Electronic Supplementary Material (ESI) for ChemComm.


# *Supporting Information*

## An Air-stable Half-sandwich $Ru^{II}$ complex as Efficient Catalyst for [3+2] Annulation of 2-Arylcyclo-2-enones with Alkynes

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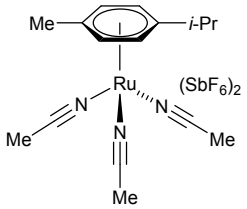
# I. General Remarks

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. All reactions were carried out under $N_2$ atmosphere. Solvents were dried by refluxing over $CaH_2$ for DCE, $P_2O_5$ for MeCN, and sodium for 1,4-dioxane and DME, and freshly distilled prior to use. 2-Arylcyclo-2-enones **1a-1q** were prepared according to the literature procedure.[1] Alkynes **2b-2g**, **2i**, **2j** and **2k** were obtained on the basis of previous reports.[2]

NMR spectra were obtained on a Bruker AV II-400 MHz. The $^1H$ NMR (400 MHz) chemical shifts were measured relative to $CDCl_3$ or $CD_3CN$ as the internal reference ($CDCl_3$: δ 7.26 ppm, $CD_3CN$: δ 1.94 ppm). The $^{13}C$ NMR (100 MHz) chemical shifts were given using $CDCl_3$/$CD_3CN$ as the internal standard ($CDCl_3$: δ 77.16 ppm, $CD_3CN$: δ 1.32 ppm). High resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). X-Ray single-crystal diffraction data were collected on an Agilent Technologies Gemini single crystal diffractometer. Melting points were determined with XRC-1 and are uncorrected.

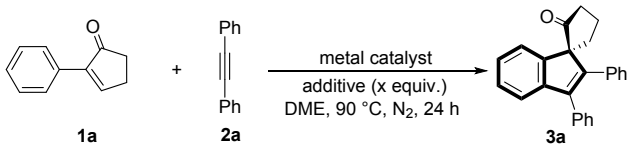
# II. Preparation of ruthenium complex II




To a suspension of [Ru(*p*-cymene)$Cl_2$]$_2$ (306 mg, 0.5 mmol) in dry MeCN (5 mL), a solution of $AgSbF_6$ (752 mg, 2.2 mmol) in dry MeCN (10 mL) was added dropwise. A precipitate formed immediately. The mixture was stirred at 90 ºC for 1 h. The solid was filtered off by a celite pad and washed with MeCN (3×10 mL). The filtrate was concentrated in vacuo to 5 mL, and $Et_2O$ (50 mL) was added with sonication. The yellow-orange solid precipitated out was collected by filtration, washed with $Et_2O$ (50 mL), dried in vacuo to give [Ru(*p*-cymene)$(MeCN)_3$]$(SbF_6)_2$ (730 mg, 88%). $^1H$ NMR (400 MHz, $CD_3CN$): $\delta$ = 1.30 (dd, $J$ = 6.8 Hz, 1.2 Hz, 6H), 2.27 (s, 3H), 2.48 (d, 9H), 2.83-2.92 (m, 1H), 5.86 (d, $J$ = 5.6 Hz, 2H), 6.09 (d, $J$ = 6.0 Hz, 2H) ppm. $^{13}C$ NMR (100 MHz, $CD_3CN$): $\delta$ = 4.5, 19.1, 22.1, 31.9, 85.4, 88.2, 106.8, 109.4, 129.0 ppm.

## III. Optimization of the reaction conditions

**Table S1 Optimization of the reaction conditions.**[a]



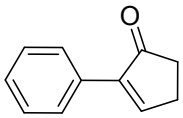

1a 2a 3a

| Entry | catalyst [M] (x mol%) | Additive (x equiv.) | T. (°C) | Yield (%)[b] |
|---|---|---|---|---|
| 1 | **II** (10 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | 71 |
| 2 | **II** (10 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.5 eq.) | 90 °C | 70 |
| 3 | **II** (10 mol%) | $Cu(OAc)_2 \cdot H_2O$ (0.5 eq.) | 90 °C | 38 |
| 4 | **II** (10 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 110 °C | 56 |
| 5 | **II** (10 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 70 °C | 30 |
| 6 | **II** (10 mol%) | $Cu(OAc)_2$ (1.0 eq.) | 90 °C | 68 |
| 7 | **II** (10 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | 52[c] |
| 8 | $[RuCl_2(p\text{-cymene})]_2/AgSbF_6$ (5 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | 23 |
| 9 | $Ru(COD)Cl_2/AgSbF_6$ (10 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | ND |
| 10 | $Ru(PPh_3)_3Cl_2/AgSbF_6$ (10 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | ND |
| 11 | $[Cp^*RuCl_2]_2/AgSbF_6$ (10 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | ND |
| 12 | $[RuCl_2(p\text{-cymene})]_2/AgSbF_6$ (5 mol%/20 mol%) | NaOAc (1.0 eq.) | 90 °C | ND |
| 13 | $[RuCl_2(p\text{-cymene})]_2/AgSbF_6$ (5 mol%/20 mol%) | AgOAc (1.0 eq.) | 90 °C | ND |
| 14 | $[RuCl_2(p\text{-cymene})]_2/AgSbF_6$ (5 mol%/20 mol%) | HOAc (1.0 eq.) | 90 °C | ND |
| 15 | $[RuCl_2(p\text{-cymene})]_2/AgPF_6$ (5 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | 6% |
| 16 | $[RuCl_2(p\text{-cymene})]_2/AgBF_4$ (5 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | trace |
| 17 | $[RuCl_2(p\text{-cymene})]_2/AgOTf$ (5 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | trace |
| 18 | $[RuCl_2(p\text{-cymene})]_2/AgOAc$ (5 mol%/20 mol%) | $Cu(OAc)_2 \cdot H_2O$ (1.0 eq.) | 90 °C | ND |

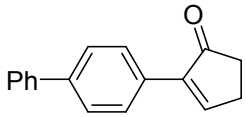
[a]Reaction conditions: **2a** (0.2 mmol), **1a** (0.25 mmol), catalyst and additive in DME (0.4 M) at 90 °C under $N_2$ for 24 h. [b]Isolated yield. [c]**a**:**2a** = 1:1.2.

## IV. General procedure for the synthesis of 2-arylcyclo-2-enones

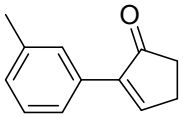
To a stirring solution of iodoenone (5 mmol) in a mixed solvent of DME (10 mL) and $H_2O$ (10 mL) were added $Na_2CO_3$ (1.1 g, 10 mmol), $ArB(OH)_2$ (10 mmol), and 10 % Pd/C (0.5 g, 5 mol%). After stirred at room temperature for 20 h, the reaction mixture was filtered and the filtrate was extracted with $Et_2O$ (2×20 mL). The combined organic extracts were washed with 1M NaOH (2×20 mL) and water, dried over anhydrous $Na_2SO_4$, and concentrated in vacuo. The residue was passed through a silica gel column with ethyl acetate/petroleum ether as the eluent to provide the desired products.



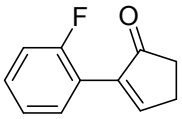

**2-Phenylcyclopent-2-enone (1a):**[1a] 78% yield, a white solid. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.60-2.61 (m, 2H), 2.71-2.73 (m, 2H), 7.33 (t, $J$ = 7.2 Hz, 1H), 7.39 (t, $J$ = 7.2 Hz, 2H), 7.69 (d, $J$ = 7.2 Hz, 2H), 7.83 (t, $J$ = 2.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.4, 36.0, 127.2, 128.5, 128.6, 131.8, 143.7, 159.1, 207.8 ppm.



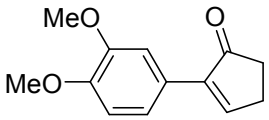

**2-([1,1'-biphenyl]-4-yl)cyclopent-2-enone (1h):** 75% yield, a white solid. M.p.: 140-142 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.62-2.65 (m, 2H), 2.72-2.76 (m, 2H), 7.35 (t, $J$ = 7.6 Hz, 1H), 7.45 (t, $J$ = 7.6 Hz, 2H), 7.60-7.63 (m, 4H), 7.79 (d, $J$ = 8.4 Hz, 2H), 7.88 (t, $J$ = 3.2 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.4, 36.0, 127.2, 127.3, 127.6, 128.9, 130.8, 140.8, 141.3, 143.2, 158.9, 207.8 ppm. HRMS (ESI$^+$): calcd for $C_{17}H_{15}O$ $[M+H]^+$ 235.1123, fonud 235.1120.



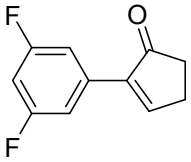

**2-(m-tolyl)cyclopent-2-enone (1i):** 69% yield, a white solid. M.p.: 103-105 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.38 (s, 3H), 2.58-2.61 (m, 2H), 2.69-2.72 (m, 2H), 7.15 (d, $J$ = 7.6 Hz, 1H), 7.28 (t, $J$ = 7.6 Hz, 1H), 7.47 (d, $J$ = 7.6 Hz, 1H), 7.50 (s, 1H), 7.81 (t, $J$ = 2.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.6, 26.3, 35.9, 124.3, 127.8, 128.4, 129.2, 131.7, 138.1, 143.7, 159.1, 207.9 ppm. HRMS (ESI$^+$): calcd for $C_{12}H_{13}O$ $[M+H]^+$ 173.0966, found 173.0965.




**2-(2-fluorophenyl)cyclopent-2-enone (1k):** 73% yield, a white solid. M.p.: 86-88 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.56-2.58 (m, 2H), 2.77 (m, 2H), 7.07-7.12 (m, 1H), 7.16 (td, $J$ = 7.6 Hz, 1.2 Hz, 1H), 7.26-7.30 (m, 1H), 7.79 (td, $J$ = 7.6 Hz, 1.6 Hz, 1H), 7.99-8.01 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.9, 34.9, 115.8 (d, $J_{CF}$ = 22.3 Hz), 119.7 (d, $J_{CF}$ = 22.1 Hz), 124.09 (d, $J_{CF}$ = 3.5 Hz), 129.75 (d, $J_{CF}$ = 8.5 Hz), 130.0 (d, $J_{CF}$ = 3.2 Hz), 138.0 (d, $J_{CF}$ = 1.9 Hz), 160.4 (d, $J_{CF}$ = 247.7 Hz), 163.0 (d, $J_{CF}$ = 7.4 Hz), 207.5 ppm. HRMS (ESI$^+$): calcd for $C_{11}H_{10}FO$ $[M+H]^+$ 177.0716, found 117.0710.



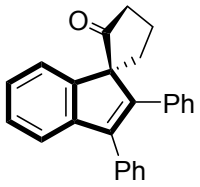

**2-(3,4-dimethoxyphenyl)cyclopent-2-enone (1l):** 80% yield, a white solid. M.p.: 117-119 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.55-2.58 (m, 2H), 2.67-2.68 (m, 2H), 3.87-3.91 (m, 6H), 6.85-6.89 (m, 1H), 7.26-7.32 (m, 2H), 7.73-7.76 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.1, 36.0, 56.0, 110.3, 111.2, 119.8, 124.7, 142.8, 148.9, 149.3, 157.6, 208.0 ppm. HRMS (ESI$^+$): calcd for $C_{13}H_{15}O_3$ $[M+H]^+$ 219.1021, found 219.1014.



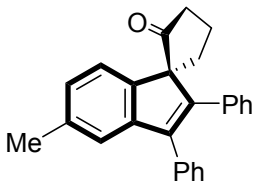

**2-(3,5-difluorophenyl)cyclopent-2-enone (1m):** 65% yield, a white solid. M.p.: 96-98 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.61-2.63 (m, 2H), 2.73-2.75 (m, 2H), 6.77 (tt, $J$ = 8.8 Hz, 2.4 Hz, 1H), 7.29 (m, 2H), 7.88 (t, $J$ = 2.8 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 26.4, 35.9, 103.9 (t, $J_{CF}$ = 25.2 Hz), 110.0 (m), 134.6 (t, $J_{CF}$ = 10.1 Hz), 141.5 (t, $J_{CF}$ = 2.8 Hz), 160.6, 163.1 (dd, $J_{CF}$ = 246.0 Hz, 12.9 Hz), 206.7 ppm. HRMS (ESI$^-$): calcd for $C_{11}H_9F_2O$ $[M+H]^+$ 195.0621, found 195.0622.

## V. General procedure for the Ru-catalyzed [3+2] Annulation of 2-arylcyclo-2-enones with alkynes

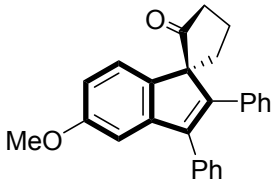
A Schlenk tube with a magnetic stir bar was charged with Ru complex (II) (16.7 mg, 10 mol%), 2-arylcyclo-2-enone 1 (0.25 mmol), alkyne 2 (0.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (39.6 mg, 0.2 mmol) and DME (0.5 mL) under $N_2$. The tube was sealed with a teflon-coated screw cap and the reaction was heated at 90 °C for 24 h. After cooled down to room temperature, the reaction mixture was filtered through a celite pad and washed with EtOAc. The filtrate was then concentrated and the residue was purified by column chromatography on silica gel (method A: PE/EA=50:1~20:1, method B: PE/DCM=3:1~1:1) to provide the desired product.



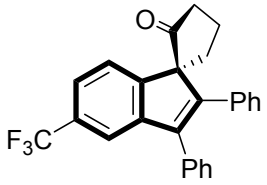

**2',3'-Diphenylspiro[cyclopentane-1,1'-inden]-2-one (3aa):** Purified by method A to give **3aa** as an off-white solid (48 mg, 71% yield). M.p.: 139-141 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.94-2.04 (m, 1H), 2.27-2.55 (m, 4H), 2.68-2.77 (m, 1H), 7.04-7.07 (m, 2H), 7.22-7.38 (m, 12H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.8, 40.0, 69.9, 121.4, 121.7, 126.0, 127.36, 127.45, 127.6, 128.3, 129.7, 129.8, 134.5, 135.9, 142.5, 144.9, 146.4, 148.5, 218.7 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{21}O$ $[M+H]^+$ 337.1592, found 337.1588.



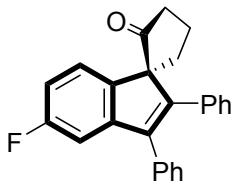

**5'-Methyl-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ba):** Purified by method A to give **3ba** as an off-white solid (50 mg, 71% yield). M.p.: 156-158 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.94-2.04 (m, 1H), 2.34-2.54 (m, 7H), 2.67-2.76 (m, 1H), 7.02-7.07 (m, 3H), 7.17 (s, 1H), 7.20-7.32 (m, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 21.7, 32.8, 39.9, 69.5, 121.4, 122.1, 126.7, 127.3, 127.4, 128.29, 128.34, 129.69, 129.78, 134.6, 135.9, 137.4, 142.5, 145.0, 145.7, 146.6, 219.0 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{23}O$ $[M+H]^+$ 351.1749, found 373.1745.




**5'-Methoxy-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ca):** Purified by method A to give **3ca** as an off-white solid (53 mg, 73% yield). M.p.: 142-144 ºC. $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.93-2.02 (m, 1H), 2.22-2.38 (m, 2H), 2.41-2.53 (m, 2H), 2.67-2.75 (m, 1H), 3.79 (s, 3H), 6.78 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.91 (d, *J* = 2.0 Hz, 1H), 7.02-7.04 (m, 2H), 7.21-7.34 (m, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 20.2, 32.9, 39.8, 55.7, 69.2, 107.3, 111.6, 122.2, 127.4, 127.5, 128.3, 128.4, 129.6, 129.7, 134.4, 135.8, 140.8, 142.4, 146.4, 147.6, 159.7, 219.0 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{23}O_2$ $[M+H]^+$ 367.1698, found 367.1693.

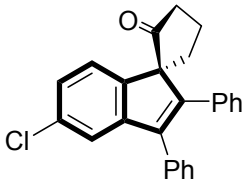



**2',3'-Diphenyl-5'-(trifluoromethyl)spiro[cyclopentane-1,1'-inden]-2-one (3da):** Purified by method A to give **3da** as an off-white solid (54 mg, 67% yield). M.p.: 178-180 ºC. $^1$H NMR (400 MHz, $CDCl_3$): *δ* = 1.94-2.04 (m, 1H), 2.23-2.35 (m, 1H), 2.39-2.56 (m, 3H), 2.68-2.76 (m, 1H), 7.03-7.05 (m, 2H), 7.23-7.34 (m, 8H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 20.3, 32.6, 40.1, 70.0, 118.0 (q, $J_{CF}$ = 3.7 Hz), 121.8, 123.0 (q, $J_{CF}$ = 3.9 Hz), 124.5 (q, $J_{CF}$ = 270.7 Hz), 127.8, 127.9, 128.5, 128.6, 129.56, 129.58, 130.1 (q, $J_{CF}$ = 31.9 Hz), 133.7, 135.2, 141.7, 145.7, 148.2, 151.9, 217.5 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{20}F_3O$ $[M+H]^+$ 405.1466, found 405.1460.

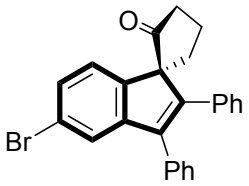



**5'-Fluoro-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ea):** Purified by method A to give **3ea** as an off-white solid (48 mg, 67% yield). M.p.: 122-124 ºC. $^1$H NMR (400 MHz, $CDCl_3$): *δ* = 1.93-2.03 (m, 1H), 2.21-2.54 (m, 4H), 2.66-2.74 (m, 1H), 6.89 (td, *J* = 9.2 Hz, 2.4 Hz, 1H), 7.02-7.06 (m, 3H), 7.22-7.30 (m, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): *δ* = 20.3, 32.7, 39.9, 69.3, 108.7 (d, $J_{CF}$ = 23.8 Hz), 112.5 (d, $J_{CF}$ = 23.1 Hz), 122.5 (d, $J_{CF}$ = 9.1 Hz), 127.6, 127.7, 128.4,

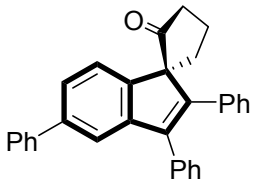
128.5, 129.56, 129.58, 133.9, 135.5, 141.9 (d, $J_{CF}$ = 3.1 Hz), 143.9 (d, $J_{CF}$ = 2.5 Hz), 147.1 (d, $J_{CF}$ = 8.7 Hz), 148.3, 163.0 (d, $J_{CF}$ = 242.4 Hz), 218.3 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{20}FO$ $[M+H]^+$ 355.1498, found 355.1498.




**5'-Chloro-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3fa):** Purified by method A to give **3fa** as an off-white solid (48 mg, 65% yield). M.p.: 148-150 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.94-2.04 (m, 1H), 2.24-2.56 (m, 4H), 2.68-2.77 (m, 1H), 7.03-7.04 (m, 2H), 7.20-7.36 (m, 11H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.7, 40.0, 69.5, 121.6, 122.6, 125.8, 127.6, 127.8, 128.4, 128.5, 129.55, 129.60, 133.7, 133.8, 135.4, 141.7, 146.7, 146.8, 148.0, 218.0 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{20}ClO$ $[M+H]^+$ 371.1203, found 371.1198.

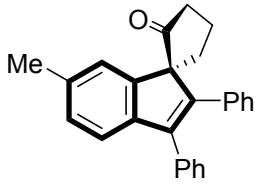



**5'-Bromo-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ga):** Purified by method A to give **3ga** as an off-white solid (54 mg, 65% yield). M.p.: 174-176 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.92-2.02 (m, 1H), 2.20-2.54 (m, 4H), 2.65-2.74 (m, 1H), 7.01-7.03 (m, 2H), 7.19-7.37 (m, 10H), 7.46 (d, $J$ =1.4 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.6, 40.0, 69.6, 121.8, 123.0, 124.5, 127.7, 127.8, 128.4, 128.5, 128.7, 129.58, 129.61, 133.8, 135.3, 141.7, 147.1, 147.2, 147.9, 217.8 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{20}BrO$ $[M+H]^+$ 415.0698, found 415.0698.

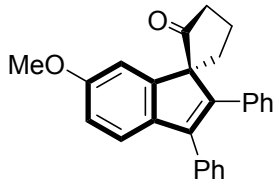



**2',3',5'-Triphenylspiro[cyclopentane-1,1'-inden]-2-one (3ha):** Purified by method A to give **3ha** as an off-white solid (67 mg, 82% yield). M.p.: 177-179 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.97-2.07 (m, 1H), 2.28-2.58 (m, 4H), 2.72-2.80 (m, 1H), 7.05-7.07 (m, 2H), 7.23-7.37 (m, 9H), 7.40-7.47 (m, 4H), 7.55-7.57 (m, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.9, 40.0, 69.7, 120.3, 121.9, 125.2, 127.3, 127.4, 127.5, 128.36,

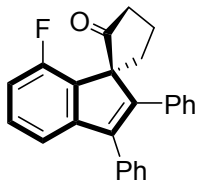
128.44, 128.8, 129.7, 129.8, 134.0, 135.8, 141.1, 141.6, 142.5, 145.5, 147.0, 147.6, 218.8 ppm. HRMS (ESI$^+$): calcd for $C_{31}H_{25}O$ $[M+H]^+$ 413.1905, found 413.1897.




**6'-methyl-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ia):** Purified by method A to give **3ia** as an off-white solid (48 mg, 69% yield). M.p.: 148-150 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.92-2.02 (m, 1H), 2.26-2.54 (m, 7H), 2.68-2.76 (m, 1H), 7.02-7.05 (m, 2H), 7.12 (d, $J$ = 8.0 Hz, 1H), 7.16 (s, 1H), 7.20-7.33 (m, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 21.8, 32.9, 40.1, 69.6, 121.1, 122.6, 127.2, 127.4, 128.2, 128.3, 129.7, 134.7, 135.9, 136.0, 142.2, 142.3, 145.4, 148.9, 219.1 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{23}O$ $[M+H]^+$ 351.1749, found 351.1743.

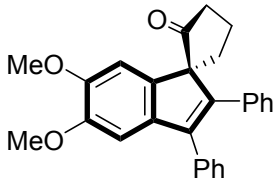



**6'-methoxy-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ja):** Purified by method A to give **3ba** as an off-white solid (50 mg, 71% yield). M.p.: 152-154 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.90-2.01 (m, 1H), 2.21-2.53 (m, 4H), 2.66-2.74 (m, 1H), 3.84 (s, 3H), 6.84 (dd, $J$ = 8.4 Hz, 2.0 Hz, 1H), 6.92 (d, $J$ = 2.4 Hz, 1H), 7.02-7.04 (m, 2H), 7.20-7.33 (m, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.2, 33.0, 39.9, 55.8, 69.6, 109.2, 111.9, 121.8, 127.2, 127.4, 128.3, 129.7, 129.8, 134.7, 136.0, 137.8, 142.0, 144.3, 150.2, 158.6, 218.7 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{23}O_2$ $[M+H]^+$ 367.1698, found 367.1692.

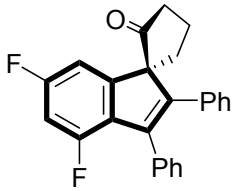



**7'-fluoro-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ka):** Purified by method A to give **3ka** as an off-white solid (30 mg, 42% yield). M.p.: 148-150 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.59-1.69 (m, 1H), 2.17-2.27 (m, 1H), 2.40-2.48 (m, 2H), 2.68-2.76 (m, 2H), 6.92 (t, $J$ = 8.4 Hz, 1H), 7.05-7.07 (m, 2H), 7.14 (d, $J$ = 7.6 Hz, 1H), 7.23-7.30 (m, 9H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.1 (d, $J_{CF}$ = 3.1 Hz), 31.4, 40.7, 68.1 (d, $J_{CF}$

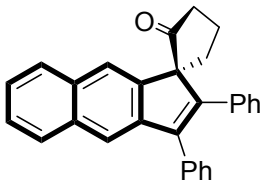
= 2.5 Hz), 113.3 (d, $J_{CF}$ = 21.0 Hz), 117.3 (d, $J_{CF}$ = 2.8 Hz), 127.6, 127.8, 128.3, 128.5, 129.56 (d, $J_{CF}$ = 8.6 Hz), 129.62, 129.64, 133.6 (d, $J_{CF}$ = 15.6 Hz), 133.9, 135.6, 141.3 (d, $J_{CF}$ = 2.4 Hz), 147.9, 148.3 (d, $J_{CF}$ = 6.1 Hz), 157.8 (d, $J_{CF}$ = 244.9 Hz), 218.5 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{20}FO$ $[M+H]^+$ 355.1498, found 355.1494.



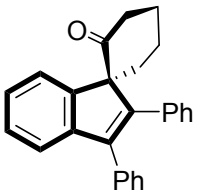

**5',6'-dimethoxy-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3la):** Purified by method A to give **3ma** as an off-white solid (38 mg, 48% yield). M.p.: 178-180 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.87-1.97 (m, 1H), 2.17-2.28 (m, 1H), 2.36-2.53 (m, 3H), 2.65-2.74 (m, 1H), 3.83 (s, 3H), 3.92 (s, 3H), 6.88 (s, 1H), 6.89 (s, 1H), 7.01-7.03 (m, 2H), 7.20-7.31 (m, 8H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 33.0, 40.1, 56.3, 56.6, 69.6, 105.1, 106.2, 127.2, 127.4, 128.3, 128.4, 129.6, 129.7, 134.7, 136.0, 137.9, 141.0, 142.1, 145.4, 148.1, 149.2, 219.2 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{25}O_3$ $[M+H]^+$ 397.1804, found 397.1806.



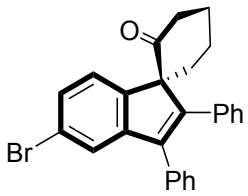

**4',6'-difluoro-2',3'-diphenylspiro[cyclopentane-1,1'-inden]-2-one (3ma):** Purified by method A to give **3la** as an off-white solid (30 mg, 41% yield). M.p.: 118-120 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.83-1.94 (m, 1H), 2.14-2.25 (m, 1H), 2.37-2.52 (m, 3H), 2.62-2.71 (m, 1H), 6.75 (t, $J$ = 8.4 Hz, 1H), 6.88 (dd, $J$ = 8.0 Hz, 2.0 Hz, 1H), 6.97-6.99 (m, 2H), 7.20-7.28 (m, 8H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.2, 33.0, 40.0, 70.4 (dd, $J_{CF}$ = 1.5 Hz, 1.0 Hz), 103.7 (t, $J_{CF}$ = 25.6 Hz), 105.9 (dd, $J_{CF}$ = 23.4 Hz, 3.9 Hz), 127.5, 127.6, 127.7, 128.4, 129.7, 129.8 (d, $J_{CF}$ = 2.2 Hz), 134.5 (d, $J_{CF}$ = 1.6 Hz), 135.1, 139.6 (dd, $J_{CF}$ = 3.9 Hz, 1.3 Hz), 146.8 (dd, $J_{CF}$ = 3.8 Hz, 1.4 Hz), 152.1 (dd, $J_{CF}$ = 9.1 Hz, 6.6 Hz), 156.2 (dd, $J_{CF}$ = 253.5 Hz, 12.5 Hz), 161.7 (dd, $J_{CF}$ = 246.1 Hz, 10.2 Hz), 216.9 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{19}F_2O$ $[M+H]^+$ 373.1404, found 373.1397.



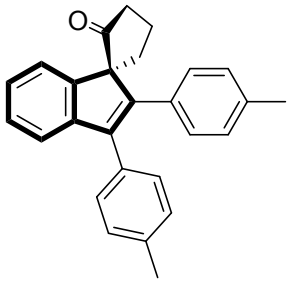
**1,2-diphenylspiro[cyclopenta[a]naphthalene-3,1'-cyclopentan]-2'-one (3na):** Purified by method A to give **3na** as an off-white solid (45 mg, 59% yield). M.p.: 179-181 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.00-2.08 (m, 1H), 2.38-2.58 (m, 4H), 2.78-2.85 (m, 1H), 7.07-7.10 (m, 2H), 7.23-7.45 (m, 10H), 7.71 (s, 1H), 7.74 (s, 1H), 7.78-7.83 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 33.6, 39.7, 69.0, 119.5, 120.5, 125.6, 126.0, 127.5, 127.6, 128.0, 128.3, 128.36, 128.45, 129.7, 129.9, 132.4, 133.5, 134.5, 135.8, 142.6, 143.4, 146.8, 147.4, 218.8 ppm. HRMS (ESI$^+$): calcd for $C_{29}H_{23}O$ $[M+H]^+$ 387.1749, found 387.1749.



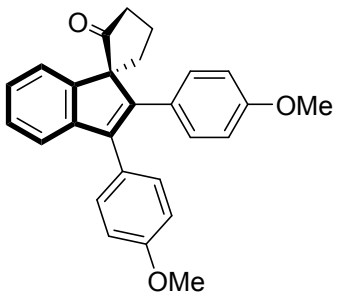

**2',3'-diphenylspiro[cyclohexane-1,1'-inden]-2-one (3oa):** Purified by method A to give **3oa** as an off-white solid (52 mg, 74% yield). M.p.: 152-154 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.83-1.91 (m, 3H), 2.18-2.31 (m, 3H), 2.69-2.74 (m, 1H), 2.92-3.01 (m, 1H), 7.12-7.38 (m, 13H), 7.74-7.77 (m, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 22.0, 25.3, 34.2, 41.1, 70.2, 121.6, 123.2, 125.4, 127.1, 127.5, 127.8, 128.0, 128.5, 129.9, 130.6, 135.0, 136.0, 142.0, 144.9, 147.1, 148.6, 208.8 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{23}O$ $[M+H]^+$ 351.1749, found 351.1743.



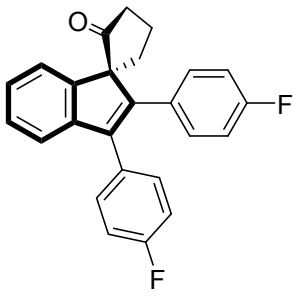

**5'-bromo-2',3'-diphenylspiro[cyclohexane-1,1'-inden]-2-one (3pa):** Purified by method A to give **3pa** as an off-white solid (52 mg, 61% yield). M.p.: 162-164 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.81-1.91 (m, 3H), 2.19-2.26 (m, 3H), 2.68-2.72 (m, 1H), 2.84-2.93 (m, 1H), 7.08-7.10 (m, 2H), 7.17-7.20 (m, 3H), 7.28-7.37 (m, 6H), 7.42 (d, $J$ = 2.0 Hz, 1H), 7.59 (d, $J$ = 8.0 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 21.9, 25.2, 34.1, 41.0, 69.8, 122.1, 124.4, 124.6, 127.4, 127.8, 128.07, 128.13, 128.6, 129.8, 130.5, 134.3, 135.4, 141.2, 145.9, 147.1, 150.2, 208.1 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{22}BrO$ $[M+H]^+$ 429.0854, found 429.0853.




**2',3'-di-p-tolylspiro[cyclopentane-1,1'-inden]-2-one (3ab):** Purified by method A to give **3ab** as an off-white solid (49 mg, 68% yield). M.p.: 182-184 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.96-2.04 (m, 1H), 2.24-2.40 (m, 8H), 2.43-2.55 (m, 2H), 2.68-2.76 (m, 1H), 6.94 (d, $J$ = 8.4 Hz, 2H), 7.04 (d, $J$ = 8.0 Hz, 2H), 7.12 (d, $J$ = 8.0 Hz, 2H), 7.20-7.24 (m, 3H), 7.28-7.38 (m, 3H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 21.35, 21.45, 32.9, 40.0, 69.8, 121.3, 121.6, 125.8, 127.5, 129.0, 129.5, 129.6, 131.6, 132.9, 136.9, 137.0, 142.0, 145.1, 146.0, 148.6, 219.0 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{25}O$ $[M+H]^+$ 365.1905, found 365.1900.

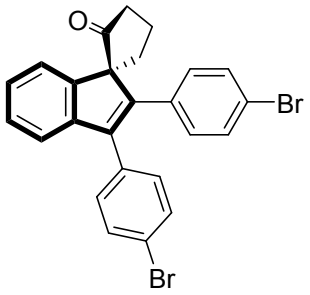



**2',3'-bis(4-methoxyphenyl)spiro[cyclopentane-1,1'-inden]-2-one (3ac):** Purified by method A to give **3ac** as an off-white solid (47 mg, 59% yield). M.p.: 126-128 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.97-2.07 (m, 1H), 2.25-2.38 (m, 2H), 2.40-2.55 (m, 2H), 2.67-2.76 (m, 1H), 3.78 (s, 3H), 3.80 (s, 3H), 6.76 (d, $J$ = 8.8 Hz, 2H), 6.84 (d, $J$ = 8.8 Hz, 2H), 6.96 (d, $J$ = 8.8 Hz, 2H), 7.21 (t, $J$ = 7.2 Hz, 1H), 7.25-7.37 (m, 5H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.9, 40.0, 55.26, 55.29, 69.7, 113.8, 121.2, 121.6, 125.8, 127.0, 127.5, 128.2, 130.9, 131.0, 141.5, 145.1, 145.4, 148.5, 158.7, 158.8, 219.2 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{25}O_3$ $[M+H]^+$ 397.1804, found 397.1796.

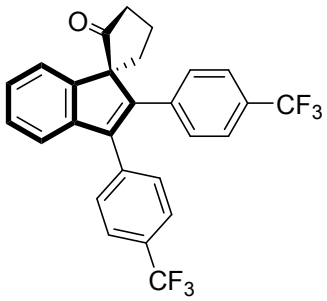



**2',3'-bis(4-fluorophenyl)spiro[cyclopentane-**

**1,1'-inden]-2-one (3ad)**: Purified by method A to give **3ad** as an off-white solid (54 mg, 73% yield). M.p.: 140-142 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.96-2.06 (m, 1H), 2.29-2.52 (m, 4H), 2.69-2.77 (m, 1H), 6.94 (t, $J$ = 8.8 Hz, 2H), 6.98-7.02 (m, 4H), 7.23-7.29 (m, 3H), 7.32 (d, $J$ = 8.0 Hz, 2H), 7.36 (d, $J$ = 7.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.6, 39.9, 69.9, 115.52 (d, $J_{CF}$ =21.3 Hz), 115.56 (d, $J_{CF}$ =21.2 Hz), 121.2, 121.8, 126.3, 127.7, 130.2 (d, $J_{CF}$ = 3.4 Hz), 131.35 (d, $J_{CF}$ = 8.0 Hz), 131.38 (d, $J_{CF}$ =8.0 Hz), 131.6 (d, $J_{CF}$ = 3.4 Hz), 142.0, 144.4, 145.4, 148.2, 162.1 (d, $J_{CF}$ = 246.0 Hz), 162.2 (d, $J_{CF}$ = 245.4 Hz), 218.5 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{19}F_2O$ $[M+H]^+$ 373.1404, found 373.1399.

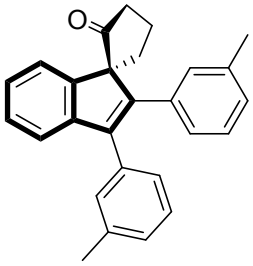



**2',3'-bis(4-bromophenyl)spiro[cyclopentane-1,1'-inden]-2-one (3ae)**: Purified by method A to give **3ae** as an off-white solid (62 mg, 63% yield). M.p.: 208-210 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.99-2.07 (m, 1H), 2.30-2.53 (m, 4H), 2.70-2.78 (m, 1H), 6.89 (d, $J$ = 8.4 Hz, 2H), 7.18 (d, $J$ = 8.4 Hz, 2H), 7.23-7.38 (m, 6H), 7.45 (d, $J$ = 8.0 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.6, 39.8, 69.9, 121.3, 121.79, 121.82, 121.8, 126.5, 127.8, 131.2, 131.3, 131.76, 131.78, 133.1, 134.5, 142.1, 144.0, 145.4, 148.3, 218.2 ppm. HRMS (ESI$^+$): calcd for $C_{25}H_{19}Br_2O$ $[M+H]^+$ 492.9803, found 492.9799.

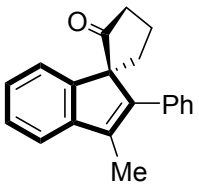



**2',3'-bis(4-(trifluoromethyl)phenyl)spiro[cyclopentane-1,1'-inden]-2-one (3af)**: Purified by method A to give **3af** as an off-white solid (57 mg, 60% yield). M.p.: 166-168 ºC. $^{1}$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.00-2.09 (m, 1H), 2.34-2.55 (m, 4H), 2.74-2.82 (m, 1H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.27-7.34 (m, 3H), 7.39-7.44 (m, 3H), 7.51 (d, $J$ = 8.0 Hz, 2H), 7.59 (d, $J$ = 8.4 Hz, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 32.4, 39.7,

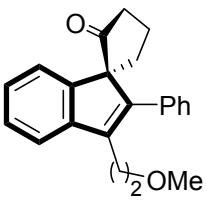
70.2, 121.4, 121.9, 124.1 (q, $J_{CF}$ = 270.5 Hz), 124.2 (q, $J_{CF}$ = 270.8 Hz), 125.48-125.55 (m), 126.9, 127.9, 129.8 (q, $J_{CF}$ = 32.3 Hz), 129.92 (q, $J_{CF}$ = 32.3 Hz), 129.98, 130.0, 142.8, 143.7, 145.8, 148.2, 217.6 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{19}F_6O$ $[M+H]^+$ 473.1340, found 473.1337.



**2',3'-di-m-tolylspiro[cyclopentane-1,1'-inden]-2-one (3ag)**: Purified by method A to give **3ag** as a light yellow oil (48 mg, 66% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.94-2.04 (m, 1H), 2.25 (s, 3H), 2.30-2.54 (m, 7H), 2.67-2.76 (m, 1H), 6.84 (d, $J$ = 7.6 Hz, 1H), 6.86 (s, 1H), 7.02 (d, $J$ = 7.6 Hz, 1H), 7.06-7.12 (m, 3H), 7.16-7.20 (m, 2H), 7.23 (td, $J$ = 7.6 Hz, 1.2 Hz, 1H), 7.30 (td, $J$ = 7.6 Hz, 1.2 Hz, 1H), 7.33-7.36 (m, 2H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.3, 21.56, 21.6, 32.8, 40.0, 69.8, 121.4, 121.6, 125.9, 126.9, 127.0, 127.5, 128.09, 128.11,128.15, 128.2, 130.1, 130.3, 134.5, 135.8, 137.7, 142.4, 145.1, 146.3, 148.5, 218.9 ppm. HRMS (ESI$^+$): calcd for $C_{27}H_{25}O$ $[M+H]^+$ 365.1905, found 365.1904.

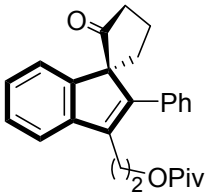


**3'-methyl-2'-phenylspiro[cyclopentane-1,1'-inden]-2-one (3ah)**: Purified by method A to give **3ah** as an off-white solid (28 mg, 51% yield). M.p.: 142-143 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.88-1.98 (m, 1H), 2.10 (s, 3H), 2.21-2.46 (m, 4H), 2.61-2.69 (m, 1H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.19-7.23 (m, 1H), 7.29 (d, $J$ = 7.6 Hz, 1H), 7.32-7.40 (m, 5H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 10.6, 19.3, 31.6, 38.9, 68.6, 119.0, 120.3, 124.8, 126.5, 126.6, 127.5, 128.3, 135.2, 136.8, 144.1, 145.0, 147.2, 218.6 ppm. HRMS (ESI$^+$): calcd for $C_{20}H_{19}O$ $[M+H]^+$ 275.1436, found 275.1439.

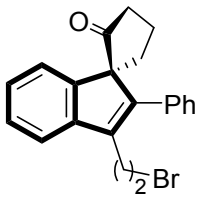


**3'-(2-methoxyethyl)-2'-phenylspiro[cyclopentane-1,1'-inden]-2-one (3ai)**: Purified by method B

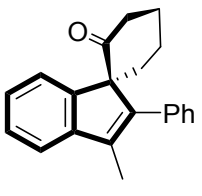
to give **3ai** as a light yellow oil (31 mg, 49% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.77-1.87 (m, 1H), 2.13-2.24 (m, 1H), 2.28-2.44 (m, 3H), 2.55-2.63 (m, 1H), 2.71-2.84 (m, 2H), 3.29 (s, 3H), 3.49-3.60 (m, 2H), 7.16-7.22 (m, 3H), 7.27 (d, $J$ = 8.4 Hz, 1H), 7.31-7.42 (m, 5H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.2, 26.8, 32.4, 39.9, 58.7, 69.8, 71.5, 120.2, 121.6, 125.8, 127.5, 127.8, 128.6, 129.3, 136.0, 138.3, 145.0, 147.3, 148.3, 218.9 ppm. HRMS (ESI$^+$): calcd for $C_{22}H_{23}O_2$ $[M+H]^+$ 319.1698, found 319.1696.




**2-(2-oxo-2'-phenylspiro[cyclopentane-1,1'-inden]-3'-yl)ethyl pivalate (3aj)**: Purified by method B to give **3aj** as an off-white solid (49 mg, 63% yield). M.p.: 108-110 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.13 (s, 9H), 1.77-1.87 (m, 1H), 2.14-2.25 (m, 1H), 2.27-2.43 (m, 3H), 2.55-2.63 (m, 1H), 2.74-2.88 (m, 2H), 4.22 (t, $J$ = 7.6 Hz, 2H), 7.16-7.22 (m, 3H), 7.27 (d, $J$ = 7.2 Hz, 1H), 7.32-7.41 (m, 4H), 7.50 (d, $J$ = 7.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.2, 25.8, 27.3, 32.5, 38.8, 39.9, 63.2, 69.9, 120.4, 121.6, 125.9, 127.6, 127.9, 128.7, 129.2, 135.9, 137.6, 144.8, 147.6, 148.2, 178.8, 218.6 ppm. HRMS (ESI$^+$): calcd for $C_{26}H_{29}O_3$ $[M+H]^+$ 389.2117, found 389.2119.




**3'-(2-bromoethyl)-2'-phenylspiro[cyclopentane-1,1'-inden]-2-one (3ak)**: Purified by method A to give **3ak** as a light yellow oil (31 mg, 42% yield). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.75-1.85 (m, 1H), 2.13-2.45 (m, 4H), 2.54-2.63 (m, 1H), 2.95-3.12 (m, 2H), 3.42-3.53 (m, 2H), 7.15 (dd, $J$ = 7.6 Hz, 1.2 Hz, 2H), 7.22 (td, $J$ = 7.6 Hz, 1.2 Hz, 1H), 7.29 (d, $J$ = 7.6 Hz, 1H), 7.32-7.42 (m, 5H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 20.2, 30.17, 30.23, 32.3, 39.9, 70.0, 119.8, 121.8, 126.1, 127.7, 128.1, 128.8, 129.1, 135.6, 138.7, 144.1, 148.01, 148.21, 218.3 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{20}BrO$ $[M+H]^+$ 367.0698, found 367.0696.

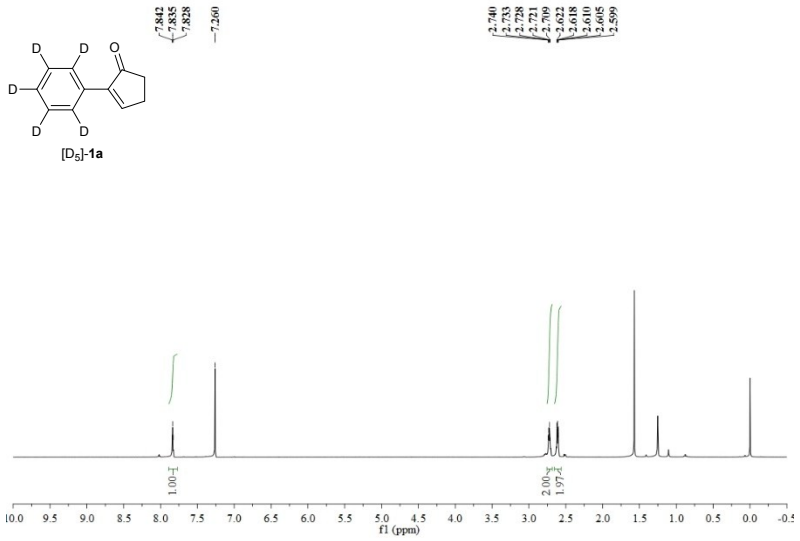


**3'-methyl-2'-phenylspiro[cyclohexane-1,1'-inden]-2-one (3oh)**: Purified by method A to give **3oh** as an off-white solid (36 mg, 63% yield). M.p.: 123-125 ºC. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 1.73-1.85 (m, 3H), 2.09-2.21 (m, 6H), 2.60-2.65 (m, 1H), 2.84-2.93 (m, 1H), 7.19-7.40 (m, 8H), 7.66 (d, $J$ = 7.6 Hz, 1H) ppm. $^{13}$C NMR (100 MHz, $CDCl_3$): $\delta$ = 11.9, 22.1, 25.4, 34.3, 41.2, 70.1, 120.2, 122.9, 125.2, 127.2, 127.8, 128.3, 130.2, 136.6, 137.1, 145.9, 146.9, 147.3, 209.4 ppm. HRMS (ESI$^+$): calcd for $C_{21}H_{21}O$ $[M+Na]^+$ 311.1412, found 311.1413.

## VI. Mechanism Study

**Synthesis of 2-([D]$_5$-phenyl)cyclopent-2-enone:**

Following the general procedure by using ([$D_5$]-phenyl)boronic acid instead of phenylboronic acid. 2-([$D_5$]-Phenyl)cyclopent-2-enone was obtained as a white solid in 75% yield, (>98% D). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ = 2.60-2.63 (m, 2H), 2.70-2.74 (m, 2H), 7.84 (t, $J$ = 2.8 Hz, 1H) ppm.

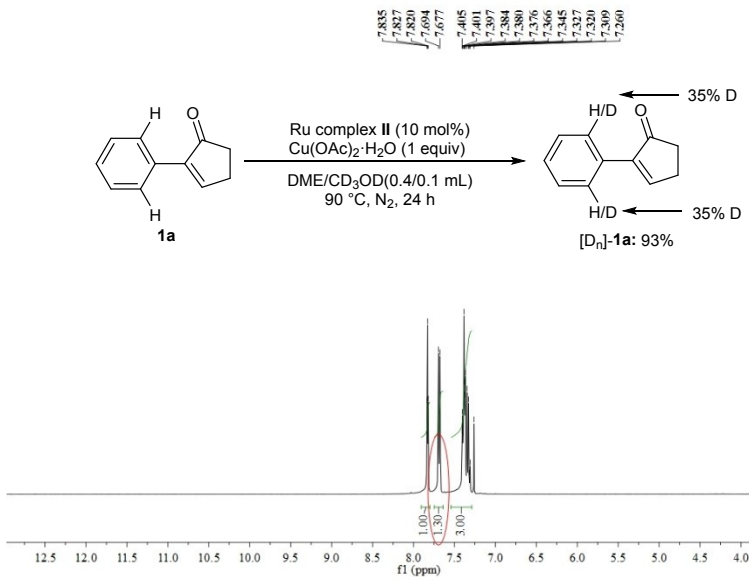



**H/D Exchange Experiment:**

a) H/D exchange in substrate **1a** with $CD_3OD$ as the cosolvent without **2a**:

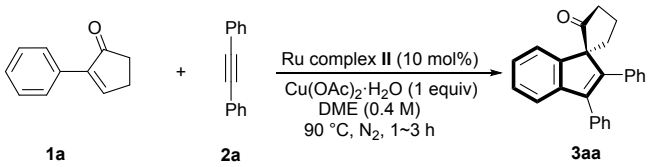
A suspension of Ru complex **II** (16.7 mg, 10 mol%), **1a** (40 mg, 0.25 mmol), and $Cu(OAc)_2 \cdot H_2O$ (40 mg, 0.2 mmol) in a solvent mixture of DME and $CD_3OD$ (0.4/0.1 mL) was stirred at 90 °C for 24 h under an atmosphere of $N_2$. After cooled to ambient temperature, the reaction mixture was filtered through a celite pad and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (PE/EA) to provide [$D_n$]-**1a** (37 mg, 93%) as a

slight yellow solid. The D-incorporation in [$D_n$]-**1a** was estimated by $^1$H-NMR spectroscopy.

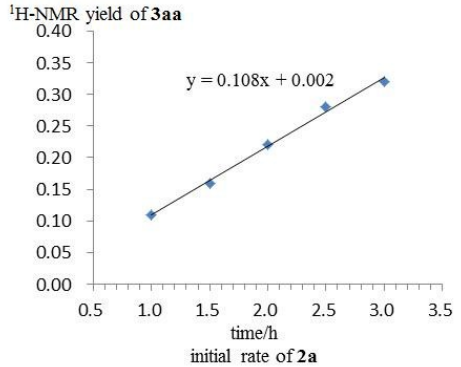


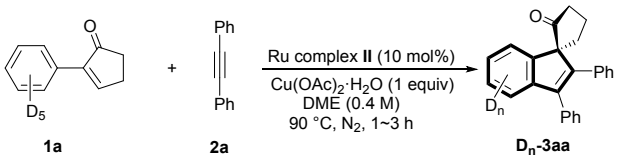

b) KIE experiments with 1a and [$D_5$]-**1a** as substrates:

Two parallel reactions with **1a** and deuterated substrate [$D_5$]-**1a** under the standard conditions were conducted: A suspension of Ru complex **II** (16.7 mg, 10 mol%), substrates **1a** (40 mg, 0.25 mmol) or [$D_5$]-**1a** (41 mg, 0.25 mmol), **2a** (36mg, 0.2 mmol), and $Cu(OAc)_2{\cdot}H_2O$ (40 mg, 0.2 mmol) in DME (0.5 mL) was stirred at 90 °C for 1.0 h, 1.5 h, 2.0 h, 2.5 h, 3.0 h, under an atmosphere of $N_2$, respectively. The consumption of substrate **2a** and the appearance of the products **3aa** or [$D_n$]-**3aa** were monitored by $^1$H-NMR spectroscopy using 0.2 mmol $CH_2Br_2$ as an internal standard. These experiments indicated that the C–H bond cleavage is not involved in the rate-limiting step.



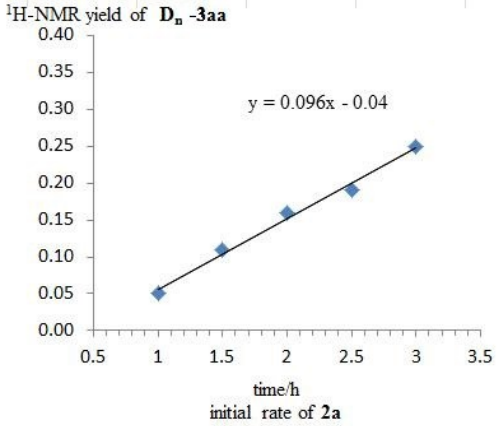

| t/(h) | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| **3aa** | 0.11 | 0.16 | 0.22 | 0.28 | 0.32 |
| **2a** | 0.88 | 0.84 | 0.76 | 0.72 | 0.67 |






1a 2a $D_n$-3aa

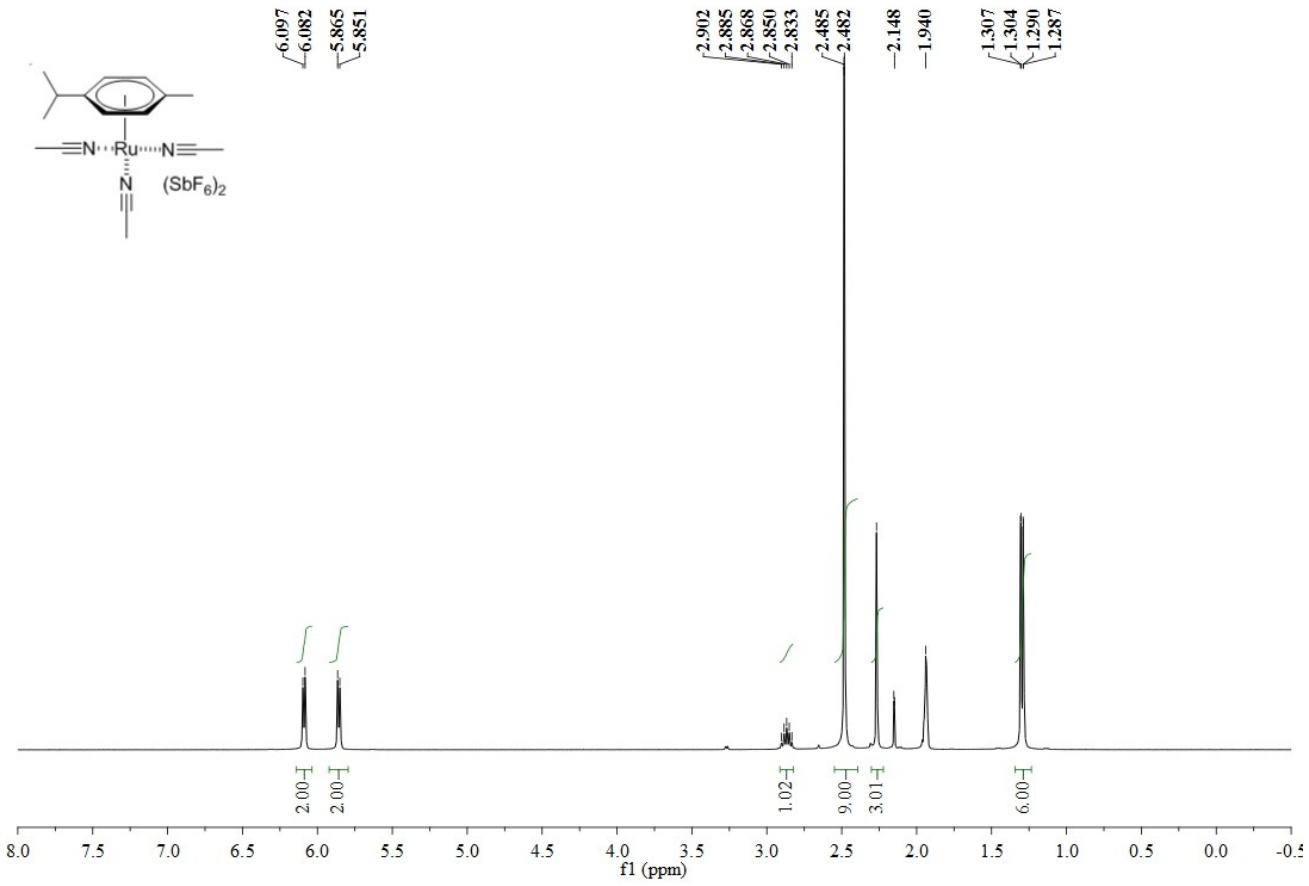
| t/(h) | 1.0 | 1.5 | 2.0 | 2.5 | 3.0 |
|---|---|---|---|---|---|
| [$D_n$]-**3aa** | 0.05 | 0.11 | 0.16 | 0.19 | 0.25 |
| **2a** | 0.92 | 0.85 | 0.80 | 0.78 | 0.74 |

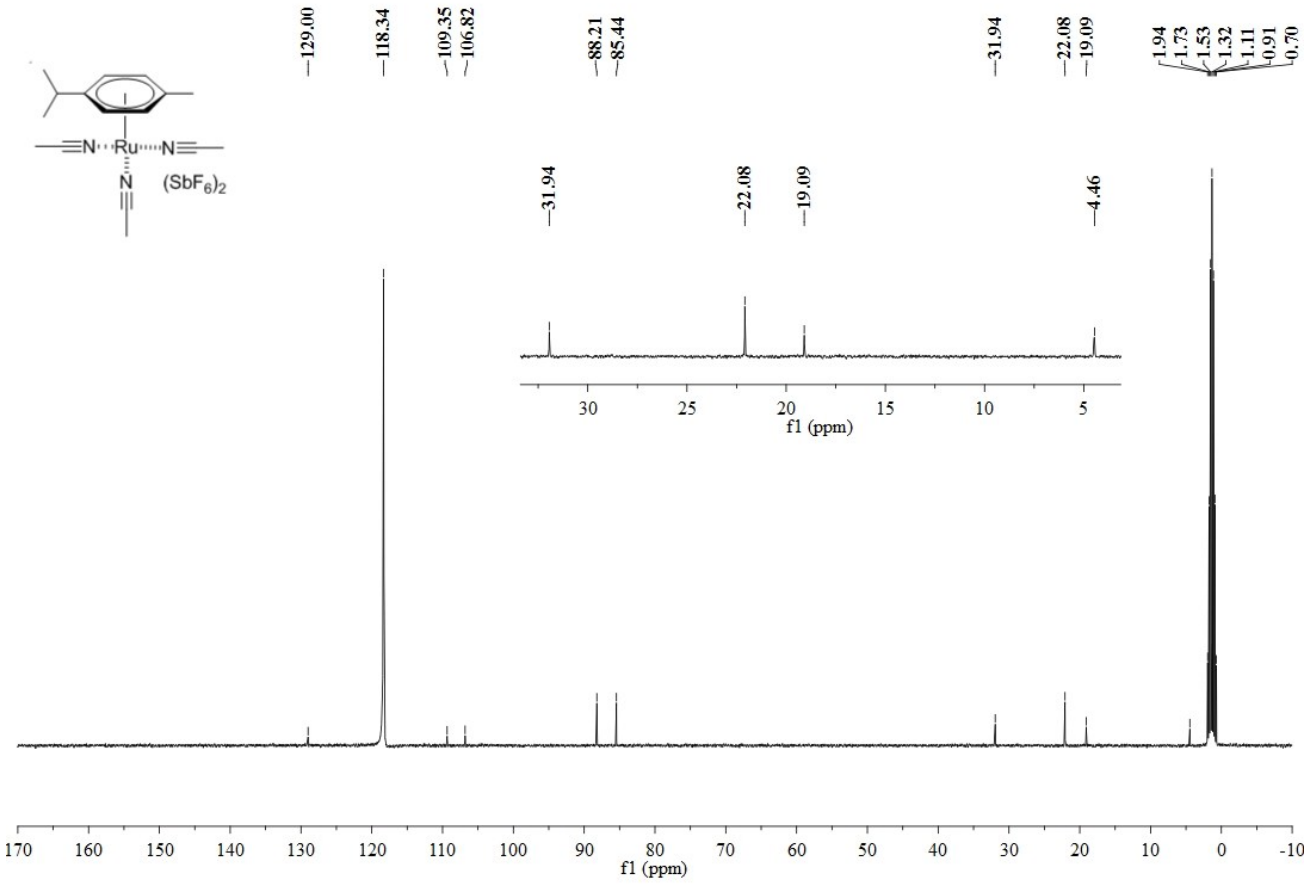


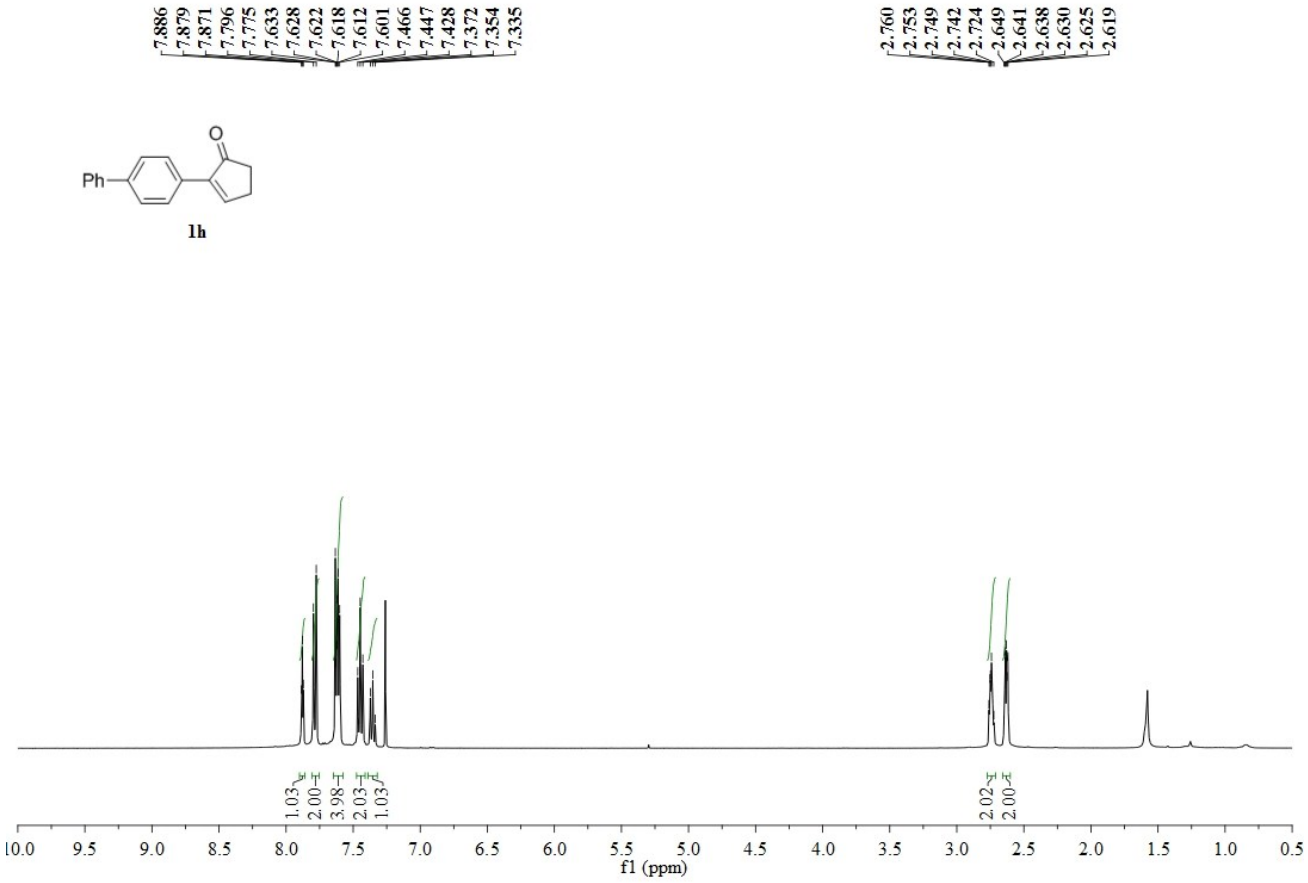

## VII. References


1. (a) Liu, C.; Xie, J.-H.; Li, Y.-L.; Chen, J.-Q.; Zhou, Q.-L. Angew. Chem., Int. Ed. **2013**, *52*, 593. (b) Chiba, S.; Xu, Y.-J.; Wang, Y.-F. *J. Am. Chem. Soc.* **2009**, *131*, 12886.
2. (a) Park, K.; Bae, G.; Moon, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2010**, *75*, 6244; (b) Wang, R.; Falck, J. R. *J. Organomet. Chem.* **2014**, *759*, 33; (c) Paul A. W.; Daniel S. *J. Am. Chem. Soc.* **2009**, *131*, 7528; (d) Fuji, K.; Tsutsumi, K.; Kakiuchi, K.; Morimoto, T. Chem. Commun. **2005**, 3295.

## VIII. Copies of $^{1}H$ and $^{13}C$ NMR Spectra

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7.622
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7.612
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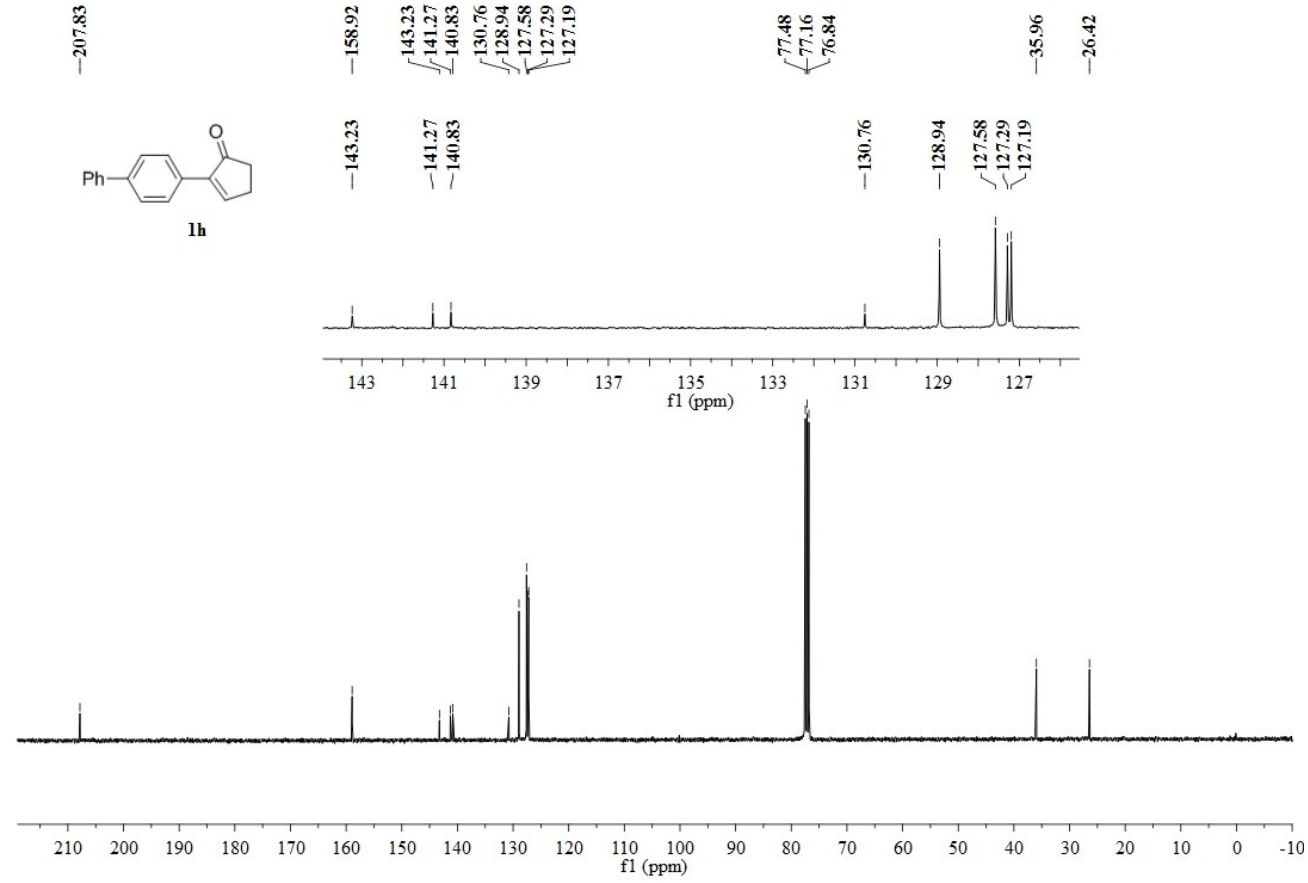
7.447
7.428
7.372
7.354
7.335
2.760
2.753
2.749
2.742
2.724
2.649
2.641
2.638
2.630
2.625
2.619
O
Ph
1h
1.03
2.00
3.98
2.03
1.03
2.02
2.00
f1 (ppm)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158.92
143.23
141.27
140.83
130.76
128.94
127.58
127.29
127.19
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77.16
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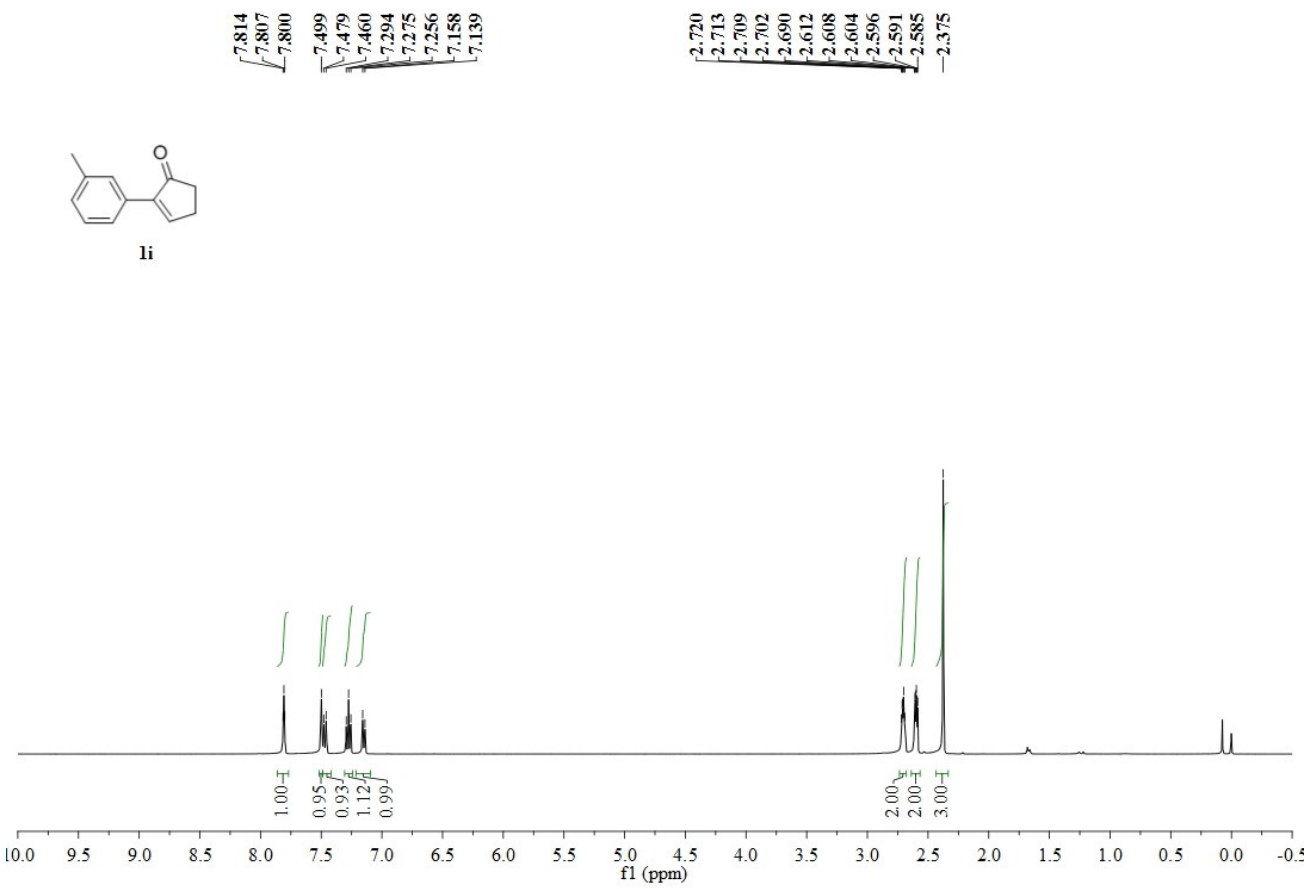
35.96
26.42
O
Ph
1h
f1 (ppm)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7.807
7.800
7.499
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7.460
7.294
7.275
7.256
7.158
7.139
2.720
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2.709
2.702
2.690
2.612
2.608
2.604
2.596
2.591
2.585
2.375
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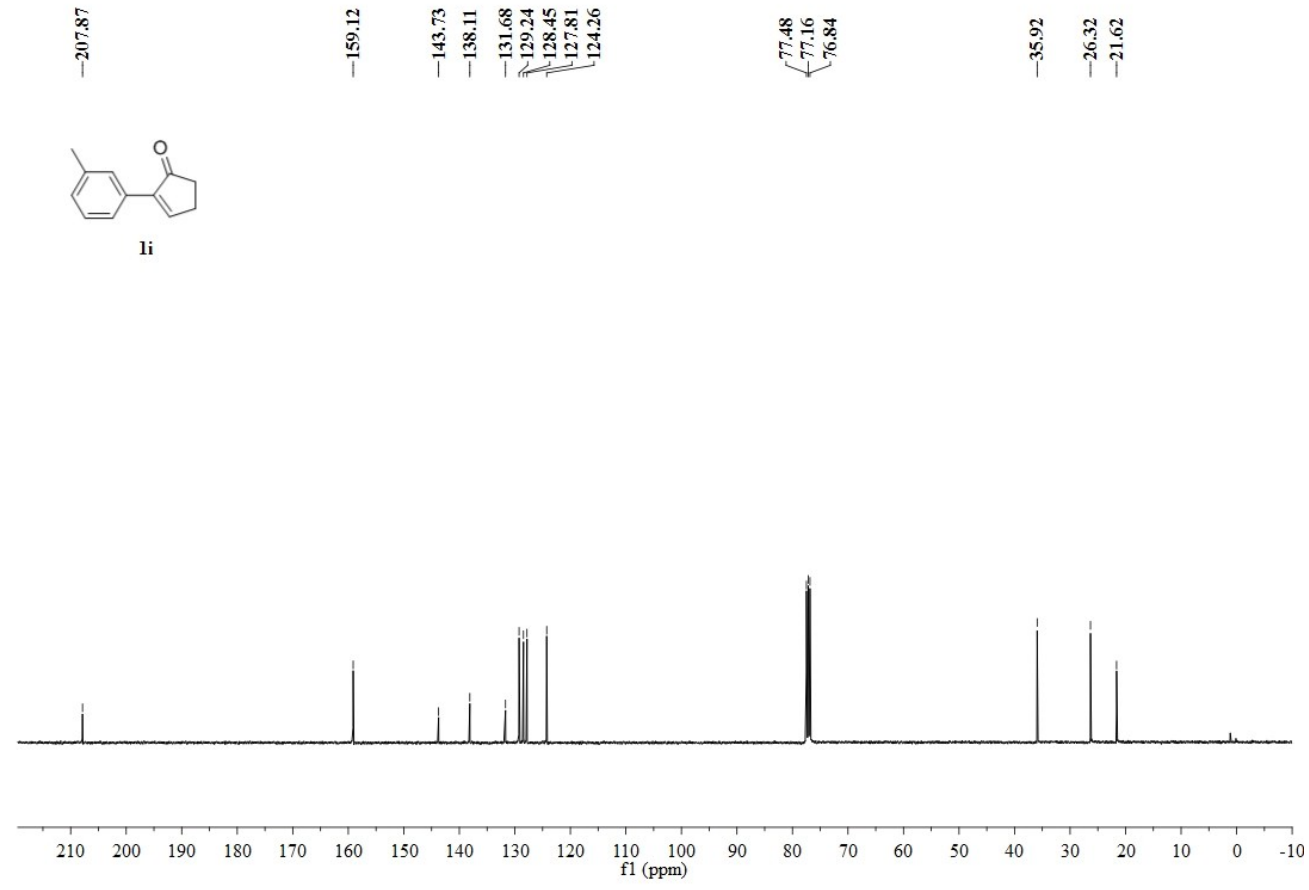
0.95
0.93
1.12
0.99
2.00
2.00
3.00
f1 (ppm)

**1i**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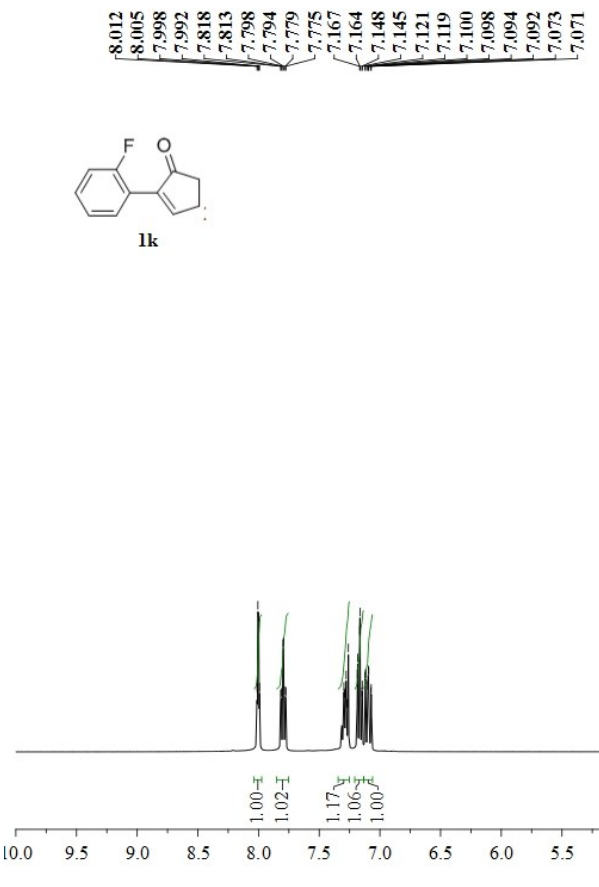
26.32
21.62
f1 (ppm)

**1i**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2.773
2.766
2.761
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2.579
2.573
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2.562
2.561
2.556
F
O
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1.02
1.17
1.06
1.00
2.19
2.15
f1 (ppm)
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162.970
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138.002
137.983
129.711
124.076
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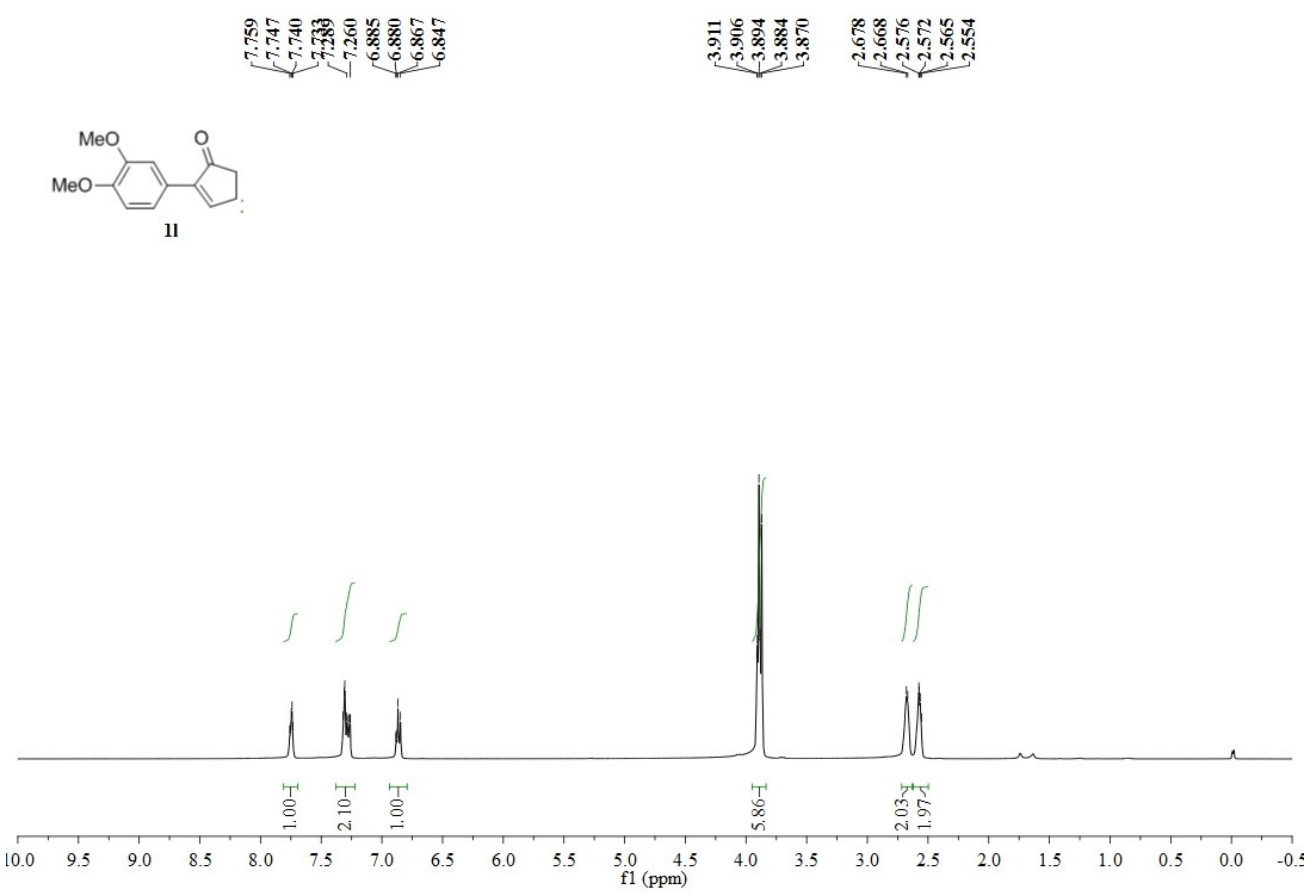
1k
f1 (ppm)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6.880
6.867
6.847
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3.906
3.894
3.884
3.870
2.678
2.668
2.576
2.572
2.565
2.554
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MeO
O
1l
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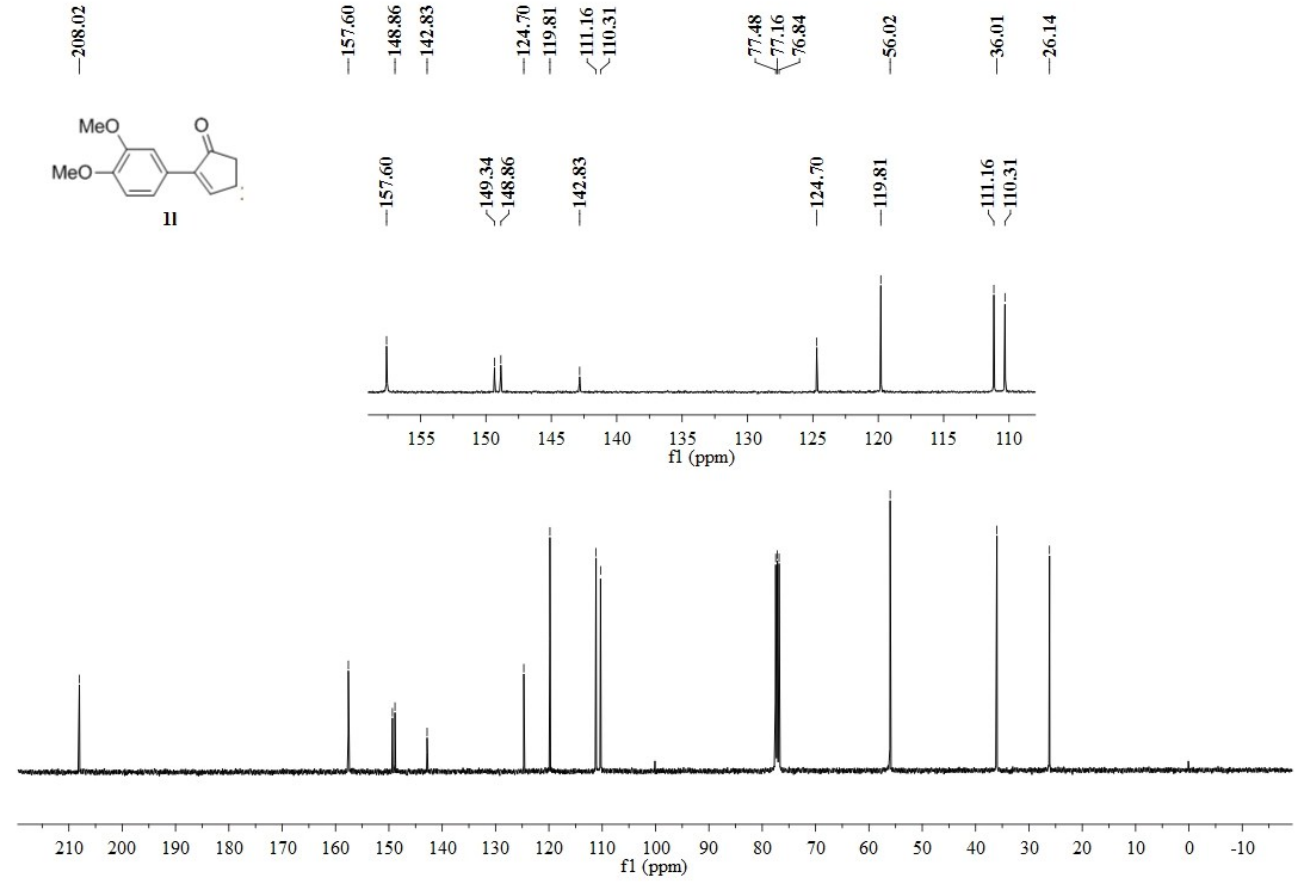
2.10
1.00
5.86
2.03
1.97
f1 (ppm)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110.31
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26.14
MeO
MeO
O
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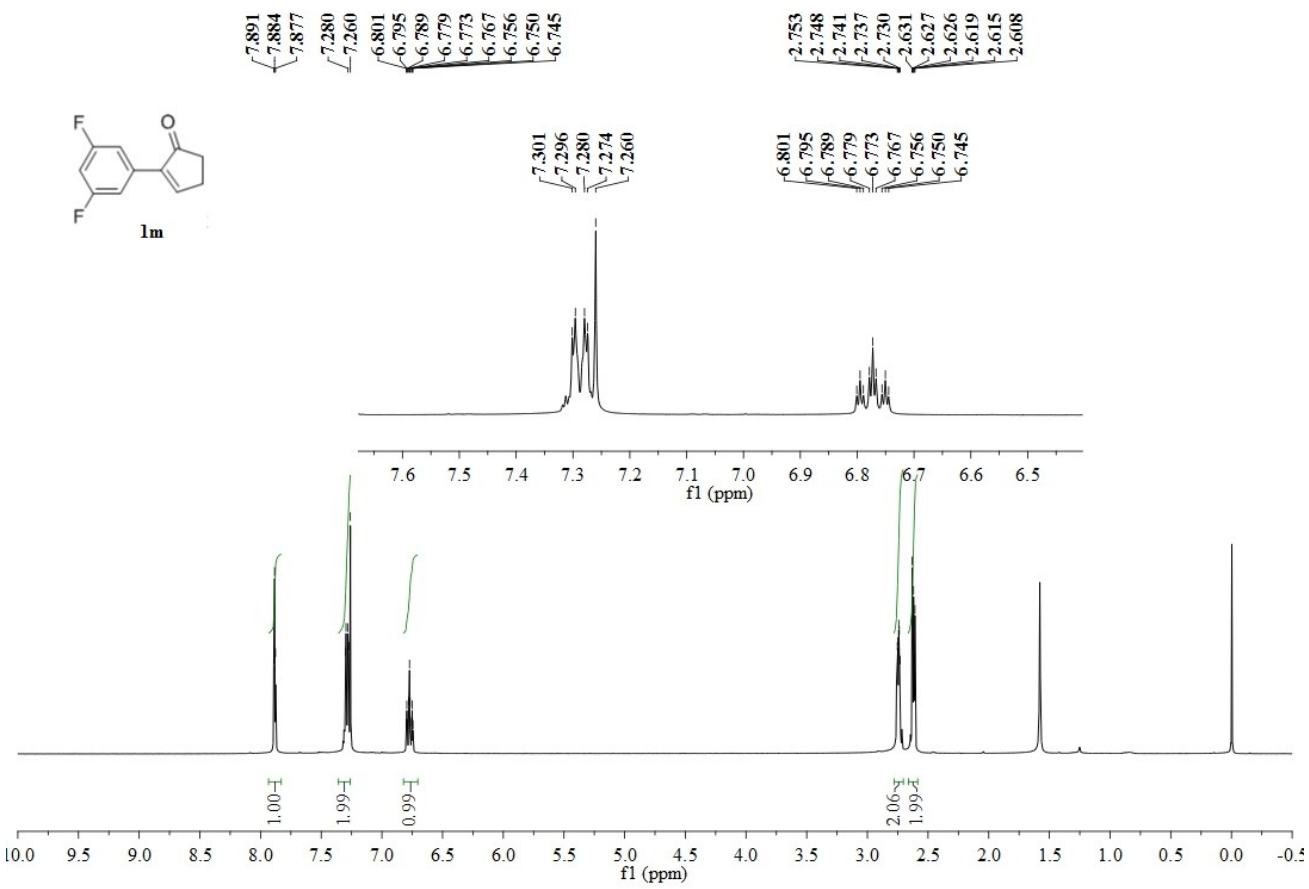
f1 (ppm)
f1 (ppm)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6.789
6.779
6.773
6.767
6.756
6.750
6.745
f1 (ppm)
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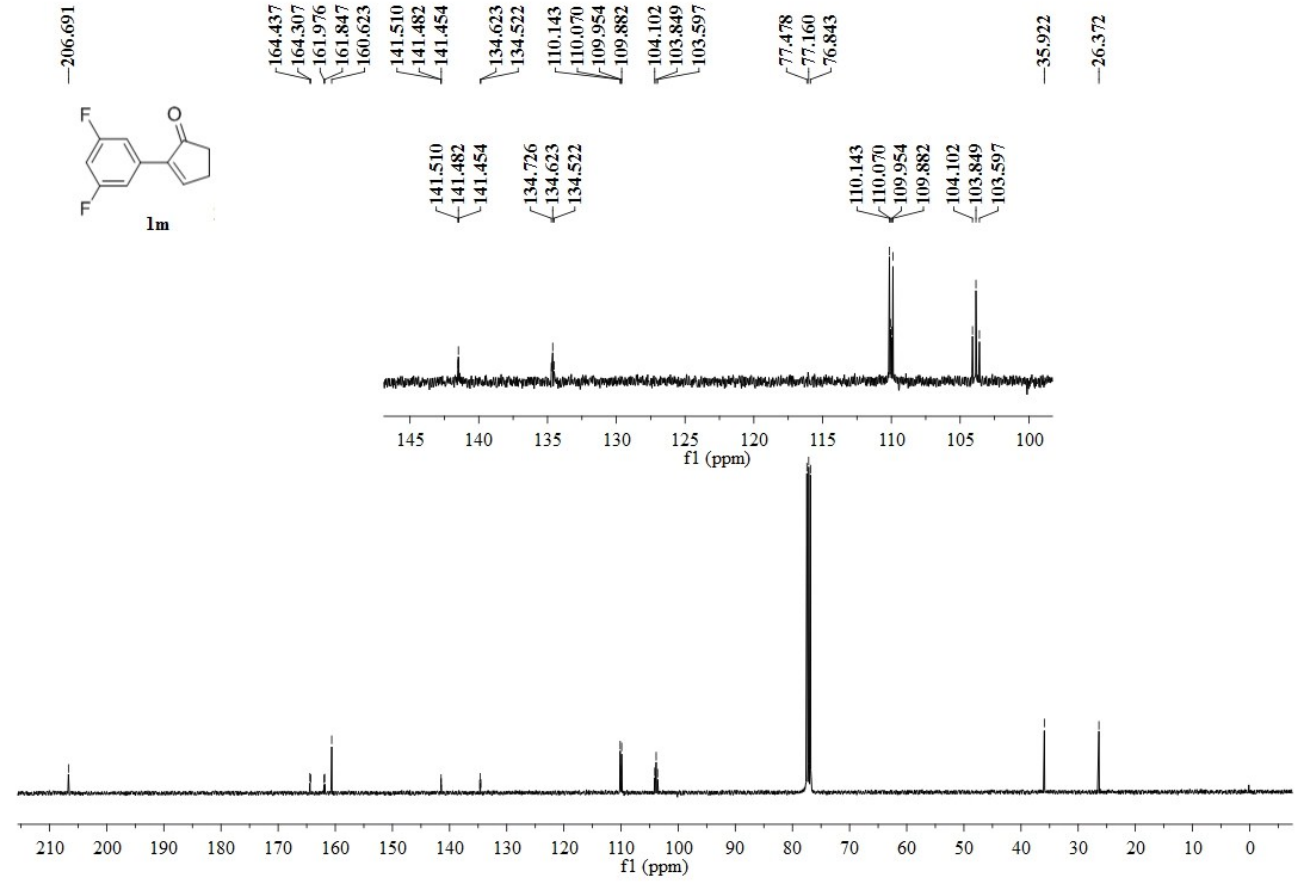
1.99
0.99
2.06
1.99
f1 (ppm)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164.307
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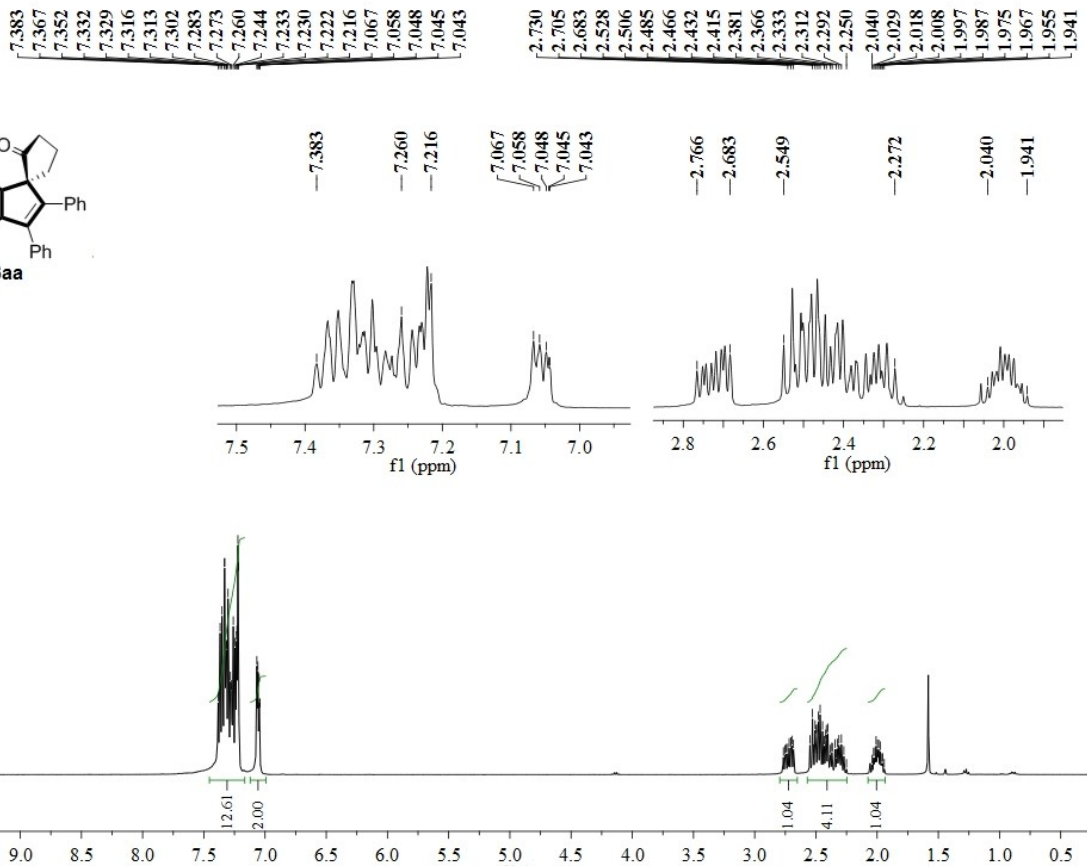
141.482
141.454
134.623
134.522
110.143
110.070
109.954
109.882
104.102
103.849
103.597
77.478
77.160
76.843
35.922
26.372
F
O
F
1m
141.510
141.482
141.454
134.726
134.623
134.522
110.143
110.070
109.954
109.882
104.102
103.849
103.597
f1 (ppm)
f1 (ppm)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7.367
7.352
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7.316
7.313
7.302
7.283
7.273
7.260
7.244
7.233
7.230
7.222
7.216
7.067
7.058
7.048
7.045
7.043
2.730
2.705
2.683
2.528
2.506
2.485
2.466
2.432
2.415
2.381
2.366
2.333
2.312
2.292
2.250
2.040
2.029
2.018
2.008
1.997
1.987
1.975
1.967
1.955
1.941
O
Ph
Ph
3aa
7.383
7.260
7.216
7.067
7.058
7.048
7.045
7.043
2.766
2.683
2.549
2.272
2.040
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f1 (ppm)
f1 (ppm)
12.61
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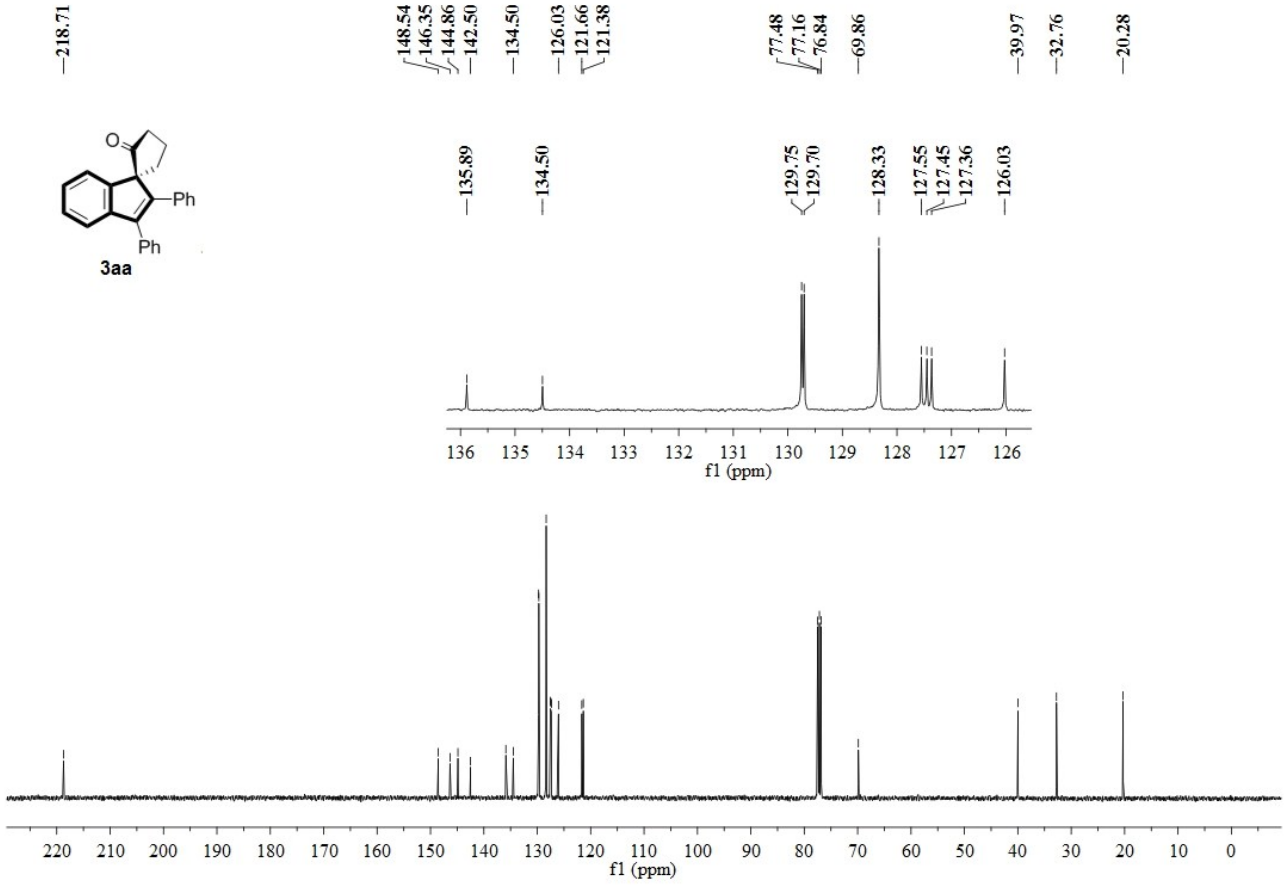
1.04
4.11
1.04
f1 (ppm)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134.50
126.03
121.66
121.38
77.48
77.16
76.84
69.86
39.97
32.76
20.28
O
Ph
Ph
3aa
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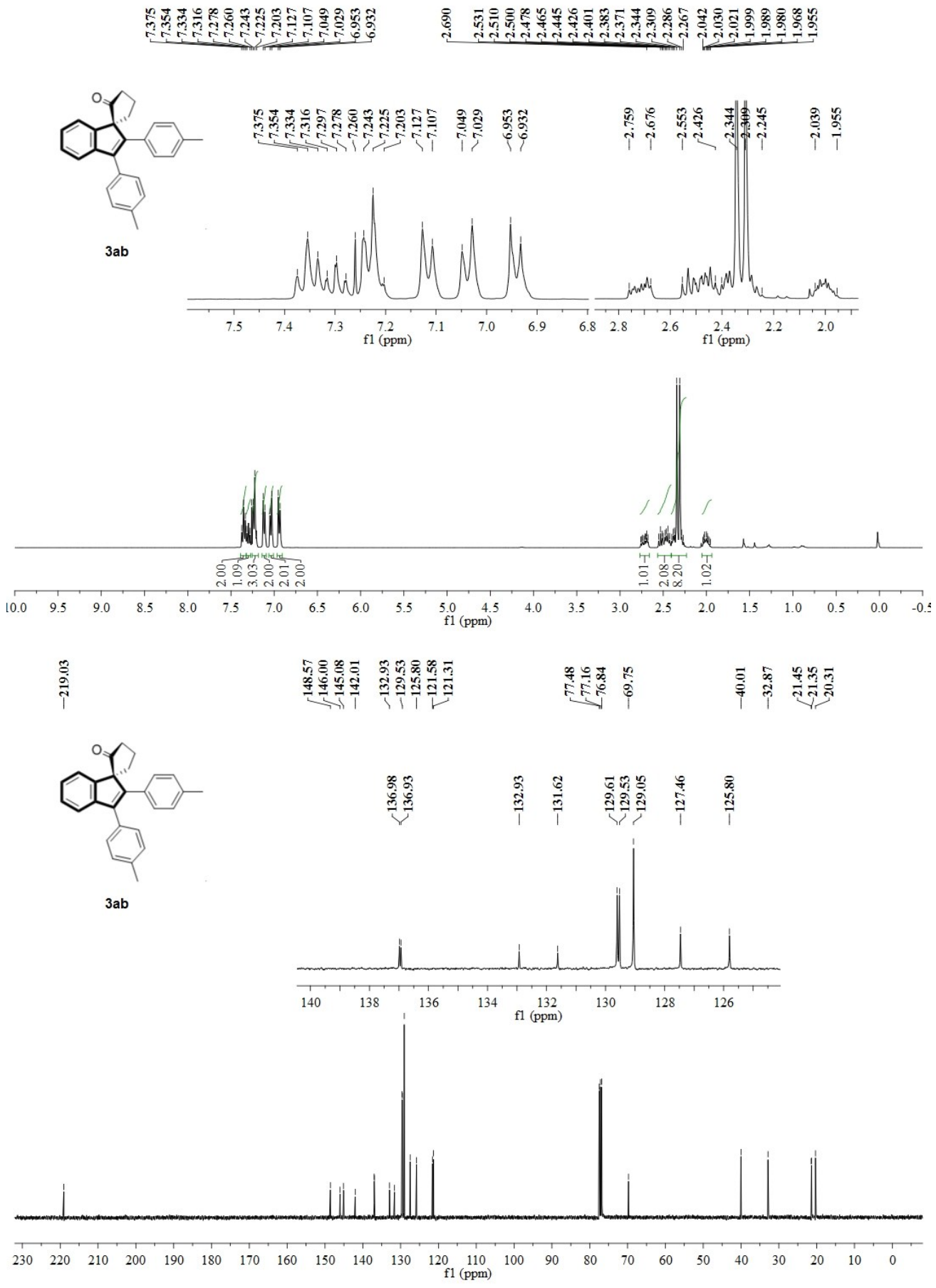
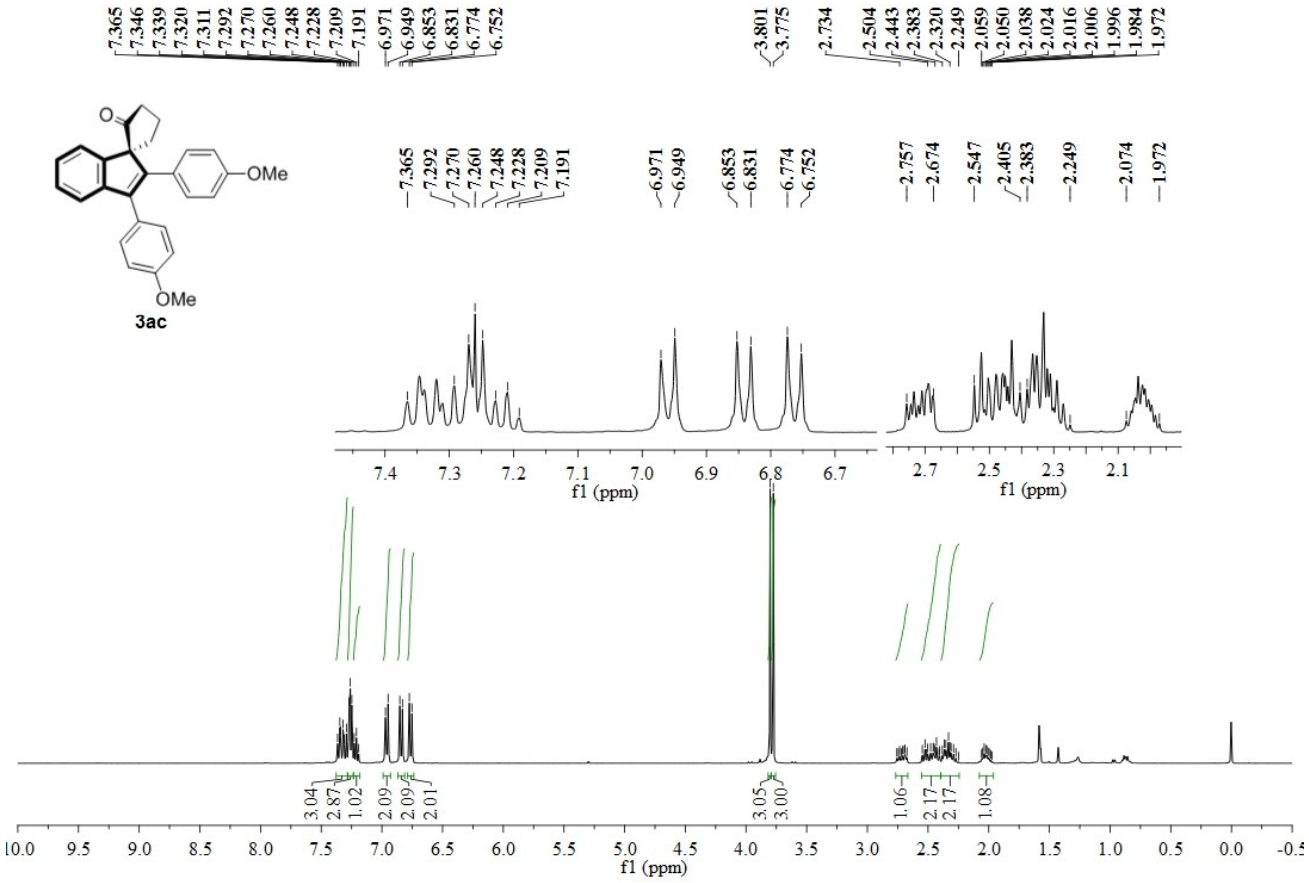
129.75
129.70
128.33
127.55
127.45
127.36
126.03
f1 (ppm)
f1 (ppm)


3ab
f1 (ppm)
3ab
f1 (ppm)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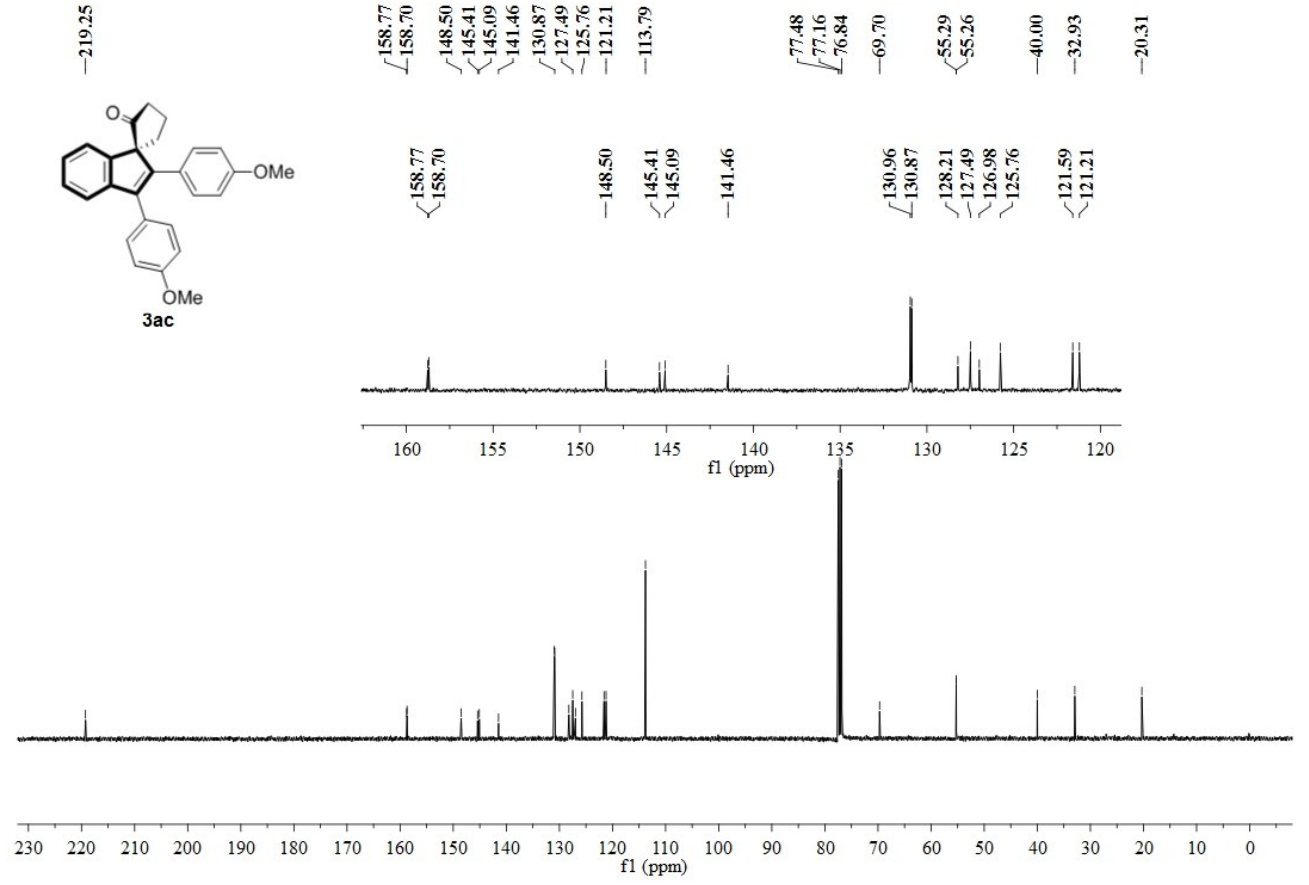
7.339
7.320
7.311
7.292
7.270
7.260
7.248
7.228
7.209
7.191
6.971
6.949
6.853
6.831
6.774
6.752
3.801
3.775
2.734
2.504
2.443
2.383
2.320
2.249
2.059
2.050
2.038
2.024
2.016
2.006
1.996
1.984
1.972
OMe
OMe
3ac
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
f1 (ppm)
2.7
2.5
2.3
2.1
f1 (ppm)
3.04
2.87
1.02
2.09
2.09
2.01
3.05
3.00
1.06
2.17
2.17
1.08
f1 (ppm)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158.77
158.70
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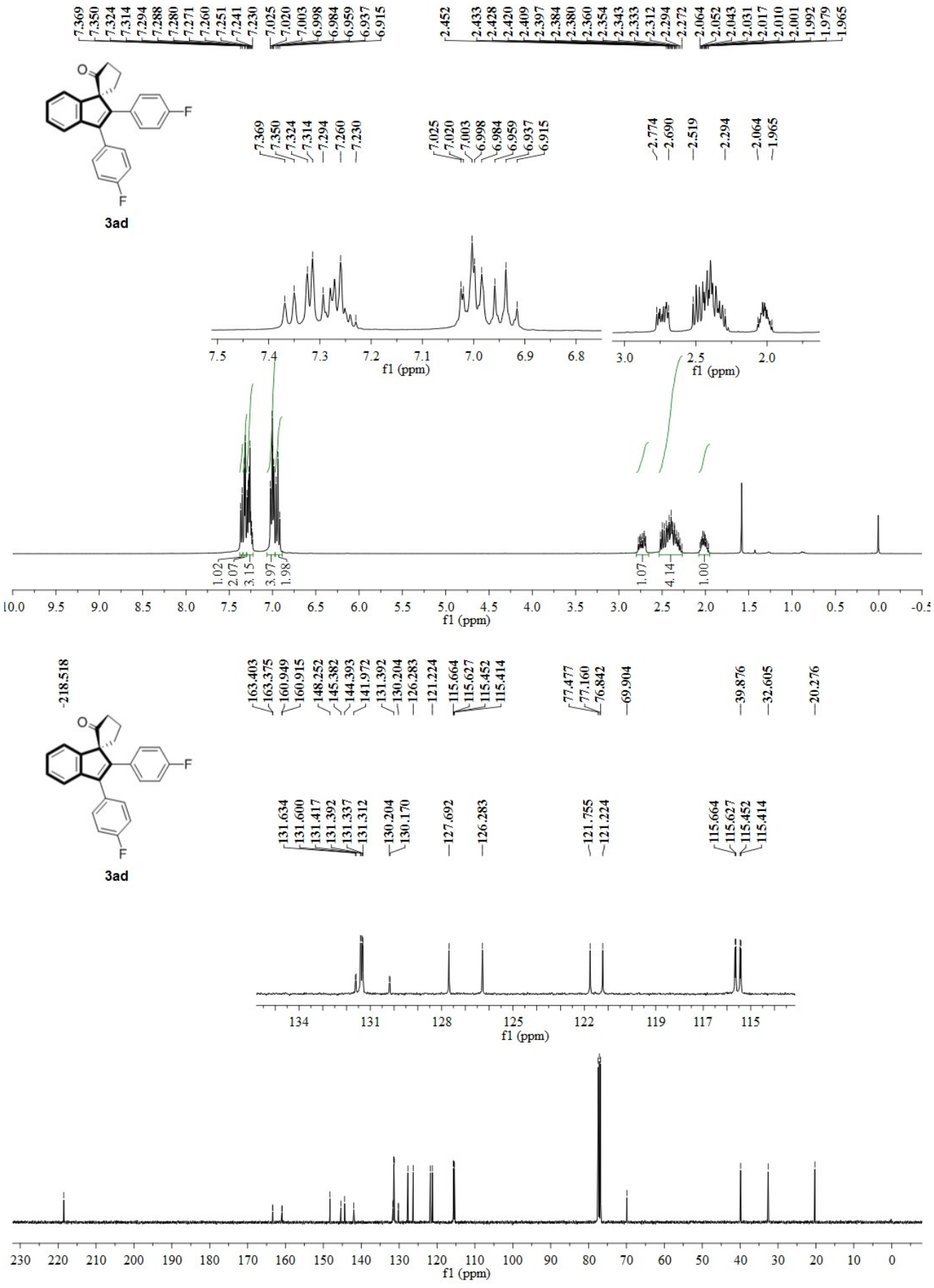
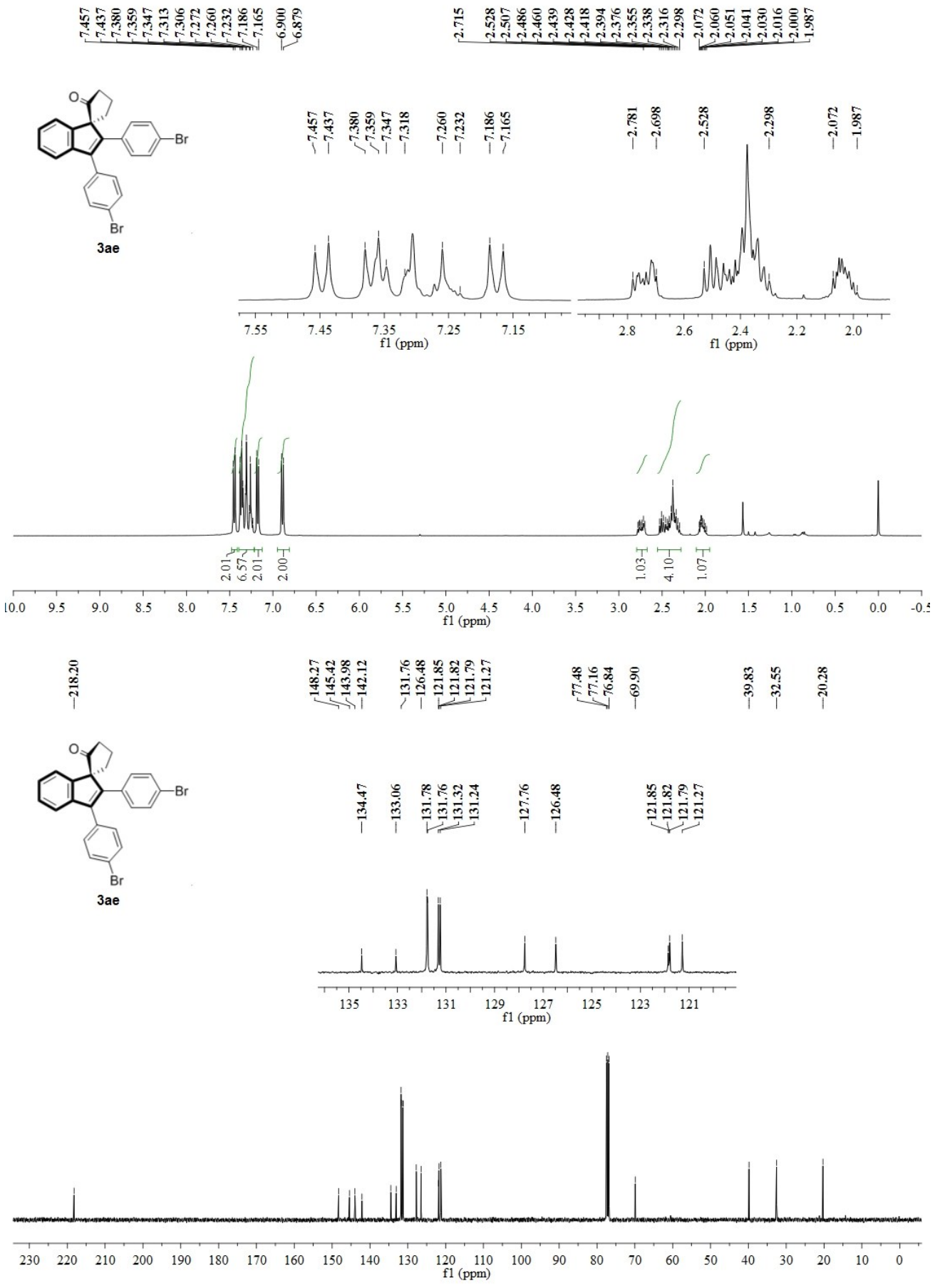
145.41
145.09
141.46
130.87
127.49
125.76
121.21
113.79
77.48
77.16
76.84
69.70
55.29
55.26
40.00
32.93
20.31
OMe
OMe
3ac
160
155
150
145
140
135
130
125
120
f1 (ppm)
f1 (ppm)


3ad
f1 (ppm)
3ad
f1 (ppm)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7.380
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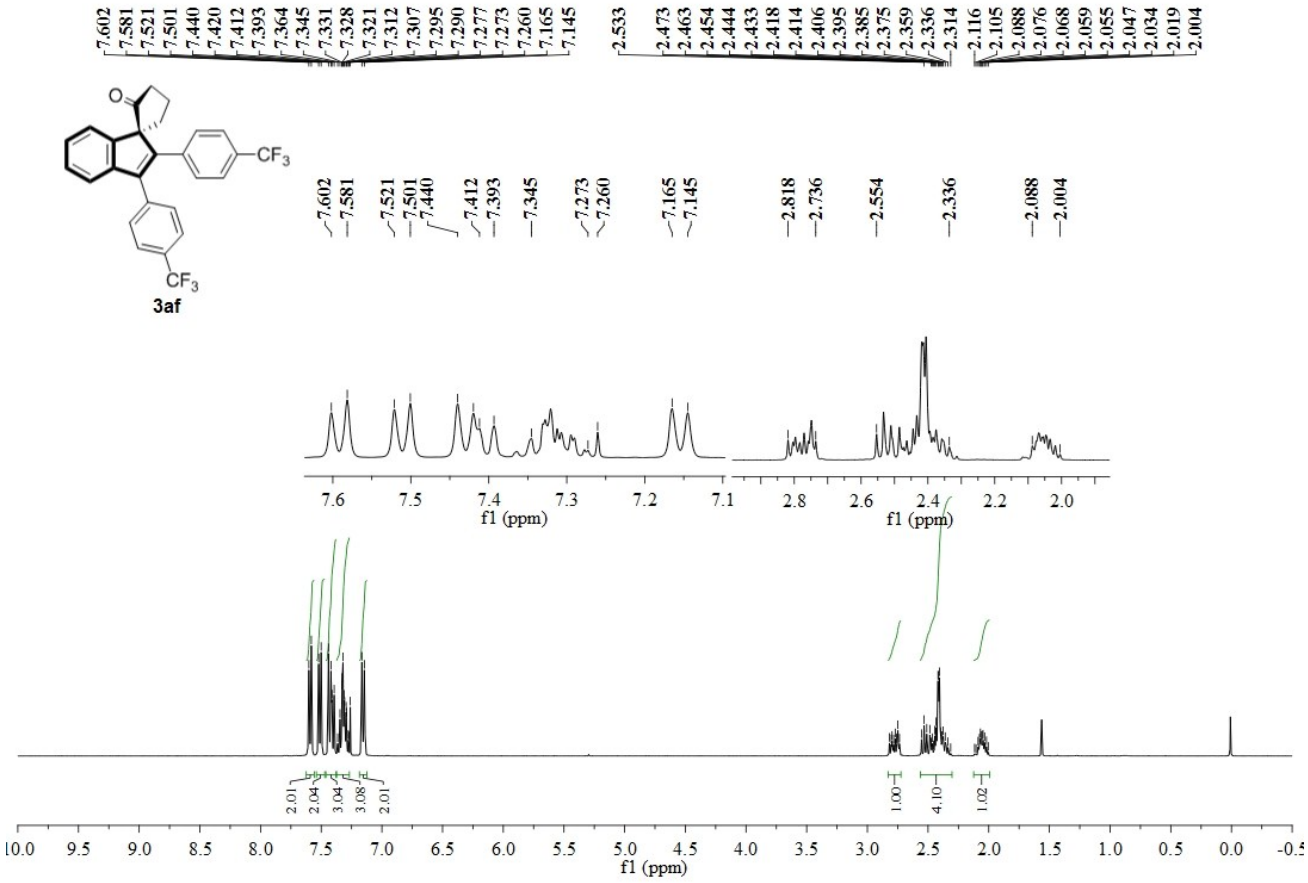
7.313
7.306
7.272
7.260
7.232
7.186
7.165
6.900
6.879
2.715
2.528
2.507
2.486
2.460
2.439
2.428
2.418
2.394
2.376
2.355
2.338
2.316
2.298
2.072
2.060
2.051
2.041
2.030
2.016
2.000
1.987
Br
Br
3ae
f1 (ppm)
2.01
6.57
2.01
2.00
1.03
4.10
1.07
218.20
148.27
145.42
143.98
142.12
131.76
126.48
121.85
121.82
121.79
121.27
77.48
77.16
76.84
69.90
39.83
32.55
20.28
134.47
133.06
131.78
131.76
131.32
131.24
127.76
126.48
121.85
121.82
121.79
121.27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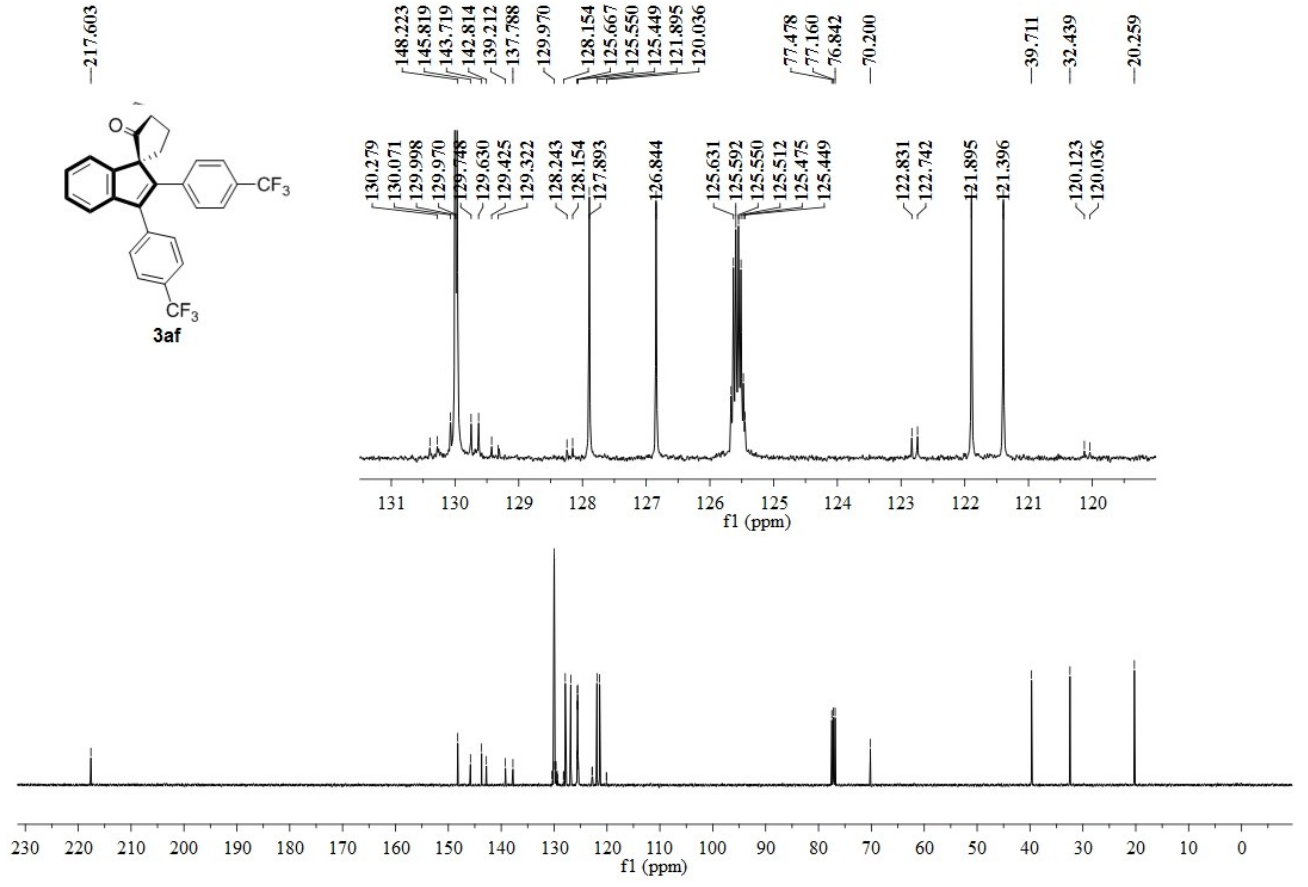
7.581
7.521
7.501
7.440
7.420
7.412
7.393
7.364
7.345
7.331
7.328
7.321
7.312
7.307
7.295
7.290
7.277
7.273
7.260
7.165
7.145
2.533
2.473
2.463
2.454
2.444
2.433
2.418
2.414
2.406
2.395
2.385
2.375
2.359
2.336
2.314
2.116
2.105
2.088
2.076
2.068
2.059
2.055
2.047
2.034
2.019
2.004
CF3
CF3
3af
f1 (ppm)
2.01
2.04
3.04
3.08
2.01
1.00
4.10
1.02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143.719
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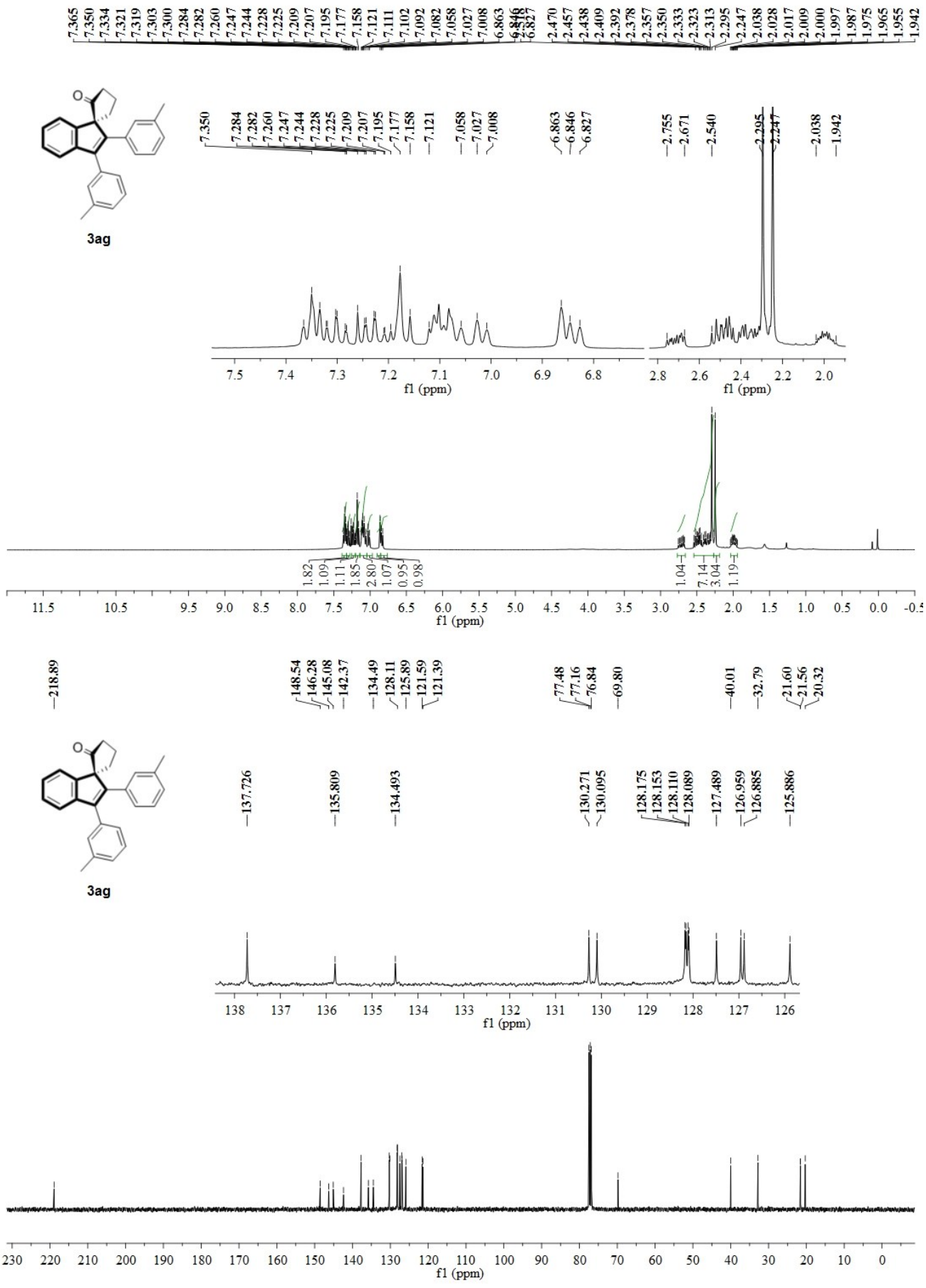
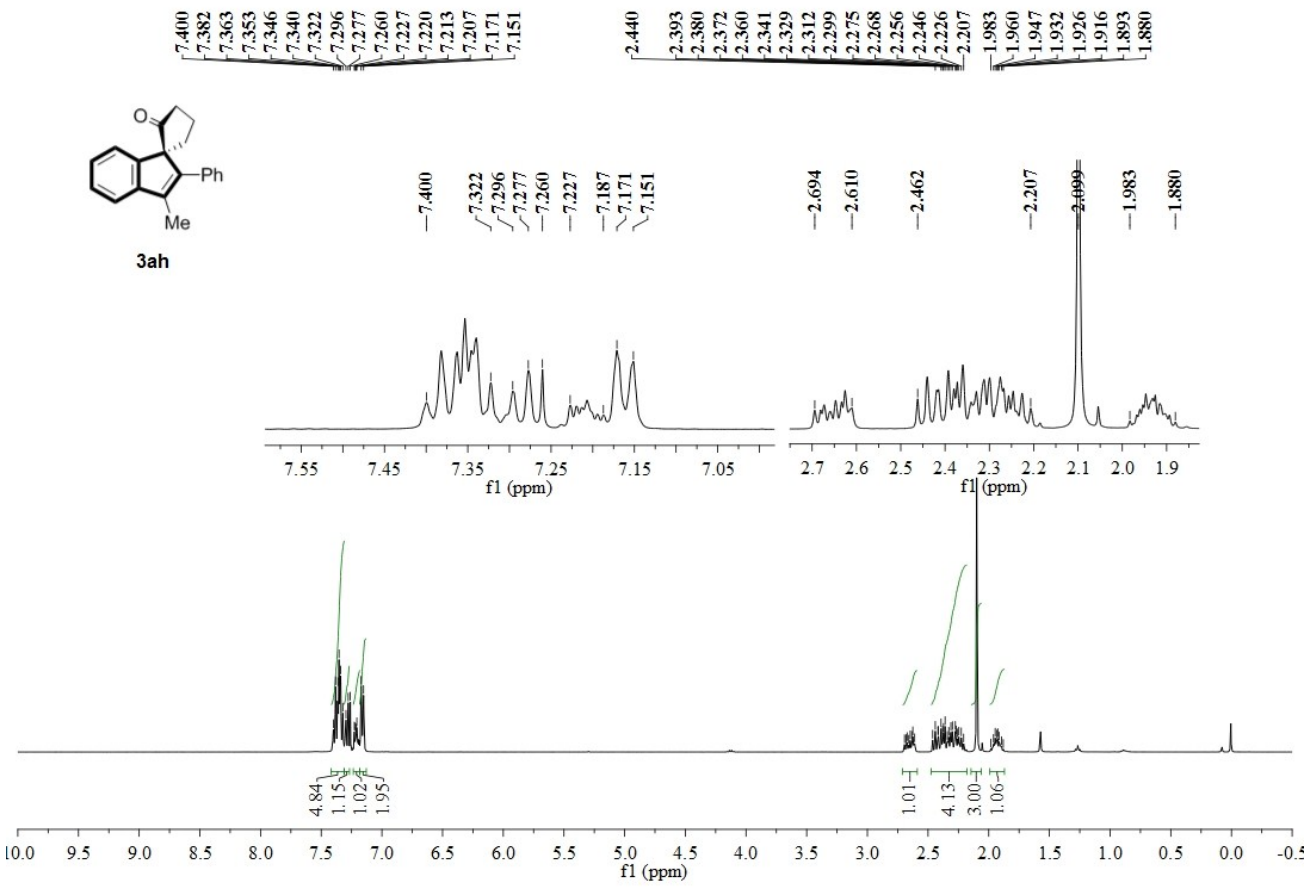
139.212
137.788
129.970
128.154
125.667
125.550
125.449
121.895
120.036
77.478
77.160
76.842
70.200
39.711
32.439
20.259
130.279
130.071
129.998
129.970
129.748
129.630
129.425
129.322
128.243
128.154
127.893
126.844
125.631
125.592
125.550
125.512
125.475
125.449
122.831
122.742
121.895
121.396
120.123
120.036
CF3
CF3
3af
f1 (ppm)


3ag
f1 (ppm)
3ag
f1 (ppm)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7.353
7.346
7.340
7.322
7.296
7.277
7.260
7.227
7.220
7.213
7.207
7.171
7.151
2.440
2.393
2.380
2.372
2.360
2.341
2.329
2.312
2.299
2.275
2.268
2.256
2.246
2.226
2.207
1.983
1.960
1.947
1.932
1.926
1.916
1.893
1.880
O
Ph
Me
3ah
7.400
7.322
7.296
7.277
7.260
7.227
7.187
7.171
7.151
2.694
2.610
2.462
2.207
2.099
1.983
1.880
f1 (ppm)
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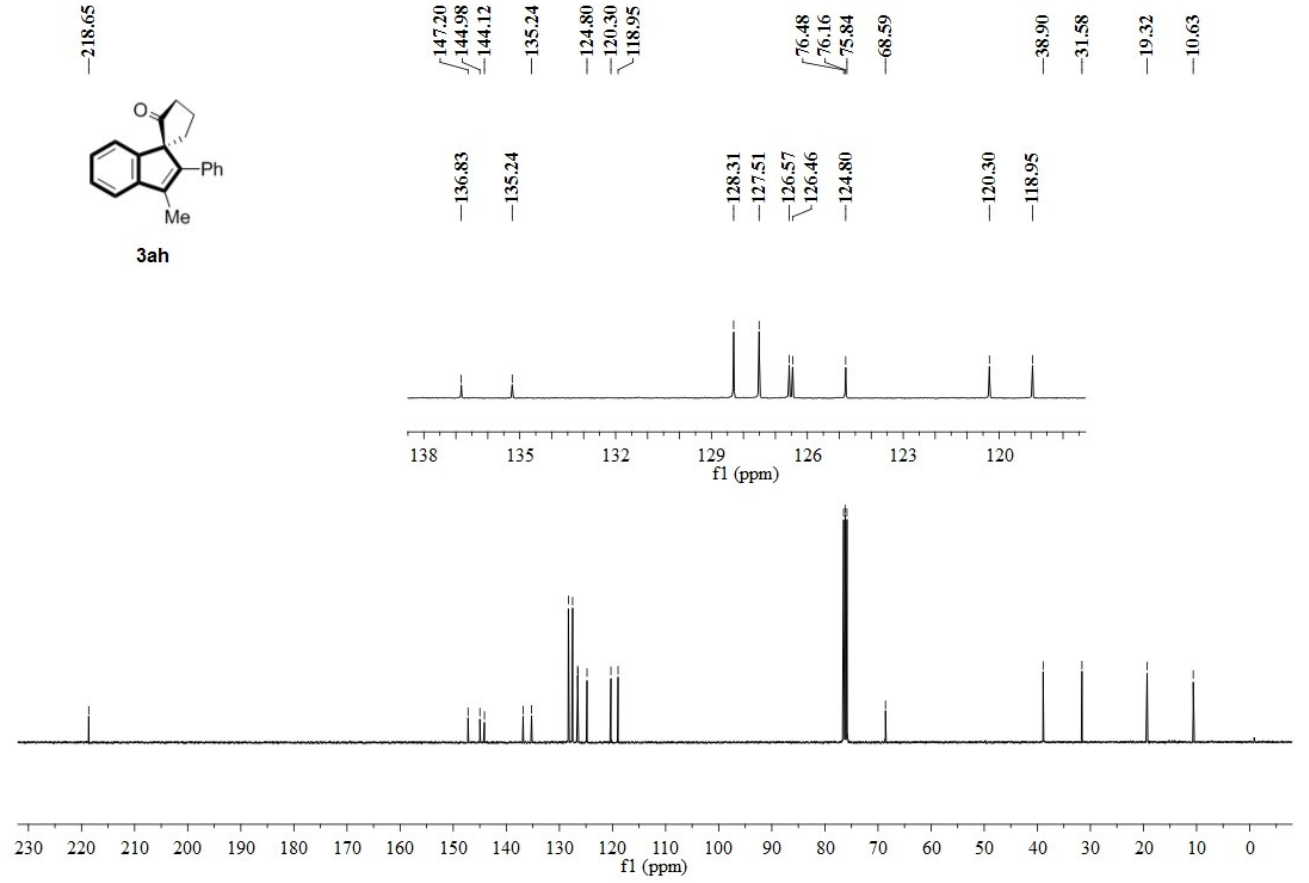
1.15
1.02
1.95
1.01
4.13
3.00
1.06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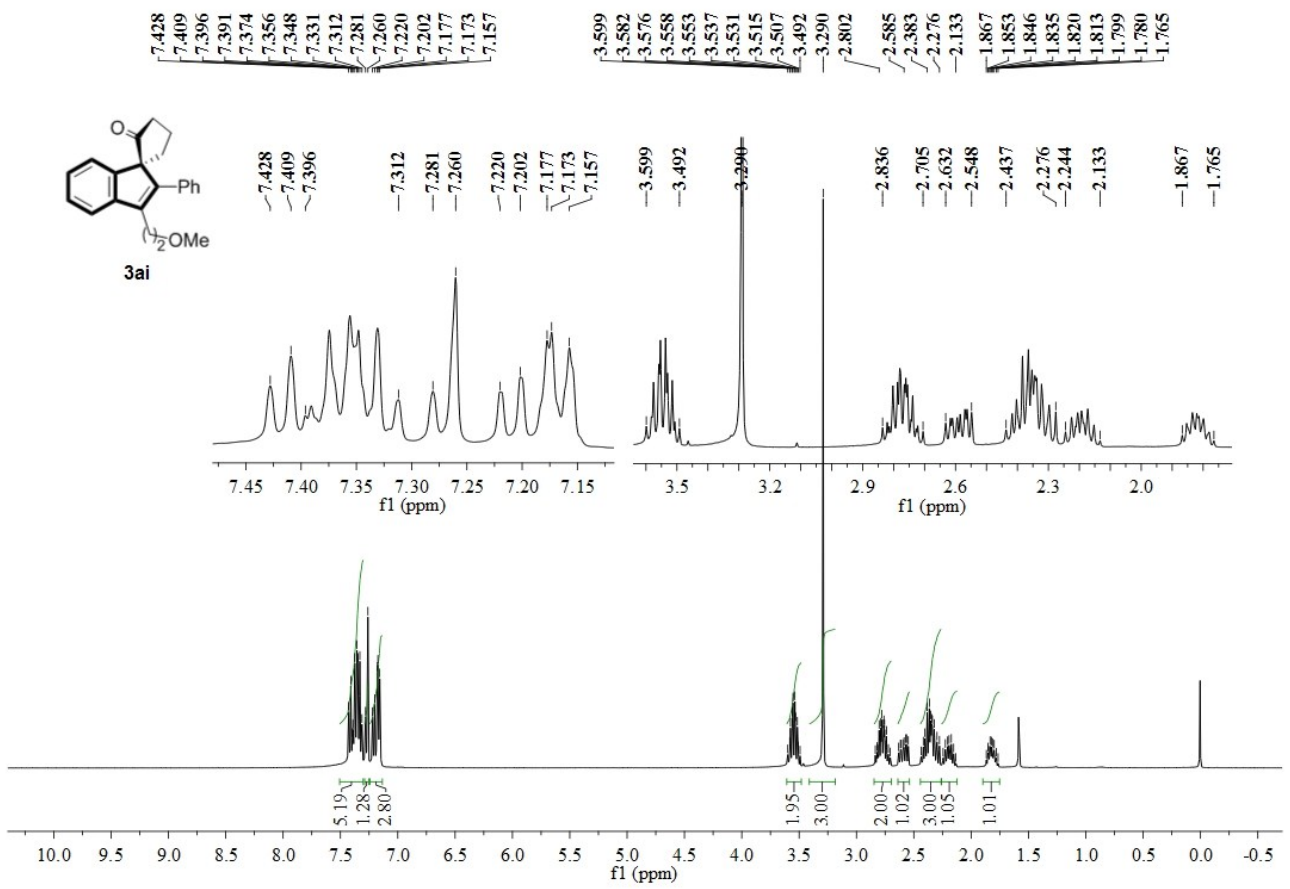
135.24
124.80
120.30
118.95
76.48
76.16
75.84
68.59
38.90
31.58
19.32
10.63
O
Ph
Me
3ah
136.83
135.24
128.31
127.51
126.57
126.46
124.80
120.30
118.95
f1 (ppm)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7.396
7.391
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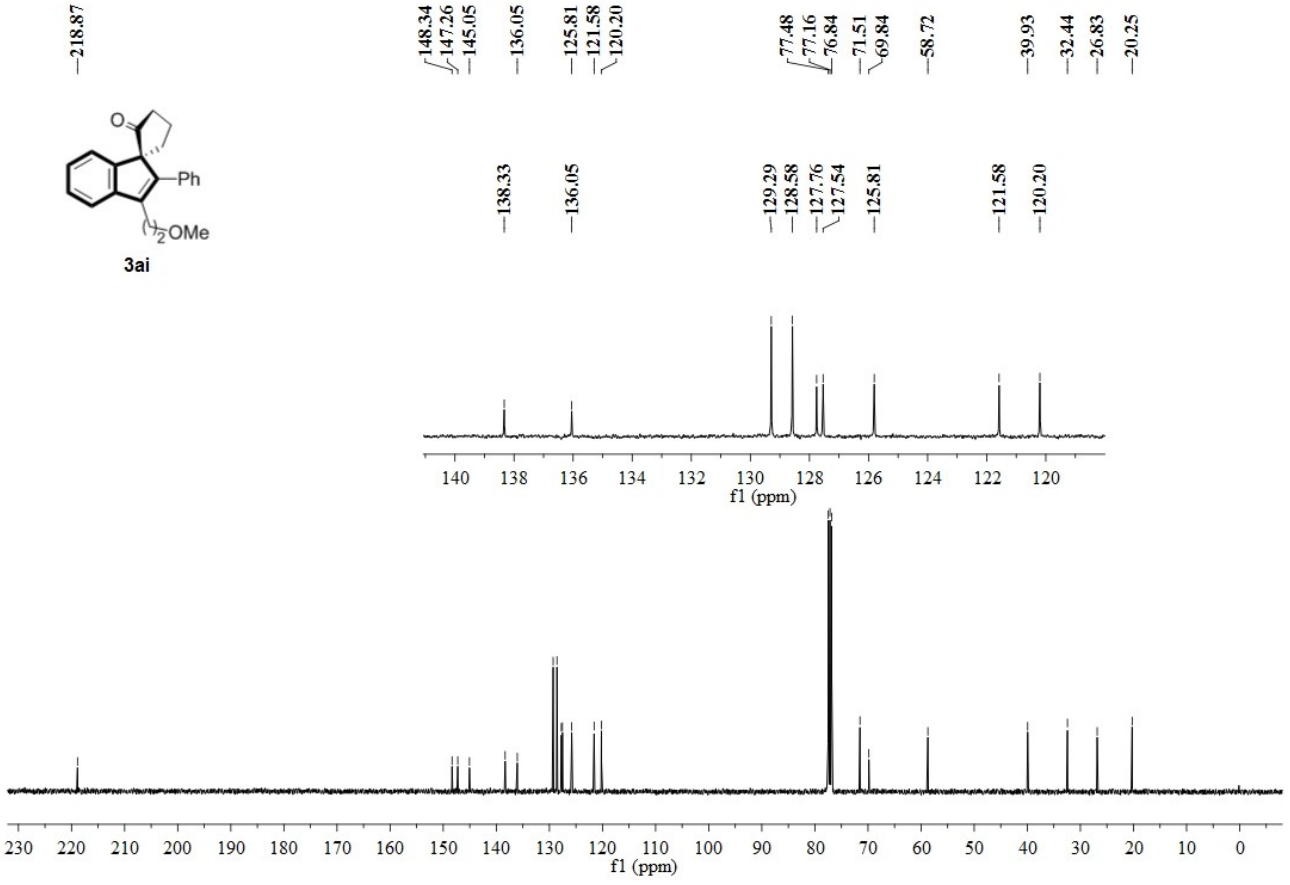
7.356
7.348
7.331
7.312
7.281
7.260
7.220
7.202
7.177
7.173
7.157
3.599
3.582
3.576
3.558
3.553
3.537
3.531
3.515
3.507
3.492
3.290
2.802
2.585
2.383
2.276
2.133
1.867
1.853
1.846
1.835
1.820
1.813
1.799
1.780
1.765
Ph
OMe
3ai
f1 (ppm)
5.19
1.28
2.80
1.95
3.00
2.00
1.02
3.00
1.05
1.01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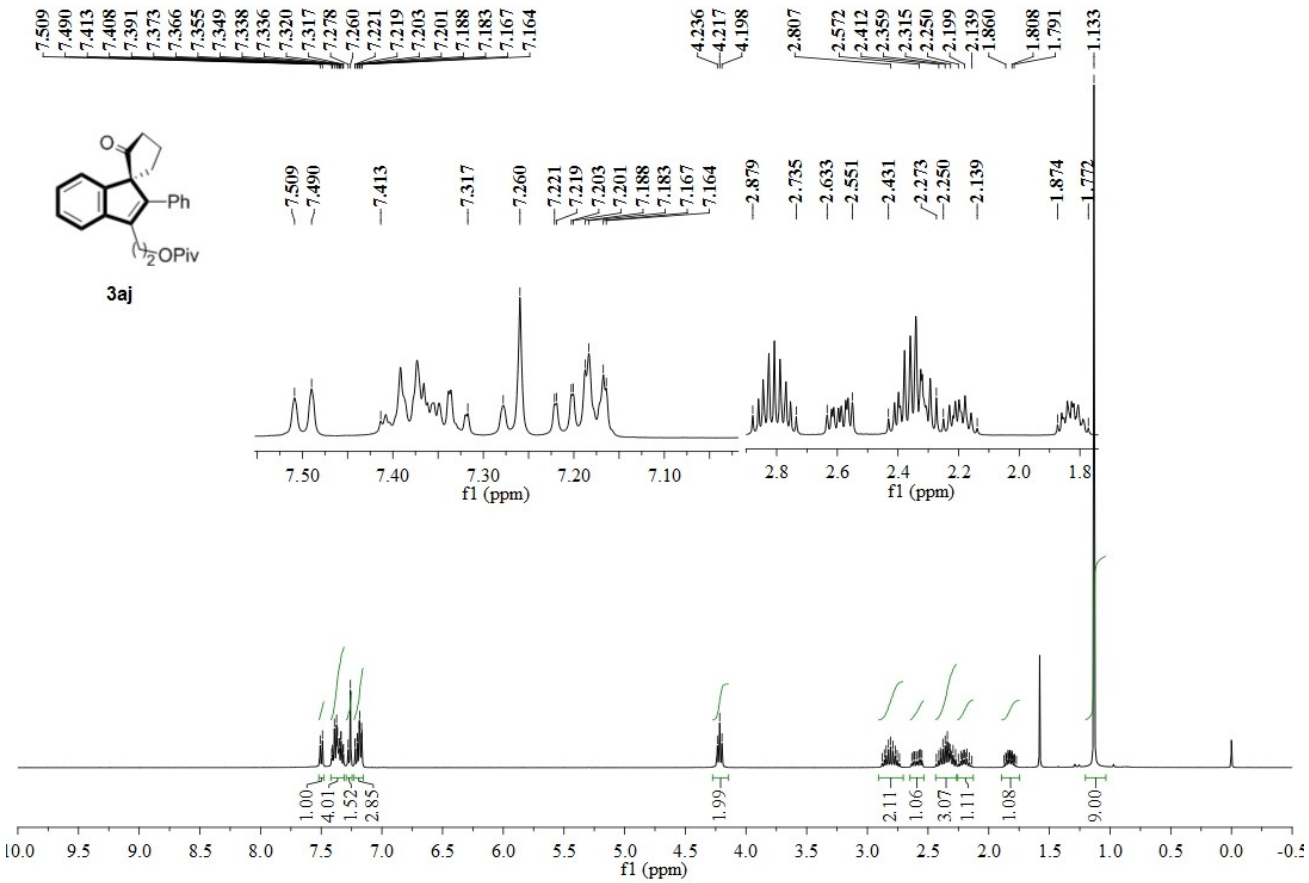
77.48
77.16
76.84
71.51
69.84
58.72
39.93
32.44
26.83
20.25
138.33
136.05
129.29
128.58
127.76
127.54
125.81
121.58
120.20
Ph
OMe
3ai
f1 (ppm)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7.355
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7.338
7.336
7.320
7.317
7.278
7.260
7.221
7.219
7.203
7.201
7.188
7.183
7.167
7.164
4.236
4.217
4.198
2.807
2.572
2.412
2.359
2.315
2.250
2.199
2.139
1.860
1.808
1.791
1.133
Ph
OPiv
3aj
f1 (ppm)
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4.01
1.52
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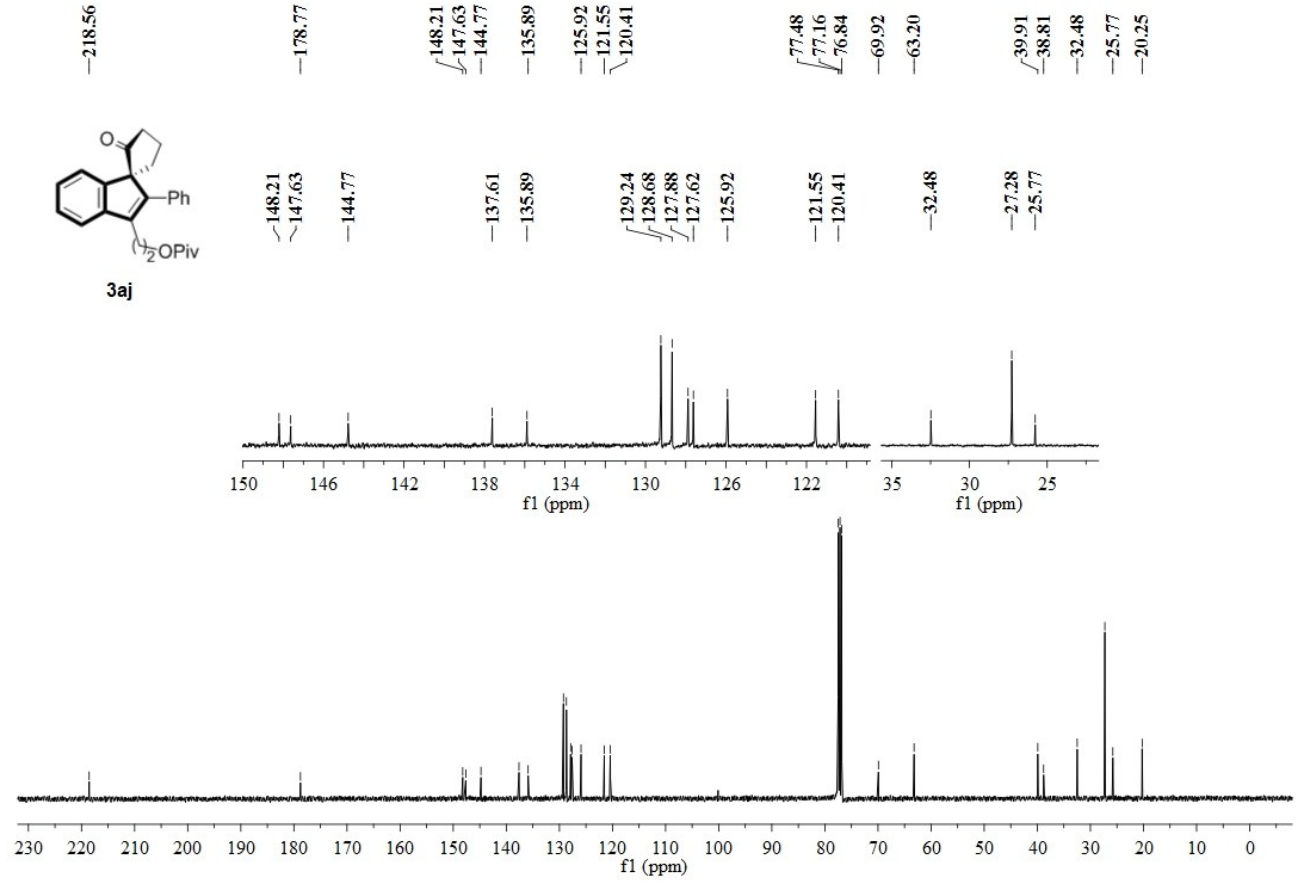
1.99
2.11
1.06
3.07
1.11
1.08
9.00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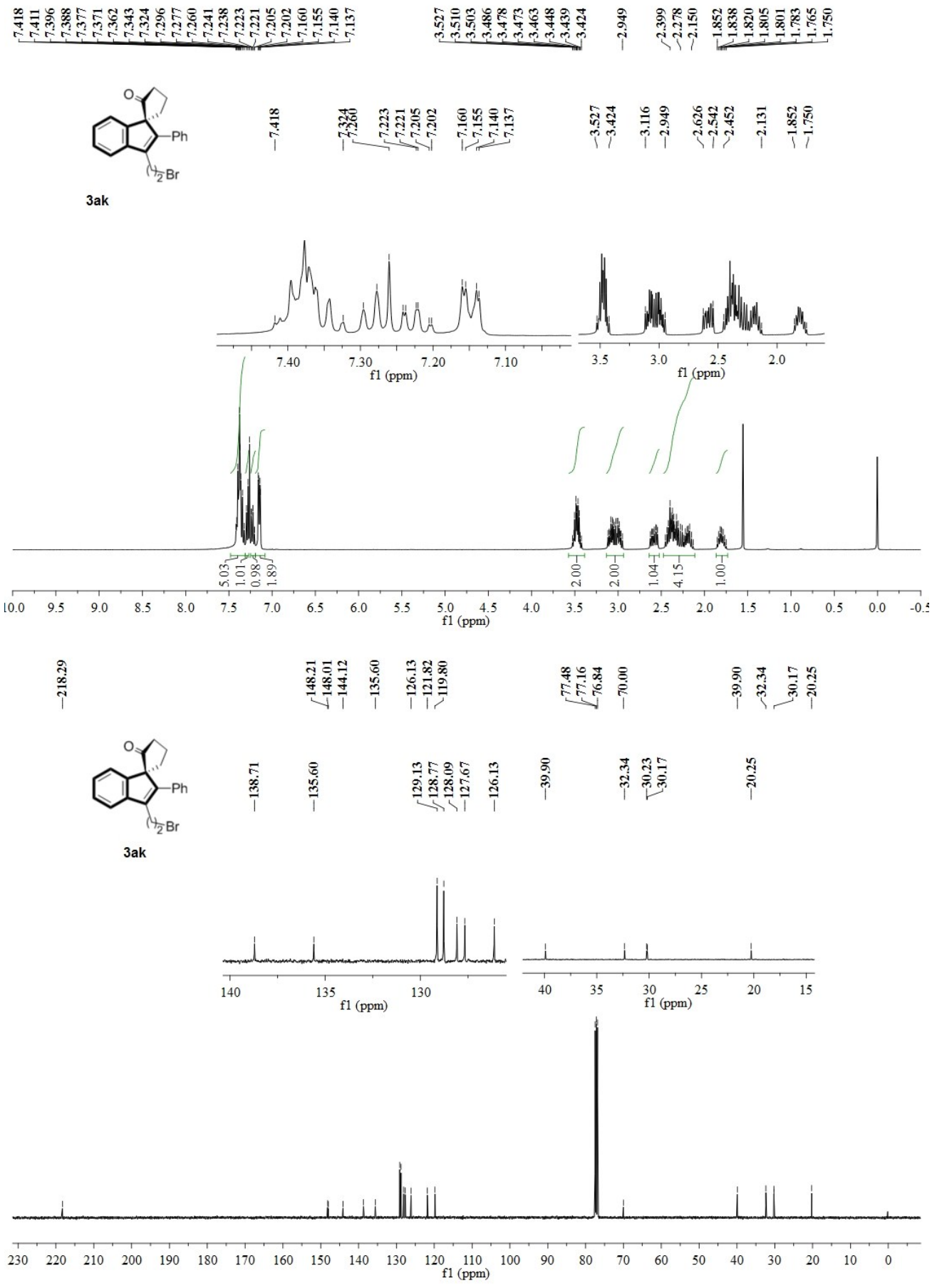
121.55
120.41
77.48
77.16
76.84
69.92
63.20
39.91
38.81
32.48
25.77
20.25
Ph
OPiv
3aj
137.61
129.24
128.68
127.88
127.62
27.28
f1 (ppm)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7.362
7.343
7.324
7.296
7.277
7.260
7.241
7.238
7.223
7.221
7.205
7.202
7.160
7.155
7.140
7.137
3.527
3.510
3.503
3.486
3.478
3.473
3.463
3.448
3.439
3.424
2.949
2.399
2.278
2.150
1.852
1.838
1.820
1.805
1.801
1.783
1.765
1.750
Ph
Br
3ak
f1 (ppm)
5.03
1.01
0.98
1.89
2.00
2.00
1.04
4.15
1.00
218.29
148.21
148.01
144.12
135.60
126.13
121.82
119.80
77.48
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39.90
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30.17
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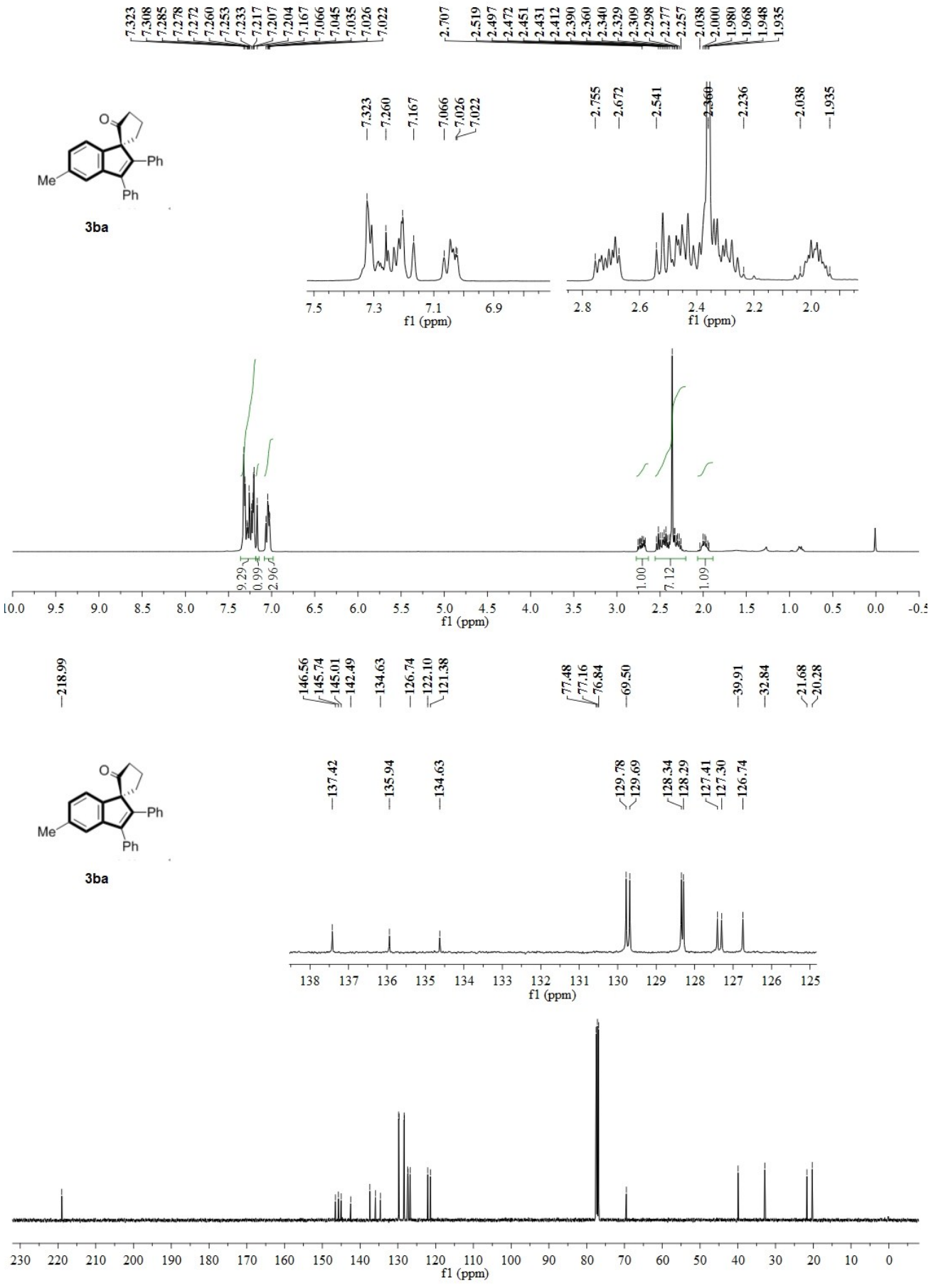
127.67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7.278
7.272
7.260
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7.233
7.217
7.207
7.204
7.167
7.066
7.045
7.035
7.026
7.022
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2.519
2.497
2.472
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2.431
2.412
2.390
2.360
2.340
2.329
2.309
2.298
2.277
2.257
2.038
2.000
1.980
1.968
1.948
1.935
Me
Ph
Ph
3ba
f1 (ppm)
9.29
0.99
2.96
1.00
7.12
1.09
218.99
146.56
145.74
145.01
142.49
134.63
126.74
122.10
121.38
77.48
77.16
76.84
69.50
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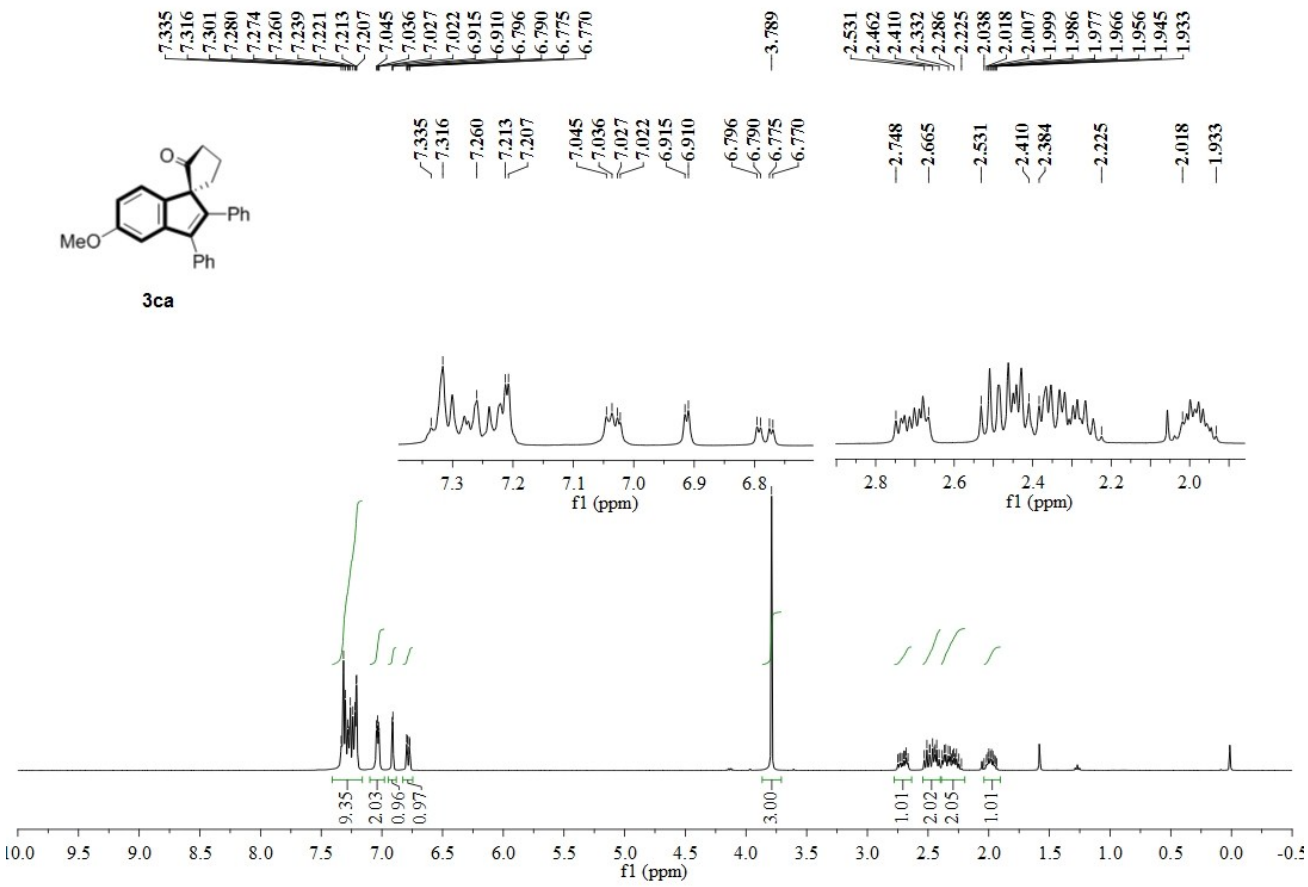
126.74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7.274
7.260
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7.221
7.213
7.207
7.045
7.036
7.027
7.022
6.915
6.910
6.796
6.790
6.775
6.770
3.789
2.531
2.462
2.410
2.332
2.286
2.225
2.038
2.018
2.007
1.999
1.986
1.977
1.966
1.956
1.945
1.933
MeO
Ph
Ph
3ca
f1 (ppm)
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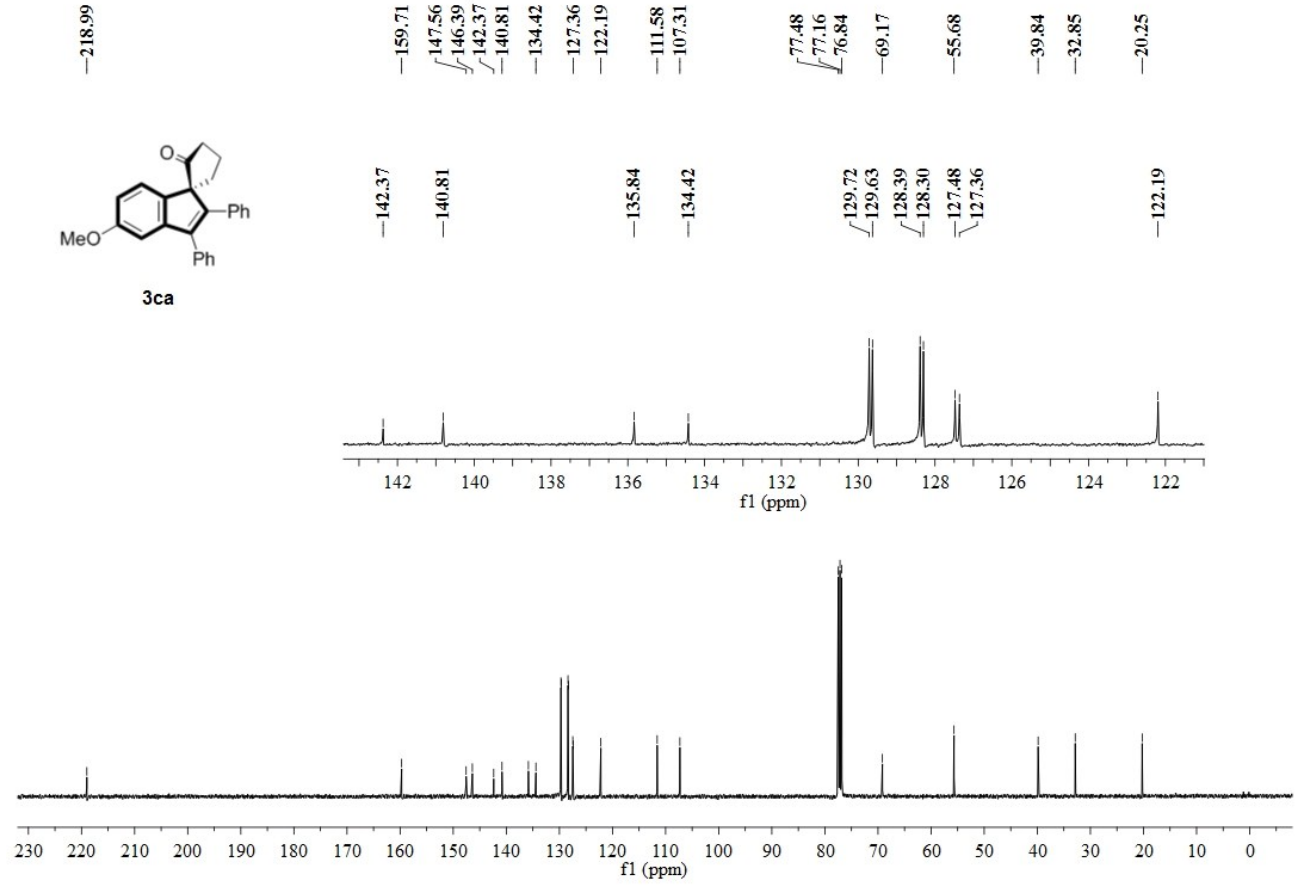
0.96
0.97
3.00
1.01
2.02
2.05
1.01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142.37
140.81
134.42
127.36
122.19
111.58
107.31
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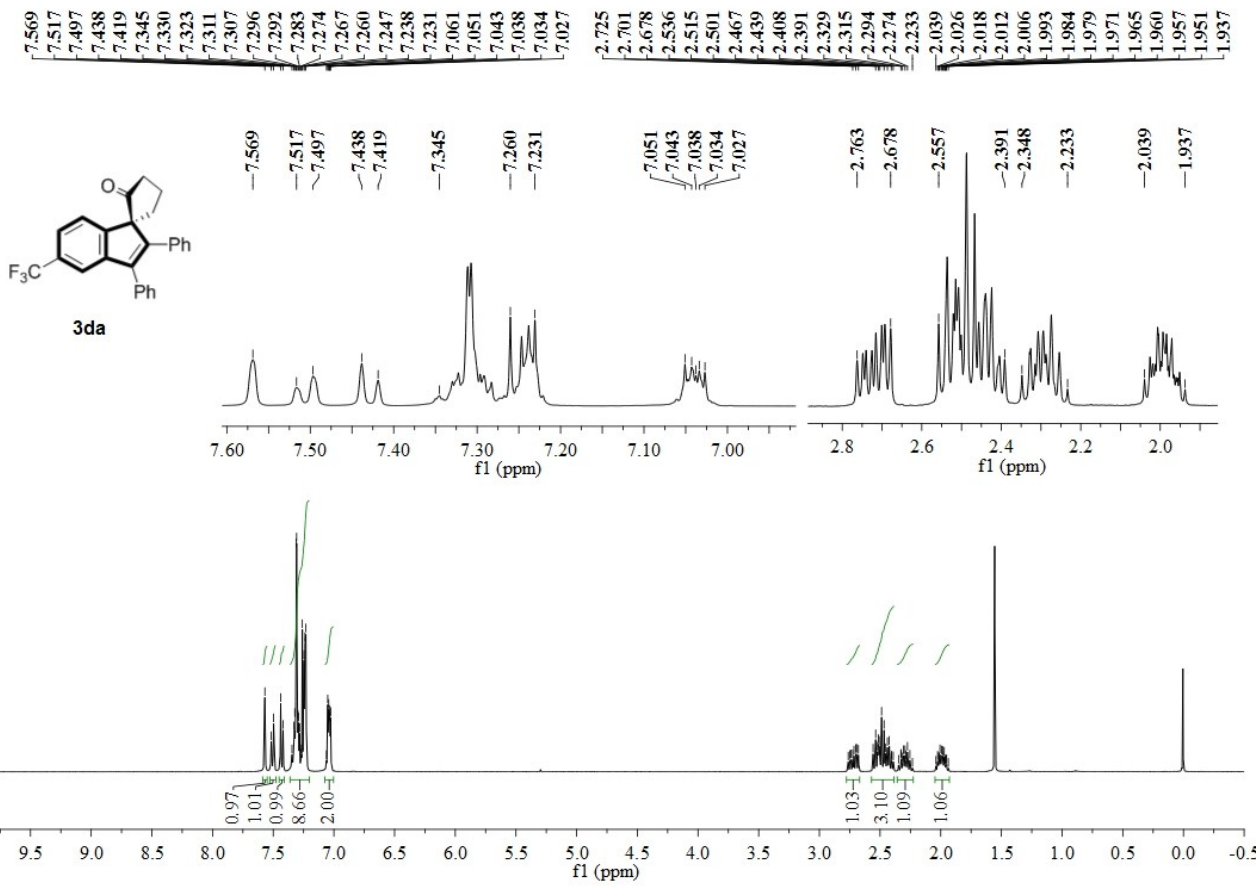
77.16
76.84
69.17
55.68
39.84
32.85
20.25
MeO
Ph
Ph
3ca
f1 (ppm)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7.419
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7.323
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7.307
7.296
7.292
7.283
7.274
7.267
7.260
7.247
7.238
7.231
7.061
7.051
7.043
7.038
7.034
7.027
2.725
2.701
2.678
2.536
2.515
2.501
2.467
2.439
2.408
2.391
2.329
2.315
2.294
2.274
2.233
2.039
2.026
2.018
2.012
2.006
1.993
1.984
1.979
1.971
1.965
1.960
1.957
1.951
1.937
O
Ph
F3C
Ph
3da
f1 (ppm)
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0.99
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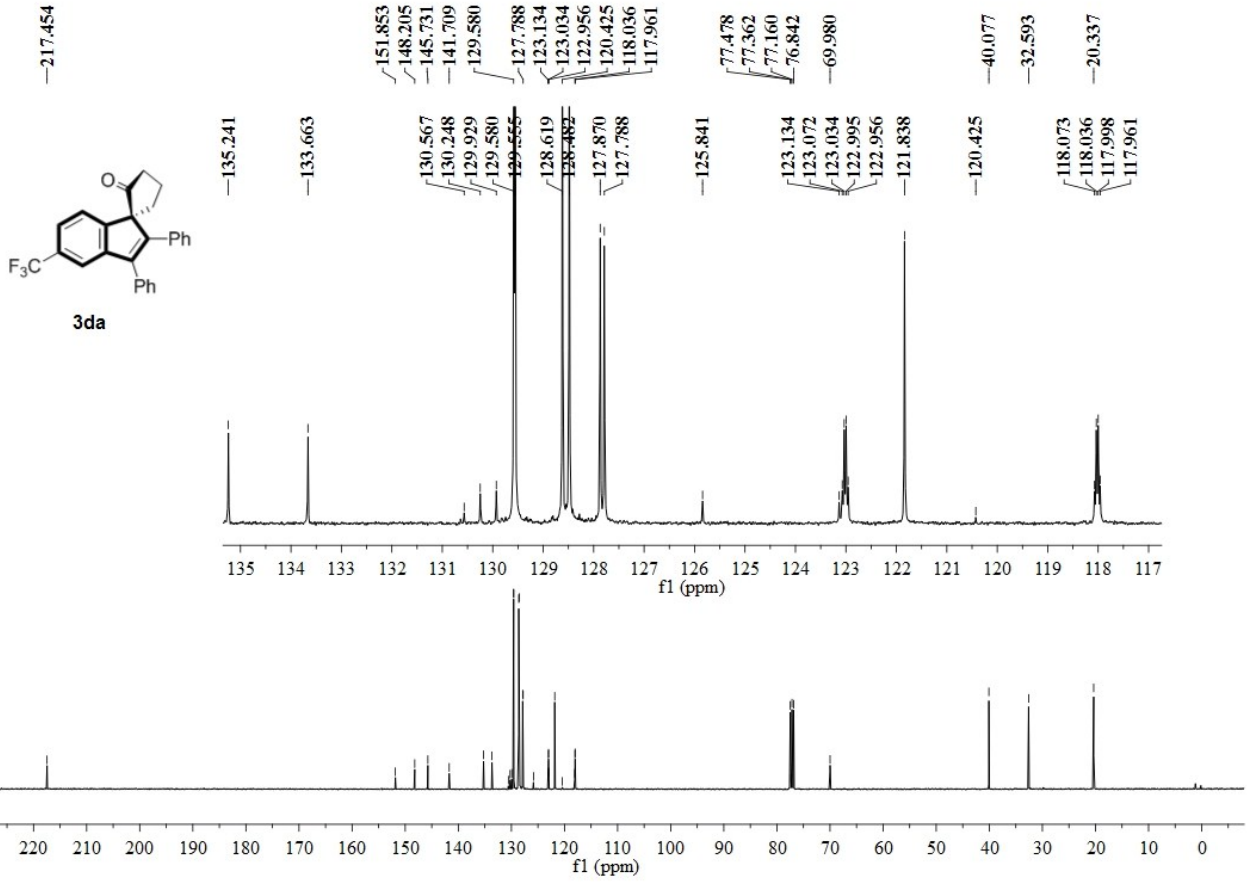
2.00
1.03
3.10
1.09
1.06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123.034
122.956
120.425
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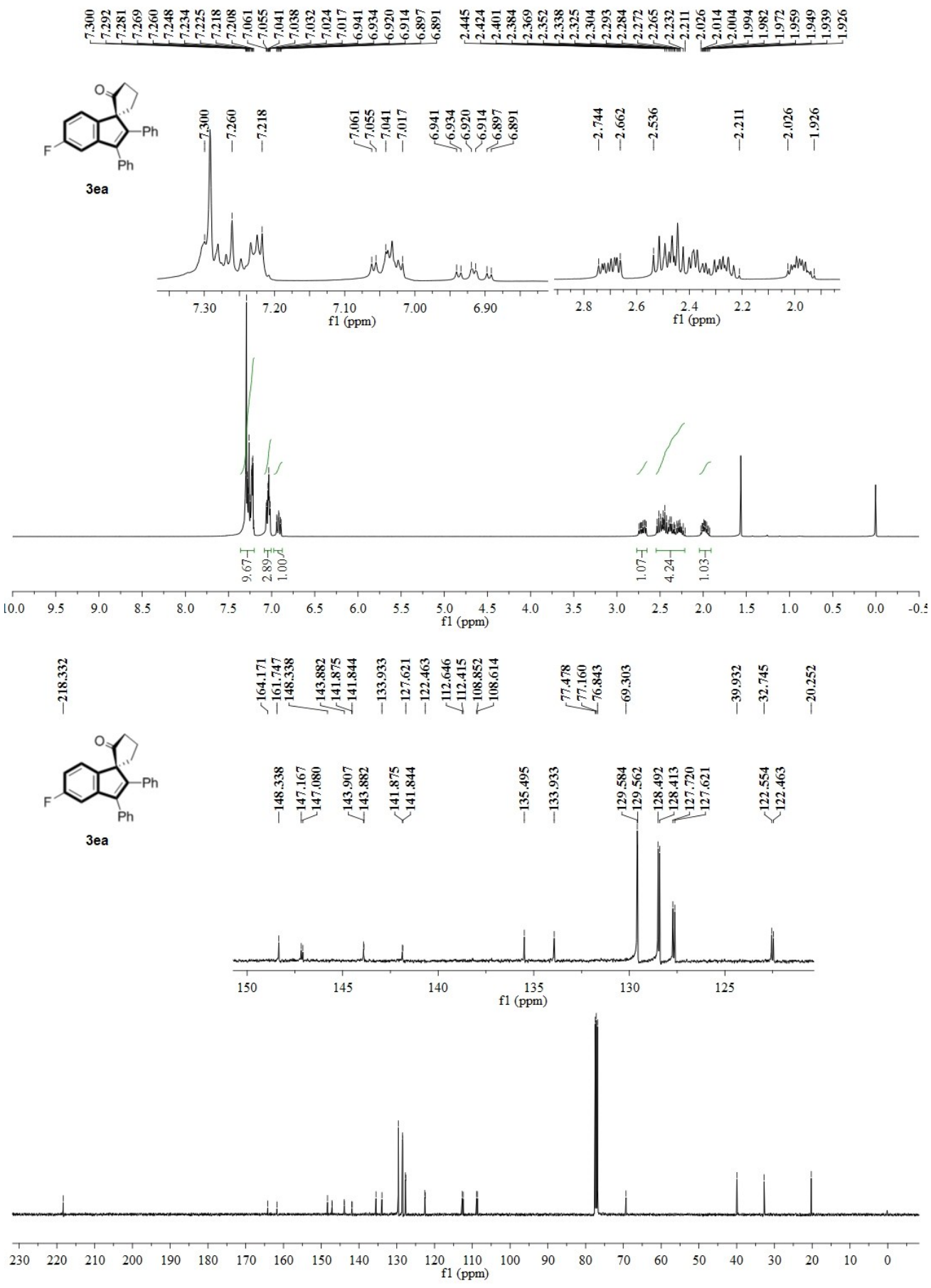
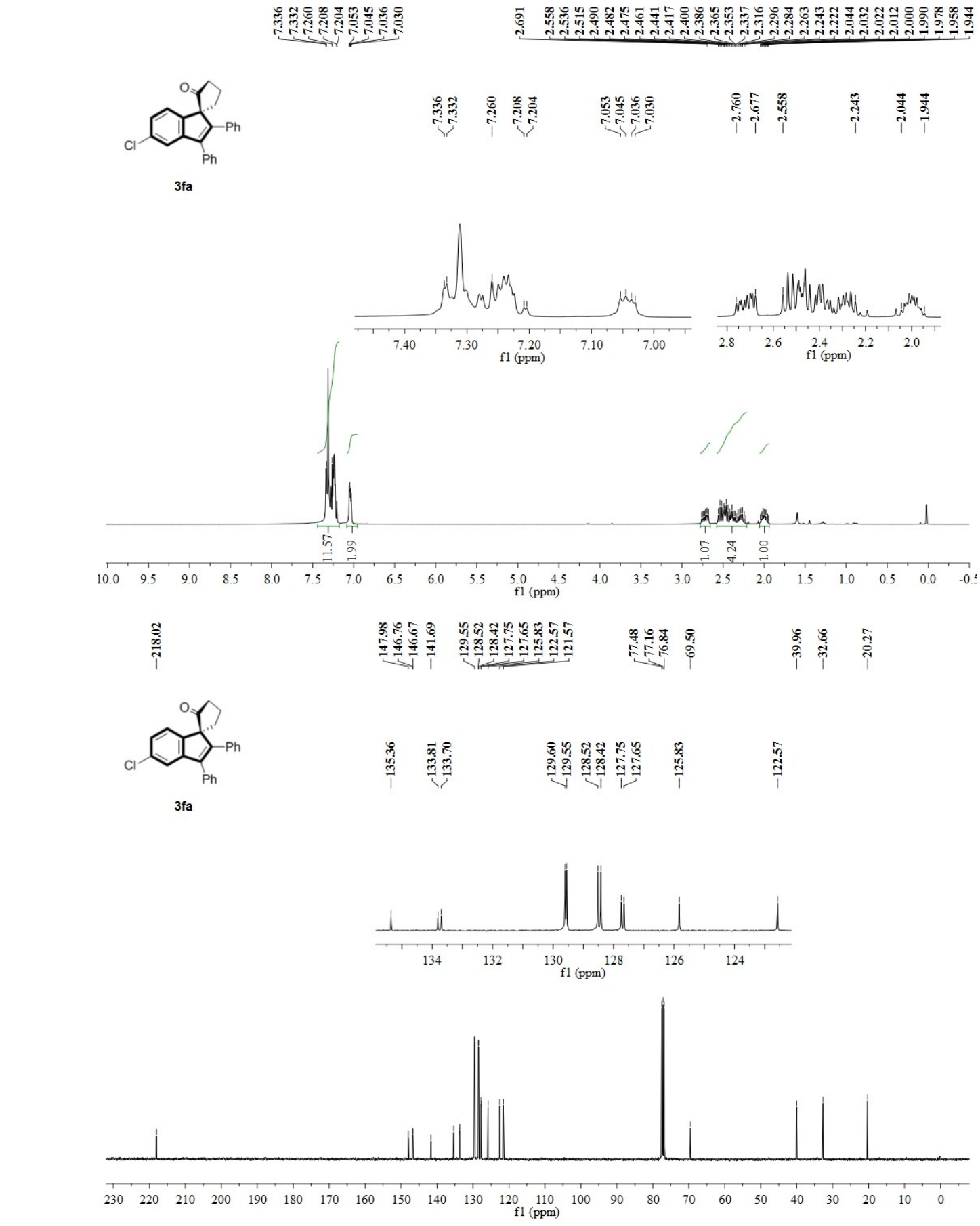
117.961
77.478
77.362
77.160
76.842
69.980
40.077
32.593
20.337
135.241
133.663
130.567
130.248
129.929
129.580
129.555
128.619
128.482
127.870
127.788
125.841
123.134
123.072
123.034
122.995
122.956
121.838
120.425
118.073
118.036
117.998
117.961
O
Ph
F3C
Ph
3da
f1 (ppm)


7.300 7.292 7.281 7.269 7.260 7.248 7.234 7.225 7.218 7.208 7.061 7.055 7.041 7.038 7.032 7.024 7.017 6.941 6.934 6.920 6.914 6.897 6.891
2.445 2.424 2.401 2.384 2.369 2.352 2.338 2.325 2.304 2.293 2.284 2.272 2.265 2.232 2.211 2.026 2.014 2.004 1.994 1.982 1.972 1.959 1.949 1.939 1.926
O
Ph
F
Ph
3ea
7.300 7.260 7.218 7.061 7.055 7.041 7.017 6.941 6.934 6.920 6.914 6.897 6.891 2.744 2.662 2.536 2.211 2.026 1.926
f1 (ppm)
9.67 2.89 1.00 1.07 4.24 1.03
f1 (ppm)
218.332 164.171 161.747 148.338 143.882 141.875 141.844 133.933 127.621 122.463 112.646 112.415 108.852 108.614 77.478 77.160 76.843 69.303 39.932 32.745 20.252
148.338 147.167 147.080 143.907 143.882 141.875 141.844 135.495 133.933 129.584 129.562 128.492 128.413 127.720 127.621 122.554 122.463
f1 (ppm)
f1 (ppm)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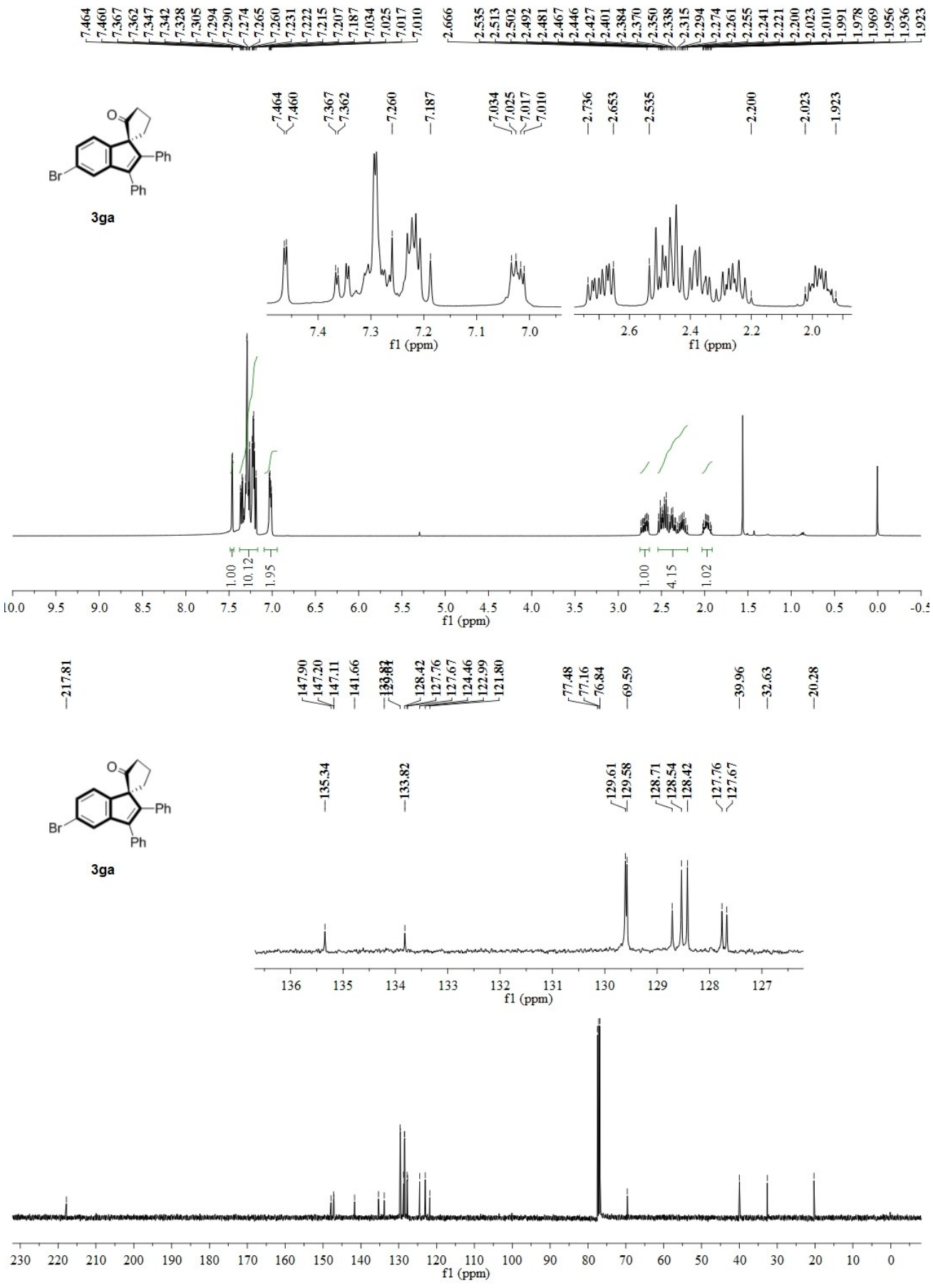
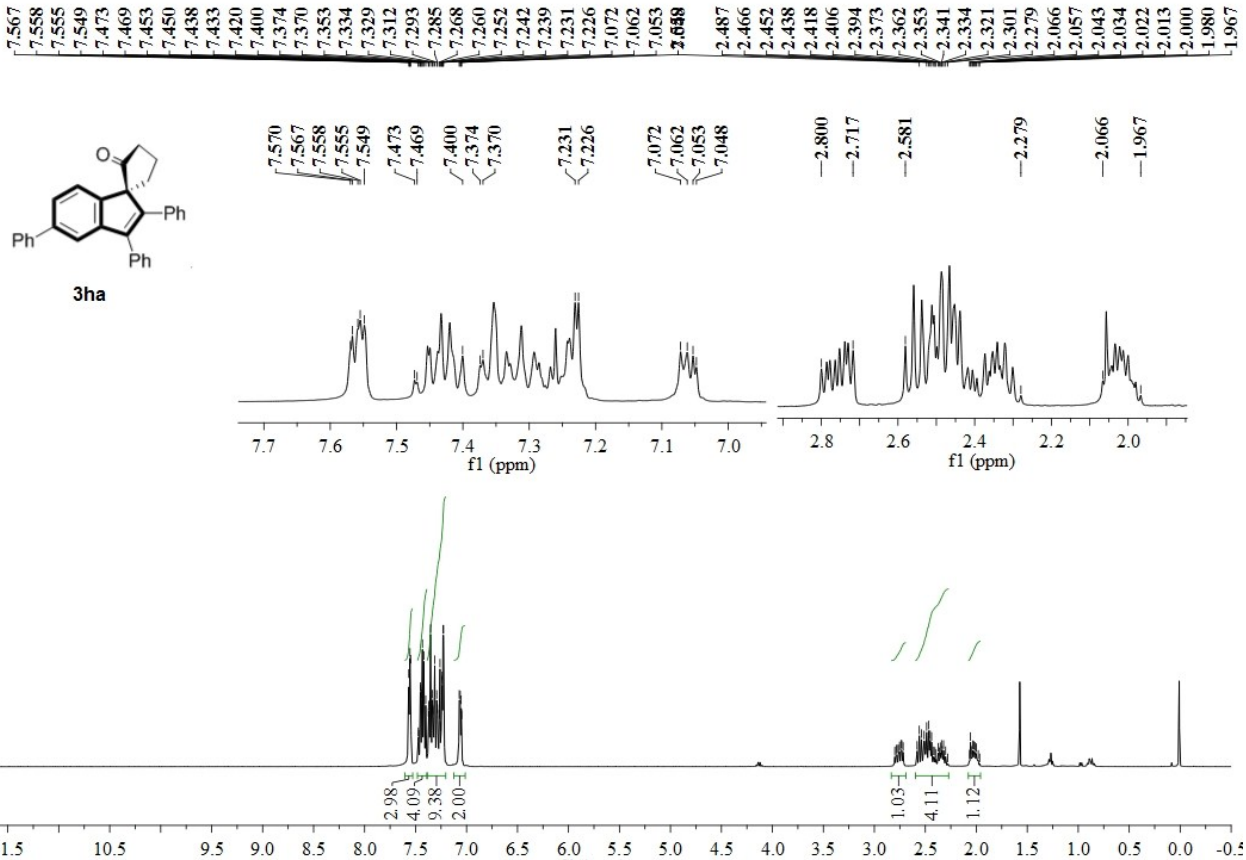
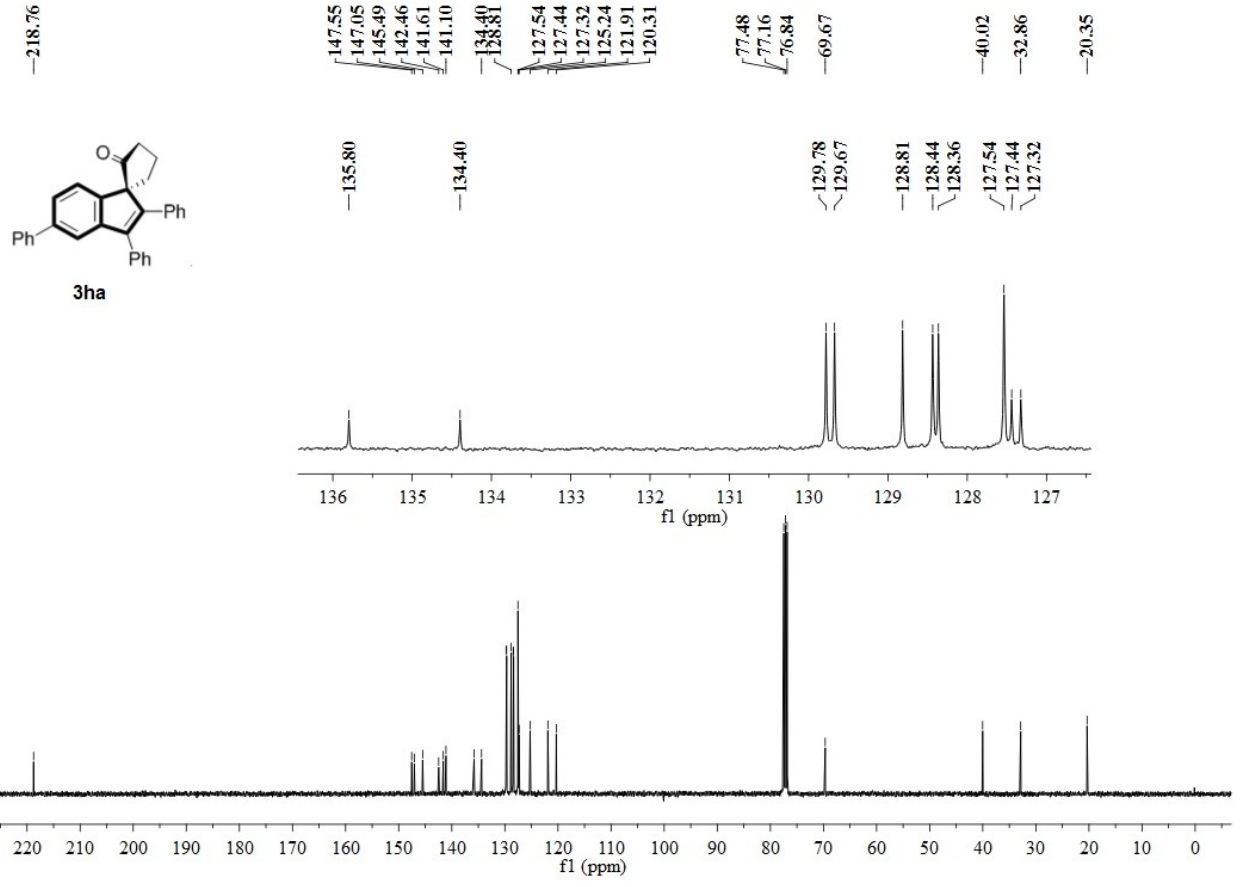
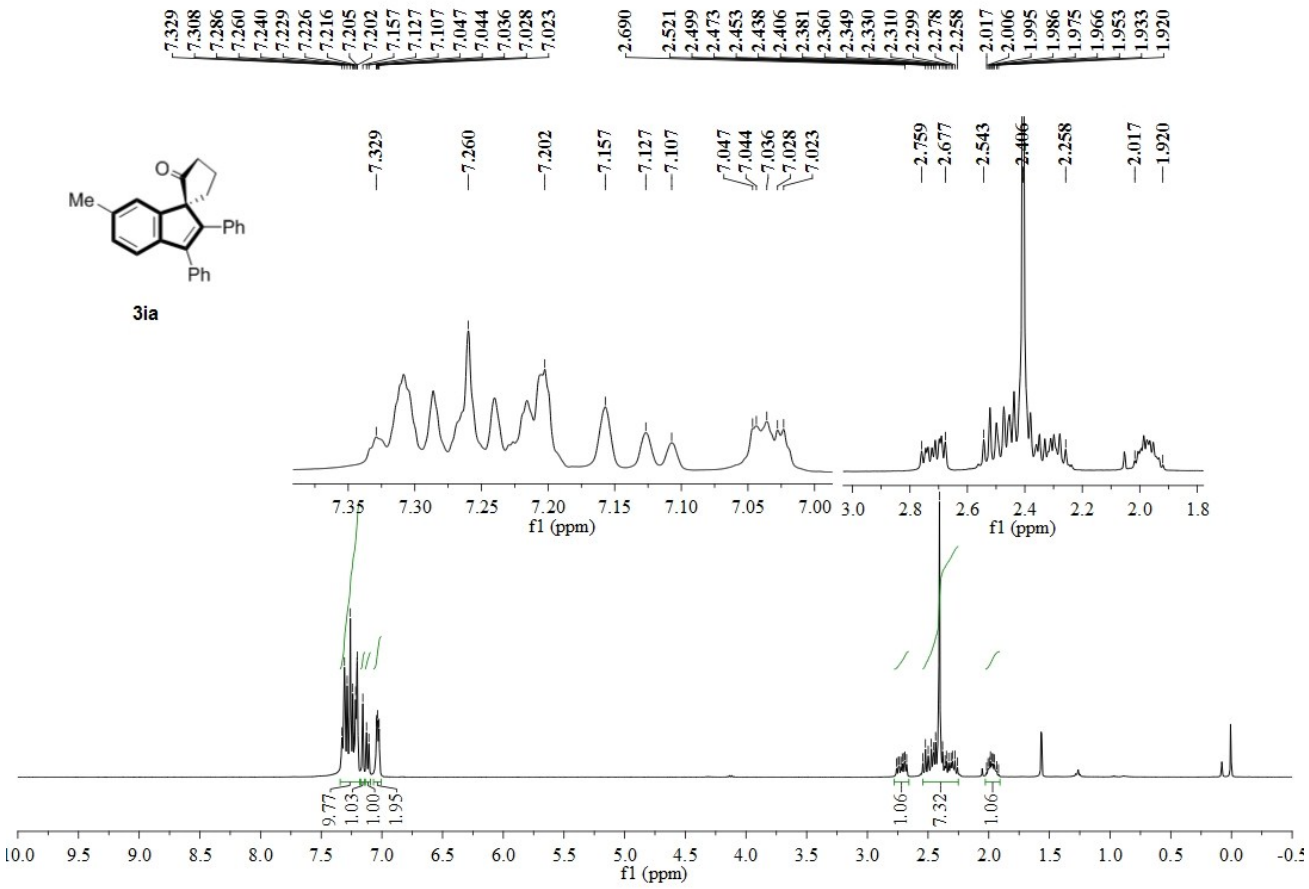
7.260
7.208
7.204
7.053
7.045
7.036
7.030
2.691
2.558
2.536
2.515
2.490
2.482
2.475
2.461
2.441
2.417
2.400
2.386
2.365
2.353
2.337
2.316
2.296
2.284
2.263
2.243
2.222
2.044
2.032
2.022
2.012
2.000
1.990
1.978
1.958
1.944
Cl
Ph
Ph
O
3fa
7.336
7.332
7.260
7.208
7.204
7.053
7.045
7.036
7.030
2.760
2.677
2.558
2.243
2.044
1.944
7.40
7.30
7.20
7.10
7.00
f1 (ppm)
2.8
2.6
2.4
2.2
2.0
f1 (ppm)
11.57
1.99
1.07
4.24
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
f1 (ppm)
218.02
147.98
146.76
146.67
141.69
129.55
128.52
128.42
127.75
127.65
125.83
122.57
121.57
77.48
77.16
76.84
69.50
39.96
32.66
20.27
Cl
Ph
Ph
O
3fa
135.36
133.81
133.70
129.60
129.55
128.52
128.42
127.75
127.65
125.83
122.57
134
132
130
128
126
124
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


3ga
f1 (ppm)
3ga
f1 (ppm)


3ha
f1 (ppm)


3ha
f1 (ppm)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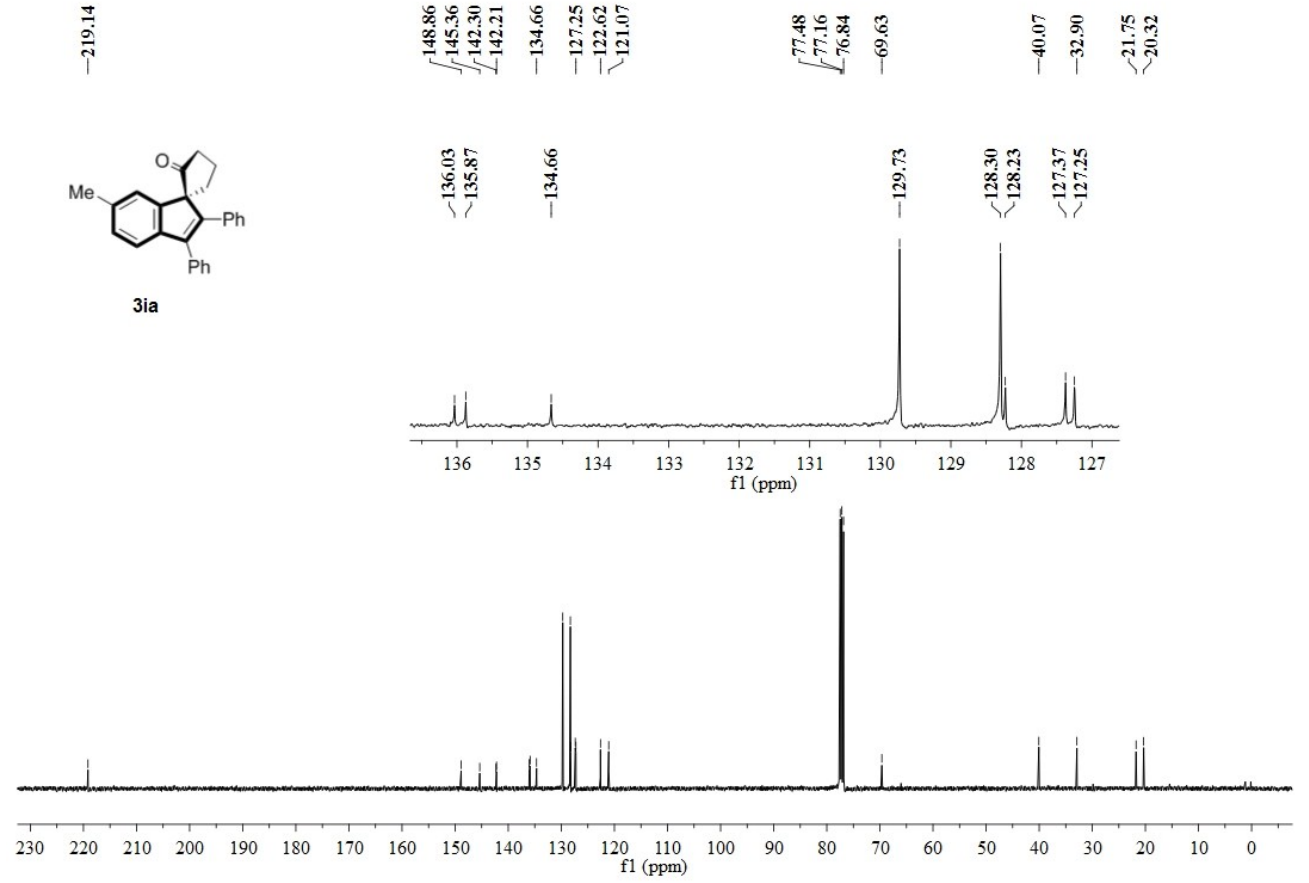
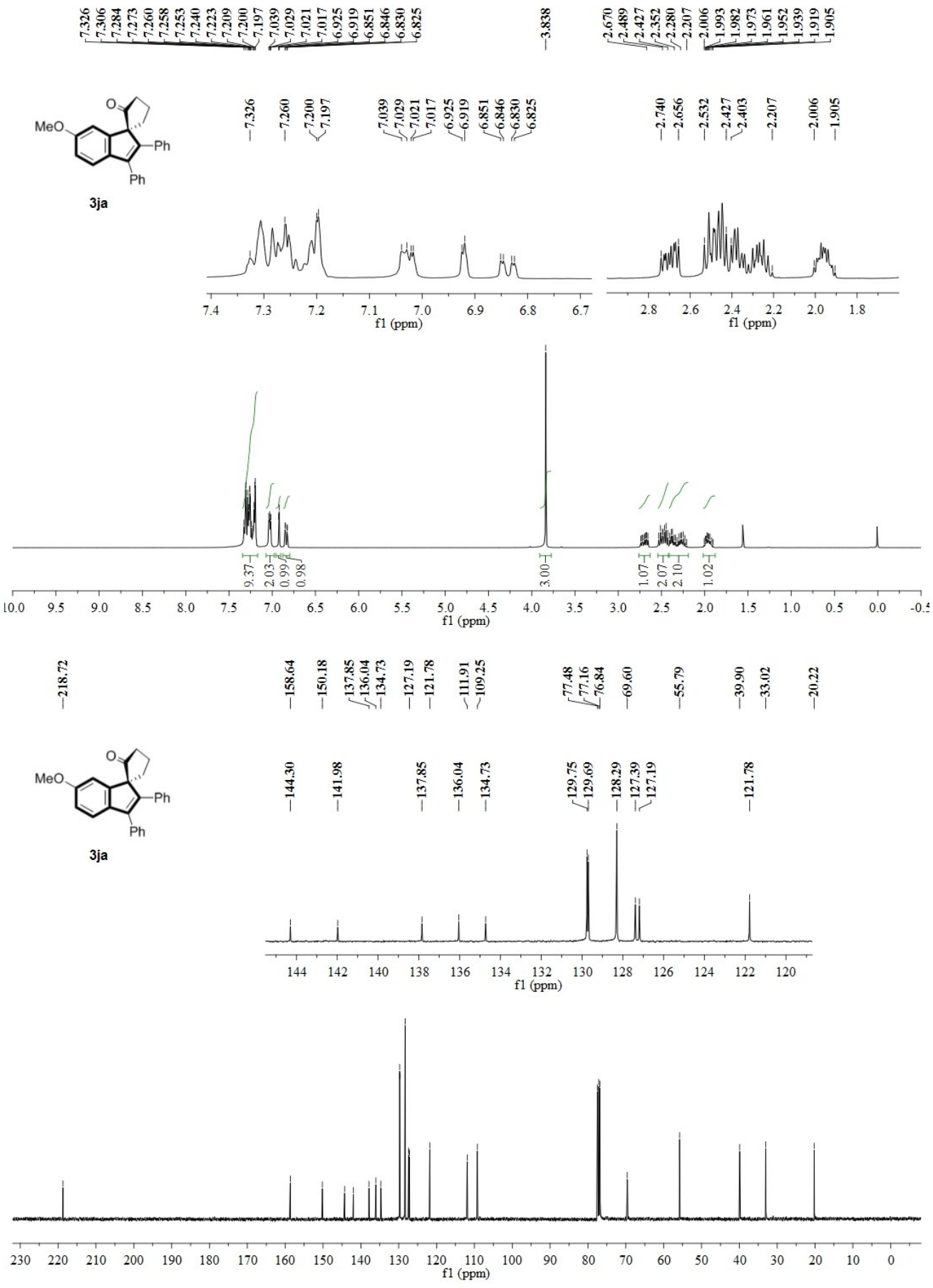
7.308
7.286
7.260
7.240
7.229
7.226
7.216
7.205
7.202
7.157
7.127
7.107
7.047
7.044
7.036
7.028
7.023
2.690
2.521
2.499
2.473
2.453
2.438
2.406
2.381
2.360
2.349
2.330
2.310
2.299
2.278
2.258
2.017
2.006
1.995
1.986
1.975
1.966
1.953
1.933
1.920
Me
Ph
Ph
3ia
f1 (ppm)
9.77
1.03
1.00
1.95
1.06
7.32
1.06


219.14
148.86
145.36
142.30
142.21
134.66
127.25
122.62
121.07
77.48
77.16
76.84
69.63
40.07
32.90
21.75
20.32
136.03
135.87
134.66
129.73
128.30
128.23
127.37
127.25
Me
Ph
Ph
3ia
f1 (ppm)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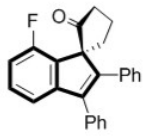
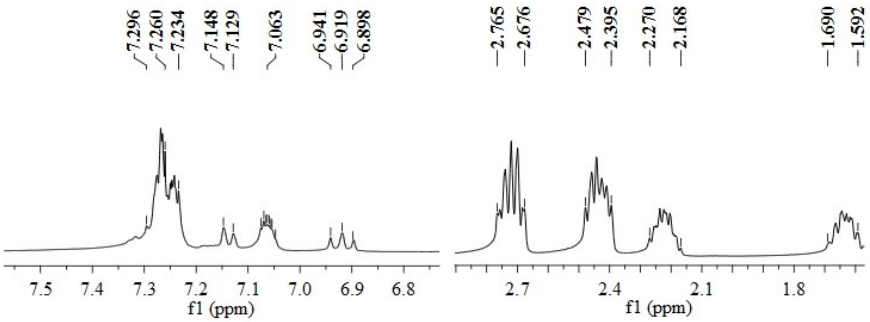
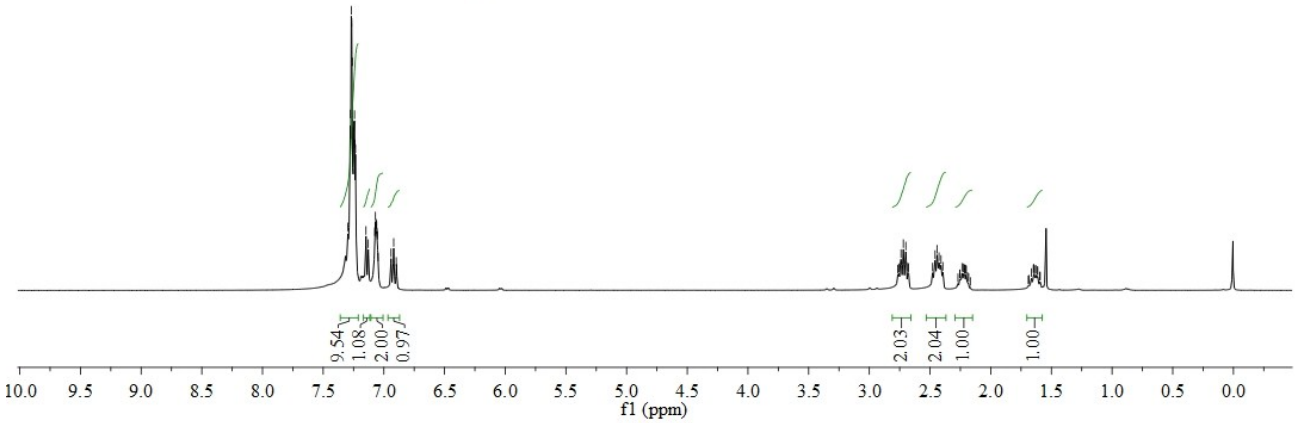
7.284
7.273
7.260
7.258
7.253
7.240
7.223
7.209
7.200
7.197
7.039
7.029
7.021
7.017
6.925
6.919
6.851
6.846
6.830
6.825
3.838
2.670
2.489
2.427
2.352
2.280
2.207
2.006
1.993
1.982
1.973
1.961
1.952
1.939
1.919
1.905
MeO
Ph
Ph
3ja
f1 (ppm)
9.37
2.03
0.99
0.98
3.00
1.07
2.07
2.10
1.02
218.72
158.64
150.18
137.85
136.04
134.73
127.19
121.78
111.91
109.25
77.48
77.16
76.84
69.60
55.79
39.90
33.02
20.22
144.30
141.98
137.85
136.04
134.73
129.75
129.69
128.29
127.39
127.19
121.78


7.296
7.275
7.268
7.265
7.260
7.256
7.250
7.247
7.242
7.239
7.234
7.148
7.129
7.075
7.070
7.065
7.063
7.059
7.056
7.054
7.047
6.941
6.919
6.898
2.765
2.757
2.739
2.720
2.699
2.684
2.676
2.253
2.168
1.690
1.685
1.665
1.649
1.644
1.639
1.629
1.618
1.612
1.596
1.592


F
O
Ph
Ph

3ka


7.296
7.260
7.234
7.148
7.129
7.063
6.941
6.919
6.898
2.765
2.676
2.479
2.395
2.270
2.168
1.690
1.592
7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)
2.7 2.4 2.1 1.8
f1 (ppm)


9.54
1.08
2.00
0.97
2.03
2.04
1.00
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
f1 (ppm)


218.526
158.986
156.537
147.862
141.280
129.622
127.589
117.350
117.322
113.370
113.160
77.478
77.160
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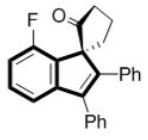
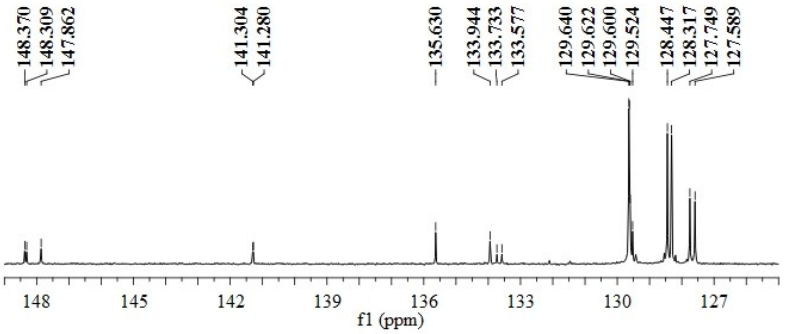
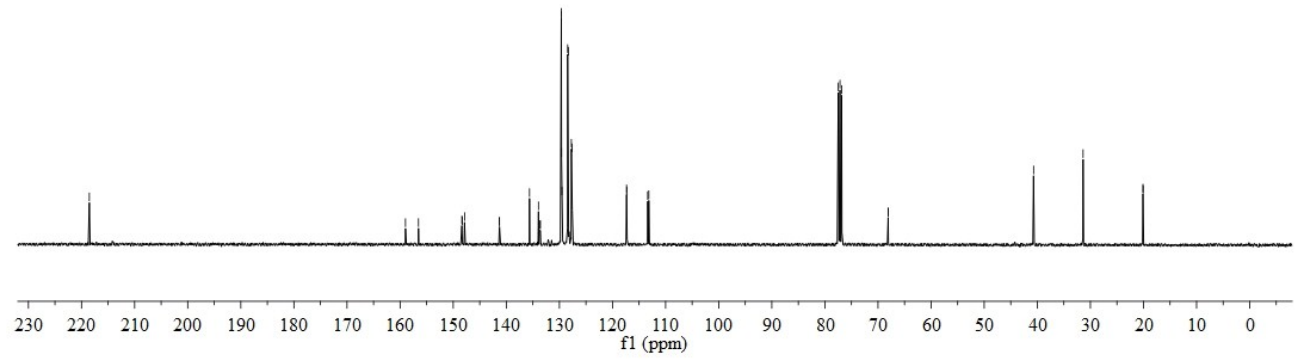
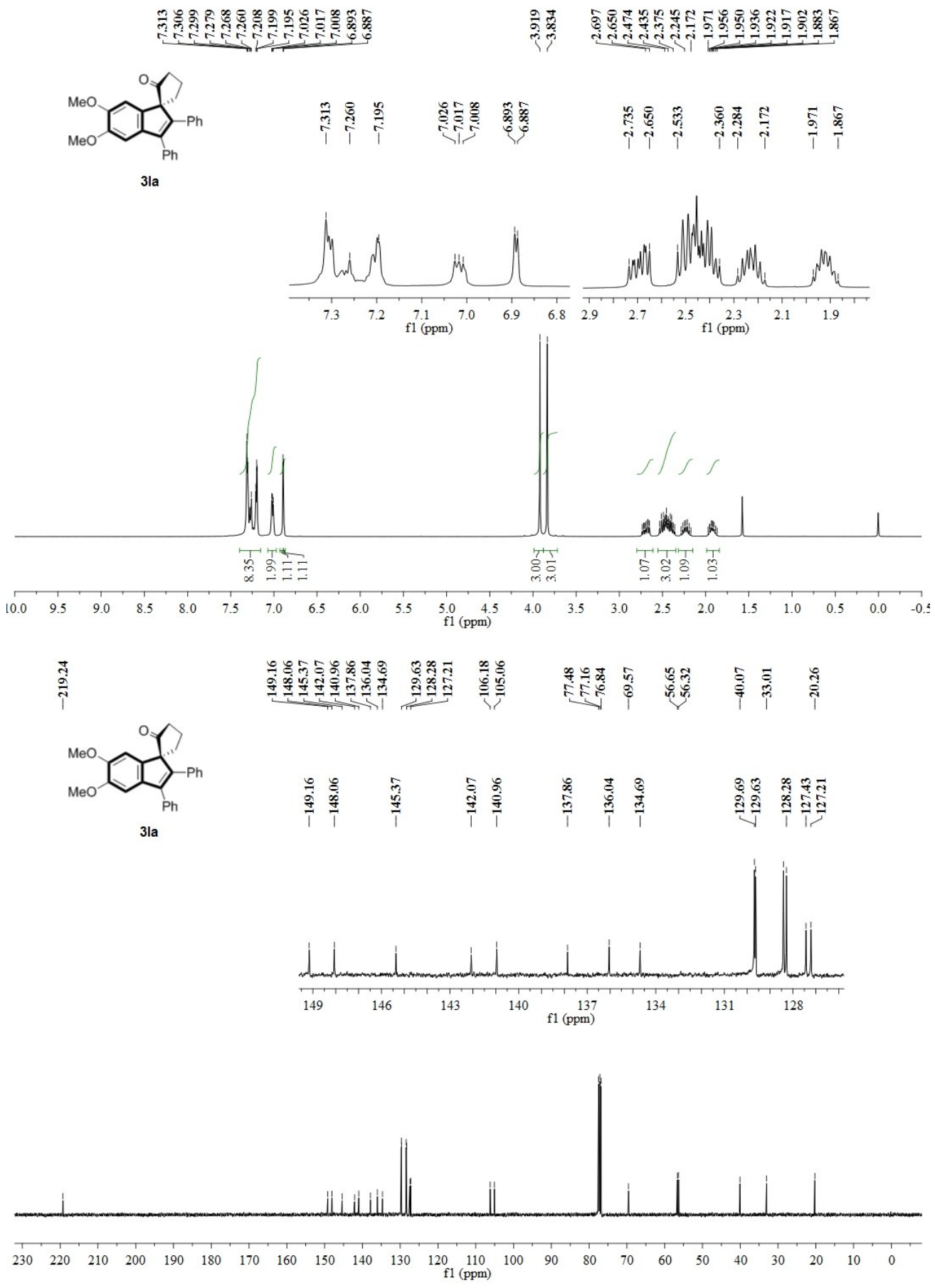
68.085
68.060
40.698
31.375
20.101
20.070


F
O
Ph
Ph

3ka


148.370
148.309
147.862
141.304
141.280
135.630
133.944
133.733
133.577
129.640
129.622
129.600
129.524
128.447
128.317
127.749
127.589
148 145 142 139 136 133 130 127
f1 (ppm)


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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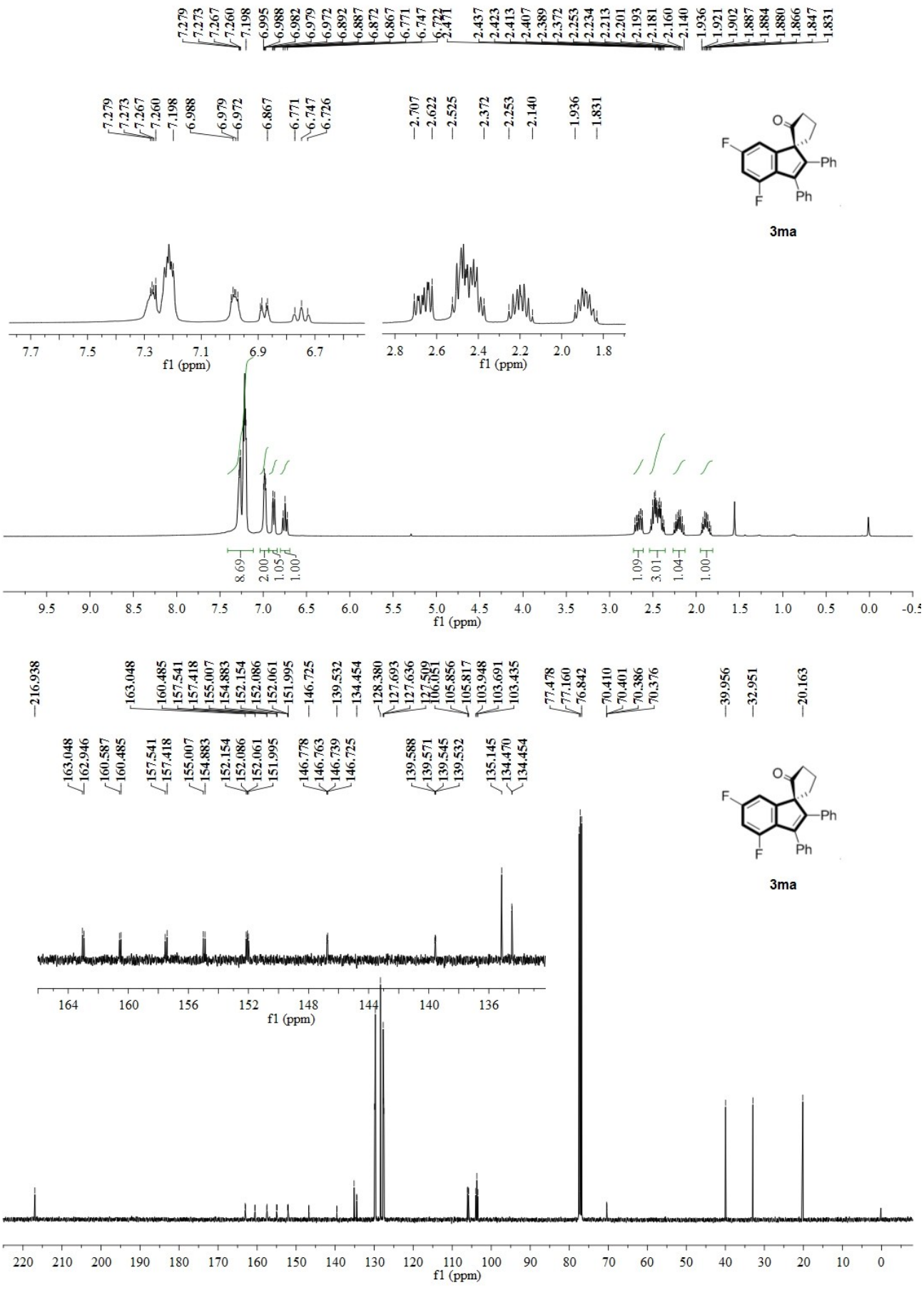
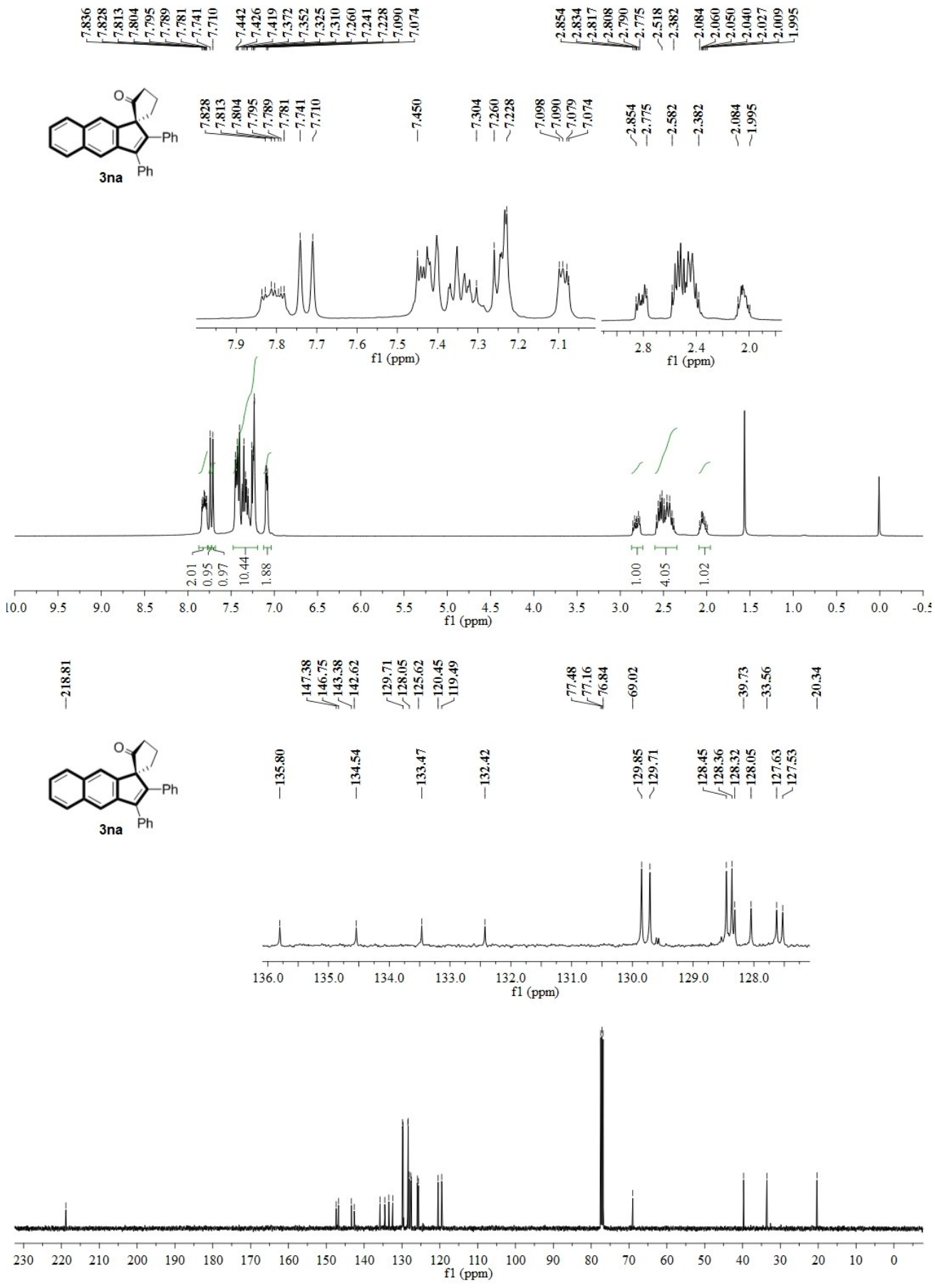
7.279
7.268
7.260
7.208
7.199
7.195
7.026
7.017
7.008
6.893
6.887
3.919
3.834
2.697
2.650
2.474
2.435
2.375
2.245
2.172
1.971
1.956
1.950
1.936
1.922
1.917
1.902
1.883
1.867
MeO
MeO
Ph
Ph
3la
f1 (ppm)
8.35
1.99
1.11
1.11
3.00
3.01
1.07
3.02
1.09
1.03
219.24
149.16
148.06
145.37
142.07
140.96
137.86
136.04
134.69
129.63
128.28
127.21
106.18
105.06
77.48
77.16
76.84
69.57
56.65
56.32
40.07
33.01
20.26


3ma
f1 (ppm)
3ma
f1 (ppm)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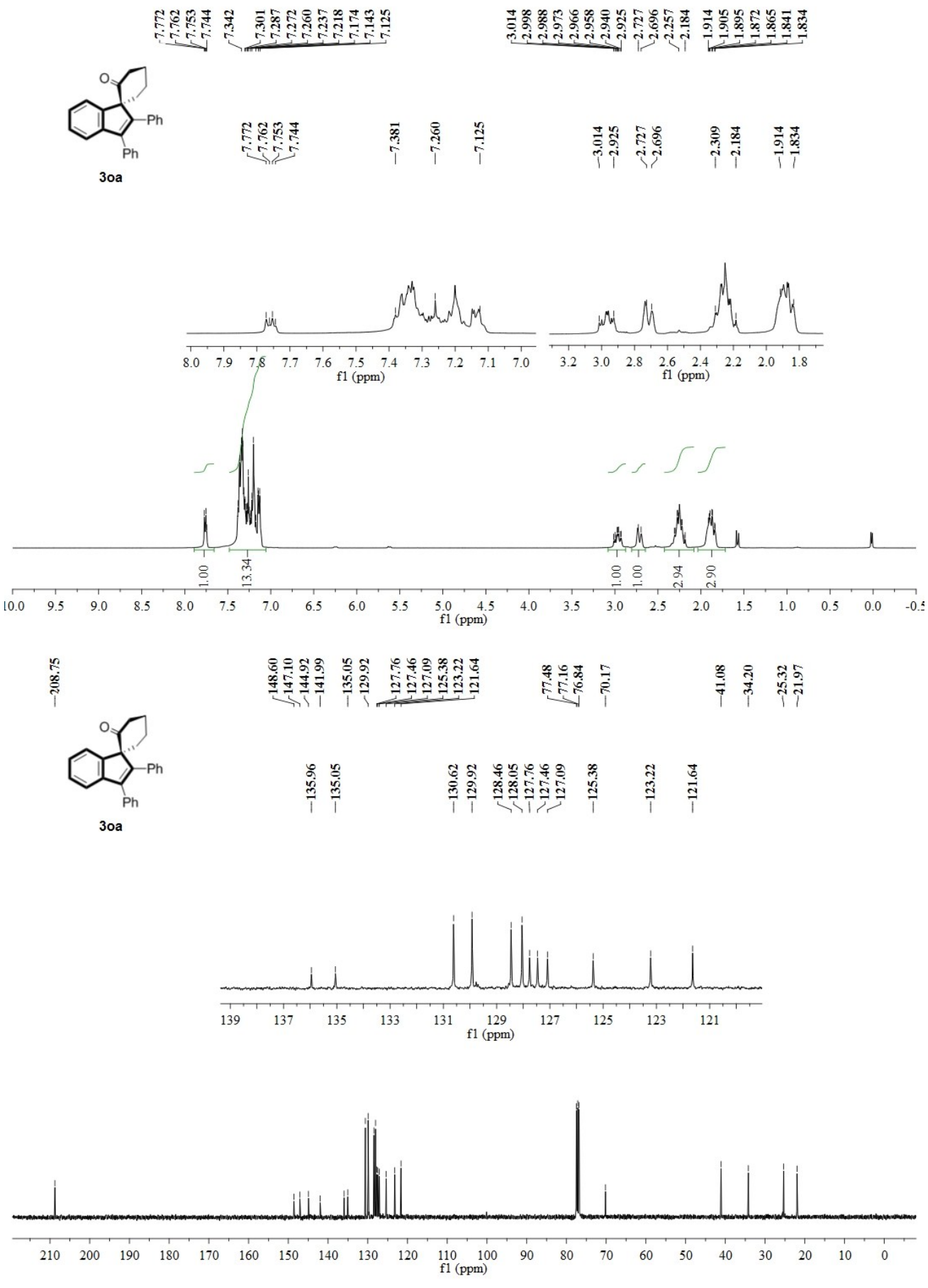
7.795
7.789
7.781
7.741
7.710
7.442
7.426
7.419
7.372
7.352
7.325
7.310
7.260
7.241
7.228
7.090
7.074
2.854
2.834
2.817
2.808
2.790
2.775
2.518
2.382
2.084
2.060
2.050
2.040
2.027
2.009
1.995
O
Ph
Ph
3na
7.828
7.813
7.804
7.795
7.789
7.781
7.741
7.710
7.450
7.304
7.260
7.228
7.098
7.090
7.079
7.074
2.854
2.775
2.582
2.382
2.084
1.995
f1 (ppm)
f1 (ppm)
2.01
0.95
0.97
10.44
1.88
1.00
4.05
1.02
f1 (ppm)
218.81
147.38
146.75
143.38
142.62
129.71
128.05
125.62
120.45
119.49
77.48
77.16
76.84
69.02
39.73
33.56
20.34
135.80
134.54
133.47
132.42
129.85
129.71
128.45
128.36
128.32
128.05
127.63
127.53
O
Ph
Ph
3na
f1 (ppm)
f1 (ppm)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7.301
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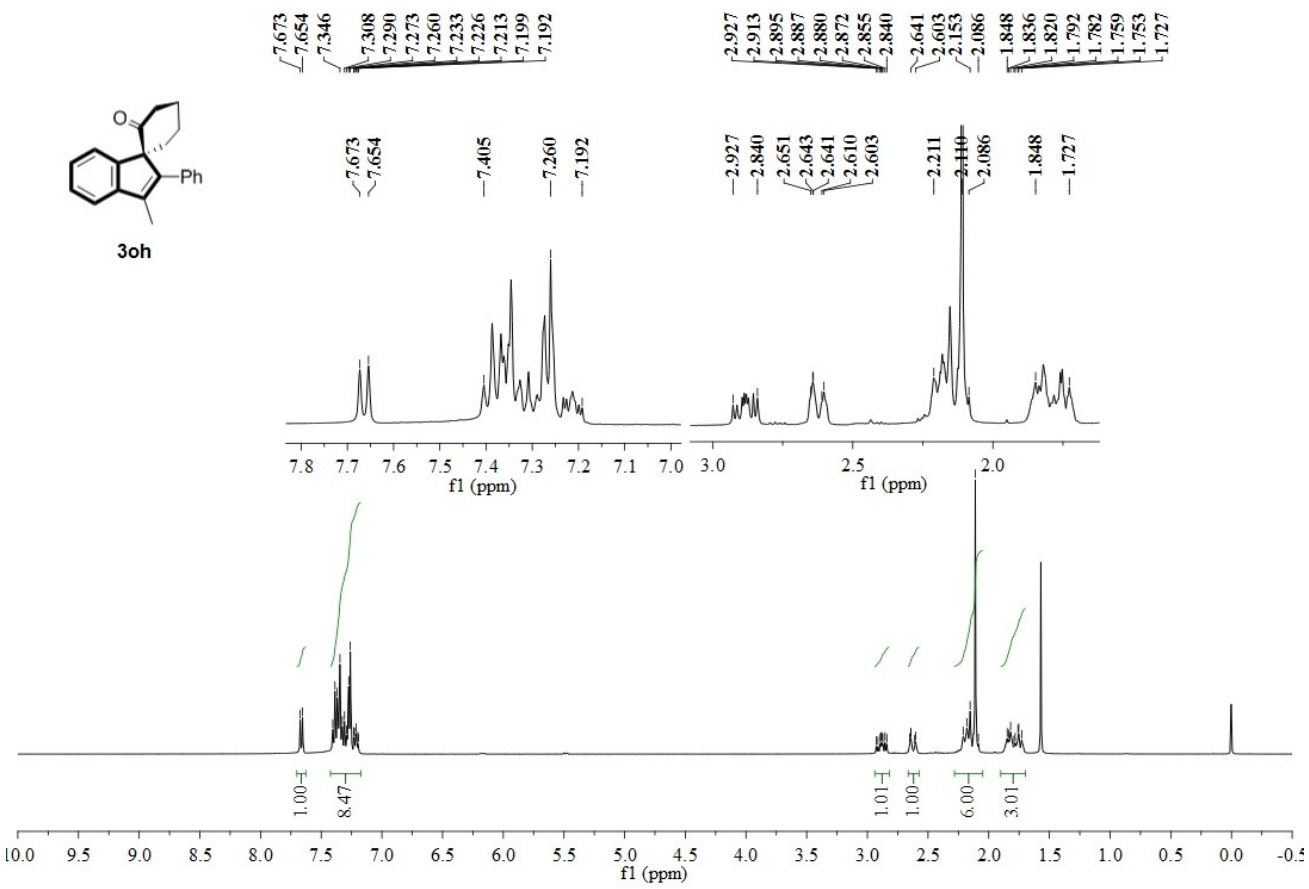
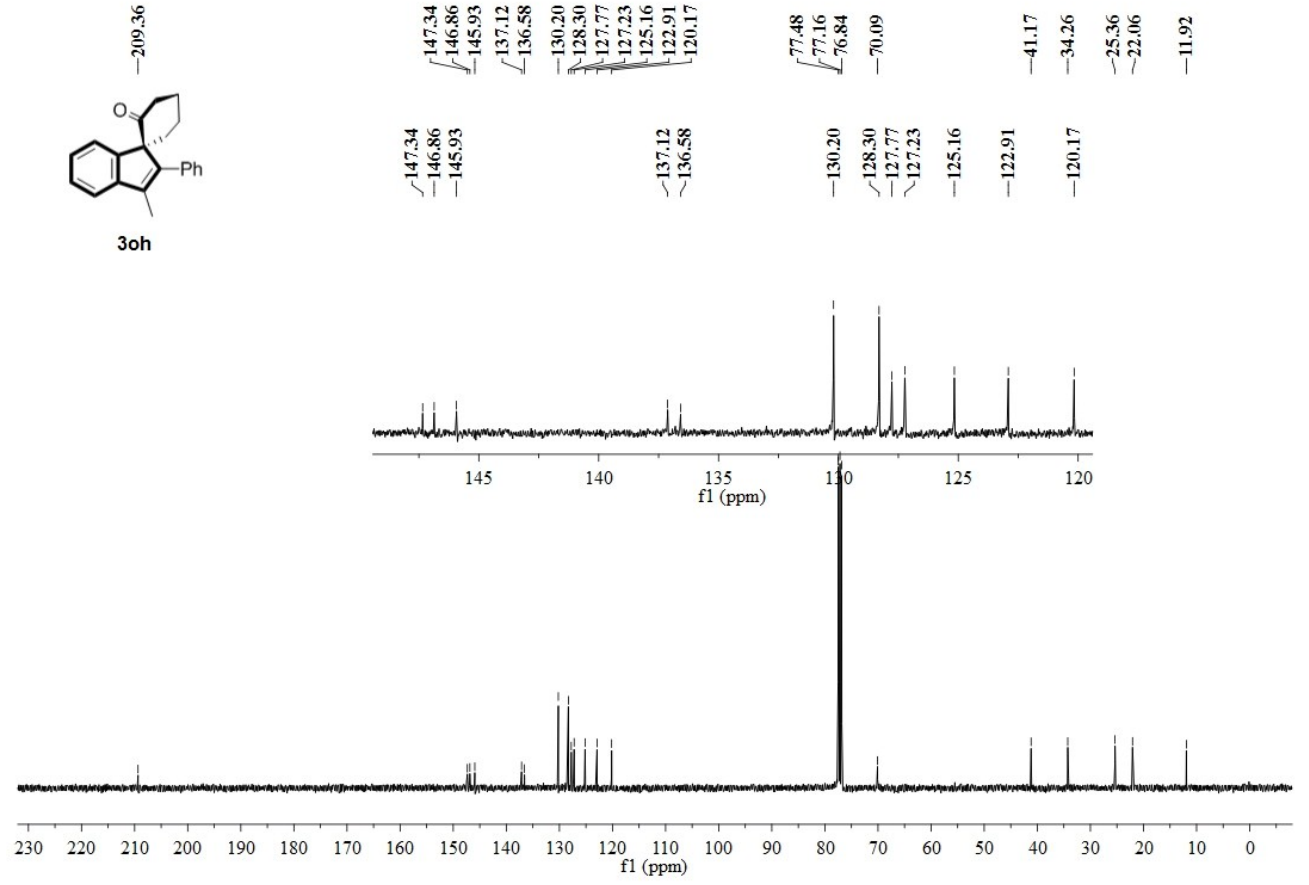
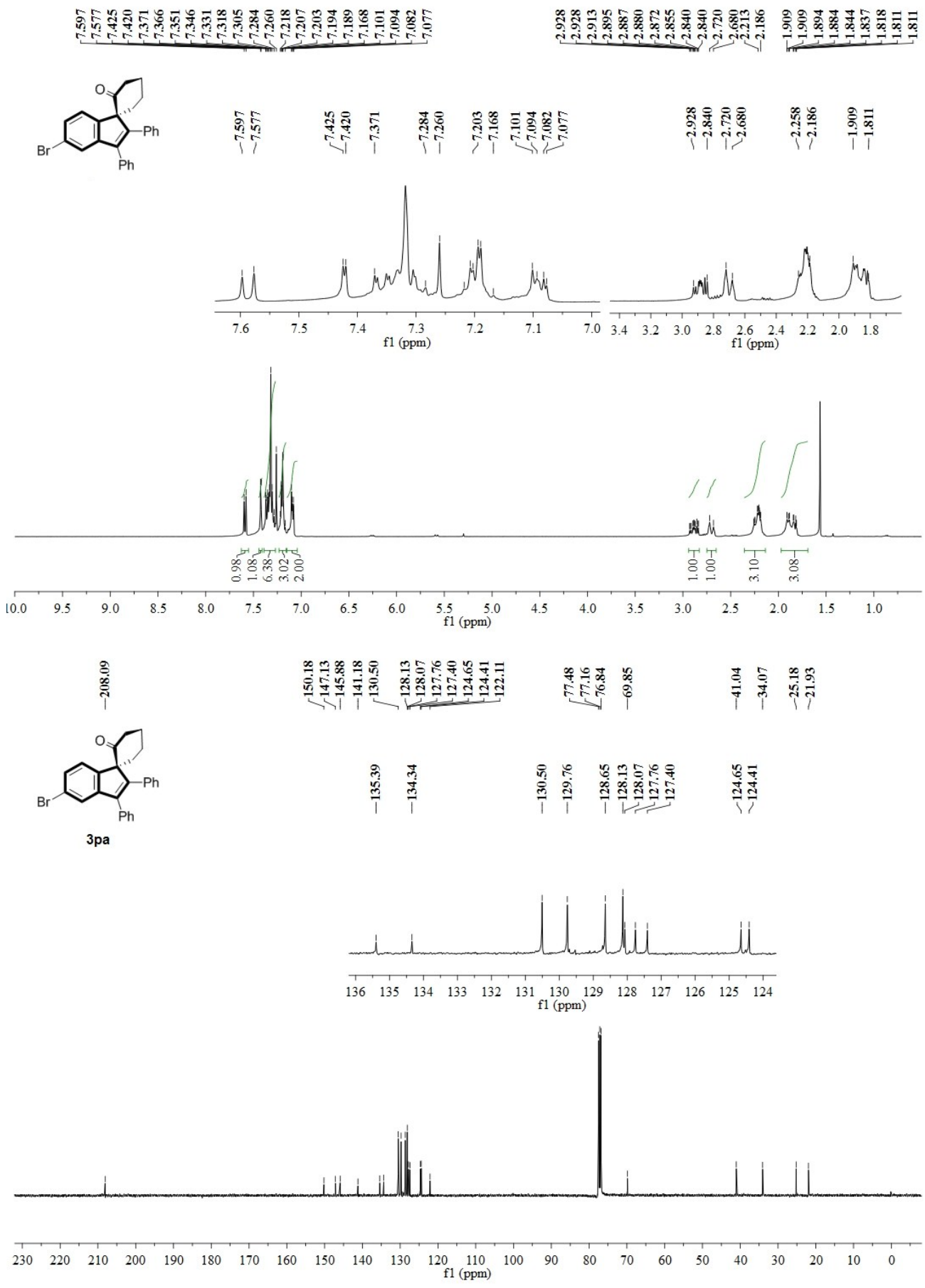
7.272
7.260
7.237
7.218
7.174
7.143
7.125
3.014
2.998
2.988
2.973
2.966
2.958
2.940
2.925
2.727
2.696
2.257
2.184
1.914
1.905
1.895
1.872
1.865
1.841
1.834
O
Ph
Ph
3oa
7.772
7.762
7.753
7.744
7.381
7.260
7.125
3.014
2.925
2.727
2.696
2.309
2.184
1.914
1.834
f1 (ppm)
f1 (ppm)
1.00
13.34
1.00
1.00
2.94
2.90
f1 (ppm)
208.75
148.60
147.10
144.92
141.99
135.05
129.92
127.76
127.46
127.09
125.38
123.22
121.64
77.48
77.16
76.84
70.17
41.08
34.20
25.32
21.97
O
Ph
Ph
3oa
135.96
135.05
130.62
129.92
128.46
128.05
127.76
127.46
127.09
125.38
123.22
121.64
f1 (ppm)
f1 (ppm)


3oh
f1 (ppm)


3oh
f1 (ppm)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2.928 2.928 2.913 2.895 2.887 2.880 2.872 2.855 2.840 2.840 2.720 2.680 2.213 2.186 1.909 1.909 1.894 1.884 1.844 1.837 1.818 1.811 1.811
O
Ph
Br
Ph
f1 (ppm)
0.98 1.08 6.38 3.02 2.00 1.00 1.00 3.10 3.08
208.09 150.18 147.13 145.88 141.18 130.50 128.13 128.07 127.76 127.40 124.65 124.41 122.11 77.48 77.16 76.84 69.85 41.04 34.07 25.18 21.93
135.39 134.34 130.50 129.76 128.65 128.13 128.07 127.76 127.40 124.65 124.41
3pa