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Supporting Information

Rhodium(III)-Catalyzed Synthesis of Indanones via C-H Activation of Phenacyl Phosphoniums and Coupling with Olefins

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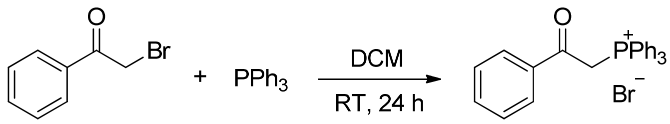
I. General Information

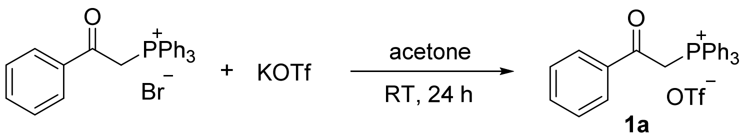
Commercially available reagents were used as received without further purification, unless stated otherwise. All reactions were carried out in a nitrogen-filled dry box or using standard Schlenk techniques. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker NMR spectrometer (400 MHz and 100 MHz, respectively) and internally referenced to the tetramethylsilane signal in the solvent indicated. ^{19}F NMR spectra were recorded on a Bruker NMR spectrometer instrument (376 MHz). HRMS were obtained on an Agilent Q-TOF 6540. Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate (EA)/petroleum ether (PE) or dichloromethane (DCM)/methanol (MeOH) as eluents. The abundance of ^{18}O in $Et^{18}OH$ and $CH_3C^{18}O_2Na$ was 95% and 98% respectively.

II. Experimental Information for the Preparation of Starting Materials

Representative Procedure of Preparation of a Phenacyl Phosphonium Salt.[1]



A solution of α-bromoacetophenone (50.0 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 20 min to a solution of triphenylphosphine (50.0 mmol) in CH_2Cl_2 (60 mL). The reaction mixture was stirred at room temperature for 24 h, and the mixture was concentrated under reduced pressure and the resulting precipitate was washed with Et_2O. The phosphonium bromide was obtained in quantitative yield, and was used without further purification.



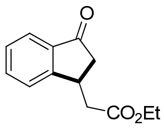
1a

A solution of KOTf (4 equiv) in acetone (10 mL) was added to a solution of (2-oxo-2-phenylethyl)triphenylphosphonium bromide (20 mmol) in acetone (40 mL) and the mixture was stirred for at rt for 24 h. All the solvent was removed under reduced pressure and the residue was washed with DCM. The solution was concentrated to give product **1a** in 95% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.1 Hz, 2H), 7.84 – 7.74 (m, 9H), 7.69 – 7.61 (m, 7H), 7.50 (t, J = 7.6 Hz, 2H), 5.60 (d, J = 12.4 Hz, 2H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 191.7, 135.1, 135.0 (d, J = 3.1 Hz), 133.8, 133.7, 130.4, 130.2, 129.5, 129.1, 118.6 (d, J = 89.5 Hz), 36.5 (d, J = 59.2 Hz). HRMS: $[M-OTf]^+$ calculated for $C_{26}H_{22}OP^+$: 381.1403, found 381.1403, $[OTf]^-$ calculated for CF_3O_3S: 148.9520, found 148.9524.

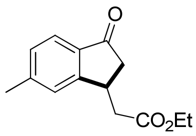
III. Experimental Details and Characterization Data

Representative procedures for the synthesis of indanone derivatives. Phenacyl phosphonium salts **1a** (0.2 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (10 mol %), CsOAc (0.4 mmol), and $Cu(OAc)_2$ (0.42 mmol) were charged into a pressure tube. Ethanol (2 mL) was then added to this tube. The resulting mixture was stirred for seconds under N_2 atmosphere, to which ethyl acrylate (**2a**, 0.4 mmol) was next added. The mixture was stirred at 120 ^oC for 18 hours. The solvent was then removed under vacuum and the residue was purified by silica gel chromatography using PE/EA (30:1 – 10:1) to afford product **3aa** as a colorless oil (34.7 mg, 80%).



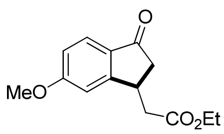
3aa, 80%

Product **3aa** was obtained as a colorless oil in 80% yield (34.7 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.76 (d, J = 7.7 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.4 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 – 3.79 (m, 1H), 3.01 (dd, J = 19.2, 7.7 Hz, 1H), 2.89 (dd, J = 15.9, 5.1 Hz, 1H), 2.56 (dd, J = 16.0, 9.3 Hz, 1H), 2.47 (dd, J = 19.2, 3.4 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 205.4, 171.7, 156.7, 136.8, 134.9, 128.0, 125.4, 123.7, 60.8, 43.3, 40.4, 34.6, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{15}O_3^+$: 219.1016, found 219.1017.



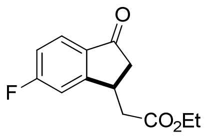
3ba, 85%

Product **3ba** was obtained as a colorless oil in 85% yield (39.4 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.64 (d, J = 7.8 Hz, 1H), 7.30 (s, 1H), 7.22 (d, J = 7.8 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.80 – 3.74 (m, 1H), 2.98 (dd, J = 19.1, 7.7 Hz, 1H), 2.87 (dd, J = 15.9, 5.1 Hz, 1H), 2.52 (dd, J = 15.9, 9.3 Hz, 1H), 2.47 – 2.40 (m, 4H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 204.9, 171.8, 157.2, 146.1, 134.6, 129.3, 125.8, 123.5, 60.8, 43.5, 40.5, 34.4, 22.2, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{17}O_3^+$: 233.1172, found 233.1174.



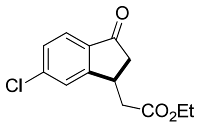
3ca, 56%

Product **3ca** was obtained as a colorless oil in 56% yield (28.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, J = 9.2 Hz, 1H), 6.95 – 6.93 (m, 2H), 4.18 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 3.81 – 3.73 (m, 1H), 2.98 (dd, J = 19.0, 7.7 Hz, 1H), 2.86 (dd, J = 15.9, 5.3 Hz, 1H), 2.54 (dd, J = 15.9, 9.2 Hz, 1H), 2.43 (dd, J = 19.0, 3.3 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 203.5, 171.8, 165.4, 159.7, 130.1, 125.4, 115.7, 108.9, 60.8, 55.7, 43.5, 40.5, 34.5, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{17}O_4^+$: 249.1121, found 249.1124.



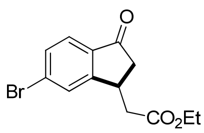
3da, 76%

Product **3da** was obtained as a colorless oil in 76% yield (35.8 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (dd, J = 8.4, 5.3 Hz, 1H), 7.18 (dd, J = 8.6, 1.9 Hz, 1H), 7.11 (ddd, J = 8.5, 2.2, 1.1 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.85 – 3.77 (m, 1H), 3.02 (dd, J = 19.2, 7.8 Hz, 1H), 2.85 (dd, J = 16.1, 5.5 Hz, 1H), 2.59 (dd, J = 16.1, 8.8 Hz, 1H), 2.48 (dd, J = 19.2, 3.4 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 203.3, 171.4, 167.2 (d, J = 256.5 Hz), 159.6 (d, J = 9.5 Hz), 133.3 (d, J = 1.8 Hz), 126.1 (d, J = 10.4 Hz), 116.3 (d, J = 23.8 Hz), 112.3 (d, J = 22.6 Hz), 60.9, 43.4, 40.1, 34.4, 14.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -102.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}FO_3^+$: 237.0921, found 237.0923.



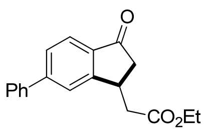
3ea, 90%

Product **3ea** was obtained as a white solid in 90% yield (40.1 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.68 (d, J = 8.2 Hz, 1H), 7.51 (s, 1H), 7.39 (dd, J = 8.2, 1.2 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.85 – 3.76 (m, 1H), 3.01 (dd, J = 19.2, 7.8 Hz, 1H), 2.86 (dd, J = 16.1, 5.4 Hz, 1H), 2.58 (dd, J = 16.1, 8.8 Hz, 1H), 2.48 (dd, J = 19.2, 3.5 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 203.7, 171.4, 158.1, 141.4, 135.3, 128.8, 125.8, 124.9, 60.9, 43.3, 40.1, 34.3, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}ClO_3^+$: 253.0626, found 253.0626.



3fa, 73%

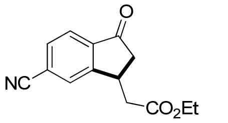
Product **3fa** was obtained as a yellow solid in 73% yield (43.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.69 (s, 1H), 7.61 (d, J = 8.1 Hz, 1H), 7.55 (dd, J = 8.2, 1.1 Hz, 1H), 4.18 (q, J = 7.2 Hz, 2H), 3.86 – 3.77 (m, 1H), 2.99 (dd, J = 19.3, 7.8 Hz, 1H), 2.86 (dd, J = 16.1, 5.3 Hz, 1H), 2.58 (dd, J = 16.1, 8.9 Hz, 1H), 2.46 (dd, J = 19.3, 3.4 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 203.9, 171.4, 158.2, 135.7, 131.7, 130.2, 128.9, 125.0, 60.9, 43.2, 40.1, 34.3, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}BrO_3^+$: 297.0121, found 297.0125.



3ga, 73%

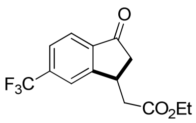
Product **3ga** was obtained as a yellow oil in 73% yield (42.7 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.81 (d, J = 8.0 Hz, 1H), 7.69 (s, 1H), 7.65 – 7.59 (m, 3H), 7.50 – 7.45 (m, 2H), 7.43 – 7.39 (m, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.90 – 3.84 (m, 1H), 3.04 (dd, J = 19.2, 7.7 Hz, 1H), 2.94 (dd, J = 15.9, 5.1 Hz, 1H), 2.60 (dd, J = 15.9, 9.3 Hz, 1H), 2.51 (dd, J = 19.2, 3.4 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 204.9, 171.7, 157.4, 148.0, 140.1, 135.7, 129.0, 128.5, 127.5, 127.5, 124.1, 124.0, 60.8, 43.6, 40.5, 34.6, 14.2. HRMS:

m/z: $[M + H]^+$ calculated for $C_{19}H_{19}O_3^+$: 295.1329, found 295.1331.



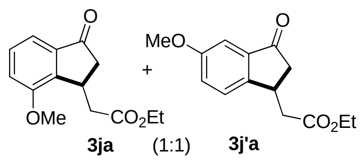
3ha, 38%

Product **3ha** was obtained as a white solid in 38% yield (18.7 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.88 – 7.81 (m, 2H), 7.70 (d, J = 7.8 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.92 – 3.85 (m, 1H), 3.07 (dd, J = 19.5, 7.9 Hz, 1H), 2.87 (dd, J = 16.4, 5.6 Hz, 1H), 2.66 (dd, J = 16.4, 8.2 Hz, 1H), 2.55 (dd, J = 19.5, 3.5 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 203.6, 171.1, 156.5, 139.8, 131.7, 129.9, 124.5, 118.0, 117.9, 61.1, 43.2, 39.8, 34.4, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{14}NO_3^+$: 244.0968, found 244.0970.



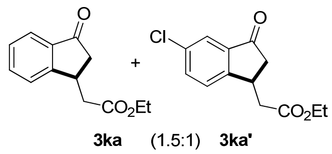
3ia, 66%

Product **3ia** was obtained as a white solid in 66% yield (37.7 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.86 (d, J = 8.0 Hz, 1H), 7.80 (s, 1H), 7.68 (d, J = 8.0 Hz, 1H), 4.18 (qd, J = 7.1, 1.7 Hz, 2H), 3.94 – 3.85 (m, 1H), 3.08 (dd, J = 19.4, 7.8 Hz, 1H), 2.91 (dd, J = 16.1, 5.4 Hz, 1H), 2.64 (dd, J = 16.1, 8.7 Hz, 1H), 2.55 (dd, J = 19.4, 3.5 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 204.1, 171.3, 156.7, 139.5, 136.2 (q, J = 32.3 Hz), 125.2 (q, J = 3.5 Hz), 124.3, 123.6 (q, J = 273.2 Hz), 122.8 (q, J = 3.9 Hz), 61.0, 43.4, 40.0, 34.6, 14.1. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -62.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{14}F_3O_3^+$: 287.0890, found 287.0890.



3ja+3ja', 67% (1:1)

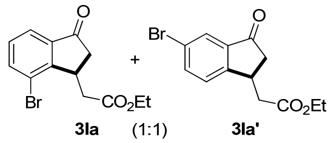
Product **3ja** and **3ja'** was obtained as a white solid in 67% yield as a 1:1 mixture (37.7 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.42 – 7.33 (m, 3H), 7.22 – 7.18 (m, 2H), 7.06 (dd, J = 7.5, 1.2 Hz, 1H), 4.20 – 4.11 (m, 4H), 3.91 (s, 3H), 3.89 – 3.83 (m, 4H), 3.80 – 3.72 (m, 1H), 3.27 (dd, J = 16.1, 3.5 Hz, 1H), 3.05 – 2.94 (m, 2H), 2.84 (dd, J = 15.9, 5.2 Hz, 1H), 2.56 – 2.44 (m, 3H), 2.38 (dd, J = 16.1, 10.3 Hz, 1H), 1.27 – 1.23 (m, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 205.8, 205.2, 172.2, 171.8, 159.8, 157.2, 149.5, 144.6, 138.7, 138.1, 129.7, 126.2, 124.1, 115.5, 115.3, 104.9, 60.8, 60.6, 55.6, 55.5, 43.9, 43.4, 40.6, 38.3, 34.0, 32.8, 14.205, 14.20. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{17}O_4^+$: 249.1121, found 249.1125.



3ka+3ka', 65% (1.5:1)

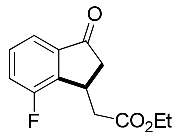
Product **3ka** and **3ka'** was obtained as a colorless oil in 65% yield as a 1.5:1 mixture (33.0 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** Mixture： δ 7.70 (d, J = 2.0 Hz, 1H), 7.67 (d, J = 7.5 Hz, 1.5H), 7.63 – 7.54 (m, 2.5H), 7.46 (d, J = 8.2 Hz, 1H), 7.39 (t, J = 7.7 Hz, 1.5H), 4.20 – 4.10

(m, 5H), 3.95 – 3.89 (m, 1.5H), 3.85 – 3.76 (m, 1H), 3.26 (dd, J = 16.3, 3.2 Hz, 1H), 3.08 – 2.96 (m, 2.5H), 2.85 (dd, J = 16.1, 5.3 Hz, 1H), 2.62 – 2.43 (m, 5H), 1.27 – 1.20 (m, 7.5H). 13C NMR (100 MHz, CDCl3) Major: δ 204.4, 171.5, 152.9, 139.2, 135.2, 132.5, 129.7, 122.2, 60.8, 43.4, 37.9, 34.2, 14.2. Minor: δ 203.8, 154.7, 138.4, 134.9, 134.5, 126.8, 123.6, 60.9, 43.6, 40.2, 34.3, 14.15. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}ClO_3^+$: 253.0626, found 253.0626.

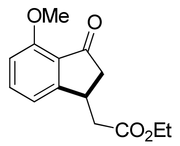


3la+3la', 58% (1:1)

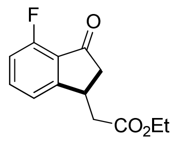
Product **3la** and **3la'** was obtained as a yellow oil in 58% yield as a 1:1 mixture (34.6 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.87 (d, J = 1.9 Hz, 1H), 7.78 (dd, J = 7.8, 0.9 Hz, 1H), 7.73 – 7.70 (m, 2H), 7.41 (d, J = 8.2 Hz, 1H), 7.32 (t, J = 7.7 Hz, 1H), 4.19 – 4.10 (m, 4H), 3.90 – 3.83 (m, 1H), 3.82 – 3.74 (m, 1H), 3.29 (dd, J = 16.3, 3.1 Hz, 1H), 3.04 (dd, J = 7.7, 5.0 Hz, 1H), 2.99 (dd, J = 7.8, 5.0 Hz, 1H), 2.85 (dd, J = 16.1, 5.3 Hz, 1H), 2.63 – 2.54 (m, 2H), 2.52 – 2.43 (m, 2H), 1.26 – 1.22 (m, 6H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 204.5, 203.7, 171.4, 155.2, 154.8, 139.3, 138.7, 138.4, 137.6, 129.9, 127.1, 126.7, 122.8, 122.4, 121.4, 60.9, 60.8, 43.5, 43.4, 40.1, 38.1, 35.7, 34.3, 14.2, 14.15. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}BrO_3^+$: 297.0121, found 297.0125.

 **3ma,** 66%

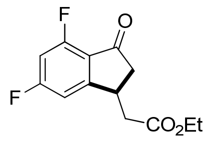
Product **3ma** was obtained as a yellow solid in 66% yield (31.2 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.57 (d, J = 7.5 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.31 – 7.27 (m, 1H), 4.14 (q, J = 7.1 Hz, 2H), 4.01 – 3.91 (m, 1H), 3.13 (dd, J = 16.2, 3.8 Hz, 1H), 3.03 (dd, J = 19.4, 7.8 Hz, 1H), 2.58 – 2.50 (m, 2H), 1.23 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 204.1 (d, J = 2.0 Hz), 171.4, 160.3 (d, J = 251.1 Hz), 141.8 (d, J = 17.0 Hz), 140.0 (d, J = 4.3 Hz), 130.2 (d, J = 6.5 Hz), 121.3 (d, J = 20.5 Hz), 119.6 (d, J = 3.9 Hz), 60.8, 43.2, 38.6, 32.2, 14.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -118.3. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}FO_3^+$: 237.0921, found 237.0924.

 **3na**, 77%

Product **3na** was obtained as a yellow oil in 77% yield (38.2 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.55 (t, J = 7.9 Hz, 1H), 7.04 (d, J = 7.6 Hz, 1H), 6.83 (d, J = 8.2 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.78 – 3.71 (m, 1H), 2.97 (dd, J = 18.9, 7.8 Hz, 1H), 2.86 (dd, J = 15.9, 5.0 Hz, 1H), 2.51 (dd, J = 15.9, 9.4 Hz, 1H), 2.44 (dd, J = 18.9, 3.5 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 203.0, 171.7, 159.4, 158.0, 136.7, 124.8, 117.1, 109.6, 60.8, 55.8, 43.8, 40.6, 34.1, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{14}H_{17}O_4^+$: 249.1121, found 249.1118.

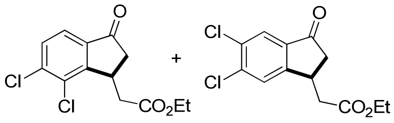
 **3oa**, 76%

Product **3oa** was obtained as a colorless oil in 76% yield (36.0 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.62 – 7.57 (m, 1H), 7.29 (d, J = 7.7 Hz, 1H), 7.02 (t, J = 8.7 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.86 – 3.80 (m, 1H), 3.02 (dd, J = 19.1, 7.9 Hz, 1H), 2.88 (dd, J = 16.1, 5.1 Hz, 1H), 2.59 (dd, J = 16.1, 9.0 Hz, 1H), 2.50 (dd, J = 19.1, 3.5 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 201.5, 171.4, 158.9 (d, J = 2.2 Hz), 158.8 (d, J = 264.3 Hz), 136.9 (d, J = 8.3 Hz), 124.6 (d, J = 12.9 Hz), 121.2 (d, J = 4.2 Hz), 114.9 (d, J = 19.3 Hz), 60.9, 43.8, 40.2, 34.5, 14.2. **^{19}F NMR (376 MHz, CDCl$_3$)** δ -114.6. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{14}FO_3^+$: 237.0921, found 237.0924.

 **3pa**, 71%

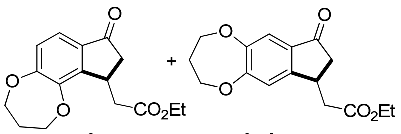
Product **3pa** was obtained as a white solid in 71% yield (35.9 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.01 (d, J = 7.8 Hz, 1H), 6.78 (td, J = 9.0, 1.6 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.86 – 3.76 (m, 1H), 3.03 (dd, J = 19.1, 7.9 Hz, 1H), 2.84 (dd, J = 16.3, 5.5 Hz, 1H), 2.61 (dd,

J = 16.3, 8.6 Hz, 1H), 2.51 (dd, J = 19.1, 3.6 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 199.72 (d, J = 1.9 Hz), 171.11, 167.60 (dd, J = 259.1, 11.1 Hz), 160.76 (dd, J = 10.7, 4.0 Hz), 159.36 (dd, J = 262.1, 8.9 Hz), 121.45 (dd, J = 13.2, 2.4 Hz), 108.70 (dd, J = 22.5, 4.3 Hz), 104.22 (dd, J = 26.9, 22.9 Hz), 61.0, 43.9, 39.9, 34.7, 14.2 . **^{19}F NMR (376 MHz, $CDCl_3$)** δ -97.7 (d, J = 13.3 Hz), -109.4 (d, J = 13.3 Hz). HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{13}F_2O_3^+$: 255.0827, found 255.0826.



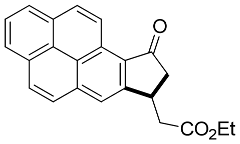
3qa (1.7:1) 3qa' **3qa+3qa'**, 47% (1.7:1)

Product **3qa** and **3qa'** was obtained as a yellow oil in 47% yield as a 1.7:1 mixture (27.1 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** Mixture: δ 7.81 (s, 1H), 7.64 (s, 1H), 7.61 (d, J = 8.1 Hz, 1.7H), 7.54 (d, J = 8.1 Hz, 1.7H), 4.21 – 4.09 (m, 5.4H), 3.98 – 3.89 (m, 1.7H), 3.82 – 3.76 (m, 1H), 3.23 (dd, J = 16.4, 3.2 Hz, 1.7H), 3.03 (dd, J = 19.3, 7.8 Hz, 2.7H), 2.83 (dd, J = 16.2, 5.6 Hz, 1H), 2.65 – 2.56 (m, 2.7H), 2.56 – 2.46 (m, 2.7H), 1.25 – 1.20 (m, 8.1H). **^{13}C NMR (100 MHz, $CDCl_3$)** Major: δ 203.2, 171.2, 154.8, 139.8, 137.4, 130.9, 130.85, 122.5, 60.9, 43.6, 37.7, 34.8, 14.14. Minor: δ 202.6, 155.4, 139.4, 136.5, 133.2, 127.7, 125.2, 61.0, 43.4, 39.9, 34.0, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{13}H_{13}Cl_2O_3^+$: 287.0236, found 287.0236.



3ra (2:1) 3ra' **3ra+3ra'**, 67% (2:1)

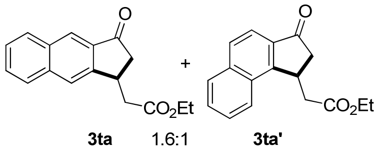
Product **3ra** and **3ra'** was obtained as a colorless oil in 67% yield as a 2:1 mixture (38.9 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** Mixture: δ 7.35 – 7.29 (m, 3H), 7.01 (d, J = 0.6 Hz, 1H), 6.98 (d, J = 8.2 Hz, 2H), 4.37 – 4.33 (m, 10H), 4.29 – 4.22 (m, 2H), 4.20 – 4.10 (m, 6H), 3.86 – 3.80 (m, 2H), 3.75 – 3.65 (m, 1H), 3.17 (dd, J = 15.9, 3.6 Hz, 2H), 2.95 (dd, J = 19.2, 7.8 Hz, 3H), 2.80 (dd, J = 15.9, 5.3 Hz, 1H), 2.54 – 2.37 (m, 6H), 2.32 – 2.21 (m, 6H), 1.28 – 1.19 (m, 9H). **^{13}C NMR (100 MHz, $CDCl_3$)** Major: δ 204.0, 172.0, 156.5, 148.7, 147.8, 132.8, 122.5, 118.4, 70.27, 60.6, 43.7, 38.8, 32.8, 30.8, 14.19. Minor: δ 203.7, 171.7, 157.5, 152.5, 151.4, 132.0, 117.2, 115.9, 70.3, 70.2, 60.8, 43.8, 40.5, 33.9, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{16}H_{19}O_5^+$: 291.1227, found 291.1230.



3sa, 47%

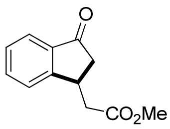
Product **3sa** was obtained as a yellow solid in 47% yield (32.0 mg). **^{1}H NMR (400 MHz, acetone-d_6)** δ 9.47 (d, J = 9.1 Hz, 1H), 8.46 – 8.42 (m, 4H), 8.34 (d, J = 9.0 Hz, 1H), 8.22 (d, J = 9.0 Hz, 1H), 8.16 (t, J = 7.7 Hz, 1H), 4.22 – 4.11 (m, 3H), 3.25 (dd, J = 12.7, 3.4 Hz, 1H), 3.22 – 3.16 (m, 1H), 2.91 – 2.82 (m, 1H), 2.72 (dd, J = 18.7, 3.6 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, DMSO-d_6)** δ 206.6, 172.1, 156.1, 136.1, 131.2, 130.9, 130.6, 130.4, 128.1, 127.8, 127.7, 127.5, 127.1, 123.8, 123.3, 122.5, 121.6, 60.5, 44.3, 34.4, 14.5.

HRMS: m/z: $[M + H]^+$ calculated for $C_{23}H_{19}O_3^+$: 343.1329, found 343.1329.



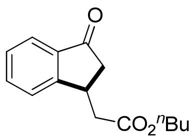
3ta+3ta', 72% (1.6:1)

Product **3ta** and **3ta'** was obtained as a yellow oil in 72% yield as a 1.6:1 mixture (38.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** Mixture: δ 8.31 (s, 1.6H), 8.11 – 8.07 (m, 1H), 8.00 – 7.95 (m, 2.6H), 7.91 (s, 1.6H), 7.88 – 7.84 (m, 2.6H), 7.74 (d, J = 8.5 Hz, 1H), 7.69 – 7.65 (m, 1.6H), 7.61 – 7.57 (m, 2H), 7.54 – 7.49 (m, 1.6H), 4.34 – 4.29 (m, 1H), 4.22 – 4.14 (m, 5.2H), 4.02 – 3.96 (m, 1.6H), 3.20 (dd, J = 16.1, 3.0 Hz, 1H), 3.15 – 3.06 (m, 2.6H), 2.99 (dd, J = 16.0, 5.3 Hz, 1.6H), 2.70 – 2.62 (m, 2.6H), 2.57 (dd, J = 19.2, 4.1 Hz, 1.6H), 2.39 (dd, J = 16.1, 10.9 Hz, 1H), 1.27 – 1.23 (m, 7.8H). **^{13}C NMR (100 MHz, CDCl$_3$)** Major: δ 205.6, 171.8, 149.8, 137.1, 134.4, 130.4, 129.5, 129.46, 128.7, 128.0, 126.5, 124.5, 124.0, 119.4, 60.8, 44.0, 40.9, 34.2, 14.23. Minor: δ 205.3, 171.8, 157.1, 137.1, 134.7, 132.6, 129.5, 129.1, 127.3, 124.4, 60.9, 44.0, 41.1, 34.0, 14.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{17}H_{17}O_3^+$: 269.1172, found 269.1173.



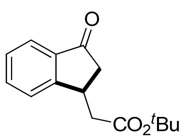
3ab, 87%

Product **3ab** was obtained as a colorless oil in 87% yield (35.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (d, J = 7.7 Hz, 1H), 7.62 (td, J = 7.7, 1.2 Hz, 1H), 7.51 (dd, J = 7.8, 0.8 Hz, 1H), 7.44 – 7.39 (m, 1H), 3.86 – 3.80 (m, 1H), 3.72 (s, 3H), 3.01 (dd, J = 19.2, 7.7 Hz, 1H), 2.90 (dd, J = 16.1, 5.2 Hz, 1H), 2.57 (dd, J = 16.1, 9.3 Hz, 1H), 2.45 (dd, J = 19.2, 3.4 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 205.2, 172.2, 156.6, 136.8, 134.9, 128.1, 125.4, 123.7, 51.9, 43.3, 40.2, 34.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{12}H_{13}O_3^+$: 205.0859, found 205.0862.



3ac, 74%

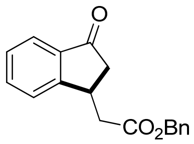
Product **3ac** was obtained as a colorless oil in 74% yield (29.8 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.76 (d, J = 7.7 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 4.12 (t, J = 6.7 Hz, 2H), 3.88 – 3.79 (m, 1H), 3.00 (dd, J = 19.2, 7.7 Hz, 1H), 2.90 (dd, J = 15.9, 5.1 Hz, 1H), 2.56 (dd, J = 15.9, 9.2 Hz, 1H), 2.46 (dd, J = 19.2, 3.4 Hz, 1H), 1.64 – 1.56 (m, 2H), 1.40 – 1.31 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 205.3, 171.8, 156.7, 136.8, 134.9, 128.0, 125.4, 123.7, 64.7, 43.3, 40.4, 34.6, 30.6, 19.1, 13.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{15}H_{19}O_3^+$: 247.1329, found 247.1331.



3ad, 57%

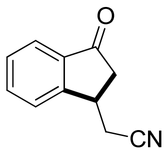
Product **3ad** was obtained as a colorless oil in 57% yield (27.8 mg). **^{1}H NMR (400 MHz,

CDCl$_3$) δ 7.75 (d, J = 7.7 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.52 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7.4 Hz, 1H), 3.82 – 3.76 (m, 1H), 2.98 (dd, J = 19.2, 7.7 Hz, 1H), 2.82 (dd, J = 15.6, 5.1 Hz, 1H), 2.52 – 2.46 (m, 2H), 1.42 (s, 9H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 205.6, 170.9, 157.0, 136.9, 134.8, 127.9, 125.5, 123.7, 81.1, 43.2, 41.5, 34.7, 28.0. HRMS: m/z: [M + H]$^+$ calculated for $C_{15}H_{19}O_3^+$: 247.1329, found 247.1328.



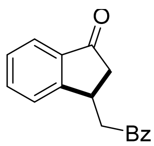
3ae, 78%

Product **3ae** was obtained as a colorless oil in 78% yield (43.5 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.74 (d, J = 7.6 Hz, 1H), 7.58 (t, J = 7.3 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.42 – 7.30 (m, 6H), 5.20 – 5.11 (m, 2H), 3.88 – 3.79 (m, 1H), 3.02 – 2.89 (m, 2H), 2.61 (dd, J = 16.0, 9.2 Hz, 1H), 2.44 (dd, J = 19.2, 3.3 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 205.2, 171.6, 156.5, 136.8, 135.6, 134.9, 128.7, 128.5, 128.4, 128.1, 125.4, 123.8, 66.7, 43.3, 40.4, 34.6. HRMS: m/z: [M + H]$^+$ calculated for $C_{18}H_{17}O_3^+$: 281.1172, found 281.1172.



3af, 75%

Product **3af** was obtained as a yellow oil in 75% yield (25.6 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.80 (d, J = 7.7 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.52 – 7.47 (m, 1H), 3.80 – 3.74 (m, 1H), 3.05 (dd, J = 19.1, 7.8 Hz, 1H), 2.85 – 2.72 (m, 2H), 2.51 (dd, J = 19.1, 3.4 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 203.2, 154.0, 136.8, 135.4, 129.0, 125.4, 124.1, 117.7, 42.5, 34.5, 23.8. HRMS: m/z: [M + H]$^+$ calculated for $C_{11}H_{10}NO^+$: 172.0757, found 172.0755.

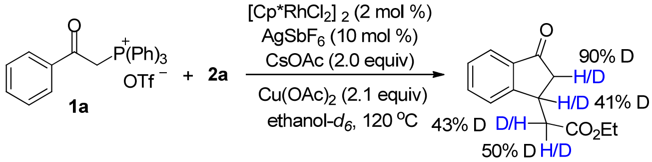


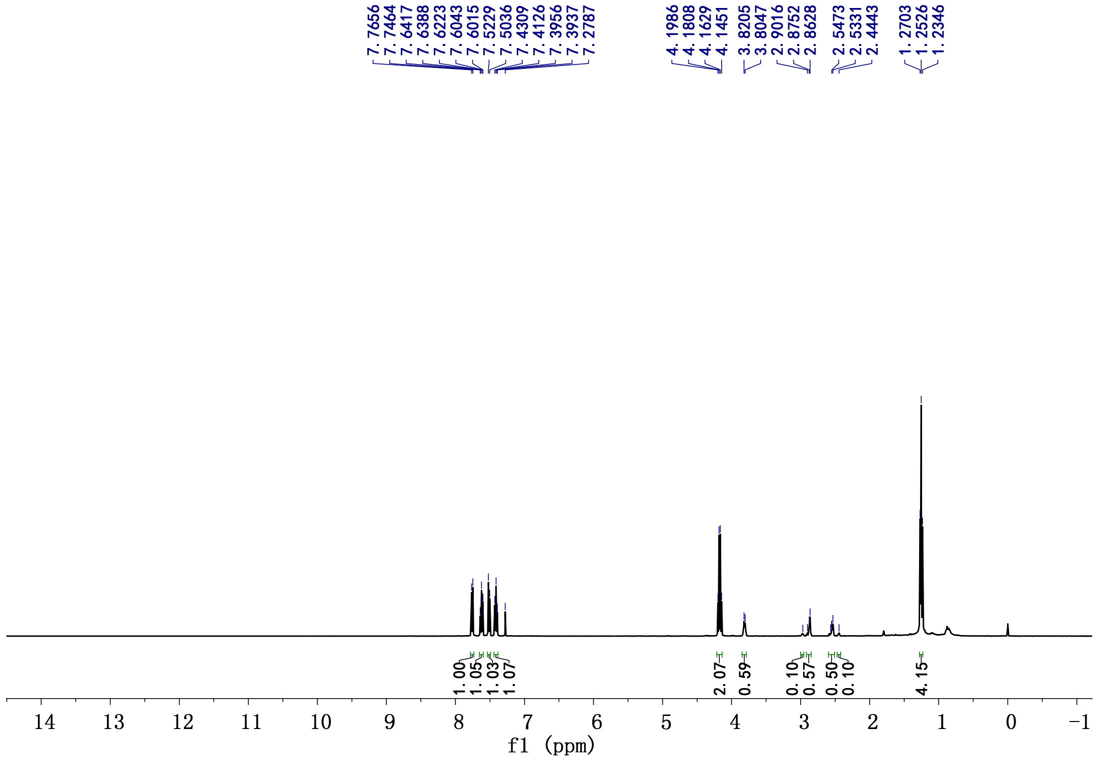
3ag, 56%

Product **3ag** was obtained as a colorless oil in 56% yield (27.9 mg). **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.99 – 7.95 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.64 – 7.53 (m, 3H), 7.49 – 7.45 (m, 2H), 7.41 (t, J = 7.4 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.57 (dd, J = 17.8, 4.8 Hz, 1H), 3.25 (dd, J = 17.8, 9.1 Hz, 1H), 3.12 (dd, J = 19.3, 7.7 Hz, 1H), 2.36 (dd, J = 19.3, 3.3 Hz, 1H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 205.7, 198.1, 157.6, 136.9, 136.6, 134.9, 133.5, 128.8, 128.1, 127.9, 125.7, 123.8, 45.3, 44.0, 33.7. HRMS: [M+H]$^+$ calculated for $C_{17}H_{15}O_2^+$: 251.1067, found 251.1068.

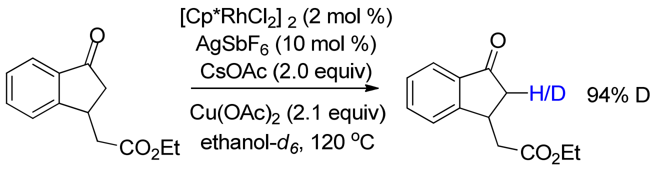
IV. Mechanistic Studies

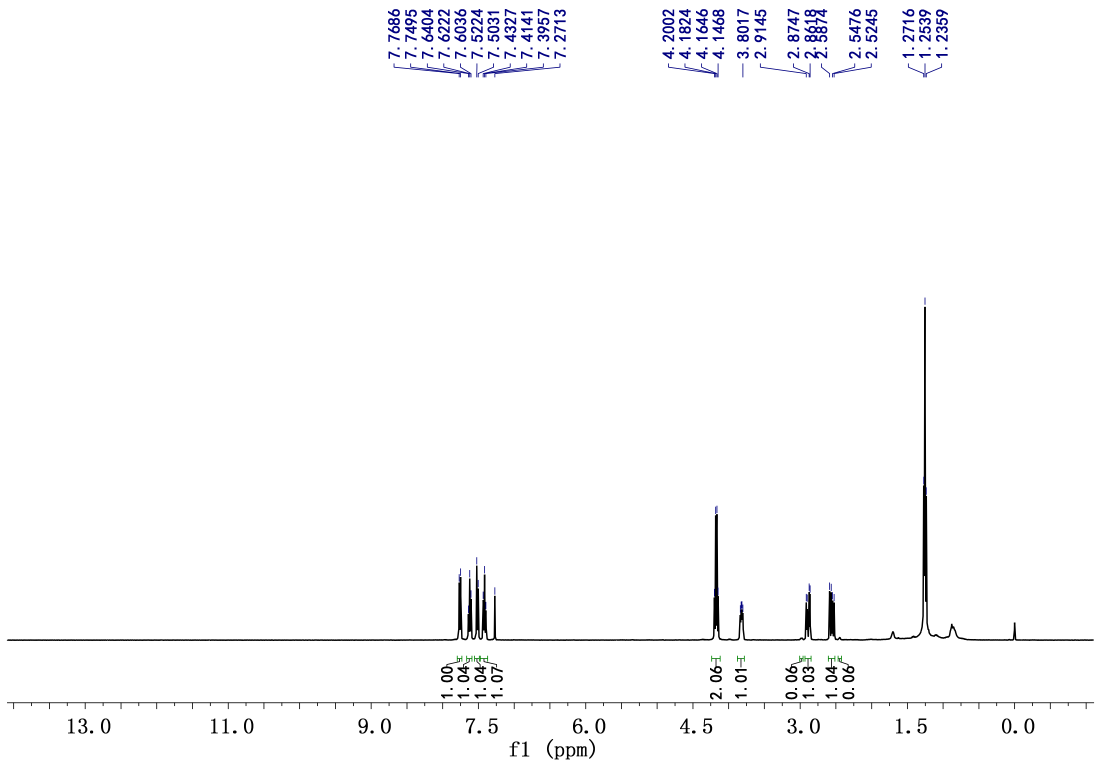
H/D Exchange Experiment of the Coupling Reaction between 1a and Ethyl Acrylate 2a. To a mixture of **1a** (0.2 mmol), CsOAc (0.4 mmol), $Cu(OAc)_2$ (0.42 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), and $AgSbF_6$ (10 mol %) in ethanol-d_6 (2 mL) was added ethyl acrylate **2a** (0.4 mmol) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 18 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford colorless oil product, which was characterized by ^1H NMR spectroscopy.



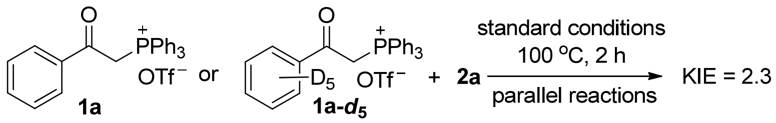


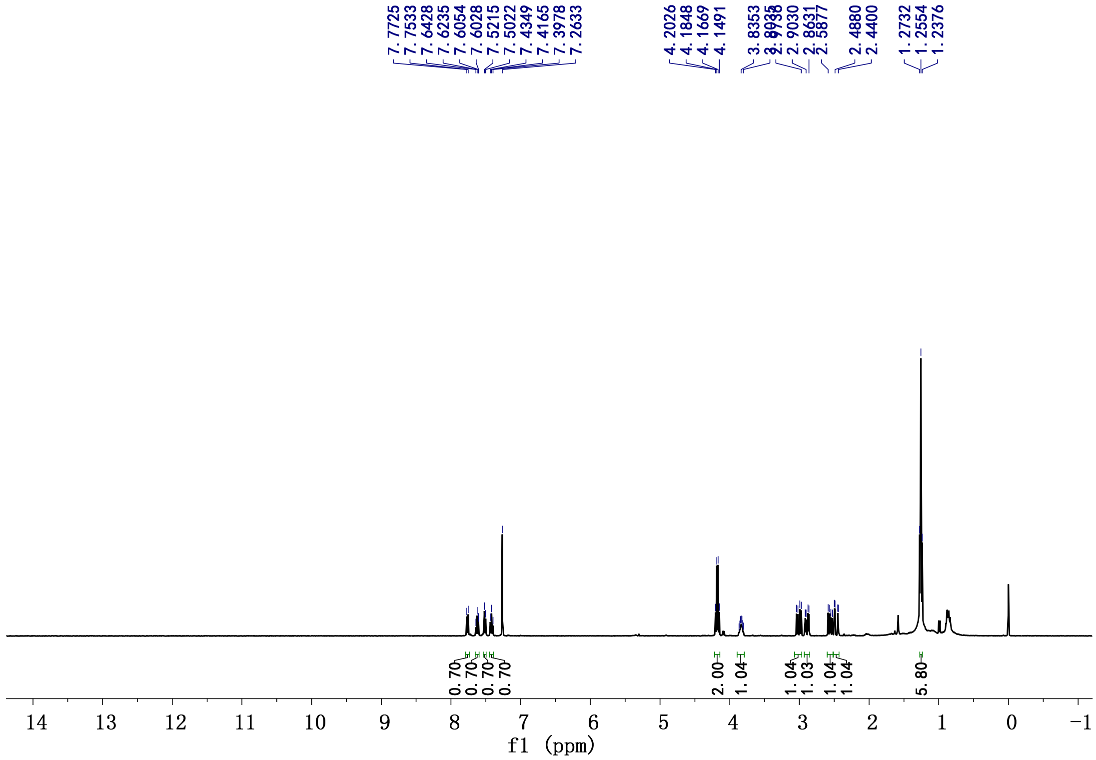
Post-Coupling H/D Exchange Experiment of the Product 3aa. A control experiment was conducted to exclude the H/D exchange originating from post-coupling H/D exchange. A mixture of **3aa** (0.1 mmol), CsOAc (0.4 mmol), $Cu(OAc)_2$ (0.42 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (10 mol %) in ethanol-d_6 (1 mL) was stirred at 120 °C for 18 h under N_2 atmosphere. Then the solvent was removed under vacuum and the residue was purified by silica gel chromatography. The product was characterized by ^1H NMR spectroscopy.



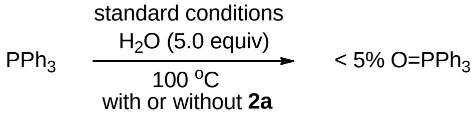


Measurement of Kinetic Isotope Effect (Parallel Reactions). Two pressure tubes were separately charged with **1a** (0.24 mmol) and **1a**-d_5 (0.24 mmol). To each tube was added [Cp*RhCl$_2$]$_2$ (2 mol %), AgSbF$_6$ (10 mol %), CsOAc (0.4 mmol), Cu(OAc)$_2$ (0.42 mmol), ethyl acrylate **2a** (0.2 mmol), and EtOH (2 mL) under N_2 atmosphere. The two reaction mixtures were stirred side by side in an oil bath preheated at 100 °C for 2 hour. After that, the reaction was cooled to 0 °C rapidly and was quenched with pentane. The two mixtures were combined and the solvent was removed under vacuum.The residue was purified by silica gel chromatography using PE/EA to afford a mixture of **3aa** and **3aa**-d_n as a colorless oil (6.5 mg, 7% yield). The KIE value was determined to be k_H/k_D = 2.3 on the basis of ^{1}H NMR analysis.

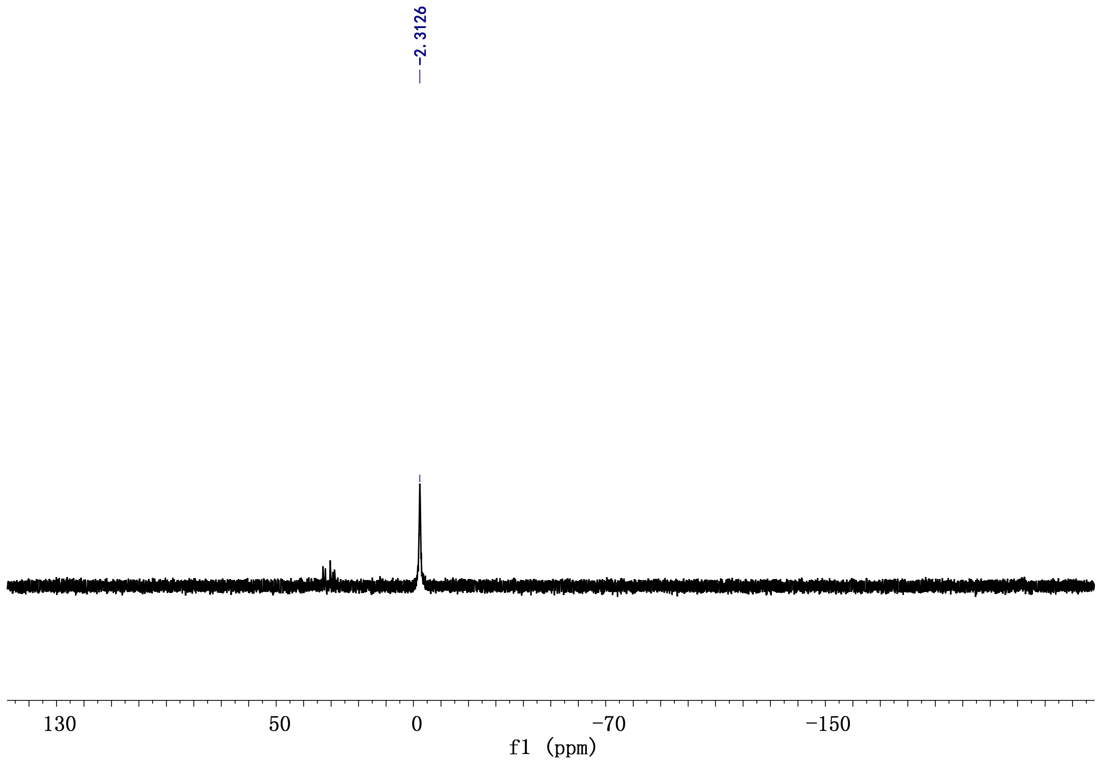




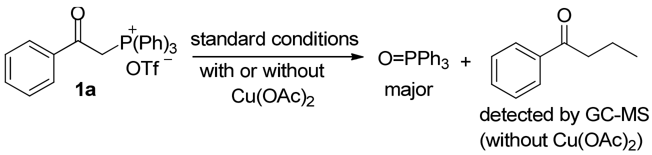
Studies on a Possible Sequence of Phosphine Elimnation-Oxidation. To a pressure tube loaded with PPh_3 (0.1 mmol) was added H_2O (5.0 equiv.) with or without ethyl acrylate **2a** under standard conditions at 100 °C for 18 h. After that, the reaction mixture was analyzed by GC-MS and ^{31}P NMR spectroscopy, and essentially no (<5%) O=PPh_3 was detected.



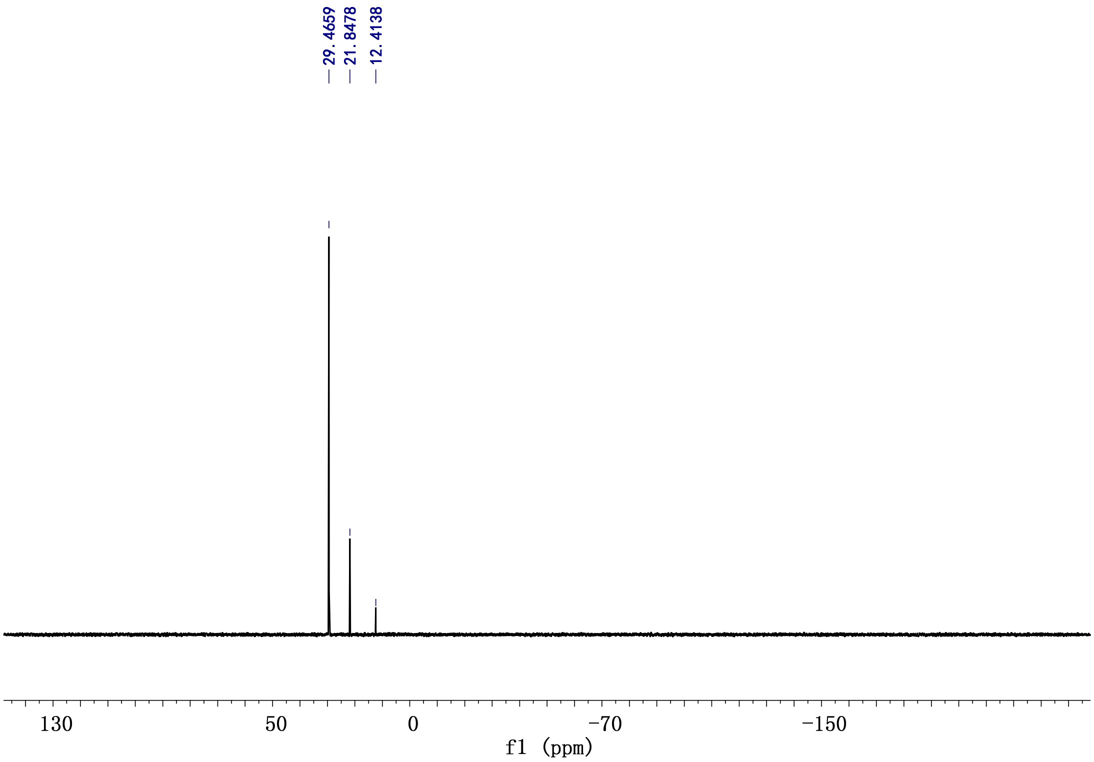
^{31}P NMR Spectrum of the Product of Mixture without **2a**



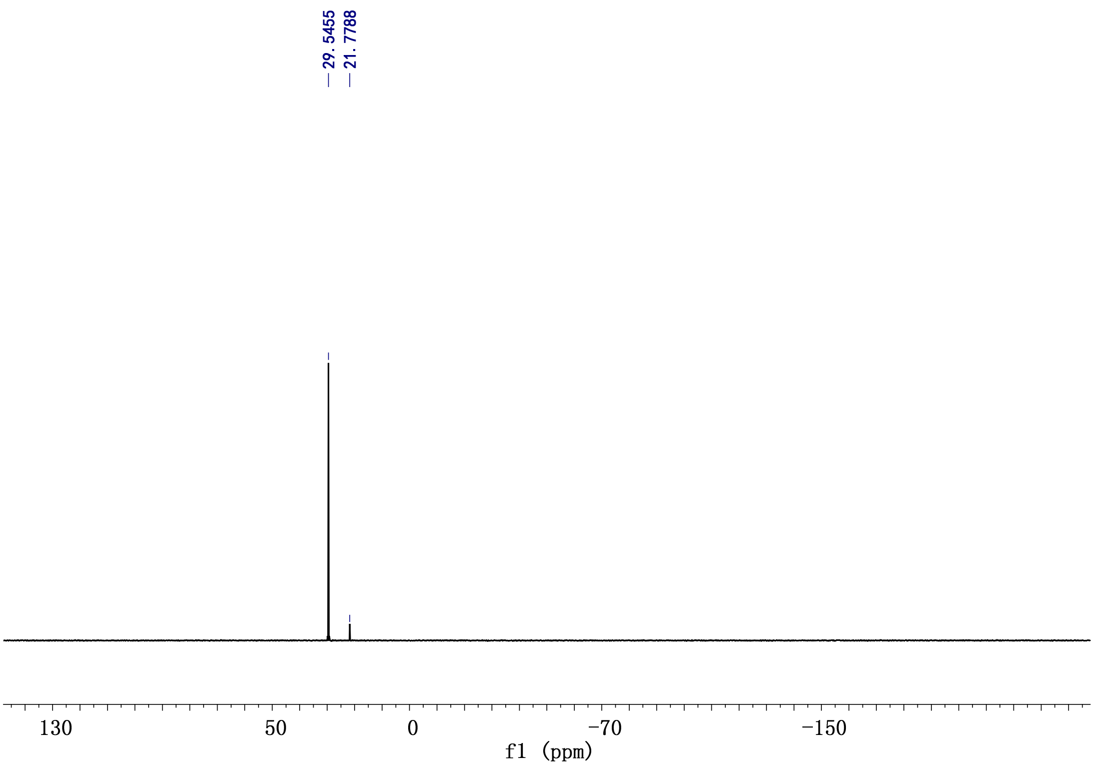
Two pressure tubes were both charged with phosphonium **1a** (0.2 mmol), and to one of the tube was added $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (10 mol %), CsOAc (0.4 mmol), $Cu(OAc)_2$ (0.42 mmol), and EtOH (2 mL) under N_2 atmosphere. To the other tube was added $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (10 mol %), CsOAc (0.4 mmol), and EtOH (2 mL) under N_2 atmosphere. The two reaction mixtures were stirred at 120 ^{o}C for 12 hour. After that, the reaction mixtures were characterized by ^{31}P NMR spectroscopy and GC-MS analysis. Phenacyl phosphonium salt was mostly converted to O=PPh$_3$ even without $Cu(OAc)_2$.



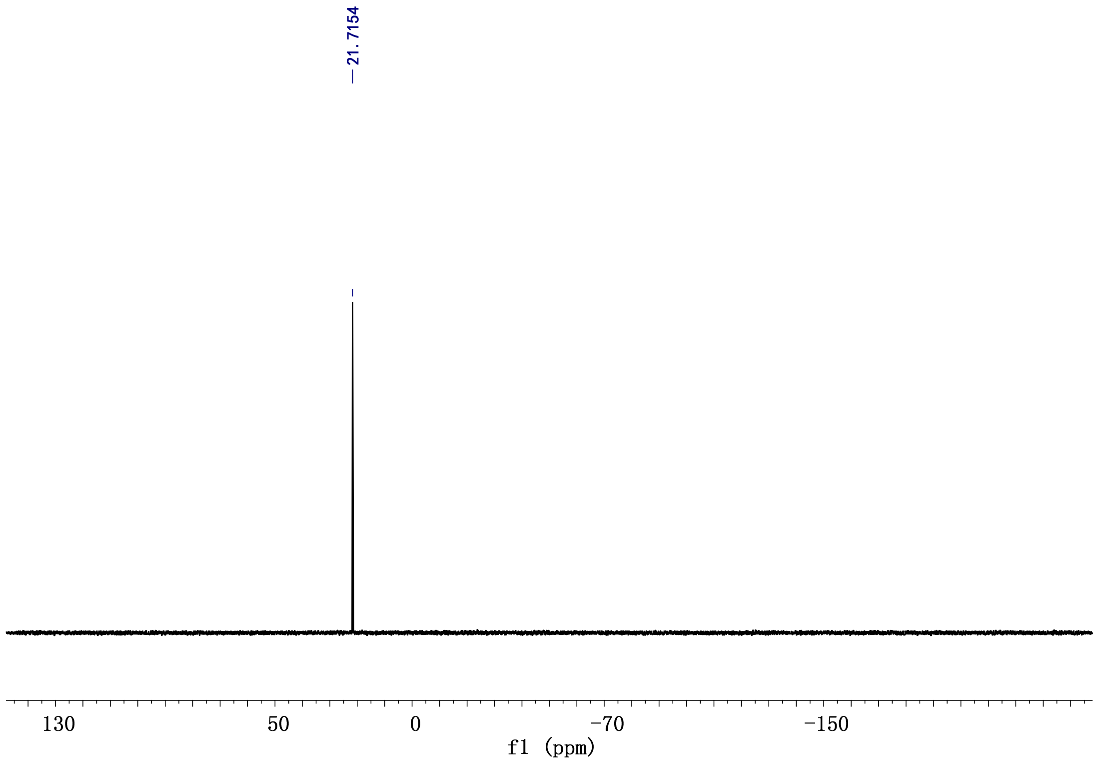
^{31}P NMR Spectra of the Mixture Obtained with $Cu(OAc)_2$



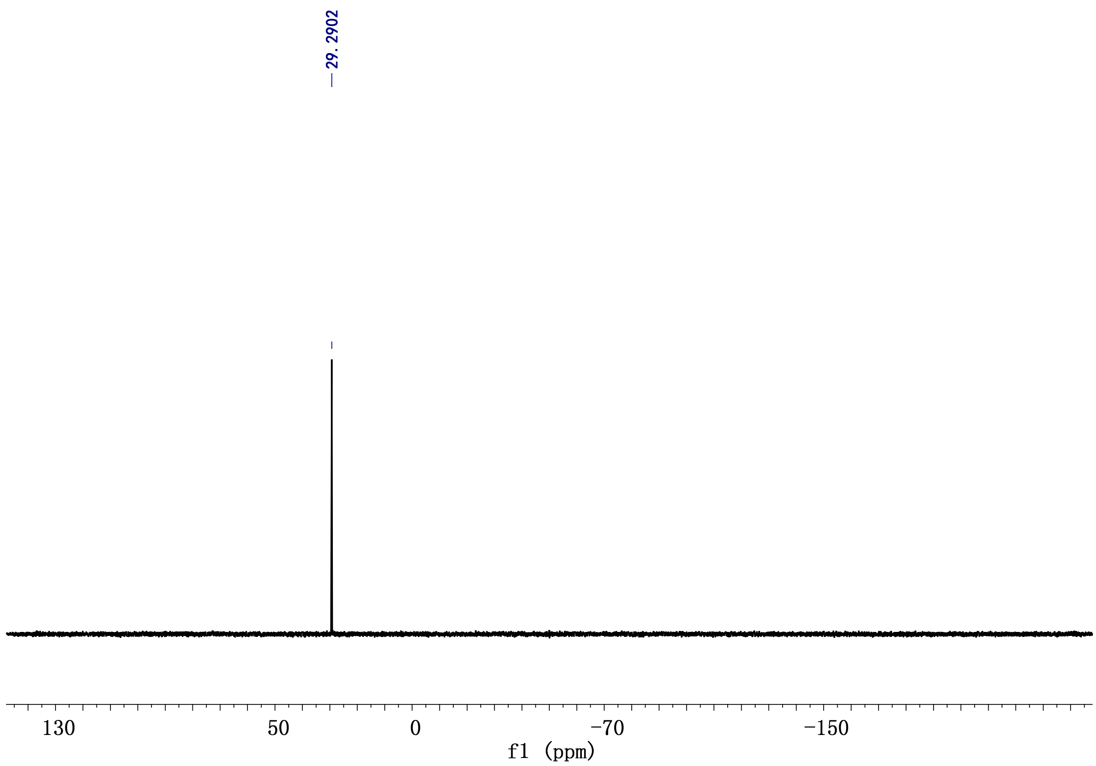
^{31}P NMR Spectra of the Mixture Obtained without $Cu(OAc)_2$



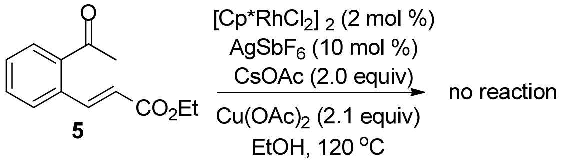
^{31}P NMR Spectra of **1a**



^{31}P NMR Spectra of O=PPh$_3$

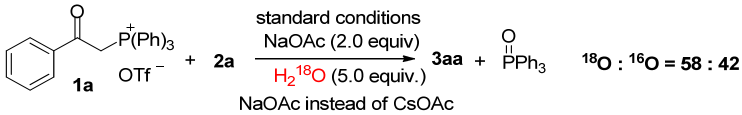


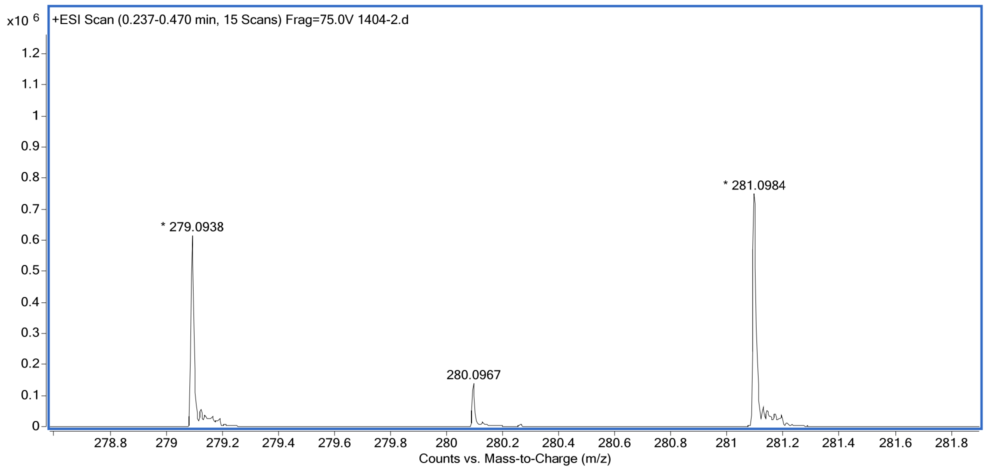
Studies on the Possible Intermediacy of an Olefin. A possible olefin intermediate **5** was prepared[2] and was subjected to the standard conditions. No conversion was detected by GC-MS.



^{1}H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, J = 15.9 Hz, 1H), 7.75 (dd, J = 7.6, 1.2 Hz, 1H), 7.61 – 7.57 (m, 1H), 7.52 (td, J = 7.4, 1.1 Hz, 1H), 7.46 (td, J = 7.5, 1.4 Hz, 1H), 6.28 (d, J = 15.9 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 2.62 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 200.9, 166.5, 143.9, 138.2, 134.8, 132.0, 129.4, 129.3, 128.4, 121.0, 60.6, 29.3, 14.3.

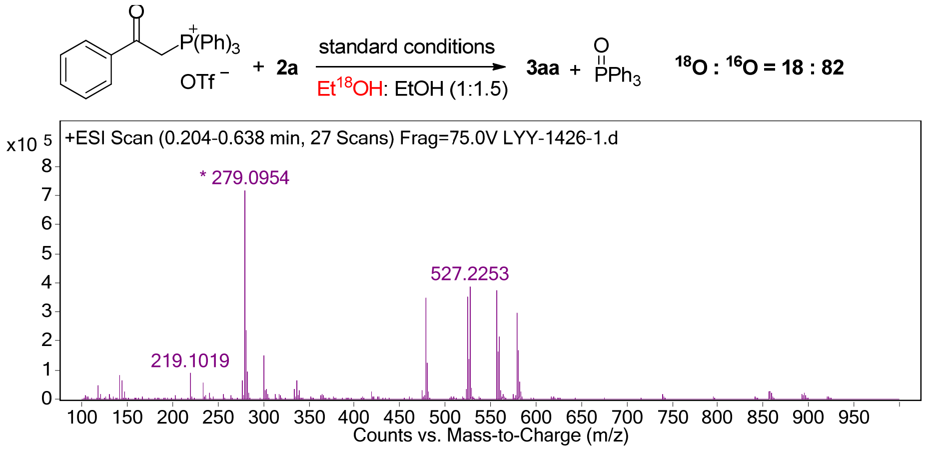
^{18}O-Labeling Experiments. To a mixture of **1a** (0.2 mmol), NaOAc (0.4 mmol), Cu(OAc)$_2$ (0.42 mmol), [Cp*RhCl$_2$] $_2$ (2 mol %), and AgSbF$_6$ (10 mol %) in EtOH (2 mL) was added ethyl acrylate (**2a**, 0.4 mmol) and H$_2$^{18}O (1 mmol) under N$_2$ atmosphere. The reaction mixture was stirred at 120 °C for 18 h. After that, the solvent was removed under reduced pressure. The residue was characterized by HRMS analysis. The ratio of the ^{18}O:^{16}O in O=PPh$_3$ was 58:42.





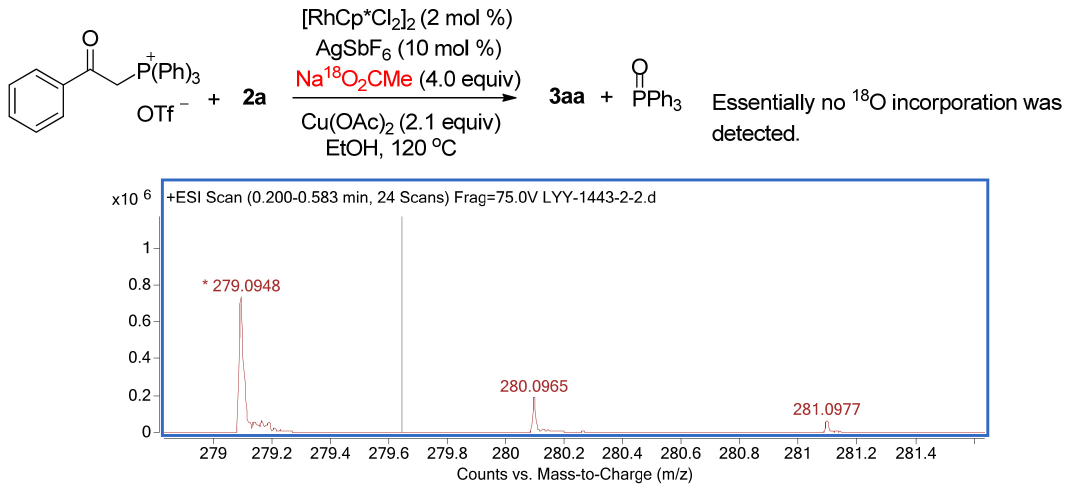
m/z	Abund	Abund %	Area	End	Start
279.0938	616386.6	56.62	7830	279.1164	278.9914
280.0967	138694.5	12.74	1539	280.1204	280.0446
281.0984	761465.5	69.94	10797	281.1232	280.9919
282.101	169991.5	15.61	1902	282.1249	282.0343
282.279	59690.4	5.48	692	282.3032	282.2447

To a mixture of **1a** (0.1 mmol), NaOAc (0.2 mmol), Cu(OAc)$_2$ (0.21 mmol), [Cp*RhCl$_2$] $_2$ (2 mol %), AgSbF$_6$ (10 mol %) in Et^{18}OH/EtOH (1:1.5, 1 mL in total) was added ethyl acrylate **2a** (0.2 mmol) under N$_2$ atmosphere. The reaction mixture was stirred at 120 °C for 18 h. The reaction mixture was characterized by HRMS analysis. The ratio of the ^{18}O:^{16}O in O=PPh$_3$ was 18:82.



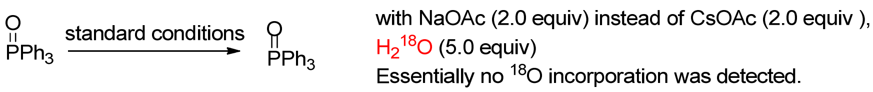
m/z	Abund	Abund %	Area	End	Start
277.1146	68399.2	9.43	779	277.1389	277.052
279.0954	725356.4	100	13515	279.1211	278.999
279.1881	51057.8	7.04	854	279.1997	279.1764
280.0973	200680.8	27.67	2327	280.1193	280.0144
281.0985	237372.1	32.72	2789	281.1221	281.0229
282.1014	45015.4	6.21	543	282.1267	281.9777
282.2794	94922	13.09	1067	282.3021	282.2407
301.076	154819	21.34	1850	301.0987	301.0172

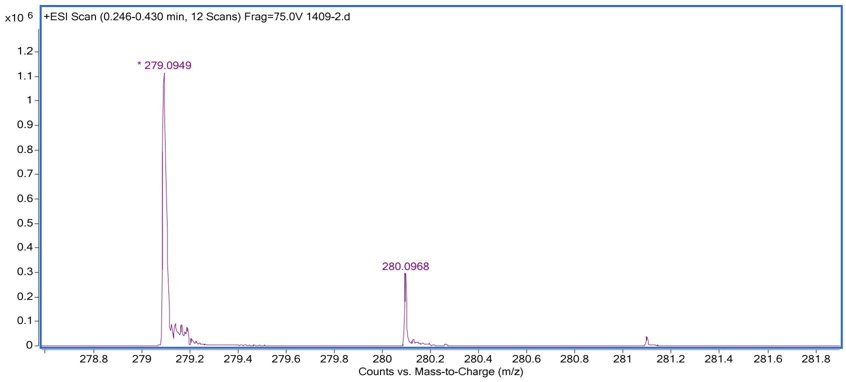
To a mixture of **1a** (0.2 mmol), $Na^{18}OAc$ (0.8 mmol), $Cu(OAc)_2$ (0.42 mmol), $[Cp^*RhCl_2]_2$ (2 mol %), $AgSbF_6$ (10 mol %) in EtOH (2 mL) was added ethyl acrylate **2a** (0.4 mmol) under N_2 atmosphere. The reaction mixture was stirred at 120 °C for 18 h. The reaction mixture was characterized by HRMS analysis. Essentially no ^{18}O was incorporated.



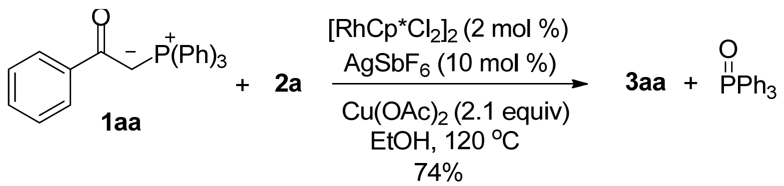
m/z	Abund	Area	End	Start
277.114	43828.7	523	277.1382	277.0831
279.0951	650907.8	12420	279.1204	278.9896
280.0969	175298.8	2140	280.1185	280.034
281.0983	62120.1	763	281.1213	281.063
282.2788	52635.4	629	282.3014	282.2283
288.1387	308379.9	3914	288.1617	288.0849
289.1415	68930.8	851	289.164	289.1078

To a mixture of O=PPh$_3$ (0.2 mmol), [Cp*RhCl$_2$]$_2$ (2 mol %), AgSbF$_6$ (10 mol %), NaOAc (0.4 mmol), Cu(OAc)$_2$ (0.42 mmol) in EtOH (2 mL) was added H$_2$^{18}O (1 mmol) at 120 °C for 18 h. The reaction mixture was characterized by HRMS analysis. No ^{18}O-labled was detected.





m/z	Abund	Abund %	Area	End	Start
146.9802	94679.3	8.25	668	146.9971	146.9507
279.0949	1120694.4	97.69	20506	279.1205	278.9926
279.1876	76357.8	6.66	1285	279.2019	279.1758
280.0968	308432.4	26.89	3474	280.1186	280.0283
301.0765	959399	83.63	16457	301.1008	300.9438
301.173	57691.1	5.03	1003	301.1854	301.1612

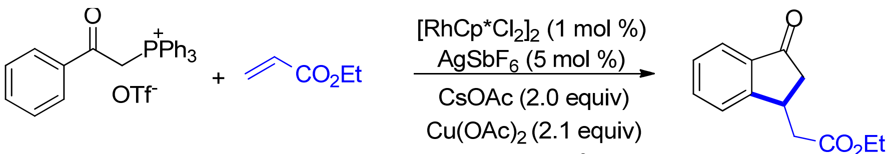


To a mixture of 1-phenyl-2-(triphenylphosphoranylidene)ethanone **1aa** (the ylidic form of **1a**, 0.2 mmol), [Cp*RhCl$_2$]$_2$ (2 mol%), AgSbF$_6$ (10 mol%), and Cu(OAc)$_2$ (0.42 mmol) in EtOH (2 mL) was added ethyl acrylate **2a** (0.4 mmol) under N$_2$ atmosphere. The reaction mixture was stirred at 120 °C for 18 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford product **3aa** in

74% yield.

V. Gram-scale Synthesis

Phenacyl phosphonium salts **1a** (5.0 mmol), $[Cp^*RhCl_2]_2$ (1 mol %), $AgSbF_6$ (5 mol %), CsOAc (2.0 equiv), and $Cu(OAc)_2$ (2.1 equiv) were charged into a pressure tube. Ethanol (40 mL) was then added to this tube. The resulting mixture was stirred for seconds under N_2 atmosphere, to which ethyl acrylate (**2a**, 2.0 equiv) was added. The mixture was stirred at 120 ^oC for 18 hours. The solvent was then removed under vacuum and the residue was purified by silica gel chromatography using PE/EA (30:1 – 10:1) to afford product **3aa** as a colorless oil (0.74 g, 68%).



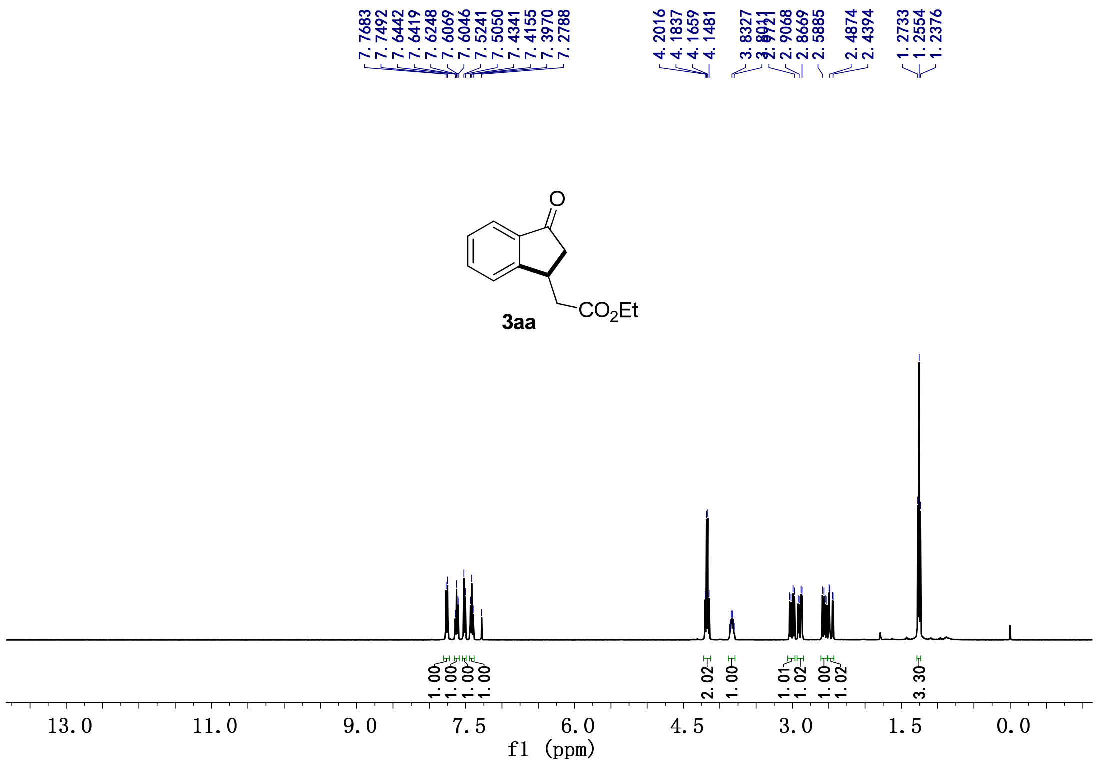
1a, 5 mmol **2a** **3aa**, 68%

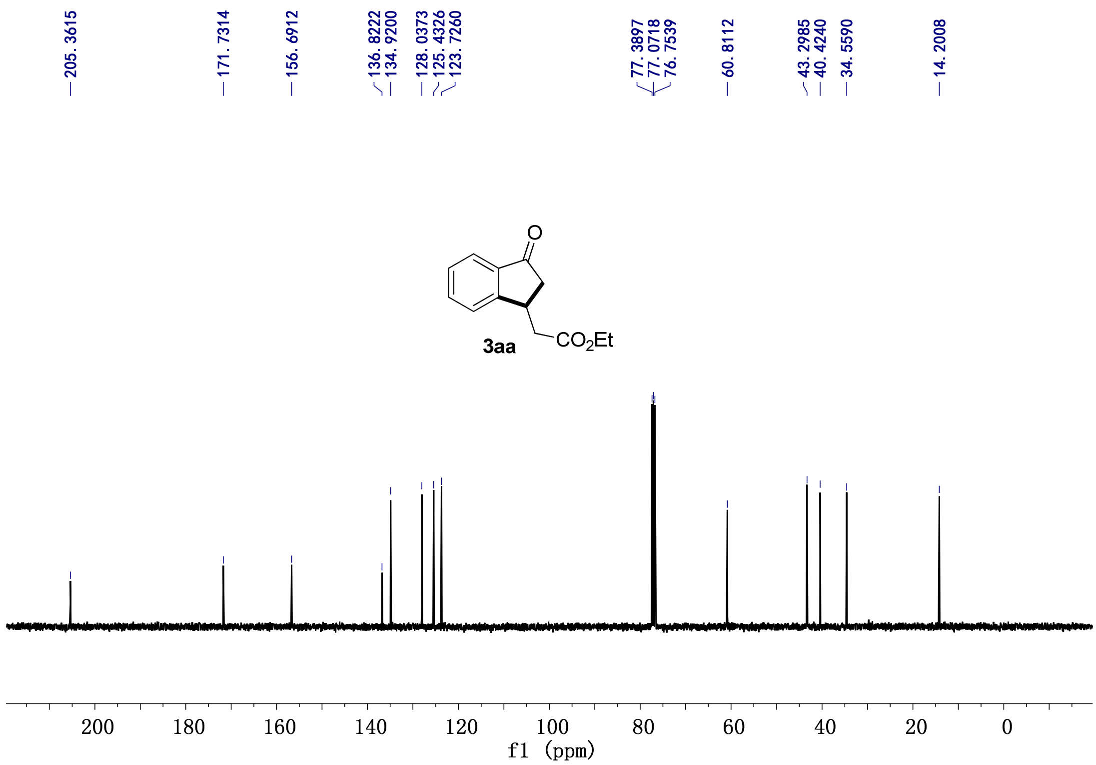
Reference

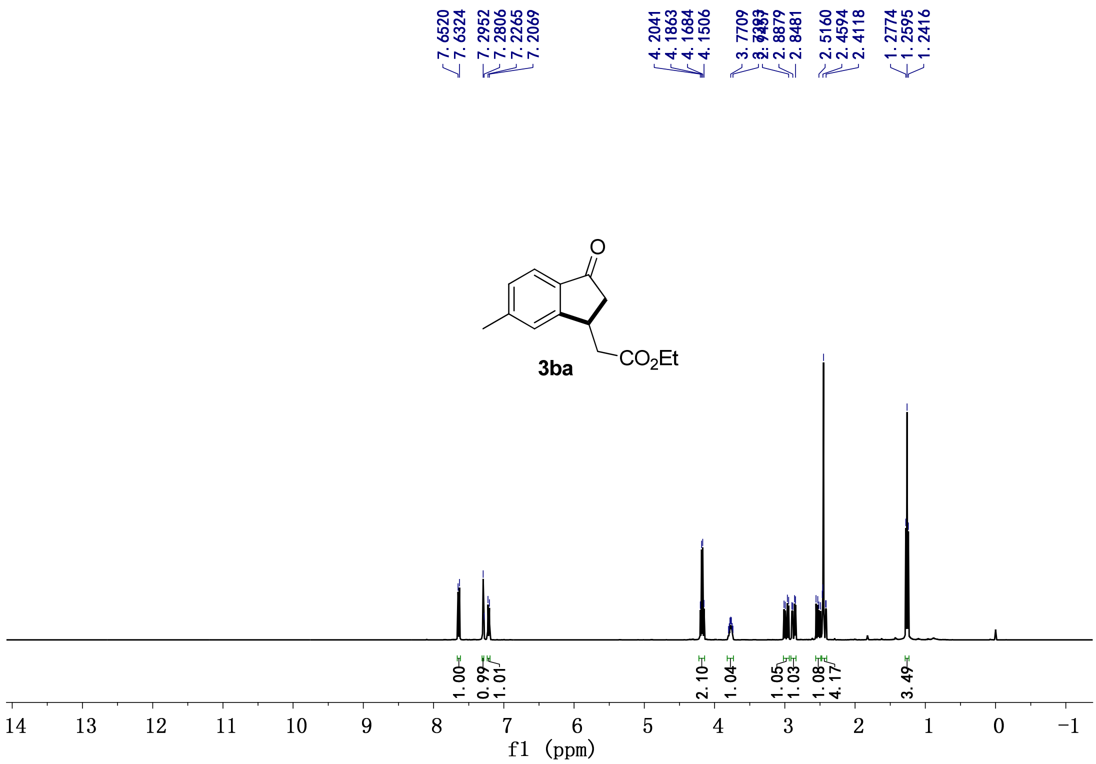
[1] (a) Nanteuil, F. D.; Loup,J.; Waser, J. *Org. Lett.* **2013**, *15*, 3738. (b) Xu, X.; Shabashov, D.; Zavalij, P. Y.; Doyle, M. P. *Org. Lett.* **2012**, *14*, 800. (c) Koduri, N. D.; Scott, H.; Hileman, B.; Cox, J. D.; Coffin, M.; Glicksberg, L.; Hussaini, S. R. *Org. Lett.* **2012**, *14*, 440.

[2] Patureau, F.W.; Besset, T.; Glorius, F. *Angew. Chem. Int. Ed.* **2011**, *50*, 1064.

VI. NMR Spectra



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2.8879
2.8481
2.5160
2.4594
2.4118
1.2774
1.2595
1.2416
3ba
CO_2Et
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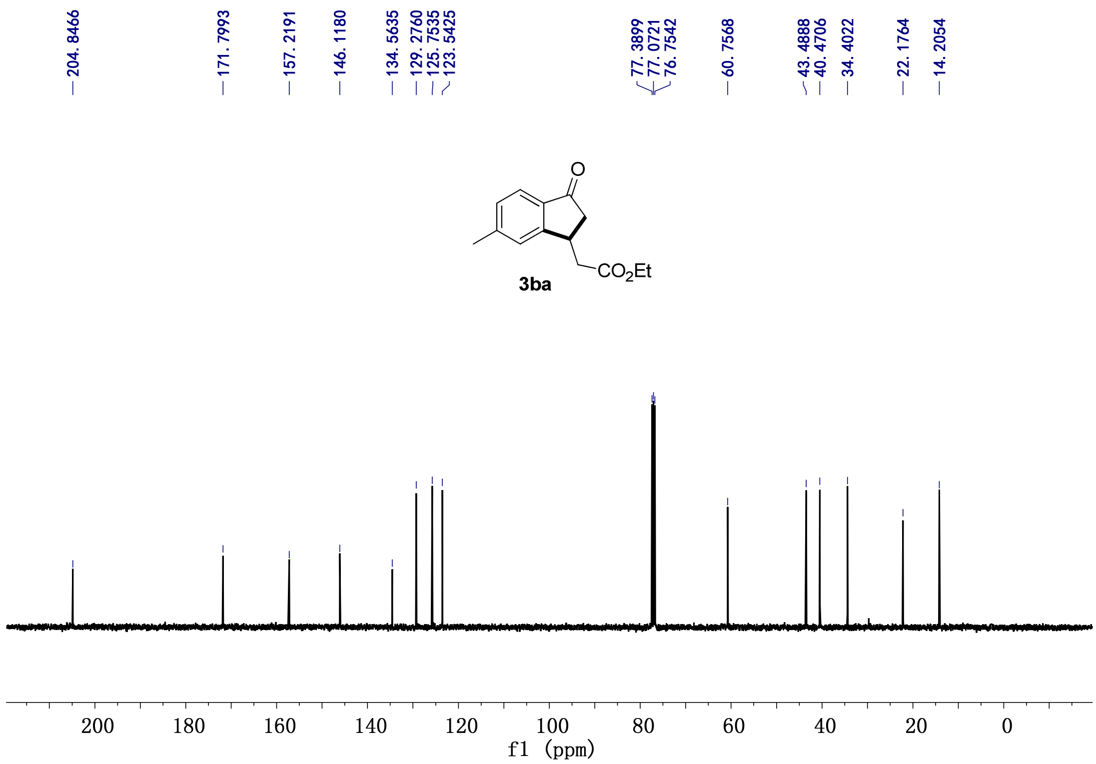
0.99
1.01
2.10
1.04
1.05
1.03
1.08
4.17
3.49
f1 (ppm)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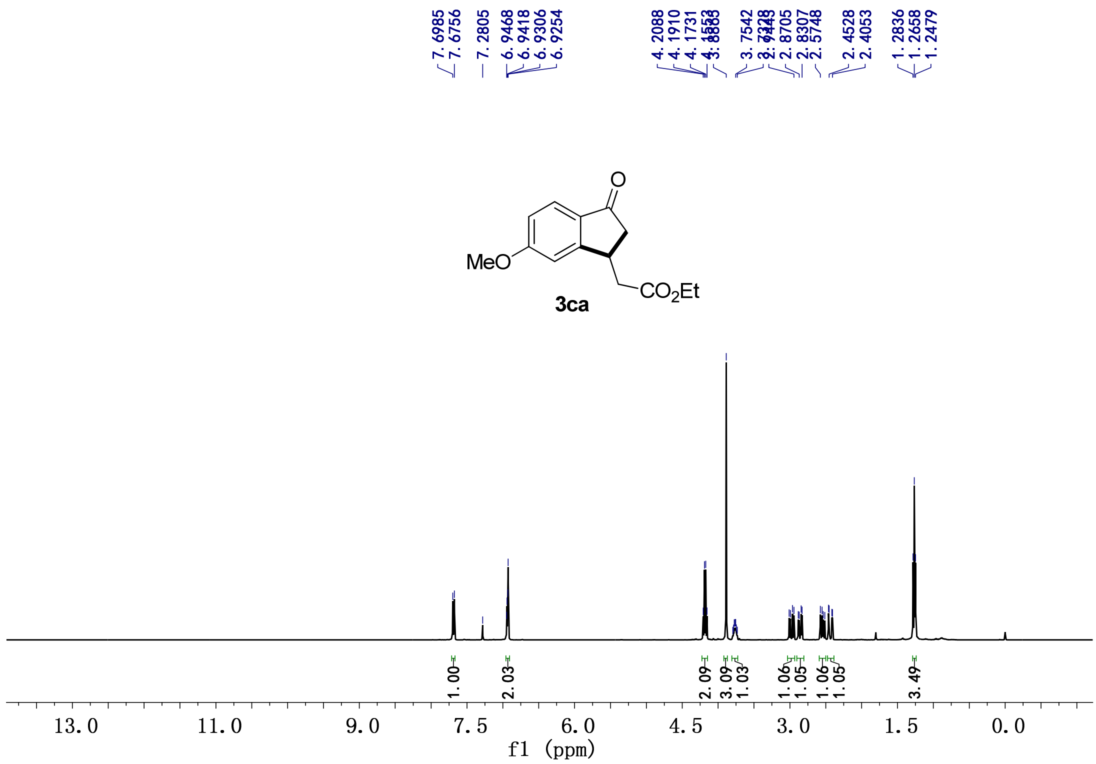
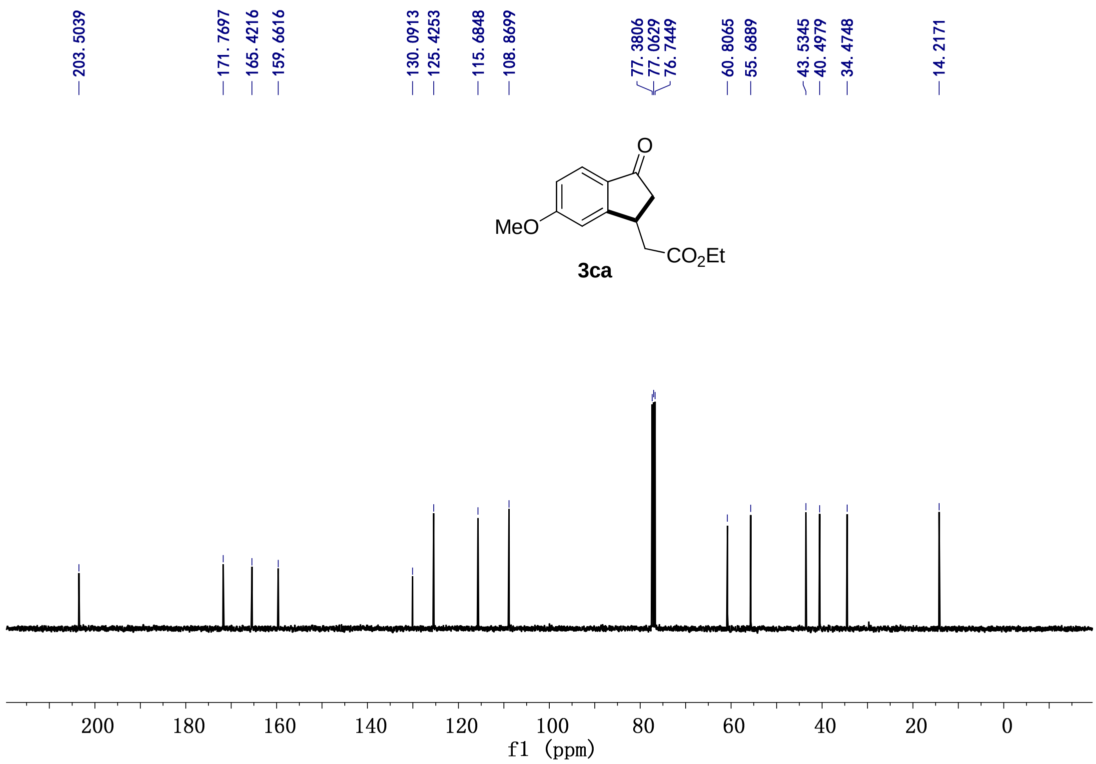
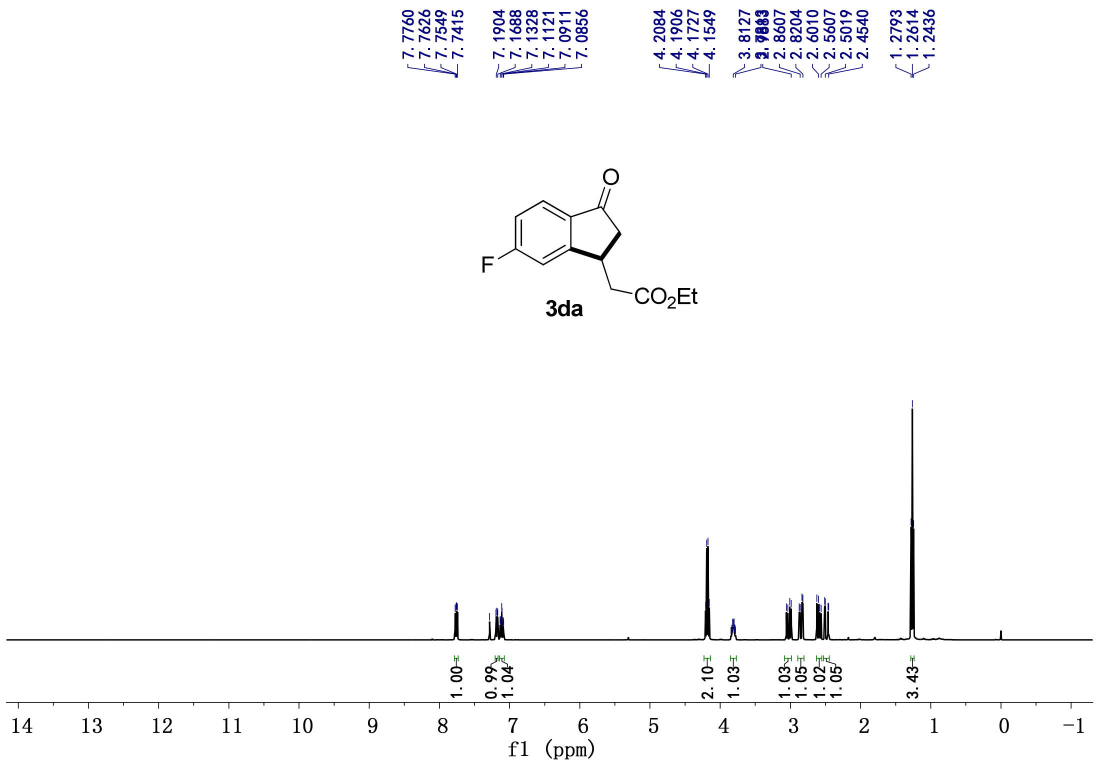
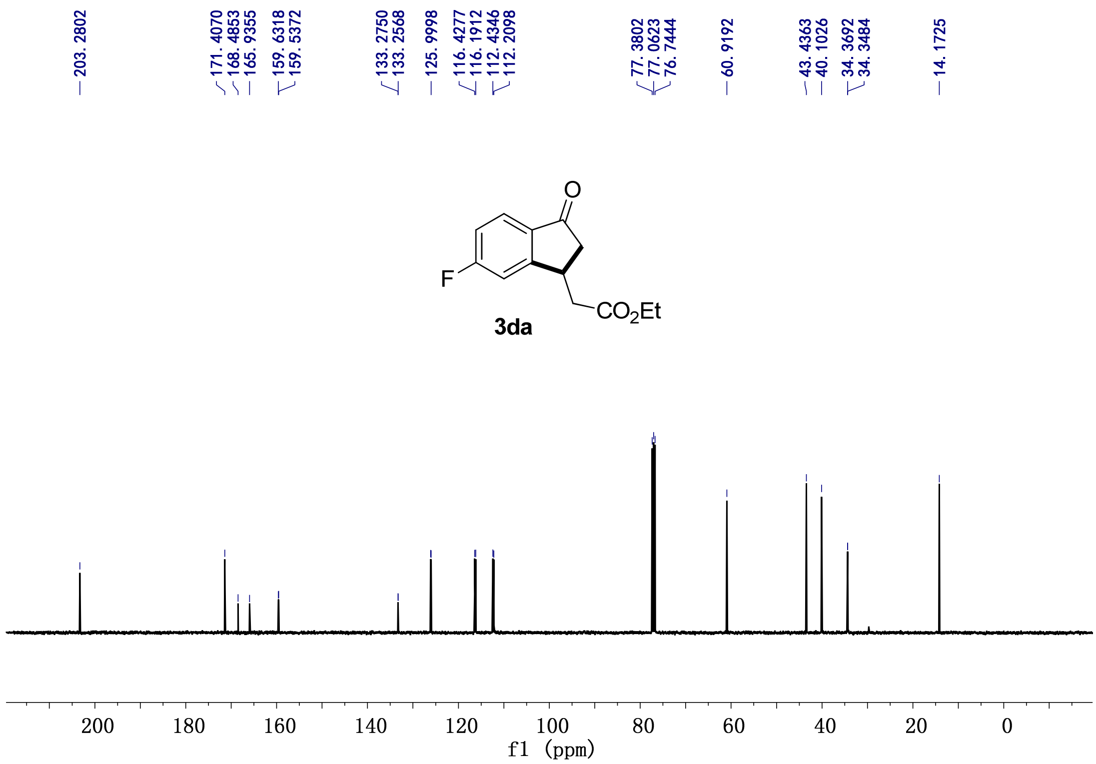
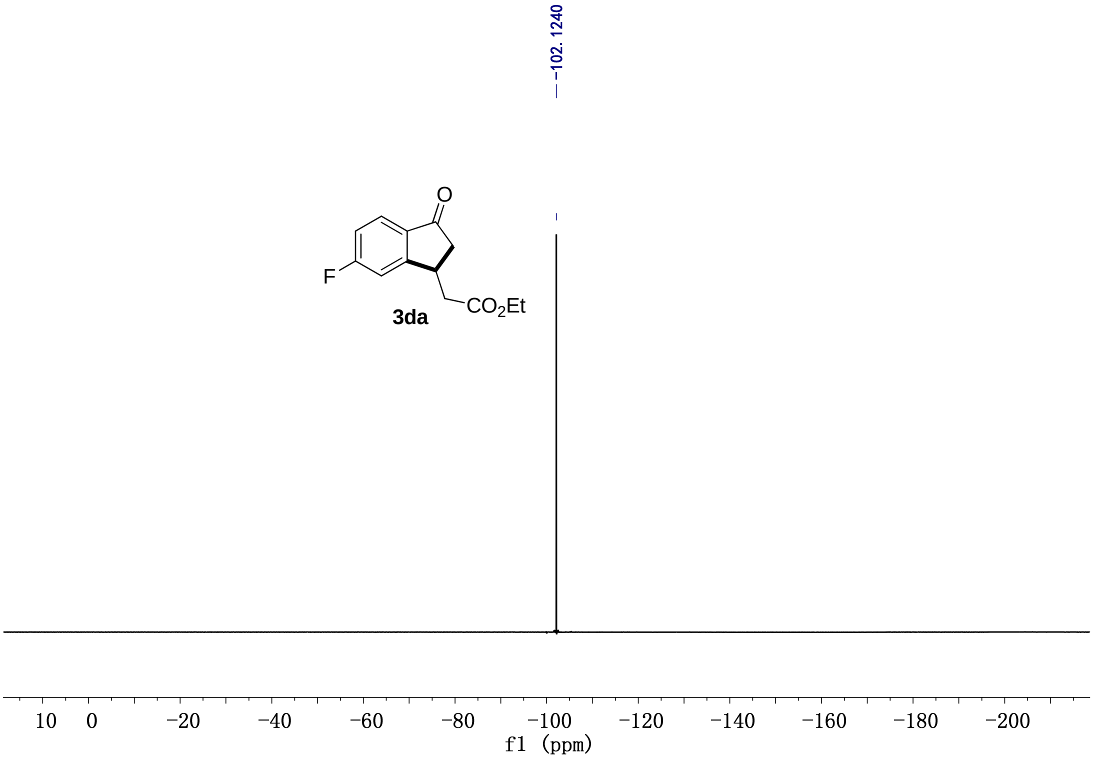
123.5425
77.3899
77.0721
76.7542
60.7568
43.4888
40.4706
34.4022
22.1764
14.2054
3ba
CO_2Et
f1 (ppm)







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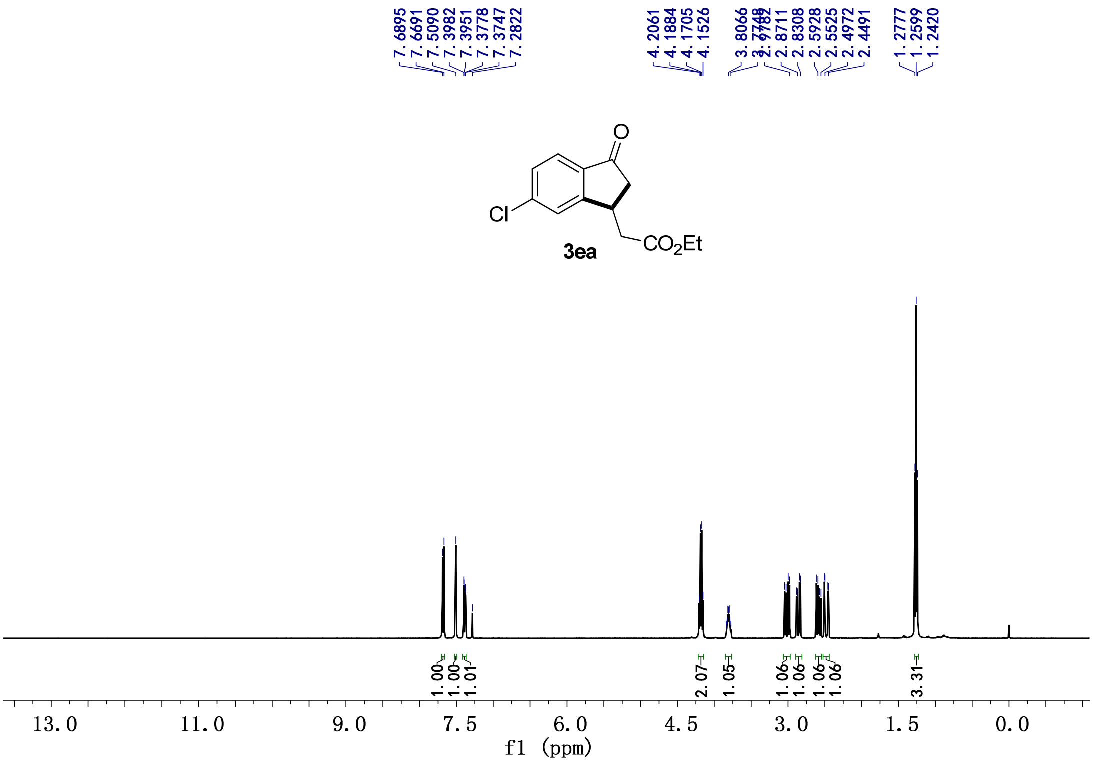
O
F
3da
CO_2Et
10 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200
f1 (ppm)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4.1705
4.1526
3.8066
2.8711
2.8308
2.5928
2.5525
2.4972
2.4491
1.2777
1.2599
1.2420
O
Cl
3ea
CO_2Et
1.00
1.00
1.01
2.07
1.05
1.06
1.06
1.06
1.06
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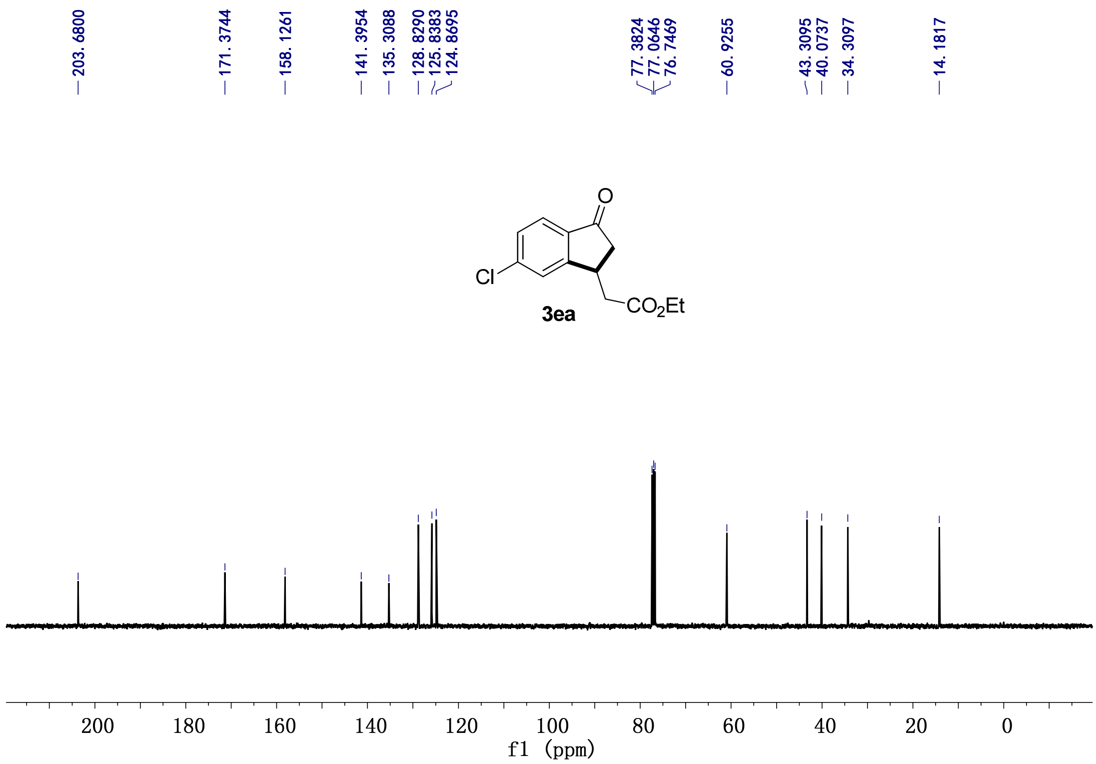
f1 (ppm)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34.3097
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60
40
20
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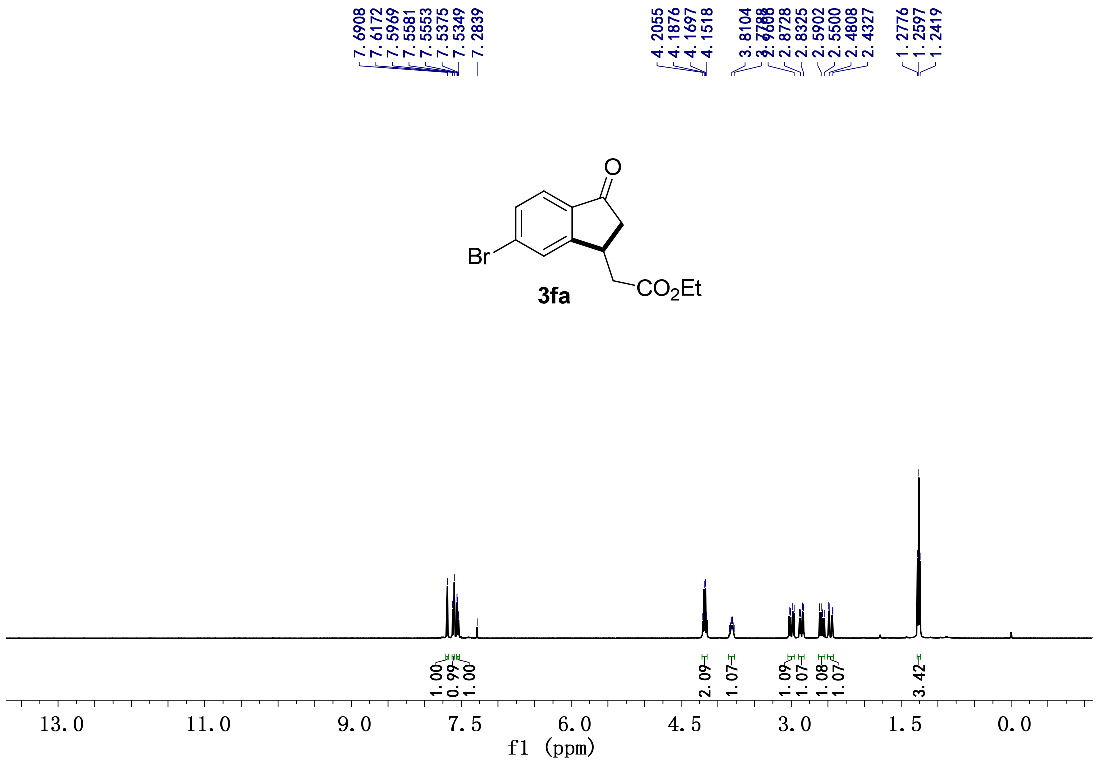
f1 (ppm)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3.8104
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2.8325
2.5902
2.5500
2.4808
2.4327
1.2776
1.2597
1.2419
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O
CO2Et
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0.97
1.00
2.09
1.07
1.09
1.07
1.08
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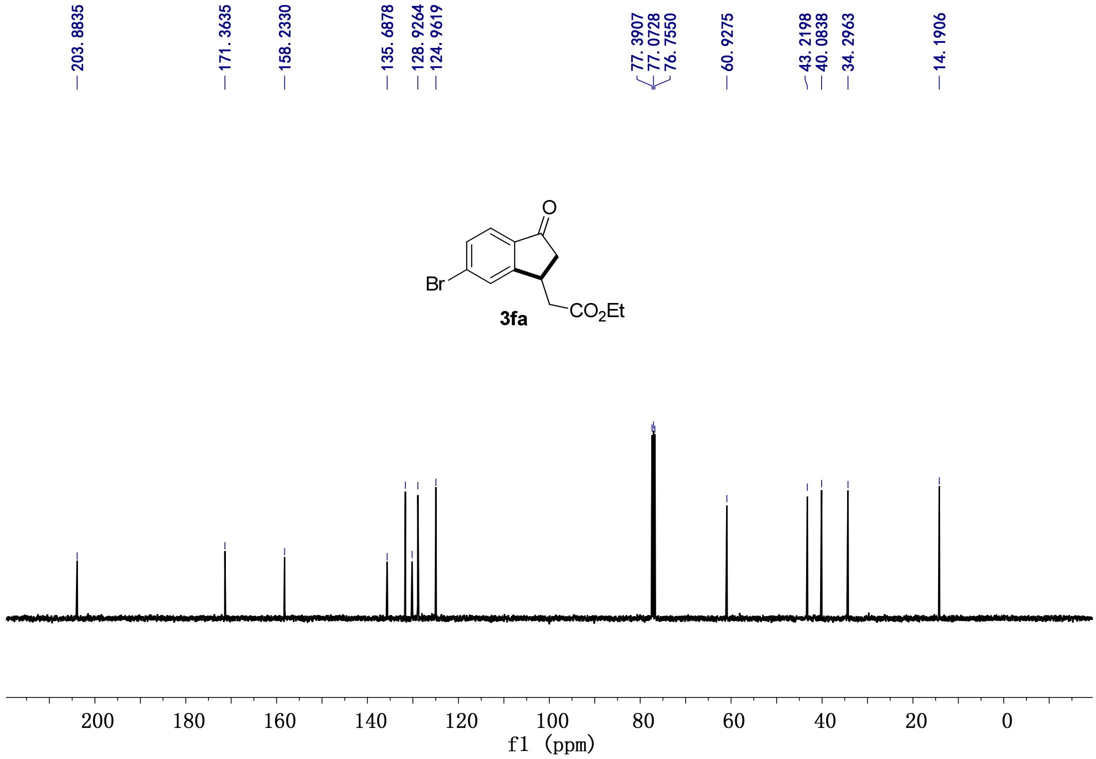
f1 (ppm)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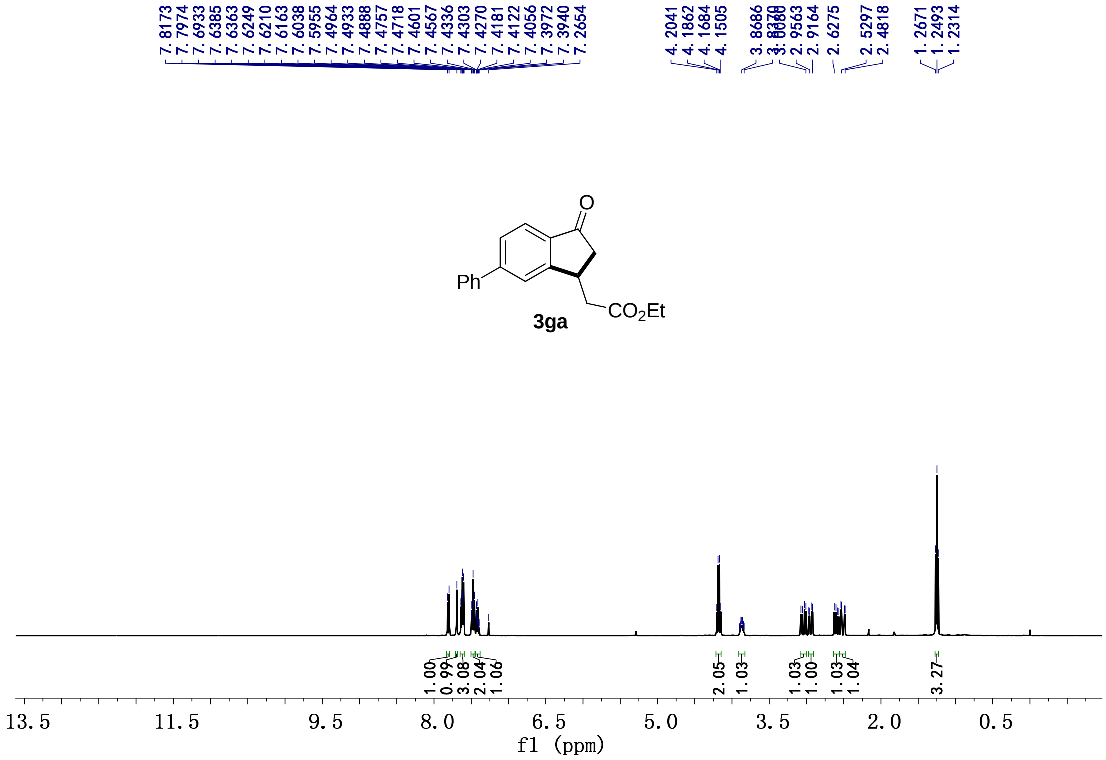
f1 (ppm)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2.05
1.03
1.03
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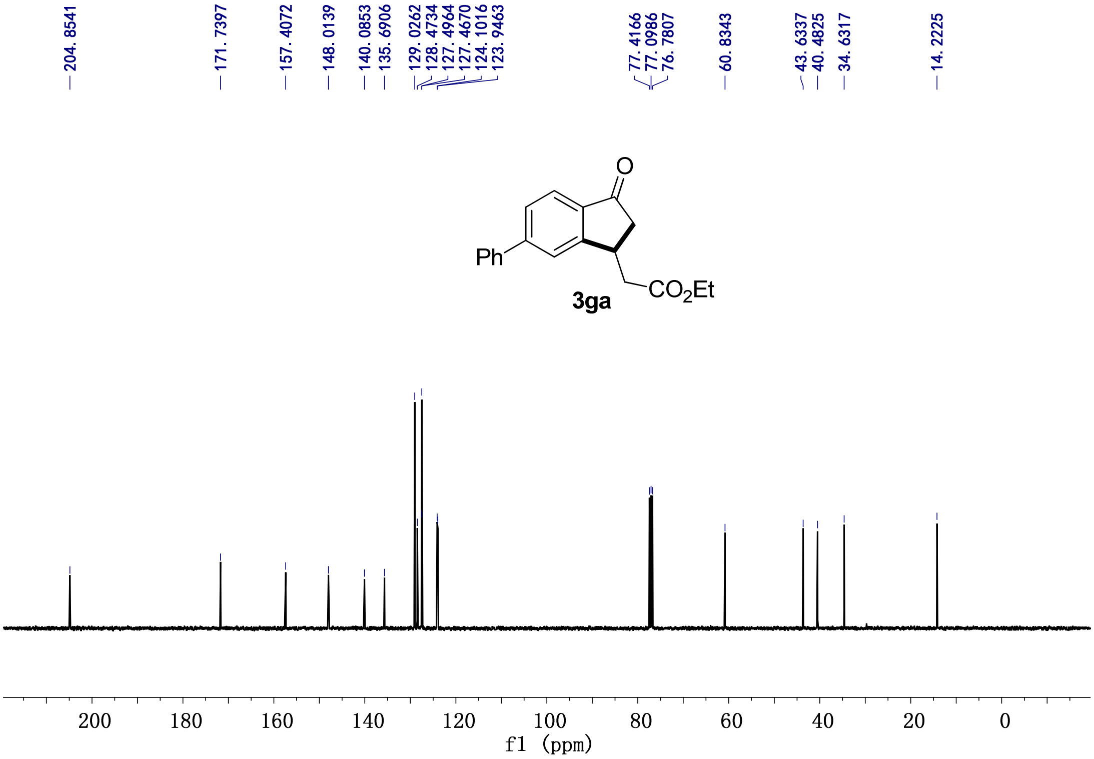
f1 (ppm)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123.9463
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77.0986
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Ph
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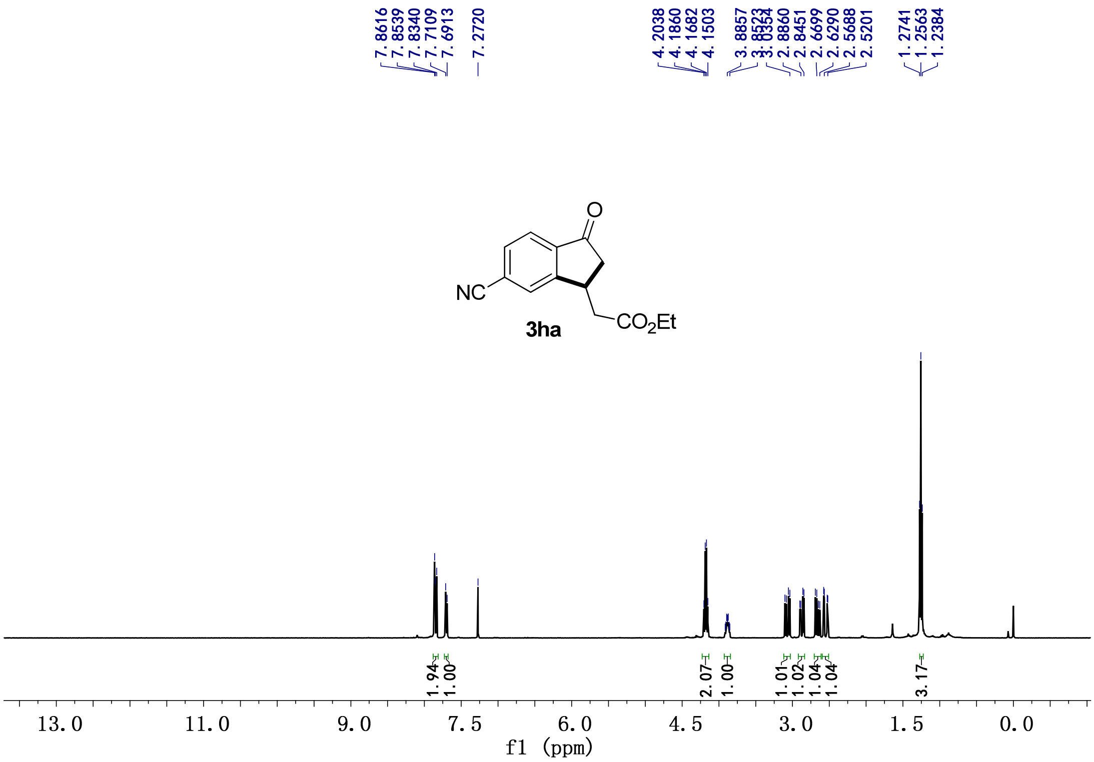
CO_2Et
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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1.00
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1.04
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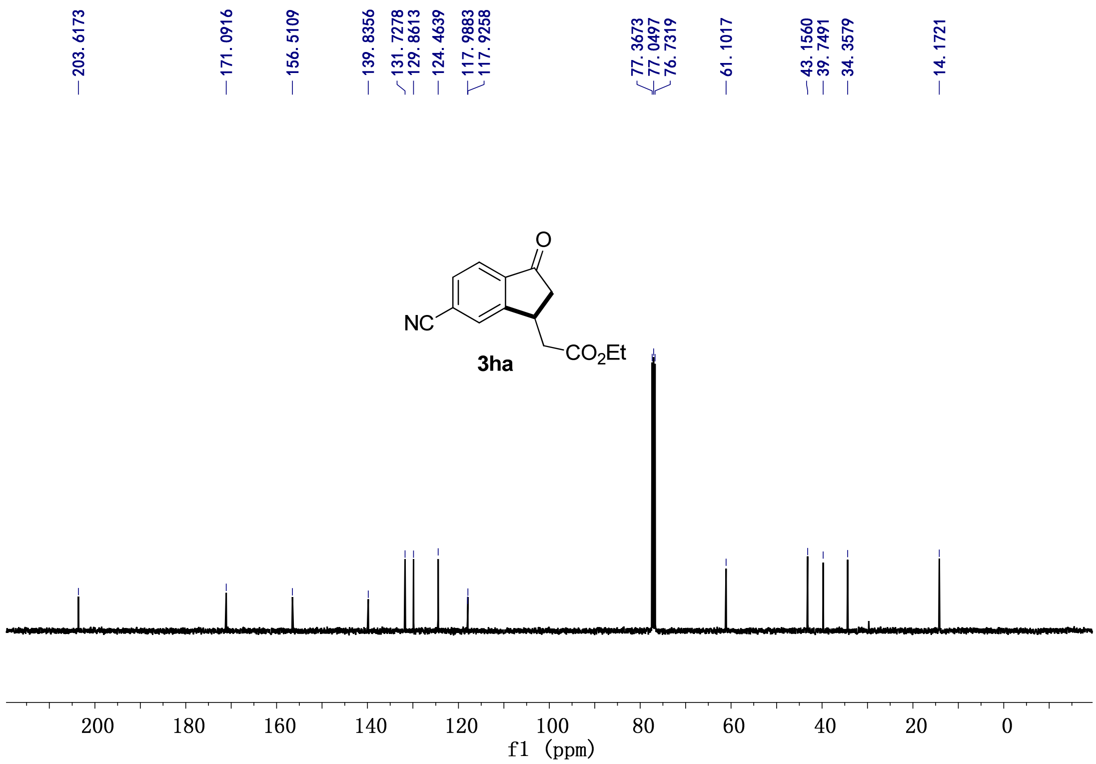
f1 (ppm)



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76.7319
61.1017
43.1560
39.7491
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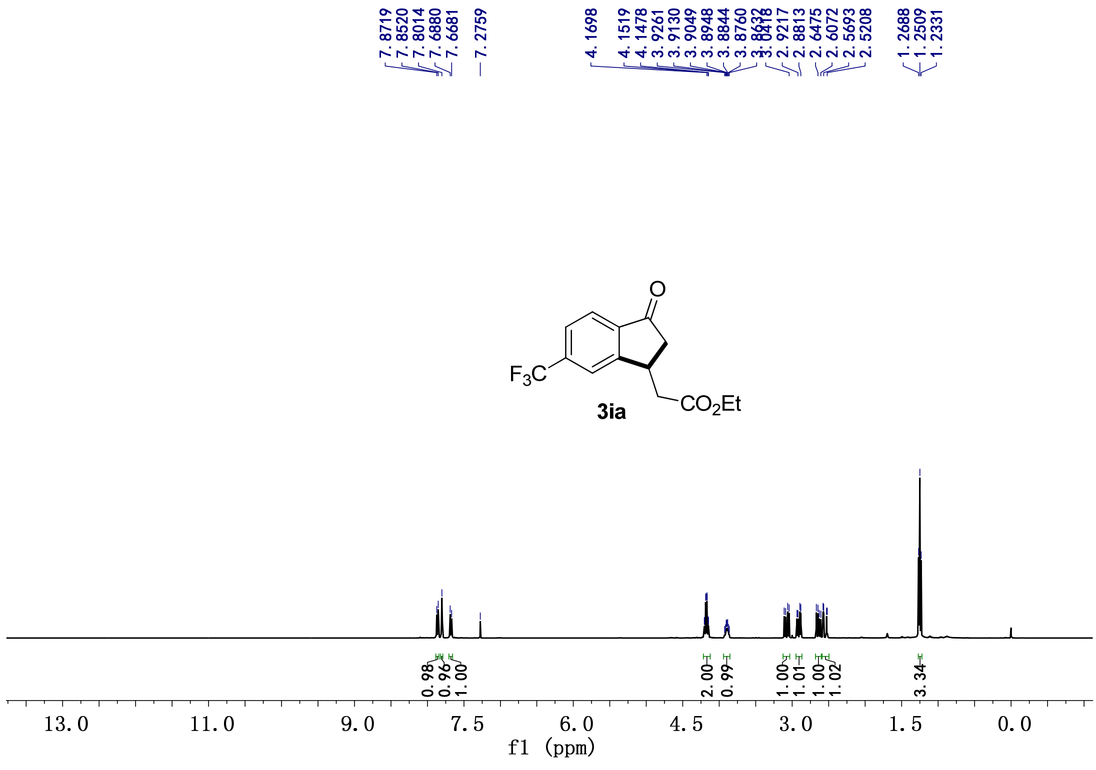

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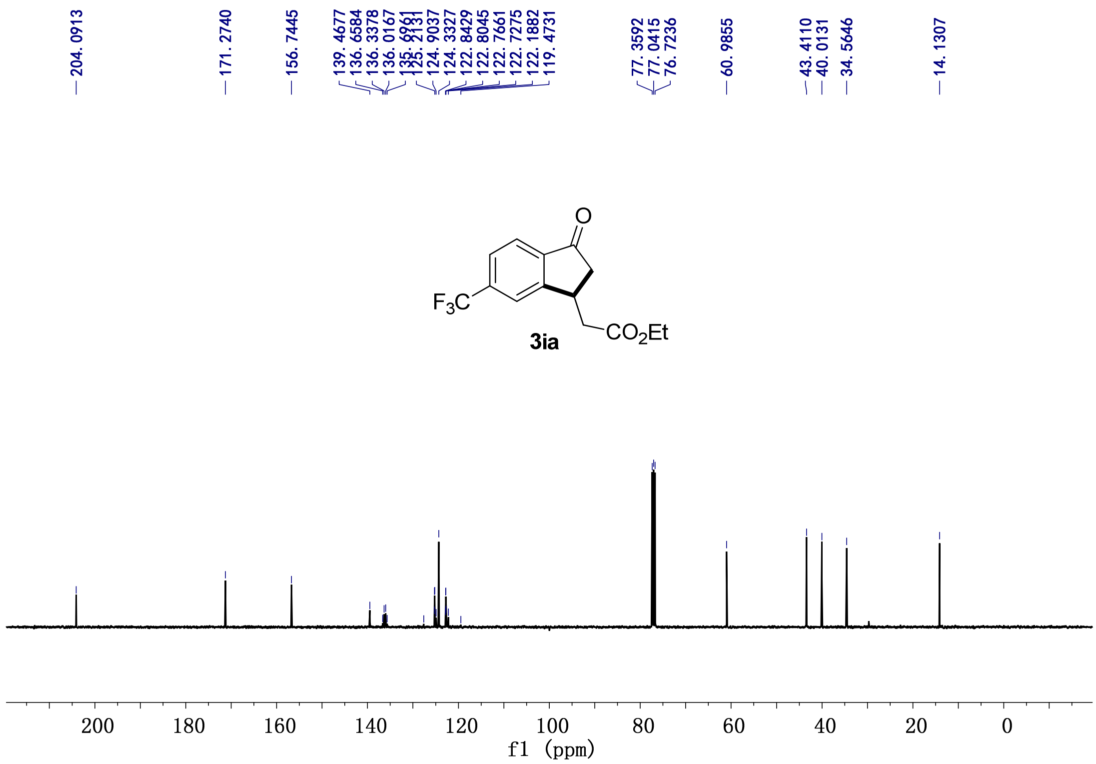
f1 (ppm)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CO2Et
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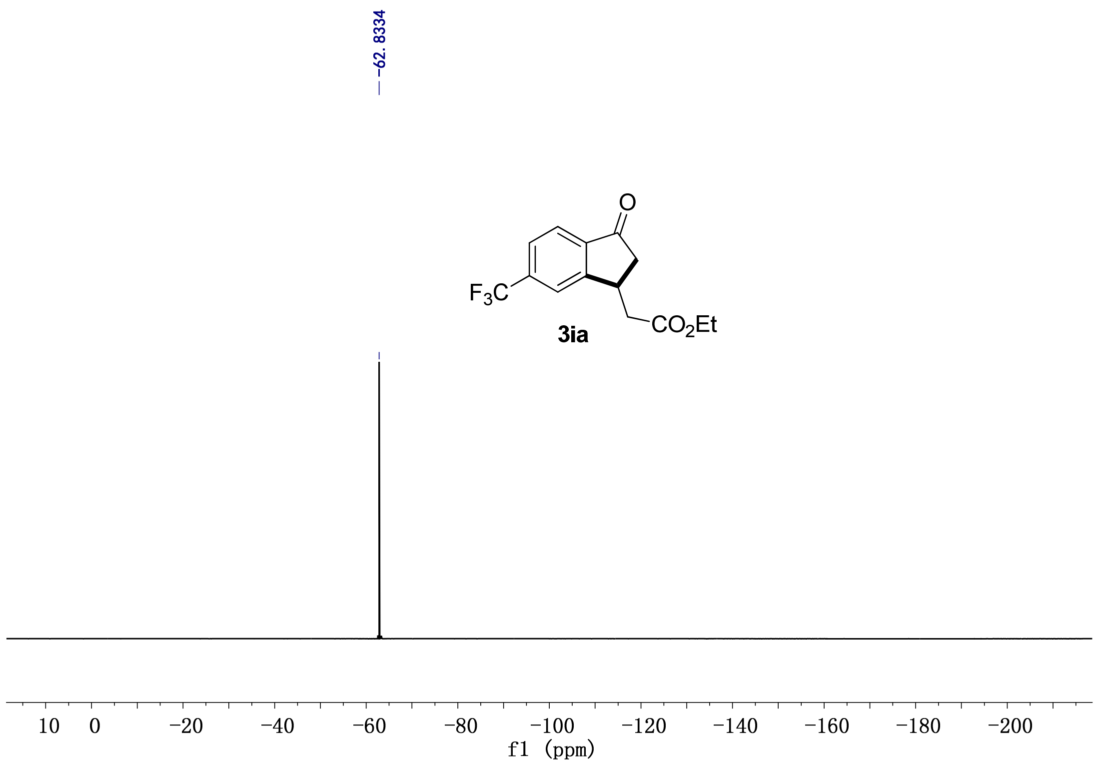
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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CO2Et
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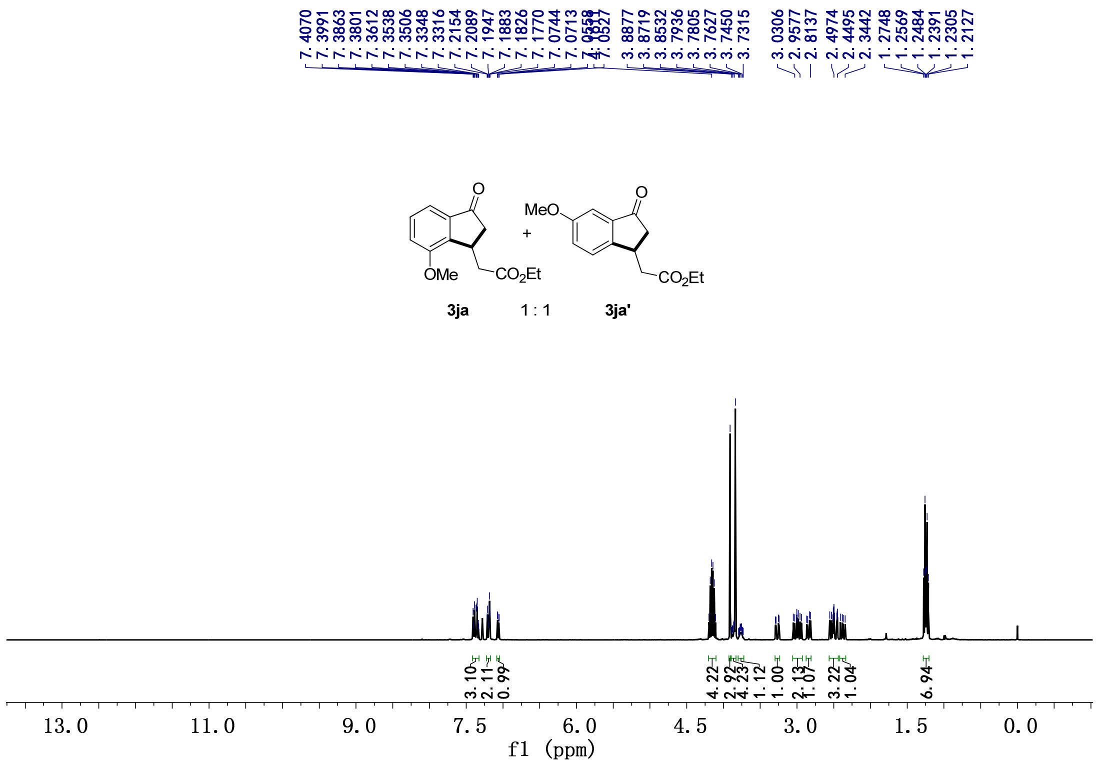
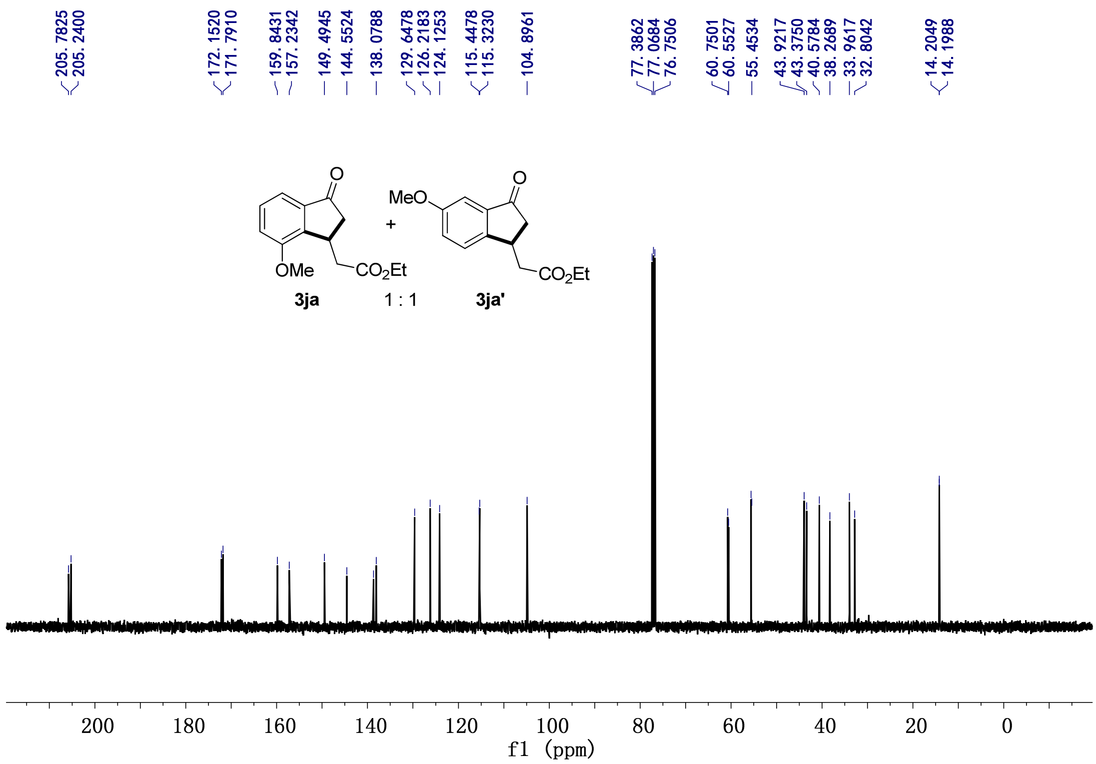
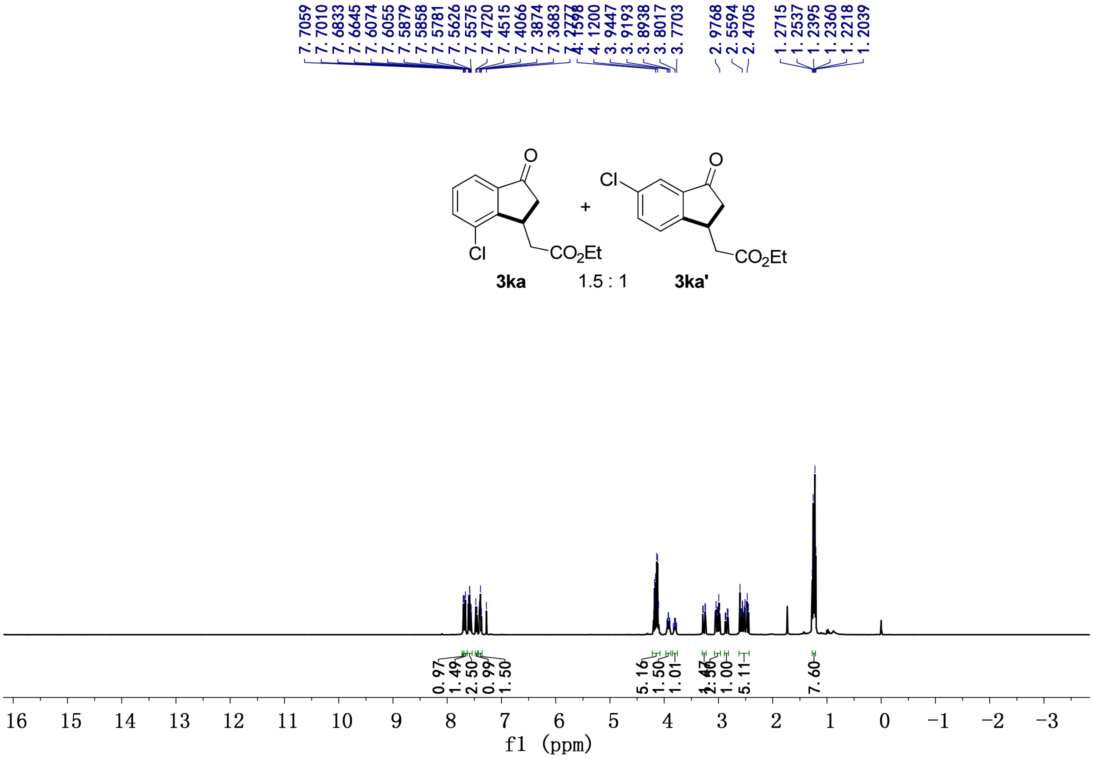
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)



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7.5879
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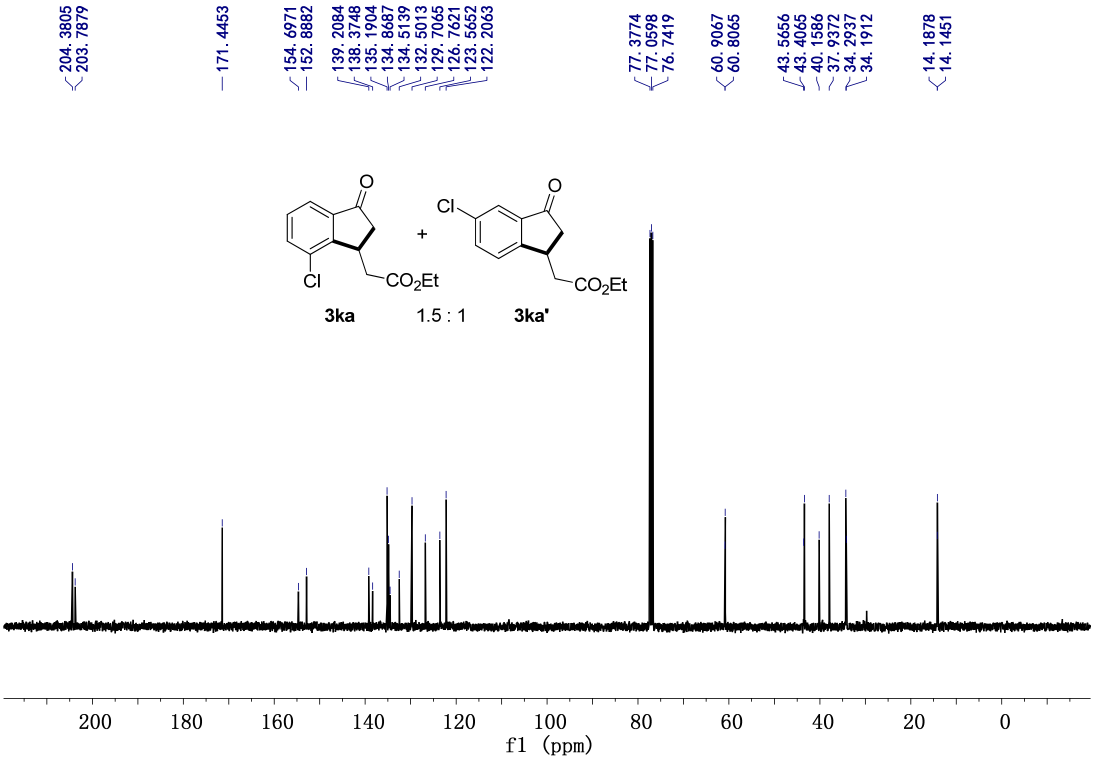
7.5781
7.5626
7.5575
7.4720
7.4515
7.4066
7.3874
7.3683
4.1200
3.9447
3.9193
3.8938
3.8017
3.7703
2.9768
2.5594
2.4705
1.2715
1.2537
1.2395
1.2360
1.2218
1.2039
Cl
CO2Et
3ka
1.5 : 1
3ka'
0.97
1.49
2.50
0.99
1.50
5.16
1.50
1.01
1.00
5.11
7.60
f1 (ppm)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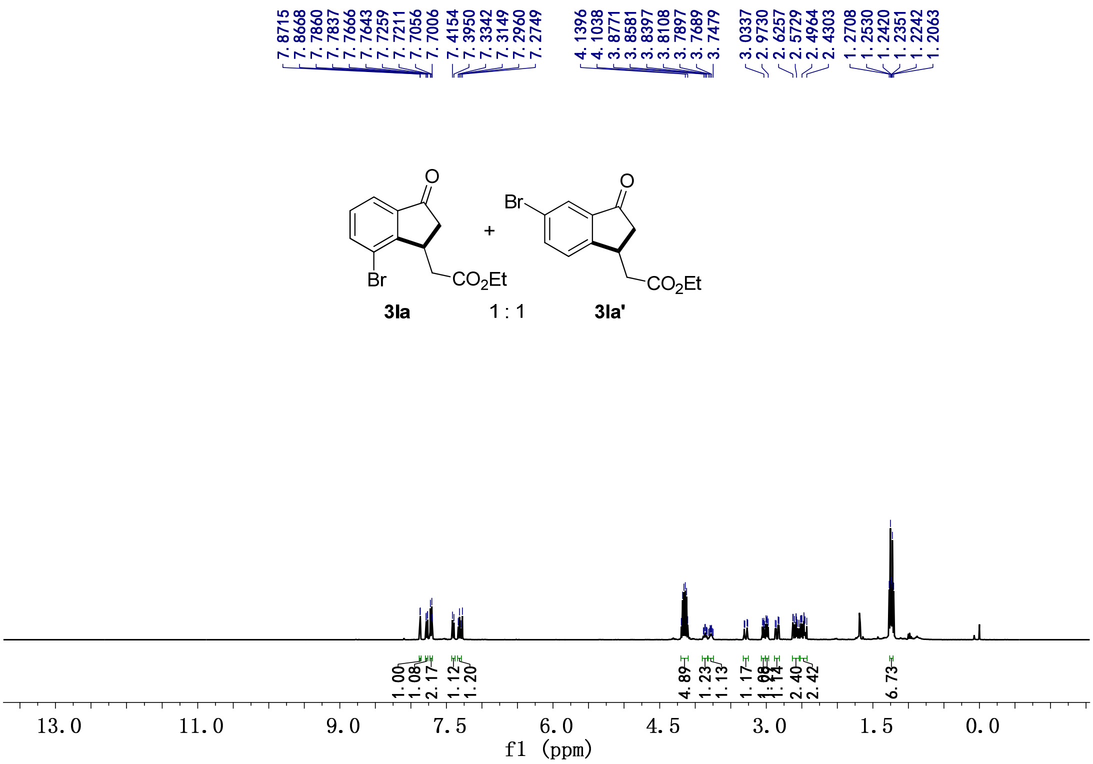
129.7065
126.7621
123.5652
122.2063
77.3774
77.0598
76.7419
60.9067
60.8065
43.5656
43.4065
40.1586
37.9372
34.2937
34.1912
14.1878
14.1451
Cl
CO2Et
3ka
1.5 : 1
3ka'
f1 (ppm)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7.4154
7.3950
7.3342
7.3149
7.2960
7.2749
4.1396
4.1038
3.8771
3.8581
3.8397
3.8108
3.7897
3.7689
3.7479
3.0337
2.9730
2.6257
2.5729
2.4964
2.4303
1.2708
1.2530
1.2420
1.2351
1.2242
1.2063
O
Br
+
Br
O
CO2Et
CO2Et
3la
1 : 1
3la'
1.00
1.08
2.17
1.12
1.20
4.89
1.23
1.13
1.17
1.08
1.14
2.40
2.42
6.73
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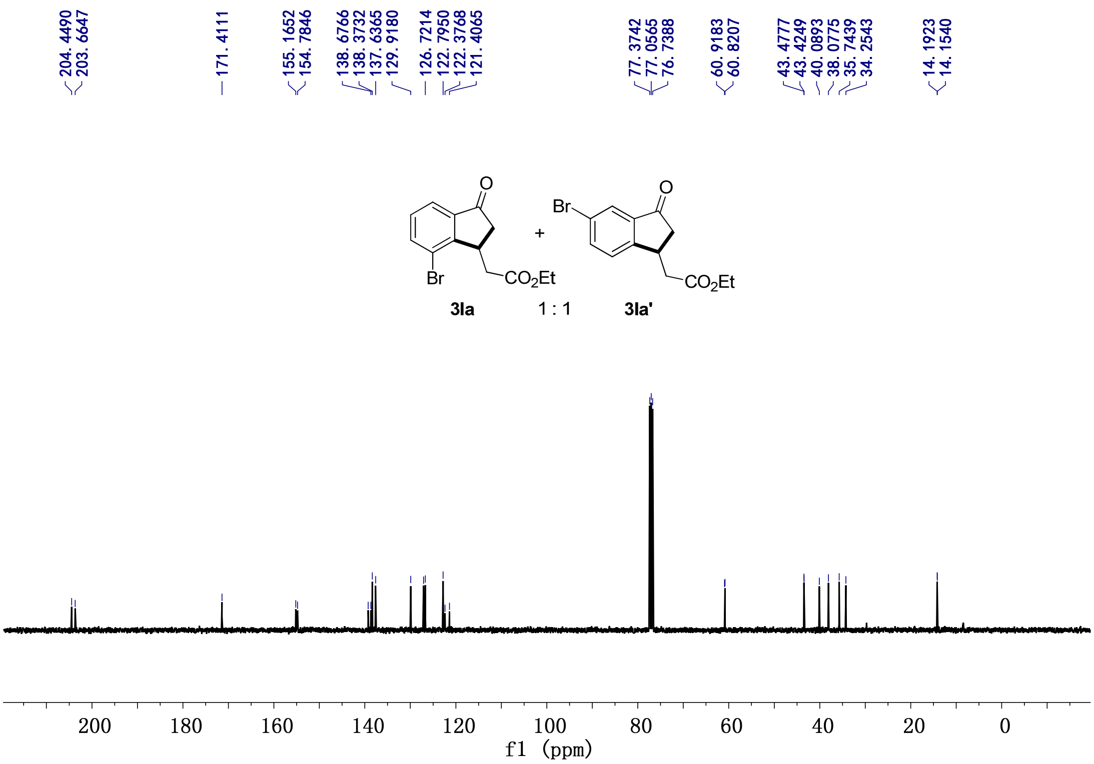
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)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121.4065
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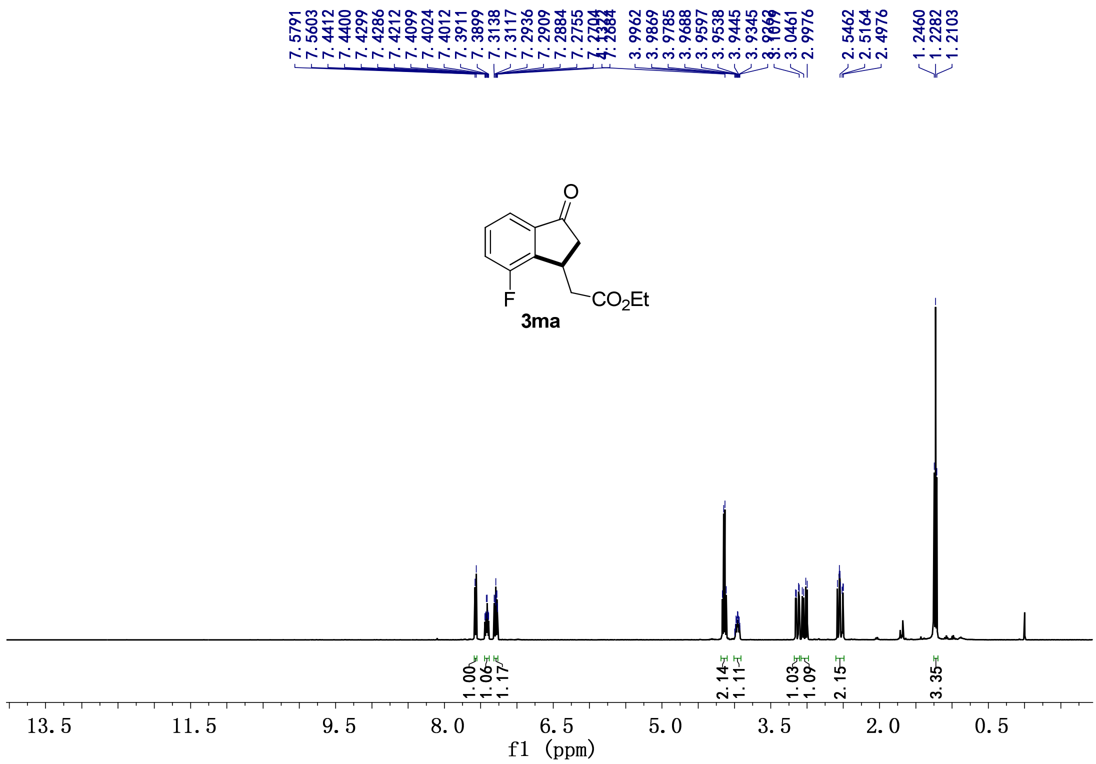
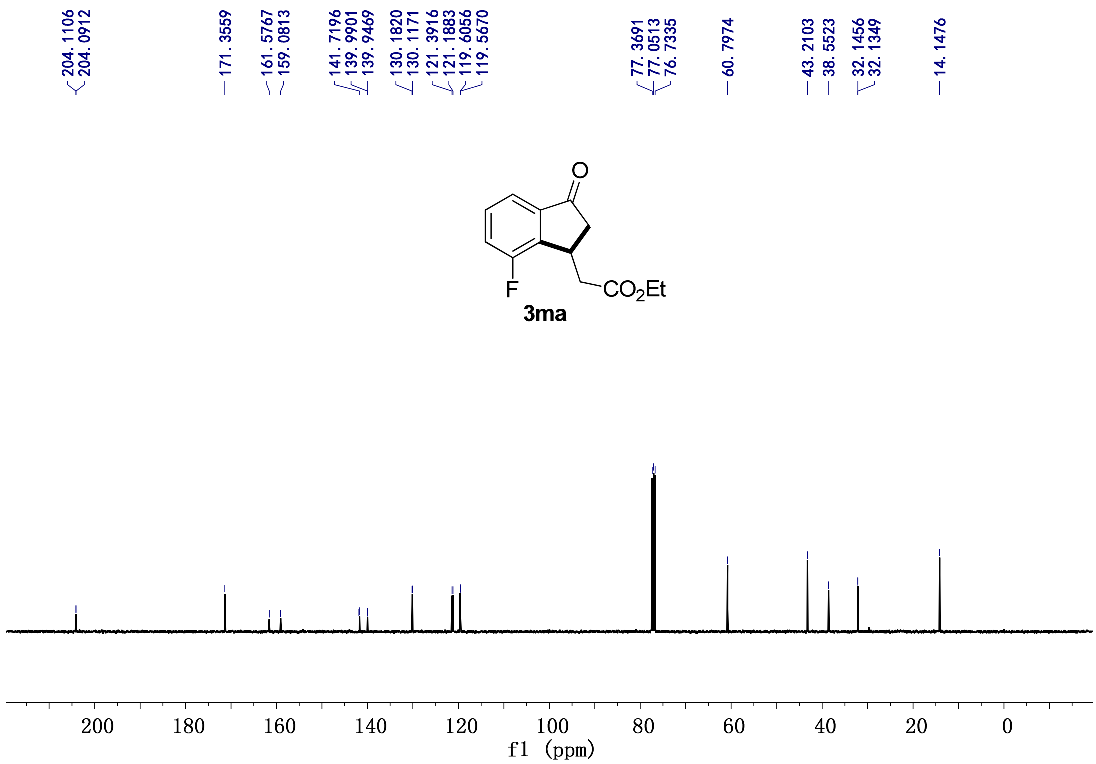
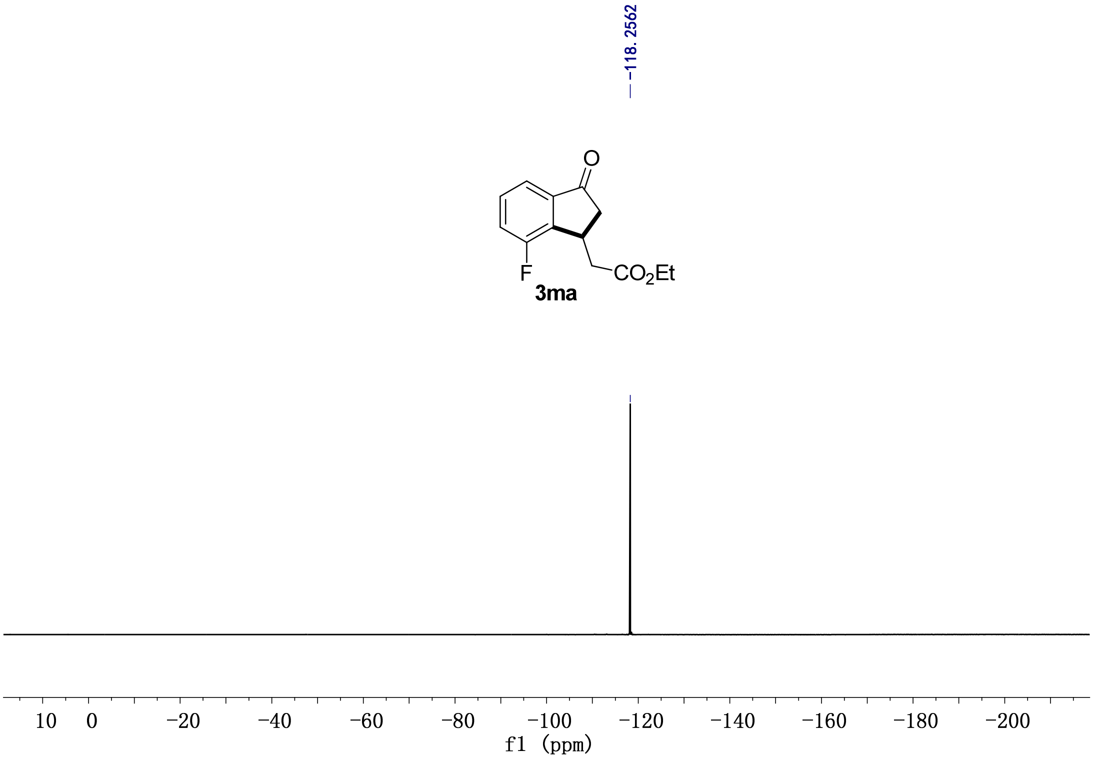
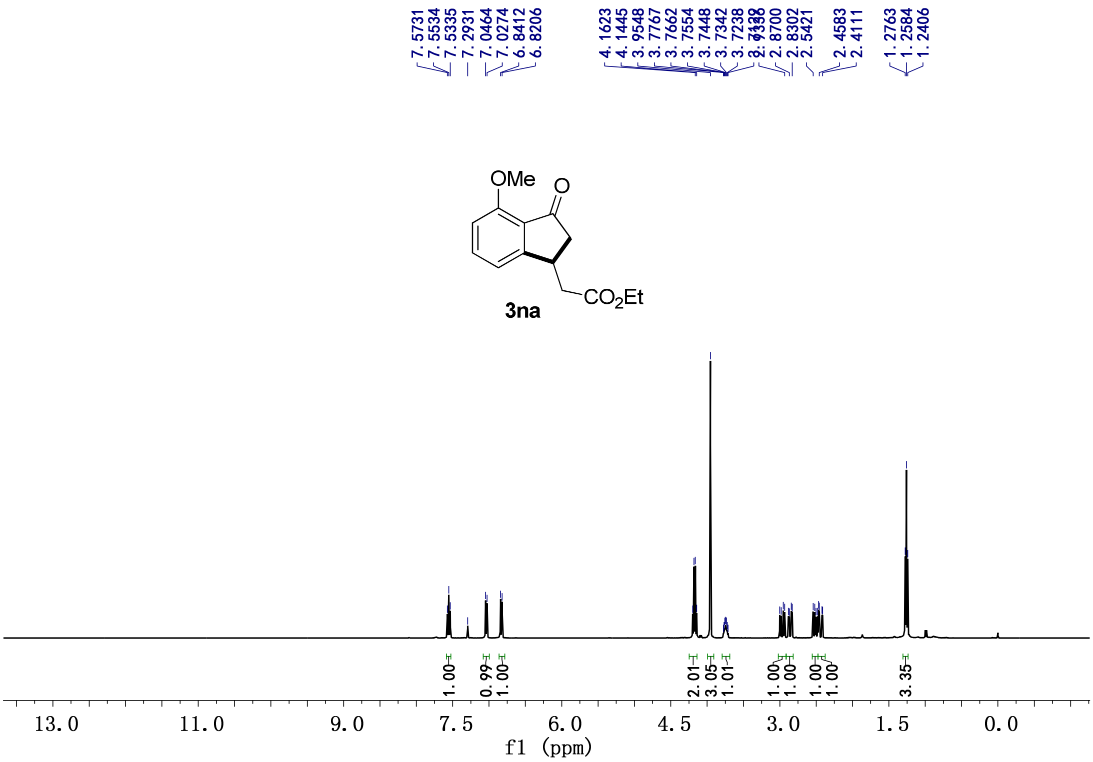
76.7388
60.9183
60.8207
43.4777
43.4249
40.0893
38.0775
35.7439
34.2543
14.1923
14.1540
O
Br
+
Br
O
CO2Et
CO2Et
3la
1 : 1
3la'
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)







−118.2562
O
F
CO2Et
3ma
10 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200
f1 (ppm)



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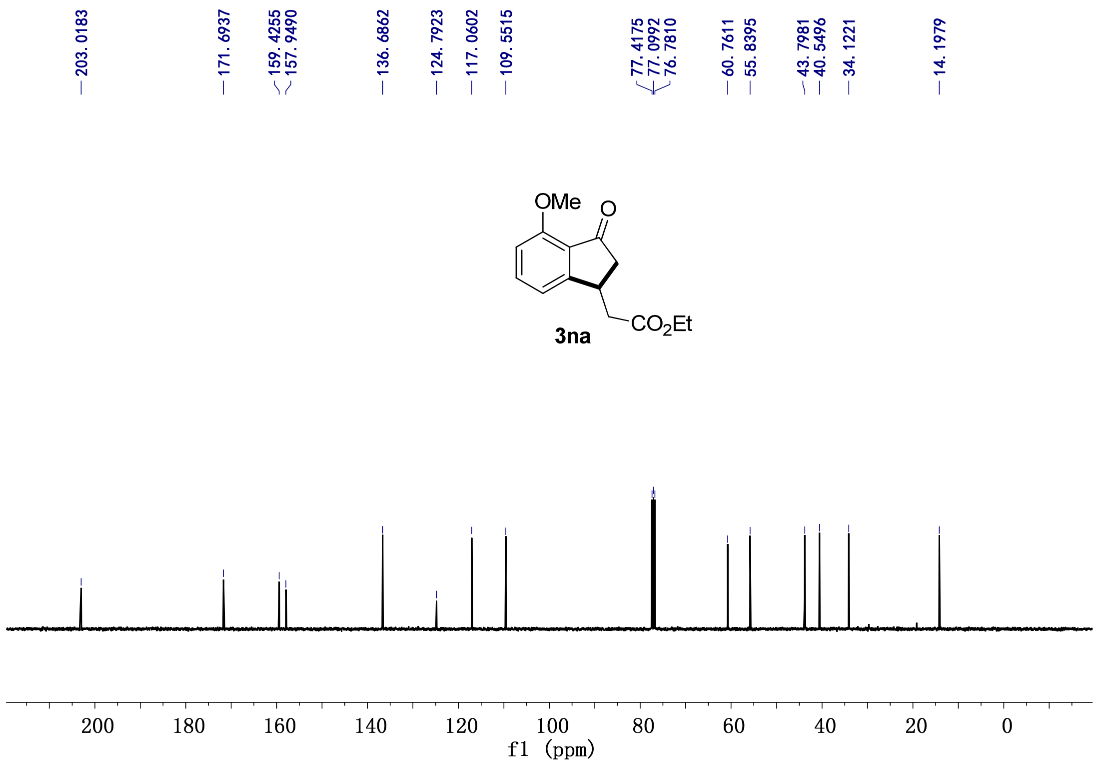
7.5335
7.2931
7.0464
7.0274
6.8412
6.8206
4.1623
4.1445
3.9548
3.7767
3.7662
3.7554
3.7448
3.7342
3.7238
2.8700
2.8302
2.5421
2.4583
2.4111
1.2763
1.2584
1.2406
OMe
O
CO2Et
3na
1.00
0.99
1.00
2.01
3.05
1.01
1.00
1.00
1.00
1.00
3.35
13.0 11.0 9.0 7.5 6.0 4.5 3.0 1.5 0.0
f1 (ppm)



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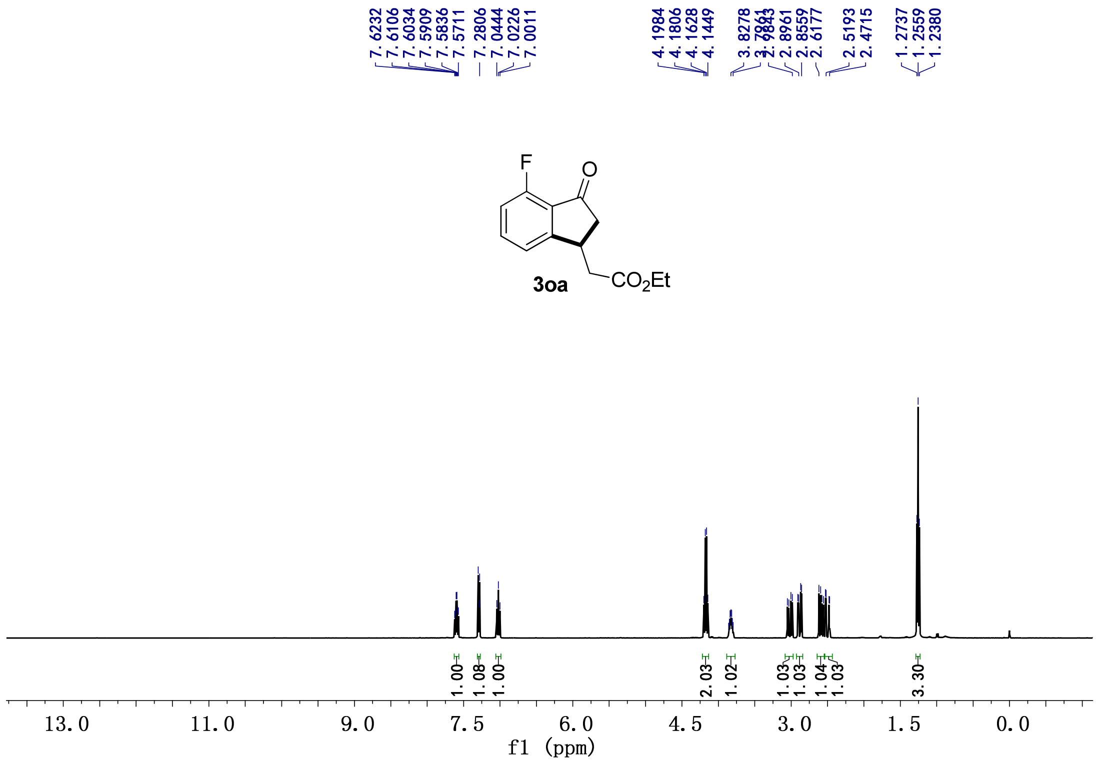

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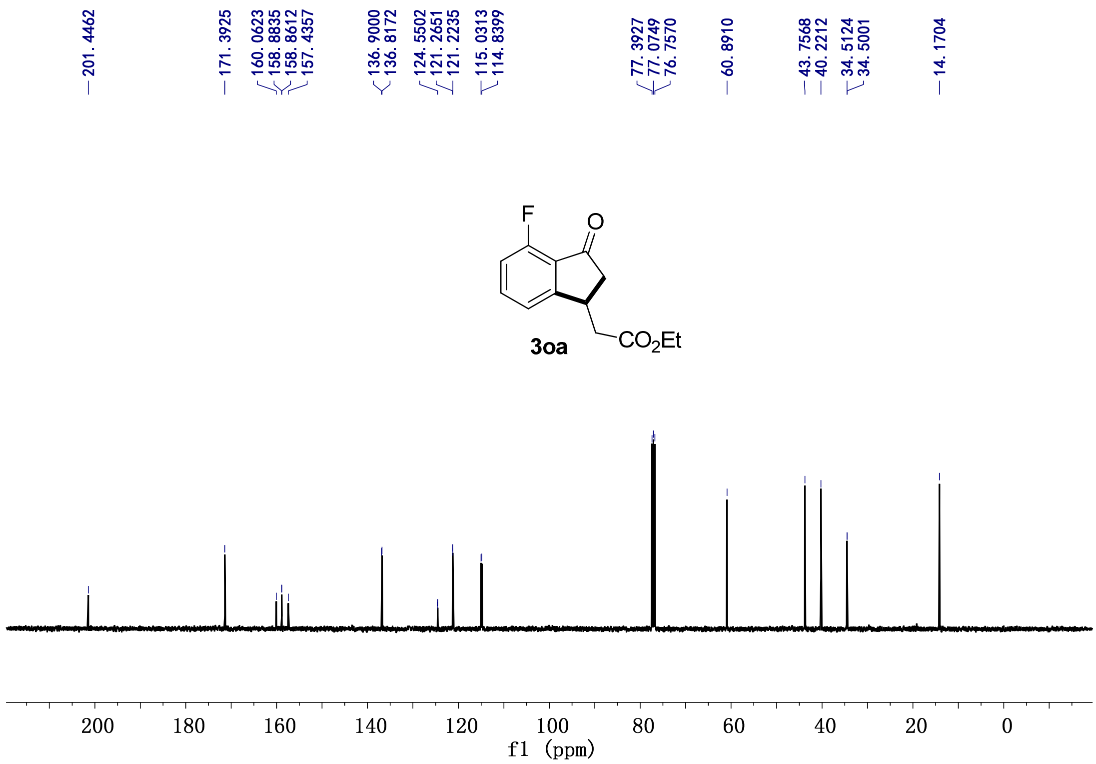
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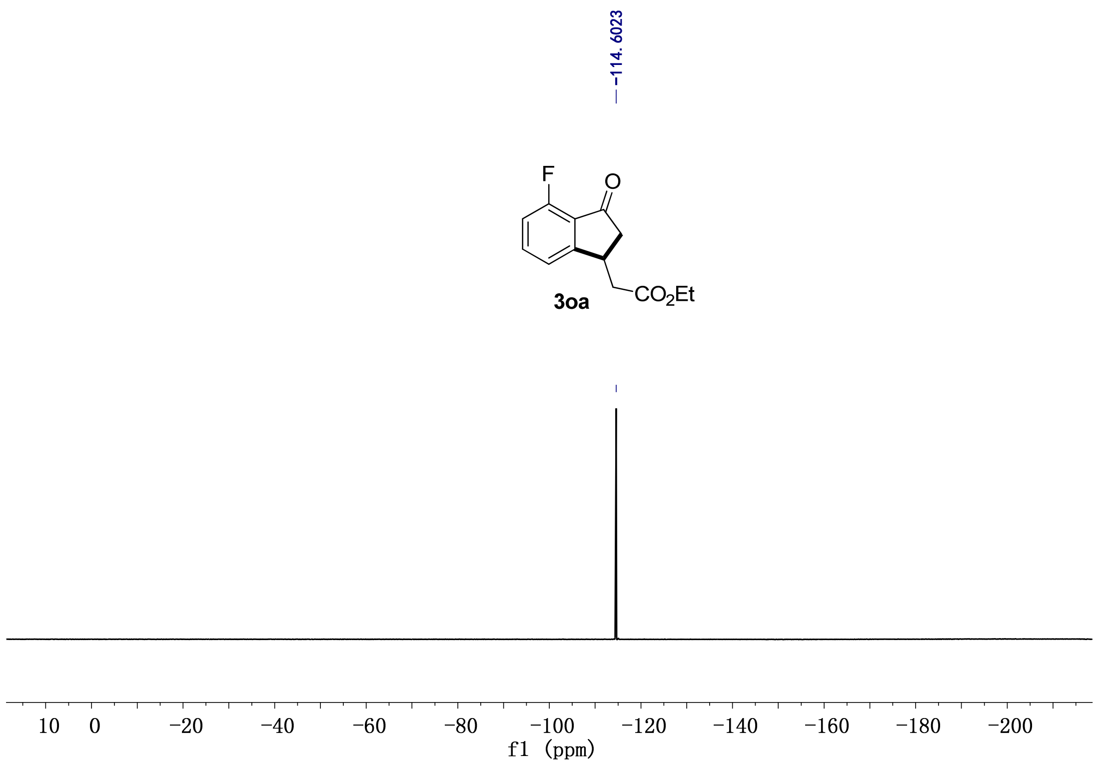
121.2235
115.0313
114.8399
77.3927
77.0749
76.7570
60.8910
43.7568
40.2212
34.5124
34.5001
14.1704
F
O
3oa
CO2Et
f1 (ppm)


-114.6023
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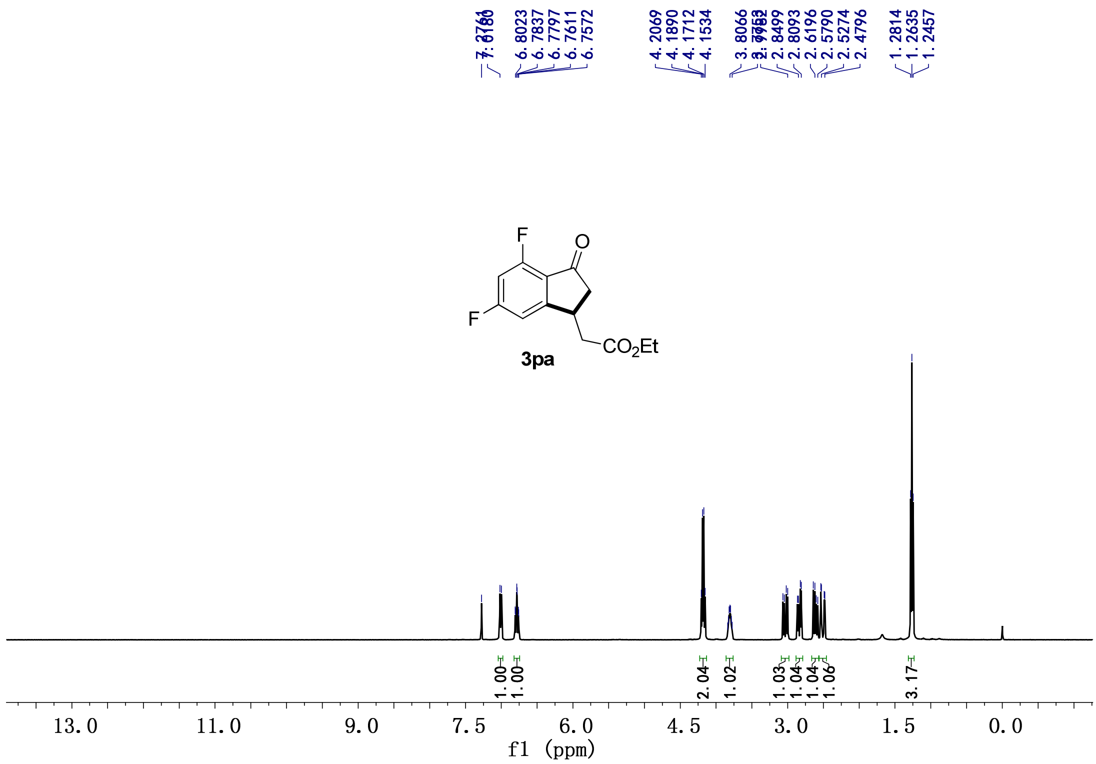
O
3oa
CO2Et
f1 (ppm)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1.00
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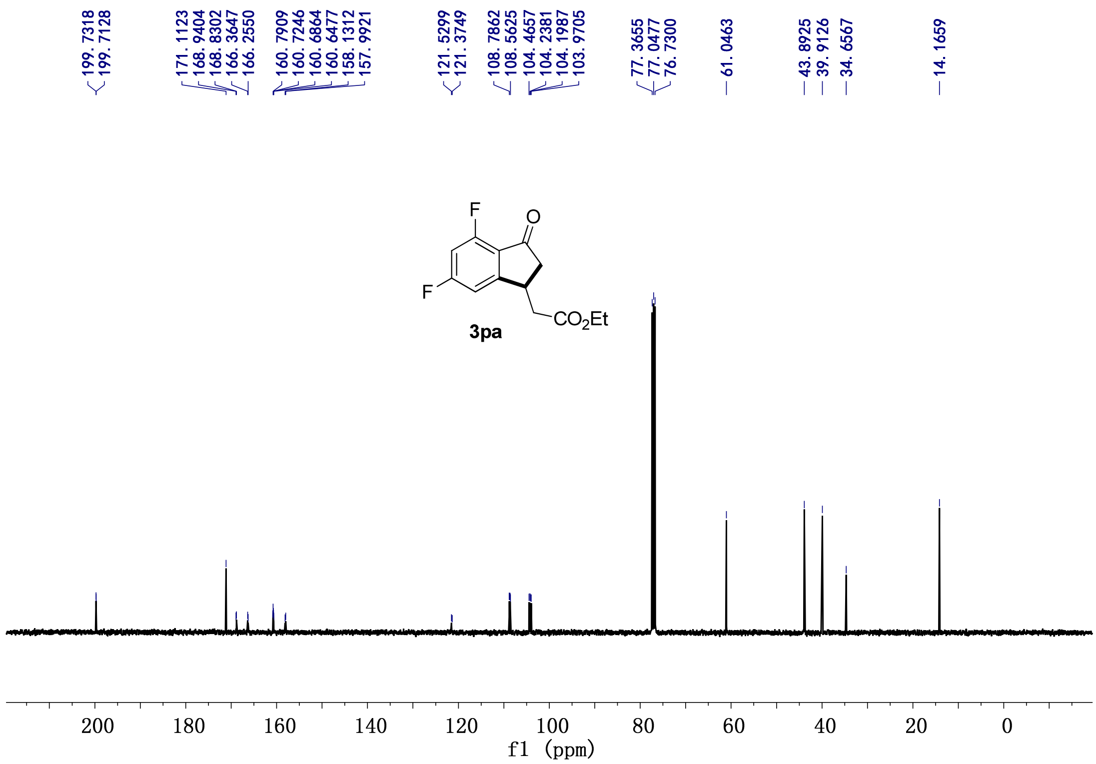
1.02
1.03
1.04
1.04
1.06
3.17
13.0
11.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)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158.1312
157.9921
121.5299
121.3749
108.7862
108.5625
104.4657
104.2381
104.1987
103.9705
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77.0477
76.7300
61.0463
43.8925
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14.1659
3pa
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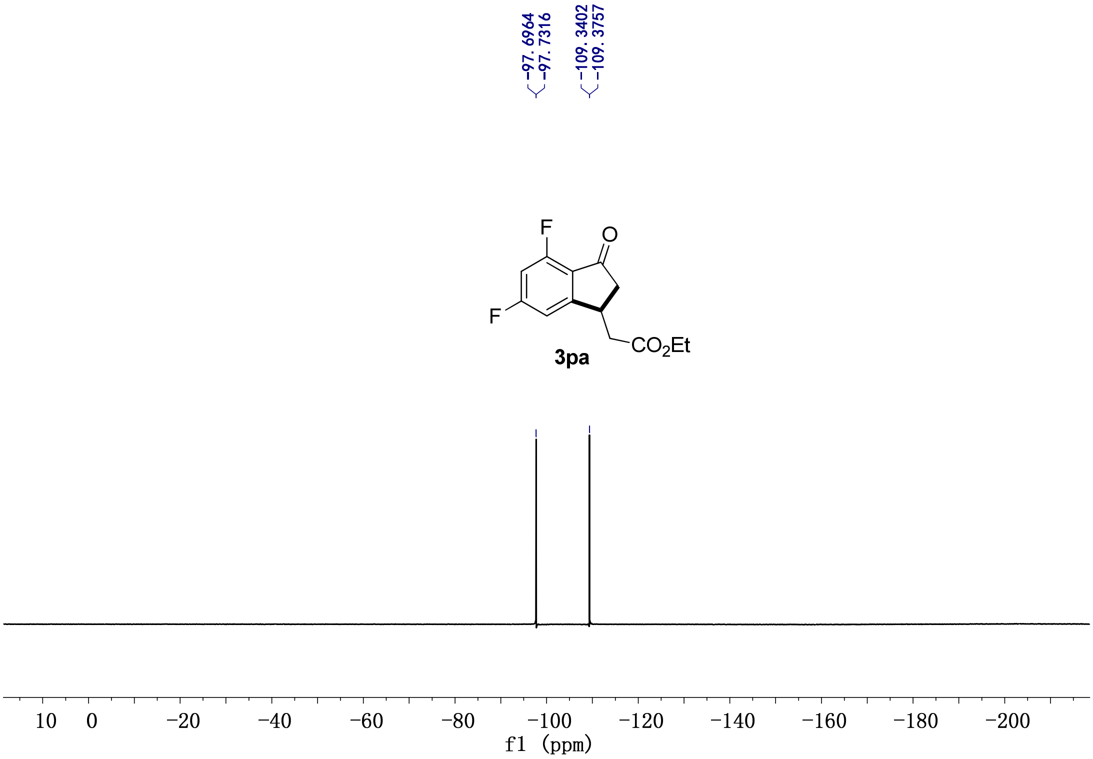
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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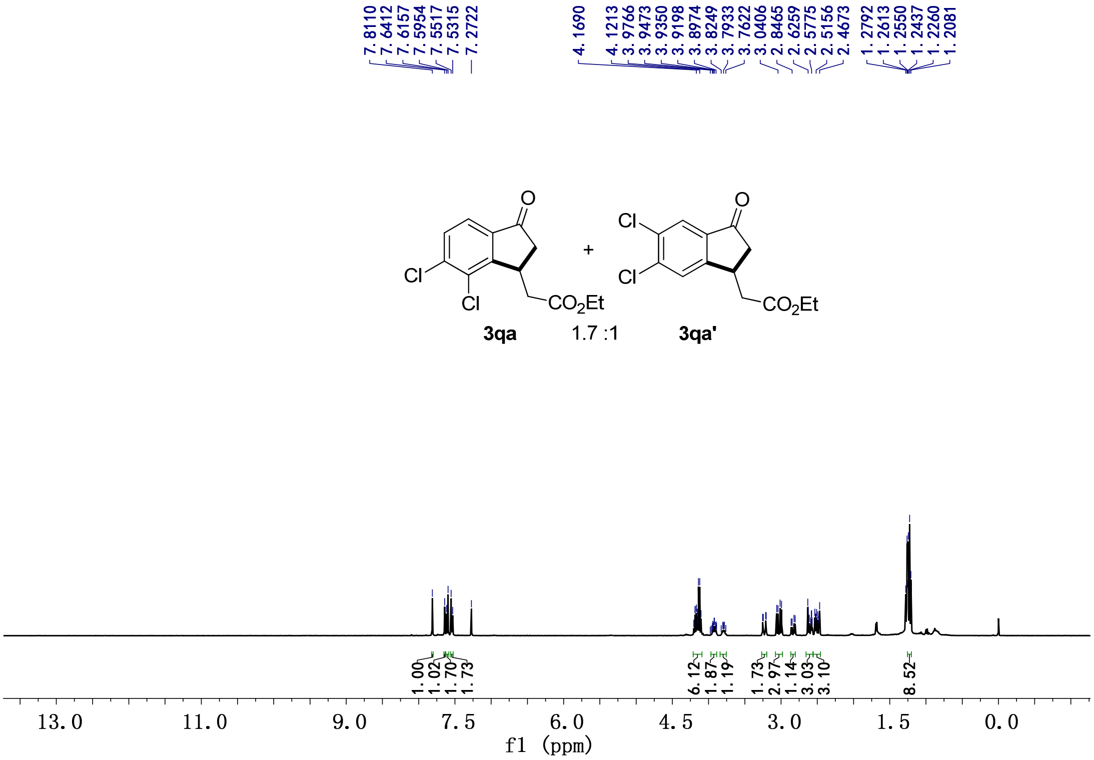
f1 (ppm)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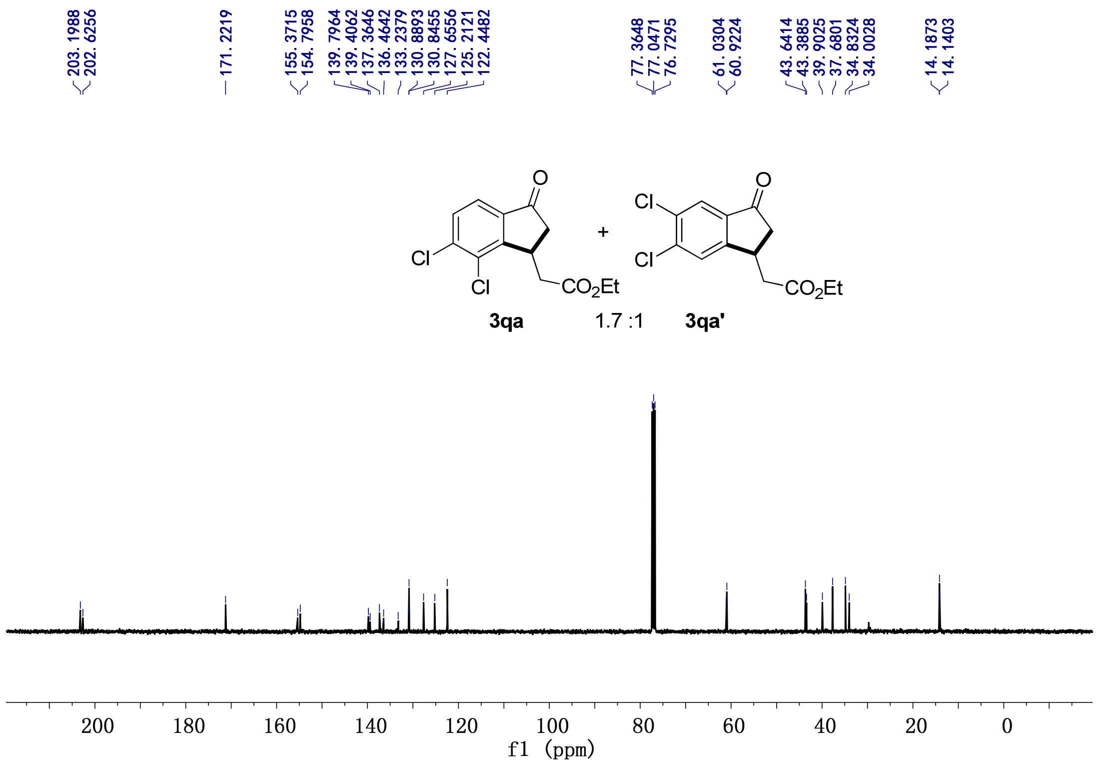
1.7 :1
3qa'
f1 (ppm)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1.7 :1
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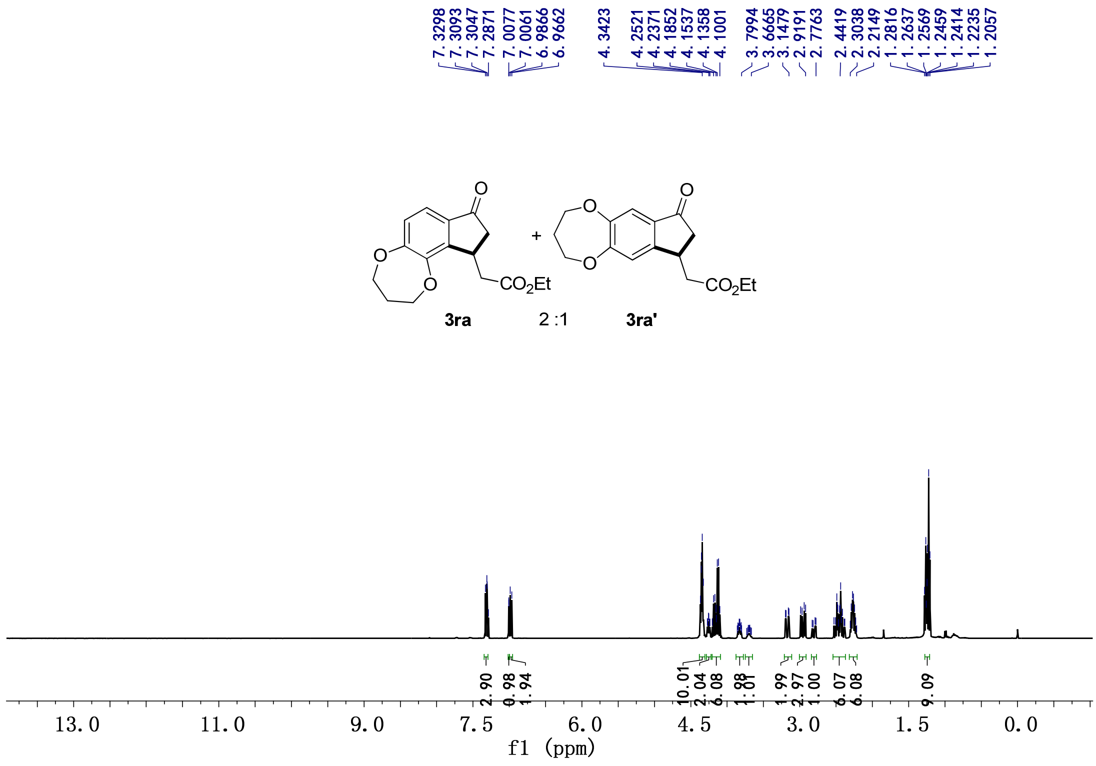
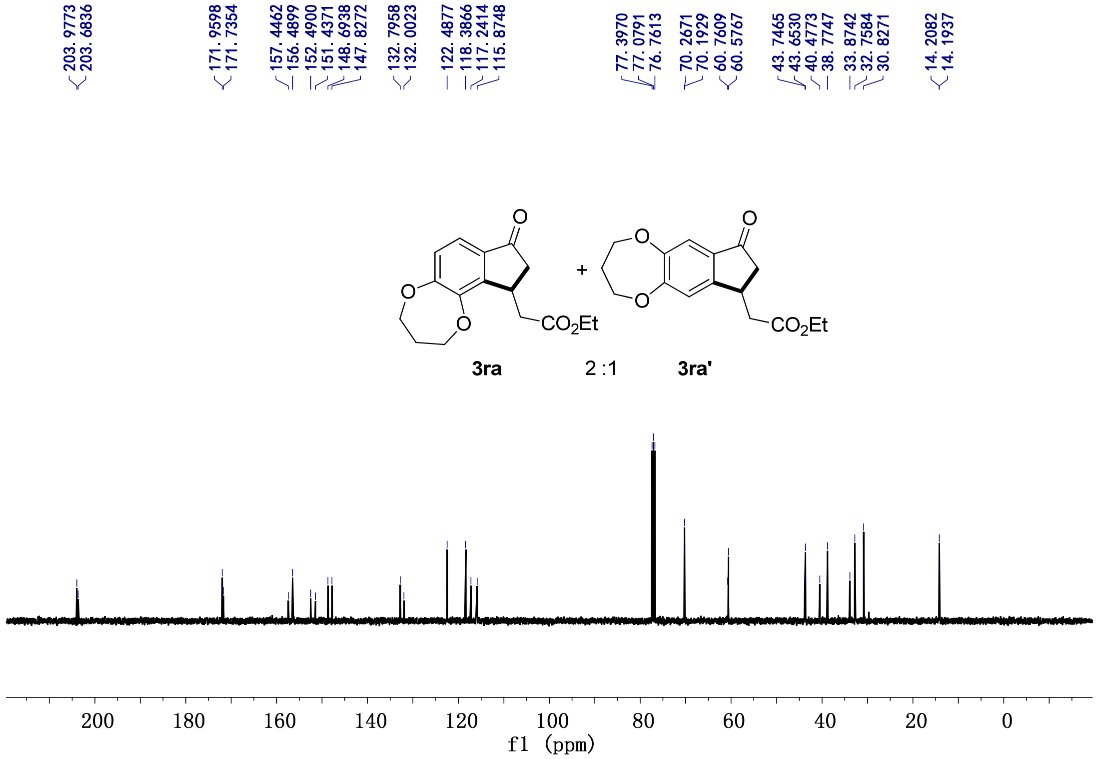
f1 (ppm)


3ra
2 :1
3ra'
f1 (ppm)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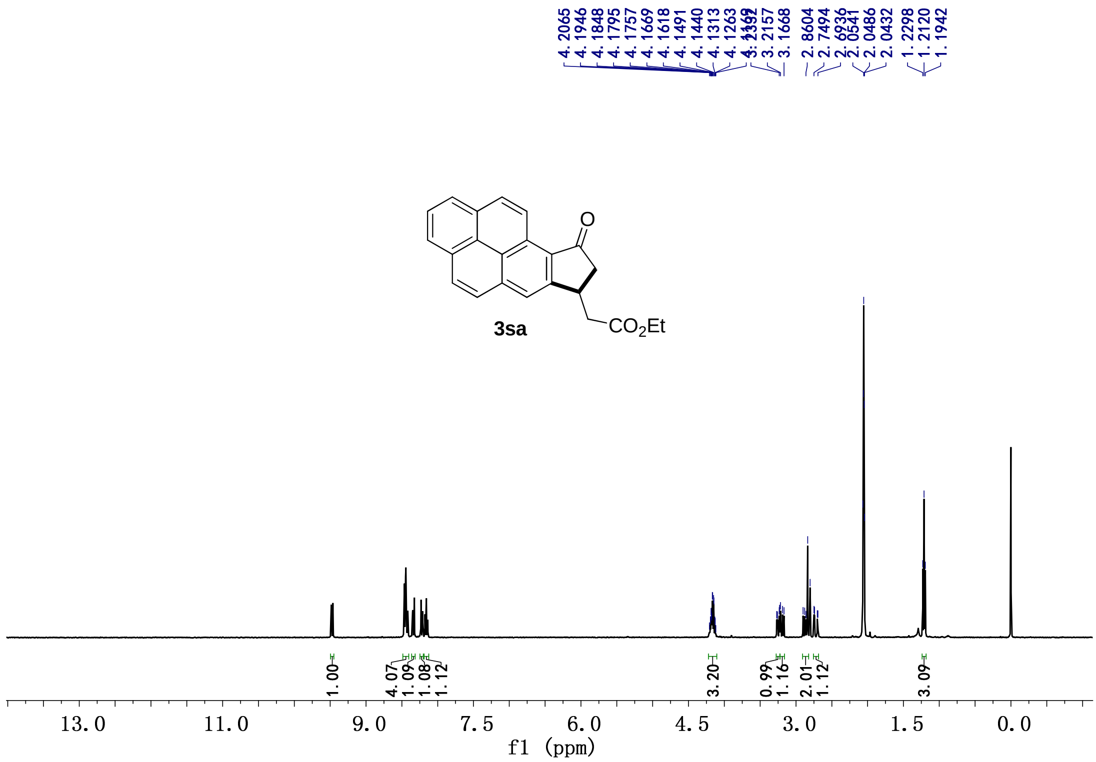
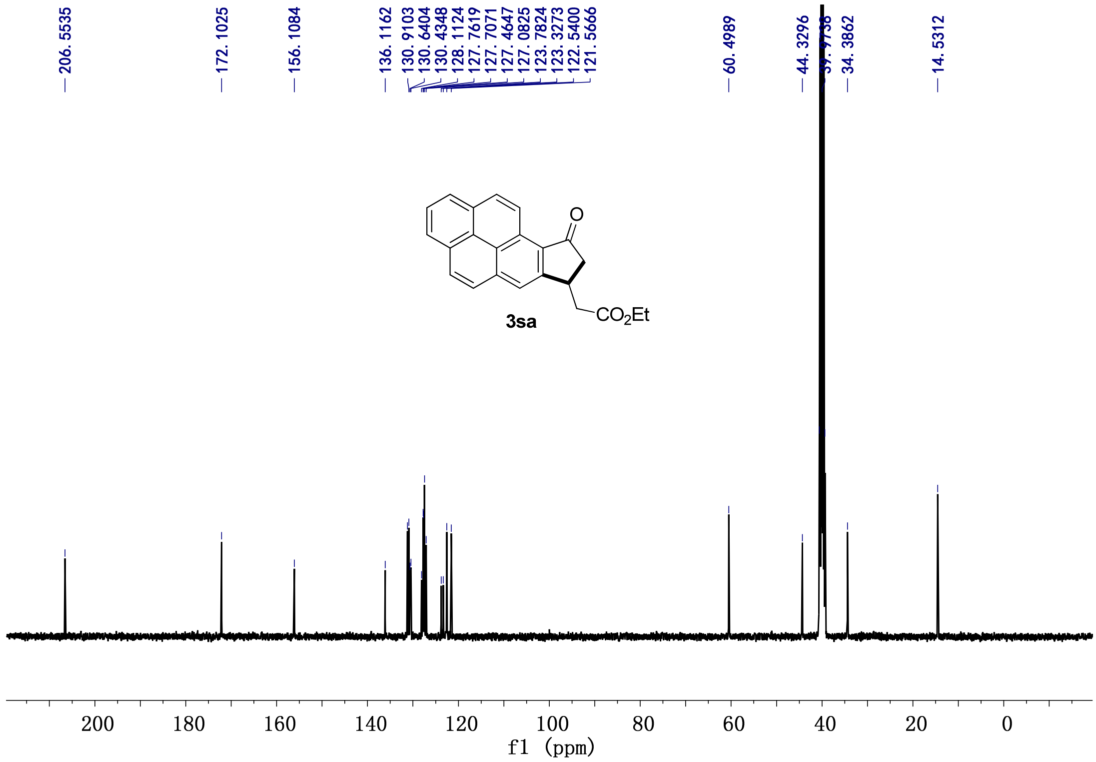
2 :1
3ra'
f1 (ppm)


3sa
f1 (ppm)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123.7824
123.3273
122.5400
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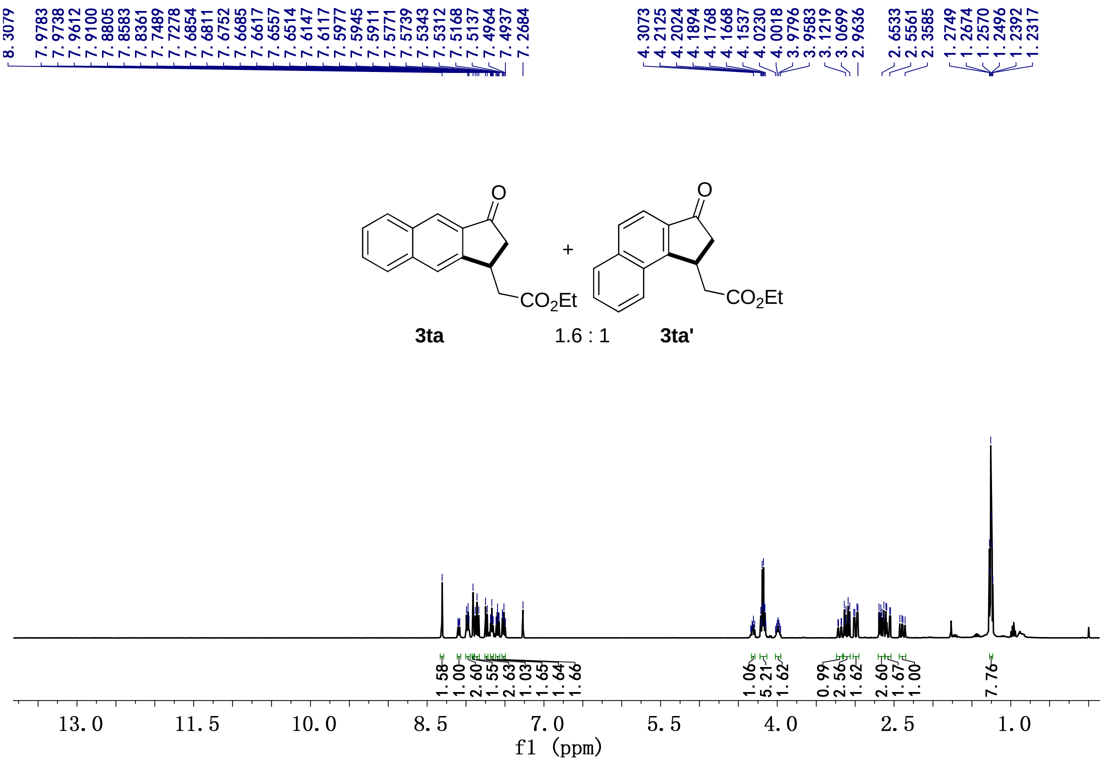
34.3862
14.5312
O
3sa
CO2Et
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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7.5911
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7.5739
7.5343
7.5312
7.5168
7.5137
7.4964
7.4937
7.2684
4.3073
4.2125
4.2024
4.1894
4.1768
4.1668
4.1537
4.0230
4.0018
3.9796
3.9583
3.1219
3.0699
2.9636
2.6533
2.5561
2.3585
1.2749
1.2674
1.2570
1.2496
1.2392
1.2317
O
+
O
CO2Et
CO2Et
3ta
1.6 : 1
3ta'
1.58
1.00
2.60
1.55
2.63
1.03
1.65
1.64
1.66
1.06
5.21
1.62
0.99
2.56
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2.60
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1.00
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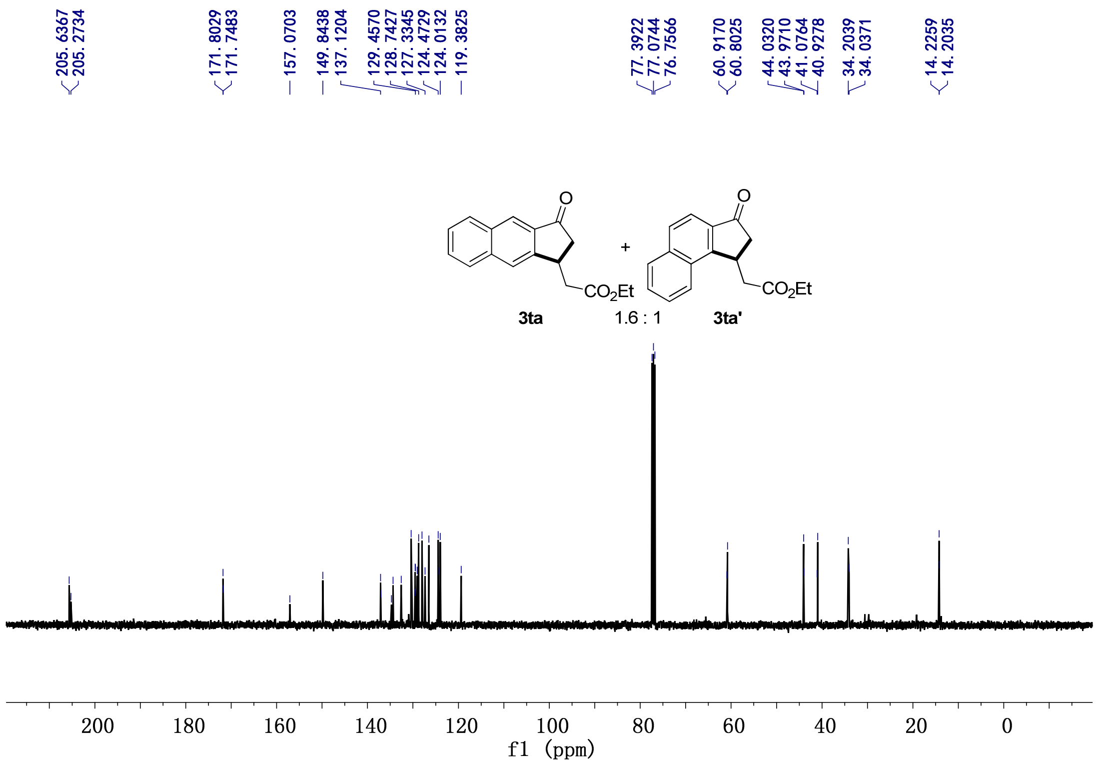
f1 (ppm)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124.4729
124.0132
119.3825
77.3922
77.0744
76.7566
60.9170
60.8025
44.0320
43.9710
41.0764
40.9278
34.2039
34.0371
14.2259
14.2035
O
+
O
CO_2Et
CO_2Et
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1.6 : 1
3ta'
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100
80
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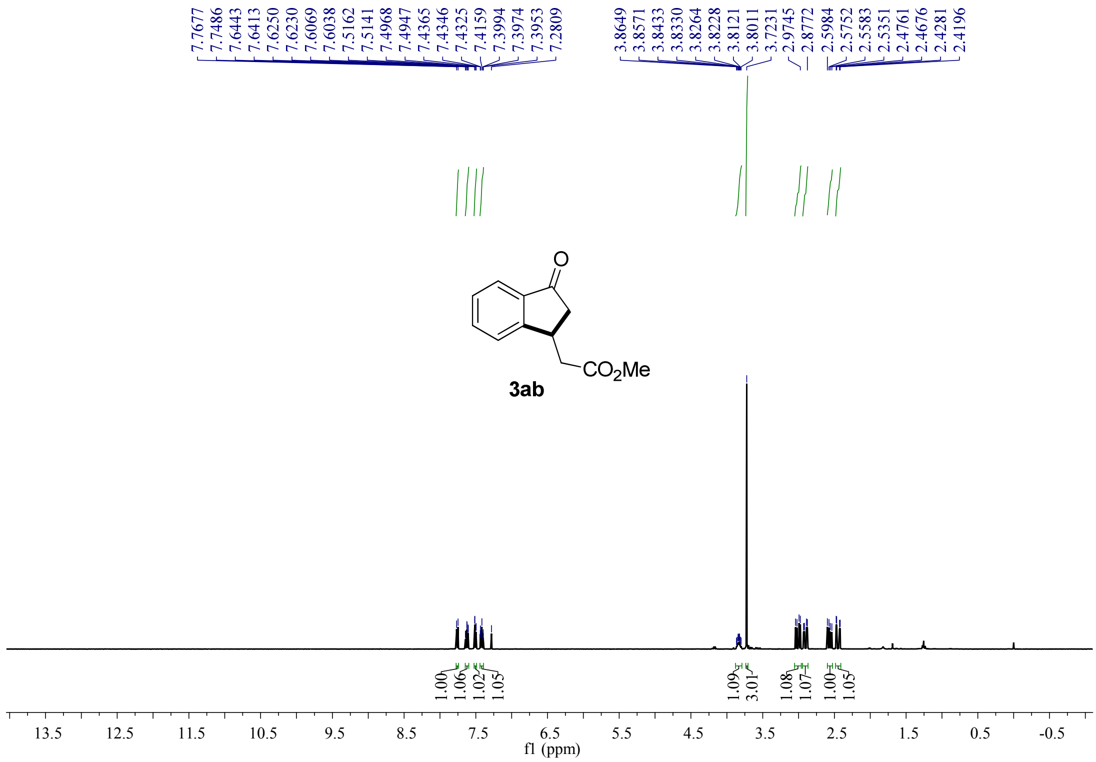
40
20
0
f1 (ppm)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7.4968
7.4947
7.4365
7.4346
7.4325
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7.3974
7.3953
7.2809
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3.8228
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2.5752
2.5583
2.5351
2.4761
2.4676
2.4281
2.4196
O
CO_2Me
3ab
1.00
1.06
1.02
1.05
1.09
3.01
1.08
1.07
1.00
1.05
13.5
12.5
11.5
10.5
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1.5
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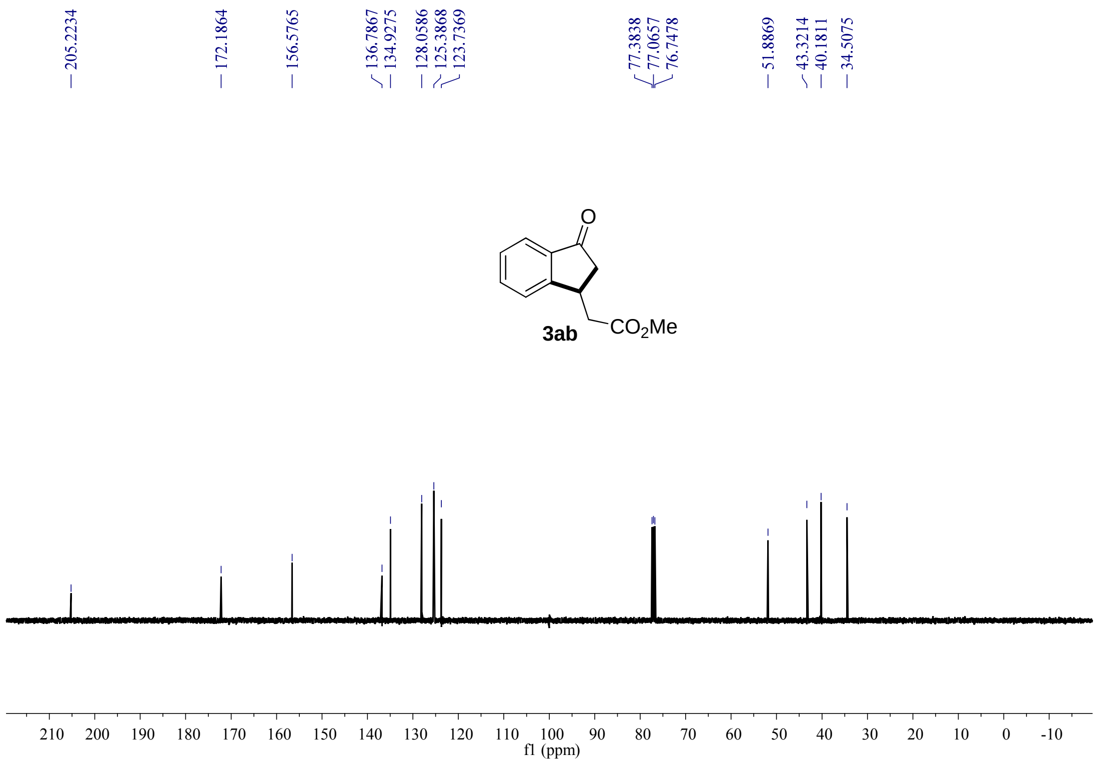
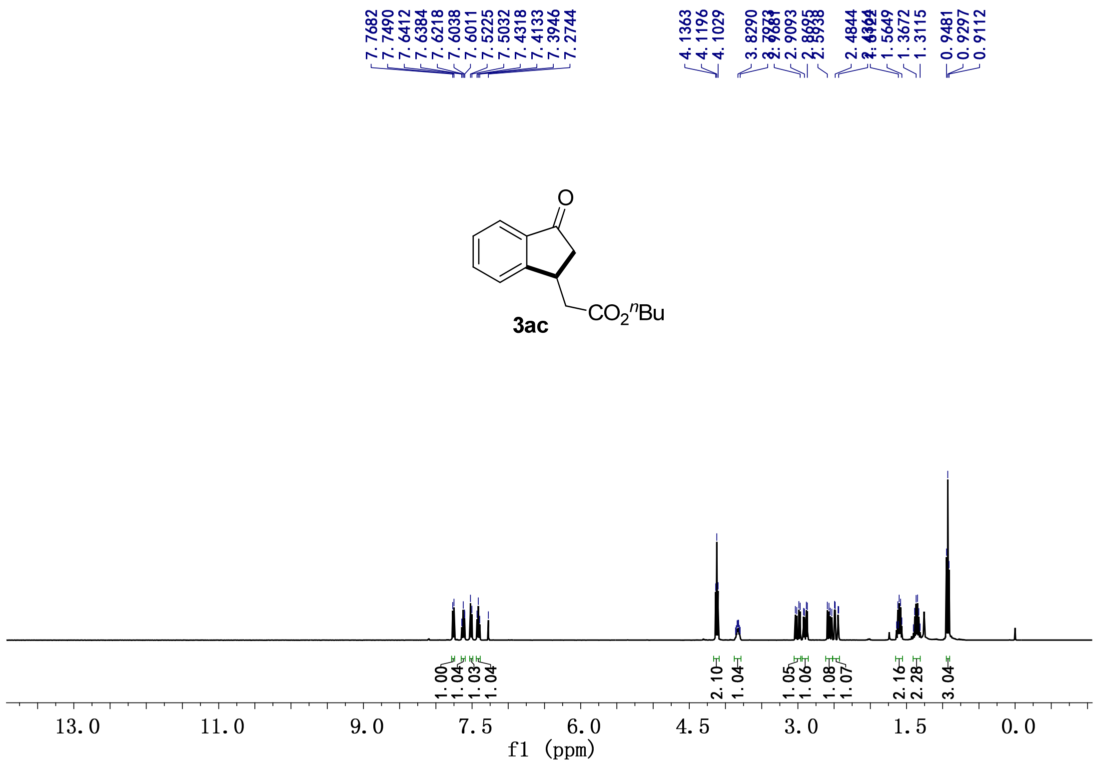
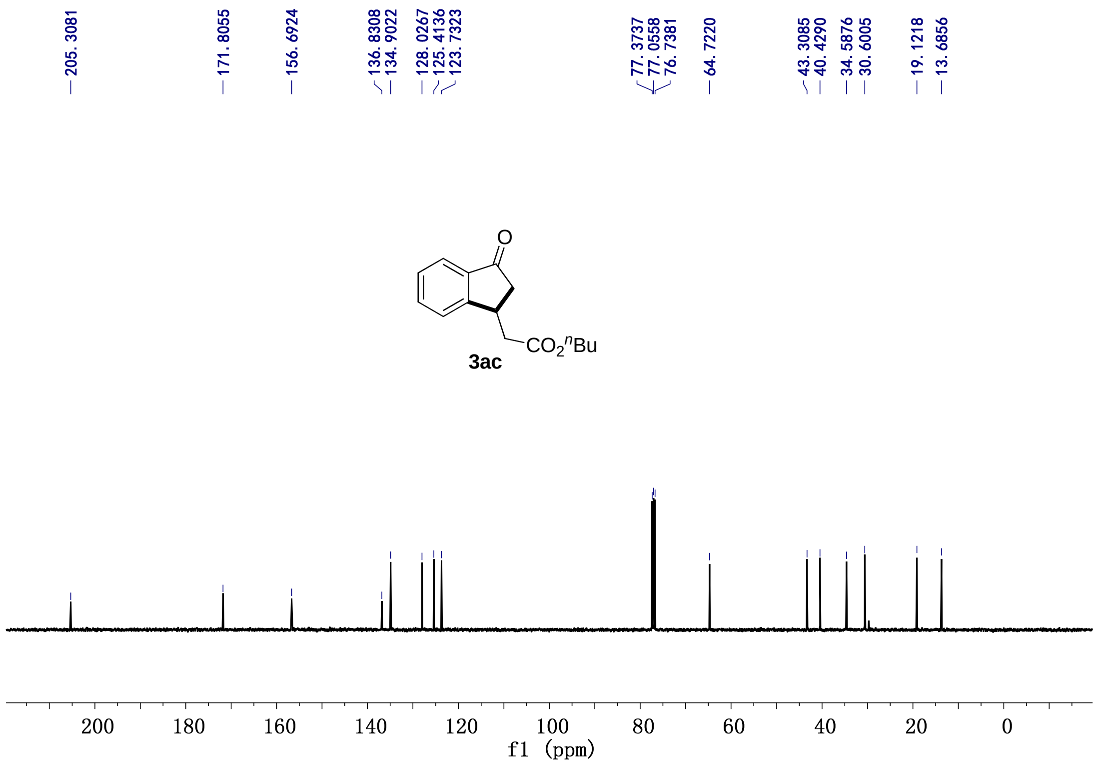
f1 (ppm)



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76.7381
64.7220
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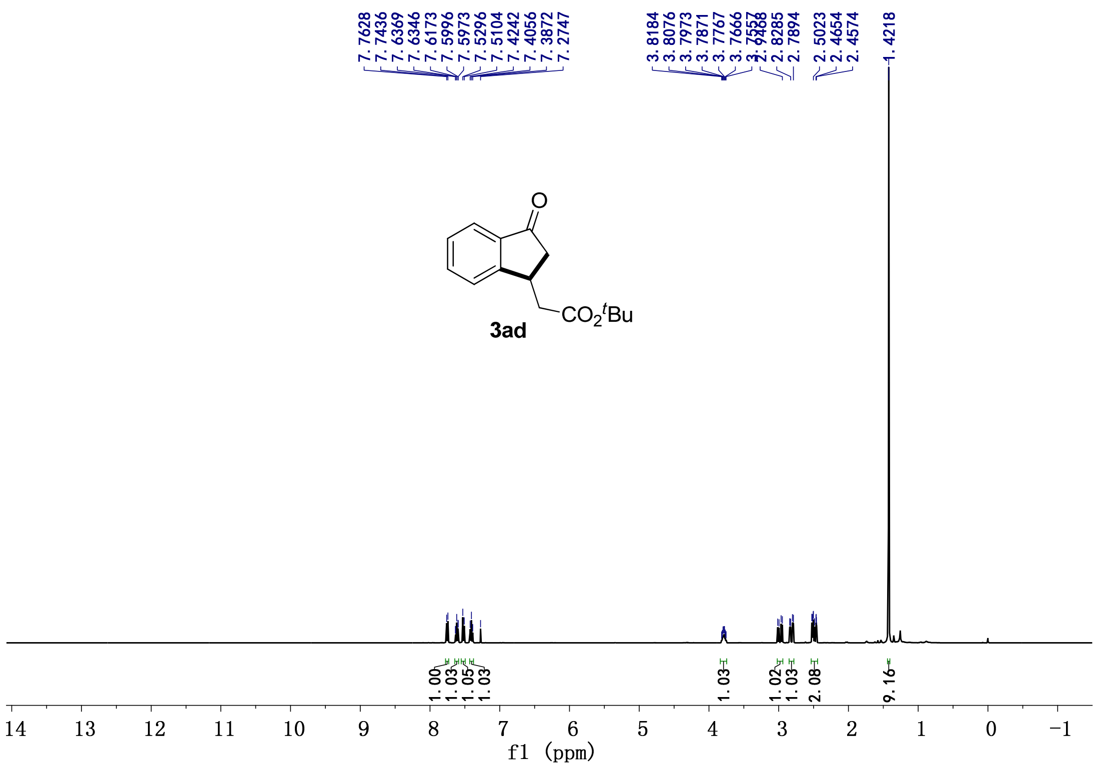
34.5876
30.6005
19.1218
13.6856
O
$CO_2{}^nBu$
3ac
f1 (ppm)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7.5296
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7.4242
7.4056
7.3872
7.2747
3.8184
3.8076
3.7973
3.7871
3.7767
3.7666
1.4218
O
$CO_2{}^tBu$
3ad
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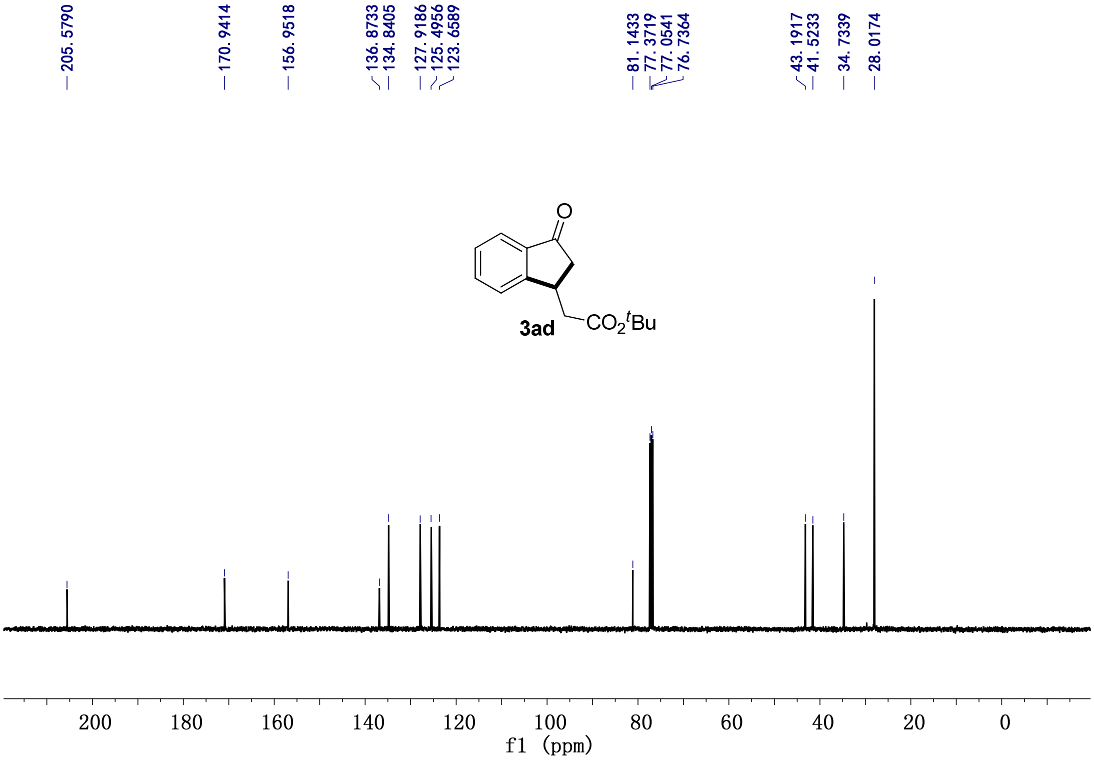
1.05
1.03
1.03
1.02
1.03
2.08
9.16
f1 (ppm)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77.0541
76.7364
43.1917
41.5233
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28.0174
3ad
CO2tBu
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180
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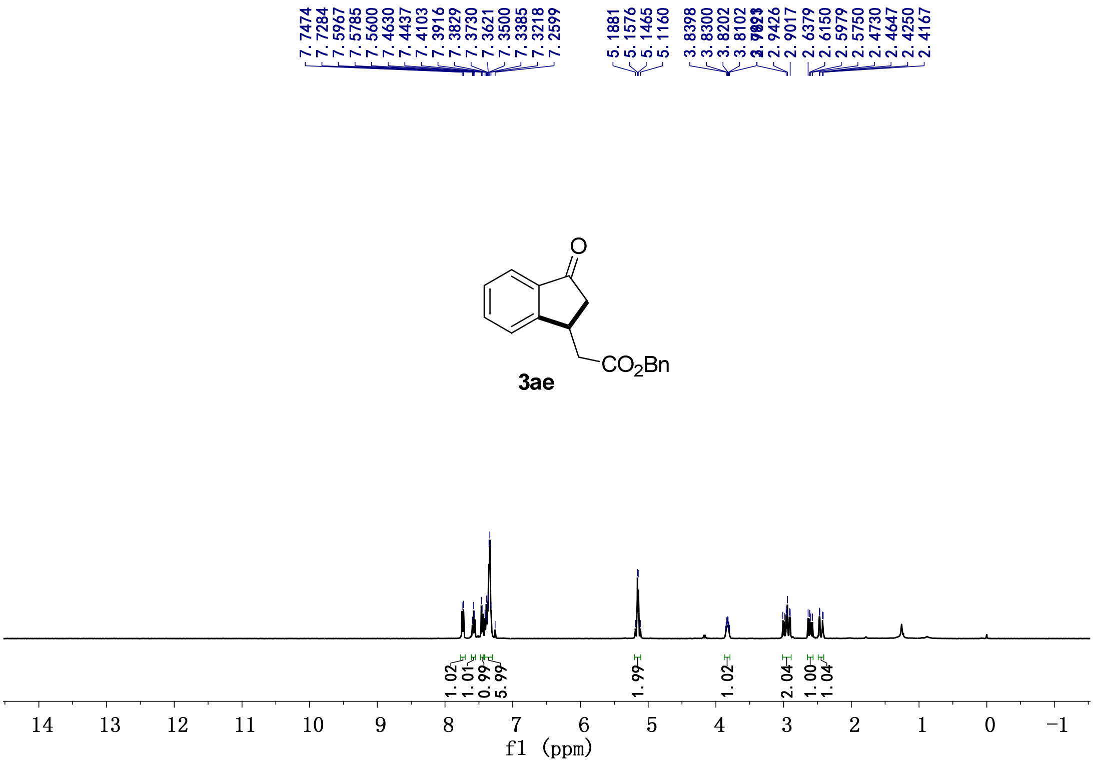
140
120
100
80
60
40
20
0
f1 (ppm)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7.2599
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5.1576
5.1465
5.1160
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2.9017
2.6379
2.6150
2.5979
2.5750
2.4730
2.4647
2.4250
2.4167
3ae
CO2Bn
1.02
1.01
0.99
5.99
1.99
1.02
2.04
1.00
1.04
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12
11
10
9
8
7
6
5
4
3
2
1
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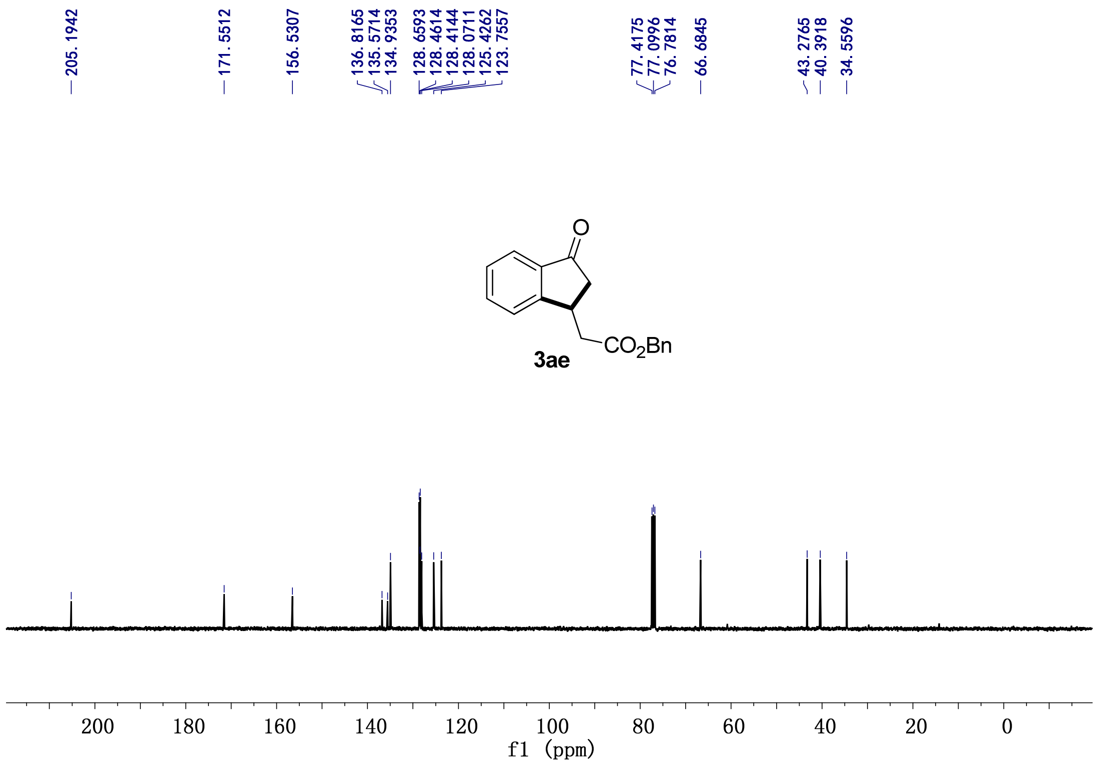
−1
f1 (ppm)



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43.2765
40.3918
34.5596
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CO2Bn
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120
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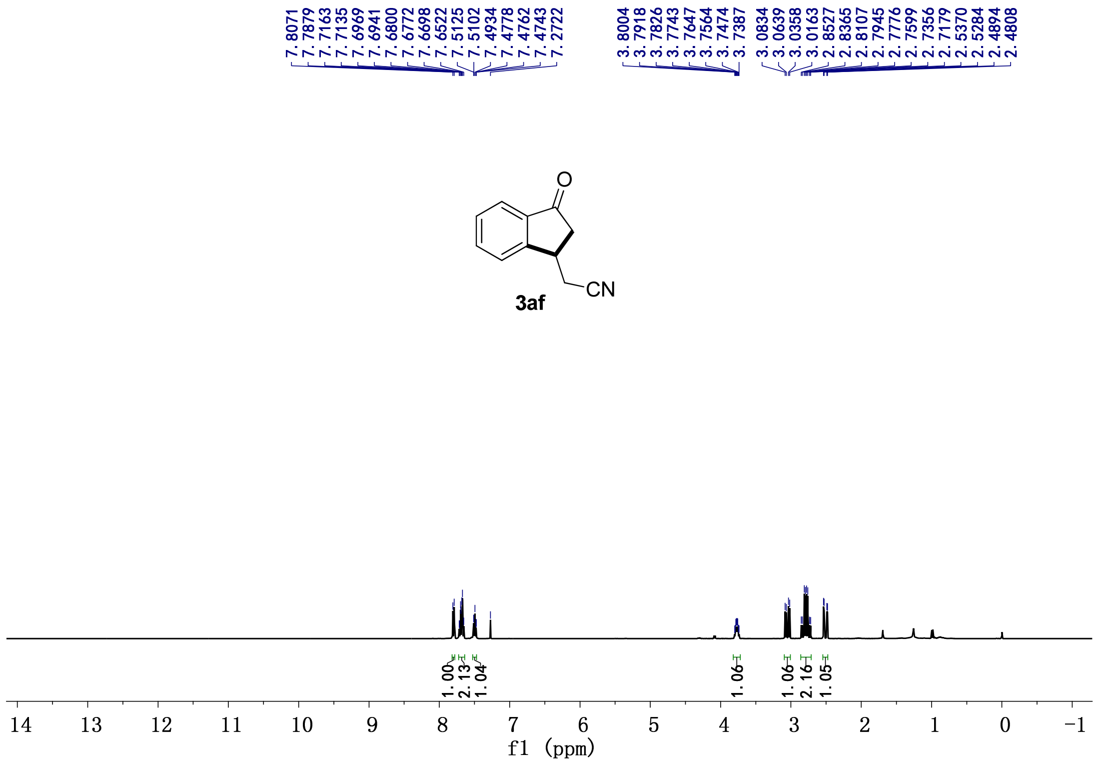
80
60
40
20
0
f1 (ppm)

3ae



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O
CN
1.00
2.13
1.04
1.06
1.06
2.16
1.05
14
13
12
11
10
9
8
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6
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4
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2
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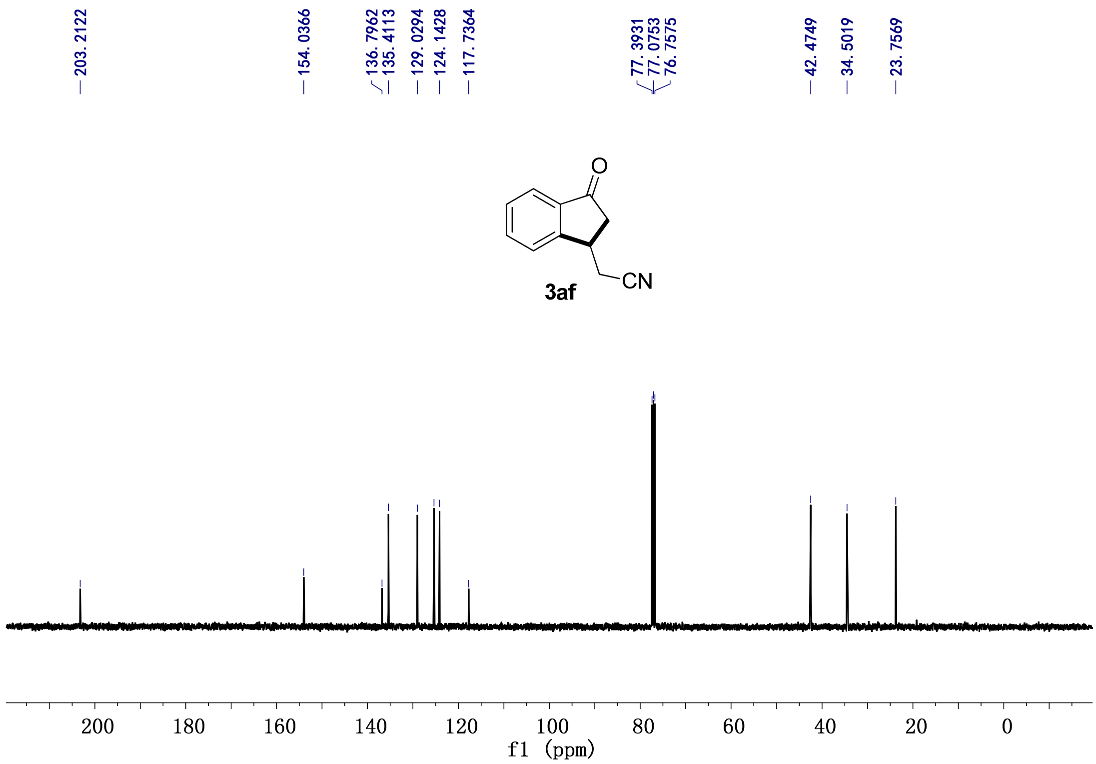
f1 (ppm)

3af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CN
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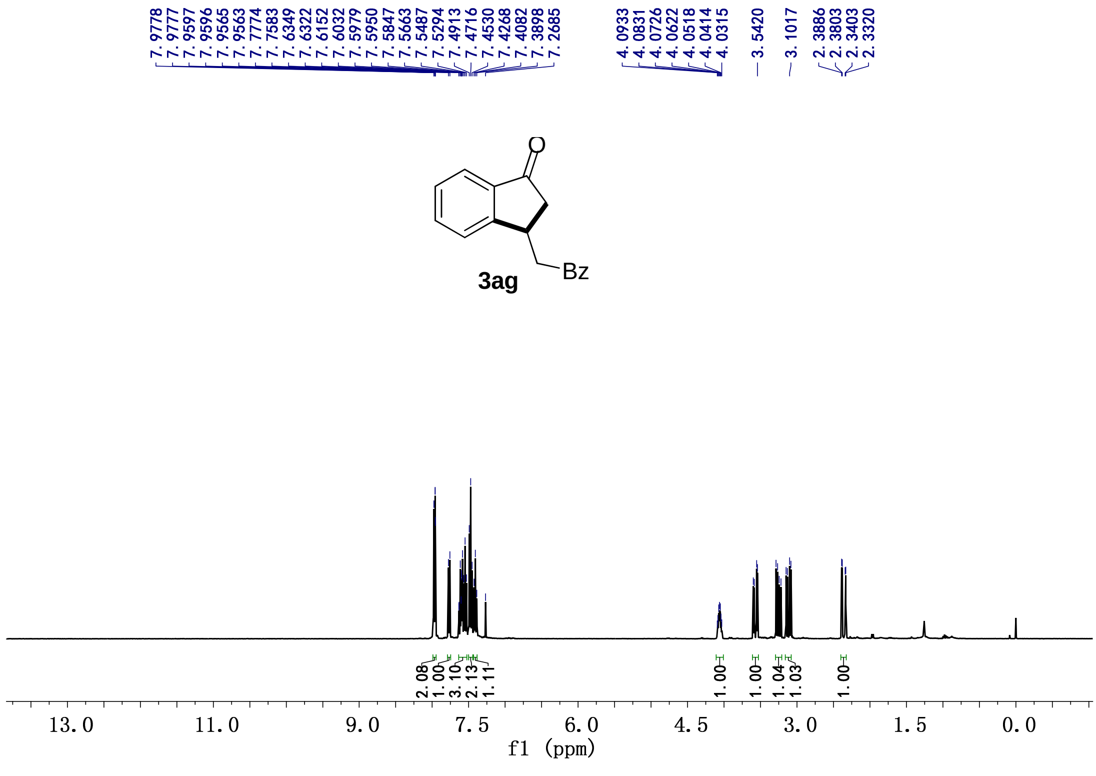
f1 (ppm)

3af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7.5950
7.5847
7.5663
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7.4268
7.4082
7.3898
7.2685
4.0933
4.0831
4.0726
4.0622
4.0518
4.0414
4.0315
3.5420
3.1017
2.3886
2.3803
2.3403
2.3320
Bz
2.08
1.00
3.10
2.13
1.11
1.00
1.00
1.04
1.03
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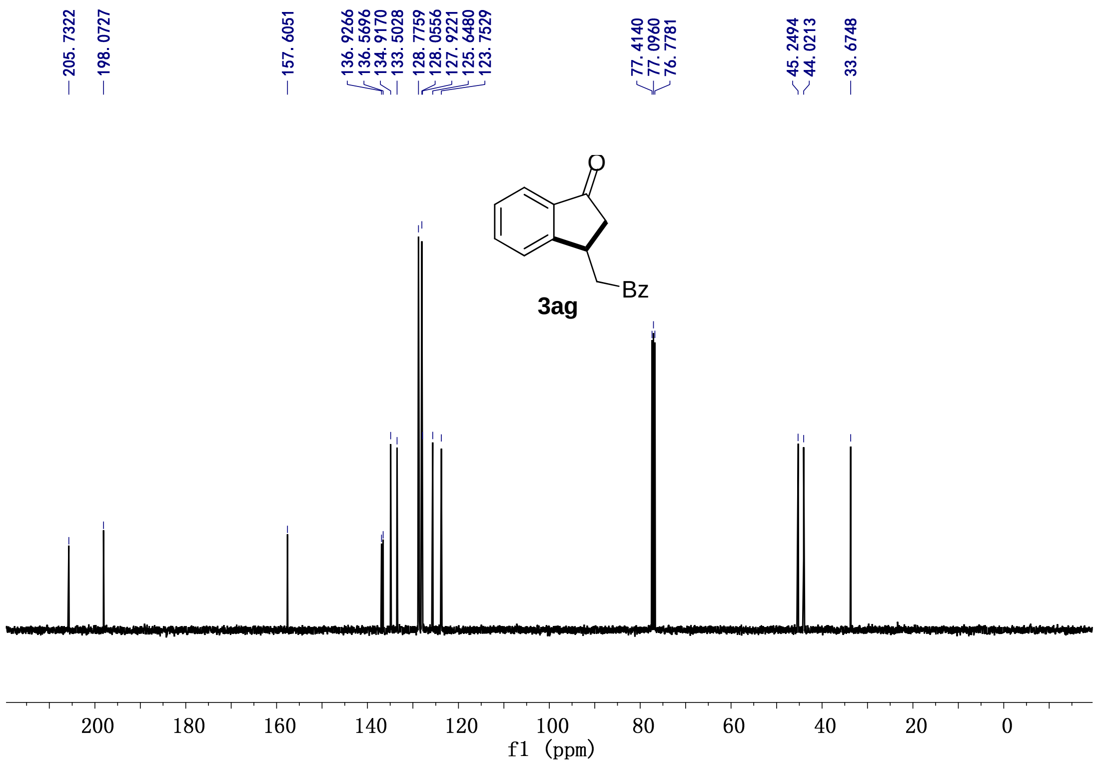
7.5
6.0
4.5
3.0
1.5
0.0
f1 (ppm)

3ag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128.0556
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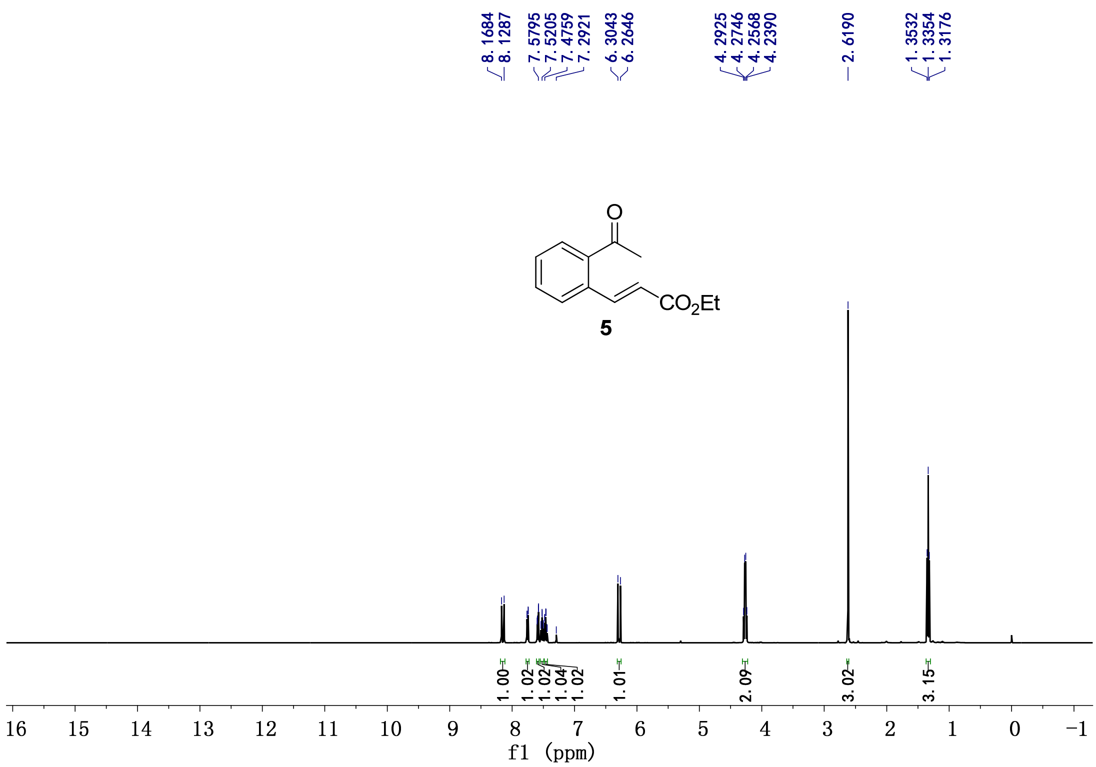
125.6480
123.7529
77.4140
77.0960
76.7781
45.2494
44.0213
33.6748
O
Bz
3ag
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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4.2390
2.6190
1.3532
1.3354
1.3176
O
CO_2Et
5
1.00
1.02
1.02
1.04
1.02
1.01
2.09
3.02
3.15
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3
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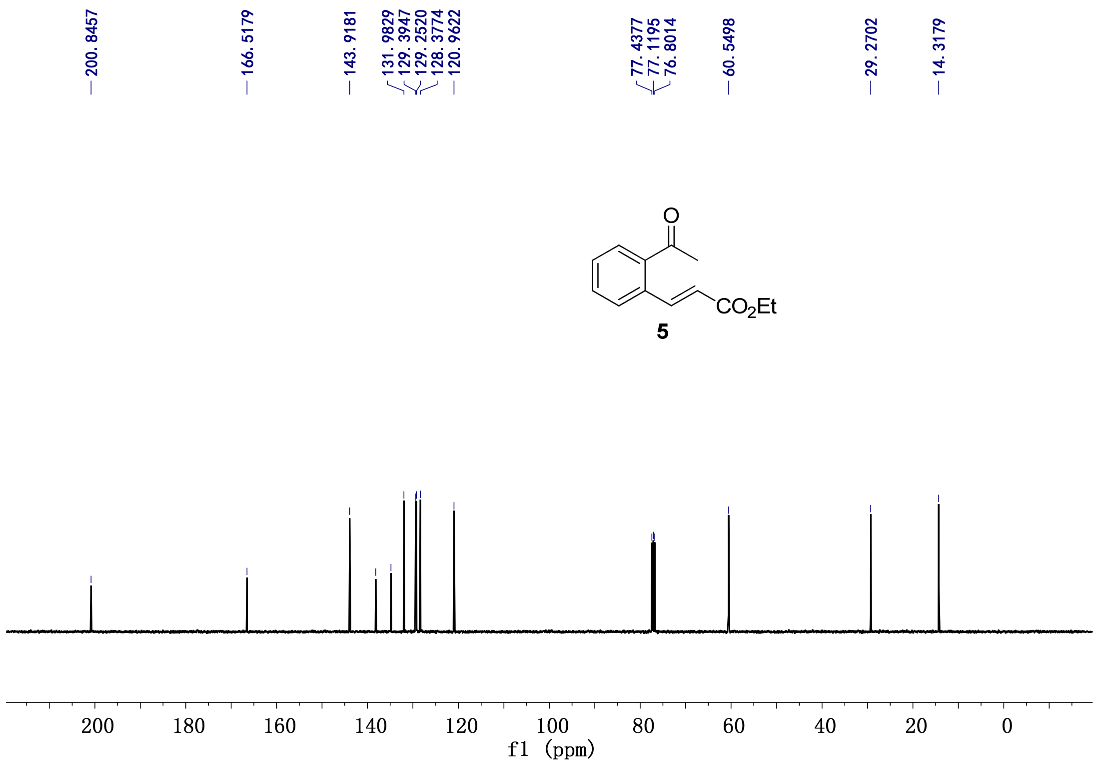
f1 (ppm)



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129.2520
128.3774
120.9622
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77.1195
76.8014
60.5498
29.2702
14.3179
O
CO2Et
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

5