Supporting Information

In Situ Generation of Highly Reactive Allenes from Nitrocyclopropanes: Controllable Synthesis of Enynes and Enesters

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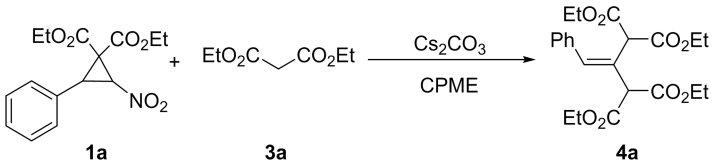
1. General information

NMR data were obtained on Bruker AVANCE 400MHz for ^{1}H at 400 MHz and for ^{13}C at 101 MHz, Bruker AVANCE 500MHz for ^{1}H at 500 MHz and for ^{13}C at 126 MHz, or Bruker AVANCE 600MHz for ^{1}H at 600 MHz and for ^{13}C at 151 MHz with TMS as the internal standard. HRMS data were measured on an Agilent 6120 LC/TOF-MS with ESI source or Waters Premier GC/ TOF-MS with EI source. experiments were conducted using silica gel GF254 (200-300mesh) eluting with ethyl ether and petroleum ether. TLC experiments were carried out on glass-backed silica plates. The commercial supplier of the soybean lecithin is Energy Chemical, the Item No. is E1201331000. Unless otherwise noted, chemicals were used without purification as commercially available.

2. Optimization of reaction conditions[a]

Table S1. Screening of reaction conditions

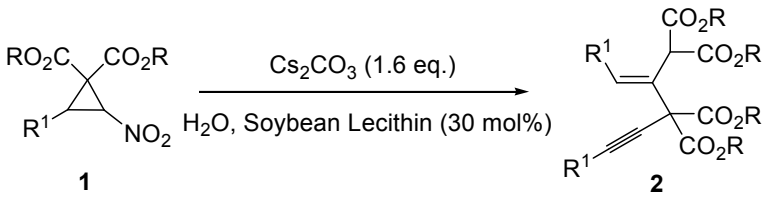


1a **3a** **4a**

entry	base (x eq.)	solvent	yield[b] (%)
1	Cs_2CO_3 (1.0)	Toluene	51
2	Cs_2CO_3 (1.0)	CH_2Cl_2	51
3	Cs_2CO_3 (1.0)	EtOAC	48
4	Cs_2CO_3 (1.0)	THF	57
5	Cs_2CO_3 (1.0)	Et_2O	58
6	Cs_2CO_3 (1.0)	DIPE	53
7	Cs_2CO_3 (1.0)	CPME[c]	55
8	Cs_2CO_3 (1.0)	CH_3CN	n.d
9	Cs_2CO_3 (1.0)	DMF	n.d
10	Cs_2CO_3 (1.0)	Acetone	39
11	Cs_2CO_3 (1.2)	CPME[c]	66
12	Cs_2CO_3 (1.4)	CPME[c]	77
13	Cs_2CO_3 (1.6)	CPME[c]	83
14	Cs_2CO_3 (1.8)	CPME[c]	87
15	Cs_2CO_3 (2.0)	CPME[c]	82

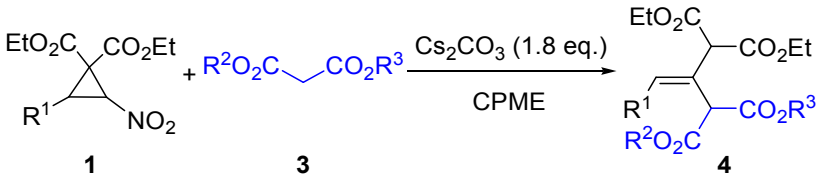
[a]Reaction conditions: **1a** (0.13 mmol), **3a** (0.21 mmol) and Cs_2CO_3 (1 eq., 0.13mmol) were added in a solvent (1.3 mL) , then the resulting mixture was stirred at r.t. for 2h. [b]Isolated yields. [c]Cyclopentyl Methyl Ether.

3. General experimental procedure for synthesis of compounds 2, 4 and 6, and characterization of compounds 2a-2t, 4a-4y and 6



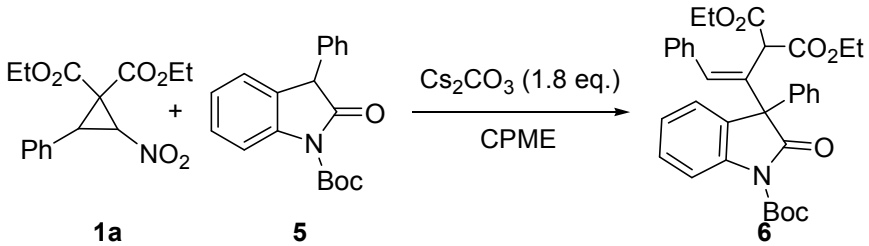
1 2

Conditions: the reactions were conducted in H_2O (1.3 mL) using surfactant soybean lecithin (30 mol%), **1** (0.13 mmol), and Cs_2CO_3 (1.6 eq.) with stirring for 4 h at r.t. After completion, the reaction mixture was dried and concentrated. The residue was purified by flash chromatography to give products **2a-2t** (eluent: petroleum ether-ethyl acetate).



1 3 4

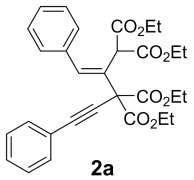
Conditions: the reactions were conducted in CPME (1.3 mL) using **1** (1.6 eq.), **3** (0.13 mmol) and Cs_2CO_3 (1.8 eq.) with stirring for 4 h at room temperature. After completion, the reaction mixture was dried and concentrated. The residue was purified by flash chromatography to give products **4a-4y** (eluent: petroleum ether-ethyl acetate).



1a 5 6

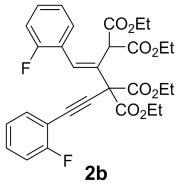
Conditions: the reaction was conducted in CPME (1.3 mL) using **1** (1.6 eq.), **5** (0.13 mmol) and Cs_2CO_3 (1.8 eq.) with stirring for 4 h at room temperature. After completion, the reaction mixture was dried and concentrated. The residue was

purified by flash chromatography to give the product **6** (eluent: petroleum ether-ethyl acetate).



2a

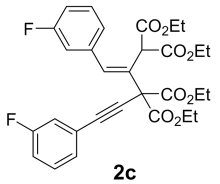
(E)-2-benzylidene-5-phenylpent-4-yne-1,1,3,3-tetracarboxylate, yield: 28.0 mg, 82.8%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 5H), 7.35 – 7.30 (m, 5H), 7.28 (s, 1H), 4.74 (s, 1H), 4.41 – 4.23 (m, 4H), 4.05 – 3.84 (m, 4H), 1.36 (t, J = 7.0 Hz, 6H), 1.14 (t, J = 7.0 Hz, 6H); 13C NMR (126 MHz, $CDCl_3$) δ 167.5(×2), 167.0(×2), 135.8, 131.8(×2), 128.7, 128.6(×2), 128.2(×2), 128.0(×2), 127.9, 127.8, 122.4, 88.8, 83.3, 62.9(×2), 62.2, 61.5(×2), 53.5, 13.9(×2), 13.8(×2). RMS (ESI+) calcd for $[C_{30}H_{32}O_8 + Na]^+$ *m/z* 543.2198, found 543.2002.



2b

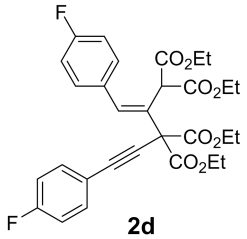
(E)-2-(2-fluorobenzylidene)-5-(2-fluorophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 25.0 mg, 69.2%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.74 – 7.47 (m, 2H), 7.42 (s, 1H), 7.37 – 7.21 (m, 2H), 7.15 – 6.98 (m, 4H), 4.74 (s, 1H), 4.37 – 4.30 (m, 4H), 4.03 – 3.84 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H), 1.16 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.3(×2), 166.5(×2), 163.1 ($^{1}J_{C\text{-}F}$ = 253.1 Hz), 160.0 ($^{1}J_{C\text{-}F}$ = 249.0 Hz), 133.7, 131.7 ($^{4}J_{C\text{-}F}$ = 3.3 Hz), 130.9 ($^{4}J_{C\text{-}F}$ = 2.4 Hz), 130.5 ($^{3}J_{C\text{-}F}$ = 7.8 Hz), 129.9 ($^{3}J_{C\text{-}F}$ = 8.1 Hz), 129.5, 123.8 ($^{3}J_{C\text{-}F}$ = 3.9 Hz), 123.6 ($^{3}J_{C\text{-}}$

$_F$ = 3.7 Hz), 123.5 ($^2J_{C\text{-}F}$ = 14.5 Hz), 115.5 ($^2J_{C\text{-}F}$ = 20.8 Hz), 114.8 ($^2J_{C\text{-}F}$ = 21.0 Hz), 111.0 ($^2J_{C\text{-}F}$ = 15.6 Hz), 88.2 ($^3J_{C\text{-}F}$ = 3.3 Hz), 82.6, 63.0(×2), 62.3, 61.6(×2), 53.7, 13.8(×2), 13.7(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}F_2O_8 + Na]^+$ *m/z* 579.1809, found 579.1813.



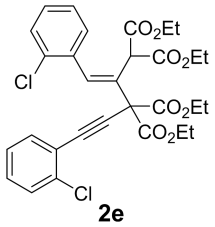
2c

(E)-2-(3-fluorobenzylidene)-5-(3-fluorophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 22.1 mg, 61.2%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 4H), 7.23 – 7.17 (m, 3H), 7.08 – 7.03 (m, 1H), 7.01 – 6.95 (m, 1H), 4.71 (s, 1H), 4.36 – 4.31 (m, 4H), 4.04 – 3.92 (m, 4H), 1.36 (t, *J* = 7.00 Hz, 6H), 1.17 (t, *J* = 7.00 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.2(×2), 166.6(×2), 163.3 ($^1J_{C\text{-}F}$ = 16.3 Hz), 161.3 ($^1J_{C\text{-}F}$ = 17.0 Hz), 137.7 ($^3J_{C\text{-}F}$ = 7.9 Hz), 136.8, 129.9 ($^3J_{C\text{-}F}$ = 8.7 Hz), 129.6 ($^3J_{C\text{-}F}$ = 8.4 Hz), 128.8, 127.7 ($^4J_{C\text{-}F}$ = 3.0 Hz), 124.4 ($^4J_{C\text{-}F}$ = 2.9 Hz), 124.1 $^3J_{C\text{-}F}$ = 9.7 Hz), 118.6 ($^2J_{C\text{-}F}$ = 23.1 Hz), 116.2 ($^2J_{C\text{-}F}$ = 21.3 Hz), 115.6 ($^2J_{C\text{-}F}$ = 22.2 Hz), 114.7 ($^2J_{C\text{-}F}$ = 21.2 Hz), 87.6 ($^4J_{C\text{-}F}$ = 3.4 Hz), 84.0, 63.1(×2), 62.0, 61.6(×2), 53.4, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}F_2O_8 + Na]^+$ *m/z* 579.1809, found 579.1811.



2d

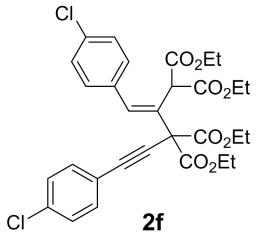
(E)-2-(4-fluorobenzylidene)-5-(4-fluorophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 26.1 mg, 72.2%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 – 7.40 (m, 4H), 7.33 – 7.26 (m, 1H), 7.06 – 6.97 (m, 4H), 4.69 (s, 1H), 4.38 – 4.28 (m, 4H), 4.01 – 3.87 (m, 4H), 1.35 (t, J = 7.00 Hz, 6H), 1.15 (t, J = 7.00 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.4(×2), 166.8(×2), 163.6 ($^{1}J_{C\text{-}F}$ = 52.7 Hz), 161.6 ($^{1}J_{C\text{-}F}$ = 49.9 Hz), 136.9, 133.8 ($^{3}J_{C\text{-}F}$ = 8.3 Hz) (×2), 131.6 ($^{3}J_{C\text{-}F}$ = 3.4 Hz), 130.6 ($^{3}J_{C\text{-}F}$ = 8.2 Hz) (×2), 128.1, 118.4, 115.6 ($^{2}J_{C\text{-}F}$ = 22.1 Hz) (×2), 114.9 ($^{2}J_{C\text{-}F}$ = 21.4 Hz) (×2), 87.8, 82.9, 63.0(×2), 62.1, 61.6(×2), 53.5, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}F_2O_8 + Na]^+$ *m/z* 579.1809, found 579.1812.



2e

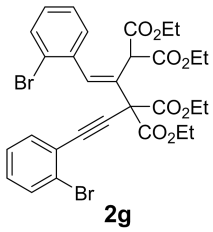
(E)-2-(2-chlorobenzylidene)-5-(2-chlorophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 26.1 mg, 68.4%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83 – 7.77 (m, 1H), 7.56 – 7.49 (m, 2H), 7.42 – 7.33 (m, 2H), 7.30 – 7.18 (m, 4H), 4.71 (s, 1H), 4.38 – 4.31 (m, 4H), 4.09 – 3.73 (m, 4H), 1.36 (t, J = 7.0 Hz, 6H), 1.16 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.4(×2), 166.5(×2), 136.4, 135.9, 134.0, 133.8, 133.6, 130.9, 129.7, 129.4, 129.2, 128.7, 128.6, 126.4, 126.3, 122.3,

88.1, 85.9, 63.0(×2), 62.3, 61.6(×2), 53.7, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}Cl_2O_8 + Na]^+$ *m/z* 611.1220, found 611.1224.



2f

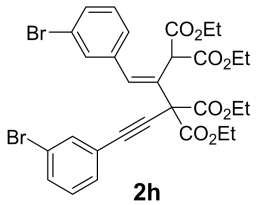
(E)-2-(4-chlorobenzylidene)-5-(4-chlorophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 21.7 mg, 56.9%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.42 (m, 2H), 7.40 (s, 1H), 7.38 (s, 1H), 7.34 – 7.27 (m, 4H), 7.29 – 7.27 (m, 1H), 4.68 (s, 1H), 4.37 – 4.29 (m, 4H), 4.03 – 3.85 (m, 4H), 1.35 (t, *J* = 7.00 Hz, 6H), 1.15 (t, *J* = 7.00 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.3(×2), 166.6(×2), 136.8, 134.9, 134.0, 133.9, 133.1(×2), 130.1(×2), 128.6(×2), 128.6, 128.2(×2), 120.7, 87.8, 84.1, 63.1(×2), 62.2, 61.6(×2), 53.5, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}Cl_2O_8 + Na]^+$ *m/z* 611.1220, found 611.1226.



2g

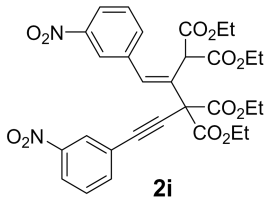
(E)-2-(2-bromobenzylidene)-5-(2-bromophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 29.6 mg, 67.4%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 – 7.53 (m, 4H), 7.47 (s, 1H), 7.29 – 7.24 (m, 2H), 7.22 – 7.11 (m, 2H), 4.70 (s, 1H), 4.38 – 4.30 (m, 4H), 4.01 – 3.81 (m, 4H), 1.37 (t, *J* = 7.00 Hz, 6H), 1.17 (t, *J* =

7.00 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.3(×2), 166.4(×2), 137.8, 135.7, 133.8, 132.4, 131.9, 131.1, 129.9, 129.5, 128.2, 126.9(×2), 125.8, 124.6, 124.0, 87.5, 87.5, 63.0(×2), 62.2, 61.6(×2), 53.8, 14.0(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}Br_2O_8 + Na]^+$ *m/z* 701.0307, found 701.0314.



2h

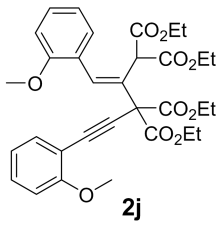
(E)-2-(3-bromobenzylidene)-5-(3-bromophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 26.0 mg, 59.2%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.66 – 7.57 (m, 2H), 7.52 – 7.38 (m, 4H), 7.32 – 7.16 (m, 3H), 4.68 (s, 1H), 4.37 – 4.29 (m, 4H), 4.09 – 3.88 (m, 4H), 1.36 (t, *J* = 7.0 Hz, 6H), 1.18 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.2(×2), 166.5(×2), 137.7, 136.5, 134.5, 132.0, 131.4, 130.8, 130.4, 129.7, 129.6, 129.1, 127.4, 124.2, 122.1, 122.0, 87.4, 84.4, 63.1(×2), 62.1, 61.7(×2), 53.5, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}Br_2O_8 + Na]^+$ *m/z* 701.0307, found 701.0311.



2i

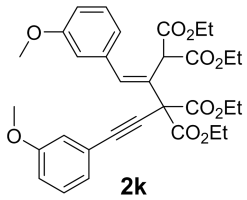
(E)-2-(3-nitrobenzylidene)-5-(3-nitrophenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 17.2 mg, 43.5%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 – 8.09 (m, 4H), 7.87 – 7.80 (m, 2H), 7.59 – 7.48 (m, 2H), 7.28 (s, 1H), 4.69 (s,

1H), 4.40 – 4.33 (m, 4H), 4.13 – 3.78 (m, 4H), 1.38 (t, J = 7.0 Hz, 6H), 1.18 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.0(×2), 166.1(×2), 148.1, 147.9, 137.6, 137.1, 135.6, 135.0, 130.3, 129.5, 129.1, 126.7, 123.9, 123.7(×2), 122.8, 86.8, 85.5, 63.4(×2), 62.2, 62.0(×2), 53.5, 14.0(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{30}H_{30}N_2O_{12} + Na]^+$ *m/z* 633.1701, found 633.1707.



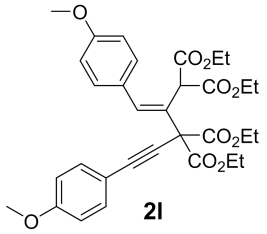
2j

(E)-2-(2-methoxybenzylidene)-5-(2-methoxyphenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 31.0 mg, 82.3%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.67 (dt, J = 6.7, 0.8 Hz, 1H), 7.49 (s, 1H), 7.48 – 7.44 (m, 1H), 7.32 – 7.21 (m, 2H), 6.93 – 6.86 (m, 2H), 6.84 (dd, J = 18.6, 8.3 Hz, 2H), 4.80 (s, 1H), 4.36 – 4.28 (m, 4H), 3.97 – 3.89 (m, 2H), 3.88 – 3.76 (m, 8H), 1.35 (t, J = 7.0 Hz, 6H), 1.13 (t, J = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.8(×2), 167.1(×2), 160.7, 157.2, 134.7, 133.7, 130.3, 129.9, 129.4, 127.2, 125.0, 120.3, 120.0, 112.1, 111.1, 110.1, 87.4, 85.3, 62.6(×2), 62.4, 61.2(×2), 55.8, 55.5, 53.9, 13.8(×2), 13.7(×2). HRMS (ESI+) calcd for $[C_{32}H_{36}O_{10} + Na]^+$ *m/z* 603.2208, found 603.2214.



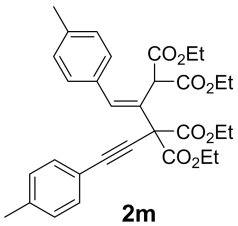
2k

(E)-2-(3-methoxybenzylidene)-5-(3-methoxyphenyl)pent-4-yne-1,1,3,3-tetracarboxylate, 26.1 mg, 69.1%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.18 (m, 1), 7.18 – 7.02 (m, 5H), 6.99 – 6.79 (m, 3H), 4.75 (s, 1H), 4.38 – 4.29 (m, 4H), 4.00 – 3.88 (m, 4H), 3.81 (s, 3H), 3.80 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6(×2), 166.9(×2), 159.2, 159.2, 138.0, 137.0, 129.3, 128.9, 127.9, 124.4, 123.4, 120.9, 116.6, 115.4, 114.3, 113.4, 88.7, 83.1, 62.9(×2), 62.2, 61.5(×2), 55.3, 55.2, 53.6, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{32}H_{36}O_{10} + Na]^+$ *m/z* 603.2208, found 603.2210.



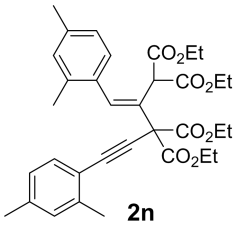
2l

(E)-2-(4-methoxybenzylidene)-5-(4-methoxyphenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 28.1 mg, 74.3%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 7.25 (m, 5H), 6.88 – 6.79 (m, 4H), 4.74 (s, 1H), 4.36 – 4.28 (m, 4H), 4.03 – 3.90 (m, 4H), 3.82 (s, 3H), 3.80 (s, 3H), 1.34 (t, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.7(×2), 167.2(×2), 159.9, 159.2, 137.5, 133.3(×2), 130.1(×2), 128.2, 126.8, 114.6, 113.8(×2), 113.3(×2), 88.7, 82.0, 62.8(×2), 62.3, 61.4(×2), 55.3, 55.2, 53.6, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{32}H_{36}O_{10} + Na]^+$ *m/z* 603.2210, found 603.2213.



2m

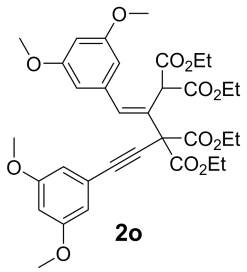
(E)-2-(4-methylbenzylidene)-5-(p-tolyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 29.0 mg, 81.5%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.10 (m, 9H), 4.74 (s, 1H), 4.36 – 4.29 (m, 4H), 4.02 – 3.88 (m, 4H), 2.36 (s, 3H), 2.33 (s, 3H), 1.35 (t, *J* = 7.0 Hz, 6H), 1.14 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6(×2), 167.1(×2), 138.8, 137.9, 137.5, 132.8, 131.7(×2), 128.9(×2), 128.6(×2), 128.6(×2), 127.4, 119.4, 88.8, 82.6, 62.8(×2), 62.1, 61.4(×2), 53.5, 21.5, 21.2, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{32}H_{36}O_8 + Na]^+$ *m/z* 571.2303, found 571.2309.



2n

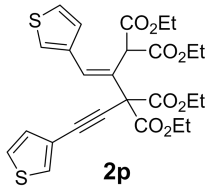
(E)-2-(2,4-dimethylbenzylidene)-5-(2,4-dimethylphenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 31.2 mg, 83.2%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.24 (m, 3H), 7.03 – 6.91 (m, 4H), 4.61 (s, 1H), 4.36 – 4.31 (m, 4H), 3.95 – 3.83 (m, 4H), 2.44 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 1.36 (t, *J* = 7.00 Hz, 6H), 1.14 (t, *J* = 7.00 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.4(×2), 167.3(×2), 140.7, 138.7, 137.7(×2), 136.6, 132.2, 131.9, 130.2, 130.1, 128.7, 127.9, 126.2, 126.0,

119.3, 87.9, 86.4, 62.8(×2), 62.0, 61.3(×2), 53.5, 21.43, 21.1, 20.4, 19.7, 14.0(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{34}H_{40}O_8 + Na]^+$ *m/z* 599.2622, found 599.2626.



2o

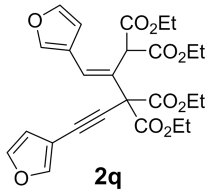
(E)-2-(3,5-dimethoxybenzylidene)-5-(3,5-dimethoxyphenyl)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 35.7 mg, 85.8%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 – 6.62 (m, 5H), 6.49 – 6.34 (m, 2H), 4.76 (s, 1H), 4.37 – 4.28 (m, 4H), 4.04 – 3.87 (m, 4H), 3.79 (s, 6H), 3.78 (s, 6H), 1.35 (t, *J* = 7.1 Hz, 6H), 1.16 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.6(×2), 166.9(×2), 160.4(×2), 160.4(×2), 138.0, 137.5, 128.0, 123.6, 109.7(×2), 106.2(×2), 102.2, 100.8, 88.7, 82.7, 62.9(×2), 62.1, 61.6(×2), 55.4(×2), 55.3(×2), 53.7, 13.9(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{34}H_{40}O_{12} + Na]^+$ *m/z* 633.2428, found 633.2430.



2p

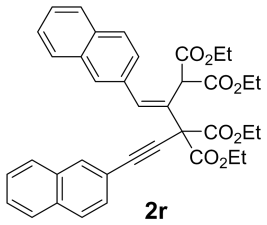
(E)-5-(thiophen-3-yl)-2-(thiophen-3-ylmethylene)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 21.0 mg, 60.7%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 – 6.28 (m, 8H), 4.37 – 4.18 (m, 4H), 4.17 – 3.92 (m, 4H), 1.29 (t, *J* = 7.0 Hz, 6H), 1.00 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.4(×2), 167.1(×2), 150.7,

147.7, 142.7(×2), 135.3, 131.4, 125.5, 119.9, 112.5, 111.6(×2), 111.1, 69.92, 68.4, 62.2(×2), 61.6(×2), 14.0(×2), 13.6(×2). HRMS (ESI+) calcd for $[C_{26}H_{28}O_8S_2 + Na]^+$ *m/z* 555.1129, found 555.1131.



2q

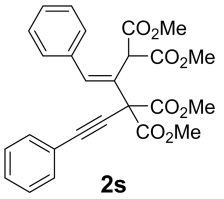
(E)-5-(furan-3-yl)-2-(furan-3-ylmethylene)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 21.2 mg, 65.2%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 – 6.90 (m, 7H), 6.45 (s, 1H), 4.38 – 4.19 (m, 4H), 4.10 – 3.95 (m, 4H), 1.31 (t, *J* = 7.0 Hz, 6H), 1.01 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3(×2), 166.9(×2), 139.5, 137.7, 135.9, 133.1, 129.0, 127.6, 127.5(×2), 127.4, 126.8, 125.8, 125.0, 70.3, 69.5, 62.2(×2), 61.9(×2), 14.1(×2), 13.5(×2). HRMS (ESI+) calcd for $[C_{26}H_{28}O_{10} + Na]^+$ *m/z* 523.0774, found 523.0779.



2r

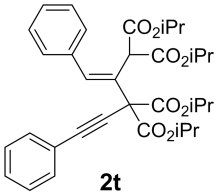
(E)-5-(naphthalen-2-yl)-2-(naphthalen-2-ylmethylene)pent-4-yne-1,1,3,3-tetracarboxylate, yield: 22.2 mg, 55.0%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 – 8.04 (m, 2H), 7.85 – 7.78 (m, 6H), 7.61 – 7.55 (m, 2H), 7.53 – 7.45 (m, 5H), 4.84 (s, 1H), 4.44 – 4.35 (m, 4H), 3.93 – 3.84 (m, 4H), 1.40 (t, *J* = 7.0 Hz, 6H), 1.09 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.5(×2), 167.0(×2), 138.0, 133.2,

133.0, 132.9, 132.8, 132.7, 132.0, 128.4(×2), 128.3, 127.9, 127.8(×2), 127.7, 127.5(×2), 126.8, 126.6, 126.5, 126.2(×2), 119.7, 89.1, 83.6, 63.0, 62.3(×2), 61.5(×2), 53.7, 14.0(×2), 13.7(×2). HRMS (ESI+) calcd for $[C_{38}H_{36}O_8 + Na]^+$ *m/z* 643.2306, found 643.2308.



2s

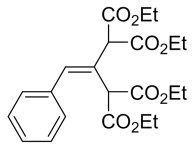
(E)-2-benzylidene-5-phenylpent-4-yne-1,1,3,3-tetracarboxylate, yield: 20.1 mg, 66.7%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 – 7.48 (m, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.29 (m, 6H), 7.28 (s, 1H), 4.76 (s, 1H), 3.88 (s, 5H), 3.85 (s, 1H), 3.51 (s, 5H), 3.44 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.9(×2), 167.5(×2), 138.3, 135.4, 131.9(×2), 128.9, 128.6(×2), 128.2(×2), 128.0(×2), 127.9, 127.6, 122.0, 89.2, 82.6, 53.9(×2), 53.3, 53.0, 52.5(×2). HRMS (ESI+) calcd for $[C_{26}H_{24}O_8 + Na]^+$ *m/z* 487.1368, found 487.1370



2t

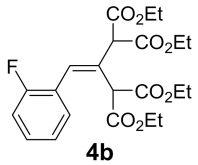
(E)-2-benzylidene-5-phenylpent-4-yne-1,1,3,3-tetracarboxylate, yield: 16.3 mg, 43.5%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 – 7.42 (m, 4H), 7.35 – 7.25 (m, 7H), 5.19 – 5.13 (m, 2H), 4.84 – 4.78 (m, 2H), 4.68 (s, 1H), 1.36 – 1.33 (m, 12H), 1.15 – 1.10 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.9(×2), 166.4(×2), 137.8,

136.1, 131.8(×2), 128.7(×2), 128.5, 128.2(×2), 128.0(×2), 128.0, 127.7, 122.8, 88.3, 83.9, 70.5(×2), 69.2(×2), 54.0, 29.7, 21.6(×2), 21.5(×2), 21.5(×2), 21.4(×2). HRMS (ESI+) calcd for $[C_{34}H_{40}O_8 + Na]^+$ *m/z* 599.2614, found 599.2628.



4a

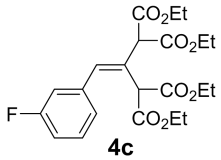
2-benzylidenepropane-1,1,3,3-tetracarboxylate, yield: 46.7 mg, 87.3%; off wite oil; 1H NMR (500 MHz, $CDCl_3$): δ 7.40 – 7.26 (m, 5H), 7.17 (s, 1H), 4.80 (s, 1H), 4.65 (s, 1H), 4.31 – 4.16 (m, 8H), 1.33 – 1.25 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.2(×2), 167.4(×2), 137.7, 135.7, 128.8(×2), 128.4(×2), 127.7, 125.1, 61.9(×2), 61.7(×2), 54.2, 53.2, 14.0 (×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{28}O_8 + Na]$+ m/z 296.0754, found 296.0758.



4b

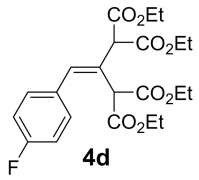
2-(2-fluorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 45.4 mg, 79.7%; off wite oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.34 – 7.05 (m, 3H), 7.01 (s, 1H), 7.01 – 6.98 (m, 1H), 4.60 (s, 1H), 4.56 (s, 1H), 4.41 – 3.91 (m, 8H), 1.26 – 1.15 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9(×2), 167.2(×2), 160.2 (d, $^1J_{C\text{-}F}$ = 166.4 Hz), 131.0 (d, $^3J_{C\text{-}F}$ = 1.9 Hz), 130.5 (d, $^4J_{C\text{-}F}$ = 1.8 Hz), 129.9 (d, $^3J_{C\text{-}F}$ = 5.4 Hz), 127.3, 124.0 (d, $^3J_{C\text{-}F}$ = 2.5 Hz), 123.4 (d, $^2J_{C\text{-}F}$ = 10.0 Hz), 115.6 (d, $^2J_{C\text{-}F}$ = 14.5 Hz),

62.0(×2), 61.8(×2), 54.4, 53.8, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}FO_8 + Na]^+$ *m/z* 461.1596, found 461.1598.



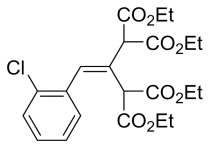
4c

2-(3-fluorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 38.9 mg, 68.3%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 6.97 (m, 5H), 4.75 (s, 1H), 4.65 (s, 1H), 4.30 – 4.15 (m, 8H), 1.38 – 1.18 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0(×2), 167.2(×2), 162.7 (d, $^1J_{C\text{-}F}$ = 247.5 Hz), 137.7 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 136.5 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 130.0 (d, $^3J_{C\text{-}F}$ = 8.5 Hz), 126.2, 124.6 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 115.7 (d, $^2J_{C\text{-}F}$ = 22.0 Hz), 114.7 (d, $^2J_{C\text{-}F}$ = 21.1 Hz), 62.0(×2), 61.8(×2), 54.2, 53.2, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}FO_8 + Na]^+$ *m/z* 461.1596, found 461.1609.



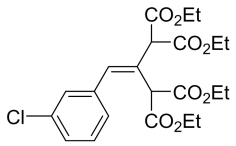
4d

2-(4-fluorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 44.2 mg, 77.6%; off wite oil; 1H NMR (400 MHz, Chloroform-*d*): δ 7.39 – 7.33 (m, 2H), 7.12 (s, 1H), 7.10 – 7.04 (m, 2H), 4.73 (s, 1H), 4.64 (s, 1H), 4.37 – 4.06 (m, 8H), 1.51 – 1.11 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1(×2), 167.3(×2), 162.3 (d, $^1J_{C\text{-}F}$ = 165.7 Hz), 136.8, 131.6 (d, $^4J_{C\text{-}F}$ = 2.3 Hz), 130.6 (d, $^3J_{C\text{-}F}$ = 5.4 Hz) (×2), 125.3, 115.4 (d, $^2J_{C\text{-}F}$ = 14.3 Hz) (×2), 62.0(×2), 61.8(×2), 54.2, 53.1, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}FO_8 + Na]^+$ *m/z* 461.1596, found 461.1608.



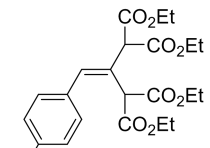
4e

2-(2-chlorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 42.3 mg, 71.7%; off wite oil; ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.46 – 7.25 (m, 4H), 7.14 (s, 1H), 4.68 (s, 1H), 4.57 (s, 1H), 4.32 – 4.15 (m, 8H), 1.39 – 1.19 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9(×2), 167.1(×2), 135.3, 134.3, 134.1, 130.4, 129.5, 129.3, 126.7, 126.7, 61.9(×2), 61.8(×2), 54.3, 53.6, 14.1(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}ClO_8 + Na]^+$ *m/z* 477.1296, found 477.1301.



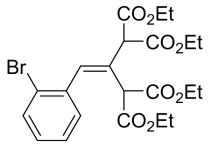
4f

2-(3-chlorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 50.2 mg, 85.1%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (s, 1H), 7.34 – 7.22 (m, 3H), 7.11 (s, 1H), 4.71 (s, 1H), 4.65 (s, 1H), 4.41 – 4.15 (m, 8H), 1.46 – 1.12 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0(×2), 167.2(×2), 137.4, 136.4, 134.4, 129.8, 128.9, 127.9, 127.0, 126.5, 62.0(×2), 61.8(×2), 54.2, 53.2, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}ClO_8 + Na]^+$ *m/z* 477.1296, found 477.1305.



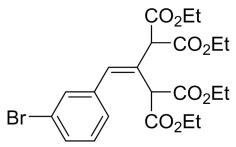
4g

2-(4-chlorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 47.9 mg, 81.2%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.28 (m, 4H), 7.11 (s, 1H), 4.70 (s, 1H), 4.64 (s, 1H), 4.29 – 4.16 (m, 8H), 1.63 – 0.89 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.1(×2), 167.2(×2), 136.6, 134.1, 133.8, 130.2(×2), 128.7(×2), 125.87, 62.0(×2), 61.8(×2), 54.2, 53.1, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}ClO_8 + Na]^+$ *m/z* 477.1296, found 477.1302.



4h

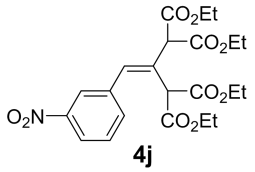
2-(2-bromobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 51.1 mg, 78.9%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 – 7.16 (m, 4H), 7.08 (s, 1H), 4.67 (s, 1H), 4.55 (s, 1H), 4.31 – 4.13 (m, 8H), 1.42 – 1.17 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9(×2), 167.1(×2), 137.2, 136.2, 132.7, 130.5, 129.4, 127.3, 126.4, 124.1, 61.9(×2), 61.8(×2), 54.2, 53.6, 14.1(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}BrO_8 + Na]^+$ *m/z* 521.0777, found 521.0781.



4i

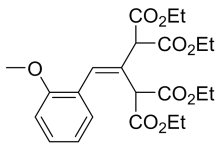
2-(3-bromobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 49.2 mg, 76.0%; off wite oil; 1H NMR (500 MHz, $CDCl_3$) δ 7.58 – 7.21 (m, 5H), 7.10 (s, 1H), δ 4.69 (s, 1H), 4.64 (s, 1H).4.28 – 4.16 (m, 8H), 1.32 – 1.27 (m, 12H); ^{13}C NMR (101

MHz, $CDCl_3$): δ 167.9(×2), 167.2(×2), 137.6, 136.3, 131.7, 130.8, 130.0, 127.4, 126.5, 122.5, 62.0(×2), 61.8(×2), 54.2, 53.2, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}BrO_8 + Na]^+$ *m/z* 521.0777, found 521.0783.



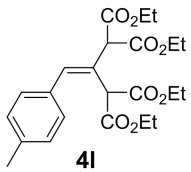
4j

2-(3-nitrobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 46.8 mg, 77.4%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 8.24 – 7.51 (m, 3H), 7.21 (s, 1H), 4.70 (s, 1H), 4.64 (s, 1H), 4.32 – 4.18 (m, 8H), 1.39 – 1.26 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8(×2), 166.9(×2), 148.3, 137.2, 135.4, 135.0, 129.5, 127.9, 123.8, 122.7, 62.3(×2), 62.0(×2), 54.2, 53.1, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{27}NO_{10} + Na]^+$ *m/z* 488.1547, found 488.1550.



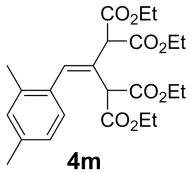
4k

2-(2-methoxybenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 52.7 mg, 90.1%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.25 (m, 2H), 7.12 (s, 1H), 7.00 – 6.86 (m, 2H), 4.72 (s, 1H), 4.68 (s, 1H), 4.39 – 4.00 (m, 8H), 3.79 (s, 3H), 1.57 – 0.97 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3(×2), 167.6(×2), 157.4, 134.0, 130.8, 129.4, 124.8, 124.7, 120.4, 110.9, 61.7(×2), 61.6(×2), 55.6, 54.4, 53.7, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{23}H_{30}O_9 + Na]^+$ *m/z* 473.1801, found 473.1804.



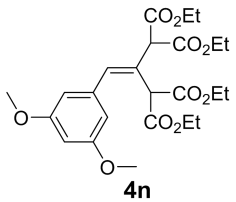
4l

2-(4-methylbenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 50.2 mg, 89.0%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 4H), 7.13 (s, 1H), 4.82 (s, 1H), 4.64 (s, 1H), 4.33 – 4.15 (m, 8H), 2.37 (s, 3H), 1.39 – 1.18 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3(×2), 167.5(×2), 137.7, 137.6, 132.8, 129.1(×2), 128.7(×2), 124.5, 61.8(×2), 61.7(×2), 54.2, 53.2, 21.2, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{23}H_{30}O_8 + Na]^+$ *m/z* 457.1838, found 457.1856.



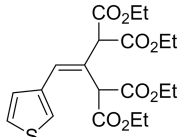
4m

2-(2,4-dimethylbenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 51.4 mg, 88.3%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.08 (m, 3H), 7.04 (s, 1H), 4.64 (s, 1H), 4.59 (s, 1H), 4.36 – 4.10 (m, 8H), 2.34 (s, 3H), 2.26 (s, 3H), 1.51 – 1.11 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.3(×2), 167.5(×2), 137.7, 137.6, 136.8, 132.2, 130.7, 128.5, 126.4, 125.2, 61.7(×2), 61.6(×2), 54.2, 53.5, 21.2, 19.7, 14.1(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{24}H_{32}O_8 + Na]^+$ *m/z* 471.1995, found 471.2010.



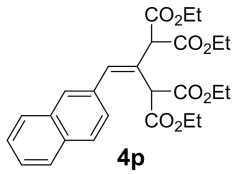
4n

2-(3,5-dimethoxybenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 52.6 mg, 84.3%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11 (s, 1H), 6.55 (s, 2H), 6.42 (s, 1H), 4.88 (s, 1H), 4.64 (s, 1H), 4.28 – 4.16 (m, 8H), 3.80 (s, 6H), 1.44 – 1.11 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2(×2), 167.4(×2), 160.7(×2), 137.8, 137.5, 125.3, 106.5(×2), 100.6, 61.9(×2), 61.7(×2), 55.4(×2), 54.1, 53.3, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{24}H_{32}O_{10} + Na]^+$ *m/z* 503.1893, found 503.1906.



4o

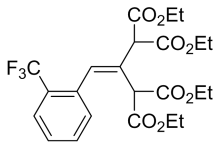
2-(thiophen-3-ylmethylene)propane-1,1,3,3-tetracarboxylate yield: 42.5 mg, 76.7%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 – 7.21 (m, 2H), 7.14 (s, 1H), 7.08 – 7.04 (m, 1H), 5.13 (s, 1H), 4.64 (s, 1H), 4.31 – 4.11 (m, 8H), 1.39 – 1.20 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.0(×2), 167.2(×2), 137.8, 129.8, 129.0, 127.4, 126.8, 123.6, 62.0(×2), 61.8(×2), 54.4, 53.8, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{20}H_{26}O_8S + Na]^+$ *m/z* 499.1246, found 499.1252.



4p

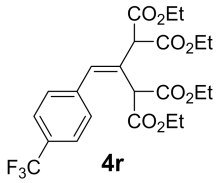
2-(naphthalen-1-ylmethylene)propane-1,1,3,3-tetracarboxylate, yield: 46.4 mg, 75.9%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 – 7.44 (m, 7H), 7.34 (s, 1H), 4.92 (s, 1H), 4.73 (s, 1H), 4.33 – 4.15 (m, 8H), 1.49 – 1.19 (m, 12H); ^{13}C NMR (101

MHz, $CDCl_3$): δ 168.2(×2), 167.5(×2), 137.8, 133.2, 133.2, 132.7, 128.2, 128.1, 127.9, 127.7, 126.8, 126.3(×2), 125.5, 61.9(×2), 61.8(×2), 54.3, 53.3, 14.1(×2), 14.0(×2). HRMS (ESI+) calcd for $[C_{26}H_{30}O_8 + Na]^+$ *m/z* 493.1838, found 493.1852.



4q

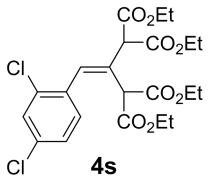
2-(2-(trifluoromethyl)benzylidene)propane-1,1,3,3-tetracarboxylate, yield: 42.4 mg, 66.8%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.27 (m, 4H), 7.27 (s, 1H), 4.68 (s, 1H), 4.40 (s, 1H), 4.30 – 4.11 (m, 8H), 1.35 – 1.18 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8(×2), 167.0(×2), 134.5, 131.8, 130.8, 128.8 ($^2J_{C\text{-}F}$ = 40.4 Hz, 20.3 Hz), 128.0, 127.4, 126.0 ($^3J_{C\text{-}F}$ = 7.0 Hz, 3.5 Hz) (×2), 123.8 ($^1J_{C\text{-}F}$ = 366.5 Hz, 183.3 Hz), 61.9(×2), 61.8(×2), 54.1, 53.9, 14.0(×2), 13.8(×2). HRMS (ESI+) calcd for $[C_{23}H_{27}F_3O_8 + Na]^+$ *m/z* 511.1580, found 511.1584.



4r

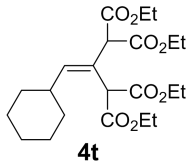
2-(4-(trifluoromethyl)benzylidene)propane-1,1,3,3-tetracarboxylate, yield: 50.9 mg, 80.2%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 – 7.44 (m, 4H), 7.19 (s, 1H), 4.67 (d, *J* = 2.0 Hz, 2H), 4.31 – 4.09 (m, 8H), 1.46 – 1.15 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.9(×2), 167.1(×2), 139.3, 136.4, 129.8 ($^2J_{C\text{-}F}$ = 21.7 Hz, 40.3 Hz),129.1(×2), 127.0, 125.4 ($^3J_{C\text{-}F}$ = 5.1 Hz, 2.5 Hz) (×2), 124.1 ($^1J_{C\text{-}F}$ = 364.1 Hz,

182.1 Hz), 62.1(×2), 61.9(×2), 54.2, 53.2, 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{23}H_{27}F_3O_8 + Na]^+$ *m/z* 511.1580, found 511.1583.



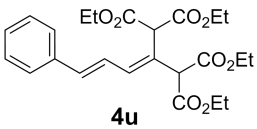
4s

2-(2,4-dichlorobenzylidene)propane-1,1,3,3-tetracarboxylate, yield: 51.2 mg, 80.7%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 – 7.24 (m, 3H), 7.06 (s, 1H), 4.67 (s, 1H), 4.49 (s, 1H), 4.35 – 4.05 (m, 8H), 1.39 – 1.19 (m, 12H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8(×2), 166.9(×2), 134.9, 134.5, 134.2, 132.8, 131.2, 129.4, 127.5, 127.1, 62.0(×2), 61.9(×2), 54.3, 53.6, 14.1(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{26}Cl_2O_8 + Na]^+$ *m/z* 511.0902, found 511.0909.



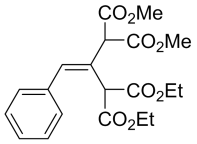
4t

2-(cyclohexylmethylene)propane-1,1,3,3-tetracarboxylate, yield: 24.1 mg, 43.5%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (d, J = 9.8 Hz, 1H), 4.59 (s, 1H), 4.38 (s, 1H), 4.26 – 4.07 (m, 8H), 2.37 – 2.23 (m, 1H), 1.78 – 1.63 (m, 6H), 1.35 – 1.07 (m, 16H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 168.4(×2), 167.7(×2), 144.6, 121.3, 61.7(×2), 61.4(×2), 55.5, 52.8, 37.8, 32.3(×2), 25.9, 25.5(×2), 14.0(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{22}H_{34}O_8 + Na]^+$ *m/z* 449.2151, found 449.2164.



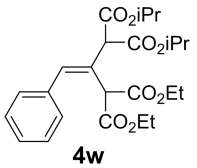
4u

2-(3-phenylallylidene)propane-1,1,3,3-tetracarboxylate, yield: 48.4 mg, 83.4%; off wite oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37 – 7.15 (m, 5H), δ 6.99 – 6.92 (m, 1H).6.67 – 6.55 (m, 2H), 4.73 (s, 1H), 4.40 (s, 1H), 4.28 – 4.01 (m, 8H), 1.49 – 0.95 (m, 12H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 167.9(×2), 167.5(×2), 137.2, 136.9, 136.8, 128.7(×2), 128.2, 126.8(×2), 123.6, 123.4, 61.9(×2), 61.8(×2), 56.75, 53.2, 14.0(×2), 14.0(×2). HRMS (ESI+) calcd for $[C_{24}H_{30}O_8 + Na]^+$ *m/z* 469.1838, found 469.1841.



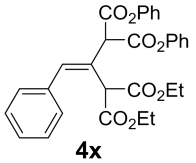
4v

1,1-diethyl 3,3-dimethyl-2-benzylidenepropane-1,1,3,3-tetracarboxylate, yield: 28 mg, 55.0%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.28 (m, 5H), 7.18 (s, 1H), 4.81 (s, 1H), 4.71 (s, 1H), 4.23 – 4.17 (m, 4H), 3.80 (s, 6H), 1.28 (t, J = 4.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7(×2), 167.5(×2), 137.9, 135.5, 128.8(×2), 128.5(×2), 127.8, 124.8, 62.0(×2), 53.8, 53.1, 52.9(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{20}H_{24}O_8 + Na]^+$ *m/z* 415.1387, found 415.1398.



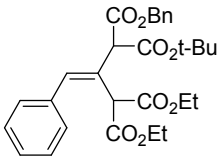
4w

1,1-diethyl 3,3-diisopropyl-2-benzylidenepropane-1,1,3,3-tetracarboxylate, yield: 34.3 mg, 58.9%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 – 7.20 (m, 5H), 7.16 (s, 1H), 5.21 – 4.99 (m, 2H), 4.78 (s, 1H), 4.58 (s, 1H), 4.30 – 4.08 (m, 4H), 1.48 – 1.04 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7(×2), 167.4(×2), 137.6, 135.8, 128.8(×2), 128.4(×2), 127.7, 125.3, 69.1(×2), 61.8(×2), 54.6, 53.3, 21.6(×2), 21.5(×2), 13.9(×2). HRMS (ESI+) calcd for $[C_{24}H_{32}O_8 + Na]^+$ *m/z* 471.2001, found 471.2006.



4x

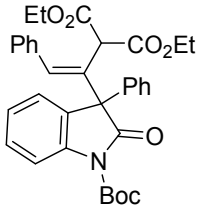
1,1-diethyl 3,3-diphenyl-2-benzylidenepropane-1,1,3,3-tetracarboxylate, yield: 40.1 mg, 60.1%; off wite oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 – 7.15 (m, 16H), 5.23 (s, 1H), 4.96 (s, 1H), 4.36 – 4.16 (m, 4H), 1.35 – 1.23 (m, 6H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5(×2), 166.7(×2), 150.8, 138.7, 135.3, 129.6(×4), 129.4, 128.8(×2), 128.6(×2), 128.1, 126.2(×2), 124.8, 121.3(×4), 62.2(×2), 54.1, 53.1, 14.0(×2). HRMS (ESI+) calcd for $[C_{30}H_{28}O_8 + Na]^+$ *m/z* 539.1687, found 539.1692.



4y

1-benzyl 1-(tert-butyl) 3,3-diethyl (E)-2-benzylidenepropane-1,1,3,3-tetracarboxylate, yield: 34.5 mg, 52%; off wite oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ

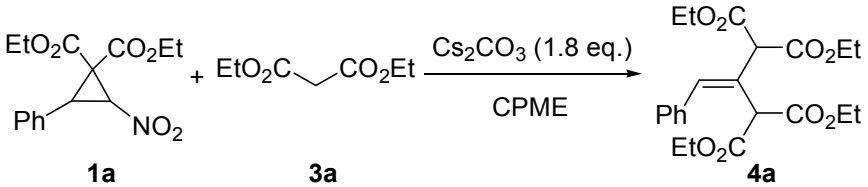
7.42 – 7.25 (m, 10H), 7.13 (s, 1H), 5.24 (s, 2H), 4.78 (s, 1H), 4.63 (s, 1H), 4.26 – 4.00 (m, 4H), 1.45 (s, 9H), 1.28 (t, 3H), 1.19 (t, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 167.5, 167.4, 166.9, 137.6, 135.8, 135.7, 128.8(×2), 128.5(×2), 128.4(×2), 128.3(×2), 128.2, 127.7, 125.3, 82.0, 67.2, 61.8 (×2), 55.2, 53.3, 27.8(×3), 14.0, 13.9. HRMS (ESI+) calcd for $[C_{29}H_{34}O_8 + Na]^+$ *m/z* 510.5830, found 510.5834.



6

diethyl (E)-2-(1-(1-(tert-butoxycarbonyl)-2-oxo-3-phenylindolin-3-yl)-2-phenylvinyl)malonate, yield: 65.8 mg, 89%; off wite oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.48 (m, 5H), 7.39 – 7.25 (m, 4H), 7.22 – 7.19 (m, 5H), 6.84 (s, 1H), 4.39 (s, 1H), 3.91 (dd, 2H), 3.82 – 3.65 (m, 2H), 1.66 (s, 9H), 1.12 (t, 3H), 1.09 (t, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.6, 167.6, 167.4, 149.3, 139.4, 139.4, 137.8, 135.7, 133.1, 129.6, 128.9, 128.8(×2), 128.7(×2), 128.6(×2), 127.8, 127.7(×2), 127.6, 126.6, 124.3, 115.4, 84.4, 64.8, 61.4(×2), 53.7, 28.1(×3), 13.8, 13.7. HRMS (ESI+) calcd for $[C_{34}H_{35}NO_7 + Na]^+$ *m/z* 569.6540, found 569.6545.

4. Scale-up experiment

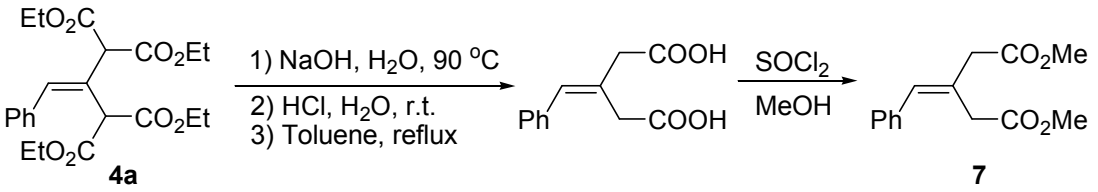


1a **3a** **4a**

The reaction was conducted in CPME (15 mL) using **1a** (3.9 mmol, 1.2 g), **3a** (6.3 mmol), and Cs_2CO_3 (7.2 mmol) with stirring for 4 h at room temperature. After

completion, the reaction mixture was dried and concentrated. The residue was purified by flash chromatography to give the product **4a** in 84% yield (eluent: petroleum ether-ethyl acetate).

5. Synthetic application of 4a



NaOH (5 equiv.) was added into a stirred solution of **4a** (11.7 mmol) in H_2O (21 mL) at 90 °C, and the resulting mixture was stirred vigorously for 2h. Then, the aqueous layer was separated, washed with Et_2O (2 × 50 mL), acidified to pH=2 with aqueous HCl solution (6 M), and extracted with EtOAc (5× 50 mL). The combined organic layer was washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure to give the acid as an oily yellow liquid that was used in the next step without further purification.

The oily yellow liquid was dissolved in toluene (10 mL), and the mixture was stirred vigorously at 120 °C for 6h. Then the mixture was concentrated under reduced pressure to leave an oily yellow liquid. Finally, the resulting mixture was dissolved in MeOH (15 mL), added $SOCl_2$ (2.5 equiv.) at 0 °C, and stirred vigorously for 2h, then mixture was washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (1/13 EtOAc/petroleum ether) to give the compound **7** in 18.8 mg, 76% yield; off white oil; ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.53 – 7.28 (m, 2H), 7.26 (m, 3H), 6.64 (s, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 3.39 (s, 2H), 3.33 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7(×2), 136.5, 133.2, 128.6(×2), 128.3(×2), 127.9, 127.2, 52.1, 52.0, 42.8, 36.4. HRMS (ESI+) calcd for $[C_{14}H_{16}O_4 + Na]^+$ *m/z* 248.2780, found 248.2776.

6. Further confirmation of allene intermediate

6.1 High-resolution ESI-MS spectrum of the dimerization reaction

Figure S1 High-resolution ESI-MS spectrum (positive mode) of the reaction mixture

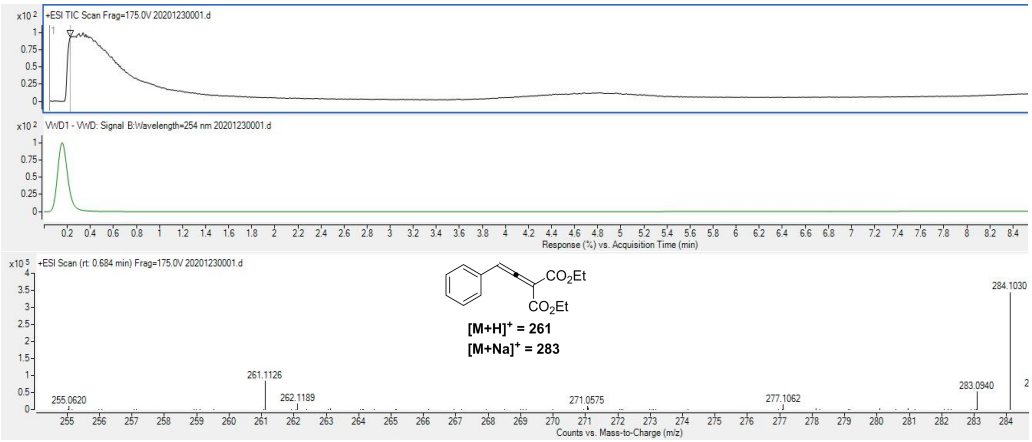
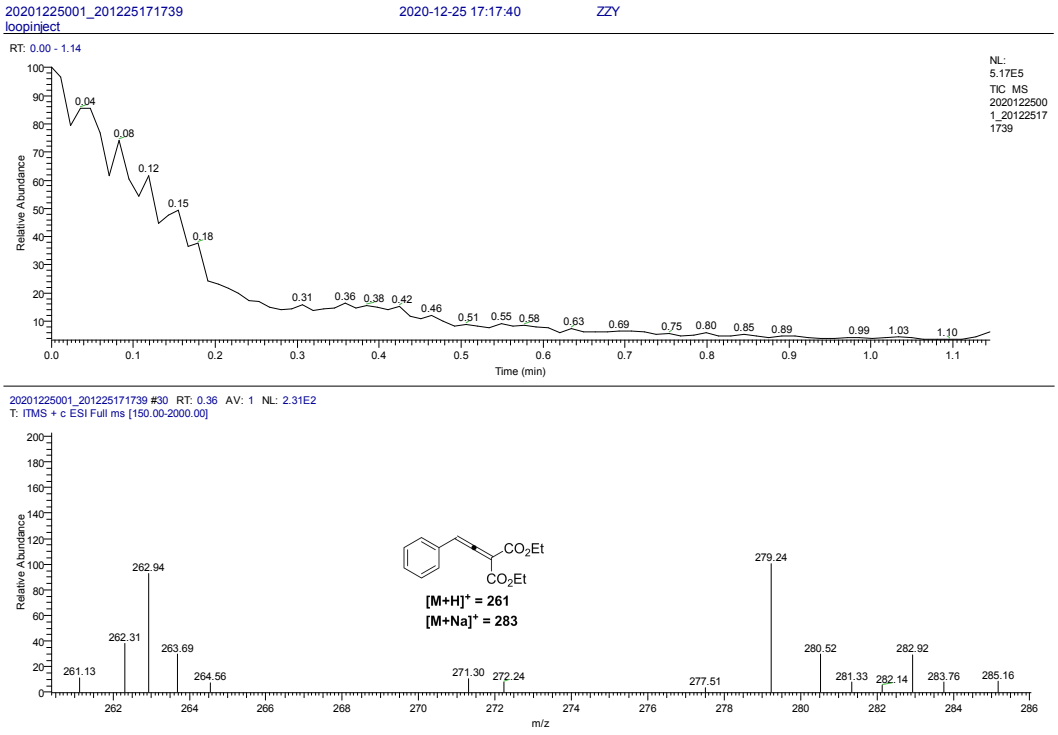


Table S2. High-resolution mass data of detected intermediates **A**

Species	Formula	Mass (measured)	Mass (calculated)	Error [ppm]
$[M+H]^+$	$C_{15}H_{17}O_4^+$	261.1126	261.1121	1.8
$[M+Na]^+$	$C_{15}H_{16}O_4Na^+$	283.0940	283.0941	0.4

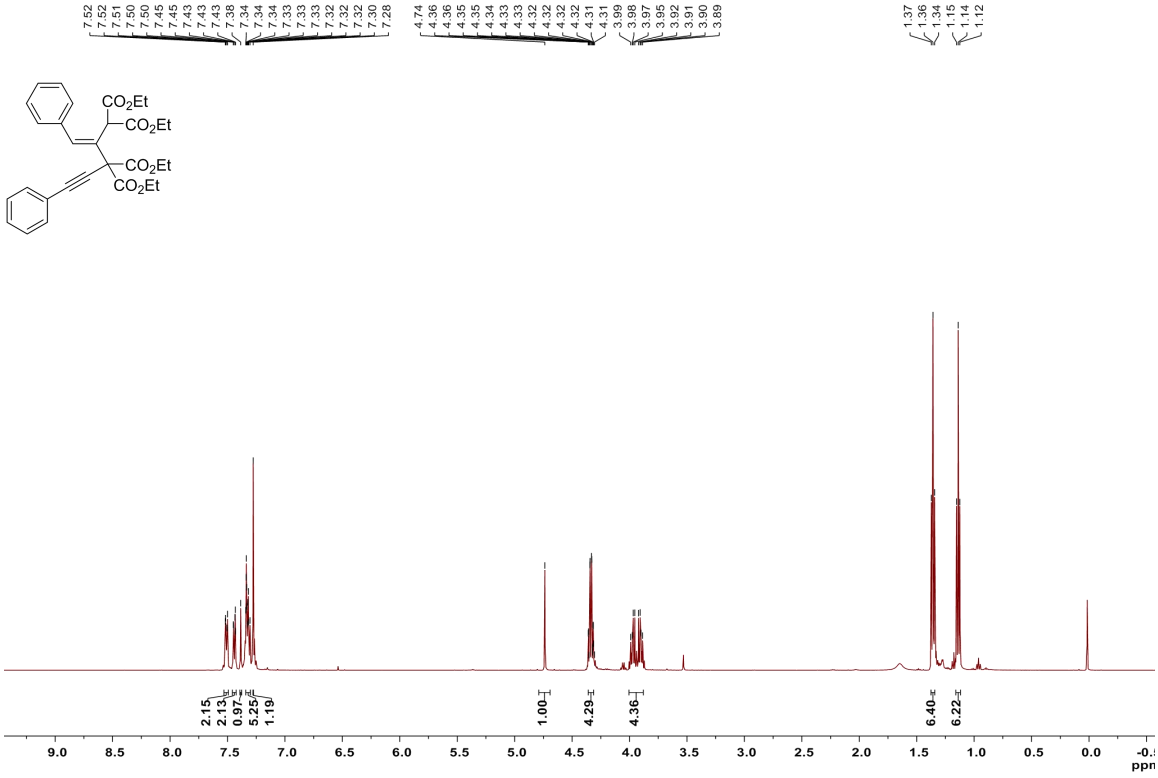
6.2 ESI-MS spectrum of the allene-synthesized reaction using phosphorus ylide and acyl chloride

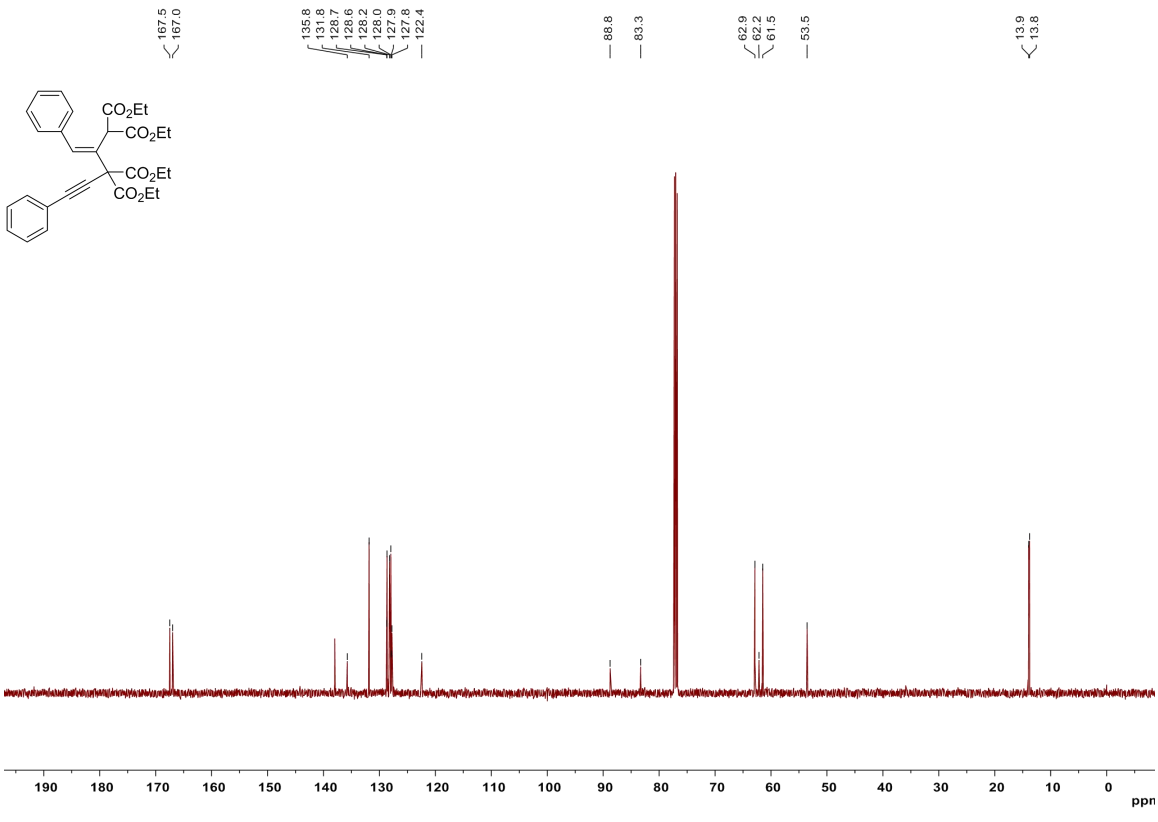
Figure S2 ESI-MS spectrum (positive mode) of the reaction mixture



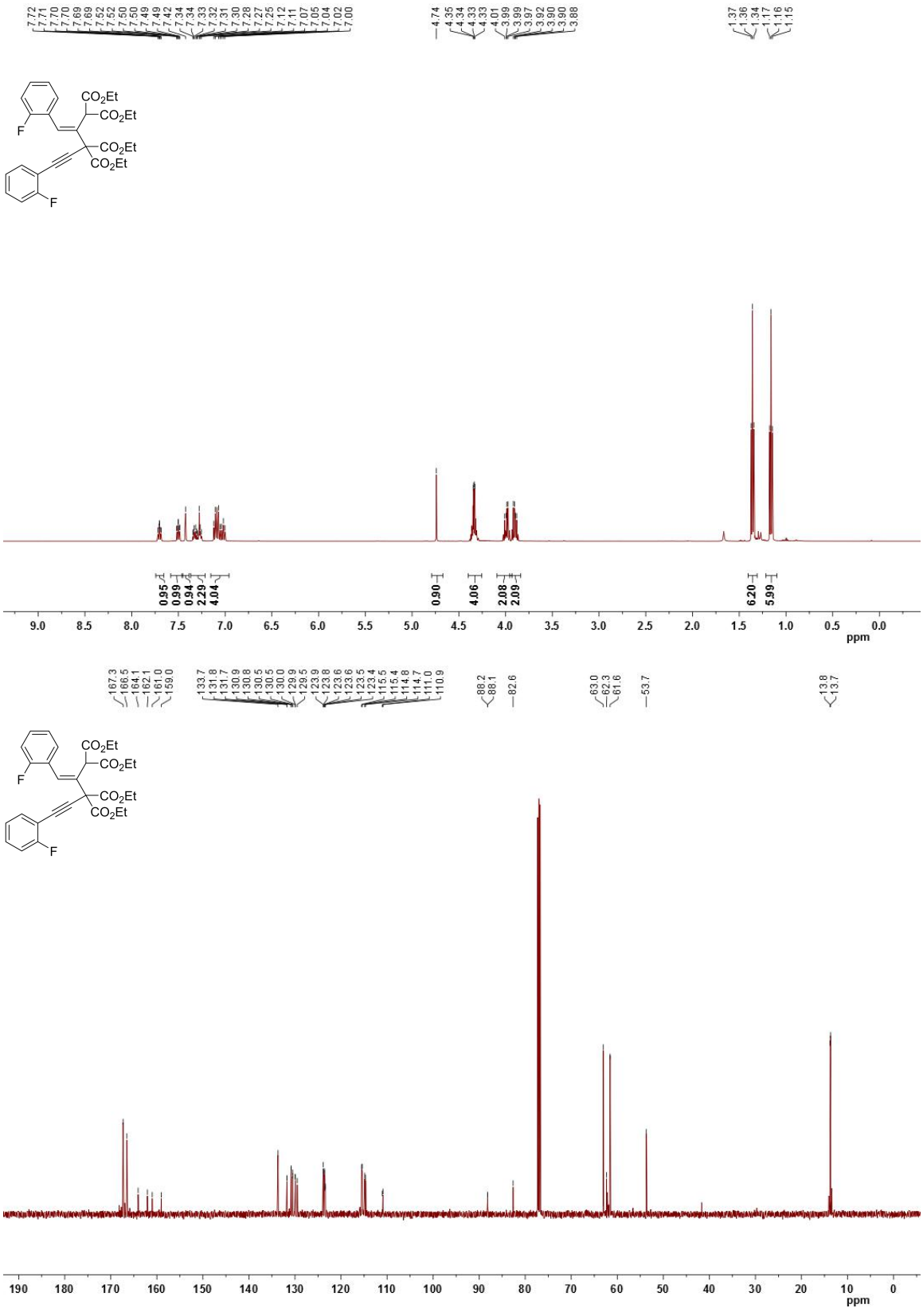
7. ^{1}H and ^{13}C NMR spectra of compounds 2a-2t, 4a-4y, 6 and 7

Compound 2a

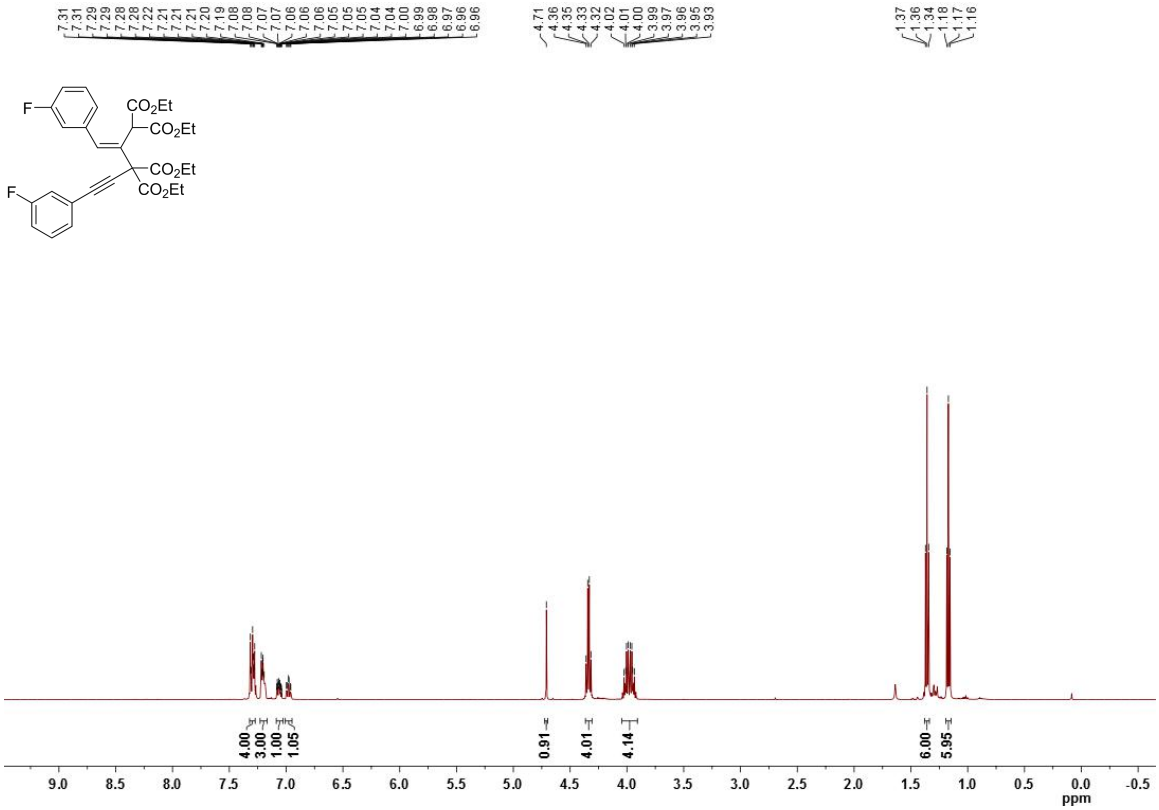




Compound 2b


7.72 7.71 7.70 7.70 7.69 7.69 7.52 7.52 7.50 7.50 7.49 7.49 7.42 7.34 7.34 7.33 7.32 7.31 7.30 7.28 7.27 7.25 7.12 7.11 7.07 7.05 7.04 7.02 7.00
4.74 4.35 4.34 4.33 4.33 4.01 3.99 3.99 3.97 3.92 3.90 3.90 3.88
1.37 1.36 1.34 1.17 1.16 1.15
CO2Et CO2Et CO2Et CO2Et
F F
0.95 0.99 0.94 2.23 4.04 0.90 4.06 2.08 2.09 6.20 5.99
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
ppm
167.3 166.5 164.1 162.1 161.0 159.0
133.7 131.8 131.7 130.9 130.8 130.5 130.5 130.0 129.9 129.5 123.9 123.8 123.6 123.6 123.5 123.4 115.5 115.4 114.8 114.7 111.0 110.9
88.2 88.1 82.6
63.0 62.3 61.6
53.7
13.8 13.7
CO2Et CO2Et CO2Et CO2Et
F F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Compound 2c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7.08
7.08
7.07
7.07
7.06
7.06
7.06
7.05
7.05
7.05
7.04
7.04
7.00
6.99
6.98
6.97
6.96
6.96
4.71
4.36
4.35
4.33
4.32
4.02
4.01
4.00
3.99
3.97
3.96
3.95
3.93
1.37
1.36
1.34
1.18
1.17
1.16
F
CO2Et
CO2Et
CO2Et
CO2Et
F
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3.00
1.00
1.05
0.91
4.01
4.14
6.00
5.95
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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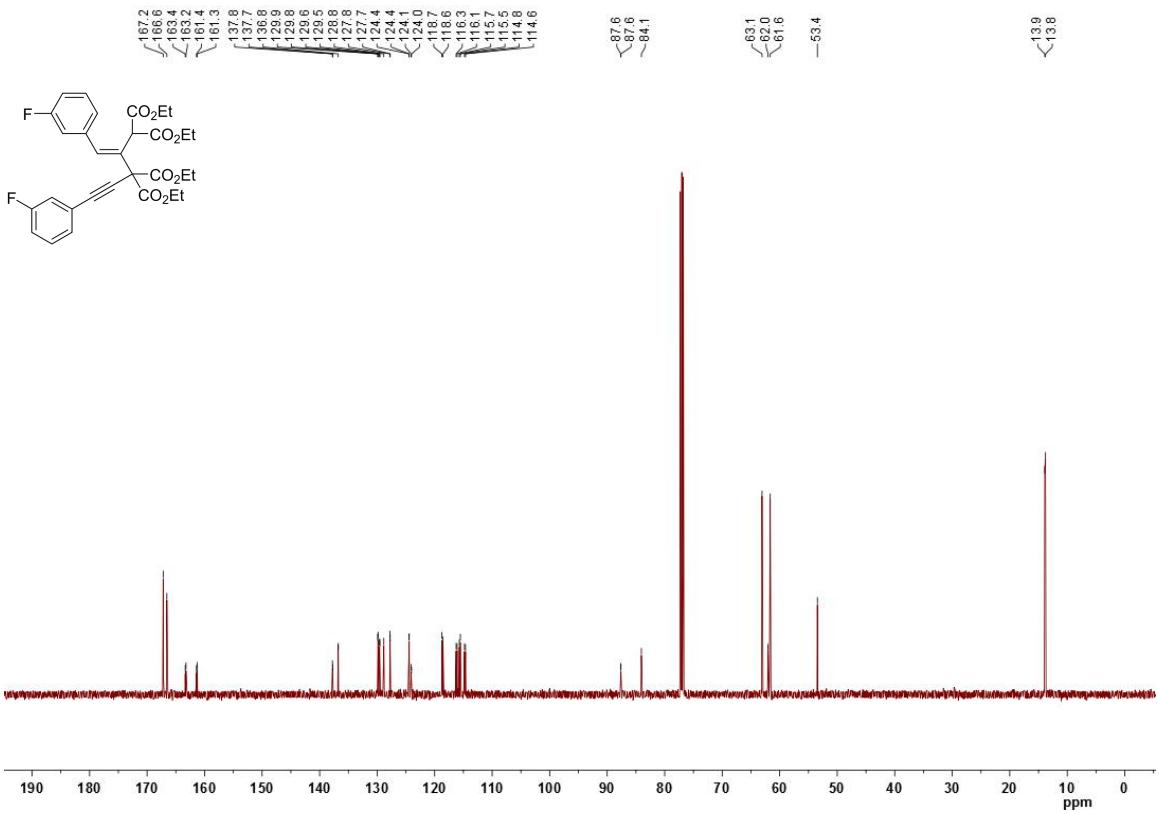
ppm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166.6
163.4
163.2
161.4
161.3
137.8
137.7
136.8
129.9
129.8
129.6
129.5
128.8
127.8
127.7
124.4
124.4
124.1
124.0
118.7
118.6
116.3
116.1
115.7
115.5
114.8
114.6
87.6
87.6
84.1
63.1
62.0
61.6
53.4
13.9
13.8
F
CO2Et
CO2Et
CO2Et
CO2Et
F
190
180
170
160
150
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120
110
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90
80
70
60
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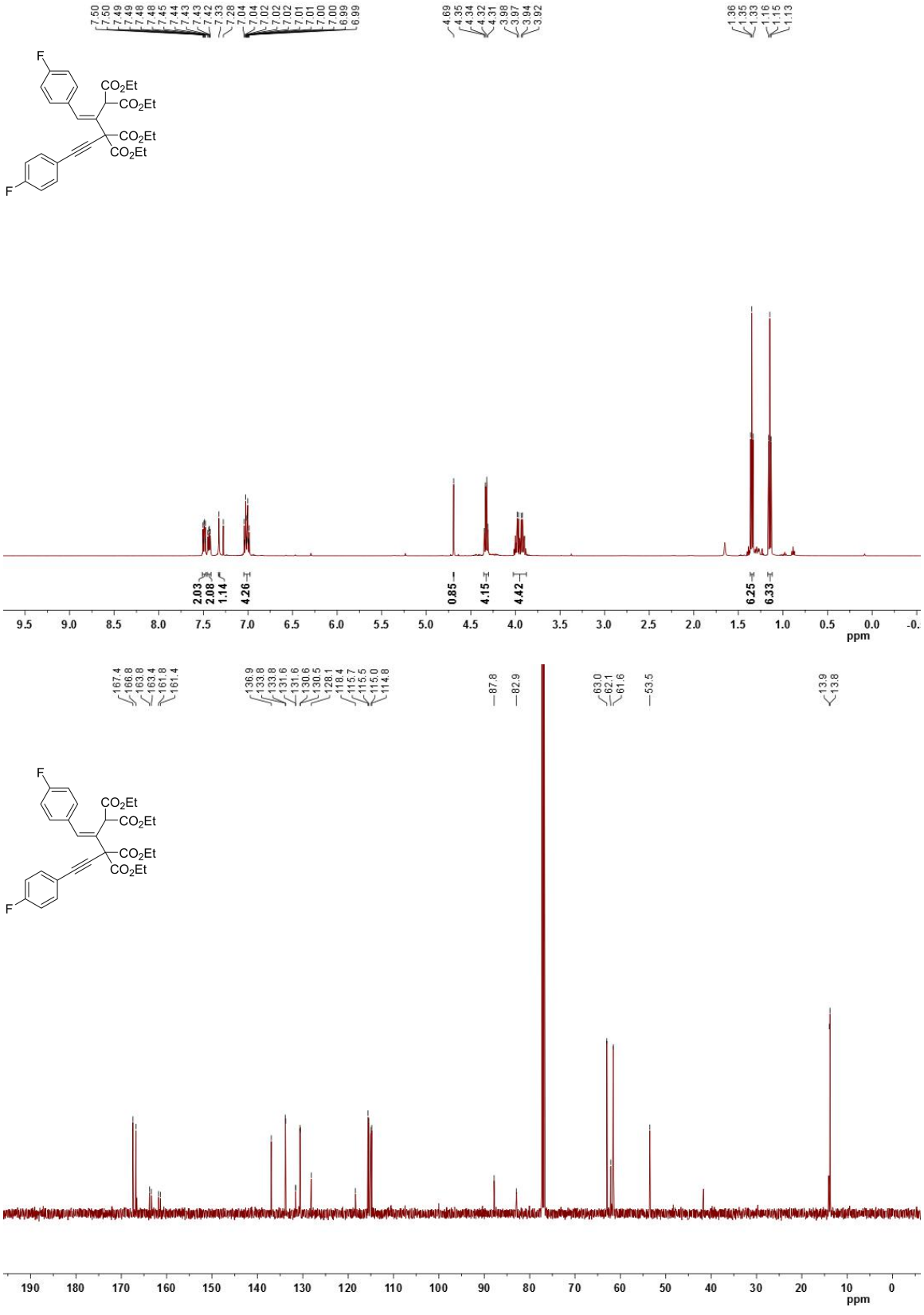
40
30
20
10
0
ppm

Compound 2d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7.43
7.42
7.33
7.28
7.04
7.04
7.02
7.02
7.02
7.01
7.01
7.00
7.00
6.99
6.99
4.69
4.35
4.34
4.32
4.31
3.98
3.97
3.94
3.92
1.36
1.35
1.33
1.16
1.15
1.13
F
CO2Et
CO2Et
CO2Et
CO2Et
F
2.03
2.08
1.14
4.26
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4.15
4.42
6.25
6.33
ppm
167.4
166.8
163.8
163.4
161.8
161.4
136.9
133.8
133.8
131.6
131.6
130.6
130.5
128.1
118.4
115.7
115.5
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53.5
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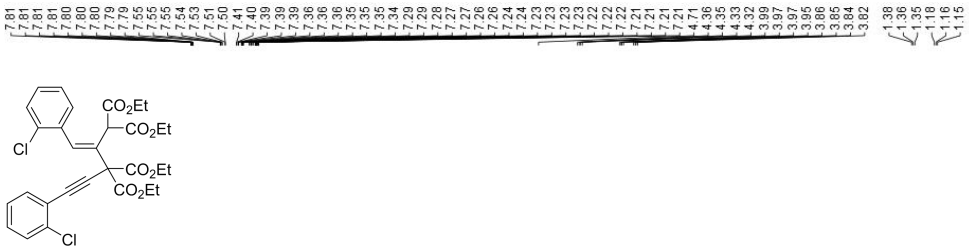
13.8
ppm

Compound 2e



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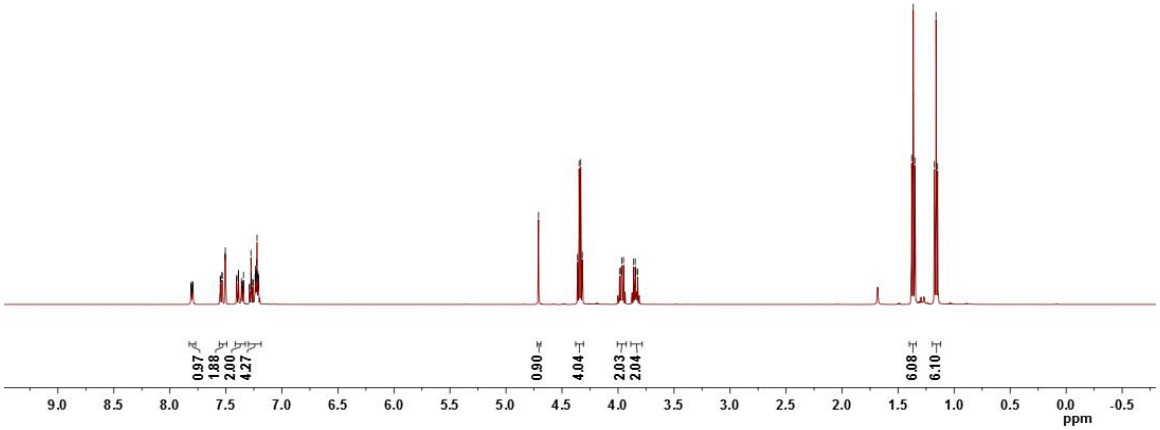
CO2Et
Cl
CO2Et
CO2Et
Cl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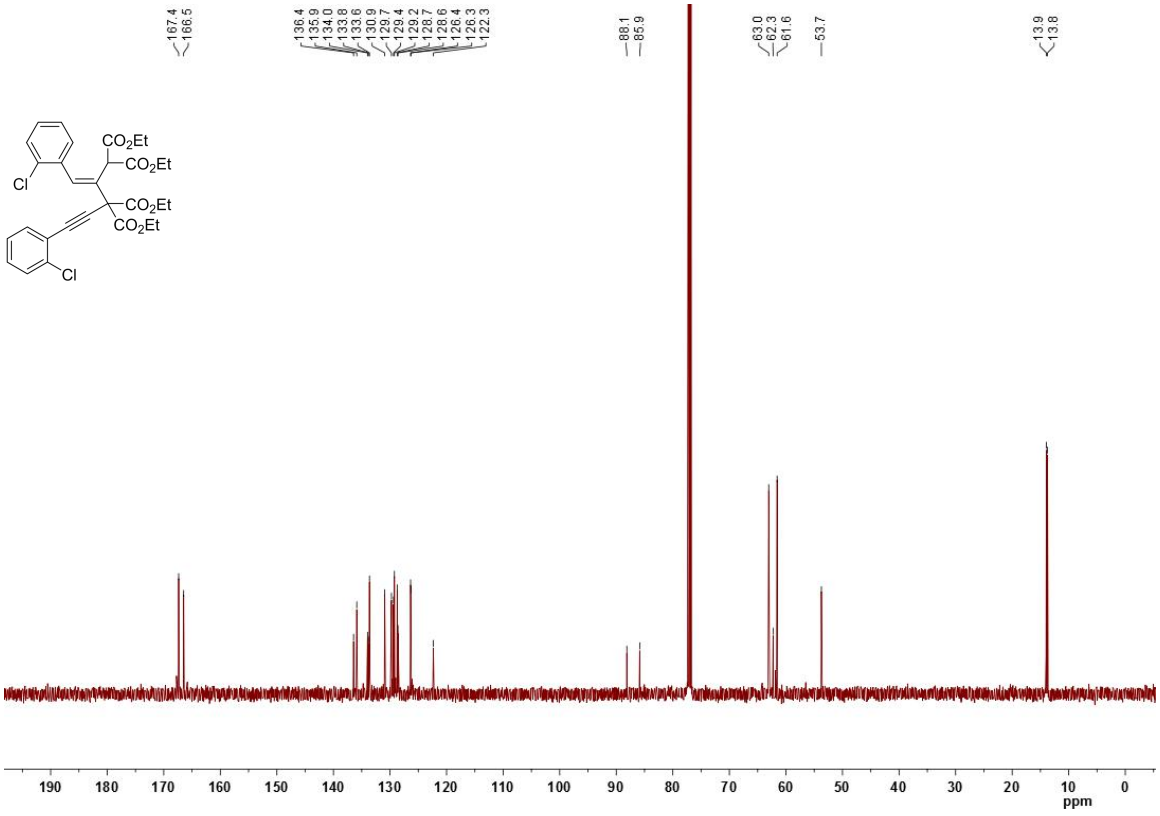
2.04
6.08
6.10
ppm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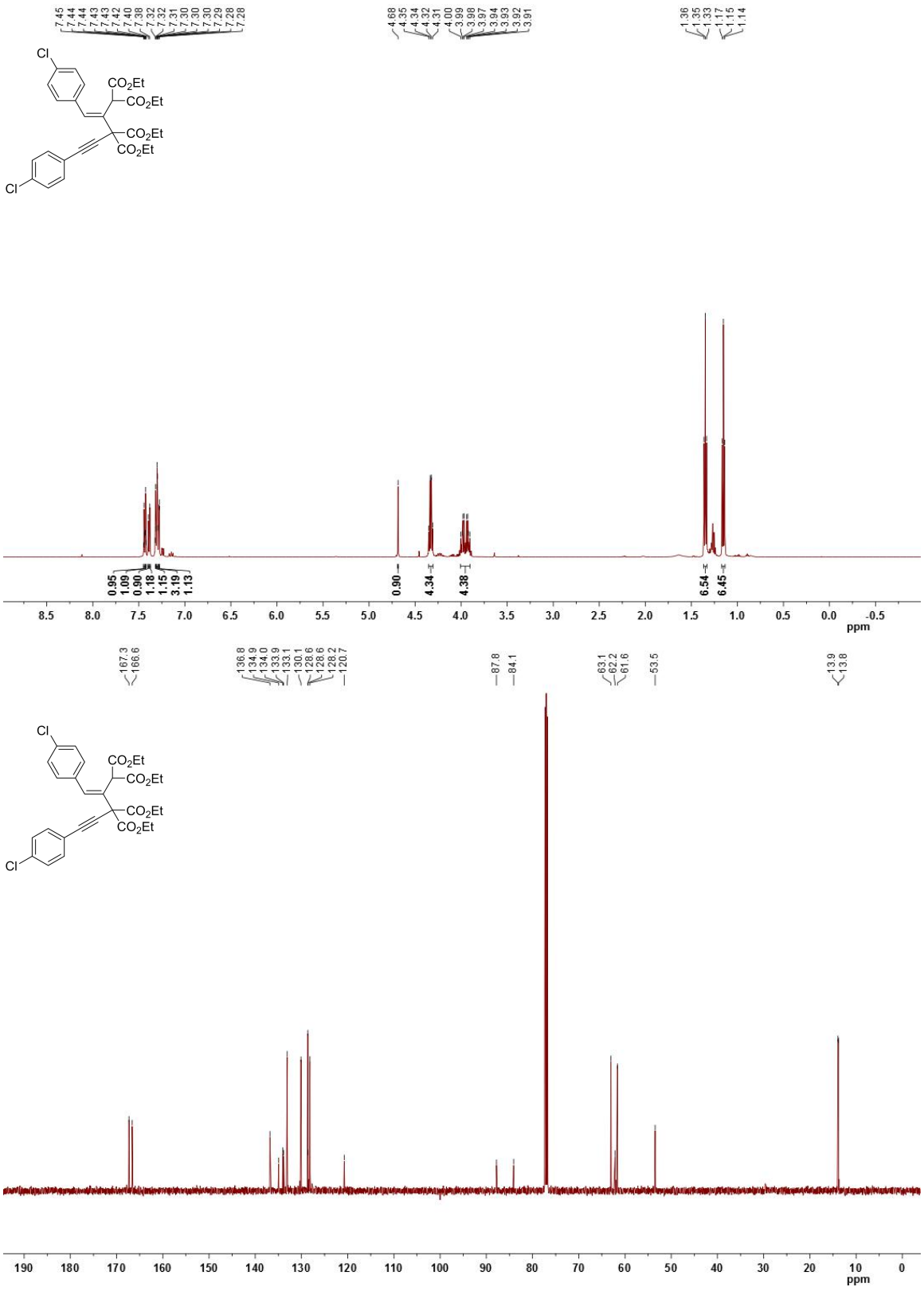
166.5
136.4
135.9
134.0
133.8
133.6
130.9
129.7
129.4
129.2
128.7
128.6
126.4
126.3
122.3
88.1
85.9
63.0
62.3
61.8
53.7
13.9
13.8
ppm

CO2Et
CO2Et
Cl
CO2Et
CO2Et
Cl

Compound 2f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7.32
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7.31
7.30
7.30
7.29
7.28
7.28
4.68
4.35
4.34
4.32
4.31
4.00
3.99
3.98
3.97
3.94
3.93
3.92
3.91
1.36
1.35
1.33
1.17
1.15
1.14
Cl
CO2Et
CO2Et
CO2Et
CO2Et
Cl
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0.90
1.18
1.15
3.19
1.13
0.90
4.34
4.38
6.54
6.45
ppm
167.3
166.6
136.8
134.9
134.0
133.9
133.1
130.1
128.6
128.6
128.2
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87.8
84.1
63.1
62.2
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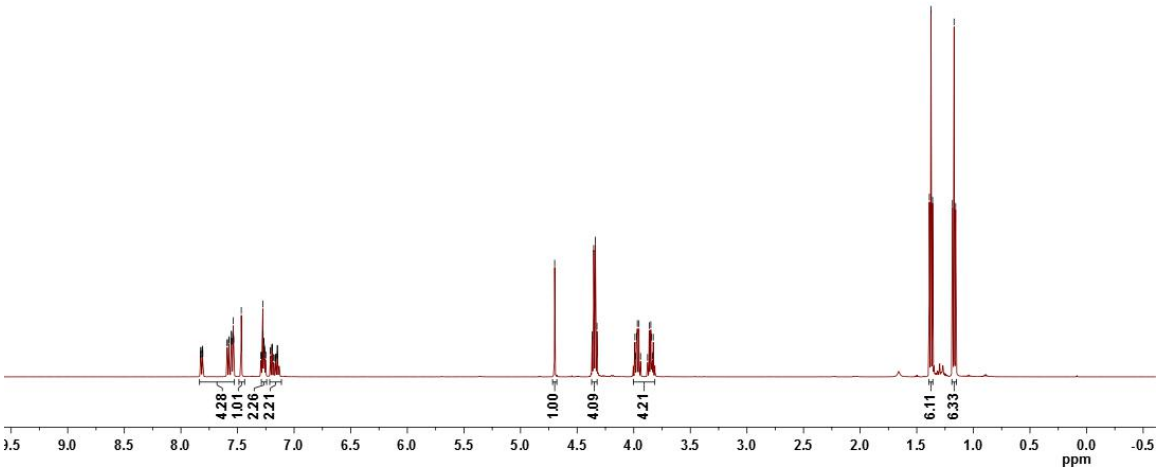
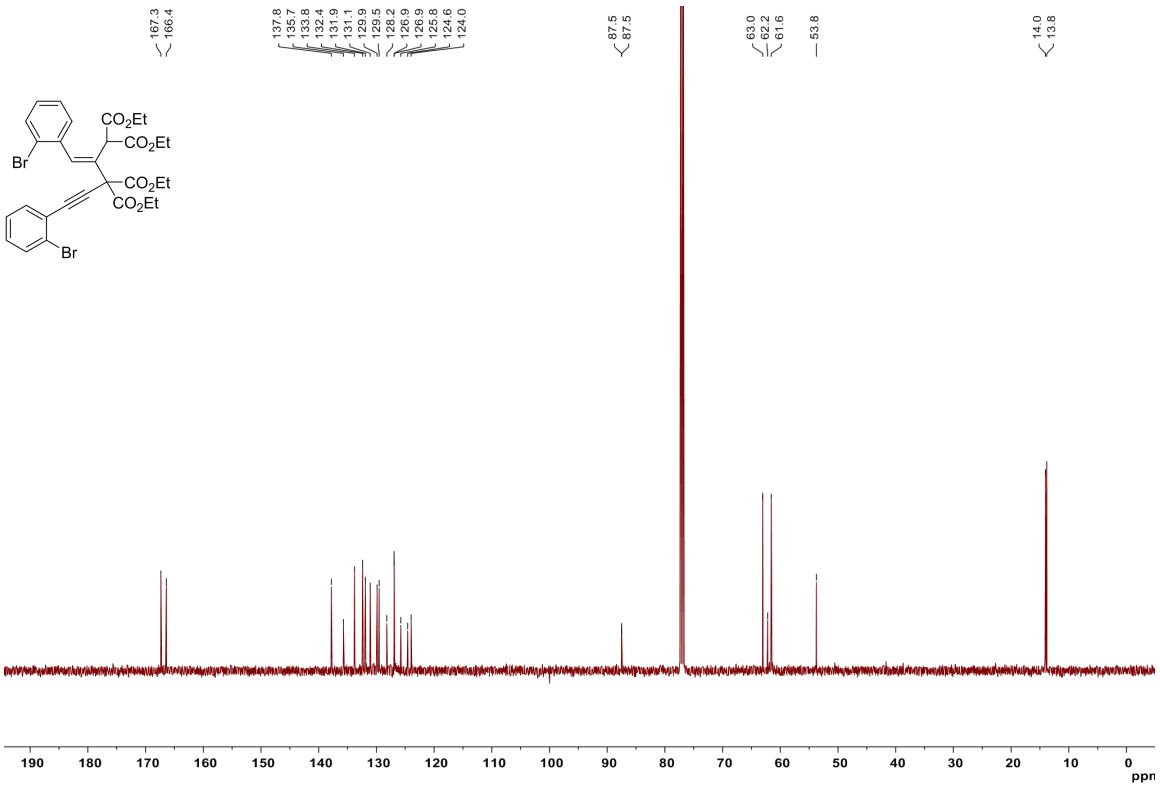
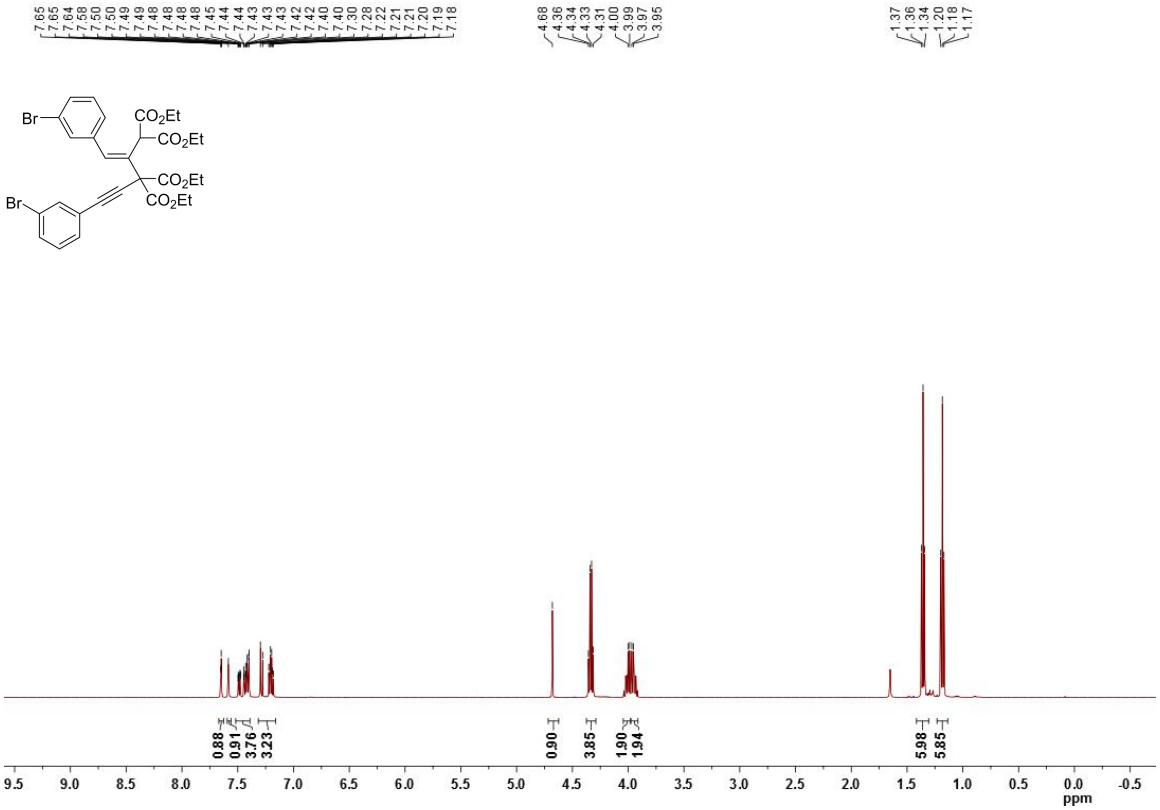
53.5
13.9
13.8
ppm

Compound 2g





Compound 2h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7.64
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7.50
7.49
7.49
7.48
7.48
7.48
7.48
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7.44
7.44
7.43
7.43
7.43
7.42
7.42
7.40
7.40
7.30
7.28
7.22
7.21
7.21
7.20
7.19
7.18
4.68
4.36
4.34
4.33
4.31
4.00
3.99
3.97
3.95
1.37
1.36
1.34
1.20
1.18
1.17
Br
CO2Et
CO2Et
CO2Et
CO2Et
Br
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0.91
3.76
3.23
0.90
3.85
1.90
1.94
5.98
5.85
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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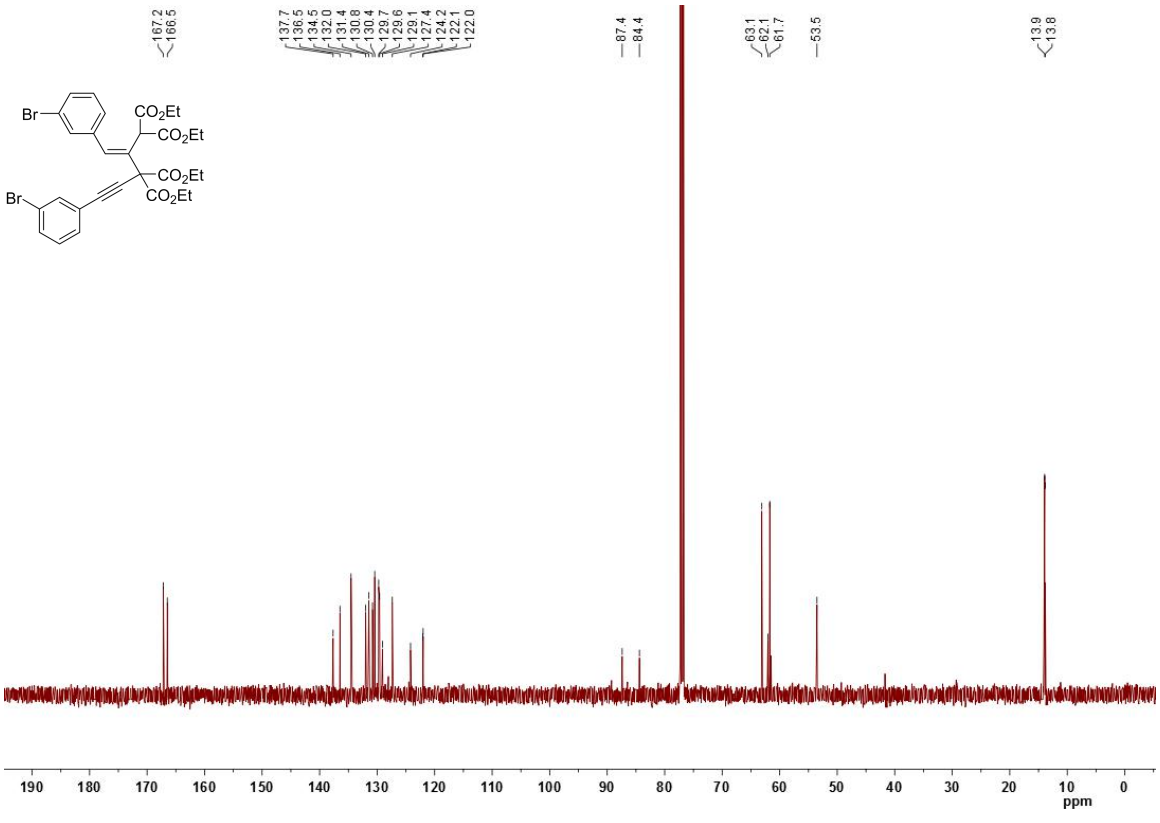
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm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130.8
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129.6
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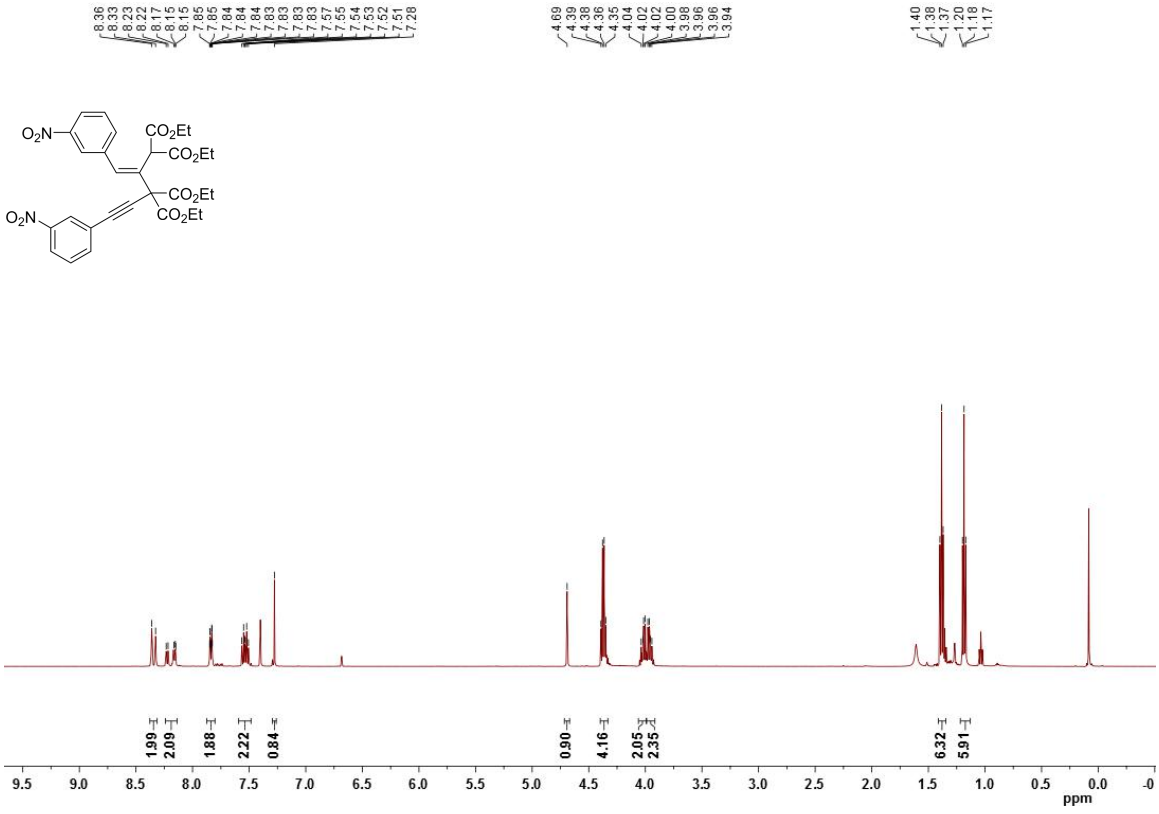
127.4
124.2
122.1
122.0
87.4
84.4
63.1
62.1
61.7
53.5
13.9
13.8
Br
CO2Et
CO2Et
CO2Et
CO2Et
Br
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 2i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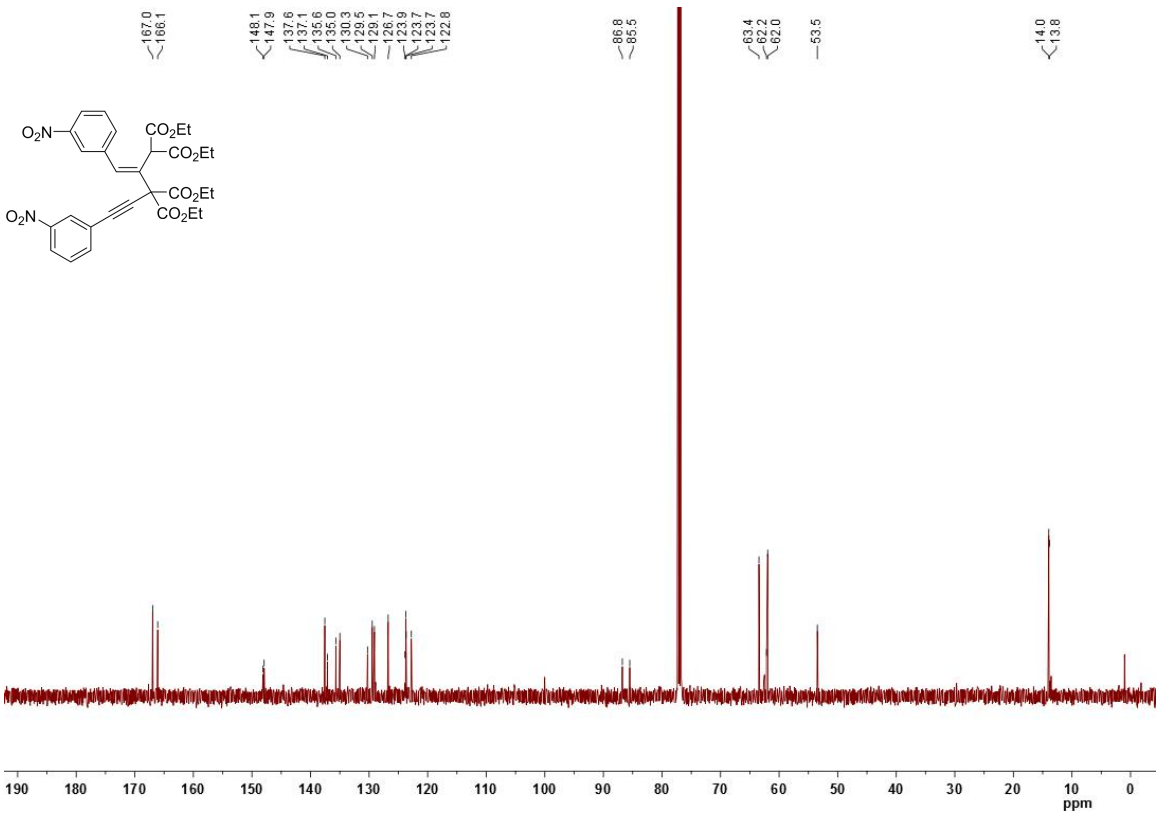
7.83
7.57
7.55
7.54
7.53
7.52
7.51
7.28
4.69
4.39
4.38
4.36
4.35
4.04
4.02
4.02
4.00
3.98
3.96
3.96
3.94
1.40
1.38
1.37
1.20
1.18
1.17
O2N
CO2Et
CO2Et
CO2Et
CO2Et
O2N
1.99
2.09
1.88
2.22
0.84
0.90
4.16
2.05
2.35
6.32
5.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
ppm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129.5
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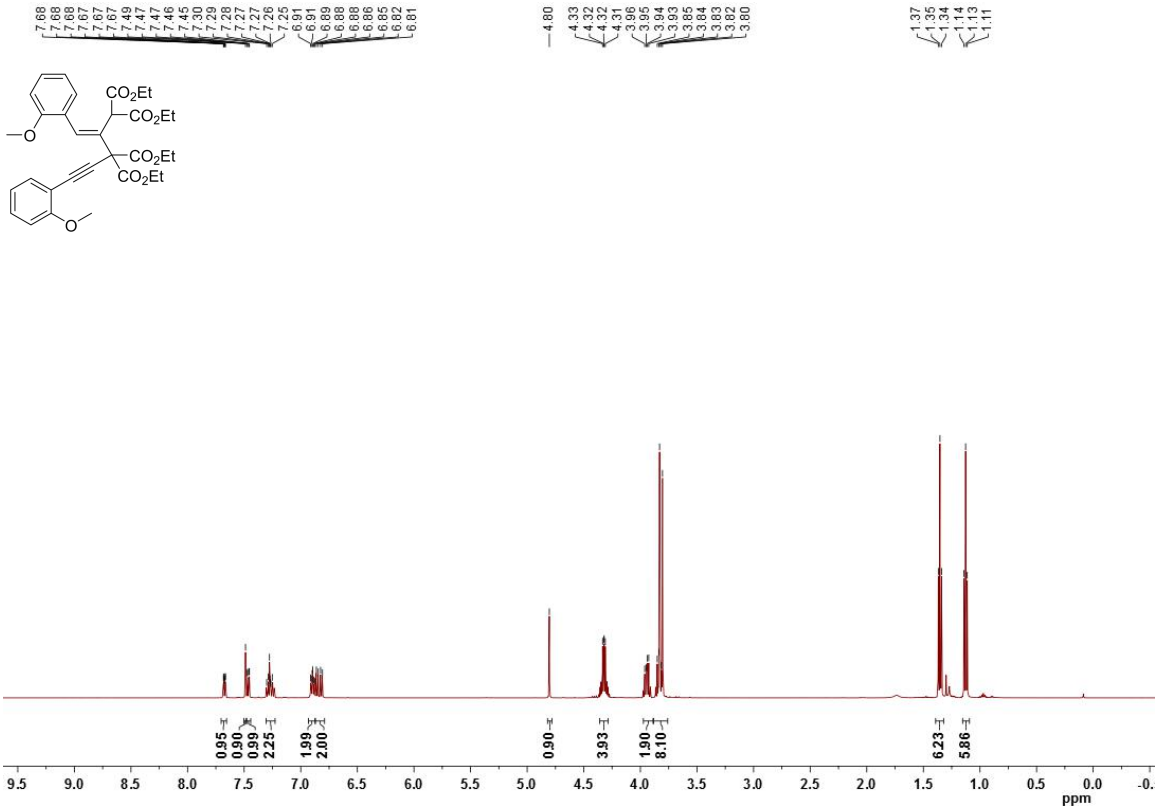
123.9
123.7
123.7
122.8
86.8
85.5
63.4
62.2
62.0
53.5
14.0
13.8
O2N
CO2Et
CO2Et
CO2Et
CO2Et
O2N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

Compound 2j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7.67
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7.46
7.45
7.30
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7.28
7.27
7.27
7.26
7.25
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6.91
6.89
6.88
6.88
6.86
6.85
6.82
6.81
4.80
4.33
4.32
4.32
4.31
3.96
3.95
3.94
3.93
3.85
3.84
3.83
3.82
3.80
1.37
1.35
1.34
1.14
1.13
1.11
CO2Et
CO2Et
CO2Et
CO2Et
O
O
0.95
0.90
0.99
2.25
1.99
2.00
0.90
3.93
1.90
8.10
6.23
5.86
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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1.5
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0.5
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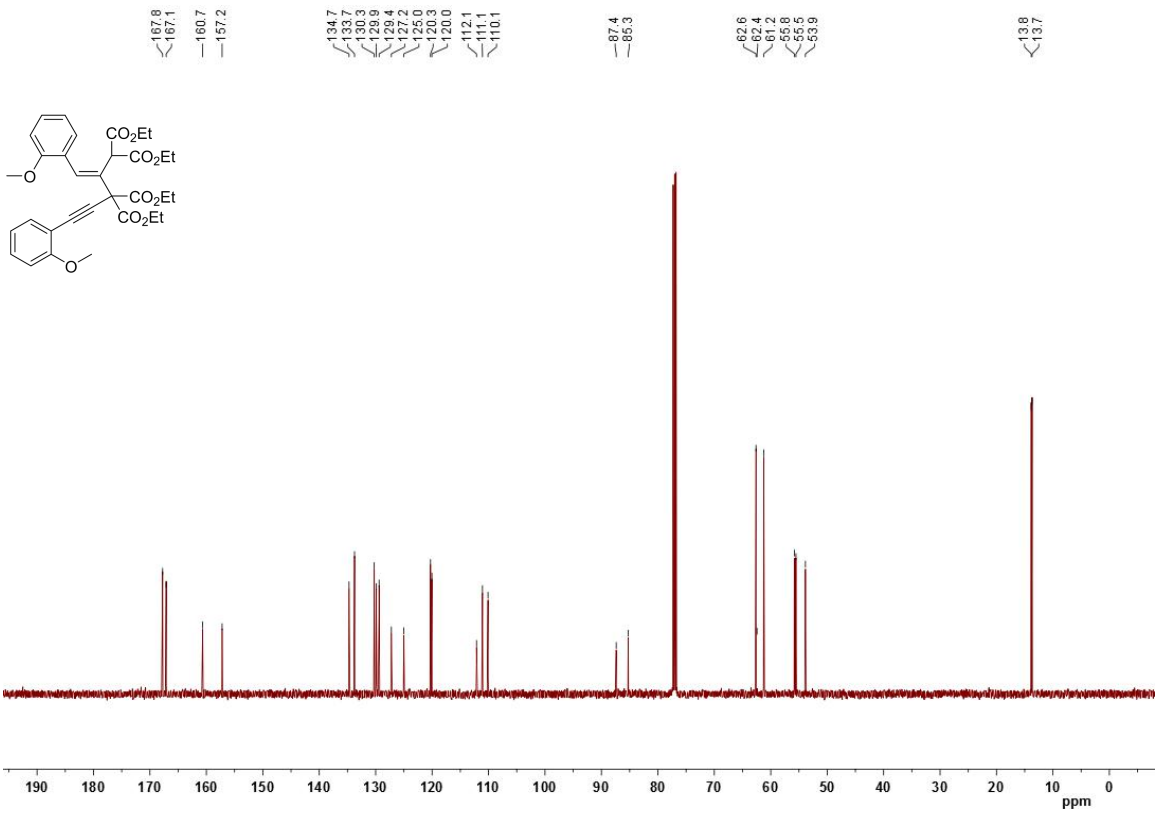
ppm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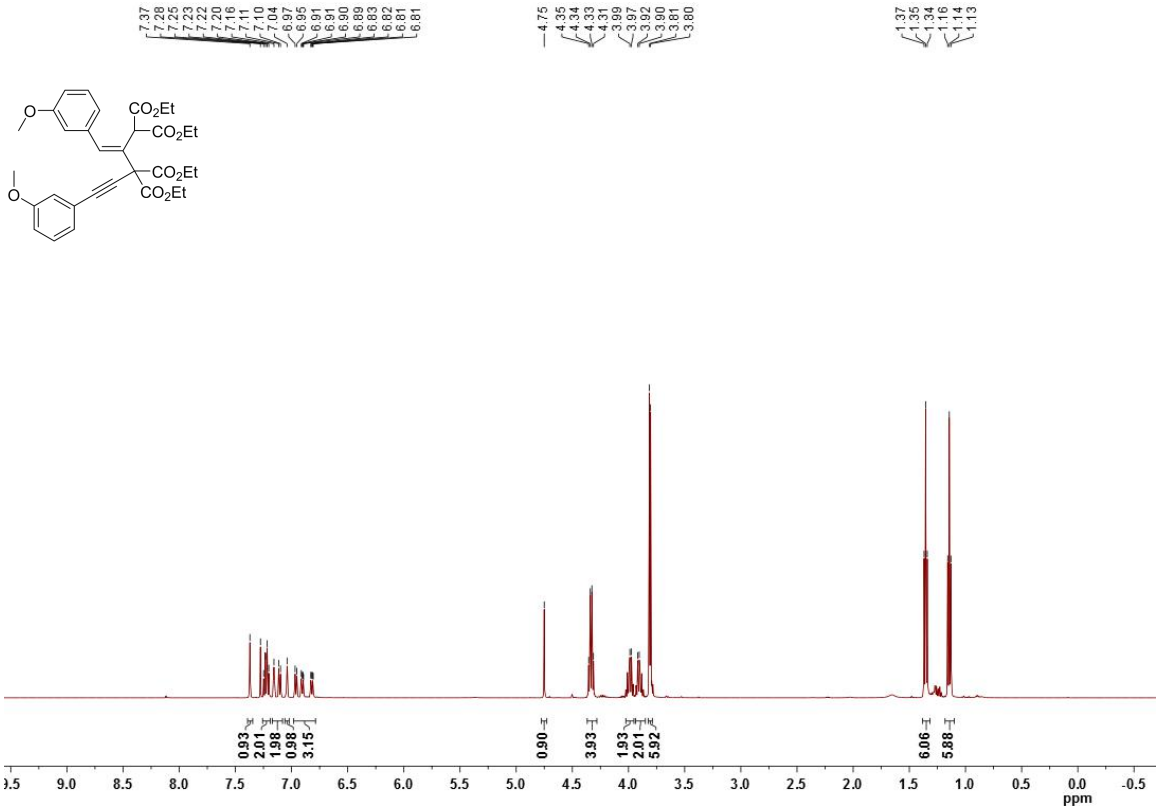
134.7
133.7
130.3
129.9
129.4
127.2
125.0
120.3
120.0
112.1
111.1
110.1
87.4
85.3
62.6
62.4
61.2
55.8
55.5
53.9
13.8
13.7
CO2Et
CO2Et
CO2Et
CO2Et
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 2k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7.04
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6.91
6.91
6.90
6.89
6.83
6.82
6.81
6.81
4.75
4.35
4.34
4.33
4.31
3.99
3.97
3.92
3.80
3.61
3.80
1.37
1.35
1.34
1.16
1.14
1.13
CO2Et
CO2Et
CO2Et
CO2Et
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0.98
3.15
0.90
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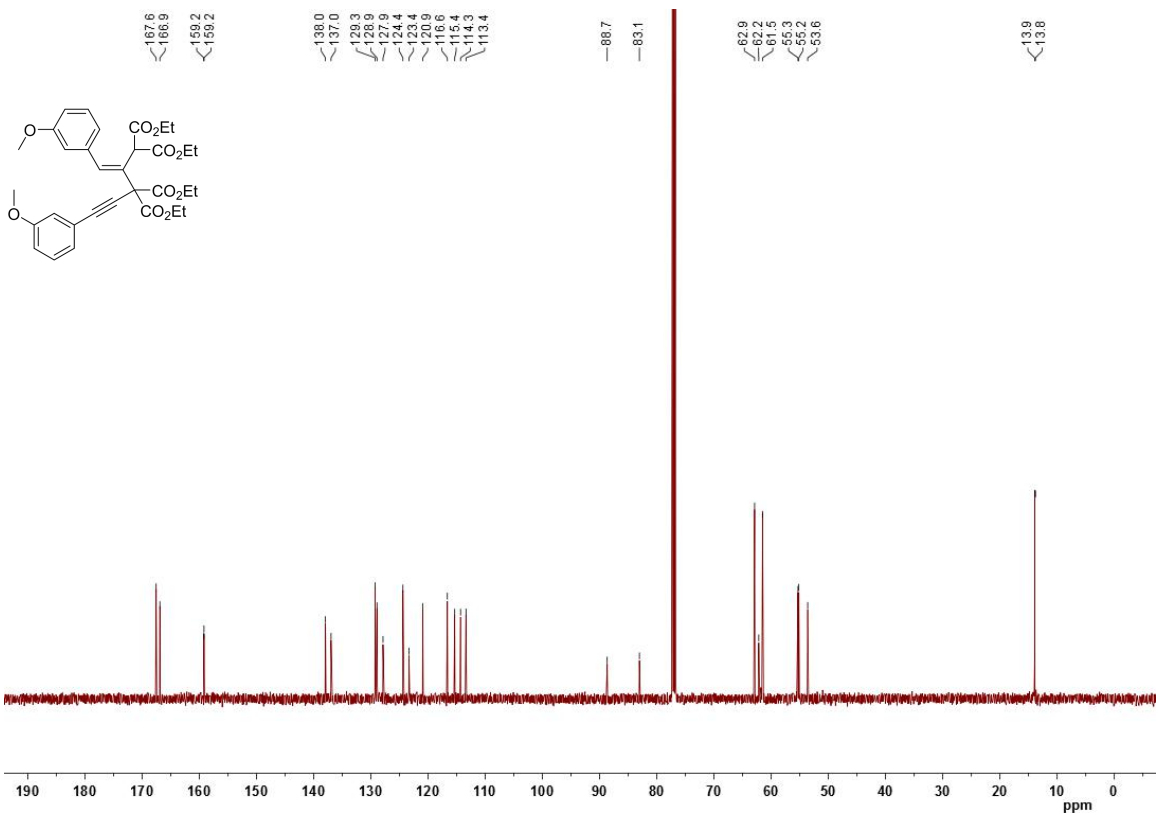
1.93
2.01
5.92
6.06
5.88
ppm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159.2
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137.0
129.3
128.9
127.9
124.4
123.4
120.9
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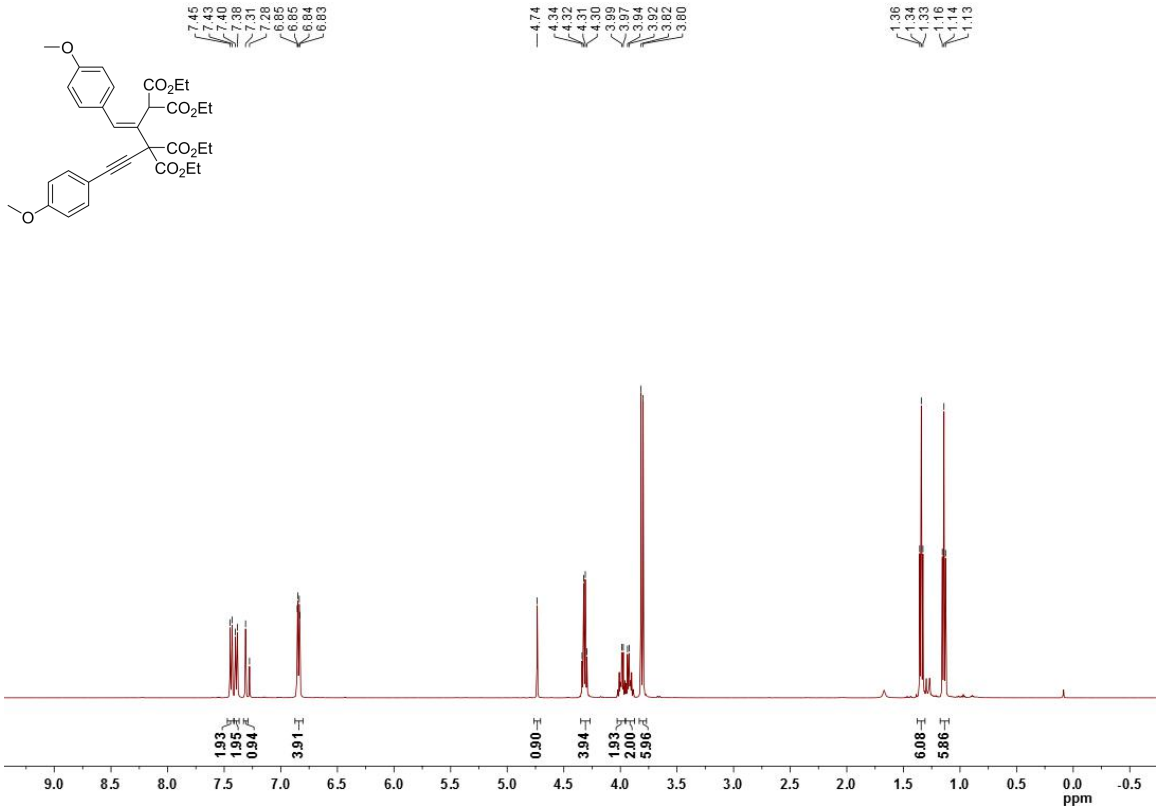
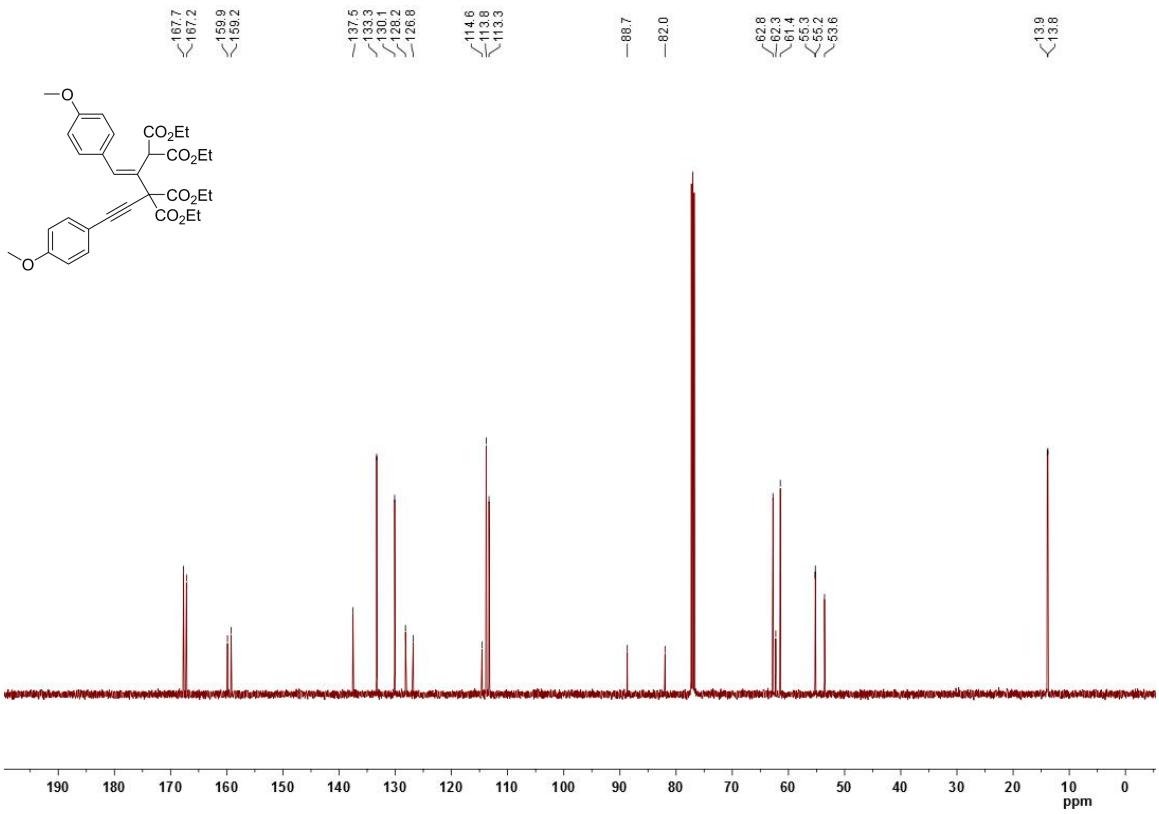
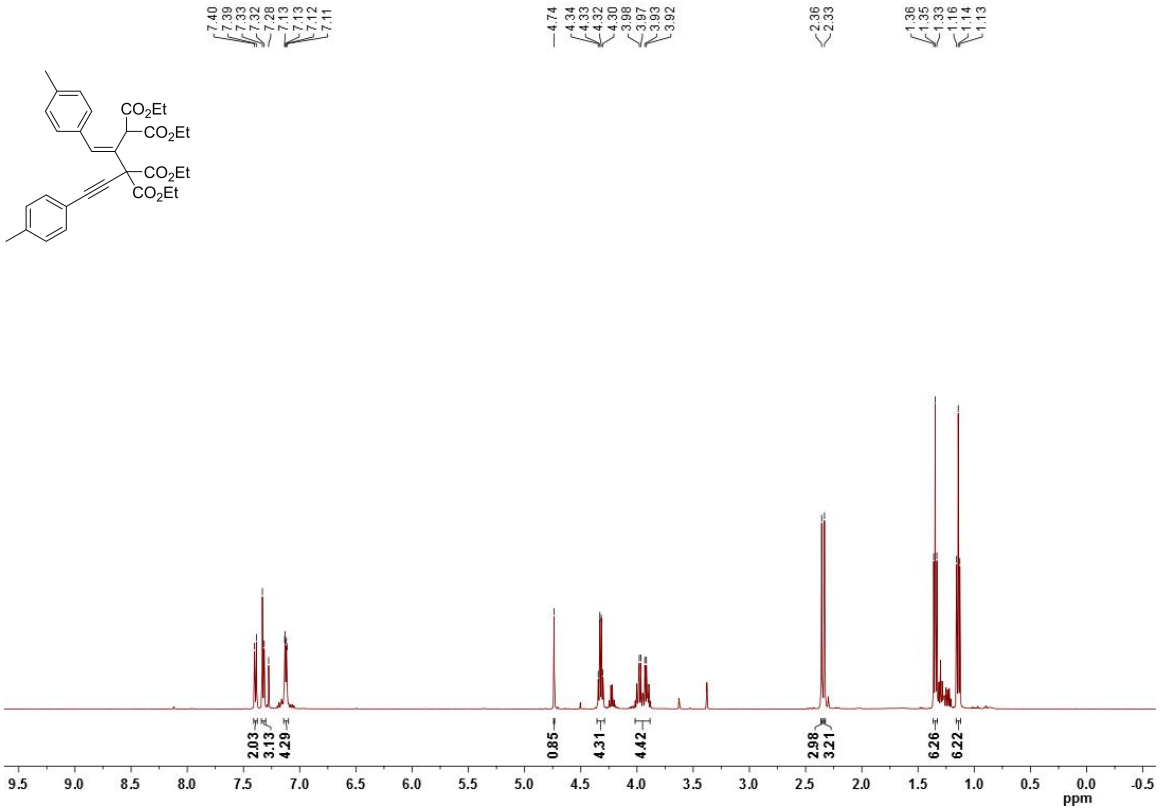
115.4
114.3
113.4
88.7
83.1
62.9
62.2
61.5
55.3
55.2
53.6
13.9
13.8
CO2Et
CO2Et
CO2Et
CO2Et
ppm

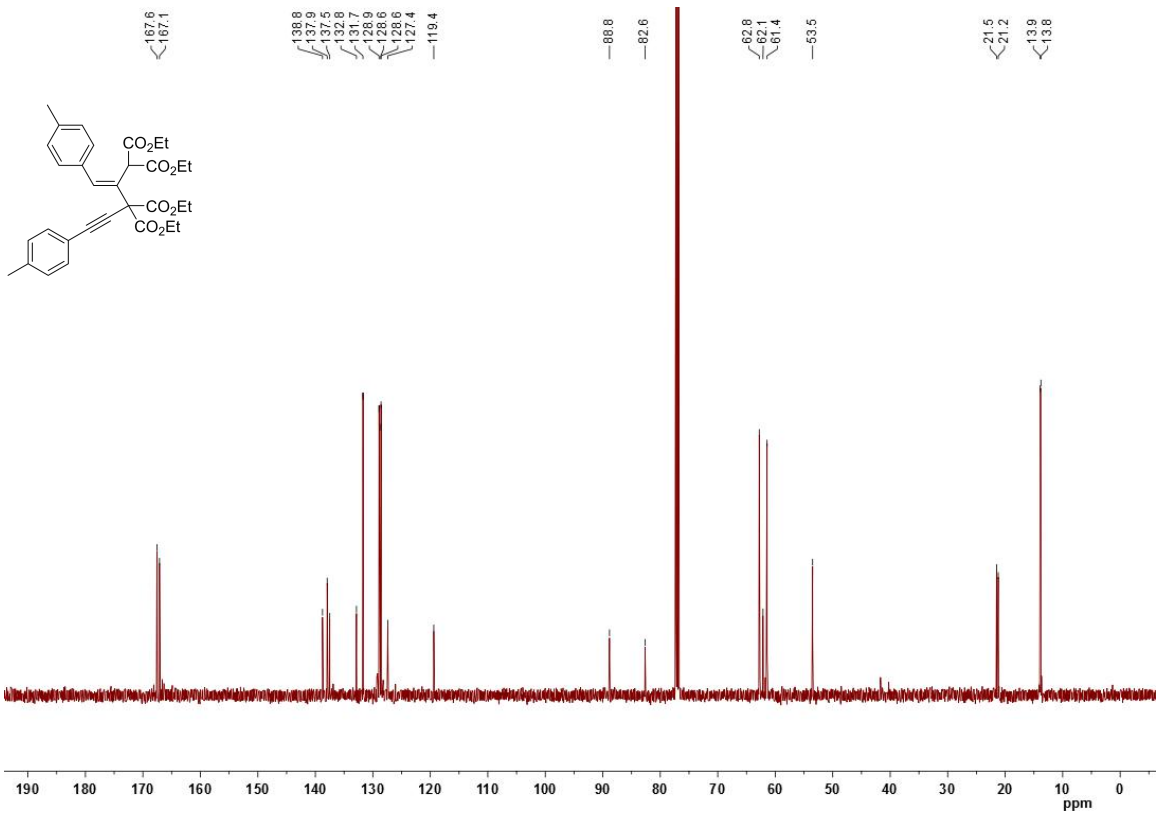
Compound 2l


7.45
7.43
7.40
7.38
7.31
7.28
6.85
6.85
6.84
6.83
4.74
4.34
4.32
4.31
4.30
3.99
3.97
3.94
3.92
3.82
3.80
1.36
1.34
1.33
1.16
1.14
1.13
CO2Et
CO2Et
CO2Et
CO2Et
O
O
1.93
1.95
0.94
3.91
0.90
3.94
1.93
2.00
5.90
6.08
5.86
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm

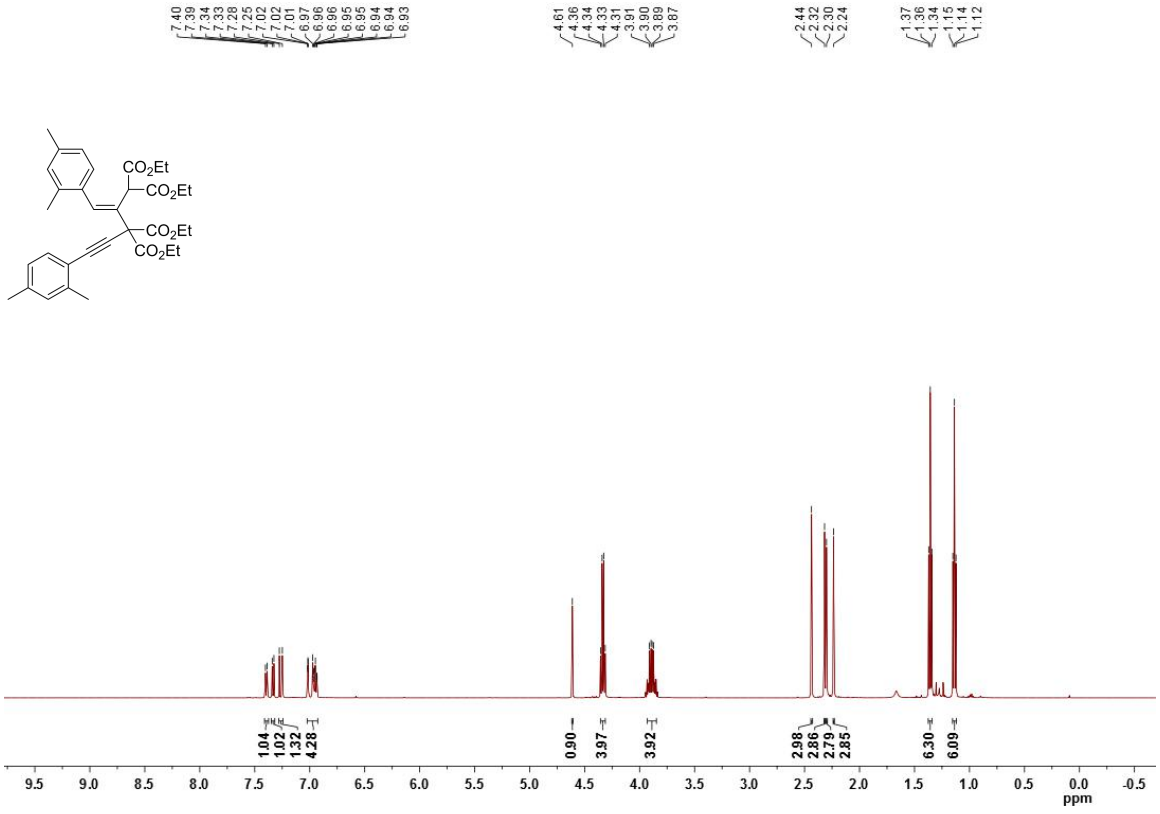

167.7
167.2
159.9
159.2
137.5
133.3
130.1
128.2
126.8
114.6
113.8
113.3
88.7
82.0
62.8
62.3
61.4
55.3
55.2
53.6
13.9
13.8
CO2Et
CO2Et
CO2Et
CO2Et
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

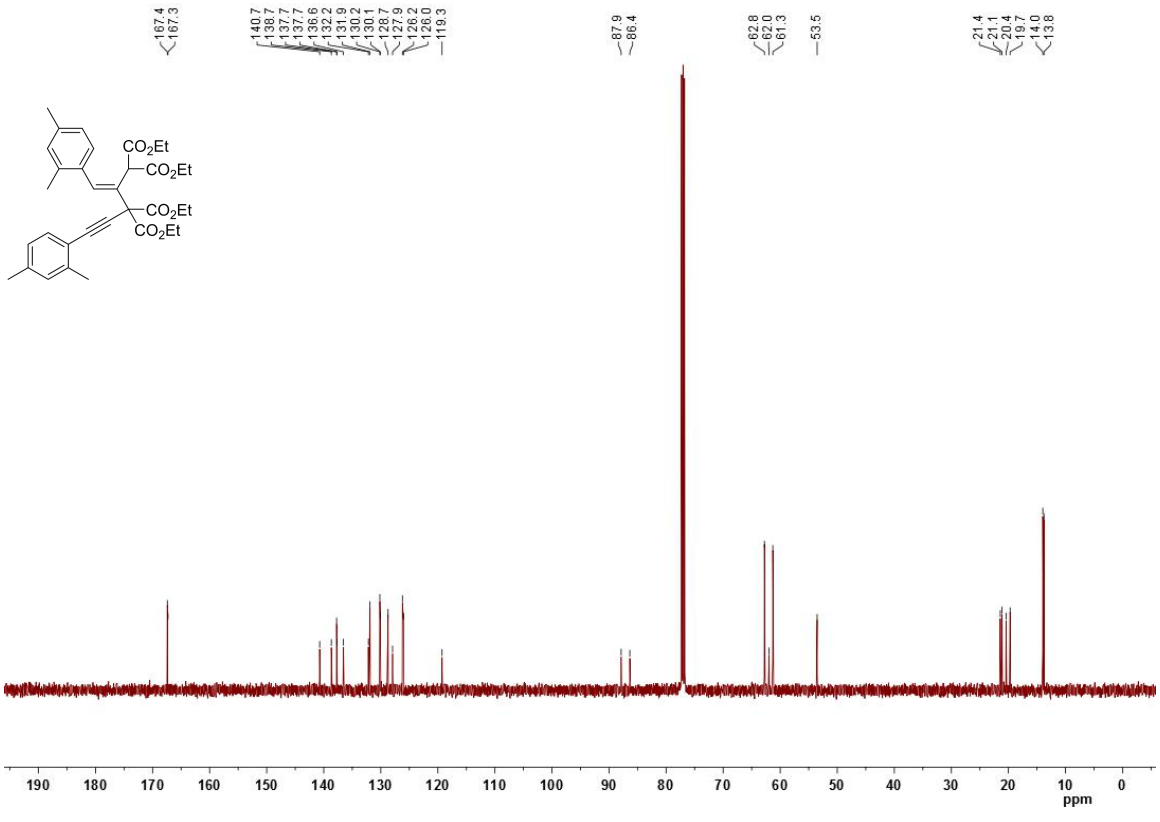
Compound 2m


7.40
7.39
7.33
7.32
7.28
7.13
7.13
7.12
7.11
4.74
4.34
4.33
4.32
4.30
3.98
3.97
3.93
3.92
2.36
2.33
1.36
1.35
1.33
1.16
1.14
1.13
CO2Et
CO2Et
CO2Et
CO2Et
2.03
3.13
4.29
0.85
4.31
4.42
2.98
3.21
6.26
6.22
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

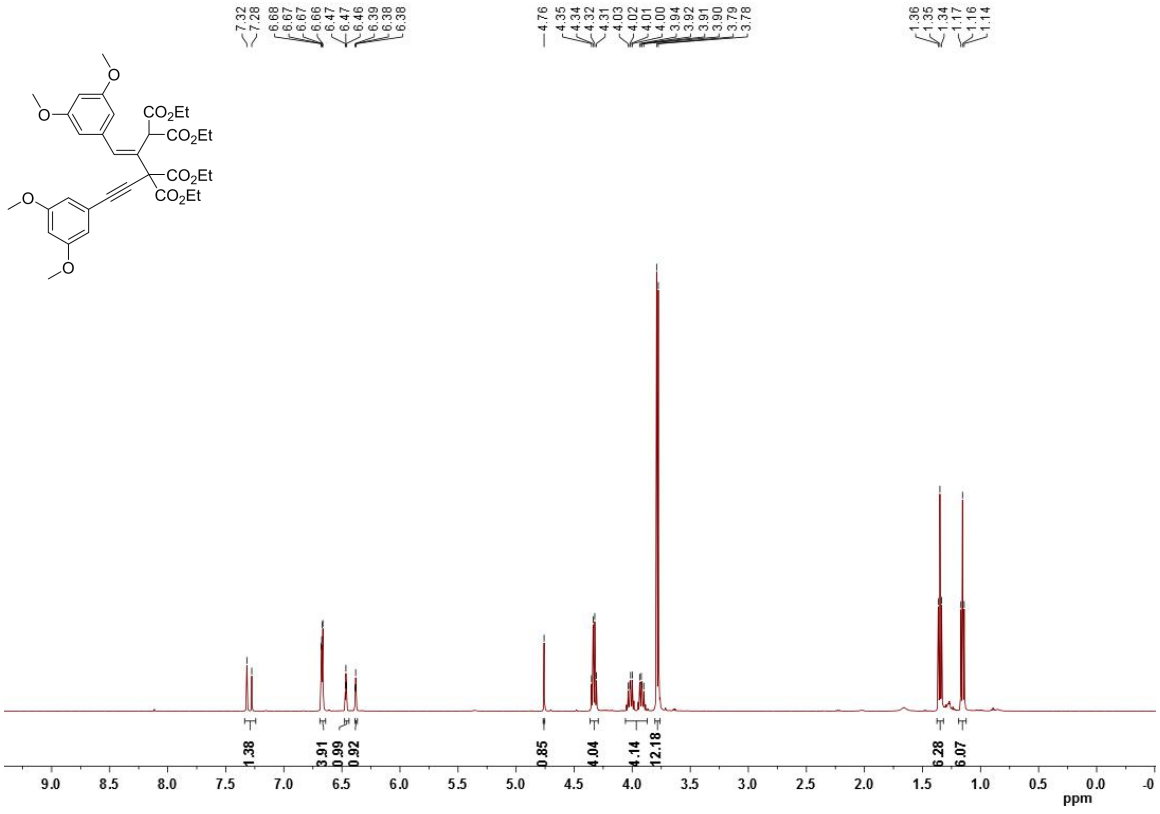

167.6
167.1
138.8
137.9
137.5
132.8
131.7
128.9
128.6
128.6
127.4
119.4
88.8
82.6
62.8
62.1
61.4
53.5
21.5
21.2
13.9
13.8
CO2Et
CO2Et
CO2Et
CO2Et
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

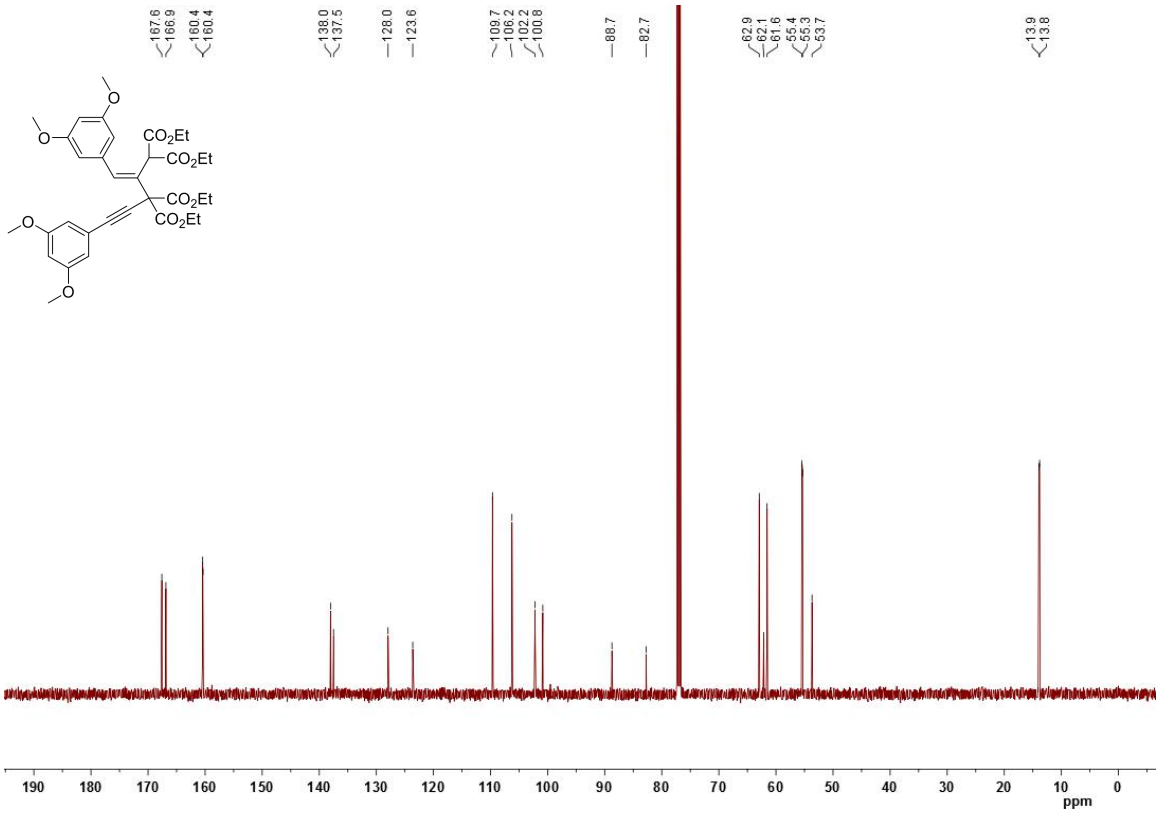
Compound 2n


7.40
7.39
7.34
7.33
7.28
7.25
7.02
7.02
7.01
6.97
6.96
6.96
6.95
6.95
6.94
6.94
6.93
4.61
4.36
4.34
4.33
4.31
3.91
3.90
3.89
3.87
2.44
2.32
2.30
2.24
1.37
1.36
1.34
1.15
1.14
1.12
CO2Et
CO2Et
CO2Et
CO2Et
1.04
1.02
1.32
4.28
0.90
3.97
3.92
2.98
2.86
2.79
2.85
6.30
6.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

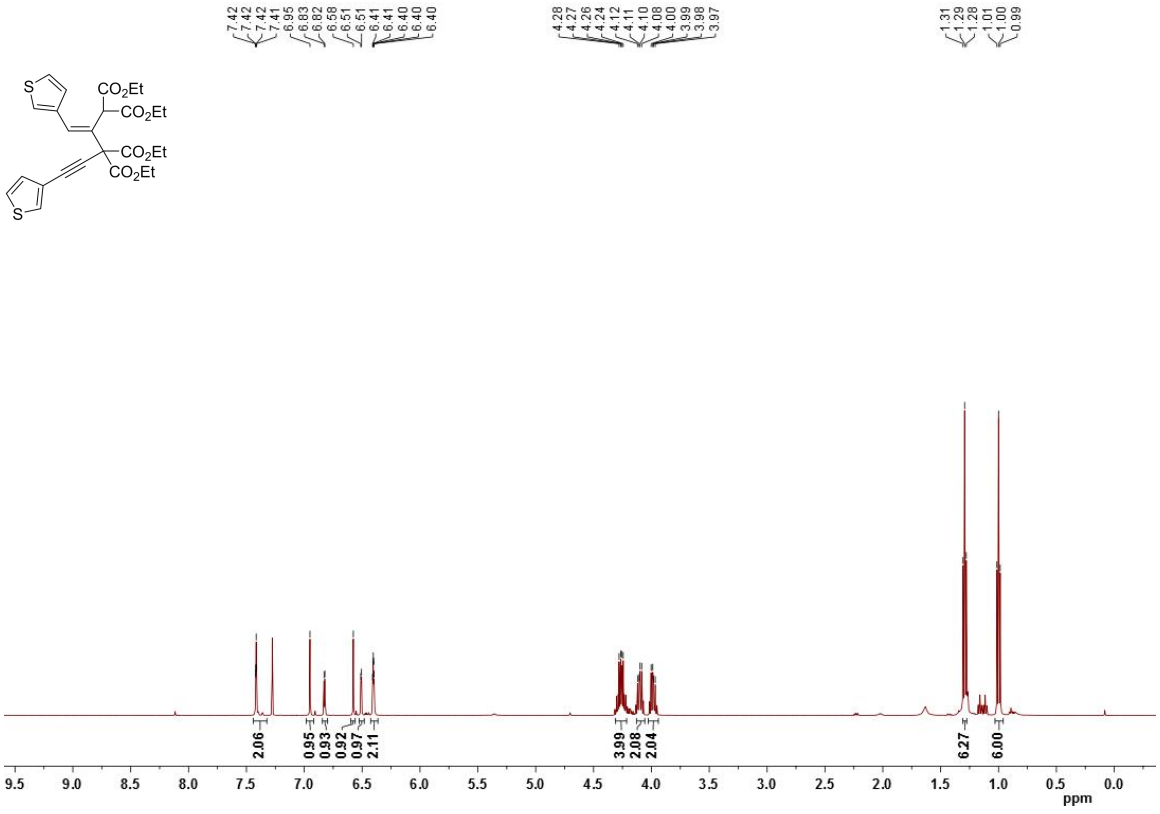

167.4
167.3
140.7
138.7
137.7
137.7
136.6
132.2
131.9
130.2
130.1
128.7
127.9
126.2
126.0
119.3
87.9
86.4
62.8
62.0
61.3
53.5
21.4
21.1
20.4
19.7
14.0
13.8
CO2Et
CO2Et
CO2Et
CO2Et
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

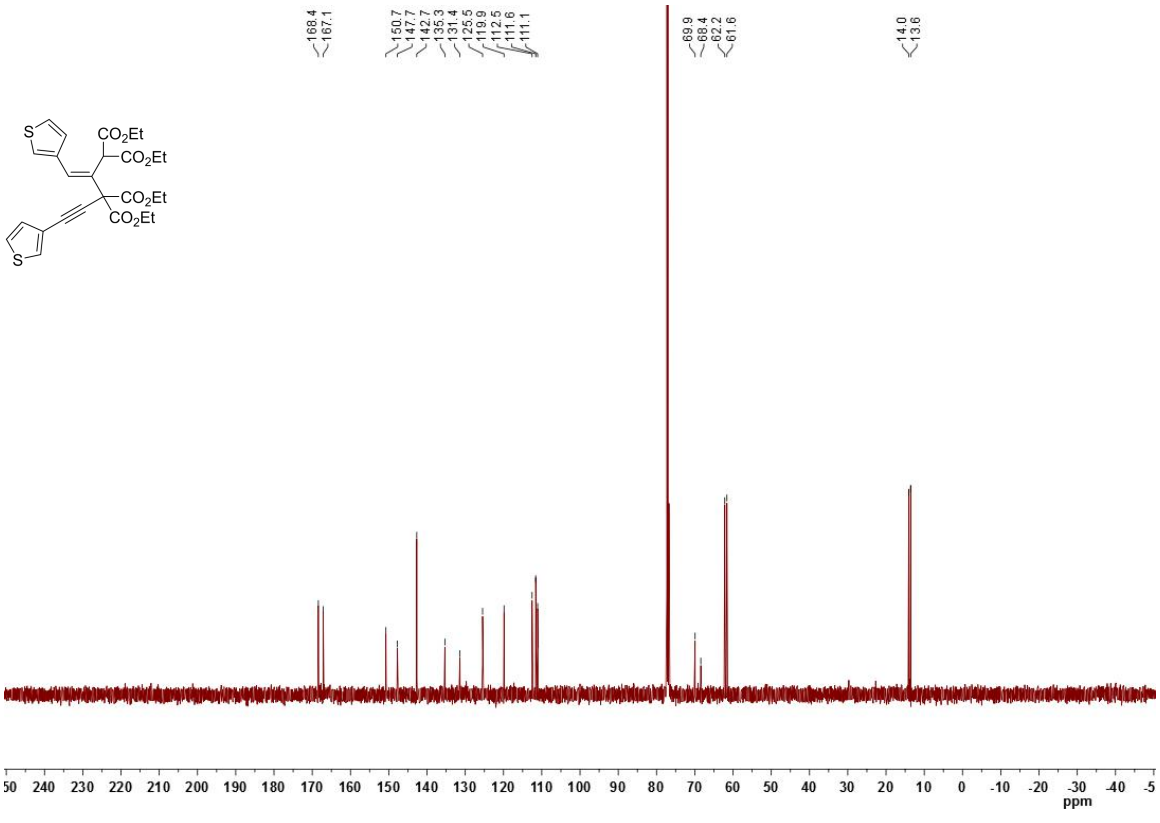
Compound 2o


7.32
7.28
6.68
6.67
6.67
6.66
6.47
6.47
6.46
6.39
6.38
6.38
4.76
4.35
4.34
4.32
4.31
4.03
4.02
4.01
4.00
3.94
3.92
3.91
3.90
3.79
3.78
1.36
1.35
1.34
1.17
1.16
1.14
CO2Et
CO2Et
CO2Et
CO2Et
1.38
3.91
0.99
0.92
0.85
4.04
4.14
12.18
6.28
6.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
ppm

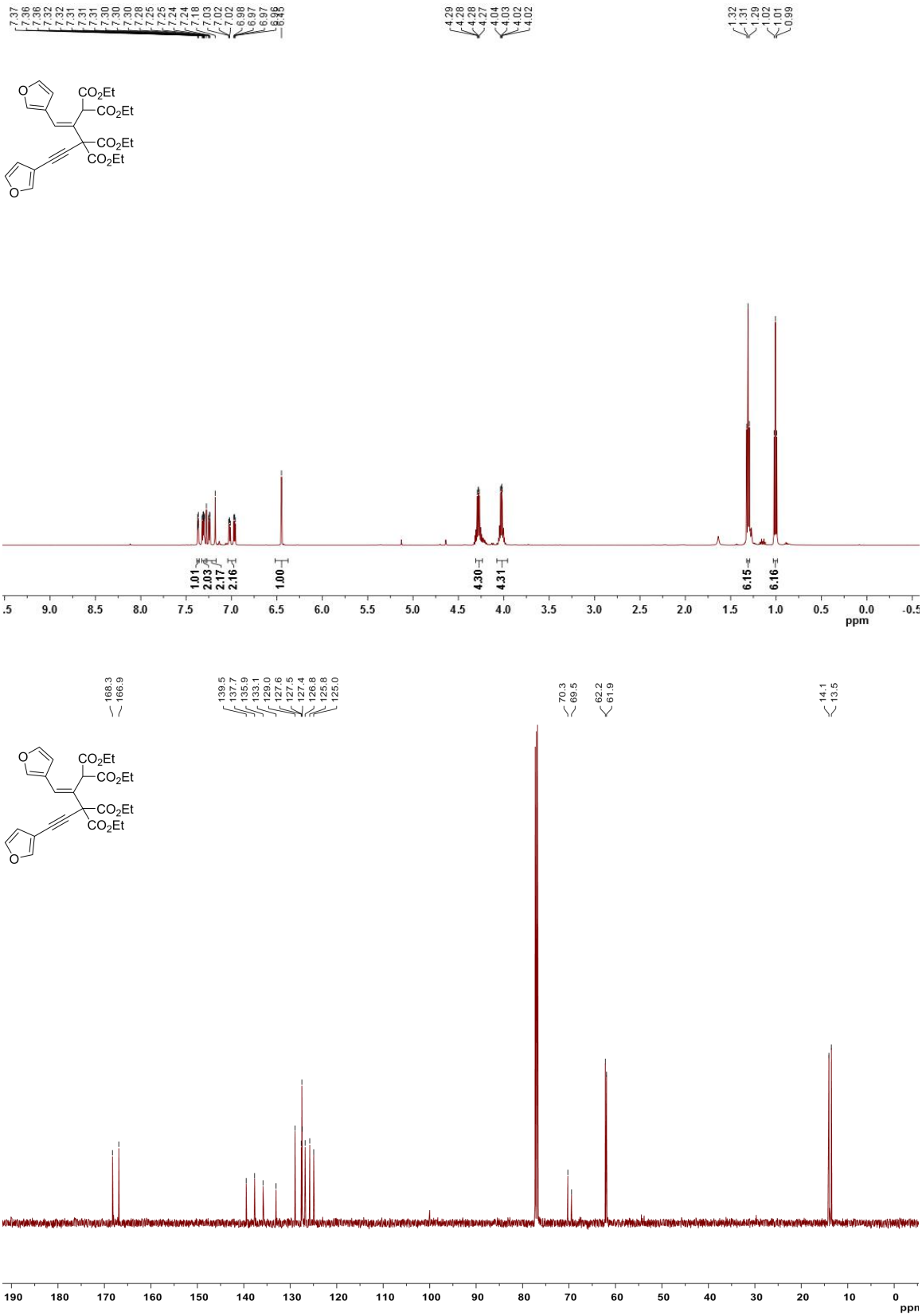

167.6
166.9
160.4
160.4
138.0
137.5
128.0
123.6
109.7
106.2
102.2
100.8
88.7
82.7
62.9
62.1
61.6
55.4
55.3
53.7
13.9
13.8
CO2Et
CO2Et
CO2Et
CO2Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 2p

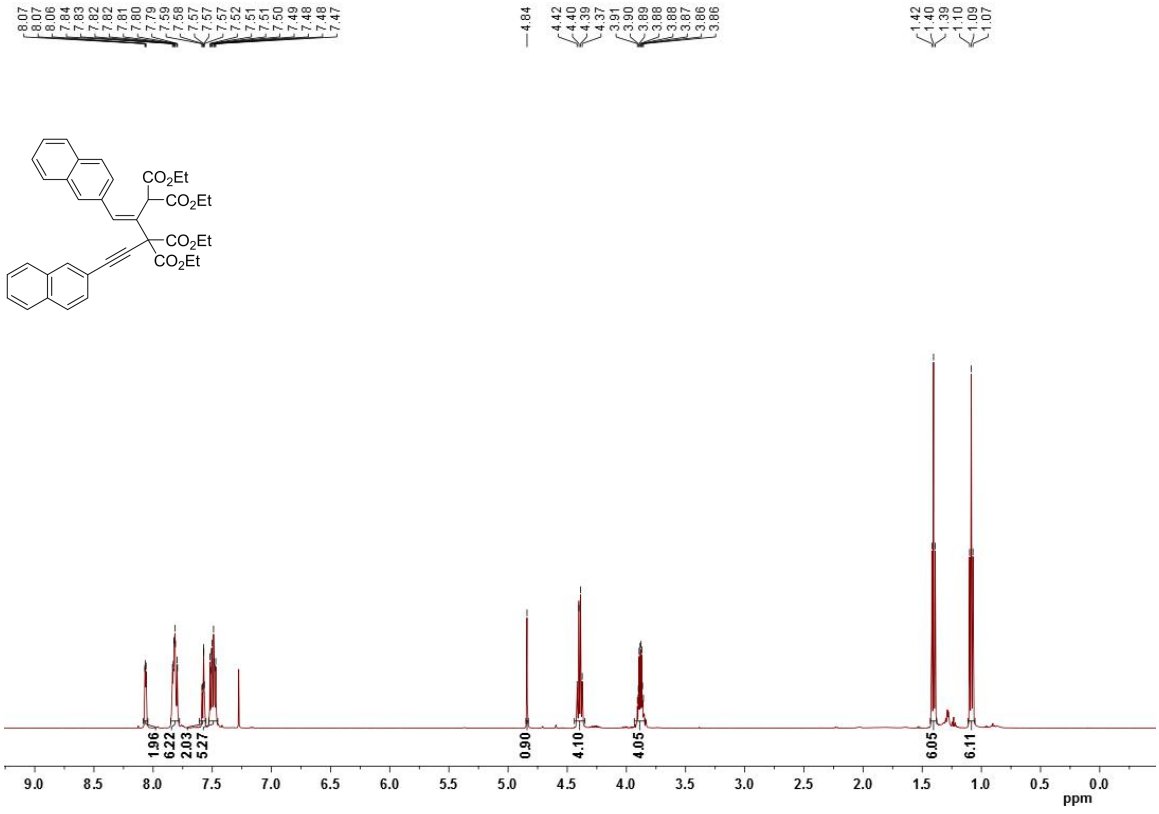

7.42
7.42
7.42
7.41
6.95
6.83
6.82
6.58
6.51
6.51
6.41
6.41
6.40
6.40
6.40
4.28
4.27
4.26
4.24
4.12
4.11
4.10
4.08
4.00
3.99
3.98
3.97
1.31
1.29
1.28
1.01
1.00
0.99
CO2Et
CO2Et
CO2Et
CO2Et
S
S
2.06
0.95
0.93
0.92
0.97
2.11
3.99
2.08
2.04
6.27
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

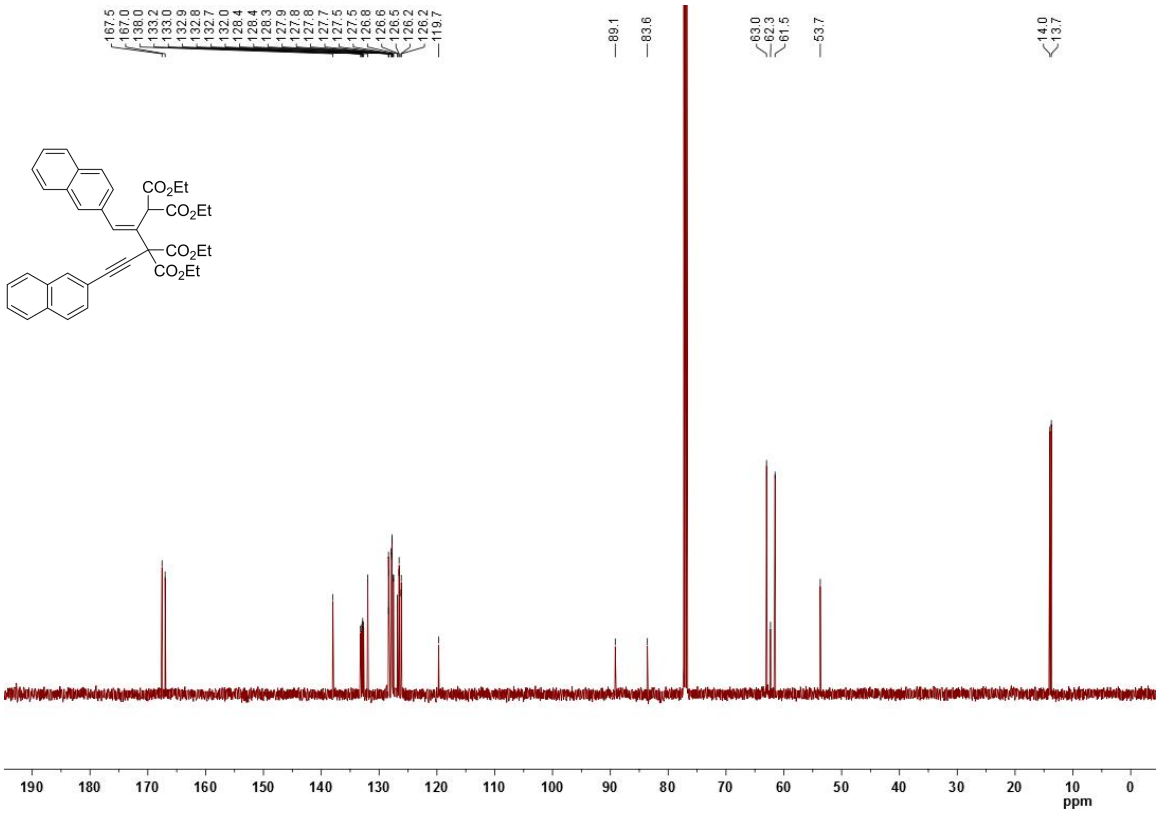

168.4
167.1
150.7
147.7
142.7
135.3
131.4
125.5
119.9
112.5
111.6
111.1
69.9
68.4
62.2
61.6
14.0
13.6
CO2Et
CO2Et
CO2Et
CO2Et
S
S
50 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -5
ppm

Compound 2q

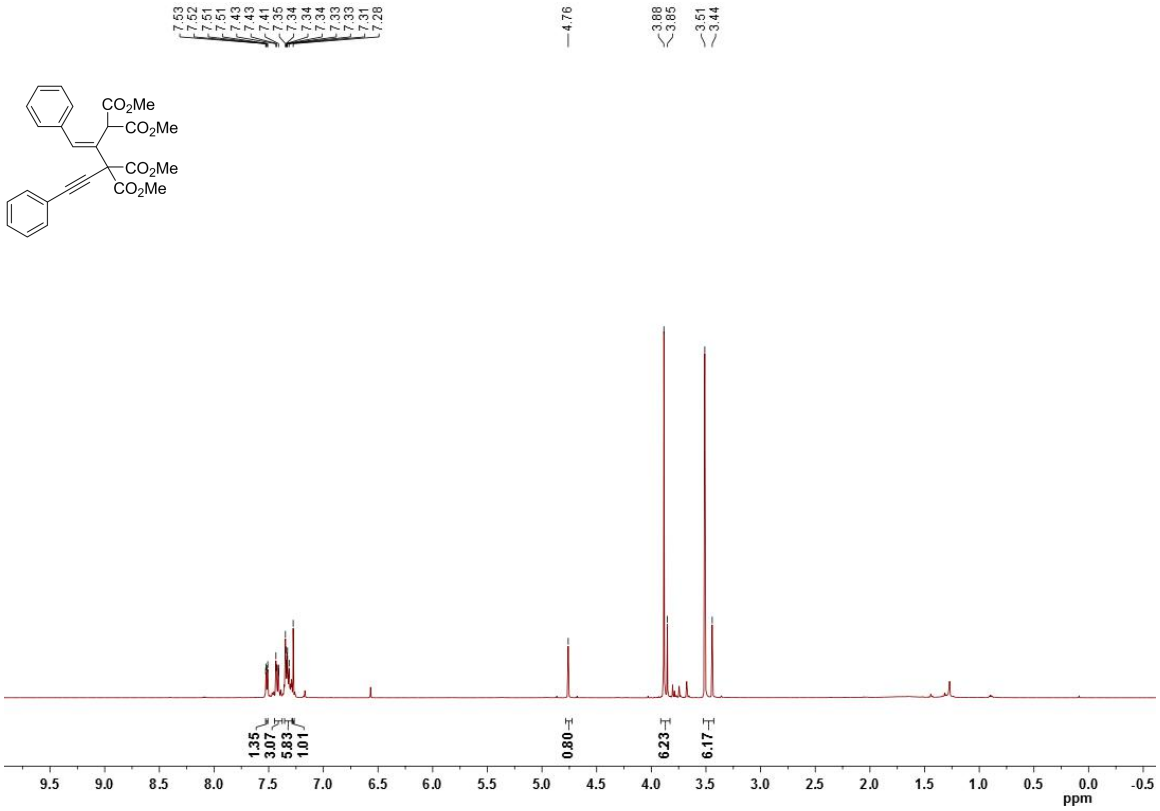

7.37
7.36
7.36
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
7.28
7.25
7.25
7.24
7.24
7.18
7.03
7.02
7.02
6.98
6.97
6.97
6.96
6.95
4.29
4.28
4.28
4.27
4.04
4.03
4.02
4.02
1.32
1.31
1.29
1.02
1.01
0.99
CO2Et
CO2Et
CO2Et
CO2Et
1.01
2.03
2.17
2.16
1.00
4.30
4.31
6.15
6.16
ppm
168.3
166.9
139.5
137.7
135.9
133.1
129.0
127.6
127.5
127.4
126.8
125.8
125.0
70.3
69.5
62.2
61.9
14.1
13.5
ppm

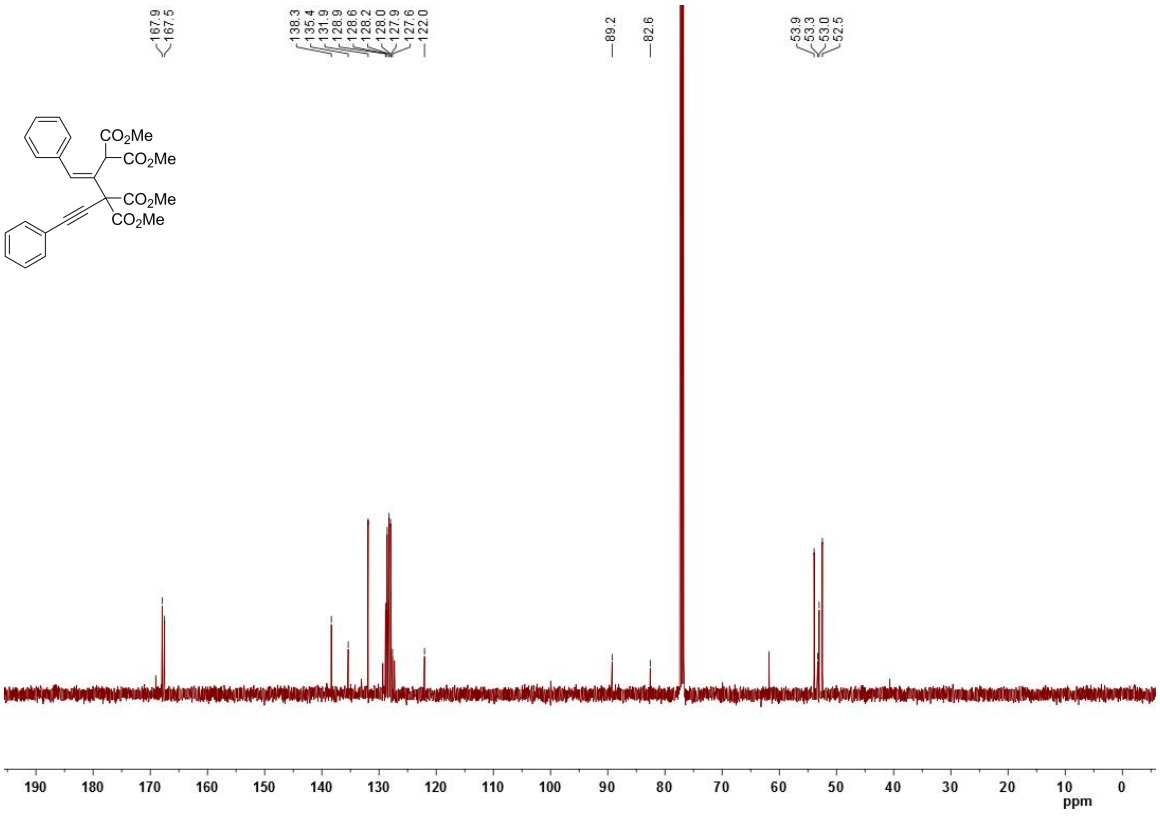
Compound 2r


8.07
8.07
8.06
7.84
7.83
7.82
7.82
7.81
7.80
7.79
7.59
7.58
7.57
7.57
7.57
7.52
7.51
7.51
7.50
7.49
7.48
7.48
7.47
4.84
4.42
4.40
4.39
4.37
3.91
3.90
3.89
3.88
3.88
3.87
3.86
3.86
1.42
1.40
1.39
1.10
1.09
1.07
CO2Et
CO2Et
CO2Et
CO2Et
1.96
6.22
2.03
5.27
0.90
4.10
4.05
6.05
6.11
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
ppm

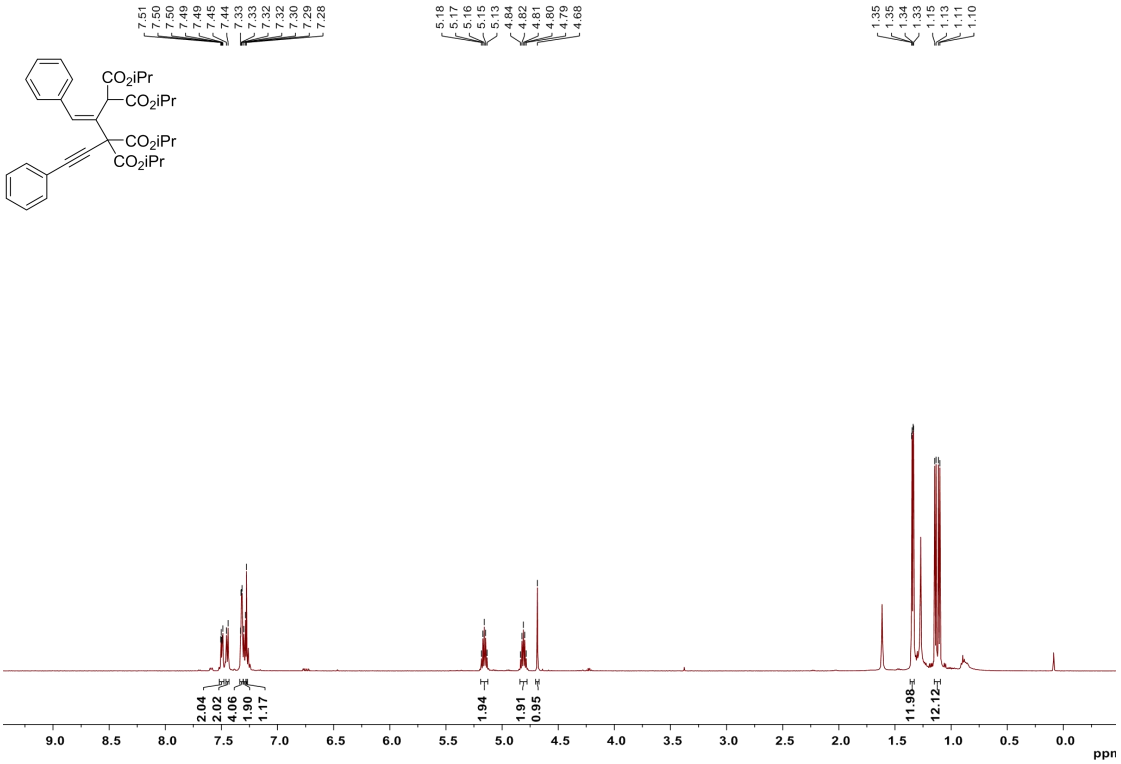

167.5
167.0
138.0
133.2
133.0
132.9
132.8
132.7
132.0
128.4
128.3
127.9
127.8
127.8
127.7
127.5
127.5
126.8
126.6
126.5
126.2
126.2
119.7
89.1
83.6
63.0
62.3
61.5
53.7
14.0
13.7
CO2Et
CO2Et
CO2Et
CO2Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

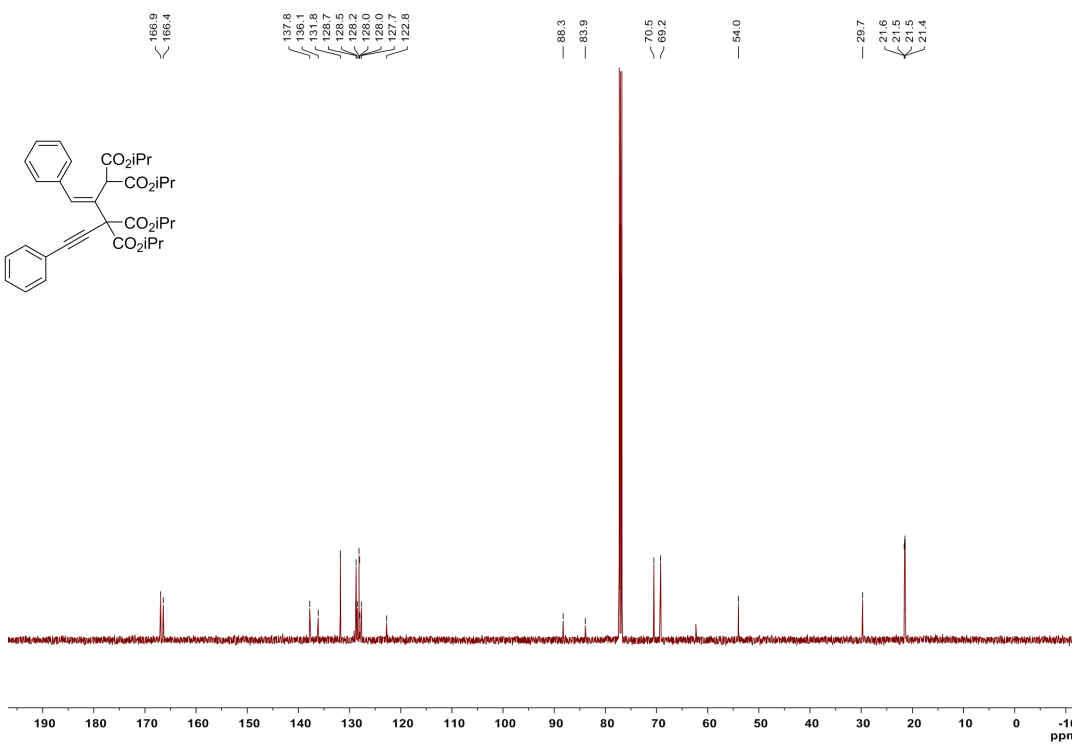
Compound 2s


7.53
7.52
7.51
7.51
7.43
7.43
7.41
7.35
7.34
7.34
7.34
7.33
7.33
7.31
7.28
4.76
3.88
3.85
3.51
3.44
CO2Me
CO2Me
CO2Me
CO2Me
1.35
3.07
5.83
1.01
0.80
6.23
6.17
ppm

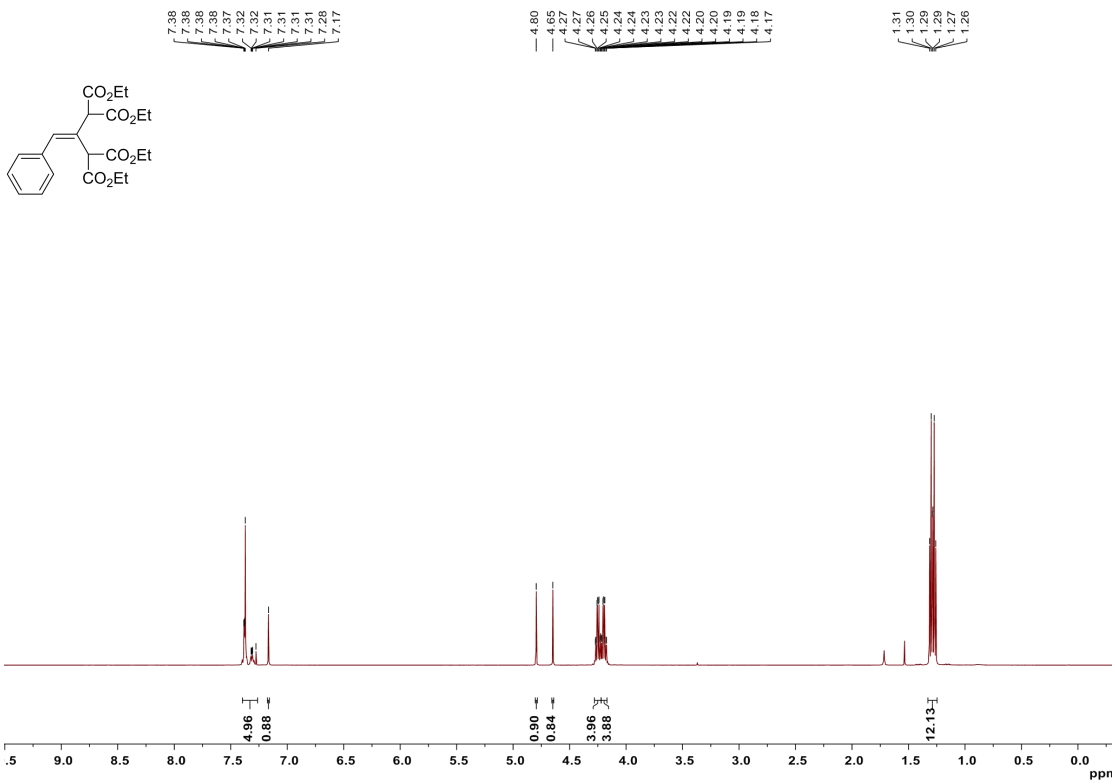

167.9
167.5
138.3
135.4
131.9
128.9
128.6
128.2
128.0
127.9
127.6
122.0
89.2
82.6
53.9
53.3
53.0
52.5
CO2Me
CO2Me
CO2Me
CO2Me
ppm

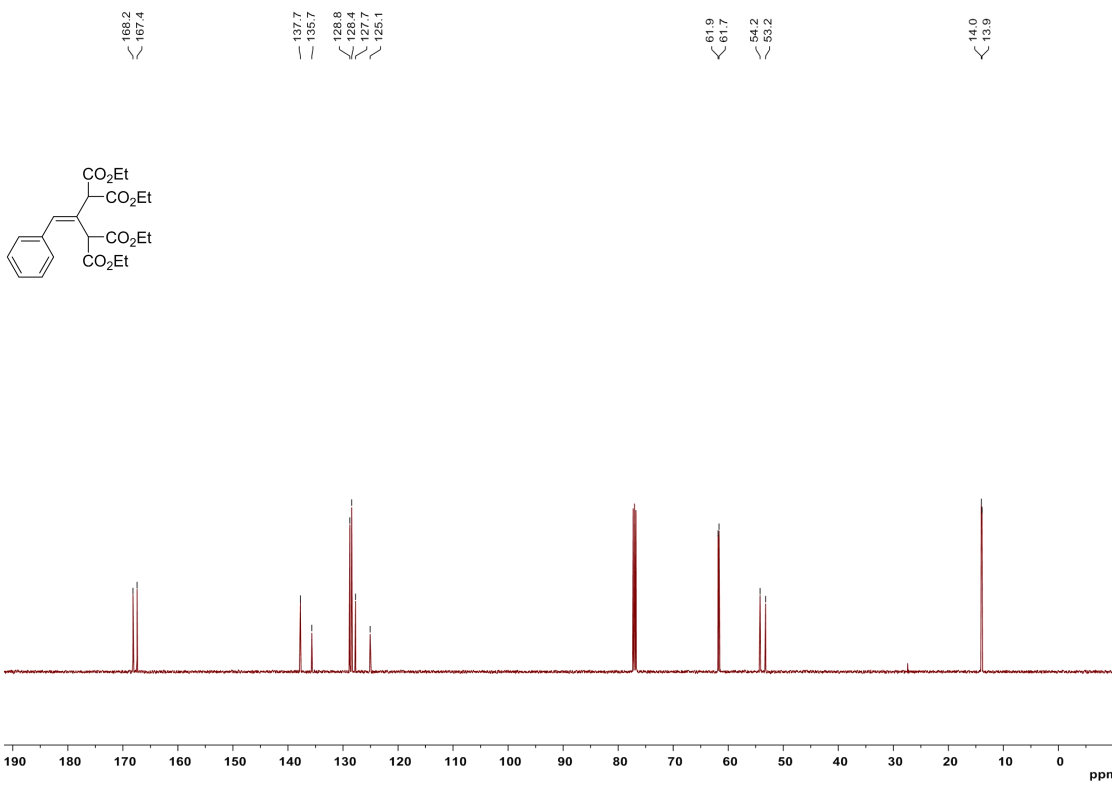
Compound 2t


7.51
7.50
7.50
7.49
7.49
7.45
7.44
7.33
7.32
7.32
7.30
7.29
7.28
5.18
5.17
5.16
5.15
5.13
4.84
4.82
4.81
4.80
4.79
4.68
1.35
1.35
1.34
1.33
1.15
1.13
1.11
1.10
CO2iPr
CO2iPr
CO2iPr
CO2iPr
2.04
2.02
4.06
1.90
1.17
1.94
1.91
0.95
11.98
12.12
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
ppm

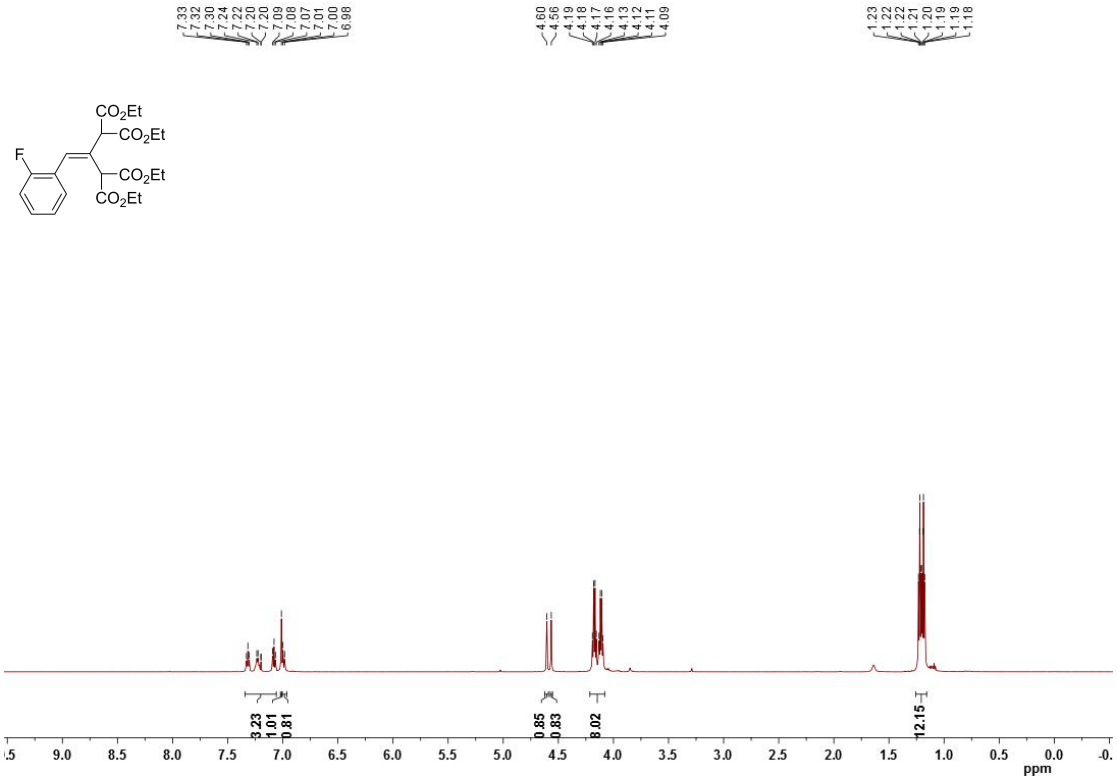

166.9
166.4
137.8
136.1
131.8
128.7
128.5
128.2
128.0
128.0
127.7
122.8
88.3
83.9
70.5
69.2
54.0
29.7
21.6
21.5
21.5
21.4
CO2iPr
CO2iPr
CO2iPr
CO2iPr
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

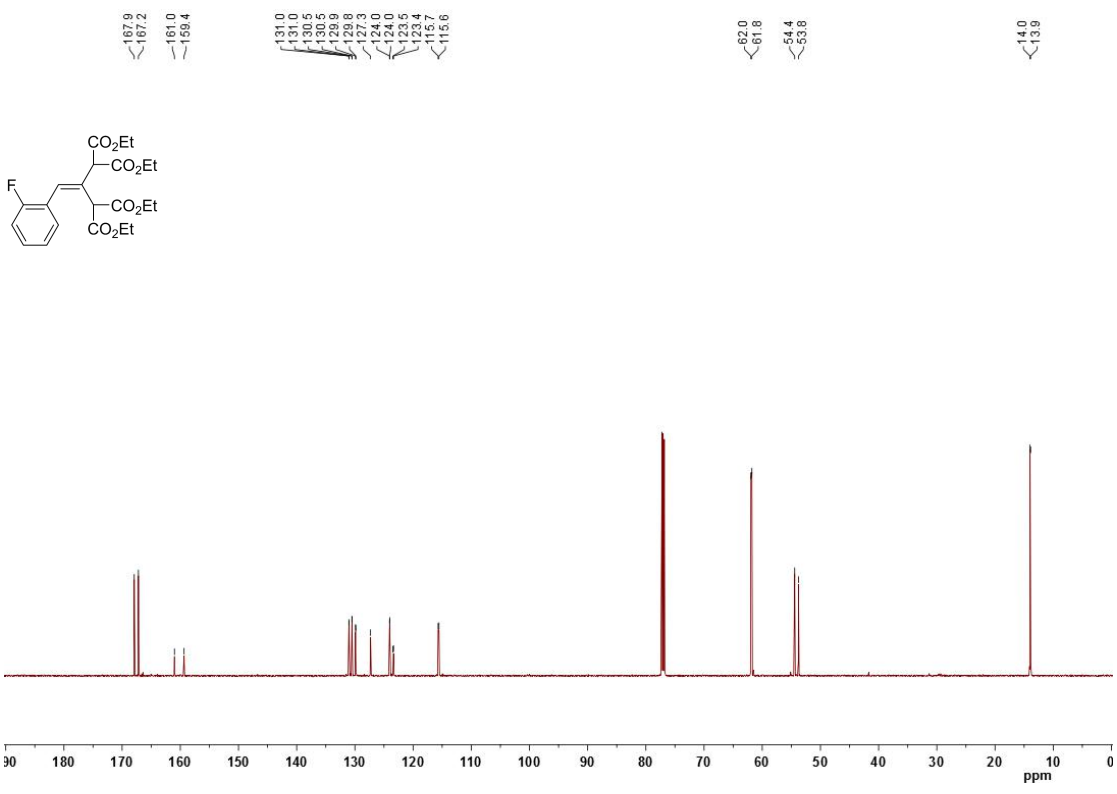
Compound 4a


7.38
7.38
7.38
7.38
7.37
7.32
7.32
7.31
7.31
7.31
7.31
7.28
7.17
4.80
4.65
4.27
4.27
4.26
4.25
4.24
4.24
4.23
4.23
4.22
4.22
4.20
4.20
4.19
4.19
4.18
4.17
1.31
1.30
1.29
1.29
1.27
1.26
CO2Et
CO2Et
CO2Et
CO2Et
4.96
0.88
0.90
0.84
3.96
3.88
12.13
ppm

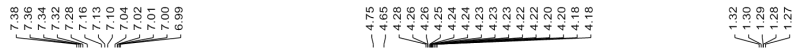

168.2
167.4
137.7
135.7
128.8
128.4
127.7
125.1
61.9
61.7
54.2
53.2
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
ppm

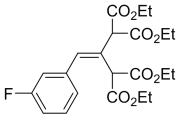
Compound 4b

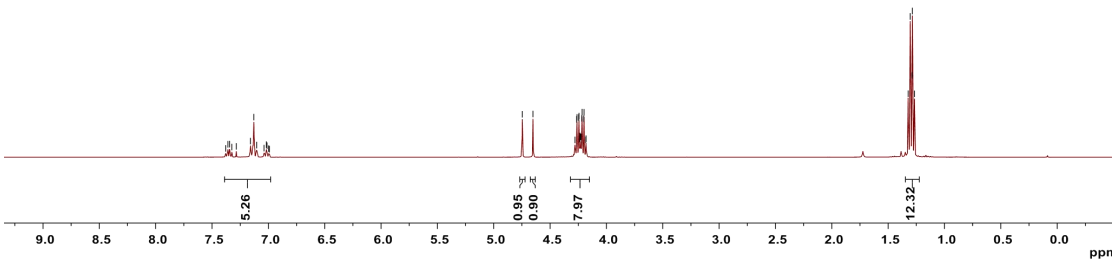

7.33
7.32
7.30
7.24
7.22
7.20
7.20
7.09
7.08
7.07
7.01
7.00
6.98
4.60
4.56
4.19
4.18
4.17
4.16
4.13
4.12
4.11
4.09
1.23
1.22
1.22
1.21
1.20
1.19
1.19
1.19
1.18
CO2Et
CO2Et
F
CO2Et
CO2Et
3.23
1.01
0.81
0.85
0.83
8.02
12.15
ppm


167.9
167.2
161.0
159.4
131.0
131.0
130.5
130.5
129.9
129.8
127.3
124.0
124.0
123.5
123.4
115.7
115.6
62.0
61.8
54.4
53.8
14.0
13.9
CO2Et
CO2Et
F
CO2Et
CO2Et
ppm

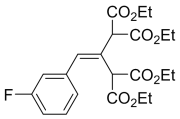
Compound 4c

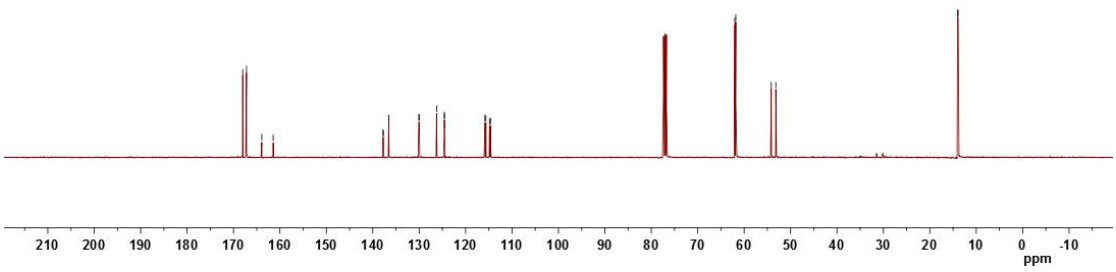

7.38
7.36
7.34
7.32
7.28
7.16
7.13
7.10
7.04
7.02
7.01
7.00
6.99
4.75
4.65
4.28
4.26
4.26
4.25
4.24
4.24
4.23
4.23
4.23
4.22
4.22
4.20
4.20
4.18
4.18
1.32
1.30
1.29
1.28
1.27


CO2Et
CO2Et
CO2Et
CO2Et
F

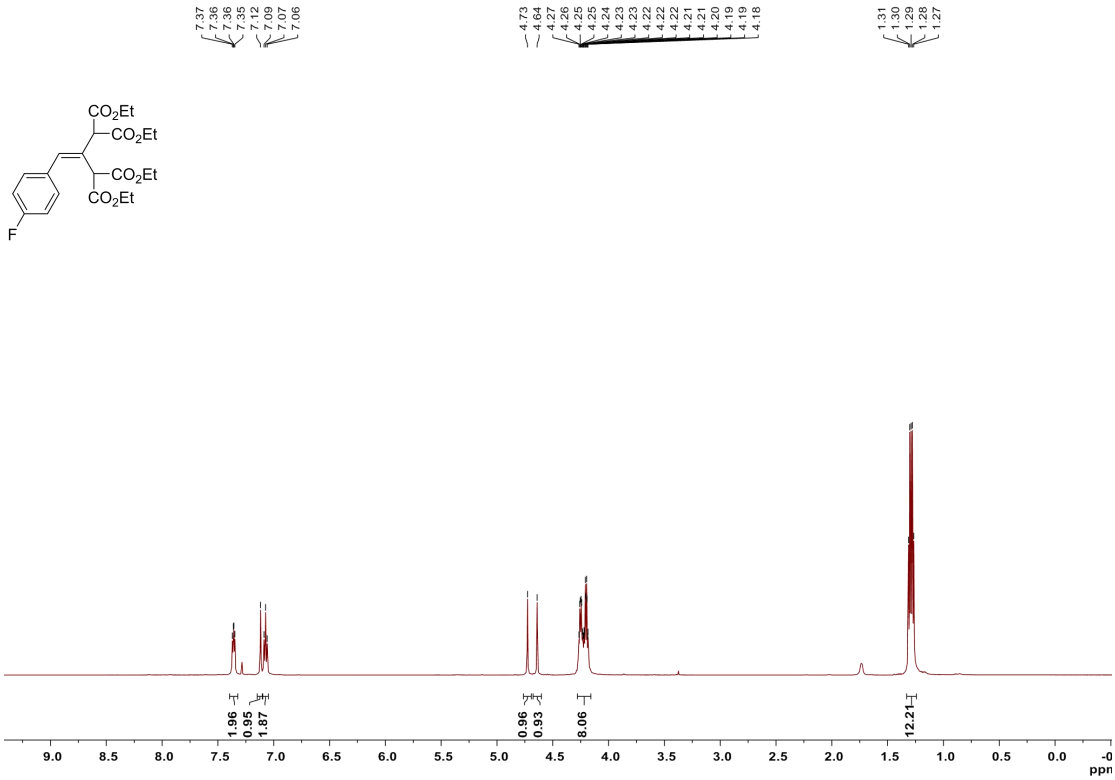

5.26
0.95
0.90
7.97
12.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

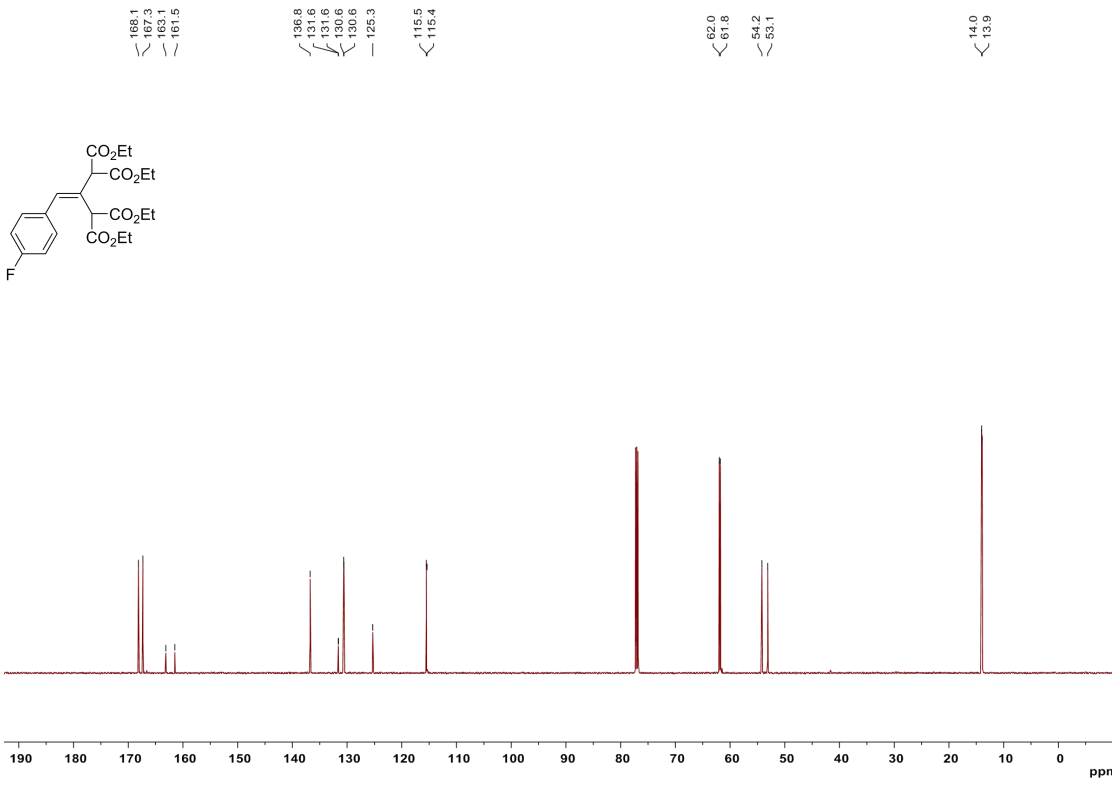

168.0
167.2
163.9
161.5
137.8
137.7
136.6
136.5
130.1
130.0
126.2
124.6
124.6
115.8
115.6
114.8
114.6
62.0
61.8
54.2
53.2
14.0
13.9


CO2Et
CO2Et
CO2Et
CO2Et
F

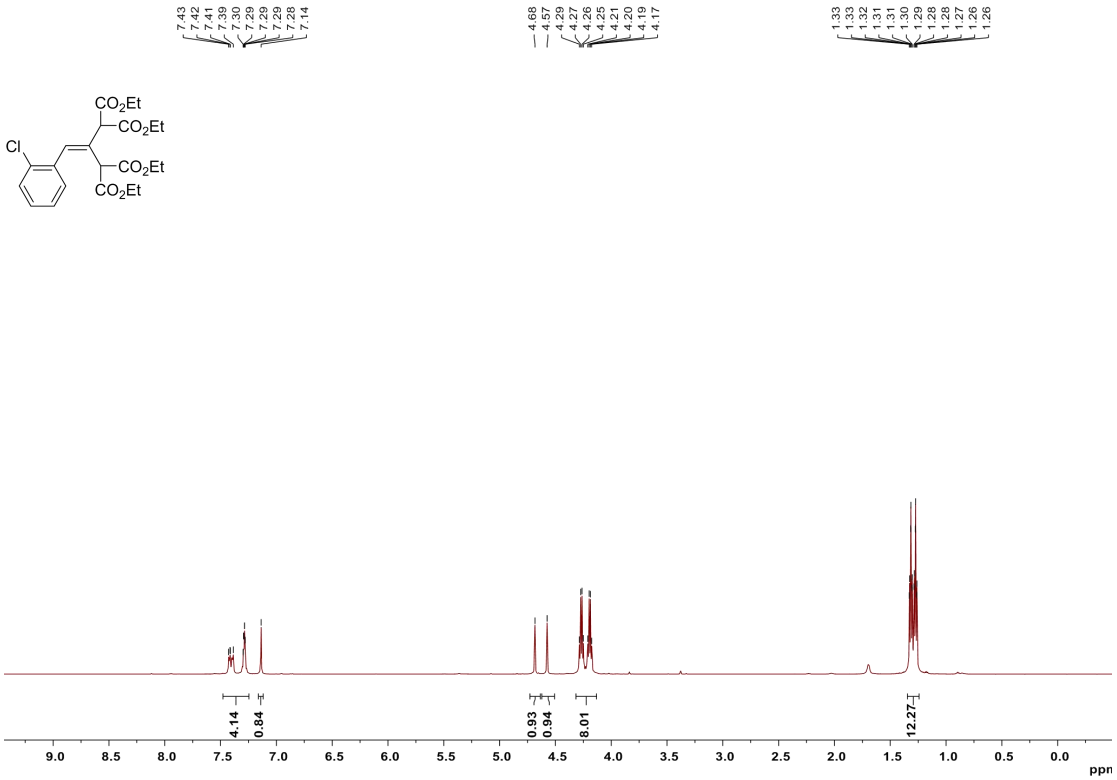

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
ppm

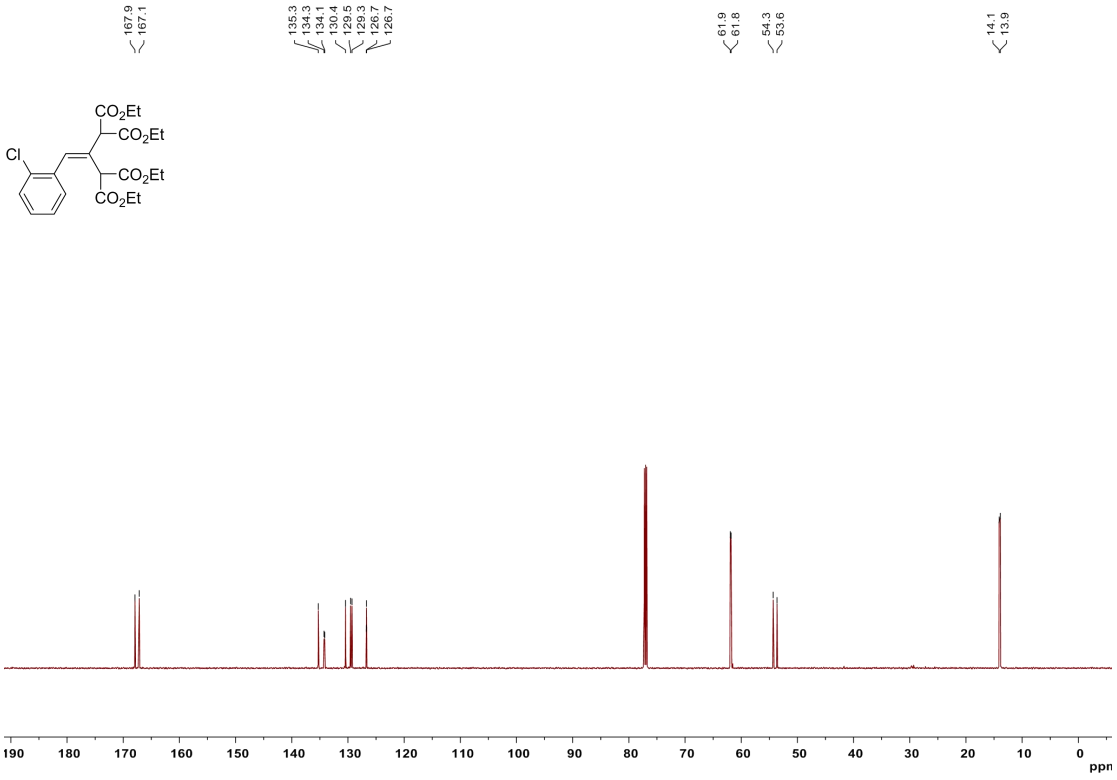
Compound 4d


7.37
7.36
7.36
7.35
7.12
7.09
7.07
7.06
4.73
4.64
4.27
4.26
4.25
4.25
4.24
4.23
4.23
4.22
4.22
4.22
4.21
4.21
4.20
4.19
4.19
4.18
1.31
1.30
1.29
1.28
1.27
CO2Et
CO2Et
CO2Et
CO2Et
F
1.96
0.95
1.87
0.96
0.93
8.06
12.21
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
ppm

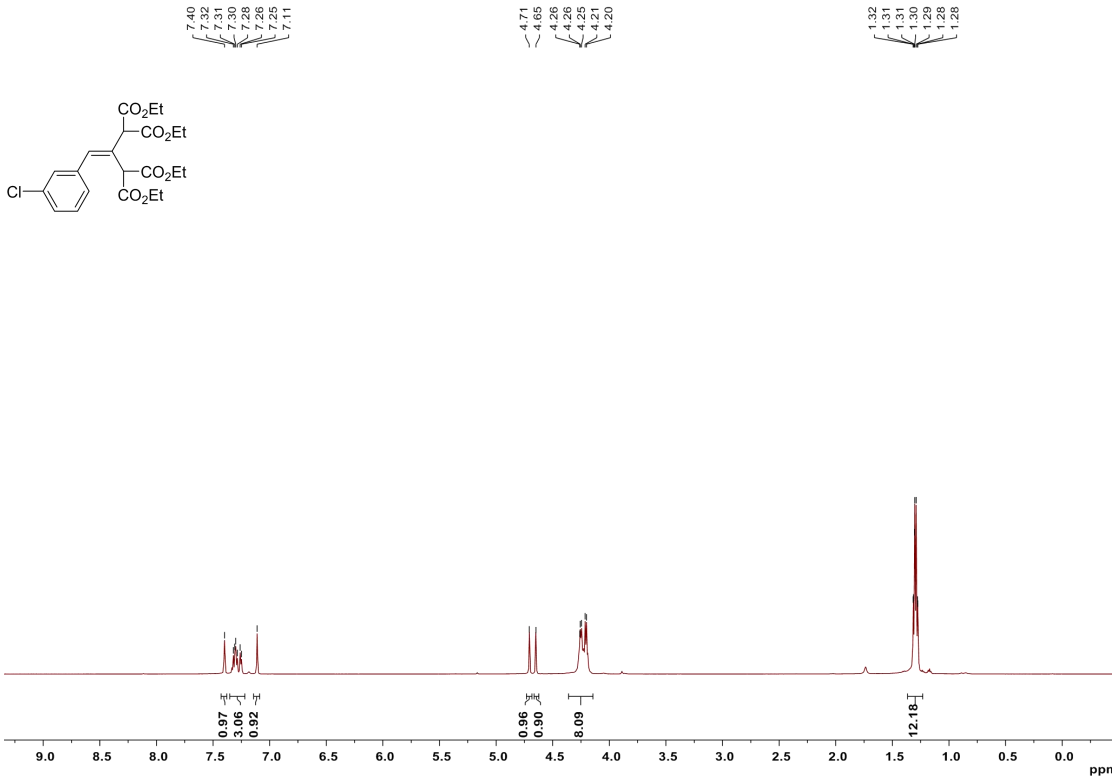

168.1
167.3
163.1
161.5
136.8
131.6
131.6
130.6
130.6
125.3
115.5
115.4
62.0
61.8
54.2
53.1
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
F
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

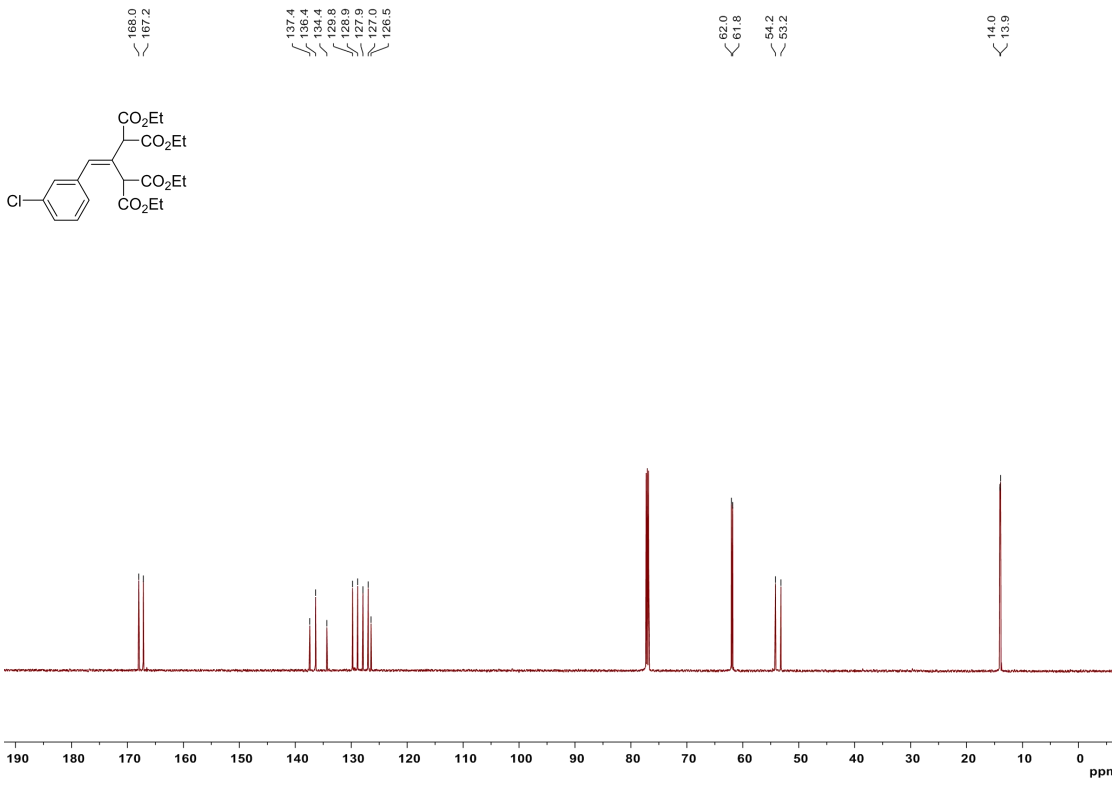
Compound 4e


7.43
7.42
7.41
7.39
7.30
7.29
7.29
7.29
7.28
7.14
4.68
4.57
4.29
4.27
4.26
4.25
4.21
4.20
4.19
4.17
1.33
1.33
1.32
1.31
1.31
1.30
1.29
1.28
1.28
1.27
1.26
1.26
CO2Et
CO2Et
Cl
CO2Et
CO2Et
4.14
0.84
0.93
0.94
8.01
12.27
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
ppm

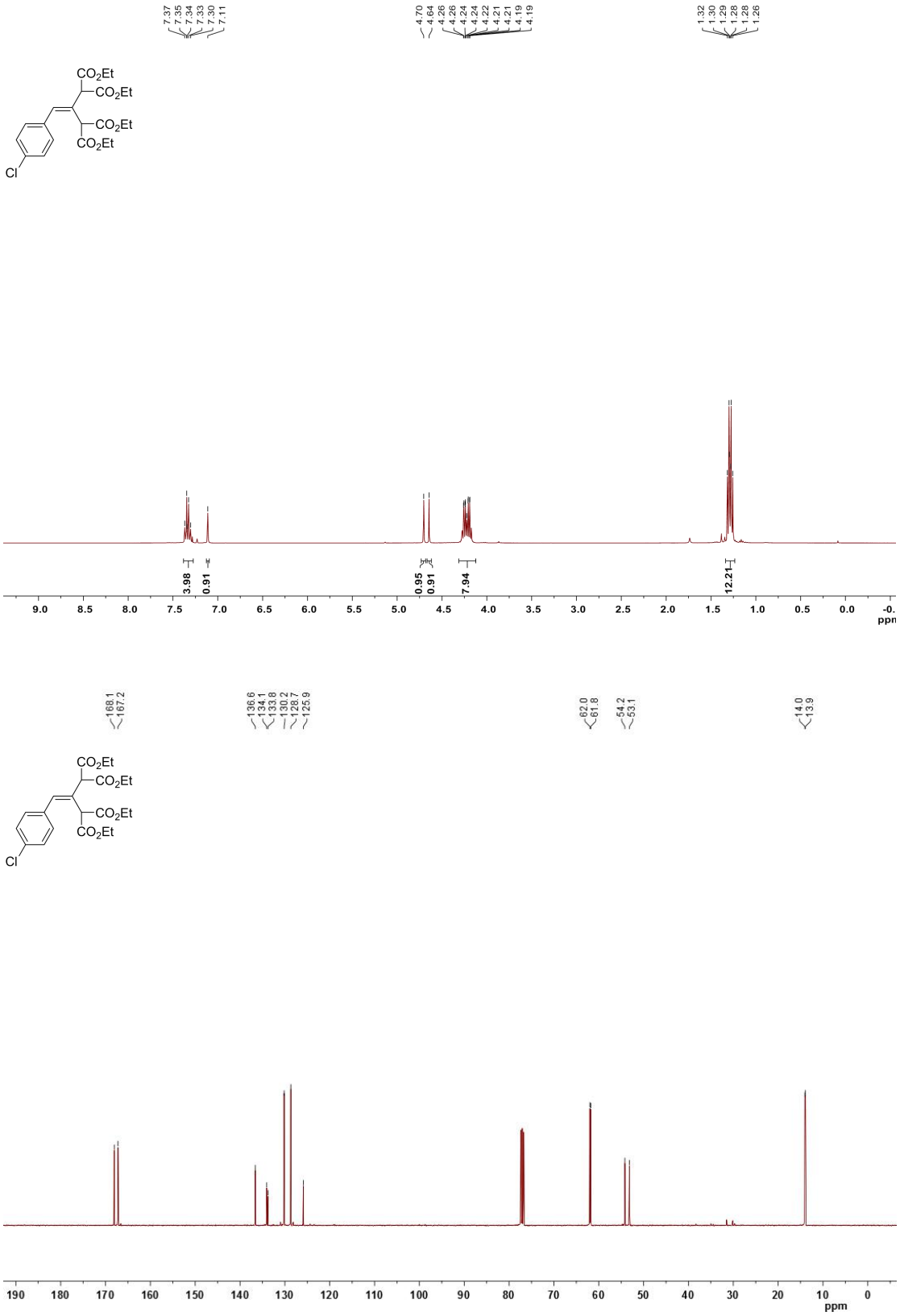

167.9
167.1
135.3
134.3
134.1
130.4
129.5
129.3
126.7
126.7
61.9
61.8
54.3
53.6
14.1
13.9
CO2Et
CO2Et
Cl
CO2Et
CO2Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 4f

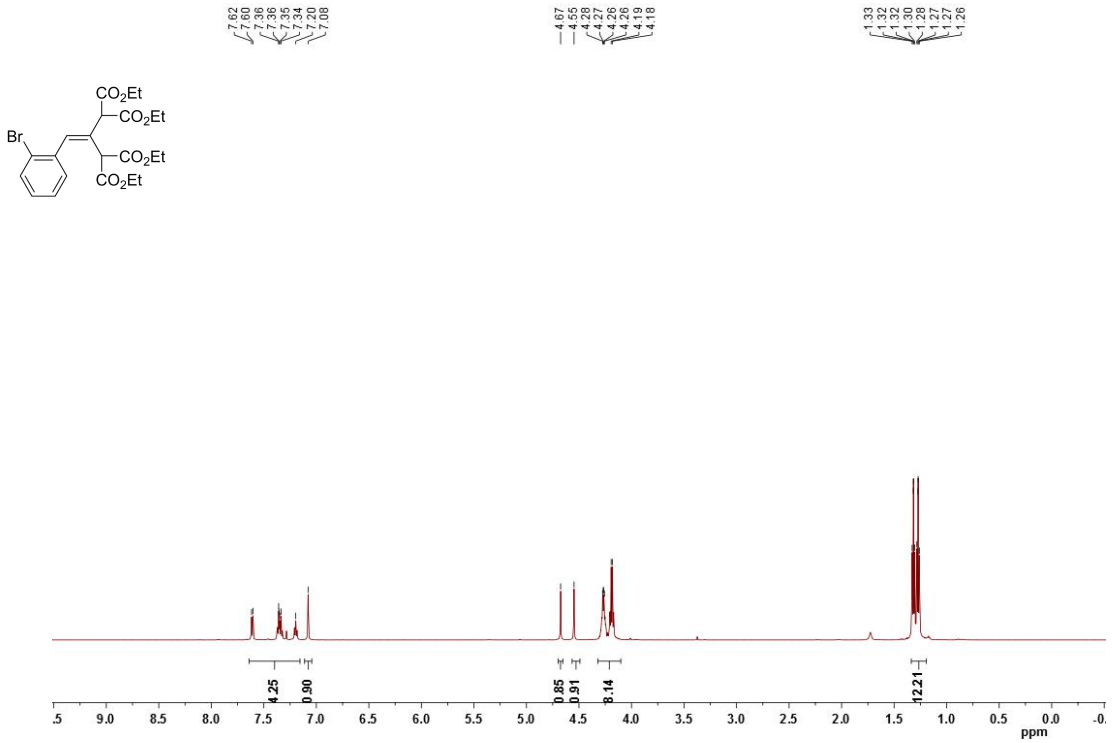

7.40
7.32
7.31
7.30
7.28
7.26
7.25
7.11
4.71
4.65
4.26
4.26
4.25
4.21
4.20
1.32
1.31
1.31
1.30
1.29
1.28
1.28
CO2Et
CO2Et
CO2Et
CO2Et
Cl
0.97
3.06
0.92
0.96
0.90
8.09
12.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

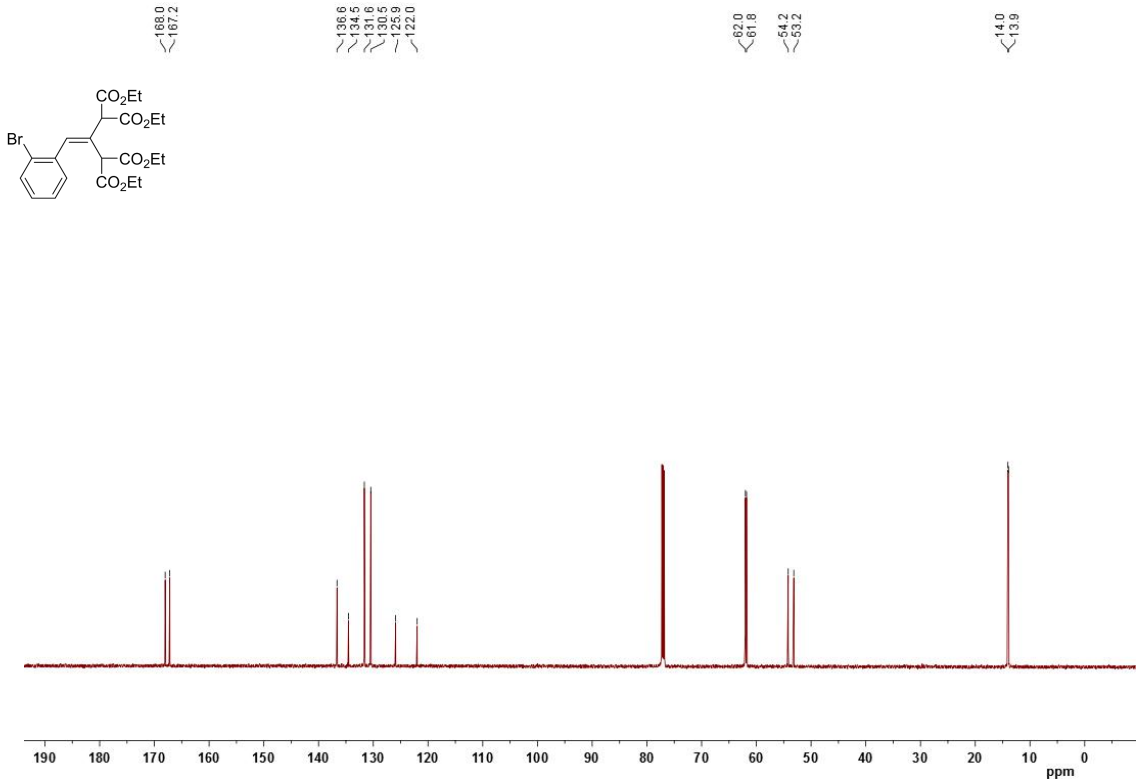

168.0
167.2
137.4
136.4
134.4
129.8
128.9
127.9
127.0
126.5
62.0
61.8
54.2
53.2
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 4g

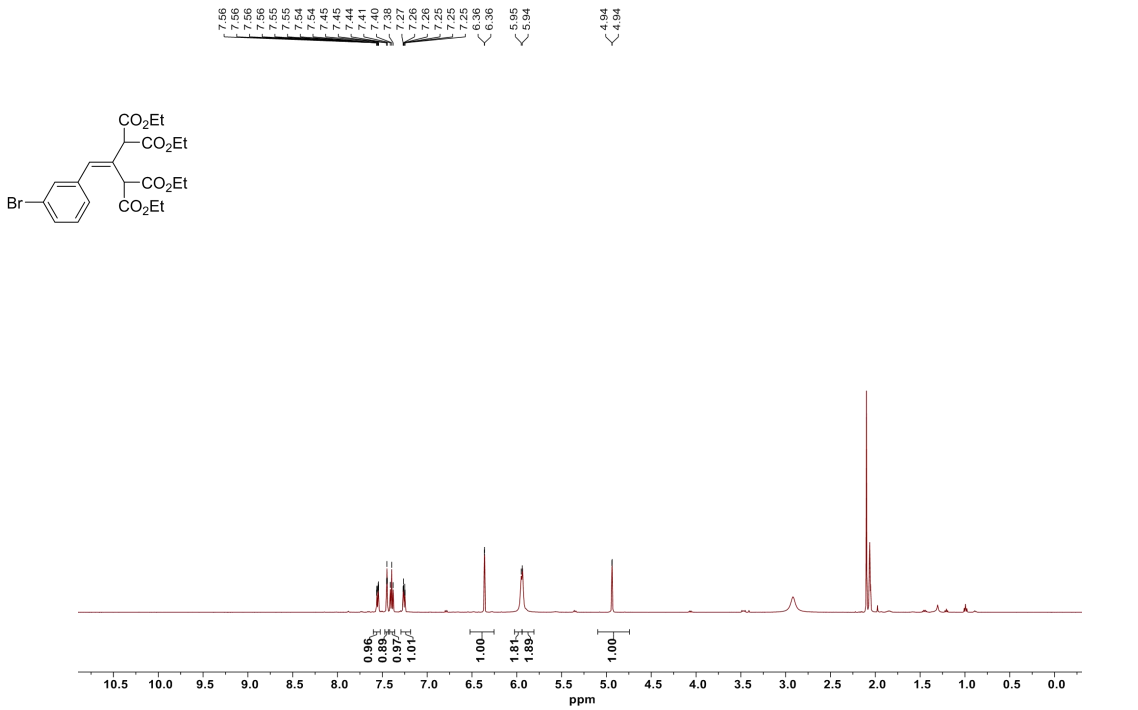

7.37
7.35
7.34
7.33
7.30
7.11
4.70
4.64
4.26
4.25
4.24
4.22
4.21
4.21
4.19
4.19
1.32
1.30
1.29
1.28
1.28
1.26
CO2Et
CO2Et
CO2Et
CO2Et
Cl
3.98
0.91
0.95
0.91
7.94
12.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
168.1
167.2
136.6
134.1
133.8
130.2
128.7
125.9
62.0
61.8
54.2
53.1
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

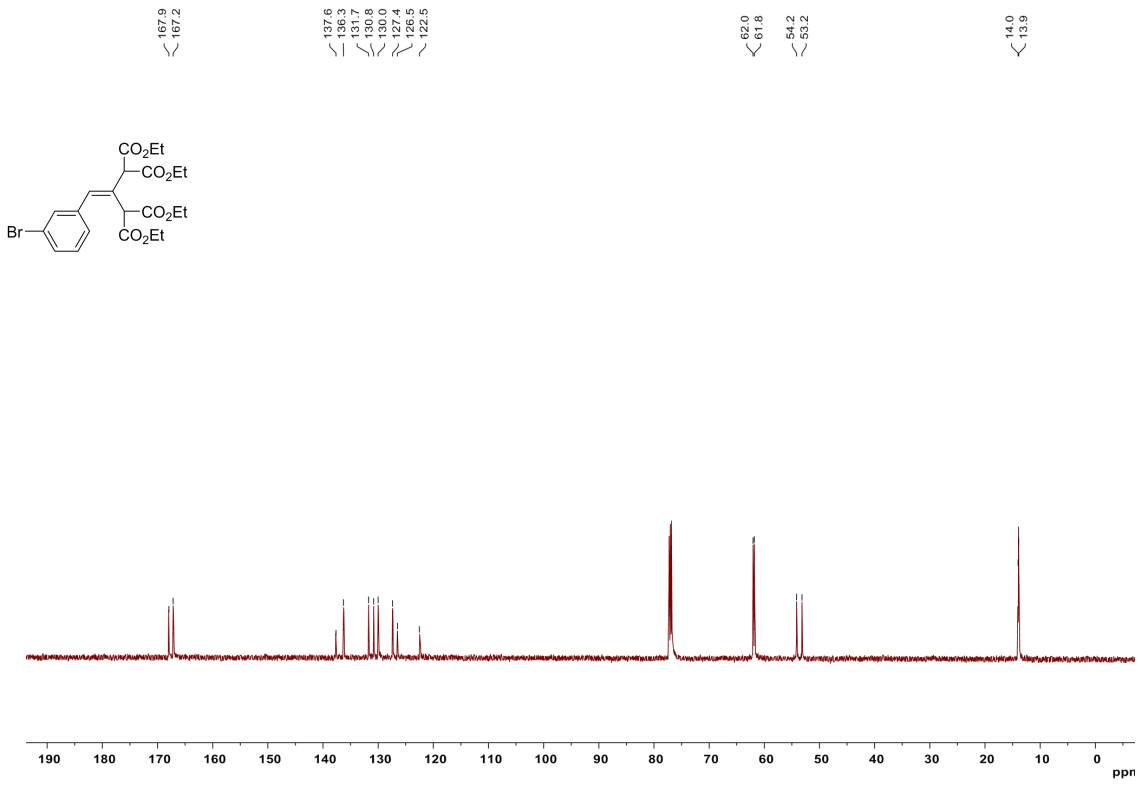
Compound 4h


7.62
7.60
7.36
7.36
7.35
7.34
7.20
7.08
4.67
4.55
4.28
4.27
4.26
4.26
4.19
4.18
1.33
1.32
1.32
1.30
1.28
1.27
1.27
1.26
CO2Et
CO2Et
Br
CO2Et
CO2Et
4.25
0.90
0.85
0.91
8.14
12.21
ppm

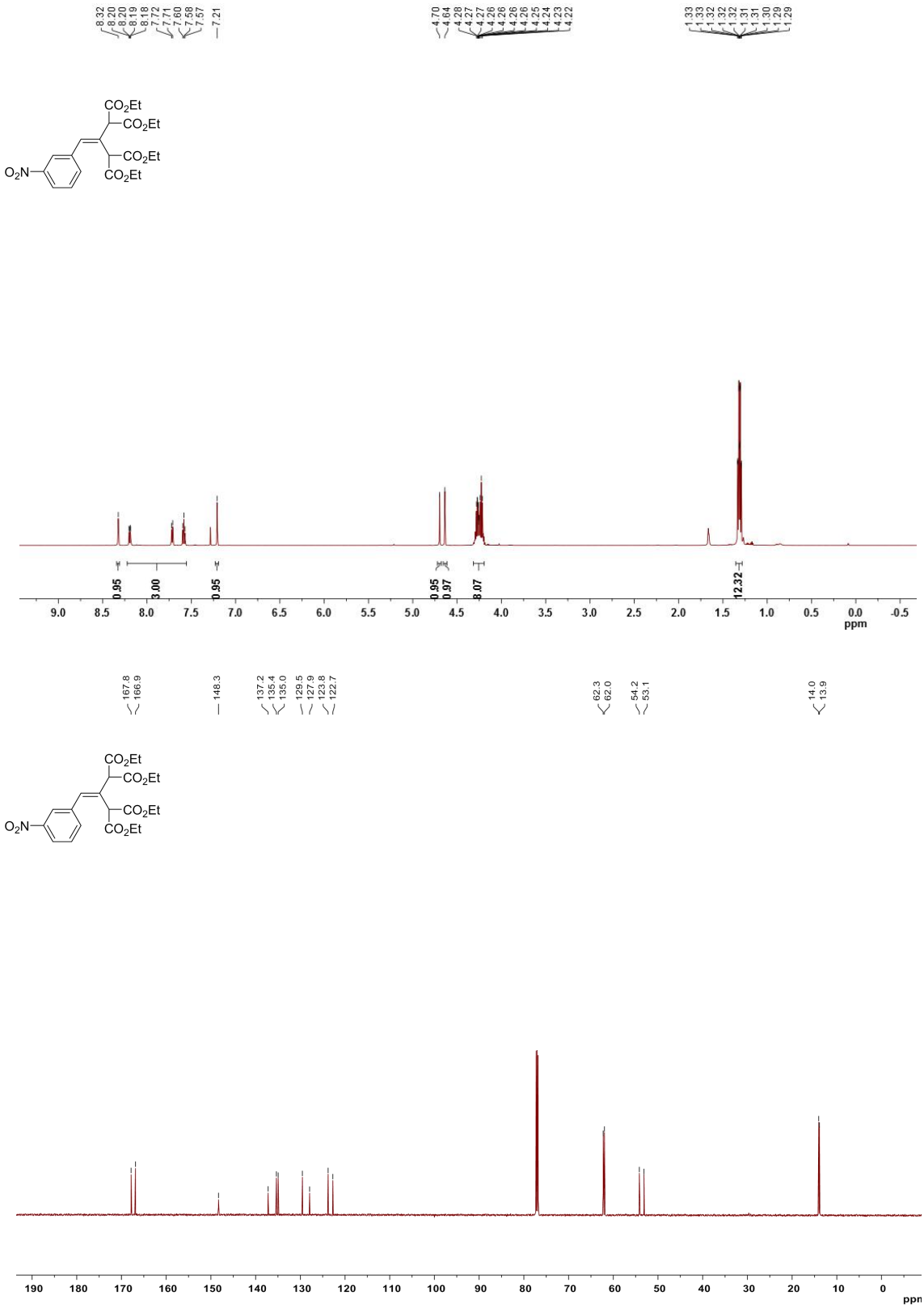

168.0
167.2
136.6
134.5
131.6
130.5
125.9
122.0
62.0
61.8
54.2
53.2
14.0
13.9
CO2Et
CO2Et
Br
CO2Et
CO2Et
ppm

Compound 4i

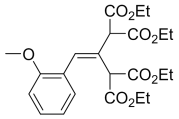

7.56
7.56
7.56
7.56
7.55
7.55
7.54
7.54
7.45
7.45
7.44
7.41
7.40
7.38
7.27
7.26
7.26
7.25
7.25
7.25
6.36
6.36
5.95
5.94
4.94
4.94
CO2Et
CO2Et
CO2Et
CO2Et
Br
0.96
0.89
0.97
1.01
1.00
1.81
1.89
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

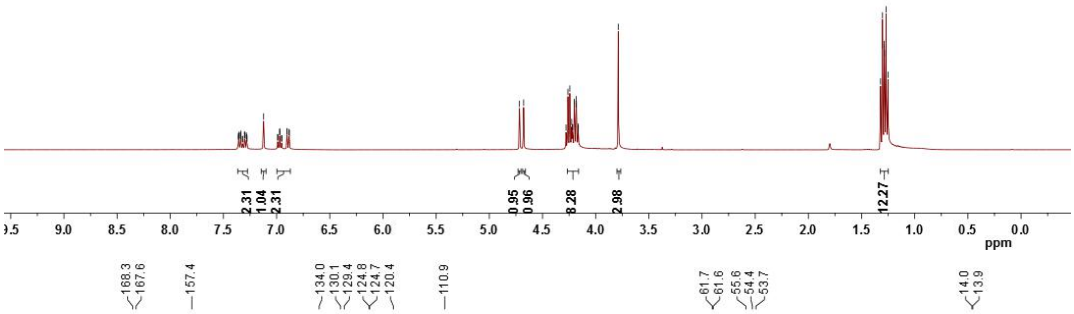

167.9
167.2
137.6
136.3
131.7
130.8
130.0
127.4
126.5
122.5
62.0
61.8
54.2
53.2
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

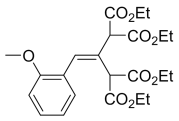
Compound 4j

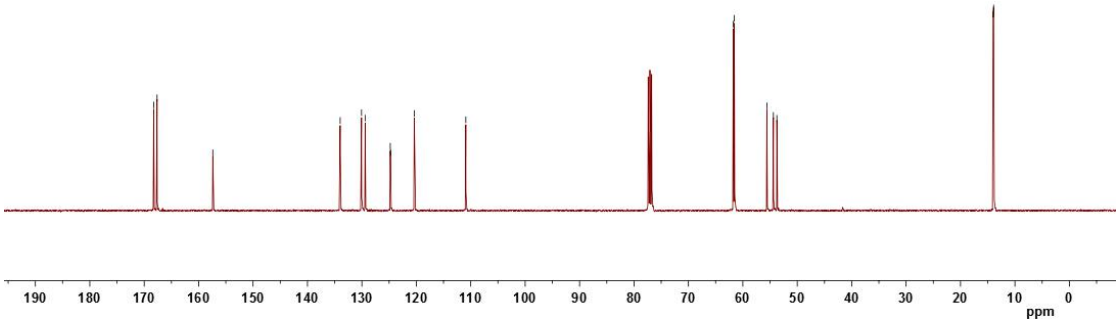

8.32
8.20
8.20
8.19
8.18
7.72
7.71
7.60
7.58
7.57
7.21
4.70
4.64
4.28
4.27
4.27
4.26
4.26
4.26
4.26
4.25
4.24
4.23
4.22
1.33
1.33
1.32
1.32
1.32
1.31
1.31
1.30
1.29
1.29
CO2Et
CO2Et
CO2Et
CO2Et
O2N
0.95
3.00
0.95
0.95
0.97
8.07
12.32
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm
167.8
166.9
148.3
137.2
135.4
135.0
129.5
127.9
123.8
122.7
62.3
62.0
54.2
53.1
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
O2N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Compound 4k

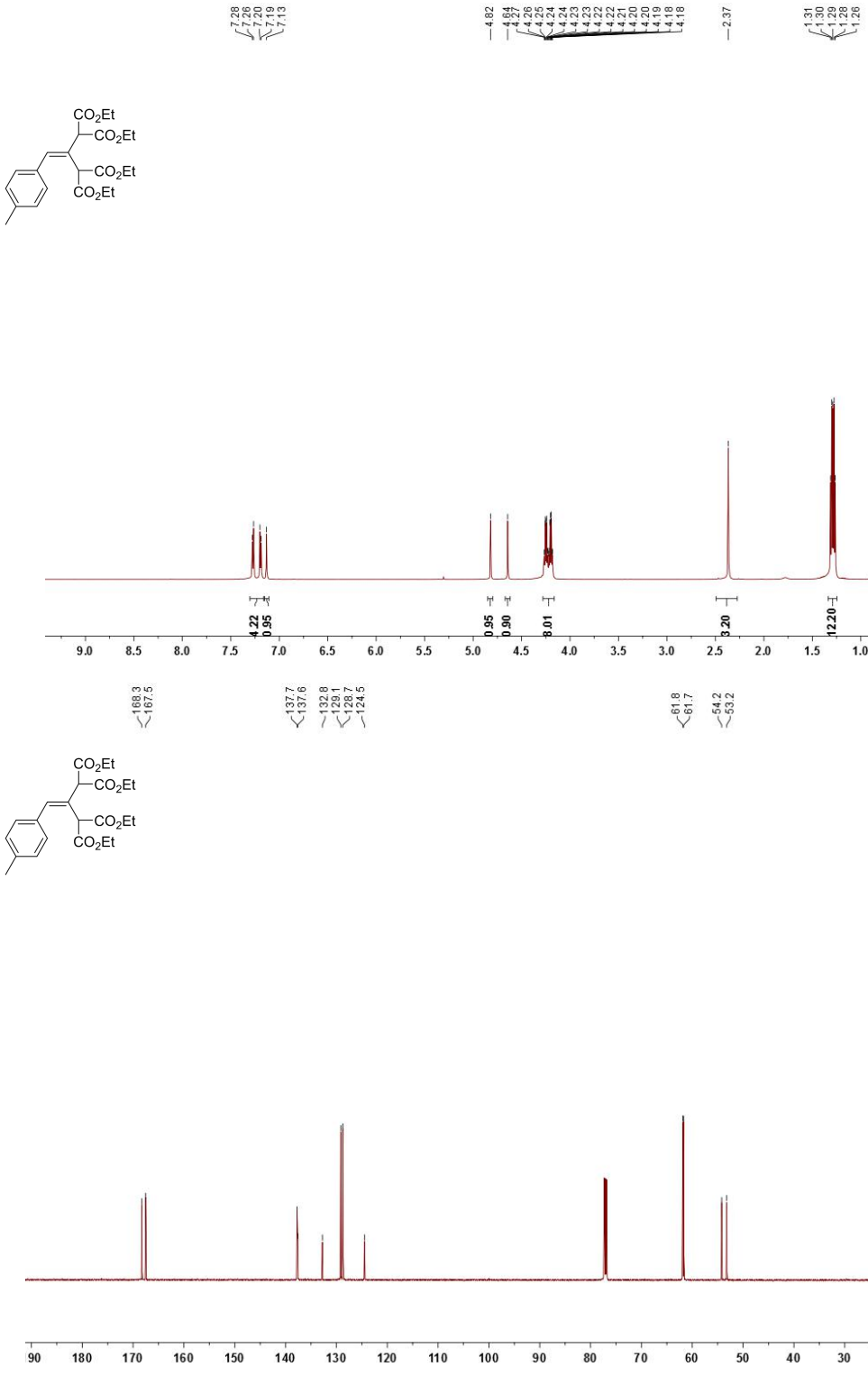




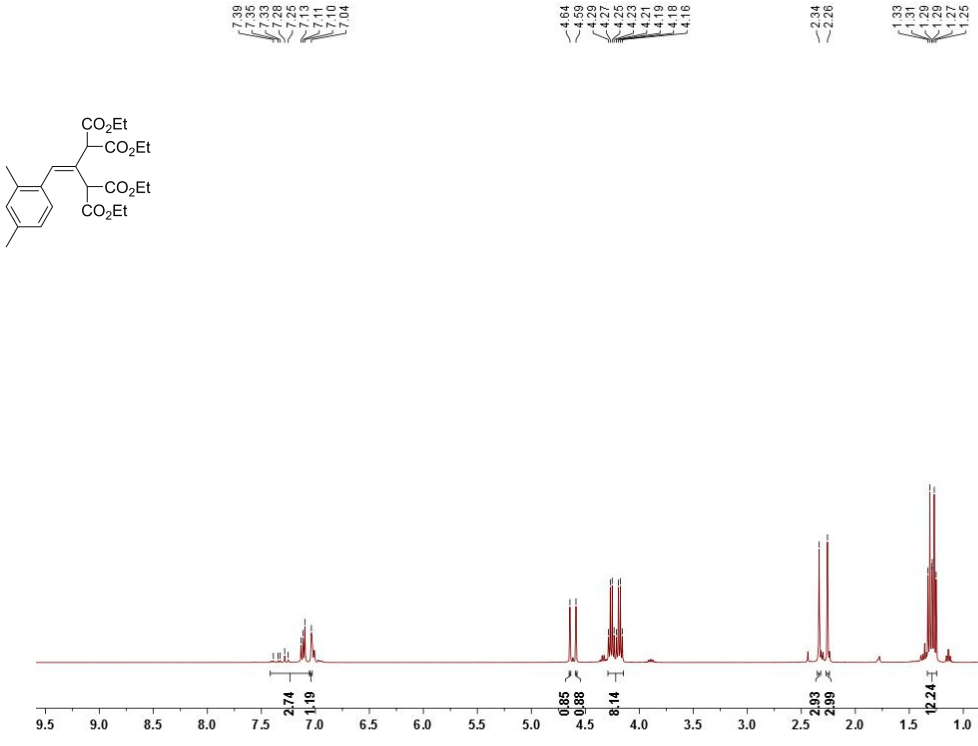


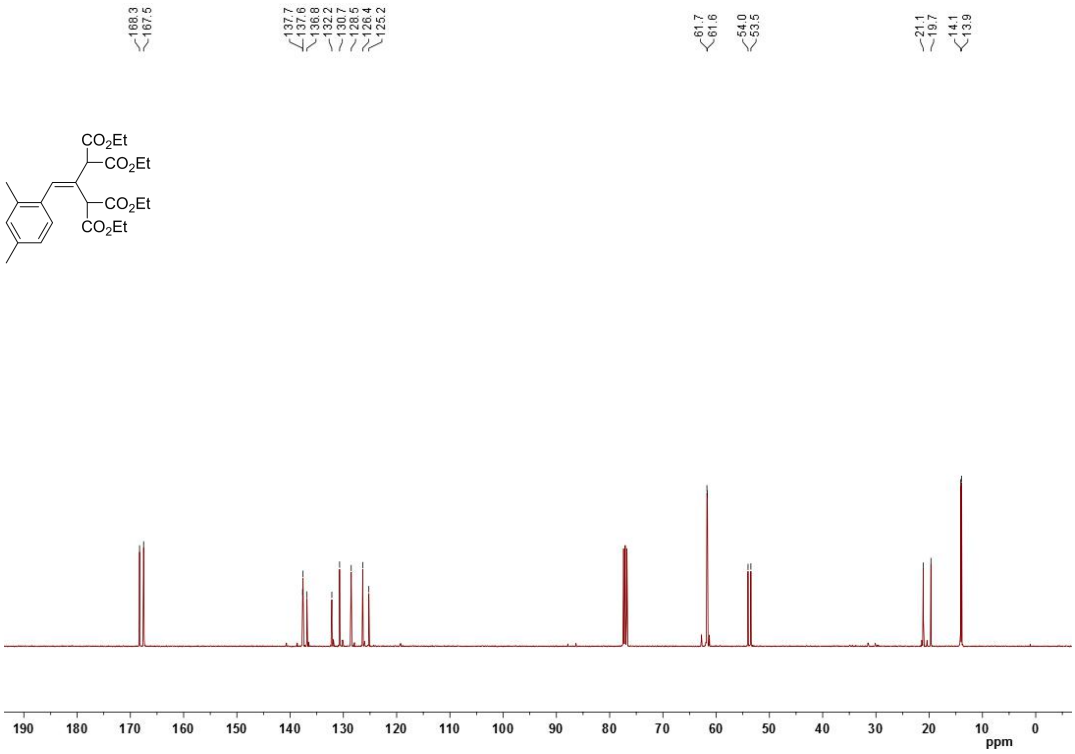


Compound 4l

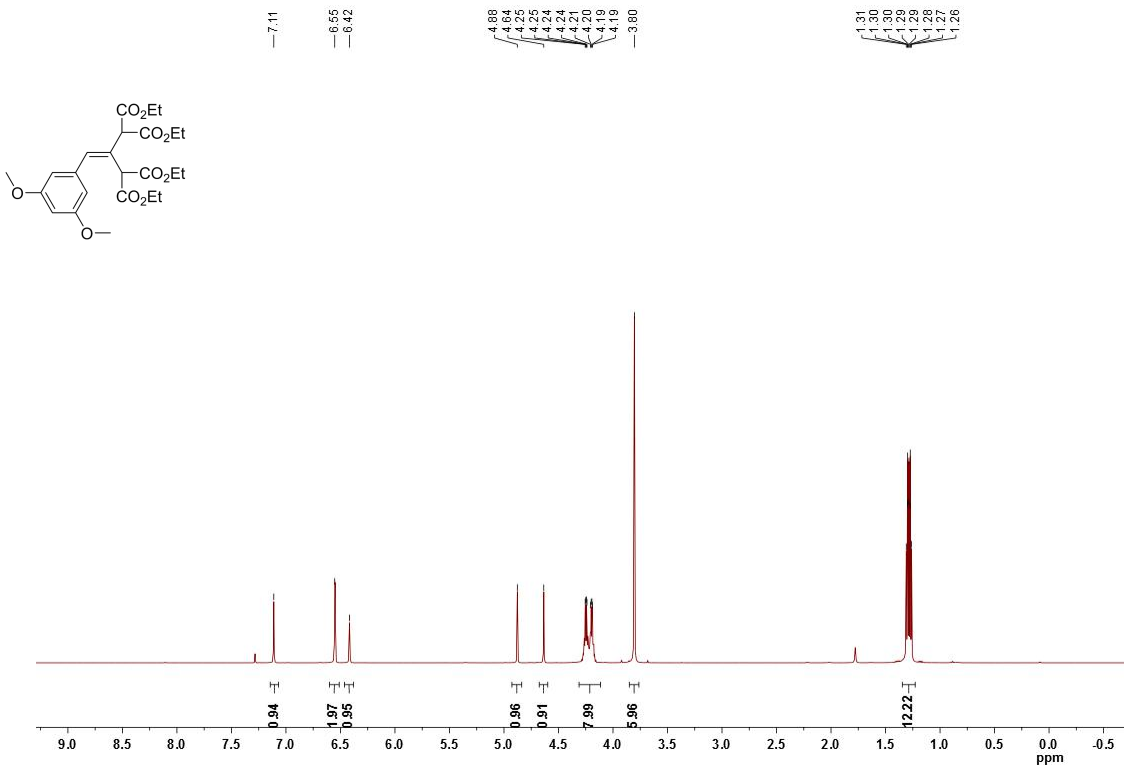

7.28
7.26
7.20
7.19
7.13
4.82
4.64
4.27
4.26
4.25
4.24
4.24
4.23
4.23
4.22
4.22
4.21
4.20
4.20
4.19
4.18
4.18
2.37
1.31
1.30
1.29
1.28
1.26
CO2Et
CO2Et
CO2Et
CO2Et
4.22
0.95
0.95
0.90
8.01
3.20
12.20
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
168.3
167.5
137.7
137.6
132.8
129.1
128.7
124.5
61.8
61.7
54.2
53.2
21.2
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

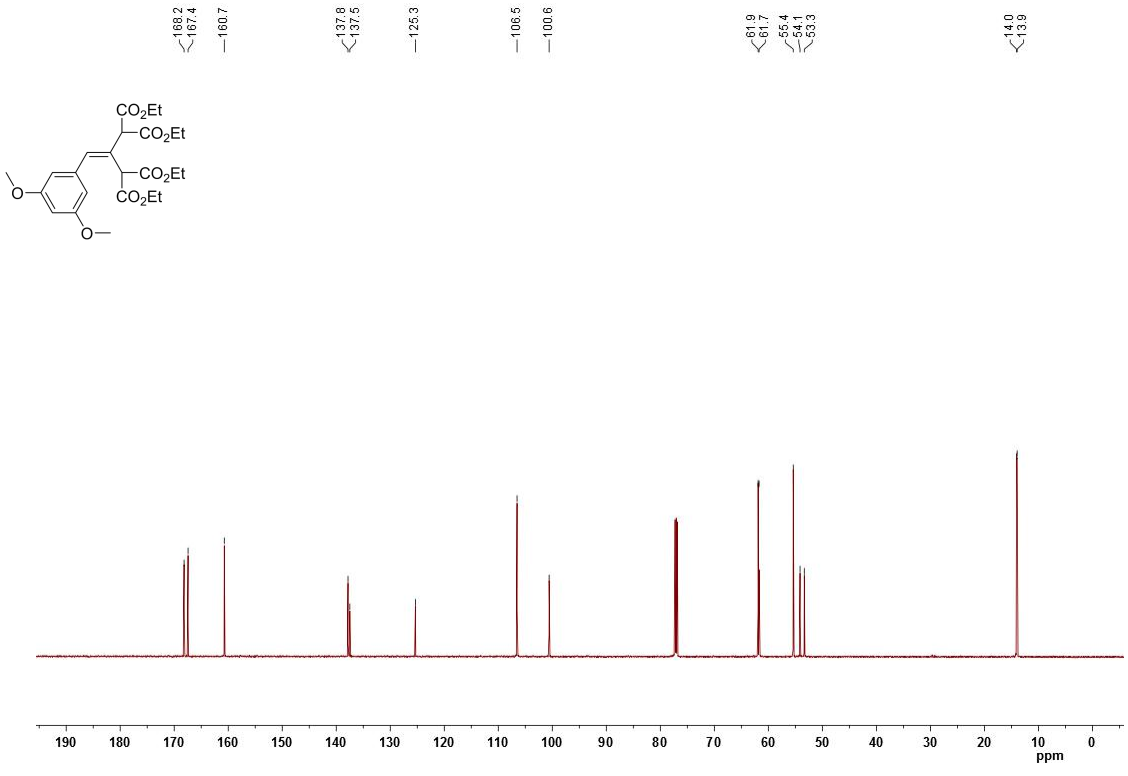
Compound 4m


7.39
7.35
7.33
7.28
7.25
7.13
7.11
7.10
7.04
4.64
4.59
4.29
4.27
4.25
4.23
4.21
4.19
4.18
4.16
2.34
2.26
1.33
1.31
1.29
1.29
1.27
1.25
CO2Et
CO2Et
CO2Et
CO2Et
2.74
1.19
0.85
0.88
8.14
2.03
2.99
12.24
ppm

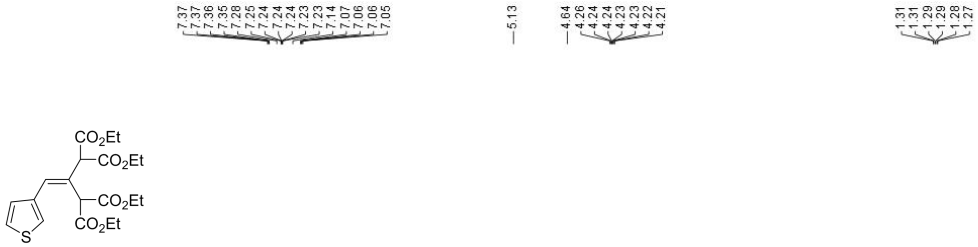

168.3
167.5
137.7
137.6
136.8
132.2
130.7
128.5
128.4
125.2
61.7
61.6
54.0
53.5
21.1
19.7
14.1
13.9
CO2Et
CO2Et
CO2Et
CO2Et
ppm

Compound 4n

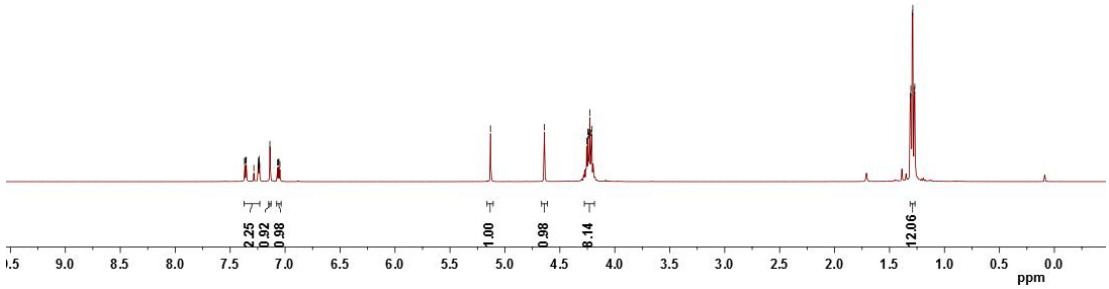

7.11
6.55
6.42
4.88
4.04
4.25
4.25
4.24
4.24
4.21
4.20
4.19
4.19
3.80
1.31
1.30
1.30
1.29
1.29
1.28
1.27
1.26
CO2Et
CO2Et
CO2Et
CO2Et
O
O
0.94
1.97
0.95
0.96
0.91
7.99
5.96
12.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


168.2
167.4
160.7
137.8
137.5
125.3
106.5
100.6
61.9
61.7
55.4
54.1
53.3
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

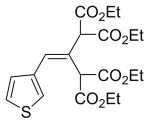
Compound 4o

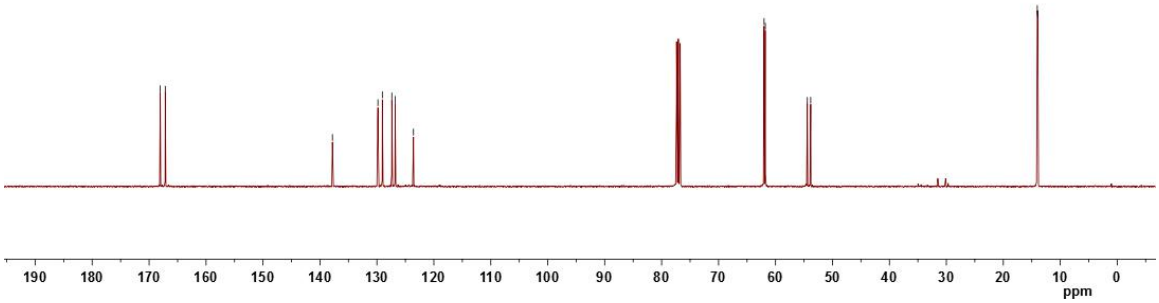

7.37
7.37
7.36
7.35
7.28
7.25
7.24
7.24
7.24
7.23
7.23
7.14
7.07
7.06
7.06
7.05
5.13
4.64
4.26
4.24
4.24
4.23
4.23
4.22
4.21
1.31
1.31
1.29
1.29
1.28
1.27

CO2Et
CO2Et
CO2Et
CO2Et
S

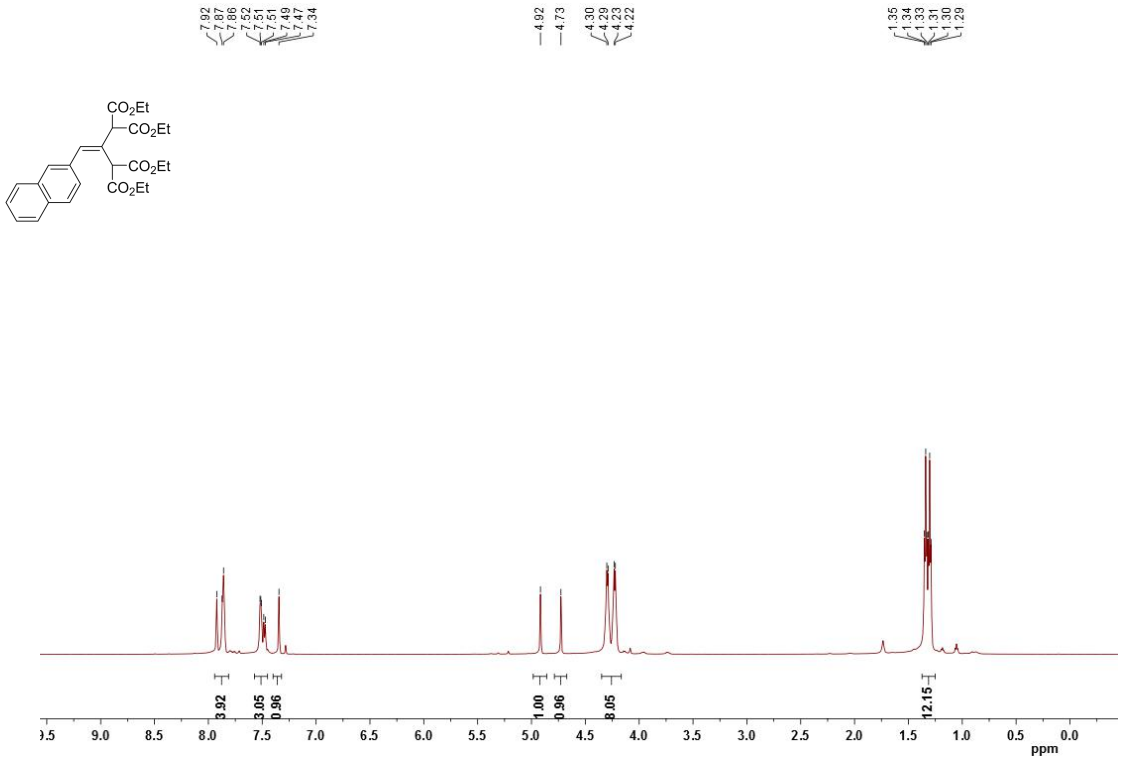

2.25
0.92
0.98
1.00
0.98
8.14
12.06
ppm


168.0
167.2
137.8
129.8
129.0
127.4
126.8
123.6
62.0
61.8
54.4
53.8
14.0
13.9


CO2Et
CO2Et
CO2Et
CO2Et
S


ppm

Compound 4p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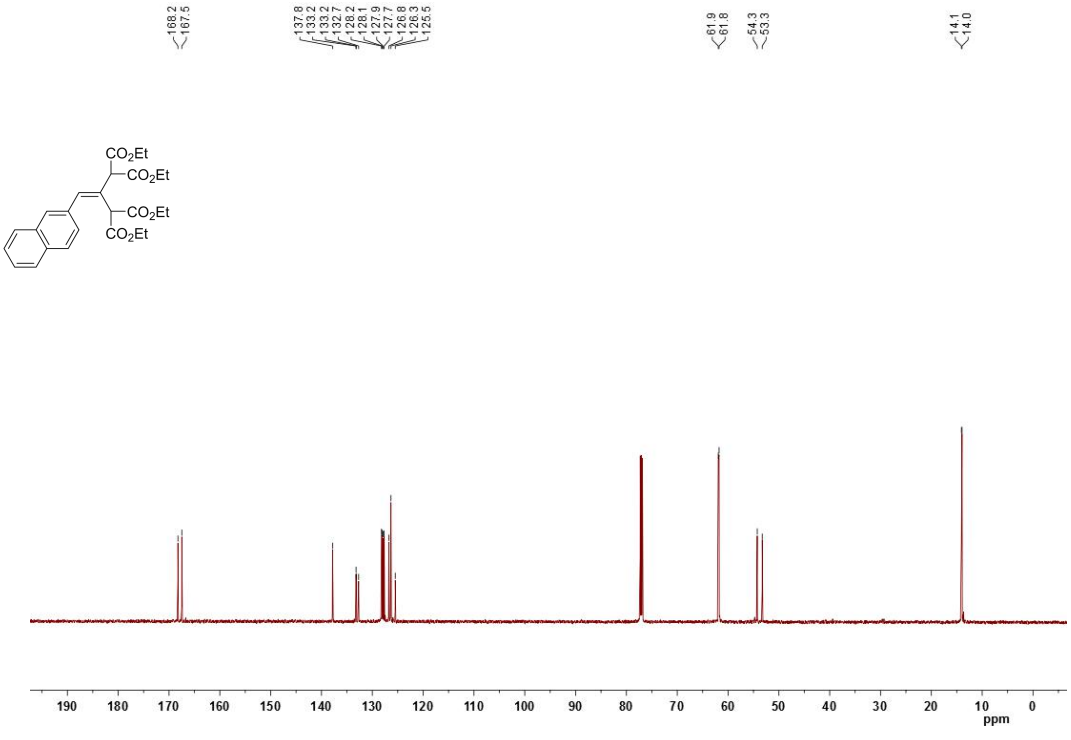
7.87
7.86
7.52
7.51
7.51
7.49
7.47
7.34
4.92
4.73
4.30
4.29
4.23
4.22
1.35
1.34
1.33
1.31
1.30
1.29
CO2Et
CO2Et
CO2Et
CO2Et
3.92
3.05
0.96
1.00
0.96
8.05
12.15
ppm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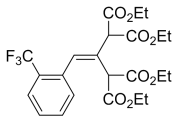
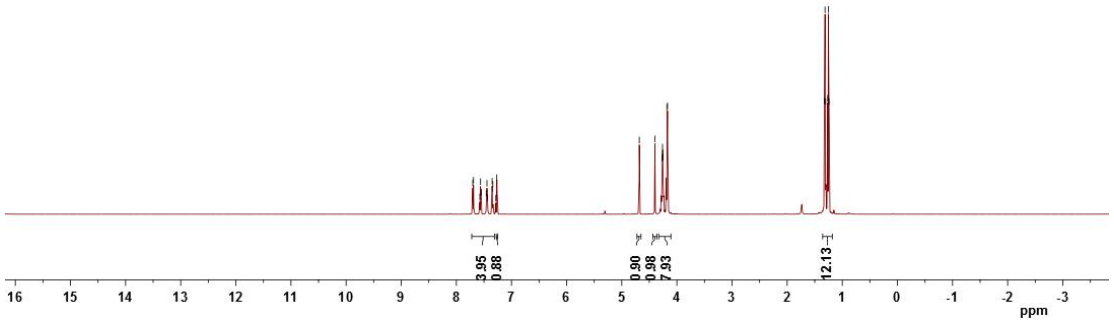
167.5
137.8
133.2
133.2
132.7
128.2
128.1
127.9
127.7
126.8
126.3
125.5
61.9
61.8
54.3
53.3
14.1
14.0
CO2Et
CO2Et
CO2Et
CO2Et
ppm

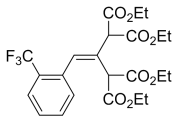
Compound 4q

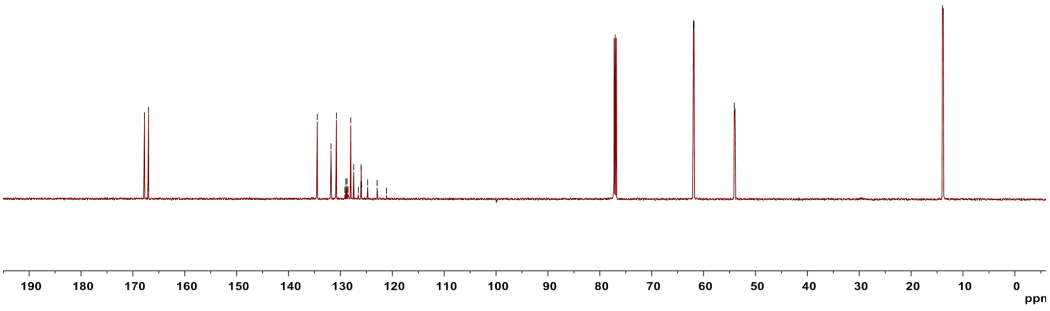

7.70
7.69
7.57
7.56
7.55
7.46
7.44
7.43
7.35
7.34
7.28
7.27
4.68
4.40
4.27
4.26
4.26
4.25
4.18
4.17
1.32
1.31
1.30
1.26
1.25
1.24


CO2Et
CO2Et
F3C
CO2Et
CO2Et

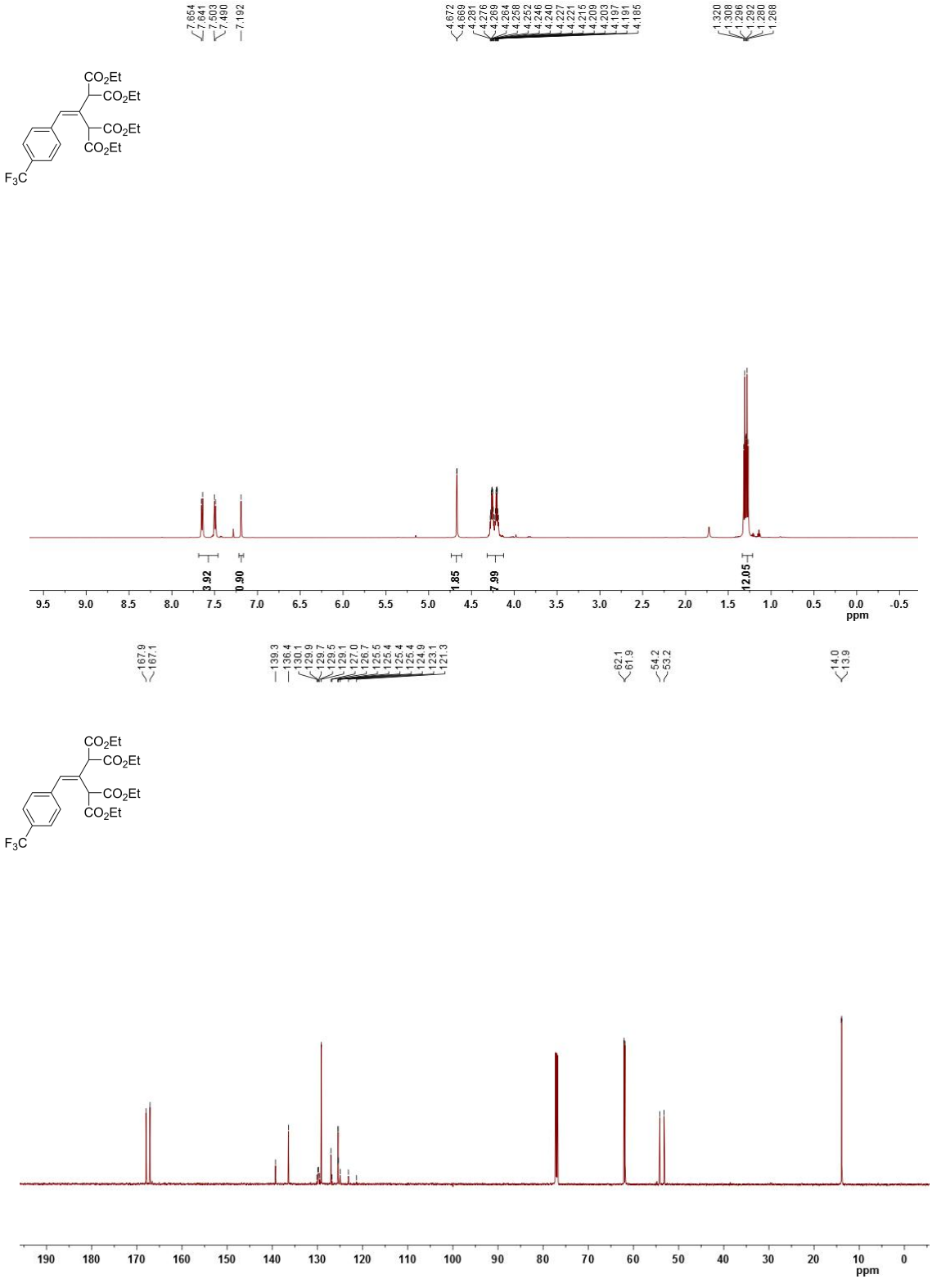

3.95
0.88
0.90
0.98
7.93
12.13
ppm


167.8
167.0
134.5
131.8
130.8
129.1
128.9
128.7
128.5
128.0
127.4
126.6
126.0
126.0
126.0
125.9
124.7
122.9
121.1
61.9
61.8
54.1
53.9
14.0
13.8

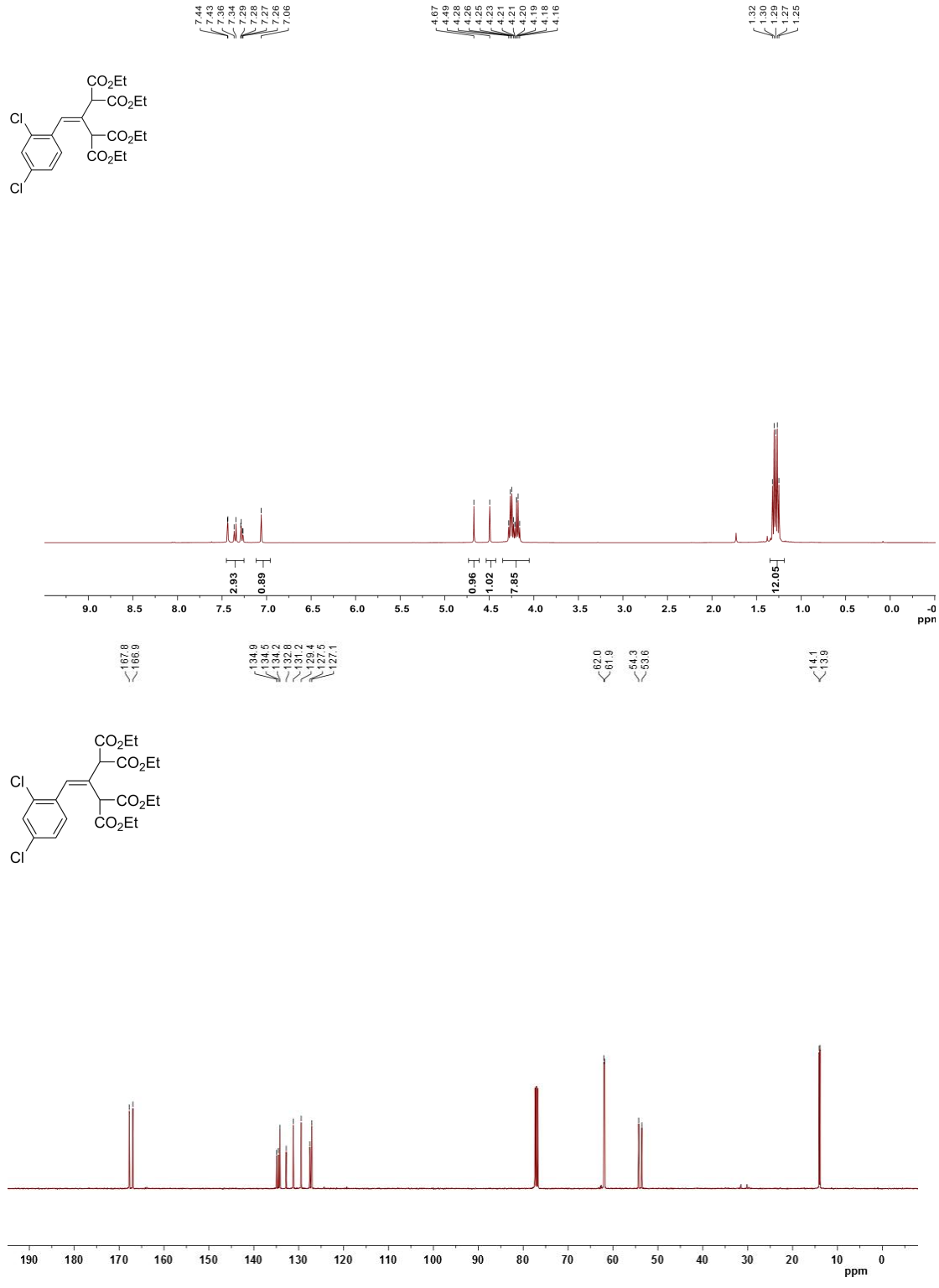

CO2Et
CO2Et
F3C
CO2Et
CO2Et


ppm

Compound 4r


7.654
7.641
7.503
7.490
7.192
4.672
4.669
4.281
4.276
4.269
4.264
4.258
4.252
4.246
4.240
4.227
4.221
4.215
4.209
4.203
4.197
4.191
4.185
1.320
1.308
1.296
1.292
1.280
1.268
CO2Et
CO2Et
CO2Et
CO2Et
F3C
3.92
0.90
1.85
7.99
12.05
ppm
167.9
167.1
139.3
136.4
130.1
129.9
129.7
128.5
128.1
127.0
126.7
125.5
125.4
125.4
125.4
124.9
123.1
121.3
62.1
61.9
54.2
53.2
14.0
13.9

Compound 4s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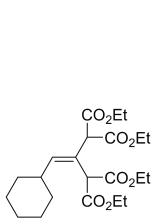
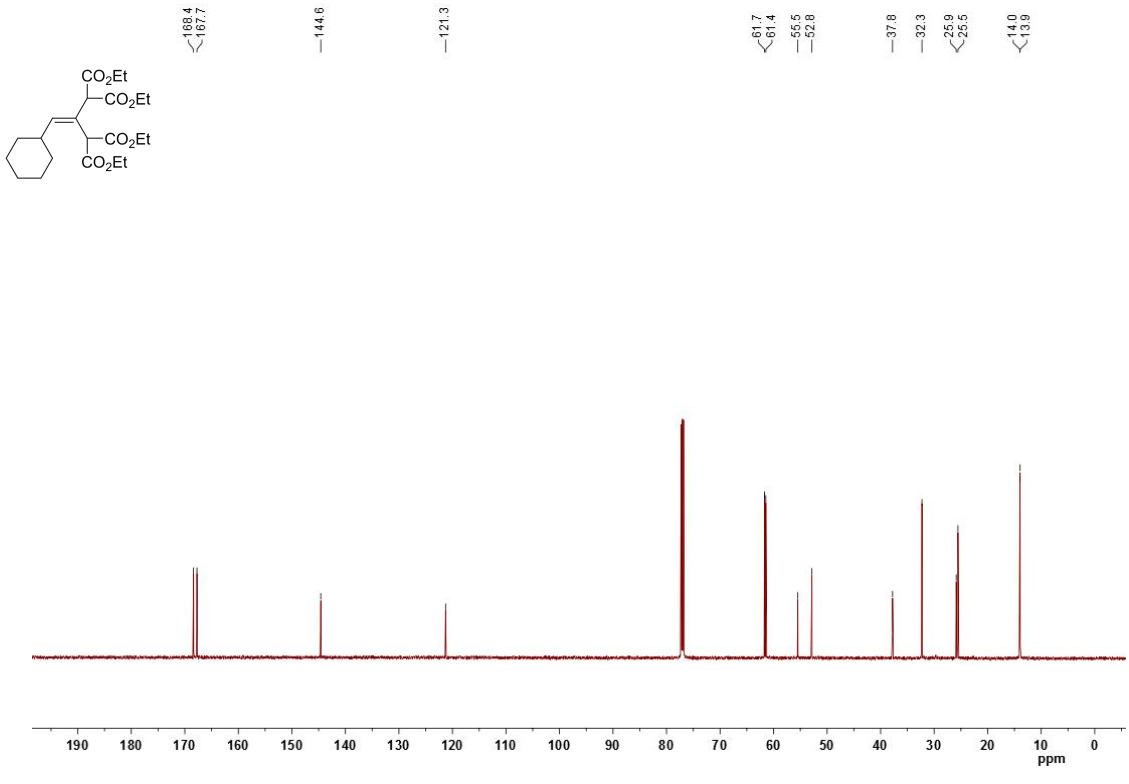
7.43
7.36
7.34
7.29
7.28
7.27
7.26
7.06
4.67
4.49
4.28
4.26
4.25
4.23
4.21
4.21
4.20
4.19
4.18
4.16
1.32
1.30
1.29
1.27
1.25
CO2Et
CO2Et
CO2Et
CO2Et
Cl
Cl
2.93
0.89
0.96
1.02
7.85
12.05
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
167.8
166.9
134.9
134.5
134.2
132.8
131.1
129.4
127.5
127.1
62.0
61.9
54.3
53.6
14.1
13.9
CO2Et
CO2Et
CO2Et
CO2Et
Cl
Cl
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

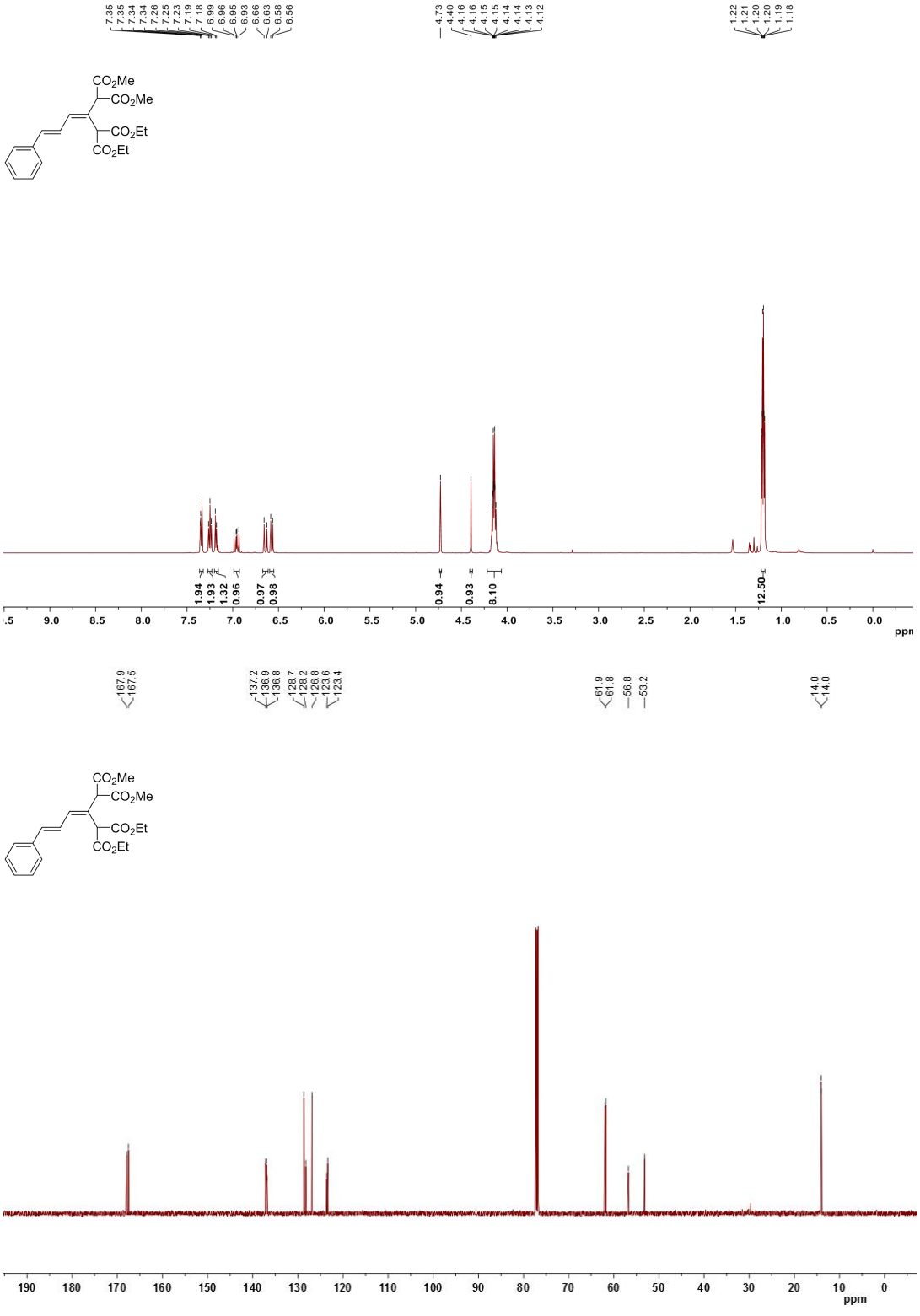
Compound 4t


CO2Et
CO2Et
CO2Et
CO2Et

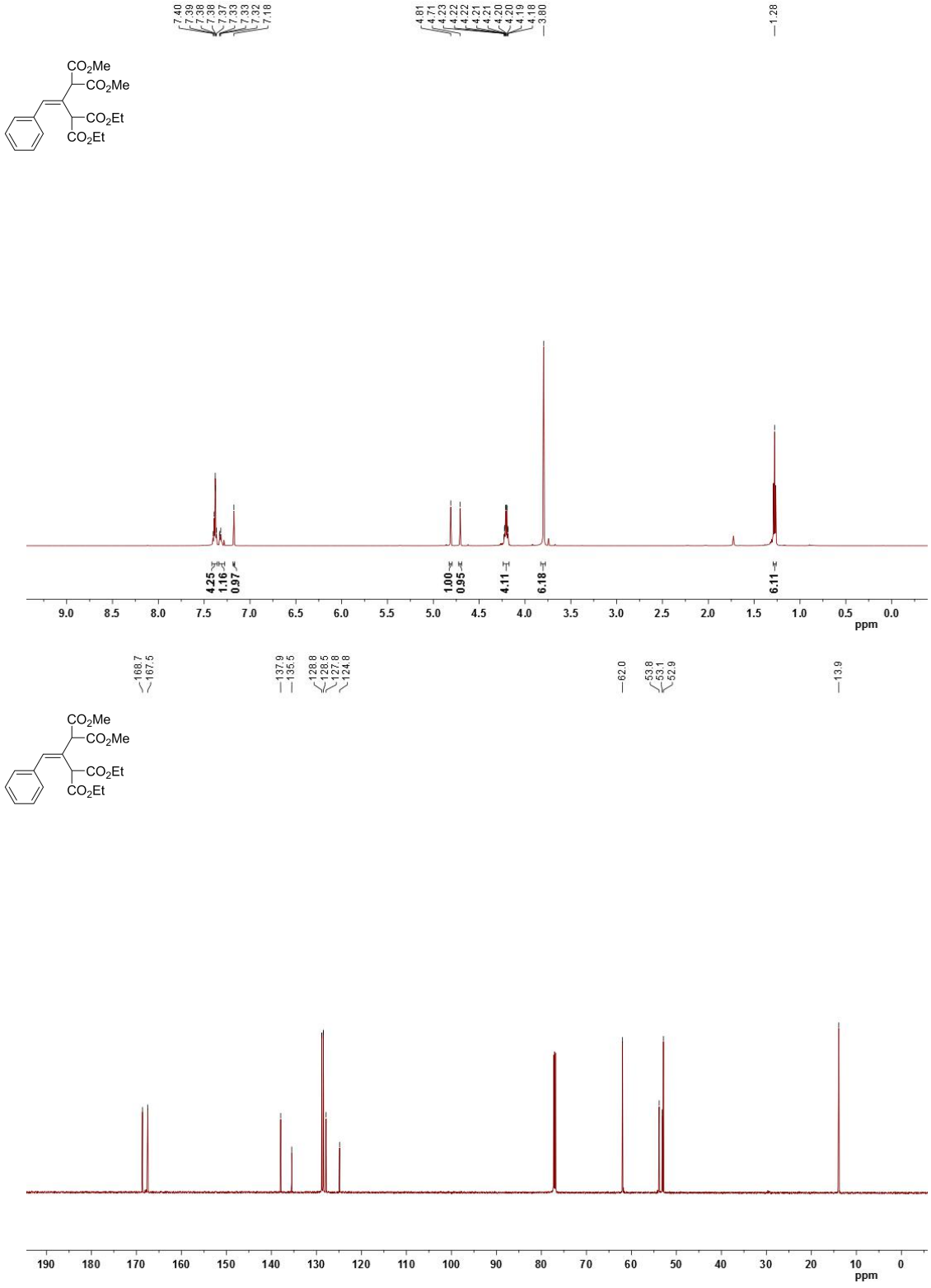
5.76
5.74
4.59
4.38
4.21
4.20
4.19
4.18
4.18
4.17
2.32
2.31
2.30
2.30
2.29
2.28
2.27
1.73
1.72
1.71
1.69
1.29
1.29
1.28
1.28
1.27
1.26
1.25
1.24
0.90
0.93
0.95
7.85
0.95
5.92
16.27
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


168.4
167.7
144.6
121.3
61.7
61.4
55.5
52.8
37.8
32.3
25.9
25.5
14.0
13.9
CO2Et
CO2Et
CO2Et
CO2Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

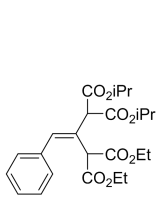
Compound 4u


7.35
7.35
7.34
7.34
7.26
7.25
7.23
7.19
7.18
6.99
6.96
6.95
6.93
6.66
6.63
6.58
6.56
4.73
4.40
4.16
4.16
4.15
4.15
4.14
4.14
4.13
4.12
1.22
1.21
1.20
1.20
1.19
1.18
CO2Me
CO2Me
CO2Et
CO2Et
1.94
1.93
1.32
0.96
0.97
0.98
0.94
0.93
8.10
12.50
ppm
167.9
167.5
137.2
136.9
136.8
128.7
128.2
126.8
123.6
123.4
61.9
61.8
56.8
53.2
14.0
14.0
CO2Me
CO2Me
CO2Et
CO2Et
ppm

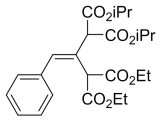
Compound 4v


7.40
7.39
7.38
7.38
7.37
7.33
7.33
7.32
7.18
4.81
4.71
4.23
4.22
4.22
4.21
4.21
4.20
4.20
4.19
4.18
3.80
1.28
CO2Me
CO2Me
CO2Et
CO2Et
4.25
1.16
0.97
1.00
0.95
4.11
6.18
6.11
ppm
168.7
167.5
137.9
135.5
128.8
128.5
127.8
124.8
62.0
53.8
53.1
52.9
13.9
ppm

Compound 4w

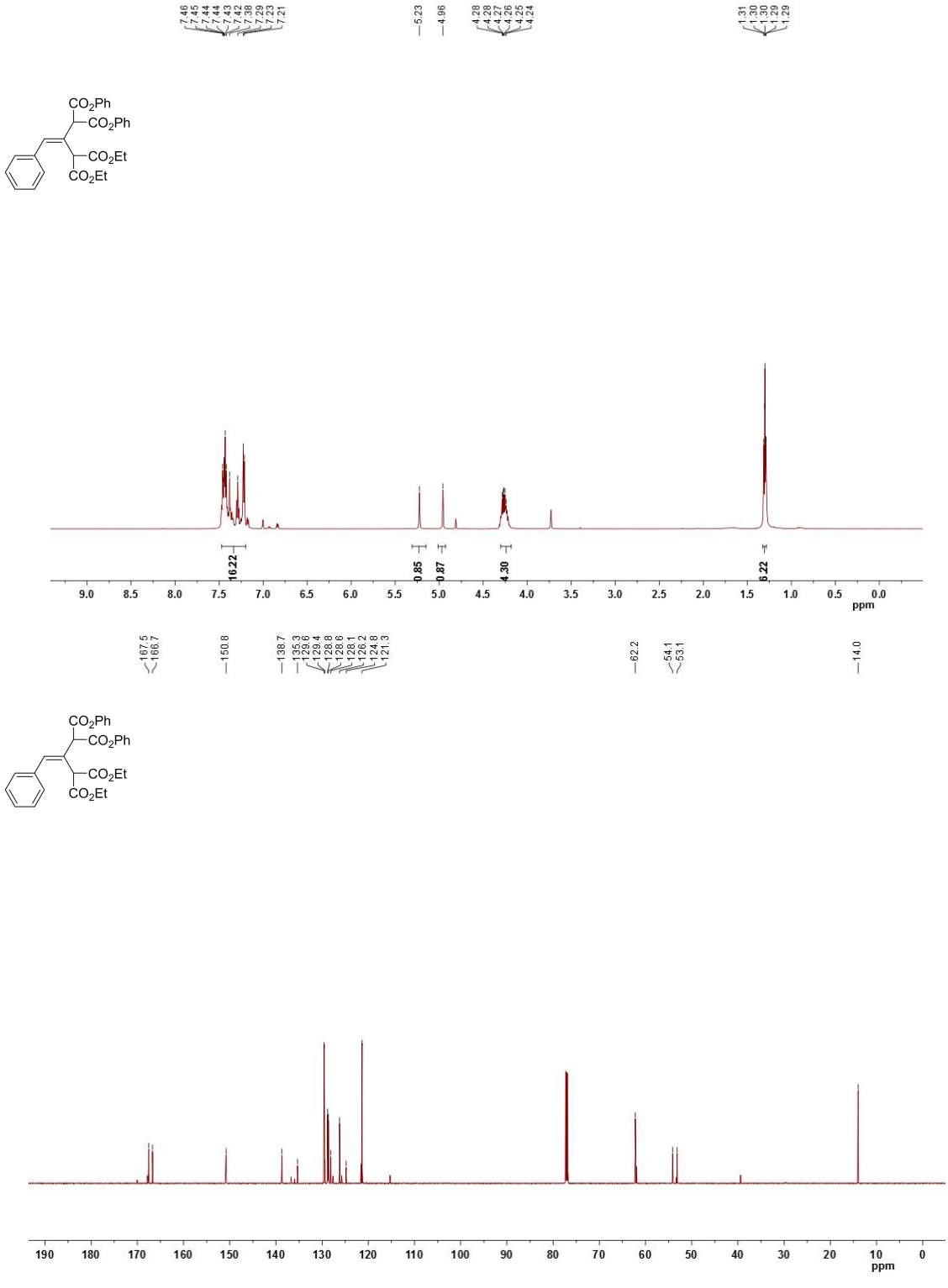

CO_2iPr
CO_2iPr
CO_2Et
CO_2Et

7.39
7.38
7.38
7.37
7.32
7.18
4.81
4.71
4.22
4.22
4.21
4.21
4.20
4.20
4.19
4.18
3.80
1.29
1.28
1.27
5.18
0.94
0.95
0.88
4.05
5.99
6.10
ppm


CO_2iPr
CO_2iPr
CO_2Et
CO_2Et

167.7
167.4
137.6
135.8
128.8
128.4
127.7
125.3
69.1
61.8
54.6
53.3
21.6
21.5
13.9
ppm

Compound 4x


7.46
7.45
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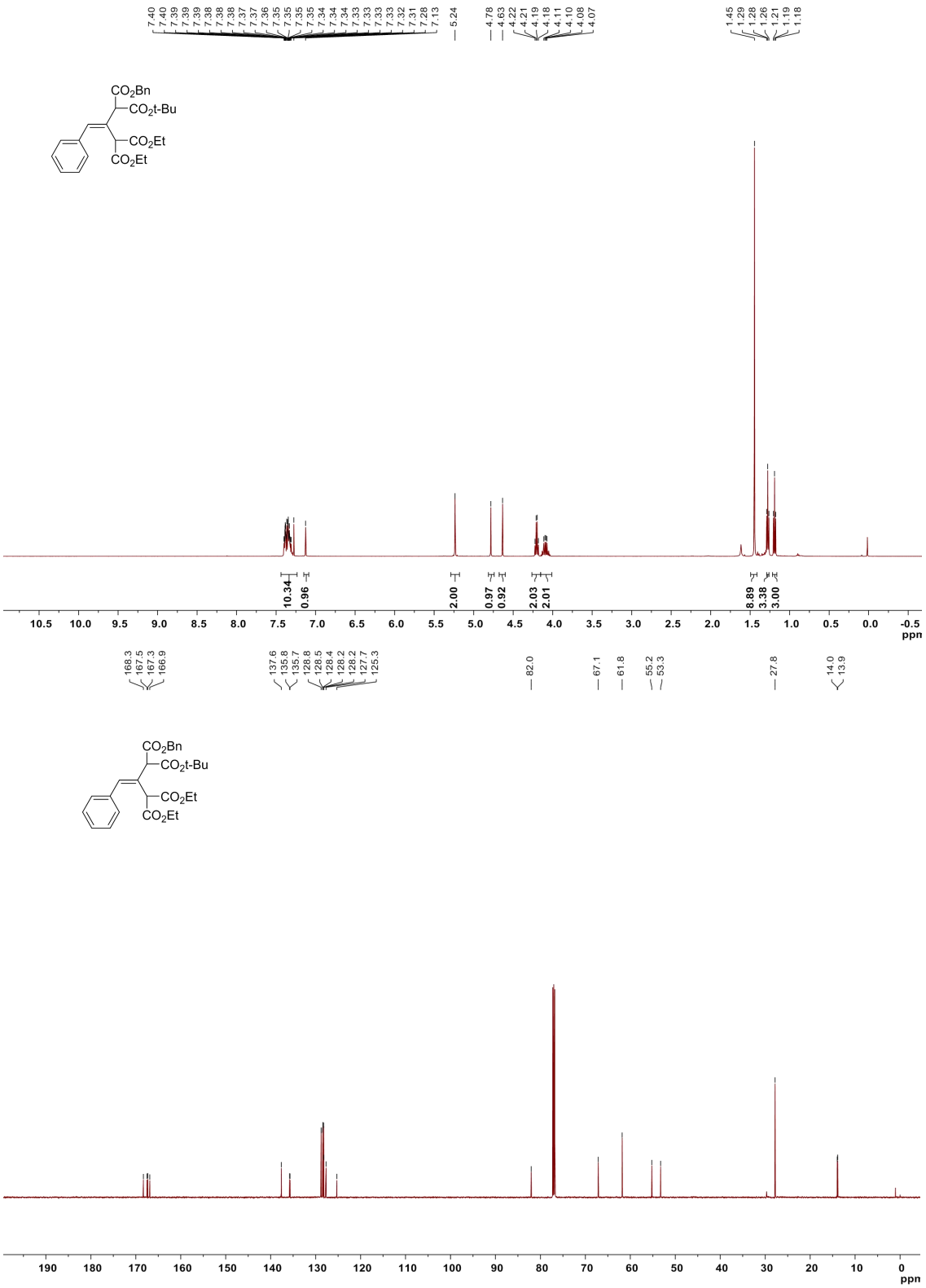
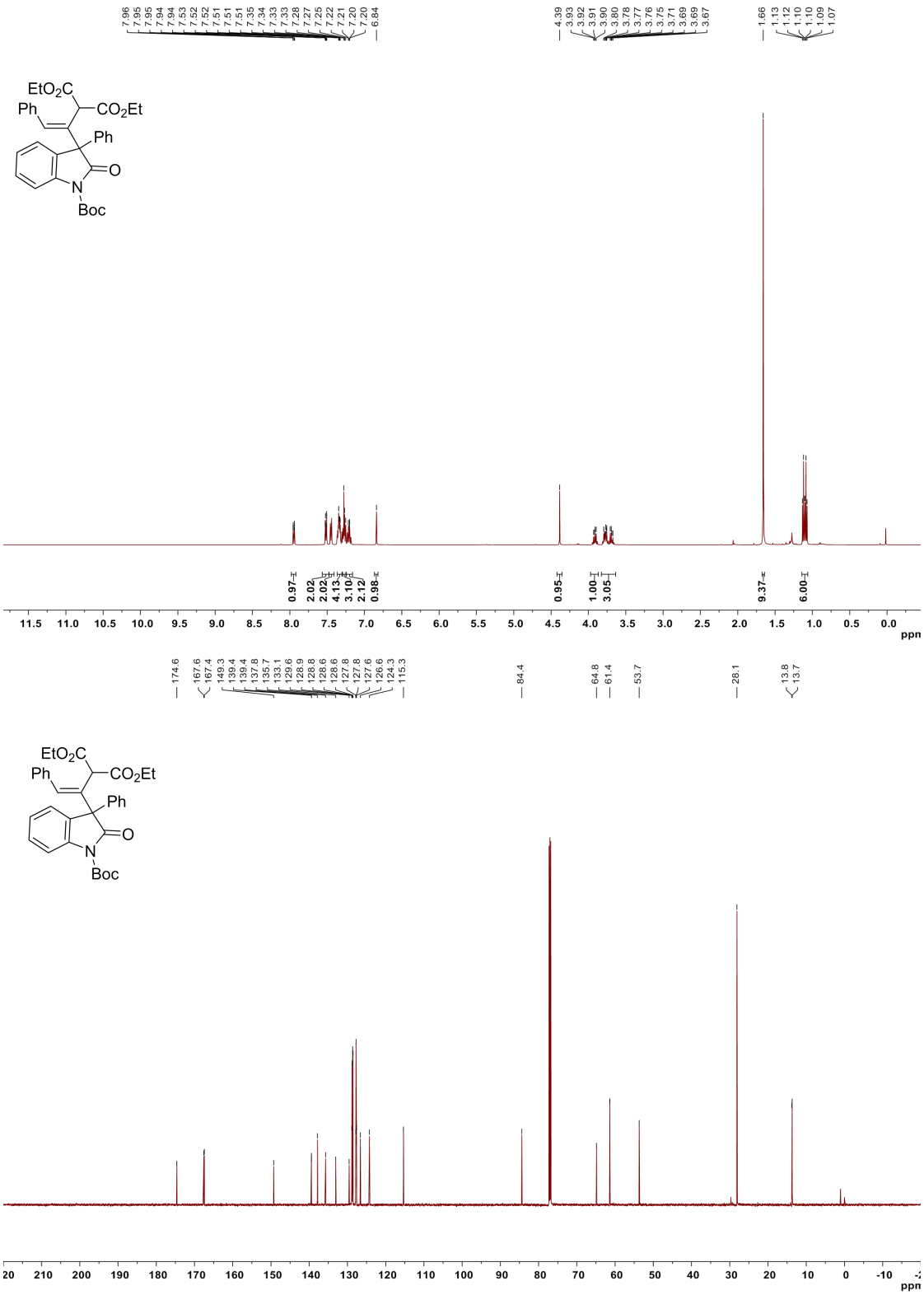
7.44
7.43
7.42
7.30
7.29
7.23
7.21
5.23
4.96
4.28
4.28
4.27
4.26
4.25
4.24
1.31
1.30
1.30
1.29
1.29
CO2Ph
CO2Ph
CO2Et
CO2Et
16.22
0.85
0.87
4.30
6.22
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
167.5
166.7
150.8
138.7
135.3
130.6
129.4
128.8
128.6
128.1
126.2
124.8
121.3
62.2
54.1
53.1
14.0
CO2Ph
CO2Ph
CO2Et
CO2Et
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

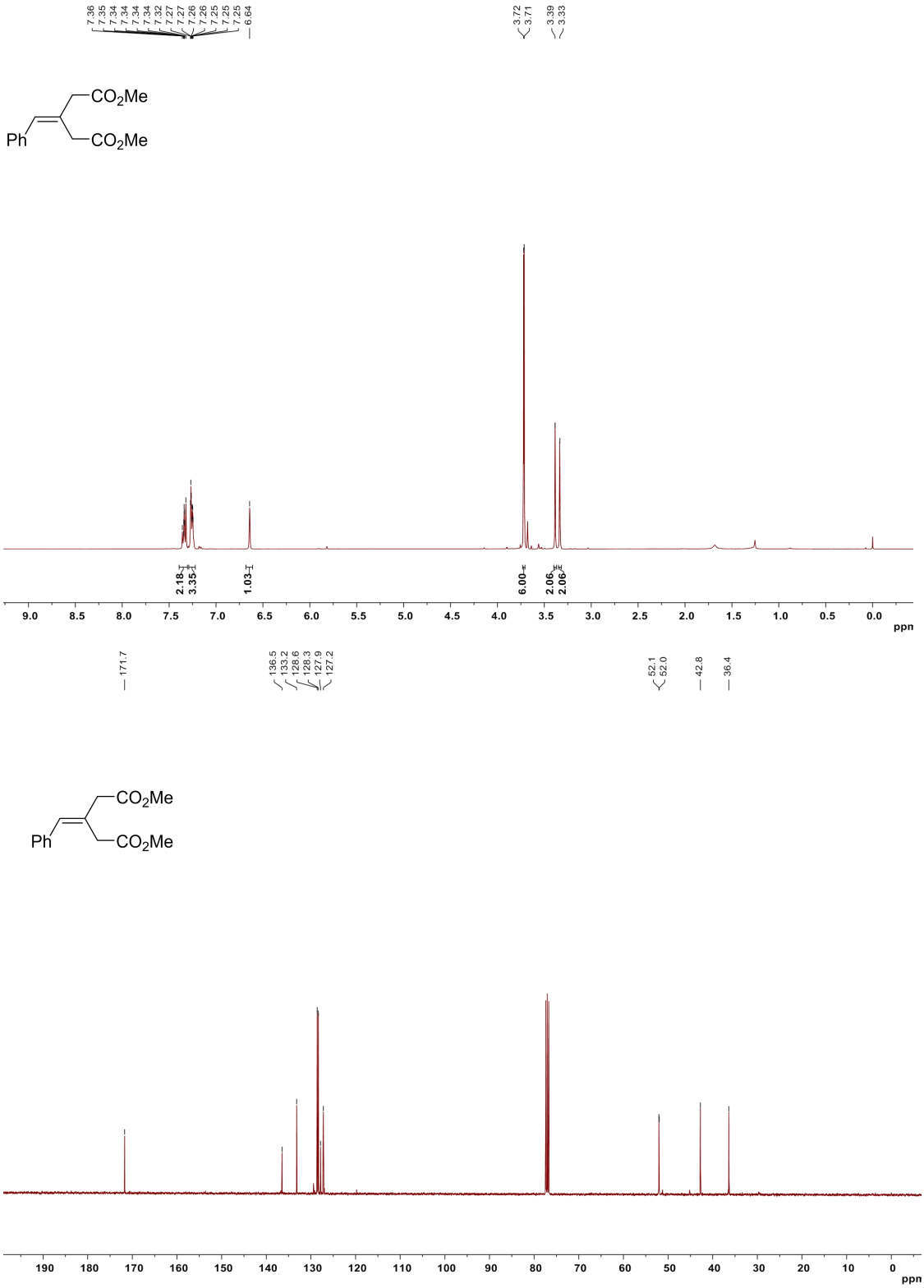
Compound 4y



Compound 6


7.96
7.95
7.95
7.94
7.94
7.53
7.52
7.52
7.51
7.51
7.51
7.35
7.34
7.33
7.33
7.28
7.27
7.25
7.22
7.21
7.20
6.84
4.39
3.93
3.92
3.91
3.90
3.80
3.78
3.77
3.76
3.75
3.71
3.69
3.69
3.67
1.66
1.13
1.12
1.10
1.10
1.09
1.07
EtO2C
Ph
CO2Et
Ph
O
N
Boc
0.97
2.02
2.02
4.13
3.10
2.12
0.98
0.95
1.00
3.05
9.37
6.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm
174.6
167.6
167.4
149.3
139.4
138.4
137.8
135.7
133.1
129.6
128.9
128.8
128.6
128.6
127.8
127.8
127.6
126.6
124.3
115.3
84.4
64.8
61.4
53.7
28.1
13.8
13.7
EtO2C
Ph
CO2Et
Ph
O
N
Boc
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

Compound 7


7.36
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7.34
7.34
7.34
7.34
7.32
7.27
7.27
7.26
7.26
7.25
7.25
7.25
6.64
3.72
3.71
3.39
3.33
CO2Me
Ph
CO2Me
2.18
3.35
1.03
6.00
2.06
2.06
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
ppm
171.7
136.5
133.2
128.6
128.3
127.9
127.2
52.1
52.0
42.8
36.4
CO2Me
Ph
CO2Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

8. X-ray crystal structure of compounds 2a and 9

8.1 X-ray crystal structure of the compound 2a

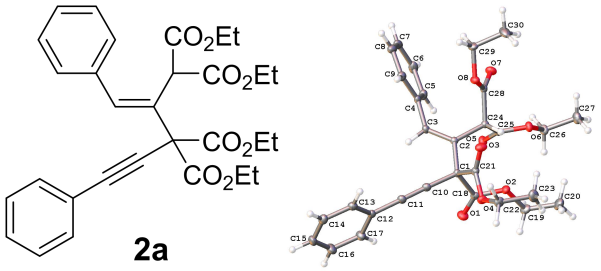

Figure S3. X-ray crystal structure of the compound **2a**

Table S3. Crystal data and structure refinement parameters of the compound **2a**

Parameter	Value	
CCDC deposition number	1950633	
Empirical formula	$C_{30}H_{32}O_8$	
Formula weight	520.55	
Temperature	170.01 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Cell dimensions	a = 9.5108(2) Å	α= 87.7580(10)°.
	b = 9.9970(2) Å	β= 89.5710(10)°.
	c = 14.6139(3) Å	γ= 80.9690(10)°.
Volume	1371.21(5) Å^3	
Z	2	
Density (calculated)	1.261 Mg/m^3	
Absorption coefficient	0.482 mm^{-1}	
F_{000}	552	
Crystal size	0.15 × 0.12 × 0.1 mm^3	
Theta range for data collection	3.985° to 54.974°	
Index ranges	$-11 \le h \le 11$	
	$-12 \le k \le 12$	
	$-17 \le l \le 17$	
Refinement method	Full-matrix least-squares on F^2	
restraints /parameters	5192 / 0 / 347	
Goodness of fit on F^2	1.074	
Extinction coef	n/a	

8.2 X-ray crystal structure of the compound 9

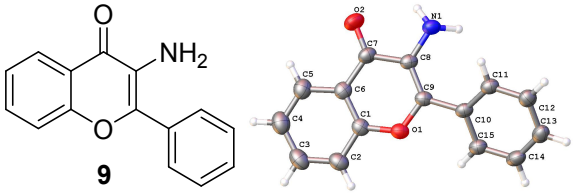

Figure S4. X-ray crystal structure of the compound **9**

Table S4. Crystal data and structure refinement parameters of the compound **9**

Parameter	Value
CCDC deposition number	1950634
Empirical formula	$C_{15}H_{11}NO_2$
Formula weight	237.25
Temperature	296.15 K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Hall group	$P2_12_12_1$
Cell dimensions	a = 4.1619 (7)Å α= 90°
	b = 13.023 (2) Å β= 90°
	c = 21.315 (4)Å γ= 90°
Volume	1155.2(3) Å^3
Z	4
Density (calculated)	1.364 Mg/m^3
Absorption coefficient	0.091 mm^{-1}
F_{000}	496
Crystal size	0.12 × 0.1 × 0.05 mm^3
Theta range for data collection	1.833° to 27.659°
Index ranges	$-5 \leq h \leq -5$
	$-17 \leq k \leq 16$
	$-27 \leq l \leq 27$
Refinement method	Full-matrix least-squares on F^2
restraints /parameters	2697/0/171
Goodness of fit on F^2	0.835
Extinction coef	n/a