Supporting Information

Mechanically Processed Sardinian Wool Promotes C-C Bond Synthesis Under Solvent-Free Conditions

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Number of pages: 50

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Number of schemes: 0

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SEM Analysis

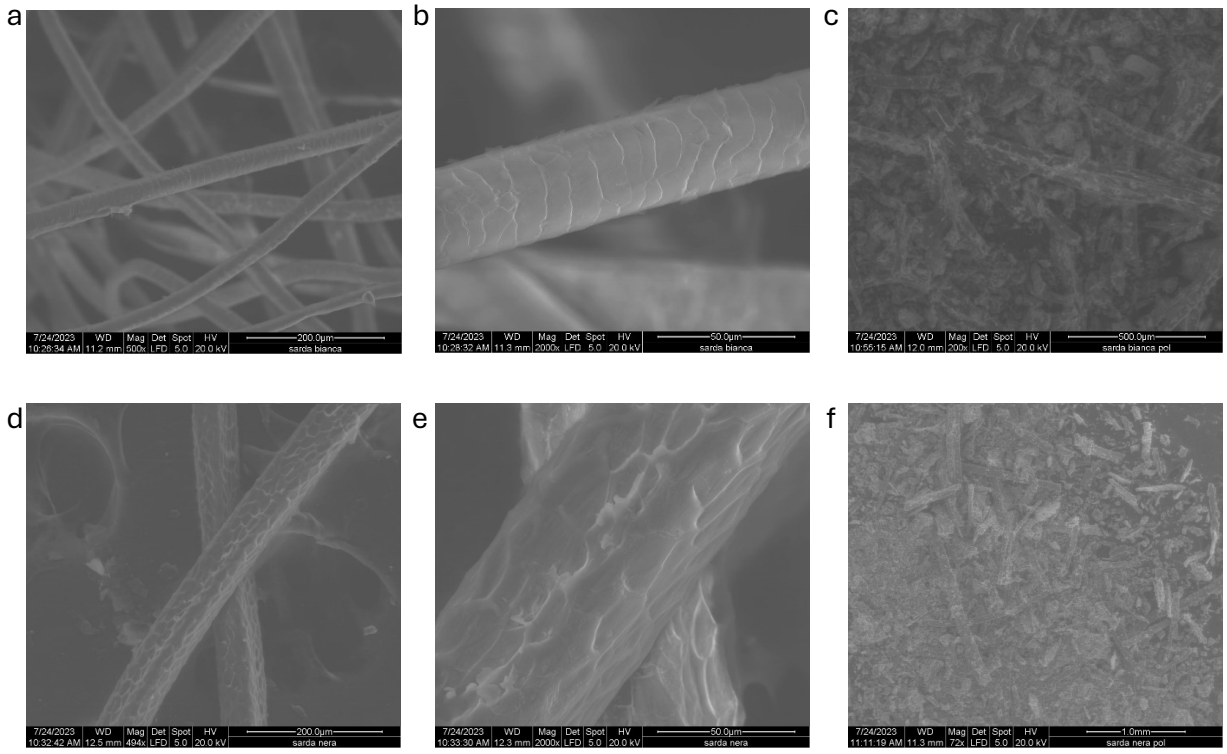


Figure 1. SEM images for wool samples before and after the treatment; a) White Wool Fibre (WWF); b) White Wool Fibre (WWF) – magnification; c) White Wool Powder (WWP); d) Black Wool Fibre (BWF); e) Black Wool Fibre (BWF)– magnification; f) Black Wool Powder (BWP).

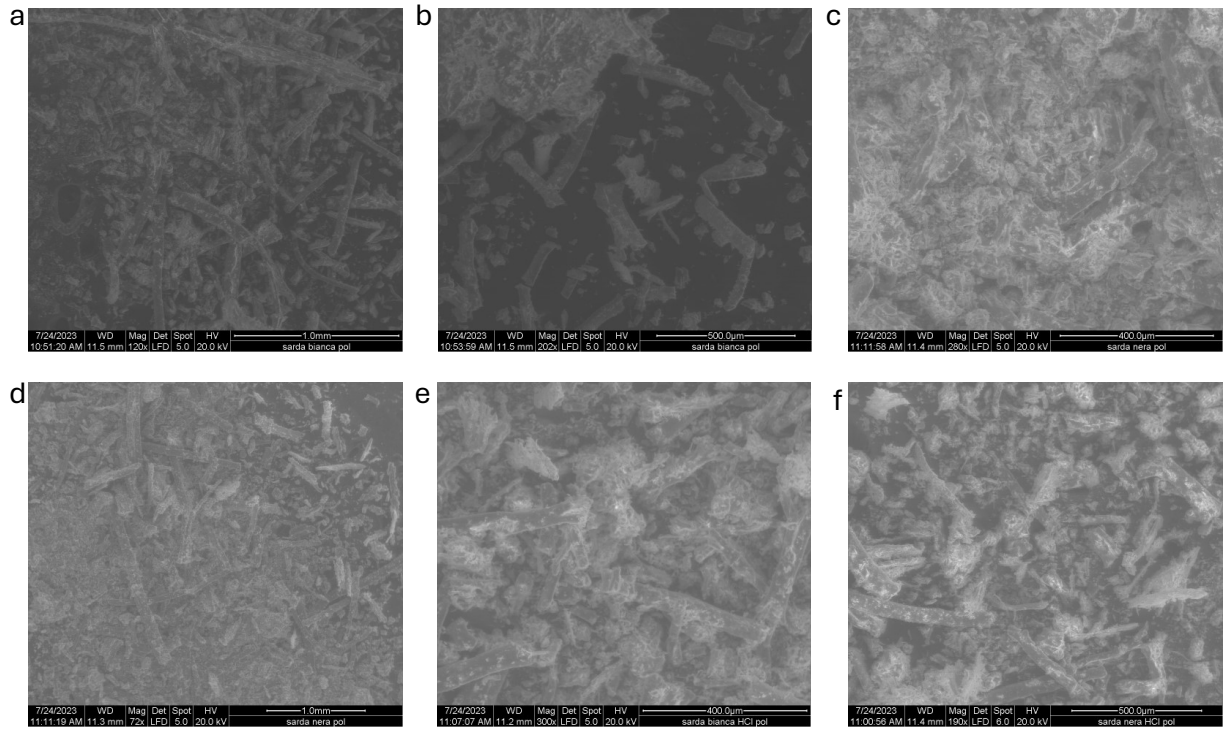
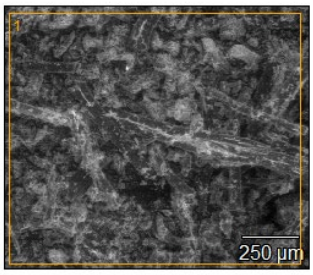


Figure 2. SEM images for wool powder samples with and without HCl treatment; a) White Wool Powder (WWP); b) White Wool Powder (WWP) – magnification; c) White Wool Powder-HCl (WWP-HCl); d) Black Wool Fibre (BWP); e) Black Wool Powder (BWP) – magnification; f) Black Wool Powder- HCl (BWP-HCl).



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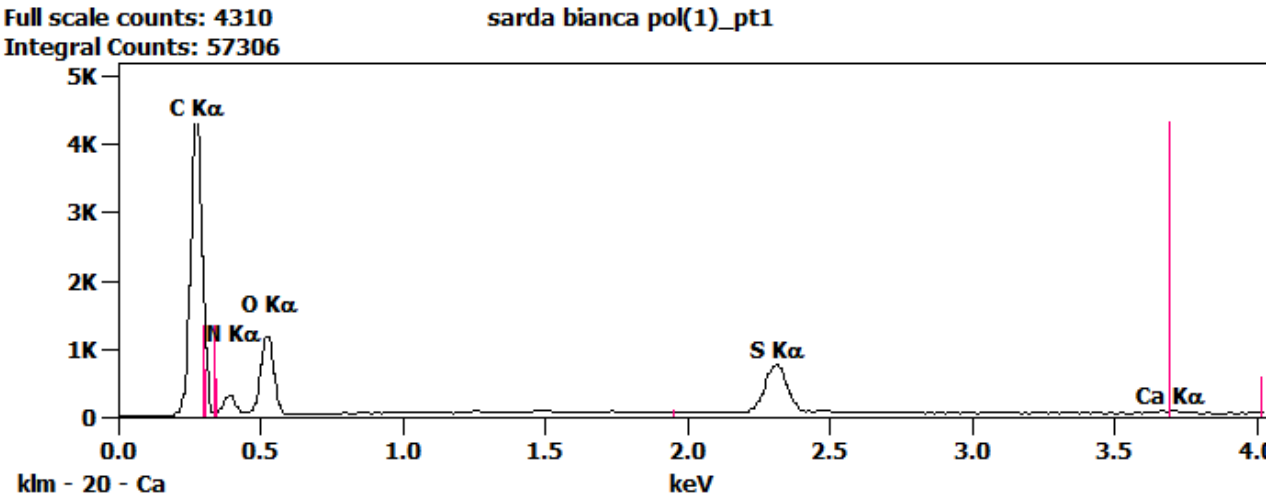

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N K (C)	K	21.7	21.3	2.7
O K (C)	K	30.4	26.1	0.5
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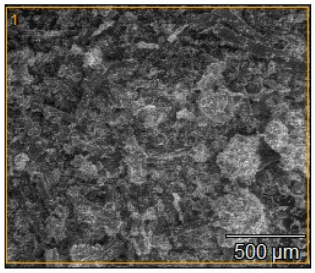

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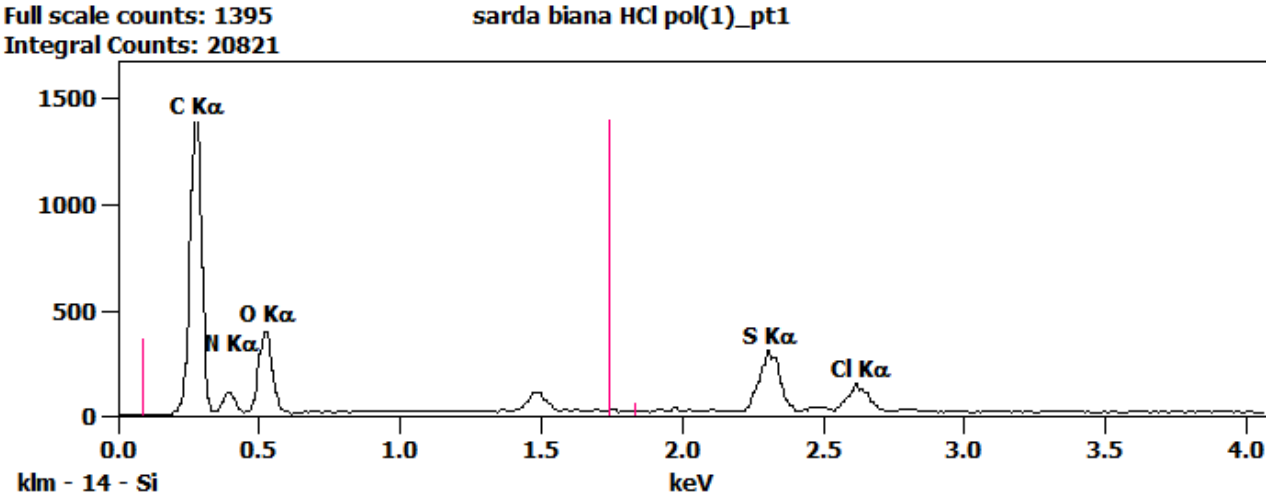

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	Line Type	Weight %	Atom %	Atom % err
C K (C)	K	39.8	46.0	0.5
N K (C)	K	28.4	28.1	2.2
O K (C)	K	28.1	24.4	0.7
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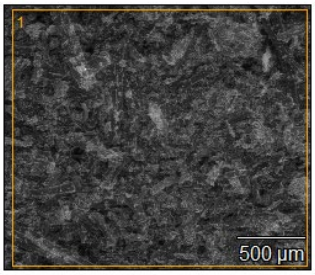

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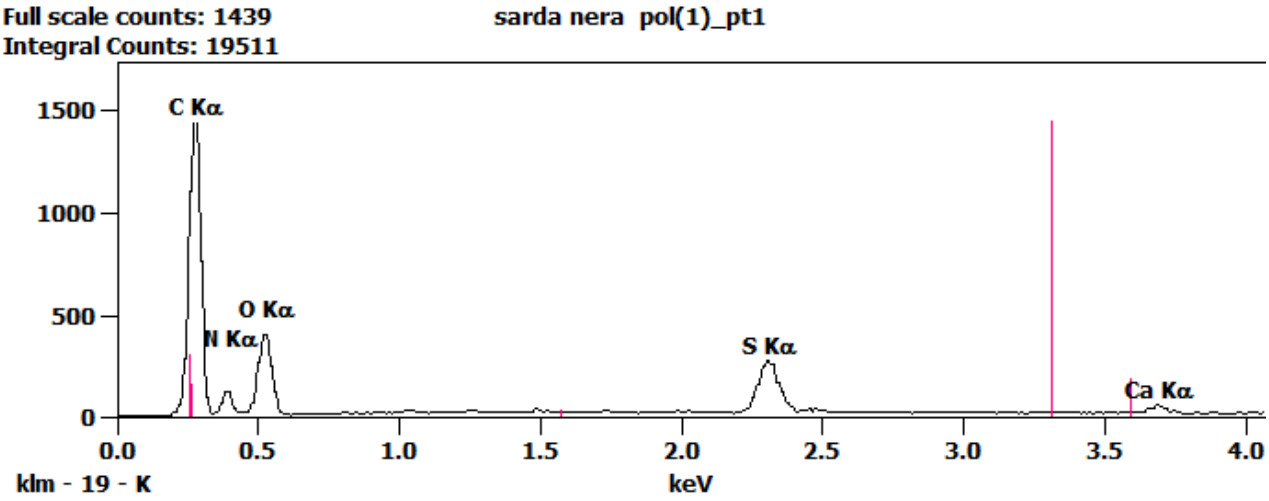

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C K (C)	K	43.2	49.7	0.6
N K (C)	K	23.1	22.8	4.4
O K (C)	K	30.3	26.1	0.8
S K	K	2.7	1.2	0.0
Ca K	K	0.6	0.2	0.0
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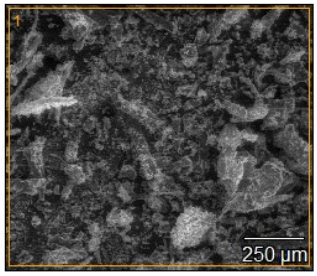

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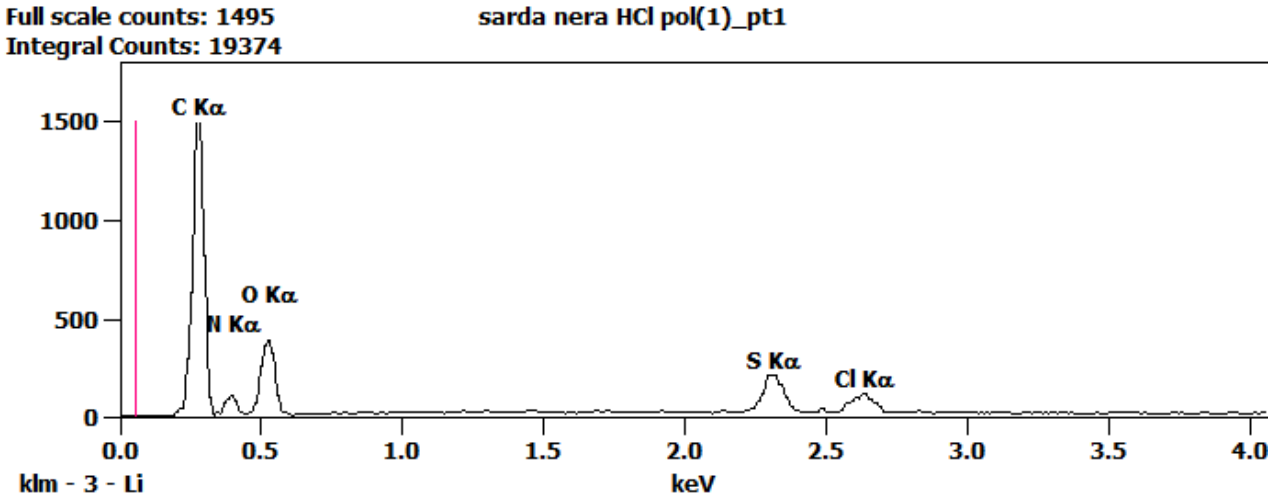

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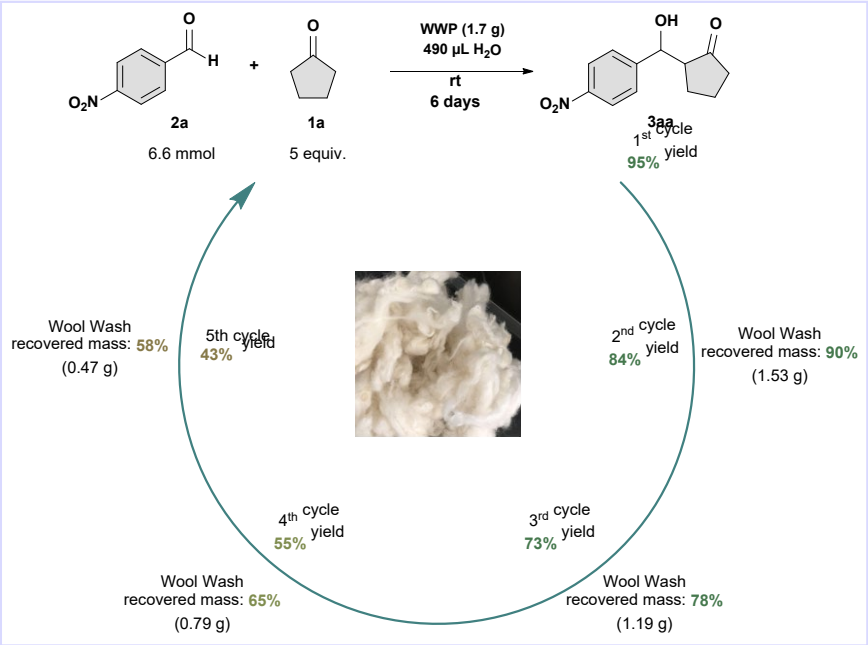
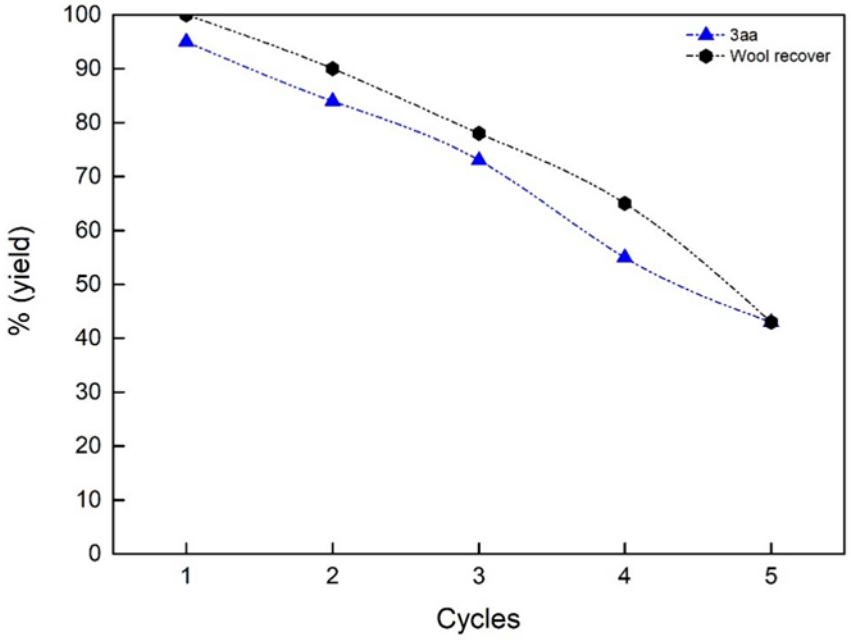
	Line Type	Weight %	Atom %	Atom % err
C K (C)	K	41.2	47.3	0.5
N K (C)	K	28.1	27.6	2.2
O K (C)	K	27.8	23.9	0.7
S K	K	1.7	0.7	0.0
Cl K	K	1.1	0.4	0.0
		100.0	100.0	

Recycling experiments and gram scale synthesis



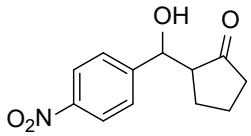
Inside a 50 mL glass vial with a magnetic stirrer, aldehyde (6.7 mmol), ketone (5 equiv.), and 1.7 g of wool powder were placed in 3 mL of distilled water. The mixture was gently stirred, and the reaction progress was monitored using TLC (Heptane/AcOEt 5:1) upon completion. The product was recovered by implementing simple filtration using AcOEt on a paper filter. After that, the solvent was evaporated under reduced pressure to obtain the pure products. The wool powder was then thoroughly washed with water and acetone, dried overnight at 50 °C and then reused.



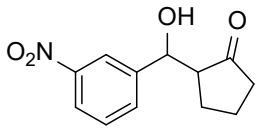
Wool sample preparation

The wool samples were prepared using the following procedure: the raw material was thoroughly rinsed and washed with tap water and soap to eliminate hydrophilic impurities. Afterward, the fibers were rinsed with heptane and then with acetone to remove the hydrophobic impurities. After several washes, the fibers have been dried overnight inside an oven. To prepare the acidic wool samples, 10 g of washed wool fibers were placed inside a beaker containing 500 mL of HCl solution (10%) and left untouched for 72 hours. Afterward, the treated fibers were washed with regular tap water and dried overnight in an oven. The dried long fibers have been finely cut into 1cm pieces to obtain the desired wool fibers (WF) size. The cut fibers were ground with ball mills using zirconia jars and balls. The best results in terms of finer powder were achieved using the Fritsch P7 Premium planetary ball mill (3.00 g of cut fiber inside a 20 mL zirconia jar with 35 balls with diameter Φ = 5 mm and mtot = 13.75 g). After grinding, black wool powder (BWP) and white wool powder (WWP) have been obtained. Wool powders were also obtained from the hydrochloric acid-treated wool fibers (BWP(HCl) and WWP(HCl)) using the same ball milling methodology.

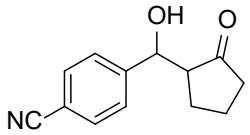
Compounds characterization



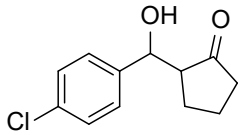
2-(hydroxy(4-nitrophenyl)methyl)cyclopentan-1-one (**3aa**). Yellow solid (45.3 mg, 96%). **M.P.**: 95 °C **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 70/30*) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 – 8.15 (m, 2H), 7.51 (t, J = 7.0 Hz, 2H), 5.42 – 4.82 (m, *diastereoisomeric proton*, 1H), 2.49 – 2.32 (m, 2H), 2.29 – 2.09 (m, *diastereoisomeric proton*, 1H), 2.04 – 1.91 (m, 2H), 1.78 – 1.64 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 219.78 (*diastereoisomeric C=O is missing*), 150.4, 148.7, 147.7, 147.3, 127.5, 126.5, 123.8, 123.7, 74.5, 70.5, 56.2, 55.2, 39.1, 38.7, 26.9, 22.5, 20.5, 20.4. Data closely matches with those reported in the literature.[1a]



2-(hydroxy(3-nitrophenyl)methyl)cyclopentan-1-one (**3ab**) Yellowish solid (37.0 mg, 91%). **M.P.**: 102 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.22 (m, 1H), 8.17 – 8.10 (m, 1H), 7.70 – 7.64 (m, 1H), 7.52 (m 1H), 5.41 – 4.83 (d, *J* = 9.2 Hz, *diastereoisomeric proton*, 1H), 2.52 – 2.35 (m, 2H), 2.33 – 2.12 (m, *diastereoisomeric proton,* 1H), 2.11 – 1.83 (m, 2H), 1.80 – 1.69 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 222.4, 219.7, 148.5, 145.1, 143.8, 132.8, 131.8, 129.7, 129.6, 129.5, 123.1, 122.4, 121.7, 120.8, 74.6, 70.4, 56.2, 55.2, 39.1, 38.7, 27.0, 22.6, 20.5, 20.4. Data closely matches with those reported in the literature.[1a]

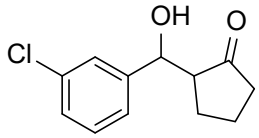


4-(hydroxy(2-oxocyclopentyl)methyl)benzonitrile (**3ac**). Off-white solid (39.9 mg, 87%). **M.P.**: 112-113 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 68/32*) δ 7.61 (dd, *J* = 8.1, 5.9 Hz, 2H), 7.44 (dd, *J* = 8.1, 5.9 Hz, 2H), 5.35 – 4.75 (m, *diastereoisomeric proton,* 1H), 2.45 – 2.28 (m, 2H), 2.27 – 2.08 (m, *diastereoisomeric proton,* 1H), 2.07 – 1.88 (m, 2H), 1.76 – 1.63 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 219.9, 207.7, 148.5, 148.4, 146.7, 132.3, 132.2, 127.3, 126.3, 118.8, 118.7, 111.7, 111.0, 74.5, 70.5, 56.1, 55.1, 39.0, 38.6, 26.7, 22.4, 20.4. Data closely matches with those reported in the literature.[1a]

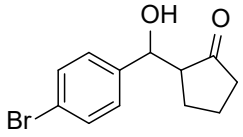


2-((4-chlorophenyl)(hydroxy)methyl)cyclopentan-1-one (**3ad**). Yellow oil (27.2 mg, 61%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 58:42*) δ 7.27 (dd, *J* = 8.8, 4.9 Hz, 2H), 7.25 – 7.20 (dd, 8.8, 4.9 Hz, 2H), 5.24 – 4.64 (m, *diastereoisomeric proton*, 1H), 2.42 – 2.30 (m, 2H), 2.24 – 2.05 (m, *diastereoisomeric proton*, 1H), 2.04 – 1.89 (m, 2H), 1.78 – 1.60 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 208.10, (*diastereoisomeric C=O is missing*), 141.4, 140.1, 131.7,

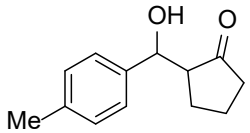
129.1, 128.7, 128.6, 128.1, 127.1, 74.7, 70.9, 70.8, 56.2, 55.4, 39.3, 38.8, 27.0, 22.8, 20.5. Data closely matches with those reported in the literature.[1a]



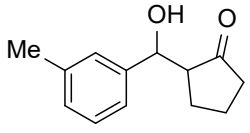
2-((3-chlorophenyl)(hydroxy)methyl)cyclopentan-1-one (**3ae**). Yellowish oil (28.9 mg, 65%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 60:40*) δ 7.37 – 7.34 (m, 1H), 7.32 – 7.26 (m, 1H), 7.24 (m, 1H), 7.20 (m, 1H), 5.30 – 5.26 (m, *diastereoisomeric proton*, 1H), 2.48 – 2.32 (m, 2H), 2.29 – 2.10 (m, *diastereoisomeric proton*, 1H), 2.08 – 1.95 (m, 2H), 1.82 – 1.65 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 208.0, (*diastereoisomeric C=O is missing*), 145.1, 143.6, 134.5, 134.5, 129.8, 129.7, 128.3, 127.5, 126.8, 125.9, 124.9, 123.8, 74.8, 70.8, 56.2, 55.3, 39.2, 38.8, 27.0, 22.7, 20.5, 20.4. Data closely matches with those reported in the literature.[1a]



2-((4-bromophenyl)(hydroxy)methyl)cyclopentan-1-one (**3af**). Off-white solid (16.9 mg, 31%). **M.P.**: 99 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 56:44*) δ 7.44 (dd, *J* = 7.1, 1.4 Hz, 2H), 7.19 (ddd, *J* = 7.1, 1.4 Hz, 2H), 5.23 – 4.65 (m, *diastereoisomeric proton*, 1H), 2.42 – 2.30 (m, 2H), 2.26 – 2.07 (m, *diastereoisomeric proton*, 1H), 2.05 – 1.88 (m, 2H), 1.79 – 1.64 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 208.0, (*diastereoisomeric C=O is missing*), 141.9, 140.5, 131.6, 131.4, 128.3, 127.4, 121.8, 121.0, 74.6, 70.8, 56.1, 55.2, 39.2, 38.7, 26.9, 22.6, 20.4, 20.4. Data closely matches with those reported in the literature.[1a]

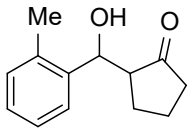


2-(hydroxy(p-tolyl)methyl)cyclopentan-1-one (**3ag**). Yellow oil (17.6 mg, 43%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 7.9, 5.6 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H), 5.26 (m, *diastereoisomeric proton*, 1H), 2.47 – 2.39 (m, 2H), 2.34 (s, 3H), 2.28 – 2.10 (m, *diastereoisomeric proton*, 1H), 2.07 – 1.88 (m, 2H), 1.87 – 1.66 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.3, (*diastereoisomeric C=O is missing*), 142.9, 132.7, 131.4, 128.9, 127.3, 126.4, 123.8, 122.7, 75.3, 71.6, 56.2, 55.4, 39.3, 38.9, 37.9, 29.5, 27.1, 22.9, 21.6, 20.6. Data closely matches with those reported in the literature.[1a]

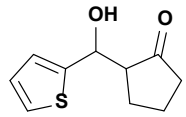


2-(hydroxy(m-tolyl)methyl)cyclopentan-1-one (**3ah**). Yellow oil (16.3 mg, 40%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 50:50*) δ 7.38 – 7.28 (dd, 15.6, 7.6 Hz, 1H), 7.22 (td, *J* = 15.6, 7.6 Hz, 1H), 7.15 (dd, *J* = 15.6, 7.6 Hz, 1H), 7.12 – 7.05 (dd, 15.6, 7.6 Hz 1H), 5.27 – 4.64 (m,

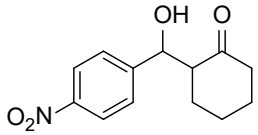
diastereoisomeric proton, 1H), 2.47 – 2.39 (m, 2H), 2.35 (s, 3H), 2.28 – 2.10 (m, *diastereoisomeric proton*, 1H), 2.06 – 1.90 (m, 2H), 1.87 – 1.61 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 208.3, (*diastereoisomeric C=O is missing*), 142.8, 141.4, 132.6, 131.3, 130.2, 128.8, 128.3, 128.1, 127.2, 126.3, 123.8, 122.6, 75.3, 71.6, 56.2, 55.3, 39.2, 38.8, 37.8, 29.4, 27.1, 22.8, 20.5, 20.4. Data closely matches with those reported in the literature.[1a]



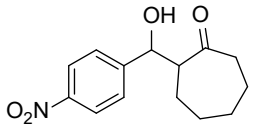
2-(hydroxy(o-tolyl)methyl)cyclopentan-1-one (**3ai**). Colourless oil (13.5 mg, 33%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 1H), 7.27 – 7.23 (m, 2H), 7.18 (m, 1H), 5.30 – 4.68 (m, *diastereoisomeric proton*, 1H), 2.48 – 2.42 (m, 2H), 2.37 (s, 3H), 2.30 – 2.12 (m, *diastereoisomeric proton*, 1H), 2.09 – 1.99 (m, 2H), 1.92 – 1.66 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 208.3, 196.5, 139.8, 139.7, 137.0, 135.1, 132.5, 130.8, 130.6, 129.5, 129.1, 129.1, 126.5, 125.6, 75.1, 71.6, 56.1, 55.4, 39.3, 37.8, 29.4, 22.9, 21.5, 21.1, 20.5, 20.2. Data closely matches with those reported in the literature.[1a]



2-(hydroxy(thiophen-2-yl)methyl)cyclopentan-1-one (**3am**). Colourless paste (33.5, 85%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 50:50; inseparable mixture with elimination product*) δ 7.27 (m, 1H), 6.97 – 6.94 (m, 2H), 5.49 – 5.01 (m, *diastereoisomeric proton*, 1H), 2.44 – 2.32 (m, 2H), 2.26 – 2.16 (m, *diastereoisomeric proton*, 1H), 2.02 – 1.88 (m, 2H), 1.82 – 1.71 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 207.8, (*diastereoisomeric C=O is missing*), 130.1, 129.6, 128.1, 126.8, 126.5, 125.3, 124.7, 124.6, 124.0, 71.4, 68.9, 56.0, 55.9, 39.3, 38.9, 27.1, 23.5, 20.7. Data closely matches with those reported in the literature.[1b]

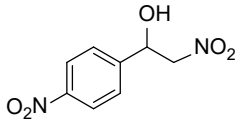


2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (**3ba**). Off-white solid (47.2 mg, 96%). **M.P.**: 98 °C. **^{1}H NMR** (600 MHz, $CDCl_3$, *mixture of diastereoisomers, syn/anti ratio: 55/45*) δ 8.18 (dd, *J* = 8.7, 3.6 Hz, 2H), 7.49 (dd, *J* = 8.7, 3.6 Hz, 2H), 5.48 – 4.88 (m, *diastereoisomeric proton*, 1H), 2.60 (m, 1H), 2.50 – 2.44 (m, 1H), 2.36 (m, 2H), 2.12 – 2.05 (m, *diastereoisomeric proton*, 1H), 1.73 – 1.49 (m, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$, *mixture of diastereoisomers*) δ 214.9, 214.2, 149.3, 148.5, 147.7, 147.1, 128.0, 126.7, 123.7, 123.5, 74.1, 70.2, 57.3, 56.9, 42.8, 42.7, 30.9, 27.9, 27.7, 26.0, 24.8, 24.7. Data closely matches with those reported in the literature.[1a]

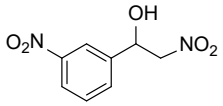


2-(hydroxy(4-nitrophenyl)methyl)cycloheptan-1-one (**3ca**). Off-white solid (43.9 mg, 83%). **M.P.** 121-123 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.18 (ddd, *J* = 8.8, 3.7, 1.6 Hz, 2H), 7.49 (ddd, *J* = 8.8, 3.7, 1.6 Hz, 2H), 5.47 – 4.89 (m, *diastereoisomeric proton*, 1H), 2.60 (qd, *J* = 17.1, 8.6 Hz, 1H), 2.51 – 2.44 (qd, *J* = 17.1, 8.6 Hz, 1H), 2.36 (qt, *J* = 17.1, 8.6 Hz, 2H), 2.14 – 2.06 (m, *diastereoisomeric proton*, 1H), 1.76 – 1.46 (m, 6H).

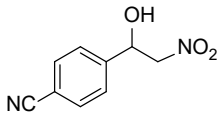
^{13}C NMR (151 MHz, $CDCl_3$) δ 214.9, 214.2, 149.3, 148.5, 147.7, 147.1, 128.0, 126.7, 123.7, 123.5, 74.1, 70.2, 57.3, 56.9, 42.8, 42.7, 30.9, 29.2, 27.9, 27.7, 26.0, 24.8, 24.8. Data closely matches with those reported in the literature.[1a]



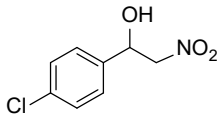
2-nitro-1-(4-nitrophenyl)ethan-1-ol (**5a**). Yellow oil (36.5 mg, 93%). **M.P.** n/a. **^{1}H NMR** (600 MHz, DMSO) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 5.44 (m, 1H), 4.97 – 4.60 (m, 2H), 3.35 (bs, 1H). **^{13}C NMR** (151 MHz, DMSO) δ 148.0, 147.1, 127.6, 123.4, 81.2, 69.1. Data closely matches with those reported in the literature.[2a]



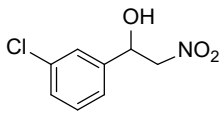
2-nitro-1-(3-nitrophenyl)ethan-1-ol (**5b**). Pale orange oil (35.3 mg, 90%). **M.P.** n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.26 (m, 1H), 8.16 (m, 1H), 7.72 – 7.68 (m, 1H), 7.55 (m, 1H), 5.54 (m, 1H), 4.59 – 4.49 (m, 2H), 3.10 (bs, 1H). **^{13}C NMR** (151 MHz, DMSO) δ 142.8, 136.9, 133.0, 129.9, 122.8, 121.0, 81.2, 68.8. Data closely matches with those reported in the literature.[2a]



4-(1-hydroxy-2-nitroethyl)benzonitrile (**5c**). Colourless oil (31.9 mg, 83%). **M.P.** n/a. **^{1}H NMR** (600 MHz, DMSO) δ 7.85 (dt, *J* = 8.0, 4.1 Hz, 1H), 7.66 (dt, *J* = 8.0, 4.1 Hz, 2H), 5.37 (m, 1H), 4.96 – 4.55 (m, 2H), 3.34 (bs, 1H). **^{13}C NMR** (151 MHz, DMSO) δ 146.0, 132.3, 127.3, 118.7, 110.7, 81.2, 69.3. Data closely matches with those reported in the literature.[2a]

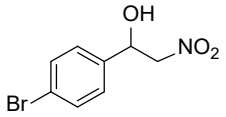


1-(4-chlorophenyl)-2-nitroethan-1-ol (**5d**). Colourless oil (25.8 mg, 64%). **M.P.** n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 – 7.37 (m, 2H), 7.37 – 7.34 (m, 2H), 5.46 (m, 1H), 4.58 (m, 1H), 4.50 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) 146.0, 132.3, 127.3, 118.7, 110.7, 81.2, 69.3. Data closely matches with those reported in the literature.[2a]

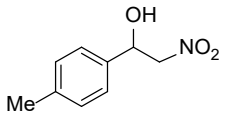


1-(3-chlorophenyl)-2-nitroethan-1-ol (**5e**). Pale yellow oil (23.4 mg, 58%). **M.P.** n/a. **^{1}H NMR** (600 MHz, DMSO) δ 7.52 (t, *J* = 1.5 Hz, 1H), 7.41 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.34 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.28 – 6.23 (m, 1H), 5.33 (dd, *J* = 9.7, 3.4 Hz, 1H), 4.89 (dd, *J* = 12.6, 3.4 Hz, 1H), 4.61 (dd, *J*

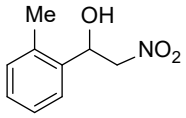
= 12.6, 9.7 Hz, 1H). **^{13}C NMR** (151 MHz, DMSO) 146.0, 132.3, 127.3, 118.7, 110.7, 81.2, 69.3. Data closely matches with those reported in the literature.[2a]



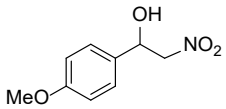
1-(4-bromophenyl)-2-nitroethan-1-ol (**5f**). Yellowish oil (30.1 mg, 61%). **M.P.** n/a. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 – 7.54 (m, 2H), 7.41 – 7.40 (m, 2H), 5.30 – 5.27 (m, 1H), 4.86 – 4.84 (m, 1H), 4.59 – 4.56 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) 137.1, 132.5, 131.0, 128.8, 83.2, 70.4. Data closely matches with those reported in the literature.[2a]



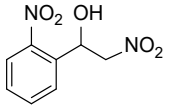
2-nitro-1-(*p*-tolyl)ethan-1-ol (**5g**). Pale yellow oil (17.2 mg, 47%). **M.P.** n/a. **^{1}H NMR** (600 MHz, DMSO) δ 7.85 – 7.83 (m, 1H), 7.30 – 7.28 (m, 1H), 7.17 (d, *J* = 7.8 Hz, 2H), 6.03 (s, 1H), 5.23 (dd, *J* = 9.9, 3.5 Hz, 1H), 4.79 (dd, *J* = 12.4, 3.5 Hz, 1H), 4.54 (dd, *J* = 12.4, 9.8 Hz, 1H), 2.28 (s, 3H). **^{13}C NMR** (151 MHz, DMSO) δ 167.8, 143.5, 138.0, 137.6, 82.4, 70.3, 21.6. Data closely matches with those reported in the literature.[2a]



2-nitro-1-(o-tolyl)ethan-1-ol (**5ai**). Yellow oil (14.9 mg, 83%). **M.P.** n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 3H), 7.11 – 7.08 (m, 1H), 4.75 (m, 3H), 2.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 136.3, 134.5, 130.8, 128.6, 126.7, 125.6, 80.2, 67.9, 18.8. Data closely matches with those reported in the literature.[2a]

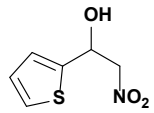


1-(4-methoxyphenyl)-2-nitroethan-1-ol (**5j**). Colourless oil (13.9 mg, 35%). **M.P.** n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.16 – 7.12 (m, 2H), 6.91 – 6.88 (m, 2H), 4.77 – 4.71 (m, 3H), 3.80 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.1, 128.5, 125.8, 115.0, 55.3, 41.2. Data closely matches with those reported in the literature.[2a]

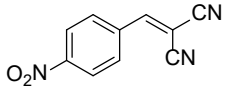


1-(2-nitrophenyl)-2-nitroethan-1-ol (**5l**). Pale orange paste (12.7 mg, 30%). **M.P.** n/a. **^{1}H NMR** (600 MHz, DMSO) δ 8.06 – 8.04 (dd, *J* = 8.4, 1.4 Hz, 1H), 7.92 – 7.90 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.82 – 7.80 (td, *J* = 7.8, 1.4 Hz, 1H), 7.63 – 7.60 (ddd, *J* = 8.4, 7.8, 1.4 Hz, 1H), 6.38 (dd, *J* = 4.9, 1.2 Hz, 1H), 5.80 – 5.78 (ddd, *J* = 9.5, 4.9, 2.8 Hz, 1H), 4.98 – 4.95 (ddd, *J* = 12.9, 2.8, 1.2 Hz, 1H), 4.62 – 4.58 (dd, *J* = 12.9, 9.5 Hz, 1H). **^{13}C**

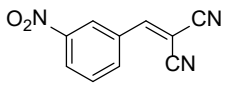
NMR (151 MHz, DMSO) δ 147.7, 136.0, 134.4, 129.9, 129.6, 124.9, 81.4, 66.6. Data closely matches with those reported in the literature.[2a]



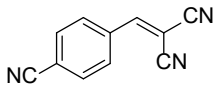
2-nitro-1-(thiophen-2-yl)ethan-1-ol (**5m**). Yellowish oil (22.9 mg, 66%). **M.P.** n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.07 (dt, *J* = 3.6, 1.1 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.73 (dd, *J* = 9.3, 3.2 Hz, 1H), 4.72 (dd, *J* = 13.4, 9.3 Hz, 1H), 4.62 (dd, *J* = 13.4, 3.2 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.4, 135.6, 134.7, 133.9, 132.2, 131.7, 129.0, 127.4, 126.3, 125.2, 80.9, 67.3. Data closely matches with those reported in the literature.[2b]



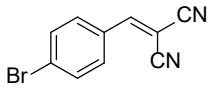
2-(4-nitrobenzylidene)malononitrile (**8a**). Yellowish solid (38.3 mg, 96%). **M.P.**: 164-165 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (m, 3H), 8.04 (s, 1H), 7.92 (m, 2H), 7.83 – 7.79 (m, 3H), 7.70 – 7.66 (m, 2H), 7.55 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 187.7, 152.4, 135.7, 135.1, 134.0, 132.9, 131.0, 129.4, 128.9, 117.7, 116.0, 113.5. Data closely matches with those reported in the literature.[3]



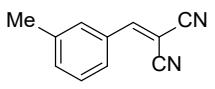
2-(3-nitrobenzylidene)malononitrile (**8b**). White solid (36.3 mg, 91%). **M.P.**: 105 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.66 (d, *J* = 2.3 Hz, 1H), 8.47 (dd, *J* = 8.2, 2.3 Hz, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 7.89 (s, 1H), 7.79 (t, *J* = 8.2 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.1, 148.8, 134.9, 132.1, 131.1, 128.4, 125.7, 112.8, 111.8, 87.0. Data closely matches with those reported in the literature.[3]



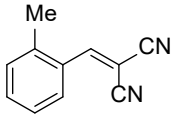
2-(4-cyanobenzylidene)malononitrile (**8c**). Off-white solid (31.9 mg, 89%). **M.P.**: 157-158 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 – 7.97 (m, 2H), 7.84 (s, 1H), 7.84 – 7.79 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 157.4, 134.4, 133.3, 130.8, 117.4, 117.4, 112.9, 111.8. Data closely matches with those reported in the literature.[3]



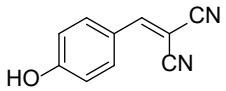
2-(4-bromobenzylidene)malononitrile (**8f**). Pale brownish solid (32.8 mg, 62%). **M.P.**: 163 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.78 – 7.76 (dd, *J* = 8.6, 1.8 Hz, 2H), 7.71 (s, 1H), 7.70 – 7.68 (dd, *J* = 8.6, 1.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.4, 133.1, 131.8, 129.9, 129.7, 113.4, 112.3, 83.6. Data closely matches with those reported in the literature.[3]



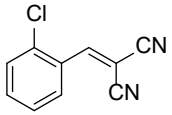
2-(3-methylbenzylidene)malononitrile (**8h**). White solid (26.1 mg, 72%). **M.P.**: 136-137 °C **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.68 (s, 1H), 7.46 – 7.41 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 160.3, 139.8, 135.7, 131.4, 131.1, 129.6, 128.0, 113.9, 112.7, 82.5, 21.4. Data closely matches with those reported in the literature.[3]



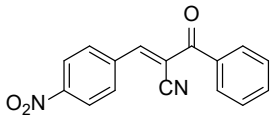
2-(2-methylbenzylidene)malononitrile (**8i**). White solid (16.3 mg, 45%). **M.P.**: 105 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.08 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 2.45 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 158.3, 139.9, 134.3, 131.5, 130.1, 128.4, 127.2, 113.9, 112.6, 84.2, 19.9. Data closely matches with those reported in the literature.[3]



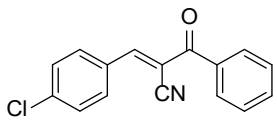
2-(4-hydroxybenzylidene)malononitrile (**8j**). Pale yellow solid (18.5 mg, 51%). **M.P.**: 184 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) 7.91 – 7.89 (m, 2H), 7.65 – 7.62 (m, 2H), 7.01 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.7, 158.9, 133.7, 130.6, 124.5, 116.8, 116.3, 114.4. Data closely matches with those reported in the literature.[3]



2-(2-chlorobenzylidene)malononitrile (**8l**). White solid (15.3 mg, 38%). **M.P.**: 91-92 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.18 (m, 1H), 7.58 – 7.53 (m, 2H), 7.48 – 7.42 (m, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 156.1, 136.4, 135.1, 130.7, 129.5, 129.1, 127.8, 113.2, 111.9, 85.8. Data closely matches with those reported in the literature.[3]

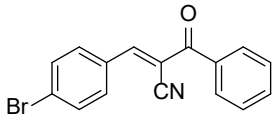


2-benzoyl-3-(4-nitrophenyl)acrylonitrile (**9a**). Pale brown solid (57.8 mg, 99%). **M.P.**: 115-117 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.99 – 7.96 (m, 2H), 7.90 (m, 2H), 7.67 – 7.63 (m, 1H), 7.56 – 7.52 (m, 2H), 7.52 – 7.49 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.5, 153.8, 139.6, 135.6, 133.5, 132.2, 131.1, 130.2, 130.0, 129.7, 129.3, 129.1, 128.7, 128.4, 116.7, 110.5. Data closely matches with those reported in the literature.[4]

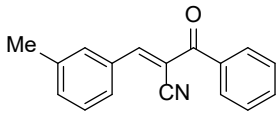


2-benzoyl-3-(4-chlorophenyl)acrylonitrile (**9d**). Pale yellowish solid (38.2 mg, 69%). **M.P.**: 89-90 °C **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.91 – 7.88 (m, 4H), 7.69 – 7.66 (m, 2H), 7.66 – 7.63 (m, 2H), 7.56

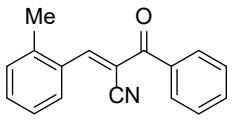
– 7.52 (m, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.9, 154.3, 136.0, 134.0, 133.1, 132.6, 132.4, 131.2, 131.0, 129.7, 129.1, 128.7, 117.1, 111.0. Data closely matches with those reported in the literature.[4]



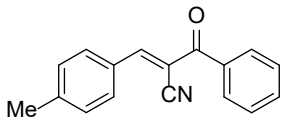
2-benzoyl-3-(4-bromophenyl)acrylonitrile (**9f**). Pale brownish solid (35.8 mg, 56%). **M.P.**: 103. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.90 – 7.86 (m, 4H), 7.65 (m, 3H), 7.53 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 188.6, 154.1, 135.7, 133.7, 132.8, 130.7, 129.4, 129.2, 128.8, 128.4, 116.8, 110.8. Data closely matches with those reported in the literature.[4]



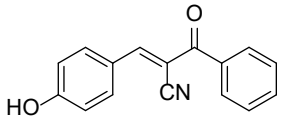
2-benzoyl-3-(m-tolyl)acrylonitrile (**9h**). Yellowish paste (35.4 mg, 71%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.90 – 7.86 (dd, *J* = 14.1, 7.7 Hz, 3H), 7.81 (s, 1H), 7.66 – 7.62 (ddd, 14.1, 7.7, 1.8 Hz, 1H), 7.53 (td, *J* = 7.7, 1.8 Hz, 2H), 7.43 – 7.39 (m, 2H), 2.43 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.3, 156.0, 139.4, 136.0, 134.5, 133.5, 131.9, 129.5, 129.4, 128.8, 128.4, 117.1, 110.1, 21.5. Data closely matches with those reported in the literature.[4]



2-benzoyl-3-(o-tolyl)acrylonitrile (**9i**). Yellow paste (21.4 mg, 43%). **M.P.**: n/a. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 8.24 – 8.22 (d, *J* = 7.8 Hz, 1H), 7.94 – 7.89 (m, 2H), 7.67 – 7.62 (m, 1H), 7.55 – 7.52 (t, *J* = 7.8 Hz, 2H), 7.46 – 7.43 (t, *J* = 7.6 Hz, 1H), 7.37 – 7.35 (t, *J* = 7.6 Hz, 1H), 7.31 – 7.30 (d, *J* = 7.6 Hz, 1H), 2.41 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.1, 154.0, 139.8, 136.0, 133.6, 132.9, 131.2, 131.1, 129.5, 128.8, 128.7, 126.9, 116.8, 111.8, 20.0. Data closely matches with those reported in the literature.[4]



2-benzoyl-3-(p-tolyl)acrylonitrile (**9g**). Yellow solid (25.3 mg, 47%). **M.P.**: 95 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.95 – 7.92 (m, 2H), 7.89 – 7.86 (m, 2H), 7.63 – 7.61 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.52 (ddd, *J* = 8.4, 7.8, 1.8 Hz, 2H), 7.32 (dd, *J* = 7.8, 1.8 Hz, 2H), 2.44 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 189.3, 155.7, 144.9, 136.1, 133.3, 131.4, 130.2, 129.4, 129.3, 128.7, 117.2, 109.0, 22.0. Data closely matches with those reported in the literature.[4]



2-benzoyl-3-(4-hydroxyphenyl)acrylonitrile (**9j**). Off-white solid (12.2 mg, 23%). **M.P.**: 123 °C. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 8.01 (m, 2H), 7.93 (m, 1H), 7.87 (m, 2H), 7.53 (m, 2H), 6.95 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 191.4, 155.3, 151.0, 149.2, 143.9, 143.5, 142.6, 134.1, 133.1, 129.2, 128.6, 116.5. Data closely matches with those reported in the literature.[4]

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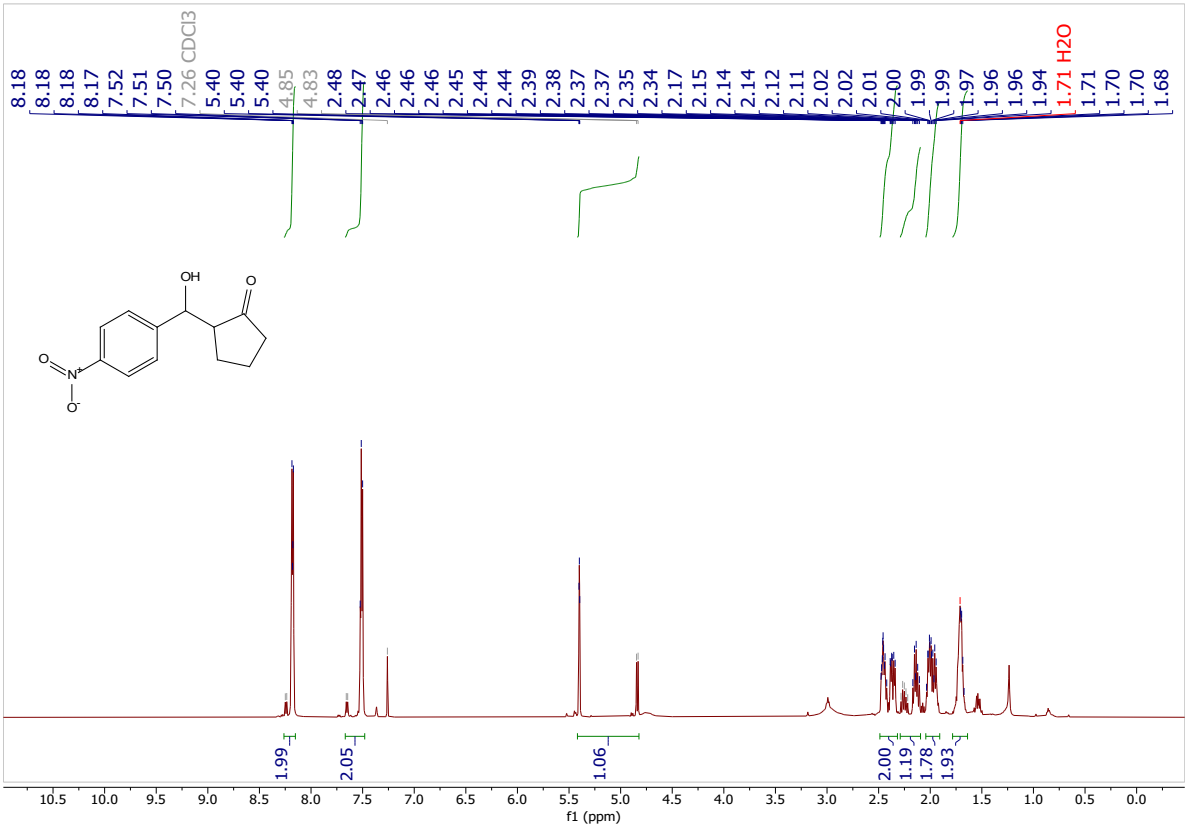
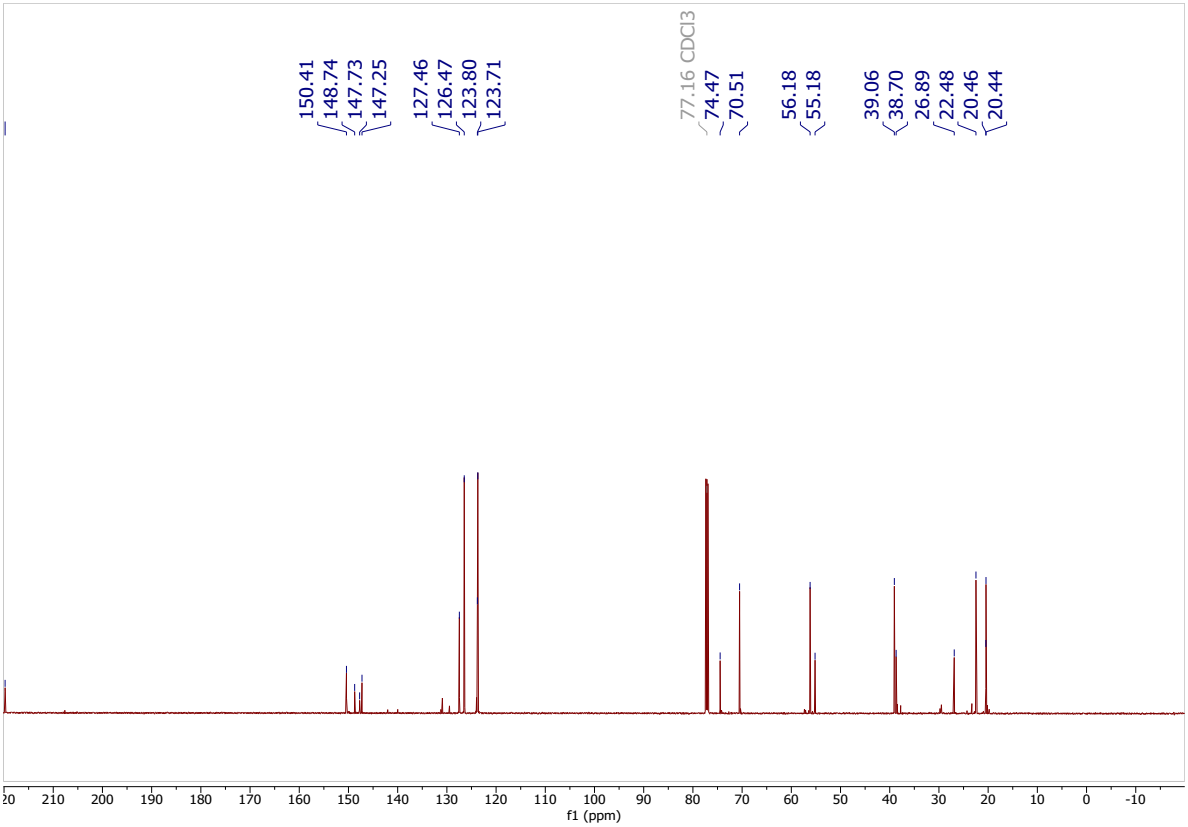
1) a) R. Rani, R. K. Peddinti, Tetrahedron: Asymmetry, 2010, 21, 775-779; b) Ikishima, H., Sekiguchi, Y., Ichikawa, Y., Kotsuki, H., *Tetrahedron*, 2006, **62**, 311–316.
2) a) Sharma, S., Kumar, M., Bhatt, V. Nayal, O. S., Thakur, M.S., Kumar, N., Singh, B., Sharma, U. *Tetrahedron Lett.,* **2016**, *57*, 5003–5008; b) Gao, N., Chen, Y.-L., He, Y.-H., Guan, Z., *RSC Adv.*, 2013, **3**, 16850–16856.
3) Hesamaldin, M., Malakooti, *R. Reaction Kinetics, Mechanisms and Catalysis*, **2014**, *113*, 241-255
4) Kao, T-T. Syu, S. Jhang, Y-W., Lin, W. *Org. Lett.* **2010**, *13*, 3066–3069

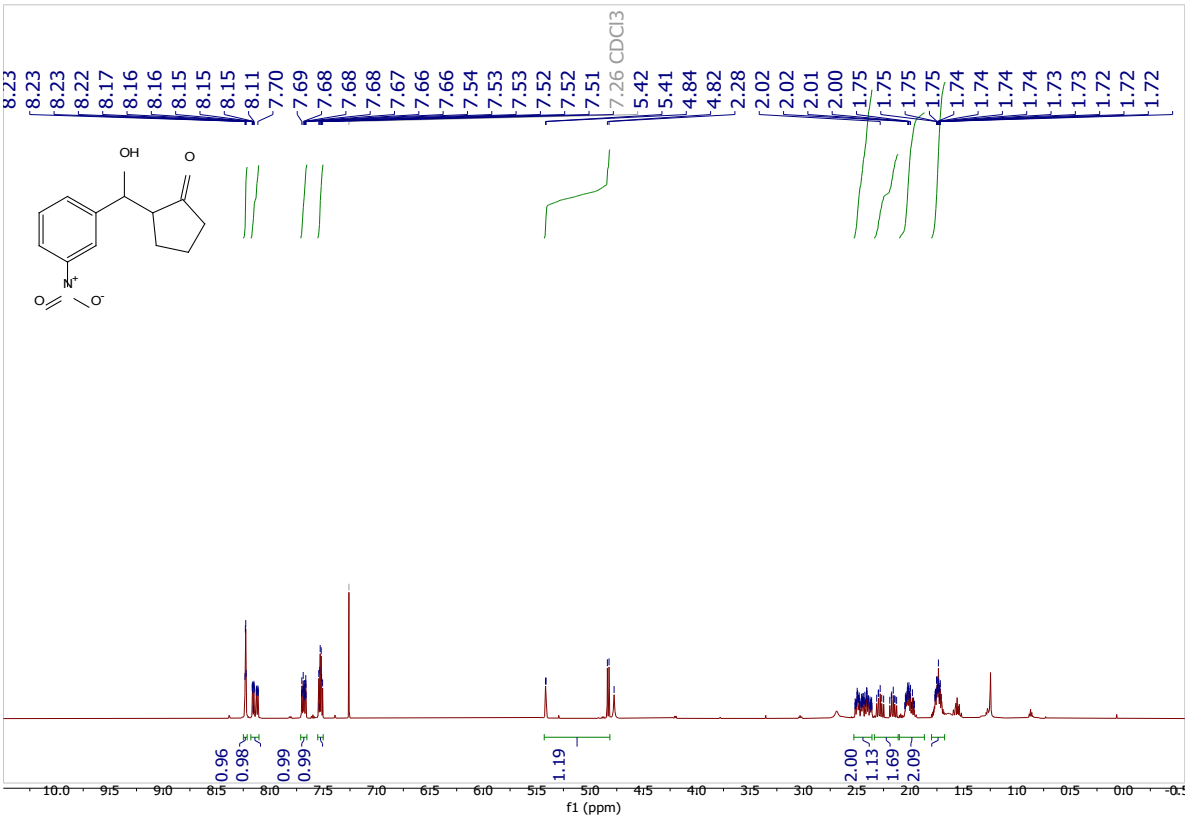
^{1}H and ^{13}C NMR Spectra

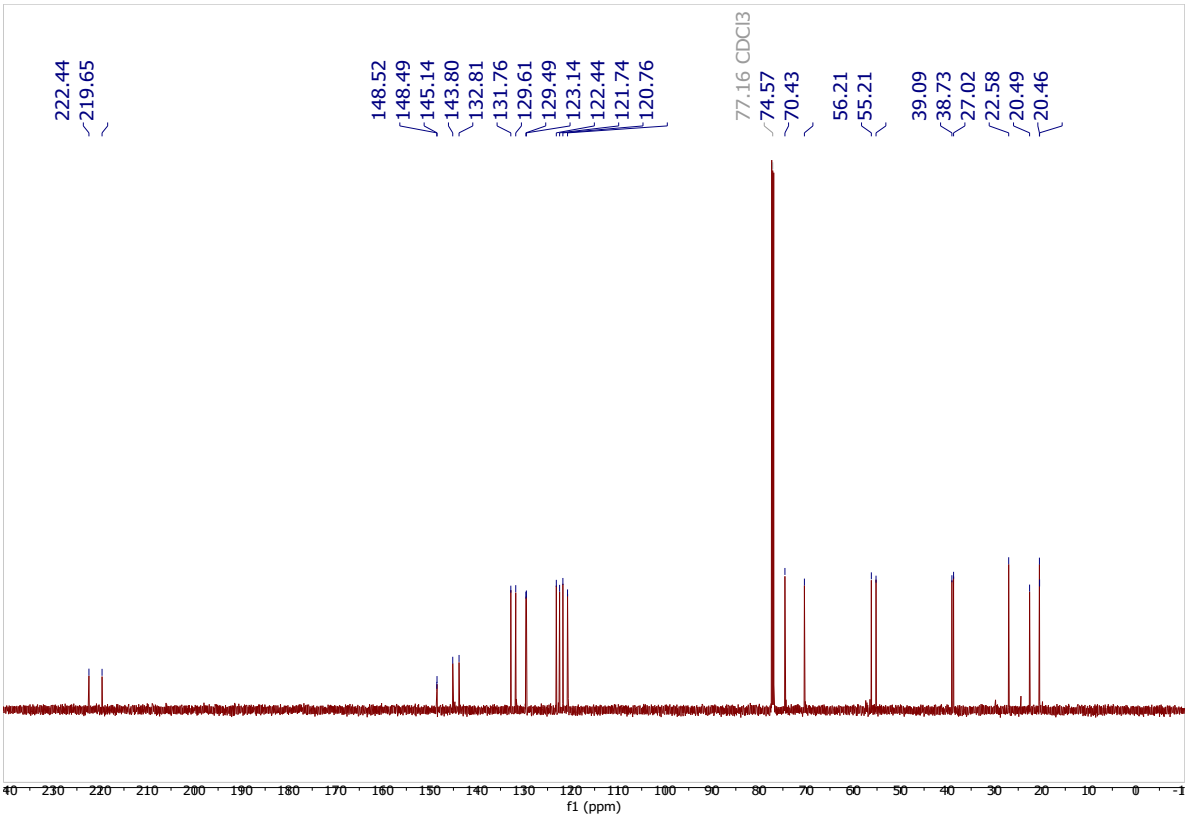
*2-(hydroxy(4-nitrophenyl)methyl)cyclopentan-1-one (**3aa**)*



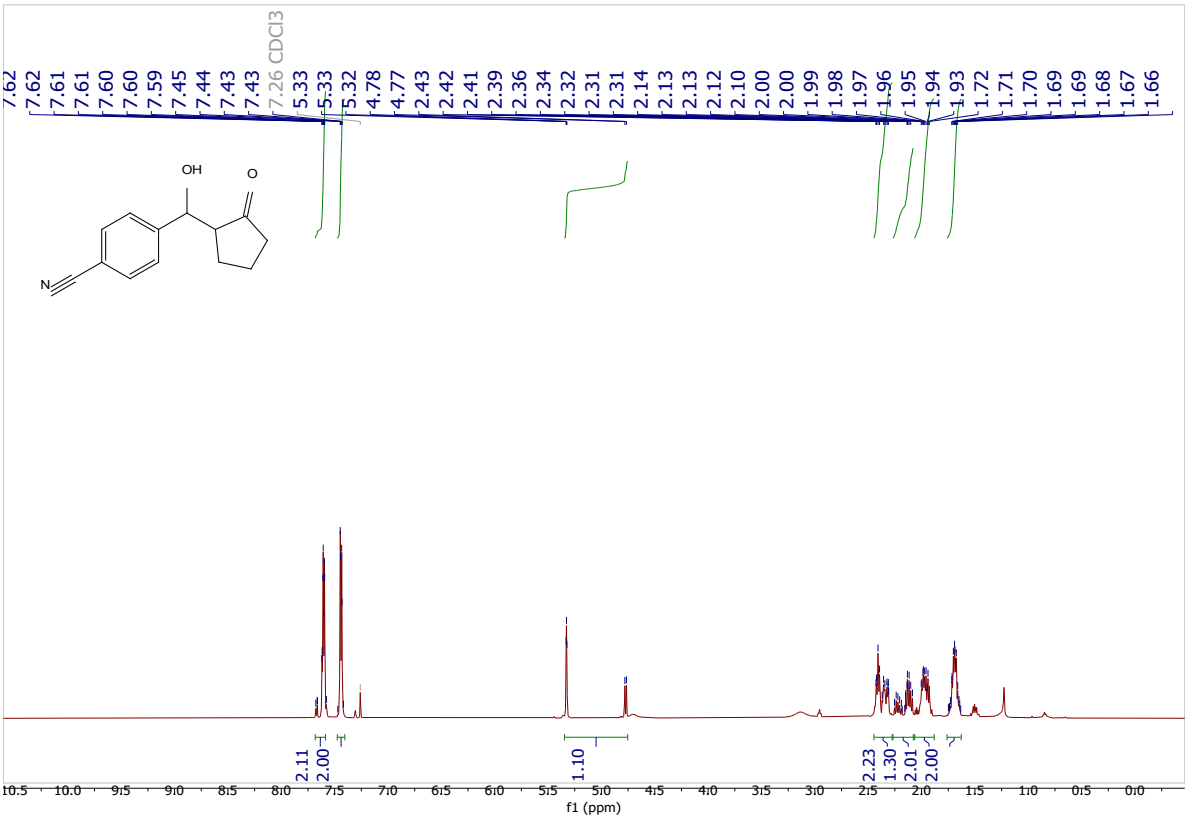


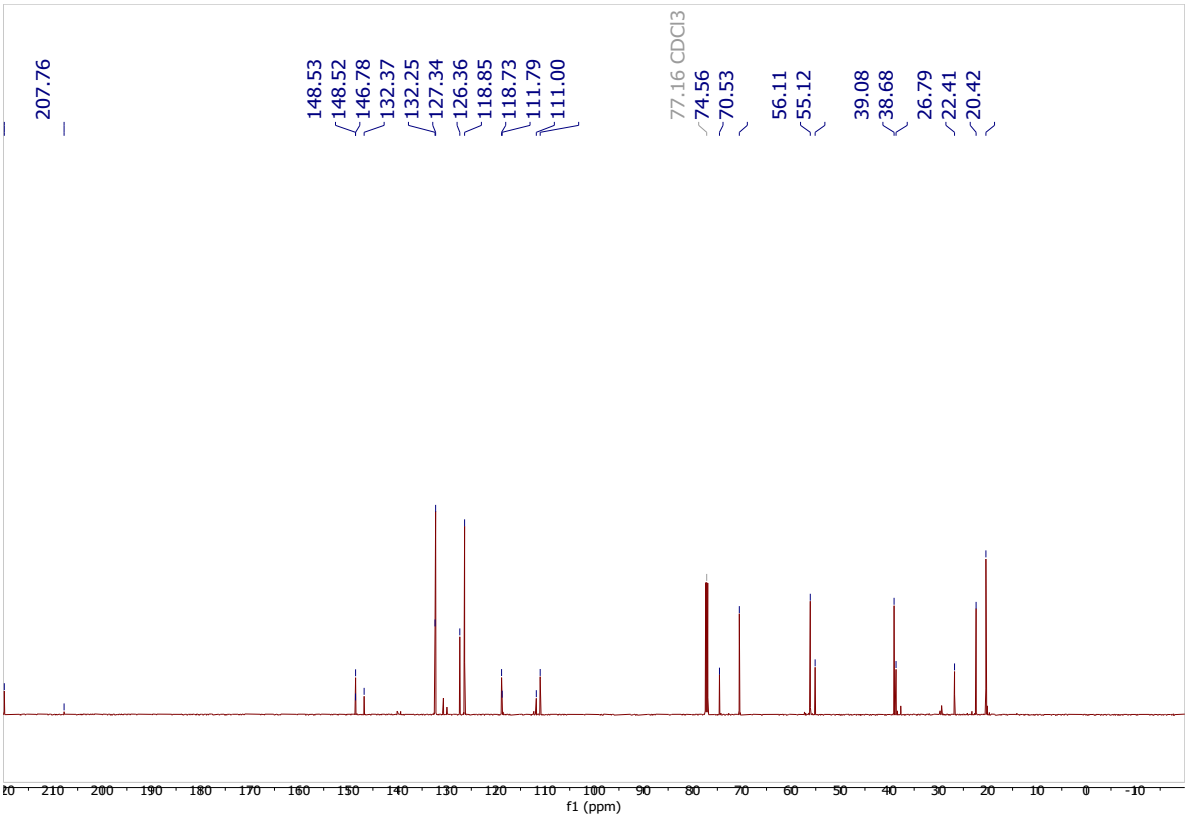
*2-(hydroxy(3-nitrophenyl)methyl)cyclopentan-1-one (**3ab**)*





*4-(hydroxy(2-oxocyclopentyl)methyl)benzonitrile (**3ac**)*





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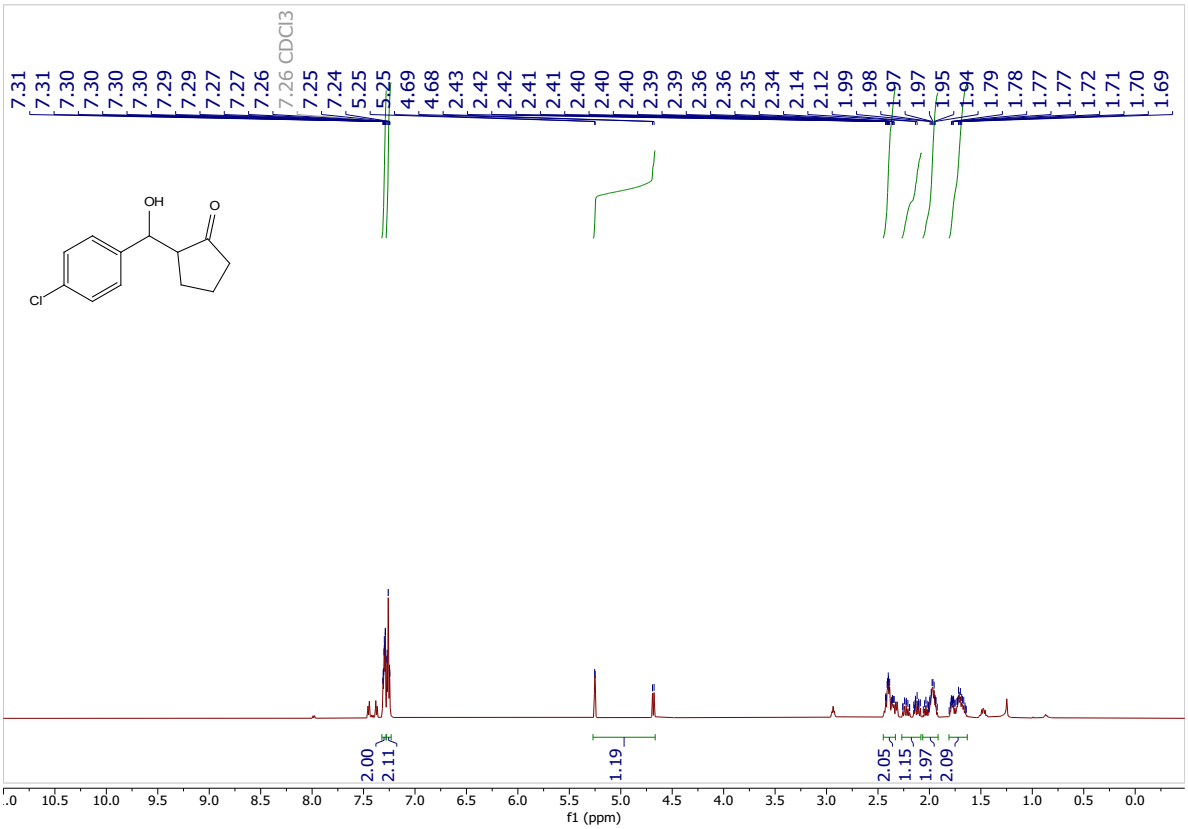

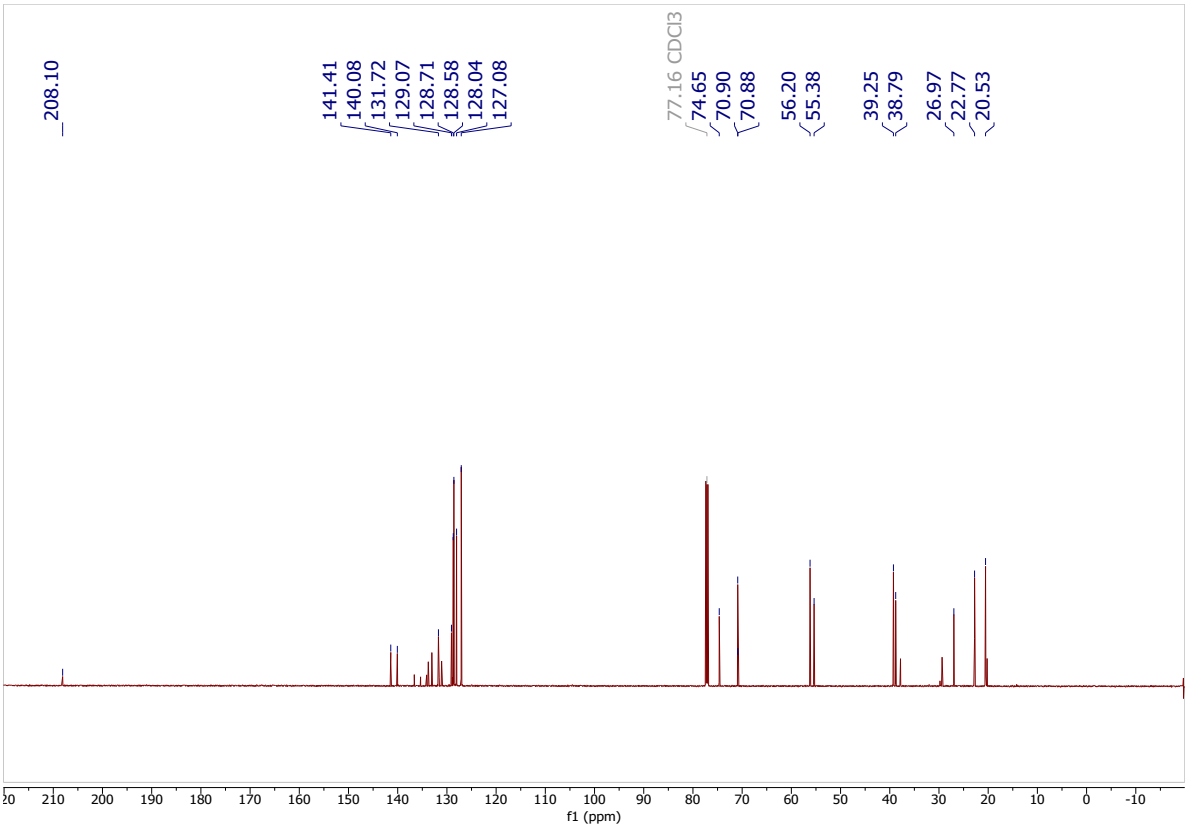

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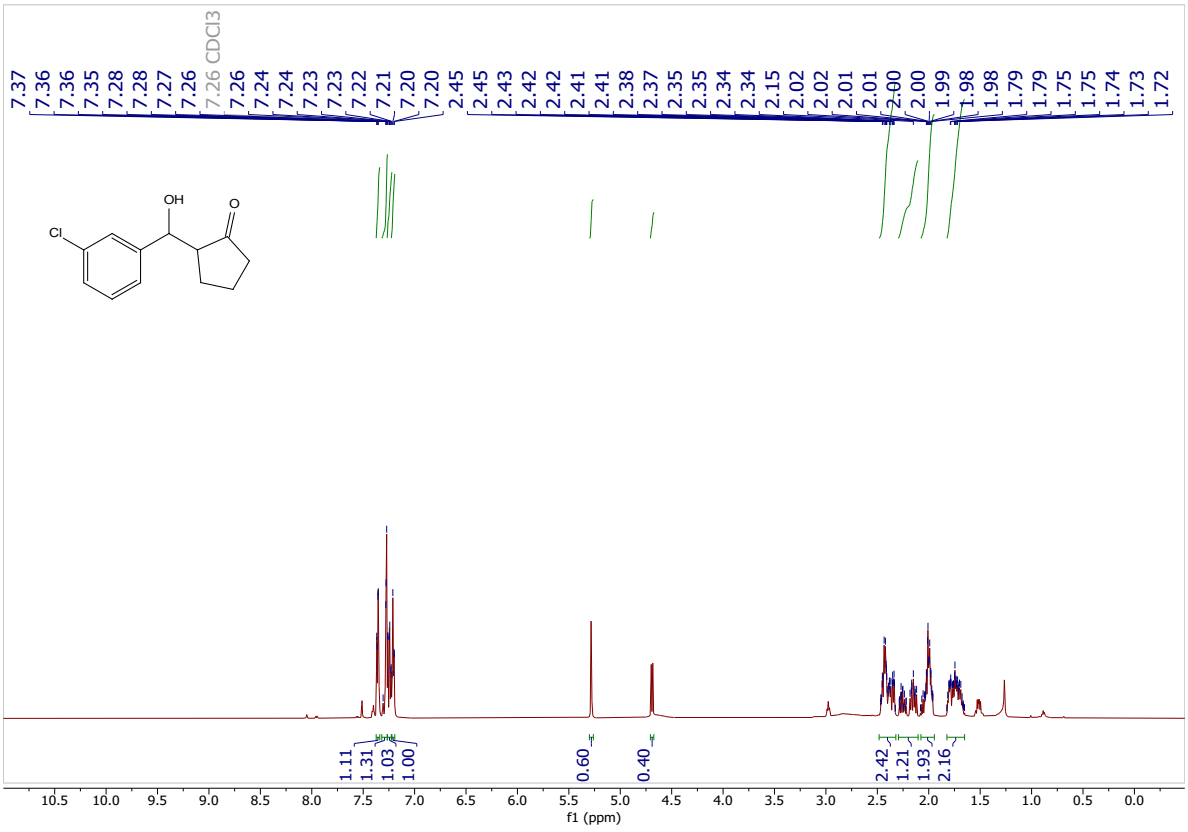

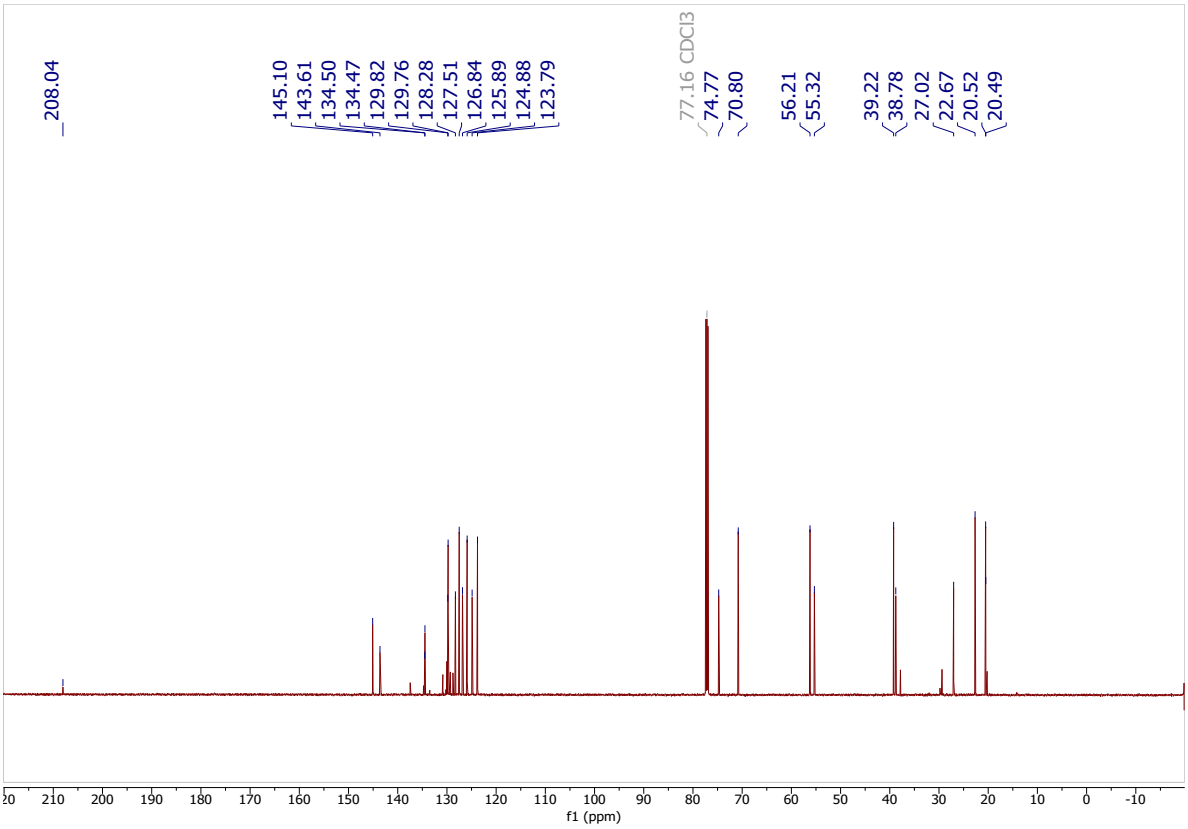

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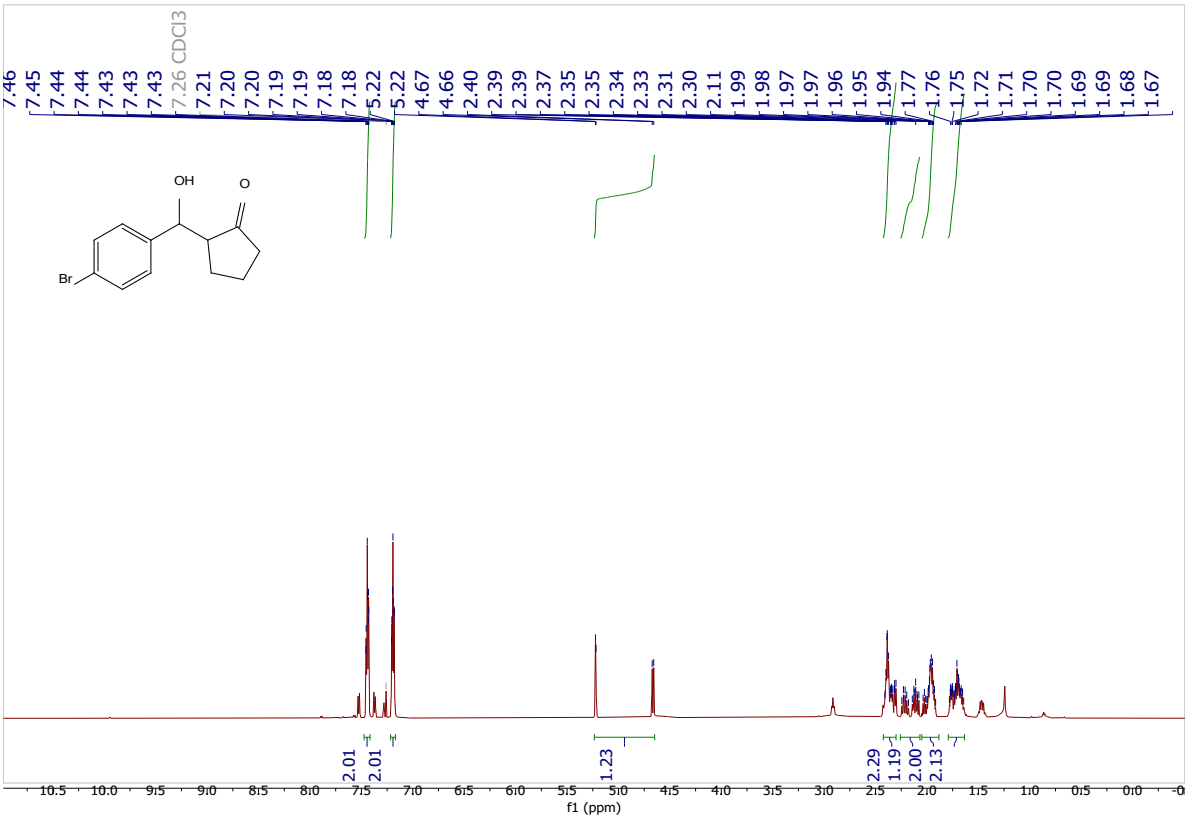
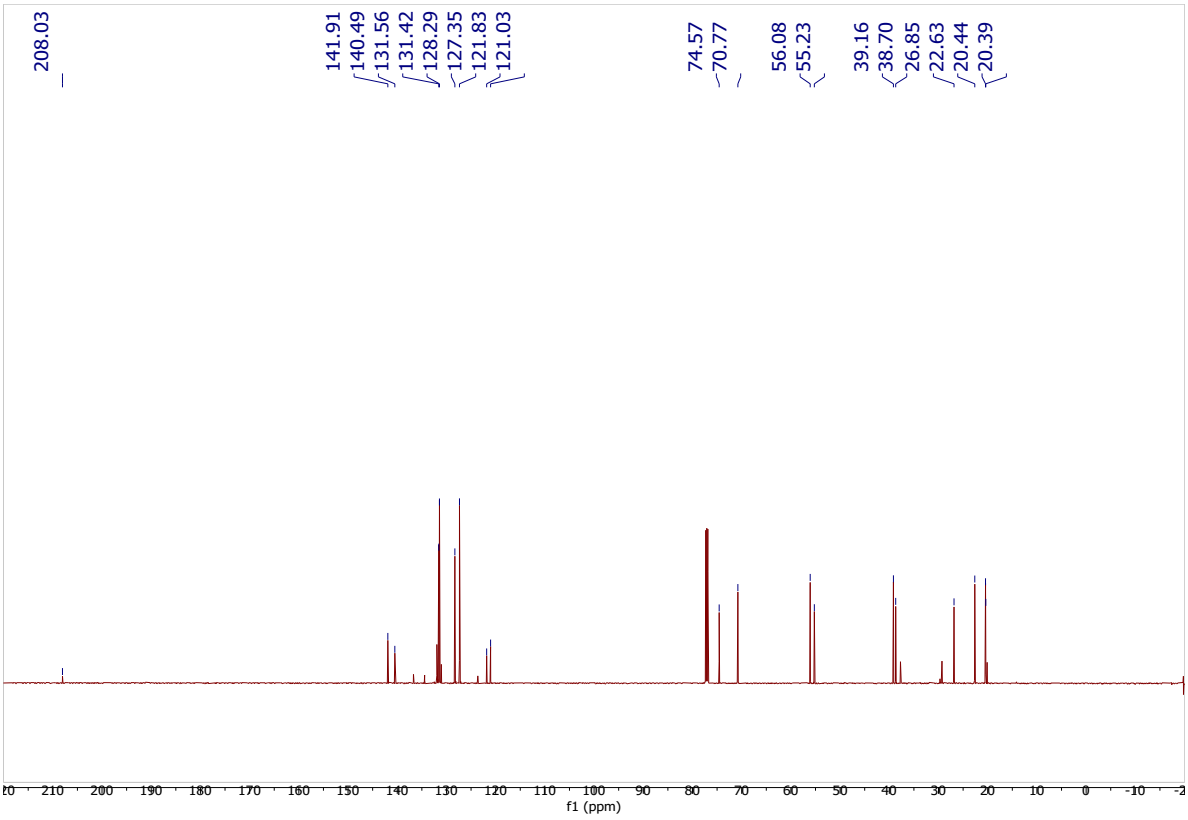
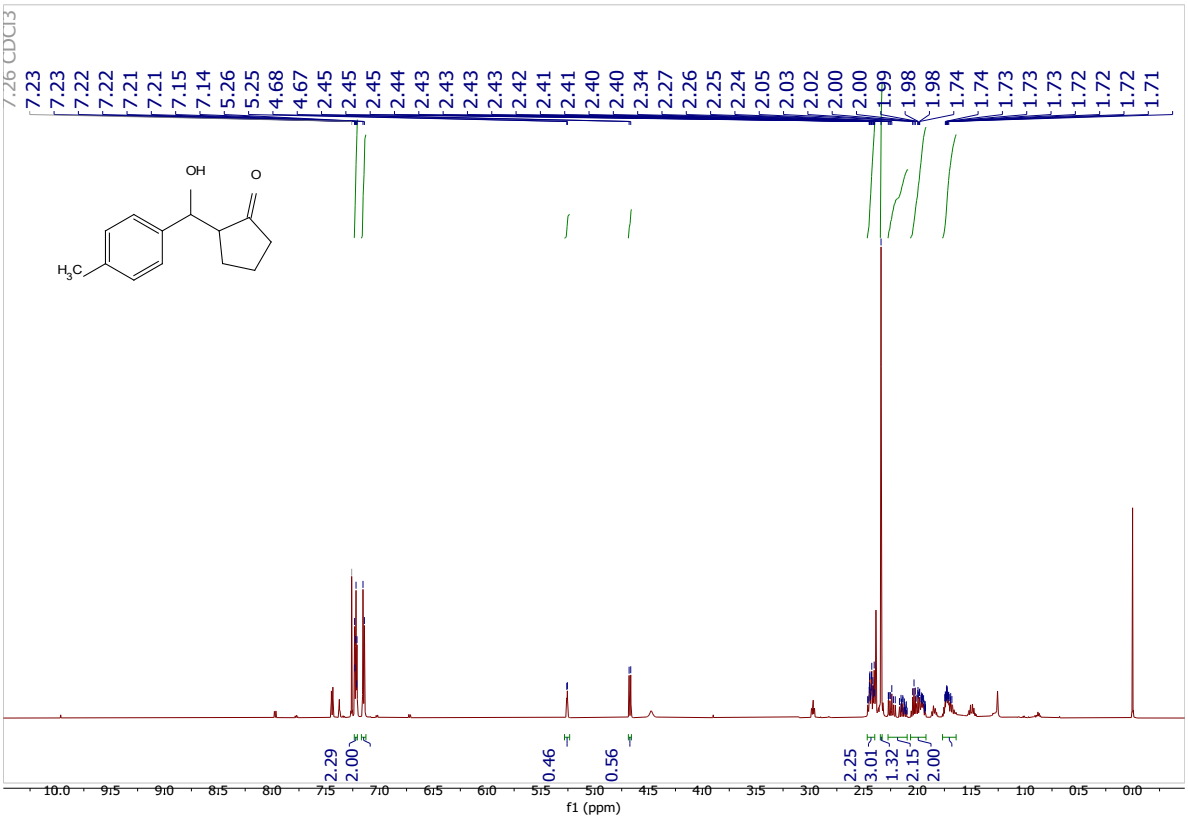
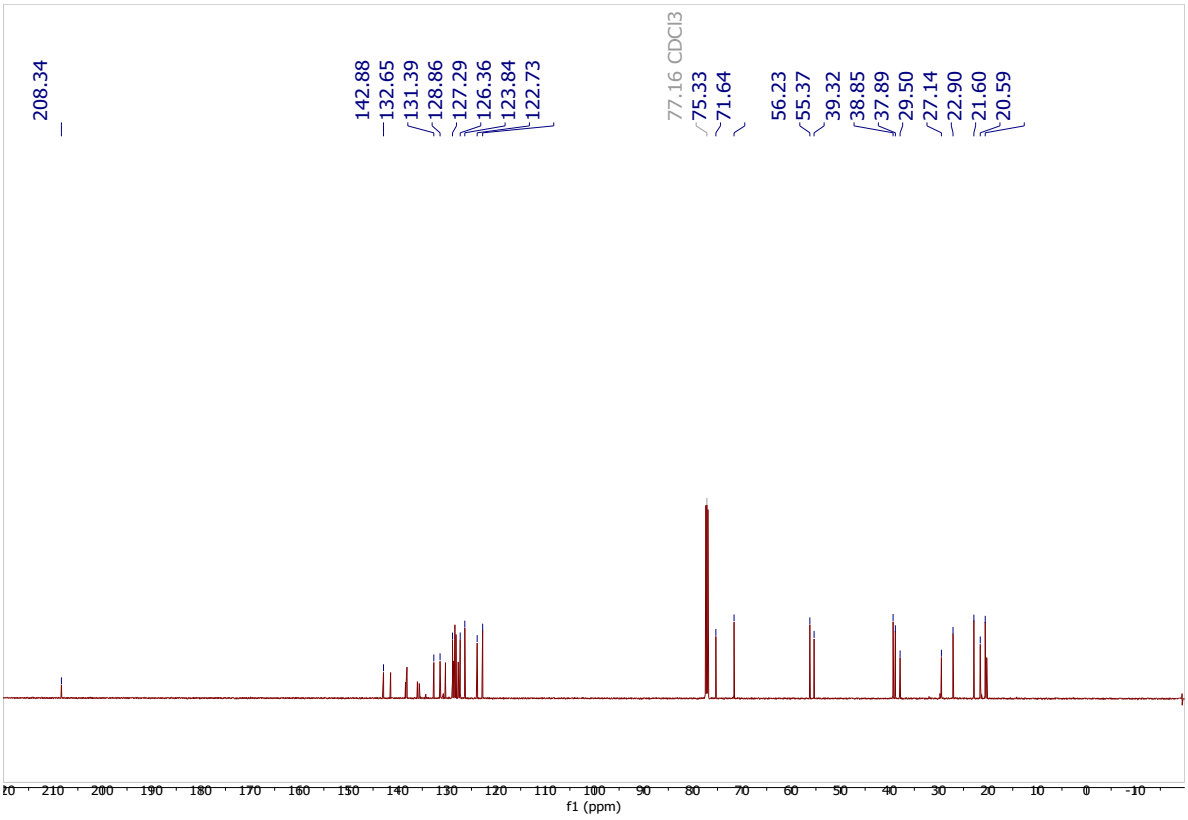


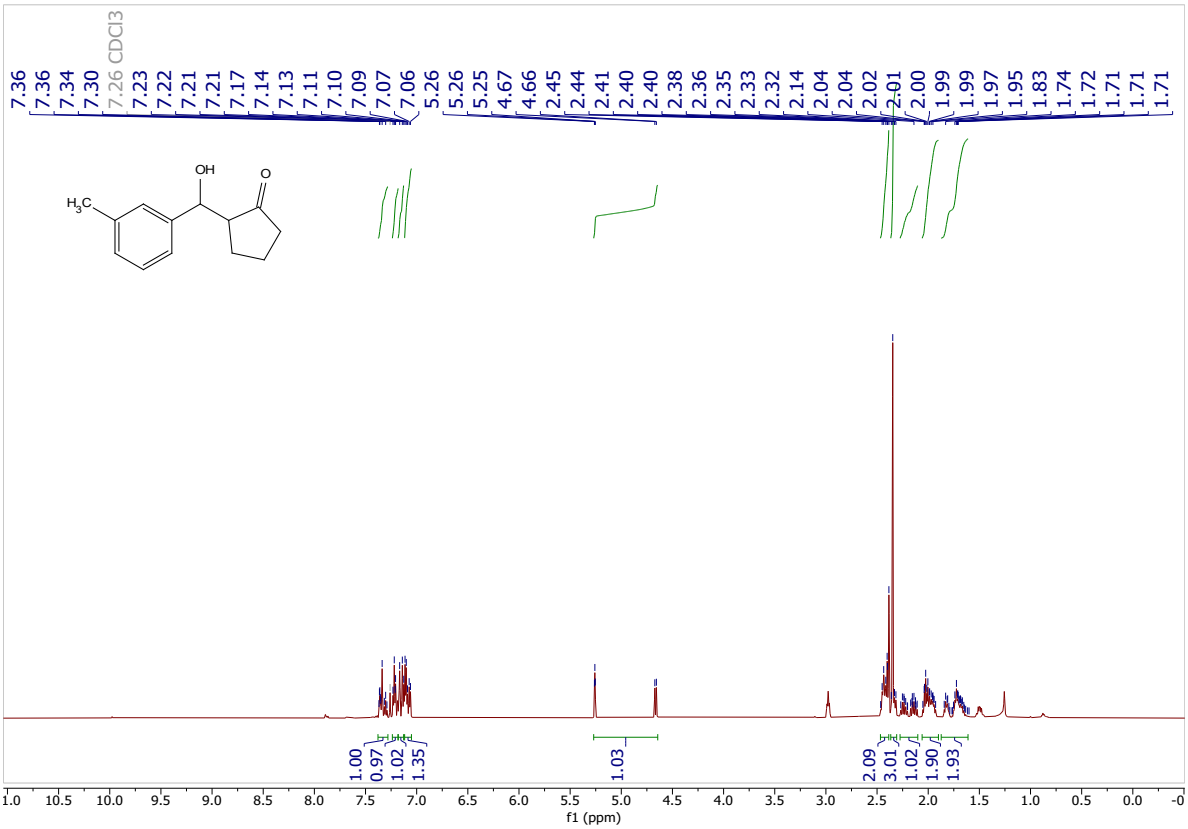


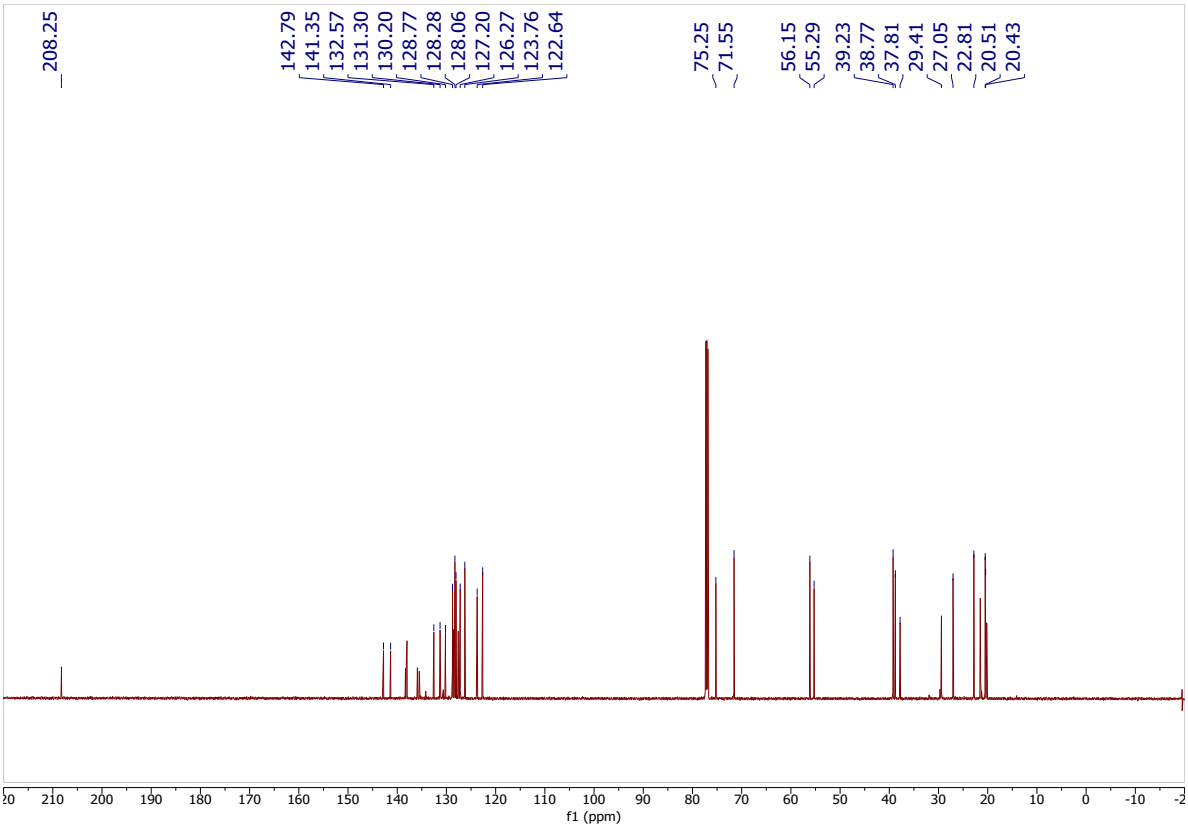
*2-(hydroxy(p-tolyl)methyl)cyclopentan-1-one (**3ag**)*



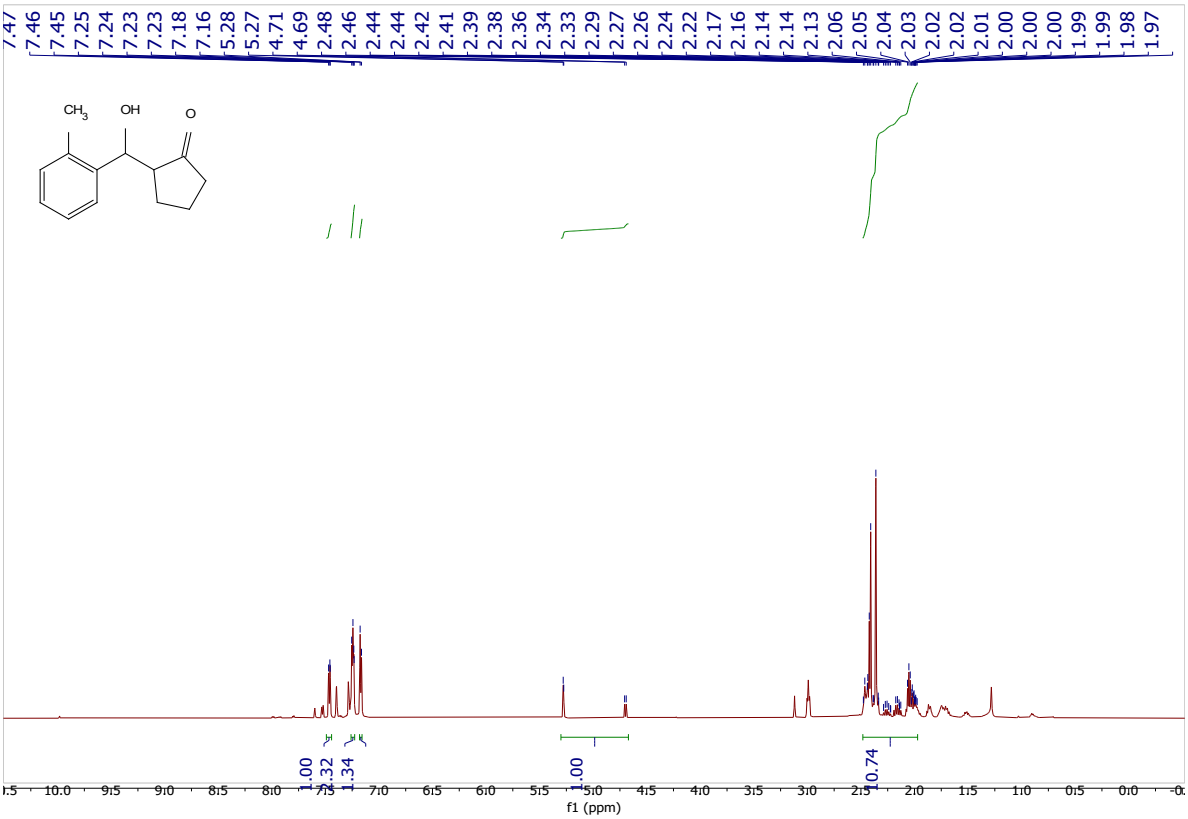


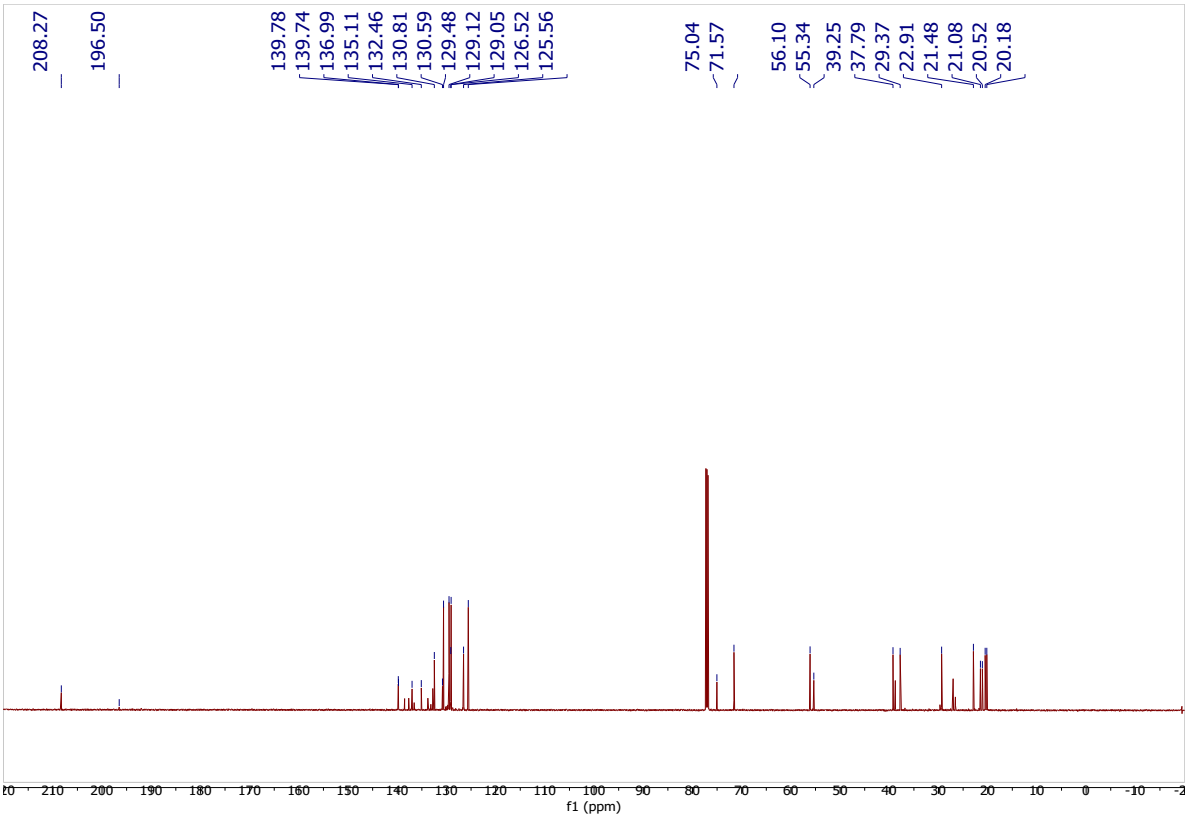
*2-(hydroxy(m-tolyl)methyl)cyclopentan-1-one (**3ah**)*



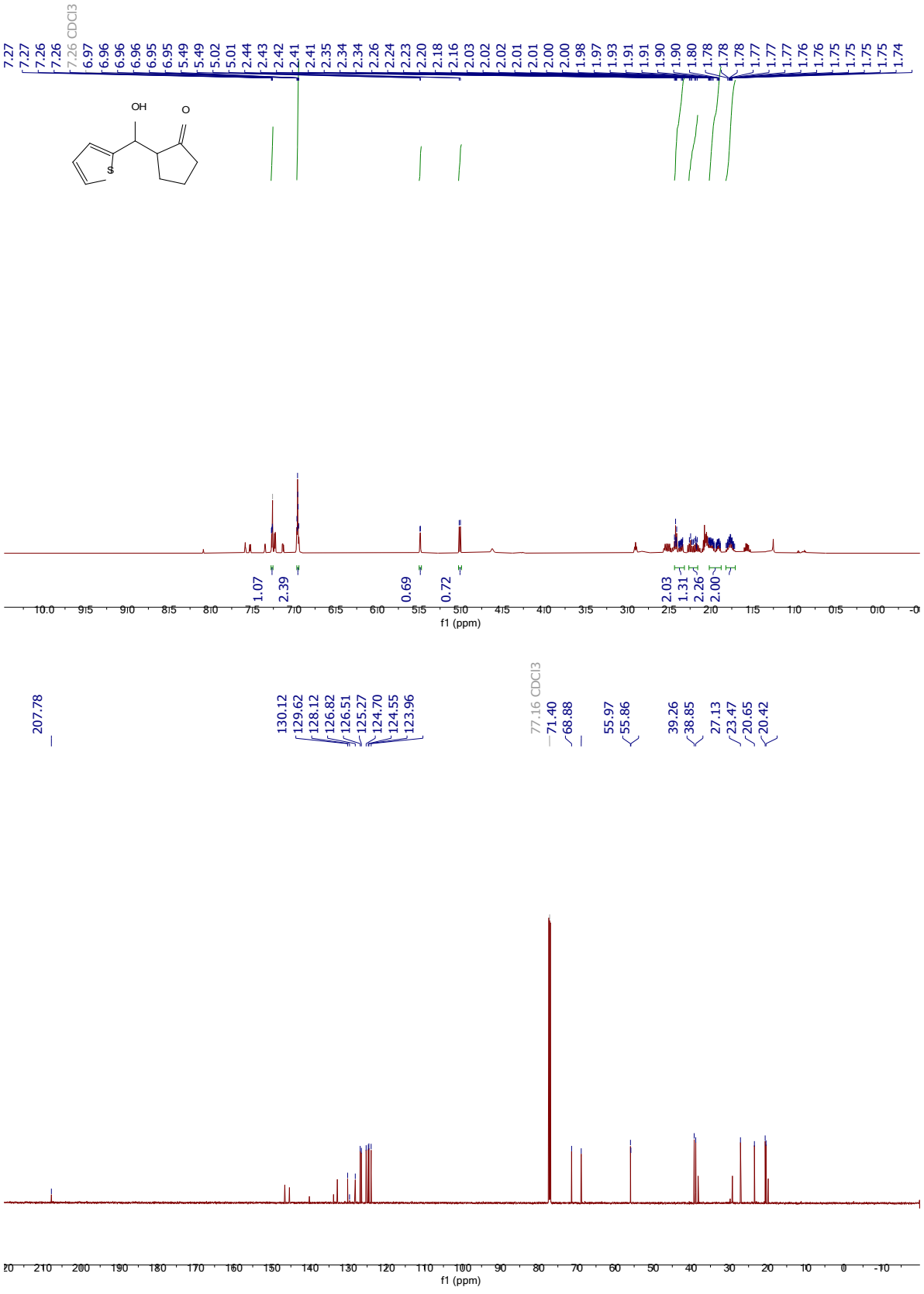


*2-(hydroxy(o-tolyl)methyl)cyclopentan-1-one (**3ai**)*

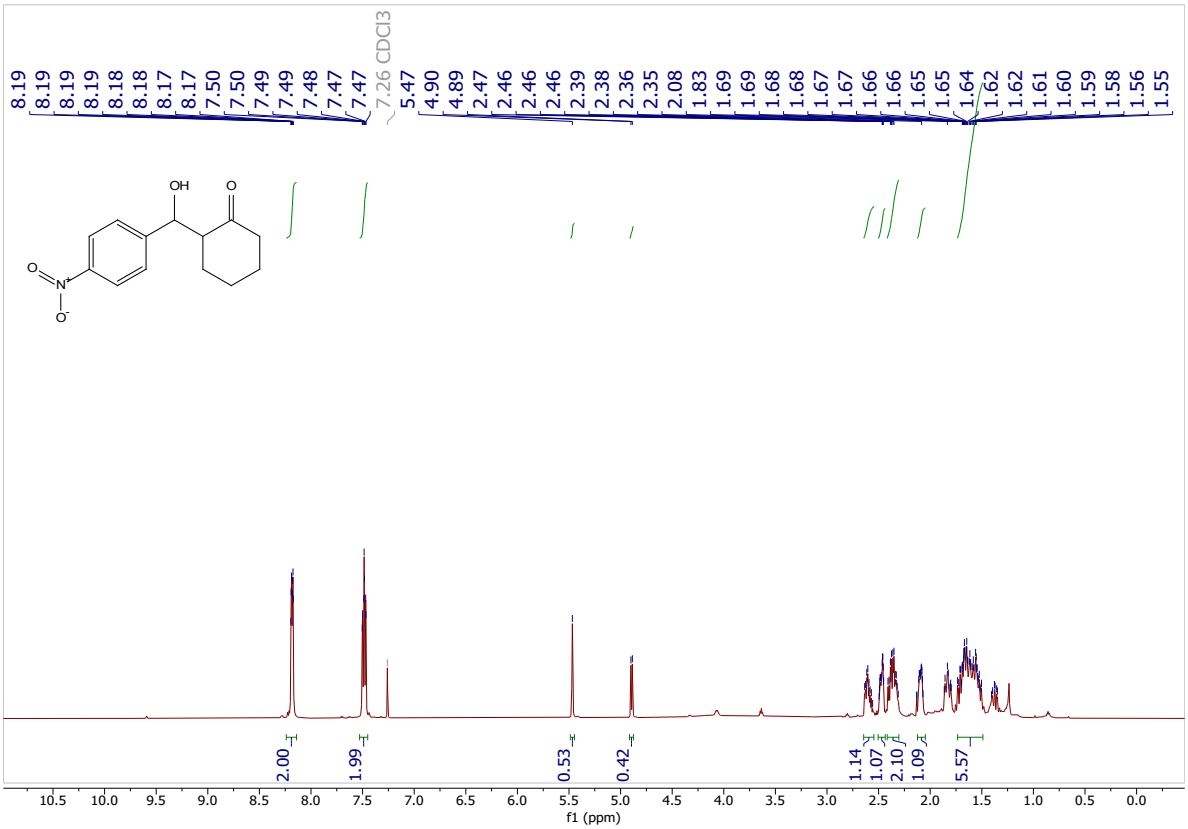


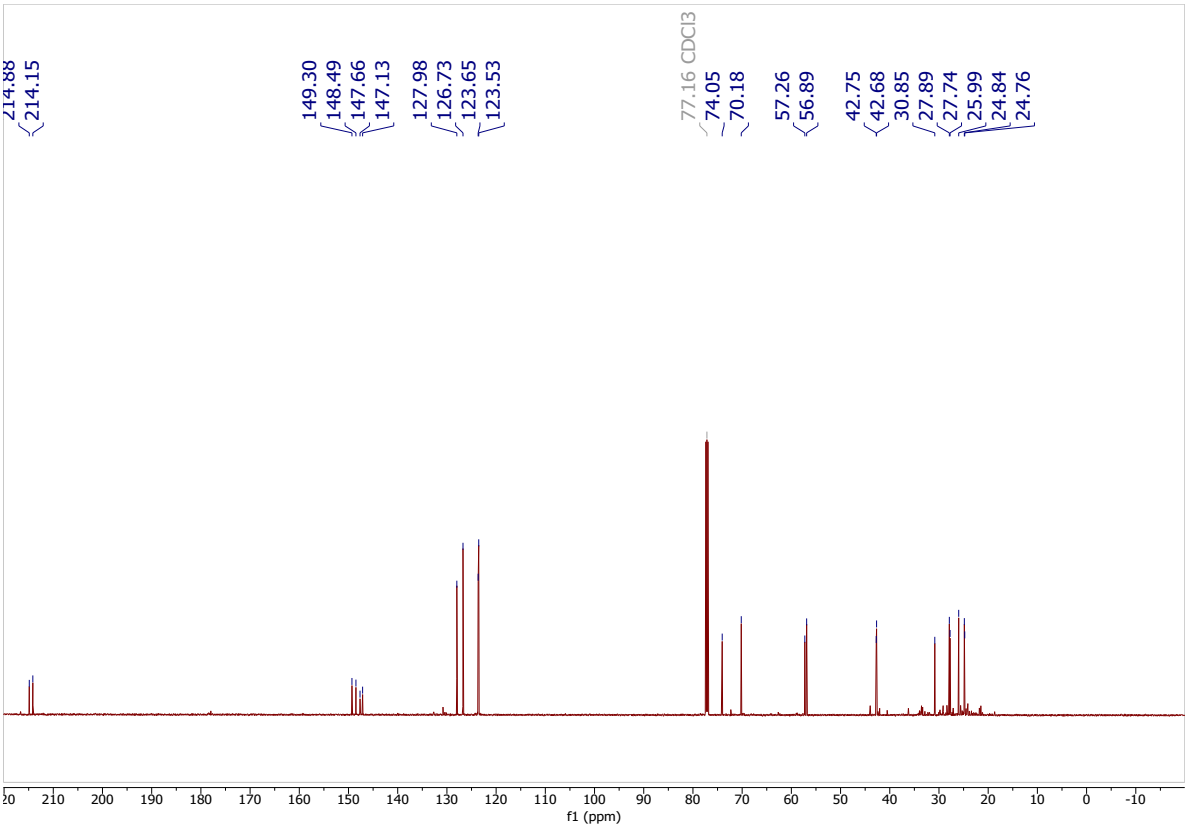


*2-(hydroxy(thiophen-2-yl)methyl)cyclopentan-1-one (**3am**)*

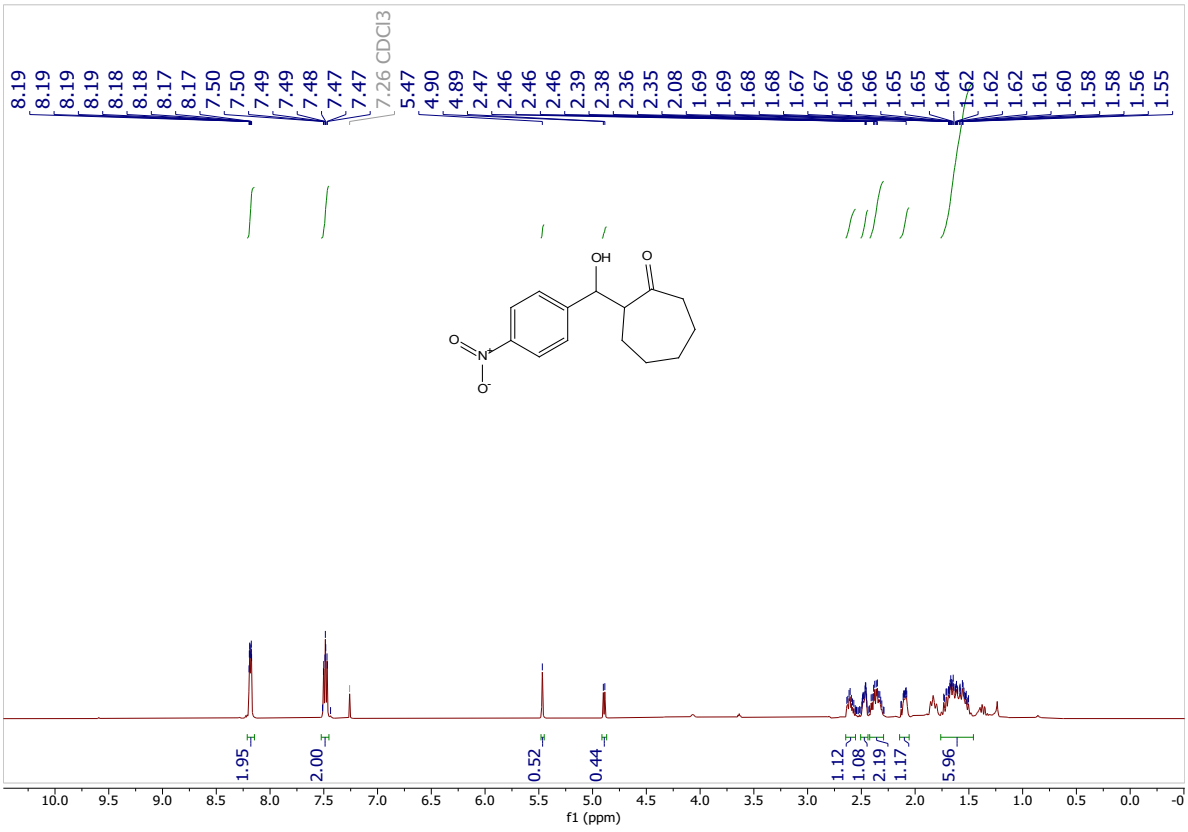


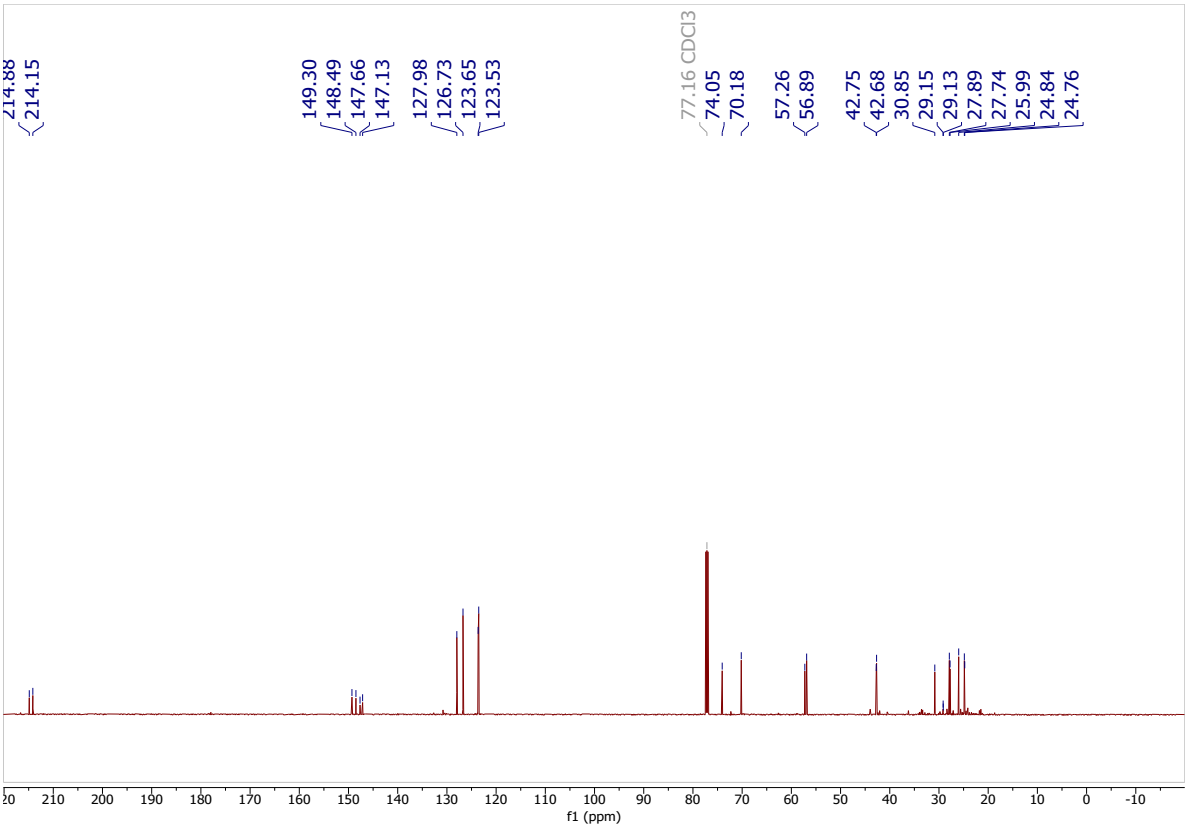
*2-(hydroxy(4-nitrophenyl)methyl)cyclohexan-1-one (**3ba**)*



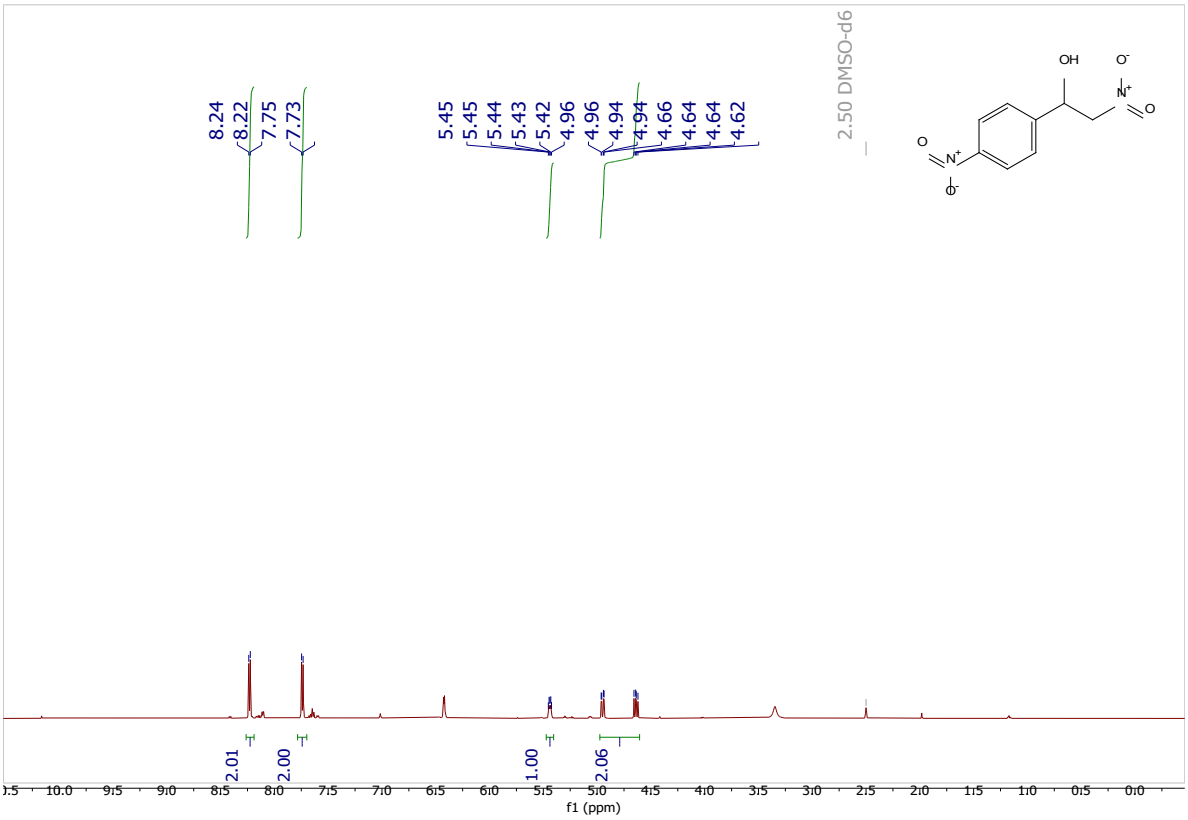


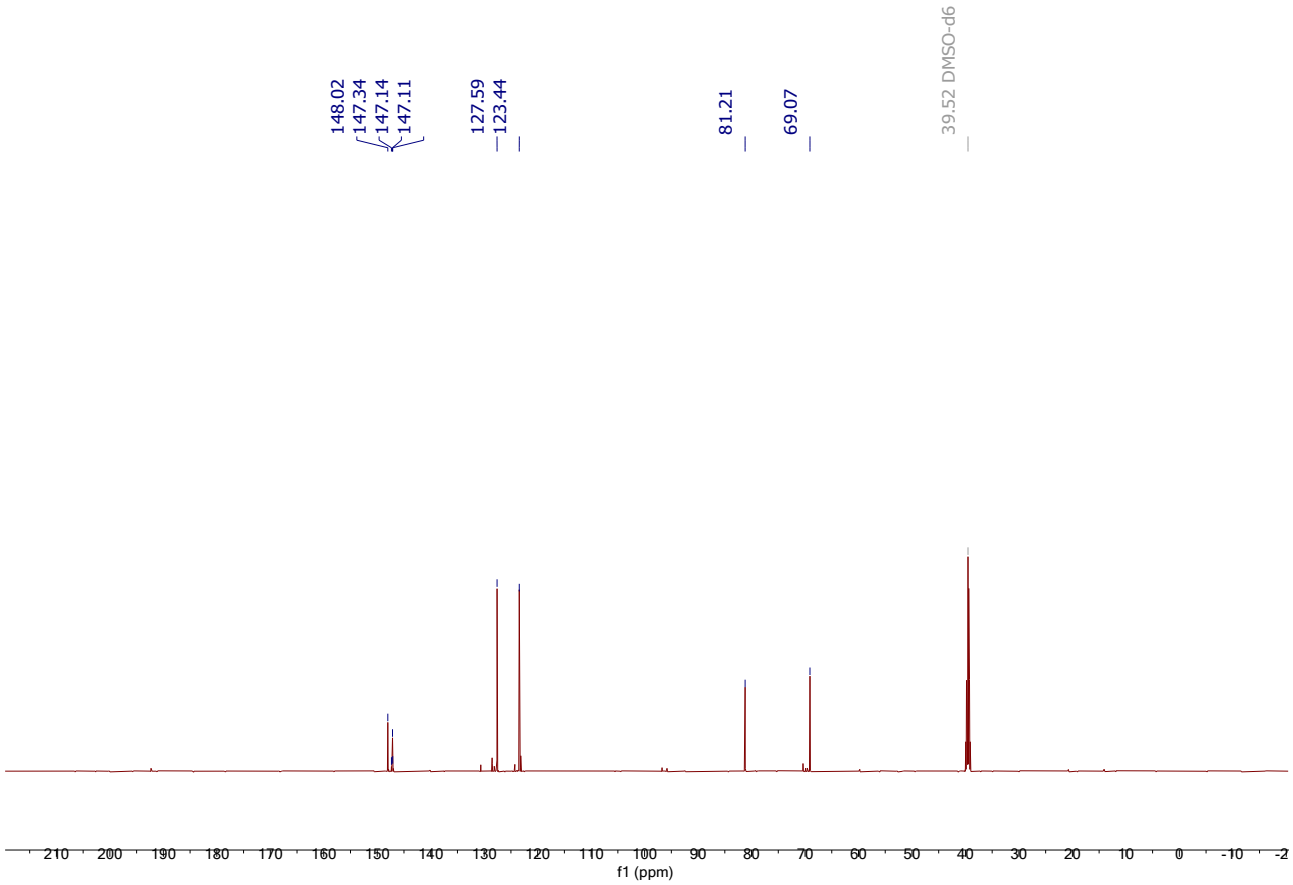
*2-(hydroxy(4-nitrophenyl)methyl)cycloheptan-1-one (**3ca**)*



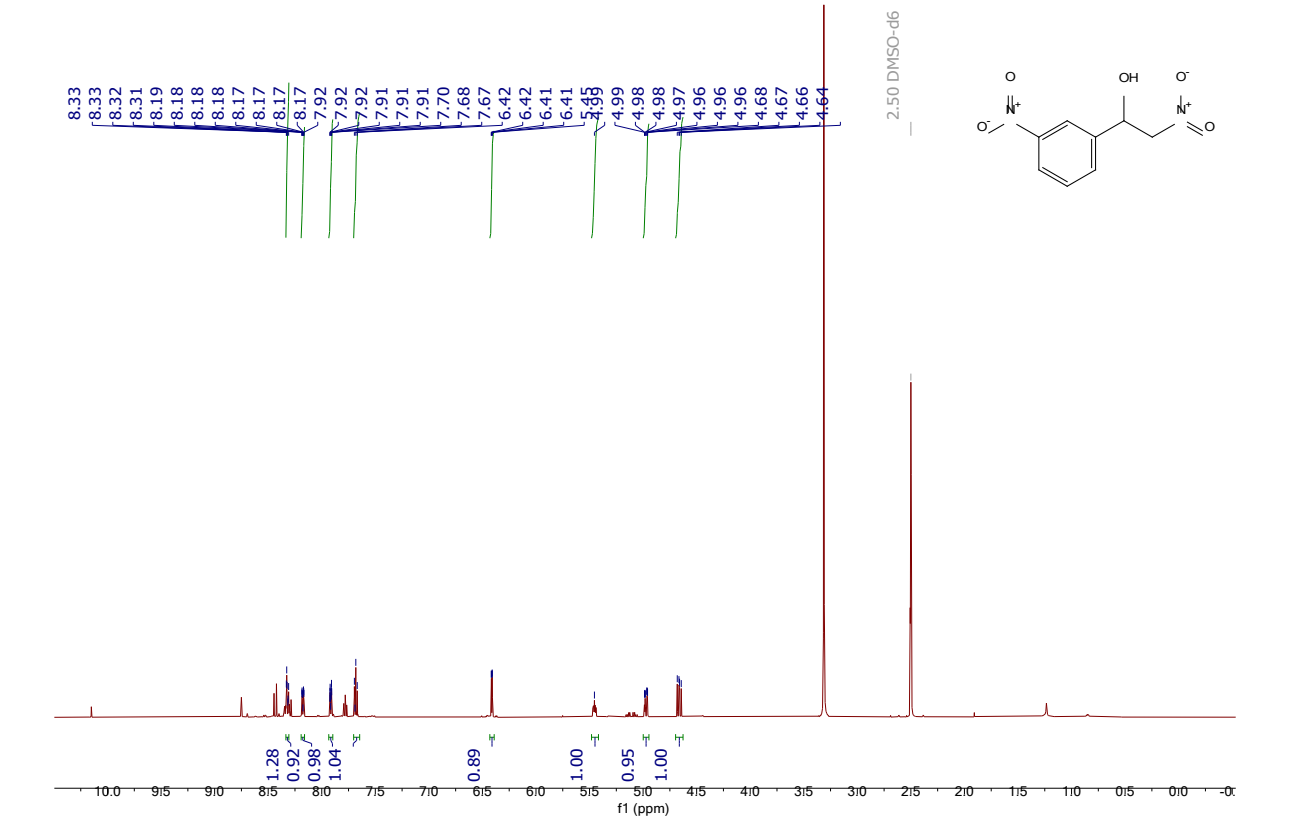


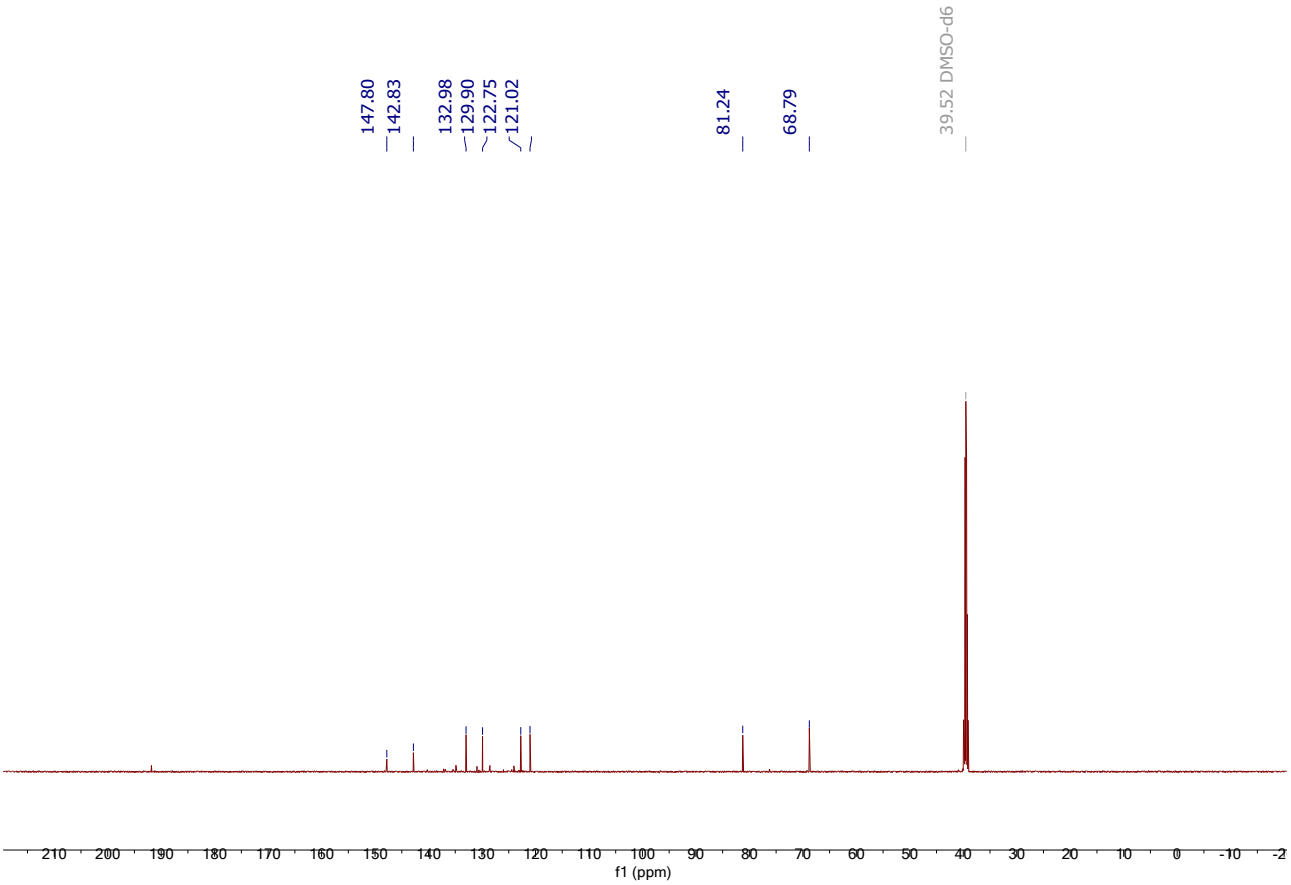
*2-nitro-1-(4-nitrophenyl)ethan-1-ol (**5a**)*



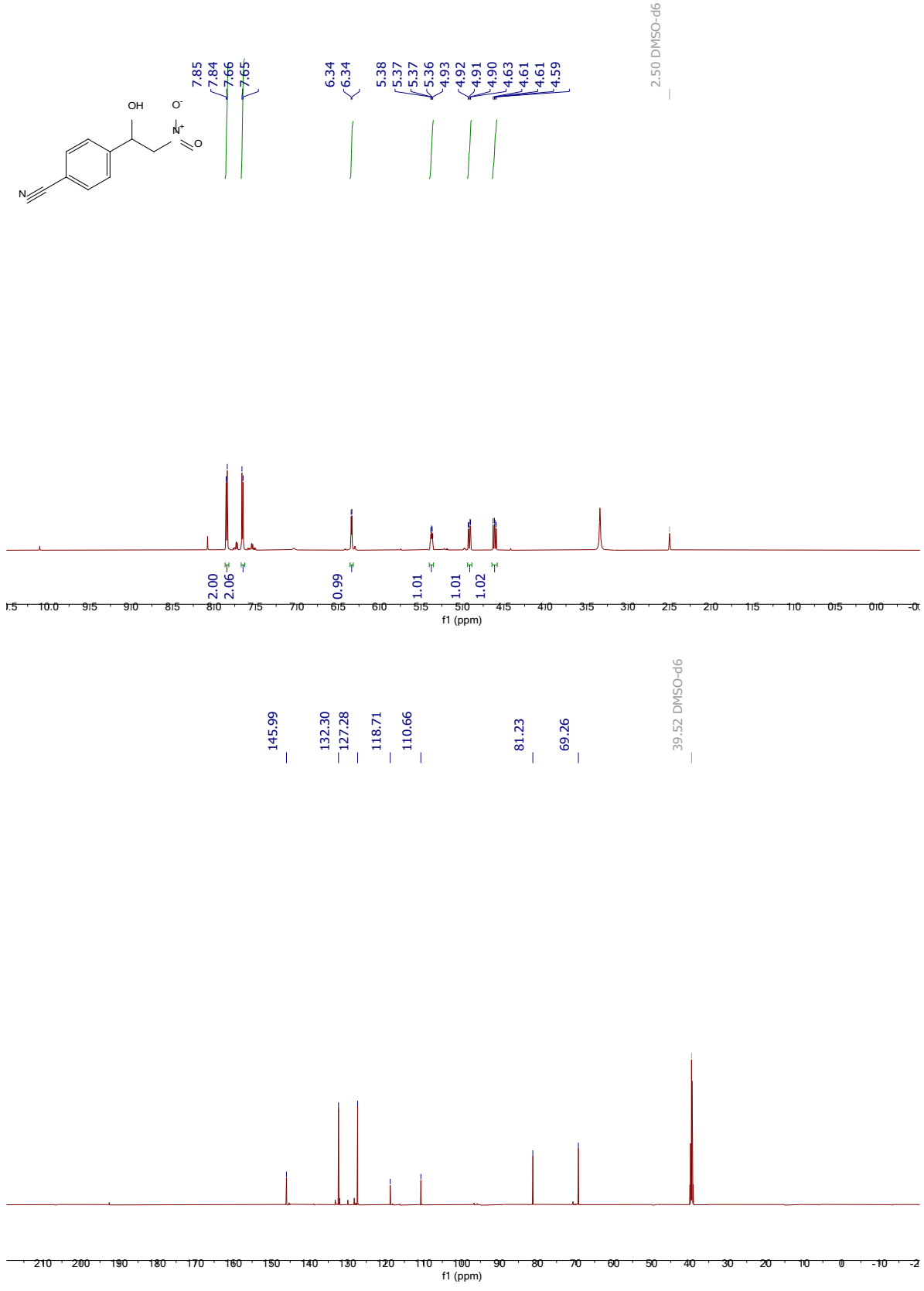


*2-nitro-1-(3-nitrophenyl)ethan-1-ol (**5b**)*

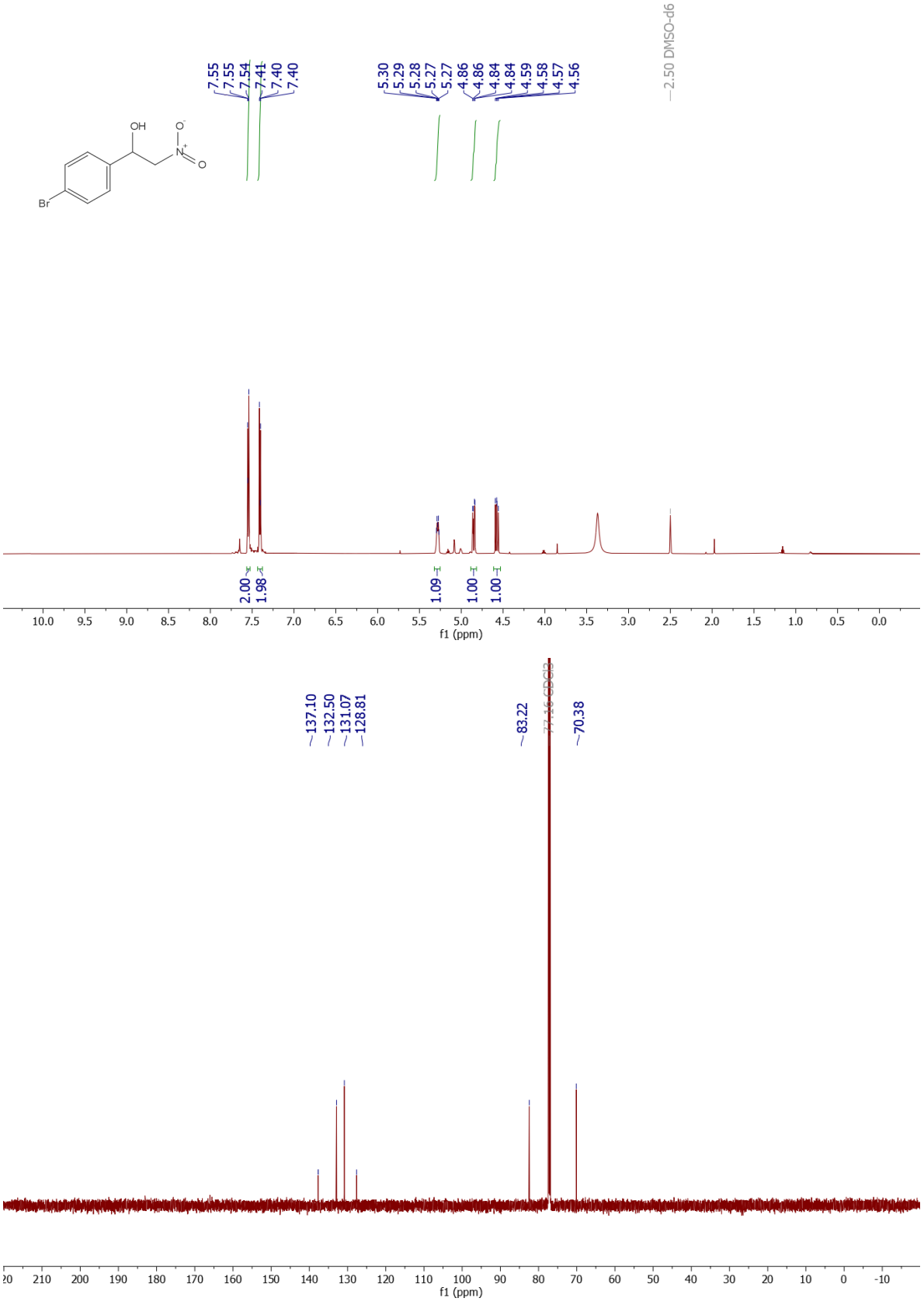




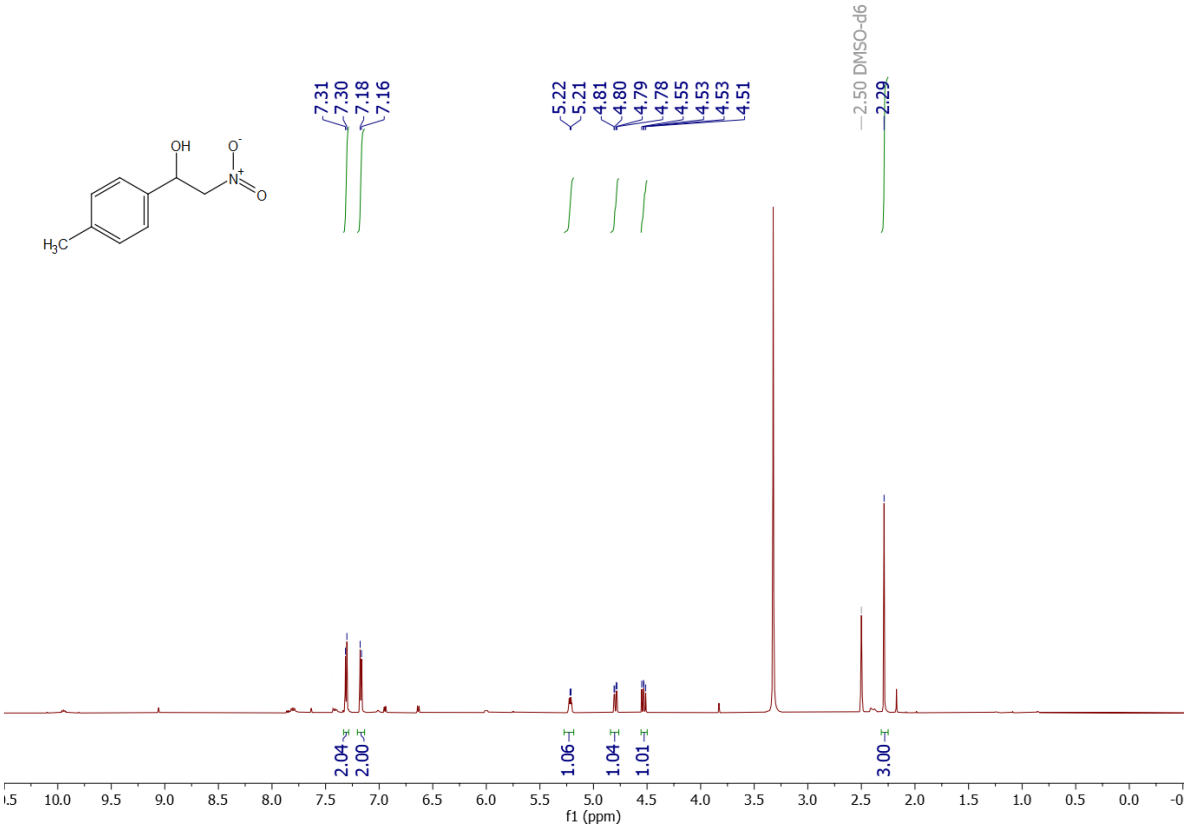
*4-(1-hydroxy-2-nitroethyl)benzonitrile (**5c**)*

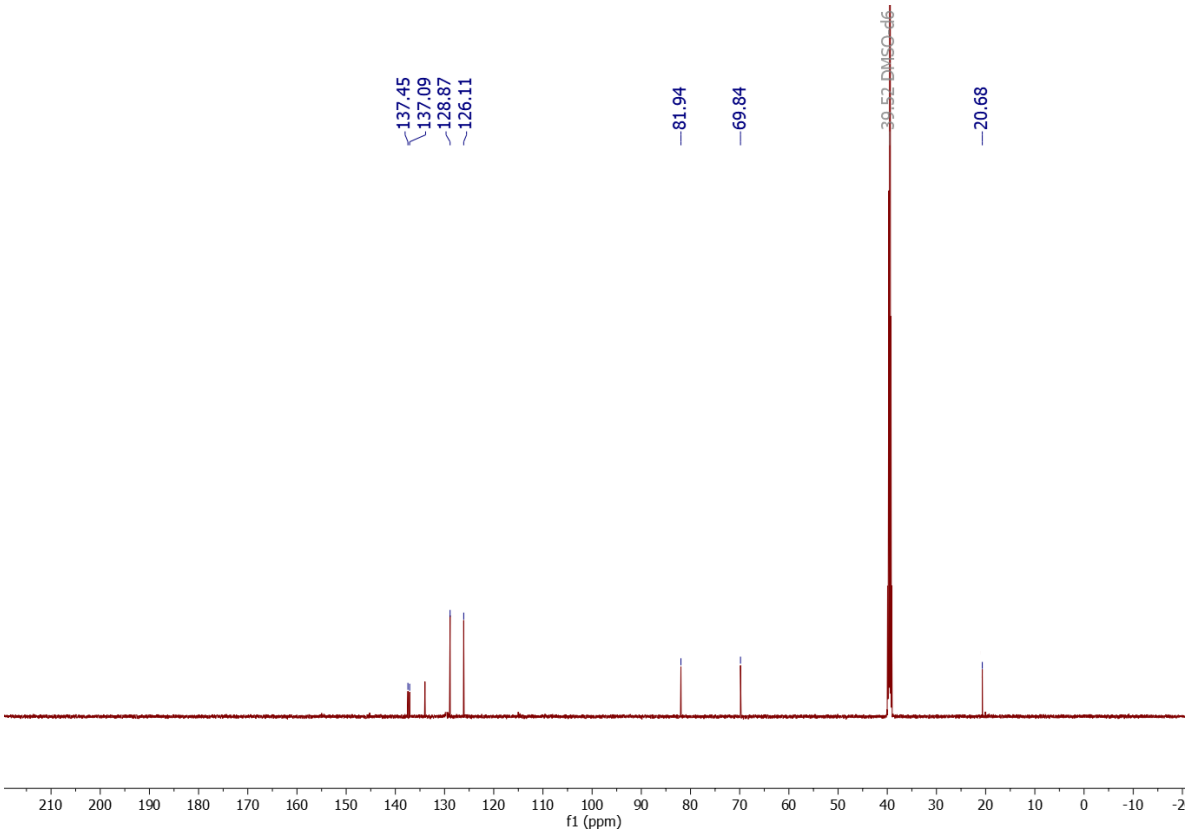


*1-(4-bromophenyl)-2-nitroethan-1-ol (**5f**)*

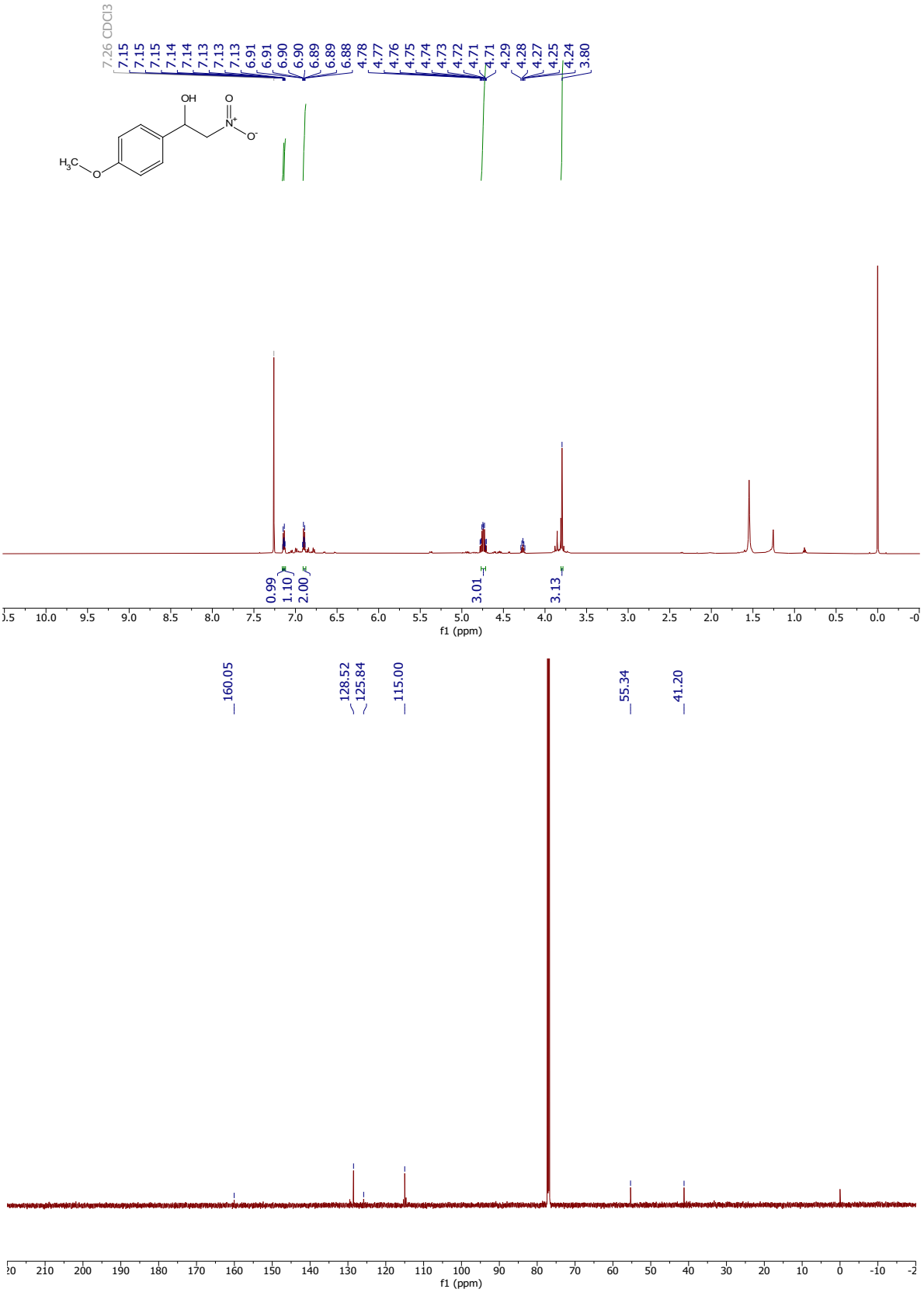


*2-nitro-1-(p-tolyl)ethan-1-ol (**5g**)*

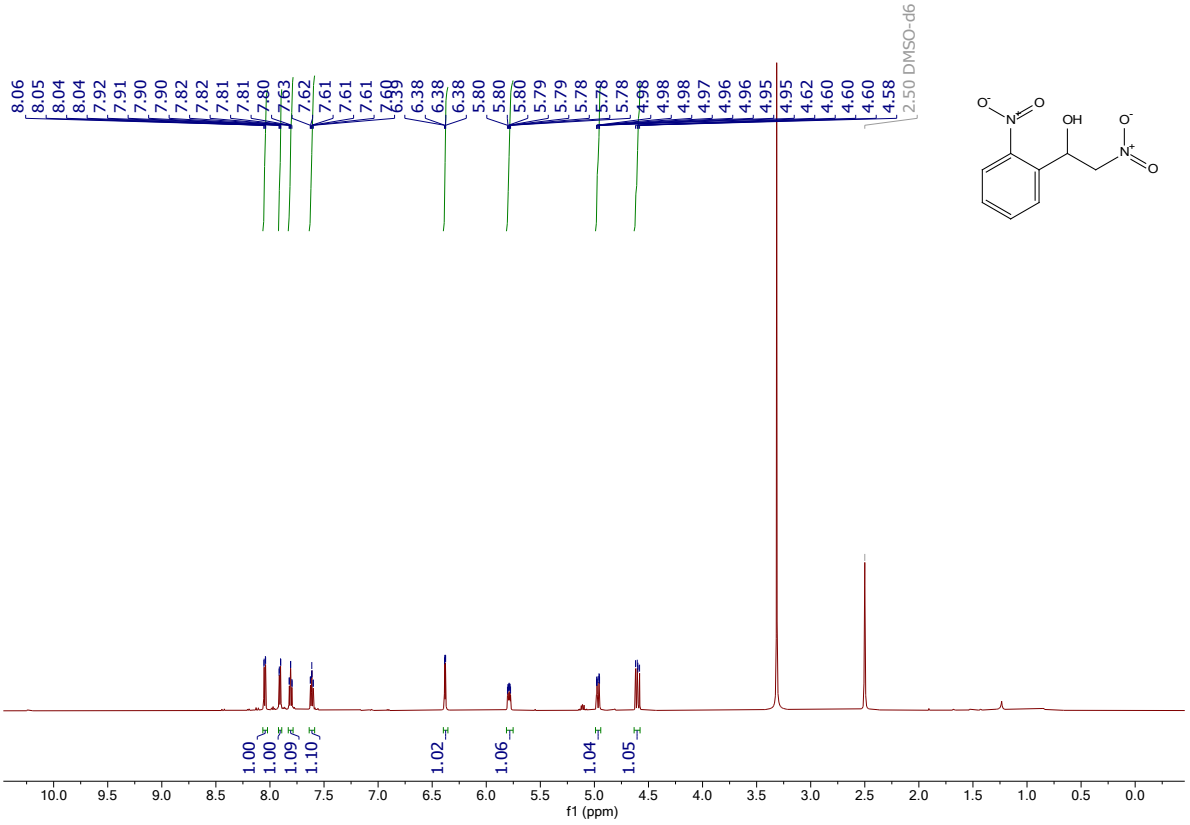


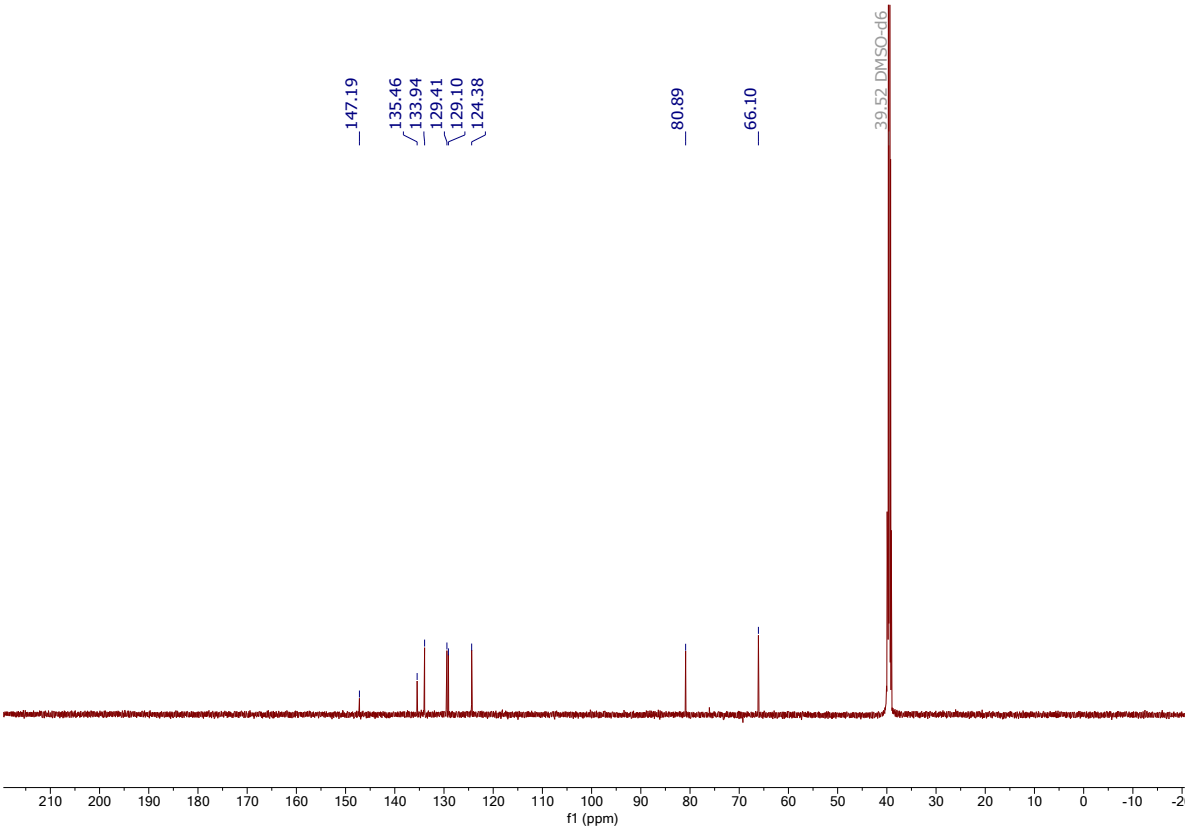


*1-(4-methoxyphenyl)-2-nitroethan-1-ol (**5j**)*

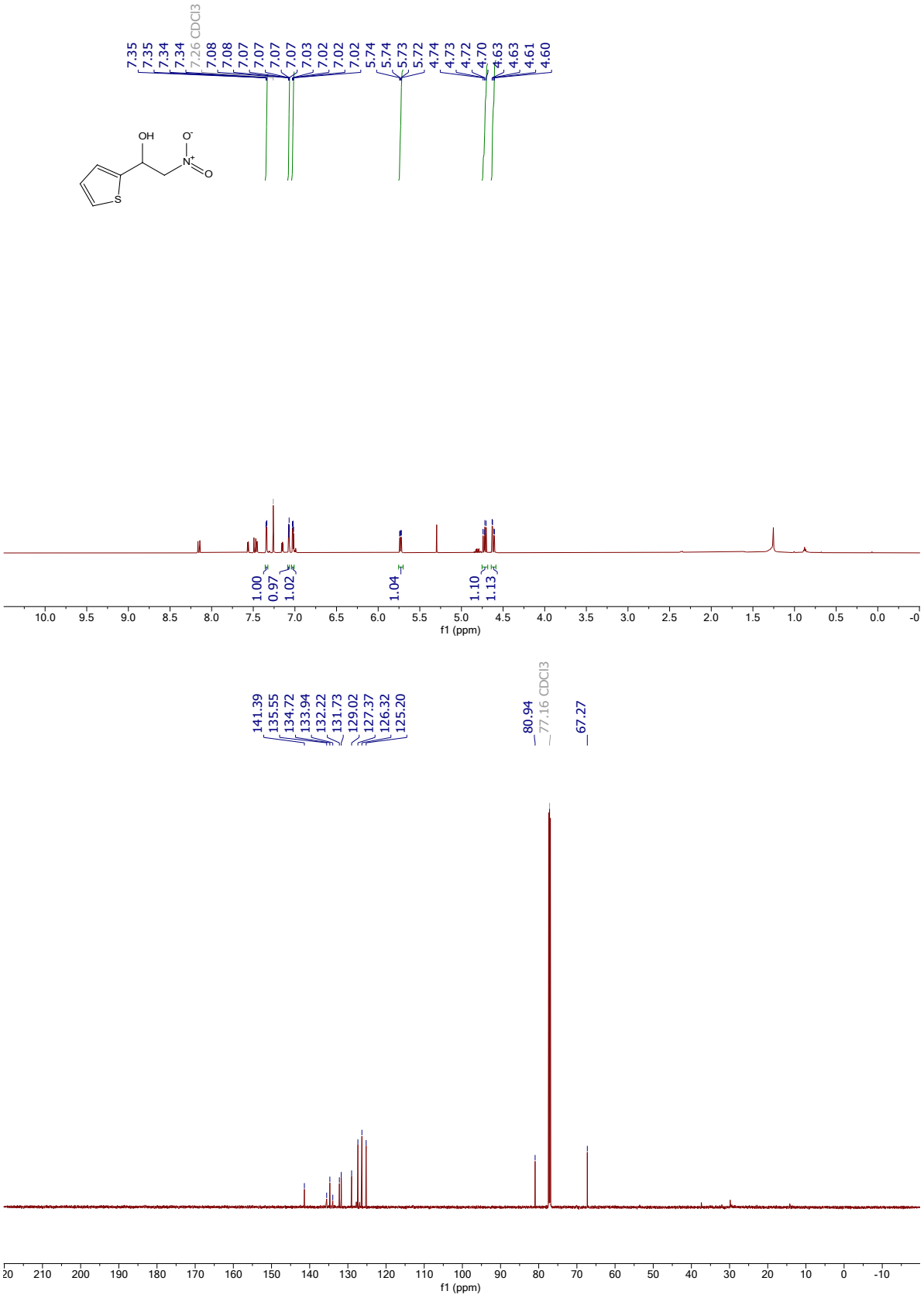


*1-(2-nitrophenyl)-2-nitroethan-1-ol (**5l**)*

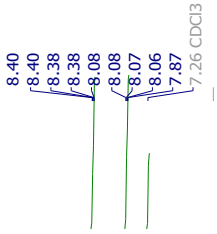


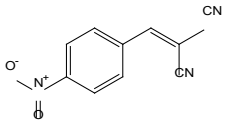


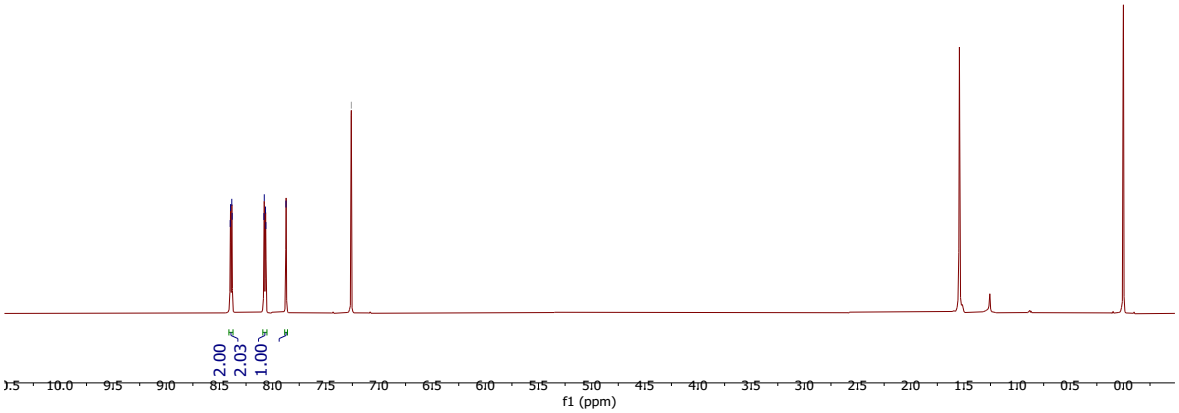
*2-nitro-1-(thiophen-2-yl)ethan-1-ol (**5m**)*

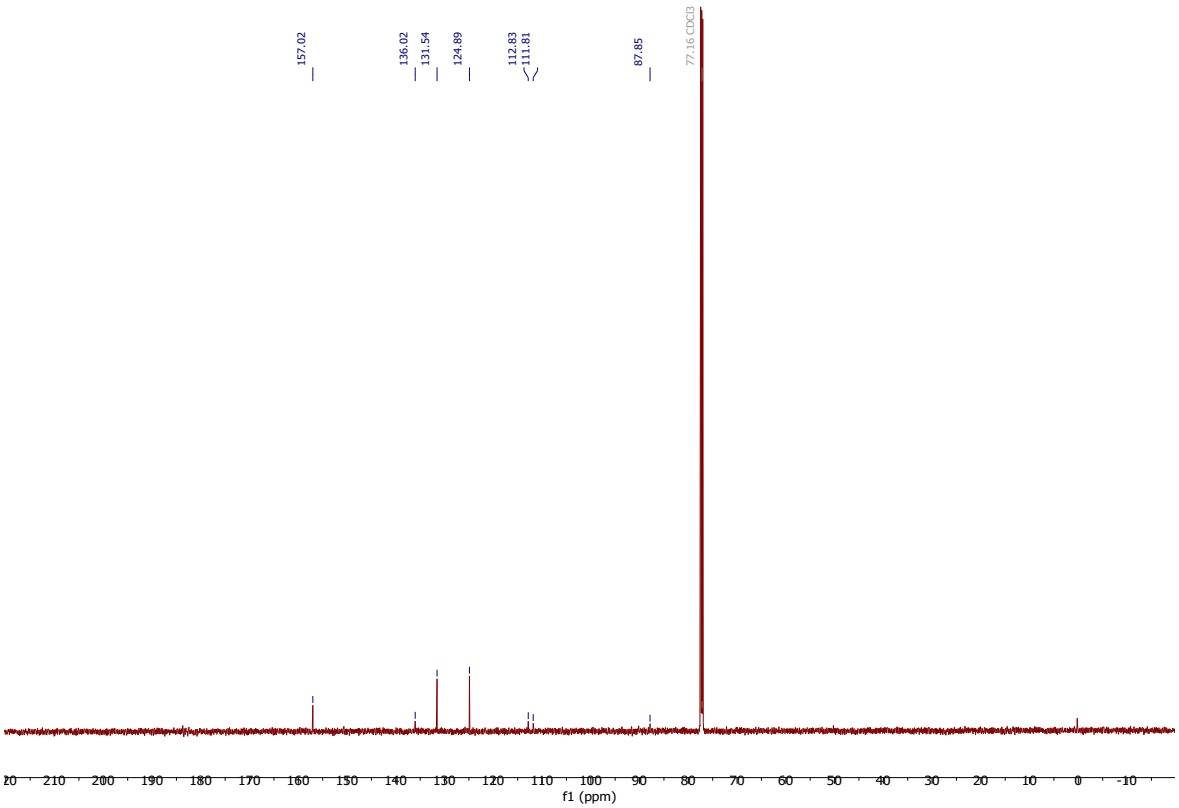


*2-(4-nitrobenzylidene)malononitrile (**8a**)*

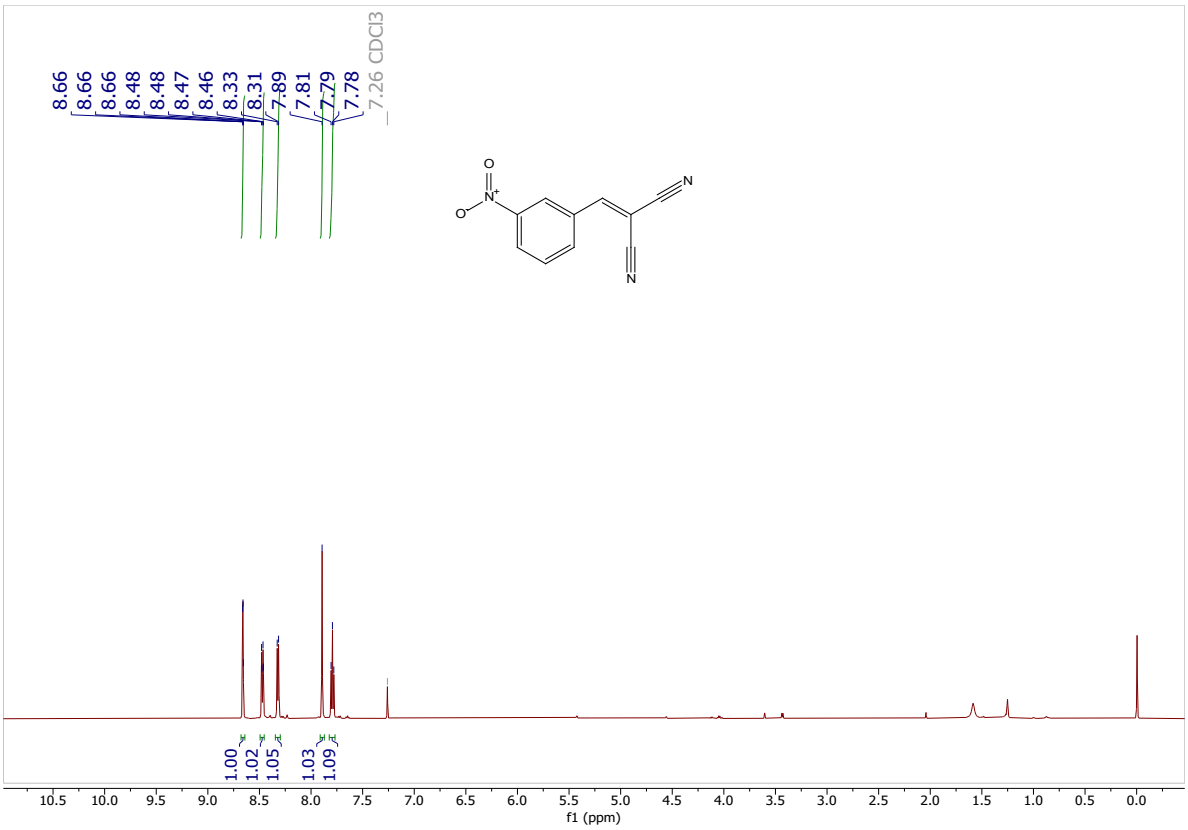


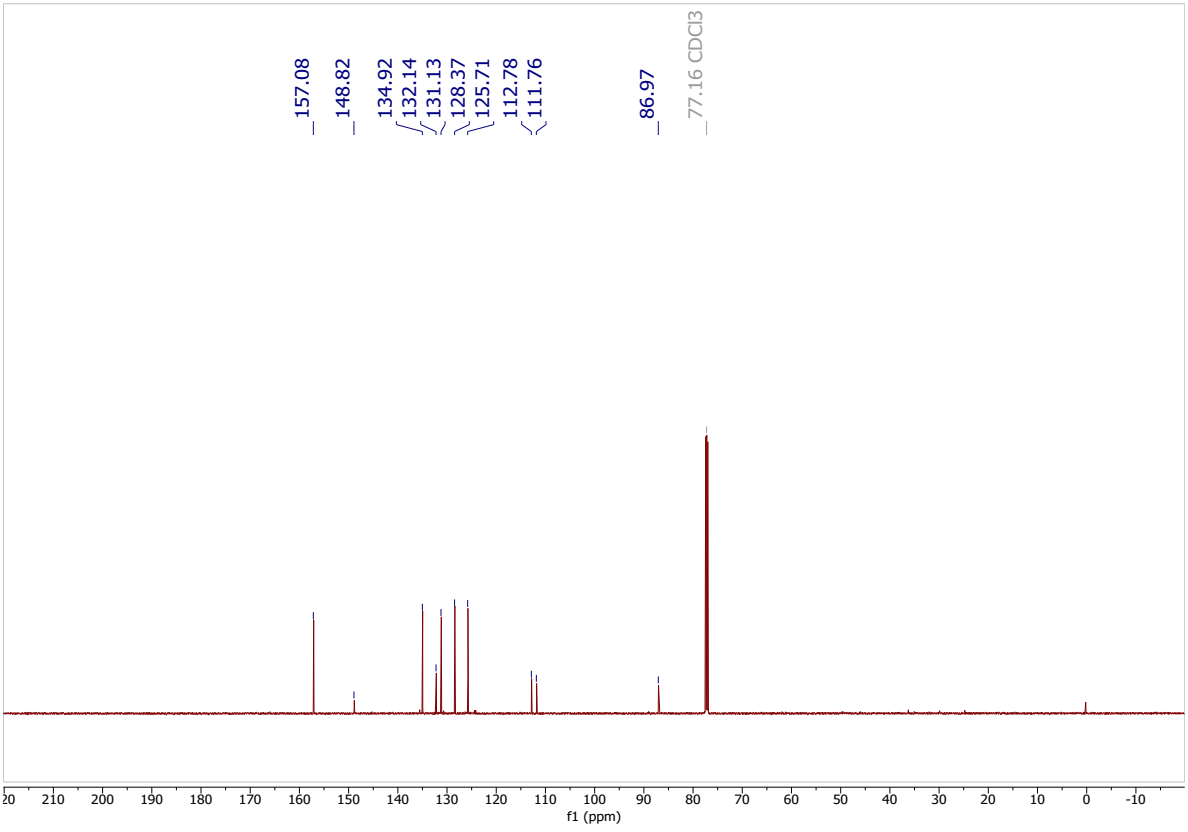




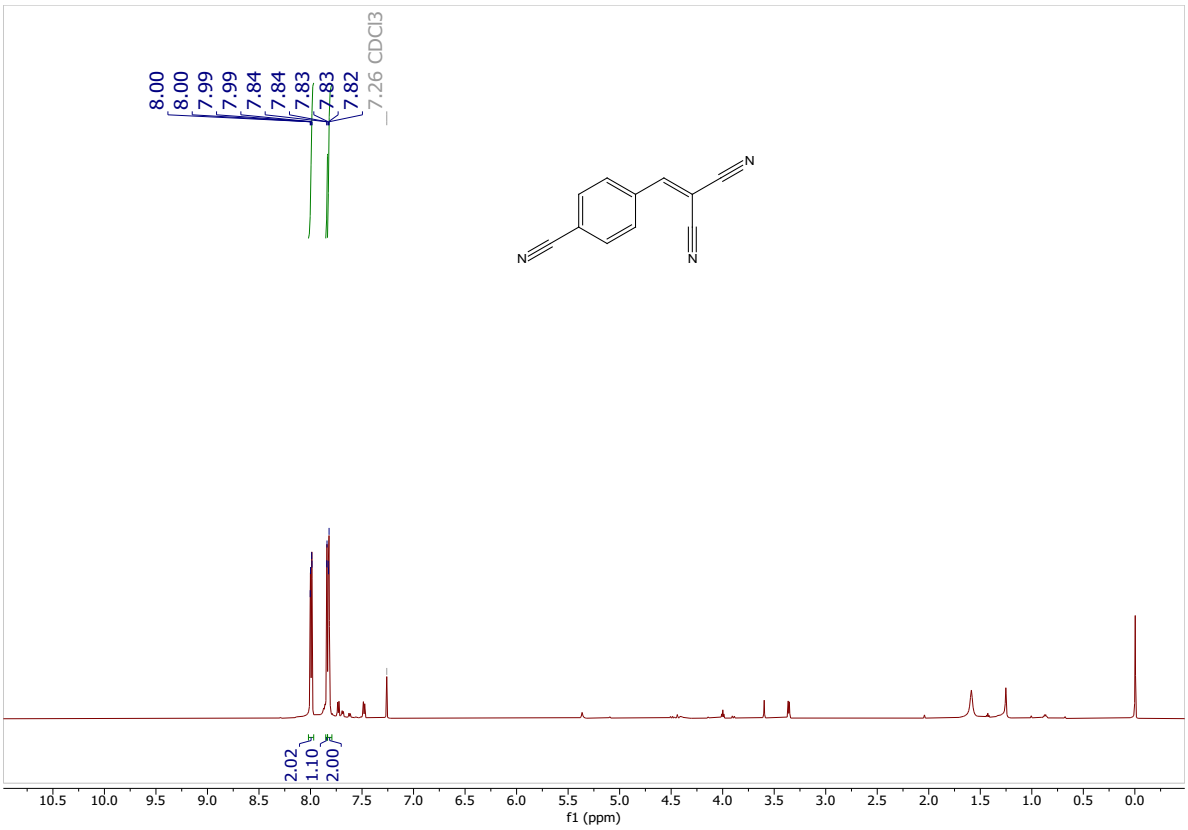


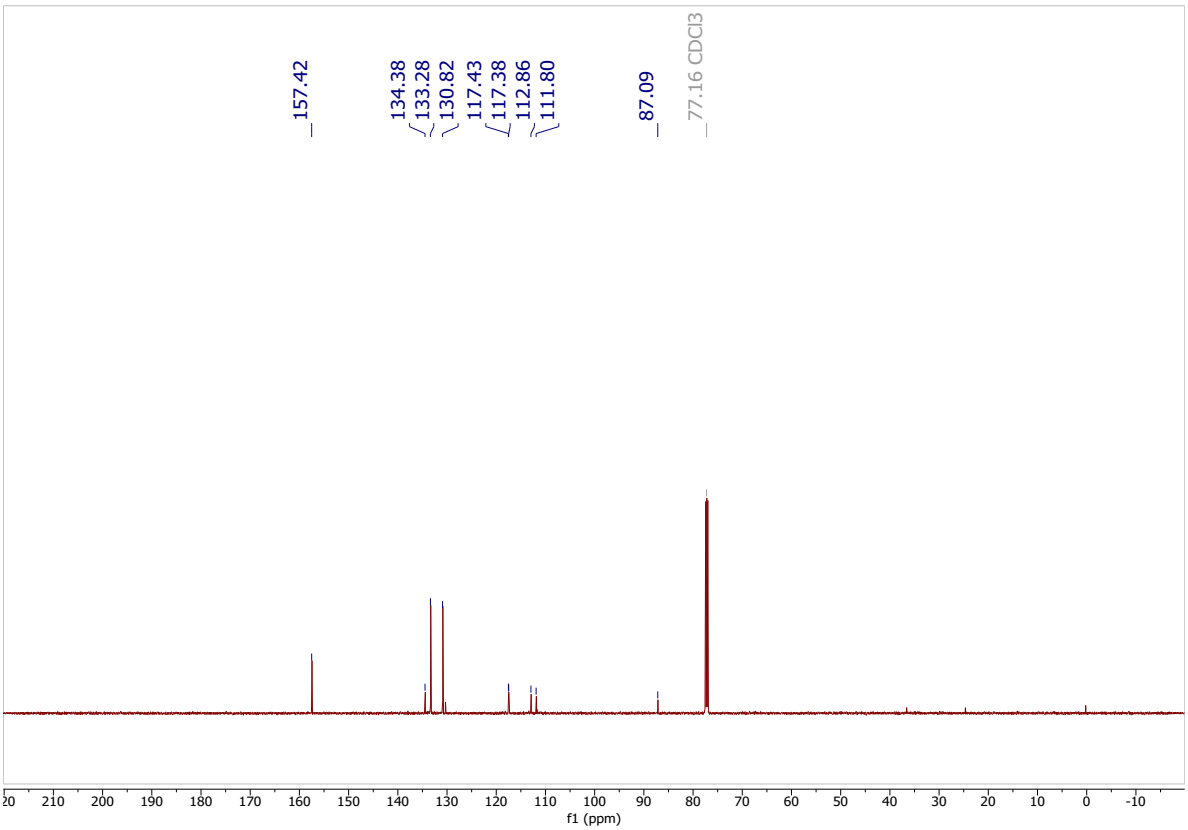
*2-(3-nitrobenzylidene)malononitrile (**8b**)*



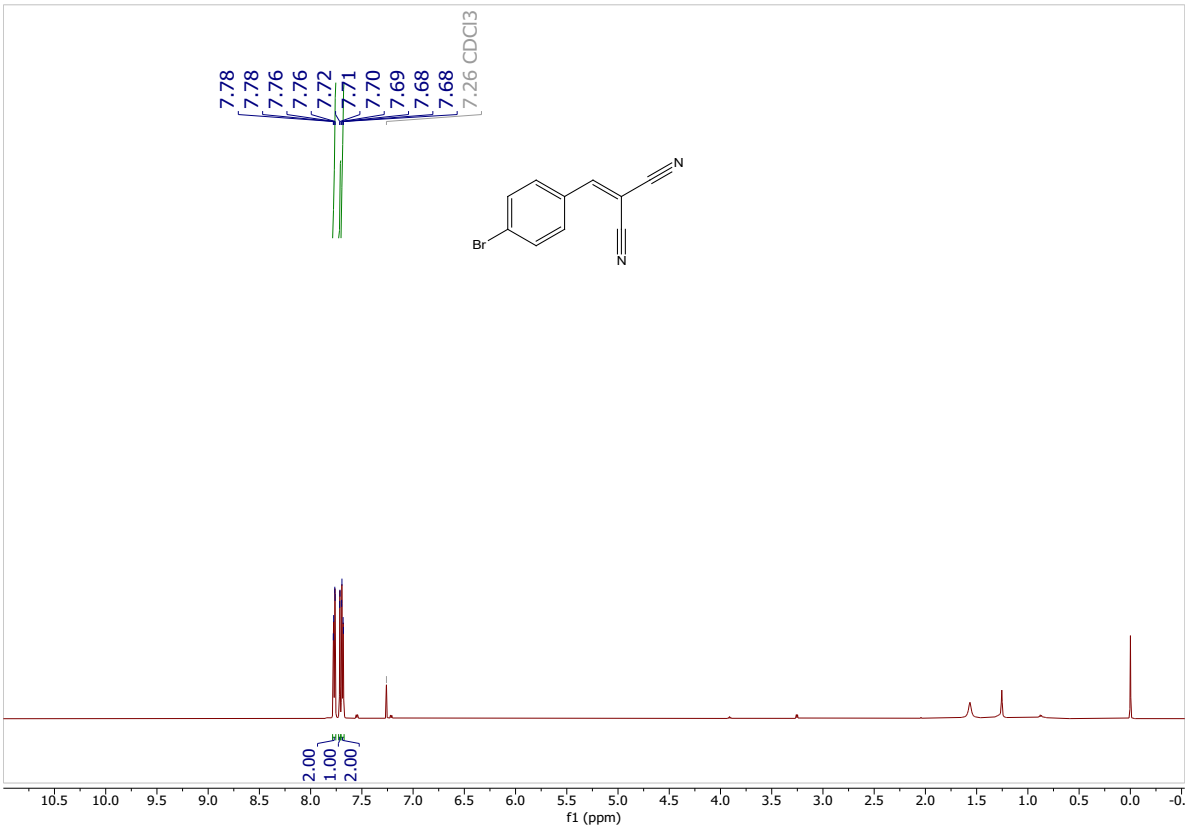


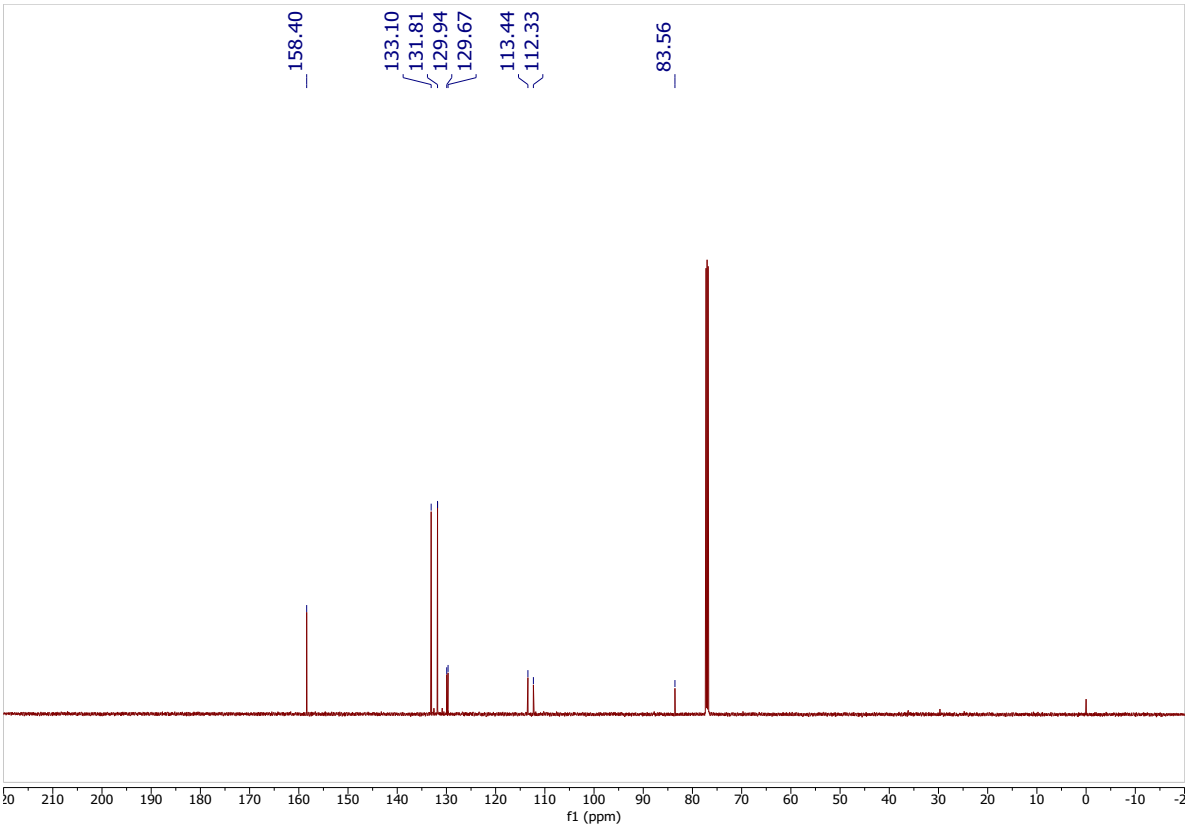
*2-(4-cyanobenzylidene)malononitrile (**8c**)*



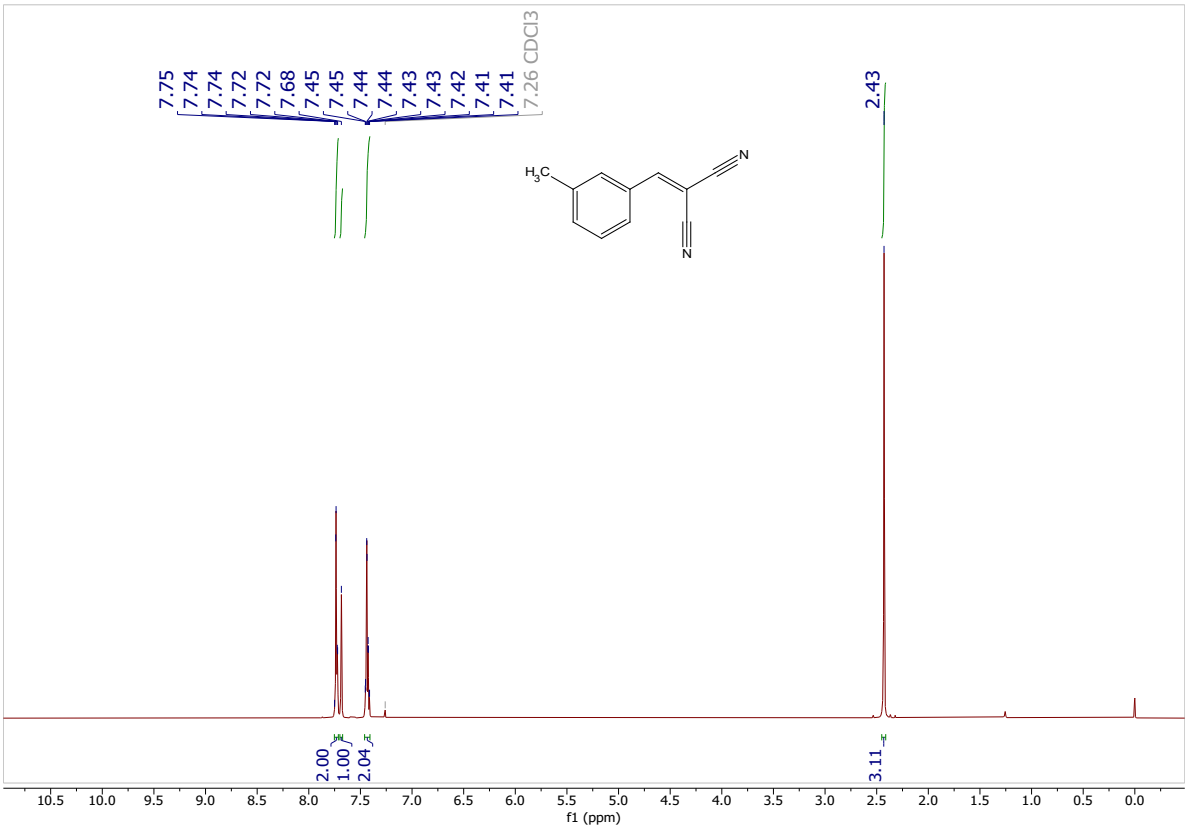


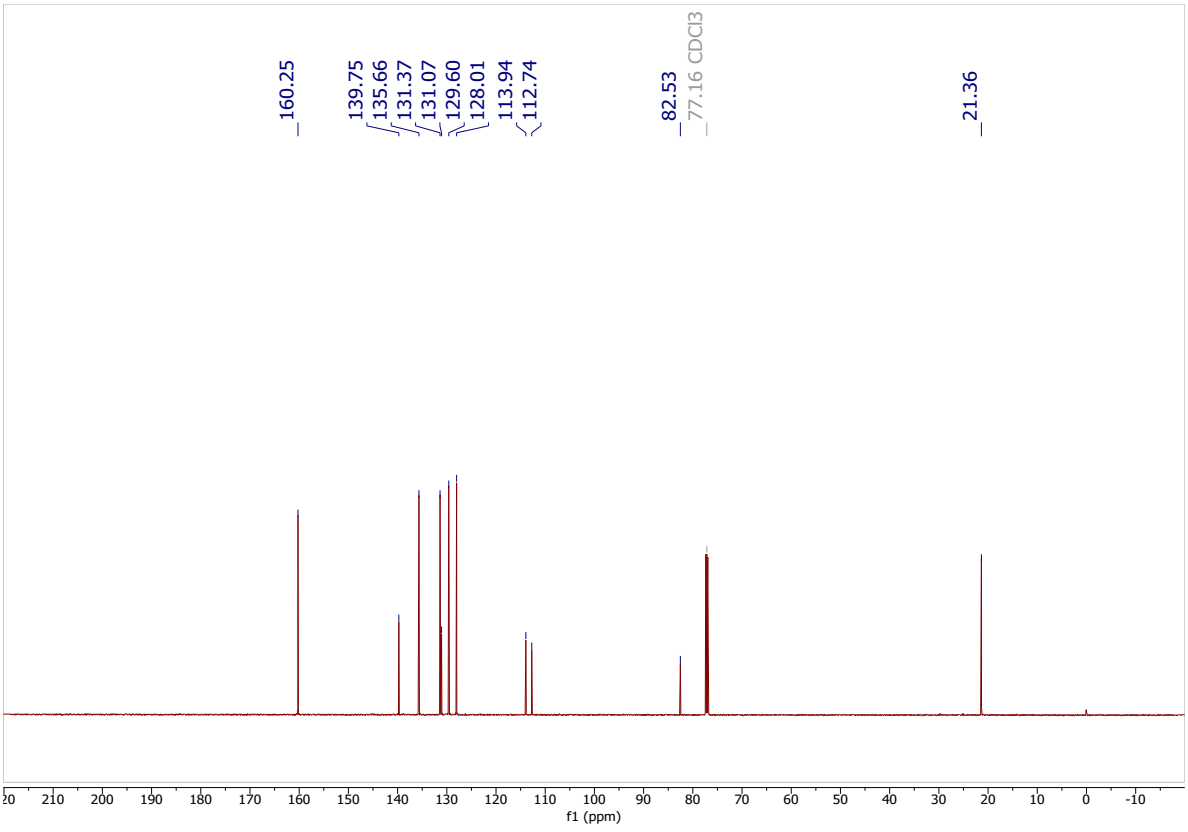
2-(4-bromobenzylidene)malononitrile ***(8f)***



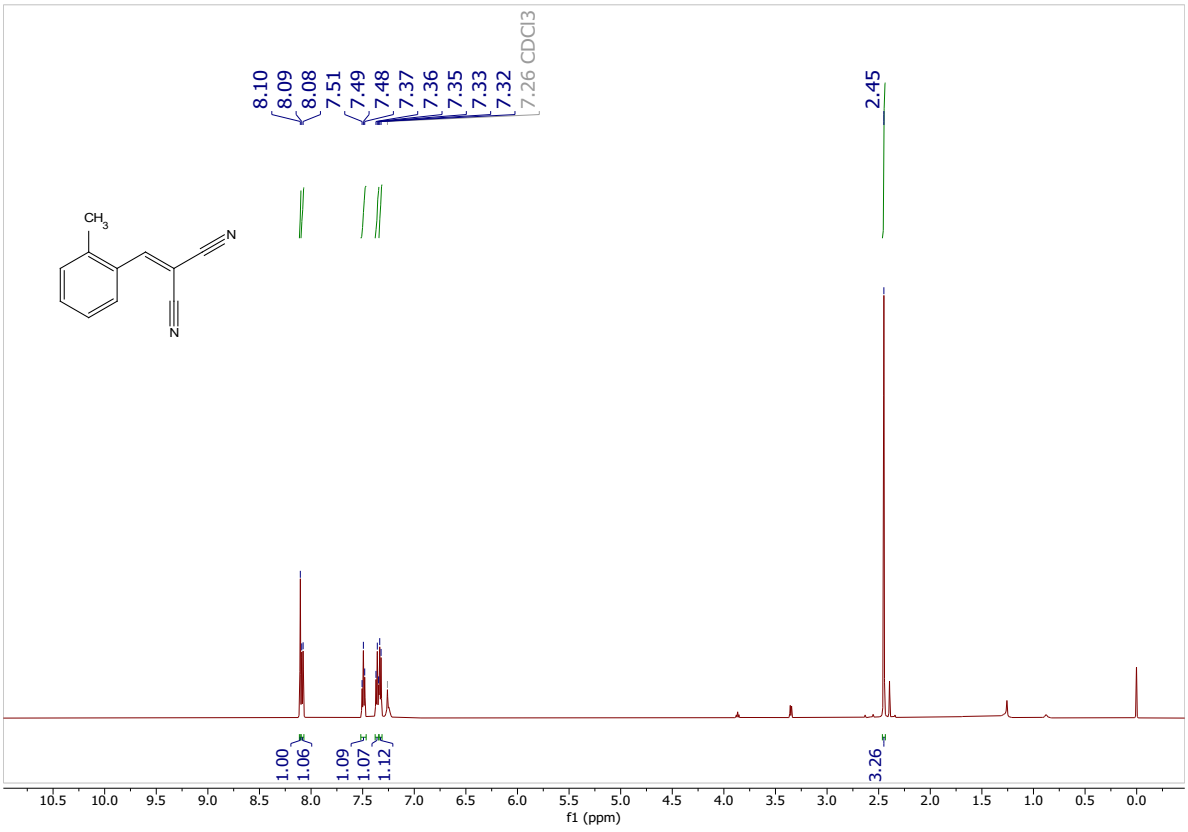


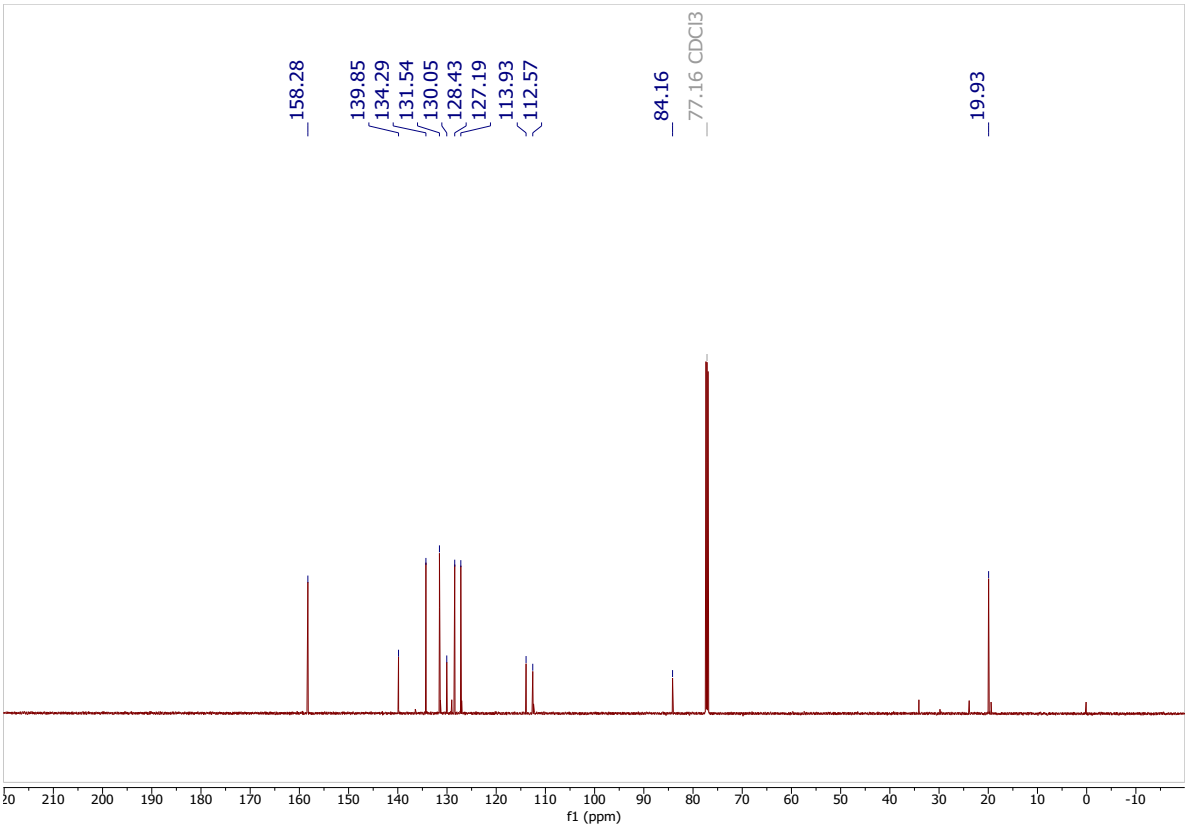
*2-(3-methylbenzylidene)malononitrile (**8h**)*



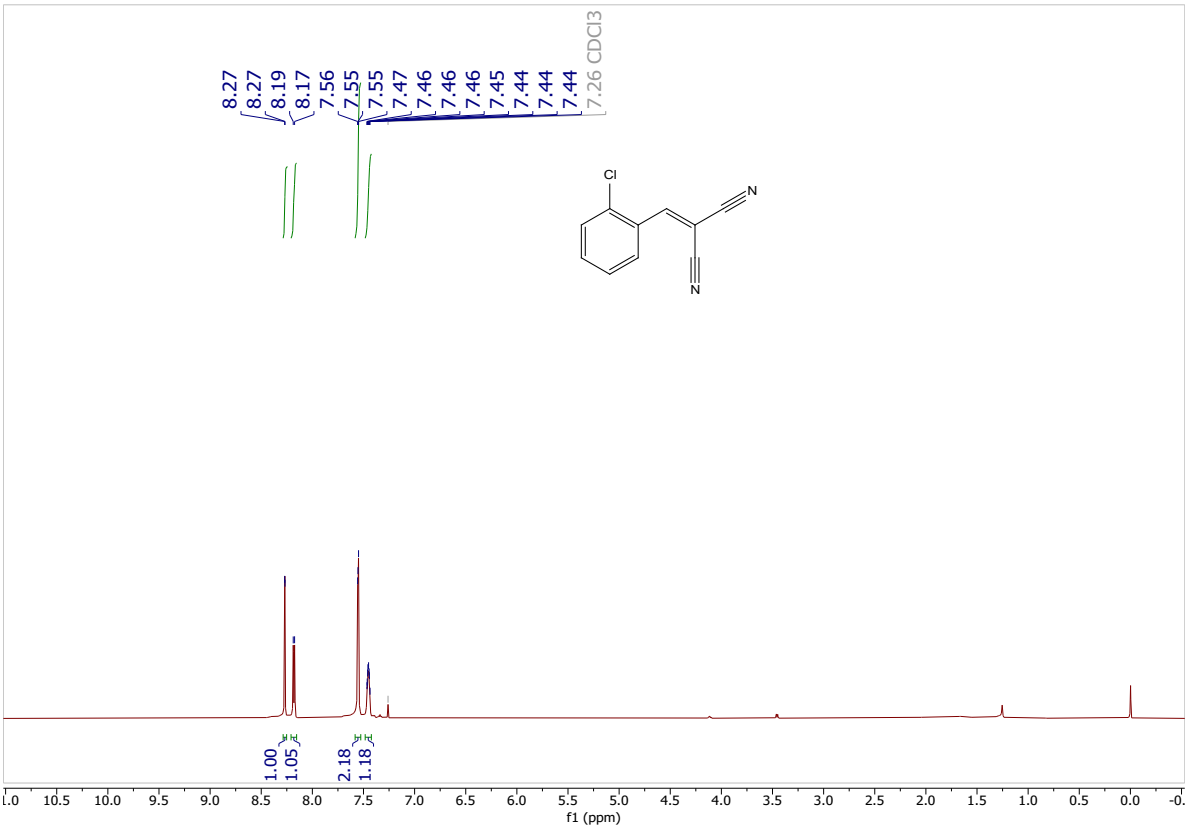


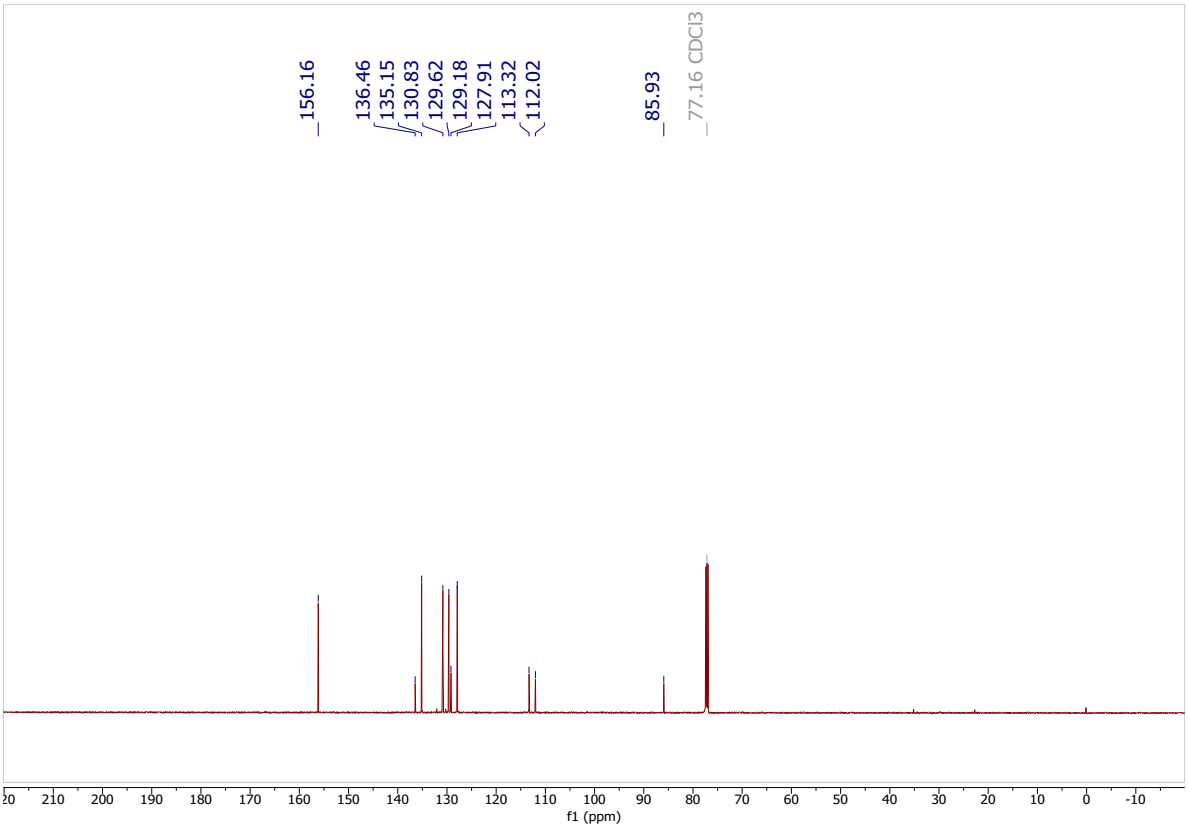
*2-(2-methylbenzylidene)malononitrile (**8i**)*



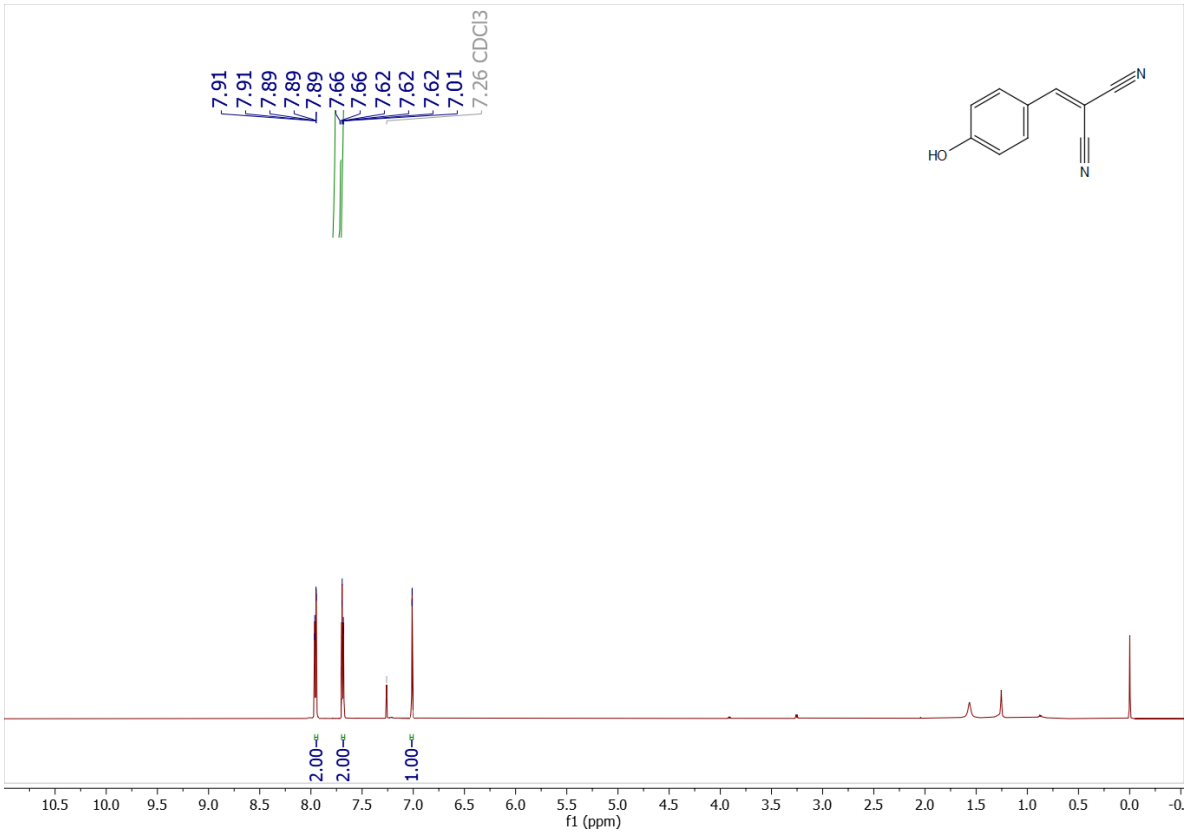


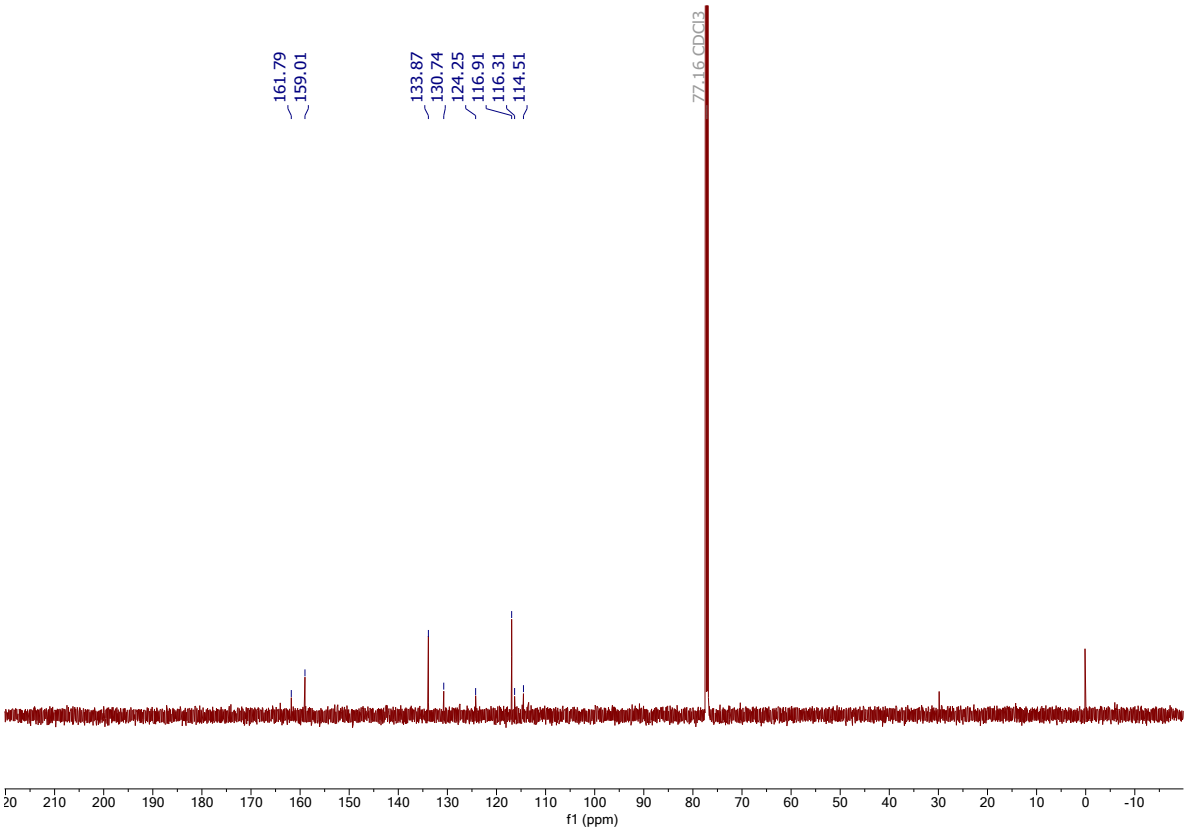
*2-(2-chlorobenzylidene)malononitrile (**8l**).*



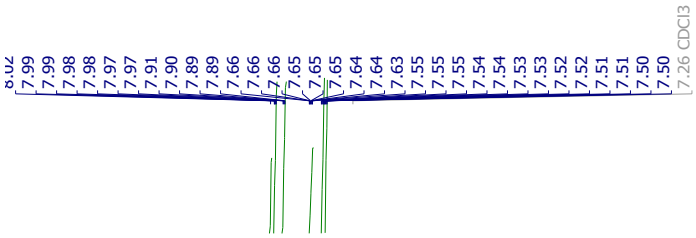


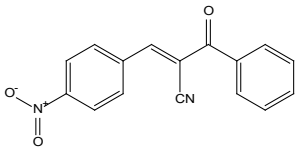
*2-(2-chlorobenzylidene)malononitrile (**8l**).*

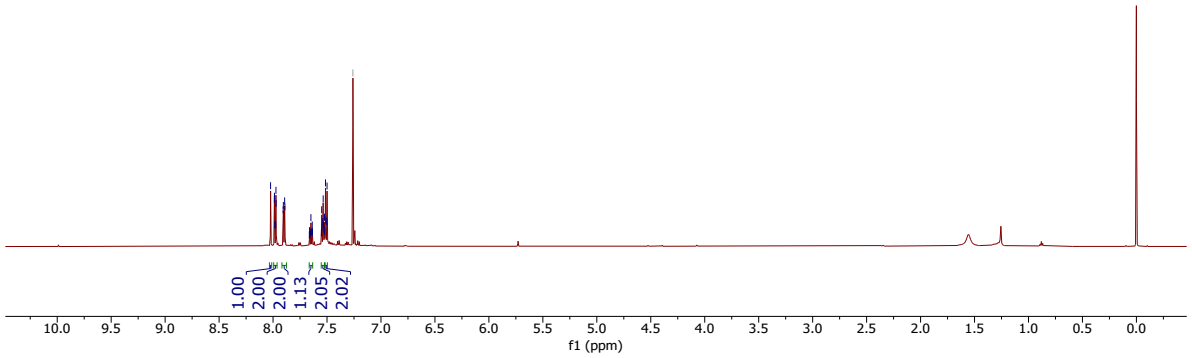


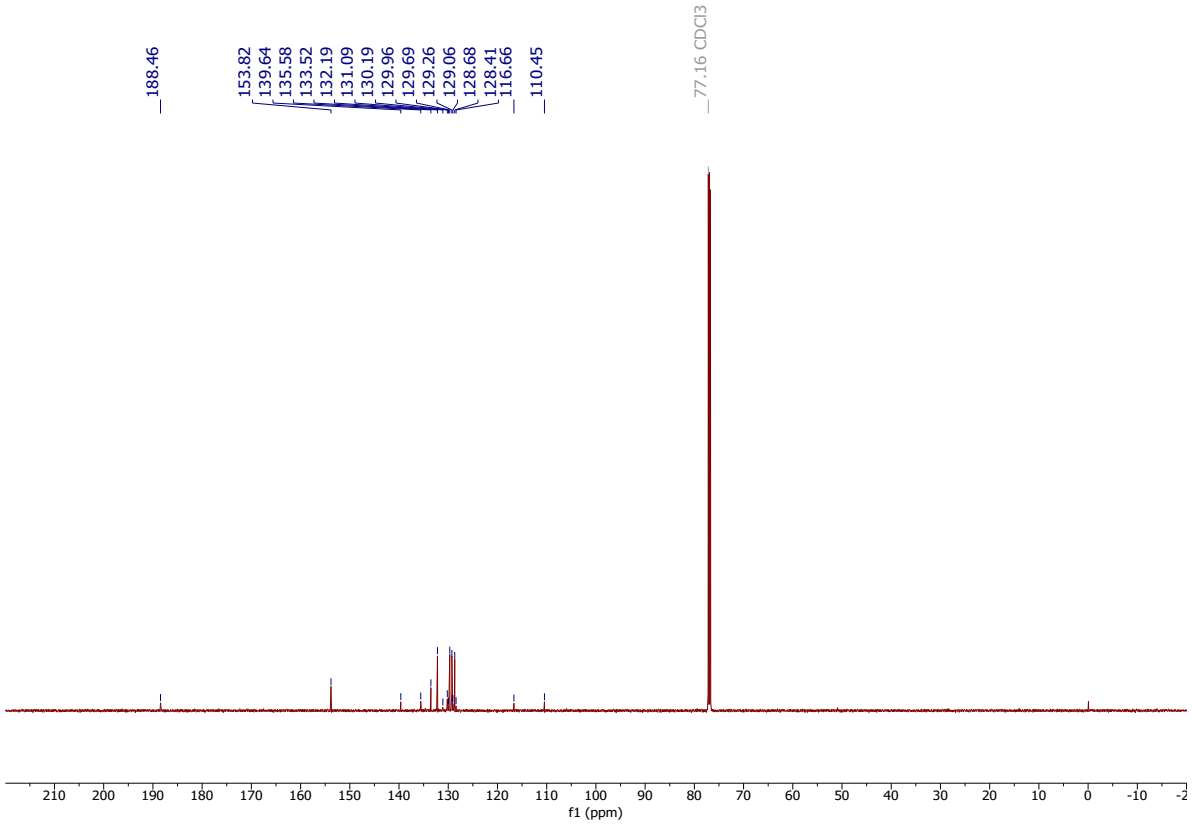


*2-benzoyl-3-(4-nitrophenyl)acrylonitrile (**9a**)*

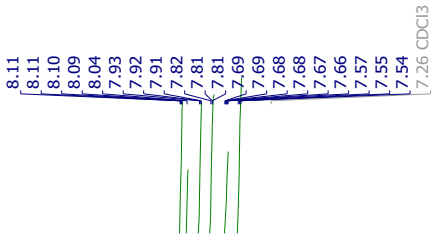


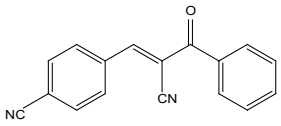


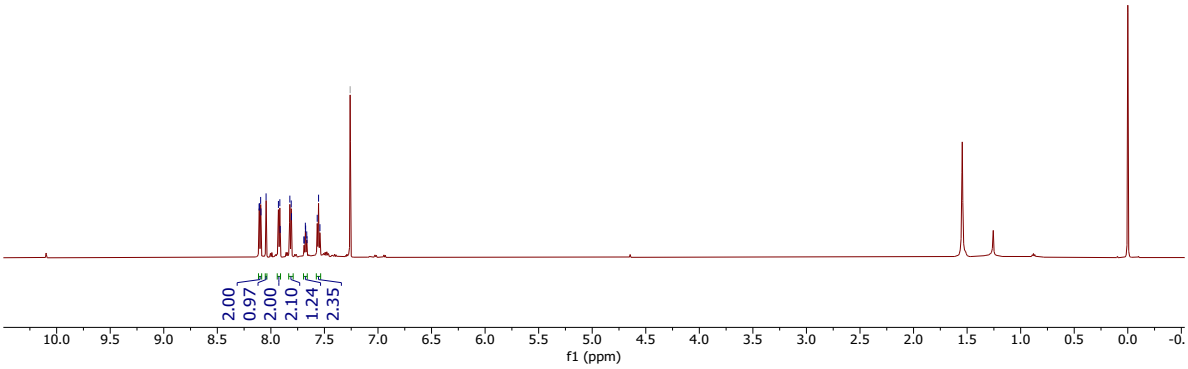


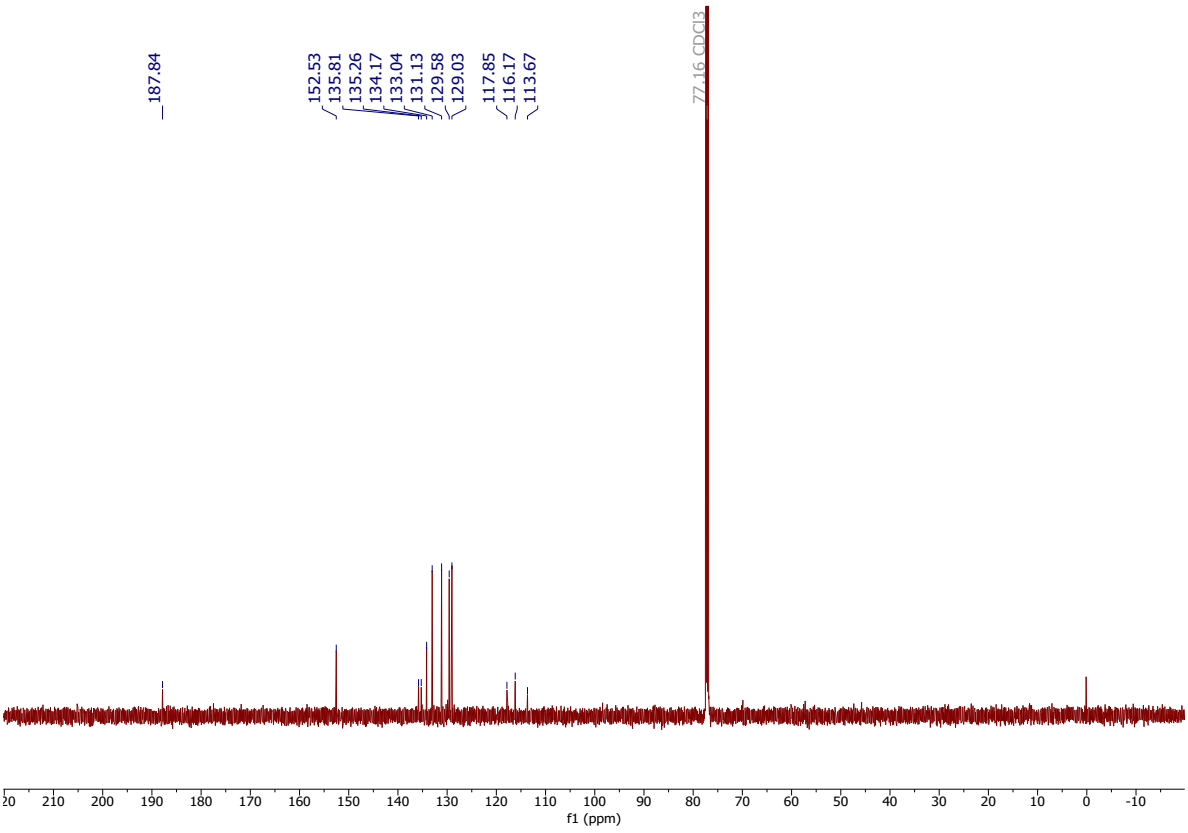


*2-benzoyl-3-(4-cyanophenyl)acrylonitrile (**9c**)*

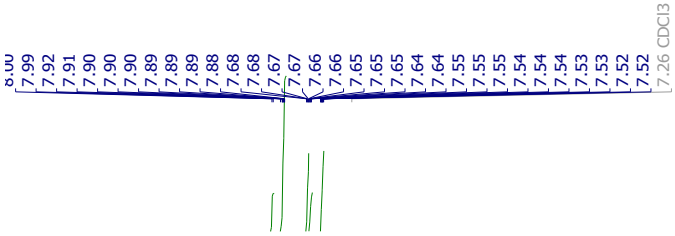


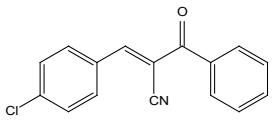


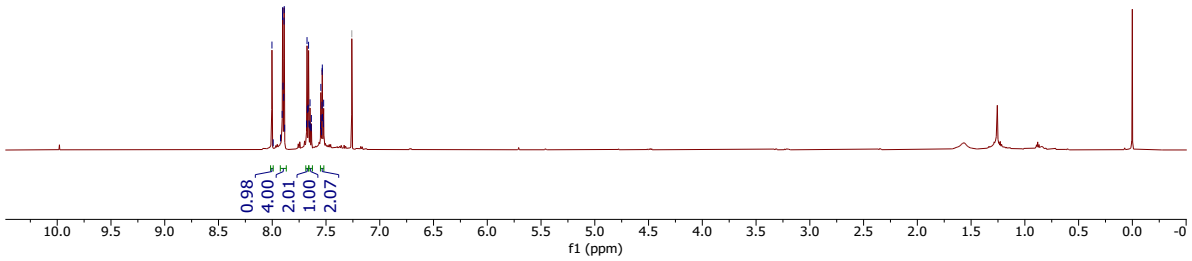


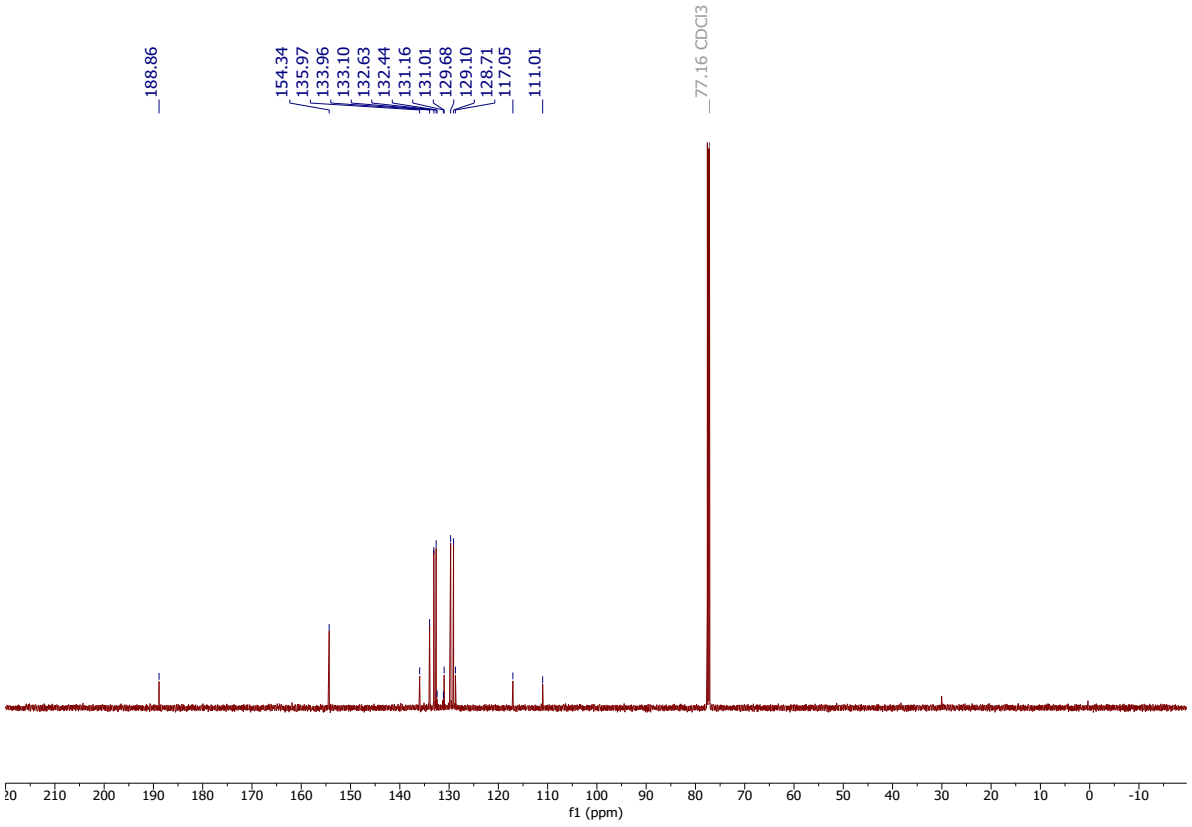


*2-benzoyl-3-(4-chlorophenyl)acrylonitrile (**9d**)*

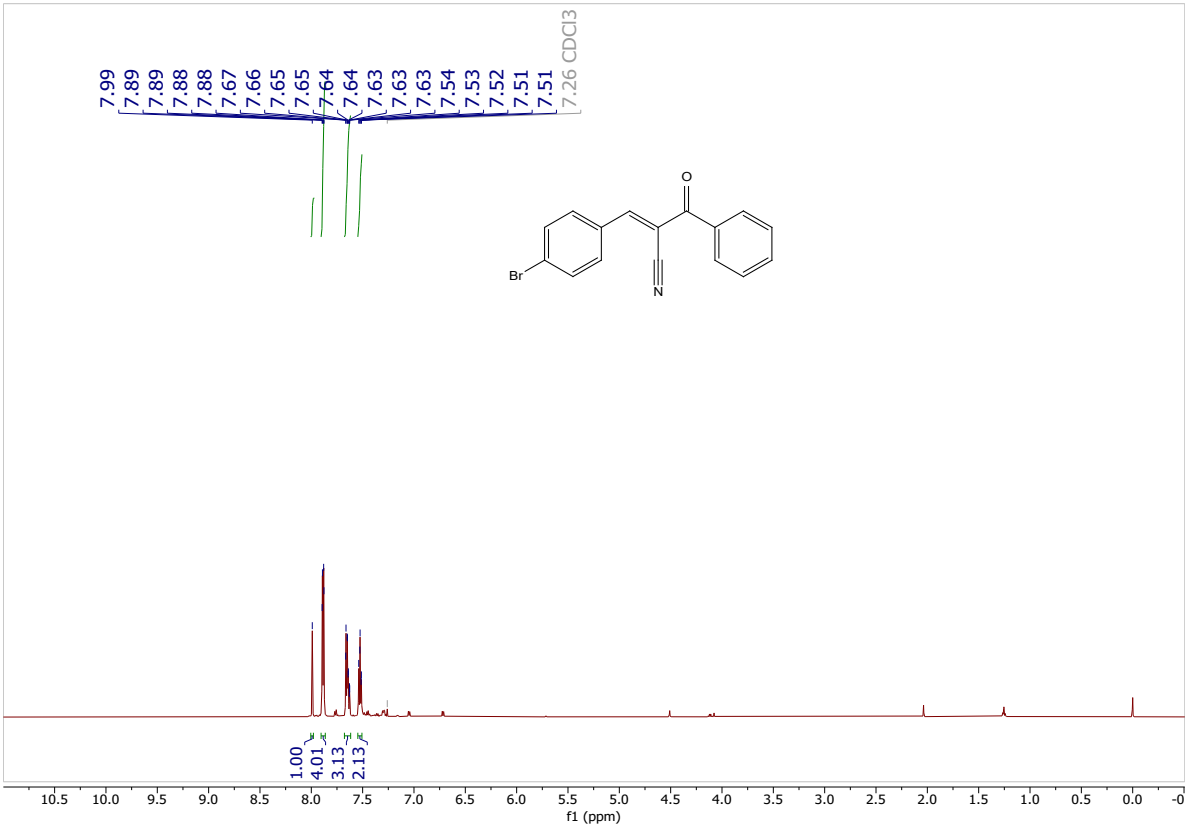


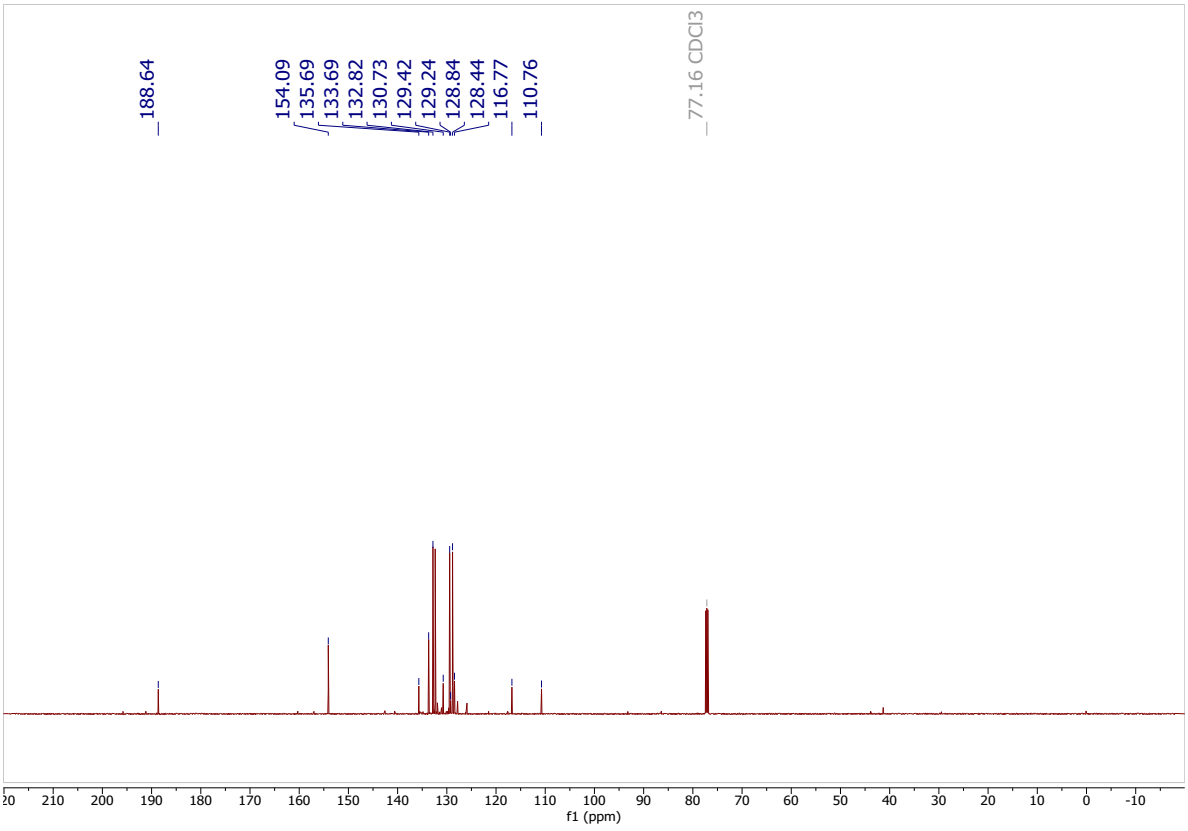




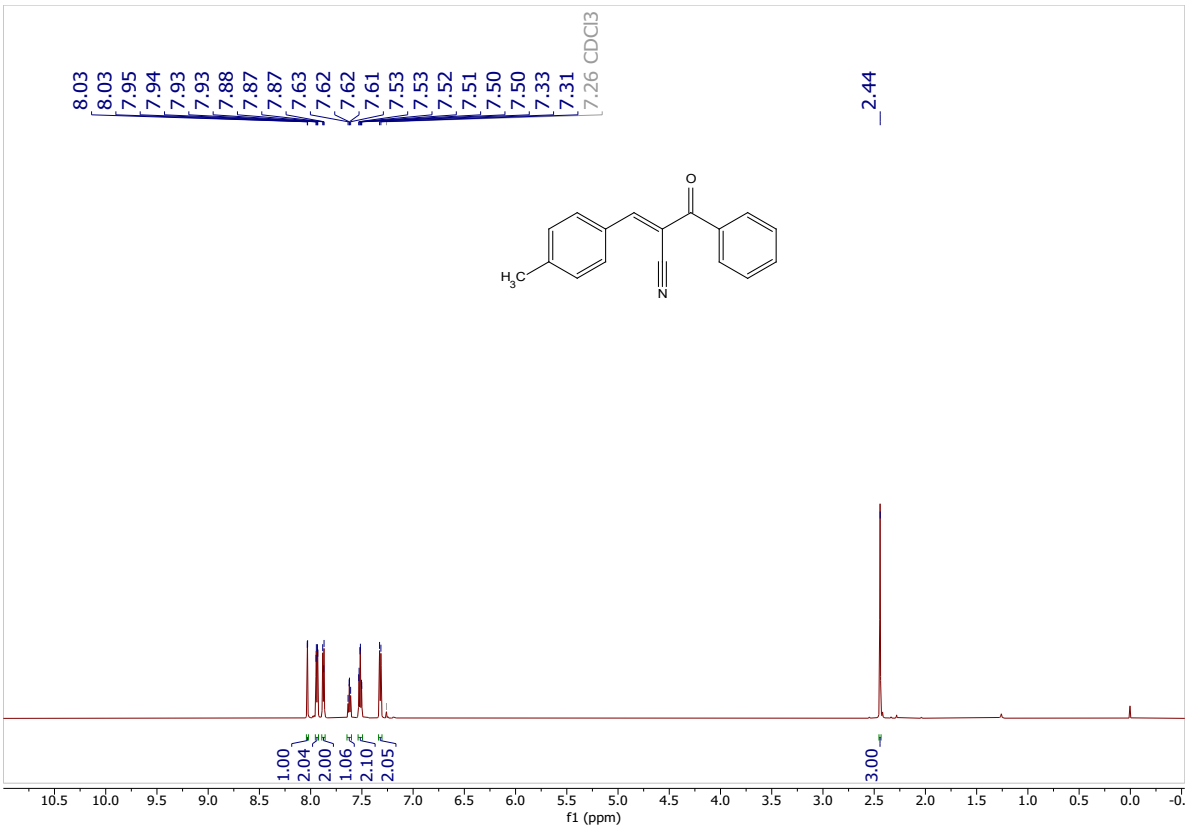


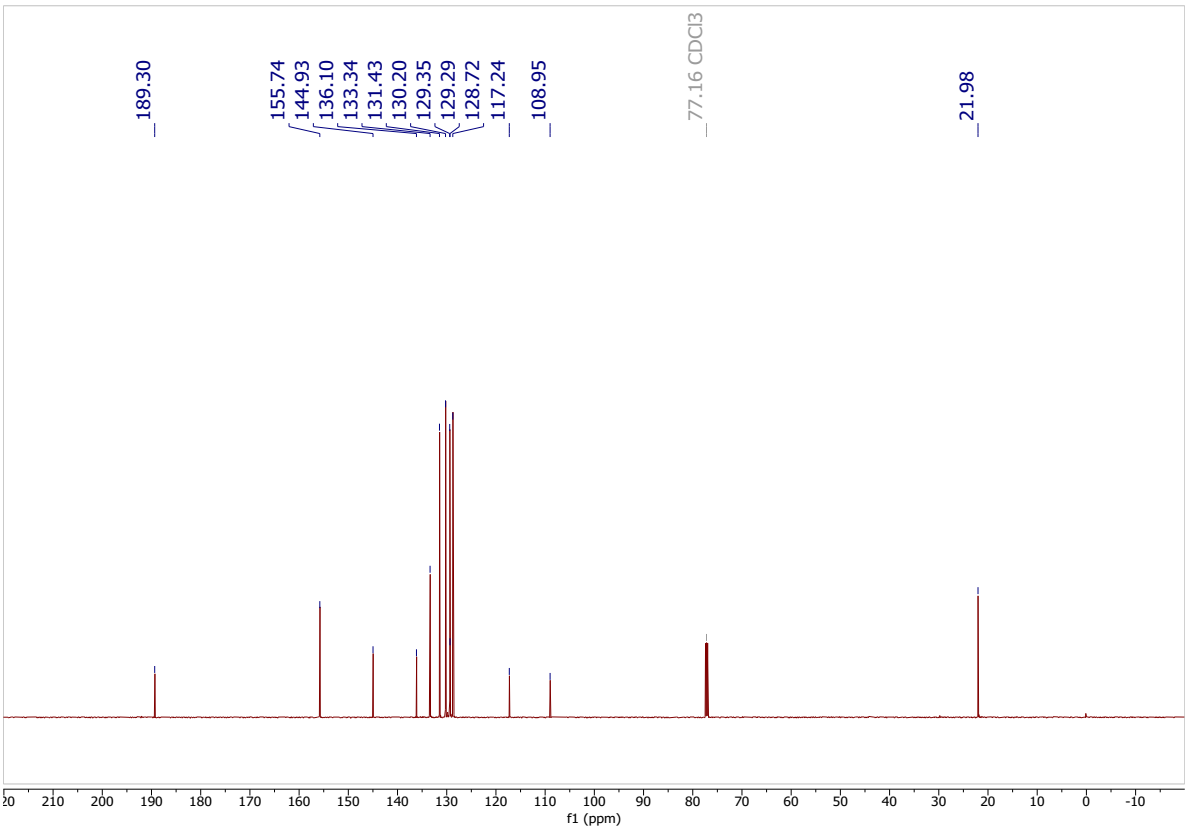
*2-benzoyl-3-(4-bromophenyl)acrylonitrile (**9f**)*



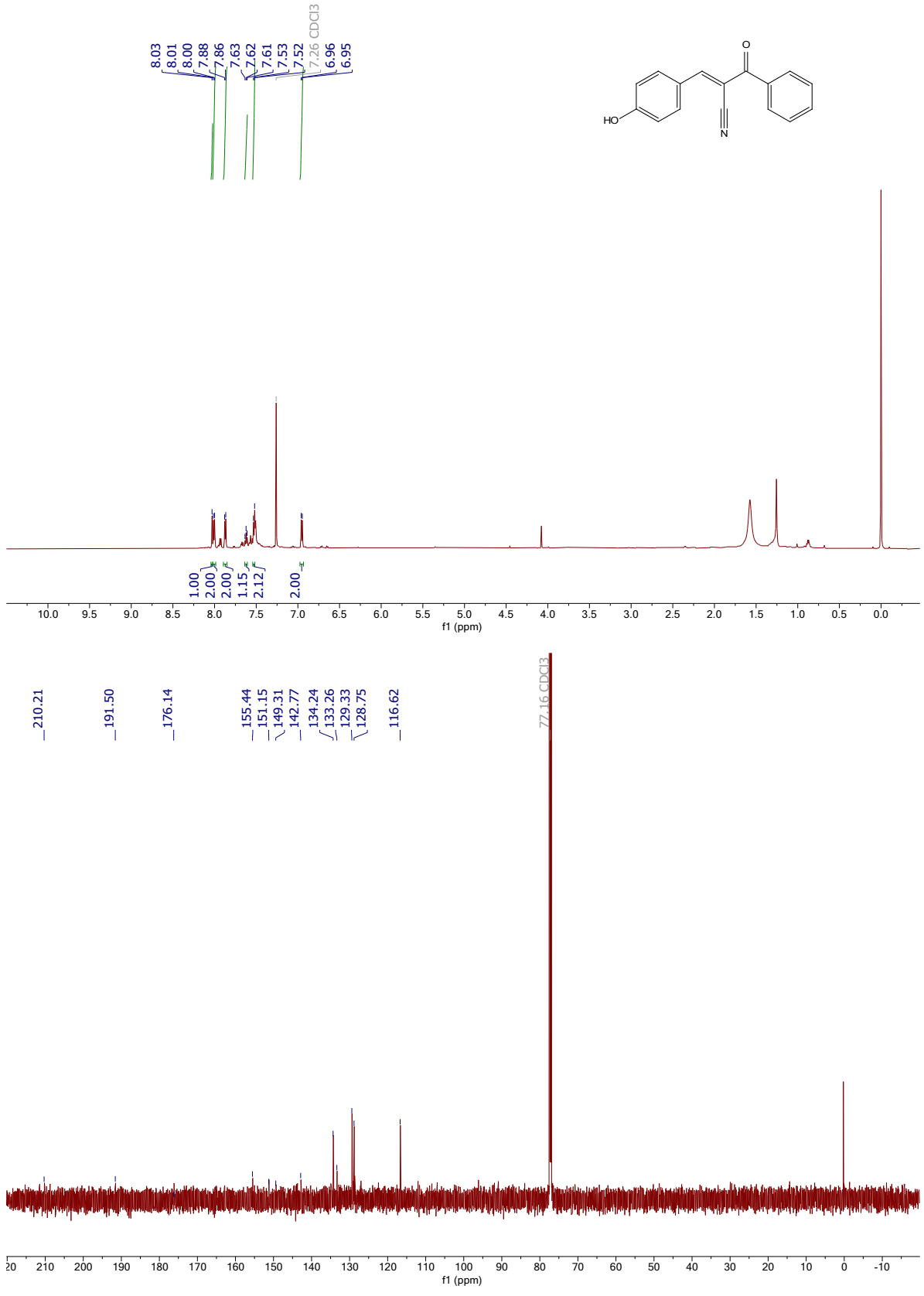


*2-benzoyl-3-(p-tolyl)acrylonitrile (**9g**)*

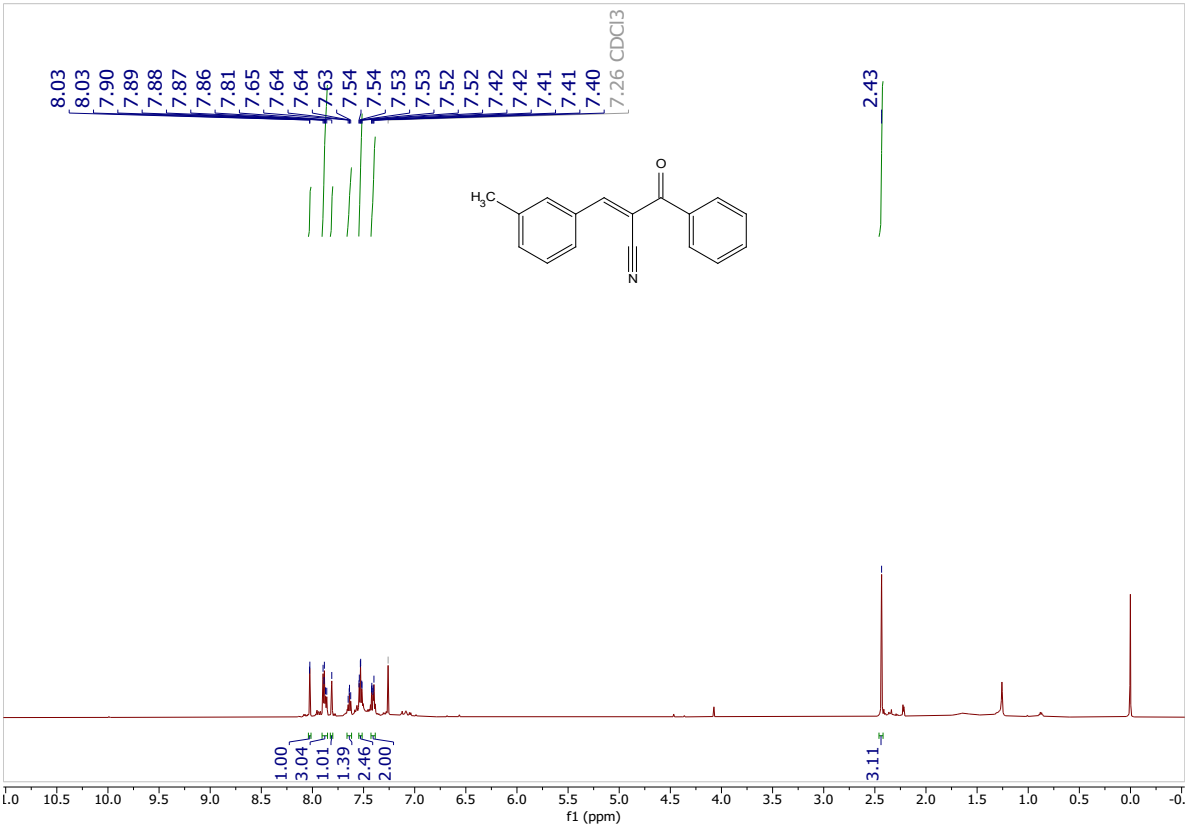


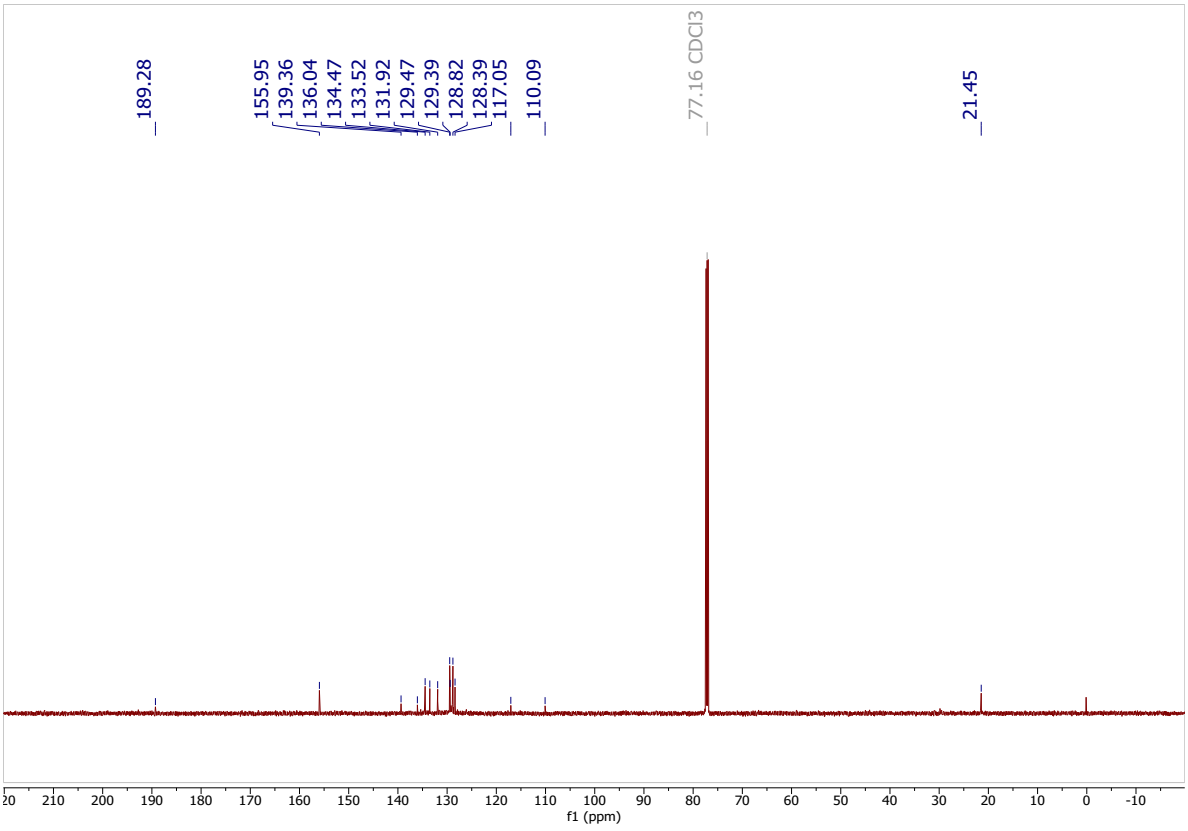


*2-benzoyl-3-(4-hydroxyhenyl)acrylonitrile (**9j**)*



*2-benzoyl-3-(m-tolyl)acrylonitrile (**9h**)*





*2-benzoyl-3-(o-tolyl)acrylonitrile (**9i**)*