Electronic Supplementary Material (ESI) for ChemComm.

Arylation and Alkenylation of Activated Alkyl Halides using Sulfonamides

*Stuart Johnson, Ervin Kovács and Michael F. Greaney**

School of Chemistry, University of Manchester, Oxford Road, Manchester, UK, M13 9PL, UK

Supporting Information

1. General remarks

^{1}H NMR, ^{13}C {^{1}H} NMR and ^{19}F NMR were recorded at 500/400 MHz, 126/101 MHz, 470/376 MHz on Bruker Avance 500 or 400 spectrometers. All ^{1}H NMR and ^{13}C chemical shifts were referenced to the residual solvent peak of $CDCl_3$ (^{1}H referenced to 7.26 ppm and ^{13}C referenced to 77.16 ppm), $(CD_3)_2SO$ (^{1}H referenced to 2.50 ppm and ^{13}C referenced to 39.52 ppm), methanol (^{1}H referenced to 3.31 ppm and ^{13}C referenced to 49.00 ppm), CD_3CN (^{1}H referenced to 1.94 ppm and ^{13}C referenced to 1.32 ppm), and acetone (^{1}H referenced to 2.05 ppm and ^{13}C referenced to 29.84 ppm). All ^{19}F chemical shifts were unadjusted from raw data. All chemical shifts are quoted in parts per million (ppm), measured from the centre of the signal except in the case of multiplets, which are quoted as a range. Coupling constants are quoted to the nearest 0.1 Hz. Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sxt), multiplet (m), broad singlet (br. s) and combinations thereof. Assignment of spectra was aided by DEPT 135 and 2D NMR spectroscopy (COSY, HSQC and HMBC). Assignments are provided in the following format: chemical shift (multiplicity, coupling constant, integration, description of functional group, letter referenced to molecule drawn above).

Low resolution mass spectrometry was performed on an Agilent 6100 mass spectrometer (ESI ionisation) and Hewlett Packard 5971 MSD (GC/MS with EI). High resolution mass spectrometry was performed on a Waters QTOF with ESI/APCI ionisation and a Thermo Finnigan MAT95XP (EI).

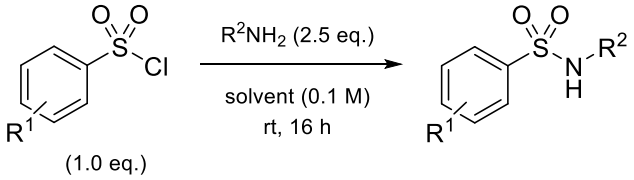
Melting points were determined using a Kofler hot-stage apparatus and are uncorrected.

Thin layer chromatography (TLC) was performed on commercially available pre-coated TLC plates (Merck Silica gel 60 F254 aluminium sheets). Visualisation was either achieved under UV light at 254 nm or with a $KMnO_4$ stain.

Column chromatography was conducted on silica gel (Sigma Aldrich, 40-63 µm, 60 Å) or Biotage KP-Sil or Snap Ultra cartridges on a Biotage Isolera automated columning machine.

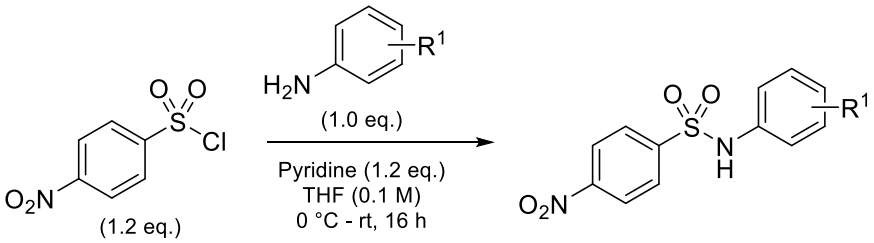
2. Synthesis of Arylsulfonamides

General Procedure A for the synthesis of *N*-methyl arylsulfonamides



To a solution of sulfonyl chloride (1.0 eq.) in diethyl ether or ethyl acetate (0.10 M), alkylamine (2.5 eq.) was added dropwise. The reaction mixture was stirred for 16 hours at room temperature, then it was concentrated under reduced pressure. HCl (1.0 M) was added, the organic compounds were extracted with DCM. The combined organic layers were washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel.

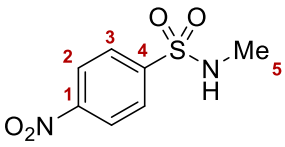
General Procedure B for the synthesis of *N*-phenyl arylsulfonamides



To a solution of substituted aniline (1.0 eq.) in freshly distilled THF (0.10 M), pyridine (1.2 eq.) and 4-nitrobenzenesulfonyl chloride (1.2 eq.) were added at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for 16 hours. The reaction was quenched with aqueous saturated NH_4Cl. The organic layers were extracted with EtOAc, washed with H_2O and brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure to give the crude product, which was purified by column chromatography on silica gel.

2.1 *N*-Alkyl Sulfonamide Syntheses

4-nitro-*N*-methylbenzenesulfonamide 6a



Prepared according to **General Procedure A** from 4-nitrobenzenesulfonyl chloride (4.5 mmol, 1.00 g), methylamine (30 wt% in EtOH, 11 mmol, 1.17 mL), Et_2O (45.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6a** as a pale yellow solid (888 mg, 4.1 mmol, 91%), m.p. 93–95 °C.

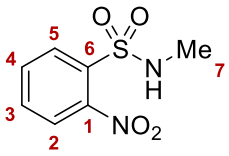
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 8.09 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 4.67 (q, *J* = 5.2 Hz, 1H, N*H*), 2.76 (d, *J* = 5.2 Hz, 3H, C*H*$_3$-5); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.3 (C-1), 145.0 (C-4), 128.6 (C-3), 124.6 (C-2), 29.5 (C-5).

IR (neat film, cm^{-1}): 3302, 3107, 2985, 1733, 1536, 1383, 1354, 1174, 854, 739.

MS (ES$^-$) found *m*/*z* 215 [M–H]$^-$; **HRMS** (ES$^-$) found 215.0110, $C_7H_7N_2O_4S$ [M–H]$^-$ requires 215.0121.

Data is in accordance with literature reports.[1]

2-nitrobenzene-*N*-methyl-sulfonamide 6b

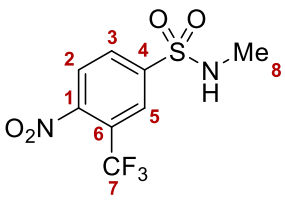


Prepared according to **General Procedure A** from 2-nitrobenzenesulfonyl chloride (2.3 mmol, 510 mg), methylamine (30 wt% in EtOH, 5.8 mmol, 595 µL), Et_2O (23.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6b** as a white solid (218 mg, 1.0 mmol, 44%).

^{1}H NMR (400 MHz, CD_3CN): δ 8.16–8.11 (m, 1H, C*H*$_{ar}$-5), 7.90–7.85 (m, 1H, C*H*$_{ar}$-2), 7.78–7.73 (m, 2H, C*H*$_{ar}$-3, 4), 5.23 (br. s, 1H, NH), 2.79 (d, J = 5.3 Hz); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.4 (C-1), 133.8 (C-4), 132.8 (C-3), 132.6 (C-6), 131.7 (C-5), 125.6 (C-2), 29.9 (C-7).

Data is in accordance with literature reports.[2]

4-nitro-3-(trifluoromethyl)-*N*-methylbenzenesulfonamide 6c



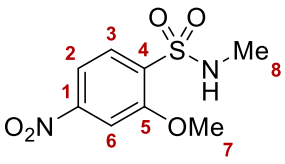
Prepared according to **General Procedure A** from 4-nitro-3-(trifluoromethyl)benzenesulfonyl chloride (0.92 mmol, 263 mg), methylamine (30 wt% in EtOH, 2.3 mmol, 239 µL), Et_2O (10.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6c** as a dark brown solid (225 mg, 0.79 mmol, 86%), m.p. 81–84 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 1.9 Hz, 1H, CH_{ar}-5), 8.25 (dd, *J* = 8.4, 1.9 Hz, 1H, CH_{ar}-3), 8.04 (d, *J* = 8.4 Hz, 1H, CH_{ar}-2), 4.65 (q, *J* = 5.2 Hz, 1H, N*H*), 2.80 (d, *J* = 5.2 Hz, 3H, CH_3-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 150.2 (C-1), 143.9 (C-4), 132.2 (C-3), 127.2–127.1 (m, C-5), 126.3 (q, *J* = 22.6 Hz, C-6), 126.1 (C-2), 123.8 (q, *J* = 225.5 Hz, C-7), 29.5 (C-8); **^{19}F NMR** (376 MHz, $CDCl_3$): δ –60.16.

IR (neat film, cm^{-1}): 3307, 3114, 3089, 3043, 2770, 1614, 1543, 1307, 1291, 836, 639.

MS (ES^-) found *m*/*z* 283 $[M–H]^-$; **HRMS** (ES^-) found 283.0005, $C_8H_6F_3N_2O_4S$ $[M–H]^-$ requires 282.9995.

4-nitro-2-methoxy-*N*-methylbenzenesulfonamide 6d



Prepared according to **General Procedure A** from 4-nitro-2-methoxybenzenesulfonyl chloride (1.0 mmol, 256 mg), methylamine (30 wt% in EtOH, 2.6 mmol, 269 µL), Et_2O (10.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6d** as a clear yellow solid (237 mg, 0.96 mmol, 94%), m.p. 169–172 °C.

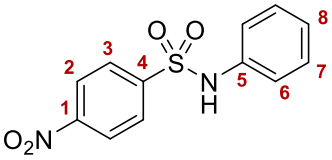
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.5 Hz, 1H, CH_{ar}-3), 7.97 (dd, *J* = 8.5, 2.0 Hz, 1H, CH_{ar}-2), 7.91 (d, *J* = 2.0 Hz, 1H, CH_{ar}-6), 4.92 (q, *J* = 5.5 Hz, 1H, N*H*), 4.13 (s, 3H, CH_3-7), 2.67 (d, *J* = 5.5, 3H, CH_3-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 156.9 (C-1), 151.7 (C-4), 132.4 (C-3), 132.0 (C-2), 115.8 (C-6), 107.5 (C-5), 57.4 (C-7), 29.6 (C-8).

IR (neat film, cm^{-1}): 3310, 3108, 2925, 2853, 1717, 1406, 1313, 1265, 1164, 1025, 802, 611.

MS (ES^-) found *m/z* 245 $[M-H]^-$, 247 $[M+H]^+$; **HRMS** (ES^-) found 245.0239, $C_8H_9N_2O_5S$ $[M-H]^-$ requires 245.0227.

2.2 *N*-Aryl Sulfonamide Syntheses

4-nitro-*N*-phenylbenzenesulfonamide 6e



Prepared according to **General Procedure A** from 4-nitrobenzenesulfonyl chloride **147a** (4.5 mmol, 1.00 mg), aniline (11 mmol, 1.03 mL), EtOAc (45.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6e** as a light pink solid (834 mg, 3.0 mmol, 67%), m.p. 157–159 °C.

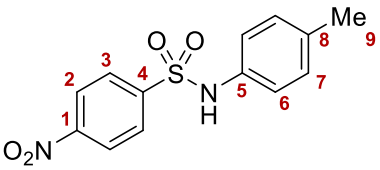
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28 (app. d, *J* = 8.5 Hz, 2H, C*H*$_{ar}$-2), 7.92 (app. d, *J* = 8.5 Hz, 2H, C*H*$_{ar}$-3), 7.31–7.25 (m, 2H, C*H*$_{ar}$-7), 7.21–7.17 (m, 1H, C*H*$_{ar}$-8), 7.09–7.06 (m, 2H, C*H*$_{ar}$-6), 6.68 (br. s, 1H, N*H*); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.4 (C-1), 144.8 (C-4), 135.4 (C-5), 129.8 (C-6), 128.7 (C-3), 126.7 (C-8), 124.4 (C-2), 122.6 (C-7).

IR (neat film, cm^{-1}): 3275, 3133, 2922, 2857, 1918, 1608, 1520, 1400, 1332, 1163, 854, 739, 669, 616.

MS (ES^-) found *m/z* 277 $[M-H]^-$; **HRMS** (ES^-) found 277.0281, $C_{12}H_9N_2O_4S$ $[M-H]^-$ requires 277.0289.

Data is in accordance with literature reports.[3]

4-nitro-*N*-(*p*-tolyl)benzenesulfonamide 6f



Prepared according to **General Procedure B** from *p*-toluidine (1.0 mmol, 107 mg), pyridine (1.2 mmol, 35 µL), 4-nitrobenzenesulfonyl chloride (1.2 mmol, 265 mg), THF (10.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6f** as a yellow solid (214 mg, 0.73 mmol, 73%), m.p. 176–178 °C.

^{1}H NMR (400 MHz, CD_3CN): δ 8.26 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 8.01 (br. s, 1H, N*H*), 7.91 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.08 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-6), 6.97 (d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-7), 2.24 (s, 3H, C*H*$_3$-9); **^{13}C NMR** (101 MHz, CD_3CN): δ 151.1 (C-4),

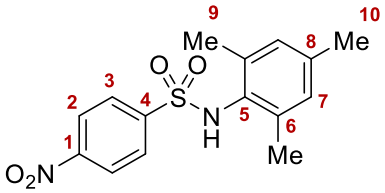
145.8 (C-1), 136.8 (C-8), 134.7 (C-5), 130.9 (C-6), 129.5 (C-3), 125.3 (C-2), 123.3 (C-7), 20.2 (C-9).

IR (neat film, cm^{-1}): 3269, 3106, 3039, 2920, 2866, 1607, 1528, 1509, 1348, 1313, 1302, 1162, 1090, 855, 745, 736, 683, 643, 607.

MS (ES^+) found *m/z* 337 $[M+2Na-H]^+$; **HRMS** (ES^+) found 337.0225, $C_{13}H_{11}N_2O_4SNa_2$ $[M+2Na-H]^+$ requires 337.0229.

Data is in accordance with literature reports.[4]

4-nitro-*N*-mesitylbenzenesulfonamide 6g



Prepared according to **General Procedure B** from 2,4,6-trimethylaniline (1.0 mmol, 141 µL), pyridine (1.2 mmol, 35 µL), 4-nitrobenzenesulfonyl chloride (1.2 mmol, 265 mg), THF (10.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6g** as a light brown solid (220 mg, 0.69 mmol, 69%), m.p. 144–146 °C.

^{1}H NMR (400 MHz, CD_3CN): δ 8.34 (app. d, *J* = 8.9 Hz, 2H, C*H*$_{ar}$-2), 7.94 (app. d, *J* = 8.9 Hz, 2H, C*H*$_{ar}$-3), 7.43 (br. s, 1H, N*H*), 6.90 (s, 2H, C*H*$_{ar}$-7), 2.26 (s, 3H, C*H*$_3$-10), 1.97 (s, 6H, C*H*$_3$-9); **^{13}C NMR** (101 MHz, CD_3CN): δ 151.2 (C-4), 148.2 (C-1), 139.0 (C-8), 138.8 (C-6), 130.7 (C-5), 130.3 (C-7), 129.2 (C-3), 125.5 (C-2), 20.9 (C-10), 18.9 (C-9).

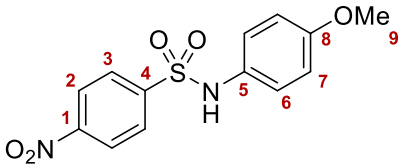
IR (neat film, cm^{-1}): 3281, 3105, 2924, 2862, 1524, 1349, 1311, 1163, 1091, 854, 738, 685, 622.

MS (ES^-) found *m/z* 319 $[M-H]^-$; **HRMS** (ES^-) found 319.0754, $C_{15}H_{15}N_2O_4S$ $[M-H]^-$ requires 319.0758.

Data is in accordance with literature reports.[5]

4-nitro-*N*-(4-methoxyphenyl)benzenesulfonamide 6h

Prepared according to **General Procedure B** from *p*-anisidine (1.0 mmol, 123 mg), pyridine (1.2 mmol, 35 µL), 4-nitrobenzenesulfonyl chloride (1.2 mmol, 265 mg), THF (10.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6h** as a light yellow solid (180 mg, 0.59 mmol, 58%), m.p. 174–176 °C.



^{1}H NMR (400 MHz, CD_3CN): δ 8.26 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.90 (br. s, 1H, N*H*), 7.85 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 6.98 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-7), 6.80 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-6), 3.72 (s, 3H, C*H*$_3$-9); **^{13}C NMR** (101 MHz, CD_3CN): δ 159.2 (C-8), 152.3 (C-4), 145.7 (C-1), 129.7 (C-5), 129.5 (C-3), 126.3 (C-7), 125.3 (C-2), 115.4 (C-6), 56.1 (C-9).

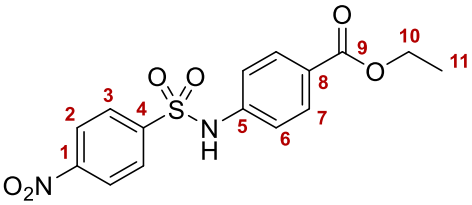
IR (solid, cm^{-1}): 3275, 3131, 2965, 2846, 1607, 1524, 1506, 1347, 1305, 1286, 1243, 1170, 1158, 1087, 1030, 852, 750, 739, 680, 660.

MS (ES$^-$) found *m*/*z* 307 [M–H]$^-$; **HRMS** (ES$^-$) found 307.0389, $C_{13}H_{11}N_2O_5S$ [M–H]$^-$ requires 307.0394.

Data is in accordance with literature reports.[6]

Ethyl 4-((4-nitrophenyl)sulfonamido)benzoate 6i

Prepared according to **General Procedure B** from *p*-aminoethylbenzoate (1.0 mmol, 165 mg), pyridine (1.2 mmol, 35 µL), 4-nitrobenzenesulfonyl chloride (1.2 mmol, 265 mg), THF (10.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6i** as a light salmon pink solid (112 mg, 0.32 mmol, 32%), m.p. 180–184 °C.



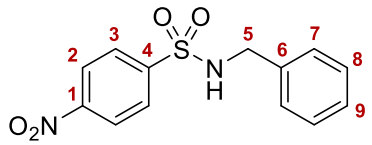
^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.40 (app. d, *J* = 8.9 Hz, 2H, C*H*$_{ar}$-2), 8.14 (app. d, *J* = 8.9 Hz, 2H, C*H*$_{ar}$-3), 7.92 (app. d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-7), 7.36 (app. d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-6), 4.29 (q, *J* = 7.2 Hz, 2H, C*H*$_2$-10), 2.83 (br. s, 1H, N*H*), 1.32 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-

11) ; **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 166.0 (C-9), 145.9 (C-1), 142.3 (C-4), 132.0 (C-5), 131.7 (C-7), 129.5 (C-3), 127.5 (C-8), 125.4 (C-2), 120.3 (C-6), 61.4 (C-10), 14.5 (C-11).

IR (neat film, cm^{-1}): 3228, 3107, 2983, 1712, 1691, 1607, 1531, 1368, 1349, 1132, 1280, 1165, 1109, 1090, 855, 736, 609, 605.

MS (ES^-) found *m/z* 349 $[M–H]^-$; **HRMS** (ES^-) found 349.0495, $C_{15}H_{13}N_2O_6S$ $[M–H]^-$ requires 349.0500.

4-nitro-*N*-benzylbenzenesulfonamide 6j



Prepared according to **General Procedure A** from 4-nitrobenzenesulfonyl chloride (4.5 mmol, 1.00 g), benzylamine (11 mmol, 1.23 mL), EtOAc (45.0 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **6j** as a yellow solid (1.07 g, 3.7 mmol, 81%), m.p. 111–113 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.30 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-2), 7.98 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-3), 7.28–7.24 (m, 3H, C*H*$_{ar}$-7,9), 7.18–7.15 (m, 2H, C*H*$_{ar}$-8), 5.06 (t, *J* = 6.1 Hz, 1H, N*H*), 4.22 (d, *J* = 6.1 Hz, 2H, C*H*$_2$-5) ; **^{13}C NMR** (126 MHz, $CDCl_3$): δ 150.1 (C-1), 146.2 (C-4), 135.6 (C-6), 129.0 (C-8), 128.44 (C-3), 128.41 (C-9), 128.0 (C-7), 124.4 (C-2), 47.5 (C-5).

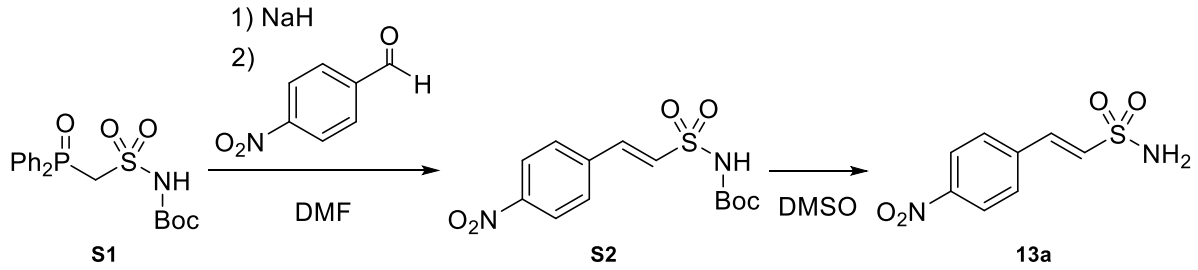
IR (neat film, cm^{-1}): 3289, 3099, 1520, 1421, 1347, 1330, 1312, 1153, 1051, 806, 754, 747, 736, 621.

MS (ES^-) found *m/z* 291 $[M–H]^-$; **HRMS** (ES^-) found 291.0441, $C_{13}H_{11}N_2O_4S$ $[M–H]^-$ requires 291.0445.

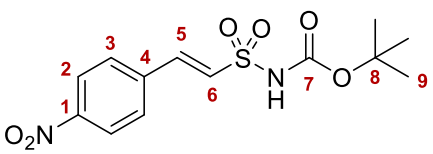
Data is in accordance with literature reports.[7]

2.3 Phenylethenesulfonamide Syntheses

(*E*)-4-Nitrophenylethenesulfonamide 13a[8]



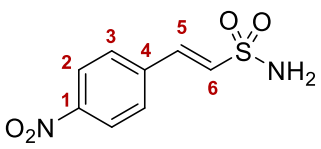
In a 100 mL Schenk flask under nitrogen atmosphere, **S1** tert-butyl (((diphenylphosphoryl)methyl)sulfonyl)carbamate (1.0 eq., 1.0 mmol, 395 mg) was dissolved in dry DMF (25.0 mL) and cooled to 0°C. To a well-stirred solution of the reagent NaH (55% in mineral oil, 2.6 eq., 2.6 mmol, 111 mg) was added. The reaction was allowed to warm to r.t. and stirred for 30 minutes. Cooled down to 0 °C, 4-nitrobenzaldehyde (1.2 eq., 1.2 mmol, 185 mg) was then added in ten portions and the reaction mixture (dark purple) was stirred vigoursly overnight at room temperature. Distilled water (50.0 mL), EtOAc (40.0 mL) and 2% aq. HCl (10.0 mL) were added to the mixture and the layers were separated. The aqueous layer was extracted with EtOAc (4 × 20 mL). The organic solution was washed with distilled water (2 × 30 mL), brine (2 × 30 mL), and dried over sodium sulfate, filtered and concentrated under reduced pressure to give the crude product (590 mg dark brown oil). The crude mixture was purified by column chromatography (10–60% EtOAc in hexanes). The Boc protected **S2** compound was obtained as a yellow solid (220 mg, 0.69 mmol, 69% yield.



^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 9.99 (br. s, 1H, N*H*), 8.33 (d, *J* = 8.9 Hz, 2H, CH_{ar}-2), 8.07 (d, *J* = 8.9 Hz, 2H, CH_{ar}-3), 7.73 (d, *J* = 15.6 Hz, 1H, C*H*-5), 7.53 (d, *J* = 15.6 Hz, 1H, C*H*-6), 1.44 (s, 9H, CH_3-9); **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 149.9 (C-1), 149.1 (C-4), 140.3 (C-5), 138.9 (C-6), 129.7 (C-2), 124.1 (C-3), 82.5 (C-8), 27.2 (C-9). **HRMS** (APCI$^-$) $C_{13}H_{15}N_2O_6S^-$ ([M–H]$^-$) requires 327.0656; found 327.0657.

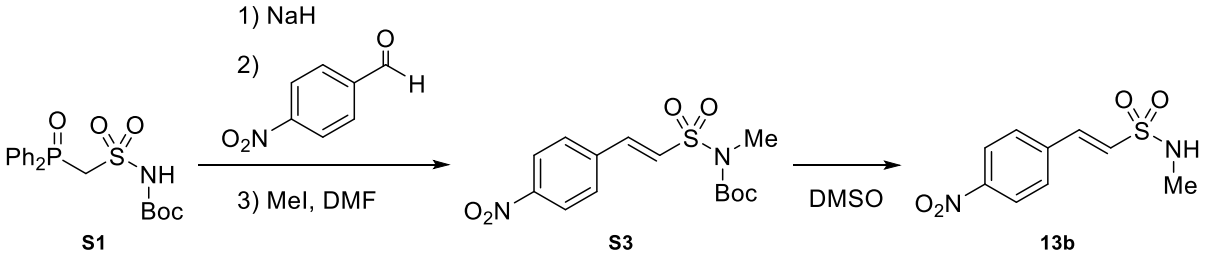
Boc-protected sulfonamide (**S2**, 2.1 mmol, 689 mg) was dissolved in DMSO (6.0 mL) and stirred for 8 hours at 80°C. The reaction mixture was cooled to room temperature,

poured into distilled water (40.0 mL) and extracted with EtOAc (4 × 20 mL). The organic solution was concentrated under reduced pressure to give the crude product (650 mg). The crude mixture was purified by column chromatography (20–80% EtOAc in hexanes) to afford **13a** as a yellow solid (345 mg, 1.5 mmol, 72% yield).

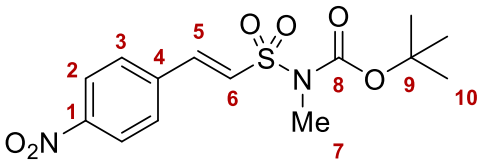


^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.30 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-2), 7.97 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-3), 7.52 (d, *J* = 15.6 Hz, 1H, C*H*-5), 7.43 (d, *J* = 15.6 Hz, 1H, C*H*-6), 6.51 (br. s, 2H, N*H*$_2$); **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 140.9 (C-1), 135.8 (C-5), 134.8 (C-4 and C-6), 130.1 (C-3), 124.9 (C-2). **HRMS** (APCI$^+$) found 229.0274, $C_8H_9N_2O_4S$ $[M+H]^+$ requires 229.0278.

(*E*)-*N*-Methyl-(4-nitrophenyl)ethenesulfonamide 13b[9]

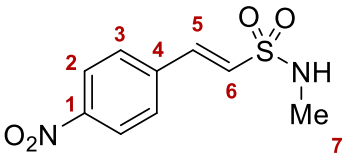


In a 100 mL Schenk flask under nitrogen atmosphere, **S1** tert-butyl (((diphenylphosphoryl)methyl)sulfonyl)carbamate (1.0 eq., 1.3 mmol, 494 mg) was dissolved in dry DMF (35.0 mL) and cooled to 0 °C. To a well-stirred solution of the reagent NaH (55% in mineral oil, 2.6 eq., 3.2 mmol, 139 mg) was added in five portions. The reaction was allowed to warm to r.t. and stirred for 30 minutes. Cooled down to 0 °C, 4-nitrobenzaldehyde (1.2 eq., 1.5 mmol, 231 mg) was then added in three portions and the reaction mixture (dark purple) was stirred vigoursly overnight (16 hours) at r.t. Cooled to 0 °C, MeI (5.0 eq., 6.3 mmol, 0.390 mL) was added, stirred at 40 °C for 4 hours. Ice and EtOAc (50.0 mL) were added to the reaction and the layers were separated. The aqueous layer was extracted with EtOAc (4 × 50 mL). The organic solution was washed with 2% aq. HCl (50.0 mL), distilled water (2 × 100 mL), brine (2 × 100 mL), and dried over sodium sulfate, filtered and concentrated under reduced pressure to give the crude product (610 mg dark brown oil). The crude mixture was purified by column chromatography (10–35% EtOAc in hexanes). The compound **S3** was obtained as an orange solid (259 mg, 0.757 mmol, 61% yield).



^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.32 (d, *J* = 8.7 Hz, 2H, C*H*$_{ar}$-2), 8.03 (d, *J* = 8.7 Hz, 2H, C*H*$_{ar}$-3), 7.72 (d, *J* = 15.5 Hz, 1H, C*H*-5), 7.55 (d, *J* = 15.5 Hz, 1H, C*H*-6), 3.22 (s, 3H, CH_3-7), 1.44 (s, 9H, CH_3-10); **^{13}C NMR** (101 MHz, $(CD_3)_2CO$, ppm): δ 152.1 (C-8), 149.9 (C-1), 141.0 (C-4), 139.7 (C-5), 130.6 (C-2), 130.2 (C-6), 125.0 (C-3), 84.6 (C-9), 33.1 (C-7), 28.1 (C-10). **HRMS** (APCI$^+$) found 343.0952, $C_{14}H_{19}N_2O_6S$ $[M+H]^+$ requires 343.0958.

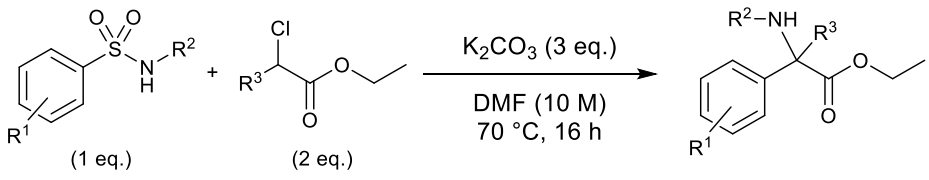
The Boc-sulfonamide (**S3**, 0.75 mmol, 256 mg) was dissolved in DMSO (3.75 mL) and heated to 120 °C for 8 hours. The reaction mixture was cooled to r.t., poured into distilled water (35.0 mL) and extracted with EtOAc (3 × 30 mL). The organic solution was concentrated under reduced pressure to give the crude product (240 mg). The crude mixture was purified by column chromatography (10–80% EtOAc in hexanes). The title compound **13b** was obtained as an orange solid (153 mg, 0.632 mmol, 84% yield).



^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.30 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-2), 8.00 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-3), 7.52 (d, *J* = 15.6 Hz, 1H, C*H*-5), 7.29 (d, *J* = 15.6 Hz, 1H, C*H*-6), 6.24 (br. s, 1H, N*H*), 2.72 (s, 3H, CH_3-7); **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 149.6 (C-1), 140.6 (C-4), 138.5 (C-5), 130.8 (C-6), 130.2 (C-2), 124.9 (C-3), 28.8 (C-7). **HRMS** (APCI$^+$) found 242.0367, $C_9H_{10}N_2O_4S$ $[M]^+$ requires 242.0361.

3. Sulfonamide Coupling Reactions with Smiles Rearrangement

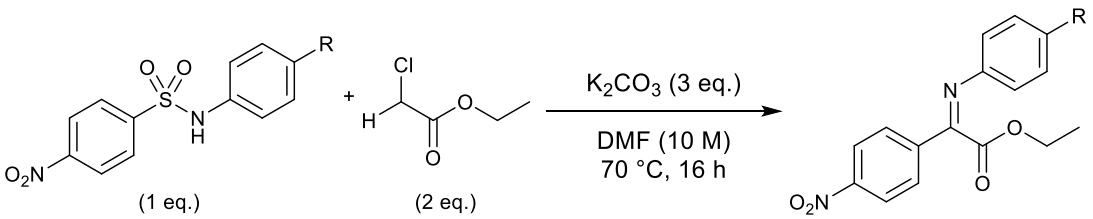
General Procedure E



In a microwave vial dried in the oven, sulfonamide (1.0 eq.), potassium carbonate (3.0 eq.) were weighted. A stirrer bar was added, the vial was sealed and the air was evacuated then the vial was filled with nitrogen. Dry DMF (0.10 M for sulfonamide),

substituted ethyl 2-chloroacetate (2.0 eq.) was added to a stirred mixture and the vial was put in a pre-warmed 70 °C oil bath to stir for 16 hours. The reaction was cooled, the vial was opened, ethyl acetate and water were added and the layers were separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were then washed three times with a 10% aqueous LiCl solution, brine, and dried over magnesium sulfate, filtered and concentrated under reduced pressure to give the crude product. The crude mixture was purified by column chromatography on silica gel.

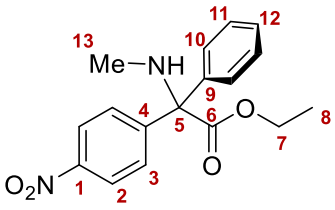
General Procedure F



To a solution of an *N*-aryl sulfonamide (1.0 eq.), K_2CO_3 (3.0 eq.), DMF (0.10 M for sulfonamide) within a metal-capped, oven-dried microwave vial, ethyl 2-chloroacetate (2.0 eq.) was added. The vial was put in a pre-warmed 70 °C oil bath to stir for 16 hours. The reaction was cooled, the vial was opened, ethyl acetate and water were added and the layers were separated. The aqueous layer was extracted with ethyl acetate. The combined organic layers were then washed three times with a 10% aqueous LiCl solution, brine, and dried over magnesium sulfate, filtered and concentrated under reduced pressure to give the crude product. The crude mixture was purified by column chromatography on silica gel.

3.1 Compound Data for Smiles products

Ethyl 2-(methylamino)-2-(4-nitrophenyl)-2-phenylacetate 8a



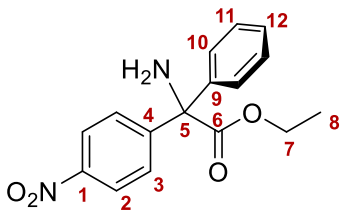
Prepared according to **General Procedure E** from 4-nitro-*N*-methylbenzenesulfonamide **6a** (0.10 mmol, 21.6 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 52 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8a** as a light yellow solid (87.0 mg, 0.28 mmol, 92%); m.p. 53–55 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.73 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.39–7.27 (m, 5H, C*H*$_{ar}$-10, 11, 12), 4.32–4.21 (m, 2H, C*H*$_2$-7), 2.34 (br. s, 1H, N*H*), 2.10 (s, 3H, C*H*$_3$-13), 1.15 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.6 (C-6), 148.6 (C-4), 147.1 (C-1), 140.7 (C-9), 129.7 (C-3), 128.5 (C-10), 128.0 (C-12), 127.9 (C-11), 123.1 (C-2), 73.2 (C-5), 62.1 (C-7), 30.9 (C-13), 14.1 (C-8).

IR (neat film, cm^{-1}): 3349, 3063, 2981, 2804, 1821, 1728, 1510, 1320, 1223, 1211, 1158, 1026, 853, 734, 701, 633.

MS (ES$^+$) found *m*/*z* 315 [M+H]$^+$; **HRMS** (ES$^+$) found 315.1336, $C_{17}H_{19}N_2O_4$ [M+H]$^+$ requires 315.1326.

Ethyl 2-amino-2-(4-nitrophenyl)-2-phenylacetate 8b



Prepared according to **General Procedure E** from 4-nitro-benzenesulfonamide (0.30 mmol, 66.5 mg), K_2CO_3 (0.90 mmol, 124 mg), ethyl α-chlorophenylacetate **7a** (0.60 mmol, 103 µL), DMF (3.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8b** as a clear colourless oil (13.5 mg, 0.045 mmol, 15%).

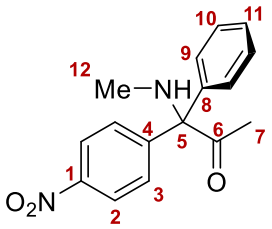
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.74 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.29–7.24 (m, 3H, C*H*$_{ar}$-10, 12), 7.23–7.19 (m, 2H, C*H*$_{ar}$-11), 4.25–4.18 (m, 2H, C*H*$_2$-7), 2.30 (br. s, 2H, NH_2), 1.17 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz,

$CDCl_3$): δ 173.8 (C-6), 150.8 (C-1), 147.3 (C-4), 143.5 (C-9), 129.2 (C-3), 128.7 (C-10), 128.2 (C-12), 127.2 (C-11), 123.2 (C-2), 68.4 (C-5), 62.6 (C-7), 14.1 (C-8).

IR (neat film, cm^{-1}): 3106, 2923, 2853, 2360, 2343, 1737, 1530, 1368, 1348, 1307, 1193, 1146, 1080, 1014, 854, 750, 734, 696, 683, 612.

MS (ES^+) found *m/z* 301 $[M+H]^+$; **HRMS** (ES^+) found 323.0998, $C_{16}H_{16}N_2O_4$ $[M+Na]^+$ requires 323.1002.

1-(Methylamino)-1-(4-nitrophenyl)-1-phenylpropan-2-one 8c



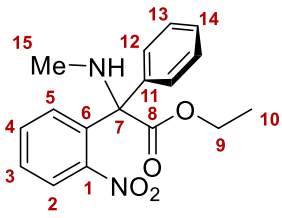
Prepared according to **General Procedure E** from 4-nitro-*N*-methylbenzenesulfonamide **6a** (0.10 mmol, 21.6 mg), K_2CO_3 (0.30 mmol, 41.5 mg), 1-chloro-1-phenylpropan-2-one (0.20 mmol, 30 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8c** as a yellow oil (10.2 mg, 0.036 mmol, 36%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.64 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.39–7.30 (m, 5H, C*H*$_{ar}$-9,10,11), 2.15 (s, 3H, C*H*$_3$-7), 2.11 (s, 3H, C*H*$_3$-12); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 205.8 (C-6), 147.6 (C-1), 147.1 (C-4), 139.4 (C-8), 130.2 (C-3), 128.9 (C-10), 128.3 (C-9), 128.2 (C-11), 123.4 (C-2), 77.7 (C-5), 30.3 (C-12), 26.3 (C-7).

IR (neat film, cm^{-1}): 3353, 3063, 2944, 2804, 1709, 1593, 1517, 1490, 1448, 1346, 1172, 1141, 1110, 850, 764, 747, 701, 668, 613.

MS (ES^+) found *m/z* 301 $[M+Na]^+$; **HRMS** (ES^+) found 285.1220, $C_{16}H_{17}N_2O_3$ $[M+H]^+$ requires 285.1234.

Ethyl 2-(methylamino)-2-(2-nitrophenyl)-2-phenylacetate 8d



Prepared according to **General Procedure E** from 2-nitro-*N*-methylbenzenesulfonamide **6b** (0.10 mmol, 21.6 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes)

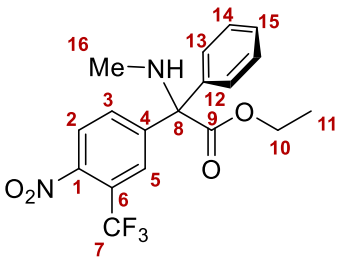
afforded **8d** as a yellow solid (15.5 mg, 0.049 mmol, 49%), m.p. 103–105 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (app. d, *J* = 8.0 Hz, 1H, C*H*$_{ar}$-2), 7.62–7.58 (m, 2H, C*H*$_{ar}$-13), 7.53–7.48 (m, 1H, C*H*$_{ar}$-3), 7.47–7.43 (m, 1H, C*H*$_{ar}$-5), 7.36–7.29 (m, 4H, C*H*$_{ar}$-4, 12, 14), 4.19–4.02 (m, 2H, C*H*$_2$-9), 2.72 (br. s, 1H, N*H*), 2.19 (s, 3H, C*H*$_3$-15), 1.13 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-10); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.1 (C-8), 150.0 (C-1), 138.9 (C-11), 135.8 (C-6), 132.8 (C-4), 131.8 (C-3), 129.0 (C-13), 128.4 (C-5), 128.2 (C-12), 128.1 (C-14), 125.4 (C-2), 72.2 (C-7), 61.9 (C-9), 30.9 (C-15), 13.9 (C-10).

IR (neat film, cm^{-1}): 3324, 3075, 2951, 2806, 1819, 1724, 1524, 1445, 1350, 1236, 1206, 1176, 1163, 1100, 1022, 968, 851, 799, 772, 744, 738, 709, 699, 692, 635.

MS (ES$^+$) found *m*/*z* 315 [M+H]$^+$; **HRMS** (ES$^+$) found 315.1339, $C_{17}H_{19}N_2O_4$ [M+H]$^+$ requires 315.1347.

Ethyl 2-(methylamino)-2-(4-nitro-3-(trifluoromethyl)phenyl)-2-phenylacetate 8e



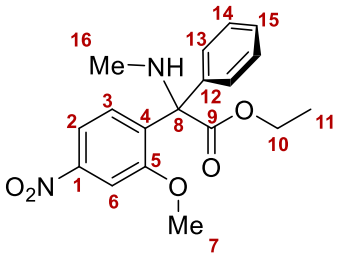
Prepared according to **General Procedure E** from 4-nitro-3-(trifluoromethyl)-*N*-methylbenzenesulfonamide **6c** (0.11 mmol, 31.6 mg), K_2CO_3 (0.33 mmol, 45.6 mg), ethyl α-chlorophenylacetate **7a** (0.22 mmol, 38 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **150g** as a clear yellow oil (17.9 mg, 0.047 mmol, 42%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (app. d, *J* = 1.8 Hz, 1H, C*H*$_{ar}$-5), 7.97 (app. dd, *J* = 8.6, 1.8 Hz, 1H, C*H*$_{ar}$-3), 7.82 (app. d, *J* = 8.6 Hz, 1H, C*H*$_{ar}$-2), 7.38–7.28 (m, 5H, C*H*$_{ar}$-13, 14, 15), 4.34–4.23 (m, 2H, C*H*$_2$-10), 2.46 (br. s, 1H, N*H*), 2.18 (s, 3H, C*H*$_3$-16), 1.24 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-11); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.1 (C-9), 146.9 (C-4), 140.5 (C-12), 138.5 (C-1), 133.7 (C-3), 128.8 (C-13), 128.5 (C-5), 128.3 (C-15), 127.7 (q, *J* = 206.5 Hz, C-7), 127.4 (C-14), 124.7 (C-2), 123.3 (q, *J* = 33.8, C-6), 73.0 (C-8), 62.4 (C-10), 30.9 (C-16), 14.2 (C-11); **^{19}F NMR** (376 MHz, $CDCl_3$): δ –59.83.

IR (neat film, cm^{-1}): 3356, 3066, 2983, 2929, 2807, 2362, 1729, 1539, 1360, 1311, 1215, 1179, 1141, 1048, 1027, 858, 758, 701, 657.

MS (ES^+) found *m/z* 383 $[M+H]^+$; **HRMS** (ES^+) found 383.1205, $C_{18}H_{18}F_3N_2O_4$ $[M+H]^+$ requires 383.1213.

Ethyl 2-(2-methoxy-4-nitrophenyl)-2-(methylamino)-2-phenylacetate 8f



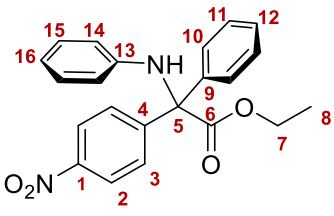
Prepared according to **General Procedure E** from 4-nitro-2-methoxy-*N*-methylbenzenesulfonamide **6d** (0.11 mmol, 26.4 mg), K_2CO_3 (0.32 mmol, 44.2 mg), ethyl α-chlorophenylacetate **152a** (0.21 mmol, 36 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8f** as a clear yellow oil (17.7 mg, 0.059 mmol, 56%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (app. dd, *J* = 8.6, 2.2 Hz, 1H, C*H*$_{ar}$-2), 7.73–7.68 (m, 3H, C*H*$_{ar}$-6, 14), 7.47 (app. d, *J* = 8.6 Hz, 1H, C*H*$_{ar}$-3), 7.38–7.32 (m, 2H, C*H*$_{ar}$-13), 7.32–7.27 (m, 1H, C*H*$_{ar}$-15), 4.23–4.12 (m, 2H, C*H*$_2$-10), 3.91 (s, 3H, C*H*$_3$-7), 2.12 (s, 3H, C*H*$_3$-16), 1.17 (t, 3H, *J* = 7.2 Hz, C*H*$_3$-11); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.2 (C-9), 157.2 (C-5), 148.1 (C-1), 138.7 (C-4), 137.6 (C-12), 129.5 (C-3), 129.0 (C-14), 128.1 (C-13), 127.9 (C-15), 115.6 (C-2), 106.1 (C-6), 69.9 (C-8), 61.4 (C-10), 56.1 (C-7), 30.6 (C-16), 14.3 (C-11).

IR (neat film, cm^{-1}): 3379, 3331, 3090, 3059, 2979, 2943, 2853, 2803, 1733, 1590, 1520, 1485, 1344, 1251, 1179, 1094, 1028, 867, 767, 739, 700.

MS (ES^+) found *m/z* 345 $[M+H]^+$; **HRMS** (ES^+) found 345.1445, $C_{18}H_{21}N_2O_5$ $[M+H]^+$ requires 345.1431

Ethyl 2-(4-nitrophenyl)-2-phenyl-2-(phenylamino) acetate 8g

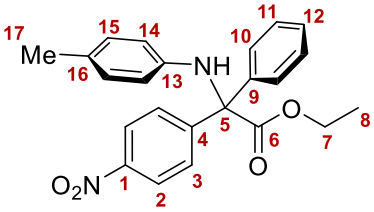


Prepared according to **General Procedure E** from 4-nitro-*N*-phenylbenzenesulfonamide **6e** (0.10 mmol, 27.8 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8g** as a yellow oil (32.3 mg, 0.086 mmol, 86%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-2), 7.84 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-3), 7.49–7.46 (m, 2H, C*H*$_{ar}$-11), 7.38–7.28 (m, 3H, C*H*$_{ar}$-10, 12), 7.03 (app. dd, *J* = 8.6, 7.5 Hz, 2H, C*H*$_{ar}$-15), 6.71 (app. tt, *J* = 7.5, 1.1 Hz, 1H, C*H*$_{ar}$-16), 6.44 (app. dd, *J* = 8.6, 1.1 Hz, 2H, C*H*$_{ar}$-14), 5.33 (s, 1H, N*H*), 4.26–4.12 (m, 2H, C*H*$_2$-7), 1.03 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.1 (C-6), 147.4 (C-4), 147.2 (C-1), 145.0 (C-13), 140.5 (C-9), 129.9 (C-3), 129.0 (C-10), 128.9 (C-15), 128.5 (C-12), 127.5 (C-11), 123.2 (C-2), 119.1 (C-16), 115.7 (C-14), 71.7 (C-5), 62.7 (C-7), 13.8 (C-8).

IR (neat film, cm^{-1}): 3392, 3054, 2981, 1731, 1602, 1518, 1498, 1347, 1257, 1224, 1196, 1023, 1015, 854, 750, 736, 720, 694.

MS (ES$^+$) found *m*/*z* 399 [M+Na]$^+$; **HRMS** (ES$^+$) found 399.1315, $C_{22}H_{20}N_2O_4Na$ [M+Na]$^+$ requires 399.1305.



Ethyl 2-(4-nitrophenyl)-2-phenyl-2-(*p*-tolylamino)acetate 8h

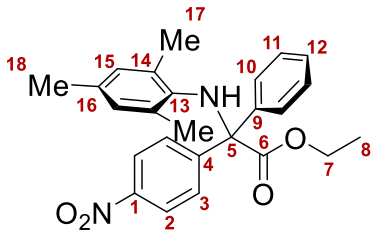
Prepared according to **General Procedure E** from 4-nitro-*N*-(*p*-tolyl)benzenesulfonamide **6f** (0.10 mmol, 29.2 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8h** as a yellow oil (36 mg, 0.092 mmol, 92%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.84 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.49–7.46 (m, 2H, C*H*$_{ar}$-11), 7.37–7.28 (m, 3H, C*H*$_{ar}$-10, 12), 6.84 (app. d, *J* = 8.3 Hz, 2H, C*H*$_{ar}$-15), 6.35 (app. d, *J* = 8.3 Hz, 2H, C*H*$_{ar}$-14), 5.21 (s, 1H, N*H*), 4.25–4.13 (m, 2H, C*H*$_2$-7), 2.17 (s, 3H, C*H*$_3$-17), 1.05 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.2 (C-6), 147.6 (C-1), 147.1 (C-4), 142.5 (C-16), 140.7 (C-13), 129.9 (C- 3), 129.5 (C-15), 128.8 (C-10), 128.4 (C-12), 128.3 (C-9), 127.5 (C-11), 123.2 (C-2), 115.8 (C-14), 71.7 (C-5), 62.7 (C-7), 20.5 (C-17), 13.9 (C-8).

IR (neat film, cm^{-1}): 3390, 2980, 2920, 2865, 2359, 1731, 1515, 1348, 1301, 1254, 1226, 1195, 1024, 1015, 855, 812, 736, 703.

MS (ES^+) found *m/z* 413 $[M+Na]^+$; **HRMS** (ES^+) found 413.1469, $C_{23}H_{22}N_2O_4Na$ $[M+Na]^+$ requires 413.1472.

Ethyl 2-(mesitylamino)-2-(4-nitrophenyl)-2-phenylacetate 8i



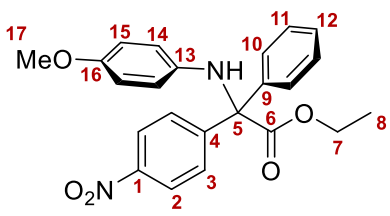
Prepared according to **General Procedure E** from 4-nitro-*N*-mesitylbenzenesulfonamide **6g** (0.10 mmol, 32.0 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8i** as a light red solid (9.7 mg, 0.023 mmol, 23%), m.p. 155–157 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (app. d, *J* = 8.9 Hz, 2H, C*H*$_{ar}$-2), 7.85 (app. d, *J* = 8.9 Hz, 2H, C*H*$_{ar}$-3), 7.21–7.15 (m, 3H, C*H*$_{ar}$-10, 12), 7.11–7.07 (m, 2H, C*H*$_{ar}$-11), 6.72 (br. s, 1H, C*H*$_{ar}$-15), 6.55 (br. s, 1H, C*H*$_{ar}$-15), 5.74 (s, 1H, NH), 4.19 (m, 2H, C*H*-7), 2.15 (s, 3H, C*H*-17), 2.13 (s, 3H, C*H*$_3$-17), 1.79 (s, 3H, C*H*$_3$-18), 1.22 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 170.6 (C-6), 150.1 (C-4), 145.7 (C-1), 140.7 (C-9), 139.6 (C-16), 138.8 (C-13), 131.9 (C-14), 131.3 (C-14), 130.2 (C-10), 129.94 (C-3), 129.86 (C-12), 129.7 (C-15), 129.3 (C-15), 128.2 (C-11), 123.8 (C-2), 68.5 (C-5), 62.0 (C-7), 21.0 (C-17), 20.0 (C-18), 19.1 (C-17), 14.1 (C-8).

IR (neat film, cm^{-1}): 3105, 3066, 2982, 2926, 2867, 1743, 1530, 1378, 1311, 1203, 1165, 1090, 1020, 853, 738, 699, 689, 625.

MS (ES^+) found *m/z* 441 $[M+Na]^+$; **HRMS** (ES^+) found 441.1783, $C_{25}H_{26}N_2O_4Na$ $[M+Na]^+$ requires 441.1785.

Ethyl 2-((4-methoxyphenyl)amino)-2-(4-nitrophenyl)-2-phenylacetate 8j



Prepared according to **General Procedure E** from 4-nitro-*N*-(4-methoxyphenyl)benzenesulfonamide **6h** (0.10 mmol, 30.8 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica

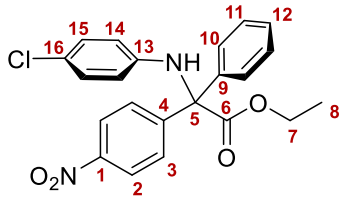
gel (0–40% EtOAc in hexanes) afforded **8j** as a clear yellow oil (38.7 mg, 0.095 mmol, 95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (app. d, *J* = 9.2 Hz, 2H, C*H*$_{ar}$-2), 7.83 (app. d, *J* = 9.2 Hz, 2H, C*H*$_{ar}$-3), 7.48–7.44 (m, 2H, C*H*$_{ar}$-11), 7.36–7.27 (m, 3H, C*H*$_{ar}$-10, 12), 6.61 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-15), 6.39 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-14), 5.04 (br. s, 1H, N*H*), 4.25–4.11 (m, 2H, C*H*$_2$-7), 3.67 (s, 3H, C*H*$_3$-17), 1.04 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.3 (C-6), 153.1 (C-16), 147.9 (C-1), 147.1 (C-4), 140.9 (C-9), 138.8 (C-13), 129.8 (C-3), 128.8 (C-10), 128.4 (C-12), 127.4 (C-11), 123.2 (C-2), 117.3 (C-14), 114.4 (C-15), 72.1 (C-5), 62.6 (C-7), 55.6 (C-17), 13.9 (C-8).

IR (neat film, cm^{-1}): 3378, 3062, 2979, 2933, 2833, 1731, 1510, 1347, 1237, 1195, 1179, 1026, 1015, 854, 823, 763, 735, 701.

MS (ES$^+$) found *m/z* 429 [M+Na]$^+$; **HRMS** (ES$^+$) found 407.1593, $C_{23}H_{23}N_2O_5$ [M+H]$^+$ requires 407.1601.

Ethyl 2-((4-chlorophenyl)amino)-2-(4-nitrophenyl)-2-phenylacetate 8k



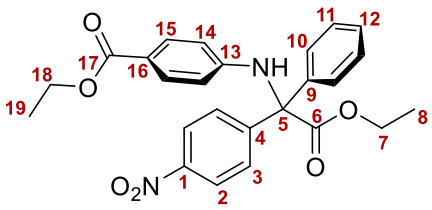
Prepared according to **General Procedure E** from 4-nitro-*N*-(4-chlorophenyl)benzenesulfonamide **6i** (0.10 mmol, 31.3 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8k** as a vibrant yellow solid (32.3 mg, 0.076 mmol, 76%), m.p. 48–51 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.72 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.38–7.35 (m, 2H, C*H*$_{ar}$-10), 7.29–7.25 (m, 2H, C*H*$_{ar}$-11), 7.25–7.21 (m, 1H, C*H*$_{ar}$-12), 6.89 (app. dt, *J* = 8.8, 3.4 Hz, 2H, C*H*$_{ar}$-15), 6.27 (app. dt, *J* = 8.8, 3.4 Hz, 2H, C*H*$_{ar}$-14), 5.35 (s,1H, N*H*), 4.18–4.08 (m, 2H, C*H*$_2$-7), 0.99 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 171.9 (C-6), 147.3 (C-1), 146.7 (C-4), 143.4 (C-13), 139.7 (C-9), 129.9 (C-3), 128.9 (C-11), 128.8 (C-15), 128.6 (C-16), 127.7 (C-10), 123.9 (C-12), 123.3 (C-2), 116.8 (C-14), 71.6 (C-5), 63.0 (C-7), 13.9 (C-8).

IR (neat film, cm^{-1}): 3389, 2981, 1732, 1595, 1525, 1498, 1447, 1347, 1314, 1294, 1255, 1226, 1015, 819, 735, 702.

MS (ES^+) found *m/z* 449 $[M+K]^+$; **HRMS** (ES^+) found 449.0665, $C_{22}H_{19}ClN_2O_4K$ $[M+K]^+$ requires 449.0655.

Ethyl 4-((2-ethoxy-1-(4-nitrophenyl)-2-oxo-1-phenylethyl)amino)benzoate 8l



Prepared according to **General Procedure E** from ethyl 4-((4-nitrophenyl)sulfonamido)benzoate **6j** (0.10 mmol, 35.0 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8l** as a light yellow oil (11.3 mg, 0.025 mmol, 25%).

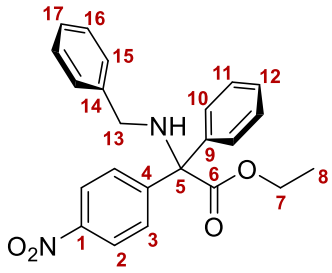
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.79 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.72 (app. d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-14), 7.47–7.41 (m, 2H, C*H*$_{ar}$-11), 7.39–7.32 (m, 3H, C*H*$_{ar}$-10, 12), 6.40 (app. d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-15), 5.91 (br. s, 1H, N*H*), 4.29–4.18 (m, 4H, C*H*$_2$-7, 18), 1.31 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-19), 1.08 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 171.8 (C-6), 166.6 (C-17), 148.6 (C-16), 147.4 (C-4), 146.1 (C-1), 138.8 (C-9), 131.0 (C-14), 130.0 (C-3), 129.0 (C-10), 128.8 (C-12), 127.9 (C-11), 123.4 (C-2), 120.6 (C-13), 114.6 (C-15), 71.2 (C-5), 63.3 (C-18), 60.5 (C-7), 14.6 (C-19), 13.8 (C-8).

IR (neat film, cm^{-1}): 3379, 2981, 2930, 2856, 1733, 1703, 1601, 1519, 1348, 1266, 1229, 1178, 1108, 771, 701.

MS (ES^-) found *m/z* 447 $[M-H]^-$; **HRMS** (ES^-) found 447.1565, $C_{25}H_{23}N_2O_6$ $[M-H]^-$ requires 447.1562.

Ethyl 2-(benzylamino)-2-(4-nitrophenyl)-2-phenylacetate 8m

Prepared according to **General Procedure E** from 4-nitro-*N*-benzylbenzenesulfonamide **6m** (0.10 mmol, 29.2 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **7a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8m** as a clear, colourless oil (86.7 mg, 0.22 mmol, 74%).

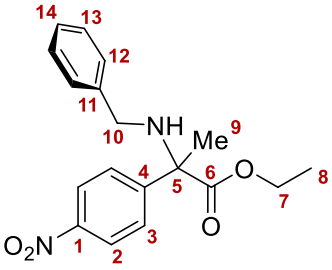


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-2), 7.74 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-3), 7.39–7.35 (m, 2H, C*H*$_{ar}$-10), 7.29–7.21 (m, 6H, C*H*$_{ar}$-11, 15, 16), 7.20–7.15 (m, 2H, C*H*$_{ar}$-12, 17), 4.26–4.15 (m, 2H, C*H*$_2$-7), 3.37 (s, 2H, C*H*-13), 2.56 (br. s, 1H, N*H*), 1.16 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 172.5 (C-6), 149.0 (C-4), 147.1 (C-1), 141.0 (C-9), 139.8 (C-14), 129.5 (C-3), 128.7 (C-15), 128.6 (C-16), 128.2 (C-11), 128.1 (C-12), 127.7 (C-10), 127.4 (C-17), 123.2 (C-2), 72.7 (C-5), 62.2 (C-7), 48.6 (C-13), 14.2 (C-8).

IR (neat film, cm^{-1}): 3334, 3062, 2980, 2853, 1728, 1518, 1346, 1220, 1993, 1026, 1015, 853, 733, 699.

MS (ES$^+$) found *m*/*z* 391 [M+H]$^+$; **HRMS** (ES$^+$) found 391.1652, $C_{23}H_{23}N_2O_4$ [M+H]$^+$ requires 391.1647.

Ethyl 2-(benzylamino)-2-(4-nitrophenyl)propanoate 8n



Prepared according to **General Procedure E** from 4-nitro-*N*-benzylbenzenesulfonamide **6o** (0.10 mmol, 29.2 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloropropionate (0.20 mmol, 25 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8n** as a light yellow solid (18.7 mg, 0.057 mmol, 57%), m.p. 73–75 °C.

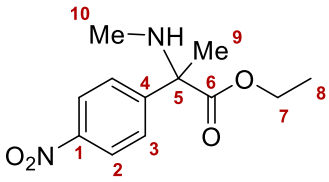
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 7.73 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.39–7.32 (m, 4H, C*H*$_{ar}$-12, 13), 7.30–7.26 (m, 1H, C*H*$_{ar}$-14), 4.25 (d, *J* = 7.2 Hz, 2H, C*H*$_2$-7), 3.70 (d, *J* = 12.2 Hz, 1H, C*H*-10), 3.62 (d, *J* = 12.2 Hz, 1H, C*H*-10), 2.30 (br. s, 1H, N*H*), 1.74 (s, 3H, C*H*$_3$-9), 1.27 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz,

$CDCl_3$): δ 174.2 (C-6), 150.9 (C-4), 147.3 (C-1), 140.0 (C-11), 128.7 (C-12), 128.3 (C-13), 127.4 (C-14), 127.2 (C-3), 123.7 (C-2), 65.8 (C-5), 61.8 (C-7), 48.4 (C-10), 25.0 (C-9), 14.3 (C-8).

IR (neat film, cm^{-1}): 3106, 1535, 1382, 1361, 1347, 1173, 854, 718, 703, 678.

MS (ES^+) found *m/z* 329 $[M+H]^+$; **HRMS** (ES^+) found 329.1496, $C_{18}H_{21}N_2O_4$ $[M+H]^+$ requires 329.1486.

Ethyl 2-(methylamino)-2-(4-nitrophenyl)propanoate 8o



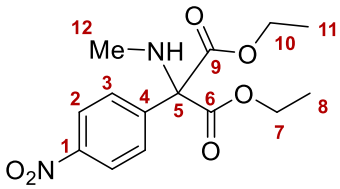
Prepared according to **General Procedure E** from 4-nitro-*N*-methylbenzenesulfonamide **6a** (0.10 mmol, 21.6 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloropropionate (0.20 mmol, 25 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8o** as a yellow oil (18.1 mg, 0.0718 mmol, 72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.19 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-2), 7.64 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-3), 4.22 (q, *J* = 7.1 Hz, 2H, C*H*$_2$-7), 2.32 (s, 3H, C*H*$_3$-10), 2.05 (br. s, 1H, N*H*), 1.64 (s, 3H, C*H*$_3$-9), 1.24 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 174.2 (C-6), 150.8 (C-4), 147.3 (C-1), 127.2 (C-3), 123.7 (C-2), 66.0 (C-5), 61.8 (C-7), 30.5 (C-10), 23.9 (C-9), 14.3 (C-8).

IR (neat film, cm^{-1}): 3352, 2982, 2942, 2854, 2803, 1727, 1605, 1520, 1491, 1449, 1347, 1234, 1149, 1109, 1098, 1014, 855, 757, 741, 700.

MS (ES^+) found *m/z* 253 $[M+H]^+$; **HRMS** (ES^+) found 253.1176, $C_{12}H_{17}N_2O_4$ $[M+H]^+$ requires 253.1183.

Diethyl 2-(methylamino)-2-(4-nitrophenyl)-malonate 8p



Diethyl 2-chloromalonate (4.0 eq., 3.0 mmol, 491 μL) was added to a solution of 4-nitro-*N*-methylbenzenesulfonamide **6a** (1.0 eq., 0.76 mmol, 165 mg), K_2CO_3 (3.0 eq., 2.3 mmol, 318 mg), DMF (8.00 mL) within a

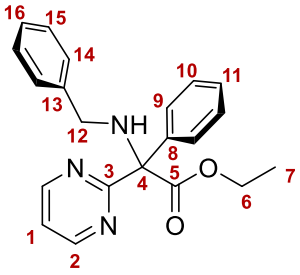
metal-capped, oven-dried microwave vial. The reaction was stirred at room temperature for 16 h, after completion EtOAc was added to the mixture and washed with 10% $LiCl_{(aq.)}$. The organic layers were extracted using EtOAc, washed with H_2O and sat. $NaCl_{(aq.)}$, dried using $MgSO_4$, filtered, and concentrated *in vacuo* to give the crude product. Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8p** as a clear colourless oil (124 mg, 0.40 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-2), 7.89 (app. d, *J* = 9.1 Hz, 2H, C*H*$_{ar}$-3), 4.31–4.19 (m, 4H, C*H*$_2$-7), 2.58 (br. s, 1H, N*H*), 2.27 (s, 3H, C*H*$_3$-9), 1.26 (t, *J* = 7.0 Hz, 6H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 168.5 (C-6), 147.9 (C-4), 142.4 (C-1), 130.2 (C-3), 123.1 (C-2), 73.7 (C-5), 62.5 (C-7), 30.3 (C-9), 14.2 (C-8).

IR (neat film, cm^{-1}): 3370, 2983, 2905, 2809, 1732, 1521, 1350, 1298, 1242, 1206, 1152, 1096, 1030, 1016, 856, 737.

MS (ES^+) found *m/z* 311 $[M+H]^+$, 333 $[M+Na]^+$; **HRMS** (ES^+) found 311.1230, $C_{14}H_{19}N_2O_6$ $[M+H]^+$ requires 311.1238.

Ethyl 2-(benzylamino)2-phenyl-2-(pyrimidin-2-yl)acetate 8q



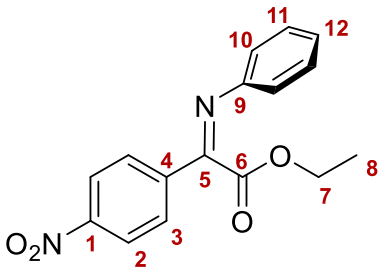
Prepared according to **General Procedure E** from *N*-benzylpyrimidine-2-sulfonamide (0.10 mmol, 24.9 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl α-chlorophenylacetate **152a** (0.20 mmol, 34 μL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **8q** as a light yellow solid (18.9 mg, 0.054 mmol, 54%), 62–64 °C.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.72 (app. d, *J* = 4.9 Hz, 2H, C*H*$_{ar}$-2), 7.79 (app. d, *J* = 7.4 Hz, 2H, C*H*$_{ar}$-9), 7.39–7.35 (m, 4H, C*H*$_{ar}$-14, 15), 7.33–7.29 (m, 3H, C*H*$_{ar}$-10, 16), 7.24 (app. t, *J* = 7.3 Hz, 1H, C*H*$_{ar}$-11), 7.16 (app. t, *J* = 4.9 Hz, 1H, C*H*$_{ar}$-1), 4.27–4.20 (m, 2H, C*H*$_2$-6), 3.71 (d, *J* = 12.9 Hz, 1H, C*H*$_2$-12), 3.56 (d, *J* = 12.9 Hz, 1H, C*H*$_2$-12), 3.31 (br. s, 1H, N*H*), 1.18 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-7); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.1 (C-5), 170.0 (C-3), 157.0 (C-2), 140.5 (C-13), 138.5 (C-8), 129.4 (C-9), 128.7 (C-16), 128.5 (C-10), 128.3 (C-15), 127.9 (C-14), 127.0 (C-11), 119.4 (C-1), 75.0 (C-4), 61.6 (C-6), 48.1 (C-12), 14.2 (C-7).

IR (neat film, cm^{-1}): 3349, 3031, 2979, 2364, 1737, 1562, 1453, 1403, 1217, 1028, 755, 699, 634.

MS (ES^+) found *m/z* 349 $[M+H]^+$; **HRMS** ($APCI^+$) found 348.1707, $C_{21}H_{22}N_3O_2$ $[M+H]^+$ requires 348.1698.

Ethyl (Z)-2-(4-nitrophenyl)-2-(phenylimino)acetate 11a



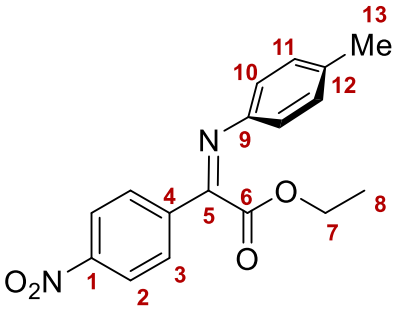
Prepared according to **General Procedure F** from 4-nitro-*N*-phenylbenzenesulfonamide **6g** (0.36 mmol, 100 mg), K_2CO_3 (1.1 mmol, 152 mg), ethyl 2-chloroacetate **7b** (0.72 mmol, 77 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **11a** as a vibrant yellow solid (121 mg, 0.41 mmol, 56%), m.p. 71–74 °C. Imine stereochemistry assigned as Z by comparison with literature data for E-**11a**.[10]

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (app. d, *J* = 8.9 Hz, 2H, CH_{ar}-2), 8.08 (app. d, *J* = 8.9 Hz, 2H, CH_{ar}-3), 7.36 (app. dd, *J* = 8.4, 7.5 Hz, 2H, CH_{ar}-11), 7.19 (app. tt, *J* = 7.5, 1.3 Hz, 1H, CH_{ar}-12), 6.97 (app. dd, *J* = 8.4, 1.3 Hz, 2H, CH_{ar}-10), 4.16 (q, *J* = 7.1 Hz, 2H, CH_2-7), 1.00 (t, *J* = 7.1 Hz, 3H, CH_3-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.2 (C-6), 158.1 (C-5), 149.67 (C-4), 149.59 (C-1), 139.4 (C-9), 129.13 (C-3), 129.09 (C-11), 125.8 (C-12), 124.0 (C-2), 119.5 (C-10), 62.1 (C-7), 13.8 (C-8).

IR (neat film, cm^{-1}): 3067, 2989, 2922, 2855, 1725, 1617, 1601, 1595, 1579, 1521, 1483, 1464, 1349, 1307, 1301, 1174, 1009, 794, 691.

MS (ES^+) found *m/z* 321 $[M+Na]^+$; **HRMS** (ES^+) found 321.0846, $C_{16}H_{14}N_2O_4Na$ $[M+Na]^+$ requires 321.0847.

Ethyl (Z)-2-(4-nitrophenyl)-2-(p-tolylimino)acetate 11b



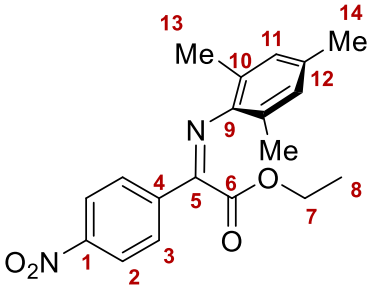
Prepared according to **General Procedure F** from 4-nitro-*N*-(*p*-tolyl)benzenesulfonamide **6h** (0.10 mmol, 29.2 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloroacetate **7b** (0.20 mmol, 22 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **11b** as a clear brown oil (21.6 mg, 0.069 mmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 8.06 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 7.16 (app. d, *J* = 8.1 Hz, 2H, C*H*$_{ar}$-11), 6.89 (app. d, *J* = 8.1 Hz, 2H, C*H*$_{ar}$-10), 4.19 (q, *J* = 7.1 Hz, 2H, C*H*$_2$-7), 2.35 (s, 3H, C*H*-13), 1.06 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.6 (C-6), 157.6 (C-5), 149.6 (C-4), 147.0 (C-12), 139.7 (C-1), 135.8 (C-9), 129.7 (C-11), 129.0 (C-3), 124.0 (C-2), 119.7 (C-10), 62.1 (C-7), 21.1 (C-13), 13.9 (C-8).

IR (neat film, cm^{-1}): 3082, 3024, 2982, 2923, 2860, 1728, 1521, 1502, 1343, 1320, 1303, 1224, 1188, 1170, 1022, 1012, 863, 850, 818, 698.

MS (ES$^+$) found *m*/*z* 335 [M+Na]$^+$; **HRMS** (ES$^+$) found 335.0998, $C_{17}H_{16}N_2O_4Na$ [M+Na]$^+$ requires 335.1002.

Ethyl (Z)-2-(mesitylimino)-2-(4-nitrophenyl)acetate 11c



Prepared according to **General Procedure F** from 4-nitro-*N*-mesitylbenzenesulfonamide **6i** (0.10 mmol, 32.0 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloroacetate **7b** (0.20 mmol, 22 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **11c** as a red-orange solid (25.4 mg, 0.075 mmol, 75%), m.p. 68–69 °C.

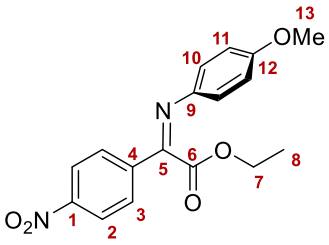
H NMR (400 MHz, $CDCl_3$): δ 8.33 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 8.11 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 6.82 (s, 2H, C*H*$_{ar}$-11), 4.10 (q, *J* = 7.1 Hz, 2H, C*H*$_2$-7), 2.26 (s, 3H, C*H*$_3$-14), 2.04 (s, 6H, C*H*$_3$-13), 0.95 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ

164.1 (C-6), 159.5 (C-5), 149.8 (C-4), 145.3 (C-9), 139.0 (C-1), 133.7 (C-12), 128.9 (C-3), 128.4 (C-11), 125.7 (C-10), 124.0 (C-2), 61.9 (C-7), 20.9 (C-14), 18.0 (C-13), 13.7(C-8).

IR (neat film, cm^{-1}): 2980, 2917, 2857, 1732, 1601, 1523, 1341, 1304, 1216, 1193, 1143, 1021, 1012, 853, 701.

MS (ES^+) found *m/z* 363 $[M+Na]^+$; **HRMS** (ES^+) found 363.1312, $C_{19}H_{20}N_2O_4Na$ $[M+Na]^+$ requires 363.1315.

Ethyl (Z)-2-((4-methoxyphenyl)imino)-2-(4-nitrophenyl)acetate 11d



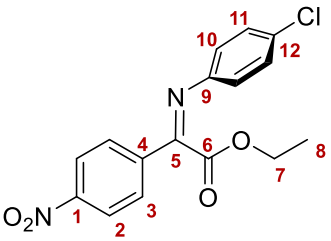
Prepared according to **General Procedure F** from 4-nitro-*N*-(4-methoxyphenyl)benzenesulfonamide **6j** (0.10 mmol, 30.8 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloroacetate **7b** (0.20 mmol, 22 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **11d** as a vibrant orange oil (16.8 mg, 0.051 mmol, 51%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (app. d, *J* = 9.0 Hz, 2H, CH_{ar}-2), 8.05 (app. d, *J* = 9.0 Hz, 2H, CH_{ar}-3), 7.00 (app. d, *J* = 8.9 Hz, 2H, CH_{ar}-11), 6.90 (app. d, *J* = 8.9 Hz, 2H, CH_{ar}-10), 4.23 (q, *J* = 7.2 Hz, 2H, CH_2-7), 3.82 (s, 3H, CH_3-13), 1.11 (t, *J* = 7.2 Hz, 3H, CH_3-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 165.0 (C-6), 158.2 (C-12), 156.8 (C-5), 149.5 (C-4), 142.5 (C-9), 139.8 (C-1), 128.9 (C-3), 124.0 (C-2), 121.6 (C-11), 114.4 (C-10), 62.1 (C-7), 55.6 (C-13), 14.0 (C-8).

IR (neat film, cm^{-1}): 3108, 3077, 2981, 2937, 2838, 1728, 1600, 1521, 1503, 1345, 1295, 1246, 1226, 1189, 1163, 1022, 1012, 851, 830, 700.

MS (ES^+) found *m/z* 351 $[M+Na]^+$; **HRMS** (ES^+) found 351.0944, $C_{17}H_{16}N_2O_5Na$ $[M+Na]^+$ requires 351.0951.

Ethyl (Z)-2-((4-chlorophenyl)imino)-2-(4-nitrophenyl)acetate 11e



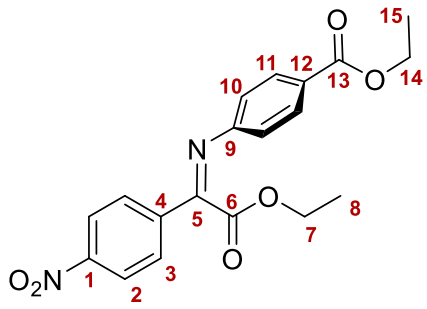
Prepared according to **General Procedure F** from 4-nitro-*N*-(4-chlorophenyl)benzenesulfonamide **6k** (0.10 mmol, 31.3 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloroacetate **7b** (0.20 mmol, 22 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **11e** as a yellow oil (16.7 mg, 0.050 mmol, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25 (app. d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-2), 7.99 (app. d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-3), 7.25 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-11), 6.85 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-10), 4.13 (q, *J* = 7.1 Hz, 2H, C*H*$_2$-7), 1.00 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 164.0 (C-6), 158.6 (C-5), 149.8 (C-4), 148.0 (C-9), 139.1 (C-1), 131.4 (C-12), 129.22 (C-3), 129.18 (C-10), 124.0 (C-2), 121.0 (C-11), 62.4 (C-7), 13.9 (C-8).

IR (neat film, cm^{-1}): 3320, 3112, 3087, 2987, 2962, 2940, 2857, 1714, 1522, 1479, 1347, 1309, 1229, 1186, 1168, 1090, 1021, 1012, 851, 836, 752, 704, 696, 664.

MS (ES$^+$) found *m*/*z* 333 [M+H]$^+$; **HRMS** (ES$^+$) found 333.0637, $C_{16}H_{14}ClN_2O_4$ [M+H]$^+$ requires 333.0637.

Ethyl (Z)-4-((2-ethoxy-1-(4-nitrophenyl)-2-oxoethylidene)imino)benzoate 11f



Prepared according to **General Procedure F** from ethyl 4-((4-nitrophenyl)sulfonamido)benzoate **6l** (0.10 mmol, 35.0 mg), K_2CO_3 (0.30 mmol, 41.5 mg), ethyl 2-chloroacetate **7b** (0.20 mmol, 22 µL), DMF (1.00 mL). Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **11f** as a yellow solid (13.5 mg, 0.037 mmol, 37%), m.p. 76–79 °C.

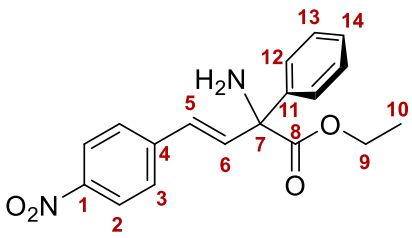
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-2), 8.09 (app. d, *J* = 9.0 Hz, 2H, C*H*$_{ar}$-3), 8.06 (app. d, *J* = 8.6 Hz, 2H, C*H*$_{ar}$-10), 6.99 (app. d, *J* = 8.6 Hz, 2H, C*H*$_{ar}$-11), 4.38 (q, *J* = 7.2 Hz, 2H, C*H*$_2$-14), 4.15 (q, *J* = 7.1 Hz, 2H, C*H*$_2$-7), 1.40 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-15), 1.01 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 166.3 (C-

13), 163.5 (C-6), 158.7 (C-5), 153.5 (C-9), 149.9 (C-4), 138.9 (C-1), 130.8 (C-10), 129.3 (C-3), 127.7 (C-12), 124.1 (C-2), 119.2 (C-11), 62.4 (C-7), 61.2 (C-14), 14.5 (C-15), 13.9 (C-8).

IR (neat film, cm^{-1}): 2981, 2936, 2355, 1713, 1601, 1524, 1347, 1272, 1226, 1190, 1166, 1101, 1021, 1013, 858, 697.

MS (ES^+) found *m/z* 393 $[M+Na]^+$; **HRMS** (ES^+) found 393.1056, $C_{19}H_{18}N_2O_6Na$ $[M+Na]^+$ requires 393.1057.

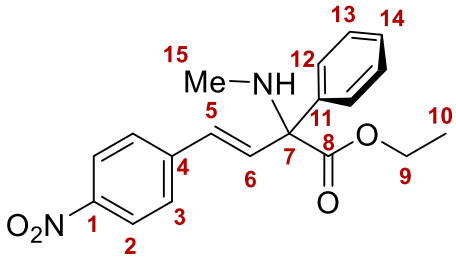
Ethyl (E)-2-amino-4-(4-nitrophenyl)-2-phenylbut-3-enoate 14a



Prepared following General Procedure E using 2-(4-nitrophenyl)ethylene-1-sulfonamide **13a** (0.20 mmol, 45.6 mg), K_2CO_3 (0.60 mmol, 83.0 mg), ethyl α-chlorophenylacetate (0.40 mmol, 69 μL), DMF (2.0 mL), after purification by column chromatography on silica gel (10–80% EtOAc in hexane) to give **14a** as a yellow oil (23.0 mg, 0.070 mmol, 35% yield).

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.22 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-2), 7.77 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-3), 7.53 (d, 2H, *J* = 7.5 Hz, C*H*$_{ar}$-12), 7.37 (t, *J* = 7.5 Hz, 2H, C*H*$_{ar}$-13), 7.29 (m, 1H, C*H*$_{ar}$-14), 7.15 (d, *J* = 15.5 Hz, 1H, C*H*-5), 7.03 (d, *J* = 15.5 Hz, 1H, C*H*-6), 4.23 (qd, *J* = 7.2 Hz, 2.2 Hz, 2H, C*H*$_2$-9), 2.49 (br. s, 1H, N*H*), 1.23 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-10). **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 174.8 (C-8), 147.9 (C-1), 144.7 (C-4), 144.4 (C-11), 138.5 (C-6), 129.3 (C-13), 128.4 (C-5), 128.4 (C-14), 128.2 (C-2), 127.0 (C-12), 124.7 (C-3), 66.4 (C-7), 62.28 (C-9), 14.4 (C-10). **HRMS** ($APCI^+$) found 327.1323, $C_{18}H_{19}N_2O_4$ $[M+H]^+$ requires 327.1339.

Ethyl (E)-2-methlyamino-4-(4-nitrophenyl)-2-phenylbut-3-enoate 14b



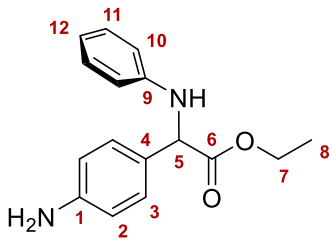
Prepared following General Procedure E using *N*-methyl-2-(4-nitrophenyl)ethylene-1-sulfonamide **13b** (0.20 mmol, 48.4 mg), K_2CO_3 (0.60 mmol, 83.0 mg), ethyl α-chlorophenylacetate (0.40 mmol, 69

µL), DMF (2.00 mL), after purification by column chromatography on silica gel (10–80% EtOAc in hexane) to give **14b** as a yellow oil (40.1 mg, 0.12 mmol, 59% yield).

^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ 8.21 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-2), 7.77 (d, *J* = 8.8 Hz, 2H, C*H*$_{ar}$-3), 7.48 (m, 2H, , C*H*$_{ar}$-12), 7.37 (t, *J* = 7.5 Hz, 2H, C*H*$_{ar}$-13), 7.29 (m, 1H, C*H*$_{ar}$-14), 7.06 (d, *J* = 15.5 Hz, 1H, C*H*-5), 6.95 (d, *J* = 15.5 Hz, 1H, C*H*-6), 4.25 (qd, *J* = 7.2 Hz, 2.2 Hz, 2H, C*H*$_2$-9), 2.66 (bs, 1H, N*H*), 2.27 (s, 3H, C*H*$_3$-15), 1.22 (t, *J* = 7.2 Hz, 3H, C*H*$_3$-10). **^{13}C NMR** (101 MHz, $(CD_3)_2CO$): δ 172.9 (C-8), 147.0 (C-1), 143.8 (C-4), 141.6 (C-11), 135.1 (C-6), 128.5 (C-5), 128.4 (C-13), 127.5 (C-14), 127.4 (C-2), 126.7 (C-12), 123.8 (C-3), 70.7 (C-7), 61.1 (C-9), 42.3 (C-15), 13.6 (C-10). **HRMS** (APCI$^+$) found 341.1488, $C_{19}H_{21}N_2O_4$ $[M+H]^+$ requires 341.1496.

4. Reduction of Imine to Arylglycine Derivative

Ethyl 2-(4-aminophenyl)-2-(phenylamino)acetate 12a



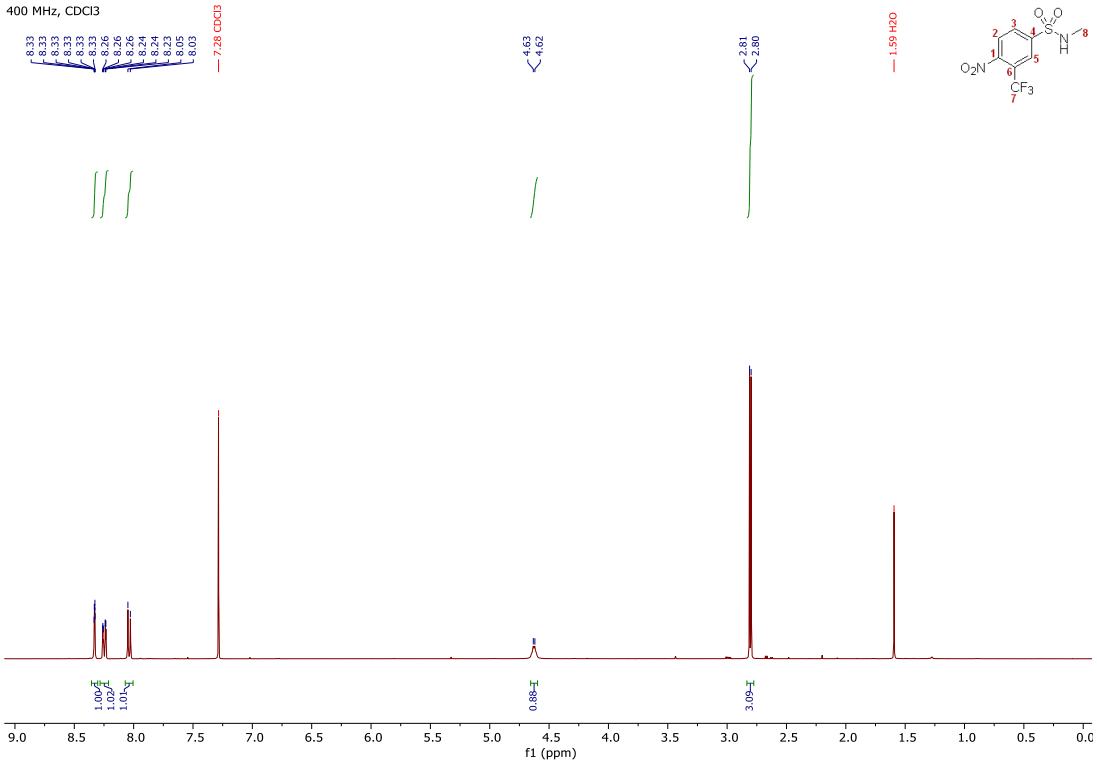
Method adapted from Mangas-Sánchez *et al.*[11] $NiCl_2.6H_2O$ (1.5 eq., 0.17 mmol, 40.4 mg) was added to a solution of ethyl 2-(4-nitrophenyl)-2-(phenylimino)acetate **11a** (1.0 eq., 0.11 mmol, 33.8 mg) in EtOH (1.00 mL). The solution was cooled to 0 °C and $NaBH_4$ (4.0 eq., 0.44 mmol, 16.6 mg) added. After 15 mins the reaction was allowed to warm to room temperature and stirred for 16 h. The mixture was filtered over Celite®, the solvents removed under reduced pressure. Purification by column chromatography on silica gel (0–40% EtOAc in hexanes) afforded **12a** as a light yellow oil (21.4 mg, 0.079 mmol, 72%).

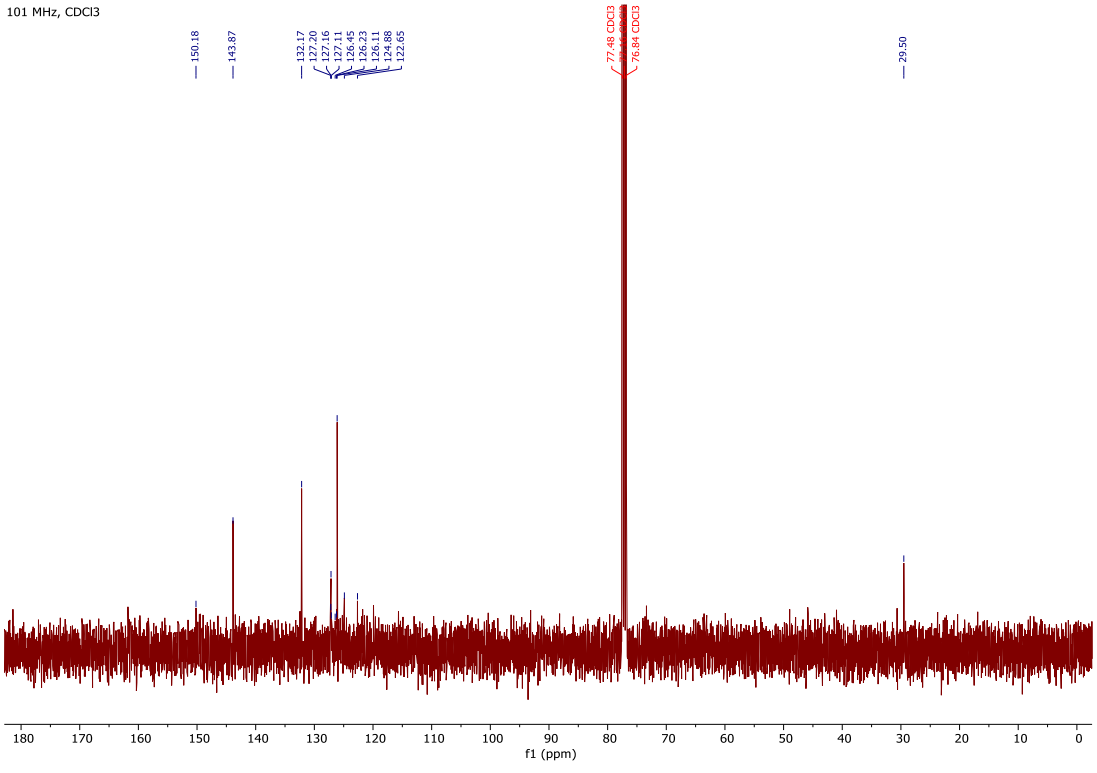
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-2), 7.12 (app. dd, *J* = 8.5, 7.5 Hz, 2H, C*H*$_{ar}$-11), 6.69 (app. tt, *J* = 7.5, 1.2 Hz, 1H, C*H*$_{ar}$-12), 6.65 (app. d, *J* = 8.4 Hz, 2H, C*H*$_{ar}$-3), 6.57 (app. dd, *J* = 8.5, 1.2 Hz, 2H, C*H*$_{ar}$-10), 4.95 (s, 1H, C*H*-5), 4.83 (br. s, 1H, N*H*), 4.26–4.19 (m, 1H, C*H*$_2$-7), 4.16–4.10 (m, 1H, C*H*$_2$-7), 3.68 (br. s, 2H, N*H*$_2$), 1.22 (t, *J* = 7.1 Hz, 3H, C*H*$_3$-8); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 172.5 (C-6), 146.5 (C-1), 146.3 (C-9), 129.3 (C-10), 128.4 (C-2), 127.5 (C-4), 118.0 (C-12), 115.4 (C-3), 113.5 (C-11), 61.7 (C-7), 60.4 (C-5), 14.2 (C-8).

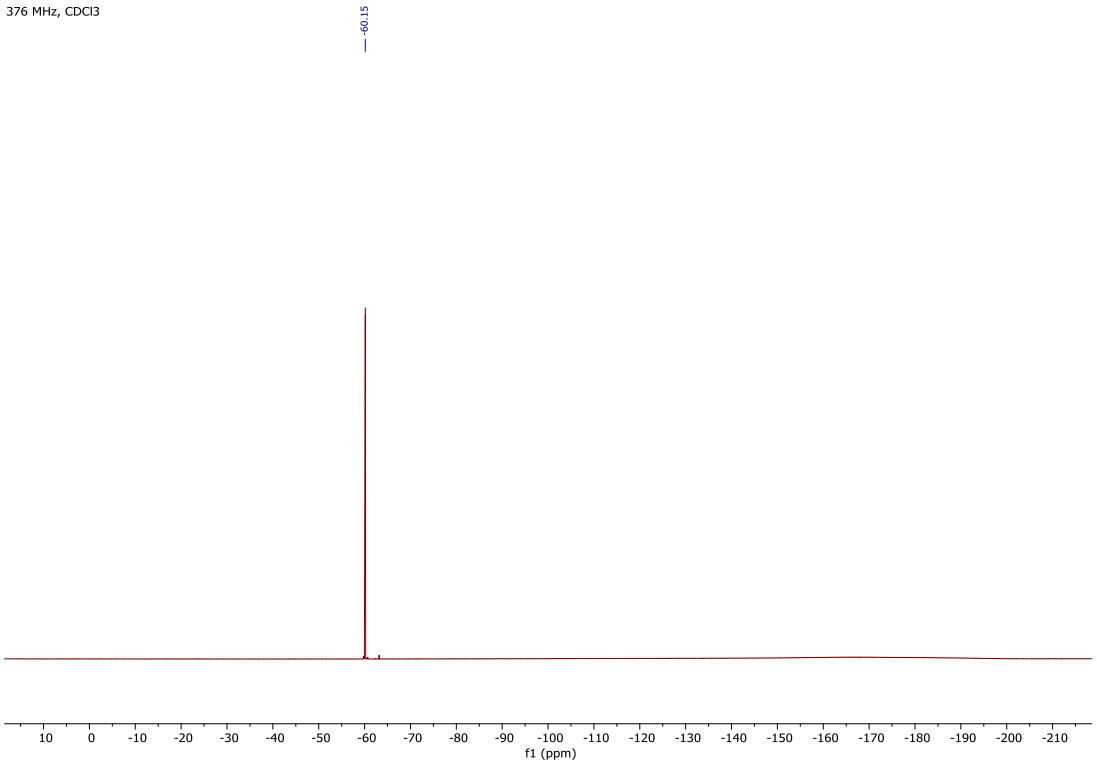
Data is in accordance with previous literature reports.[12]

5. NMR Spectra

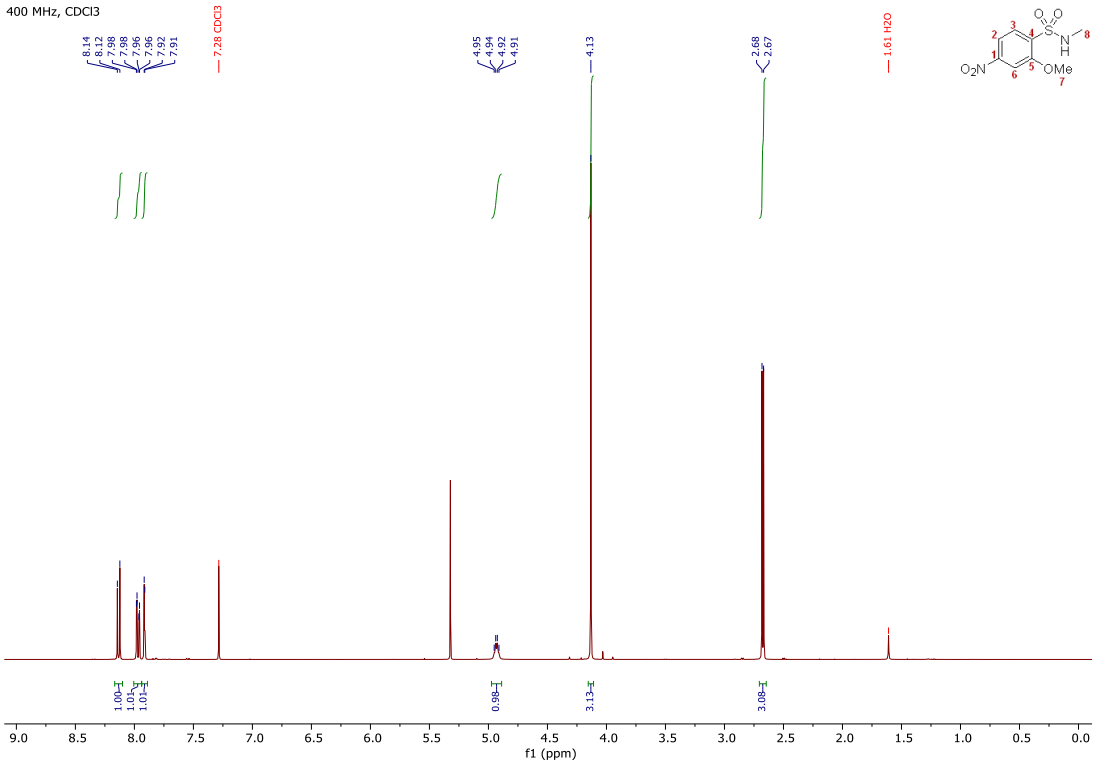
6c

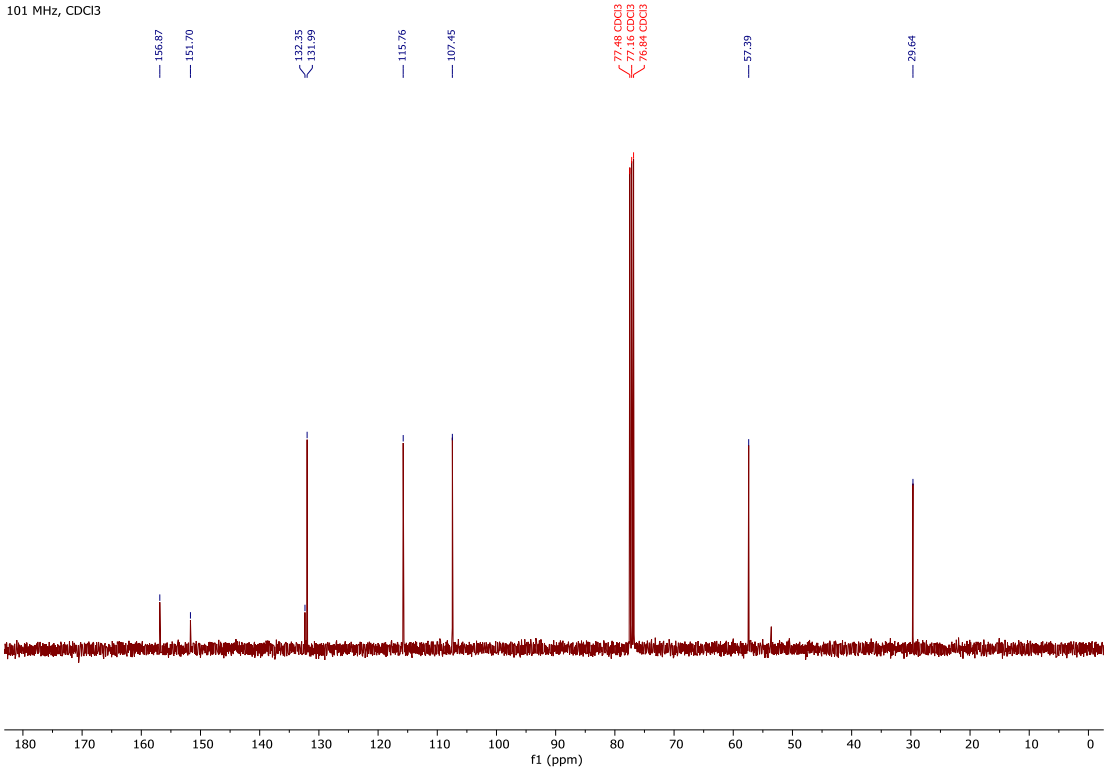




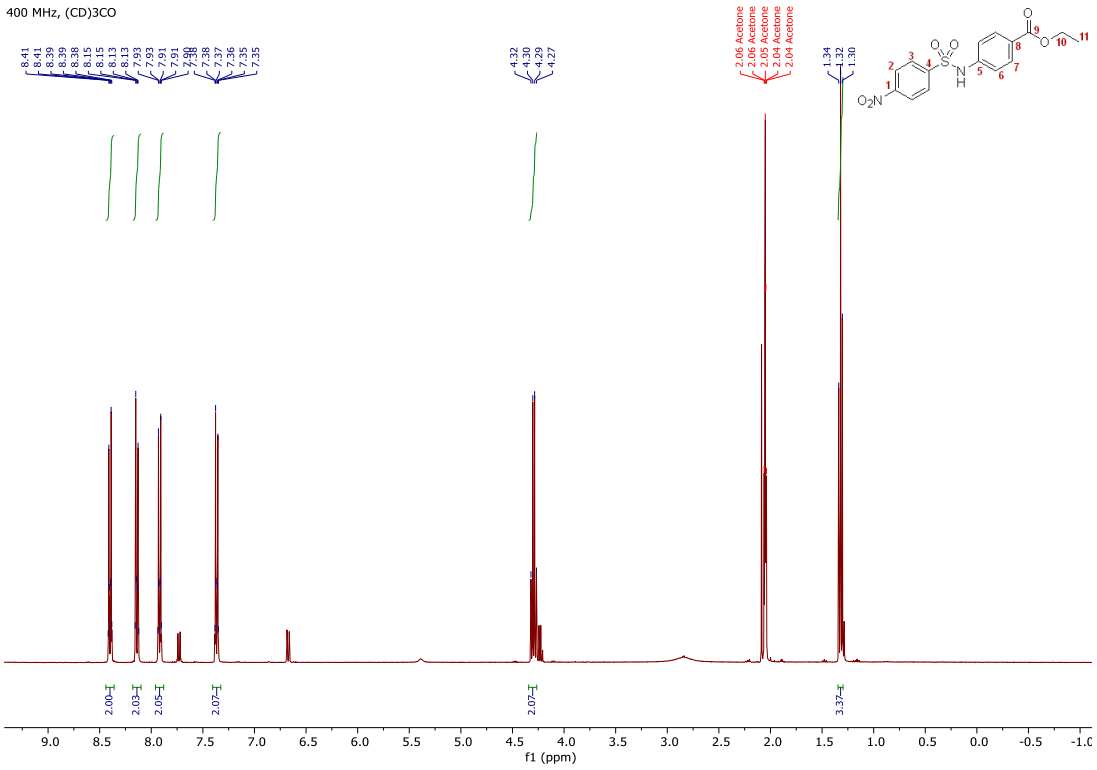

376 MHz, CDCl3
-60.15
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

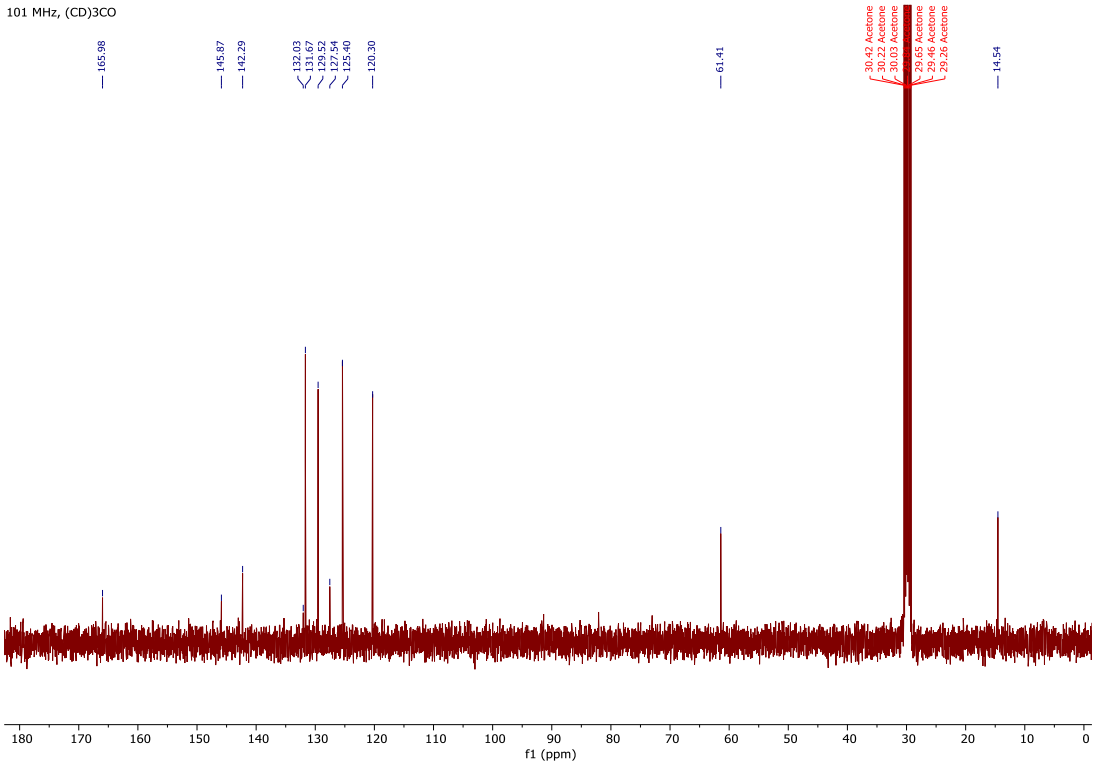
6d

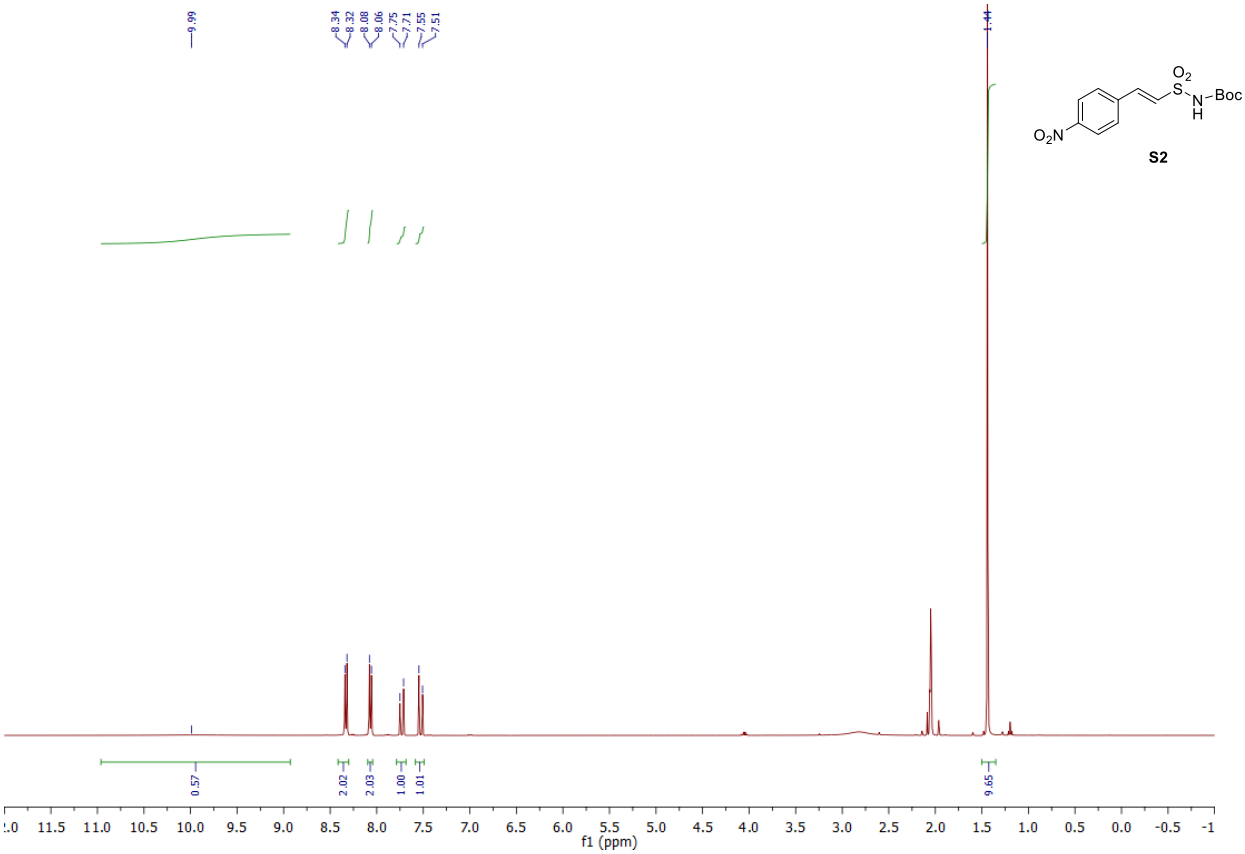

400 MHz, CDCl3
8.14
8.12
7.98
7.98
7.96
7.96
7.92
7.91
7.28 CDCl3
4.95
4.94
4.92
4.91
4.13
2.68
2.67
1.61 H2O
1.00
1.01
1.01
0.98
3.13
3.08
f1 (ppm)

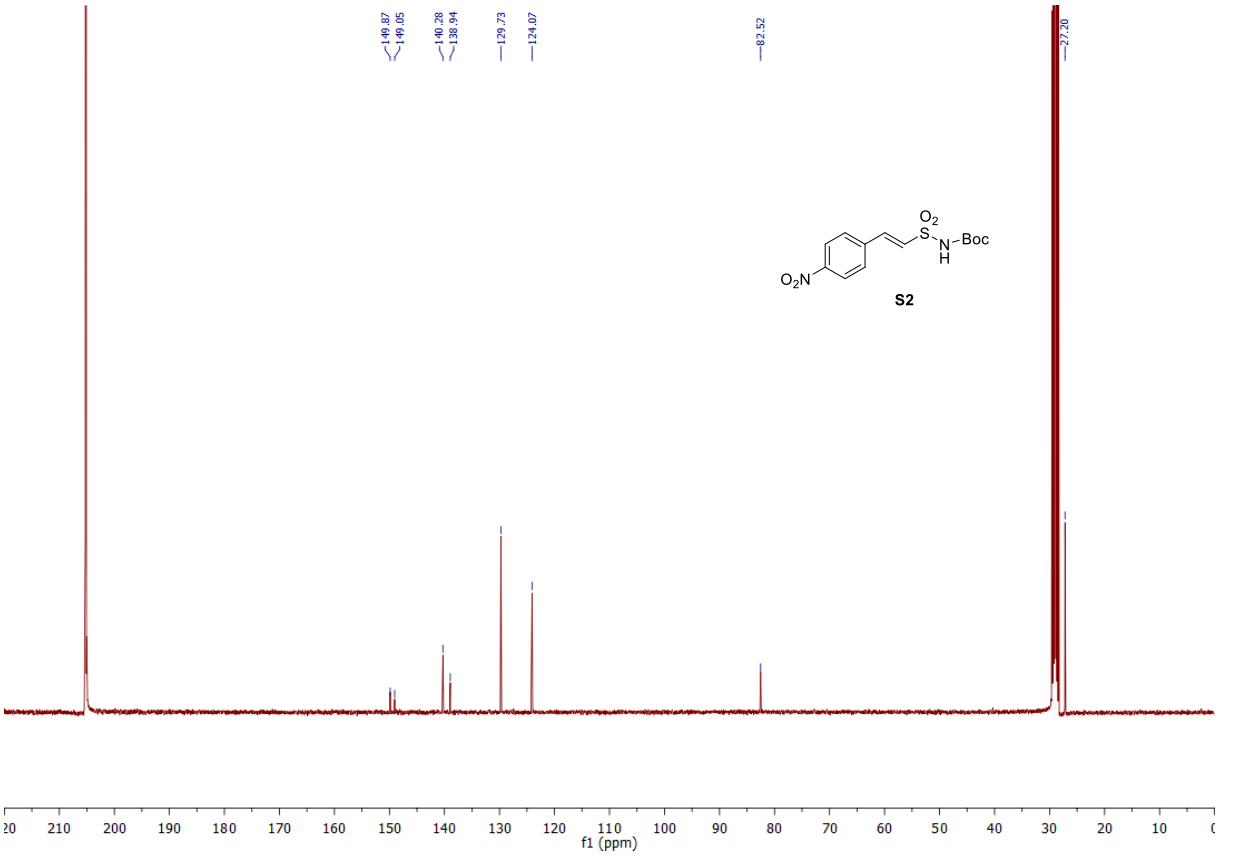

101 MHz, CDCl3
156.87
151.70
132.35
131.99
115.76
107.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
57.39
29.64
f1 (ppm)

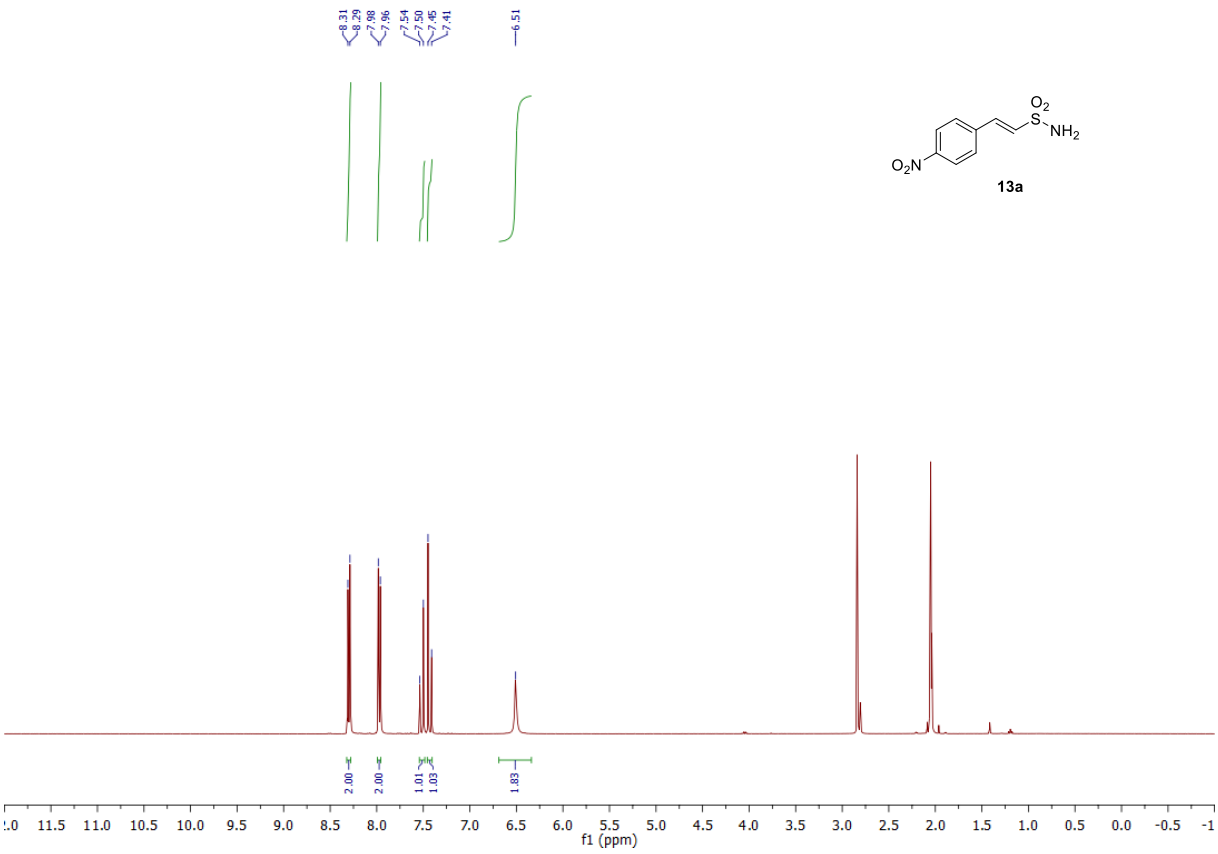
6i


400 MHz, (CD)3CO
8.41
8.41
8.39
8.39
8.38
8.15
8.15
8.13
8.13
7.93
7.93
7.91
7.91
7.38
7.38
7.37
7.36
7.35
7.35
4.32
4.30
4.29
4.27
2.06 Acetone
2.06 Acetone
2.05 Acetone
2.04 Acetone
2.04 Acetone
1.34
1.32
1.30
2.00
2.03
2.05
2.07
2.07
3.37
f1 (ppm)


101 MHz, (CD)3CO
165.98
145.87
142.29
132.03
131.67
129.52
127.54
125.40
120.30
61.41
30.42 Acetone
30.22 Acetone
30.03 Acetone
29.65 Acetone
29.46 Acetone
29.26 Acetone
14.54
f1 (ppm)

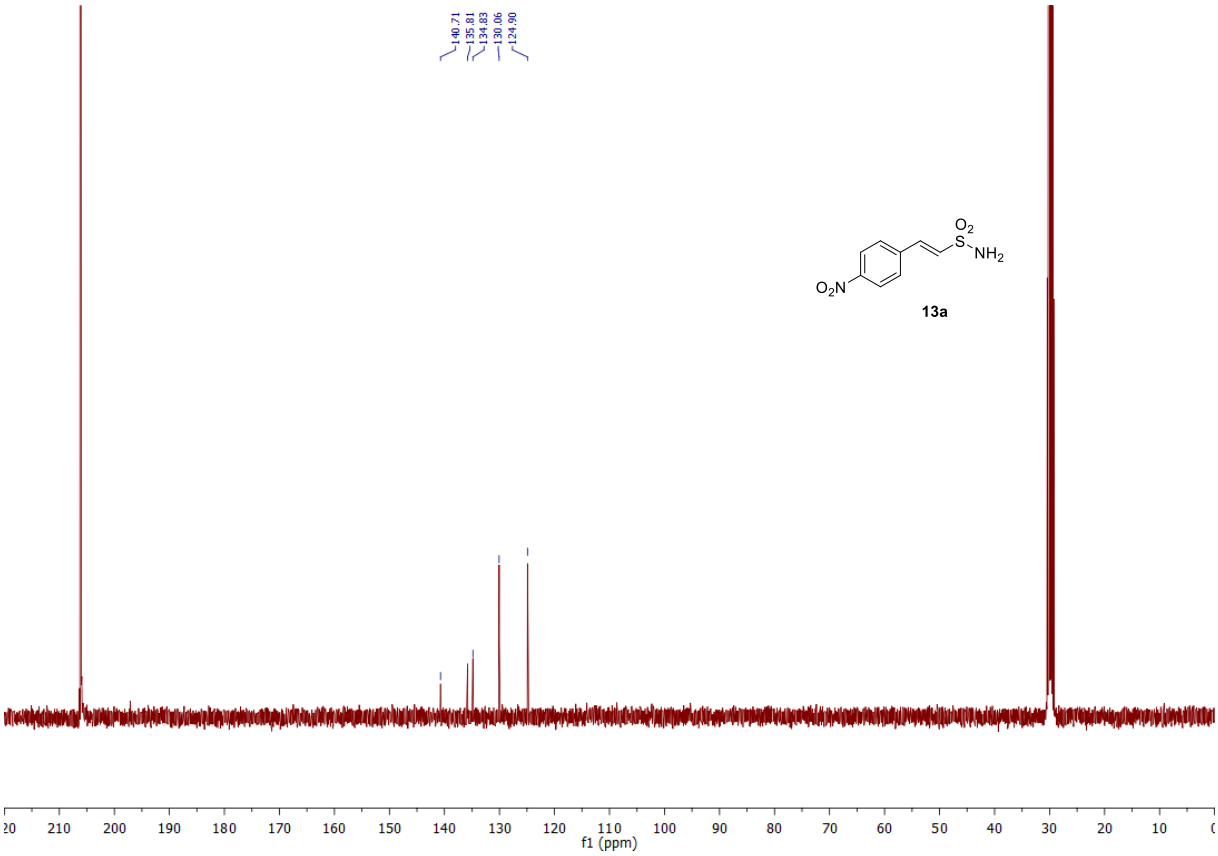

9.99
8.34
8.32
8.08
8.06
7.75
7.71
7.55
7.51
1.44
0.57
2.02
2.03
1.00
1.01
9.65
f1 (ppm)
S2


149.87
149.05
140.28
138.94
129.73
124.07
82.52
27.20
f1 (ppm)
S2


8.31
8.29
7.98
7.96
7.54
7.50
7.45
7.41
6.51
2.00
2.00
1.01
1.03
1.83
f1 (ppm)

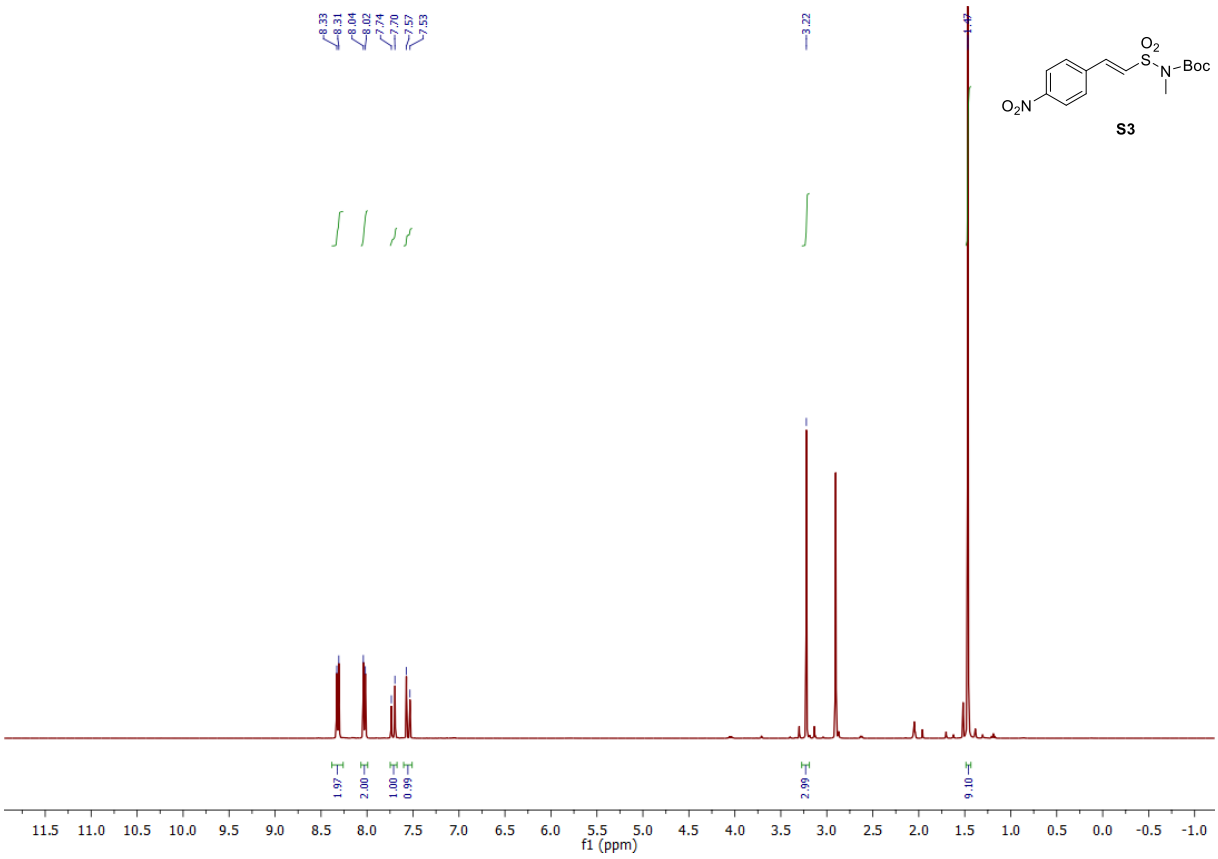
O2
S
NH2
O2N

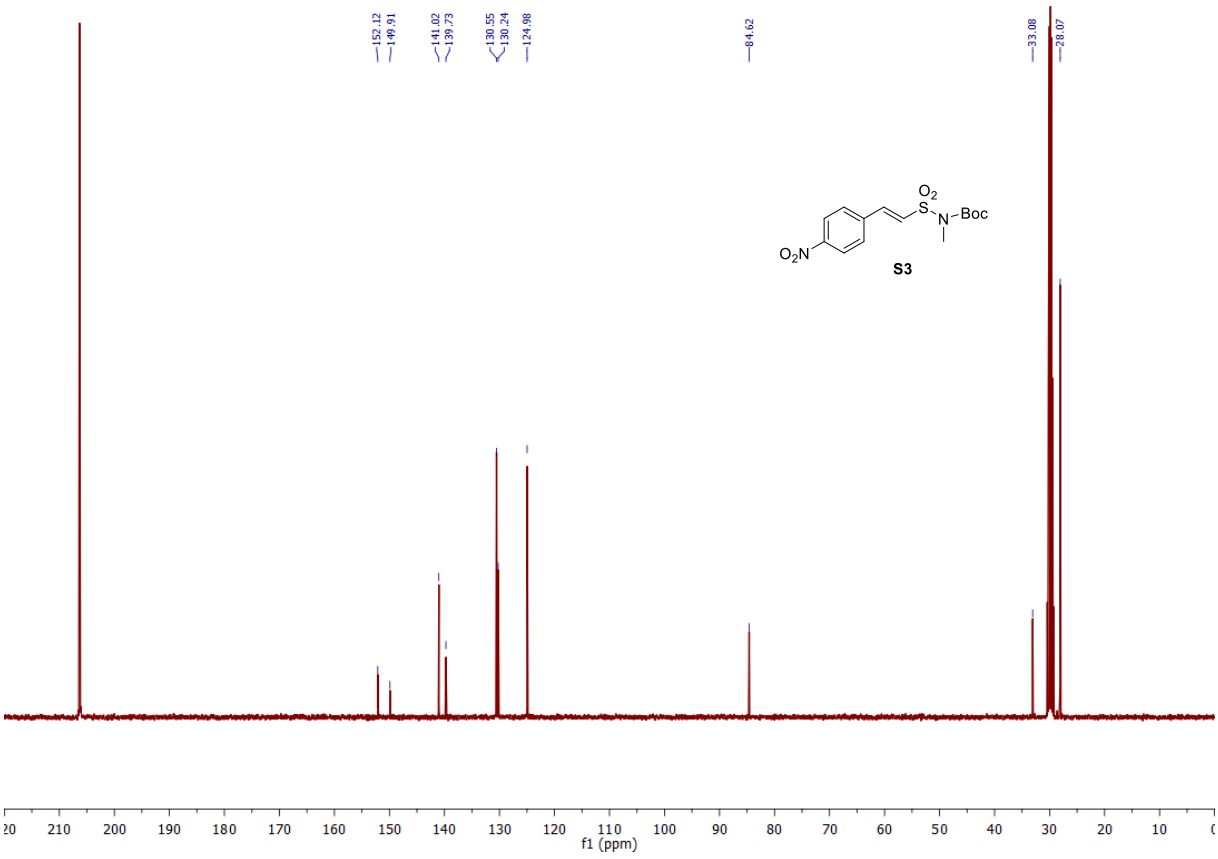
13a

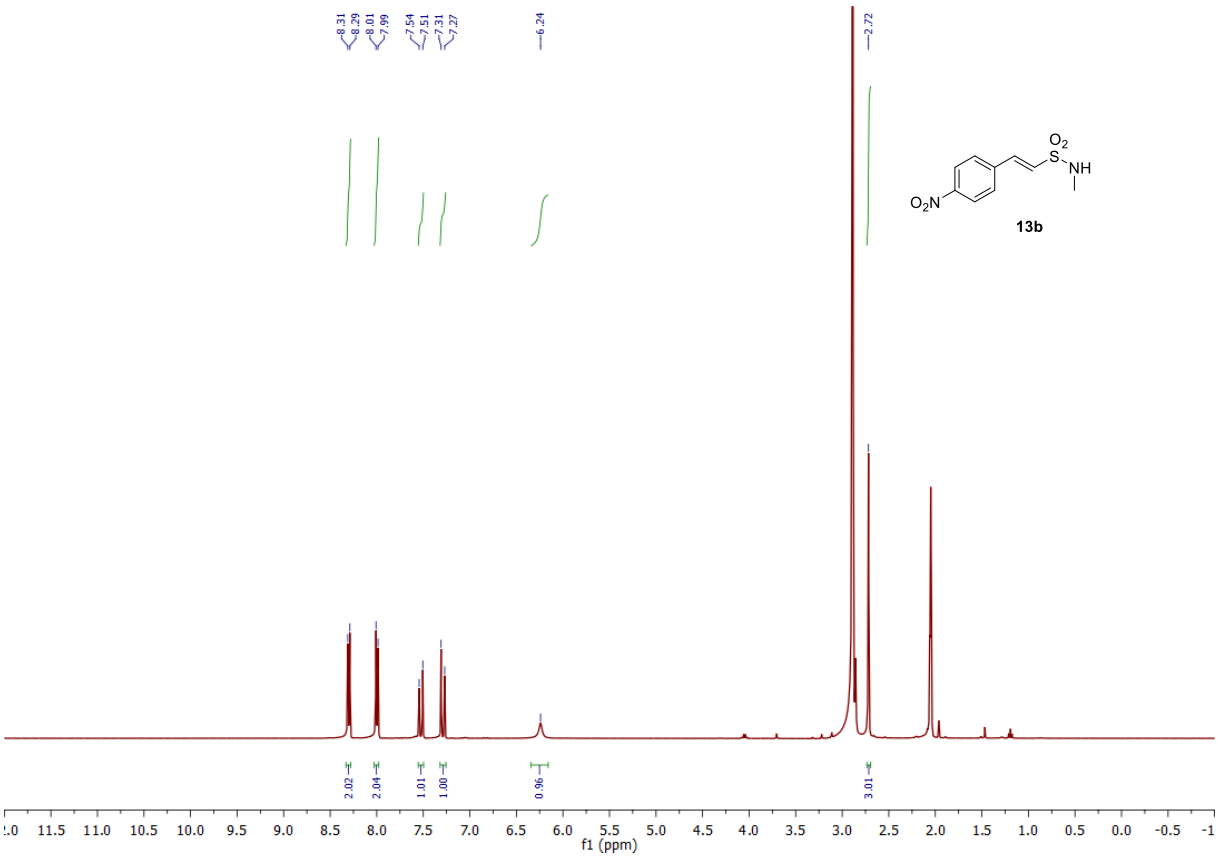

140.71
135.81
134.83
130.06
124.90
f1 (ppm)

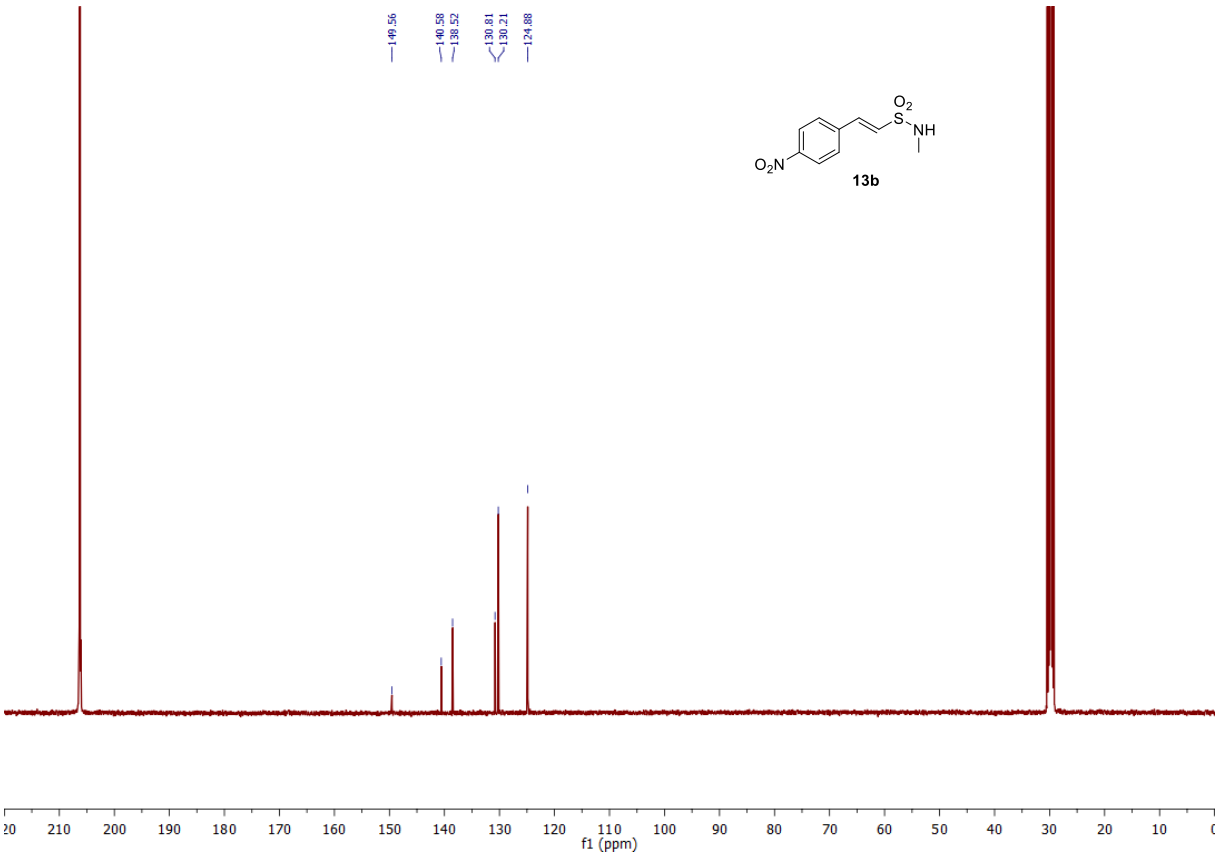
O2
S
NH2
O2N

13a

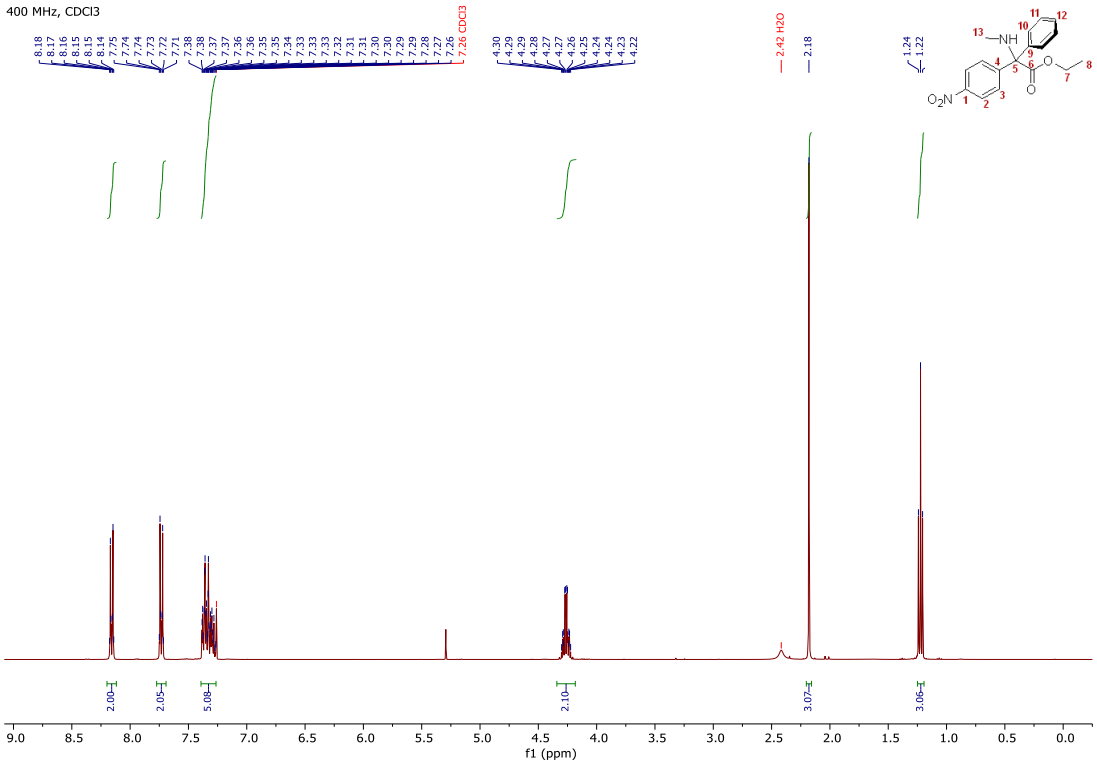

8.33
8.31
8.04
8.02
7.74
7.70
7.57
7.53
3.22
1.47
1.97
2.00
1.00
0.99
2.99
9.10
f1 (ppm)
S3

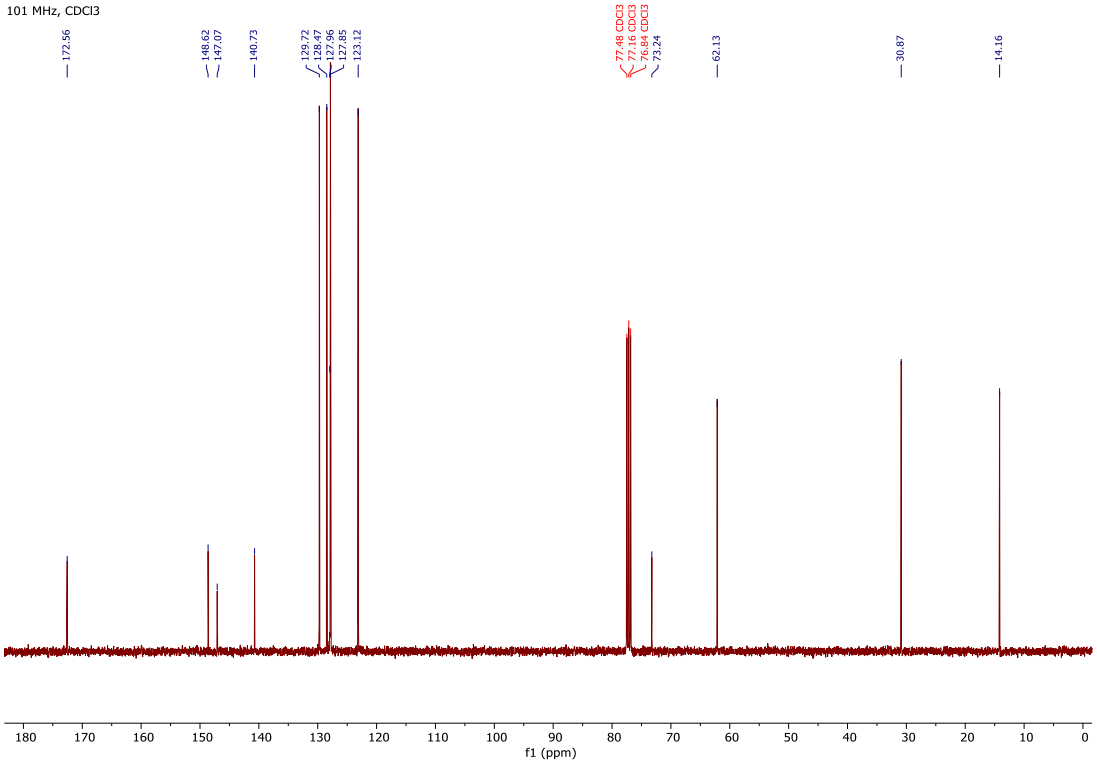

152.12
149.91
141.02
139.73
130.55
130.24
124.98
84.62
33.08
28.07
f1 (ppm)
S3


8.31
8.29
8.01
7.99
7.54
7.51
7.31
7.27
6.24
2.72
2.02
2.04
1.01
1.00
0.96
3.01
f1 (ppm)
O2
S
NH
O2N
13b

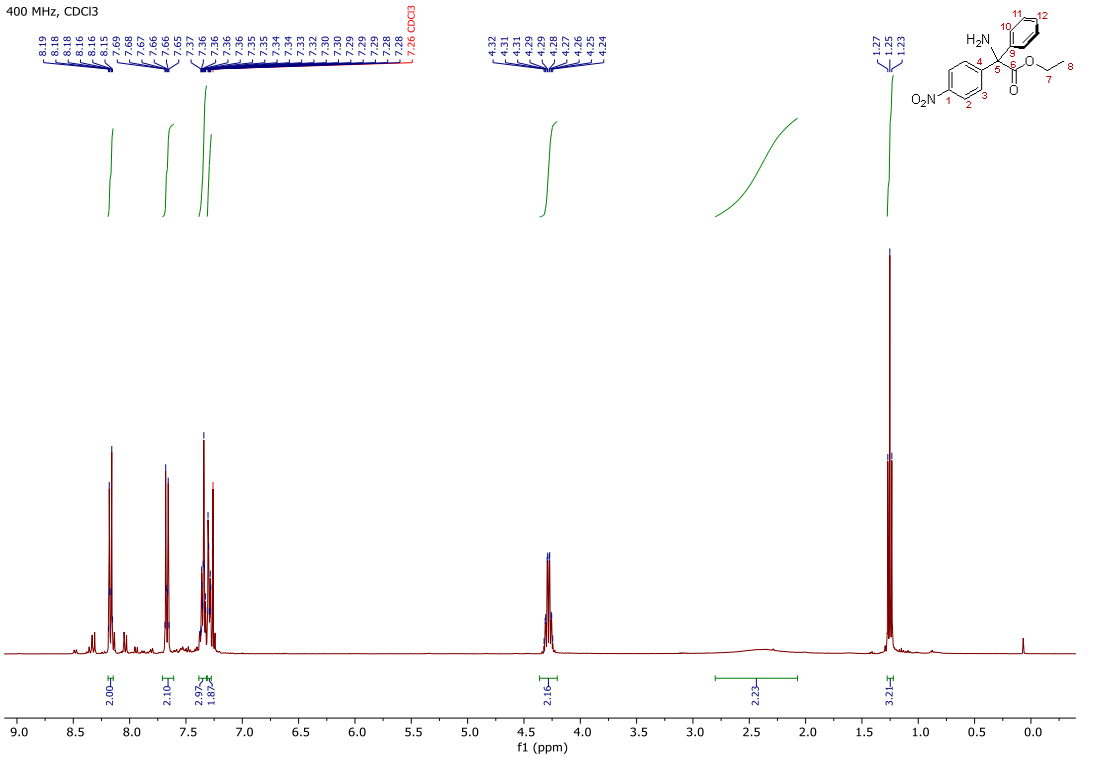

149.56
140.58
138.52
130.81
130.21
124.88
f1 (ppm)
O2
S
NH
O2N
13b

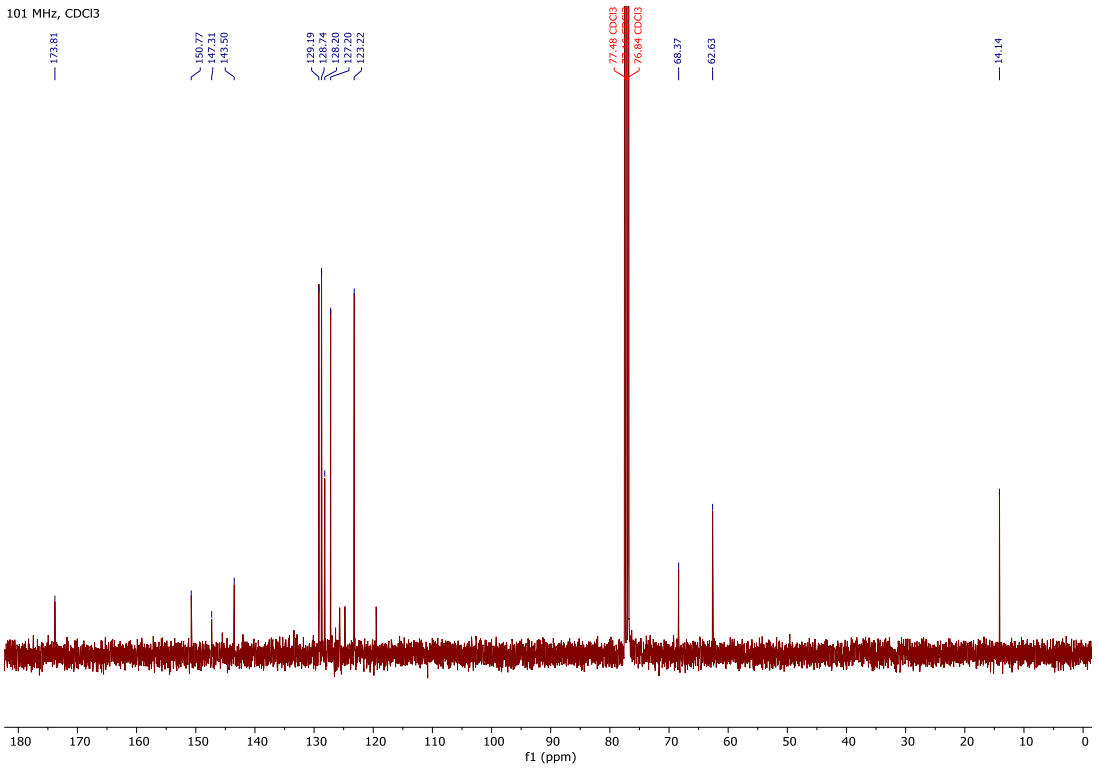
8a


400 MHz, CDCl3
8.18
8.17
8.16
8.15
8.15
8.14
7.75
7.74
7.74
7.73
7.72
7.71
7.38
7.38
7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.26
7.26 CDCl3
4.30
4.29
4.29
4.28
4.27
4.27
4.26
4.25
4.24
4.24
4.23
4.22
2.42 H2O
2.18
1.24
1.22
2.00
2.05
5.08
2.10
3.07
3.06
f1 (ppm)

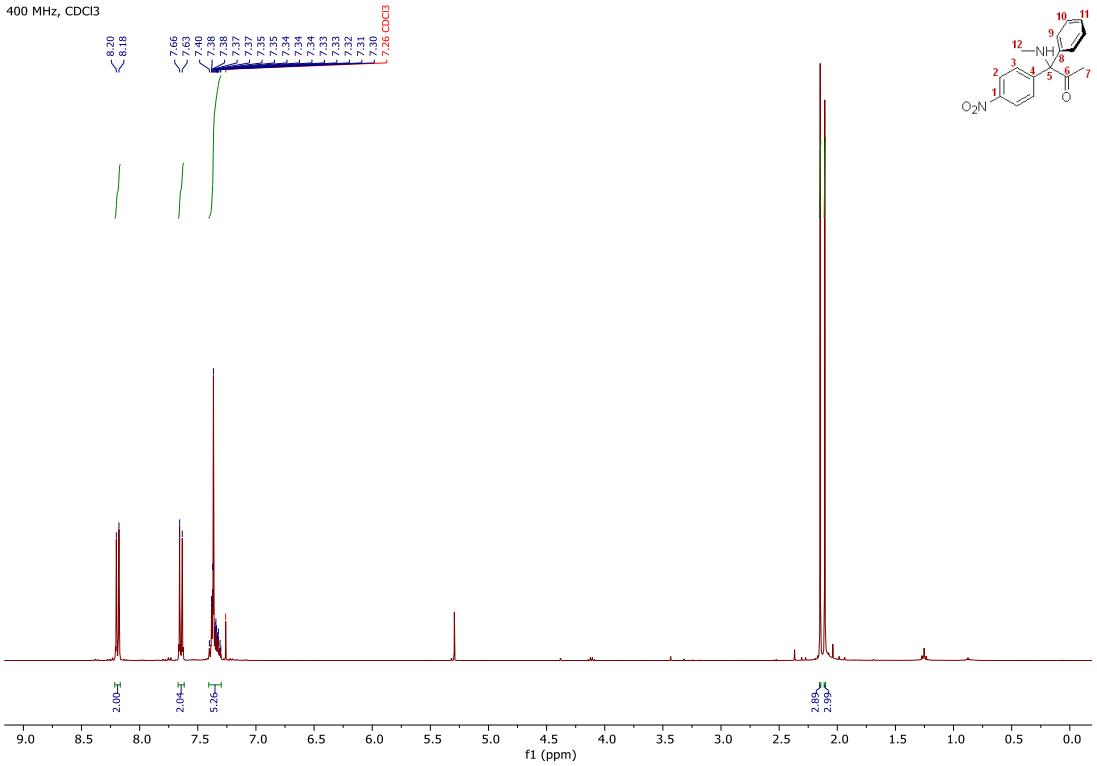

101 MHz, CDCl3
172.56
148.62
147.07
140.73
129.72
128.47
127.96
127.85
123.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.24
62.13
30.87
14.16
f1 (ppm)

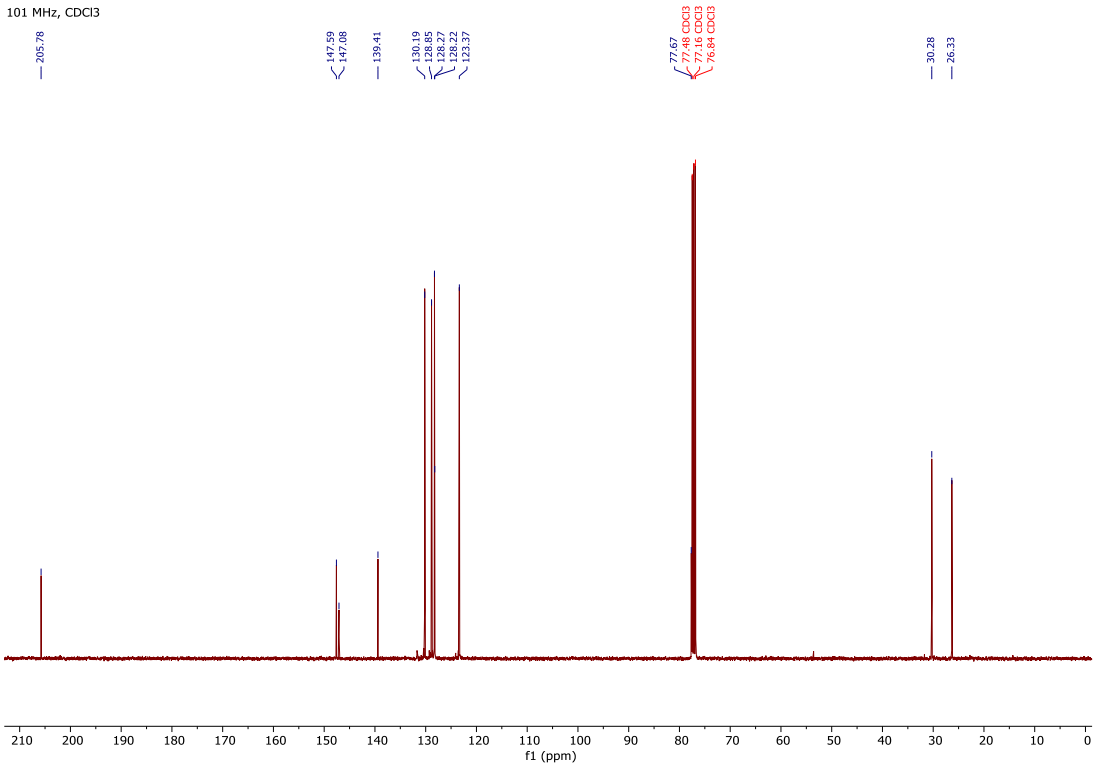
8b


400 MHz, CDCl3
7.26 CDCl3
f1 (ppm)

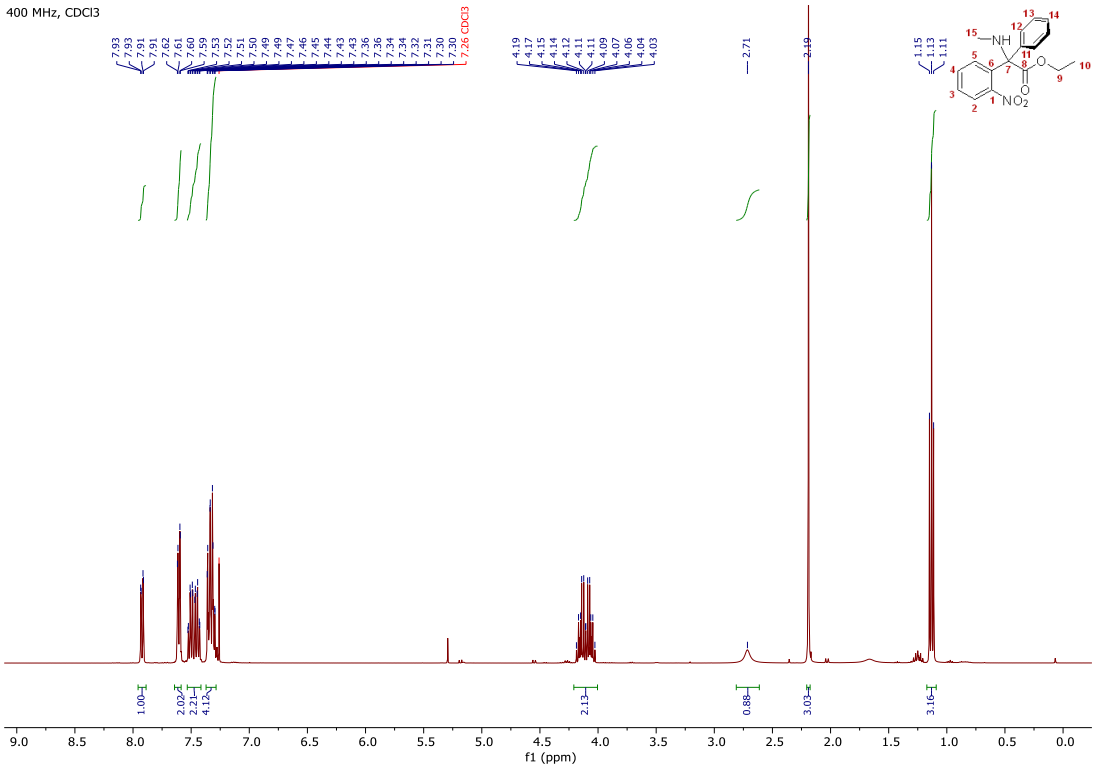

101 MHz, CDCl3
173.81
150.77
147.31
143.50
129.19
128.74
128.20
127.20
123.22
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
68.37
62.63
14.14
f1 (ppm)

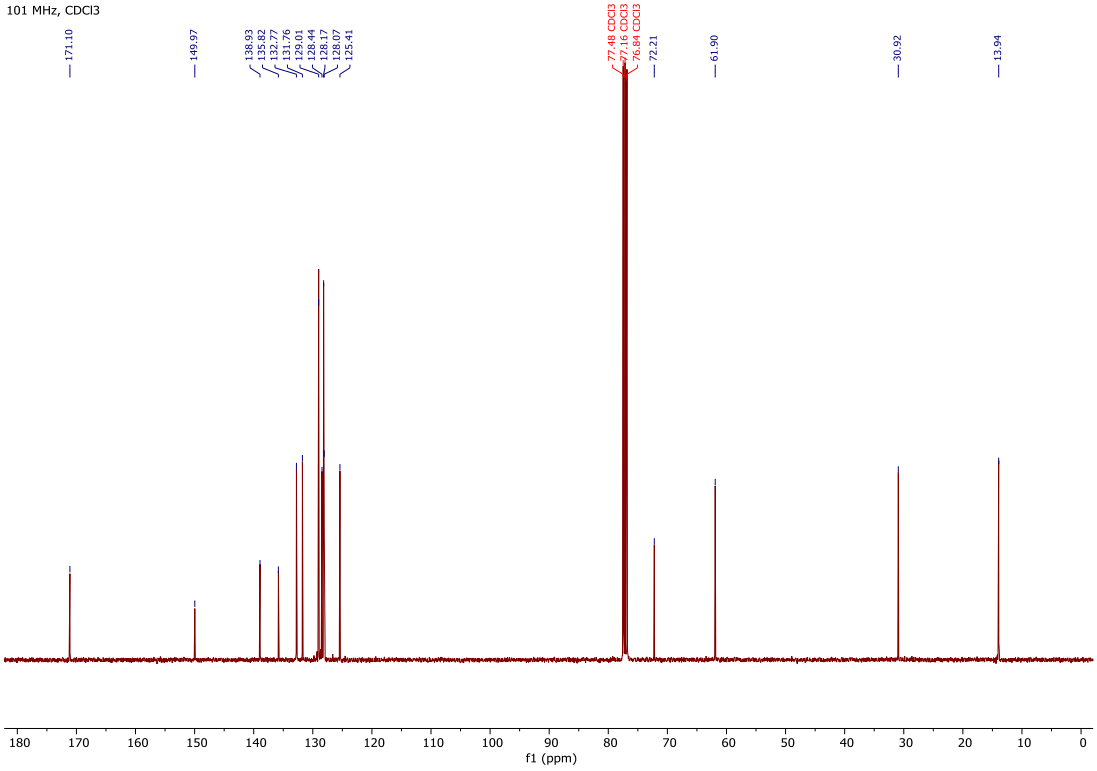
8c


400 MHz, CDCl3
8.20
8.18
7.66
7.63
7.40
7.38
7.38
7.37
7.37
7.35
7.35
7.34
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.26 CDCl3
2.00
2.04
5.26
2.89
2.99
f1 (ppm)

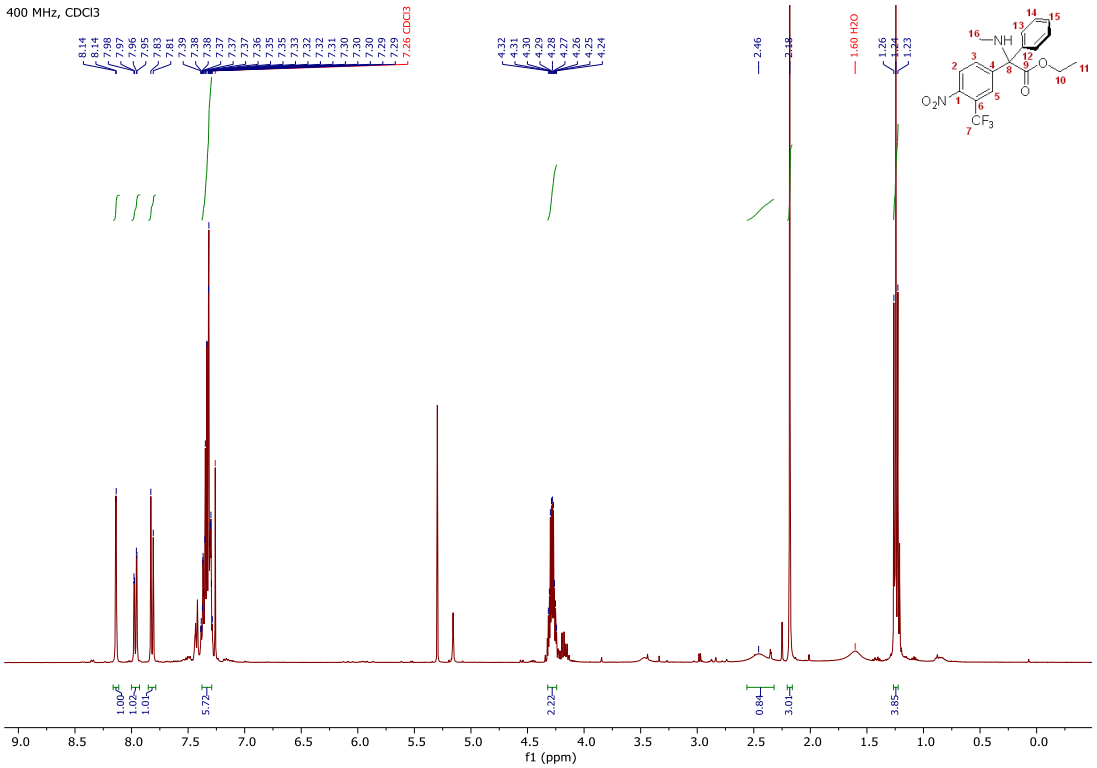

101 MHz, CDCl3
205.78
147.59
147.08
139.41
130.19
128.85
128.27
128.22
123.37
77.67
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
30.28
26.33
f1 (ppm)

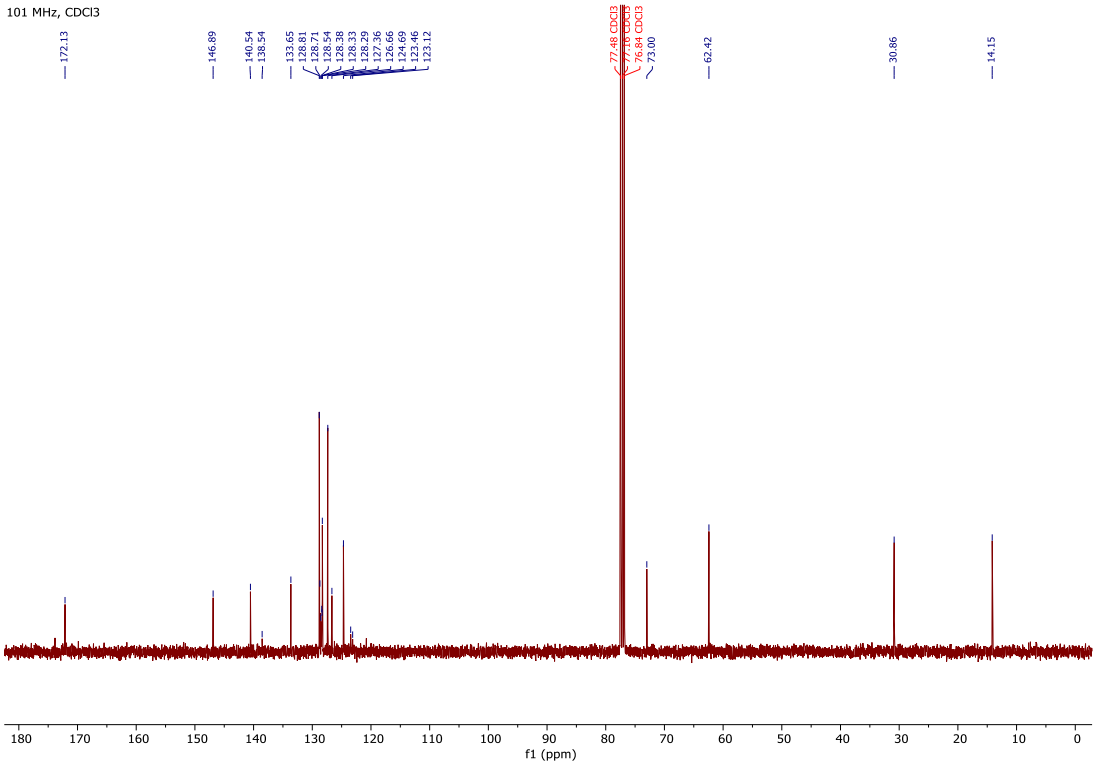
8d

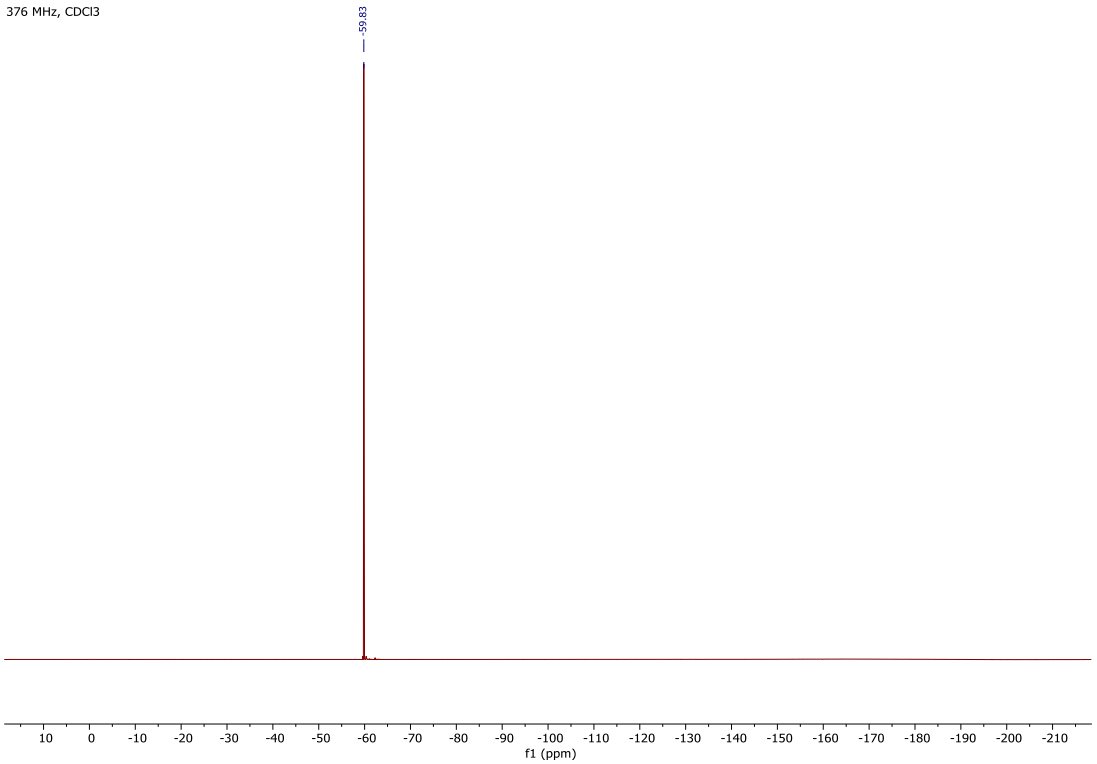

400 MHz, CDCl3
7.93
7.91
7.62
7.61
7.60
7.59
7.53
7.52
7.51
7.50
7.49
7.47
7.46
7.45
7.44
7.43
7.36
7.34
7.32
7.31
7.30
7.26 CDCl3
4.19
4.17
4.15
4.14
4.12
4.11
4.09
4.07
4.06
4.04
4.03
2.71
2.19
1.15
1.13
1.11
NH
NO2
1.00
2.02
2.21
4.12
2.13
0.88
3.03
3.16
f1 (ppm)


101 MHz, CDCl3
171.10
149.97
138.93
135.82
133.77
131.76
129.01
128.44
128.17
128.07
125.41
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.21
61.90
30.92
13.94
f1 (ppm)

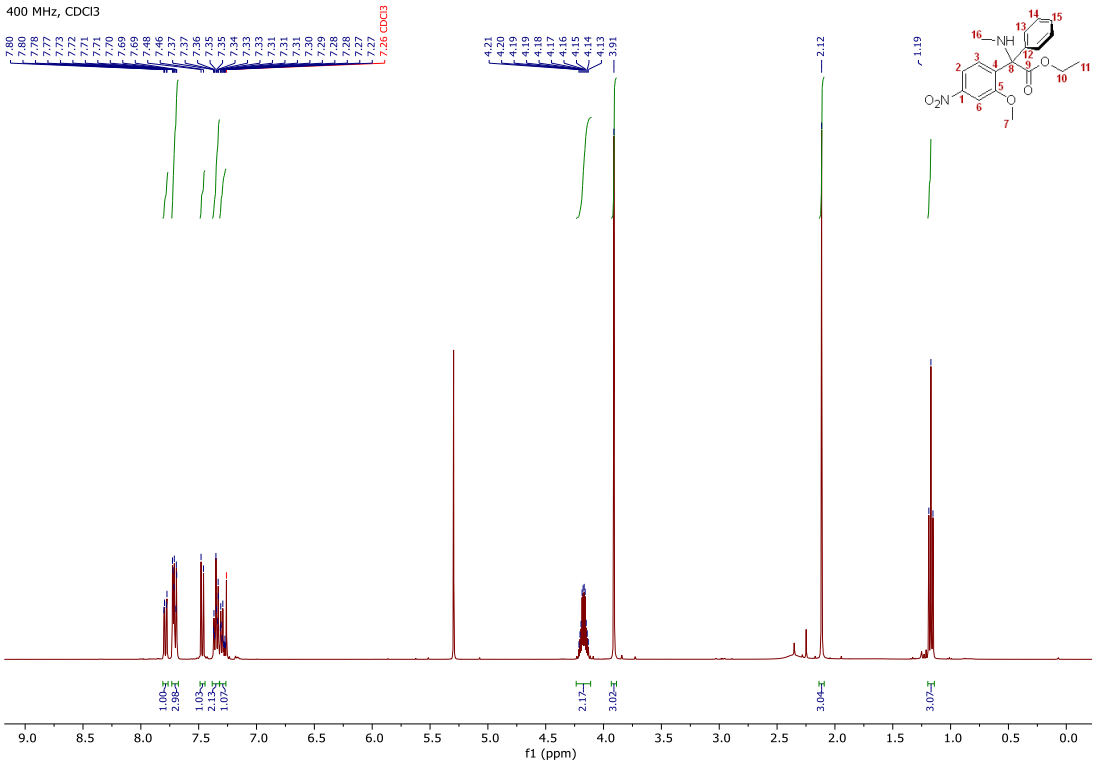
8e

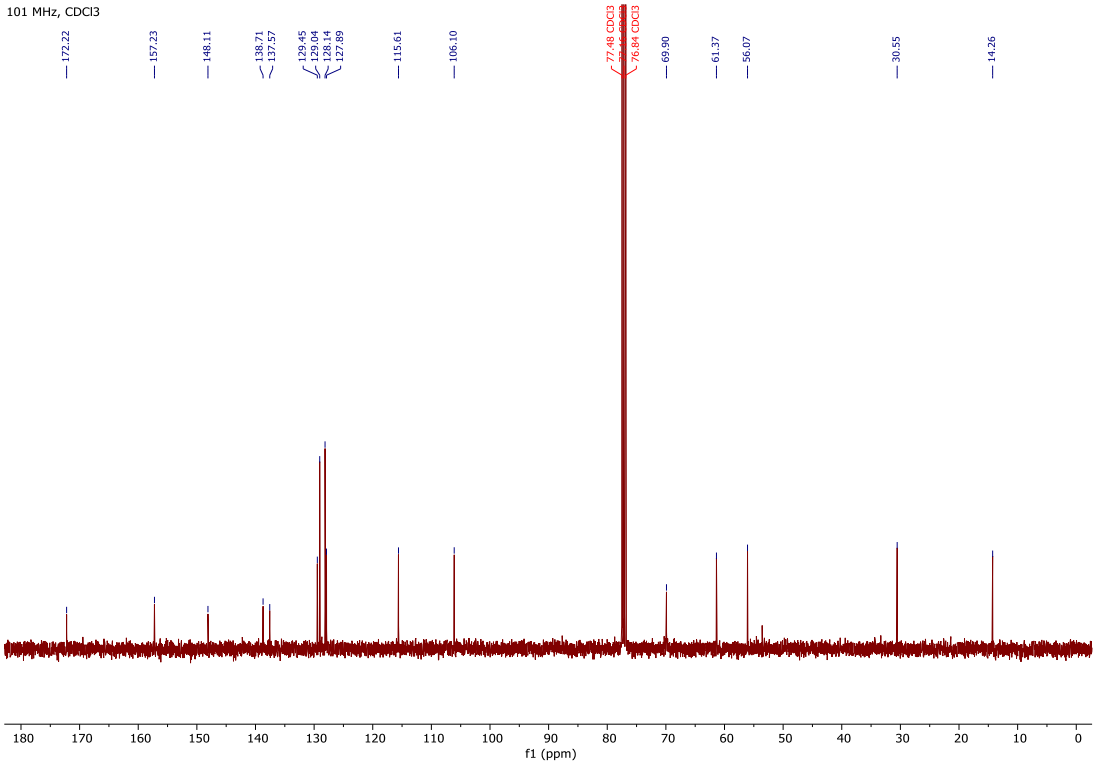

400 MHz, CDCl3
8.14
8.14
8.13
7.98
7.97
7.96
7.95
7.83
7.81
7.39
7.38
7.38
7.37
7.37
7.37
7.36
7.35
7.35
7.33
7.32
7.32
7.31
7.30
7.30
7.30
7.29
7.29
7.26 CDCl3
4.32
4.31
4.30
4.29
4.28
4.27
4.26
4.25
4.24
2.46
2.18
1.60 H2O
1.26
1.24
1.23
1.00
1.02
1.01
5.72
2.22
0.84
3.01
3.85
f1 (ppm)


101 MHz, CDCl3
172.13
146.89
140.54
138.54
133.65
128.81
128.71
128.54
128.38
128.33
128.29
127.36
126.66
124.69
123.46
123.12
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.00
62.42
30.86
14.15
f1 (ppm)

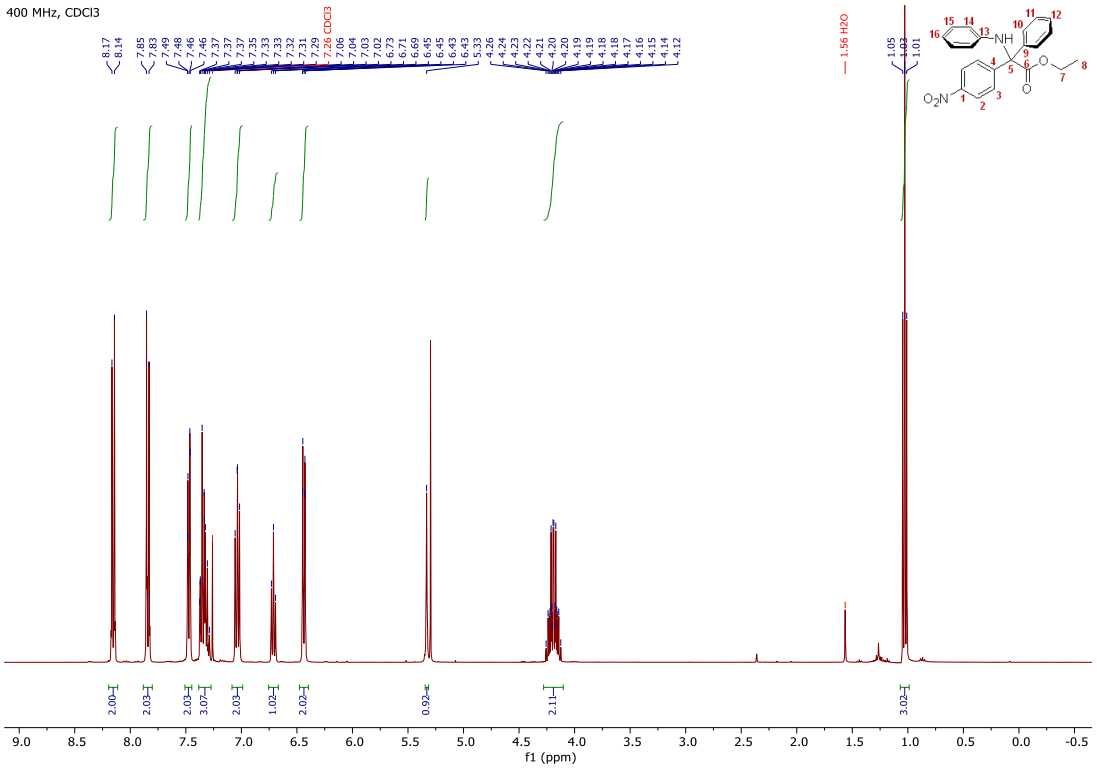

376 MHz, CDCl3
-59.83
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

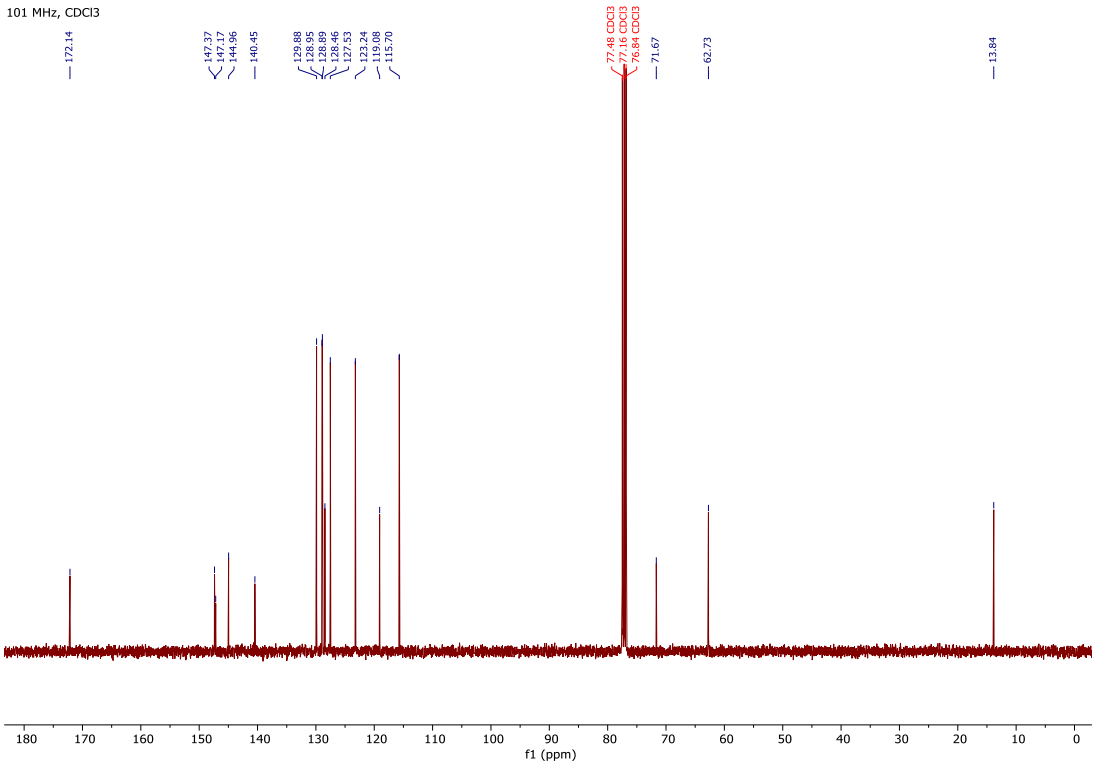
8f


400 MHz, CDCl3
7.80
7.78
7.77
7.73
7.72
7.71
7.70
7.69
7.48
7.46
7.37
7.36
7.35
7.34
7.33
7.31
7.30
7.29
7.28
7.27
7.26 CDCl3
4.21
4.20
4.19
4.18
4.17
4.16
4.15
4.14
4.13
3.91
2.12
1.19
1.00
2.98
1.03
2.13
1.07
2.17
3.03
3.04
3.07
f1 (ppm)

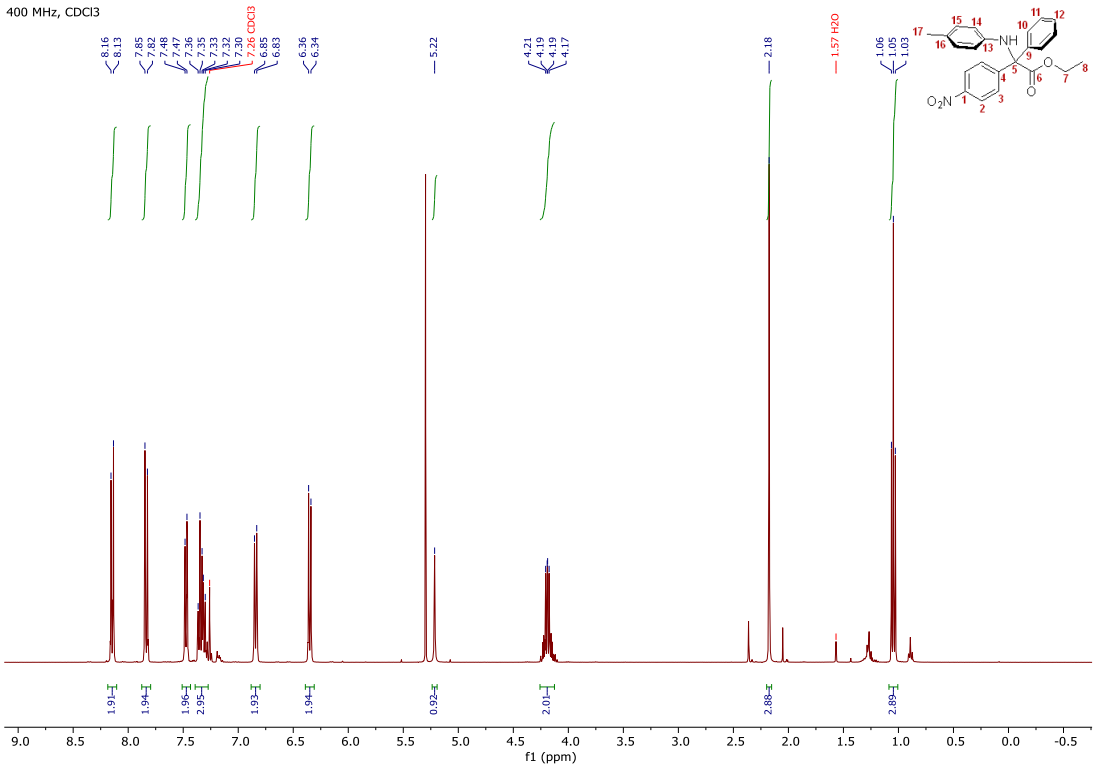

101 MHz, CDCl3
172.22
157.23
148.11
138.71
137.57
129.45
129.04
128.14
127.89
115.61
106.10
77.48 CDCl3
76.84 CDCl3
69.90
61.37
56.07
30.55
14.26
f1 (ppm)

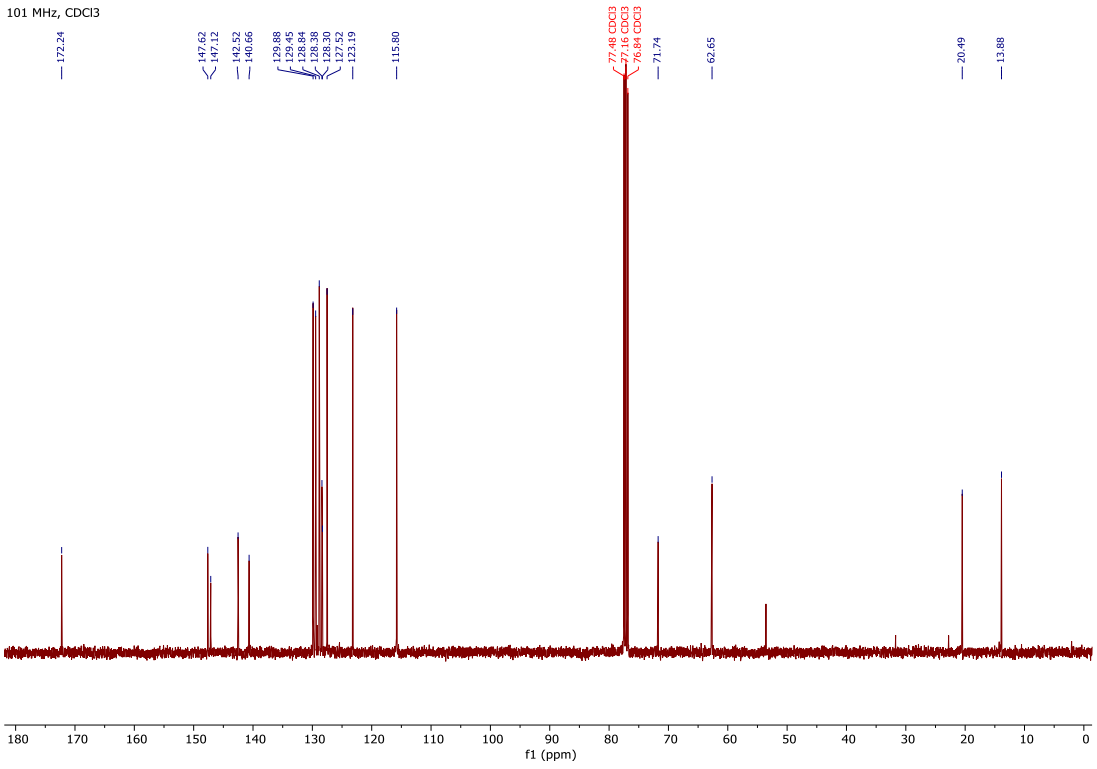
8g


400 MHz, CDCl3
8.17
8.14
7.85
7.83
7.49
7.48
7.46
7.46
7.37
7.37
7.35
7.33
7.33
7.32
7.31
7.29
7.26 CDCl3
7.06
7.04
7.03
7.02
6.73
6.71
6.69
6.45
6.45
6.43
6.43
5.33
4.26
4.24
4.23
4.22
4.21
4.20
4.20
4.19
4.19
4.18
4.18
4.17
4.16
4.15
4.14
4.12
1.56 H2O
1.05
1.03
1.01
2.00
2.03
2.03
3.07
2.03
1.02
2.02
0.92
2.11
3.02
f1 (ppm)

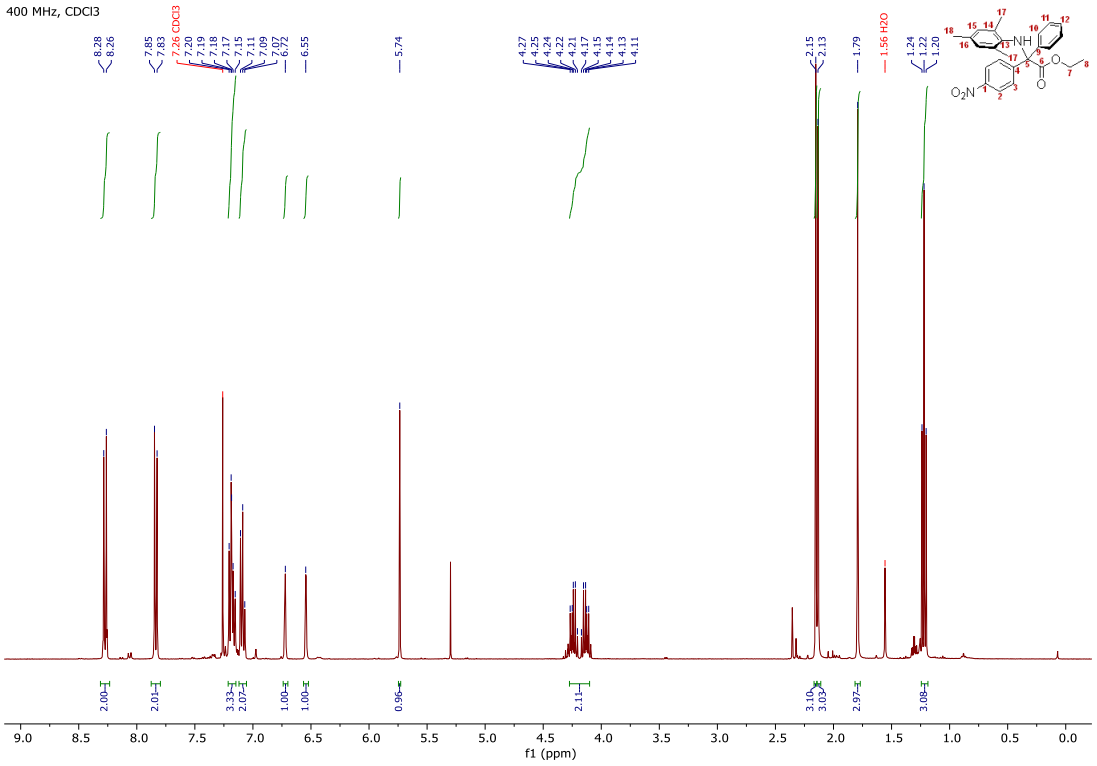

101 MHz, CDCl3
172.14
147.37
147.17
144.96
140.45
129.88
128.95
128.89
128.46
127.53
123.24
119.08
115.70
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.67
62.73
13.84
f1 (ppm)

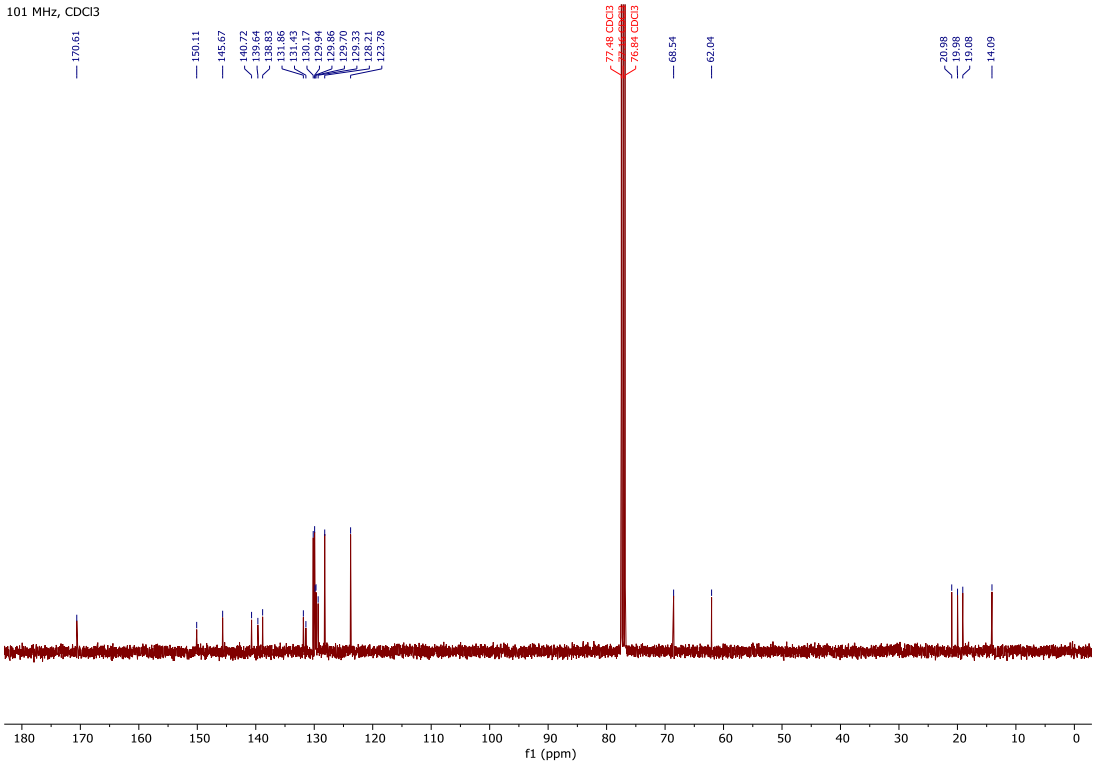
8h


400 MHz, CDCl3
8.16
8.13
7.85
7.82
7.48
7.47
7.36
7.35
7.33
7.32
7.30
7.26 CDCl3
6.85
6.83
6.36
6.34
5.22
4.21
4.19
4.19
4.17
2.18
1.57 H2O
1.06
1.05
1.03
1.91
1.94
1.96
2.95
1.93
1.94
0.92
2.01
2.88
2.89
f1 (ppm)

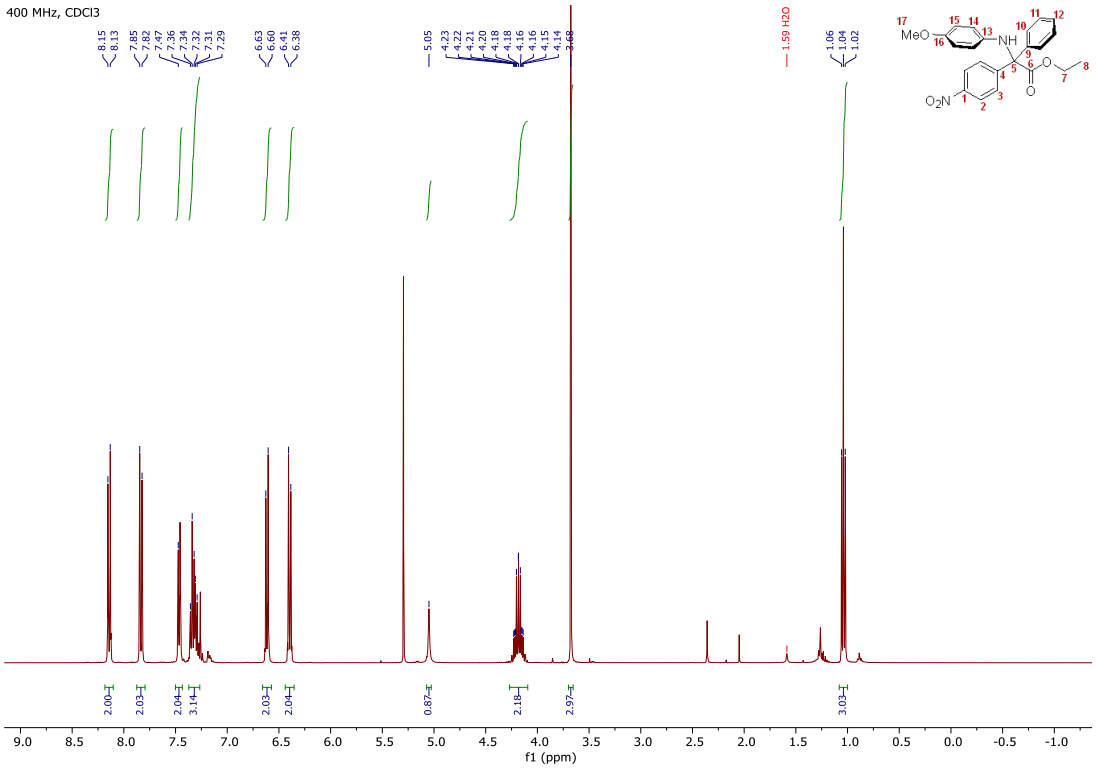

101 MHz, CDCl3
172.24
147.62
147.12
142.52
140.66
129.88
129.45
128.84
128.38
128.30
127.52
123.19
115.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.74
62.65
20.49
13.88
f1 (ppm)

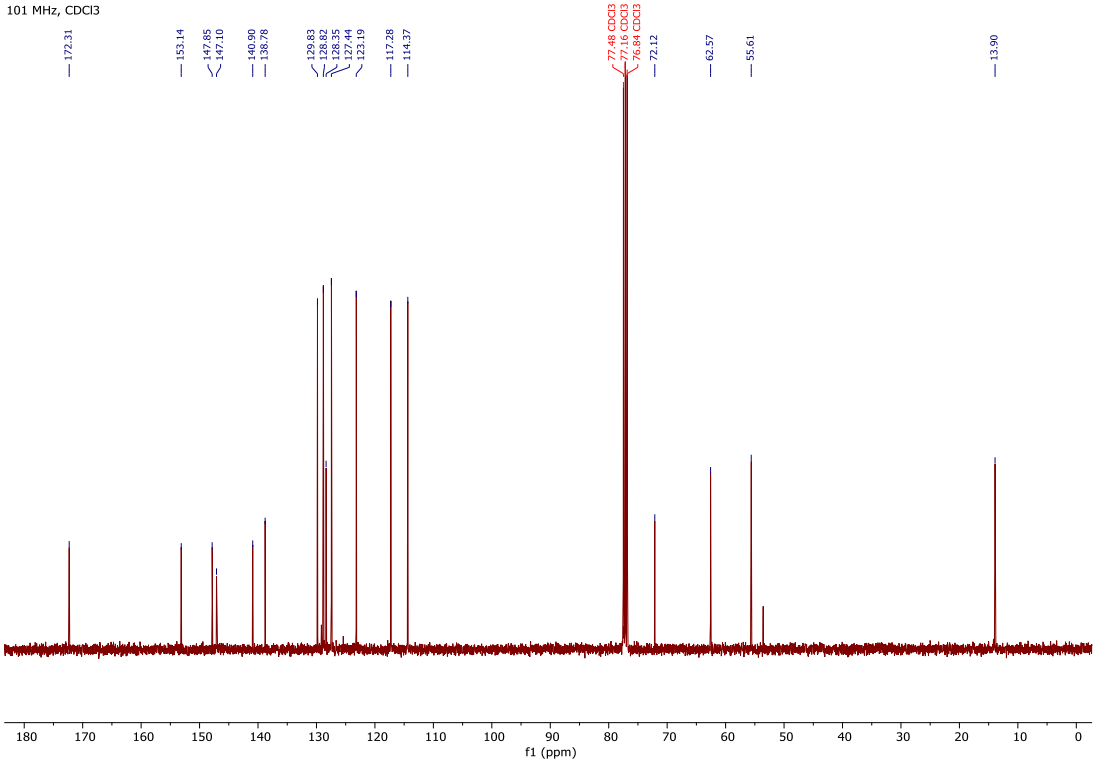
8i


400 MHz, CDCl3
8.28
8.26
7.85
7.83
7.26 CDCl3
7.20
7.19
7.18
7.17
7.15
7.11
7.09
6.72
6.55
5.74
4.27
4.25
4.24
4.22
4.21
4.17
4.15
4.14
4.13
4.11
2.15
2.13
1.79
1.56 H2O
1.24
1.22
1.20
2.00
2.01
3.33
2.07
1.00
1.00
0.96
2.11
3.10
3.03
2.97
3.08
f1 (ppm)

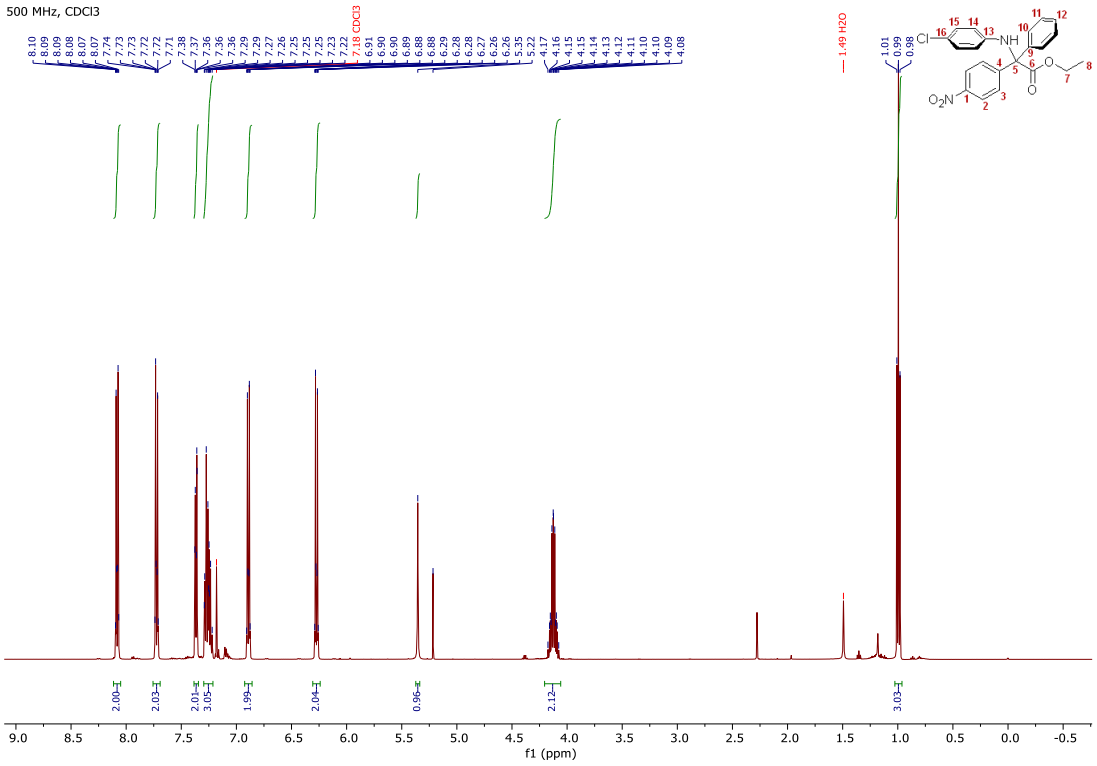

101 MHz, CDCl3
170.61
150.11
145.67
140.72
139.64
138.83
131.86
131.43
130.17
129.94
129.86
129.70
129.33
128.21
123.78
77.48 CDCl3
76.84 CDCl3
68.54
62.04
20.98
19.98
19.08
14.09
f1 (ppm)

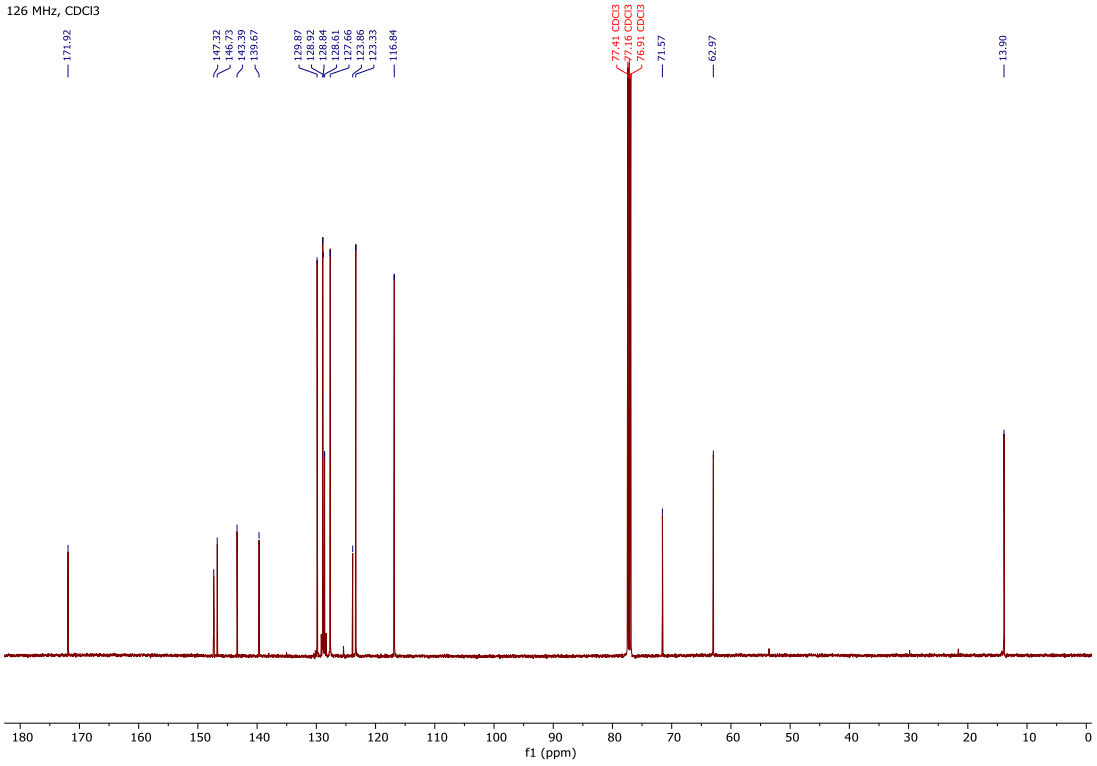
8j


400 MHz, CDCl3
8.15
8.13
7.85
7.82
7.47
7.36
7.34
7.32
7.31
7.29
6.63
6.60
6.41
6.38
5.05
4.23
4.22
4.21
4.20
4.18
4.18
4.16
4.16
4.15
4.14
3.48
1.59 H2O
1.06
1.04
1.02
MeO
NH
O2N
2.00
2.03
2.04
3.14
2.03
2.04
0.87
2.18
2.97
3.03
f1 (ppm)

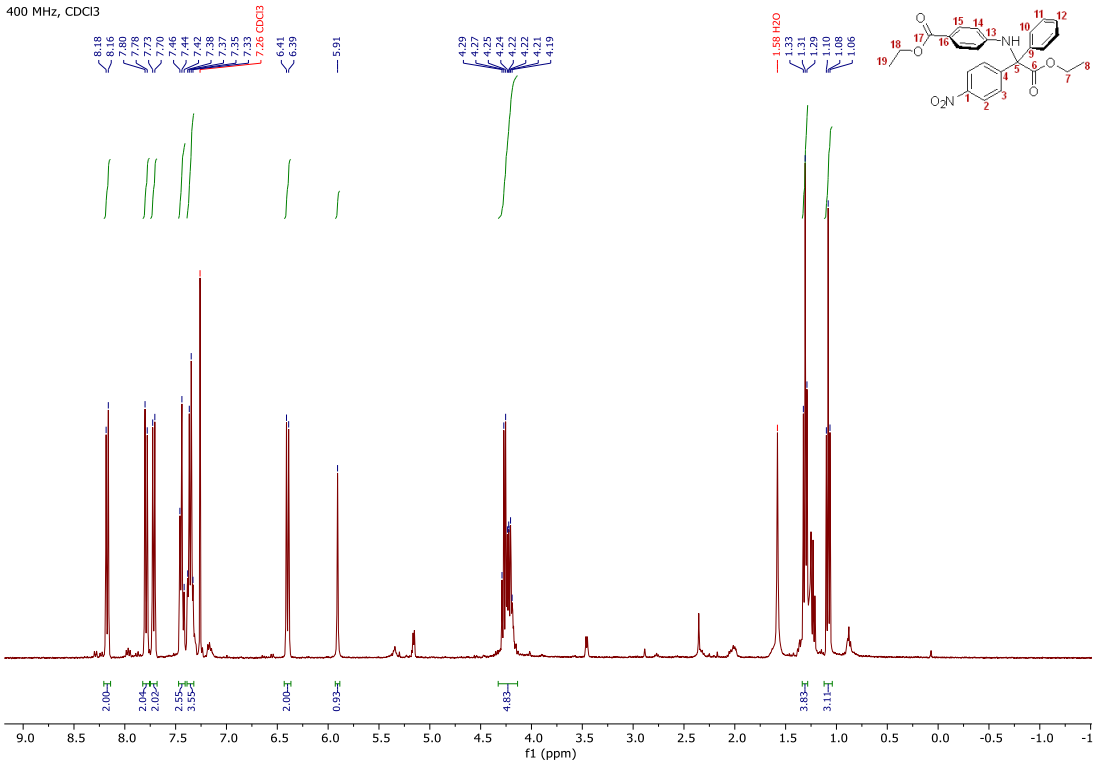

101 MHz, CDCl3
172.31
153.14
147.85
147.10
140.90
138.78
129.83
128.82
128.35
127.44
123.19
117.28
114.37
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.12
62.57
55.61
13.90
f1 (ppm)

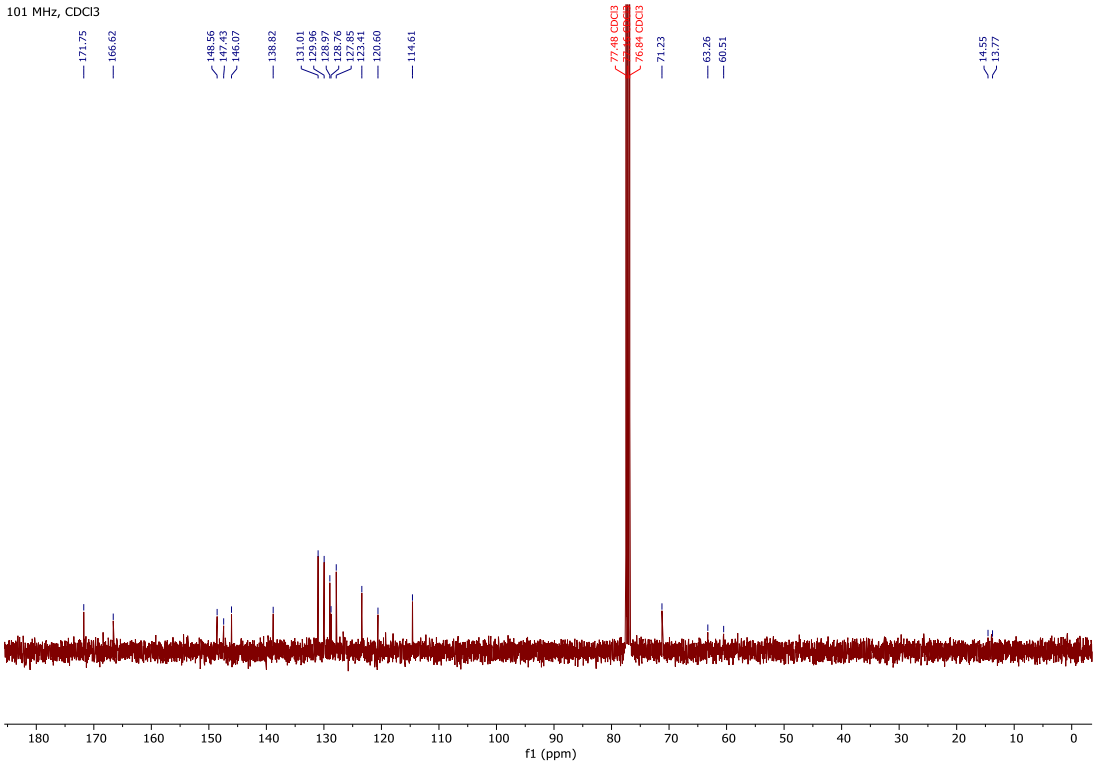
8k


500 MHz, CDCl3
7.18 CDCl3
1.49 H2O
f1 (ppm)

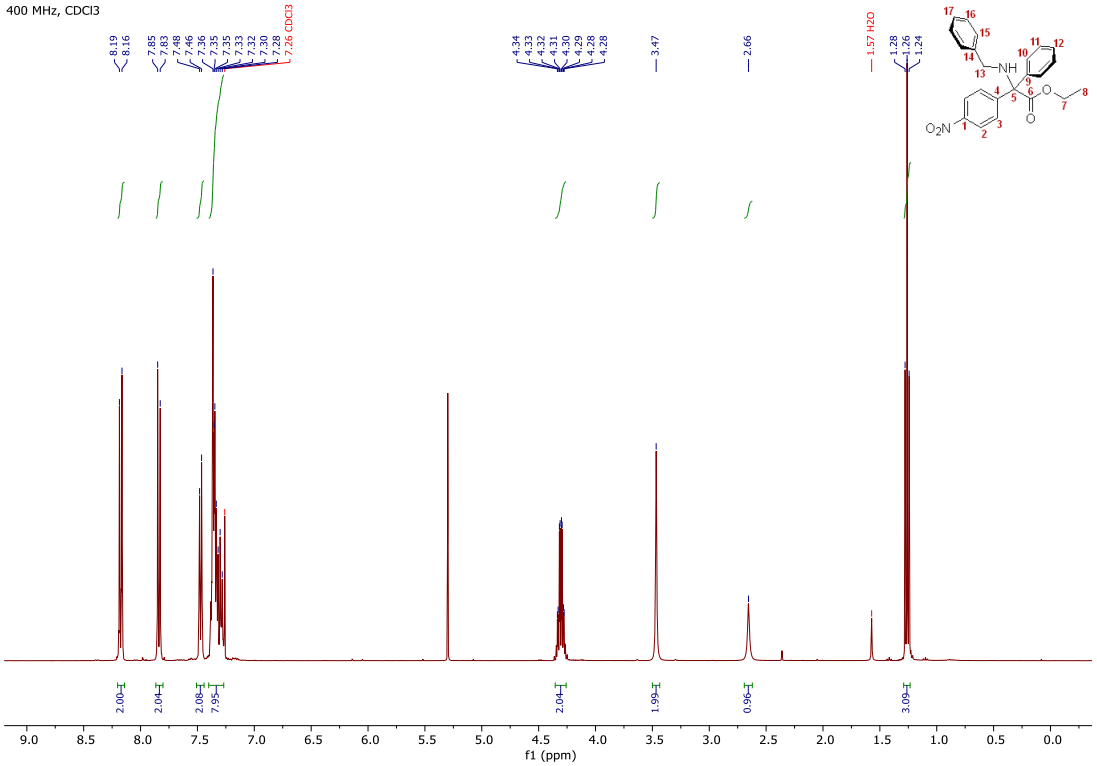

126 MHz, CDCl3
171.92
147.32
146.73
143.39
139.67
129.87
128.92
128.84
128.61
127.66
123.86
123.33
116.84
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
71.57
62.97
13.90
f1 (ppm)

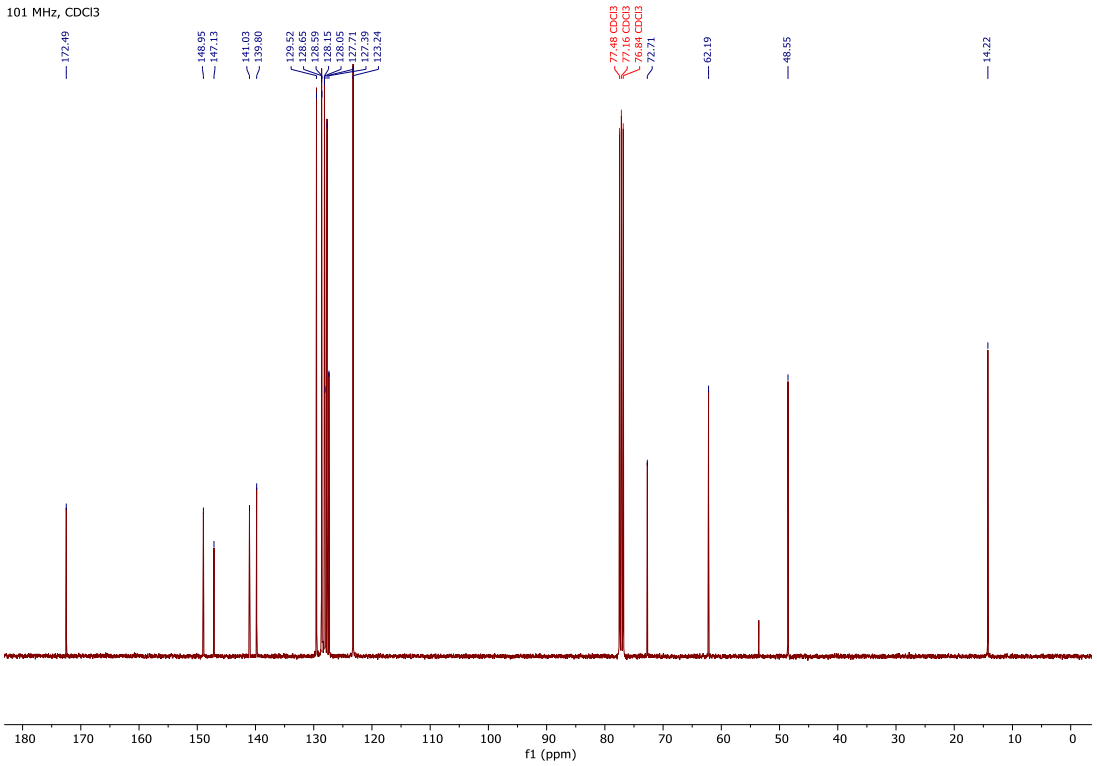
8l


400 MHz, CDCl3
8.18
8.16
7.80
7.78
7.73
7.70
7.46
7.44
7.42
7.38
7.37
7.35
7.33
7.26 CDCl3
6.41
6.39
5.91
4.29
4.27
4.25
4.24
4.22
4.22
4.21
4.19
1.58 H2O
1.33
1.31
1.29
1.10
1.08
1.06
2.00
2.04
2.02
2.55
3.55
2.00
0.93
4.83
3.83
3.11
f1 (ppm)

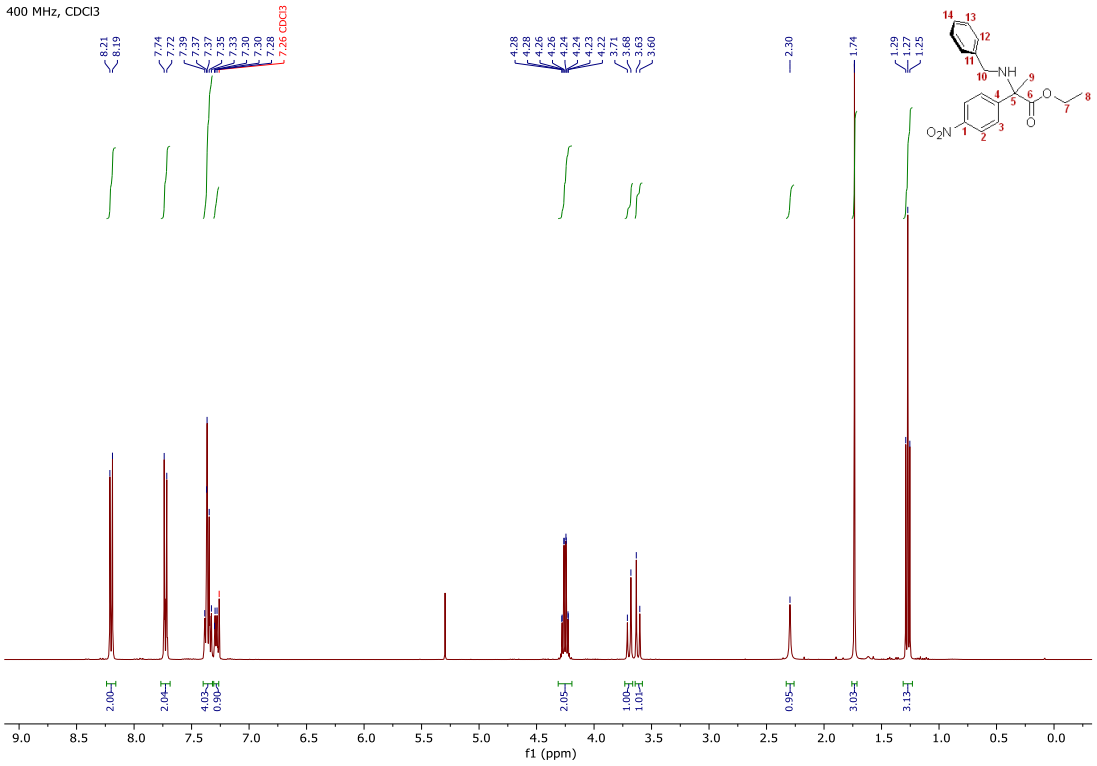

101 MHz, CDCl3
171.75
166.62
148.56
147.43
146.07
138.82
131.01
129.96
128.97
128.76
127.85
123.41
120.60
114.61
77.48 CDCl3
76.84 CDCl3
71.23
63.26
60.51
14.55
13.77
f1 (ppm)

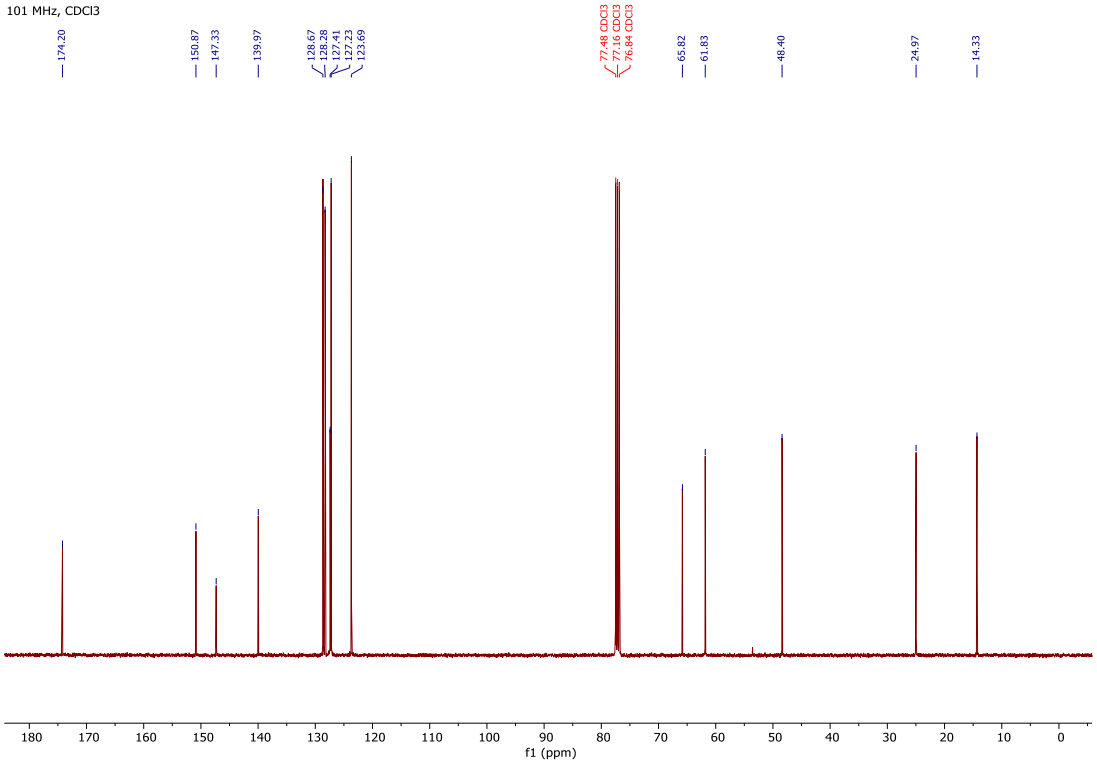
8m


400 MHz, CDCl3
8.19
8.16
7.85
7.83
7.48
7.46
7.36
7.35
7.33
7.32
7.30
7.28
7.26 CDCl3
4.34
4.33
4.32
4.31
4.30
4.29
4.28
4.28
3.47
2.66
1.57 H2O
1.28
1.26
1.24
2.00
2.04
2.08
7.95
2.04
1.99
0.96
3.09
f1 (ppm)


101 MHz, CDCl3
172.49
148.95
147.13
141.03
139.80
129.52
128.65
128.59
128.15
128.05
127.71
127.39
123.24
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
72.71
62.19
48.55
14.22
f1 (ppm)

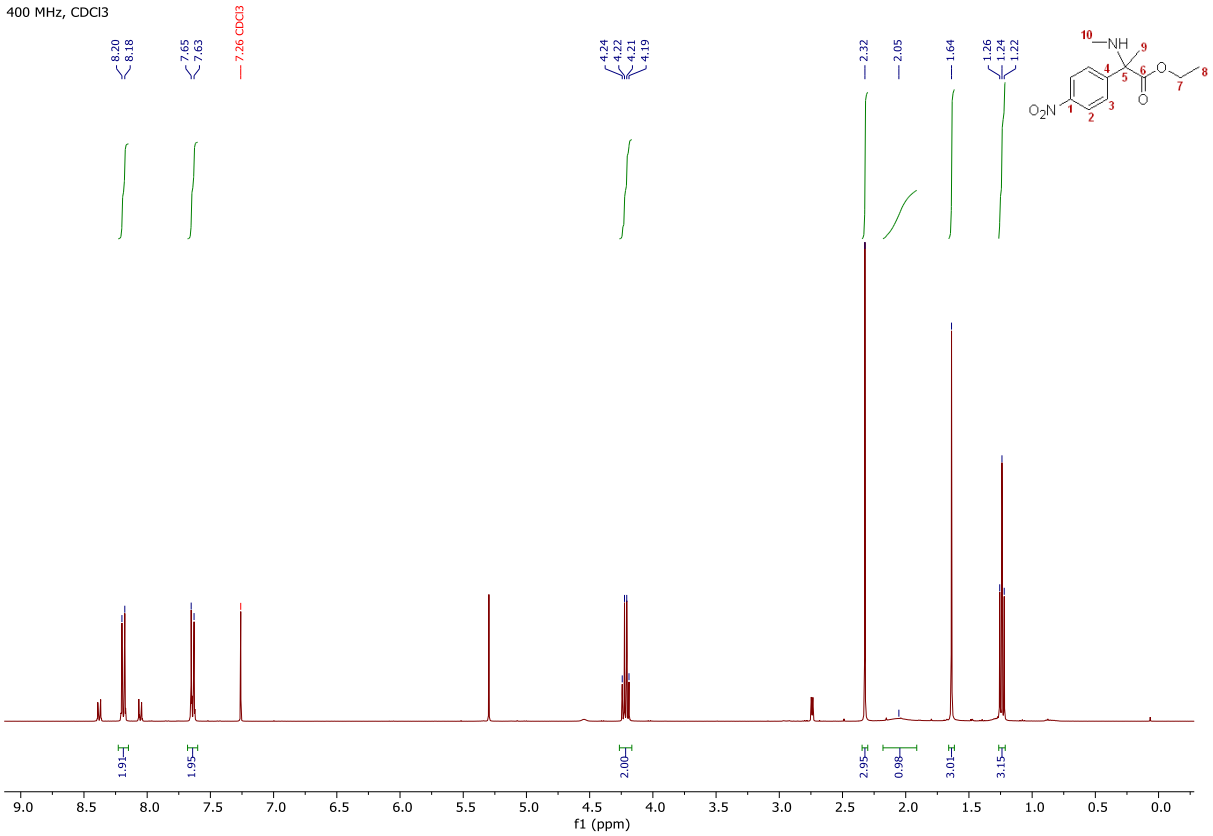
8n


400 MHz, CDCl3
8.21
8.19
7.74
7.72
7.39
7.37
7.35
7.33
7.30
7.30
7.28
7.26 CDCl3
4.28
4.28
4.26
4.26
4.24
4.24
4.23
4.22
3.71
3.68
3.63
3.60
2.30
1.74
1.29
1.27
1.25
NH
O2N
2.00
2.04
4.03
0.90
2.05
1.00
1.01
0.95
3.03
3.13
f1 (ppm)

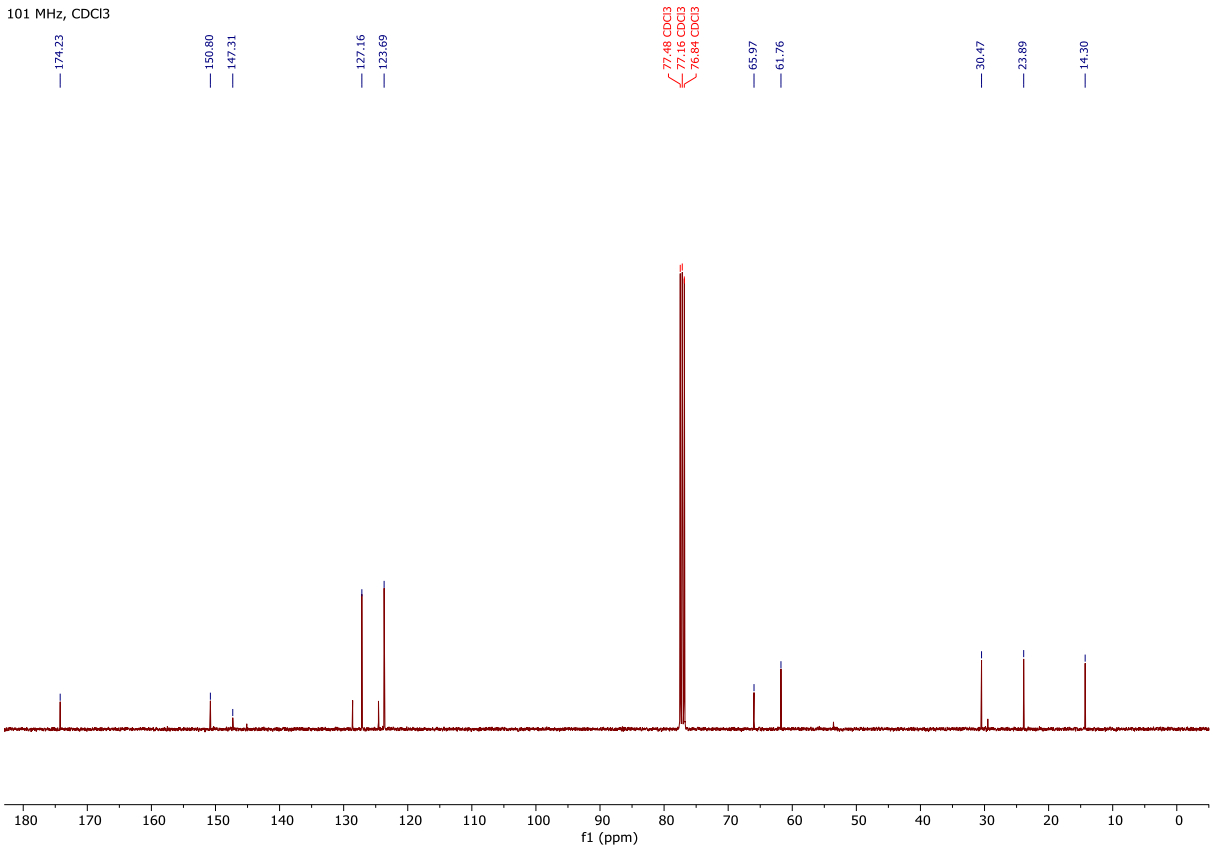

101 MHz, CDCl3
174.20
150.87
147.33
139.97
128.67
128.28
127.41
127.23
125.69
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
65.82
61.83
48.40
24.97
14.33
f1 (ppm)

8o

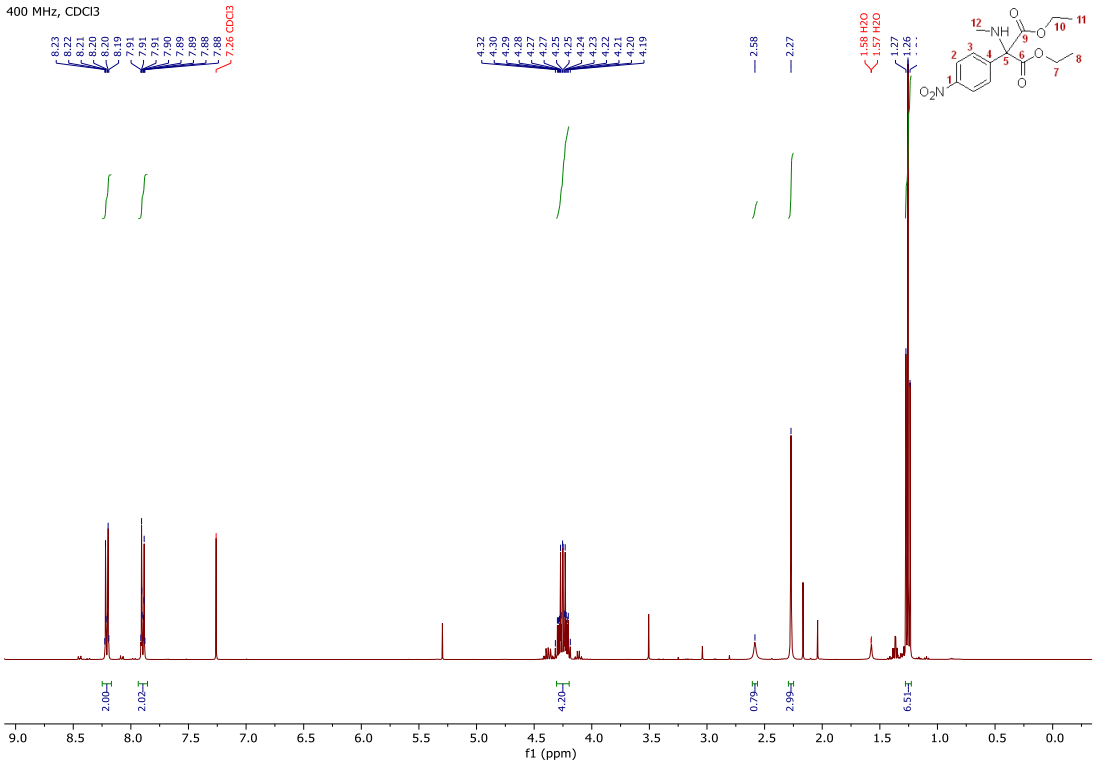
400 MHz, CDCl3

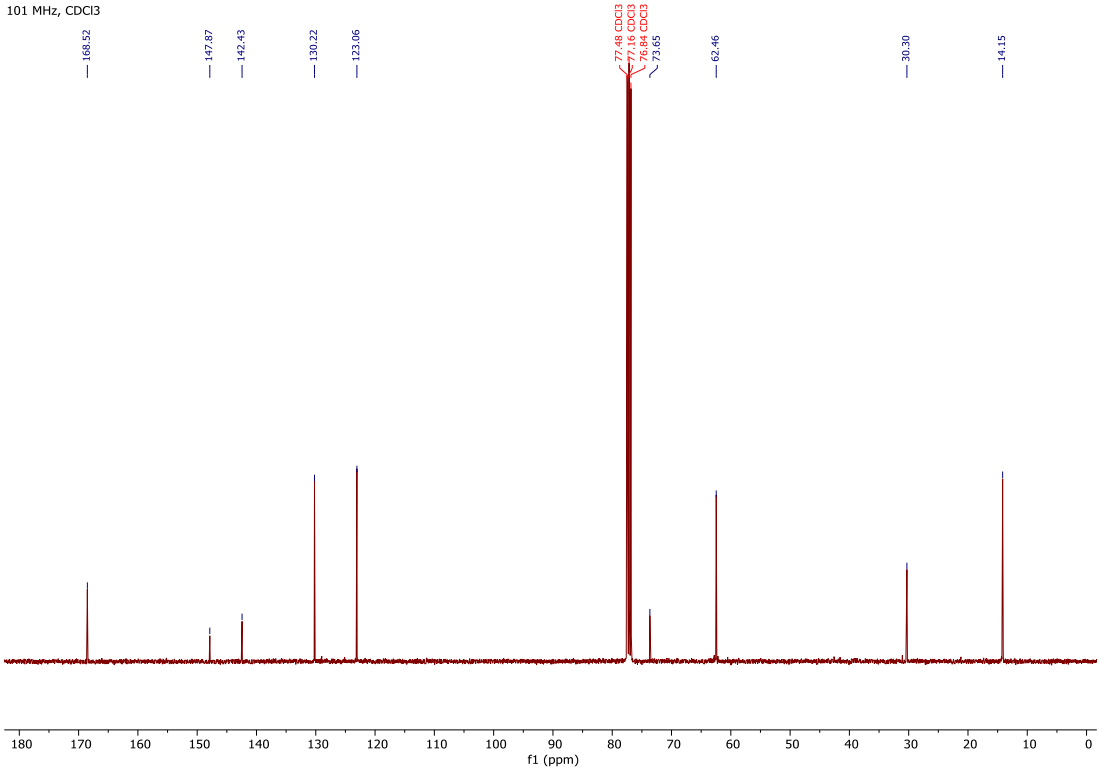


101 MHz, CDCl3

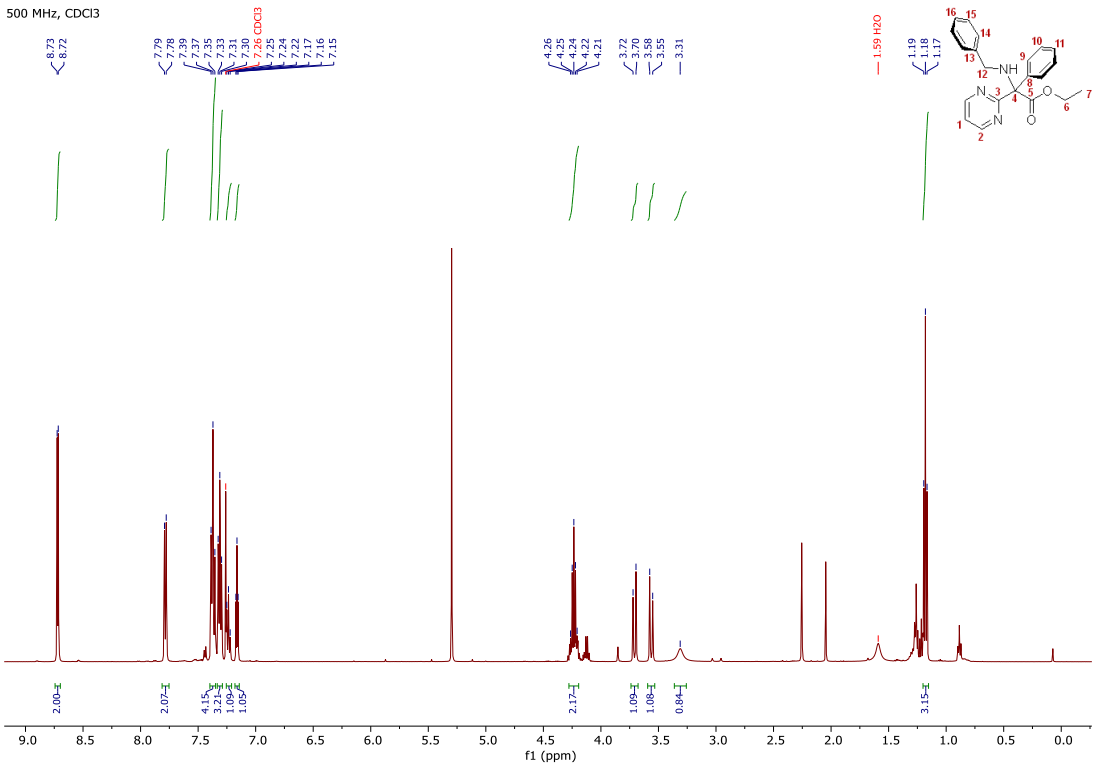


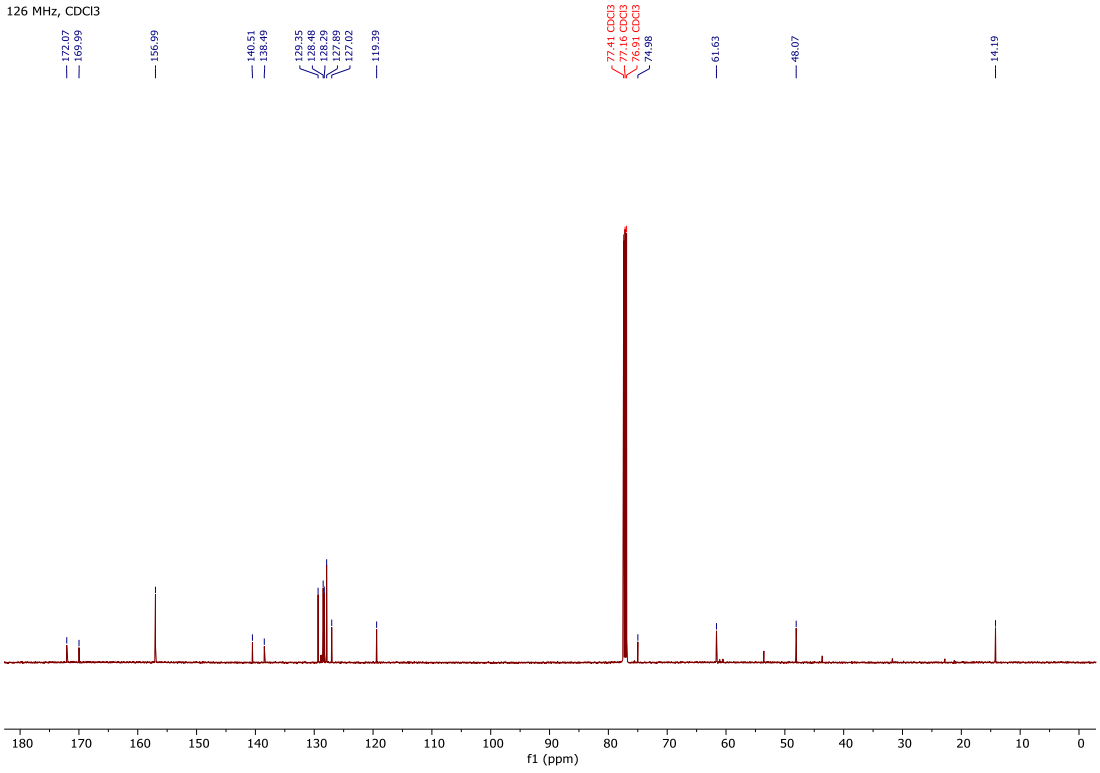
8p


400 MHz, CDCl3
8.23
8.22
8.21
8.20
8.19
7.91
7.91
7.91
7.90
7.89
7.89
7.88
7.88
7.26 CDCl3
4.32
4.30
4.29
4.28
4.27
4.27
4.25
4.25
4.24
4.23
4.22
4.21
4.20
4.19
2.58
2.27
1.58 H2O
1.57 H2O
1.27
1.26
2.00
2.02
4.20
0.79
2.99
6.51
f1 (ppm)

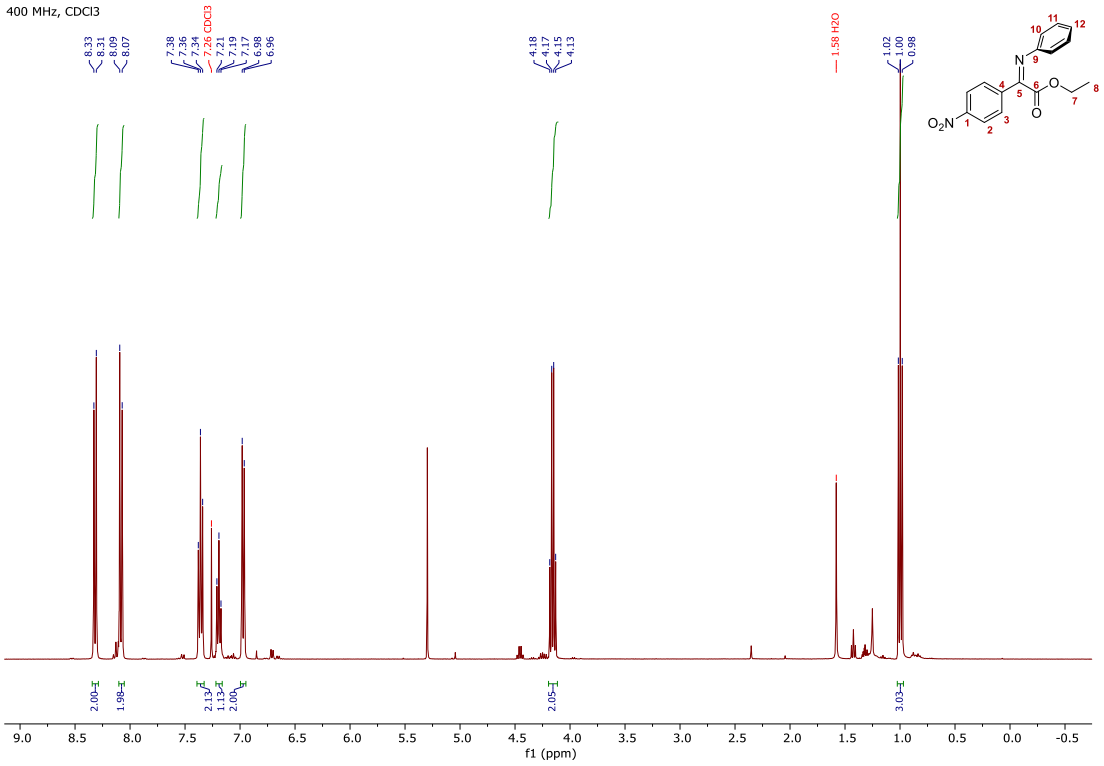

101 MHz, CDCl3
168.52
147.87
142.43
130.22
123.06
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
73.65
62.46
30.30
14.15
f1 (ppm)

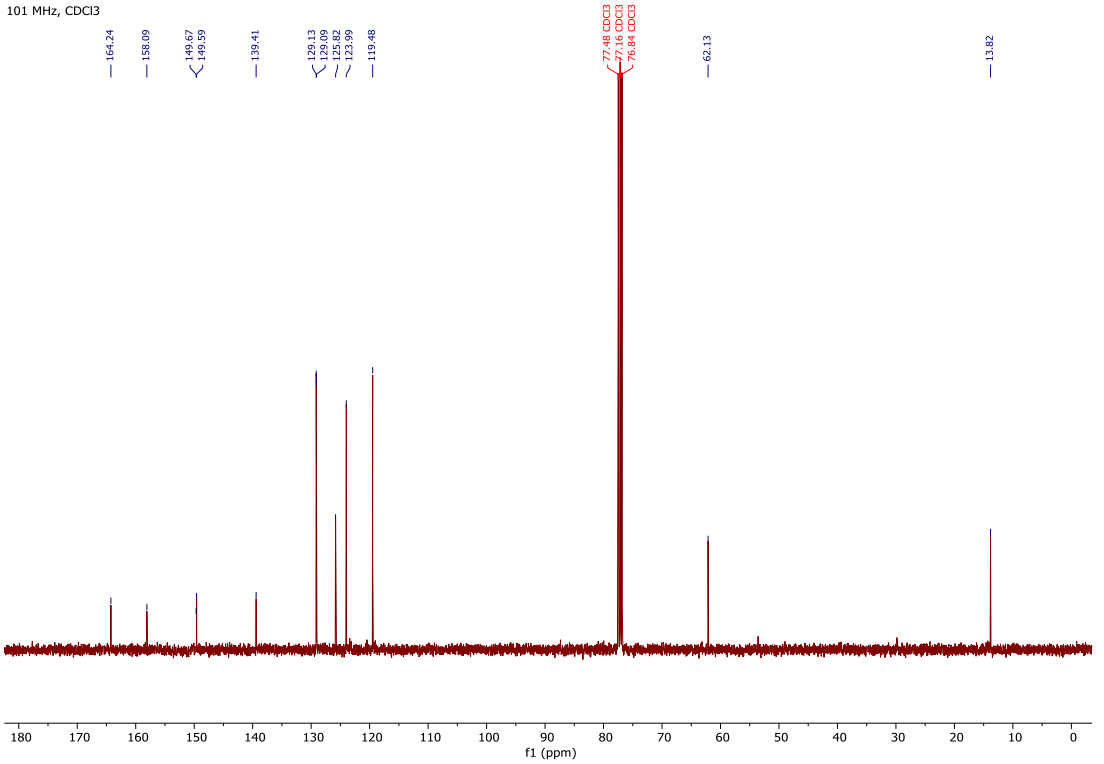
8q


500 MHz, CDCl3
8.73
8.72
7.79
7.78
7.39
7.37
7.35
7.33
7.31
7.30
7.26 CDCl3
7.25
7.24
7.22
7.17
7.16
7.15
4.26
4.25
4.24
4.22
4.21
3.72
3.70
3.58
3.55
3.31
1.59 H2O
1.19
1.18
1.17
2.00
2.07
4.15
3.22
1.09
1.05
2.17
1.09
1.08
0.84
3.15
f1 (ppm)

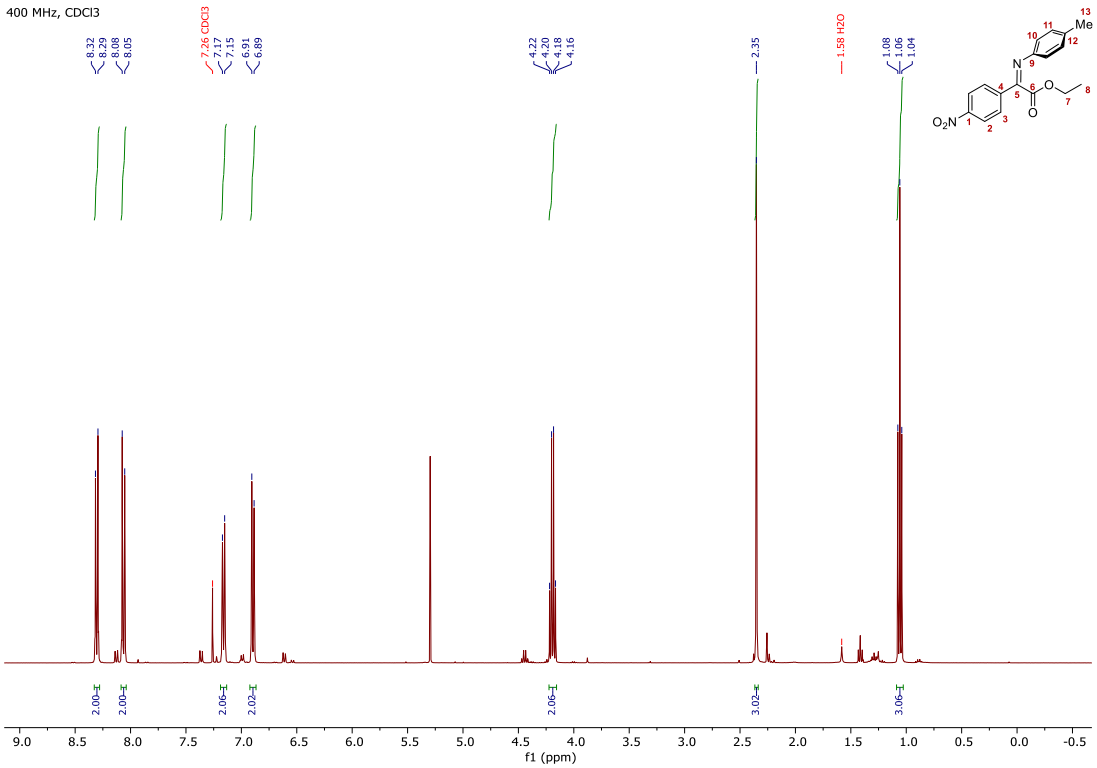

126 MHz, CDCl3
172.07
169.99
156.99
140.51
138.49
129.35
128.48
128.29
127.89
127.02
119.39
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
74.98
61.63
48.07
14.19
f1 (ppm)

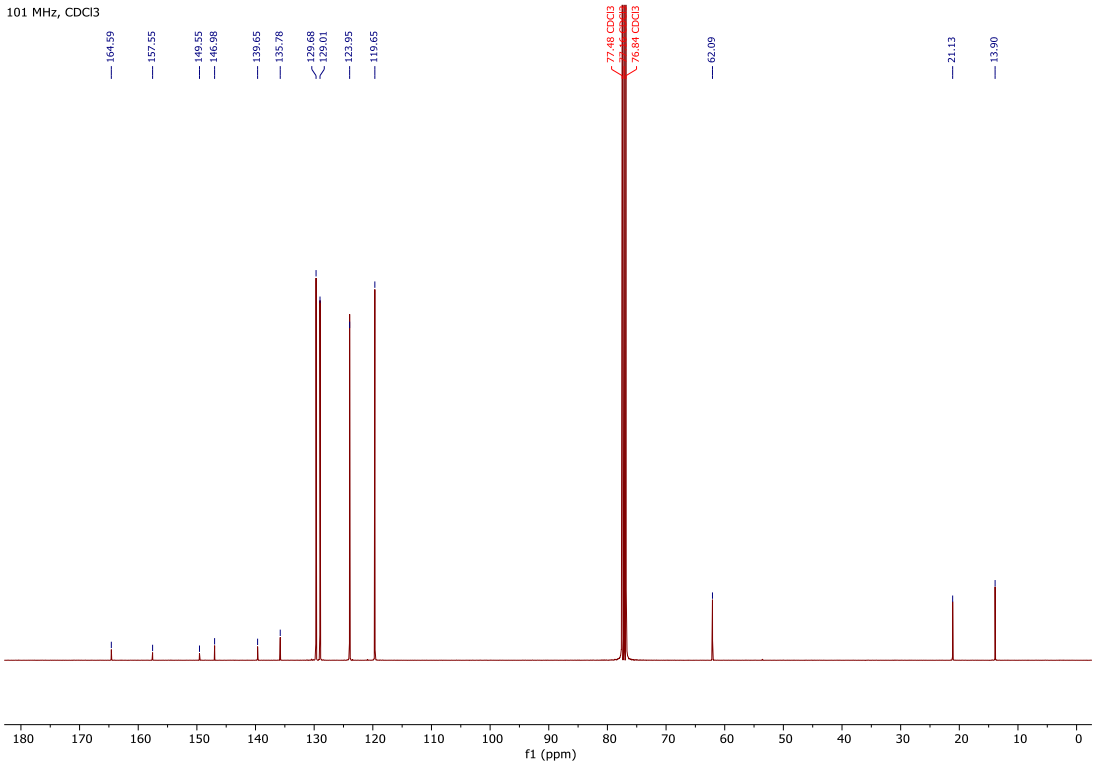
11a


400 MHz, CDCl3
8.33
8.31
8.09
8.07
7.38
7.36
7.34
7.26 CDCl3
7.21
7.19
7.17
6.98
6.96
4.18
4.17
4.15
4.13
1.58 H2O
1.02
1.00
0.98
2.00
1.98
2.13
2.14
2.00
2.05
3.03
f1 (ppm)

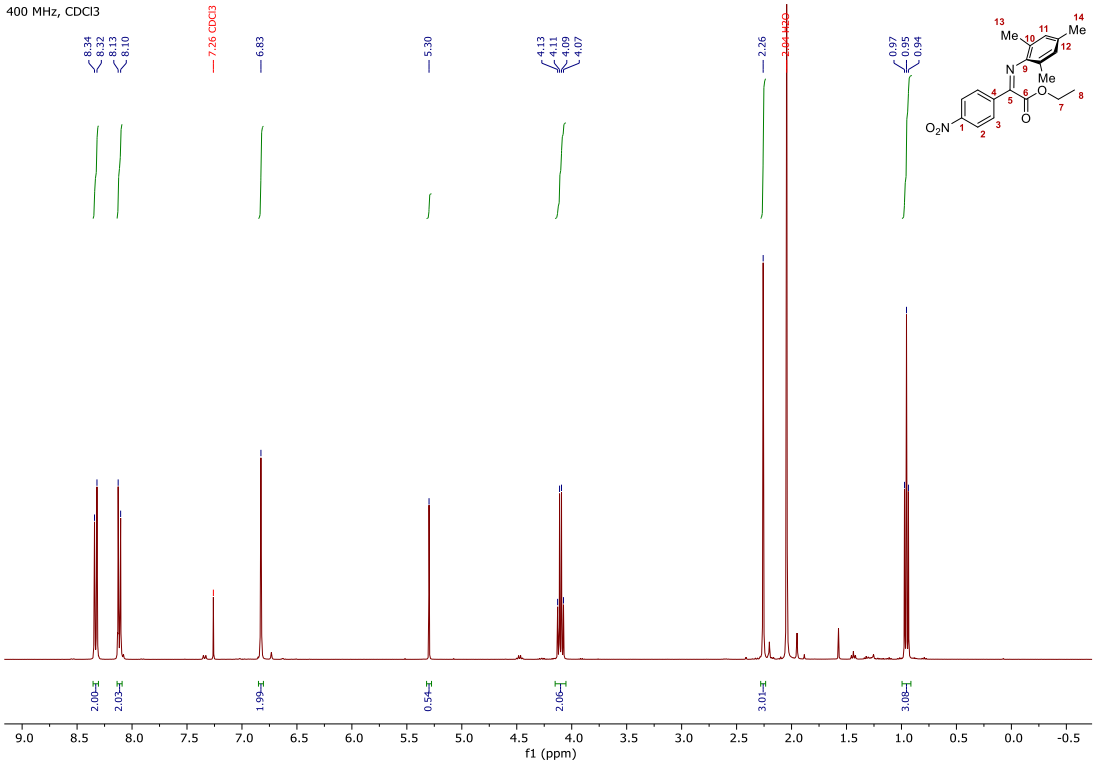

101 MHz, CDCl3
164.24
158.09
149.67
149.59
139.41
129.13
129.09
125.82
123.99
119.48
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.13
13.82
f1 (ppm)

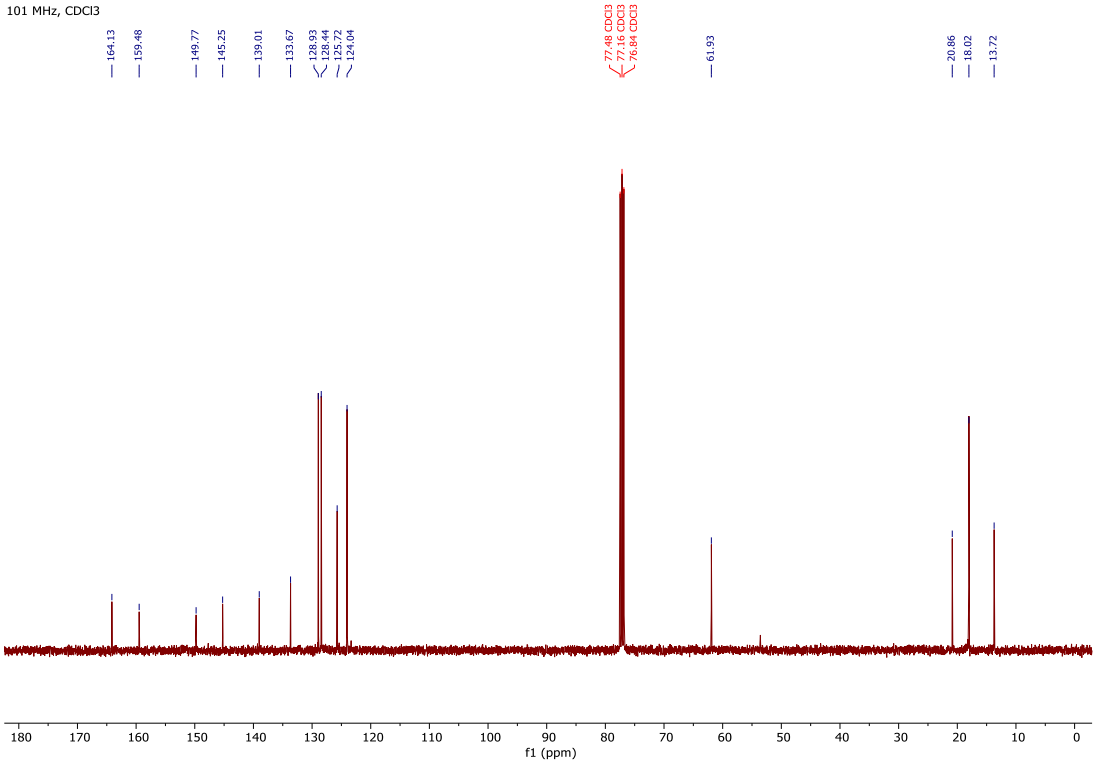
11b


400 MHz, CDCl3
8.32
8.29
8.08
8.05
7.26 CDCl3
7.17
7.15
6.91
6.89
4.22
4.20
4.18
4.16
2.35
1.58 H2O
1.08
1.06
1.04
Me
O2N
2.00
2.00
2.06
2.02
2.06
3.02
3.06
f1 (ppm)

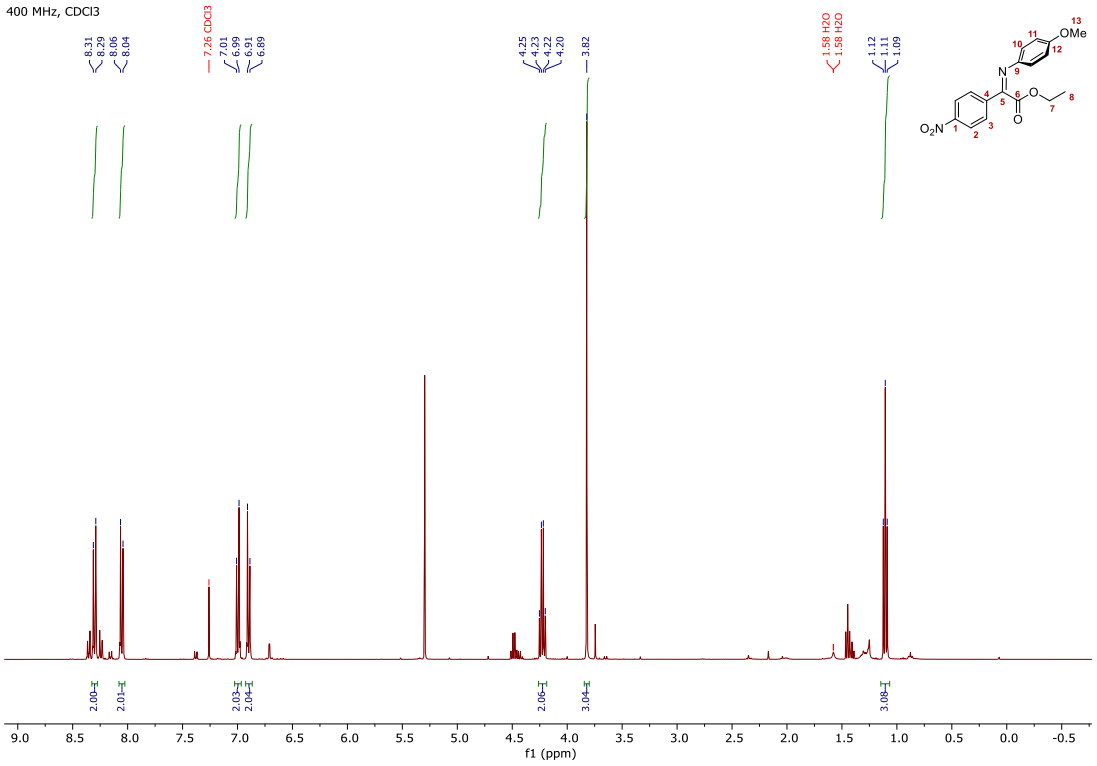

101 MHz, CDCl3
164.59
157.55
149.55
146.98
139.65
135.78
129.68
129.01
123.95
119.65
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.09
21.13
13.90
f1 (ppm)

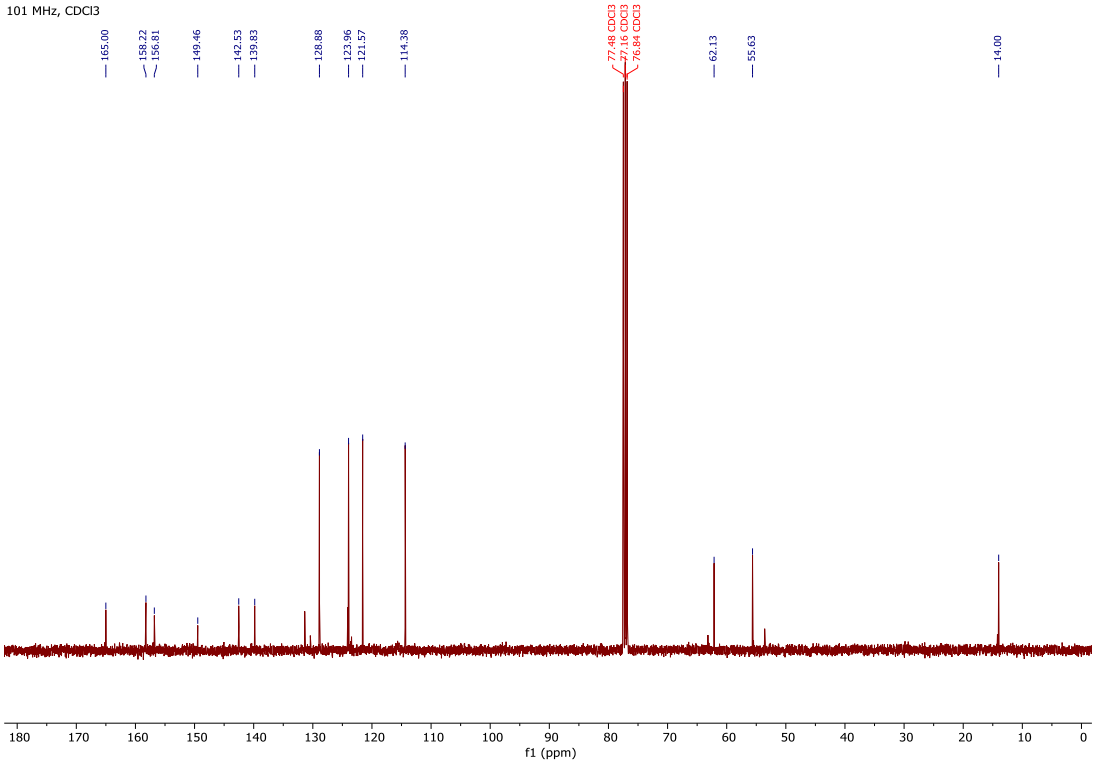
11c


400 MHz, CDCl3
8.34
8.32
8.13
8.10
7.26 CDCl3
6.83
5.30
4.13
4.11
4.09
4.07
2.26
3.04 H30
0.97
0.95
0.94
Me
Me
Me
N
O
O
O2N
2.00
2.03
1.99
0.54
2.06
3.01
3.08
f1 (ppm)

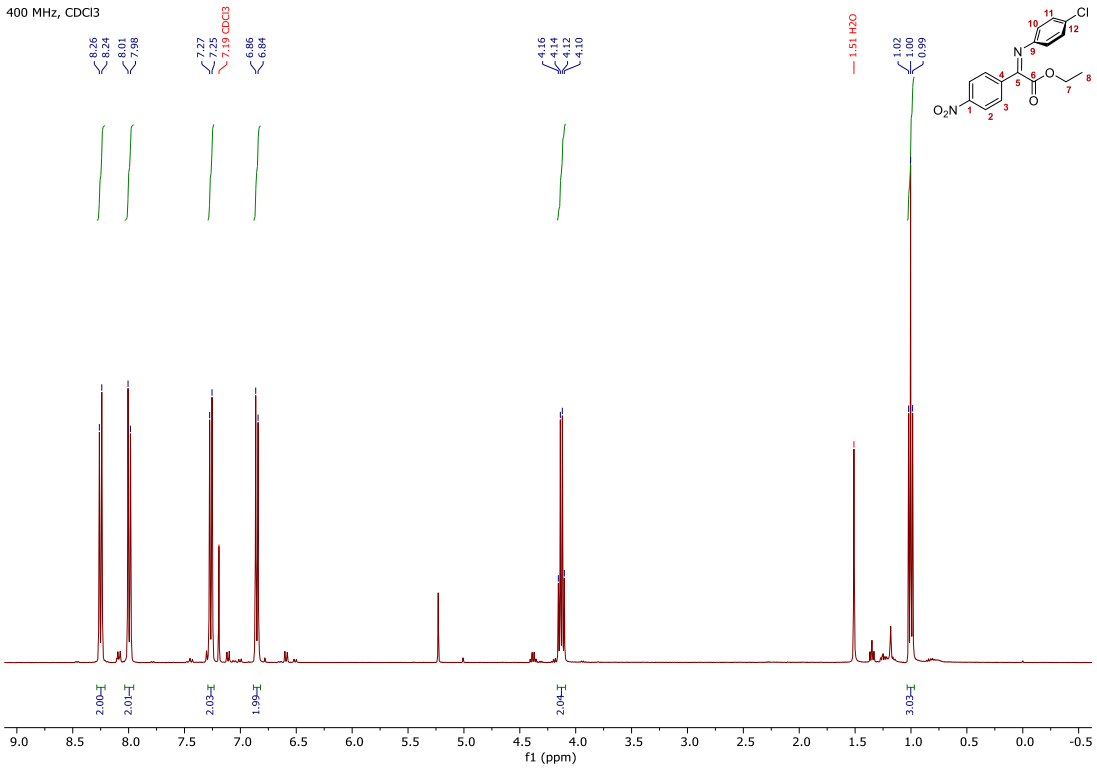

101 MHz, CDCl3
164.13
159.48
149.77
145.25
139.01
133.67
128.93
128.44
125.72
124.04
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
61.93
20.86
18.02
13.72
f1 (ppm)

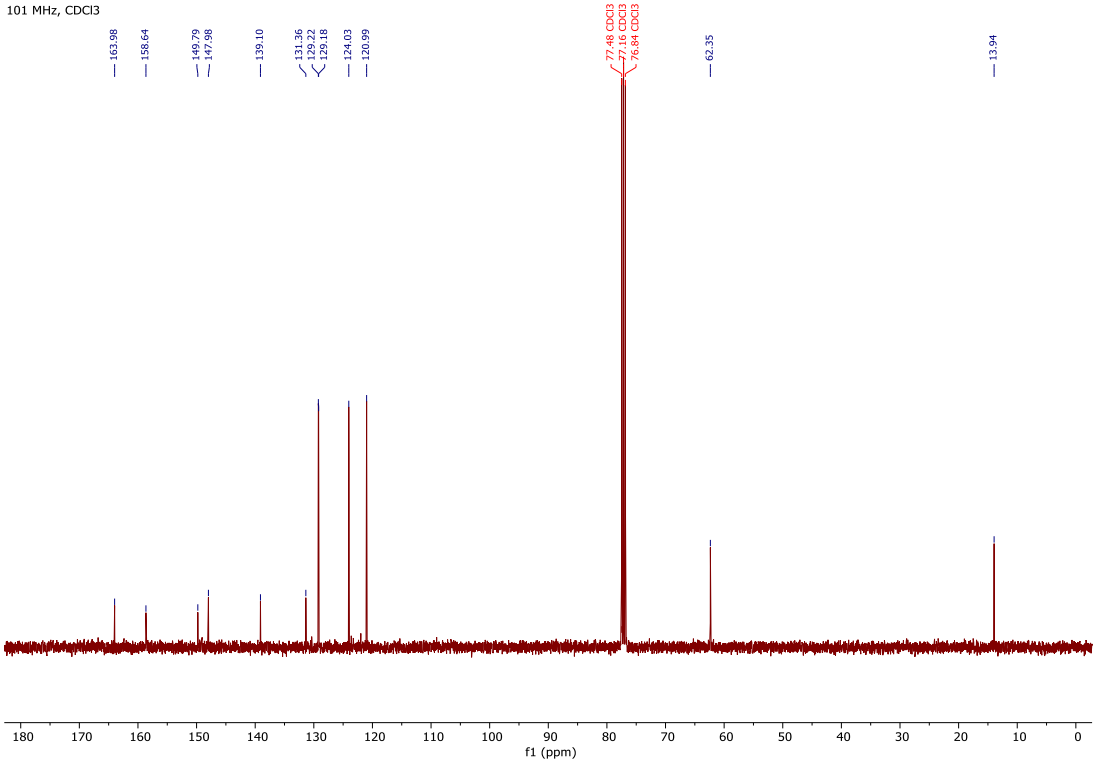
11d


400 MHz, CDCl3
8.31
8.29
8.06
8.04
7.26 CDCl3
7.01
6.99
6.91
6.89
4.25
4.23
4.22
4.20
3.82
1.58 H2O
1.58 H2O
1.12
1.11
1.09
OMe
2.00
2.01
2.03
2.04
2.06
3.04
3.08
f1 (ppm)

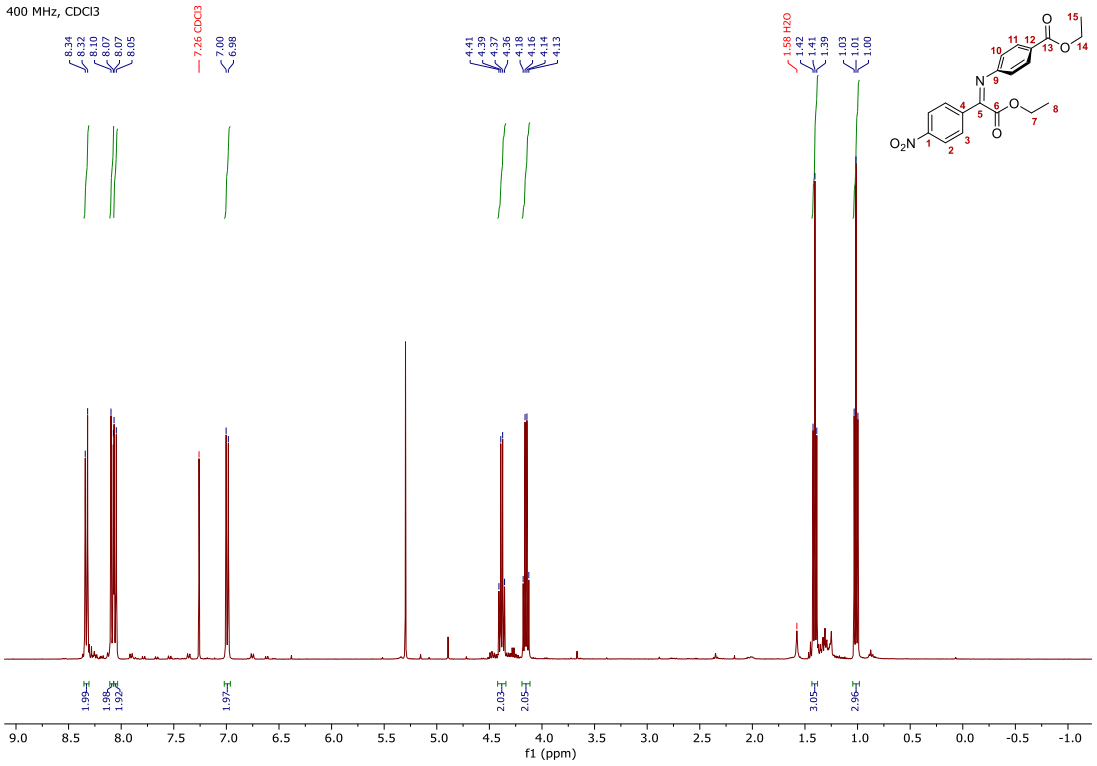

101 MHz, CDCl3
165.00
158.22
156.81
149.46
142.53
139.83
128.88
123.96
121.57
114.38
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.13
55.63
14.00
f1 (ppm)

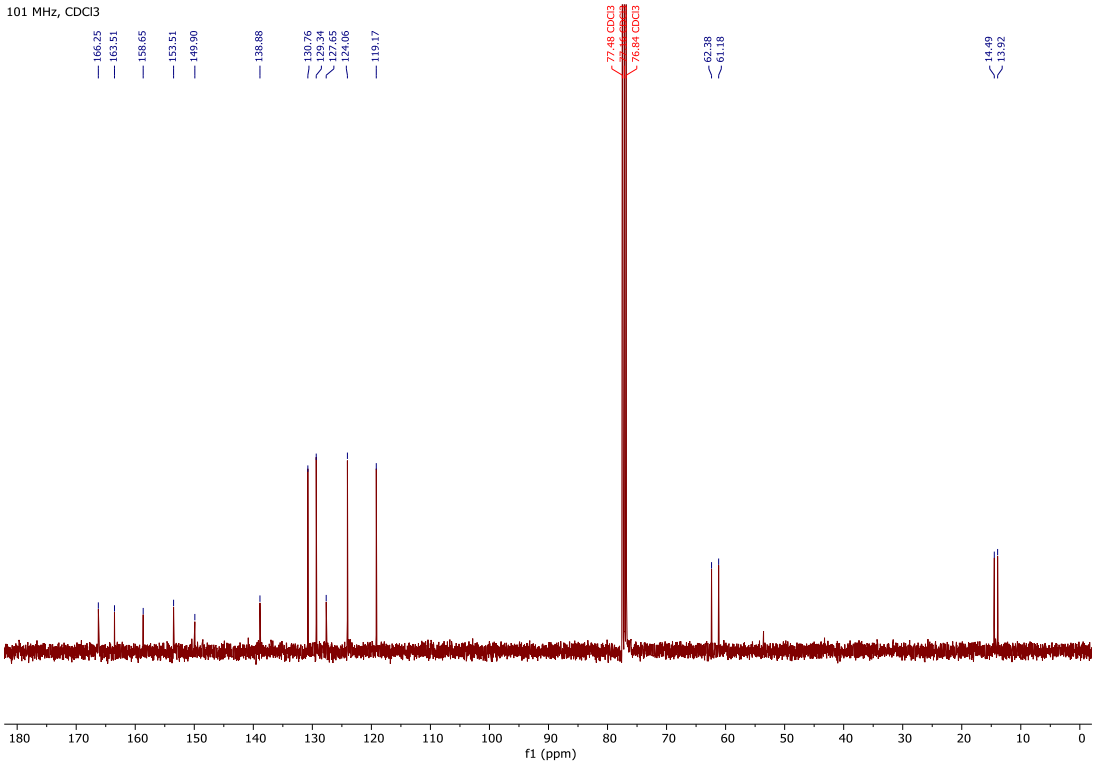
11e

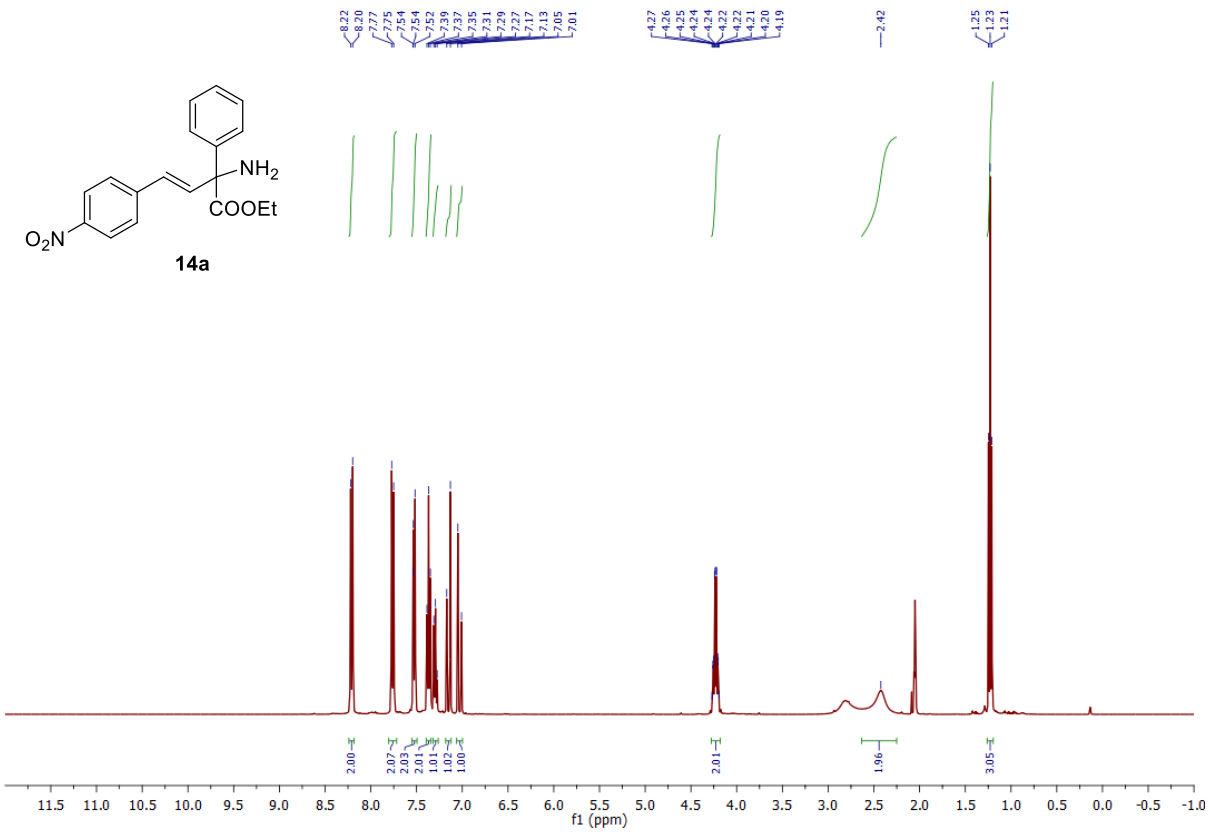

400 MHz, CDCl3
8.26
8.24
8.01
7.98
7.27
7.25
7.19 CDCl3
6.86
6.84
4.16
4.14
4.12
4.10
1.51 H2O
1.02
1.00
0.99
2.00
2.01
2.03
1.99
2.04
3.03
f1 (ppm)

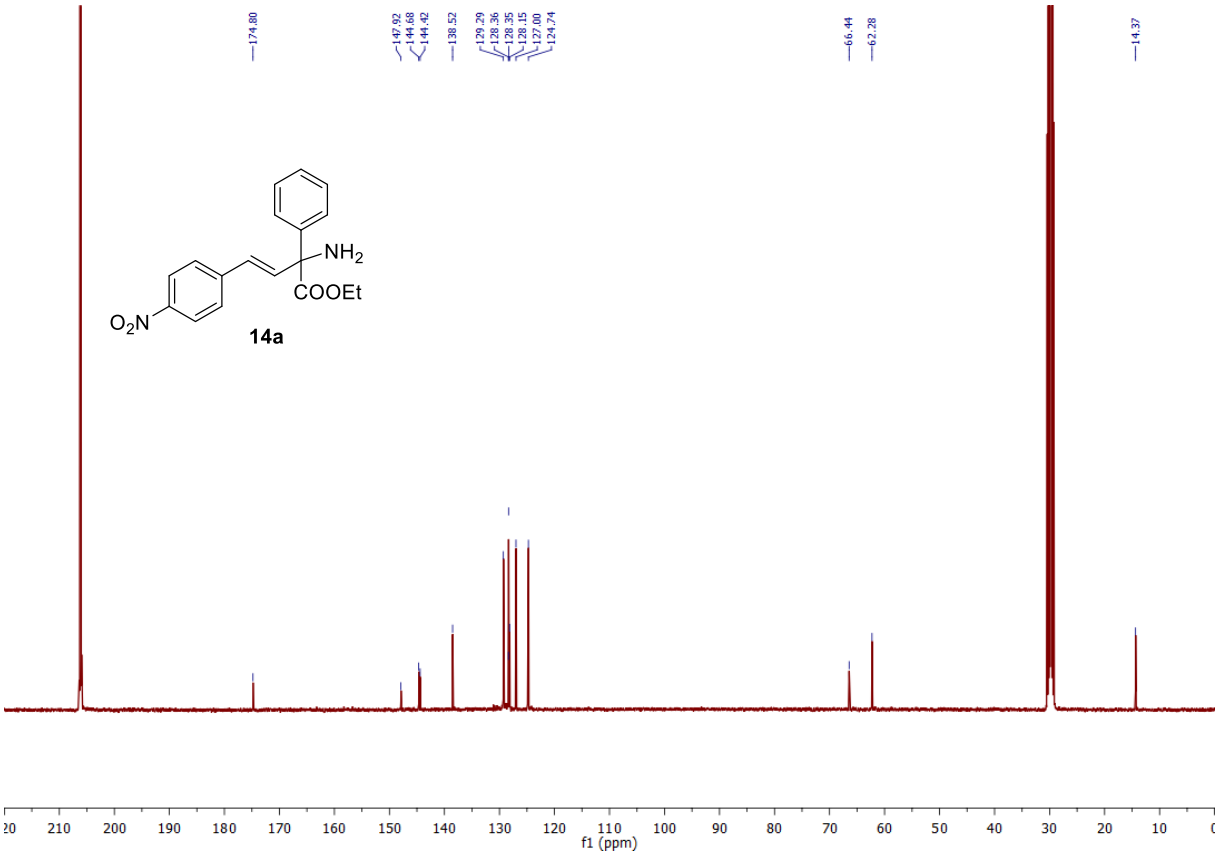

101 MHz, CDCl3
163.98
158.64
149.79
147.98
139.10
131.36
129.22
129.18
124.03
120.99
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.35
13.94
f1 (ppm)

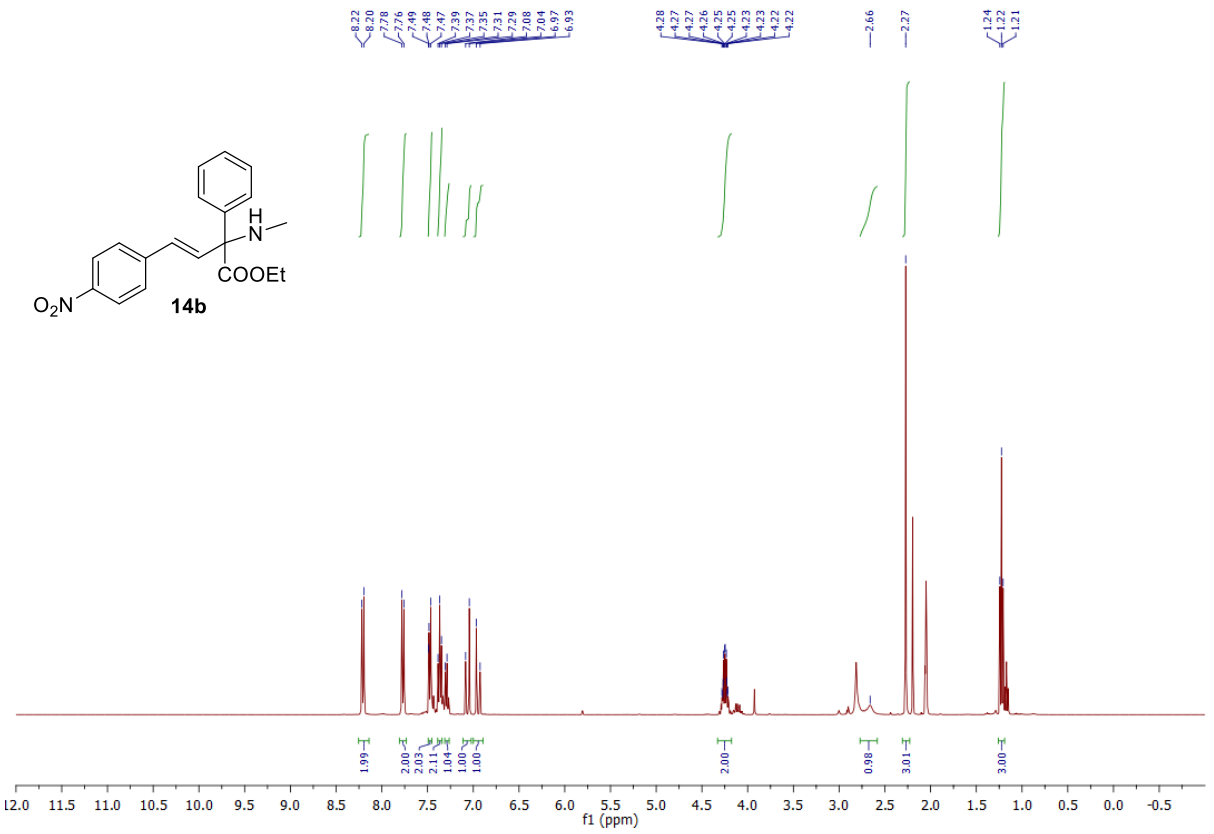
11f

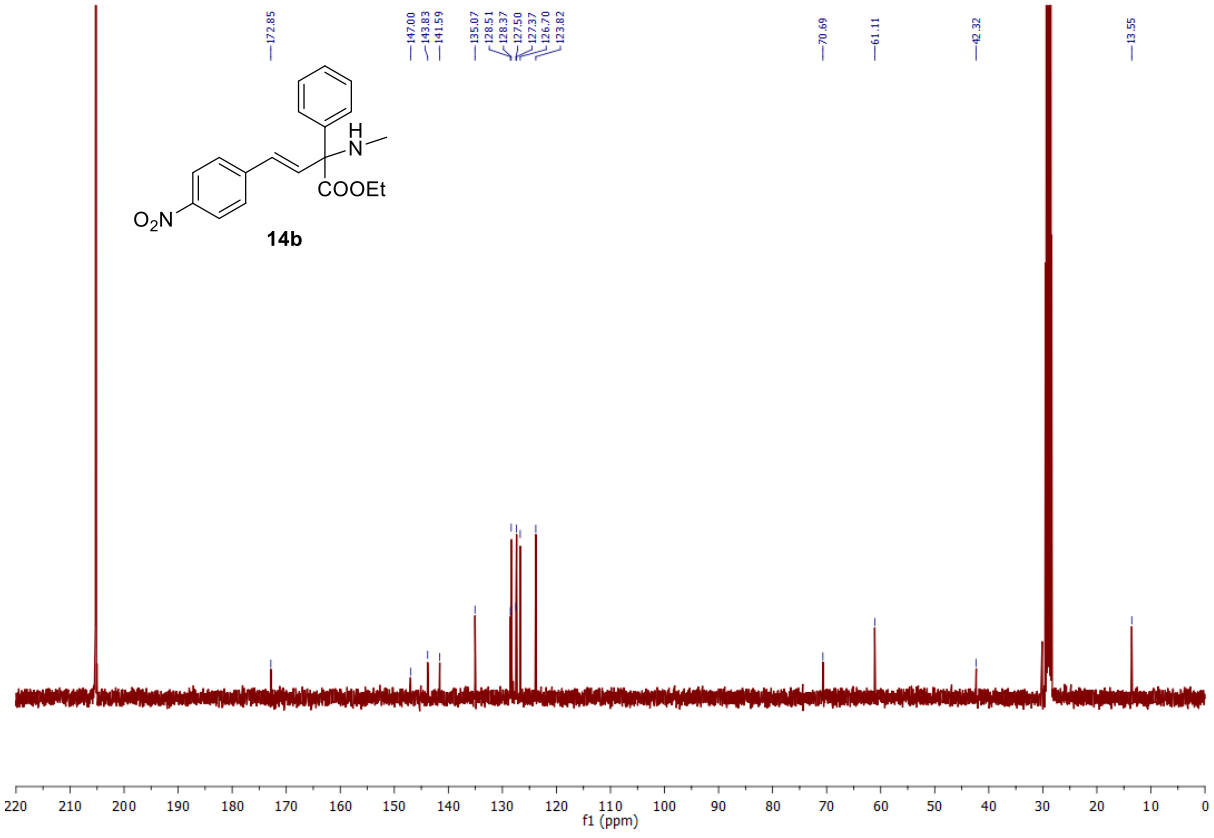

400 MHz, CDCl3
8.34
8.32
8.10
8.07
8.07
8.05
7.26 CDCl3
7.00
6.98
4.41
4.39
4.37
4.36
4.18
4.16
4.14
4.13
1.58 H2O
1.42
1.41
1.39
1.03
1.01
1.00
1.99
1.98
1.92
1.97
2.03
2.05
3.05
2.96
f1 (ppm)


101 MHz, CDCl3
166.25
163.51
158.65
153.51
149.90
138.88
130.76
129.34
127.65
124.06
119.17
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.38
61.18
14.49
13.92
f1 (ppm)


8.22
8.20
7.77
7.75
7.54
7.52
7.39
7.37
7.35
7.31
7.29
7.27
7.17
7.13
7.05
7.01
4.27
4.26
4.25
4.24
4.22
4.21
4.20
4.19
2.42
1.25
1.23
1.21
NH2
COOEt
O2N
14a
2.00
2.07
2.03
2.01
1.01
1.02
1.00
2.01
1.96
3.05
f1 (ppm)


174.80
147.92
144.68
144.42
138.52
129.29
128.36
128.35
128.15
127.00
124.74
66.44
62.28
14.37
NH2
COOEt
O2N
14a
f1 (ppm)


8.22
8.20
7.78
7.76
7.49
7.48
7.47
7.39
7.37
7.35
7.31
7.29
7.08
7.04
6.97
6.93
4.28
4.27
4.27
4.26
4.25
4.25
4.23
4.23
4.22
4.22
2.66
2.27
1.24
1.22
1.21
H
N
COOEt
O2N
14b
1.99
2.00
2.03
2.11
1.04
1.00
1.00
2.00
0.98
3.01
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
f1 (ppm)


172.85
147.00
143.83
141.59
135.07
128.51
128.37
127.50
127.37
126.70
123.82
70.69
61.11
42.32
13.55
H
N
COOEt
O2N
14b
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

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