Rhodium(I)-catalyzed Pauson-Khand-type reaction using formic acid as a CO surrogate: an alternative approach for indirect CO_2 utilization

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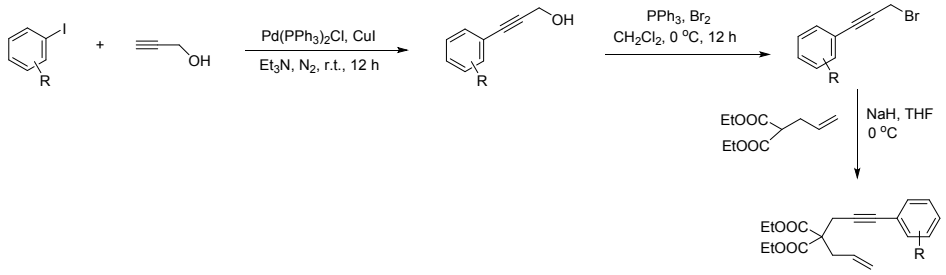
1. Materials and methods

Commercial reagents including aryl iodides, propargyl alcohol, rhodium precursors and phosphine ligands were used without further purification. All of the solvents were dried following the standard procedure or super-dry solvents were commercially available. All reactions were carried out under nitrogen atmosphere. ^{1}H NMR spectra were recorded on Bruker 400 MHz spectrometer using $CDCl_3$ as solvent referenced to $CHCl_3$ (7.26 ppm). ^{13}C NMR spectra were recorded at 100.6 MHz in $CDCl_3$ using $CDCl_3$ (77.0 ppm) as an internal reference. GC analysis were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-50, 30 m × 0.25 μm) using a flame ionization detector. High resolution mass spectrometry was conducted using a Varian 7.0 T FTICR-MS by ESI technique. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets.

2. Representative procedure for the preparation of substituted 1,6-enynes

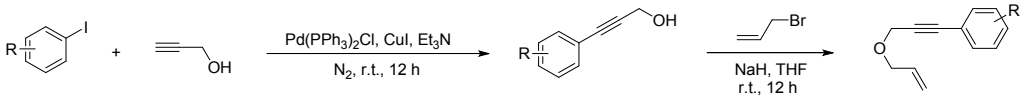


According to the general procedure,[1-3] $Pd(PPh_3)_2Cl_2$ (280.8 mg, 0.4 mmol, 1 mol%) and CuI (152.4 mg, 0.8 mmol, 2 mol%) were suspended in Et_3N (160 mL) under nitrogen atmosphere. Subsequently, iodobenzene (8.16 g, 4.55 mL, 40 mmol) was added, followed by propargyl alcohol (2.47 g, 2.63 mL, 44 mmol, 1.1 equiv), and the reaction was stirred at room temperature for 12 hours. Subsequent workup and column chromatography (hexanes : EtOAc = 7 : 3) yielded the 3-phenylprop-2-yn-1-ol as an orange oil in quantitative yield. Rf = 0.37 (hexanes : EtOAc 7 : 3).

To a solution of Ph_3P (855 mg, 3.26 mmol, 1.10 equiv) in CH_2Cl_2 (10 mL) at 0 °C under air was added Br_2 (514 mg, 3.22 mmol, 1.09 equiv) dropwise. The solution was stirred at 0 °C for 30 min, turning into a yellow mixture. A solution of 3-phenylprop-2-yn-1-ol (393 mg, 2.97 mmol, 1.00 equiv) in CH_2Cl_2 (5 mL) was added dropwise. The yellow solution was maintained at 0 °C

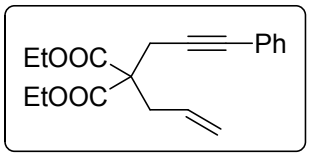
for 1 h, and then n-pentane (20 mL) was added. The reaction mixture was further stirred at r.t. for 30 min. Then the reaction mixture was purified by flash column chromatography on silica gel using *n*-pentane : ethyl acetate = 30 : 1 as eluent to afford analytically pure propargyl bromides as a yellow oil.

Sodium hydride was suspended in dry THF (0.18 g, 7.6 mmol, 1.2 equiv) and the suspension was cooled to 0 °C, then diethyl allyl malonate (1.26 g, 1.2 mL, 6.3 mmol, 1.0 equiv) was added dropwise at 0 °C. The solution was allowed to reach room temperature and stirred for 1.5 h. Then the solution was cooled to 0 °C and the propargyl bromide (1.482 g, 7.6 mmol, 1.2 equiv) was added dropwise at 0 °C. The solution was then allowed to reach room temperature and stirred overnight. After the reaction reached to completion, saturated brine (15 mL) was added and the solution was extracted with ether (3 × 20 mL). The extracts were dried over $MgSO_4$, filtered and concentrated to provide the crude material which was then purified by column chromatography on silica gel (5% EtOAc/hexanes) to afford the diester-linked 1,6-enyne as an light yellow oil.

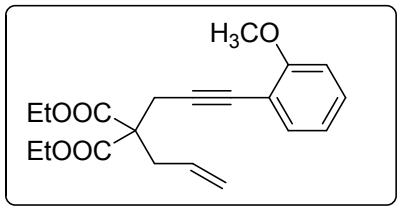


To a solution of 3-phenyl-2-propyn-1-ol (5.28 g, 40 mmol) in freshly distilled THF (80 mL) was added NaH (1.44 g, 60 mmol, pre-washed with dry hexane) portionwise at 0 ºC. The white suspension was slowly warmed to room temperature and stirred for 2 hours. The reaction mixture was then cooled to 0 °C and allyl bromide (6.8 mL, 80 mmol) was added dropwise. After complete addition, the reaction was warmed to room temperature and further stirred for 2 hours. Water (~30 mL) was slowly added and the aqueous layer was extracted with diethyl ether (3 ×100 mL). The combined organic layers were washed with water (~50 mL), brine (~50 mL) and dried over sodium sulfate. Solvent was removed by rotary evaporation and the light yellow crude product was purified by flash column chromatography on silica gel to give title compound as a colorless liquid.[4-5]

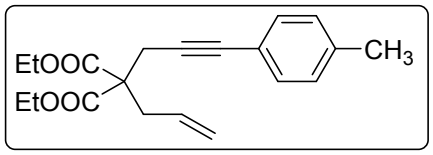
3. Characterization and NMR spectral copies of the substrates



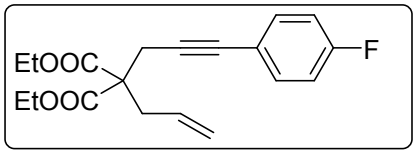
diethyl 2-allyl-2-(3-phenylprop-2-yn-1-yl)malonate **1a**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, 6H), 2.78 - 2.93 (m, 4H), 4.11 - 4.16 (t, 4H), 5.05 - 5.15 (m, 2H), 5.58 - 5.64 (m, 1H), 7.19-7.28 (m, 4H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 169.90, 132.01, 131.67, 128.26, 128.00, 123.32, 119.79, 84.46, 83.57, 61.66, 57.08, 36.70, 23.57, 14.17 ppm; IR (KBr) *v*/cm^{-1} 3079, 2981, 1734, 1490, 1442, 1289, 1241. 924, 757, 692; ESI-MS calcd for $[C_{19}H_{23}O_4]^+$ 318.4, found 318.4 $(M+H)^+$.



diethyl 2-allyl-2-(3-(2-methoxyphenyl)prop-2-yn-1-yl)malonate **1b**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 - 7.19 (m, 1H), 7.11 (m, 1H), 6.83 - 6.88 (m, 2H), 5.74 (m, 1H), 5.27 (m, 1H), 5.13 (m, 1H), 6.41 (t, *J* = 8.4 Hz, 1H), 6.28 (m, 1H), 4.64 (d, *J* = 10.9 Hz, 1H), 4.14 (d, *J* = 7.9 Hz, 4H), 3.85 (s, 3H), 3.07 (s, 2H), 2.90 - 2.92 (d, 2H), 1.26 (t, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02, 160.18, 133.71, 132.20, 129.39, 120.40, 119.78, 112.61,110.66, 88.62, 79.87, 61.67, 57.22, 55.75, 36.65, 23.93, 14.19.

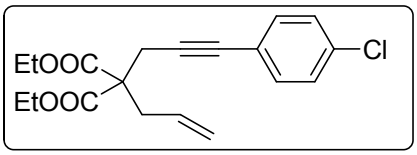


diethyl 2-allyl-2-(3-(p-tolyl)prop-2-yn-1-yl)malonate **1c**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 - 7.21 (m, 2H), 7.07 (d, *J* = 7.9 Hz, 2H), 5.69 (ddt, *J* = 17.4, 10.0, 7.5 Hz, 1H), 5.25 - 5.10 (m, 1H), 4.28 - 4.14 (m, 1H), 3.00 (s, 1H), 2.86 (d, *J* = 7.5 Hz, 1H), 2.32 (s, 1H), 1.26 (t, *J* = 7.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02, 138.07, 137.34, 132.15, 131.62, 131.30, 129.05, 120.36, 119.76, 83.72, 83.69, 61.69, 57.23, 36.78, 23.69, 21.51, 14.23.

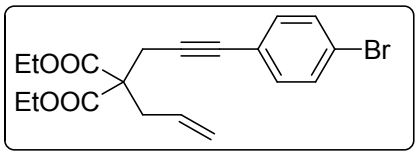


diethyl 2-allyl-2-(3-(4-fluorophenyl)prop-2-yn-1-yl)malonate **1d**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (dt, J = 1.9, 3.5 Hz, 2H), δ 6.96 (t, J = 8.6 Hz, 2H), 5.74 - 5.63 (m, 1H), 5.20 (d, J =

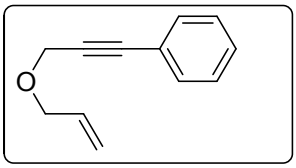
16.8 Hz, 1H), 5.15 (d, J = 9.8 Hz, 1H), 4.22 (q, J = 7.0 Hz, 4H), 2.99 (s, 2H,), 2.85 (d, J = 7.4 Hz, 2H), 1.26 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.7, 163.6 (d, J = 247.8 Hz), 133.5 (d, J = 8.8 Hz), 131.9, 119.8, 119.4 (d, J = 3.3 Hz), 115.6 (d, J = 22.0 Hz), 84.2, 82.5, 61.7, 57.0, 36.7, 23.5, 14.1.



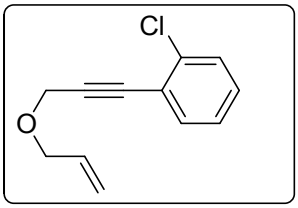
diethyl 2-allyl-2-(3-(4-chlorophenyl)prop-2-yn-1-yl)malonate **1e**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 7.4 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 5.54 - 5.61 (m, 1H), 5.14 - 5.18 (m, 2H), 4.21 (m, 4H), 2.97 (s, 2H), 2.76 (d, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.72, 133.92, 132.15, 131.62, 128.55, 121.82, 119.76, 85.62, 82.49, 61.69, 57.15, 36.78, 23.69, 14.13.



diethyl 2-allyl-2-(3-(4-bromophenyl)prop-2-yn-1-yl)malonate **1f**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.67 (m, 1H), 5.09 (m, 2H), 4.14 (q, *J* = 7.2 Hz, 4H), 2.92 (s, 2H), 2.77 (d, *J* = 7.2 Hz, 2H), 1.18 (t, J = 7.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.02, 132.15, 131.62, 122.44, 122.32, 120.36, 85.72, 82.49, 61.79, 57.13, 36.78, 23.69, 14.33.

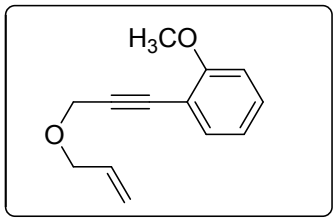


3-(allyloxy)-1-phenyl-1-propyne **1g**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 5.3, 2.3 Hz, 2H), 7.41 - 7.29 (m, 3H), 5.99 (m, *J* = 10.4, 5.8, 2.9 Hz, 1H), 5.38 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.27 (d, *J* = 10.4 Hz, 1H), 4.41 (d, *J* = 1.0 Hz, 2H), 4.17 (dd, *J* = 5.7, 1.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.17, 131.87, 128.54, 128.39, 122.75, 118.03, 86.36, 85.14, 70.81, 58.03.

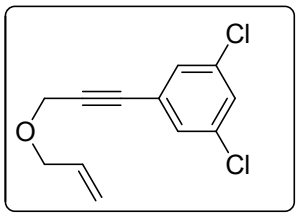


3-(allyloxy)-1-(2-clorophenyl)-1-propyne **1h**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.44 - 7.39 (m, 1H), 7.31 - 7.20 (m, 2H), 6.08 - 5.88 (m, 1H), 5.39 (dd, *J* =

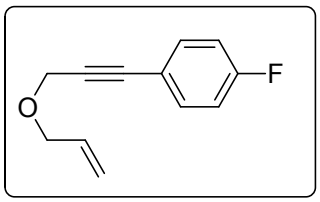
17.2, 1.4 Hz, 1H), 5.28 (d, *J* = 10.3 Hz, 1H), 4.47 (s, 2H), 4.21 (d, *J* = 5.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.11, 134.11, 133.61, 129.59, 129.37, 126.55, 122.72, 118.24, 90.54, 83.19, 70.75, 57.91.



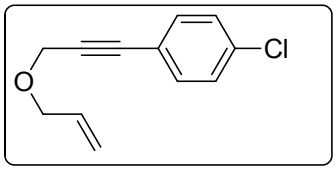
3-(allyloxy)-1-(2-methoxyphenyl)-1-propyne **1i**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.11 (dd, *J* = 12.4, 5.1 Hz, 2H), 6.70 (dd, *J* = 15.8, 8.0 Hz, 1H), 5.76 (m, *J* = 26.3, 10.7 Hz, 1H), 5.17 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.05 (d, *J* = 10.3 Hz, 1H), 4.25 (s, 2H), 3.98 (d, *J* = 5.8 Hz, 2H), 3.68 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.11, 134.18, 133.76, 129.92, 120.41, 117.89, 111.80, 110.61, 89.12, 82.69, 70.56, 58.12, 55.75.



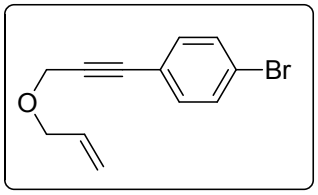
1-(3-(allyloxy)prop-1-yn-1-yl)-3,5-dichlorobenzene **1j**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 3H), 6.05 - 5.83 (m, 1H), 5.35 (dd, *J* = 17.2, 1.4 Hz, 1H), 5.25 (d, *J* = 10.4 Hz, 1H), 4.36 (s, 2H), 4.11 (dd, *J* = 5.7, 1.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.97, 133.92, 130.05, 128.94, 125.54, 118.27, 87.81, 83.70, 71.01, 57.76.



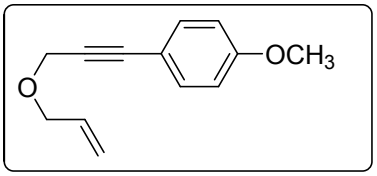
3-(allyloxy)-1-(4-fluorophenyl)-1-propyne **1k**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.24 (t, *J* = 8.6 Hz, 2H), 6.18 (m, *J* = 22.9, 11.0, 5.8 Hz, 1H), 5.58 (d, *J* = 17.2 Hz, 1H), 5.48 (d, *J* = 10.5 Hz, 1H), 4.61 (s, 2H), 4.37 (d, *J* = 5.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.98, 163.83, 161.35, 133.94, 133.73, 133.65, 118.05, 115.83, 115.69, 115.47, 85.24, 84.70, 70.77, 57.84.



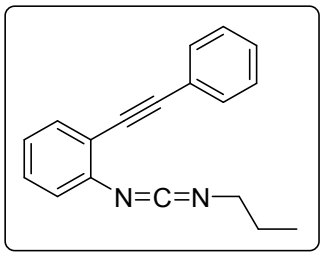
3-(allyloxy)-1-(4-clorophenyl)-1-propyne **1l**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 - 7.36 (m, 2H), 7.36 - 7.28 (m, 2H), 5.96 (ddd, *J* = 16.1, 10.6, 5.7 Hz, 1H), 5.37 (d, *J* = 17.2 Hz, 1H), 5.27 (d, *J* = 10.3 Hz, 1H), 4.39 (s, 2H), 4.15 (d, *J* = 5.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.58, 134.05, 133.08, 128.73, 121.21, 118.10, 86.17, 85.20, 70.91, 57.94.



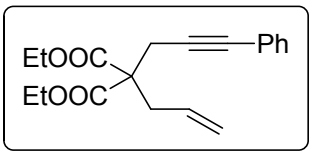
3-(allyloxy)-1-(4-bromophenyl)-1-propyne **1m**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 6.04 - 5.85 (m, 1H), 5.34 (d, *J* = 17.2 Hz, 1H), 5.24 (d, *J* = 10.4 Hz, 1H), 4.36 (s, 2H), 4.12 (d, *J* = 4.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.11, 133.33, 131.71, 122.85, 121.76, 118.11, 86.44, 85.31, 70.97, 58.01.

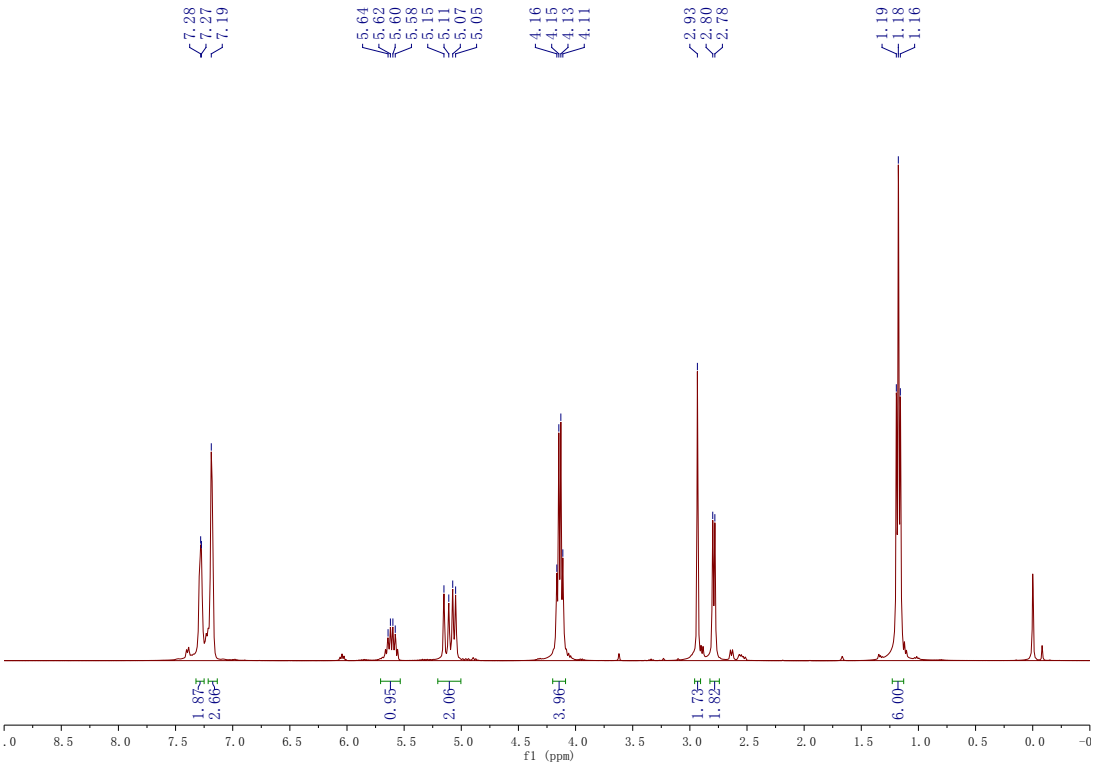


3-(allyloxy)-1-(4-methoxyphenyl)-1-propyne **1n**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 5.81 (ddd, *J* = 16.3, 10.9, 5.8 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.3 Hz, 1H), 5.10 (d, *J* = 10.3 Hz, 1H), 4.23 (s, 2H), 4.00 (d, *J* = 5.7 Hz, 2H), 3.66 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.71, 134.12, 133.26, 117.88, 114.72, 113.92, 86.23, 83.60, 70.64, 58.01, 55.27.



2-phenylethynylphenyl)propylcarbodiimide **1o**, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 5.5, 2.2 Hz, 2H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.38 (dd, *J* = 6.6, 3.0 Hz, 3H), 7.28 (dd, *J* = 11.0, 4.4 Hz, 1H), 7.17 - 7.07 (m, 2H), 3.35 (t, *J* = 6.9 Hz, 2H), 1.74 - 1.60 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.47, 133.55, 133.26, 131.59, 129.35, 128.48, 128.35, 124.21, 124.06, 123.31, 118.83, 95.24, 86.44, 77.44, 77.12, 76.81, 48.55, 24.51, 11.43; IR (KBr) *v*/cm^{-1} 3062, 2845, 2252, 2144, 1164, 910, 647.


EtOOC
EtOOC
Ph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4.11
2.93
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0.95
2.06
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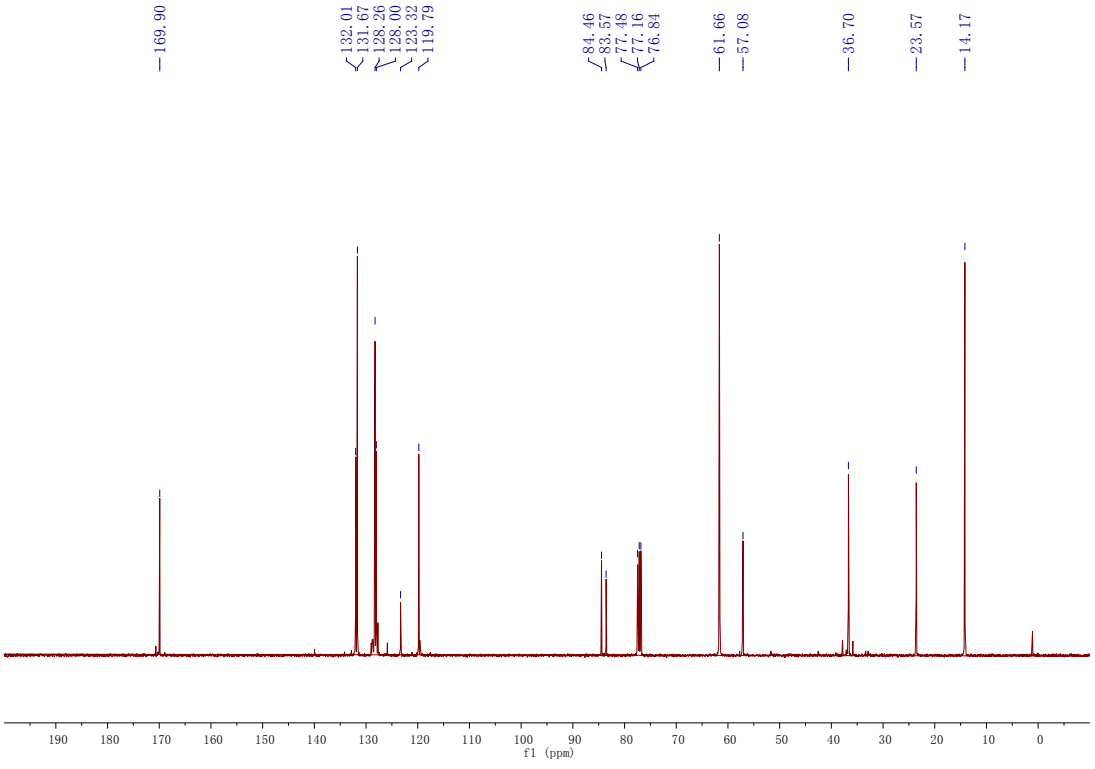
6.00
f1 (ppm)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77.16
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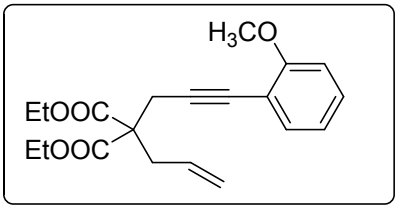
61.66
57.08
36.70
23.57
14.17
f1 (ppm)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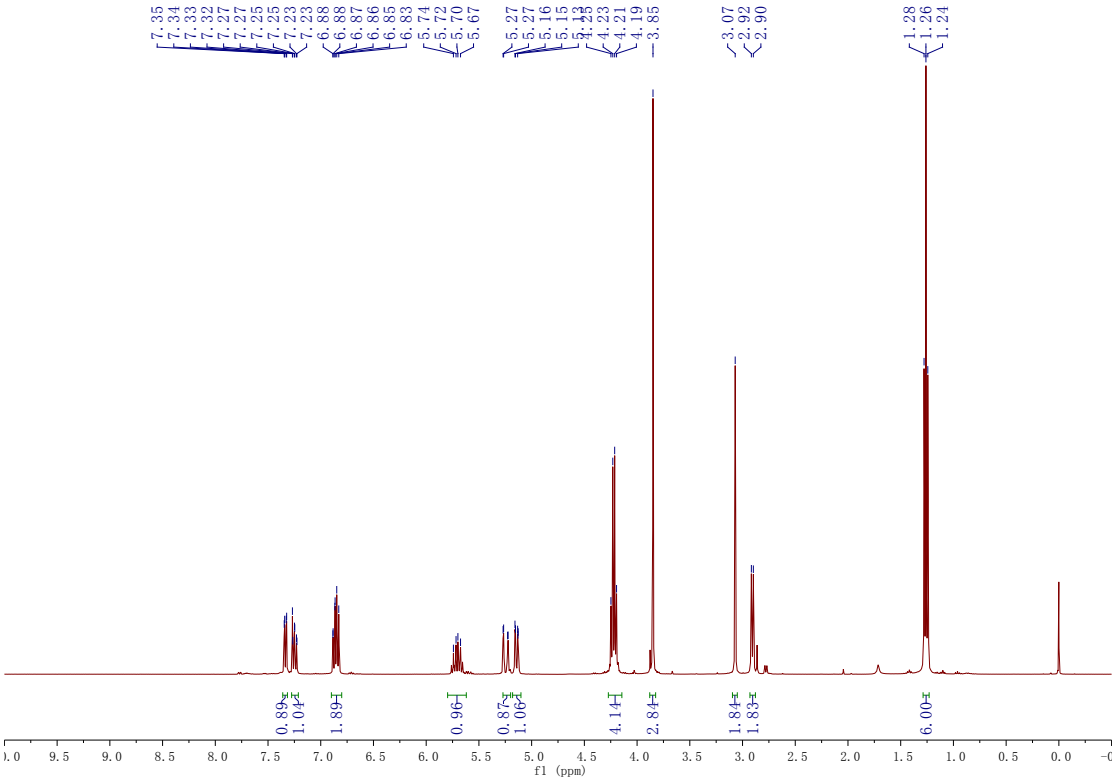
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6.85
6.83
5.74
5.72
5.70
5.67
5.27
5.27
5.16
5.15
4.23
4.23
4.21
4.19
3.85
3.07
2.92
2.90
1.28
1.26
1.24
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1.83
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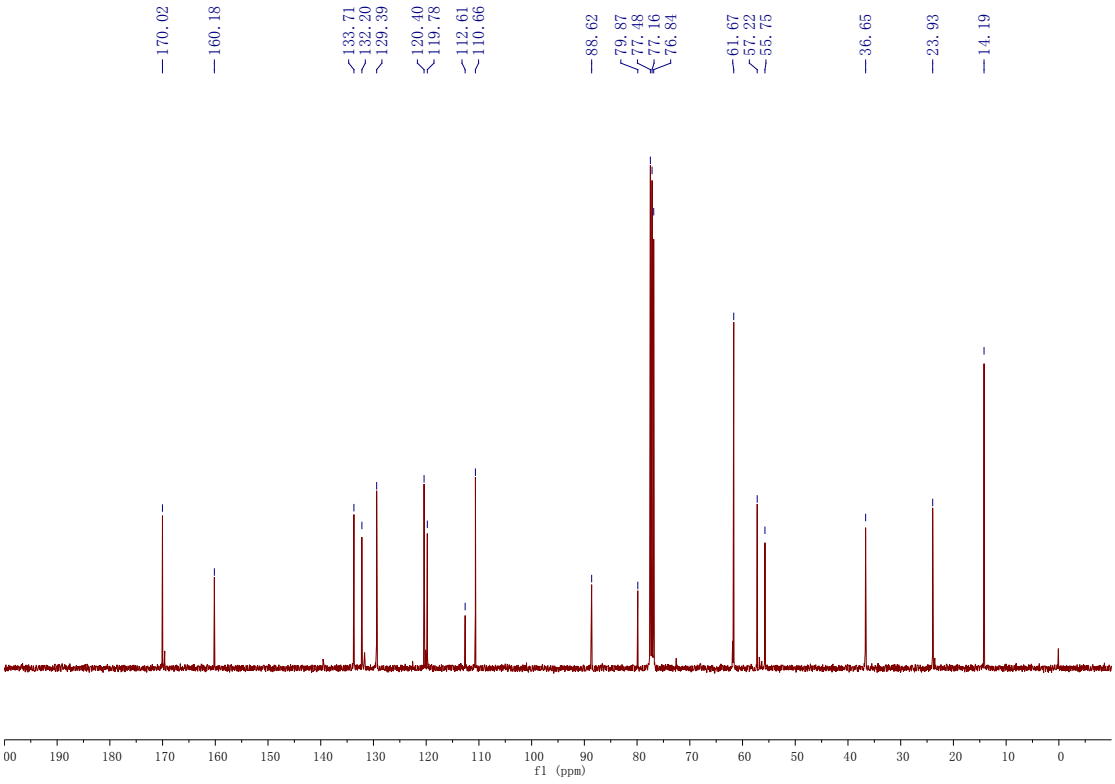
f1 (ppm)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57.22
55.75
36.65
23.93
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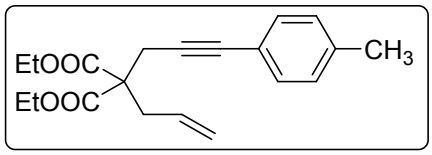
f1 (ppm)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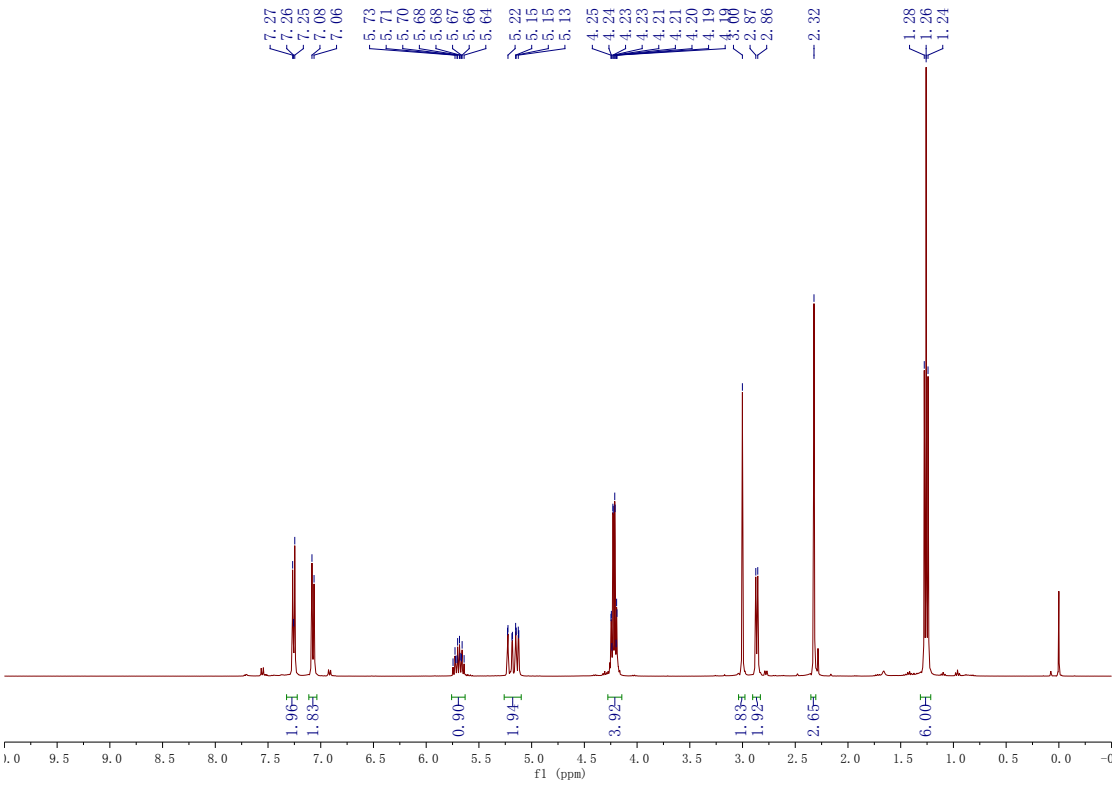
EtOOC
CH3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5.15
5.13
4.25
4.24
4.23
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4.21
4.21
4.20
4.19
3.00
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2.86
2.32
1.28
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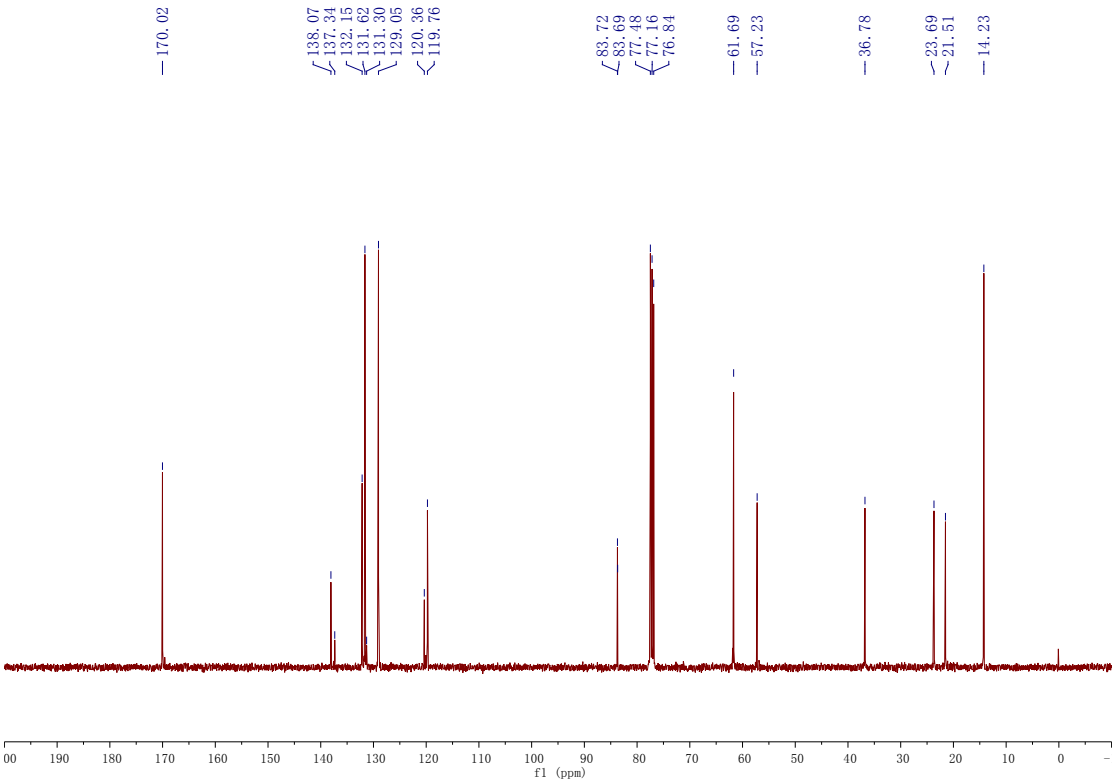
6.00
f1 (ppm)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120.36
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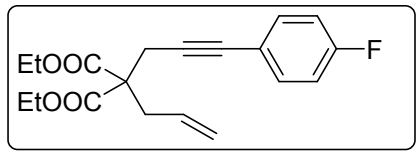
57.23
36.78
23.69
21.51
14.23
f1 (ppm)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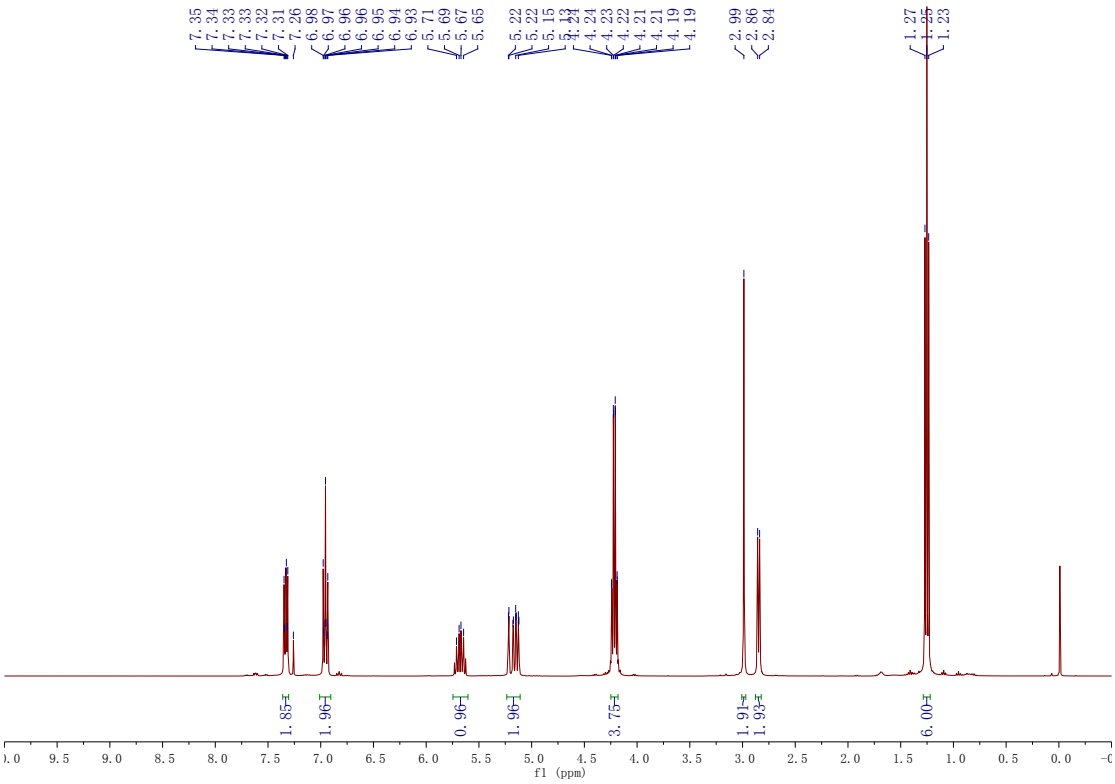
EtOOC
F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4.21
4.21
4.19
4.19
2.99
2.86
2.84
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0.96
1.96
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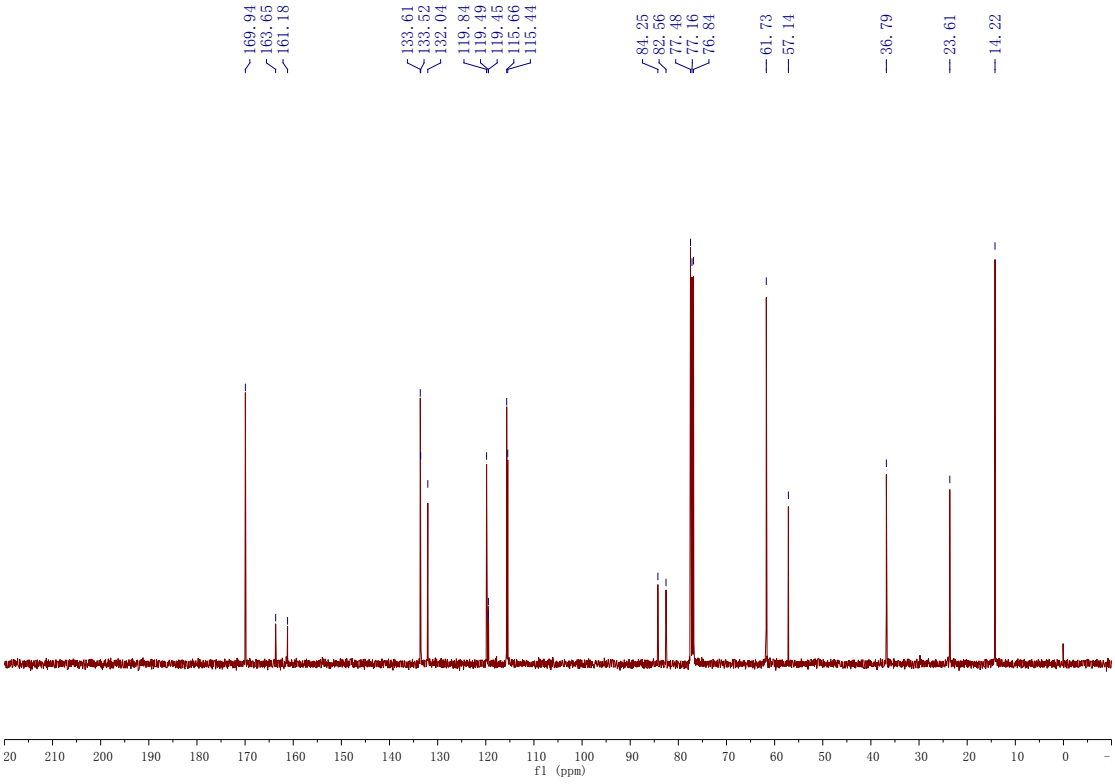
1.93
6.00
f1 (ppm)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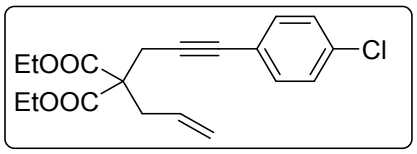
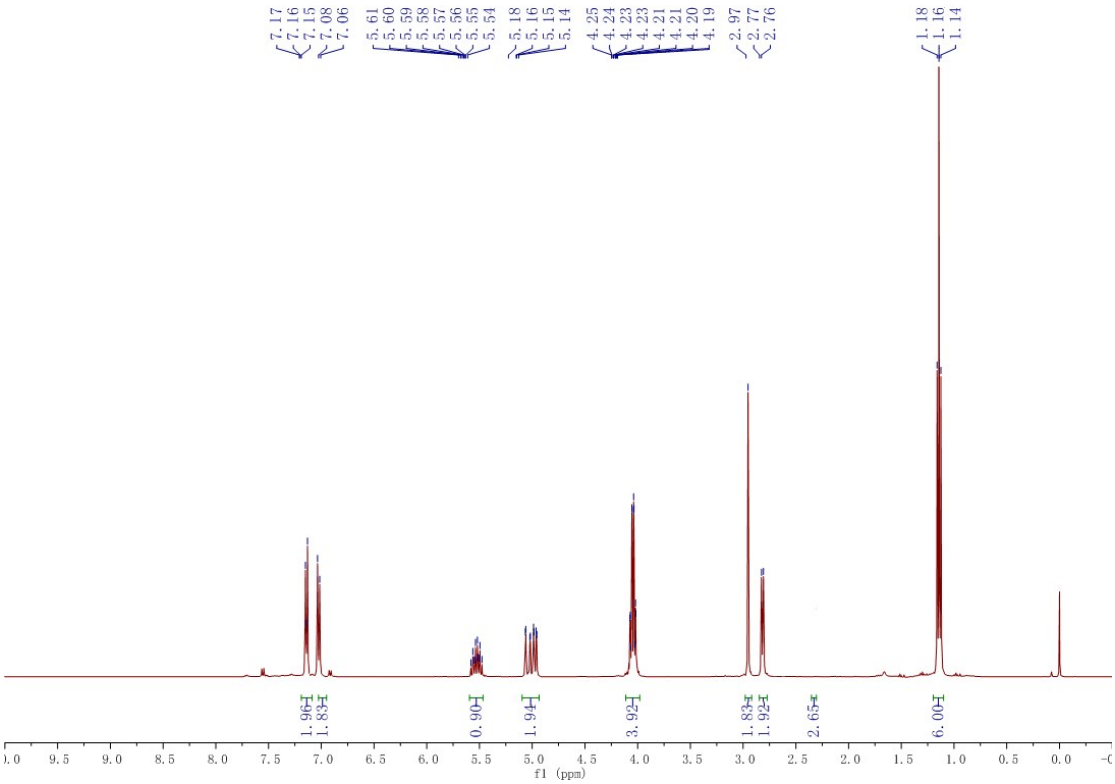
57.14
36.79
23.61
14.22
f1 (ppm)


EtOOC
EtOOC
Cl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4.23
4.21
4.21
4.20
4.19
2.97
2.77
2.76
1.18
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1.14
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1.83
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1.94
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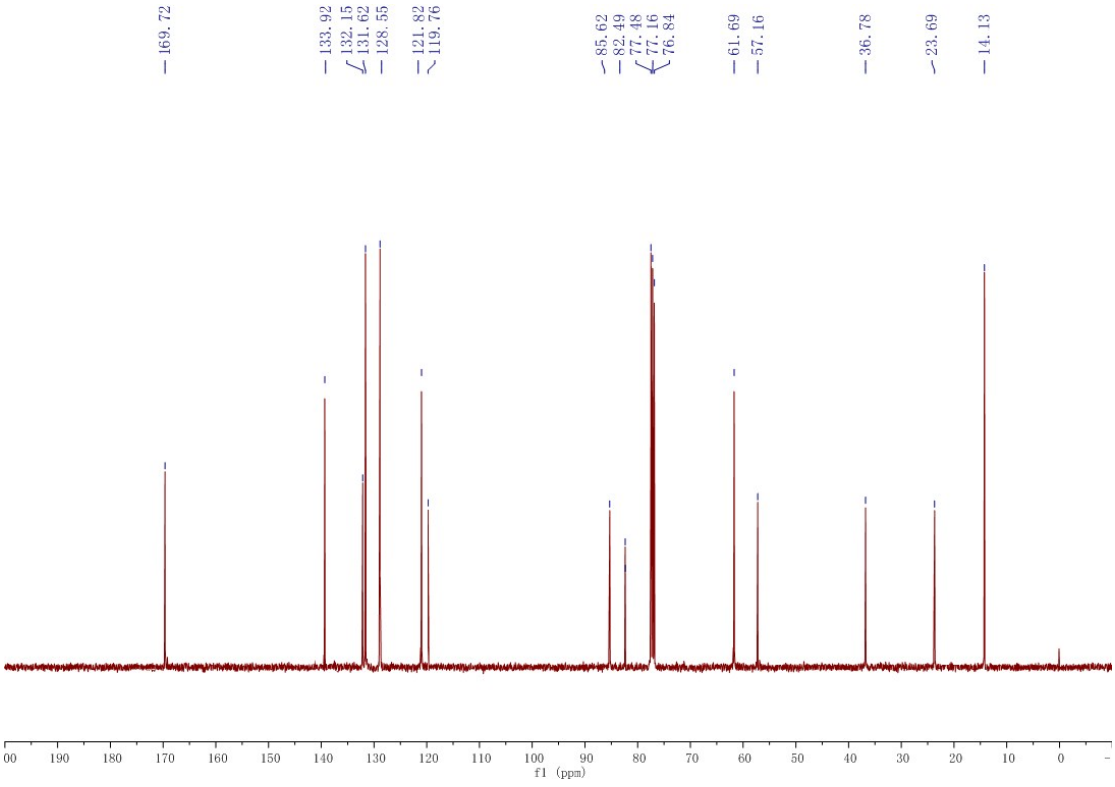
1.83
1.92
2.65
6.00
f1 (ppm)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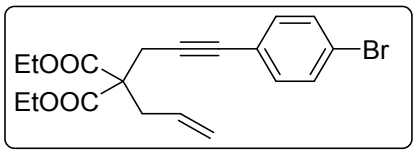
23.69
14.13
f1 (ppm)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EtOOC
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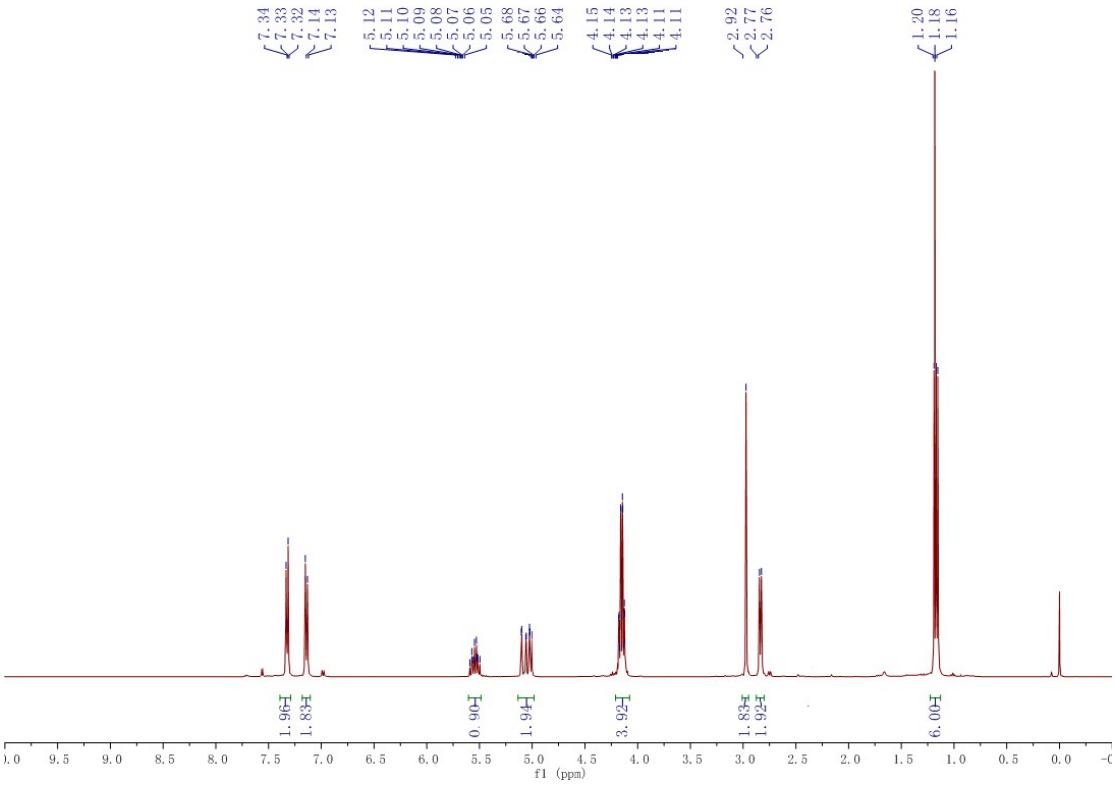
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4.14
4.13
4.11
4.11
2.92
2.77
2.76
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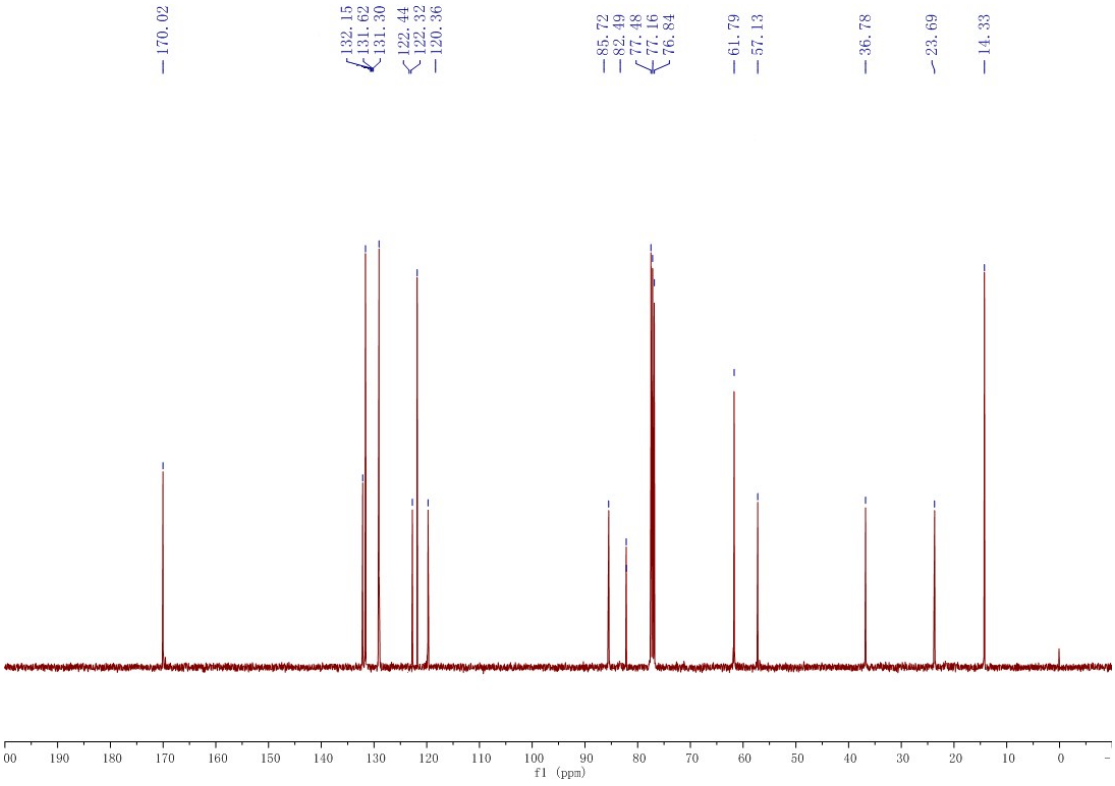
1.92
6.00
f1 (ppm)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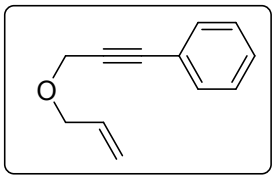
36.78
23.69
14.33
f1 (ppm)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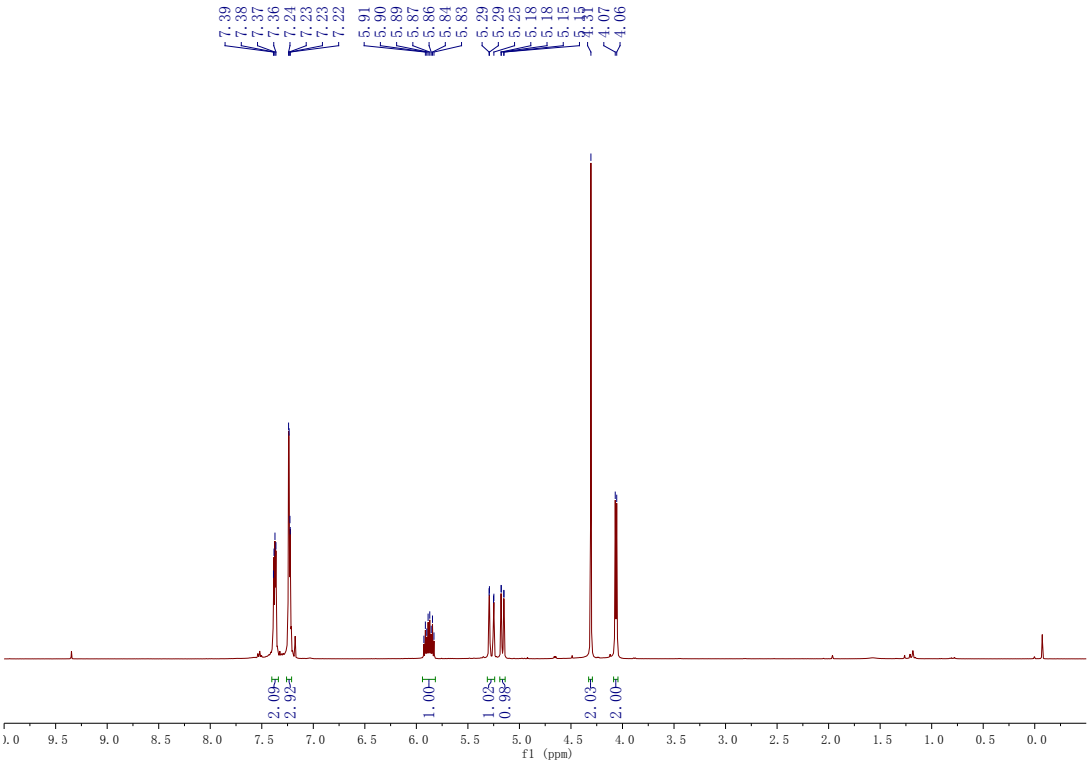
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5.29
5.25
5.18
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5.15
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0.98
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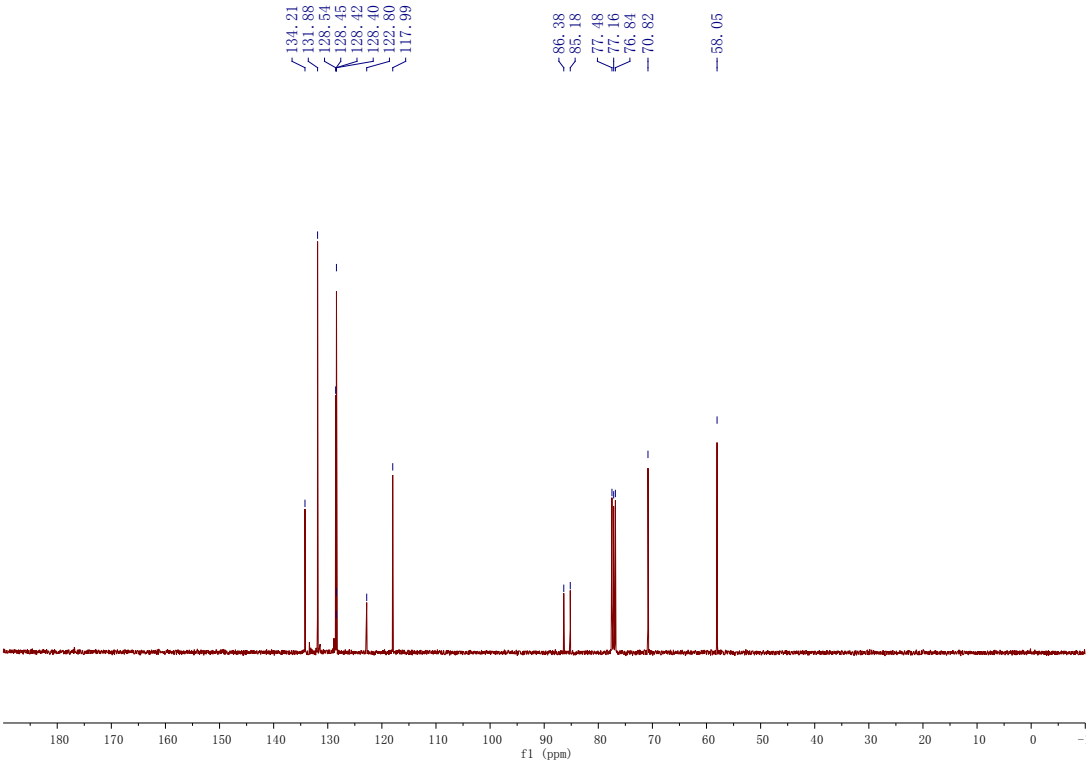
2.00
f1 (ppm)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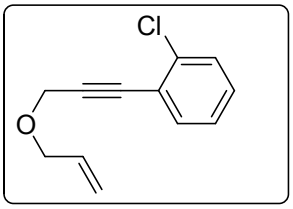
76.84
70.82
58.05
f1 (ppm)


Cl
O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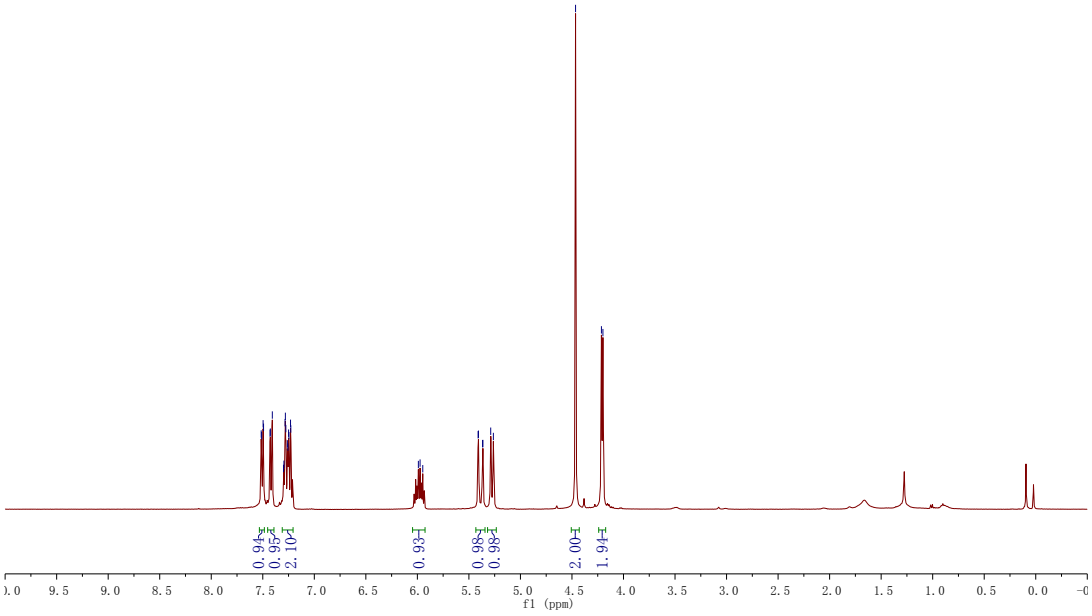
4.20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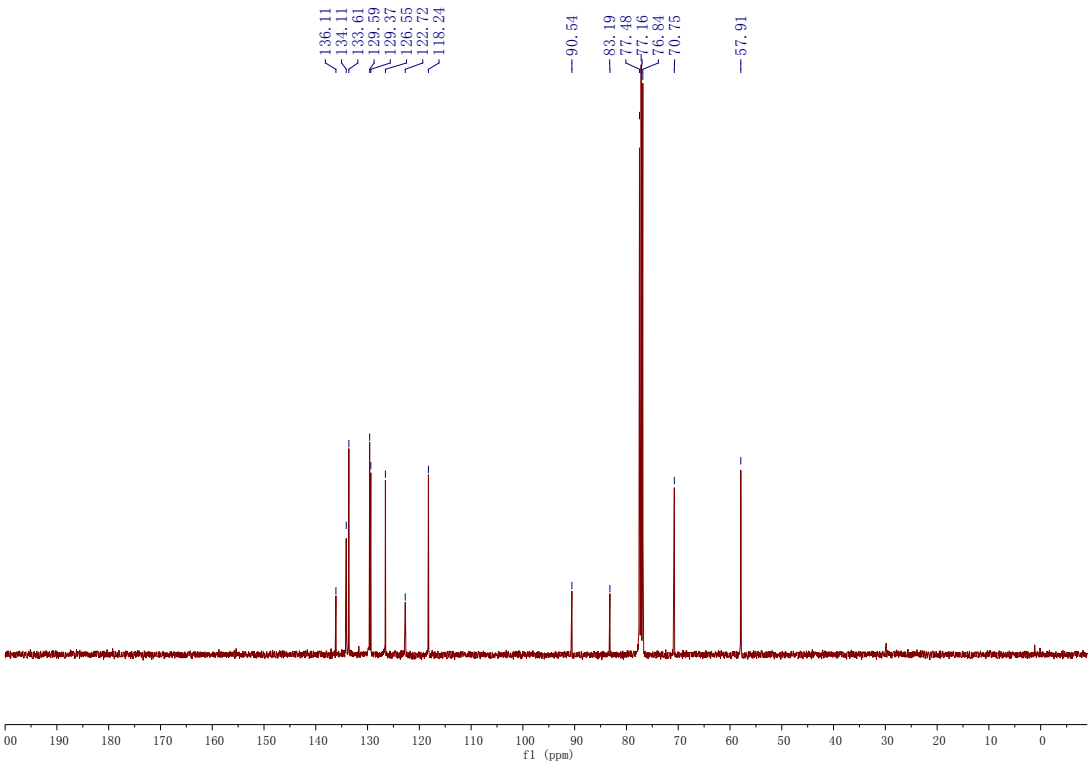
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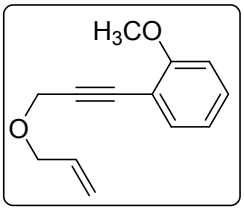
76.84
70.75
57.91
f1 (ppm)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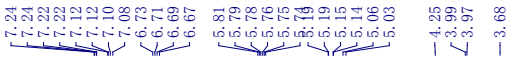
O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5.03
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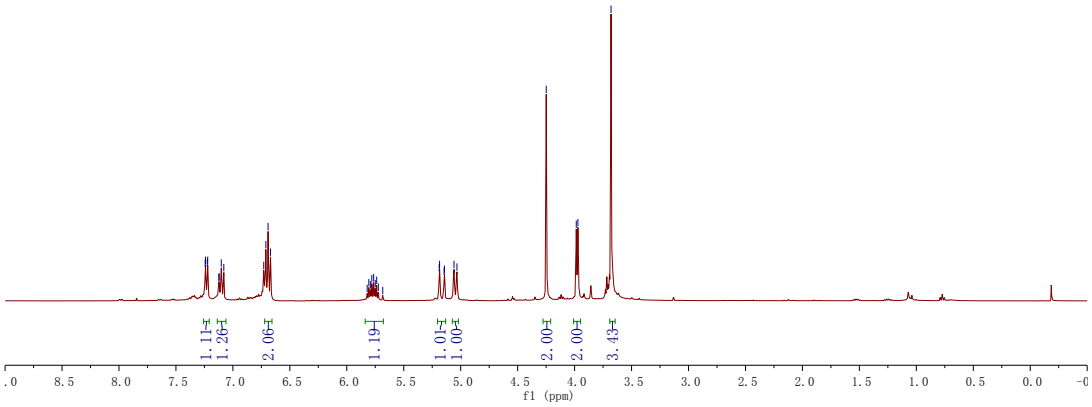
3.68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1.19
1.01
1.00
2.00
2.00
3.43
f1 (ppm)


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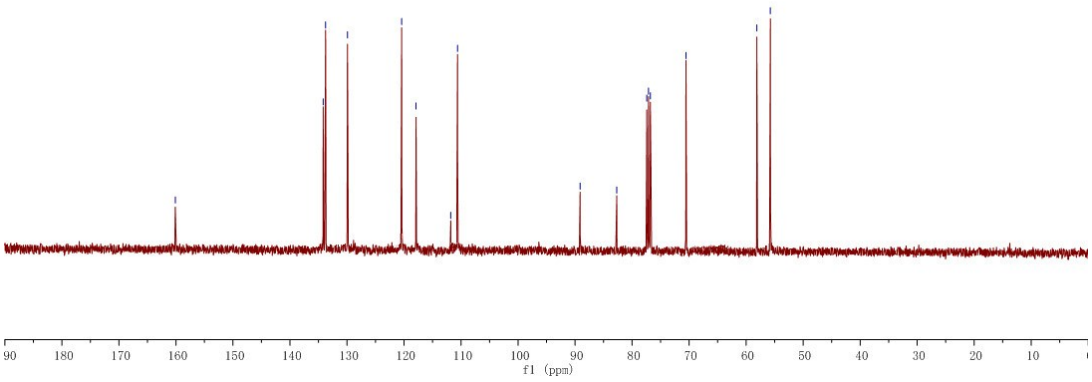
58.12
55.75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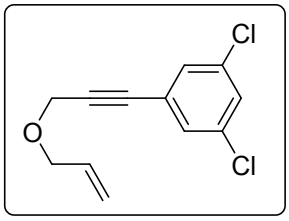
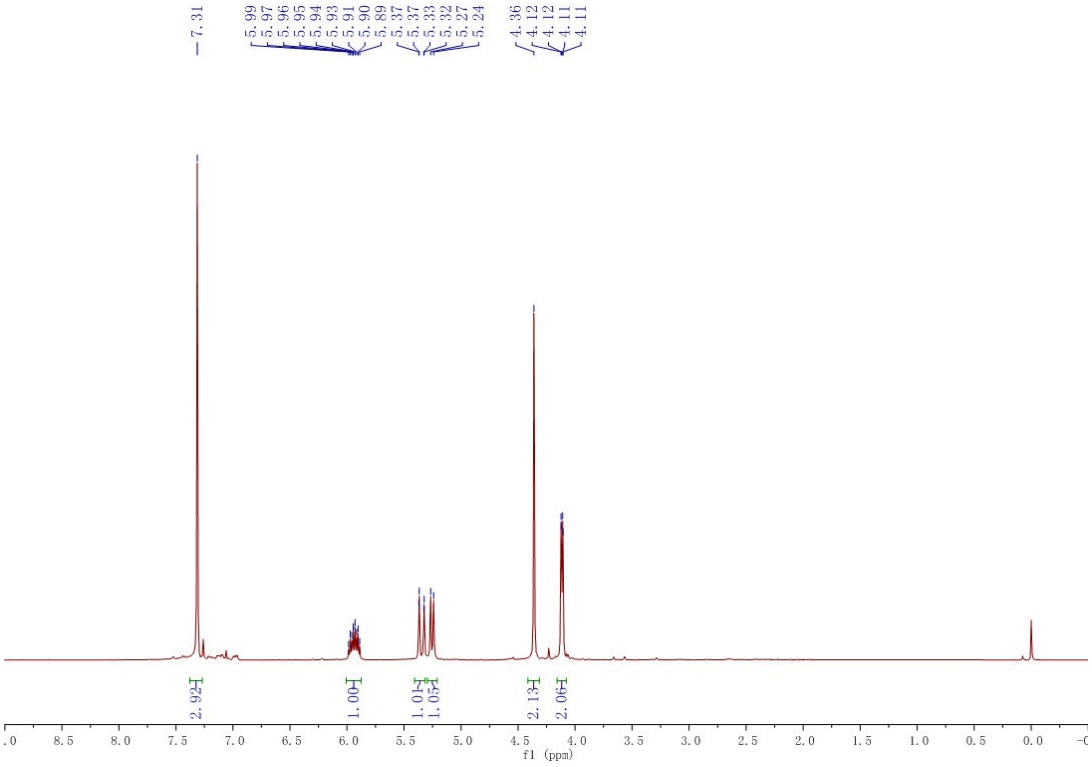

Cl
O
Cl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5.27
5.24
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4.11
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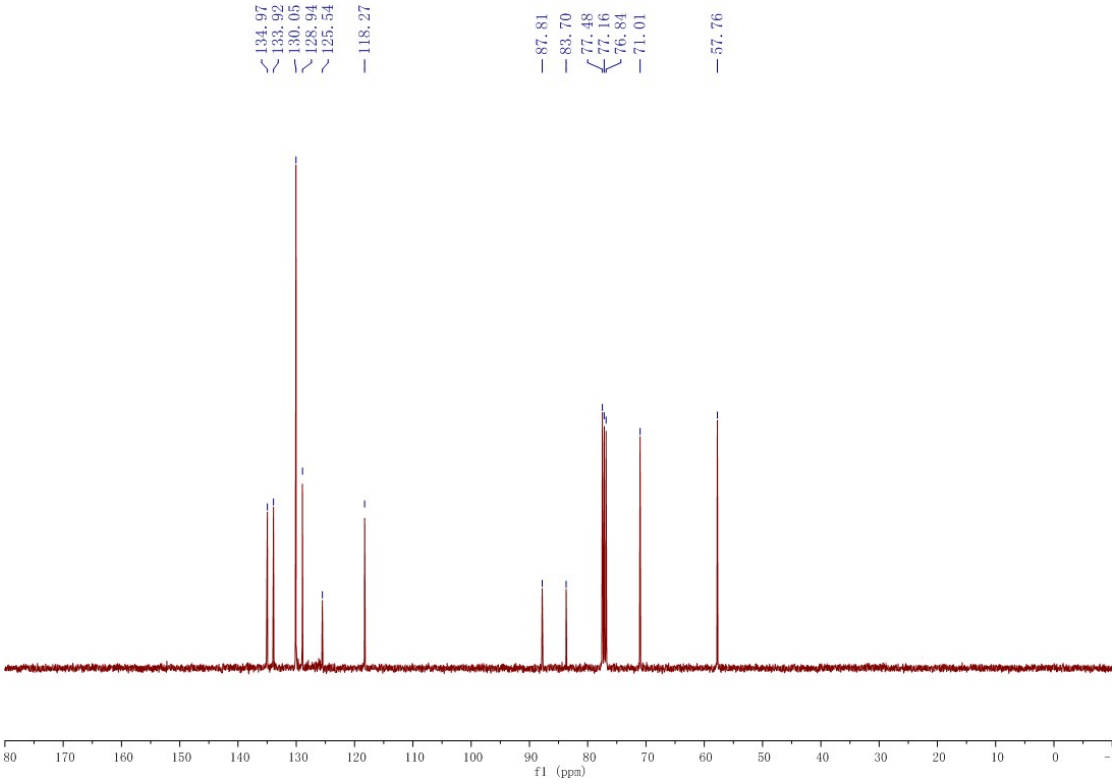
1.01
1.05
2.13
2.06
f1 (ppm)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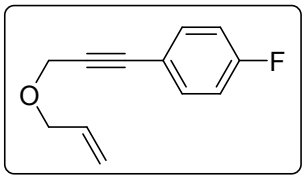
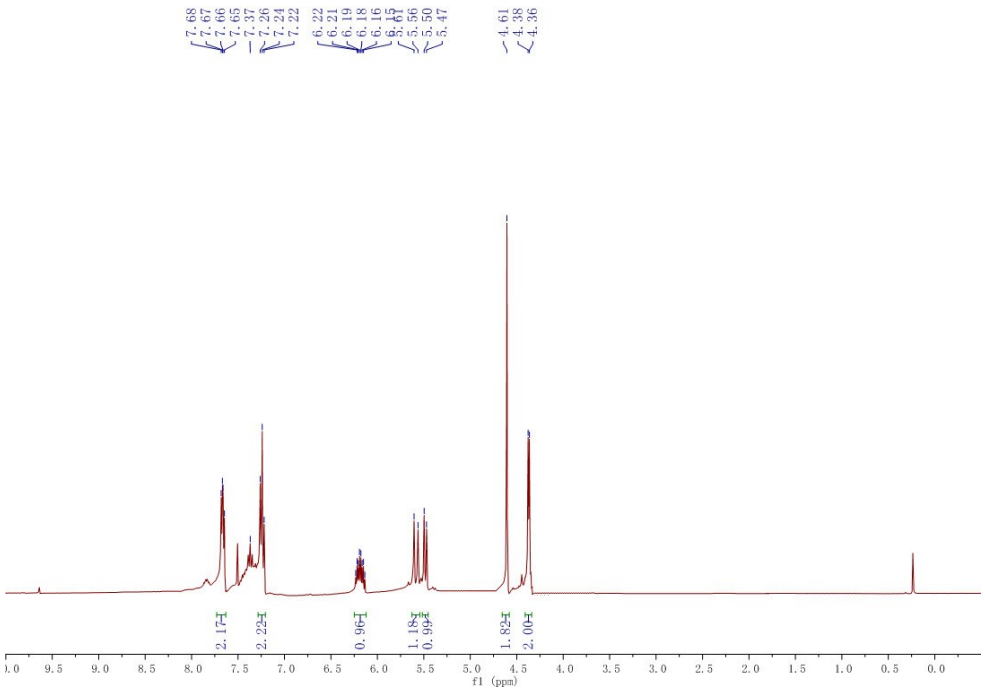
76.84
71.01
57.76
f1 (ppm)


F
O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5.56
5.50
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2.22
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0.99
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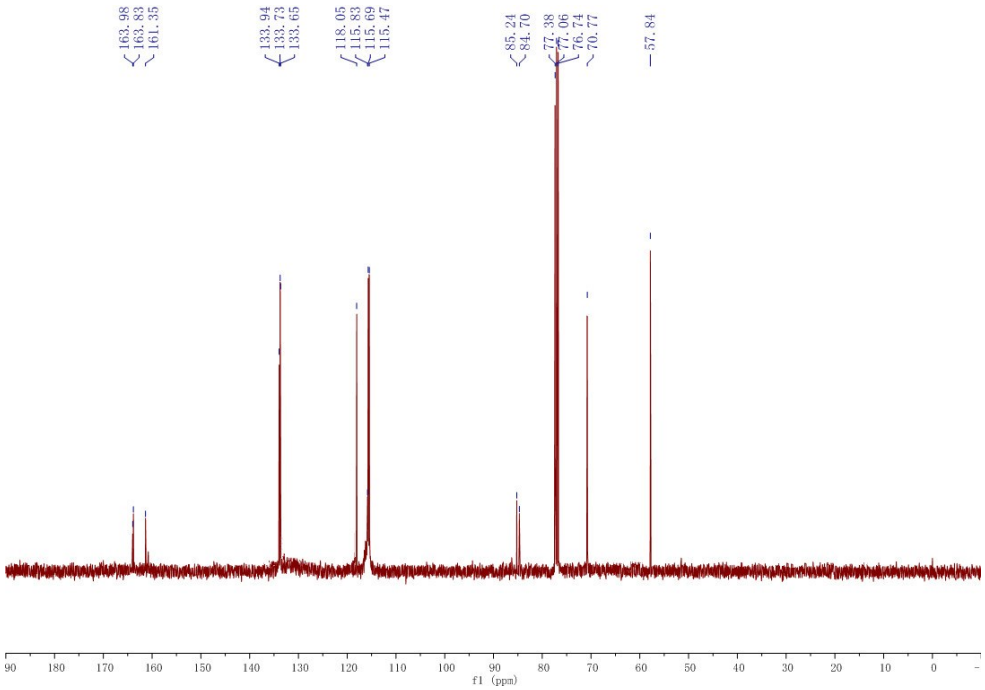
2.00
f1 (ppm)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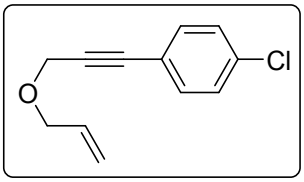
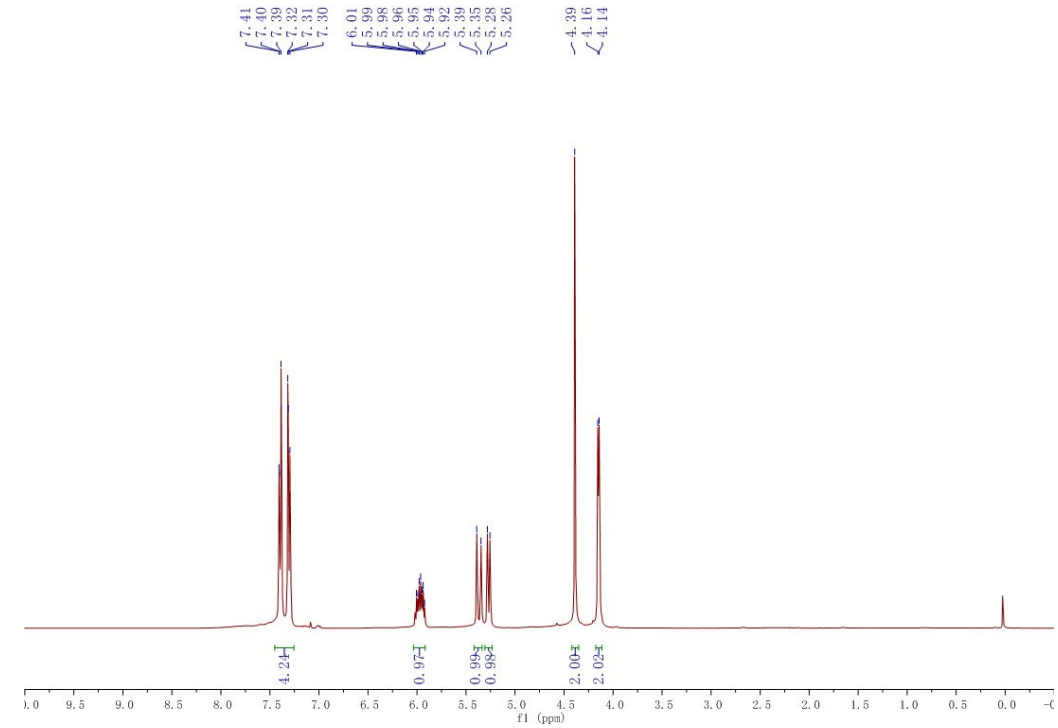
76.74
70.77
57.84
f1 (ppm)


Cl
O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5.95
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5.92
5.39
5.35
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5.26
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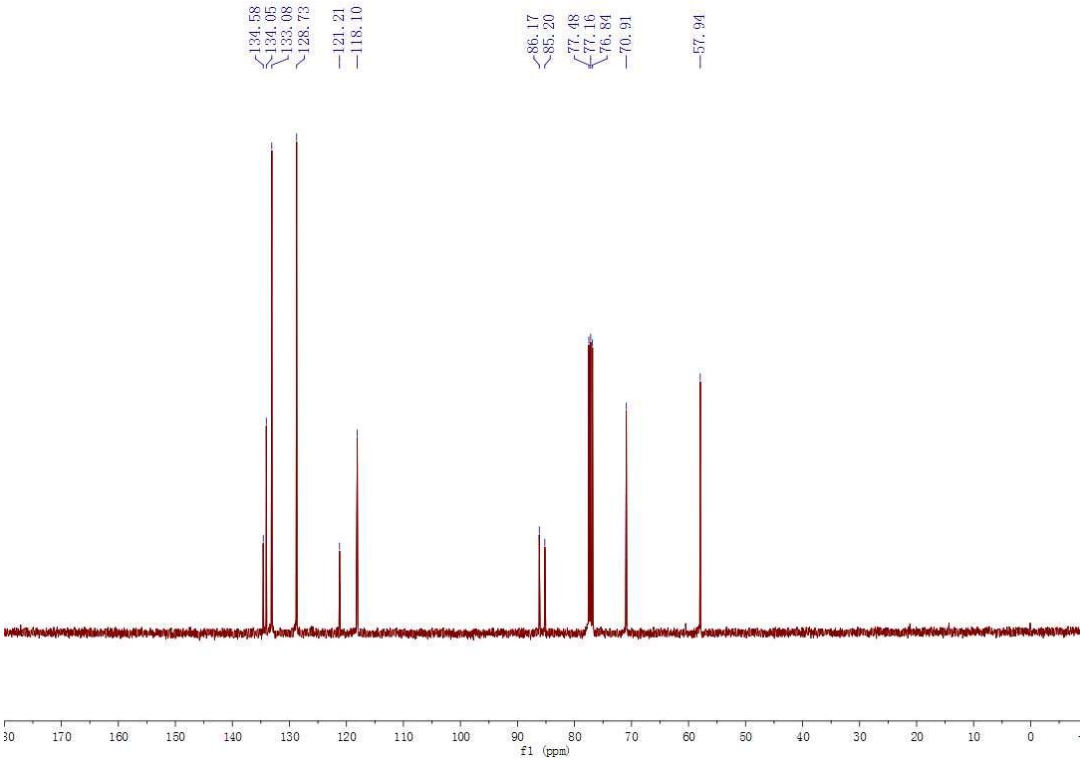
4.16
4.14
4.24
0.97
0.99
0.98
2.00
2.02
f1 (ppm)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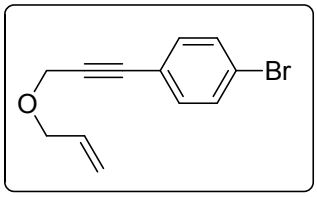
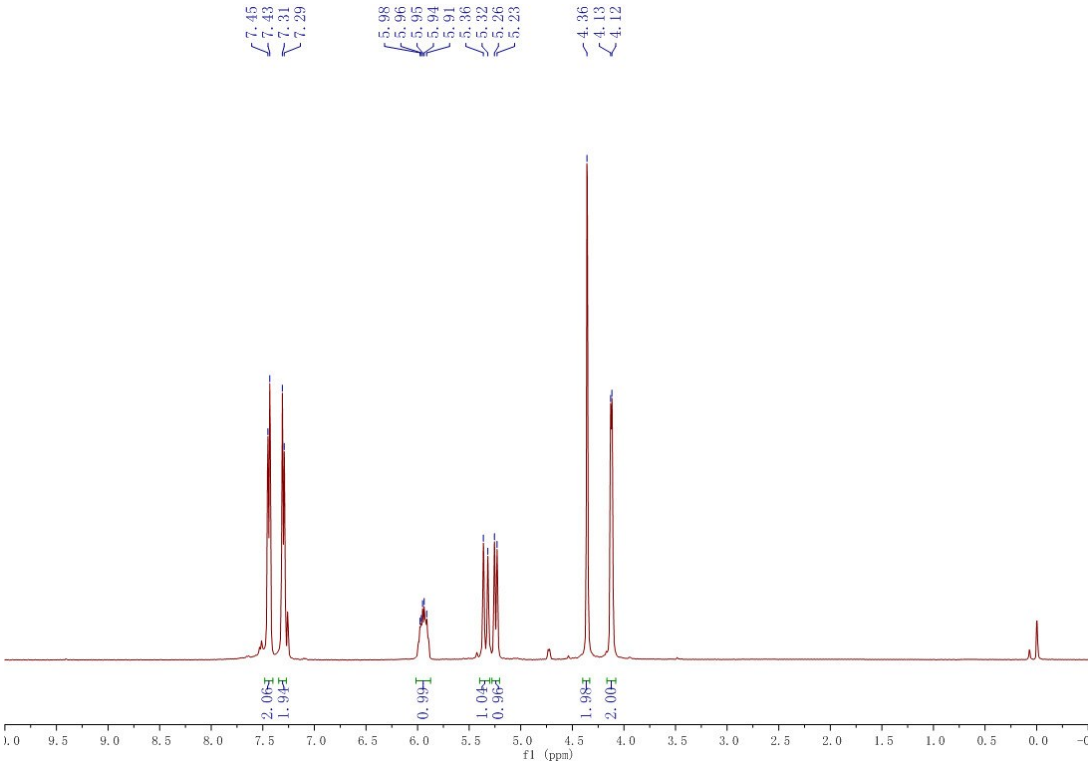
76.84
70.91
57.94
f1 (ppm)


Br
O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0.96
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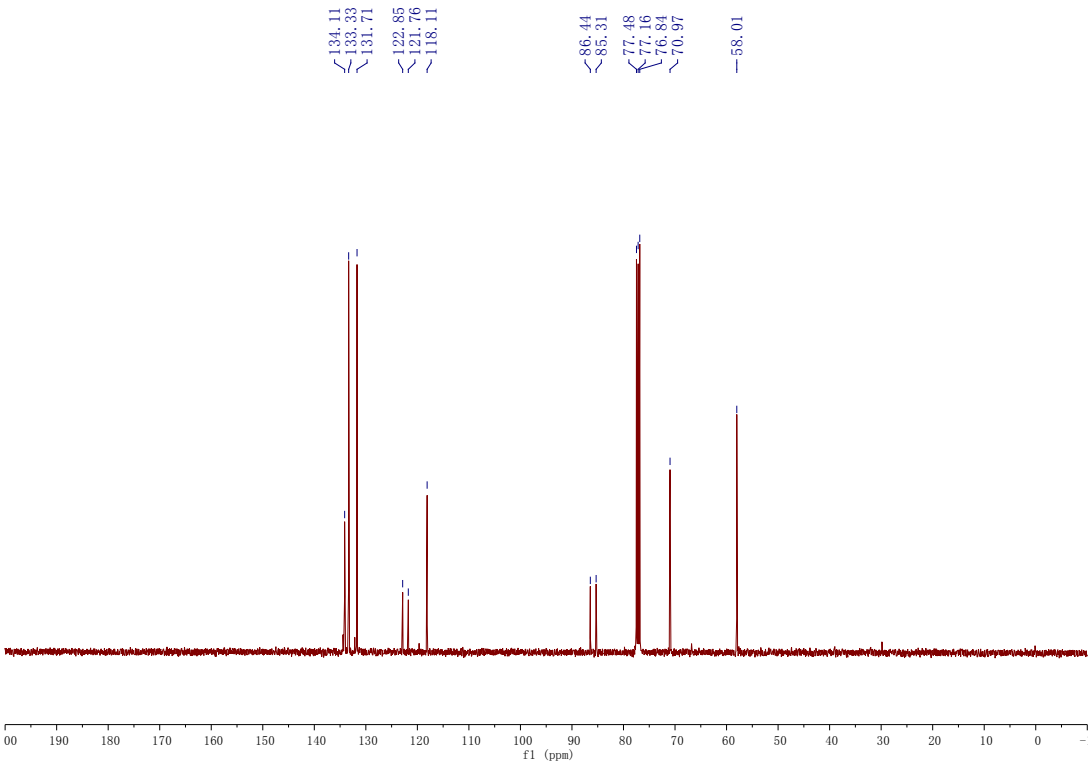
2.00
f1 (ppm)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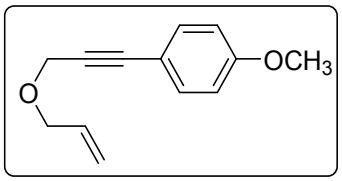
77.48
77.16
76.84
70.97
58.01
f1 (ppm)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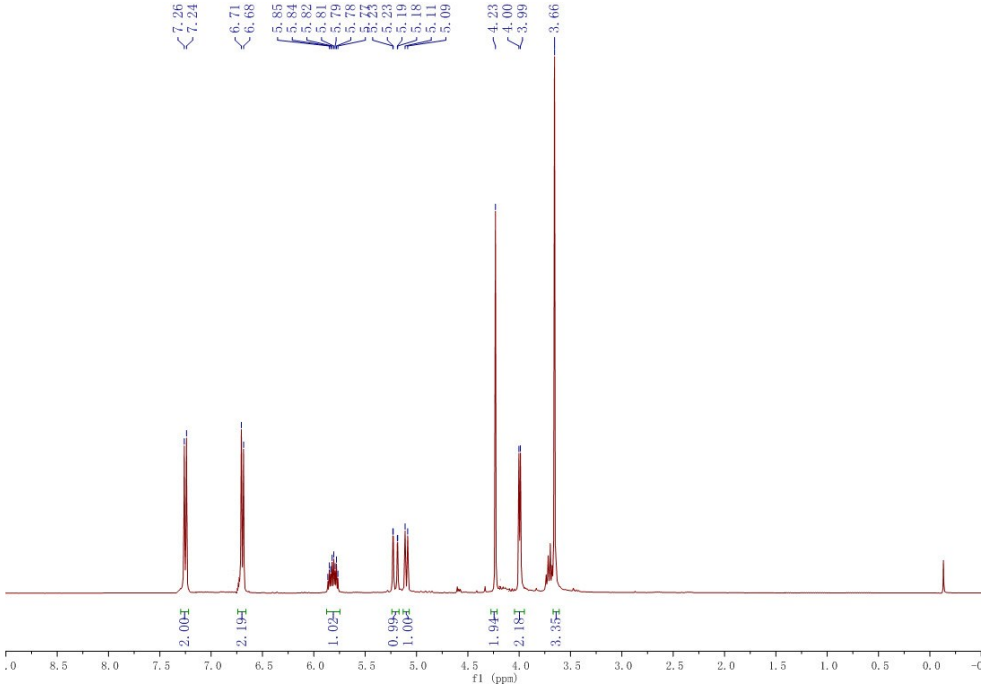
O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5.11
5.09
4.23
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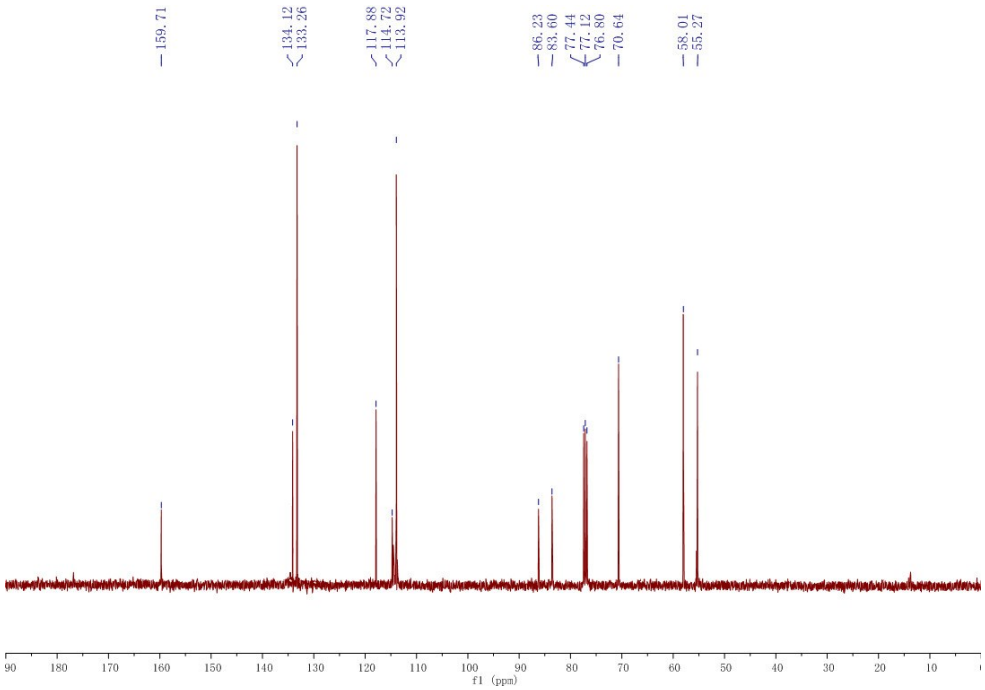
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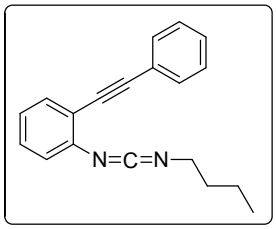
f1 (ppm)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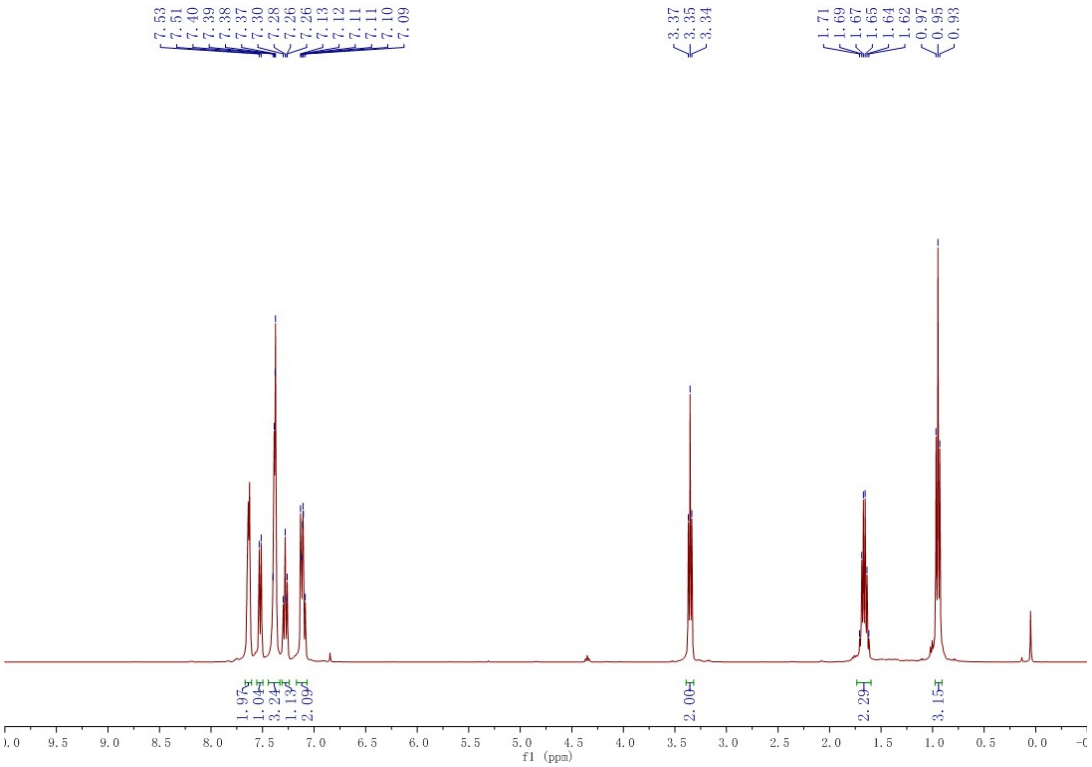
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7.11
7.10
7.09
3.37
3.35
3.34
1.71
1.69
1.67
1.65
1.64
1.62
0.97
0.95
0.93
1.97
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3.24
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2.00
2.00
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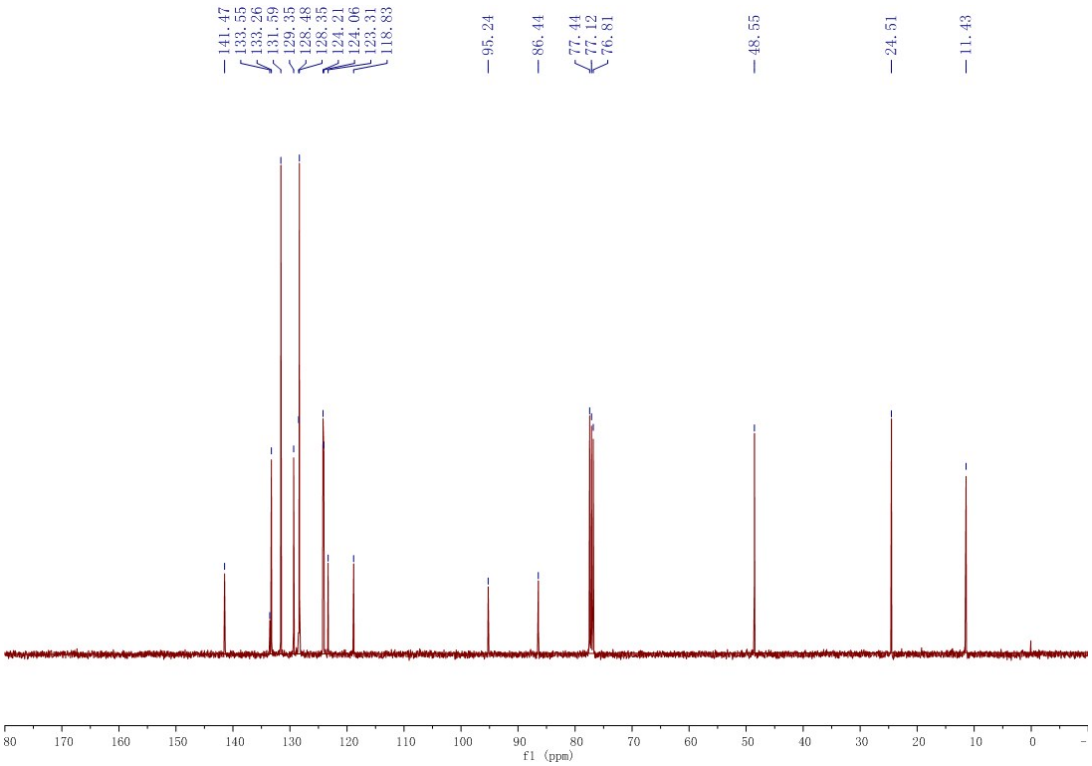
3.15
f1 (ppm)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123.31
118.83
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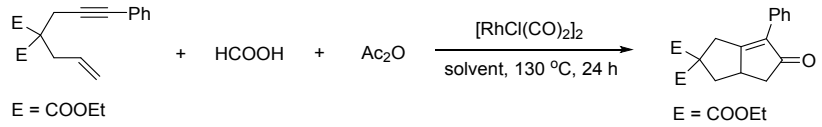
86.44
77.44
77.12
76.81
48.55
24.51
11.43
f1 (ppm)

4. Typical procedure for the rhodium-catalyzed Pauson-Khand-type reaction

Take the cyclocarbonylation of **1a** under optimized conditions as an example: in a glassic pressure tube, formic acid (0.0684 g, 1.5 mmol) and acetic anhydride (0.0766 g, 0.75 mmol) were pre-stirred at room temperature under the atmosphere of argon for 1.5 h. Subsequently, solution of $[RhCl(cod)]_2$ (4.9 mg, 2 mol%) and **1a** (0.1714 g, 0.5 mmol) in 3 mL butyl ether was added to the mixture of formic acid and acetic anhydride via a syringe under argon atmosphere. Then the vial was tightly sealed and stirred at 130 °C for 24 h. After the reaction, 20 mg diphenyl was used as internal standard for GC yield determination. To obtain pure products, 20 mL water was added to the reaction mixture, extracted with ethyl acetate (20 mL × 3). Then the organic layers were washed with saturated NaCl solution, dried with anhydrous Na_2SO_4, purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) was conducted.

5. Investigation of the key reaction parameters

Table S1. Effect of formic acid and its alkali salts on the reaction[a]



Entry	Catalyst (mol%)	Source of CO	Additive	Conversion[b] (%)	Yield[b] (%)
1	$[RhCl(CO)_2]_2$ (2 mol%)	HCOONa (1.5 mmol)	Ac_2O (1 mmol)	36	34
2	$[RhCl(CO)_2]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	61	56
3	$[RhCl(CO)_2]_2$ (2 mol%)	$HCOOLi·H_2O$ (1.5 mmol)	Ac_2O (1.5 mmol)	14	13
4	$[RhCl(CO)_2]_2$ (2 mol%)	HCOONa (1.5 mmol)	Ac_2O (1.5 mmol)	7	4
5	$[RhCl(CO)_2]_2$ (2 mol%)	HCOOK (1.5 mmol)	Ac_2O (1.5 mmol)	9.3	3
6	$[RhCl(CO)_2]_2$ (2 mol%)	HCOOCs (1.5 mmol)	Ac_2O (1.5 mmol)	0	0
7	$[RhCl(CO)_2]_2$ (2 mol%)	$HCOONH_4$ (1.5 mmol)	Ac_2O (1.5 mmol)	12	3
8	$[RhCl(CO)_2]_2$ (2 mol%)	HCOOH (1.5 mmol)	-	11	8
9	$[RhCl(CO)_2]_2$	-	Ac_2O	16	10

	(2 mol%)		(1.5 mmol)		
10	$[RhCl(CO)_2]_2$ (2 mol%)	-	-	0	0
11	-	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	0	0

[a]Reaction condition: Diethyl1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (0.1714 g, 0.5 mmol), $[RhCl(CO)_2]_2$ (3.8 mg, 2 mol%), Ac_2O (0.160 g, 1.5 mmol), dibutyl ether (5 mL), 130 °C, 24 h. [b]Yield of diethyl7-oxo-8-phenyl-bicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate, as determined by GC using biphenyl as internal standard.

Table S2. Effect of rhodium and iridium catalysts on the reaction[a]

Entry	Catalyst (mol%)	Source of CO	Additive	Conversion[b] (%)	Yield[b] (%)
1	$[RhCl(CO)_2]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	61	56
2	$RhCl_3 \cdot 3H_2O$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	40	35
3	$Rh(PPh_3)_3Cl$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	38	33
4	$Rh(acac)_3$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	15	5
5	$[RhCl(coe)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	67	63
6	$[Cp^*RhCl_2]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	28	10
7	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	81	78
8	$[Rh(CO)_2acac$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	67	60
9	$[IrCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	70	46

[a]Reaction condition: Diethyl1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (0.1714 g, 0.5 mmol), catalyst (2 mol%), dibutyl ether (5 mL), HCOOH (0.0684 g, 1.5 mmol), Ac_2O (0.160 g, 1.5 mmol), dibutyl ether (5 mL), 130 °C, 24 h. [b]Yield of diethyl7-oxo-8-phenyl-bicyclo[3.3.0]oct-1(8)-ene-3,3- dicarboxylate, as determined by GC using biphenyl as internal standard.

Table S3. Effect of acetic anhydride amounts on the reaction[a]

Entry	Catalyst	Source of CO	Additive	Conversion[b] (%)	Yield[b] (%)
1	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (0.1 mmol)	10	8
2	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (0.25 mmol)	15	13
3	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (0.5 mmol	17	14
4	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (0.75 mmol)	94	86
5	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1 mmol)	92	85
6	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (1.5 mmol)	81	78
7	$[RhCl(cod)]_2$ (2 mol%)	HCOOH (1.5 mmol)	Ac_2O (2 mmol)	51	45

[a]Reaction condition: Diethyl1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (0.1714 g, 0.5 mmol), $[RhCl(cod)]_2$ (4.9 mg, 2 mol%), dibutyl ether (5 mL), HCOOH (0.0684 g, 1.5 mmol), dibutyl ether (5 mL), 130 °C, 24 h. [b]Yield of diethyl7-oxo-8-phenyl-bicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate, as determined by GC using biphenyl as internal standard.

Table S4. Solvent effect on the reaction[a]

Entry	Catalyst	Solvent	Conversion[b] (%)	Yield[b] (%)
1	$[RhCl(cod)]_2$ (2 mol%)	Bu_2O	94	86
2	$[RhCl(cod)]_2$ (2 mol%)	DMF	15	9
3	$[RhCl(cod)]_2$ (2 mol%)	DMAC	12	11
4	$[RhCl(cod)]_2$ (2 mol%)	DMSO	4	3
5	$[RhCl(cod)]_2$ (2 mol%)	THF	23	21
6	$[RhCl(cod)]_2$ (2 mol%)	Toluene	71	68
7	$[RhCl(cod)]_2$ (2 mol%)	NMP	0	0

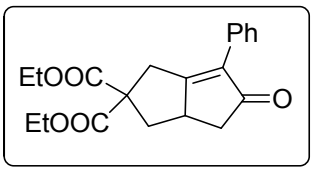
[a]Reaction condition: Diethyl1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (0.1714 g, 0.5 mmol), $[RhCl(cod)]_2$ (4.9 mg, 2 mol%), HCOOH (0.0684 g, 1.5 mmol), Ac_2O (0.0766 g, 0.75 mmol), solvent (5 mL), 130 °C, 24 h. [b]Yield of diethyl7-oxo-8-phenyl-bicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate, as determined by GC using biphenyl as internal standard.

Table S5. Effect of temperature and reaction time on the reaction[a]

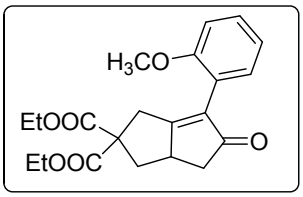
Entry	T (°C)	t (h)	Conversion[b] (%)	Yield[b] (%)
1	140	24	95	86
2	130	24	94	86
3	120	24	86	82
4	130	20	89	80
5	130	16	73	67

[a]Reaction condition: Diethyl1-phenyl-6-hepten-1-yne-4,4-dicarboxylate (0.1714 g, 0.5 mmol), $[RhCl(cod)]_2$ (4.9 mg, 2 mol%), HCOOH (0.0684 g, 1.5 mmol), Ac_2O (0.0766 g, 0.75 mmol), solvent (5 mL), 130 °C, 24 h. [b]Yield of diethyl7-oxo-8-phenyl-bicyclo[3.3.0]oct-1(8)-ene-3,3-dicarboxylate, as determined by GC using biphenyl as internal standard.

6. Characterization and NMR spectral copies of the products

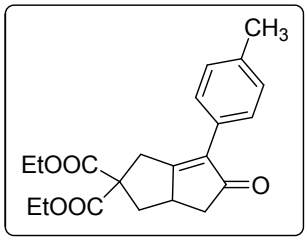


5-oxo-6-phenyl-3,3a,4,5-tetrahydro-1H-pentalene-2,2-dicarboxylic acid diethyl ester **2a**, white solid. Mp: 78-79 °C, (lit.[6] 78-80 °C). ^{1}H NMR δ 1.20 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H), 1.74 (dd, J = 12.7, 12.7 Hz, 1H), 2.28 (dd, J = 3.4, 17.8 Hz, 1H), 2.78 - 2.83 (m, 2H), 3.07 - 3.16 (m, 1H), 3.27 (d, J = 19.2 Hz, 1H), 3.62 (d, J = 19.2 Hz, 1H), 4.10 - 4.20 (m, 2H), 4.26 (q, J = 7.1 Hz, 2H), 7.31 (dd, J = 7.5, 7.5 Hz, 1H), 7.39 (dd, J = 7.5, 7.5 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 14.08, 14.16, 35.97, 38.82, 42.75, 42.96, 61.38, 62.09, 62.30, 128.30, 128.52, 131.00, 135.57, 170.82, 171.70, 179.12, 207.26.

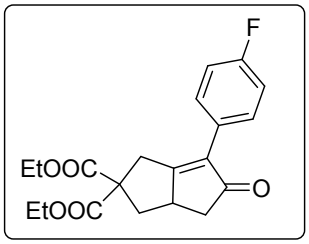


diethyl 6-(2-methoxyphenyl)-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate **2b**, light yellow solid. Mp: 92-93 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (m, 2H), 7.03 - 6.97 (m, 1H), 6.93 (d, J = 8.2 Hz, 1H), 4.32 - 4.22 (m, 2H), 4.21 - 4.10 (m, 2H), 3.81 (s, 3H), 3.40 (d, J = 19.4 Hz, 1H), 3.25 - 3.14 (m, 1H), 3.07 (d, J = 19.4 Hz, 1H), 2.87 - 2.74 (m, 2H), 2.29 (dd, J = 17.8, 3.3 Hz, 1H), 1.82 (t, J = 12.7 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.35, 181.19, 171.92, 171.08, 157.03, 132.80, 130.91, 129.72, 120.53, 119.86, 111.03, 62.11, 61.94, 60.77, 55.45, 42.95, 42.51, 39.47, 36.41, 14.15,

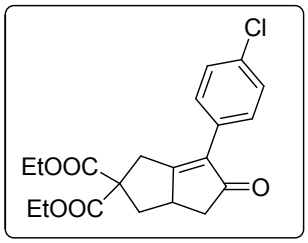
14.08.



diethyl 5-oxo-6-(p-tolyl)-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate **2c**, white solid. Mp: 99-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.21 - 4.10 (m, 2H), 3.63 (d, *J* = 19.2 Hz, 1H), 3.27 (d, *J* = 19.2 Hz, 1H), 3.12 (d, *J* = 5.0 Hz, 1H), 2.87 - 2.75 (m, 2H), 2.41 - 2.24 (m, 4H), 1.76 (t, *J* = 12.7 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.48, 178.29, 171.86, 170.97, 138.33, 135.61, 129.36, 128.54, 128.29, 62.38, 62.16, 61.58, 43.01, 42.88, 39.01, 36.14, 21.53, 14.28, 14.20.

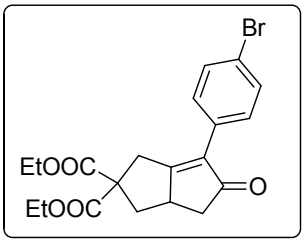


diethyl 6-(4-fluorophenyl)-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate **2d**, white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 4.32 - 4.25 (m, 2H), 4.17 (dt, *J* = 7.1, 3.8 Hz, 2H), 3.61 (d, *J* = 19.2 Hz, 1H), 3.26 (d, *J* = 19.2 Hz, 1H), 3.13 (d, *J* = 5.4 Hz, 1H), 2.89 - 2.76 (m, 2H), 2.29 (dd, *J* = 17.9, 3.3 Hz, 1H), 1.74 (t, *J* = 12.7 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.30, 178.94, 171.74, 170.91, 163.94, 161.47, 160.96, 134.67, 130.46, 130.37, 115.78, 115.57, 62.46, 62.26, 61.50, 43.08, 42.75, 38.89, 36.06, 14.27, 14.20.

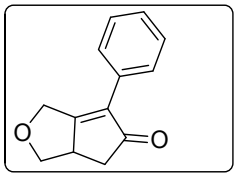


diethyl 6-(4-chlorophenyl)-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate **2e**, white solid. Mp: 84-85 °C, (lit.[7] 83 - 85 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.11 (dt, *J* = 10.8, 3.7 Hz, 2H), 3.54 (d, *J* = 19.3 Hz, 1H), 3.19 (d, *J* = 19.3 Hz, 1H), 3.13 - 2.97 (m, 2H), 2.81 - 2.70 (m, 1H), 2.23 (dd, *J* = 18.0, 3.3 Hz, 1H), 1.69 (t, *J* = 12.7 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR

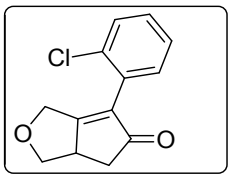
(101 MHz, $CDCl_3$) δ 206.85, 179.64, 171.57, 170.73, 134.49, 131.72, 130.04, 129.89, 122.48, 62.37, 62.16, 61.36, 43.09, 42.65, 38.70, 36.01, 14.16, 14.09.



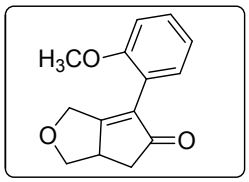
diethyl 6-(4-bromophenyl)-5-oxo-3,3a,4,5-tetrahydropentalene-2,2(1H)-dicarboxylate **2f**, white solid. Mp: 94 - 95 °C, (lit.[7] 94 - 95 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.11 (dt, *J* = 10.8, 3.7 Hz, 2H), 3.54 (d, *J* = 19.3 Hz, 1H), 3.19 (d, *J* = 19.3 Hz, 1H), 3.13 - 2.97 (m, 1H), 2.81 - 2.70 (m, 2H), 2.23 (dd, *J* = 18.0, 3.3 Hz, 1H), 1.69 (t, *J* = 12.7 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.85, 179.64, 171.57, 170.73, 134.49, 131.72, 130.04, 129.89, 122.48, 62.37, 62.16, 61.36, 43.09, 42.65, 38.70, 36.01, 14.16, 14.09.



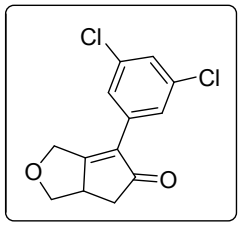
2-phenyl-7-oxabicyclo[3.3.0]oct-1-en-3-one **2g**, light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.45 - 7.34 (m, 3H), 4.95 (d, *J* = 16.3 Hz, 1H), 4.60 (d, *J* = 16.2 Hz, 1H), 4.38 (t, *J* = 7.6 Hz, 1H), 3.40 – 3.18 (m, 2H), 2.86 (dd, *J* = 17.7, 6.2 Hz, 1H), 2.35 (dd, *J* = 17.6, 3.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.99, 177.52, 134.92, 130.74, 128.81, 128.79, 128.19, 127.86, 71.54, 66.46, 43.46, 40.48.



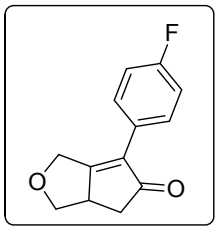
3a,4-dihydro-6-(2-chlorophenyl)-1H-cyclopenta[c]furan-5-one **2h**, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 - 7.45 (m, 4 H), 4.74 (d, J = 15.0 Hz, 1 H), 4.42 (d, J = 15.0 Hz, 1 H), 4.40 (d, dd, J = 12.0, 6.0 Hz, 1 H), 3.42 (m, 1 H), 3.36 (dd, J = 12.0, 6.0 Hz, 1 H), 2.87 (dd, J = 17.9, 6.0 Hz, 1H), 2.36 (dd, J = 17.9, 3.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz,): δ 206.5, 180.6, 134.1, 133.4, 131.3, 130.2, 130.1, 129.7, 126.9, 72.3, 67.0, 43.8, 39.9.



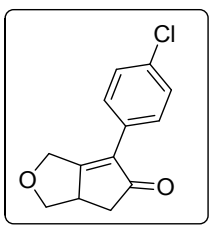
3a,4-dihydro-6-(2-methoxyphenyl)-1H-cyclopenta[c]furan-5-one **2i**, colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 7.04 (d, J = 8.0 Hz, 1H), 6.90 (dd, J = 2.5 Hz, 8.0 Hz, 1H), 4.92 (d, J = 16.0 Hz, 1H), 4.59 (d, J = 16.0 Hz, 1H), 4.37 (t, J = 7.5 Hz, 1H), 3.82 (s, 3H), 3.29-3.33 (m, 1H), 3.23 (dd, J = 7.5 Hz, 11.5 Hz, 1H), 2.84 (dd, J = 6.5 Hz, 17.5 Hz, 1H), 2.33 (dd, J = 4.0 Hz, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 206.7, 177.7, 159.6, 134.5, 131.8, 129.6, 120.5, 114.3, 113.4, 71.3, 66.3, 55.2, 43.3, 40.3.



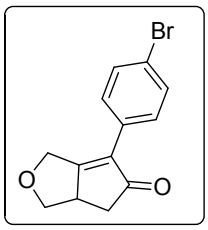
6-(3,5-dichlorophenyl)-3a,4-dihydro-1H-cyclopenta[c]furan-5(3H)-one **2j**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H), 7.25 (s, 1H), 4.87 (d, *J* = 16.7 Hz, 1H), 4.51 (d, *J* = 16.7 Hz, 1H), 4.32 (t, *J* = 7.7 Hz, 1H), 3.28 (d, *J* = 6.6 Hz, 1H), 3.18 (dd, *J* = 11.1, 7.9 Hz, 1H), 2.78 (dd, *J* = 17.8, 6.3 Hz, 1H), 2.27 (dd, *J* = 17.8, 3.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 205.80, 180.03, 135.33, 133.47, 132.39, 128.63, 126.29, 71.35, 66.26, 43.77, 40.20.



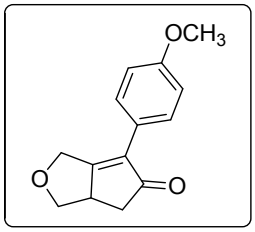
2-(4-fluorophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one **2k**, yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (dd, J = 5.5 Hz, 8.0 Hz, 2H), 7.09 (t, J = 8.0 Hz, 2H), 4.91 (d, J = 16.5 Hz, 1H), 4.56 (d, J = 16.5 Hz, 1H), 4.37 (t, J = 7.5 Hz, 1H), 3.29-3.33 (m, 1H), 3.24 (dd, J = 7.5 Hz, 11.0 Hz, 1H), 2.84 (dd, J = 6.5 Hz, 18.0 Hz, 1H), 2.33 (dd, J = 3.5 Hz, 17.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 204.1, 177.0, 161.7, 133.6, 129.8 (d, J = 8.4 Hz), 126.7, 115.6 (d, J = 22.0 Hz), 71.3, 66.2, 43.2, 40.1.



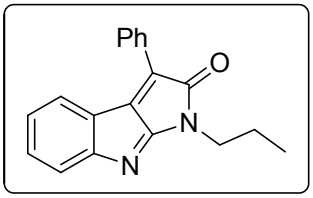
2-(4-chlorophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one **2l**, yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.48 (d, J = 9.0 Hz, 2H), 7.38 (d, J = 9.0 Hz, 1H), 4.92 (d, J = 16.0 Hz, 1H), 4.57 (d, J = 16.0 Hz, 1H), 4.38 (t, J = 8.0 Hz, 1H), 3.30 - 3.37 (m, 1H), 3.25 (dd, J = 7.5 Hz, 11.0 Hz, 1H), 2.85 (dd, J = 6.0 Hz, 18.0 Hz, 1H), 2.33 (dd, J = 3.5 Hz, 18.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 101 MHz) δ 205.3, 175.1, 159.7, 134.0, 129.3, 123.3, 114.1, 71.1, 66.3, 43.2, 40.2.



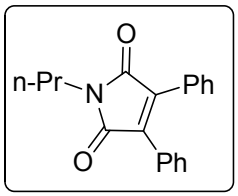
2-(4-bromophenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one **2m**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 - 7.32 (m, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 4.74 (d, *J* = 16.4 Hz, 1H), 4.39 (d, *J* = 16.5 Hz, 1H), 4.20 (t, *J* = 7.4 Hz, 1H), 3.25 - 3.01 (m, 2H), 2.67 (dd, *J* = 17.7, 6.1 Hz, 1H), 2.26 - 2.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.59, 178.12, 133.74, 131.93, 129.61, 122.99, 71.40, 66.36, 43.56, 40.32.



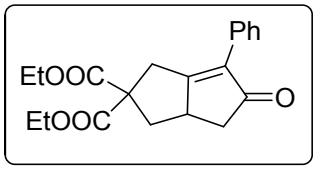
2-(4-Methoxyphenyl)-7-oxabicyclo[3.3.0]oct-1-en-3-one **2n**, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 6.3 Hz, 2H), 6.97 (s, 2H), 4.93 (d, *J* = 16.0 Hz, 1H), 4.60 (d, *J* = 16.2 Hz, 1H), 4.38 (s, 1H), 3.84 (s, 3H), 3.42 - 3.18 (m, 2H), 2.85 (d, *J* = 17.1 Hz, 1H), 2.34 (d, *J* = 17.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.24, 175.25, 159.84, 134.22, 129.40, 123.27, 114.09, 71.42, 66.36, 55.31, 43.14, 40.29.



3-Phenyl-1-propylpyrrolo[2,3-b]indol-2-one **2o**, brown solid, mp 128-129 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): 0.99 (t, J = 7.3 Hz, 3H), 1.79 (m, J = 7.3 Hz, 2H), 3.62 (t, J = 7.3Hz, 2H), 6.91 (m, J = 1.2 , 1.2, 7.3Hz, 1H), 7.14 - 7.22 (m, 1H), 7.20 (m, J = 1.2, 7.3, 7.3 Hz, 1H), 7.47-7.57(m, 4H), 7.90-7.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) 11.27, 21.69, 41.70, 120.13, 124.60, 124.63, 124.93, 128.88, 129.15, 129.73, 129.76, 130.55, 132.99, 138.20, 161.92, 172.02, 173.33. IR (KBr/cm^{-1}) 2904, 1724, 1628, 1586, 1427, 1347, 1302, 1154, 750, 732.



N-propyl diphenylmaleinide **2q**, green solid, Mp: 67 - 69 ^{o}C, (lit.[8] 66-68 ^{o}C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 - 7.45 (m, 5H), 7.42 - 7.32 (m, 4H), 3.67 - 3.57 (m, 2H), 1.71 (dd, J = 14.7, 7.4 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.03, 136.19, 130.02, 129.91, 128.84, 128.69, 40.18, 22.10, 11.53.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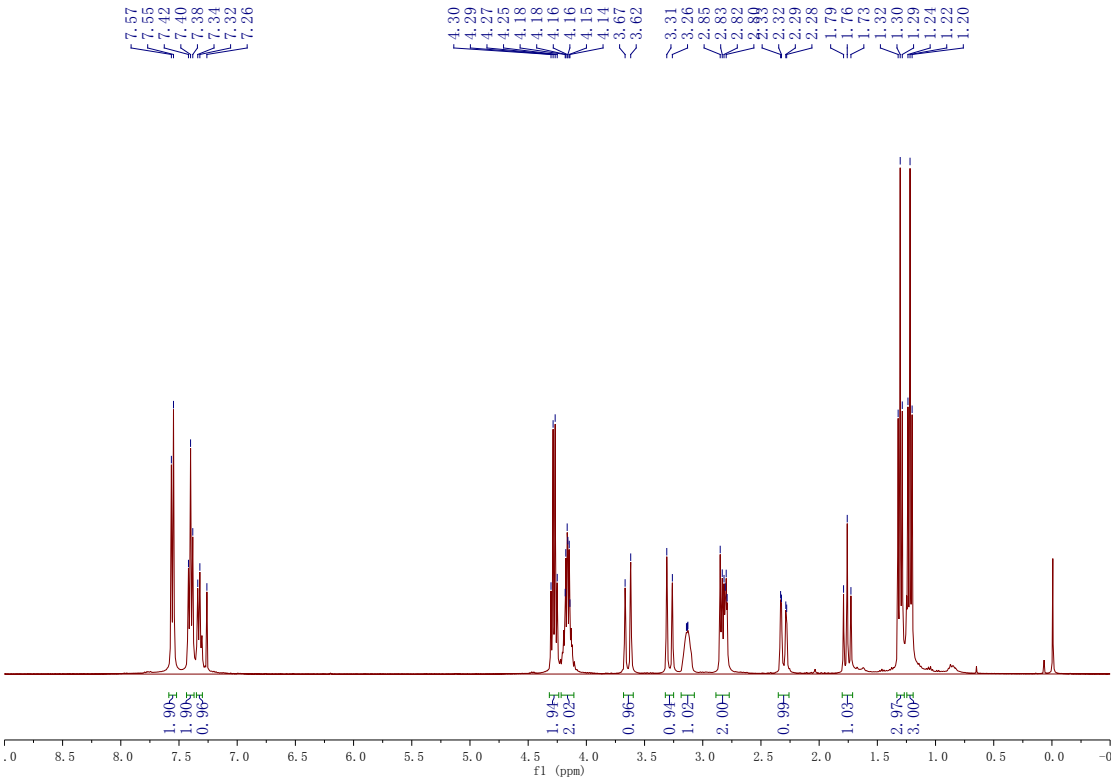
EtOOC
O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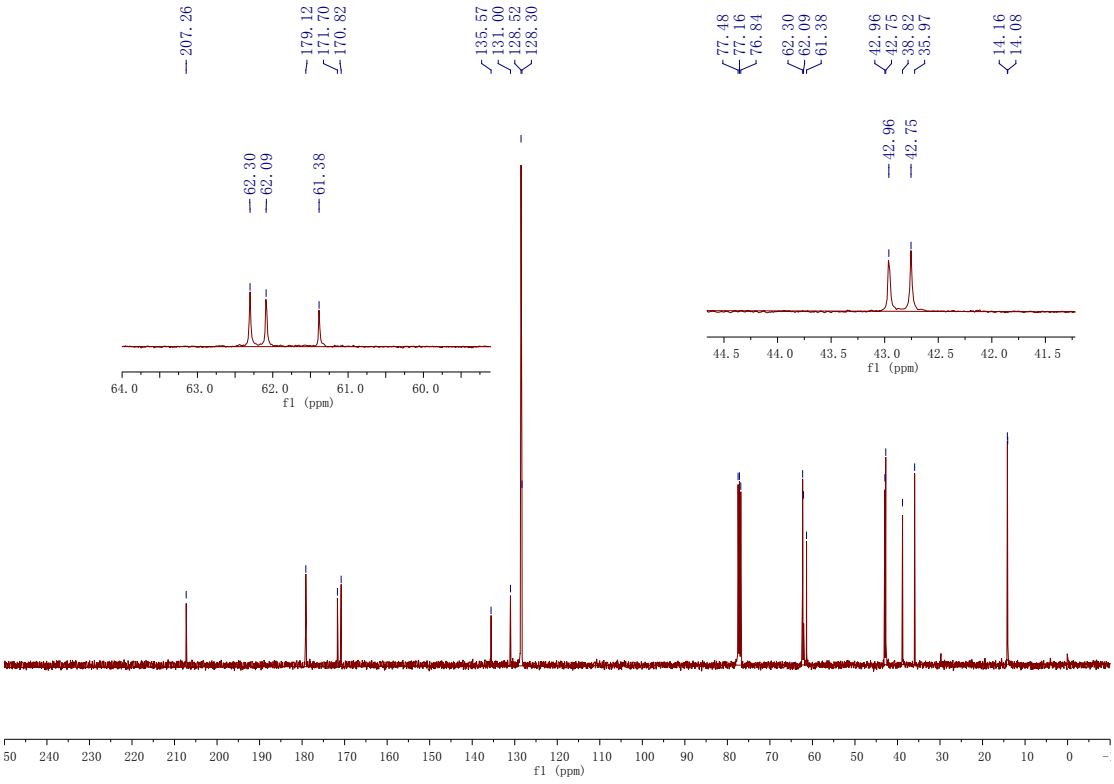
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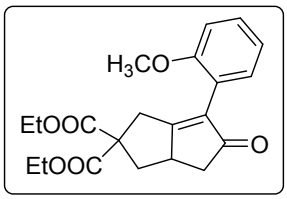
f1 (ppm)
f1 (ppm)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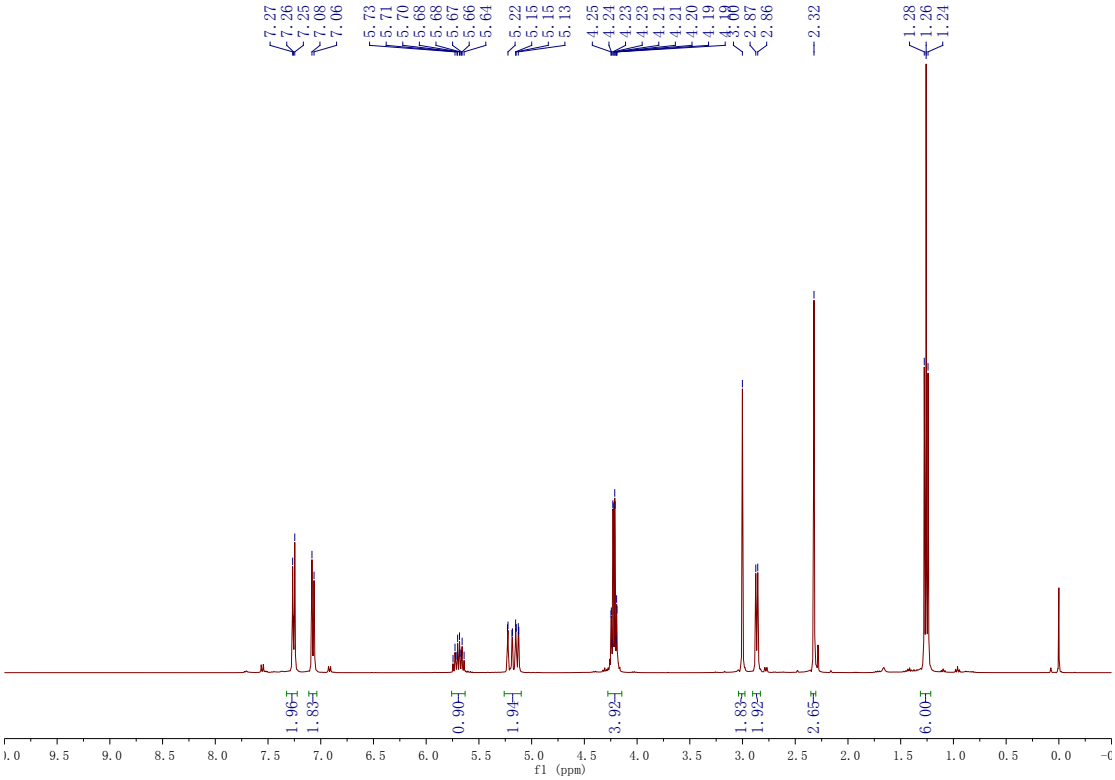
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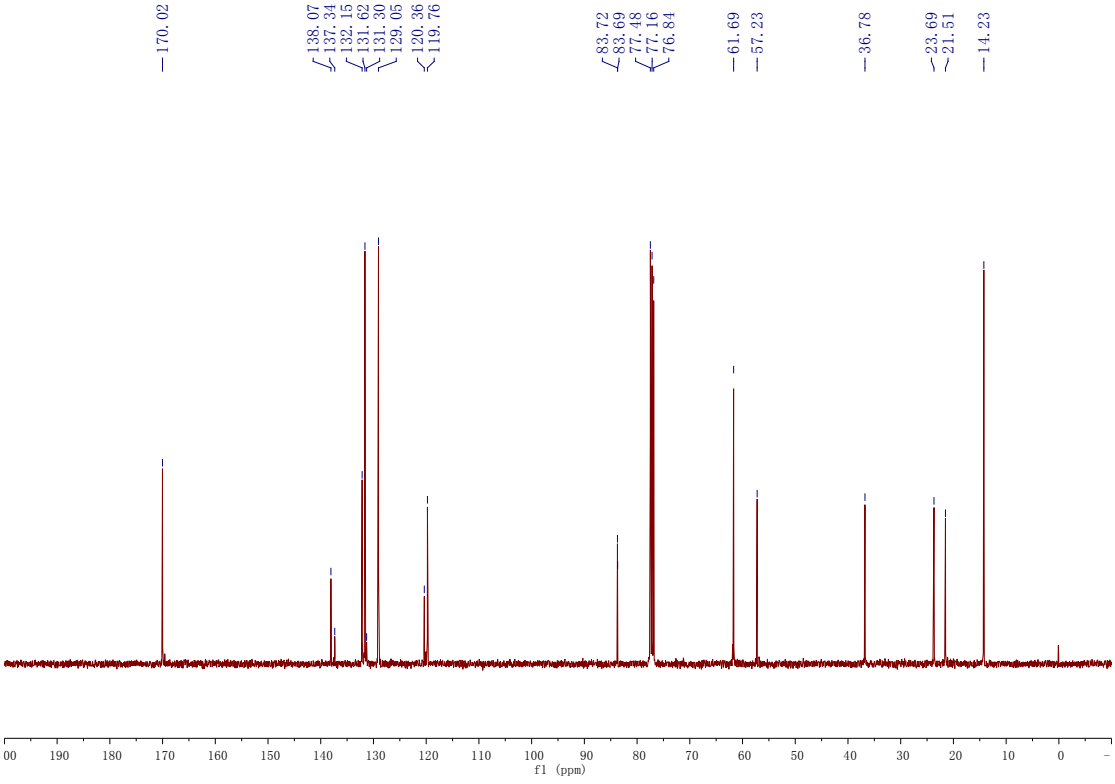
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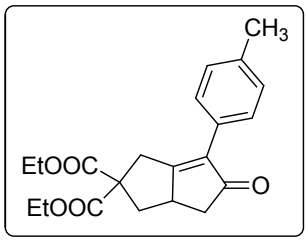
f1 (ppm)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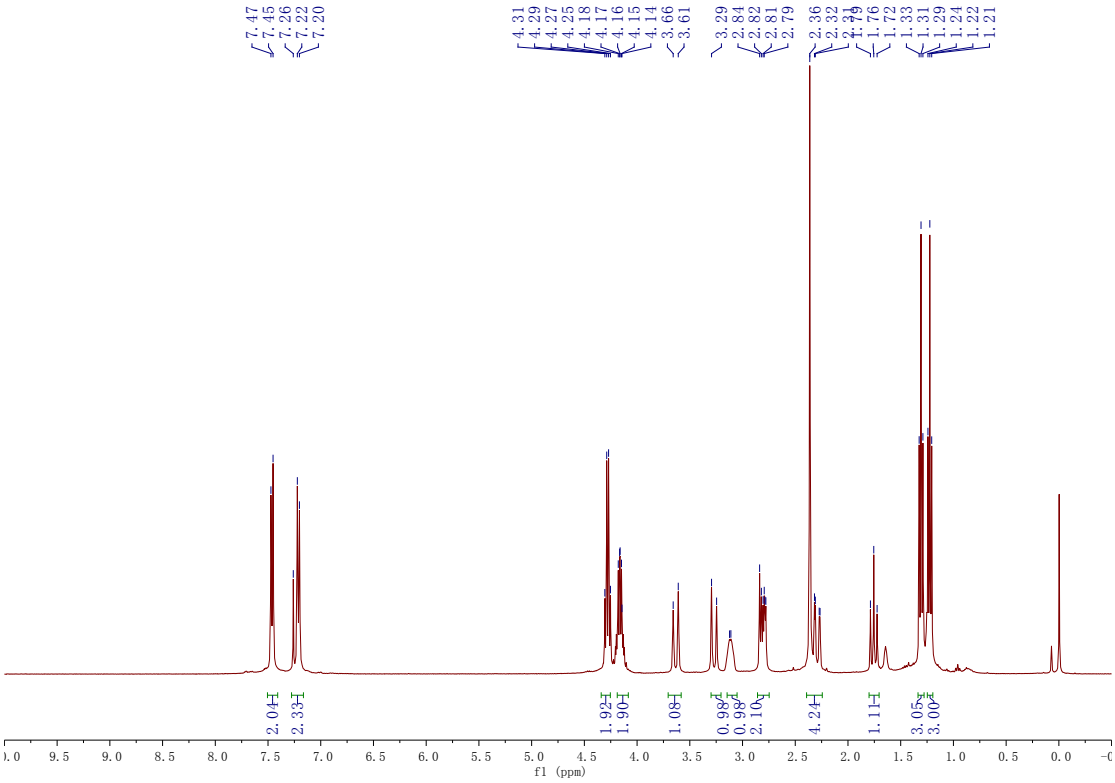
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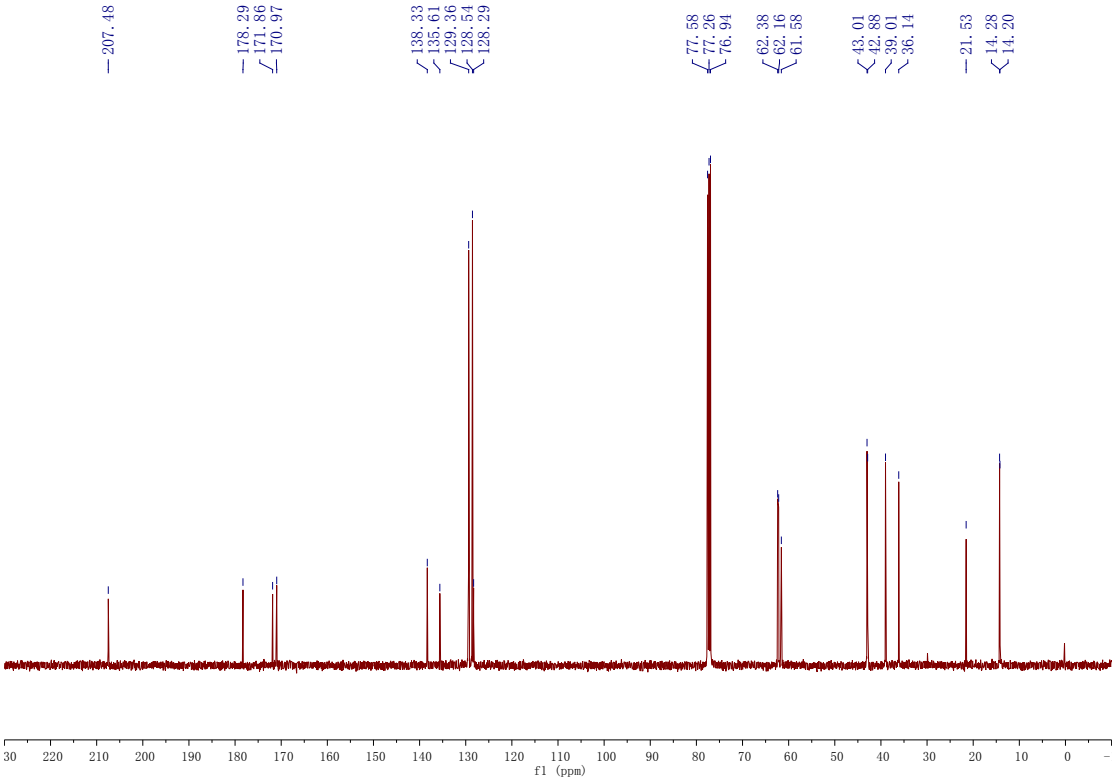
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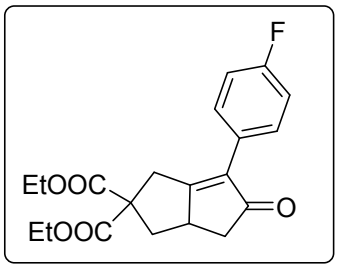
f1 (ppm)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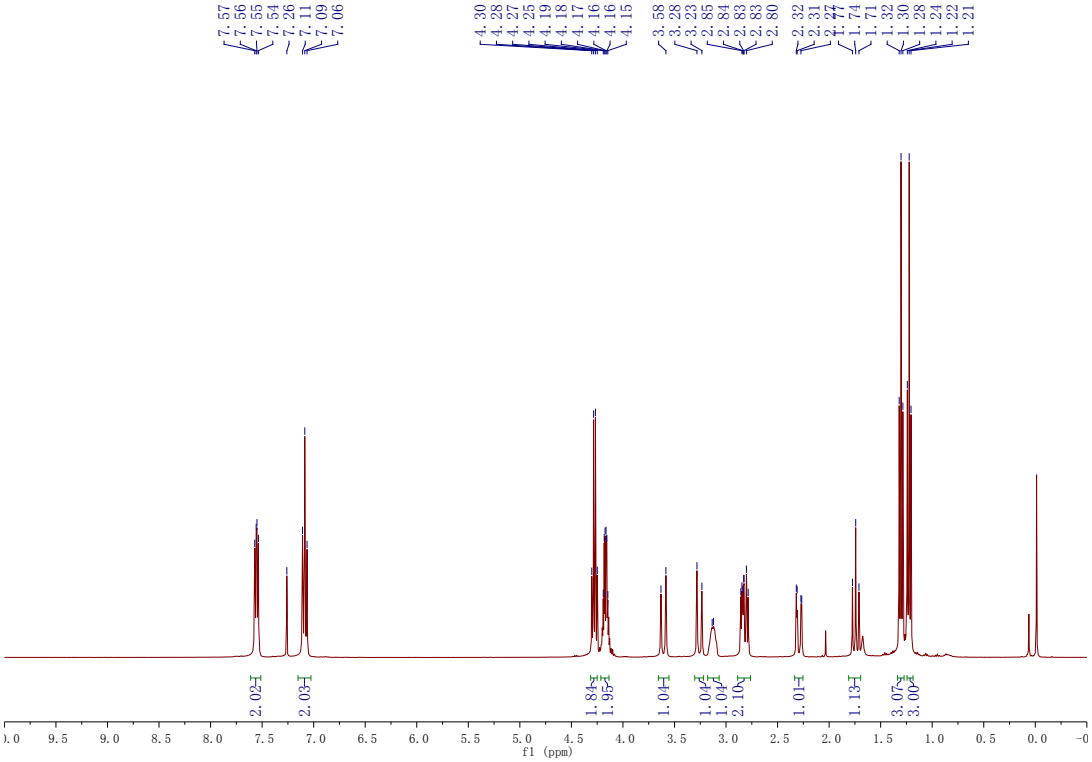
O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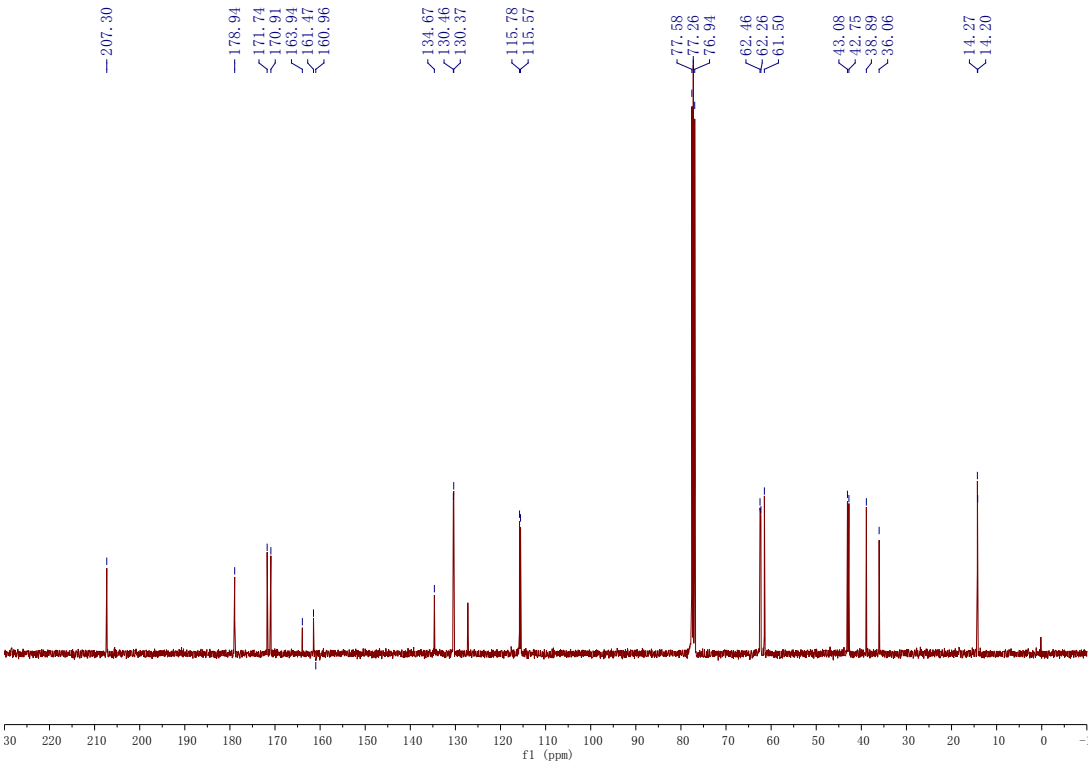
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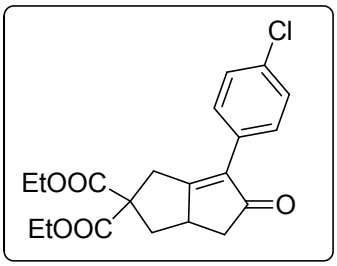
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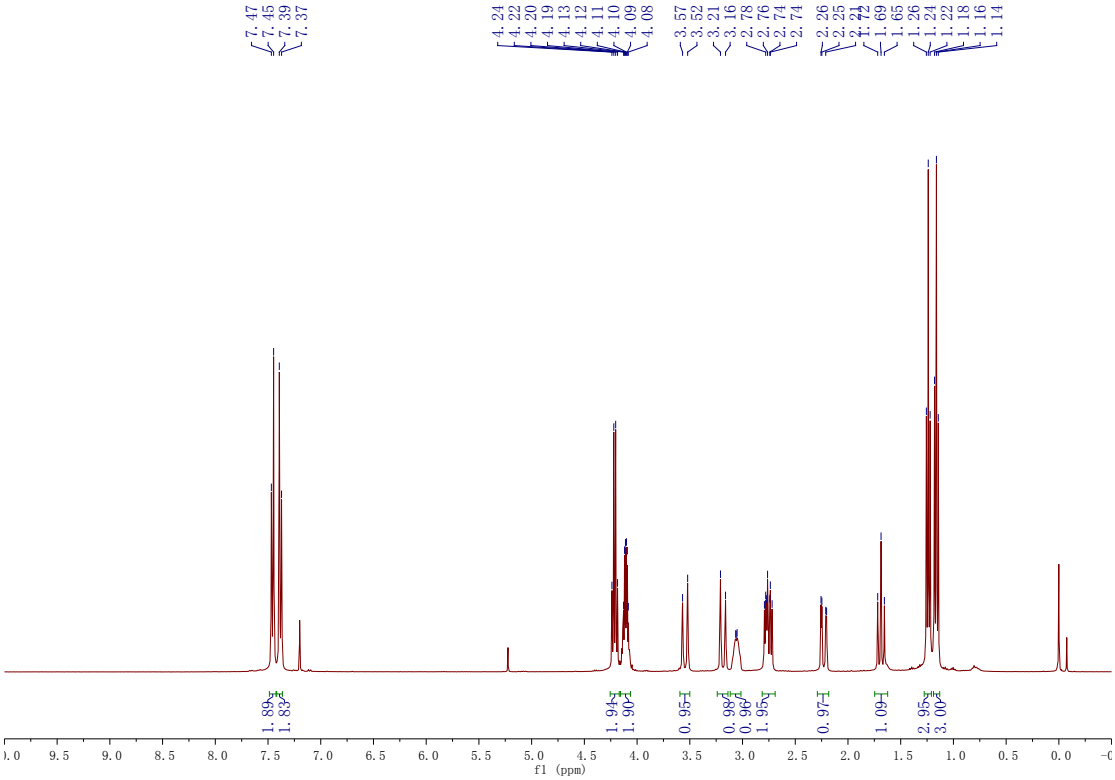
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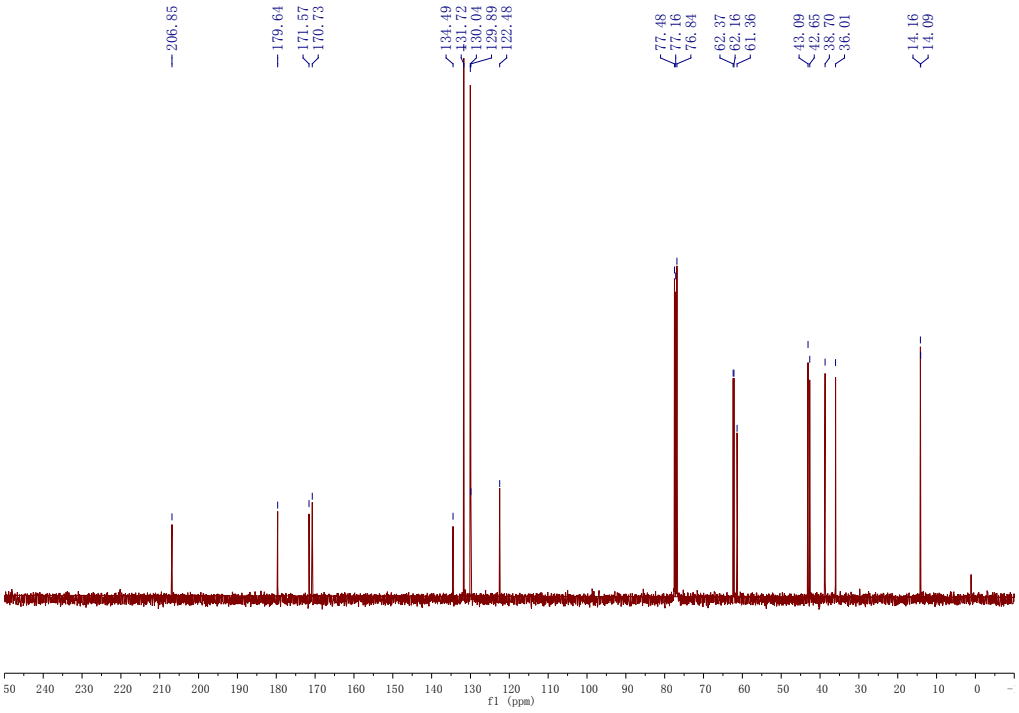
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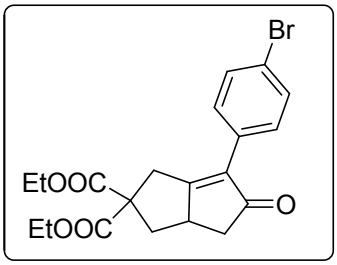
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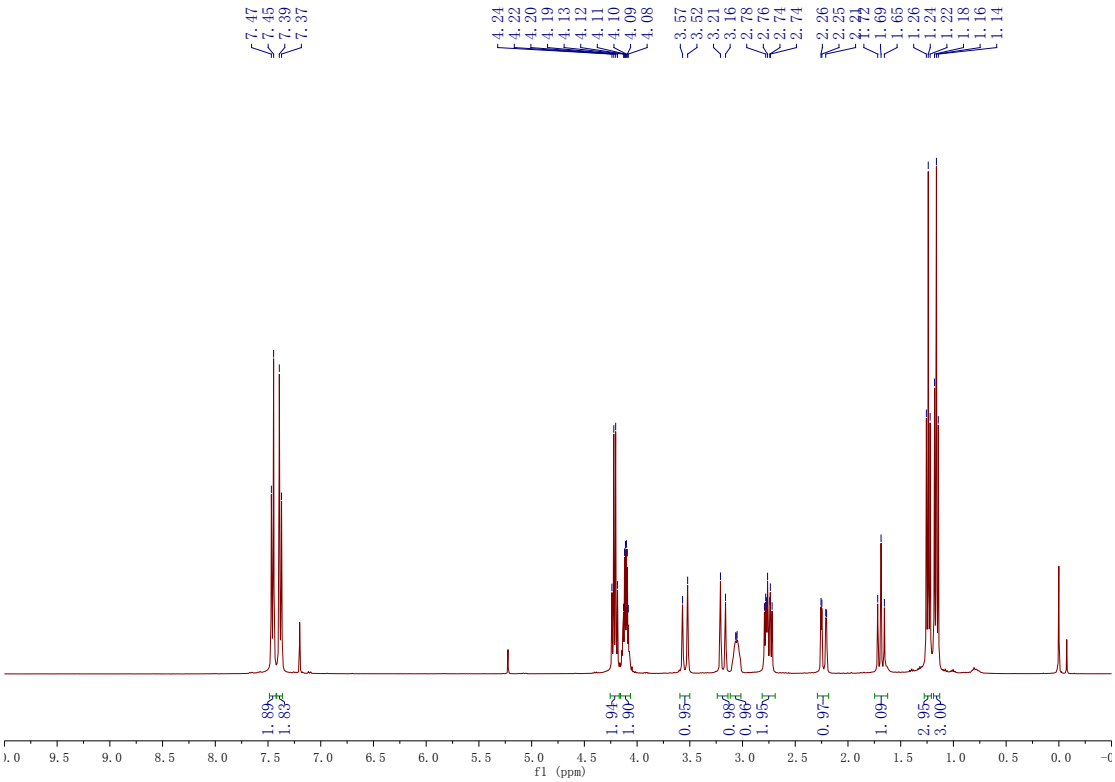
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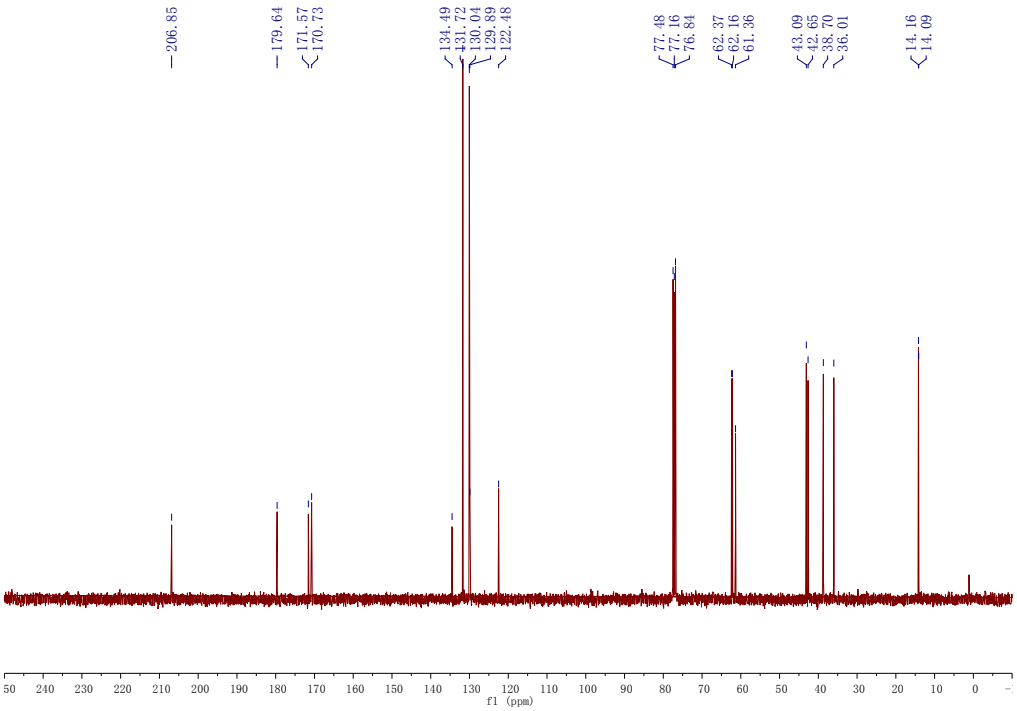
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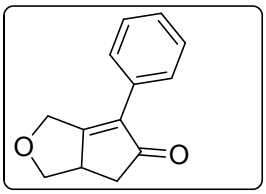
f1 (ppm)



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7.26

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4.40
4.38
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3.24
3.22

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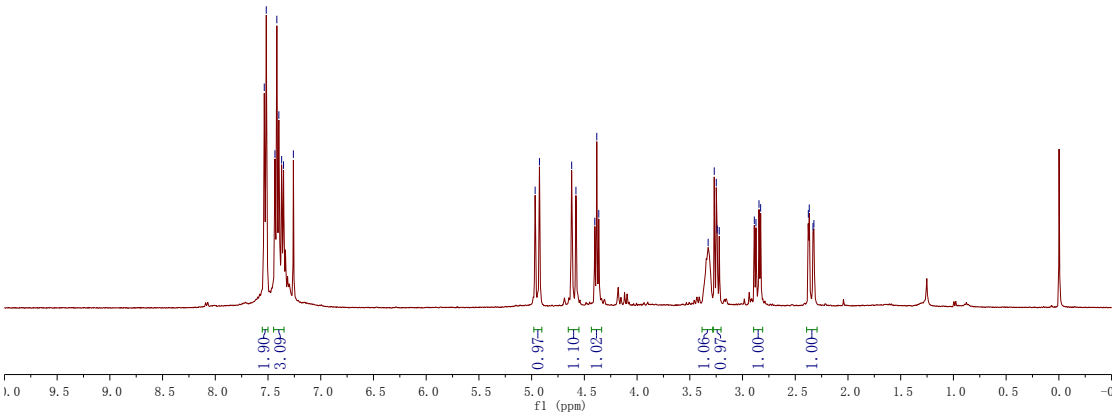
2.32



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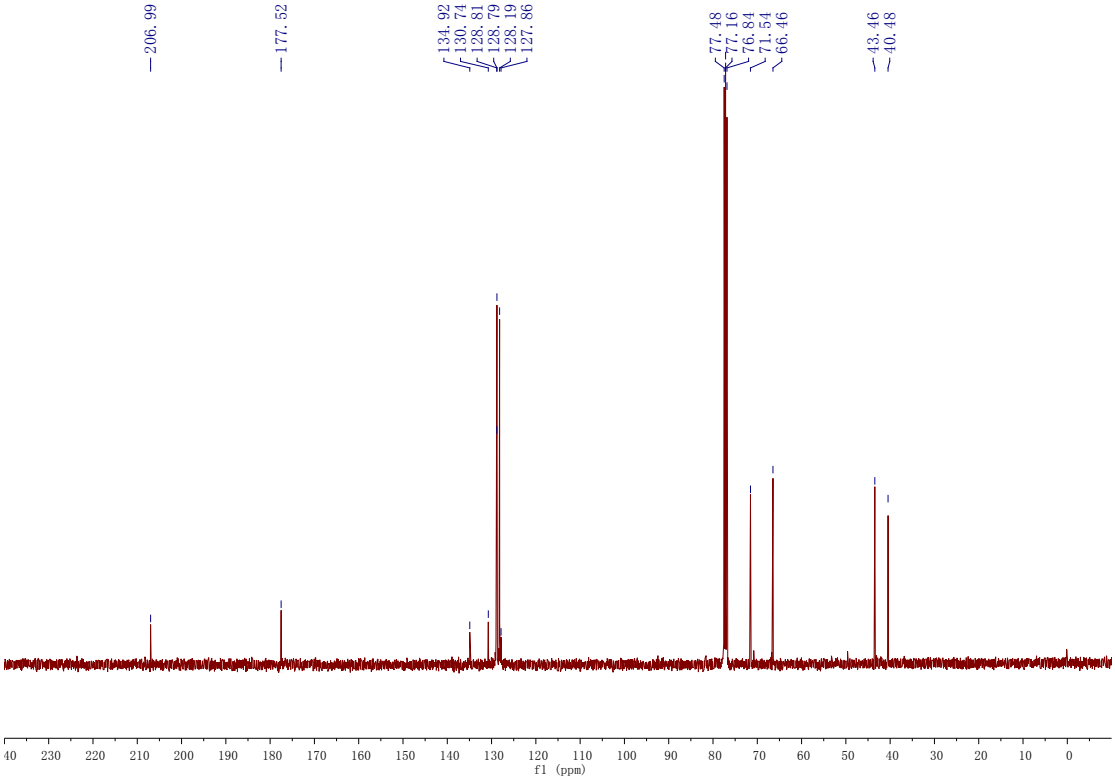
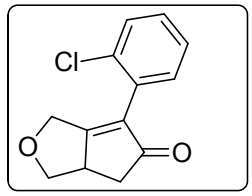
40.48

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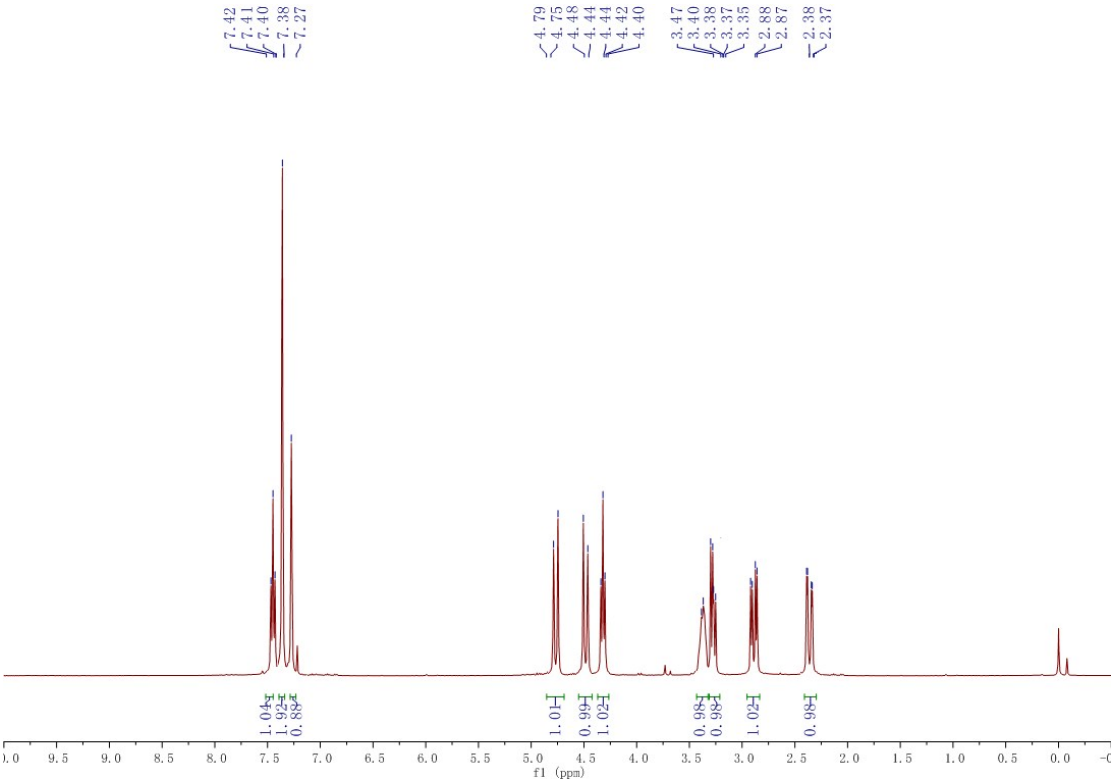
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4.42
4.40
3.47
3.40
3.38
3.37
3.35
2.88
2.87
2.38
2.37
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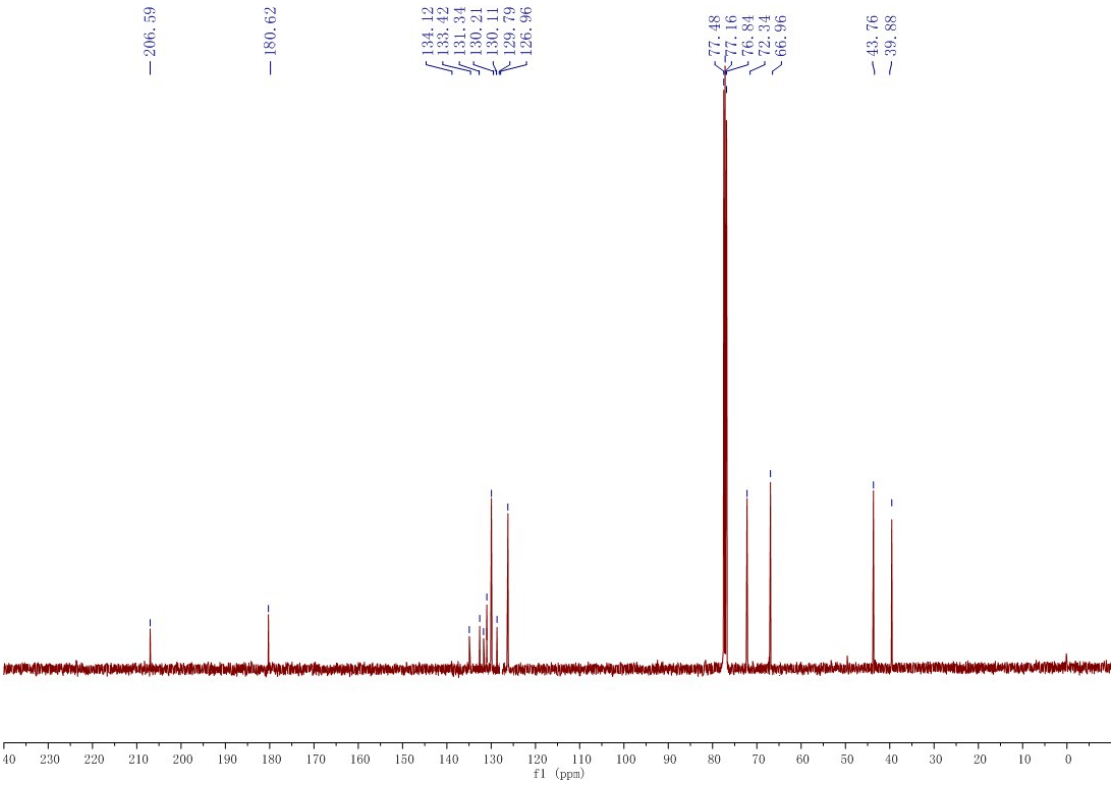
0.88
1.01
0.99
1.02
0.98
0.98
1.02
0.98
f1 (ppm)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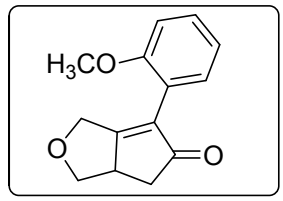
43.76
39.88
f1 (ppm)



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6.87
6.85

4.61
4.57
4.33
4.31
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3.73

3.30
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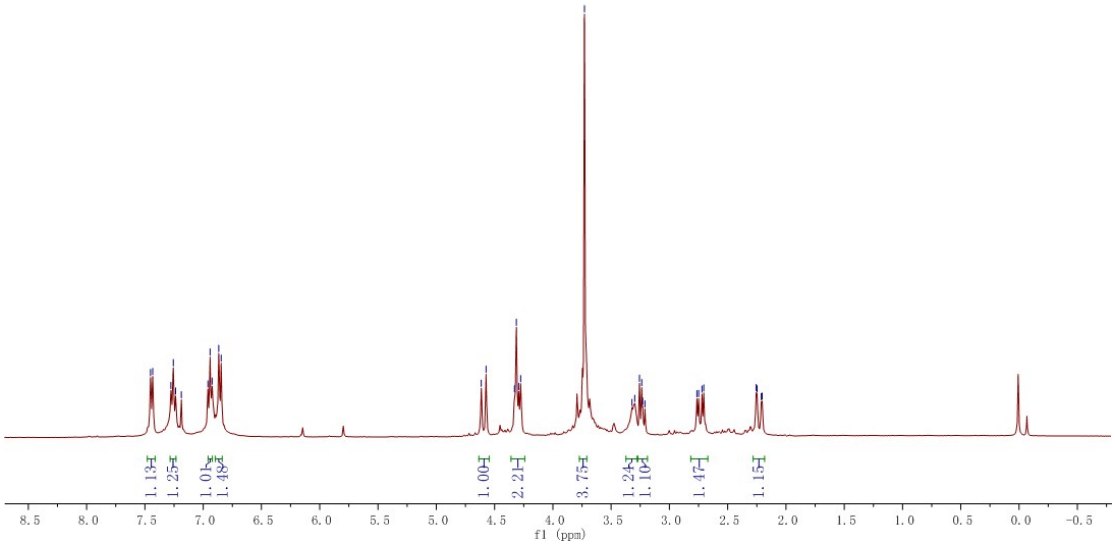
3.23

2.75
2.72
2.25
2.21
2.20



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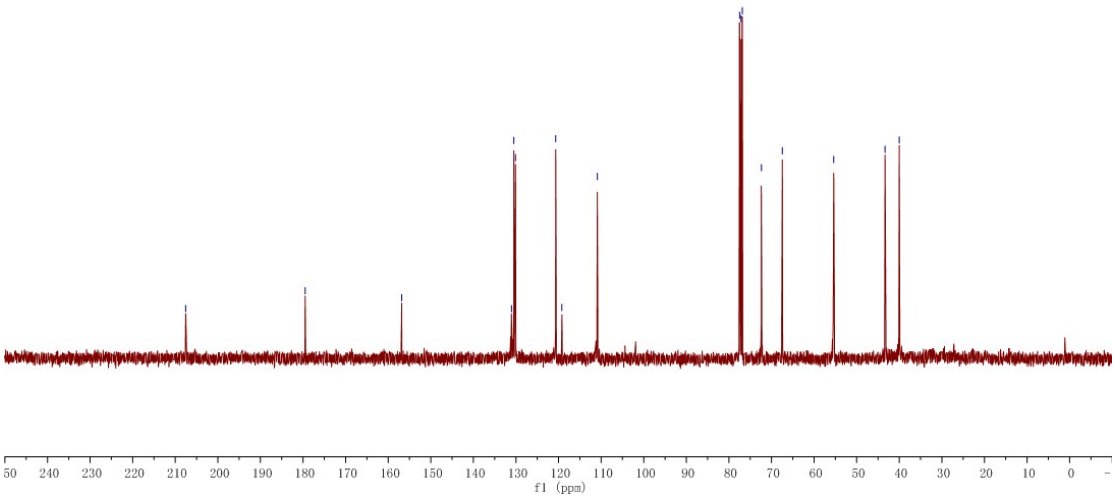
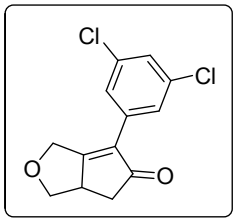
43.33
40.01

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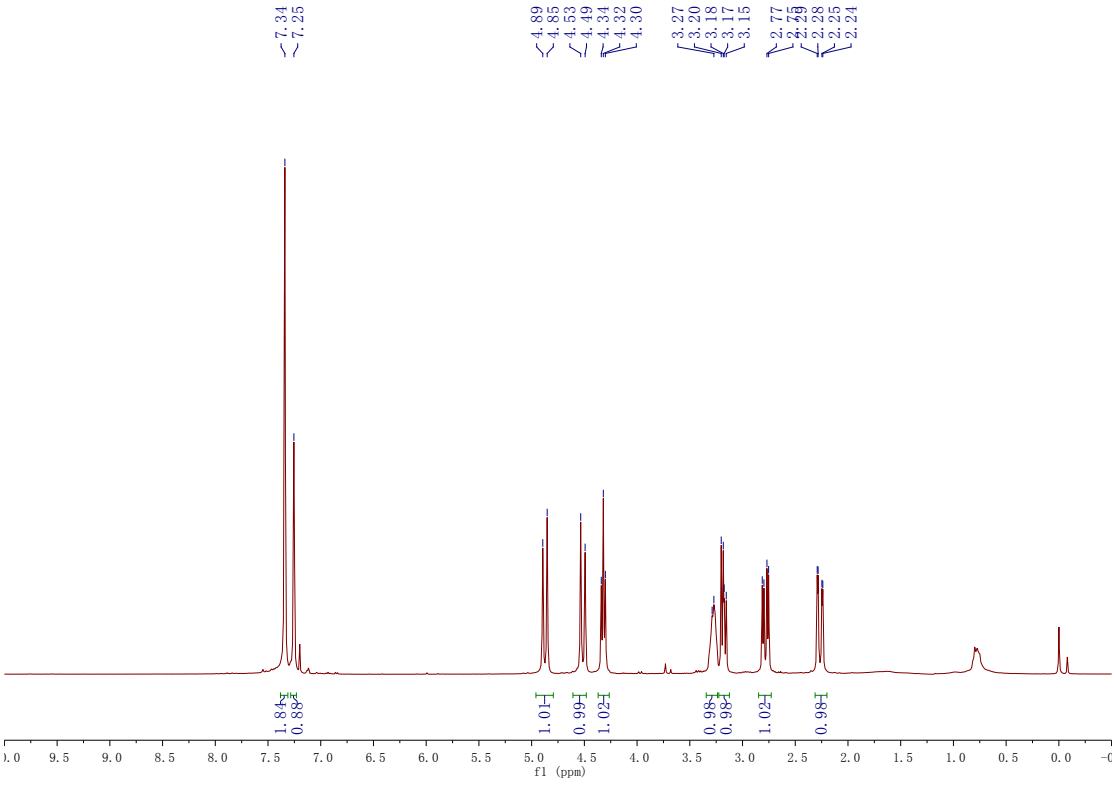
Cl
O
O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3.27
3.20
3.18
3.17
3.15
2.77
2.28
2.25
2.24
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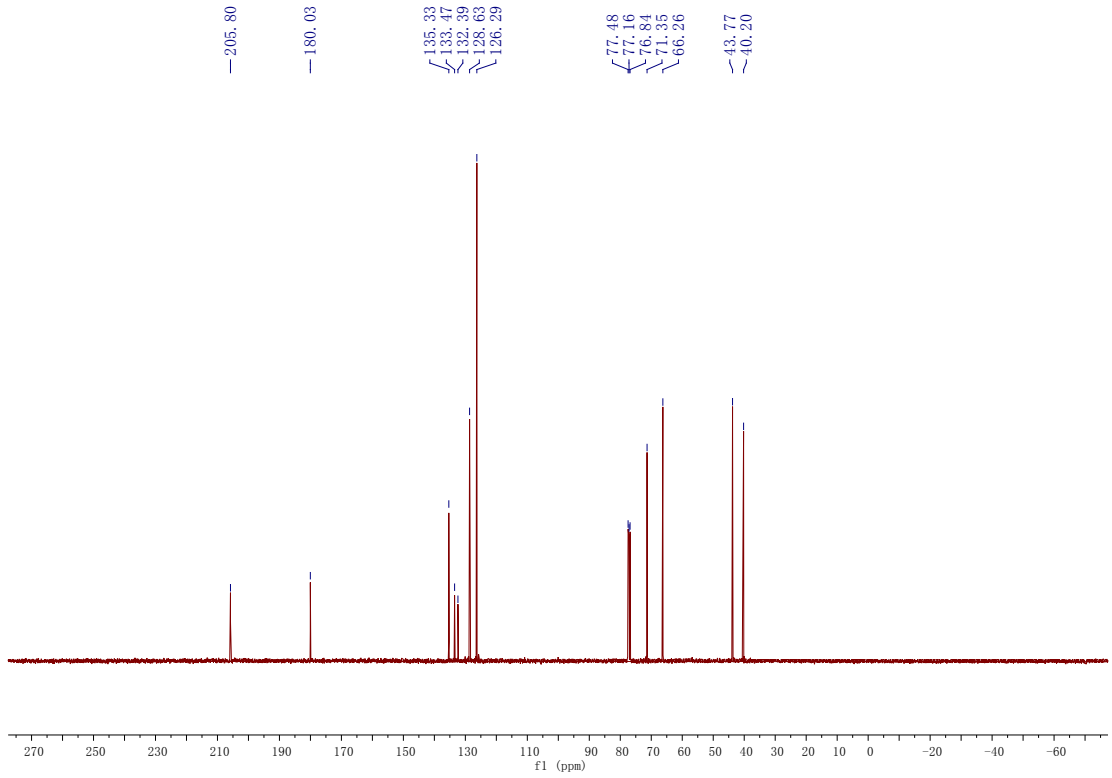
0.88
1.01
0.99
1.02
0.98
0.98
1.02
0.98
f1 (ppm)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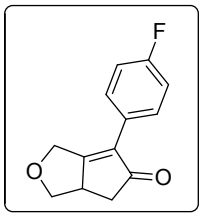
f1 (ppm)



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4.29
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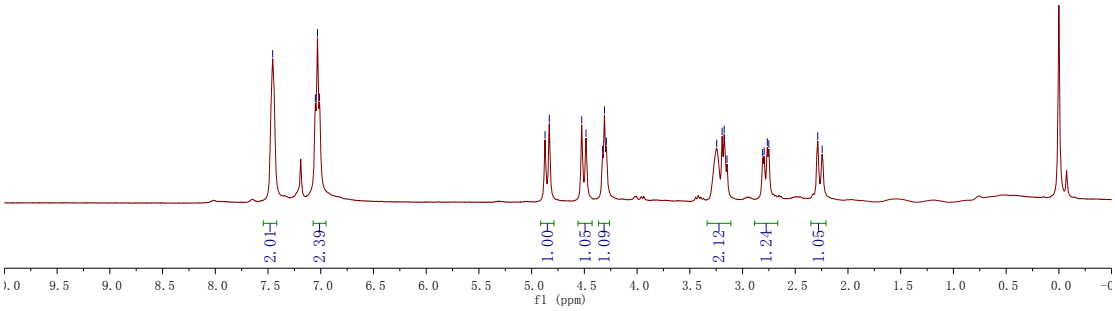
2.24



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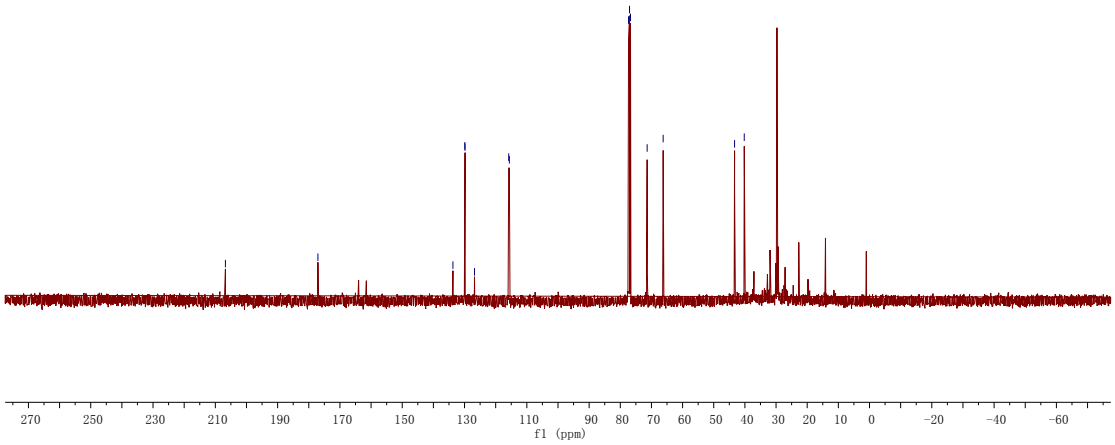

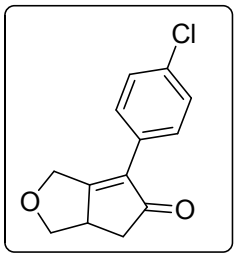

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7.26

4.97
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4.38
4.36

3.37
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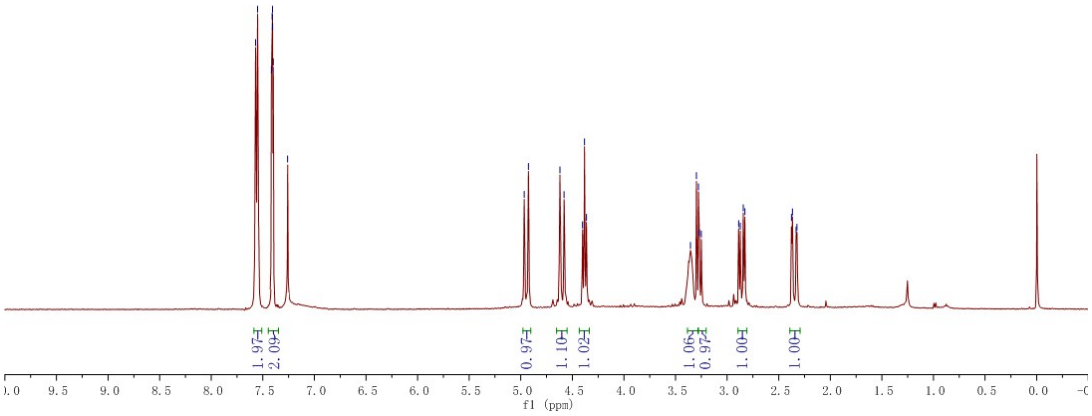
2.32



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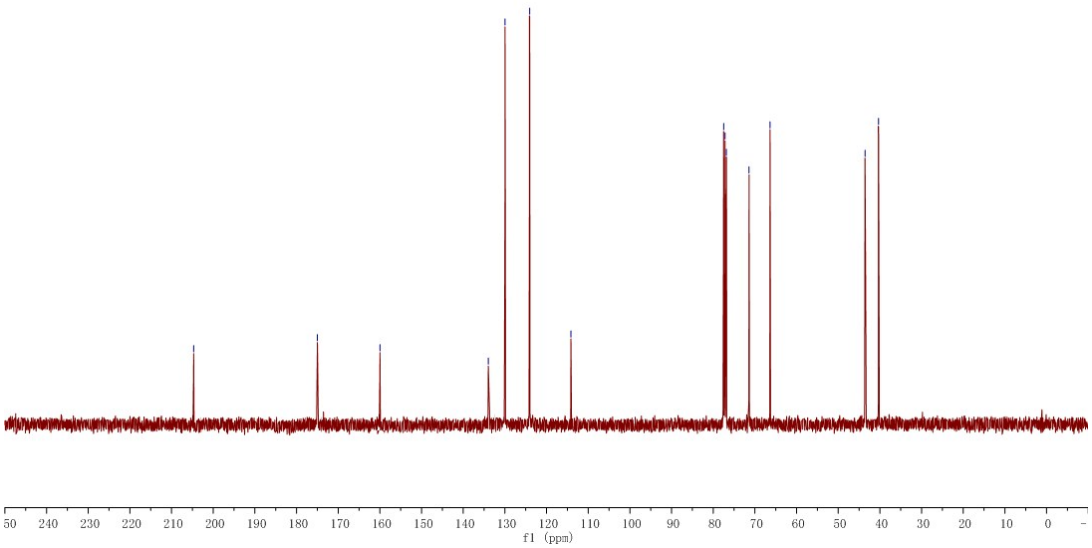

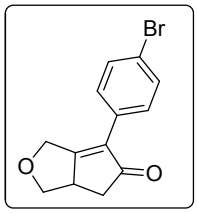
Br
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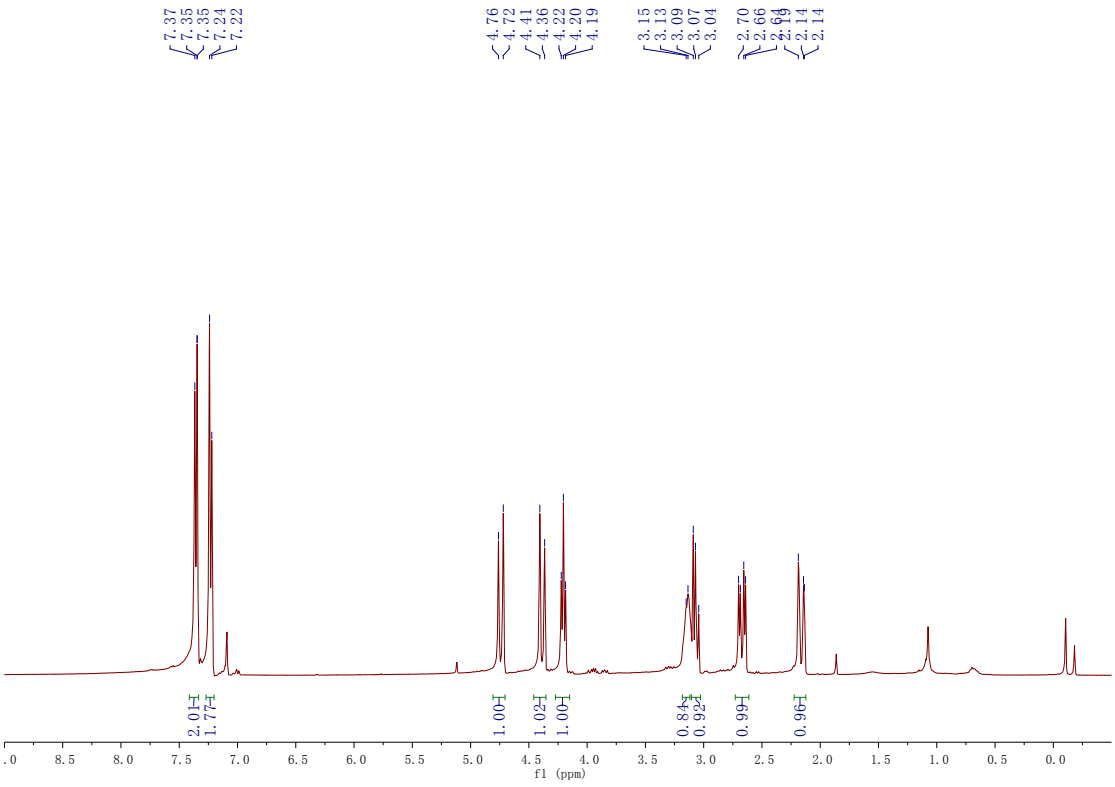
O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4.22
4.20
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3.15
3.13
3.09
3.07
3.04
2.70
2.66
2.64
2.19
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2.14
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1.77
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1.02
1.00
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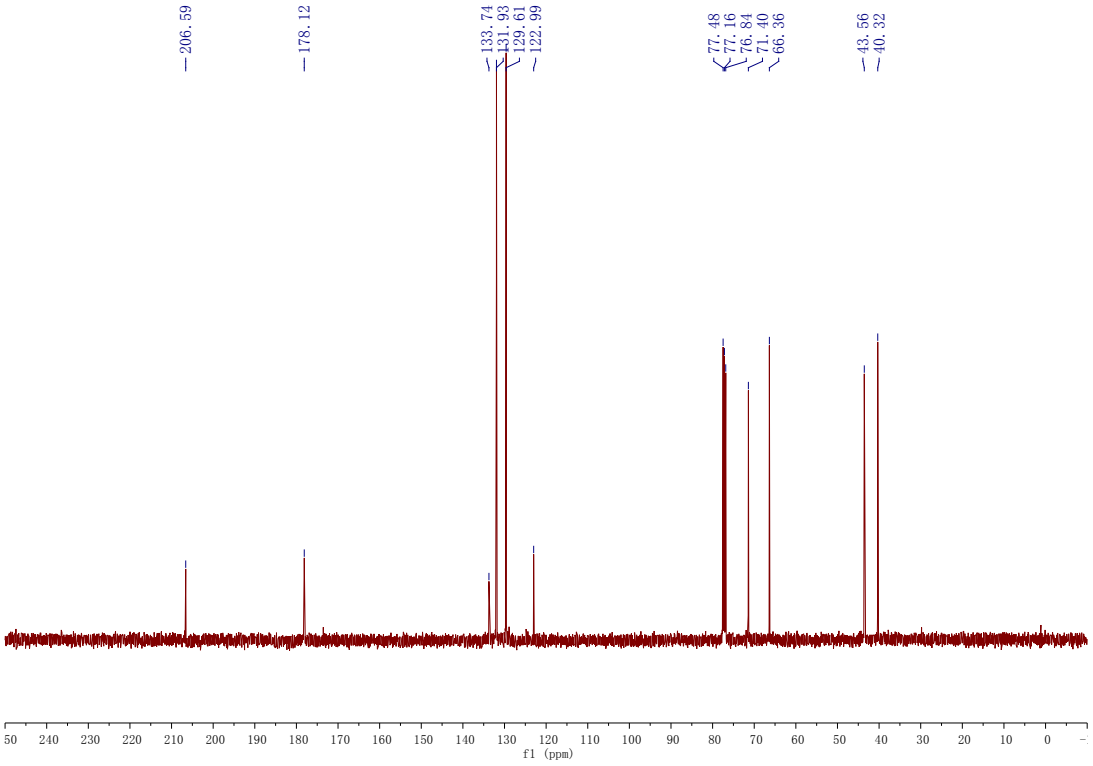
0.92
0.99
0.96
f1 (ppm)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66.36
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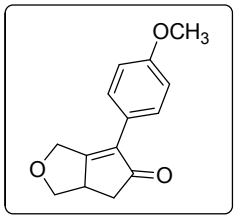
40.32
f1 (ppm)


OCH3
O
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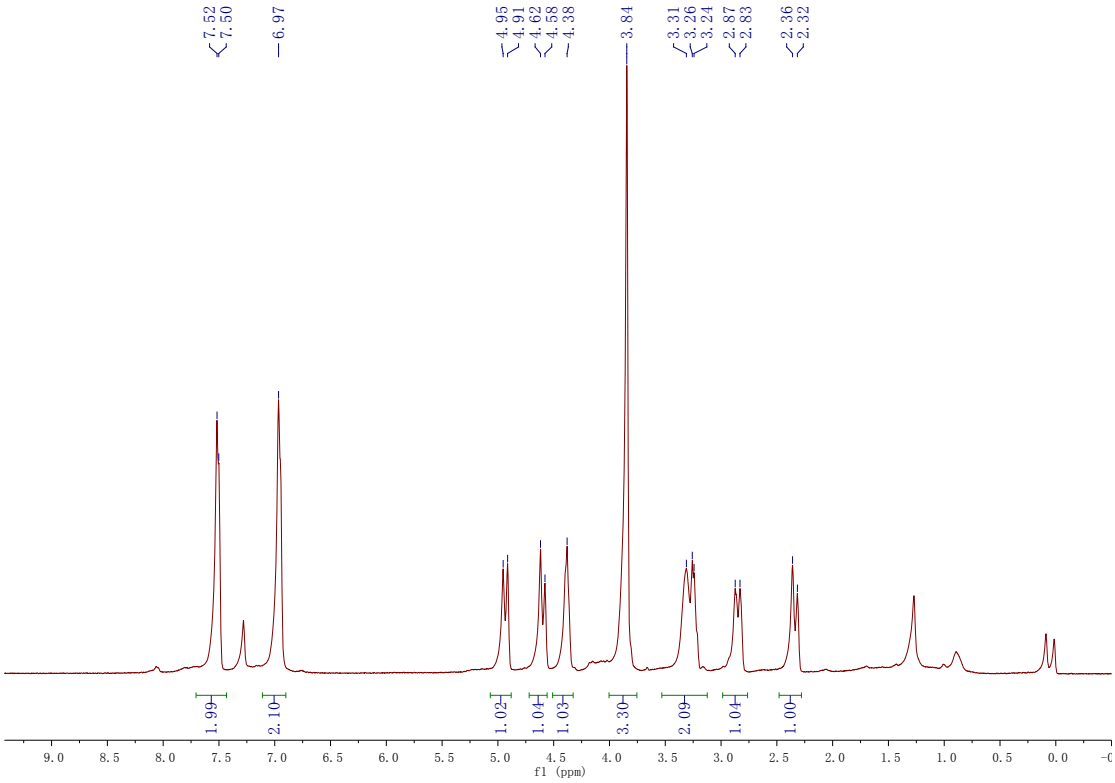
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2.83
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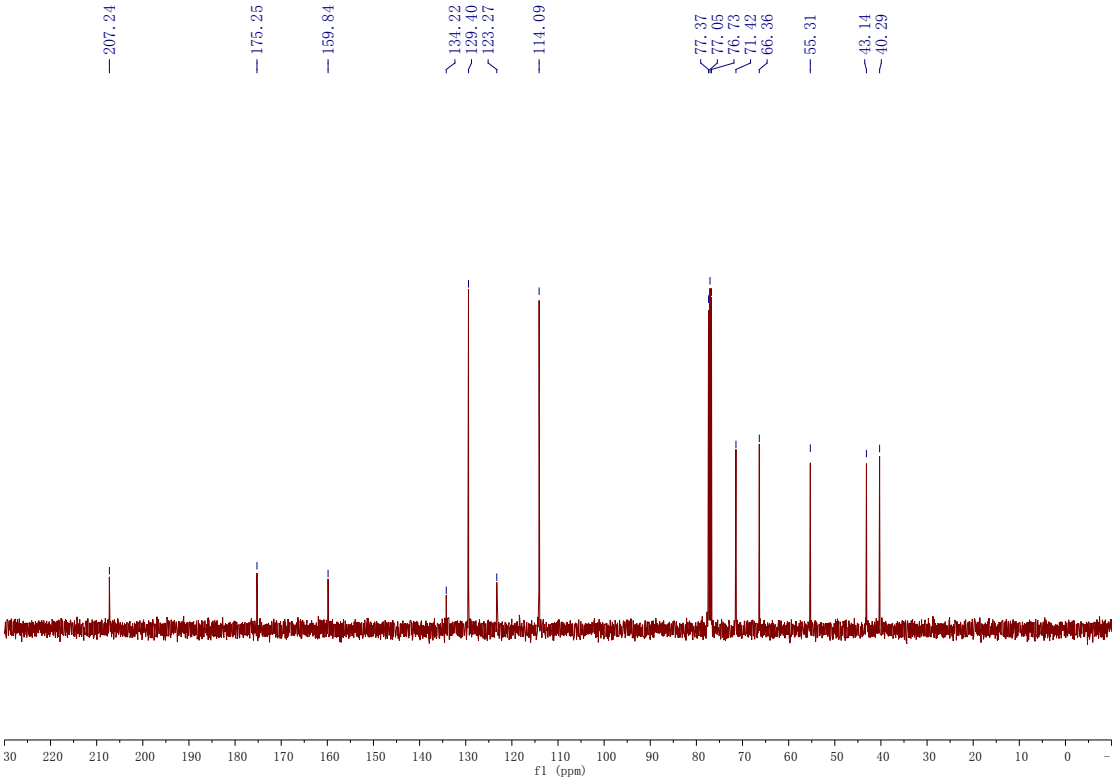
3.30
2.09
1.04
1.00
f1 (ppm)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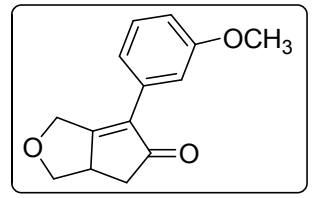
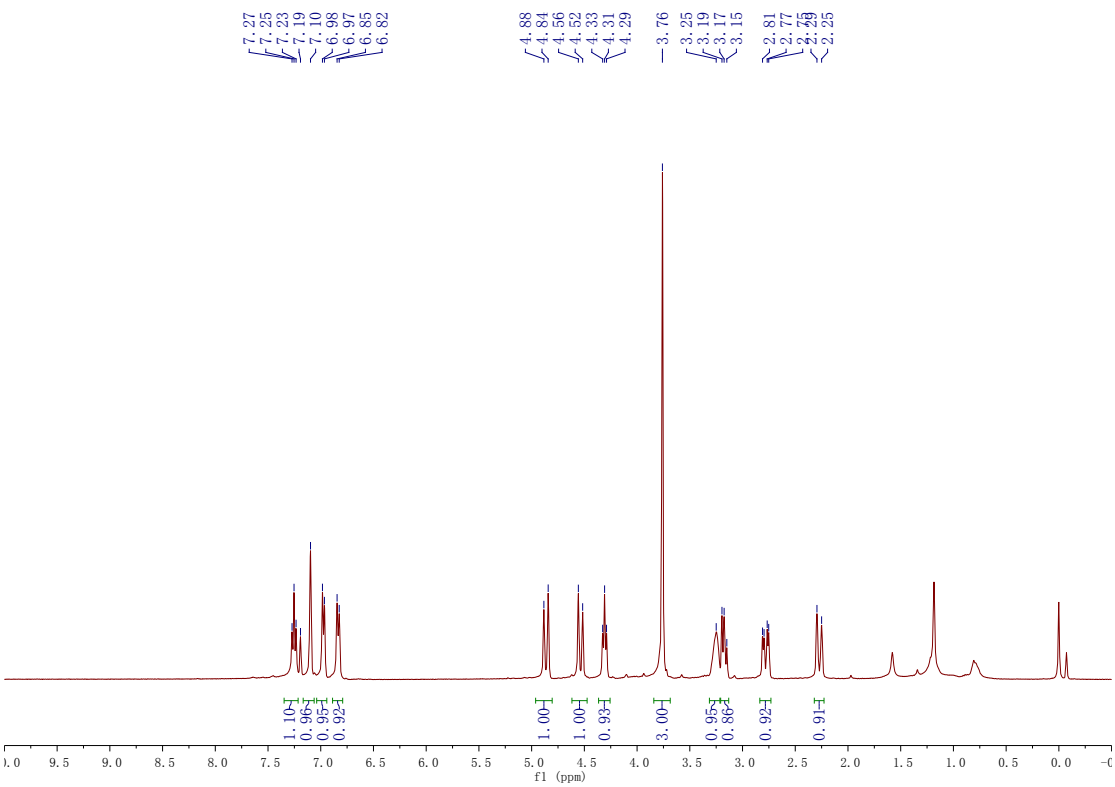
40.29
f1 (ppm)


OCH3
O
O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4.31
4.29
3.76
3.25
3.19
3.17
3.15
2.81
2.77
2.25
1.10
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0.95
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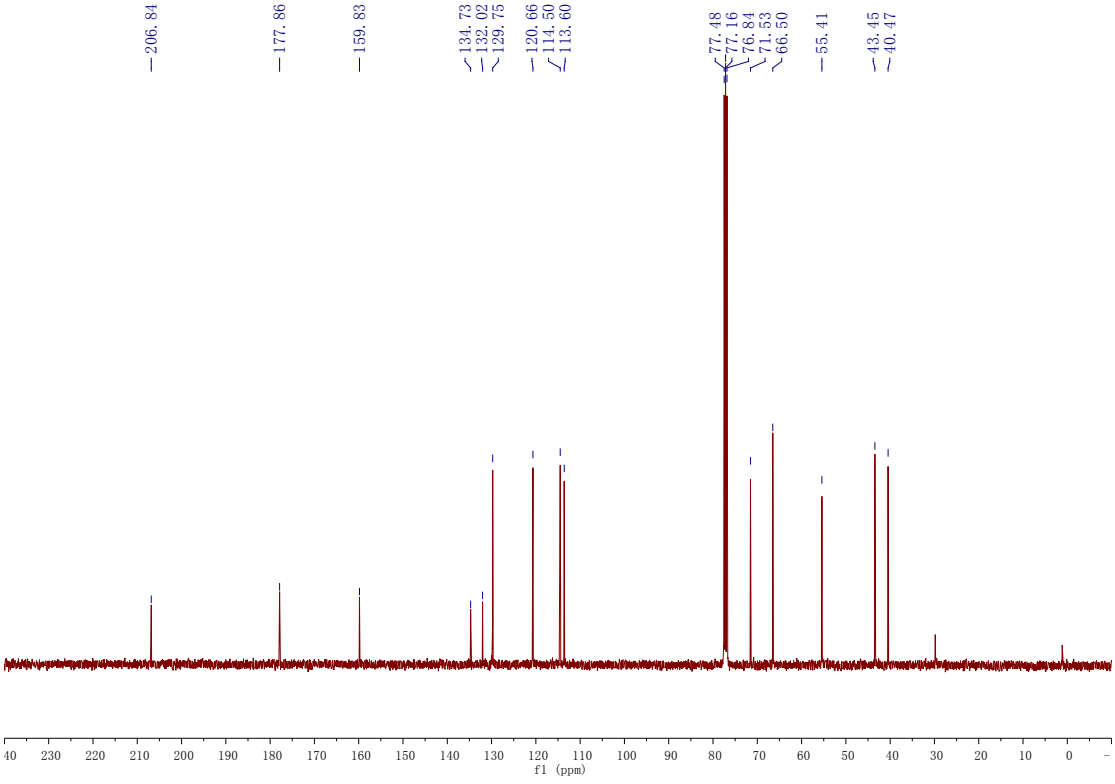
1.00
1.00
0.93
3.00
0.95
0.86
0.92
0.91
f1 (ppm)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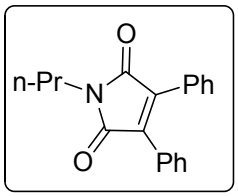
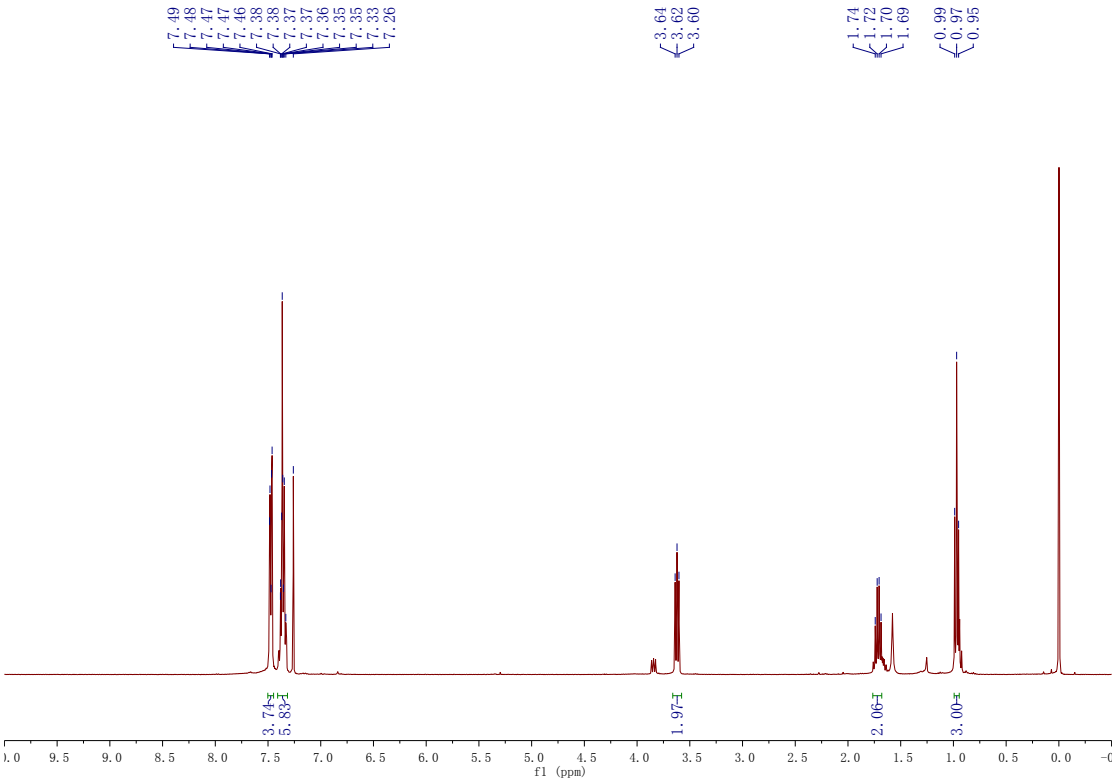
66.50
55.41
43.45
40.47
f1 (ppm)


O
n-Pr
N
Ph
O
Ph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7.33
7.26
3.64
3.62
3.60
1.74
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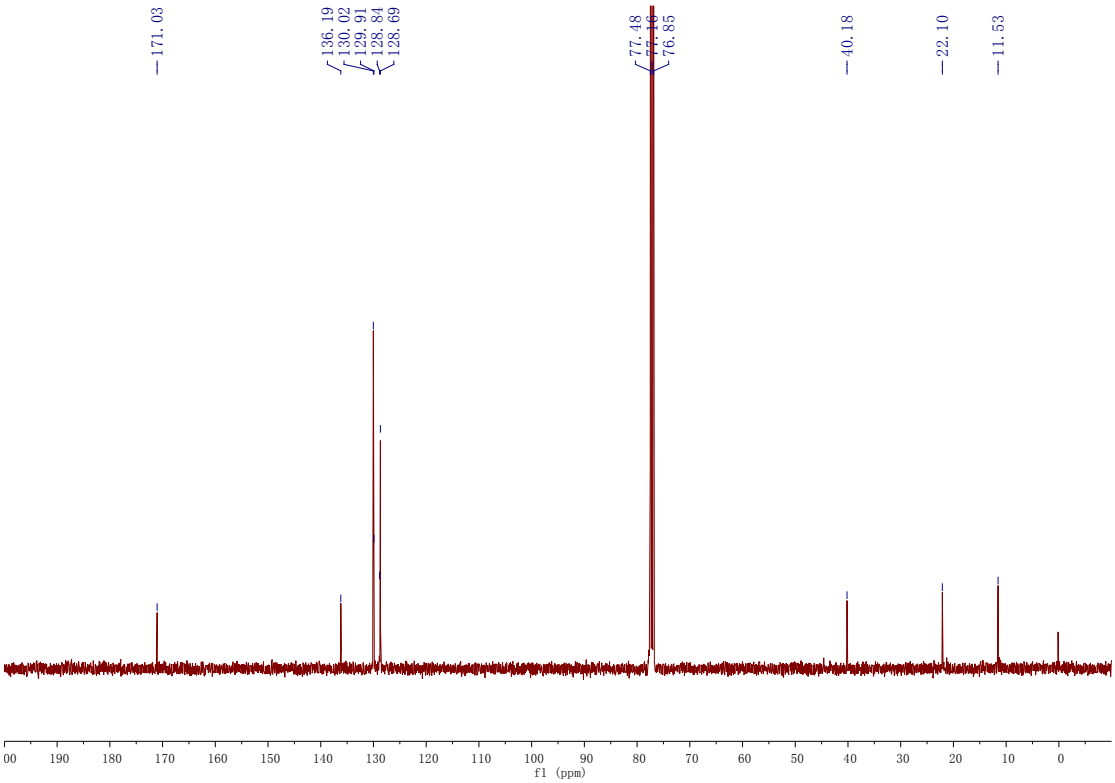
0.99
0.97
0.95
3.74
5.83
1.97
2.06
3.00
f1 (ppm)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129.91
128.84
128.69
77.48
77.16
76.85
40.18
22.10
11.53
f1 (ppm)

7. References

(1) J. Panteleev, R. Y. Huang, E. K. J. Lui and M. Lautens, *Org. Lett*., 2011, **13**, 5314-5317.

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(4) J. Panteleev, R. Y. Huang, E. K. J. Lui and M. Lautens, *Org. Lett*., 2011, **13**, 5314-5317.

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(6) K. Fuji, T. Morimoto, K. Tsutsumi and K. Kakiuchi, *Tetrahedron Lett.*, 2004, **45**, 9163-9166.

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