Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cobalt(III)-Catalyzed Efficient Synthesis of Indenones through Carboannulation of Benzoates and Alkynes

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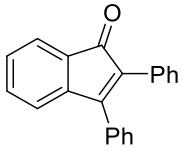
Table of Contents

I. General

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. Diphenylacetylenes[1] and $[CoCp^*(CO)I_2]$[2] were prepared by following literature reports. All reactions were carried out using Schlenk techniques or in an N_2-filled glovebox. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^1H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using dichloromethane (DCM)/petroleum ether (PE).

II. General procedures for the synthesis of compound 3

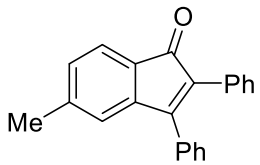
Benzoates (0.2 mmol), alkynes (0.24 mmol), $[Cp^*Co(CO)I_2]$ (10 mol %), $AgNTf_2$ (20 mol %), $Zn(OAc)_2$ (2.0 equiv), and HFIP (2.0 mL) were charged into the pressure tube. The reaction mixture was stirred under N_2 at 120 ºC for 12 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/DCM to afford the product **3**.



2,3-Diphenyl-1H-inden-1-one **(3aa)**

3aa was obtained according to the general procedure in 86% yield (48.5 mg). red solid;

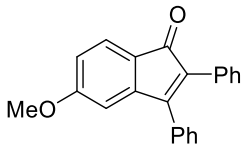
^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 6.8 Hz, 1H), 7.44 – 7.32 (m, 6H), 7.29 – 7.25 (m, 6H), 7.14 (d, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 155.4, 145.3, 133.5, 132.8, 132.4, 130.8, 130.7, 130.0, 129.3, 129.0, 128.8, 128.5, 128.1, 127.8, 123.0, 121.3. The NMR data agree with those in a literature report.[3]



5-Methyl-2,3-diphenyl-1H-inden-1-one **(3ba)**

3ba was obtained according to the general procedure in 91% yield (53.9 mg). red solid;

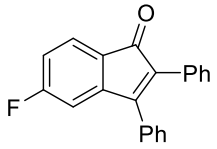
^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.2 Hz, 1H), 7.30 – 7.35 (m, 5H), 7.27 – 7.23 (m, 5H), 7.06 (d, J = 7.1 Hz, 1H), 6.93 (s, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 154.9, 145.6, 144.4, 132.8, 132.7, 130.8, 129.9, 129.1, 128.9, 128.7, 128.5, 128.3, 128.0, 127.6, 123.0, 122.5, 22.1. The NMR data agree with those in a literature report.[3]



5-Methoxy-2,3-diphenyl-1H-inden-1-one **(3ca)**

3ca was obtained according to the general procedure in 77% yield (47.8 mg). red solid;

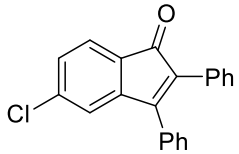
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 7.9 Hz, 1H), 7.40 – 7.34 (m, 5H), 7.30 – 7.20 (m, 5H), 6.73 – 6.63 (m, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 164.5, 153.2, 147.9, 133.9, 132.7, 130.9, 130.0, 129.2, 128.8, 128.6, 128.1, 127.8, 124.9, 123.5, 110.5, 110.3, 55.8. The NMR data agree with those in a literature report.[3]



5-Fluoro-2,3-diphenyl-1H-inden-1-one **(3da)**

3da was obtained according to the general procedure in 51% yield (30.3 mg). red solid;

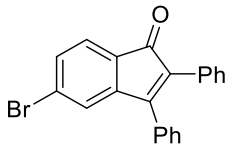
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dd, J = 7.8, 5.2 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.37 – 7.34 (m, 2H), 7.26 – 7.24 (m, 5H), 6.96 – 6.89 (m, 1H), 6.86 (dd, J = 8.5, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 166.5 (d, $J_{C\text{-}F}$ = 252.9 Hz), 153.2 (d, $J_{C\text{-}F}$ = 2.4 Hz), 148.6 (d, $J_{C\text{-}F}$ = 9.3Hz), 133.7 (d, $J_{C\text{-}F}$ = 1.0 Hz), 132.2, 130.4, 120.0, 129.5, 129.0, 128.4, 128.2, 128.1, 126.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 124.8 (d, $J_{C\text{-}F}$ = 9.7 Hz), 114.4 (d, $J_{C\text{-}F}$ = 23.0 Hz), 110.2 (d, $J_{C\text{-}F}$ = 25.7 Hz). The NMR data agree with those in a literature report.[3]



5-Chloro-2,3-diphenyl-1H-inden-1-one **(3ea)**

3ea was obtained according to the general procedure in 58% yield (36.6 mg). red solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.6 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.38 – 7.34 (m, 2H), 7.28 – 7.24 (m, 6H), 7.11 (d, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.0, 154.0, 147.3, 139.8, 133.5, 132.2, 130.3, 130.0, 129.6, 129.0, 128.9, 128.5, 128.4, 128.2, 128.1, 123.9, 122.0. The NMR data agree with those in a literature report.[3]

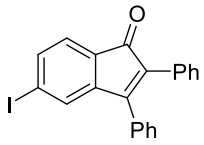


5-Bromo-2,3-diphenyl-1H-inden-1-one **(3fa)**

3fa was obtained according to the general procedure in 54% yield (39.1 mg). red solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.40 (m, 5H), 7.36 – 7.34 (m, 2H), 7.27 – 7.24 (m, 6H). ^{13}C NMR

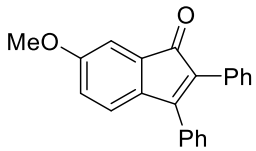
(100 MHz, $CDCl_3$) δ 195.3, 154.3, 147.4, 133.5, 132.3, 131.8, 130.4, 130.1, 129.7, 129.5, 129.1, 128.5, 128.44, 128.3, 128.2, 124.8, 124.2. The NMR data agree with those in a literature report.[3]



5-Iodo-2,3-diphenyl-1H-inden-1-one **(3ga)**

3ga was obtained according to the general procedure in 55% yield (44.5 mg). red solid;

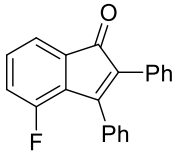
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 7.5, 1.1 Hz, 1H), 7.46 (d, J = 0.8 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.36 – 7.33 (m, 2H), 7.30 (d, J = 7.5 Hz, 1H), 7.27 – 7.24 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 154.4, 146.9, 138.0, 133.1, 132.2, 130.2, 130.0, 129.6, 129.0, 128.4, 128.2, 128.1, 124.2, 100.9. HRMS: $[M + H]^+$ calculated for $C_{21}H_{14}IO^+$: 409.0084, found: 409.0084.



6-Methoxy-2,3-diphenyl-1H-inden-1-one **(3ha)**, major : minor = 1.2:1

3ha was obtained according to the general procedure in 87% yield (54.6 mg). red solid;

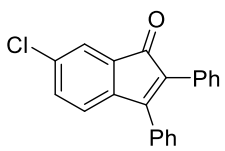
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.35 (m, 3H), 7.34 – 7.28 (m, 2H), 7.26 – 7.22 (m, 4H), 7.21 – 7.12 (m, 3H), 7.03 (d, J = 8.0 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 161.1, 154.0, 136.9, 131.1, 130.1, 129.9, 129.4, 128.8, 128.5, 128.1, 127.9, 127.6, 122.3, 119.7, 116.1, 110.7, 55.7. HRMS: $[M + H]^+$ calculated for $C_{22}H_{17}O_2^+$: 313.1223, found: 313.1222.



6-Fluoro-2,3-diphenyl-1H-inden-1-one **(3ia)**, major : minor = 15:1

3ia was obtained according to the general procedure in 90% yield (54.0 mg). red solid;

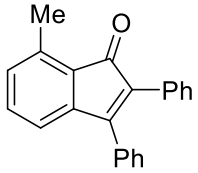
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 6H), 7.30 – 7.15 (m, 6H), 7.06 (t, J = 9.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 156.1 (d, $J_{C\text{-}F}$ = 255.9 Hz), 154.4 (d, $J_{C\text{-}F}$ = 3.4 Hz), 133.7 (d, $J_{C\text{-}F}$ = 2.6 Hz), 133.5 (d, $J_{C\text{-}F}$ = 3.8 Hz), 133.46, 133.4, 131.4 (d, $J_{C\text{-}F}$ = 6.8 Hz), 130.3, 130.1, 129.3, 128.54 (d, $J_{C\text{-}F}$ = 2.7 Hz), 128.3, 128.1, 127.9, 123.4 (d, $J_{C\text{-}F}$ = 23.1 Hz), 119.2 (d, $J_{C\text{-}F}$ = 2.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.2. HRMS: $[M + H]^+$ calculated for $C_{21}H_{14}FO^+$: 301.1023, found: 301.1027.



6-Chloro-2,3-diphenyl-1H-inden-1-one **(3ja)**, major : minor = 3.2:1

3ja was obtained according to the general procedure in 47% yield (30.0 mg). red solid;

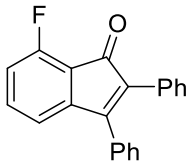
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, J = 1.8 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.39 – 7.34 (m, 3H), 7.27 – 7.24 (m, 5H), 7.08 (d, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.1, 155.1, 143.3, 135.0, 132.6, 132.6, 132.4, 130.4, 129.9, 129.6, 128.9, 128.4, 128.2, 128.0, 127.9, 123.6, 122.2. HRMS: $[M + H]^+$ calculated for $C_{21}H_{14}ClO^+$: 317.0728, found: 317.0730.



7-Methyl-2,3-diphenyl-1H-inden-1-one **(3ka)**

3ka was obtained according to the general procedure in 85% yield (50.3 mg). red solid;

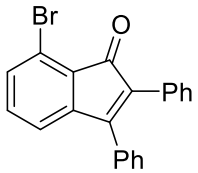
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 5H), 7.28 – 7.17 (m, 6H), 7.04 (d, J = 7.8 Hz, 1H), 6.95 (d, J = 7.2 Hz, 1H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 154.3, 145.7, 138.0, 133.0, 132.6, 132.4, 132.2, 131.0, 130.1, 129.1, 128.8, 128.6, 128.0, 127.6, 127.1, 119.3, 17.4. The NMR data agree with those in a literature report.[3]



7-Fluoro-2,3-diphenyl-1H-inden-1-one **(3la)**

3la was obtained according to the general procedure in 29% yield (17.4 mg). red solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 3H), 7.30 – 7.24 (m, 3H), 7.20 – 7.15 (m, 5H), 6.88 (t, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6 (d, $J_{C\text{-}F}$ = 1.4 Hz), 157.9 (d, $J_{C\text{-}F}$ = 262.3 Hz), 154.5 (d, $J_{C\text{-}F}$ = 4.7 Hz), 147.4 (d, $J_{C\text{-}F}$ = 3.5 Hz), 135.8 (d, $J_{C\text{-}F}$ = 8.3 Hz), 133.0 (d, $J_{C\text{-}F}$ = 1.3 Hz), 132.5, 130.2, 130.1, 129.4, 128.9, 128.5, 128.1, 128.0, 118.3 (d, $J_{C\text{-}F}$ = 21.5 Hz), 117.7 (d, $J_{C\text{-}F}$ = 2.4 Hz), 115.6 (d, $J_{C\text{-}F}$ = 12.4 Hz). HRMS: $[M + H]^+$ calculated for $C_{21}H_{14}FO^+$: 301.1023, found: 301.1021.

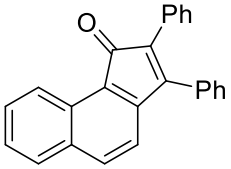


7-Bromo-2,3-diphenyl-1H-inden-1-one **(3ma)**

3ma was obtained according to the general procedure in 42% yield (30.3 mg). red solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.32 (m, 6H), 7.30 – 7.18 (m, 6H), 7.09 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.7, 153.4, 148.2, 134.1, 134.0, 132.9, 132.2, 130.1, 129.4, 128.9, 128.5, 128.1, 128.0, 127.6, 120.5, 119.1. HRMS: $[M + H]^+$ calculated for $C_{21}H_{14}BrO^+$: 361.0223, found:

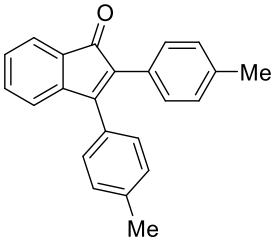
361.0227.



2,3-Diphenyl-1H-cyclopenta[a]naphthalen-1-one **(3na)**

3na was obtained according to the general procedure in 70% yield (46.8 mg). red solid;

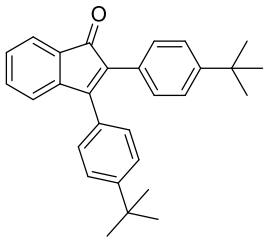
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 8.1 Hz, 1H), 7.73 (d, J = 8.3 Hz, 1H), 7.53 (t, J = 7.4 Hz, 1H), 7.47 – 7.41 (m, 5H), 7.36 (t, J = 7.4 Hz, 1H), 7.33 – 7.23 (m, 6H) ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 153.8, 146.7, 134.7, 134.2, 132.8, 131.2, 130.8, 130.1, 129.4, 129.3, 129.2, 128.9, 128.6, 128.4, 128.1, 127.7, 126.0, 123.9, 122.4, 119.3. HRMS: $[M + H]^+$ calculated for $C_{25}H_{17}O^+$: 333.1274, found: 333.1277.



2,3-Di-p-tolyl-1H-inden-1-one **(3ab)**

3ab was obtained according to the general procedure in 38% yield (23.6 mg). red solid;

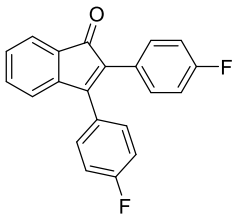
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 6.9 Hz, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.18 (m, 6H), 7.17 – 7.13 (m, 2H), 7.09 – 7.07 (m, 2H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 154.8, 145.5, 139.4, 137.5, 133.3, 132.1, 130.9, 129.9, 129.8, 129.5, 128.9, 128.7, 128.5, 128.0, 122.8, 121.1, 21.5, 21.4. The NMR data agree with those in a literature report.[3]



2,3-Bis(4-(tert-butyl)phenyl)-1H-inden-1-one **(3ac)**

3ac was obtained according to the general procedure in 45% yield (35.5 mg). red solid;

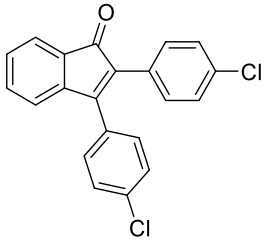
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 6.9 Hz, 1H), 7.44 – 7.41 (m, 2H), 7.36 – 7.33 (m, 3H), 7.30 – 7.22 (m, 5H), 7.16 (d, J = 7.2 Hz, 1H), 1.36 (s, 9H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 154.7, 152.5, 150.6, 145.6, 133.3, 131.8, 130.9, 129.9, 129.6, 128.7, 128.3, 127.9, 125.6, 125.0, 122.8, 121.3, 34.9, 34.6, 31.3. The NMR data agree with those in a literature report.[5]



2,3-Bis(4-fluorophenyl)-1H-inden-1-one **(3ad)**

3ad was obtained according to the general procedure in 90% yield (57.6 mg). red solid;

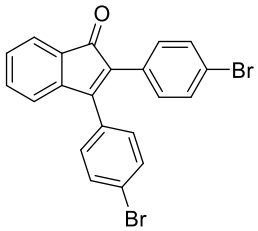
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.0 Hz, 1H), 7.40 – 7.35 (m, 3H), 7.31 – 7.27 (m, 1H), 7.25 – 7.21 (m, 2H), 7.14 – 7.10 (m, 3H), 7.00 – 6.94 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 163.2 (d, $J_{C\text{-}F}$ = 248.7 Hz), 162.4 (d, $J_{C\text{-}F}$ = 247.0 Hz), 154.2, 144.9, 133.6, 131.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 131.5, 130.6, 130.5 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.2, 128.5 (d, $J_{C\text{-}F}$ = 3.4 Hz), 126.6 (d, $J_{C\text{-}F}$ = 3.4 Hz), 123.2, 121.1, 116.2 (d, $J_{C\text{-}F}$ = 21.6 Hz), 115.4 (d, $J_{C\text{-}F}$ = 21.4 Hz). HRMS: $[M + H]^+$ calculated for $C_{21}H_{13}F_2O^+$: 319.0929, found: 319.0929.



2,3-Bis(4-chlorophenyl)-1H-inden-1-one **(3ae)**

3ae was obtained according to the general procedure in 86% yield (60.4 mg). red solid;

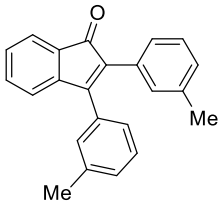
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 6.9 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.33 – 7.27 (m, 3H), 7.27 – 7.23 (m, 2H), 7.19 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 7.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 154.3, 144.6, 135.6, 134.1, 133.7, 131.5, 131.2, 130.9, 130.5, 129.9, 129.4, 129.3, 128.9, 128.6 123.3, 121.2. The NMR data agree with those in a literature report.[4]



2,3-Bis(4-bromophenyl)-1H-inden-1-one **(3af)**

3af was obtained according to the general procedure in 73% yield (64.4 mg). red solid;

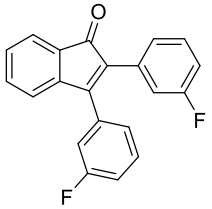
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 3H), 7.41 – 7.38 (m, 3H), 7.33 – 7.22 (m, 3H), 7.13 – 7.09 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 154.4, 144.6, 133.7, 132.3, 131.5, 131.4, 131.3, 130.5, 130.1, 129.4, 129.3, 123.9, 123.3, 122.4, 121.2. The NMR data agree with those in a literature report.[5]



2,3-Di-m-tolyl-1H-inden-1-one **(3ag)**

3ag was obtained according to the general procedure in 56% yield (35.0 mg). red solid;

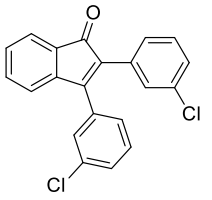
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.0 Hz, 1H), 7.36 (t, J = 7.0 Hz, 1H), 7.29 – 7.24 (m, J = 8.2, 4.3 Hz, 2H), 7.22 – 7.18 (m, 2H), 7.17 – 7.09 (m, 4H), 7.05 (d, J = 7.5 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 2.34 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 155.4, 145.4, 138.4, 137.5, 133.4, 132.8, 132.4, 130.8, 130.7, 130.6, 130.0, 128.9, 128.7, 128.5, 127.9, 127.1, 125.7, 122.9, 121.3, 21.5, 21.4. The NMR data agree with those in a literature report.[3]



2,3-Bis(3-fluorophenyl)-1H-inden-1-one **(3ah)**

3ah was obtained according to the general procedure in 88% yield (56.0 mg). red solid;

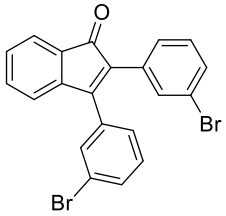
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 6.8 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.22 (m, 1H), 7.17 – 7.12 (m, 1H), 7.09 – 6.97 (m, 4H), 6.97 – 6.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 162.9 (d, $J_{C\text{-}F}$ = 246.4 Hz), 162.5 (d, $J_{C\text{-}F}$ = 243.9 Hz), 154.7 (d, $J_{C\text{-}F}$ = 1.9 Hz), 144.6, 134.5 (d, $J_{C\text{-}F}$ = 8.0 Hz), 133.8, 132.4 (d, $J_{C\text{-}F}$ = 8.4 Hz), 131.7 (d, $J_{C\text{-}F}$ = 2.1 Hz), 130.8 (d, $J_{C\text{-}F}$ = 8.2 Hz), 130.4, 129.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 129.5, 125.7 (d, $J_{C\text{-}F}$ = 2.7 Hz), 124.2 (d, $J_{C\text{-}F}$ = 2.9 Hz), 123.4, 121.4, 116.8 (d, $J_{C\text{-}F}$ = 22.2 Hz), 116.6 (d, $J_{C\text{-}F}$ = 21.0 Hz), 115.4 (d, $J_{C\text{-}F}$ = 22.3 Hz), 115.0 (d, $J_{C\text{-}F}$ = 20.8 Hz). The NMR data agree with those in a literature report.[6]



2,3-Bis(3-chlorophenyl)-1H-inden-1-one **(3ai)**

3ai was obtained according to the general procedure in 84% yield (59.1 mg). red solid;

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 6.4 Hz, 1H), 7.32 – 7.22 (m, 6H), 7.18 – 7.08 (m, 3H), 7.04 – 6.99 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 154.5, 144.5, 135.0, 134.1, 134.12, 133.8, 132.08, 131.6, 130.4, 130.3, 129.9, 129.7, 129.5, 129.4, 128.2, 128.19, 128.1, 126.8, 123.4, 121.4. The NMR data agree with those in a literature report.[3]



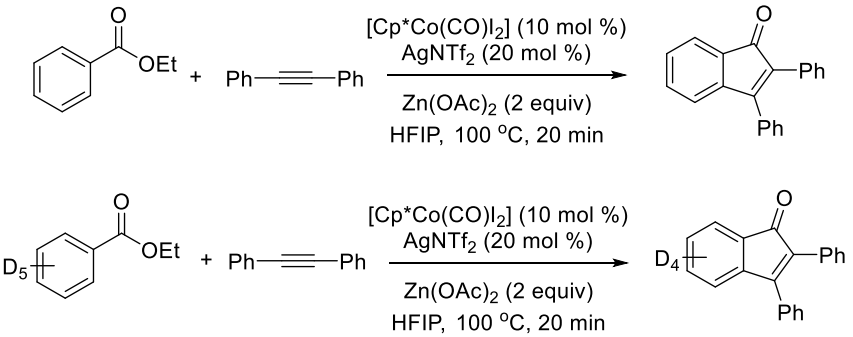
2,3-Bis(3-bromophenyl)-1H-inden-1-one **(3aj)**

3aj was obtained according to the general procedure in 83% yield (73.0 mg). red solid;

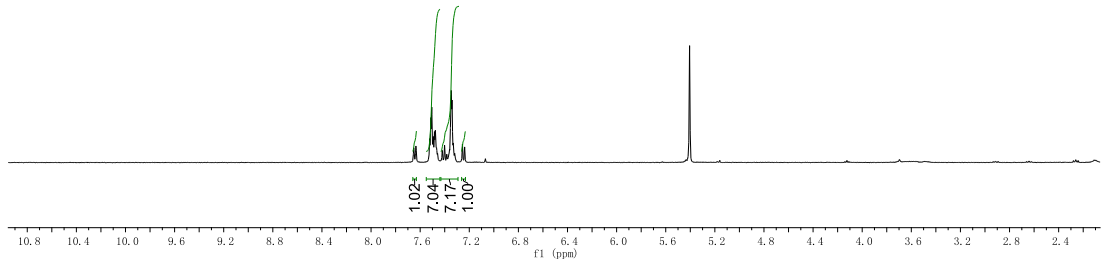
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.53 (m, 3H), 7.46 (s, 1H), 7.43 – 7.37 (m, 2H), 7.34 – 7.22 (m, 3H), 7.16 – 7.08 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 154.4, 144.4, 134.4, 133.8, 132.7, 132.6, 132.3, 131.5, 131.1, 131.0, 130.6, 130.3, 129.7, 129.6, 128.5, 127.2, 123.4, 123.0, 122.3, 121.4. HRMS: $[M + H]^+$ calculated for $C_{21}H_{13}Br_2O^+$: 438.9328, found: 438.9326.

III. Mechanistic Studies

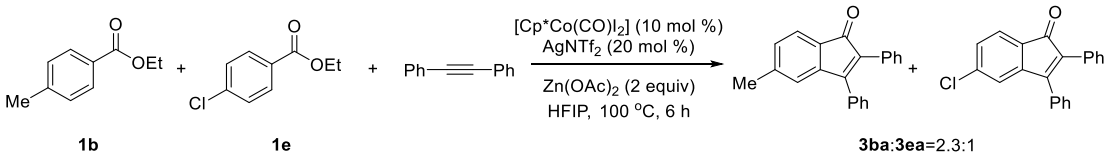
1. KIE measurements of reaction for indenones



A mixture of ethyl benzoate **1a** (0.2 mmol, 30.0 mg), diphenylacetylene **2a** (0.24 mmol, 42.8 mg), [Cp*Co(CO)I_2] (10 mol %, 9.5 mg), $AgNTf_2$ (20 mol %, 16.0 mg), $Zn(OAc)_2$ (2.0 equiv, 73.4 mg), and HFIP (2.0 mL) were charged into a pressure tube under N_2. In another tube were added a mixture of ethyl benzoate-d_5 **1a'** (0.2 mmol, 31.0 mg), diphenylacetylene **2a** (0.24 mmol, 42.8 mg), [Cp*Co(CO)I_2] (10 mol %, 9.5 mg), $AgNTf_2$ (20 mol %, 16.0 mg), $Zn(OAc)_2$ (2.0 equiv, 73.4 mg), and HFIP (2.0 mL) were charged into a pressure tube under N_2 These two reaction mixtures were stirred side-by-side in the same oil bath at 100 °C for 20 min. These two mixtures were rapidly combined and all the volatiles were rapidly removed under reduced pressure. The residue was purified by silica gel chromatography using PE/DCM to afford the mixed product. KIE value (k_H/k_D = 4.5) was estimated on the basis of ^{1}H NMR analysis. No H/D exchanged in the reaction product was observed.[3] If the relative amount of D is x and 1*14 + 10*x = 16.23, then x = 0.223. KIE = 1/x = 4.5.

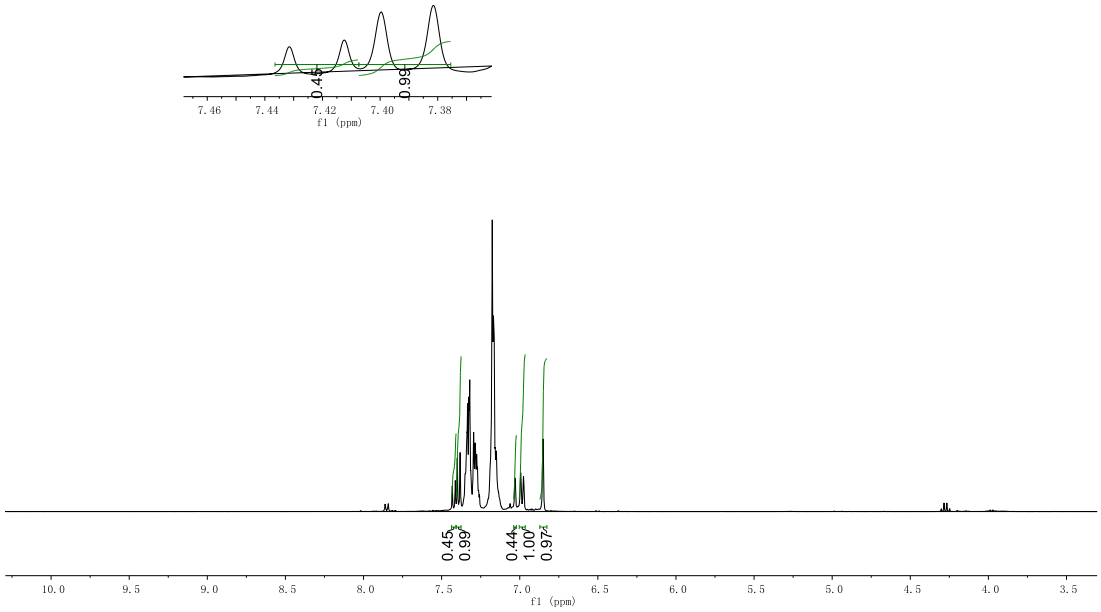


2. Competitive Experiment



1b **1e** **3ba**:**3ea**=2.3:1

An equimolar mixture of acetanilide **1b** (0.2 mmol, 32.0 mg) and **1e** (0.2 mmol, 37.0 mg), diphenylacetylene **2a** (0.2 mmol, 36.0 mg), [Cp*Co(CO)I_2] (10 mol %, 9.5 mg), $AgNTf_2$ (20 mol %, 16.0 mg), $Zn(OAc)_2$ (2.0 equiv, 73.4 mg), and HFIP (2.0 mL) were charged into a pressure tube under N_2. The reaction mixture was stirred at 120 °C for 6 h. The solvent was rapidly removed under reduced pressure and the residue was purified by silica gel chromatography using PE/DCM to afford the mixed product. The yield ratio (**3ba**/**3ea** = 2.3:1) was determined on the basis of ^{1}H NMR analysis.



IV. References

(1) M. J. Mio, L. C. Kopel, , J. B. Braun, T. L. Gadzikwa, K. L. Hull, R. G. Brisbois, C. J. Markworth and P. A. Grieco, *Org. Lett.*, 2002, **4**, 3199.

(2) T. Yoshino, H. Ikemoto, S. Matsunaga and M. Kanai, *Angew. Chem., Int. Ed*., 2013, **52**, 2207.

(3) B.-J. Li, H.-Y. Wang, Q.-L. Zhu and Z.-J. Shi, *Angew. Chem., Int. Ed.*, 2012, **51**, 3948.

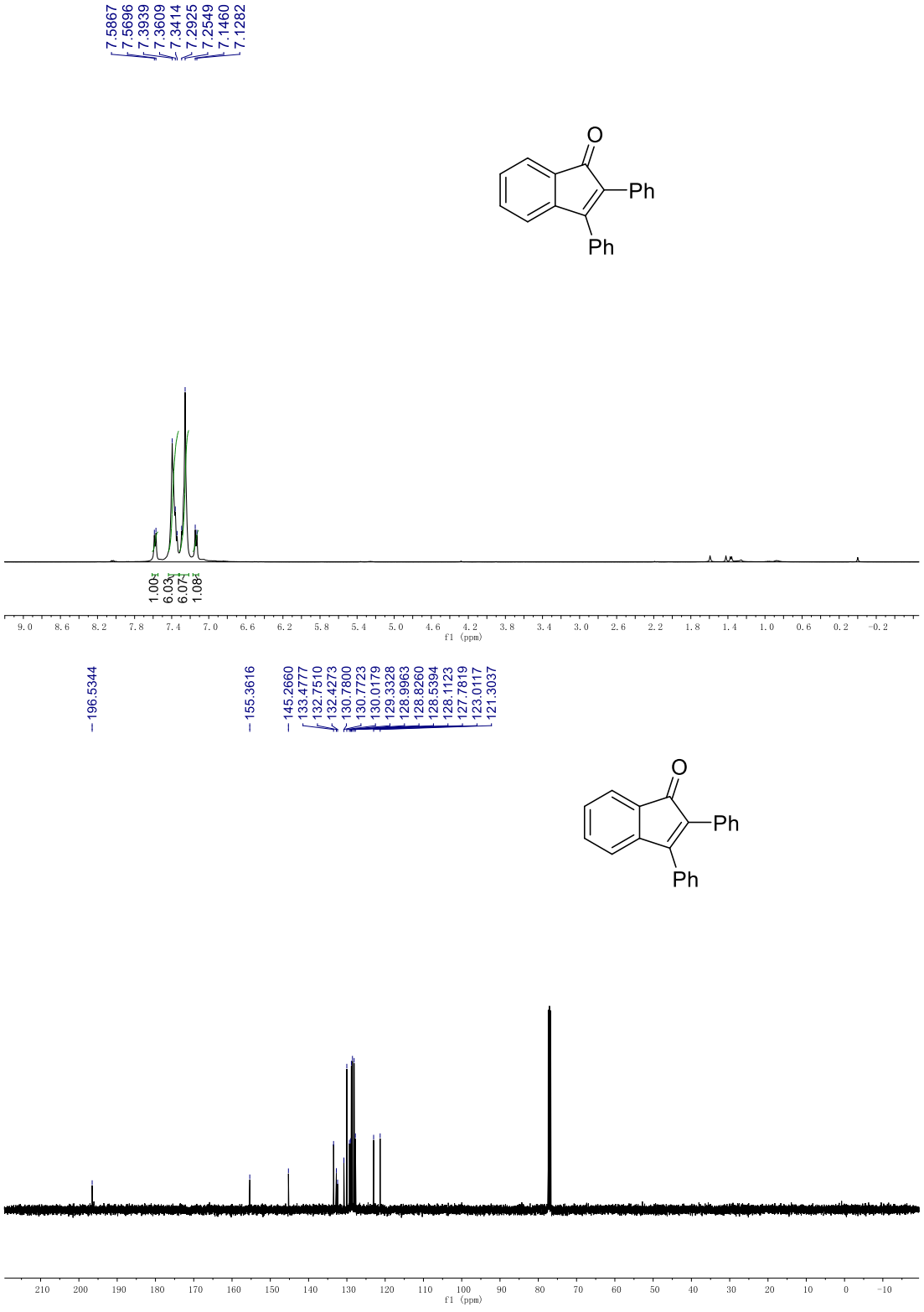
(4) A. A. Pletnev, Q. Tian and R. C. Larock, *J. Org. Chem.*, 2002, **67**, 9276.

(5) Z. Qi, M. Wang and X. Li, *Org. Lett.*, 2013, **15**, 5440.

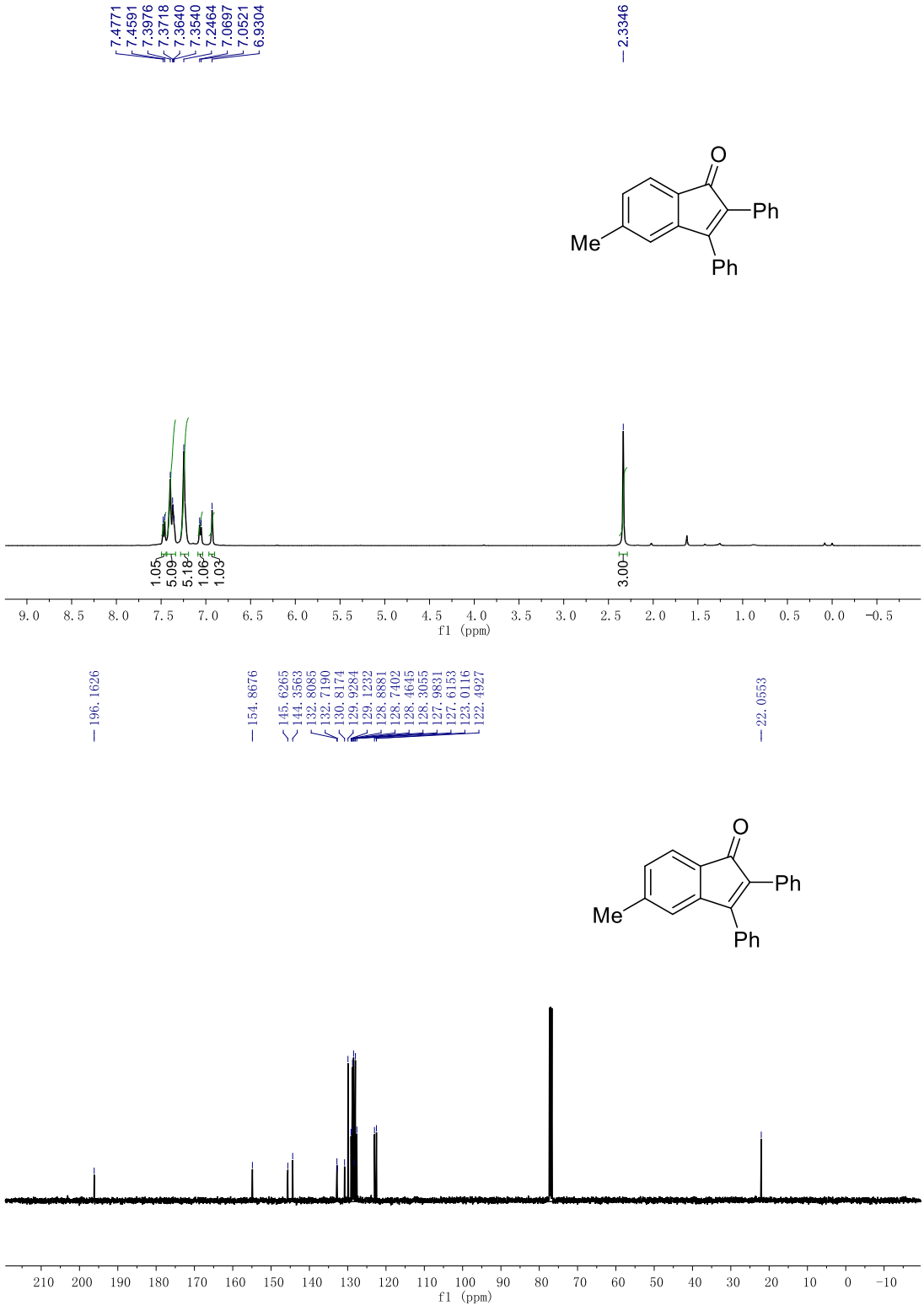
(6) S. Chen, J. Yu, Y. Jiang, F. Chen and J. Cheng, *Org. Lett.*, 2013, **15**, 4754.

V. NMR Spectra

3aa



3ba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7.3640
7.3540
7.2464
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7.0521
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2.3346
O
Ph
Me
Ph
1.05
5.09
5.18
1.06
1.03
3.00
f1 (ppm)
196.1626
154.8676
145.6265
144.3563
132.8085
132.7190
130.8174
129.9284
129.1232
128.8881
128.7402
128.4645
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127.6153
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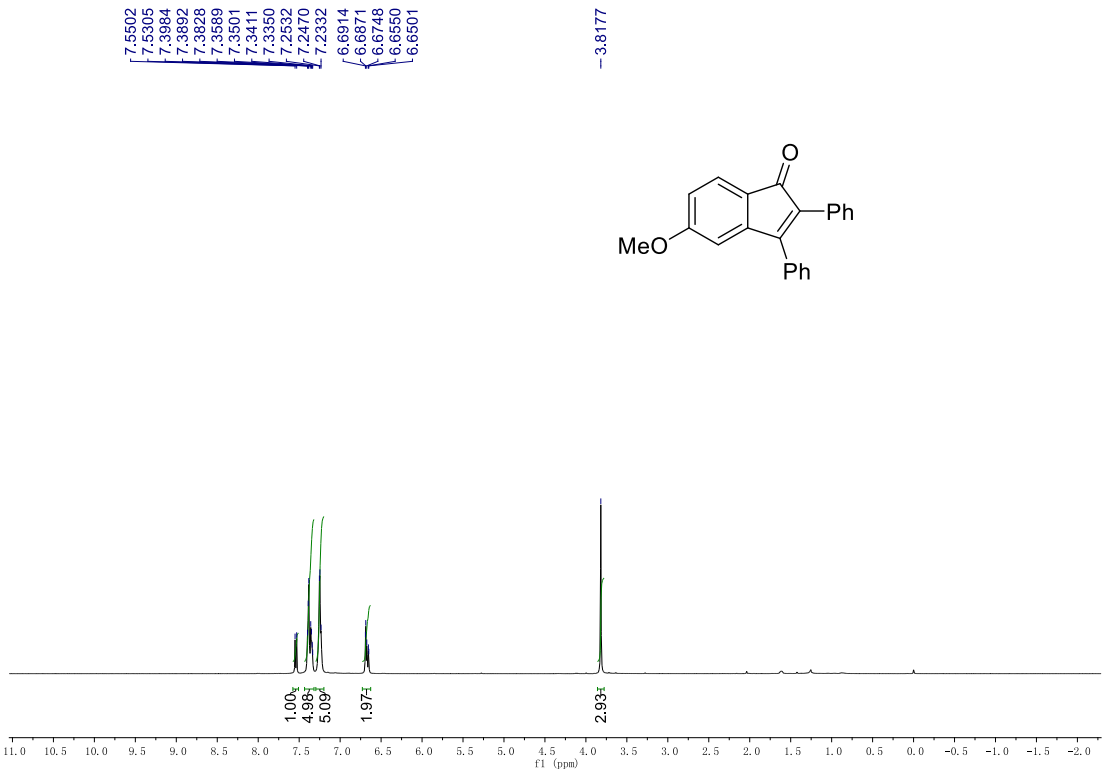
O
Ph
Me
Ph
f1 (ppm)

3ca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7.3984
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7.3828
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7.3350
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7.2470
7.2332
6.6914
6.6871
6.6748
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O
Ph
MeO
Ph
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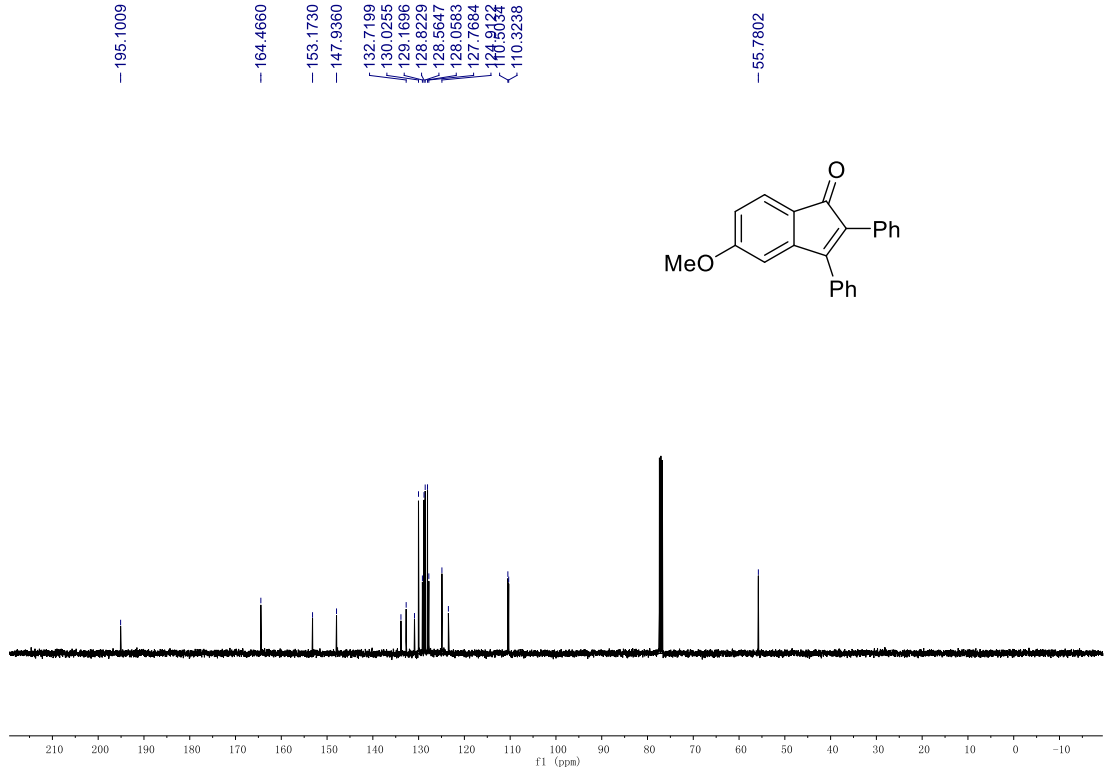
4.95
5.09
1.97
2.93
f1 (ppm)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129.1696
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128.5647
128.0583
127.7684
110.3238
55.7802
O
Ph
MeO
Ph
f1 (ppm)

3da


7.5702
7.5636
7.5506
7.4272
7.4186
7.4115
7.3658
7.3582
7.3491
7.3422
7.2613
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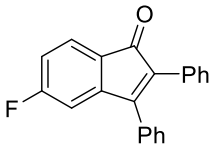
6.8692
6.8528
6.8480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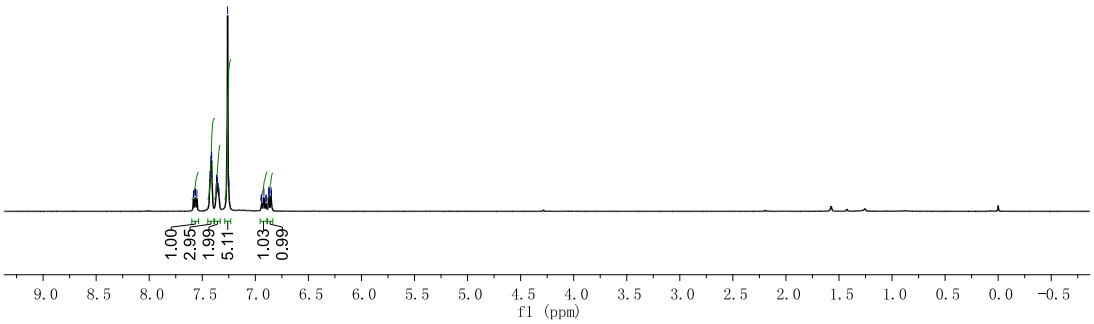
Ph
F
Ph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2.95
1.99
5.11
1.03
0.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


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167.7459
165.2188
153.1634
153.1390
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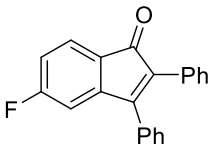
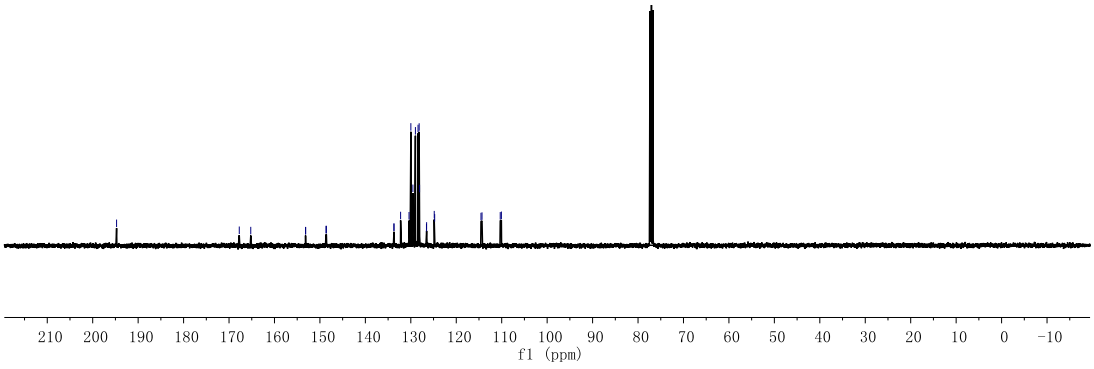
110.0646


O
Ph
F
Ph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f1 (ppm)

3ea


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7.4181
7.4092
7.3756
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7.3477
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7.2579
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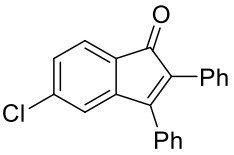
7.1094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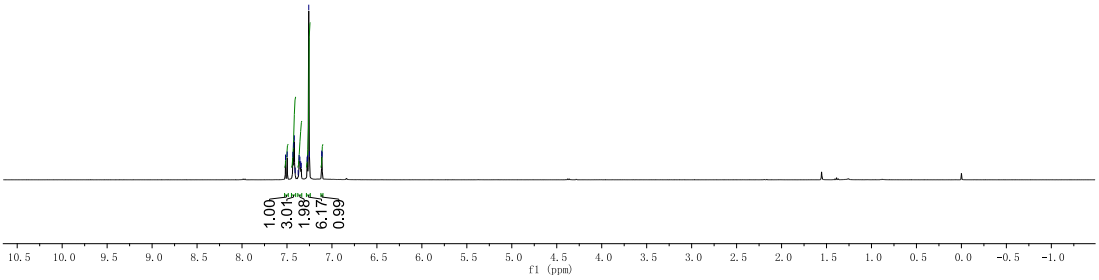
Cl
Ph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3.01
1.99
6.17
0.99
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


195.0092
154.0297
147.2841
139.7541
133.5294
132.2028
130.3274
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129.0092
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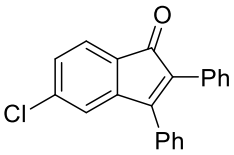
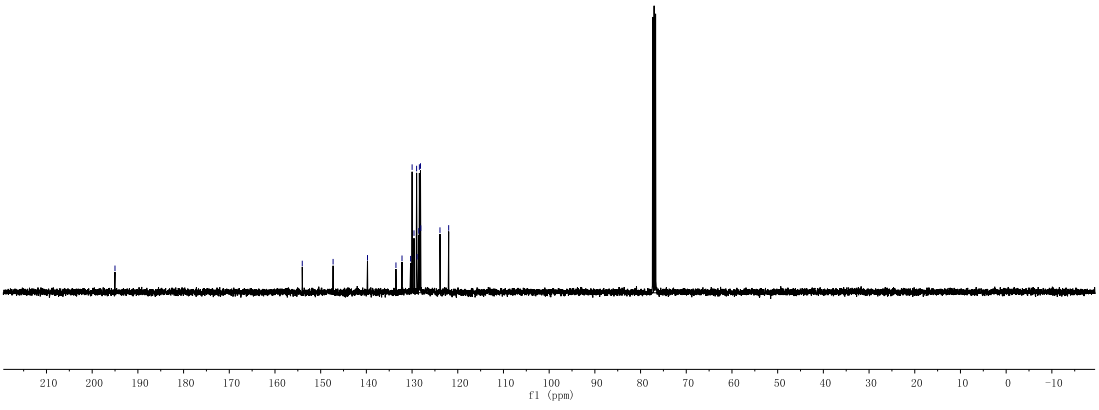
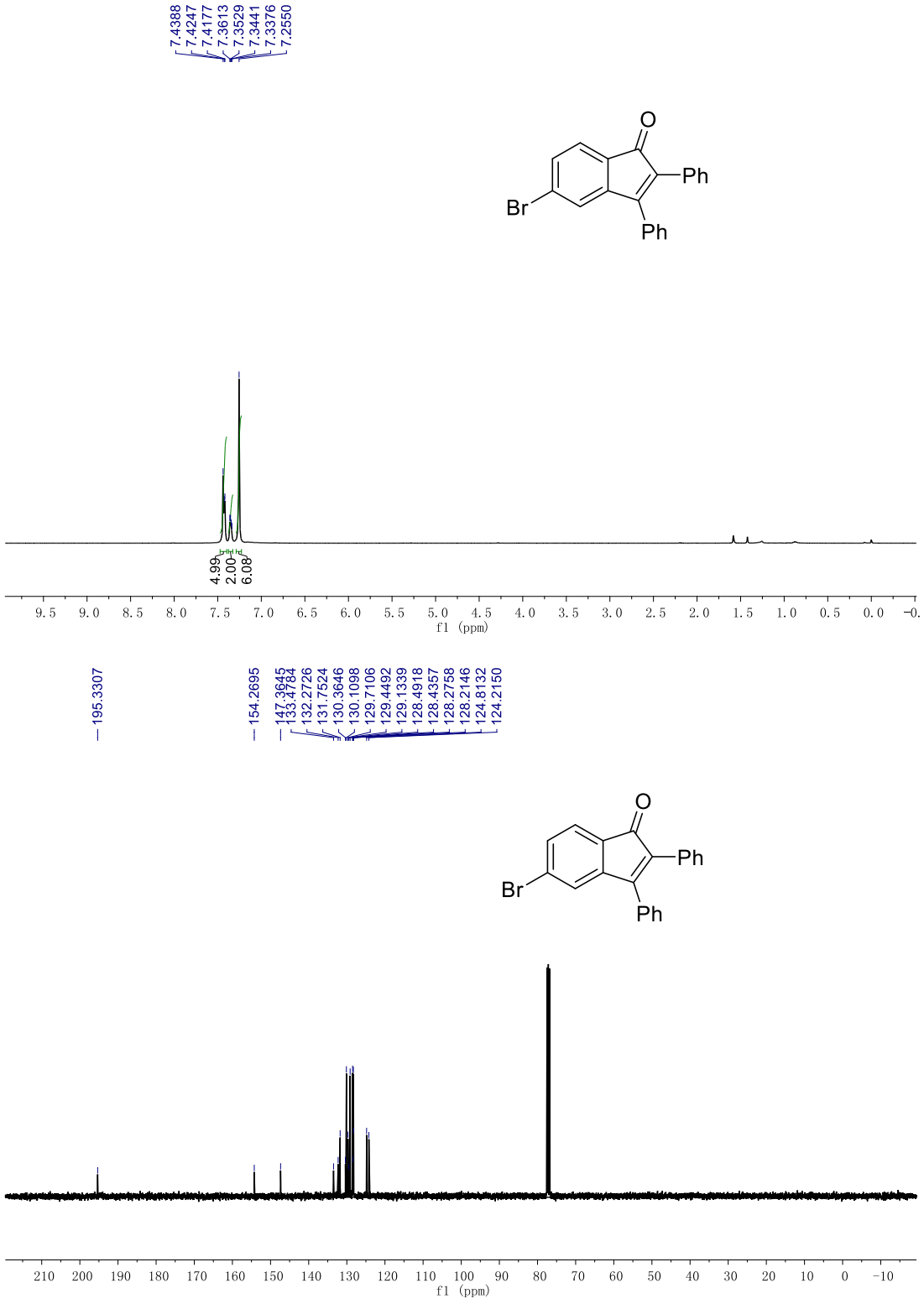
128.4023
128.1597
128.0928
123.8958
121.9924


O
Ph
Cl
Ph


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3fa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7.3529
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Ph
Br
Ph
4.99
2.00
6.08
f1 (ppm)
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147.3645
133.4784
132.2726
131.7524
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129.7106
129.4492
129.1339
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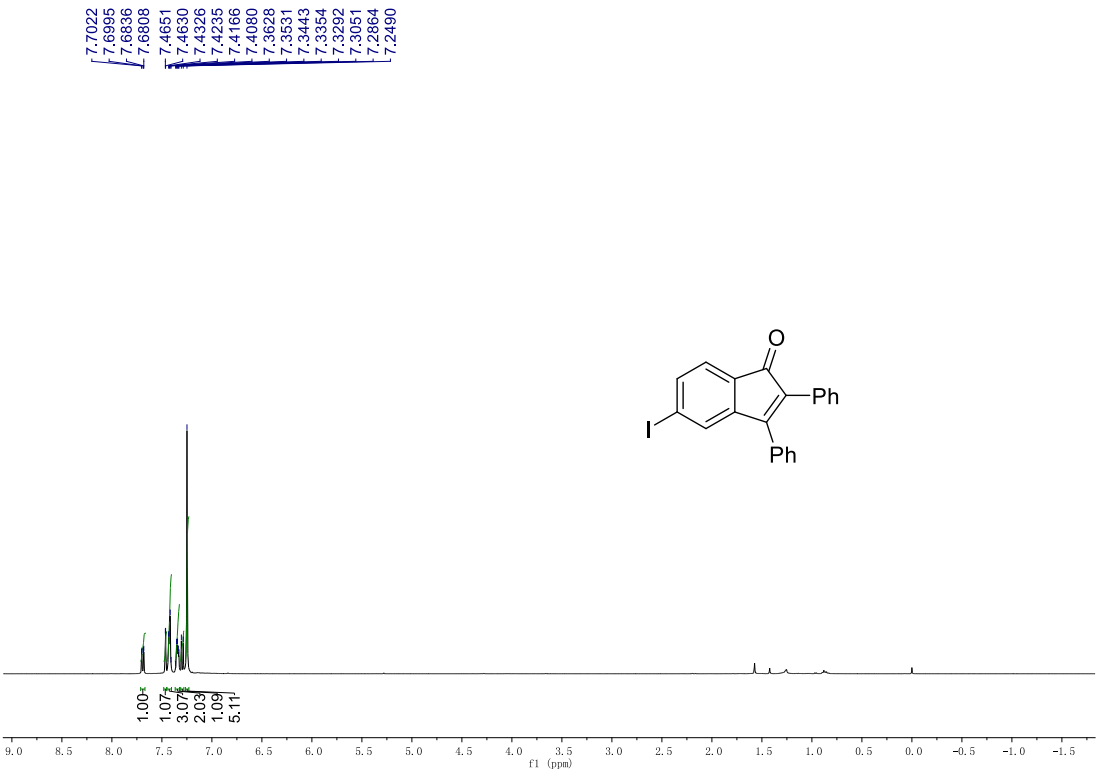
O
Ph
Br
Ph
f1 (ppm)

3ga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7.4326
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7.4166
7.4080
7.3628
7.3531
7.3443
7.3354
7.3292
7.3051
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7.2490
O
Ph
I
Ph
1.00
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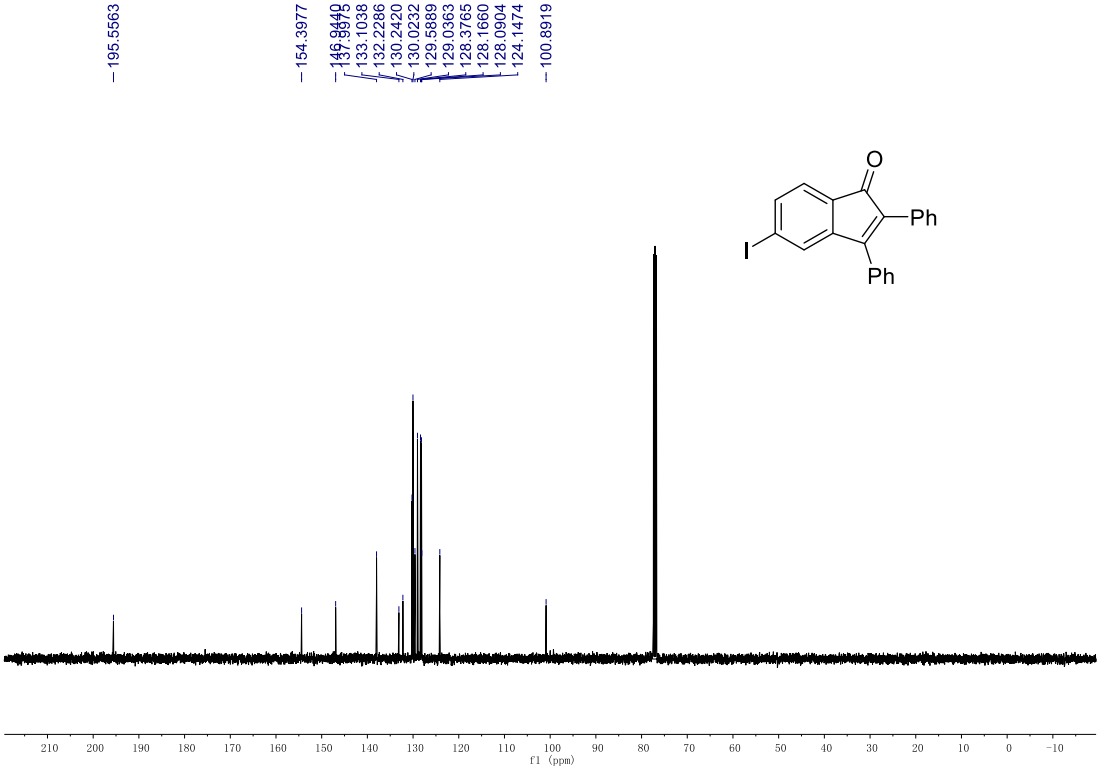
3.07
2.03
1.09
5.11
f1 (ppm)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132.2286
130.2420
130.0232
129.5889
129.0363
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128.1660
128.0904
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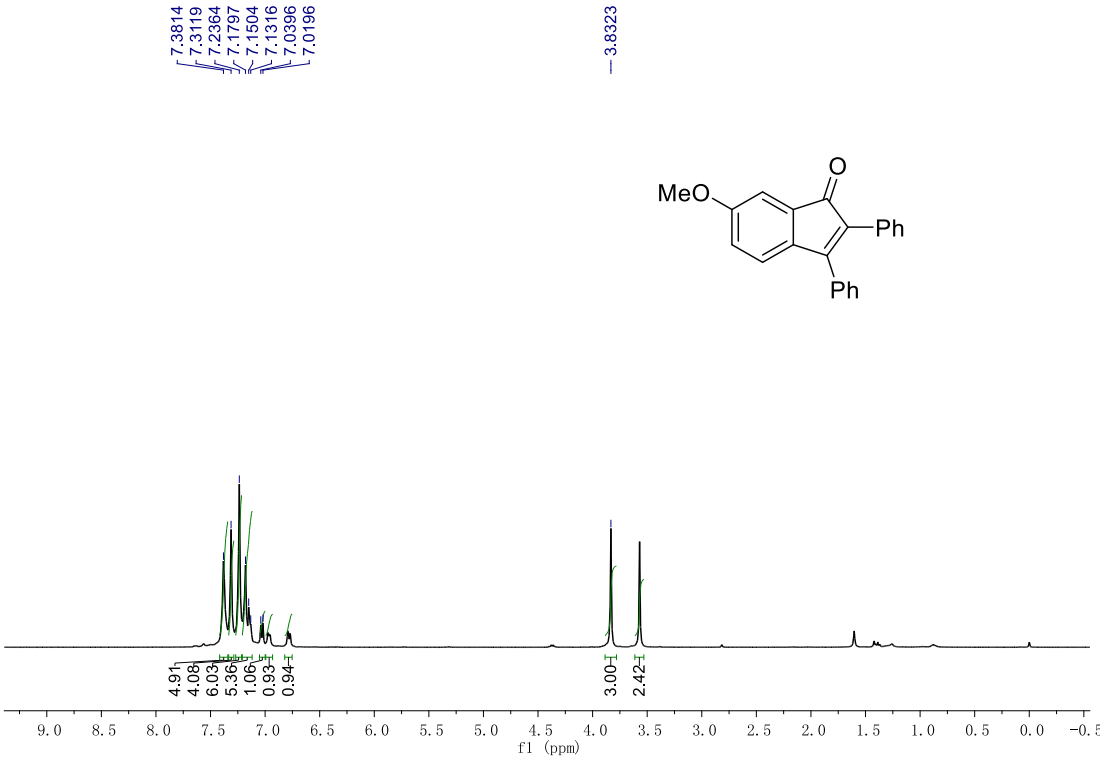
O
Ph
I
Ph
f1 (ppm)

3ha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7.1316
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MeO
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Ph
Ph
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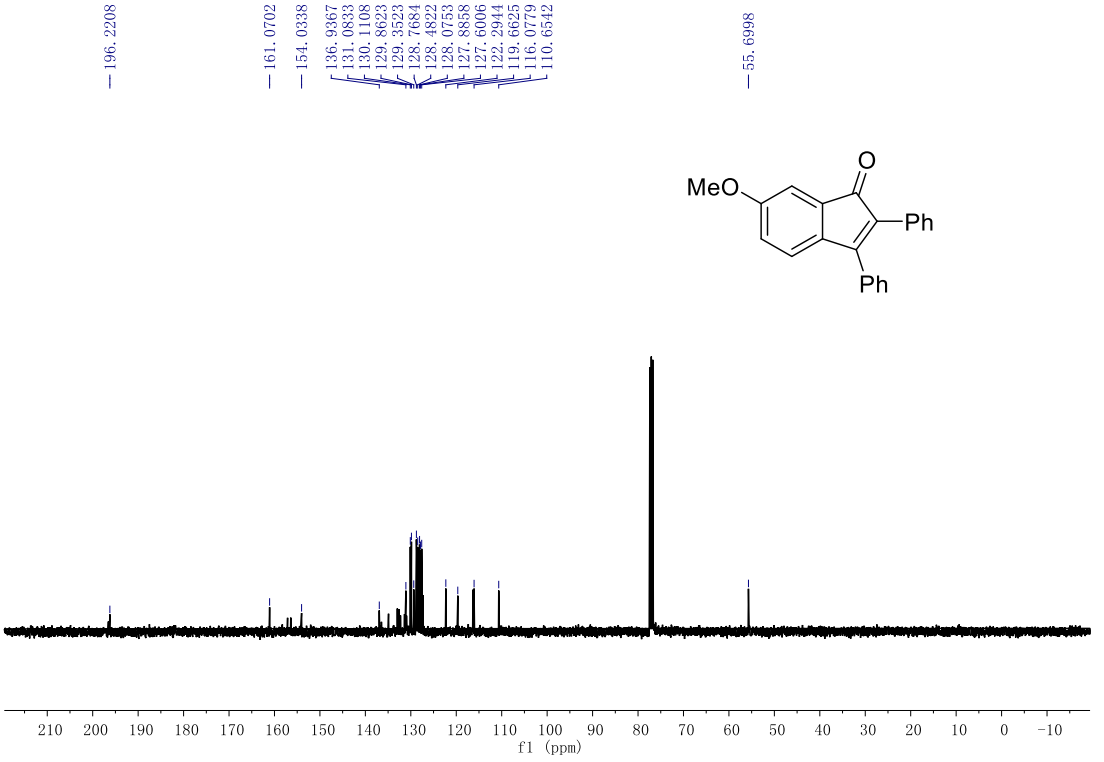
4.08
6.03
5.36
1.06
0.93
0.94
3.00
2.42
f1 (ppm)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127.8858
127.6006
122.2944
119.6625
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55.6998
MeO
O
Ph
Ph
f1 (ppm)

3ia


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7.3600
7.2863
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7.2655
7.2548
7.2434
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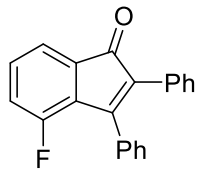
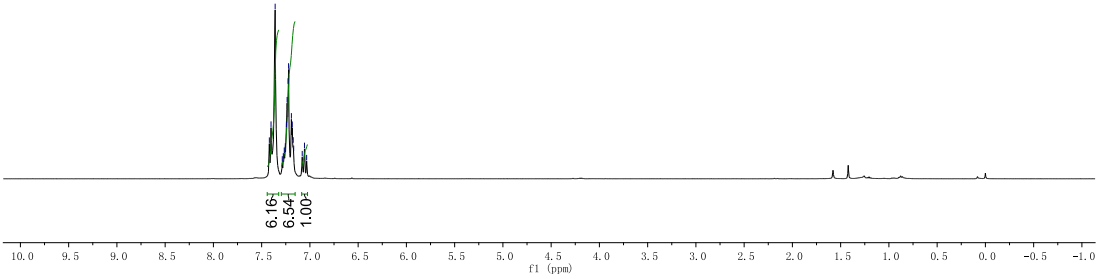

O
Ph
Ph
F


6.16
6.54
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


195.1560
157.4098
154.8504
154.3877
154.3536
133.7260
133.7003
133.4806
133.4619
133.4425
133.4128
131.4485
131.3802
130.3196
130.0913
129.2688
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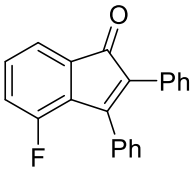
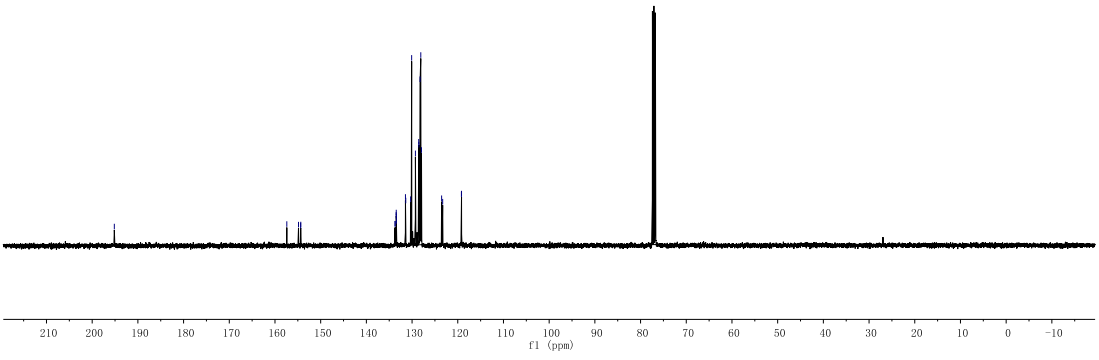
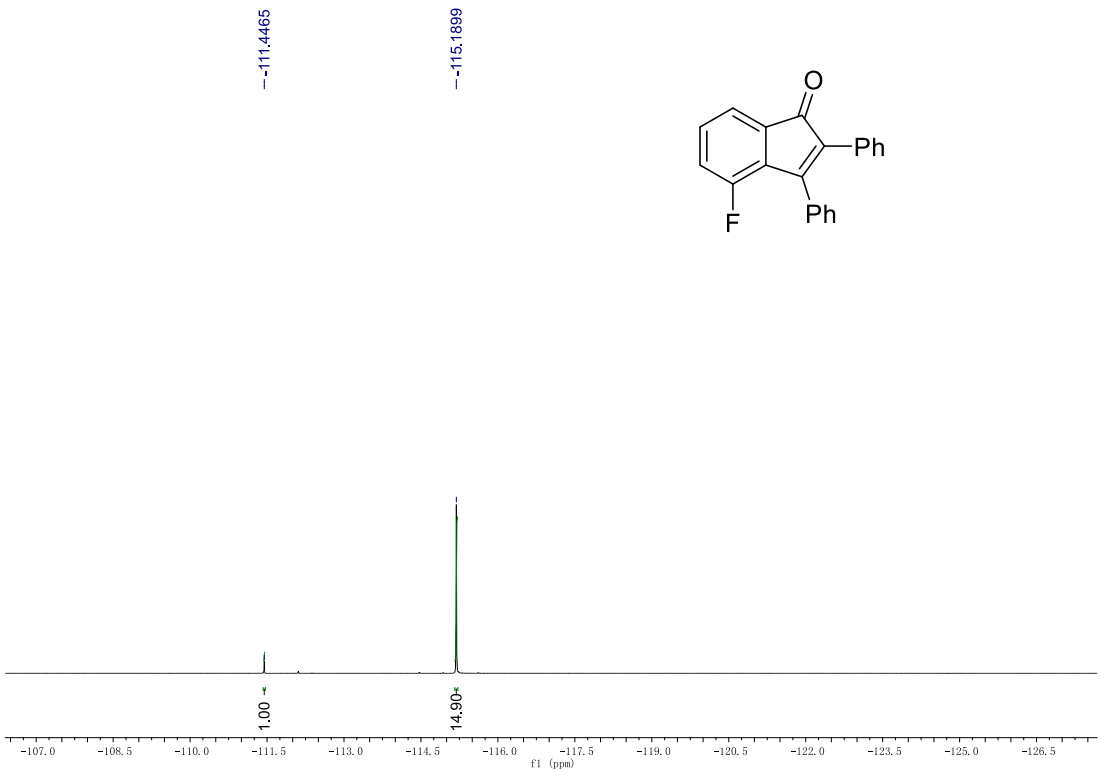
128.5165
128.2565
128.0936
127.9423
123.5345
123.3035
119.2037
119.1777


O
Ph
Ph
F


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-111.4465
-115.1899
O
Ph
Ph
F
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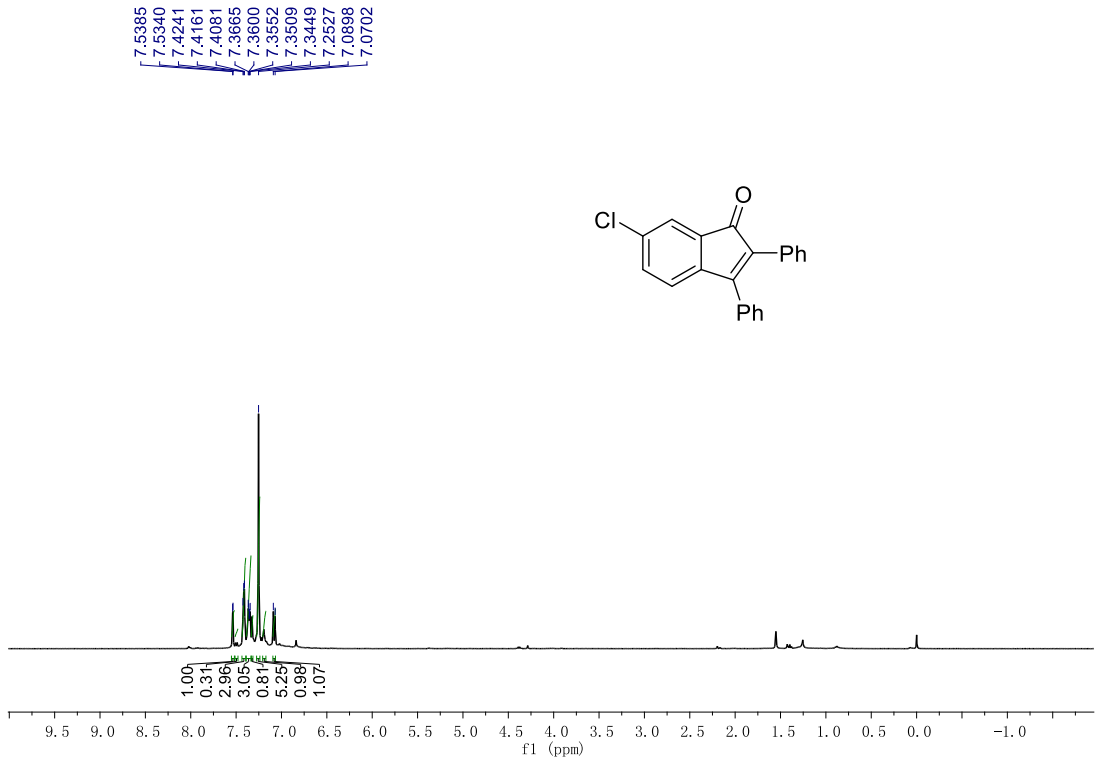
14.90
-107.0
-108.5
-110.0
-111.5
-113.0
-114.5
-116.0
-117.5
-119.0
-120.5
-122.0
-123.5
-125.0
-126.5
f1 (ppm)

3ja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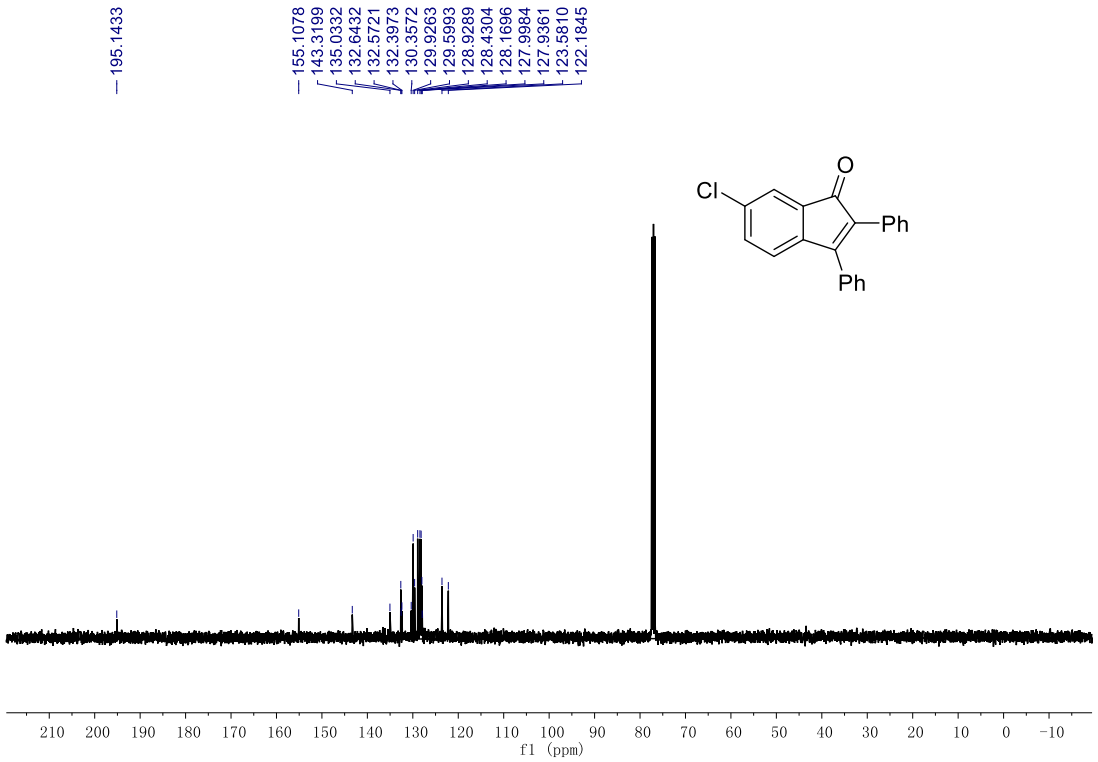
7.4081
7.3665
7.3600
7.3552
7.3509
7.3449
7.2527
7.0898
7.0702
O
Cl
Ph
Ph
1.00
0.31
2.96
3.05
0.81
5.25
0.98
1.07
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


195.1433
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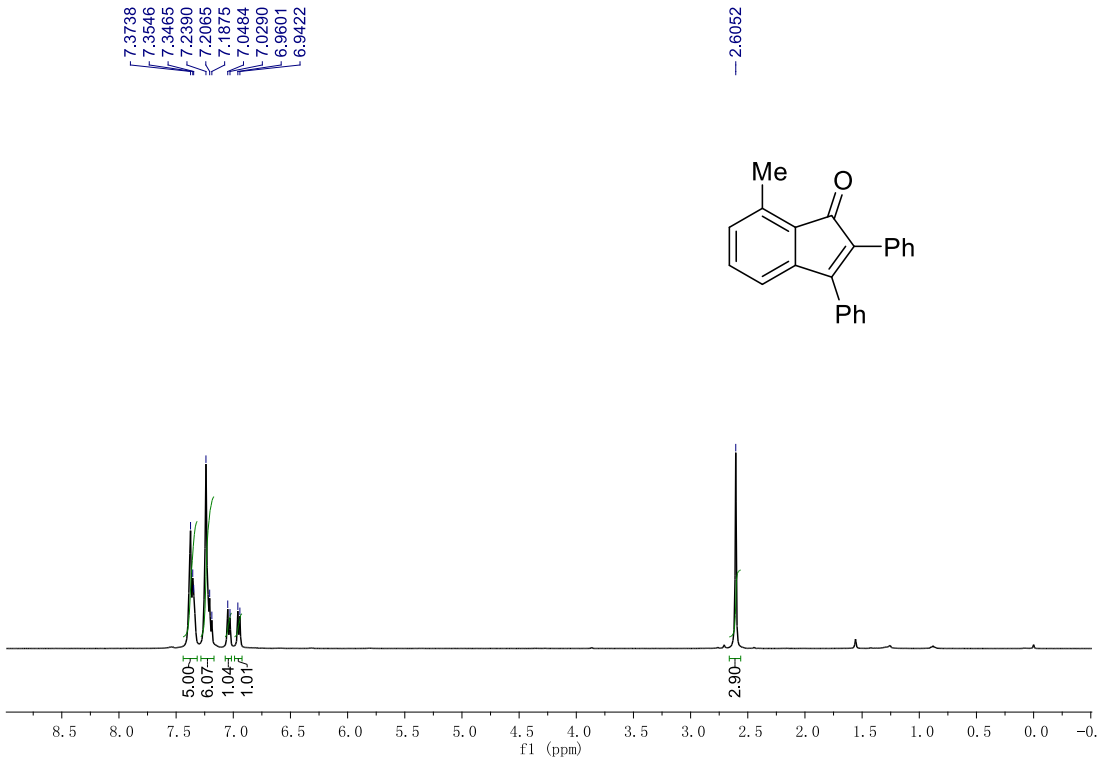
143.3199
135.0332
132.6432
132.5721
132.3973
130.3572
129.9263
129.5993
128.9289
128.4304
128.1696
127.9984
127.9361
123.5810
122.1845
Cl
O
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3ka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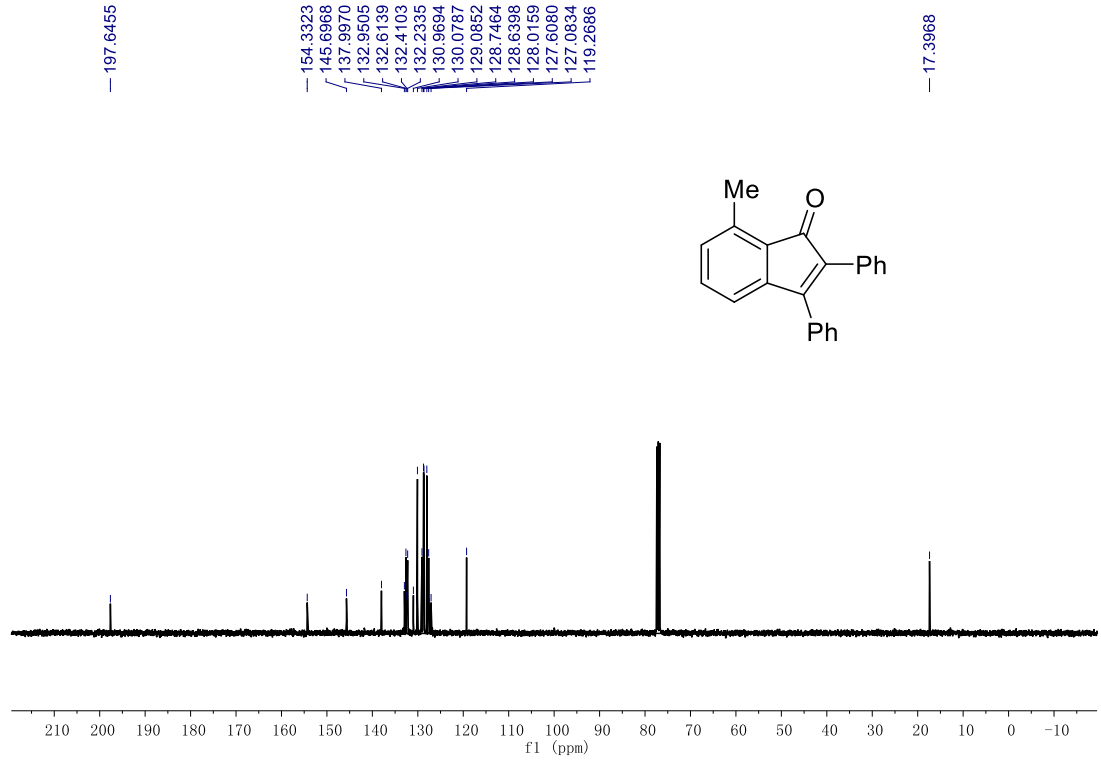
7.3546
7.3465
7.2390
7.2065
7.1875
7.0484
7.0290
6.9601
6.9422
2.6052
Me
O
Ph
Ph
5.00
6.07
1.04
1.01
2.90
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)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132.4103
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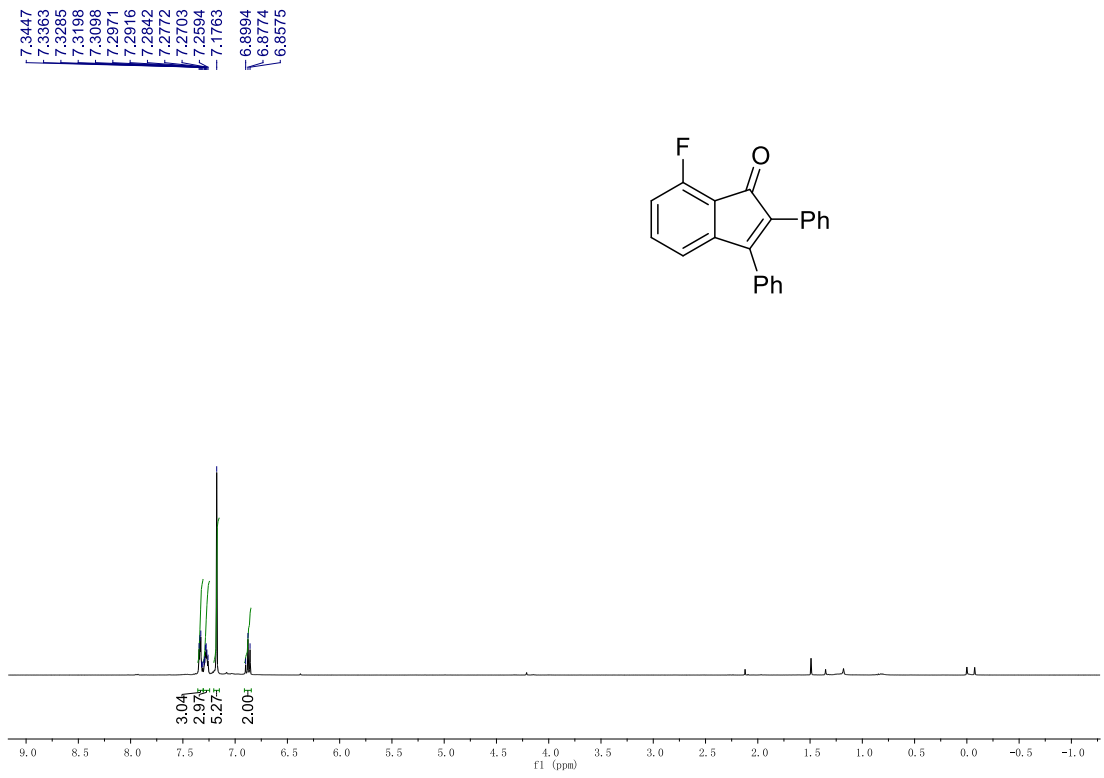
130.9694
130.0787
129.0852
128.7464
128.6398
128.0159
127.6080
127.0834
119.2686
17.3968
Me
O
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

3la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7.3285
7.3198
7.3098
7.2971
7.2916
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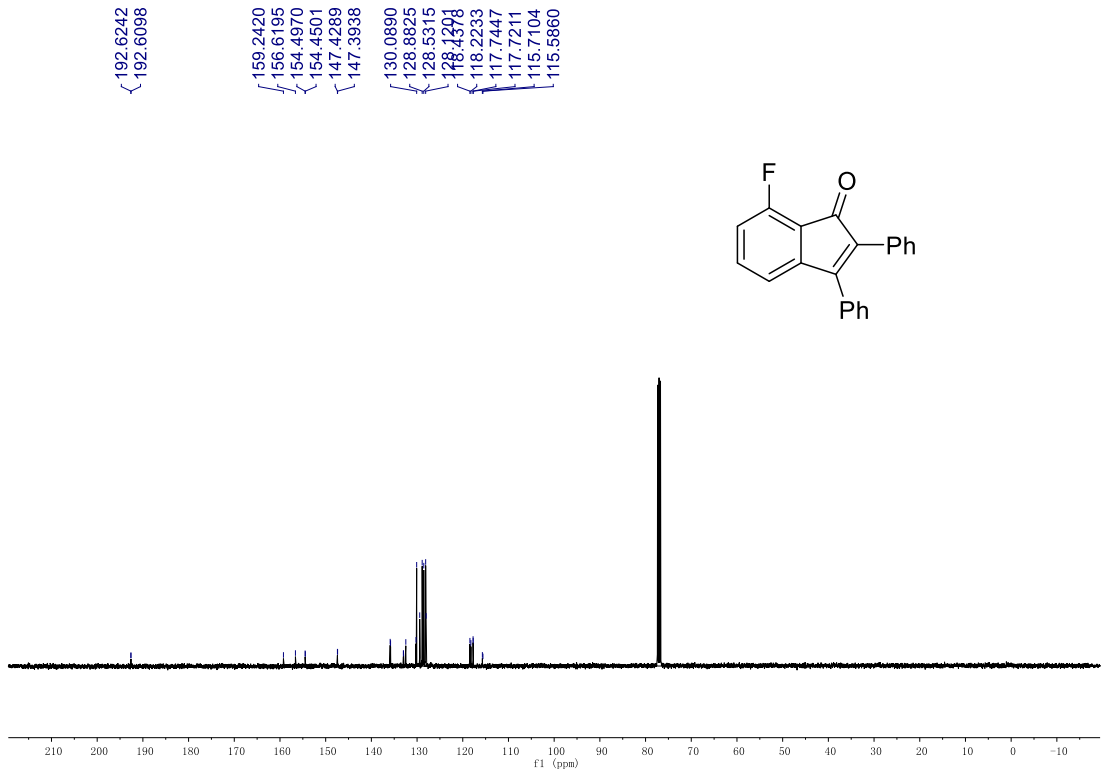
7.2772
7.2703
7.2594
7.1763
6.8994
6.8774
6.8575
F
O
Ph
Ph
3.04
2.97
5.27
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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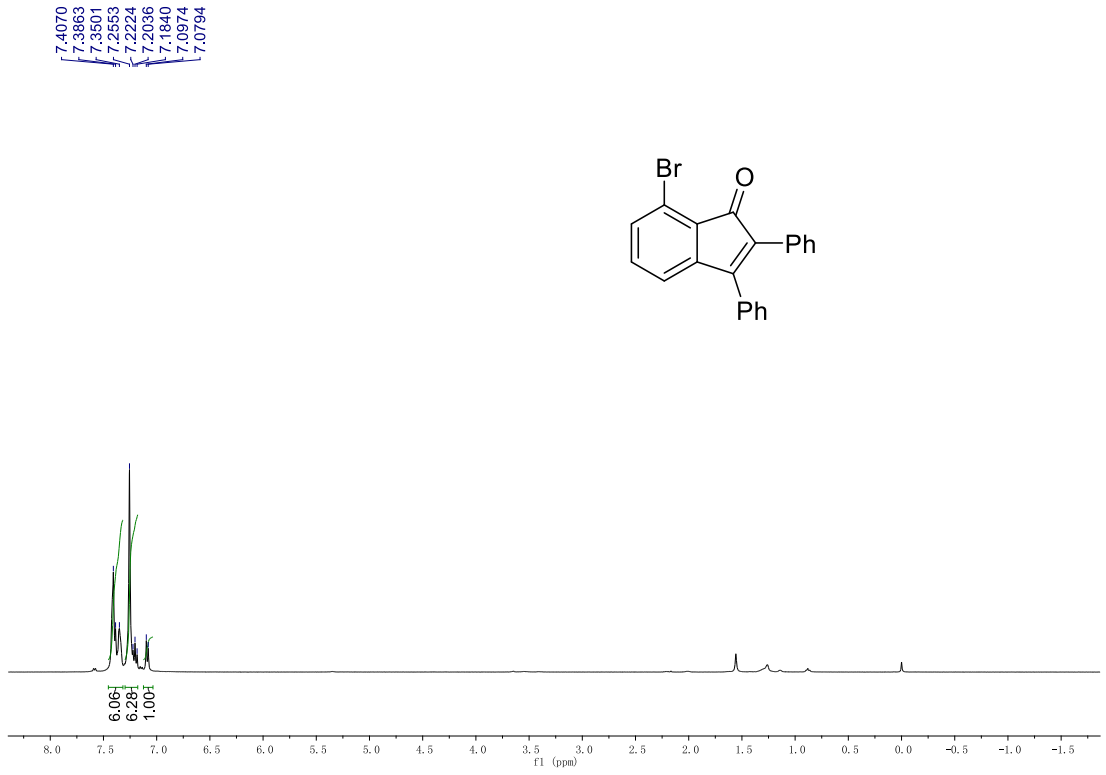
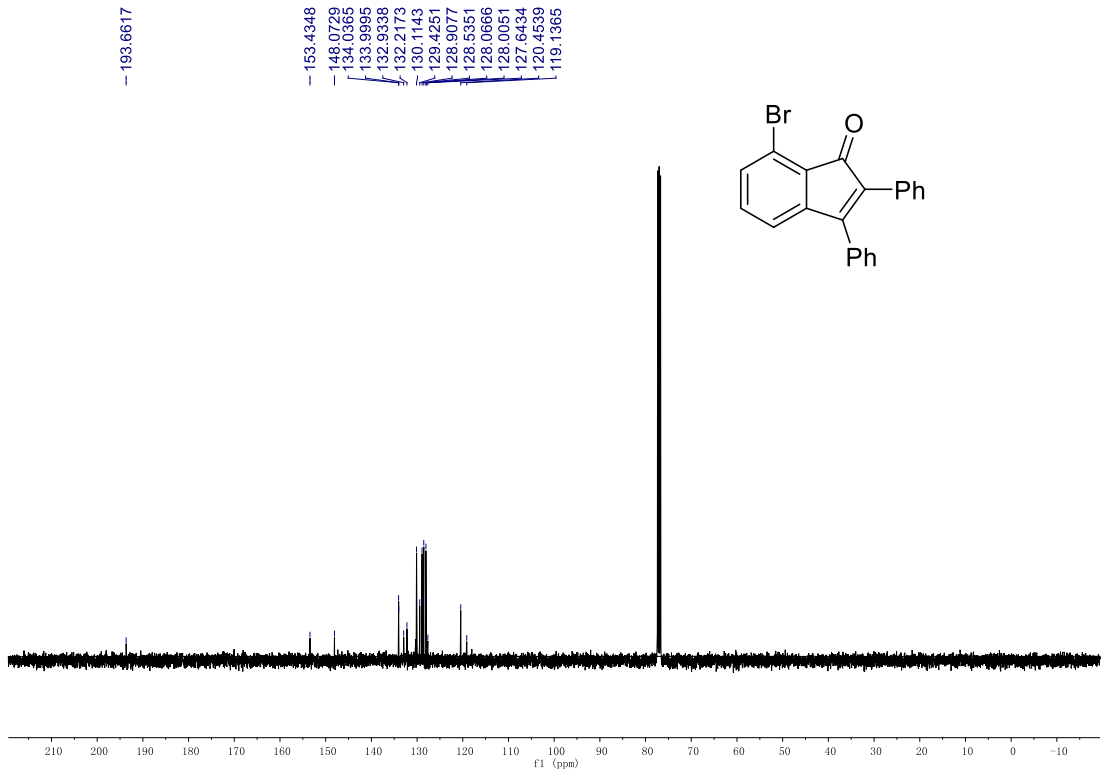
192.6098
159.2420
156.6195
154.4970
154.4501
147.4289
147.3938
130.0890
128.8825
128.5315
118.2233
117.7447
117.7211
115.7104
115.5860
F
O
Ph
Ph
f1 (ppm)

3ma


7.4070
7.3863
7.3501
7.2553
7.2224
7.2036
7.1840
7.0974
7.0794
Br
O
Ph
Ph
6.06
6.28
1.00
f1 (ppm)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153.4348
148.0729
134.0365
133.9995
132.9338
132.2173
130.1143
129.4251
128.9077
128.5351
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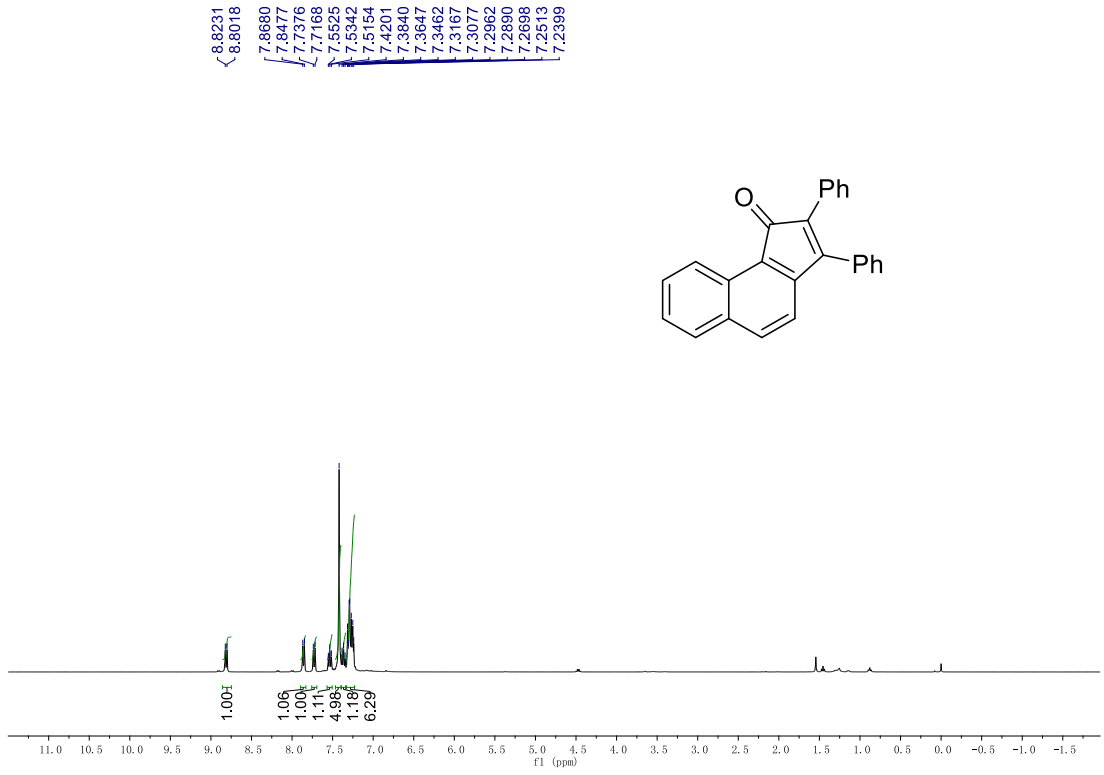
128.0051
127.6434
120.4539
119.1365
Br
O
Ph
Ph
f1 (ppm)

3na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7.8680
7.8477
7.7376
7.7168
7.5525
7.5342
7.5154
7.4201
7.3840
7.3647
7.3462
7.3167
7.3077
7.2962
7.2890
7.2698
7.2513
7.2399
O
Ph
Ph
1.00
1.06
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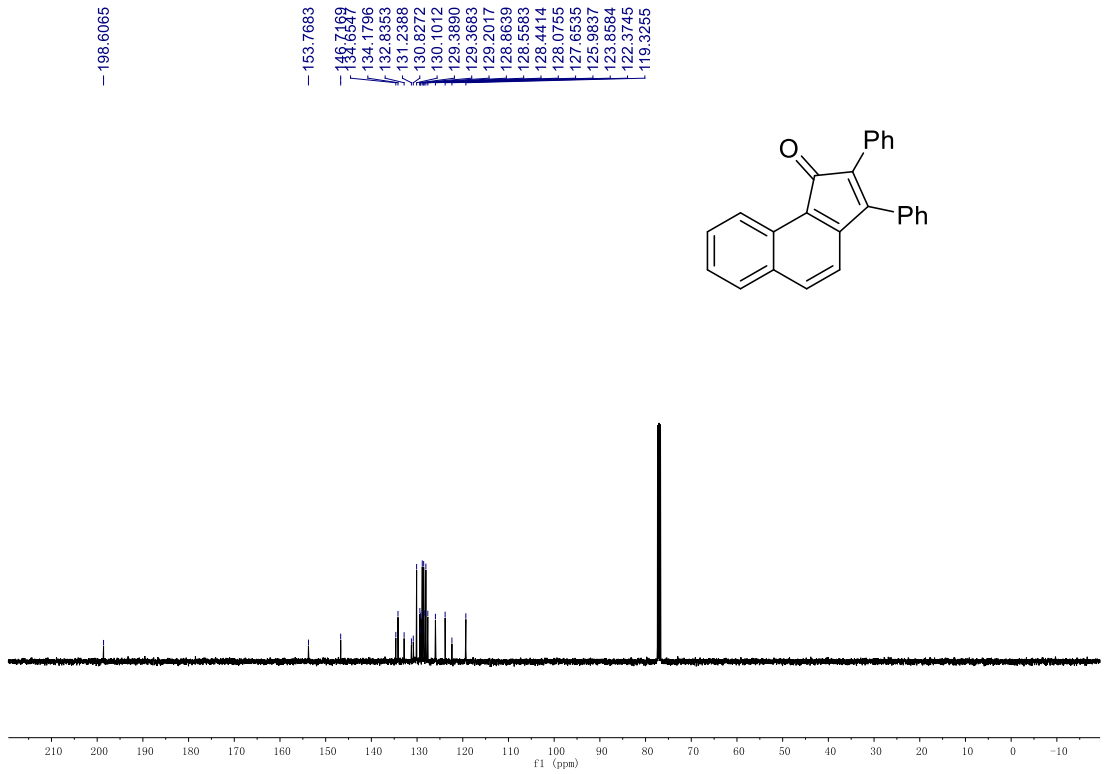
1.11
4.98
1.18
6.29
f1 (ppm)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134.1796
132.8353
131.2388
130.8272
130.1012
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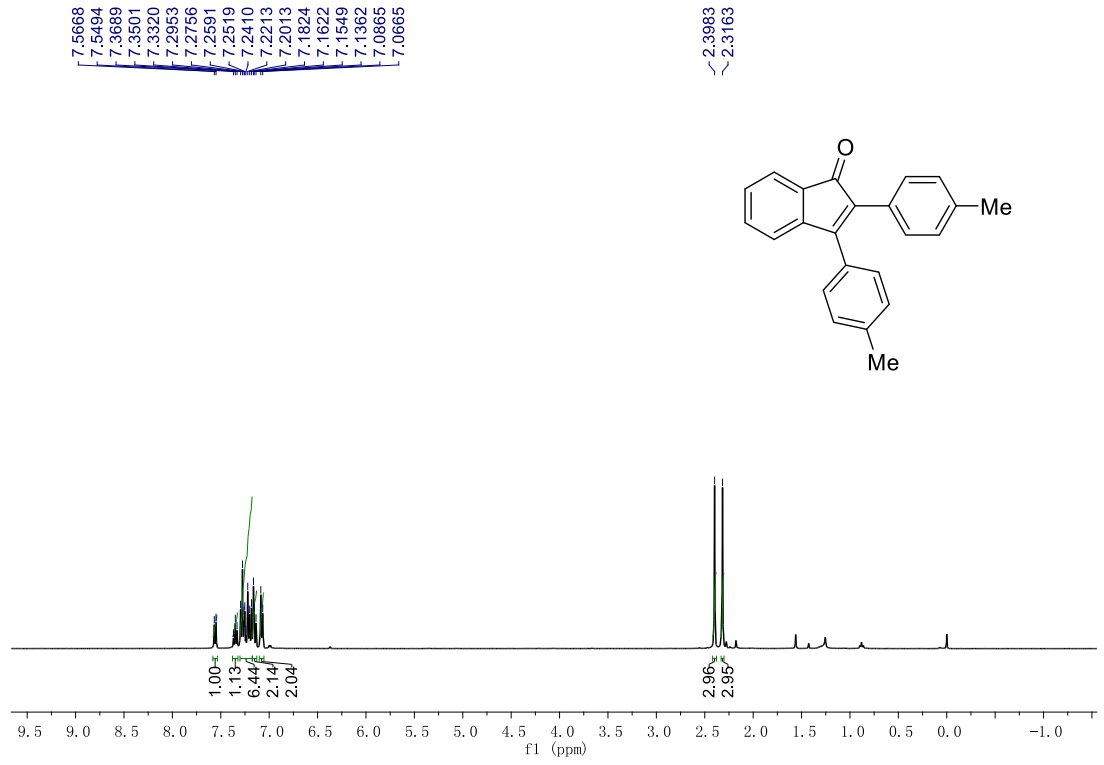
129.2017
128.8639
128.5583
128.4414
128.0755
127.6535
125.9837
123.8584
122.3745
119.3255
O
Ph
Ph
f1 (ppm)

3ab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7.3501
7.3320
7.2953
7.2756
7.2591
7.2519
7.2410
7.2213
7.2013
7.1824
7.1622
7.1549
7.1362
7.0865
7.0665
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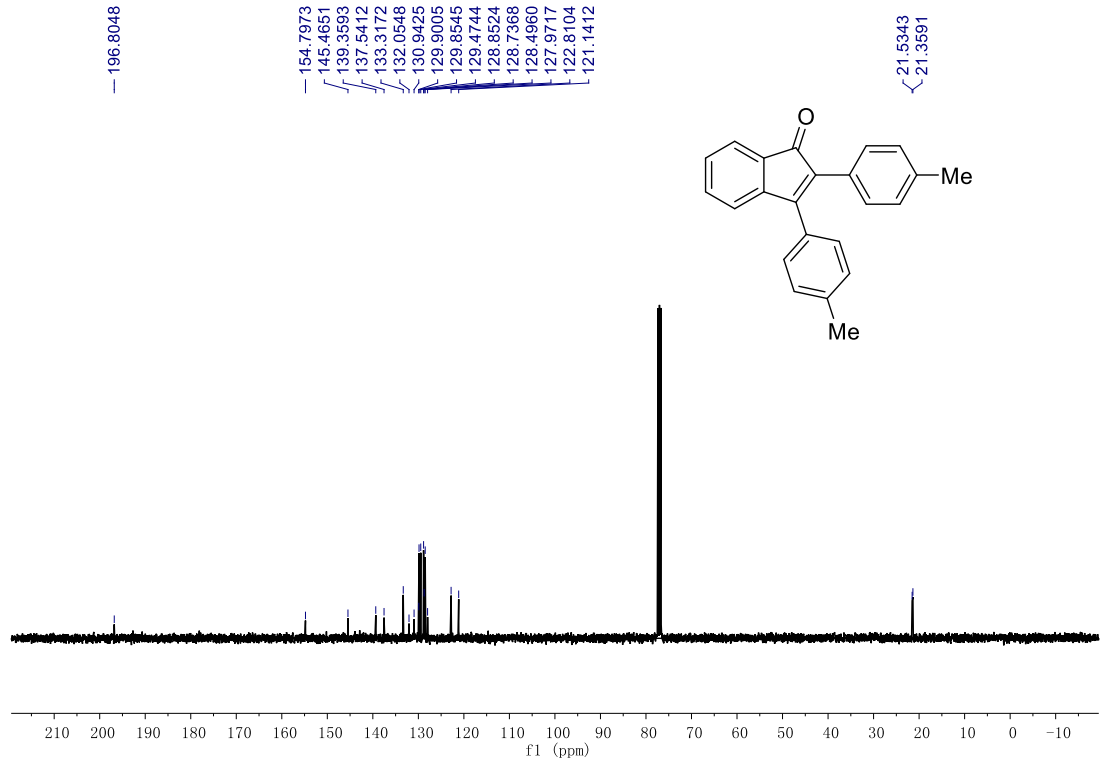
2.3163
O
Me
Me
1.00
1.13
6.44
2.14
2.04
2.96
2.95
f1 (ppm)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137.5412
133.3172
132.0548
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129.9005
129.8545
129.4744
128.8524
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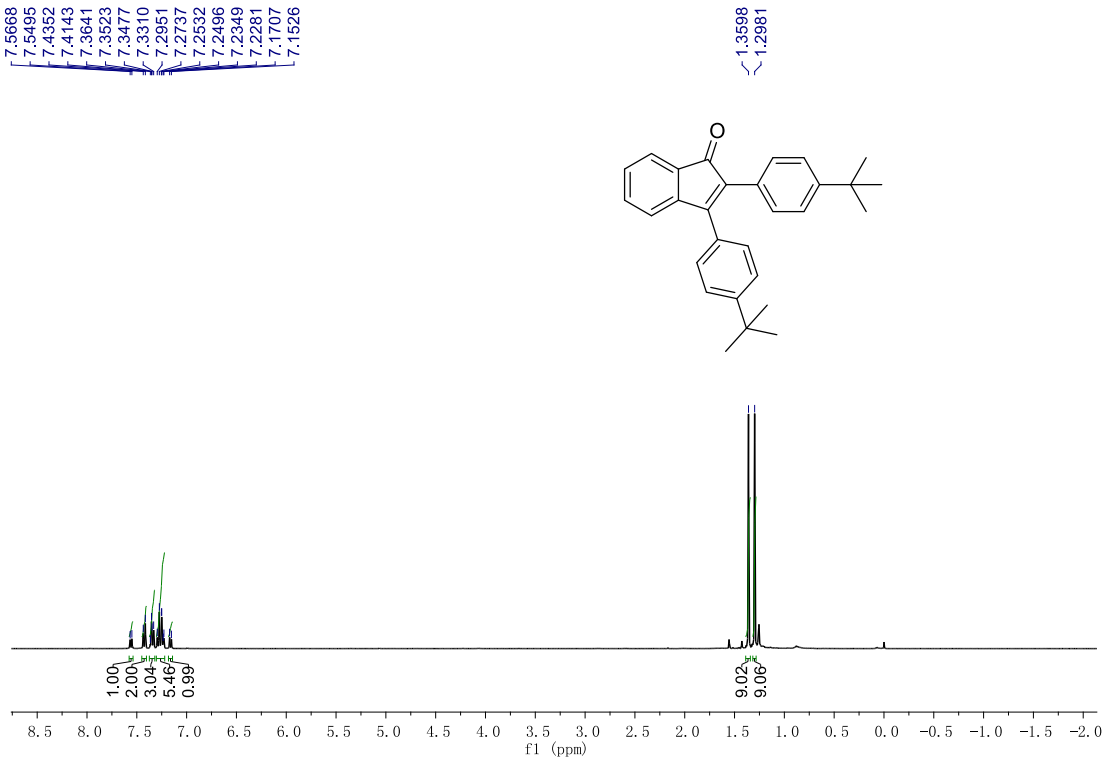
127.9717
122.8104
121.1412
21.5343
21.3591
O
Me
Me
f1 (ppm)

3ac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7.4352
7.4143
7.3641
7.3523
7.3477
7.3310
7.2951
7.2737
7.2532
7.2496
7.2349
7.2281
7.1707
7.1526
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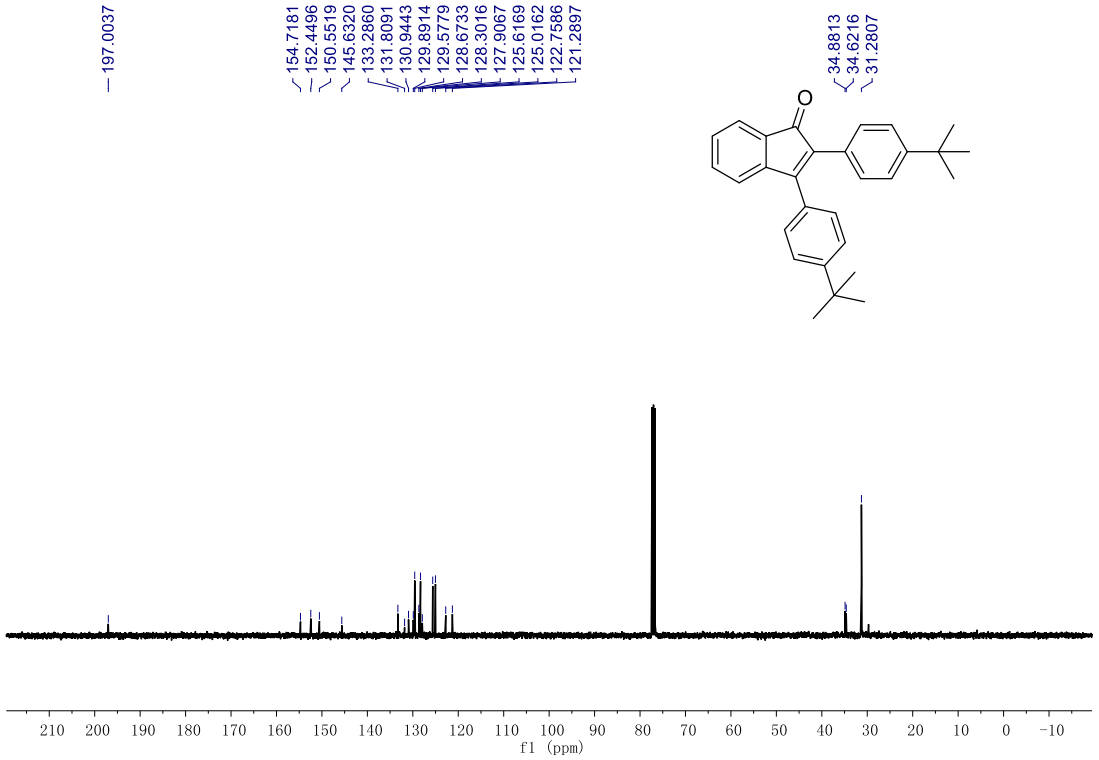
1.2981
O
1.00
2.00
3.04
5.46
0.99
9.02
9.06
f1 (ppm)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129.8914
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128.6733
128.3016
127.9067
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122.7586
121.2897
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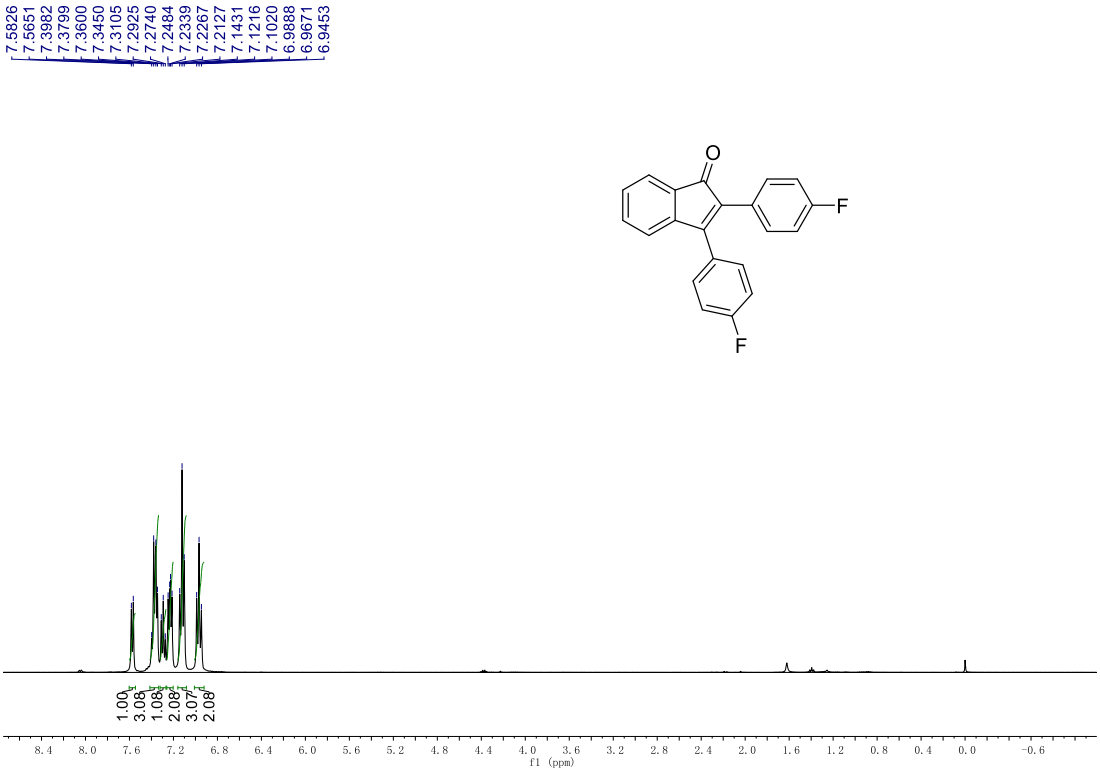
34.6216
31.2807
O
f1 (ppm)

3ad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7.3450
7.3105
7.2925
7.2740
7.2484
7.2339
7.2267
7.2127
7.1431
7.1216
7.1020
6.9888
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O
F
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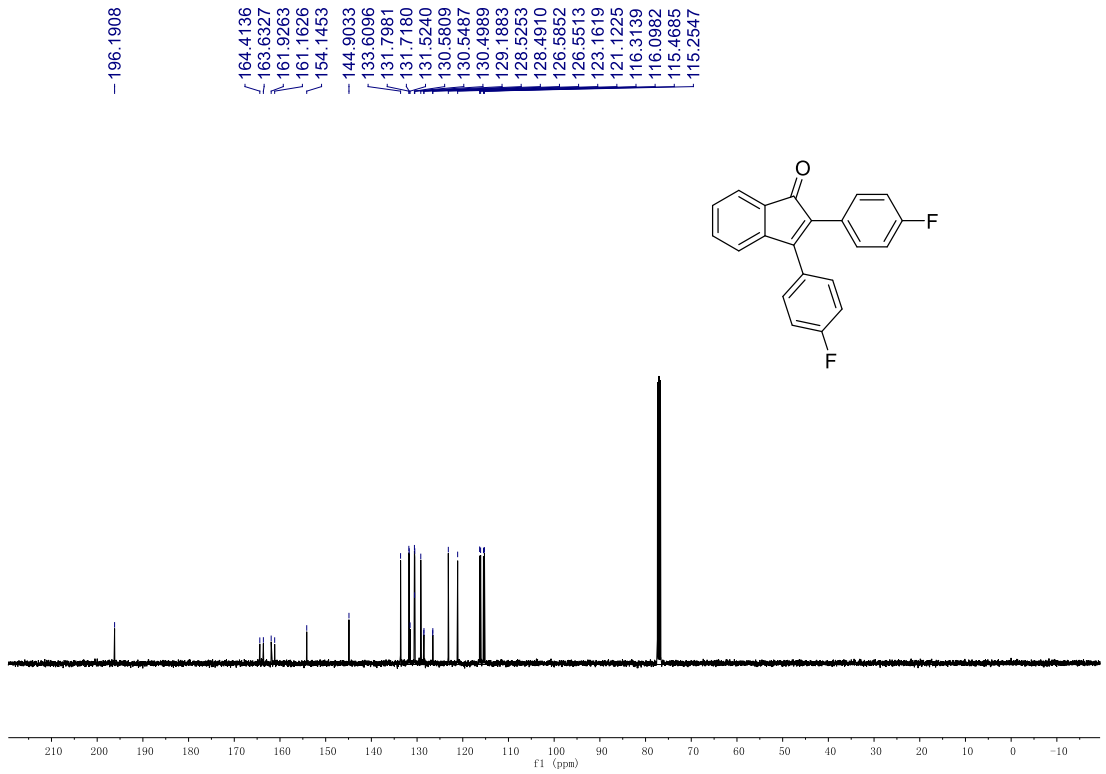
1.08
2.08
3.07
2.08
f1 (ppm)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144.9033
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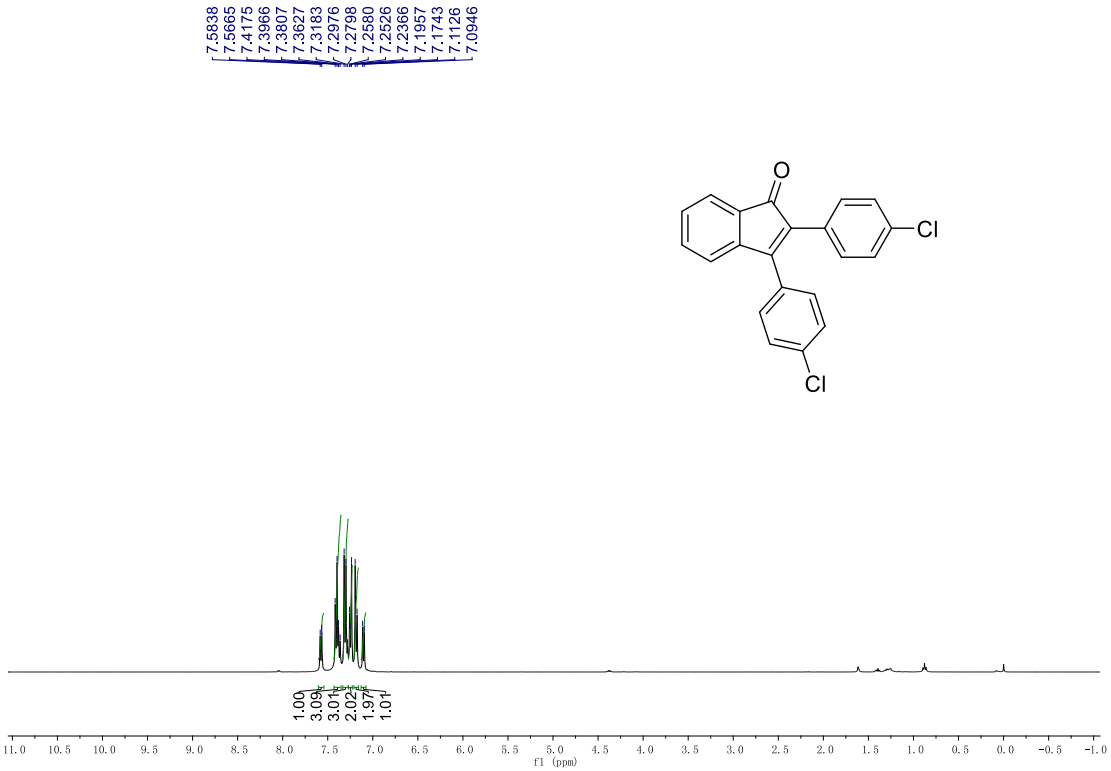
130.5809
130.5487
130.4989
129.1883
128.5253
128.4910
126.5852
126.5513
123.1619
121.1225
116.3139
116.0982
115.4685
115.2547
O
F
F
f1 (ppm)

3ae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7.3183
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7.2798
7.2580
7.2526
7.2366
7.1957
7.1743
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O
Cl
Cl
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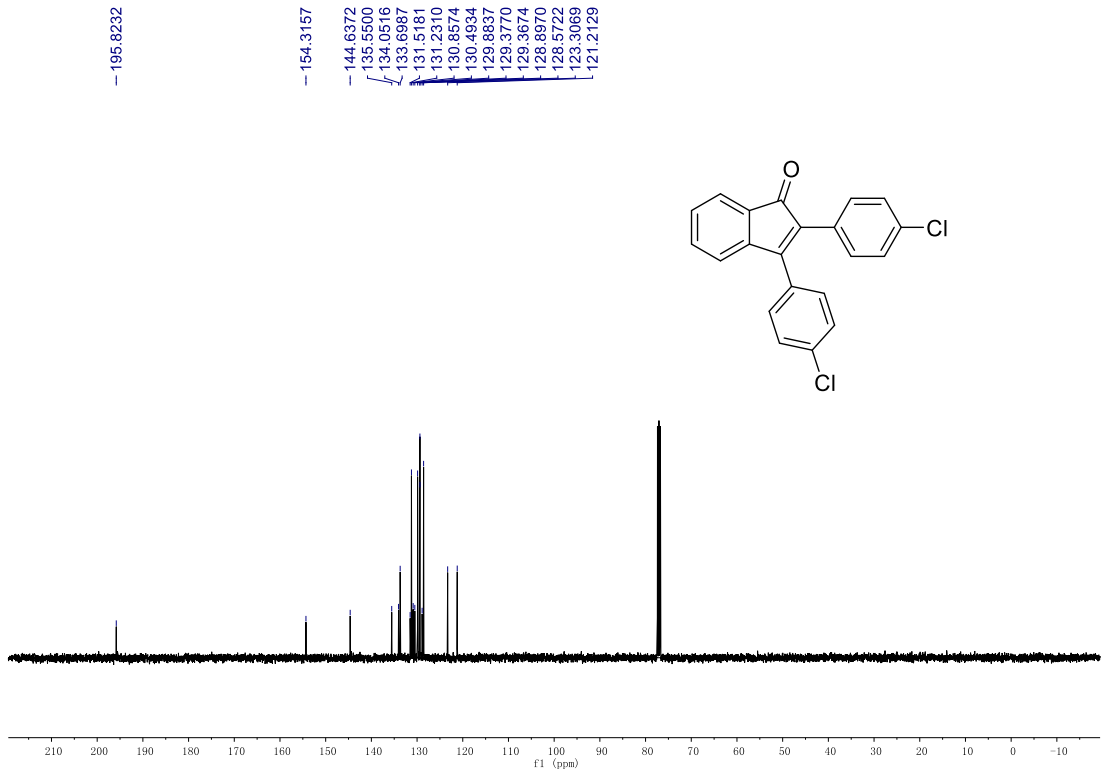
3.01
2.02
1.97
1.01
f1 (ppm)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128.8970
128.5722
123.3069
121.2129
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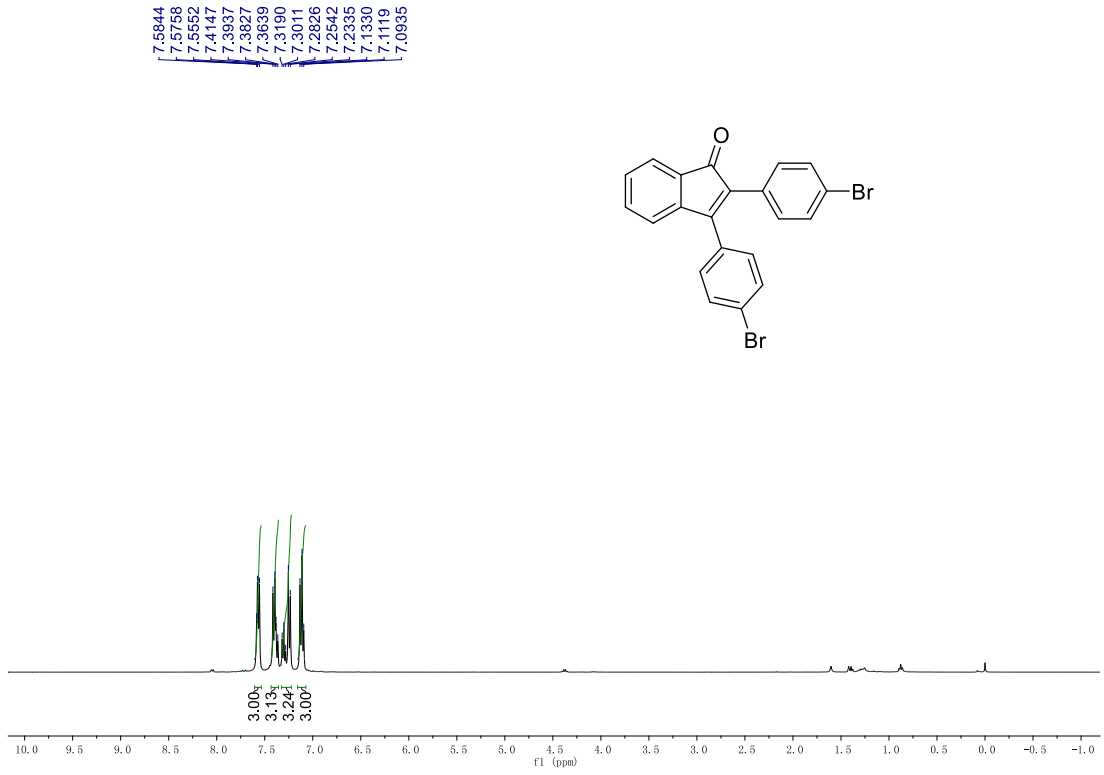
Cl
Cl
f1 (ppm)

3af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7.2542
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7.1119
7.0935
O
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Br
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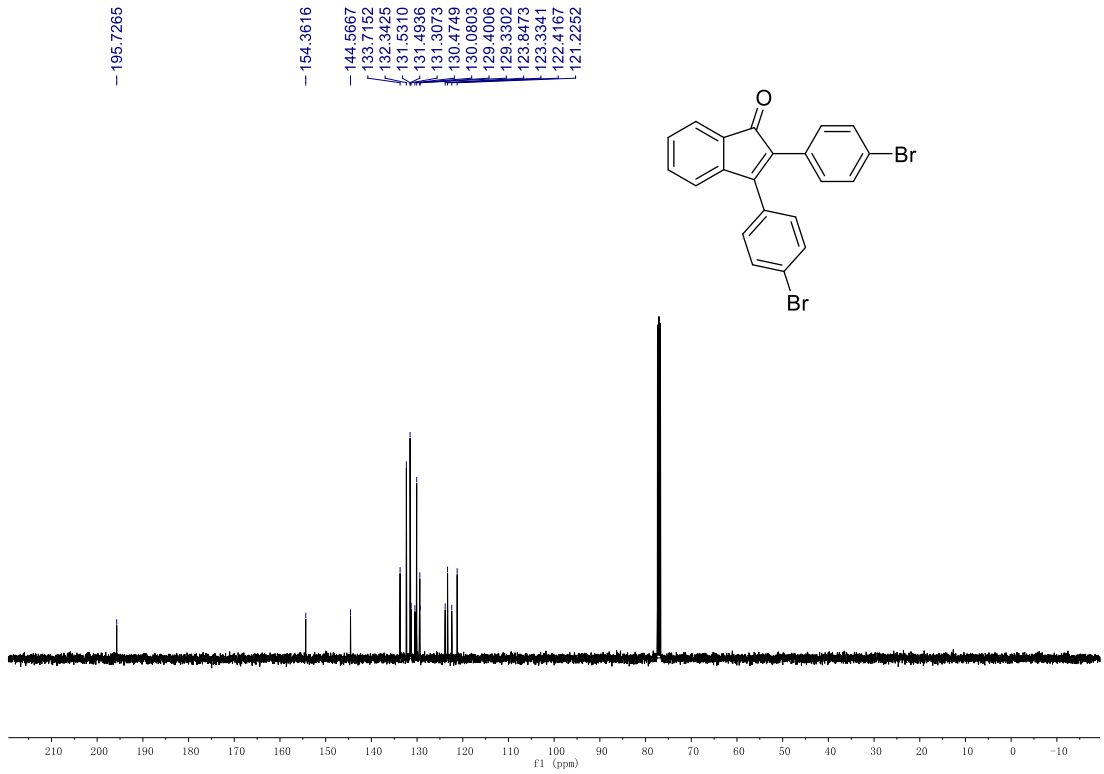
3.13
3.24
3.00
f1 (ppm)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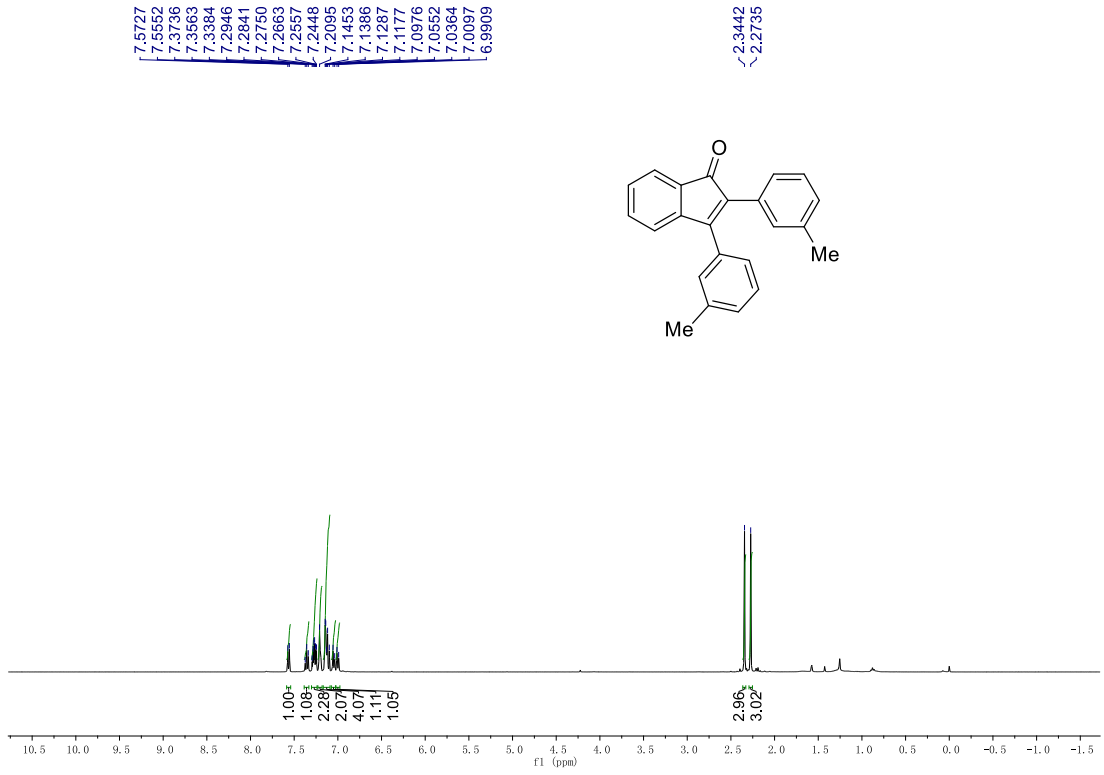
Br
Br
f1 (ppm)

3ag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7.2663
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7.2448
7.2095
7.1453
7.1386
7.1287
7.1177
7.0976
7.0552
7.0364
7.0097
6.9909
2.3442
2.2735
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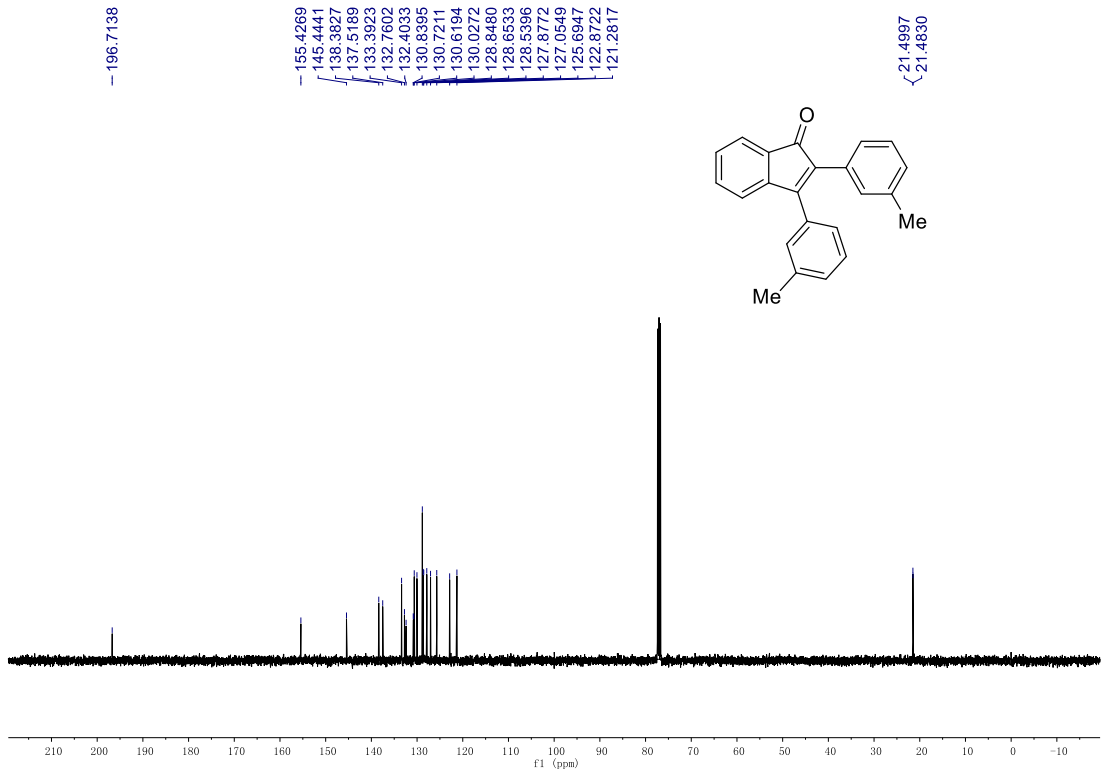
2.28
2.07
4.07
1.11
1.05
2.96
3.02
f1 (ppm)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128.8480
128.6533
128.5396
127.8772
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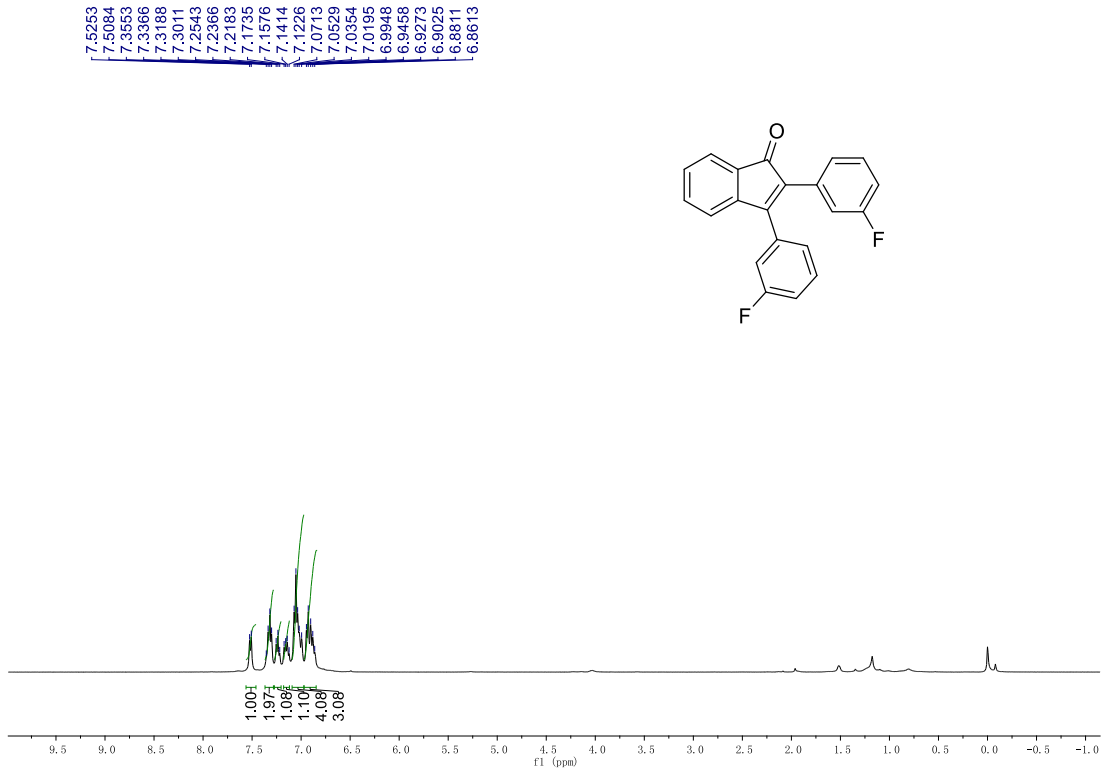
21.4830
O
Me
Me
f1 (ppm)

3ah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7.1414
7.1226
7.0713
7.0529
7.0354
7.0195
6.9948
6.9458
6.9273
6.9025
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O
F
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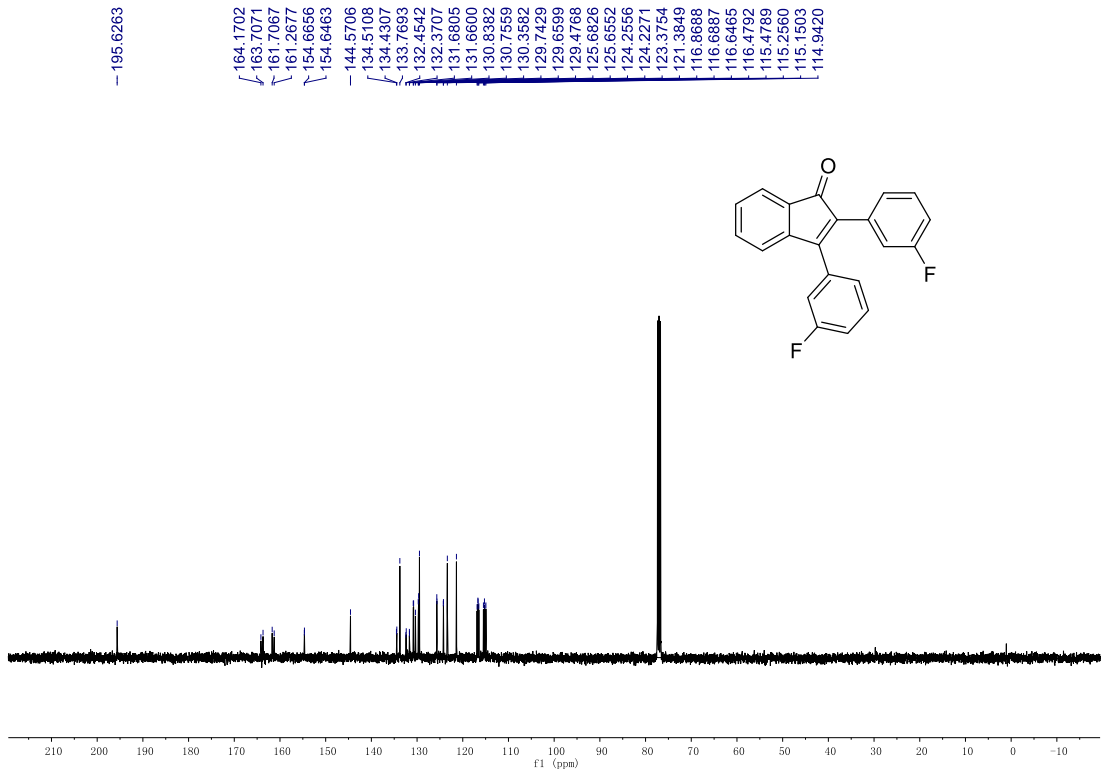
1.97
1.08
1.10
4.08
3.08
f1 (ppm)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132.4542
132.3707
131.6805
131.6600
130.8382
130.7559
130.3582
129.7429
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125.6552
124.2556
124.2271
123.3754
121.3849
116.8688
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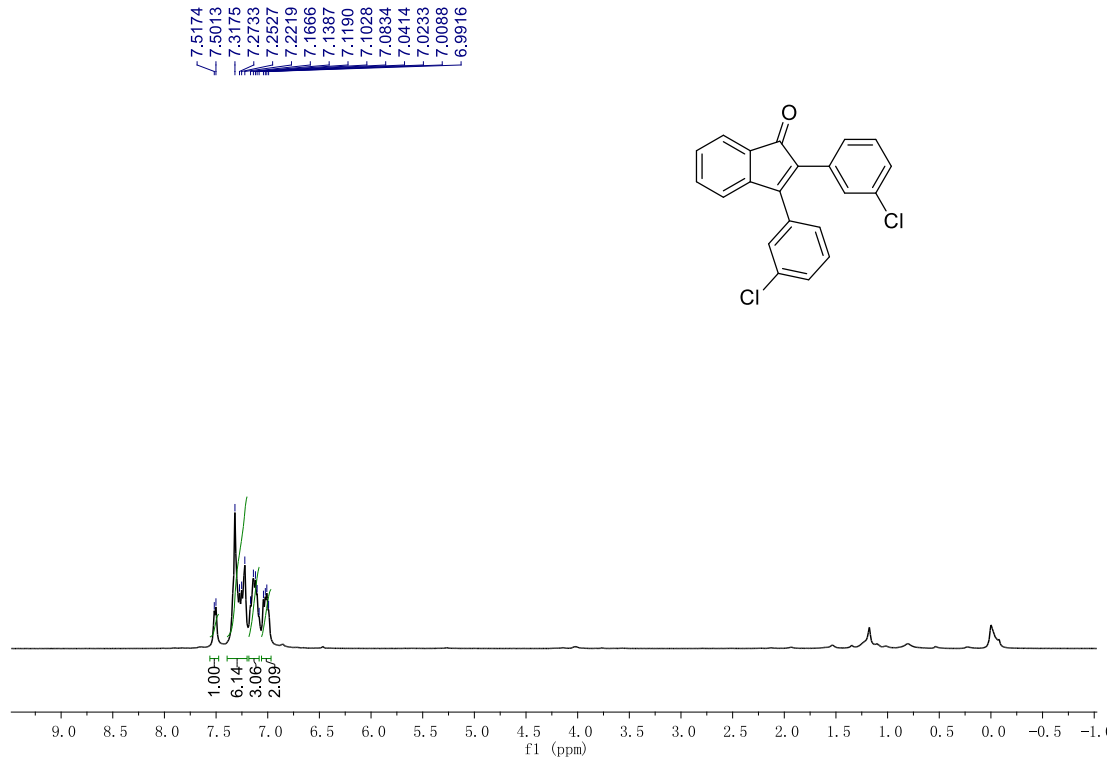
116.4792
115.4789
115.2560
115.1503
114.9420
O
F
F
f1 (ppm)

3ai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7.1028
7.0834
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7.0088
6.9916
O
Cl
Cl
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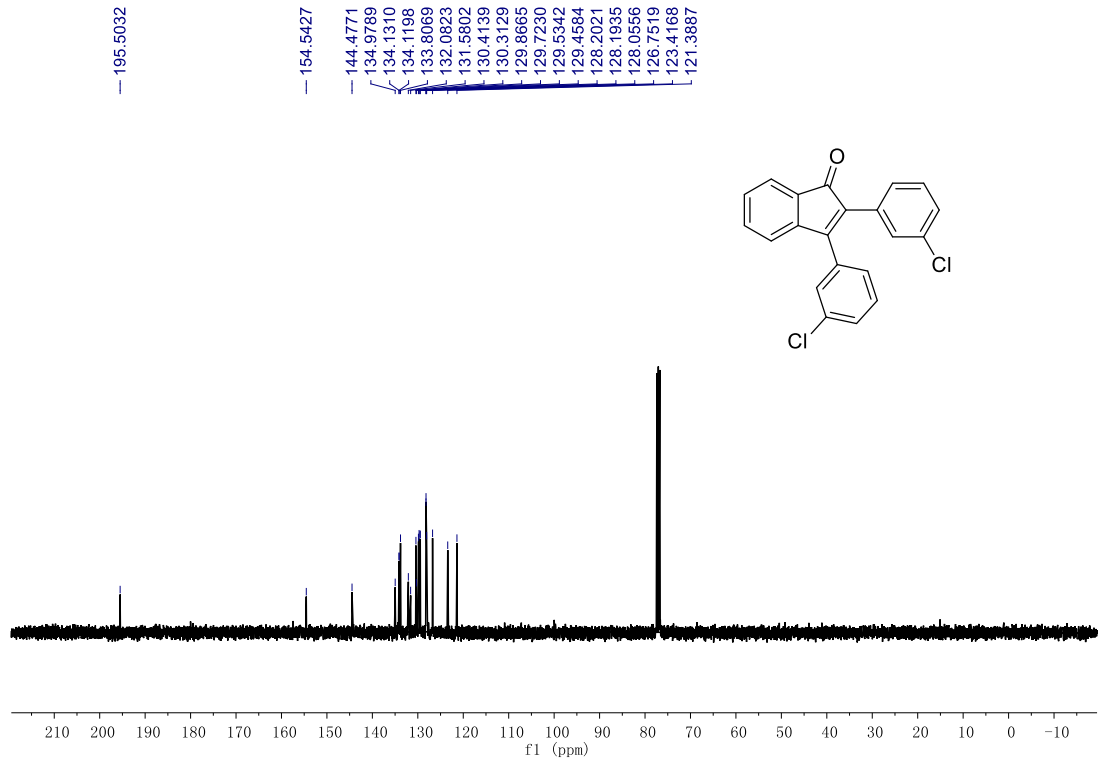
6.14
3.06
2.09
f1 (ppm)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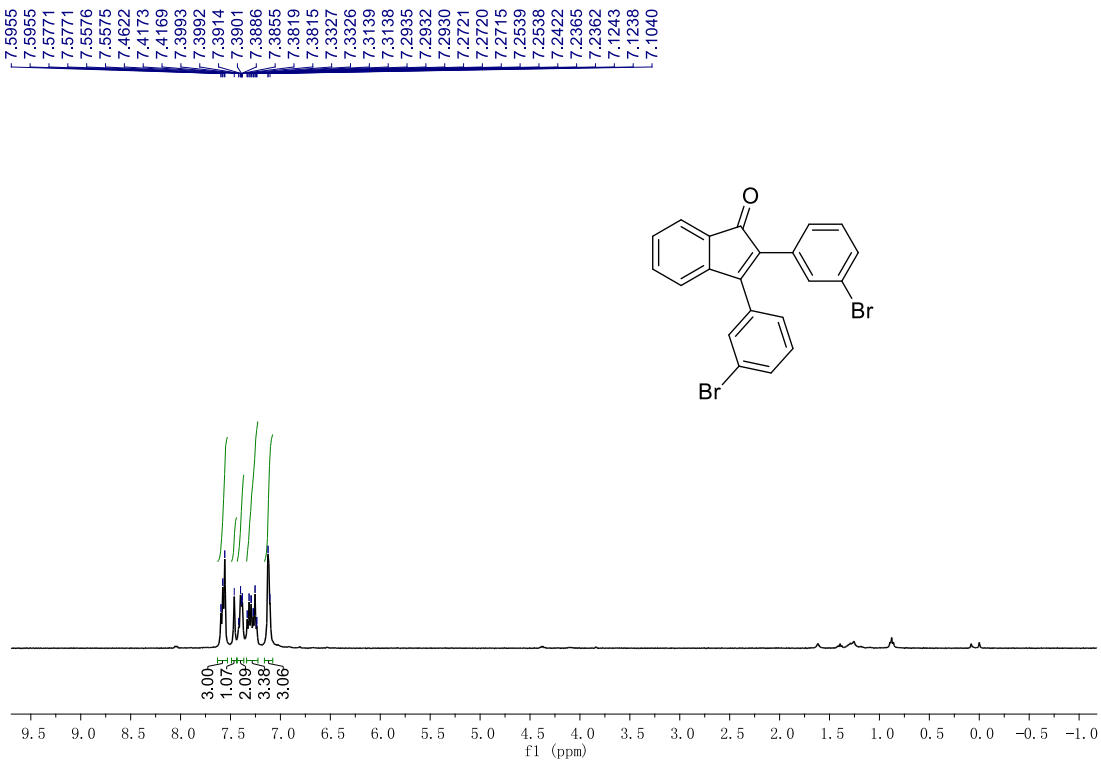
129.7230
129.5342
129.4584
128.2021
128.1935
128.0556
126.7519
123.4168
121.3887
O
Cl
Cl
f1 (ppm)

3aj


7.5955
7.5955
7.5771
7.5771
7.5576
7.5575
7.4622
7.4173
7.4169
7.3993
7.3992
7.3914
7.3901
7.3886
7.3855
7.3819
7.3815
7.3327
7.3326
7.3139
7.3138
7.2935
7.2932
7.2930
7.2721
7.2720
7.2715
7.2539
7.2538
7.2422
7.2365
7.2362
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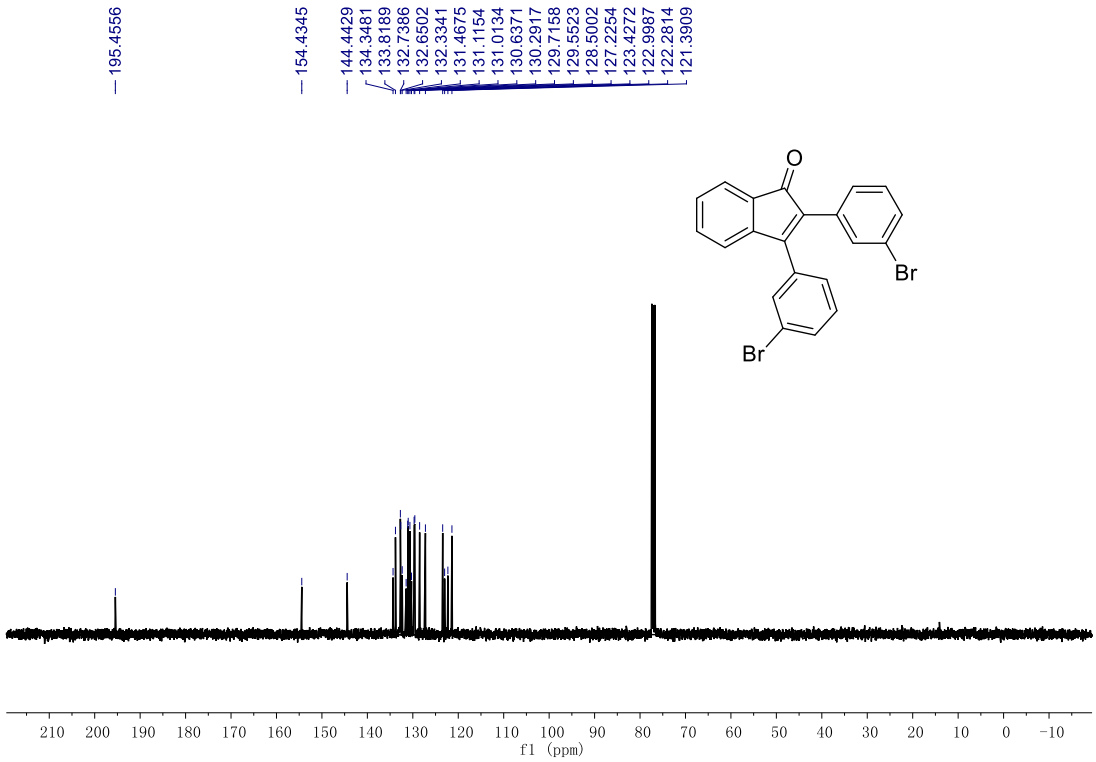
7.1040
O
Br
Br
3.00
1.07
2.09
3.38
3.06
f1 (ppm)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144.4429
134.3481
133.8189
132.7386
132.6502
132.3341
131.4675
131.1154
131.0134
130.6371
130.2917
129.7158
129.5523
128.5002
127.2254
123.4272
122.9987
122.2814
121.3909
O
Br
Br
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)