Electronic Supplementary Material (ESI) for New Journal of Chemistry.


Supporting information

# Michael addition reaction of malonates to nitro olefins catalyzed by 1,1-diaminobenzalazine, A bifunctional hydrogen bonding organocatalyst

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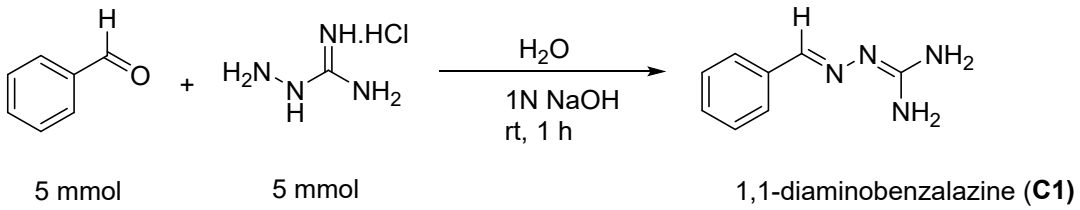
## General Information

The reagents and chemicals required for the study were procured and all the reagents were used as such without further purification unless otherwise mentioned. The progress of the reaction was monitored by Thin Layer Chromatography (TLC) performed on silica gel aluminium plates and visualization was done by UV light. $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded at 500 MHz and 125 MHz respectively, with TMS as an internal standard. $^{31}P$ NMR was recorded at 202.4 MHz with TMS as an internal standard. The $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded using $CDCl_3$ at 7.25 ppm and 77.31 ppm and for a few compounds DMSO-$d_6$ at 2.50 ppm and 39.51 ppm respectively. Chemical shift (δ) are reported in parts per million (ppm). Coupling constants (J) were reported in Hertz (Hz). The abbreviations used to characterize the signals are as follows: s = singlet, m = multiplet, d = doublet, br. s. = broad singlet, dd = doublet of doublet, t = triplet. High resolution mass spectra were recorded using ESI-TOF method.

Synthetic Procedures: Synthesis of organocatalyst (**C1**): To the benzaldehyde and aminoguanidine hydrochloride solution in $H_2O$ was added 1N NaOH (2 mL) and the reaction mixture was stirred for 1-2 h, until precipitate is formed. (Scheme S1) The resultant precipitate was filtered and dried to afford the desired organocatalysts in 88.5 to 70 % yields.




Scheme S1: Synthesis of Catalyst (**C1**)

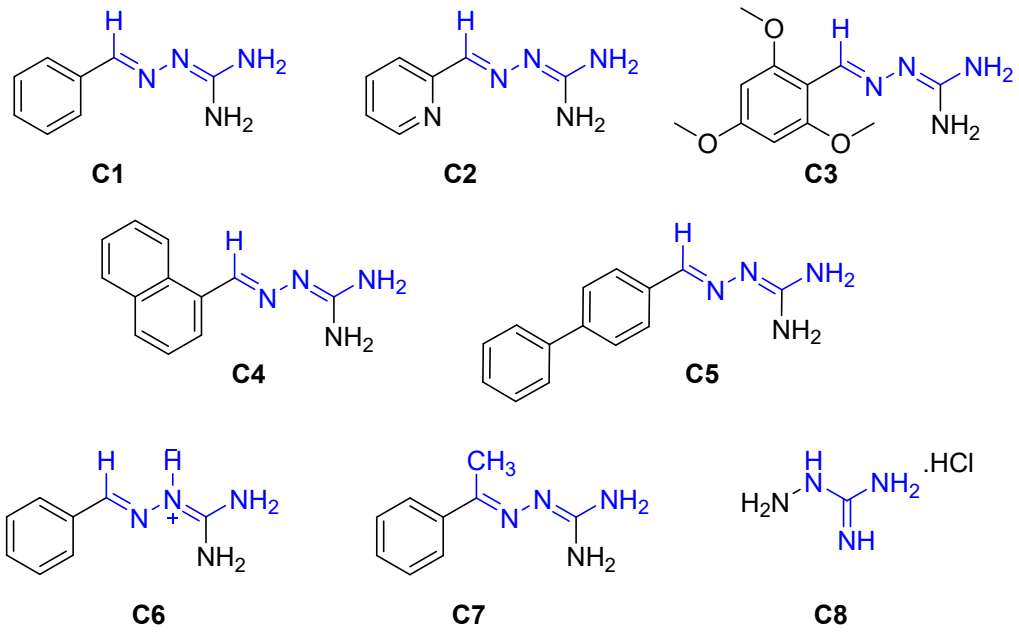



**Figure S1**. 1,1-diaminoazines used as organocatalysts for Michael addition reaction.

**General Procedure for the Preparation of 3a**

To the neat and dried round bottom flask with 25 mL capacity diethylmalonate **1a** (50 mg, 0.33mmol),*β*-nitrostyrene **2a** (107 mg, 0.67mmol), and azine **C1**(6 mg, 10 mol%) were charged followed by addition of 1mL MeCN. The reaction mass was stirred at rt for 24 hours. The progress of the reaction was monitored by TLC. The reaction mass was extracted with ethyl acetate/water (3×50 mL). The organic layers were combined and subjected to drying by rotary evaporator to get crude **3a** which were purified by usingcolumn chromatography (hexane-EtOAc). The product was obtained in 80% yield (83 mg).The representative procedure was employed for the synthesis of **3b-3w**.

***diethyl 2-(2-nitro-1-phenylethyl)malonate (3a)***

The title compound was isolated by column chromatography (hexane-EtOAc 9:1), Yield: 80% (82mg), yellow liquid; $^{1}$H NMR (500MHz, $CDCl_3$) □ = 7.31 – 7.27 (m, 3H), 7.25 – 7.21 (m, 2 H), 4.93 – 4.8 (dd, *J* = 5.0 Hz, 1 H), 4.87 – 4.82 (dd, *J* = 5.0 Hz, 1 H), 4.75 – 4.71 (m, 1 H), 4.23 – 4.14 (m, 3 H), 4.09 – 4.04 (q, *J* = 7.0 Hz , 2 H), 1.24 – 1.21 (t, *J* = 5.0 Hz , 3 H), 1.11 – 1.08 (t, *J* = 10.0 Hz , 3 H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ =□167.5, 166.9, 136.2, 129.0, 128.4, 128.1, 77.7, 62.2, 61.9, 39.4, 29.7, 14.0, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{20}NO_6^+$ 310.1285; Found 310.1287.

***diethyl 2-(1-(2-chlorophenyl)-2-nitroethyl)malonate (3b)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 68% (64 mg),yellow liquid; $^{1}$H NMR (500MHz, $CDCl_3$) $\delta$ = 7.40 – 7.38 (m,1 H), 7.24 – 7.21 (m, 3 H), 5.11 – 5.07 (dd, *J* = 7.0 Hz, 1 H), 4.95 – 4.91 (dd, *J* = 5.0 Hz, 1 H), 4.75 – 4.71 (m, 1 H), 4.23 – 4.14 (m, 2 H), 4.09 – 4.04 (q, *J* = 7.0 Hz , 3 H), 1.24 – 1.21 (t, *J* = 5.0 Hz , 3 H), 1.11 – 1.08 (t, *J* = 10.0 Hz , 3 H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) $\delta$ =□167.5, 166.9, 134.2, 133.7, 130.5, 129.5, 128.9, 127.3, 75.7, 62.2, 53.1, 39.4, 29.7, 14.0, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}ClNO_6^+$ 344.0895; Found 344.0899.

***diethyl 2-(1-(2,4-dichlorophenyl)-2-nitroethyl)malonate (3c)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 54% (47 mg),yellow liquid; $^{1}$H NMR (500MHz, $CDCl_3$) $\delta$ = 7.42 (s,1 H), 7.23 – 7.19 (m, 2 H), 5.09 – 5.05 (dd, *J* = 7.0 Hz, 1 H), 4.93 – 4.89 (dd, *J* = 5.0 Hz, 1 H), 4.70 – 4.65(td, *J* = 5.0 Hz, 1 H), 4.24 – 4.16 (m, 2 H), 4.11 – 4.06 (q, *J* = 7.0 Hz , 2 H), 4.03 – 4.02 (d, *J* = 5.0 Hz , 1 H), 1.25 – 1.22 (t, *J* = 5.0 Hz , 3 H), 1.14 – 1.12 (t, *J* = 5.0 Hz , 3 H); $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) $\delta$ =167.3, 166.7, 134.9, 134.9, 132.4, 130.3, 128.8, 127.6, 75.5, 62.3, 53.0, 39.4, 29.7, 14.0, 13.9; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}Cl_2NO_6^+$ 378.0506; Found 378.0506.

***diethyl 2-(1-(2,6-dichlorophenyl)-2-nitroethyl)malonate(3d)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 74% (86 mg),yellow liquid; $^{1}$H NMR (500MHz, DMSO-$d_6$) $\delta$ = 7.46 – 7.43 (t, *J* = 7.0 Hz, 2 H), 7.32 – 7.29 (t, *J* = 7.0 Hz, 1 H), 5.21 – 5.16 (dd, *J* = 7.0 Hz, 1 H), 5.13 – 5.08 (m, 1 H), 5.05 –

5.02 (dd, *J* = 5.0 Hz,1 H), 4.44 – 4.42 (d, *J* = 10.0 Hz,1 H), 4.22 – 4.09 (m, 2 H), 3.83 – 3.69 (m, 2 H), 1.17 – 1.15 (t, *J* = 5.0 Hz , 3 H), 0.80 – 0.77 (t, *J* = 7.0 Hz , 3 H); $^{13}C\{^{1}H\}$ NMR (125 MHz, DMSO-$d_6$) $\delta$ =167.7, 166.6, 137.2, 135.2, 132.4, 131.2, 130.6, 129.5, 76.6, 62.3, 61.7, 52.0, 38.8, 14.3, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}Cl_2NO_6^+$ 378.0506; Found 378.0508.

***diethyl 2-(1-(2-methoxyphenyl)-2-nitroethyl)malonate(3e)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 52% (50 mg), yellow liquid; $^{1}H$ NMR (600MHz, $CDCl_3$) □ = 7.24 – 7.22 (m, 1 H), 7.14 – 7.13 (d, *J* = 6.0 Hz, 1 H), 6.87 – 6.84 (m, 2 H), 5.03 – 4.99 (dd, *J* = 9.0 Hz, 1 H),4.88 – 4.84 (dd, *J* = 9.0 Hz,1 H), 4.39 – 4.34 (m, 1 H), 4.24 – 4.17 (m, 2 H), 4.15 – 4.13 (d, *J* = 12.0 Hz, 1 H),3.96 – 3.91 (q, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 1.27 – 1.24 (t, *J* = 9.0 Hz, 3 H),1.01 – 0.98 (t, *J* = 9.0 Hz, 3 H), ; $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$) $\delta$= 168.0, 167.7, 157.4, 130.9, 129.7, 123.7, 120.8, 111.1,76.2, 62.0, 61.6, 55.5, 52.7, 40.5, 14.0, 13.8 ; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{22}NO_7^+$ 340.1391; Found 340.1396.

***diethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (3f)***

The title compound was isolated by column chromatography (hexane-EtOAc 9:1), Yield: 73% (79 mg), yellow liquid; $^{1}$H NMR (500MHz, $CDCl_3$) $\delta$ = 7.29 – 7.28 (d, *J* = 6.0 Hz, 2 H), 7.18 – 7.17 (d, *J* = 6.0 Hz, 2 H), 4.91 – 4.88 (dd, *J* = 9.0 Hz, 1 H), 4.84 – 4.820 (dd, *J* = 9.0 H, 1 H), 4.24 – 4.18 (m, 2 H), 4.04 – 4.00 (q, *J* = 9.0 Hz, 2 H), 3.77 – 3.76 (d, *J* = 6.0 Hz, 1 H), 1.26 – 1.24 (t, *J* = 6.0 Hz , 3 H), 1.08 – 1.06 (t, *J* = 6.0 Hz , 3 H) ; $^{13}$C{$^{1}$H} NMR (125MHz, $CDCl_3$) $\delta$=167.3, 166.7, 134.7, 134.4, 129.5, 129.2, 77.5, 62.4, 62.1, 54.8, 42.4, 14.0, 13.8.

***diethyl 2-(2-nitro-1-(p-tolyl)ethyl)malonate (3g)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 59% (59 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.10 (s, 4 H), 4.89 – 4.80 (m, 2 H),4.24 – 4.16 (m, 3 H), 4.02 – 3.98 (q, *J* = 9.0 Hz, 2 H),3.79 – 3.77 (d, *J* = 12.0 Hz, 1 H), 2.28 (m, 3 H),1.26 – 1.24 (t, *J* = 9.0 Hz, 3 H), 1.06 – 1.04 (t, *J* = 9.0 Hz, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =167.6, 166.9, 138.1, 133.1, 129.6, 127.9, 77.8, 62.2, 61.9, 55.1, 42.6, 21.1, 14.0, 13.8 ; HRMS (ESI) m/z: [M+Na] Calcd for $C_{14}H_{21}NaNO_6$ 346.1267; Found 346.1256.

***diethyl 2-(1-(4-(benzyloxy)phenyl)-2-nitroethyl)malonate (3h)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 58% (81 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.40 – 7.35 (m, 4 H), 7.33 – 7.31 (m, 1 H),7.16 – 7.14 (d, *J* = 12.0 Hz, 2H), 6.91 – 6.89 (d, *J* = 12.0 Hz, 2 H),5.01 (s, 2 H), 4.90 – 4.86 (dd, *J* = 9.0 Hz, 1 H),4.83 – 4.78 (dd, *J* = 9.0 Hz, 1 H),4.23 – 4.19 (m, 3 H),4.03 – 3.98 (q, *J* = 9.0 Hz, 2 H),3.78– 3.76 (d, *J* = 12.0 Hz, 1 H),1.27 – 1.25 (t, *J* = 12.0 Hz, 3 H),1.06 – 1.04 (d, *J* = 12.0 Hz, 3H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =167.6, 166.9, 158.7, 136.7, 129.2, 128.6, 128.1, 127.5, 115.2, 77.9, 62.2, 61.9, 55.1, 42.4, 14.0, 13.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_7^+$ 416.1704; Found 416.1708.

***dimethyl 2-(2-nitro-1-phenylethyl)malonate (3i)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 61% (60 mg), yellow liquid; $^{1}$H NMR (500MHz, $CDCl_3$) □ = 7.31 – 7.27 (dd, *J* = 7.0 Hz, 3 H), 7.22 – 7.21 (d, *J* = 5.0 Hz, 2 H), 4.92 – 4.86 (m, 2 H), 4.26 – 4.21 (m, 1 H), 3.86 – 3.85 (d, *J* = 5.0 Hz,1 H), 3.75 (s, 3 H), 3.55 (s, 3 H), ; $^{13}$C{$^{1}$H} NMR (125 MHz, $CDCl_3$) $\delta$ =167.9, 167.3, 136.1, 129.1, 128.5, 127.9, 77.4, 54.8, 53.1, 52.9, 43.0; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}NO_6^+$ 282.0972; Found 288.0971.

***dimethyl 2-(1-(2-chlorophenyl)-2-nitroethyl)malonate (3j)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 96% (87 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.41 – 7.39 (m, *J* = 6.0 Hz, 1 H), 7.23 – 7.22 (m,*J* = 6.0 Hz, 3 H), 5.12 – 5.09 (dd, *J* = 6.0 Hz, 1 H), 4.96 – 4.93 (dd, *J* = 6.0 Hz,1 H), 4.76 – 4.72 (m, 1 H), 4.11 – 4.10 (d, *J* = 6.0 Hz, 1 H), 3.72 (s, 3 H), 3.62 (s, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 167.8, 167.3, 134.1, 133.6, 130.6, 129.6, 127.4, 75.5 53.0, 53.0, 52.8; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}ClNO_6^+$ 316.0582; Found 316.0586.

***dimethyl 2-(1-(2,4-dichlorophenyl)-2-nitroethyl)malonate (3k)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 87% (70 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.43 – 7.42 (d, *J* = 6.0 Hz, 1 H), 7.23 – 7.21 (dd, *J* = 6.0 Hz, 1 H),7.19 – 7.18 (d, *J* = 6.0 Hz, 1 H),5.10 – 5.06 (dd, *J* = 9.0 Hz, 1 H), 4.94 – 4.91 (dd, *J* = 6.0 Hz,1 H), 4.71 – 4.67 (m, 1 H), 4.06 – 4.05 (d, *J* = 6.0 Hz, 1 H), 3.73 (s, 3 H), 3.65 (s, 3 H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =167.6, 167.1, 134.9, 134.9 , 132.3, 130.4, 127.7, 75.3 60.5, 53.2, 53.2, 52.7; HRMS (ESI) m/z: [M+Na] Calcd for $C_{13}H_{13}Cl_2NaNO_6^+$ 372.0018; Found 372.0016.

***dimethyl 2-(1-(2,6-dichlorophenyl)-2-nitroethyl)malonate (3l)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 55% (44 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.37 – 7.35 (dd, *J* = 12.0 Hz, 1 H), 7.29 – 7.27 (dd, *J* = 6.0 Hz, 1 H), 7.18 – 7.15 (t, *J* = 9.0 Hz, 1 H), 5.38 – 5.34 (m, 1 H), 5.16 – 5.12 (dd, *J* = 9.0 Hz, 1 H), 4.98 – 4.95 (dd, *J* = 9.0 Hz, 1 H), 4.45 – 4.44 (d, *J* = 6.0 Hz, 1 H), 3.81 (s, 3 H), 3.48 (s, 3 H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =167.8, 166.6, 137.9, 134.7, 131.8, 130.1, 130.0, 129.4, 75.4, 53.3, 52.7, 51.8, 38.7; HRMS (ESI) m/z: [M+Na] Calcd for $C_{13}H_{13}Cl_2NaNO_6$ 372.0018; Found 372.0021.

***dimethyl 2-(1-(2-methoxyphenyl)-2-nitroethyl)malonate (3m)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 85% (74 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.25 – 7.23 (d, *J* = 12.0 Hz, 1 H), 7.14 – 7.12 (dd, *J* = 6.0 Hz, 1 H),6.88 – 6.85 (m, 2 H), 5.04 – 4.99 (dd, *J* = 7.0 Hz, 1 H),4.89 – 4.85 (dd, *J* = 9.0 Hz,1 H), 4.41 – 4.36 (m, 1 H),4.18 – 4.16 (d, *J* = 12.0 Hz,1 H), 3.86 (s, 3 H), 3.74 (s, 3 H), 3.50 (s, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =168.3, 167.7, 157.3, 130.6, 129.7, 123.7, 120.9, 111.2,76.0, 55.5, 52.9, 52.7, 52.6, 40.3, ; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO_7^+$ 312.1078; Found 312.1083.

***dimethyl 2-(1-(4-chlorophenyl)-2-nitroethyl)malonate (3n)***

The title compound was isolated by column chromatography (hexane-EtOAc 9:1), Yield: 63% (58 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.30 – 7.28 (d, *J* = 12.0 Hz, 2 H), 7.17 – 7.16 (d, *J* = 6.0 Hz, 2 H), 4.91 – 4.88 (dd, *J* = 9.0 Hz, 1 H),4.85 – 4.82 (dd, *J* = 6.0 Hz,1 H), 4.23 – 4.19 (m, 1 H),3.82 – 3.80 (d, *J* = 12.0 Hz,1 H), 3.75 (s, 3 H), 3.58 (s, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =167.7, 167.1, 134.6, 134.5, 129.3, 129.3, 77.2, 54.5, 53.2, 53.0, 42.3, ; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{15}ClNO_6^+$ 316.0582; Found 316.0588.

***dimethyl 2-(2-nitro-1-(p-tolyl)ethyl)malonate (3o)***

The title compound was isolated by column chromatography (hexane-EtOAc 9:1), Yield: 62% (56 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) □ = 7.11 – 7.08 (m, 4 H), 4.90 – 4.82 (m, 2 H),4.21 – 4.17 (m, 1H), 3.84 – 3.82 (d, *J* = 12.0 Hz, 1 H),3.74 – 3.73 (d, *J* = 6.0 Hz, 3 H), 3.56 (m, 3 H),2.29 (m, 3 H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =168.0, 167.3, 138.2, 133.0, 129.8, 127.7, 77.6, 54.8, 53.0, 52.9, 42.6, 21.7; HRMS (ESI) m/z: [M+Na] Calcd for $C_{14}H_{17}NaNO_6$ 318.0954; Found 318.0952.

***dimethyl 2-(1-(4-(benzyloxy)phenyl)-2-nitroethyl)malonate (3p)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 82% (75 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.40 – 7.37 (m, 5 H), 7.15 – 7.14 (d, *J* = 6.0 Hz, 2 H), 6.92 – 6.91 (d, *J* = 6.0 Hz, 2 H), 5.02 (s, 2 H), 4.90 – 4.87 (dd, *J* = 6.0 Hz, 1 H), 4.85 – 4.81 (dd, *J* = 9.0 Hz, 1 H), 4.21 – 4.17 (m, 1 H), 3.83 – 3.82 (d, *J* = 6.0 Hz, 1 H),3.76 (s, 3 H), 3.56 (s, 3 H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =167.9, 167.3, 158.7, 136.7, 129.1, 128.7, 128.2, 127.6, 115.3, 70.1, 54.9, 52.8, 42.3, 41.2, 29.7, 14.9; HRMS (ESI) m/z: [M+Na] Calcd for $C_{20}H_{21}NaNO_7$ 410.1216; Found 410.1215.

***dimethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl) malonate (3q)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 93% (81 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.14 – 7.12 (d, $J$ = 12.0 Hz, 2 H), 6.83 – 6.82 (d, $J$ = 6.0 Hz, 2 H), 4.89 – 4.86 (dd, $J$ = 6.0 Hz, 1 H),4.83 – 4.80 (dd, $J$ = 6.0 Hz, 1 H), 4.20 – 4.16 (m, $J$ = 6.0 Hz,1 H),3.82 – 3.81 (d, $J$ = 6.0 Hz,1 H), 3.76 (s, 3 H), 3.75 (s, 3 H), 3.56 (s, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$ =168.0, 167.4, 159.5, 129.1, 129.0, 127.8, 114.4, 114.4, 55.2, 54.9, 52.9, 52.9, 42.3, ; HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{18}NO_7^+$ 312.1078; Found 312.1083.

***1-ethyl 3-methyl 2-chloro-2-(2-nitro-1-phenylethyl)malonate (3r)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 76% (80 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.36 – 7.34 (m, 2 H), 7.30 – 7.29 (m, 3 H),4.94 – 4.92 (dd, $J$ = 9.0 Hz ,1 H), 4.84 – 4.82 (dd, $J$ = 9.0 Hz, 1 H), 4.66 – 4.64 (dd, $J$ = 9.0 Hz, 1 H),4.05 – 3.96 (m, 2 H), 2.30 (s, 3 H), 1.09 – 1.06 (t, $J$ = 9.0 Hz, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 196.5, 164.8, 133.7, 129.3, 129.1, 128.8, 77.2, 77.0, 63.9, 46.6, 25.6, 13.7; HRMS (ESI) m/z: [M+Na] Calcd for $C_{14}H_{16}ClNaNO_5$ 336.0615; Found 336.0617.

***dimethyl 2-(1-(furan-2-yl)-2-nitroethyl)malonate (3s)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 72% (70 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.37 – 7.35 (d, 1 H), 6.30 – 6.22 (m, 2 H),4.94 – 4.87 (m, 2 H), 4.41 – 4.37 (m, 1 H), 3.96 – 3.94 (m, 1 H), 3.77 (s, 3 H), 3.70 (s, 3 H) ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 167.4, 167.3, 149.3, 143.0, 110.7, 108.56, 53., 36.9; HRMS (ESI) m/z: [M+Na] Calcd for $C_{11}H_{13}NO_7$ 294.0692; Found 294.0589.

***diethyl 2-(1-(furan-2-yl)-2-nitroethyl)malonate (3t)***

The title compound was isolated by column chromatography (hexane-EtOAc9:1), Yield: 84% (80 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.35 – 7.34 (d, 1 H), 6.30 – 6.22 (m, 2 H),4.94 – 4.87 (m, 2 H), 4.40 – 4.36 (m, 1 H), 4.24-4.20 (m, 1 H), 4.17 – 4.13 (m, 2 H), 3.91– 3.90 (d, 1 H), 1.28-1.25 (t, 3 H), 1.21– 1.19 (t, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 167.2, 166.9, 149.6, 142.8, 110.64, 108.56, 62.2, 53.1, 36.9, 14.01, 14.0; HRMS (ESI) m/z: [M+Na] Calcd for $C_{13}H_{13}NO_7$ 322.1005; Found 322.0907.

***2-(3-oxo-1,3-diphenylpropyl)malononitrile (3u)***

The title compound was isolated by column chromatography (hexane-EtOAc 9.5:0.5), Yield: 94% (62 mg), white solid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.99 – 7.97 (m, 2 H), 7.66 – 7.62 (m, 1 H), 7.52 – 7.50 (m, 2 H), 7.48-7.41 (m, 5H), 4.67 – 4.66 (dd, 1 H), 3.99 – 3.98 (dd, *J* = 9.0 Hz, 1 H),3.75 – 3.64 (m, 2 H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 196.7, 136.6, 135.9, 134.3, 129.4, 129.3, 129.0, 128.2, 128.1, 111.9, 111.8, 41.3, 40.2, 28.9; HRMS (ESI) m/z: [M+Na] Calcd for $C_{18}H_{14}N_2O$ 297.1004; Found 297.0977.

***diethyl 2-(3-oxo-1,3-diphenylpropyl)malonate (3v)***

The title compound was isolated by column chromatography (hexane-EtOAc 9.2:0.8), Yield: 92% (81 mg), white solid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.36 – 7.34 (m, 2 H), 7.30 – 7.29 (m, 3 H),4.94 – 4.92 (dd, *J* = 9.0 Hz ,1 H), 4.84 – 4.82 (dd, *J* = 9.0 Hz, 1 H), 4.66 – 4.64 (dd, *J* = 9.0 Hz, 1 H),4.05 – 3.96 (m, 2 H), 2.30 (s, 3 H), 1.09 – 1.06 (t, *J* = 9.0 Hz, 3 H), ; $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 197.7, 168.5, 167.8, 140.5, 136.9, 133.16, 128.6, 128.5, 128.3, 128.2, 127.2, 61.8, 61.4, 57.7, 42.7, 40.9, 14.1, 13.8; HRMS (ESI) m/z: [M+Na] Calcd for $C_{14}H_{16}ClNaNO_5$ 391.1624; Found 391.1529.

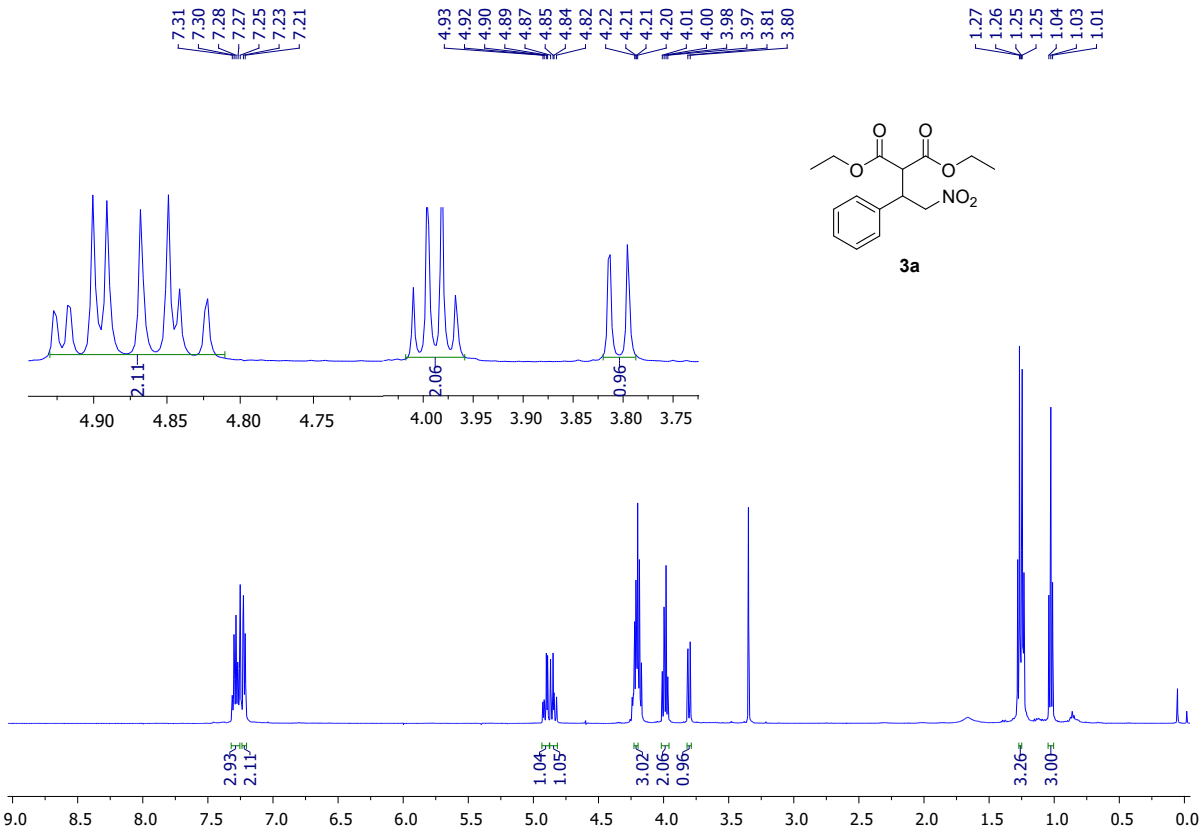
***dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate (3w)***

The title compound was isolated by column chromatography (hexane-EtOAc 9.2:0.8), Yield: 76% (80 mg), white solid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.90 – 7.89 (m, 2 H), 7.54 – 7.52 (m, 1 H), 7.44-7.41 (m, 2H), 7.25-7.15 (m, 5 H), 4.22 – 4.20 (m,1 H), 3.87 – 3.86 (d, 1 H), 3.73 (s, 3 H), 3.57 – 3.46 (m, 5 H); $^{13}$C{$^{1}$H} NMR (150MHz, $CDCl_3$) $\delta$= 197.6, 168.8, 168.2, 140.9, 136.9, 133.2, 128.8, 128.6, 128.3, 127.3, 57.4, 52.7, 52.5, 42.4, 40.8, 29.8; HRMS (ESI) m/z: [M+Na] Calcd for $C_{22}H_{24}O_5$ 363.1311; Found 363.1206.

***2-(1-(4-(benzyloxy)phenyl)-3-oxo-3-phenylpropyl)malononitrile (3x)***

The title compound was isolated by column chromatography (hexane-EtOAc 9:1), Yield: 78% (47 mg), yellow liquid; $^{1}$H NMR (600MHz, $CDCl_3$) $\delta$ = 7.96 – 7.95 (m, 2 H), 7.63 – 7.60 (m,

1 H), 7.50-7.01 (m, 11 H), 5.06 (s, 2 H), 4.61 – 4.60 (d, 1 H), 3.93 – 3.89 (m, 1 H), 3.69 – 3.58 (m, 2 H); $^{13}C\{^{1}H\}$ NMR (150MHz, $CDCl_3$) $\delta$= 196.8, 159.4, 136.7, 135.9, 134.2, 129.3, 129.0, 128.8, 128.7, 128.2, 127.6, 115.6, 112.0, 111.8, 70.2, 40.6, 40.3, 29.1; HRMS (ESI) m/z: [M+Na] Calcd for $C_{22}H_{18}O_{23}$ 337.1307; Found 337.1313.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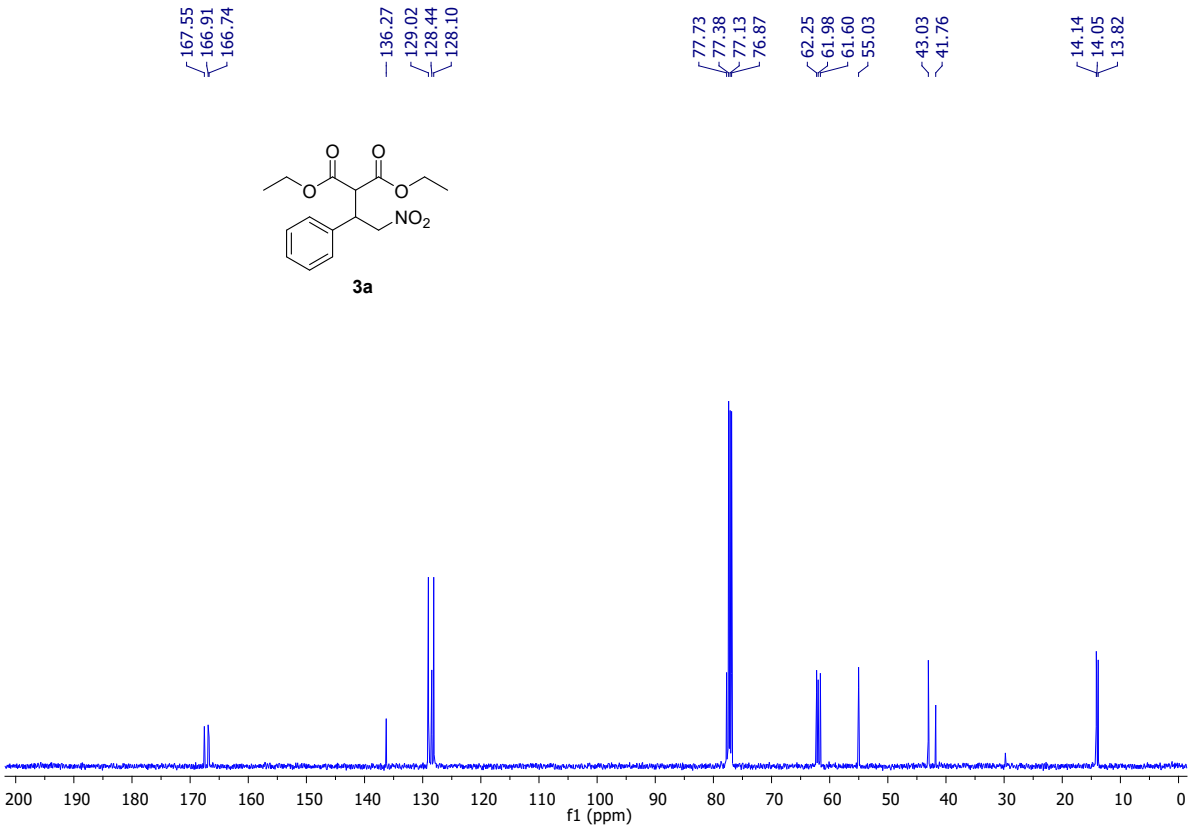
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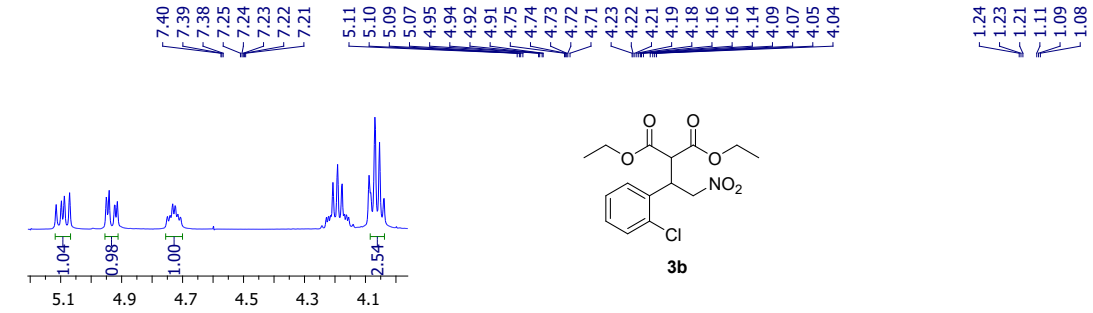
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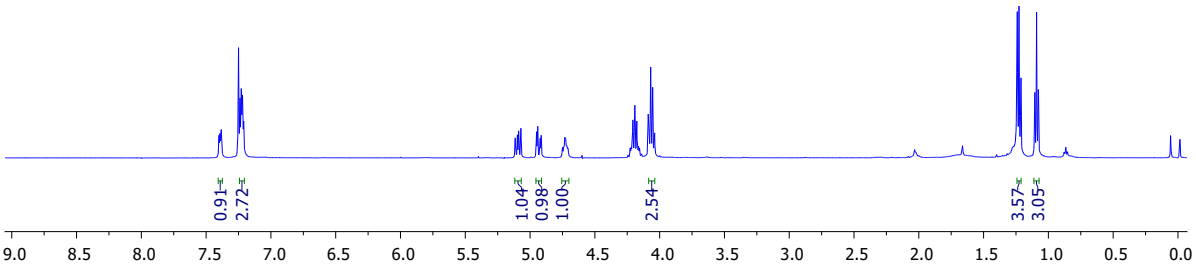
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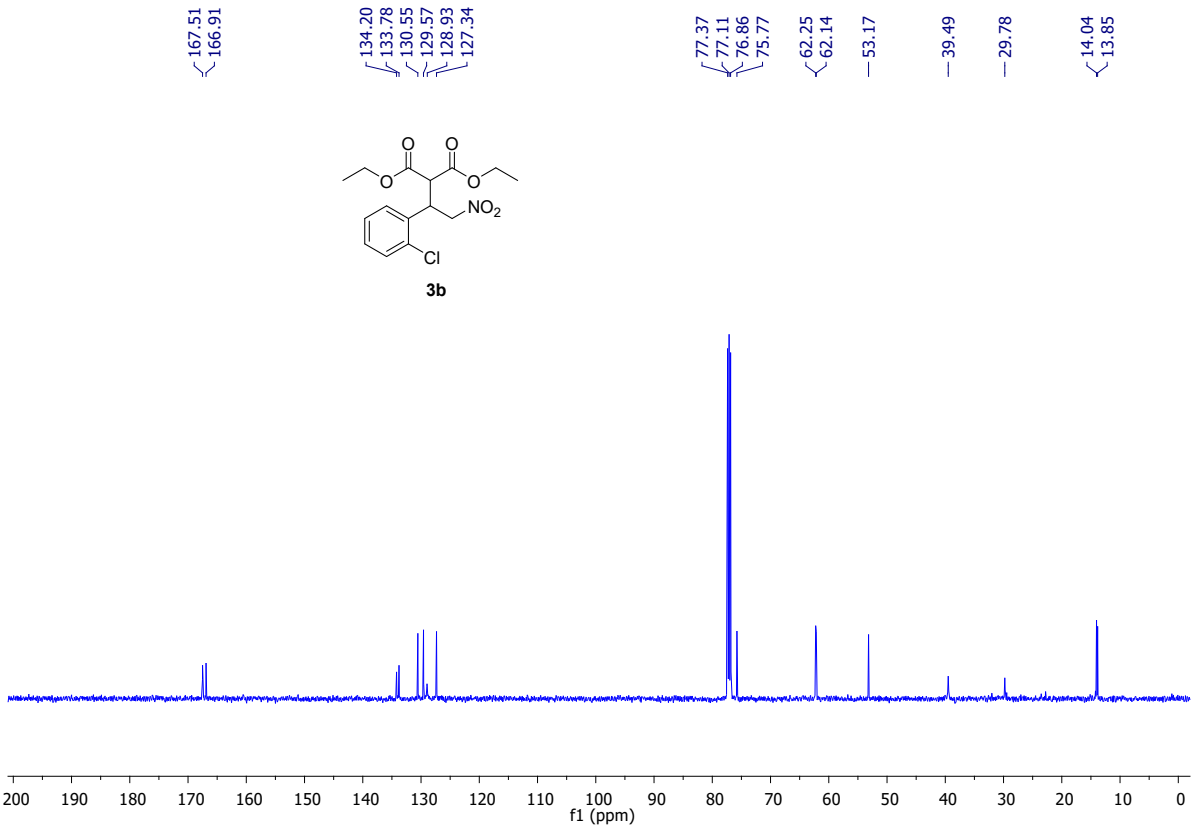
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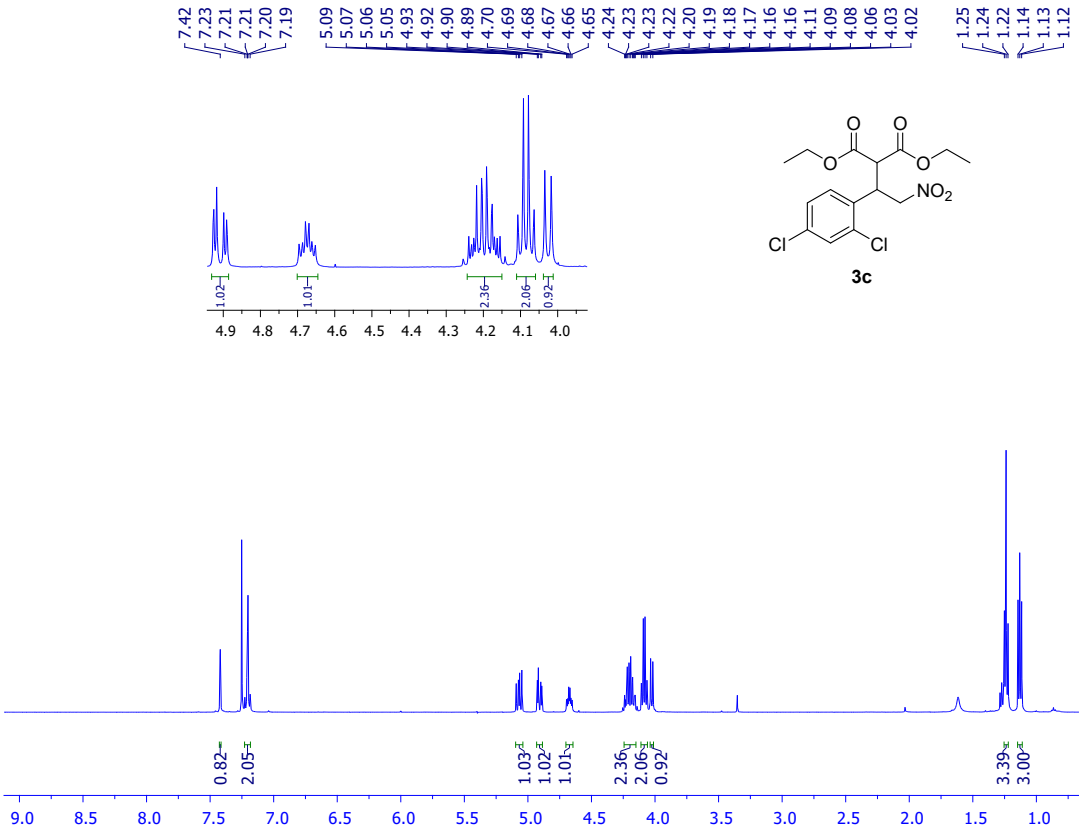
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1.02 1.01 2.36 2.06 0.92
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O O O O NO2 Cl Cl
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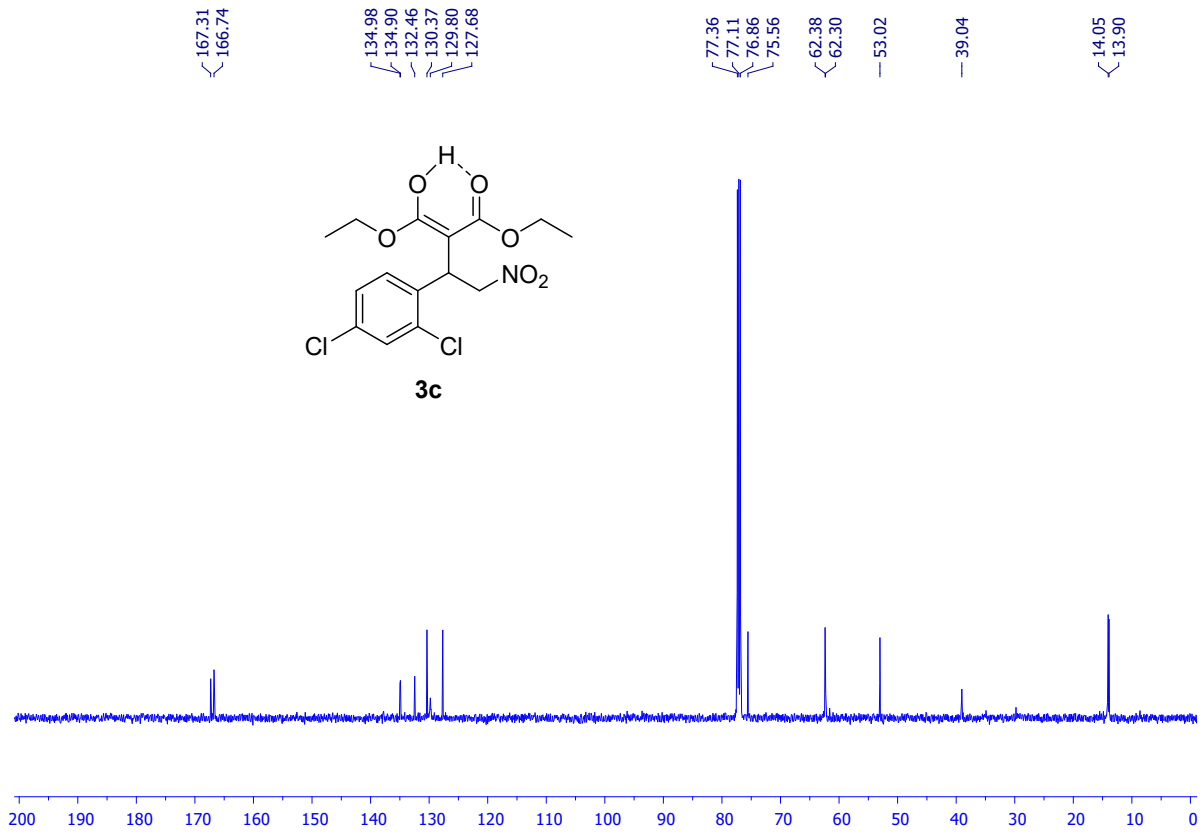
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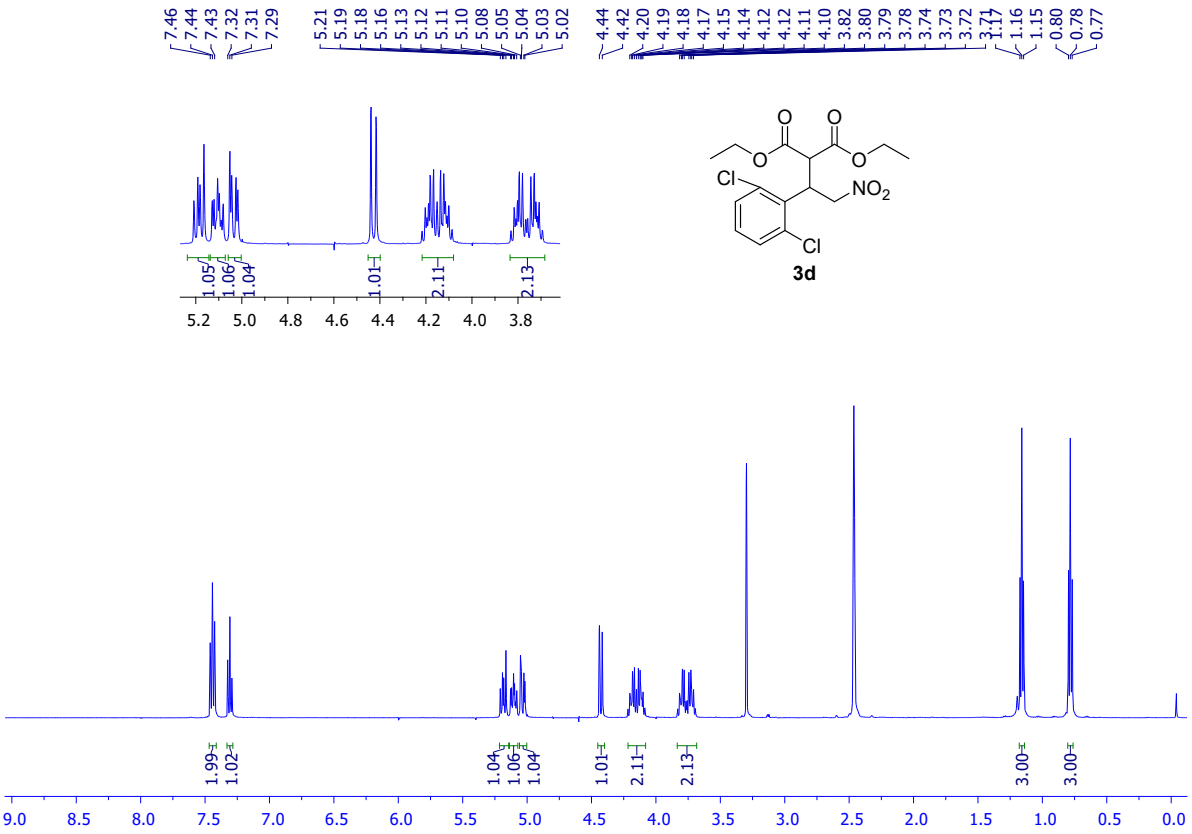
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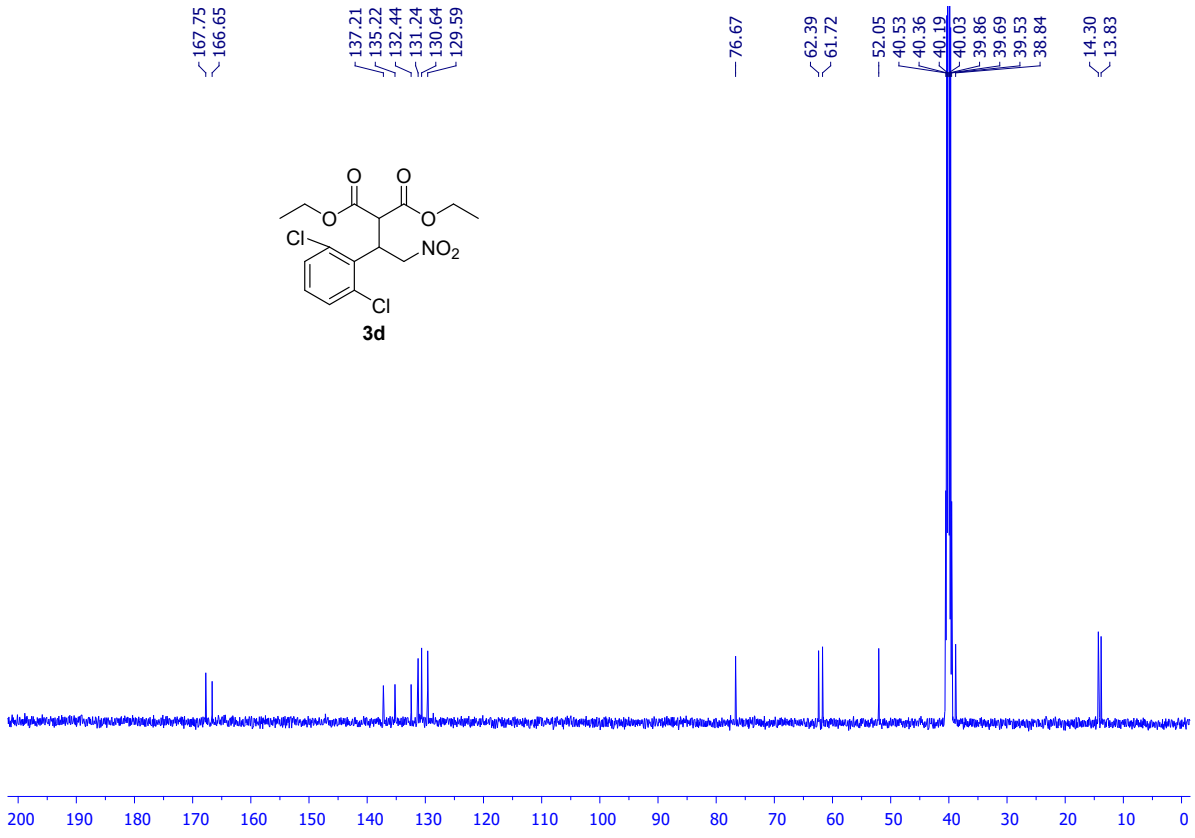
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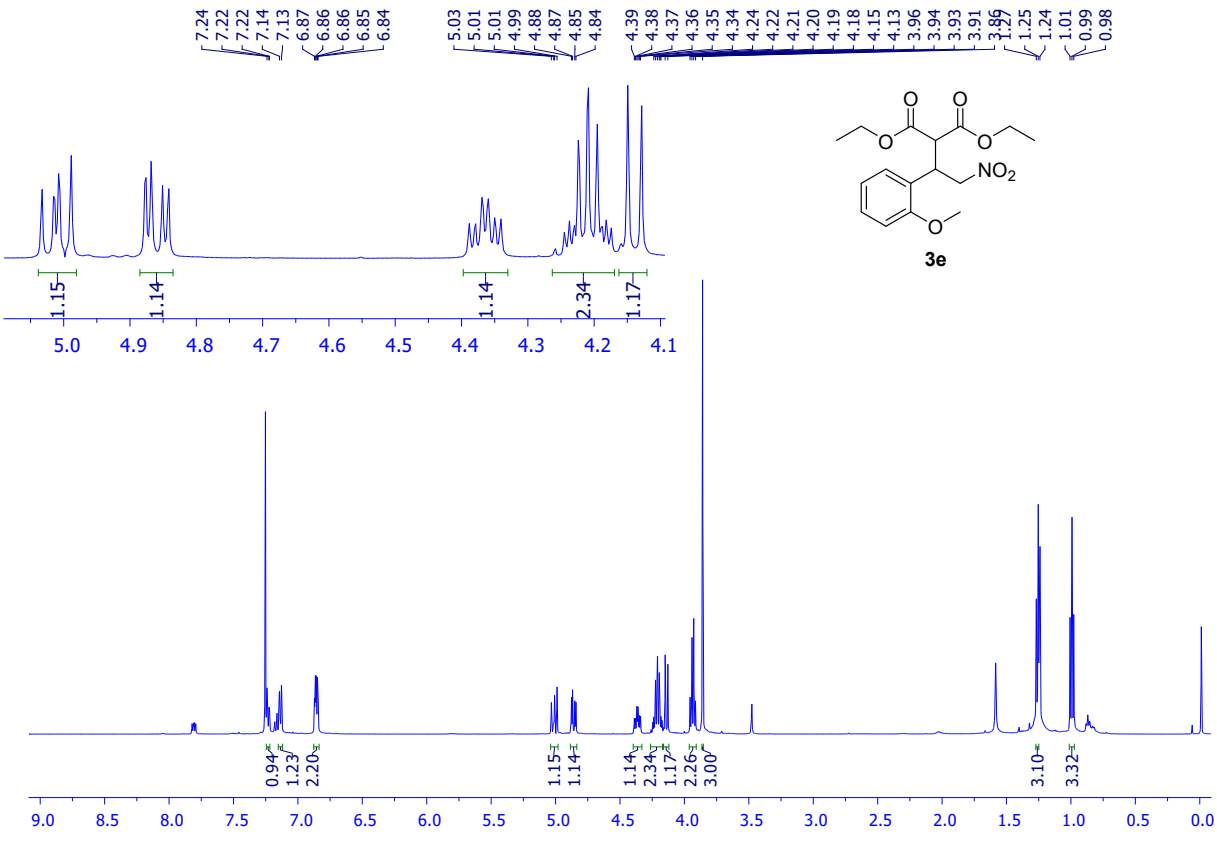
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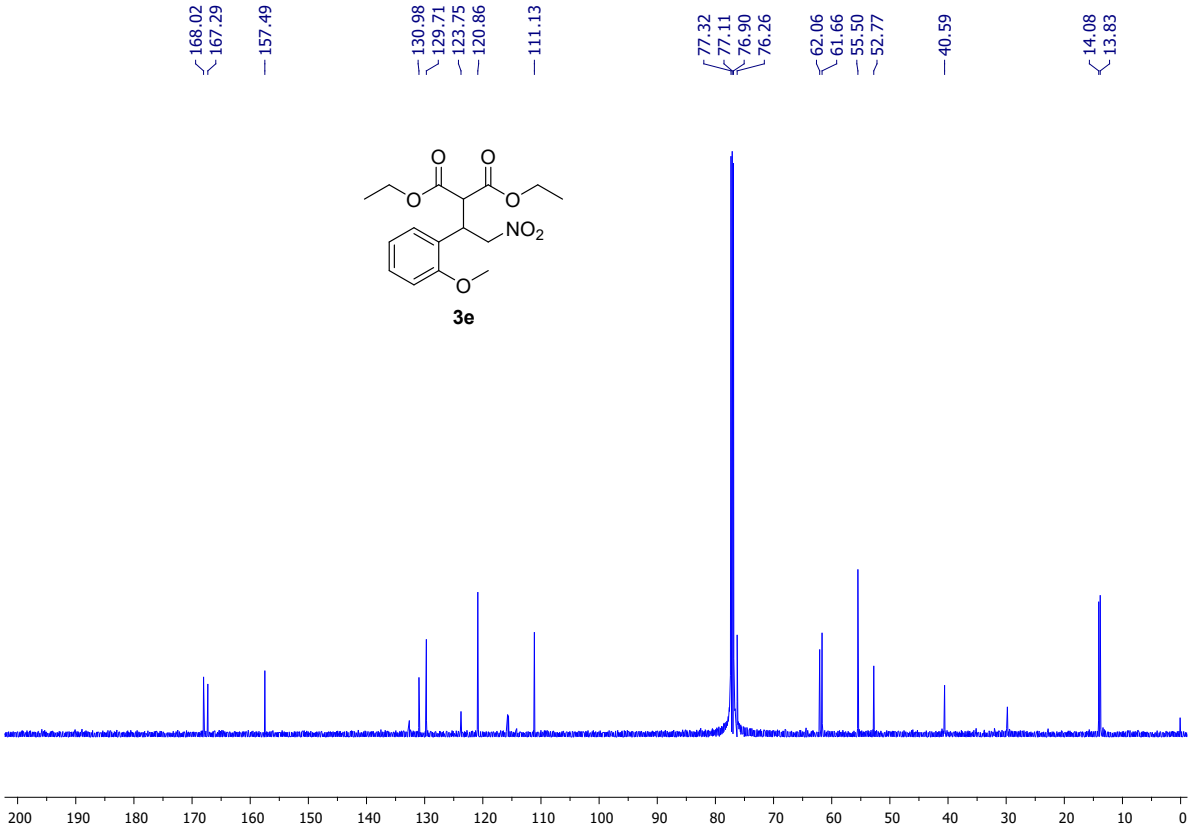
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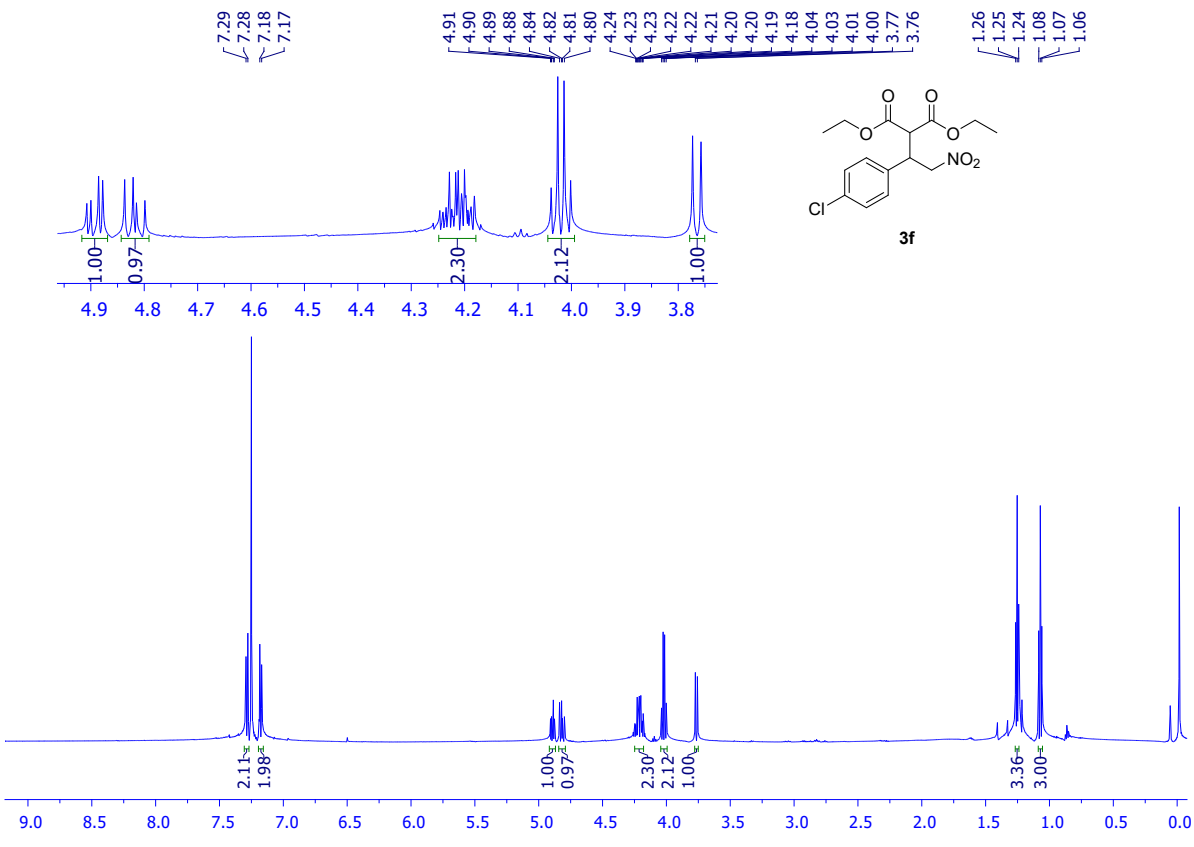
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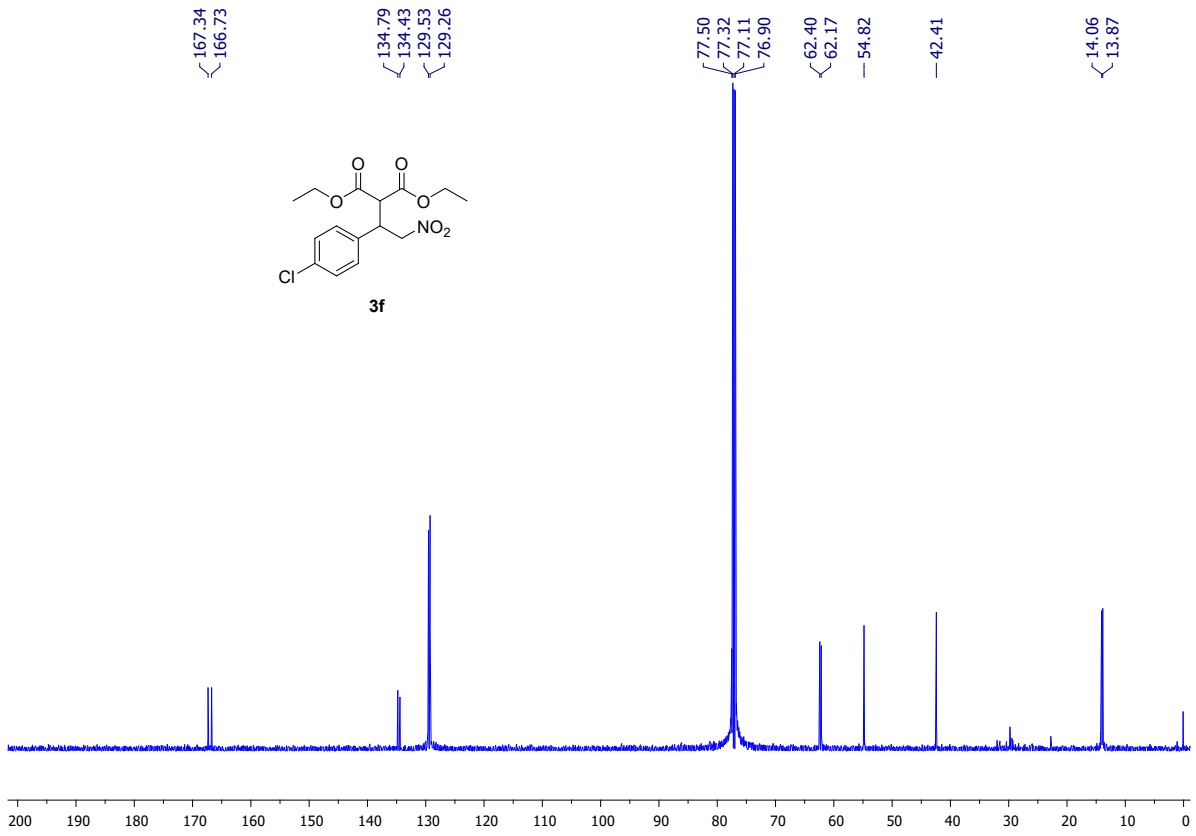
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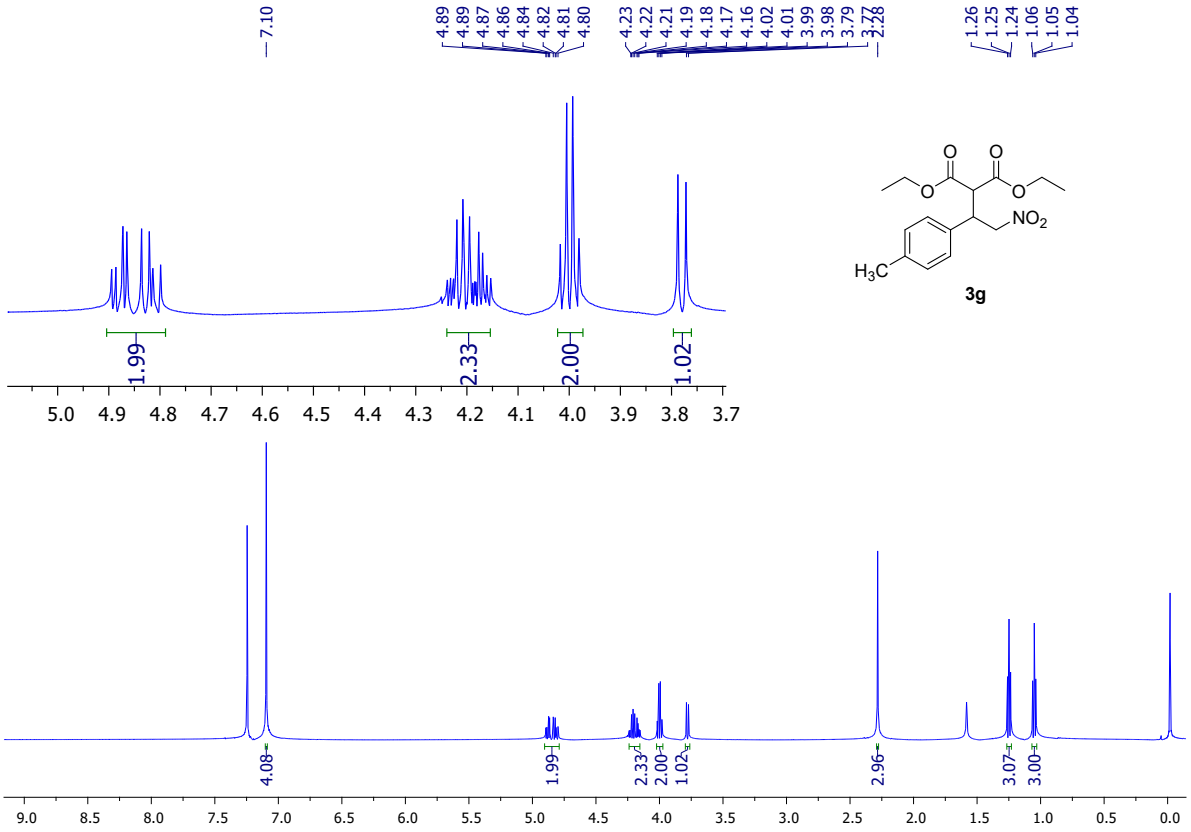
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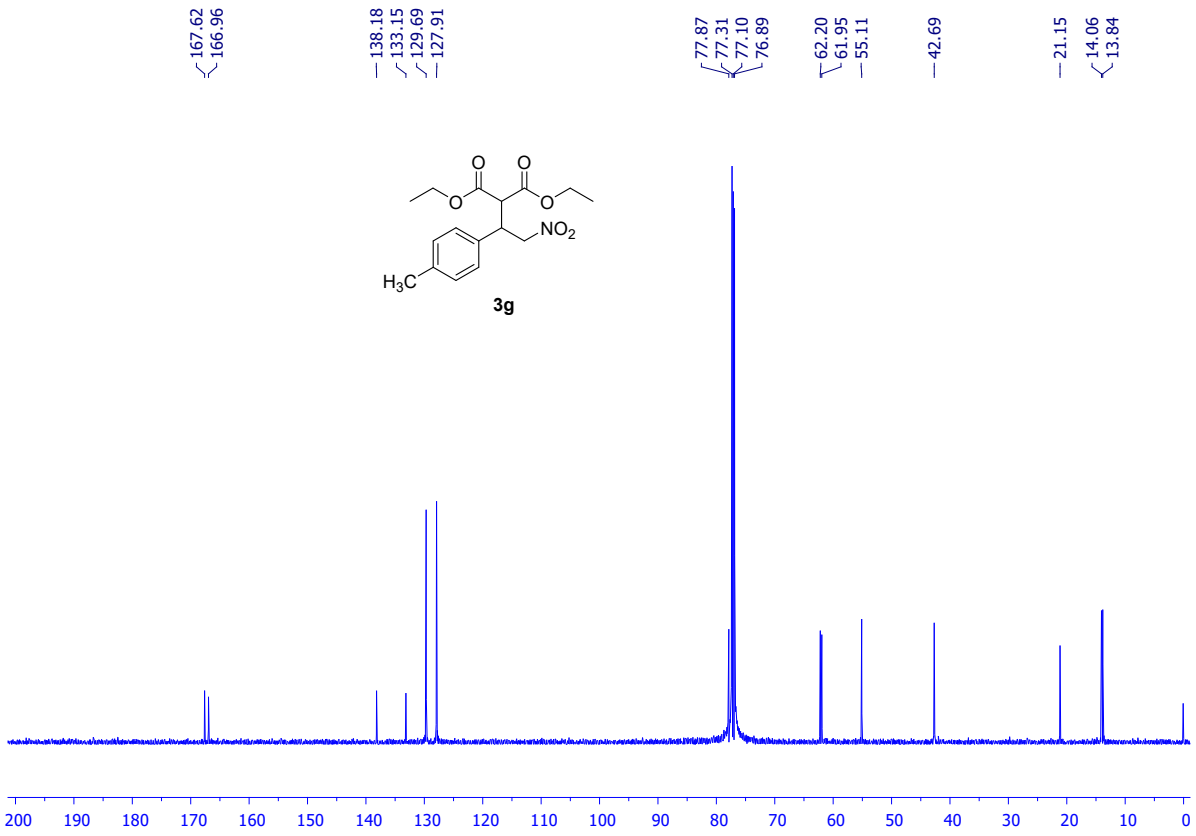
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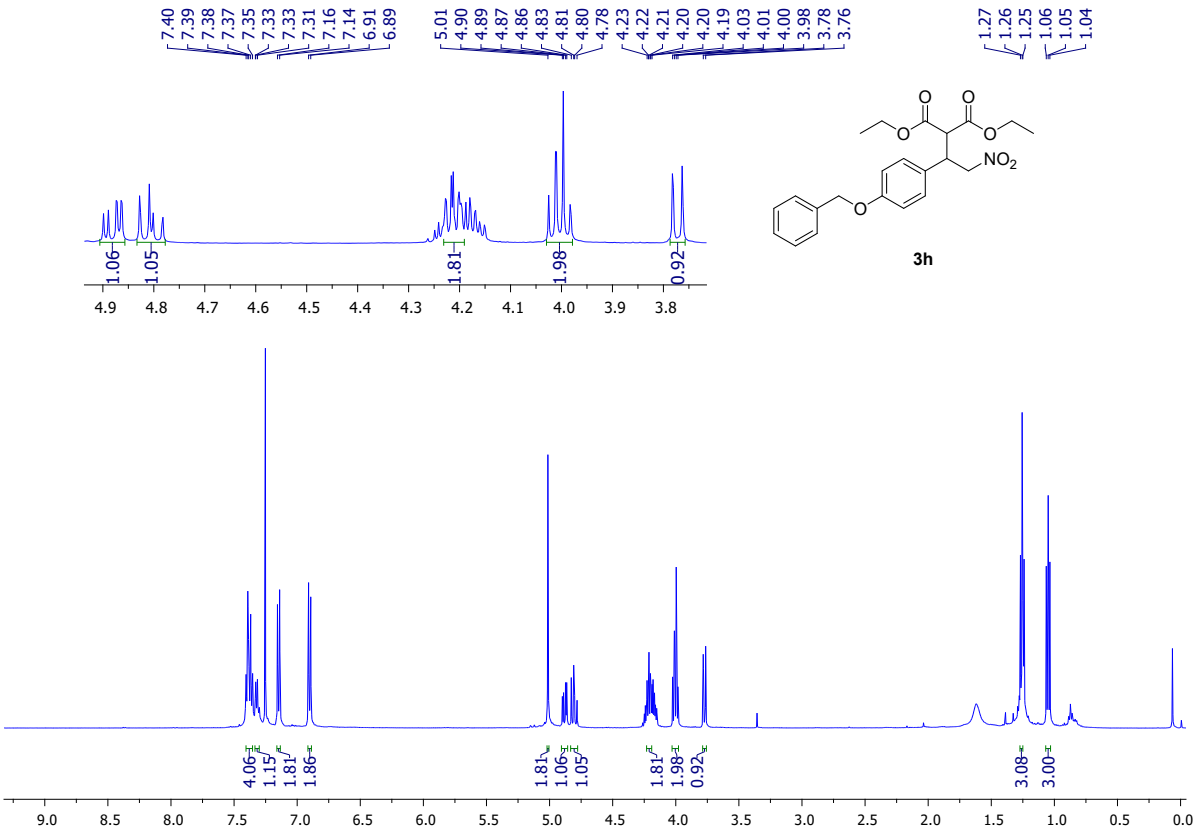
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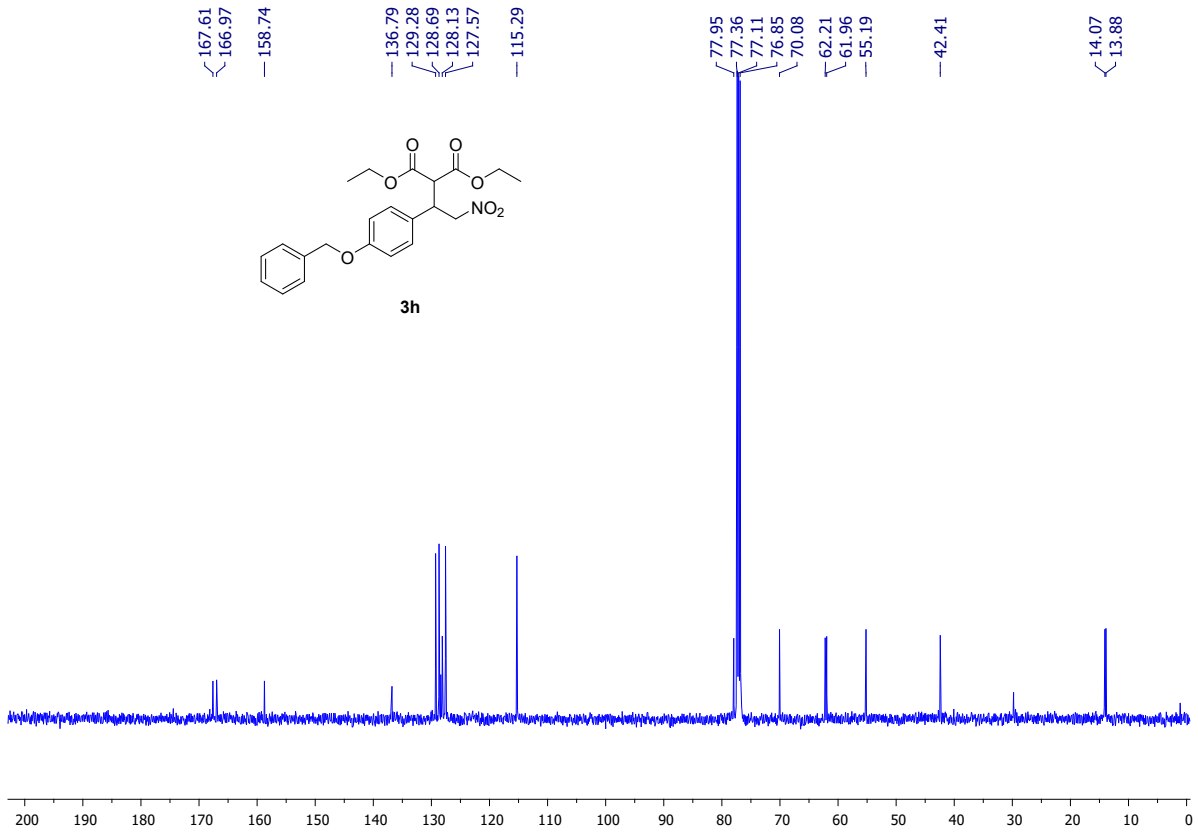
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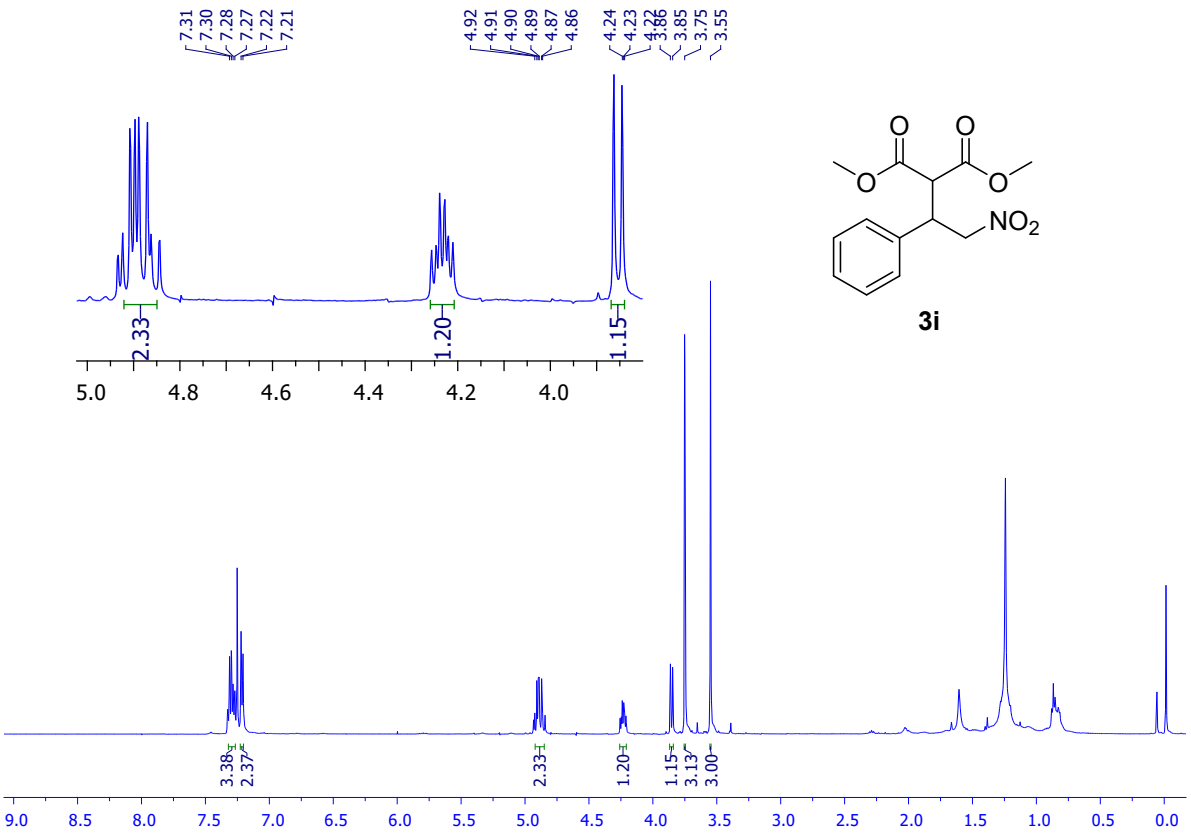
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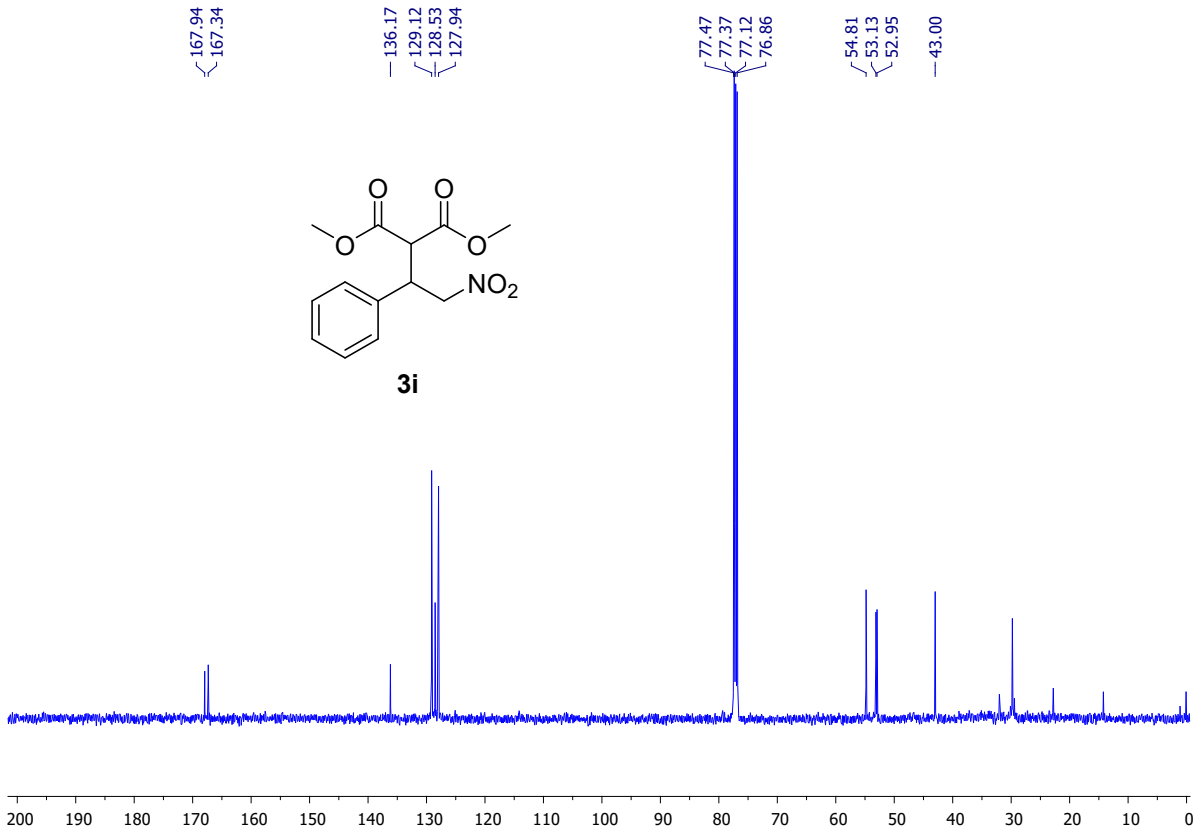
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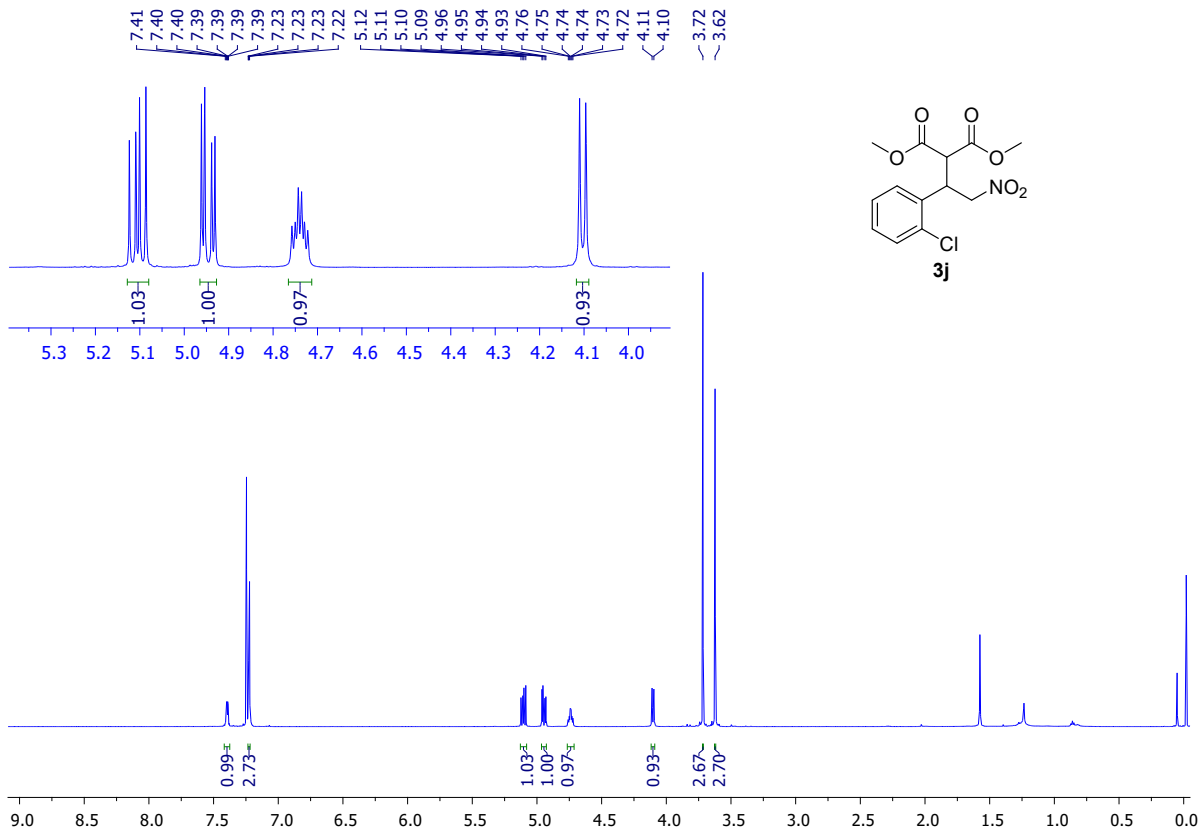
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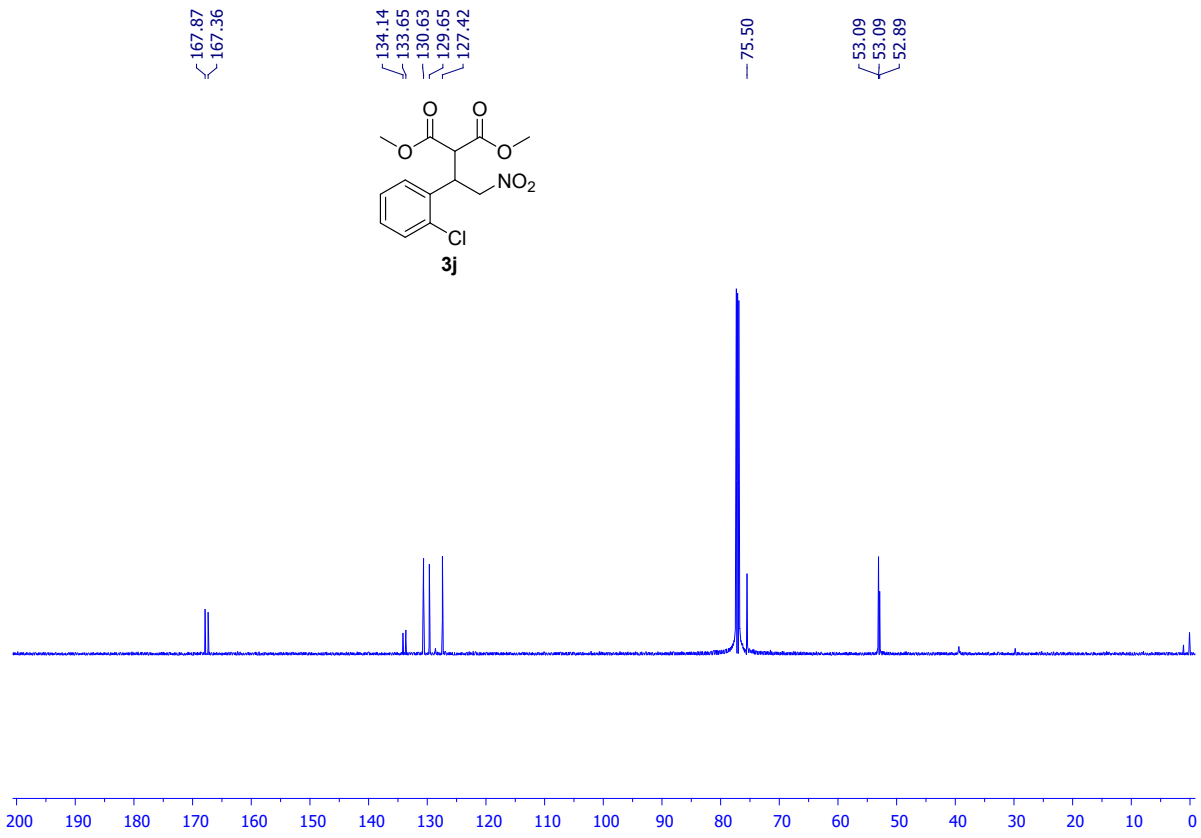
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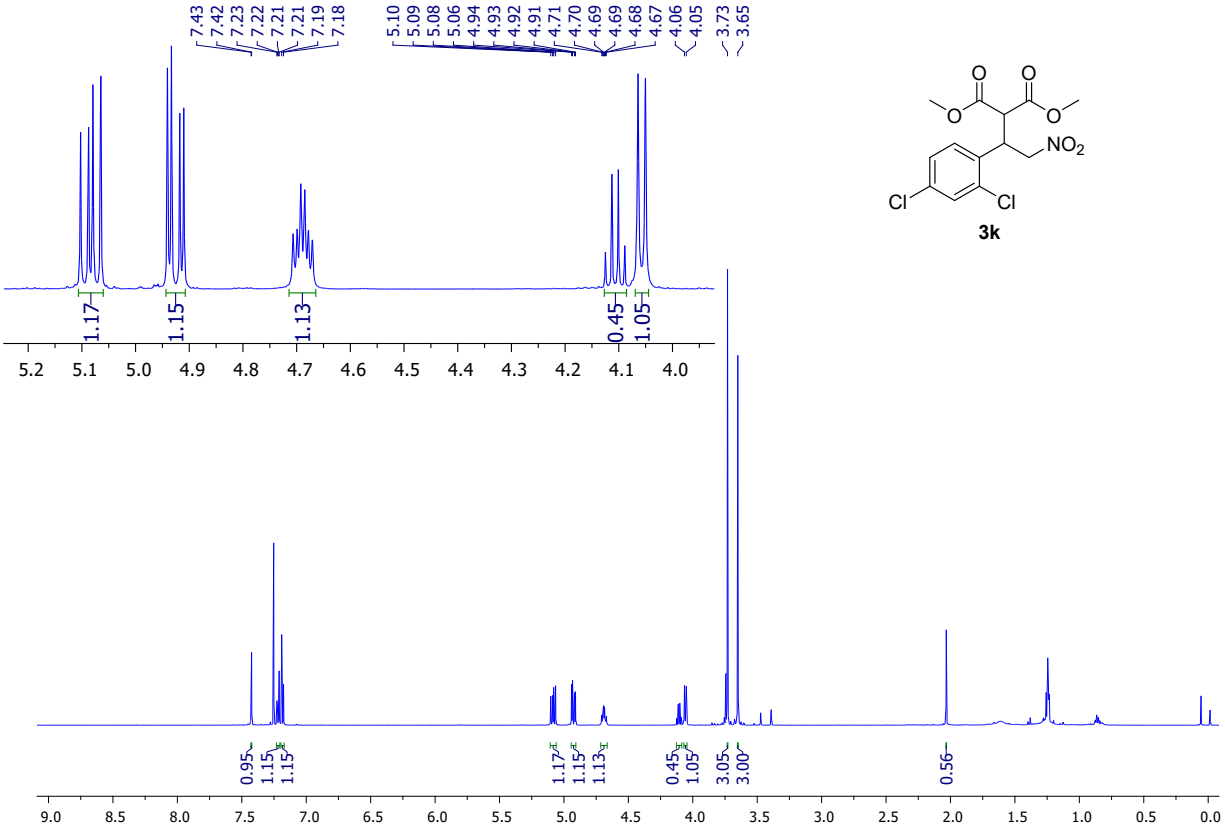
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1.05
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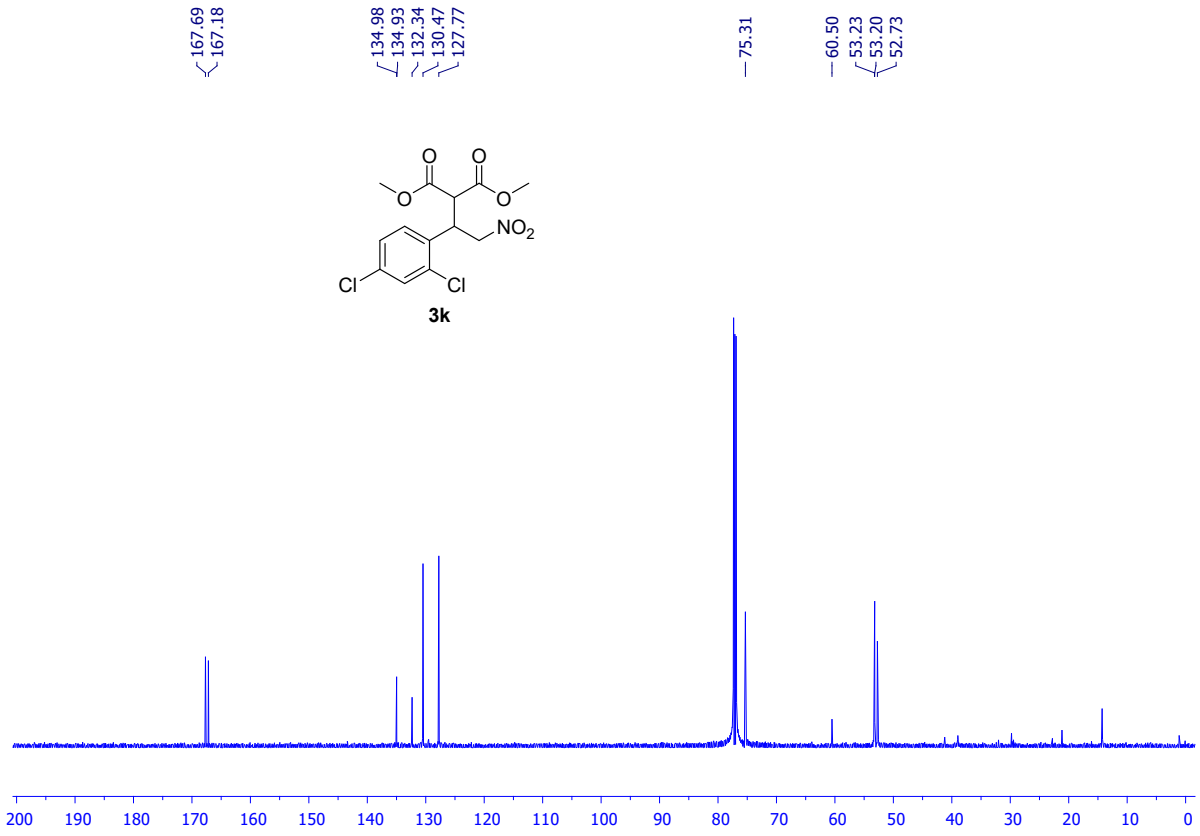
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Cl
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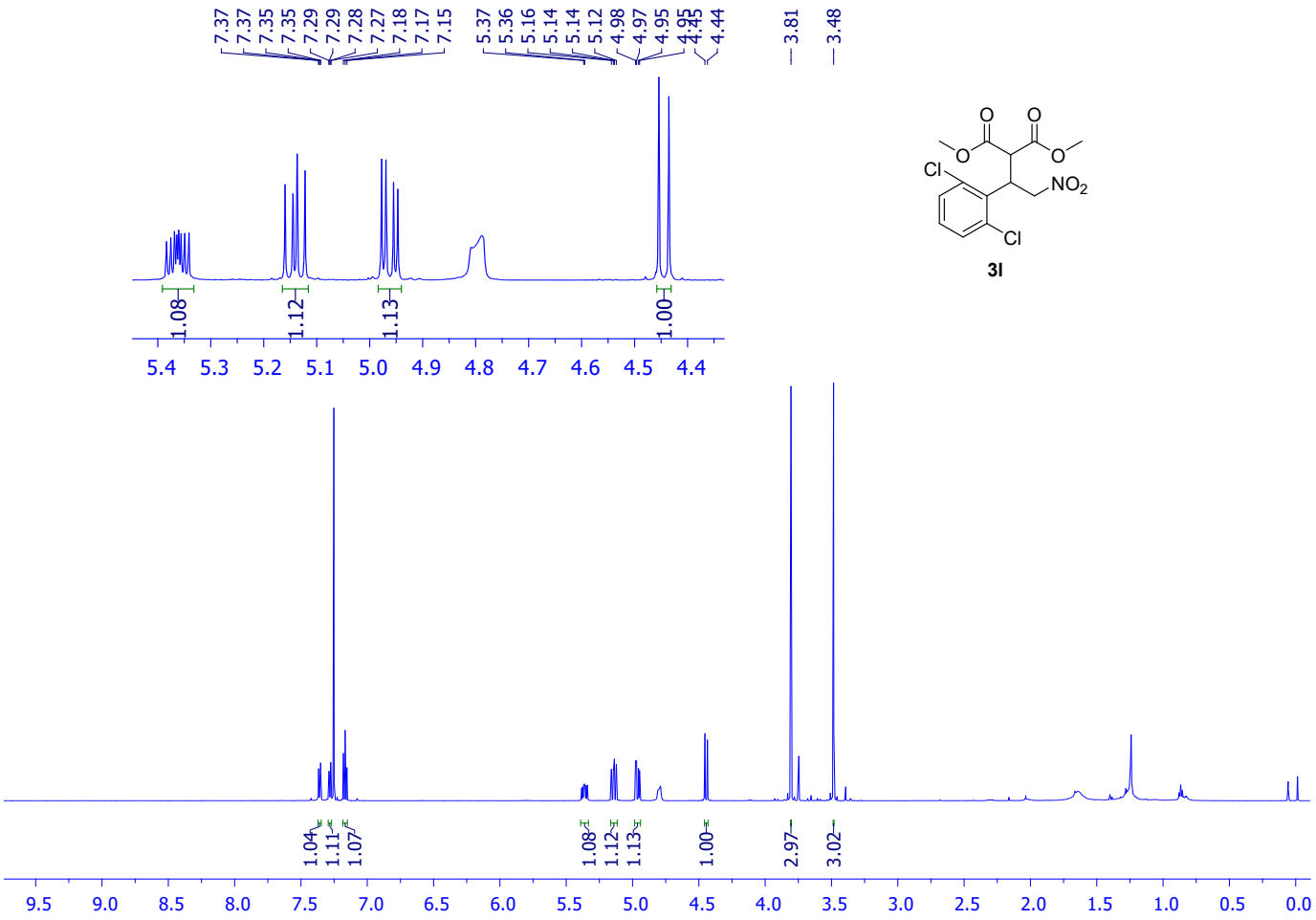
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5.14
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4.97
4.95
4.45
4.44
3.81
3.48
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1.13
1.00
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O
O
Cl
NO2
Cl
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1.08
1.12
1.13
1.00
2.97
3.02
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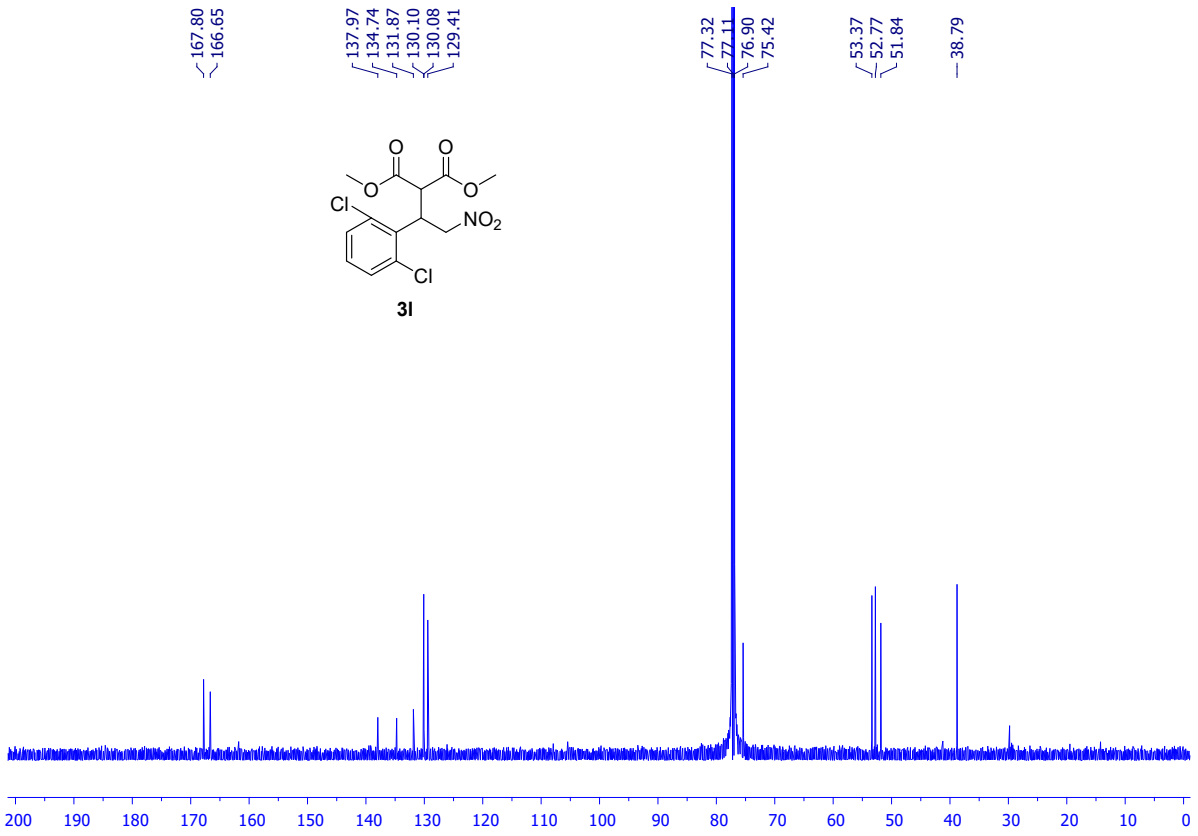
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52.77
51.84
38.79
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O
O
O
Cl
NO2
Cl
3l
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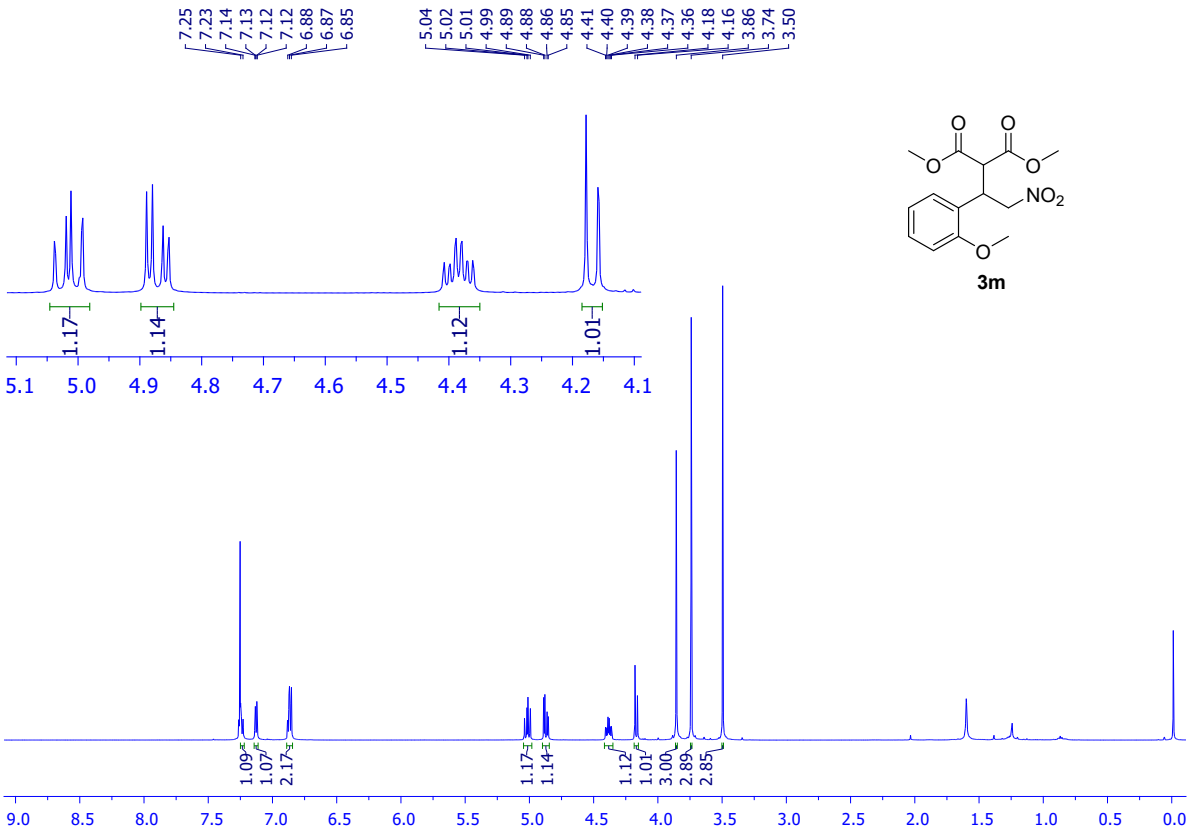
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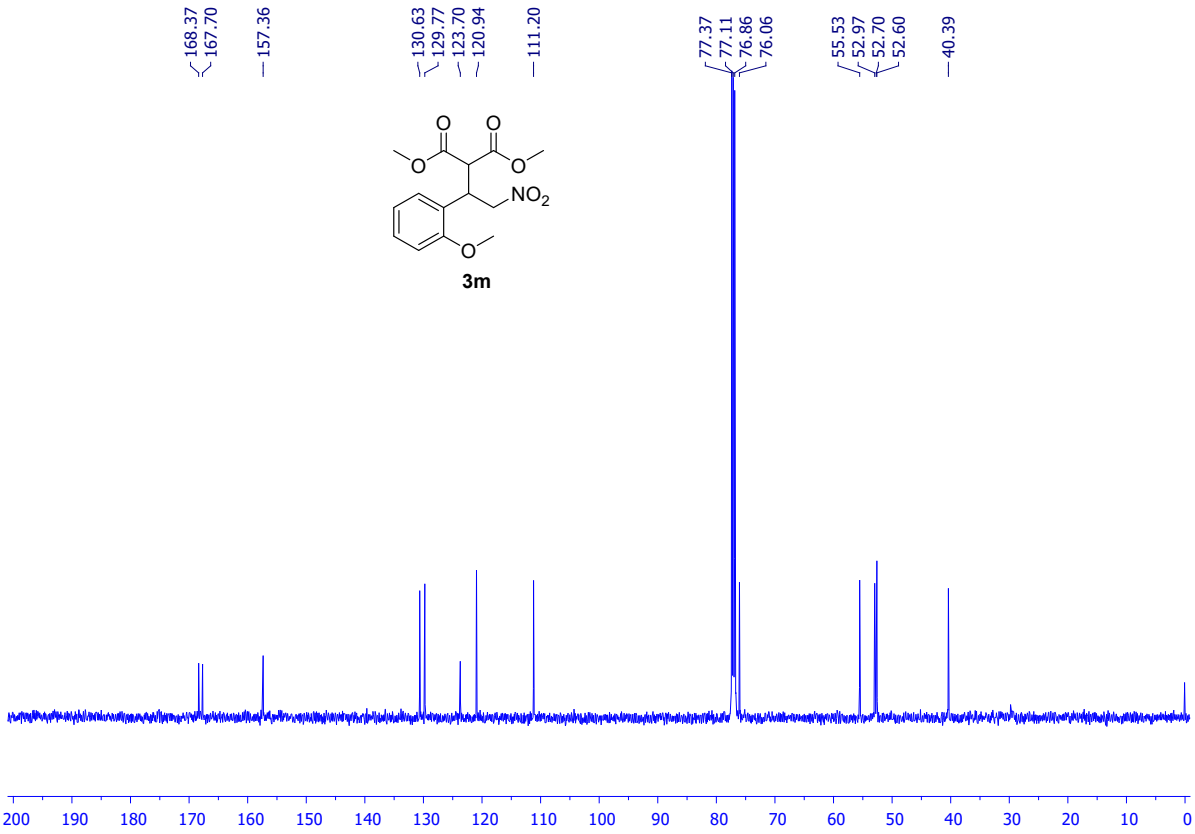
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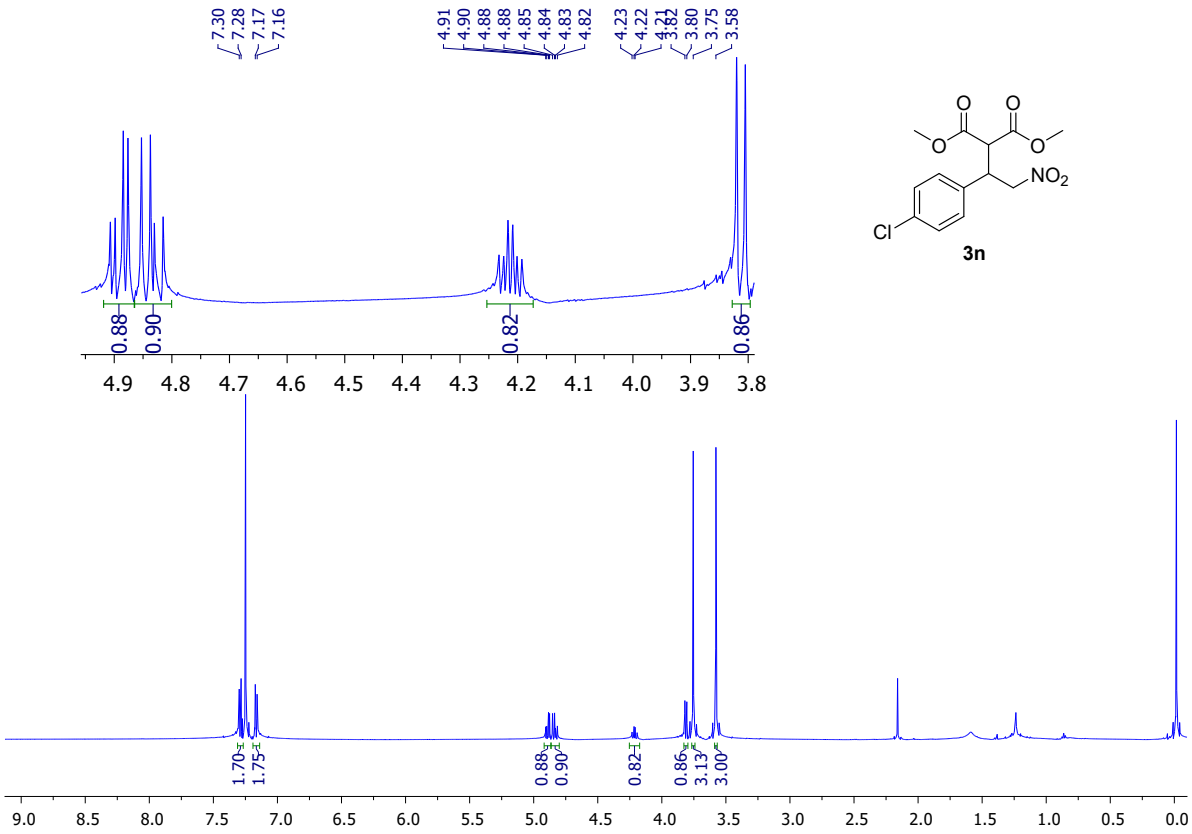
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0.82
0.86
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3.13
3.00
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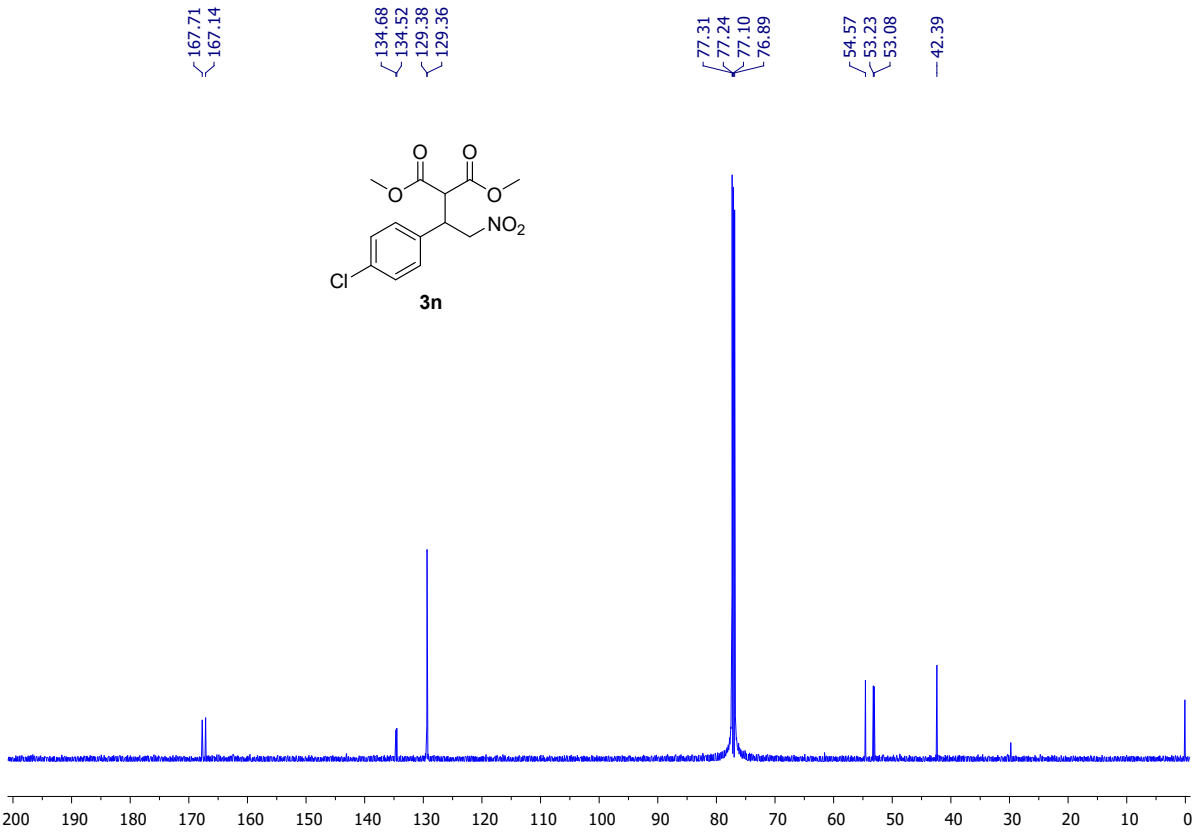
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O
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3n
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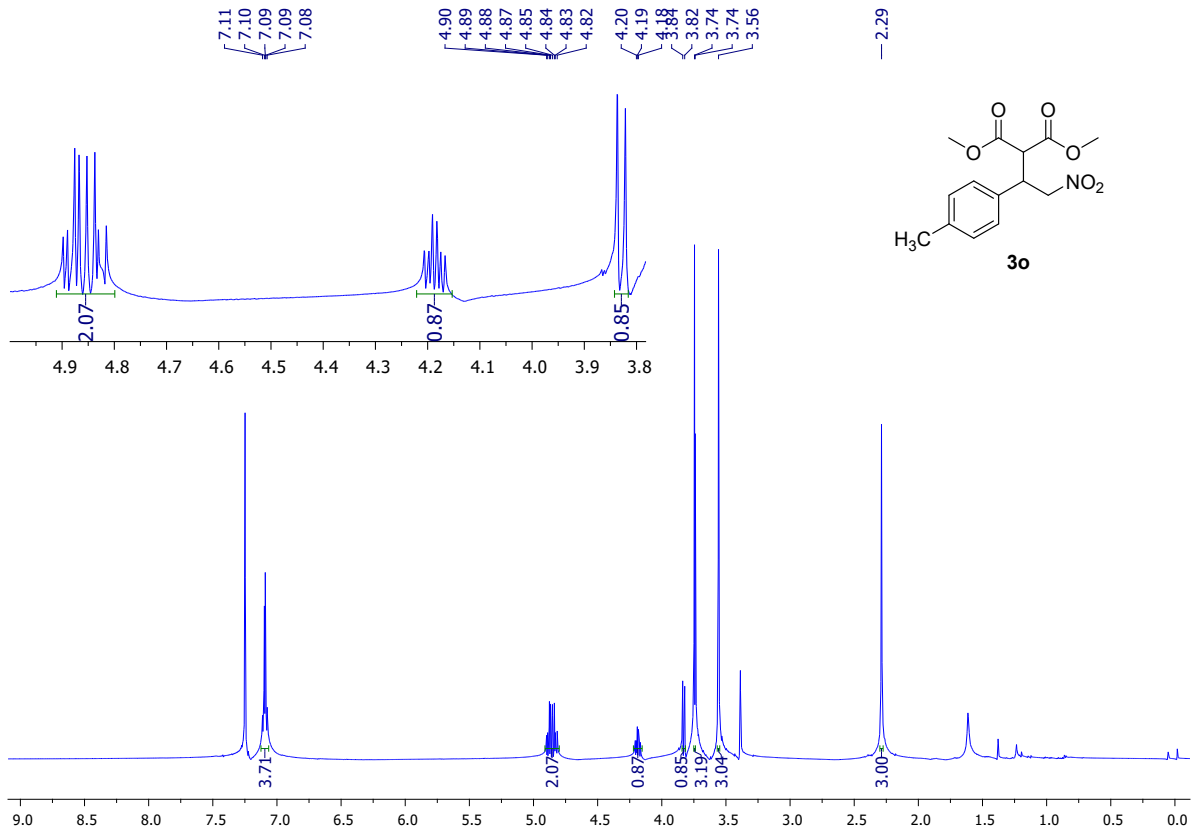
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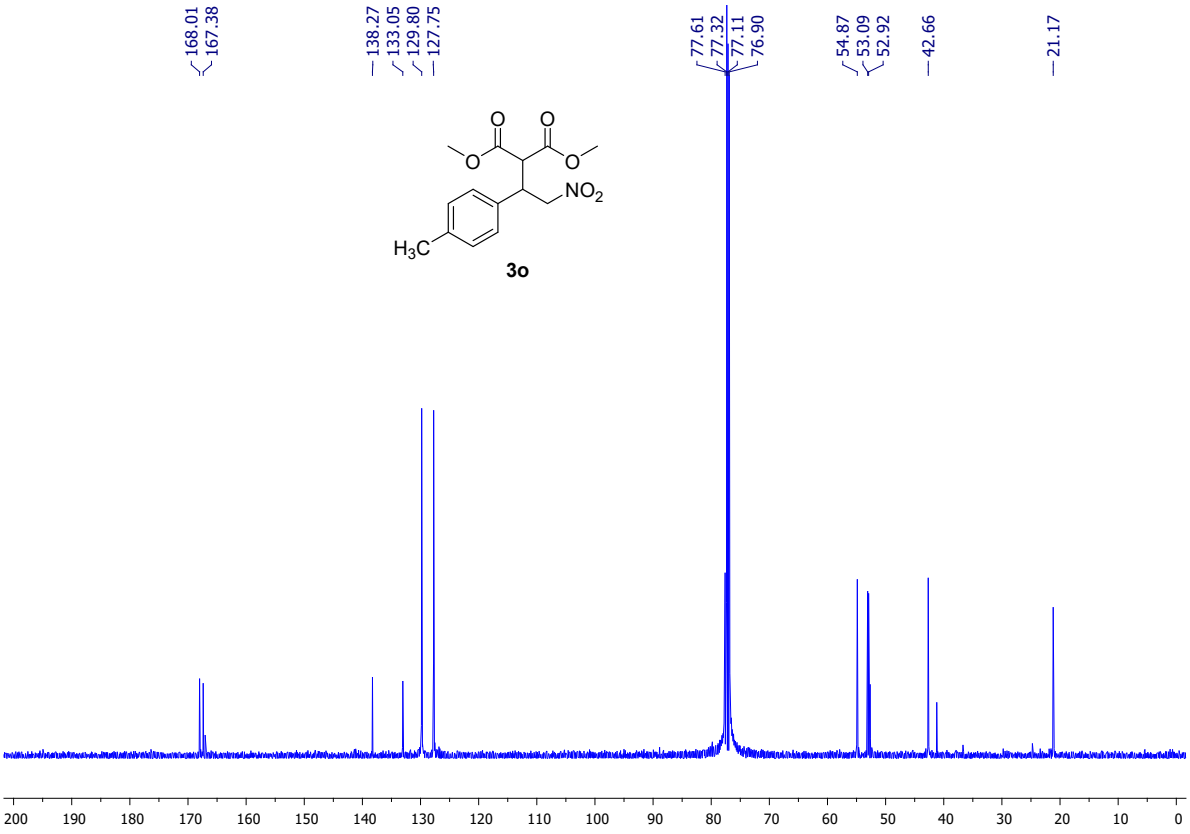
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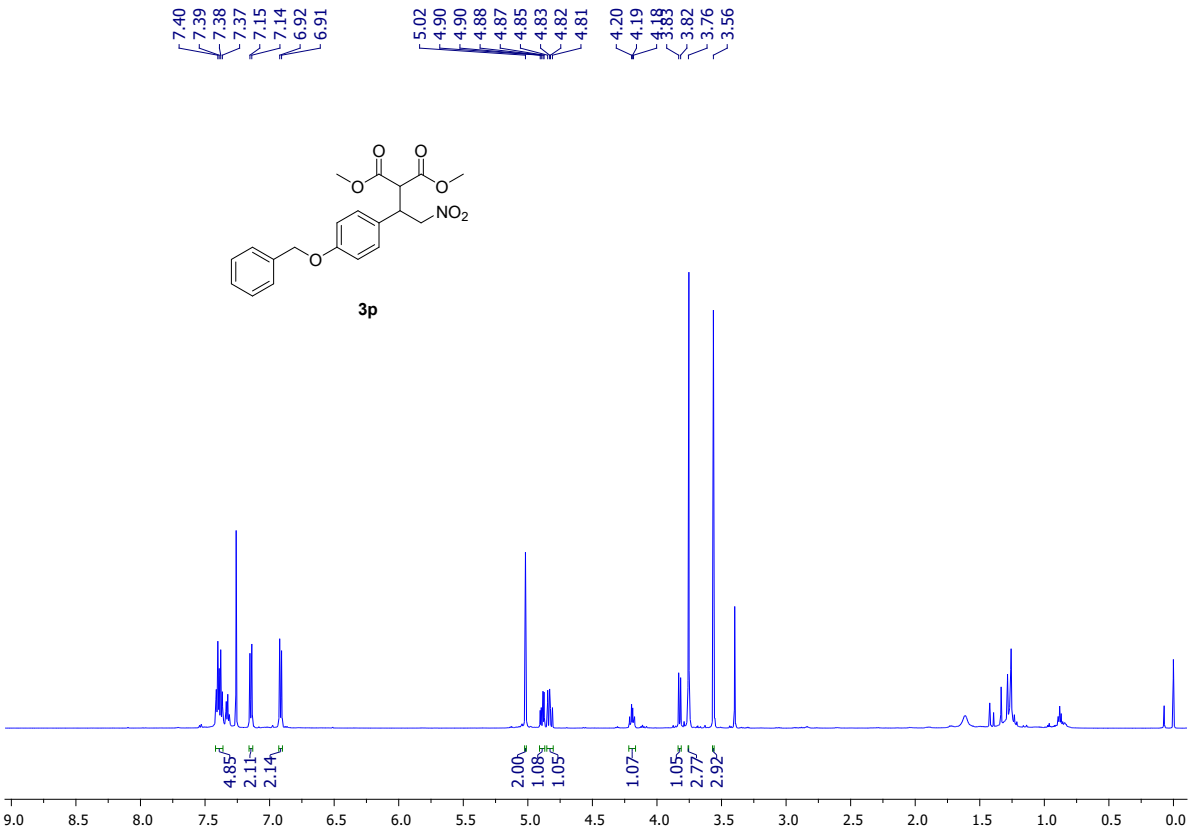
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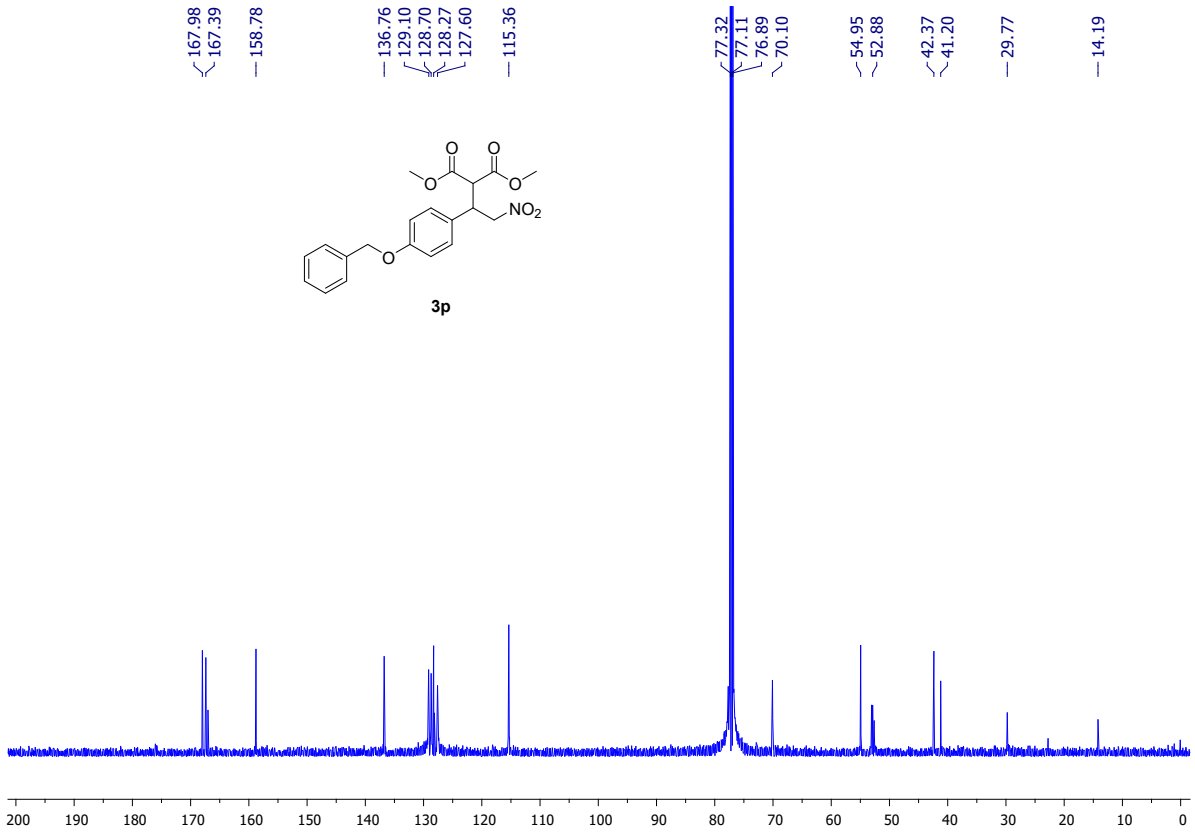
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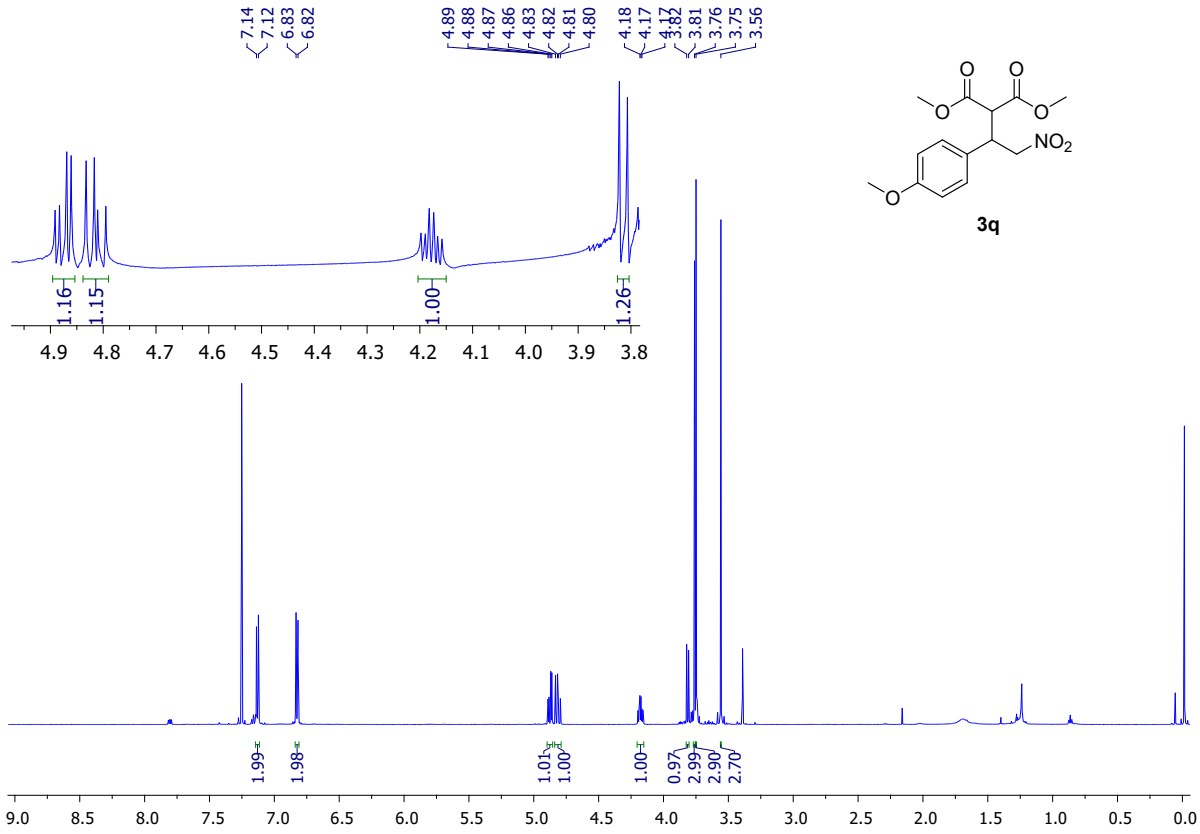
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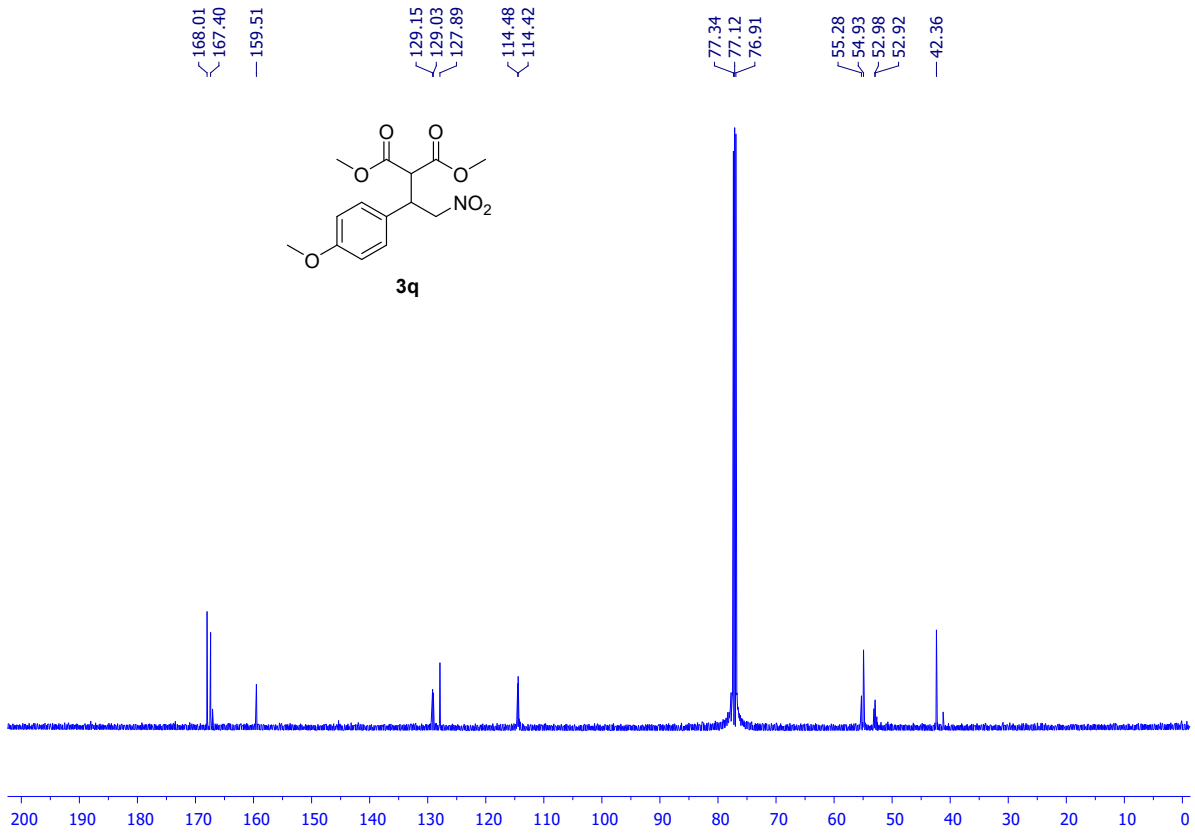
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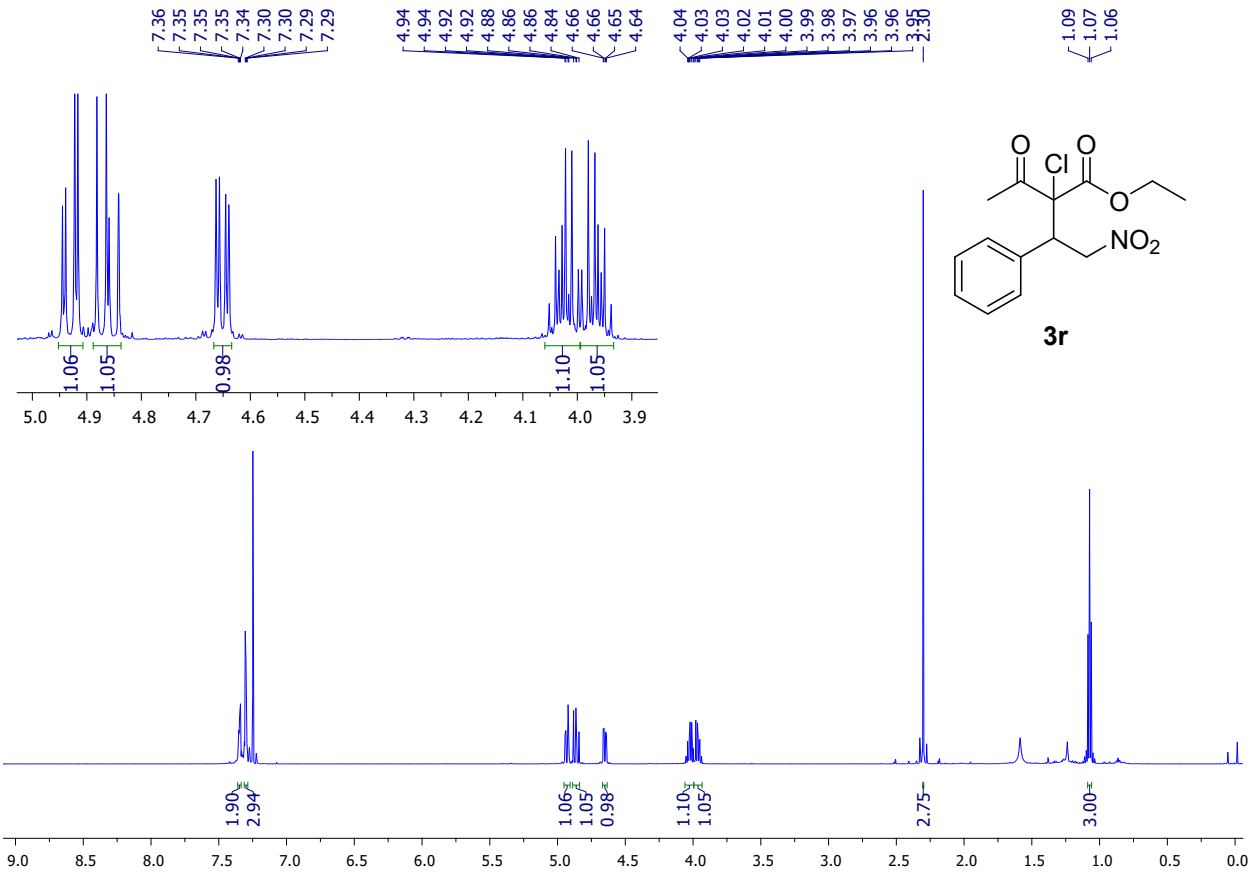
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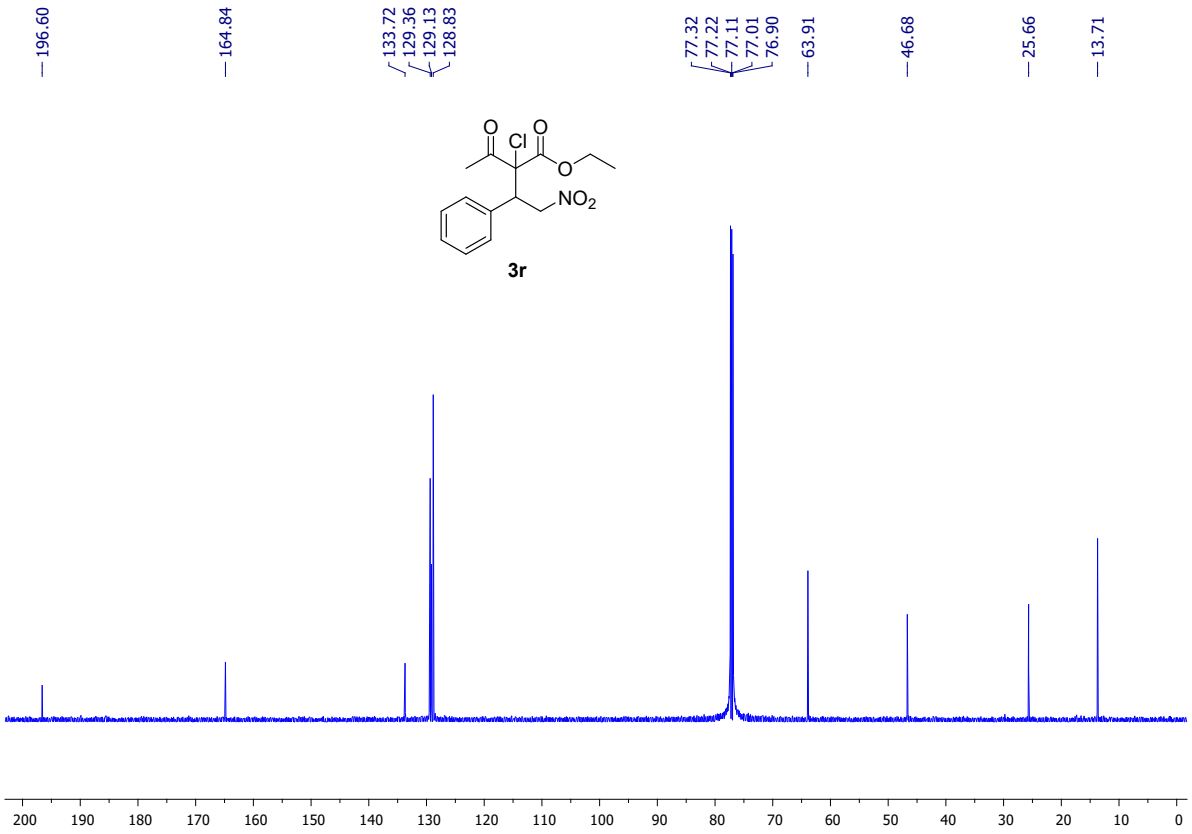
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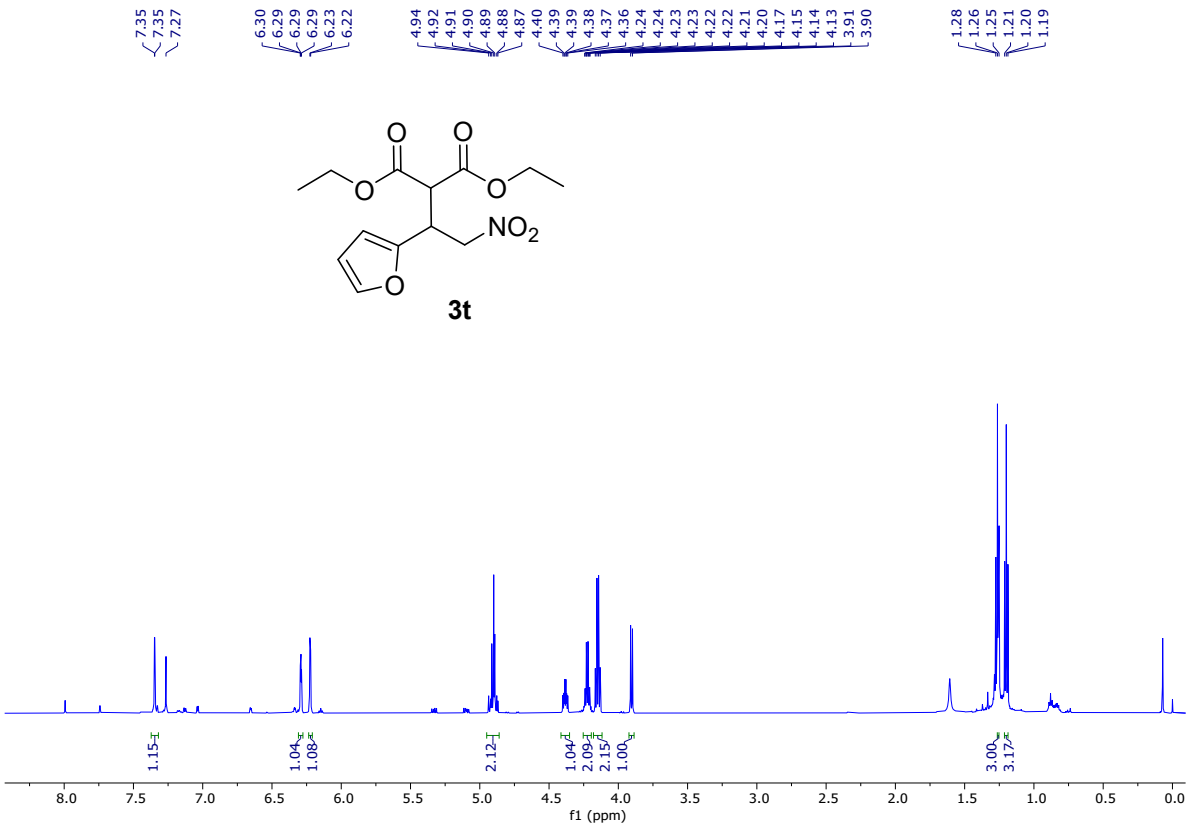
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1.0
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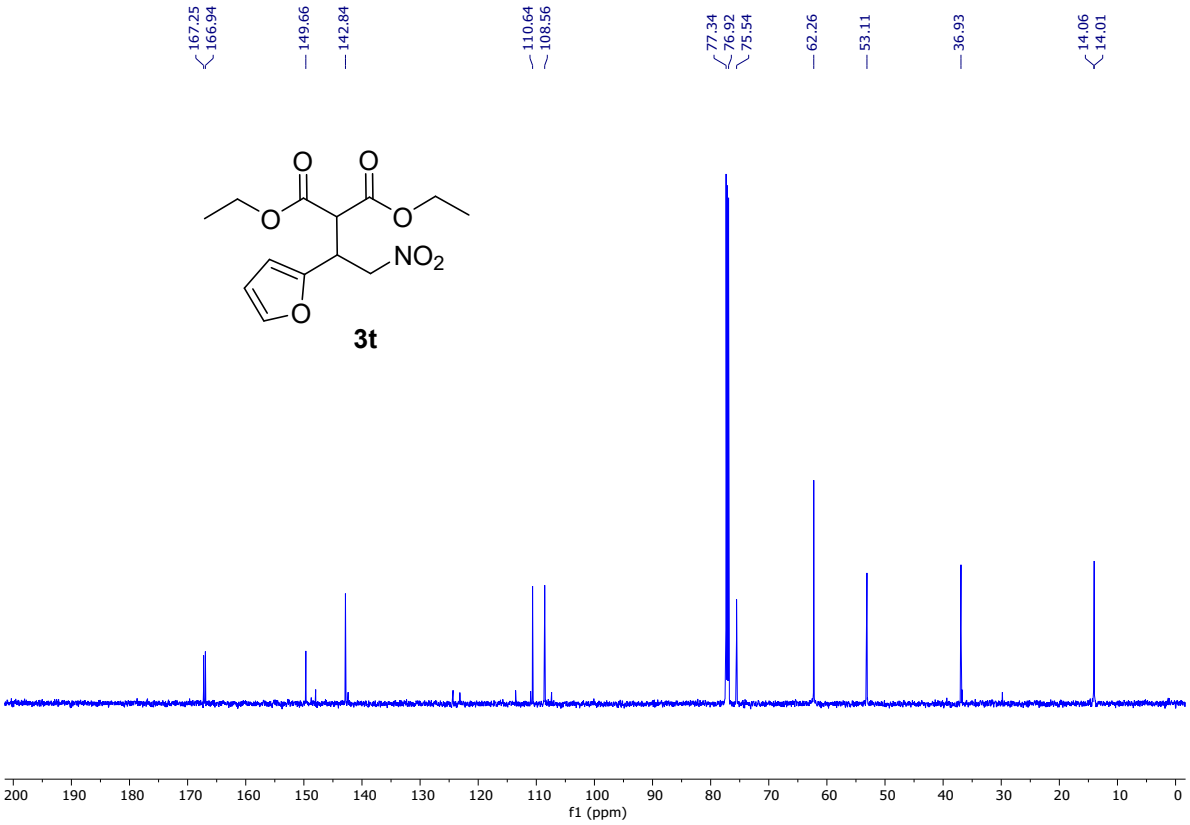
f1 (ppm)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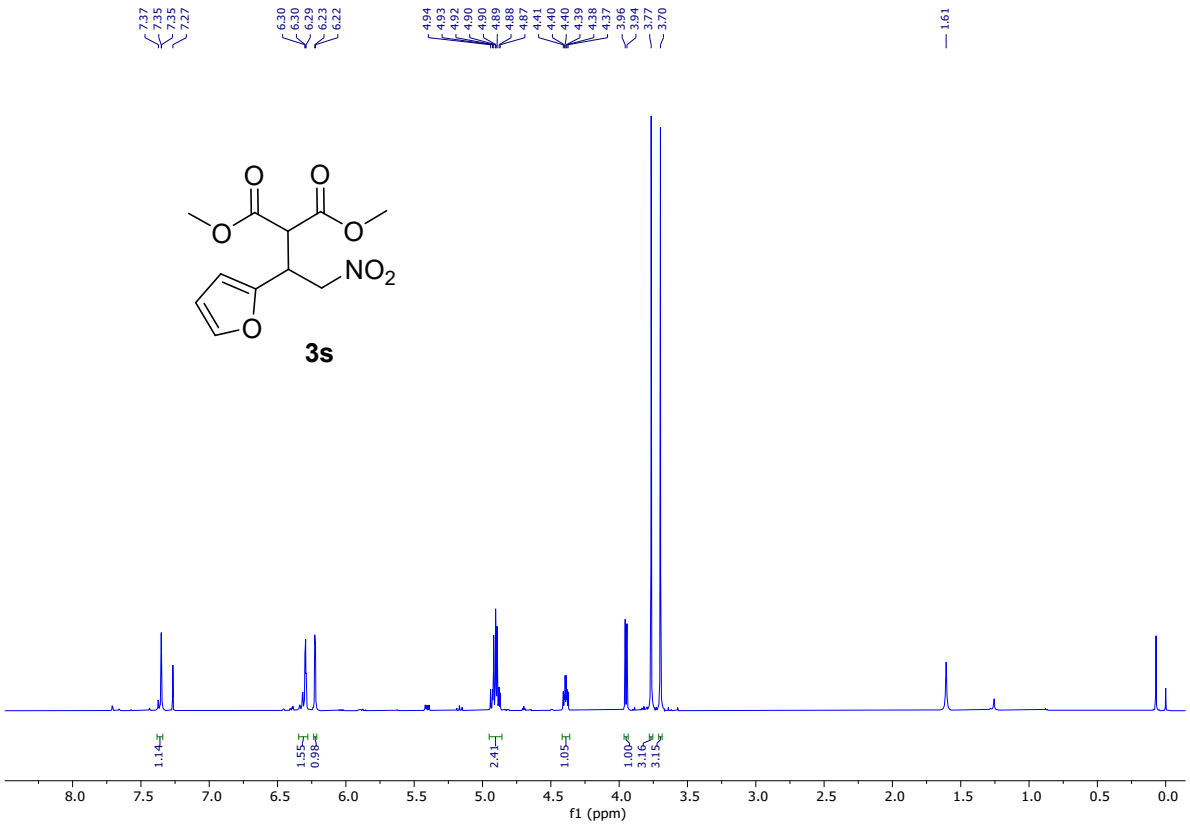
NO2
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**3t**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3.15
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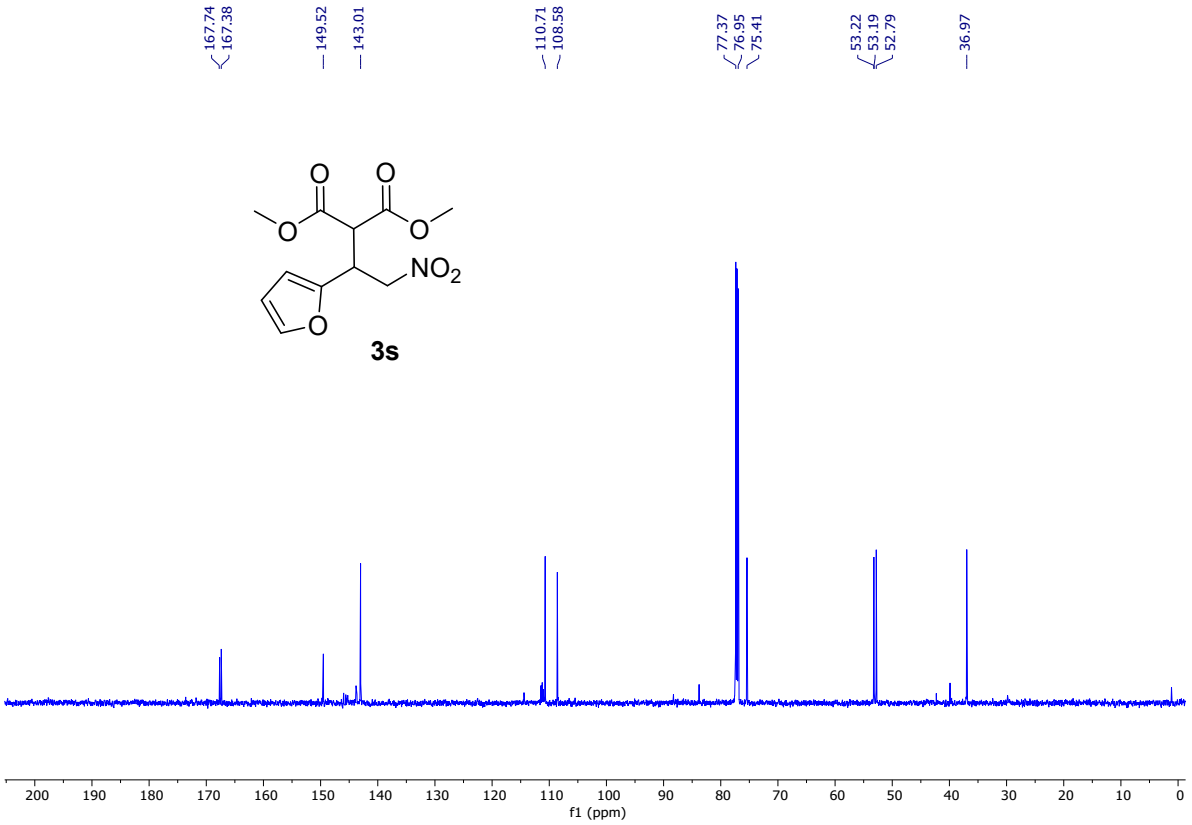
f1 (ppm)

**3s**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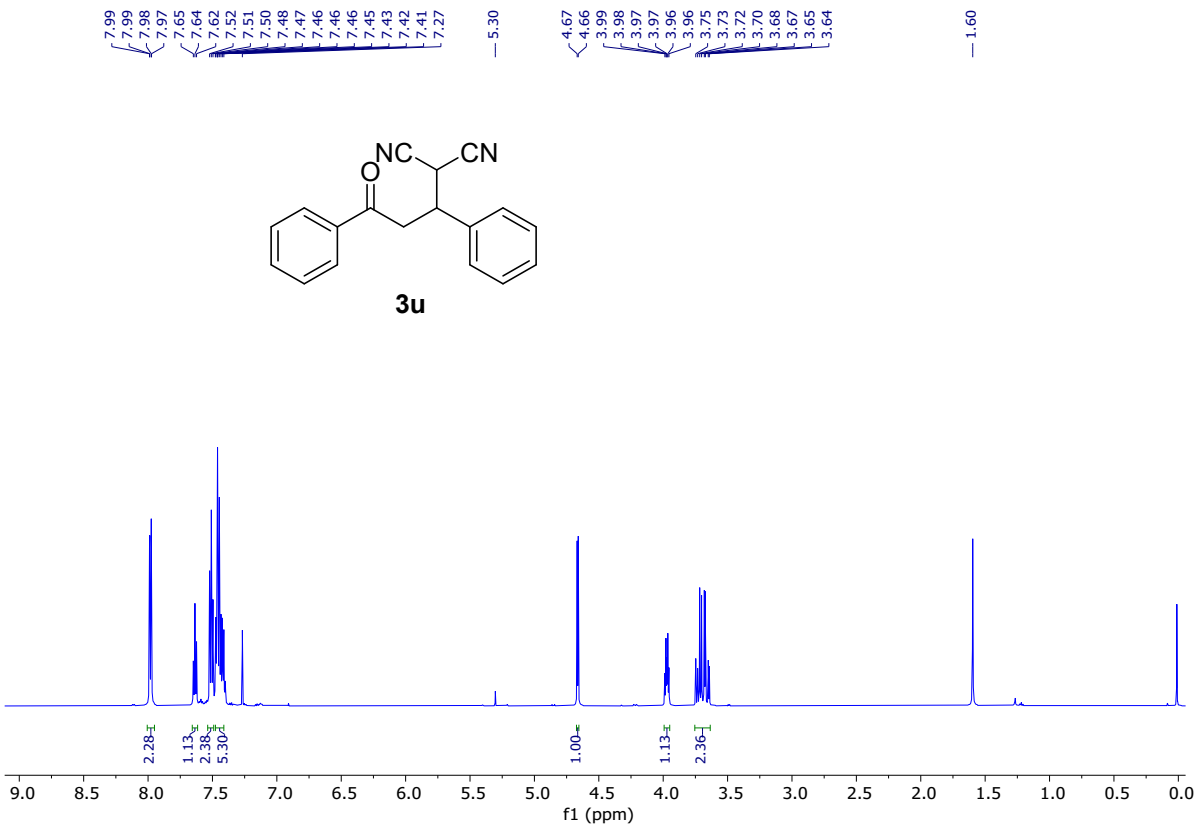
O
O
O
NO2
O
f1 (ppm)

**3s**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3.97
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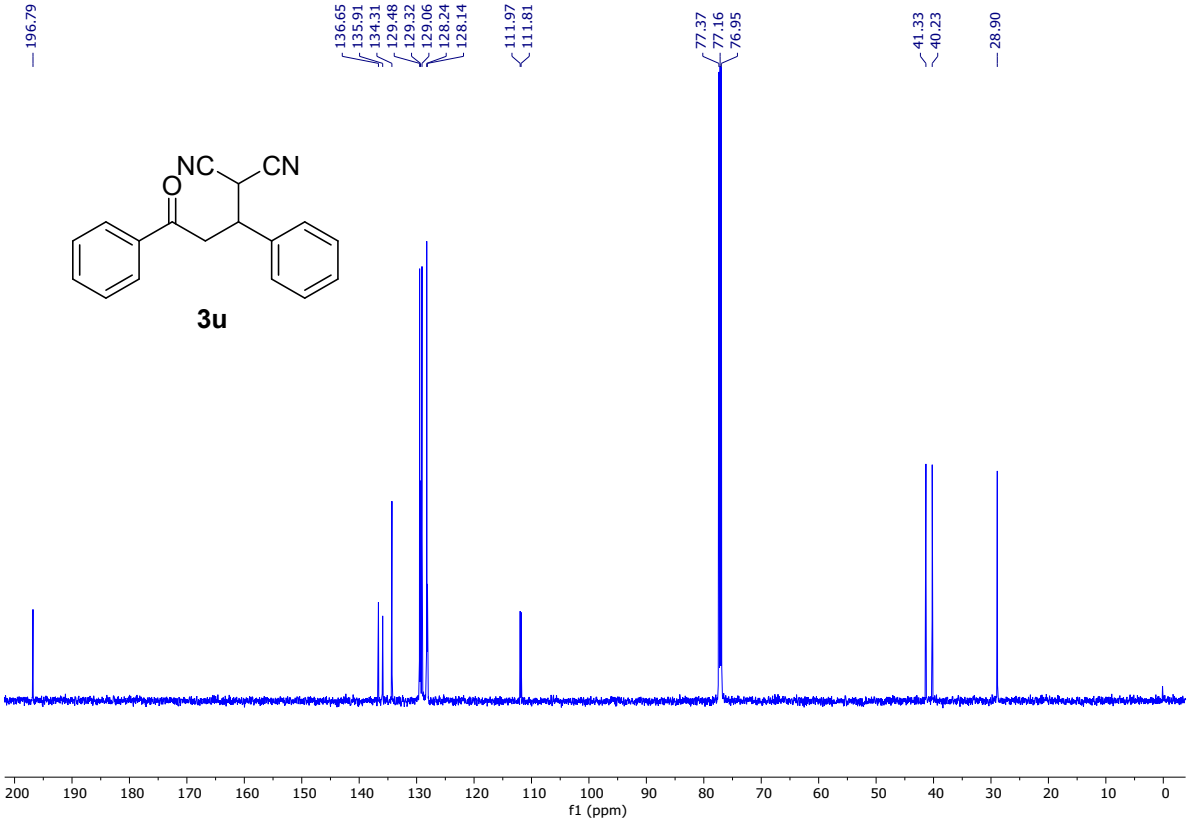
f1 (ppm)

**3u**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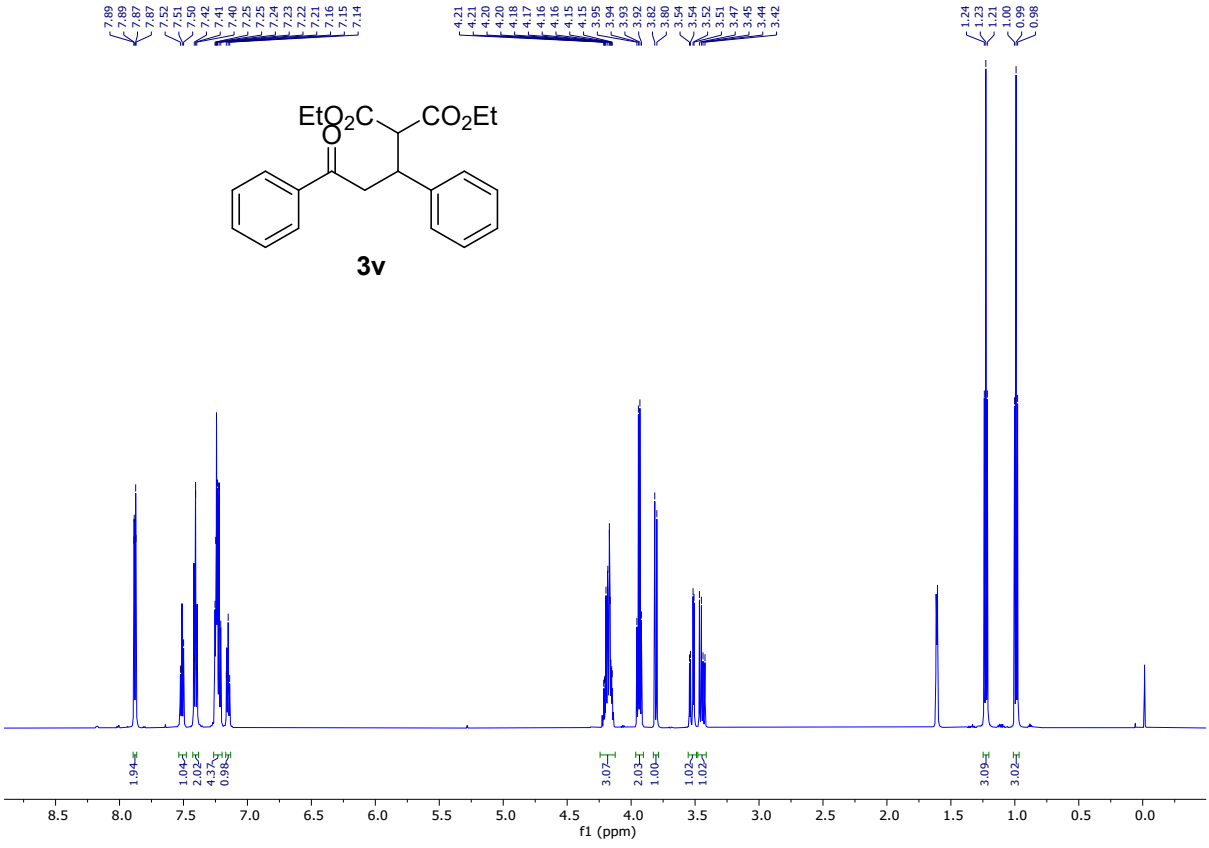
f1 (ppm)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1.21
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0.98
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CO2Et
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3v
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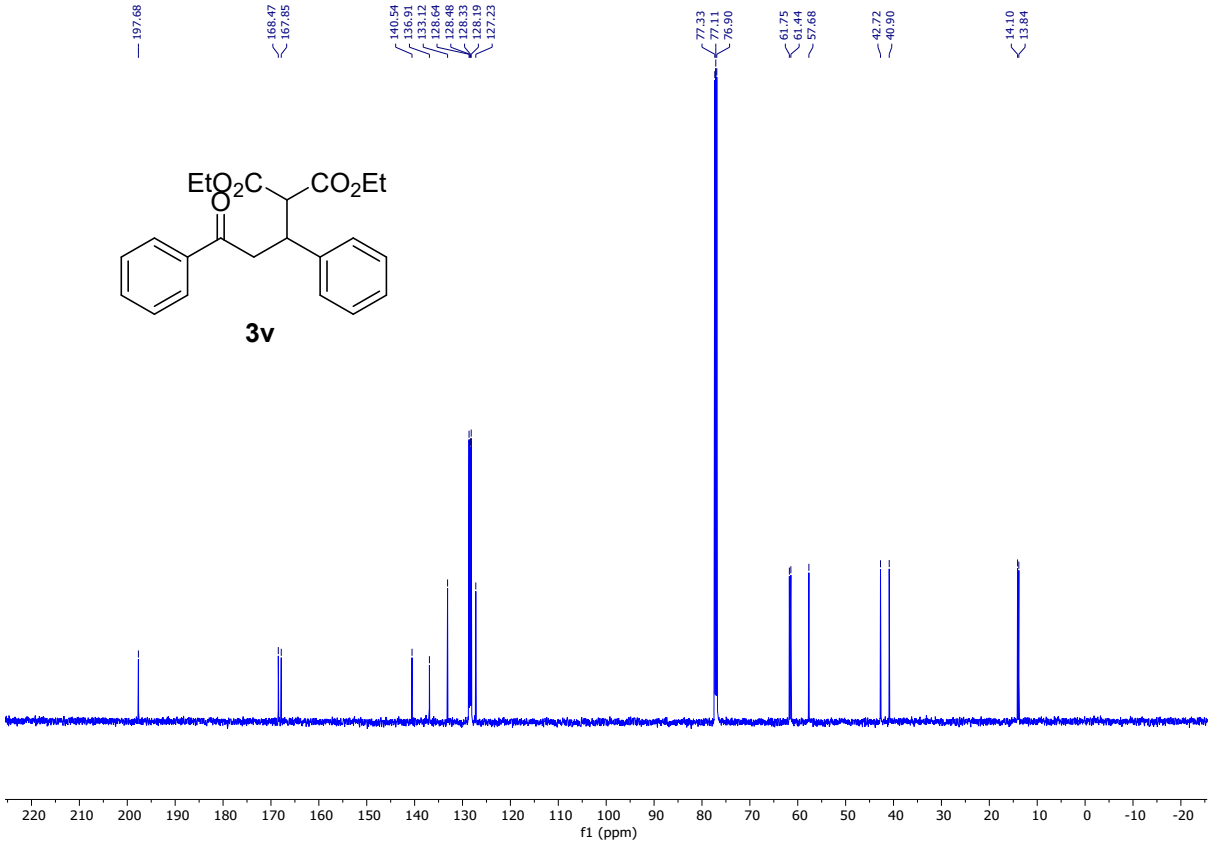
f1 (ppm)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61.75
61.44
57.68
42.72
40.90
14.10
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CO2Et
O
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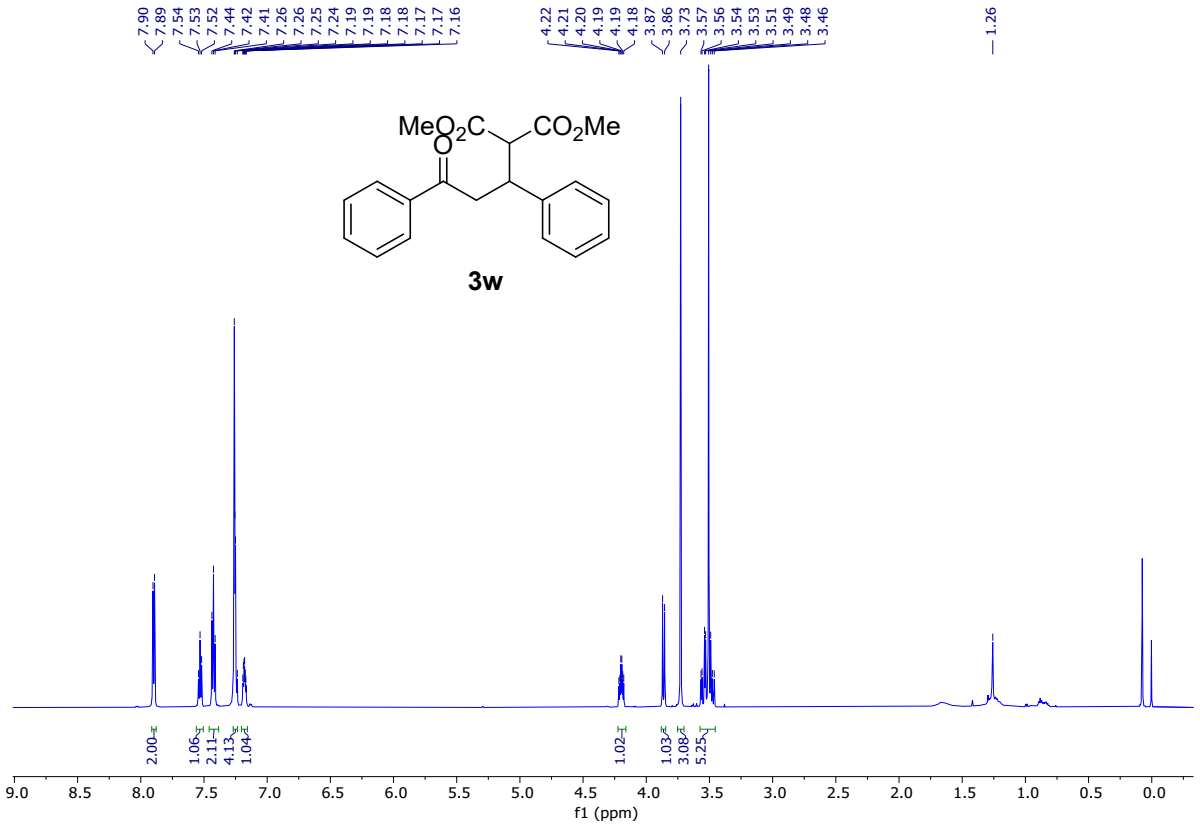
f1 (ppm)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7.18
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CO2Me
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1.03
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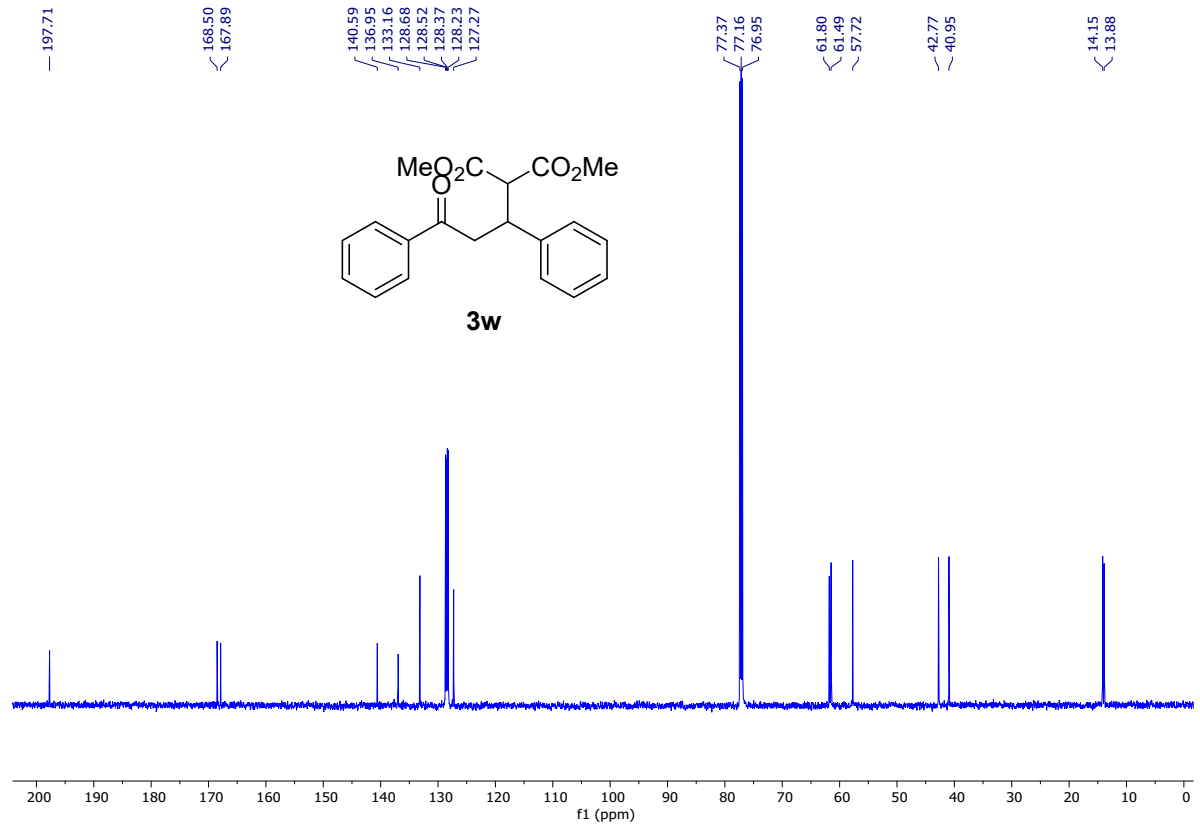
f1 (ppm)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128.52
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128.23
127.27
77.37
77.16
76.95
61.80
61.49
57.72
42.77
40.95
14.15
13.88
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CO2Me
O
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50
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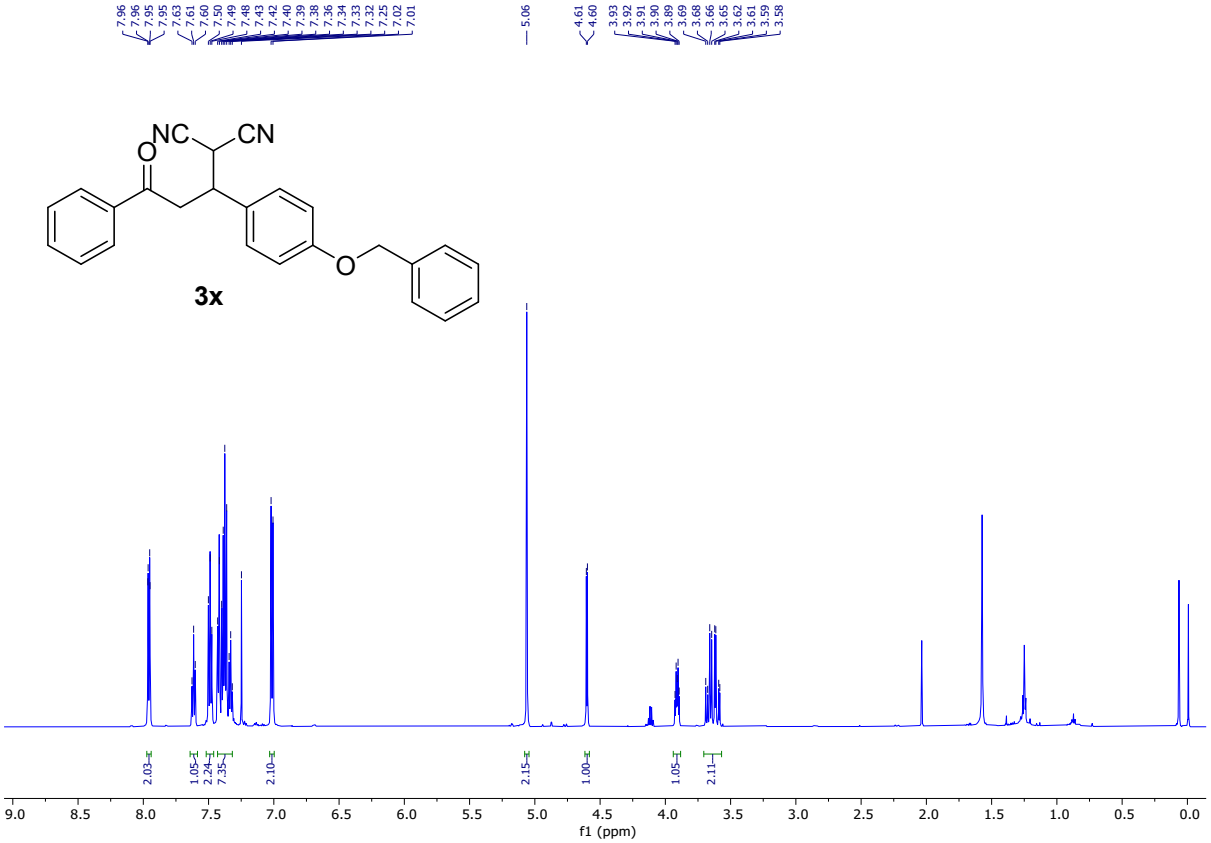
f1 (ppm)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7.32
7.25
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4.60
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3.92
3.91
3.90
3.89
3.69
3.68
3.66
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CN
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O
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1.05
2.24
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2.10
2.15
1.00
1.05
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7.0
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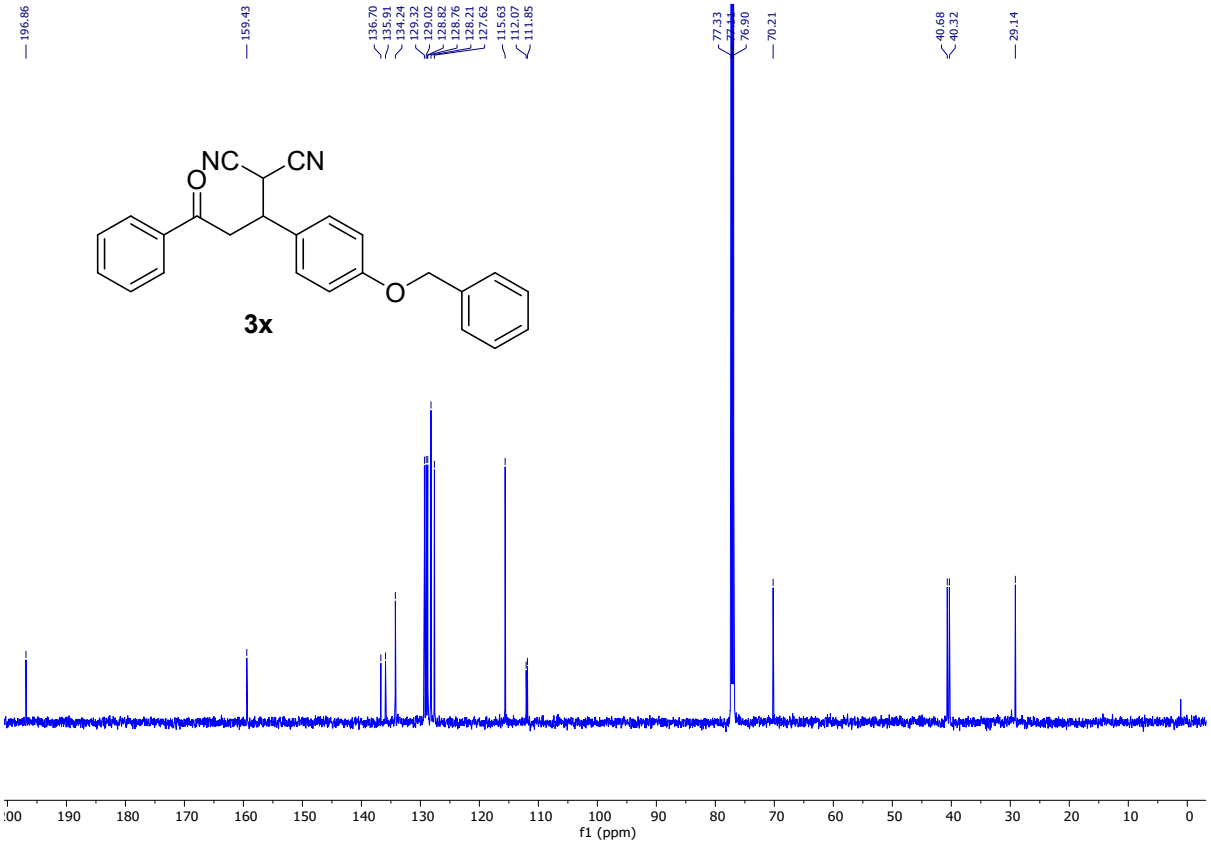
0.0
f1 (ppm)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160
150
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60
50
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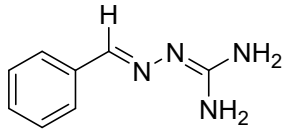
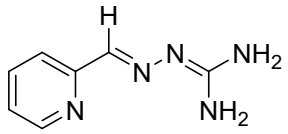
30
20
10
0
f1 (ppm)

**Characterization Data of the catalysts:**



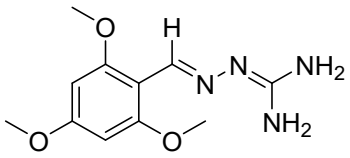
**C1**

Yield: 580 mg, 95%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 7.95 (s, 1H), 7.63-7.62 (d, *J* = 7.62 Hz, 2H), 7.30-7.27 (t, *J* = 7.28 Hz, 2H), 7.22-7.19 (t, *J* = 7.21 Hz, 1H), 5.89 (br.s, 1H), 5.80 (br. s., 1H) - ; $^{13}$C NMR 161.10, 143.66, 137.49, 128.86, 128.20, 126.73; IR (FTIR) -NH (3428 $cm^{-1}$), C=N (1637 $cm^{-1}$). HRMS (ESI) m/z 163.0978 ($M+H^+$), calc. for $C_8H_{11}N_4^+$ 163.1024.



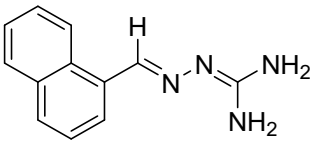
**C2**

Yield: 510 mg, 84%, white solid; $^1$H NMR (500 MHz, DMSO- *d6*) δ 8.43 – 8.42 (d, *J* = 8.42 Hz, 1H), 8.04 – 8.03 (d, *J* = 8.03 Hz, 1H), 7.93 (br. s., 1H), 7.68 - 7.65 (t, *J* = 7.66 Hz, 1H), 7.18 – 7.16 (dd, *J* = 7.17 Hz, 1H), 6.15 (br.s, 1H), 5.87 (br. s., 1H); $^{13}$C NMR 161.73, 156.26, 149.39, 143.87, 136.40, 122.74, 119.80; IR (FTIR) -NH (3456 $cm^{-1}$), C=N (1567 $cm^{-1}$). HRMS (ESI) m/z 164.0953 ($M+H^+$), calc. for $C_7H_{10}N_5^+$ 164.0931.



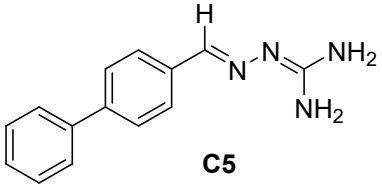
**C3**

Yield: 464 mg, 90%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 8.09 (br. s., 1H), 6.19 (br. s., 2H), 5.54 (br. s., 2H), 5.23 (br. s., 2H), 3.75 (br. s., 3H), 3.75 (br. s., 6H); 13C NMR 160.87, 159.89, 159.78, 139.54, 107.23, 91.73, 56.37, 55.76; IR (FTIR) CN (2342 cm-1), P=O (1182 cm-1). HRMS (ESI) m/z 253.1280 ($M+H^+$), calc. for $C_{11}H_{17}N_4O_3^+$ 253.1295.



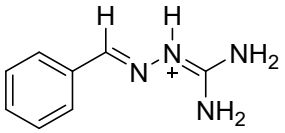
**C4**

Yield: 502 mg, 92%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 8.68 (br. s., 1H), 8.63 – 8.62 (d, *J* = 8.62 Hz, 1H), 7.98 – 7.96 (d, *J* = 7.97 Hz, 1H), 7.90 – 7.88 (d, *J* = 7.87 Hz, 1H), 7.81 – 7.79 (d, *J* = 7.80 Hz, 1H), 7.54 – 7.44 (m, 4H), 5.94 (br. s., 2H), 5.60 (br. s., 2H),; 13C NMR 161.24, 142.51, 134.08, 132.71, 130.73, 129.02, 128.39, 126.96, 126.25 126.08, 125.48, 124.52; IR (FTIR) -NH (3451 cm-1), C=N (1637 cm-1). HRMS (ESI) m/z 213.1187 ($M+H^+$), calc. for $C_{12}H_{13}N_4^+$ 213.1135.



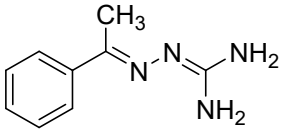
**C5**

Yield: 495 mg, 94%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 7.99 (br. s., 1H), 7.73 – 7.71 (d, *J* = 7.72 Hz, 2H), 7.66 – 7.64 (d, *J* = 7.65 Hz, 2H), 7.61 – 7.59 (d, *J* = 7.60 Hz, 2H), 7.44 – 7.41 (t, *J* = 7.42 Hz, 2H), 7.33 – 7.30 (t, *J* = 7.32 Hz, 1H), 6.04 (br. s., 2H), 5.67 (br. s., 2H); 13C NMR 161.10, 143.16, 140.32, 139.72, 136.67, 129.47, 127.91, 127.30, 127.12, 126.98; IR (FTIR) -NH (3450 cm-1), C=N (1586 cm-1). HRMS (ESI) m/z 239.1345 ($M+H^+$), calc. for $C_{14}H_{15}N_4^+$ 239.1291.



**C6**

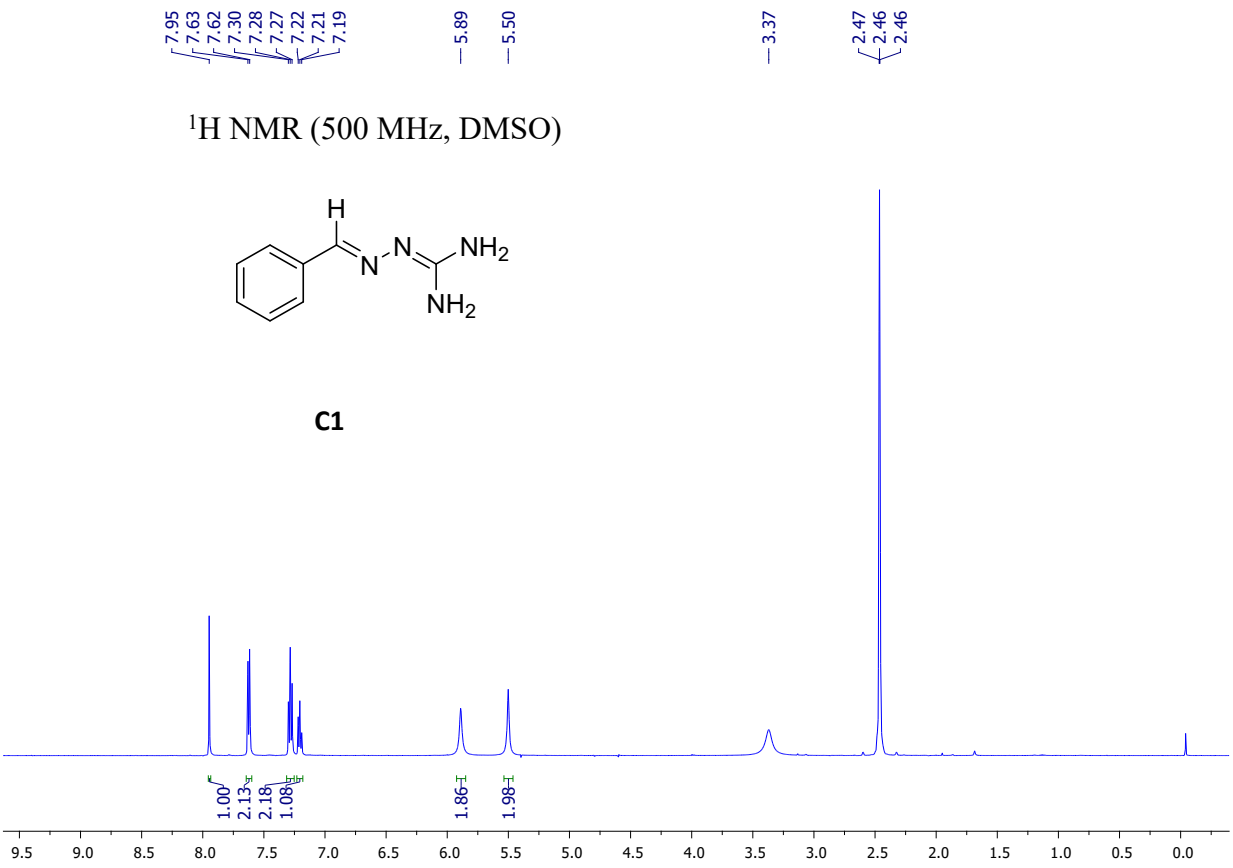
Yield: 563 mg, 92%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 12.10(br. s., 1H), 8.15 (br. s., 1H), 7.82 (br. s., 4H), 7.59 (br. s., 1H), 7.40 (br. s., 3H); 13C NMR 156.01, 147.23, 133.95, 130.99, 129.21, 128.10; IR (FTIR) -NH (3099 cm-1), C=N (1657 cm-1). HRMS (ESI) m/z 163.1003 (M+H+), calc. for $C_8H_{11}N_4^+$ 163.0978.



**C7**

Yield: 525 mg, 88%, white solid; 1H NMR (500 MHz, DMSO- *d6*) δ 7.75 – 7.74 (d, *J* = 7.74 Hz, 2H), 7.29 – 7.26 (t, *J* = 7.20 Hz, 2H), 7.21 – 7.19 (t, *J* = 7.20 Hz, 1H), 5.84 (br. s., 1H), 5.45 (br. s., 1H), 3.34 (br. s., 1H), 3.32 (br. s., 1H), 2.18 (br. s., 3H); 13C NMR 160.29, 140.70, 128.45, 127.65, 125.82, 13.86; IR (FTIR) -NH (3458 cm-1), C=N (1621 cm-1). HRMS (ESI) m/z 177.1135 (M+H+), calc. for $C_9H_{13}N_4^+$ 177.1182.

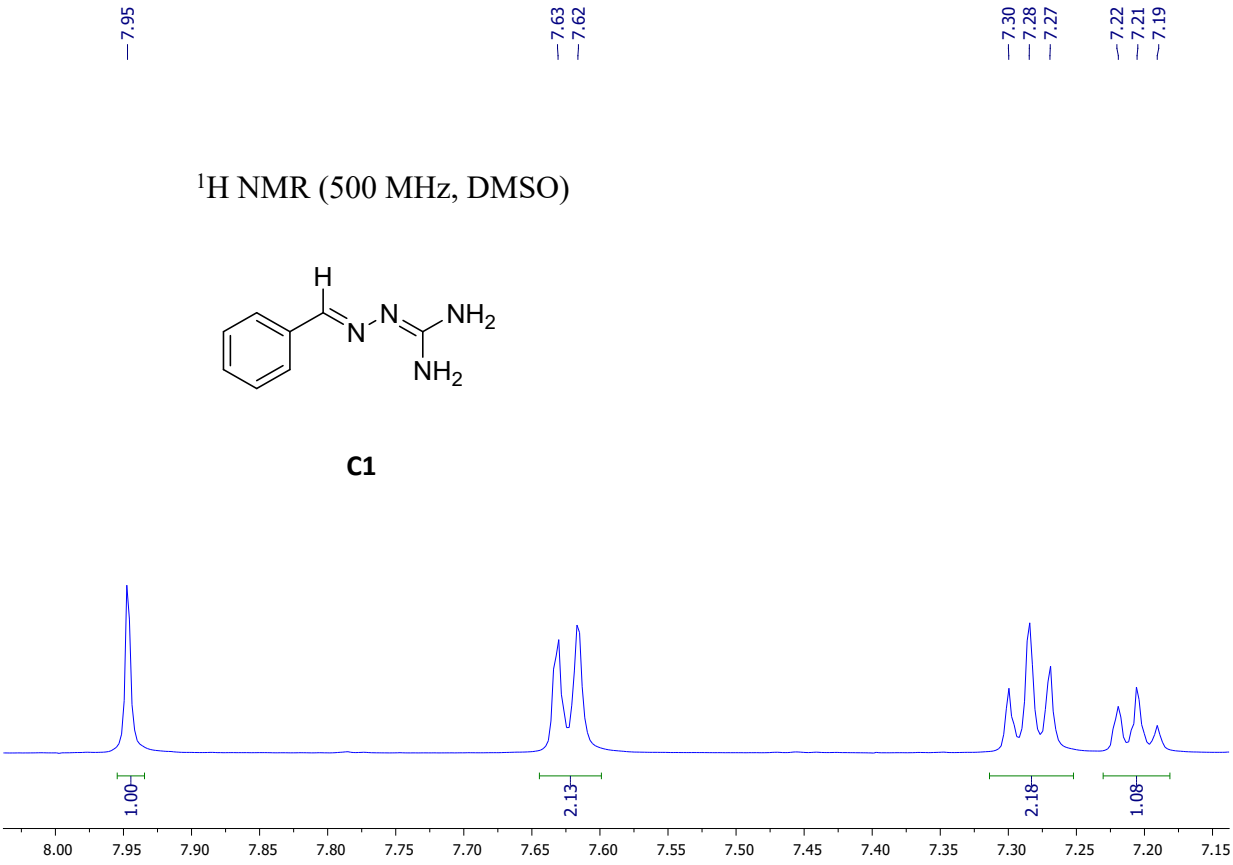
**$^{1}$H and $^{13}$C NMR spectra of catalysts:**




$^{1}$H NMR (500 MHz, DMSO)



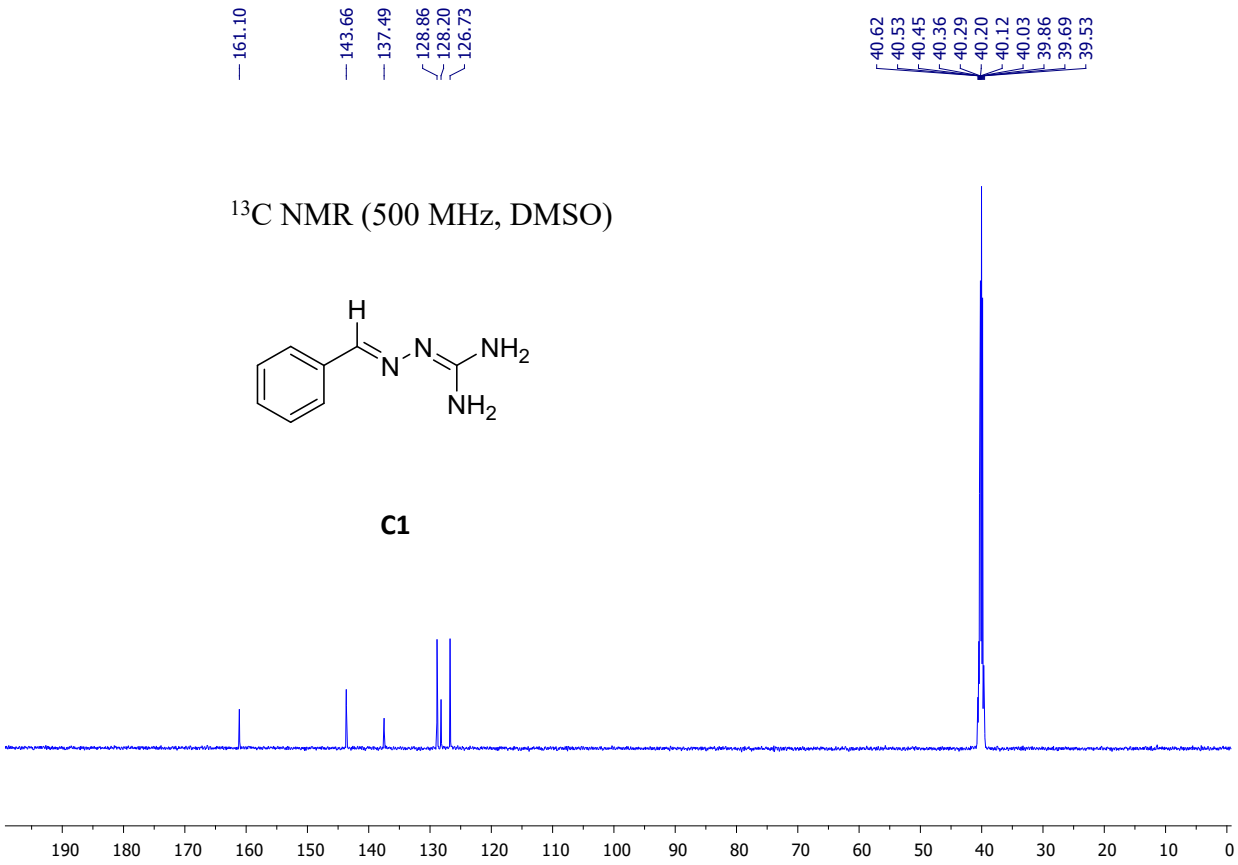

**C1**




$^{1}$H NMR (500 MHz, DMSO)



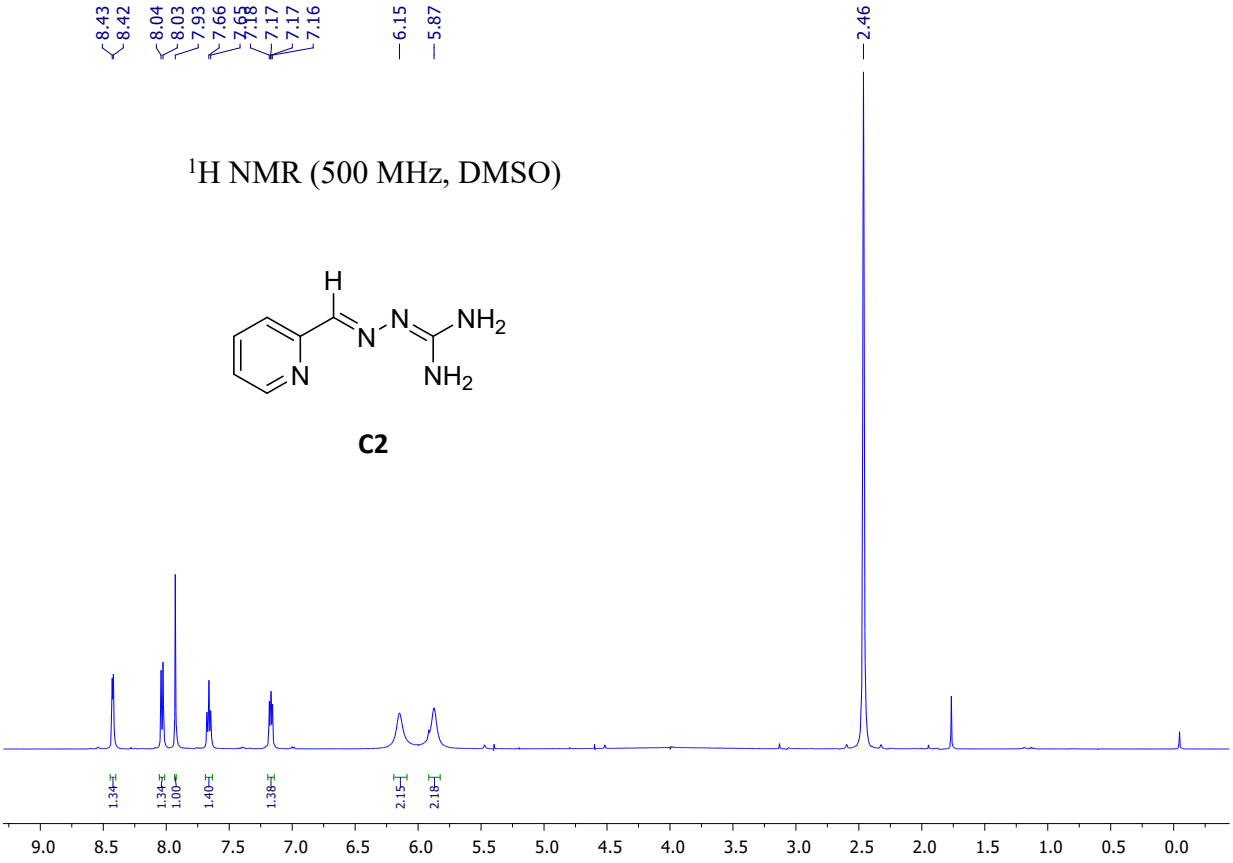

**C1**




$^{13}$C NMR (500 MHz, DMSO)



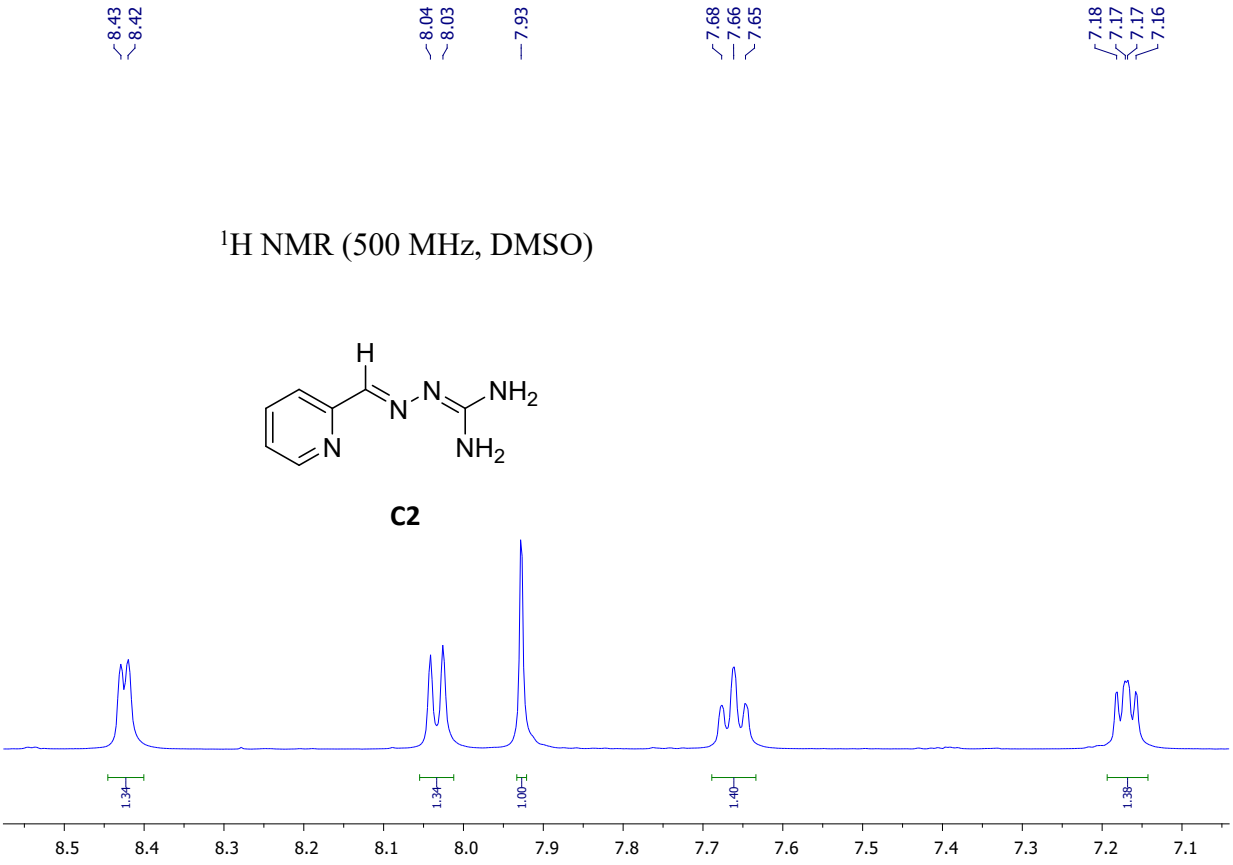

**C1**




$^{1}$H NMR (500 MHz, DMSO)

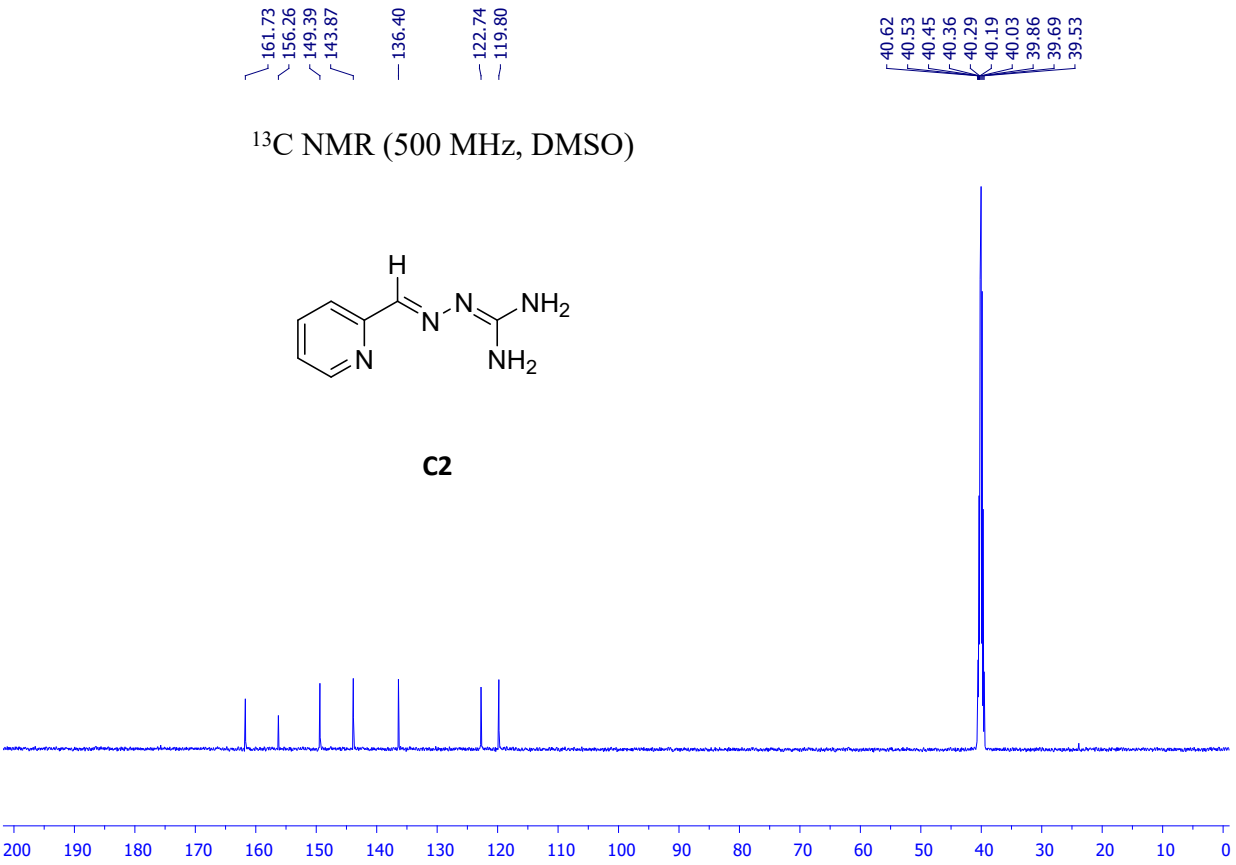



**C2**



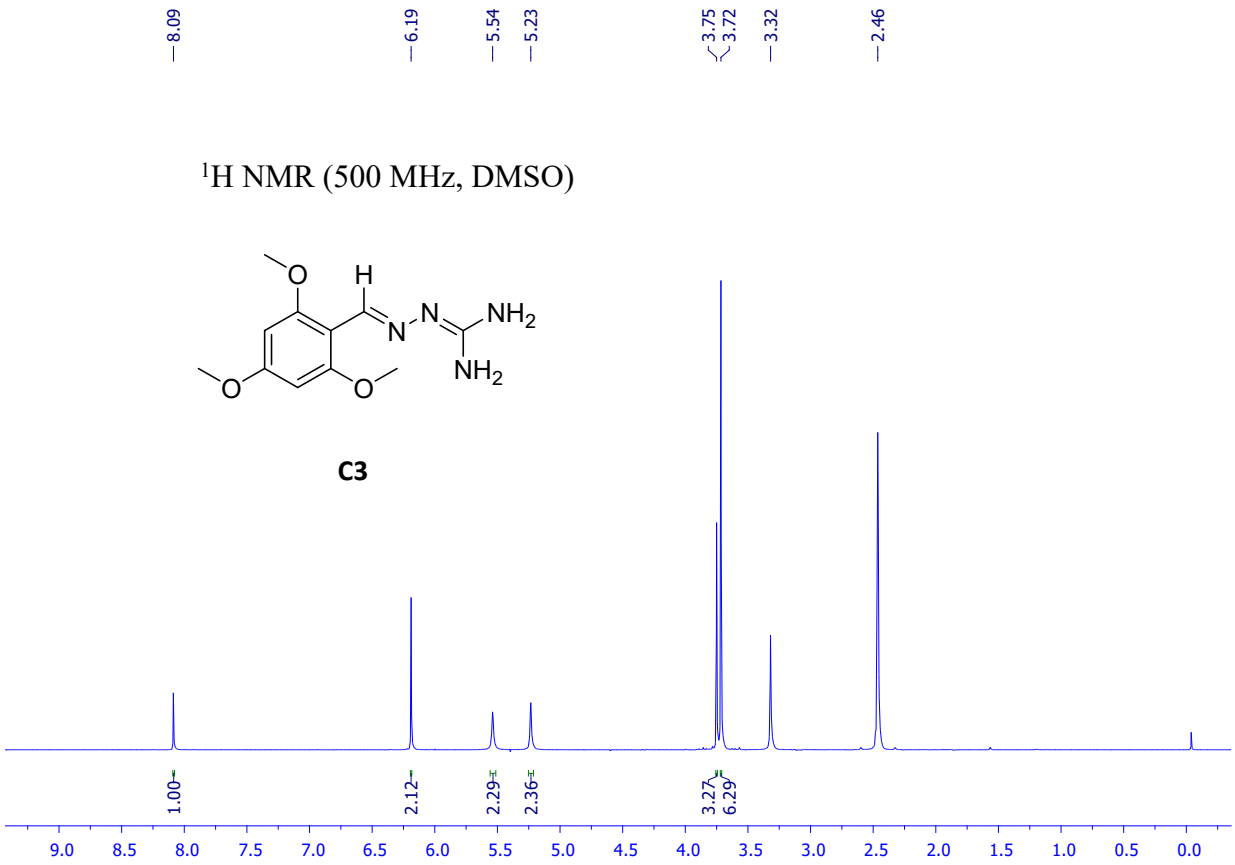

$^{1}$H NMR (500 MHz, DMSO)

**C2**



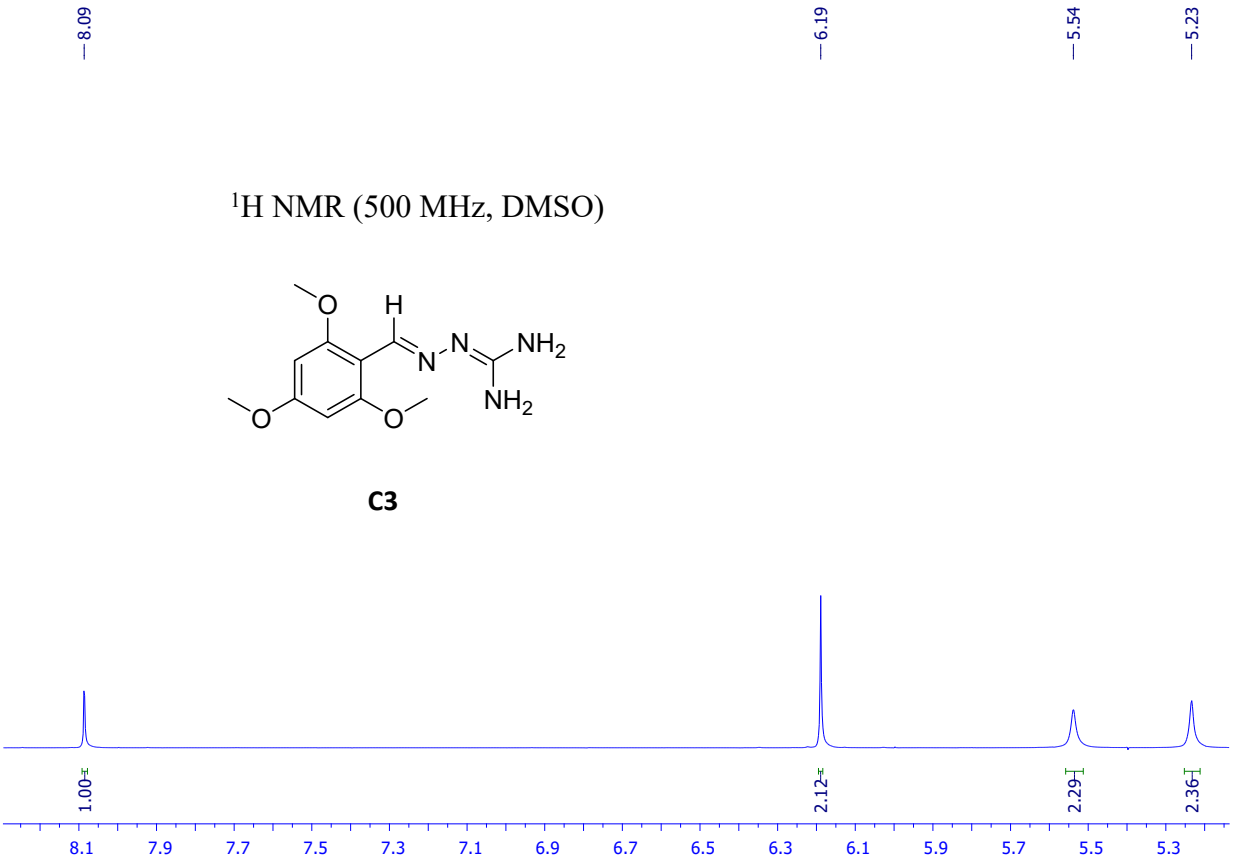

$^{13}$C NMR (500 MHz, DMSO)

**C2**




$^{1}$H NMR (500 MHz, DMSO)

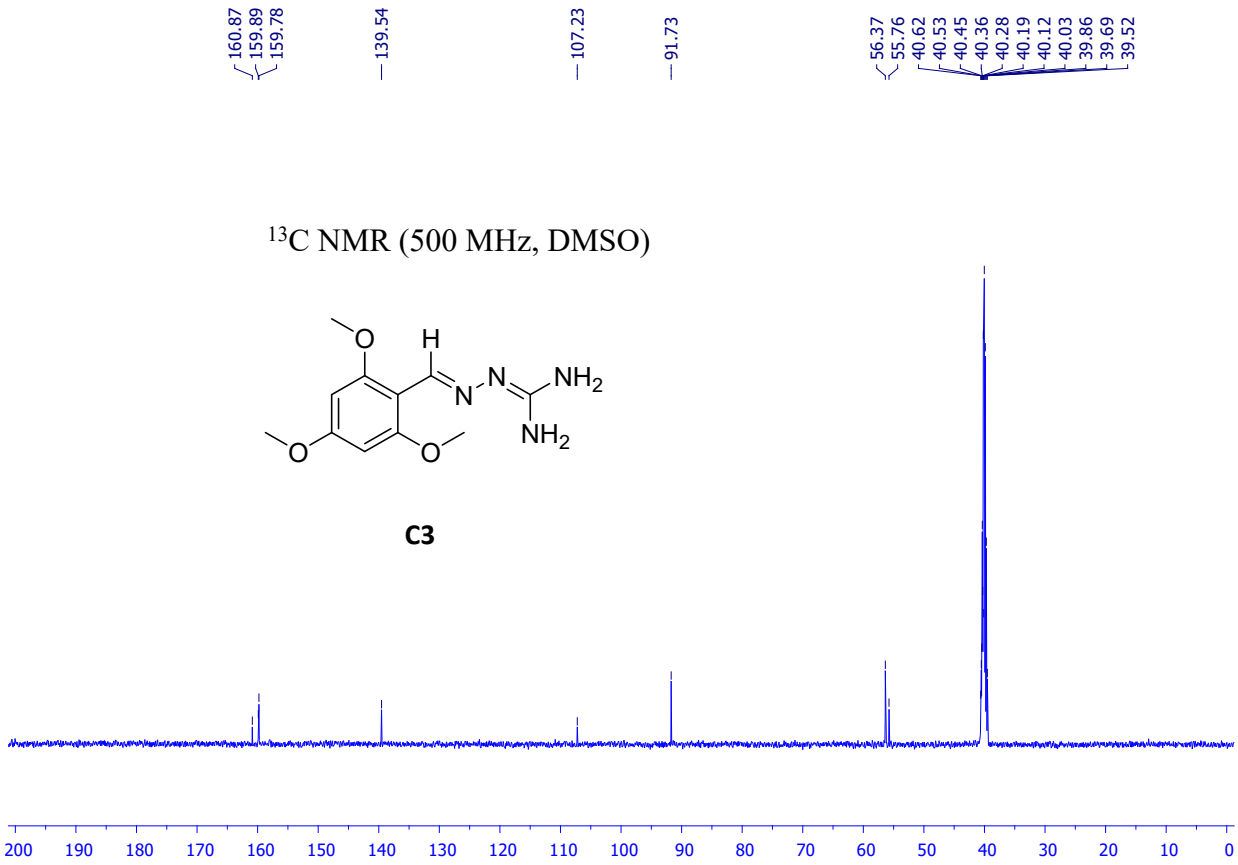
**C3**




$^{1}$H NMR (500 MHz, DMSO)




**C3**

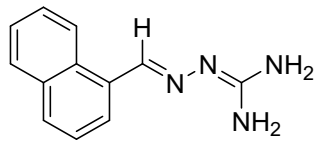



$^{13}$C NMR (500 MHz, DMSO)



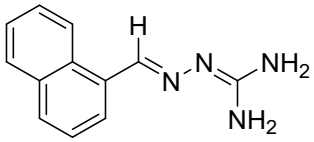

**C3**


$^{1}$H NMR (500 MHz, DMSO)

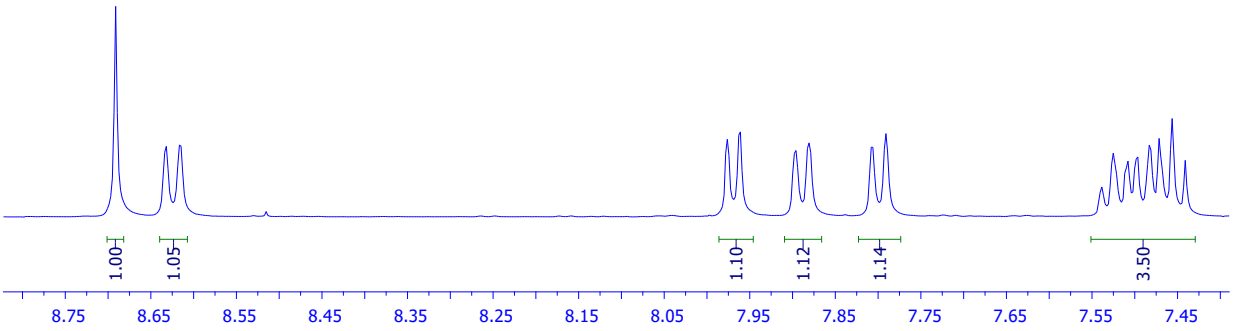


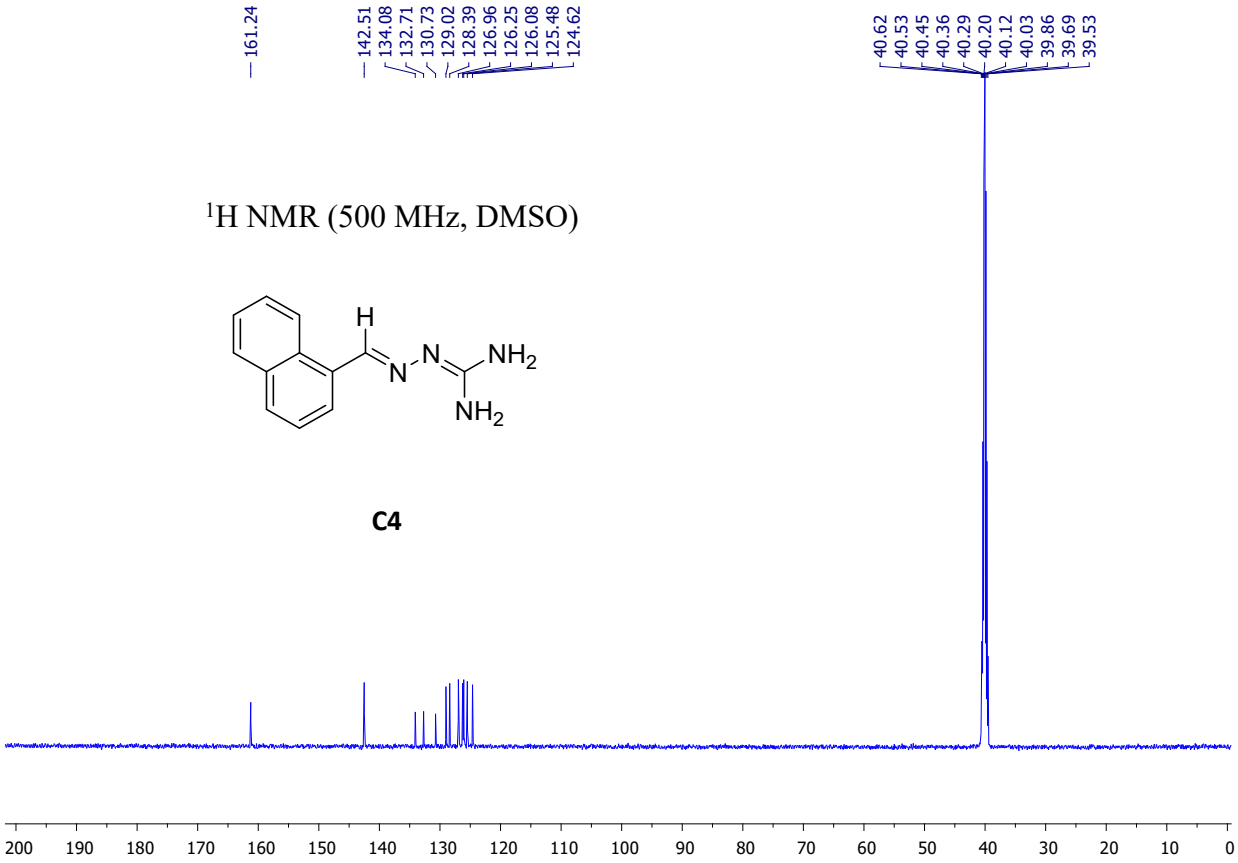

**C4**


$^{1}$H NMR (500 MHz, DMSO)




**C4**

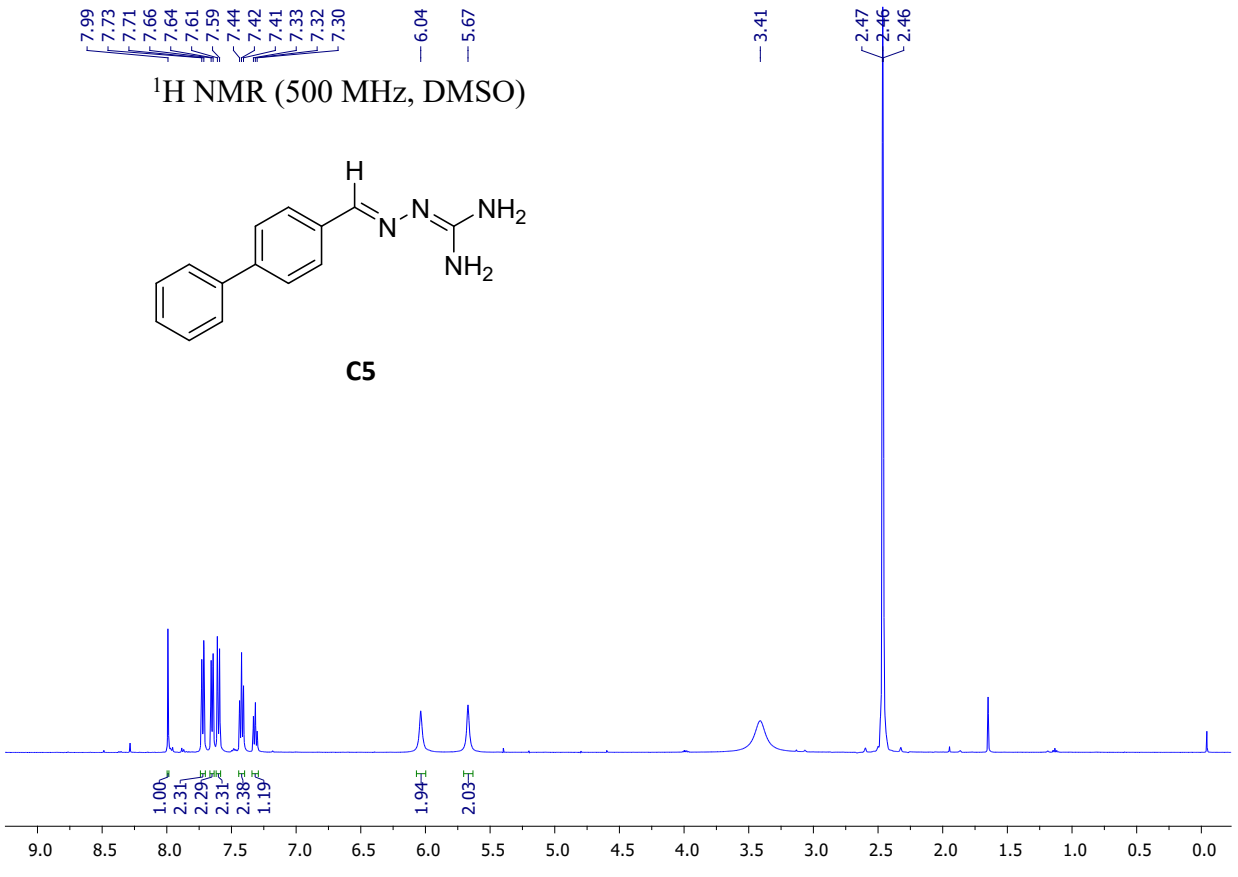





$^1$H NMR (500 MHz, DMSO)



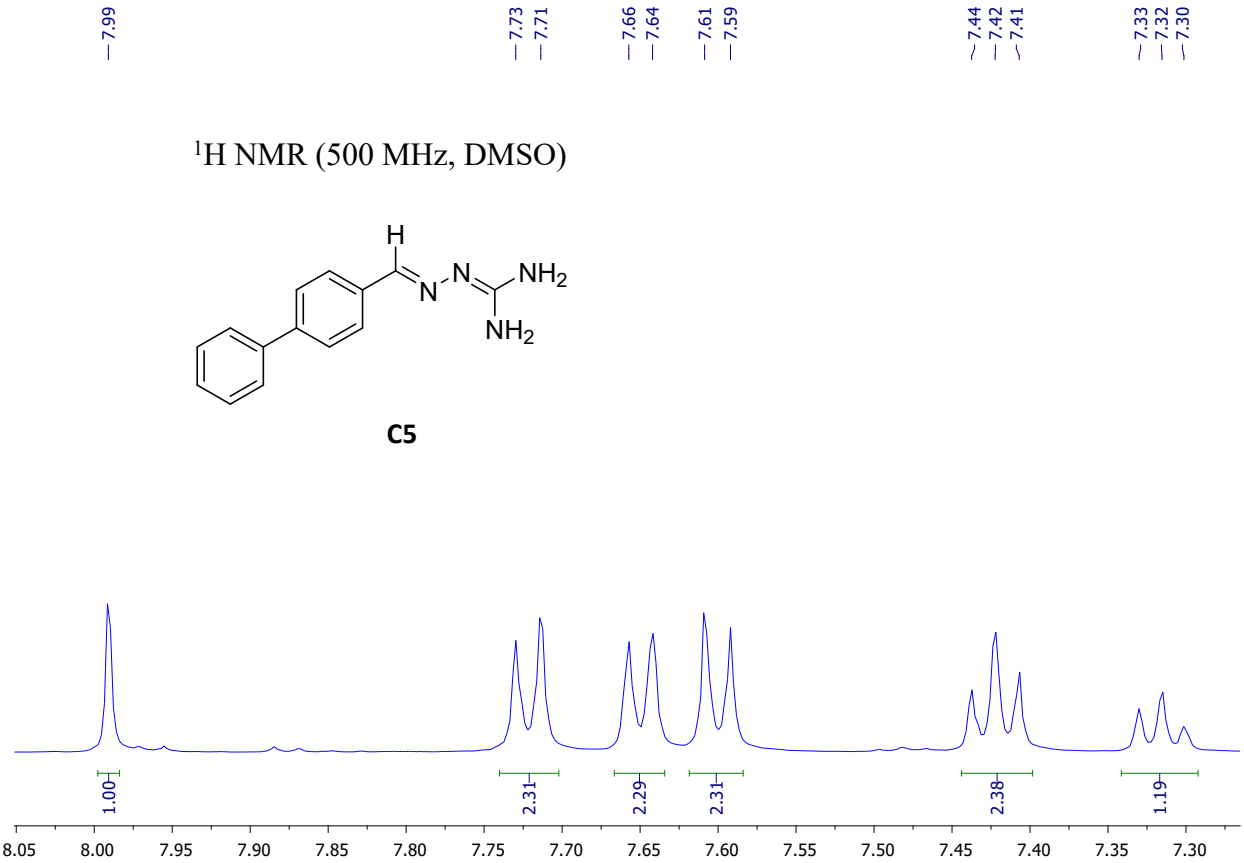

**C4**




$^1$H NMR (500 MHz, DMSO)



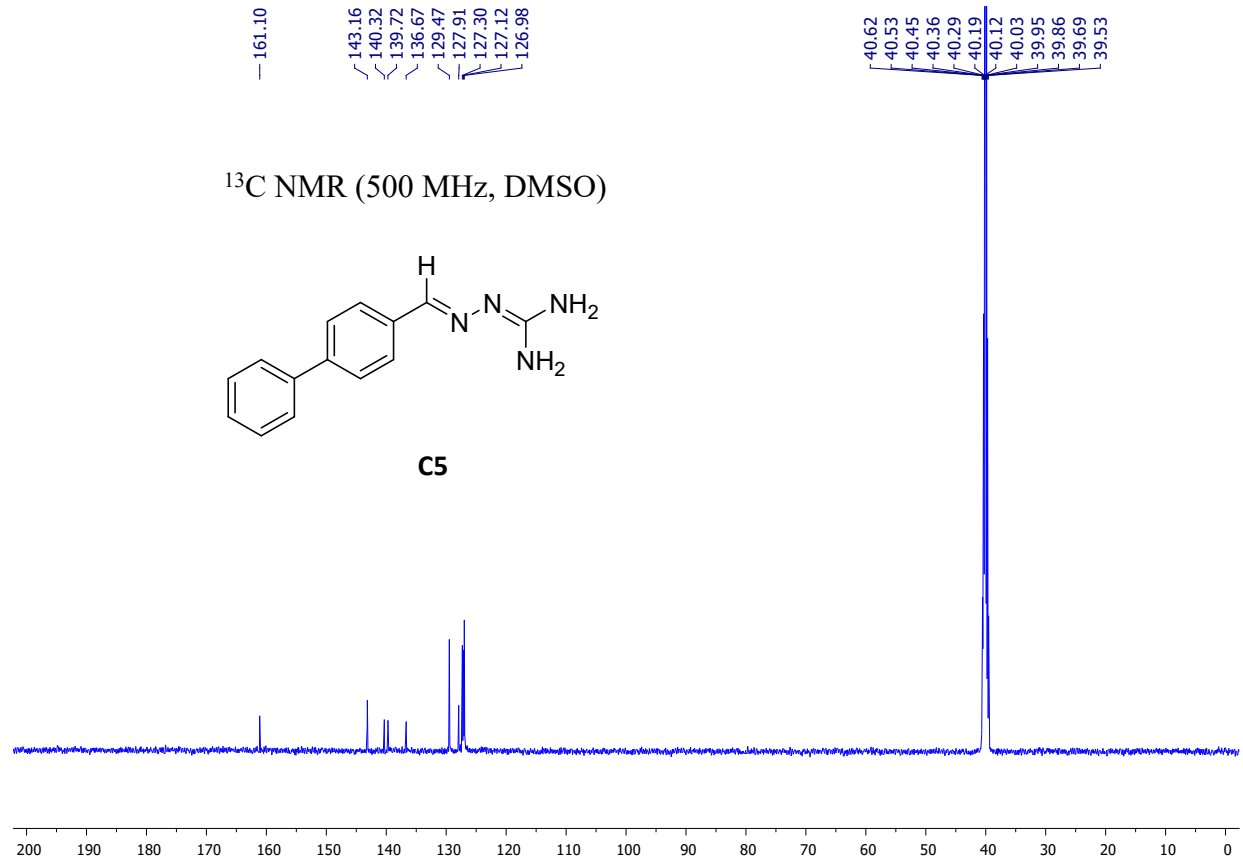

**C5**




$^{1}$H NMR (500 MHz, DMSO)



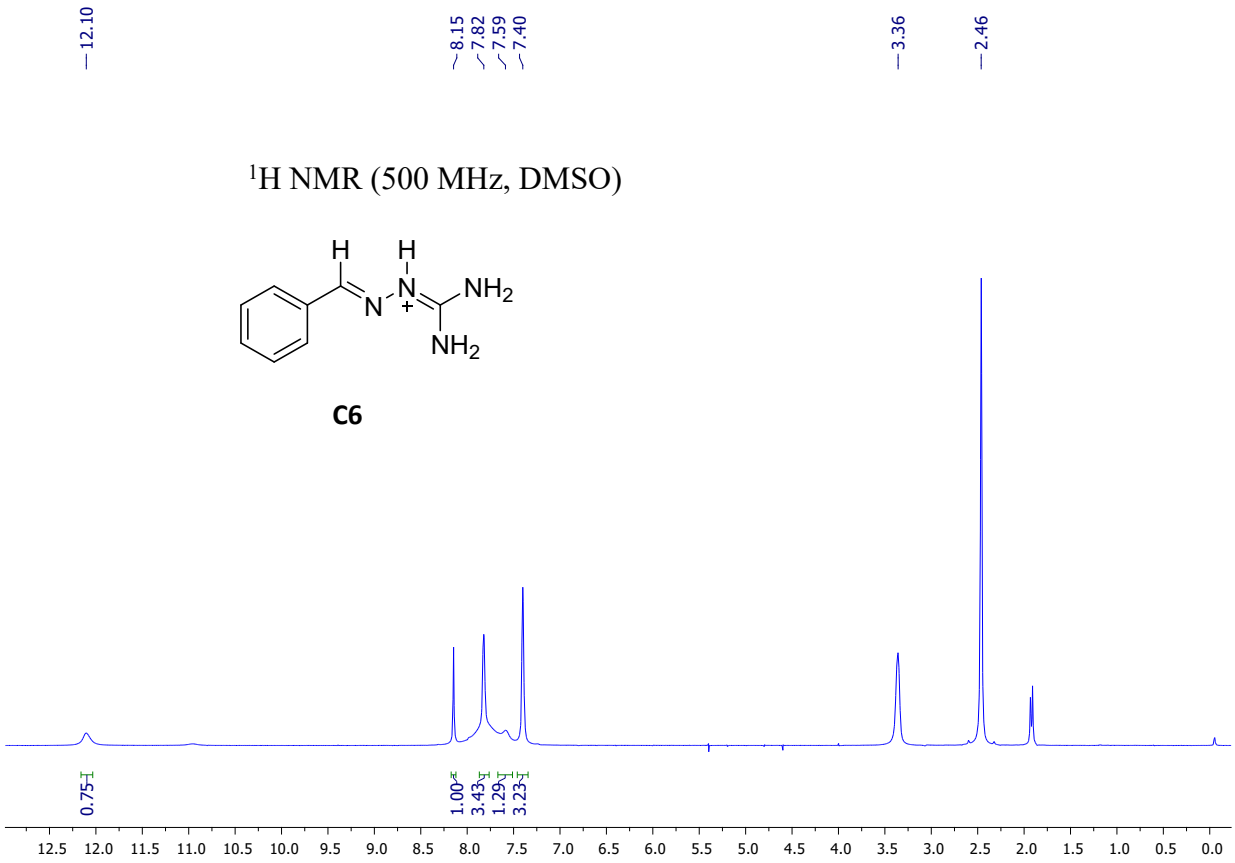

**C5**




$^{13}$C NMR (500 MHz, DMSO)



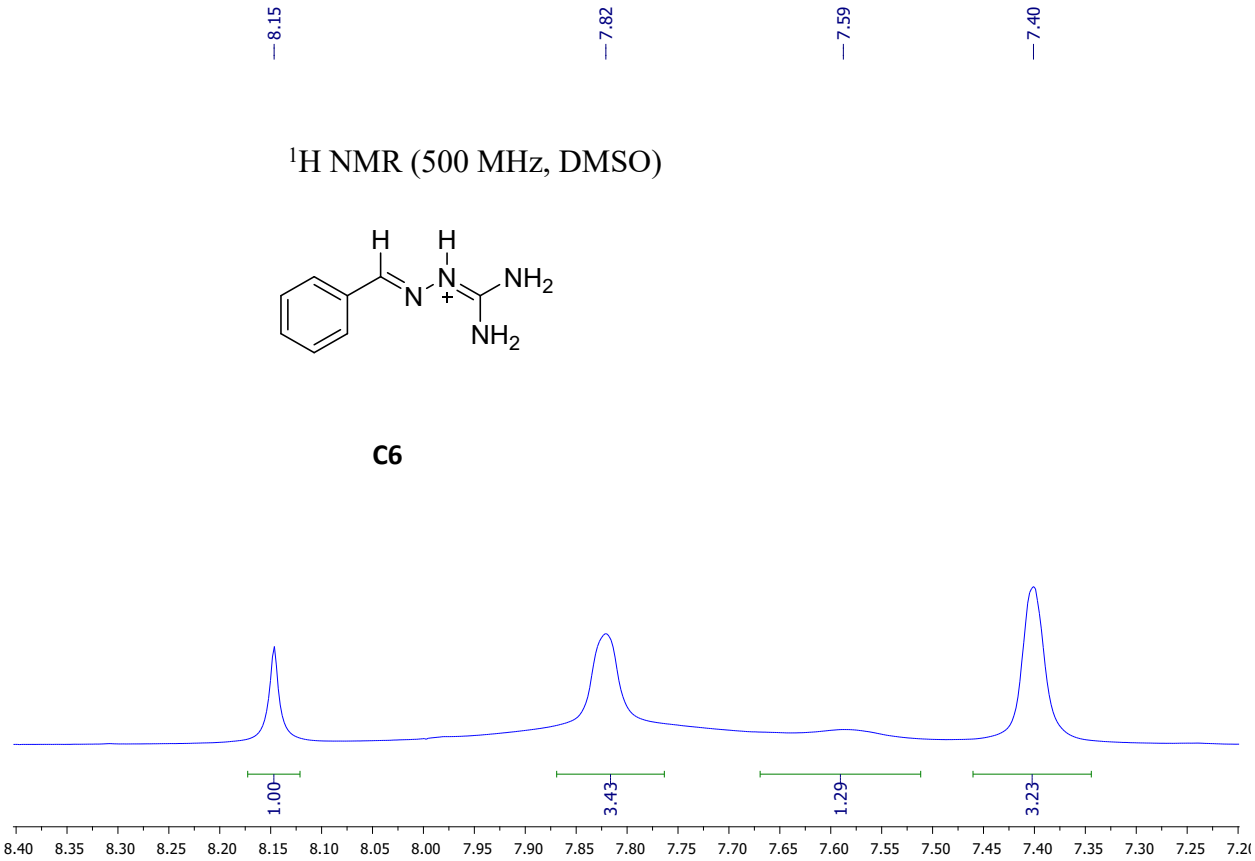

**C5**




$^{1}$H NMR (500 MHz, DMSO)



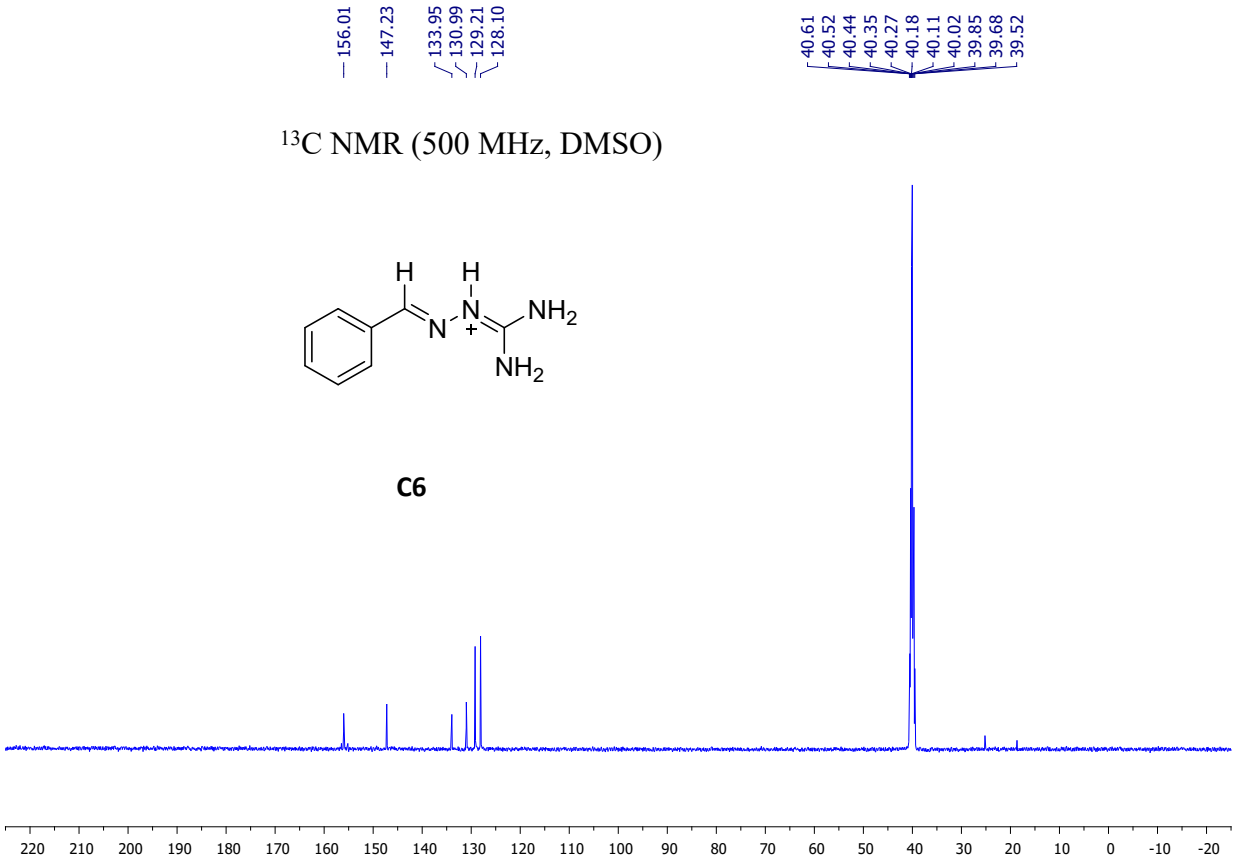

**C6**




$^{1}$H NMR (500 MHz, DMSO)



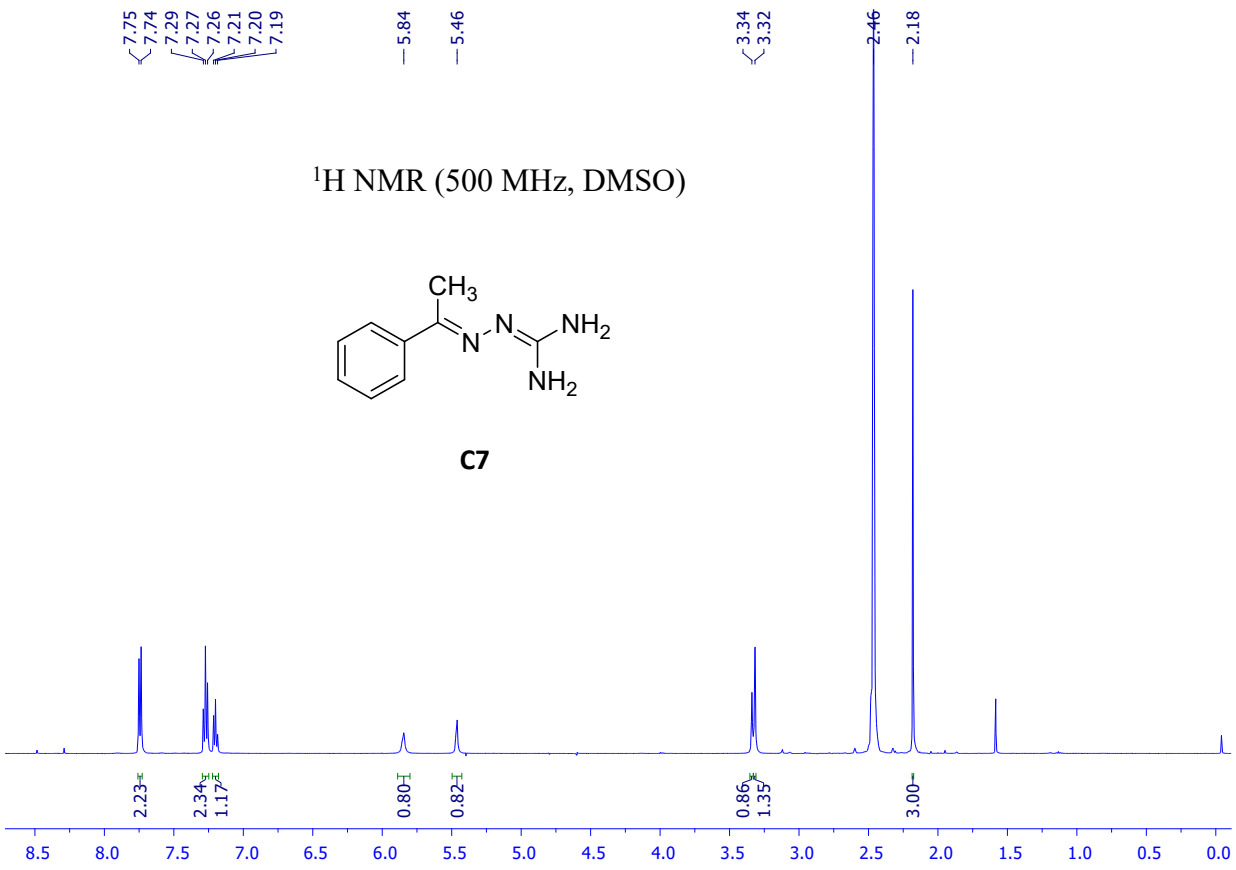

**C6**




$^{13}$C NMR (500 MHz, DMSO)



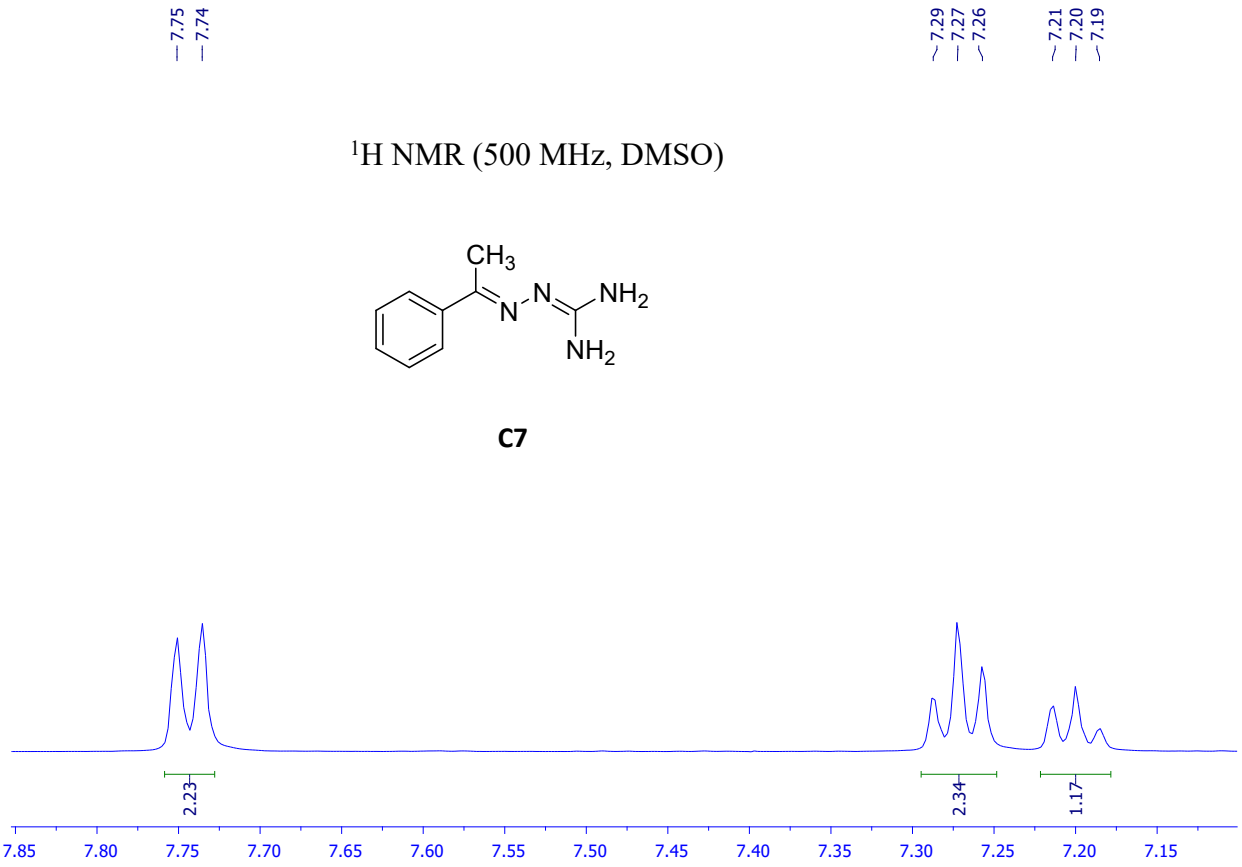

**C6**




$^{1}$H NMR (500 MHz, DMSO)

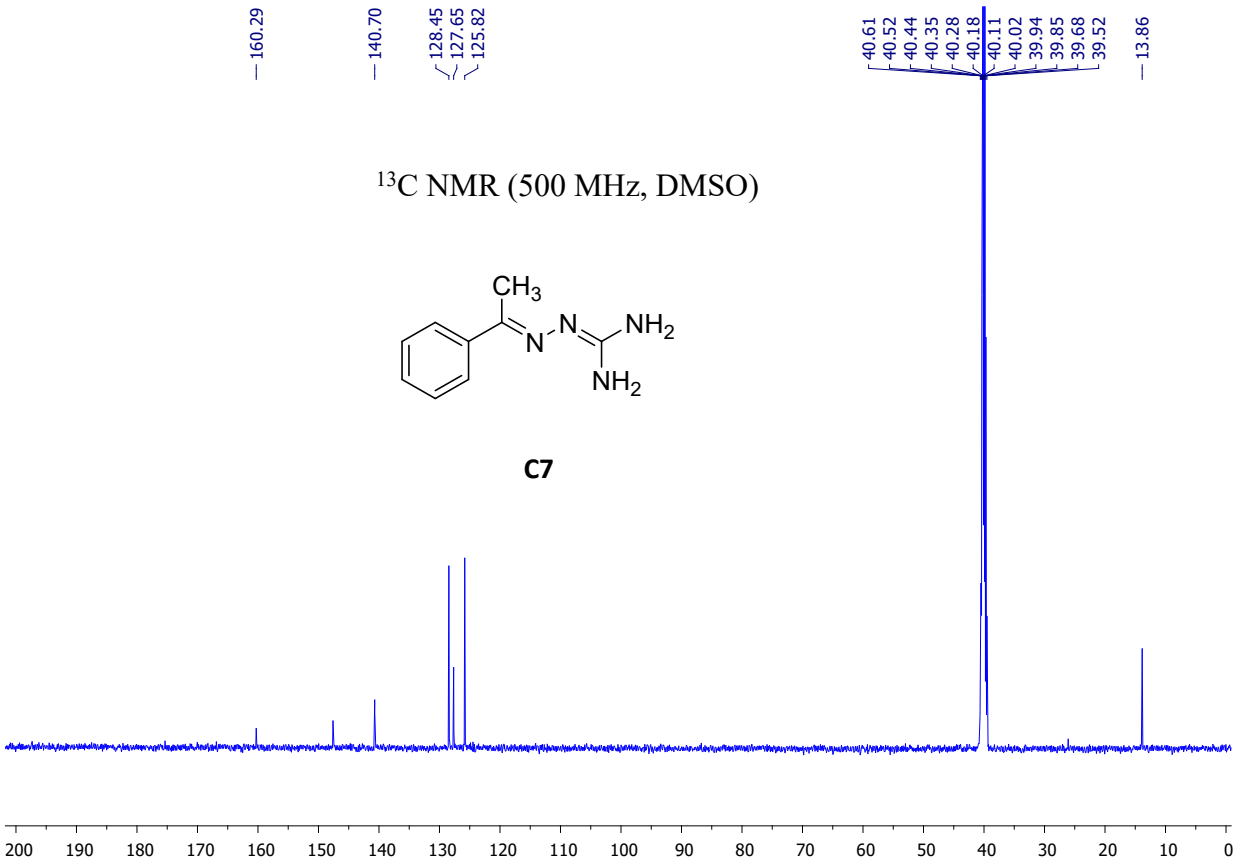



**C7**




$^{1}$H NMR (500 MHz, DMSO)

**C7**




$^{13}$C NMR (500 MHz, DMSO)




**C7**