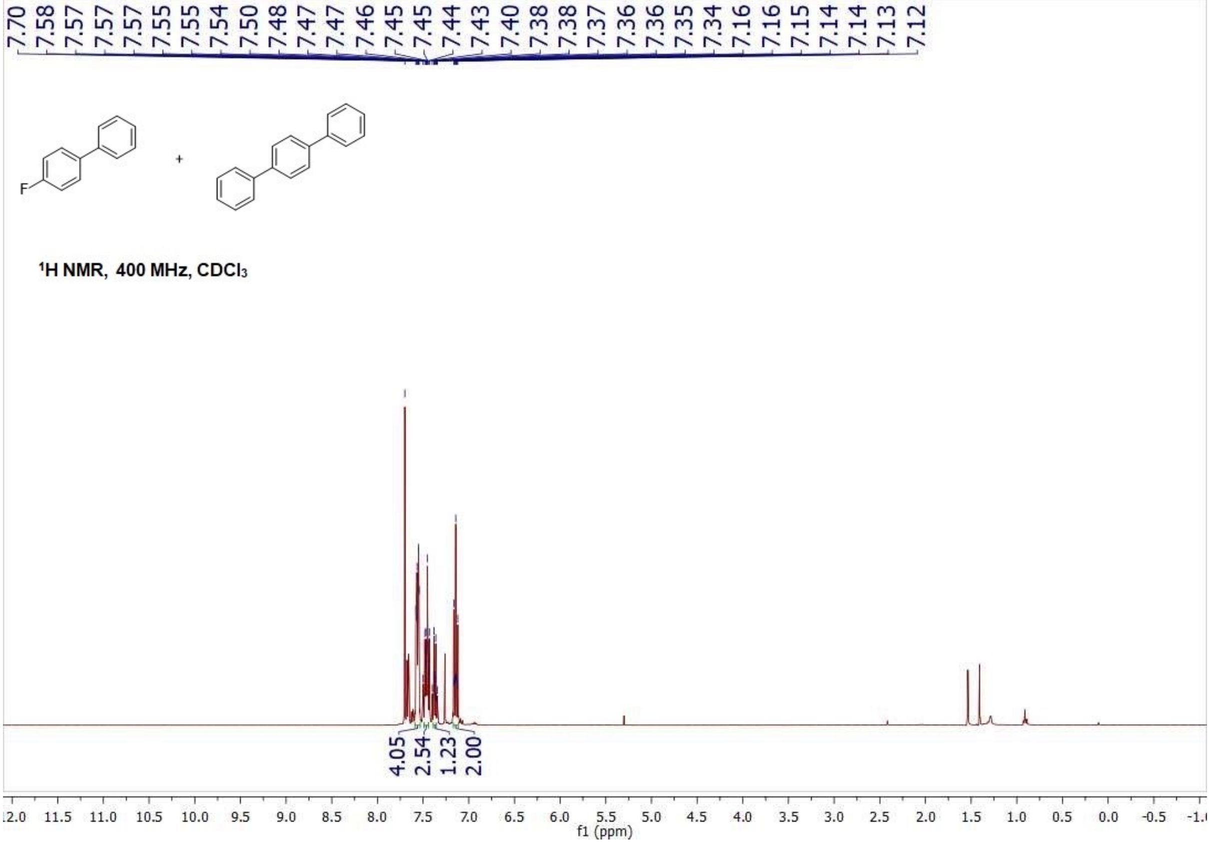

7.71
7.70
7.70
7.69
7.68
7.68
7.55
7.55
7.53
7.52
7.52
7.52
7.52
7.51
7.51
7.51
7.50
7.50
7.49
7.45
7.45
7.45
7.43
7.41
7.41
7.27
7.26
7.26
2.52
Me
1H NMR, 400 MHz, CDCl3
2.05
4.02
1.94
0.99
3.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


141.50
141.37
138.42
128.82
128.13
128.10
127.30
124.41
21.65
Me
^{13}C NMR, 101 MHz, CDCl$_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

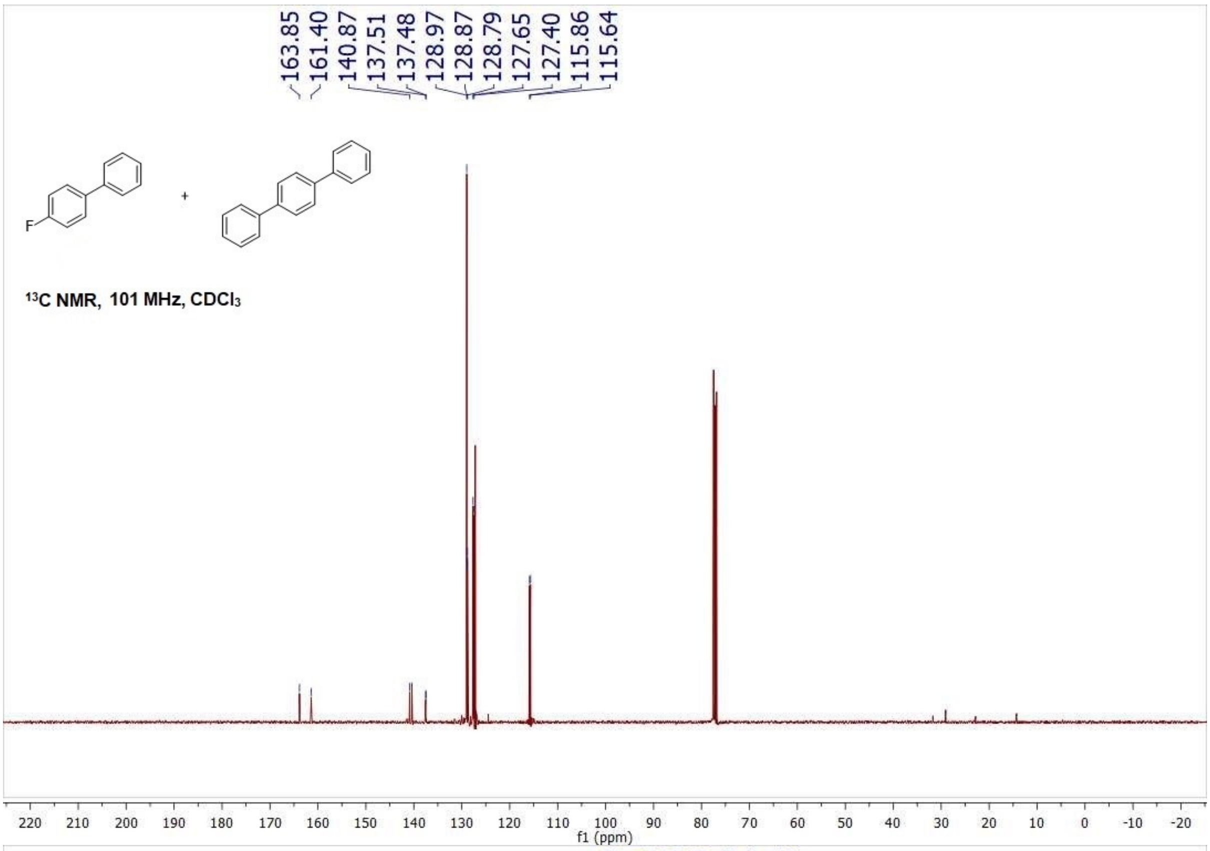

7.74
7.74
7.73
7.72
7.70
7.69
7.68
7.68
7.61
7.60
7.59
7.58
7.58
7.51
7.51
7.49
7.48
7.47
7.47
7.45
7.44
7.44
7.43
7.41
NC
^{1}H NMR, 400 MHz, CDCl$_3$
4.00
1.93
2.02
1.00
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



^{13}C NMR, 101 MHz, $CDCl_3$



^{1}H NMR, 400 MHz, $CDCl_3$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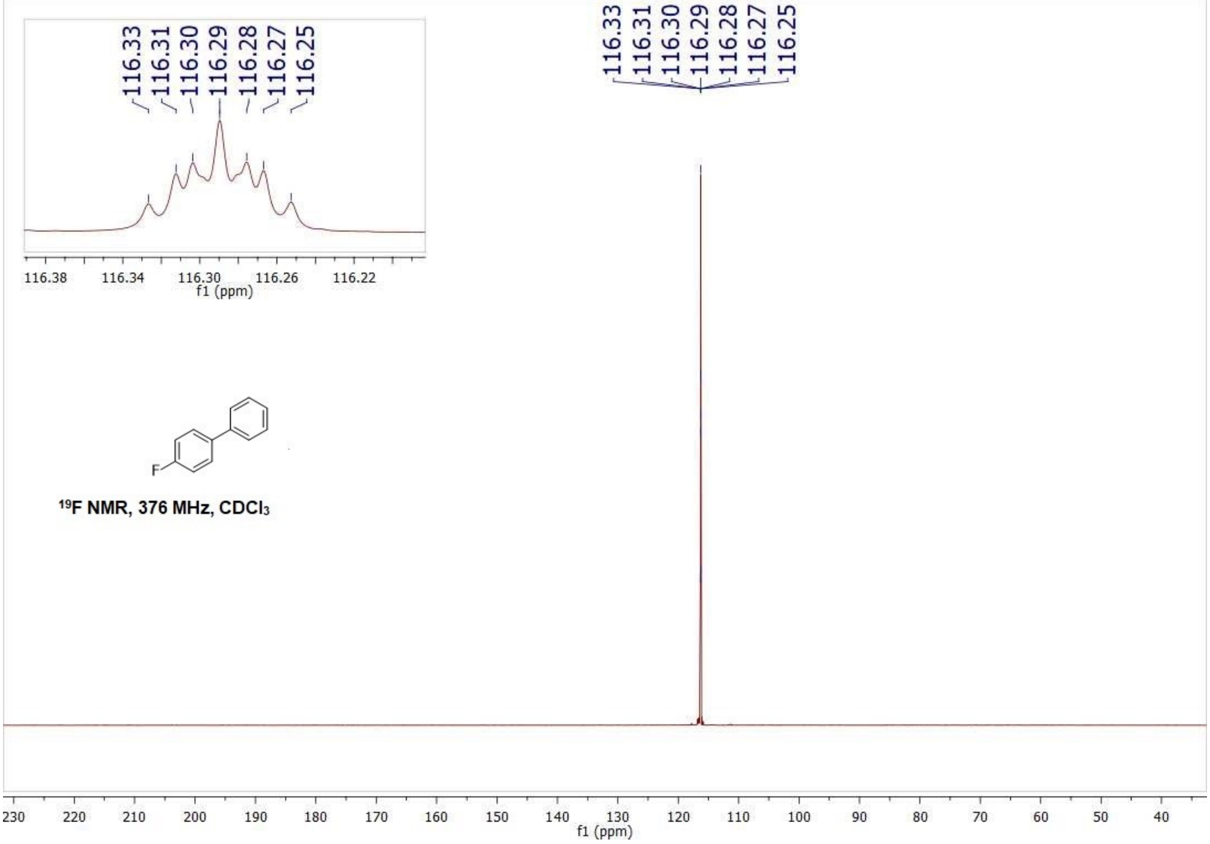
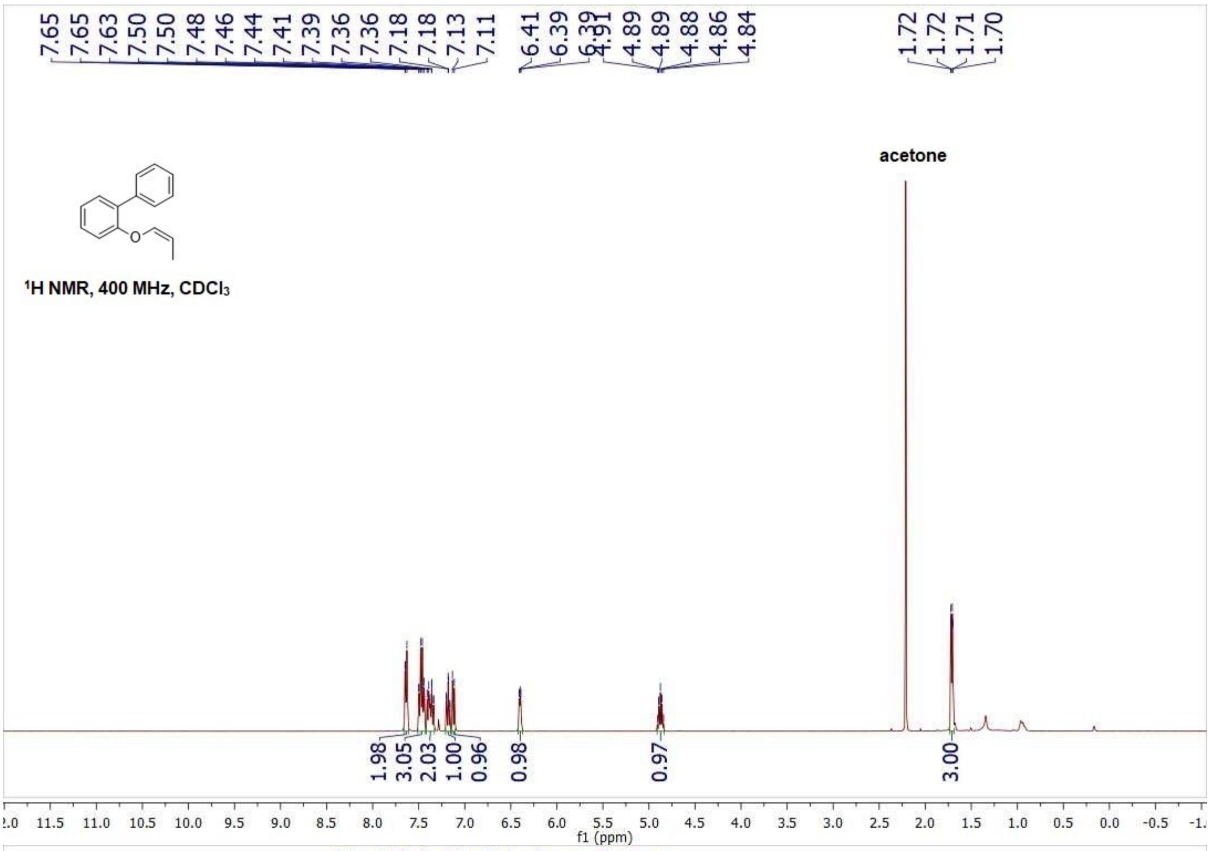
140.87
137.51
137.48
128.97
128.87
128.79
127.65
127.40
115.86
115.64
F
+
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


116.33
116.31
116.30
116.29
116.28
116.27
116.25
116.38
116.34
116.30
116.26
116.22
f1 (ppm)
F
19F NMR, 376 MHz, CDCl3
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)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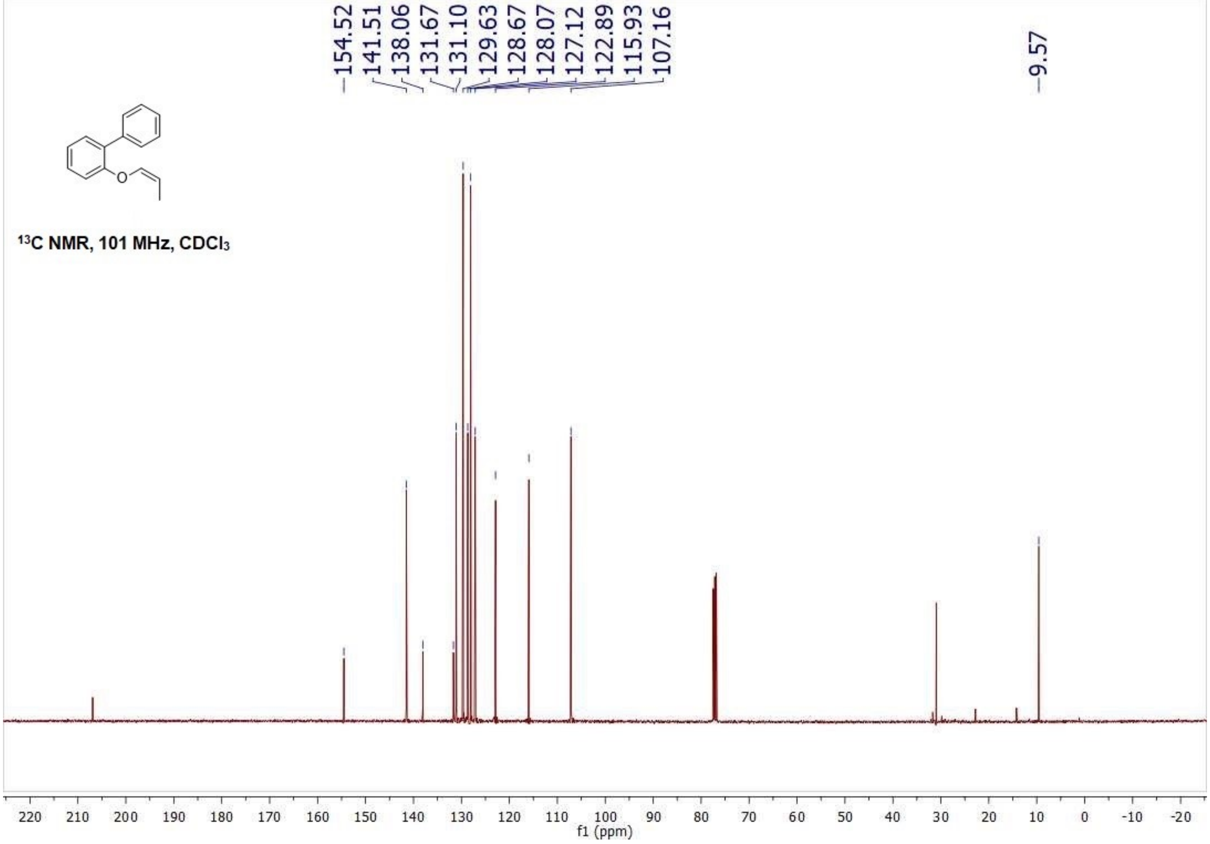
7.65
7.63
7.50
7.50
7.48
7.46
7.44
7.41
7.39
7.36
7.36
7.18
7.18
7.13
7.11
6.41
6.39
6.39
4.91
4.89
4.89
4.88
4.86
4.84
1.72
1.72
1.71
1.70
acetone
O
1H NMR, 400 MHz, CDCl3
1.98
3.05
2.03
1.00
0.96
0.98
0.97
3.00
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)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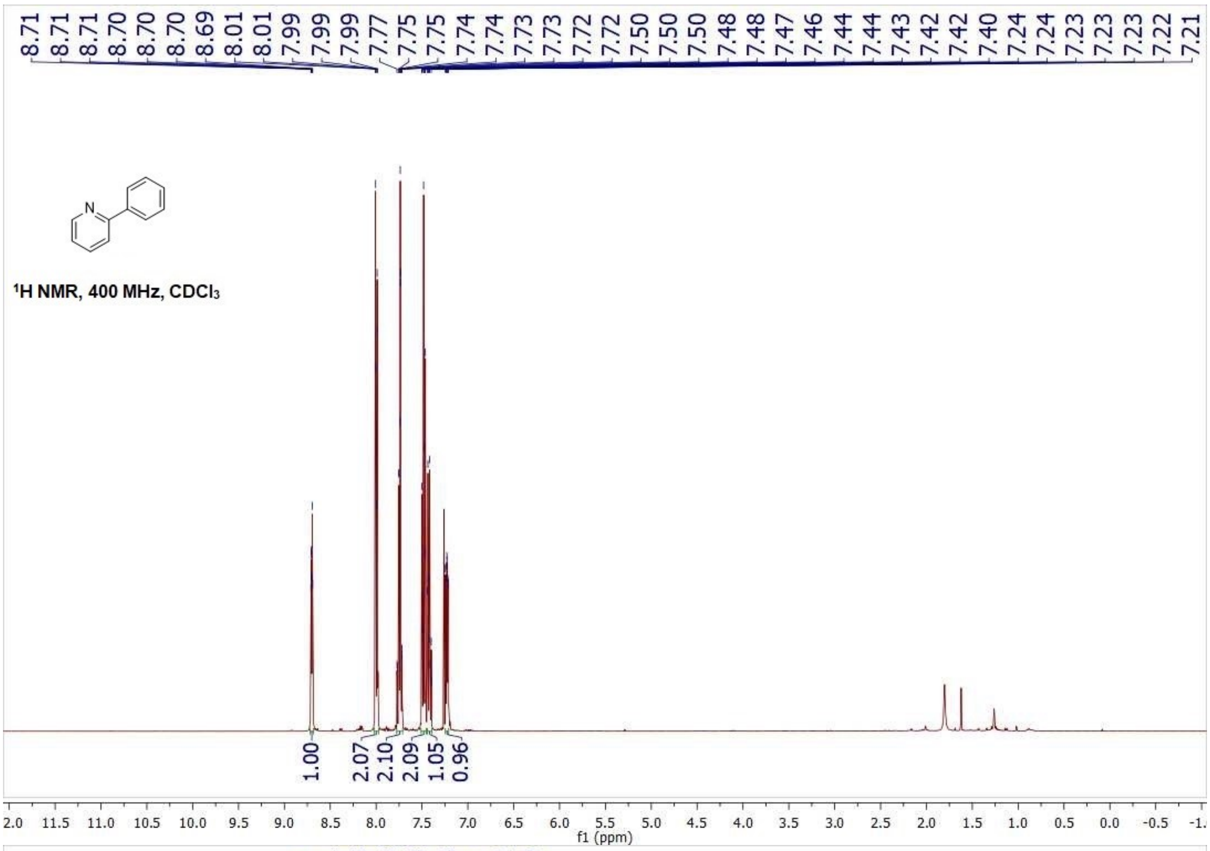
141.51
138.06
131.67
131.10
129.63
128.67
128.07
127.12
122.89
115.93
107.16
9.57
O
13C NMR, 101 MHz, CDCl3
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)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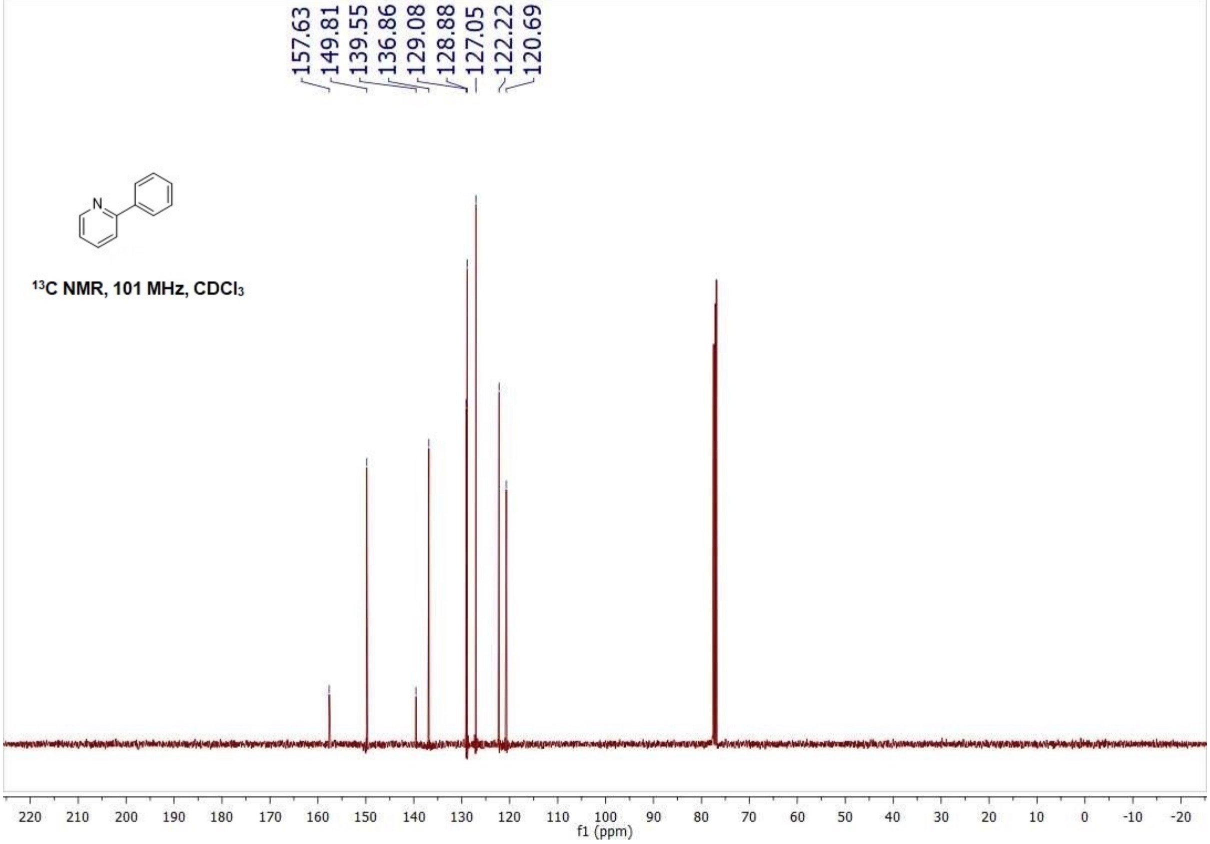
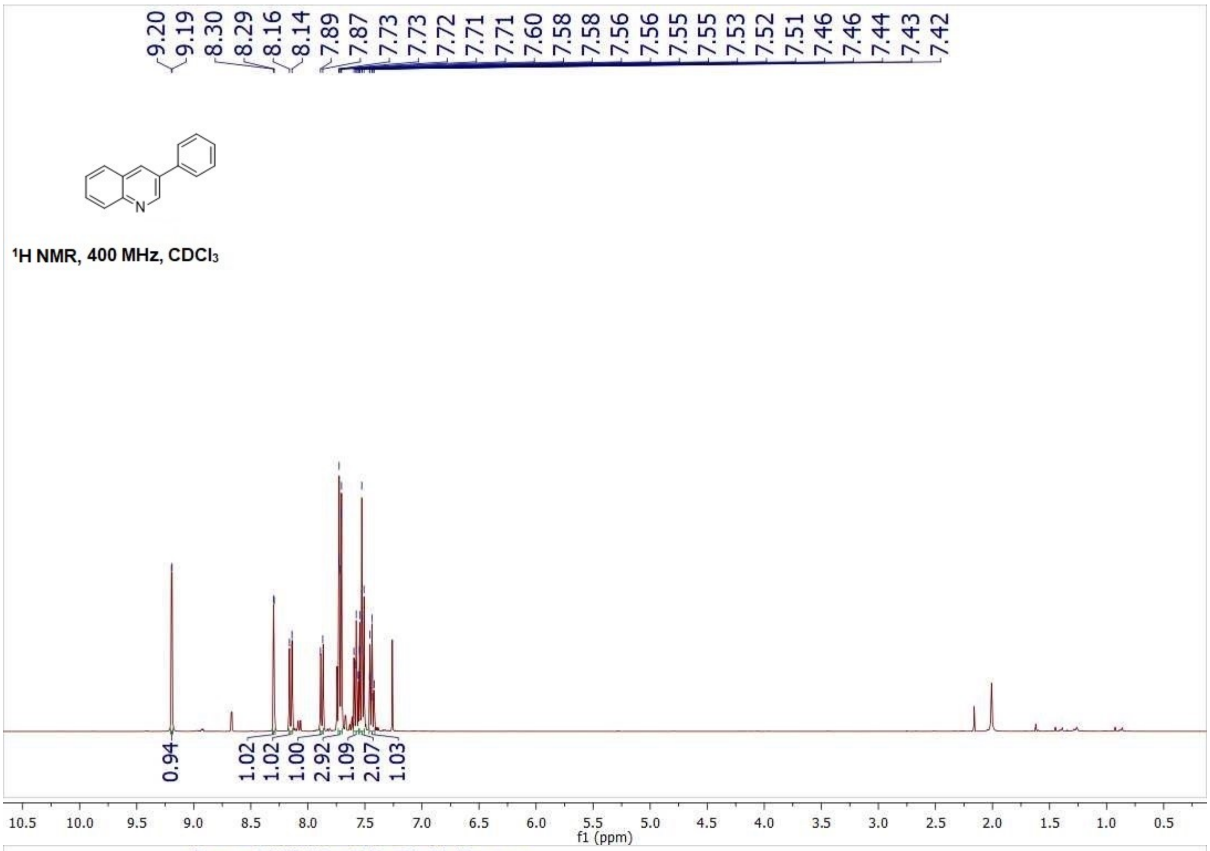
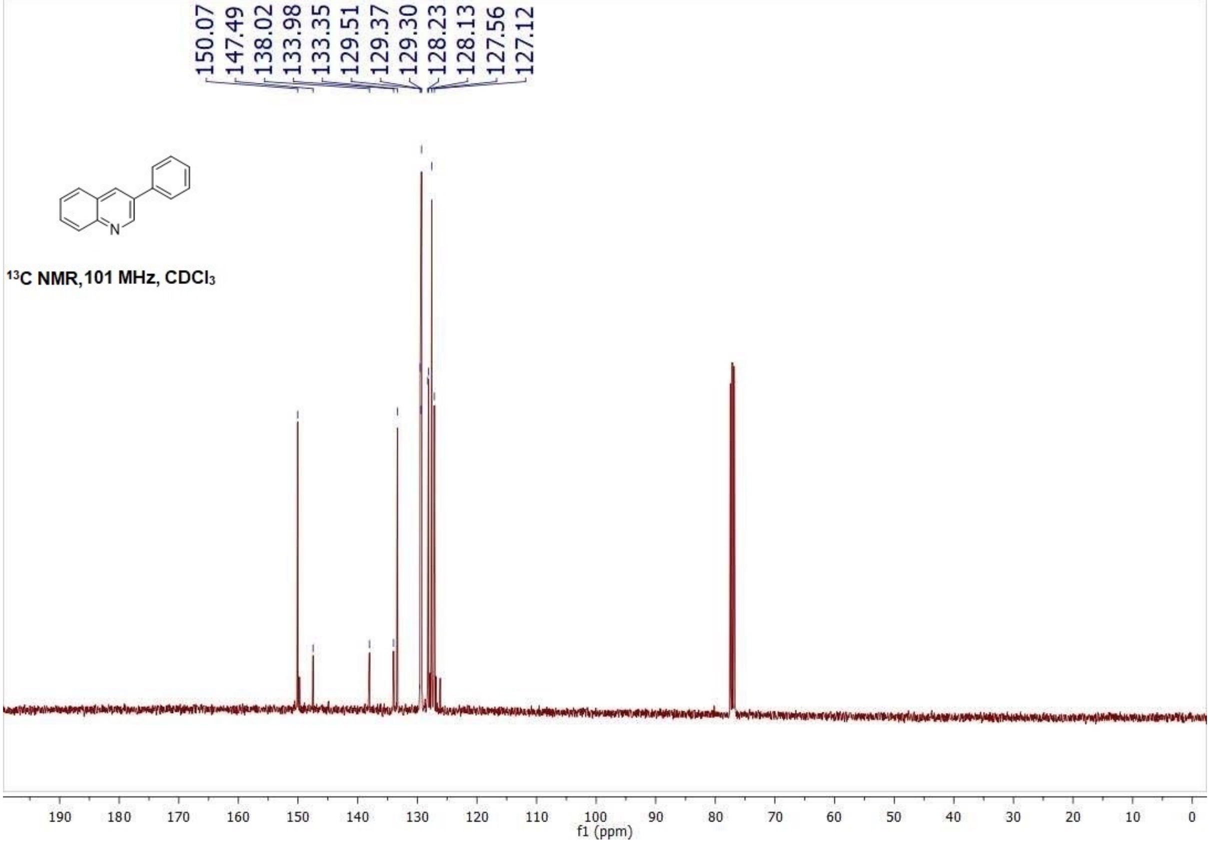
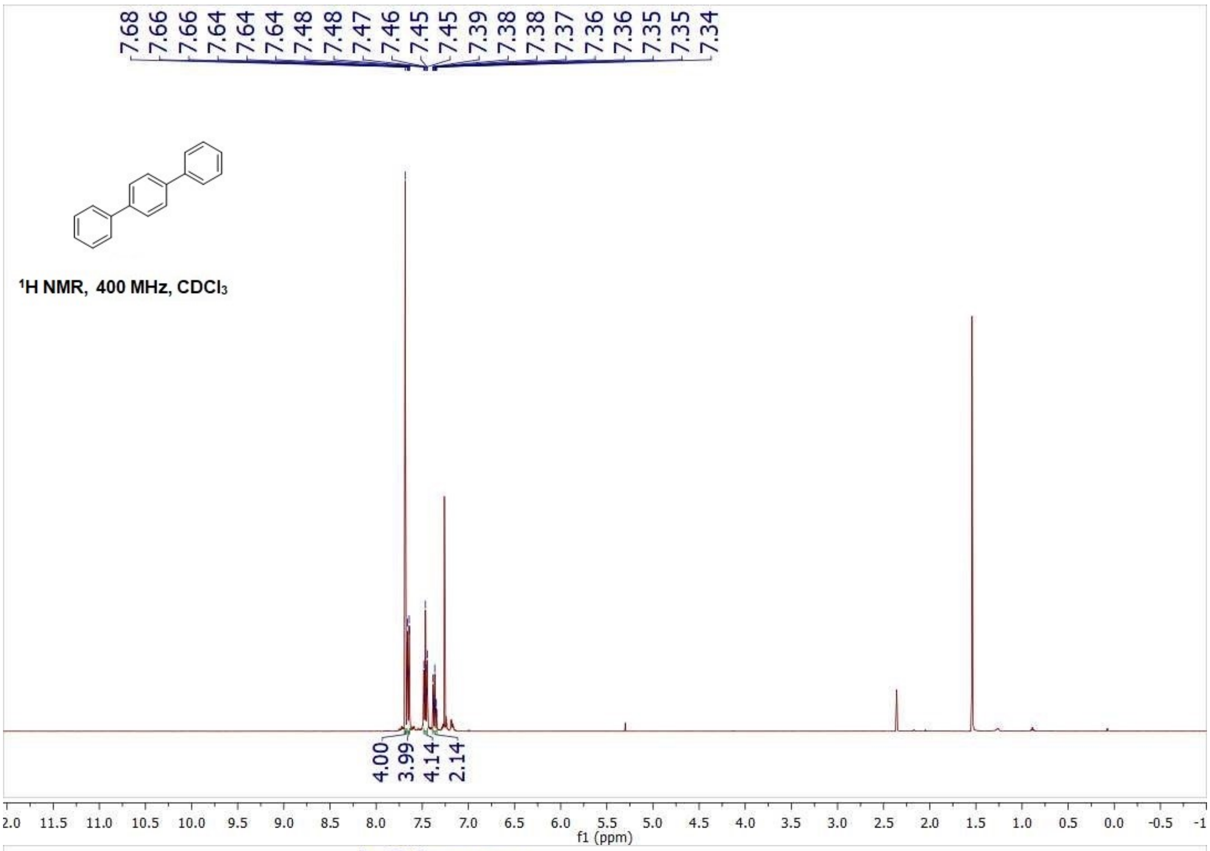
8.71
8.71
8.70
8.70
8.70
8.69
8.01
8.01
7.99
7.99
7.77
7.75
7.75
7.74
7.74
7.73
7.73
7.72
7.72
7.50
7.50
7.50
7.48
7.48
7.47
7.46
7.44
7.44
7.43
7.42
7.42
7.40
7.24
7.24
7.23
7.23
7.23
7.22
7.21
N
^{1}H NMR, 400 MHz, CDCl$_3$
1.00
2.07
2.10
2.09
1.05
0.96
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


157.63
149.81
139.55
136.86
129.08
128.88
127.05
122.22
120.69
N
^{13}C NMR, 101 MHz, CDCl$_3$
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


9.20
9.19
8.30
8.29
8.16
8.14
7.89
7.87
7.73
7.73
7.72
7.71
7.71
7.60
7.58
7.58
7.56
7.56
7.55
7.55
7.53
7.52
7.51
7.46
7.46
7.44
7.43
7.42
N
^{1}H NMR, 400 MHz, CDCl$_3$
0.94
1.02
1.02
1.00
2.92
1.09
2.07
1.03
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


150.07
147.49
138.02
133.98
133.35
129.51
129.37
129.30
128.23
128.13
127.56
127.12
N
^{13}C NMR,101 MHz, CDCl$_3$
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.66
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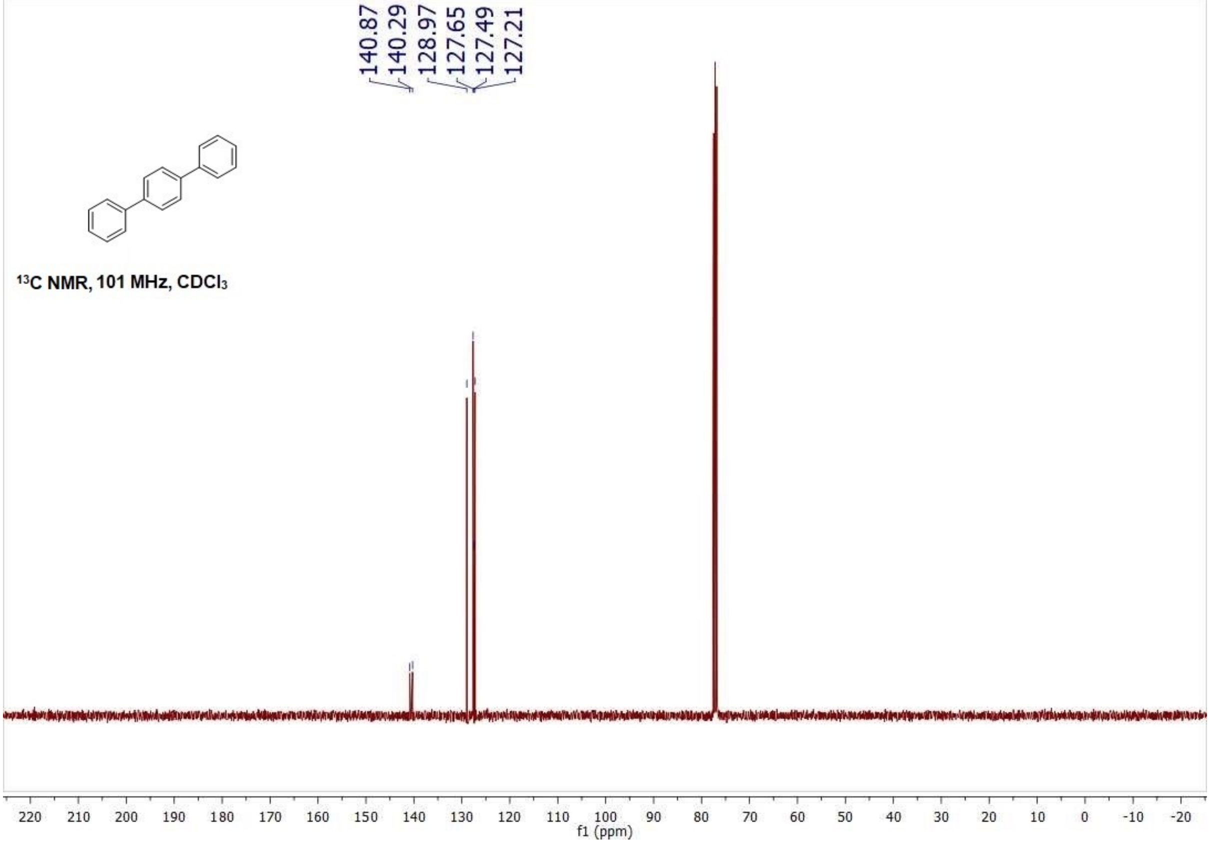
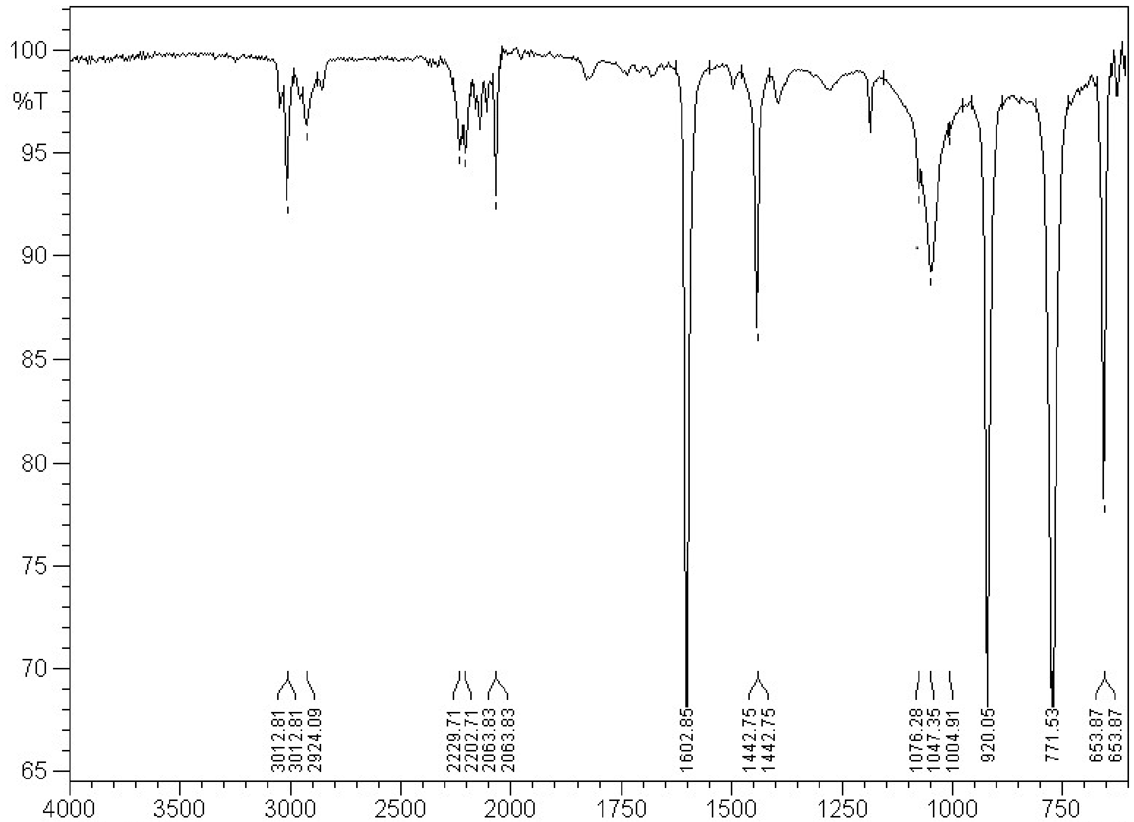
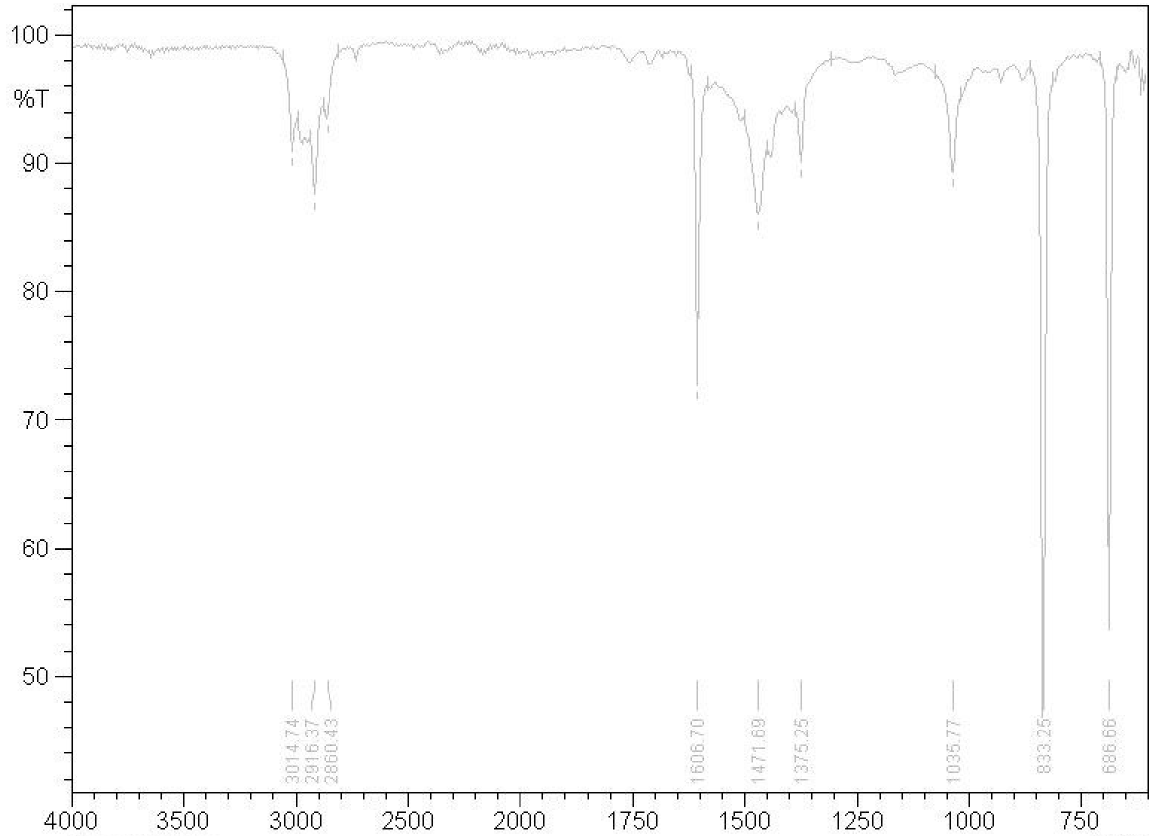
7.64
7.64
7.48
7.48
7.47
7.46
7.45
7.45
7.39
7.38
7.38
7.37
7.36
7.36
7.35
7.35
7.34
¹H NMR, 400 MHz, CDCl₃
4.00
3.99
4.14
2.14
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


140.87
140.29
128.97
127.65
127.49
127.21
¹³C NMR, 101 MHz, CDCl₃
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

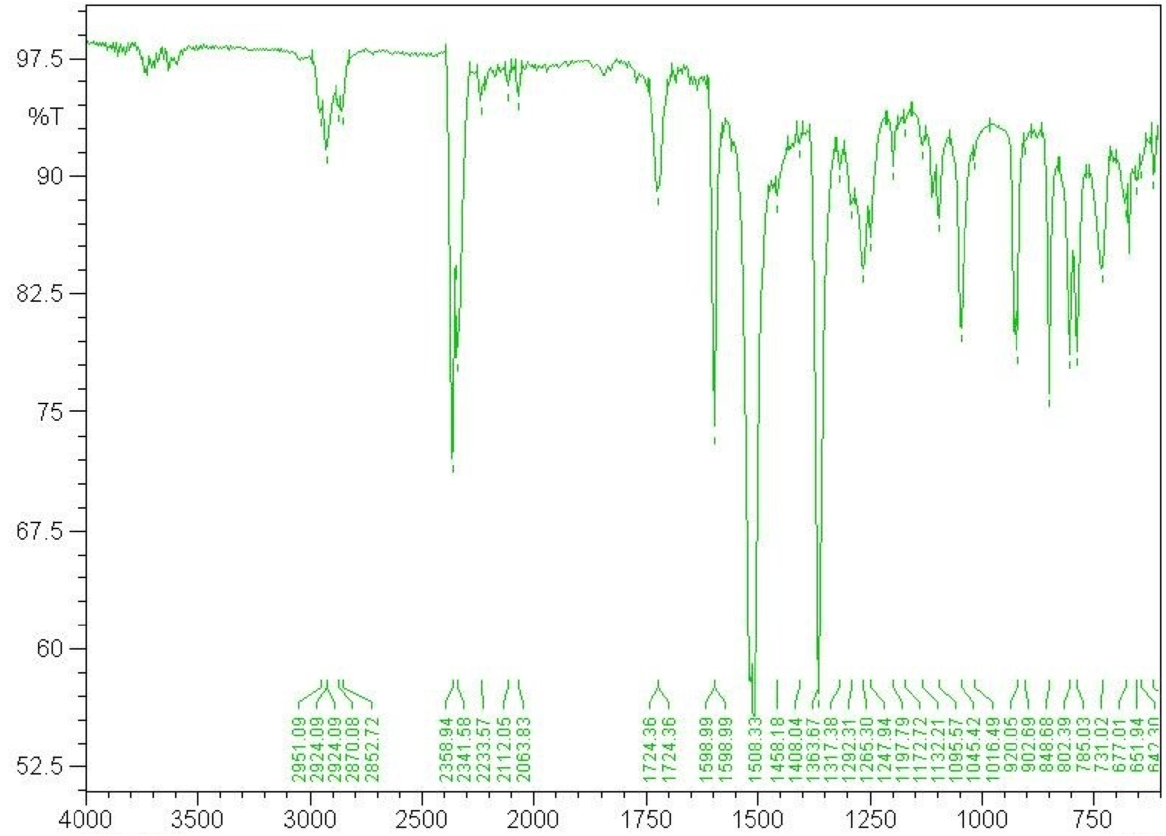
IR spectra



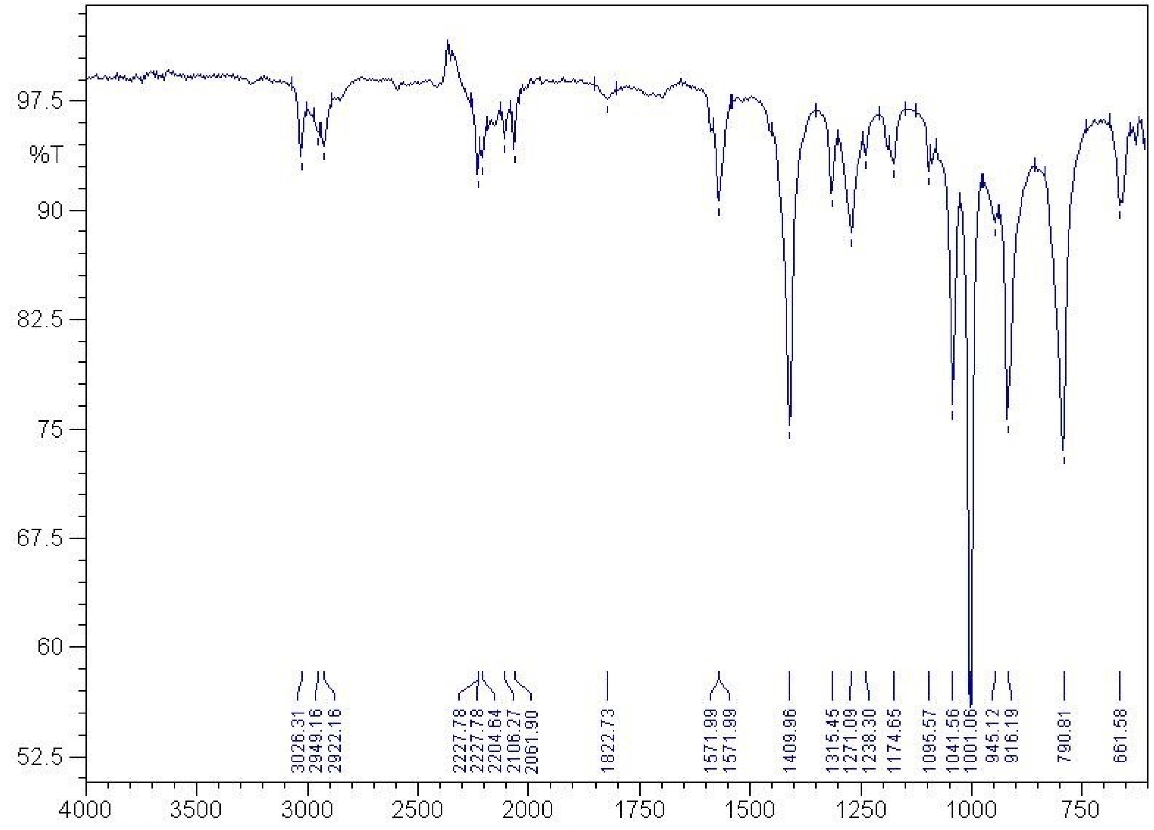
FTIR spectrum of d_9-mesitylene ***S1***



FTIR spectrum of commercial non-deuterated mesitylene



*FTIR spectrum of d_9-nitromesitylene **S4***

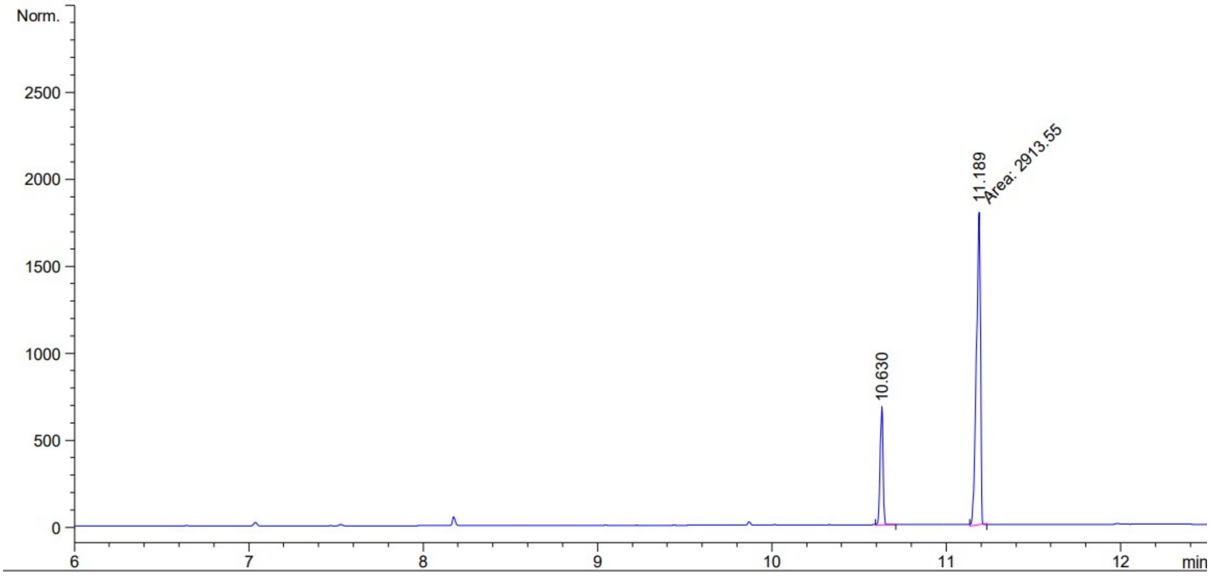


*FTIR spectrum of d_9-iodomesitylene **S6***

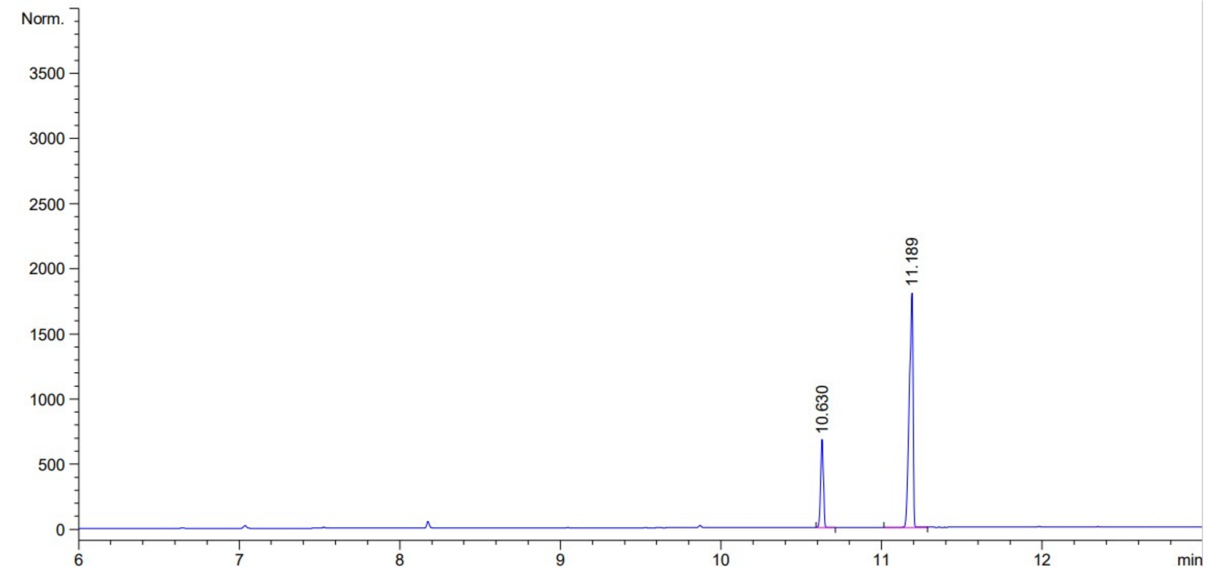
GC-FID traces

Approximate retention times: **6** RT = 11.2 min, **7** RT = 12.4 min, **5** RT = 12.0 min, **8** RT = 7.1 min, *n*-dodecane RT = 10.6 min.

GC-FID traces for reaction condition screen (Page S15, Table S1)



Entry 1



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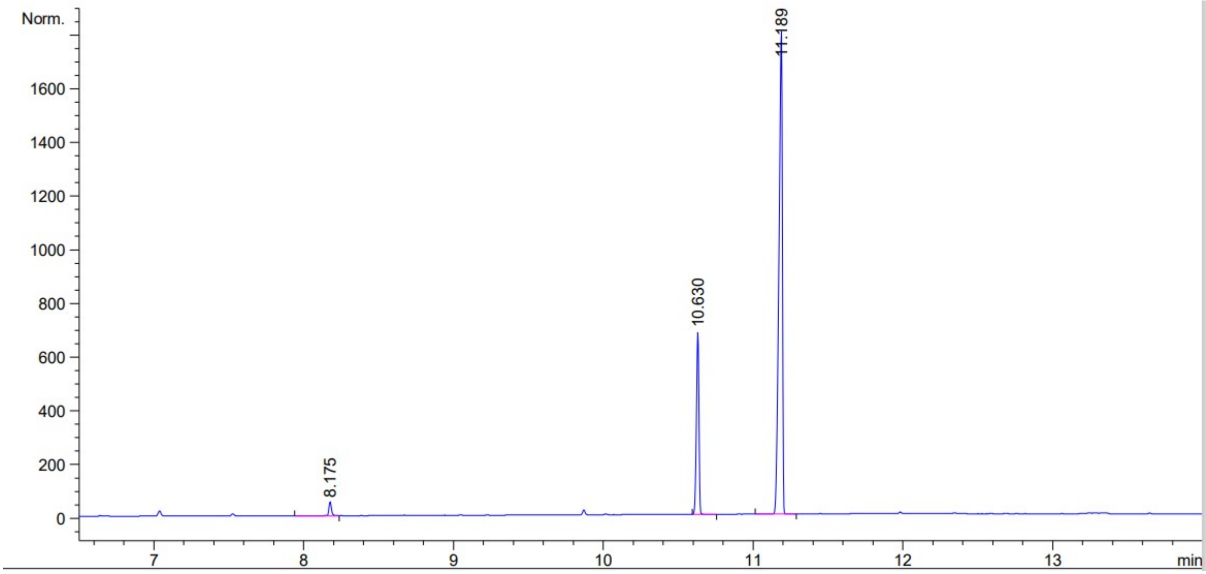

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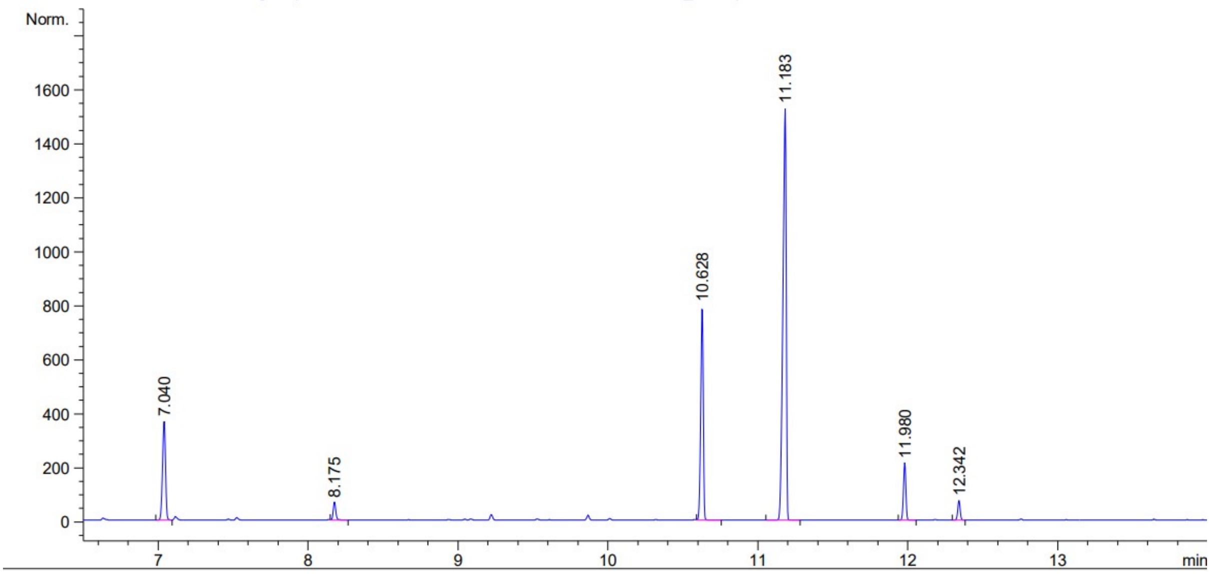

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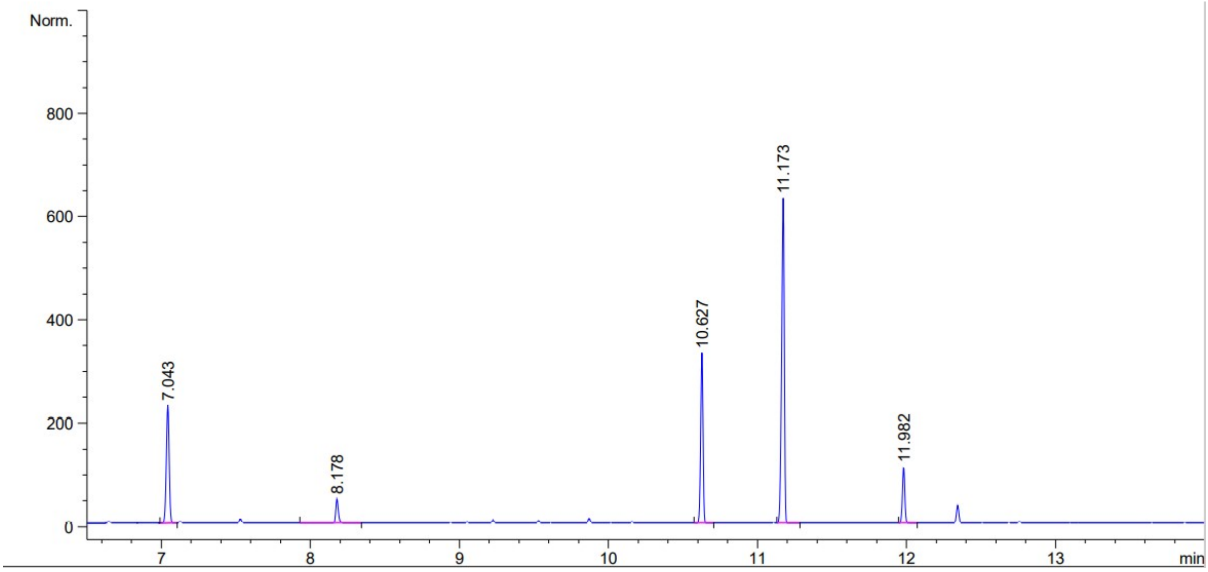

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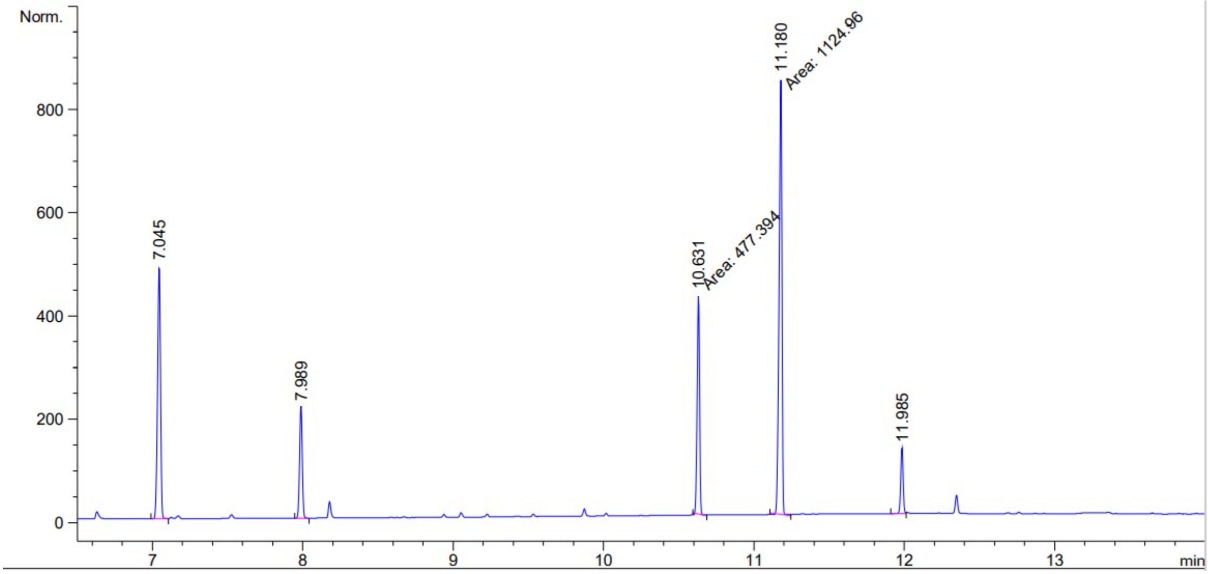

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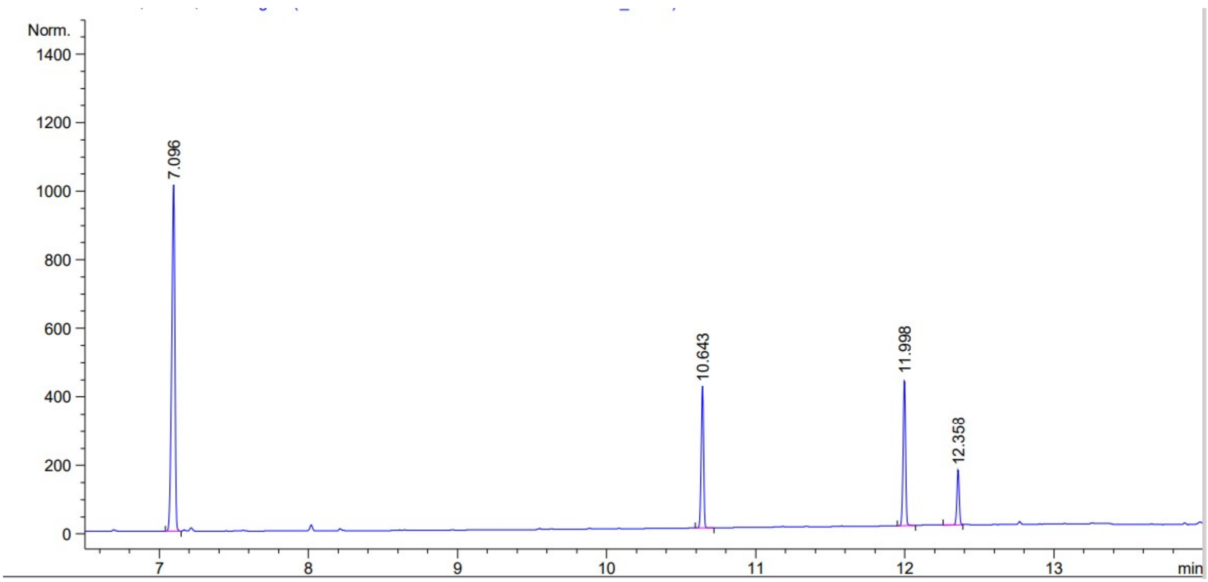

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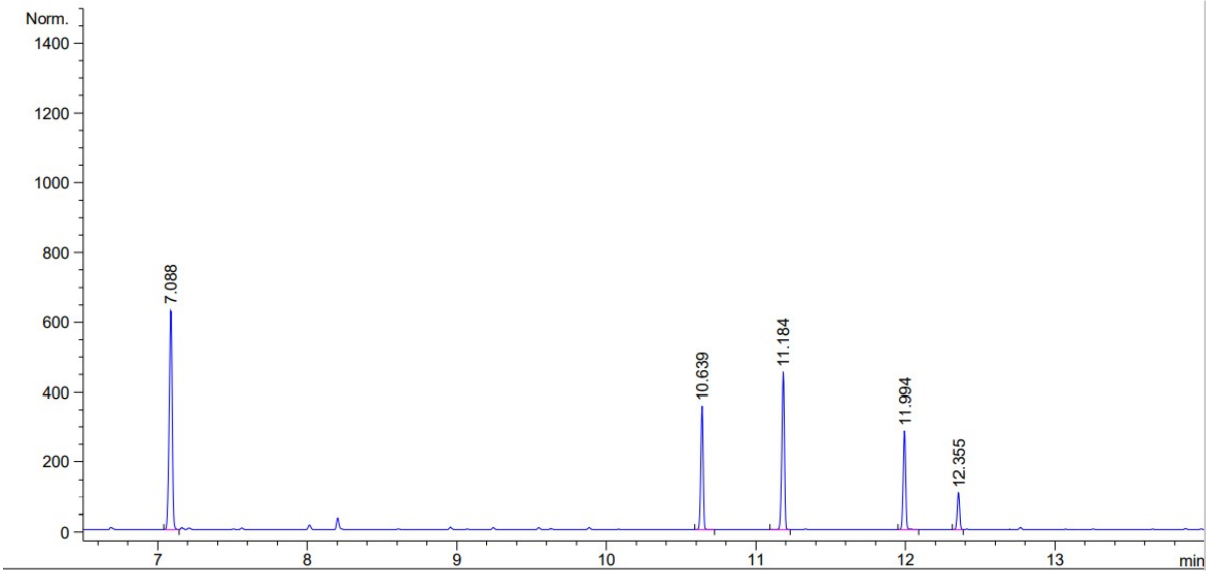

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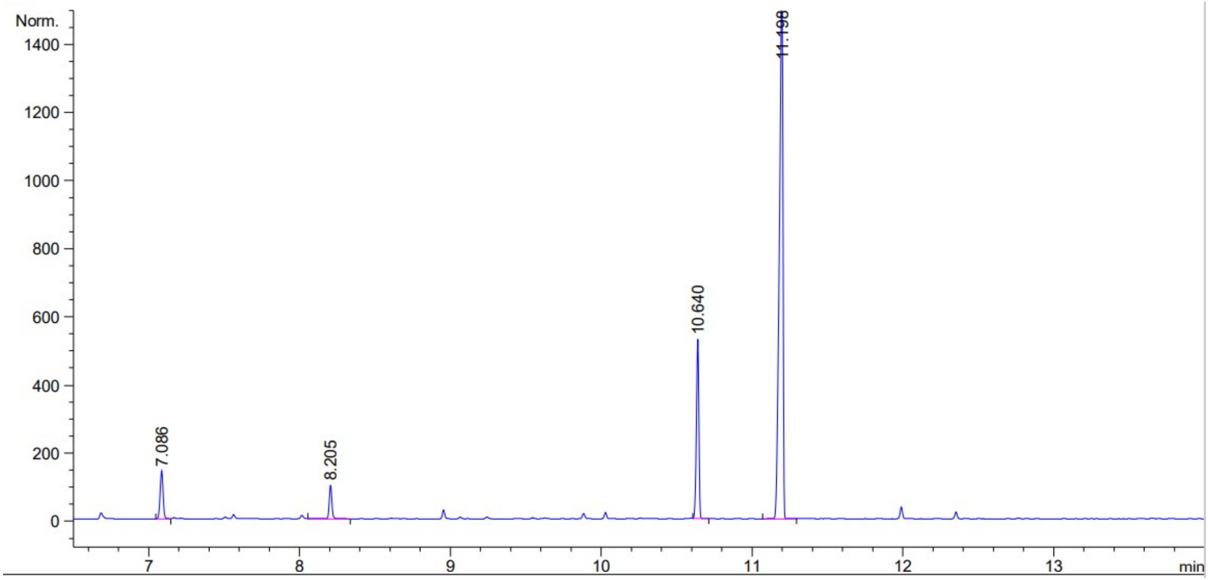

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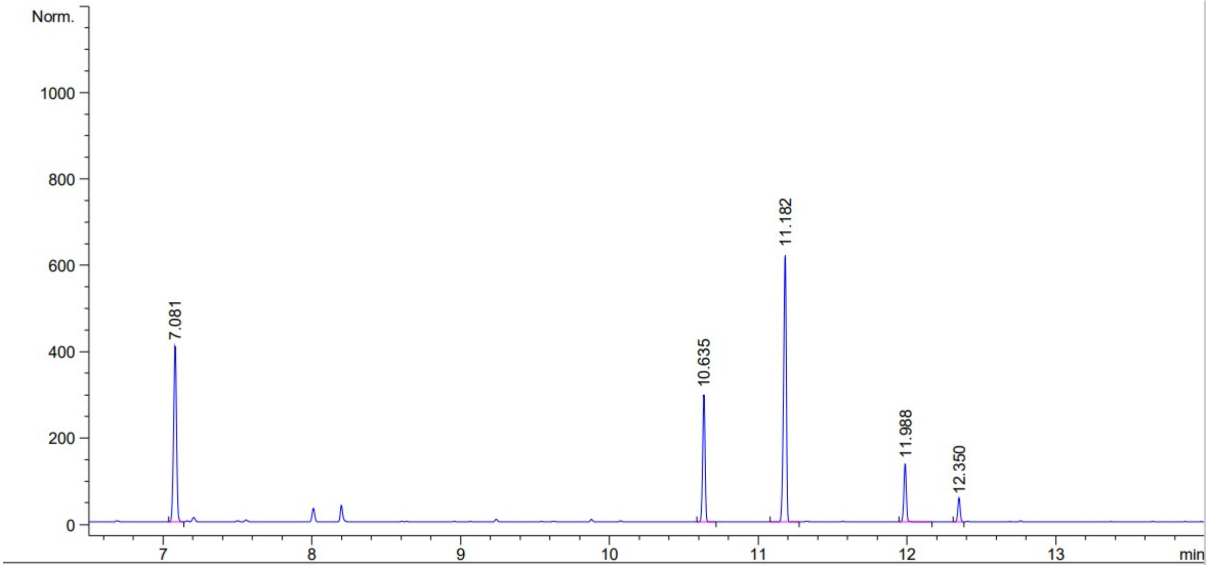

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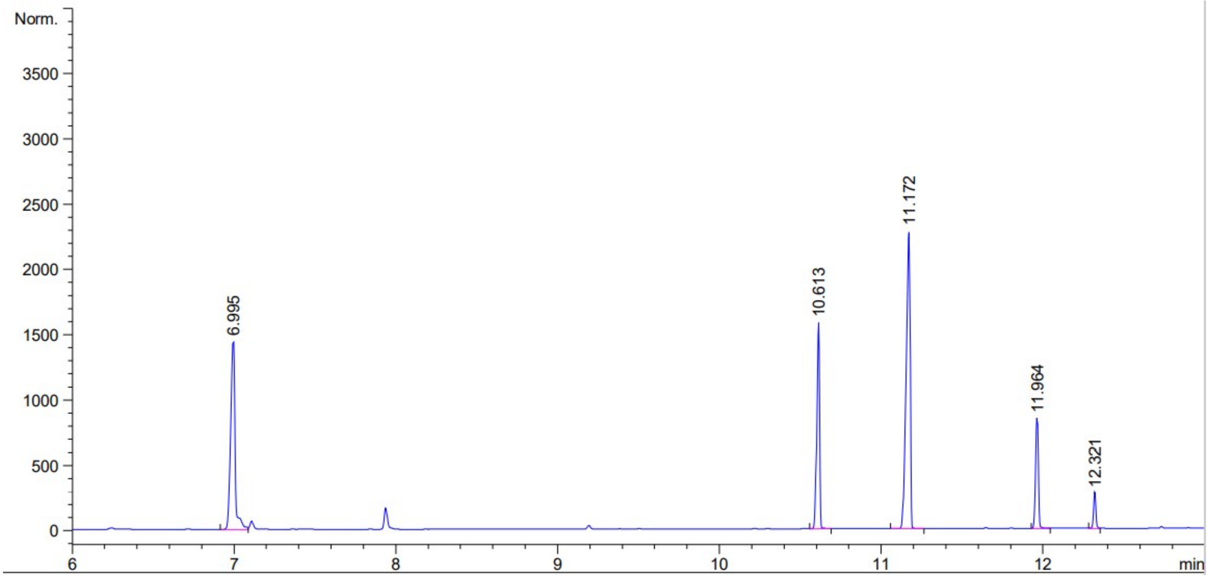

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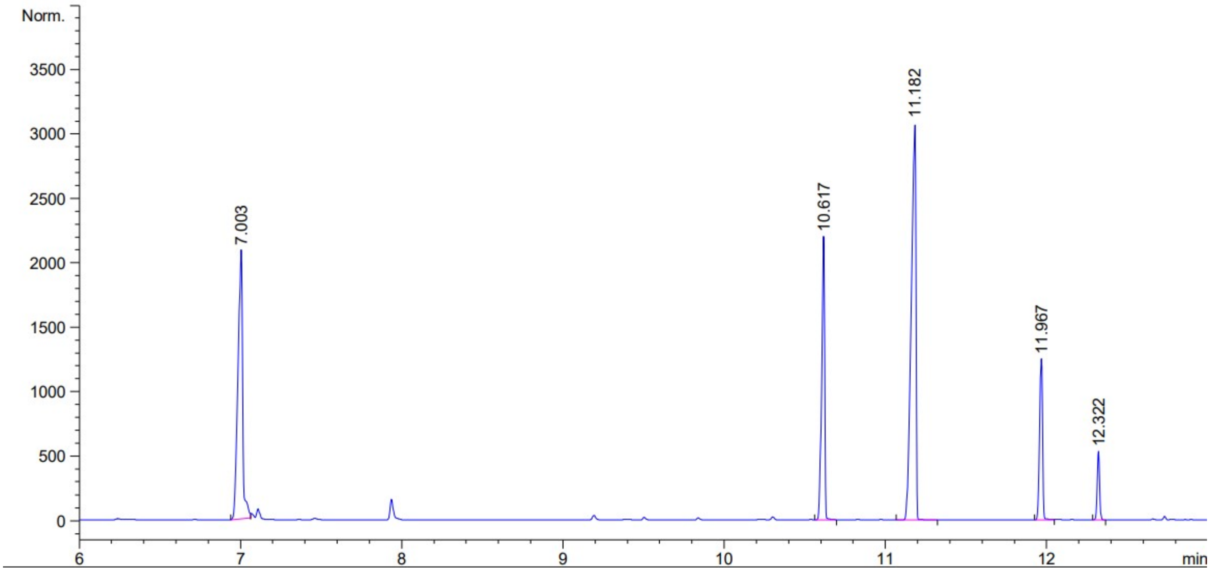

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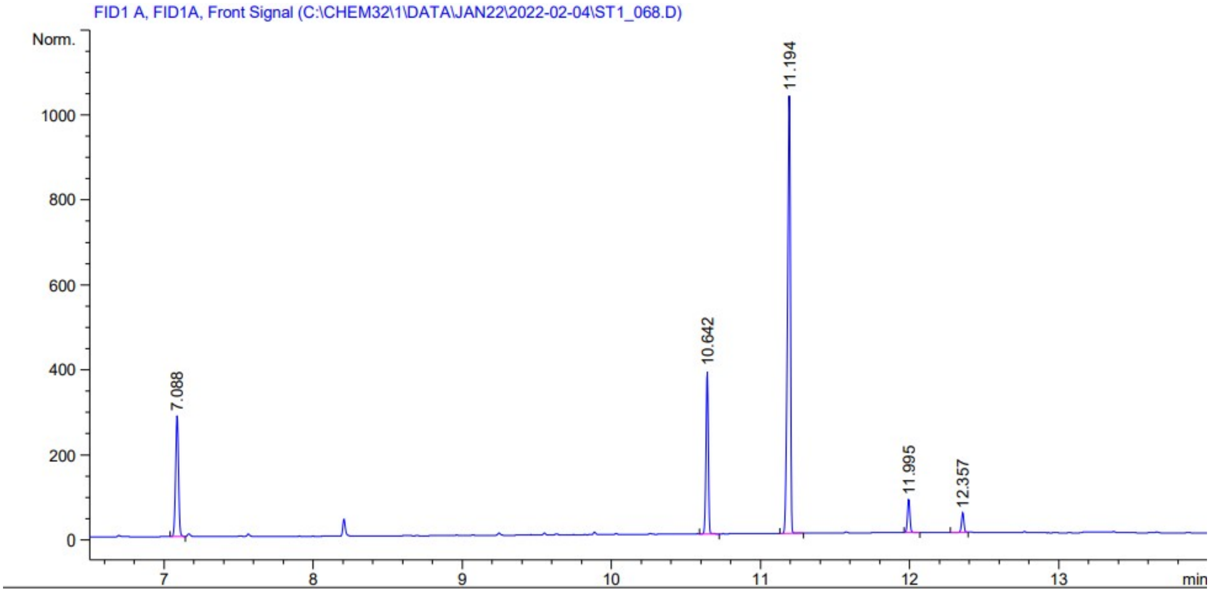

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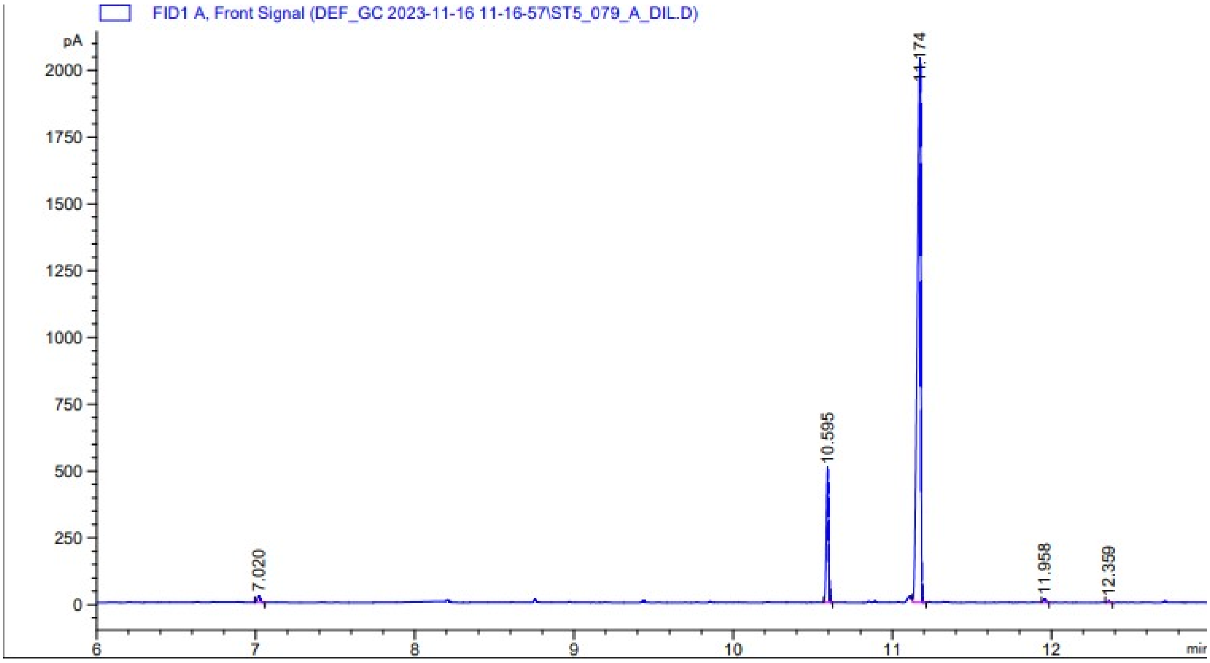

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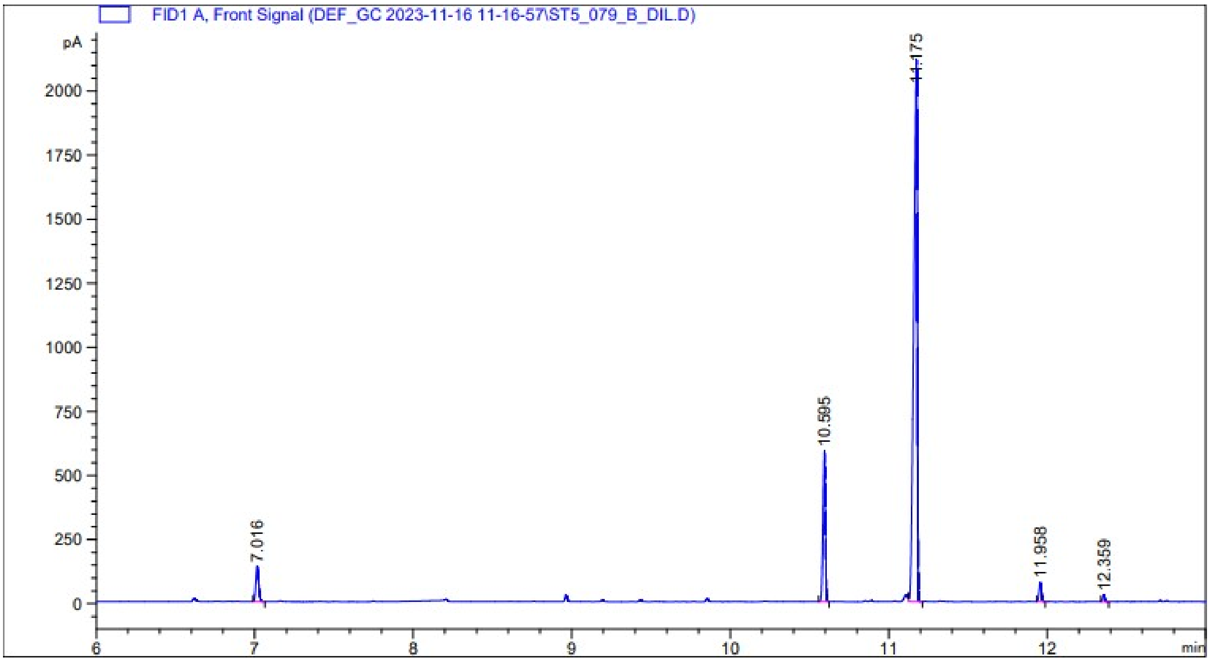

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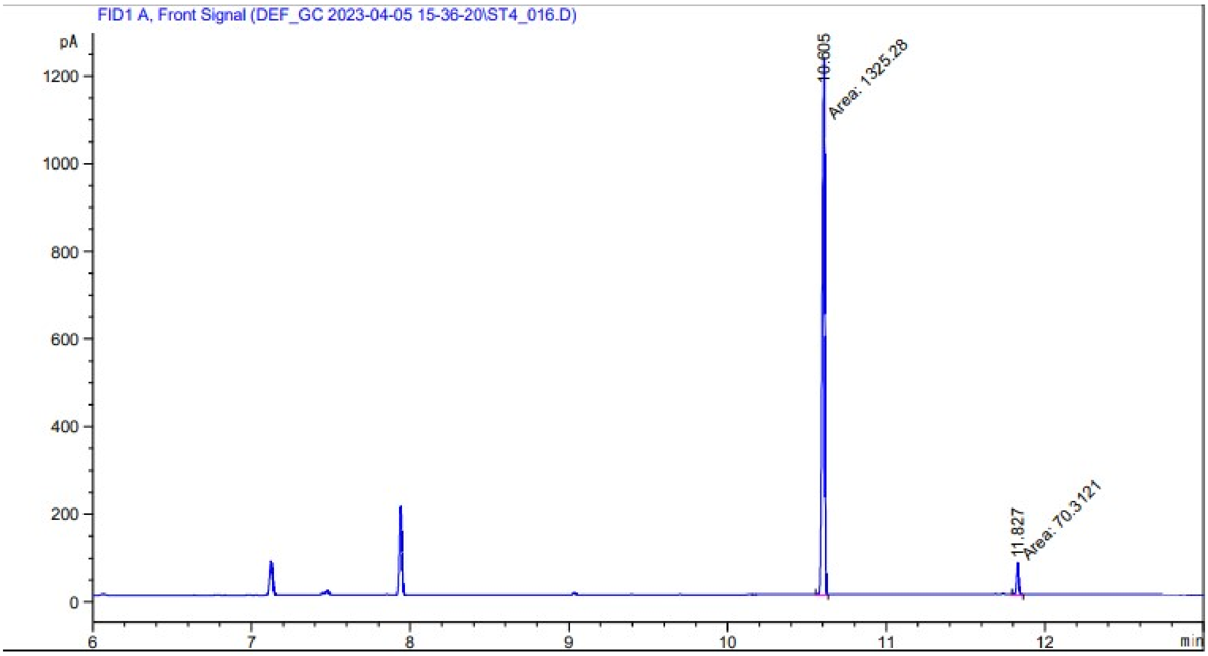
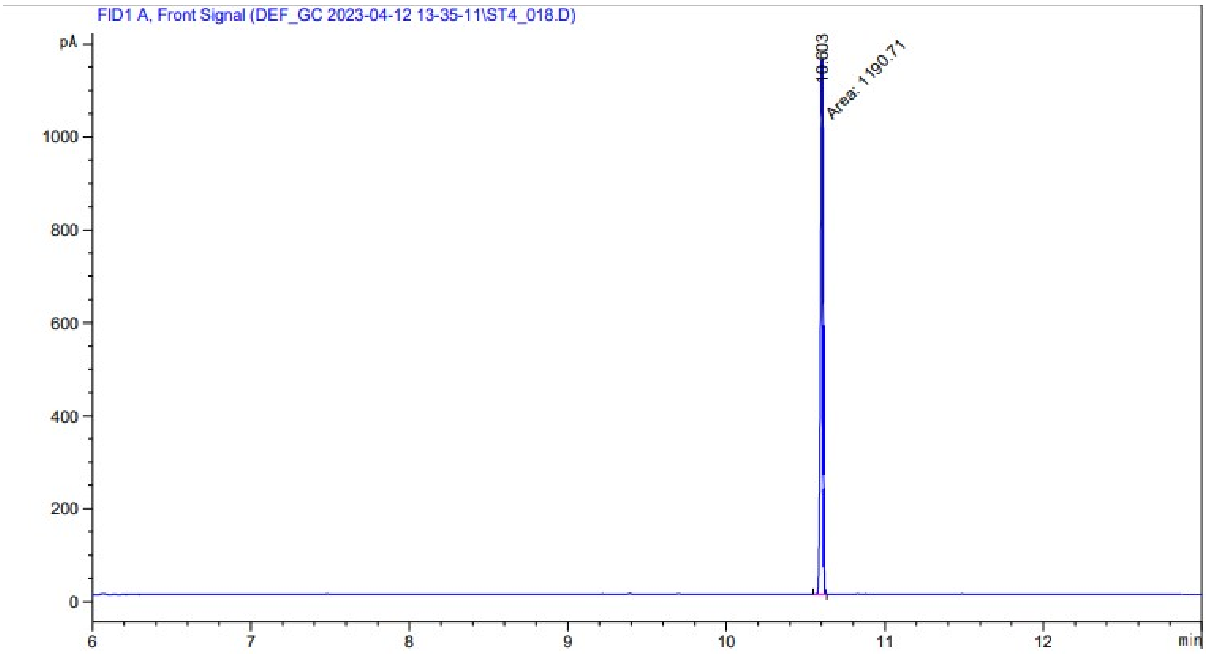


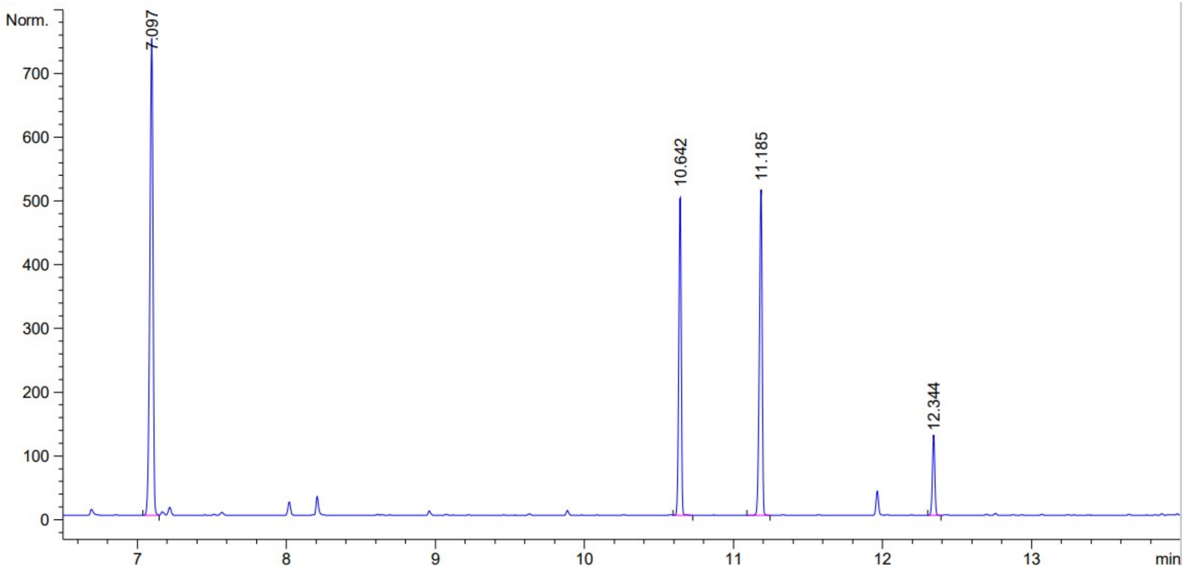
Entry 16



Entry 17

GC-FID traces for solvent deuteration experiments (Page S15, Table S2)

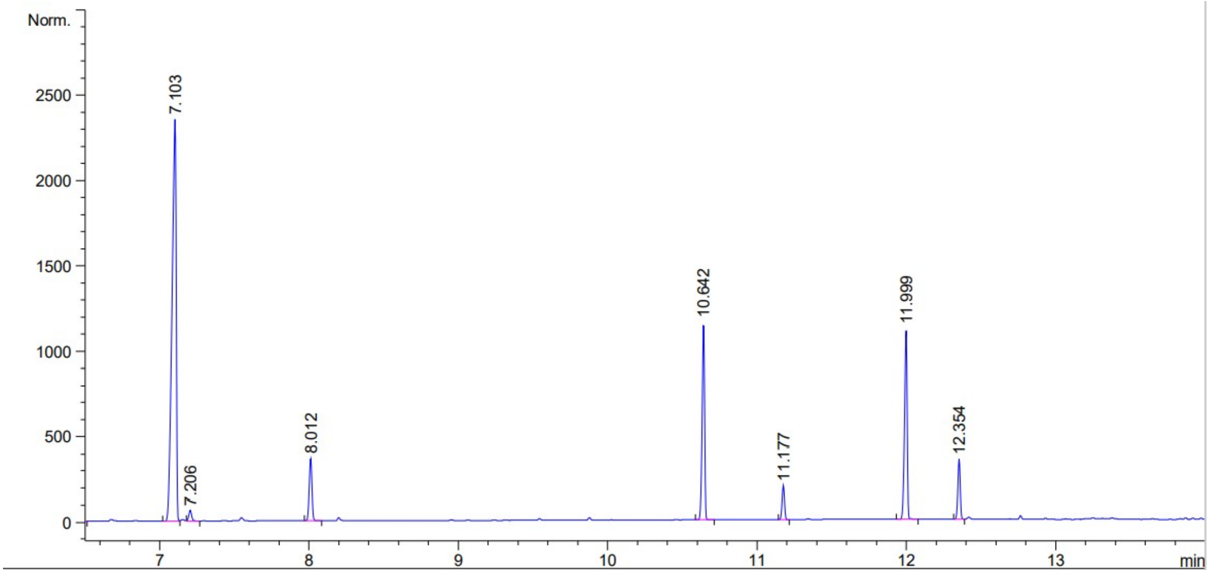
Yields for deuterated analogues of compounds were measured in the same way as non-deuterated analogues.



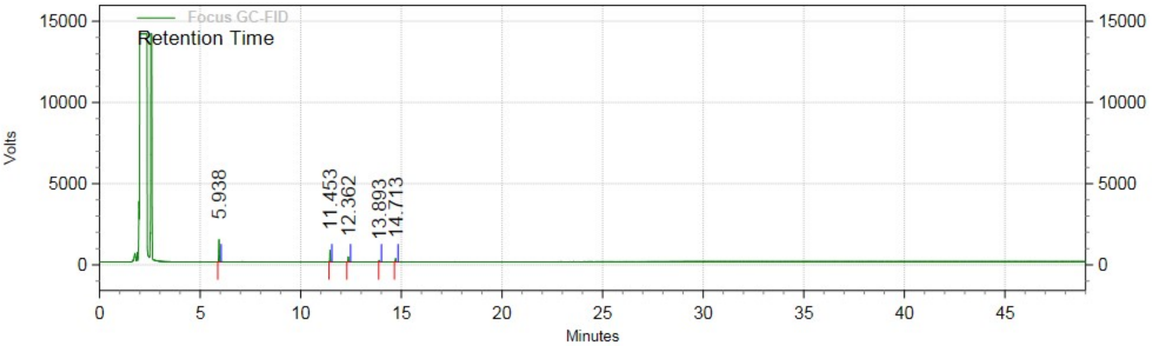
Entry 2

GC-FID traces for COD/d_9-KO^{t}Bu experiments (Page S16, Table S3)

Yields for deuterated analogues of compounds were measured in the same way as non-deuterated analogues.

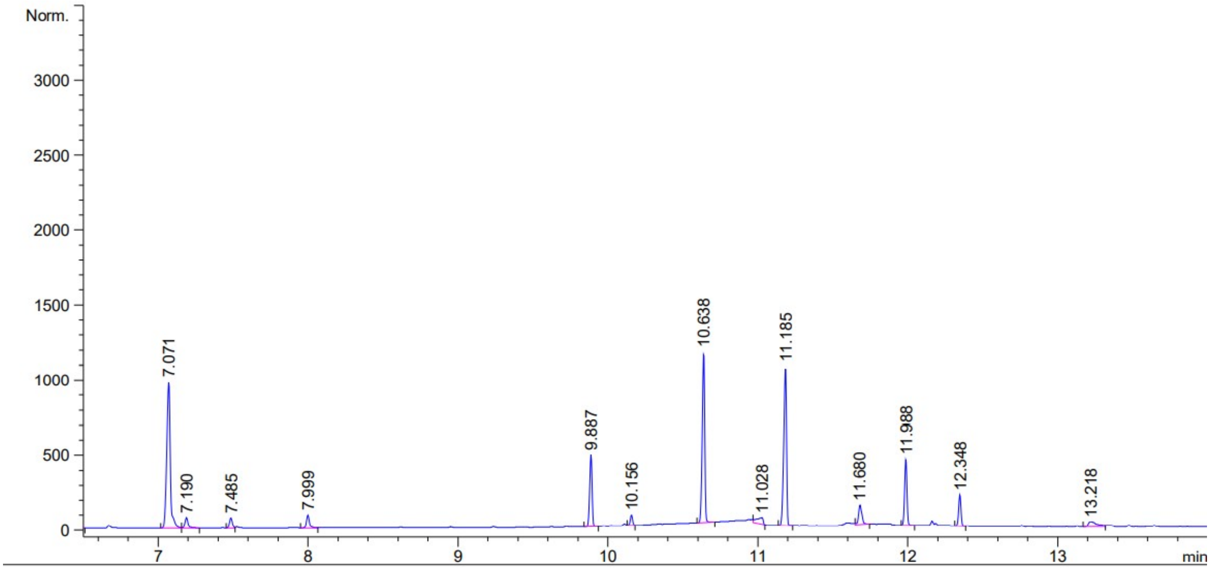


Entry 2



Entry 3 – For this single experiment, due to breakage of the GC-FID used in the rest of the study, a different GC-FID instrument was used to obtain data. New calibration curves were constructed for the new instrument, however this turned out to be unnecessary because results on either machine could be input into either set of calibrations to obtain identical yields. This is because our calibration method simply compares peak ratios between the internal standard and the target compound. The approximate retention times on this instrument are: m-xylene RT = 5.9 min, n-dodecane RT = 11.5 min, 2-iodo-m-xylene RT = 12.4 min, biphenyl RT = 13.9 min, 2,6-dimethylbiphenyl RT = 14.7.

GC-FID traces for TEMPO reactions (Page S23, Table S4)



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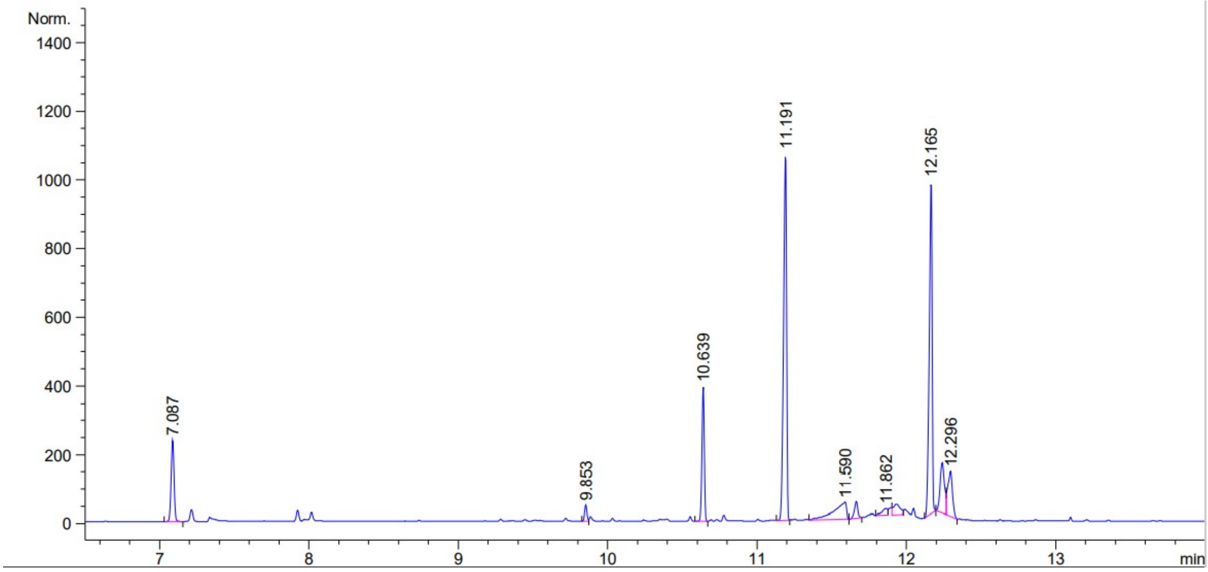
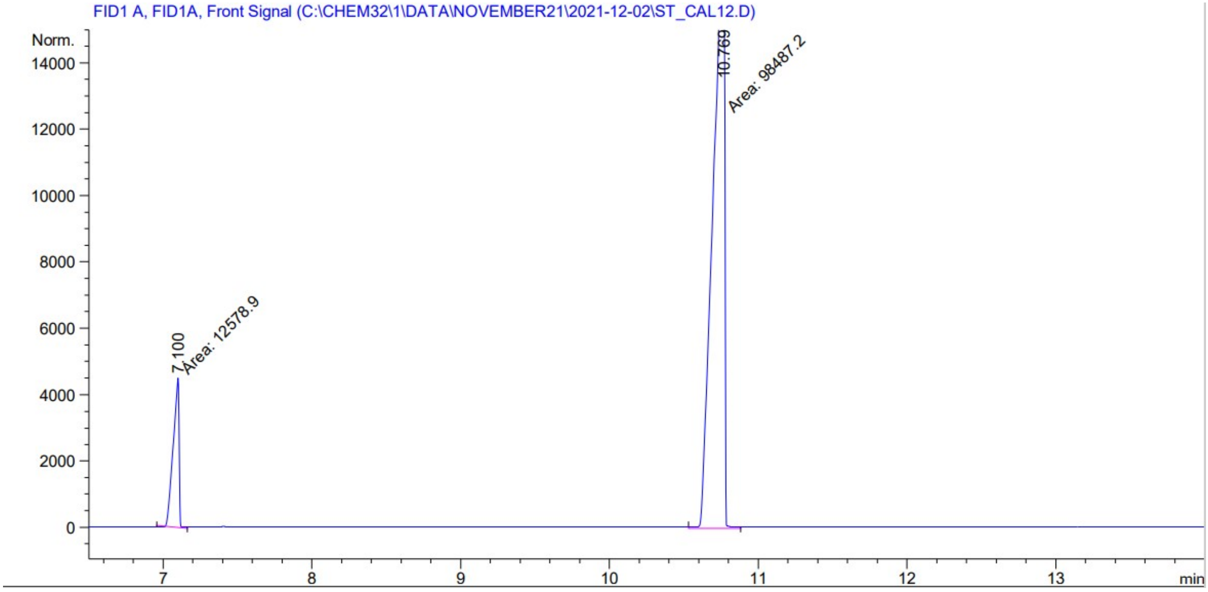


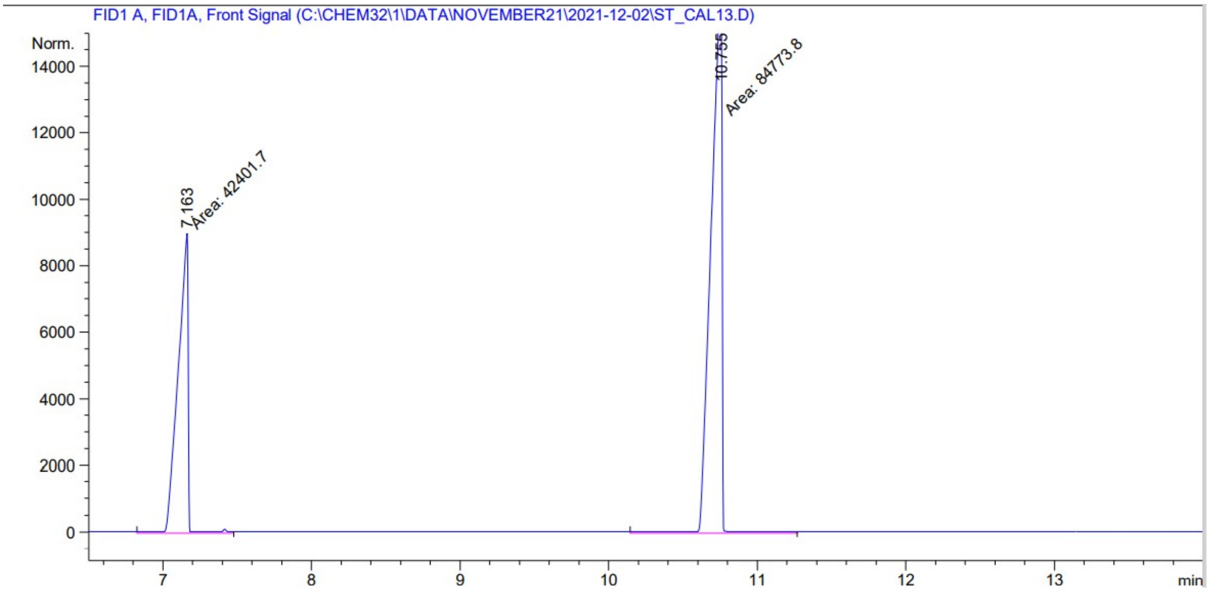
Entry 3

GC-FID traces for *m*-xylene calibration curve (Page S23, Table S5)

Samples of 0.02-1.0 mmol *m*-xylene **8** (RT = 7.1 min) and 0.1 mmol dodecane (RT = 10.7 min).



Entry 1



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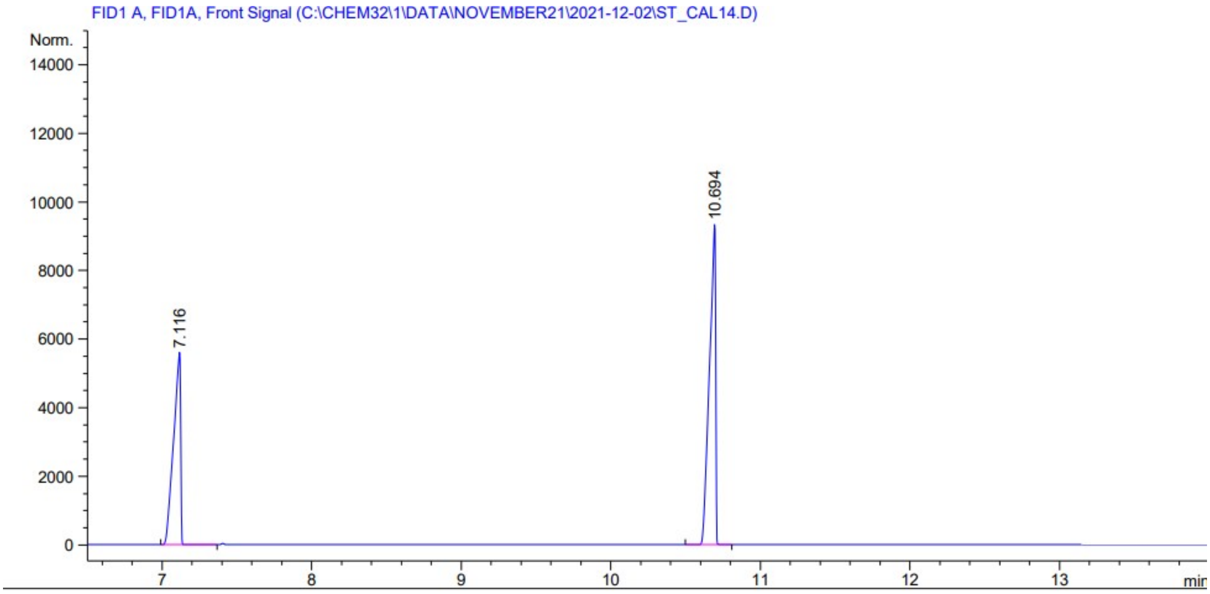

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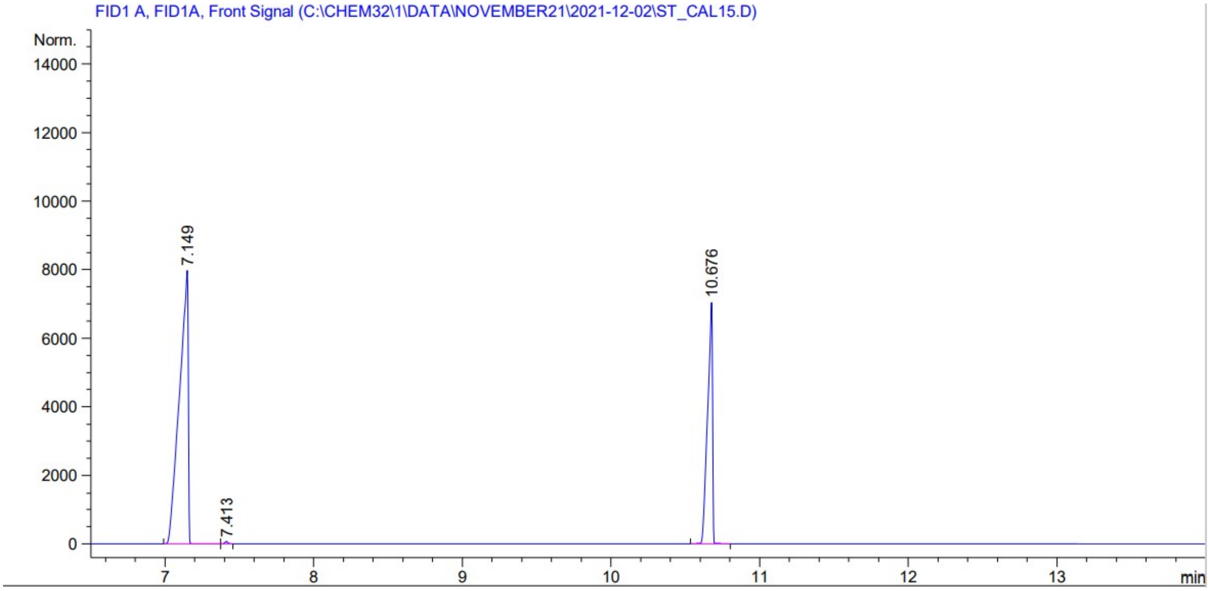

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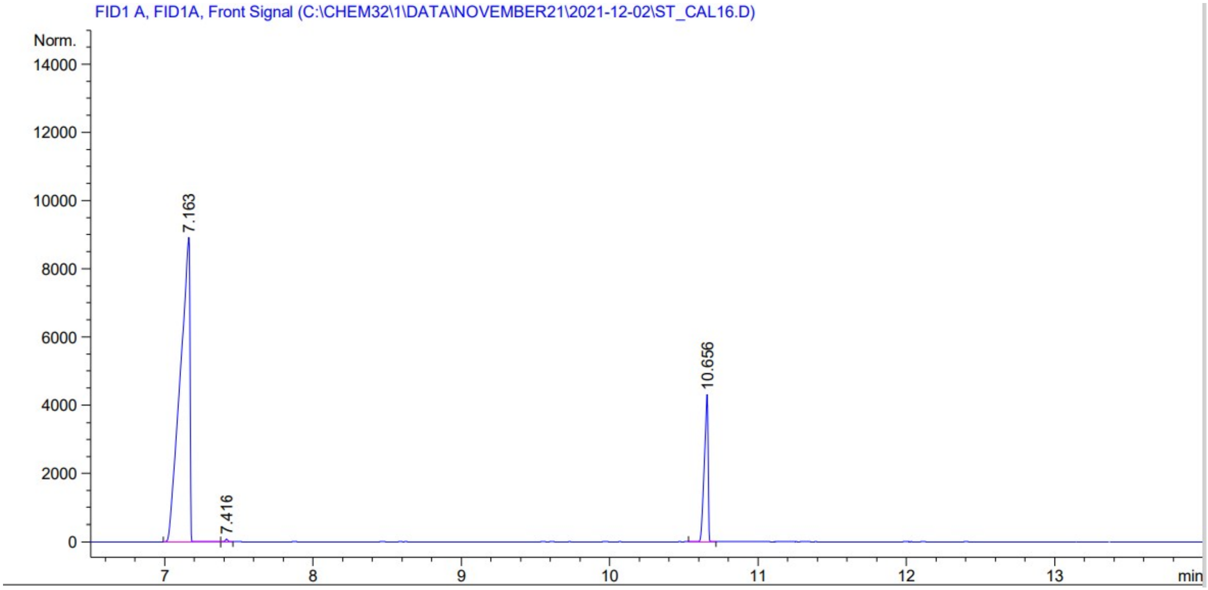
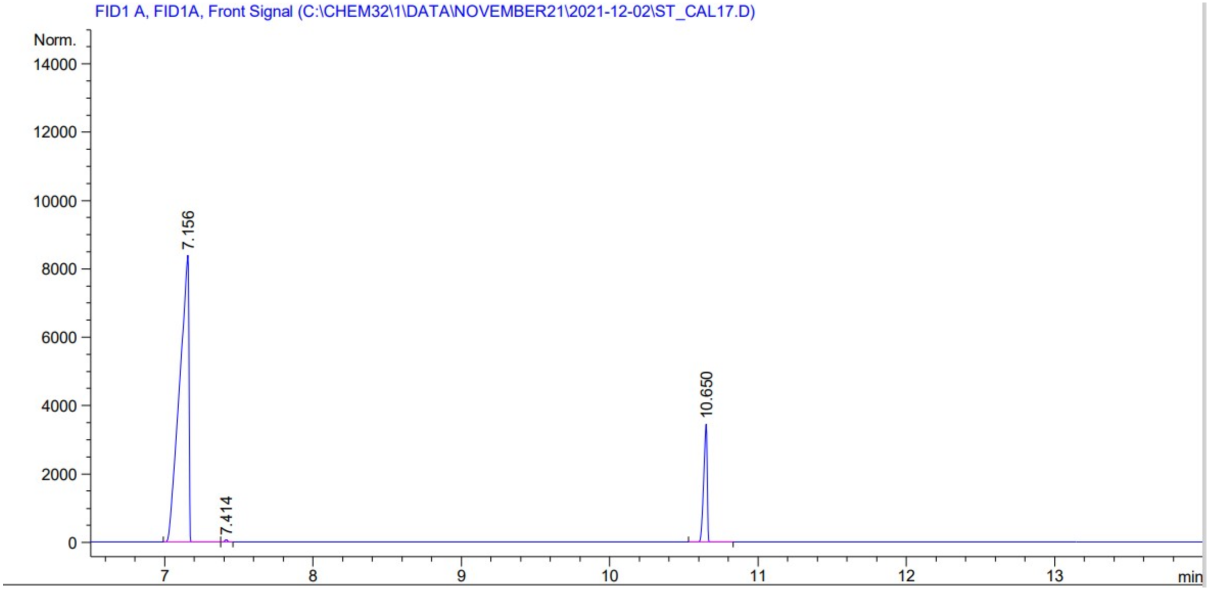


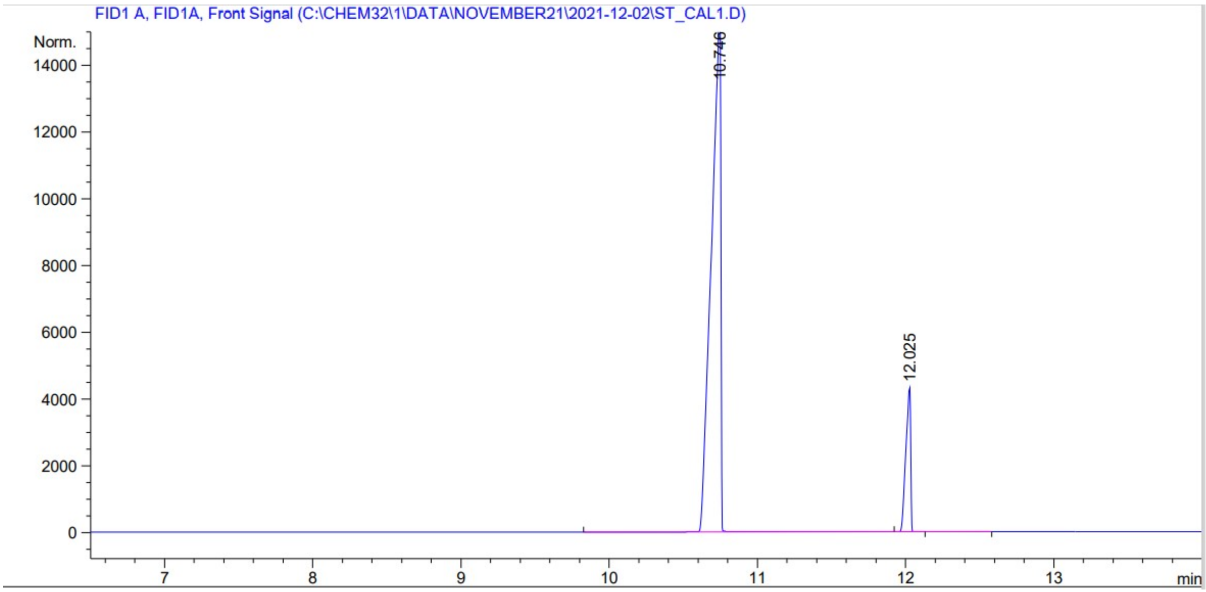
Entry 5



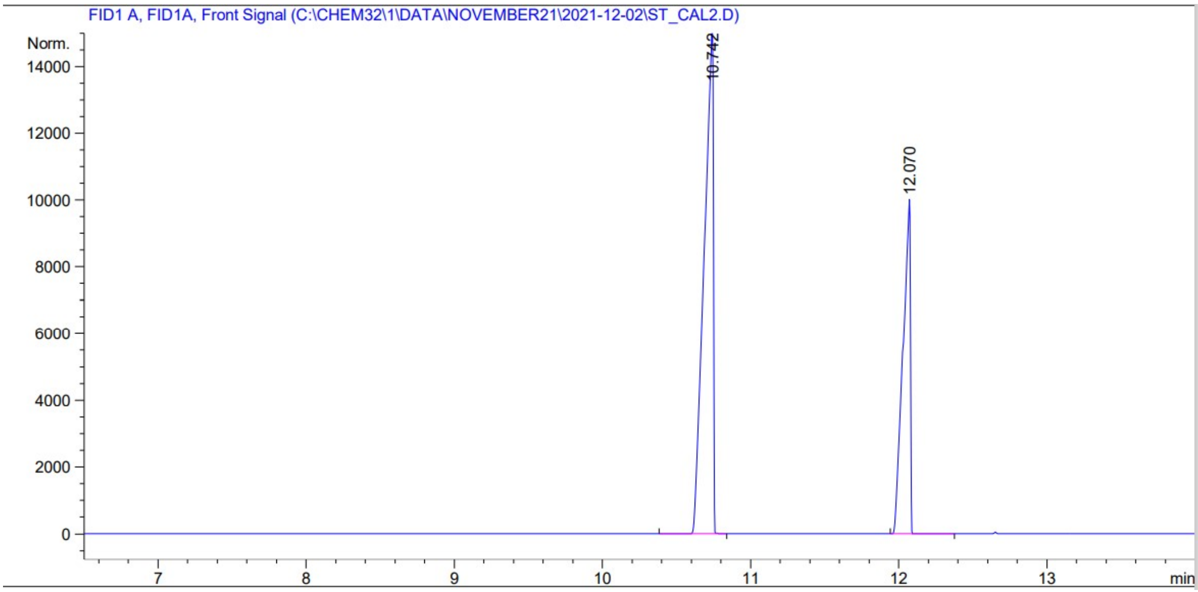
Entry 6

GC-FID traces for biphenyl calibration curve (Page S23, Table S6)

Samples of 0.014-0.7 mmol biphenyl **5** (RT = 12.0 min) and 0.1 mmol dodecane (RT = 10.7 min).



Entry 1



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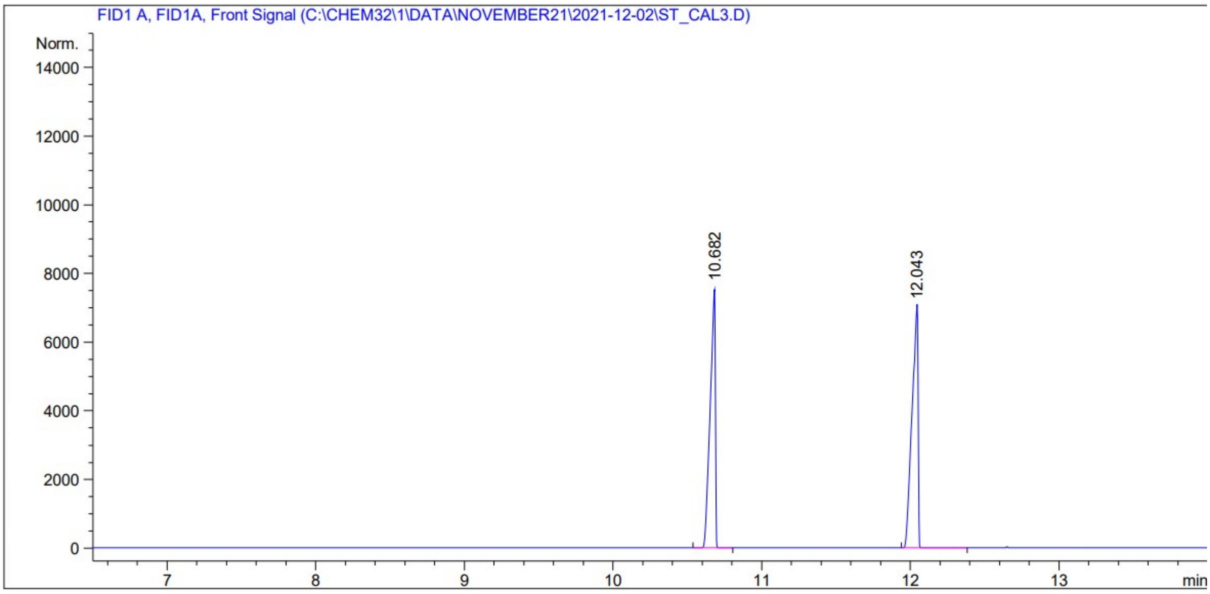
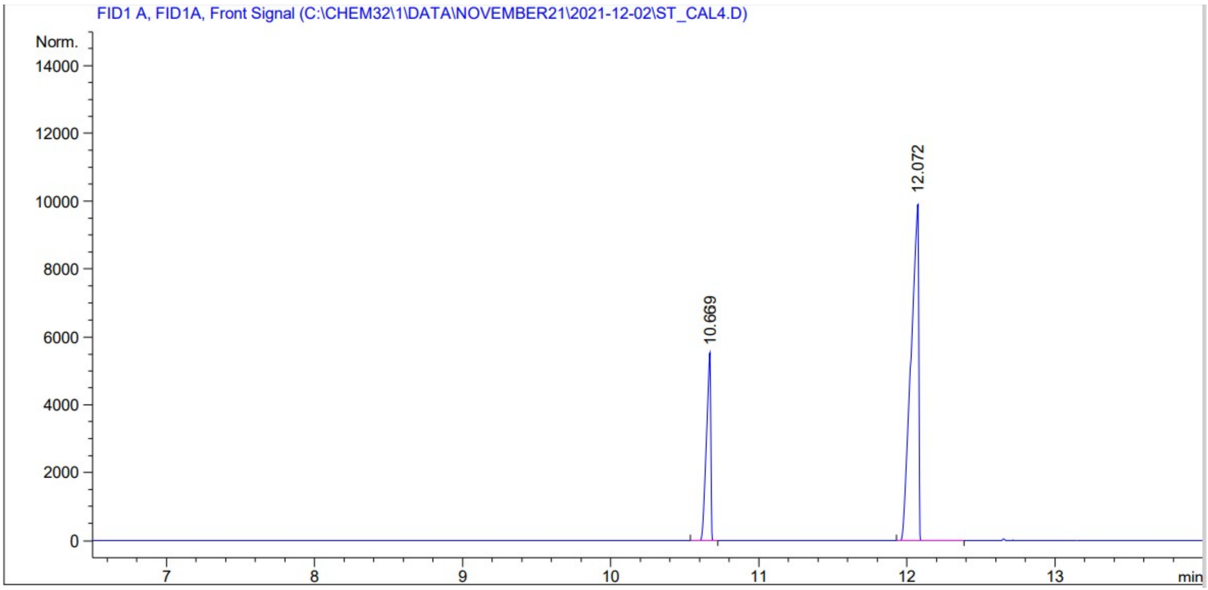
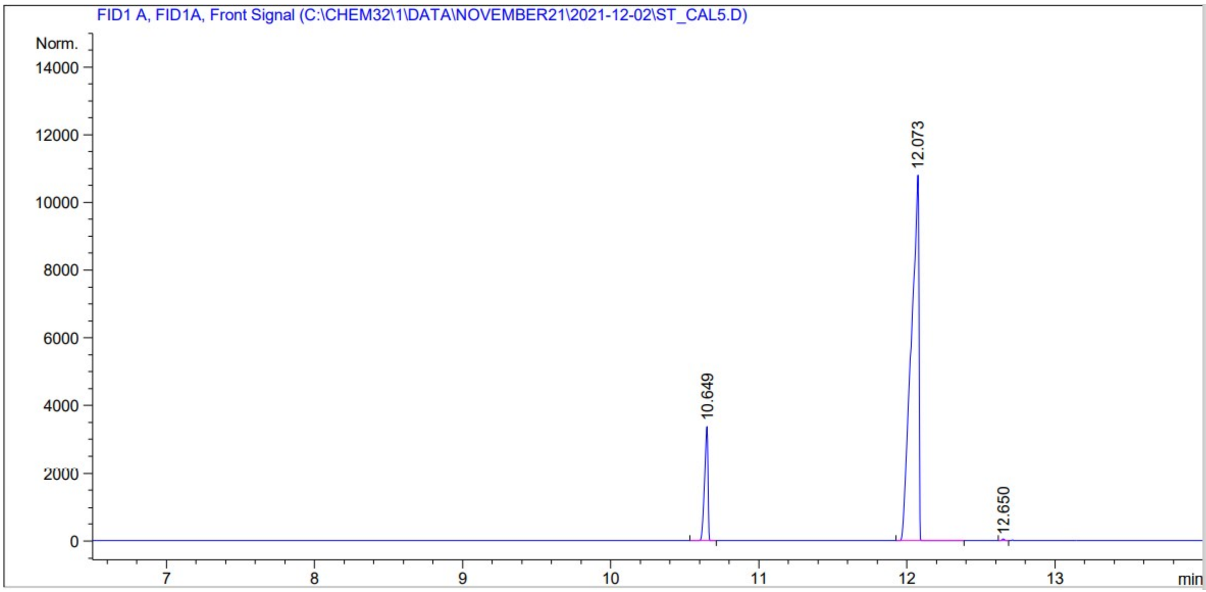


Entry 3



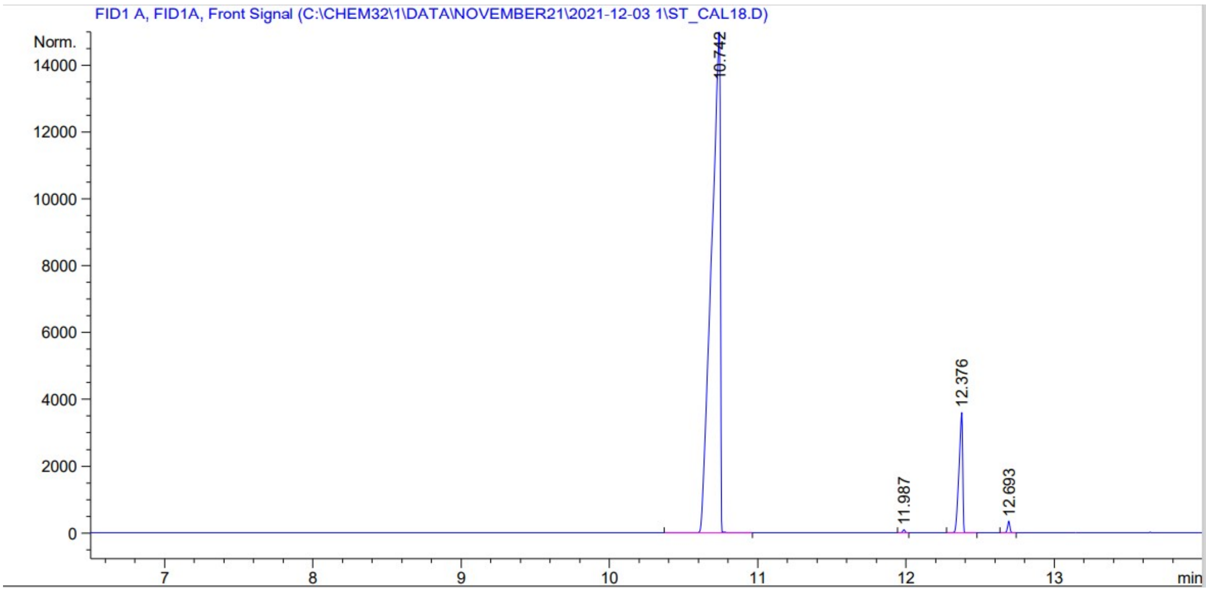
Entry 4


FID1 A, FID1A, Front Signal (C:\CHEM32\1\DATA\NOVEMBER21\2021-12-02\ST_CAL5.D)
Norm.
14000
12000
10000
8000
6000
4000
2000
0
7
8
9
10
11
12
13
min
10.649
12.073
12.650

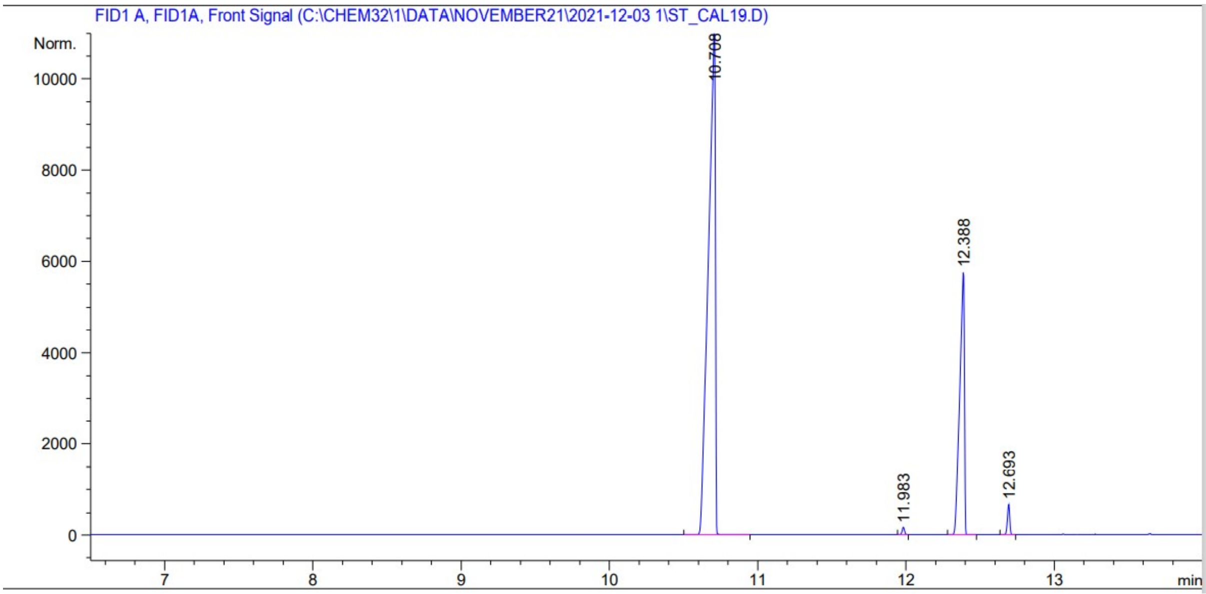
Entry 5

GC-FID traces for 2,6-dimethylbiphenyl calibration curve (Page S24, Table S7)

Samples of 0.01-0.5 mmol 2,6-dimethlybiphenyl **7** (RT = 12.4 min) and 0.1 mmol dodecane (RT = 10.7 min).



Entry 1



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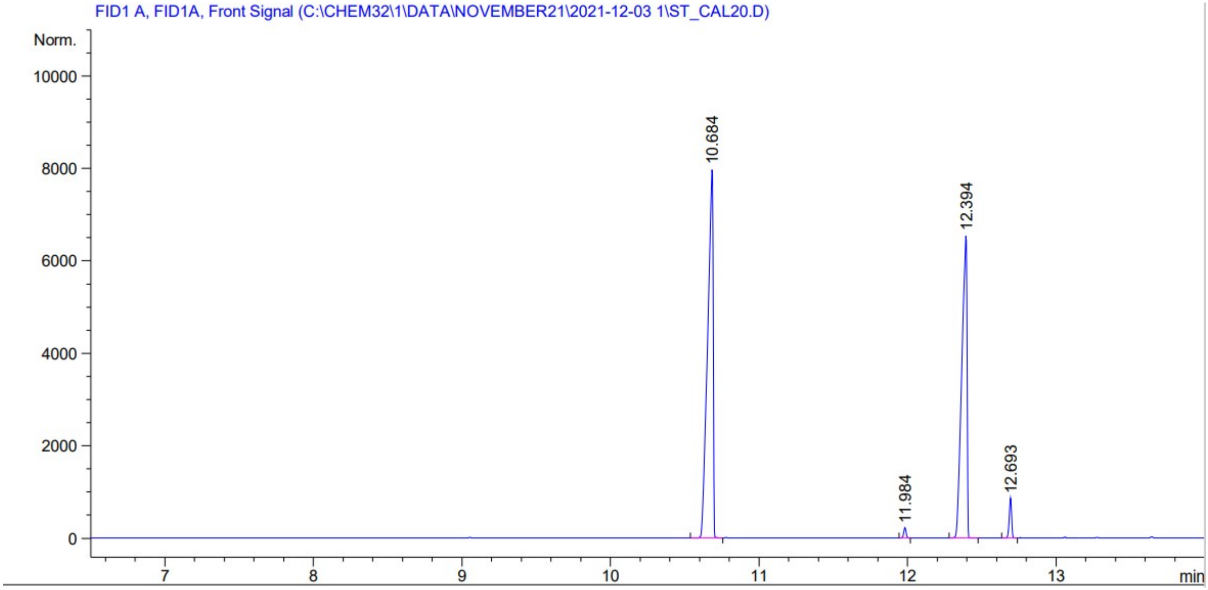

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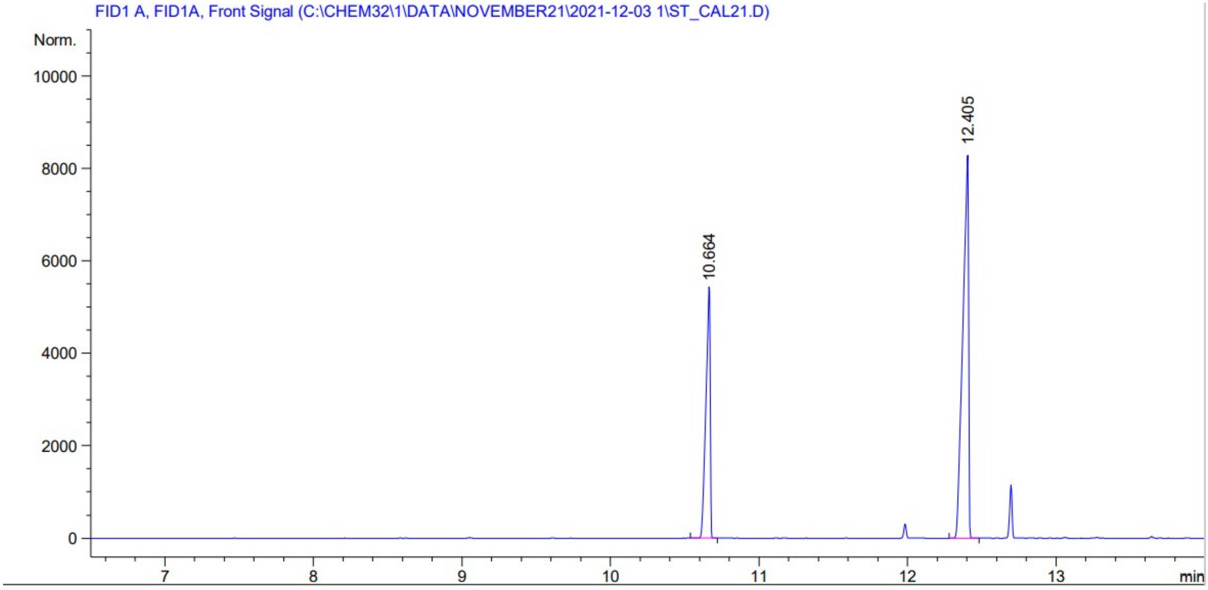
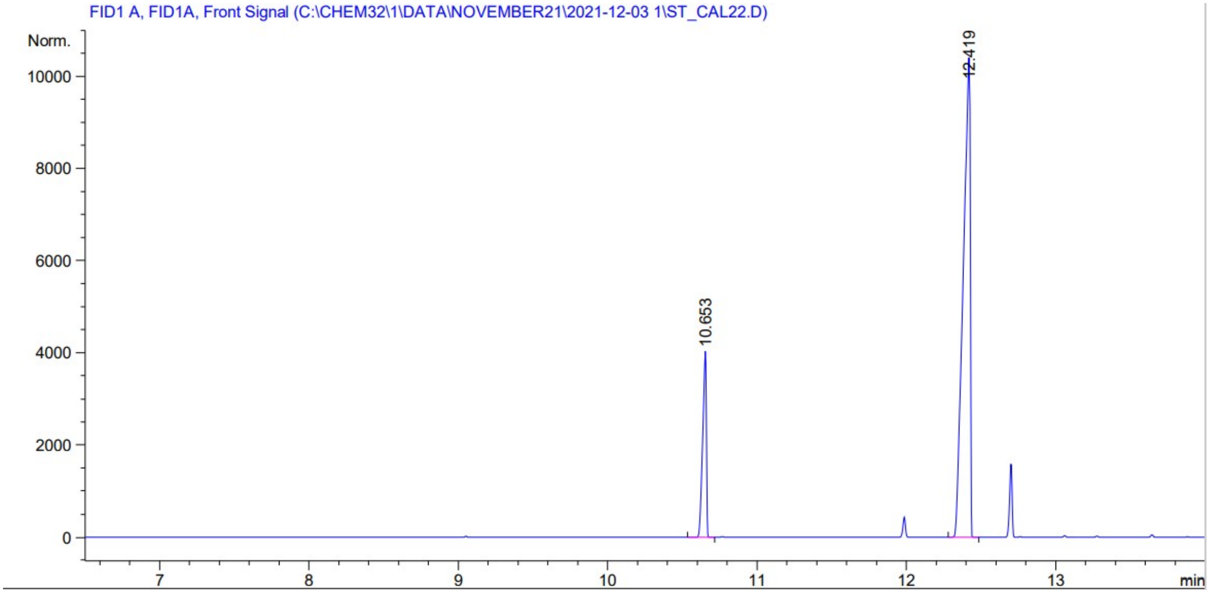


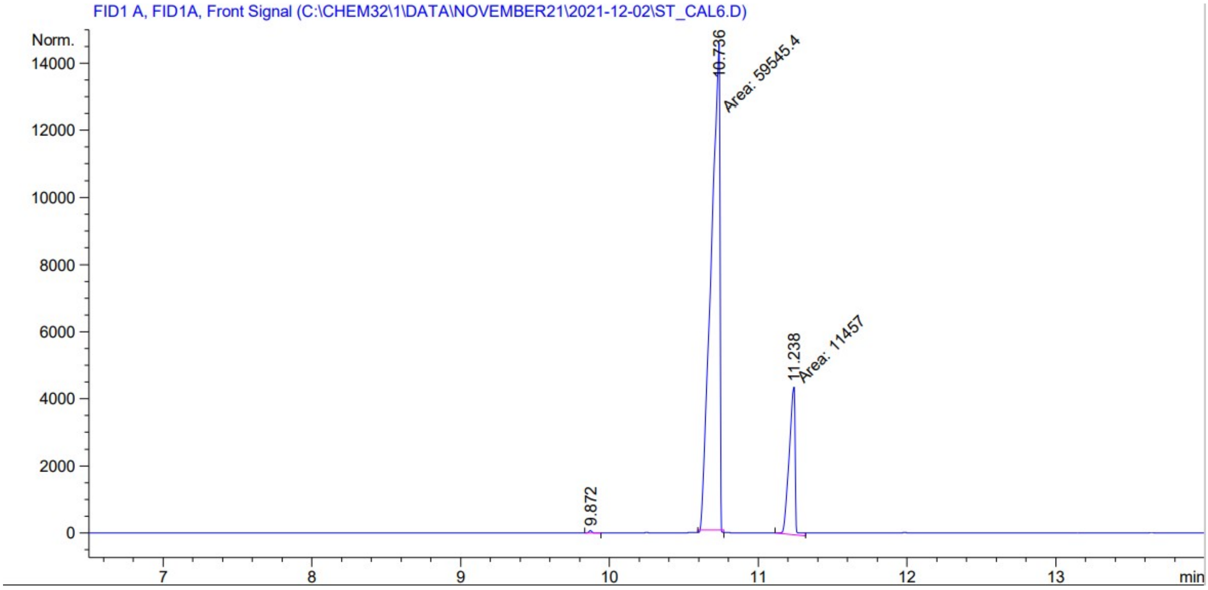
Entry 4



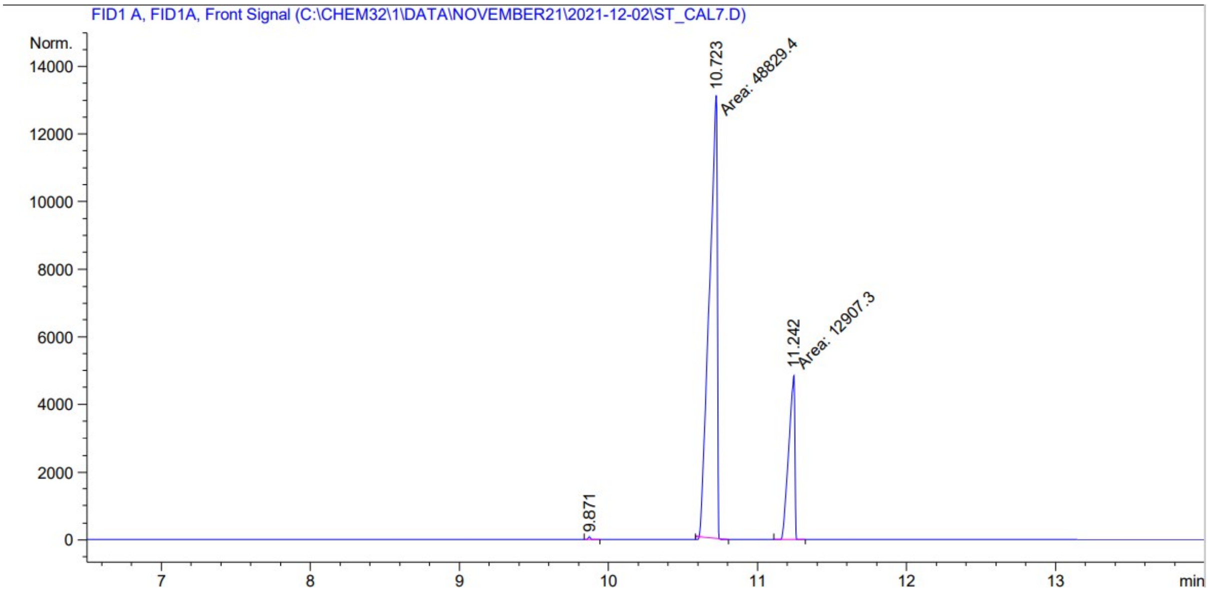
Entry 5

GC-FID traces for 2,6-dimethyliodobenzene calibration curve (Page S24, Table S8)

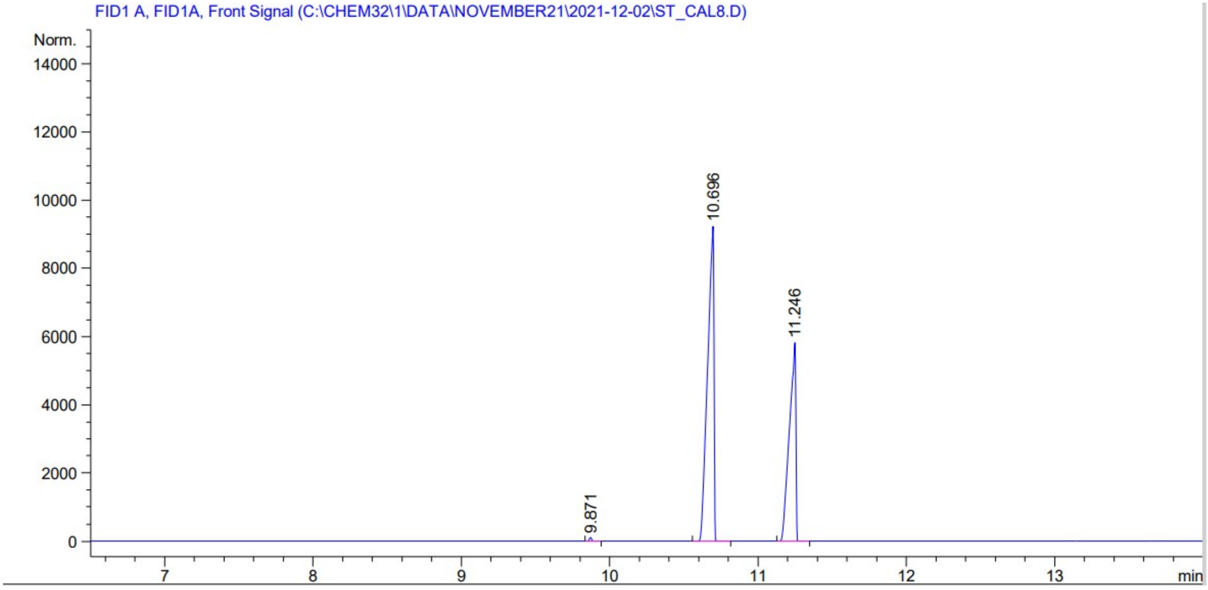
Samples of 0.02-0.6 mmol 2,6-dimethlyiodobenzene **6** (RT = 11.2 min) and 0.1 mmol dodecane (RT = 10.7 min).



Entry 1



Entry 2



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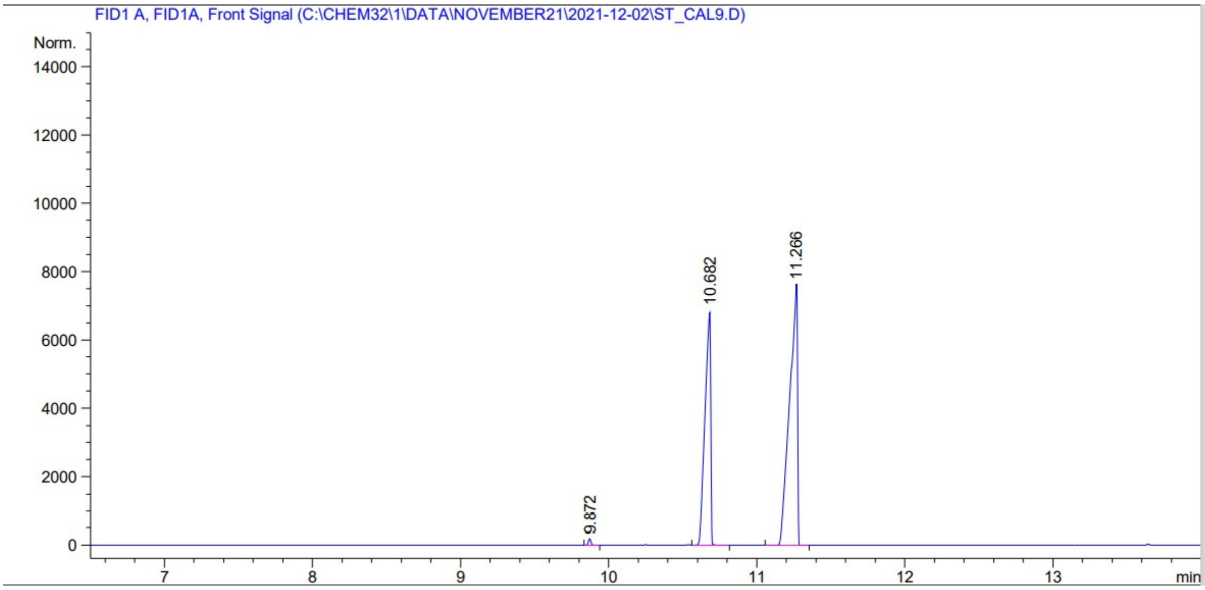

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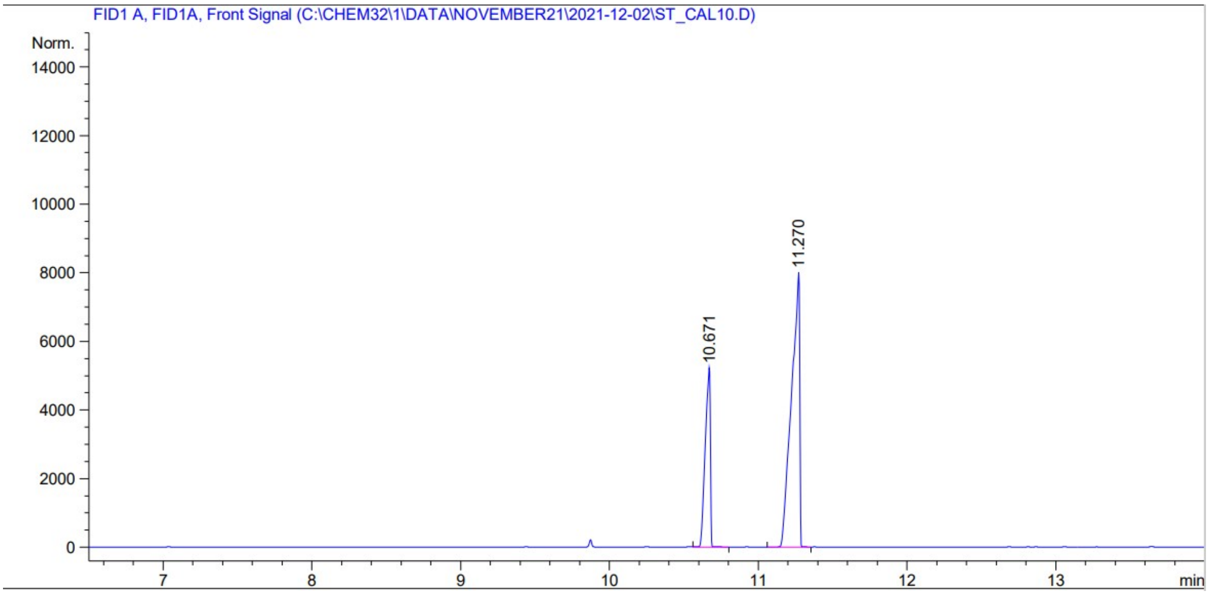
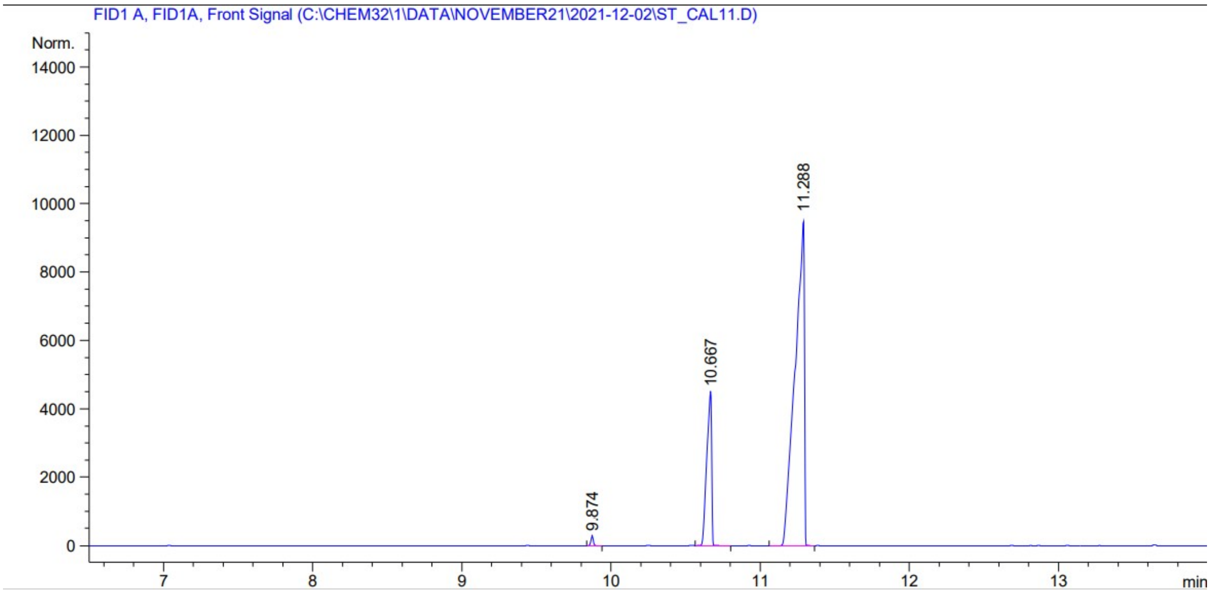


Entry 5



Entry 6

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(2) E. Shirakawa, K. I. Itoh, T. Higashino and T. Hayashi, *J. Am. Chem. Soc.* 2010, **132**, 15537–15539.

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