Supporting Information

for

New Strategy to Construct Spiro/Fused/Bridged Carbocyclic Scaffolds Based on the Design of Novel 6-C Synthon Precursor

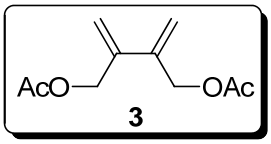
*Jia Liu, Xi Wang, Chang-Liang Sun, Bi-Jie Li, Zhang-jie shi and Min Wang**

I. General

All the reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. $Pd(OAc)_2$ (99.99% pure) was purchased from Alfa, DPPF (99% pure) was purchased from Zilai and DBU (99% pure) was purchased from Alfa. CH_2Cl_2 was distilled over CaH_2. ^1H NMR (300 MHz) and ^{13}C NMR (50 MHz) was recored on Varian Inc spectrometers or ^{13}C NMR (60 MHz) was registered on Jeol spectrometers with $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal standard. Chemical shifts are reported in ppm by assigning TMS resonance in the ^1H spectrum as 0.00 ppm and $CDCl_3$ resonance in the ^{13}C spectrum as 77.0 ppm. All coupling constants (*J* values) are reported in Hertz (Hz). Column chromatography was performed on silica gel 200-300 mesh. IR, GC, MS, and HRMS were performed by the State-authorized Analytical Center in Peking University. The following compounds were prepared according to known literature procedures: citations after punctuation **3**[1], **8a**[2], **8b**[3].

II. Synthesis of Substrates

Experimental Procedure of synthesis of 2,3-dimethylenebutane-1,4-diyl diacetate (3): To an three-neck flask (250 mL) equipped with a magnetic stir bar was added 2.12 g (2.5 mmol, 5 mol %) of 1,3-dimesityl-4,5-dihydroimidazol-2-ylidenetricyclohexylphos-phine benzylidene ruthenium dichloride (Grubbs II catalyst)[4] under ethylene balloon. A solution of 8.5 g of but-2-yne-1,4-diyl diacetate (50 mmol) in 200 mL of DCM was added to the flask. The mixture was stirred at room temperature for 12 hours. The reaction mixture was purified by silica gel column chromatography with ether/ petroleum ether = 1/4 to afford compound **3** as white solid (8.11 g, 82% yield). Spectra were identical to those reported in ref 1.

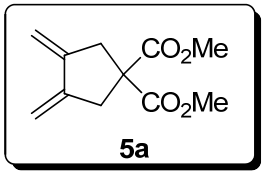


3

Dimethyl 3,4-dimethylenecyclopentane-1,1-dicarboxylate ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.34 (bs, 2H), 5.31 (bs, 2H), 4.78 (s, 4H), 2.10 (s, 6H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 170.5, 139.3, 115.8, 64.9, 20.9. **MS** ($C_{10}H_{14}O_4$): 198 (M^+). HRMS (EI): Anal. Calcd. (M^+) 198.08, Found: 198.1. **IR** (cm^{-1}): ν 1742, 1405, 1318, 1260, 1178

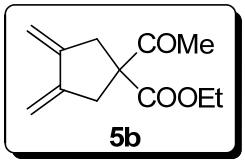
III. Synthesis and analytical data of product 5, 7, 9

Dimethyl 3,4-dimethylenecyclopentane-1,1-dicarboxylate



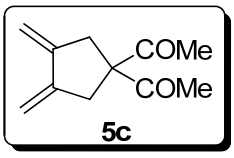
Following the general procedure, starting from 32 mg (0.24 mmol) of dimethyl malonate **4a**, product **5a** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 33.4 mg, 79% yield. colorless oil. **^{1}H NMR ($CDCl_3$, 300 MHz)**: δ 5.40 (s, 2H), 4.96 (s, 2H), 3.73 (s, 6H), 3.04 (s, 4H). **^{13}C NMR ($CDCl_3$, 50 MHz)**: δ 171.6, 144.4, 105.6, 57.6, 52.8, 41.2. **MS** ($C_{11}H_{14}O_4$): 210 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 233.07843, Found: 233.07831. **IR** (cm^{-1}): ν 1735, 1435, 1288, 1247, 1178.

Ethyl 1-acetyl-3,4-dimethylenecyclopentanecarboxylate (5b)



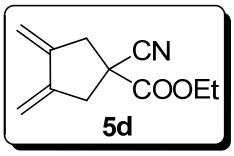
Following the general procedure, starting from 32 mg (0.24 mmol) of Ethyl acetoacetate **4b**, product **5b** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 35.4 mg, 85% yield, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.39 (s, 2H), 4.96 (s, 2H), 4.24-4.16 (m, 2H), 3.04-2.91 (m, 4H), 2.19 (s, 3H), 1.26 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 203.2, 171.9, 144.6, 105.6, 64.0, 61.7, 39.9, 26.3, 14.0. **MS** ($C_{12}H_{16}O_3$): 208 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 231.09917, Found: 231.09911. **IR** (cm^{-1}): ν 1713, 1357, 1235, 1180, 1151.

1,1'-(3,4-Dimethylenecyclopentane-1,1-diyl)diethanone (5c)



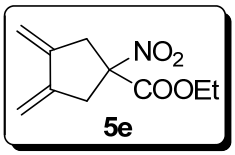
Following the general procedure, starting from 24 mg (0.24 mmol) of pentane-2,4-dione **4c**, product **5c** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 29.2 mg, 82% yield, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.39 (s, 2H), 4.98 (s, 2H), 2.97 (s, 4H), 2.14 (s, 6H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 205.0, 144.4, 105.9, 71.7, 38.8, 26.6. **MS** ($C_{11}H_{14}O_2$): 178 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 179.10666, Found: 179.10634. **IR** (cm^{-1}): ν 1718, 1699, 1421, 1356, 1210.

Ethyl 1-cyano-3,4-dimethylenecyclopentanecarboxylate (5d)



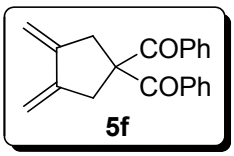
Following the general procedure, starting from 27 mg (0.24 mmol) of ethyl cyanoacetate **4d**. product **5d** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 34.8 mg, 91% yield, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.52 (s, 2H), 5.07 (s, 2H), 4.32-4.25 (m, 2H), 3.15-3.00 (m, 4H), 1.33 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 168.0, 142.1, 119.5, 107.3, 63.1, 45.5, 43.3, 13.9. **MS** ($C_{11}H_{13}NO_2$): 191 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 214.08385, Found: 214.08361. **IR** (cm^{-1}): ν 1743, 1239, 1069, 1023, 907.

Ethyl 3,4-dimethylene-1-nitrocyclopentanecarboxylate (5e)



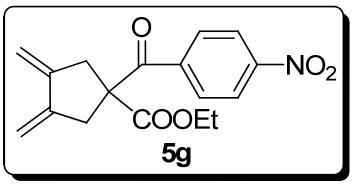
Following the general procedure, starting from 32 mg (0.24 mmol) of ethyl nitroacetate **4e**, product **5e** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 21.5 mg, 51% yield, pale yellow oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.48 (s, 2H), 5.05 (s, 2H), 4.32-4.25 (m, 2H), 3.48 (d, 2H, *J* = 8.7 Hz), 3.26 (d, 2H, *J* = 8.7 Hz), 1.29 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 166.3, 141.8, 107.2, 96.7, 63.2, 42.5, 13.8. **MS** ($C_{10}H_{13}NO_4$): 234 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 234.07368, Found: 234.07362. **IR** (cm^{-1}): ν 1749, 1554, 1414, 1369, 1240.

(3,4-Dimethylenecyclopentane-1,1-diyl)bis(phenylmethanone) (5f)



Following the general procedure, starting from 54 mg (0.24 mmol) of 1,3-diphenylpropane-1,3-dione **4f**, product **5f** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 54.4 mg, 90% yield, white solid; mp: 73-74 ℃. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.86 (d, 4H, *J* = 3.9 Hz), 7.42 (t, 2H, *J* = 7.5 Hz), 7.31 (t, 4H, *J* = 7.5 Hz), 5.42 (s, 2H), 4.96 (s, 2H), 3.40 (s, 4H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 197.6, 144.9, 135.5, 133.2, 129.2, 128.6, 105.5, 67.4, 41.9. **MS** ($C_{21}H_{18}O_2$): 302 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 303.13796, Found: 303.13820. **IR** (cm^{-1}): ν 1725, 1682, 1427, 1325, 1210.

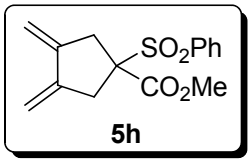
Ethyl 3,4-dimethylene-1-(4-nitrobenzoyl)cyclopentanecarboxylate (5g)



Following the general procedure, starting from 50 mg (0.24 mmol) of ethyl 4-nitrophenylacetate **4g**, product **5g** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 55.4 mg, 88% yield, pale yellow sticky oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.30 (d, 2H, *J* = 4.5 Hz), 8.04 (d, 2H,

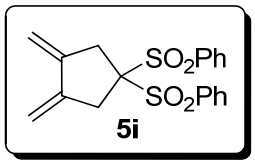
J = 4.5 Hz), 5.4 (s, 2H), 4.99 (s, 2H), 4.17-4.10 (m, 2H), 3.20 (s, 4H), 1.06 (t, 3H, *J* = 7.2 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 193.7, 172.5, 150.1, 144.0, 139.7, 129.6, 123.7, 105.9, 62.1, 61.4, 41.2, 13.8. **MS** ($C_{17}H_{17}NO_5$): 315 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 338.09989, Found: 338.10013. **IR** (cm^{-1}): ν 1738,1693, 1521, 1349, 1280, 1203.

Methyl 3,4-dimethylene-1-(phenylsulfonyl)cyclopentanecarboxylate (5h)



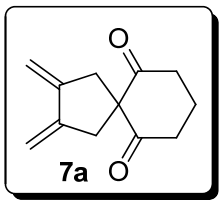
Following the general procedure, starting from 51 mg (0.24 mmol) of methyl phenylsulfonylacetate **4h**, product **5h** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 41.5 mg, 71% yield, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.85-7.82 (m, 2H), 7.72-7.67 (m, 1H), 7.59-7.54 (m, 2H), 5.39 (s, 2H), 4.96 (s, 2H), 3.66(s, 3H), 3.27 (d, 2H, *J* = 8.3 Hz), 3.15 (d, 2H, *J* = 8.3 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 168.0, 142.8, 134.3, 129.8, 128.9, 128.8, 106.4, 76.0, 53.3, 38.9. **MS** ($C_{15}H_{16}O_4S$): 292 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 315.06615, Found: 315.06527. **IR** (cm^{-1}): ν 1742,1680, 1540, 1470, 1280.

1,1-Biphenylsulfonyl-3,4-dimethylenecyclopentane (5i):



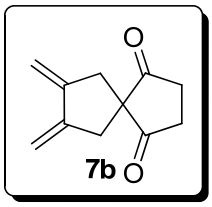
Following the general procedure, starting from 71 mg (0.24 mmol) of bis(phenylsulfonyl)methane **4i**, product **5i** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 48.6 mg, 65% yield, white solid, 123-124 ℃. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.03-8.01 (m, 4H), 7.74-7.69 (m, 2H), 7.59-7.54 (m, 4H), 5.29 (s, 2H), 4.84 (s, 2H), 3.40 (s, 4H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 142.5, 136.6, 134.7, 131.1, 128.7, 106.3, 90.2, 38.4. **MS** ($C_{19}H_{18}O_4S_2$): 374 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 375.15909, Found: 375.15869. **IR** (cm^{-1}): ν 1740, 1603, 1374, 1224, 1028.

2,3-Dimethylenespiro[4.5]decane-6,10-dione (7a)



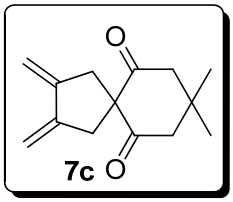
Following the general procedure, starting from 27 mg (0.24 mmol) of 1,3-Cyclohexanedione **6a**, product **5a** was obtained using ether/petroleum ether (1:2) as the eluant. yield: 33.1 mg, 87% yield, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.39 (s, 2H), 4.94 (s, 2H), 2.93 (t, 4H, *J* =1.8 Hz), 2.71 (t, 4H, *J* = 6.6 Hz), 2.03-1.94 (m, 2H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 207.3, 144.6, 105,5, 69.8, 39.7, 37.8, 17.9. **MS** ($C_{12}H_{14}O_2$): 190 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 191.10666, Found: 191.10626. **IR** (cm^{-1}): ν 1727, 1695, 1423, 866, 713.

7,8-Dimethylenespiro[4.4]nonane-1,4-dione (7b)



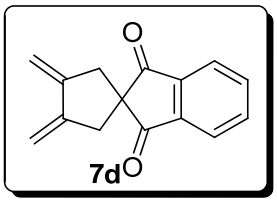
Following the general procedure, starting from 20 mg (0.24 mmol) of 1,3-Cyclopentanedione **6b** , product 7**b** was obtained using ether/petroleum ether (1:2) as the eluant. yield: 24.7 mg, 70% yield, white solid, mp: 83-84 ℃. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.46 (s, 2H), 4.97 (s, 2H), 2.82 (s, 4H), 2.70 (t, 4H, *J* = 1.8 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 214.2, 144.3, 106.0, 59.8, 40.5, 35.0. **MS** ($C_{11}H_{12}O_2$): 176 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 177.09101, Found: 177.09059. **IR** (cm^{-1}): ν 1720, 1420, 1297, 1205, 937.

8,8-Dimethyl-2,3-dimethylenespiro[4.5]decane-6,10-dione (7c)



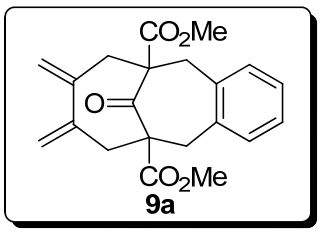
Following the general procedure, starting from 34 mg (0.24 mmol) of dimedone **6c**, product **7c** was obtained using ether/petroleum ether (1:3) as the eluant. yield: 31.0 mg, 71% yield, white solid, mp: 103-104 ℃. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.38 (s, 2H), 4.93 (s, 2H), 2.91 (s, 4H), 2.63 (s, 4H), 1.01 (s, 6H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 207.0, 144.6, 105.4, 68.5, 51.6, 39.6, 30.7, 28.4. **MS** ($C_{14}H_{18}O_2$): 218 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 219.13796, Found: 219.13773. **IR** (cm^{-1}): ν 1720, 1696, 1422, 1327, 1239.

3,4-Dimethylenespiro[cyclopentane-1,2'-indene]-1',3'-dione (7d)



Following the general procedure, starting from 34 mg (0.24 mmol) of 35 mg (0.24 mmol) of 1,3-indanedione **6d**, product **7d** was obtained using ether/petroleum ether (1:3) as the eluant. yield: 43.0 mg, 96% yield, white solid, mp: 70-71 ℃. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 8.00-7.98 (m, 2H), 7.88-7.85 (m, 2H), 5.53 (s, 2H), 5.01 (s, 2H), 2.83 (s, 4H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 202.6, 145.2, 141.2, 135.8, 123.5, 105.6, 56.8, 40.7. **MS** ($C_{15}H_{12}O_2$): 224 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 225.09101, Found: 225.09088. **IR** (cm^{-1}): ν 1739, 1701, 1593, 1333, 1232.

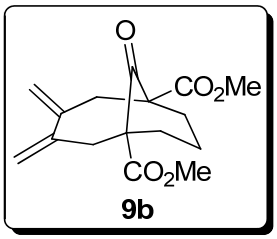
Dimethyl 8,9- benzo-3,4-dimethylene-11-oxobicyclo[4.3.1]undecane-1,6-dicarboxylate (9a)



9a

Following the general procedure, starting from 66 mg (0.24 mmol) of dimethyl 3-oxo-1,2,4,5-tetrahydrobenzo[*d*]cycloheptene-2,4-dicarboxylate **8a**, product **7d** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 65.2 mg, 92% yield, white solid, mp: 94-95 ℃. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.27-7.20 (m, 4H), 5.58 (s, 2H), 5.04 (s, 2H), 3.73 (s, 6H), 3.22 (dd, 4H, J_1 = 23.4 Hz, J_2 = 14.7 Hz), 2.90 (d, 2H, J = 7.5 Hz), 2.55 (d, 2H, J = 7.5 Hz). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 206.0, 172.6, 142.2, 137.0, 131.1, 127.3, 115.7, 63.5, 52.2, 38.4, 37.4. **MS** ($C_{21}H_{22}O_5$): 354 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 355.15400, Found: 355.15369. **IR** (cm^{-1}): ν 1735, 1696, 1433, 1268, 1237, 1202, 1180.

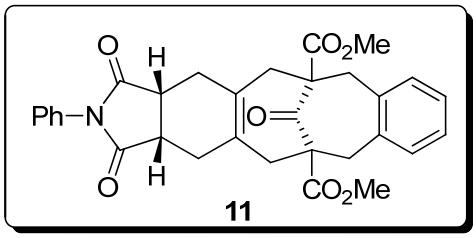
Dimethyl 3,4-dimethylene-11-oxobicyclo[4.4.1]decane-1,6-dicarboxylate (9b)



9b

Following the general procedure, starting from dimethyl cyclohexanone-2,6-dicaboxylate **8b**, product 9**d** was obtained using ether/petroleum ether (1:4) as the eluant. yield: 44.4 mg, 76% yield, colorless oil. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.48 (s, 2H), 5.11 (s, 2H), 3.74 (s, 6H), 2.92 (s, 4H), 2.55-2.45 (m, 2H), 2.26-2.17 (m, 1H), 2.12-2.01 (m, 2H), 1.97-1.83 (m, 1H). **^{13}C NMR** ($CDCl_3$, 60 MHz): δ 206.2, 172.8, 142.1, 114.4, 61.1, 52.3, 37.5, 34.8, 17.1. **MS** ($C_{16}H_{20}O_5$): 292 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 315.12029, Found: 315.11968. **IR** (cm^{-1}): ν 1735, 1706, 1458, 1431, 1277, 1214, 1139.

Synthesis of compound 11 (Eq 4).

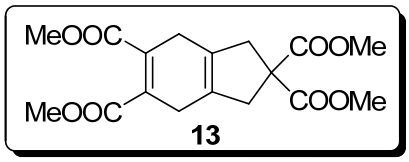


11

A solution of dimethyl 8,9- benzo-3,4-dimethylene-11-oxobicyclo[4.3.1] undecane-1,6-dicarboxylate **9a** (65 mg, 0.184 mmol), N-phenylmaleimide **10** (34.6 mg, 0.2 mol) in acetone (5.0 mL) was stirred for 12 hours at RT. After removing the solvent under vacuum, the residue was purified by silica gel column chromatography with EtOAc/ petroleum ether = 1/4 to afford compound **11** as a white solid (79.7 mg, 84% yield, dr > 20: 1), mp: 273-274 □. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.41- 7.33 (m, 3H), 7.30- 7.27 (m, 2H), 7.20- 7.16 (m, 2H), 7.10- 7.02 (m, 2H), 3.81 (s, 6H), 3.48 (s, 1H), 3.43 (s, 1H), 3.16- 3.14(m, 2H), 3.06 (s, 1H), 3.00 (s, 1H), 2.67-2.49 (m, 6H), 2.22 (s, 1H), 2.18 (s, 1H). **^{13}C NMR** ($CDCl_3$, 60 MHz): δ 206.6, 178.9, 172.7, 135.9, 134.0, 131.8, 131.7, 128.9, 128.3, 128.0, 126.1, 63.2, 52.4, 39.7,

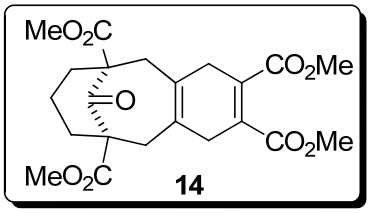
39.3, 35.8, 31.5. **MS** ($C_{31}H_{29}NO_7$): 527 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 528.20168, Found: 528.20046. **IR** (cm^{-1}): ν 2923, 2852, 1738, 1708, 1476, 1285.

Synthesis of compound 13 (Eq 5).



To an oven dried Schlenk tube was added 2,3-dimethylenebutane-1,4-diyl diacetate **3** (39.6 mg, 0.20 mmol), dimethyl malonate **4a** (0.24 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), DPPF (5.54 mg, 0.01 mmol), DBU (76 mg, 0.50 mmol). The tube was evacuated and refilled with N_2, and this process was repeated 3 times. Then 2.5 mL of CH_2Cl_2 was added into the tube by syringe. The mixture was stirred at room temperature for 24 hours. After removing the solvent under vacuum, the solvent of DMAD **12** (170.4 mg, 1.2 mmol) in ether (5 mL) was add to the reaction mixture. After refluxing for 4 hours, the solvent was removed under vacuum. the residue was purified by silica gel column chromatography with EtOAc/ petroleum ether = 1/1 to afford compound **13** as a white solid (51.9 mg, 74% yield), mp: 117-118 □. **Tetramethyl 1H-indene-2,2,5,6(3H,4H,7H)-tetracarboxylate ^{1}H NMR** ($CDCl_3$, 300 MHz): δ 3.78 (s, 6H), 3.75 (s, 6H), 2.99 (s, 4H), 2.98 (s, 4H). **^{13}C NMR** ($CDCl_3$, 60 MHz): δ 172.4, 166.3, 132.8, 127.8, 57.6, 52.8, 52.1, 42.7, 28.3. **MS** ($C_{17}H_{20}O_8$): 352 (M^+). HRMS (ESI): Anal. Calcd. ($M+H^+$) 353.12309, Found: 353.12280. **IR** (cm^{-1}): ν 1730, 1647, 1434, 1317, 1255, 1202, 1152.

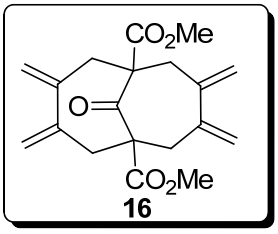
Synthesis of compound 14 (Eq 6).



To an oven dried Schlenk tube was added 2,3-dimethylenebutane-1,4-diyl diacetate **3** (39.6 mg, 0.20 mmol), nucleophile (0.24 mmol), $Pd(OAc)_2$ (1.12 mg, 0.005 mmol), dppf (5.54 mg, 0.01 mmol), DBU (76 mg, 0.50 mmol). The tube was evacuated and refilled with N_2, and this process was repeated 3 times. Then 2.5 mL of CH_2Cl_2 was added into the tube by syringe. The mixture was stirred at room temperature for 24 hours. After removing the solvent under vacuum, the solvent of DMAD **12** (170.4 mg, 1.2 mmol) in ether (5 mL) was add to the reaction mixture. The mixture was refluxed for 4 hours. After removing the solvent under vacuum, the residue was purified by silica gel column chromatography with EtOAc/ petroleum ether = 1/1 to afford compound **14** as a white solid (59.4 mg, 69% yield), mp: 122-123 □. **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 3.77 (s, 6H), 3.75 (s, 6H), 3.53-3.43 (m, 2H), 3.04-2.95 (m, 4H), 2.53-2.47 (m, 2H), 2.42-2.37 (m, 2H), 2.02-1.97 (m, 2H), 1.86-1.80 (m, 2H). **^{13}C NMR** ($CDCl_3$, 60 MHz): δ 205., 172.8, 168.1, 132.4, 128.7, 61.0, 52.4, 52.0, 35.3, 34.1, 33.4, 16.7. **MS** ($C_{22}H_{26}O_9$): 434 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 457.14690, Found: 457.14691. **IR** (cm^{-1}): ν 1734, 1434, 1286, 1249, 1071.

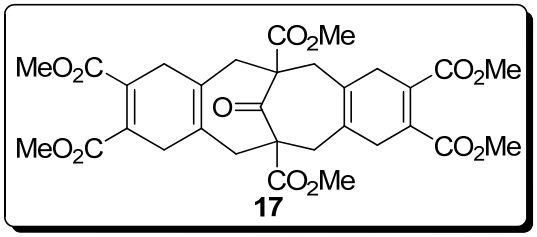
Synthesis of compounds 16 and 17 (Eq 7).

To an oven dried Schlenk tube was added 2,3-dimethylenebutane-1,4-diyl diacetate **3** (99 mg, 0.50 mmol), dimethyl acetone -1,3-dicarboxylate **15** (0.2 mmol), $Pd(OAc)_2$ (2.24 mg, 0.01 mmol), DPPF (11.8 mg, 0.02 mmol), DBU (182.4 mg, 1.2 mmol). The tube was evacuated and refilled with N_2, and this process was repeated 3 times. Then 5 mL of CH_2Cl_2 was added into the tube by syringe. The mixture was stirred at room temperature for 24 hours. The reaction mixture was purified by silica gel column chromatography with ether/ petroleum ether = 1/4 to afford compound **16** as colorless oil (51.1 mg, 74% yield). **Dimethyl 3,4,8,9-tetramethylene-11-oxobicyclo[4.4.1]undecane-1,6-dicarboxylate** **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 5.45 (s, 4H), 5.00 (s, 4H), 3.72 (s, 6H), 2.82 (d, 8H, *J* = 1.7 Hz). **^{13}C NMR** ($CDCl_3$, 60 MHz): δ 206.8, 172.7, 143.9, 115.8, 63.3, 52.3, 37.8. **MS** ($C_{19}H_{22}O_5$): 330 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 353.13594, Found: 353.13586. **IR** (cm^{-1}): ν 1735, 1696, 1432, 1269, 1209.



16

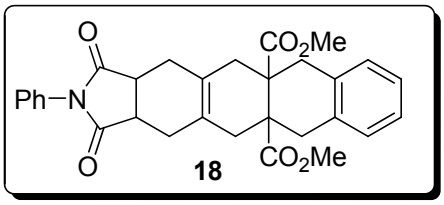
A solution of **16** (66 mg, 0.2 mmol), DMAD **12** (71 mg, 0.5 mol) in CH_2Cl_2/ ether = 1/1 (5.0 mL) was stirred for 12 hours in reflux. After removing the solvent under vacuum, the residue was purified by silica gel column chromatography with EtOAc/ petroleum ether = 2:1 to afford compound **17** as a white solid (105.6 mg, 86% yield), mp: 253-254 □. **Dimethyl 3,4,8,9-tetramethylene-11-oxobicyclo[4.4.1]undecane-1,6-dicarboxylate** **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 3.79 (s, 12H), 3.76 (s, 6H), 3.40-3.30 (m, 4H), 3.03-2.92 (m, 4H), 2.58 (s, 8H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 205.6, 172.7, 167.8, 132.2, 128.0, 62.5, 52.5, 52.3, 35.5, 34.8. **MS** ($C_{31}H_{34}O_{13}$): 614 (M^+). HRMS (ESI): Anal. Calcd. ($M+Na^+$) 637.18818, Found: 637.18916. **IR** (cm^{-1}): ν 2952, 1734, 1696, 1434, 1271, 1235, 1066.



17

Synthesis of compound 18 (Eq 8).

Compound **18** was obtained from CH_2Cl_2 by slow solvent evaporation with using compound sample obtained by irradiation of **11** in the solid state with *k* > 290 nm (Pyrex filter). Compound 18 is a white solid (yield > 95%), mp: 261-262 □**.** **^{1}H NMR** ($CDCl_3$, 300 MHz): δ 7.33-7.23 (m, 5H), 7.16-6.99 (m, 4H), 3.77 (s, 6H), 3.44 (s, 1H), 3.39 (s, 1H), 3.11- 3.05 (m, 2H), 3.02 (s, 1H), 3.00 (s, 1H), 2.62-2.45 (m, 6H), 2.19 (s, 1H), 2.14 (s, 1H). **^{13}C NMR** ($CDCl_3$, 60 MHz): δ 179.2, 173.0, 136.1, 134.3, 132.0, 131.6, 129.1, 128.6, 128.3, 126.3, 63.3, 52.5, 39.8, 39.4, 35.9, 31.4. **MS** ($C_{30}H_{29}NO_6$): 499 (M^+). HRMS (ESI): Anal. Calcd. (M^+) 499.19894, Found: 499.20023. **IR** (cm^{-1}): ν 2904, 1710, 1699, 1480, 1206.



18

References

1. Atsushi K.; Norikazu S.; Miwako M. *Tetrahedron*, **1999**, *55,*8155.
2. Shuntaro Mataka. *J. Org. Chem*. **1989**, *54*, 5237.
3. Blicke, F. F.; McCarty, F. J. *J. Org. Chem*. **1959**, *24*, 1069.
4. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999***, 1*, 953.

IV. X-ray Crystal Structure of 11 and 17

Experimental Details

A colorless Toluene and Hexane solution of **11** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of solvent at room temperature. A colorless prism crystal of C_{31} H_{28} NO_7 having approximate dimensions of 0.19 x 0.18 x 0.10 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

A colorless CH_2Cl_2 and Hexane solution of **17** was prepared. Crystals suitable for X-ray analysis were obtained by slow evaporation of solvent at room temperature. A colorless prism crystal of C_{31} H_{28} NO_7 having approximate dimensions of 0.40 x 0.40 x 0.30 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

Crystal Data

	11	**17**
formula	$C_{31}H_{29}NO_7$, C_7H_8	$C_{31}H_{34}O_{13}$
fw	618.68	614.58
cryst syst	triclinic	Monoclinic
space group	P-1	P2(1)/n
a (Å)	9.851(2)	12.624(3)
b (Å)	11.303(2)	10.895(2)
c (Å)	15.868(3)	21.852(4)
α(deg)	82.36(3)	90.00
β(deg)	76.88(3)	104.90(3)
γ(deg)	64.54(3)	90.00
V (Å^3)	1552.4(5)	2904.7(10)
Z	2	4
D_{calcd} (g cm^{-3})	1.324	1.405
μ (mm^{-1})	0.091	0.110
F(000)	645	1296
cryst size (mm)	0.19×0.18× 0.10	0.40×0.40×0.30
max. 2θ(deg)	50.0	55.0
no. of reflns collected	5470	6634
no. of indep reflns/R_{int}	4872/ 0.0457	2441/0.0903
no. of params	417	404
goodness-of-fit on F^2	1.211	0.990
R1, wR2 ($I > 2\sigma(I)$)	0.0775, 0.1767	0.0649, 0.0734
R1, wR2 (all data)	0.0883 , 0.1831	0.1659 , 0.0734

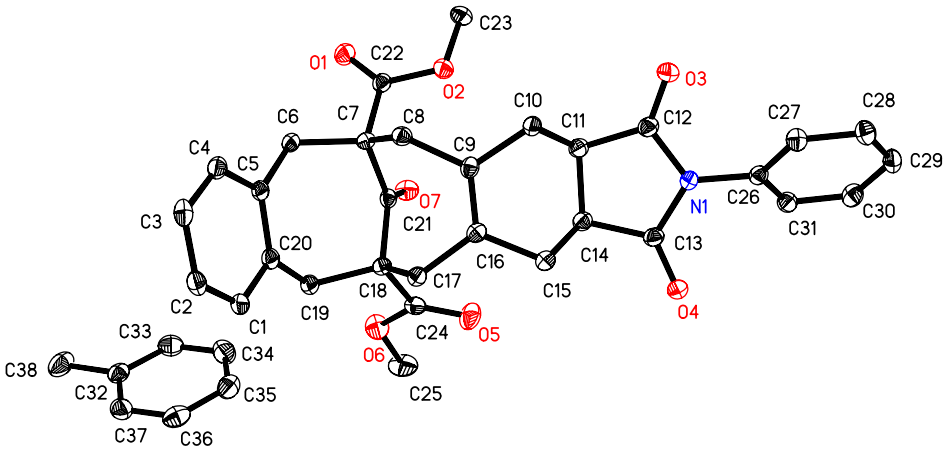


Figure 1. X-ray crystallographic of compound **11**

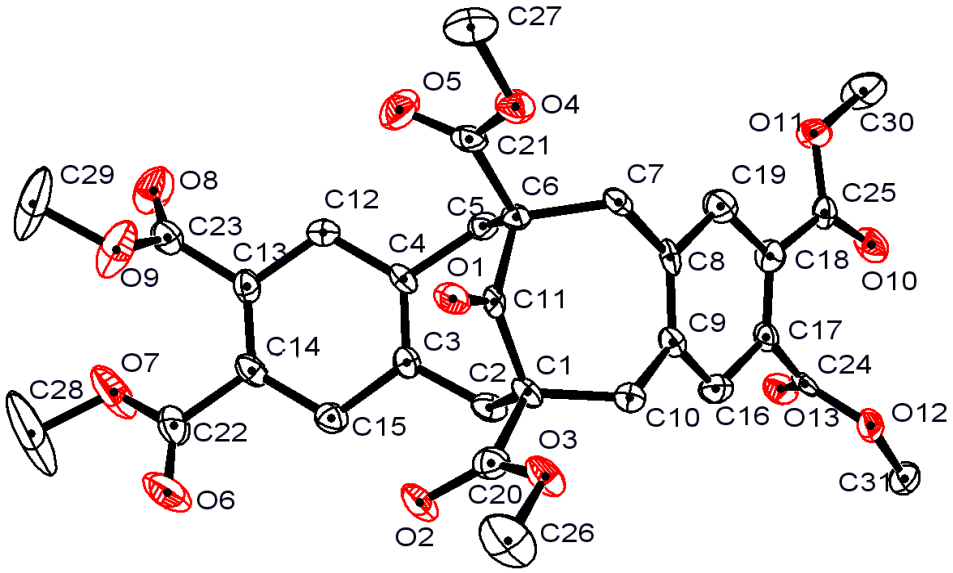
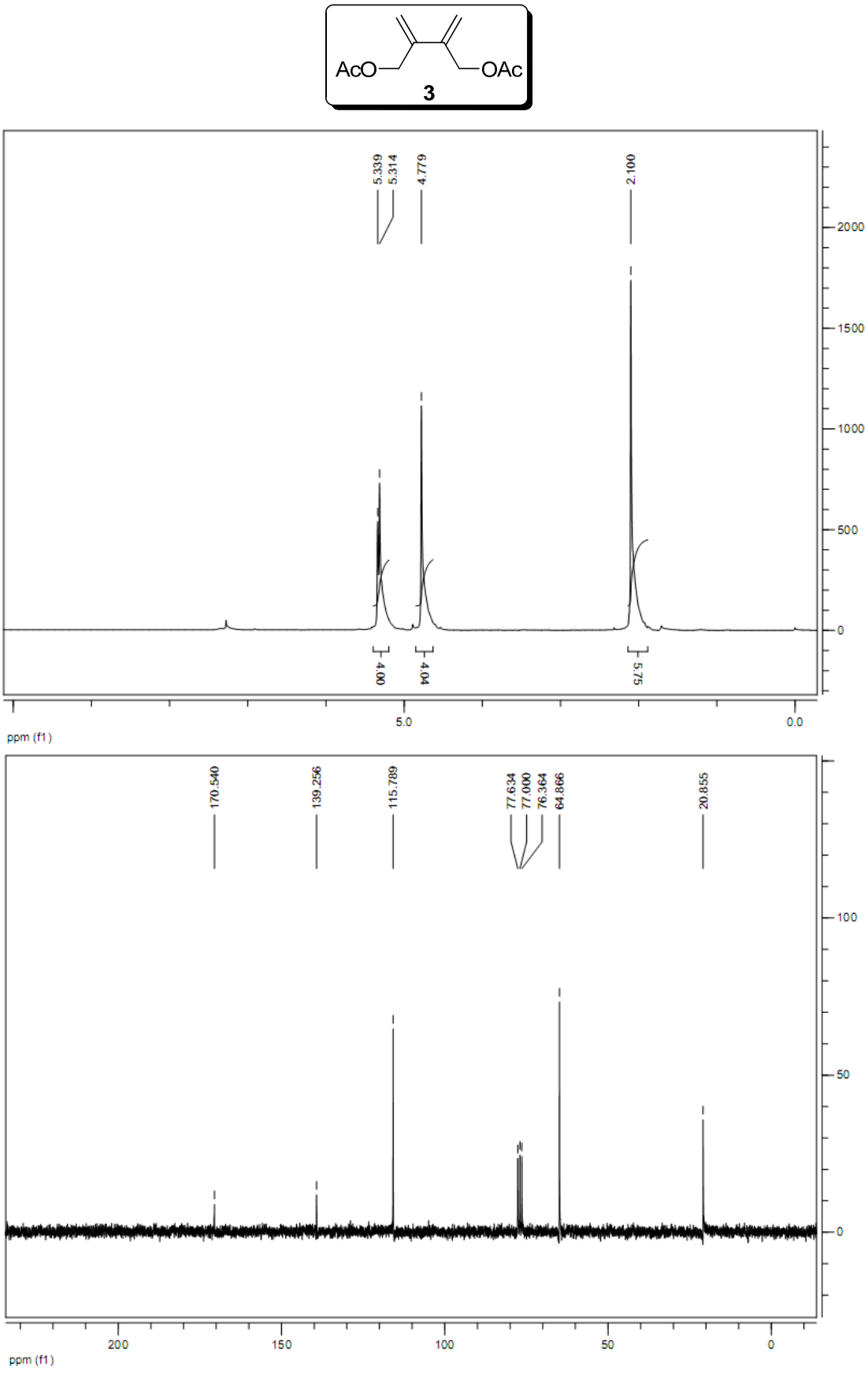


Figure 2. X-ray crystallographic of compound **17**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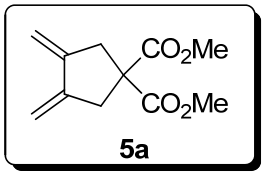
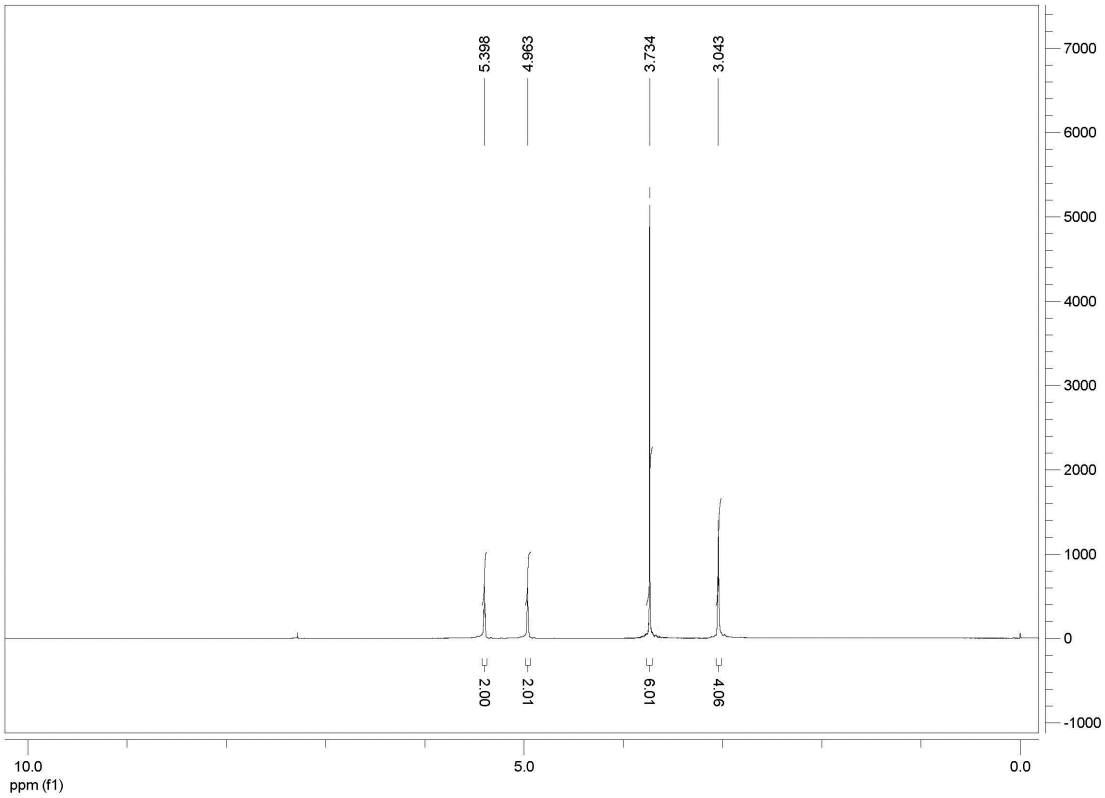
20.855
ppm (f1)


CO2Me
CO2Me

5a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3.734
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2.00
2.01
6.01
4.06
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5000
4000
3000
2000
1000
0
-1000
10.0
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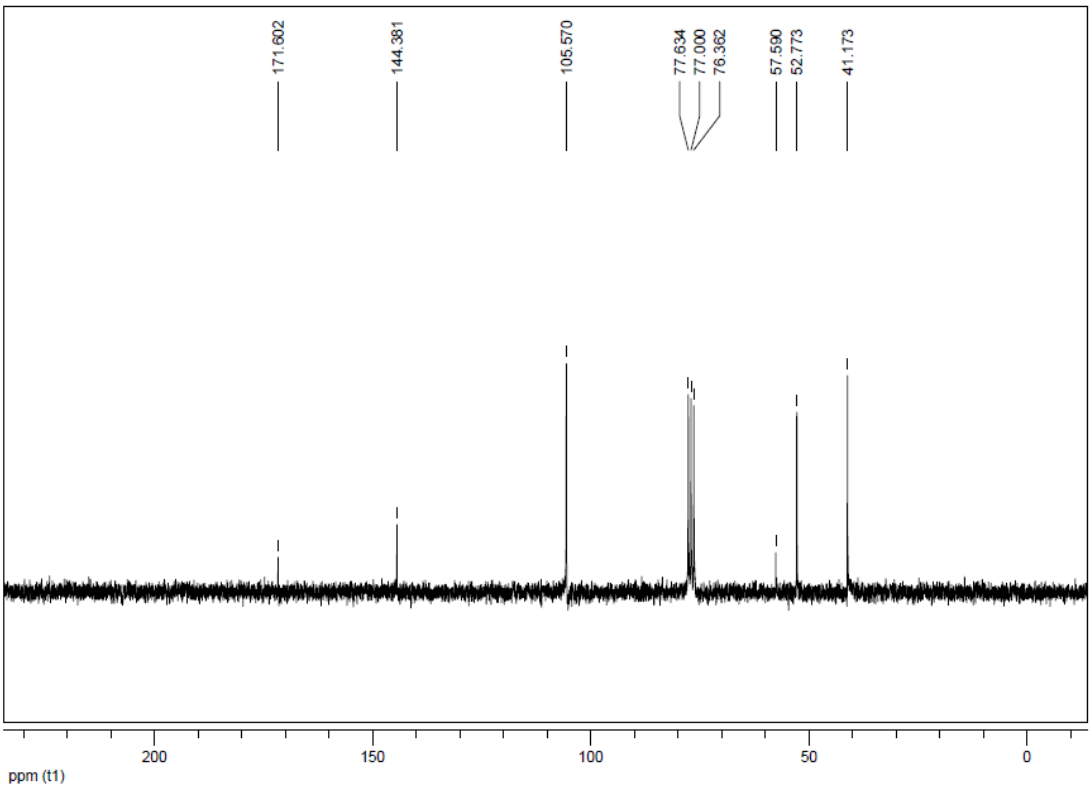
0.0
ppm (f1)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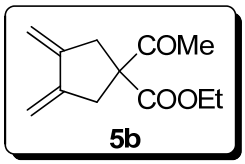
COMe
COOEt
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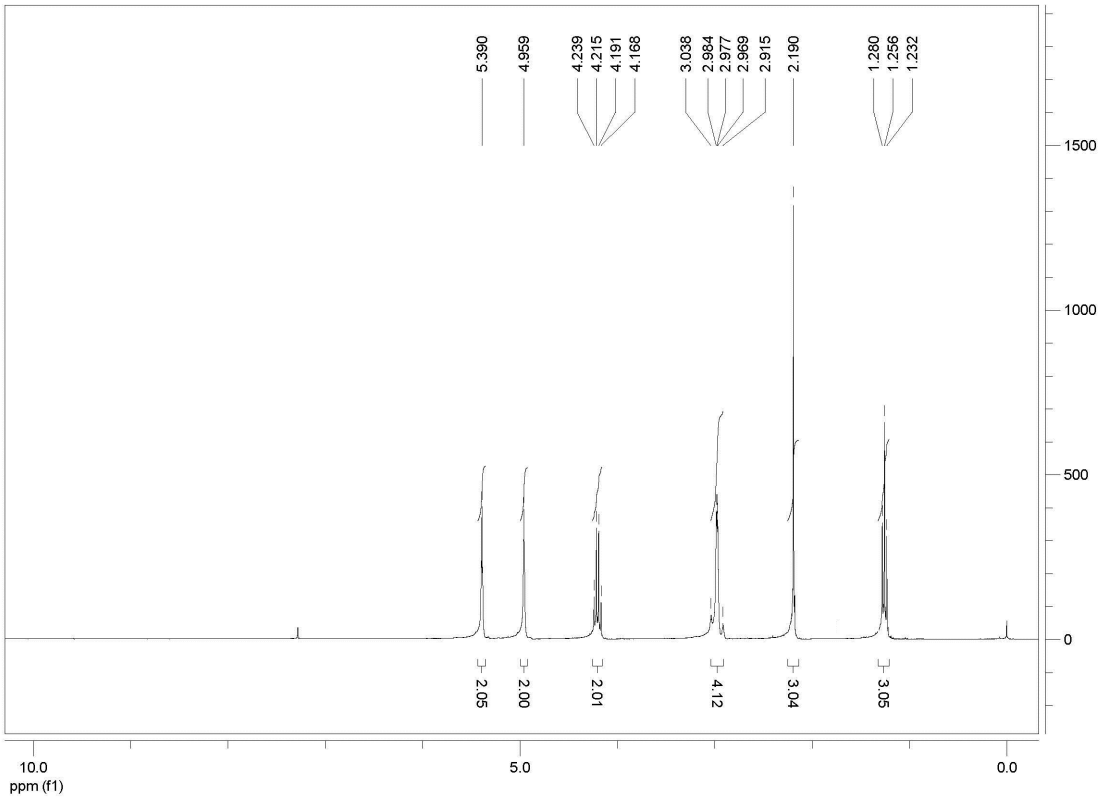
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1.256
1.232
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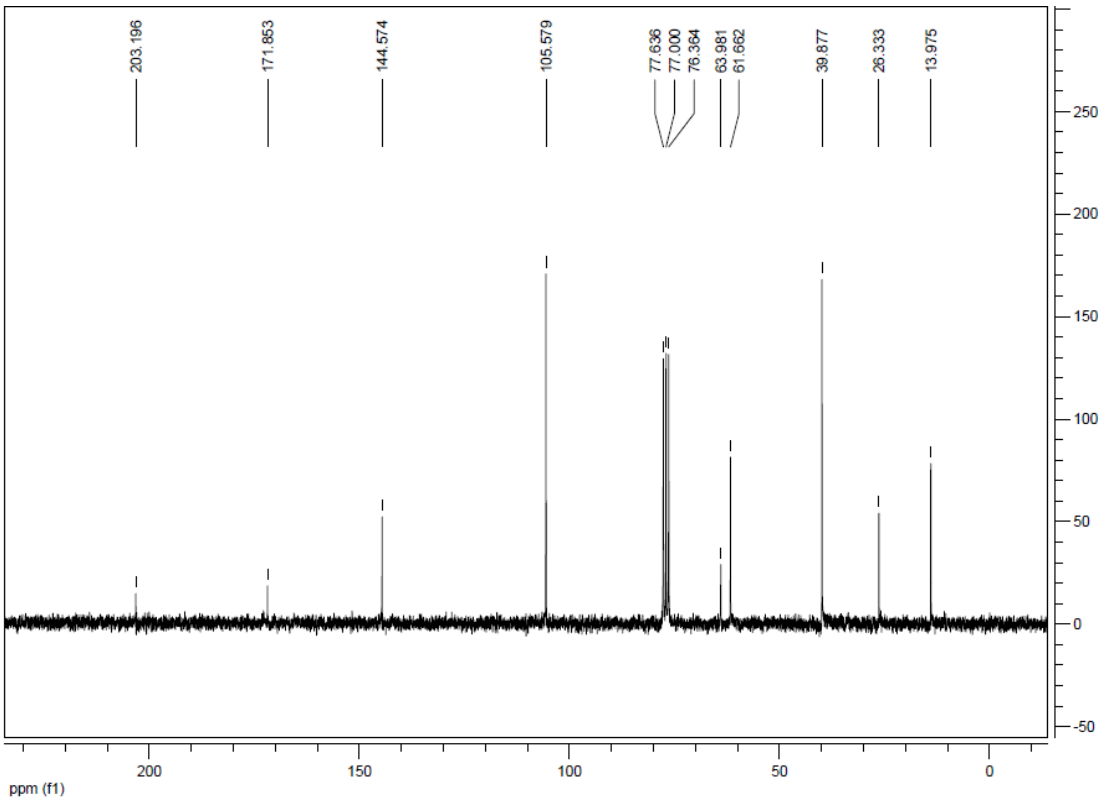
ppm (f1)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-50
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100
50
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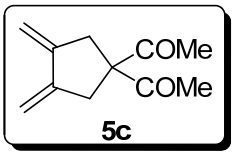
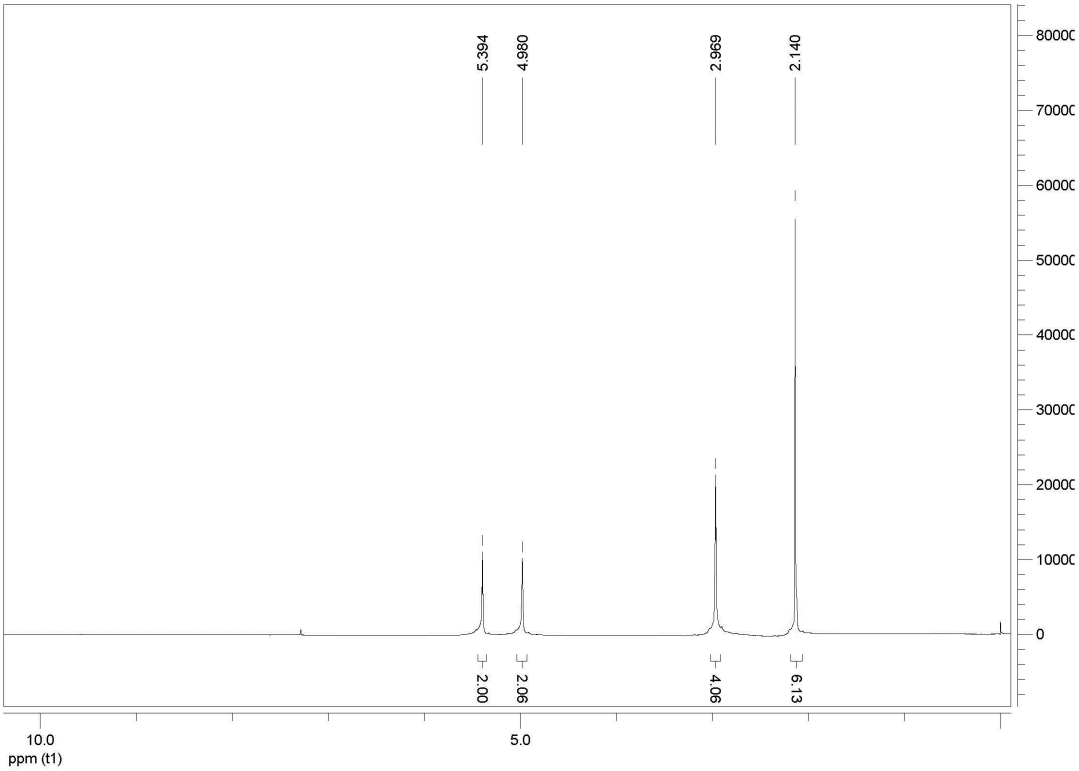
ppm (f1)


COMe
COMe

5c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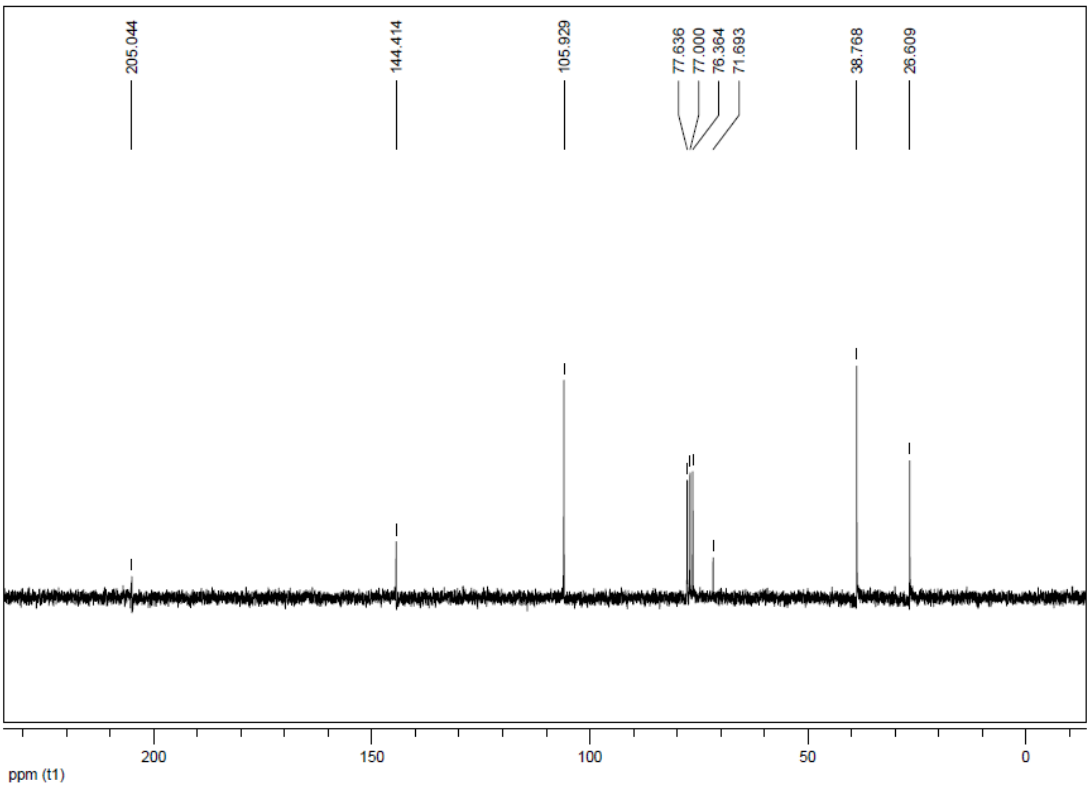
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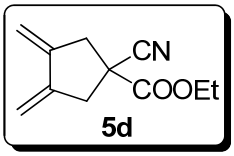
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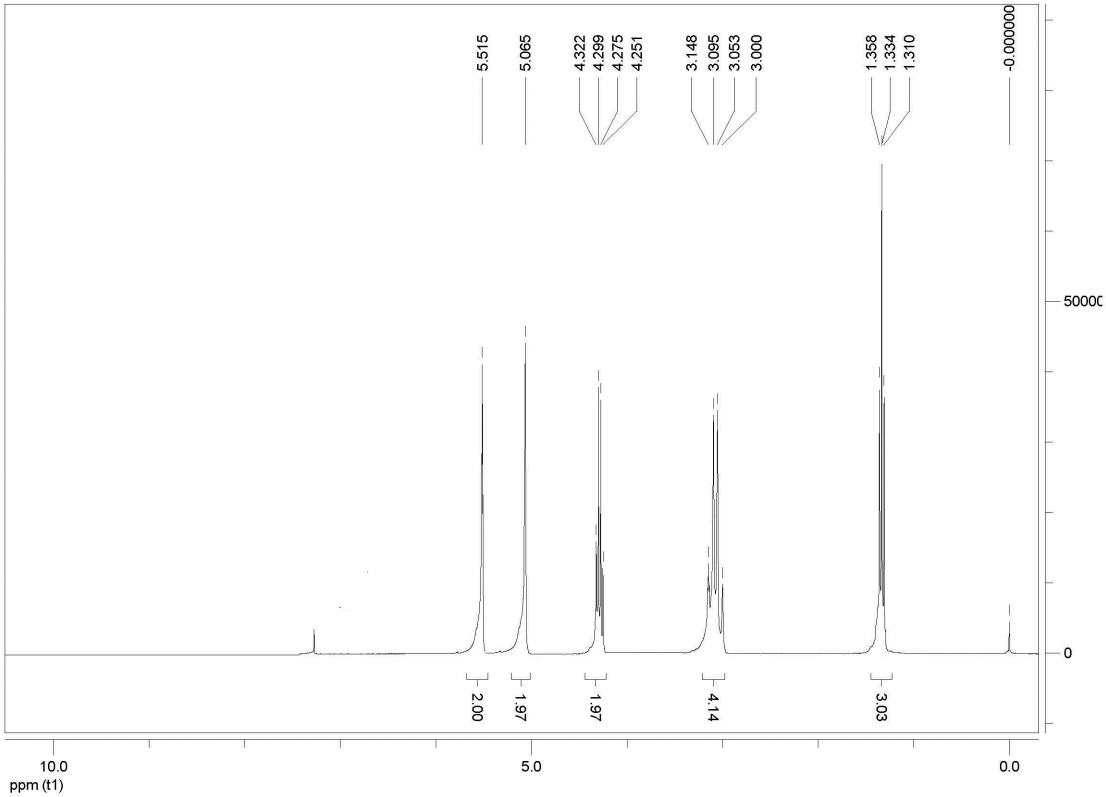
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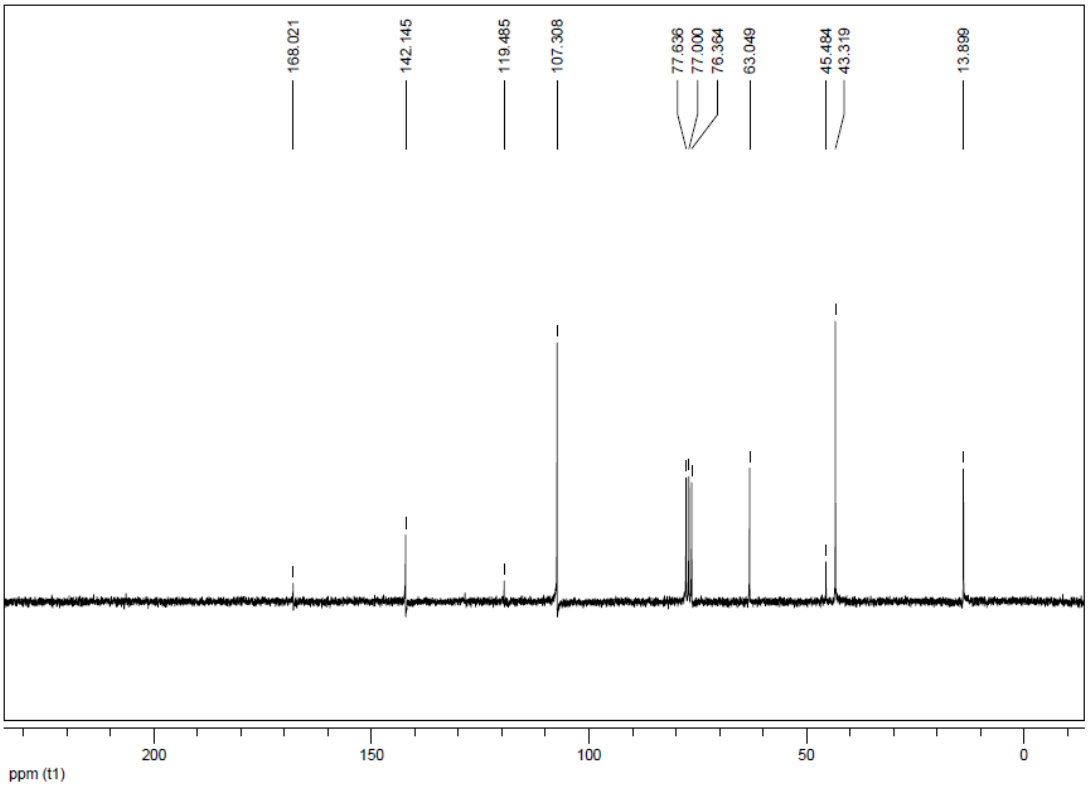
ppm (t1)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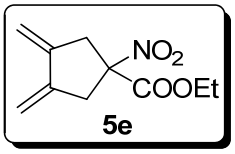
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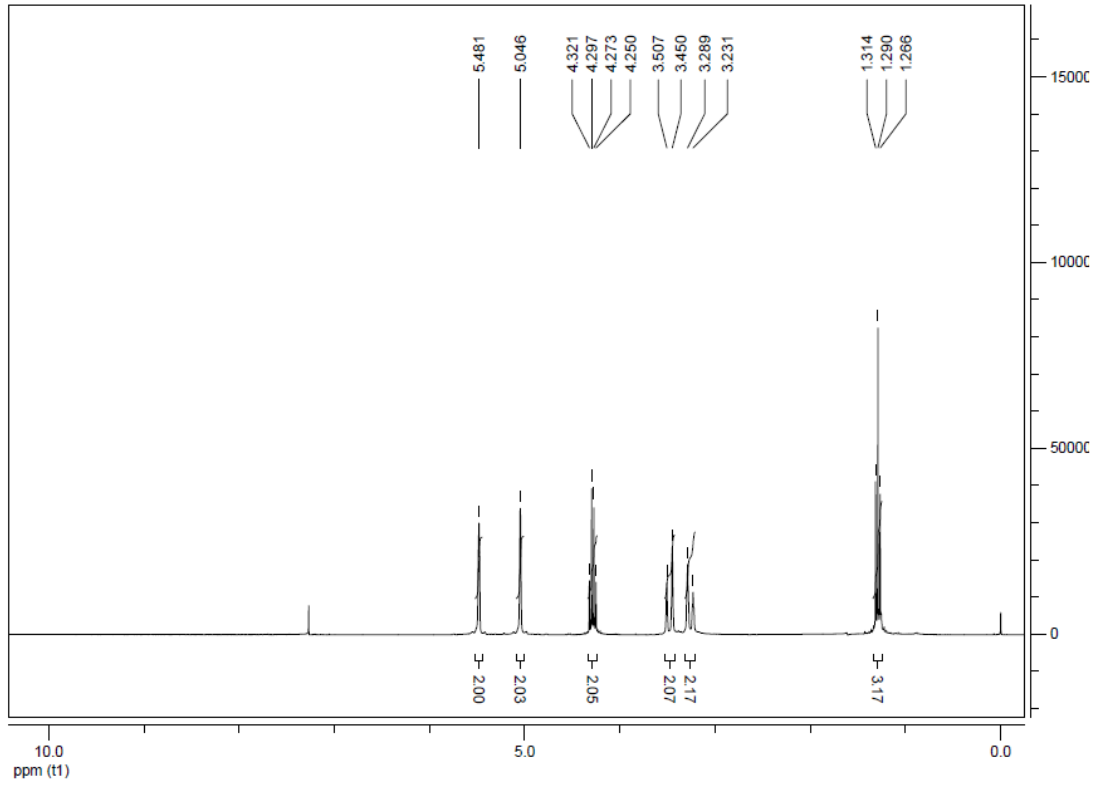
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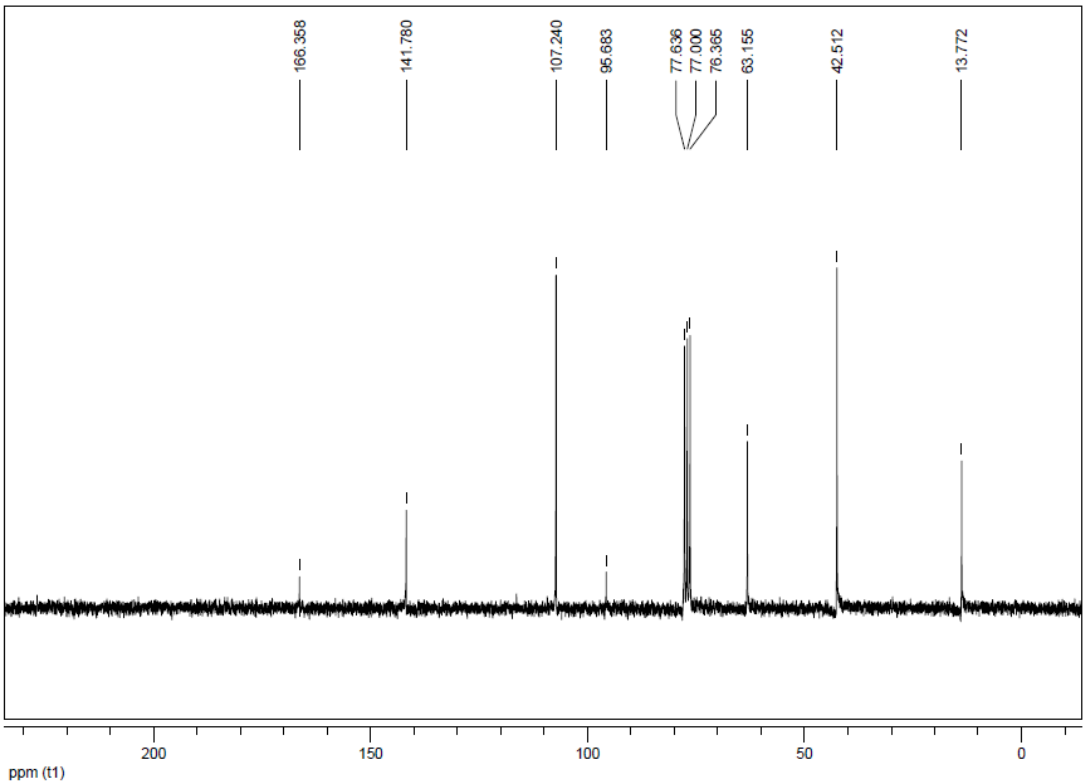
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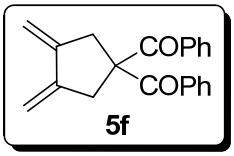
ppm (t1)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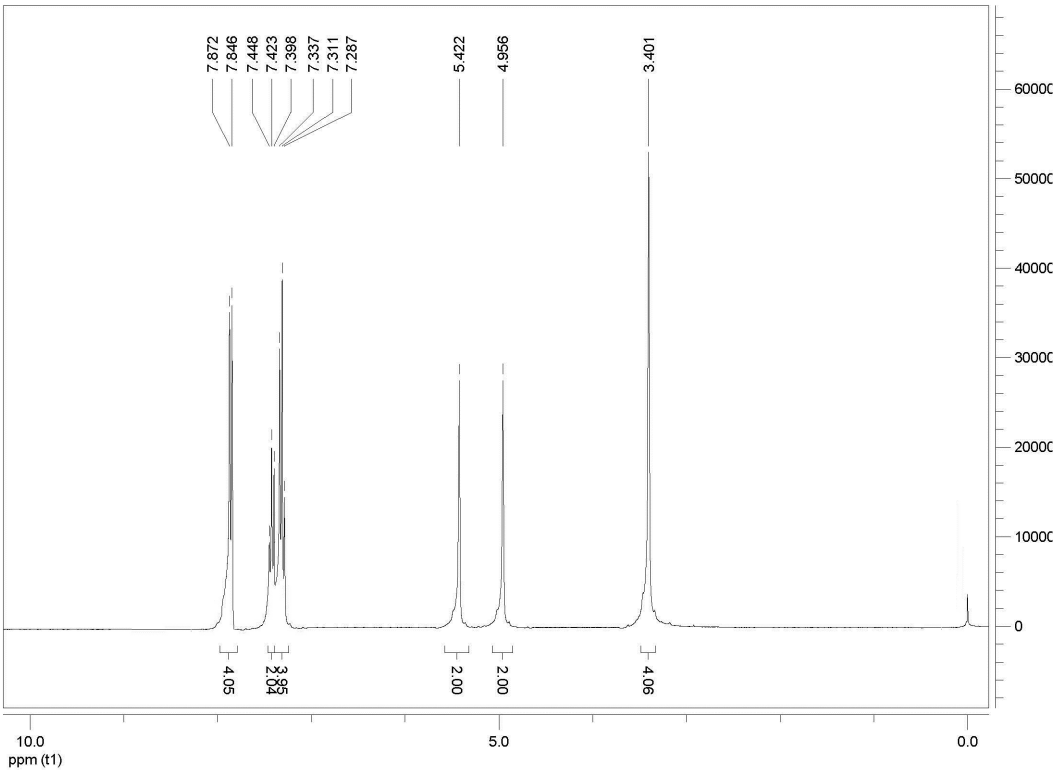
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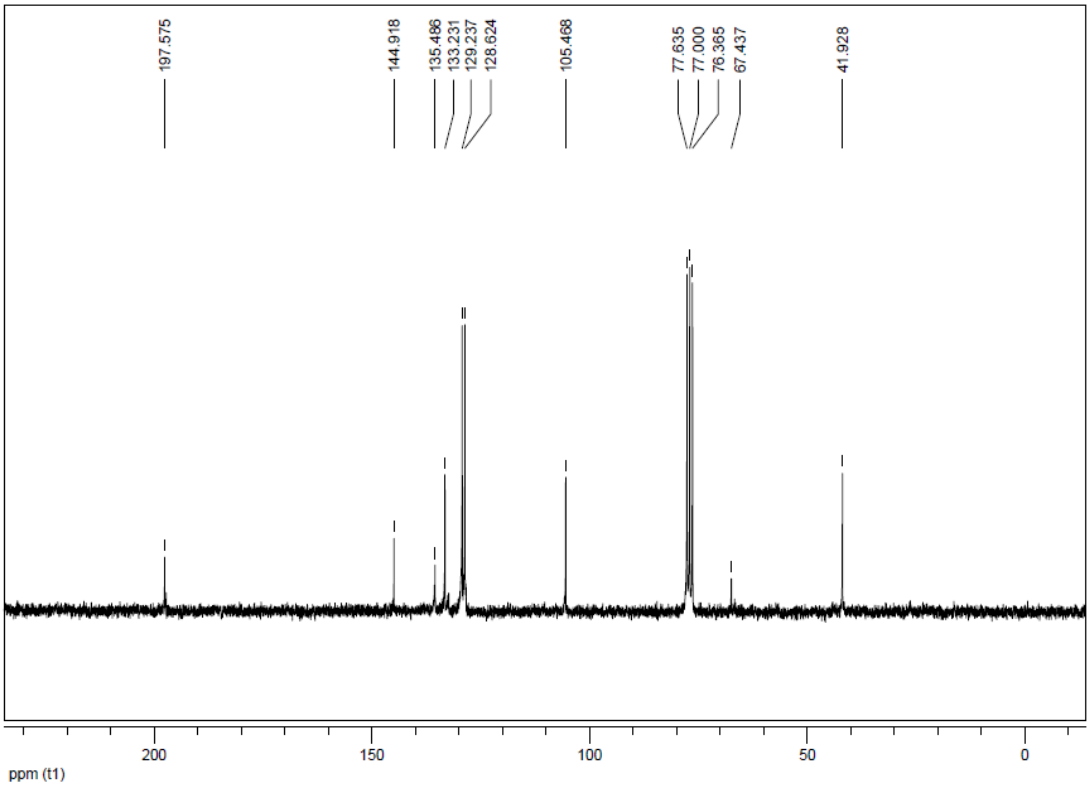
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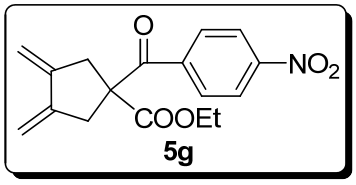
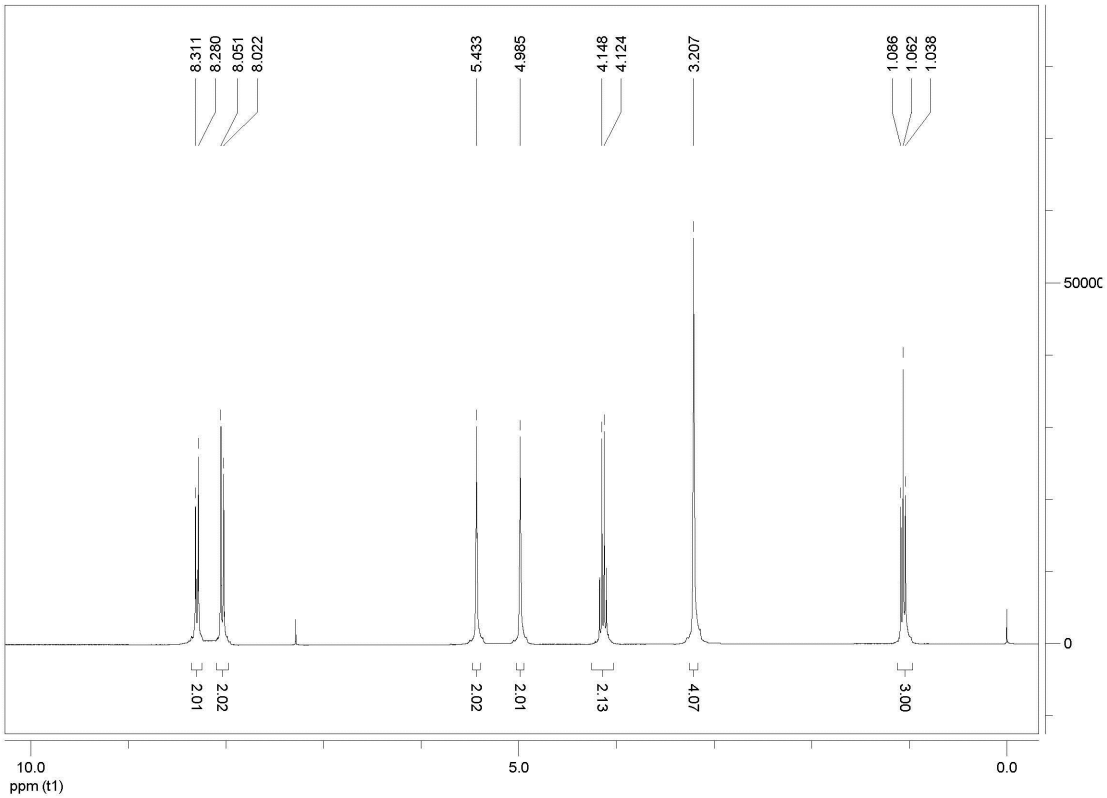
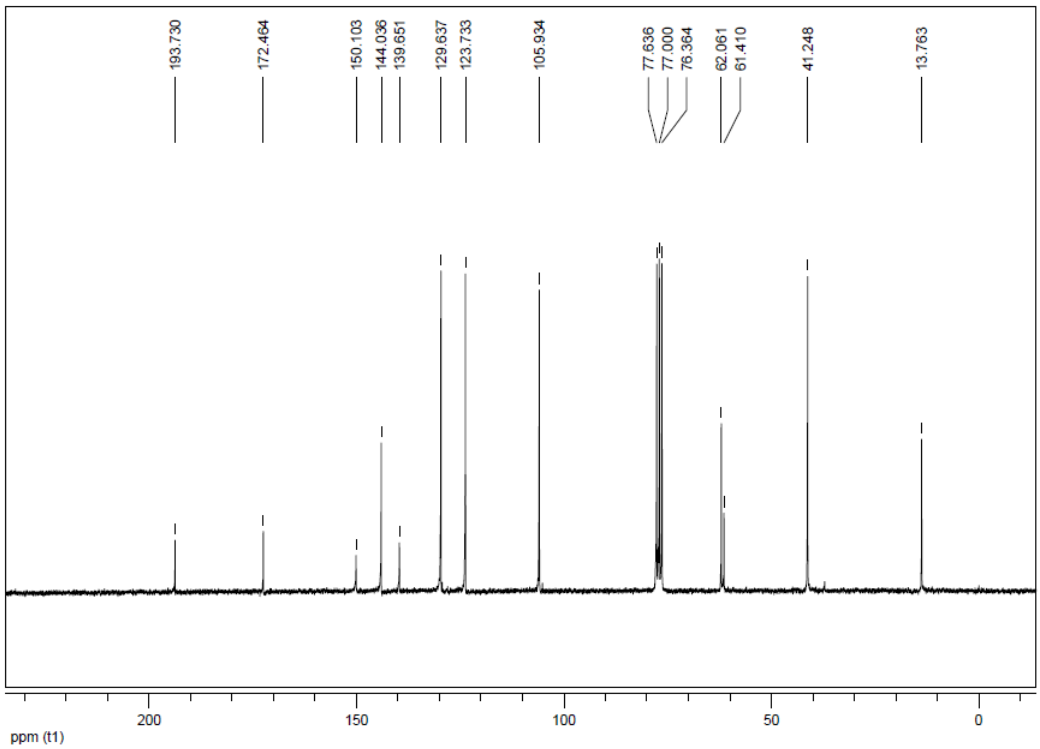
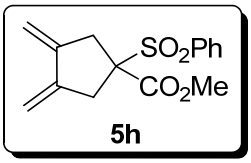
144.918
135.486
133.231
129.237
128.624
105.468
77.635
77.000
76.365
67.437
41.928
200
150
100
50
0
ppm (t1)


O
NO2
COOEt

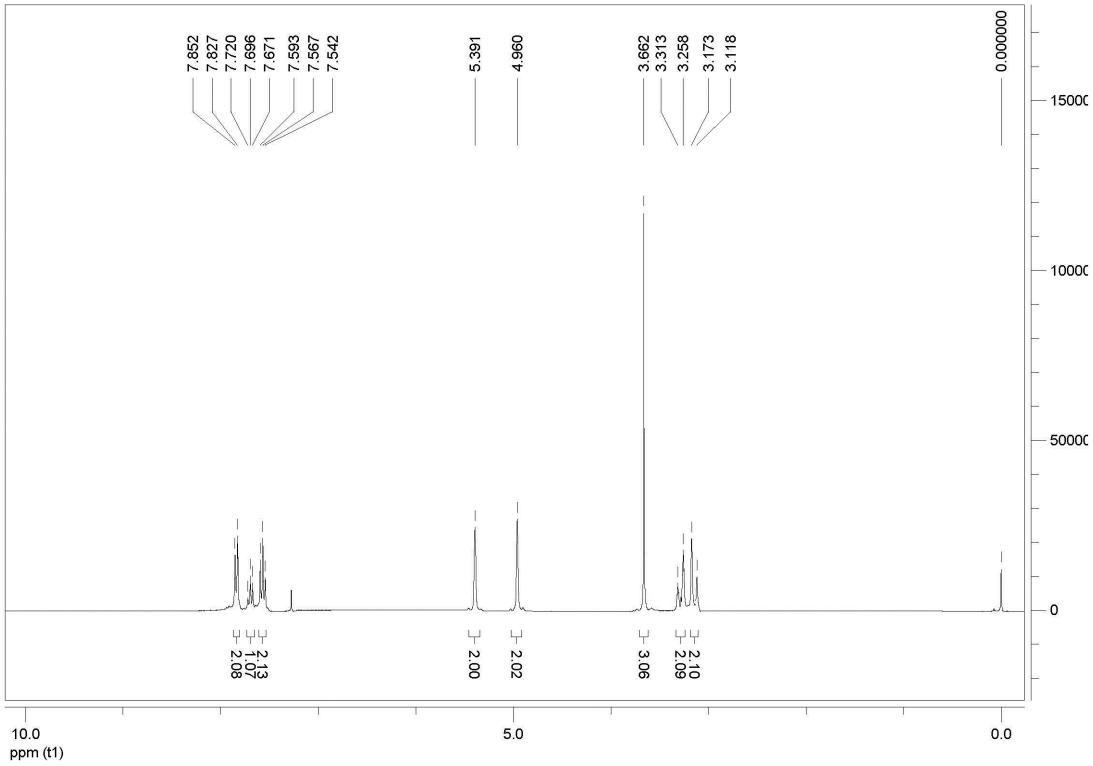
5g

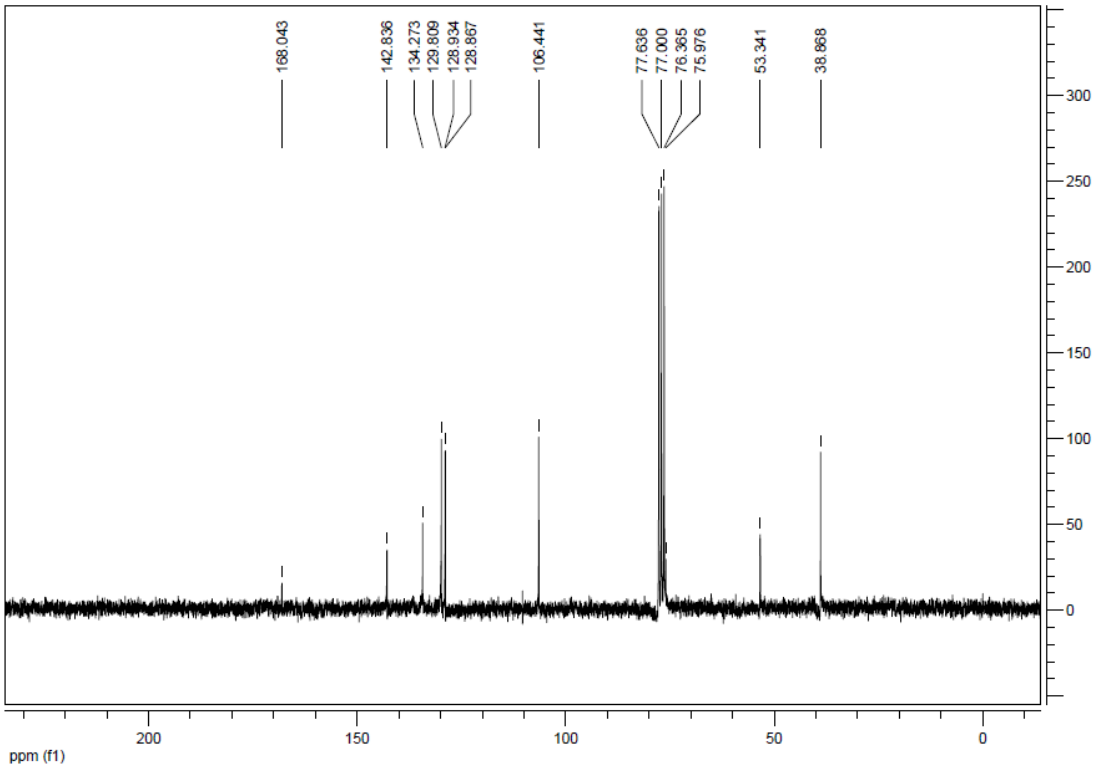

8.311
8.280
8.051
8.022
5.433
4.985
4.148
4.124
3.207
1.086
1.062
1.038
50000
0
2.01
2.02
2.02
2.01
2.13
4.07
3.00
10.0
5.0
0.0
ppm (t1)

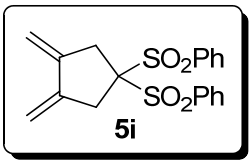

193.730
172.464
150.103
144.036
139.651
129.637
123.733
105.934
77.636
77.000
76.364
62.061
61.410
41.248
13.763
200
150
100
50
0
ppm (t1)


SO2Ph
CO2Me

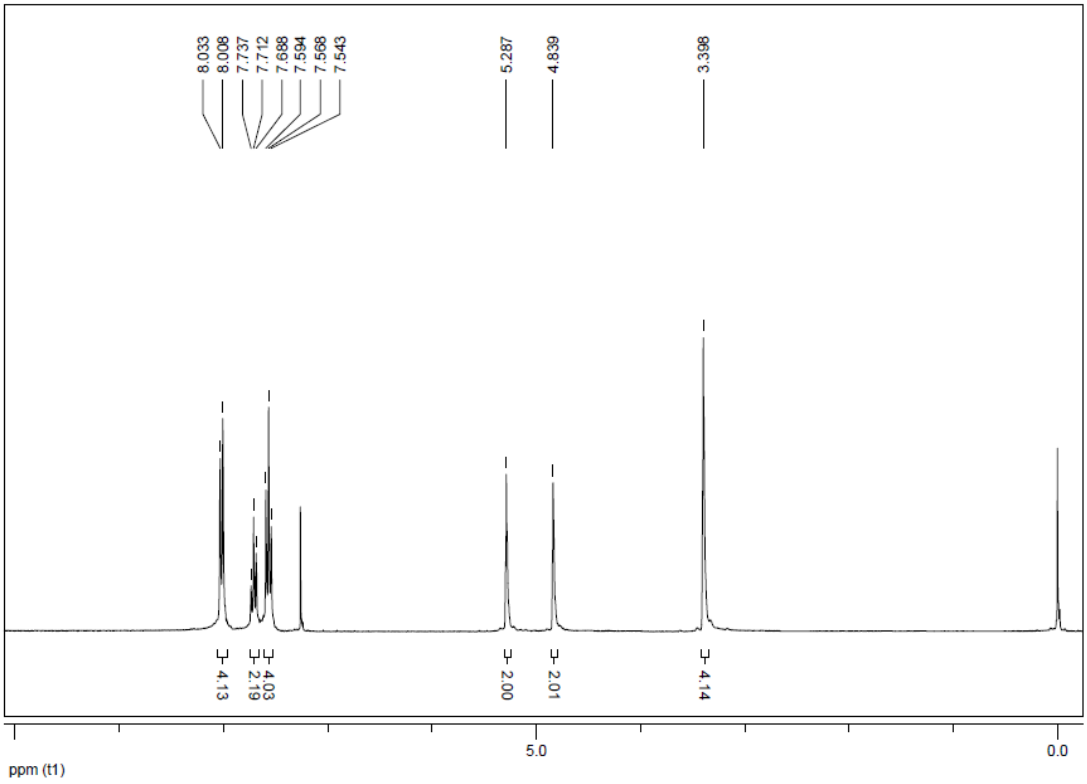
5h

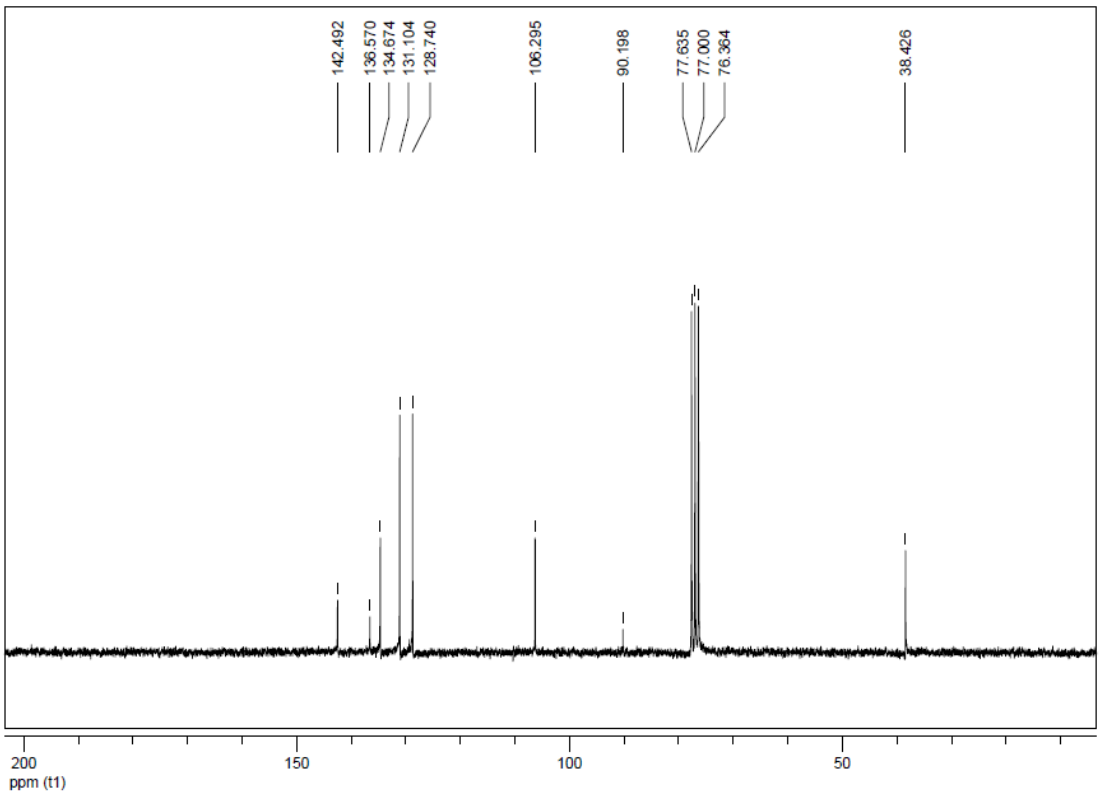

7.852
7.827
7.720
7.696
7.671
7.593
7.567
7.542
5.391
4.960
3.662
3.313
3.258
3.173
3.118
0.000000
15000
10000
5000
0
2.08
1.07
2.13
2.00
2.02
3.06
2.09
2.10
10.0
5.0
0.0
ppm (t1)

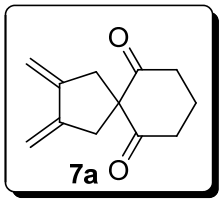

168.043
142.836
134.273
129.809
128.934
128.867
106.441
77.636
77.000
76.365
75.976
53.341
38.868
300
250
200
150
100
50
0
200
150
100
50
0
ppm (f1)

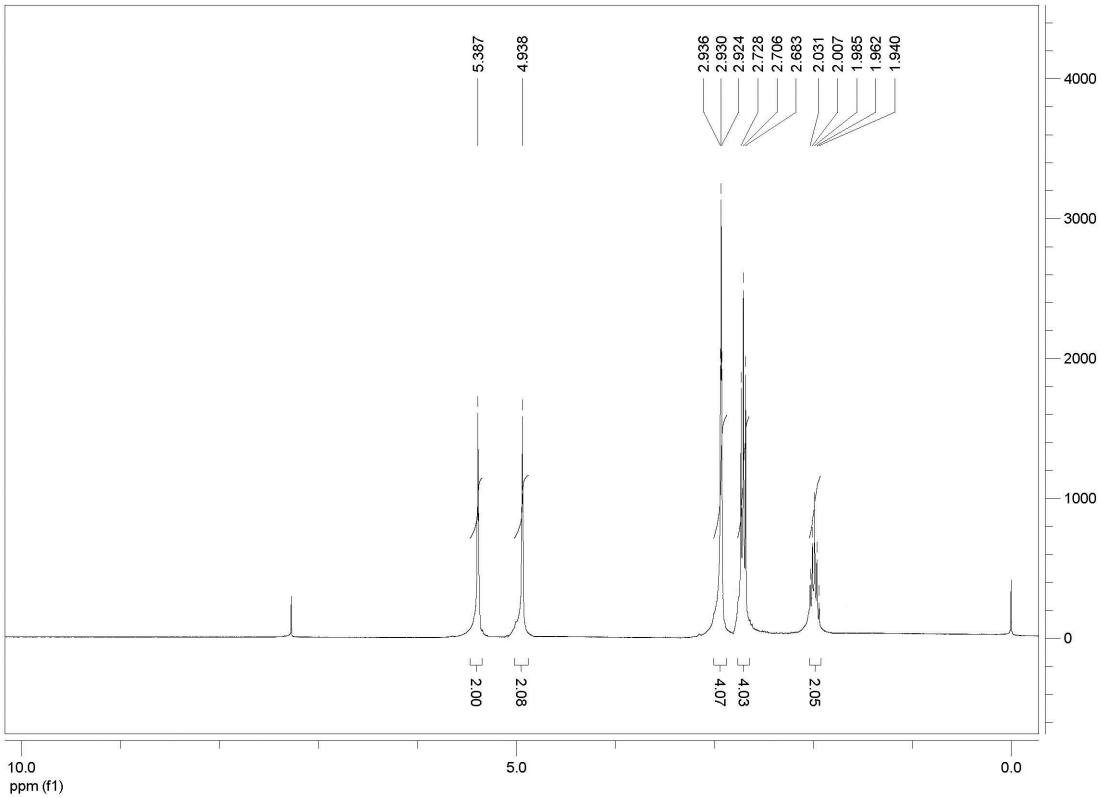

SO2Ph
SO2Ph

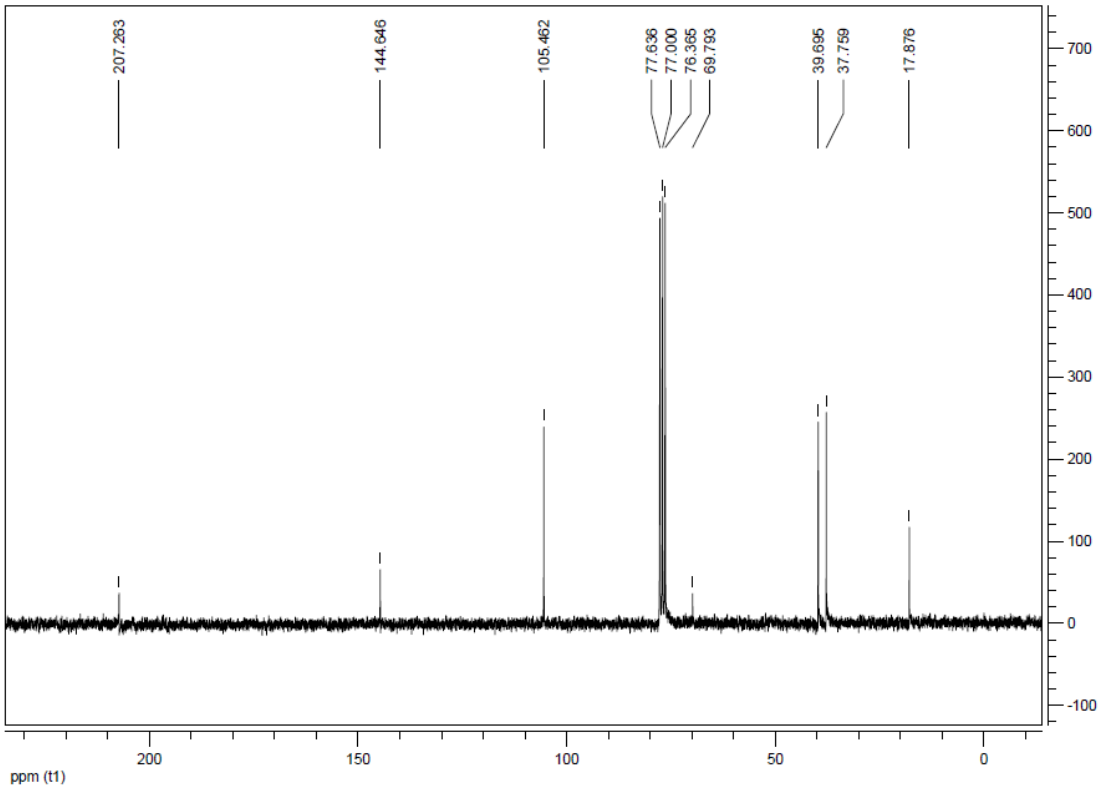
5i

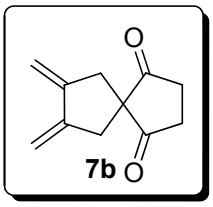

8.033
8.008
7.737
7.712
7.688
7.594
7.568
7.543
5.287
4.839
3.398
4.13
2.19
4.03
2.00
2.01
4.14
5.0
0.0
ppm (t1)

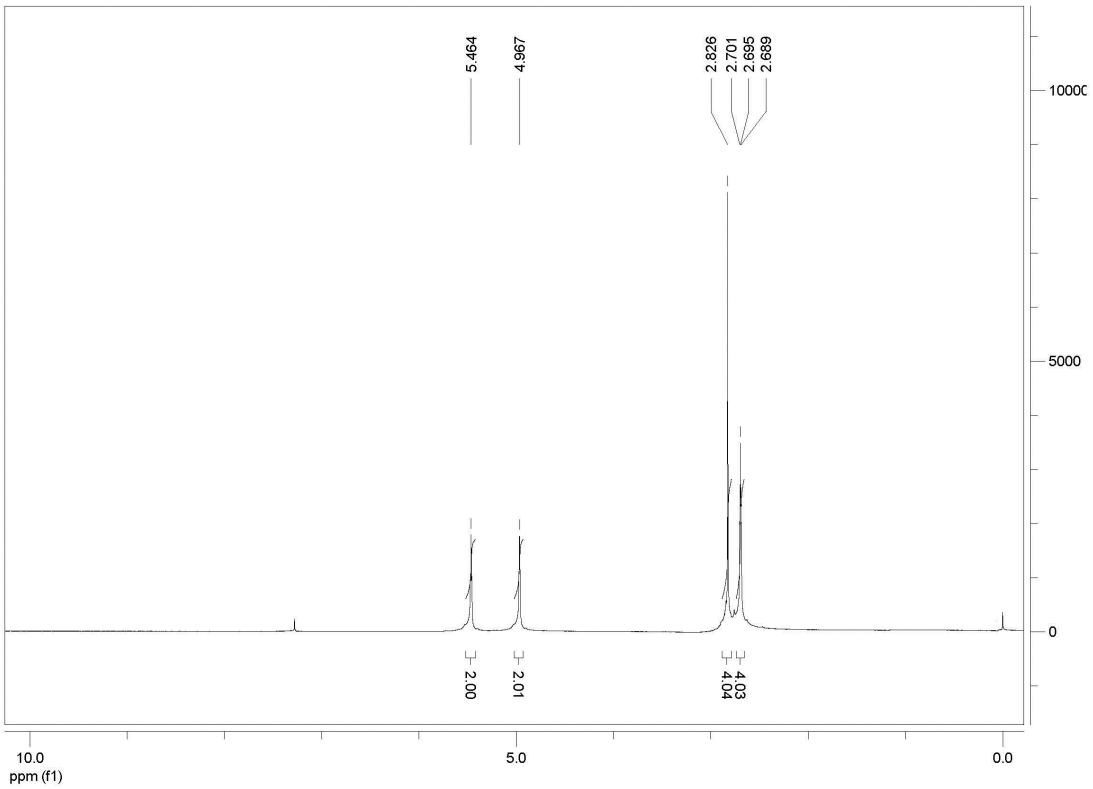

142.492
136.570
134.674
131.104
128.740
106.295
90.198
77.635
77.000
76.364
38.426
200
150
100
50
ppm (t1)

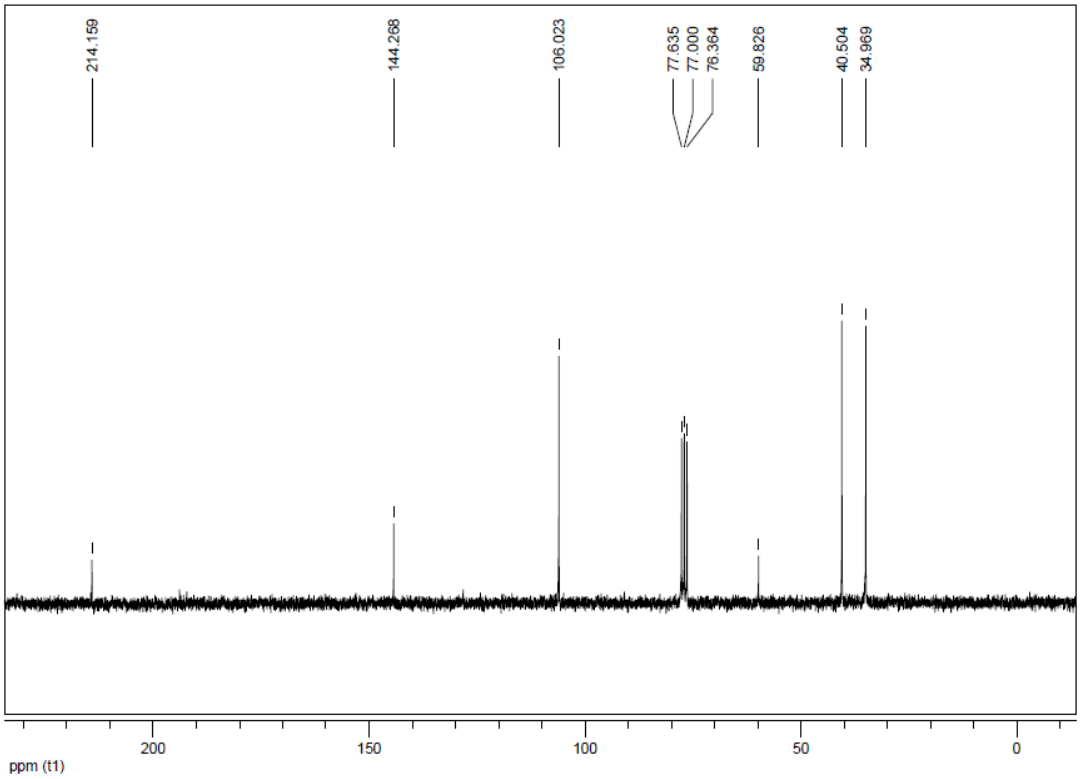

O
7a
O

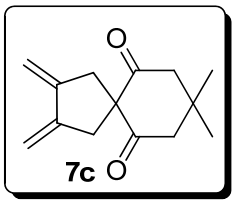

5.387
4.938
2.936
2.930
2.924
2.728
2.706
2.683
2.031
2.007
1.985
1.962
1.940
2.00
2.08
4.07
4.03
2.05
4000
3000
2000
1000
0
10.0
5.0
0.0
ppm (f1)

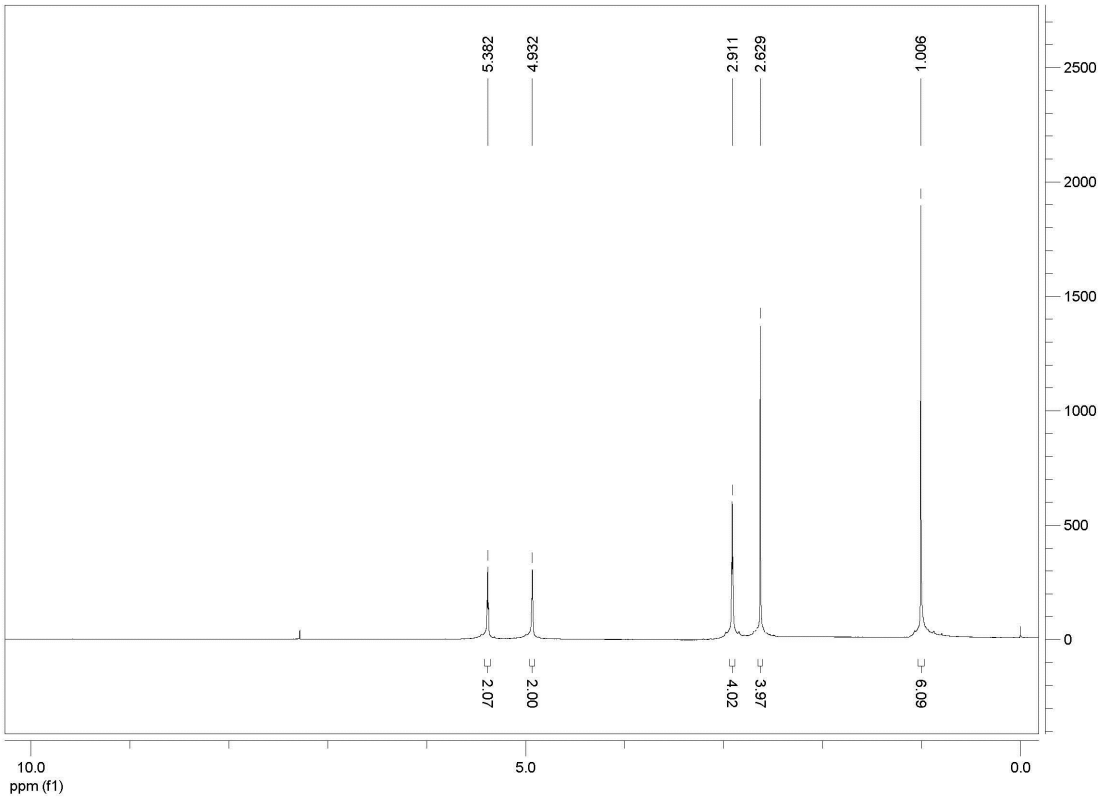

207.263
144.646
105.462
77.636
77.000
76.365
69.793
39.695
37.759
17.876
700
600
500
400
300
200
100
0
-100
200
150
100
50
0
ppm (t1)

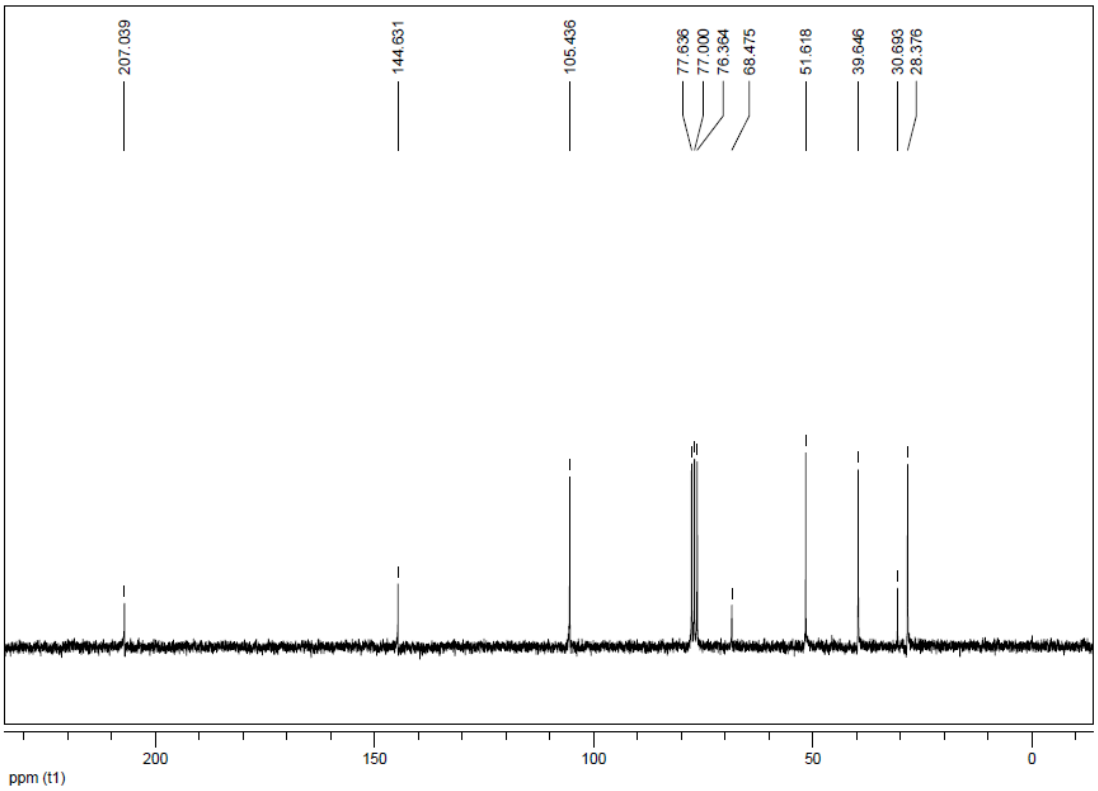

O
7b
O

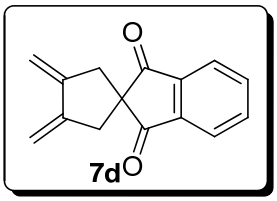

5.464
4.967
2.826
2.701
2.695
2.689
10000
5000
0
2.00
2.01
4.03
4.04
10.0
5.0
0.0
ppm (f1)

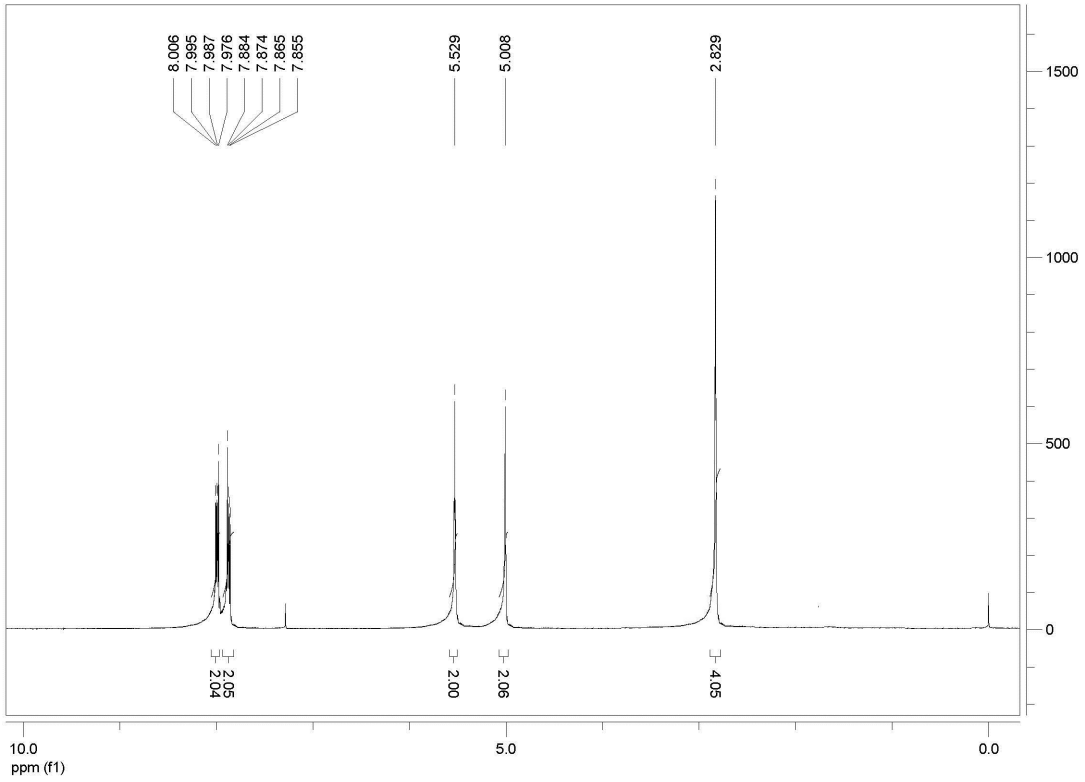

214.159
144.268
106.023
77.635
77.000
76.364
59.826
40.504
34.969
200
150
100
50
0
ppm (t1)

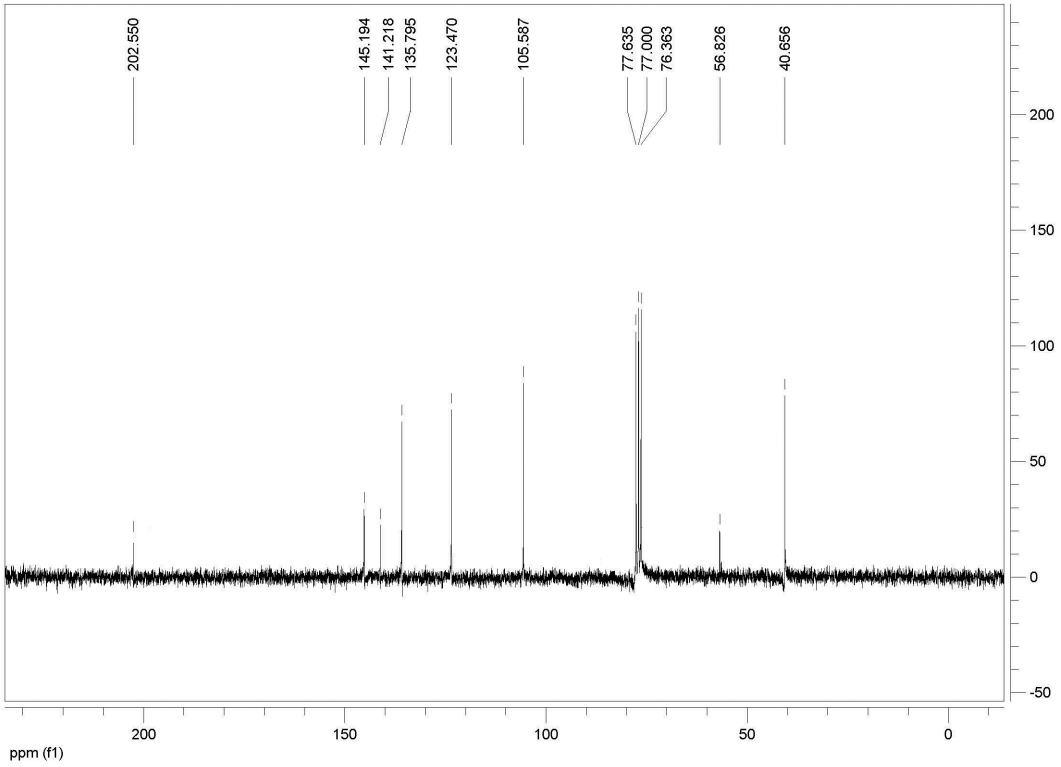

O
7c O

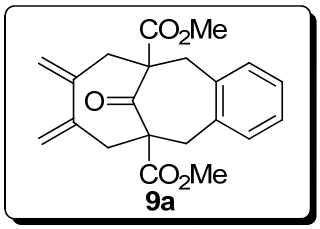

5.382
4.932
2.911
2.629
1.006
2500
2000
1500
1000
500
0
2.07
2.00
4.02
3.97
6.09
10.0
5.0
0.0
ppm (f1)


207.039
144.631
105.436
77.636
77.000
76.364
68.475
51.618
39.646
30.693
28.376
200
150
100
50
0
ppm (t1)

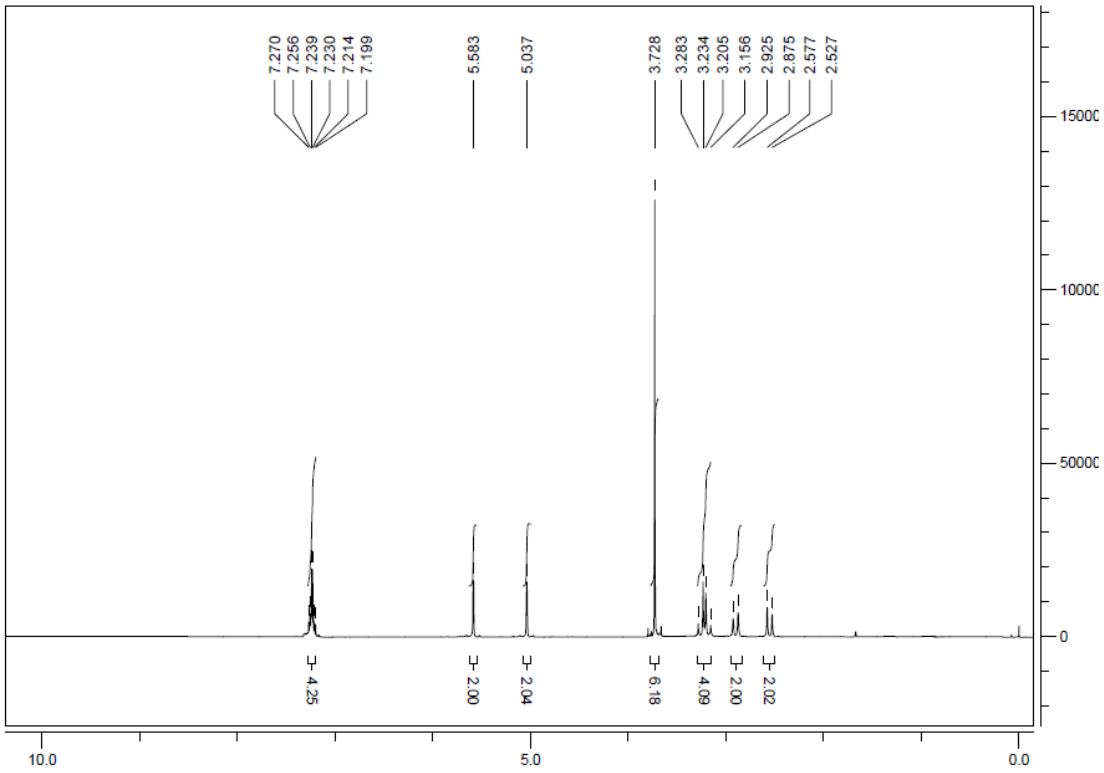

O
O
7d

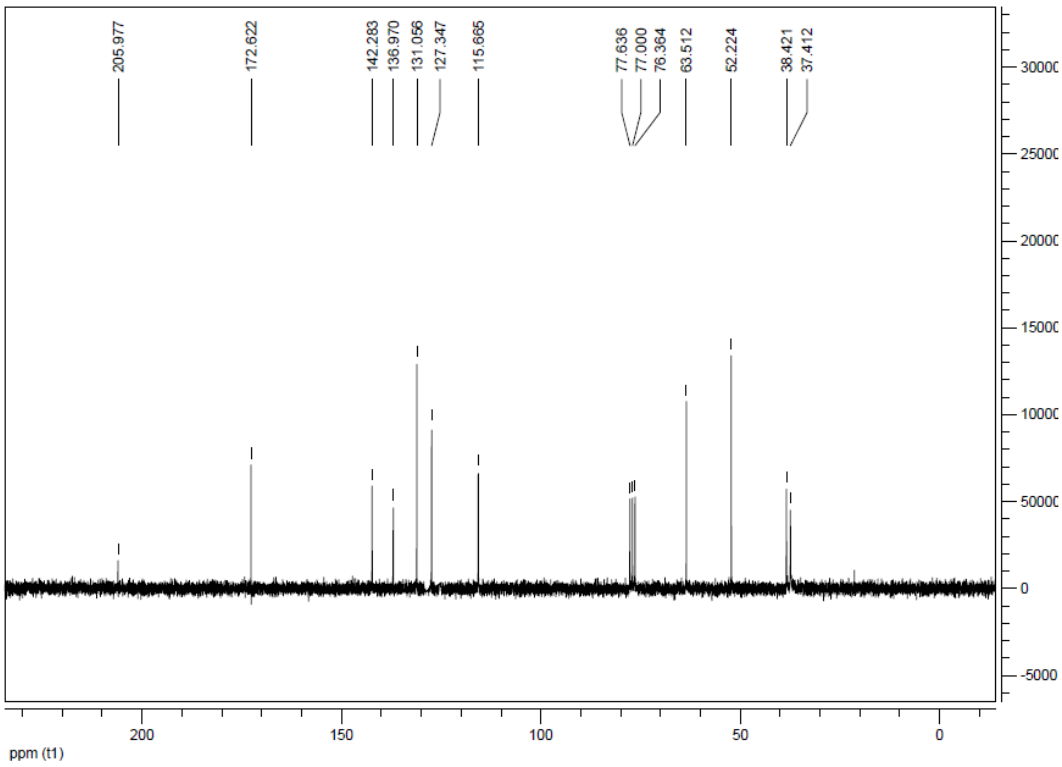

8.006
7.995
7.987
7.976
7.884
7.874
7.865
7.855
5.529
5.008
2.829
1500
1000
500
0
2.04
2.05
2.00
2.06
4.05
10.0
5.0
0.0
ppm (f1)

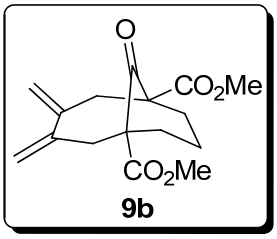

202.550
145.194
141.218
135.795
123.470
105.587
77.635
77.000
76.363
56.826
40.656
200
150
100
50
0
-50
200
150
100
50
0
ppm (f1)


CO2Me
O
CO2Me

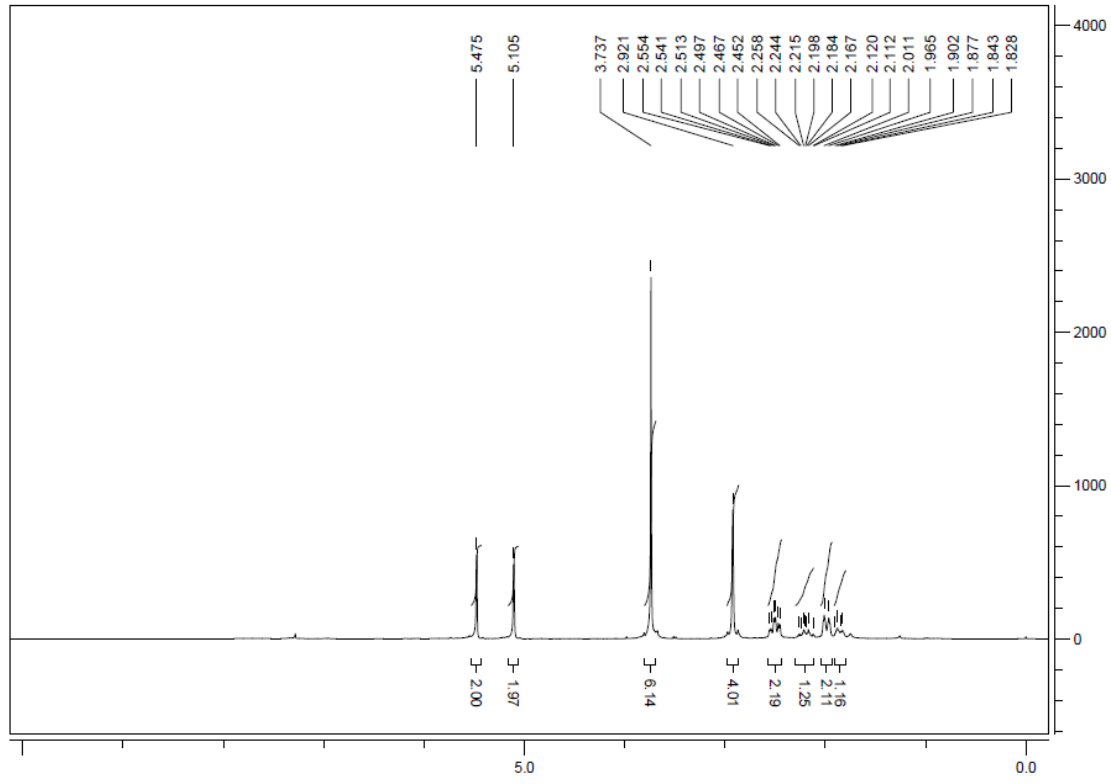
9a

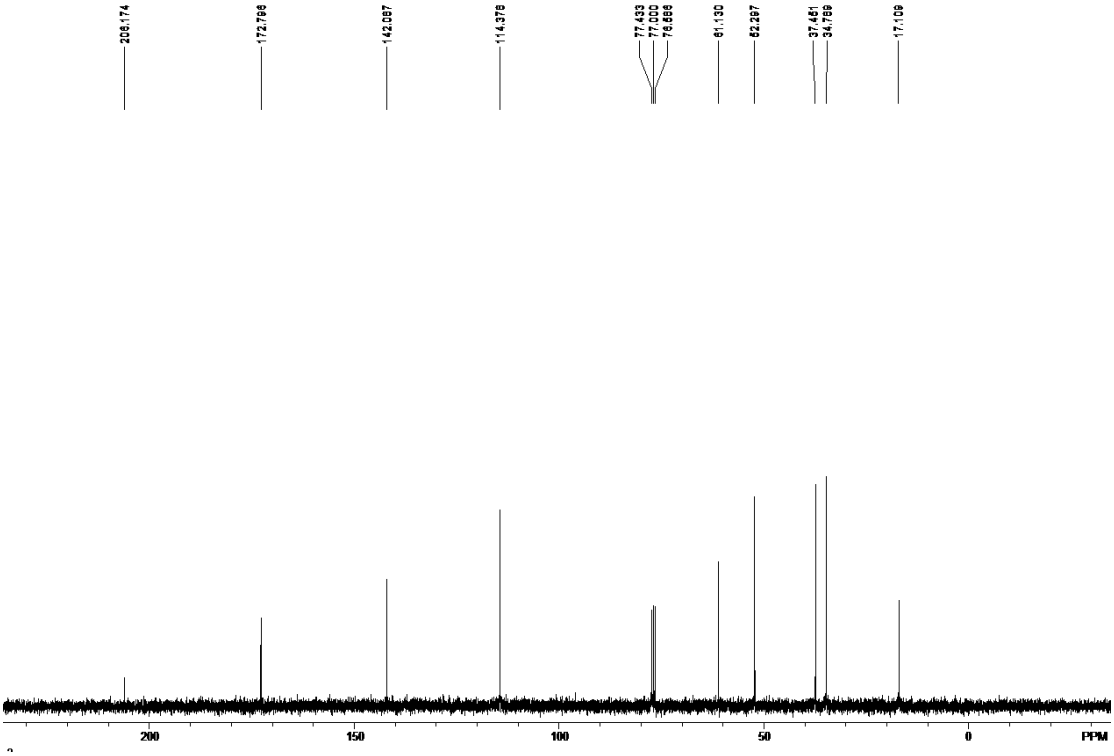

7.270
7.256
7.239
7.230
7.214
7.199
5.583
5.037
3.728
3.283
3.234
3.205
3.156
2.925
2.875
2.577
2.527
4.25
2.00
2.04
6.18
4.09
2.00
2.02
10.0
5.0
0.0

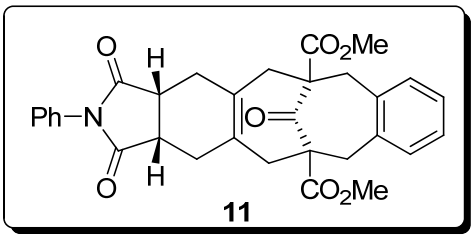

205.977
172.622
142.283
136.970
131.056
127.347
115.665
77.636
77.000
76.364
63.512
52.224
38.421
37.412
200
150
100
50
0
ppm (t1)


O
CO2Me
CO2Me

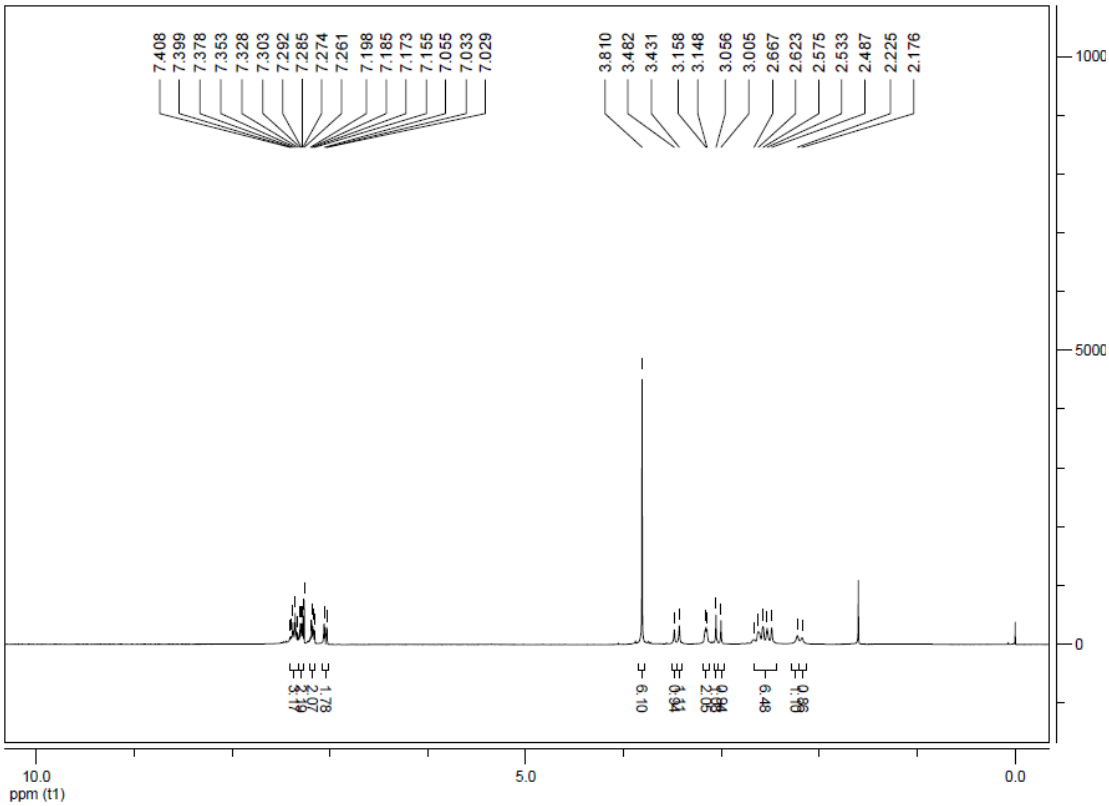
9b

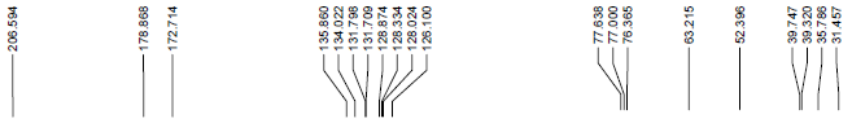

5.475
5.105
3.737
2.921
2.554
2.541
2.513
2.497
2.467
2.452
2.258
2.244
2.215
2.198
2.184
2.167
2.120
2.112
2.011
1.965
1.902
1.877
1.843
1.828
4000
3000
2000
1000
0
2.00
1.97
6.14
4.01
2.19
1.25
2.11
1.16
5.0
0.0


208.174
172.796
142.087
114.376
77.433
77.000
76.566
61.130
52.287
37.461
34.769
17.109
200
150
100
50
0
PPM


O
H
CO2Me
Ph–N
O
O
H
CO2Me

11


7.408
7.399
7.378
7.353
7.328
7.303
7.292
7.285
7.274
7.261
7.198
7.185
7.173
7.155
7.055
7.033
7.029
3.810
3.482
3.431
3.158
3.148
3.056
3.005
2.667
2.623
2.575
2.533
2.487
2.225
2.176
1000
5000
0
3.19
2.07
1.78
6.10
0.94
2.00
6.48
1.96
10.0
ppm (t1)
5.0
0.0


206.594
178.868
172.714
135.860
134.022
131.798
131.709
128.874
128.334
128.024
126.100
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77.000
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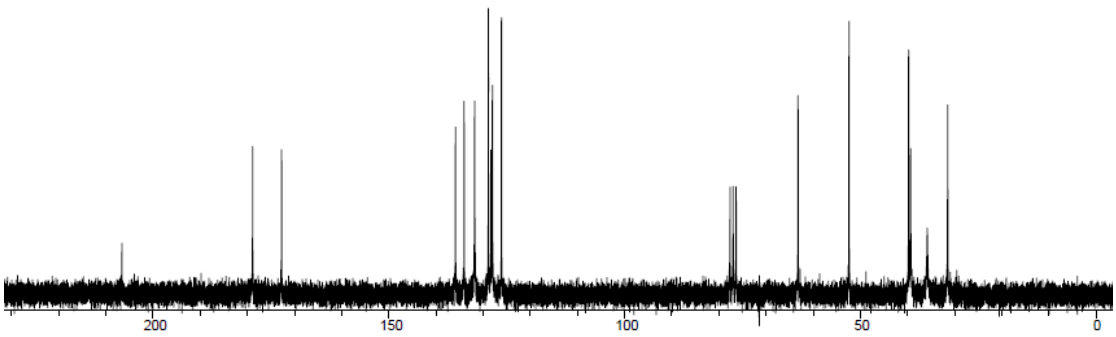
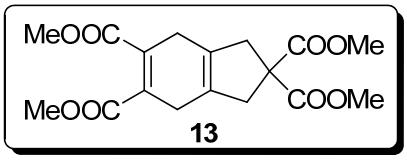
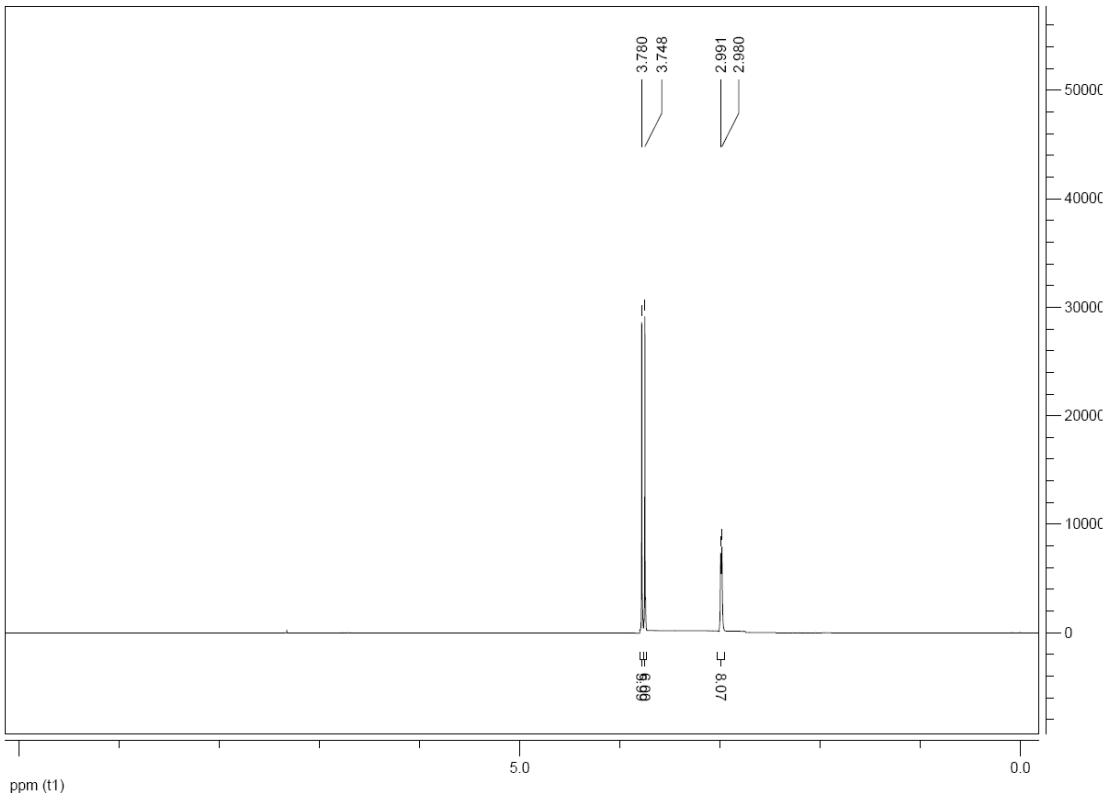
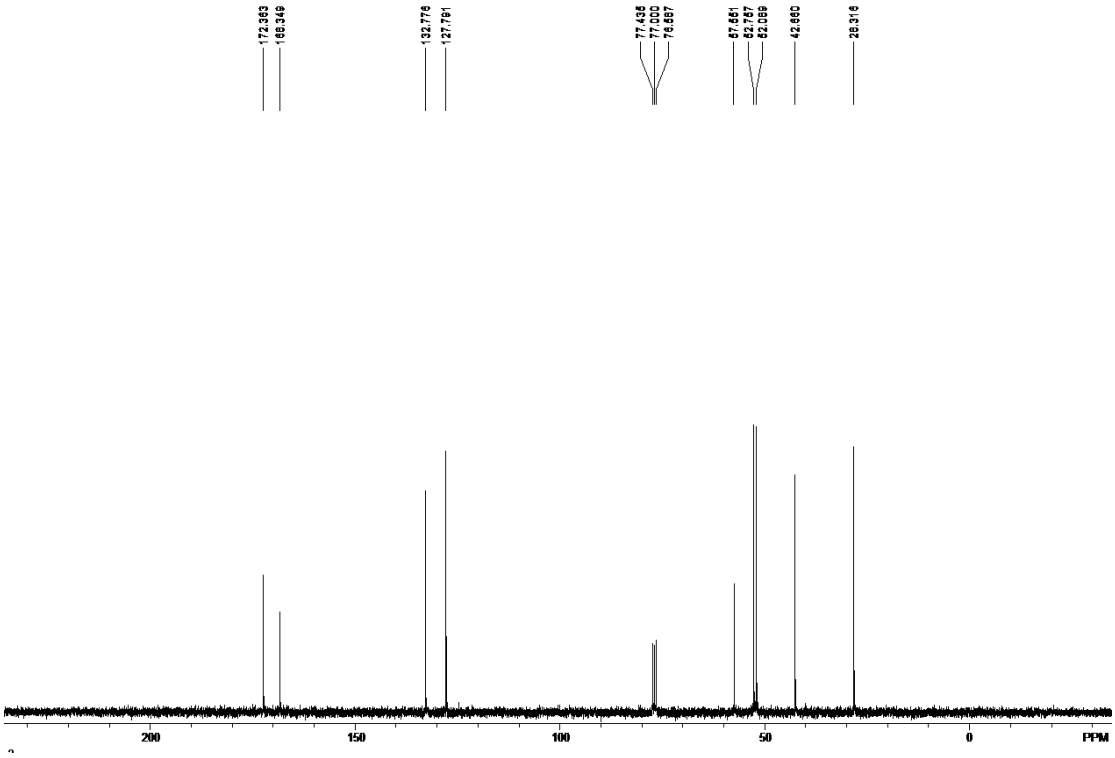
63.215
52.396
39.747
39.320
35.786
31.457

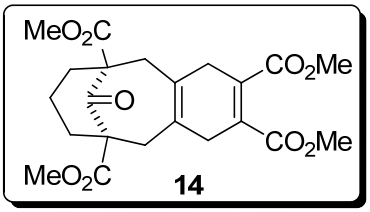

200
150
100
50
0


MeOOC
COOMe
MeOOC
COOMe

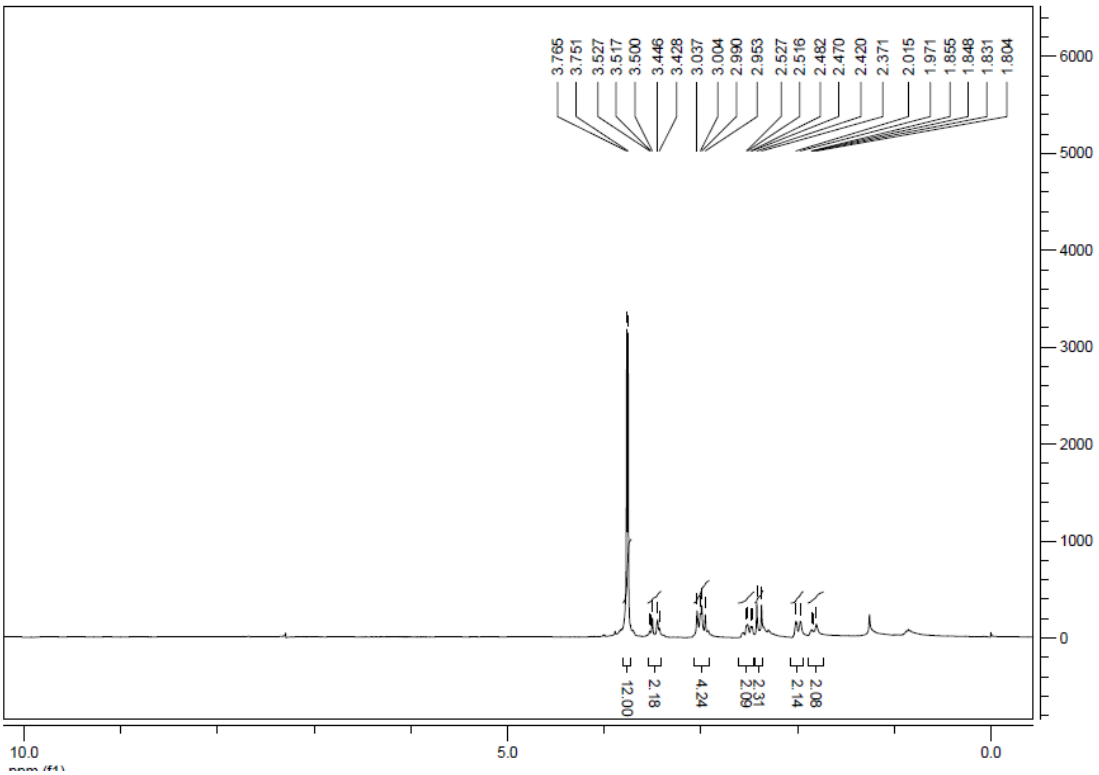
13

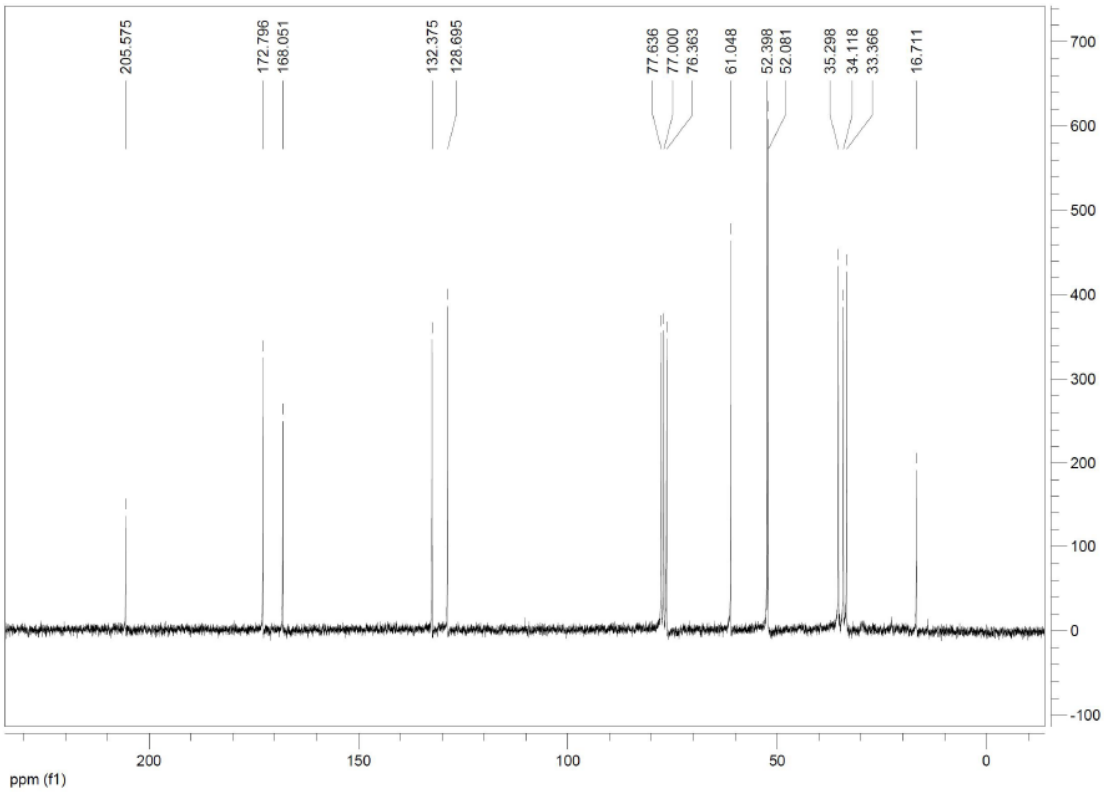

3.780
3.748
2.991
2.980
5000
4000
3000
2000
1000
0
6.99
8.07
5.0
0.0
ppm (t1)

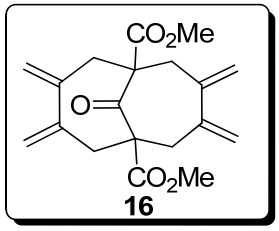

172.353
168.349
132.776
127.791
77.435
77.000
76.687
67.881
62.787
62.089
42.860
28.316
200
150
100
50
0
PPM


MeO2C
CO2Me
O
CO2Me
MeO2C

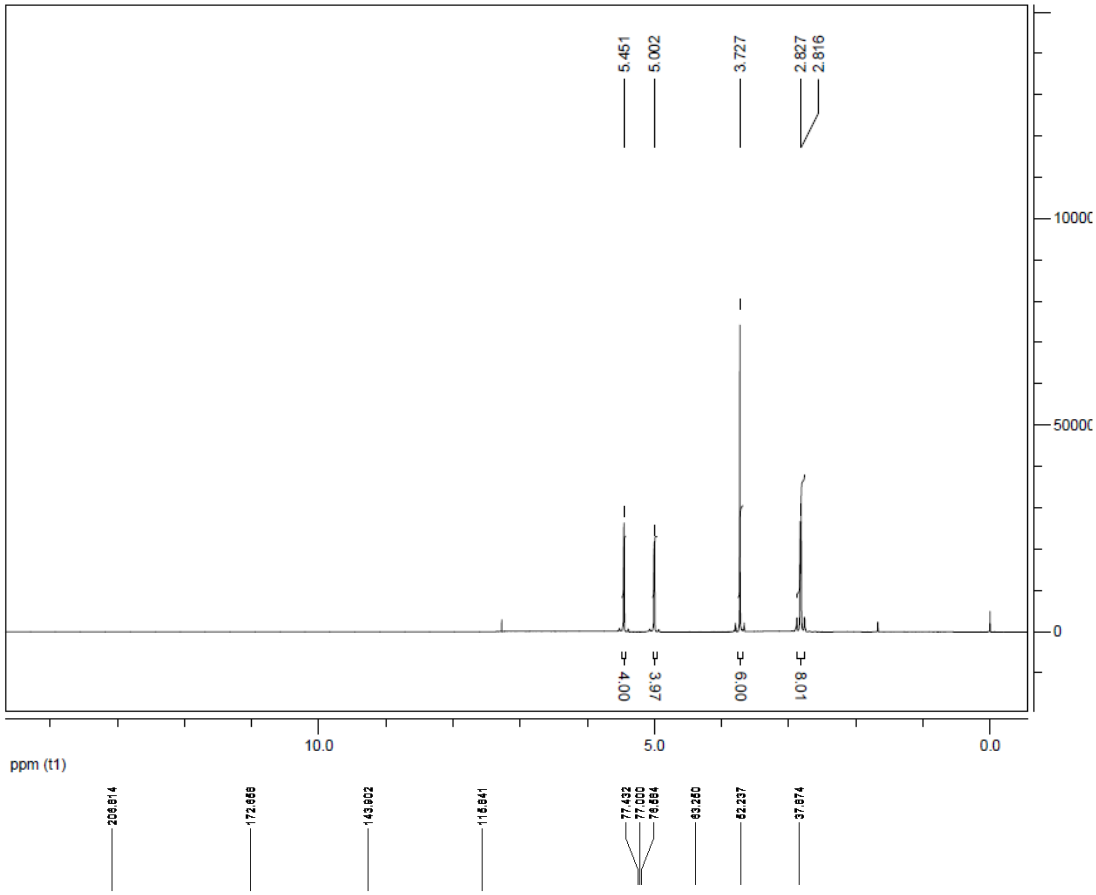
14

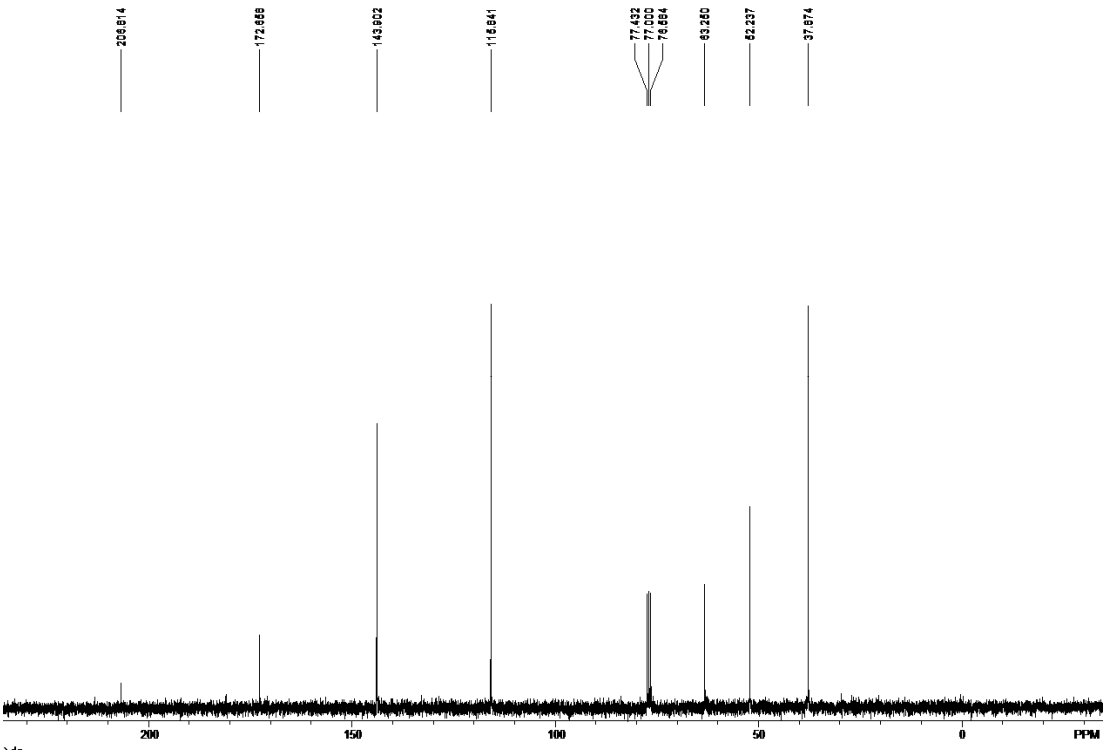

3.765
3.751
3.527
3.517
3.500
3.446
3.428
3.037
3.004
2.990
2.953
2.527
2.516
2.482
2.470
2.420
2.371
2.015
1.971
1.855
1.848
1.831
1.804
2.00
2.18
4.24
2.31
2.09
2.14
2.08
10.0
5.0
0.0

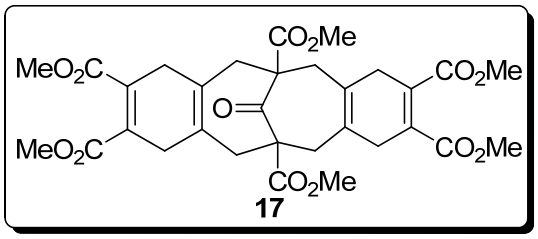

205.575
172.796
168.051
132.375
128.695
77.636
77.000
76.363
61.048
52.398
52.081
35.298
34.118
33.366
16.711
200
150
100
50
0
ppm (f1)


CO2Me
O
CO2Me

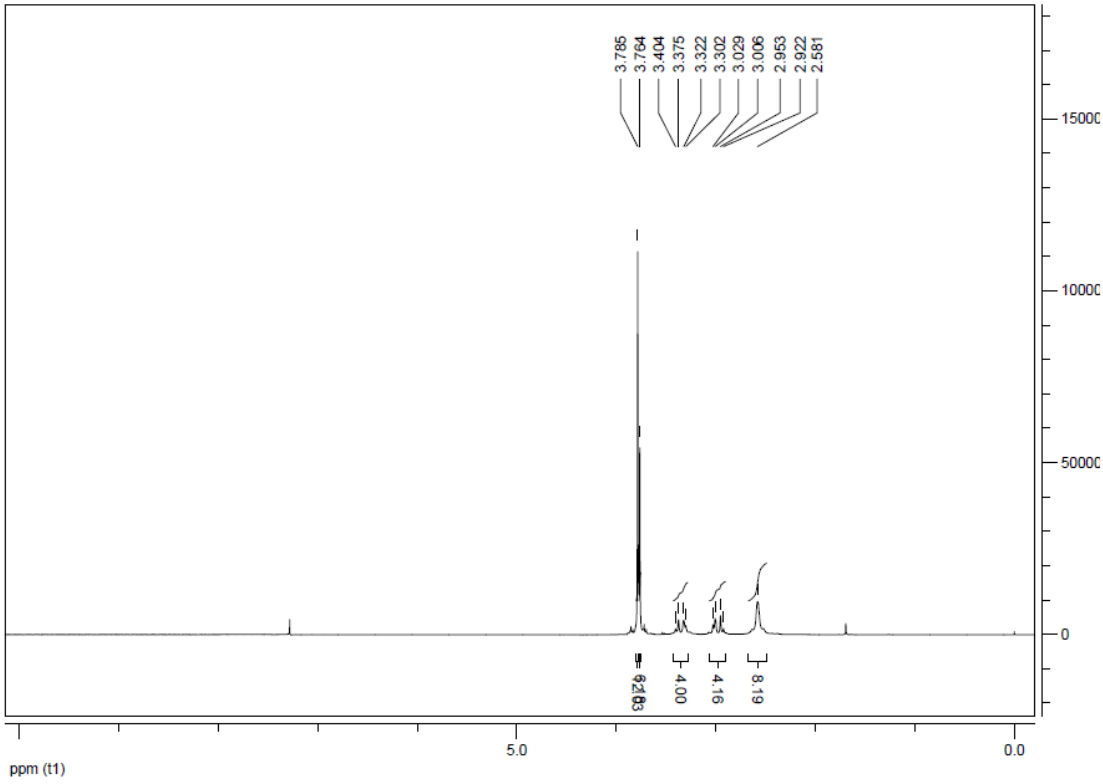
16

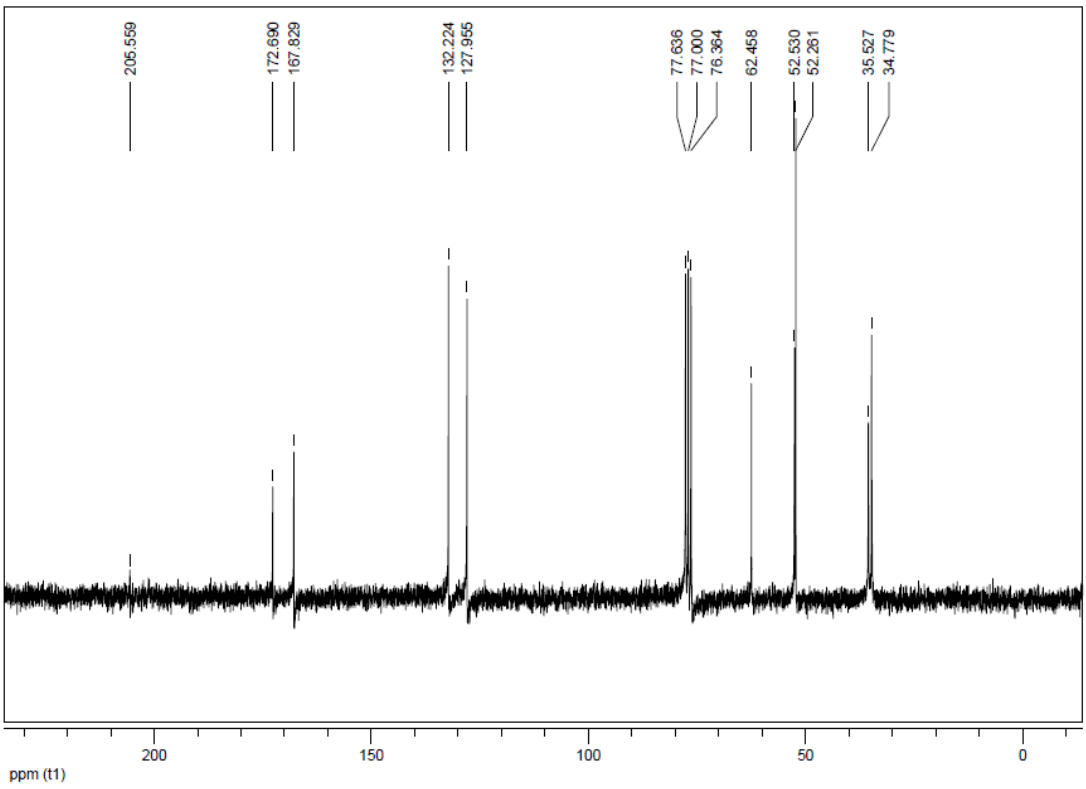

5.451
5.002
3.727
2.827
2.816
4.00
3.97
6.00
8.01
10000
50000
0
10.0
5.0
0.0
ppm (t1)

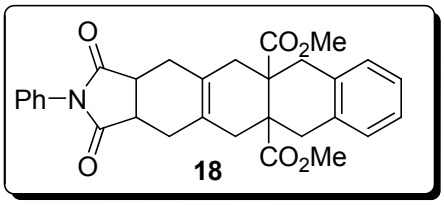

206.814
172.868
143.902
118.841
77.432
77.000
76.564
63.260
62.237
37.874
200
150
100
50
0
PPM


CO2Me
MeO2C
CO2Me
O
MeO2C
CO2Me
CO2Me

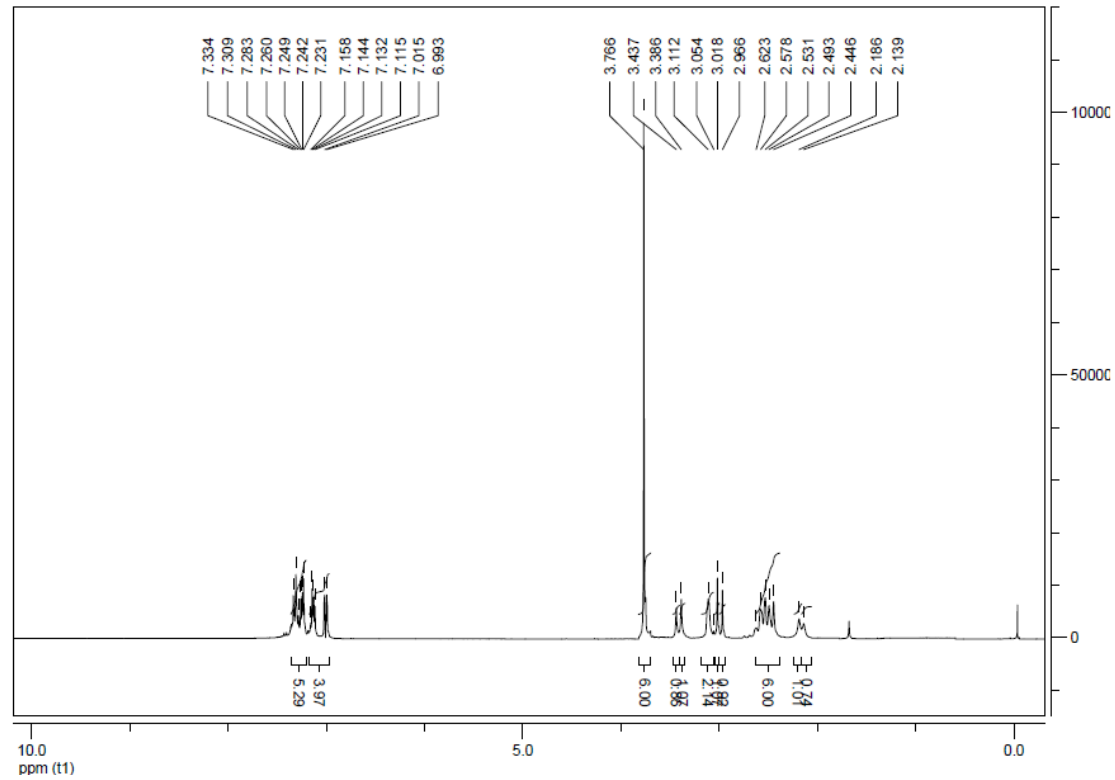
17

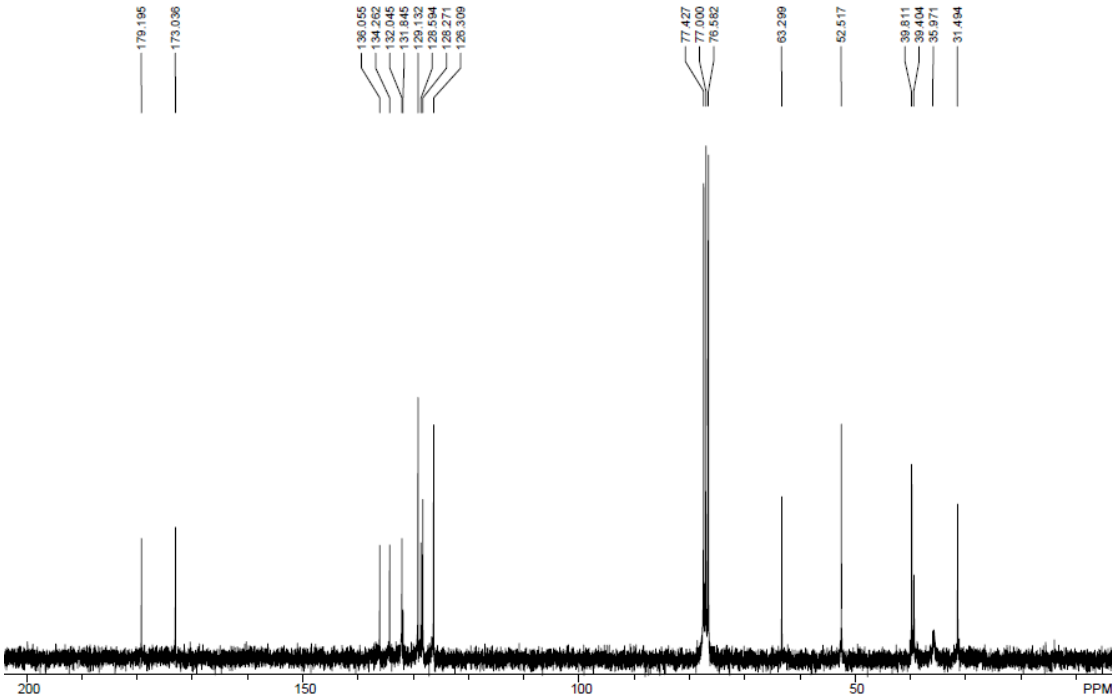

3.785
3.764
3.404
3.375
3.322
3.302
3.029
3.006
2.953
2.922
2.581
15000
10000
50000
0
6.00
4.00
4.16
8.19
5.0
0.0
ppm (t1)


205.559
172.690
167.829
132.224
127.955
77.636
77.000
76.364
62.458
52.530
52.261
35.527
34.779
200
150
100
50
0
ppm (t1)


O
CO2Me
Ph–N
O
CO2Me

18


7.334
7.309
7.283
7.260
7.249
7.242
7.231
7.158
7.144
7.132
7.115
7.015
6.993
3.766
3.437
3.386
3.112
3.054
3.018
2.966
2.623
2.578
2.531
2.493
2.446
2.186
2.139
10000
50000
0
5.29
3.97
6.00
6.00
10.0
ppm (t1)
5.0
0.0


179.195
173.036
136.055
134.262
132.045
131.845
129.132
128.594
128.271
126.309
77.427
77.000
76.582
63.299
52.517
39.811
39.404
35.971
31.494
200
150
100
50
PPM