A Convenient Regioselective Synthesis of Cyclopentadienones *via* Palladium-Catalyzed [2+2+1] Cyclocarbonylation of Alkynes

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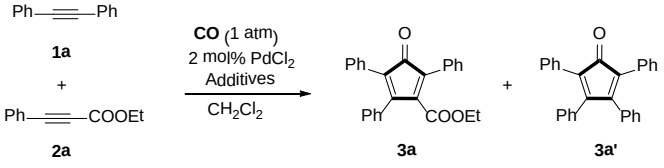
Supporting Information

I. General Information

Solvents and all reagents were used as received. ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and ^{13}C NMR spectra recorded in $CDCl_3$ at 100 MHz. The chemical shifts (d) were referenced to TMS. GC-MS was obtained using electron ionization (EI). High-resolution mass spectra (ESI) were obtained with a LCMS-IT-TOF mass spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. Melting points were measured with a micro melting point apparatus. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF_{254}), and visualization was effected at 254 nm.

II. Screening Reaction Conditions

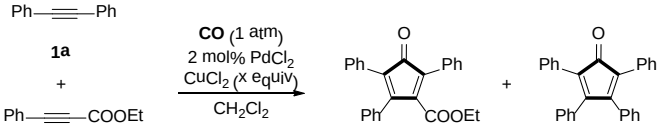
Table S1. Optimization of Different Additives[a]



Entry	Catalyst	Additive	Solvent	Yield (%)[b]	
				3a	**3a'**
1	$PdCl_2$	-	CH_2Cl_2	0	42
2	$PdCl_2$	LiCl	CH_2Cl_2	5	60
3	$PdCl_2$	LiBr	CH_2Cl_2	0	5
4	$PdCl_2$	KI	CH_2Cl_2	0	0
5	$PdCl_2$	CuCl	CH_2Cl_2	46	15
6	$PdCl_2$	$CuCl_2$	CH_2Cl_2	92	6
7	$PdCl_2$	Bu_4NCl	CH_2Cl_2	0	0
8	$PdCl_2$	$ZnCl_2$	CH_2Cl_2	0	0
9	$PdCl_2$	$CuBr_2$	CH_2Cl_2	0	0
10[c]	$PdCl_2$	$CuBr_2$	CH_2Cl_2	35	5

[a] Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.22 mmol), **2a** (0.2 mmol), $PdCl_2$ (2 mol%), additives (0.2 mmol) in CH_2Cl_2 (3 mL) at 40 °C (bath temperature) for 16 h. [b] Determined by GC using dodecane as the internal standard. [c] 1 equiv of LiCl was added.

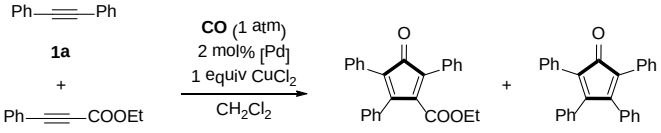
Table S2. Optimization of the Ratio of $CuCl_2$[a]



Entry	Catalyst	$CuCl_2$ (x equiv)	Solvent	Yield (%)[b]	
				3a	**3a'**
1	$PdCl_2$	-	CH_2Cl_2	0	42
2	$PdCl_2$	0.2	CH_2Cl_2	15	37
3	$PdCl_2$	0.5	CH_2Cl_2	48	30
4	$PdCl_2$	1.0	CH_2Cl_2	92	6
5	$PdCl_2$	2.0	CH_2Cl_2	73	20
6	$PdCl_2$	5.0	CH_2Cl_2	74	16

[a] Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.22 mmol), **2a** (0.2 mmol), $PdCl_2$ (2 mol%), in CH_2Cl_2 (3 mL) at 40 °C (bath temperature) for 16 h. [b] Determined by GC using dodecane as the internal standard.

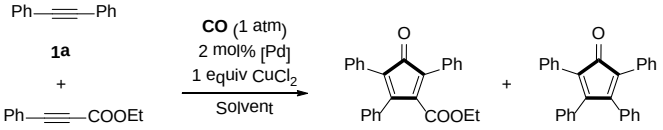
Table S3. Optimization of Different Pd-Catalysts[a]



Entry	[Pd]	Additives	Solvent	Yield (%)[b]	
				3a	**3a'**
1	$Pd(OAc)_2$	$CuCl_2$	CH_2Cl_2	0	0
2	$Pd(PPh_3)_2Cl_2$	$CuCl_2$	CH_2Cl_2	0	0
3	$Pd_2(dba)_3$	$CuCl_2$	CH_2Cl_2	0	0
4	$Pd(PPh_3)_4$	$CuCl_2$	CH_2Cl_2	0	0
5	$PdCl_2$	$CuCl_2$	CH_2Cl_2	92	6
6	$PdBr_2$	$CuCl_2$	CH_2Cl_2	53	8
7	PdI_2	$CuCl_2$	CH_2Cl_2	0	0

[a] Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.22 mmol), **2a** (0.2 mmol), Pd-catalyst (2 mol%), $CuCl_2$ (0.2 mmol) in CH_2Cl_2 (3 mL) at 40 °C (bath temperature) for 16 h. [b] Determined by GC using dodecane as the internal standard.

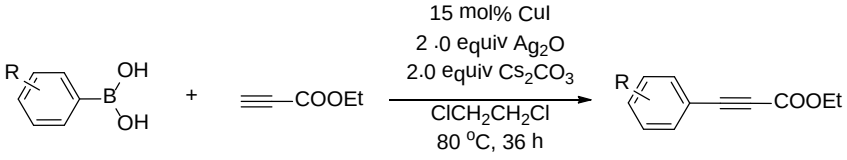
Table S4. Optimization of Different Solvents[a]



Entry	[Pd]	Additives	Solvent	Yield (%)[b]	
				3a	**3a'**
1	$PdCl_2$	$CuCl_2$	THF	10	7
2	$PdCl_2$	$CuCl_2$	Toluene	15	5
3	$PdCl_2$	$CuCl_2$	DCE	8	25
4	$PdCl_2$	$CuCl_2$	CH_2Cl_2	92	6
5	$PdCl_2$	$CuCl_2$	CH_3CN	0	0

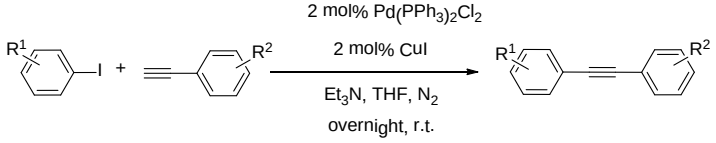
[a] Reaction conditions: unless otherwise noted, all reactions were performed with **1a** (0.22 mmol), **2a** (0.2 mmol), Pd-catalyst (2 mol%), $CuCl_2$ (0.2 mmol) in indicated solvent (3 mL) at 40 °C (bath temperature) for 16 h. [b] Determined by GC using dodecane as the internal standard.

III. Preparation of Penylpropiolate Esters Derivative[1]



Under air atmosphere, a reaction tube was charged with arylboronic acid (0.25 mmol), alkyne (0.375 mmol), CuI (7.2 mg, 15 mol %), Ag_2O (115 mg, 0.5 mmol), Cs_2CO_3 (163 mg, 0.5 mmol), and DCE (2 mL). After the mixture was heated at 80 °C for 36 h, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography on silica gel to give the product.

IV. Preparation of Alkynes[2]



$Pd(PPh_3)_2Cl_2$ (2 mol%) and CuI (2 mol%) were weighed out to a round bottom flask

equipped with a magnetic stir bar and fitted with a rubber septa. The flask was purged with argon and THF (3 mL) followed by triethylamine (3 mL) were added via syringe. Iodobenzene (6 mmol, 1.1 equiv) followed by phenylacetylene (5 mol, 1 equiv) were added to the stirring mixture and the reaction was stirred overnight at room temperature. The volatiles were evaporated under reduced pressure and the residue was extracted with ethyl acetate/ether/brine. The organics were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the product.

V. Synthesis of 3 from Alkynes and Phenylpropiolate Esters

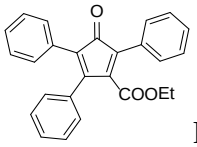
Alkynes **1** (0.3 mmol), phenylpropiolate esters **2** (0.33 mmol), $PdCl_2$ (2 mol%), $CuCl_2$ (0.3 mmol), and 3 mL of dichloromethane were added to a tube equipped with magnetic stirrer bar. Then the tube was charged with CO (1 atm), and was stirred at 40 ^oC (oil bath temperature) for the desired reaction time. After the reaction was finished (monitored by TLC), the crude product was cooled to room temperature and then directly separated by flash column chromatography on silica gel to afford the pure product cyclopentadienones **3**.

VI. Synthesis of 5 Directly from Diynes

Diynes **1** (0.2 mmol), $PdCl_2$ (2 mol%), and 3 mL of dichloromethane were added to a tube equipped with magnetic stirrer bar. Then the tube was charged with CO (1 atm), and was stirred at 40 ^oC (oil bath temperature) for the desired reaction time. After the reaction was finished (monitored by TLC), the crude product was cooled to room temperature and then directly separated by flash column chromatography on silica gel to give the pure product cyclopentadienones **6**.

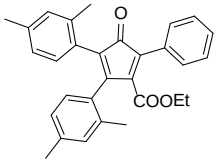
VII. Analytical Data for 3a-3w, and 5a-5c.

Ethyl 3-oxo-2,4,5-triphenylcyclopenta-1,4-dienecarboxylate (3a).[3]



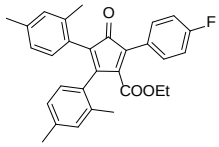
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52-7.46 (m, 2H), 7.34-7.20 (m, 8H), 7.17-7.12 (m, 5H), 4.04 (q, *J* = 7.1 Hz, 2H), 0.93 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 165.6, 153.0, 144.9, 133.1, 130.2, 129.9, 129.4, 129.3, 129.2, 129.0, 128.6, 128.3, 128.1, 127.9, 124.5, 61.5, 13.7; IR (KBr): 3019, 1720, 1647, 1494, 1445, 1373, 1354, 1217, 1118, 1020, 765, 694 cm^{-1}; MS (EI) m/z: 380, 309, 276, 202, 178, 105, 77.

Ethyl 4,5-bis(2,4-dimethylphenyl)-3-oxo-2-phenylcyclopenta-1,4-dienecarboxylate (3b).



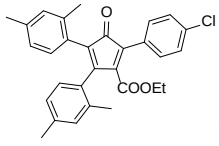
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 6.6 Hz, 2H), 7.45-7.36 (m, 3H), 7.04 (d, J = 7.5 Hz, 1H), 6.95 (d, J = 6.6 Hz, 3H), 6.83 (d, J = 7.8 Hz, 2H), 4.06 (d, J = 7.1, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 2.08 (s, 6H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 165.3, 155.3, 144.6, 138.5, 137.9, 137.0, 135.5, 131.1, 131.0, 130.5, 130.2, 129.6, 129.5, 128.9, 128.3, 128.2, 127.8, 127.5, 127.4, 126.3, 126.2, 61.2, 21.2, 21.1, 20.6, 20.0, 13.5; IR (KBr): 3059, 2964, 2923, 1722, 1612, 1494, 1447, 1310, 1201, 1137, 796, 695 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{28}NaO_3$ $[M+Na]^+$ 459.1931, found 459.1933.

Ethyl 4,5-bis(2,4-dimethylphenyl)-2-(4-fluorophenyl)-3-oxocyclopenta-1,4-diene-carboxylate (3c).



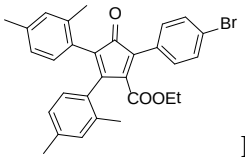
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.7Hz, 2H), 7.10 (t, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 6.0 Hz, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.09 (s, 6H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 165.2, 164.4, 161.9, 155.4, 144.3, 138.6, 138.0, 137.0, 135.4, 131.7, 131.6, 131.1, 131.1, 130.5, 130.2, 127.7, 127.4, 126.3, 126.3, 125.6, 115.5, 115.3, 61.3, 21.2, 21.1, 20.6, 20.0, 13.5; IR (KBr): 3060, 2967, 2928, 1721, 1612, 1494, 1447, 1310, 1200, 1139, 794, 696 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{27}FNaO_3$ $[M+Na]^+$ 477.1836, found 477.1837.

Ethyl 2-(4-chlorophenyl)-4,5-bis(2,4-dimethylphenyl)-3-oxocyclopenta-1,4-diene-carboxylate (3d).



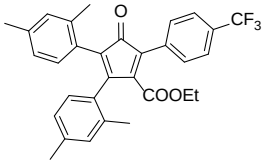
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.5 Hz, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96-6.95 (m, 3H), 6.87 (d, *J* = 7.7 Hz, 1H), 6.81 (d, *J* = 7.7Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.09 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 165.1, 155.3, 144.9, 138.6, 138.0, 137.90, 135.4, 135.1, 131.1, 131.1, 130.9, 130.4, 130.1, 128.5, 127.9, 127.3, 127.1, 126.3, 126.3, 61.4, 21.2, 21.1, 20.6, 20.0, 13.5; IR (KBr): 3058, 2964, 2928, 1720, 1612, 1494, 1446, 1310, 1204, 1139, 795, 697 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{27}ClNaO_3$ $[M+Na]^+$ 493.1541, found 493.1538.

Ethyl 2-(4-bromophenyl)-4,5-bis(2,4-dimethylphenyl)-3-oxocyclopenta-1,4-diene-carboxylate (3e).



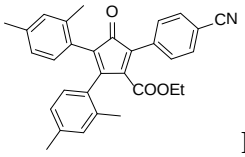
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.96-6.94 (m, 3H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.06 (q, *J* = 7.1Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 2.08 (s, 6H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 165.18, 155.3, 145.0, 138.6, 138.0, 137.0, 135.4, 131.5, 131.1, 131.1, 130.4, 130.1, 128.4, 127.9, 127.4, 127.3, 127.2, 126.4, 126.3, 123.5, 61.4, 21.2, 21.2, 20.6, 20.0, 13.5; IR (KBr): 3061, 2967, 2928, 1722, 1612, 1494, 1447, 1310, 1200, 1139, 795, 696 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{27}BrNaO_3$ $[M+Na]^+$ 537.1036, found 537.1033.

Ethyl 4,5-bis(2,4-dimethylphenyl)-3-oxo-2-(4-(trifluoromethyl)phenyl)cyclopenta-1,4-dienecarboxylate (3f).



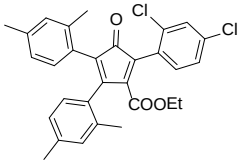
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 3H), 6.87 (d, *J* =7.8 Hz, 2H), 4.09 (d, *J* = 7.1Hz, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 2.11 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 164.9, 155.0, 146.5, 138.8, 138.1, 136.9, 135.4, 133.0, 131.2, 131.1, 130.4, 129.9, 128.2, 127.3, 127.1, 126.8, 126.4, 126.3, 125.1, 125.0, 122.6, 61.5, 21.2, 21.1, 20.6, 20.0, 13.5; IR (KBr): 3053, 2987, 1725, 1614, 1452, 1374, 1324, 1242, 1167, 1127, 1063, 843, 695 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{27}F_3NaO_3$ $[M+Na]^+$ 527.1805, found 527.1799.

Ethyl 2-(4-cyanophenyl)-4,5-bis(2,4-dimethylphenyl)-3-oxocyclopenta-1,4-diene-carboxylate (3g).



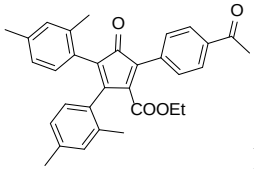
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.04-7.02 (m, 1H), 6.99-6.93 (m, 3H), 6.88-6.86 (m, 1H), 6.81-6.80 (m, 1H), 4.12-4.01 (q, *J* = 7.1 Hz, 2H), 2.28 (s, 3H), 2.26 (s, 3H), 2.06 (s, 6H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 190.0, 164.7, 154.9, 147.2, 138.9, 138.3, 136.9, 135.4, 134.0, 131.8, 131.2, 131.16, 130.4, 130.1, 128.4, 127.3, 126.9, 126.4, 126.3, 126.2, 118.6, 112.2, 61.6, 21.2, 21.1, 20.6, 20.0, 13.5; IR (KBr): 3060, 2924, 2228, 1722, 1611, 1499, 1450, 1348, 1236, 1137, 826, 737 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{27}NNaO_3$ $[M+Na]^+$ 484.1883, found 484.1878.

Ethyl 2-(2,4-dichlorophenyl)-4,5-bis(2,4-dimethylphenyl)-3-oxocyclopenta-1,4-dienecarboxylate (3h).



Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.31 (s, 2H), 7.04-6.90 (m, 4H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.79 (d, *J* = 7.7 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.14 (s, 3H), 2.10 (s, 3H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 163.5, 146.6, 138.5, 138.1, 137.0, 135.3, 135.3, 134.9, 132.5, 131.1, 130.9, 130.4, 130.2, 129.4, 129.3, 128.9, 128.1, 127.6, 127.1, 126.7, 126.3, 61.2, 21.2, 21.1, 20.5, 20.1, 13.4; IR (KBr): 3058, 2964, 2928, 1721, 1613, 1496, 1446, 1310, 1204, 1139, 795, 697 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{26}Cl_2NaO_3$ $[M+Na]^+$ 527.1151, found 527.1146.

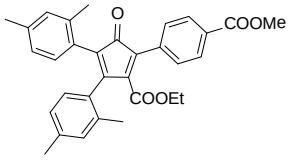
Ethyl 2-(4-acetylphenyl)-4,5-bis(2,4-dimethylphenyl)-3-oxocyclopenta-1,4-diene-carboxylate (3i).



Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.67 (d,

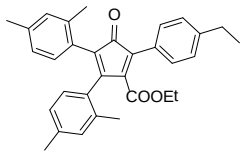
J = 8.4 Hz, 2H), 7.04 (d, *J* = 7.6 Hz, 1H), 7.00-6.92 (m, 3H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.07 (q, *J* = 7.1Hz, 2H), 2.62 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.08 (s, 6H), 0.97 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 197.5, 164.9, 155.0, 146.4, 138.7, 138.1, 136.9, 136.7, 135.4, 134.0, 131.1, 131.1, 130.4, 129.8, 129.6, 128.2, 128.0, 127.3, 127.1, 127.0, 126.3, 126.2, 61.4, 26.5, 21.1, 21.1, 20.5, 20.0, 13.5; IR (KBr): 3060, 2926, 1722, 1718, 1611, 1499, 1452, 1358, 1236, 1137, 826, 737 cm^{-1}; ESI-HRMS calcd for $C_{32}H_{30}NaO_4$ $[M+Na]^+$ 501.2036, found 501.2034.

Methyl 4-(3,4-bis(2,4-dimethylphenyl)-2-(ethoxycarbonyl)-5-oxocyclopenta-1,3-di en-1-yl)benzoate (3j).



Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.93 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.08 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.7, 166.6, 164.9, 155.0, 146.3, 138.7, 138.1, 136.9, 135.4, 133.9, 131.1, 130.4, 130.1, 130.0, 129.8, 129.4, 129.3, 128.2, 127.3, 127.2, 127.1, 126.3, 1263, 61.4, 52.1, 21.2, 21.1, 20.5, 20.0, 13.5; IR (KBr): 3060, 2985, 1724, 1610, 1443, 1372, 1280, 1240, 1200, 1104, 1020, 832, 737 cm^{-1}; ESI-HRMS calcd for $C_{32}H_{30}NaO_5$ $[M+Na]^+$ 517.1985, found 517.1983.

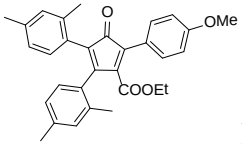
Ethyl 4,5-bis(2,4-dimethylphenyl)-2-(4-ethylphenyl)-3-oxocyclopenta-1,4-dienecar -boxylate (3k).



Red oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.1 Hz, 2H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 6.8 Hz, 3H), 6.85 (d, *J* = 7.8 Hz, 1H),

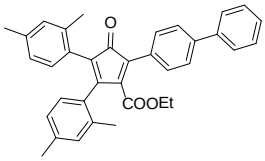
6.79 (d, *J* = 7.8 Hz, 1H), 4.06 (dd, *J* = 7.1, 3.0 Hz, 2H), 2.70-2.65 (m, 2H), 2.27 (s, 3H), 2.25 (s, 3H), 2.08 (s, 6H), 1.24 (d, *J* = 7.6 Hz, 3H), 0.96 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 165.4, 155.5, 145.4, 143.6, 138.4, 137. 8, 137.0, 135.4, 131.1, 131.0, 130.5, 129.6, 128.4, 128.1, 127.8, 127.6, 127.5, 127.4, 126.8, 126.3, 126.2, 61.1, 28.7, 21.2, 21.1, 20.6, 20.0, 15.2, 13.5; IR (KBr): 3060, 2924, 2228, 1722, 1611, 1499, 1450, 1348, 1236, 1137, 826, 737 cm^{-1}; ESI-HRMS calcd for $C_{32}H_{32}NaO_3$ $[M+Na]^+$ 487.2244, found 487.2242.

Ethyl 4,5-bis(2,4-dimethylphenyl)-2-(4-methoxyphenyl)-3-oxocyclopenta-1,4-di-enecarboxylate (3l).



Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 7.05-7.03 (m, 1H), 6.98-6.92 (m, 5H), 6.83 (d, *J* =8.9 Hz, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.09 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 165.5, 160.3, 155.9, 142.2, 138.4, 137.7, 137.0, 135.4, 131.2, 131.1, 131.0, 130.5, 128.1, 127.6, 127.3, 127.2, 126.3, 126.2, 122.0, 113.8, 61.1, 55.2, 21.2, 21.1, 20.6, 20.0, 13.5; IR (KBr): 3021, 2924, 1720, 1606, 1509, 1450, 1372, 1254, 1178, 831, 736 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{30}NaO_4$ $[M+Na]^+$ 489.2036, found 489.2037.

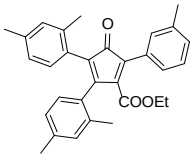
Ethyl 2-([1,1'-biphenyl]-4-yl)-4,5-bis(2,4-dimethylphenyl)-3-oxocyclopenta-1,4-di-enecarboxylate (3m).



Red oil;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.63 (m, 6H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 6.5 Hz, 3H), 6.86 (d, *J* =7.8 Hz, 2H), 4.10 (q, *J* = 7.1Hz, 2H), 2.30 (s, 3H), 2.28 (s, 3H), 2.12 (s, 6H), 1.00 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 165.4, 155.5, 144.3, 141.6, 140.5,

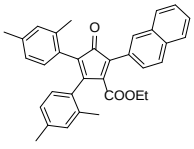
138.5, 137.9, 137.0, 135.5, 131.1, 131.1, 130.5, 130.37, 130.1, 128.8, 128.5, 127.9, 127.8, 127.6, 127.5, 127.4, 127.1, 126.9, 126.3, 126.3, 61.3, 21.2, 21.1, 20.6, 20.0, 13.6; IR (KBr): 3020, 2924, 1721, 1608, 1509, 1450, 1372, 1254, 1178, 831, 736 cm^{-1}; ESI-HRMS calcd for $C_{36}H_{32}NaO_3$ $[M+Na]^+$ 535.2244, found 535.2242.

Ethyl 4,5-bis(2,4-dimethylphenyl)-3-oxo-2-m-tolylcyclopenta-1,4-dienecarboxylate (3n).



Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 9.2 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 5.9 Hz, 3H), 6.86 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 4.08 (q, *J* = 7.1Hz, 2H), 2.39 (s, 3H), 2.29 (s, 3H), 2.26 (s, 3H), 2.09 (s, 6H), 0.99 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 165.3, 155.3, 144.4, 138.5, 137.8, 137.7, 137.0, 135.4, 131.1, 130.5, 130.1, 129.8, 129.3, 128.5, 128.1, 127.5, 127.4, 126.7, 126.3, 126.2, 61.2, 21.4, 21.2, 21.1, 20.57, 20.0, 13.5; IR (KBr): 3020, 2925, 1720, 1608, 1509, 1450, 1372, 1254, 1182, 831, 736 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{30}NaO_3$ $[M+Na]^+$ 473.2087, found 473.2084.

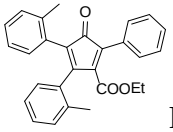
Ethyl 4,5-bis(2,4-dimethylphenyl)-2-(naphthalen-2-yl)-3-oxocyclopenta-1,4-diene-carboxylate (3o).



Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.90-7.82 (m, 3H), 7.65-7.62 (m, 1H), 7.54-7.46 (m, 2H), 7.09-7.07 (m, 1H), 6.97-6.96 (m, 3H), 6.89-6.84 (m, 2H), 4.09 (q, *J* = 7.1Hz, 2H), 2.30 (s, 3H), 2.27 (s, 3H), 2.12 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 165.4, 155.5, 144.6, 138.6, 137.9, 137.0, 135.5, 133.3, 133.0, 131.1, 130.5, 130.2, 129.9, 128.7, 128.2, 127.8, 127.6, 127.5, 127.4, 126.9, 126.8, 126.6, 126.3, 126.2, 126.1, 61.3, 21.2, 21.1, 20.6, 20.1, 13.6; IR (KBr): 3020, 2925,

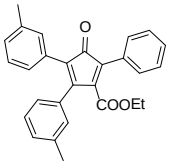
1720, 1608, 1509, 1450, 1372, 1254, 1182, 831, 736 cm^{-1}; ESI-HRMS calcd for $C_{34}H_{30}NaO_3$ $[M+Na]^+$ 509.2087, found 509.2086.

Ethyl 3-oxo-2-phenyl-4,5-dio-tolylcyclopenta-1,4-dienecarboxylate (3p).



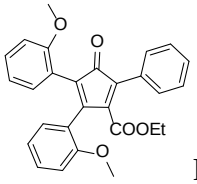
Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.45-7.38 (m, 3H), 7.23-7.11 (m, 6H), 7.06-7.03 (m, 1H), 6.93-6.92 (m, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.15 (s, 6H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 165.1, 155.5, 144.3, 137.2, 135.6, 130.5, 130.2, 129.6, 129.3, 129.0, 128.8, 128.5, 128.2, 127.9, 127.4, 125.6, 125.4, 61.3, 20.7, 20.1, 13.5; IR (KBr): 3059, 2979, 2926, 1721, 1626, 1490, 1447, 1346, 1168, 1130, 742, 698 cm^{-1}; ESI-HRMS calcd for $C_{28}H_{24}NaO_3$ $[M+Na]^+$ 431.1618, found 431.1616.

Ethyl 3-oxo-2-phenyl-4,5-di-m-tolylcyclopenta-1,4-dienecarboxylate (3q).



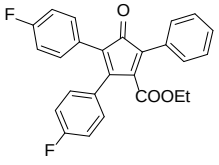
Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.58 (m, 2H), 7.47-7.39 (m, 3H), 7.26-7.08 (m, 7H), 7.03-7.01 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.34 (s, 3H), 2.31 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 165.7, 152.9, 145.0, 138.1, 137.6, 133.0, 130.5, 130.1, 130.0, 129.4, 128.9, 128.6, 128.4, 128.3, 128.1, 127.9, 127.6, 127.0, 125.0, 124.3, 61.4, 21.4, 21. 3, 13.7; IR (KBr): 3059, 2985, 1723, 1596, 1452, 1373, 1311, 1240, 1178, 1113, 792, 697 cm^{-1}; ESI-HRMS calcd for $C_{28}H_{24}NaO_3$ $[M+Na]^+$ 431.1618, found 431.1617.

Ethyl 4,5-bis(2-methoxyphenyl)-3-oxo-2-phenylcyclopenta-1,4-dienecarboxylate (3r).



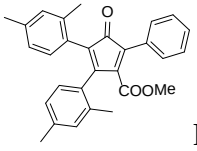
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.54 (m, 5H), 7.48-7.39 (m, 3H), 7.16-7.14 (m, 1H), 7.07-7.03 (m, 2H), 6.96-6.92 (m, 2H), 4.25 (q, *J* = 7.1 Hz,, 2H), 3.94 (s, 3H), 3.59 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 164.8, 157.5, 156.4, 153.0, 143.7, 131.6, 130.4, 129.9, 129.7, 129.3, 129.2, 128.6, 127.8, 123.4, 120.5, 120.3, 119.9, 111.0, 109.9, 60.7, 55.0, 54.9, 13.6; IR (KBr): 3057, 2982, 2938, 1718, 1596, 1449, 1461, 1249, 1196, 1132, 751, 698 cm^{-1}; ESI-HRMS calcd for $C_{28}H_{24}NaO_5$ $[M+Na]^+$ 463.1516, found 463.1517.

Ethyl 4,5-bis(4-fluorophenyl)-3-oxo-2-phenylcyclopenta-1,4-dienecarboxylate (3s).



Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.31-7.26 (m, 3H), 7.19-7.12 (m, 2H), 7.10-7.05 (m, 2H), 6.94-6.84 (4H), 4.03 (q, *J* = 7.1 Hz, 2H), 0.94 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 165.4, 164.3, 163.6, 161.9, 161.2, 151.8, 144.4, 131.7, 130.0, 129.4, 129.1, 128.8, 128.3, 125.9, 123.7, 115.8, 115.5, 61.6, 13.7; IR (KBr): 3057, 2986, 1723, 1598, 1505, 1369, 1237, 1161, 1113, 842, 698 cm^{-1}; ESI-HRMS calcd for $C_{26}H_{19}F_2O_3$ $[M+H]^+$ 417.1297, found 417.1295.

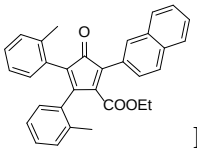
Methyl 4,5-bis(2,4-dimethylphenyl)-3-oxo-2-phenylcyclopenta-1,4-dienecarboxylate (3t).



Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.45-7.36 (m, 3H), 7.05-7.04 (d, *J* = 7.6 Hz, 1H), 6.99-6.92 (m, 3H), 6.87 (d, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.60 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$)

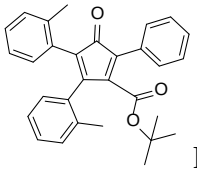
δ 199.2, 165.9, 155.1, 144.3, 138.6, 137.9, 137.0, 135.4, 131.2, 131.1, 130.5, 130.0, 129.5, 129.4, 129.0, 128.5, 128.3, 127.7, 127.5, 127.3, 126.4, 126.3, 52.0, 21.2, 21.1, 20.6, 20.0; IR (KBr): 3020, 2986, 1723, 1598, 1505, 1369, 1237, 1161, 1113, 842, 698 cm^{-1}; ESI-HRMS calcd for $C_{29}H_{26}NaO_3$ $[M+Na]^+$ 445.1774, found 445.1778.

Ethyl 2-(naphthalen-2-yl)-3-oxo-4,5-dio-tolylcyclopenta-1,4-dienecarboxylate (3u).



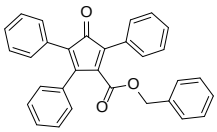
Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.92-7.84 (m, 3H), 7.67-7.65 (m, 1H), 7.55-7.49 (m, 2H), 7.25-7.15 (m, 6H), 7.10-7.04 (m, 1H), 6.97-6.95 (m, 1H), 4.08 (q, *J* = 7.1Hz, 2H), 2.19 (s, 6H), 0.95 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 165.2, 155.8, 144.3, 137.2, 135.6, 133.3, 133.0, 130.6, 130.3, 123.0, 128.8, 128.7, 128.5, 128.2, 128.0, 127.8, 127.6, 127.4, 126.9, 126.8, 126.5, 126.39, 125.6, 125.4, 61.3, 20.7, 20.1, 13.5; IR (KBr): 3059, 2980, 2926, 1720, 1635, 1598, 1453, 1344, 1187, 1095, 817, 742 cm^{-1}; ESI-HRMS calcd for $C_{32}H_{26}NaO_3$ $[M+Na]^+$ 481.1774, found 481.1773.

tert-Butyl 3-oxo-2-phenyl-4,5-dio-tolylcyclopenta-1,4-dienecarboxylate (3v).



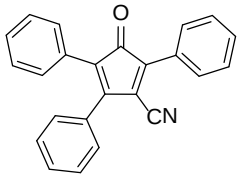
Red oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.44-7.37 (m, 3H), 7.21-7.12 (m, 6H), 7.05-7.03 (m, 1H), 6.92-6.90 (m, 1H), 2.16 (s, 3H), 2.14 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 164.2, 155.7, 145.65, 137.3, 135.6, 130.5, 130.4, 130.2, 130.1, 129.5, 129.4, 128.8, 128.6, 128.2, 127.6, 127.2, 125.5, 125.3, 83.0, 27.5, 20.7, 20.1; IR (KBr): 3053, 2981, 2938, 1719, 1595, 1449, 1461, 1249, 1193, 1136, 750, 699 cm^{-1}; ESI-HRMS calcd for $C_{30}H_{28}NaO_3$ $[M+Na]^+$ 459.1931, found 459.1925.

Benzyl 3-oxo-2,4,5-triphenylcyclopenta-1,4-dienecarboxylate (3w).



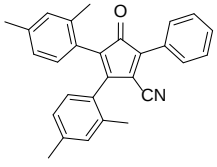
Red oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.10 (m, 20H), 5.08 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 165.5, 152.8, 144.5, 134.4, 132.8, 130.1, 129.9, 129.4, 129.3, 129.2, 129.0, 128.68, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.8, 127.7, 124.4, 67.4; IR (KBr): 3059, 2964, 1725, 1594, 1492, 1447, 1242, 1196, 1115, 740, 696 cm^{-1}; ESI-HRMS calcd for $C_{31}H_{22}NaO_3$ $[M+Na]^+$ 465.1461, found 465.1466.

3-oxo-2,4,5-triphenylcyclopenta-1,4-dienecarbonitrile(4a).[4]



Purple solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98-7.97 (m, 2H), 7.54-7.42 (m, 8H), 7.31-7.24 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 150.2, 138.6, 131.1, 131.0, 130.4, 129.9, 129.6, 129.3, 129.0, 128.9, 128.7, 128.4, 128.3, 128.0, 124.6, 122.1, 115.0. IR (KBr): 3019, 2215, 1720, 1627, 1494, 1445, 1354, 1217, 1118, 1020, 765, 727, 693 cm^{-1}; MS (EI) m/z: 333, 305, 278, 227, 178, 152, 105.

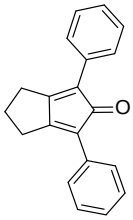
4,5-bis(2,4-dimethylphenyl)-3-oxo-2-phenylcyclopenta-1,4-dienecarbonitrile (4b).



Purple solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-7.96 (m, 2H), 7.56-7.44 (m, 3H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.99 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 7.8 Hz, 1H), 2.34 (s, 3H), 2.29 (s, 3H), 2.15 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 152.6, 139.9, 138.4, 137.7, 136.9, 135.9, 131.7, 131.3, 130.9, 130.4, 129.5, 128.9, 128.4, 128.2, 127.5, 126.8, 126.6, 126.5, 122.6, 115.1, 21.3, 21.1, 20.5, 20.3. IR (KBr): 3019, 2213, 1715, 1627, 1494, 1445, 1354, 1217, 1118, 1020, 826,

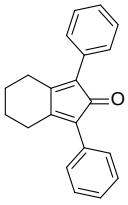
765, 727, 693 cm^{-1} ESI-HRMS calcd for $C_{28}H_{23}NNaO$ $[M+Na]^+$ 412.1672, found 412.1673.

1,3-Diphenyl-4,5-dihydropentalen-2(4H)-one (6a).[5]



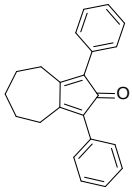
Yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (m, 4H), 7.41 (m, 4H), 7.29 (m, 2H), 2.90 (t, *J* = 7.2 Hz, 4H), 2.23 (q *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 162.6, 132.1, 128.4, 128.0, 126.9, 119.0, 28.0, 27.2; IR (KBr): 3060, 2956, 2851, 1714, 1598, 1494, 1459, 1265, 750, 697 cm^{-1}; MS (EI) m/z: 272, 243, 228, 215, 167, 115.

1,3-Diphenyl-4,5,6,7-tetrahydroinden-2-one (6b).



Reddish oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.35-7.28 (m, 7H), 7.19-7.14 (m, 3H), 2.76-2.75 (m, 4H), 1.67-1.57 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 153.5, 131. 5, 129.2, 128.2, 127.0, 122.4, 26.7, 22.7; IR (KBr): 3057, 2931, 2860, 1715, 1598, 1493, 1446, 1264, 750, 699 cm^{-1}; ESI-HRMS calcd for $C_{21}H_{18}NaO$ $[M+Na]^+$ 309.1250, found 309.1247.

1,3-Diphenyl-4,5,6,7-tetrahydroazulen-2(4H)-one (6c).



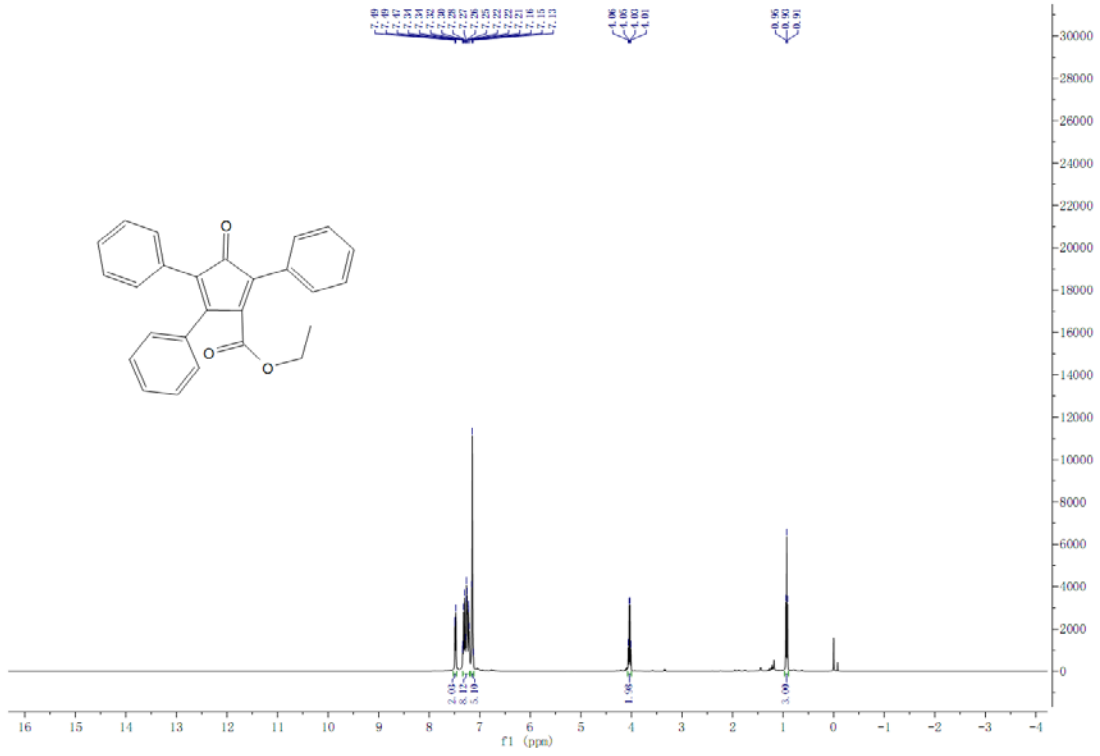
Reddish oil; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.38 (m, 4H), 7.34-7.28 (m, 6H), 2.74 (s, 4H), 1.80 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 158.5, 131.4, 129.7,

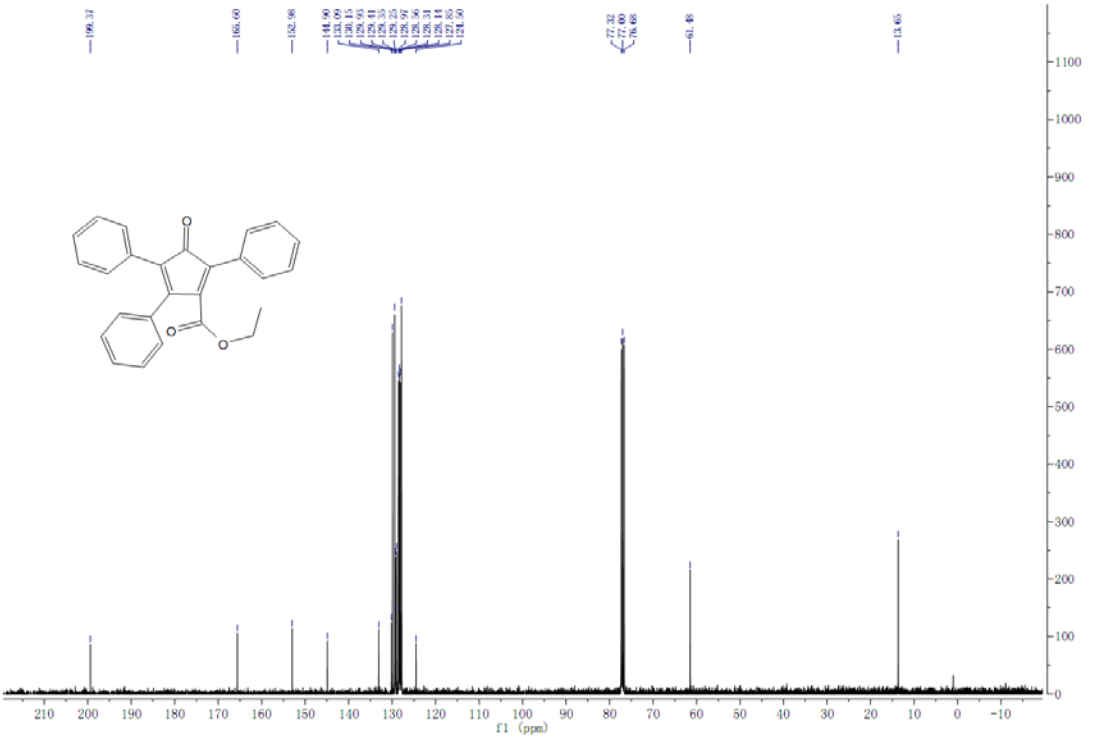
128.2, 127.2, 124.0, 31.6, 29.9, 28.2. IR (KBr): 3054, 2924, 2853, 1710, 1596, 1492, 1445, 1267, 747, 697 cm^{-1}; ESI-HRMS calcd for $C_{22}H_{20}NaO$ $[M+Na]^+$ 323.1406, found 323.1406.

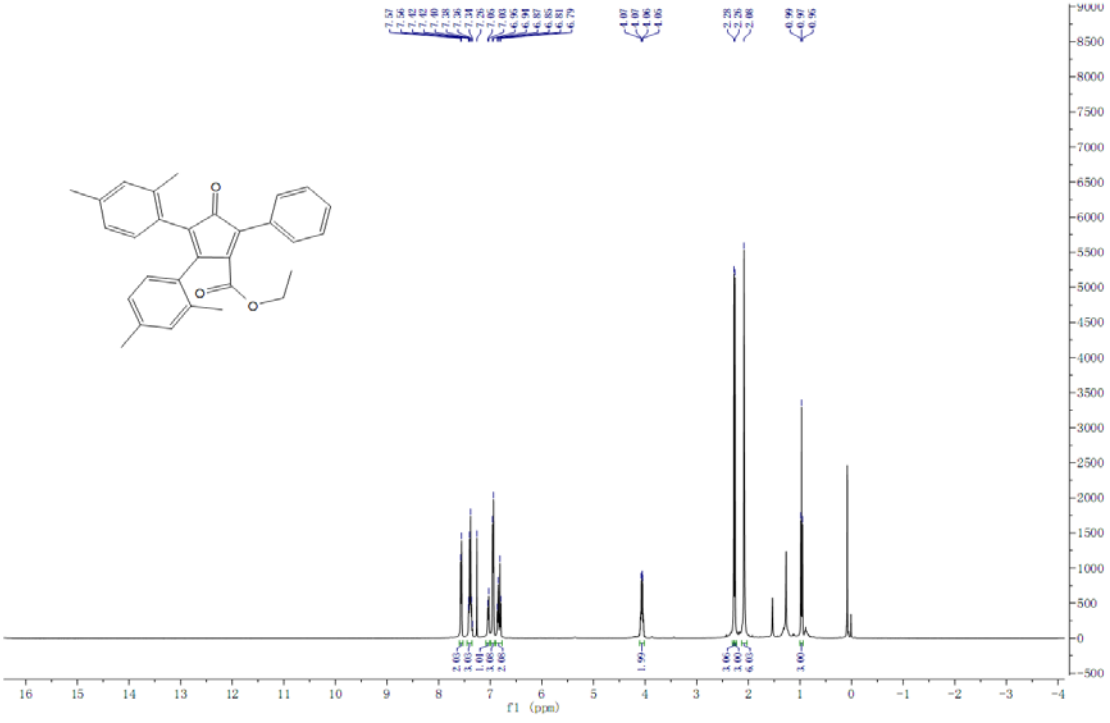
References:

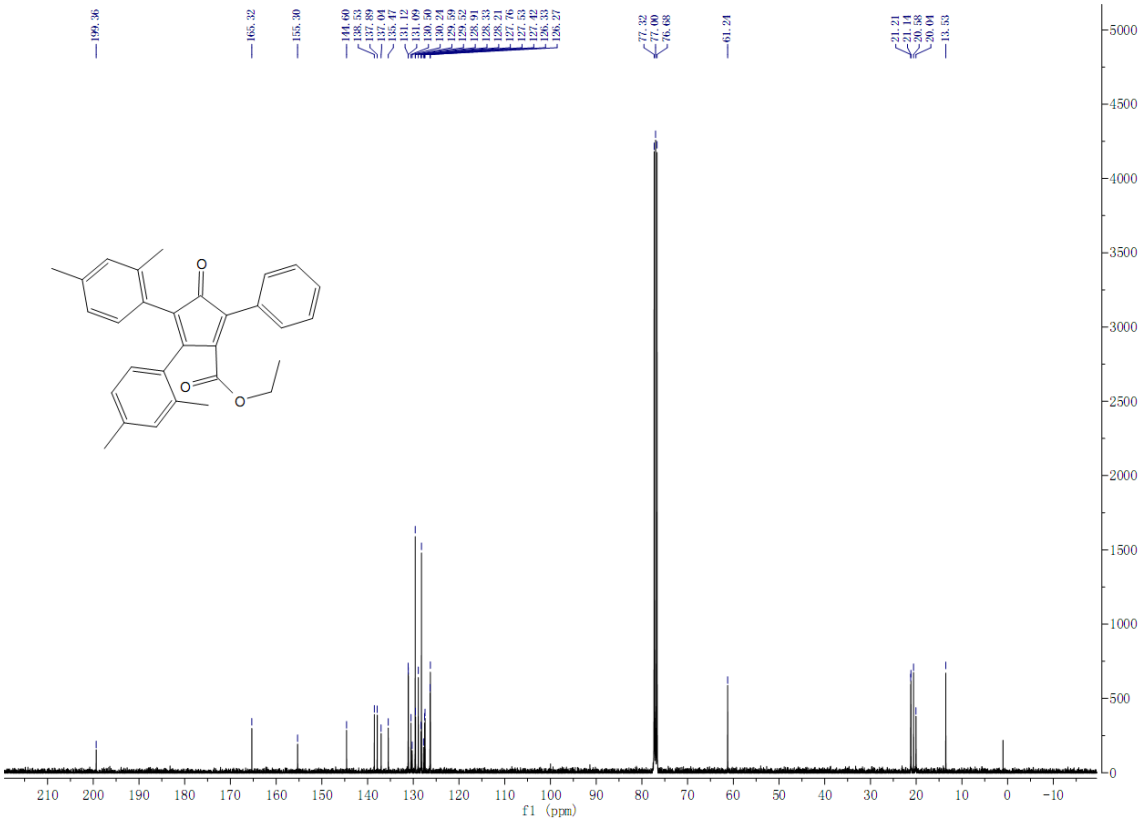
1. C.-D. Pan, F. Luo, W.-H. Wang, Z.-S. Ye, J. Cheng, *Tetrahedron* 2009, **50**, 5044.
2. D. R.Stuart, M. Bertrand-Laperle, K. M. N. Burgess, K. Fagnou, *J. Am. Chem. Soc.* 2008, **130**, 16474.
3. H.-M. Peng, R. D. Webster, X. W. Li, *Organometallics* 2008, **27**, 4484.
4. P. A. Wender, T. J. Paxton, T. J. Williams, *J. Am. Chem. Soc.* 2006, **128**, 14814;
5. T. Shibata, K. Yamashita, H. Ishida, K. Takagi, *Org. Lett.* 2001, **3**, 1217.

XI. NMR Spectra for All Compounds





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130.94
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129.52
128.91
128.53
128.21
127.76
127.53
127.42
126.33
126.27
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77.00
76.68
61.24
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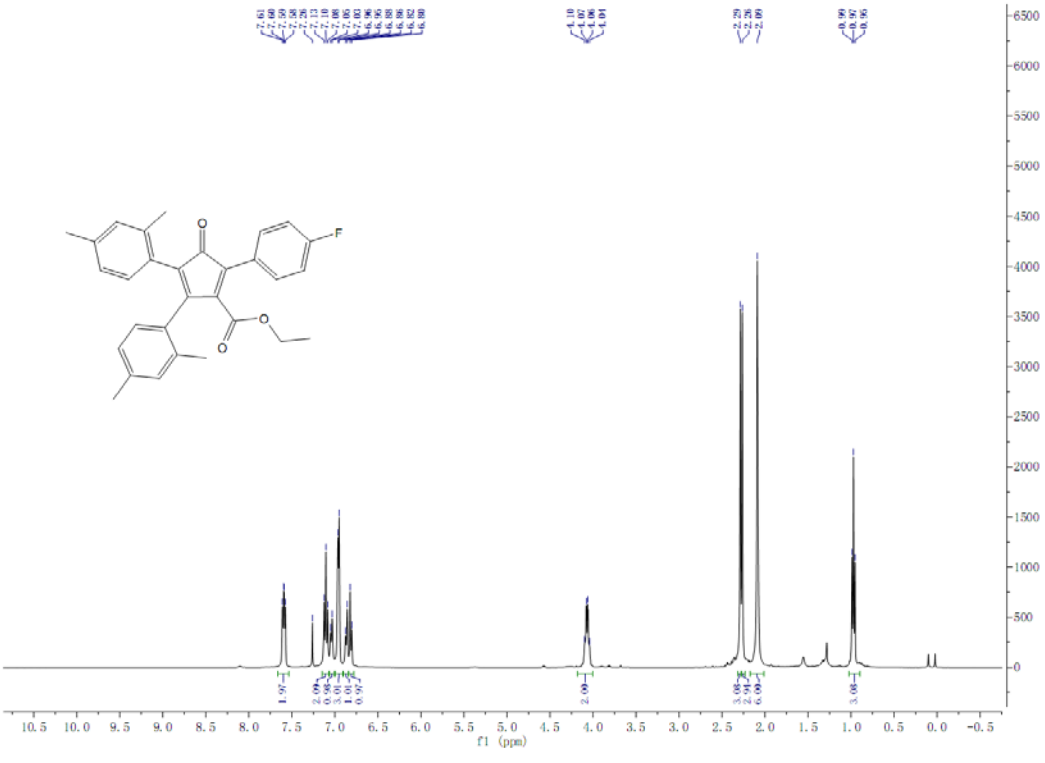
21.14
20.58
20.04
13.53
f1 (ppm)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6.95
6.88
6.86
6.82
6.80
4.10
4.07
4.06
4.01
2.29
2.26
2.09
0.99
0.97
0.96
1.97
2.09
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1.01
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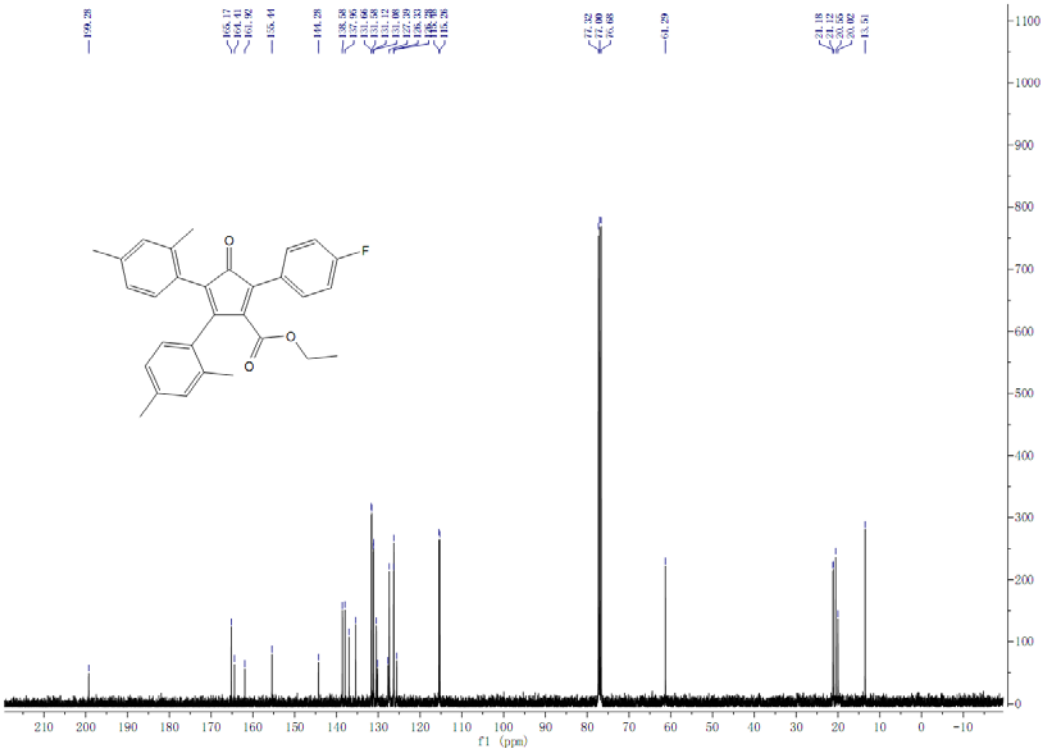
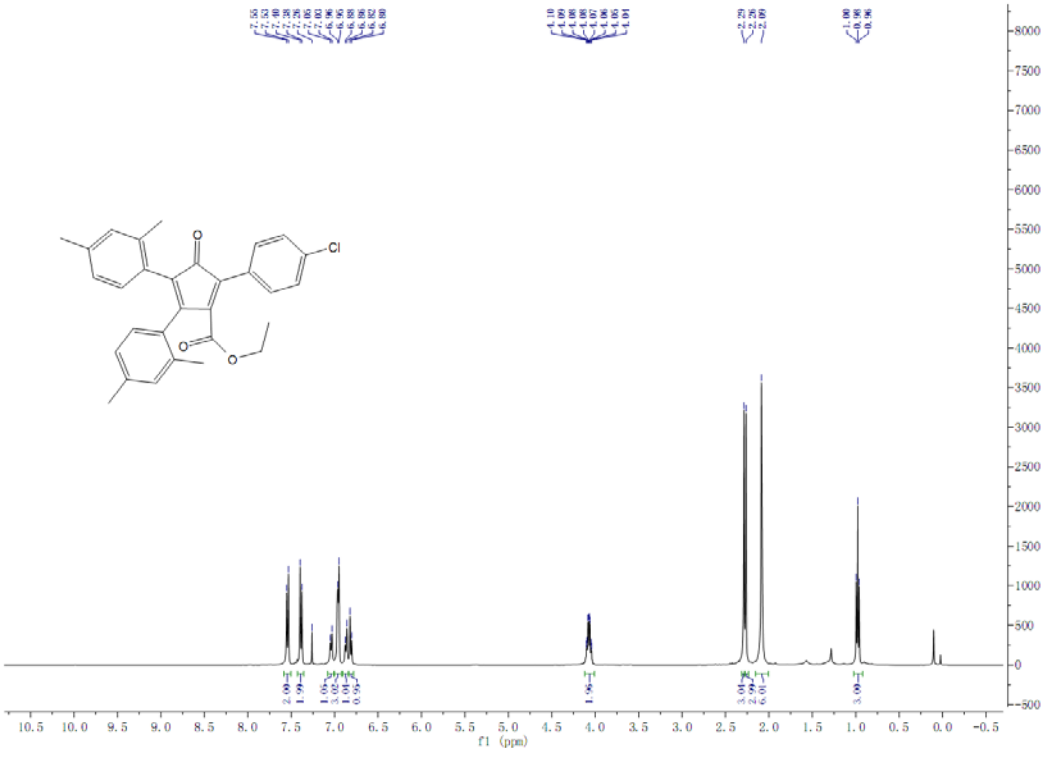
2.00
3.08
2.94
6.09
3.08
f1 (ppm)

Supporting Information





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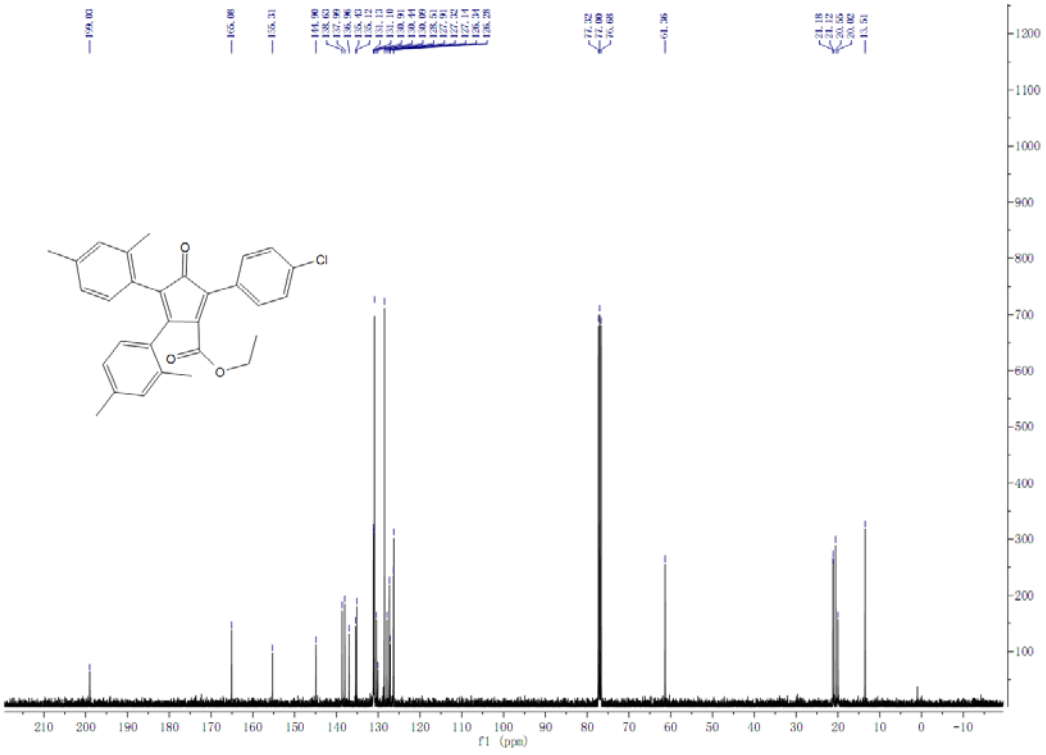

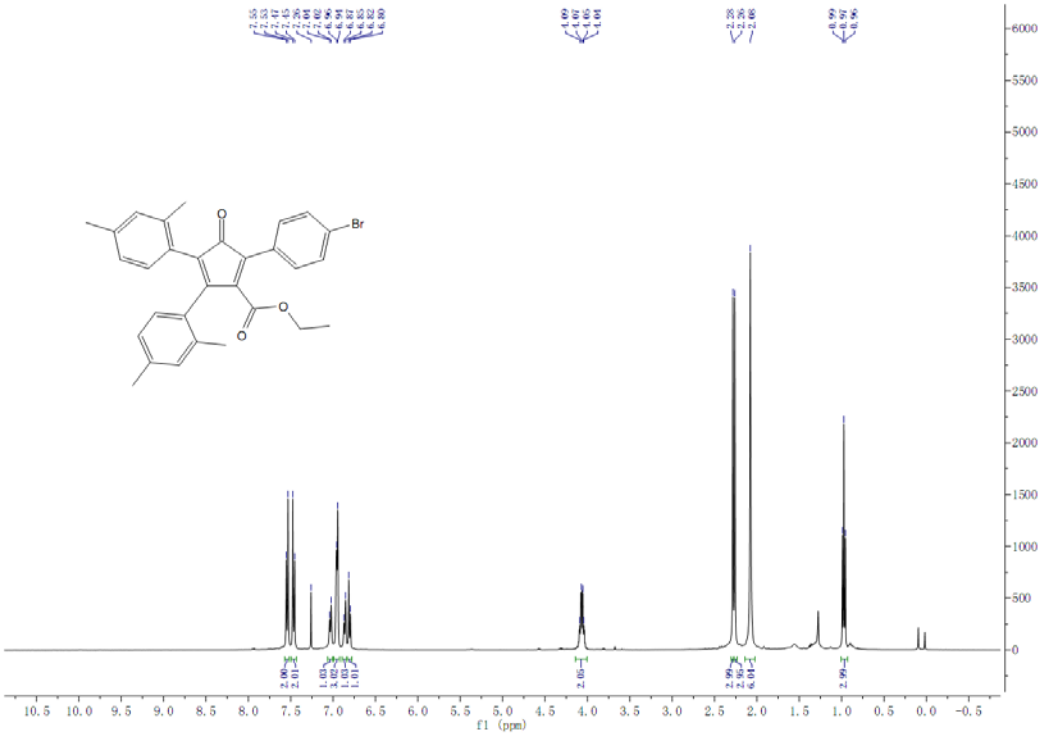

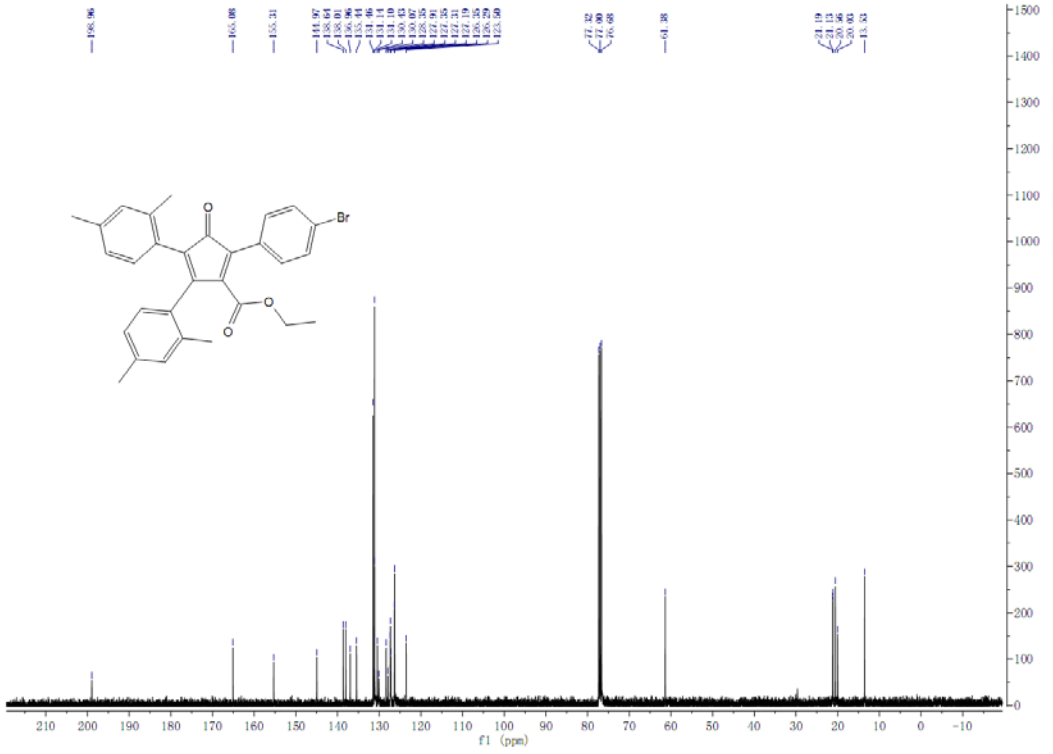
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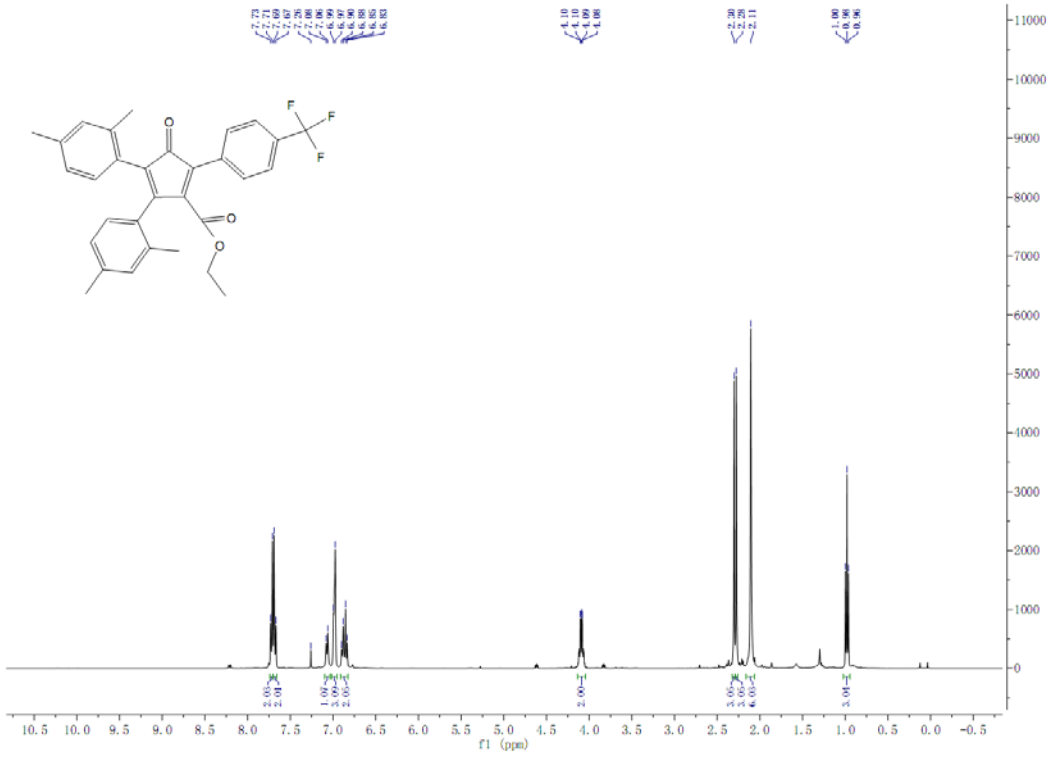
f1 (ppm)


F
F
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O
O
f1 (ppm)

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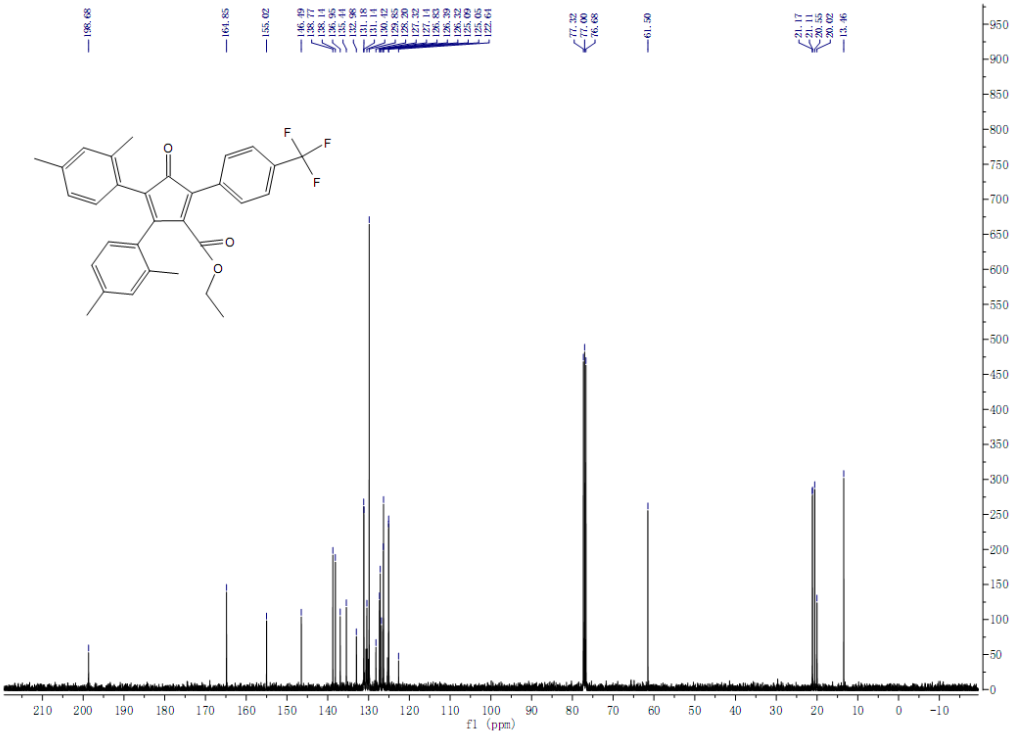

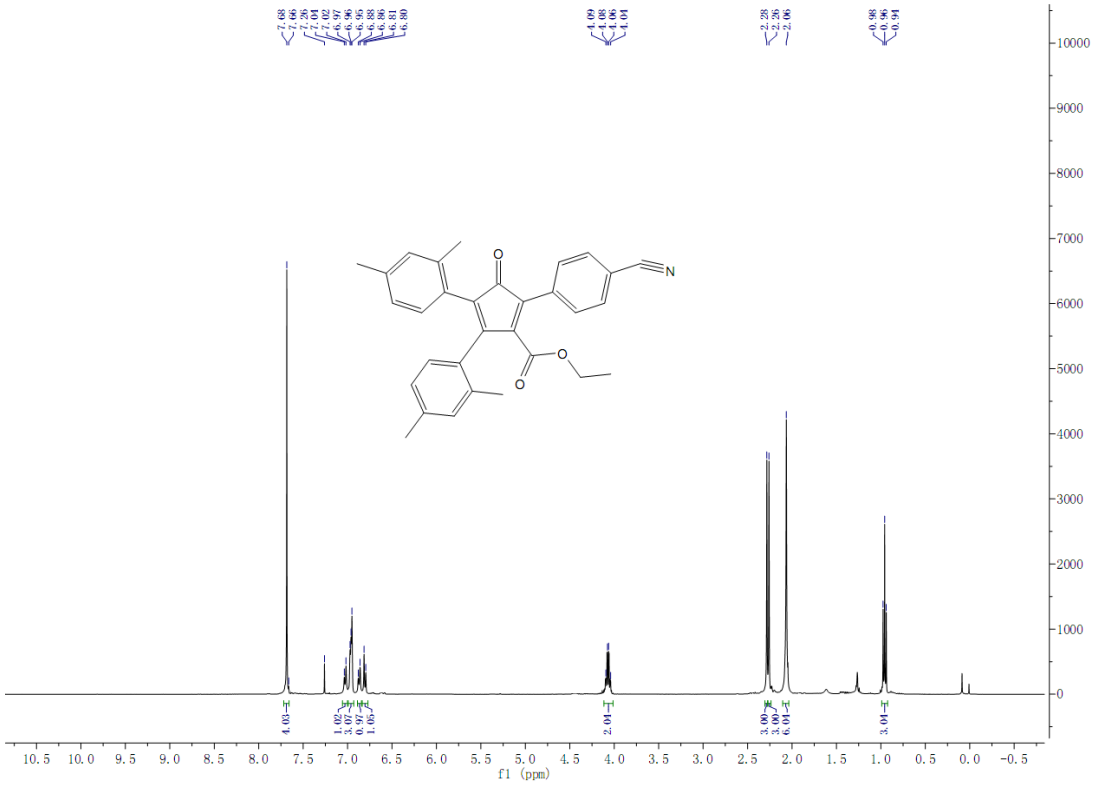

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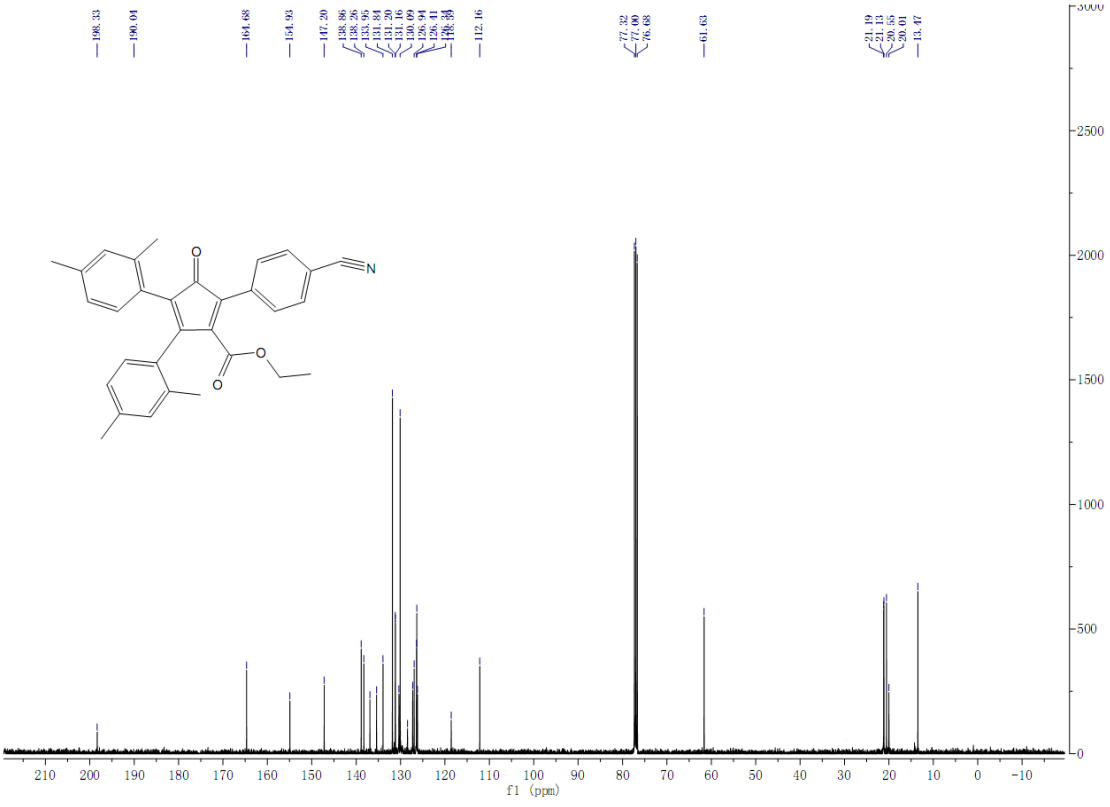

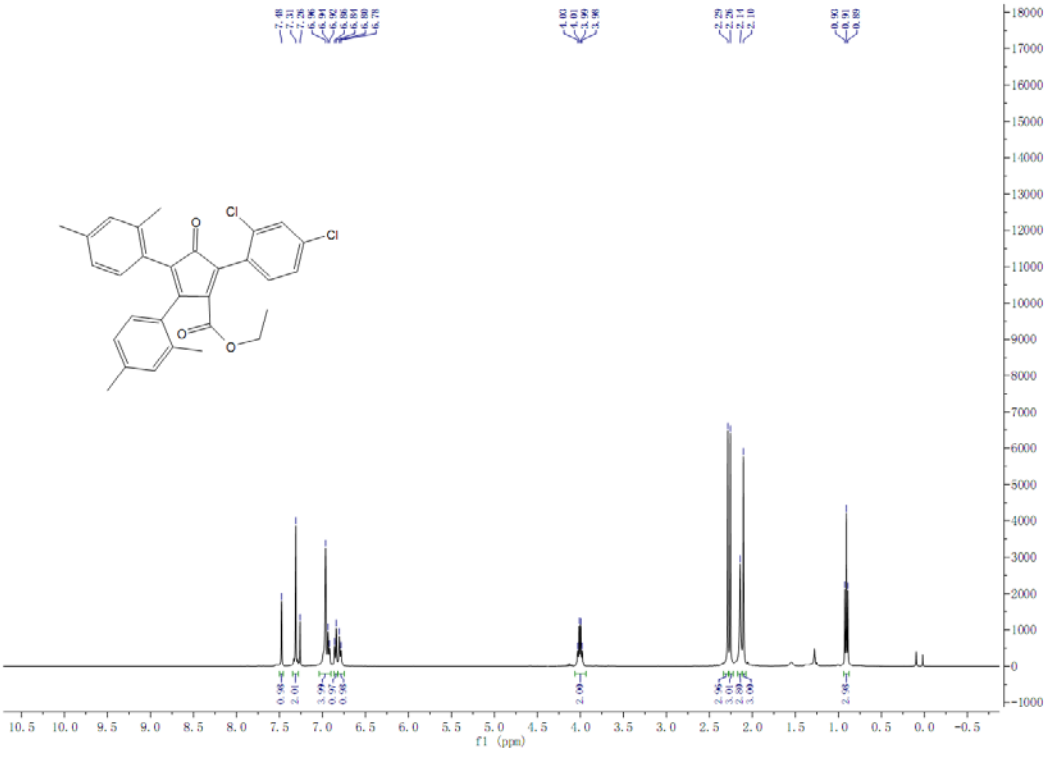

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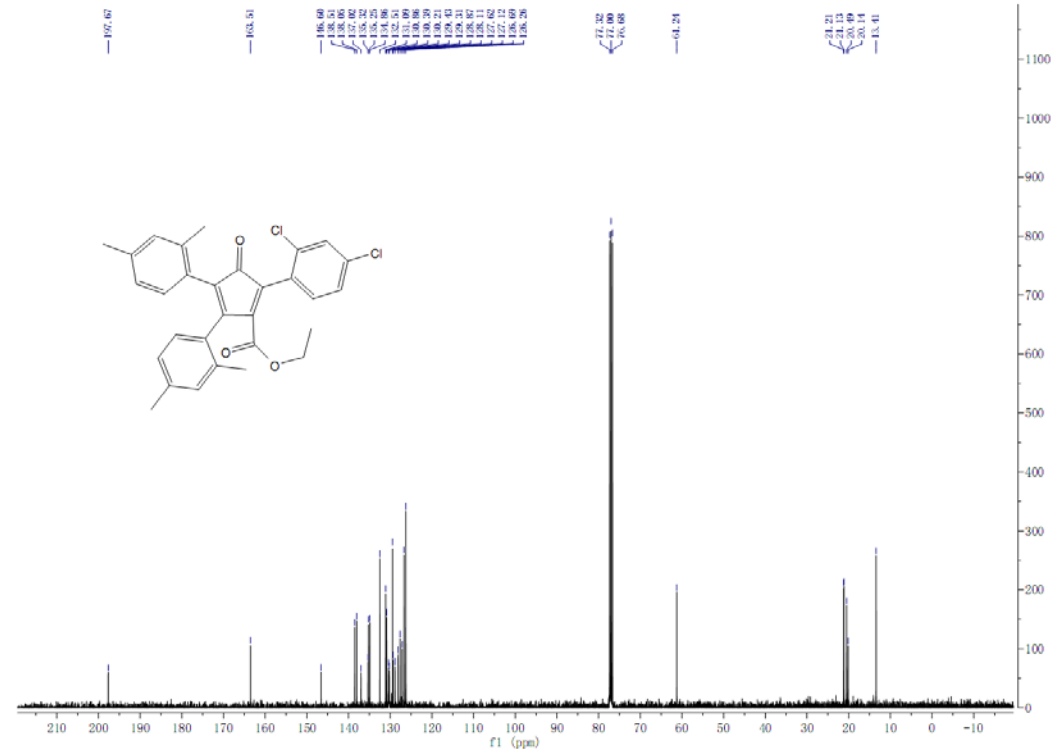

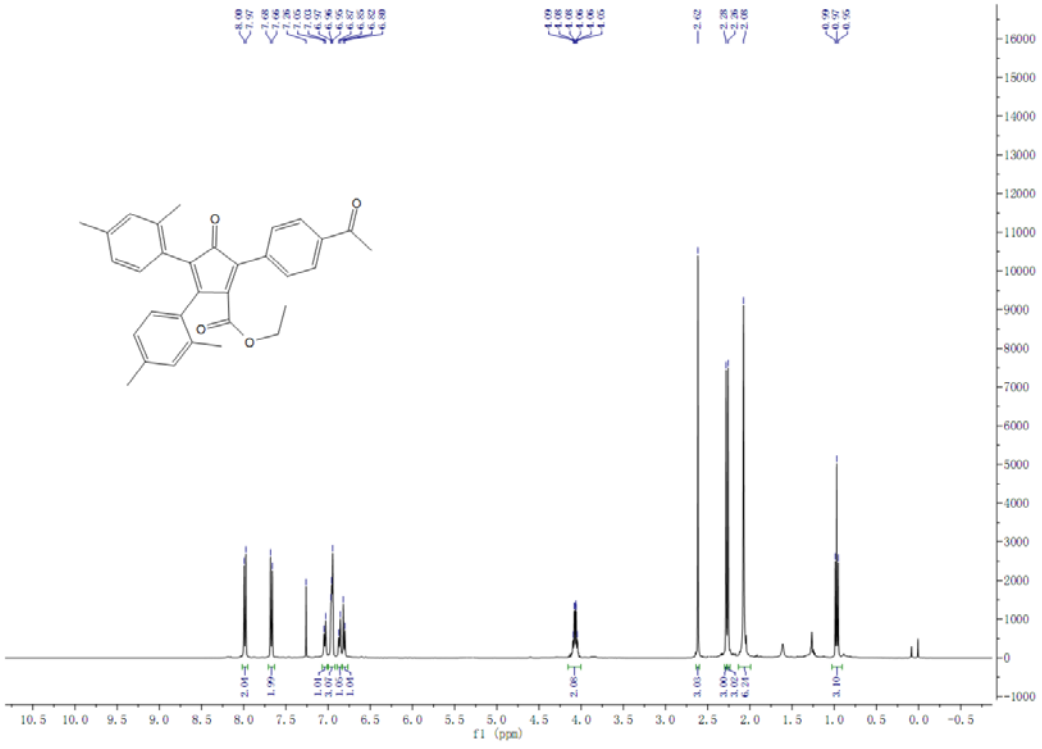

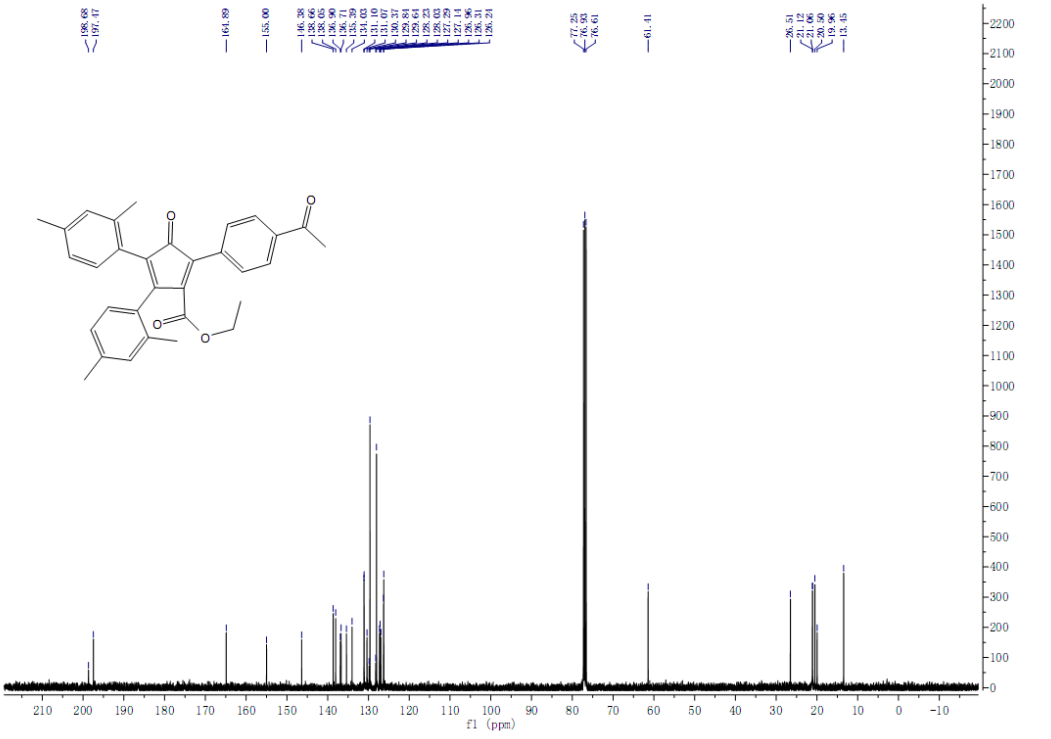
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128.03
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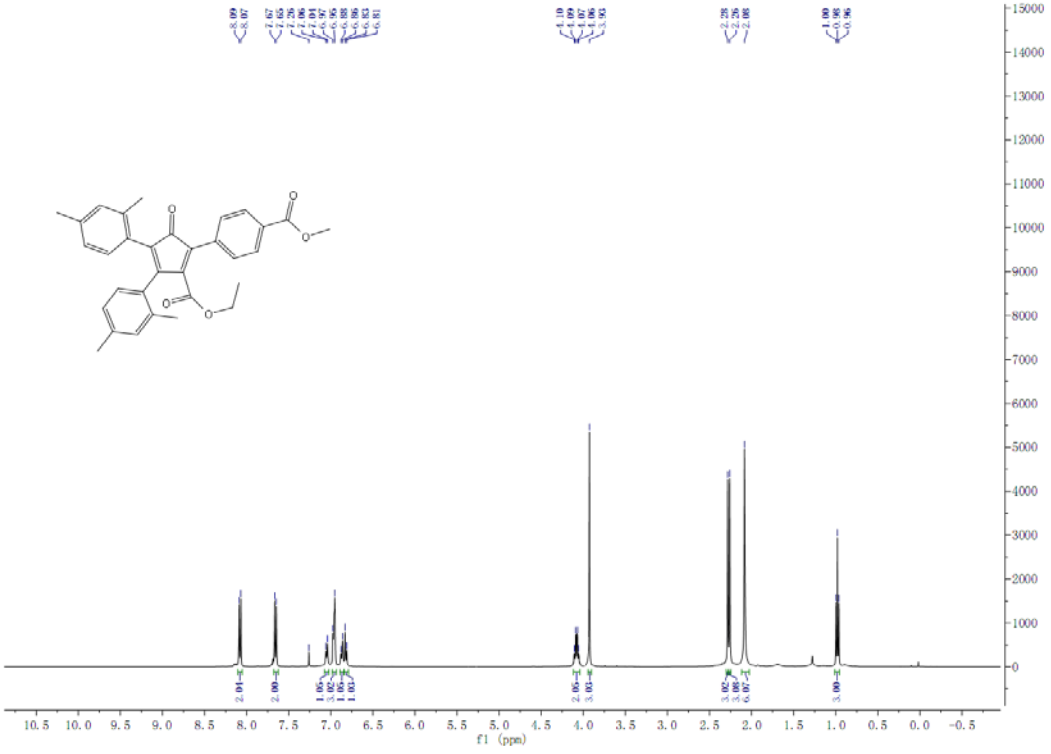
f1 (ppm)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4.07
4.06
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1.07
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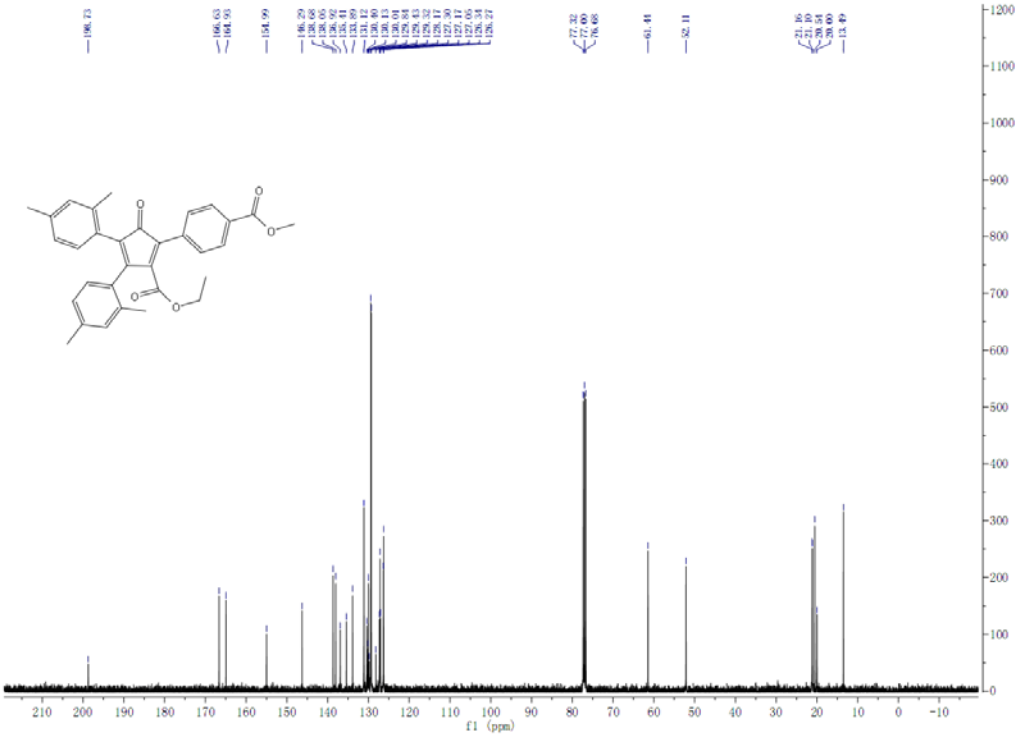
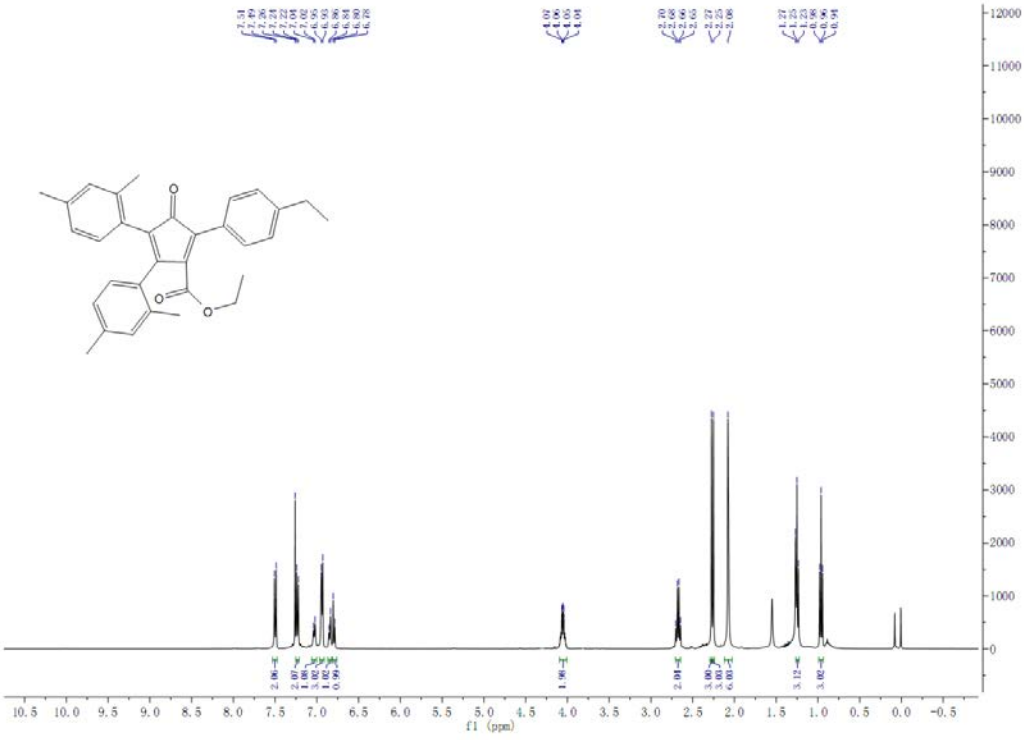
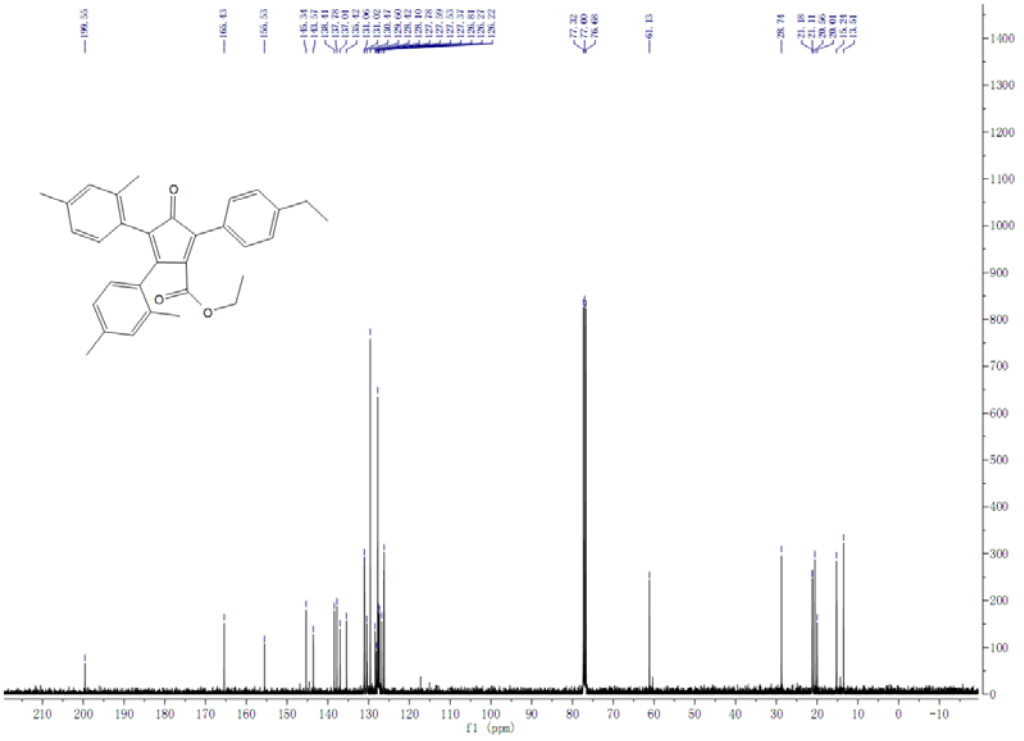
f1 (ppm)



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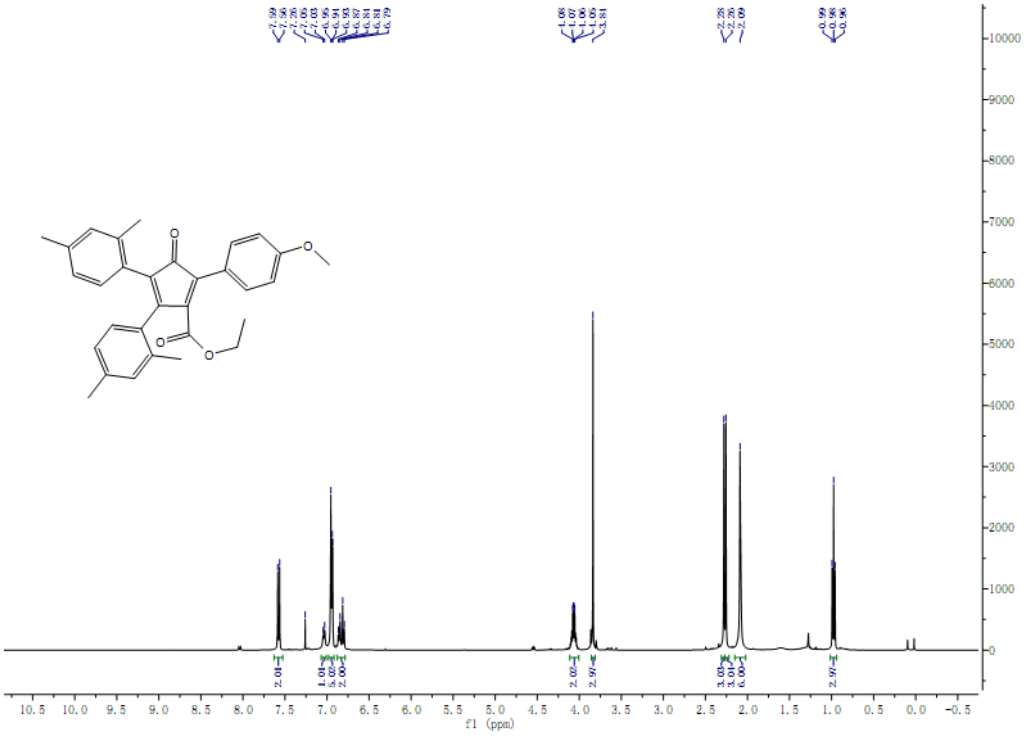
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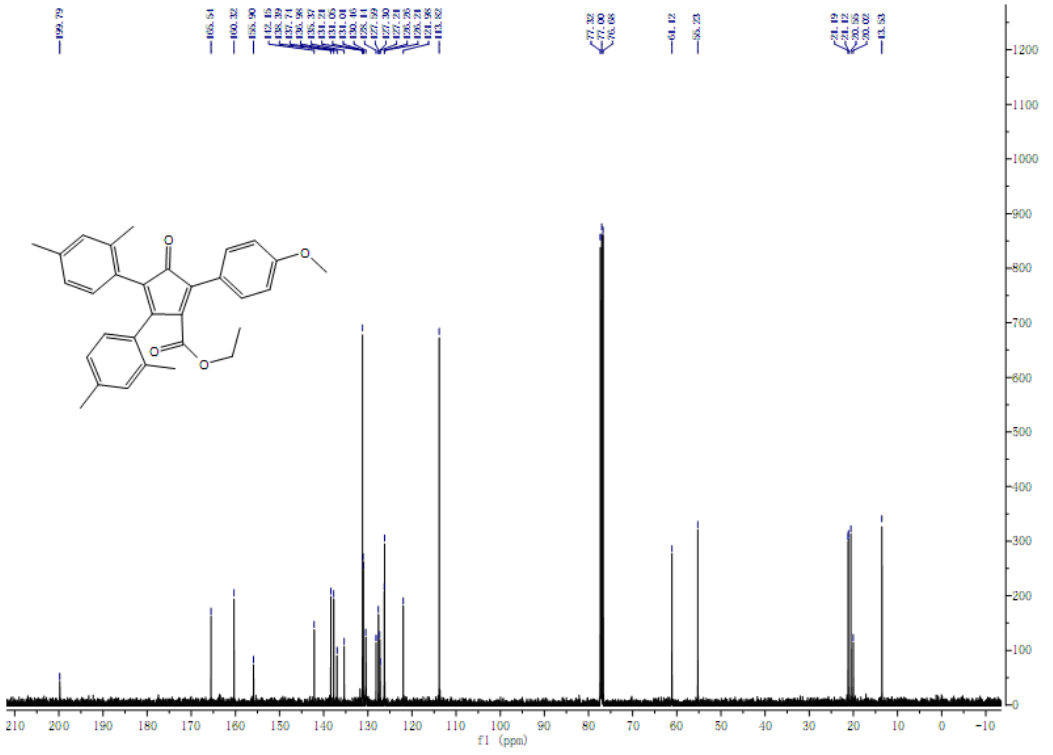

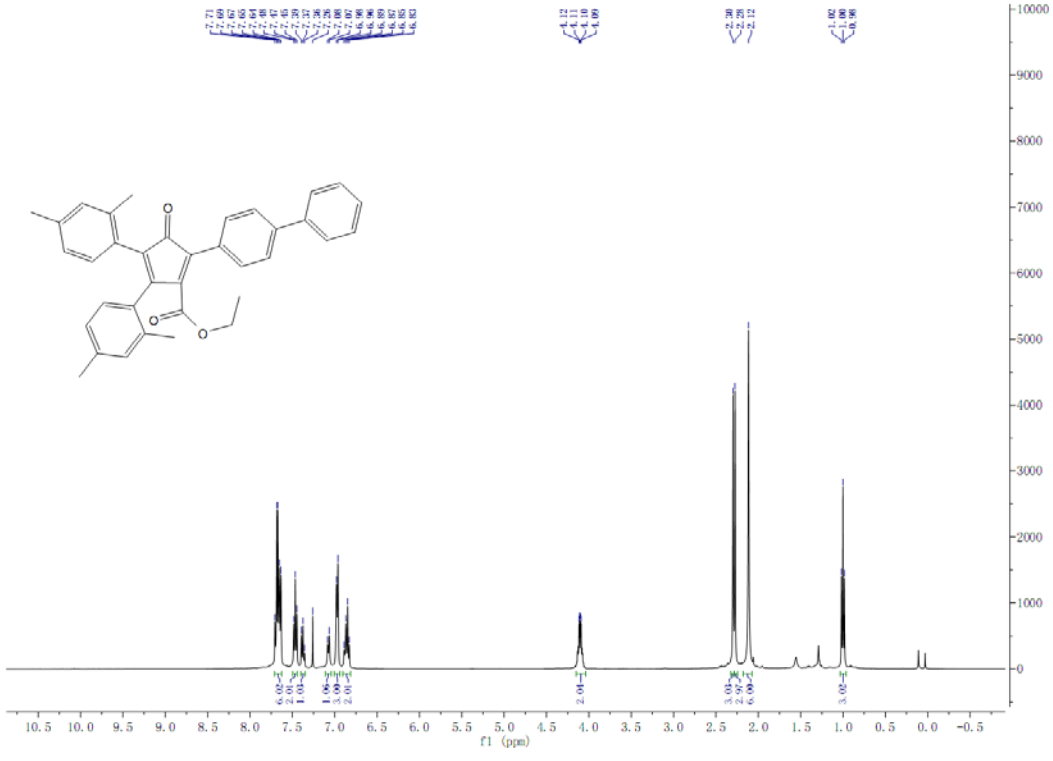

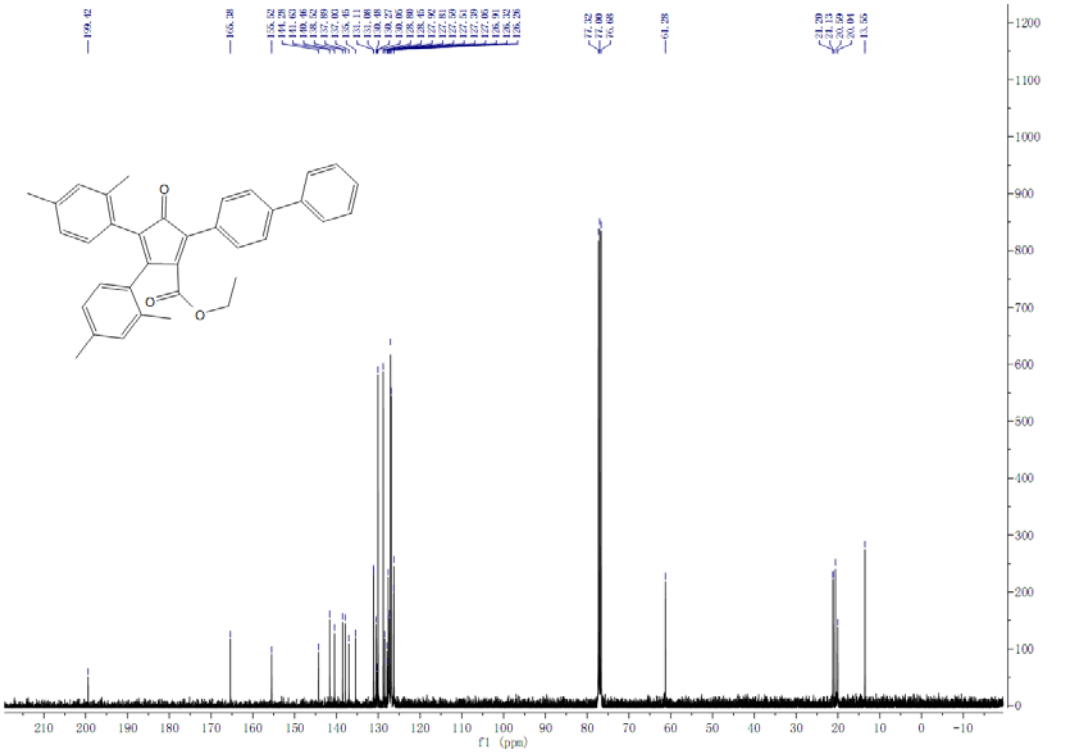

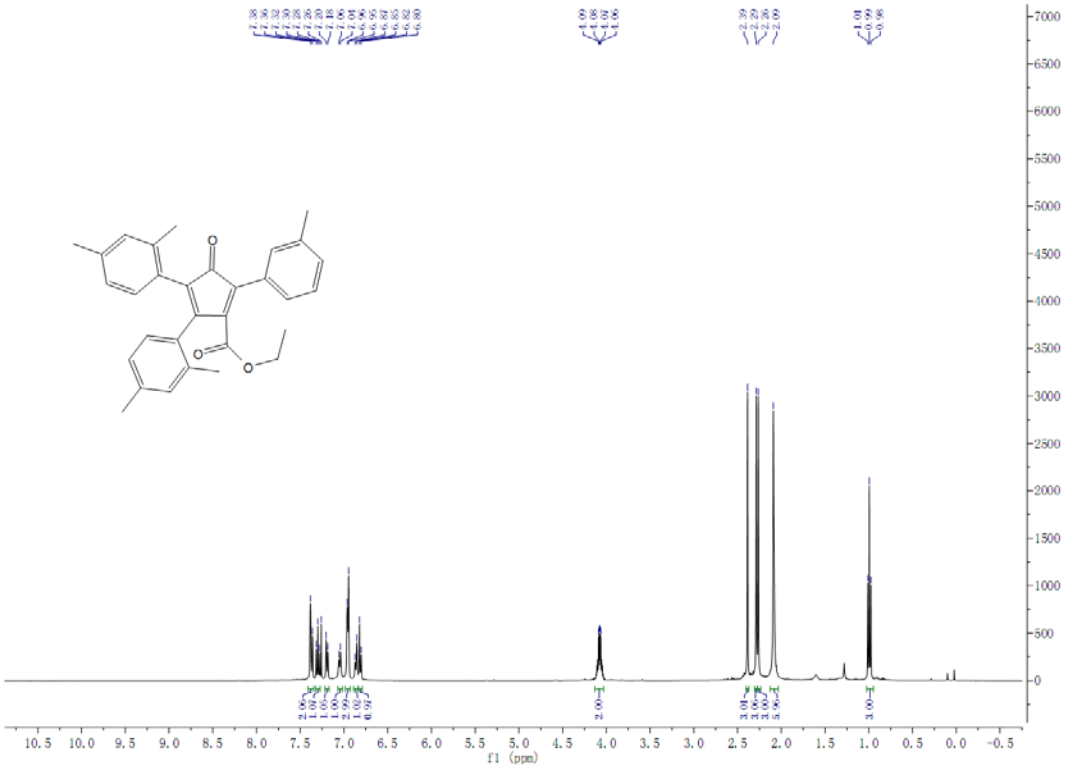

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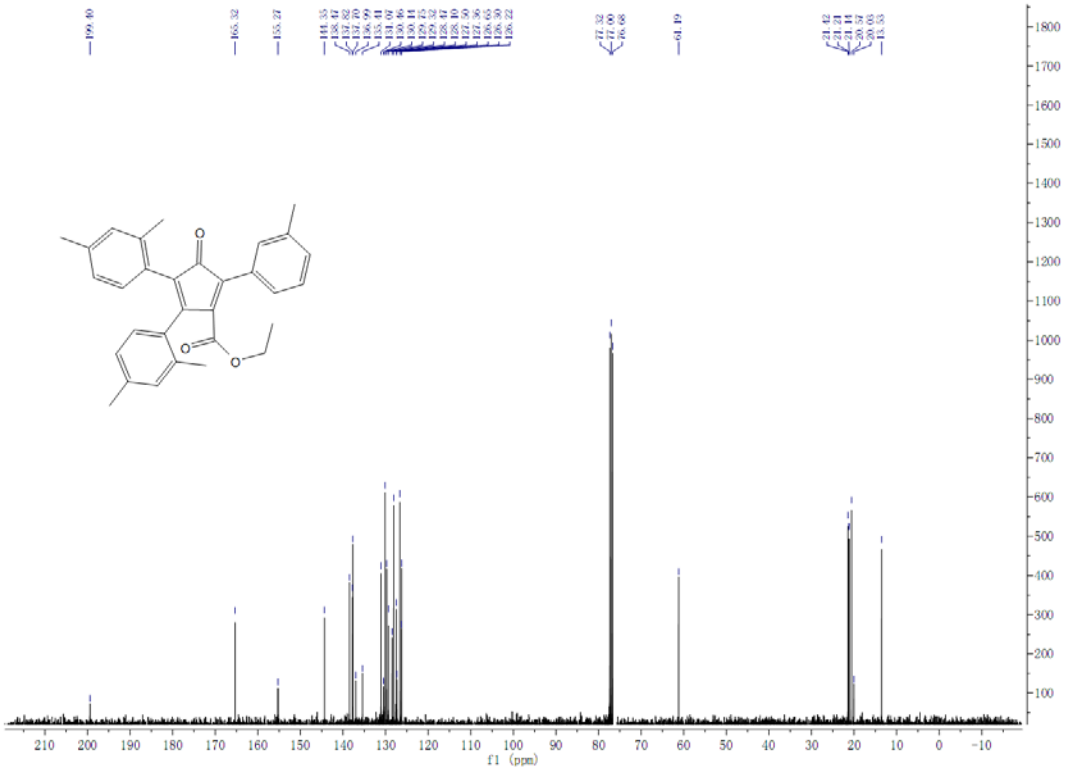

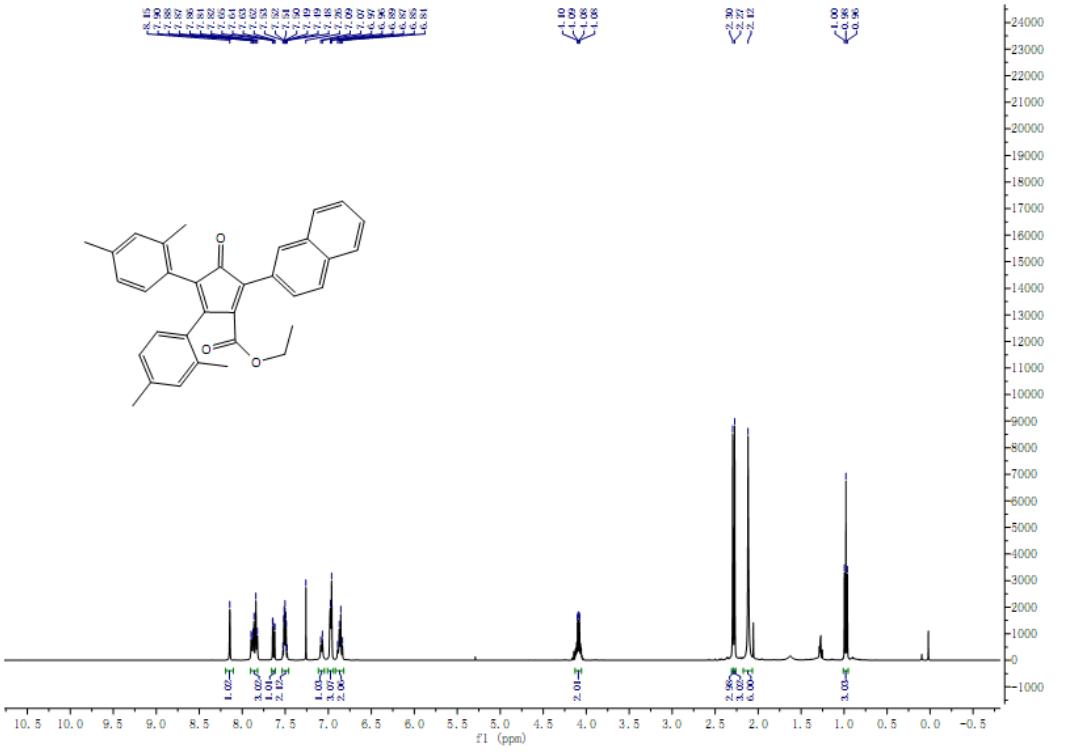

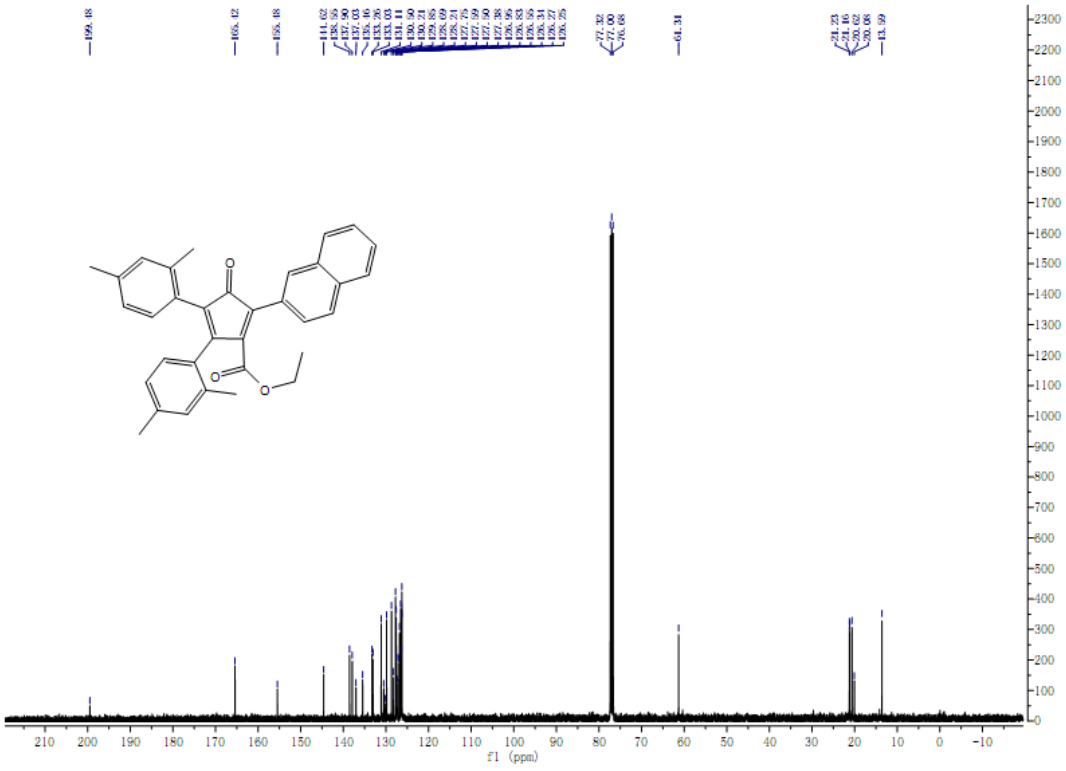
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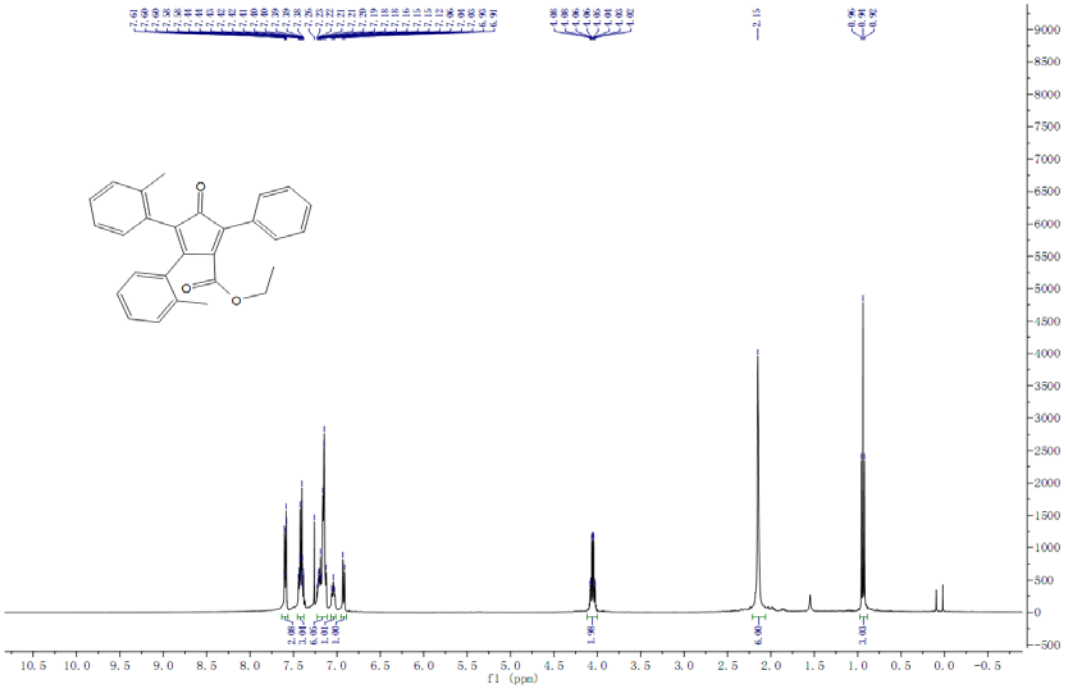
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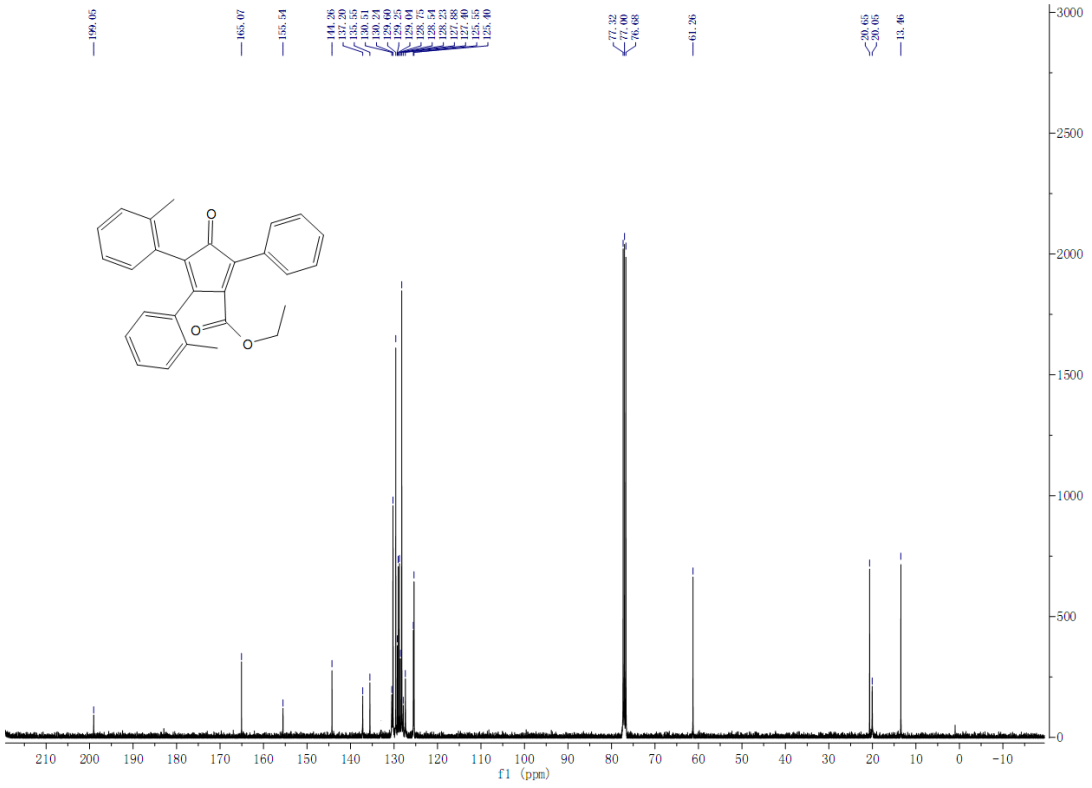

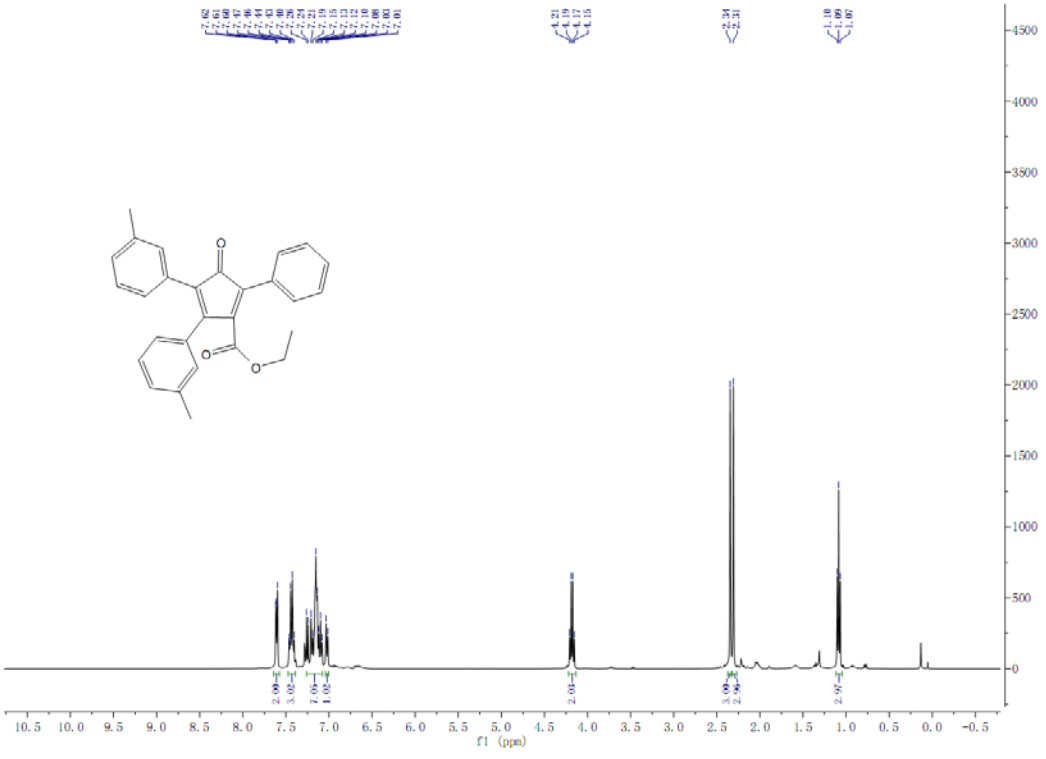

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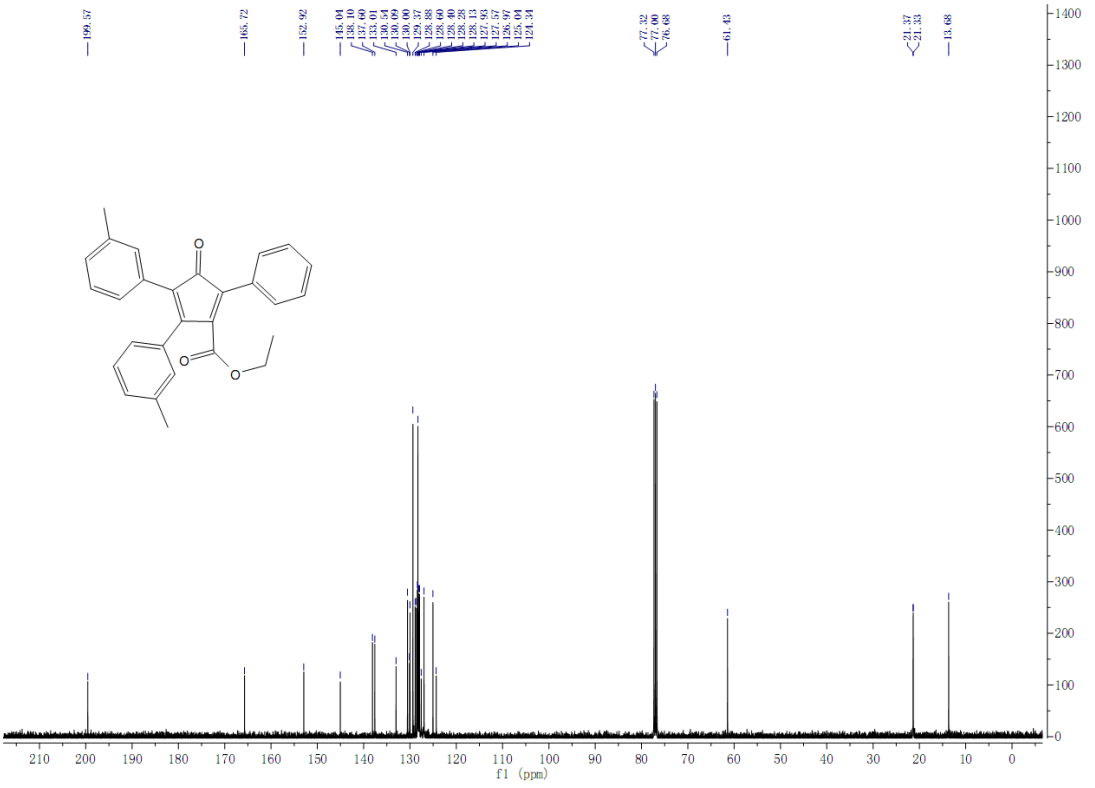

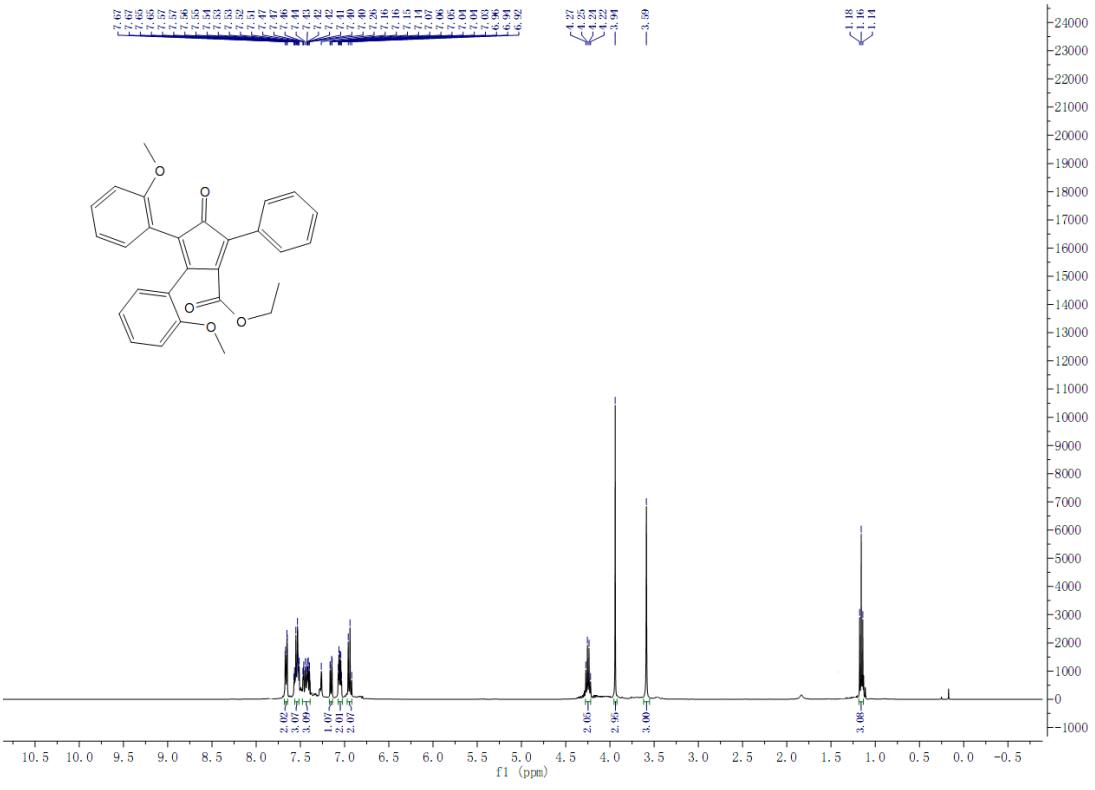

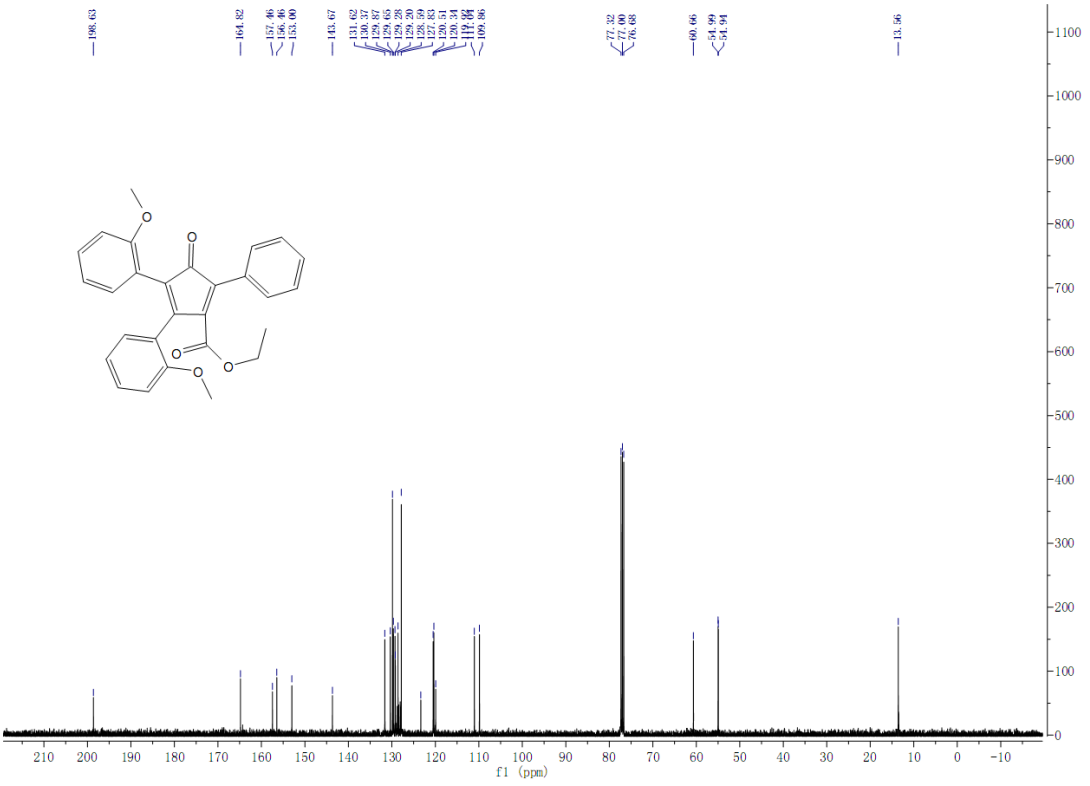
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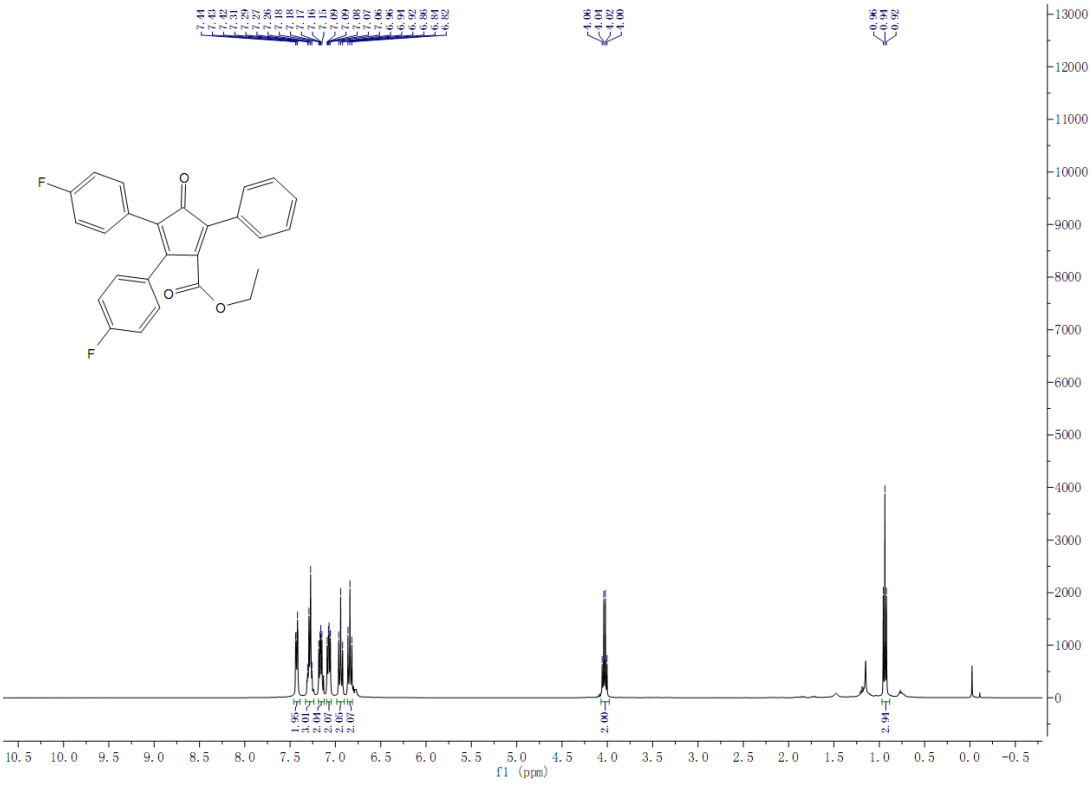
f1 (ppm)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2.05
2.07
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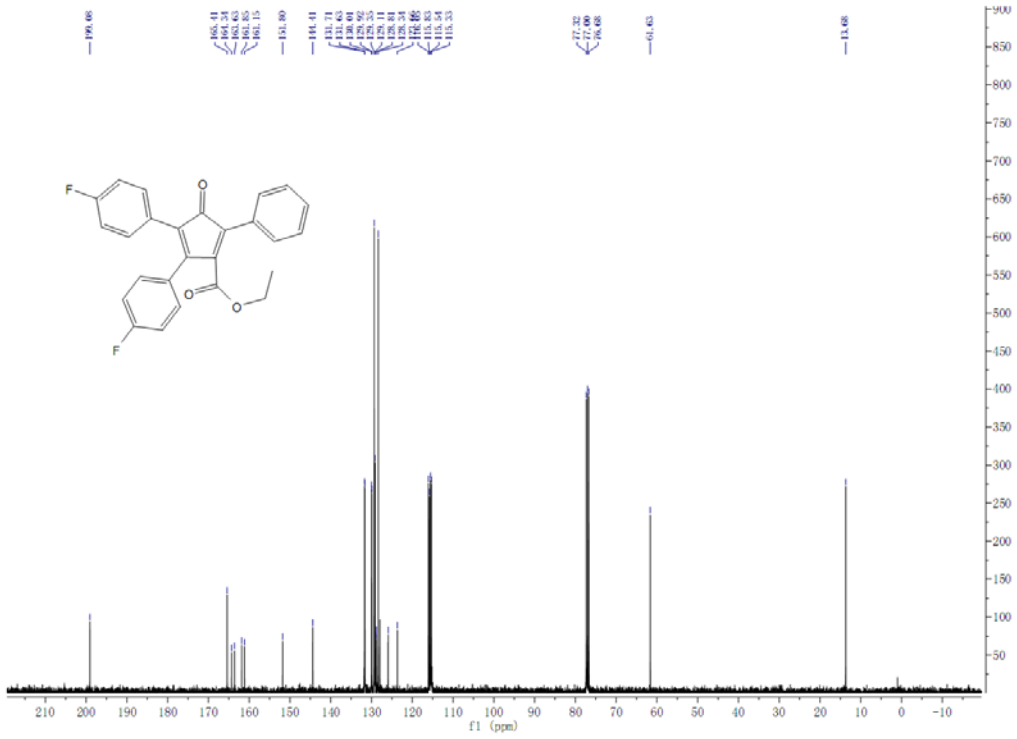
2.94
f1 (ppm)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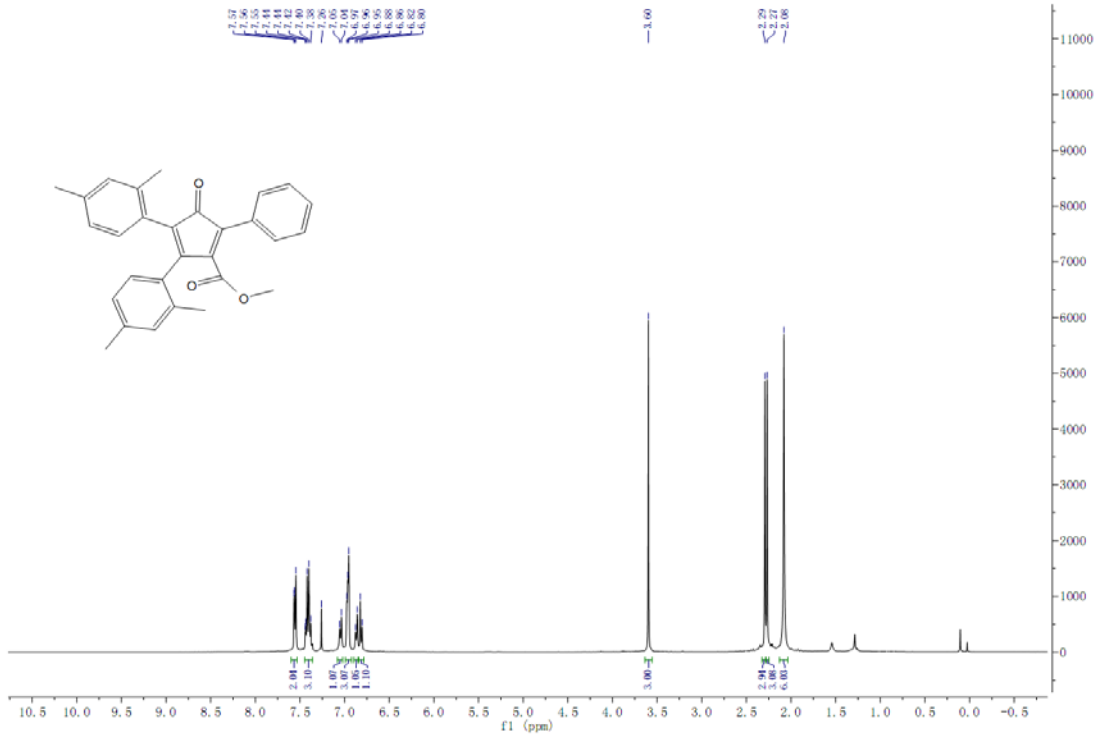
f1 (ppm)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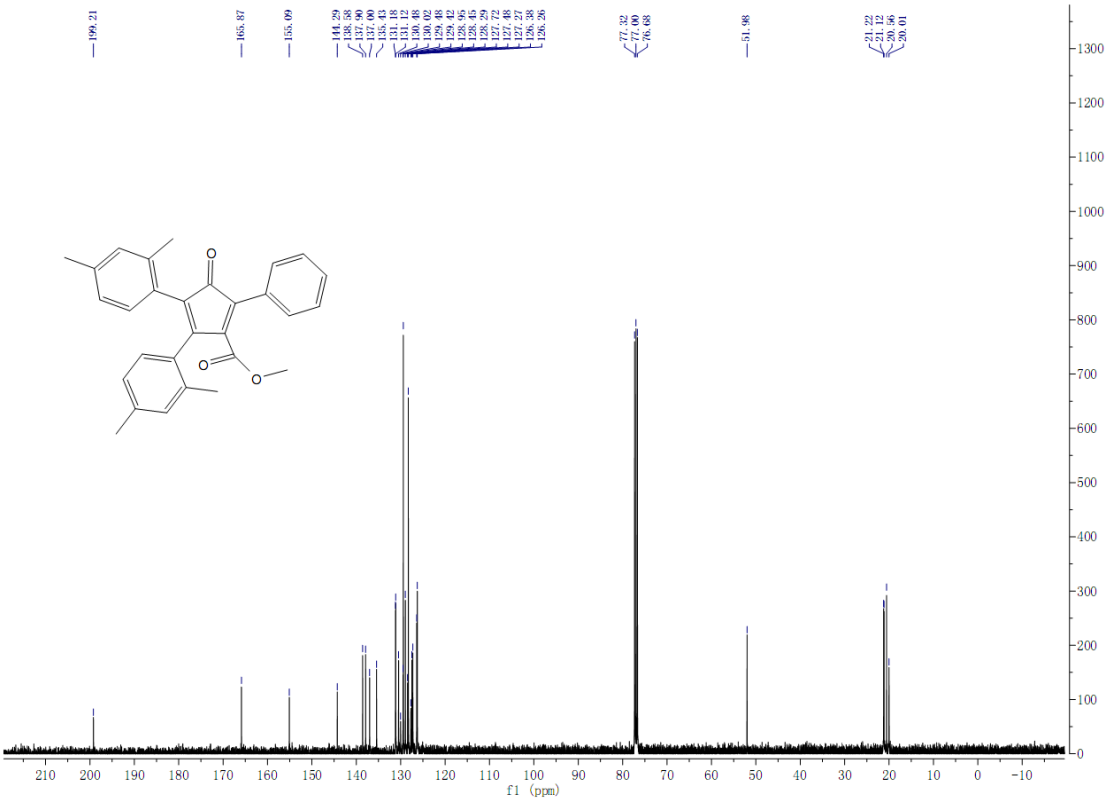
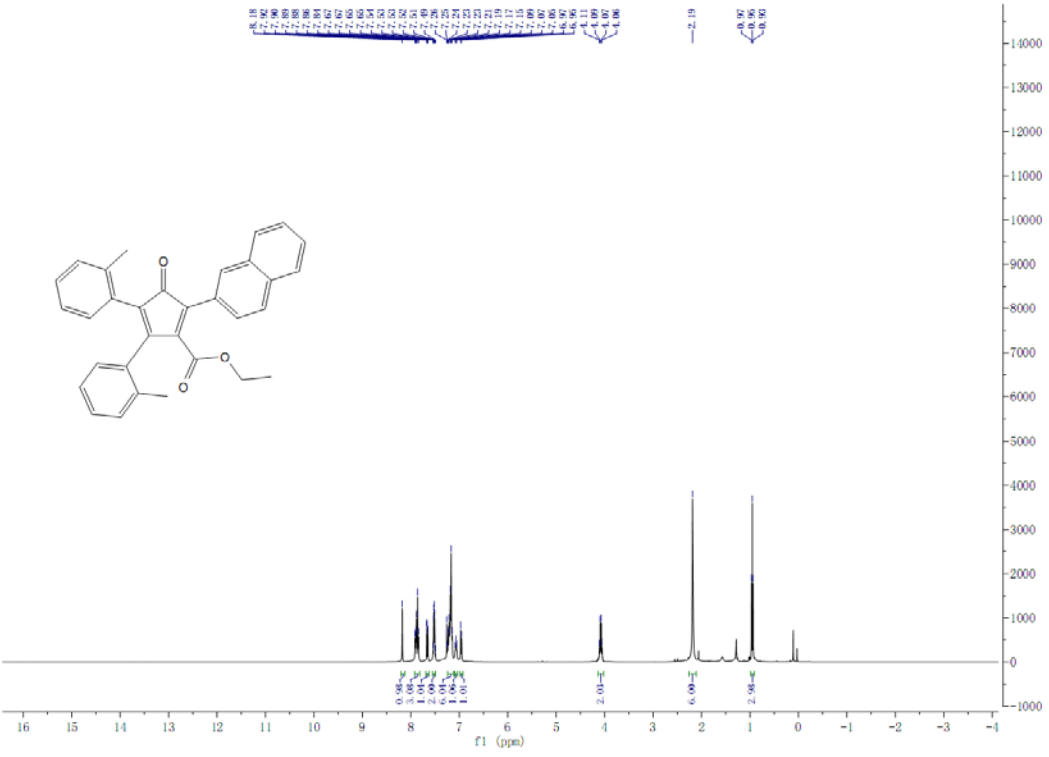
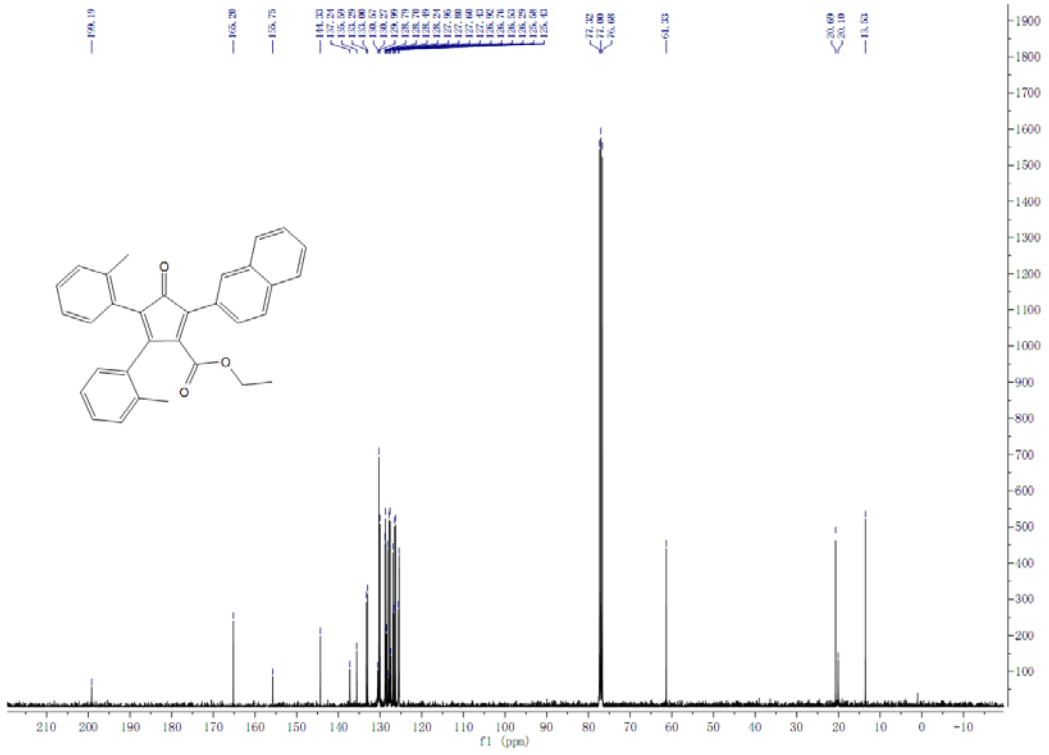
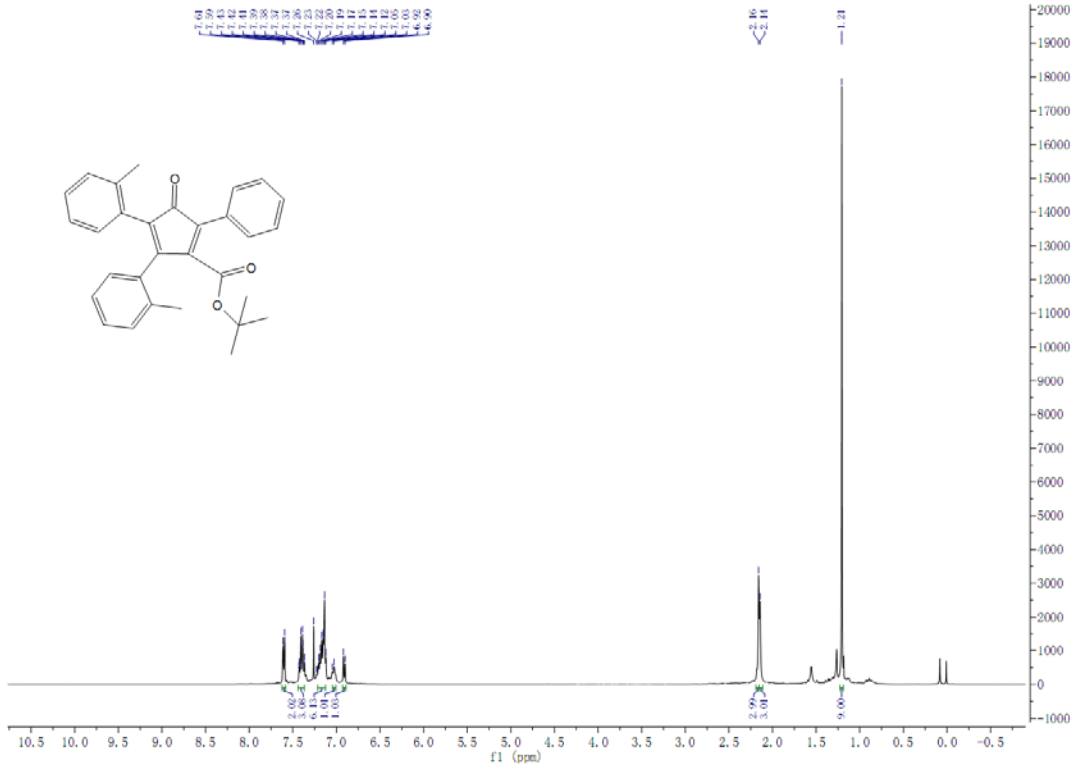
Supporting Information

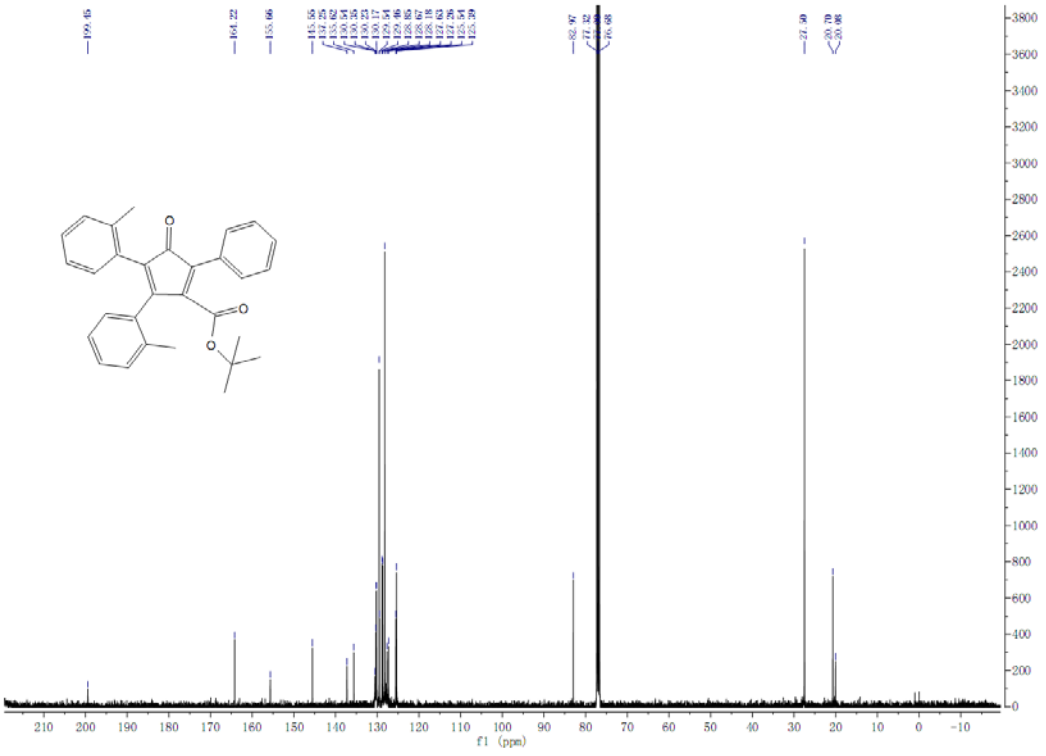


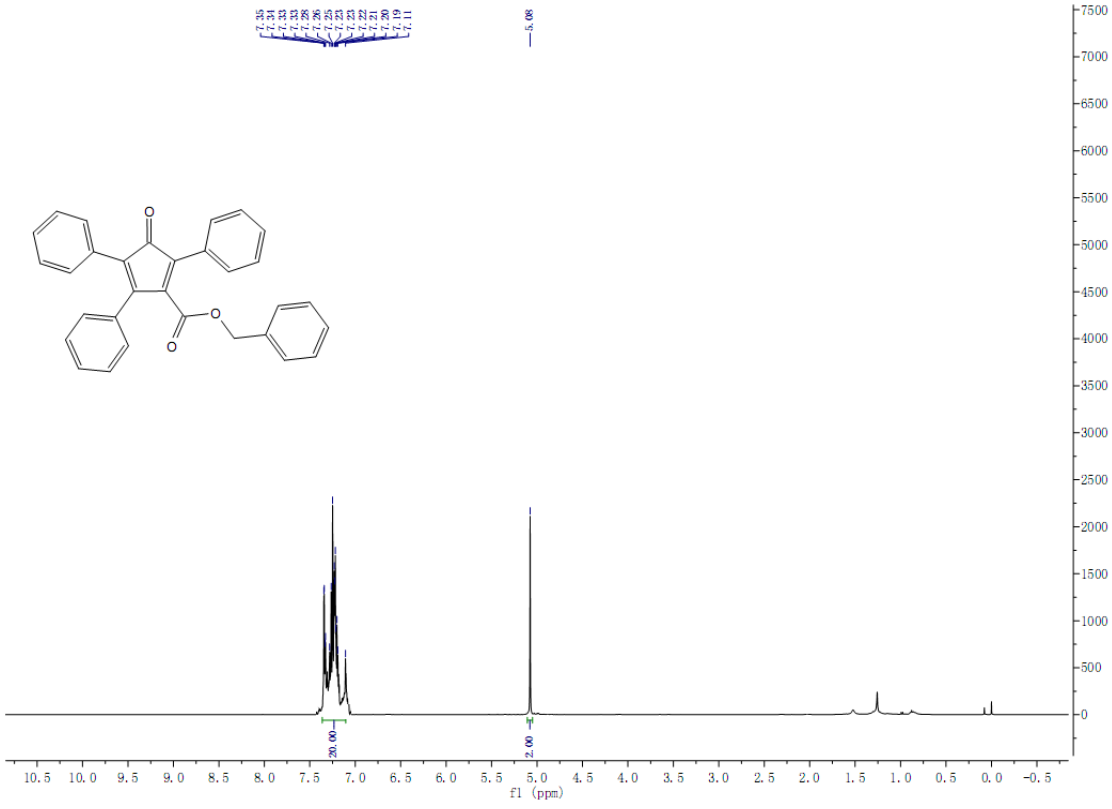


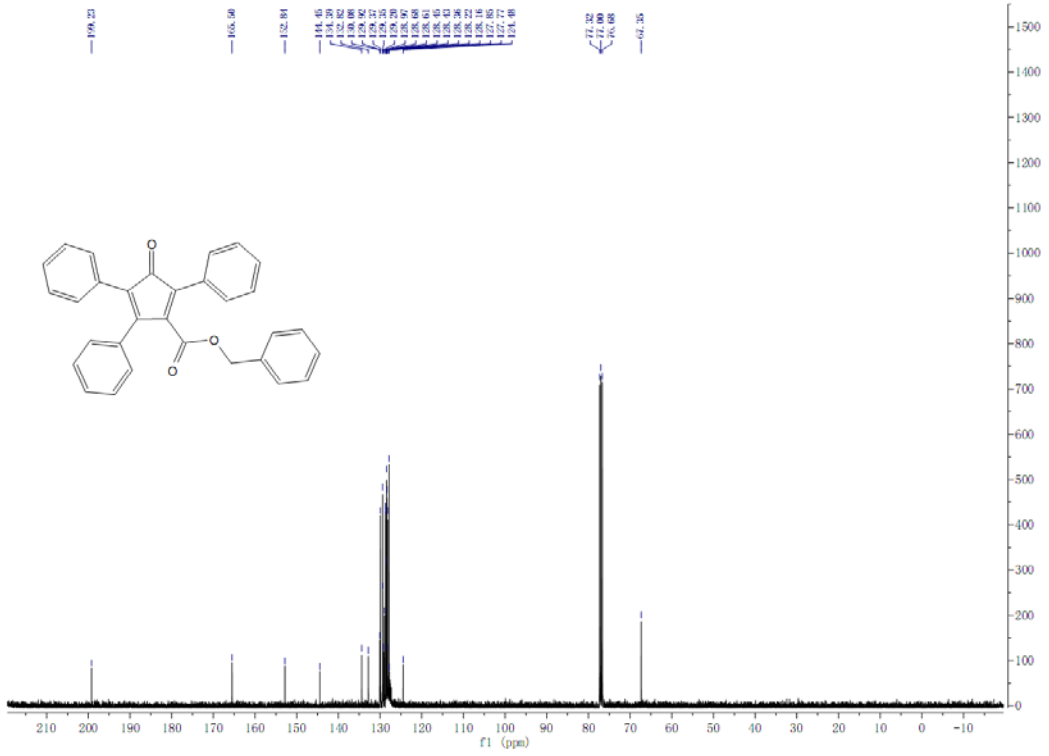




Supporting Information



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128.45
128.43
128.36
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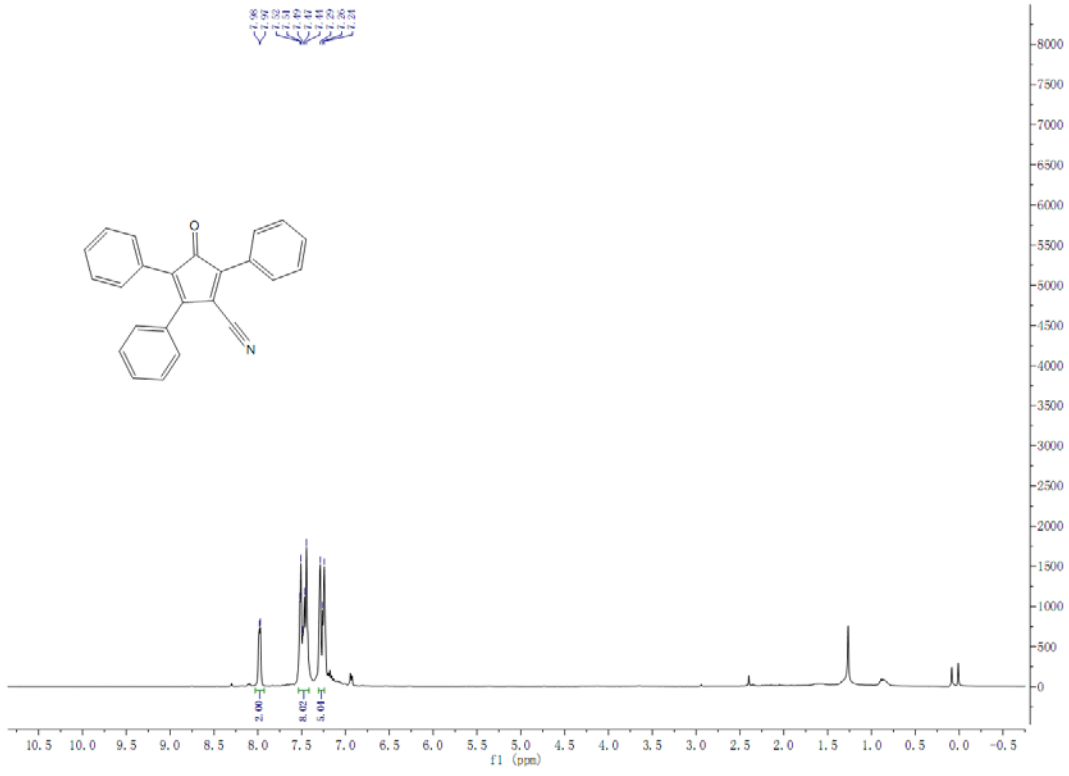
77.32
77.00
76.68
67.35
O
O
O
f1 (ppm)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O
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2.00
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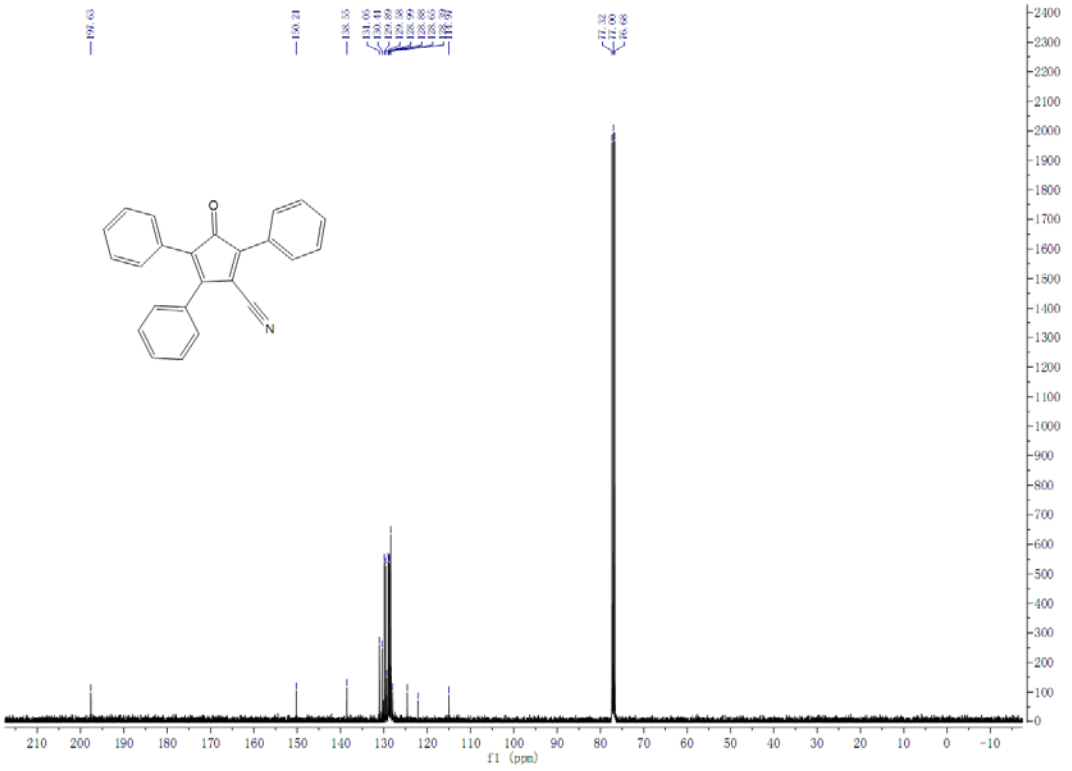
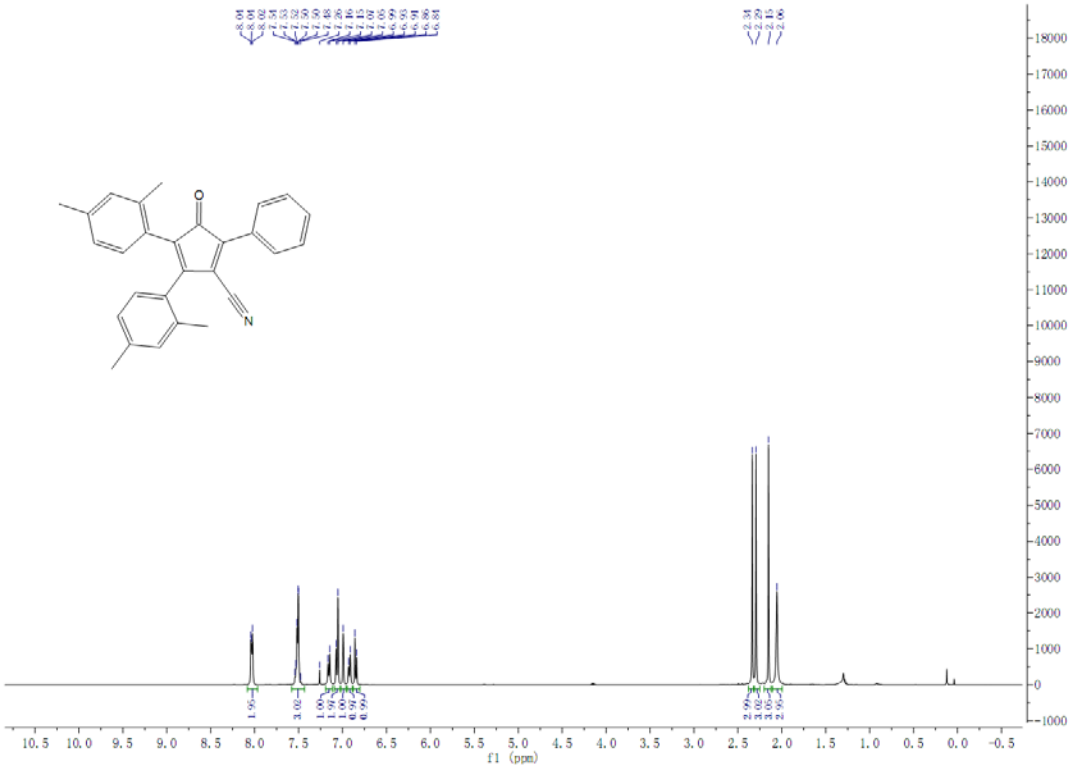
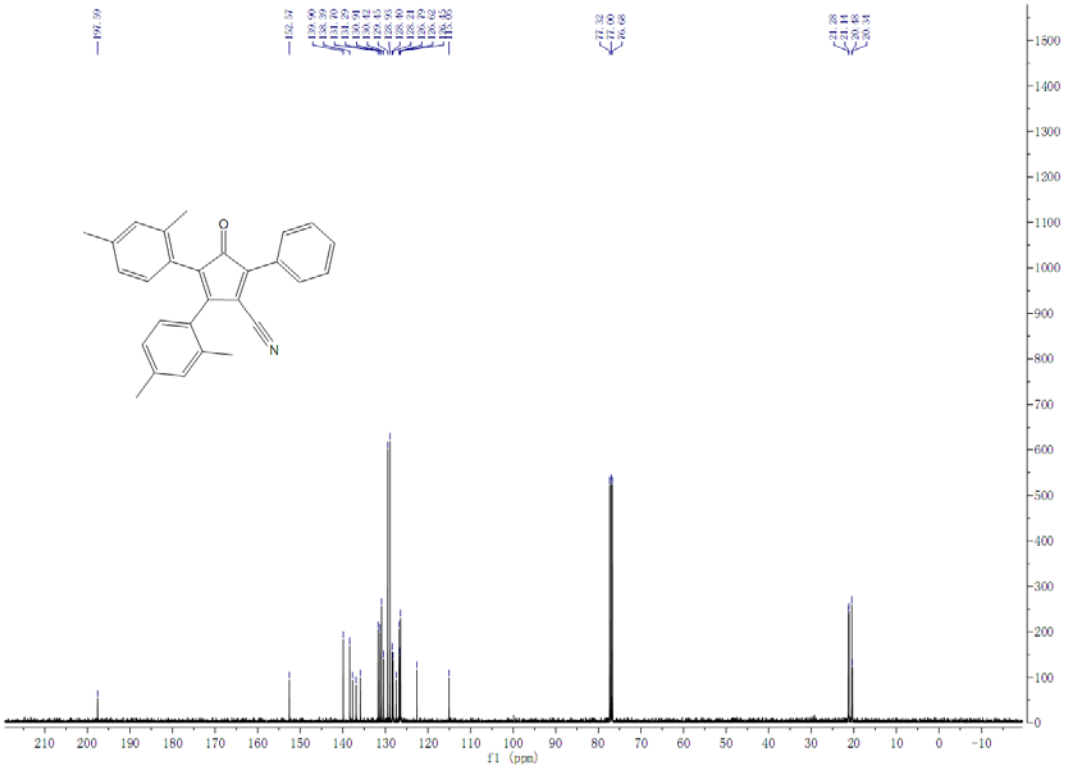
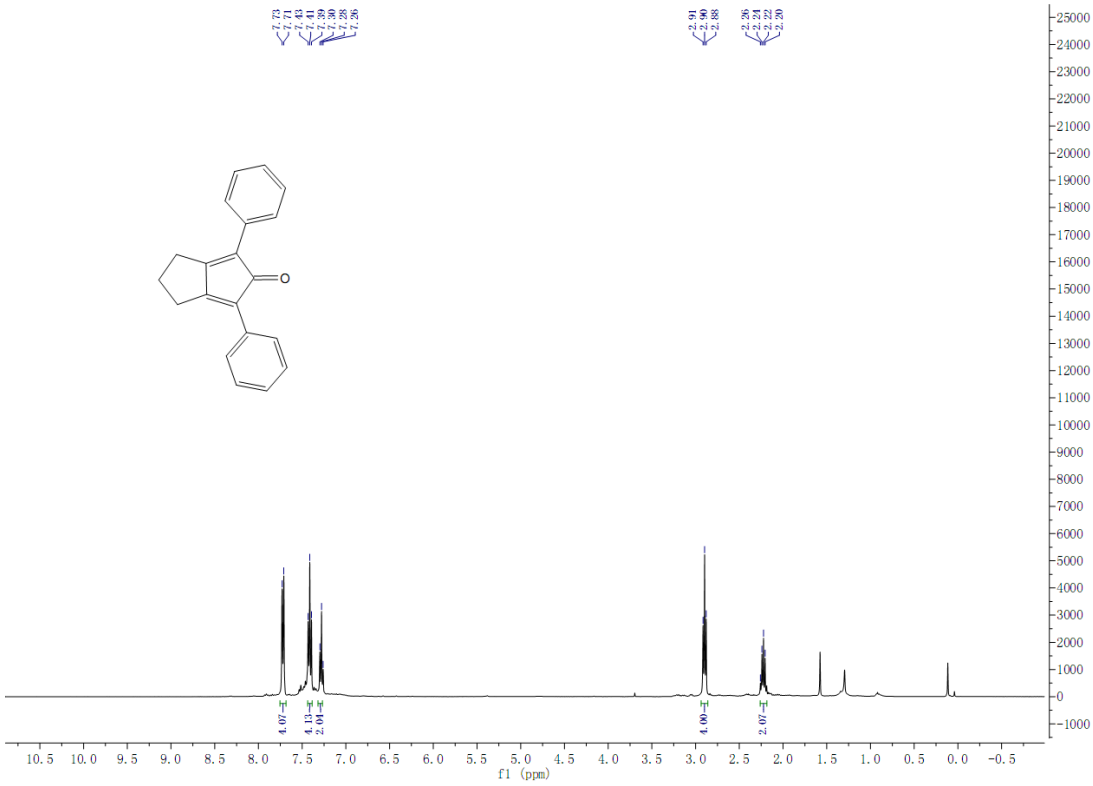
f1 (ppm)

Supporting Information

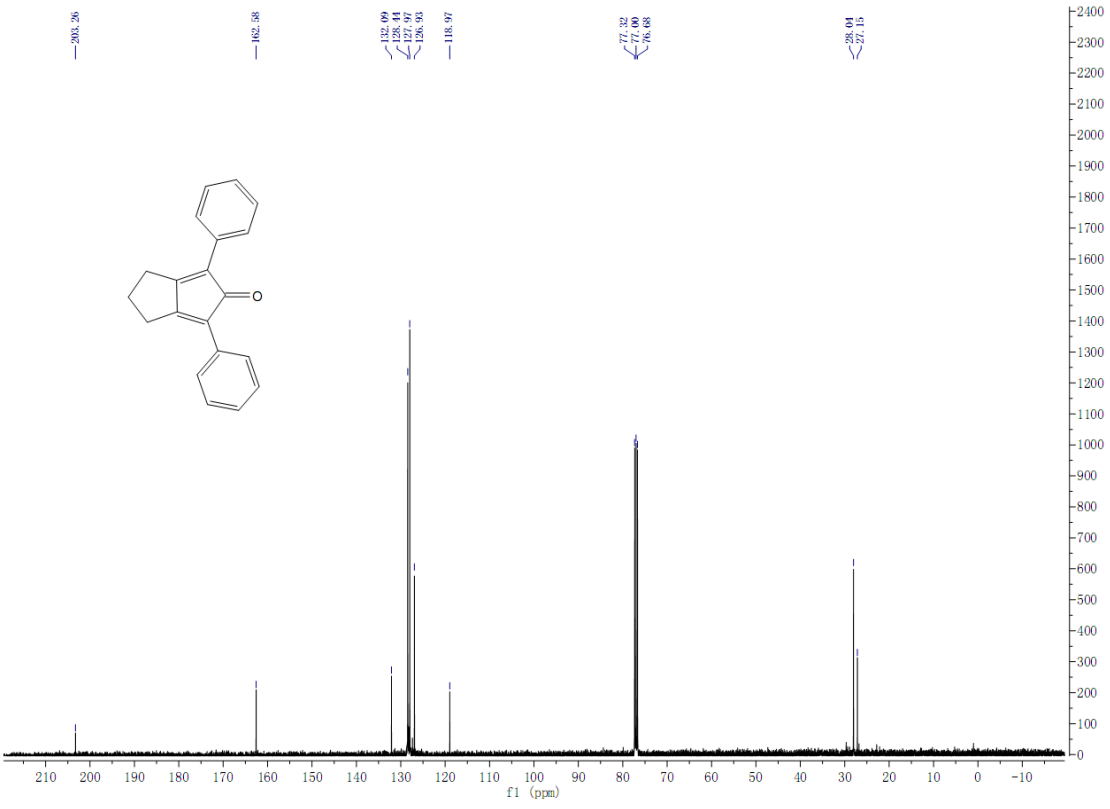


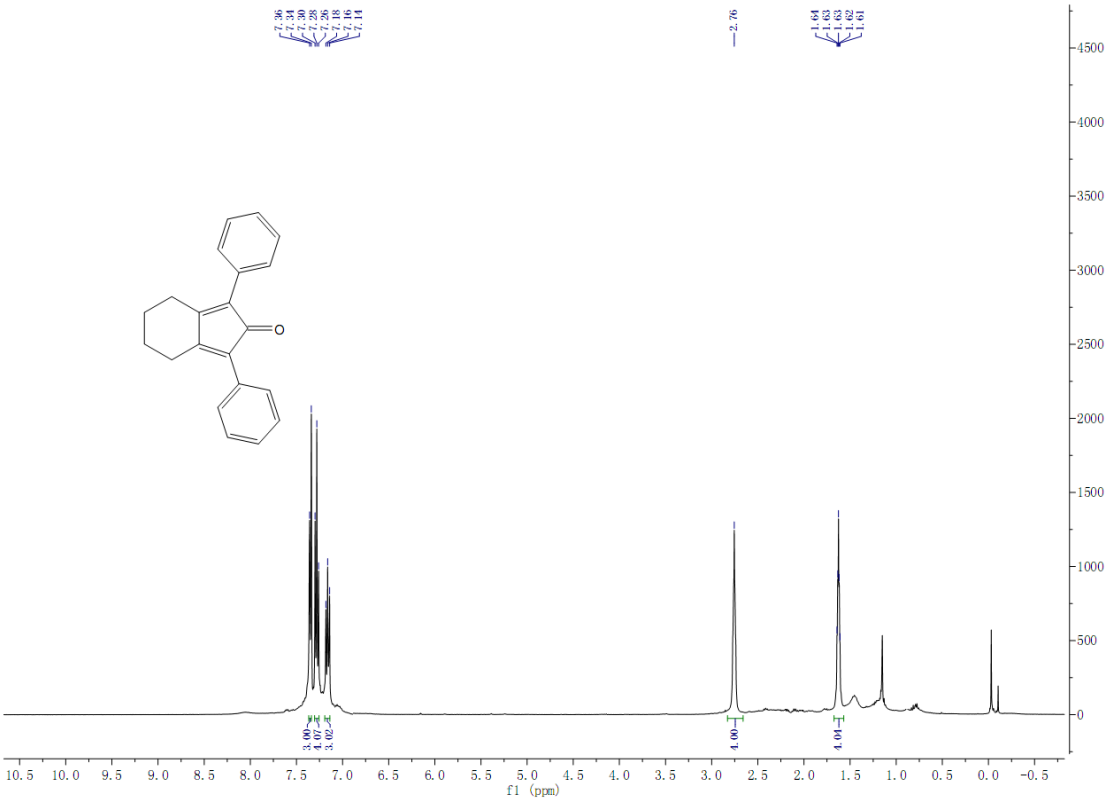



O
N
f1 (ppm)


O
f1 (ppm)

Supporting Information





Supporting Information