Supporting Information for

Metal-free C-C, C-O, C-S and C-N Bond Formation Enabled by SBA-15 Supported TFMSA

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Experimental procedures and analytical data

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1. General considerations

The solvents were dried and distilled prior to use by the literature methods. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker DRX–400 spectrometer and all chemical shift values refer to δ_{TMS} = 0.00 ppm or $CDCl_3$ ($\delta(^{1}H)$, 7.26 ppm; $\delta(^{13}C)$, 77.16 ppm). The GC analysis was obtained on Agilent 7890/5975C. Analytical TLC plates, Sigma-Aldrich silica gel $60F_{200}$ were viewed by UV light (254 nm). Column chromatographic purifications were performed on SDZF silica gel 160. All the chemical reagents were purchased from commercial sources and used as received unless otherwise indicated. Compounds **3a**-**3c**,[1] **3e**-**3g**,[1] **5b-5c**,[2] **7a**,[3] **7c**,[3] **7d**,[4] **7g**,[3] **7h**,[5] **7i**,[6] **9a-9d**,[7] **9e**,[8] **9f**[9] were known and its spectroscopic feature is in good agreement with that reported in the literatures.

Catalyst characterization. SBA-15 is commercially available from Nanjing XFNANO Materials Tech Co., Ltd. Flourier transform infrared (FT-IR, Thermo Scientific Nicolet iS5) was used to analyse the TFMSA@SBA-15. The morphology and element distribution of TFMSA@SBA-15 were examined by scanning electron microscope (SEM, Hitachi S-4800) and transmission electron microscope (JEM-2010 UHR). pH meter (METTLER TOLEDO FiveEasy Plus) was used to measure the pH value in reaction systems.

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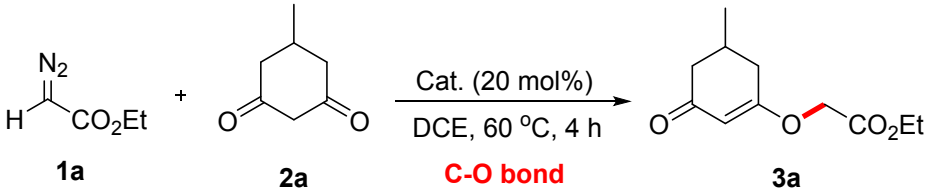
Table S1. Study on relationship between catalytic activity and p*K*a value of protic acid catalysts in forming C-O bonds reaction



1a **2a** **C-O bond** **3a**

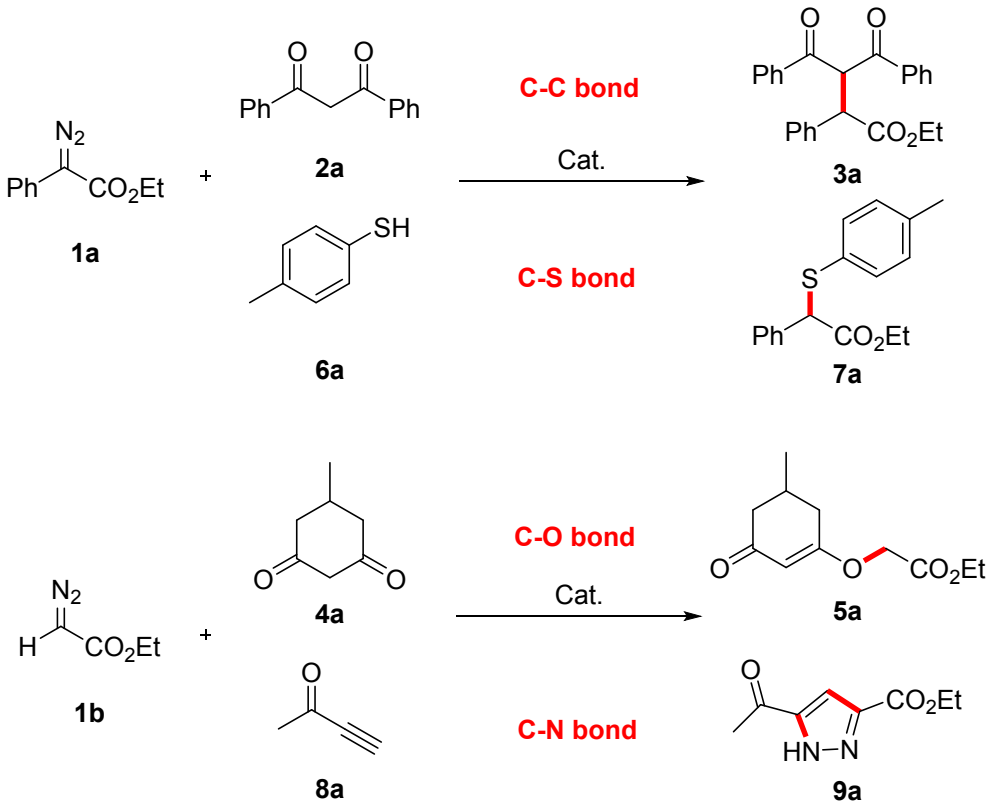
entry	cat.	p*K*a	Yield 3a (%)
1	-	-	0
2	AcOH	4.7	10
3	CSA	1.2	29
4	TFA	-0.25	13
5	MsOH	-2.6	32
6	TsOH	-2.8	40
7	H_2SO_4	-3.0	60
8	HCl	-8.0	52
9	$HClO_4$	-10.0	62
10	**TFMSA**	**-14.0**	**93**

Reaction conditions: **1a** (0.5 mmol), **2a** (1.5 mmol), catalyst (20 mol%), DCE (3 mL), 60 °C, 4 h, isolated yield.

Preparation of TFMSA@SBA-15

The preparation of TFMSA@SBA-15 was carried out the following some methods of the originally reported procedure.[10,11] The SBA (1 g) has been suspended in EtOAc (5 mL), then TFMAS (88µL, 2 mol%) was added and the mixture was stirred for 24 h. EtOAc was removed under reduced pressure, the residue was heated at 60 °C for 12 h under vacuum to afford TFMSA@SBA-15.

Table S2. Study on catalytic activity of TFMSA@SBA-15



cat.	C-C bond yield (%)	C-O bond yield (%)	C-S bond yield (%)	C-N bond yield (%)
TFMSA (20 mol%)	64	93	55	68
TFMSA (2 mol%)	67	69	66	44
TFMSA@SBA-15 (2 mol%)	**80**	**95**	**85**	**88**

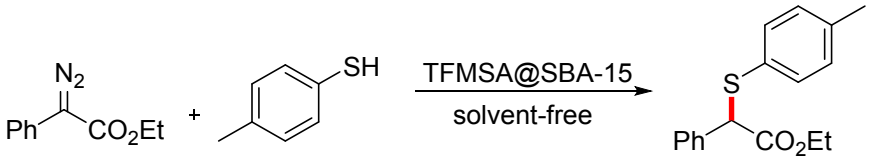
Reaction conditions: **C-C bond** formation: **1a** (0.5 mmol), **2a** (2.5 mmol), TFMSA@SBA-15 (2 mol%), DCE (3 mL), 60 °C, 1 h, isolated yield; **C-O bond** formation: **1b** (0.5 mmol), **4a** (1.5 mmol), TFMSA@SBA-15 (2 mol%), DCE (3 mL), 60 °C, 4 h, isolated yield; **C-S bond** formation: **1a** (0.5 mmol), **6a** (1.5 mmol), TFMSA@SBA-15 (2 mol%), rt, 5 min, isolated yield; **C-N bond** formation: **1b** (0.55 mmol), **8a** (0.5 mmol), TFMSA@SBA-15 (2 mol%), DCE (3 mL), 60 °C, 8 h, isolated yield.

Table S3. The comparison TON values between TFMSA@SBA-15 and other catalysts in similar reactions

Type	Cat.	Reference	Yield (%)	TON
C-C bond formation	$Sc(OTf)_3$	*Angew. Chem. Int. Ed.*, 2018, **57**, 8927.	42-95%	3
	$(ArO)_3PAuNTf_2$	*Angew. Chem. Int. Ed.*, 2014, **53**, 9817.	53-90%	20
	TFMSA@SBA-15	-	**65-87%**	**50**
C-O bond formation	$Sc(OTf)_3$	*Angew. Chem. Int. Ed.*, 2018, **57**, 8927.	54%	3
	AgOTf	*Angew. Chem. Int. Ed.*, 2018, **57**, 8927.	80%	10
	$HClO_4$-SiO_2	*Green Chem.*, 2018, **20**, 4547.	-	333
	TFMSA@SBA-15	-	**49-95%**	**50**
C-S bond formation	$Ni(OTf)_2$	*Angew. Chem. Int. Ed.*, 2019, **58**, 13492.	-	10
	AgOTf	*Org. Biomol. Chem.*, 2009, **7**, 1276.	-	10
	$[(CH_3CN)_4Cu]PF_6$	*J.Org. Chem.*, 2017, **82**, 3000.	75-90%	20
	$Ir(TTP)CH_3$	*Organometallics.*, 2017, **36**, 927.	-	1428
	$Fe(OTf)_2$	*Org. Biomol. Chem.*, 2019, **17**, 3098.	35-96%	6
	Mb-based catalysts	*Chem. Sci.*, 2015, **6**, 2488.	-	1100-5400
	TFMSA@SBA-15	-	**65-85%**	**50**
C-N bond formation	$InCl_3$	*Chem. Commun.*, 2004, 394.	54-93%	5
	$Pd(PPh_3)_4$	*J. Org. Chem.*, 2011, **76**, 5915.	40-90%	20
	Bu_4NI	*Org. Biomol. Chem.*, 2016, **14**, 8486.	42-99%	10
	TFMSA@SBA-15	-	**65-85%**	**50**

The catalytic performance of TFMSA@SBA-15 in C-C, C-O, C-S and C-N bond formation is close to those reported catalysts.

Table S4. Study on reusability of TFMSA@SBA-15



1a **6a** **C-S bond** **7a**

Run	Scale		TFMAS@SBA-15		pH	7a Yield (%)
	1a	6a	used	recovered		
1st	1.0 g	1.90 g	104 mg	90 mg	0.67	80
2nd	0.77 g	1.46 g	80 mg	74 mg	0.72	78
3rd	0.58 g	1.09 g	60 mg	54 mg	0.86	76
4th	0.38 g	0.73 g	40 mg	38 mg	1.578	50
5th	0.19 g	0.37 g	20 mg	17 mg	3.06	26

Reaction conditions: TFMSA@SBA-15 (2 mol%), rt, isolated yield. General procedure of catalyst recycling: after the completion of this reaction, the mixture was added DCM (2 mL), then the catalyst was separated by centrifugation (12000 rpm, 15 min) and washed with DCM (3 mL ×5). After that, it was dried on vacuum (60 ^{o}C) for 1 h. General procedure of pH tests: after the completion of this reaction, the mixture was added DCM (2 mL), then the catalyst was separated by centrifugation (12000 rpm, 15 min). After that, the mother liquors were taken run 1st (5.8 µL), run 2nd (7.5 µL), run 3rd (10 µL), run 4th (15 µL) and run 5th (30 µL), respectively. The sample solutions were diluted to 2 mL with DCM and the pH value of supernatant was tested with pH meter.

The reusability of TFMSA@SBA-15 was investigated in the reaction of C-S bond formation that TOF is up to 600 h^{-1}. The reaction was repeated 5 times in the presence of the recovered TFMSA@SBA-15 to afford **7a** in run 1st (80%), run 2nd (78%), run 3rd (76%), run 4th (50%) and run 5th (26%), respectively (Table S4). A reduction in the yield after run 3rd was detected. So the upper limit for reusability of TFMSA@SBA-15 is 4 cycles.

From run 1st to run 3rd, the heterogeneous mesoporous material based TFMAS catalyst is stable, exhibiting negligible acid leaching. However, the pH value (Fig. S1a) increased obviously after running 3 times, the tendency indicated that pKa value of reused TFMSA@SBA-15 increased gradually due to the leaching of TFMSA.

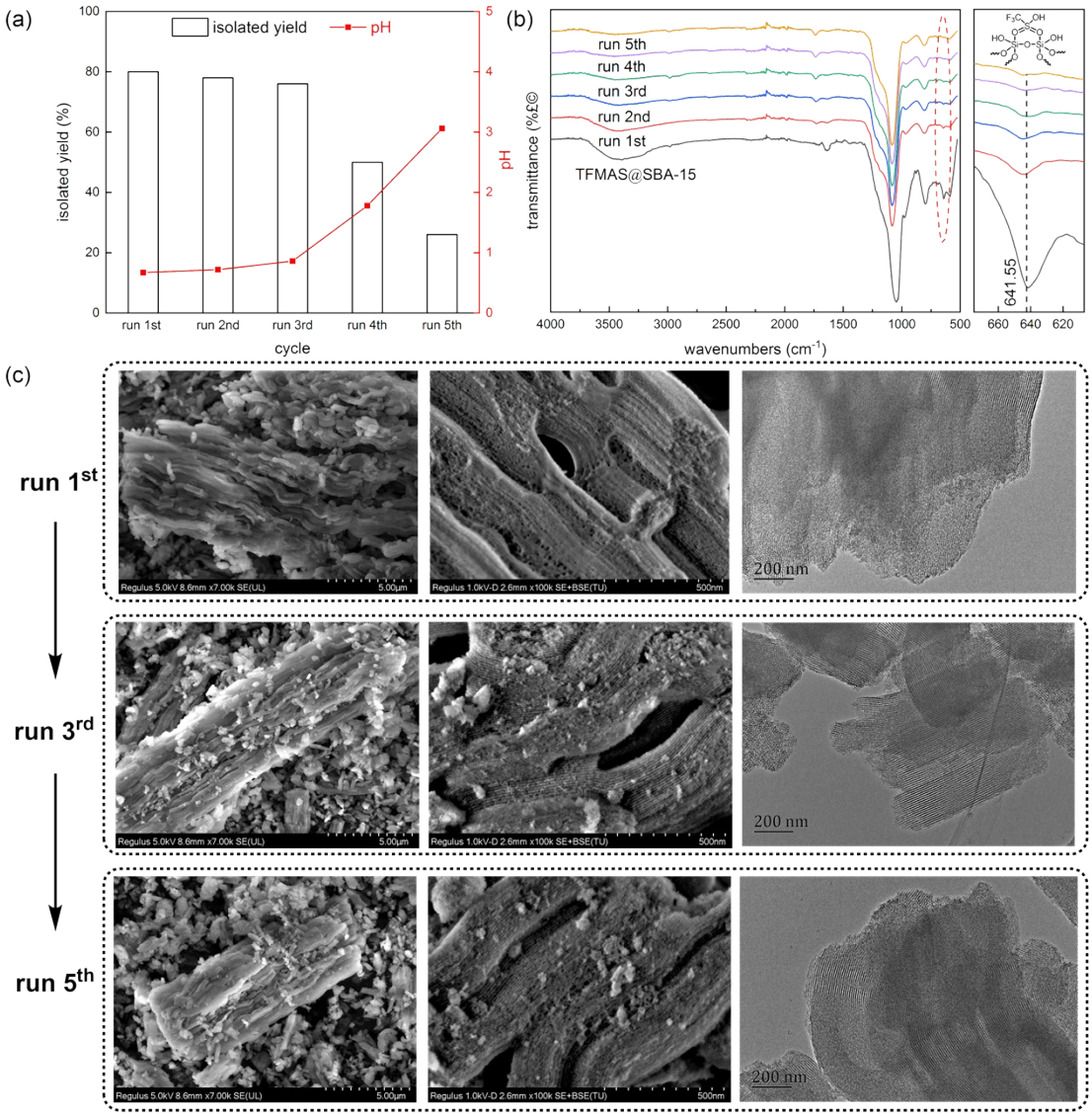
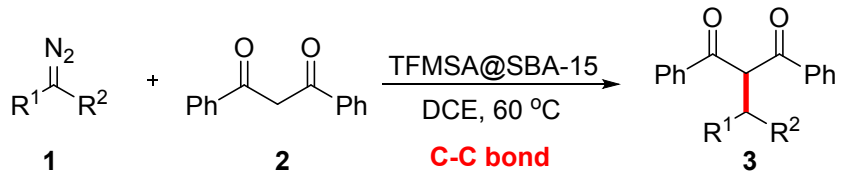


Figure S1. (a) Recycling and pH tests of TFMAS@SBA-15. (b) FT-IR spectra of TFMAS@SBA-15 and reused TFMAS@SBA-15. (c) Reused TFMSA@SBA-15 SEM images and TEM images.

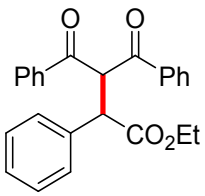
The reused catalysts were also characterized using SEM, TEM and FTIR, respectively. The results clearly show that the initial cylindrical mesoporous of SBA-15 was still preserved on the supported catalyst (Fig. S1c). Therefore, the recycling has a minor effect on the structure of the catalyst. It is notable that the peak at 641 cm^{-1} that arise from stretching vibration of the sulfonic group has gradually disappeared (Fig. S1b) after running 3 times, which provided evidences of the TFMSA leaching in recycling.

4. Synthesis and analytical data of compounds 3



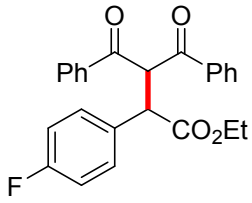
A typical general procedure for the synthesis of 3 (with **3a** as an example): A mixture of ethyl 2-diazo-2-phenylacetate **1a** (96 mg, 0.5 mmol), 1,3-diphenylpropane-1,3-dione **2a** (560 mg, 2.5 mmol) and TFMSA@SBA-15 (10 mg) in DCE (3 mL) was stirred at 60 °C for 1 h. After **1a** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/EtOAc, 50:1) to afford the corresponding **3a** as a white solid (155 mg, 80%).

1-gram scale reaction for 3a: A mixture of ethyl 2-diazo-2-phenylacetate **1a** (1 g, 5.2 mmol), 1,3-diphenylpropane-1,3-dione **2a** (5.8 g, 26 mmol) and TFMSA@SBA-15 (104 mg) in DCE (15 mL) was stirred at 60 °C for 3 h. After **1a** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/EtOAc, 50:1) to afford the corresponding **3a** as a white solid (1.54 g, 77%).

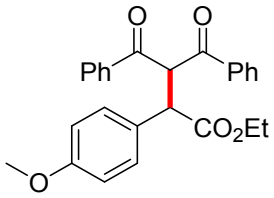


Ethyl-3-benzoyl-4-oxo-2,4-diphenylbutanoate (3a): 155 mg, yield 80%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.65 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.51 – 7.46 (m, 1H), 7.45 – 7.40 (m, 1H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.29 – 7.24 (m, 4H), 7.16 (t, *J* = 7.3 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.09 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.24 – 4.04 (m, 1H), 1.18 (t, *J* = 7.1 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.66, 194.33, 172.74, 136.76, 136.47, 135.40, 133.55, 133.44, 128.90, 128.90, 128.80, 128.79, 128.68, 128.60, 127.96, 61.58, 61.04, 52.69, 14.10. The spectroscopic

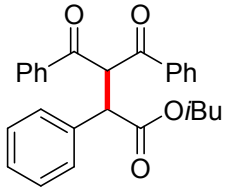
data for this product match the literature data.[1]



Ethyl-3-benzoyl-2-(4-fluorophenyl)-4-oxo-4-phenylbutanoate (3b): 175 mg, yield 87%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.89 (m, 2H), 7.72 – 7.62 (m, 2H), 7.52 – 7.43 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.17 (m, 2H), 6.85 (t, *J* = 8.7 Hz, 2H), 6.06 (d, *J* = 11.2 Hz, 1H), 4.79 (d, *J* = 11.2 Hz, 1H), 4.21 – 4.04 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.52, 194.21, 172.62, 162.41 (d, *J* = 247.0 Hz), 136.61, 136.36, 133.67, 133.65, 131.21, 131.17, 130.40, 130.32, 128.89, 128.84, 128.77, 128.73, 115.84 (d, *J* = 21.6 Hz), 61.69, 61.00, 51.84, 14.09. The spectroscopic data for this product match the literature data.[1]

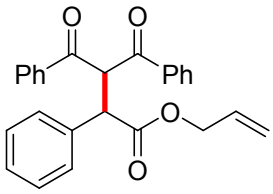


Ethyl-3-benzoyl-2-(4-methoxyphenyl)-4-oxo-4-phenylbutanoate (3c): 141 mg, yield 68%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.87 (m, 2H), 7.76 – 7.60 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.0 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.7 Hz, 2H), 6.06 (d, *J* = 11.2 Hz, 1H), 4.76 (d, *J* = 11.2 Hz, 1H), 4.22 – 4.03 (m, 2H), 3.68 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.79, 194.49, 172.98, 159.24, 136.77, 136.44, 133.56, 133.44, 129.75, 128.90, 128.82, 128.79, 128.63, 127.29, 114.31, 61.53, 61.23, 55.31, 51.83, 14.12. The spectroscopic data for this product match the literature data.[1]

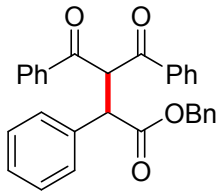


Isobutyl-3-benzoyl-4-oxo-2,4-diphenylbutanoate (3d): 155 mg, yield 75%, white solid, Mp 99.2-101.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.89 (m, 2H), 7.70 – 7.61 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.35

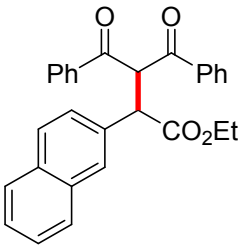
(t, *J* = 7.8 Hz, 2H), 7.29 – 7.25 (m, 4H), 7.15 (t, *J* = 7.3 Hz, 2H), 7.12 – 7.07 (m, 1H), 6.12 (d, *J* = 11.2 Hz, 1H), 4.83 (d, *J* = 11.2 Hz, 1H), 3.86 (qd, *J* = 10.6, 6.7 Hz, 2H), 1.95 – 1.73 (m, 1H), 0.79 (dd, *J* = 6.7, 3.3 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)δ 194.63, 194.26, 172.82, 136.72, 136.45, 135.45, 133.55, 133.46, 128.90, 128.86, 128.79, 128.67, 128.60, 127.94, 71.53, 60.84, 52.72, 27.79, 19.00, 18.97. HRMS (EI) calcd for $C_{27}H_{26}O_4$ $[M+H]^+$: 415.1909; Found: 415.1884.



Allyl-3-benzoyl-4-oxo-2,4-diphenylbutanoate (3e): 153 mg, yield 77%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.88 (m, 2H), 7.70 – 7.60 (m, 2H), 7.54 – 7.46 (m, 1H), 7.45 – 7.39 (m, 1H), 7.38 – 7.31 (m, 2H), 7.27 – 7.25 (m, 4H), 7.22 – 7.13 (m, 2H), 7.13 – 7.07 (m, 1H), 6.10 (d, *J* = 11.2 Hz, 1H), 5.88 – 5.72 (m, 1H), 5.27 – 5.16 (m, 1H), 5.16 – 5.10 (m, 1H), 4.85 (d, *J* = 11.2 Hz, 1H), 4.65 – 4.51 (m, 2H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)δ 194.61, 194.28, 172.48, 136.68, 136.37, 135.14, 133.62, 133.50, 131.83, 128.94, 128.92, 128.81, 128.80, 128.71, 128.62, 128.05, 118.27, 66.02, 60.95, 52.57.The spectroscopic data for this product match the literature data.[1]

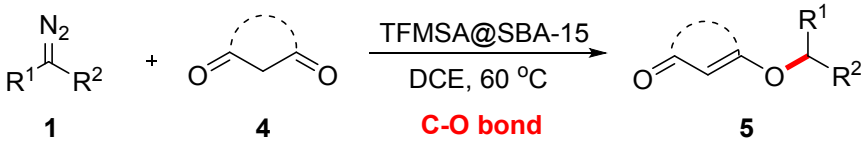


Benzyl-3-benzoyl-4-oxo-2,4-diphenylbutanoate (3f): 166 mg, yield 74%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 2H), 7.67 (d, *J* = 7.2 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.30 – 7.22 (m, 7H), 7.20 – 7.09 (m, 5H), 6.13 (d, *J* = 11.2 Hz, 1H), 5.17 (d, *J* = 12.5 Hz, 1H), 5.11 (d, *J* = 12.5 Hz, 1H), 4.92 (d, *J* = 11.2 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 194.55, 194.20, 172.53, 136.68, 136.37, 135.71, 135.04, 133.57, 133.47, 128.89, 128.78, 128.77, 128.73, 128.59, 128.47, 128.12, 128.00, 127.88, 127.30, 67.09, 60.92, 52.63.The spectroscopic data for this product match the literature data.[1]



Ethyl-3-benzoyl-2-(naphthalen-2-yl)-4-oxo-4-phenylbutanoate (3g): 142 mg, yield 65%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 7.57 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.48 (m, 1H), 7.45 – 7.35 (m, 5H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 7.05 (t, *J* = 7.1 Hz, 2H), 6.34 (d, *J* = 11.9 Hz, 1H), 5.66 (d, *J* = 11.9 Hz, 1H), 4.23 – 4.01 (m, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 194.81, 194.46, 173.28, 136.56, 136.33, 134.03, 133.49, 133.11, 131.73, 128.84, 128.81, 128.69, 128.41, 128.15, 127.31, 126.70, 125.85, 125.17, 123.71, 61.71, 60.77, 14.05. The spectroscopic data for this product match the literature data.[1]

6. Synthesis and analytical data of compounds 5

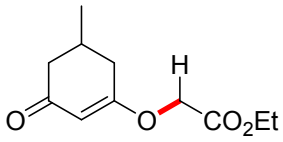


1 **4** **5**

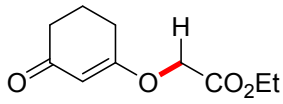
A typical general procedure for the synthesis of 5 (with **5a** as an example): A mixture of ethyl 2-diazoacetate **1b** (69 µL, 0.5 mmol), 5-methylcyclohexane-1,3-dione **4a** (187 mg, 1.5 mmol) and TFMSA@SBA-15 (10 mg) in DCE (3 mL) was stirred at 60 °C for 4 h. After **1b** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/EtOAc, 10:1) to afford the corresponding **5a** as a colorless oil (100 mg, 95%).

1-gram scale reaction for 5a: A mixture of ethyl 2-diazoacetate **1b** (1 g, 8.76 mmol), 5-methylcyclohexane-1,3-dione **4a** (3.3 g, 26.3 mmol) and TFMSA@SBA-15 (175 mg) in DCE (20 mL) was stirred at 60 °C for 10 h. After **1b** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash

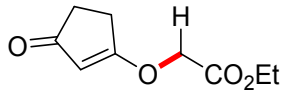
chromatography (petroleum ether (60-90 °C)/EtOAc, 10:1) to afford the corresponding **5a** as a colorless oil (1.68 g, 90%).



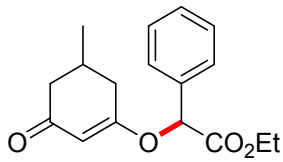
Ethyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)acetate (5a): 100 mg, yield 95%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (s, 1H), 4.43 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.57 – 2.44 (m, 1H), 2.43 – 2.34 (m, 1H), 2.27 – 2.16 (m, 2H), 2.07 – 1.94 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 3H), 1.05 (d, *J* = 6.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.59, 176.27, 166.98, 102.99, 64.82, 61.77, 44.99, 36.73, 28.75, 20.82, 14.13. HRMS (EI) calcd for $C_{11}H_{16}O_4$ $[M+H]^+$: 213.1127; Found: 213.1110



Ethyl-2-((3-oxocyclohex-1-en-1-yl)oxy)acetate (5b): 94 mg, yield 95%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (s, 1H), 4.45 (s, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 2.50 (t, *J* = 6.2 Hz, 2H), 2.37 – 2.30 (m, 2H), 2.08 – 1.91 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.56, 176.80, 167.08, 103.51, 64.81, 61.85, 36.77, 28.73, 21.15, 14.20. The spectroscopic data for this product match the literature data.[2]

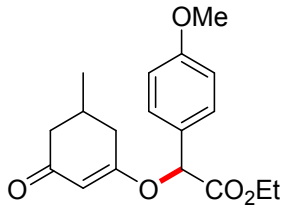


Ethyl-2-((3-oxocyclopent-1-en-1-yl)oxy)acetate (5c): 78 mg, yield 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 – 5.16 (m, 1H), 4.55 (d, *J* = 4.9 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.73 – 2.64 (m, 2H), 2.49 – 2.40 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 205.59, 189.24, 166.67, 105.65, 67.69, 61.95, 34.35, 28.28, 14.15. The spectroscopic data for this product match the literature data.[2]

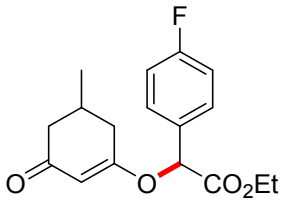


Ethyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)-2-phenylacetate (5d): 115 mg,

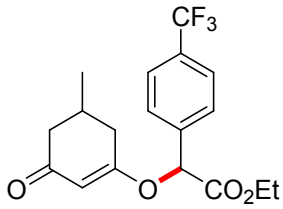
yield 80%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 2H), 7.43 – 7.35 (m, 3H), 5.43 (d, *J* = 7.7 Hz, 1H), 5.28 (d, *J* = 4.7 Hz, 1H), 4.27 – 4.08 (m, 2H), 2.69 – 2.50 (m, 1H), 2.46 – 2.17 (m, 3H), 2.11 – 1.95 (m, 1H), 1.20 (td, *J* = 7.1, 1.9 Hz, 3H), 1.07 (t, *J* = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.63, 175.74, 168.31, 133.95, 129.53, 129.01, 127.22, 103.98, 78.32, 62.15, 45.10, 37.09, 28.83, 20.93, 14.06. HRMS (EI) calcd for $C_{17}H_{20}O_4$ [M+H]$^+$: 289.1440; Found: 289.1424.



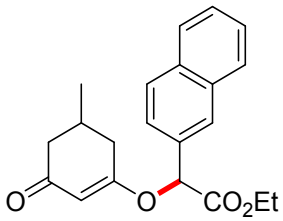
Ethyl-2-(4-methoxyphenyl)-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)acetate (5e): 140 mg, yield 86%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.33 (m, 2H), 7.00 – 6.81 (m, 2H), 5.38 (d, *J* = 7.6 Hz, 1H), 5.27 (dd, *J* = 4.8, 1.1 Hz, 1H), 4.28 – 4.06 (m, 2H), 3.81 (s, 3H), 2.67 – 2.48 (m, 1H), 2.45 – 2.16 (m, 3H), 2.11 – 1.95 (m, 1H), 1.20 (td, *J* = 7.1, 2.1 Hz, 3H), 1.10 – 1.05 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 172.45, 146.01, 137.70, 129.38, 129.02, 128.46, 127.39, 118.27, 113.54, 60.86, 52.97. HRMS (EI) calcd for $C_{18}H_{22}O_5$ [M+H]$^+$: 319.1545; Found: 319.1521.



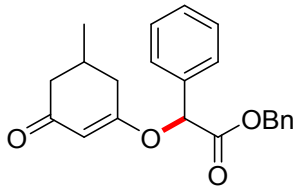
Ethyl-2-(4-fluorophenyl)-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)acetate (5f): 135 mg, yield 88%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 2H), 7.20 – 6.92 (m, 2H), 5.41 (d, *J* = 7.6 Hz, 1H), 5.26 (dd, *J* = 4.1, 1.2 Hz, 1H), 4.32 – 4.02 (m, 2H), 2.70 – 2.48 (m, 1H), 2.47 – 2.16 (m, 3H), 2.11 – 1.96 (m, 1H), 1.20 (td, *J* = 7.1, 2.1 Hz, 3H), 1.10 – 1.06 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.42, 175.43, 168.20, 163.39 (d, *J* = 248.9 Hz), 129.95, 129.21, 129.12, 116.08 (d, *J* = 21.9 Hz), 104.03, 77.61, 62.25, 45.12, 37.08, 28.84, 20.91, 14.06. HRMS (EI) calcd for $C_{17}H_{19}FO_4$ [M+H]$^+$: 307.1346; Found: 307.1327.



Ethyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)-2-(4-(trifluoromethyl)phenyl)acetate (5g): 169 mg, yield 95%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.45 (m, 4H), 5.49 (d, *J* = 7.2 Hz, 1H), 5.37 – 5.16 (m, 1H), 4.35 – 4.05 (m, 2H), 2.71 – 2.51 (m, 1H), 2.49 – 2.18 (m, 3H), 2.12 – 1.97 (m, 1H), 1.22 (td, *J* = 7.1, 2.1 Hz, 3H), 1.10 (t, *J* = 6.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.34, 175.19, 167.69, 137.86, 131.72 (q, *J* = 32.7 Hz) , 127.50, 126.03 (q, *J* = 3.8 Hz), 121.37 (q, *J* =268.9 Hz), 104.22, 77.60, 62.55, 45.12, 37.03, 28.85, 20.92, 14.07. HRMS (EI) calcd for $C_{18}H_{19}F_3O_4$ [M+H]$^+$: 357.1314; Found: 357.1295.

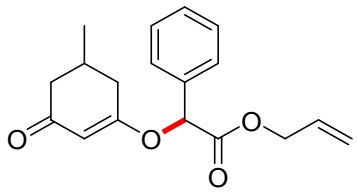


Ethyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)-2-(naphthalen-2-yl)acetate (5h): 83 mg, yield 49%, light yellow. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 – 8.09 (m, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.69 – 7.61 (m, 1H), 7.61 – 7.42 (m, 3H), 6.14 (d, *J* = 9.9 Hz, 1H), 5.40 (d, *J* = 2.4 Hz, 1H), 4.31 – 4.06 (m, 2H), 2.70 – 2.50 (m, 1H), 2.48 – 2.17 (m, 3H), 2.15 – 1.97 (m, 1H), 1.16 (td, *J* = 7.1, 1.8 Hz, 3H), 1.08 (dd, *J* = 8.5, 6.5 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 199.67, 175.83, 168.47, 134.09, 130.79, 130.39, 129.95, 129.10, 127.17, 126.71, 126.32, 125.40, 123.52, 103.99, 76.43, 62.29, 45.17, 37.19, 28.86, 20.95, 14.09. HRMS (EI) calcd for $C_{21}H_{22}O_4$ [M+H]$^+$: 339.1596; Found: 339.1572.

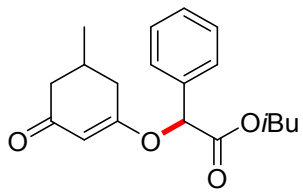


Benzyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)-2-phenylacetate (5i): 150 mg, yield 86%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 1H), 7.41 –

7.35 (m, 3H), 7.34 – 7.26 (m, 3H), 7.23 – 7.13 (m, 2H), 5.51 (d, *J* = 7.1 Hz, 1H), 5.33 – 5.25 (m, 1H), 5.21 – 5.08 (m, 2H), 2.68 – 2.48 (m, 1H), 2.44 – 2.13 (m, 3H), 2.09 – 1.95 (m, 1H), 1.07 (dd, *J* = 6.3, 1.5 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.33, 175.43, 168.14, 134.90, 133.75, 129.54, 128.99, 128.64, 128.56, 128.14, 127.22, 104.09, 78.24, 67.58, 45.07, 37.02, 28.73, 20.88. HRMS (EI) calcd for $C_{22}H_{22}O_4$ $[M+H]^+$: 351.1596; Found: 351.1575.

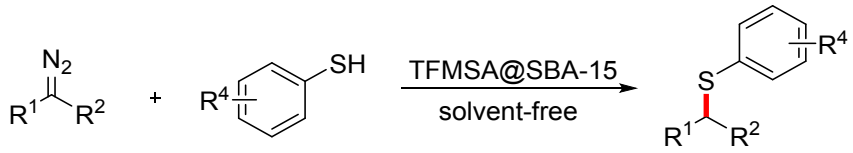


Allyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)-2-phenylacetate (5j): 134 mg, yield 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.43 (m, 2H), 7.43 – 7.34 (m, 3H), 5.86 – 5.72 (m, 1H), 5.48 (d, *J* = 7.0 Hz, 1H), 5.32 – 5.25 (m, 1H), 5.23 – 5.12 (m, 2H), 4.67 – 4.53 (m, 2H), 2.68 – 2.50 (m, 1H), 2.48 – 2.14 (m, 3H), 2.11 – 1.95 (m, 1H), 1.11 – 1.04 (m, 3H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.43, 175.51, 167.98, 133.89, 131.08, 129.58, 129.03, 127.24, 119.15, 104.04, 78.23, 66.38, 45.11, 37.07, 28.80, 20.90. HRMS (EI) calcd for $C_{18}H_{20}O_4$ $[M+H]^+$: 301.1440; Found: 301.1421.



Isobutyl-2-((5-methyl-3-oxocyclohex-1-en-1-yl)oxy)-2-phenylacetate (5k): 127 mg, yield 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.41 (m, 2H), 7.41 – 7.29 (m, 3H), 5.45 (d, *J* = 6.9 Hz, 1H), 5.35 – 5.18 (m, 1H), 4.01 – 3.76 (m, 2H), 2.68 – 2.48 (m, 1H), 2.44 – 2.14 (m, 3H), 2.08 – 1.96 (m, 1H), 1.90 – 1.79 (m, 1H), 1.11 – 1.02 (m, 3H), 0.80 (dd, *J* = 6.7, 2.5 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 199.33, 175.49, 168.29, 134.10, 129.43, 128.91, 127.10, 103.96, 78.27, 71.81, 45.07, 37.03, 28.75, 27.69, 20.86, 18.85. HRMS (EI) calcd for $C_{19}H_{24}O_4$ $[M+H]^+$: 317.1753; Found: 317.1734.

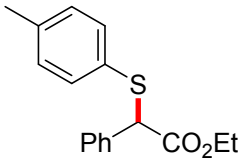
7. Synthesis and analytical data of compounds 7



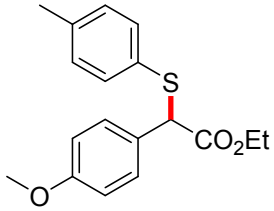
1 **6** **C-S bond** **7**

A typical general procedure for the synthesis of 7 (with **7a** as an example): A mixture of ethyl 2-diazo-2-phenylacetate **1a** (96 mg, 0.5 mmol), 4-methylbenzenethiol **6a** (186 mg, 1.5 mmol) and TFMSA@SBA-15 (10 mg) was stirred at room temperature for 5 min. After **1a** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 ^{o}C)/EtOAc, 100:1) to afford the corresponding **7a** as a colorless oil (122 mg, 85%).

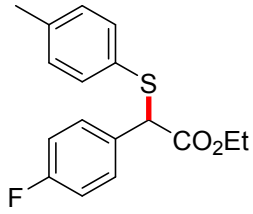
1-gram scale reaction for 7a: A mixture of ethyl 2-diazo-2-phenylacetate **1a** (1 g, 5.2 mmol), 4-methylbenzenethiol **6a** (1.9 g, 15.6 mmol) and TFMSA@SBA-15 (104 mg) was stirred at room temperature for 1 h. After **1a** was completely consumed by TLC monitoring on silica gel, the resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 ^{o}C)/EtOAc, 100:1) to afford the corresponding **7a** as a colorless oil (1.19 g, 80%).



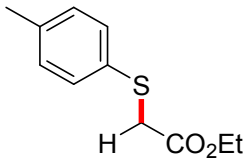
Ethyl-2-phenyl-2-(p-tolylthio)acetate (7a): 122 mg, yield 85%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 2H), 7.35 – 7.26 (m, 5H), 7.07 (d, *J* = 7.9 Hz, 2H), 4.83 (s, 1H), 4.22 – 4.03 (m, 2H), 2.31 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.66, 168.39, 138.45, 136.01, 133.47, 130.18, 129.84, 128.74, 128.69, 128.32, 61.79, 56.95, 21.29, 14.14. The spectroscopic data for this product match the literature.[3]



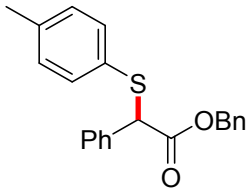
Ethyl-2-(4-methoxyphenyl)-2-(p-tolylthio)acetate (7b): 130 mg, yield 82%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.7 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.82 (s, 1H), 4.21 – 4.00 (m, 2H), 3.79 (s, 3H), 2.32 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.80, 159.57, 138.28, 133.33, 130.22, 129.81, 129.77, 127.82, 114.07, 61.64, 56.15, 55.34, 21.24, 14.09. HRMS (EI) calcd for $C_{18}H_{20}O_3S$ $[M+H]^+$: 317.1211; Found: 317.1210.



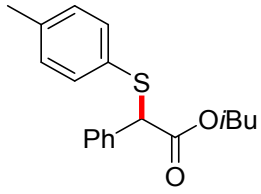
Ethyl-2-(4-fluorophenyl)-2-(p-tolylthio)acetate (7c): 119 mg, yield 78%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.35 (m, 2H), 7.29 – 7.26 (m, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 7.05 – 6.95 (m, 2H), 4.81 (s, 1H), 4.26 – 4.04 (m, 2H), 2.32 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.48, 162.68 (d, *J* = 247.3 Hz), 138.69, 133.72, 131.88, 131.85, 130.48, 130.39, 129.88, 129.72, 115.61 (d, *J* = 21.6 Hz), 61.85, 56.09, 21.28, 14.10. The spectroscopic data for this product match the literature.[3]



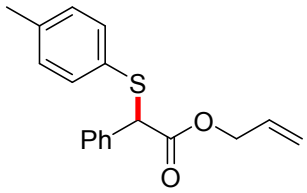
Ethyl-2-(p-tolylthio)acetate (7d): 74 mg, yield 70%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.58 (s, 2H), 2.32 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.90, 137.40, 131.30, 131.06, 129.88, 61.51, 37.53, 21.14, 14.18. The spectroscopic data for this product match the literature.[4]



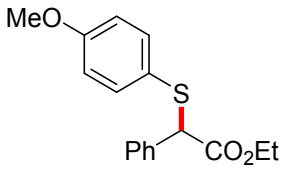
Benzyl-2-phenyl-2-(p-tolylthio)acetate (7e): 122 mg, yield 70%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.36 (m, 2H), 7.31 – 7.26 (m, 5H), 7.26 – 7.19 (m, 3H), 7.19 – 7.09 (m, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.01 (d, *J* = 12.3 Hz, 1H), 4.86 (s, 1H), 2.27 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.55, 138.49, 135.69, 135.50, 133.54, 130.00, 129.88, 128.76, 128.73, 128.58, 128.40, 128.35, 128.27, 67.38, 56.84, 21.29. HRMS (EI) calcd for $C_{22}H_{20}O_2S$ $[M+H]^+$: 349.1262; Found: 349.1238.



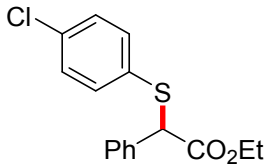
Isobutyl-2-phenyl-2-(p-tolylthio)acetate (7f): 113 mg, yield 72%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.40 (m, 2H), 7.35 – 7.27 (m, 5H), 7.07 (d, *J* = 7.9 Hz, 2H), 4.86 (s, 1H), 3.85 (d, *J* = 6.6 Hz, 2H), 2.31 (s, 3H), 0.83 (d, *J* = 6.7 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.71, 138.39, 136.07, 133.28, 130.25, 129.87, 128.72, 128.69, 128.32, 71.81, 57.11, 27.79, 21.29, 19.05. HRMS (EI) calcd for $C_{19}H_{22}O_2S$ $[M+H]^+$: 315.1419; Found: 315.1399.



Allyl-2-phenyl-2-(p-tolylthio)acetate (7g): 97 mg, yield 65%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.40 (m, 2H), 7.37 – 7.26 (m, 5H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.85 – 5.73 (m, 1H), 5.25 – 5.13 (m, 2H), 4.86 (s, 1H), 4.66 – 4.46 (m, 2H), 2.31 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.35, 138.56, 135.83, 133.57, 131.68, 130.01, 129.88, 128.77, 128.71, 128.40, 118.67, 66.24, 56.94, 21.31. The spectroscopic data for this product match the literature.[3]

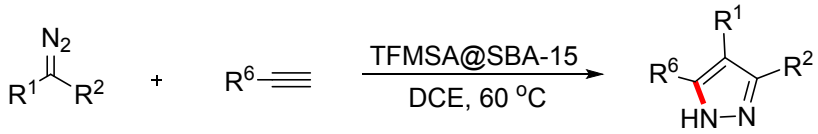


Ethyl-2-((4-methoxyphenyl)thio)-2-phenylacetate (7h): 116 mg, yield 77%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.36 – 7.27 (m, 5H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.74 (s, 1H), 4.20 – 4.03 (m, 2H), 3.78 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.69, 160.34, 136.33, 136.06, 128.75, 128.69, 128.27, 123.95, 114.60, 61.72, 57.58, 55.46, 14.17. The spectroscopic data for this product match the literature.[5]



Ethyl 2-((4-chlorophenyl)thio)-2-phenylacetate (7i): 115 mg, yield 75%, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.36 – 7.27 (m,5H), 7.24 – 7.21 (m, 2H), 4.87 (s, 1H), 4.27 – 4.00 (m, 2H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.20, 135.47, 134.40, 134.31, 132.23, 129.17, 128.80, 128.61, 128.49, 61.92, 56.55, 14.09. The spectroscopic data for this product match the literature.[6]

5. Synthesis and analytical data of compounds 9

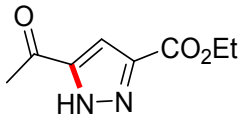


1 **8** **C-N bond** **9**

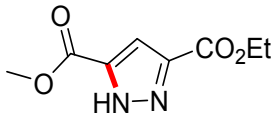
A typical general procedure for the synthesis of 9 (with **9a** as an example): A mixture of ethyl 2-diazoacetate **1b** (69 µL, 0.55 mmol), but-3-yn-2-one **8a** (39 µL, 0.5 mmol) and TFMSA@SBA-15 (10 mg) in DCE (3 mL) was stirred at 60 °C for 8 h. The resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 ºC)/EtOAc, 5:1) to afford the corresponding **9a** as a white solid (80 mg, 88%).

1-gram scale reaction for 9a: A mixture of ethyl 2-diazoacetate **1b** (1.9 mL, 16.2

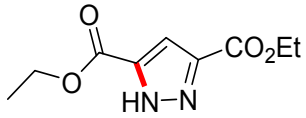
mmol), but-3-yn-2-one **8a** (1 g, 14.7 mmol) and TFMSA@SBA-15 (294 mg) in DCE (10 mL) was stirred at 60 °C for 15 h. The resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 °C)/EtOAc, 5:1) to afford the corresponding **9a** as a white solid (2.22 g, 83%).



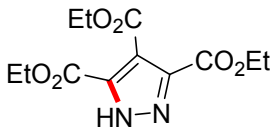
Ethyl-5-acetyl-1H-pyrazole-3-carboxylate (9a): 80 mg, yield 88%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.32 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.61 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 191.78, 160.47, 139.65, 110.15, 61.91, 26.93, 14.29. The spectroscopic data for this product match the literature data.[7]



3-ethyl-5-methyl 1H-pyrazole-3,5-dicarboxylate (9b): 68 mg, yield 68%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.44 (s, 1H), 7.32 (s, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.42, 160.33, 136.62, 136.30, 111.46, 61.81, 52.55, 14.25. The spectroscopic data for this product match the literature data.[7]

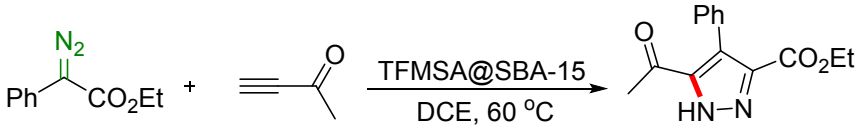


Diethyl-1H-pyrazole-3,5-dicarboxylate (9c): 67 mg, yield 63%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.08 (s, 1H), 7.33 (s, 1H), 4.41 (q, *J* = 7.1 Hz, 4H), 1.39 (t, *J* = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.72, 132.17, 111.41, 61.80, 14.32. The spectroscopic data for this product match the literature data.[7]



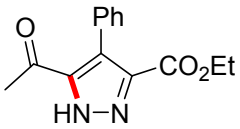
Triethyl-1H-pyrazole-3,4,5-tricarboxylate (9d): 132 mg, yield 93%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.62 (s, 1H), 4.43 – 4.31 (m, 6H), 1.40 – 1.27 (m, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 163.34, 159.34, 138.60, 119.72, 62.20, 62.10, 14.09,

14.05.The spectroscopic data for this product match the literature data.[7]

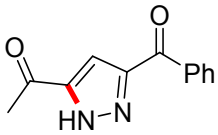


1a **8a** **9e**

A typical procedure for the synthesis of 9e: A mixture of ethyl 2-diazo-2-phenylacetate **1a** (105 mg, 0.55 mmol), but-3-yn-2-one **8a** (39 µL, 0.5 mmol) and TFMSA@SBA-15 (10 mg) in DCE (3 mL) was stirred at 60 °C for 8 h. The resultant mixture was cooled to ambient temperature and evaporated all the volatiles under reduced pressure. The residue was purified by flash chromatography (petroleum ether (60-90 ºC)/EtOAc, 5:1) to afford the corresponding **9e** as a white solid (90 mg, 70%).



Ethyl-5-acetyl-4-phenyl-1H-pyrazole-3-carboxylate (9e): 90 mg, yield 70%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.74 (s, 1H), 7.62 – 7.53 (m, 2H), 7.48 – 7.41 (m, 3H), 4.32 (q, *J* = 7.1 Hz, 2H), 2.63 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 186.68, 164.42, 141.22, 129.81, 128.98, 128.13, 112.63, 61.74, 27.88, 14.00. The spectroscopic data for this product match the literature data.[8]



1-(3-benzoyl-1H-pyrazol-5-yl)ethan-1-one (9f): 68 mg, yield 74%, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 1H), 8.08 (d, *J* = 7.7 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.40 (s, 1H), 2.66 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 192.43, 185.43, 136.44, 133.80, 129.84, 128.86, 110.97, 26.92. The spectroscopic data for this product match the literature data.[9]

8. X-Ray crystallographic studies

Single crystals of compounds **3a** were grown in petroleum ether (60-90 °C)/CH_2Cl_2

(v/v, 3/1) at 20 °C and their X-ray diffraction studies were carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1917691 for **3a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

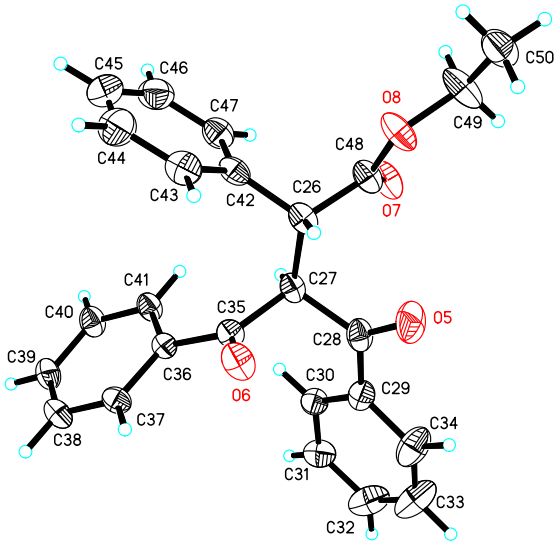


Figure S2. ***ORTEP*** diagram of compound **3a**.

Table S5. Crystal data and structure refinement for **3a**.

Identification code	mo_dd19032_0m
Empirical formula	$C_{25}H_{22}O_4$
Formula weight	386.42
Temperature	193(2) K

Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.7065(5) Å	a= 78.2880(10)°.
	b = 12.0739(5) Å	b= 83.3010(10)°.
	c = 17.4608(8) Å	g= 70.1950(10)°.
Volume	2076.61(16) $Å^3$	
Z	4	
Density (calculated)	1.236 Mg/m^3	
Absorption coefficient	0.083 mm^{-1}	
F(000)	816	
Crystal size	0.200 x 0.170 x 0.130 mm^3	
Theta range for data collection	2.332 to 25.499°.	
Index ranges	-12<=h<=12, -14<=k<=14, -21<=l<=21	
Reflections collected	39159	
Independent reflections	7692 [R(int) = 0.0378]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6502	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7692 / 1 / 526	
Goodness-of-fit on F^2	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0485, wR2 = 0.1130	
R indices (all data)	R1 = 0.0630, wR2 = 0.1239	
Extinction coefficient	0.027(2)	
Largest diff. peak and hole	0.530 and -0.229 $e.Å^{-3}$	

Single crystals of compounds **5d** were grown in petroleum ether (60-90 °C)/CH_2Cl_2 (v/v, 3/1) at 20 °C and their X-ray diffraction studies were carried out on a SMART APEX diffractometer with graphite-monochromated Mo radiation (λ = 0.71073 Å). Cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the SHELXL-97 package. The X-ray crystallographic files, in CIF format, are available from the Cambridge Crystallographic Data Centre on quoting the deposition numbers CCDC 1917690 for **5d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 IEZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

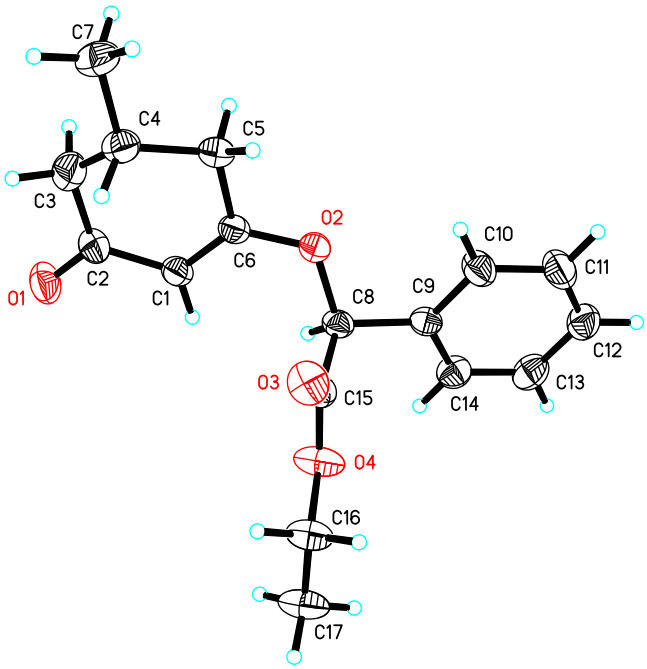
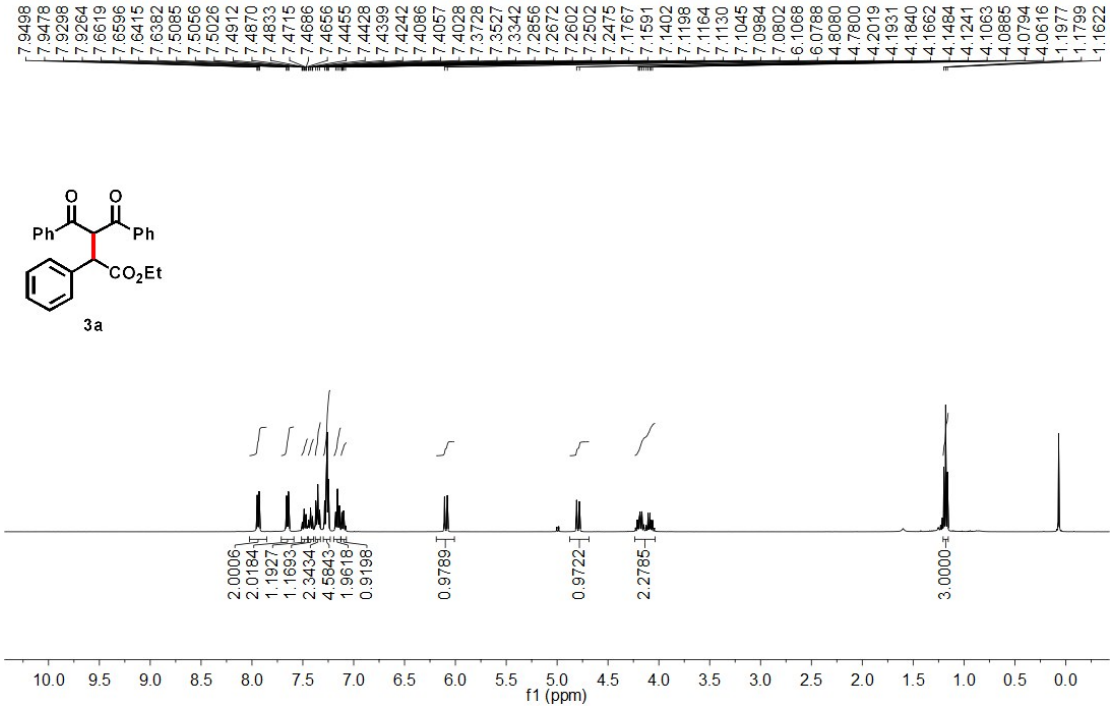


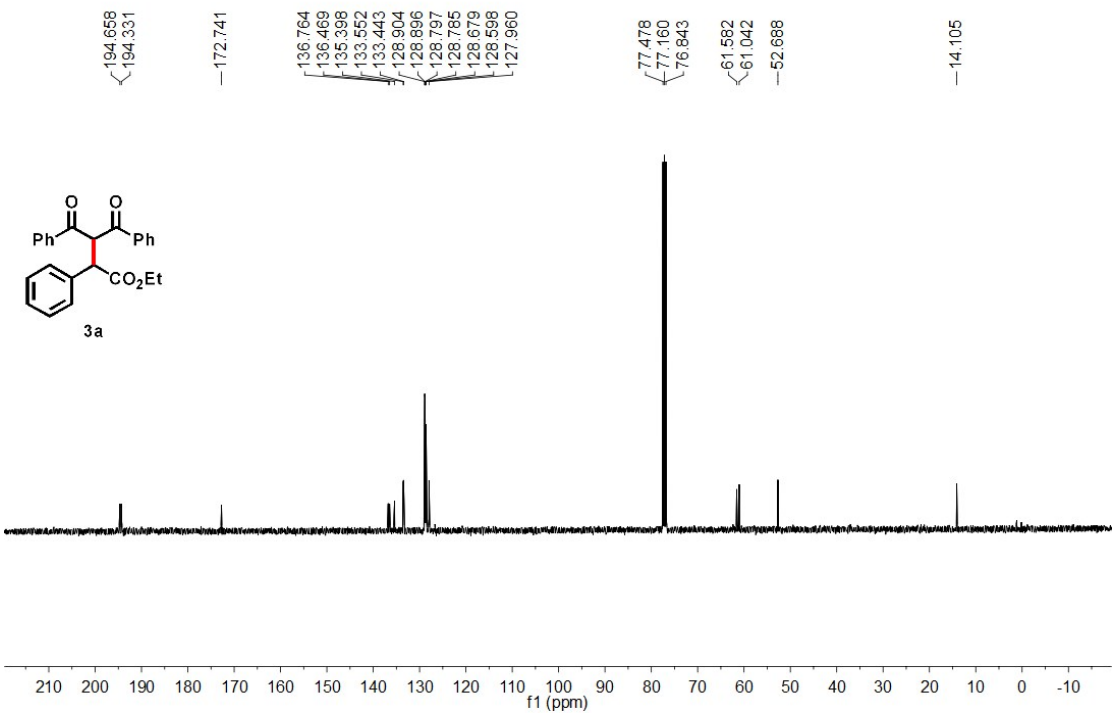
Figure S3. ***ORTEP*** diagram of compound **5d**.

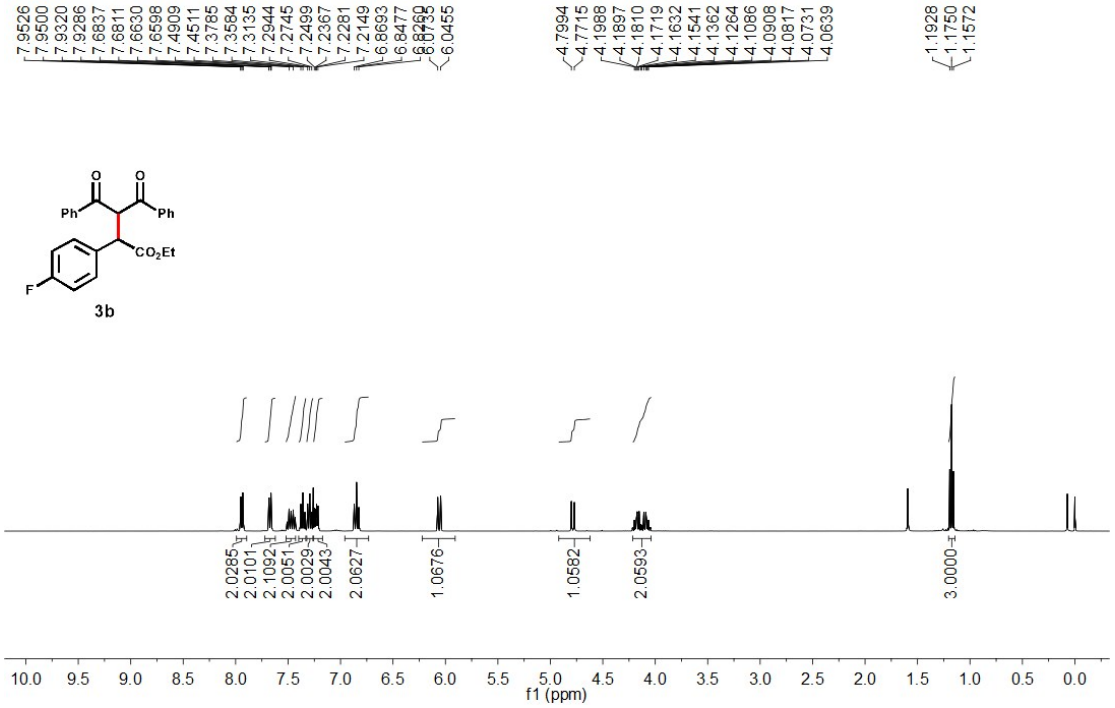
Table S6. Crystal data and structure refinement for **5d**.

Identification code	mo_dd19034_0m	
Empirical formula	$C_{17}H_{20}O_4$	
Formula weight	288.33	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.2804(4) Å	a= 90°.
	b = 8.1597(3) Å	b= 90.4030(10)°.
	c = 23.4123(9) Å	g = 90°.
Volume	1581.83(11) $Å^3$	
Z	4	
Density (calculated)	1.211 Mg/m^3	
Absorption coefficient	0.085 mm^{-1}	
F(000)	616	
Crystal size	0.200 x 0.160 x 0.140 mm^3	
Theta range for data collection	2.643 to 24.996°.	
Index ranges	-9<=h<=9, -9<=k<=9, -27<=l<=25	
Reflections collected	23273	
Independent reflections	2765 [R(int) = 0.0748]	
Completeness to theta = 25.242°	96.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4933	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2765 / 82 / 231	
Goodness-of-fit on F^2	1.054	
Final R indices [I>2sigma(I)]	R1 = 0.0580, wR2 = 0.1491	
R indices (all data)	R1 = 0.0696, wR2 = 0.1606	
Extinction coefficient	0.034(9)	
Largest diff. peak and hole	0.394 and -0.204 $e.Å^{-3}$	

9. Copies of NMR spectra



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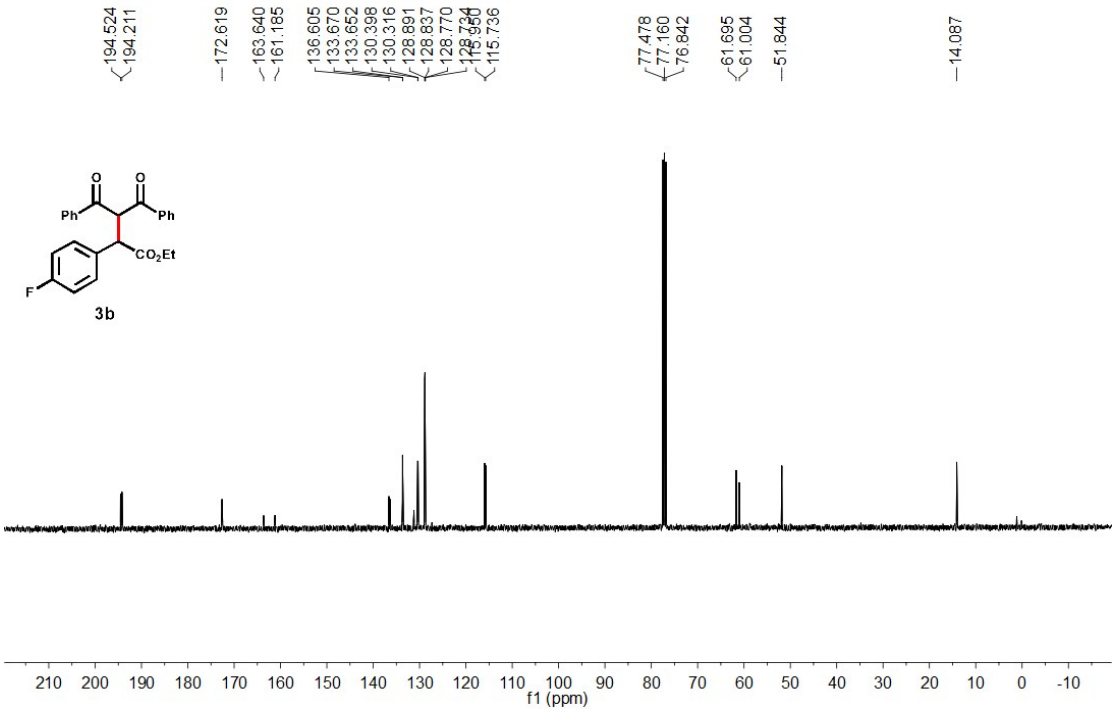
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115.736
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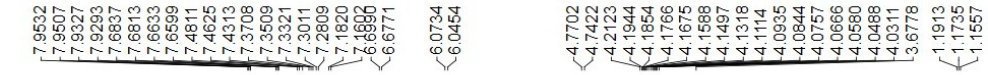
77.160
76.842
61.695
61.004
51.844
14.087
Ph
Ph
CO2Et
F
3b
f1 (ppm)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7.4313
7.3708
7.3509
7.3321
7.3011
7.2809
7.1820
7.1802
6.6990
6.6771
6.0734
6.0454
4.7702
4.7422
4.2123
4.1944
4.1854
4.1766
4.1675
4.1588
4.1497
4.1318
4.1114
4.0935
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4.0757
4.0666
4.0580
4.0488
4.0311
3.6778
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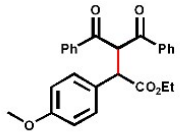
1.1735
1.1557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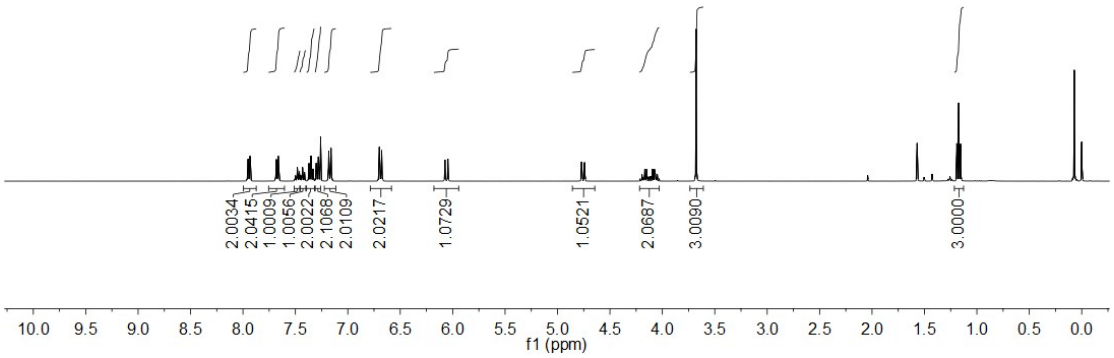
O
Ph
Ph
CO2Et
O

3c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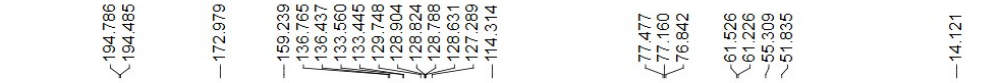
2.0415
1.0009
1.0056
2.0022
2.1068
2.0109
2.0217
1.0729
1.0521
2.0687
3.0090
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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172.979
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136.437
133.560
133.445
129.748
128.904
128.824
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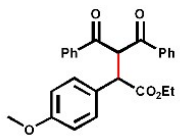
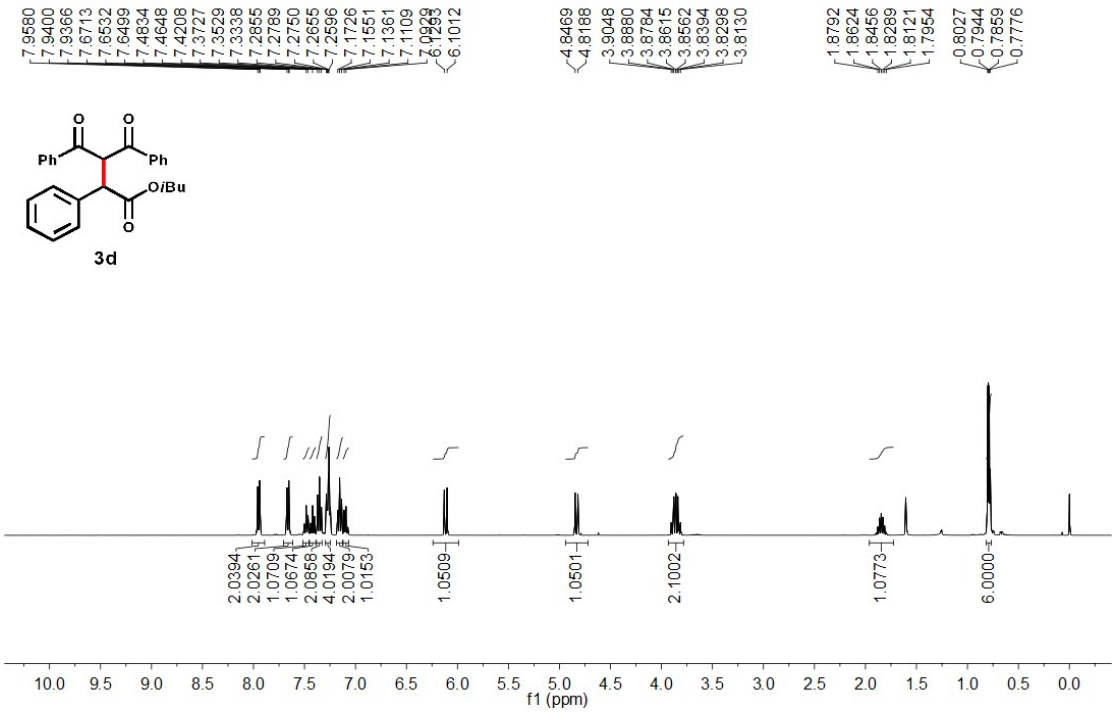
128.631
127.289
114.314
77.477
77.160
76.842
61.526
61.226
55.309
51.835
14.121


O
O
Ph
Ph
CO2Et
O

3c

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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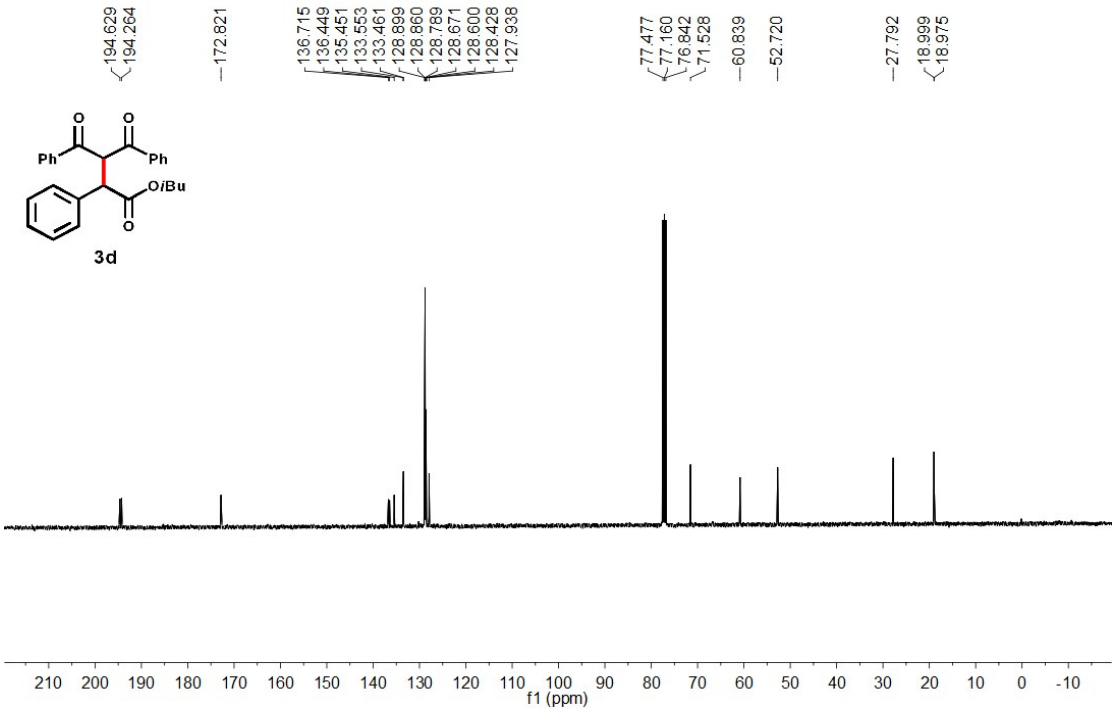
7.4208
7.3727
7.3529
7.3338
7.2855
7.2789
7.2750
7.2655
7.2596
7.1726
7.1551
7.1361
7.1109
6.1293
6.1012
4.8469
4.8188
3.9048
3.8880
3.8784
3.8615
3.8562
3.8394
3.8298
3.8130
1.8792
1.8624
1.8456
1.8289
1.8121
1.7954
0.8027
0.7944
0.7859
0.7776
Ph
Ph
O
O
O
O
OiBu
3d
2.0394
2.0261
1.0709
1.0674
2.0858
4.0194
2.0079
1.0153
1.0509
1.0501
2.1002
1.0773
6.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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133.461
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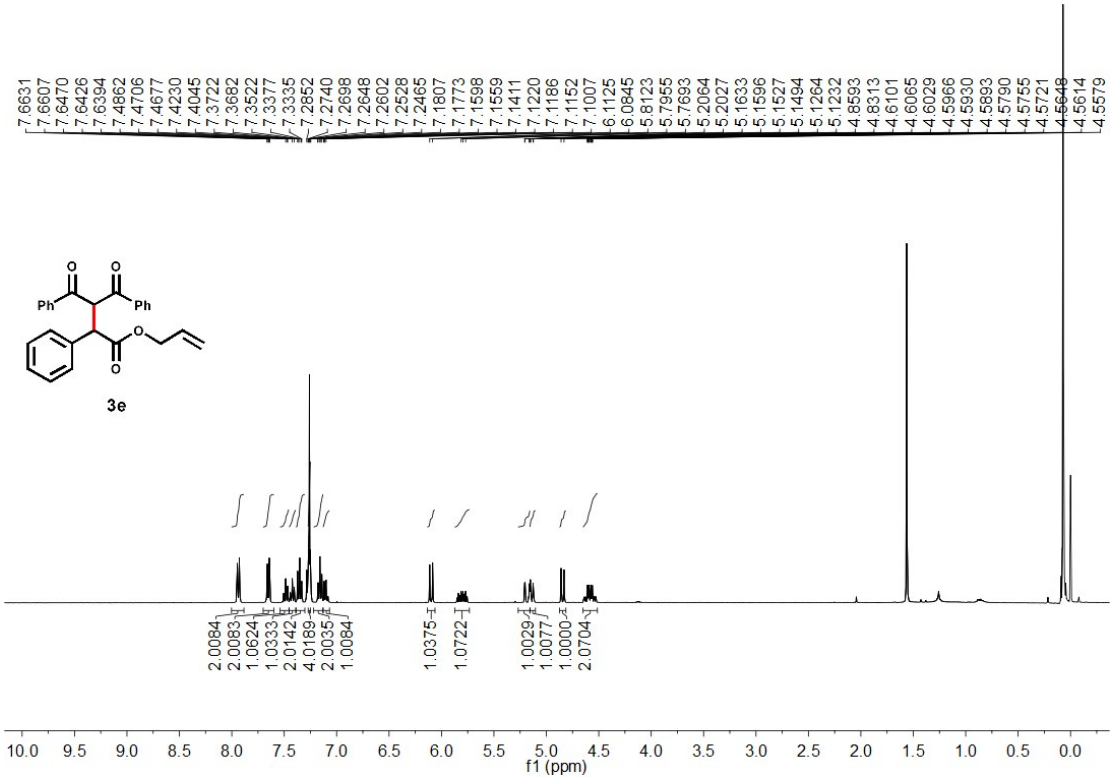
128.860
128.789
128.671
128.600
128.428
127.938
77.477
77.160
76.842
71.528
60.839
52.720
27.792
18.999
18.975
Ph
Ph
O
O
O
O
OiBu
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.6426
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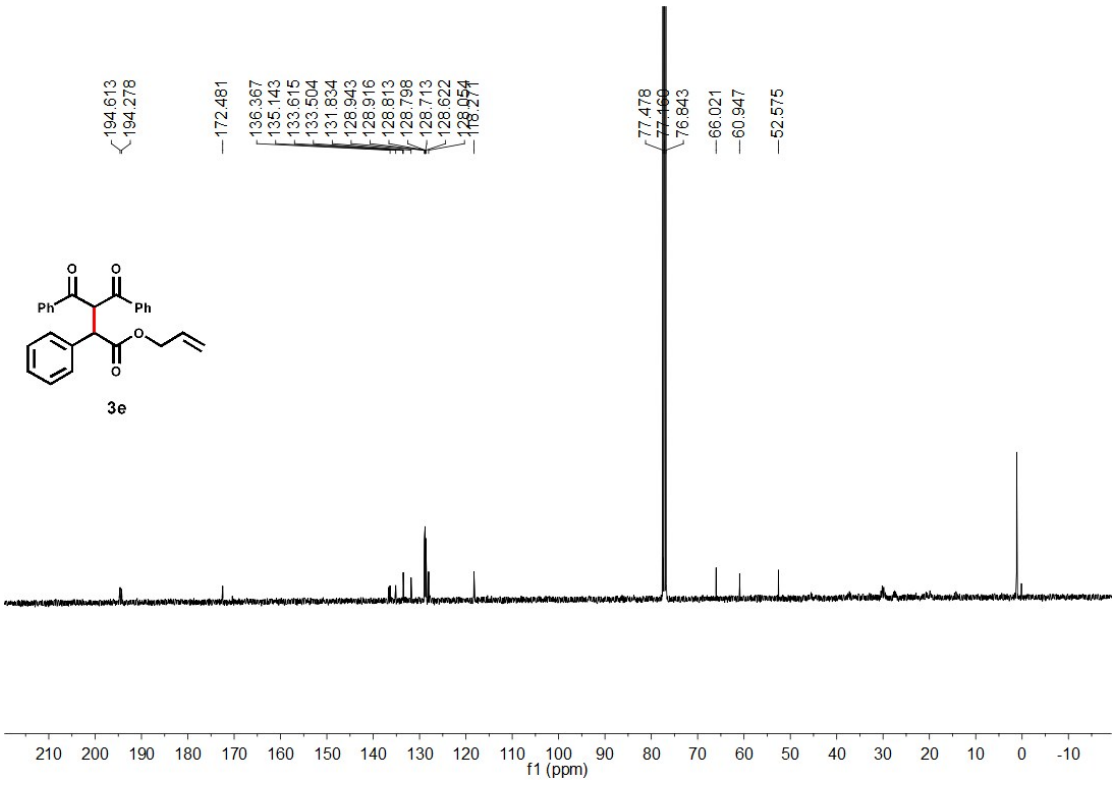
7.4045
7.3722
7.3682
7.3522
7.3377
7.3335
7.2852
7.2740
7.2698
7.2648
7.2602
7.2528
7.2465
7.1807
7.1773
7.1598
7.1559
7.1411
7.1220
7.1186
7.1152
7.1007
6.1125
6.0845
5.8123
5.7955
5.7693
5.2064
5.2027
5.1633
5.1596
5.1527
5.1494
5.1264
5.1232
4.8593
4.8313
4.6101
4.6065
4.6029
4.5966
4.5930
4.5893
4.5790
4.5755
4.5721
4.5648
4.5614
4.5579
Ph
Ph
O
O
O
O
3e
2.0084
2.0083
1.0624
1.0333
2.0142
4.0189
2.0035
1.0084
1.0375
1.0722
1.0029
1.0077
1.0000
2.0704
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.813
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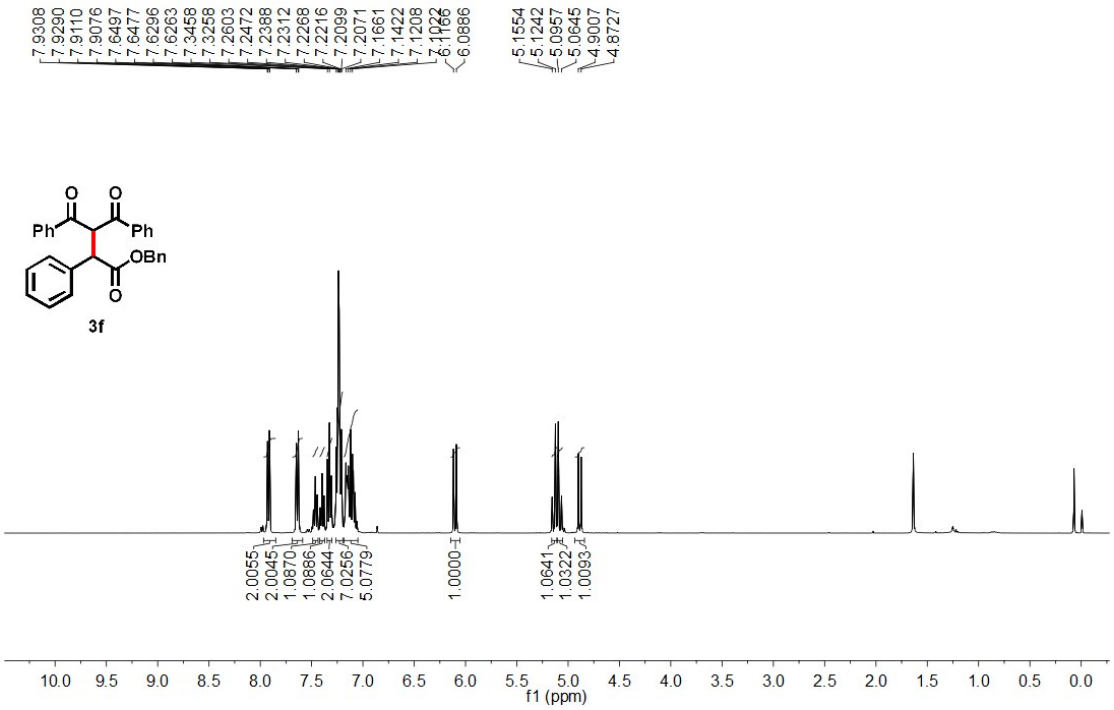
128.713
128.622
128.054
118.271
77.478
77.160
76.843
66.021
60.947
52.575
Ph
Ph
O
O
O
O
3e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.9290
7.9110
7.9076
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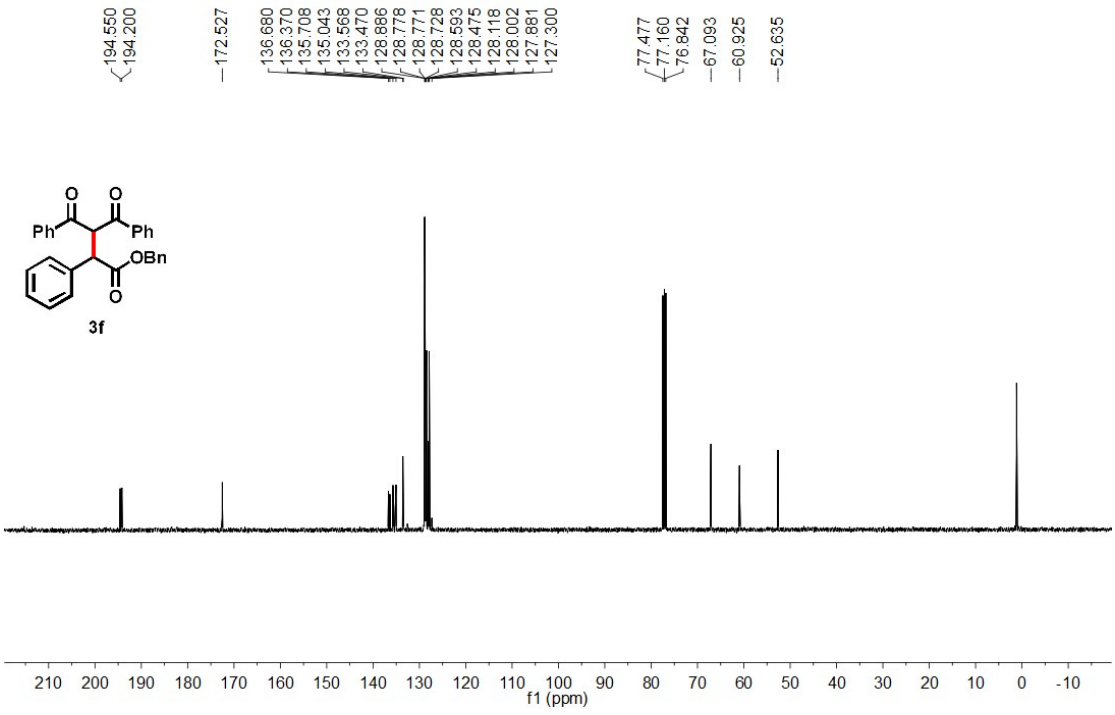
7.6477
7.6296
7.6263
7.3458
7.3258
7.2603
7.2472
7.2388
7.2312
7.2268
7.2216
7.2099
7.2071
7.1661
7.1422
7.1208
7.1022
6.1166
6.0886
5.1554
5.1242
5.0957
5.0645
4.9007
4.8727
Ph
O
O
Ph
OBn
O
3f
2.0055
2.0045
1.0870
1.0886
2.0644
7.0256
5.0779
1.0000
1.0641
1.0322
1.0093
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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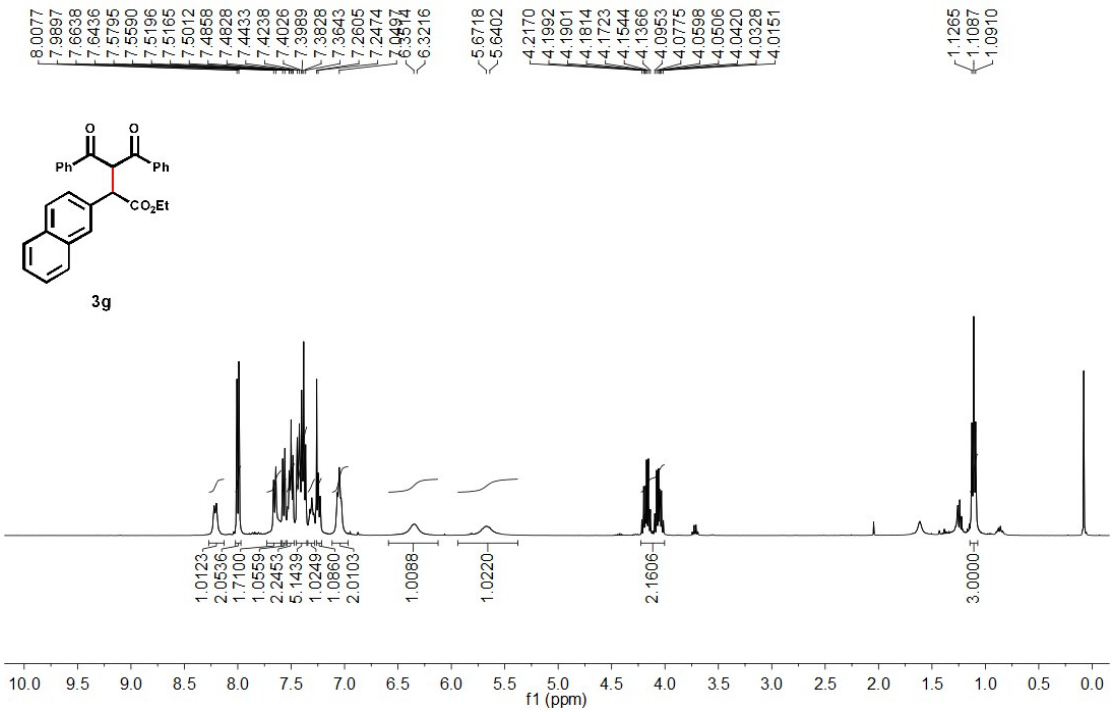
128.771
128.728
128.593
128.475
128.118
128.002
127.881
127.300
77.477
77.160
76.842
67.093
60.925
52.635
Ph
O
O
Ph
OBn
O
3f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.5590
7.5196
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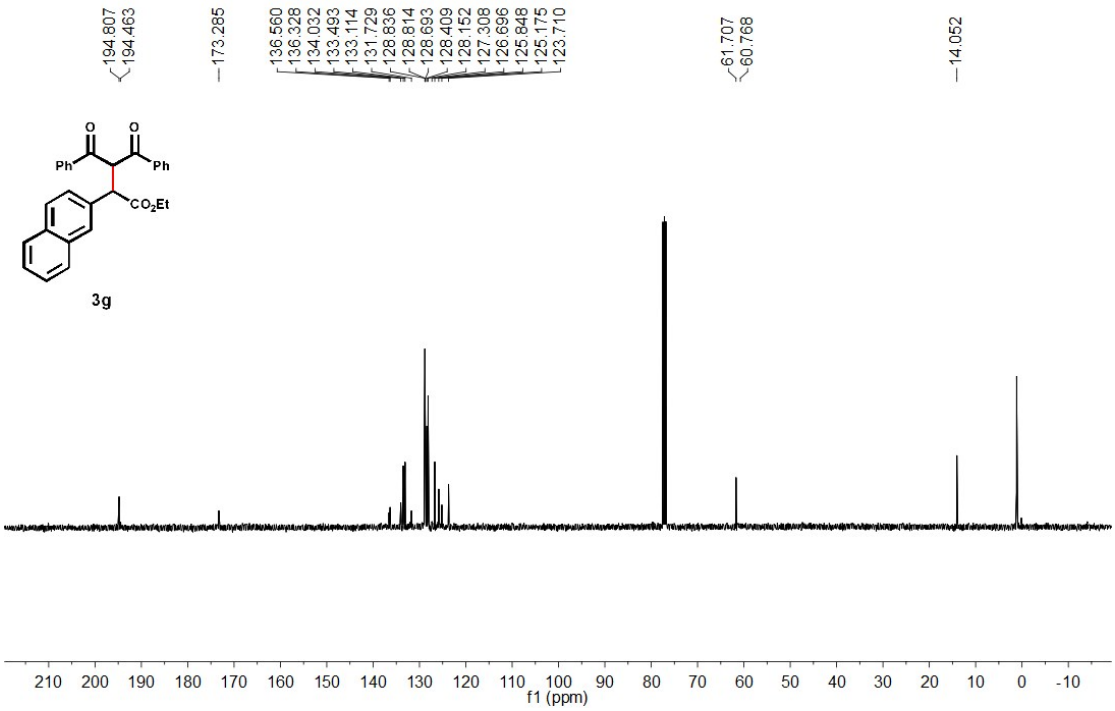
7.5012
7.4858
7.4828
7.4433
7.4238
7.4026
7.3989
7.3828
7.3643
7.2605
7.2474
6.3216
5.6718
5.6402
4.2170
4.1992
4.1901
4.1814
4.1723
4.1544
4.1366
4.0953
4.0775
4.0598
4.0506
4.0420
4.0328
4.0151
1.1265
1.1087
1.0910
Ph
Ph
CO2Et
3g
1.0123
2.0536
1.7100
1.0559
2.2453
5.1439
1.0249
1.0860
2.0103
1.0088
1.0220
2.1606
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.409
128.152
127.308
126.696
125.848
125.175
123.710
61.707
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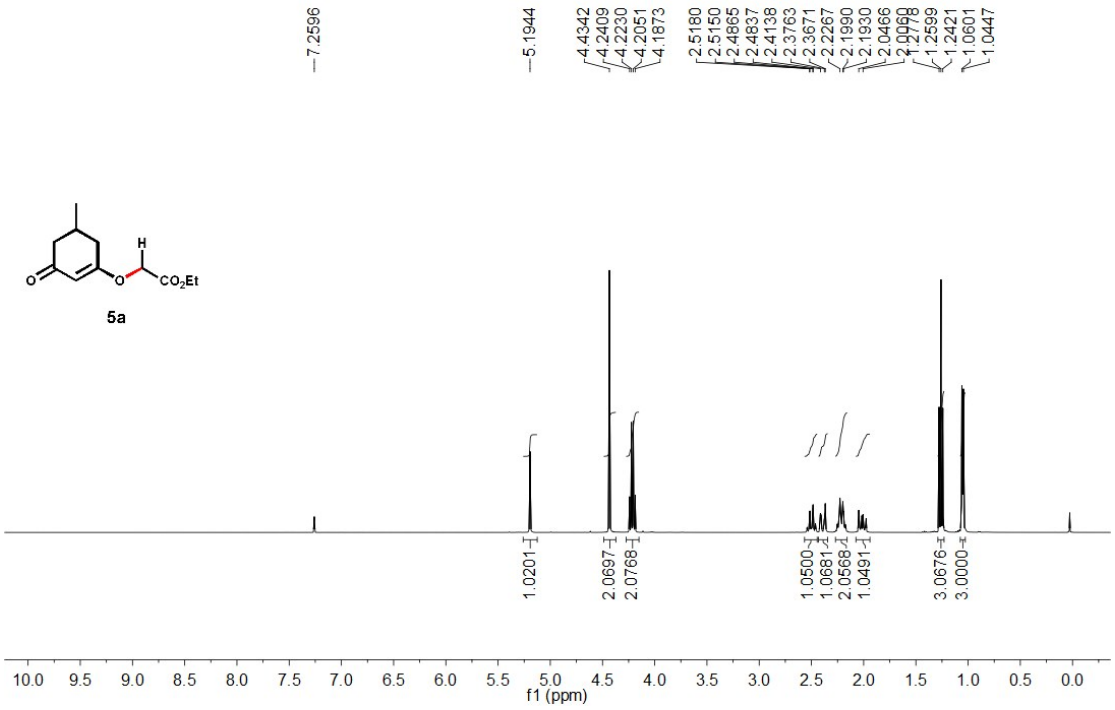
14.052
Ph
Ph
CO2Et
3g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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2.5150
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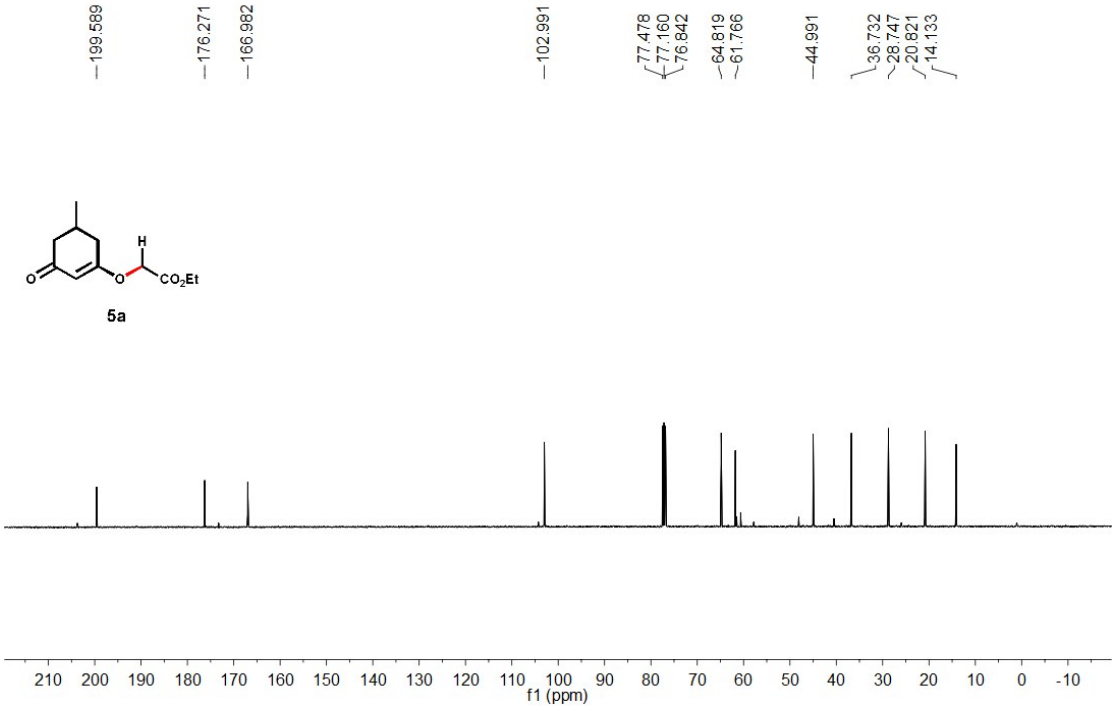
2.4837
2.4138
2.3763
2.3671
2.2267
2.1990
2.1930
2.0466
1.2778
1.2599
1.2421
1.0601
1.0447
1.0201
2.0697
2.0768
1.0500
1.0681
2.0568
1.0491
3.0676
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5a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166.982
102.991
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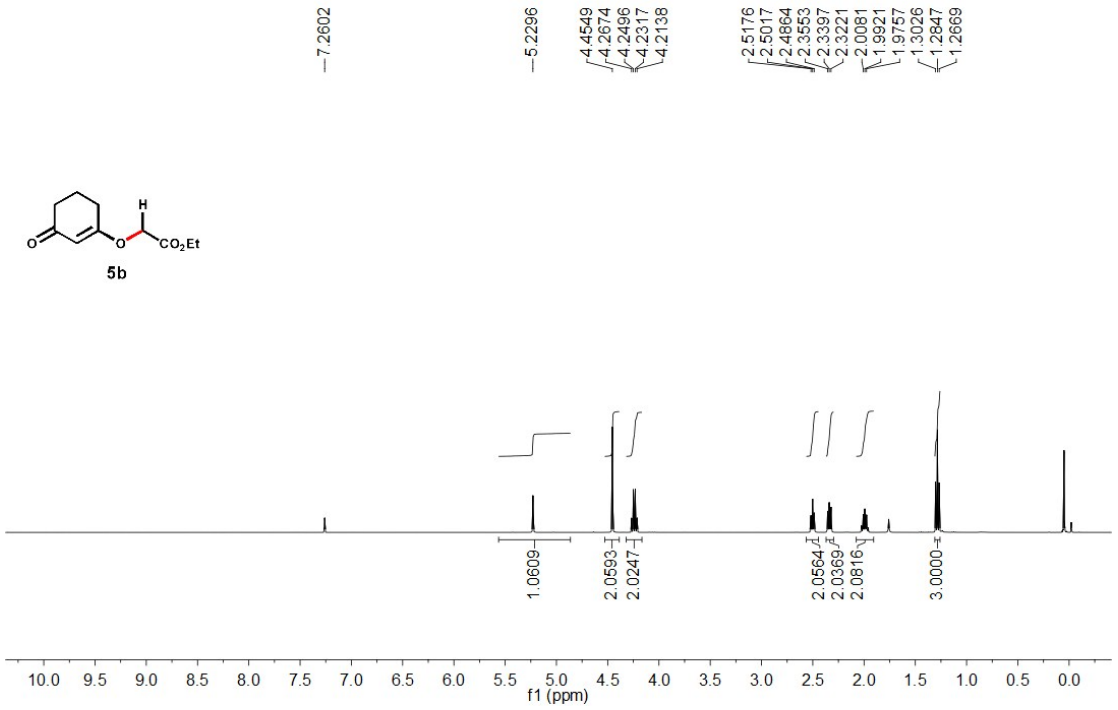
77.160
76.842
64.819
61.766
44.991
36.732
28.747
20.821
14.133
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5a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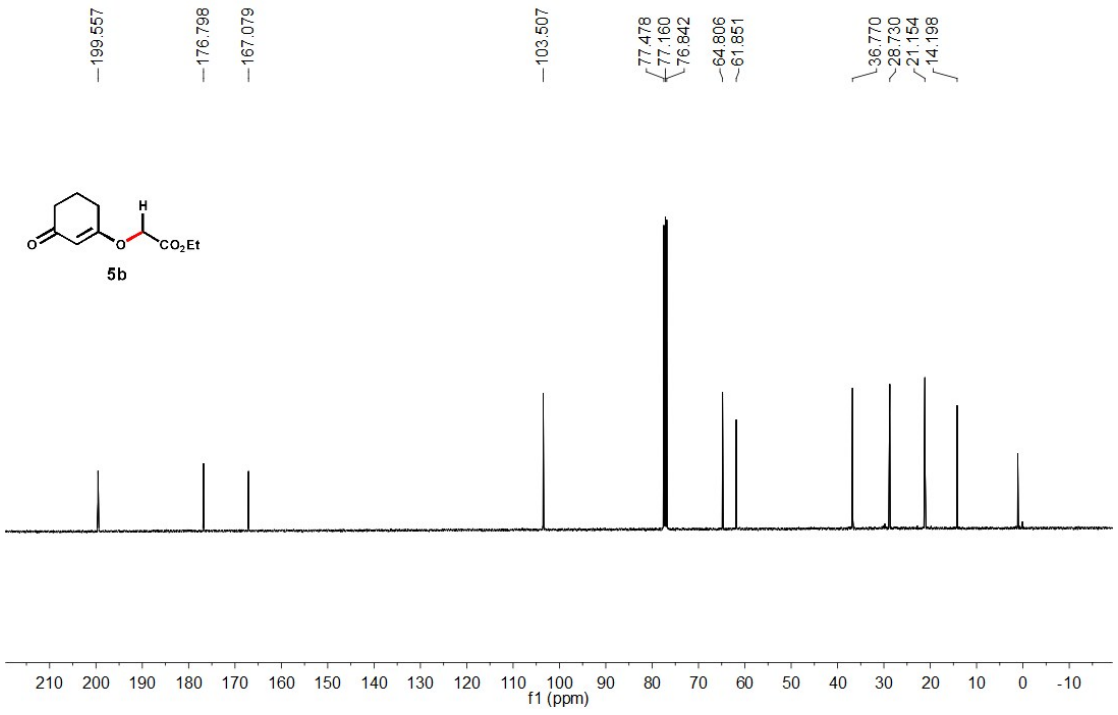
2.5017
2.4864
2.3553
2.3397
2.3221
2.0081
1.9921
1.9757
1.3026
1.2847
1.2669
O
H
O
CO2Et
5b
1.0609
2.0593
2.0247
2.0564
2.0369
2.0816
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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36.770
28.730
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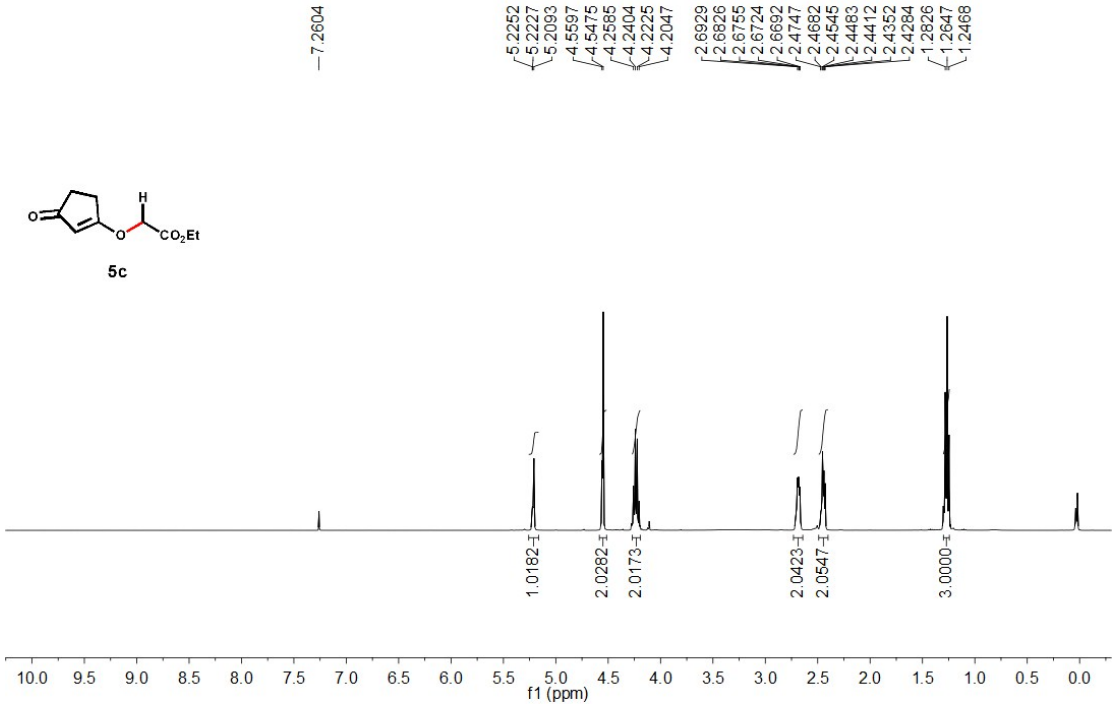
H
O
CO2Et
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.2585
4.2404
4.2225
4.2047
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2.6826
2.6755
2.6724
2.6692
2.4747
2.4682
2.4545
2.4483
2.4412
2.4352
2.4284
1.2826
1.2647
1.2468
O
H
O
CO2Et
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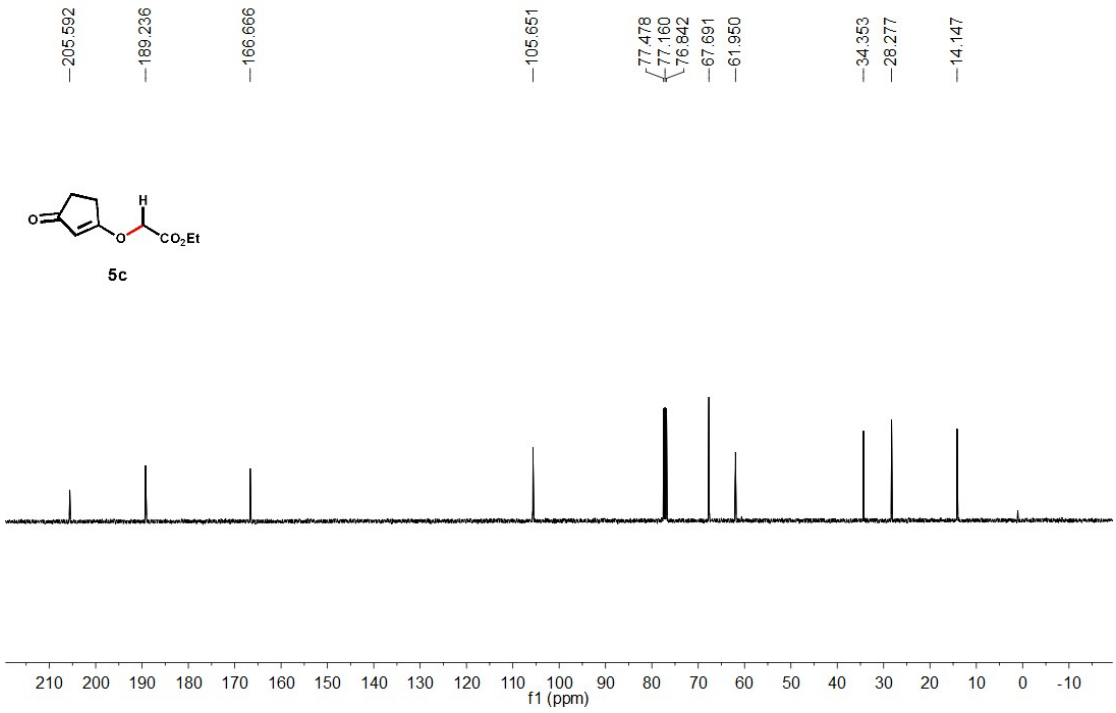
2.0173
2.0423
2.0547
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5c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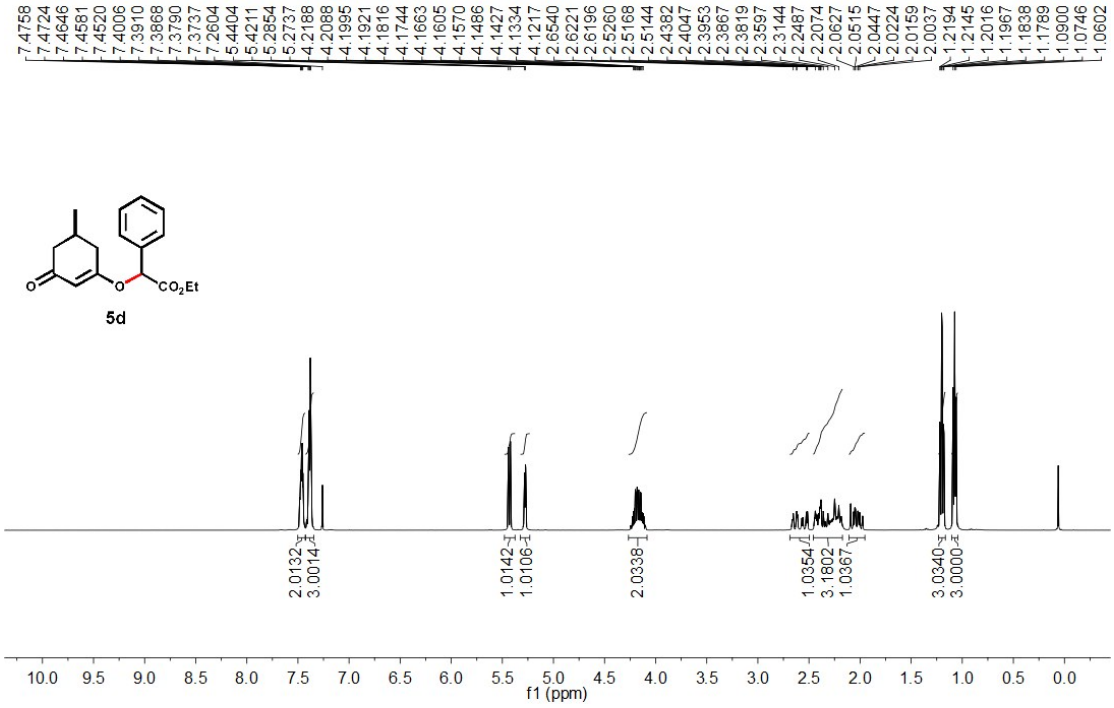
77.160
76.842
67.691
61.950
34.353
28.277
14.147
O
H
O
CO2Et
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5c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5.4404
5.4211
5.2854
5.2737
4.2188
4.2088
4.1995
4.1921
4.1816
4.1744
4.1663
4.1605
4.1570
4.1486
4.1427
4.1334
4.1217
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2.6221
2.6196
2.5260
2.5168
2.5144
2.4382
2.4047
2.3953
2.3867
2.3819
2.3597
2.3144
2.2487
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2.0515
2.0447
2.0224
2.0159
2.0037
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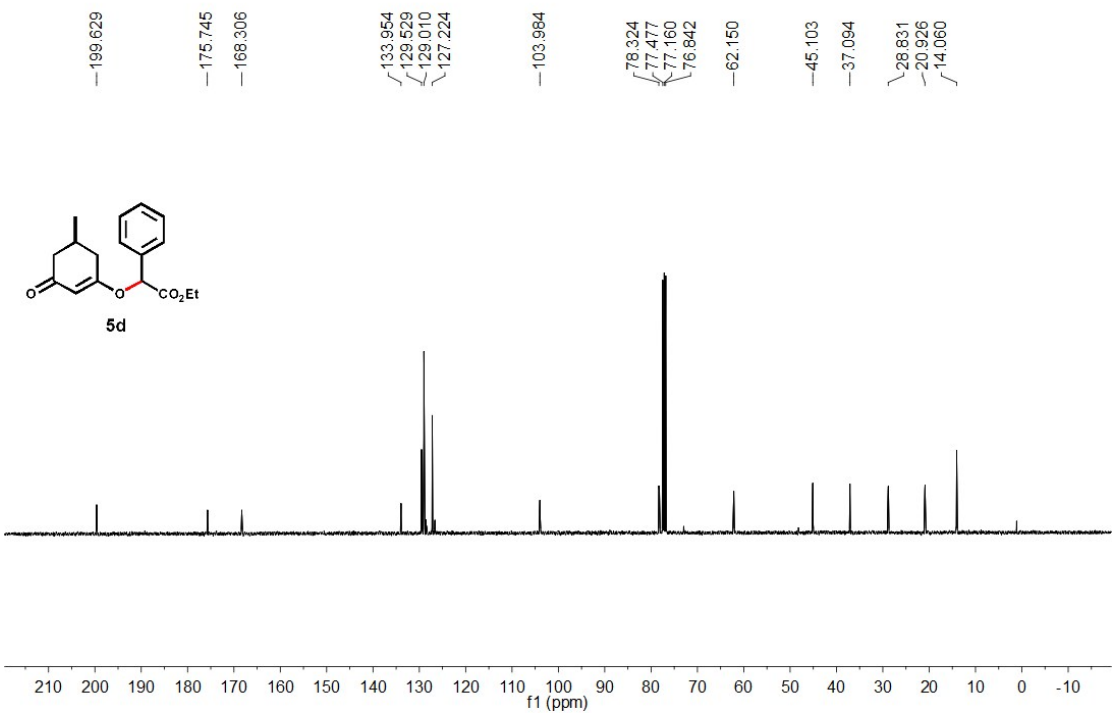
1.2145
1.2016
1.1967
1.1838
1.1789
1.0900
1.0746
1.0602
O
O
CO2Et
5d
2.0132
3.0014
1.0142
1.0106
2.0338
1.0354
3.1802
1.0367
3.0340
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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127.224
103.984
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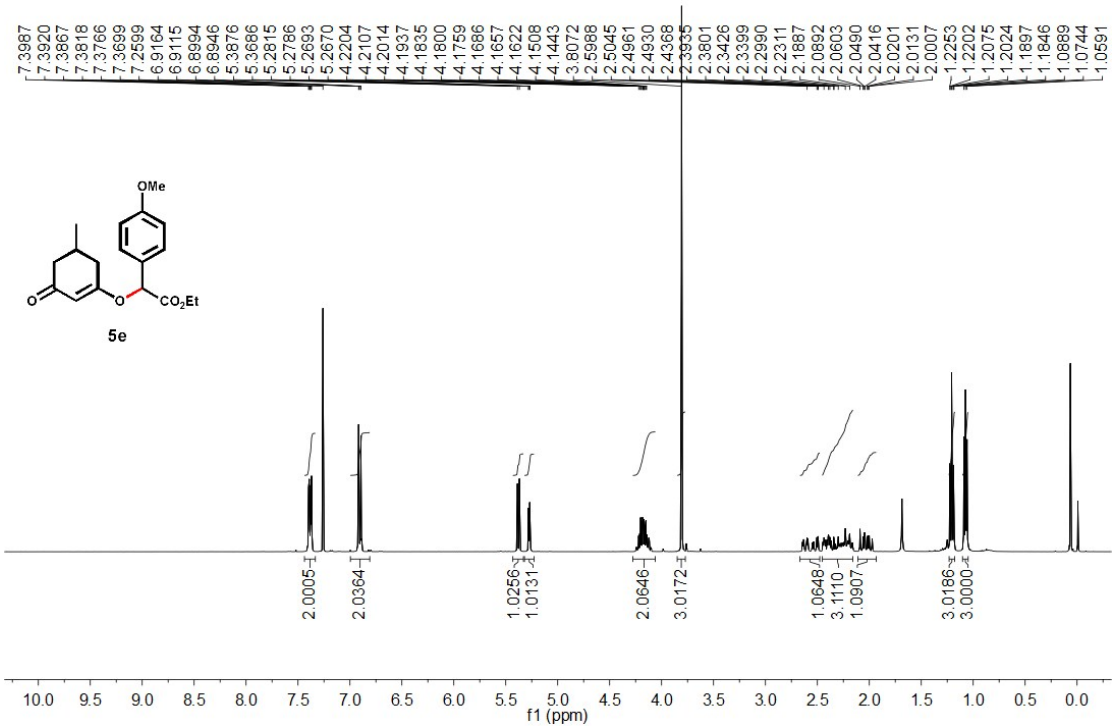
77.477
77.160
76.842
62.150
45.103
37.094
28.831
20.926
14.060
O
O
CO2Et
5d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OMe
O
O
CO2Et
5e
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3.0172
1.0648
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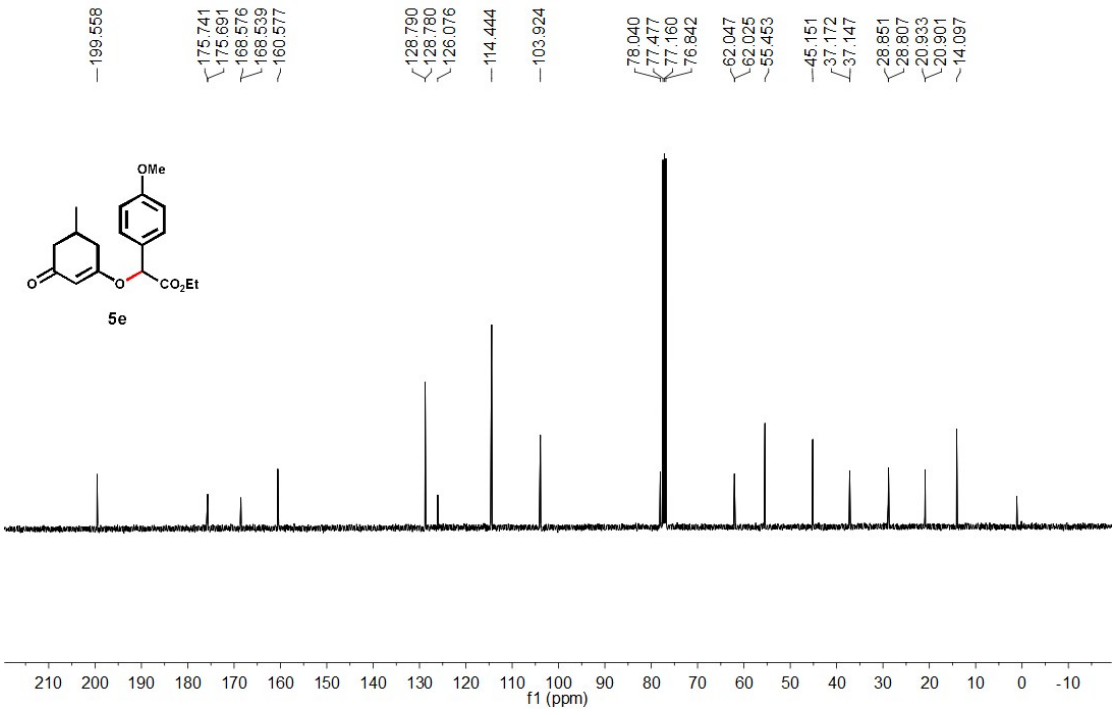
1.0907
3.0186
3.0000
f1 (ppm)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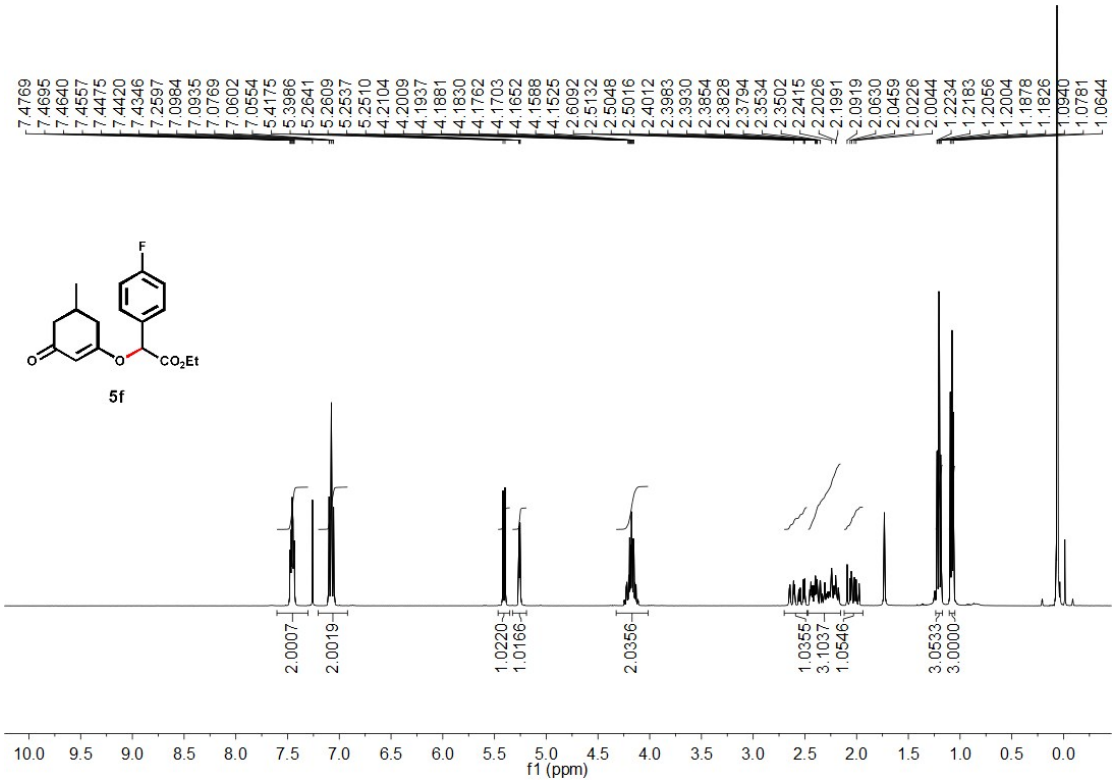
103.924
78.040
77.477
77.160
76.842
62.047
62.025
55.453
45.151
37.172
37.147
28.851
28.807
20.933
20.901
14.097
OMe
O
O
CO2Et
5e
f1 (ppm)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7.0554
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5.2641
5.2609
5.2537
5.2510
4.2104
4.2009
4.1937
4.1881
4.1830
4.1762
4.1703
4.1652
4.1588
4.1525
2.6092
2.5132
2.5048
2.5016
2.4012
2.3983
2.3930
2.3854
2.3828
2.3794
2.3534
2.3502
2.2415
2.2026
2.1991
2.0919
2.0630
2.0459
2.0226
2.0044
1.2234
1.2183
1.2056
1.2004
1.1878
1.1826
1.0940
1.0781
1.0644
F
O
O
CO2Et
5f
2.0007
2.0019
1.0220
1.0166
2.0356
1.0355
3.1037
1.0546
3.0533
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
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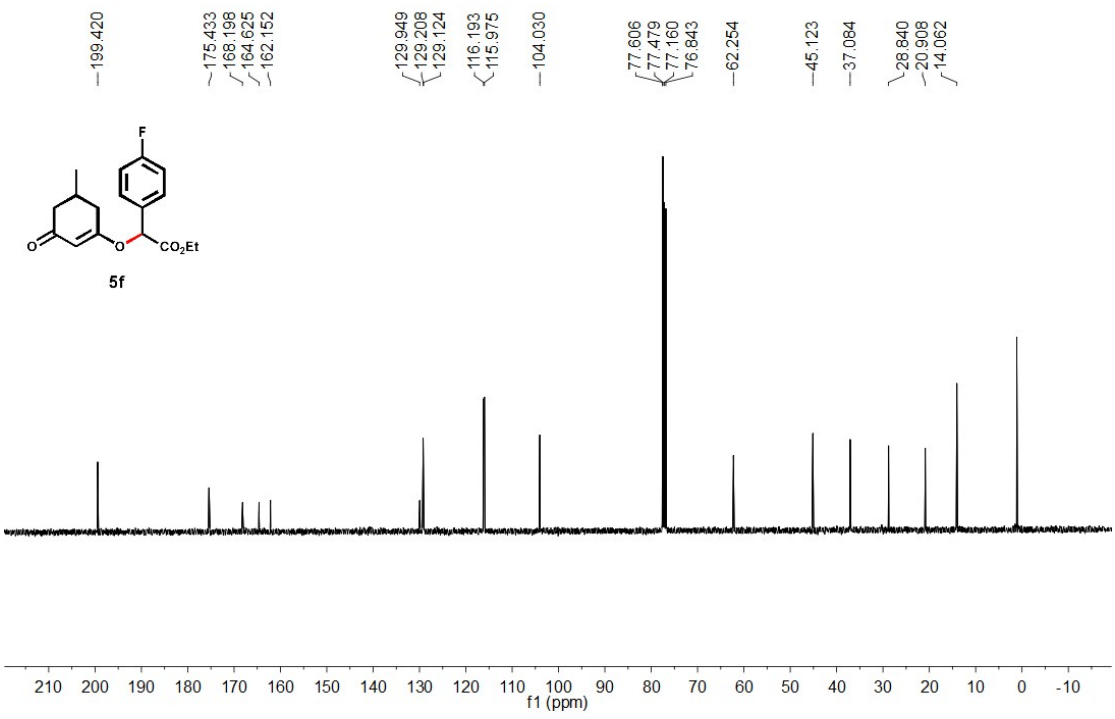
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77.479
77.160
76.843
62.254
45.123
37.084
28.840
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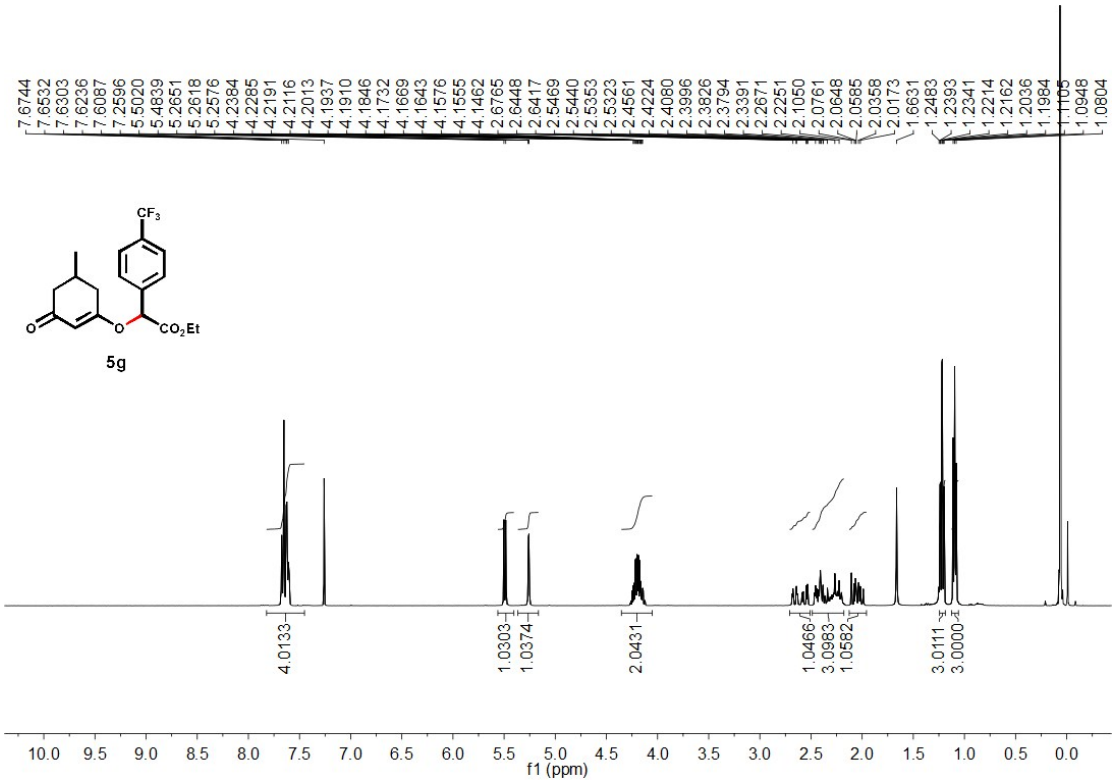
O
O
CO2Et
5f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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4.2384
4.2285
4.2191
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4.2013
4.1937
4.1910
4.1846
4.1732
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4.1643
4.1576
4.1555
4.1462
2.6765
2.6448
2.6417
2.5469
2.5440
2.5353
2.5323
2.4561
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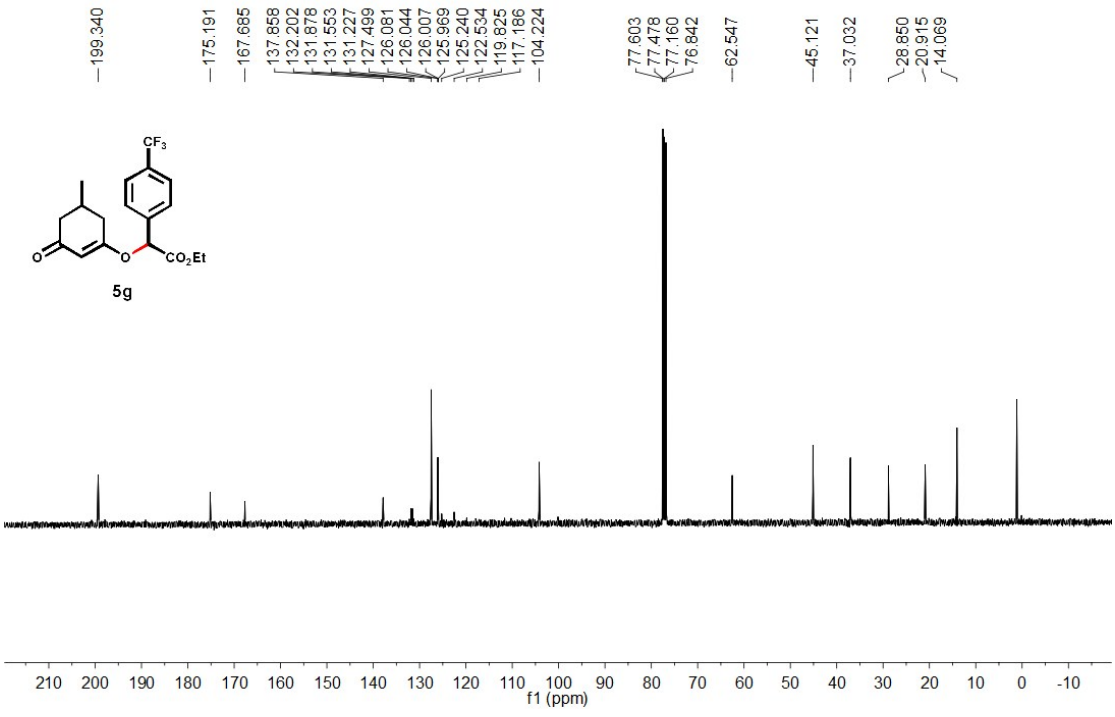
2.4080
2.3996
2.3826
2.3794
2.3391
2.2671
2.2251
2.1050
2.0761
2.0648
2.0585
2.0358
2.0173
1.6631
1.2483
1.2393
1.2341
1.2214
1.2162
1.2036
1.1984
1.1105
1.0948
1.0804
CF3
O
O
CO2Et
5g
4.0133
1.0303
1.0374
2.0431
1.0466
3.0983
1.0582
3.0111
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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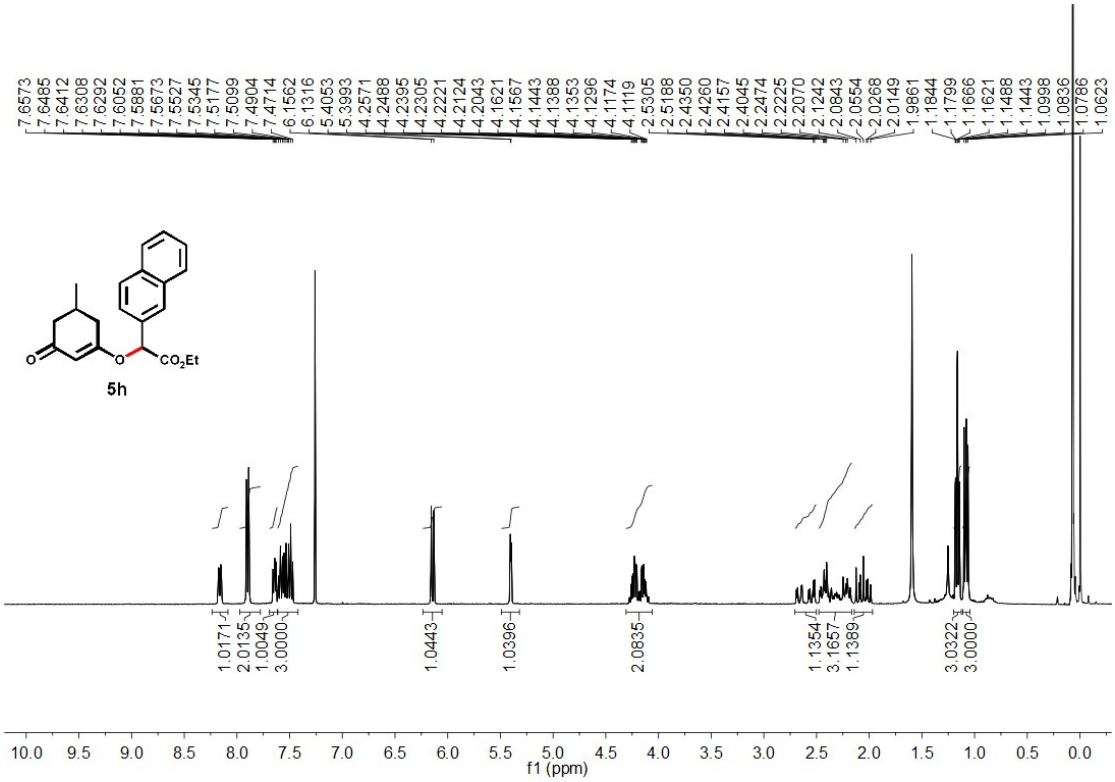
125.240
122.534
119.825
117.186
104.224
77.603
77.478
77.160
76.842
62.547
45.121
37.032
28.850
20.915
14.069
CF3
O
O
CO2Et
5g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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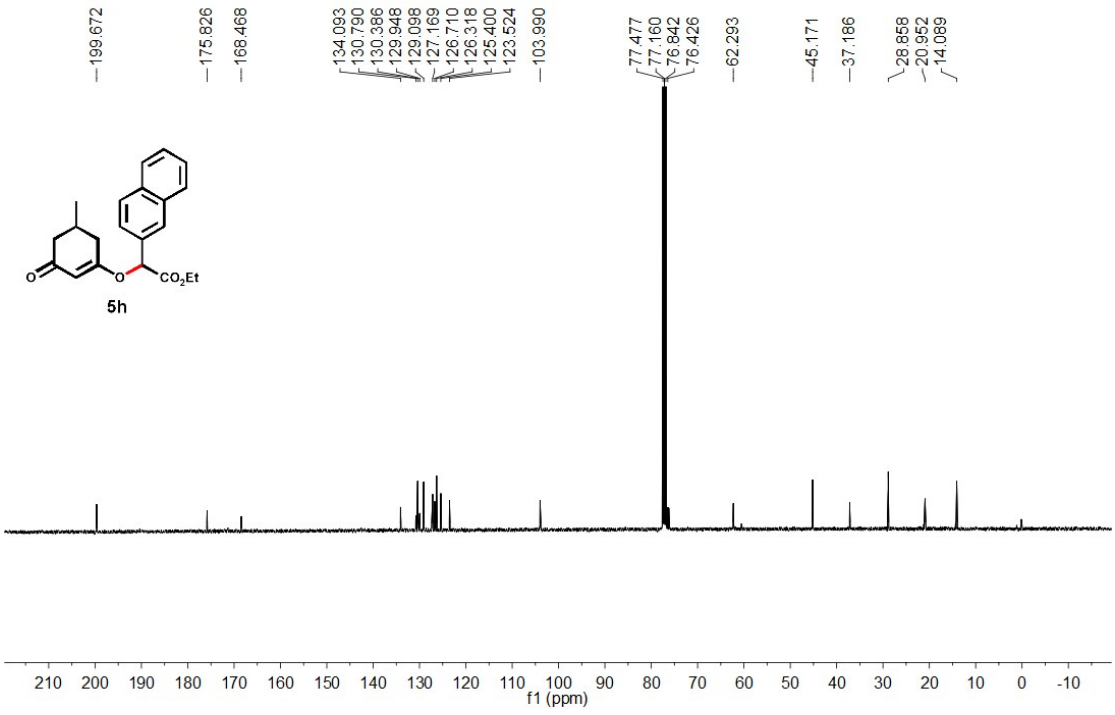
7.5099
7.4904
7.4714
6.1562
6.1316
5.4053
5.3993
4.2571
4.2488
4.2395
4.2305
4.2221
4.2124
4.2043
4.1621
4.1567
4.1443
4.1388
4.1353
4.1296
4.1174
4.1119
2.5305
2.5188
2.4350
2.4260
2.4157
2.4045
2.2474
2.2225
2.2070
2.1242
2.0843
2.0554
2.0268
2.0149
1.9861
1.1844
1.1799
1.1666
1.1621
1.1488
1.1443
1.0998
1.0836
1.0786
1.0623
O
O
CO2Et
5h
1.0171
2.0135
1.0049
3.0000
1.0443
1.0396
2.0835
1.1354
3.1657
1.1389
3.0322
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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130.386
129.948
129.098
127.169
126.710
126.318
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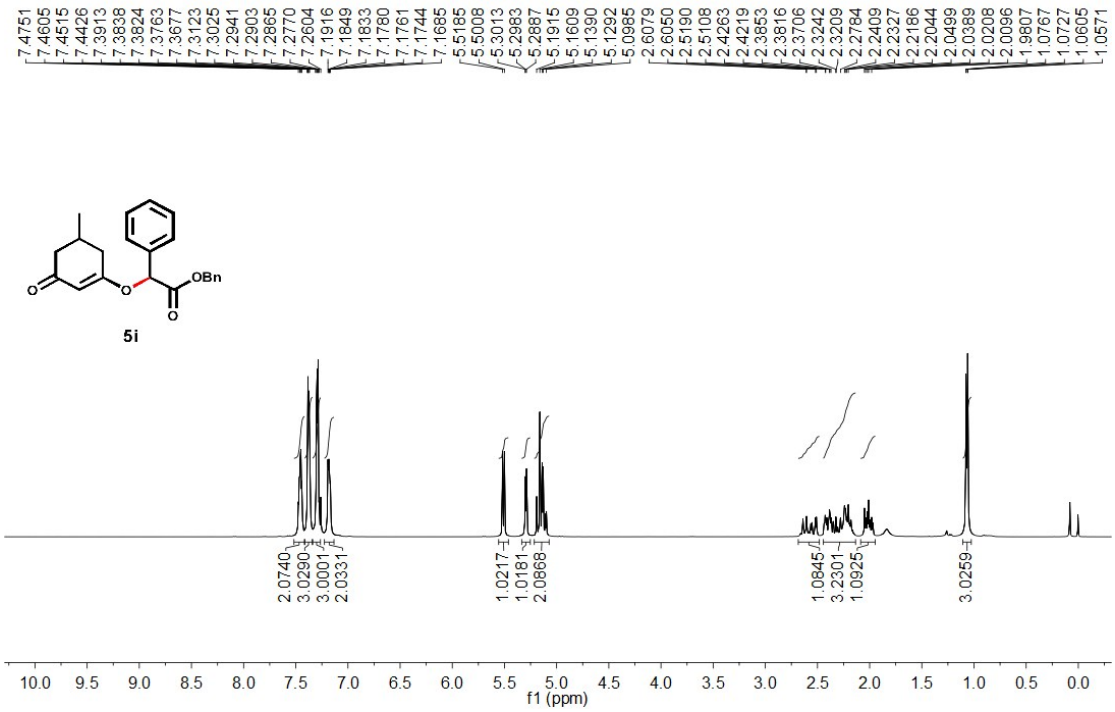
123.524
103.990
77.477
77.160
76.842
76.426
62.293
45.171
37.186
28.858
20.952
14.089
O
O
CO2Et
5h
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3123
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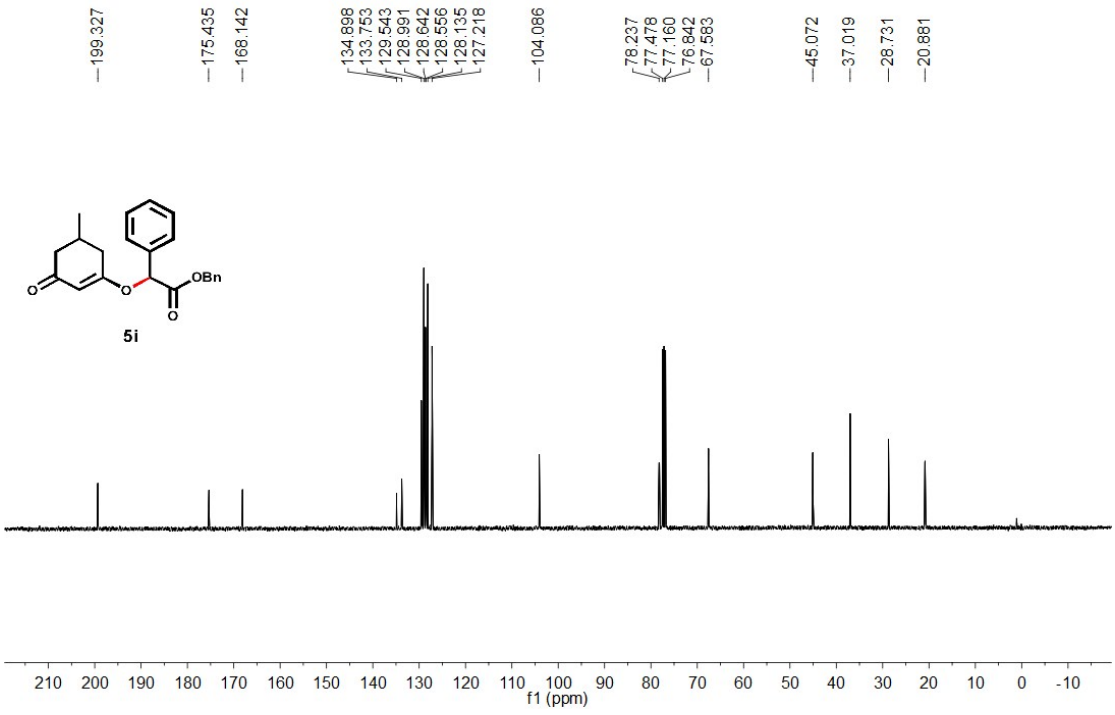
7.2941
7.2903
7.2865
7.2770
7.2604
7.1916
7.1849
7.1833
7.1780
7.1761
7.1744
7.1685
5.5185
5.5008
5.3013
5.2983
5.2887
5.1915
5.1609
5.1390
5.1292
5.0985
2.6079
2.6050
2.5190
2.5108
2.4263
2.4219
2.3853
2.3816
2.3706
2.3242
2.3209
2.2784
2.2409
2.2327
2.2186
2.2044
2.0499
2.0389
2.0208
2.0096
1.9807
1.0767
1.0727
1.0605
1.0571
OBn
O
O
O
5i
2.0740
3.0290
3.0001
2.0331
1.0217
1.0181
2.0868
1.0845
3.2301
1.0925
3.0259
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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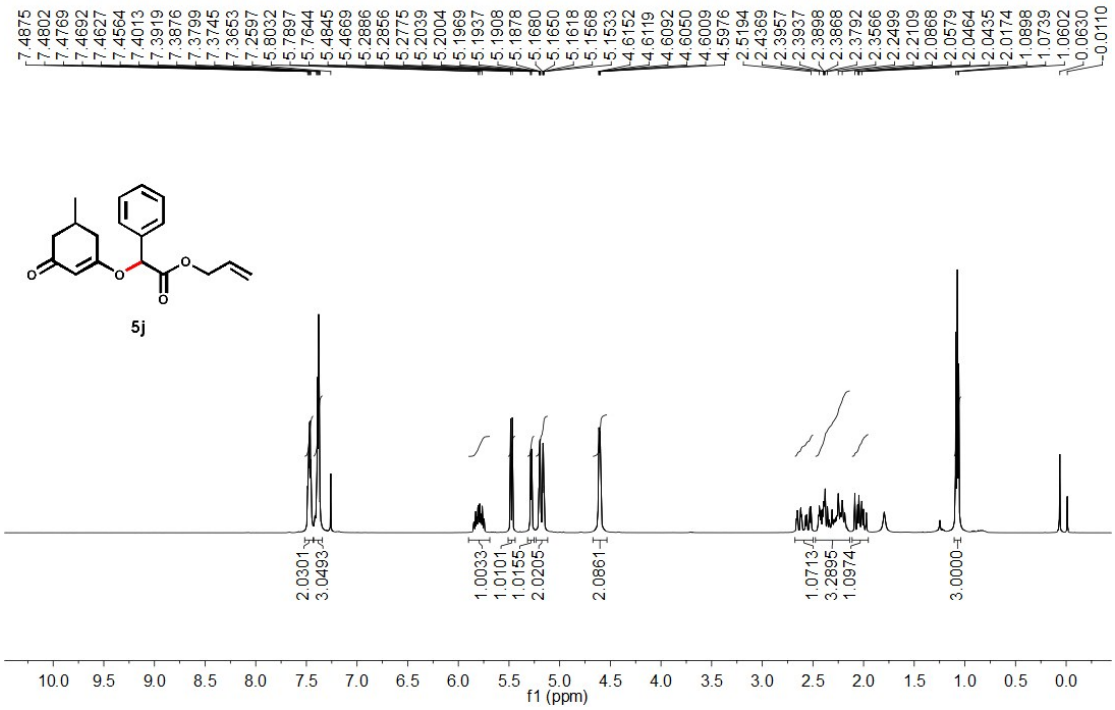
128.556
128.135
127.218
104.086
78.237
77.478
77.160
76.842
67.583
45.072
37.019
28.731
20.881
OBn
O
O
O
5i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3799
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7.3653
7.2597
5.8032
5.7897
5.7644
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5.4669
5.2886
5.2856
5.2775
5.2039
5.2004
5.1969
5.1937
5.1908
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5.1650
5.1618
5.1568
5.1533
4.6152
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4.6092
4.6050
4.6009
4.5976
2.5194
2.4369
2.3957
2.3937
2.3898
2.3868
2.3792
2.3566
2.2499
2.2109
2.0868
2.0579
2.0464
2.0435
2.0174
1.0898
1.0739
1.0602
0.0630
0.0110
5j
2.0301
3.0493
1.0033
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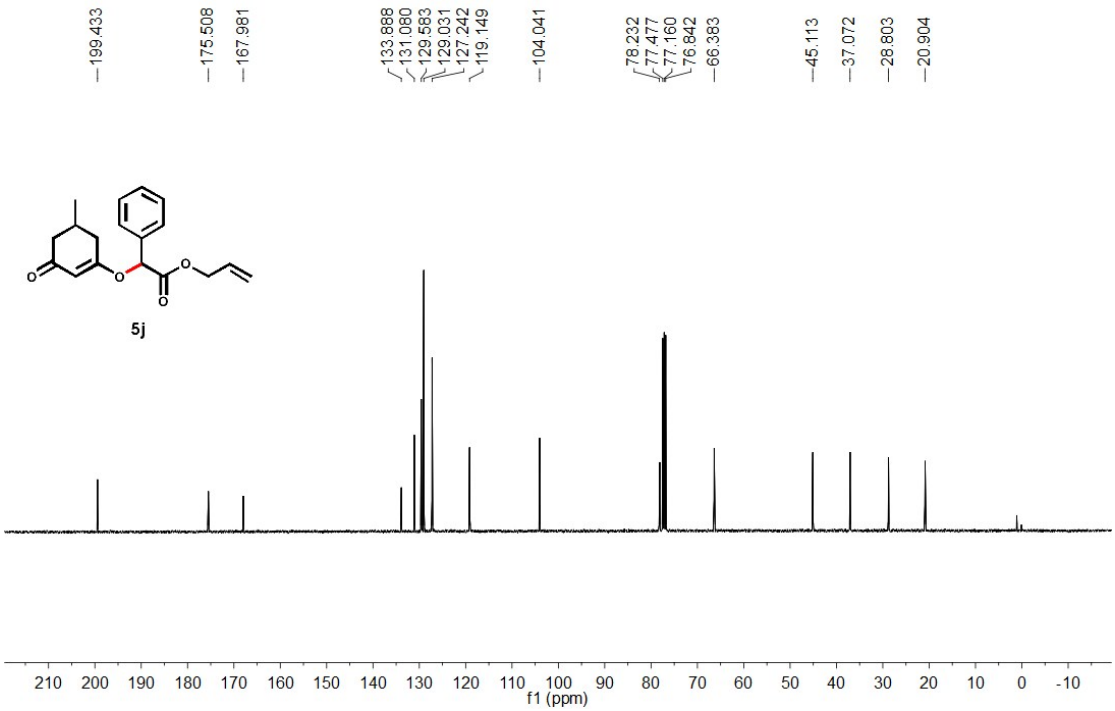
1.0155
2.0205
2.0861
1.0713
3.2895
1.0974
3.0000
f1 (ppm)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28.803
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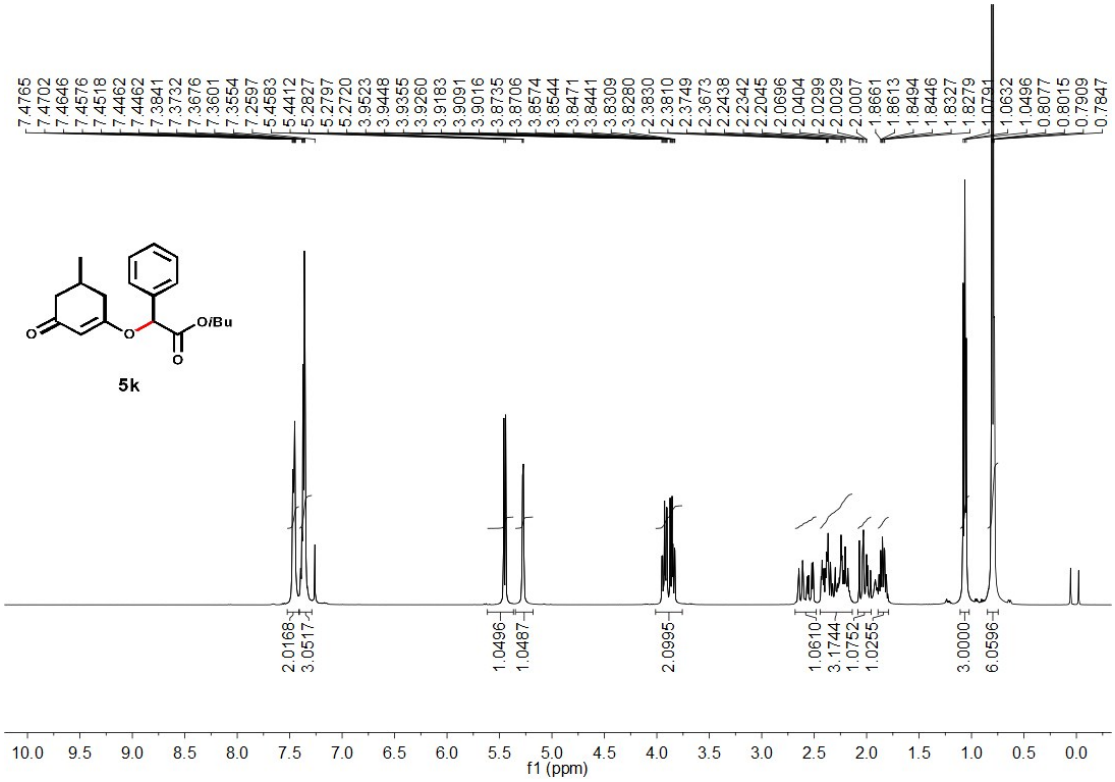
5j
f1 (ppm)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7.4462
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7.3554
7.2597
5.4583
5.4412
5.2827
5.2797
5.2720
3.9523
3.9448
3.9355
3.9260
3.9183
3.9091
3.9016
3.8735
3.8706
3.8574
3.8544
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3.8309
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3.8230
2.3810
2.3749
2.3673
2.2438
2.2342
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2.0404
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2.0029
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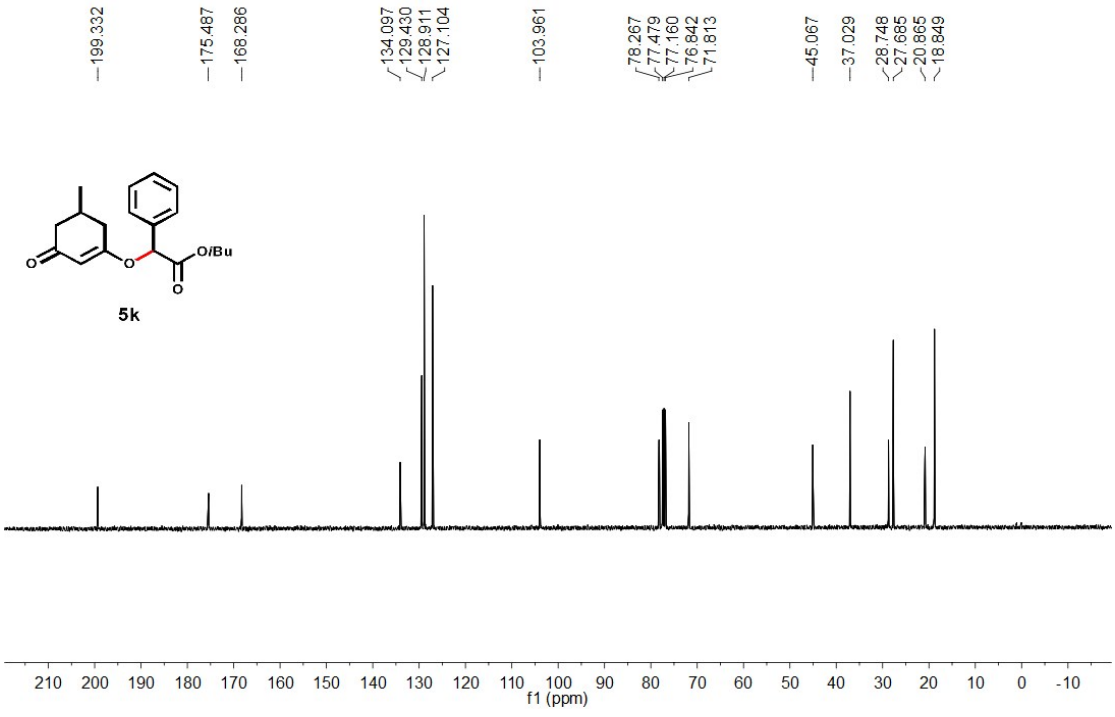
1.8613
1.8494
1.8446
1.8327
1.8279
1.0791
1.0632
1.0496
0.8077
0.8015
0.7909
0.7847
O/Bu
O
O
5k
2.0168
3.0517
1.0496
1.0487
2.0995
1.0610
3.1744
1.0752
1.0255
3.0000
6.0596
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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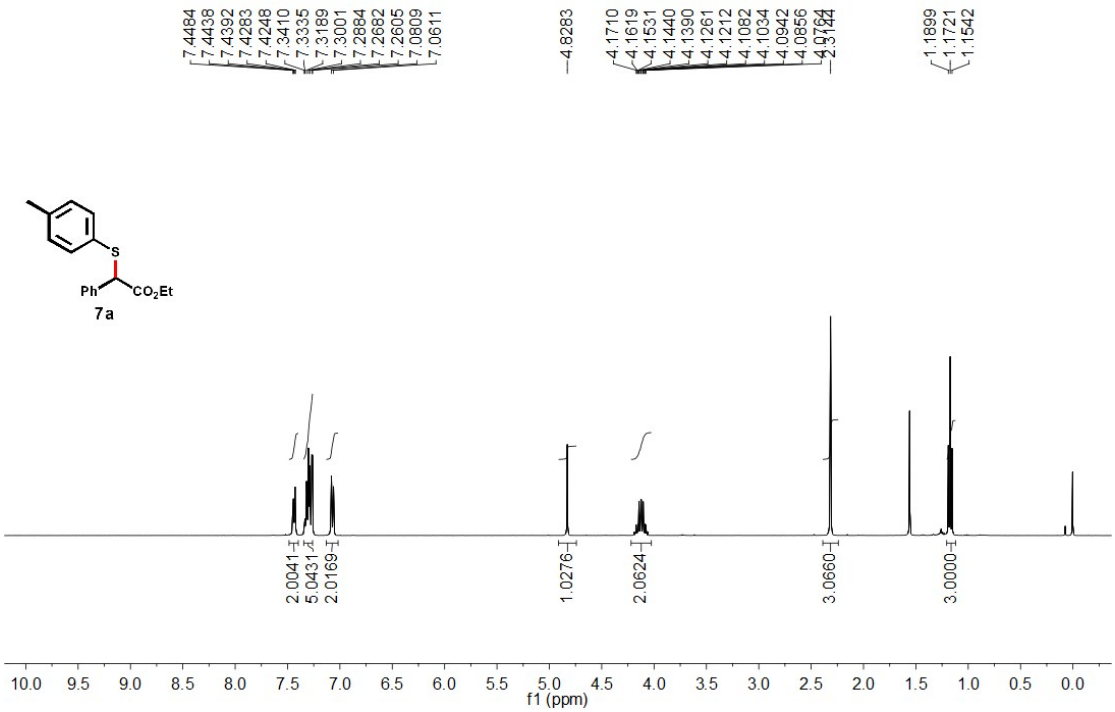
77.479
77.160
76.842
71.813
45.067
37.029
28.748
27.685
20.865
18.849
O/Bu
O
O
5k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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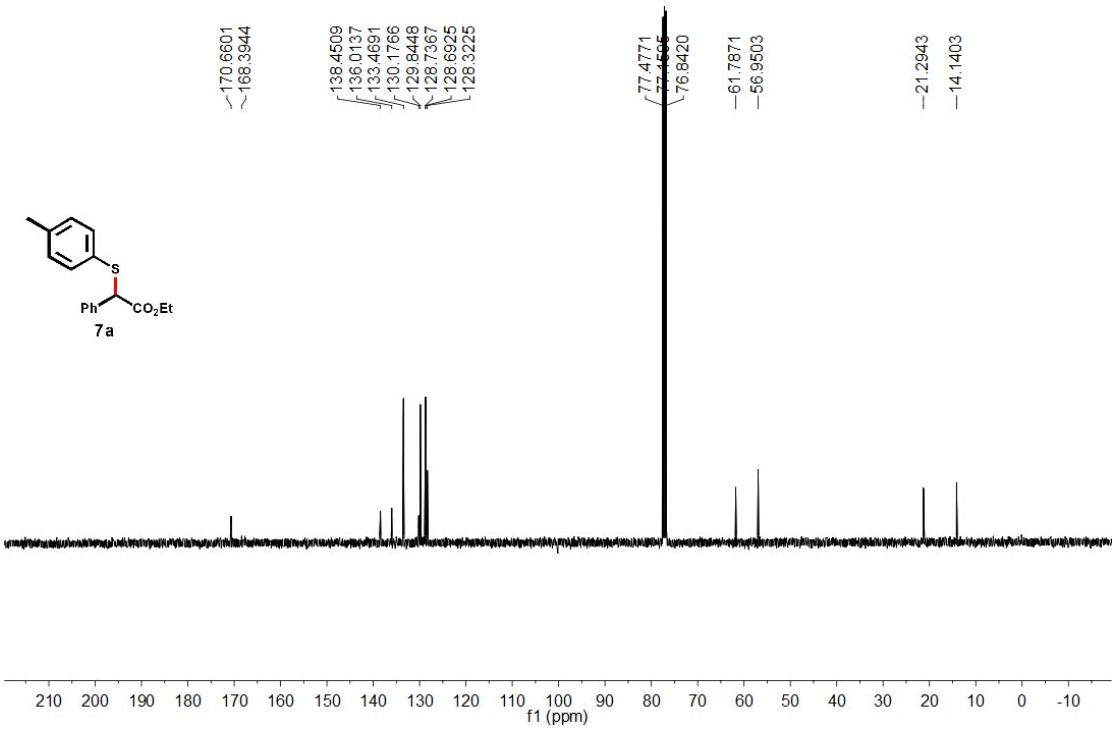
7.2605
7.0809
7.0611
4.8283
4.1710
4.1619
4.1531
4.1440
4.1390
4.1261
4.1212
4.1082
4.1034
4.0942
4.0856
2.3144
1.1899
1.1721
1.1542
S
Ph
CO2Et
7a
2.0041
5.0431
2.0169
1.0276
2.0624
3.0660
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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128.3225
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76.8420
61.7871
56.9503
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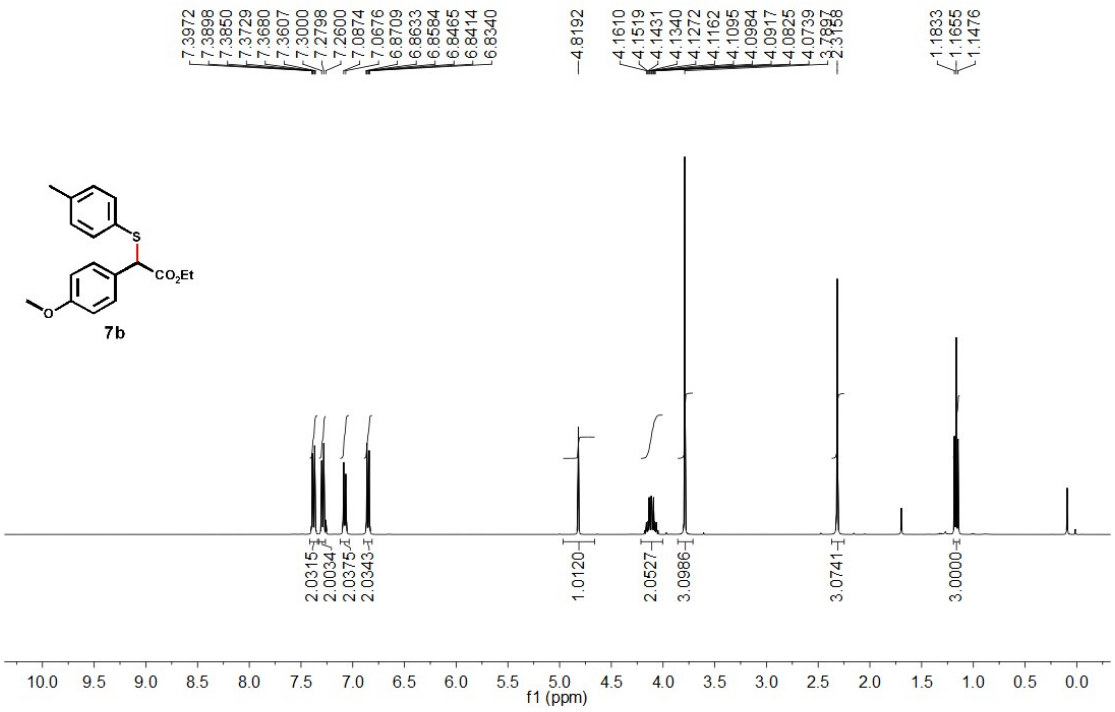
S
Ph
CO2Et
7a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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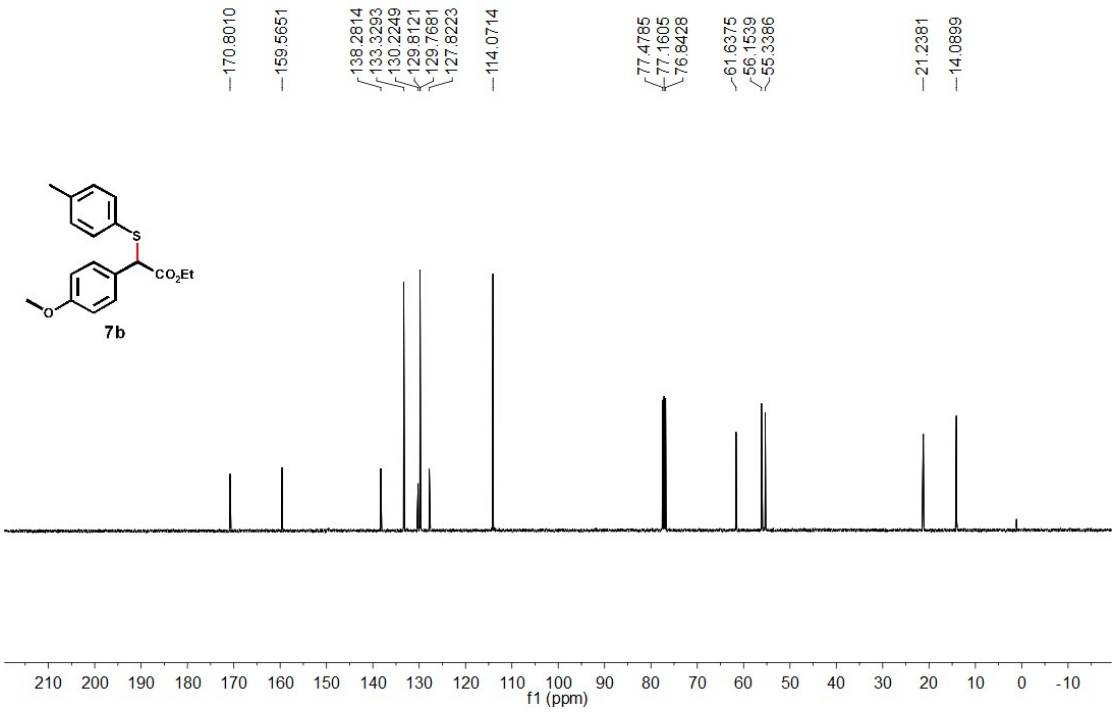
6.8633
6.8584
6.8465
6.8414
6.8340
4.8192
4.1610
4.1519
4.1431
4.1340
4.1272
4.1162
4.1095
4.0984
4.0917
4.0825
4.0739
3.7897
3.7758
1.1833
1.1655
1.1476
S
CO2Et
O
7b
2.0315
2.0034
2.0375
2.0343
1.0120
2.0527
3.0986
3.0741
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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76.8428
61.6375
56.1539
55.3386
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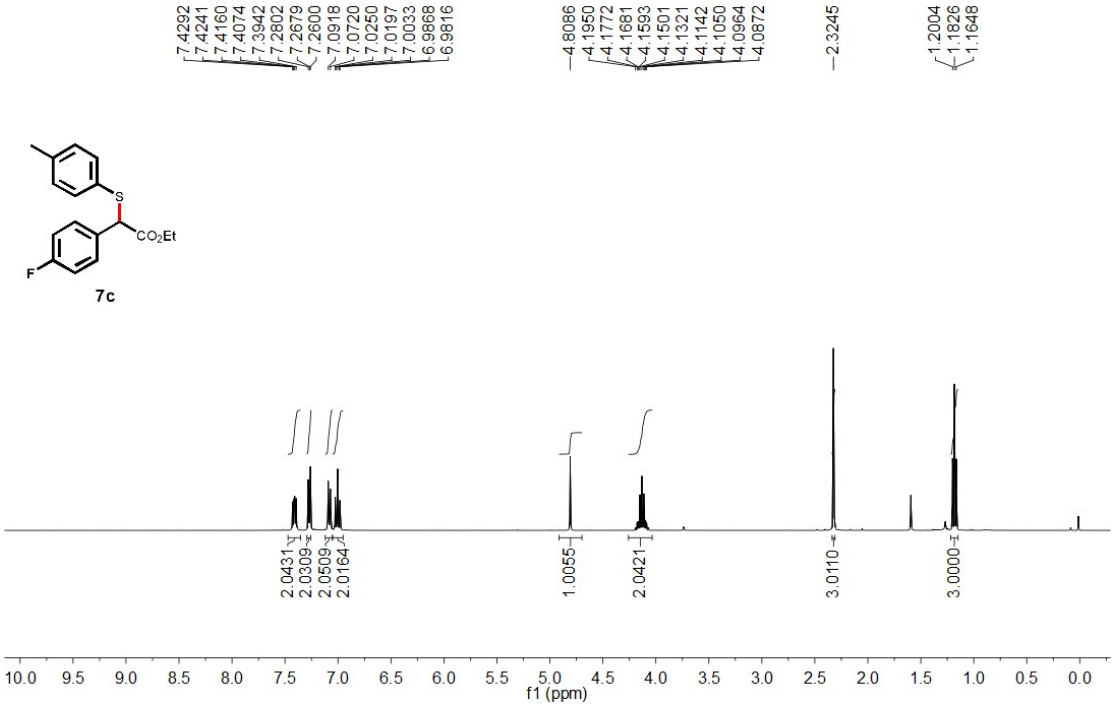
S
CO2Et
O
7b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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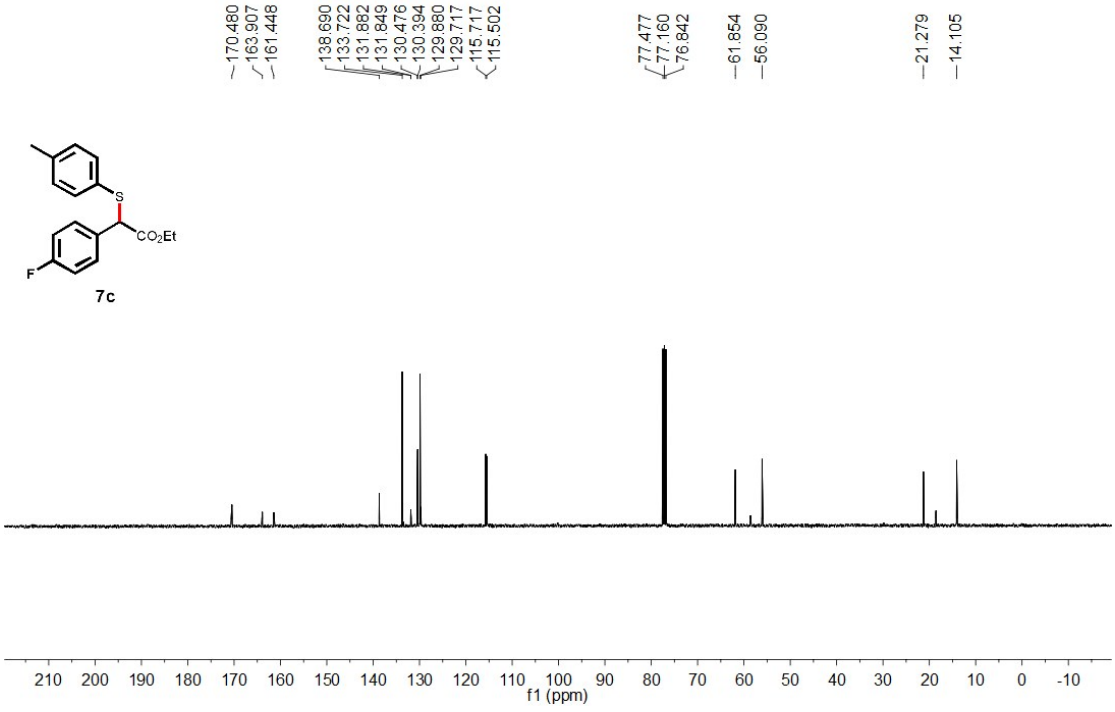
7.0197
7.0033
6.9868
6.9816
4.8086
4.1950
4.1772
4.1681
4.1593
4.1501
4.1321
4.1142
4.1050
4.0964
4.0872
2.3245
1.2004
1.1826
1.1648
S
CO2Et
F
7c
2.0431
2.0309
2.0509
2.0164
1.0055
2.0421
3.0110
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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115.502
77.477
77.160
76.842
61.854
56.090
21.279
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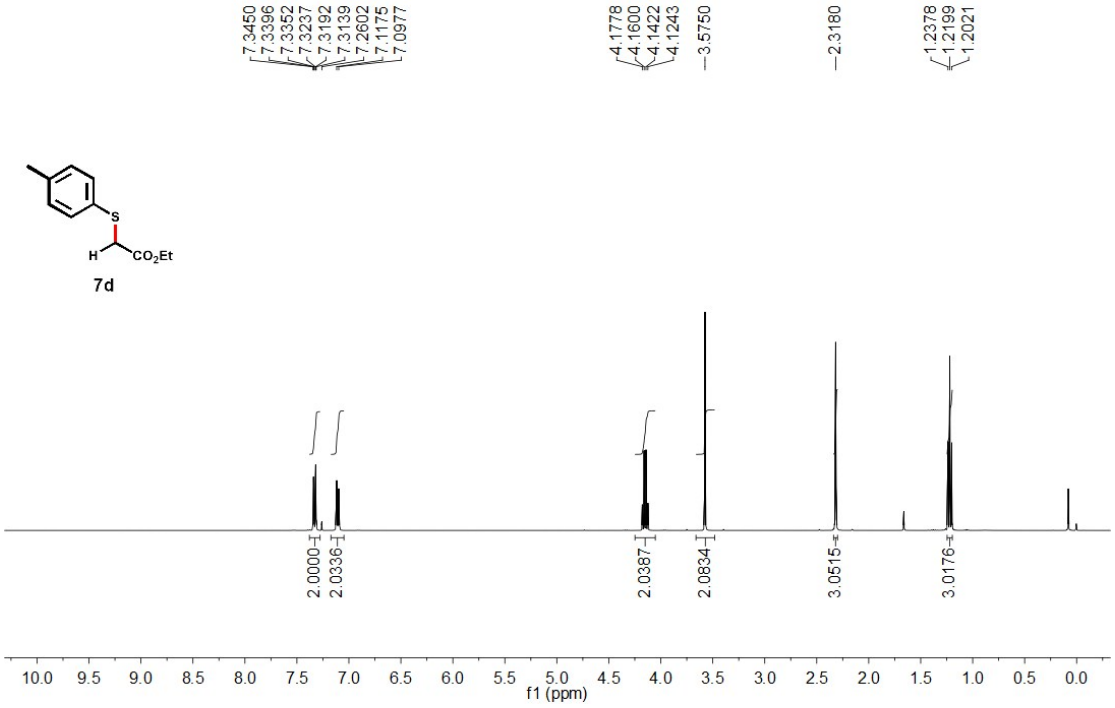
S
CO2Et
F
7c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.3237
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7.3139
7.2602
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7.0977
4.1778
4.1600
4.1422
4.1243
3.5750
2.3180
1.2378
1.2199
1.2021
S
H
CO2Et
7d
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2.0834
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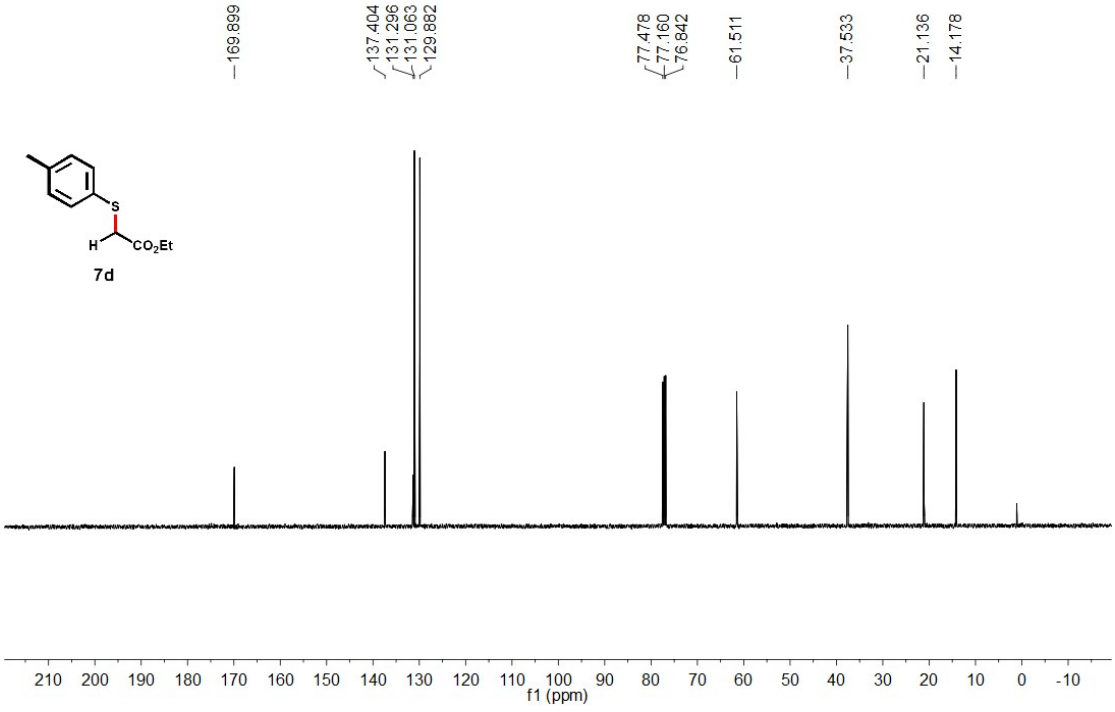
3.0176
f1 (ppm)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37.533
21.136
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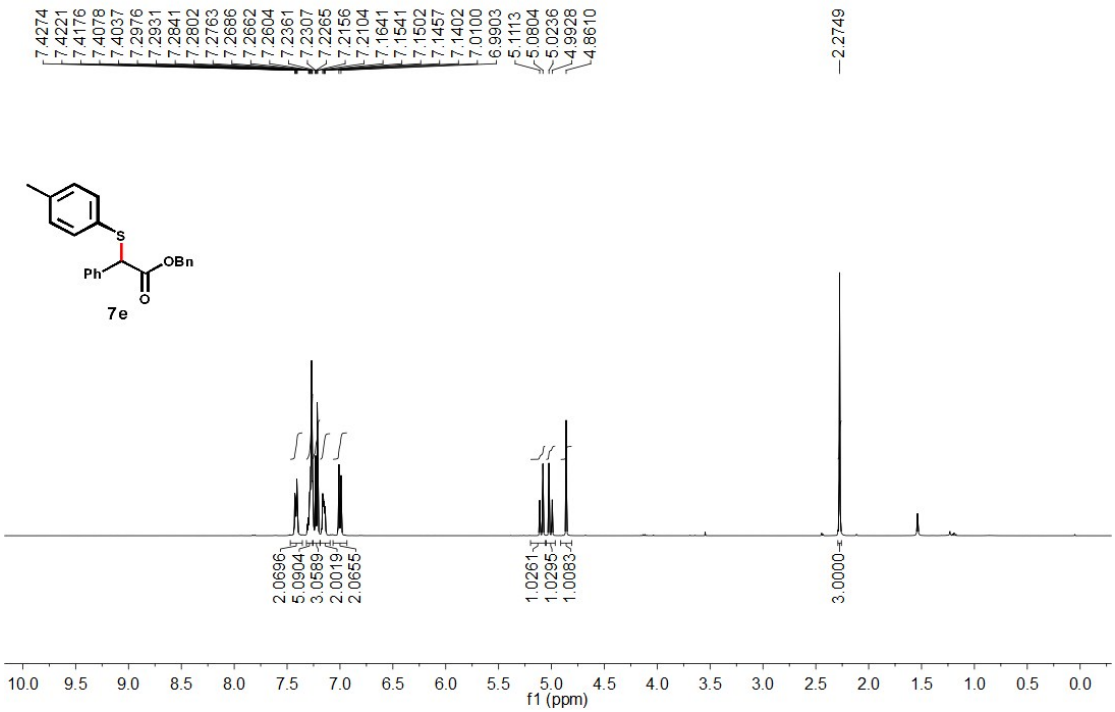
S
H
CO2Et
7d
f1 (ppm)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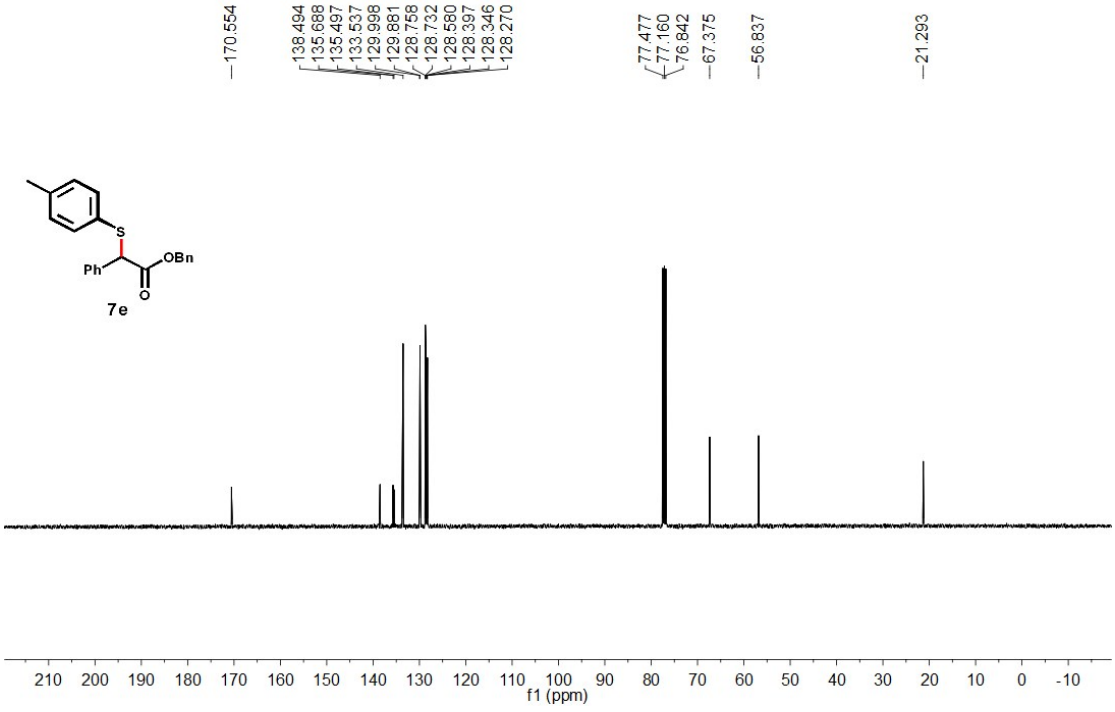
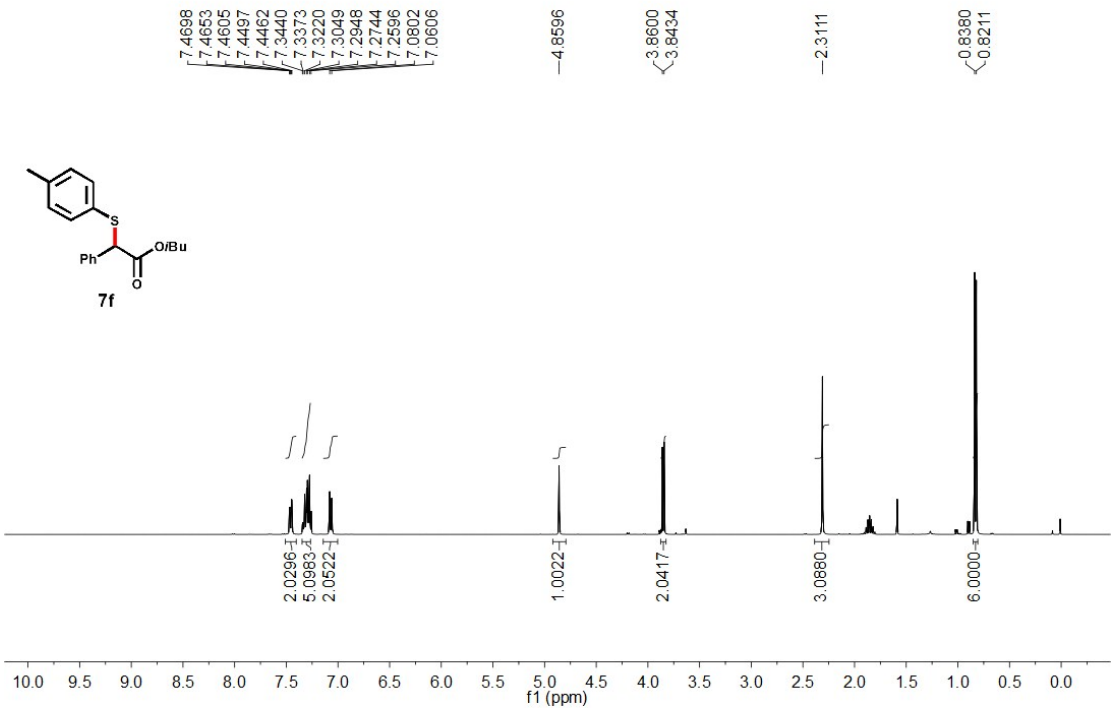
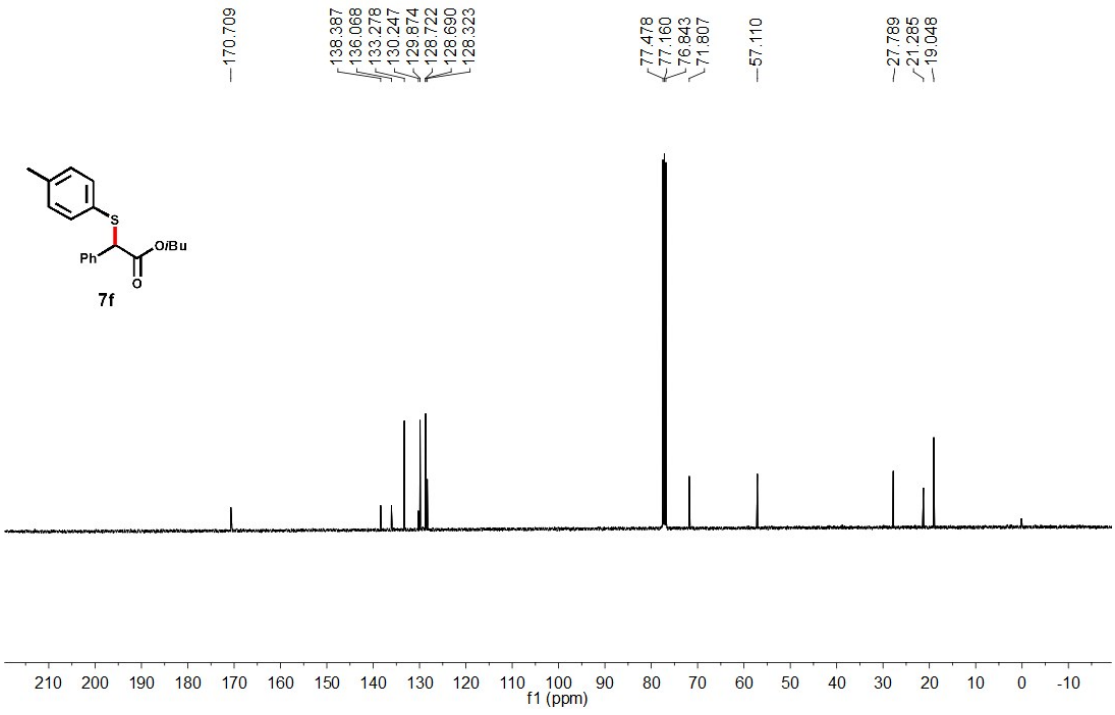
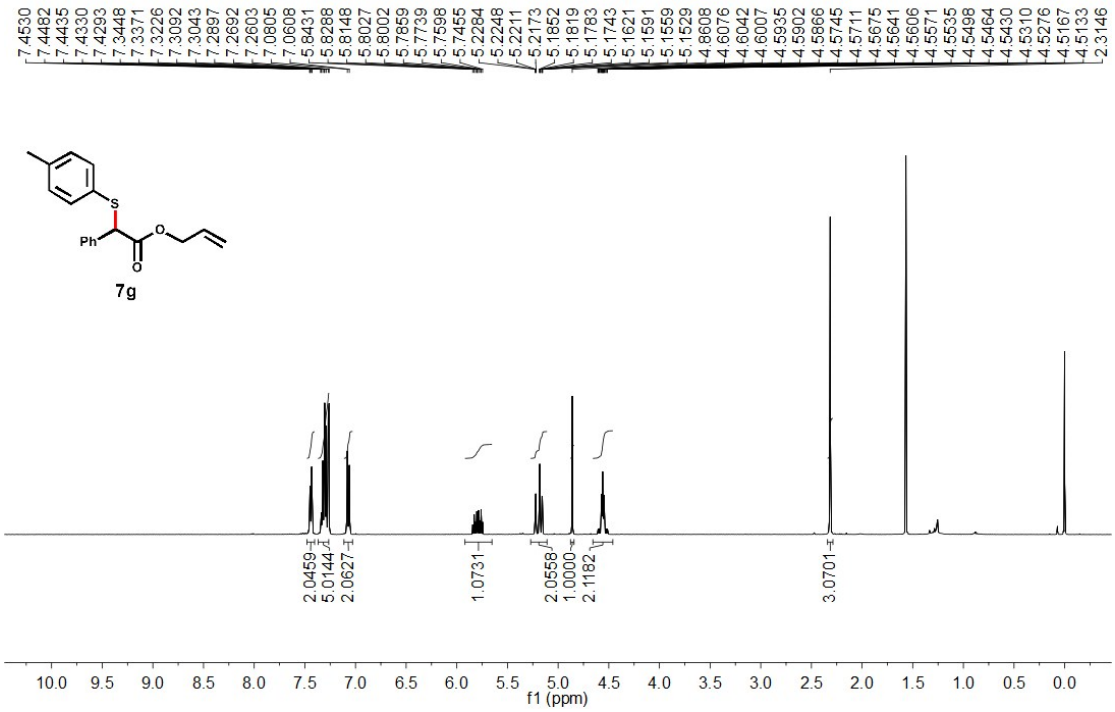
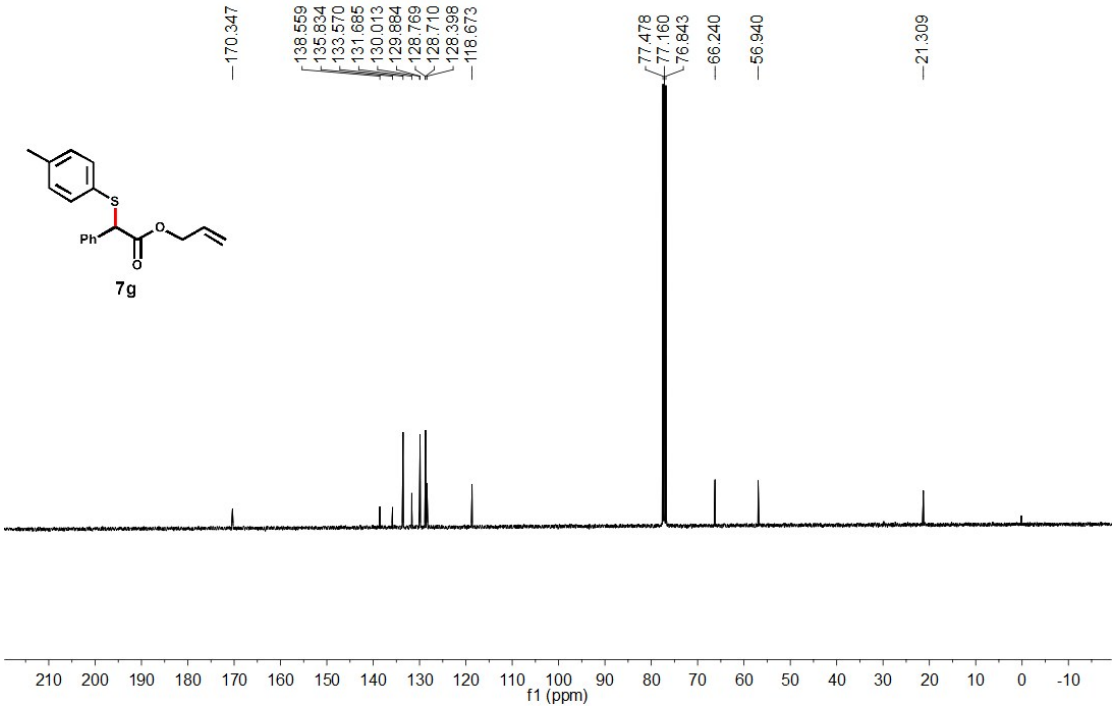
7.4221
7.4176
7.4078
7.4037
7.2976
7.2931
7.2841
7.2802
7.2763
7.2686
7.2662
7.2604
7.2361
7.2307
7.2265
7.2156
7.2104
7.1641
7.1541
7.1502
7.1457
7.1402
7.0100
6.9903
5.1113
5.0804
5.0236
4.9928
4.8610
2.2749
S
Ph
OBn
O
7e
2.0696
5.0904
3.0589
2.0019
2.0655
1.0261
1.0295
1.0083
3.0000
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


170.554
138.494
135.688
135.497
133.537
129.998
129.881
128.758
128.732
128.580
128.397
128.346
128.270
77.477
77.160
76.842
67.375
56.837
21.293
S
Ph
OBn
O
7e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.4698
7.4653
7.4605
7.4497
7.4462
7.3440
7.3373
7.3220
7.3049
7.2948
7.2744
7.2596
7.0802
7.0606
4.8596
3.8600
3.8434
2.3111
0.8380
0.8211
S
Ph
O
O/Bu
7f
2.0296
5.0983
2.0522
1.0022
2.0417
3.0880
6.0000
f1 (ppm)


170.709
138.387
136.068
133.278
130.247
129.874
128.722
128.690
128.323
77.478
77.160
76.843
71.807
57.110
27.789
21.285
19.048
S
Ph
O
O/Bu
7f
f1 (ppm)


7.4530
7.4482
7.4435
7.4330
7.4293
7.3448
7.3371
7.3226
7.3092
7.3043
7.2897
7.2692
7.2603
7.0805
7.0608
5.8431
5.8288
5.8148
5.8027
5.8002
5.7859
5.7739
5.7598
5.7455
5.2284
5.2248
5.2211
5.2173
5.1852
5.1819
5.1783
5.1743
5.1621
5.1591
5.1559
5.1529
4.8608
4.6076
4.6042
4.6007
4.5935
4.5902
4.5866
4.5745
4.5711
4.5675
4.5641
4.5606
4.5571
4.5535
4.5498
4.5464
4.5430
4.5310
4.5276
4.5167
4.5133
2.3146
S
Ph
O
O
7g
2.0459
5.0144
2.0627
1.0731
2.0558
1.0000
2.1182
3.0701
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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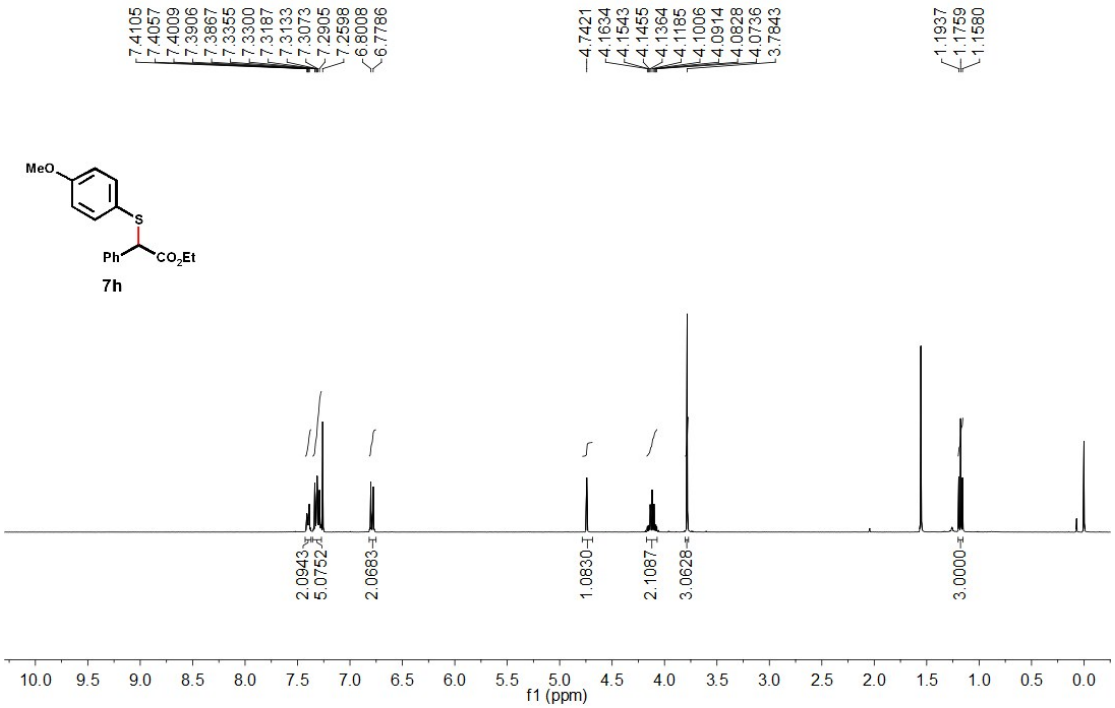
135.834
133.570
131.685
130.013
129.884
128.769
128.710
128.398
118.673
77.478
77.160
76.843
66.240
56.940
21.309
S
Ph
O
O
7g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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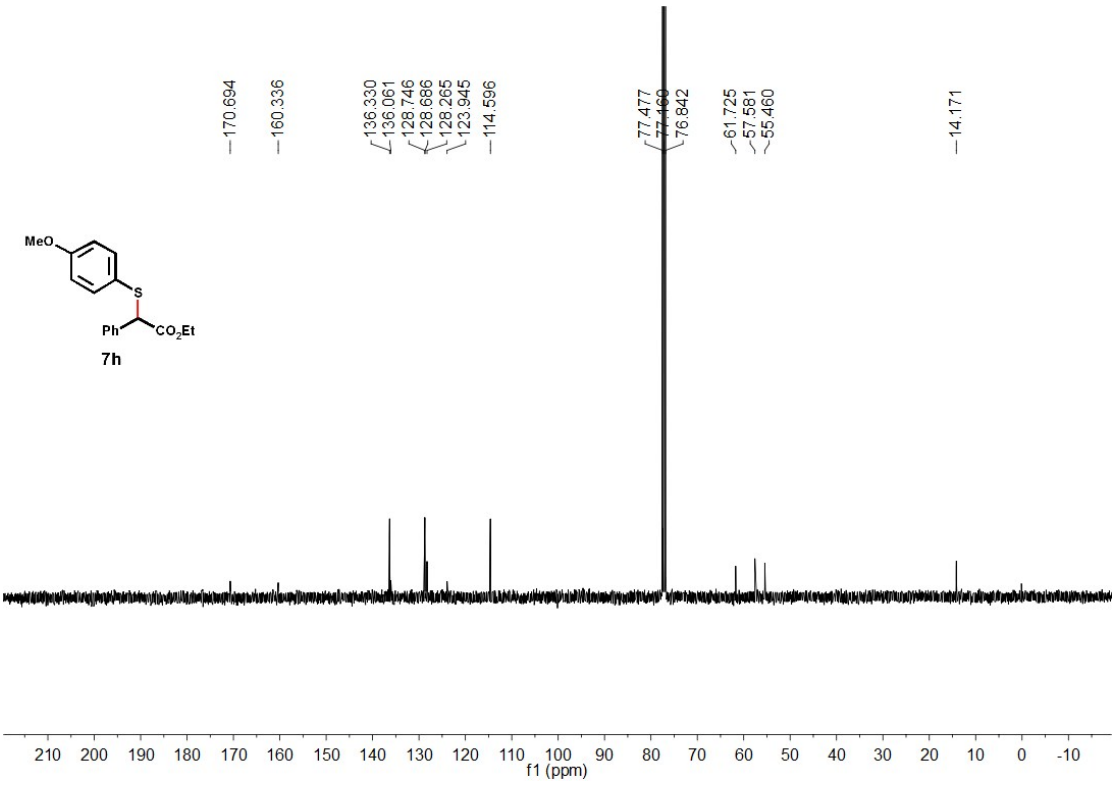
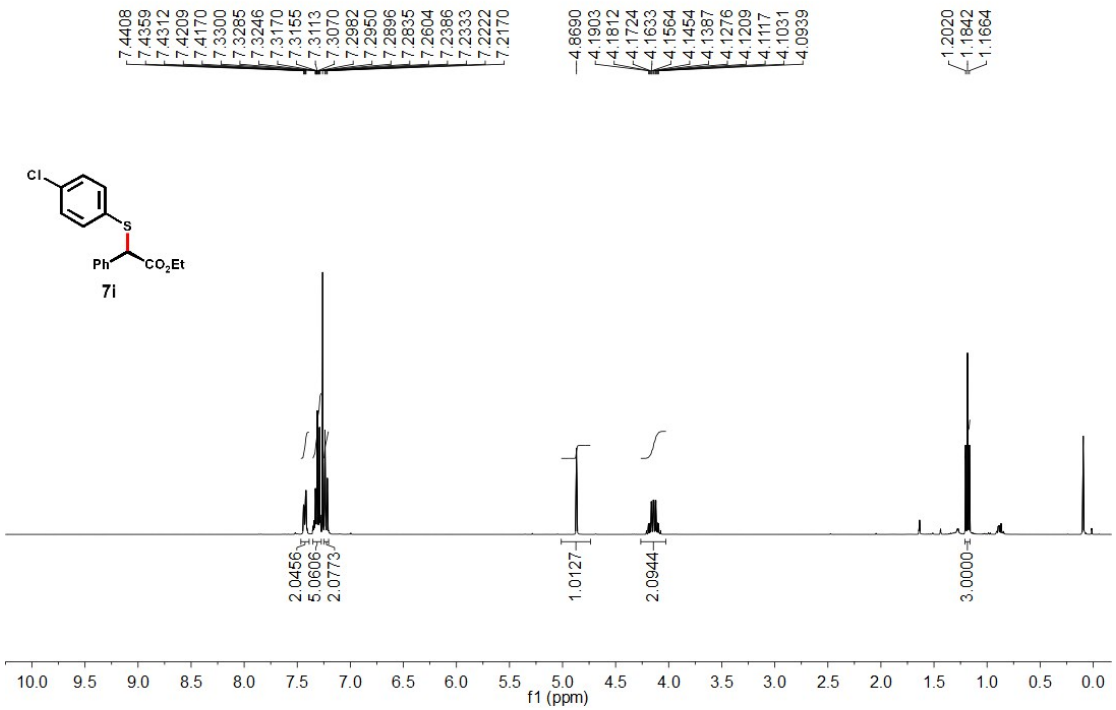
7.4057
7.4009
7.3906
7.3867
7.3355
7.3300
7.3187
7.3133
7.3073
7.2905
7.2598
6.8008
6.7786
4.7421
4.1634
4.1543
4.1455
4.1364
4.1185
4.1006
4.0914
4.0828
4.0736
3.7843
1.1937
1.1759
1.1580
MeO
S
Ph
CO2Et
7h
2.0943
5.0752
2.0683
1.0830
2.1087
3.0628
3.0000
f1 (ppm)


170.694
160.336
136.330
136.061
128.746
128.686
128.265
123.945
114.596
77.477
77.160
76.842
61.725
57.581
55.460
14.171
MeO
S
Ph
CO2Et
7h
f1 (ppm)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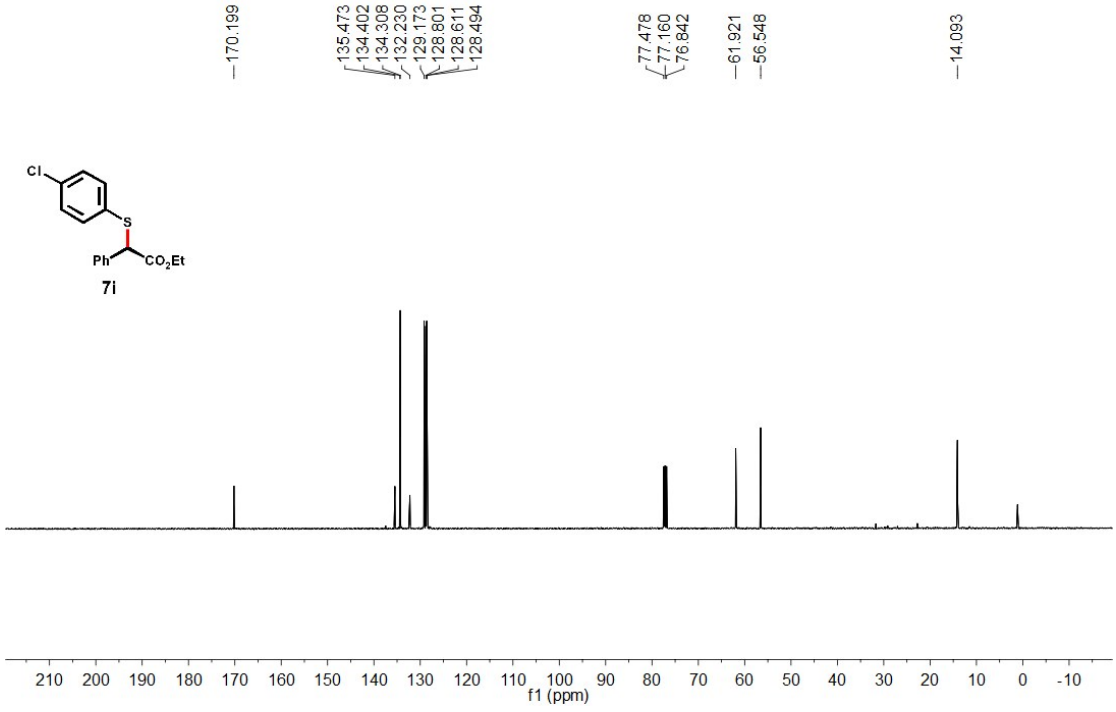
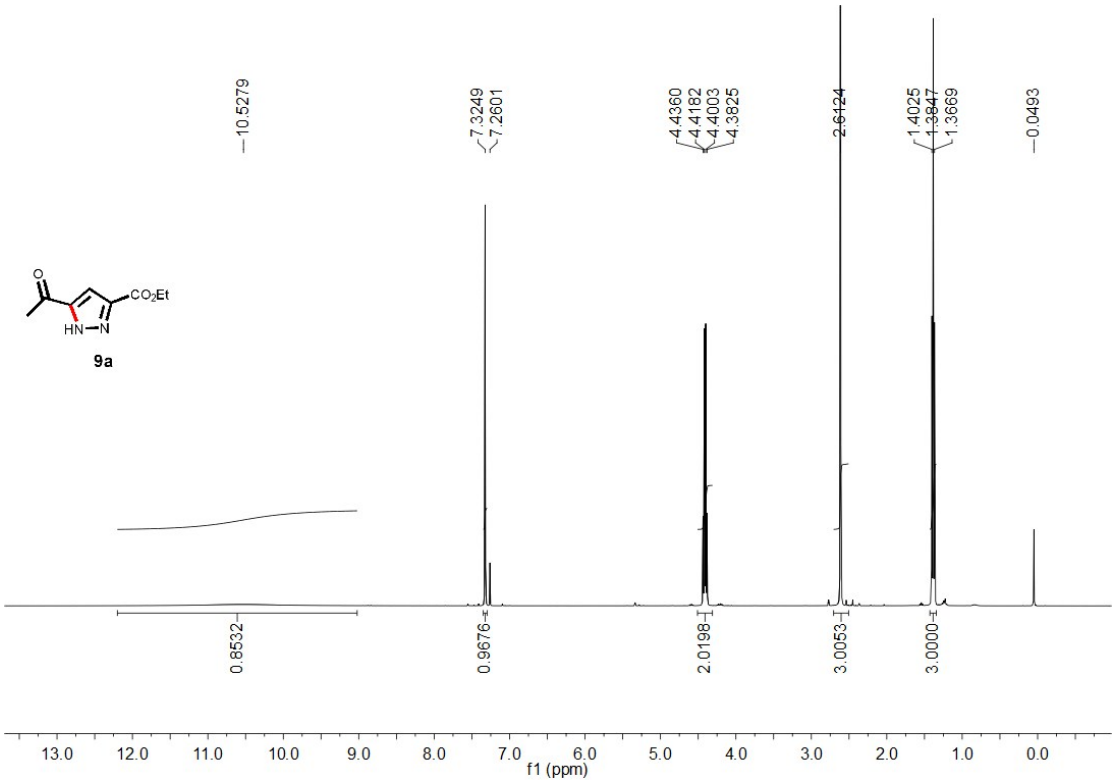
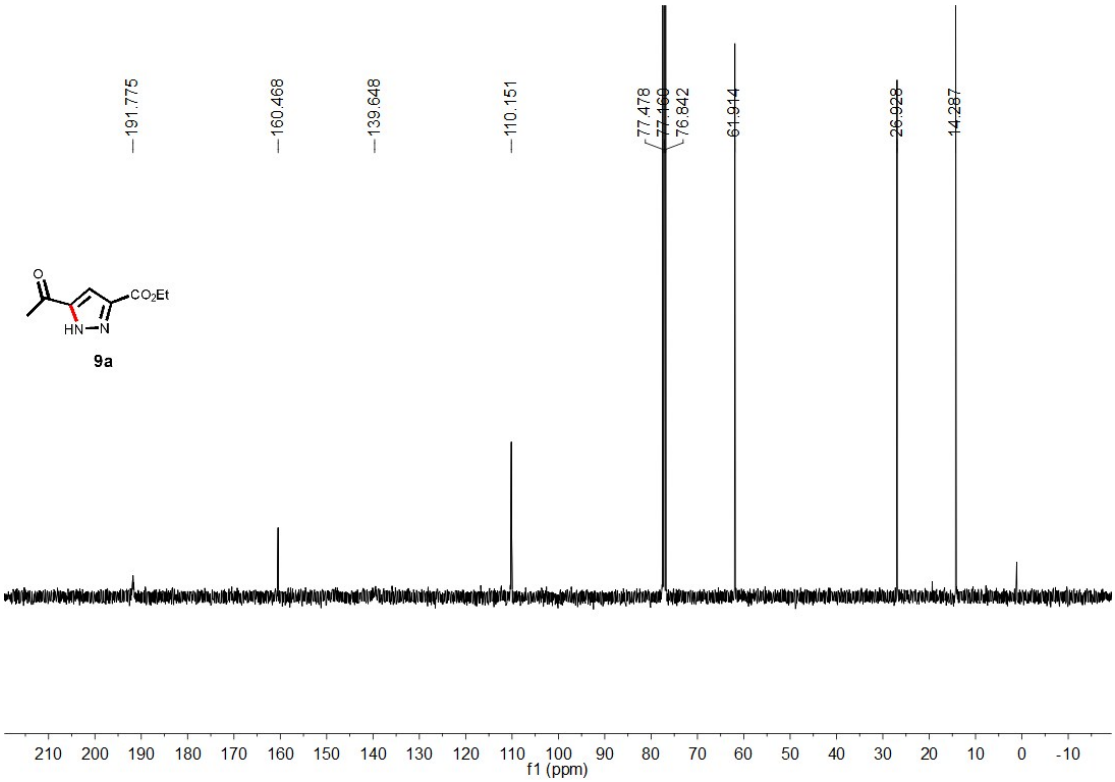
7.4359
7.4312
7.4209
7.4170
7.3300
7.3285
7.3246
7.3170
7.3155
7.3113
7.3070
7.2982
7.2950
7.2896
7.2835
7.2604
7.2386
7.2333
7.2222
7.2170
4.8690
4.1903
4.1812
4.1724
4.1633
4.1564
4.1454
4.1387
4.1276
4.1209
4.1117
4.1031
4.0939
1.2020
1.1842
1.1664
Cl
S
Ph
CO2Et
7i
2.0456
5.0606
2.0773
1.0127
2.0944
3.0000
f1 (ppm)


170.199
135.473
134.402
134.308
132.230
129.173
128.801
128.611
128.494
77.478
77.160
76.842
61.921
56.548
14.093
Cl
S
Ph
CO2Et
7i
f1 (ppm)


10.5279
7.3249
7.2601
4.4360
4.4182
4.4003
4.3825
2.6124
1.4025
1.3847
1.3669
0.0493
0.8532
0.9676
2.0198
3.0053
3.0000
f1 (ppm)


191.775
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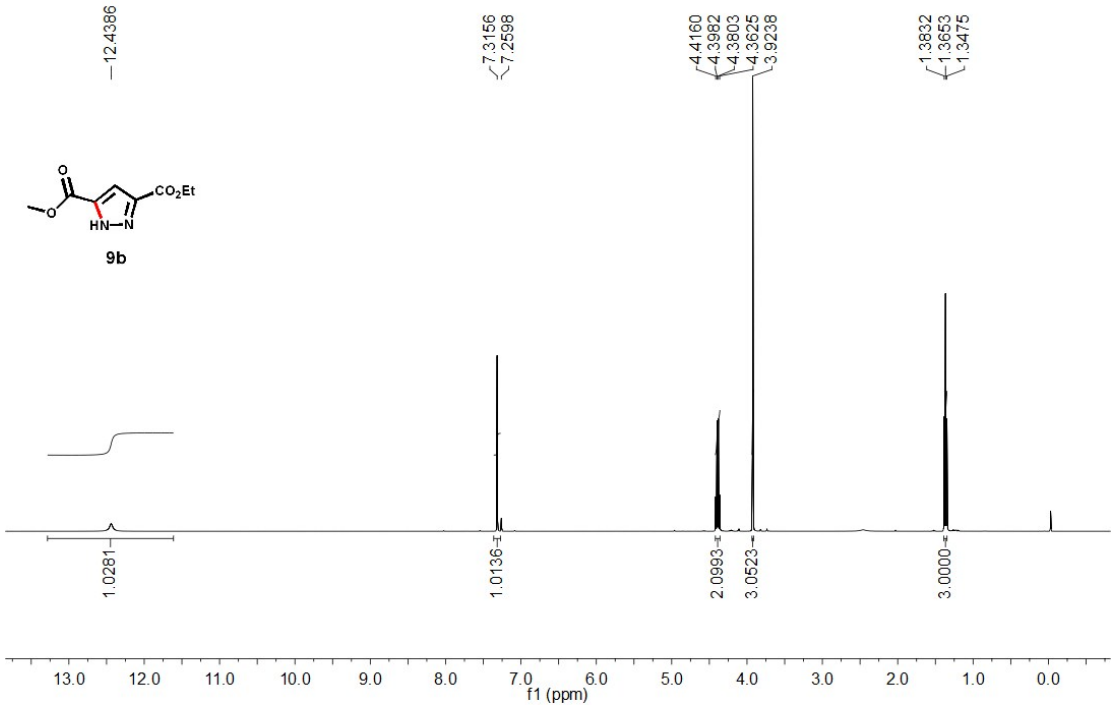
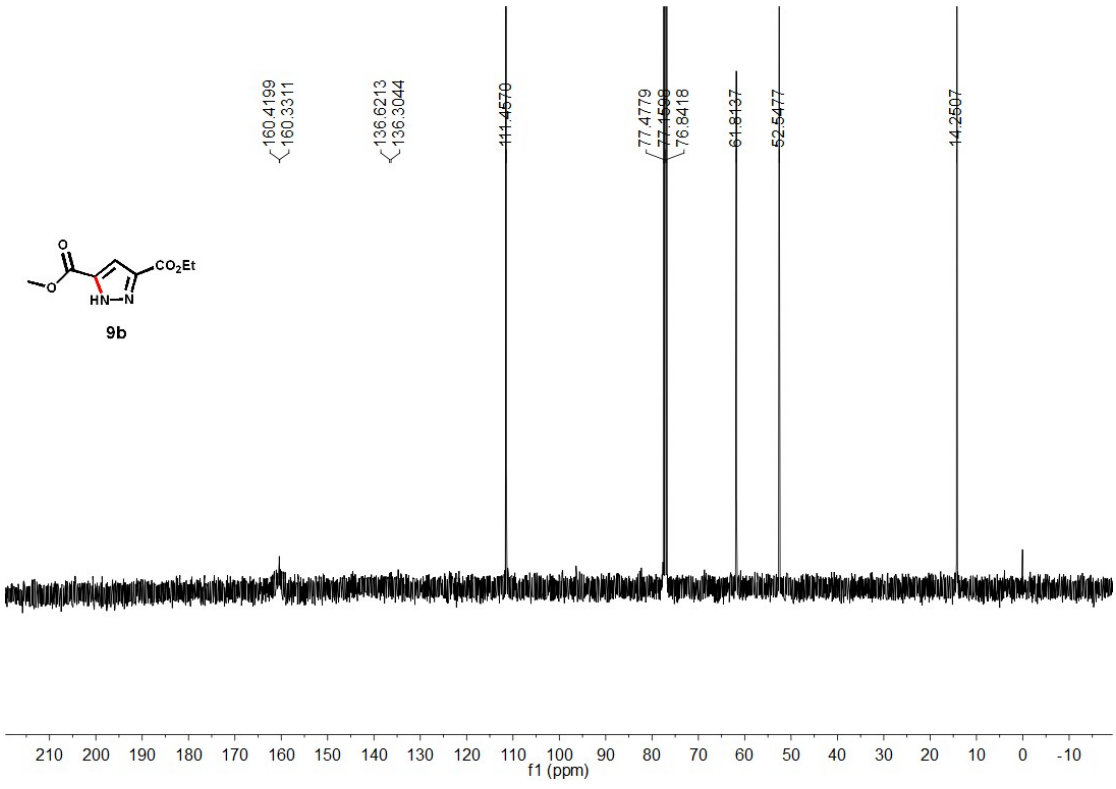
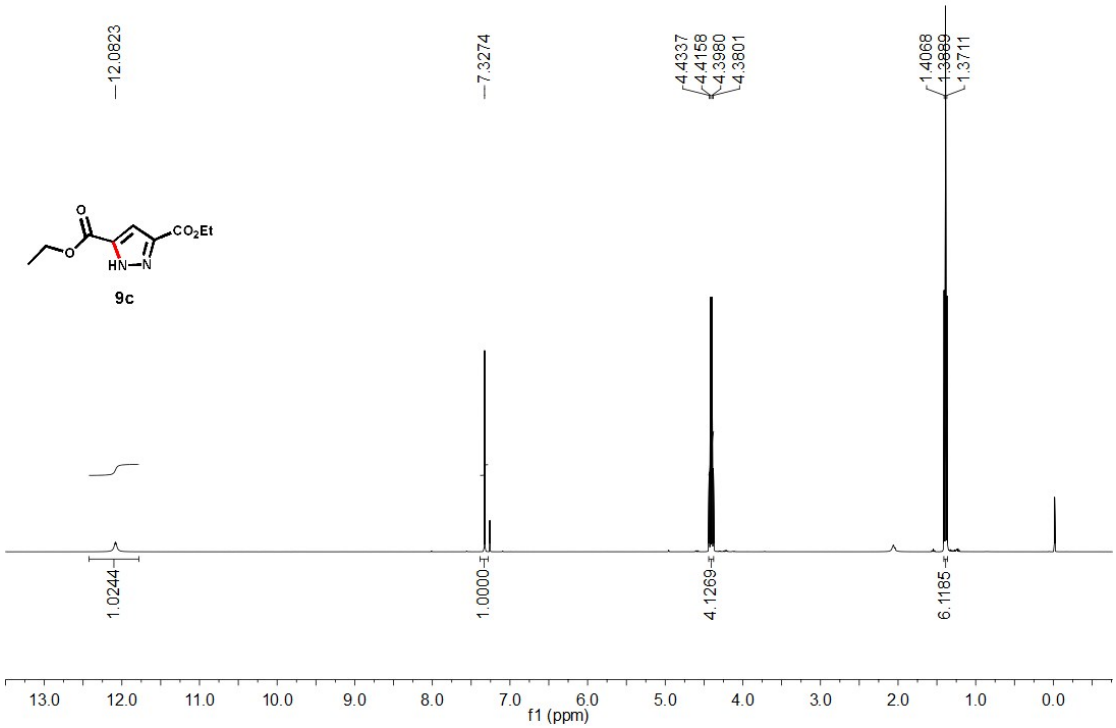
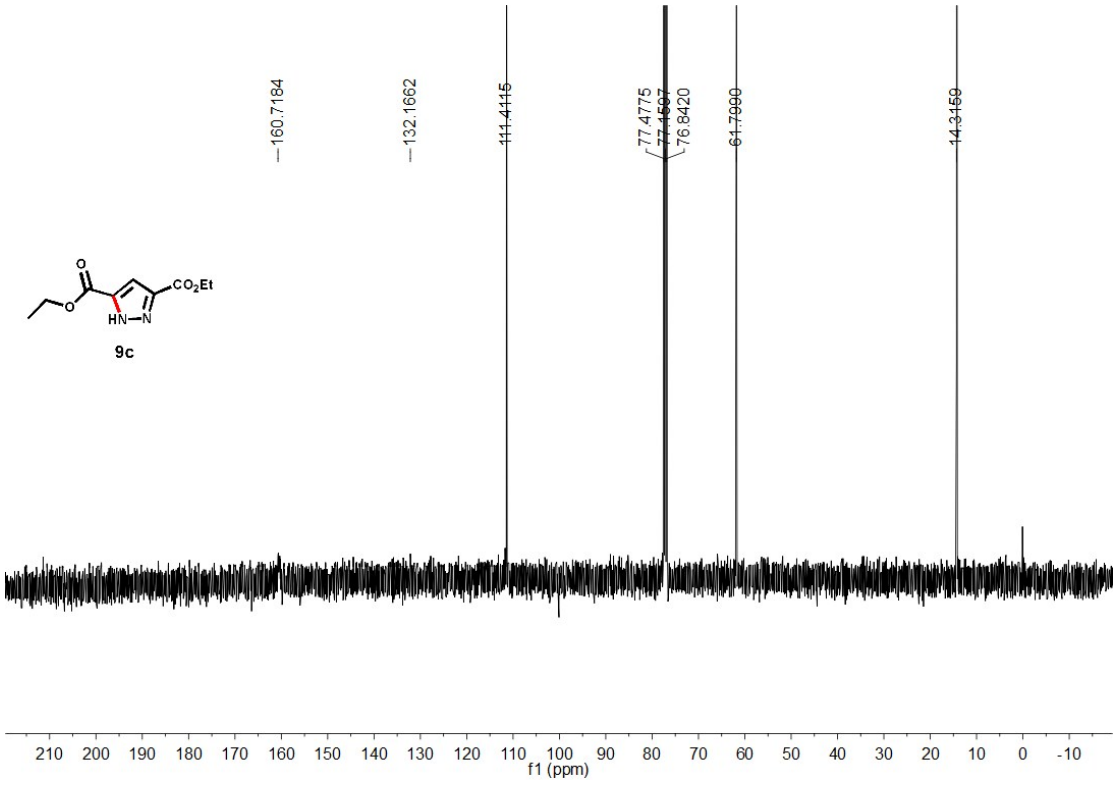
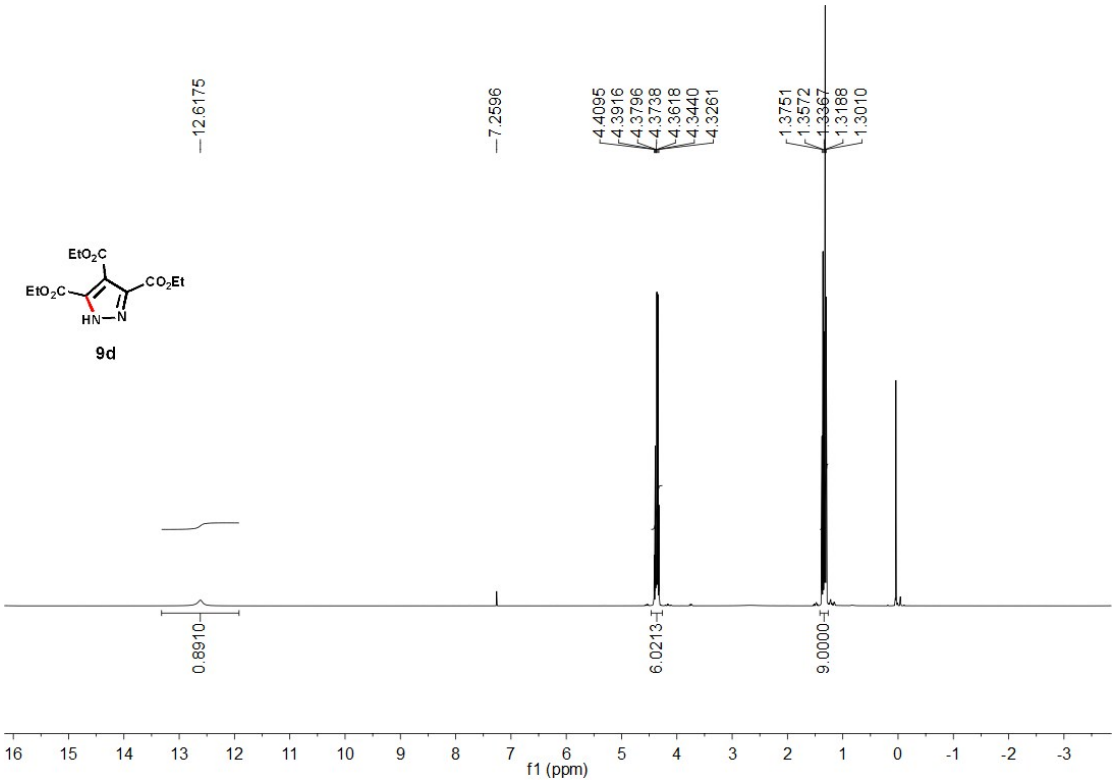
139.648
110.151
77.478
77.160
76.842
61.914
26.928
14.287
f1 (ppm)


12.4386
7.3156
7.2598
4.4160
4.3982
4.3803
4.3625
3.9238
1.3832
1.3653
1.3475
1.0281
1.0136
2.0993
3.0523
3.0000
f1 (ppm)

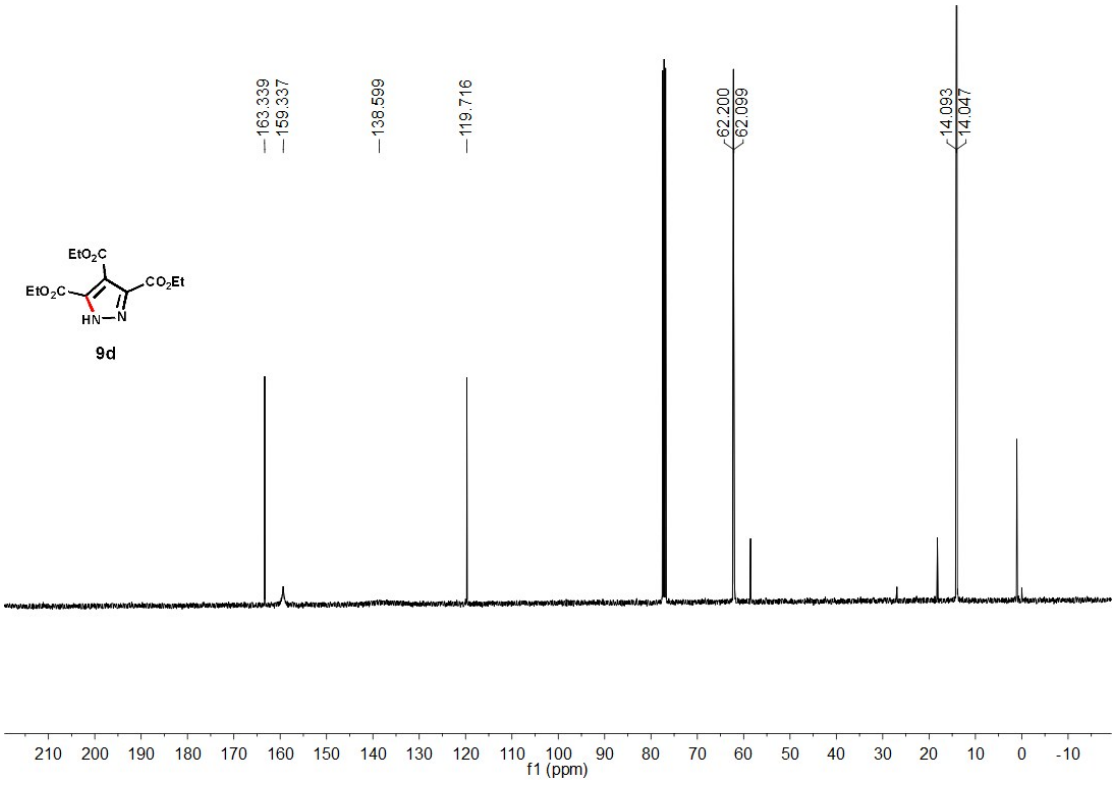

160.4199
160.3311
136.6213
136.3044
111.4570
77.4779
76.8418
61.8137
52.5477
14.2507
f1 (ppm)


12.0823
7.3274
4.4337
4.4158
4.3960
4.3801
1.4068
1.3889
1.3711
9c
1.0244
1.0000
4.1269
6.1185
f1 (ppm)


160.7184
132.1662
111.4115
77.4775
77.1607
76.8420
61.7990
14.3159
9c
f1 (ppm)


12.6175
7.2596
4.4095
4.3916
4.3796
4.3738
4.3618
4.3440
4.3261
1.3751
1.3572
1.3367
1.3188
1.3010
0.8910
6.0213
9.0000
f1 (ppm)
9d

F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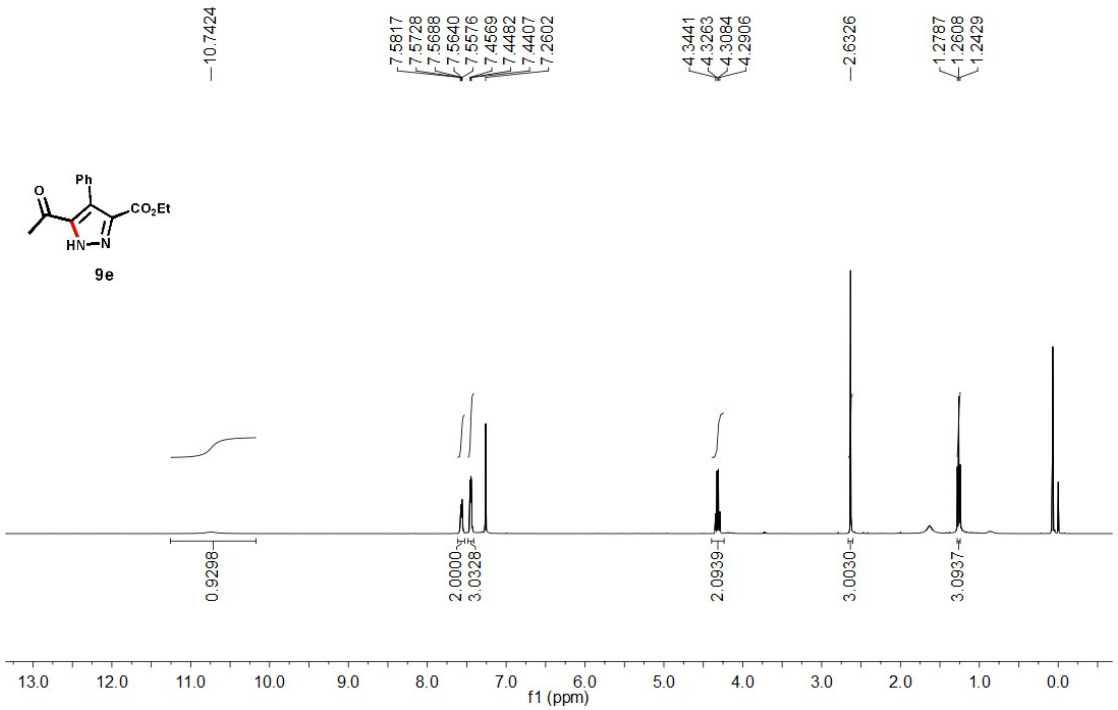
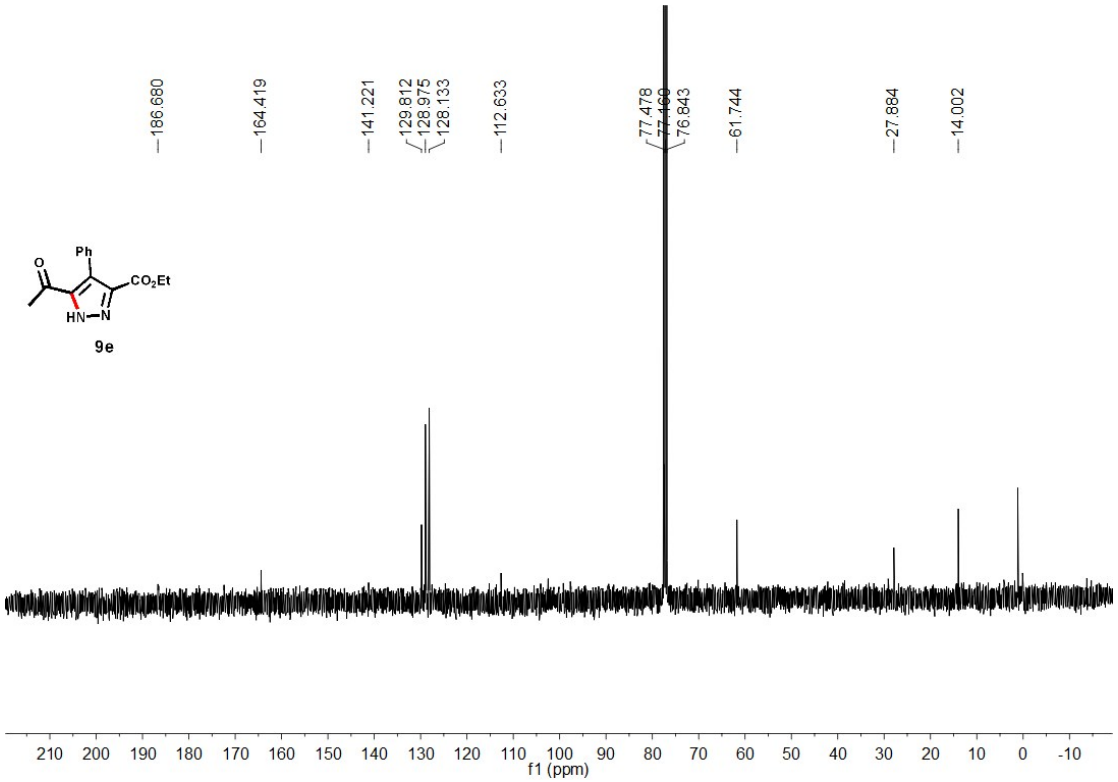
159.337
138.599
119.716
62.200
62.099
14.093
14.047
f1 (ppm)
9d


10.7424
7.5817
7.5728
7.5688
7.5640
7.5576
7.4569
7.4482
7.4407
7.2602
4.3441
4.3263
4.3084
4.2906
2.6326
1.2787
1.2608
1.2429
Ph
O
CO2Et
HN
N
9e
0.9298
2.0000
3.0328
2.0939
3.0030
3.0937
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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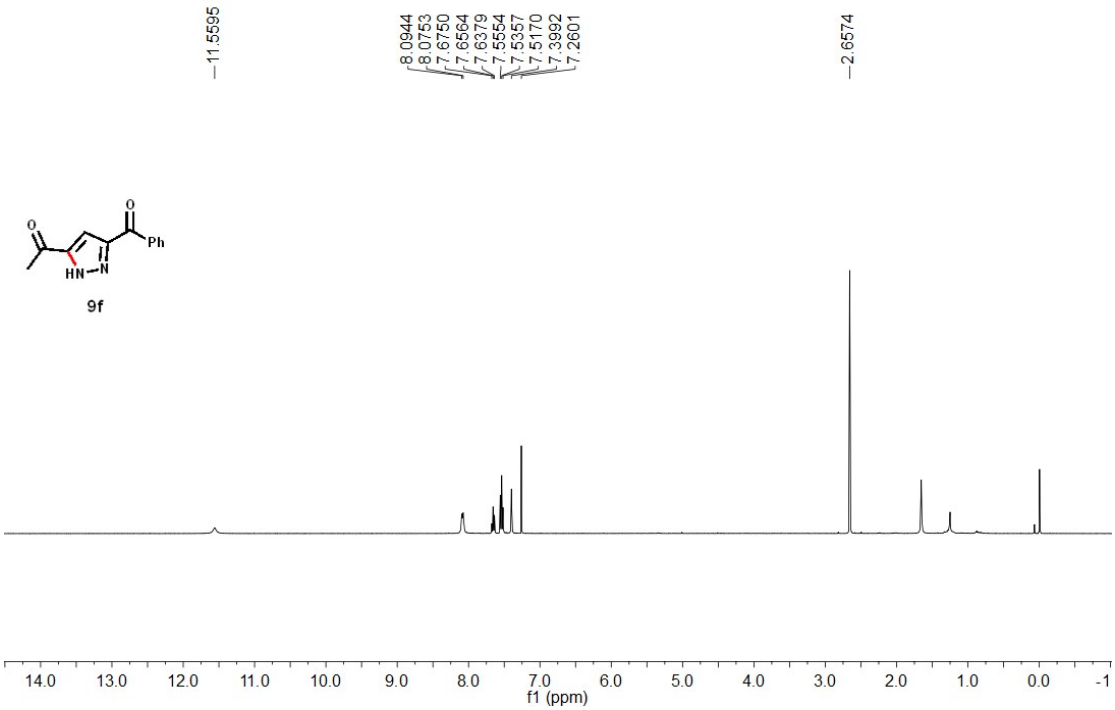
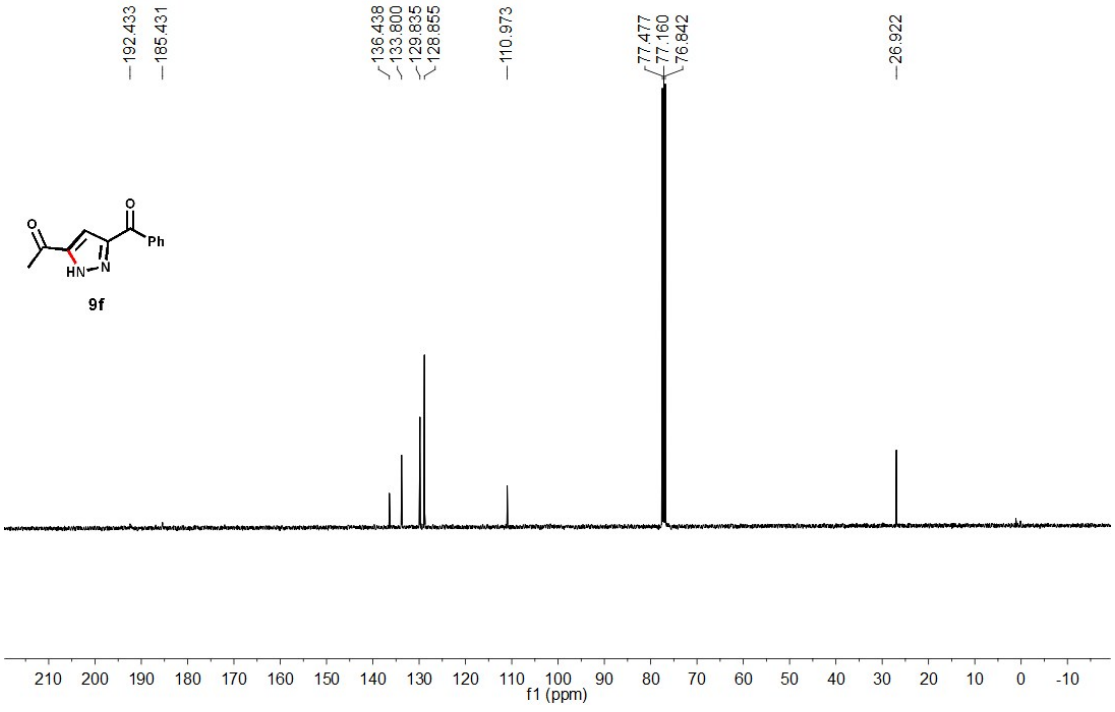
164.419
141.221
129.812
128.975
128.133
112.633
77.478
77.160
76.843
61.744
27.884
14.002
Ph
O
CO2Et
HN
N
9e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


11.5595
8.0944
8.0753
7.6750
7.6564
7.6379
7.5554
7.5357
7.5170
7.3992
7.2601
2.6574
O
O
Ph
HN
N
9f
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1
f1 (ppm)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185.431
136.438
133.800
129.835
128.855
110.973
77.477
77.160
76.842
26.922
O
O
Ph
HN
N
9f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

10. TFMSA@SBA-15 detected by energy dispersive spectrometer (EDS)