Electronic Supplementary Information

for

Peroxide promoted tunable decarboxylative alkylation of cinnamic acids to form alkenes or ketones under metal-free conditions

Jing Ji, Ping Liu and Peipei Sun*

College of Chemistry and Materials Science, Nanjing Normal University; Jiangsu Provincial Key Laboratory of Material Cycle Processes and Pollution Control; Jiangsu Collaborative Innovation Center of Biomedical Functional Materials, Nanjing 210097, China
E-mail: sunpeipei@njnu.edu.cn

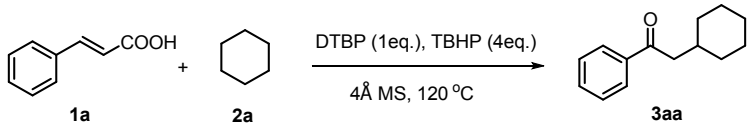
Contents:

1. General Considerations:

All reactions were run in a sealed tube with a Teflon lined cap under air atmosphere. Chemicals were commercially available and were used without purification. Disulfides were purchased or prepared according to the literature procedures.[1] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 400 spectrometers in $CDCl_3$ [using $(CH_3)_4Si$ (for ^{1}H, $\delta = 0.00$; for ^{13}C, $\delta = 77.00$) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were obtained with a Waters Q-TOF mass spectrometer. LC-MS was determined on an Agilent 1200HPLC. Melting points are uncorrected.

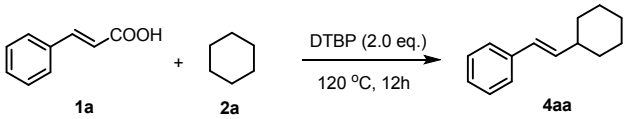
2. General Experimental Procedures

2.1 Representative procedure for decarboxylative alkylation of cinnamic acids to form ketones

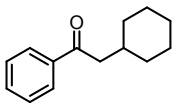


A mixture of cinnamic acid **1a** (0.5 mmol), 4A molecular sieves (200 mg), cyclohexane **2a** (2.0 mL), DTBP (0.5 mmol, 1.0 equiv.) and TBHP (2.0 mmol, 4.0 equiv., 70% aqueous solution) was sealed in a 25 mL tube with a Teflon lined cap under nitrogen atmosphere. The tube was then placed in an oil bath, stirred and heated at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (25 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified over a column of silica gel (eluent: hexane/ethyl acetate = 20 : 1) to afford the desired product **3aa**.

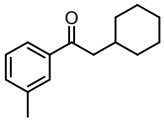
2.2 Representative procedure for decarboxylative alkylation of cinnamic acids to form alkenes:



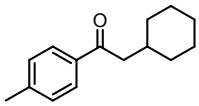
A mixture of cinnamic acid **1a** (0.5 mmol), cyclohexane **2a** (2.0 mL) and DTBP (1.0 mmol, 2.0 equiv.) was sealed in a 25 mL tube with a Teflon lined cap under nitrogen atmosphere. The tube was then placed in an oil bath, stirred and heated at 120 °C for 24 h. After cooling to room temperature, the reaction mixture was quenched with water (20 mL) and extracted with dichloromethane (25 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and the solvent was removed under vacuum. The crude product was purified over a column of silica gel (eluent: hexane/ethyl acetate = 40 : 1) to afford the desired product **4aa**.



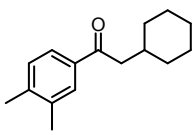
2-Cyclohexyl-1-phenylethan-1-one (**3aa**):[1] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.97 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.59–7.55 (m, 1H), 7.49–7.45 (m, 2H), 2.84 (d, *J* = 6.8 Hz, 2H), 2.05-1.95 (m, 1H), 1.80–1.66 (m, 5H), 1.36–1.16 (m, 3H), 1.09–0.99 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.3, 137.5, 132.8, 128.5, 128.1, 46.2, 34.6, 33.5, 26.3, 26.2.



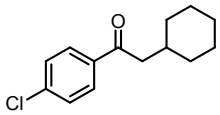
2-Cyclohexyl-1-(*m*-tolyl)ethan-1-one (**3ba**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.76 (dd, *J* = 9.2, 1.6 Hz, 2H), 7.40–7.34 (m, 2H), 2.83 (d, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.05–1.94 (m, 1H), 1.80-1.65 (m. 5H), 1.33–1.15 (m, 3H), 1.08–0.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.5, 138.3, 137.6, 133.6, 128.6, 128.4, 125.4, 46.3, 34.6, 33.4, 26.3, 26.2, 21.4; HRMS-ESI (m/z): calcd for $C_{15}H_{20}ONa$ $[M + Na]^+$ 239.1406, found 239.1412.



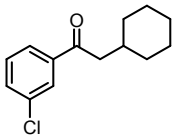
2-Cyclohexyl-1-(*p*-tolyl)ethan-1-one (**3ca**):[2] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 2.81 (d, *J* = 6.8 Hz, 2H), 2.43 (s, 3H), 2.04–1.94 (m, 1H), 1.79–1.65 (m, 5H), 1.32–1.15 (m, 3H), 1.08–0.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.0, 143.6, 135.0, 129.2, 128.3, 46.1, 34.7, 33.5, 26.3, 26.2, 21.6.



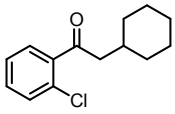
2-Cyclohexyl-1-(3,4-dimethylphenyl)ethan-1-one (**3da**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.75 (d, *J* = 1.6 Hz, 1H), 7.70 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 2.81 (d, *J* = 6.8 Hz, 2H), 2.34 (s, 6H), 2.03–1.92 (m, 1H), 1.79–1.65 (m, 5H), 1.32–1.15 (m, 3H), 1.07–0.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.3, 142.3, 136.9, 135.5, 129.7, 129.3, 126.0, 46.1, 34.7, 33.5, 26.3, 26.2, 20.0, 19.8; HRMS-ESI (m/z): calcd for $C_{16}H_{22}ONa$ $[M + Na]^+$ 253.1563, found 253.1569.



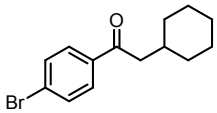
1-(4-Chlorophenyl)-2-cyclohexylethan-1-one (**3ea**):[3] White solid. Mp: 52–54 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, *J* = 8.8 Hz, 2H), 7.44 (*J* = 8.8 Hz, 2H), 2.80 (d, *J* = 6.8 Hz, 2H), 2.01–1.92 (m, 1H), 1.78–1.65 (m, 5H), 1.32–1.15 (m, 3H), 1.07–0.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.0, 139.3, 135.8, 129.6, 128.8, 46.2, 34.5, 33.4, 26.2, 26.1.



1-(3-Chlorophenyl)-2-cyclohexylethan-1-one (**3fa**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.92 (dd, *J* = 3.6, 2.0 Hz, 1H), 7.84–7.81 (m, 1H), 7.54–7.51 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 2.81 (d, *J* = 6.8 Hz, 2H), 2.02–1.93 (m, 1H), 1.78–1.65 (m, 5H), 1.32–1.15 (m, 3H), 1.07–0.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 198.9, 139.0, 134.9, 132.8, 129.9, 128.2, 126.2, 46.3, 34.4, 33.4, 26.2, 26.1; HRMS-ESI (m/z): calcd for $C_{14}H_{17}ClONa$ $[M + Na]^+$ 259.0860, found 259.0869.

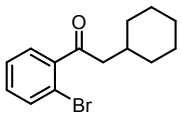


1-(2-Chlorophenyl)-2-cyclohexylethan-1-one (**3ga**): Colorless oil.. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43–7.29 (m, 4H), 2.82 (d, *J* = 6.8 Hz, 2H), 2.00–1.90 (m, 1H), 1.79–1.62 (m, 5H), 1.31–1.13 (m, 3H), 1.05–0.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 203.5, 140.1, 131.4, 130.7, 130.5, 128.6, 126.9, 50.6, 34.2, 33.2, 26.2, 26.1; HRMS-ESI (m/z): calcd for $C_{14}H_{17}ClONa$ $[M + Na]^+$ 259.0860, found 259.0866.

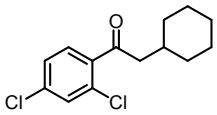


1-(4-Bromophenyl)-2-cyclohexylethan-1-one (**3ha**): White solid. Mp: 52–54 °C. ^{1}H NMR

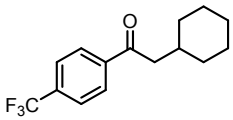
($CDCl_3$, 400 MHz) δ 7.81 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 2.79 (d, *J* = 6.8 Hz, 2H), 2.01–1.91 (m, 1H), 1.77–1.64 (m, 5H), 1.31–1.14 (m, 3H), 1.06–0.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.1, 136.1, 131.8, 129.7, 128.0, 46.1, 34.5, 33.4, 26.2, 26.1; HRMS-ESI (m/z): calcd for $C_{14}H_{17}BrONa$ $[M + Na]^+$ 303.0355, found 303.0361.



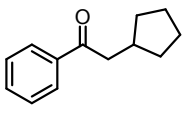
1-(2-Bromophenyl)-2-cyclohexylethan-1-one (**3ia**): Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.61 (d, *J* = 7.6 Hz, 1H), 7.38–7.35 (m, 2H), 7.31–7.27 (m, 1H), 2,82 (d, *J* = 6.8 Hz, 2H), 2.02–1.91 (m, 1H), 1.82–1.64 (m, 5H), 1.36–1.14 (m, 3H), 1.07–0.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 204.2, 142.3, 133.7, 131.3, 128.3, 127.4, 118.6, 50.4, 34.1, 33.2, 26.2, 26.1; HRMS-ESI (m/z): calcd for $C_{14}H_{17}BrONa$ $[M + Na]^+$ 303.0355, found 303.0378.



2-Cyclohexyl-1-(2,4-dichlorophenyl)ethan-1-one (**3ja**): Yellow oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, *J* = 1.6 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 8.4 Hz, 1.6 Hz, 1H), 2.81 (d, *J* = 6.8 Hz, 2H), 1.99–1.88 (m, 1H), 1.77–1.64 (m. 5H), 1.33–1.13 (m, 3H), 1.05–0.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.2, 138.2, 137.0, 131.9, 130.4, 129.9, 127.3, 50.5, 34.3, 33.2, 26.2, 26.1; HRMS-ESI (m/z): calcd for $C_{14}H_{16}Cl_2ONa$ $[M + Na]^+$ 253.1563, found 253.1568.

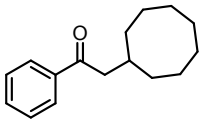


2-Cyclohexyl-1-(4-(trifluoromethyl)phenyl)ethan-1-one (**3ka**): Colorless oil. ^1H NMR ($CDCl_3$, 400MHz), δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 2.86 (d, *J* = 6.8 Hz, 2H), 2.05–1.94 (m, 1H), 1.79–1.65 (m, 5H), 1.33–1.15 (m, 3H), 1.08–0.99 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.2, 140.1, 134.2 (q, *J* = 32.4 Hz), 128.4, 125.6 (q, *J* = 3.5 Hz), 123.6 (q, *J* = 270.9 Hz), 46.5, 34.4, 33.4, 26.2, 26.1; HRMS-ESI (m/z): calcd for $C_{15}H_{17}F_3ONa$ $[M + Na]^+$ 293.1123, found 293.1136.

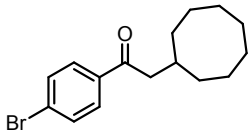


2-Cyclopentyl-1-phenylethan-1-one (**3ab**):[1] Colorless oil. ^1H NMR ($CDCl_3$, 400 MHz) δ 8.00–7.97 (m, 2H), 7.60–7.55 (m, 1H), 7.50–7.46 (m, 2H), 3.00 (d, *J* = 6.8 Hz, 2H), 2.47–2.35 (m, 1H),

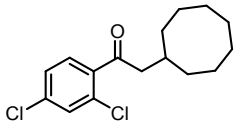
1.94–1.86 (m, 2H), 1.69–1.55 (m, 4H), 1.25–1.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.4, 137.3, 132.8, 128.5, 128.1, 44.8, 36.1, 32.7, 25.0.



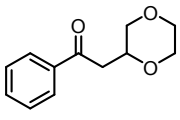
2-Cyclooctyl-1-phenylethan-1-one (**3ac**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98–7.94 (m, 2H), 7.59–7.54 (m, 1H), 7.49–7.44 (m, 2H), 2.88 (d, *J* = 6.8 Hz, 2H), 2.34–2.26 (m, 1H), 1.69–1.52 (m, 12H), 1.42–1.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.5, 137.5, 132.8, 128.5, 128.1, 46.9, 34.1, 32.5, 27.1, 26.2, 25.3; HRMS-ESI (m/z): calcd for $C_{16}H_{22}ONa$ $[M + Na]^+$ 253.1563, found 253.1568.



1-(4-Bromophenyl)-2-cyclooctylethan-1-one (**3hc**): White solid. Mp: 40–42 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 2H), 2.84 (d, *J* = 6.8 Hz, 2H), 2.30–2.23 (m, 1H), 1.67–1.51 (m, 12H), 1.41–1.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.4, 136.1, 131.9, 129.7, 128.0, 46.8, 34.0, 32.5, 27.1, 26.2, 25.3. HRMS-ESI (m/z): calcd for $C_{16}H_{21}BrOK$ $[M + K]^+$ 347.0407, found 347.0403.

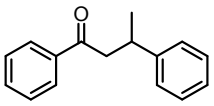


2-Cyclooctyl-1-(2,4-dichlorophenyl)ethan-1-one (**3jc**): Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44 (d, *J* = 2.0 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.85 (d, *J* = 7.2 Hz, 2H), 2.26–2.18 (m, 1H), 1.66–1.49 (m. 12H), 1.39–1.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.5, 138.2, 137.0, 131.9, 130.4, 129.9, 127.3, 51.3, 33.9, 32.4, 27.0, 26.2, 25.2; HRMS-ESI (m/z): calcd for $C_{16}H_{20}Cl_2ONa$ $[M + Na]^+$ 321.0783, found 321.0781.

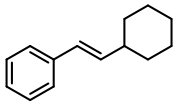


2-(1,4-Dioxan-2-yl)-1-phenylethan-1-one (**3ad**):[4] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.99–7.96 (m , 2H), 7.62–7.58 (m, 1H), 7.51–7.47 (m, 2H), 4.30–4.24 (m, 1H), 3.95 (d, *J* = 11.2 Hz, 1H), 3.82–3.74 (m, 3H), 3.68–3.62 (m, 1H), 3.41 (t, *J* = 10.4 Hz, 1H), 3.27 (dd, *J* = 16.4, 6.4 Hz, 1H), 2.91 (dd, *J* = 16.4, 6.0, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.1, 136.9, 133.4, 128.7,

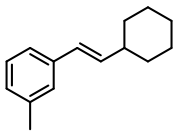
128.2, 71.8, 91.0, 66.9, 66.5, 40.7.



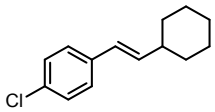
1,3-Diphenylbutan-1-one (**3ae**):[5] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.95 (dd, *J* = 7.2, 5.2 Hz, 2H), 7.59–7.55 (m, 1H), 7.49–7.45 (m, 2H), 7.35–7,.29 (m, 4H), 7.24–7.20 (m, 1H), 3.58–3.49 (m, 1H), 3.33 (dd, *J* = 16.4, 5.6 Hz, 1H), 3.21 (dd, *J* = 16.4, 8.4 Hz, 1H), 1.36 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.1, 146.6, 137.2, 133.0, 128.6, 128.5, 128.1, 126.9, 126.3, 47.0, 35.6, 21.9.



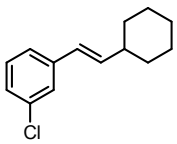
(*E*)-(2-Cyclohexylvinyl)benzene (**4aa**):[6] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40–7.37 (m, 2H), 7.33–7.29 (m, 2H), 7.23–7.19 (m, 1H), 6.37 (d, *J* = 16.0 Hz, 1H), 6.21 (dd, *J* = 16.0 Hz, 6.8 Hz, 1H), 2.20–2.12 (m, 1H), 1.86–1.69 (m, 5H), 1.41–1.16 (m, 5H); ^{13}C NMR($CDCl_3$, 100 MHz) δ 138.1, 136.9, 128.5, 127.2, 126.7, 125.9, 41.2, 33.0, 26.2, 26.1.



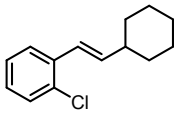
(*E*)-1-(2-Cyclohexylvinyl)-3-methylbenzene (**4ba**):[7] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27–7.20 (m, 3H), 7.07 (d, *J* = 6.8 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.40 (s, 3H), 2.24–2.15 (m, 1H), 1.89–1.73 (m, 5H), 1.44-1.20 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1, 138.0, 136.7, 128.4, 127.6, 127.3, 126.7, 123.2, 41.2, 33.0, 26.2, 26.1, 21.5.



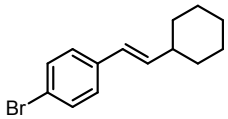
(*E*)-1-Chloro-4-(2-cyclohexylvinyl)benzene (**4ea**):[6] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.31–7.26 (m, 4H), 6.33 (dd, *J* = 16.0, 1.2 Hz, 1H), 6.18 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.20–2.11 (m, 1H), 1.86–1.70 (m, 5H), 1.42–1.16 (m, 5H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 137.5, 136.6, 132.2, 128.6, 127.2, 126.1, 41.2, 32.9, 26.2, 26.0.



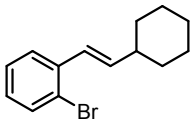
(*E*)-1-Chloro-3-(2-cyclohexylvinyl)benzene (4fa):[8] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 (s, 1H), 7.24–7.17 (m, 3H), 6.32 (d, *J* = 16.4 Hz, 1H), 6.22 (dd, *J* = 16.4, 6.8 Hz, 1H), 2.21–2.12 (m, 1H), 1.85–1.70 (m, 5H), 1.42–1.16 (m, 5H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 140.0, 138.4, 134.4, 129.6, 126.7, 126.1, 125.9, 124.2, 41.1, 32.9, 26.1, 26.0.



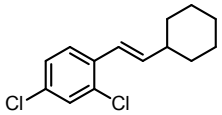
(*E*)-1-Chloro-2-(2-cyclohexylvinyl)benzene (**4ga**):[7] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.24–7.20 (m, 1H), 7.17–7.13 (m, 1H), 6.77 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 7.2 Hz, 1H), 2.27–2.18 (m, 1H), 1.89–1.71 (m, 5H), 1.42–1.19 (m, 5H); ^{13}C NMR($CDCl_3$,100 MHz) δ 139.7, 136.1, 132.7, 129.6, 127.8, 126.7, 126.5, 123.6, 41.4, 32.9, 26.2, 26.0.



(*E*)-1-Bromo-4-(2-cyclohexylvinyl)benzene (**4ha**):[6] White solid. Mp: 43–45 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.19–2.11 (m, 1H), 1.85–1.70 (m, 5H), 1.41–1.16 (m, 5H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 137.7, 137.0, 131.5, 127.5, 126.2, 120.3, 41.2, 32.9, 26.2, 26.0.

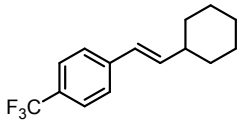


(*E*)-1-Bromo-2-(2-cyclohexylvinyl)benzene (**4ia**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57–7.52 (m, 2H), 7.28–7.24 (m, 1H), 7.10–7.06 (m, 1H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.27–2.18 (m, 1H), 1.89–1.71 (m, 5H), 1.42–1.19 (m, 5H); ^{13}C NMR ($CDCl_3$,100 MHz) δ 139.8, 137.8, 132.8, 128.1, 127.4, 126.8, 126.3, 123.4, 41.3, 32.9, 26.2, 26.0; HRMS-ESI (m/z): calcd for $C_{14}H_{18}Br$ $[M + H]^+$ 265.0592, found 265.0597.

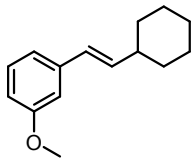


(*E*)-2,4-Dichloro-1-(2-cyclohexylvinyl)benzene (**4ja**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (d, *J* = 8.4 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.8 (dd, *J* = 8.4, 2.0 Hz, 2H), 6.67 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 16.0, 6.8 Hz, 1H), 2.24–2.15 (m, 1H), 1.86–1.69 (m, 5H), 1.38–1.17 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 134.7, 133.1, 132.6, 129.2, 127.3, 127.0, 122.7, 41.4,

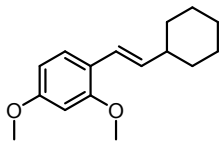
32.8, 26.1, 26.0; HRMS-ESI (m/z): calcd for $C_{14}H_{17}Cl_2$ $[M + H]^+$ 255.0707, found 255.0711.



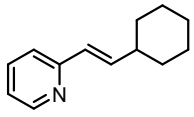
(*E*)-1-(2-Cyclohexylvinyl)-4-(trifluoromethyl)benzene (**4ka**):[9] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 6.41(d, *J* = 16.4 Hz, 1H), 6.31 (dd, *J* = 16.4, 6.4 Hz, 1H), 2.24–2.15 (m, 1H), 1.87–1.71 (m, 5H), 1.43–1.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 141.6, 139.6, 128.6 (q, *J* = 32.1 Hz), 126.2, 126.1, 125.4 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 270.1 Hz), 41.2, 32.8, 26.1, 26.0.



(*E*)-1-(2-Cyclohexylvinyl)-3-methoxybenzene (**4la**):[7] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.24 (t, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 1.8 Hz, 1H), 6.79 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.36 (d, *J* = 16.0 Hz, 1H), 6.22 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.85 (s, 3H), 2.21–2.13 (m, 1H), 1.87–1.71 (m, 5H), 1.43–1.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 139.6, 137.2, 129.4, 127.2, 118.7, 112.4, 111.3, 55.2, 41.2, 33.0, 26.2, 26.1.

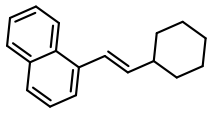


(*E*)-1-(2-Cyclohexylvinyl)-2,4-dimethoxybenzene (**4ma**): Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 16.4 Hz, 1H), 6.50–6.46 (m, 2H), 6.08 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 2.20–2.12 (m, 1H), 1.87–1.69 (m, 5H), 1.38–1.20 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 159.8, 157.3, 135.4, 126.8, 121.4, 120.2, 104.7, 98.4, 55.4, 55.3, 41.6, 33.2, 26.3, 26.2. HRMS-ESI (m/z): calcd for $C_{16}H_{23}O_2$ $[M + H]^+$ 247.1698, found 247.1687.

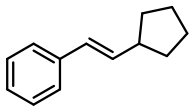


(*E*)-2-(2-Cyclohexylvinyl)pyridine (**4na**):[10] Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.53 (d, *J* = 4.8 Hz, 1H), 7.62–7.57 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.10–7.07 (m, 1H), 6.71 (dd, *J* = 16.0, 6.8 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 2.24–2.15 (m, 1H), 1.87–1.67 (m, 5H), 1.36–1.18 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.3, 149.3, 141.5, 136.4, 127.4, 121.5, 121.1, 41.0, 32.6, 26.1,

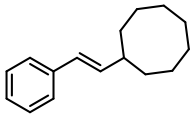
26.0.



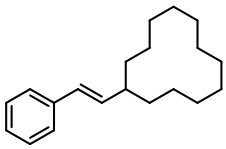
(*E*)-1-(2-Cyclohexylvinyl)naphthalene (**4oa**):[6] Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.22 (d, *J* = 9.2 Hz, 1H), 7.91 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.81 (d, *J* = 4.2 Hz, 1H), 7.65–7.48 (m, 4H), 7.17 (d, *J* = 15.6 Hz, 1H), 6.28 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.38–2.30 (m, 1H), 2.00–1.78 (m, 5H), 1.48–1.31 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 140.3, 136.0, 133.7, 131.3, 128.5, 127.2, 125.8, 125.7, 125.6, 124.4, 124.0, 123.5, 41.6, 33.1, 26.3, 26.2.



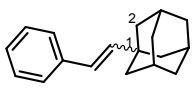
(*E*)-(2-Cyclopentylvinyl)benzene (**4ab**):[6] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.40 (m, 2H), 7.37–7.32 (m, 2H), 7.26–7.22 (m, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.71–2.61 (m, 1H), 1.97–1.89 (m, 2H), 1.82–1.64 (m, 4H), 1.51–1.42 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.0, 135.7, 128.5, 127.9, 126.7, 126.0, 43.9, 33.3, 25.3.



(*E*)-Styrylcyclooctane (**4ac**):[6] Colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.41–7.39 (m, 2H), 7.35–7.32 (m, 2H), 7.25–7.21 (m, 1H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.27 (dd, *J* =16.0, 7.6 Hz, 1H), 2.45–2.43(m, 1H), 1.86–1.57 (m, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.2, 137.9, 128.5, 126.9, 126.7, 126.0, 41.4, 31.9, 27.5, 26.0, 25.1.

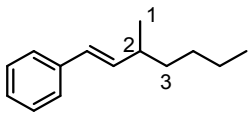


(*E*)-Styrylcyclododecane (**4af**): White solid. Mp: 38–40 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.40 (d, *J* = 7.8 Hz, 2H), 7.35–7.31 (m, 2H), 7.25–7.20 (m, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.43–2.35 (m, 1H), 1.66–1.51 (m, 2H), 1.47–1.34 (m, 20H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.1, 136.6, 128.5, 128.2, 126.7, 126.0, 37.6, 30.0, 23.9, 23.8, 23.4, 22.4; HRMS-ESI (m/z): calcd for $C_{20}H_{31}$ $[M + H]^+$ 271.2426, found 271.2413.



(3*r*,5*r*,7*r*)-1-((*E*)-Styryl)adamantine (**4ag**):[11] White solid (a mixture, 83% coupling on C(1) and

17% coupling on C(2), determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.20 (m, 5H), 6.55 (dd, *J* = 16.0, 6.4 Hz, 0.17H), 6.45 (d, *J* = 16.0 Hz, 0.17H), 6.29 (d, *J* = 16.4 Hz, 0.83H), 6.15 (d, *J* = 16.4 Hz, 0.83H), 2.61 (d, *J* = 6.0 Hz, 0.17H), 2.08–1.90 (m, 4H), 1.82–1.73 (m, 10.83H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 142.1, 138.2, 135.1, 128.9, 128.5, 126.7, 126.0, 124.5, 47.8, 47.4, 42.3, 38.8, 38.1, 36.9, 35.6, 35.2, 33.1, 32.2, 31.7, 28.5, 28.1, 27.9.



(*E*)-(3-Methylhept-1-en-1-yl)benzene (**4ah**):[6] Colorless oil (a mixture, 10% coupling on C(1), 50% coupling on C(2) and 40% coupling on C(3), determined by ^{1}H NMR). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.40 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26–7.22 (m, 1H), 6.41–6.37 (m, 1H), 6.29 (dt, *J* = 16.0, 6.8 Hz, 0.10H), 6.16 (dd, *J* = 16.0, 8.0 Hz, 0.50H), 6.01 (dd, *J* = 16.0, 8.8 Hz, 0.40H), 2.37–2.27 (m, 0.5H), 2.26–2.24 (m, 0.1H), 2.13–2.07 (m, 0.4H), 1.55–1.33 (m, 6H), 1.13 (d, *J* = 6.8 Hz, 1.5H), 0.97–0.93 (m, 4.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.0, 137.1, 135.6, 129.7, 128.5, 128.0, 126.8, 126.7, 126.0, 44.9, 37.4, 37.3, 36.9, 29.7, 28.2, 22.9, 20.7, 20.5, 14.2, 14.1, 11.9.

3. References

1 C. F. Malosh and J. M. Ready, *J. Am. Chem. Soc*., 2004, **126**, 10240-10241.

2 C. C. Wamser and W. R. Wagner, *J. Am. Chem. Soc*., 1981, **103**, 7233-7234.

3 J. Rey, H.-P. Hu, J. P. Snyder and A. G. M. Barrett, *Tetrahedron Lett*., 2012, **68**, 9211-9217.

4 K Cheng, L.-H. Huang and Y.-H. Zhang, *Org. Lett*., 2009, **11**, 2908-2911.

5 L. R. Jefferies and S. P. Cook, *Tetrahedron*, 2014, **70**, 4204-4027.

6 Y.-F. Zhu and Y.-Y. Wei, *Chem*. *Sci*., 2014, **5**, 2379-2382.

7 J.-C. Zhao, H. Fang, J.-L. Han and Y. Pan, *Beilstein J. Org. Chem*., 2013, **9**, 1718-1723.

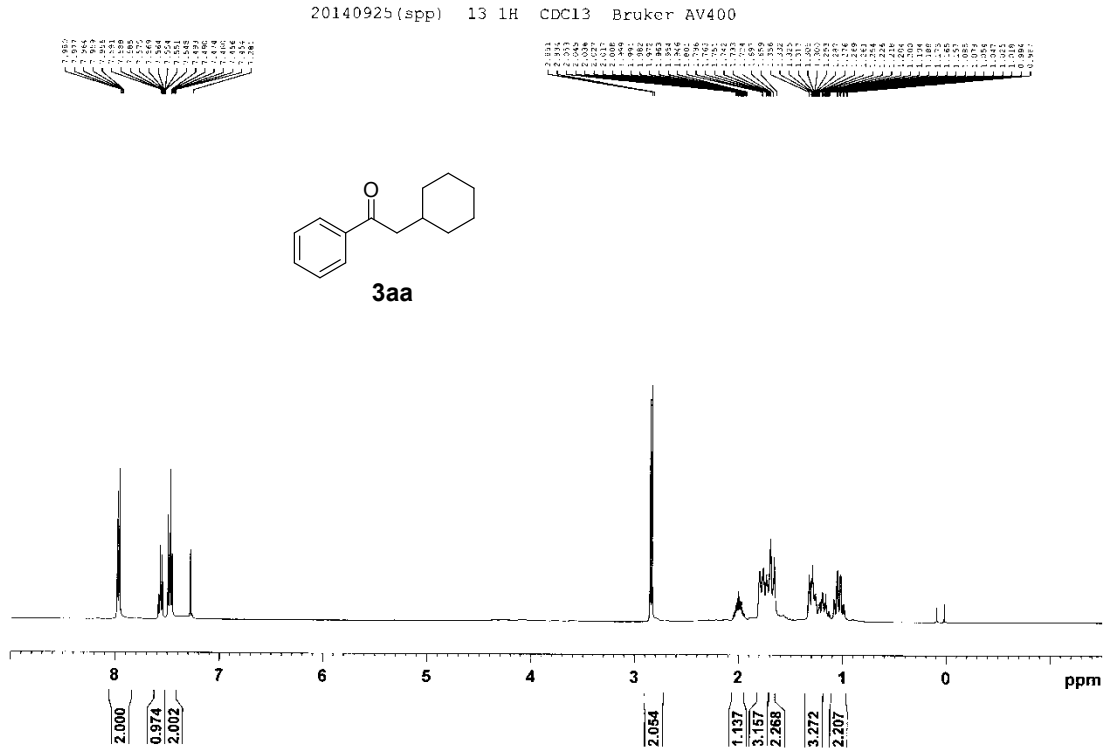
8 W. Affo, H. Ohmiya, T. Fujioka, Y. Ikeda, T. Nakamura, H. Yorimitsu, K. Oshima, Y. Imamura, T. Mizuta and K. Miyoshi, *J. Am. Chem. Soc.*, 2006, **128**, 8068-8077.

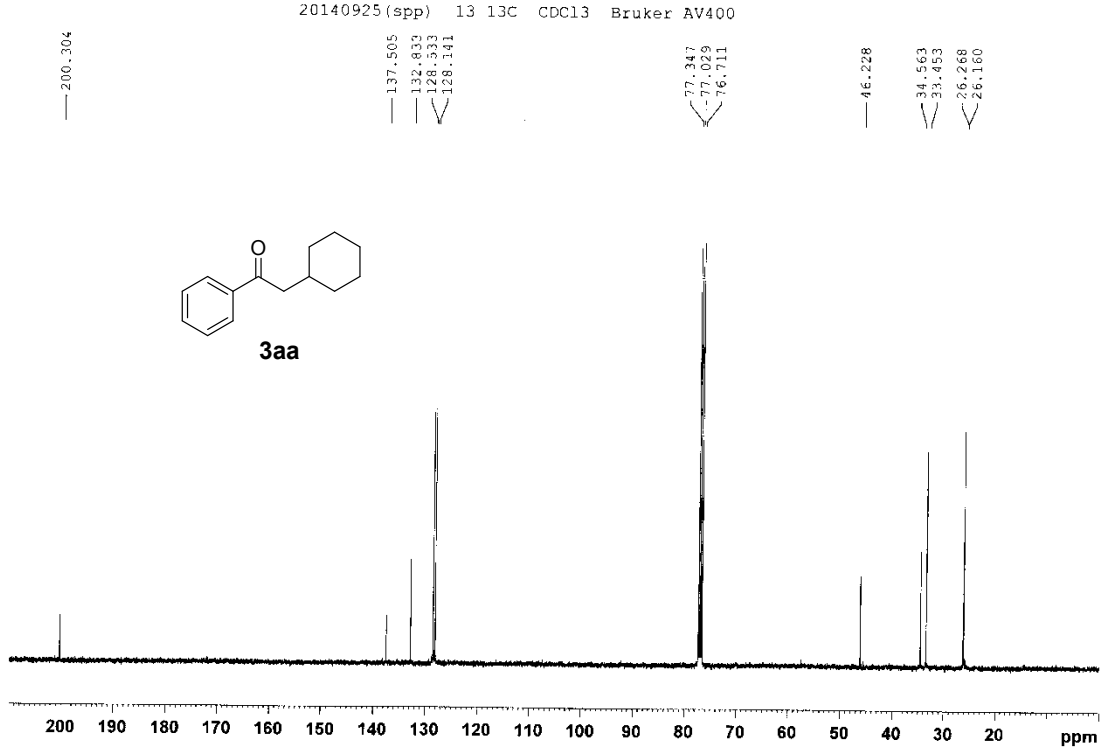
9 C. M. McMahon and E. J. Alexanian, *Angew. Chem. Int. Ed*., 2014, **53**, 5974 –5977.

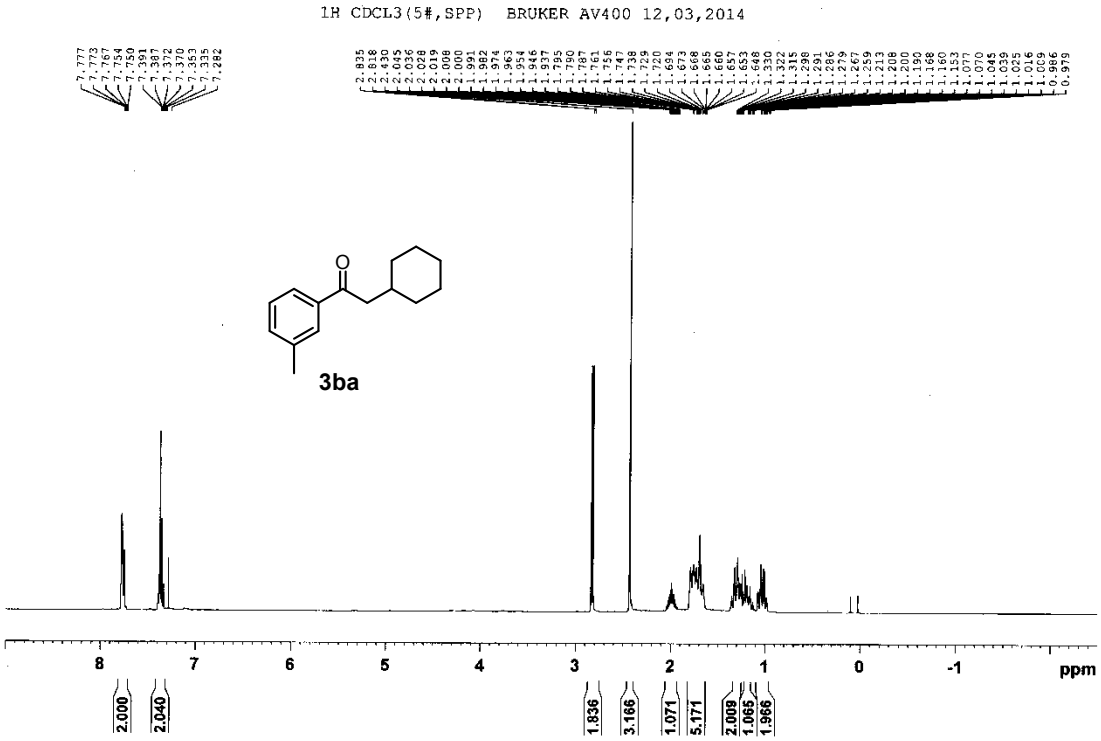
10 D. Mao, G. Hong, S.-Y. Wu, X. Liu, J.-J. Yu and L.-M. Wang, *Eur. J. Org. Chem*., 2014, **14**, 3009-3019.

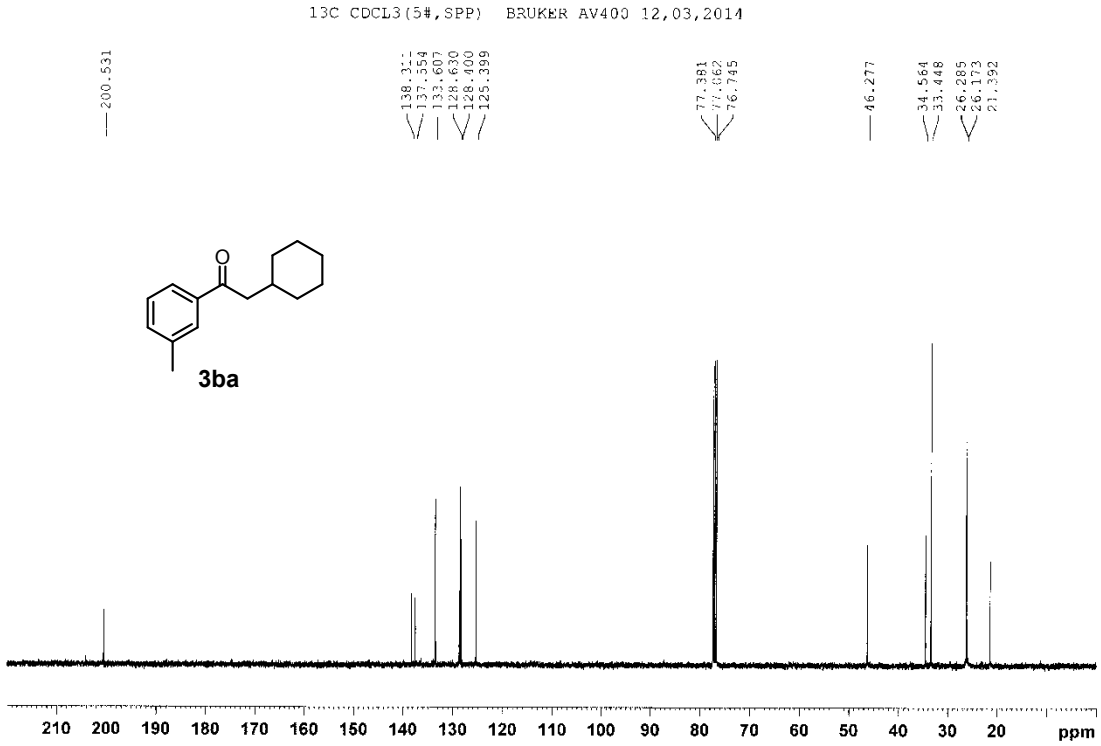
11 K. Kanagaraj and K. Pitchumani, *Chem.–Eur. J*., 2013, **19**, 14425-14431.

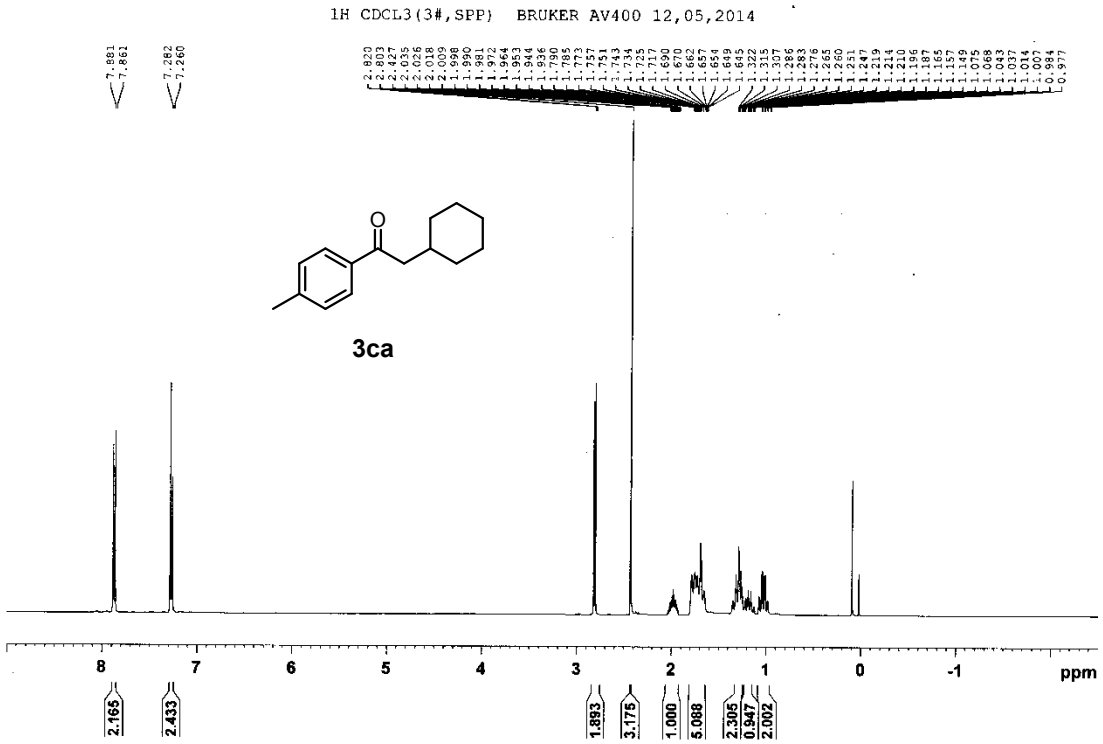
4. Copies of ^{1}H and ^{13}C NMR Spectra of the Products

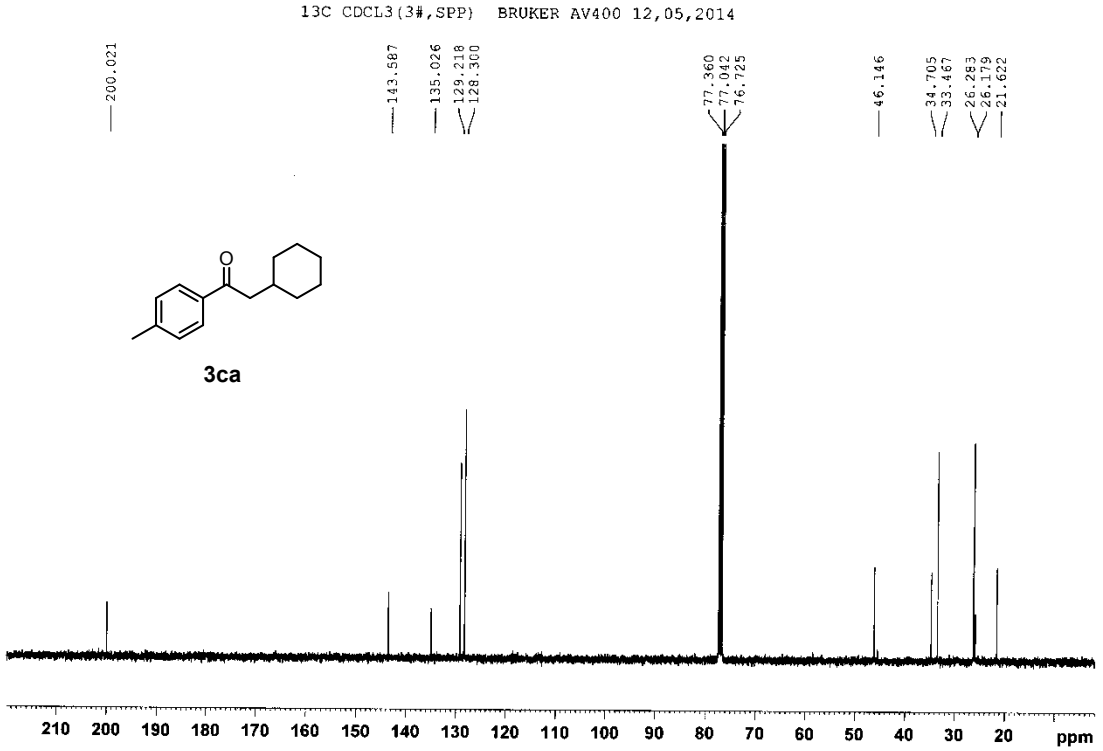


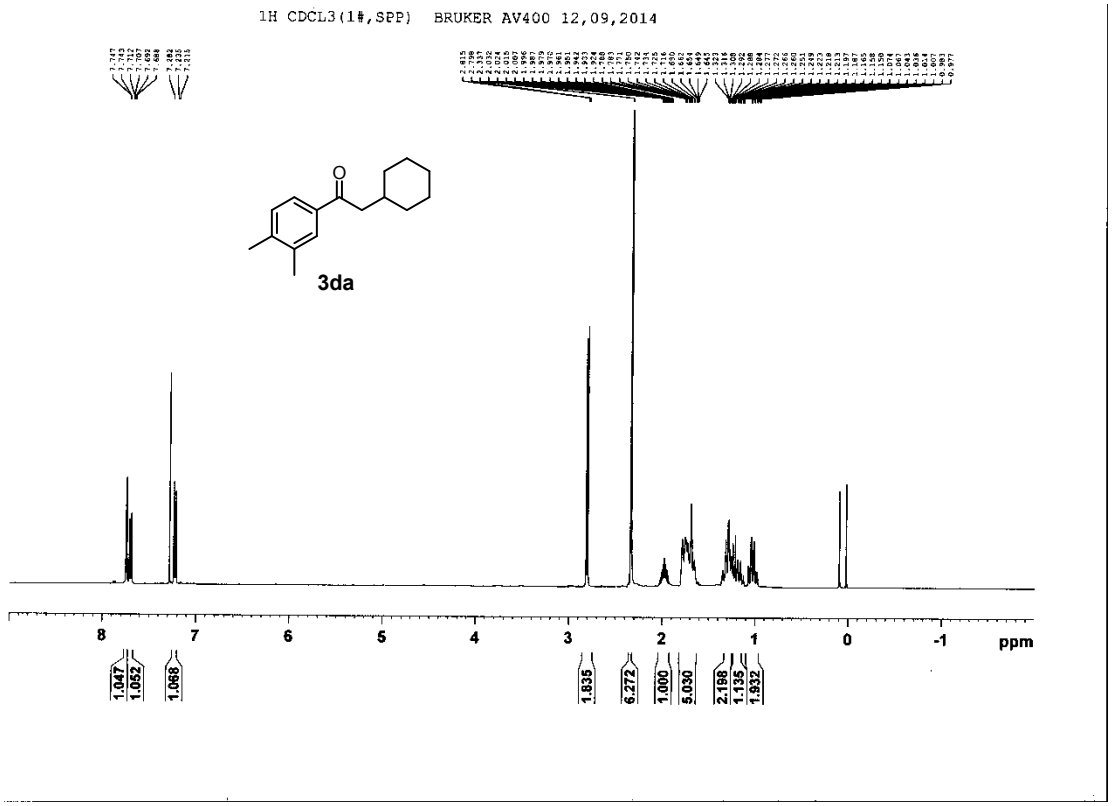


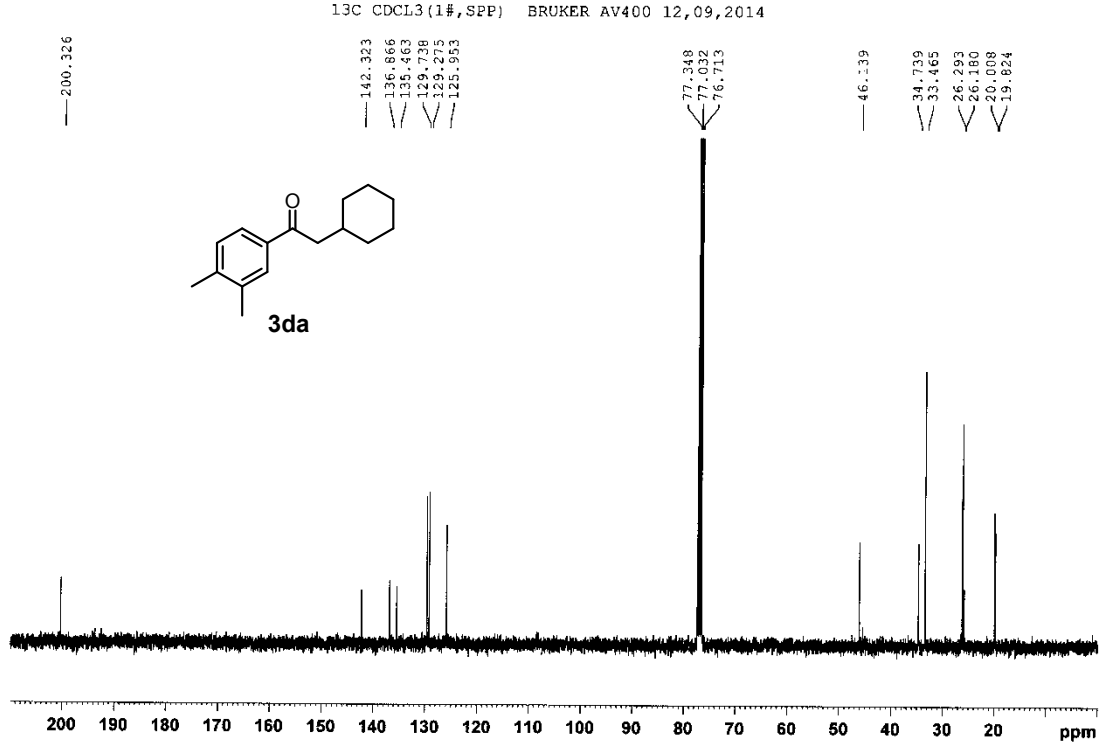

1H CDCL3(5#,SPP) BRUKER AV400 12,03,2014
3ba
8
7
6
5
4
3
2
1
0
-1
ppm
2.000
2.040
1.836
3.166
1.071
5.171
2.009
1.065
1.966

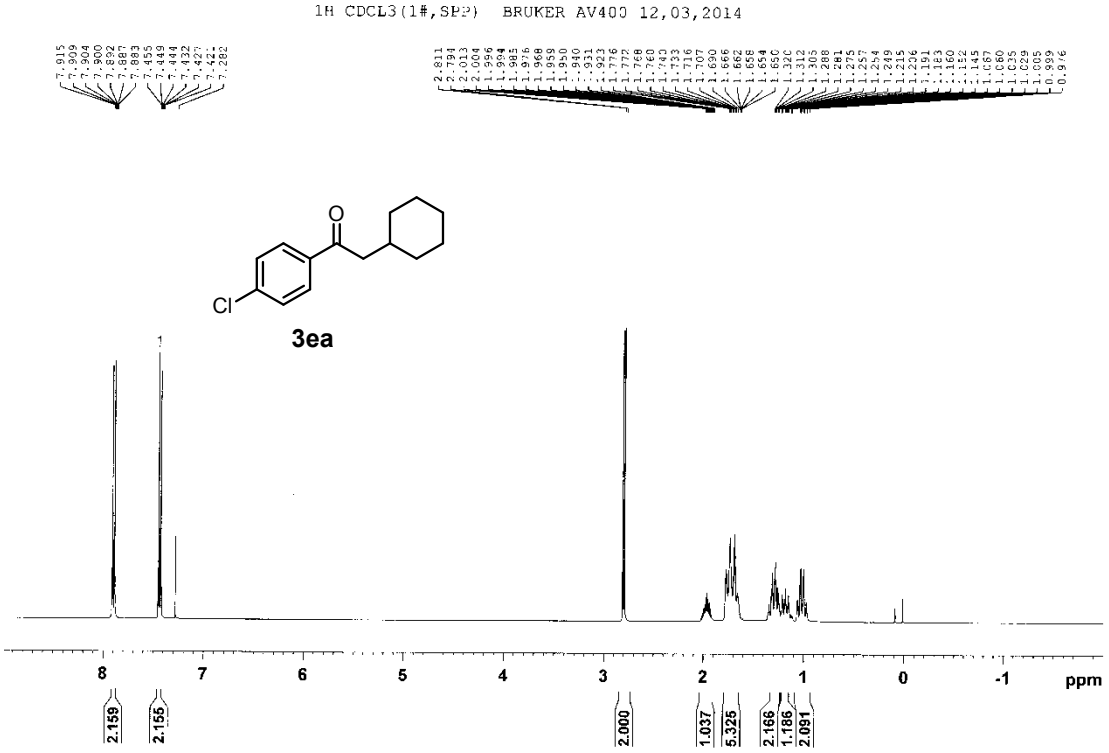

13C CDCL3(5#,SPP) BRUKER AV400 12,03,2014
200.531
138.31
137.554
133.607
128.630
128.400
125.399
77.381
77.062
76.745
46.277
34.564
33.448
26.285
26.173
21.392
3ba
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

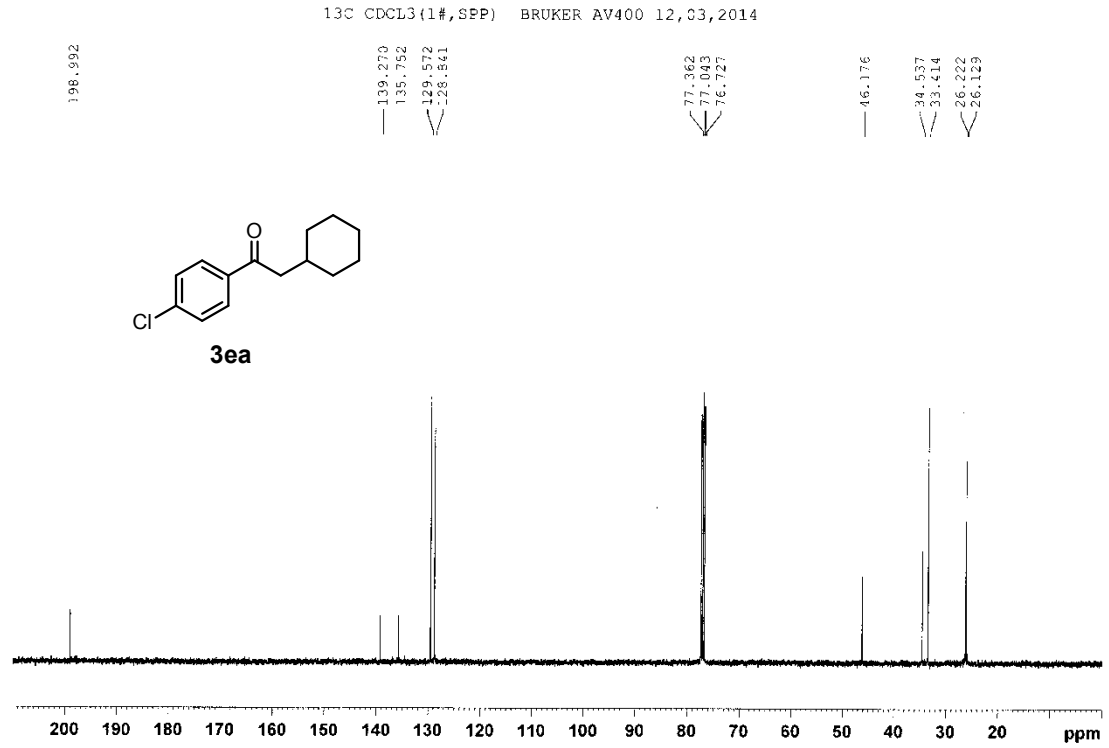

1H CDCL3(3#,SPP) BRUKER AV400 12,05,2014
7.881
7.861
7.282
7.260
3ca
8
7
6
5
4
3
2
1
0
-1
ppm
2.165
2.433
1.893
3.175
1.000
5.088
2.305
0.947
2.002

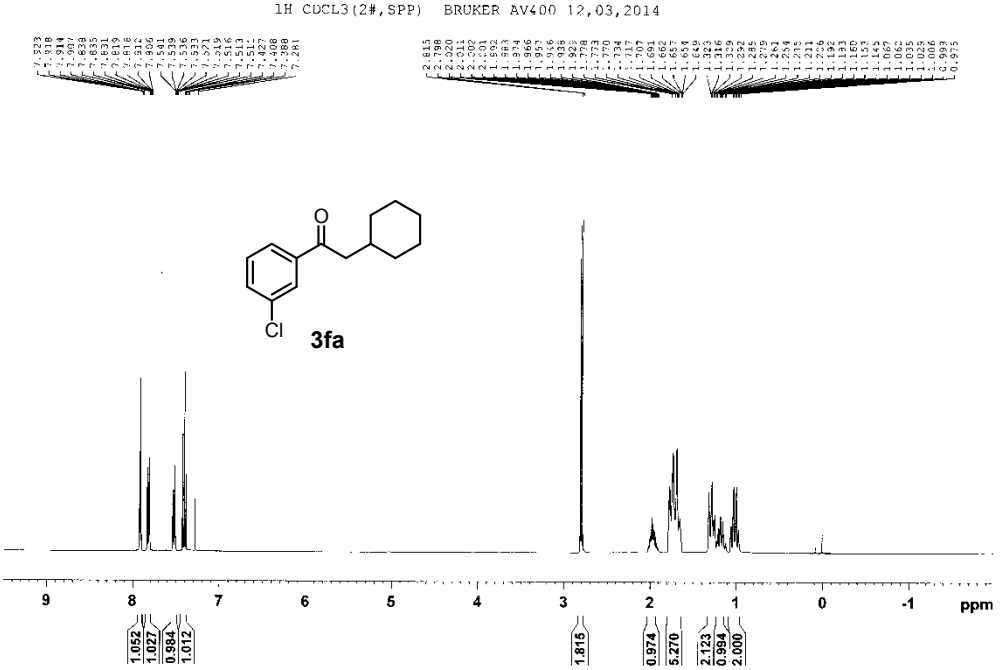

13C CDCL3(3#,SPP) BRUKER AV400 12,05,2014
200.021
143.587
135.026
129.218
128.300
77.360
77.042
76.725
46.146
34.705
33.467
26.283
26.179
21.622
3ca
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

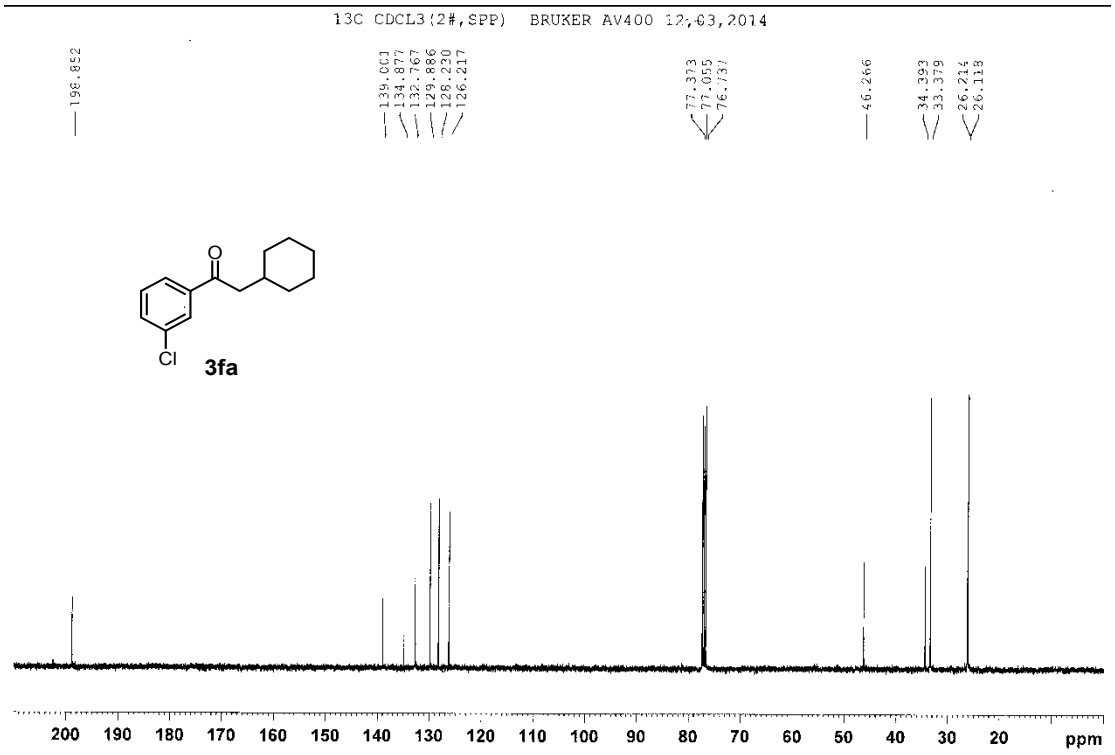

1H CDCL3(1#,SPP) BRUKER AV400 12,09,2014
3da
8
7
6
5
4
3
2
1
0
-1
ppm
1.047
1.052
1.068
1.835
6.272
1.000
5.030
2.198
1.135
1.932


13C CDCL3(1#,SPP) BRUKER AV400 12,09,2014
200.326
142.323
136.866
135.463
129.738
129.275
125.953
77.348
77.032
76.713
46.139
34.739
33.465
26.293
26.180
20.008
19.824
3da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

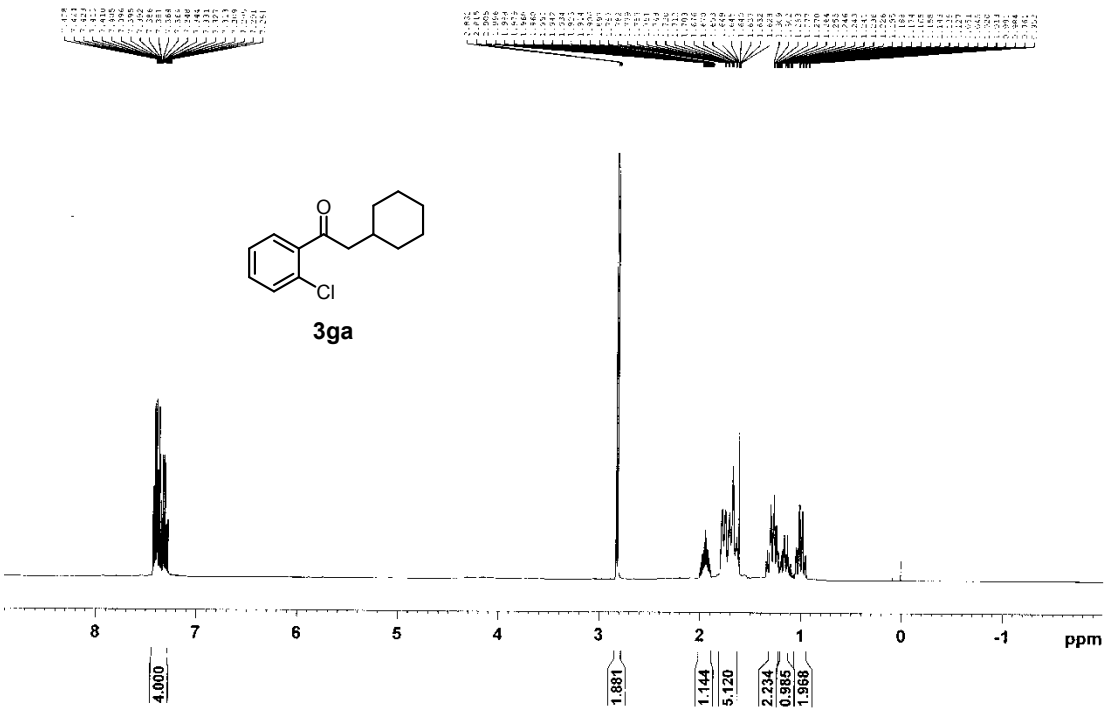

1H CDCL3(1#,SPP) BRUKER AV400 12,03,2014
3ea
ppm
2.159
2.155
2.000
1.037
5.325
2.166
1.186
2.091


13C CDCL3(1#,SPP) BRUKER AV400 12,03,2014
198.992
139.270
135.752
129.572
128.841
77.362
77.043
76.727
46.176
34.537
33.414
26.222
26.129
3ea
ppm


1H CDCL3(2#,SPP) BRUKER AV400 12,03,2014
3fa
9
8
7
6
5
4
3
2
1
0
-1
ppm
1.052
1.027
0.984
1.012
1.815
0.974
5.270
2.123
0.994
2.000

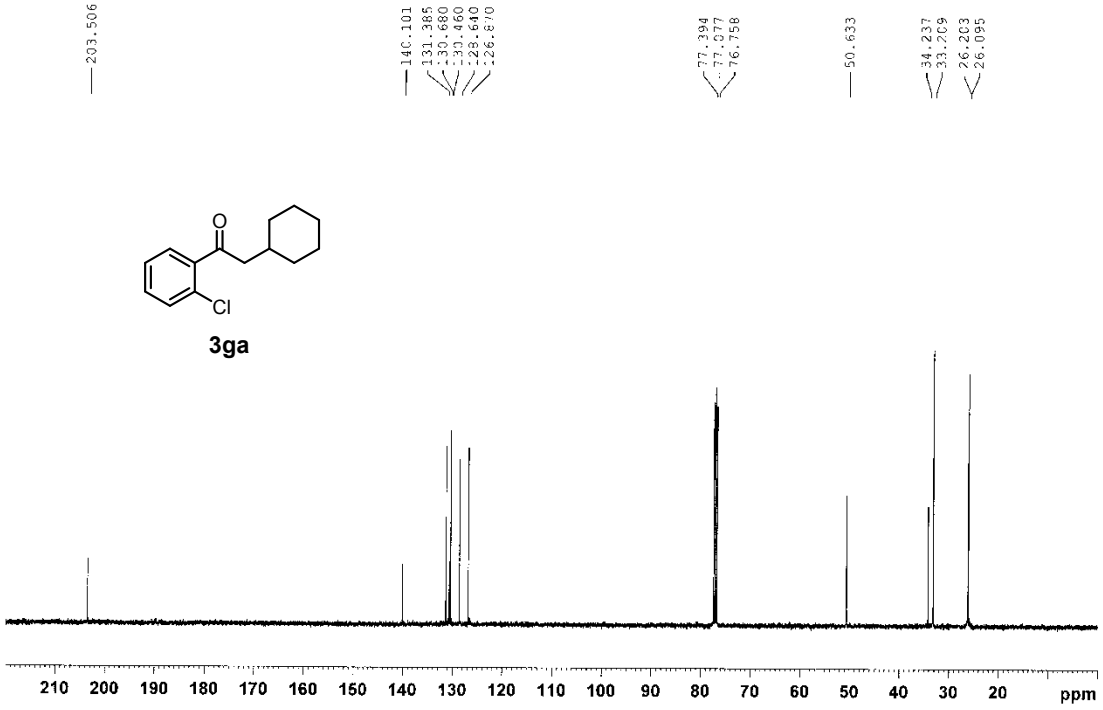

13C CDCL3(2#,SPP) BRUKER AV400 12,03,2014
198.852
139.003
134.877
132.767
129.886
128.230
126.217
77.373
77.055
76.737
46.266
34.393
33.379
26.214
26.118
3fa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

1H CDCL3(3#,SPP) BRUKER AV400 12,03,2014

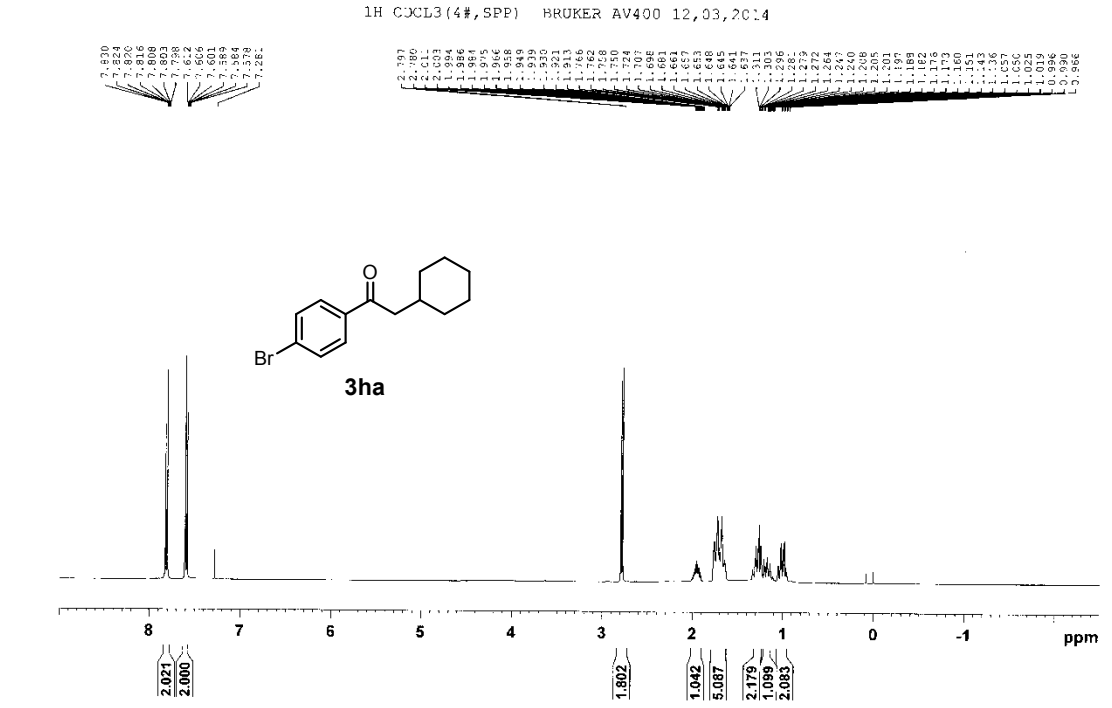


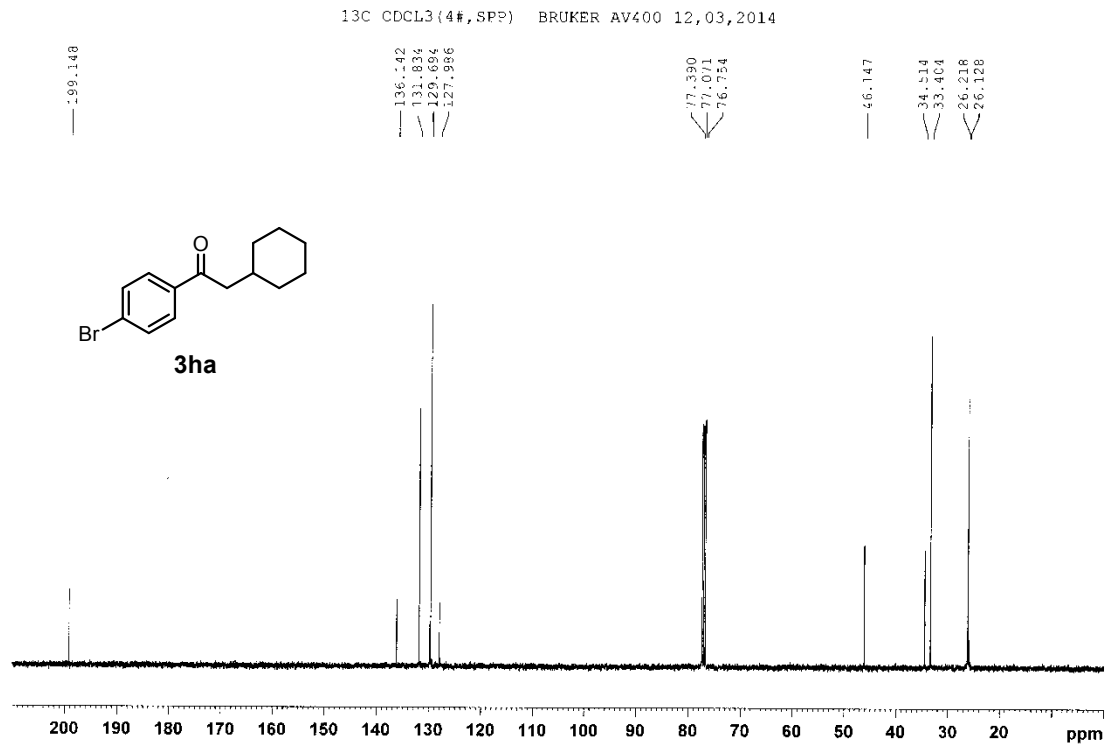
3ga

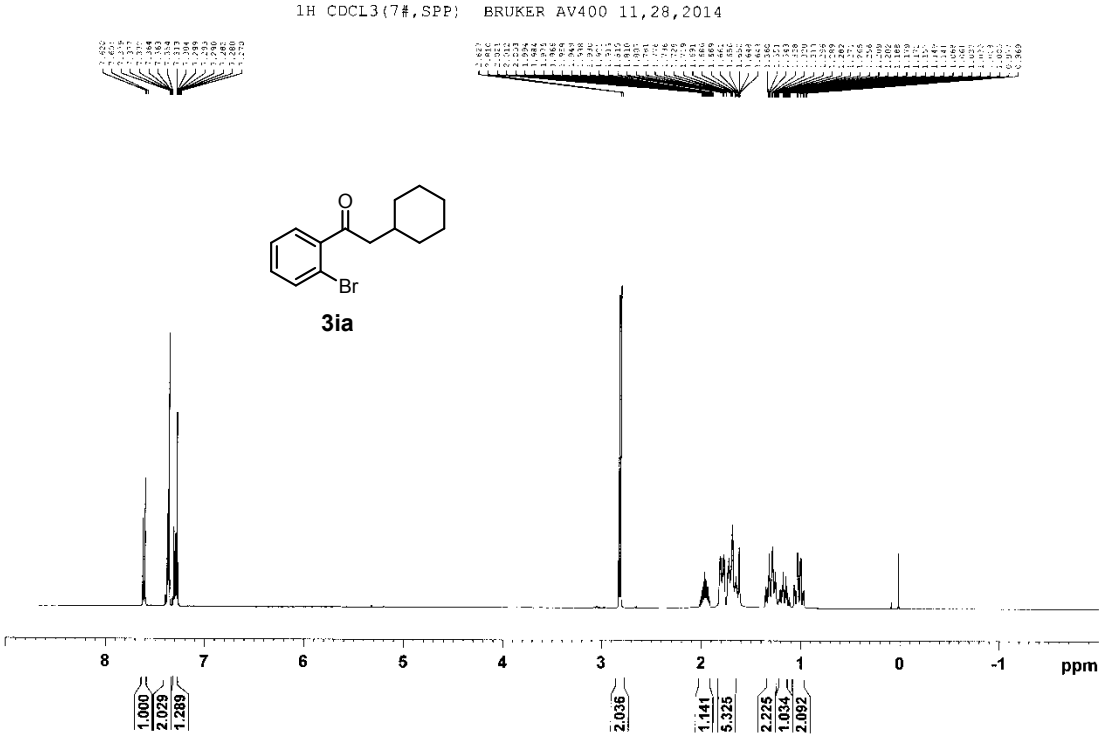
13C CDCL3(3#,SPP) BRUKER AV400 12,03,2014

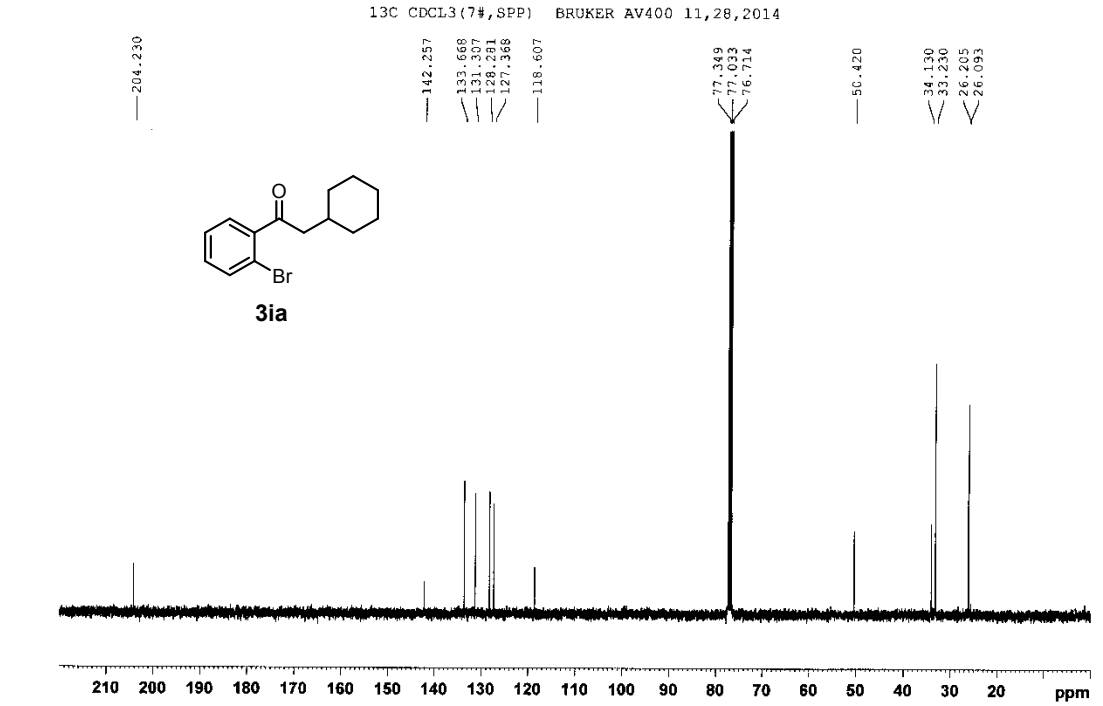


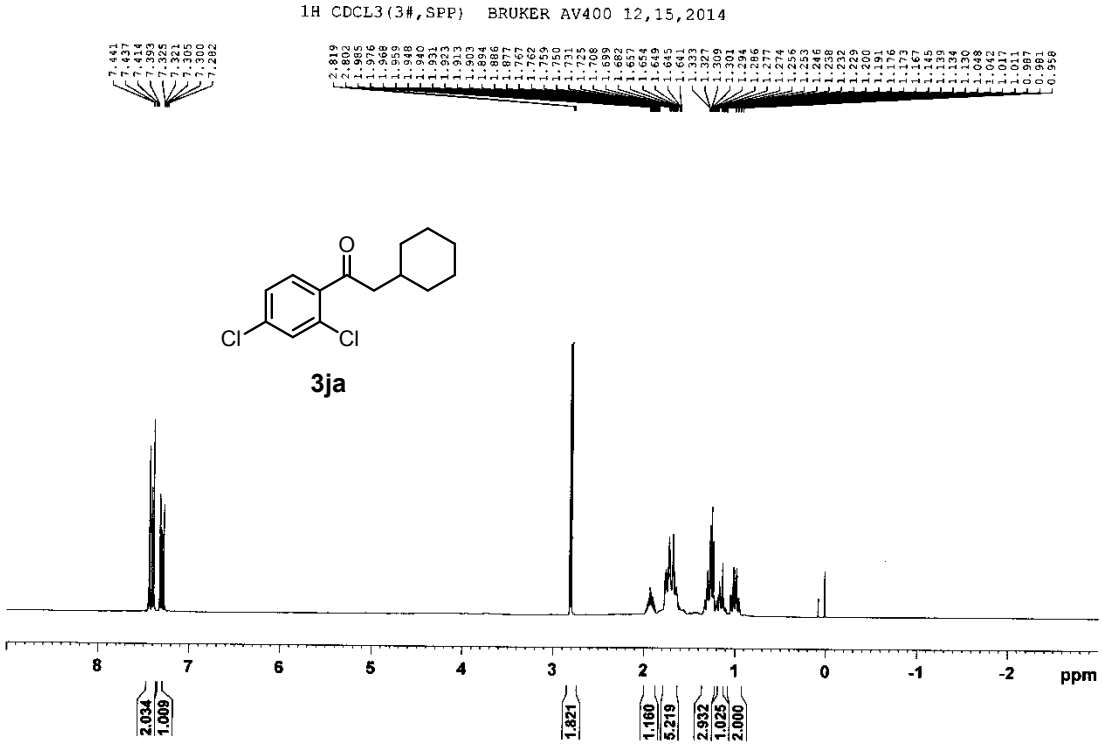
3ga

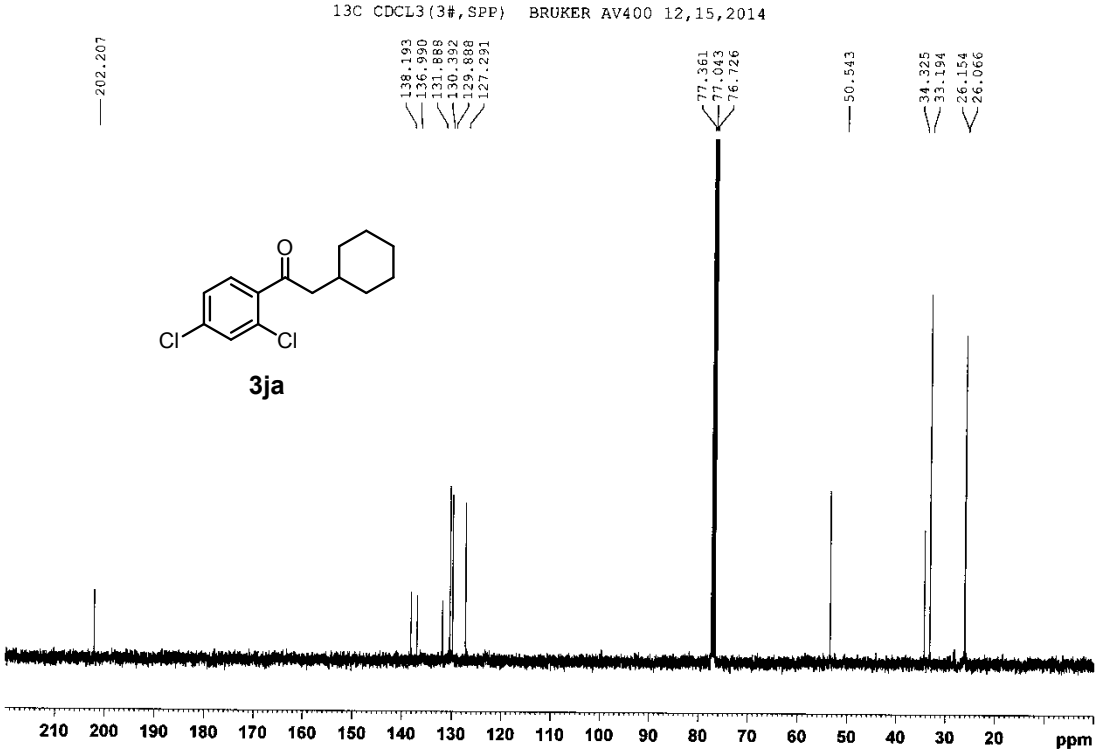

1H CDCL3(4#,SPP) BRUKER AV400 12,03,2014
Br
3ha
8
7
6
5
4
3
2
1
0
-1
ppm
2.021
2.000
1.802
1.042
5.087
2.179
1.099
2.083

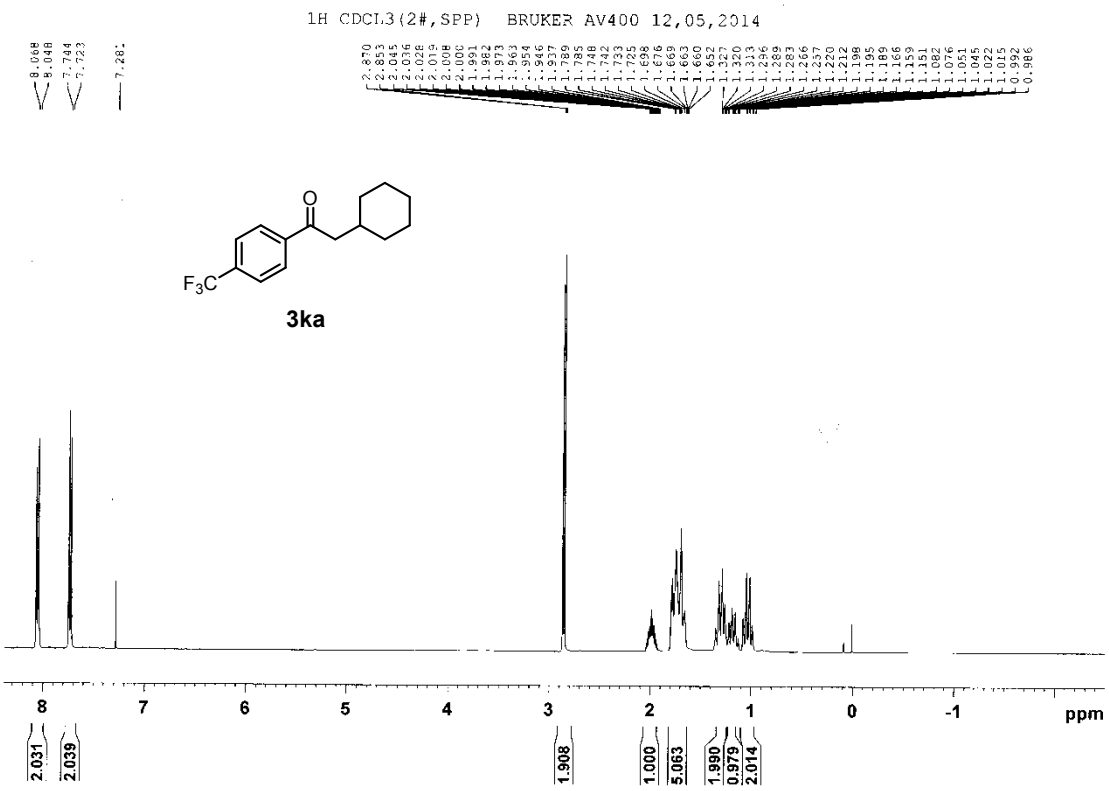

13C CDCL3(4#,SPP) BRUKER AV400 12,03,2014
199.148
136.242
131.834
129.694
127.996
77.390
77.071
76.754
46.147
34.514
33.404
26.218
26.128
Br
3ha
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

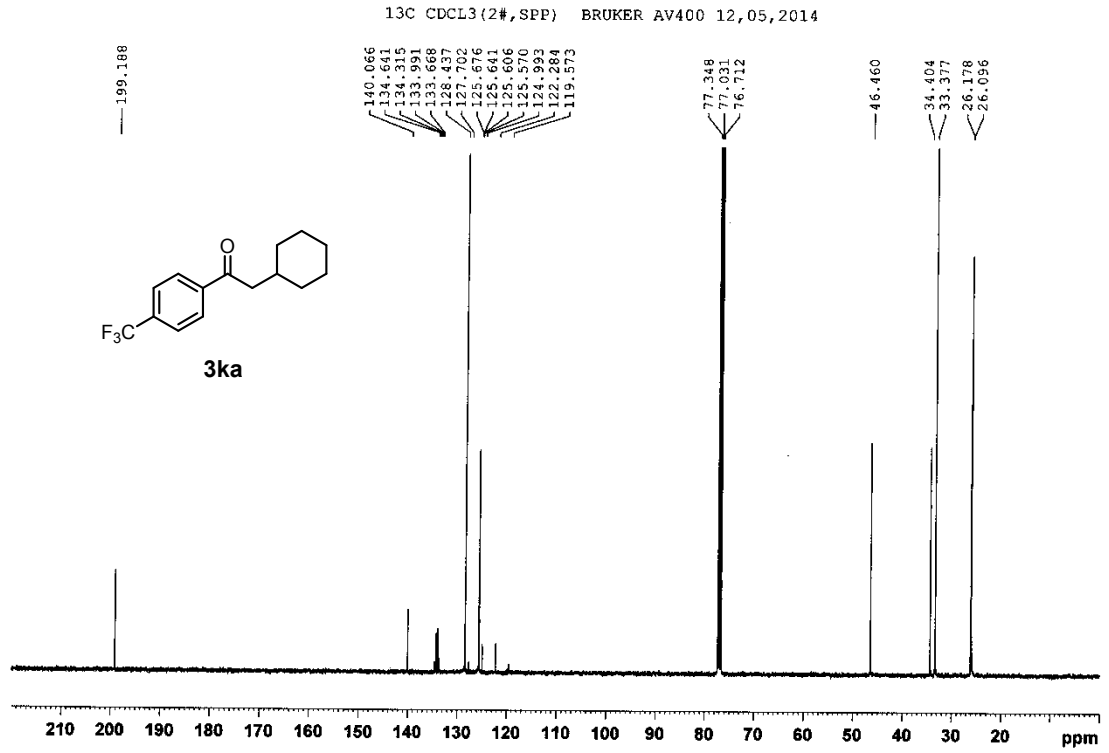

1H CDCL3(7#,SPP) BRUKER AV400 11,28,2014
O
Br
3ia
8
7
6
5
4
3
2
1
0
-1
ppm
1.000
2.029
1.289
2.036
1.141
5.325
2.225
1.034
2.092


13C CDCL3(7#,SPP) BRUKER AV400 11,28,2014
204.230
142.257
133.668
131.307
128.281
127.368
118.607
77.349
77.033
76.714
50.420
34.130
33.230
26.205
26.093
O
Br
3ia
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

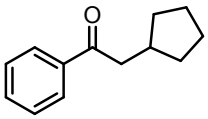

1H CDCL3(3#,SPP) BRUKER AV400 12,15,2014
3ja
ppm
2.034
1.009
1.821
1.160
5.219
2.932
1.025
2.000


13C CDCL3(3#,SPP) BRUKER AV400 12,15,2014
202.207
138.193
136.990
131.888
130.392
129.888
127.291
77.361
77.043
76.726
50.543
34.325
33.194
26.154
26.066
3ja
ppm

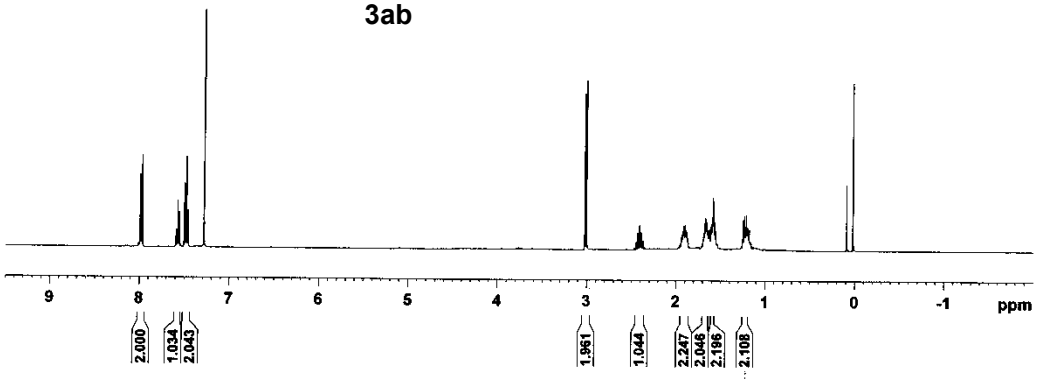

1H CDCL3(2#,SPP) BRUKER AV400 12,05,2014
3ka
ppm


13C CDCL3(2#,SPP) BRUKER AV400 12,05,2014
3ka
ppm

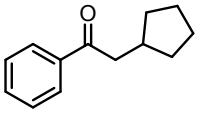
1H CDCL3(5#,SPP) BRUKER AV400 12,19,2014



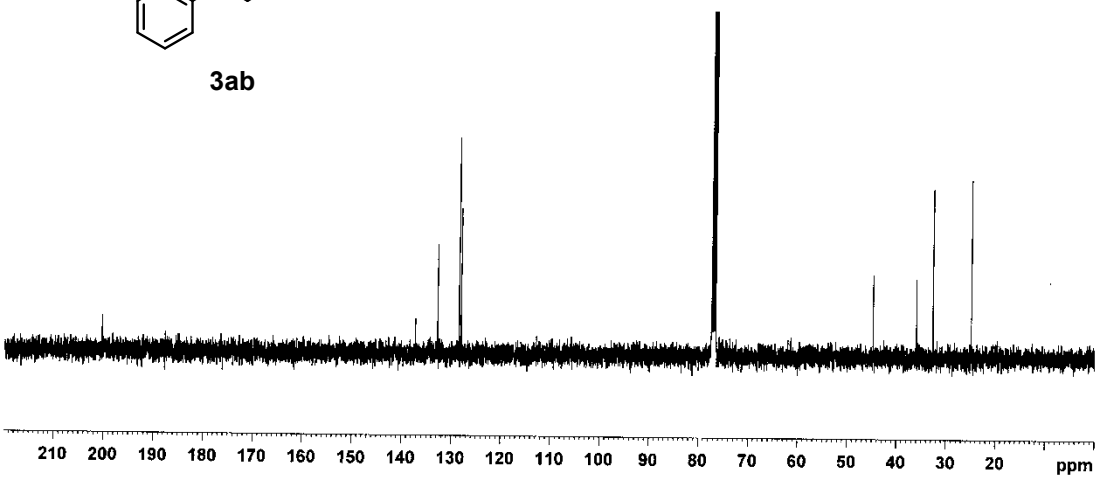
3ab

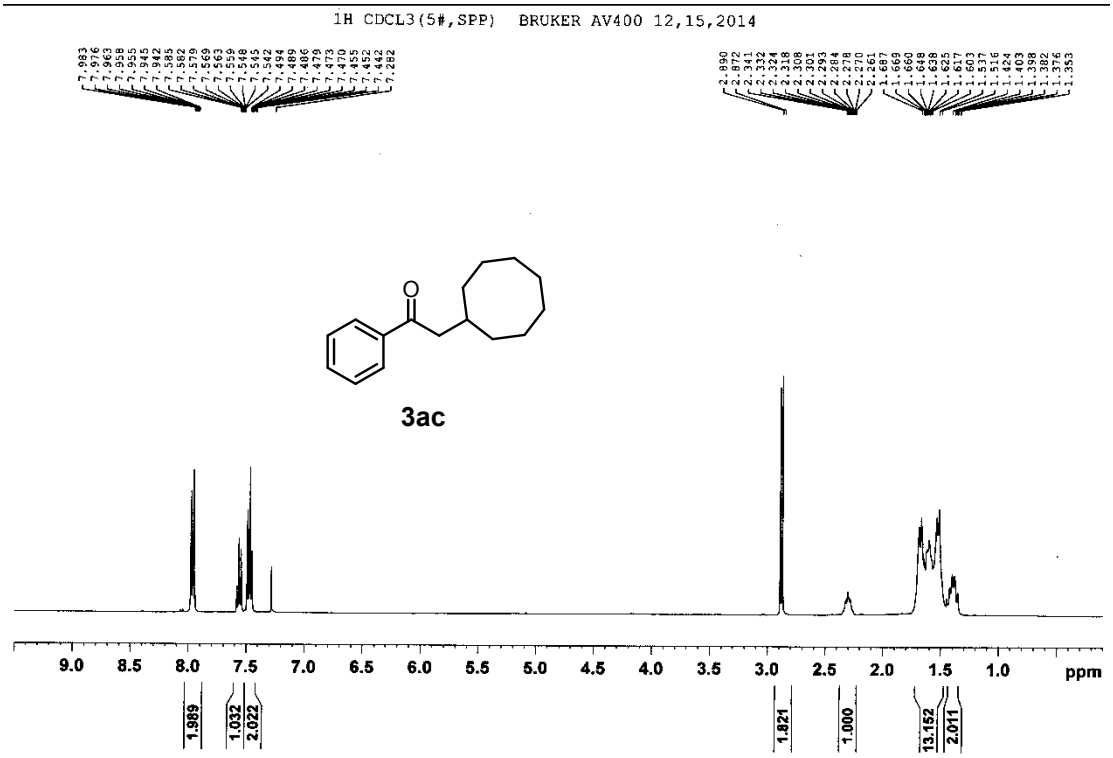


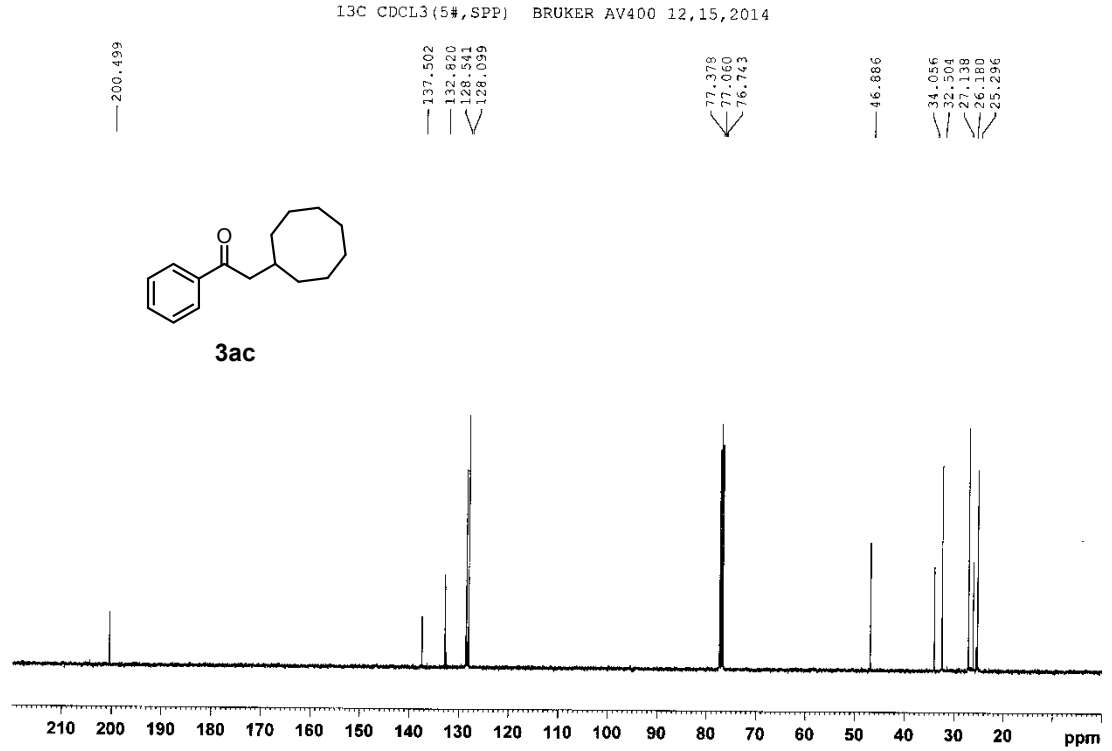
13C CDCL3(5#,SPP) BRUKER AV400 12,19,2014

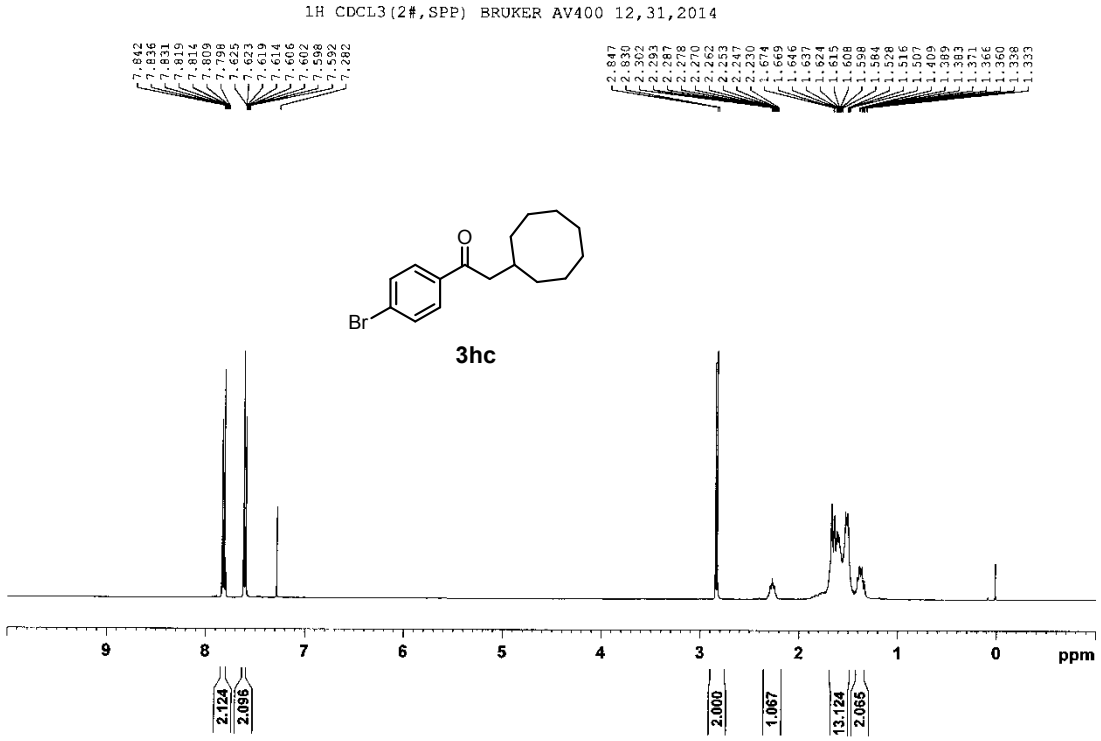


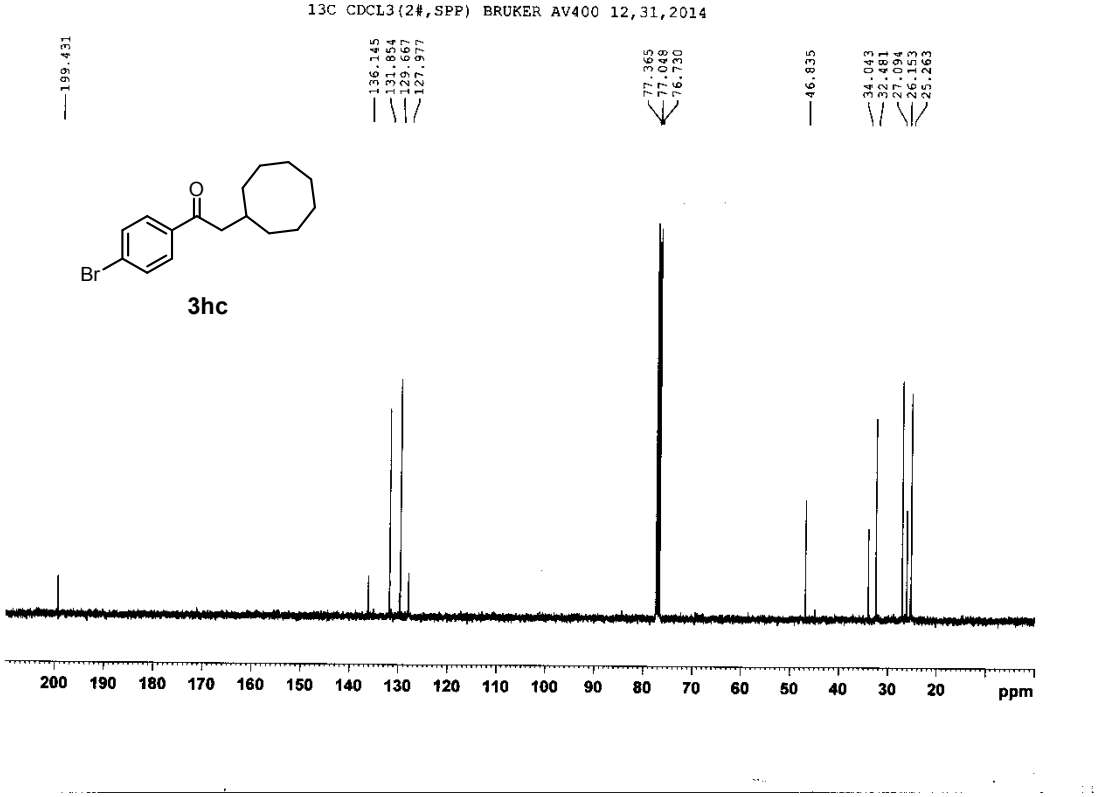
3ab

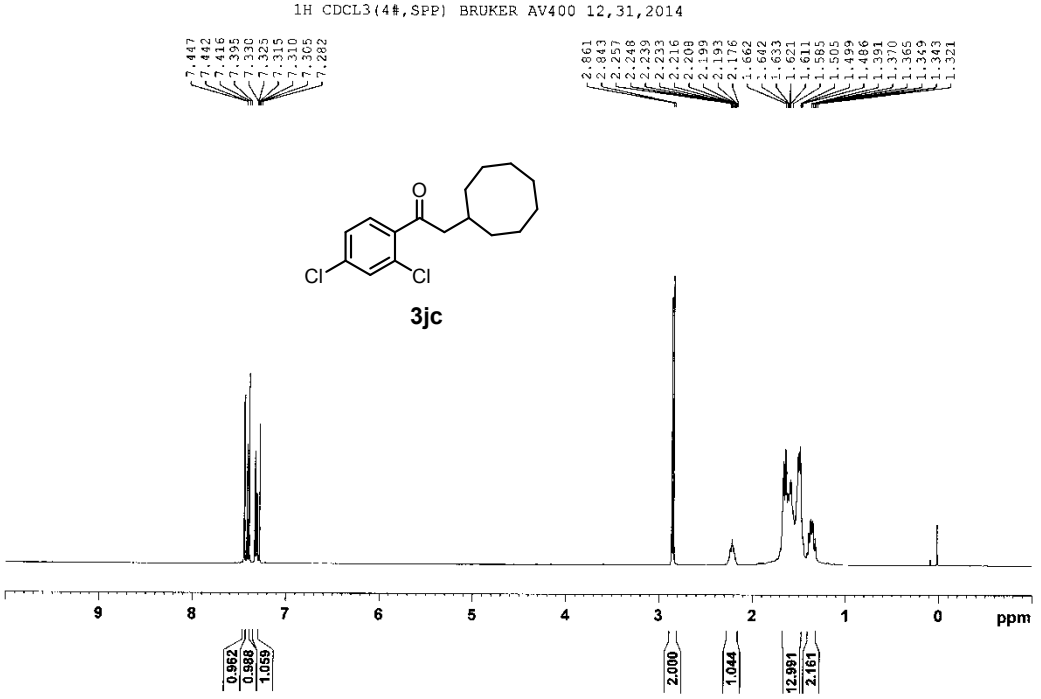


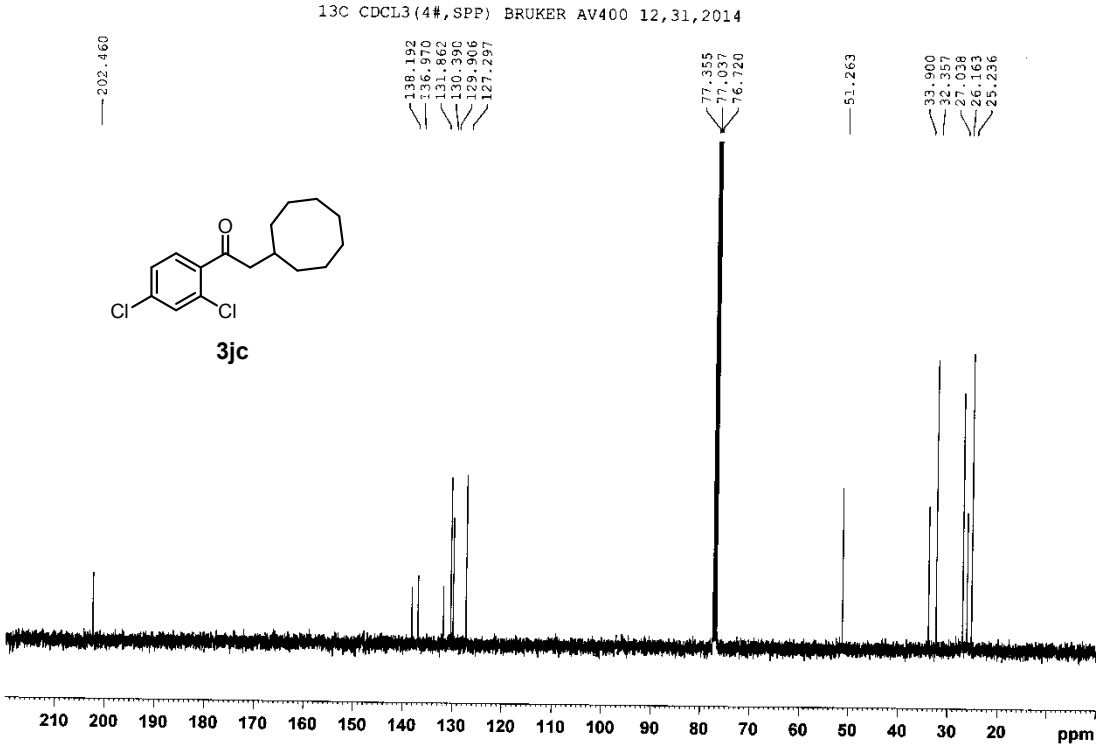

1H CDCL3(5#,SPP) BRUKER AV400 12,15,2014
7.983
7.976
7.963
7.958
7.955
7.945
7.942
7.585
7.582
7.579
7.569
7.563
7.559
7.548
7.545
7.542
7.494
7.489
7.486
7.479
7.473
7.470
7.455
7.452
7.447
7.282
2.890
2.872
2.341
2.332
2.324
2.318
2.308
2.301
2.293
2.284
2.278
2.270
2.261
1.687
1.669
1.660
1.648
1.638
1.625
1.617
1.603
1.537
1.515
1.424
1.403
1.398
1.382
1.376
1.353
O
3ac
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
ppm
1.989
1.032
2.022
1.821
1.000
13.152
2.011

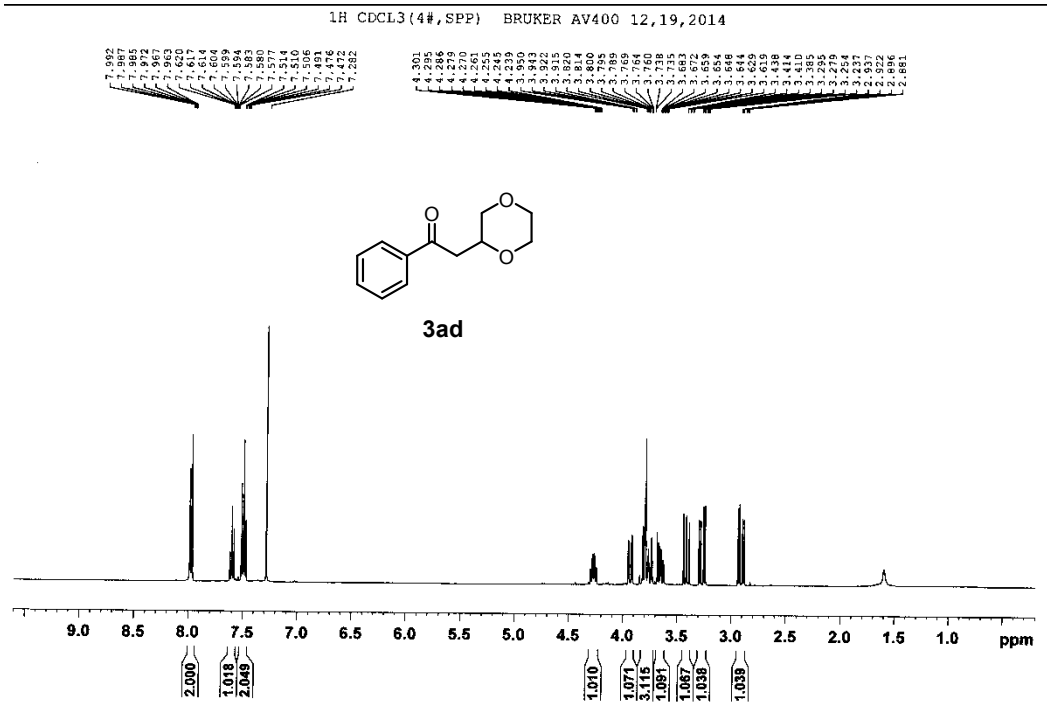

13C CDCL3(5#,SPP) BRUKER AV400 12,15,2014
200.499
137.502
132.820
128.541
128.099
77.378
77.060
76.743
46.886
34.056
32.504
27.138
26.180
25.296
O
3ac
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

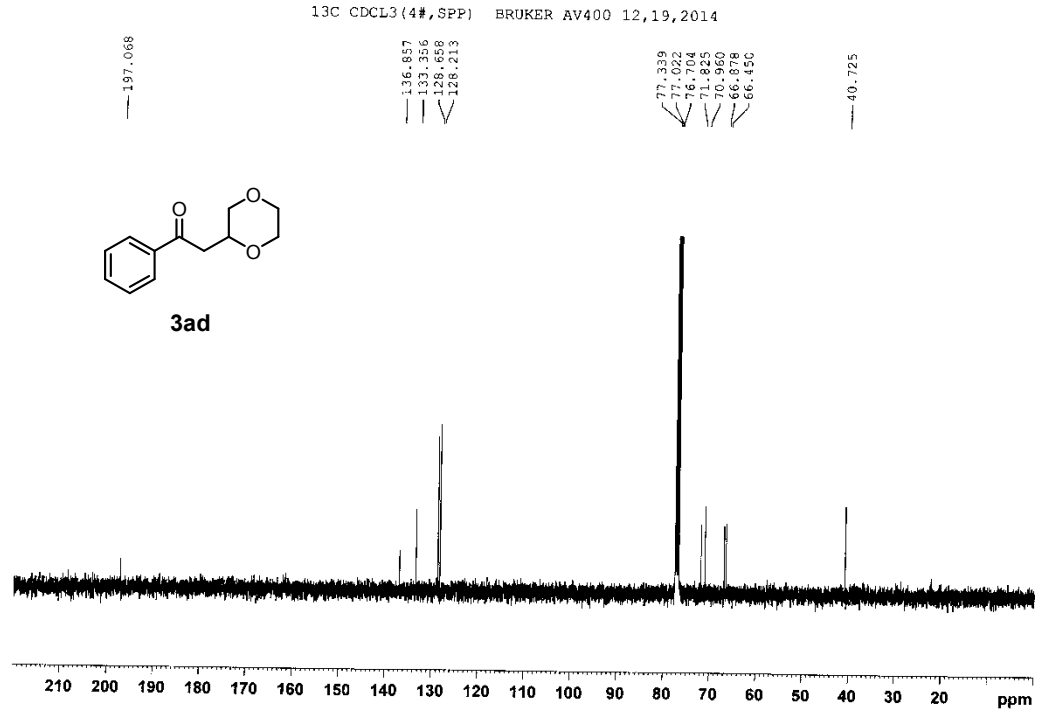

1H CDCL3(2#,SPP) BRUKER AV400 12,31,2014
7.842
7.836
7.831
7.819
7.814
7.809
7.798
7.625
7.623
7.619
7.614
7.606
7.602
7.598
7.592
7.282
2.847
2.830
2.302
2.293
2.287
2.278
2.270
2.262
2.253
2.247
2.230
1.674
1.669
1.646
1.637
1.624
1.615
1.608
1.598
1.584
1.528
1.516
1.507
1.409
1.389
1.383
1.371
1.366
1.360
1.338
1.333
O
Br
3hc
9
8
7
6
5
4
3
2
1
0
ppm
2.124
2.096
2.000
1.067
13.124
2.065

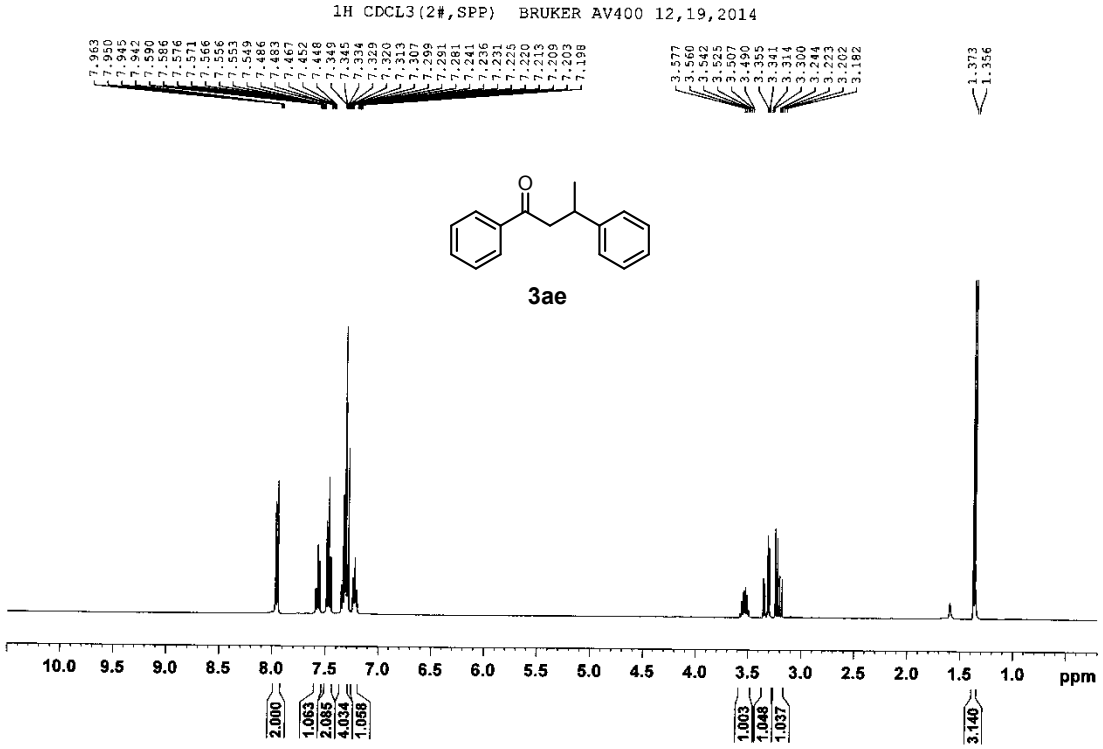

13C CDCL3(2#,SPP) BRUKER AV400 12,31,2014
199.431
136.145
131.854
129.667
127.977
77.365
77.048
76.730
46.835
34.043
32.481
27.094
26.153
25.263
O
Br
3hc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

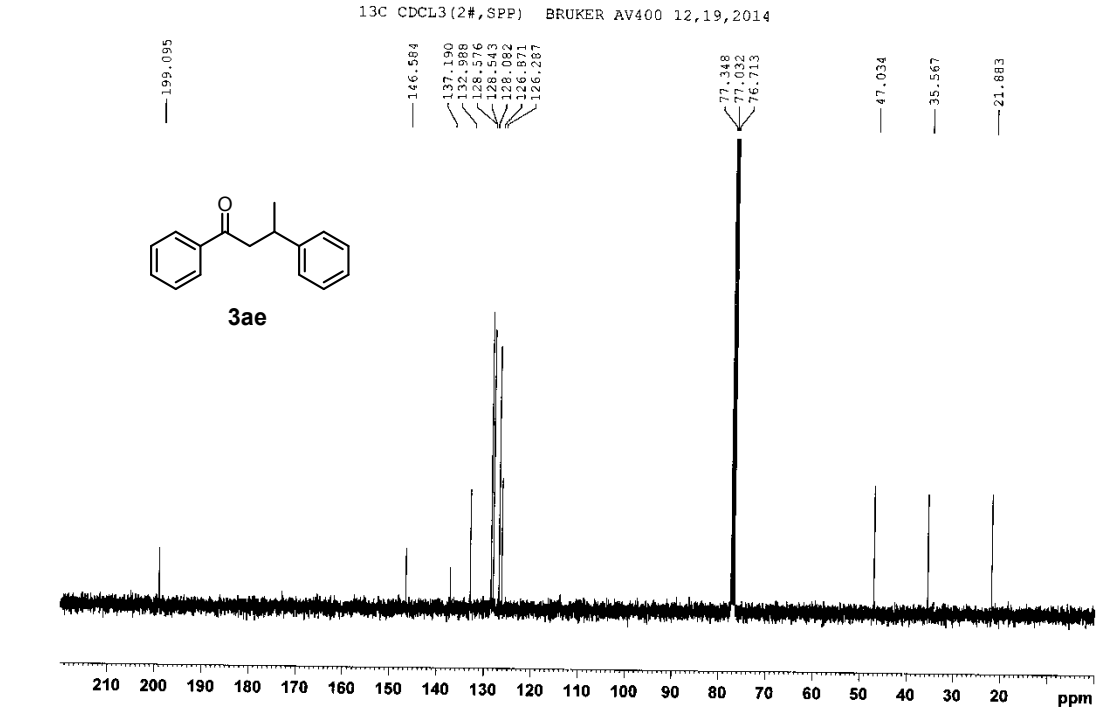

1H CDCL3(4#,SPP) BRUKER AV400 12,31,2014
7.447
7.442
7.416
7.395
7.330
7.325
7.315
7.310
7.305
7.282
2.861
2.843
2.257
2.248
2.239
2.233
2.216
2.208
2.199
2.193
2.176
1.662
1.642
1.633
1.621
1.611
1.585
1.565
1.499
1.486
1.391
1.370
1.365
1.349
1.343
1.321
O
Cl
Cl
3jc
9
8
7
6
5
4
3
2
1
0
ppm
0.962
0.988
1.059
2.000
1.044
12.991
2.161

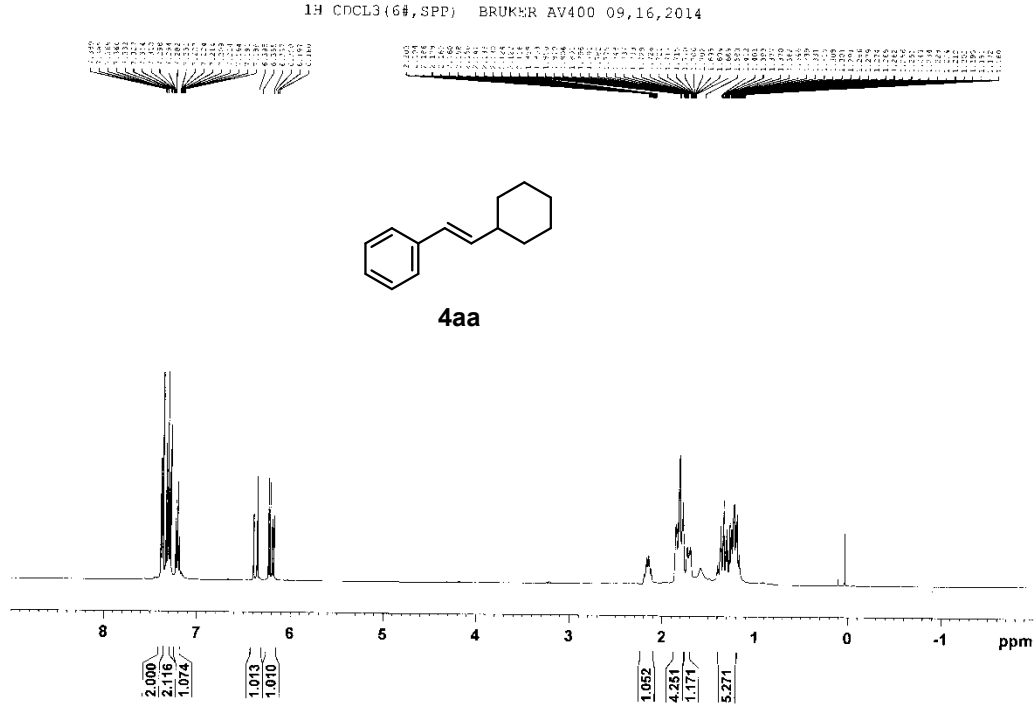

13C CDCL3(4#,SPP) BRUKER AV400 12,31,2014
202.460
138.192
136.970
131.862
130.390
129.906
127.297
77.355
77.037
76.720
51.263
33.900
32.357
27.038
26.163
25.236
O
Cl
Cl
3jc
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

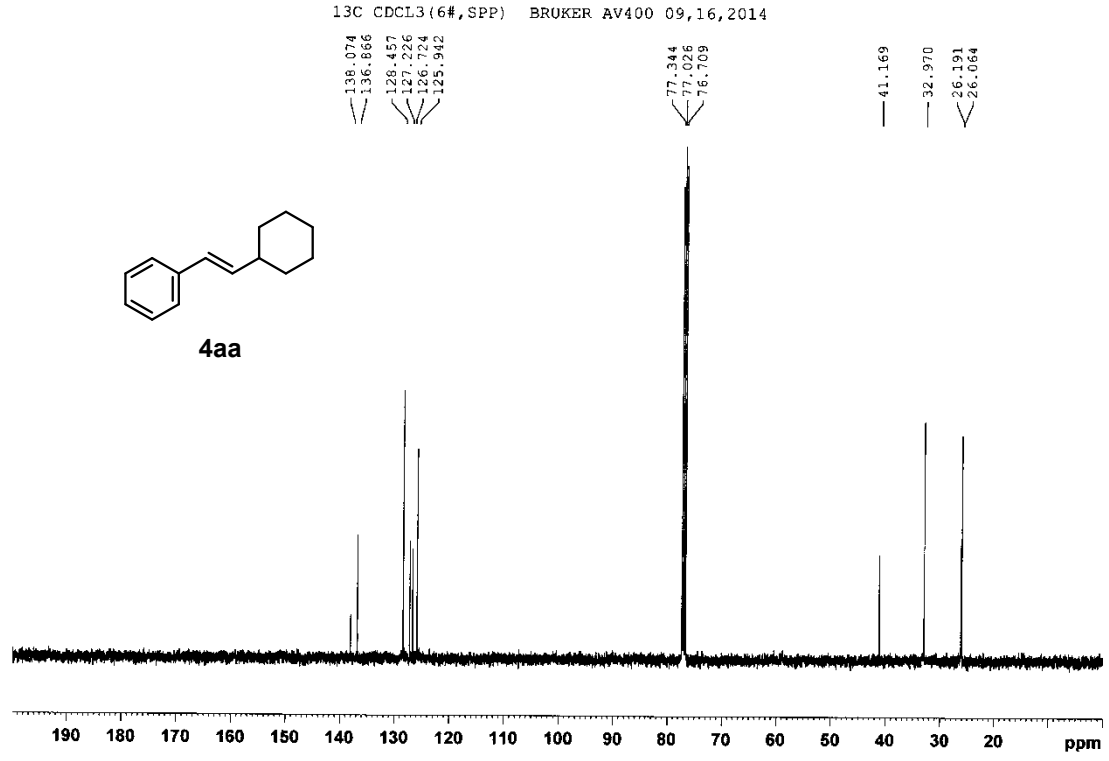

1H CDCL3(4#,SPP) BRUKER AV400 12,19,2014
3ad
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.000 1.018 2.049 1.010 1.071 3.115 1.091 1.067 1.038 1.039

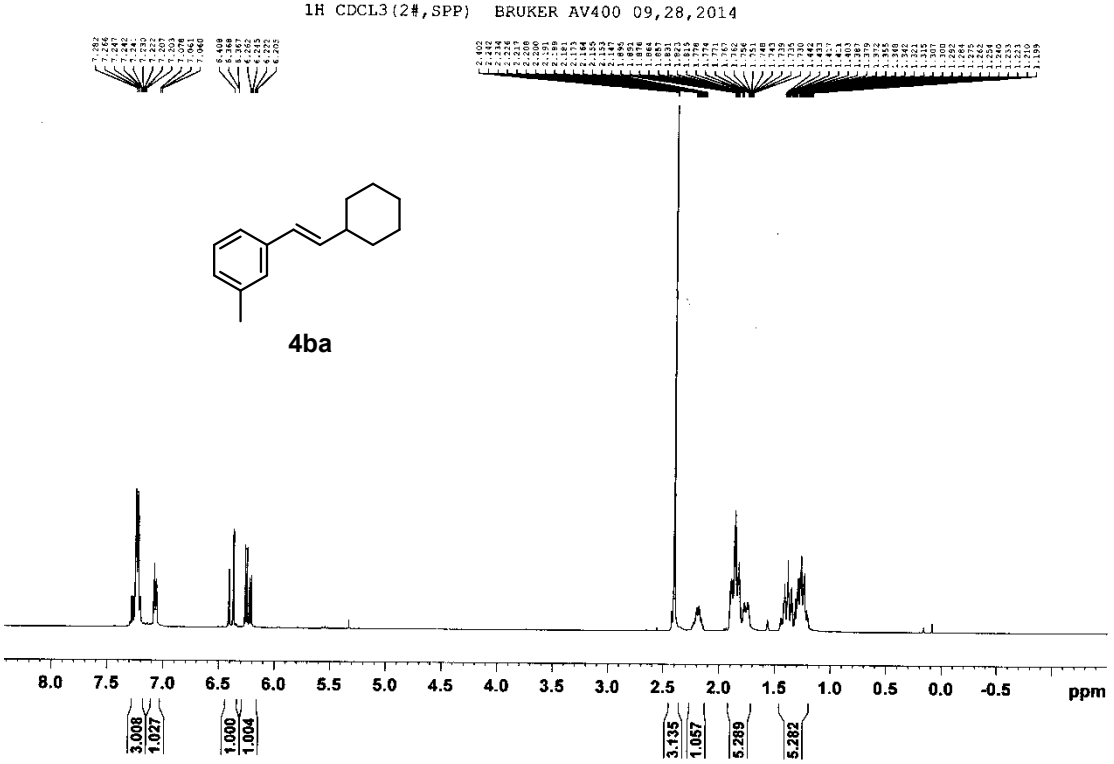

13C CDCL3(4#,SPP) BRUKER AV400 12,19,2014
197.068
136.857
133.356
128.658
128.213
77.339
77.022
76.704
71.825
70.960
66.878
66.450
40.725
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

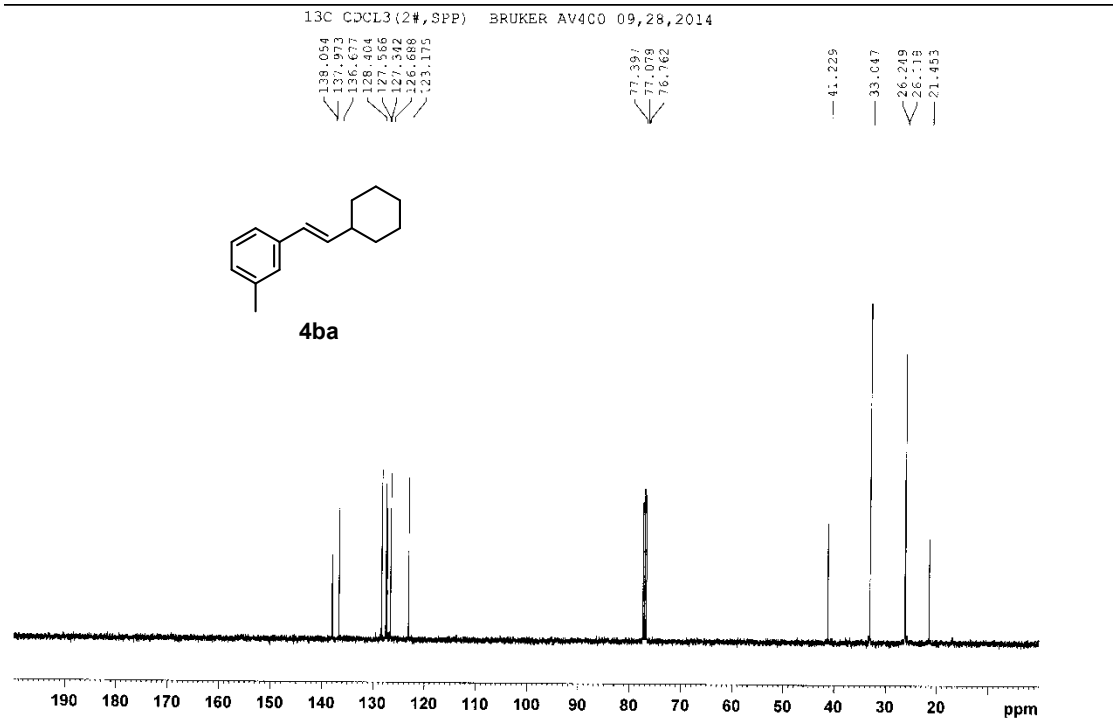

1H CDCL3(2#,SPP) BRUKER AV400 12,19,2014
7.963
7.950
7.945
7.942
7.590
7.586
7.576
7.571
7.566
7.556
7.553
7.549
7.486
7.483
7.467
7.452
7.448
7.349
7.345
7.334
7.329
7.320
7.313
7.307
7.299
7.281
7.241
7.236
7.231
7.225
7.220
7.213
7.209
7.203
7.198
3.577
3.560
3.542
3.525
3.507
3.490
3.355
3.341
3.314
3.300
3.244
3.223
3.202
3.182
1.373
1.356
O
3ae
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 ppm
2.000
1.063
2.085
4.034
1.058
1.003
1.048
1.037
3.140

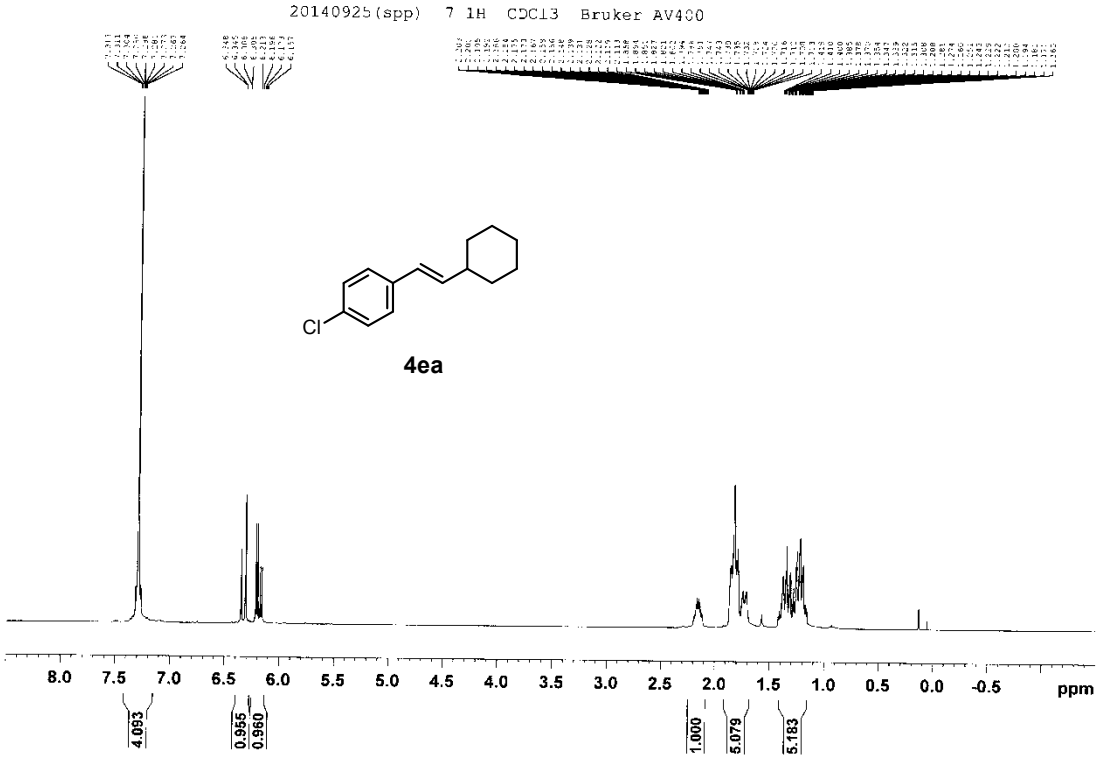

13C CDCL3(2#,SPP) BRUKER AV400 12,19,2014
199.095
146.584
137.190
132.988
128.576
128.543
128.082
126.871
126.287
77.348
77.032
76.713
47.034
35.567
21.883
O
3ae
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

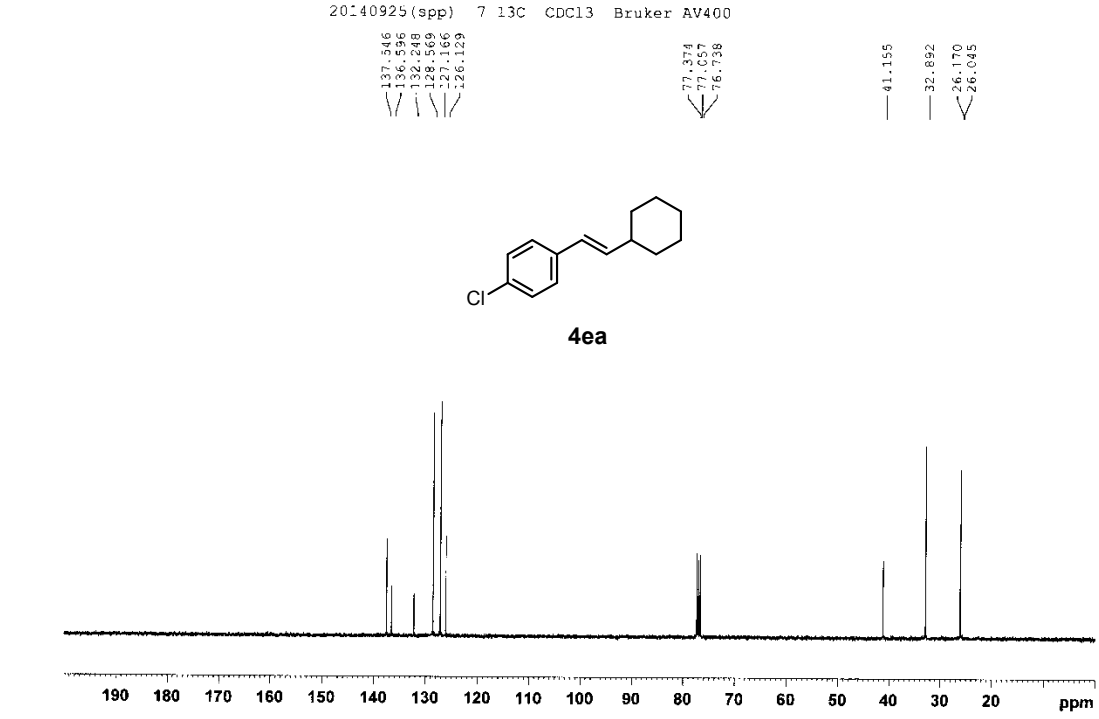

1H CDCL3(6#,SPP) BRUKER AV400 09,16,2014
4aa
8
7
6
5
4
3
2
1
0
-1
ppm
2.000
2.116
1.074
1.013
1.010
1.052
4.251
1.171
5.271

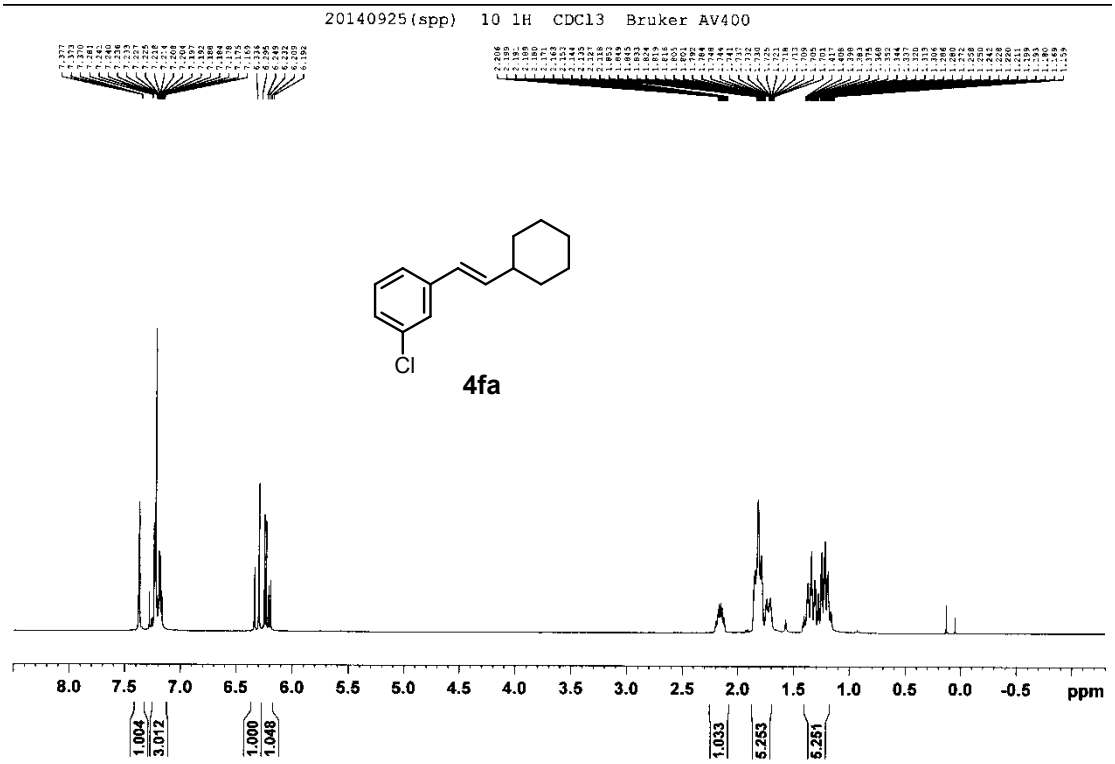

13C CDCL3(6#,SPP) BRUKER AV400 09,16,2014
138.074
136.866
128.457
127.226
126.724
125.942
77.344
77.026
76.709
41.169
32.970
26.191
26.064
4aa
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

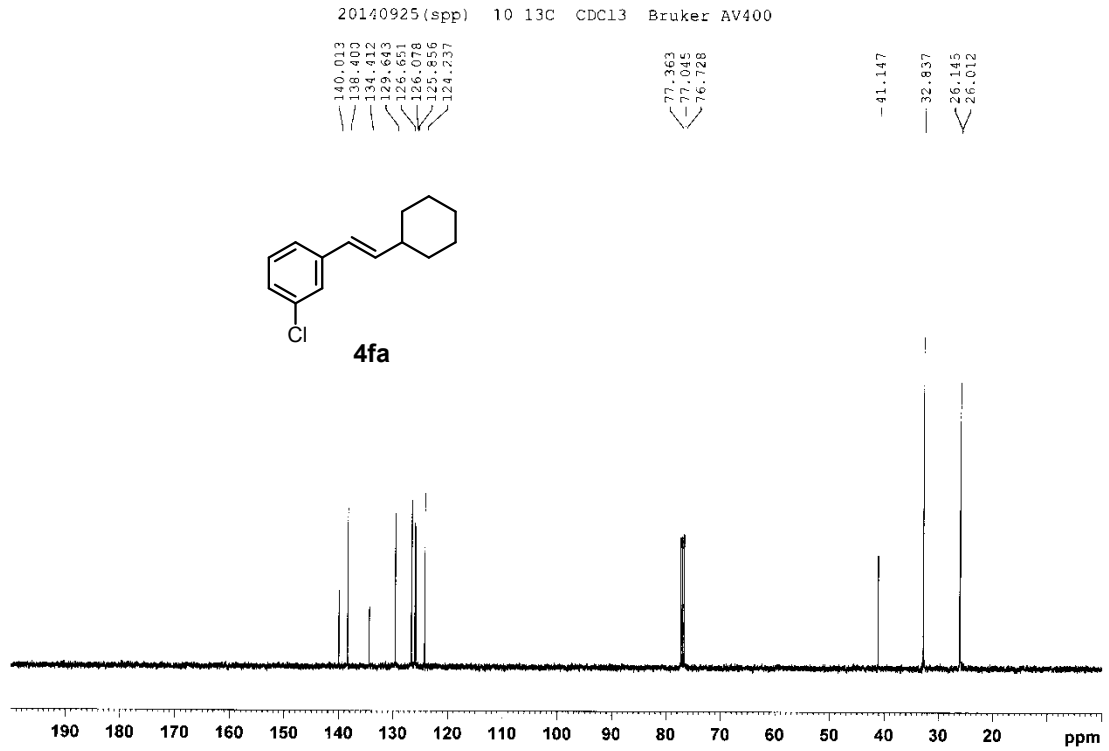

1H CDCL3(2#,SPP) BRUKER AV400 09,28,2014
4ba
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
3.008
1.027
1.000
1.004
3.135
1.057
5.289
5.282

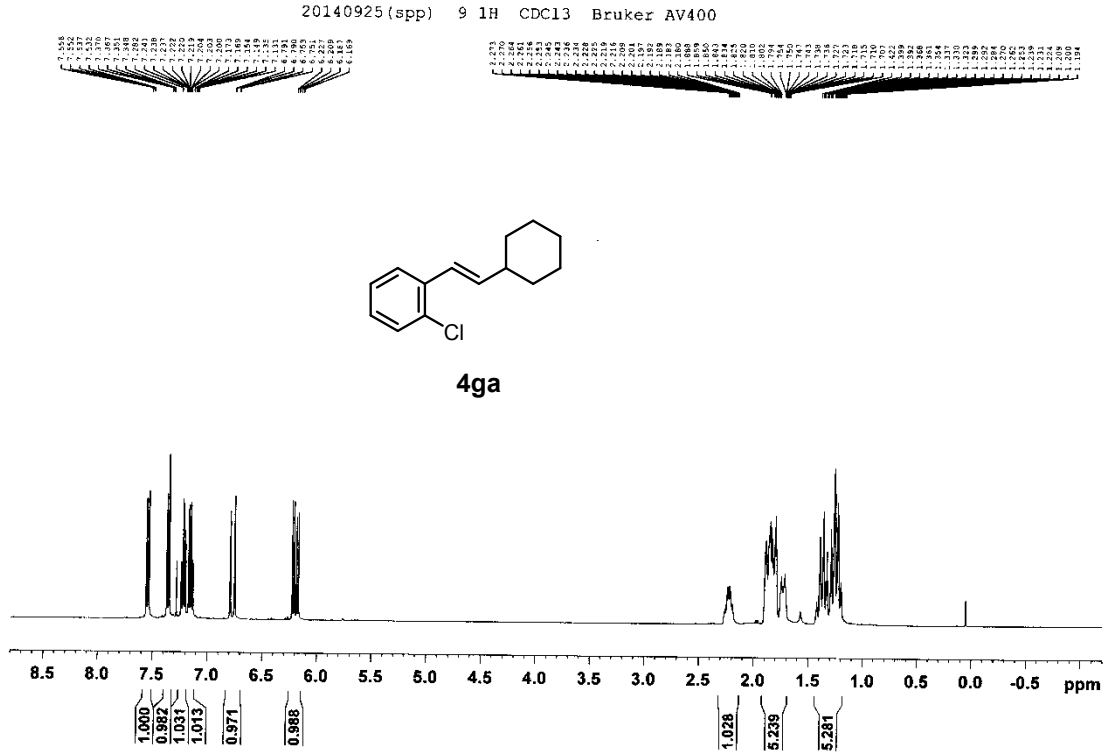

13C CDCL3(2#,SPP) BRUKER AV400 09,28,2014
139.054
137.973
136.677
128.404
127.566
127.342
126.688
123.175
77.391
77.079
76.762
41.229
33.047
26.249
26.118
21.453
4ba
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

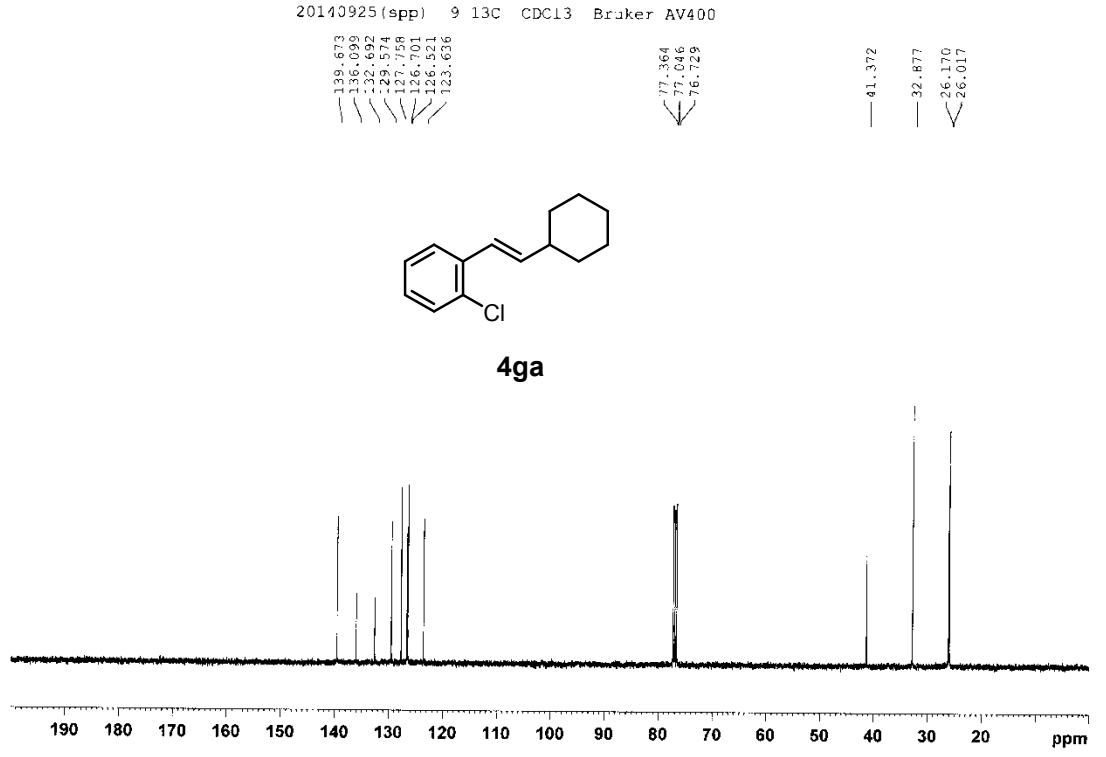

20140925(spp) 7 1H CDCl3 Bruker AV400
Cl
4ea
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
4.093
0.955
0.960
1.000
5.079
5.183

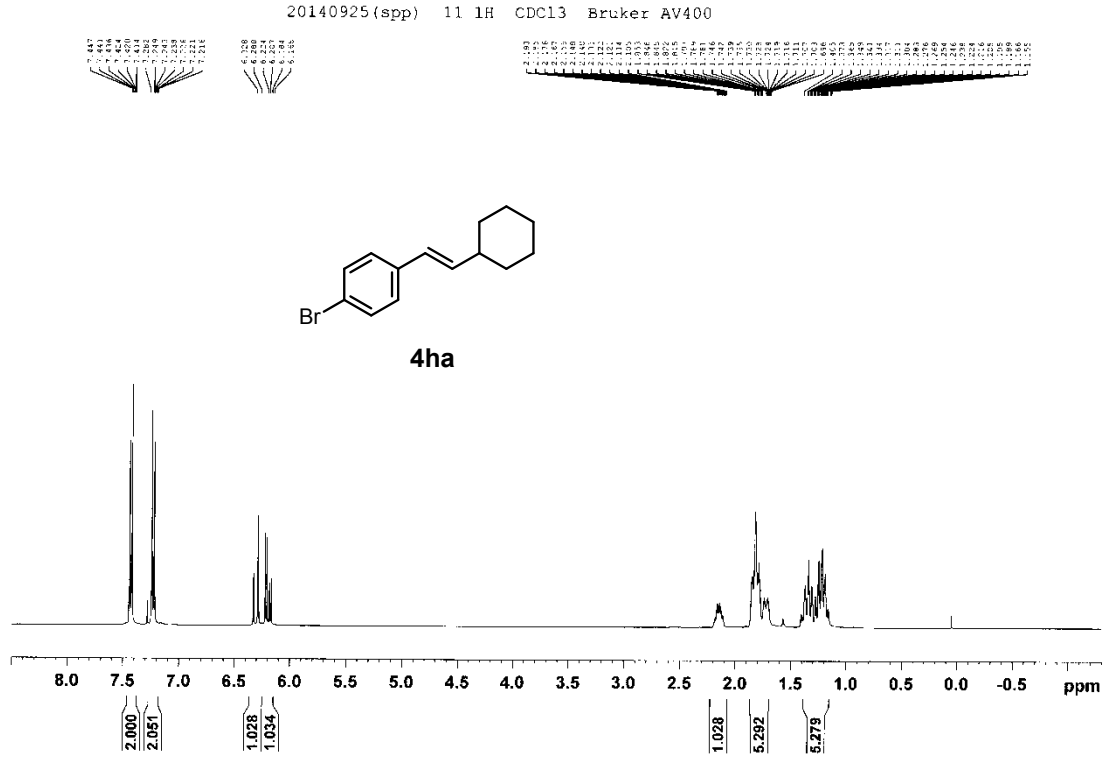

20140925(spp) 7 13C CDCl3 Bruker AV400
137.546
136.596
132.248
128.569
127.166
126.129
77.374
77.057
76.738
41.155
32.892
26.170
26.045
Cl
4ea
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


20140925(spp) 10 1H CDCl3 Bruker AV400
Cl
4fa
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.004
3.012
1.000
1.048
1.033
5.253
5.251

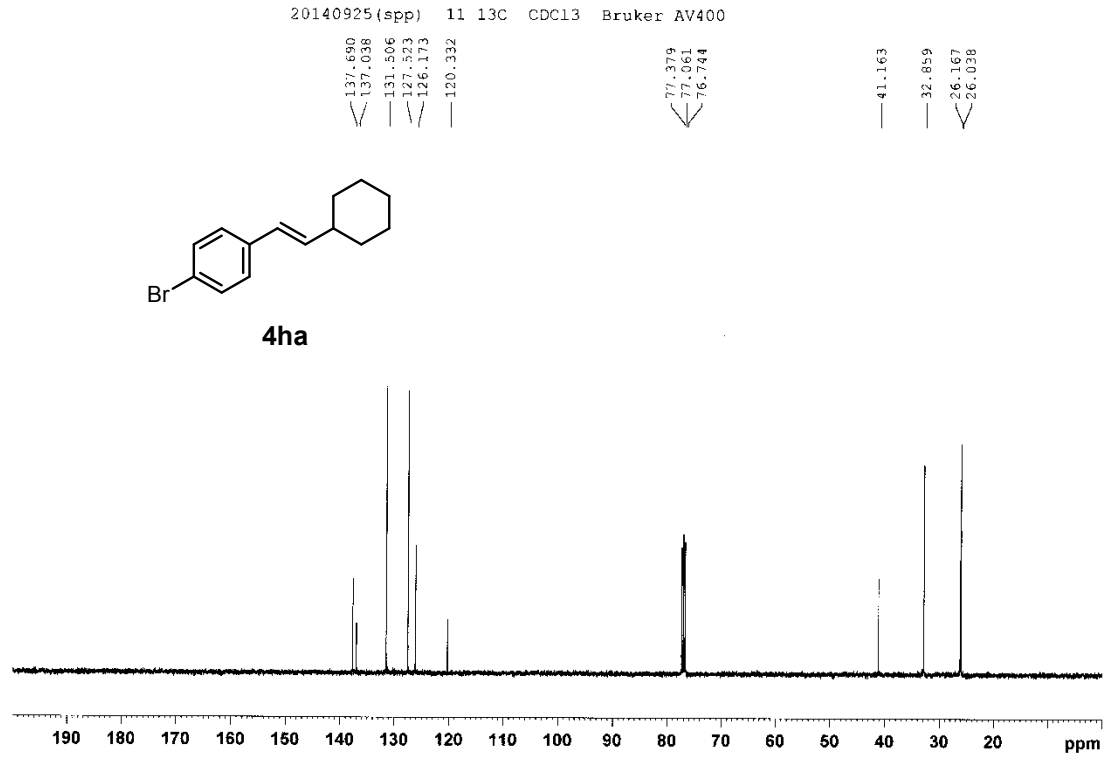

20140925(spp) 10 13C CDCl3 Bruker AV400
140.013
138.400
134.412
129.643
126.651
126.078
125.856
124.237
77.363
77.045
76.728
41.147
32.837
26.145
26.012
Cl
4fa
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


20140925(spp) 9 1H CDCl3 Bruker AV400
Cl
4ga
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.000 0.982 1.031 1.013 0.971 0.988 1.028 5.239 5.281

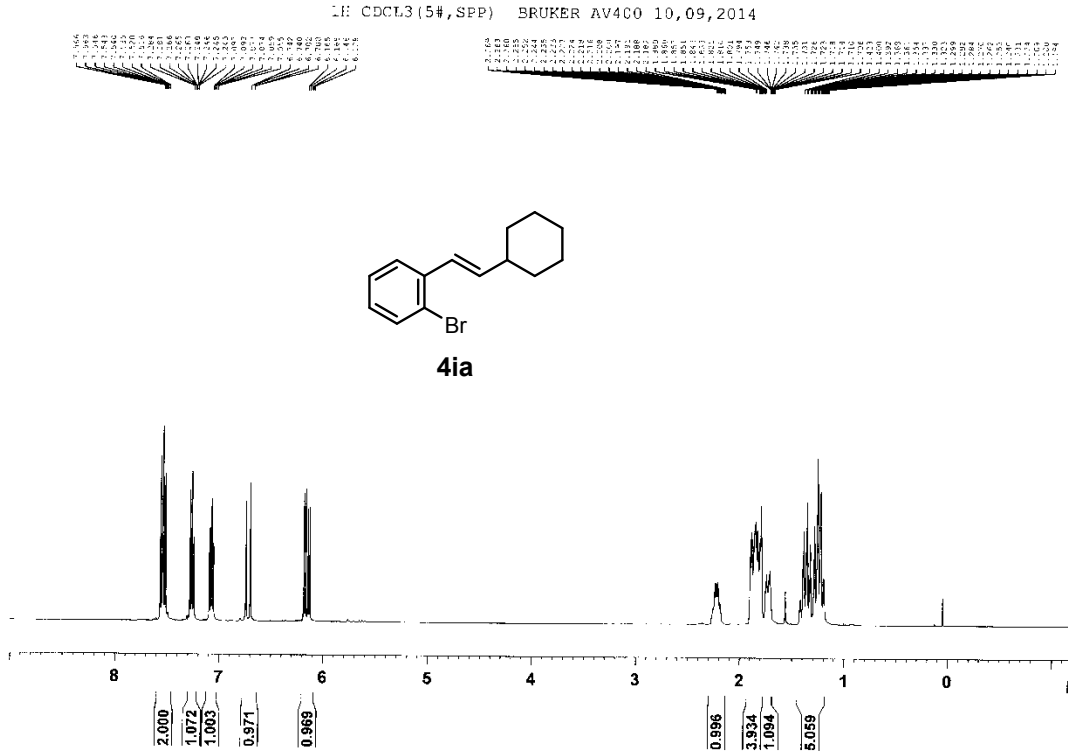

20140925(spp) 9 13C CDCl3 Bruker AV400
139.673
136.099
132.692
129.574
127.758
126.701
126.521
123.636
77.364
77.046
76.729
41.372
32.877
26.170
26.017
Cl
4ga
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

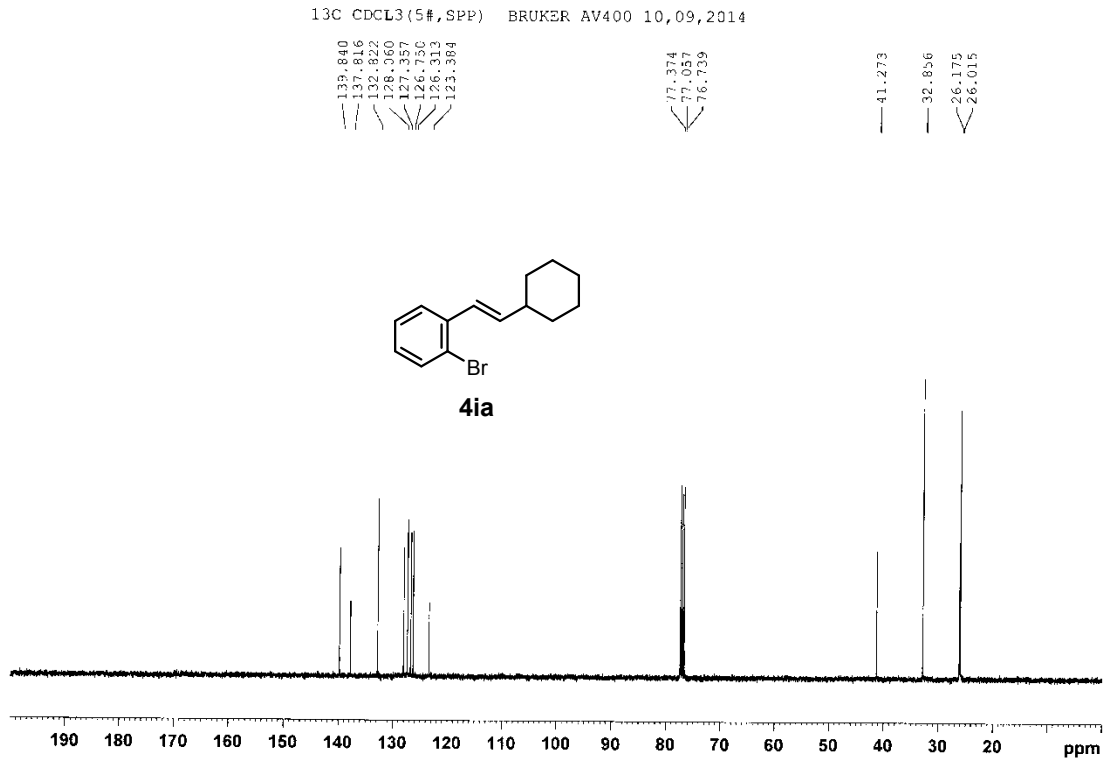

20140925(spp) 11 1H CDCl3 Bruker AV400
Br
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.000 2.051 1.028 1.034 1.028 5.292 5.279

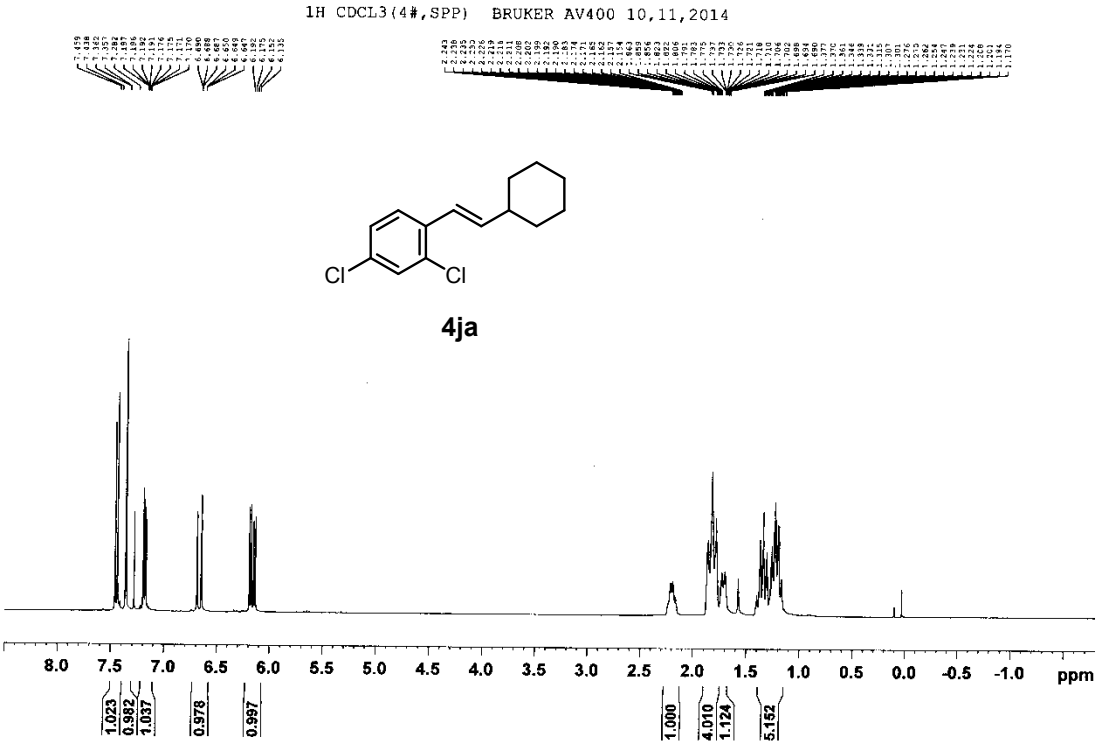
4ha

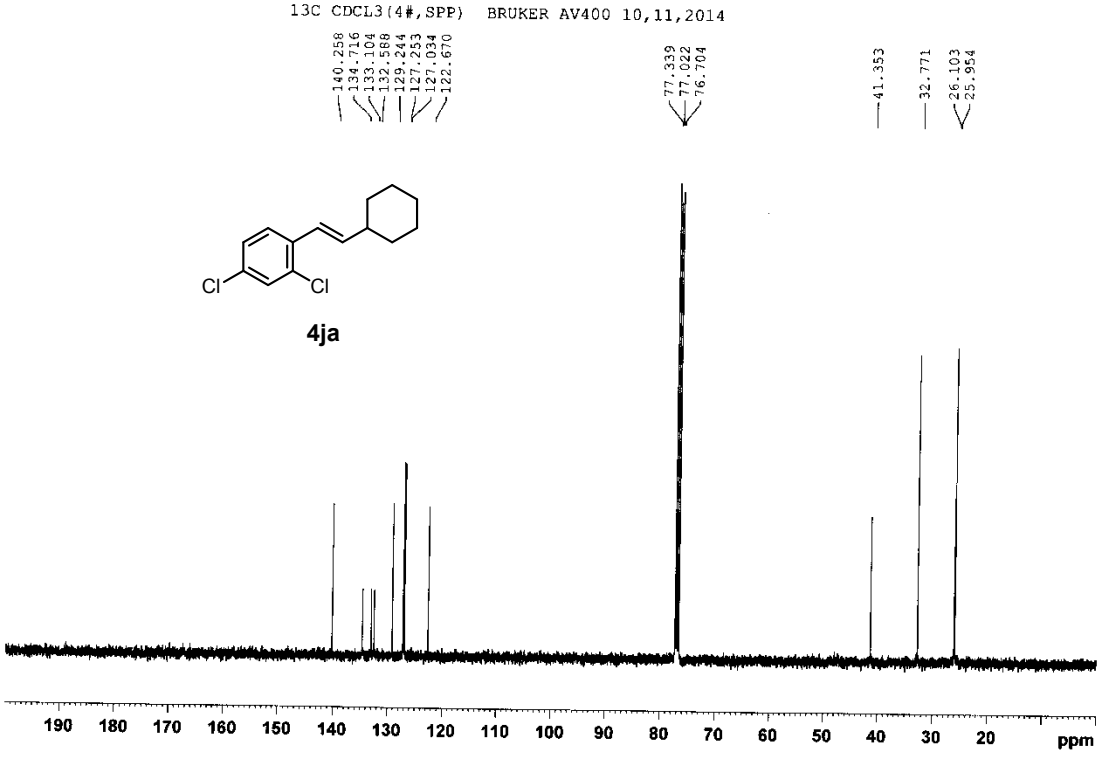

20140925(spp) 11 13C CDCl3 Bruker AV400
137.690
137.038
131.506
127.523
126.173
120.332
77.379
77.061
76.744
41.163
32.859
26.167
26.038
Br
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

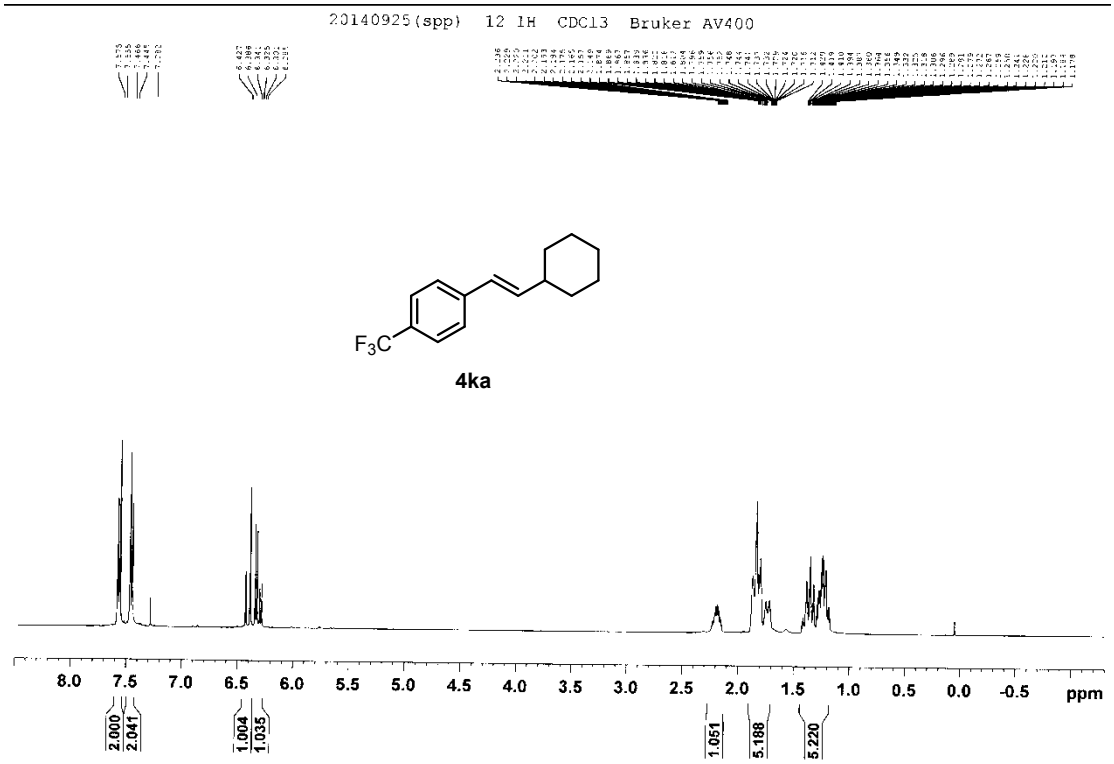
4ha

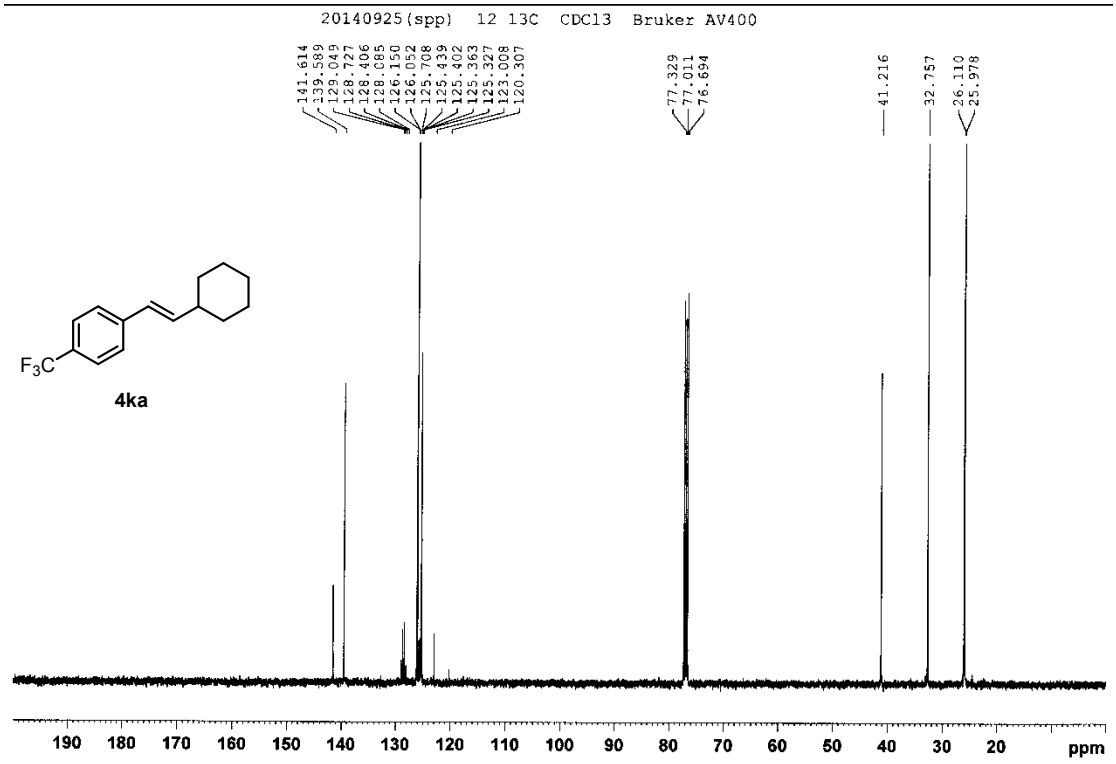

1E CDCL3(5#,SPP) BRUKER AV400 10,09,2014
Br
4ia
8
7
6
5
4
3
2
1
0
ppm
2.000
1.072
1.003
0.971
0.969
0.996
3.934
1.094
5.059

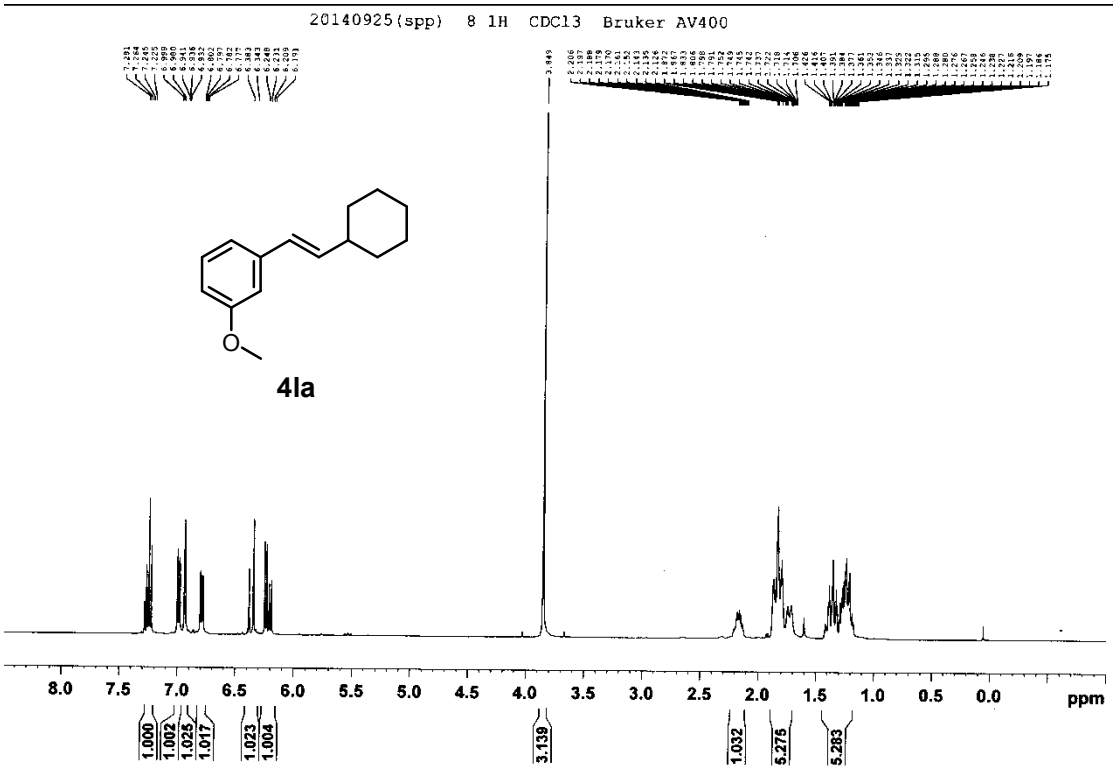

13C CDCL3(5#,SPP) BRUKER AV400 10,09,2014
139.840
137.816
132.822
128.060
127.357
126.736
126.313
123.384
77.374
77.057
76.739
41.273
32.856
26.175
26.015
Br
4ia
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

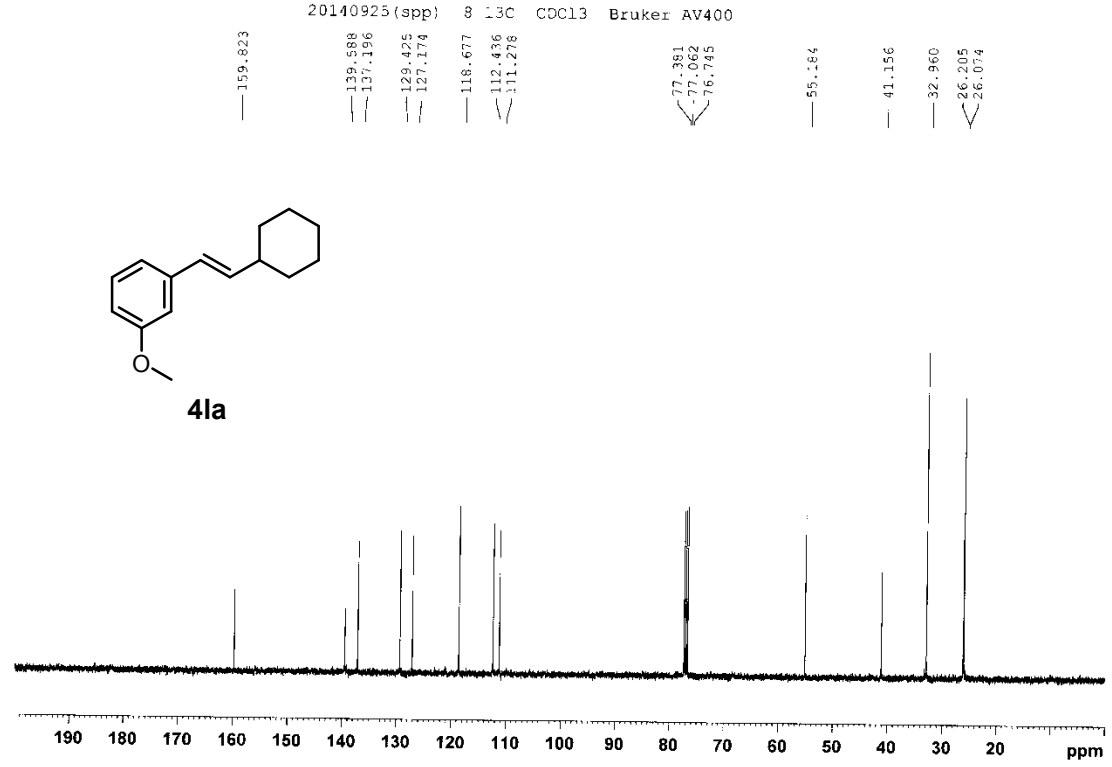

1H CDCL3(4#,SPP) BRUKER AV400 10,11,2014
Cl
Cl
4ja
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 ppm
1.023
0.982
1.037
0.978
0.997
1.000
4.010
1.124
5.152

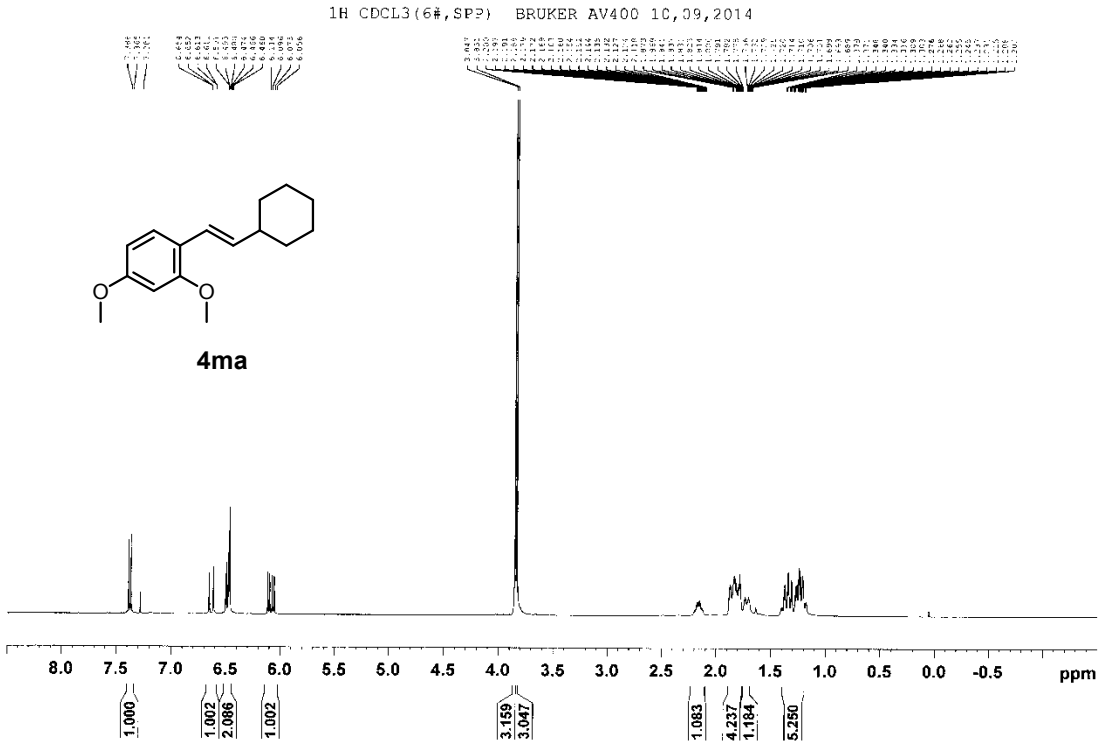

13C CDCL3(4#,SPP) BRUKER AV400 10,11,2014
140.258
134.716
133.104
132.588
129.244
127.253
127.034
122.670
77.339
77.022
76.704
41.353
32.771
26.103
25.954
Cl
Cl
4ja
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

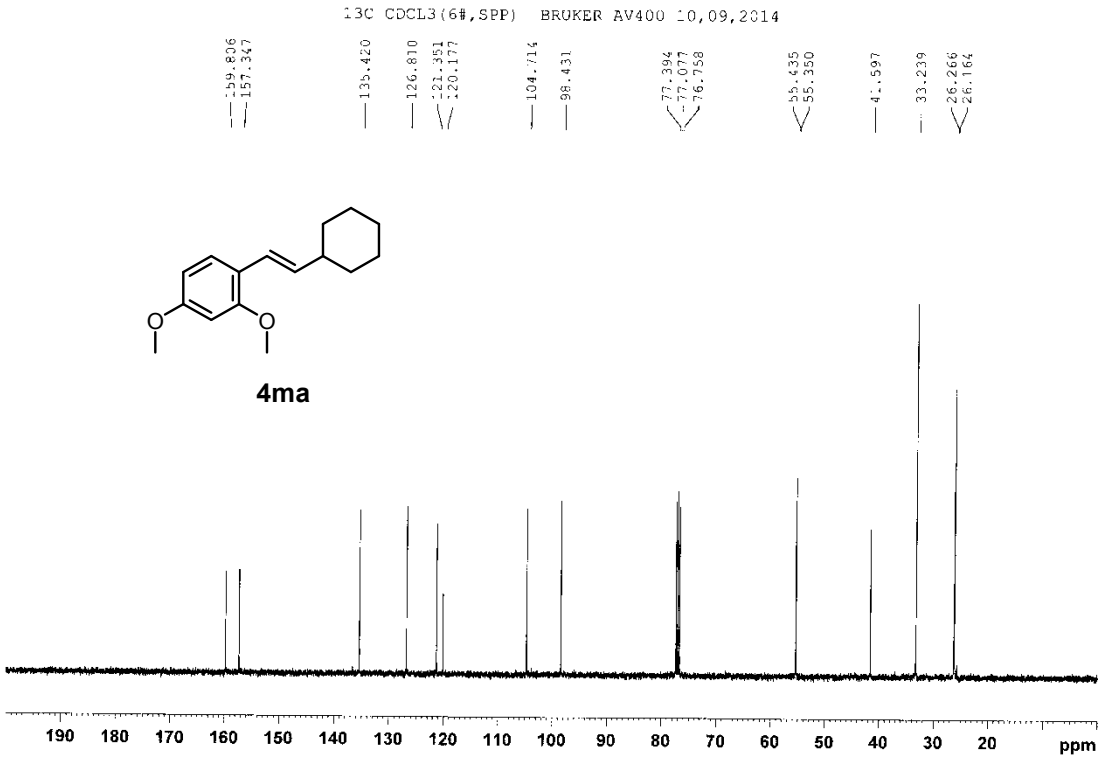

20140925(spp) 12 1H CDCl3 Bruker AV400
F3C
4ka
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.000
2.041
1.004
1.035
1.051
5.188
5.220

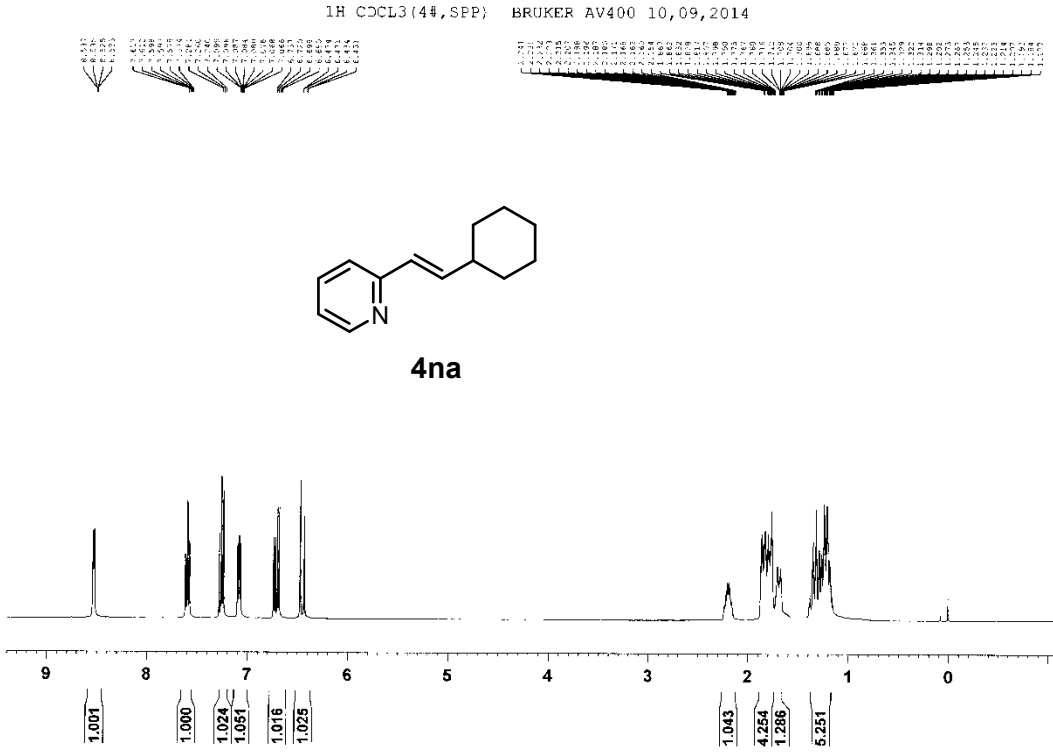

20140925(spp) 12 13C CDCl3 Bruker AV400
141.614
139.589
129.049
128.727
128.406
128.065
126.150
126.052
125.708
125.439
125.402
125.363
125.327
123.008
120.307
77.329
77.011
76.694
41.216
32.757
26.110
25.978
F3C
4ka
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

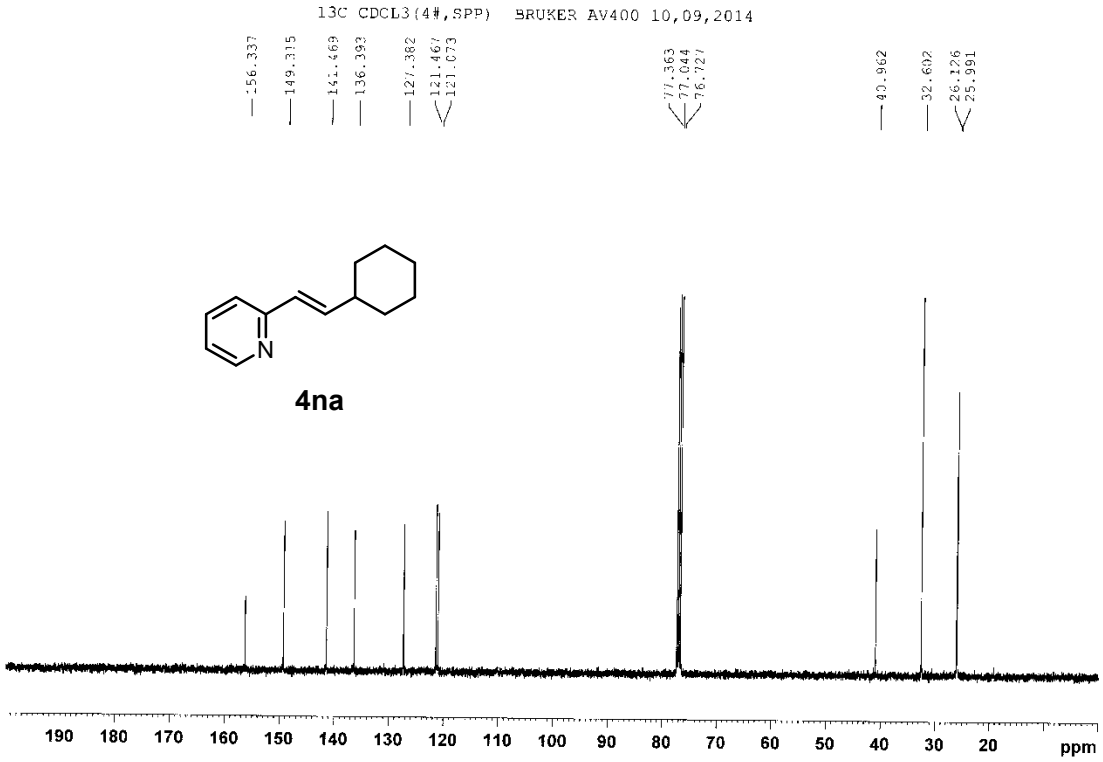

20140925(spp) 8 1H CDCl3 Bruker AV400
4la
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.000 1.002 1.025 1.017 1.023 1.004 3.139 1.032 5.275 5.283

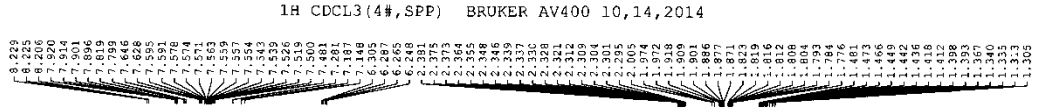

20140925(spp) 8 13C CDCl3 Bruker AV400
159.823
139.588
137.196
129.425
127.174
118.677
112.436
111.278
77.381
77.062
76.745
55.184
41.156
32.960
26.205
26.074
4la
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

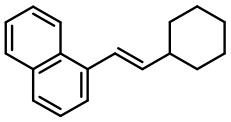

1H CDCL3(6#,SPP) BRUKER AV400 10,09,2014
4ma
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
1.000 1.002 2.086 1.002 3.159 3.047 1.083 4.237 1.184 5.250


13C CDCL3(6#,SPP) BRUKER AV400 10,09,2014
159.806
157.347
135.420
126.810
121.351
120.177
104.714
98.431
77.394
77.077
76.758
55.435
55.350
41.597
33.239
26.266
26.164
4ma
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

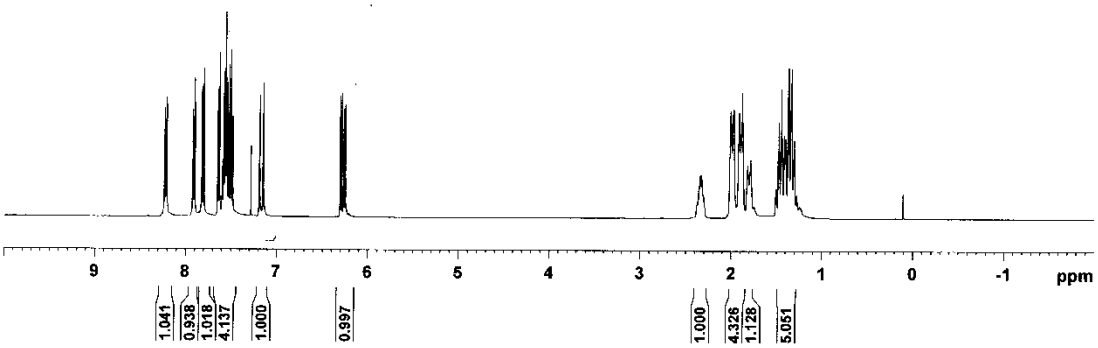

1H CDCL3(4#,SPP) BRUKER AV400 10,09,2014
4na
9
8
7
6
5
4
3
2
1
0
ppm
1.001
1.000
1.024
1.051
1.016
1.025
1.043
4.254
1.286
5.251

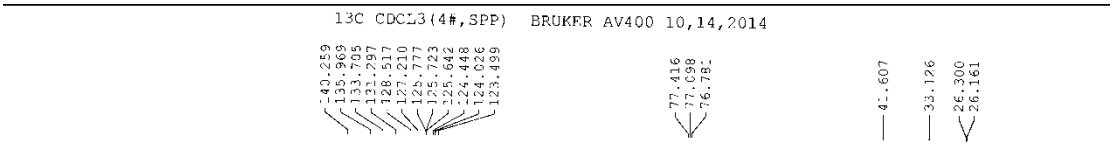

13C CDCL3(4#,SPP) BRUKER AV400 10,09,2014
156.337
149.315
145.469
136.393
127.382
121.467
121.073
77.363
77.044
76.727
40.962
32.602
26.126
25.991
4na
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

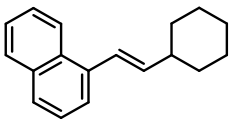

1H CDCL3(4#,SPP) BRUKER AV400 10,14,2014



4oa

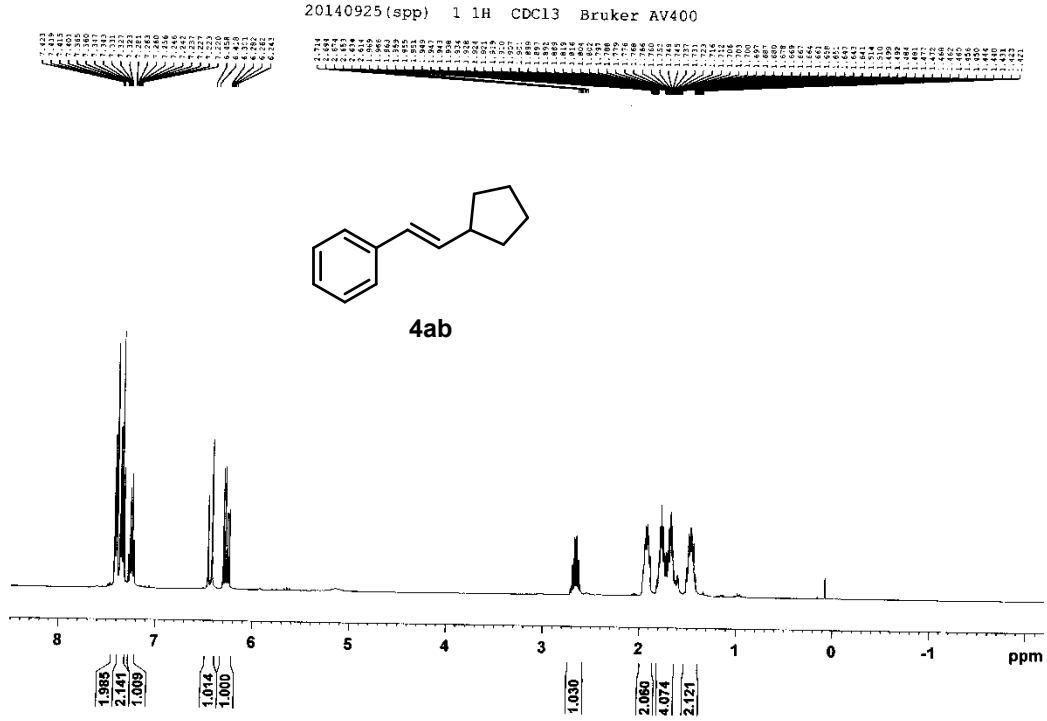

9
8
7
6
5
4
3
2
1
0
-1
ppm
1.041
0.938
1.018
4.137
1.000
0.997
1.000
4.326
1.128
5.051

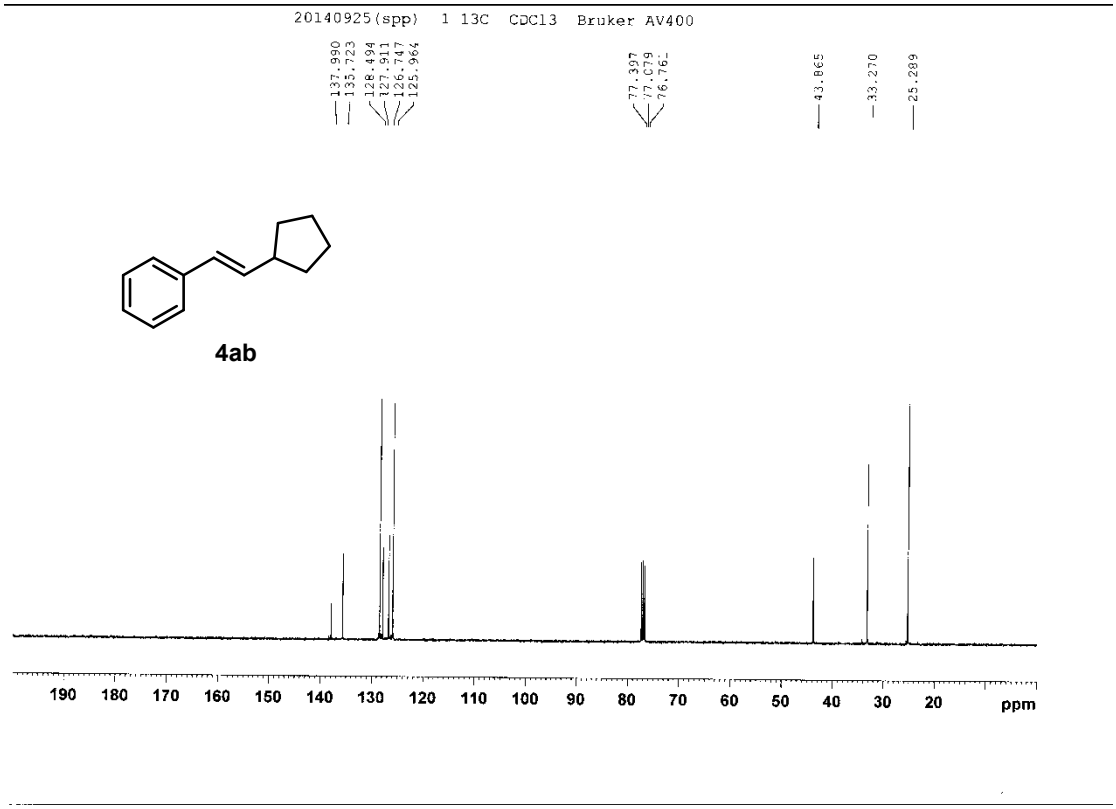

13C CDCL3(4#,SPP) BRUKER AV400 10,14,2014

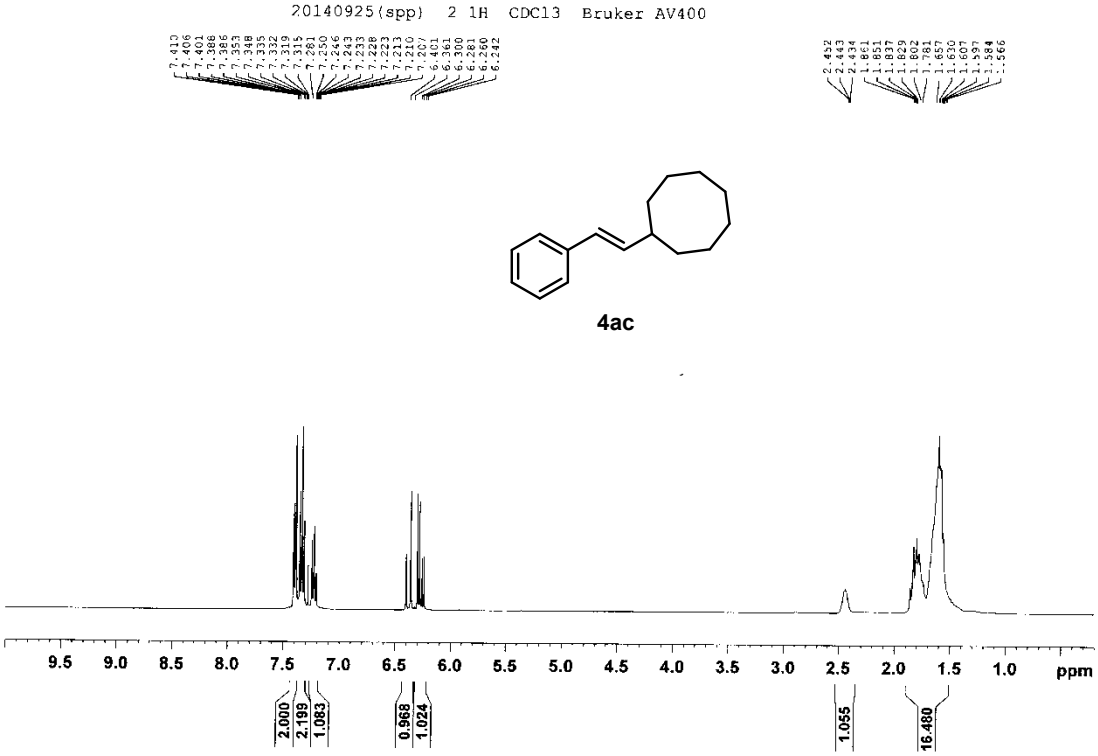


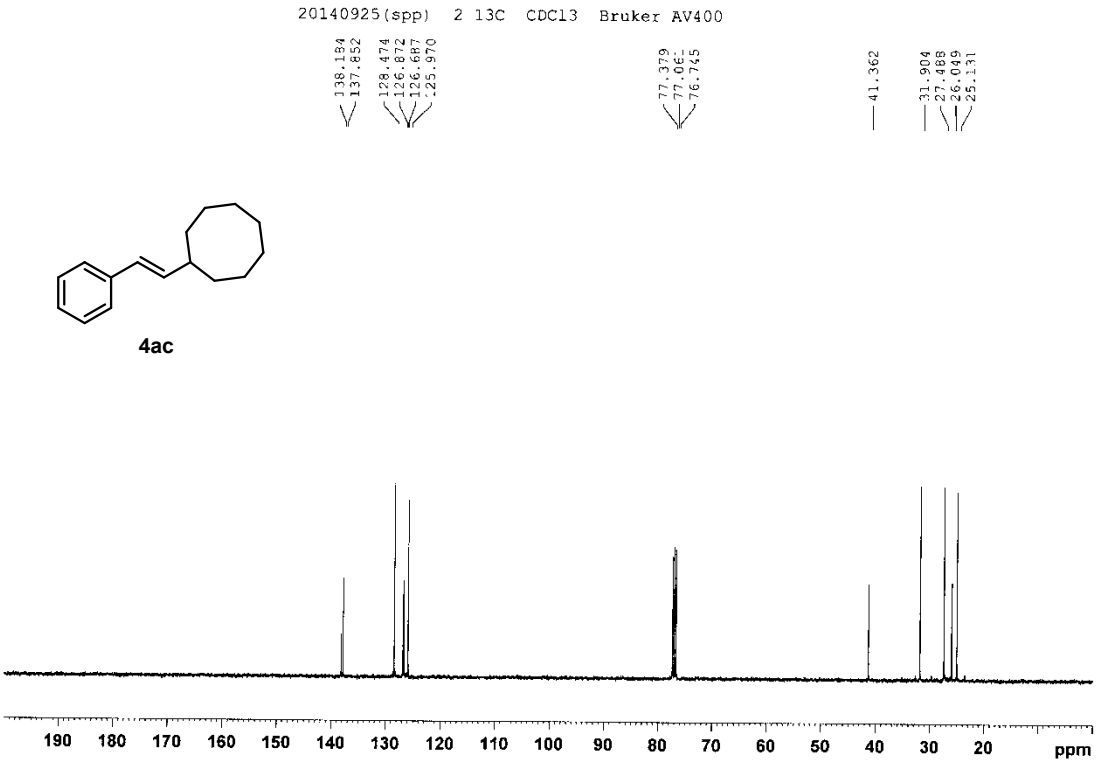
4oa

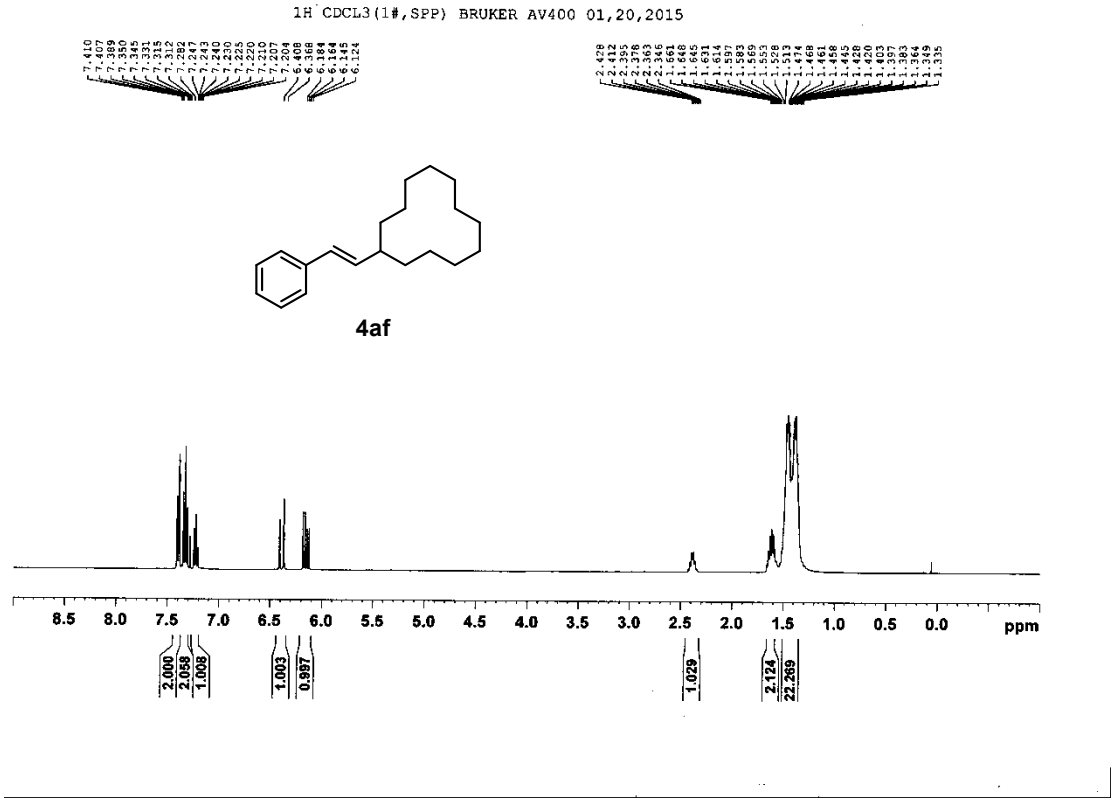
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

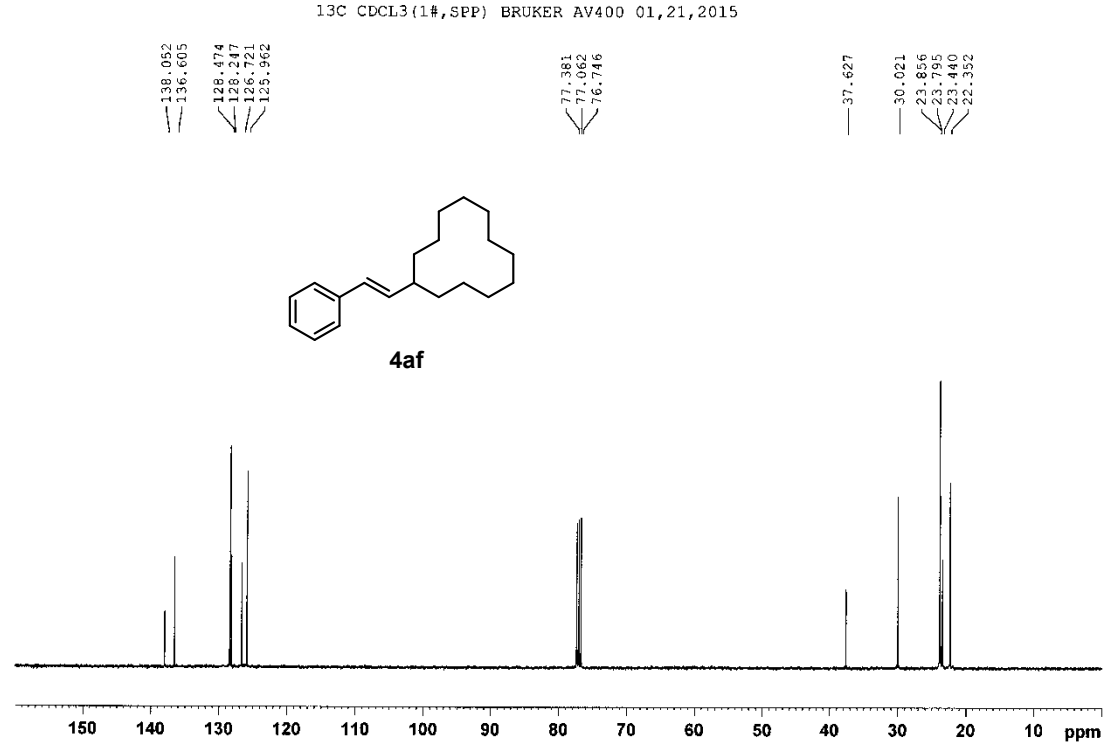

20140925(spp) 1 1H CDCl3 Bruker AV400
4ab
8
7
6
5
4
3
2
1
0
-1
ppm
1.985
2.141
1.009
1.014
1.000
1.030
2.060
4.074
2.121

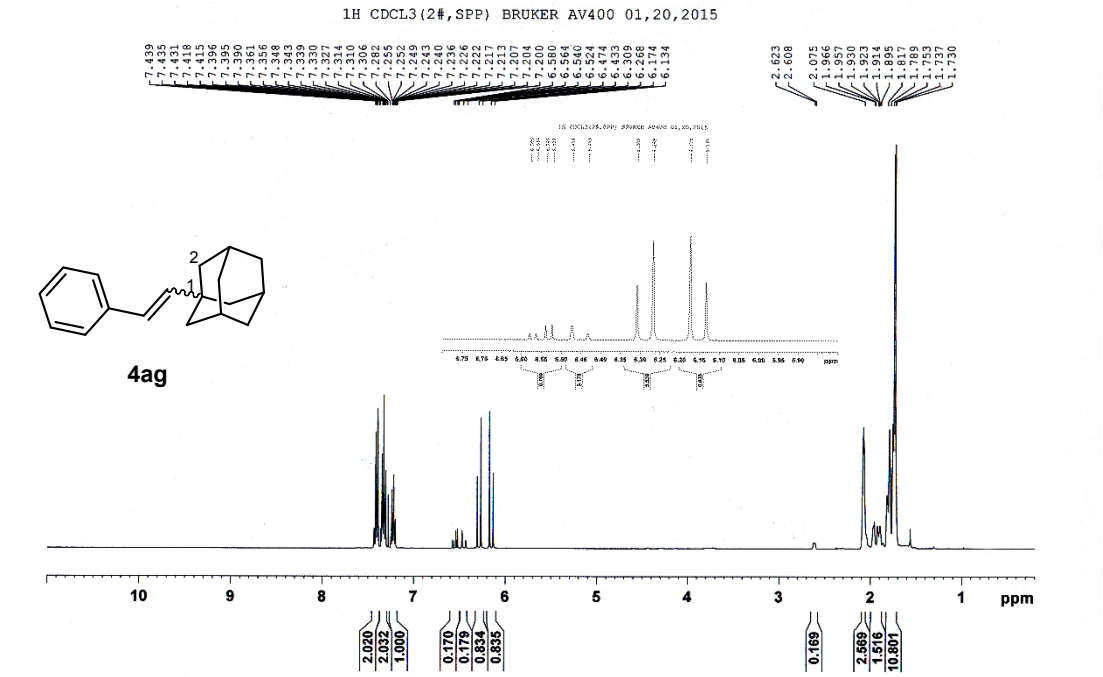

20140925(spp) 1 13C CDCl3 Bruker AV400
137.990
135.723
128.494
127.911
126.747
125.964
77.397
77.079
76.761
43.865
33.270
25.289
4ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

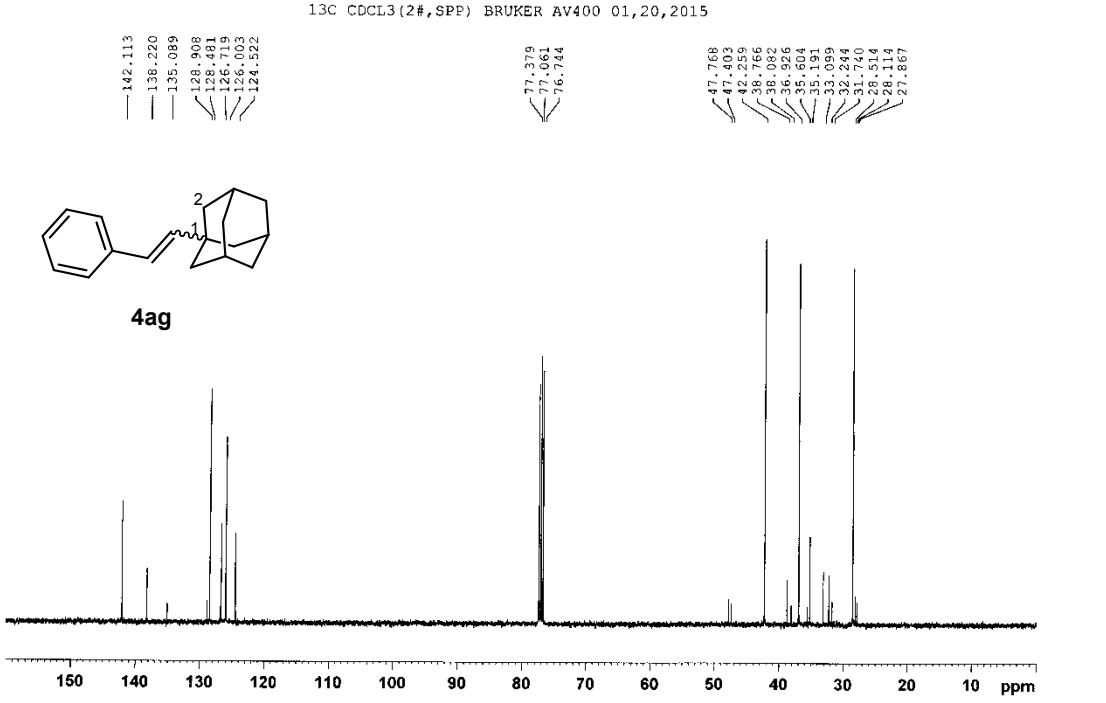

20140925(spp) 2 1H CDCl3 Bruker AV400
4ac
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.000
2.199
1.083
0.968
1.024
1.055
16.480

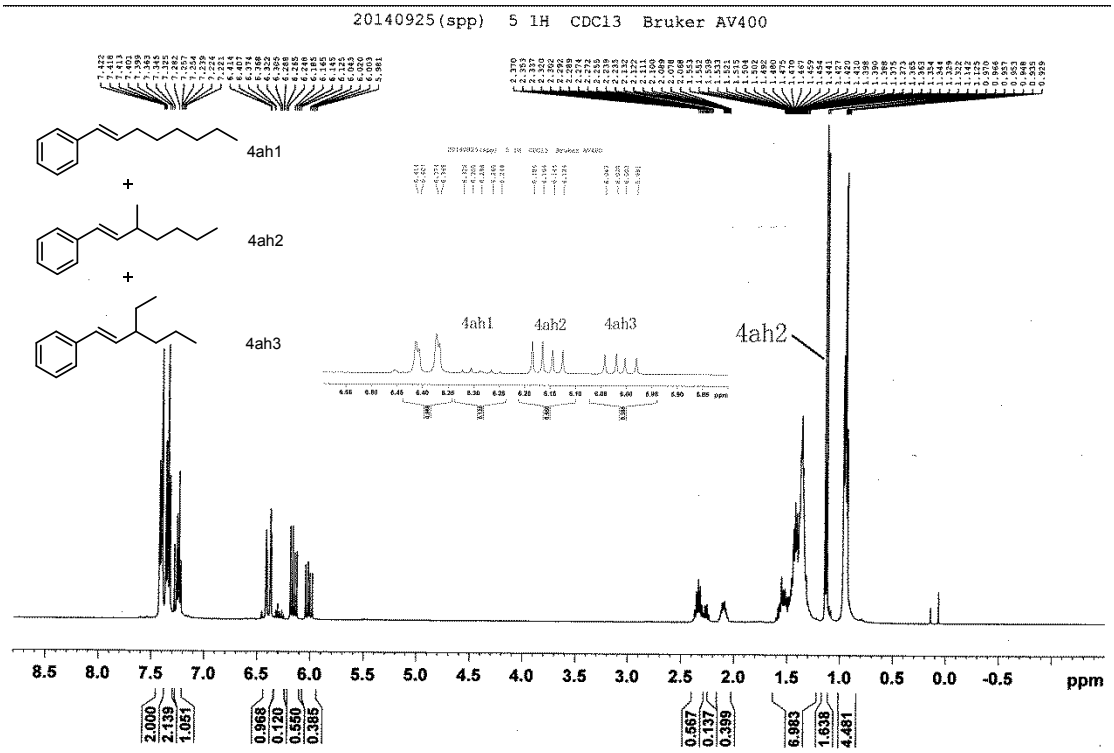

20140925(spp) 2 13C CDCl3 Bruker AV400
4ac
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

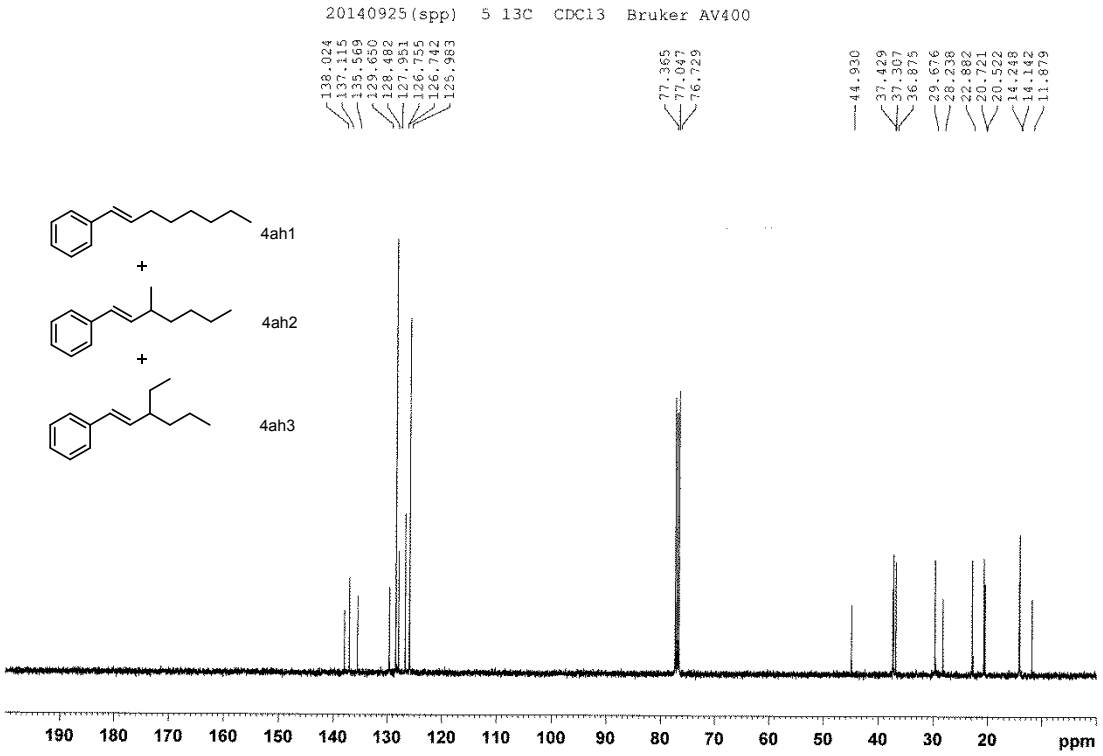

1H CDCL3(1#,SPP) BRUKER AV400 01,20,2015
4af
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.000
2.058
1.008
1.003
0.987
1.029
2.124
22.269


13C CDCL3(1#,SPP) BRUKER AV400 01,21,2015
138.052
136.605
128.474
128.247
126.721
125.962
77.381
77.062
76.746
37.627
30.021
23.856
23.795
23.440
22.352
4af
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

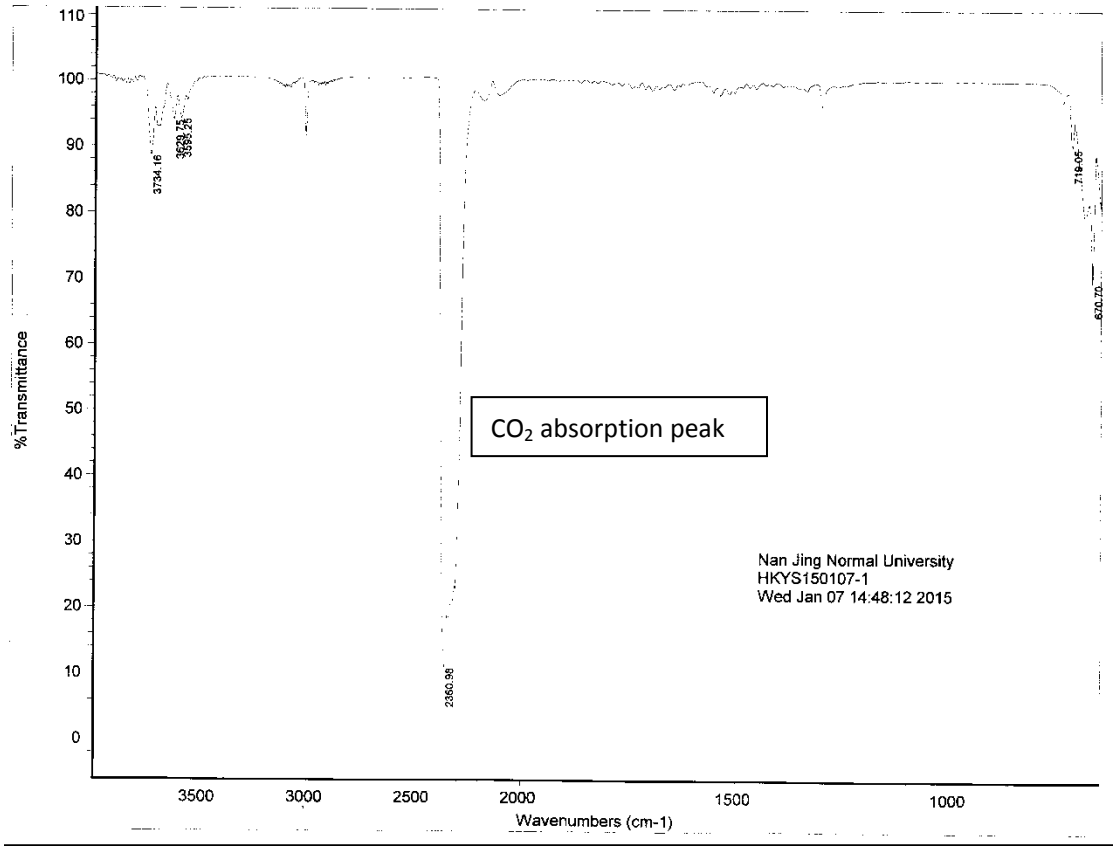

1H CDCL3(2#,SPP) BRUKER AV400 01,20,2015
4ag
ppm


13C CDCL3(2#,SPP) BRUKER AV400 01,20,2015
4ag
ppm

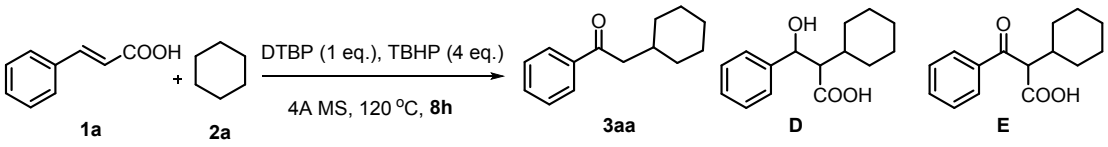

20140925(spp) 5 1H CDCl3 Bruker AV400
4ah1
4ah2
4ah3
4ah1
4ah2
4ah3
4ah2
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 ppm
2.000 2.139 1.051 0.968 0.120 0.550 0.385 0.567 0.137 0.399 6.983 1.638 4.481


20140925(spp) 5 13C CDCl3 Bruker AV400
138.024
137.115
135.569
129.650
128.482
127.951
126.755
126.742
125.983
77.365
77.047
76.729
44.930
37.429
37.307
36.875
29.676
28.238
22.882
20.721
20.522
14.248
14.142
11.879
4ah1
4ah2
4ah3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

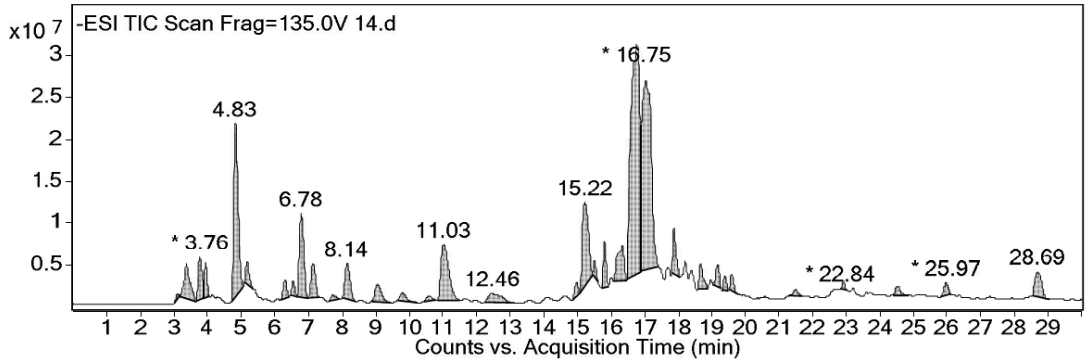
5. GC−FTIR Spectra of the Components of the Gas Generated from the Reaction to form 3aa



6. LC−MS Analysis for the Reaction Mixture to Form 3aa after Reacting for 8 h under the Standard Reaction Conditions



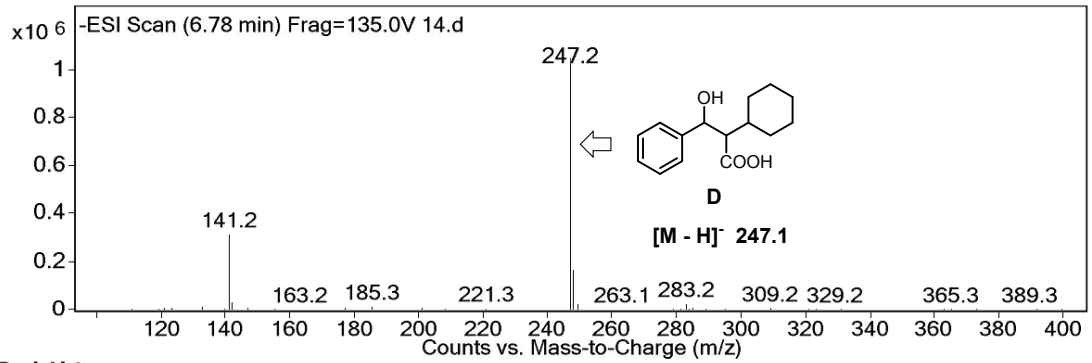
Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** ESI



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
3	3.66	3.76	3.88	5207840	41535817	8.48
5	4.7	4.83	5.06	20667638	180285856	36.79
9	6.65	6.78	6.99	10004558	89968971	18.36
12	8.01	8.14	8.41	4273206	44265062	9.03
16	10.84	11.03	11.5	6730793	109370437	22.32
19	15.07	15.22	15.44	10015550	124681471	25.45
21	15.72	15.81	15.92	5522550	31652722	6.46
23	16.47	16.75	16.87	27510111	489992868	100
24	16.87	17.03	17.4	22618896	443779158	90.57
25	17.8	17.87	18.06	5417192	36222725	7.39

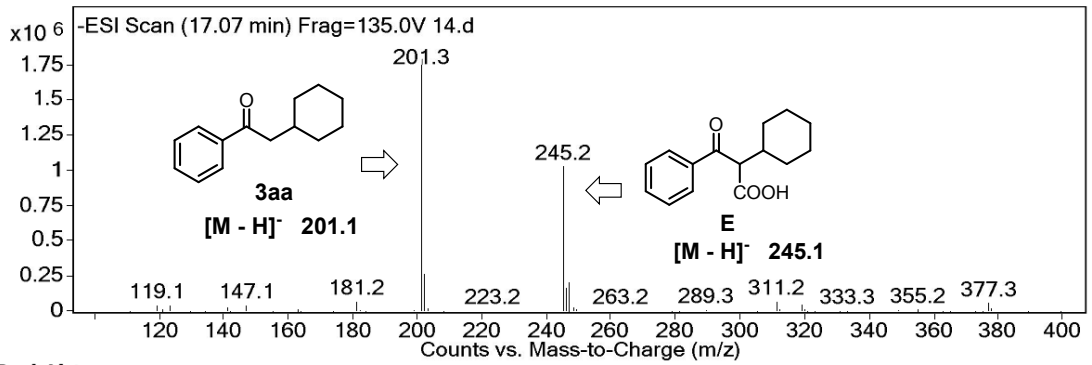
Fragmentor Voltage 135 **Collision Energy** 0 **Ionization Mode** Esi



Peak List

m/z	Abund
133.2	11290
141.2	310347
142.2	27086
185.3	10324
247.2	1047752
248.2	165041
249.2	20046
283.2	22730
285.2	6390
295.2	6312

Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Esi



Peak List

m/z	Abund
147.1	43633
181.2	70947
201.3	1791989
202.3	265696
245.2	1027350
246.2	165742
247.2	199696
311.2	72380
319.3	44338
377.3	58698