Electronic Supplementary Material (ESI) for ChemComm.

One-pot borylation/Suzuki-Miyaura sp^2–sp^3 cross coupling

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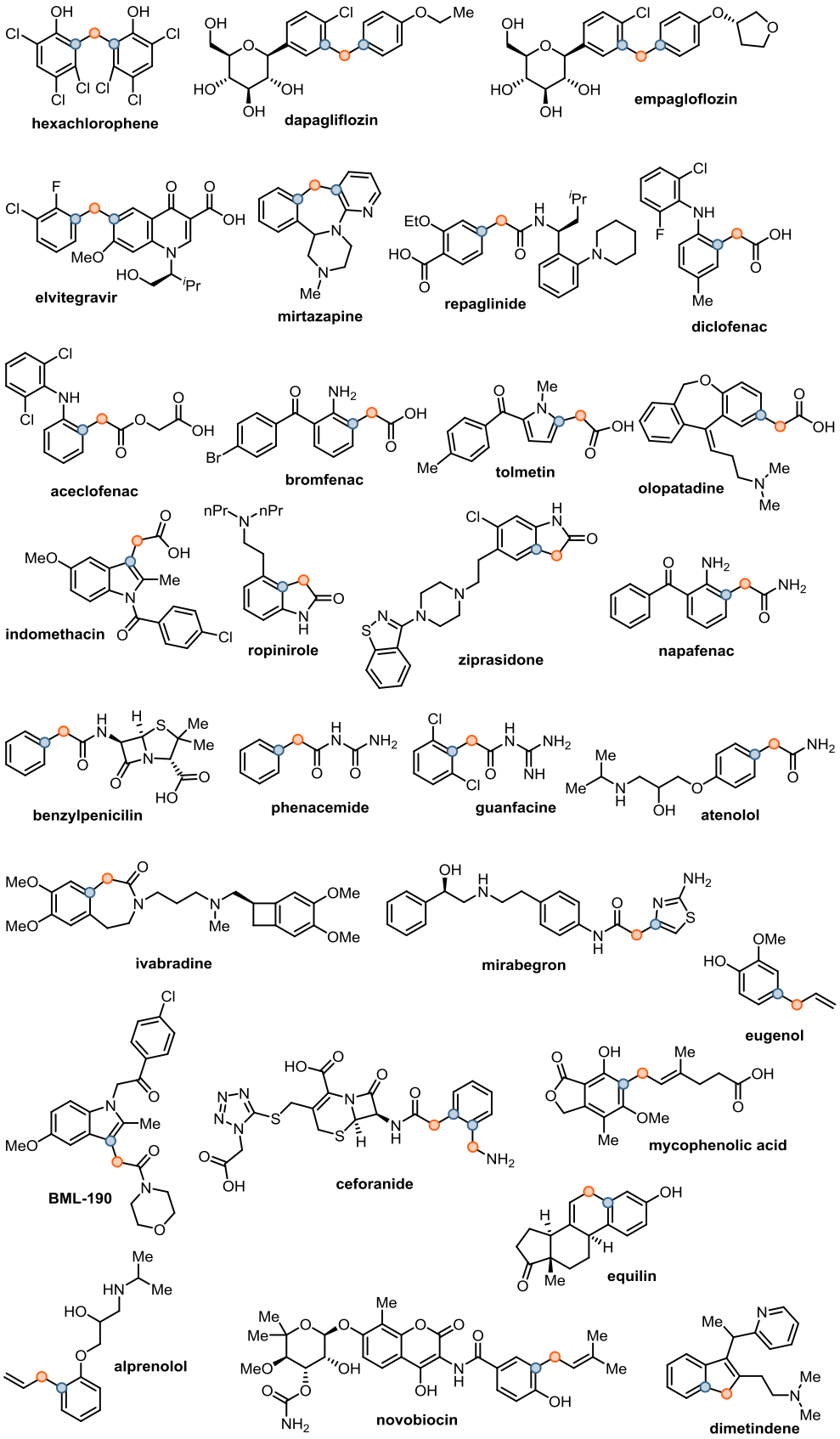
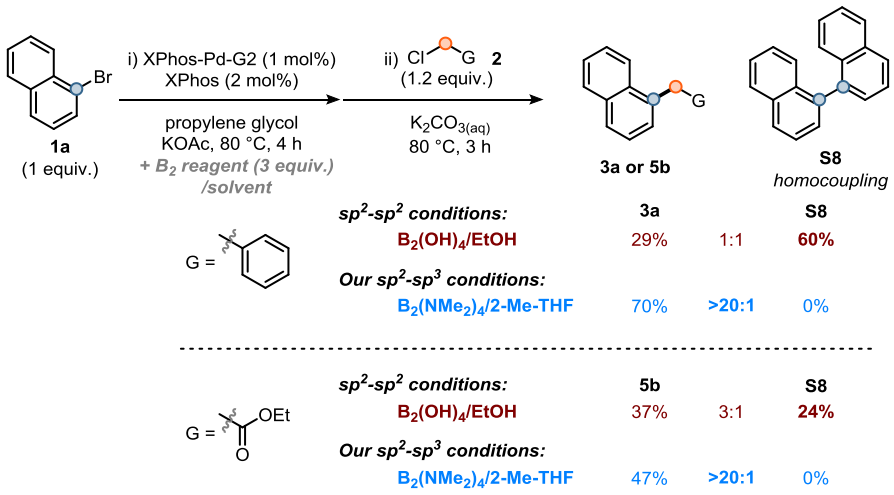
Electronic supplementary information

Contents

Supplement to Scheme 1A. Additional drug molecules containing α-arylated alkyl motifs





Scheme S1. Comparison of the previous one-pot borylation/SM sp^2-sp^2 cross coupling conditions[1] with our conditions for sp^2-sp^3 coupling.

[1] (a) G. A. Molander, S. L. J. Trice and S. D. Dreher, *J. Am. Chem. Soc.*, 2010, **132**, 17701; (b) G. A. Molander, S. L. J. Trice, S. M. Kennedy, S. D. Dreher, and M. T. Tudge, *J. Am. Chem. Soc*., 2012, **134**, 11667; (c) G. A. Molander, S. L. J. Trice and S. M. Kennedy, *J. Org. Chem*., 2012, **77**, 8678; (d) G. A. Molander, S. L. J. Trice and B. Tschaen, *Tetrahedron*, 2015, **71**, 5758.

General information

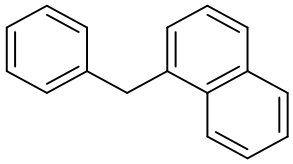
XPhos-Pd-G2 (Aldrich), XPhos (Aldrich), propylene glycol (Aldrich), tetrakis(dimethylamino)diborane (Fluorochem), inhibitor free anhydrous 2-methyl tetrahydrofuran (Aldrich) were used as received. All other solvents and reagents were purchased from commercial sources and used as supplied. ^{1}H NMR and ^{13}C NMR were recorded on 300, 400 and 500 MHz spectrometers with chemical shift values reported in parts per million (ppm) relative to the residual solvent signal, with coupling constant (*J*) values reported in Hz. All mass spectra were collected by the School of Chemistry Mass Spectrometry Service at The University of Manchester. EI (70 eV) was obtained via GCMS. Routine TLC analysis was carried out on aluminum sheets coated with silica gel 60 Å F254, 0.2 mm thickness. Plates were visualised using 254 nm ultraviolet light and/or dipped in aqueous potassium permanganate or *p*-anisaldehyde. Flash column chromatography was carried out on 40-63 μ, 60 Å silica gel. Automated reverse phase chromatography utilised Biotage Isolera (30 g SNAP C18 cartridges) with aqueous ammonium carbonate pH 10 buffer/acetonitrile as the eluent.

General procedure for one-pot borylation/Suzuki-Miyaura sp^2–sp^3 cross coupling (GP)

Potassium acetate (109 mg, 1.10 mmol), aryl halide **1** (0.37 mmol, if solid), XPhos-Pd-G2 (2.87 mg, 1.00 mol%) and XPhos (3.48 mg, 2.00 mol%) was added to an oven dried flask (cooled under a stream of nitrogen) containing a Teflon coated magnetic stirrer bar. The atmosphere was purged with nitrogen via three vacuum/nitrogen cycles. Aryl halide **1** (0.37 mmol, if liquid), propylene glycol (0.162 mL, 2.20 mmol), tetrakis(dimethylamino)diborane (0.226 mL, 1.10 mmol) and anhydrous 2-methyl tetrahydrofuran (3.00 mL) were added through a septum

and the reaction mixture was stirred and heated at 80 °C until the consumption of aryl halide **1** was observed (borylation time). Aqueous potassium carbonate (1.8 M, 1.10 mL, 1.98 mmol) was added, followed by alkyl chloride **2** (0.43 mmol), and heating continued at 80 °C until the consumption of the boronate intermediate was observed (Suzuki-Miyaura coupling time). The reaction mixture was cooled to room temperature and filtered through a pad of celite, washing the filter cake with ethyl acetate (25.0 mL). The solvent was evaporated under reduced pressure and the crude mixture purified by automated reverse phase chromatography or manual flash column chromatography to give the desired product.

Substrate scope



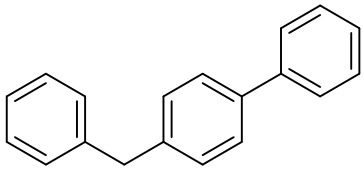
1-Benzylnaphthalene 3a[2]

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 4 h, SM time 3 h, purifying by Biotage Isolera gave **3a** (56 mg, 70 %) as a white solid.

δ_H (300 MHz, $CDCl_3$): 8.00 (d, *J* = 9.2, 1H, Ar*H*), 7.85 (m, 1H, Ar*H*), 7.75 (d, *J* = 8.2, 1H, Ar*H*), 7.49-7.41 (m, 3H, Ar*H*), 7.31-7.20 (m, 6H, Ar*H*), 4.45 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 140.60 (4°), 136.59 (4°), 133.89 (4°), 132.08 (4°), 128.73 (CH), 128.65 (CH), 128.44 (CH), 127.32 (CH), 127.14 (CH), 126.04 (CH), 125.96 (CH), 125.54 (CH), 124.27 (CH), 39.03 (CH_2).

[2] G. Tang, P. Zhang, J. Xu, Y. Gao, X. Li and Y. Zhao, *Synlett*, 2014, 25, 2928-2932.

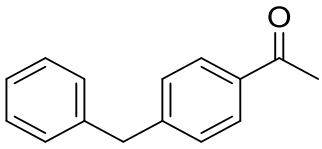


4-Benzyl-1,1'-biphenyl 3b[3]

Following GP, using 4-bromobiphenyl (0.37 mmol, 86 mg) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 1 h, SM time 3 h, purifying by Biotage Isolera gave **3b** (49 mg, 54%) as a white solid.

δ_H (300 MHz, $CDCl_3$): 7.60-7.25 (m, 14H, Ar*H*), 4.06 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 140.96 (4°), 140.22 (4°), 138.98 (4°), 129.29 (CH), 128.94 (CH), 128.69 (CH), 128.50 (CH), 127.18 (CH), 127.05 (CH), 126.98 (CH), 126.11 (CH), 41.55 (CH_2).



1-(4-Benzylphenyl)ethanone 3c[4]

Following GP, using 4-chloroacetaphenone (0.37 mmol, 48 μL) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 1 h, SM time 2 h, purifying by Biotage Isolera gave **3c** (52 mg, 67%) as a white solid.

Following GP, using 4-bromoacetaphenone (0.37 mmol, 74 mg) and benzyl chloride (0.41mmol, 47μL) with borylation time = 1 h, SM time 2 h, purifying by Biotage Isolera gave **3c** (44 mg, 56%) as a white solid.

Following GP, using 4-acetylphenyl trifluoromethanesulfonate (0.37 mmol, 99 mg) and benzyl chloride (0.41mmol, 47μL) with borylation time = 2 h, SM time 16 h, gave **3c** (58 mg, 75%) by internal standard NMR (1,5-cyclooctadiene as internal standard).

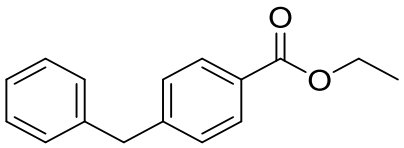
[3] G. Tang, P. Zhang, J. Xu, Y. Gao, X. Li and Y. Zhao, *Synlett*, 2014, 25, 2928-2932.

[4] S. Pal, S. Chowdhury, E. Rozwadowski, A. Auffrant and C. Gosmini, *Advanced Synthesis & Catalysis*, 2016, 358, 2431-2435.

δ_H (300 MHz, $CDCl_3$): 7.88 (d, *J* = 8.3, 2H, ArH), 7.34-7.17 (m, 7H, ArH), 4.04 (s, 2H, CH_2), 2.57 (s, 3H, $COCH_3$).

δ_C (101 MHz, $CDCl_3$): 197.76 (4°), 146.76 (4°), 139.99 (4°), 135.17 (4°), 129.06 (CH), 128.88 (CH), 128.59 (CH), 126.37 (CH), 41.85 (CH_2), 26.53 (CH_3).

LRMS (EI): [210.28], 210.1, 195.1 (100%), 165.0, 152.0



Ethyl 4-benzylbenzoate 3d[5]

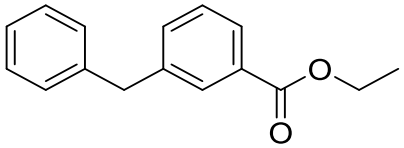
Following GP, using ethyl 4-chlorobenzoate (0.37 mmol, 68 mg) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 1 h, SM time 2 h, purifying by Biotage Isolera gave **3d** (58 mg, 65%) as a colourless oil.

δ_H (300 MHz, $CDCl_3$): 7.97 (d, J = 8.3, 2H, Ar*H*), 7.31-7.17 (m, 7H, Ar*H*), 4.37 (q, *J* = 7, 2H, OCH_2), 4.00 (s, 2H, CH_2), 1.39 (t, *J* = 7.1, 3H, CH_3).

δ_C (101 MHz, $CDCl_3$): 166.53 (4°), 146.34 (4°), 140.13 (4°), 129.73 (CH), 128.86 (CH), 128.54 (CH), 128.39 (CH), 126.31 (CH), 60.78 (CH_2), 41.85 (CH_2), 14.30 (CH_3).

LRMS (ESI+): [240.12], 241.09

[5]S. Pal, S. Chowdhury, E. Rozwadowski, A. Auffrant and C. Gosmini, *Advanced Synthesis & Catalysis*, 2016, 358, 2431-2435.



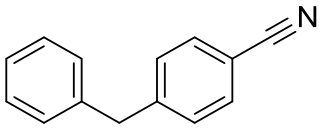
Ethyl 3-benzylbenzoate 3e[6]

Following GP, using ethyl 4-bromobenzoate (0.37 mmol, 59 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 1 h, SM time 2 h, purifying by Biotage Isolera gave **3e** (55 mg, 65%) as a colourless oil.

δ_H (300 MHz, $CDCl_3$): 7.93-7.88 (m, 2H, Ar*H*), 7.36-7.17 (m, 7H, Ar*H*), 4.37 (q, *J* = 7.1, 2H, OCH_2), 4.04 (s, 2H, CH_2), 1.39 (t, *J* = 7.2, 3H, CH_3).

δ_C (101 MHz, $CDCl_3$): 166.65 (4°), 141.35 (4°), 140.49 (4°), 133.41 (CH), 130.63 (4°), 129.98 (CH), 128.83 (CH), 128.53 (CH), 128.46 (CH), 127.37 (CH), 126.24 (CH), 60.97 (CH_2), 41.67 (CH_2), 14.30 (CH_3).

LRMS (ESI+): [240.12], 241.09



4-Benzylbenzonitrile 3f[7]

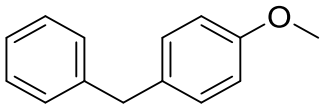
Following GP, using 4-chlorobenzonitrile (0.37 mmol, 51 mg) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 1 h, SM time 2 h, purifying by Biotage Isolera gave **3f** (48 mg, 68%) as a white solid.

δ_H (300 MHz, $CDCl_3$): 7.56 (d, *J* = 8.3, 2H, Ar*H*), 7.29-7.16 (m, 7H, Ar*H*), 4.03 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 146.72 (4°), 139.32 (4°), 132.30 (CH), 129.63 (CH), 128.96 (CH), 128.76 (CH), 126.67 (CH), 118.99 (4°), 110.04 (4°), 41.97 (CH_2).

[6] S. Pal, S. Chowdhury, E. Rozwadowski, A. Auffrant and C. Gosmini, *Advanced Synthesis & Catalysis*, 2016, 358, 2431-2435.

[7] S. Pal, S. Chowdhury, E. Rozwadowski, A. Auffrant and C. Gosmini, *Advanced Synthesis & Catalysis*, 2016, 358, 2431-2435.



1-Benzyl-4-methoxybenzene 3g[8]

Following GP, using 4-chloroanisole (0.37 mmol, 45 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 1 h, SM time 2 h, purifying by Biotage Isolera gave **3g** (40 mg, 55%) as a white solid.

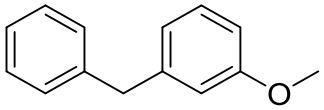
Following GP, using 4-bromoanisole (0.37 mmol, 46 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 3 h, SM time 16 h, purifying by Biotage Isolera gave **3g** (42 mg, 58%) as a white solid.

Following GP, using 4-methoxyphenyl trifluoromethanesulfonate (0.37 mmol, 95 mg) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 2 h, SM time 16 h, gave **3g** (51 mg, 70%) by internal standard NMR (1,5-cyclooctadiene as internal standard).

δ_H (300 MHz, $CDCl_3$): 7.30-7.07 (m, 7H, Ar*H*), 6.82 (d, *J* = 8.6, 2H, Ar*H*), 3.92 (s, 2H, CH_2), 3.76 (s, 3H, OCH_3).

δ_C (101 MHz, $CDCl_3$): 157.89 (4°), 141.54 (4°), 133.21 (4°), 129.84 (CH), 128.79 (CH), 128.40 (CH), 125.95 (CH), 113.81 (CH), 55.22 (CH_2), 41.00 (CH_3).

LRMS (EI): [198.27], 198.1 (100%), 183.1, 167.1, 153.1, 121.1



1-Benzyl-3-methoxybenzene 3h[9]

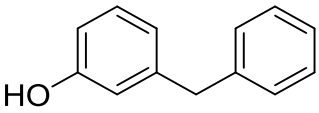
Following GP, using 3-bromoanisole (0.37 mmol, 47 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 1 h, SM time 3 h, purifying by Biotage Isolera gave **3h** (40 mg, 56%) as a colourless oil.

[8] S. Pal, S. Chowdhury, E. Rozwadowski, A. Auffrant and C. Gosmini, *Advanced Synthesis & Catalysis*, 2016, 358, 2431-2435.
[9] E. Alacid and C. Nájera, *Organic Letters*, 2008, 10, 5011-5014.

δ_H (300 MHz, $CDCl_3$): 7.31-7.19 (m, 6H, Ar*H*), 6.82-6.75 (m, 3H, Ar*H*), 3.98 (s, 2H, CH_2), 3.79 (s, 3H, OCH_3).

δ_C (101 MHz, $CDCl_3$): 159.65 (4°), 142.67 (4°), 140.87 (4°), 129.38 (CH), 128.88 (CH), 128.43 (CH), 126.07 (CH), 121.34 (CH), 114.73 (CH), 111.23 (CH), 55.10 (CH_3), 42.91 (CH_2).

LRMS (ESI+): [198.26], 199.07



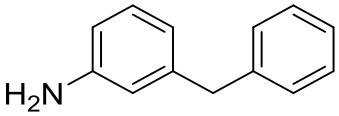
3-Benzylphenol 3i[10]

Following GP, using 3-chlorophenol (0.37 mmol, 39 µL) and benzyl chloride (0.41mmol, 47 µL) with borylation time = 1 h, SM time 3 h, purifying by Biotage Isolera gave **3i** (52 mg, 76%) as a colourless oil.

δ_H (300 MHz, $CDCl_3$): 7.31-7.15 (m, 6H, Ar*H*), 6.80 (d, *J* = 7.6, 1H, Ar*H*), 6.71-6.67 (m, 2H, Ar*H*), 4.55 (brs, 1H, O*H*), 3.94 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 155.66 (4°), 142.93 (4°), 140.78 (4°), 129.56 (CH), 128.91 (CH), 128.42 (CH), 126.07 (CH), 121.25 (CH), 115.84 (CH), 113.03 (CH), 41.68 (CH_2).

LRMS (ESI-): [184.24], 183.14



3-Benzylanaline 3j

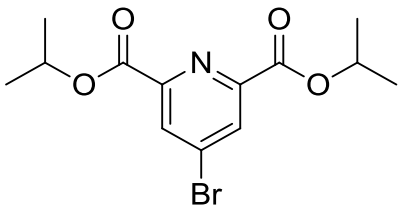
Following GP, using 3-chloroaniline (0.37 mmol, 39 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 1 h, SM time 3 h, purifying by Biotage Isolera gave **3j** (21 mg, 31%) as a colourless oil.

[10] S. Bernhardt, Z. Shen and P. Knochel, *Chemistry - A European Journal*, 2012, 19, 828-833.

δ_H (300 MHz, $CDCl_3$): 7.31-7.27 (m, 2H, Ar*H*), 7.20 (m, 3H, Ar*H*), 7.09 (app. t, *J* = 7.7, 1H, Ar*H*), 6.62 (d, *J* = 7.6, 1H, Ar*H*), 6.55 (d, *J* = 8, 1H, Ar*H*), 6.52 (s, 1H, Ar*H*), 3.90 (s, 2H, CH_2), 3.49 (br. s, 2H, NH_2).

δ_C (101 MHz, $CDCl_3$): 146.09 (4°), 142.33 (4°), 141.07 (4°), 129.32 (CH), 128.93 (CH), 128.37 (CH), 125.98 (CH), 119.55 (CH), 115.85 (CH), 113.10 (CH), 41.85 (CH_2).

HRMS (APCI): calc. for $C_{13}H_{13}N$+H; 184.1121. Found; 184.1116



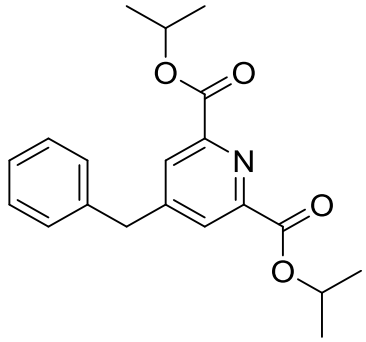
Diisopropyl 4-bromopyridine-2,6-dicarboxylate

To a stirring solution of chelidamic acid (2.73 mmol, 500 mg) in chloroform (3 mL) was added phosphorus pentabromide (13.7 mmol, 5.88 g). The mixture was heated to 90 °C for 18 h. The reaction mixture was cooled to 0 °C and anhydrous 2-propanol (4.00 mL) was added drop-wise with stirring. The mixture was stirred for a further 2 h at room temperature. The reaction mixture was diluted with dichloromethane (10 mL) and added drop-wise to a stirred solution of saturated aqueous sodium hydrogen carbonate (25 mL). The phases were separated and the aqueous phase extracted with dichloromethane (2 × 10 mL) and the combined organics were dried over magnesium sulphate. The solvent was evaporated under reduced pressure and the crude mixture was purified by column chromatography to give the desired product as a white solid (715 mg, 79%).

δ_H (500 MHz, $CDCl_3$): 8.37 (s, 2H, ArH), 5.32 (sept., *J* = 6.3, 2H, C*H*(CH_3)$_2$), 1.43 (d, *J* = 6.3, 12H, CH(C*H*$_3$)$_2$).

δ_C (126 MHz, $CDCl_3$): 162.91 (4°), 149.87 (4°), 134.67 (4°), 130.75 (CH), 70.60 (CH), 21.76 (CH_3).

HRMS (ESI+): calc. for $C_{13}H_{16}NBrO_4$+H; 330.0335. Found; 330.0330



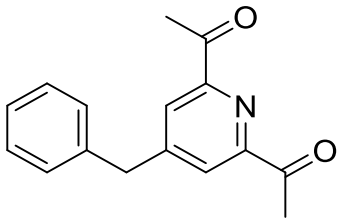
Diisopropyl 4-benzylpyridine-2,6-dicarboxylate 3k

Following GP, using diisopropyl 4-bromopyridine-2,6-dicarboxylate (0.37 mmol, 122 mg) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 2 h, SM time 2 h, purifying by Biotage Isolera gave **3k** (48 mg, 38%) as an orange solid.

δ_H (300 MHz, $CDCl_3$): 8.04 (s, 2H, Ar*H* Pyr), 7.45-7.10 (m, 5H, Ar*H* Bn), 5.28 (sept, *J* = 6.0, 2H, C*H*(CH_3)$_2$), 4.10 (s, 2H, C*H*$_2$), 1.41 (d, *J* = 6.0, 12H, CH(C*H*$_3$)$_2$)

δ_C (101 MHz, $CDCl_3$): 164.30 (4°), 152.67 (4°), 149.21 (4°), 137.84 (4°), 128.97 (CH), 127.95 (CH), 127.05 (CH), 127.2 (CH), 70.07 (CH ^{i}Pr), 41.18 (CH_2), 21.80 (CH_3).

HRMS (APCI): calc. for $C_{20}H_{24}O_4N$; 342.1700. Found; 342.1693



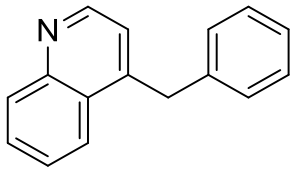
1,1'-(4-benzylpyridine-2,6-diyl)bis(ethan-1-one) 3l

Following GP, using 1,1'-(4-bromopyridine-2,6-diyl)bis(ethan-1-one) (0.37 mmol, 90 mg) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 3 h, SM time 3 h, purifying by Biotage Isolera gave **3l** (32 mg, 34%) as a white solid.

δ_H (300 MHz, $CDCl_3$): 8.05 (s, 2H, Ar*H* Pry), 7.35-7.17 (m, 5H, Ar*H* Bn), 4.08 (s, 2H, CH_2), 2.76 (s, 6H, CH_3).

δ_C (101 MHz, $CDCl_3$): 199.68 (4°), 152.88 (4°), 152.72 (4°), 138.03 (4°), 128.94 (CH), 126.98 (CH), 124.98 (CH), 41.45 (CH_2), 25.69 (CH_3).

HRMS (APCI): calc. for $C_{16}H_{16}NO_2$; 254.1176. Found; 254.1170



4-Benzylquinoline 3m[11]

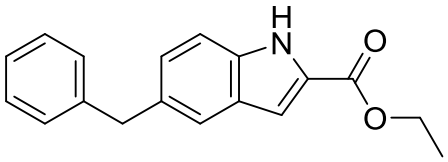
Following GP, using 4-chloroquinoline (0.37 mmol, 48 µL) and benzyl chloride (0.41 mmol, 47 µL) with borylation time = 2 h, SM time 2 h, purifying by Biotage Isolera gave **3m** (60 mg, 73%) as a white solid.

δ_H (300 MHz, $CDCl_3$): 8.79 (d, *J* = 4.5, 1H, Ar*H*), 8.10 (d, *J* = 8.3, 1H, Ar*H*), 7.99 (d, *J* = 8.6, 1H, Ar*H*), 7.65 (m, 1H, Ar*H*), 7.49 (m, 1H, Ar*H*), 7.29-7.08 (m, 6H, Ar*H*), 4.40 (s, 2H CH_2).

δ_C (101 MHz, $CDCl_3$): 150.27 (CH), 148.31 (4°), 146.50 (4°), 138.54 (4°), 130.14 (CH), 129.11 (CH), 128.88 (CH), 128.68 (CH), 127.55 (4°), 126.59 (CH), 126.53 (CH), 123.81 (CH), 121.81 (CH), 38.10 (CH_2).

LRMS (ESI+): [219.29], 220.15

[11] H. Sterckx, J. De Houwer, C. Mensch, W. Herrebout, K. Tehrani and B. Maes, *ChemInform*, 2016, 47.



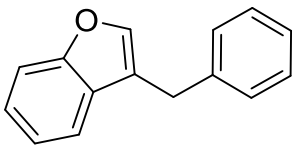
Ethyl 5-benzyl-1*H*-indole-2-carboxylate 3n

Following GP, using ethyl 5-chloro-1*H*-indole-2-carboxylate (0.37 mmol, 83 mg) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 1.5 h, SM time 2.5 h, purifying by Biotage Isolera gave **3n** (73 mg, 71%) as a white solid.

δ_H (300 MHz, $CDCl_3$): 9.14 (brs, 1H, N*H*), 7.49 (s, 1H, Ar*H* indole), 7.36-7.14 (m, 8H, Ar*H*), 4.41 (q, *J* = 7.2, 2H, OCH_2), 4.07 (s, 2H, CH_2), 1.41 (t, *J* = 7.1, 3H, CH_3).

δ_C (101 MHz, $CDCl_3$): 162.13 (4°), 141.72 (4°), 135.60 (4°), 133.51 (4°), 128.87 (CH), 128.39 (CH), 127.66 (4°), 127.59 (4°), 127.02 (CH), 125.94 (CH), 122.07 (CH), 111.90 (CH), 108.37 (CH), 60.98 (CH_2), 41.89 (CH_2), 14.36 (CH_3).

HRMS (APCI): calc. for $C_{18}H_{17}NO_2$+H; 280.1332. Found; 280.1323



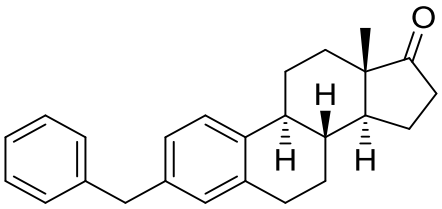
3-Benzylbenzofuran 3o

Following GP, using 3-bromo-1-benzofuran (0.37 mmol, 73 mg) and benzyl chloride (0.41 mmol, 47 μL) with borylation time = 1.5 h, SM time 2.5 h, purifying by Biotage Isolera gave **3o** (49 mg, 64%) as a white solid.

δ_H (300 MHz, $CDCl_3$): 7.50-7.37 (m, 3H, Ar*H*), 7.29-7.15 (m, 7H, Ar*H*), 4.02 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 155.51 (4°), 142.11 (CH), 139.17 (4°), 128.62 (CH), 128.50 (CH), 127.98 (4°), 126.35 (CH), 124.19 (CH), 122.33 (CH), 119.87 (CH), 119.68 (4°), 111.42 (CH), 29.97 (CH_2).

HRMS (APCI+): Found 209.0961, $C_{15}H_{13}O$ requires 209.0961.



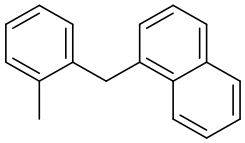
(8R,9S,13S,14S)-3-Benzyl-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one 3p

Following GP, using (8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (0.37 mmol, 149 mg) and benzyl chloride (0.41mmol, 47 μL) with borylation time = 2 h, SM time 16 h. Product **3p** was isolated by column chromatography (ethyl acetate 5:95 hexane) as a white solid (41 mg, 32%).

δ_H (300 MHz, $CDCl_3$): 7.27 (m, 6H, Ar*H*), 6.99 (m, 2H, Ar*H*), 3.94 (s, 2H Ar-CH_2-Ar), 2.89 (m, 2H, CH_2-C=O), 2.53 (dd, *J* = 18.8, 8.5, 1H, C*H*-Ar), 2.43 (m, 1H, C*H*), 2.29 (m, 1H, C*H*), 2.06 (m, 4H, 2xCH_2), 1.56 (m, 6H, 3xCH_2), 0.93 (s, 3H, CH_3).

δ_C (101 MHz, $CDCl_3$): 220.95 (4°), 141.17 (4°), 138.57 (4°), 137.42 (4°), 136.48 (4°), 129.40 (CH), 128.88 (CH), 128.41 (CH), 126.29 (CH), 125.97 (CH), 125.41 (CH), 50.44 (CH), 47.96 (4°), 44.24 (CH), 41.43 (CH_2), 38.14 (CH), 35.83 (CH_2), 31.55 (CH_2), 29.34 (CH_2), 26.50 (CH_2), 25.68 (CH_2), 21.55 (CH_2), 13.81 (CH_3).

HRMS (ESI+): Found 367.2031, $C_{25}H_{28}ONa$ requires 367.2032.

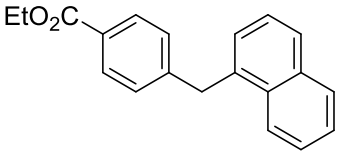


1-(2-Methylbenzyl)naphthalene 3q[12]

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 2-methylbenzyl chloride (0.43 mmol, 57 μL) with borylation time = 4 h, SM time 16 h. Yield of product **3q** was determined by internal standard NMR (1,5-cyclooctadiene) (60%).

δ_H (300 MHz, $CDCl_3$): 8.10 (m, 1H, Ar*H*), 8.00 (dd, *J* = 6.1, 3.4, 1H, Ar*H*), 7.87 (d, *J* = 8.3, 1H, Ar*H*), 7.48 (t, *J* = 7.6, 1H, Ar*H*), 7.38-7.35 (m, 3H, Ar*H*), 7.29 (t, *J* = 7.2, 1H, Ar*H*), 7.22-7.15 (m, 2H, Ar*H*), 7.03 (d, *J* = 7.3, 1H, Ar*H*), 4.52 (s, 2H, CH_2), 2.45 (s, 3H, CH_3).

LRMS (EI): [232.33], 232.2 (100%), 217.1, 202.1, 141.1, 104.1



Ethyl 4-(naphthalen-1-ylmethyl)benzoate 3r[13]

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and ethyl 4-(chloromethyl)benzoate (0.43 mmol, 47 μL) with borylation time = 4 h, SM time 16 h. Product **3r** was isolated by column chromatography (ethyl acetate 1:19 hexane) as a colourless oil (74 mg, 70%).

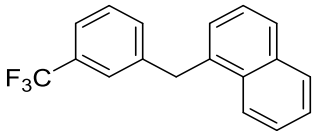
δ_H (300 MHz, $CDCl_3$): 7.96-7.87 (m, 4H, Ar*H*), 7.80 (d, *J* = 8.3, 1H, Ar*H*), 7.49-7.42 (m, 3H, Ar*H*), 7.32-7.26 (m, 3H, Ar*H*), 4.51 (s, 2H, CH_2), 4.36 (q, *J* = 7.1, 2H, OCH_2), 1.37 (t, *J* = 7.1, 3H, CH_3).

[12] X. Liu, H. Zhu, Y. Shen, J. Jiang and T. Tu, *Chinese Chemical Letters*, 2017, 28, 350-353.

[13] M. Dinesh, S. Archana, R. Ranganathan, M. Sathishkumar and A. Ponnuswamy, *Tetrahedron Letters*, 2015, 56, 6975-6979.

δ_C (101 MHz, $CDCl_3$): 166.56 (4°), 146.01 (4°), 135.67 (4°), 133.94 (4°), 131.95 (4°), 129.74 (CH), 128.73 (CH), 128.64 (CH), 128.42 (4°), 127.47 (CH), 126.09 (CH), 125.67 (CH), 125.52 (CH), 124.07 (CH), 60.79 (CH_2), 39.14 (CH_2), 14.31 (CH_3).

HRMS (APCI): calc. for $C_{20}H_{19}O_2$; 291.1380. Found; 291.1374



1-(3-(Trifluoromethyl)benzyl)naphthalene 3s

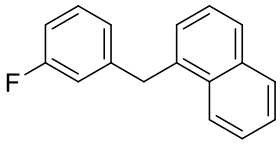
Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 3-(trifluoromethyl)benzyl chloride (0.43 mmol, 47 μL) with borylation time = 2 h, SM time 16 h. Product **3s** was isolated by column chromatography (IPA 2:98 hexane) as a colourless oil (48 mg, 45 %).

δ_H (300 MHz, $CDCl_3$): 7.96-7.89 (m, 2H, Ar*H*), 7.82 (d, *J* = 8.3, 1H, Ar*H*), 7.54-7.44 (m, 5H, Ar*H*), 7.40-7.30 (m, 3H, Ar*H*), 4.51 (s, 2H, CH_2)

δ_C (101 MHz, $CDCl_3$): 141.54 (4°), 135.48 (4°), 133.96 (4°), 132.02 (CH), 131.89 (4°), 130.73 (q, *J* = 32.3, 4°), 128.88 (CH), 128.79 (CH), 127.56 (CH), 127.45 (CH), 126.18 (CH), 125.72 (CH), 125.55 (CH), 125.38 (q, *J* = 3.91, CH), 124.18 (q, *J* = 272.9, 4°), 123.93 (CH), 123.03 (q, *J* = 3.91, CH), 38.78 (CH_2).

δ_F (376 MHz, $CDCl_3$): -62.47 (CF_3)

HRMS (APCI): calc. for $C_{18}H_{13}F_3$; 286.0964. Found; 286.0962



1-(3-Fluorobenzyl)naphthalene 3t

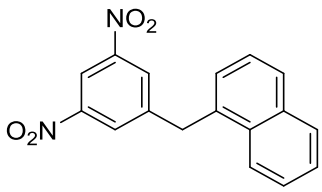
Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 3-fluorobenzyl chloride (0.43 mmol, 52 μL) with borylation time = 4 h, SM time 16 h. Product **3t** was isolated by column chromatography (ethyl acetate 1:99 hexane) as a colourless oil (61 mg, 70%).

δ_H (300 MHz, $CDCl_3$): 7.98 (d, *J* = 8.3, 1H, Ar*H*), 7.91 (d, *J* = 7.3, 1H, Ar*H*), 7.83 (d, *J* = 8.1, 1H, Ar*H*), 7.55-7.47 (m, 3H, Ar*H*), 7.34 (d, *J* = 7.1, 1H, Ar*H*), 7.26 (m, 1H, Ar*H*), 7.03 (d, *J* = 7.6, 1H, Ar*H*), 6.95-6.92 (m, 2H, Ar*H*), 4.47 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 162.98 (d, *J* = 245.51, 4°), 143.28 (d, *J* = 6.85, 4°), 135.74 (4°), 133.94 (4°), 131.96 (4°), 129.78 (d, *J* = 8.80, CH), 128.72 (CH), 127.44 (CH), 126.08 (CH), 125.58 (d, *J* = 11.74, CH), 124.28 (d, *J* = 1.96, CH), 124.08 (CH), 115.63 (CH), 115.43 (CH), 113.07 (CH), 112.85 (CH), 38.77 (CH_2)

δ_F (376 MHz, $CDCl_3$): -113.41 (Ar*F*)

HRMS (APCI): calc. for $C_{17}H_{13}F$; 236.0996. Found; 236.0993



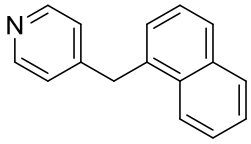
1-(3,5-Dinitrobenzyl)naphthalene 3u

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 3,5-dinitrobenzyl chloride (0.43 mmol, 93 mg) with borylation time = 2 h, SM time 16 h. Product **3u** was isolated by column chromatography (DCM 1:1 pentane) as a yellow solid (66 mg, 58%).

δ_H (300 MHz, $CDCl_3$): 8.77 (s, 1H, Ar*H*), 8.28 (s, 2H, Ar*H*), 7.81 (d, *J* = 7.6, 1H, Ar*H*), 7.77 (d, *J* = 8.3, 1H, Ar*H*), 7.70 (d, *J* = 8.1, 1H, Ar*H*), 7.42-7.37 (m, 3H, Ar*H*), 7.29 (d, *J* = 6.8, 1H, Ar*H*), 4.54 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 148.52 (4°), 145.42 (4°), 134.14 (4°), 133.08 (4°), 131.32 (4°), 129.16 (CH), 128.64 (CH), 128.57 (CH), 127.98 (CH), 126.77 (CH), 126.10 (CH), 125.65 (CH), 123.24 (CH), 116.90 (CH), 38.67(CH_2)

HRMS (APCI): calc. for $C_{17}H_{12}N_2O_4$; 308.0792. Found; 308.0787

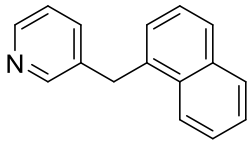


4-(Naphthalen-1-ylmethyl)pyridine 3v[14]

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 4-(chloromethyl)pyridine hydrochloride (0.43 mmol, 71 mg) with borylation time = 4 h, SM time 16 h. Yield of product **3v** was determined by internal standard NMR (1,5-cyclooctadiene) (56%).

δ_H (300 MHz, $CDCl_3$): 8.51 (d, *J* = 5.9, 2H, Ar*H*), 7.87-7.79 (m, 3H, Ar*H*), 7.48-7.41 (m, 3H, Ar*H*), 7.31 (d, *J* = 7.1, 1H, Ar*H*), 7.09 (d, *J* = 5.6, 2H, Ar*H*), 4.41 (s, 2H, CH_2).

LRMS (EI): [219.29], 219.1 (100%), 204.1, 189.1, 165.1, 141.1, 115.1



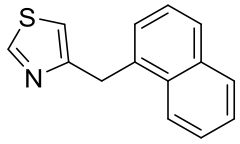
3-(Naphthalen-1-ylmethyl)pyridine 3x[15]

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 3-(chloromethyl)pyridine hydrochloride (0.43 mmol, 71 mg) with borylation time = 5 h, SM time 16 h. Product **3x** was isolated by column chromatography (diethyl ether 1:9 DCM) as a pale yellow oil (64 mg, 79%).

δ_H (300 MHz, $CDCl_3$): 8.59 (s, 1H, Ar*H*), 8.46 (d, *J* = 4.6, 1H, Ar*H*), 7.95-7.88 (m, 2H, Ar*H*), 7.80 (d, *J* = 8.3, 1H, Ar*H*), 7.51-7.41 (m, 4H, Ar*H*), 7.31 (d, *J* = 6.8, 1H, Ar*H*), 7.18-7.15 (m, 1H, Ar*H*), 4.46 (s, 2H, CH_2).

δ_C (101 MHz, $CDCl_3$): 150.08 (CH), 147.61 (CH), 136.01 (CH), 136.00 (4°), 135.21 (4°), 133.95 (4°), 131.76 (4°), 128.79 (CH), 127.59 (CH), 127.39 (CH), 126.22 (CH), 125.73 (CH), 125.50 (CH), 123.88 (CH), 123.38 (CH), 36.21 (CH_3).

[14] F. Dai, Q. Gui, J. Liu, Z. Yang, X. Chen, R. Guo and Z. Tan, *Chemical Communications*, 2013, 49, 4634.
[15] G. Stewart, P. Maligres, C. Baxter, E. Junker, S. Krska and J. Scott, *Tetrahedron*, 2016, 72, 3701-3706.



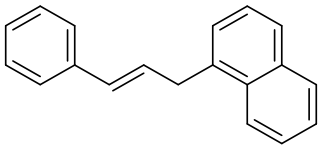
4-(Naphthalen-1-ylmethyl)thiazole 3y

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 4-(chloromethyl)thiazole hydrochloride (0.43 mmol, 73 mg) with borylation time = 4 h, SM time 16 h. Product **3y** was isolated by column chromatography (ethyl acetate 1:4 hexane) as a yellow oil (36 mg, 43%).

δ_H (300 MHz, $CDCl_3$): 8.80 (s, 1H S-C*H*=N), 8.03-7.98 (m, 1H, Ar*H*), 7.88 (d, *J* = 9, 1H, Ar*H*), 7.81 (d, *J* = 7.8, 1H, Ar*H*), 7.51-7.42 (m, 4H, Ar*H*), 6.70 (s, 1H, C=C-*H*), 4.67 (s, 2H, CH_2)

δ_C (101 MHz, $CDCl_3$): 156.98 (4°), 152.49 (CH), 135.04 (4°), 133.94 (4°), 131.88 (4°), 128.67 (CH), 127.53 (CH), 127.31 (CH), 126.04 (CH), 125.62 (CH), 124.19 (CH), 114.46 (CH), 35.32 (CH_2).

HRMS (APCI): calc. for $C_{14}H_{12}NS$; 226.0685. Found; 226.0683



1-Cinnamylnaphthalene 4a[16]

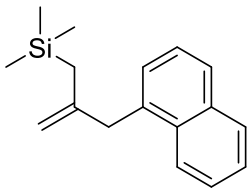
Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and cinnamyl chloride (0.43 mmol, 47 μL) with borylation time = 2 h, SM time 16 h. Product **4a** was isolated by column chromatography (DCM 1:4 pentane) as a white solid (42 mg, 47 %).

δ_H (300 MHz, $CDCl_3$): 8.11 (d, *J* = 7.8, 1H, Ar*H*), 7.89 (d, *J* = 7.8, 1H, Ar*H*), 7.78 (d, *J* = 7.8, 1H, Ar*H*), 7.55-7.41 (m, 4H, Ar*H*), 7.36-7.25 (m, 4H, Ar*H*), 7.22-7.19 (m, 1H, Ar*H*), 6.68-6.47 (m, 2H, *H*C=C*H*), 4.02 (d, *J* = 4.4, 2H, CH_2).

[16] R. Ghosh, N. Adarsh and A. Sarkar, *The Journal of Organic Chemistry*, 2010, 75, 5320-5322.

δ_C (101 MHz, $CDCl_3$): 137.42 (4°), 136.21 (4°), 133.83 (4°), 132.00 (4°), 131.27 (CH), 128.85 (CH), 128.68 (CH), 128.46 (CH), 127.06 (CH), 126.37 (CH), 126.08 (CH), 125.93 (CH), 125.63 (CH), 125.56 (CH), 123.99 (CH), 36.40 (CH_2)

LRMS (EI): [244.13], 244.1, 229.1, 168.1, 153.1 (100%)



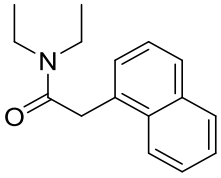
Trimethyl(2-(naphthalen-1-ylmethyl)allyl)silane 4b

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 µL) and 2-(chloromethyl)allyl-trimethylsilane (0.43 mmol, 78 µL) with borylation time = 4 h, SM time 16 h. Product **4b** was isolated by column chromatography (hexane) as a colourless oil. Product was still impure so yield was determined by internal standard NMR (35%). Following GP, using 2-(chloromethyl)allyl-trimethylsilane (3 equiv., 1.11 mmol, 201 µL) with borylation time = 4 h, SM time 16 h, gave **4b** (63%) by NMR yield (1,5-cyclooctadiene as internal standard).

δ_H (300 MHz, $CDCl_3$): 7.83-7.81 (m, 1H, Ar*H*), 7.66-7.50 (m, 3H, Ar*H*), 7.31-7.20 (m, 2H, Ar*H*), 7.14 (d, *J* = 6.6, 1H, Ar*H*), 4.48 (s, 1H, C=C*H*), 4.25 (d, *J* = 1.2, 1H, C=C*H*), 3.55 (s, 2H, Ar-CH_2), 1.44 (s, 2H, Si-CH_2), -0.10 (s, 9H, Si-CH_3).

δ_C (101 MHz, $CDCl_3$): 146.07 (4°), 135.94 (4°), 133.79 (4°), 132.54 (4°), 128.55 (CH), 127.23 (CH), 126.90 (CH), 125.64 (CH), 125.46 (CH), 125.39 (CH), 124.42 (CH), 109.91 (CH_2), 42.11 (CH_2), 26.93 (CH_2), -1.17 (CH_3).

LRMS (EI): [254.45], 254.2, 239.2, 180.1, 167.1, 141.1, 115.1, 73.1 (100%)



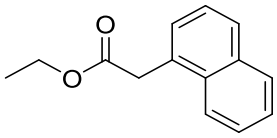
_N_,_N_-Diethyl-2-(naphthalen-1-yl)acetamide 5a[17]

Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and 2-chloro-*N*,*N*-diethylacetamide (0.43 mmol, 47 μL) with borylation time = 4 h, SM time 16 h. Product **5a** was isolated by column chromatography (ethyl acetate 1:5 hexane) as a colourless oil (51 mg, 57%).

δ_H (300 MHz, $CDCl_3$): 7.98 (d, *J* = 8.1, 1H, Ar*H*), 7.88 (d, *J* = 7.8, 1H, Ar*H*), 7.78 (d, *J* = 8.3, 1H, Ar*H*), 7.56-7.48 (m, 2H, Ar*H*), 7.43 (t, *J* = 7.6, 1H, Ar*H*), 7.34 (d, *J* = 7.1, 1H, Ar*H*), 4.14 (s, 2H, CH_2-C=O), 3.47 (q, *J* = 7.1, 2H, NCH_2), 3.33 (q, *J* = 7.2, 2H, NCH_2), 1.20 (t, *J* = 7.1, 3H, CH_3), 1.13 (t, *J* = 7.1, 3H, CH_3).

δ_C (101 MHz, $CDCl_3$): 170.16 (4°), 133.77 (4°), 132.05 (4°), 131.81 (4°), 128.74 (CH), 127.51 (CH), 126.22 (CH), 126.09 (CH), 125.68 (CH), 125.51 (CH), 123.42 (CH), 42.42 (CH_2), 40.20 (CH_2), 38.35 (CH_2), 14.23 (CH_3), 12.97 (CH_3).

LRMS (EI): [241.33], 241.2, 141.1, 115.1, 100.1 (100%)



Ethyl 2-(naphthalen-1-yl)acetate 5b[18]

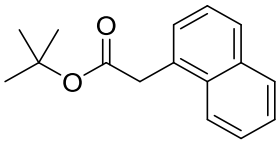
Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and ethyl chloroacetate (0.43 mmol, 47 μL) with borylation time = 5 h, SM time 16 h. Product **5b** was isolated by column chromatography (ethyl acetate 1:9 hexane) as a pale yellow oil (58 mg, 73%).

[17] B. Zheng, T. Jia and P. Walsh, *Advanced Synthesis & Catalysis*, 2014, 356, 165-178.
[18] M. Dinesh, S. Archana, R. Ranganathan, M. Sathishkumar and A. Ponnuswamy, *Tetrahedron Letters*, 2015, 56, 6975-6979.

δ_H (300 MHz, $CDCl_3$): 7.98 (d, *J* = 8.3, 1H, Ar*H*), 7.84 (d, *J* = 7.8, 1H, Ar*H*), 7.77 (d, *J* = 7.3, 1H, Ar*H*), 7.53-7.45 (m, 2H, Ar*H*), 7.41-7.38 (m, 2H, Ar*H*), 4.13 (q, 2H, *J* = 7.2, CO_2CH_2), 4.04 (s, 2H, CH_2), 1.20 (t, *J* = 7.1, 3H, CH_3).

δ_C (101 MHz, $CDCl_3$): 171.57 (4°), 133.77 (4°), 132.08 (4°), 130.65 (4°), 128.67 (CH), 127.98 (CH), 127.92 (CH), 126.27 (CH), 125.72 (CH), 125.45 (CH), 123.80 (CH), 60.93 (CH_2), 39.24 (CH_2), 14.14 (CH_3).

LRMS (EI): [214.26], 214.1, 141.1 (100%), 115.1



***tert*-Butyl 2-(naphthalen-1-yl)acetate 5c**[19]

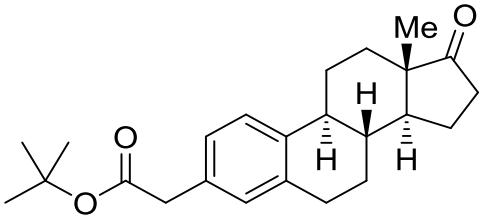
Following GP, using 1-bromonaphthalene (0.37 mmol, 52 μL) and *tert*-butyl chloroacetate (0.43 mmol, 61 μL) with borylation time = 4 h, SM time 16 h. Product **5c** was isolated by column chromatography (ethyl acetate 1:19 hexane) as a yellow oil (68 mg, 76%).

δ_H (300 MHz, $CDCl_3$): 8.03 (d, *J* = 8.3, 1H, Ar*H*), 7.89 (d, *J* = 7.8, 1H, Ar*H*), 7.81 (d, *J* = 7.8, 1H, Ar*H*), 7.58-7.41 (m, 4H, Ar*H*), 4.01 (s, 2H, CH_2), 1.44 (s, 9H, CH_3).

δ_C (101 MHz, $CDCl_3$): 170.92 (4°), 133.78 (4°), 132.13 (4°), 131.28 (4°), 128.62 (CH), 127.78 (CH), 127.76 (4°), 126.08 (CH), 125.61 (CH), 125.43 (CH), 123.90 (CH), 80.96 (4°), 40.48 (CH_2), 27.96 (CH_3).

LRMS (EI): [242.32], 242.1, 186.1, 141.1 (100%), 115.1, 57.1

[19] R. Delley, S. Bandyopadhyay, M. Fox, C. Schliehe, D. Hodgson, F. Hollfelder, A. Kirby and A. O'Donoghue, *Org. Biomol. Chem.*, 2012, 10, 590-596.



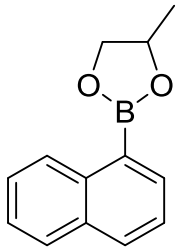
***tert*-Butyl 2-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)acetate 5d**

Following GP, using (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl trifluoromethanesulfonate (0.326 mmol, 131 mg) and *tert*-butyl 2-chloroacetate (0.391 mmol, 55.9 µl), with borylation time = 2 h, SM time 16 h. Product **1b** was isolated by column chromatography (ethyl acetate 25:75 hexane) as a white amorphous solid (112 mg, 93%).

δ_H (500 MHz, $CDCl_3$): 7.25 (d, 1H, *J* = 8.0, Ar*H*), 7.06 (d, 1H, J = 8.0, Ar*H*), 7.06 (s, 1H, Ar*H*), 3.48 (s, 2H, C*H*$_2$-CO$_2$^{t}Bu), 2.89 (app. dd, 2H, *J* = 9.0, 4.1, ArC*H*$_2$CH$_2$), 2.51 (dd, 1H, *J* = 19.0, 8.9, C*H*-Ar), 2.42 (m, 1H), 2.29 (m, 1H), 2.20-1.94 (m, 4H), 1.68-1.41 (m, 6H), 1.46 (s, 9H, tBu), 0.92 (s, 3H, C(O)CC*H*$_3$).

δ_C (101 MHz, $CDCl_3$): 220.90 (4°), 171.16 (4°), 138.24 (4°), 136.51 (4°), 132.01 (4°), 129.82 (CH), 126.57 (CH), 125.45 (CH), 80.72 (4°), 50.48 (CH), 47.96 (4°), 44.27 (CH), 41.92 (CH_2), 38.06 (CH), 35.84 (CH_2), 31.57 (CH_2), 29.30 (CH_2), 28.06 (CH_3), 26.47 (CH_2), 25.66 (CH_2), 21.57 (CH_2), 13.81 (CH_3).

HRMS (ESI+): Found 391.2237, $C_{24}H_{32}O_3Na$ requires 391.2244.



4-Methyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane 7a

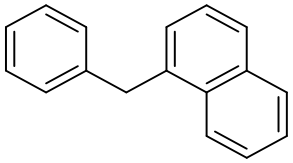
δ_H (300 MHz, $CDCl_3$): 8.68 (d, *J* = 8.3, 1H, Ar*H*), 8.03 (d, *J* = 6.1, 1H, Ar*H*), 7.88 (d, *J* = 8.1, 1H, Ar*H*), 7.77 (d, *J* = 7.8, 1H, Ar*H*), 7.48-7.39 (m, 3H, Ar*H*), 4.73 (m, 1H, H_2C-C*H*-CH_3), 4.47 (t, *J* = 8.54, 1H, C*H*$_2$), 3.19 (dd, *J* = 8.8, 7.3, 1H, C*H*$_2$), 1.41 (d, *J* = 6.1, 3H, C*H*$_3$)

δ_C (101 MHz, $CDCl_3$): 136.84, 135.98, 133.18, 131.86, 128.38, 128.25, 126.40, 125.51, 124.96, 73.64, 72.39, 21.90.

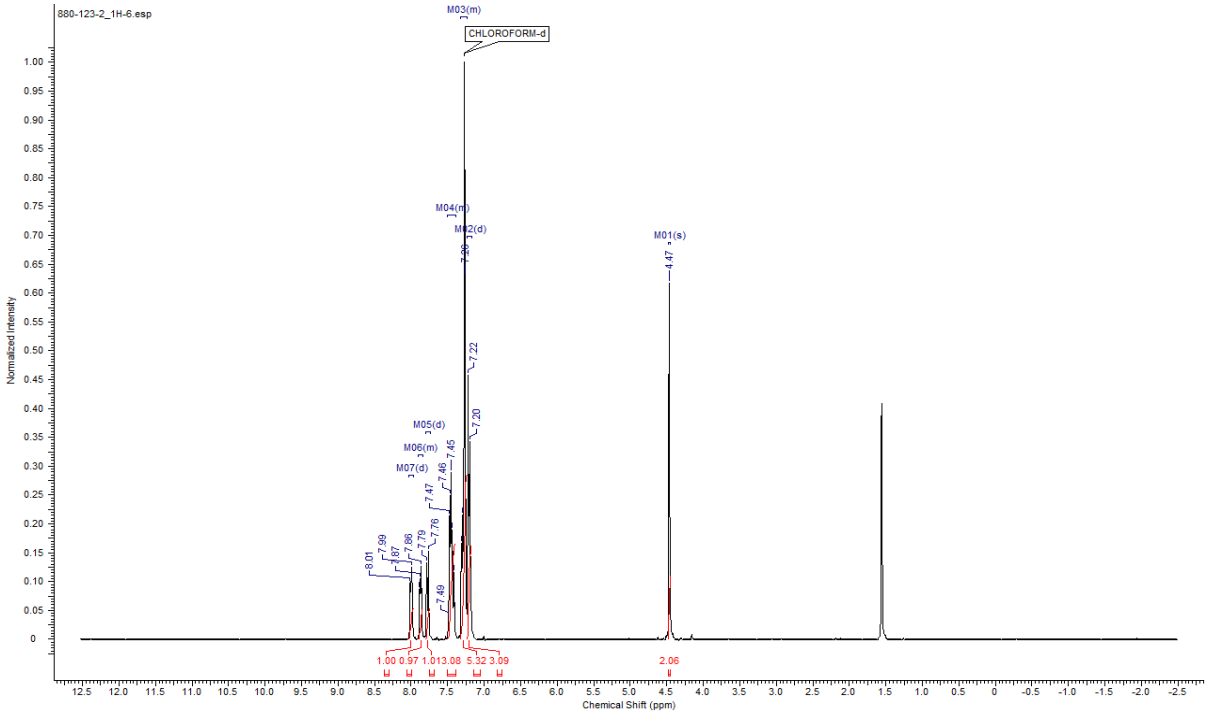
LRMS (EI): [212.10], 212.1 (100%), 197.1, 154.1, 127.1, 98.5, 77.1, 51.1.

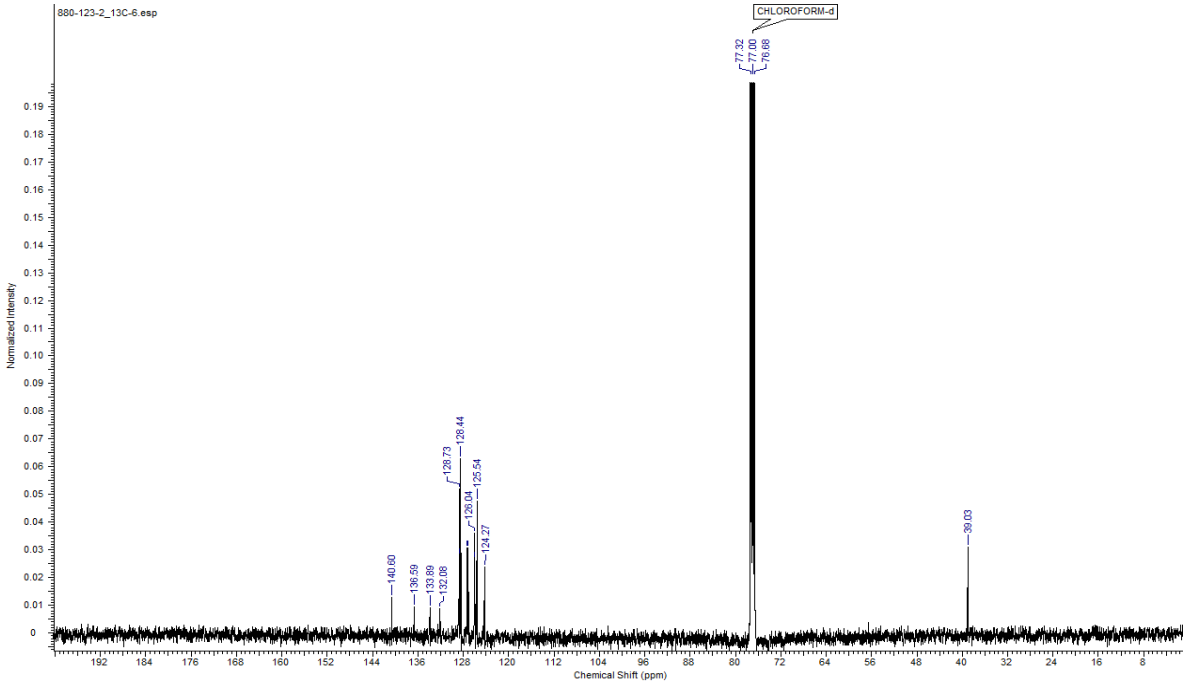
HRMS (ESI+): calc. for $C_{13}H_{13}BO_2$+H; 213.1081. Found; 213.1080.

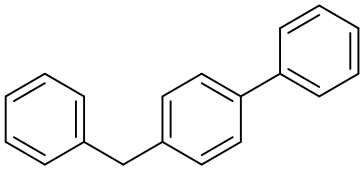
^{1}H and ^{13}C NMR spectra



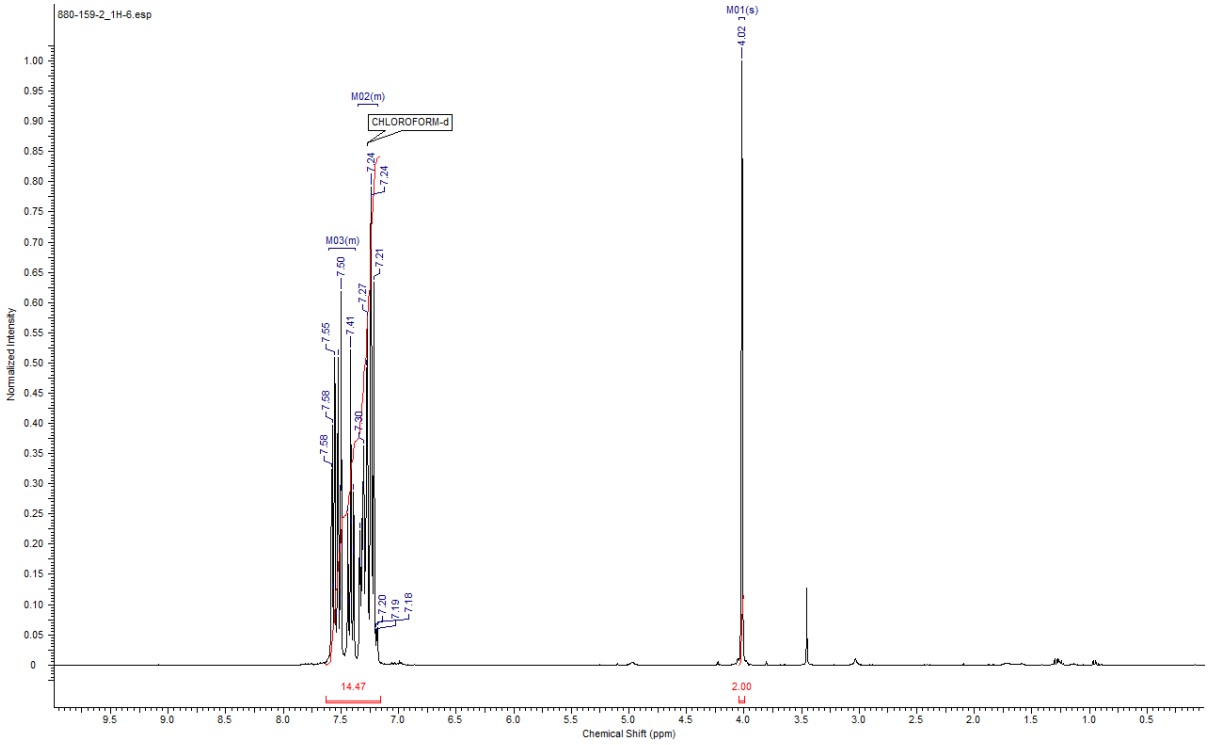
3a

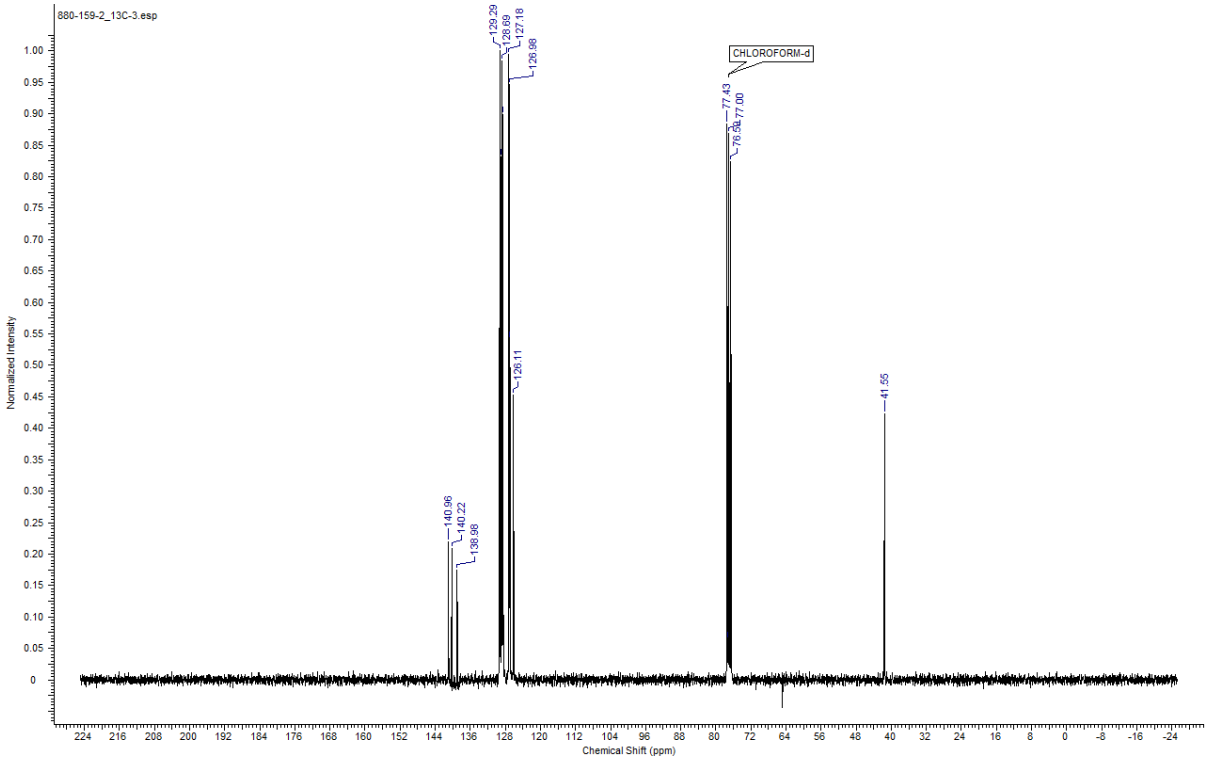


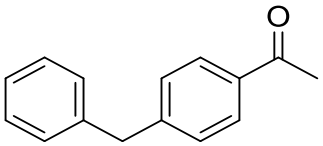




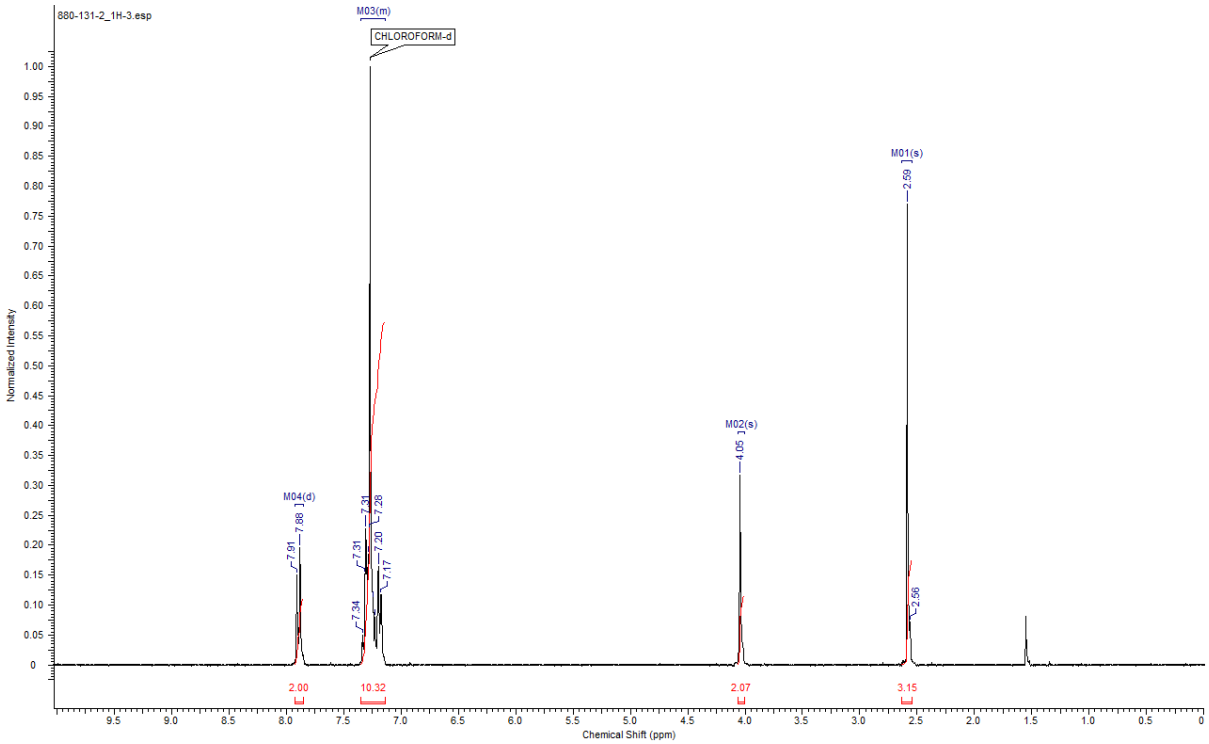
3b

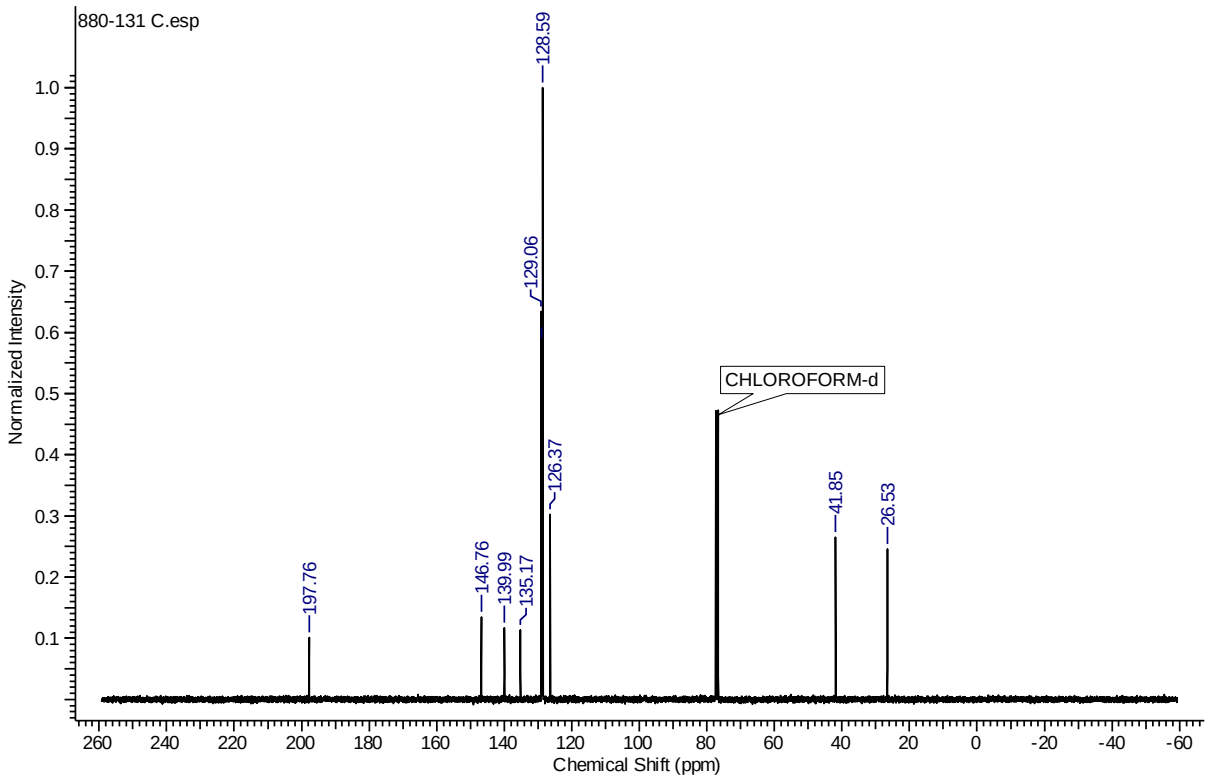

880-159-2_1H-6.esp
M01(s)
4.02
M02(m)
CHLOROFORM-d
7.24
7.24
M03(m)
7.50
7.21
7.27
7.41
7.55
7.58
7.58
7.30
7.20
7.19
7.18
14.47
2.00
Normalized Intensity
Chemical Shift (ppm)

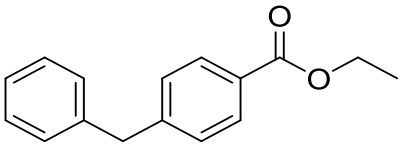

880-159-2_13C-3.esp
129.29
128.69
127.18
126.98
CHLOROFORM-d
77.43
77.00
76.58
126.11
41.55
140.96
140.22
136.98
Normalized Intensity
Chemical Shift (ppm)



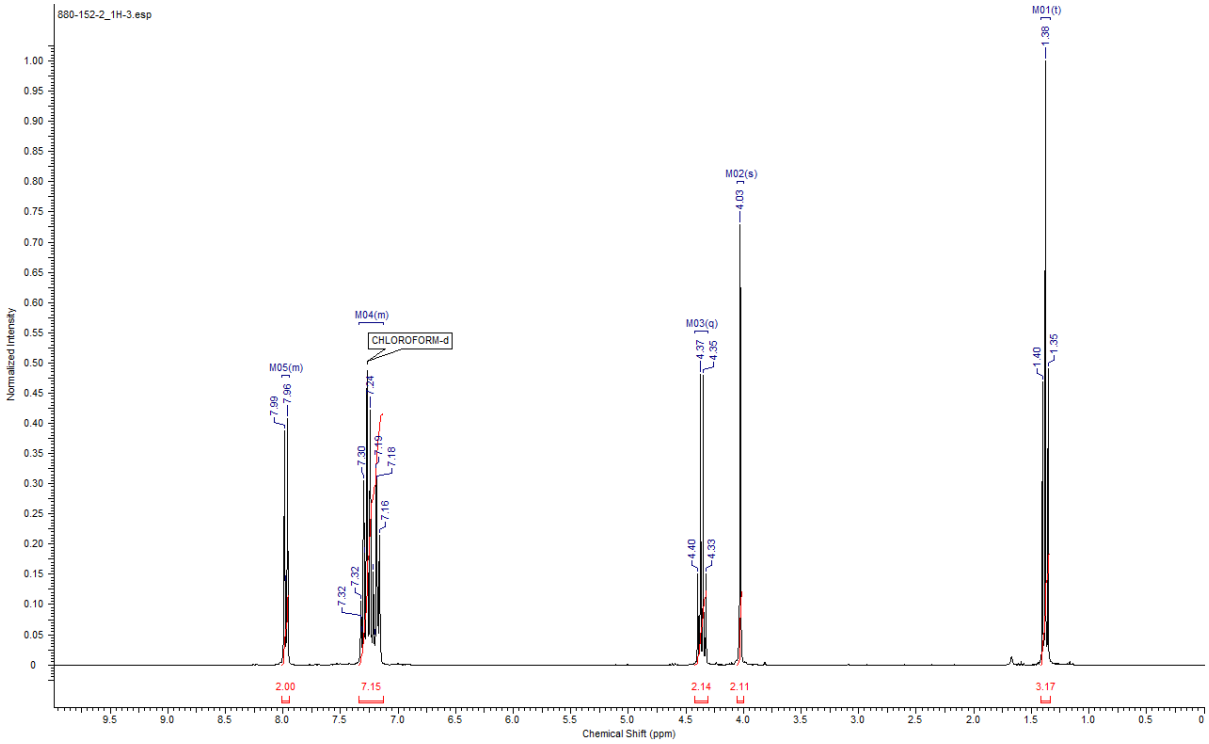
3c

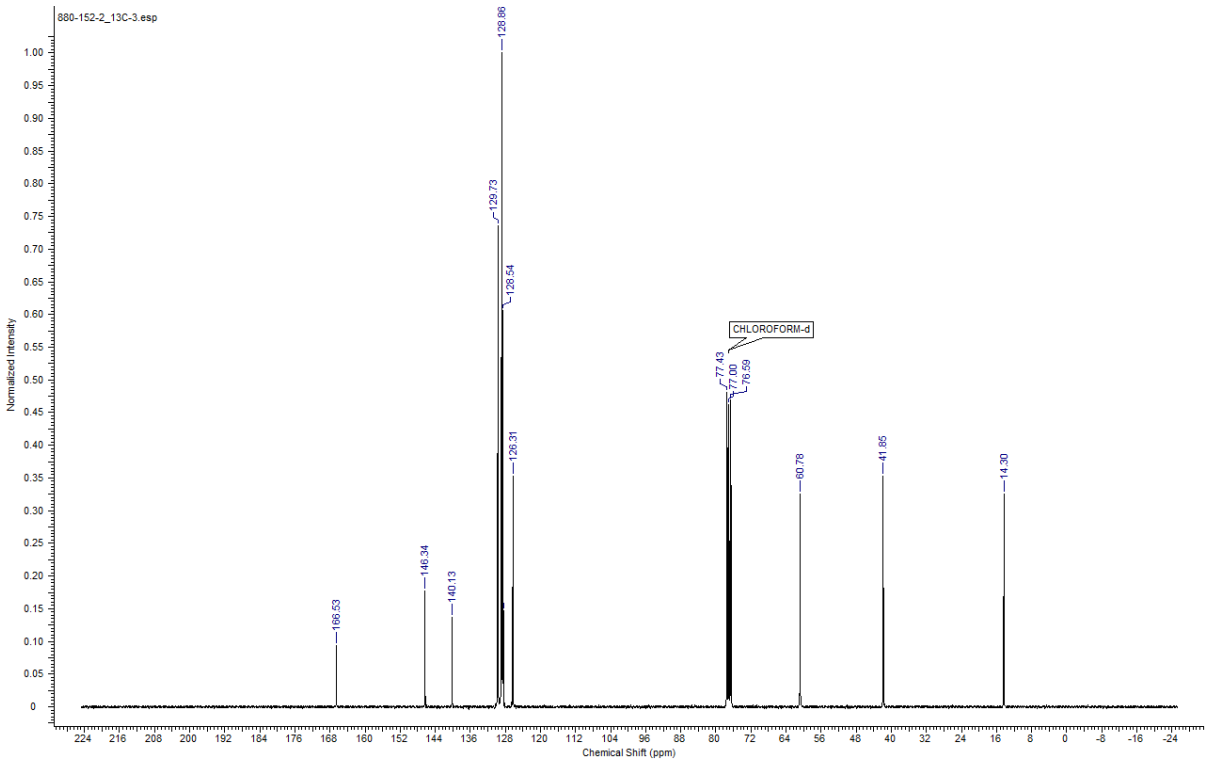

880-131-2_1H-3.esp
M03(m)
CHLOROFORM-d
M01(s)
2.59
M02(s)
4.05
M04(d)
7.88
7.91
7.31
7.28
7.20
7.17
7.34
2.66
2.00
10.32
2.07
3.15
Normalized Intensity
Chemical Shift (ppm)


880-131 C.esp
128.59
129.06
126.37
CHLOROFORM-d
41.85
26.53
197.76
146.76
139.99
135.17
Normalized Intensity
Chemical Shift (ppm)

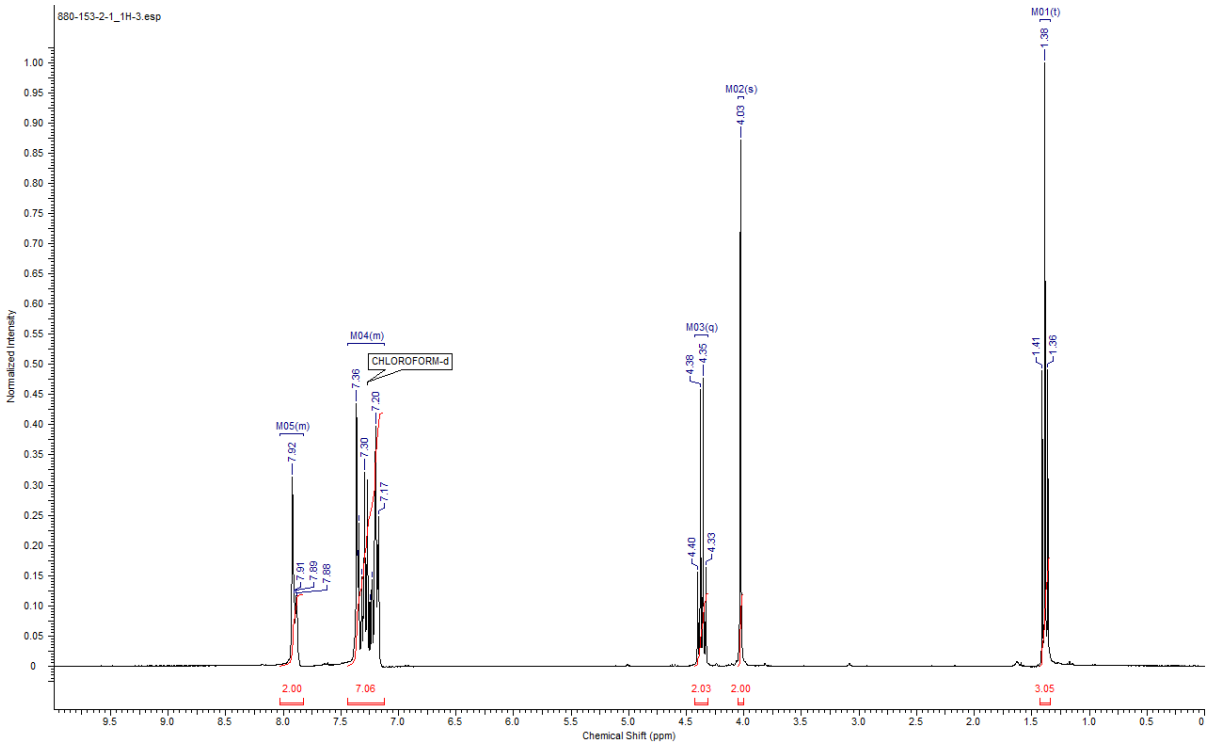


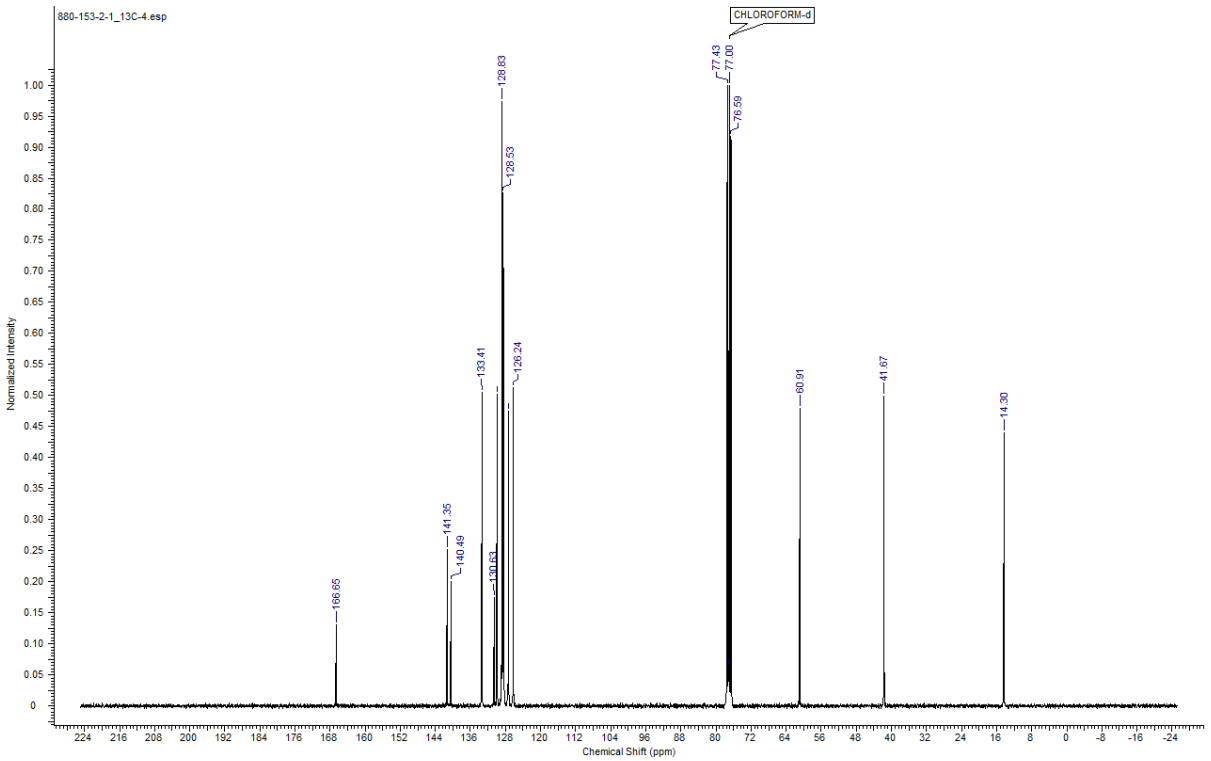
3d

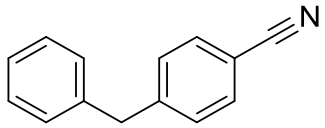

880-152-2_1H-3.esp
Normalized Intensity
Chemical Shift (ppm)
M01(t)
M02(s)
M03(q)
M04(m)
M05(m)
CHLOROFORM-d
1.38
1.40
1.35
4.03
4.37
4.35
4.40
4.33
7.99
7.98
7.24
7.30
7.19
7.18
7.16
7.32
7.32
2.00
7.15
2.14
2.11
3.17


880-152-2_13C-3.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
128.86
129.73
128.54
126.31
77.43
77.00
76.59
60.78
41.85
14.30
166.53
146.34
140.13

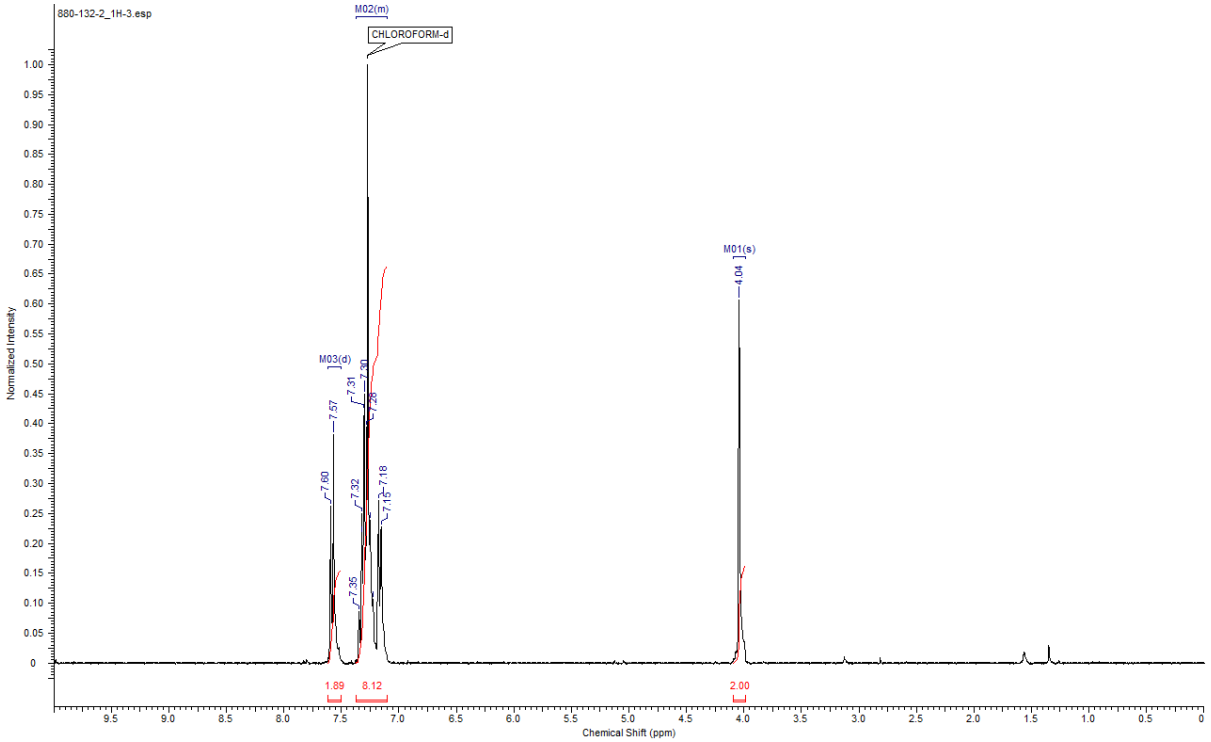
3e

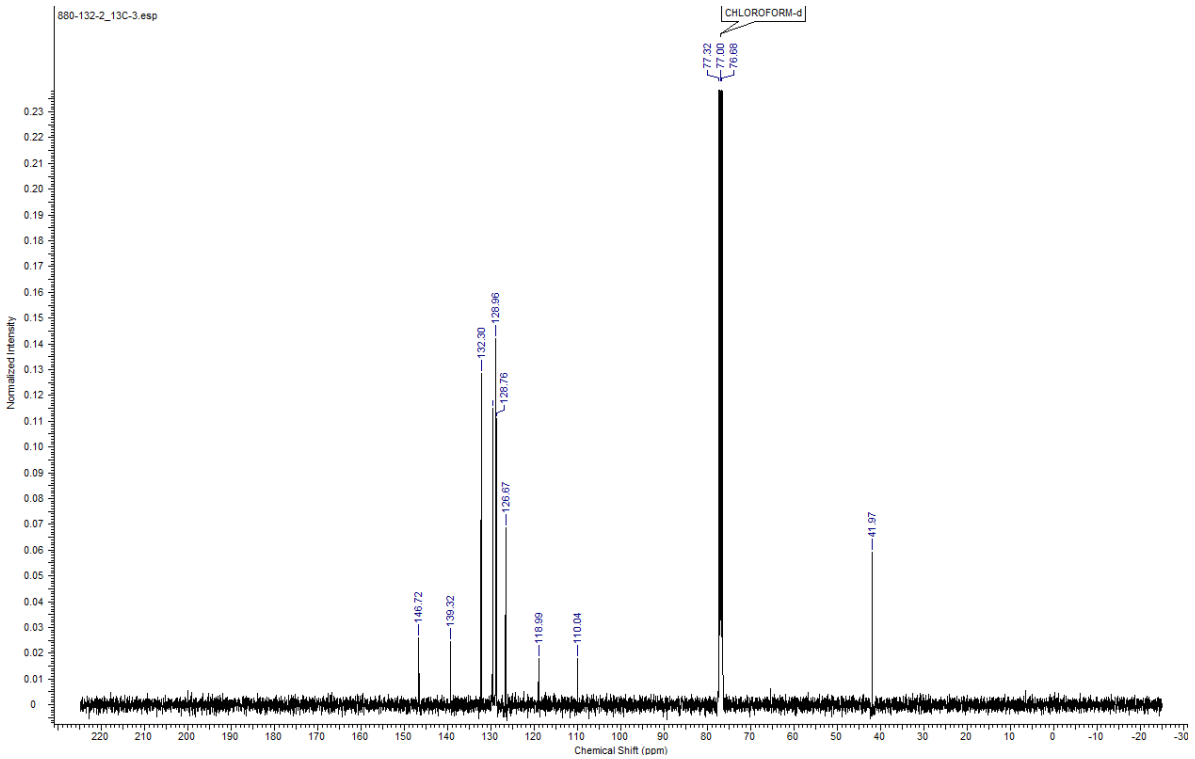

880-153-2-1_1H-3.esp
Normalized Intensity
Chemical Shift (ppm)
M01(t)
1.38
M02(s)
4.03
M03(q)
4.38
4.35
M04(m)
7.36
7.30
7.20
7.17
CHLOROFORM-d
M05(m)
7.92
7.91
7.89
7.88
1.41
1.36
1.40
4.33
2.00
7.06
2.03
2.00
3.05

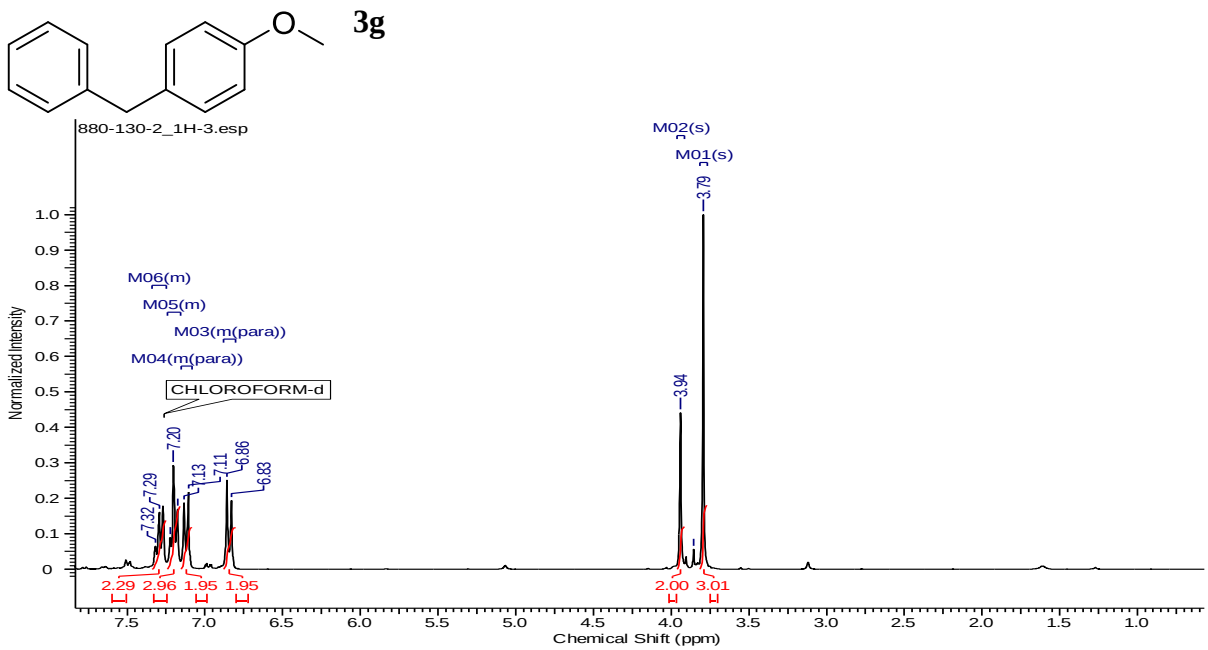

880-153-2-1_13C-4.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.43
77.00
76.59
128.83
128.53
133.41
130.24
141.35
140.49
130.63
166.65
60.91
41.67
14.30

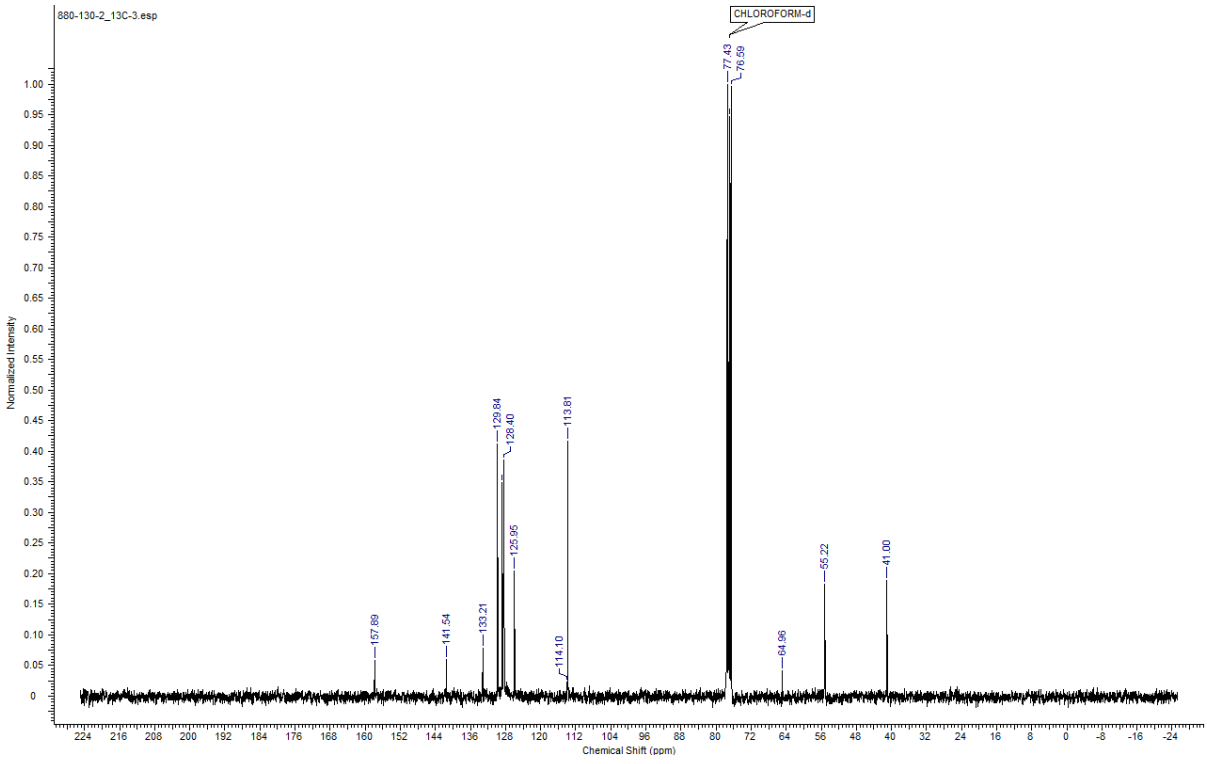


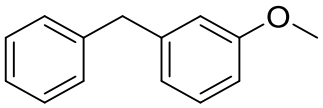
3f


880-132-2_1H-3.esp
M02(m)
CHLOROFORM-d
M01(s)
4.04
M03(d)
7.57
7.31
7.30
7.26
7.60
7.32
7.18
7.15
7.35
1.89
8.12
2.00
Normalized Intensity
Chemical Shift (ppm)

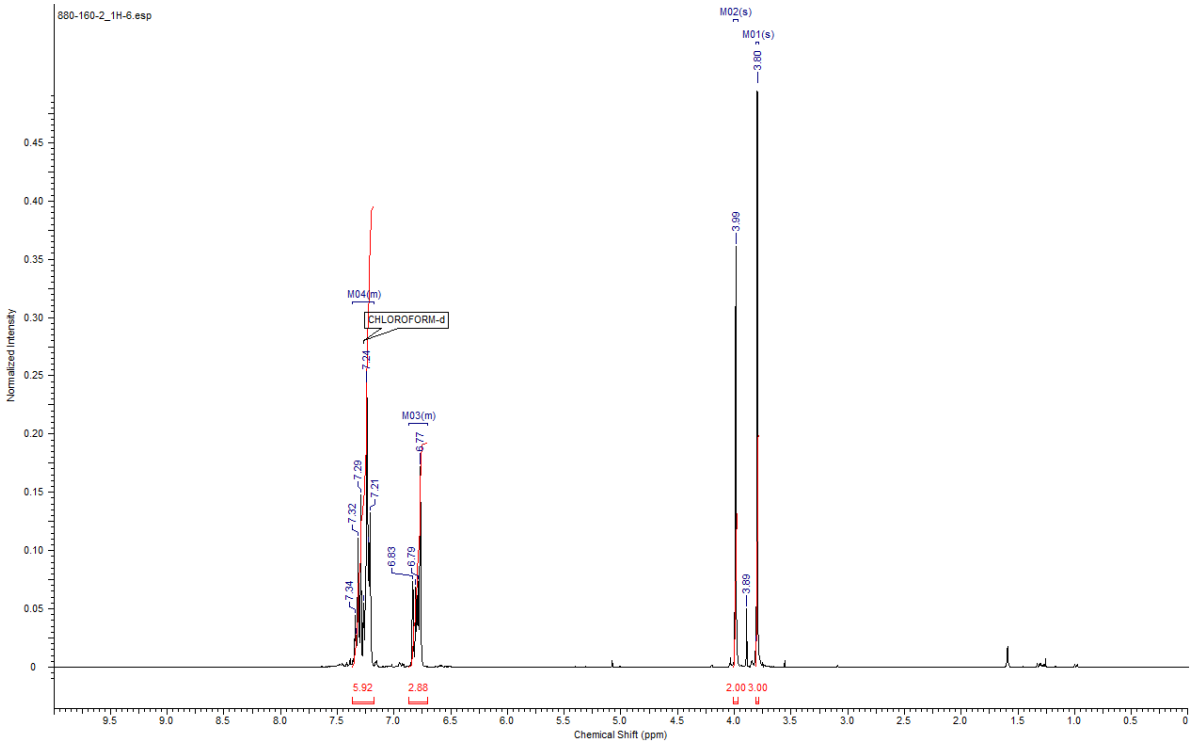

880-132-2_13C-3.esp
CHLOROFORM-d
77.32
77.00
76.68
132.30
128.96
128.76
126.67
146.72
139.32
118.99
110.04
41.97
Normalized Intensity
Chemical Shift (ppm)

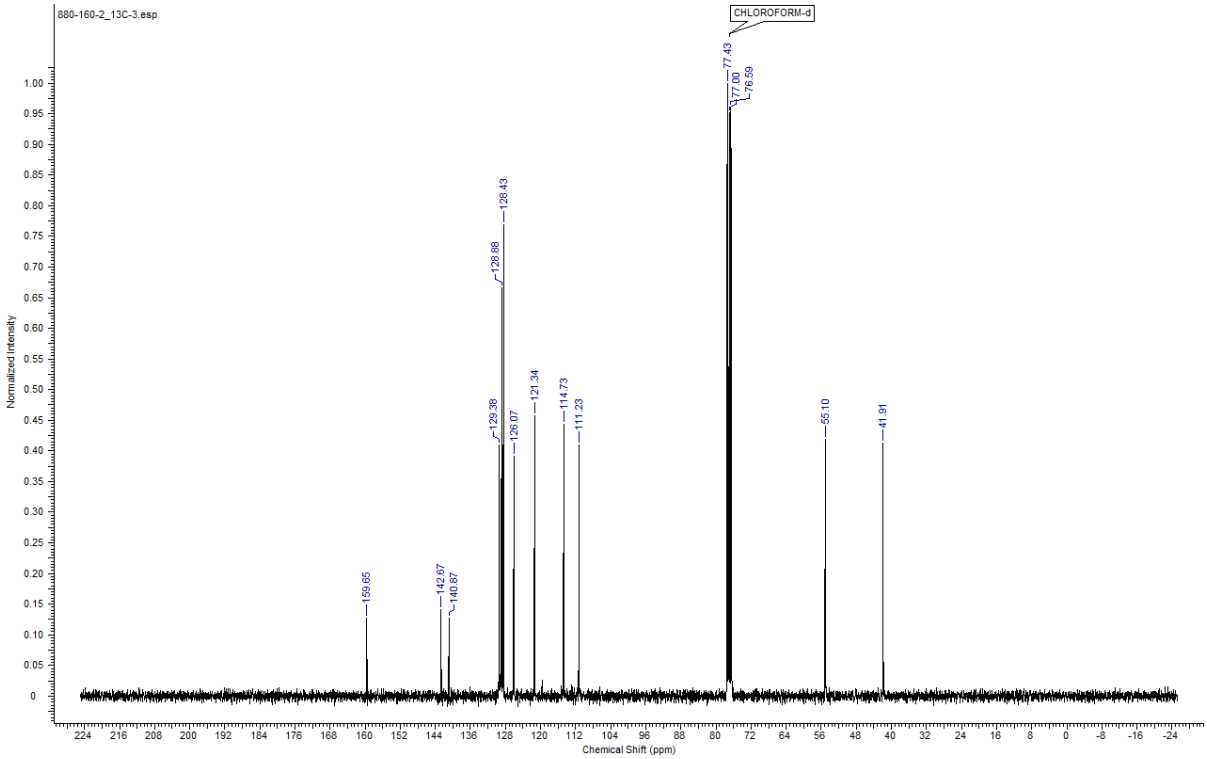

3g
880-130-2_1H-3.esp
M02(s)
M01(s)
3.79
M06(m)
M05(m)
M03(m(para))
M04(m(para))
CHLOROFORM-d
7.20
7.29
7.32
7.13
7.11
6.86
6.88
3.94
2.29
2.96
1.95
1.95
2.00
3.01
Normalized Intensity
Chemical Shift (ppm)

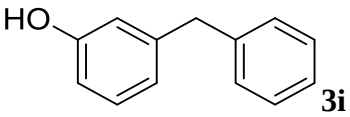

880-130-2_13C-3.esp
CHLOROFORM-d
77.43
76.59
129.84
128.40
125.95
113.81
157.89
141.54
133.21
114.10
64.96
55.22
41.00
Normalized Intensity
Chemical Shift (ppm)



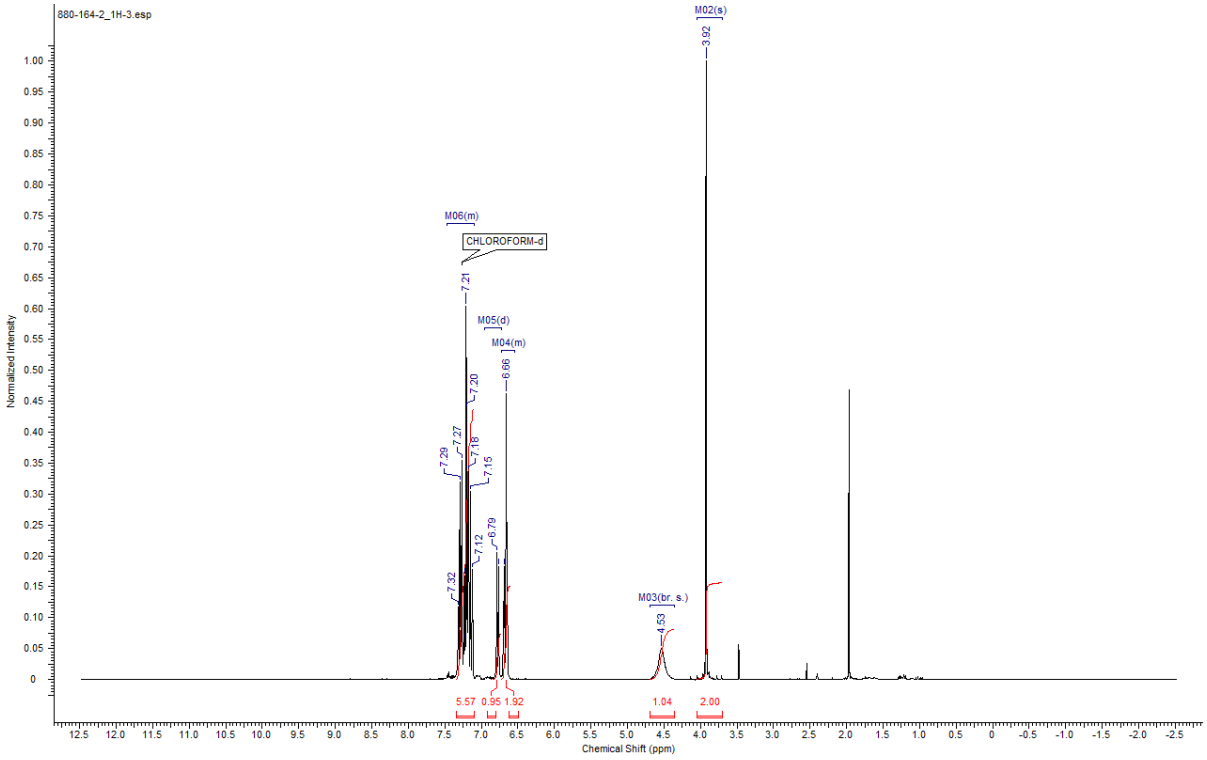
3h

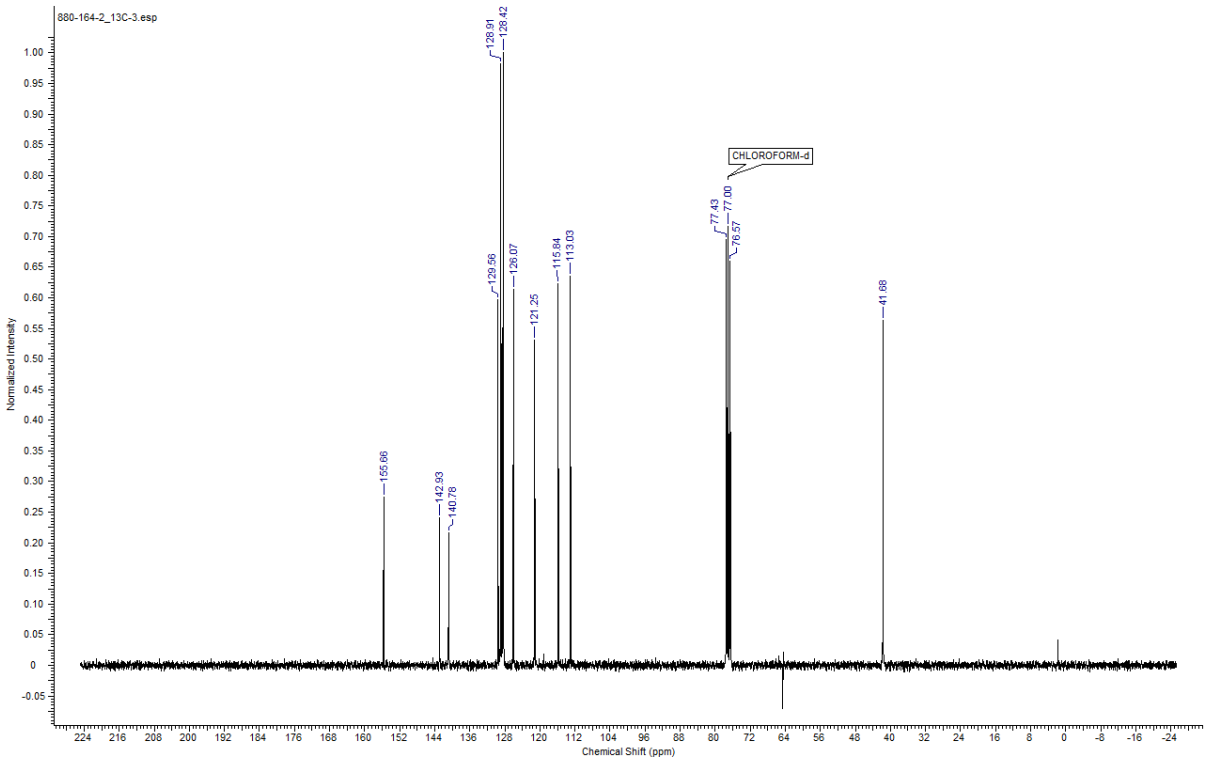

880-160-2_1H-6.esp
M02(s)
M01(s)
3.80
3.99
M04(m)
CHLOROFORM-d
7.24
M03(m)
6.77
7.29
7.21
7.32
7.34
6.83
6.79
3.89
Normalized Intensity
5.92
2.88
2.00
3.00
Chemical Shift (ppm)

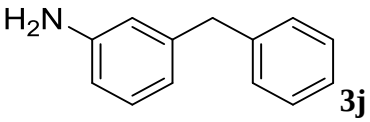

880-160-2_13C-3.esp
CHLOROFORM-d
77.43
77.00
76.59
128.43
128.88
129.38
129.07
121.34
114.73
111.23
159.65
142.67
140.87
55.10
41.91
Normalized Intensity
Chemical Shift (ppm)


HO

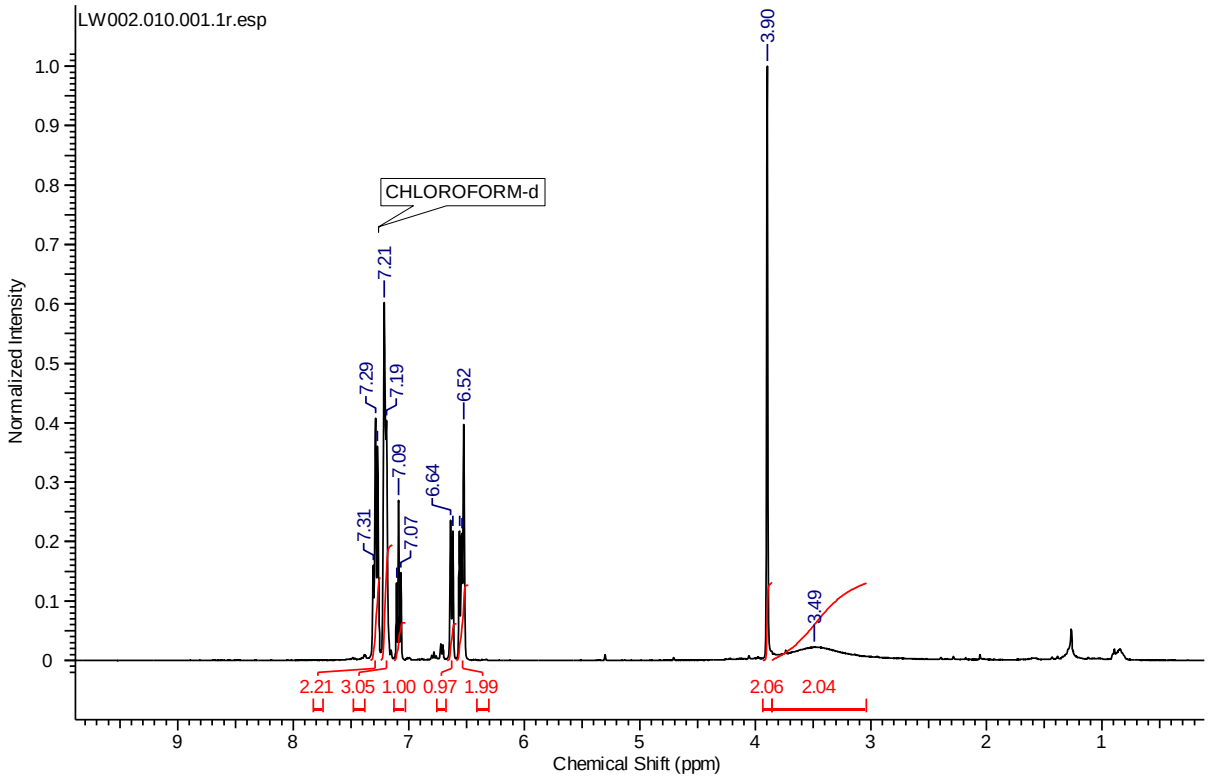
3i

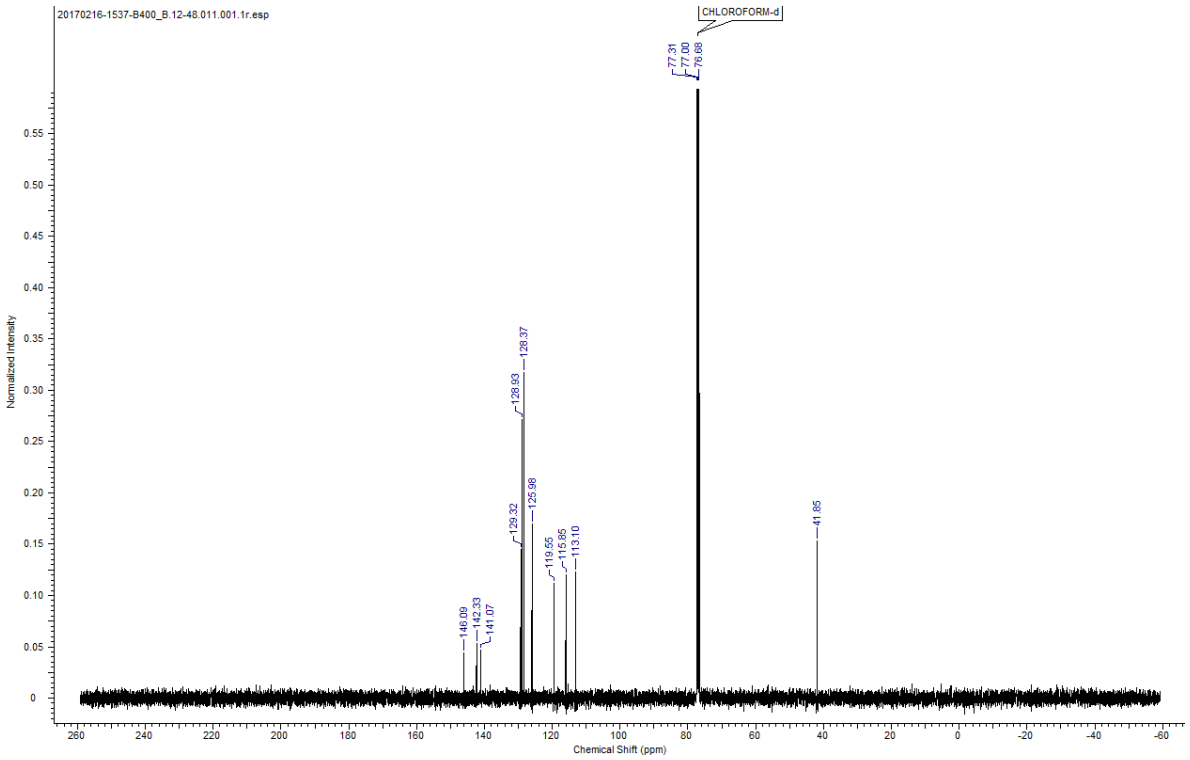

880-164-2_1H-3.esp
M02(s)
3.92
M06(m)
CHLOROFORM-d
7.21
M05(d)
M04(m)
6.66
7.20
7.27
7.29
7.18
7.15
6.79
7.12
7.32
M03(br. s.)
4.53
5.57
0.95
1.92
1.04
2.00
Normalized Intensity
Chemical Shift (ppm)

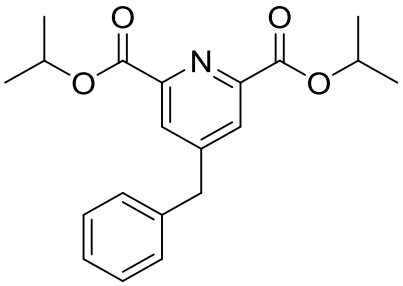

880-164-2_13C-3.esp
128.91
128.42
CHLOROFORM-d
77.43
77.00
76.57
129.56
126.07
115.84
113.03
121.25
41.68
155.66
142.93
140.78
Normalized Intensity
Chemical Shift (ppm)


H_2N

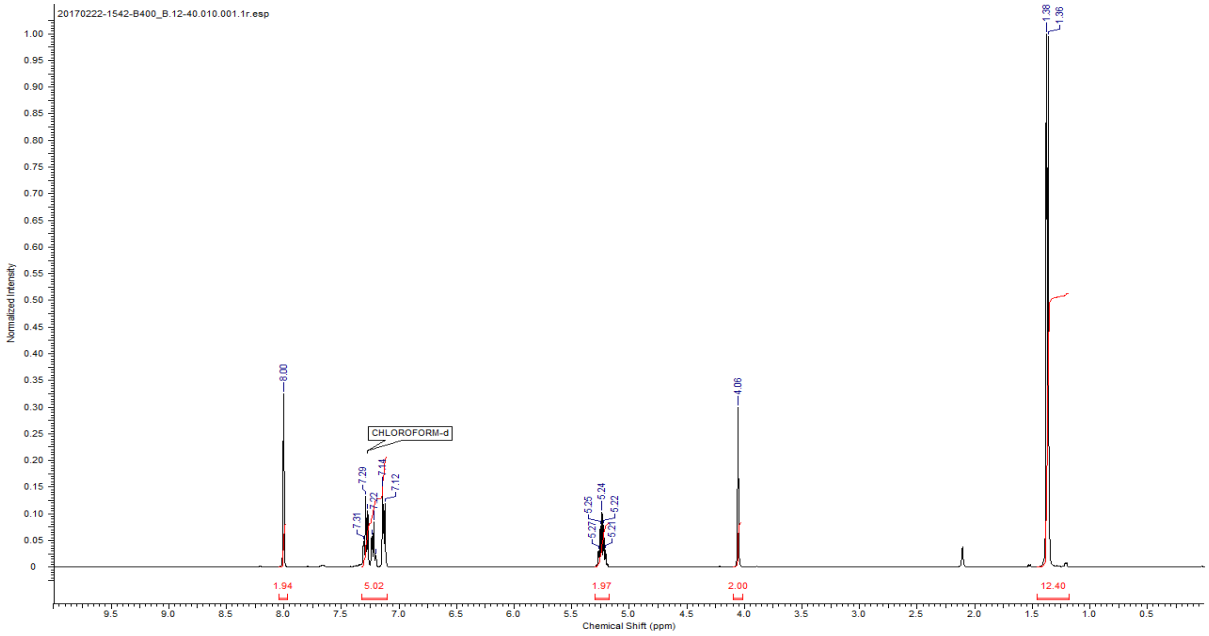
3j

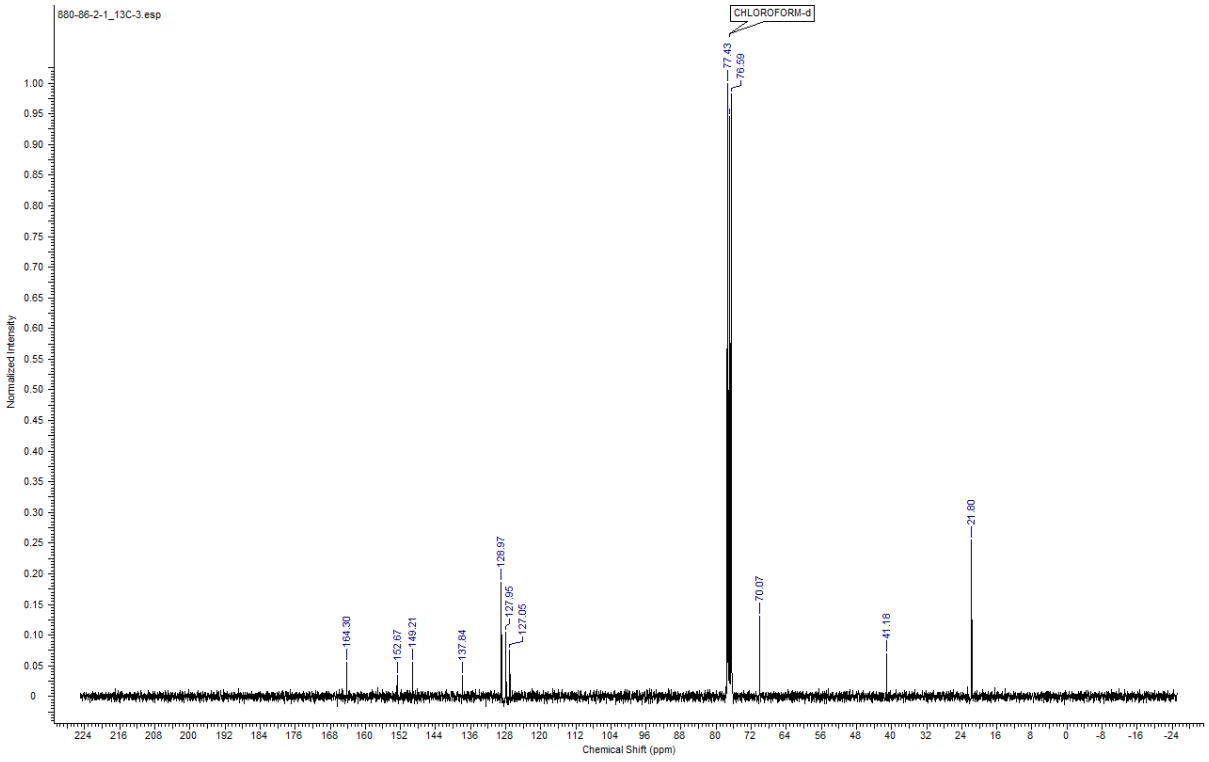

LW002.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
3.90
7.21
7.29
7.19
6.52
7.09
6.64
7.31
7.07
3.49
2.21
3.05
1.00
0.97
1.99
2.06
2.04

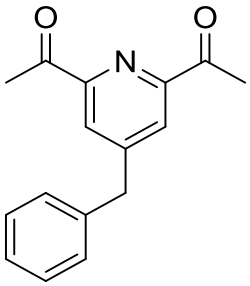

20170216-1537-B400_B.12-48.011.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.31
77.00
76.68
129.37
128.93
125.98
129.32
119.55
115.85
113.10
146.09
142.33
141.07
41.85



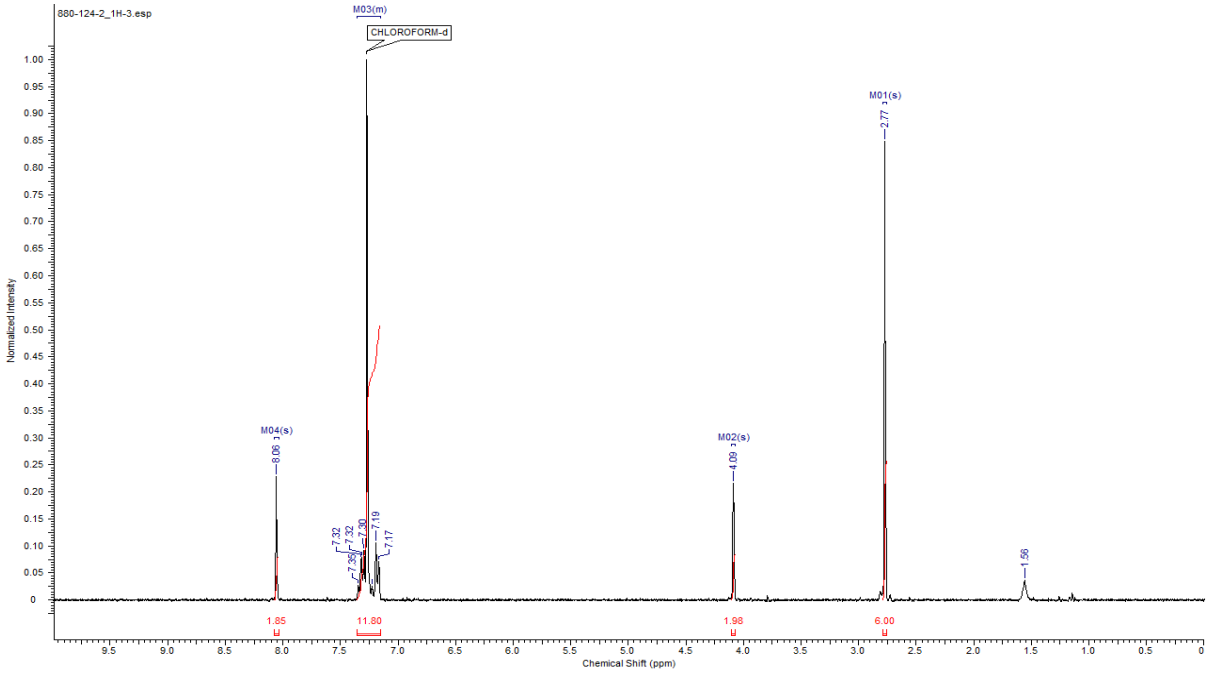
3k

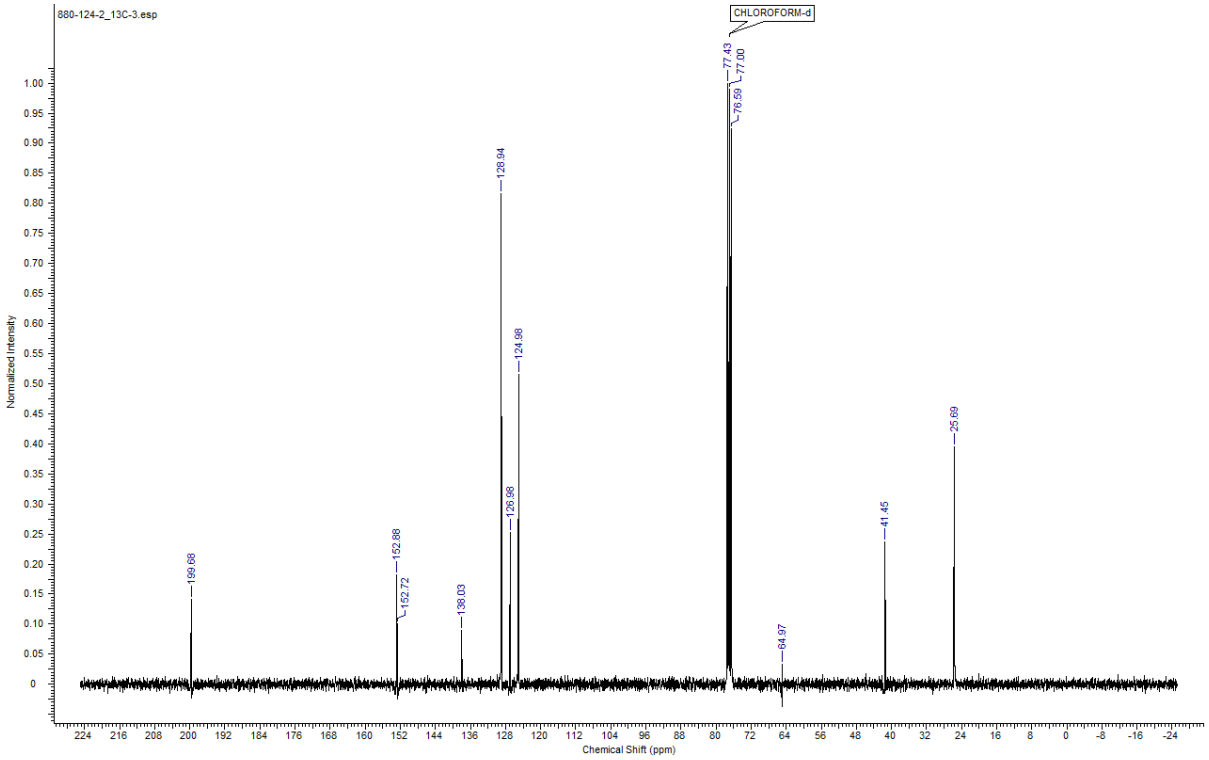

20170222-1542-B400_B.12-40.010.001.1r.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
8.00
7.31
7.29
7.22
7.44
7.12
5.27
5.25
5.24
5.22
5.21
4.06
1.38
1.36
1.94
5.02
1.97
2.00
12.40

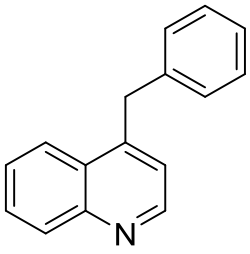

880-86-2-1_13C-3.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.43
76.59
164.30
152.67
149.21
137.84
128.97
127.95
127.05
70.07
41.18
21.80



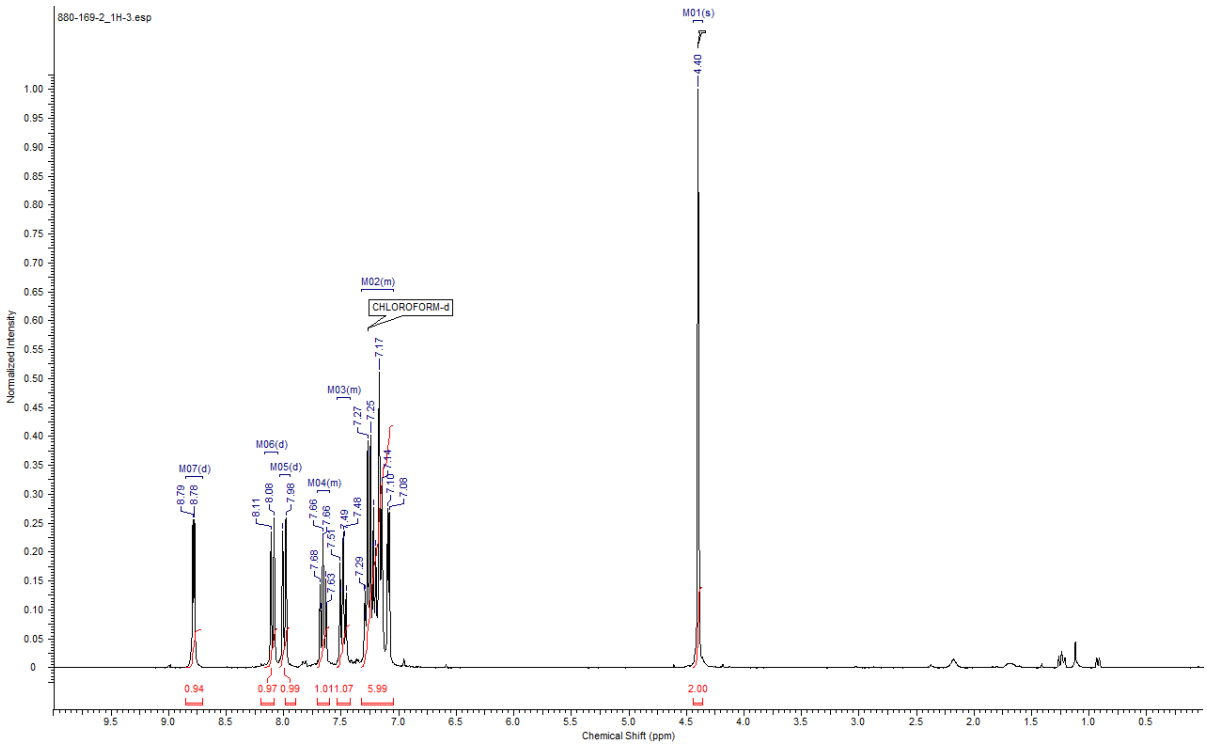
3l

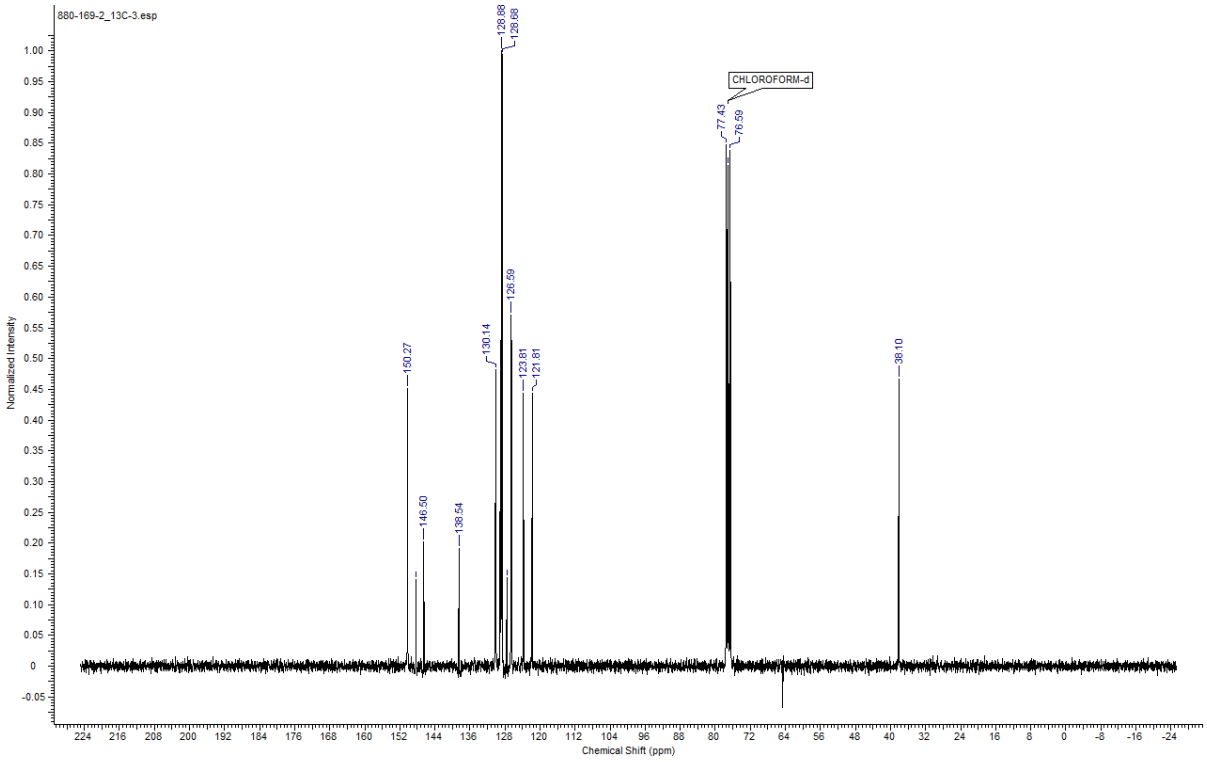

880-124-2_1H-3.esp
M03(m)
CHLOROFORM-d
M01(s)
M04(s)
M02(s)
Normalized Intensity
Chemical Shift (ppm)

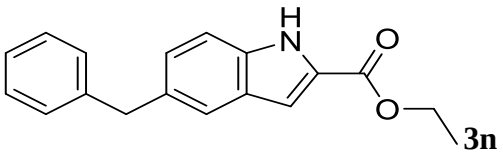

880-124-2_13C-3.esp
CHLOROFORM-d
Normalized Intensity
Chemical Shift (ppm)



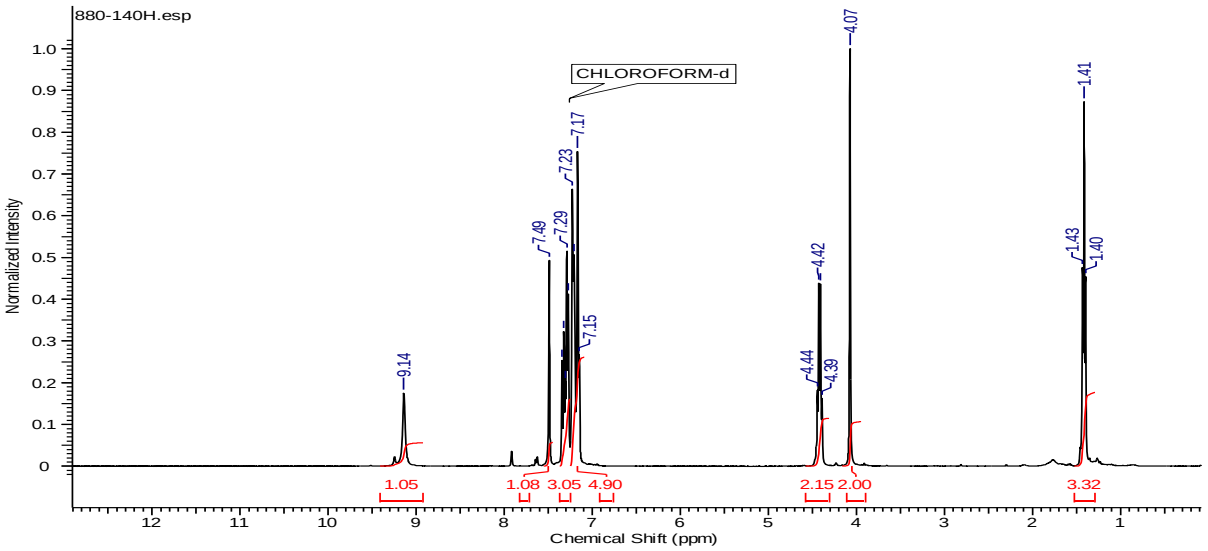
3m

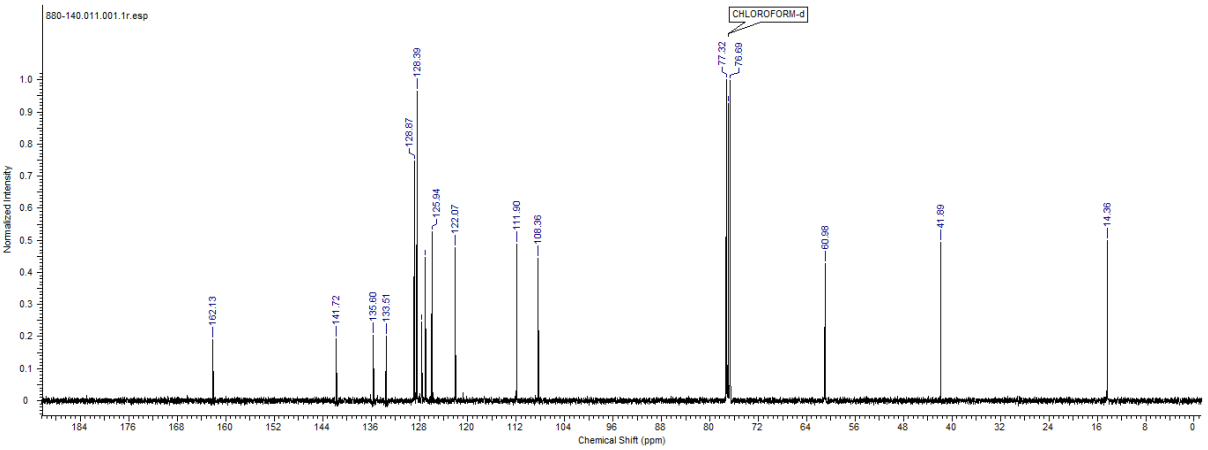

880-169-2_1H-3.esp
M01(s)
4.40
M02(m)
CHLOROFORM-d
7.17
M03(m)
7.27
7.25
M04(m)
M05(d)
M06(d)
M07(d)
8.79
8.78
8.11
8.08
7.98
7.66
7.65
7.51
7.49
7.48
7.29
7.14
7.10
7.08
0.94
0.97
0.99
1.01
1.07
5.99
2.00
Normalized Intensity
Chemical Shift (ppm)

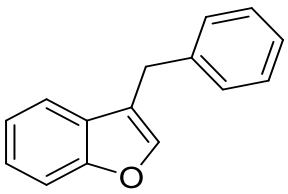

880-169-2_13C-3.esp
128.88
128.68
CHLOROFORM-d
77.43
76.59
126.59
130.14
123.81
121.81
150.27
146.50
138.54
38.10
Normalized Intensity
Chemical Shift (ppm)


H
N
O
O

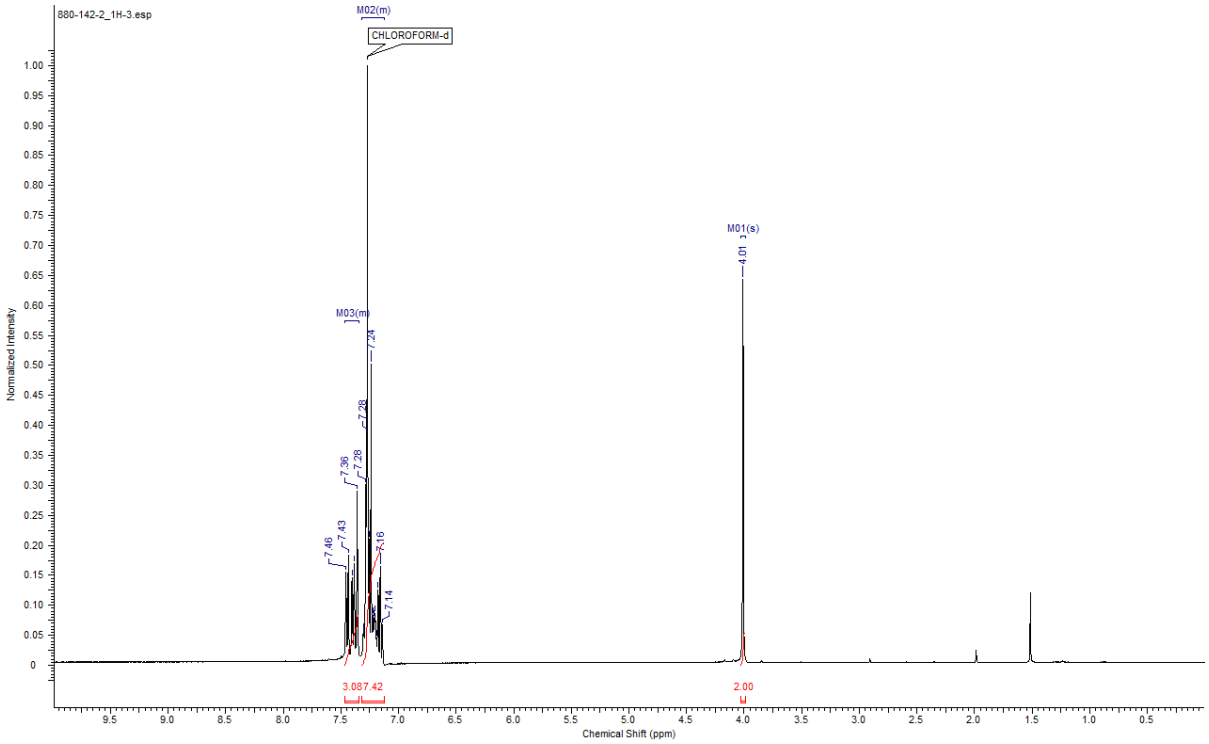
3n

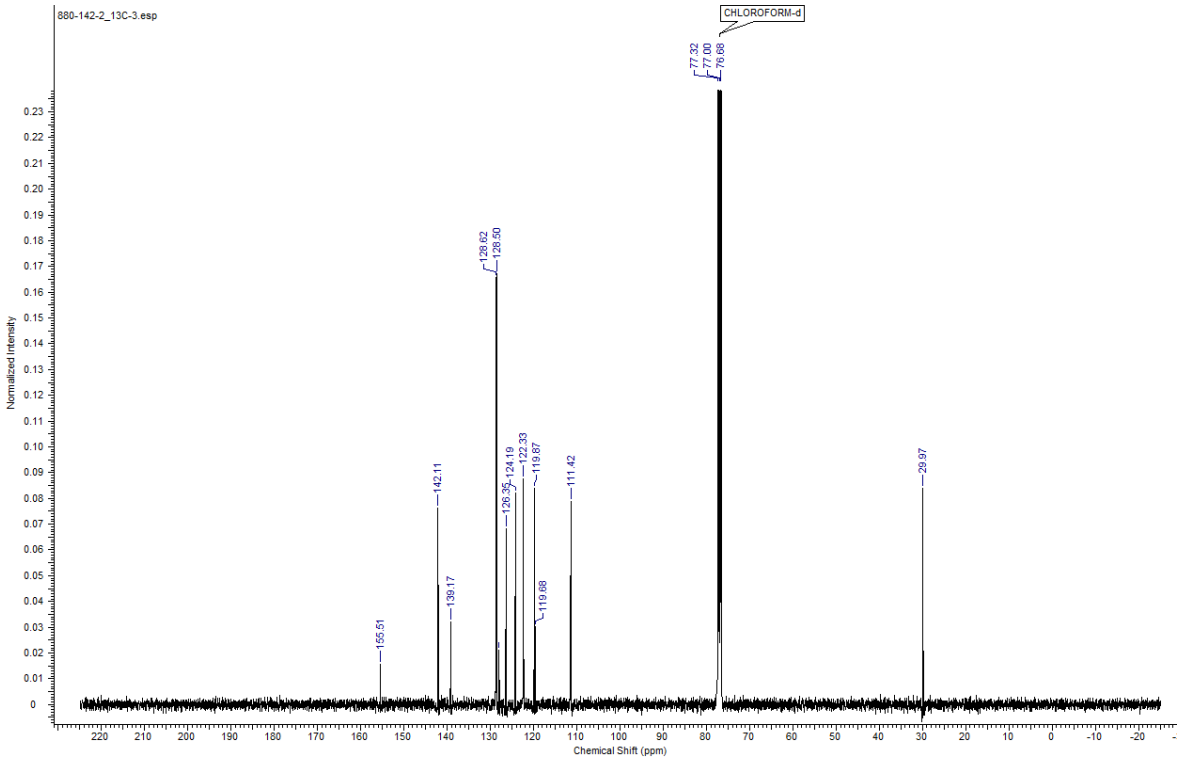

880-140H.esp
CHLOROFORM-d
9.14
7.49
7.29
7.23
7.17
7.15
4.44
4.42
4.39
4.07
1.43
1.41
1.40
1.05
1.08
3.05
4.90
2.15
2.00
3.32
Normalized Intensity
Chemical Shift (ppm)


880-140.011.001.1r.esp
CHLOROFORM-d
162.13
141.72
135.60
133.51
128.39
126.87
125.94
122.07
111.90
108.36
77.32
76.69
60.98
41.89
14.36
Normalized Intensity
Chemical Shift (ppm)

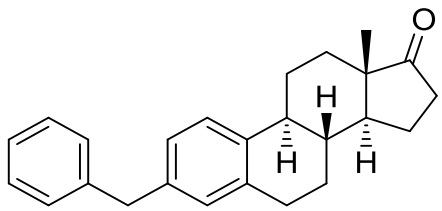


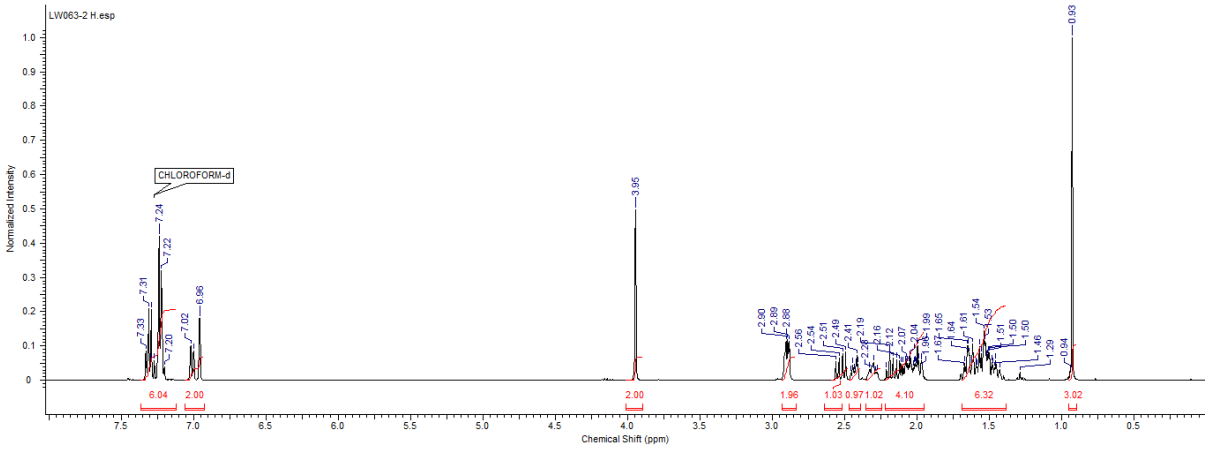
3o

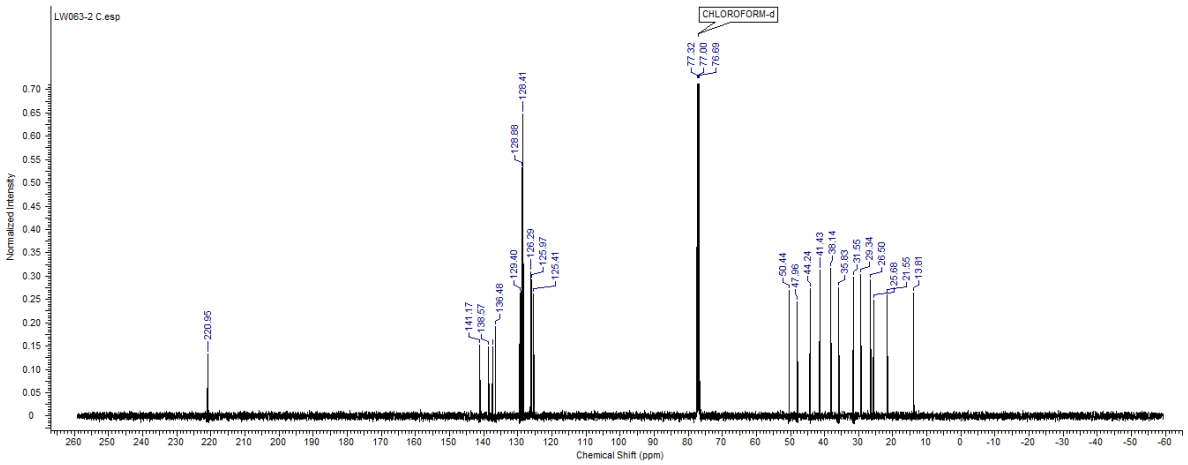

880-142-2_1H-3.esp
M02(m)
CHLOROFORM-d
M01(s)
M03(m)
7.24
7.28
7.36
7.28
7.46
7.43
7.16
7.14
4.01
3.087.42
2.00
Normalized Intensity
Chemical Shift (ppm)

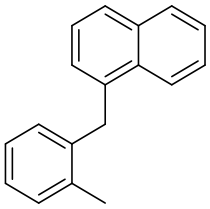

880-142-2_13C-3.esp
CHLOROFORM-d
77.32
77.00
76.68
139.62
128.50
142.11
126.35
124.19
122.33
119.87
111.42
139.17
119.68
155.51
29.97
Normalized Intensity
Chemical Shift (ppm)

3p


O
H
H
H

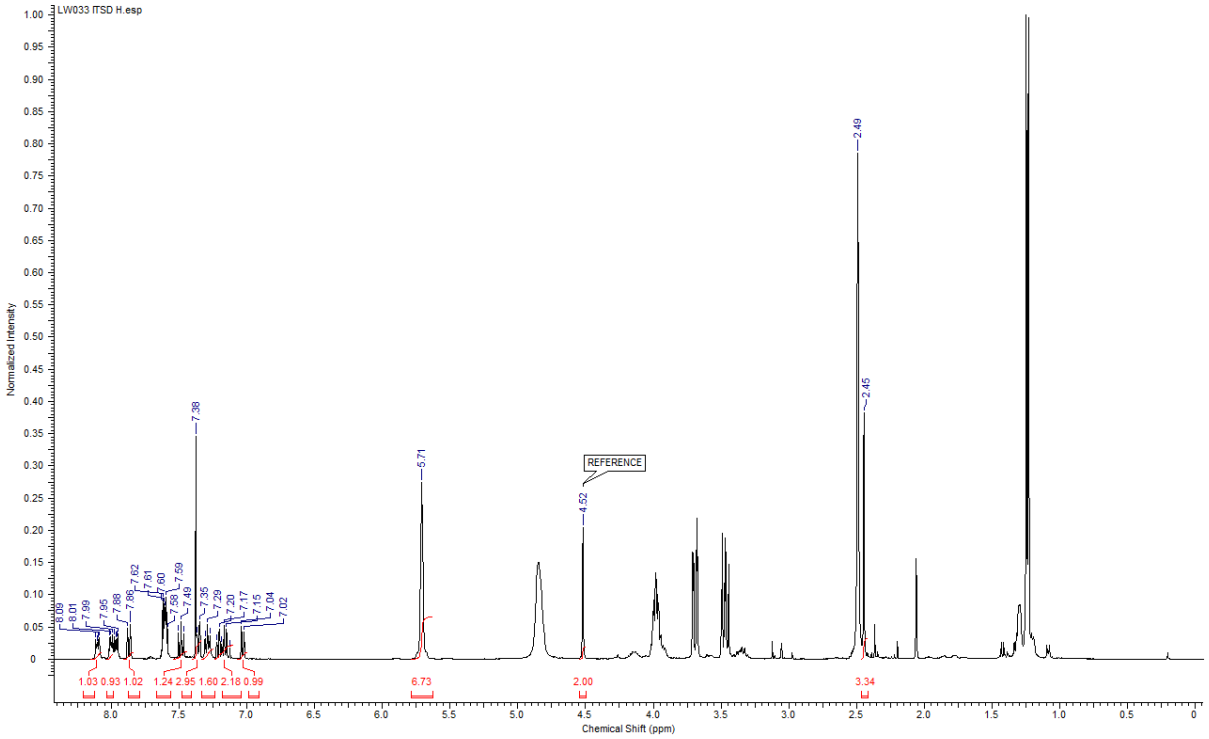

LW063-2 H.esp
Normalized Intensity
CHLOROFORM-d
7.33
7.31
7.24
7.22
7.20
7.02
6.96
3.95
2.90
2.89
2.88
2.56
2.54
2.51
2.49
2.41
2.19
2.16
2.12
2.07
2.04
1.99
1.67
1.65
1.64
1.61
1.54
1.53
1.50
1.50
1.46
1.29
0.94
0.93
6.04
2.00
2.00
1.96
1.03
0.97
1.02
4.10
6.32
3.02
Chemical Shift (ppm)

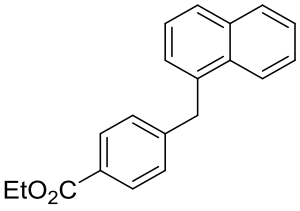

LW063-2 C.esp
Normalized Intensity
CHLOROFORM-d
77.32
77.00
76.69
220.95
141.17
138.57
136.48
129.40
128.88
126.41
126.29
125.97
125.41
60.44
47.96
44.24
41.43
38.14
35.83
31.55
29.34
26.50
25.68
21.55
13.81
Chemical Shift (ppm)



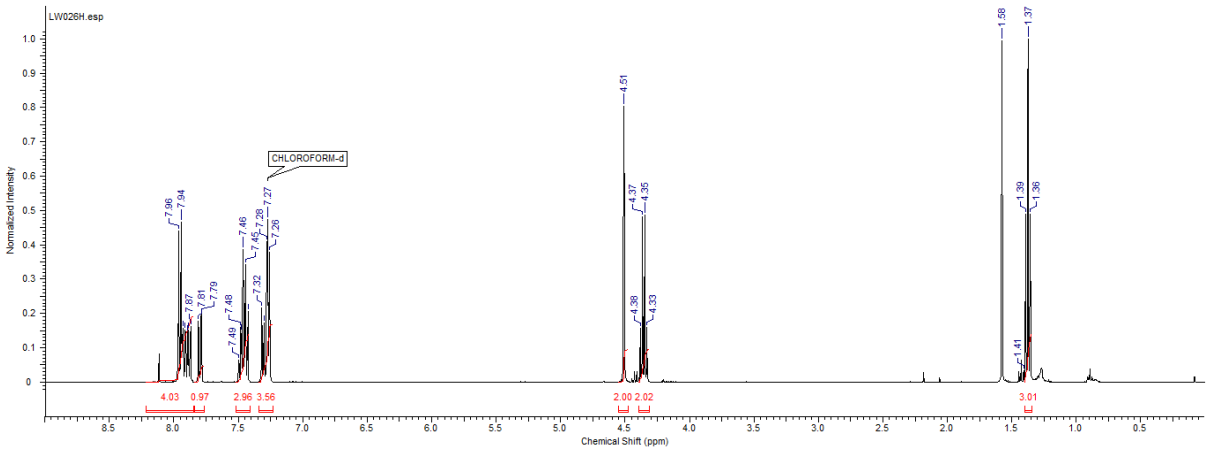
3q

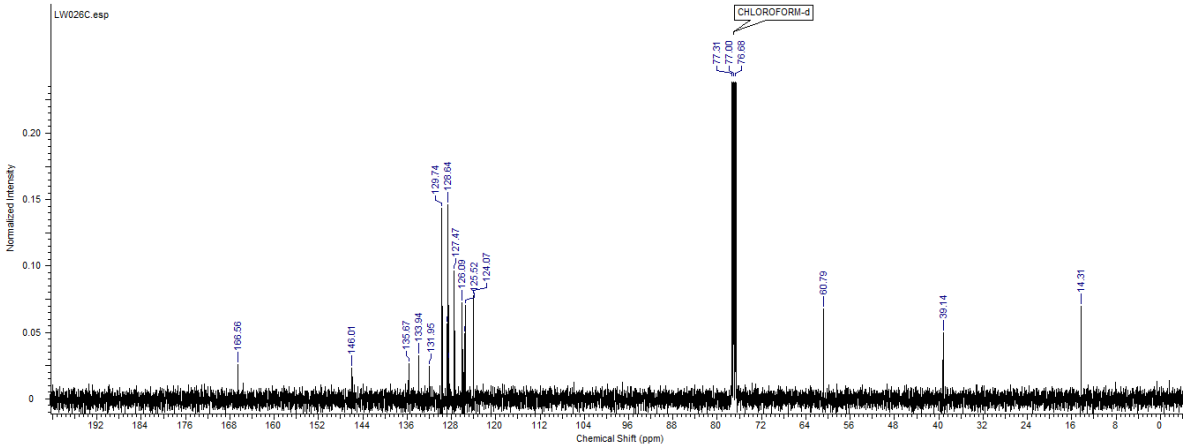
Internal standard NMR (1,5-cyclooctadiene)

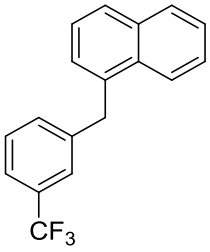



EtO2C

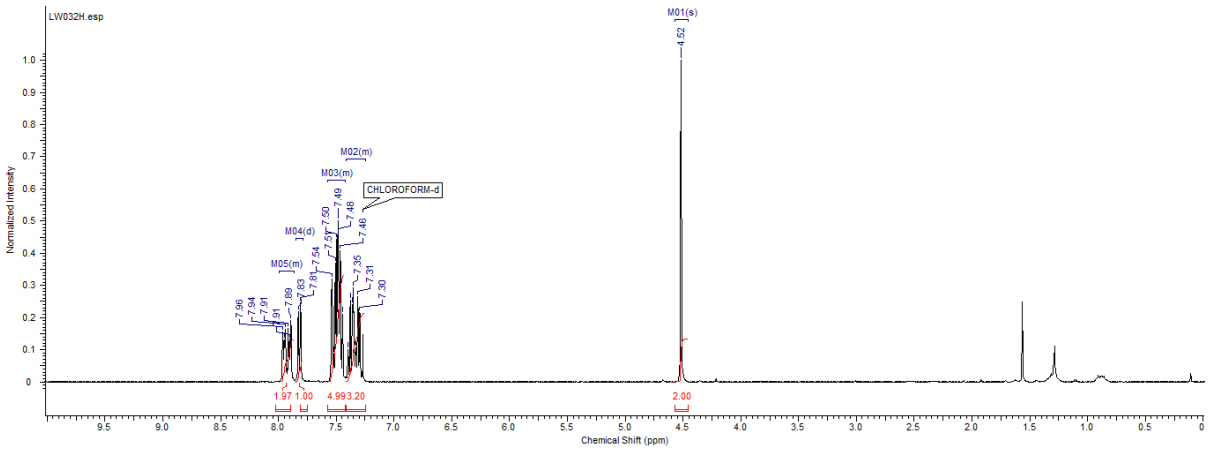
3r

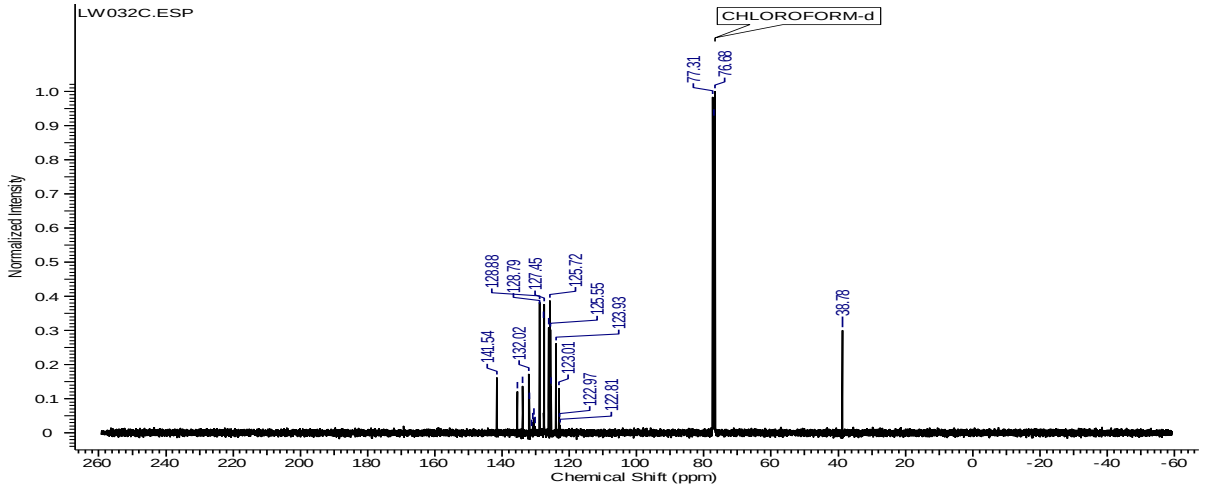

LW026H.esp
CHLOROFORM-d
Normalized Intensity
Chemical Shift (ppm)
7.96
7.94
7.87
7.81
7.79
7.48
7.46
7.45
7.32
7.28
7.27
7.26
4.51
4.38
4.37
4.35
4.33
1.58
1.41
1.39
1.37
1.36
4.03
0.97
2.96
3.56
2.00
2.02
3.01

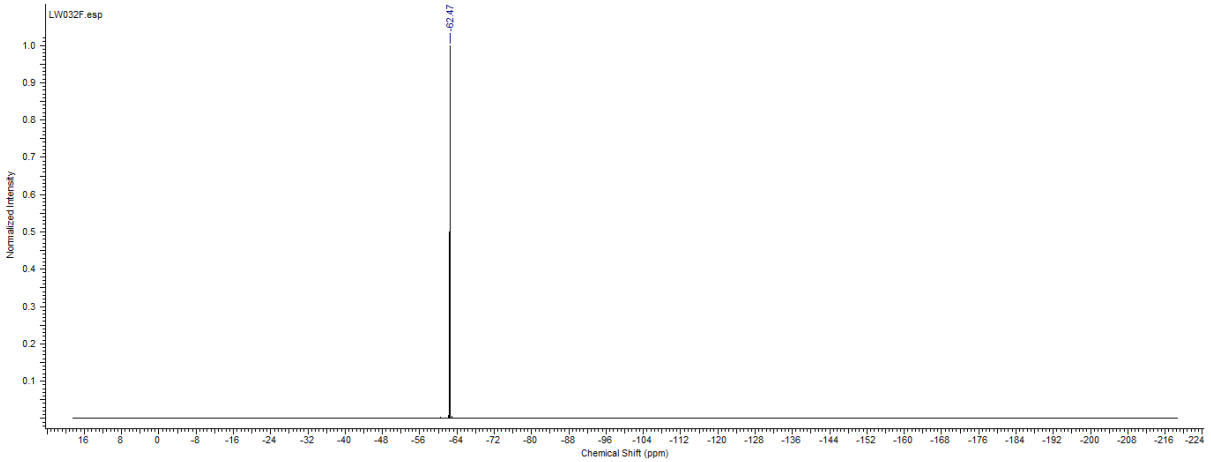

LW026C.esp
CHLOROFORM-d
Normalized Intensity
Chemical Shift (ppm)
77.31
77.00
76.68
166.56
146.01
135.67
133.94
131.95
129.74
128.64
127.47
126.09
125.52
124.07
60.79
39.14
14.31

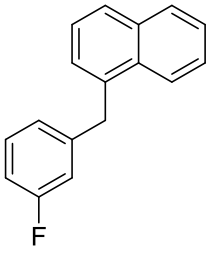

CF3

3s

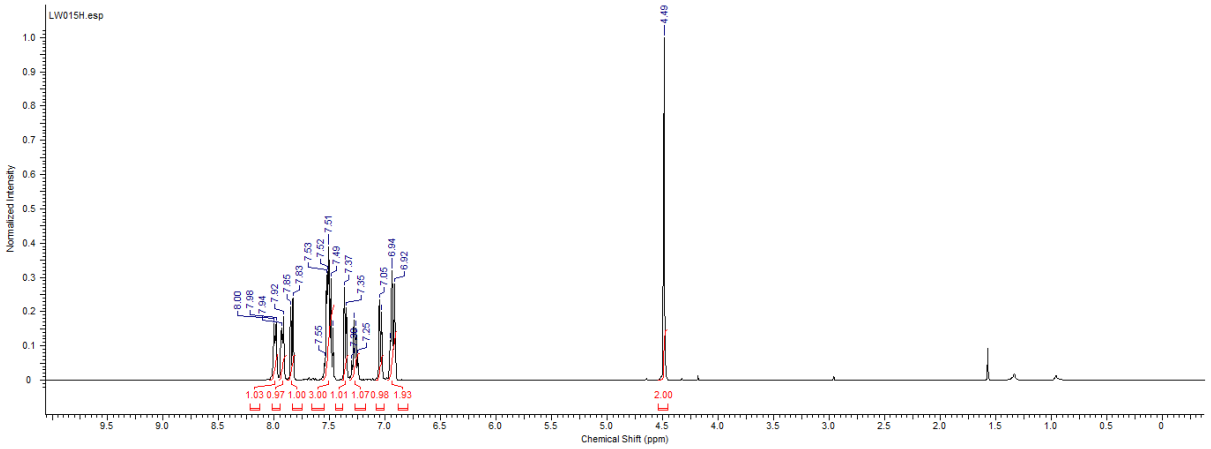

LW032H.esp
M01(s)
4.52
M02(m)
M03(m)
CHLOROFORM-d
M04(d)
M05(m)
7.96
7.94
7.91
7.89
7.83
7.81
7.54
7.50
7.49
7.48
7.46
7.35
7.31
7.30
1.97 1.00 4.99 3.20
2.00
Normalized Intensity
Chemical Shift (ppm)

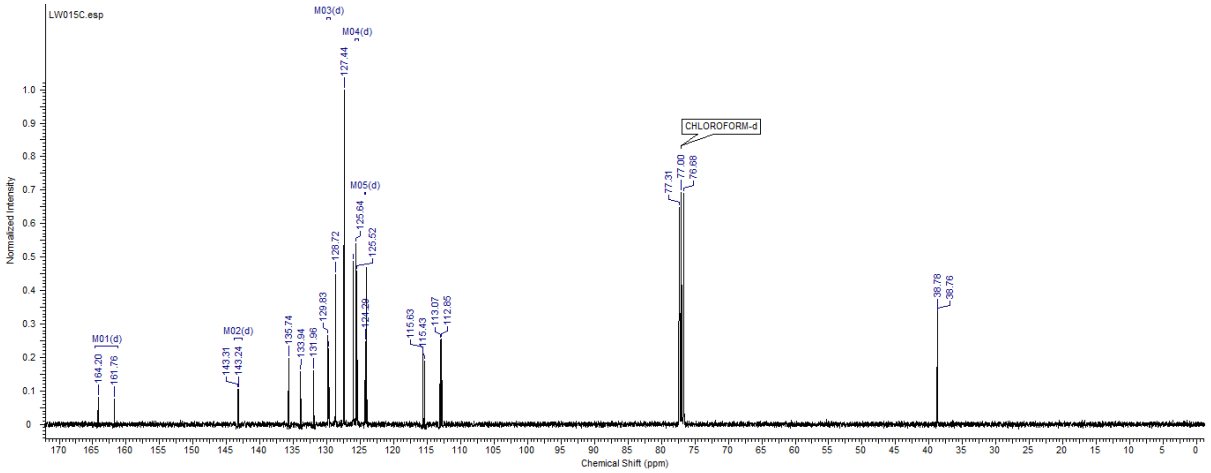

LW032C.ESP
CHLOROFORM-d
77.31
76.68
128.88
128.79
127.45
125.72
125.55
123.93
141.54
132.02
123.01
122.97
122.81
38.78
Normalized Intensity
Chemical Shift (ppm)

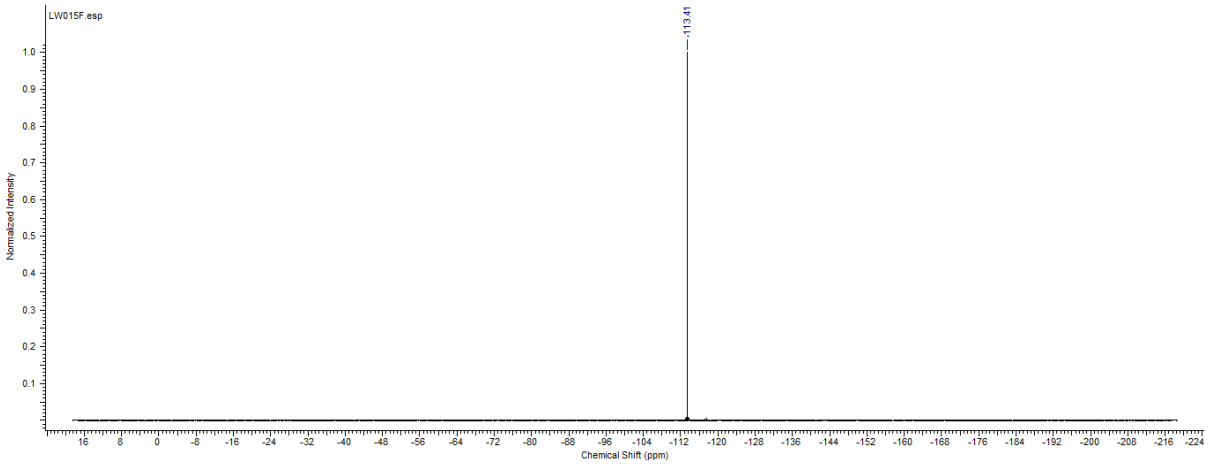

LW032F.esp
-62.47
Normalized Intensity
Chemical Shift (ppm)

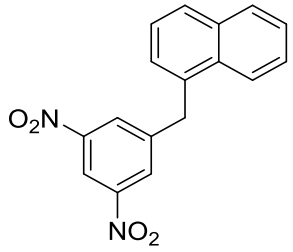

F

3t

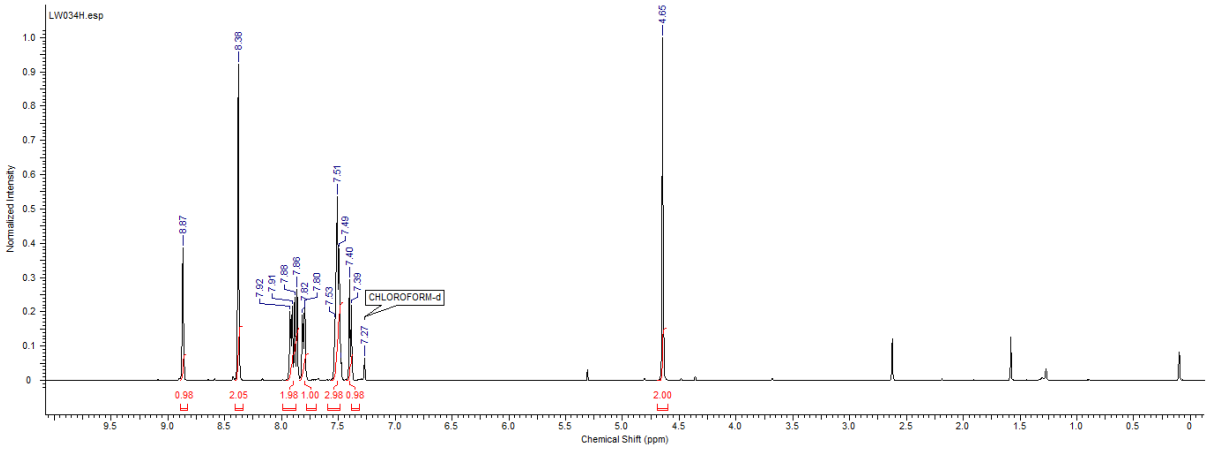

LW015H.esp
Normalized Intensity
Chemical Shift (ppm)
4.49
8.00
7.98
7.94
7.92
7.85
7.83
7.53
7.52
7.51
7.49
7.37
7.35
7.05
6.94
6.92
7.55
7.25
1.03 0.97 1.00 3.00 1.01 1.07 0.98 1.93
2.00

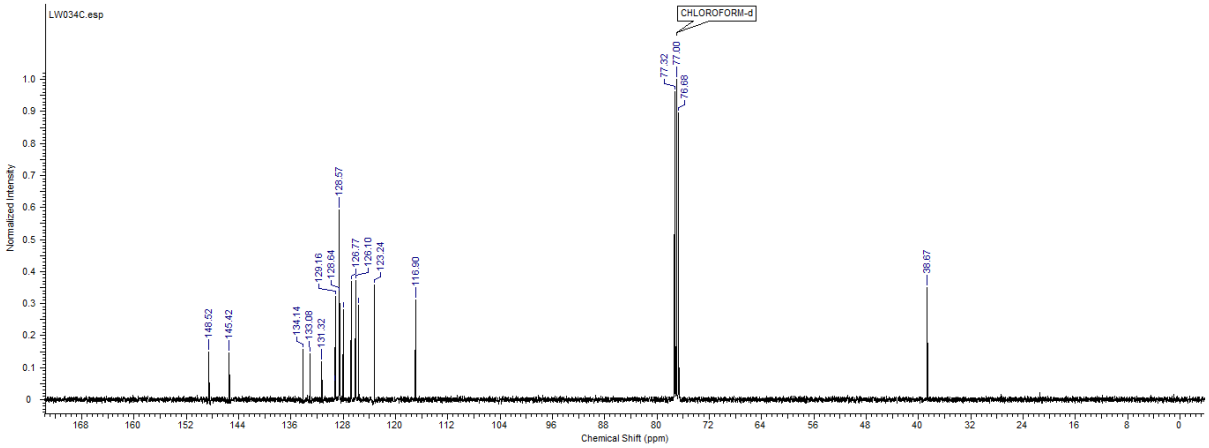

LW015C.esp
Normalized Intensity
Chemical Shift (ppm)
M01(d)
M02(d)
M03(d)
M04(d)
M05(d)
164.20
161.76
143.31
143.24
135.74
133.94
131.98
129.83
128.72
127.44
125.64
125.52
124.29
115.83
115.43
113.07
112.85
CHLOROFORM-d
77.31
77.00
76.68
38.78
38.76

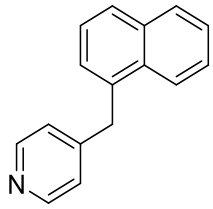

LW015F.esp
Normalized Intensity
Chemical Shift (ppm)
-113.41


O_2N
NO_2

3u

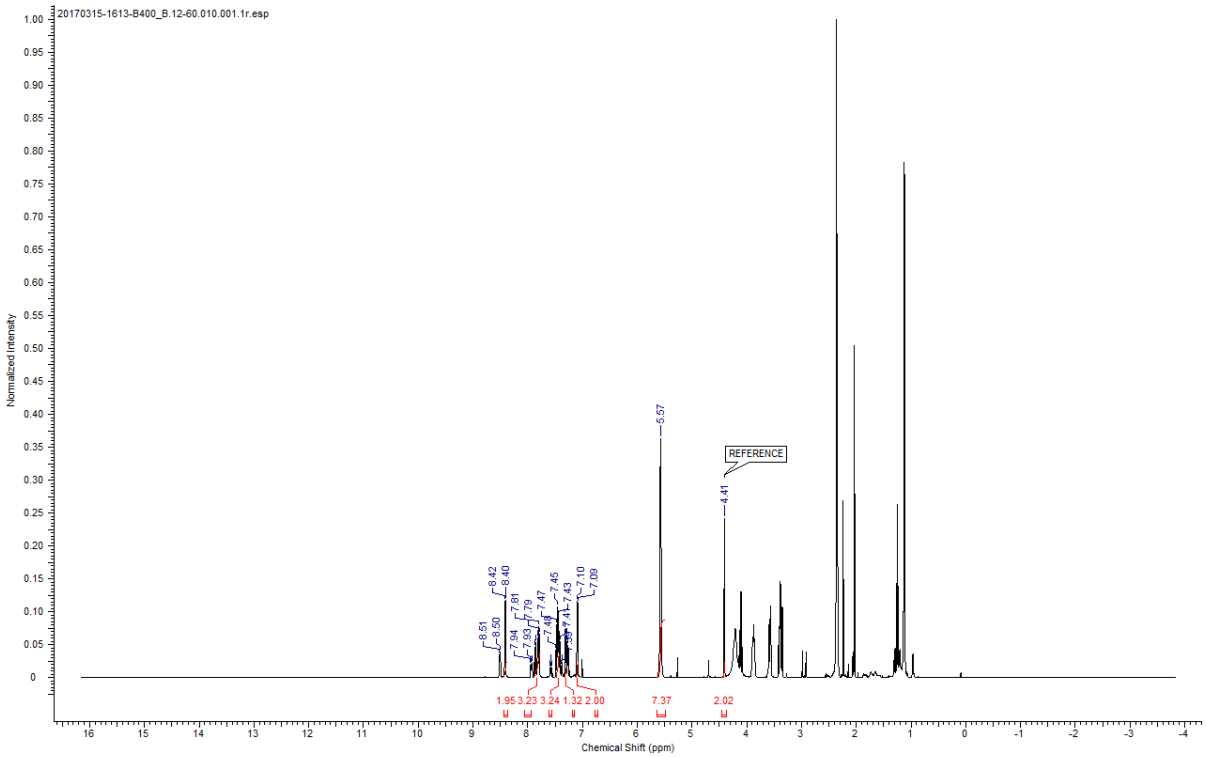

LW034H.esp
Normalized Intensity
Chemical Shift (ppm)
8.87
8.38
7.92
7.91
7.89
7.86
7.82
7.80
7.53
7.51
7.49
7.40
7.39
7.27
CHLOROFORM-d
4.65
0.98
2.05
1.98
1.00
2.98
0.98
2.00


LW034C.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.32
77.00
76.68
148.52
145.42
134.14
133.08
131.32
129.16
128.84
128.57
126.77
126.10
123.24
116.90
39.67

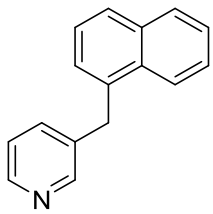


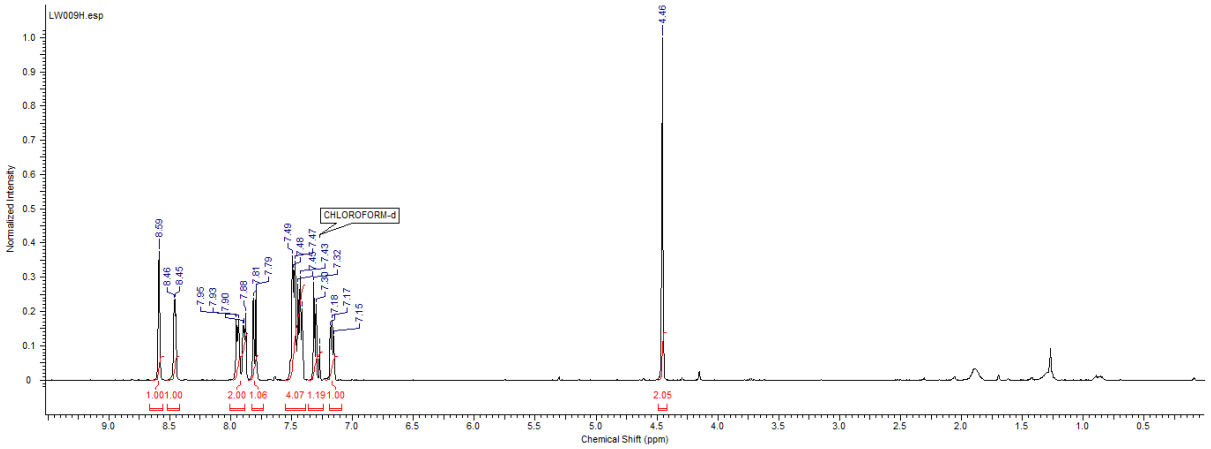
3v

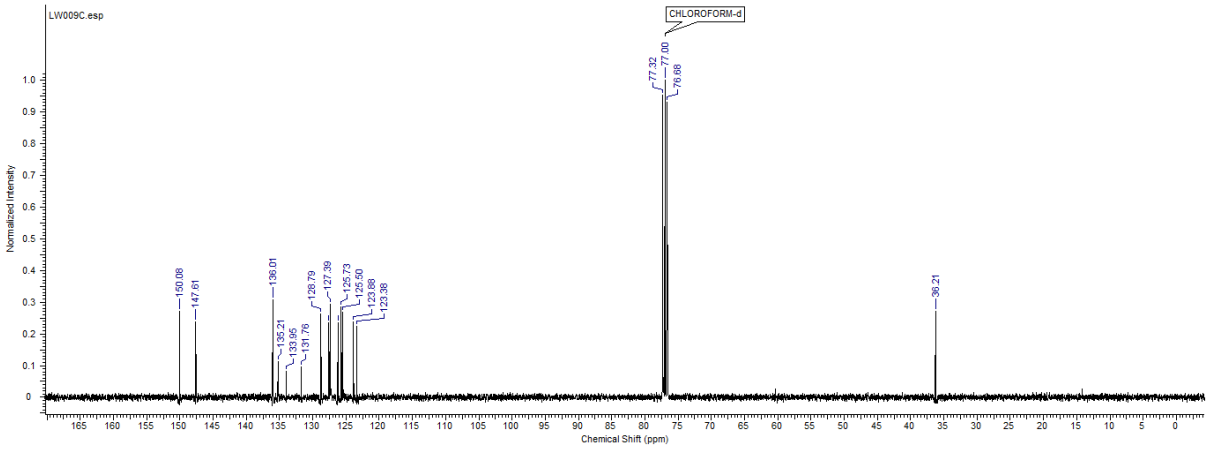
Internal standard NMR (1,5-cyclooctadiene)

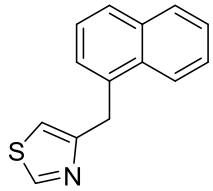


3x

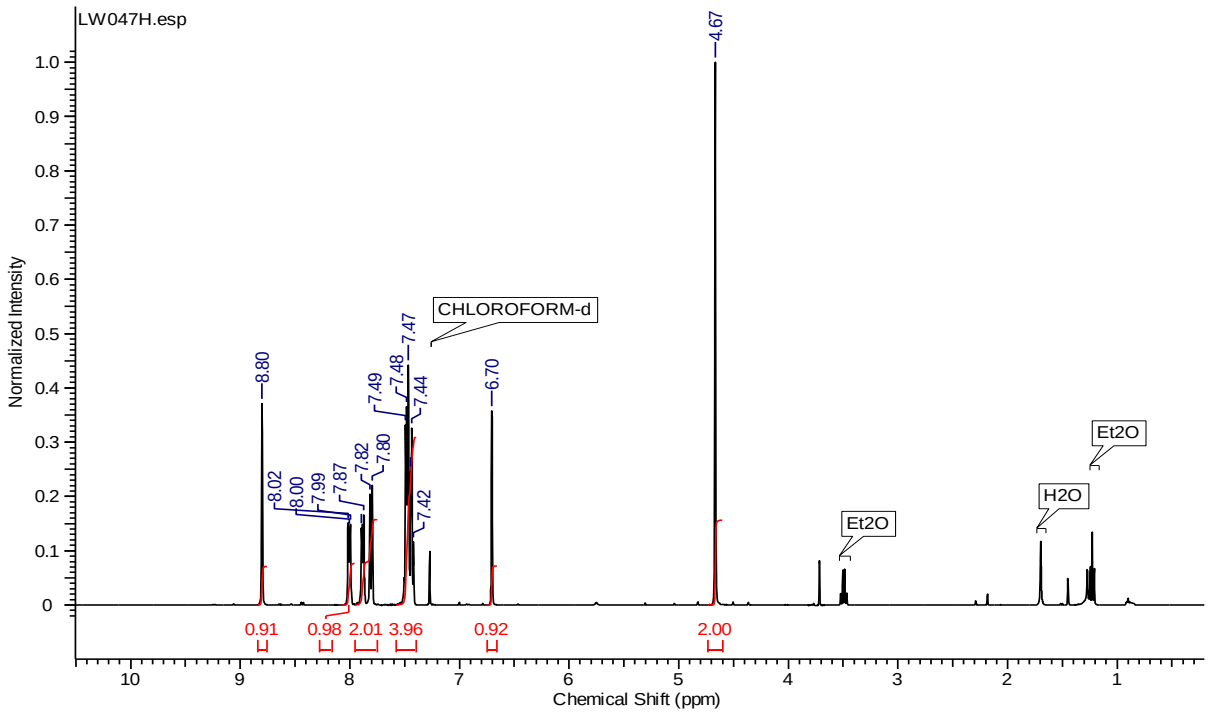


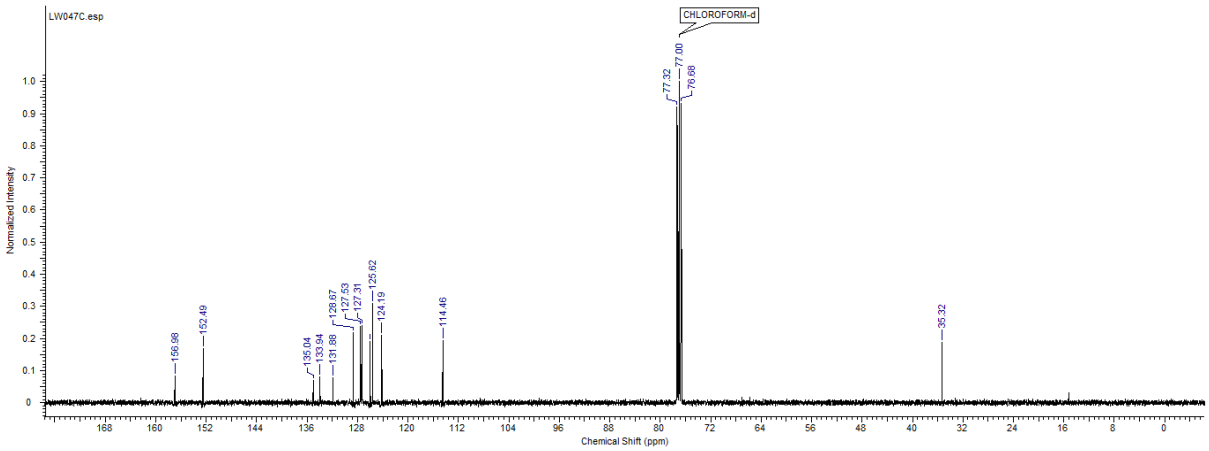

LW009H.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
8.59
8.46
8.45
7.95
7.93
7.90
7.89
7.81
7.79
7.49
7.47
7.43
7.32
7.18
7.17
7.15
4.46
1.00 1.00
2.00 1.06
4.07 1.19 1.00
2.05

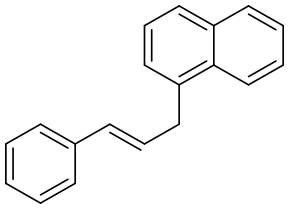

LW009C.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.32
77.00
76.68
150.08
147.61
136.01
135.21
133.95
131.76
128.79
127.39
125.73
125.50
123.88
123.38
39.21


S
N

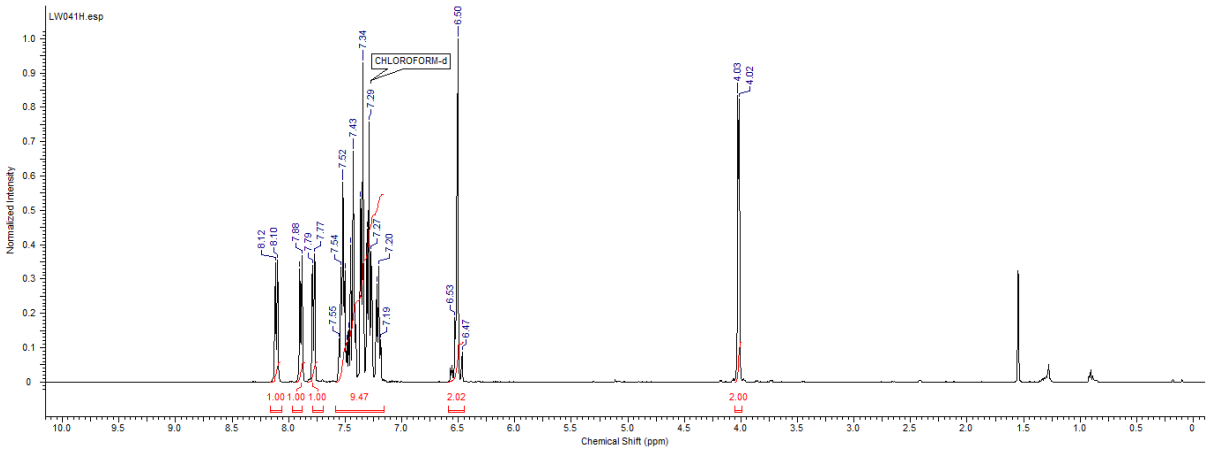
3y

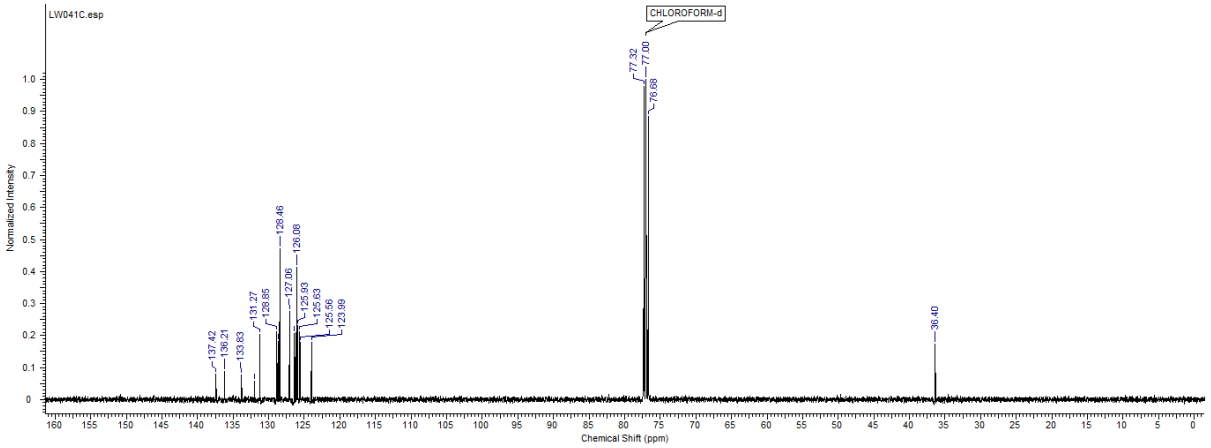

LW047H.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
Et2O
H2O
Et2O
8.80
8.02
8.00
7.99
7.87
7.82
7.80
7.49
7.48
7.47
7.44
7.42
6.70
4.67
0.91
0.98
2.01
3.96
0.92
2.00

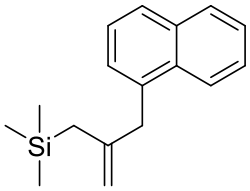

LW047C.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.32
77.00
76.68
166.98
152.49
135.04
133.94
131.88
129.67
127.53
127.31
125.62
124.19
114.46
35.32



4a

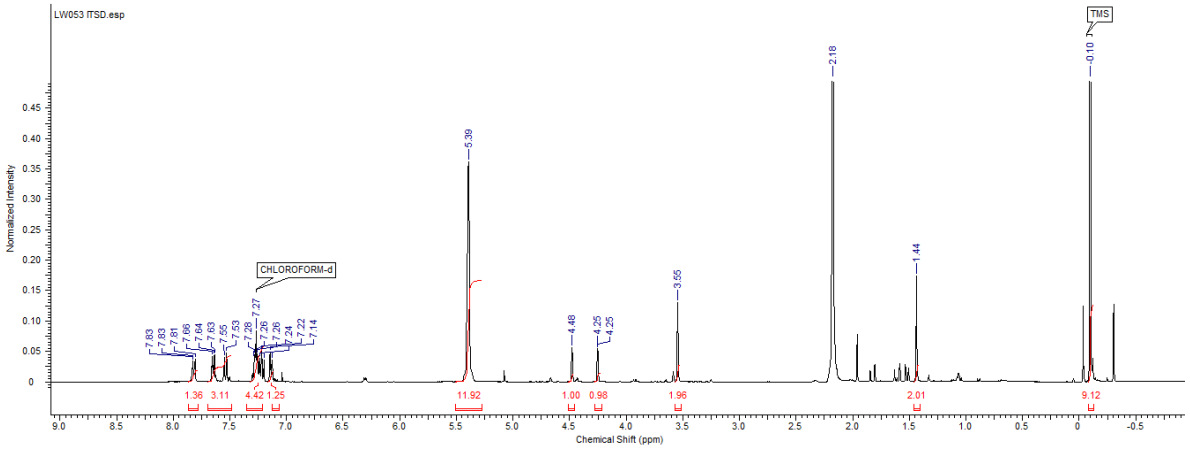

LW041H.esp
CHLOROFORM-d
8.12
8.10
7.88
7.79
7.77
7.54
7.55
7.34
7.29
7.43
7.52
7.27
7.20
7.19
6.50
6.53
6.47
4.03
4.02
1.00 1.00 1.00 9.47 2.02 2.00
Normalized Intensity
Chemical Shift (ppm)

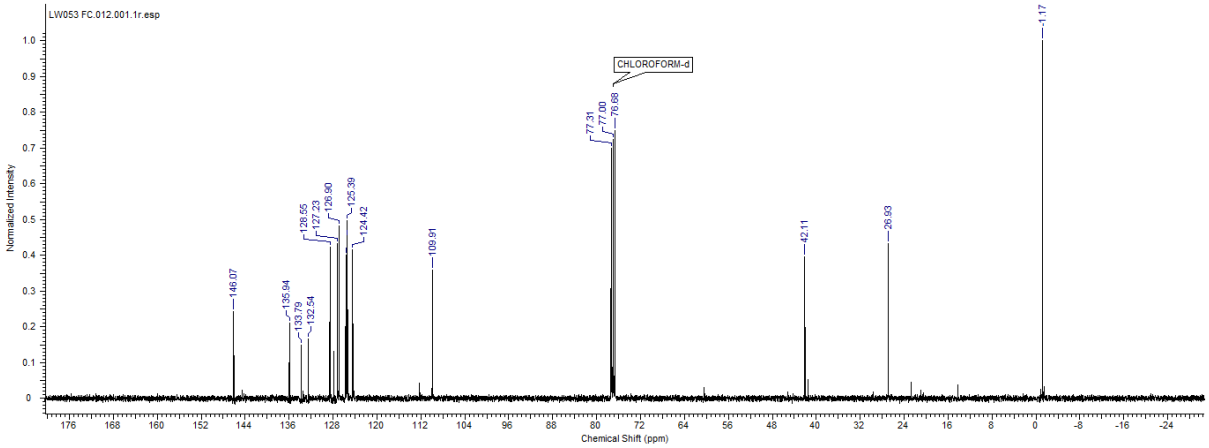

LW041C.esp
CHLOROFORM-d
77.32
77.00
76.68
128.46
126.08
127.06
125.93
125.63
125.56
123.99
131.27
128.85
137.42
136.21
133.83
36.40
Normalized Intensity
Chemical Shift (ppm)

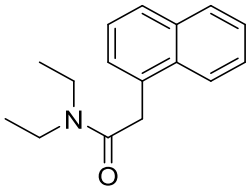


4b

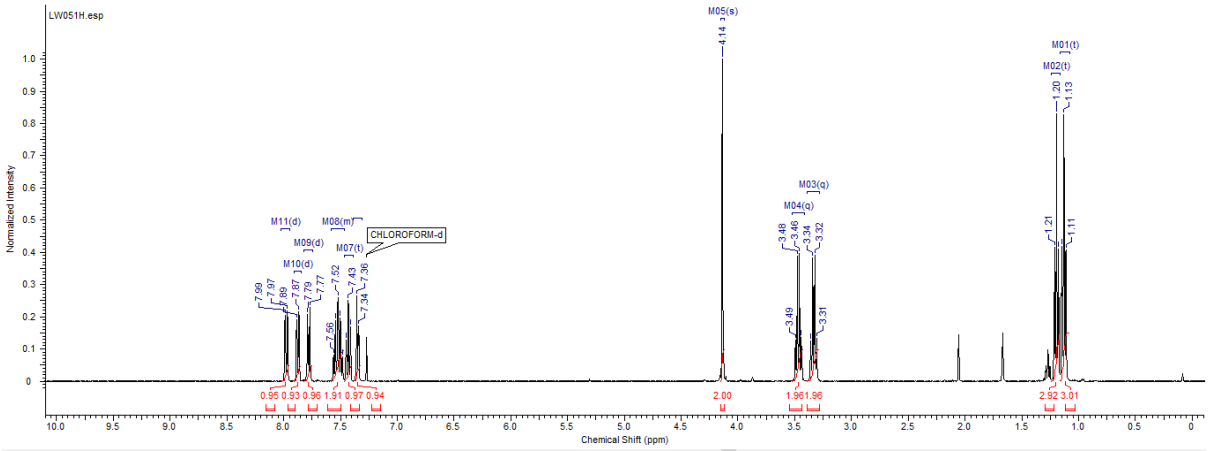
Internal standard NMR (1,5-cyclooctadiene)

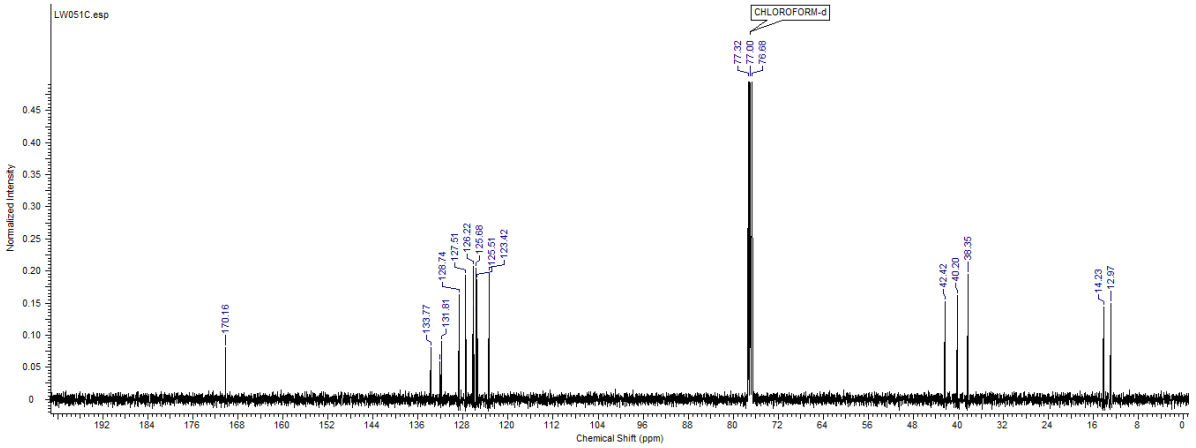


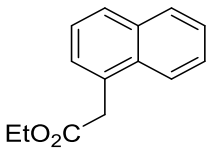




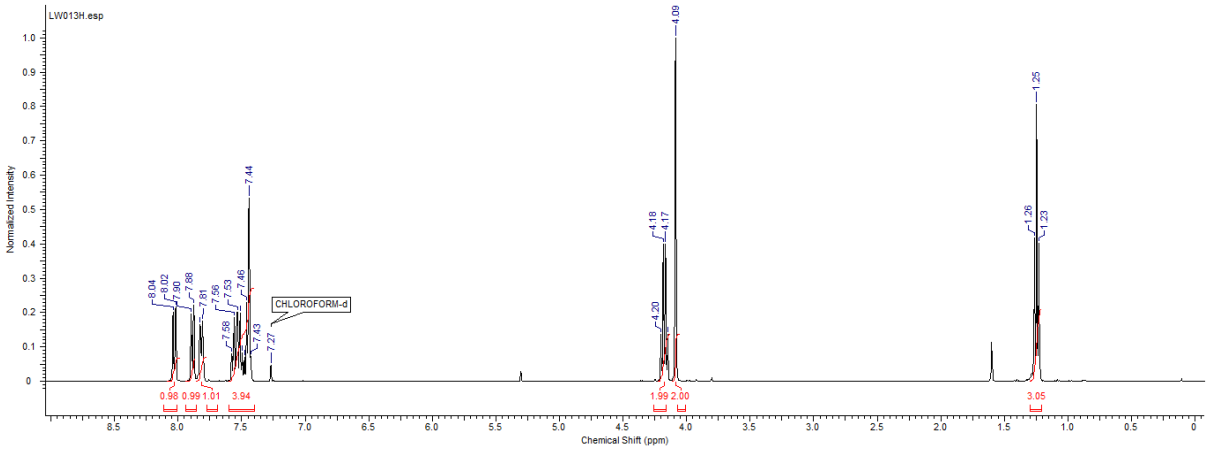
5a

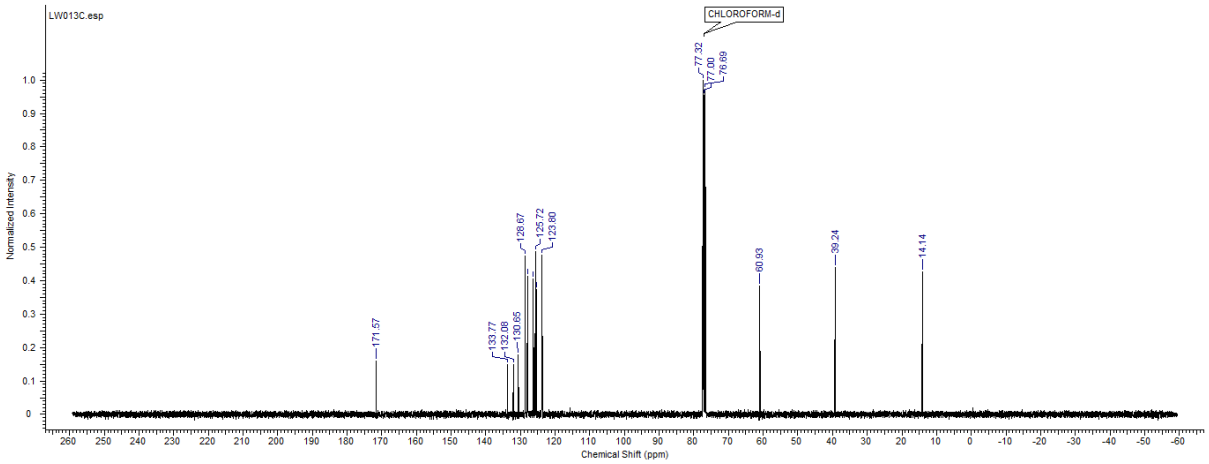

LW051H.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
M01(t)
M02(t)
M03(q)
M04(q)
M05(s)
M07(t)
M08(m)
M09(d)
M10(d)
M11(d)
7.99
7.97
7.89
7.87
7.79
7.77
7.52
7.43
7.36
7.34
7.26
3.48
3.46
3.34
3.32
3.49
3.31
1.21
1.20
1.19
1.11
0.95 0.93 0.96 1.91 0.97 0.94
2.00
1.96 1.96
2.92 3.01

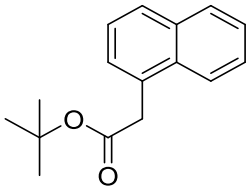

LW051C.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.32
77.00
76.68
170.16
133.77
131.81
128.74
127.51
126.22
125.68
125.51
123.42
42.42
40.20
38.35
14.23
12.97


EtO2C

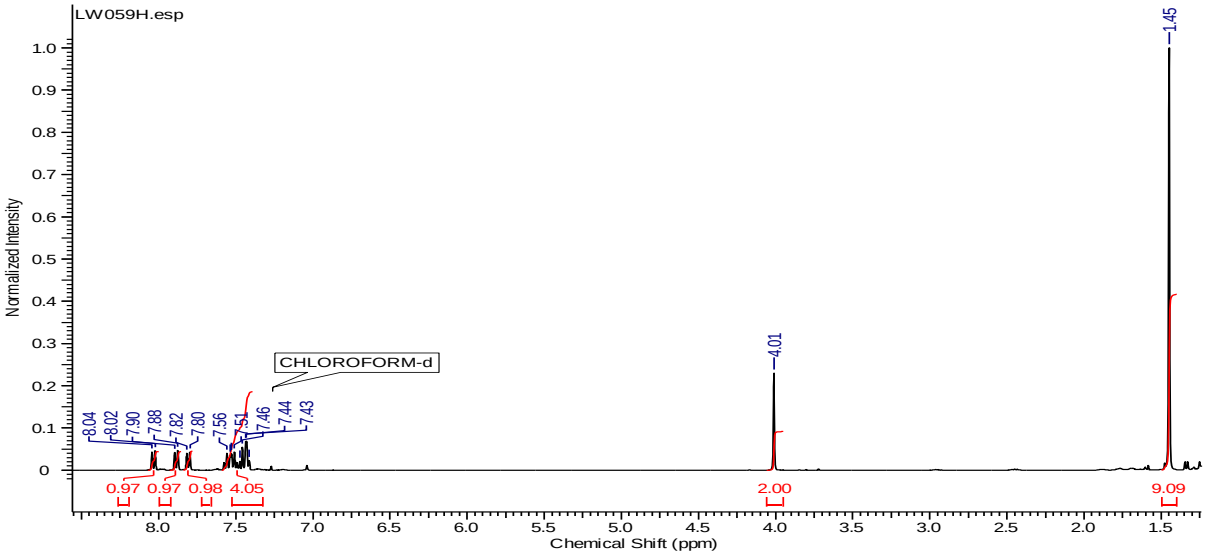
5b

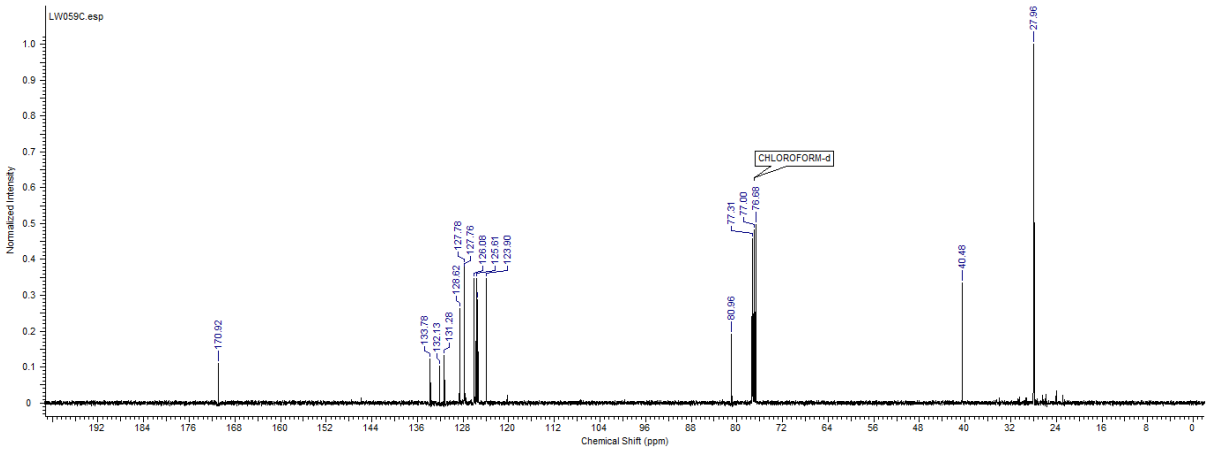

LW013H.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
8.04
8.02
7.90
7.88
7.86
7.58
7.53
7.46
7.44
7.43
7.27
4.20
4.18
4.17
4.09
1.26
1.25
1.23
0.98
0.99
1.01
3.94
1.99
2.00
3.05

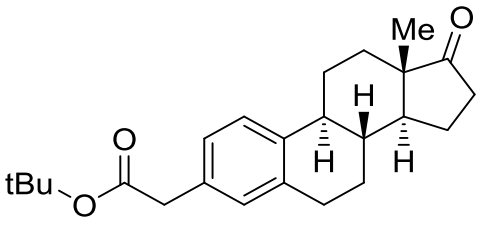

LW013C.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
77.32
77.00
76.69
171.57
133.77
132.08
130.65
128.67
125.72
123.60
60.93
39.24
14.14



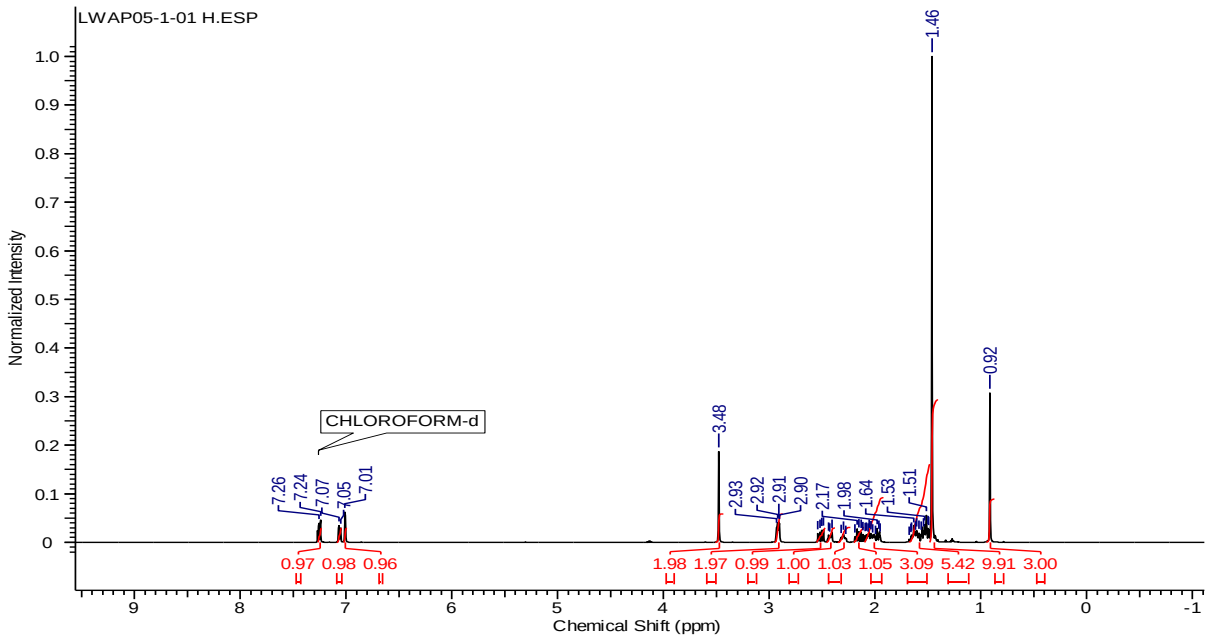
5c

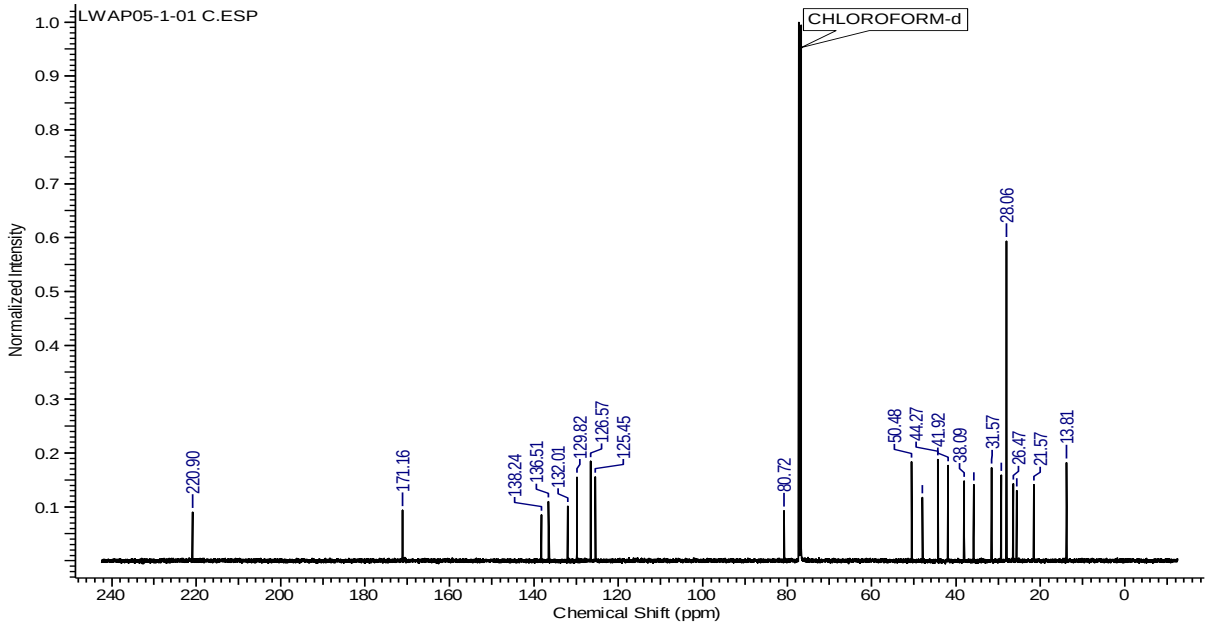

LW059H.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
8.04
8.02
7.90
7.88
7.82
7.80
7.56
7.51
7.46
7.44
7.43
4.01
1.45
0.97
0.97
0.98
4.05
2.00
9.09

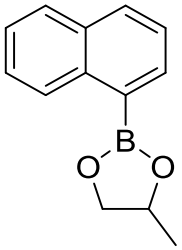

LW059C.esp
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
170.92
133.78
132.13
131.28
128.62
127.78
127.76
126.88
126.85
123.90
77.31
77.00
76.68
80.96
40.48
27.96


Me
O
H
H
H
O
tBu
O

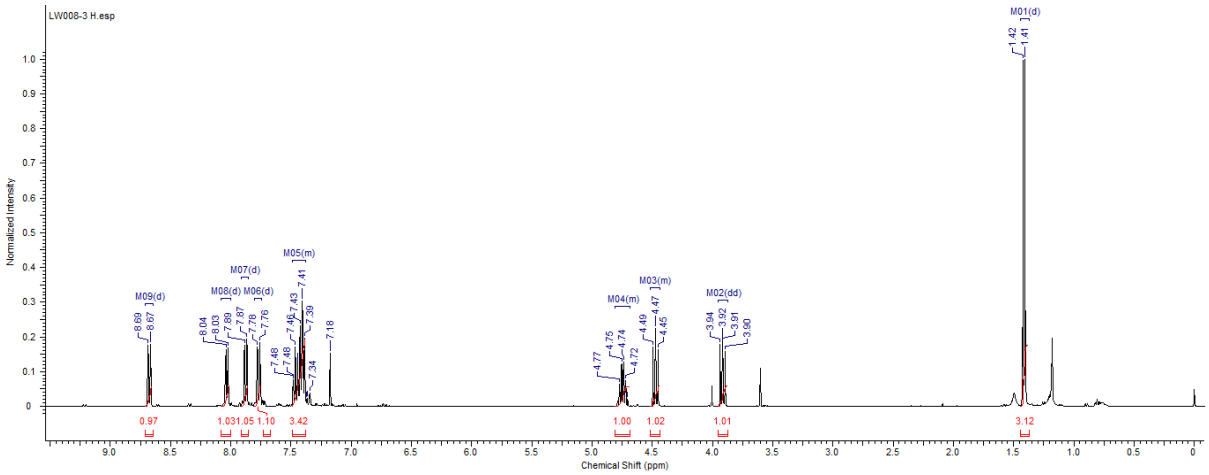
5d

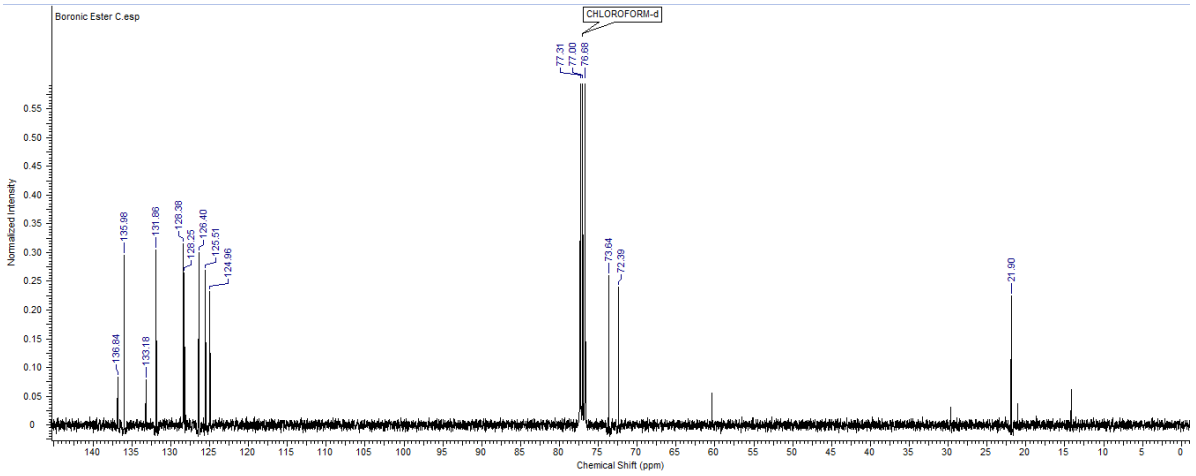

LWAP05-1-01 H.ESP
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
7.26
7.24
7.07
7.05
7.01
3.48
2.93
2.92
2.91
2.90
2.17
1.98
1.64
1.53
1.51
1.46
0.92
0.97 0.98 0.96
1.98 1.97 0.99 1.00 1.03 1.05 3.09 5.42 9.91 3.00


LWAP05-1-01 C.ESP
Normalized Intensity
Chemical Shift (ppm)
CHLOROFORM-d
220.90
171.16
138.24
136.51
132.01
129.82
126.57
125.45
80.72
50.48
44.27
41.92
38.09
31.57
28.06
26.47
21.57
13.81



7a


LW008-3 H.esp
Normalized Intensity
Chemical Shift (ppm)
M01(d)
M02(dd)
M03(m)
M04(m)
M05(m)
M06(d)
M07(d)
M08(d)
M09(d)


Boronic Ester C.esp
CHLOROFORM-d
Normalized Intensity
Chemical Shift (ppm)