Supporting Information

Synthesis of Highly Polysubstituted Cyclopentadienes through Oxypalladation Initiated Domino Heck Reactions of Internal Alkynes

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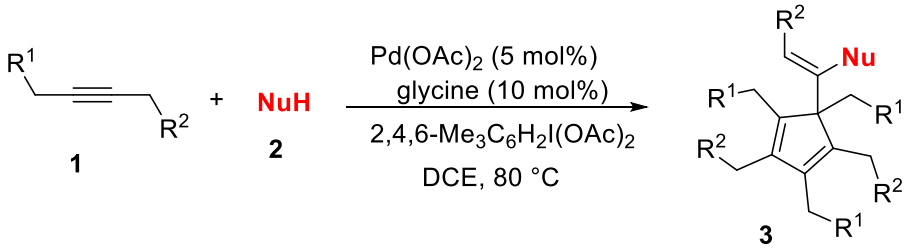
Contents

1. General experimental information

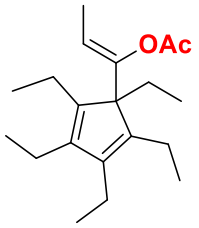
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra were recorded at ambient temperature using 400 or 500 MHz spectrometers. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Enantiomeric excesses (ee) were determined by chiral high-performance liquid chromatography (chiral HPLC). The chiral columns used for the determination of Enantiomeric ratios by chiral HPLC were Chiralpak columns. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. High resolution mass spectra were acquired on an LTQ FT spectrometer, and were obtained by peak matching. Melting points are reported uncorrected. Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Chromatography was performed using with 300-400 mesh silica gel (SiO_2). Unless otherwise noted, all reagents and solvents were obtained from commercial sources and, where appropriate, purified prior to use. alkynes **1a-1h**, carboxylic acids **2a-2p, 2q-2s** and ligands **L1-L11** were purchased from Sigma-Adrich.

2. Synthesis of cyclopentadienes 3



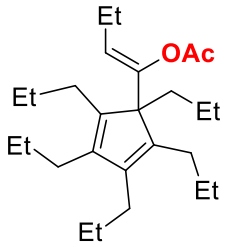
General procedure A: In a 10 mL reaction flask was charged with $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 5 mol%), glycine **L4** (2.3 mg, 0.03 mmol, 10 mol%), and DCE (1.0 mL). The mixture was stirred at room temperature for 30 min under N_2. Then, alkynes **1** (0.9 mmol), NuH **2** (1.5 mmol, 5.0 equiv.), 2,4,6-$Me_3C_6H_2I(OAc)_2$ (218.4 mg, 0.6 mmol, 2.0 equiv.) and DCE (2.0 mL) were added. The reaction vessel was once again sealed with a Teflon cap. The reaction mixture was stirred vigorously at 80 °C in an oil bath

for 16-24 h until alkyne **1** was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (1/20 to 1/5, ethyl acetate/petroleum ether) to afford cyclopentadienes **3**.



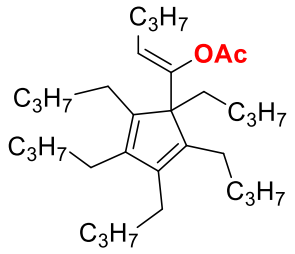
3aa

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl acetate (3aa). Light yellow liquid, 0.065 g, 71% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31 (q, J = 5.2, 1H), 2.26−2.22 (m, 4H), 2.14−2.02 (m, 4H), 1.88 (s, 3H), 1.74 (q, J = 6.0 Hz, 2H), 1.47 (d, J = 5.6 Hz, 3H), 1.04−0.99 (m, 12H), 0.46 (t, J = 5.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.0, 150.1, 143.9, 141.4, 111.0, 65.5, 22.1, 20.3, 18.8, 18.7, 14.9, 13.7, 11.6, 7.3; HRMS (ESI) *m/z* calcd for $C_{20}H_{33}O_2$ $[M+H]^+$ 305.2475, found 305.2475.



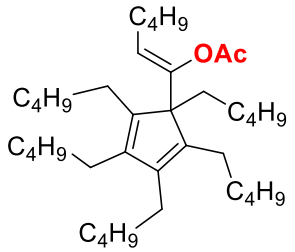
3ba

(Z)-1-(1,2,3,4,5-pentapropylcyclopenta-2,4-dien-1-yl)but-1-en-1-yl acetate (3ba). Light yellow liquid, 0.087g, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.19-5.16 (t, J = 7.2 Hz, 1H), 2.17−2.13 (m, 4H), 2.10−2.02 (m, 2H), 1.98−1.90 (m, 2H), 1.88−1.82 (m, 2H), 1.86 (s, 3H), 1.63−1.59 (m, 2H), 1.43−1.33 (m, 8H), 0.98−0.90 (m, 15H), 0.80−0.74 (m, 2H), 0.78 (d, J = 1.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 167.2, 148.5, 142.5, 141.3, 118.3, 64.8, 32.2, 28.6, 28.4, 23.5, 22.5, 20.5, 19.8, 15.8, 15.1, 14.6, 14.3, 13.6; HRMS (ESI) *m/z* calcd for $C_{26}H_{45}O_2$ $[M+H]^+$ 389.3414, found 389.3417.



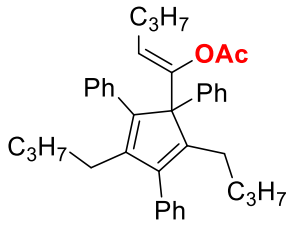
3ca

(Z)-1-(1,2,3,4,5-pentabutylcyclopenta-2,4-dien-1-yl)pent-1-en-1-yl acetate (3ca). Light yellow liquid, 0.086g, 61% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.20 (t, J = 6.8 Hz, 1H), 2.18−2.15 (m, 4H), 2.10−2.04 (m, 2H), 1.97−1.92 (m, 2H), 1.86 (s, 3H), 1.64−1.58 (m, 5H), 1.40−1.33 (m, 19H), 0.94−0.88 (m, 15H), 0.84 (t, J = 7.2 Hz, 3H), 0.75−0.73 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.2, 149.2, 142.5, 141.0 ,116.6, 64.8, 32.4, 31.4, 28.4, 26.0, 25.9, 24.6, 23.6, 23.1, 23.0, 22.2, 20.5, 14.1, 14.0, 13.9, 13.8; HRMS (ESI) *m/z* calcd for $C_{32}H_{57}O_2$ $[M+H]^+$ 473.4353, found 473.4360.



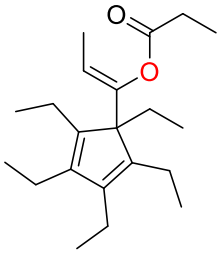
3da

(Z)-1-(1,2,3,4,5-pentapentylcyclopenta-2,4-dien-1-yl)hex-1-en-1-yl acetate (3da). Light yellow liquid, 0.097 g, 58% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.16 (t, J = 7.2 Hz, 1H), 2.17−2.14 (m, 4H), 2.10−2.02 (m, 2H), 1.98−1.91 (m, 2H), 1.86 (s, 3H), 1.63−1.59 (m, 4H), 1.38−1.25 (m, 31H), 0.91−0.87 (m, 16H), 0.84 (t, J = 7.2 Hz, 3H), 0.79−0.71 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 167.1, 149.1, 142.5, 141.2, 116.7, 64.9, 32.7, 32.3, 31.2, 29.9, 28.8, 26.2, 26.1, 26.0, 22.6, 22.5, 22.4, 22.1, 20.5, 14.1, 14.0, 13.9; HRMS (ESI) *m/z* calcd for $C_{38}H_{69}O_2$ $[M+H]^+$ 557.5292, found 557.5309.



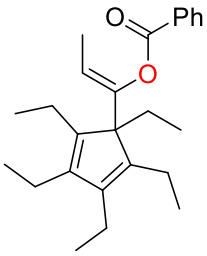
3ea

(Z)-1-(2,4-dibutyl-1,3,5-triphenylcyclopenta-2,4-dien-1-yl)pent-1-en-1-yl acetate (3ea) A yellow liquid, 0.093 g, 56% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38-7.34 (m, 5H), 7.32-7.28 (m, 5H), 7.21-7.20 (m, 3H), 7.07-7.04 (m, 3H), 5.32 (t, J = 7.0 Hz, 1H), 2.39-2.31 (m, 3H), 2.07-2.04 (m, 5H), 1.49-1.44 (m, 3H), 0.94-0.90 (m, 7H), 0.85-0.80 (m, 3H), 0.60 (t, J = 7.5 Hz, 3H), 0.53 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.7, 146.5, 146.2, 145.1, 144.9, 144.3, 137.7, 136.9, 136.0, 129.9, 129.8, 129.5, 128.4, 127.9, 127.4, 126.9, 126.7, 126.1, 119.5, 66.6, 30.5, 29.9, 29.2, 26.1, 24.4, 22.8, 22.3, 22.1, 20.9, 14.2, 14.0, 13.6; HRMS (ESI) *m/z* calcd for $C_{38}H_{44}NaO_2$ [M + Na]$^{+}$: 555.3234, found 555.3233.



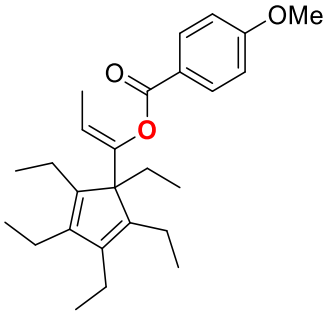
3ab

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl butyrate (3ab). Light yellow liquid, 0.096 g, 73% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (q, J = 6.8 Hz, 1H), 2.26−1.99 (m, 10H), 1.75 (q, J = 7.2 Hz, 2H), 1.46 (d, J = 6.8 Hz, 3H), 1.05−0.99 (m, 15H), 0.45 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.4, 150.0, 141.4, 110.8, 65.4, 27.3, 22.1, 18.8, 14.9, 13.7, 11.6, 9.2, 7.3; HRMS (ESI) *m/z* calcd for $C_{21}H_{34}O_2$ [M+Na]$^{+}$ 341.2451, found 341.2451.



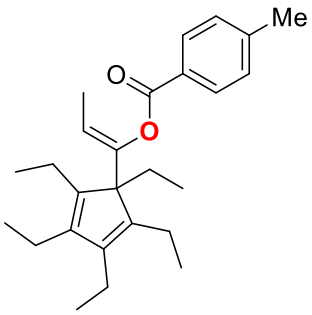
3ac

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl benzoate (3ac). Light yellow liquid, 0.075 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 2H), 5.45 (q, J = 6.8 Hz, 1H), 2.27−2.04 (m, 8H), 1.82 (q, J = 7.2, 2H), 1.54 (d, J = 6.8 Hz, 3H), 1.07 (t, J = 7.6 Hz, 6H), 0.84 (t, J = 7.6 Hz, 6H), 0.48 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 162.7, 150.0, 144.2, 141.3, 132.6, 130.1, 129.9, 128.0, 111.5, 65.5, 22.2, 18.8, 14.6, 13.8, 11.8, 7.3; HRMS (ESI) *m/z* calcd for $C_{25}H_{35}O_2$ $[M+H]^+$ 367.2632, found 367.2629.



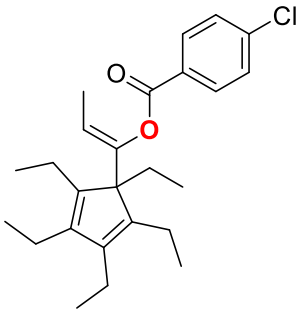
3ad

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 4-methoxybenzoate (3ad). Light yellow liquid, 0.072 g, 64% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 8.8 Hz, 2H), 6.85 (d, J = 8.4 Hz, 2H), 5.42 (q, J = 6.8 Hz, 1H), 3.84 (s, 3H), 2.26−2.04 (m, 8H), 1.81 (q, J = 7.2 Hz, 2H), 1.53 (d, J = 6.8 Hz, 3H), 1.09 (t, J = 7.6 Hz, 6H), 0.86 (t, J = 7.2 Hz, 6H), 0.47 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 163.0, 162.4, 150.0, 144.1, 141.4, 131.9, 122.6, 113.2, 111.3, 65.6, 55.4, 22.1, 18.8, 18.7, 14.7, 13.8, 11.8, 7.3; HRMS (ESI) *m/z* calcd for $C_{26}H_{37}O_3$ $[M+H]^+$ 397.2737, found 397.2737.



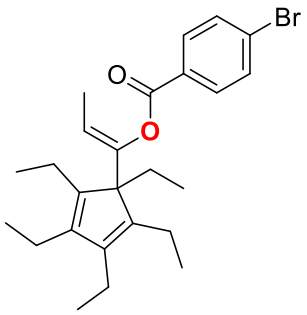
3ae

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 4-methylbenzoate (3ae). Light yellow liquid, 0.071 g, 62% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 5.43 (d, J = 6.8 Hz, 1H), 2.38 (s, 3H), 2.27−2.04 (m, 8H), 1.81 (q, J = 6.0 Hz, 2H), 1.52 (d, J = 6.8 Hz, 3H), 1.09 (t, J = 7.6 Hz, 6H), 0.86 (t, J = 7.6 Hz, 6H), 0.47 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 162.8, 150.0, 144.1, 143.2, 141.3, 129.9, 128.7, 127.4, 111.3, 65.6, 22.1, 21.6, 18.8, 18.7, 14.7, 13.8, 11.8, 7.3; HRMS (ESI) *m/z* calcd for $C_{26}H_{37}O_2$ $[M+H]^+$ 381.2788, found 381.2791.



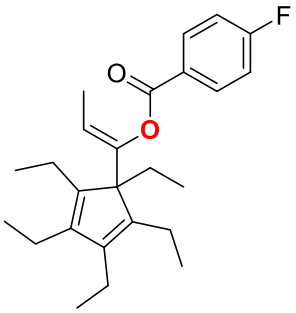
3af

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 4-chlorobenzoate (3af) A yellow liquid, 0.085 g, 71% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 5.45 (d, 6.5 Hz, 1H), 2.23-2.07 (m, 8H), 1.81 (q, J = 7.0 Hz, 2H), 1.52 (d, J = 6.5 Hz, 3H), 1.06 (t, J = 7.5 Hz, 6H), 0.82 (t, J = 7.0 Hz, 6H), 0.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.9, 150.1, 144.4, 141.4, 139.2, 131.4, 128.8, 128.6, 111.8, 65.7, 22.3, 19.0, 14.9, 14.0, 12.0, 7.4; HRMS (ESI) *m/z* calcd for $C_{25}H_{33}ClNaO_2$ $[M + Na]^+$: 423.2061, found 423.2058.



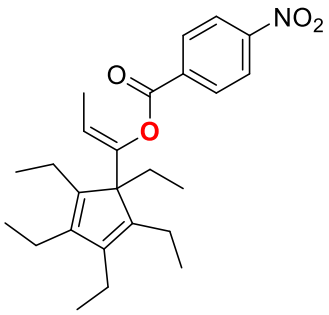
3ag

(*Z*)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 4-bromobenzoate (3ag) A yellow liquid, 0.081 g, 61% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (d, J = 8.5 Hz, 2H), 7.51 (d, J = 8.5 Hz, 2H), 5.45 (d, J = 7.0 Hz, 1H), 2.24-2.15 (m, 4H), 2.13-2.03 (m, 4H), 1.81 (q, J = 7.5 Hz, 2H), 1.52 (d, J = 6.5 Hz, 3H), 1.06 (t, J = 8.0 Hz, 6H), 0.83 (t, J = 7.5 Hz, 6H), 0.46 (t, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.1, 150.1, 144.5, 141.4, 131.6, 129.2, 127.9, 111.8, 65.7, 22.3, 19.0, 18.9, 14.9, 14.0, 12.0, 7.4; HRMS (ESI) *m/z* calcd for $C_{25}H_{33}BrNaO_2$ $[M + Na]^+$: 467.1556, found 467.1546.



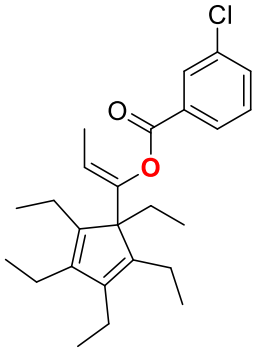
3ah

(*Z*)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 4-fluorobenzoate (3ah) A yellow liquid, 0.076 g, 66% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91-7.88 (m, 2H), 7.03 (t, J = 8.5 Hz, 2H), 5.45 (q, J = 7.0 Hz, 1H), 2.25-2.15 (m, 4H), 2.13-2.04 (m, 4H), 1.81 (q, J = 7.5 Hz, 2H), 1.53 (d, J = 7.0 Hz, 3H), 1.06 (t, J = 7.5 Hz, 6H), 0.82 (t, J = 7.5 Hz, 6H), 0.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.7 (d, J = 252.0 Hz), 161.7, 150.0, 144.3, 141.4, 132.5 (d, J = 9.1 Hz), 126.5 (d, J = 2.9 Hz), 115.3 (d, J = 21.6 Hz), 111.7, 65.6, 22.2, 18.9, 18.8, 14.7, 13.9, 11.8, 7.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ -106.2; HRMS (ESI) *m/z* calcd for $C_{25}H_{34}FO_2$ $[M + H]^+$: 385.2537, found 385.2530.



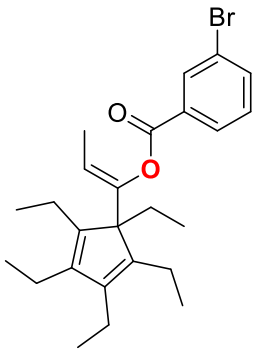
3ai

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 4-nitrobenzoate (3ai) A yellow liquid, 0.089 g, 72% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.23 (d, J = 8.5 Hz, 2H), 8.05 (d, J = 8.5 Hz, 2H), 5.50 (q, J = 6.5 Hz, 1H), 2.23-2.19 (m, 2H), 2.16-2.11 (m, 4H), 2.10-2.05 (m, 2H), 1.82 (q, J = 7.0 Hz, 2H), 1.54 (d, J = 7.0 Hz, 3H), 1.07 (t, J = 7.5 Hz, 6H), 0.81 (t, J = 7.5 Hz, 6H), 0.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.9, 150.5, 150.2, 144.6, 141.4, 135.8, 131.1, 123.4, 112.2, 65.7, 22.4, 18.9, 18.9, 14.9, 14.0, 12.0, 7.4; HRMS (ESI) *m/z* calcd for $C_{25}H_{34}NO_4$ $[M + H]^+$: 412.2482, found 412.2478.



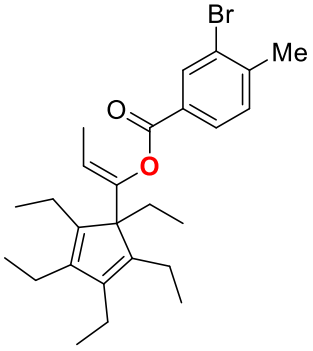
3aj

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 3-chlorobenzoate (3aj). Light yellow liquid, 0.086 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 7.6 Hz, 1H), 7.33−7.29 (m, 1H), 5.47 (q, J = 6.8 Hz, 1H), 2.23−2.05 (m, 8H), 1.82−1.76 (m, 2H), 1.54 (d, J = 6.8 Hz, 3H), 1.09 (t, J = 7.6 Hz, 6H), 0.85 (t, J = 7.2 Hz, 6H), 0.48 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4, 149.9, 144.4, 141.2, 134.2, 132.7, 131.9, 130.0, 129.4, 128.0, 111.8, 65.5, 22.2, 18.8, 18.7, 14.7, 13.8, 11.8, 7.3; HRMS (ESI) *m/z* calcd for $C_{25}H_{34}ClO_2$ $[M+H]^+$ 401.2242, found 401.2255.



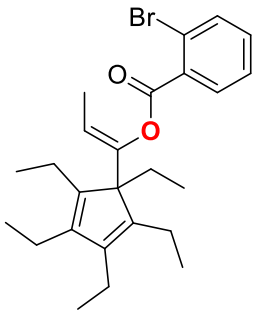
3ak

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 3-bromobenzoate (3ak) A yellow liquid, 0.097 g, 73% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.0 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.63 (d, J = 8.0 Hz, 1H), 7.24 (d, J = 8.0 Hz, 1H), 5.46 (q, J = 6.5 Hz, 1H), 2.23-2.15 (m, 6H), 2.11-2.05 (m, 2H), 1.81 (q, J = 7.5 Hz, 2H), 1.53 (d, J = 7.0 Hz, 3H), 1.07 (t, J = 7.5 Hz, 6H), 0.83 (t, J = 7.5 Hz, 6H), 0.46 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.4, 150.1, 144.6, 141.4, 135.8, 133.1, 132.2, 129.8, 128.6, 122.3, 112.0, 65.7, 22.3, 18.9, 14.9, 13.9, 12.0, 7.4; HRMS (ESI) *m/z* calcd for $C_{25}H_{34}BrO_2$ $[M + H]^+$: 445.1737, found 445.1722.



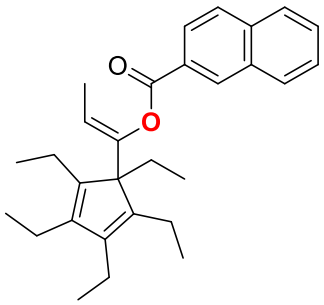
3al

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 3-bromo-4-methylbenzoate (3al). Light yellow liquid, 0.078 g, 57% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 1H), 5.45 (q, J = 6.8 Hz, 1H), 2.42 (s, 3H), 2.25−2.03 (m, 8H), 1.82 (q, J = 7.2 Hz, 2H), 1.53 (d, J = 6.8 Hz, 3H), 1.09 (t, J = 7.6 Hz, 6H), 0.86 (t, J = 7.2 Hz, 6H), 0.48 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 161.4, 149.9, 144.4, 143.0, 141.2, 133.8, 130.4, 129.5, 128.7, 124.4, 111.7, 65.5, 23.2, 22.1, 18.8, 14.7, 13.8, 11.8, 7.3; HRMS (ESI) *m/z* calcd for $C_{26}H_{36}BrO_2$ $[M+H]^+$ 459.1893, found 459.1872.



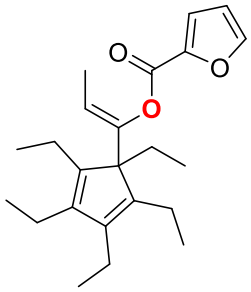
3am

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 2-bromobenzoate (3am). Light yellow liquid, 0.071 g, 52% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.8 Hz, 2H), 7.29−7.25 (m, 2H), 5.48 (q, J = 6.8 Hz, 1H), 2.26−2.05 (m, 8H), 1.83 (q, J = 7.6 Hz, 2H), 1.61 (d, J = 6.8 Hz, 3H), 1.05 (t, J = 7.6 Hz, 6H), 0.94 (t, J = 7.6 Hz, 6H), 0.49 (t, J = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.7, 149.8, 144.2, 141.5, 134.2, 132.3, 131.8, 126.6, 122.1, 65.5, 22.3, 18.9, 18.8, 14.8, 13.8, 11.9, 7.2; HRMS (ESI) *m/z* calcd for $C_{25}H_{34}BrO_2$ $[M+H]^+$ 445.1737, found 445.1731.



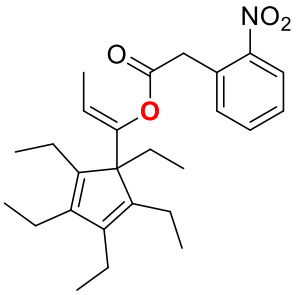
3an

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 2-naphthoate (3an) A yellow liquid, 0.076 g, 61% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.46 (s, 1H), 7.93-7.80 (m, 4H), 7.58-7.50 (m, 2H), 5.49 (q, J = 6.5 Hz, 1H), 2.31-2.23 (m, 2H), 2.17-2.12 (m, 6H), 1.85 (q, J = 7.0 Hz, 2H), 1.58 (d, J = 7.5 Hz, 3H), 1.12 (t, J = 8.0 Hz, 6H), 0.81 (t, J = 7.5 Hz, 6H), 0.47 (t, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 150.3, 144.5, 141.5, 135.6, 132.5, 131.5, 129.4, 128.2, 127.9, 127.9, 127.6, 126.6, 125.8, 111.7, 65.8, 22.4, 19.0, 19.0, 14.9, 14.0, 12.0, 7.5; HRMS (ESI) *m/z* calcd for $C_{29}H_{37}O_2$ $[M + H]^+$: 417.2788, found 417.2773.



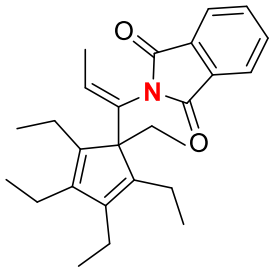
3ao

(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl furan-2-carboxylate (3ao). Light yellow liquid, 0.060 g, 56% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1H), 6.95 (d, J = 2.8 Hz, 1H), 6.43 (s, 1H), 5.44 (q, J = 6.8 Hz, 1H), 2.24−2.03 (m, 8H), 1.80 (q, J = 6.8 Hz, 2H), 1.55 (d, J = 6.8 Hz, 3H), 1.07 (t, J = 7.6 Hz, 6H), 0.85 (t, J = 7.6 Hz, 6H), 0.47 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 154.8, 149.5, 146.2, 144.4, 144.3, 141.1, 117.6, 111.9, 111.5, 65.4, 22.1, 18.8, 18.7, 14.6, 13.8, 11.7, 7.9; HRMS (ESI) *m/z* calcd for $C_{23}H_{33}O_3$ $[M+H]^+$ 357.2424, found 357.2422.



3ap

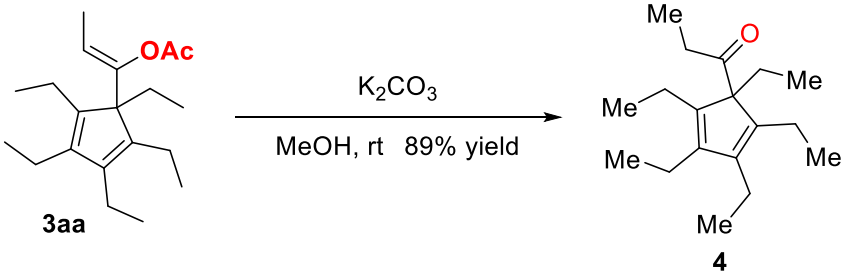
(Z)-1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl 2-(2-nitrophenyl)acetate (3ap). Light yellow liquid, 0.092 g, 72% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, J = 8.4 Hz, 1H), 7.57−7.54 (m, 1H), 7.46−7.42 (m, 1H), 7.22 (d, J = 7.6 Hz, 1H), 5.33−5.28 (m, 1H), 3.87 (s, 2H), 2.27−2.21 (m, 3H), 2.09−1.94 (m, 5H), 1.72 (q, J = 6.8 Hz, 2H), 1.50 (d, J = 6.8 Hz, 3H), 1.08 (t, J = 7.2 Hz, 6H), 0.93 (t, J = 7.2 Hz, 6H), 0.44 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 165.9, 149.8, 148.7, 143.8, 141.5, 133.3, 133.2, 129.8, 128.4, 125.2, 65.3, 39.1, 22.2, 18.9, 18.7, 15.2, 13.6, 11.5, 7.2; HRMS (ESI) *m/z* calcd for $C_{26}H_{36}NO_4$ $[M+H]^+$ 426.2639, found 426.2640.



3aq

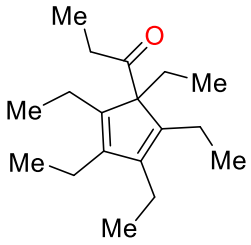
(Z)-2-(1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)prop-1-en-1-yl)isoindoline-1,3-dione (3aq). Light yellow liquid, 0.063 g, 54% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76−7.65 (m, 4H), 6.05 (q, J = 6.4 Hz, 1H), 2.34−2.02 (m, 8H), 1.89 (q, J = 7.2 Hz, 2H), 1.54 (d, J = 6.8 Hz, 3H), 1.08 (d, J = 7.6 Hz, 6H), 0.75 (d, J = 7.2 Hz, 6H), 0.58 (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 166.9, 144.4, 142.7, 134.0, 133.5, 131.8, 126.8, 112.9, 67.1, 22.0, 19.5, 18.6, 14.2, 13.8, 13.3, 8.2; HRMS (ESI) *m/z* calcd for $C_{26}H_{34}NO_2$ $[M+H]^+$ 392.2584, found 392.2594.

3. Synthesis of compounds 4 and 5



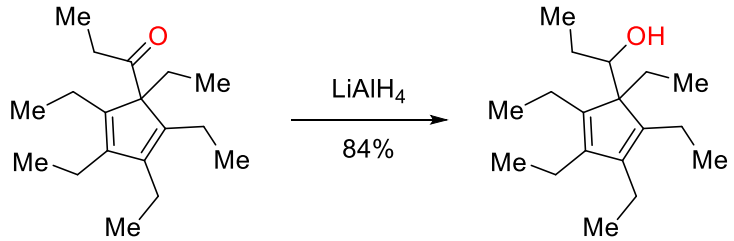
3aa **4**

In a 10 mL reaction flask was charged with **3aa** (0.060 g, 0.2 mmol), K_2CO_3 (0.033 g, 1.2 equiv.). MeOH (2 mL) was then added via syringe and the reaction vessel was sealed with a Teflon cap. The reaction mixture was stirred vigorously at room temperature for 60 h until **3aa** was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded on silica gel, eluents with a mixed eluents petroleum ether/ethyl acetate = 50/1) to afford **4**.



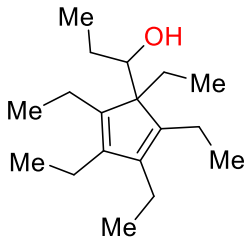
4

1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)propan-1-one (4). Yellow oil (0.046 g, 89% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.35-2.32 (m, 4H), 2.12-2.07 (m, 4H), 2.05 (q, J = 7.5 Hz, 2H), 1.97 (q, J = 7.5 Hz, 2H), 1.08 (t, J = 7.5 Hz, 6H), 0.96 (t, J = 8.0 Hz, 6H), 0.86 (t, J = 7.5 Hz, 3H), 0.37 (t, J = 7.5 Hz, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 211.6, 147.5, 140.6, 75.7, 28.3, 20.3, 19.1, 19.0, 14.7, 14.2, 8.7, 7.0; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{31}O$ 263.2369; Found 263.2370.



4 **5**

In a 10 mL reaction flask was charged with **4** (0.052 g, 0.2 mmol), $LiAlH_4$ (0.015 g, 2.0 equiv.). THF (2 mL) was then added via syringe and the reaction vessel was sealed with a Teflon cap. The reaction mixture was stirred vigorously 0 ℃ to room temperature for 1 h until **4** was consumed completely (monitored by TLC). At this time, the solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (the crude residue was dry loaded on silica gel, eluents with a mixed eluents petroleum ether/ethyl acetate = 10/1) to afford **5**.

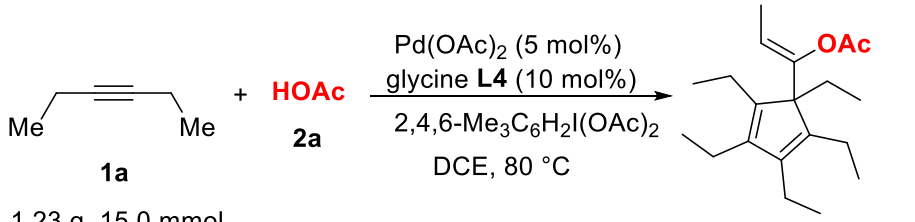


5

1-(1,2,3,4,5-pentaethylcyclopenta-2,4-dien-1-yl)propan-1-ol (5). Yellow liquid, 0.044 g, 84% yield; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.58 (d, J = 10.0 Hz, 1H), 2.36-

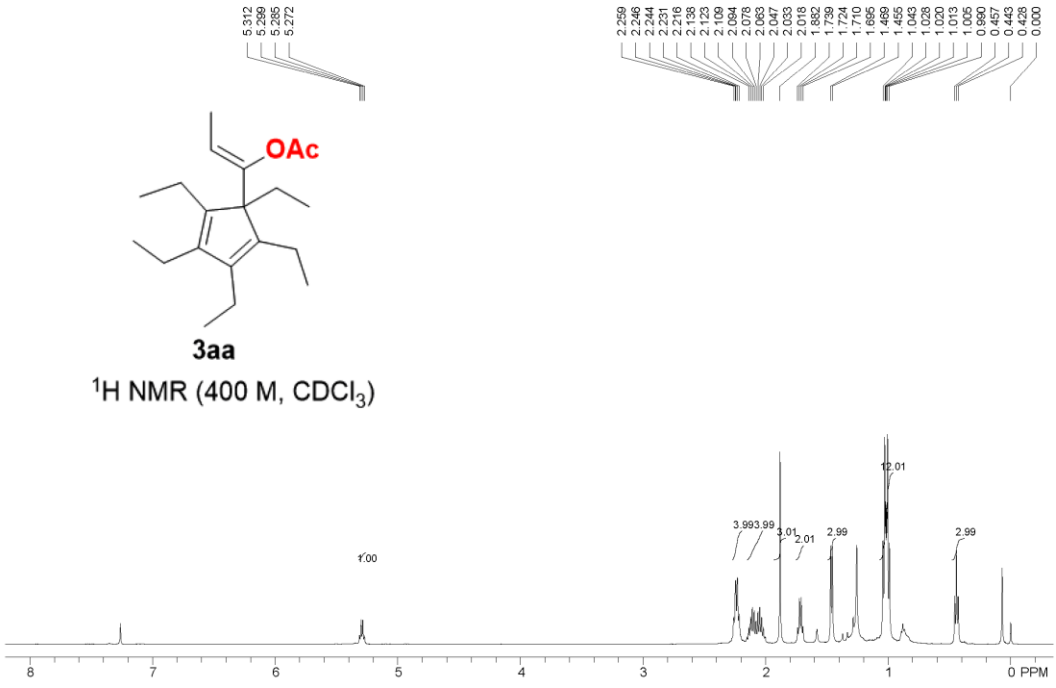
2.29 (m, 1H), 2.26-2.12 (m, 6H), 2.06-1.93 (m, 2H), 1.61-1.54 (m, 1H), 1.33-1.25 (m, 2H), 1.22-1.13 (m, 1H), 1.09 (t, J = 7.5 Hz, 3H), 1.04-1.00 (m, 9H), 0.92 (t, J = 7.5 Hz, 3H), 0.40 (t, J = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.0, 143.9, 142.7, 141.7, 78.1, 66.2, 24.5, 23.6, 19.5, 18.9, 18.8, 18.7, 15.3, 15.1, 14.3, 14.1, 11.8, 7.6.; HRMS (ESI) *m/z* calcd for $C_{18}H_{33}O$ $[M + H]^+$: 265.2526, found 265.2530.

4. Gram scale preparation of cyclopentadiene 3aa



In a 100 mL reaction flask was charged with $Pd(OAc)_2$ (56 mg, 0.25 mmol, 5 mol%), glycine **L4** (36 mg, 0.5 mmol, 10 mol%), and DCE (10.0 mL). The mixture was stirred at room temperature for 30 min under N_2. Then, 3-hexyne **1a** (1.23 g, 15.0 mmol), HOAc **2a** (1.5 g, 25.0 mmol, 5.0 equiv.), 2,4,6-$Me_3C_6H_2I(OAc)_2$ (3.6 g, 10 mmol, 2.0 equiv.) and DCE (60.0 mL) were added. The reaction vessel was once again sealed with a Teflon cap. The reaction mixture was stirred vigorously at 80 °C in an oil bath for 48 h until 3-hexyne **1a** was consumed completely (monitored by TLC). At this time, the reaction was quenched by H_2O (30 mL), extraction with DCM (30 mL × 2), and the organic layers were combined and washed with saturated $NaHCO_3$ (30 mL), dried over Na_2SO_4, and the solvent was filtered. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (1/20 to 1/10, ethyl acetate/petroleum ether) to afford cyclopentadiene **3aa** (0.988 g, 65% yield) as yellow liquid.

5. NMR spectra for compounds 3-5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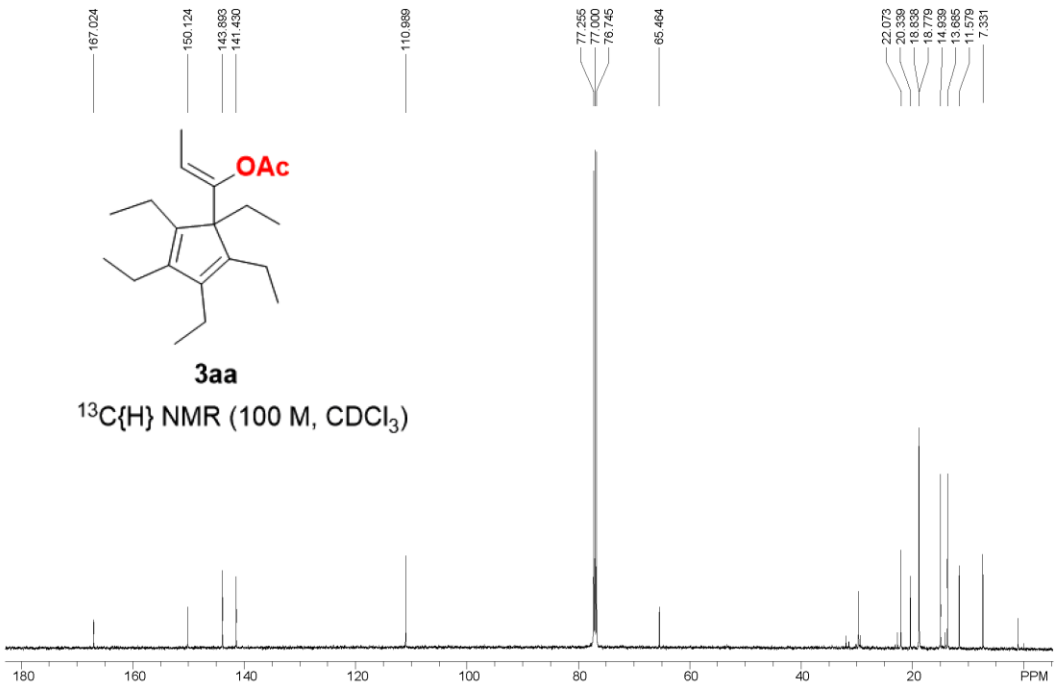
5.285
5.272
2.259
2.246
2.244
2.231
2.216
2.138
2.123
2.109
2.094
2.078
2.063
2.047
2.033
2.018
1.882
1.739
1.724
1.710
1.695
1.469
1.455
1.043
1.028
1.020
1.013
1.005
0.990
0.457
0.443
0.428
0.000
OAc
3aa
1H NMR (400 M, CDCl3)
1.00
3.99
3.99
3.01
2.01
2.99
12.01
2.99
8
7
6
5
4
3
2
1
0 PPM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141.430
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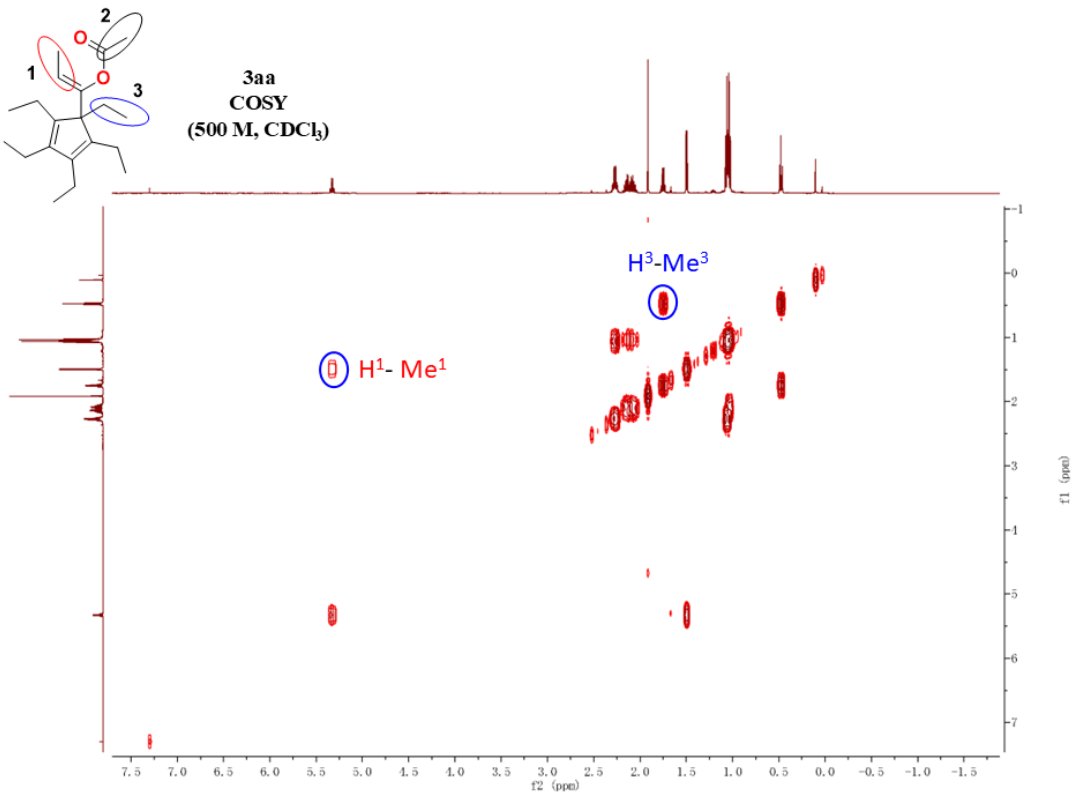
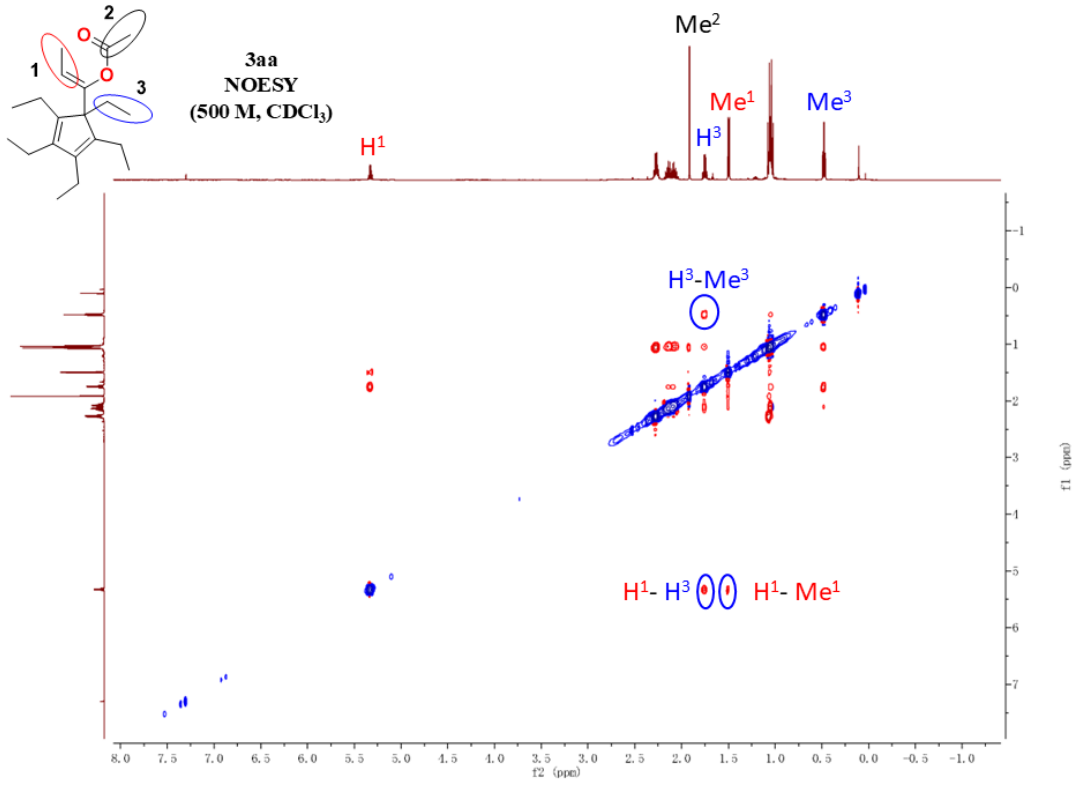
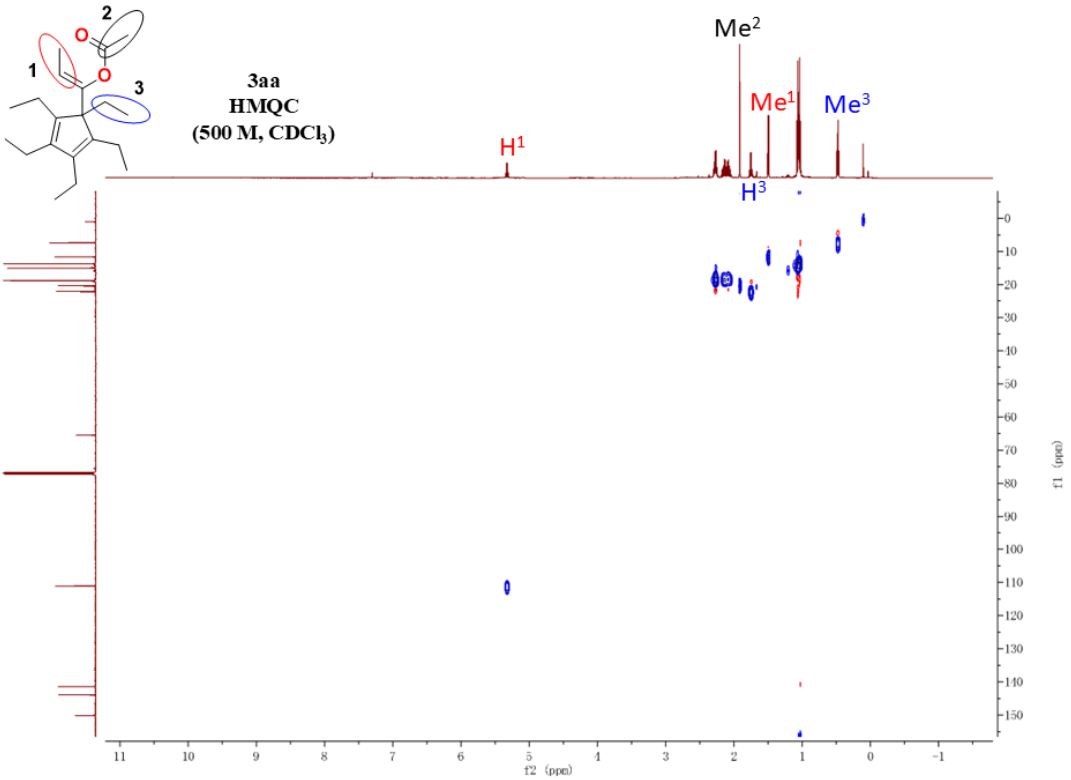
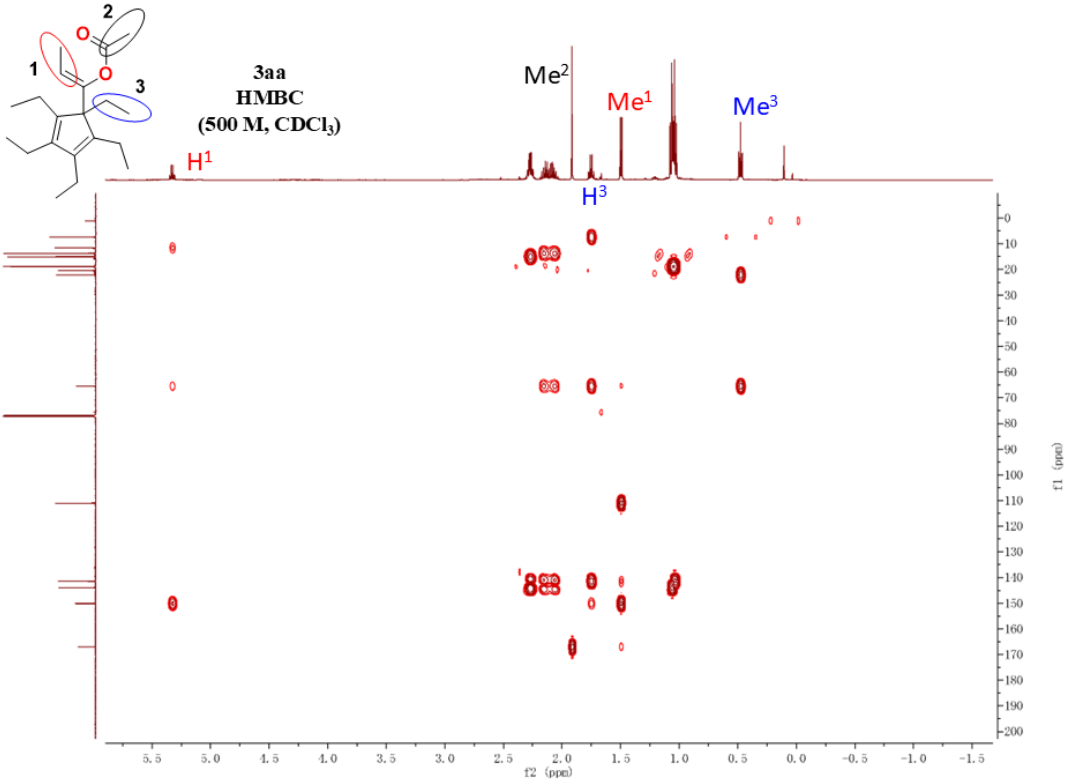
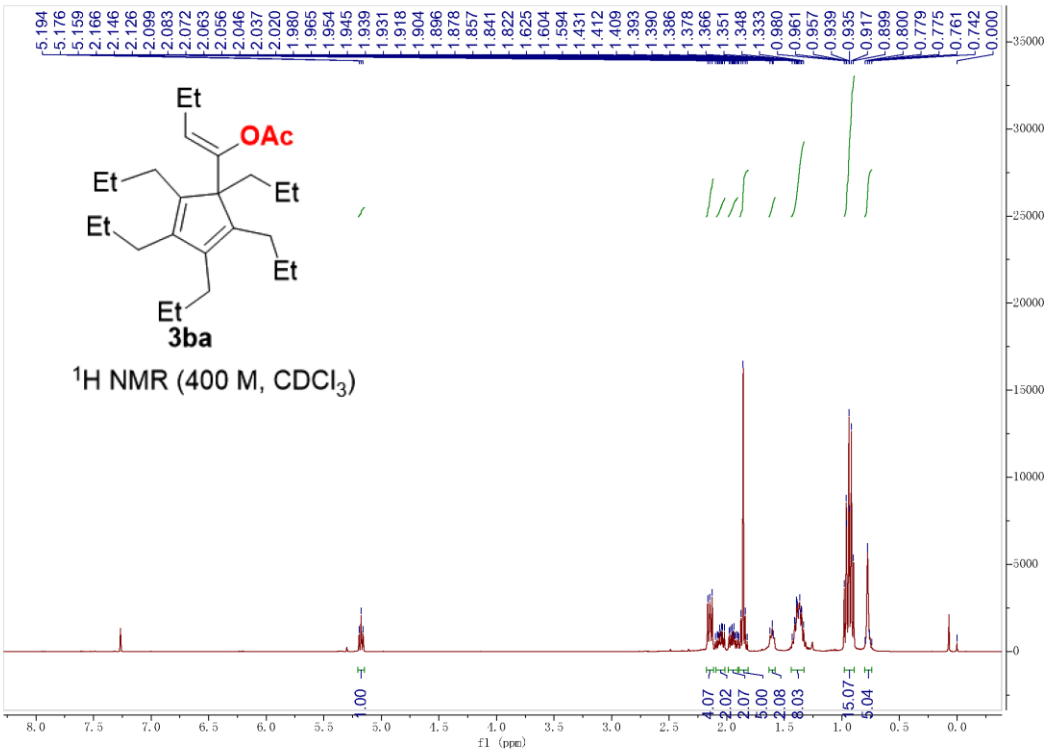
77.255
77.000
76.745
65.464
22.073
20.339
18.838
18.779
14.939
13.685
11.579
7.331
OAc
3aa
13C{H} NMR (100 M, CDCl3)
180
160
140
120
100
80
60
40
20
PPM

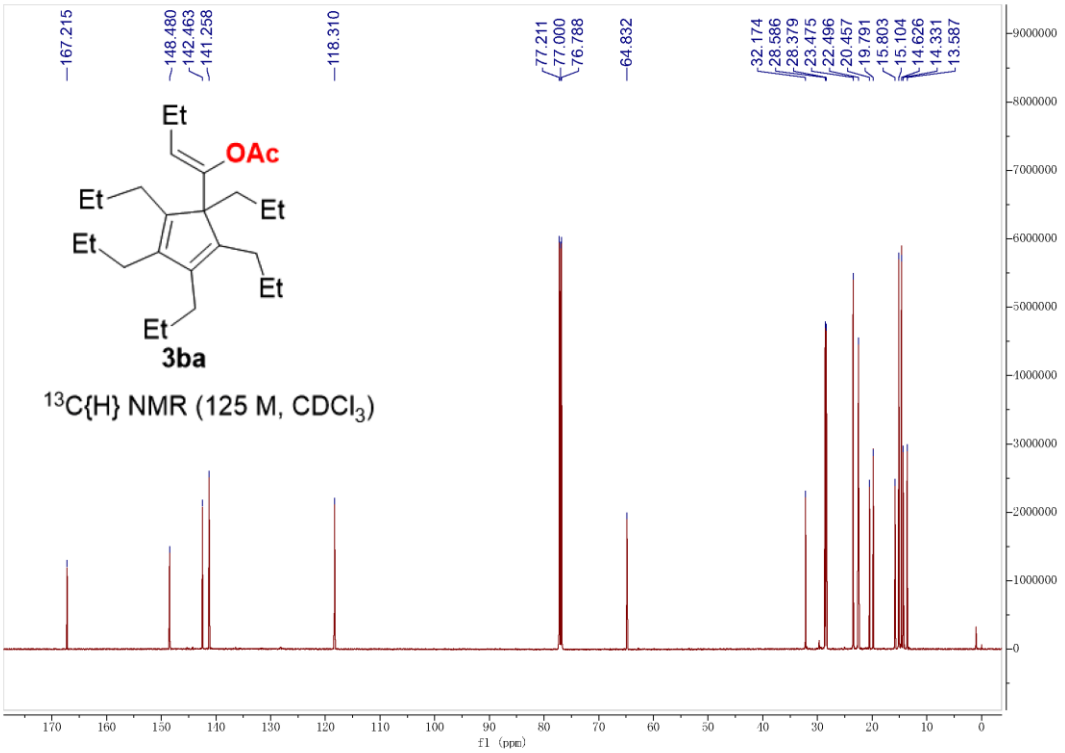

3aa
COSY
(500 M, CDCl3)
H3-Me3
H1- Me1
f2 (ppm)
f1 (ppm)

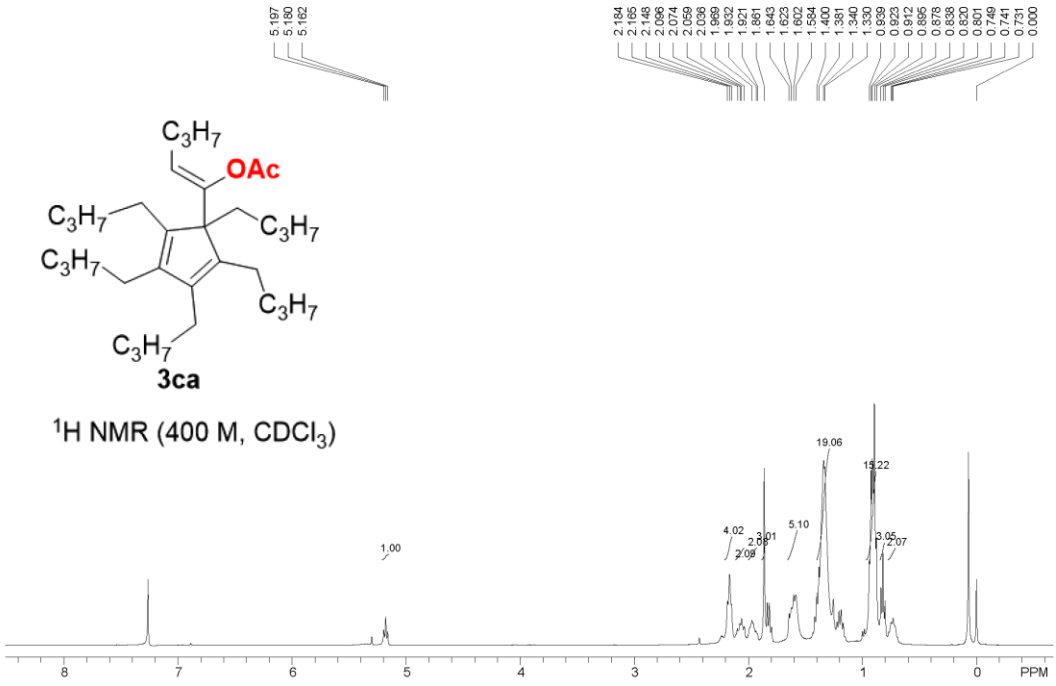

3aa
NOESY
(500 M, CDCl3)
Me2
Me1
Me3
H3
H1
H3-Me3
H1- H3
H1- Me1
f2 (ppm)
f1 (ppm)


3aa
HMQC
(500 M, CDCl3)
Me2
Me1
Me3
H1
H3
f2 (ppm)
f1 (ppm)


3aa
HMBC
(500 M, CDCl3)
Me2
Me1
Me3
H1
H3
f2 (ppm)
f1 (ppm)


Et
OAc
Et
Et
Et
Et
Et
Et
3ba
1H NMR (400 M, CDCl3)
f1 (ppm)


Et
OAc
Et
Et
Et
Et
Et
Et
3ba
13C{H} NMR (125 M, CDCl3)
f1 (ppm)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2.165
2.148
2.096
2.074
2.059
2.038
1.969
1.932
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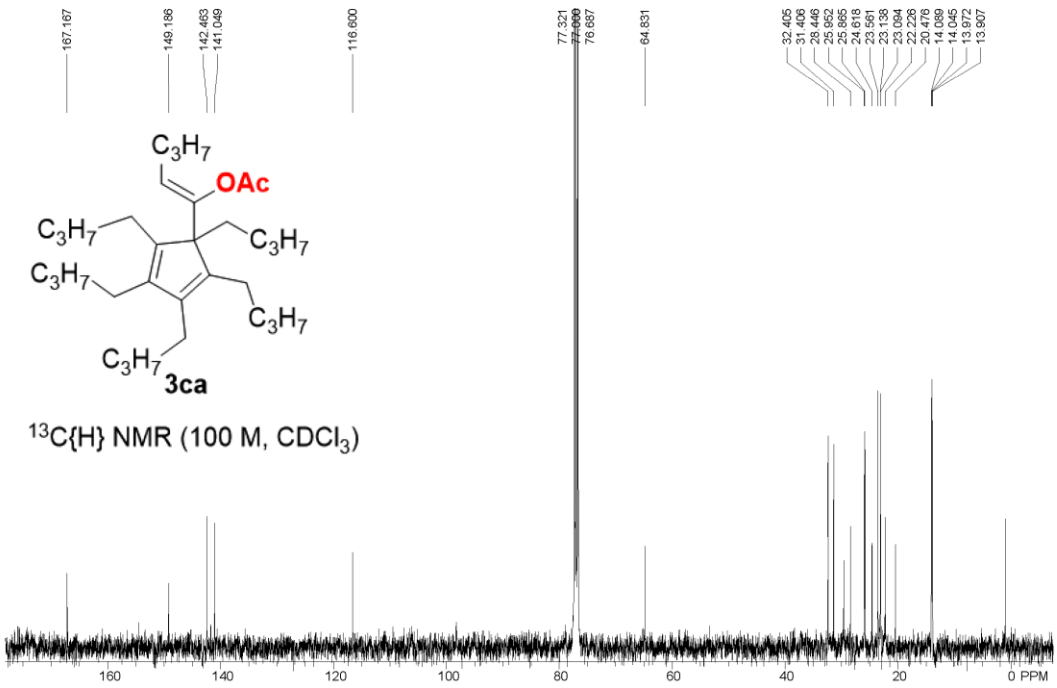
1.881
1.643
1.623
1.602
1.584
1.400
1.381
1.340
1.330
0.939
0.923
0.912
0.895
0.878
0.858
0.830
0.801
0.749
0.741
0.731
0.000
C3H7
OAc
C3H7
C3H7
C3H7
C3H7
C3H7
3ca
1H NMR (400 M, CDCl3)
19.06
15.22
4.02
3.01
2.08
2.09
5.10
3.05
2.07
1.00
8
7
6
5
4
3
2
1
0
PPM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141.049
116.600
77.321
77.000
76.687
64.831
32.405
31.406
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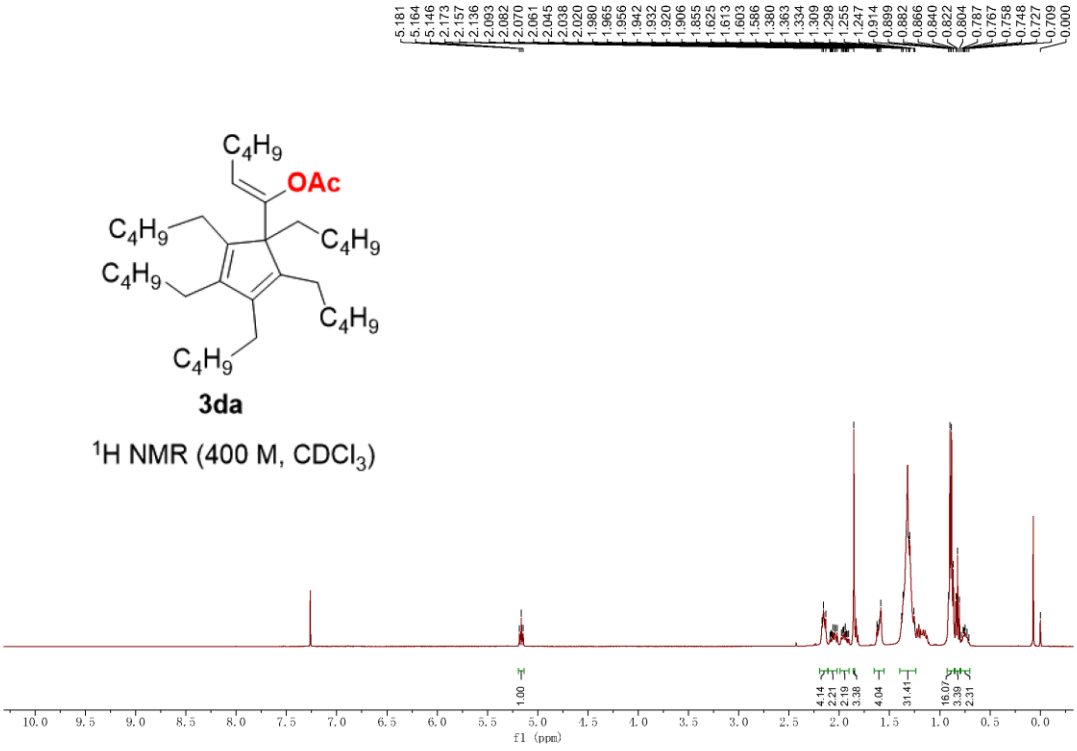
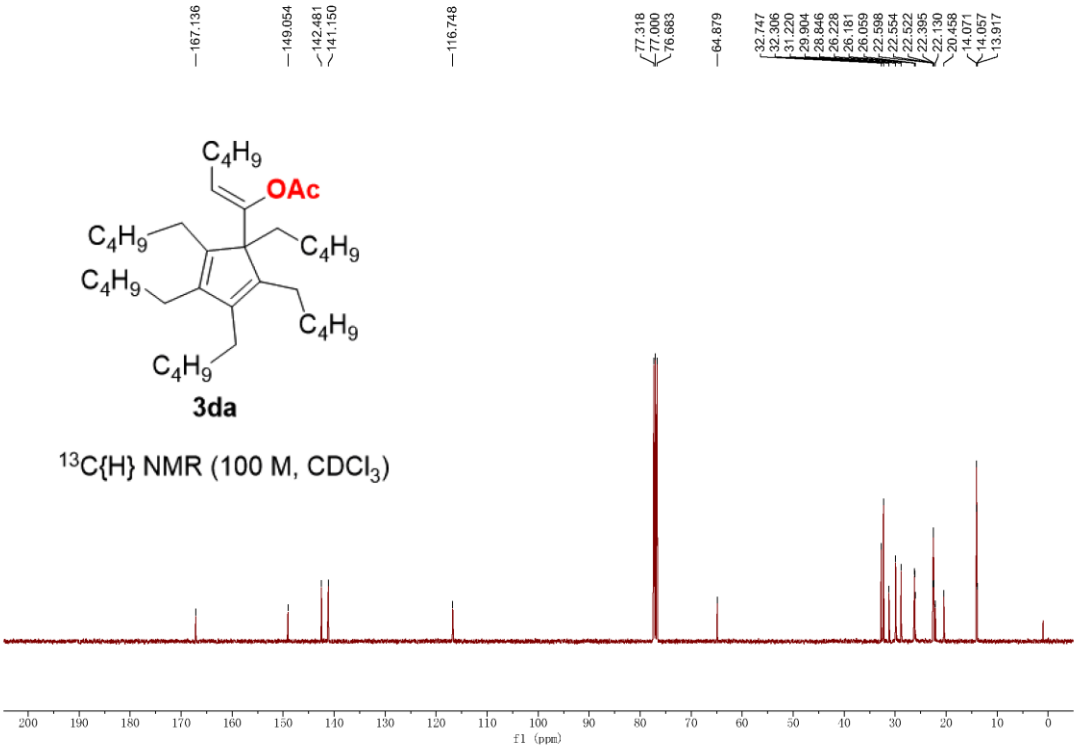
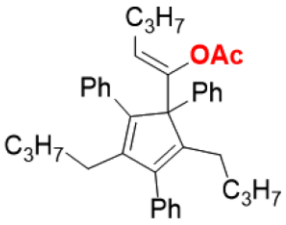
25.952
25.865
24.618
23.561
23.138
23.094
22.226
20.476
14.089
14.045
13.972
13.907
C3H7
OAc
C3H7
C3H7
C3H7
C3H7
C3H7
3ca
13C{H} NMR (100 M, CDCl3)
160
140
120
100
80
60
40
20
0 PPM

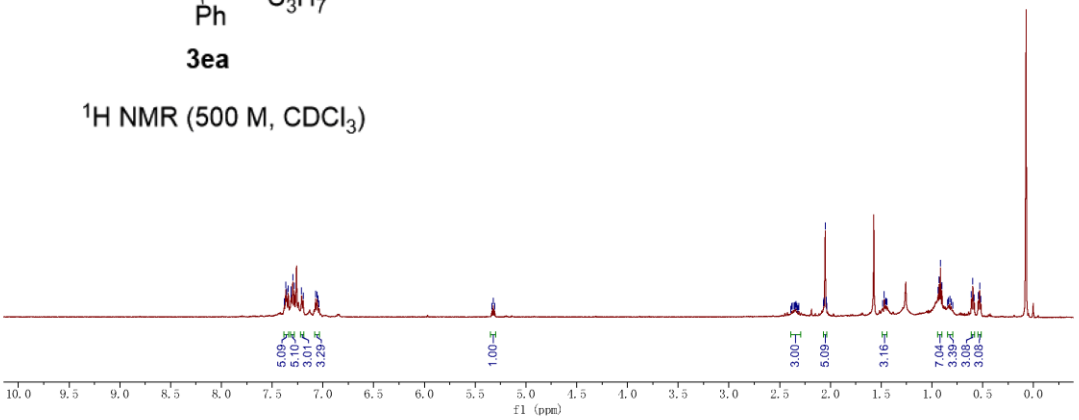

5.181
5.164
5.146
5.146
5.173
2.157
2.136
2.093
2.082
2.070
2.061
2.045
2.038
2.020
1.980
1.965
1.956
1.942
1.932
1.920
1.906
1.855
1.625
1.613
1.603
1.586
1.380
1.363
1.334
1.309
1.298
1.255
1.247
0.914
0.899
0.882
0.866
0.840
0.822
0.804
0.787
0.767
0.758
0.748
0.727
0.709
0.000
C4H9
OAc
C4H9
C4H9
C4H9
C4H9
C4H9
3da
1H NMR (400 M, CDCl3)
1.00
4.14
2.21
2.19
3.38
4.04
31.41
16.07
3.39
2.31
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)

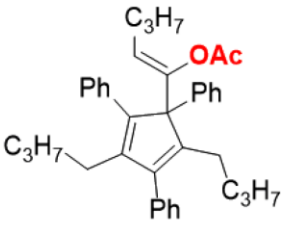

167.136
149.054
142.481
141.150
116.748
77.318
77.000
76.683
64.879
32.747
32.306
31.220
29.904
28.846
26.228
26.181
26.059
22.598
22.554
22.522
22.395
22.130
20.458
14.071
14.057
13.917
C4H9
OAc
C4H9
C4H9
C4H9
C4H9
C4H9
3da
13C{H} NMR (100 M, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



3ea

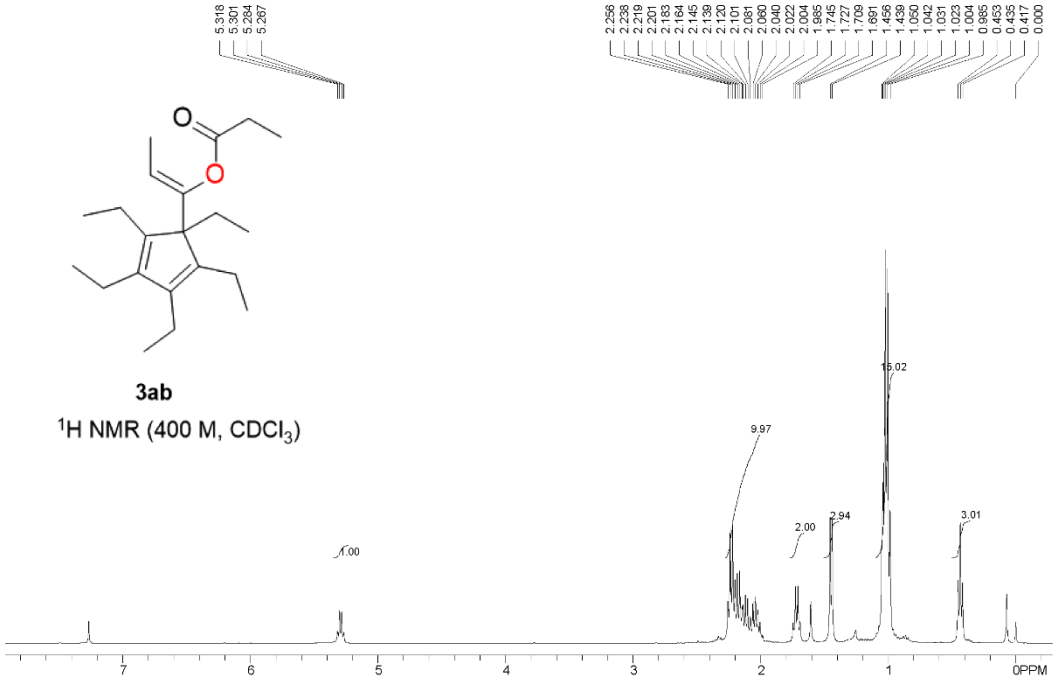
^{1}H NMR (500 M, $CDCl_3$)

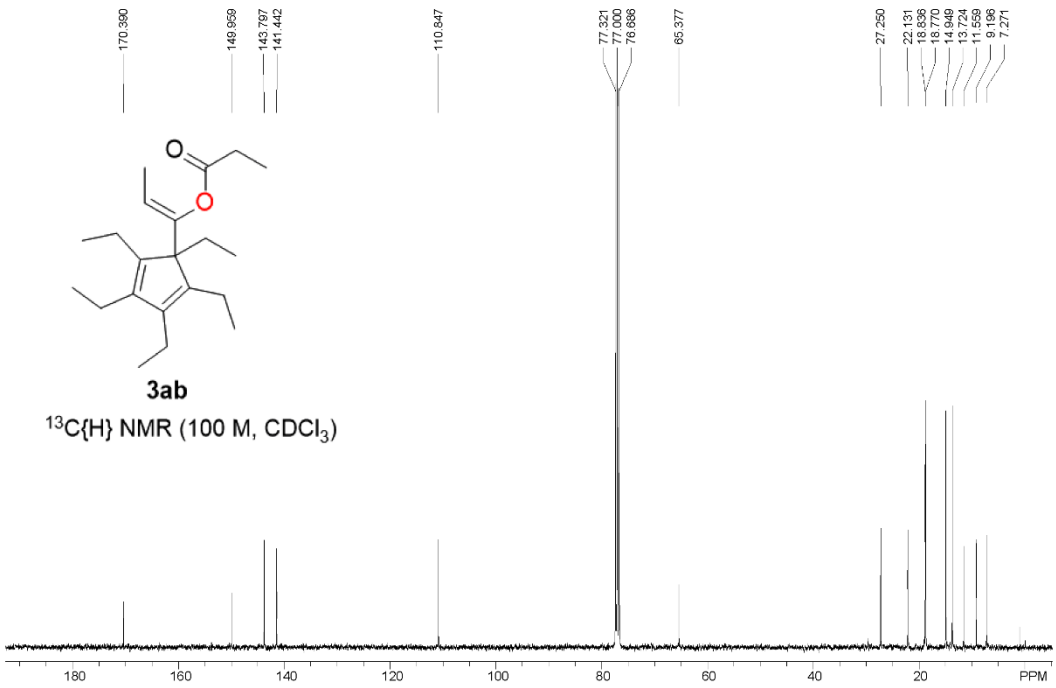


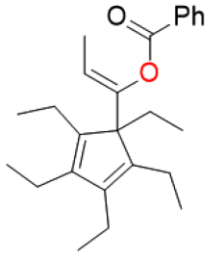


3ea

$^{13}C\{H\}$ NMR (125M, $CDCl_3$)

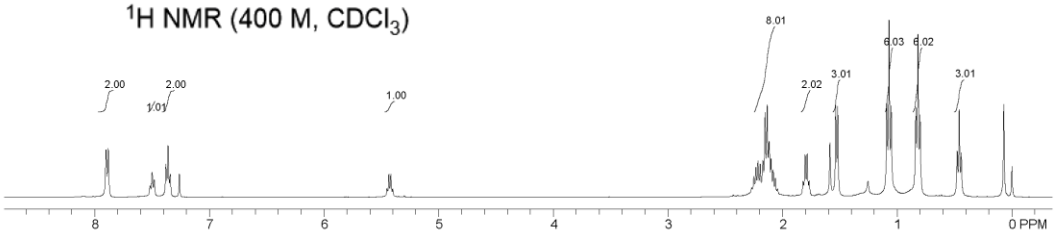

5.316
5.301
5.284
5.267
2.256
2.238
2.219
2.201
2.183
2.164
2.145
2.139
2.120
2.101
2.081
2.060
2.040
2.022
2.004
1.985
1.745
1.727
1.709
1.691
1.456
1.439
1.050
1.042
1.031
1.023
1.004
0.985
0.453
0.435
0.417
0.000
O
O
3ab
1H NMR (400 M, CDCl3)
15.02
9.97
2.00
2.94
3.01
1.00
7
6
5
4
3
2
1
0PPM

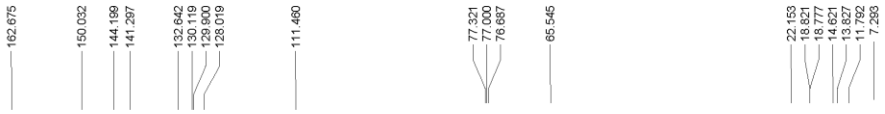

170.390
149.959
143.797
141.442
110.847
77.321
77.000
76.688
65.377
27.250
22.131
18.836
18.770
14.949
13.724
11.559
9.196
7.271
O
O
3ab
13C{H} NMR (100 M, CDCl3)
180
160
140
120
100
80
60
40
20
PPM

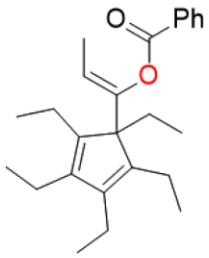


3ac

^{1}H NMR (400 M, $CDCl_3$)

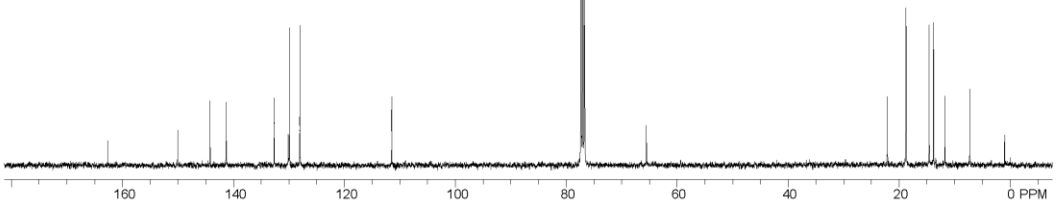


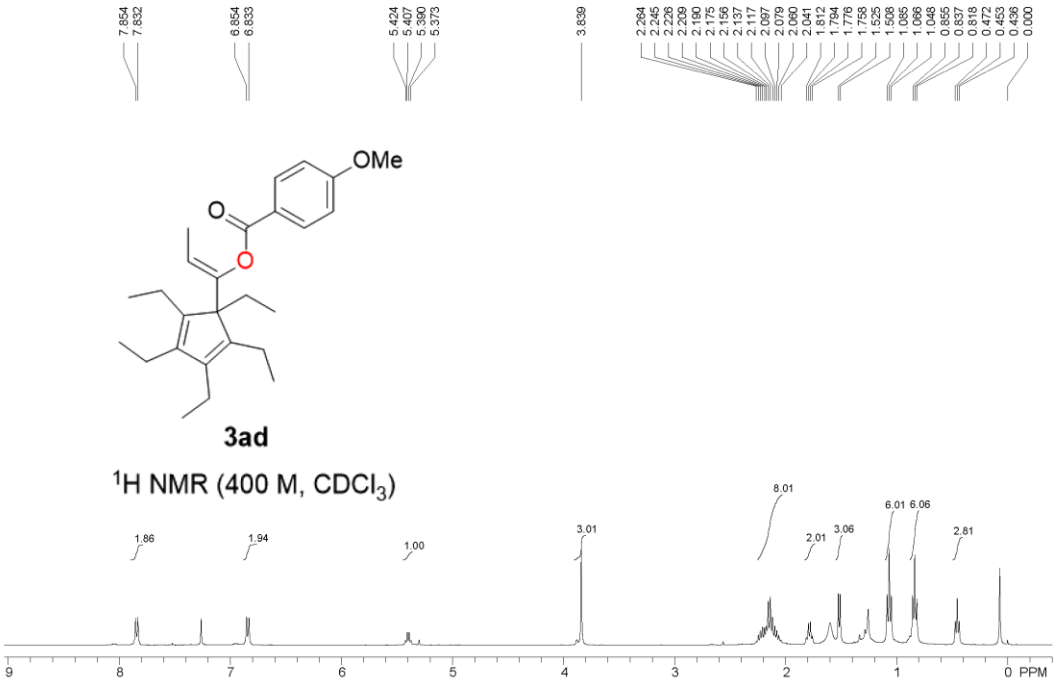


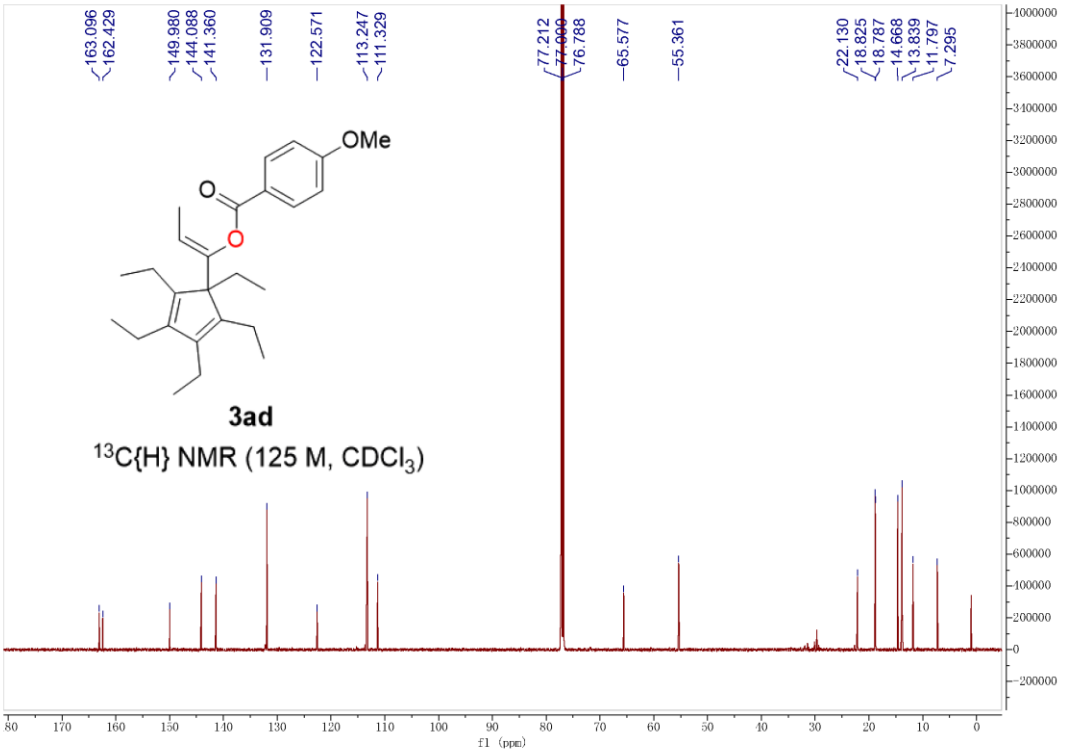


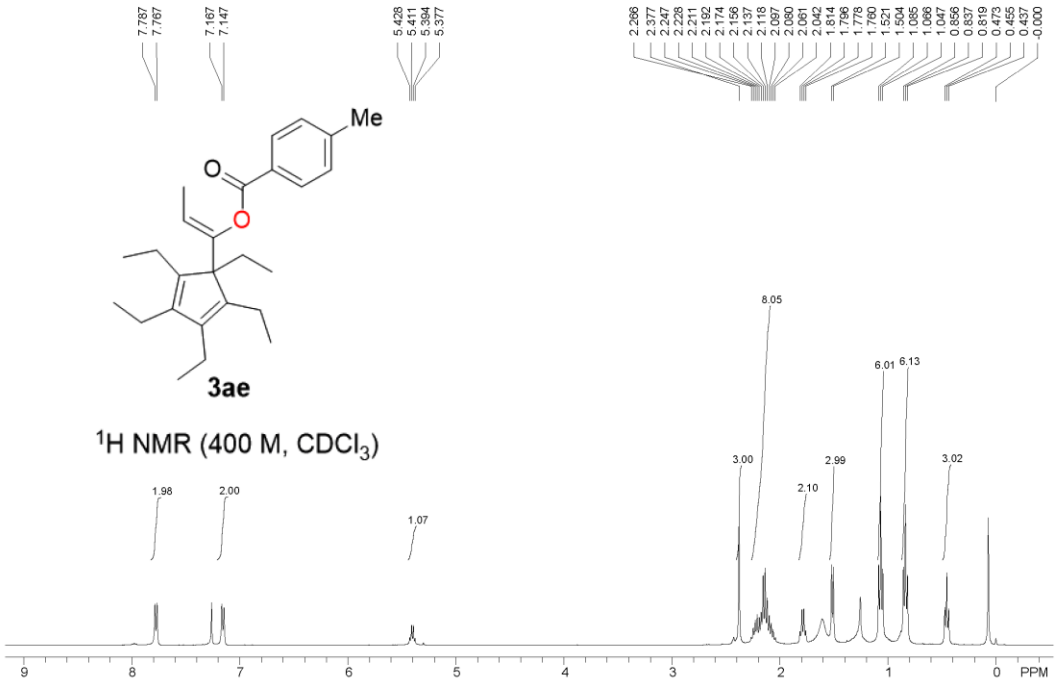
3ac

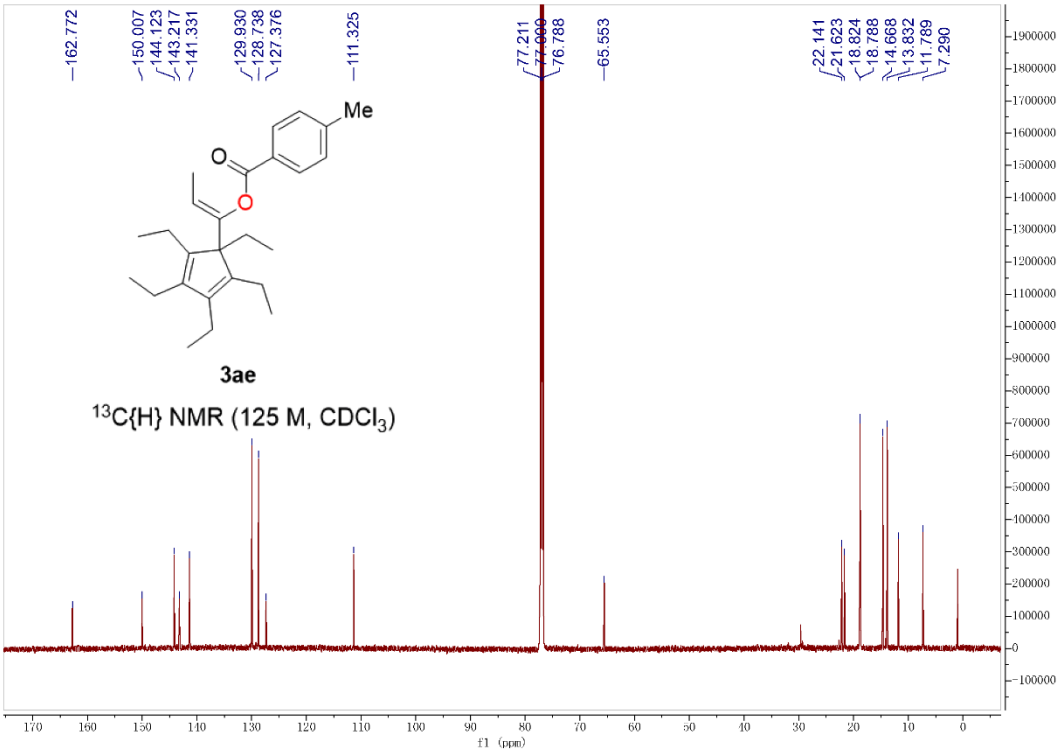
^{13}C{H} NMR (100 M, $CDCl_3$)

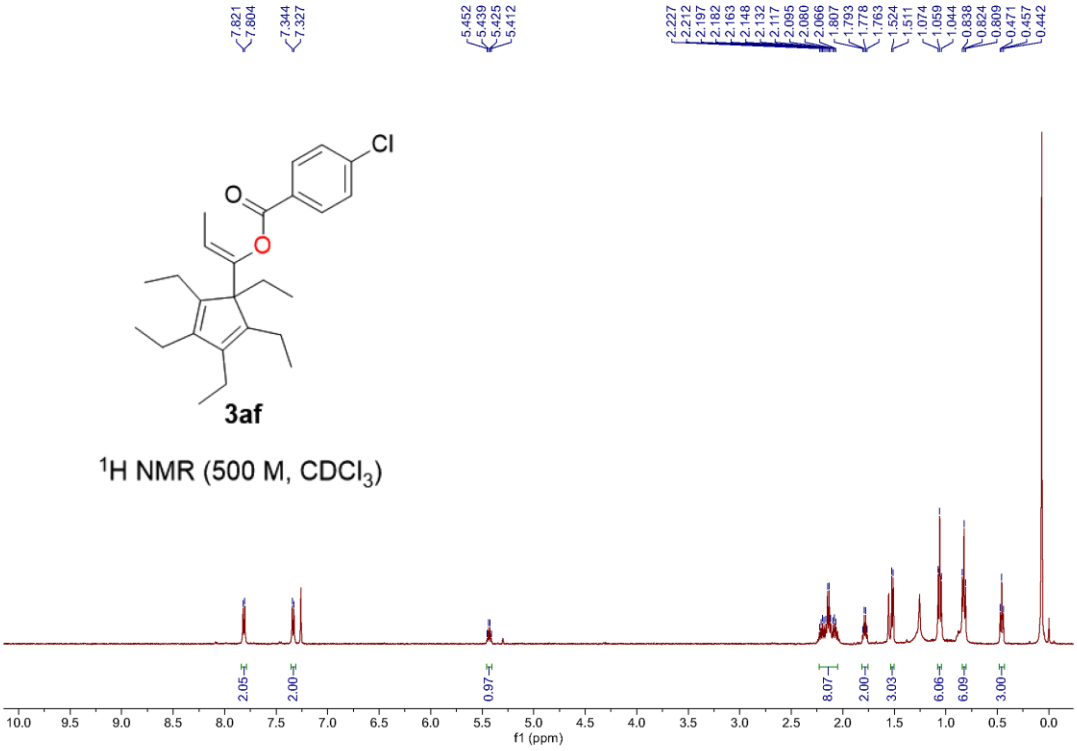


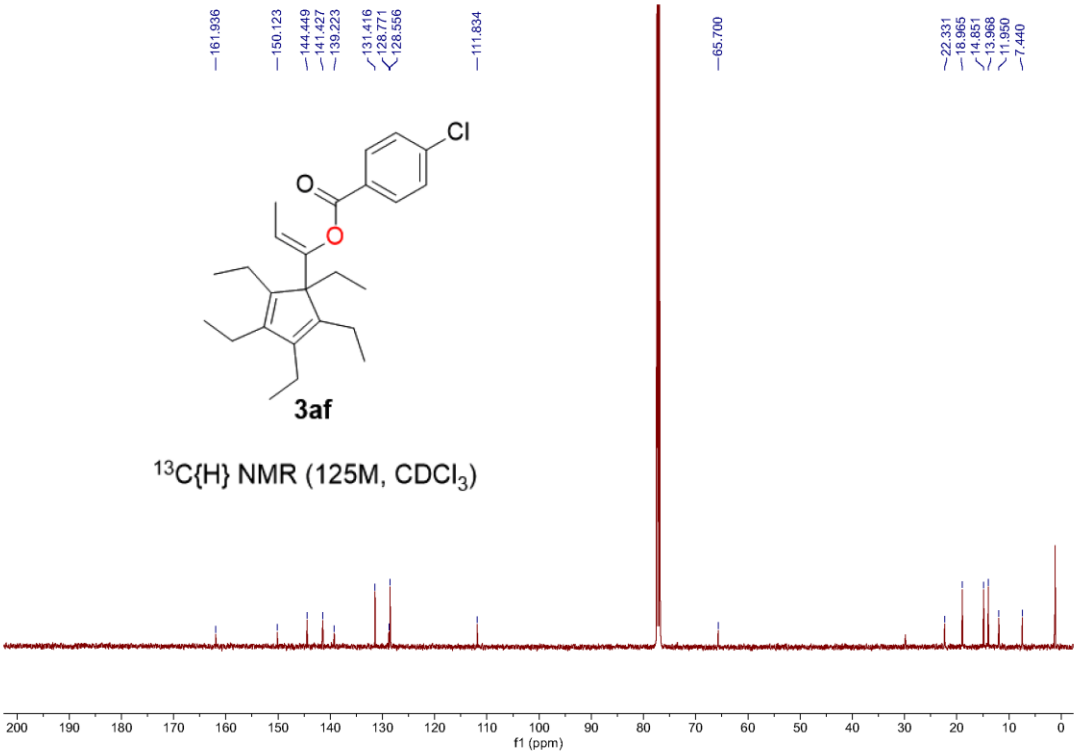

7.854
7.832
6.854
6.833
5.424
5.407
5.390
5.373
3.839
2.264
2.245
2.226
2.208
2.190
2.175
2.156
2.137
2.117
2.097
2.079
2.060
2.041
1.812
1.794
1.776
1.758
1.525
1.508
1.085
1.066
1.048
0.855
0.837
0.818
0.472
0.453
0.436
0.000
OMe
O
O
3ad
1H NMR (400 M, CDCl3)
1.86
1.94
1.00
3.01
8.01
2.01
3.06
6.01
6.06
2.81
9
8
7
6
5
4
3
2
1
0 PPM

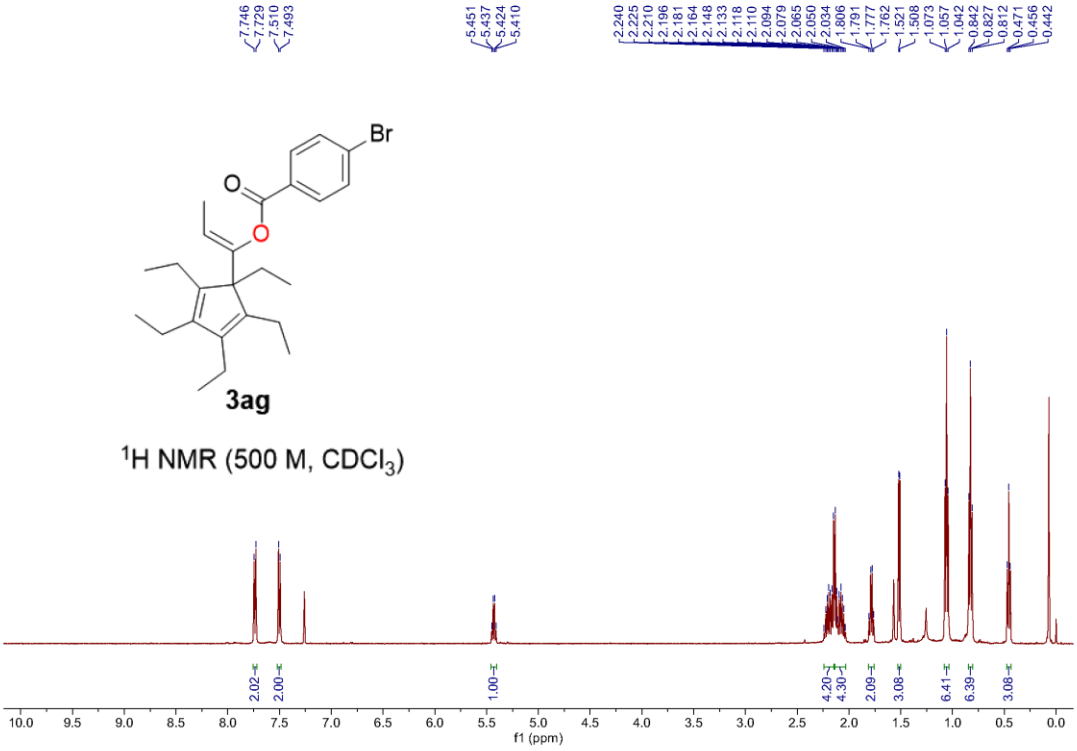

163.096
162.429
149.980
144.088
141.360
131.909
122.571
113.247
111.329
77.212
77.000
76.788
65.577
55.361
22.130
18.825
18.787
14.668
13.839
11.797
7.295
OMe
O
O
3ad
13C{H} NMR (125 M, CDCl3)
f1 (ppm)

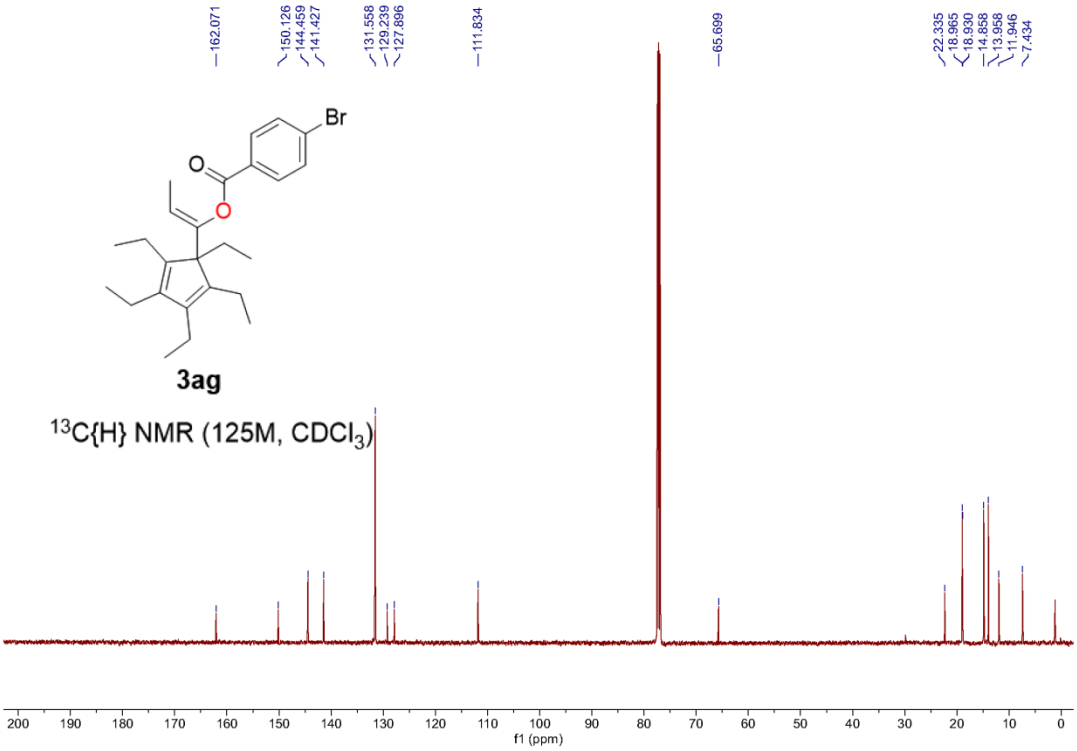

7.787
7.767
7.167
7.147
5.426
5.411
5.394
5.377
2.266
2.377
2.247
2.226
2.211
2.192
2.174
2.156
2.137
2.118
2.097
2.080
2.061
2.042
1.814
1.796
1.778
1.760
1.521
1.504
1.085
1.066
1.047
0.856
0.837
0.819
0.473
0.455
0.437
-0.000
Me
O
O
3ae
1H NMR (400 M, CDCl3)
8.05
6.01
6.13
3.00
2.99
2.10
3.02
1.98
2.00
1.07
9
8
7
6
5
4
3
2
1
0
PPM

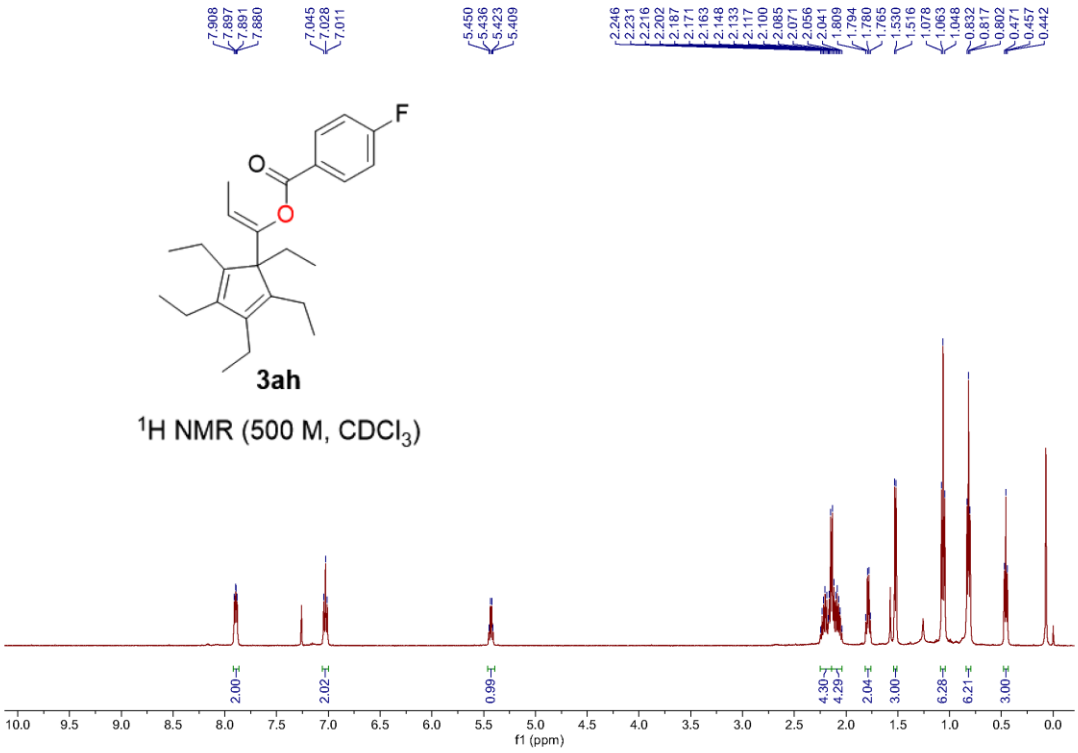

162.772
150.007
144.123
143.217
141.331
129.930
128.738
127.376
111.325
77.211
77.000
76.788
65.553
22.141
21.623
18.824
18.788
14.668
13.832
11.789
7.290
Me
O
O
3ae
13C{H} NMR (125 M, CDCl3)
f1 (ppm)

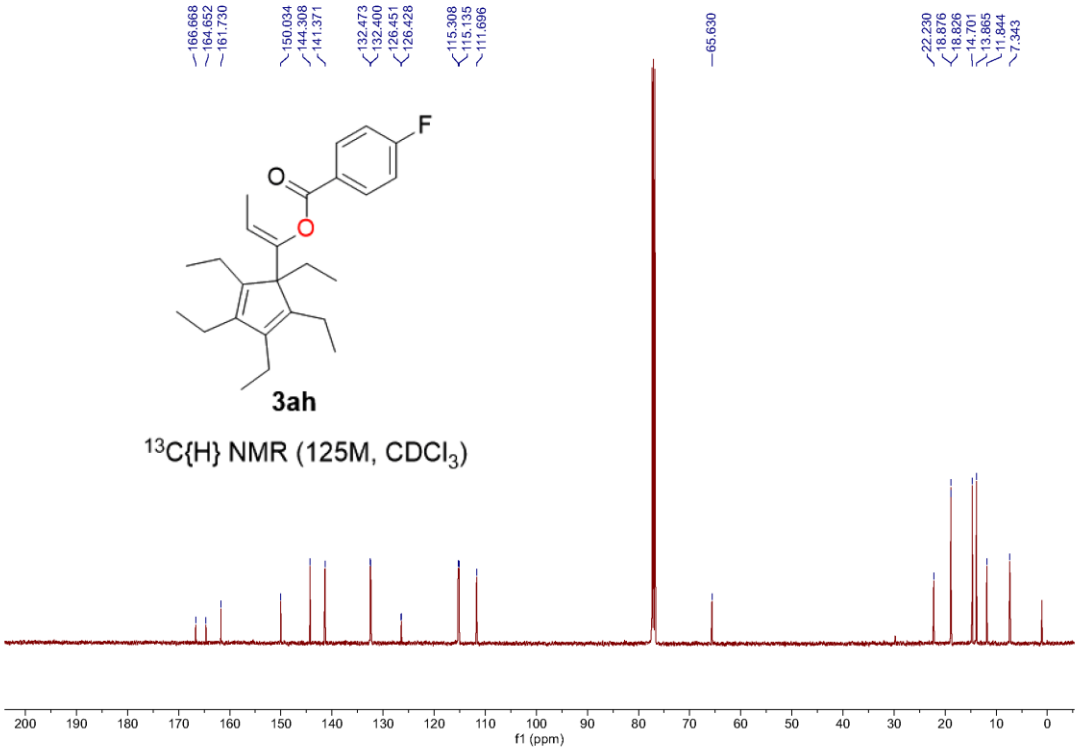

7.821
7.804
7.344
7.327
5.452
5.439
5.425
5.412
2.227
2.212
2.197
2.182
2.163
2.148
2.132
2.117
2.095
2.080
2.066
1.807
1.793
1.778
1.763
1.524
1.511
1.074
1.059
1.044
0.838
0.824
0.809
0.471
0.457
0.442
Cl
O
O
3af
^{1}H NMR (500 M, CDCl$_3$)
2.05
2.00
0.97
8.07
2.00
3.03
6.06
6.09
3.00
10.0 9.5 9.0 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)

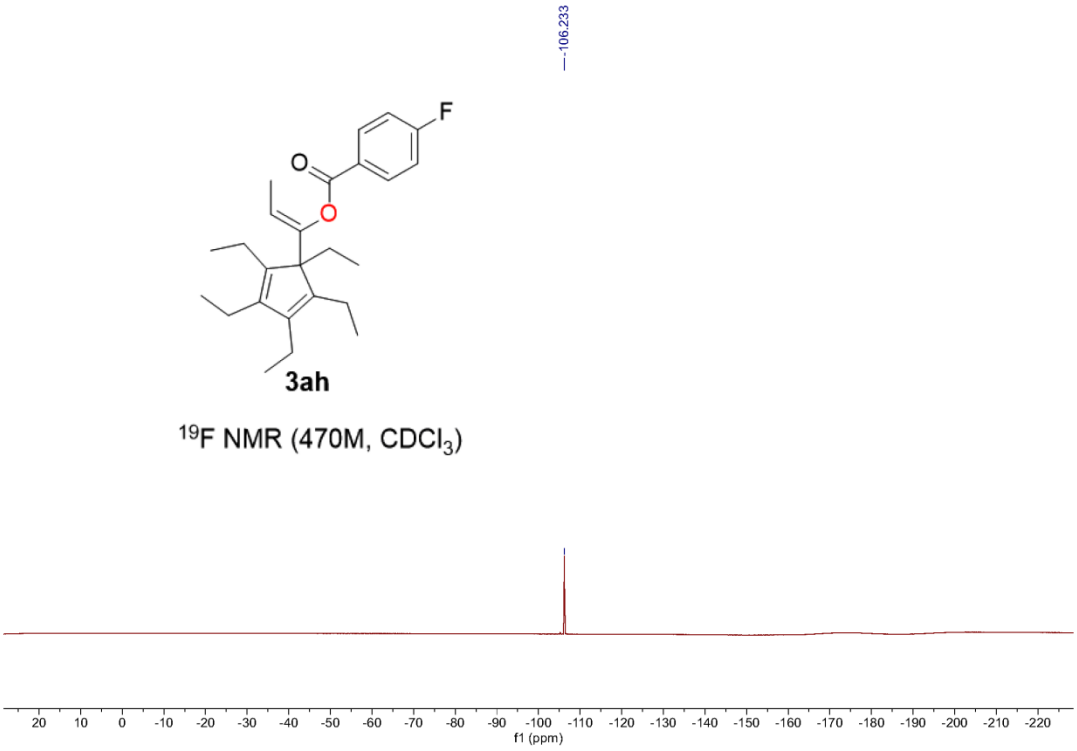

161.936
150.123
144.449
141.427
139.223
131.416
128.771
128.556
111.834
65.700
22.331
18.965
14.851
13.968
11.950
7.440
Cl
O
O
3af
^{13}C{H} NMR (125M, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

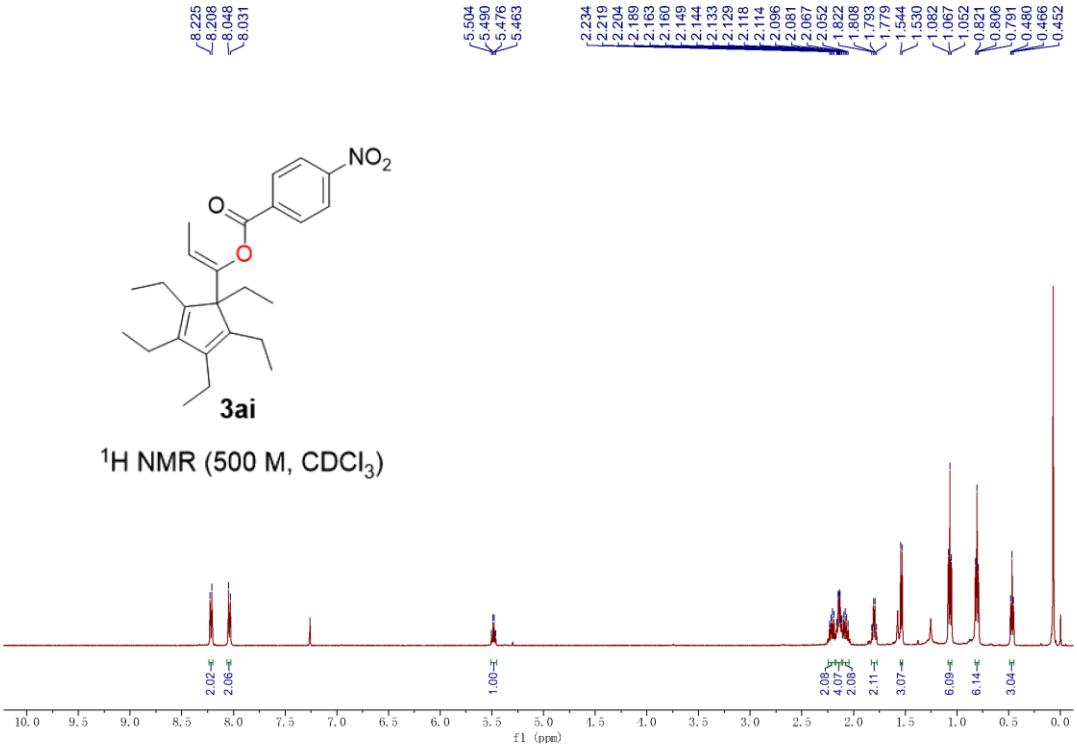

7.746
7.729
7.510
7.493
5.451
5.437
5.424
5.410
2.240
2.225
2.210
2.196
2.181
2.164
2.148
2.133
2.118
2.110
2.094
2.079
2.065
2.050
2.034
1.806
1.791
1.777
1.762
1.521
1.508
1.073
1.057
1.042
0.842
0.827
0.812
0.471
0.456
0.442
Br
O
O
3ag
^{1}H NMR (500 M, $CDCl_3$)
2.02
2.00
1.00
4.20
4.30
2.09
3.08
6.41
6.39
3.08
f1 (ppm)

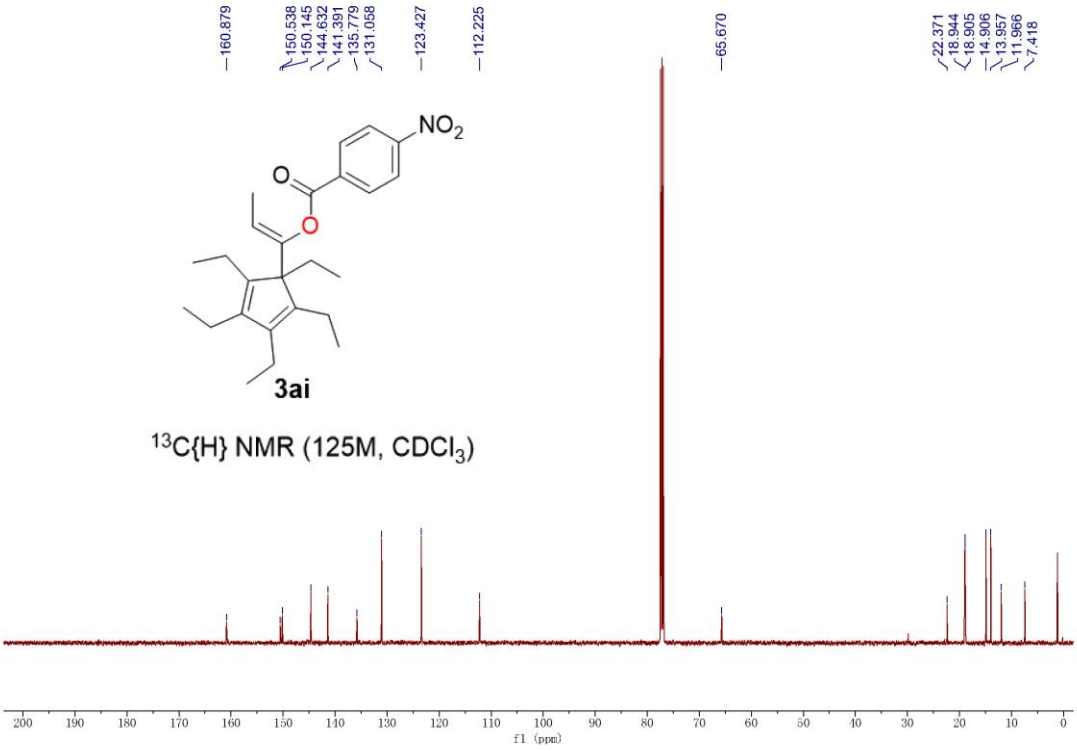

162.071
150.126
144.459
141.427
131.558
129.239
127.896
111.834
65.699
22.335
18.965
18.930
14.858
13.958
11.946
7.434
Br
O
O
3ag
^{13}C{H} NMR (125M, $CDCl_3$)
f1 (ppm)

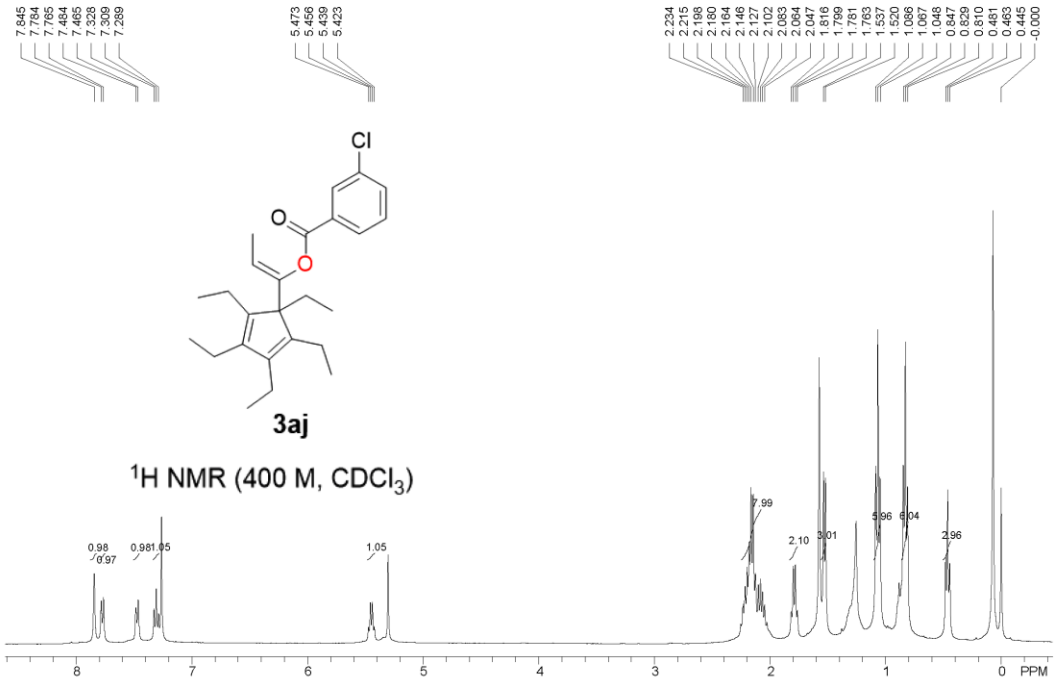

7.908
7.897
7.891
7.880
7.045
7.028
7.011
5.450
5.436
5.423
5.409
2.246
2.231
2.216
2.202
2.187
2.171
2.163
2.148
2.133
2.117
2.100
2.085
2.071
2.056
2.041
1.809
1.794
1.780
1.765
1.530
1.516
1.078
1.063
1.048
0.832
0.817
0.802
0.471
0.457
0.442
F
O
O
3ah
1H NMR (500 M, CDCl3)
2.00
2.02
0.99
4.30
4.29
2.04
3.00
6.28
6.21
3.00
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)

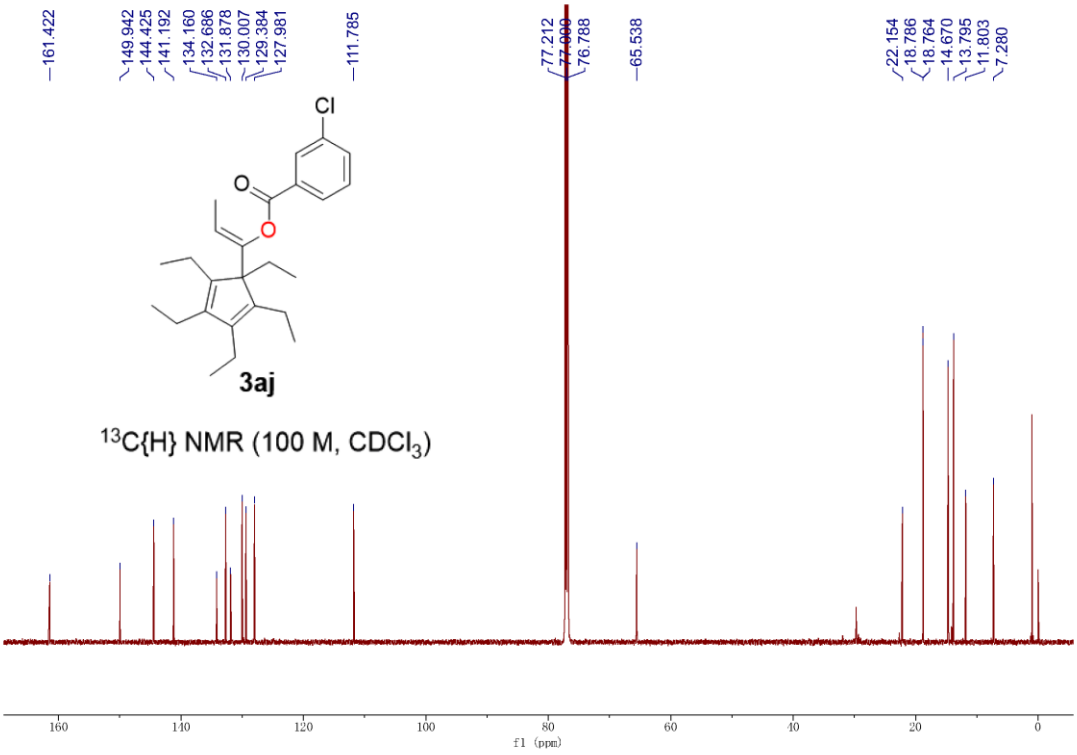

166.668
164.652
161.730
150.034
144.308
141.371
132.473
132.400
126.451
126.428
115.308
115.135
111.696
65.630
22.230
18.876
18.826
14.701
13.865
11.844
7.343
F
O
O
3ah
13C{H} NMR (125M, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

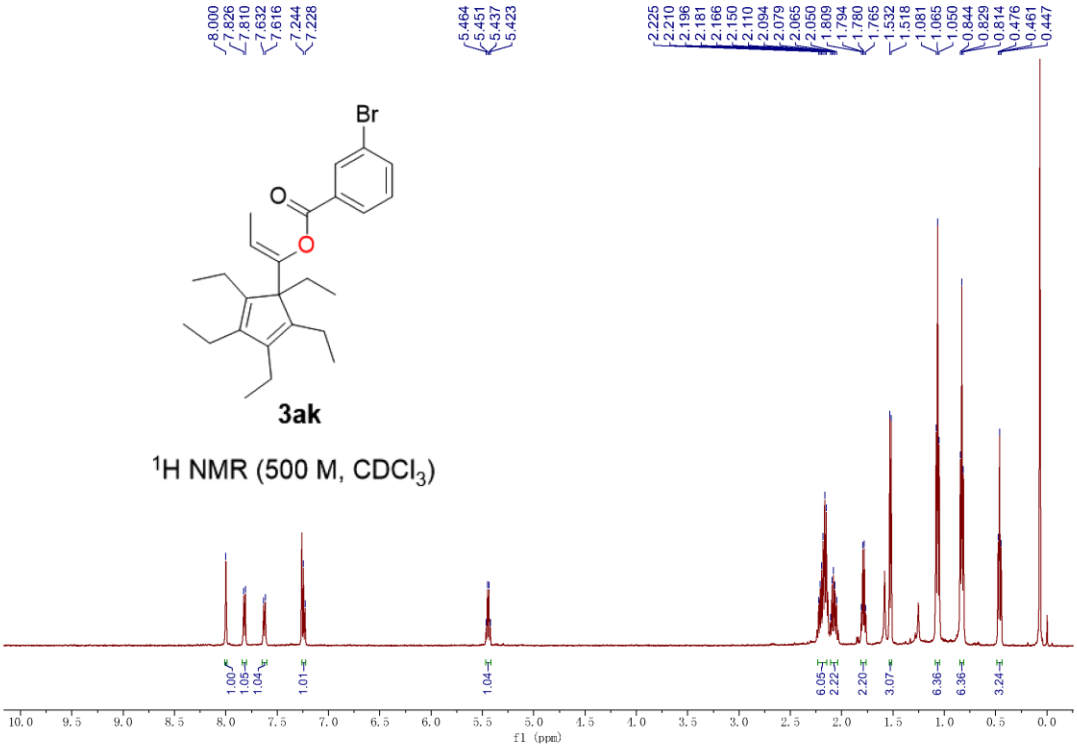

-106.233
F
O
O
3ah
19F NMR (470M, CDCl3)
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

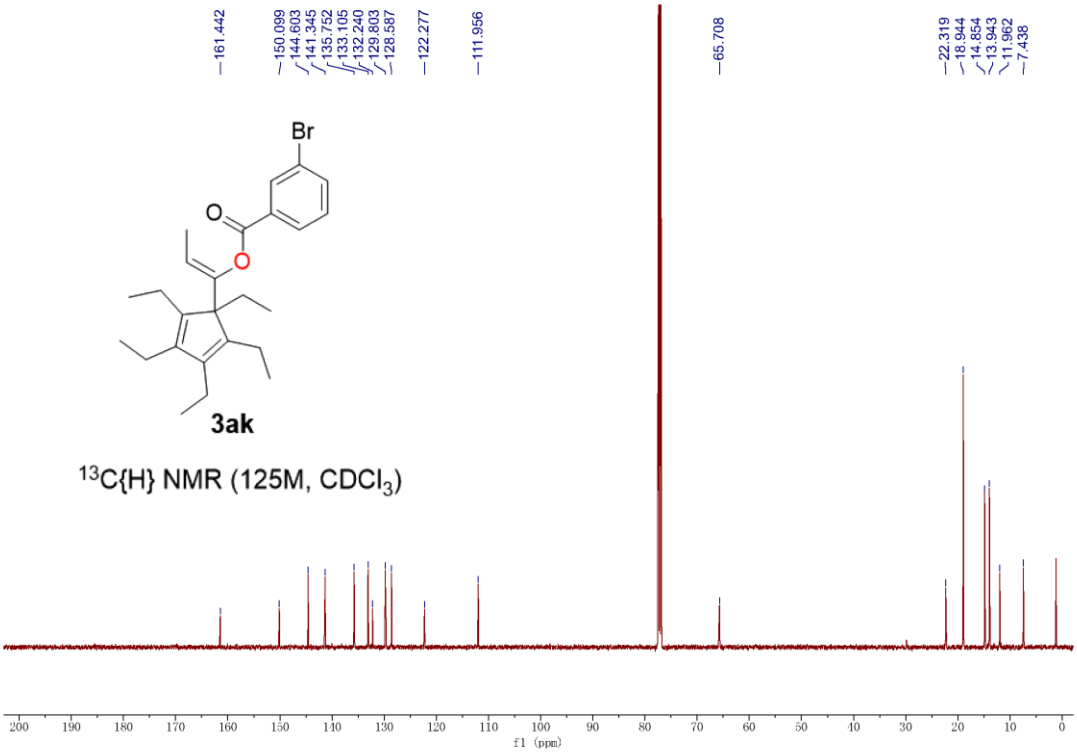

8.225
8.208
8.048
8.031
5.504
5.490
5.476
5.463
2.234
2.219
2.204
2.189
2.163
2.160
2.149
2.144
2.133
2.129
2.118
2.114
2.096
2.081
2.067
2.052
1.822
1.808
1.793
1.779
1.544
1.530
1.082
1.067
1.052
0.821
0.806
0.791
0.480
0.466
0.452
NO2
O
O
3ai
1H NMR (500 M, CDCl3)
2.02
2.06
1.00
2.08
4.07
2.08
2.11
3.07
6.09
6.14
3.04
f1 (ppm)

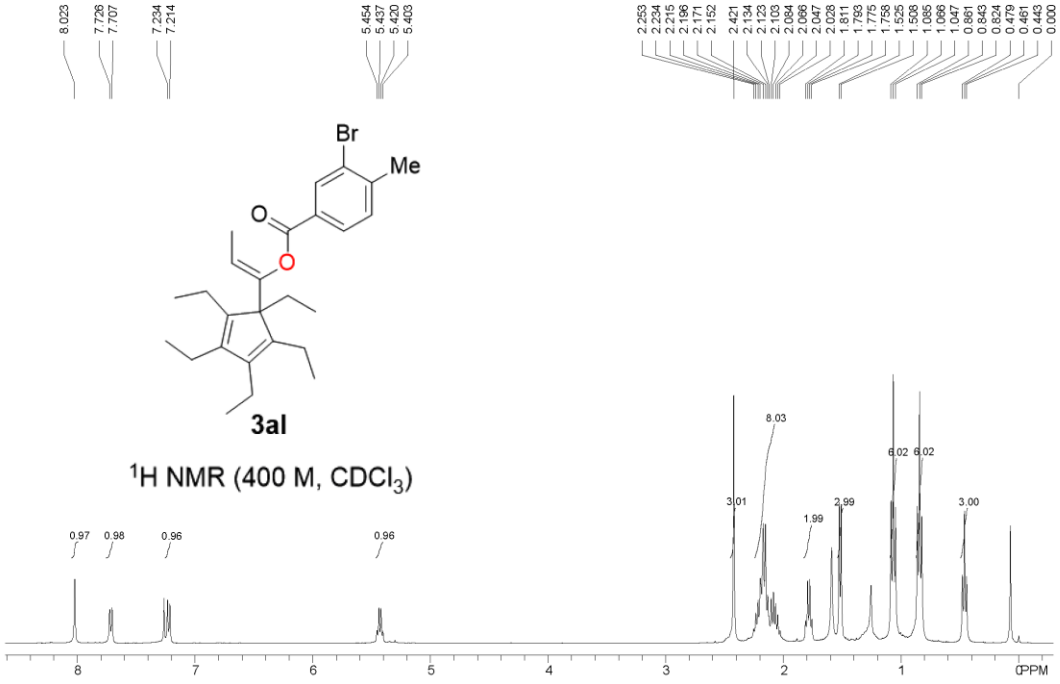

160.879
150.538
150.145
144.632
141.391
135.779
131.058
123.427
112.225
65.670
22.371
18.944
18.905
14.906
13.957
11.966
7.418
NO2
O
O
3ai
13C{H} NMR (125M, CDCl3)
f1 (ppm)

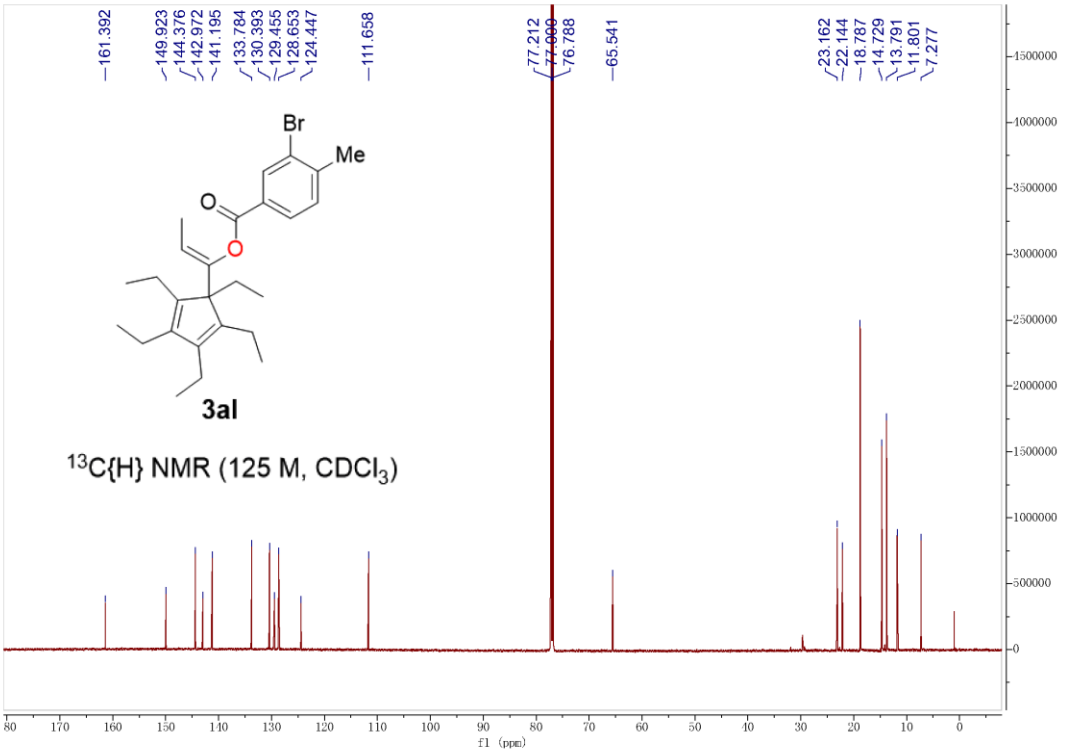

7.845
7.784
7.765
7.484
7.465
7.328
7.309
7.289
5.473
5.456
5.439
5.423
2.234
2.215
2.198
2.180
2.164
2.146
2.127
2.102
2.083
2.064
2.047
1.816
1.799
1.781
1.763
1.537
1.520
1.086
1.067
1.048
0.847
0.829
0.810
0.481
0.463
0.445
-0.000
Cl
O
O
3aj
1H NMR (400 M, CDCl3)
0.98
0.97
0.98
1.05
1.05
7.99
2.10
3.01
5.96
6.04
2.96
8
7
6
5
4
3
2
1
0
PPM

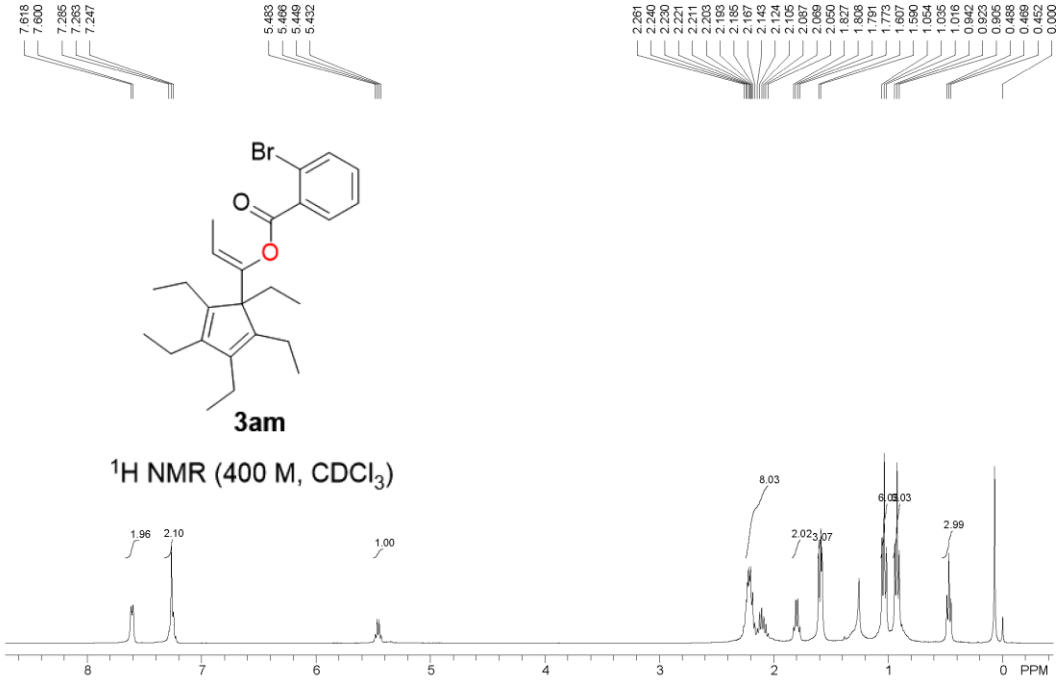

161.422
149.942
144.425
141.192
134.160
132.686
131.878
130.007
129.384
127.981
111.785
77.212
77.000
76.788
65.538
22.154
18.786
18.764
14.670
13.795
11.803
7.280
Cl
O
O
3aj
13C{H} NMR (100 M, CDCl3)
160
140
120
100
80
60
40
20
0
f1 (ppm)

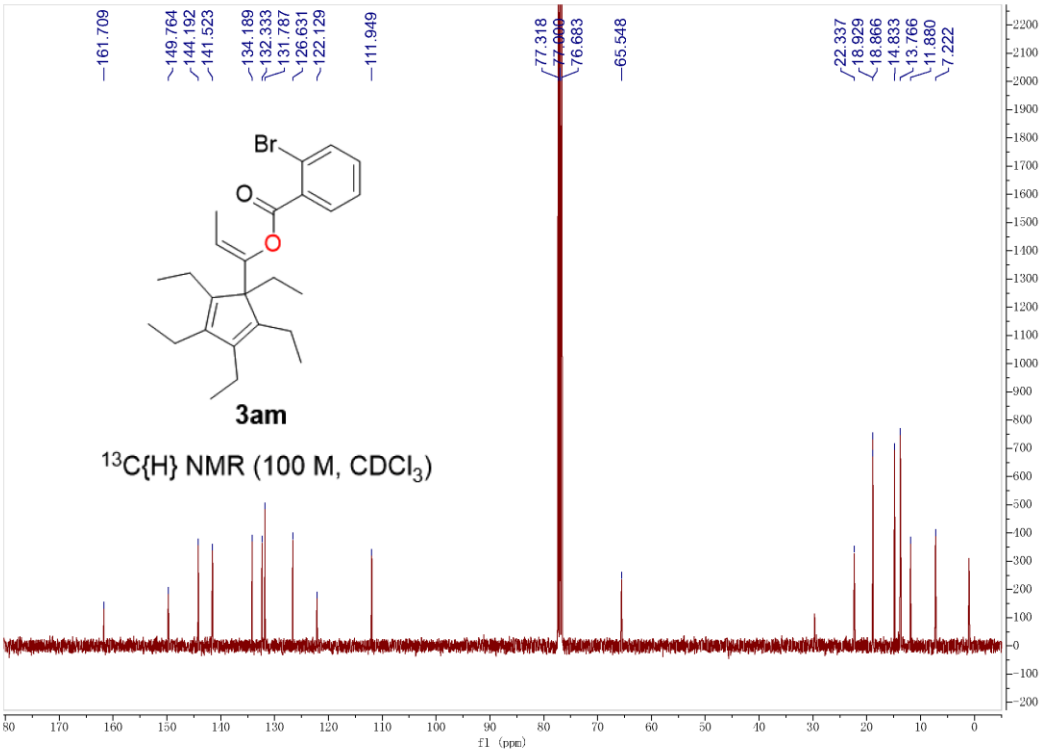

8.000
7.826
7.810
7.632
7.616
7.244
7.228
5.464
5.451
5.437
5.423
2.225
2.210
2.196
2.181
2.166
2.150
2.110
2.094
2.079
2.065
2.050
1.809
1.794
1.780
1.765
1.532
1.518
1.081
1.065
1.050
0.844
0.829
0.814
0.476
0.461
0.447
Br
O
O
3ak
1H NMR (500 M, CDCl3)
1.00
1.05
1.04
1.01
1.04
6.05
2.22
2.20
3.07
6.36
6.36
3.24
f1 (ppm)

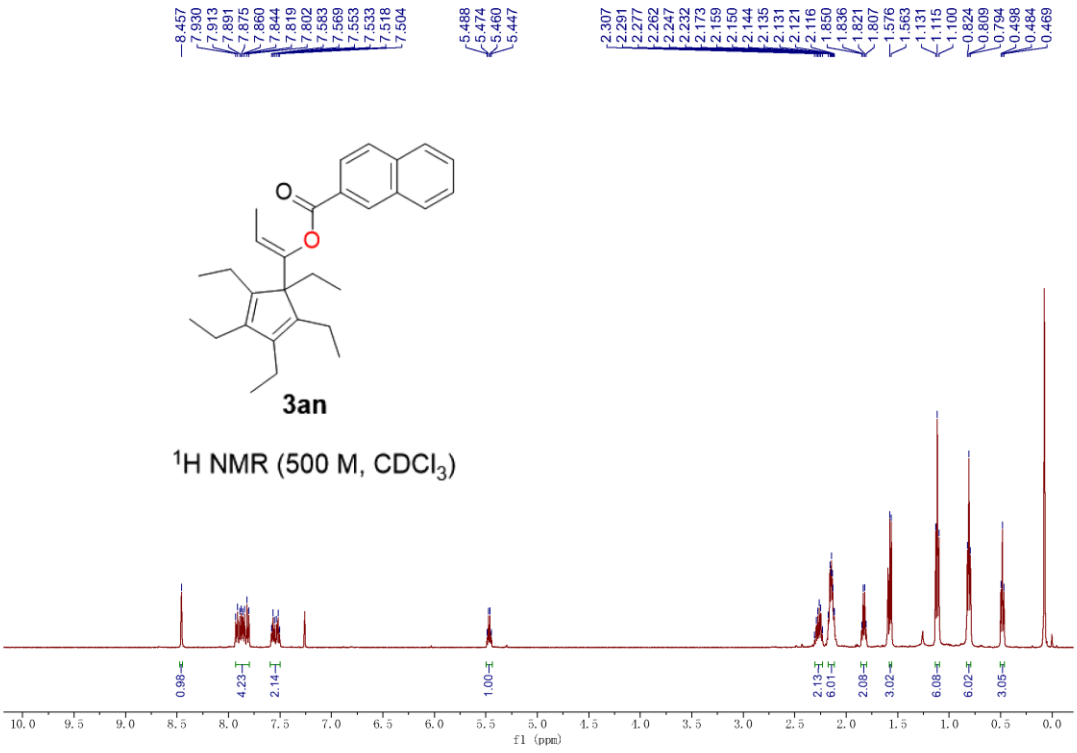

161.442
150.099
144.603
141.345
135.752
133.105
132.240
129.803
128.587
122.277
111.956
65.708
22.319
18.944
14.854
13.943
11.962
7.438
Br
O
O
3ak
13C{H} NMR (125M, CDCl3)
f1 (ppm)

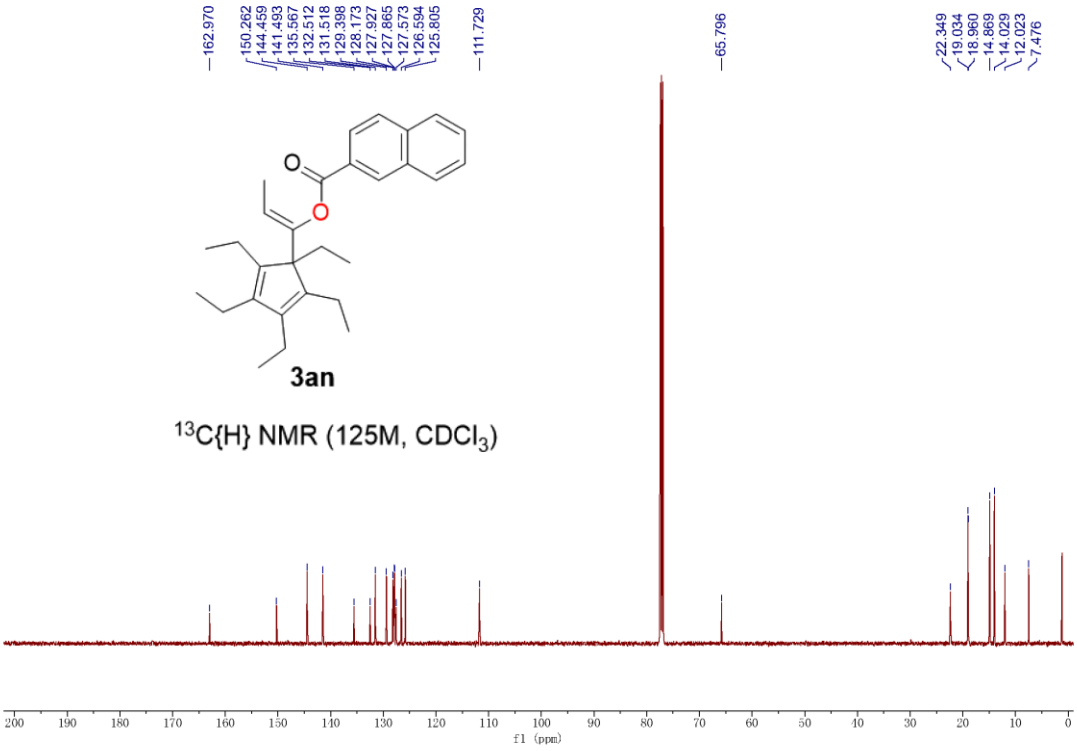

8.023
7.726
7.707
7.234
7.214
5.454
5.437
5.420
5.403
2.253
2.234
2.215
2.196
2.171
2.152
2.421
2.134
2.123
2.103
2.084
2.066
2.047
2.028
1.811
1.793
1.775
1.758
1.525
1.508
1.085
1.066
1.047
0.861
0.843
0.824
0.479
0.461
0.443
0.000
Br
Me
O
O
3al
1H NMR (400 M, CDCl3)
0.97
0.98
0.96
0.96
3.01
8.03
1.99
2.99
6.02
6.02
3.00
8
7
6
5
4
3
2
1
0PPM

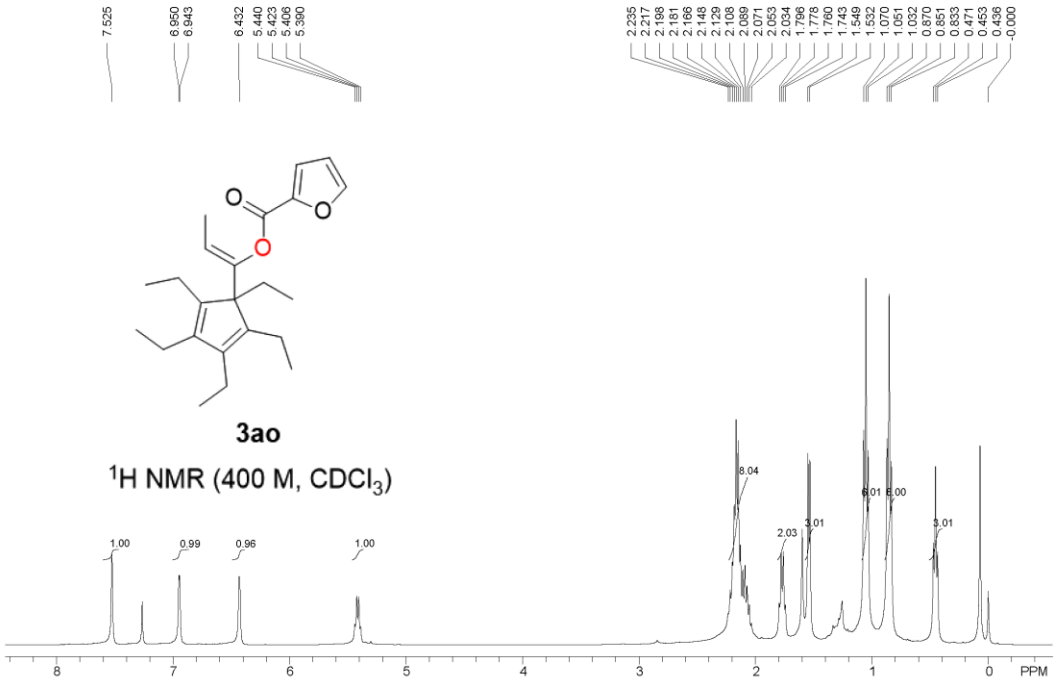

161.392
149.923
144.376
142.972
141.195
133.784
130.393
129.455
128.653
124.447
111.658
77.212
77.000
76.788
65.541
23.162
22.144
18.787
14.729
13.791
11.801
7.277
Br
Me
O
O
3al
13C{H} NMR (125 M, CDCl3)
1500000
1000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

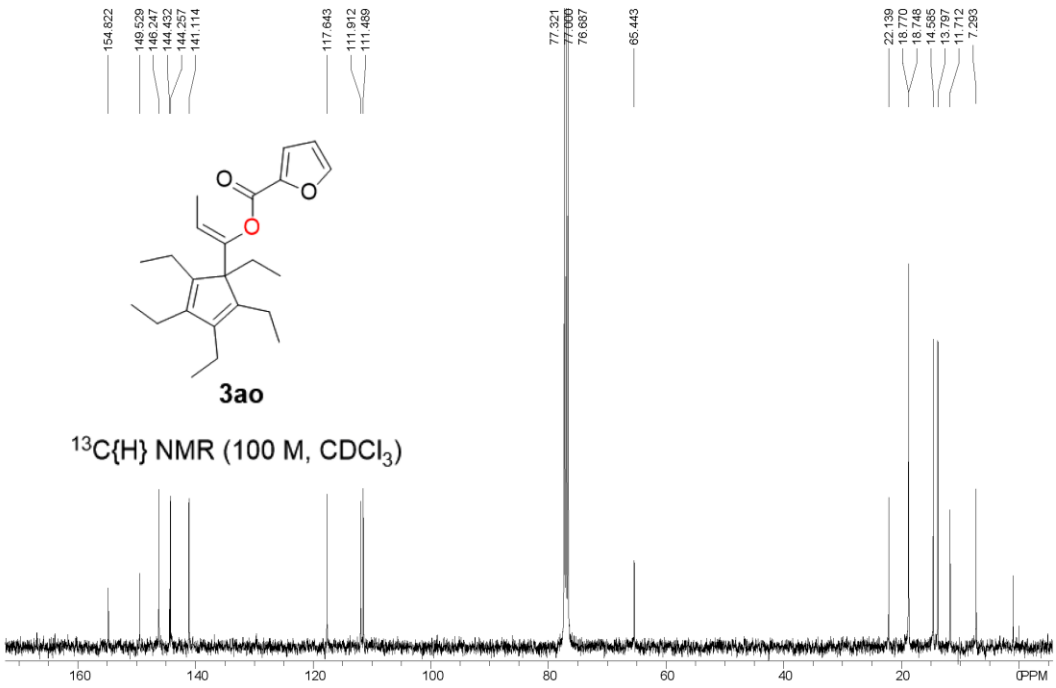

7.618
7.600
7.285
7.263
7.247
5.483
5.466
5.449
5.432
2.261
2.240
2.230
2.221
2.211
2.203
2.193
2.185
2.167
2.143
2.124
2.105
2.087
2.069
2.050
1.827
1.808
1.791
1.773
1.607
1.590
1.054
1.035
1.016
0.942
0.923
0.905
0.488
0.469
0.452
0.000
Br
O
O
3am
1H NMR (400 M, CDCl3)
1.96
2.10
1.00
8.03
2.02
3.07
6.05
5.03
2.99
8
7
6
5
4
3
2
1
0
PPM

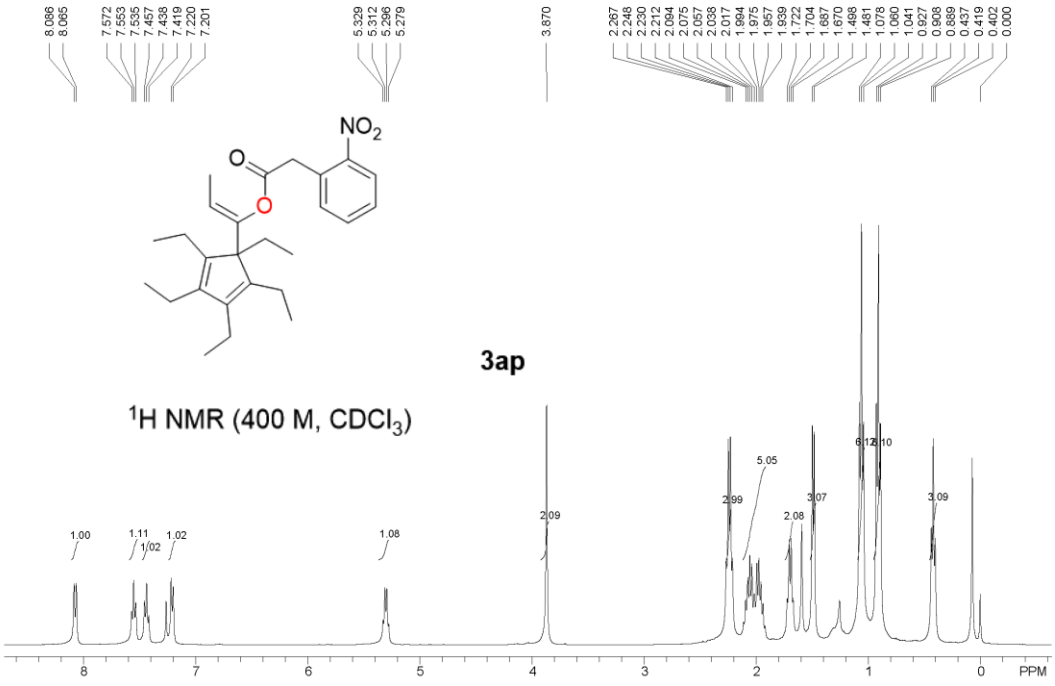

161.709
149.764
144.192
141.523
134.189
132.333
131.787
126.631
122.129
111.949
77.318
77.000
76.683
65.548
22.337
18.929
18.866
14.833
13.766
11.880
7.222
Br
O
O
3am
13C{H} NMR (100 M, CDCl3)
f1 (ppm)

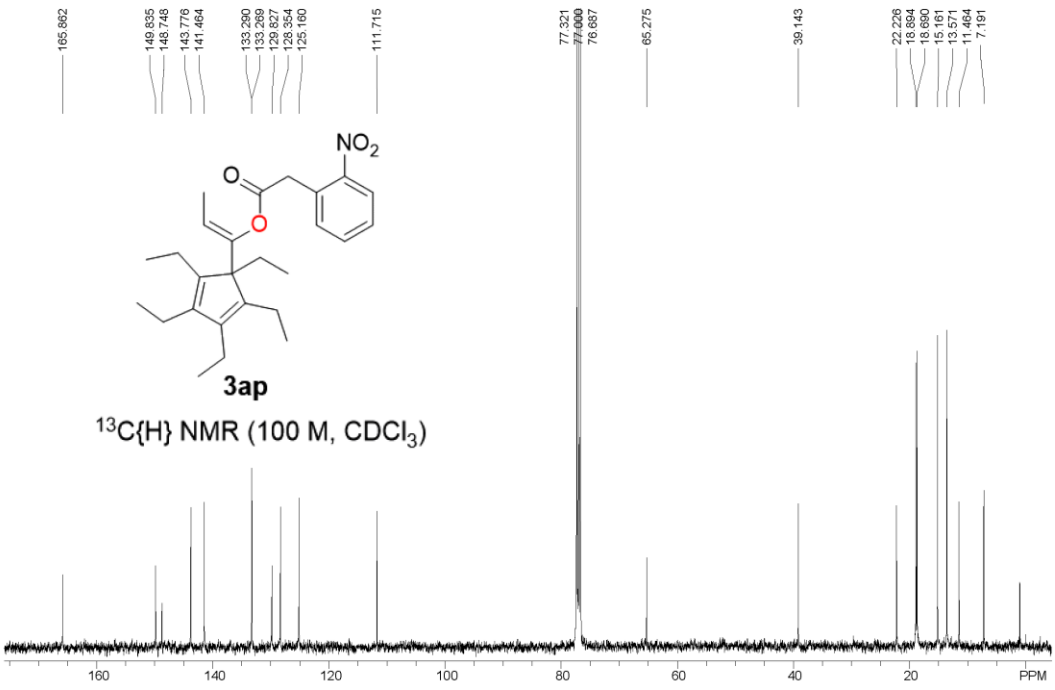

8.457
7.930
7.913
7.891
7.875
7.860
7.844
7.819
7.802
7.583
7.569
7.553
7.533
7.518
7.504
5.488
5.474
5.460
5.447
2.307
2.291
2.277
2.262
2.247
2.232
2.173
2.159
2.150
2.144
2.135
2.131
2.121
2.116
1.850
1.836
1.821
1.807
1.576
1.563
1.131
1.115
1.100
0.824
0.809
0.794
0.498
0.484
0.469
O
O
3an
^{1}H NMR (500 M, CDCl$_3$)
0.98
4.23
2.14
1.00
2.13
6.01
2.08
3.02
6.08
6.02
3.05
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)

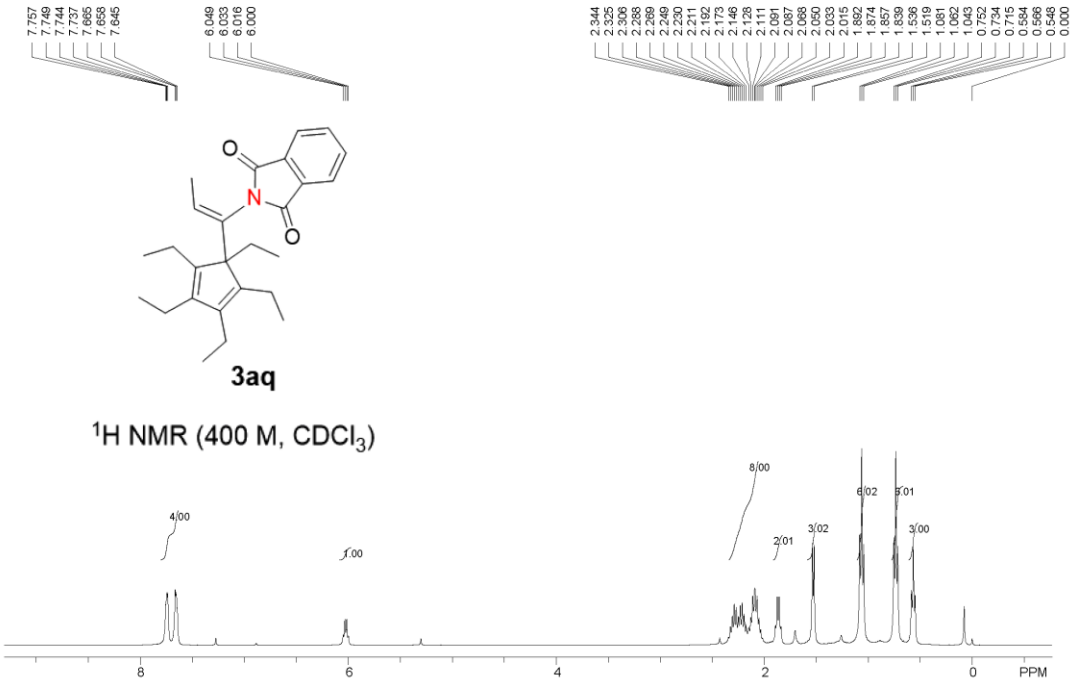

162.970
150.262
144.459
141.493
135.567
132.512
131.518
129.398
128.173
127.927
127.865
127.573
126.594
125.805
111.729
65.796
22.349
19.034
18.960
14.869
14.029
12.023
7.476
O
O
3an
^{13}C{H} NMR (125M, CDCl$_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

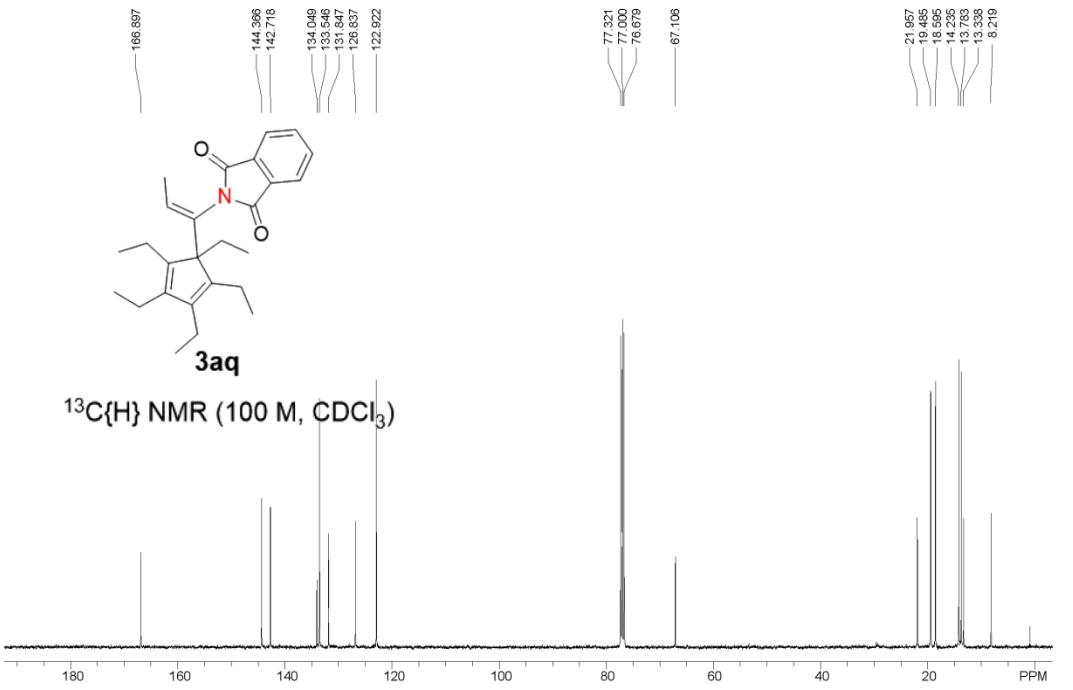

7.525
6.950
6.943
6.432
5.440
5.423
5.406
5.390
2.235
2.217
2.198
2.181
2.166
2.148
2.129
2.108
2.089
2.071
2.053
2.034
1.796
1.778
1.760
1.743
1.549
1.532
1.070
1.051
1.032
0.870
0.851
0.833
0.471
0.453
0.436
-0.000
O
O
O
3ao
1H NMR (400 M, CDCl3)
1.00
0.99
0.96
1.00
8.04
2.03
3.01
6.01
6.00
3.01
8
7
6
5
4
3
2
1
0
PPM

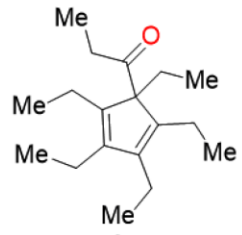

154.822
149.529
146.247
144.432
144.257
141.114
117.643
111.912
111.489
77.321
77.000
76.657
65.443
22.139
18.770
18.748
14.585
13.797
11.712
7.293
O
O
O
3ao
13C{H} NMR (100 M, CDCl3)
160
140
120
100
80
60
40
20
0
PPM


8.086
8.065
7.572
7.553
7.535
7.457
7.438
7.419
7.220
7.201
5.329
5.312
5.296
5.279
3.870
2.267
2.248
2.230
2.212
2.094
2.075
2.057
2.038
2.017
1.994
1.975
1.957
1.939
1.722
1.704
1.687
1.670
1.496
1.481
1.078
1.060
1.041
0.927
0.908
0.889
0.437
0.419
0.402
0.000
NO2
O
O
3ap
1H NMR (400 M, CDCl3)
1.00
1.11
1.02
1.02
1.08
2.09
2.99
5.05
2.08
3.07
6.12
6.10
3.09
8
7
6
5
4
3
2
1
0
PPM


165.862
149.835
148.748
143.776
141.464
133.290
133.269
129.827
128.354
125.160
111.715
77.321
77.000
76.687
65.275
39.143
22.226
18.894
18.690
15.161
13.571
11.464
7.191
NO2
O
O
3ap
13C{H} NMR (100 M, CDCl3)
160
140
120
100
80
60
40
20
PPM

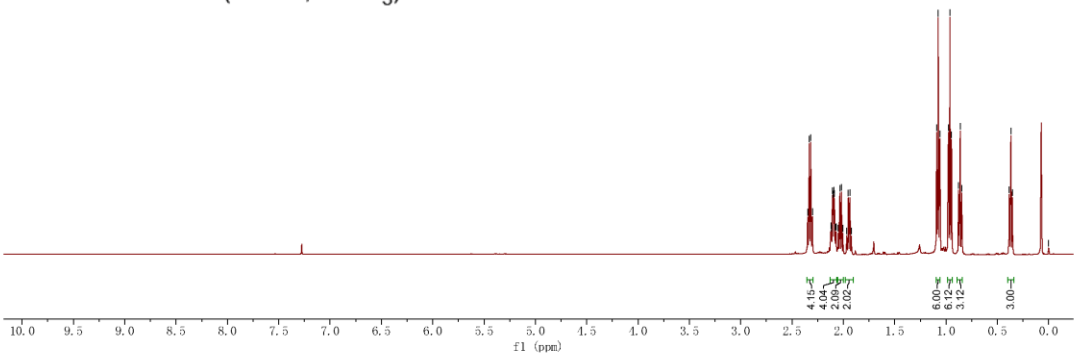

7.757
7.749
7.744
7.737
7.665
7.658
7.645
6.049
6.033
6.016
6.000
2.344
2.325
2.306
2.288
2.269
2.249
2.230
2.211
2.192
2.173
2.146
2.128
2.111
2.091
2.087
2.066
2.050
2.033
2.015
1.892
1.874
1.857
1.839
1.536
1.519
1.081
1.062
1.043
0.752
0.734
0.715
0.584
0.566
0.548
0.000
O
N
O
3aq
1H NMR (400 M, CDCl3)
4.00
1.00
8.00
6.02
5.01
3.02
3.00
2.01
8
6
4
2
0
PPM

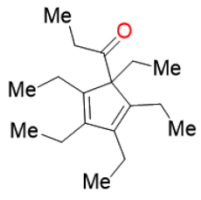

166.897
144.366
142.718
134.049
133.546
131.847
128.837
122.922
77.321
77.000
76.679
67.106
21.957
19.485
18.595
14.235
13.783
13.338
8.219
O
N
O
3aq
13C{H} NMR (100 M, CDCl3)
180
160
140
120
100
80
60
40
20
PPM



4

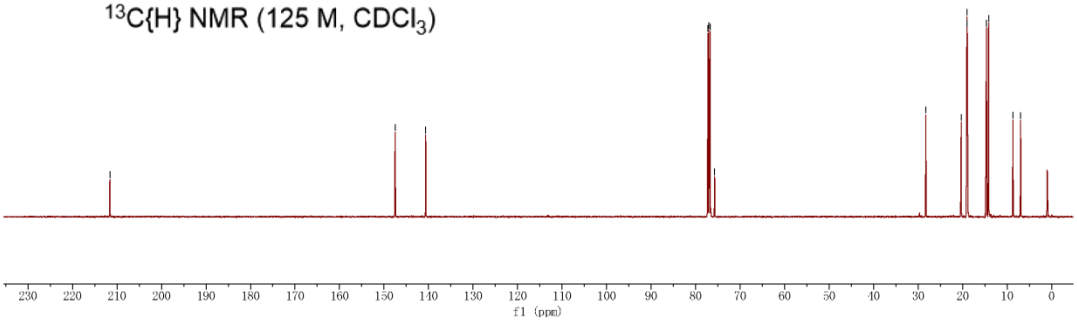
^{1}H NMR (500 M, $CDCl_3$)

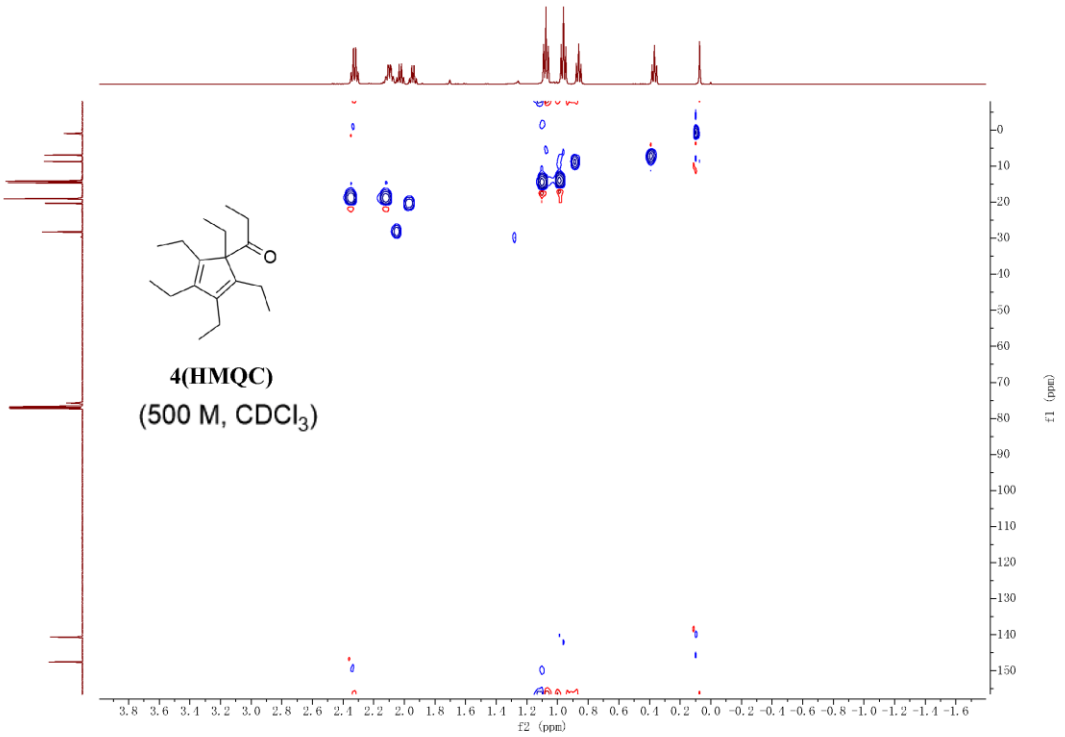


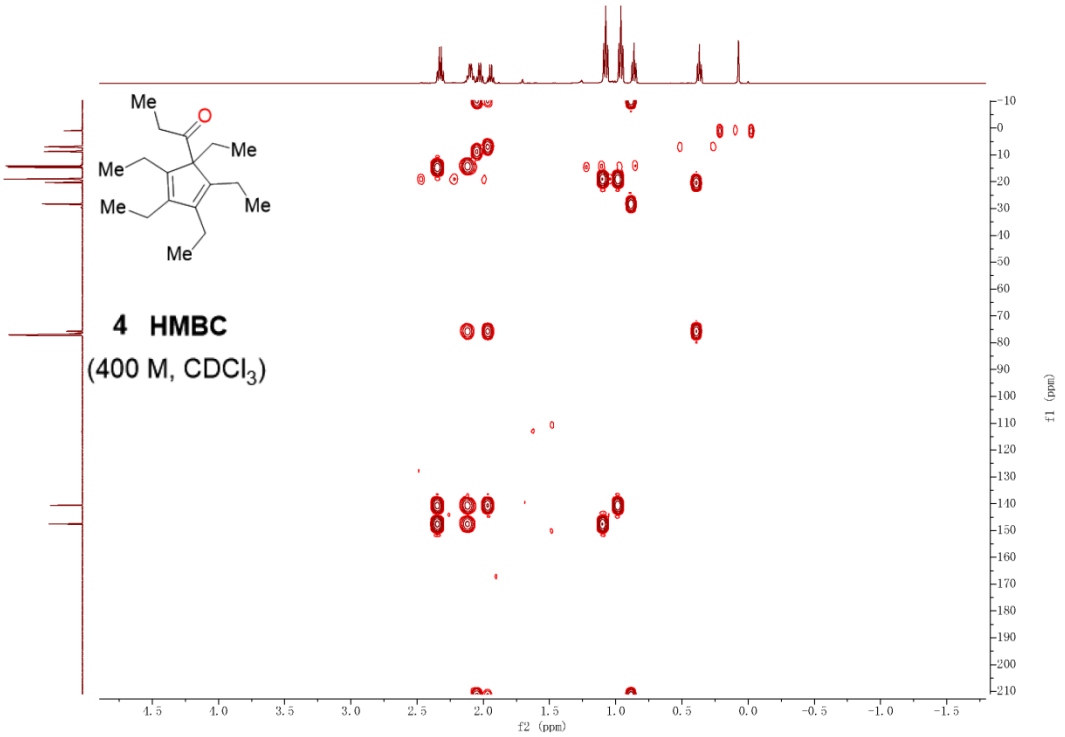


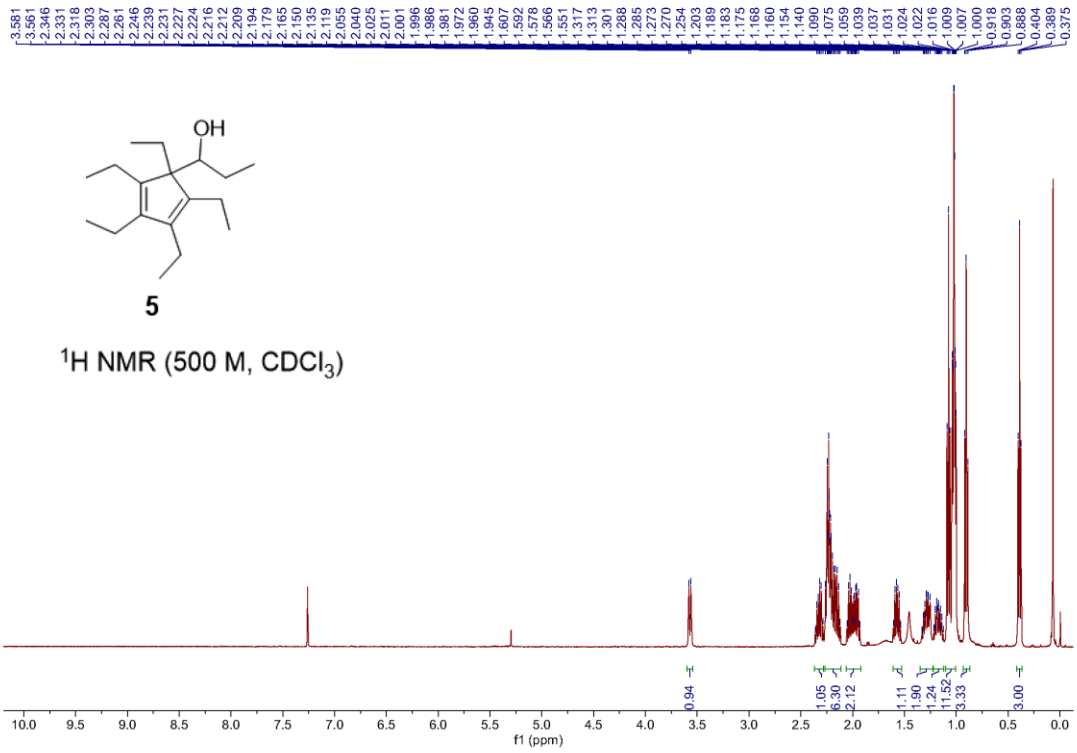
4

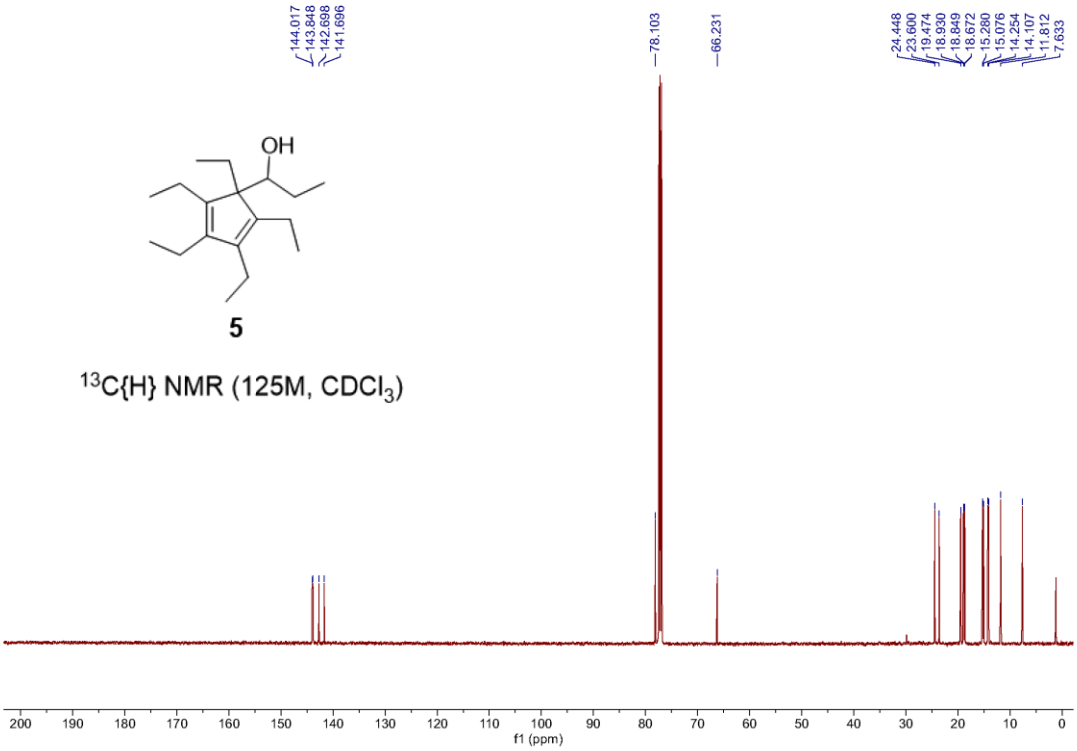
^{13}C{H} NMR (125 M, $CDCl_3$)




O
4(HMQC)
(500 M, CDCl3)
f2 (ppm)
f1 (ppm)


Me
Me
Me
Me
Me
Me
4 HMBC
(400 M, CDCl3)
f2 (ppm)
f1 (ppm)


OH
5
^{1}H NMR (500 M, $CDCl_3$)
f1 (ppm)


OH
5
^{13}C{H} NMR (125M, $CDCl_3$)
f1 (ppm)