Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Palladium Catalyzed Direct Benzylation/Allylation of Malonates with Benzyl-/Allyl-Alcohols – *In Situ* C-O Bond Activation

Xueqin Cao, Yugen Zhang*

Institute of Bioengineering and Nanotechnology
31 Biopolis Way, The Nanos
Singapore 138669
E-mail: ygzhang@ibn.a-star.edu.sg

Table of Contents

1. General Information

All anhydrous solvents were purchased from Sigma-Aldrich and used without further purification. All other reagents were used as received. All reactions were carried out under an argon or nitrogen atmosphere.

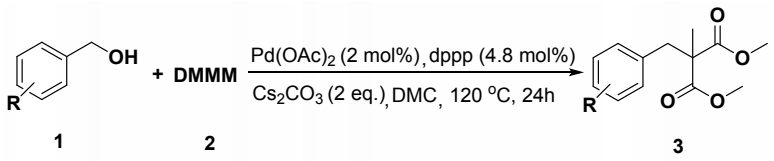
Analytical thin layer chromatography (TLC) was performed using Merck 60 F-254 silica gel plates with visualization by ultraviolet light (254 nm) and/or I_2. Flash column chromatography was carried out on Kieselgel 60 (0.040-0.063 mm) supplied by Merck under positive pressure.

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) with the residual solvent peak of tetramethylsilane used as the internal standard at 0.00 ppm. ^1H NMR data are reported in the following order: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet), coupling constants (*J*, Hz), integration and assignment. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF-QII spectrometer.

Compounds **3a**,[1] **3f**,[2] and **5f** [3] were identified by comparison with their ^1H and ^{13}C NMR spectra reported in the literature.

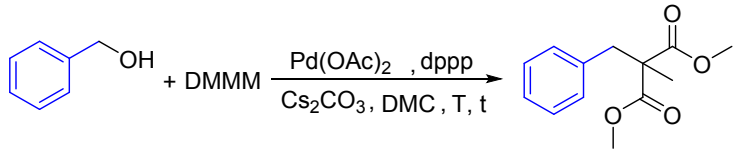
2. Procedure of the benzylation/allylation of DMMM

General procedure:



Under nitrogen atmosphere, benzyl alcohol (1.0 mmol), DMMM (1.0 mmol), $Pd(OAc)_2$ (4.5 mg, 20 μmol), dppp (20 mg, 48 μmol), Cs_2CO_3 (652 mg, 2.0 equiv) and dimethylcarbonate (DMC) (2 mL) were combined in a 20 mL headspace vial fitted with a suba seal cap. The mixture was stirred at 120 °C for 24 h, then cooled to room temperature. The mixture was filtered and washed by ethyl acetate. The obtained filtration was evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane) to give the desired product.

Table S1. Reaction conditions screening for the benzylation of DMMM.

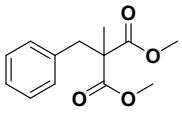


Entry	$Pd(OAc)_2$ mol%	dppp (eq.) mol%	Cs_2CO_3 eq.	DMC mL	Co-solvent mL	T (°C)	t (h)	Yield(%)[a]
1	2	4.8	1	2	-	120	24	79

2	2	4.8	1.5	2	-	120	24	85
3	2	4.8	2	2	-	120	24	90
4	2	4.8	2	2	-	120	16	76
5	2	4.8	2	2	-	120	20	83
6	2	4.8	2	2	-	100	24	29
7	2	4	2	2	-	120	24	85
8	2	2.5	2	2	-	120	24	81
9	1	2	2	2	-	120	24	80
10	2	4.8	2	0.34	Toluene (1)	120	24	< 5
11	2	4.8	2	0.34	DMF (1)	120	24	< 5

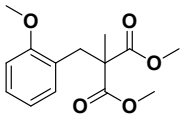
Reaction conditions: Benzyl alcohol (1.0 mmol), DMMM (1.0 mmol). [a] Yield by NMR.

Dimethyl 2-benzyl-2-methylmalonate (3a)



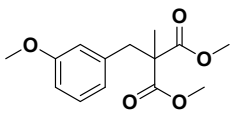
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless solid (203 mg, 86%). Spectroscopic data were in agreement with the published data. [1] **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.30-7.23 (m, 3H, ArH), 7.10-7.07 (m, 2H, ArH), 3.67 (s, 6H, 2 x CH_3), 3.12 (s, 2H, CH_2), 1.22 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.8, 135.9, 130.3, 128.4, 127.2, 54.4, 52.8, 40.7, 19.5; **HRMS** (ESI+) calc. for $C_{13}H_{16}O_4$ $[M+Na]^+$ 259.0941; found 259.0942.

Dimethyl 2-(2-methoxybenzyl)-2-methylmalonate (3b)



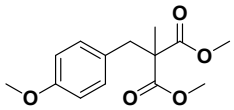
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless solid (242 mg, 91%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.22 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H, ArH), 7.00 (dd, J = 7.4, 1.8 Hz, 1H, ArH), 6.95 (dd, J = 8.3, 0.8 Hz, 1H, ArH), 6.85 (td, J = 7.4, 1.0 Hz, 1H, ArH), 3.72 (s, 3H, CH_3), 3.66 (s, 6H, 2 x CH_3), 3.17 (s, 2H, CH_2), 1.16 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 172.1, 157.8, 131.5, 128.5, 123.9, 120.2, 110.9, 55.2, 53.8, 52.6, 34.1, 19.2; **HRMS** (ESI+) calc. for $C_{14}H_{18}O_5$ $[M+Na]^+$ 289.1046; found 289.1049.

Dimethyl 2-(3-methoxybenzyl)-2-methylmalonate (3c)



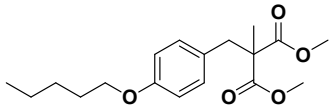
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (255 mg, 91%). %). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.21-7.17 (m, 1H, ArH), 6.81 (ddd, J = 8.2, 2.6, 0.9Hz, 1H, ArH), 6.67-6.63 (m, 2H, ArH), 3.71 (s, 3H, CH_3), 3.67 (s, 6H, 2 x CH_3), 3.10 (s, 2H, CH_2), 1.23 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.8, 159.5, 137.4, 129.3, 122.5, 115.9, 112.6, 55.3, 54.4, 52.6, 40.6, 19.5; **HRMS** (ESI+) calc. for $C_{14}H_{18}O_5$ $[M+Na]^+$ 289.1046; found 289.1049.

Dimethyl 2-(4-methoxybenzyl)-2-methylmalonate (3d)



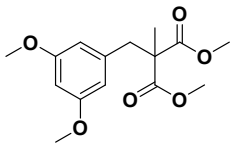
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (239 mg, 90%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.01 (d, J = 8.8Hz, 2H, ArH), 6.83 (d, J = 8.8Hz, 2H, ArH), 3.72 (s, 3H, CH_3), 3.67 (s, 6H, 2 x CH_3), 3.07 (s, 2H, CH_2), 1.22 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 158.4, 131.0, 127.8, 113.5, 55.1, 54.8, 52.4, 40.3, 19.6; **HRMS** (ESI+) calc. for $C_{14}H_{18}O_5$ $[M+Na]^+$ 289.1046; found 289.1051.

Dimethyl 2-methyl-2-(4-(pentyloxy)benzyl)malonate (3e)



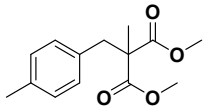
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless liquid (280 mg, 87%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 6.88 (d, J = 8.7Hz, 2H, ArH), 6.81 (d, J = 8.7Hz, 2H, ArH), 3.90 (t, J = 6.5Hz, 2H, CH_2), 3.66 (s, 6H, 2 x CH_3), 3.05 (s, 2H, CH_2), 1.72-1.65 (m, 2H, CH_2), 1.40-1.32 (m, 4H, 2 x CH_2), 1.21 (s, 3H, CH_3), 0.88 (t, J = 7.1Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 158.0, 130.9, 127.6, 114.0, 67.7, 54.9, 52.4, 40.3, 28.9, 28.1, 22.3, 19.6, 13.9; **HRMS** (ESI+) calc. for $C_{18}H_{26}O_5$ $[M+Na]^+$ 345.1672; found 345.1678.

Dimethyl 2-(3,5-dimethoxybenzyl)-2-methylmalonate (3f)



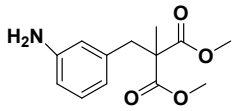
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a white solid (240 mg, 81%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 6.38 (t, J = 2.3 Hz, 1H, ArH), 6.23 (t, J = 2.5 Hz, 2H, ArH), 3.69 (s, 6H, 2 x CH_3), 3.67 (s, 6H, 2 x CH_3), 3.06 (s, 2H, CH_2), 1.24 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.8, 160.4, 138.4, 108.3, 98.8, 55.2, 54.2, 52.7, 40.8, 19.4; **HRMS** (ESI+) calc. for $C_{15}H_{20}O_6$ $[M+Na]^+$ 319.1152; found 319.1160.

Dimethyl 2-methyl-2-(4-methylbenzyl)malonate (3g)



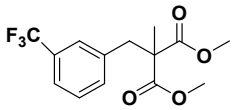
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (215 mg, 86%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.08 (d, J = 7.7 Hz, 2H, ArH), 6.97 (d, J = 8.0 Hz, 2H, ArH), 3.67 (s, 6H, 2 x CH_3), 3.08 (s, 2H, CH_2), 2.26 (s, 3H, Ar-CH_3); 1.21 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.7, 136.1, 132.7, 130.0, 128.9, 54.3, 52.6, 40.2, 20.7, 19.3; **HRMS** (ESI+) calc. for $C_{14}H_{18}O_4$ $[M+Na]^+$ 273.1097; found 273.1101.

Dimethyl 2-(3-aminobenzyl)-2-methylmalonate (3h)



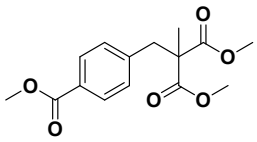
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=2/5) as a light yellow liquid (193 mg, 77%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 6.89 (t, J = 7.7Hz, 1H, ArH), 6.41 (ddd, J = 8.0, 2.2, 0.9Hz, 1H, ArH), 6.26 (t, J = 1.9Hz, 1H, ArH), 6.20 (d, J = 7.5Hz, 1H, ArH), 5.0 (s, 2H, NH_2), 3.67 (s, 6H, 2 x CH_3), 2.96 (s, 2H, CH_2), 1.22 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 172.1, 148.8, 136.3, 128.7, 117.8, 115.7, 112.6, 54.5, 52.6, 41.0, 19.4; **HRMS** (ESI+) calc. for $C_{13}H_{17}NO_4$ $[M+Na]^+$ 274.1050; found 274.1040.

Dimethyl 2-methyl-2-(3-(trifluoromethyl)benzyl)malonate (3i)



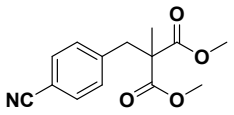
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (283 mg, 93%). **^{1}H NMR** (400 MHz, d_6-DMSO)) δ 7.63-7.61 (m, 1H, ArH), 7.53 (td, J = 8.0, 0.6Hz, 1H, ArH), 7.44-7.42 (m, 2H, ArH), 3.67 (s, 6H, 2 x CH_3), 3.25 (s, 2H, CH_2), 1.25 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.5, 137.4, 134.4, 129.3, 129.0 (q, $^2J_{CF}$ = 31Hz), 126.5 (q, $^3J_{CF}$ = 4Hz), 124.3 (q, $^1J_{CF}$ = 272Hz), 123.8 (q, $^3J_{CF}$ = 4Hz), 54.2, 52.6, 40.1, 19.3; **HRMS** (ESI+) calc. for $C_{14}H_{15}F_3O_4$ $[M+Na]^+$ 327.0815; found 327.0818.

Dimethyl 2-(4-(methoxycarbonyl)benzyl)-2-methylmalonate (3j)



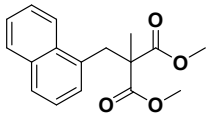
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a white solid (247 mg, 84%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.87 (d, J = 8.4 Hz, 2H, ArH), 7.25 (d, J = 8.4 Hz, 2H, ArH), 3.84 (s, 3H, CH_3), 3.67 (s, 6H, 2 x CH_3), 3.21 (s, 2H, CH_2), 1.24 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.5, 166.2, 141.7, 130.6, 129.2, 128.5, 54.2, 52.7, 52.3, 40.5, 19.4; **HRMS** (ESI+) calc. for $C_{15}H_{18}O_6$ $[M+Na]^+$ 317.0996; found 317.1002.

Dimethyl 2-(4-cyanobenzyl)-2-methylmalonate (3k)



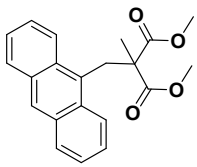
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/4) as a white solid (212 mg, 81%). %). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.76 (d, J = 8.5 Hz, 2H, ArH), 7.32 (d, J = 8.5 Hz, 2H, ArH), 3.67 (s, 6H, 2 x CH_3), 3.22 (s, 2H, CH_2), 1.23 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.3, 142.0, 132.2, 131.2, 118.8, 110.0, 54.1, 52.7, 40.4, 19.3; **HRMS** (ESI+) calc. for $C_{14}H_{15}NO_4$ $[M+Na]^+$ 284.0893; found 284.0898.

Dimethyl 2-methyl-2-(naphthalen-1-ylmethyl)malonate (3l)



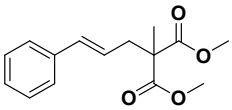
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/15) as a colourless sticky liquid (246 mg, 86%). %). **^{1}H NMR** (400 MHz, d_6-DMSO)) δ 7.89-7.82 (m, 3H, ArH), 7.63 (s, 1H, ArH), 7.51-7.46 (m, 2H, ArH), 7.24 (dd, J = 8.4, 1.8Hz, 1H, ArH), 3.70 (s, 6H, 2 x CH_3), 3.31 (s, 2H, CH_2), 1.29 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.7, 133.6, 132.9, 132.1 128.7, 128.4, 127.7, 127.5, 126.3, 125.9, 54.4, 52.7, 40.8, 19.5; **HRMS** (ESI+) calc. for $C_{17}H_{18}O_4$ $[M+Na]^+$ 309.1097; found 309.1098.

Dimethyl 2-(anthracen-9-ylmethyl)-2-methylmalonate (3m)



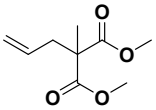
This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/15) as an orange solid (215 mg, 64%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 8.56 (s, 1H, ArH), 8.22-8.20 (m, 2H, ArH), 8.10-8.08 (m, 2H, ArH), 7.38-7.30 (m, 4H, ArH), 4.36 (s, 2H, CH_2), 3.61 (s, 6H, 2 x CH_3), 1.05 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 172.2, 131.1, 131.0, 129.2, 128.7, 127.3, 125.9, 125.1, 124.8, 54.5, 52.9, 30.5, 20.1; **HRMS** (ESI+) calc. for $C_{21}H_{20}O_4$ $[M+Na]^+$ 359.1254; found 359.1260.

Dimethyl 2-cinnamyl-2-methylmalonate (3n)



This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (249 mg, 95%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.37-7.21 (m, 5H, ArH), 6.48 (d, J = 15.2Hz, 1H, =CH), 6.11 (dt, J = 15.6, 7.8Hz, 1H, =CH), 3.67 (s, 6H, 2 x CH_3), 2.69 (dd, J = 7.5, 1.1Hz, 2H, CH_2), 1.36 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.8, 136.7, 133.9, 128.8, 127.6, 126.1, 124.0, 53.5, 52.6, 38.9, 19.7. **HRMS** (ESI+) calc. for $C_{15}H_{18}O_4$ $[M+Na]^+$ 285.1097; found 285.1110.

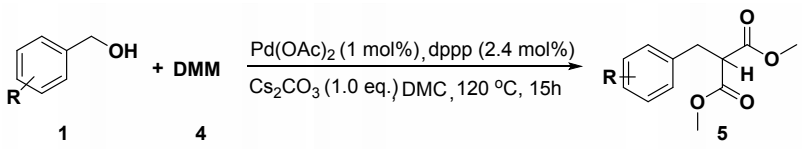
Dimethyl 2-allyl-2-methylmalonate (3o)



This compound was prepared according to general procedure and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (136 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.73-5.62 (m, 1H, =CH), 5.12-5.07 (m, 2H, $=CH_2$), 3.72 (s, 6H, 2 x CH_3), 2.61 (dt, J = 7.4, 1.1Hz, 2H, CH_2), 1.39 (s, 3H, CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.3, 132.4, 119.1, 53.4, 52.4, 40.0, 19.7; **HRMS** (ESI+) calc. for $C_9H_{14}O_4$ $[M+Na]^+$ 209.0790; found 209.0793.

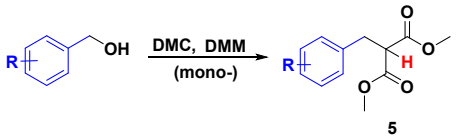
3. Procedure of the benzylation/allylation of DMM

General procedure A:



Under nitrogen atmosphere, benzyl alcohol (1.0 mmol), DMM (5.0 mmol), $Pd(OAc)_2$ (2.3 mg, 10 μmol), dppp (10 mg, 24 μmol), Cs_2CO_3 (326 mg, 1.0 equiv) and DMC (2 mL) were combined in a 20 mL headspace vial fitted with a suba seal cap. The mixture was stirred at 120 °C for 15 h, then cooled to room temperature. The mixture was filtered and washed by ethyl acetate, and the obtained solution was evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane) to give the desired product **5**.

Table S2. Reaction conditions screening for the benzylation of DMM (I).

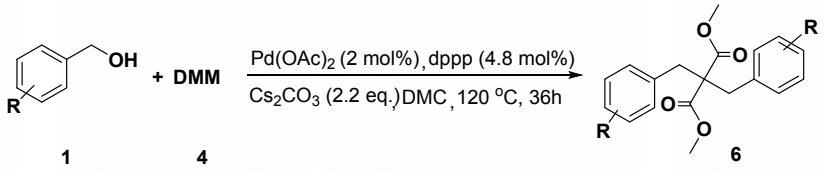


Entry	$Pd(OAc)_2$ (mol%)	dppp (mol%)	Ratio of BnOH/DMM	T(°C)	t(h)	Yield(%)[a] mono-	bis-
1	2	4.8	1:1.2	120	24	38	23
2[b]	2	4.8	1:1.2	120	24	44	20
3[b]	2	4.8	1:3	120	15	70	9

4[b]	2	4.8	1:5	120	15	78	4
5	2	4.8	1:5	120	15	84	6
6	1	2.4	1:5	120	15	86	7
7	1	2.4	1:8	120	15	86	5
8	1	2.4	1:3	120	15	74	11
9	0.5	1.2	1:5	120	15	76	7
10[b]	1	2.4	1:5	120	15	80	6
11	1	2.4	1:5	120	12	78	6
12	1	2.4	1:5	120	18	74	8
13	1	2.4	1:5	110	15	74	6

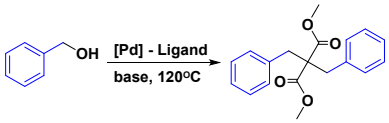
Reaction conditions: BnOH (1 mmol), Cs_2CO_3 (1.0 eq.), DMC (2 mL). [a]Yield by NMR. [b] Solvent (1 mL DMC + 1 mL Dioxane)

General procedure B:



Under nitrogen atmosphere, benzyl alcohol (2.2 mmol), DMM (1.0 mmol), $Pd(OAc)_2$ (4.5 mg, 20 μmol), dppp (20 mg, 48 μmol), Cs_2CO_3 (717 mg, 2.2 equiv) and DMC (2 mL) were combined in a 20 mL headspace vial fitted with a suba seal cap. The mixture was stirred at 120 °C for 36 h, then cooled to room temperature. The mixture was filtered and washed by ethyl acetate, and the obtained solution was evaporated under reduced pressure. The residue was purified by flash column chromatography (EtOAc/hexane) to give the desired product **6**.

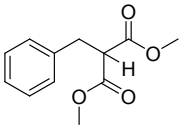
Table S3. Reaction conditions screening for the benzylation of DMM (II).



Entry	Base	(eq.)	DMC (mL)	Co-solvent (mL)	t (h)	Yield(%)[a]
1	Cs_2CO_3	(2)	-	Toluene (2)	24	0
2	Cs_2CO_3	(2)	2	-	24	56
3	Cs_2CO_3	(2)	1	-	24	45
4[b]	Cs_2CO_3	(2)	2	-	24	43
5	Cs_2CO_3	(2.2)	2	-	24	67
6	Cs_2CO_3	(2.2)	2	-	29	78
7	Cs_2CO_3	(2.2)	2	-	36	85
8	Cs_2CO_3	(2.5)	2	-	24	54
9	K_2CO_3	(2)	2	-	24	30
10	K_2CO_3	(2.2)	2	-	24	36
11	NaO^tBu	(2)	2	-	24	11
12[c]	Cs_2CO_3	(2)	1	-	24	< 5
13[d]	Cs_2CO_3	(2)	1	-	24	12
14[e]	Cs_2CO_3	(2)	1	-	24	25
15[f]	Cs_2CO_3	(2)	1	-	24	31
16	Cs_2CO_3	(2.2)	1	DMF (1)	24	43
17	Cs_2CO_3	(2.2)	1	DMF (1)	30	46

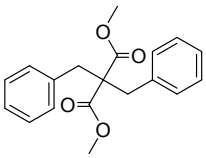
Reaction conditions: Benzyl alcohol (2.2 mmol), DMM (1.0 mmol), Pd(OAc) (2 mol%), dppp (4.8 mol%), 120 **ºC**. [a] Yield by NMR. [b] Pd(OAc) (4 mol%), dppp(10 mol%). [c] TCHP as ligand. [d] DPMP as ligand. [e] dppb as ligand. [f] TPAP as ligand.

Dimethyl 2-benzylmalonate (5a)



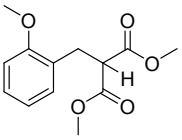
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a colourless liquid (189 mg, 85%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.30-7.19 (m, 5H, ArH), 3.87 (t, J = 8.0 Hz, 1H, CH), 3.60 (s, 6H, 2 x CH_3), 3.08 (d, J = 7.8 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.0, 137.7, 128.8, 128.5, 126.8, 52.8, 52.5, 34.2; **HRMS** (ESI+) calc. for $C_{12}H_{14}O_4$ $[M+Na]^+$ 245.0784; found 245.0775.

Dimethyl 2,2-dibenzylmalonate (6a)



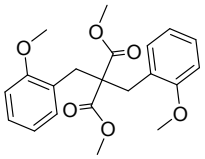
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (259 mg, 83%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.32-7.15 (m, 10H, 2 x ArH), 3.58 (s, 6H, 2 x CH_3), 3.10 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.6, 135.8, 130.1, 128.4, 127.1, 60.0, 52.3, 38.5; **HRMS** (ESI+) calc. for $C_{19}H_{20}O_4$ $[M+Na]^+$ 335.1254; found 335.1248.

Dimethyl 2-(2-methoxybenzyl)malonate (5b)



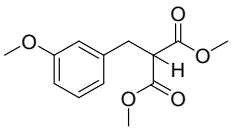
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless liquid (234 mg, 93%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.19 (m, 1H, ArH), 7.13-7.11 (m, 1H, ArH), 6.87-6.82 (m, 2H, ArH), 3.85 (t, J = 8.1 Hz, 1H, CH), 3.83 (s, 3H, Ar-OCH_3), 3.68 (s, 6H, 2 x CH_3), 3.20 (d, J = 7.7 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.1, 157.3, 130.1, 128.5, 125.4, 120.4, 110.7, 55.4, 52.4, 51.0, 29.5; **HRMS** (ESI+) calc. for $C_{13}H_{16}O_5$ $[M+Na]^+$ 275.0890; found 275.0887.

Dimethyl 2,2-bis(2-methoxybenzyl)malonate (6b)



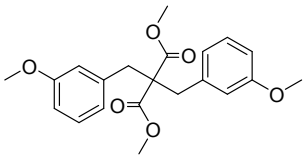
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless sticky liquid (286 mg, 77%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.20 (td, J = 8.1, 1.7 Hz, 2H, 2 x ArH), 7.02 (dd, J = 7.5, 1.7 Hz, 2H, 2 x ArH), 6.92 (dd, J = 8.2, 0.8 Hz, 2H, 2 x ArH), 7.20 (td, J = 7.4, 1.0 Hz, 2H, 2 x ArH), 3.69 (s, 6H, 2 x Ar-OCH_3), 3.53 (s, 6H, 2 x OCH_3), 3.13 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.9, 157.8, 131.1, 128.2, 124.5, 119.9, 110.3, 58.4, 55.3, 52.4, 33.0; **HRMS** (ESI+) calc. for $C_{21}H_{24}O_6$ $[M+Na]^+$ 395.1465; found 395.1472.

Dimethyl 2-(3-methoxybenzyl)malonate (5c)



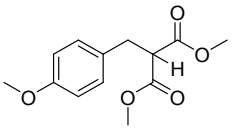
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a colourless liquid (232 mg, 92%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.20-6.74 (m, 4H, ArH), 3.88 (t, J = 8.1 Hz, 1H, CH), 3.72 (s, 3H, Ar-OCH_3), 3.61 (s, 6H, 2 x CH_3), 3.05 (d, J = 7.3 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.0, 159.4, 139.4, 129.4, 120.9, 114.4, 112.3, 55.0, 52.7, 52.5, 34.1; **HRMS** (ESI+) calc. for $C_{13}H_{16}O_5$ $[M+Na]^+$ 275.0890; found 275.0889.

Dimethyl 2,2-bis(3-methoxybenzyl)malonate (6c)



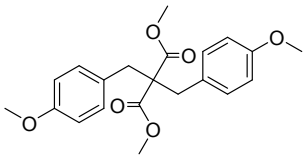
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless sticky liquid (227 mg, 71%). %). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.23 (t, J = 8.0 Hz, 2H, 2 x ArH), 6.83 (ddd, J = 8.3, 2.5, 0.6 Hz, 2H, 2 x ArH), 6.71 (d, J = 7.6 Hz, 2H, 2 x ArH), 6.67 (t, J = 2.0 Hz, 2H, 2 x ArH), 3.72 (s, 6H, 2 x Ar-OCH_3), 3.61 (s, 6H, 2 x CH_3), 3.08 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.6, 159.1, 137.4, 129.4, 122.3, 115.7, 112.5, 59.9, 54.9, 52.5, 38.5; **HRMS** (ESI+) calc. for $C_{21}H_{24}O_6$ $[M+Na]^+$ 395.1465; found 395.1473.

Dimethyl 2-(4-methoxybenzyl)malonate (5d)



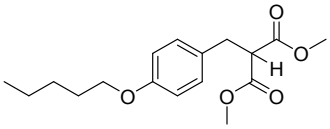
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a colourless liquid (237 mg, 94%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.11 (d, J = 8.8 Hz, 2H, ArH), 6.83 (d, J = 8.8 Hz, 2H, ArH), 3.81 (t, J = 8.0 Hz, 1H, CH), 3.71 (s, 3H, Ar-OCH_3), 3.60 (s, 6H, 2 x CH_3), 3.01 (d, J = 8.0 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.1, 158.2, 130.0, 129.6, 114.0, 55.1, 53.2, 52.5, 33.6; **HRMS** (ESI+) calc. for $C_{13}H_{16}O_5$ $[M+Na]^+$ 275.0890; found 275.0891.

Dimethyl 2,2-bis(4-methoxybenzyl)malonate (6d)



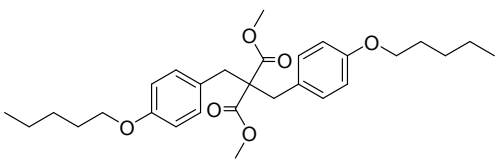
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a white solid (253 mg, 71%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.07 (d, J = 8.8 Hz, 4H, 2 x ArH), 6.81 (d, J = 8.8 Hz, 4H, 2 x ArH), 3.80 (s, 6H, 2 x Ar-OCH_3), 3.66 (s, 6H, 2 x CH_3), 3.16 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.5, 158.5, 131.1, 128.2, 113.7, 60.5, 55.4, 52.1, 38.3; **HRMS** (ESI+) calc. for $C_{21}H_{24}O_6$ $[M+Na]^+$ 395.1465; found 395.1474.

Dimethyl 2-(4-(pentyloxy)benzyl)malonate (5e)



This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless liquid (213 mg, 69%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.09 (d, J = 8.1 Hz, 2H, ArH), 6.81 (d, J = 8.1 Hz, 2H, ArH), 3.90 (t, J = 6.6 Hz, 2H, CH_2), 3.80 (t, J = 8.0 Hz, 1H, CH), 3.60 (s, 6H, 2 x CH_3), 3.01 (d, J = 7.7 Hz, 2H, CH_2), 1.72-1.64 (m, 2H, CH_2), 1.41-1.32 (m, 4H, CH_2 CH_2), 0.88 (t, J = 7.0 Hz, 3H, CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 168.9, 157.3, 130.0, 129.4, 114.3, 67.2, 53.0, 52.2, 33.6, 28.6, 28.0, 22.0, 14.1; **HRMS** (ESI+) calc. for $C_{17}H_{24}O_5$ $[M+Na]^+$ 331.1516; found 331.1523.

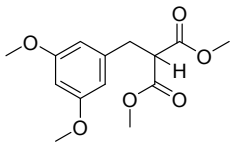
Dimethyl 2,2-bis(4-(pentyloxy)benzyl)malonate (6e)



This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless sticky liquid (368 mg, 76%). %). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.04 (d, J = 8.7 Hz, 4H, 2 x ArH), 6.84 (d, J = 8.7 Hz, 4H, 2 x ArH), 3.91 (t, J = 6.5 Hz, 4H, 2 x CH_2), 3.58 (s, 6H, 2 x CH_3), 3.00 (s, 4H, 2 x CH_2), 1.72-1.65 (m, 4H, 2 x CH_2), 1.42-1.30 (m, 8H, 2 x CH_2 CH_2), 0.89 (t, J = 7.1

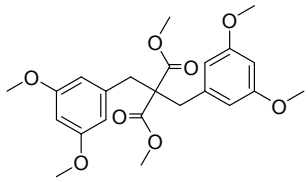
Hz, 6H, 2 x CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.9, 157.8, 131.3, 127.6, 114.3, 67.5, 60.2, 52.4, 37.6, 28.6, 27.9, 22.0, 14.2; **HRMS** (ESI+) calc. for $C_{29}H_{40}O_6$ $[M+Na]^+$ 507.2717; found 507.2724.

Dimethyl 2-(3,5-dimethoxybenzyl)malonate (5f)



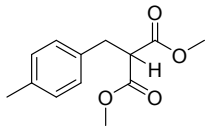
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a colourless liquid (200 mg, 71%). %). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 6.36-6.33 (m, 3H, ArH), 3.88 (t, J = 8.2 Hz, 1H, CH), 3.70 (s, 6H, 2 x Ar-OCH_3), 3.62 (s, 6H, 2 x CH_3), 3.01 (d, J = 8.2 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 168.8, 160.6, 140.1, 106.7, 98.3, 55.2, 52.6, 52.5, 34.3; **HRMS** (ESI+) calc. for $C_{14}H_{18}O_6$ $[M+Na]^+$ 305.0996; found 305.1000.

Dimethyl 2,2-bis(3,5-dimethoxybenzyl)malonate (6f)



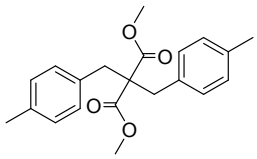
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a white solid (315 mg, 73%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 6.40 (d, J = 2.2 Hz, 2H, 2 x ArH), 6.24 (d, J = 2.2 Hz, 4H, 2 x ArH),3.71 (s, 12H, 4 x Ar-OCH_3), 3.63 (s, 6H, 2 x CH_3), 3.04 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.5, 160.3, 137.8, 108.1, 99.0, 59.6, 55.1, 52.5, 38.6; **HRMS** (ESI+) calc. for $C_{23}H_{28}O_8$ $[M+Na]^+$ 455.1676; found 455.1685.

Dimethyl 2-(4-methylbenzyl)malonate (5g)



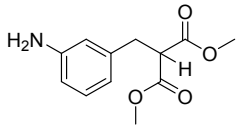
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a colourless liquid (160 mg, 68%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.08 (s, 4H, ArH), 3.83 (t, J = 8.1 Hz, 1H, CH), 3.60 (s, 6H, 2 x CH_3), 3.03 (d, J = 7.5 Hz, 2H, CH_2), 2.25 (s, 3H, Ar- CH_3),; **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.0, 136.0, 134.9, 129.1, 128.7, 52.9, 52.5, 33.8, 20.8; **HRMS** (ESI+) calc. for $C_{13}H_{16}O_4$ $[M+Na]^+$ 259.0941; found 259.0937.

Dimethyl 2,2-bis(4-methylbenzyl)malonate (6g)



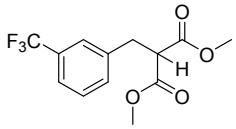
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (265 mg, 78%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.11 (d, J = 7.8 Hz, 4H, 2 x ArH), 7.03 (d, J = 8.0 Hz, 4H, 2 x ArH),3.59 (s, 6H, 2 x CH_3), 3.03 (s, 4H, 2 x CH_2), 2.27 (s, 6H, 2 x Ar-CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.8, 136.3, 132.8, 130.3, 129.2, 60.0, 52.5, 37.9, 20.9; **HRMS** (ESI+) calc. for $C_{21}H_{24}O_4$ $[M+Na]^+$ 363.1567; found 363.1570.

Dimethyl 2-(3-aminobenzyl)malonate (5h)



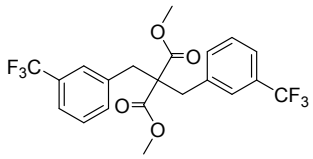
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/3) as a colourless liquid (12 mg, 5%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 6.89 (t, J = 7.7 Hz, 1H, ArH), 6.40-6.35 (m, 2H, ArH), 6.30 (t, J = 7.5 Hz, 1H, ArH), 5.00 (s, 2H, NH_2), 3.72 (t, J = 8.0 Hz, 1H, CH), 3.62 (s, 6H, 2 x CH_3), 2.91 (d, J = 8.3 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.1, 148.8, 138.2, 129.1, 116.0, 114.0, 112.5, 53.0, 52.5, 34.5; **HRMS** (ESI+) calc. for $C_{12}H_{15}NO_4$ $[M+Na]^+$ 260.0893; found 260.0888.

Dimethyl 2-(3-(trifluoromethyl)benzyl)malonate (5i)



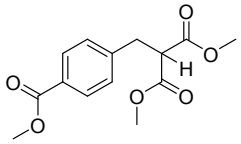
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (209 mg, 72%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.59-7.51 (m, 4H, ArH), 3.99 (t, J = 8.0 Hz, 1H, CH), 3.60 (s, 6H, 2 x CH_3), 3.18 (d, J = 7.3 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.7, 138.5, 132.2, 130.8 (q, $^2J_{CF}$ = 32Hz), 128.9, 125.4 (q, $^3J_{CF}$ = 4Hz), 123.9 (q, $^1J_{CF}$ = 272Hz), 123.6 (q, $^3J_{CF}$ = 4Hz), 53.2, 52.6, 34.3; **HRMS** (ESI+) calc. for $C_{13}H_{13}F_3O_4$ $[M+Na]^+$ 313.0658; found 313.0664.

Dimethyl 2,2-bis(3-(trifluoromethyl)benzyl)malonate (6i)



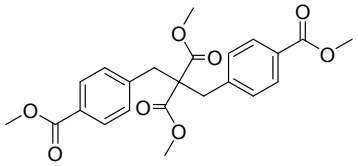
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (278 mg, 62%). %). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.64 (d, J = 7.6 Hz, 2H, 2 x ArH), 7.56 (t, J = 7.8 Hz, 2H, 2 x ArH), 7.49 (d, J = 7.6 Hz, 2H, 2 x ArH), 7.43 (s, 2H, 2 x ArH), 3.57 (s, 6H, 2 x CH_3), 3.25 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.5, 136.7, 133.3, 130.6 (q, $^2J_{CF}$ = 33Hz), 128.7, 126.6 (q, $^3J_{CF}$ = 4Hz), 124.0 (q, $^3J_{CF}$ = 4Hz), 123.9 (q, $^1J_{CF}$ = 272Hz), 60.2, 52.3, 39.5; **HRMS** (ESI+) calc. for $C_{21}H_{18}F_6O_4$ $[M+Na]^+$ 471.1001; found 471.1003.

Dimethyl 2-(4-(methoxycarbonyl)benzyl)malonate (5j)



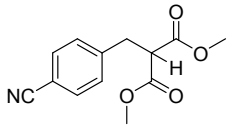
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/3) as a white solid (160 mg, 57%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.88 (d, J = 8.1 Hz, 2H, ArH), 7.37 (d, J = 8.1 Hz, 2H, ArH), 3.95 (t, J = 8.0 Hz, 1H, CH), 3.83 (s, 3H, Ar-$COOCH_3$), 3.61 (s, 6H, 2 x CH_3), 3.16 (d, J = 8.0 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 168.8, 166.1, 143.5, 129.4, 129.3, 128.2, 52.6, 52.3, 52.2, 34.0; **HRMS** (ESI+) calc. for $C_{14}H_{16}O_6$ $[M+Na]^+$ 303.0839; found 303.0846.

Dimethyl 2,2-bis(4-(methoxycarbonyl)benzyl)malonate (6j)



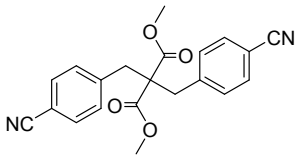
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a white solid (218 mg, 51%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 4H, 2 x ArH), 7.21 (d, J = 8.4 Hz, 4H, 2 x ArH), 3.92 (s, 6H, 2 x Ar-$COOCH_3$), 3.65 (s, 6H, 2 x CH_3), 3.27 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 170.7, 166.8, 141.2, 129.9, 129.5, 128.9, 60.1, 52.3, 52.0, 39.6; **HRMS** (ESI+) calc. for $C_{23}H_{24}O_8$ $[M+Na]^+$ 451.1363; found 451.1371.

Dimethyl 2-(4-cyanobenzyl)malonate (5k)



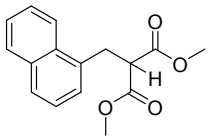
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/3) as a colourless liquid (148 mg, 60%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.76 (d, J = 8.8 Hz, 2H, ArH), 7.44 (d, J = 8.8 Hz, 2H, ArH), 3.99 (t, J = 8.0 Hz, 1H, CH), 3.61 (s, 6H, 2 x CH_3), 3.17 (d, J = 8.0 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 168.8, 143.9, 132.6, 130.1, 119.0, 109.8, 52.9, 52.1, 34.1; **HRMS** (ESI+) calc. for $C_{13}H_{13}NO_4$ $[M+Na]^+$ 270.0737; found 270.0729.

Dimethyl 2,2-bis(4-cyanobenzyl)malonate (6k)



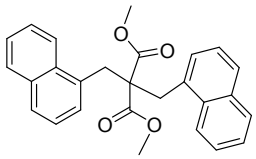
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a a white solid (217 mg, 60%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.69 (d, J = 8.6 Hz, 4H, 2 x ArH), 7.36 (d, J = 8.6 Hz, 4H, 2 x ArH), 3.57 (s, 6H, 2 x CH_3), 3.22 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.0, 141.9, 132.4, 131.2, 118.9, 110.1, 59.8, 52.6; 39.2; **HRMS** (ESI+) calc. for $C_{21}H_{18}N_2O_4$ $[M+Na]^+$ 385.1159; found 385.1161.

Dimethyl 2-(naphthalen-1-ylmethyl)malonate (5l)



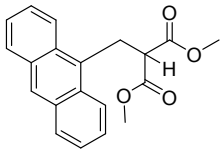
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/6) as a colourless liquid (177 mg, 65%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.88-7.83 (m, 3H, ArH), 7.03 (d, J = 0.7 Hz, 1H, ArH), 7.50-7.45 (m, 2H, ArH), 7.40 (dd, J = 8.5, 1.7 Hz, 1H, ArH), 4.00 (t, J = 8.0 Hz, 1H, CH), 3.60 (s, 6H, 2 x CH_3), 3.26 (d, J = 7.8 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.1, 135.5, 133.2, 132.0, 128.0, 127.63, 127.57, 127.3, 127.1, 126.3, 125.8, 52.7, 52.5, 34.5; **HRMS** (ESI+) calc. for $C_{16}H_{16}O_4$ $[M+Na]^+$ 295.0941; found 295.0939.

Dimethyl 2,2-bis(naphthalen-1-ylmethyl)malonate (6l)



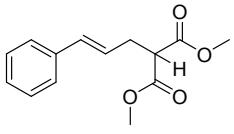
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a white solid (350 mg, 85%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.93-7.86 (m, 6H, 2 x ArH), 7.74 (s, 2H, 2 x ArH), 7.54-7.49 (m, 4H, 2 x ArH), 7.33 (dd, J = 8.5, 1.8 Hz, 2H, 2 x ArH), 3.62 (s, 6H, 2 x CH_3), 3.33 (s, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 171.3, 133.6, 133.2, 132.3, 128.9, 128.0, 127.7, 127.6, 127.5, 126.0, 125.6, 60.5, 52.2, 39.6; **HRMS** (ESI+) calc. for $C_{27}H_{24}O_4$ $[M+Na]^+$ 435.1567; found 435.1574.

Dimethyl 2-(anthracen-9-ylmethyl)malonate (5m)



This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/6) as a yellow solid (200 mg, 62%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 8.56 (s, 1H, ArH), 8.27-8.24 (m, 2H, ArH), 8.11-8.09 (m, 2H, ArH), 7.60-7.51 (m, 4H, ArH), 4.18 (d, J = 7.8 Hz, 2H, CH_2), 3.87 (t, J = 7.8 Hz, 1H, CH), 3.47 (s, 6H, 2 x CH_3); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.0, 131.2, 129.6, 129.5, 129.3, 127.1, 126.4, 125.3, 124.1, 52.5, 52.4, 26.2; **HRMS** (ESI+) calc. for $C_{20}H_{18}O_4$ $[M+Na]^+$ 345.1097; found 345.1105.

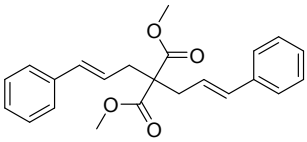
Dimethyl 2-cinnamylmalonate (5n)



This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/5) as a colourless liquid (219 mg, 94%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.37-7.28 (m, 4H, ArH), 7.25-7.20 (m, 1H, ArH),6.46 (d, J = 16.3 Hz, 1H, = CH), 6.23-6.15 (m, 1H, =CH), 3.73 (t, J =

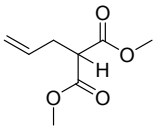
7.5 Hz, 1H, CH), 3.66 (s, 6H, 2 x CH_3), 2.67 (td, J = 7.3, 1.2 Hz, 2H, CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 169.2, 136.8, 132.2, 128.7, 127.5, 126.1, 125.9, 52.6, 51.1, 32.1; **HRMS** (ESI+) calc. for $C_{14}H_{16}O_4$ $[M+Na]^+$ 271.0941; found 271.0934.

Dimethyl 2,2-dicinnamylmalonate (6n)



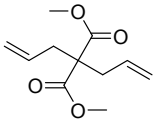
This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless sticky liquid (328 mg, 90%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 7.42-7.40 (m, 4H, 2 x ArH), δ 7.34-7.30 (m, 4H, 2 x ArH), δ 7.26-7.22 (m, 2H, 2 x ArH), 6.52 (d, J = 15.8 Hz, 2H, 2 x = CH), 6.16 (dt, J = 15.8, 8.2 Hz, 2H, 2 x =CH), 3.68 (s, 6H, 2 x CH_3), 2.75 (d, J = 7.4 Hz, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 171.0, 136.7, 134.0, 128.8, 127.6, 126.5, 124.0, 58.1, 52.7, 36.1; **HRMS** (ESI+) calc. for $C_{23}H_{24}O_4$ $[M+Na]^+$ 387.1567; found 387.1571.

Dimethyl 2-allylmalonate (5o)



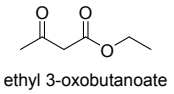
This compound was prepared according to general procedure A and isolated by flash column chromatography (ethyl acetate/hexane=1/10) as a colourless liquid (91 mg, 53%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.81-5.71 (m, 1H, =CH), 5.14-5.05 (m, 2H, =CH_2), 3.74 (s, 6H, 2 x CH_3), 3.46 (t, J = 7.6 Hz, 1H, CH), 2.67-2.62 (m, 2H, CH_2); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.5, 133.7, 117.8, 52.5, 51.3, 32.8; **HRMS** (ESI+) calc. for $C_8H_{12}O_4$ $[M+Na]^+$ 195.0628; found 195.0630.

Dimethyl 2,2-diallylmalonate (6o)

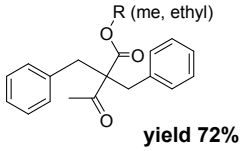


This compound was prepared according to general procedure B and isolated by flash column chromatography (ethyl acetate/hexane=1/20) as a colourless liquid (142 mg, 67%). **^{1}H NMR** (400 MHz, d_6-DMSO) δ 5.67-5.58 (m, 2H, 2 x =CH), 5.15-5.09 (m, 4H, 2 x =CH_2), 3.65 (s, 6H, 2 x CH_3), 2.53 (d, J = 8.0 Hz, 4H, 2 x CH_2); **^{13}C NMR** (101 MHz, d_6-DMSO) δ 170.5, 132.4, 119.6, 57.1, 52.5, 36.5; **HRMS** (ESI+) calc. for $C_{11}H_{16}O_4$ $[M+Na]^+$ 235.0941; found 235.0942.

Table S4. Primary screening for other substrates.

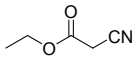


ethyl 3-oxobutanoate



yield 72%

minor product



minor product

minor product

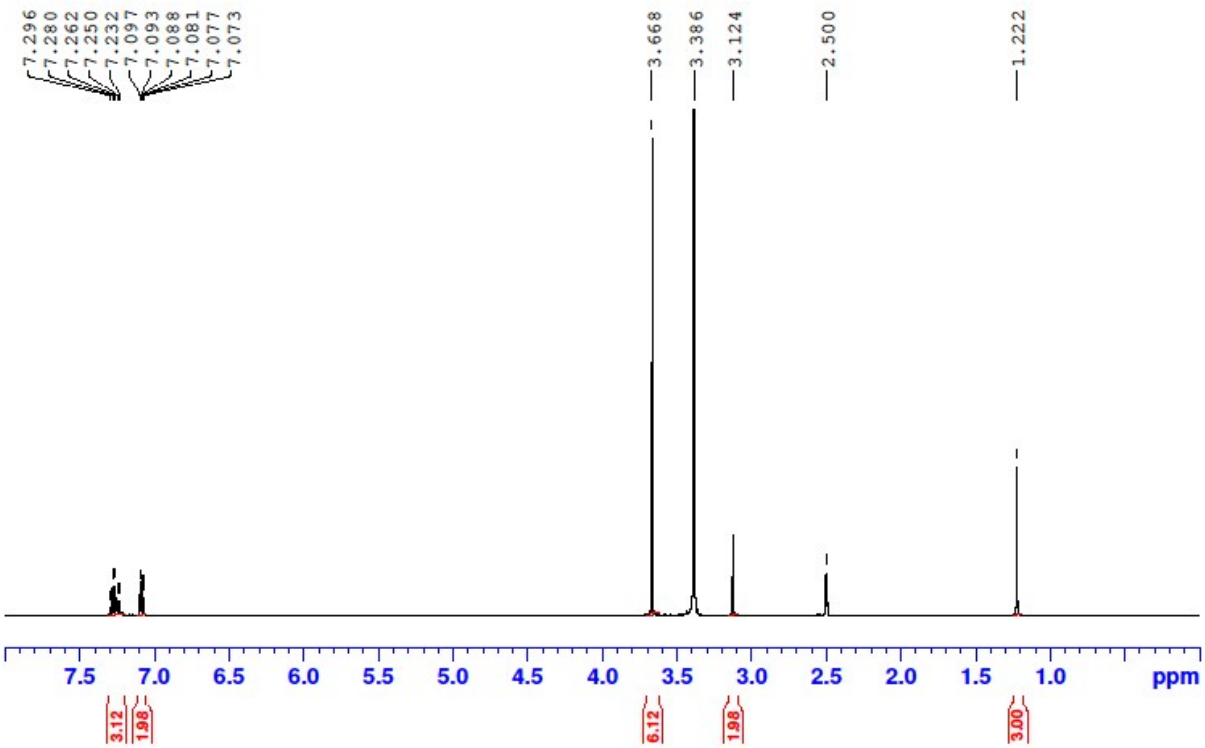
Reaction conditions: Benzyl alcohol (2.2 mmol), substrates (1.0 mmol), $Pd(OAc)_2$ (2 mol%), dppp (5 mol%), Cs_2CO_3 (2.2 eq.), DMC (3 mL), 120 ^oC, 48 h.

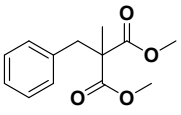
4. References

[1] F. Bjoerkling, J. Boutelje, S. Gatenbeck, K. Hult, T. Norin, P.Szmulik, *Tetrahedron* 1985, **41**, 1347.
[2] E. Fillion, D. Fishlock, A. Wilsily, J. M. Goll. *J. Org. Chem.* 2005, **70**, 1316-1327.
[3] T. Ke, C. R. Wescott, A. M. Klibanov. *J. Am. Chem. Soc.* 1996, **118**, 3366-3374.

5. ^{1}H and ^{13}C NMR Spectra of malonates

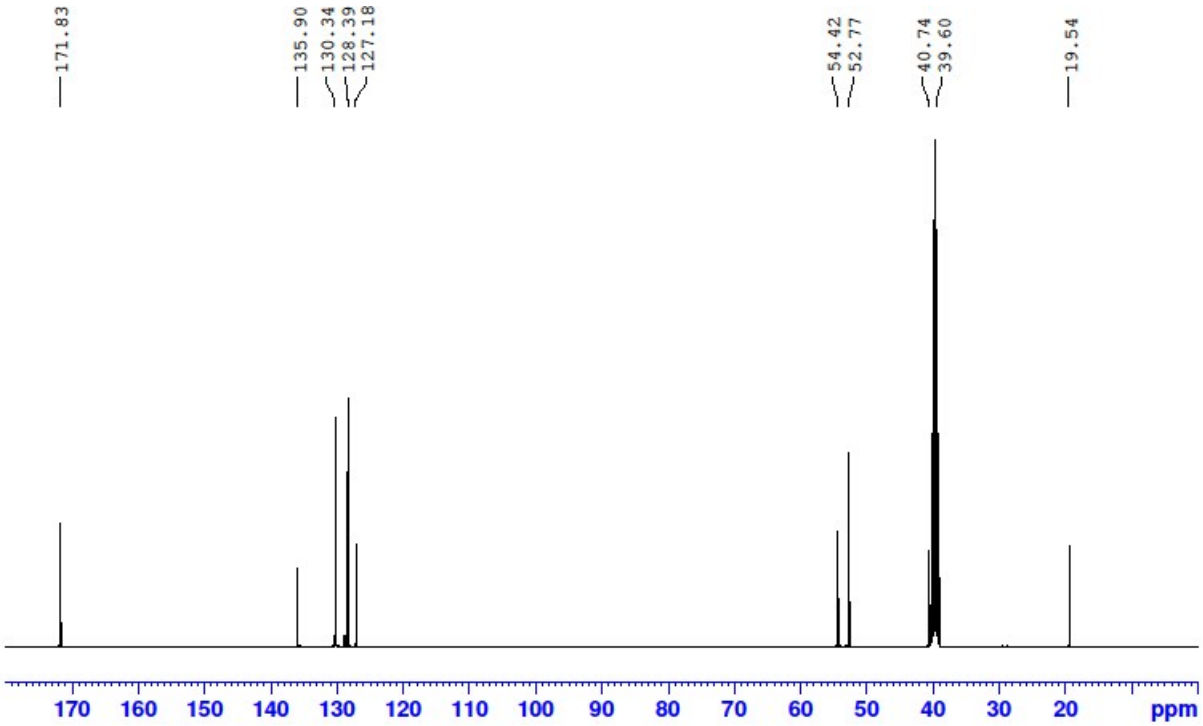
^{1}H NMR, d_6-DMSO, 400 MHz



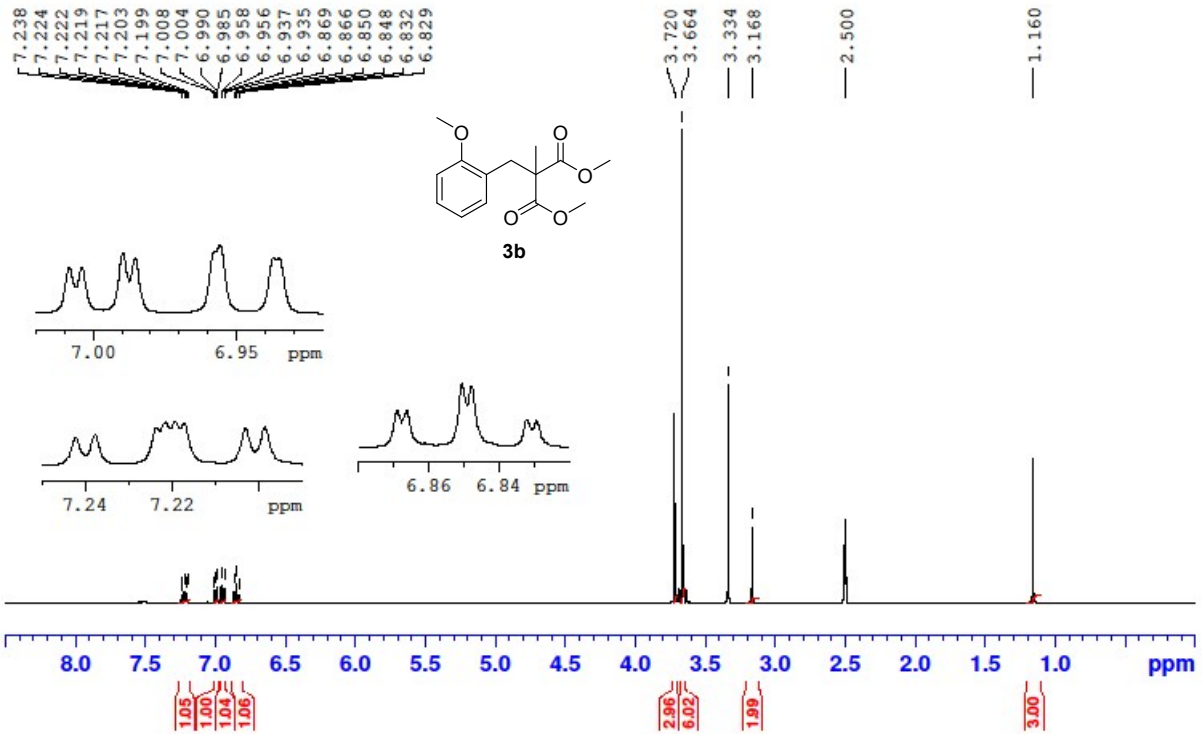


3a

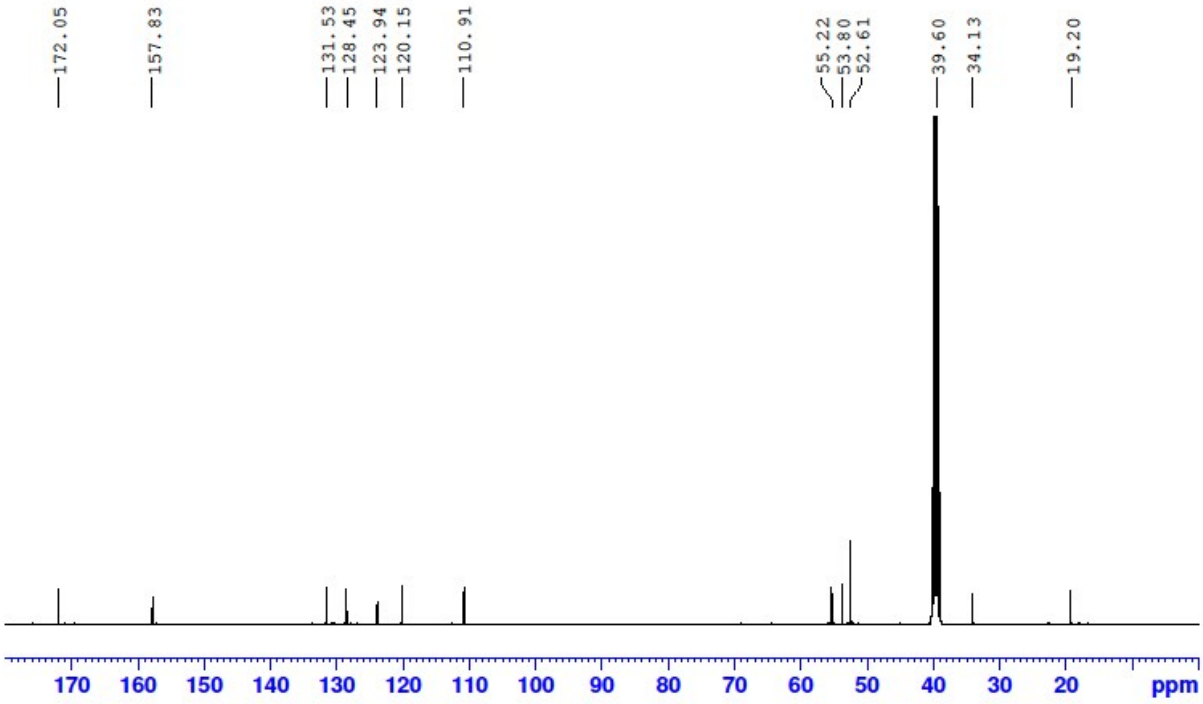
^{13}C NMR, d_6-DMSO, 101 MHz



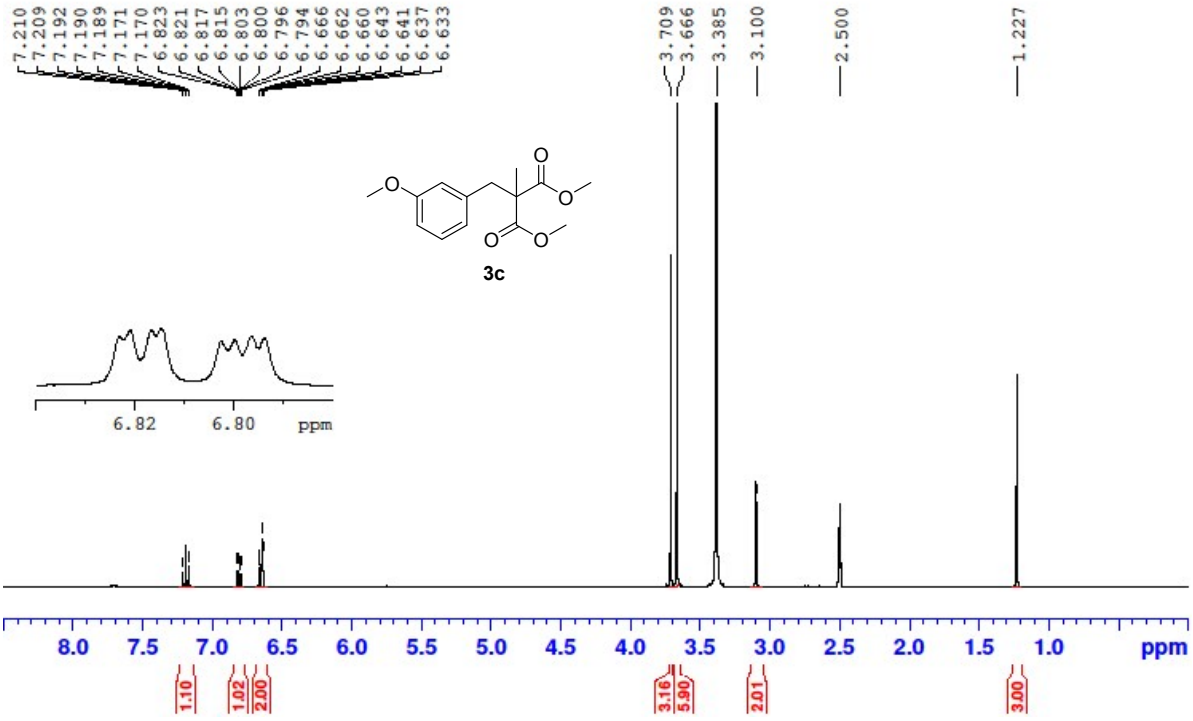
^{1}H NMR, d_6-DMSO, 400 MHz



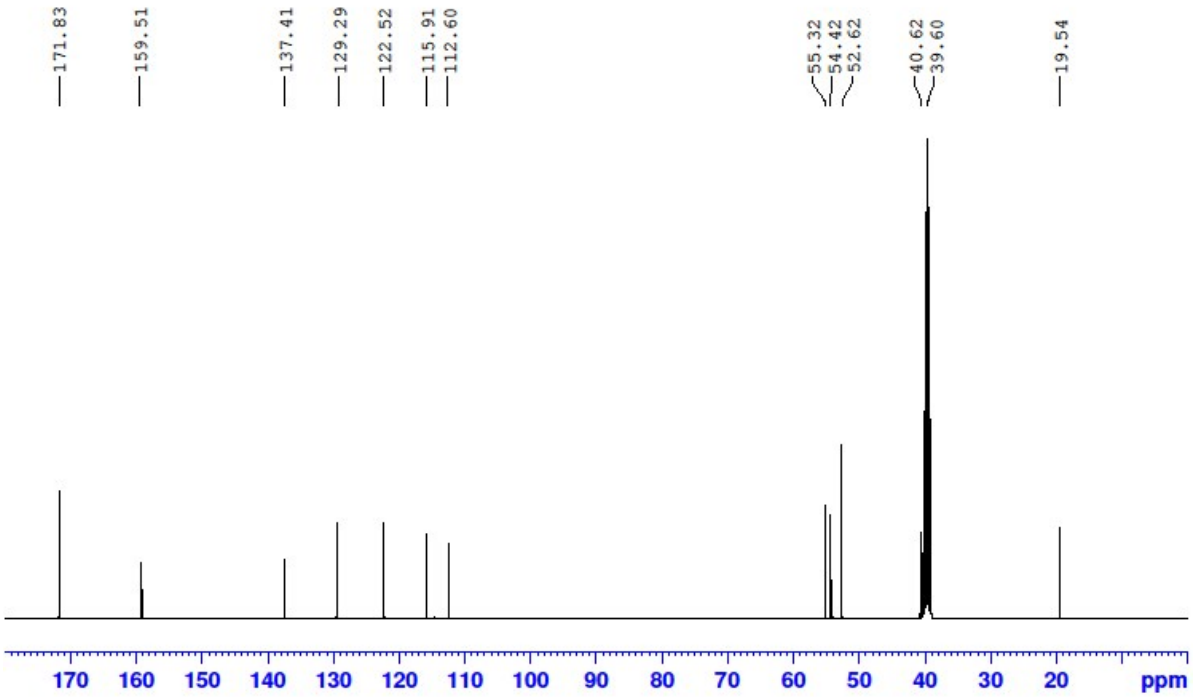
^{13}C NMR, d_6-DMSO, 101 MHz



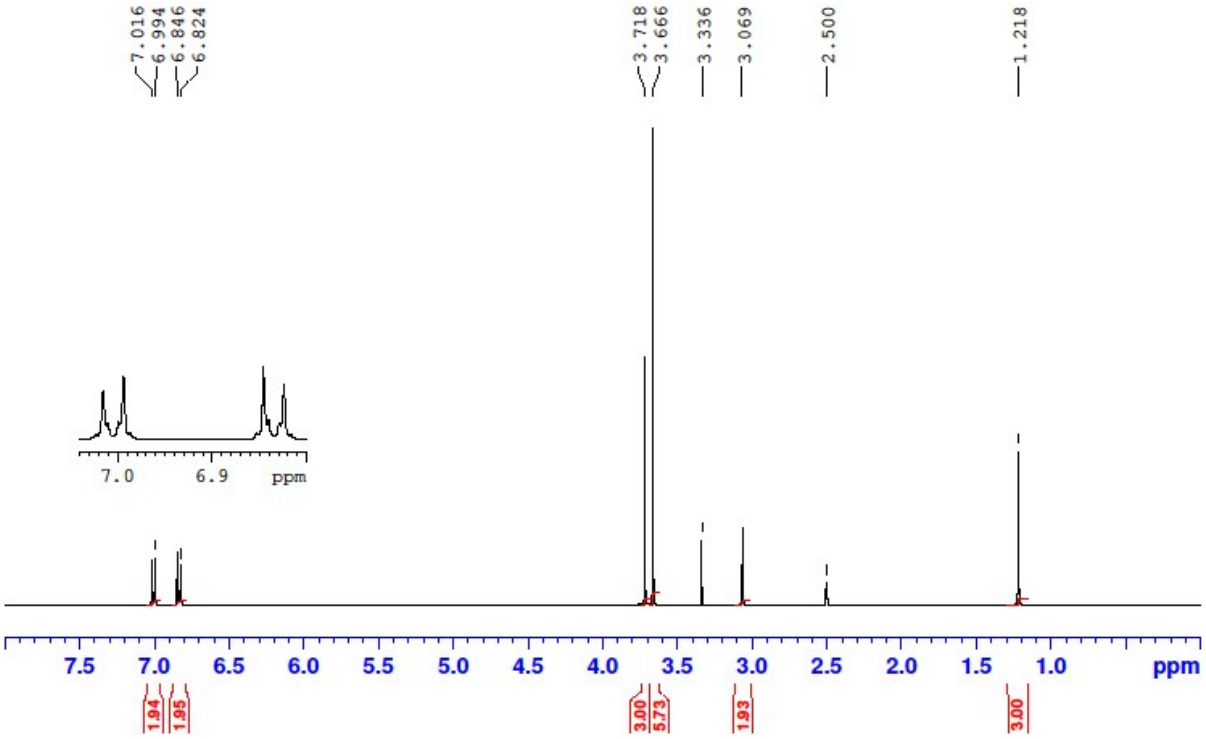
^{1}H NMR, d_6-DMSO, 400 MHz

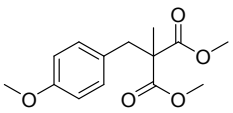


^{13}C NMR, d_6-DMSO, 101 MHz



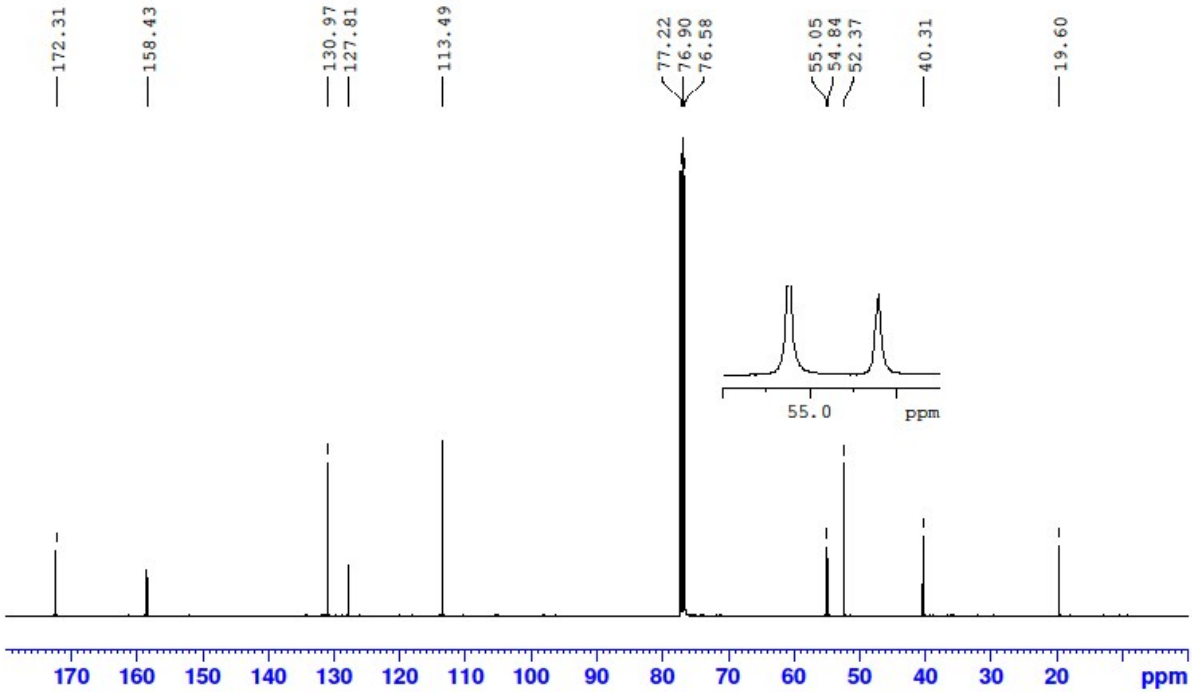
^{1}H NMR, d_6-DMSO, 400 MHz



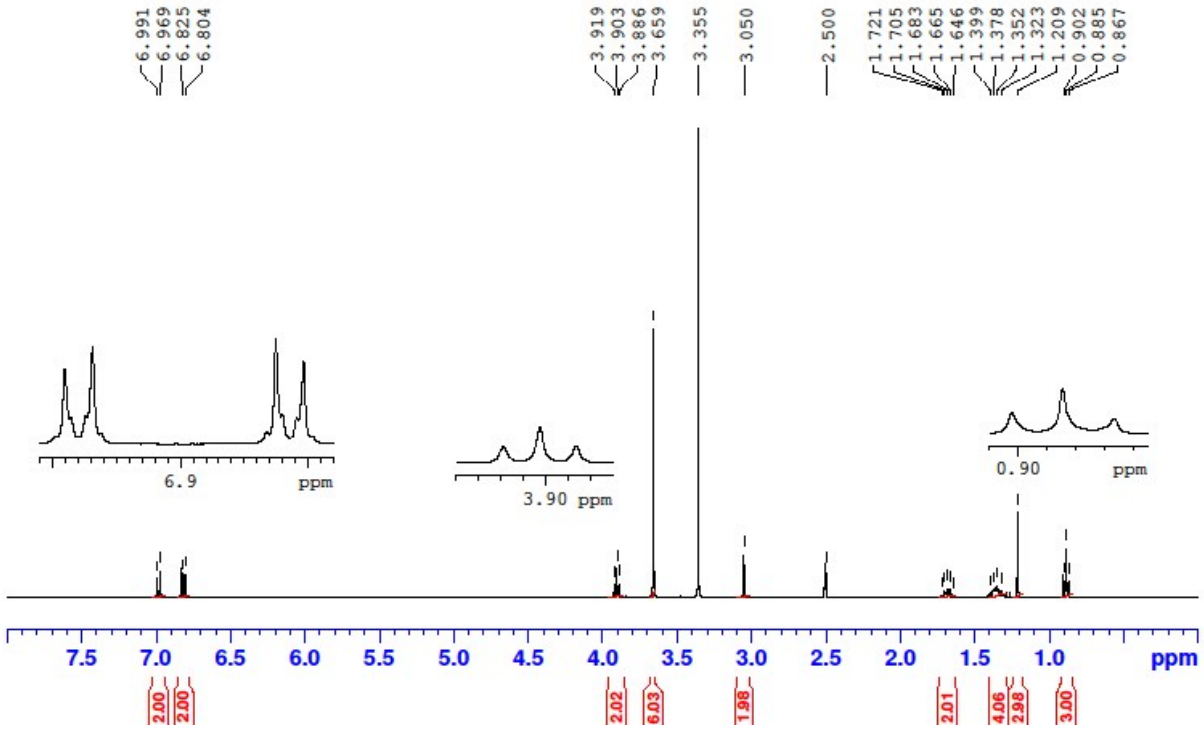


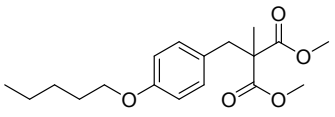
3d

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



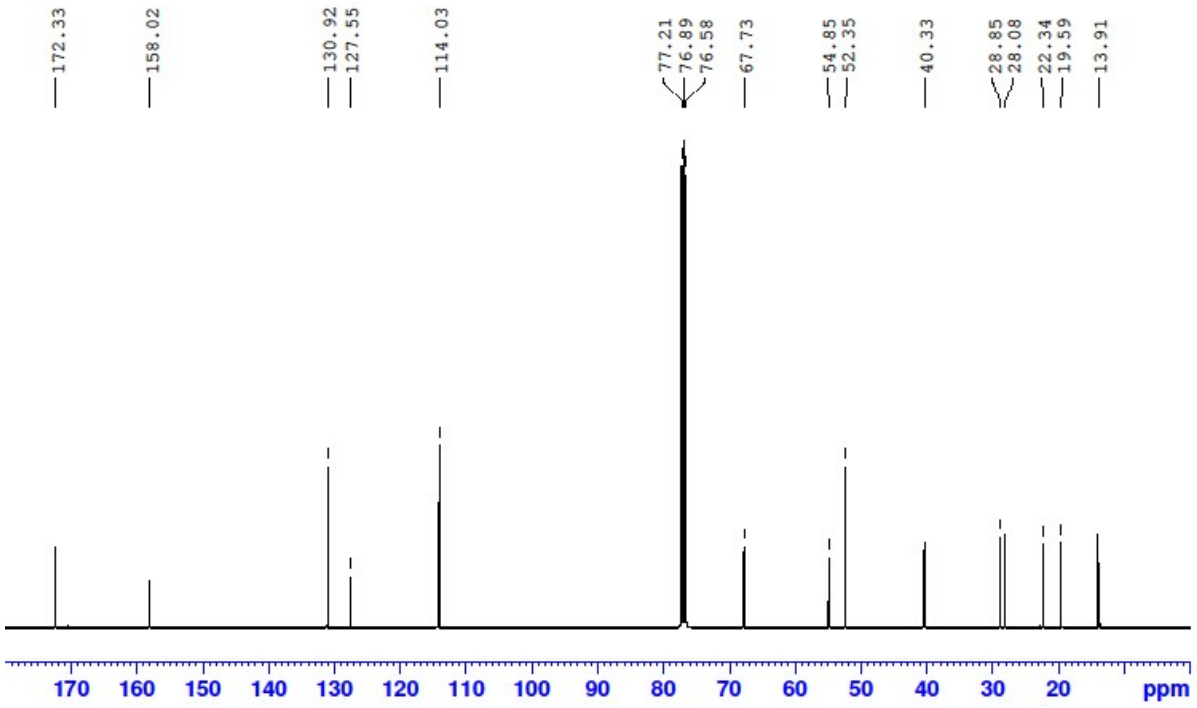
^{1}H NMR, d_6-DMSO, 400 MHz



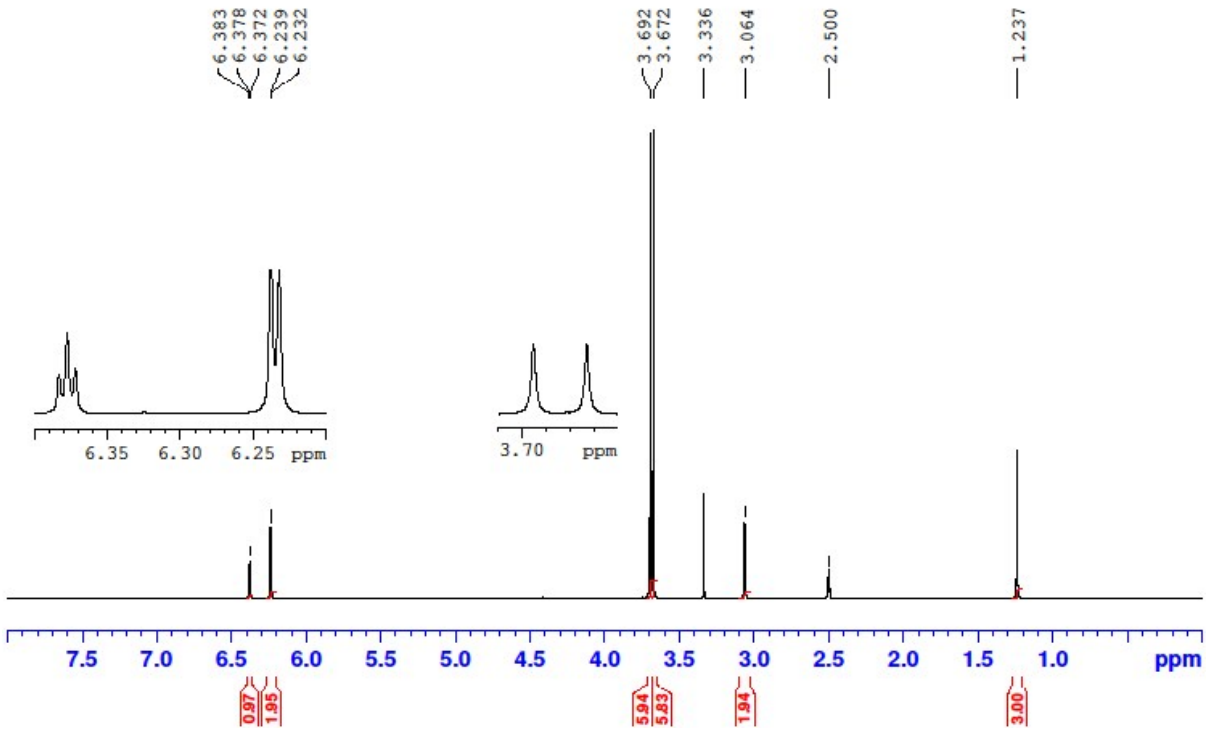


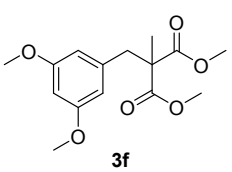
3e

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



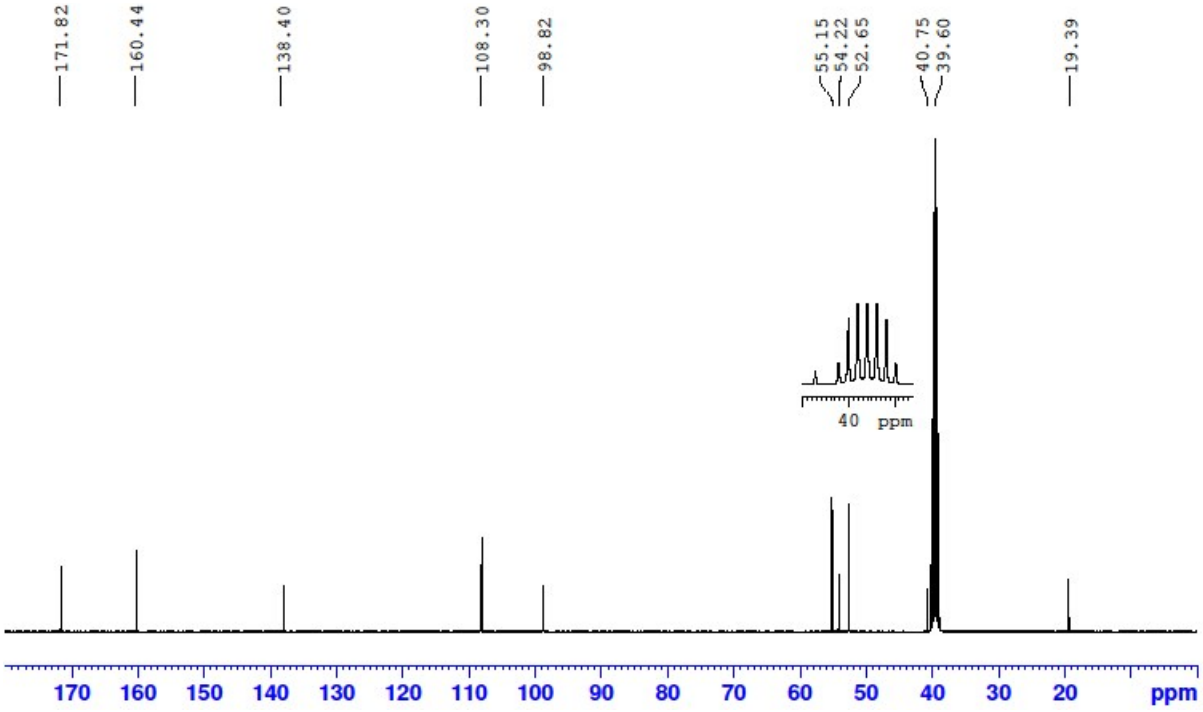
^{1}H NMR, d_6-DMSO, 400 MHz



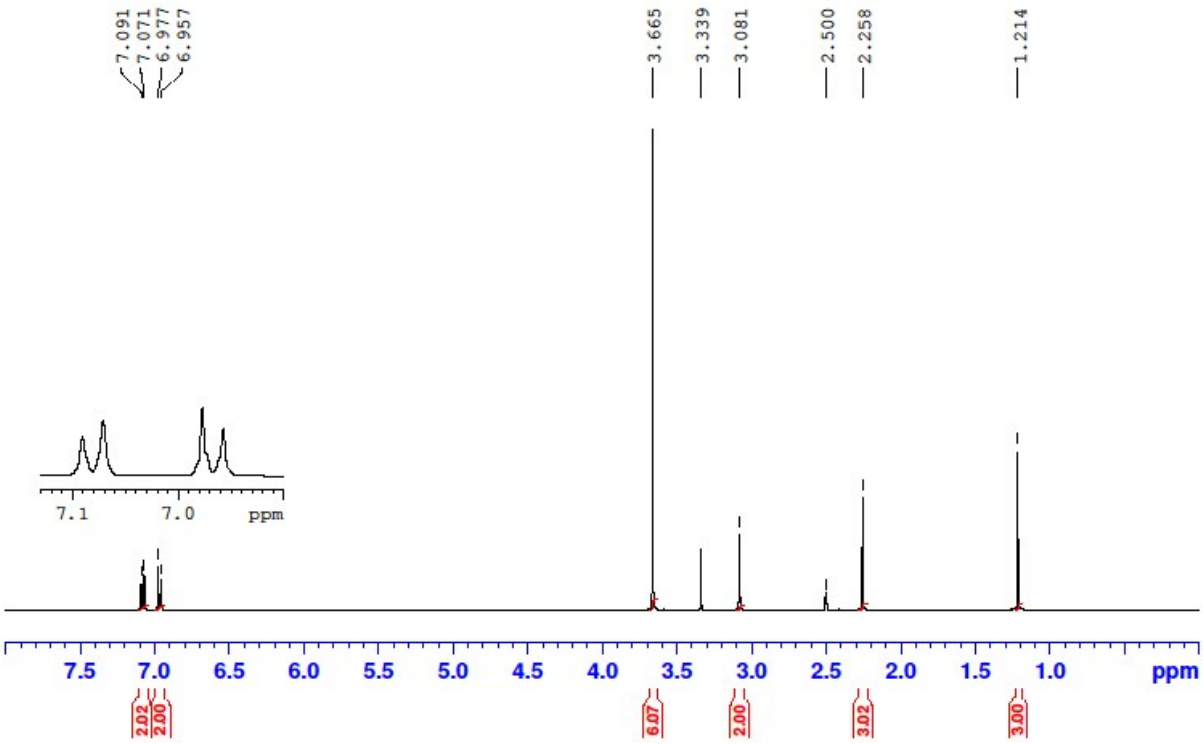


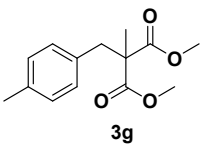
3f

^{13}C NMR, d_6-DMSO, 101 MHz



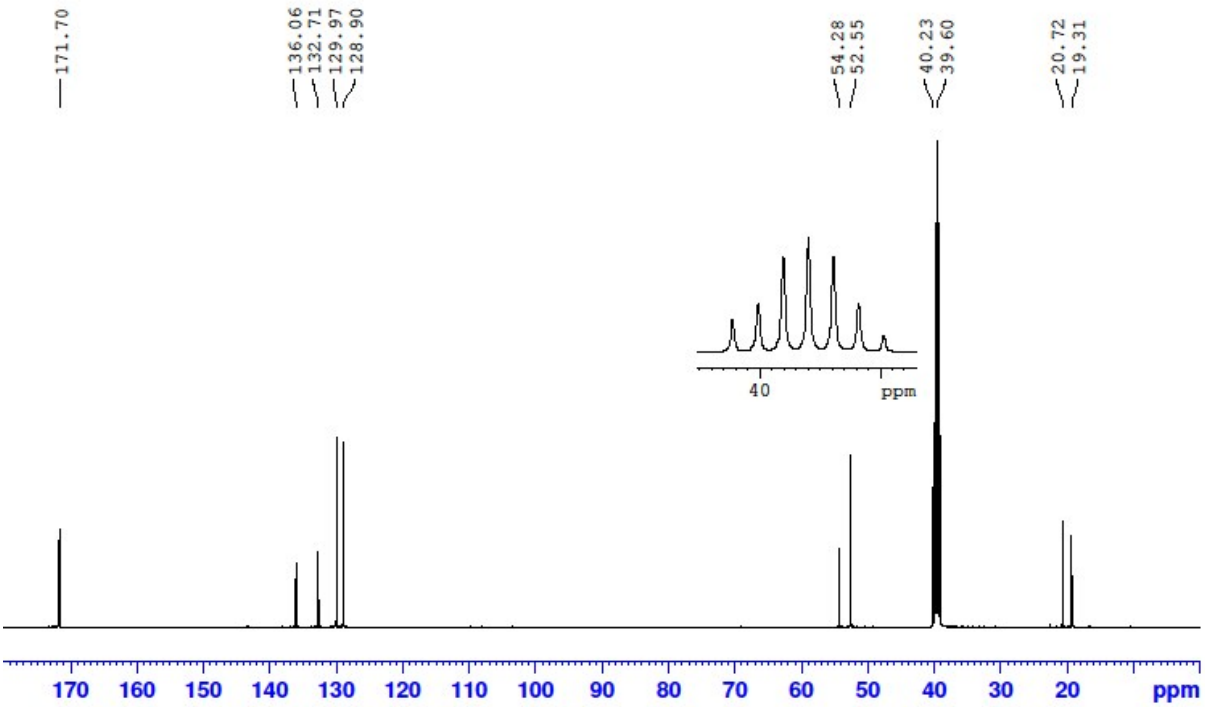
^{1}H NMR, d_6-DMSO, 400 MHz



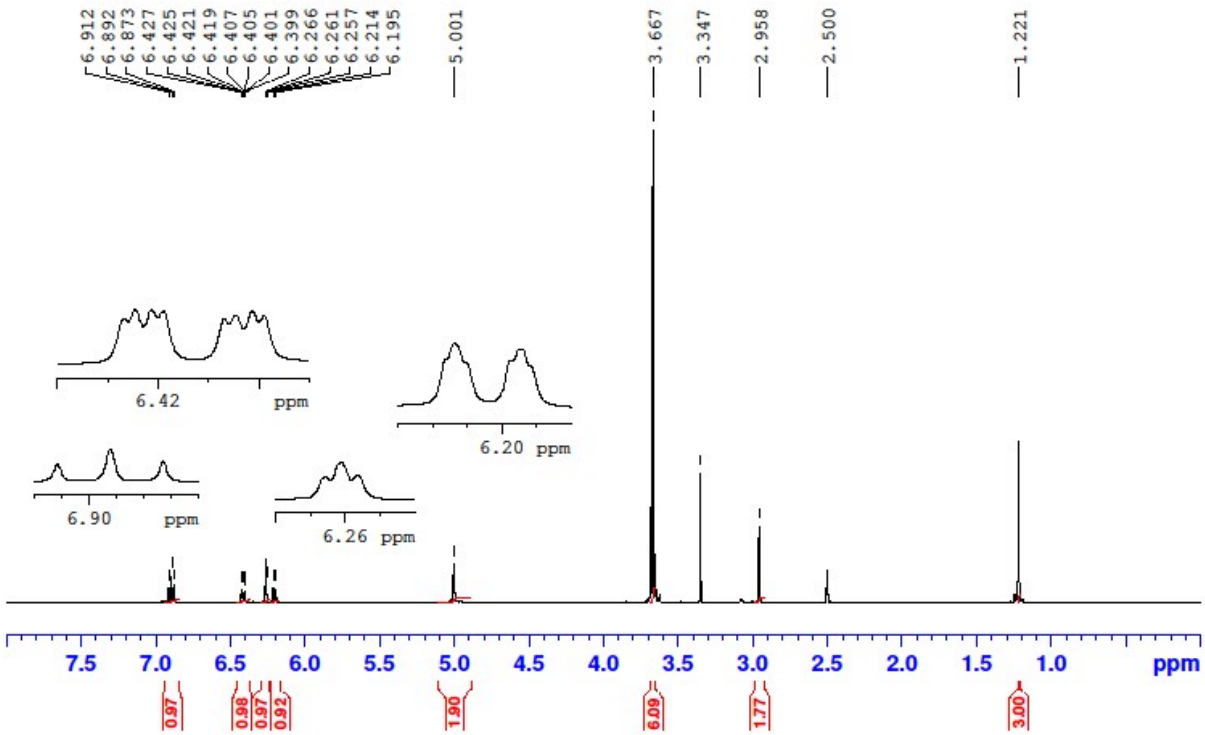


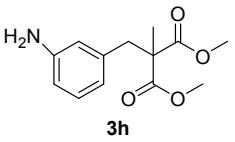
3g

^{13}C NMR, d_6-DMSO, 101 MHz



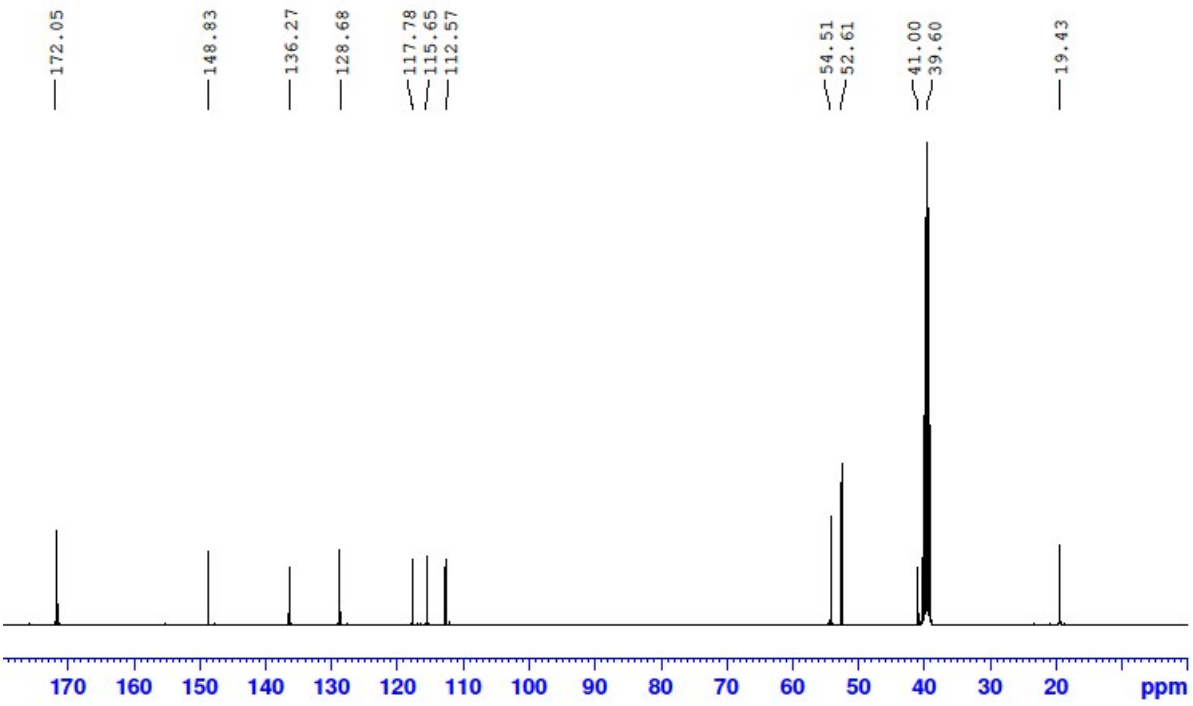
^{1}H NMR, d_6-DMSO, 400 MHz



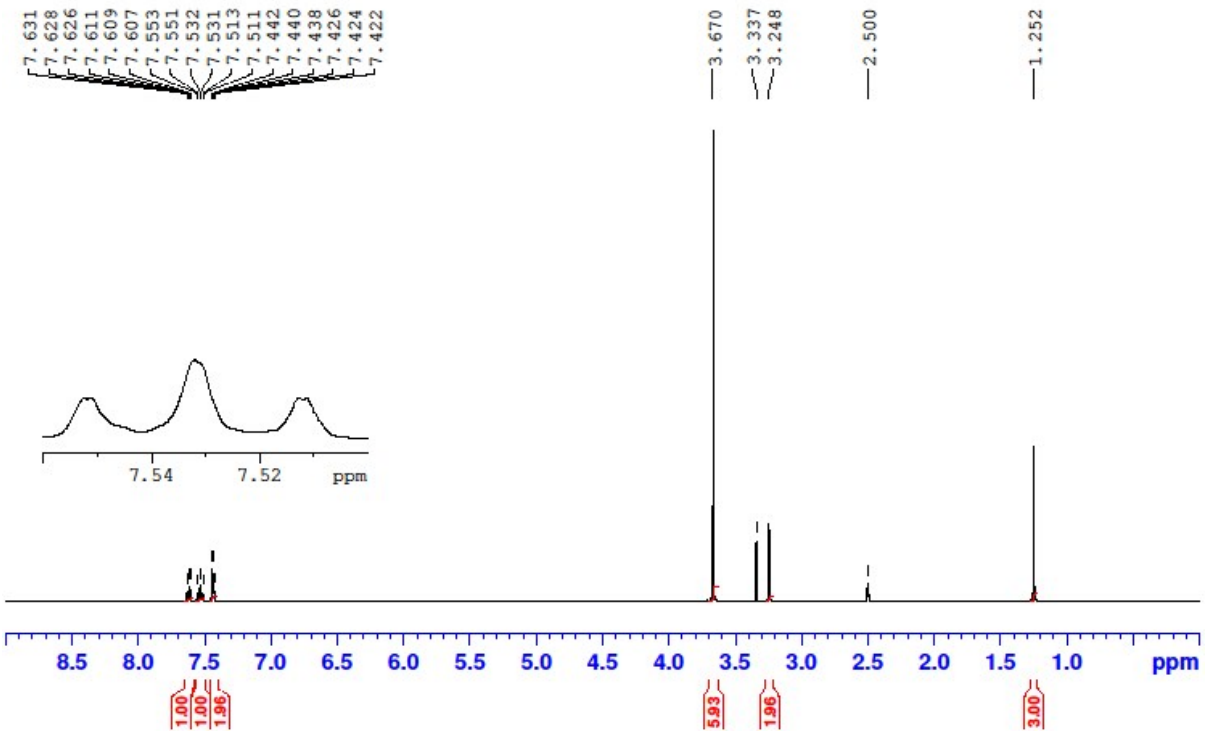


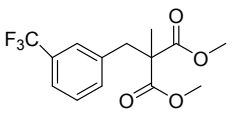
3h

^{13}C NMR, d_6-DMSO, 101 MHz



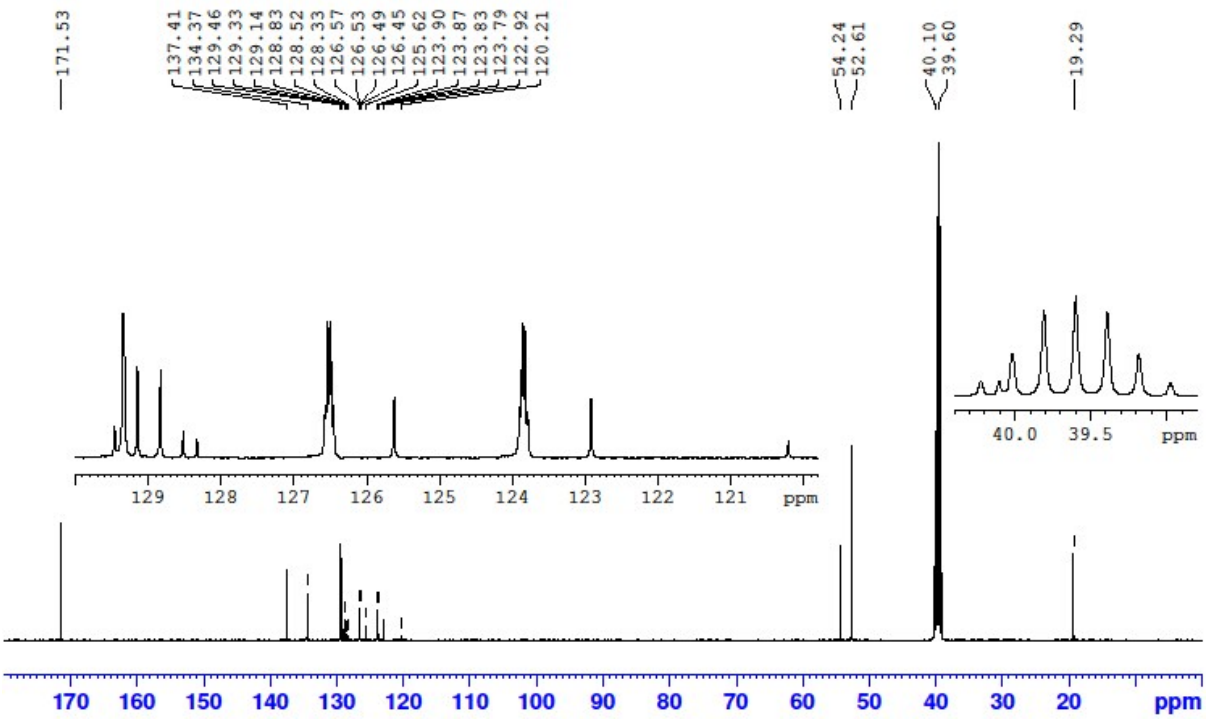
^{1}H NMR, d_6-DMSO, 400 MHz



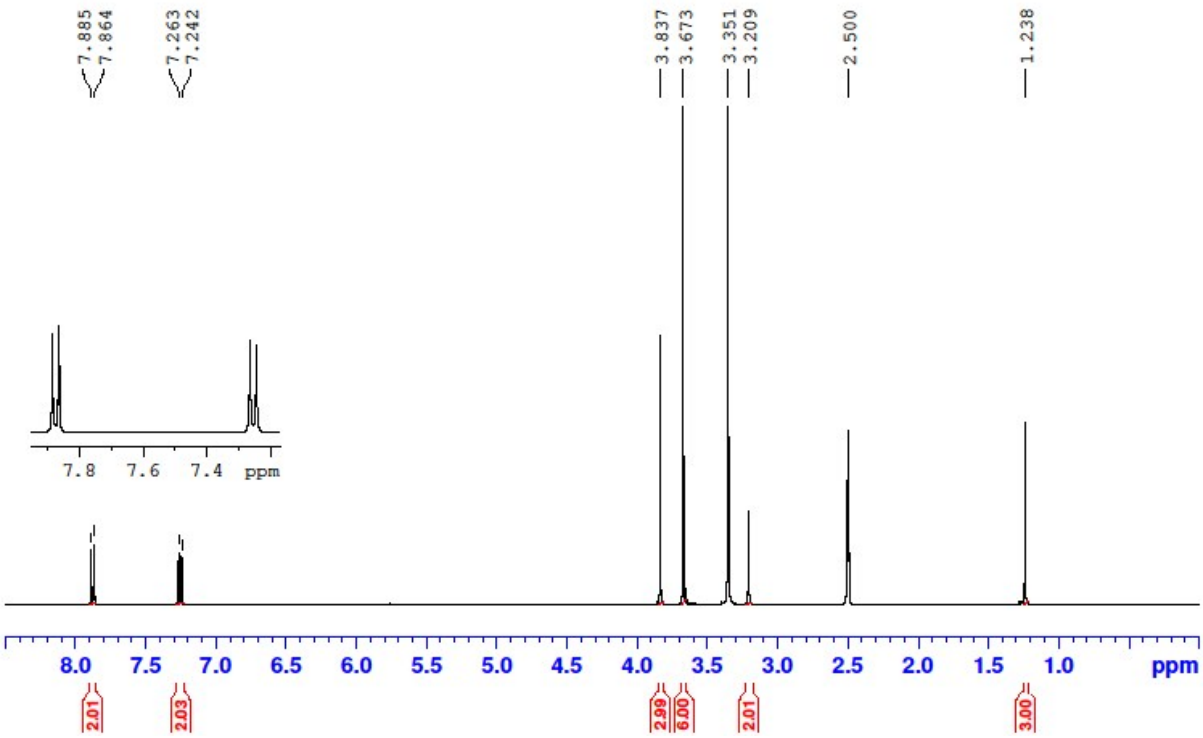


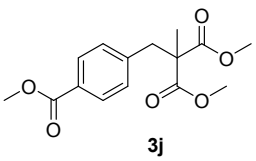
3i

^{13}C NMR, d_6-DMSO, 101 MHz



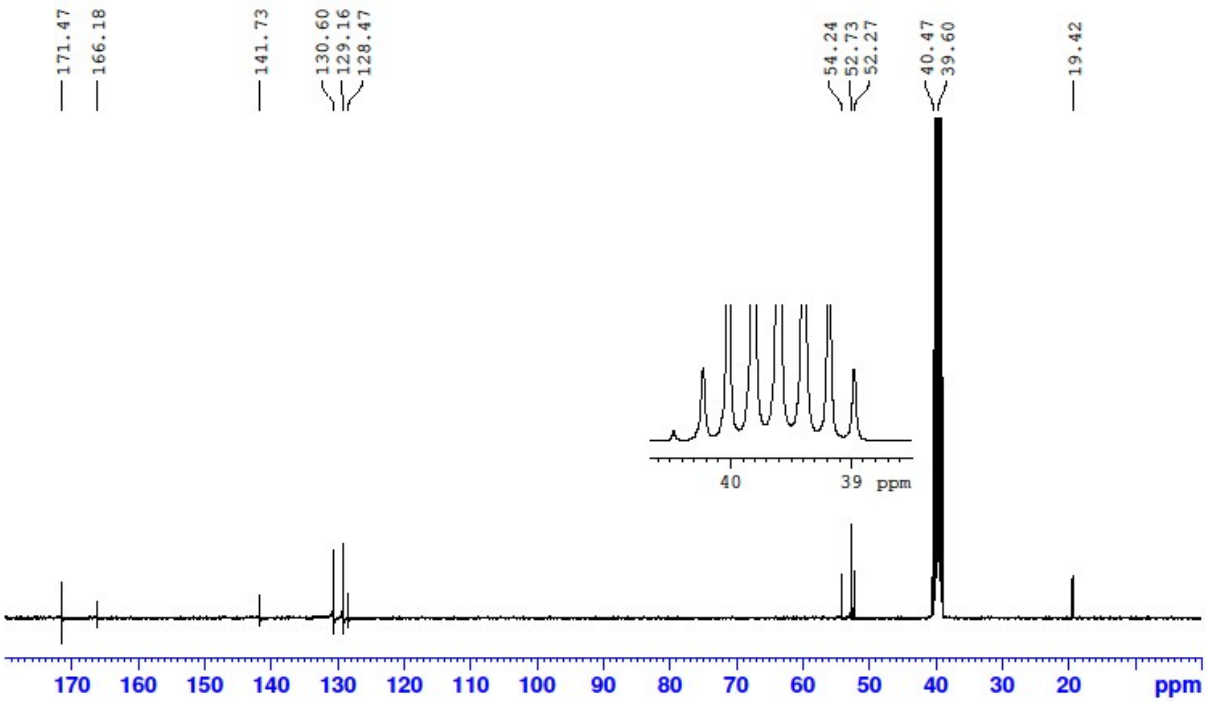
^{1}H NMR, d_6-DMSO, 400 MHz



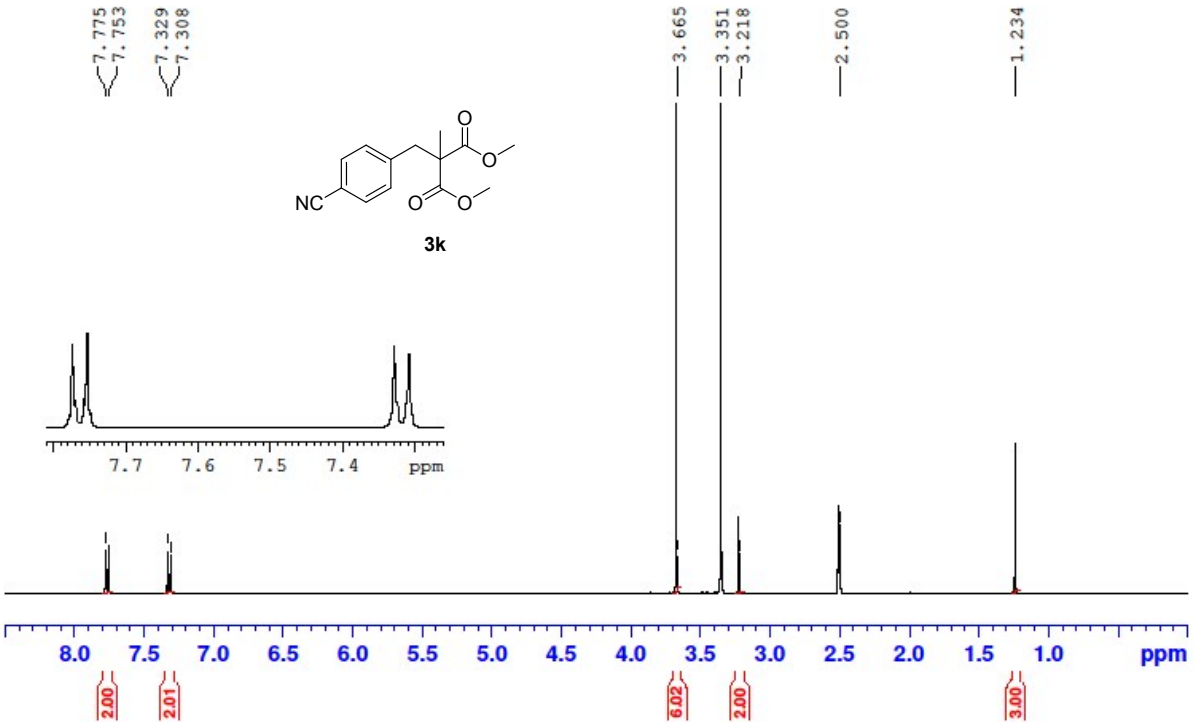


3j

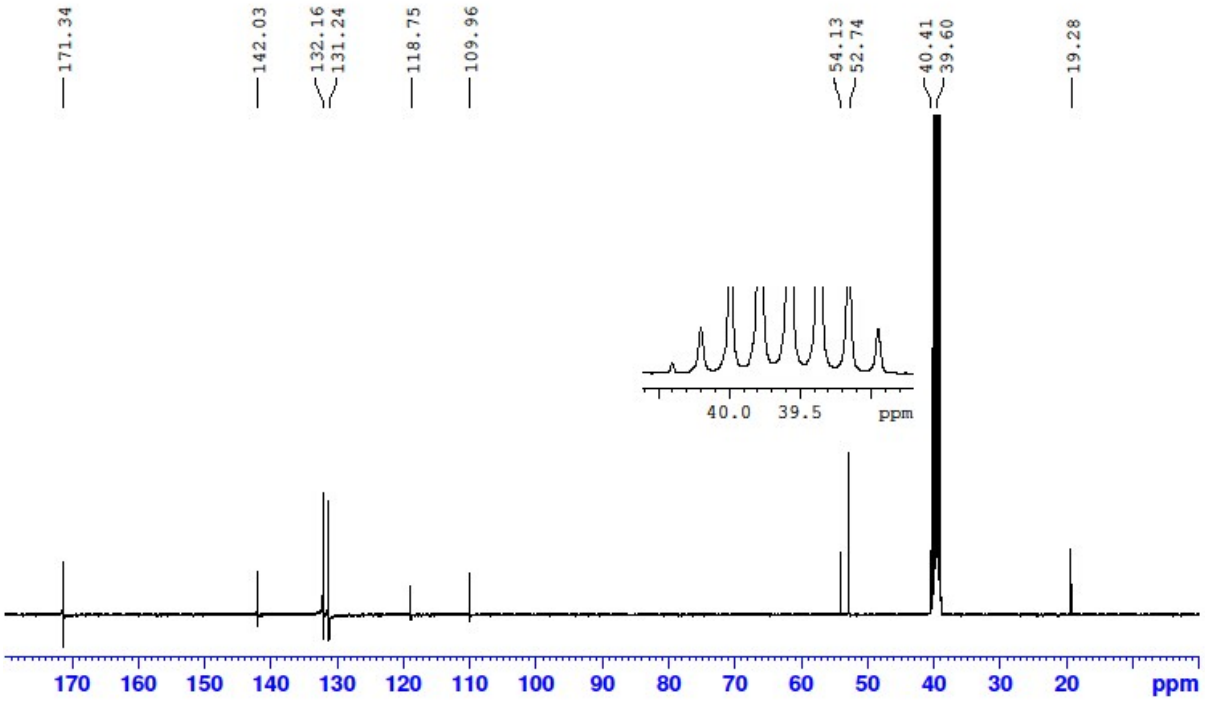
^{13}C NMR, d_6-DMSO, 101 MHz



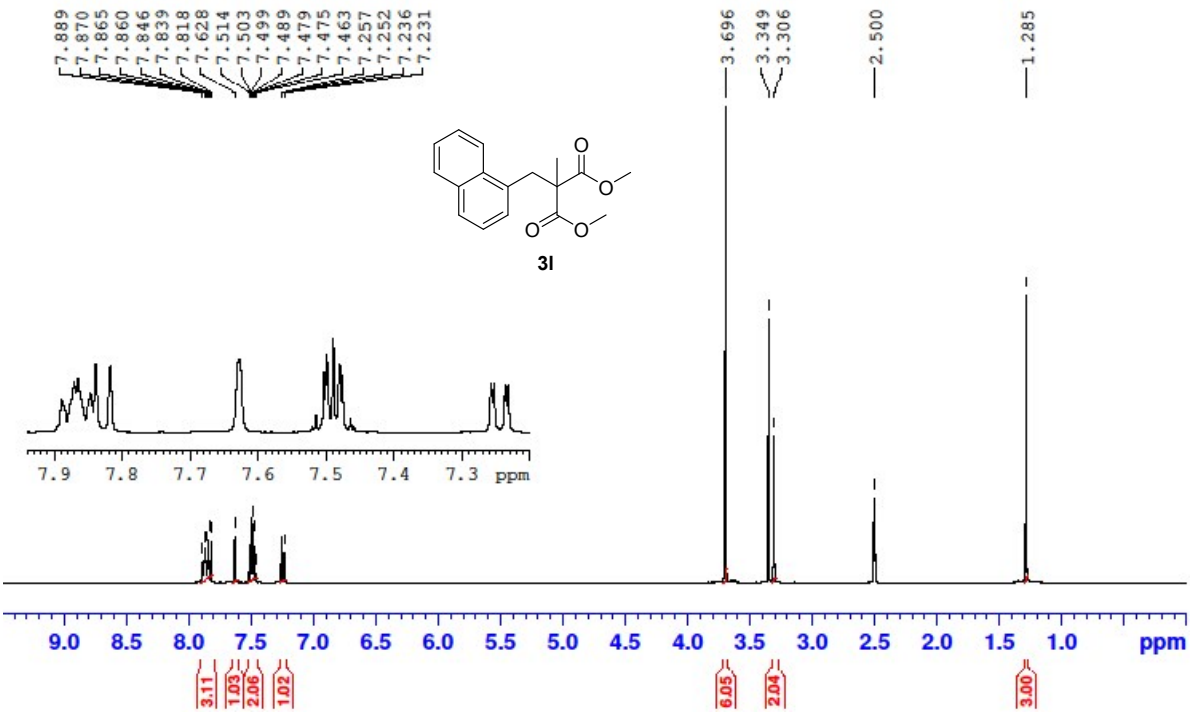
^{1}H NMR, d_6-DMSO, 400 MHz



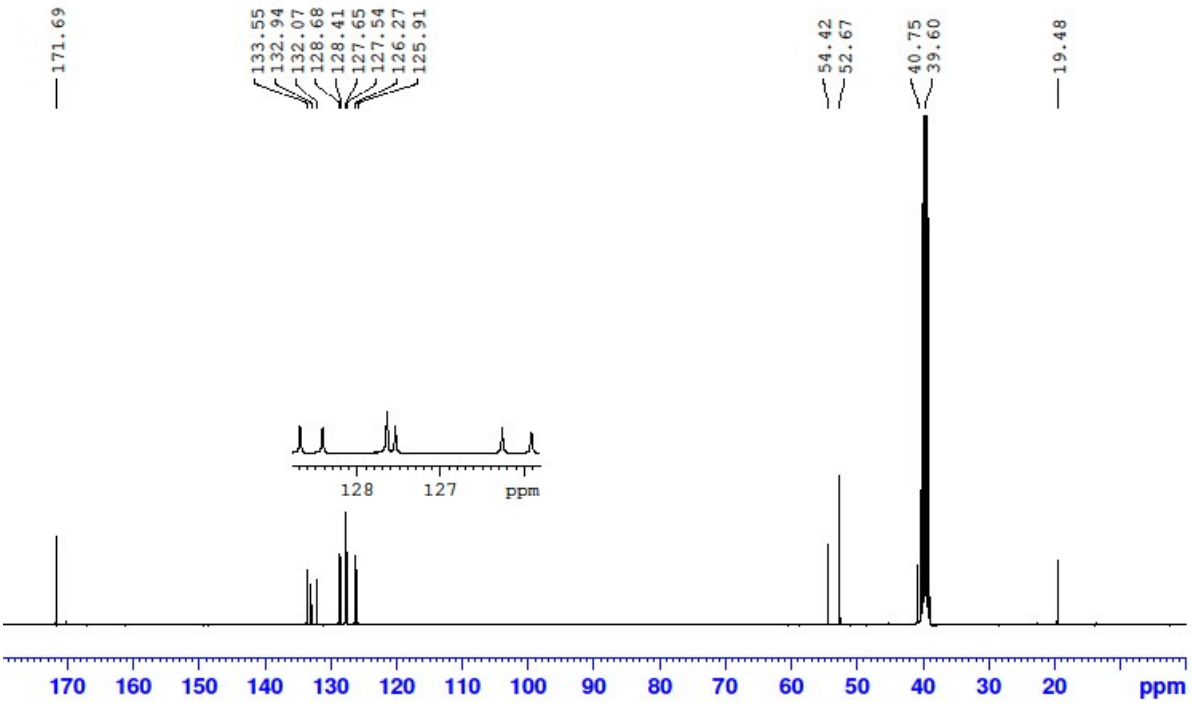
^{13}C NMR, d_6-DMSO, 101 MHz



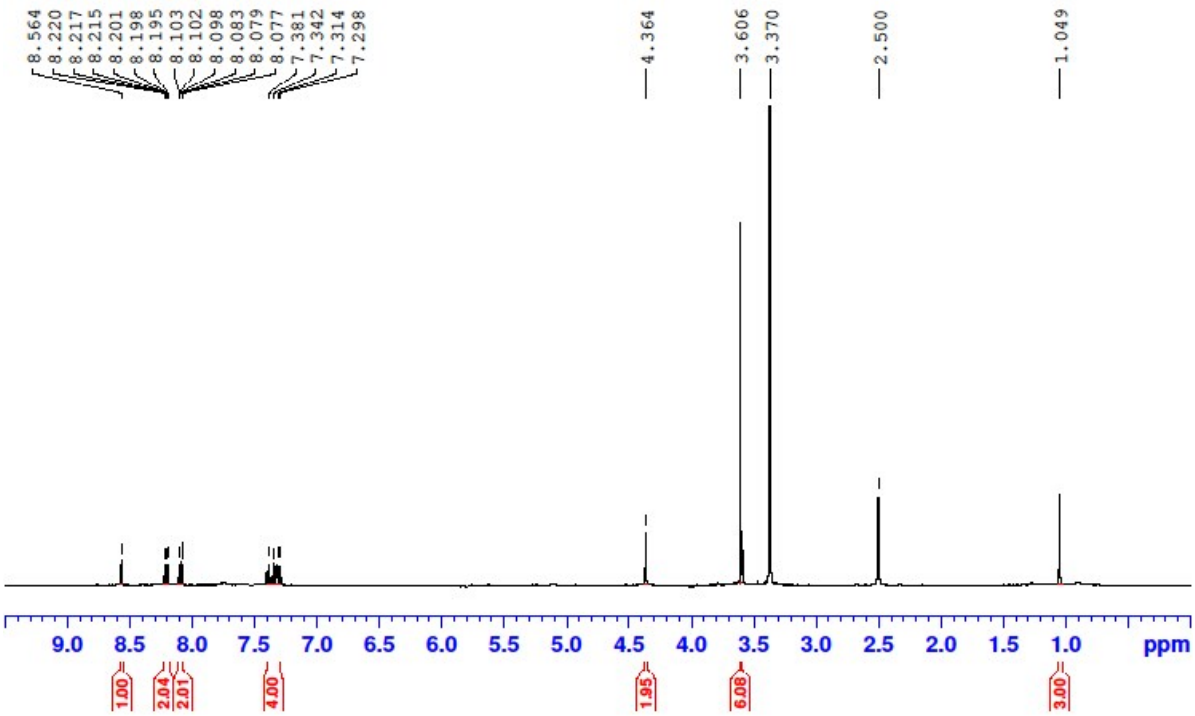
^{1}H NMR, d_6-DMSO, 400 MHz



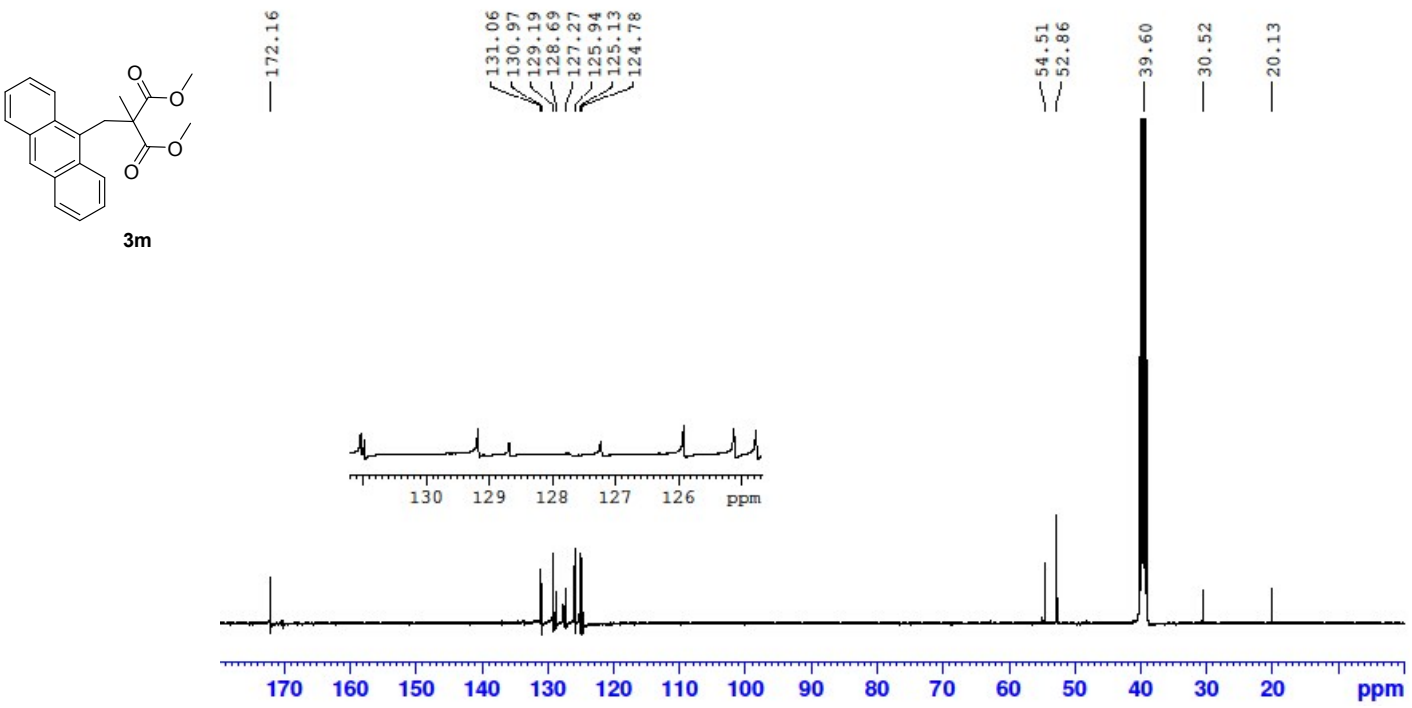
^{13}C NMR, d_6-DMSO, 101 MHz



^{1}H NMR, d_6-DMSO, 400 MHz

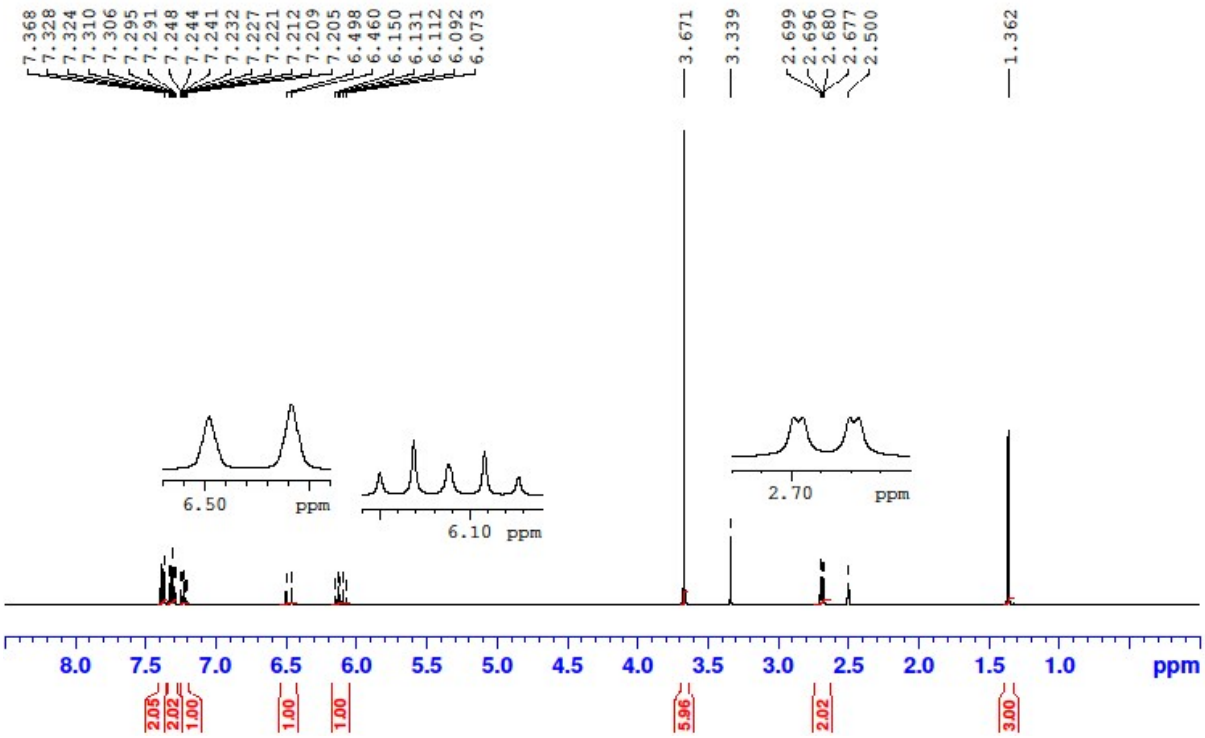


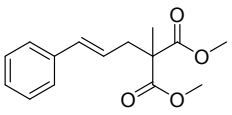
^{13}C NMR, d_6-DMSO, 101 MHz



3m

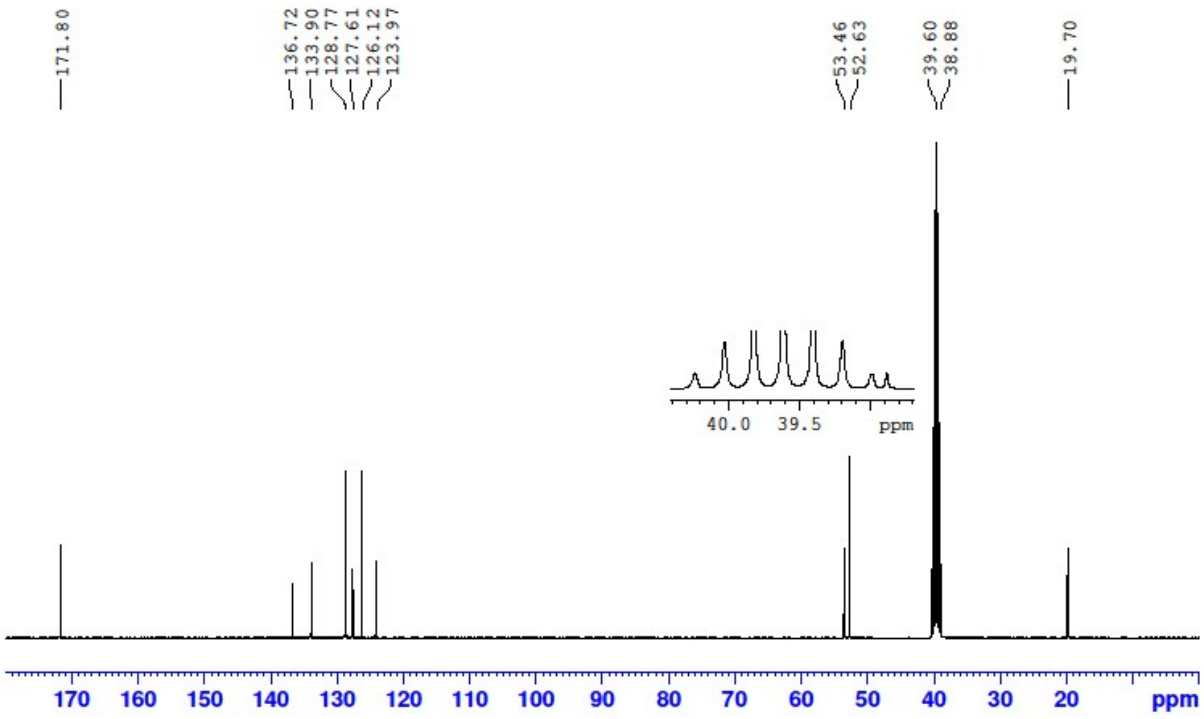
^{1}H NMR, d_6-DMSO, 400 MHz



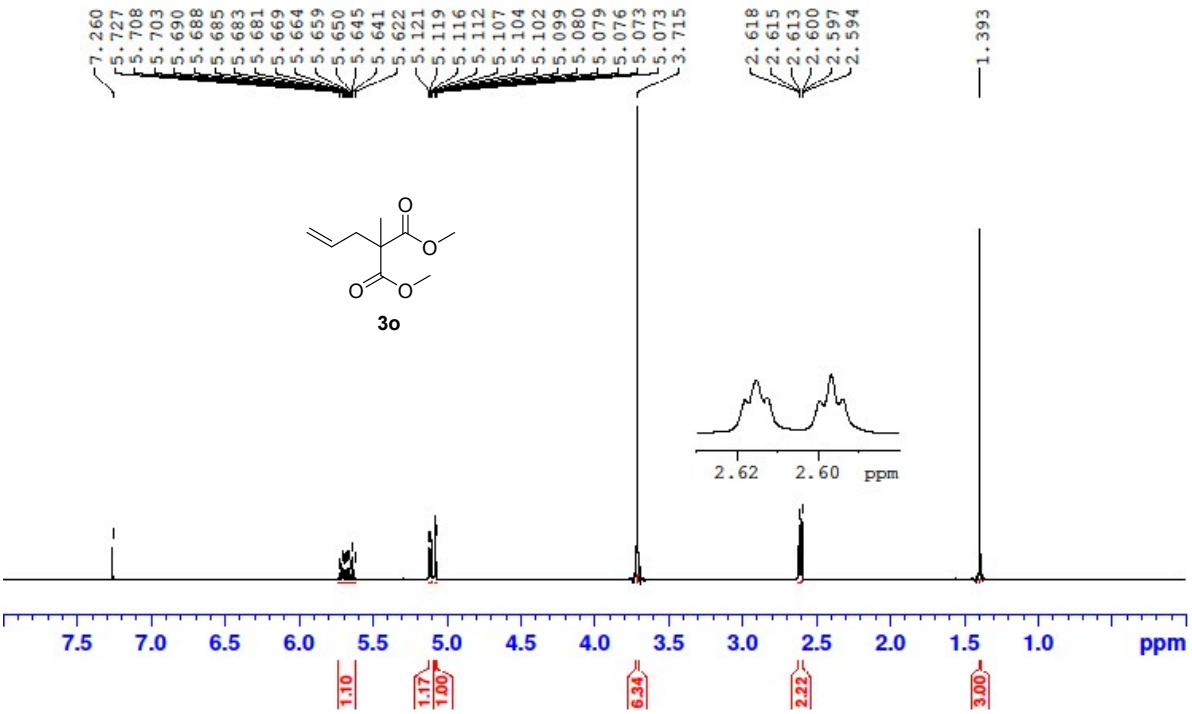


3n

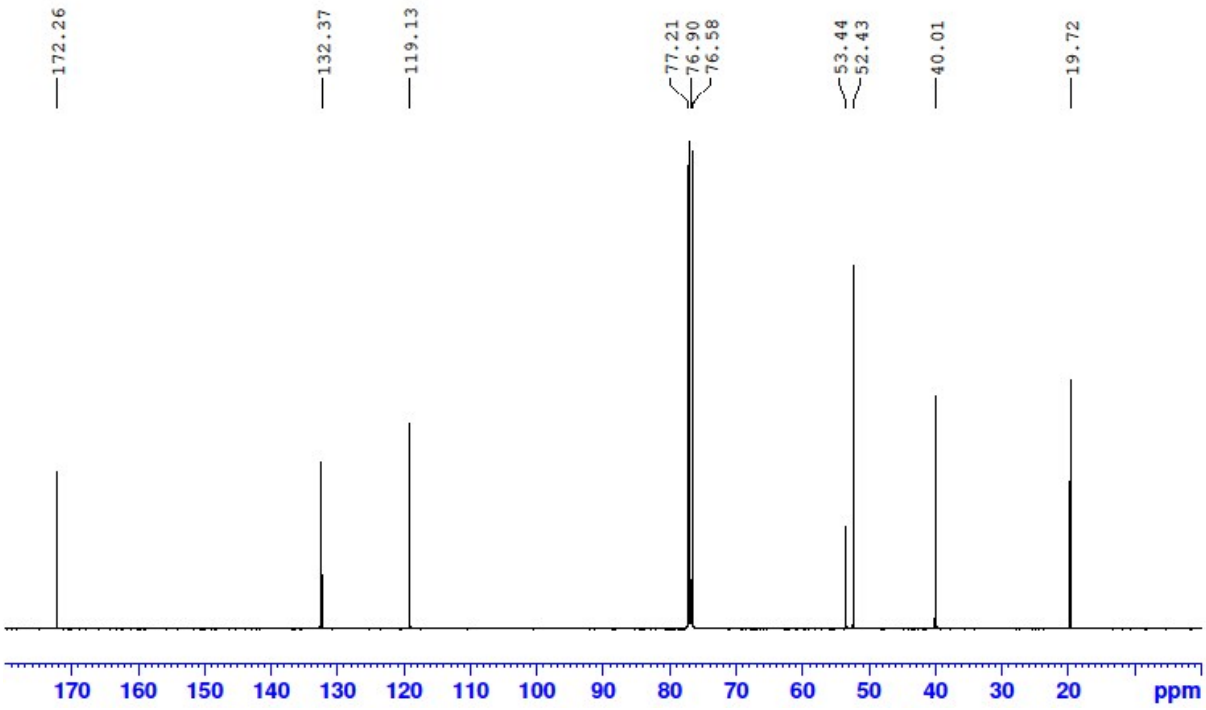
^{13}C NMR, d_6-DMSO, 101 MHz



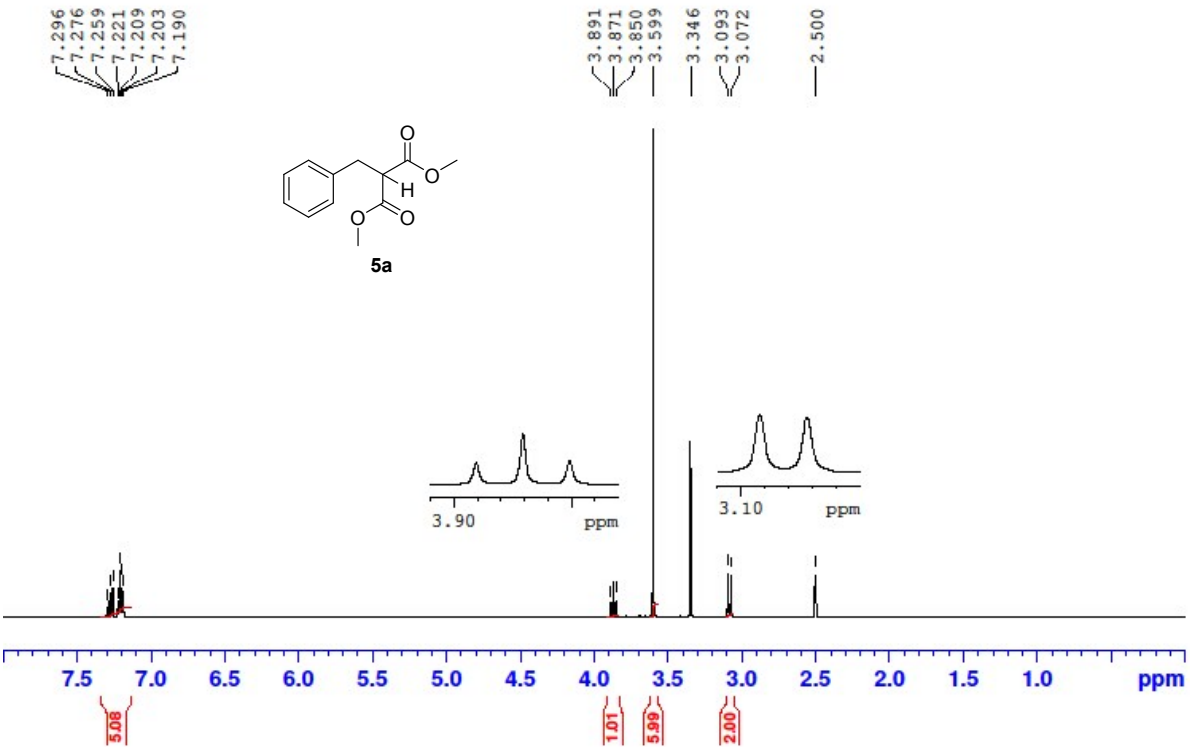
^{1}H NMR, $CDCl_3$, 400 MHz



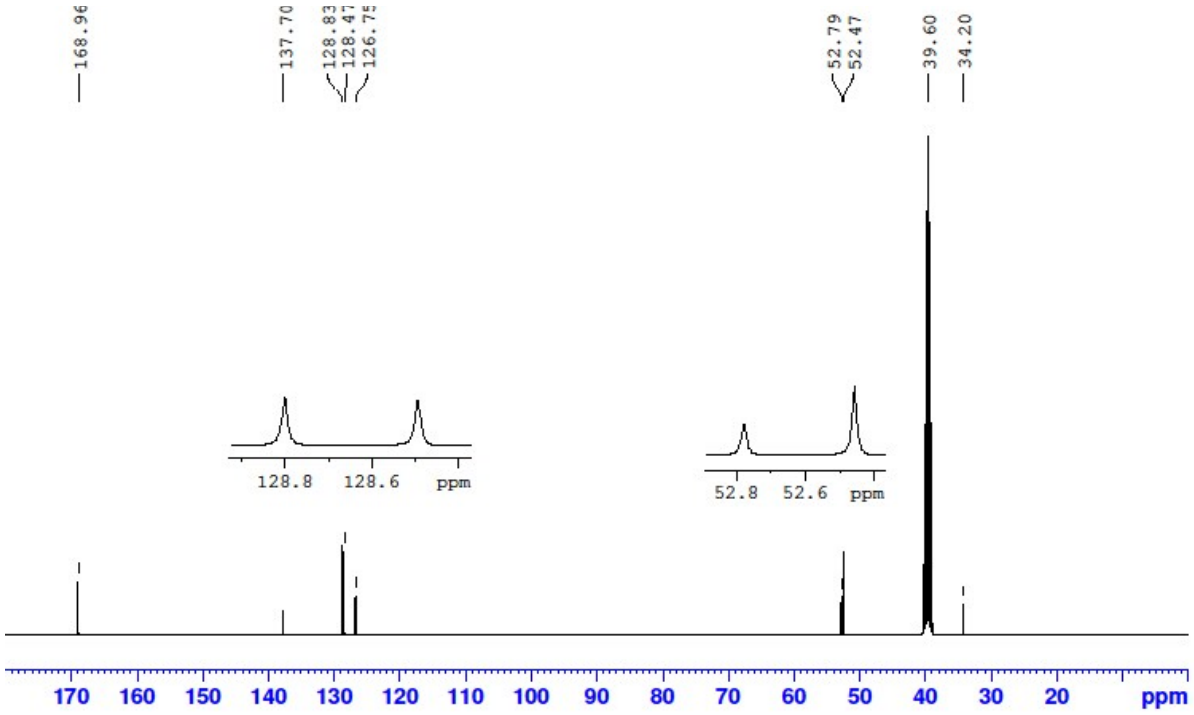
^{13}C NMR, $CDCl_3$, 101 MHz



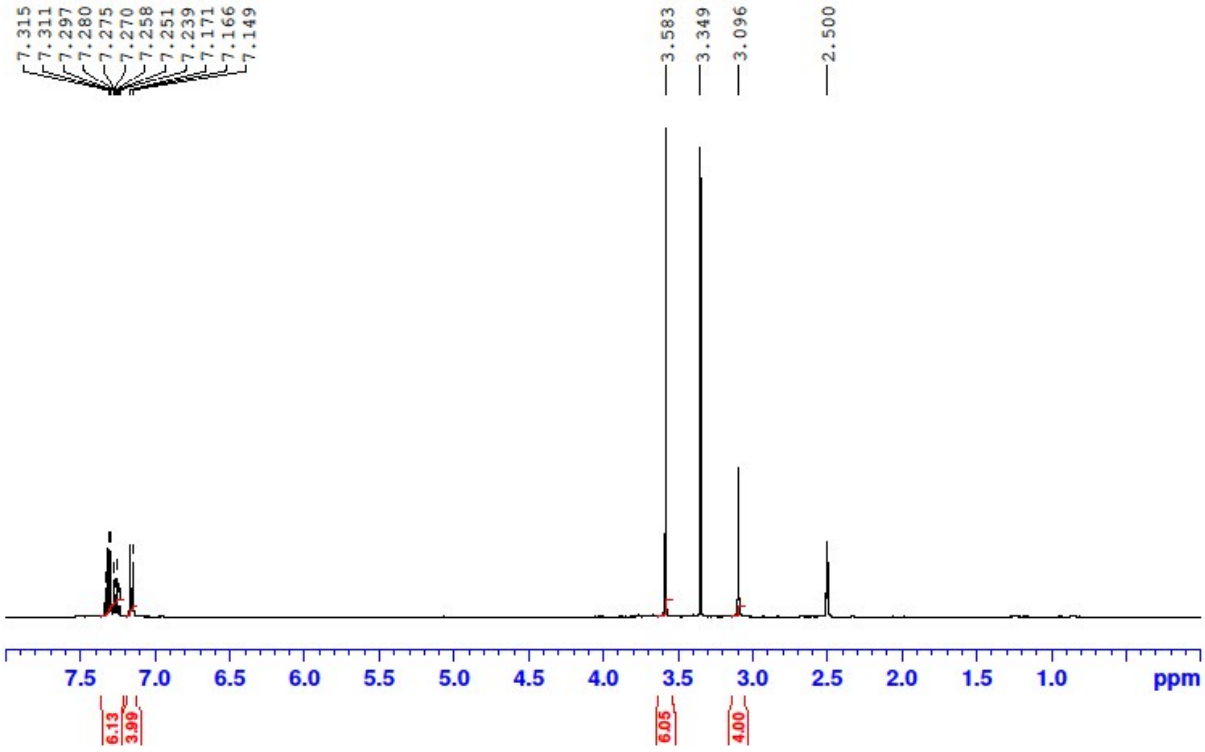
^{1}H NMR, d_6-DMSO, 400 MHz

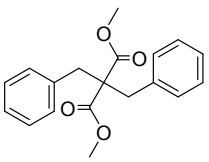


^{13}C NMR, d_6-DMSO, 101 MHz



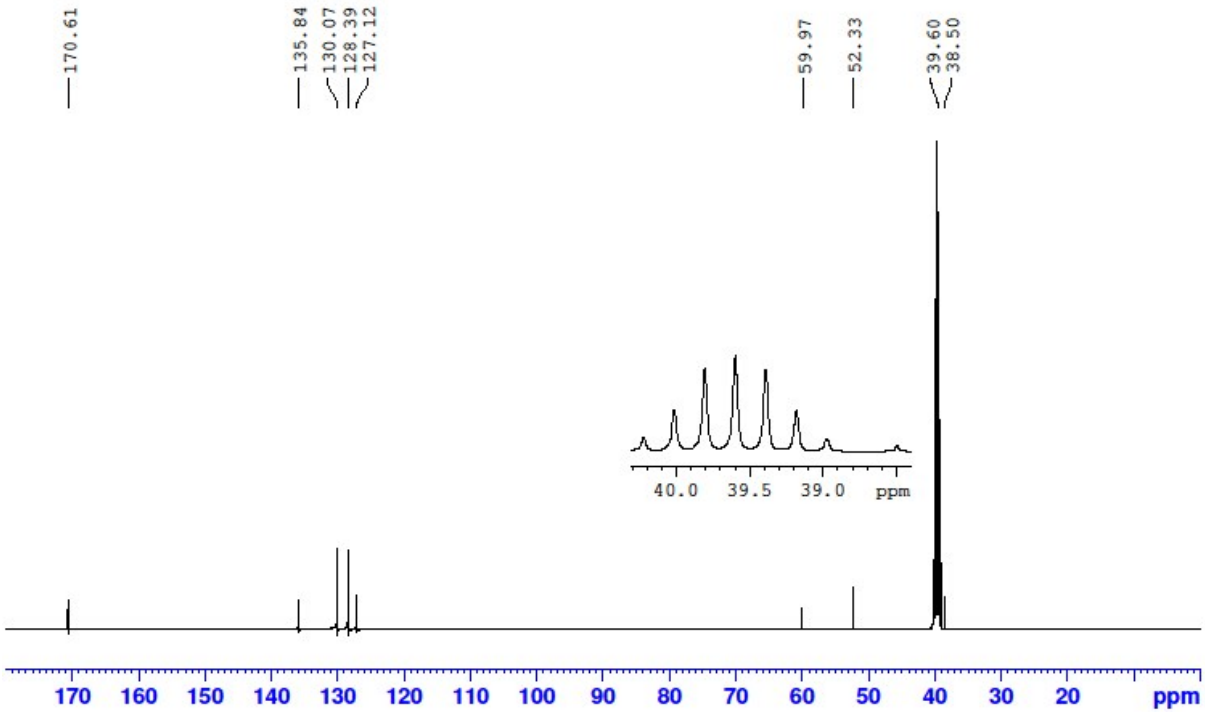
^{1}H NMR, d_6-DMSO, 400 MHz



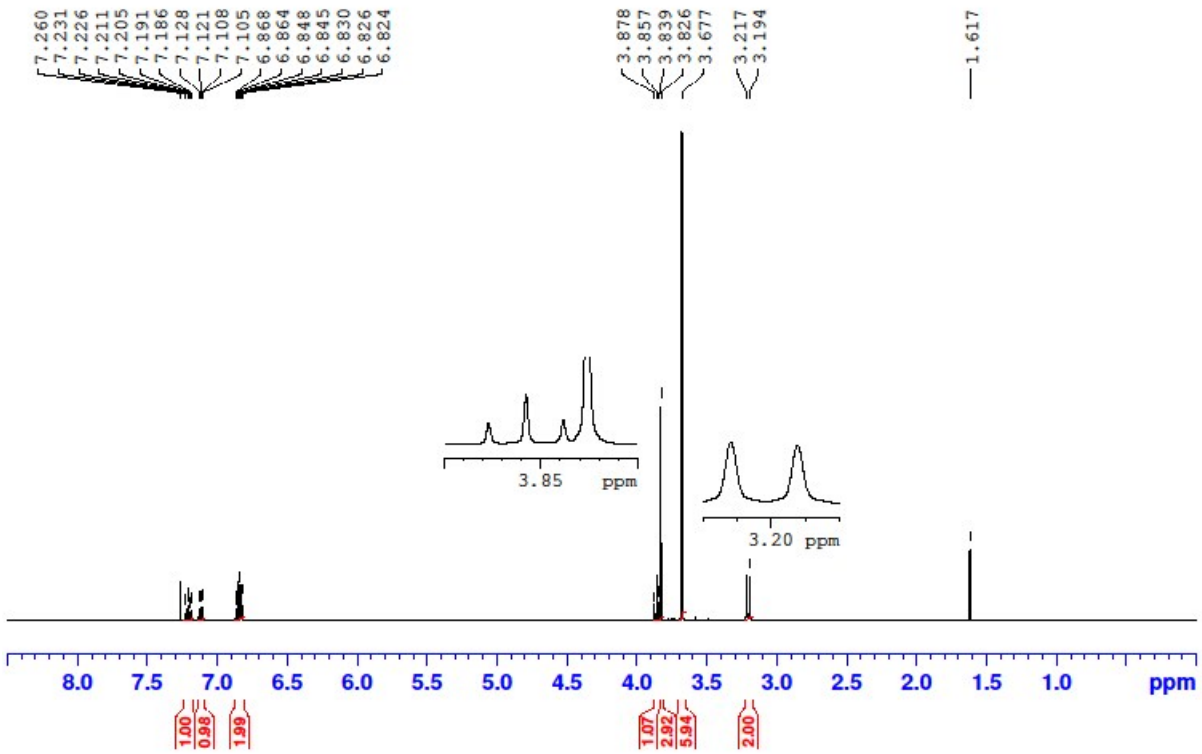


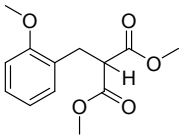
6a

^{13}C NMR, d_6-DMSO, 101 MHz



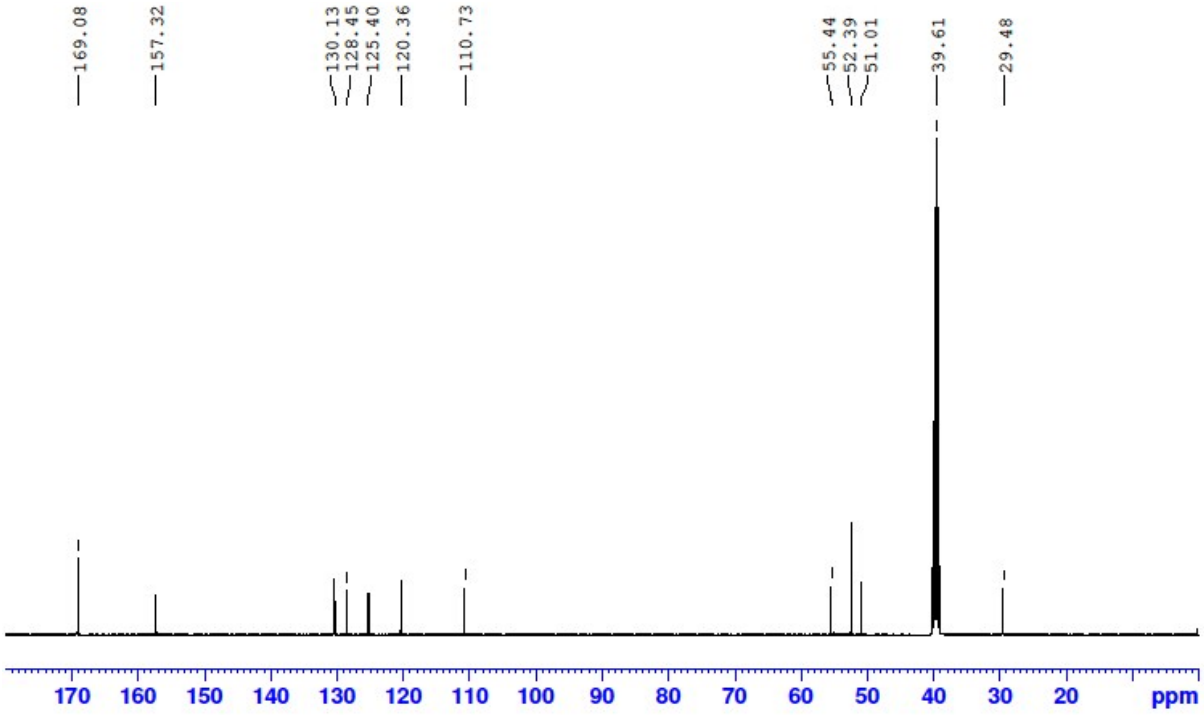
^{1}H NMR, $CDCl_3$, 400 MHz



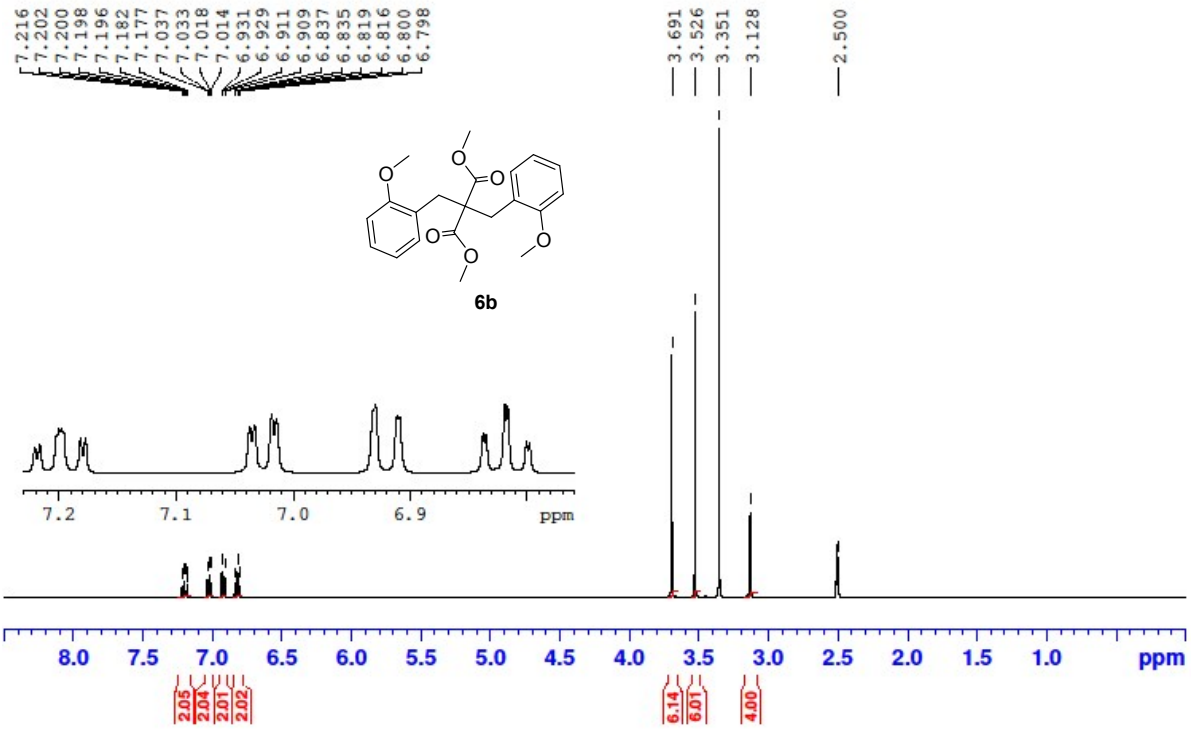


5b

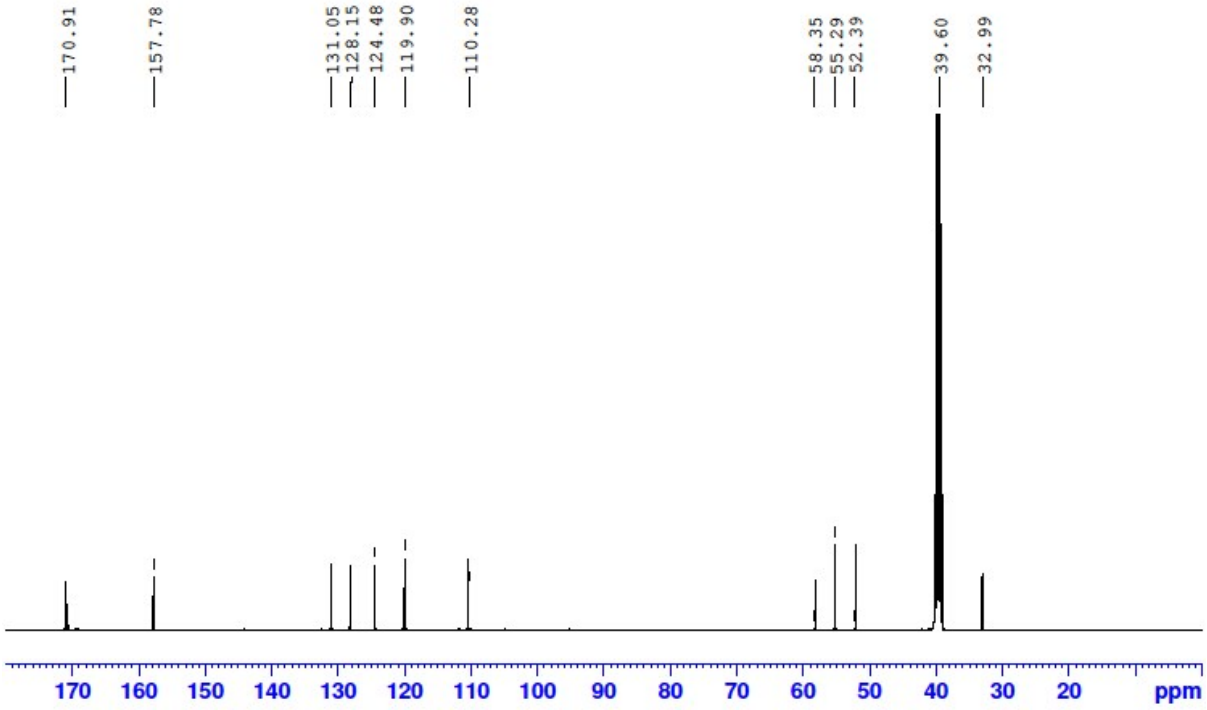
^{13}C NMR, d_6-DMSO, 101 MHz



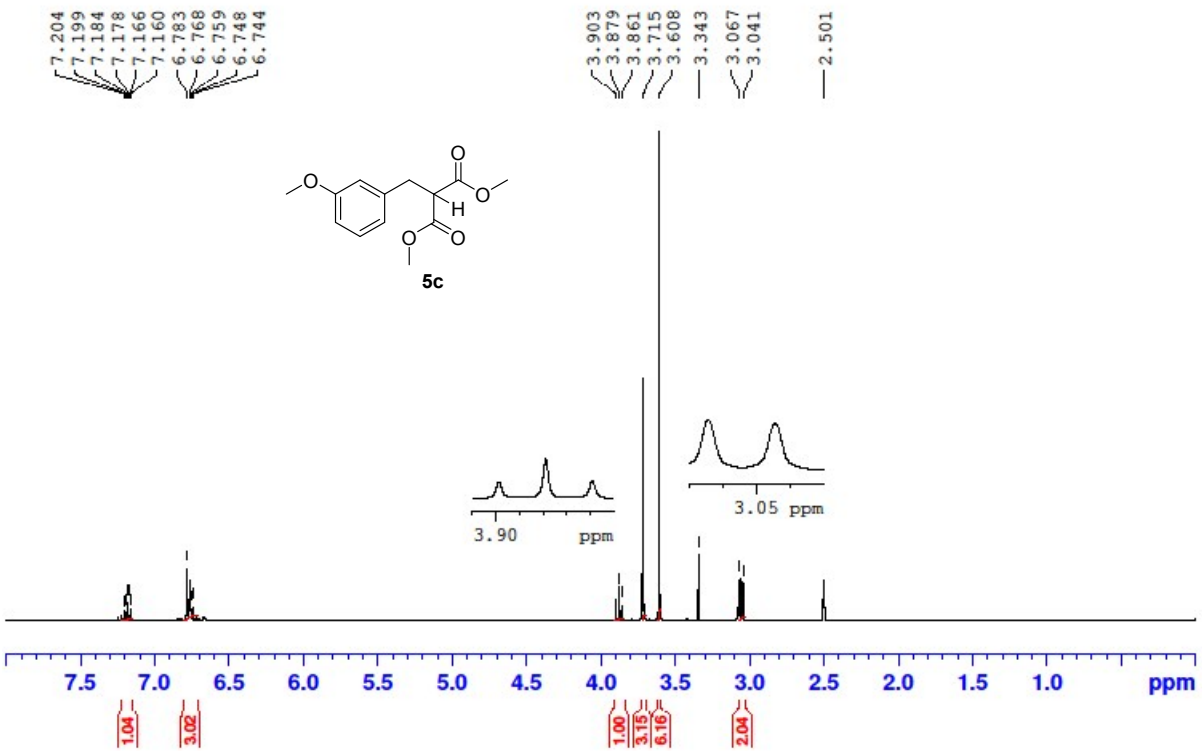
^{1}H NMR, d_6-DMSO, 400 MHz



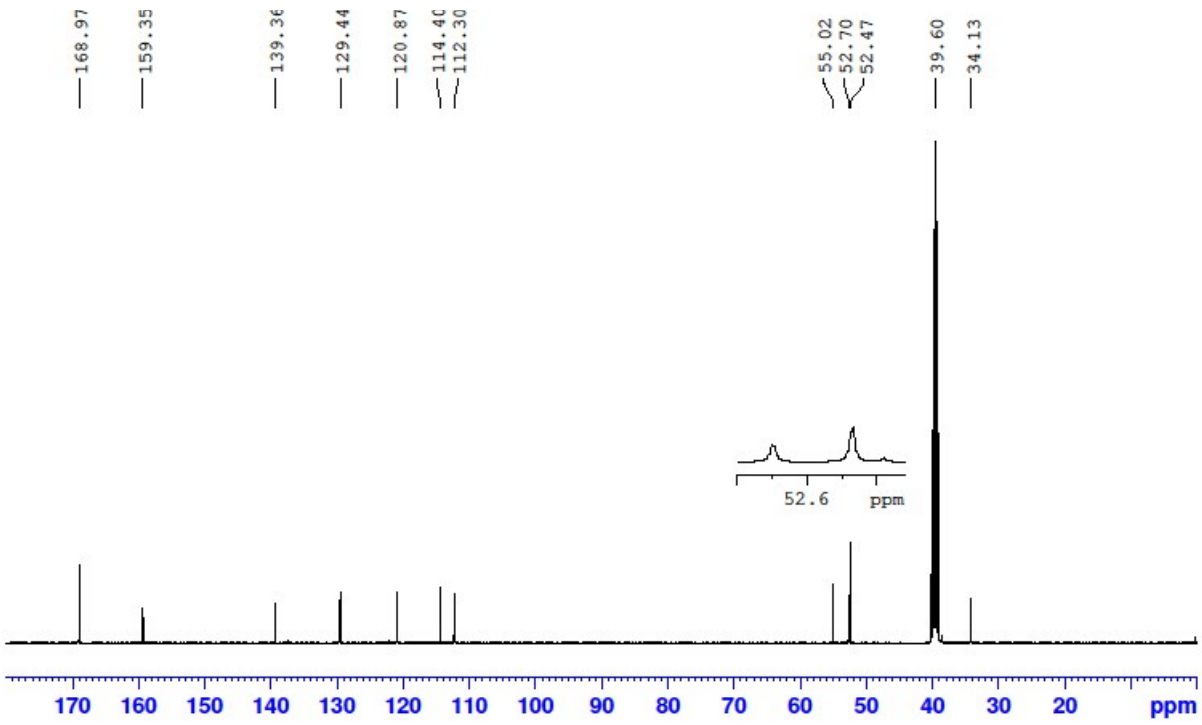
^{13}C NMR, d_6-DMSO, 101 MHz



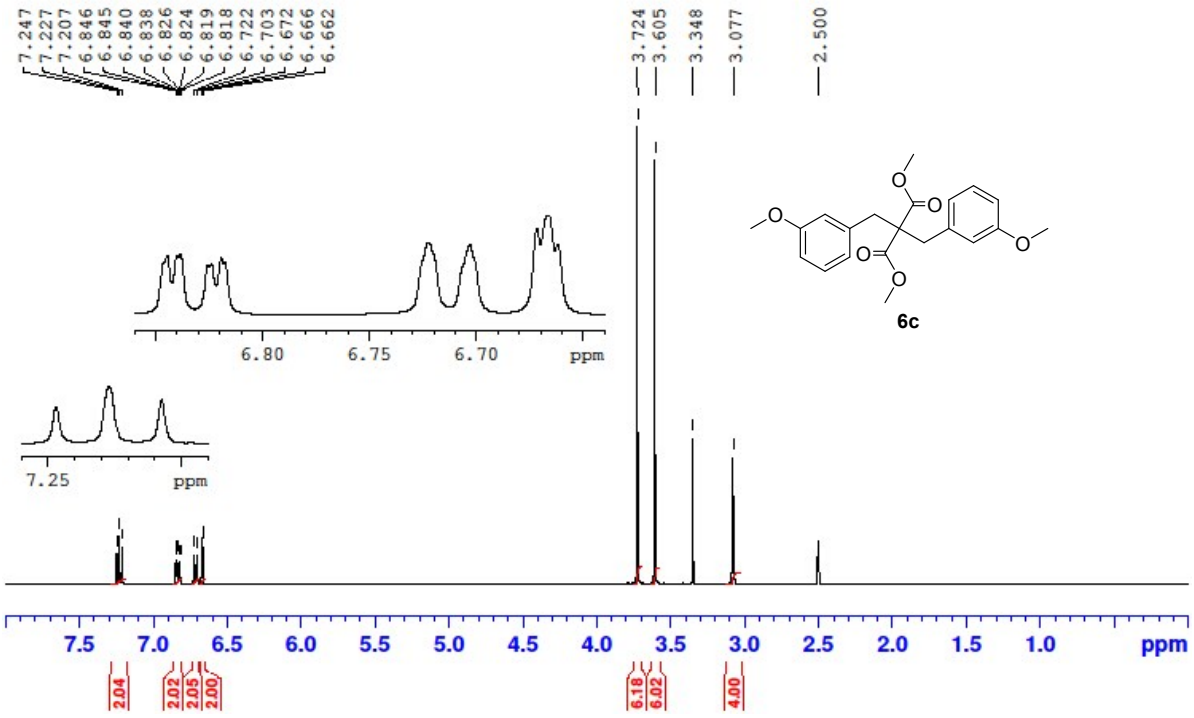
^{1}H NMR, d_6-DMSO, 400 MHz



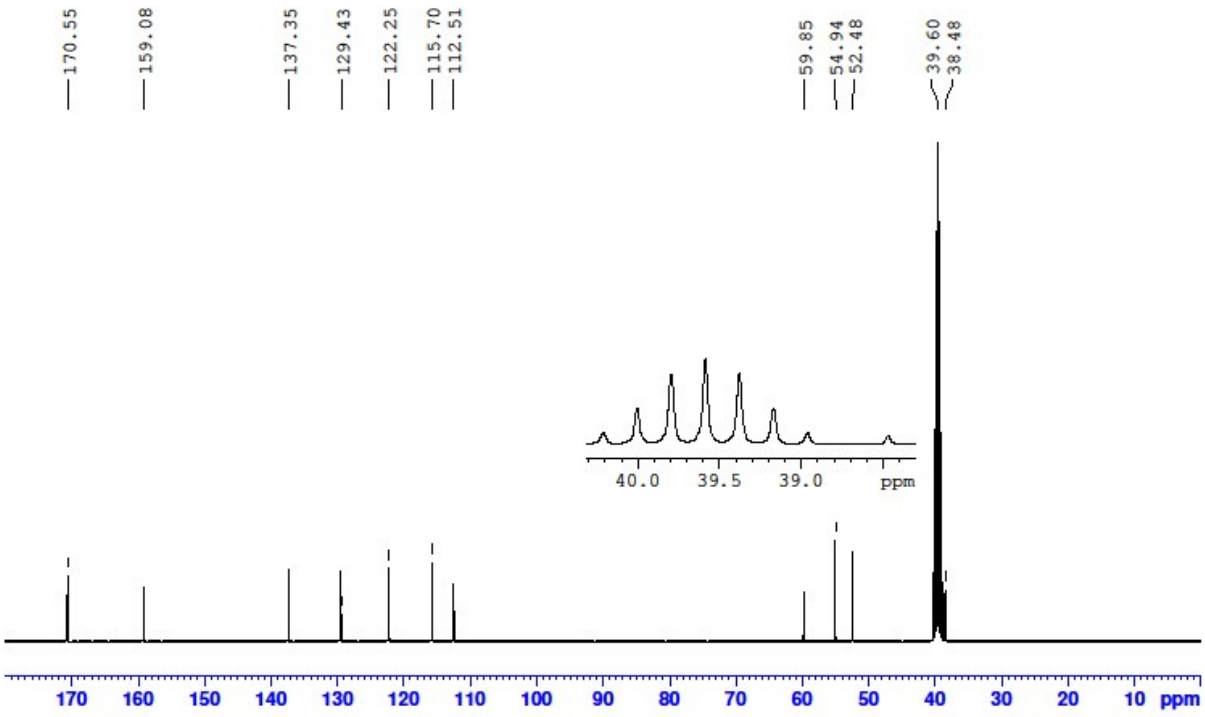
^{13}C NMR, d_6-DMSO, 101 MHz



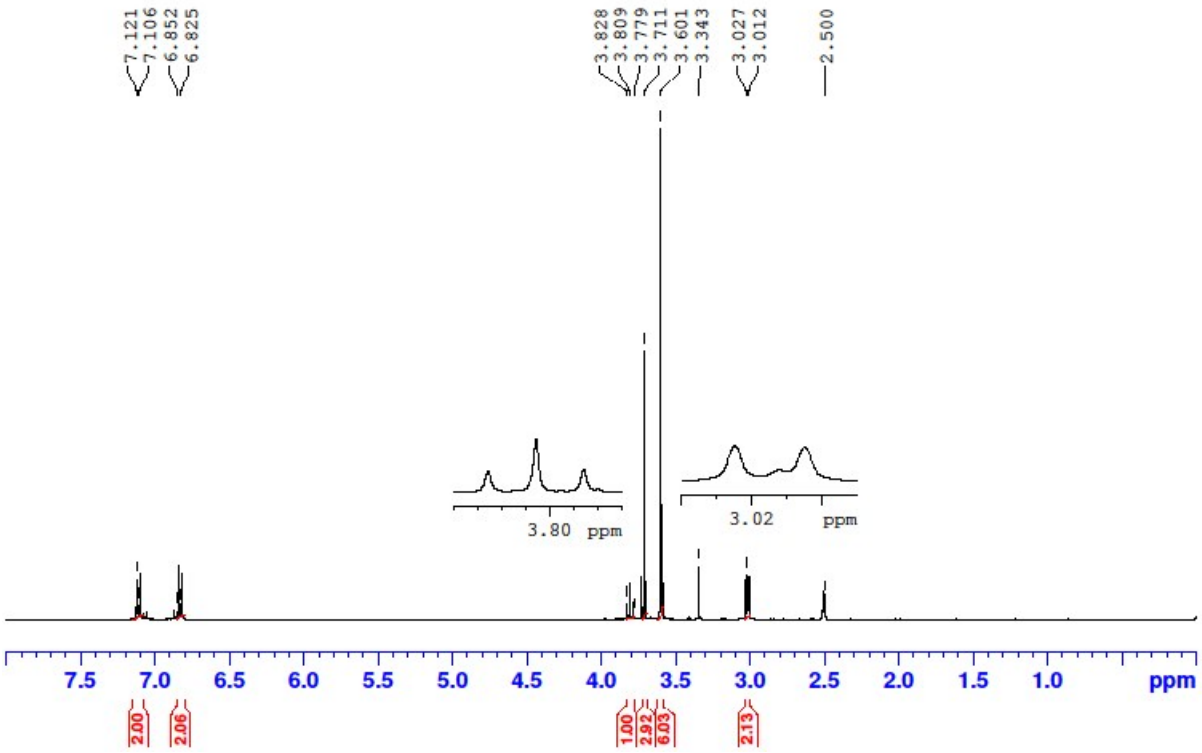
^{1}H NMR, d_6-DMSO, 400 MHz

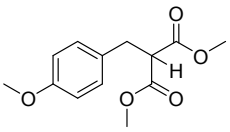


^{13}C NMR, d_6-DMSO, 101 MHz



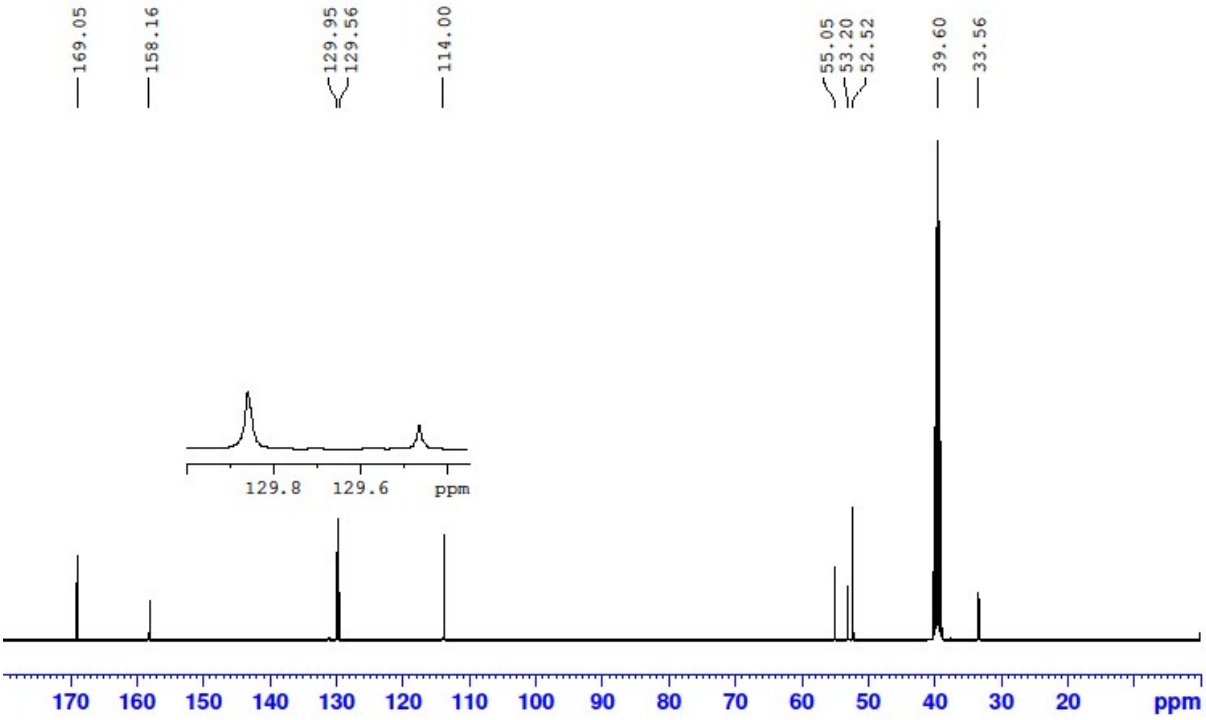
^{1}H NMR, d_6-DMSO, 400 MHz



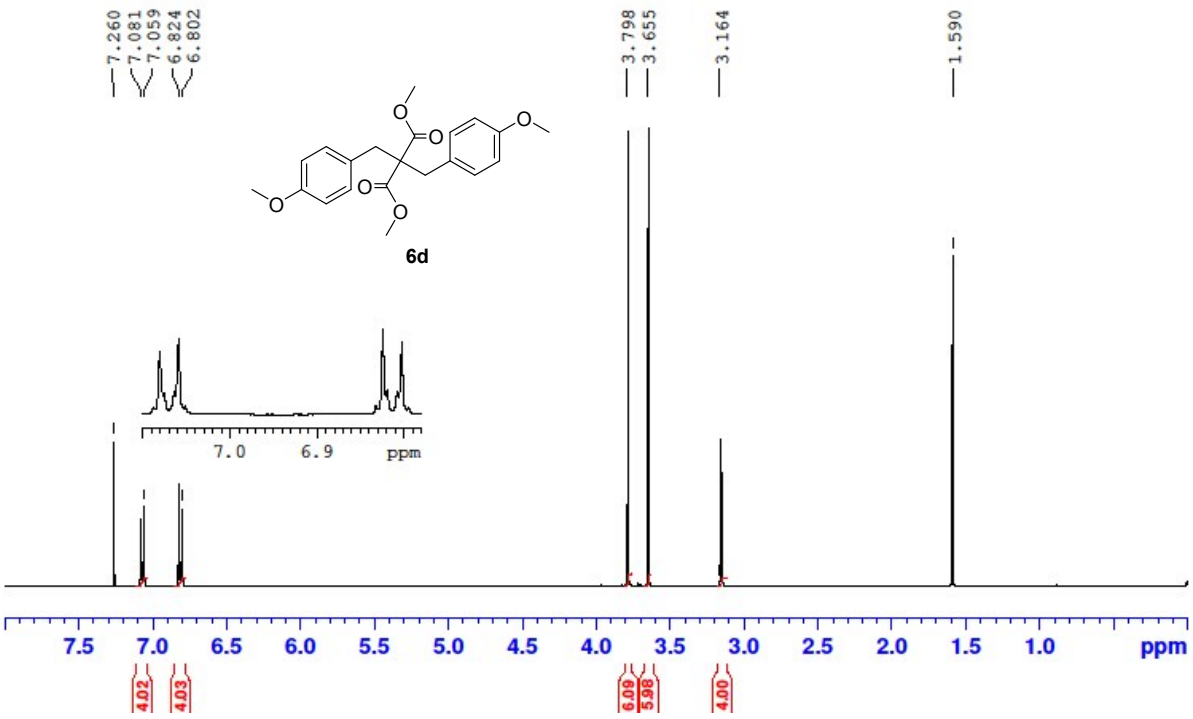


5d

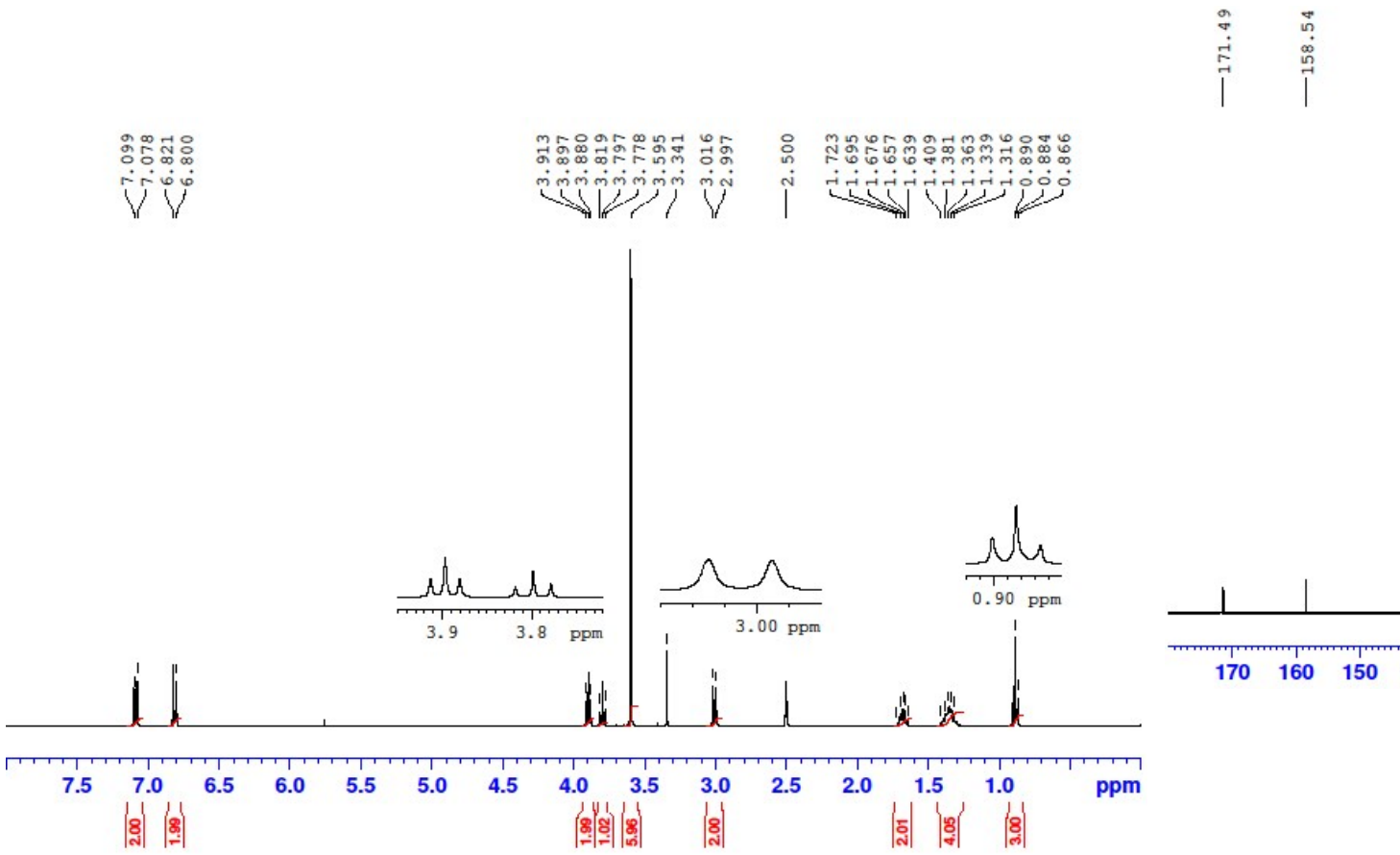
^{13}C NMR, d_6-DMSO, 101 MHz



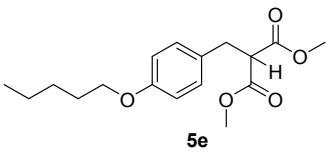
^{1}H NMR, $CDCl_3$, 400 MHz



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

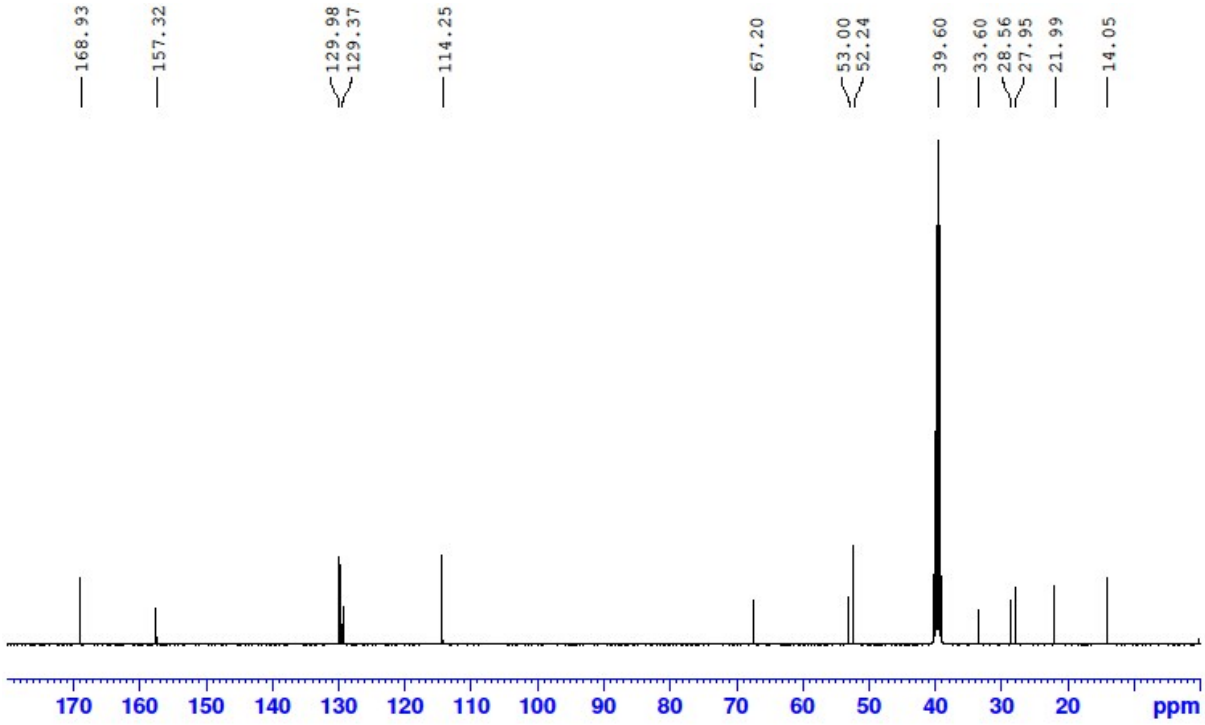


^{1}H NMR, d_6-DMSO, 400 MHz

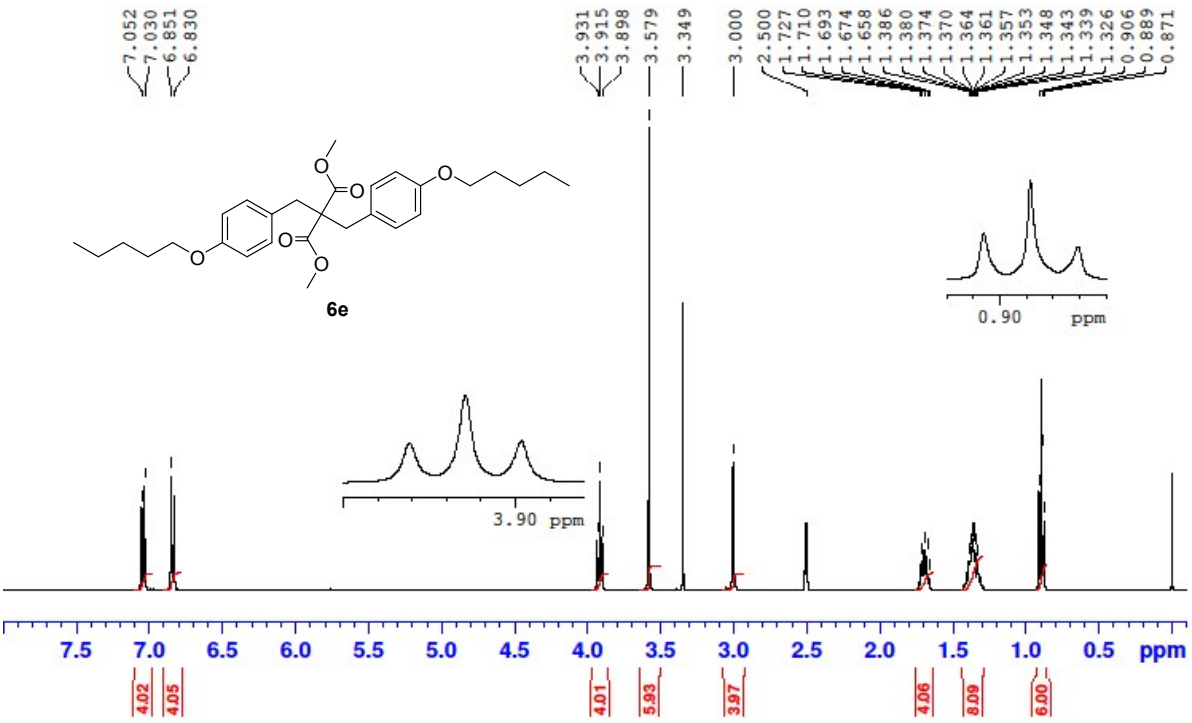


5e

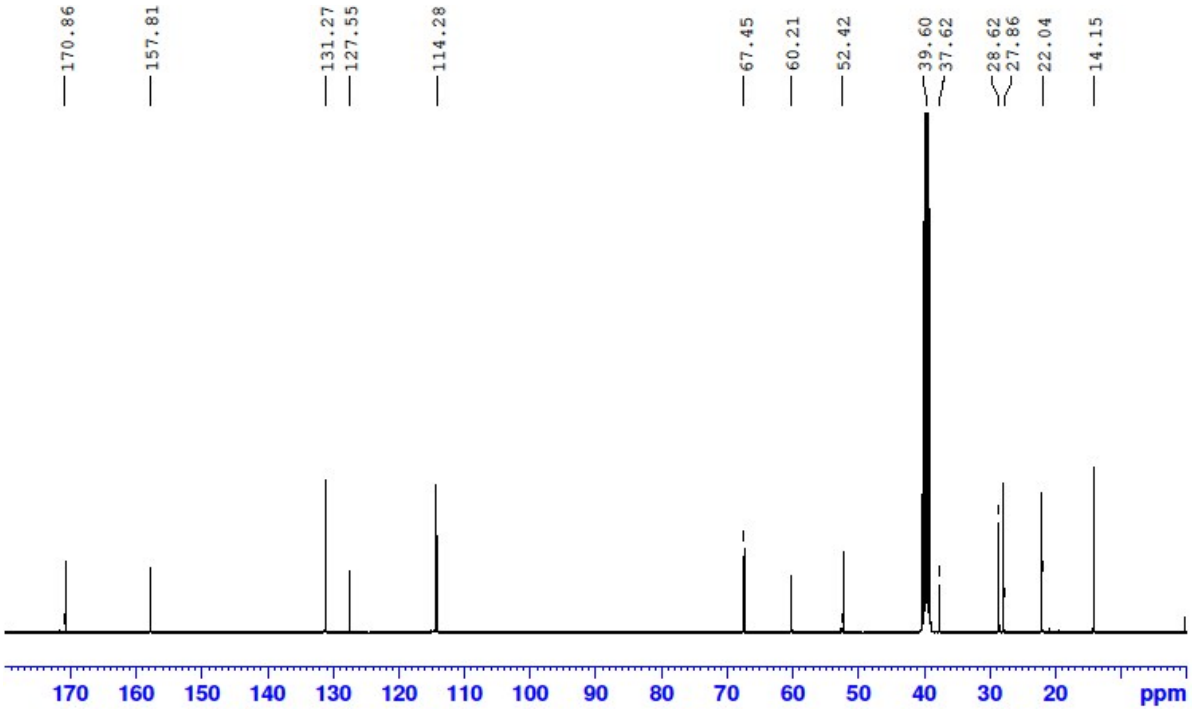
^{13}C NMR, d_6-DMSO, 101 MHz



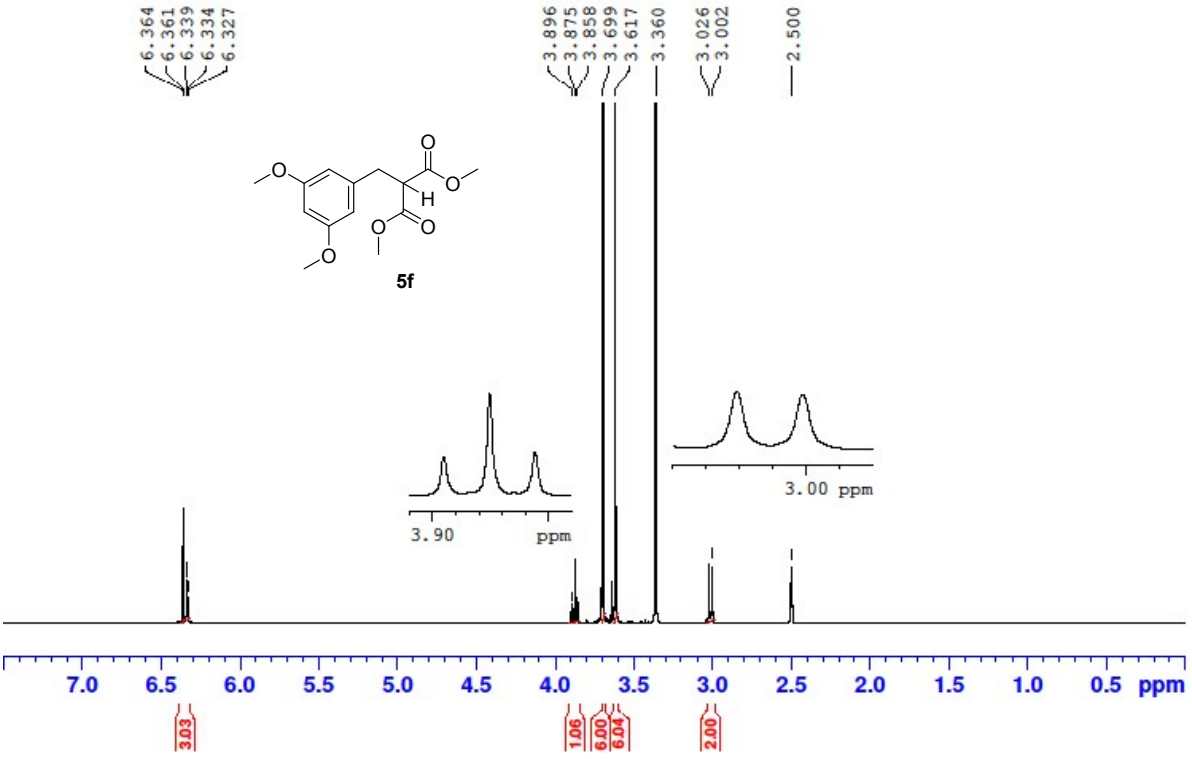
^{1}H NMR, d_6-DMSO, 400 MHz



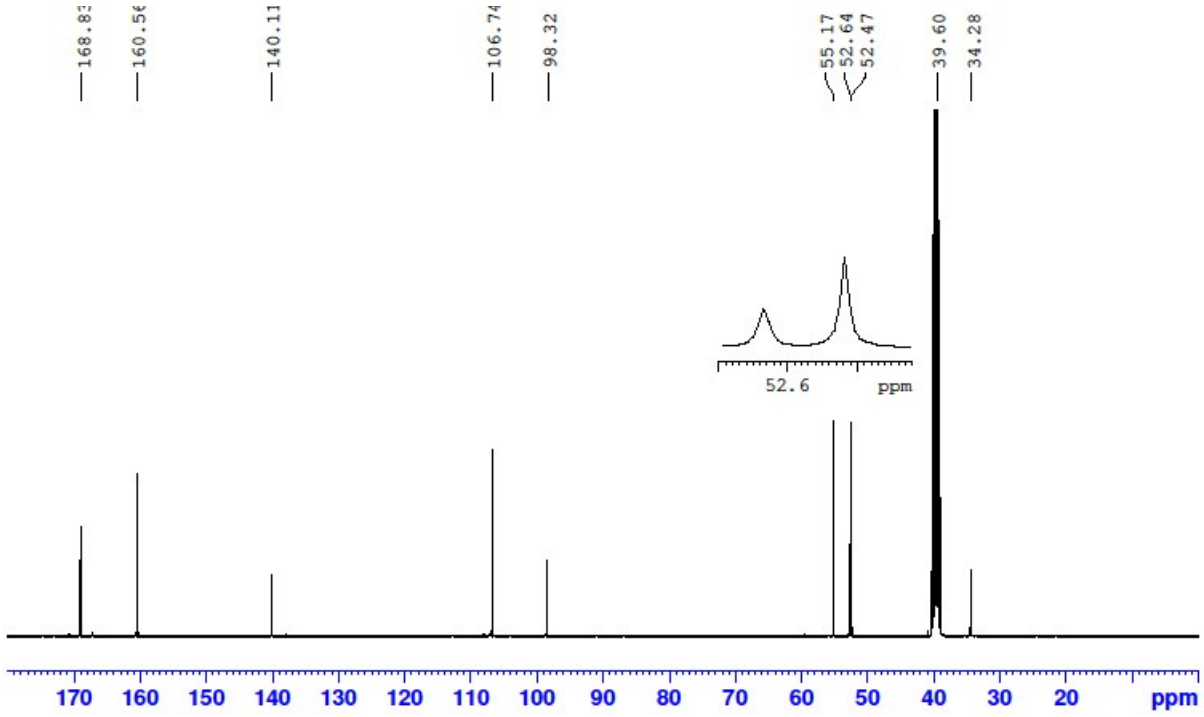
^{13}C NMR, d_6-DMSO, 101 MHz



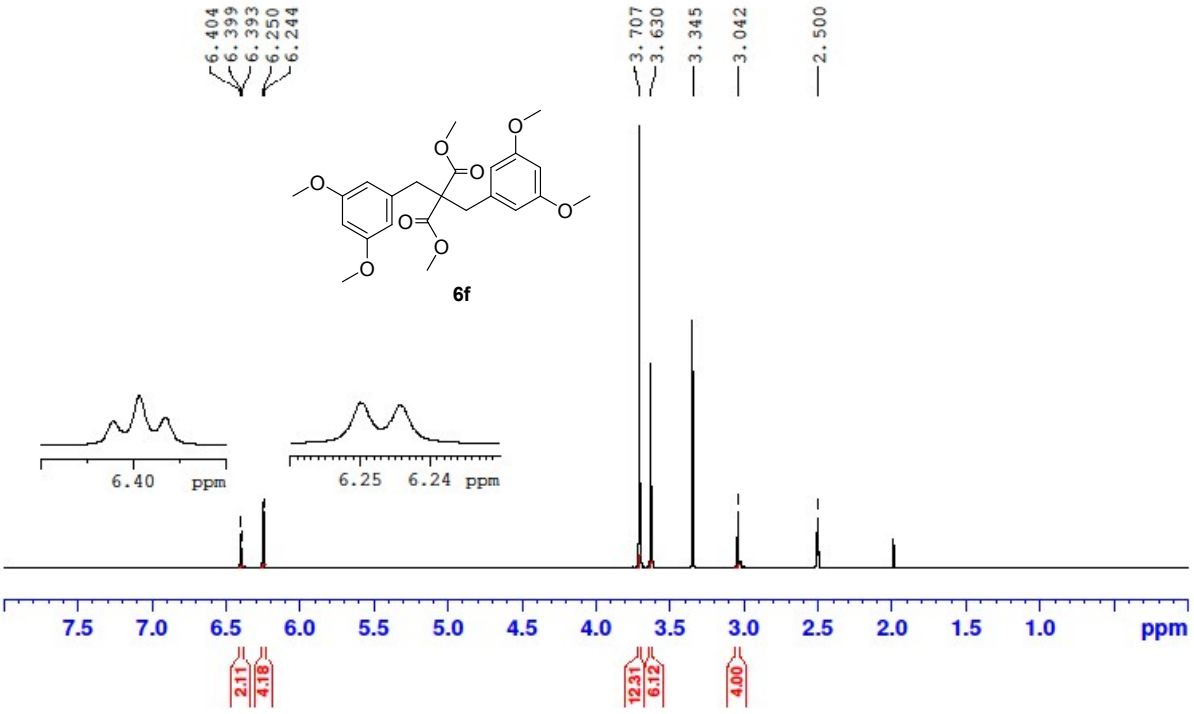
^{1}H NMR, d_6-DMSO, 400 MHz



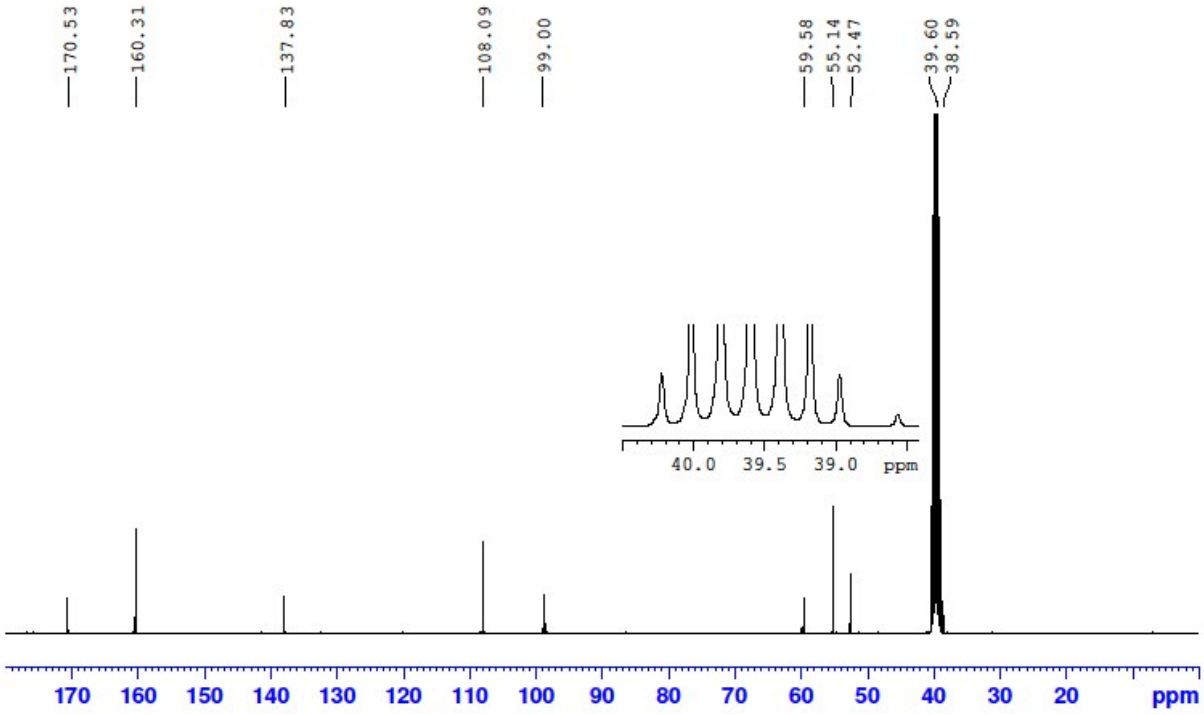
^{13}C NMR, d_6-DMSO, 101 MHz



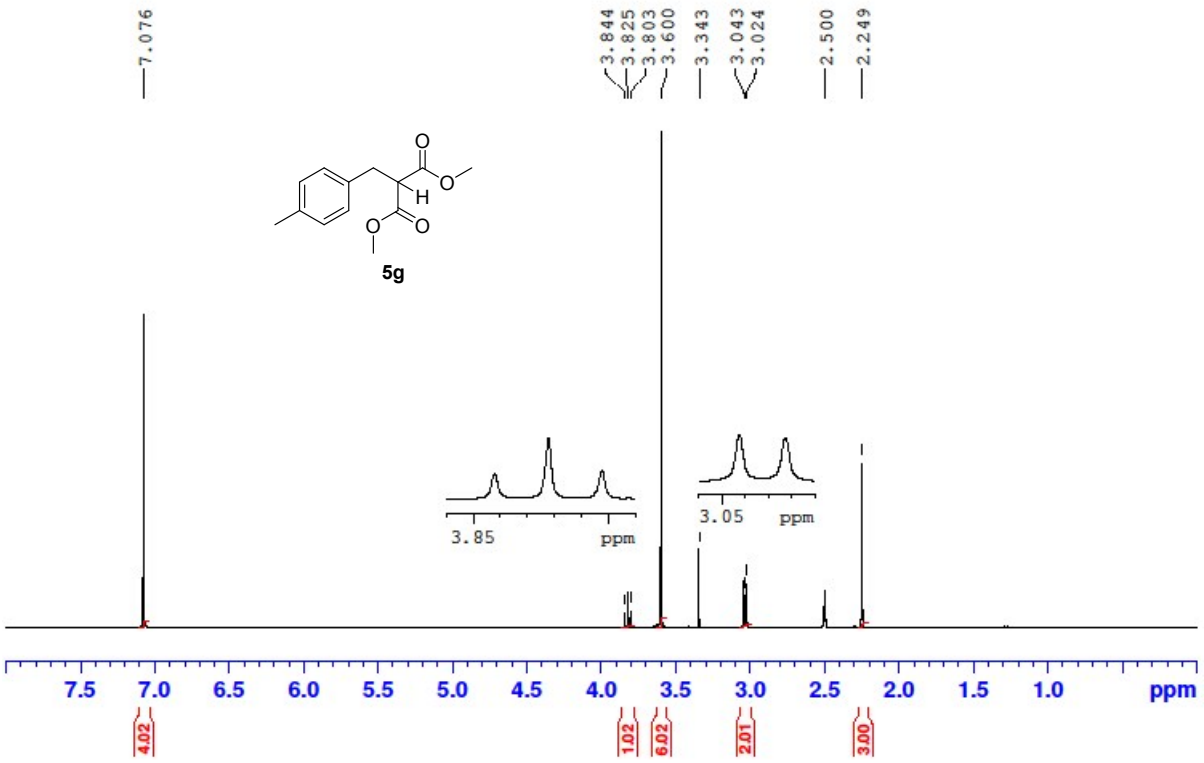
^{1}H NMR, d_6-DMSO, 400 MHz



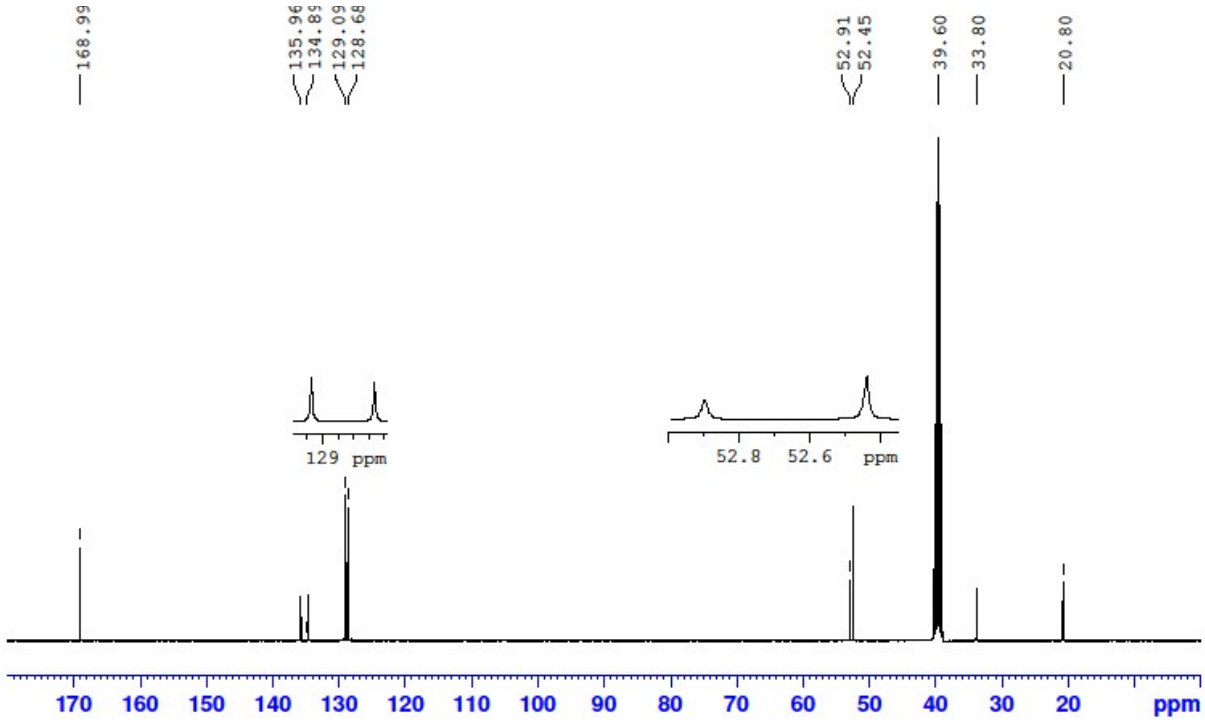
^{13}C NMR, d_6-DMSO, 101 MHz



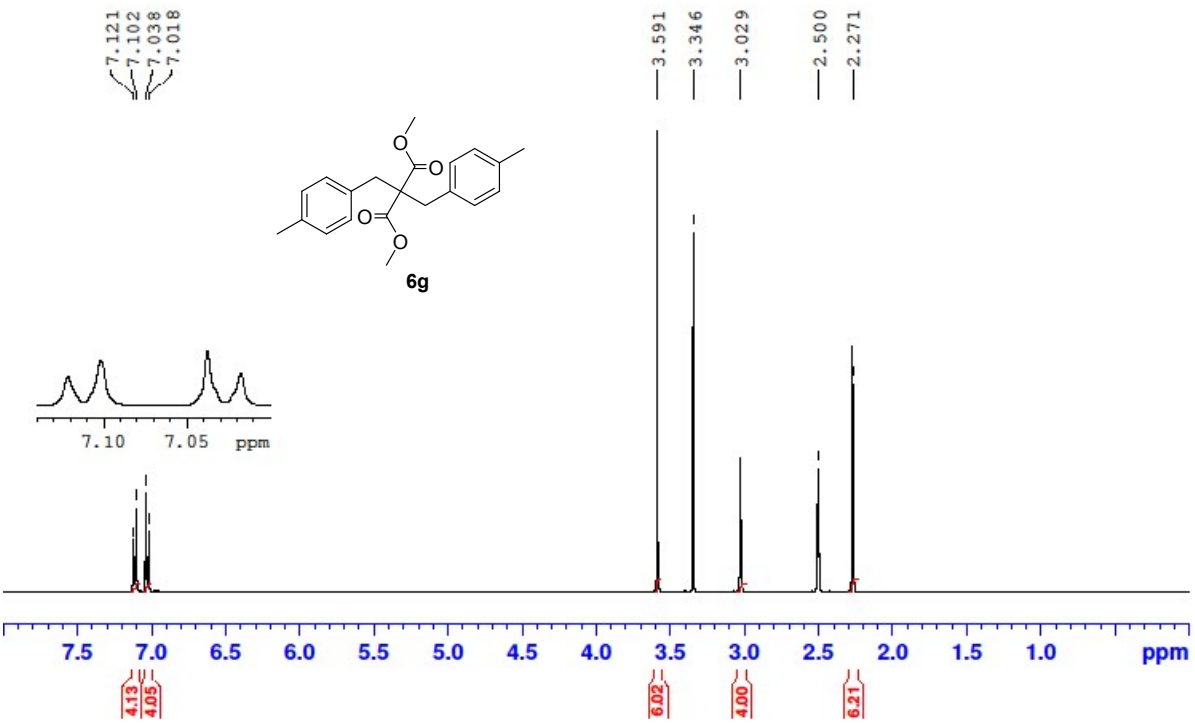
^{1}H NMR, d_6-DMSO, 400 MHz



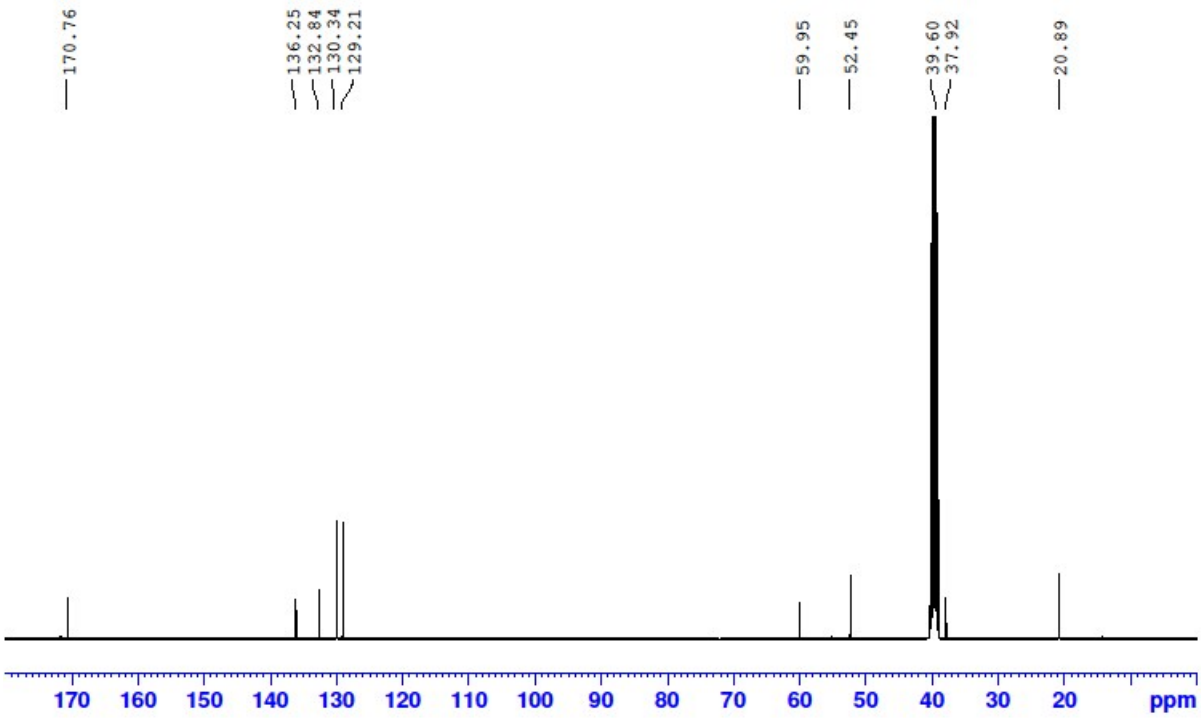
^{13}C NMR, d_6-DMSO, 101 MHz



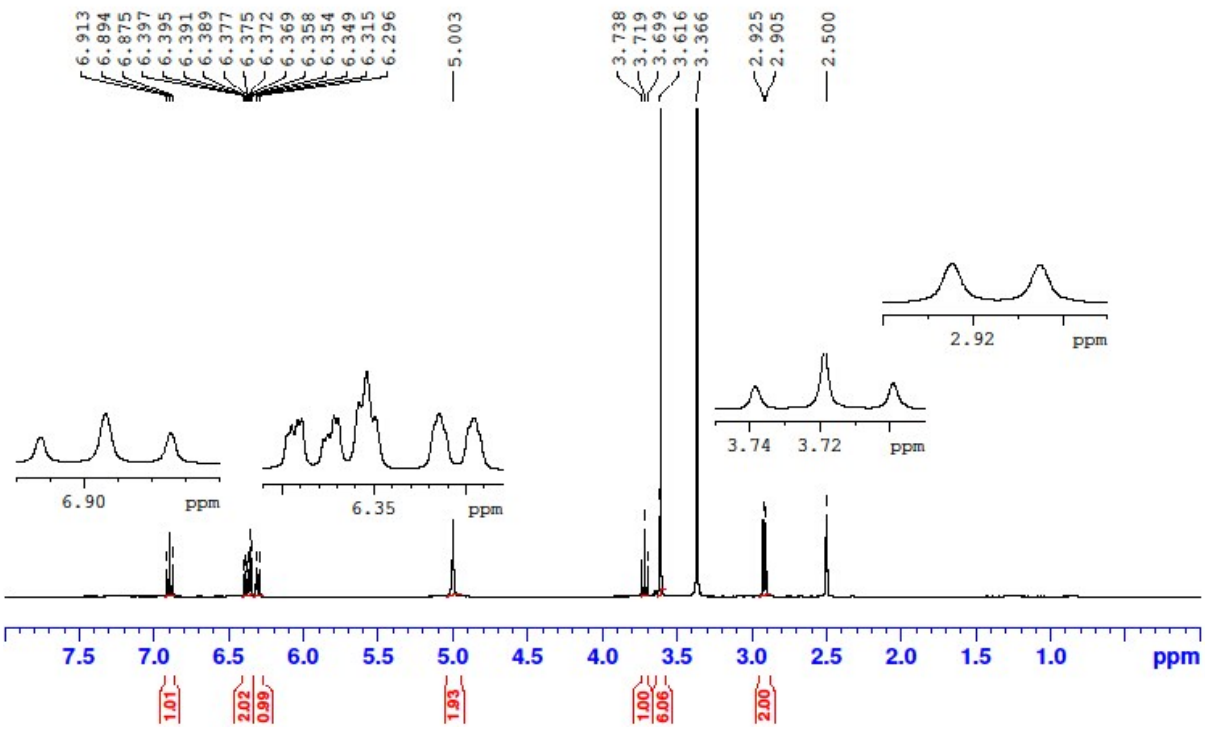
^{1}H NMR, d_6-DMSO, 400 MHz

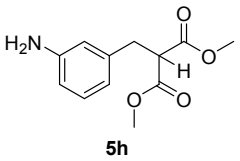


^{13}C NMR, d_6-DMSO, 101 MHz



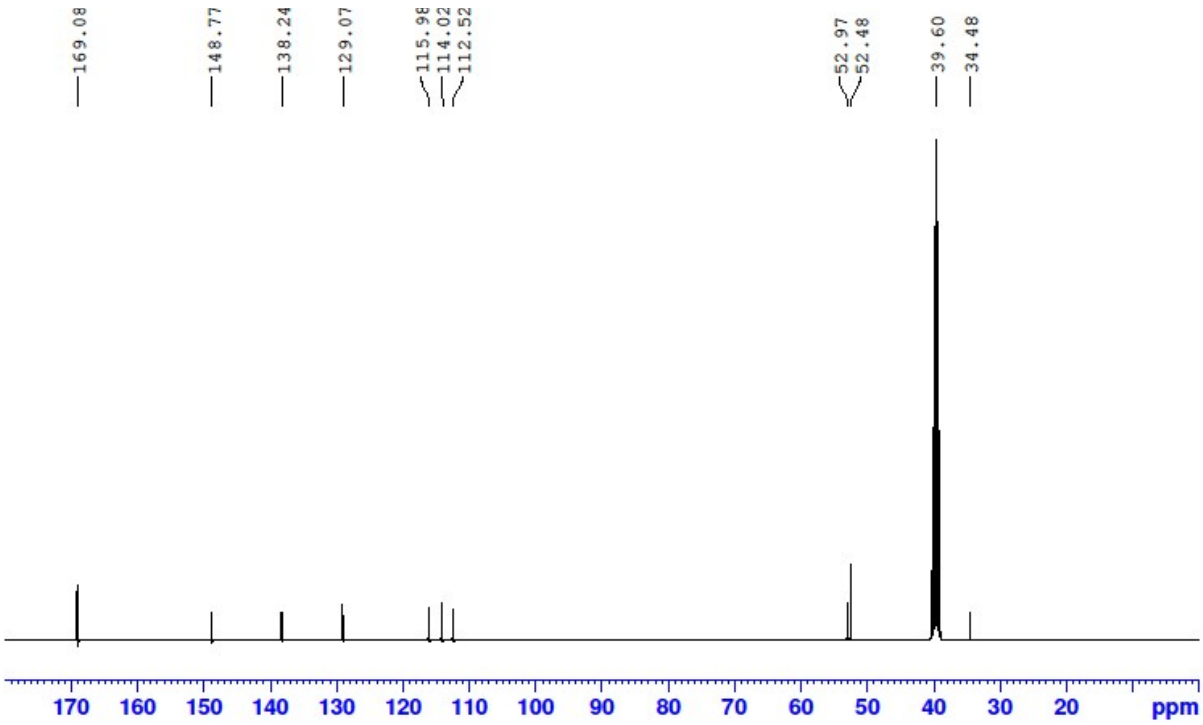
^{1}H NMR, d_6-DMSO, 400 MHz



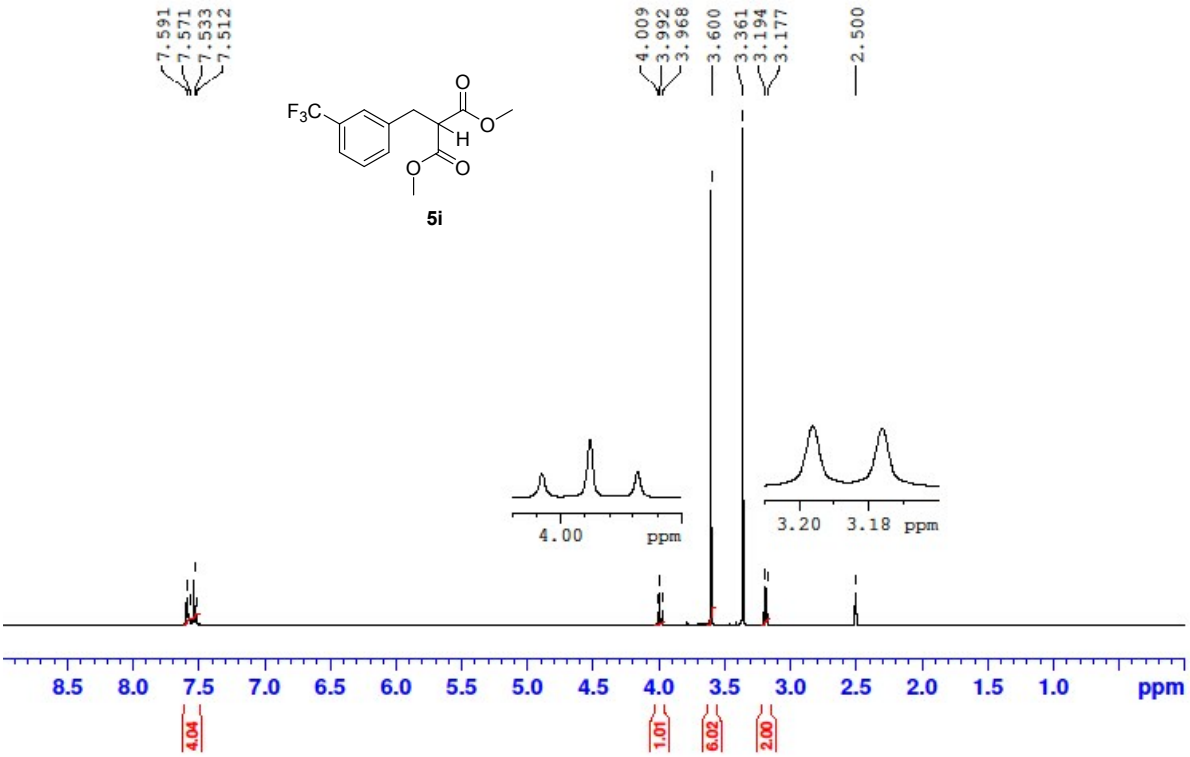


5h

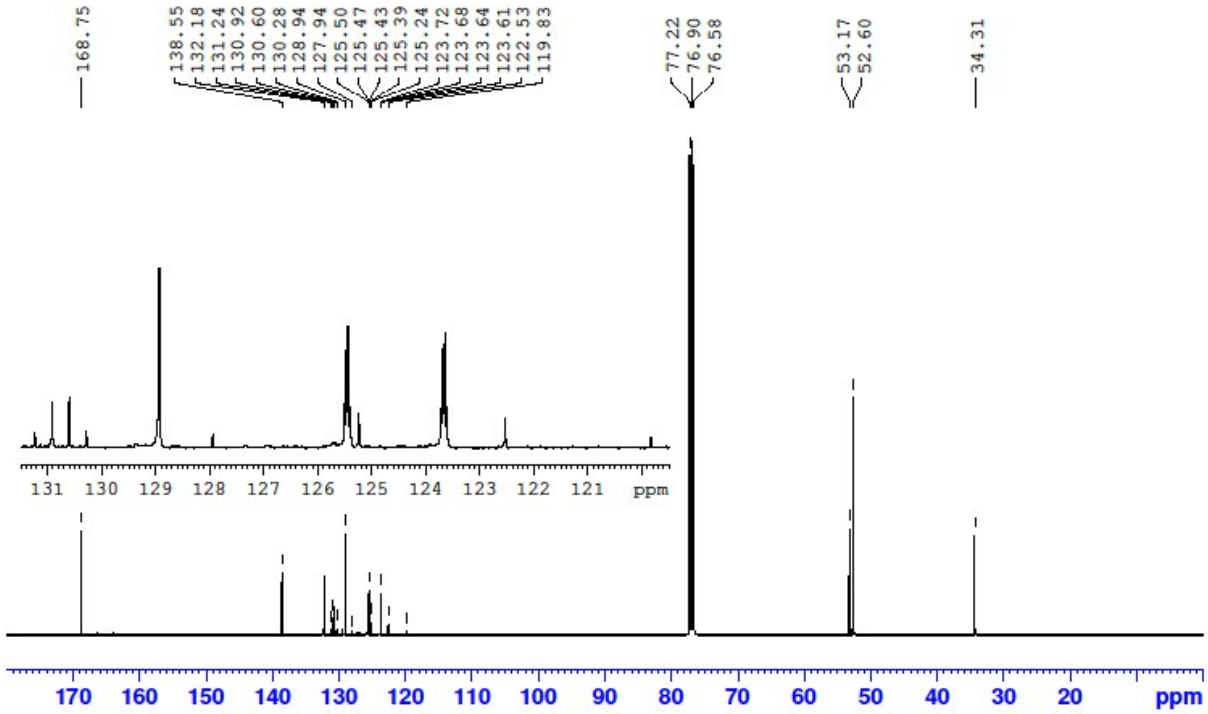
^{13}C NMR, d_6-DMSO, 101 MHz



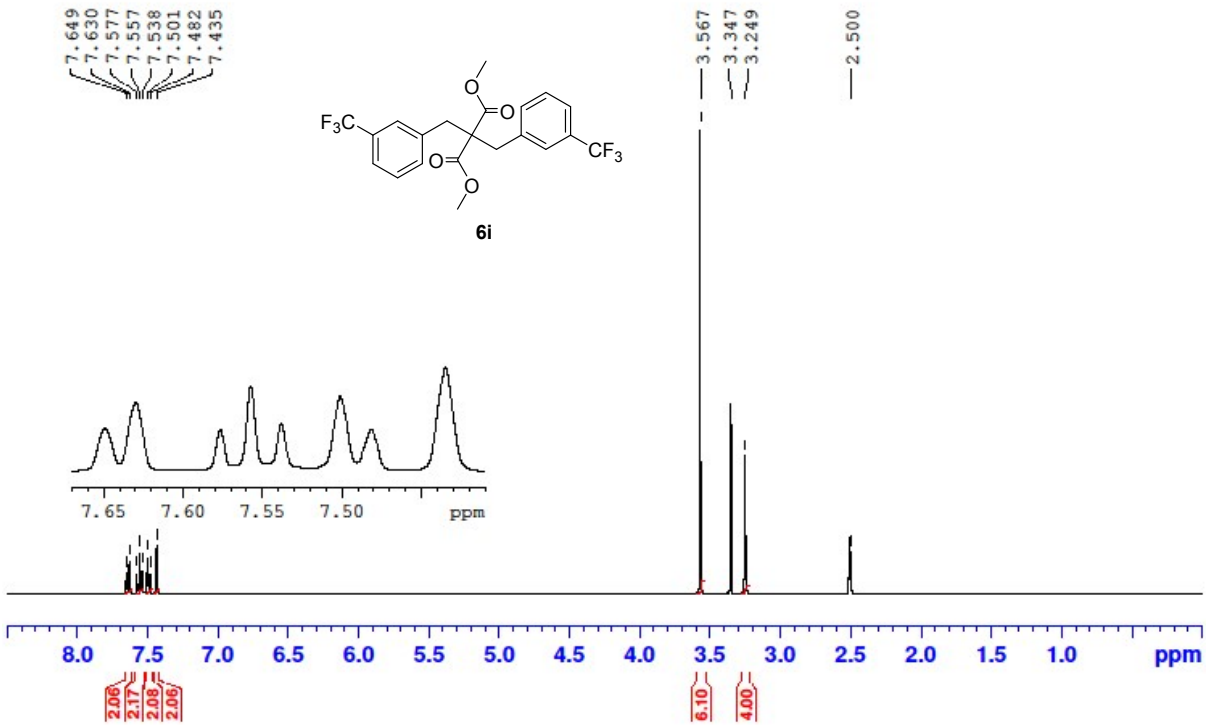
^{1}H NMR, d_6-DMSO, 400 MHz



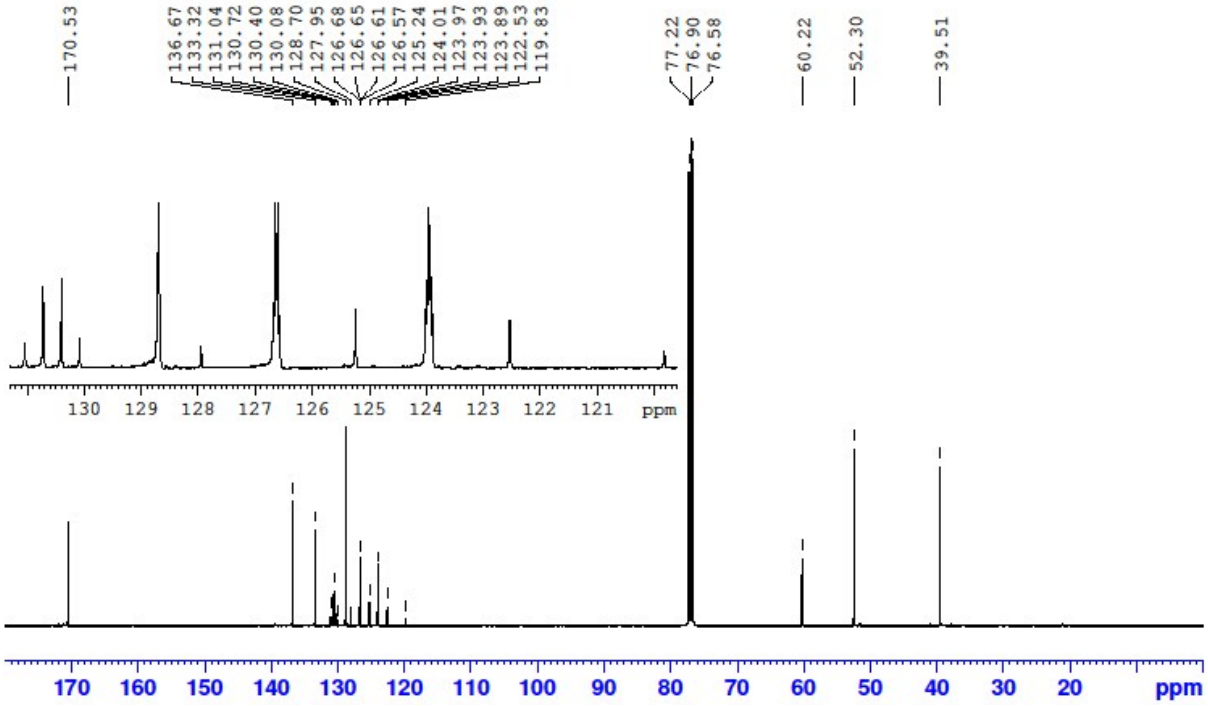
^{13}C NMR, $CDCl_3$, 101 MHz



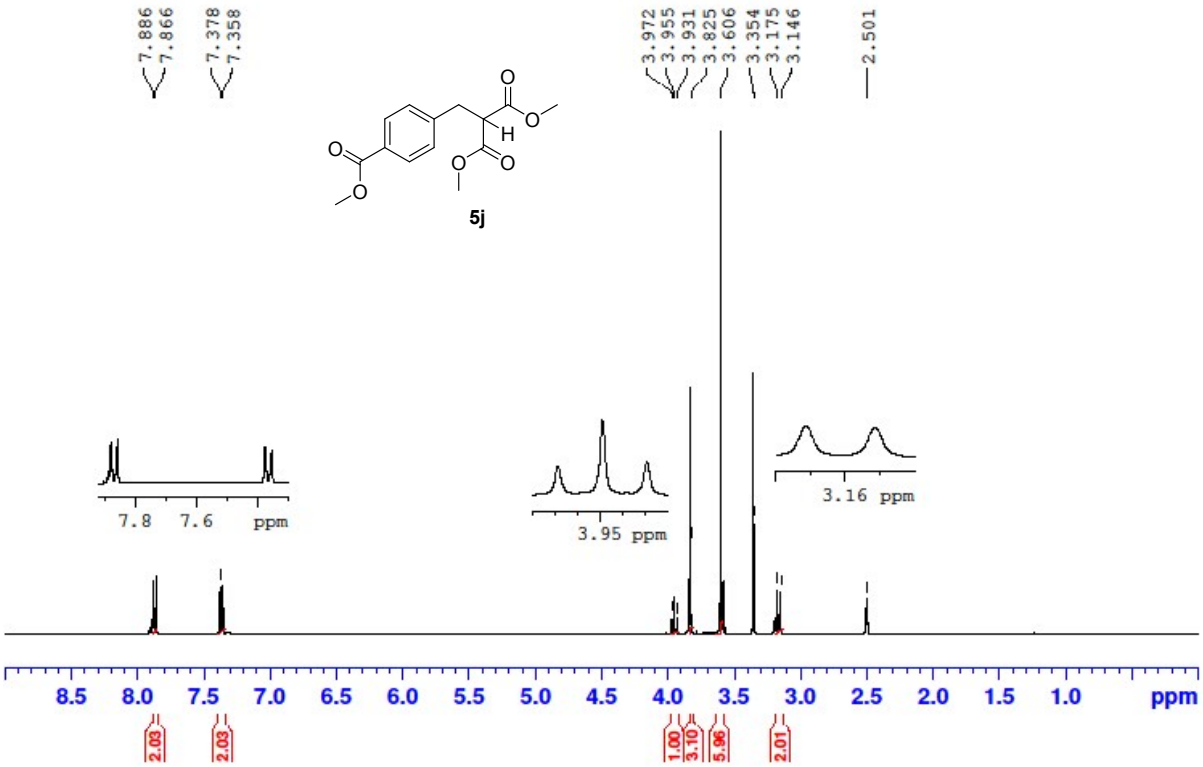
^{1}H NMR, d_6-DMSO, 400 MHz



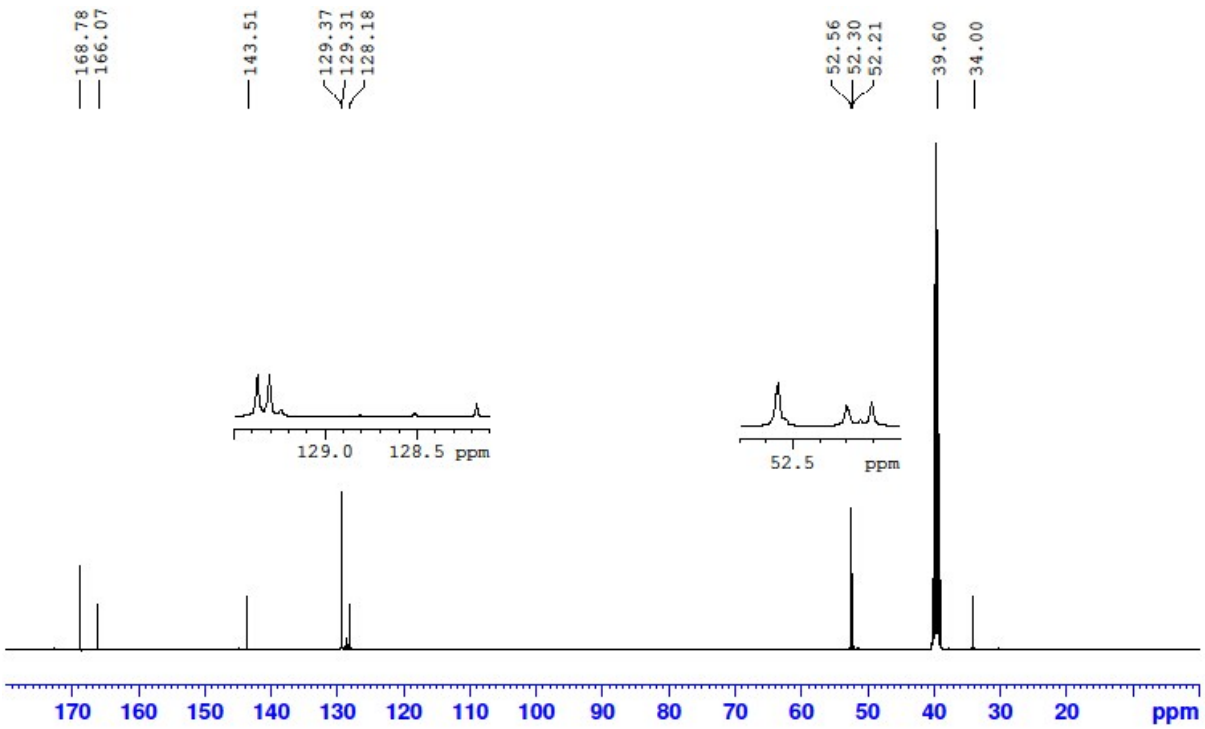
^{13}C NMR, $CDCl_3$, 101 MHz



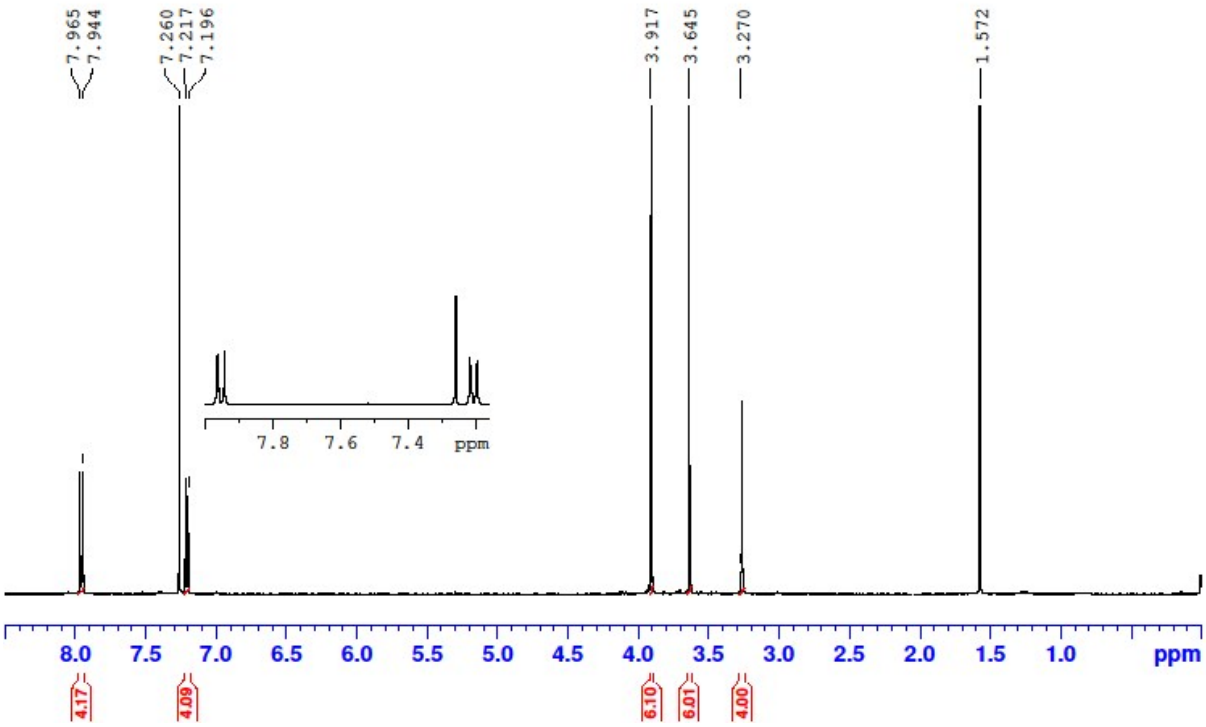
[1]H NMR, d_6-DMSO, 400 MHz

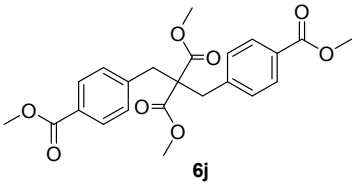


[13]C NMR, d_6-DMSO, 101 MHz



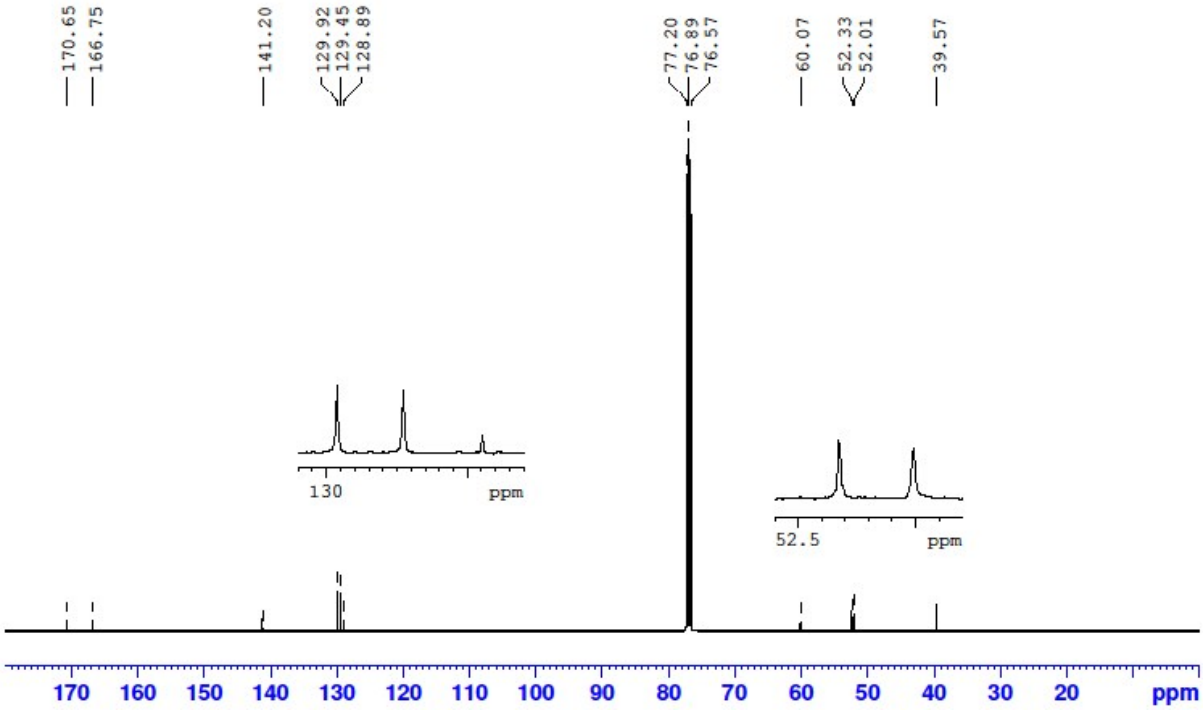
^{1}H NMR, $CDCl_3$, 400 MHz



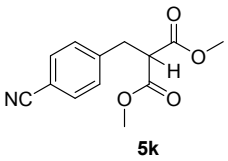


6j

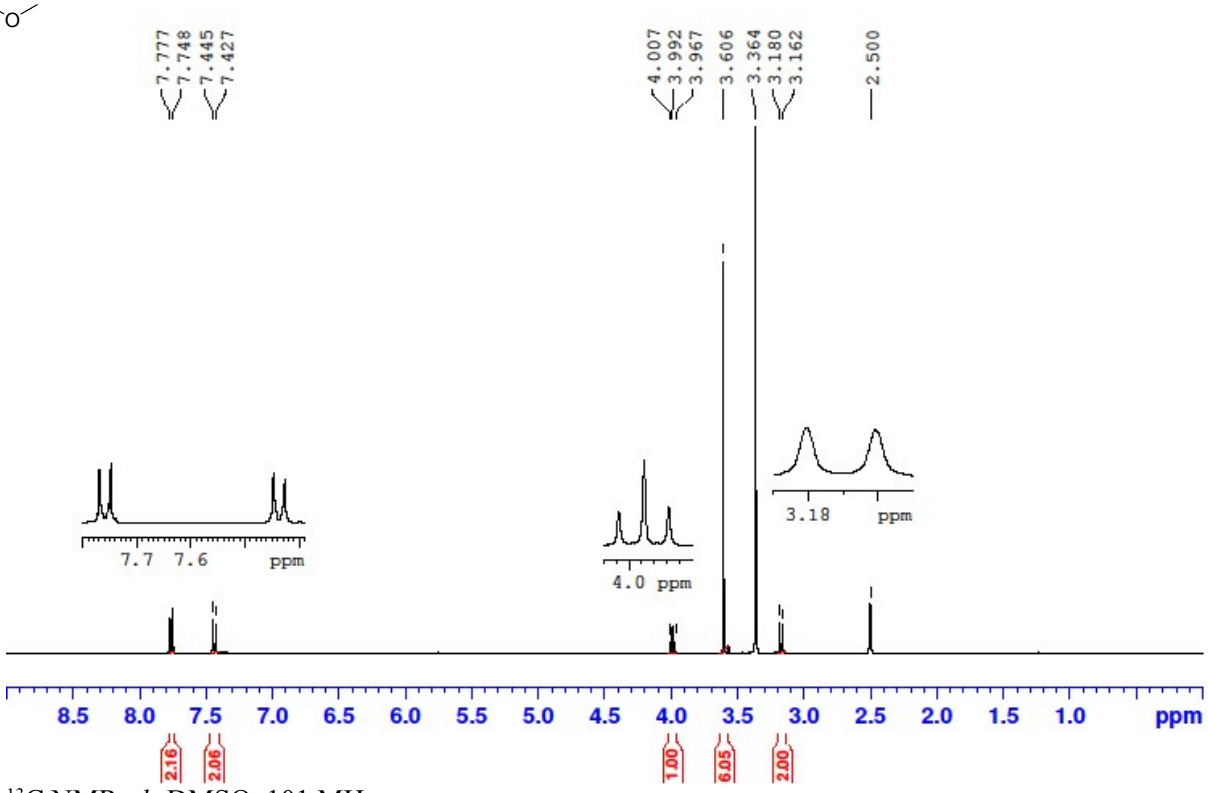
^{13}C NMR, $CDCl_3$, 101 MHz



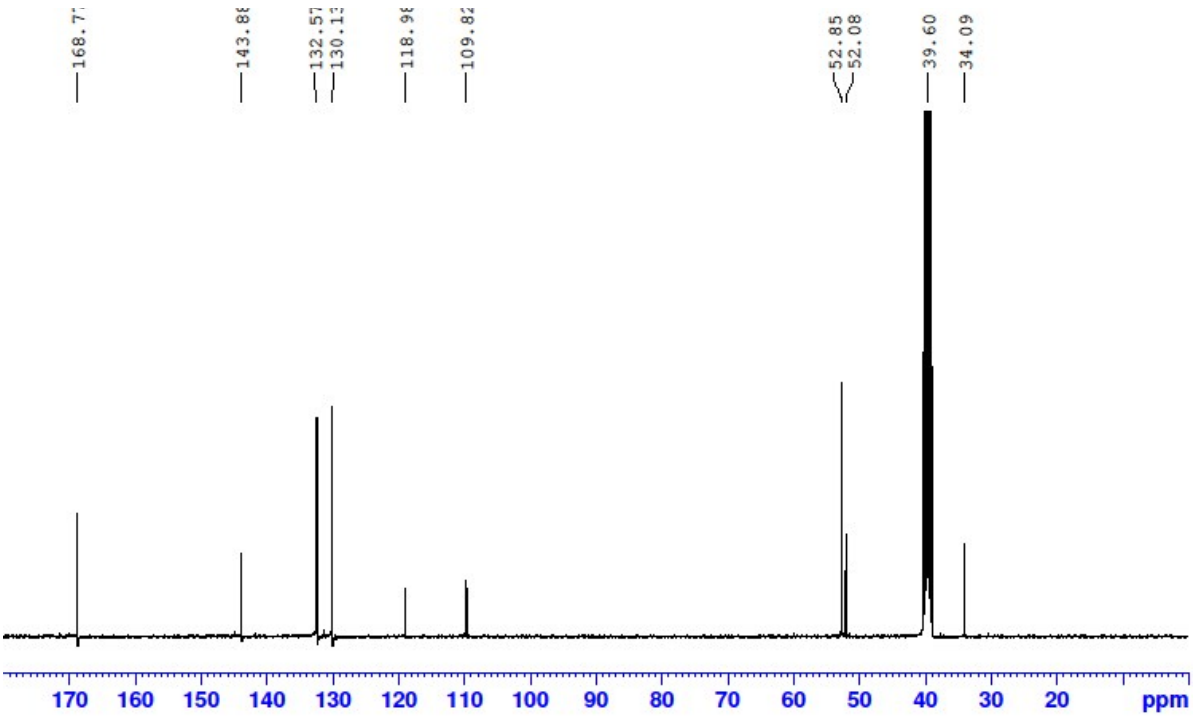
^{1}H NMR, d_6-DMSO, 400 MHz



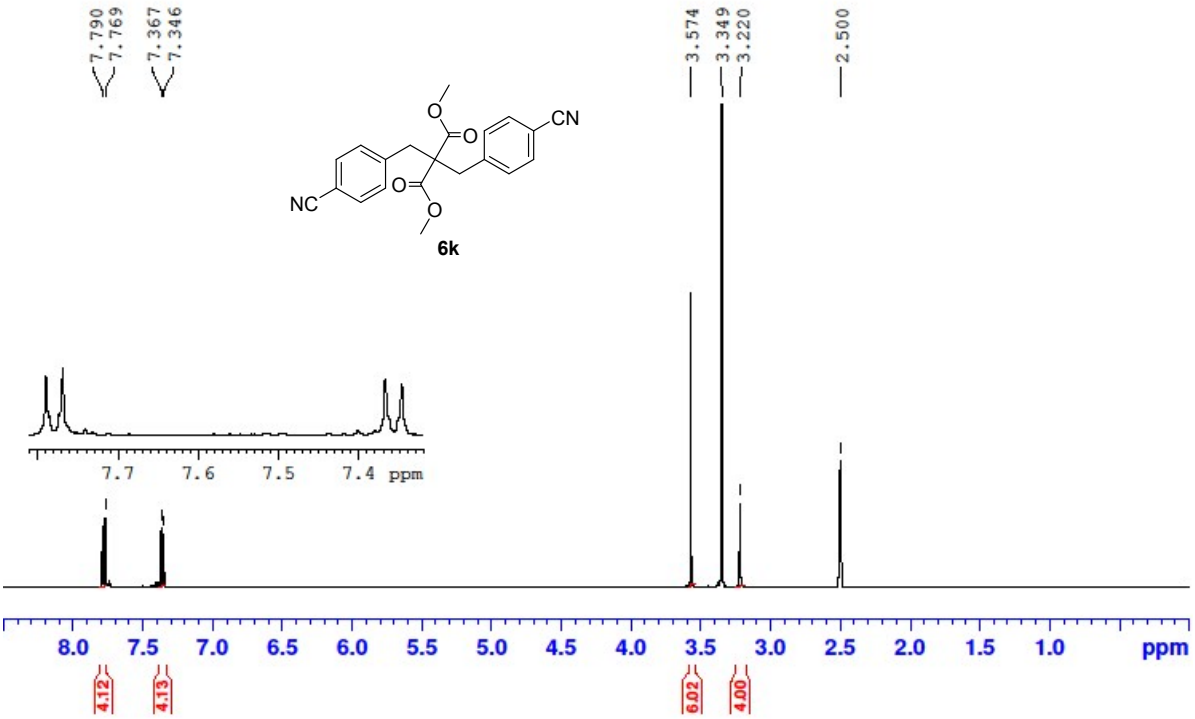
5k



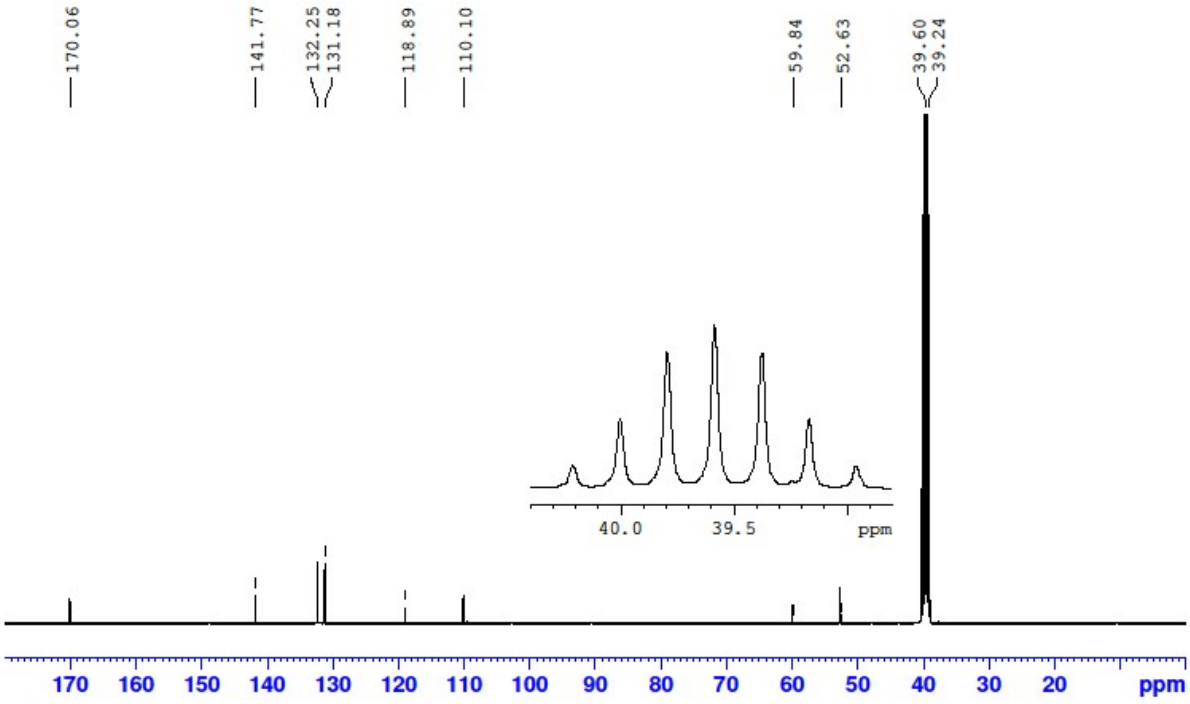
^{13}C NMR, d_6-DMSO, 101 MHz



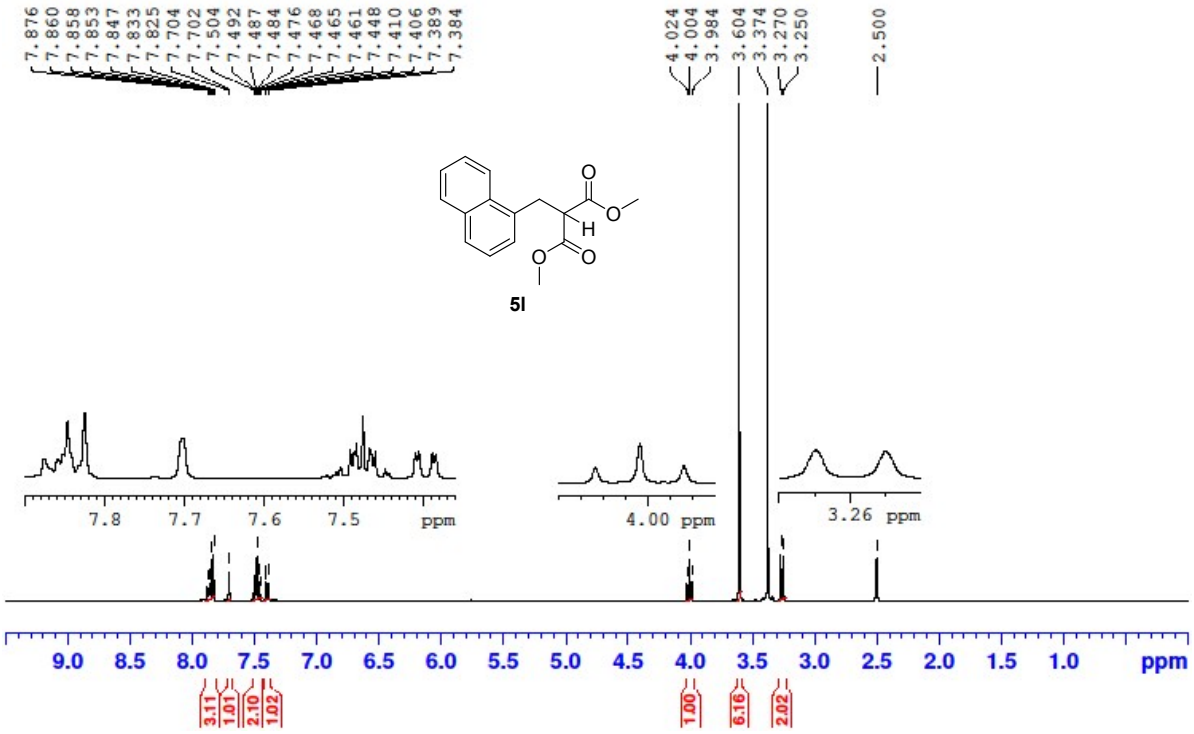
^{1}H NMR, d_6-DMSO, 400 MHz



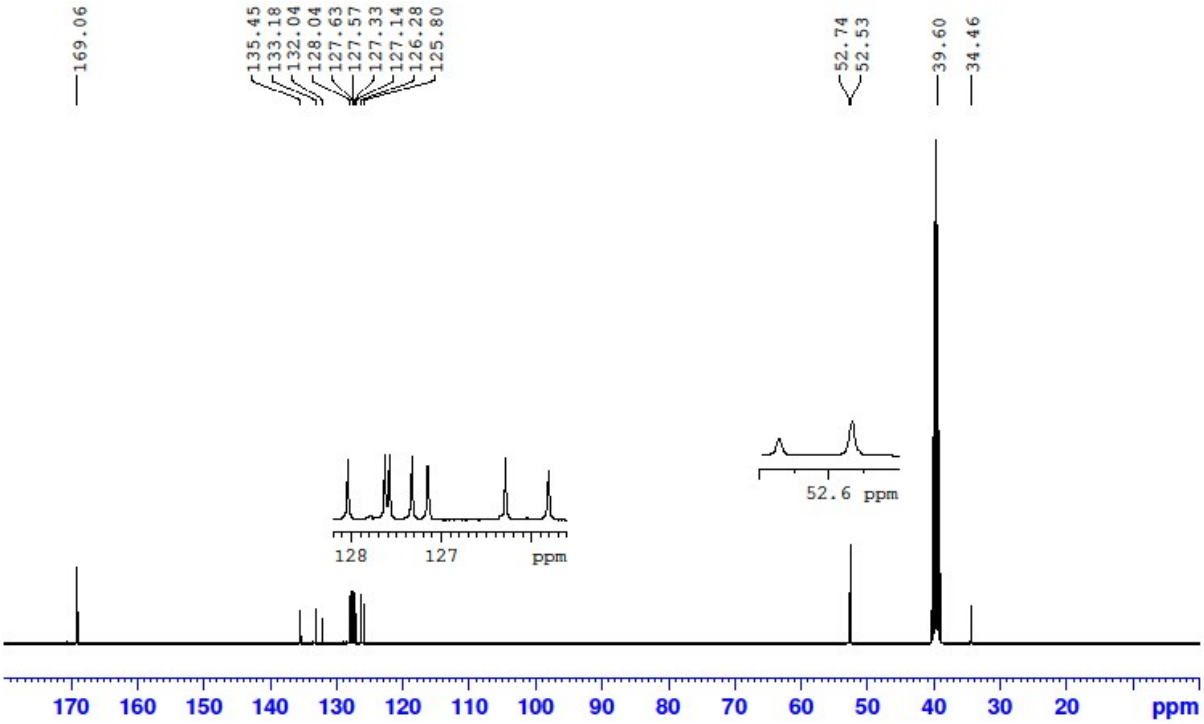
^{13}C NMR, d_6-DMSO, 101 MHz



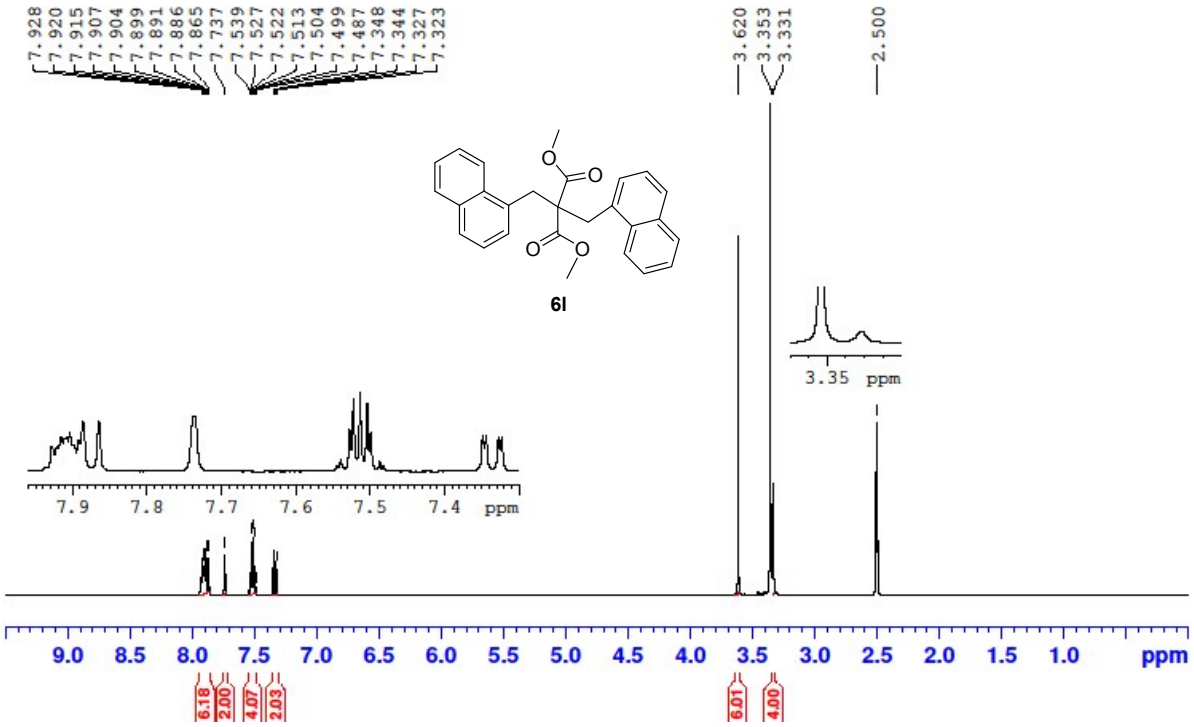
^{1}H NMR, d_6-DMSO, 400 MHz



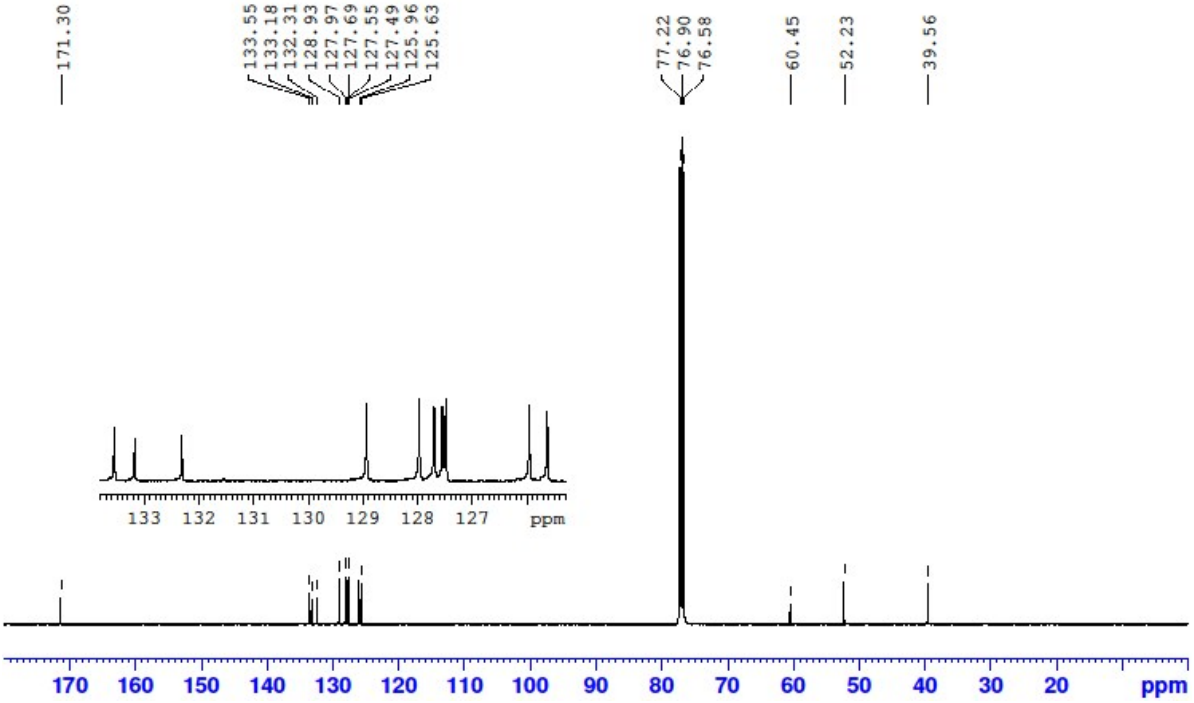
^{13}C NMR, d_6-DMSO, 101 MHz



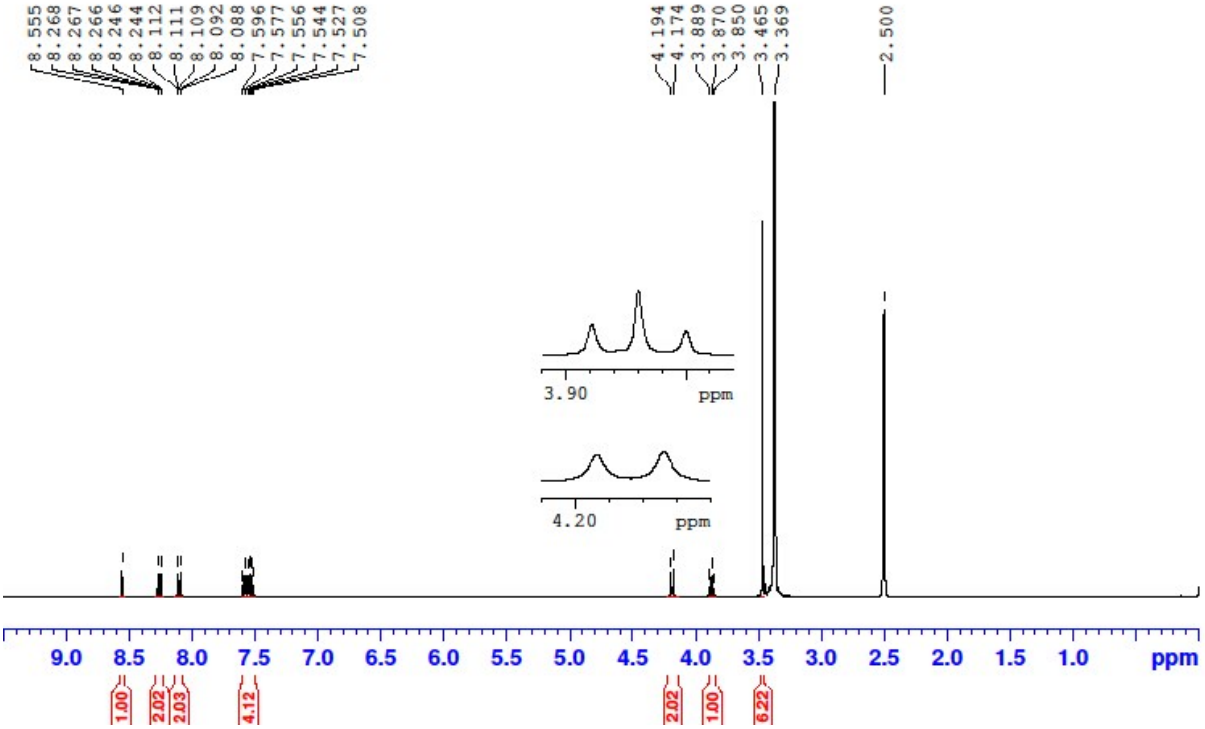
^{1}H NMR, d_6-DMSO, 400 MHz

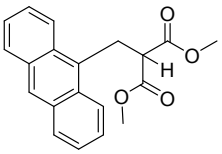


^{13}C NMR, $CDCl_3$, 101 MHz



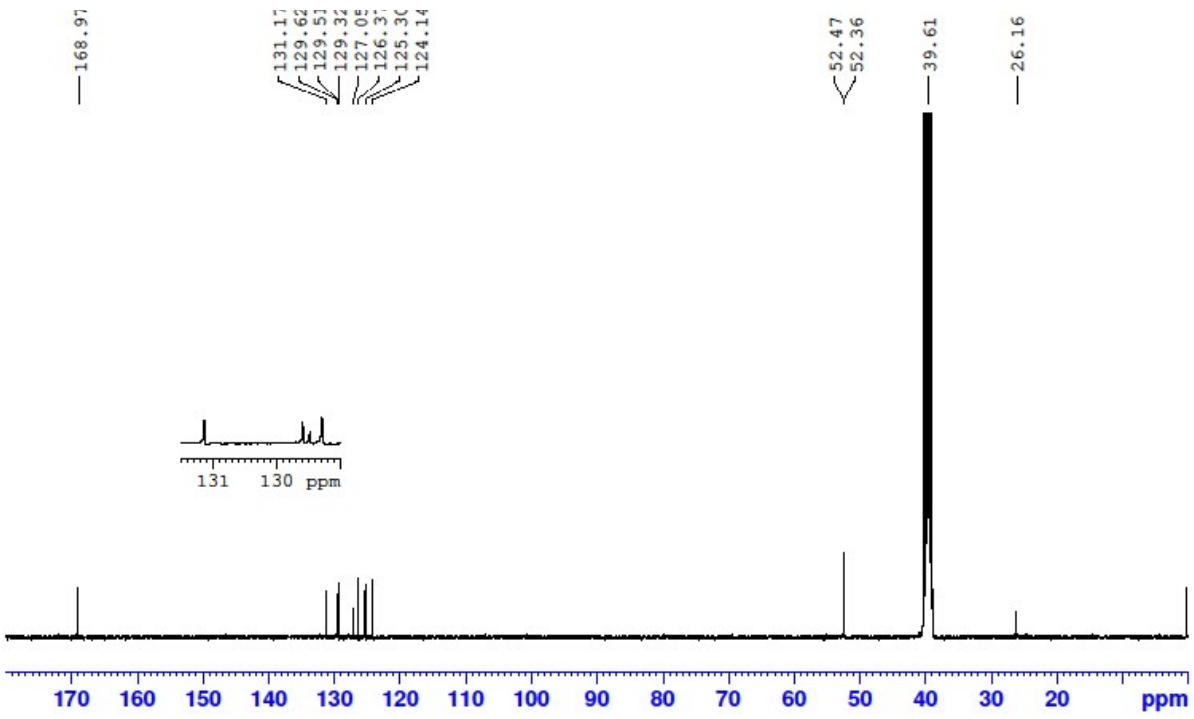
^{1}H NMR, d_6-DMSO, 400 MHz



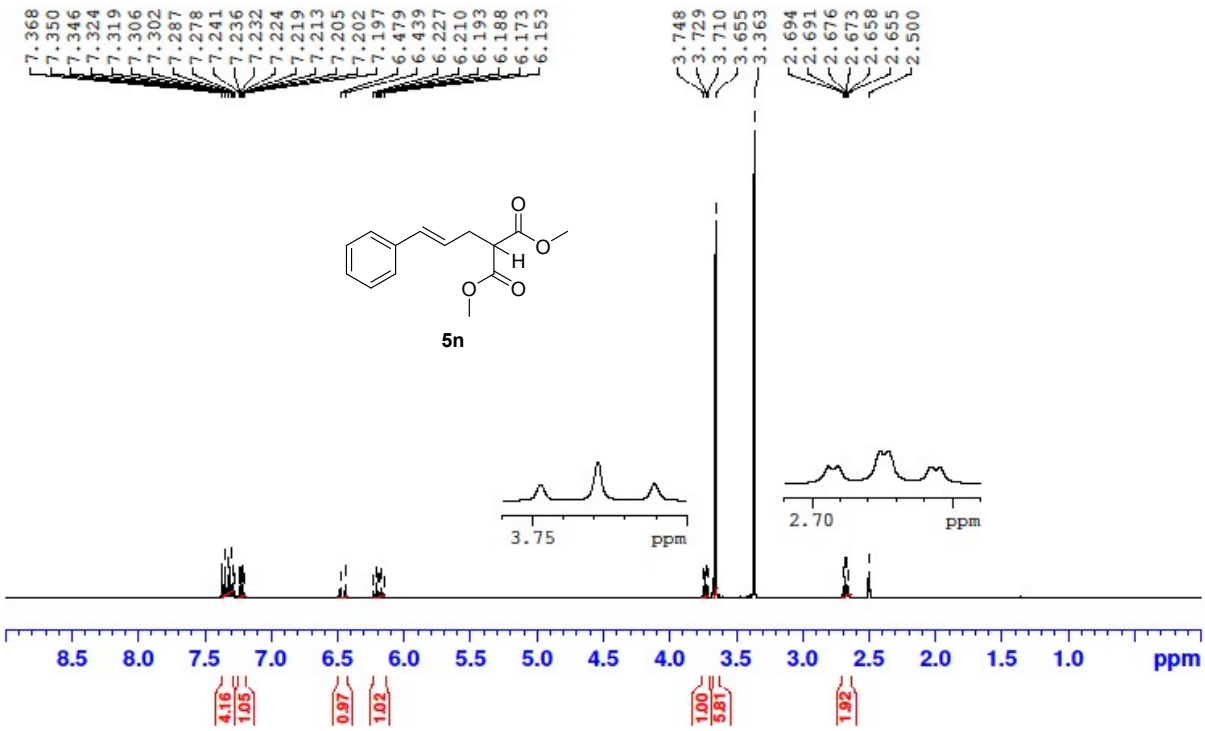


5m

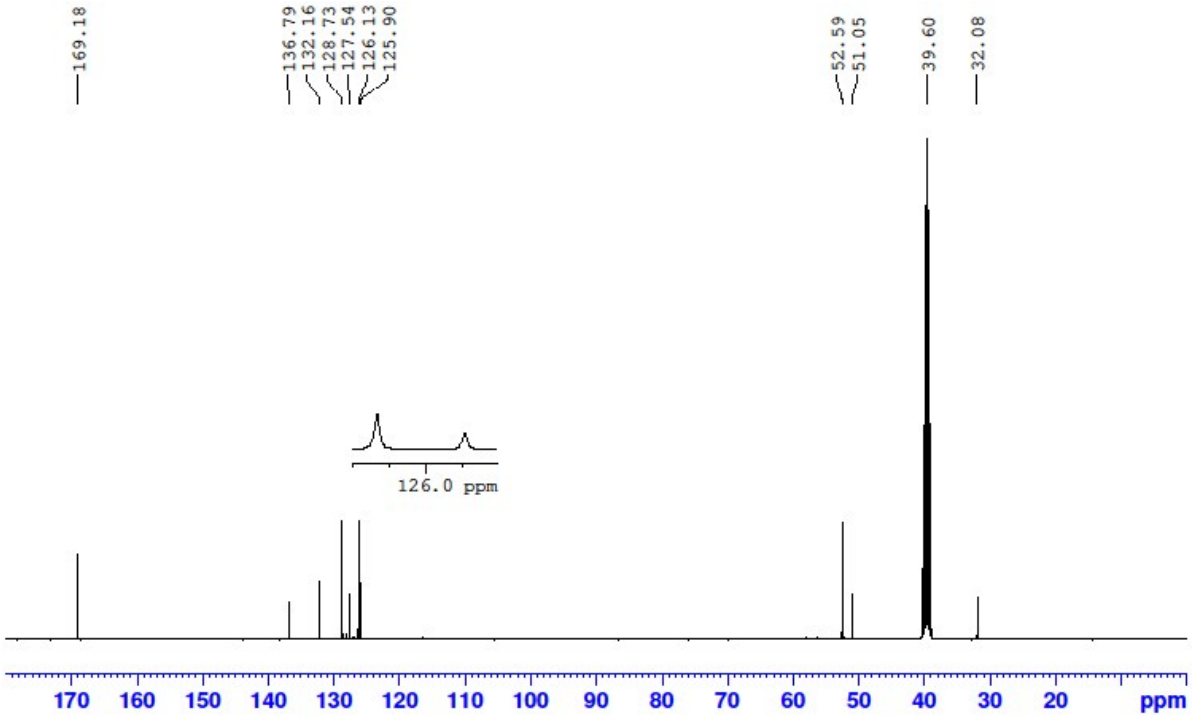
^{13}C NMR, d_6-DMSO, 101 MHz



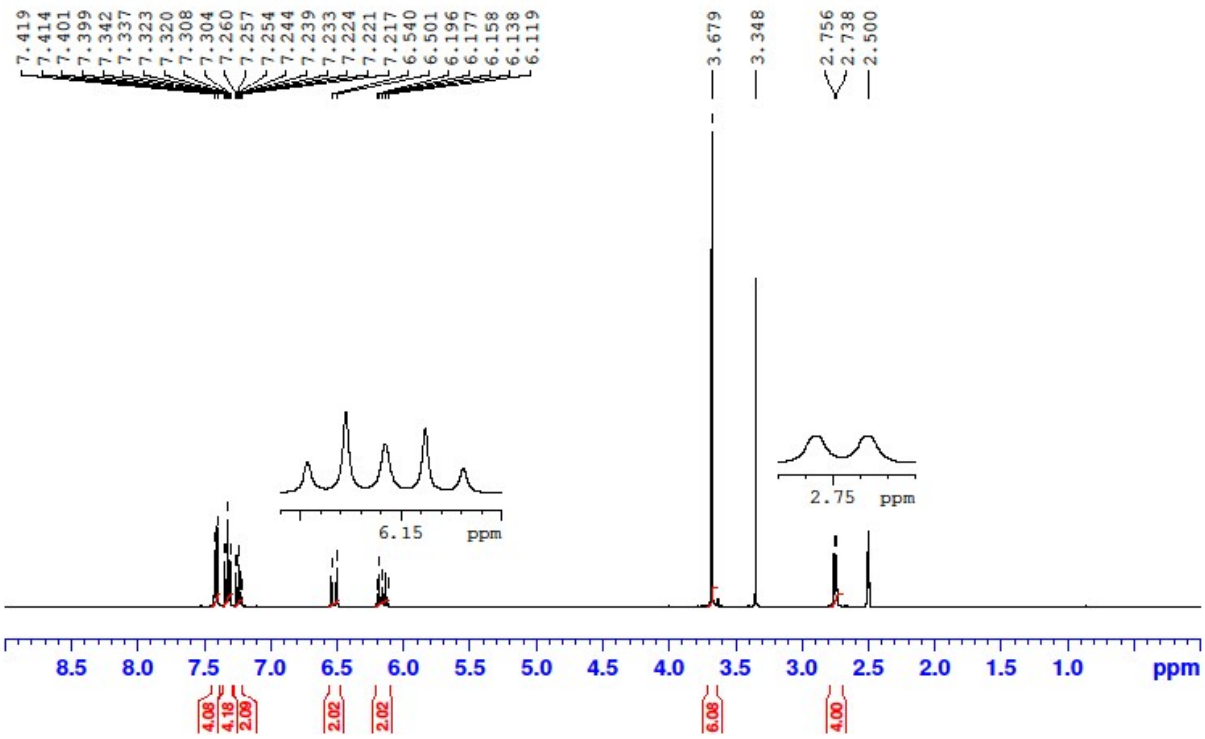
^{1}H NMR, d_6-DMSO, 400 MHz

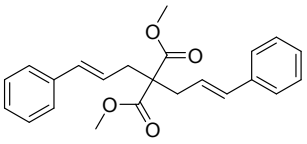


^{13}C NMR, d_6-DMSO, 101 MHz



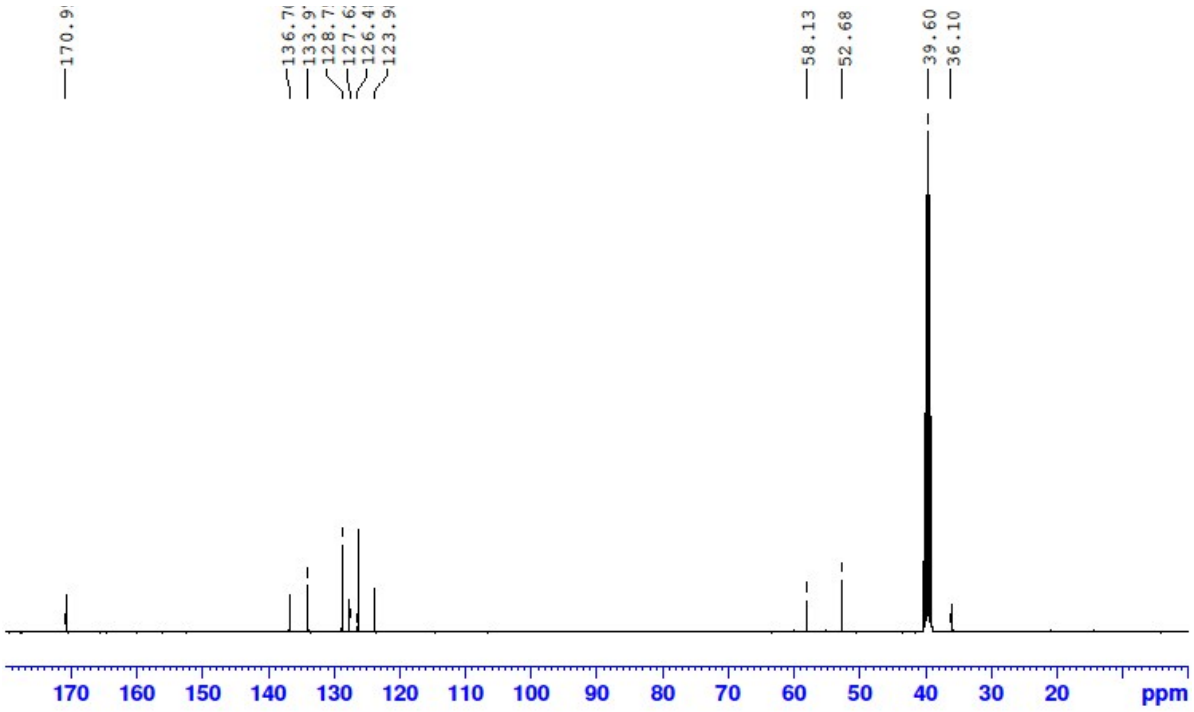
^{1}H NMR, d_6-DMSO, 400 MHz



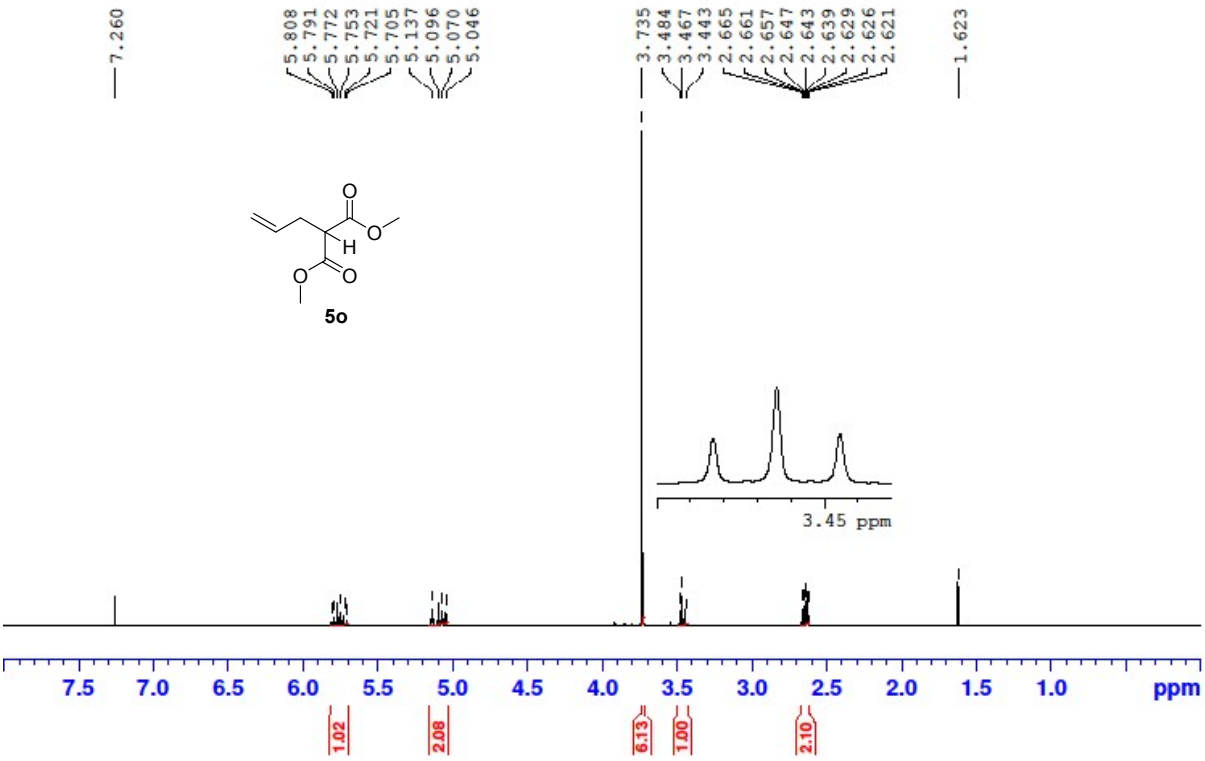


6n

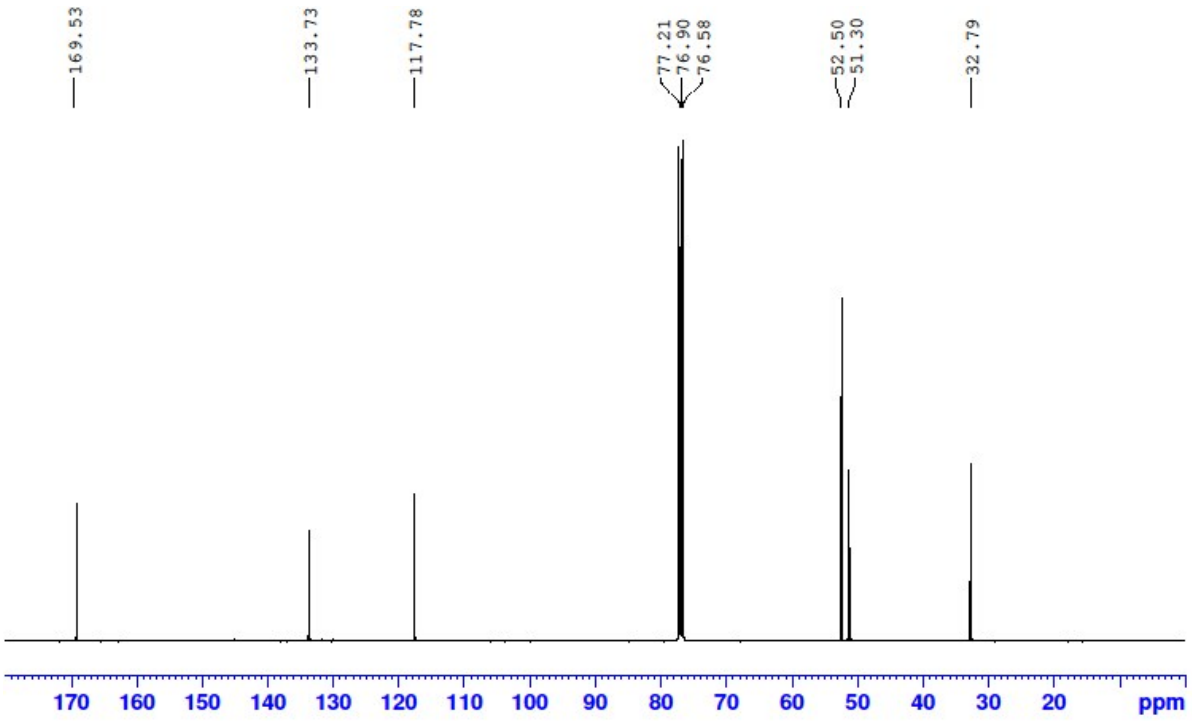
^{13}C NMR, d_6-DMSO, 101 MHz



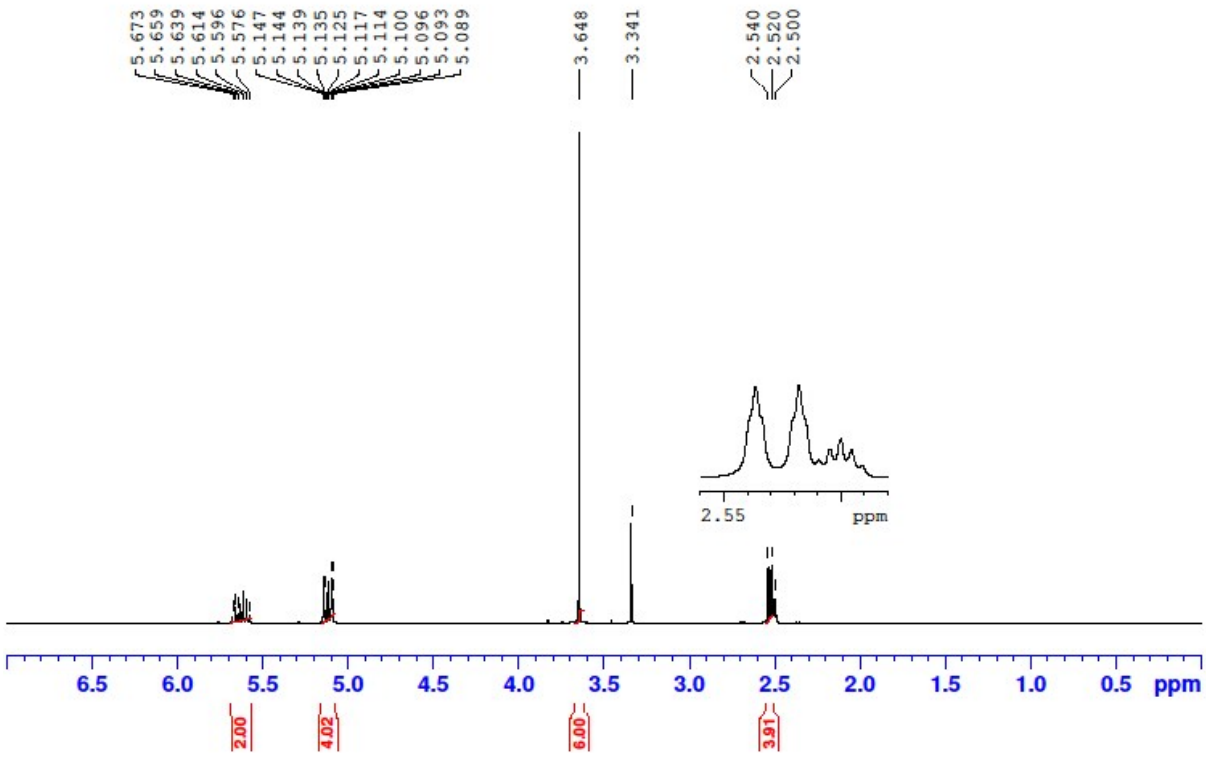
^{1}H NMR, $CDCl_3$, 400 MHz

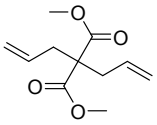


^{13}C NMR, $CDCl_3$, 101 MHz



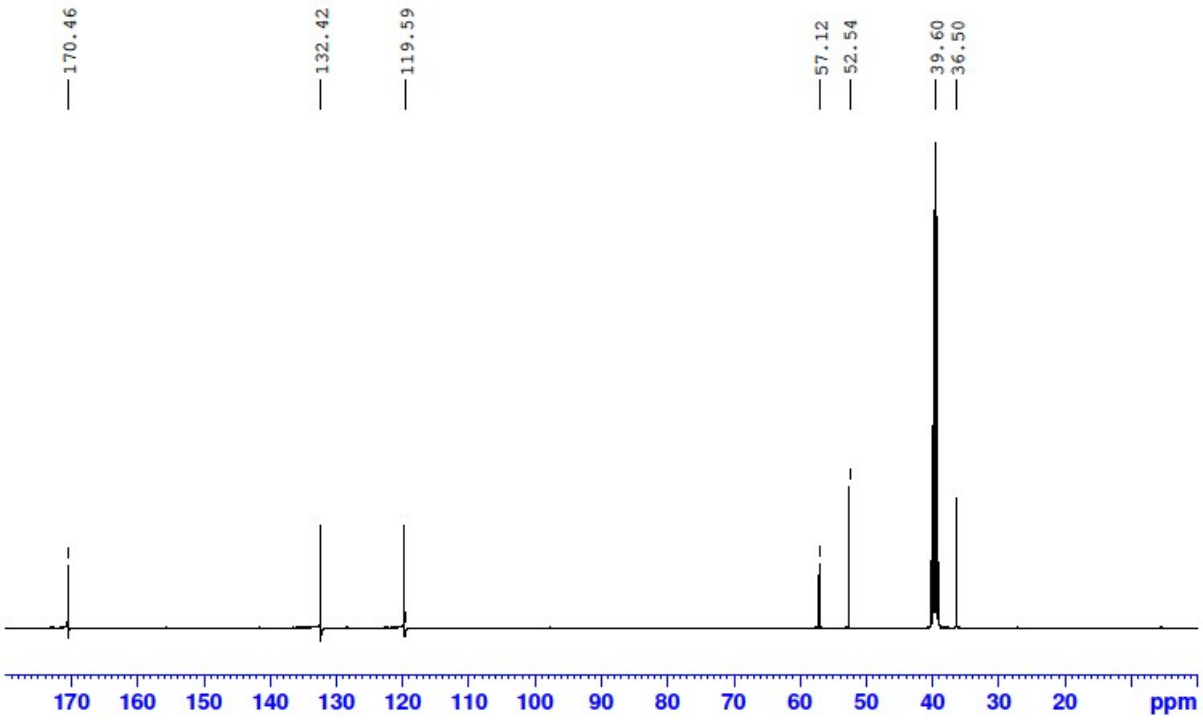
^{1}H NMR, d_6-DMSO, 400 MHz



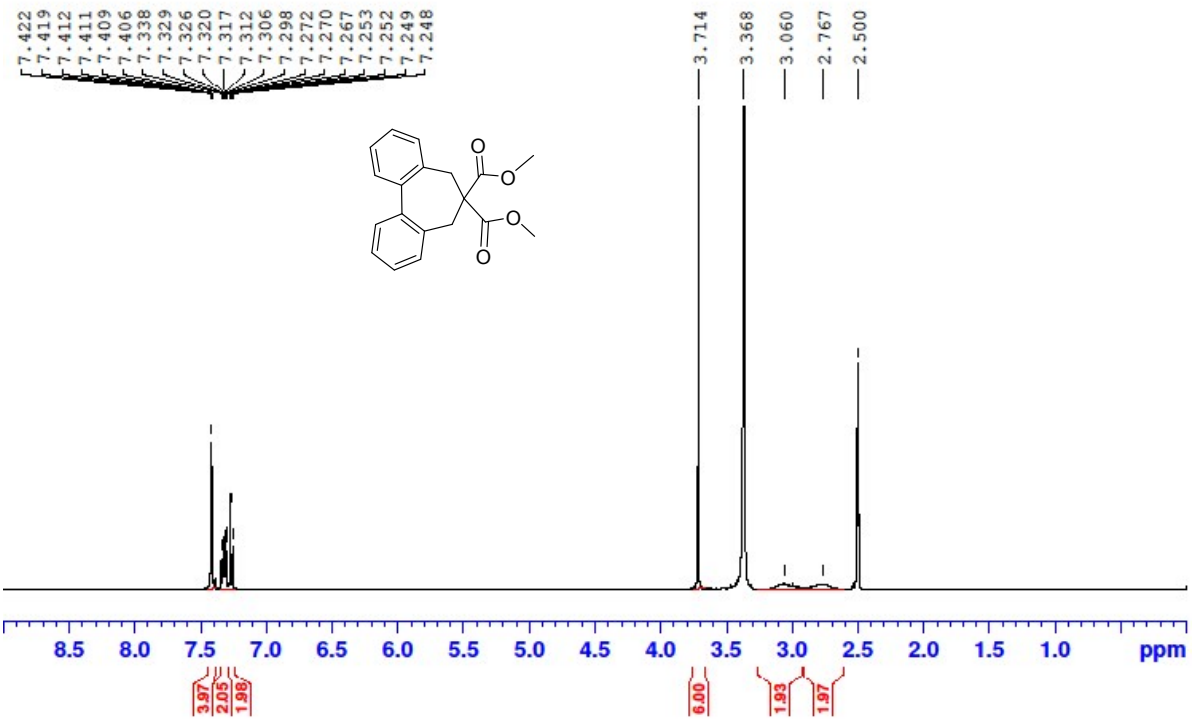


6o

^{13}C NMR, d_6-DMSO, 101 MHz



^{1}H NMR, d_6-DMSO, 400 MHz



^{13}C NMR, d_6-DMSO, 101 MHz