Supporting Information

Integration of Electrooxidative Cyclization and Chemical Oxidation via Alkoxysulfnoium Ions. Synthesis of Exocyclic Ketones from Alkenes with Cyclization

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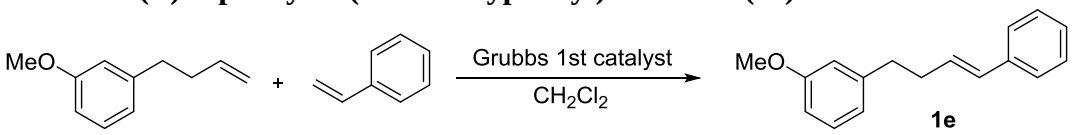
General

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Varian MERCURY plus-400 (^{1}H 400 MHz, ^{13}C 100 MHz), or JEOL ECA-600P spectrometer (^{1}H 600 MHz, ^{13}C 150 MHz). Mass spectra were obtained on JEOL JMS SX-102A mass spectrometer. IR spectra were measured on Shimadzu IRAffinity (FTIR). Merck precoated silica gel F_{254} plates (thickness 0.25 mm) was used for thin-layer chromatography (TLC) analysis. Flash chromatography was carried out on a silica gel (Kanto Chem. Co., Silica Gel N, spherical, neutral, 40-100 mm). Preparative gel permeation chromatography (GPC) was carried out on Japan Analytical Industry LC-918 equipped with JAIGEL-1H and 2H using $CHCl_3$ as an eluent. Rotating disk electrode (RDE) voltammetry was carried out using BAS 600C electrochemical analyzer and BAS RRDE-3. Measurements were carried out in 0.1 M $LiClO_4/CH_3CN$ using a glassy carbon disk working electrode, a platinum wire counter electrode, and an SCE reference electrode with sweep rate of 10 mVs^{-1} at 3000 rpm. X-ray single crystal structure analysis was performed on RIGAKU R-AXIS RAPID. All reactions were carried out under argon atmosphere unless otherwise noted. Compounds **1a**,[1] **1b**,[1] **1c**,[2] **1d**,[3] **1f**,[1] **6a**,[1] **6b**,[1] 4-(3-methoxyphenyl)-1-butene,[4] *N*-tosylpropylamine,[5] *N*-tosylcinnamylamine,[1] and *N*-methyl-*N*-tosylcinnamylamine[1] were prepared according to the reported procedures. Bu_4NBF_4 was purchased from TCI and dried at 50 ^{o}C/1 mmHg for 12 hours. $Bu_4NB(C_6F_5)_4$ was prepared according to the reported procedure.[6] Dichloromethane was washed with water, distilled from P_2O_5, redistilled from dried K_2CO_3 to remove a trace amount of acid, and stored over molecular sieves 4A. Triethylamine (Et_3N) was refluxed with calcium hydride, distilled, and stored over molecular sieves 4A. CD_2Cl_2 was dried over molecular sieves 4A before use. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. DFT calculations were performed with the Gaussian 09 program.[7] All geometry optimizations were carried out at the UB3LYP level of density functional theory with the 6-31+G(d) basis set.

Oxidative cyclization of alkenes having nucleophilic functional groups

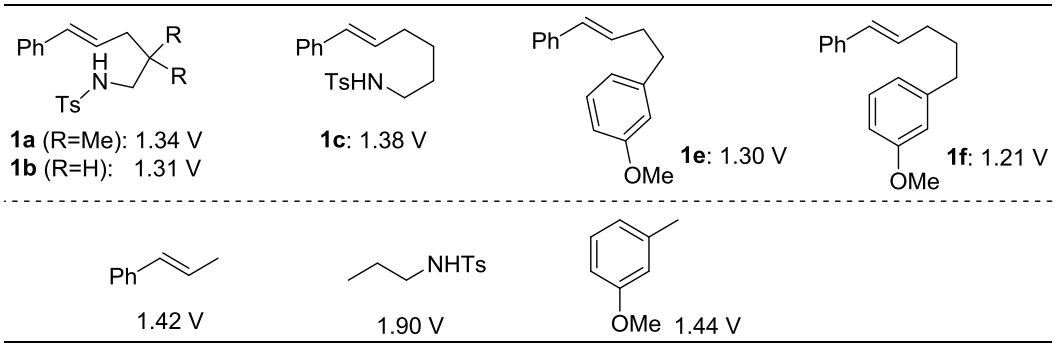
Preparation of (*E*)-1-phenyl-4-(3-methoxyphenyl)-1-butene (1e)



To a round-bottom flask were added 4-(3-methoxyphenyl)-1-butene (800 mg, 4.93 mmol), styrene (1.1 g, 10.6 mmol), benzylidenebis(tricyclohexylphosphine) dichlororuthenium (the 1st generation Grubbs catalyst) (100 mg, 0.12 mmol), and CH_2Cl_2 (20 mL). Then, the mixture was heated to 40 ^{o}C and stirred for additional 96 hours. The solvent was removed under reduced pressure and the resulting crude product was purified with flash chromatography (hexane/EtOAc 20:1) to obtain the title compound (440 mg, 36%): TLC R_f 0.44 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.53 (q, J = 7.2 Hz, 2 H), 2.77 (dd, J = 7.2, 8.4 Hz, 2 H), 3.80 (s, 3 H), 6.26 (dt, J = 6.8, 15.6 Hz, 1 H), 6.43 (d, J = 16.0 Hz, 1 H), 6.77 (m, 2 H), 6.83 (d, J = 8.0 Hz, 1 H), 7.27 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.8, 35.9, 55.1, 111.2, 114.2, 120.9, 126.0, 126.9, 128.5, 129.3, 129.9, 130.4, 137.7, 143.4, 159.6; HRMS (ESI) calcd for $C_{17}H_{19}O$ [M+H^{+}]: 237.1285, found: 237.1284.

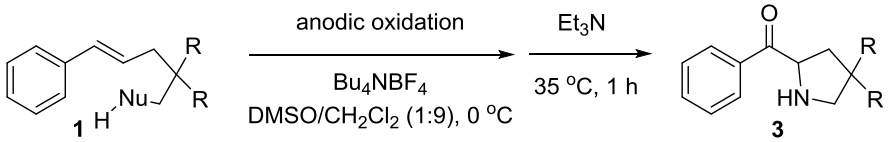
Oxidation potentials of alkenes having a nucleophilic moiety and compounds having an alkene moiety or a nucleophilic moiety

Table S1. Oxidation Potentials (V vs. SCE) of **1a-c**, **1e-g**, (*E*)-β-methylstyrene, 3-methoxytoluene, *N*-tosylpropylamine, and *n*-propylalcohol.

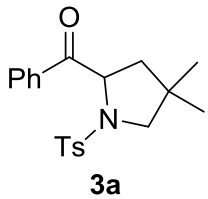


The oxidation potential of **1d** was not determined in this condition because of the high noise.

Typical procedure for oxidation of alkenes bearing a nucleophilic functional group

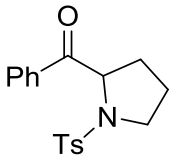


The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 300 °C/1 mmHg for 4 h before use) and a platinum plate cathode (10 mm x 10 mm). In the anodic chamber were placed 0.25 mmol of alkene **1**, Bu_4NBF_4 (980 mg, 3.0 mmol), DMSO (1.0 mL) and CH_2Cl_2 (9.0 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (55 μL, 0.62 mmol), Bu_4NBF_4 (980 mg, 3.0 mmol), and CH_2Cl_2 (10.0 mL). The constant current electrolysis (8.0 mA) was carried out at 0 °C with magnetic stirring until TLC analysis indicated that the alkene was consumed. Then 0.5 mL of Et_3N was added to both the anodic and the cathodic chambers, and the resulting mixture was heated at 35 °C with stirring for 1 h. After removal of solvent of anodic solution under reduced pressure, the residue was quickly filtered through a short column (2 x 4 cm) of silica gel to remove Bu_4NBF_4 using hexane/EtOAc 1:1 containing 1 vol% of triethylamine as an eluent. Purification of the crude product by flash chromatography gave the cyclized carbonyl compounds.



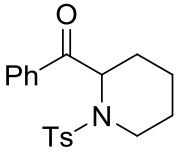
3a

***N*-Tosyl-2-benzoyl-4,4-dimethylpyrrolidine (3a):** Electrochemical oxidation (2.1 F mol^{-1}) of (*E*)-*N*-tosyl-3,3-dimethl-5-phenyl-4-pentenamine (**1a**) (85.0 mg, 0.247 mmol) followed by flash chromatography (hexane/EtOAc 4:1) gave the title compound (78.6 mg, 89%): TLC R_f 0.22 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (s, 3 H), 1.05 (s, 3 H), 1.74 (dd, *J* = 8.8, 12.4 Hz, 1 H), 2.10 (dd, *J* = 8.4, 12.8 Hz, 1 H), 2.41 (s, 3 H), 3.17 (d, *J* = 10.0 Hz, 1 H), 3.32 (d, *J* = 9.6 Hz, 1 H), 5.37 (t, *J* = 8.8 Hz, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.47 (dd, *J* = 7.2, 7.4 Hz, 2 H), 7.57 (t, *J* = 8.0 Hz, 1 H), 7.80 (d, *J* = 8.0 Hz, 2 H), 7.96 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 25.3, 26.0, 39.5, 45.3, 60.4, 63.4, 127.7, 128.5, 128.7, 129.5, 133.4, 135.3, 136.3, 143.3, 197.8; IR (neat) 1699.9, 2965.7, 3027.4 cm^{-1}; LRMS (ESI) *m/z* 358 [$M+H^+$], 357 [M^+], 252 (M-C_6H_5CO), 155 (Ts^-); HRMS (ESI) calcd for $C_{20}H_{24}O_3NS$ [$M+H^+$]: 358.1471, found 358.1475. The spectral data were reported in the preliminary communication.[1]



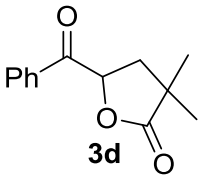
3b

***N*-Tosyl-2-benzoylpyrrolidine (3b):** Electrochemical oxidation (2.5 F mol^{-1}) of (*E*)-*N*-tosyl-5-phenyl-4-pentenamine (**1b**) (78.5 mg, 0.249 mmol) followed by flash chromatography (hexane/EtOAc 10:3) gave the title compound (70.0 mg, 85%): TLC R_f 0.27 (hexane/EtOAc 10:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80-2.02 (m, 3 H), 2.20 (m, 1 H), 2.42 (s, 3 H), 3.48 (t, *J* = 6.4 Hz, 2 H), 5.38 (dd, *J* = 3.2, 8.8 Hz, 1 H), 7.31 (d, *J* = 8.4 Hz, 2 H), 7.48 (dd, *J* = 7.6, 7.6 Hz, 2 H), 7.59 (t, *J* = 7.6 Hz, 1 H), 7.77 (d, *J* = 8.0 Hz, 2 H), 7.97 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.5, 24.6, 30.8, 48.2, 62.9, 127.5, 128.5, 128.7, 129.5, 133.4, 134.8, 135.9, 143.4, 197.4; IR (neat) 1323.2, 1693.8 cm^{-1}; LRMS (ESI) *m/z* 330 [M+H^+], 347 [M+NH_4^+]; HRMS (ESI) calcd for $C_{18}H_{20}O_3NS$ [M+H^+]: 330.1158, found 330.1147. The spectral data were reported in the preliminary communication.[1]



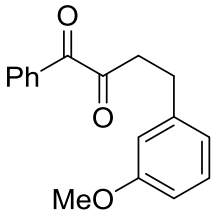
3c

***N*-Tosyl-2-benzoylpiperidine (3c):** Electrochemical oxidation (2.1 F mol^{-1}) of (*E*)-*N*-tosyl-6-phenyl-5-hexenamine (**1c**) (40.0 mg, 0.121 mmol) followed by flash chromatography (hexane/EtOAc 3:1 with 1 vol% of Et_3N) gave the title compound (5.5 mg, 13%): TLC R_f 0.21 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53-2.41 (m, 6 H), 2.41 (s, 3 H), 2.84 (t, *J* = 7.2 Hz, 1 H), 2.97 (q, *J* = 6.4 Hz, 1 H), 4.56 (m, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.49 (t, *J* = 7.2 Hz, 2 H), 7.65 (t, *J* = 7.2 Hz, 1 H), 7.74 (d, *J* = 8.8 Hz, 2 H), 7.95 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ19.6, 21.5, 29.0, 37.9, 42.7, 127.1, 128.9, 129.7, 130.2, 131.8, 134.7, 136.9, 143.5, 192.0, 202.6; HRMS (ESI Negative) calcd for $C_{19}H_{20}NO_3S$ [M-H^-]: 342.1169, found: 342.1162.



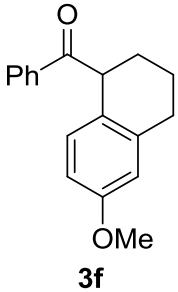
3d

3,3-Dimethyl-5-benzoyltetrahydrofuran-2-one (3d): Electrochemical oxidation (2.1 F mol^{-1}) of **1d** (49.5 mg, 0.242 mmol) followed by flash chromatography (hexane/EtOAc 4:1) gave the title compound (32.3 mg, 61%): TLC R_f 0.57 (hexane/EtOAc 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (s, 3 H), 1.36 (s, 3 H), 2.41 (m, 2 H), 5.63 (t, *J* = 7.2 Hz, 1 H), 7.50 (d, *J* = 7.2 Hz, 2 H), 7.63 (m, 1 H), 7.98 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.4, 25.6, 39.6, 39.8, 76.1, 129.1, 129.2, 134.2, 134.4, 181.1, 194.9; HRMS (ESI) calcd for $C_{13}H_{14}O_3$ [M+H^+]: 219.1016, found: 219.1015.



5e

1-Phenyl-4-(3-anysyl)butan-1,2-dione (5e): Electrochemical oxidation (3.0 F mol^{-1}) of (*E*)-1-phenyl 4-(3-methoxyphenyl)-1-butene (**1e**) (30.3 mg, 0.127 mmol) followed by flash chromatography (hexane/EtOAc 10:1) and preparative GPC gave the title compound (7.8 mg, 23%): TLC R_f 0.33 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02 (t, *J* = 7.6 Hz, 2 H), 3.23 (t, *J* = 7.2 Hz, 2 H), 3.78 (s, 3 H), 6.73-6.78 (m, 2 H), 6.82 (dd, *J* = 0.4, 7.6 Hz, 1 H), 7.20 (t, *J* = 8.0 Hz, 1 H), 7.47, (t, *J* = 7.6 Hz, 2 H), 7.63 (m, 1 H), 7.92 (dd, *J* = 1.2, 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.9, 40.1, 55.1, 111.8, 114.1, 120.7, 128.8, 129.6, 130.2, 131.8, 134.6, 141.7, 159.7, 192.0, 202.2; HRMS (ESI) calcd for $C_{17}H_{17}O_3$ [M+H^+]: 269.1172, found: 269.1165.

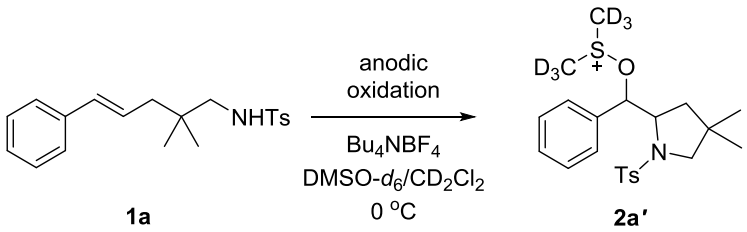


3f

1-Benzoyl-6-methoxy-1,2,3,4-tetrahydronaphthalene (3f): Electrochemical oxidation (2.1 F mol^{-1}) of **1f** (30.5 mg, 0.121 mmol) followed by flash chromatography (hexane/EtOAc 20:1 with 1 vol% of Et_3N) gave the title compound (23.5 mg, 73%): TLC R_f 0.36 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.78 (m, 1 H), 1.92 (m, 1 H), 2.07 (m, 1 H), 2.15, (m, 1 H), 2.85, (m, 2 H), 3.79 (s, 3 H), 4.77 (t, *J* = 6.8 Hz, 1 H), 6.68 (m, 2 H), 6.84, (d, *J* = 8.4 Hz, 1 H), 7.49 (dd, *J* = 7.6, 7.6 Hz, 2 H), 7.58 (m, 1 H), 8.01 (dd, *J* = 1.2, 8.4 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 20.6, 27.7, 29.6, 46.7, 55.1, 112.3, 113.9, 126.8, 128.6, 128.7, 130.3, 132.9, 136.6, 138.9, 158.1, 202.8; IR (neat) 1597.6, 1680.6, 2938.7, 3012.0

cm^{-1}; LRMS (ESI) m/z 266 (M^+), 161($PhCO^-$); HRMS (ESI) calcd for $C_{18}H_{18}O_2$ [M^+]: 266.1307, found: 266.1296. The spectral data were reported in the preliminary communication.[1]

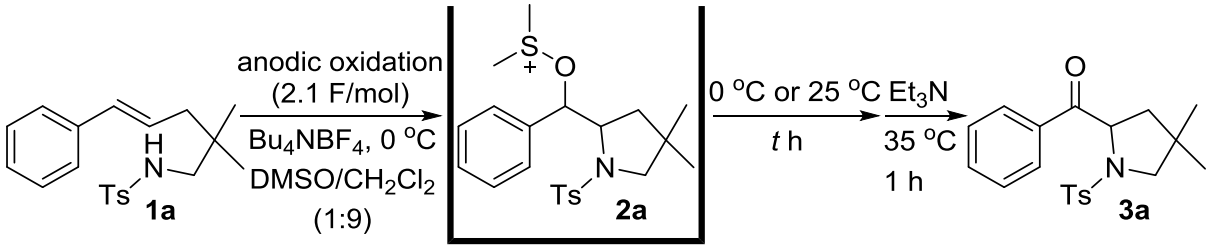
NMR analysis of alkoxysulfonium ion 2a'.



The anodic oxidation was carried out using a divided cell equipped with a carbon felt anode and a platinum plate cathode. In the anodic chamber were placed (*E*)-*N*-tosyl-3,3-dimethl-5-phenyl-4-pentenamine (**1a**) (23.5 mg, 0.068 mmol), Bu_4NBF_4 (49 mg, 0.149 mmol), DMSO-d_6, (0.5 mL), and CD_2Cl_2 (4.5 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (12 μL, 0.14 mmol) and 0.1 M Bu_4NBF_4/CD_2Cl_2 (5.0 mL). The constant current electrolysis (4.0 mA) was carried out at 0 °C with magnetic stirring until 2.1 F mol^{-1} of electricity was consumed. The reaction mixture of the anodic chamber (0.6 mL) was transferred to a 5 mm ϕ NMR tube with septum cap under argon atmosphere at room temperature, and the NMR measurement was carried out at 0 °C. Chemical shifts are reported using methylene signals of CH_2Cl_2 at δ 5.32 as an internal standard. Selected signals for **2a'** (3.5 – 10.0 ppm for ^1H NMR at 0 °C, 60.0 – 200.0 ppm for ^{13}C NMR at 0 °C). ^1H NMR (600 MHz, CD_2Cl_2) δ 3.68 (m, 1 H), 6.15 (s, 1 H), 7.28 (d, *J* = 8.2 Hz, 2 H), 7.39 (m, 5 H), 7.74 (d, *J* = 8.2 Hz, 2 H); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 62.1, 64.8, 90.3, 125.6, 127.6, 129.1, 129.3, 130.3, 135.0, 145.1. The spectral data were reported in the preliminary communication.[1]

Thermal stability of the cyclized alkoxysulfonium ion 2a

After electrochemical oxidation of **1a**, the reaction mixture was stirred at 0 °C or 25 °C for pre-set hours. Then 0.5 mL of Et_3N was added to both the anodic and the cathodic chambers, and the resulting mixture was heated at 35 °C with stirring for 1 h. After removal of solvent of anodic solution under reduced pressure, the residue was quickly filtered through a short column (2 x 4 cm) of silica gel to remove Bu_4NBF_4 using hexane/EtOAc 1:1 containing 1 vol% of triethylamine as an eluent. The reaction yield was determined by ^1H NMR analysis using tetrachloroethane as an internal standard (Figure S1).



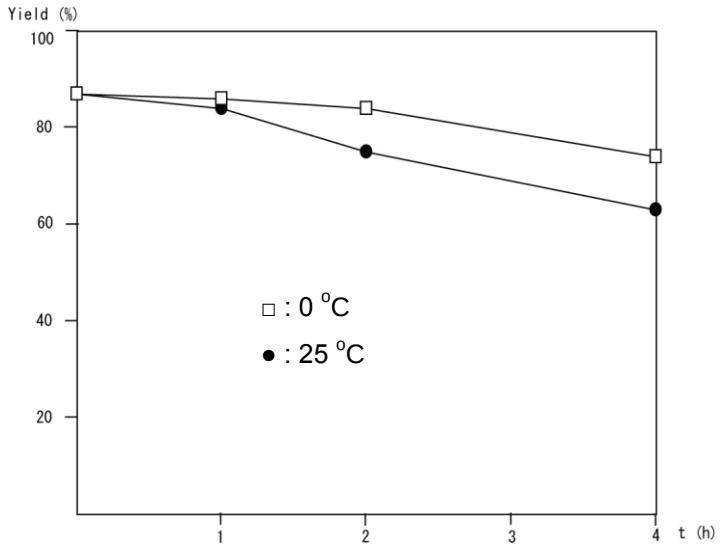
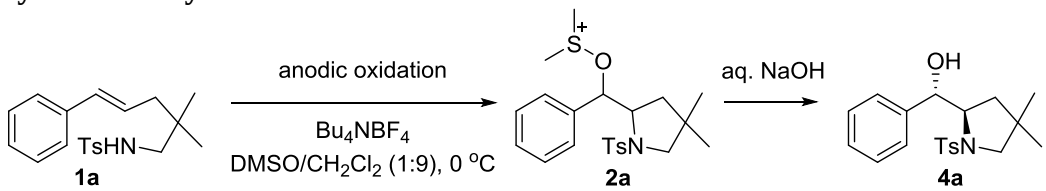


Figure S1. Thermal Stability of Alkoxysulfonium Ion **2a**.

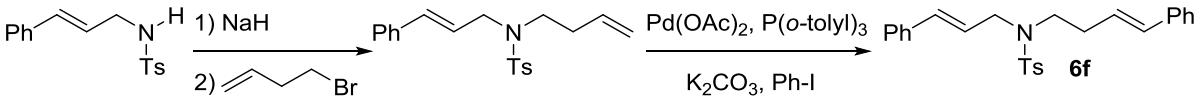
Hydrolysis of alkoxysulfonium ion 2a.



The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 160 mg, dried at 300 °C/1 mmHg for 4 h before use) and a platinum plate cathode (10 mm x 10 mm). In the anodic chamber were placed (*E*)-*N*-tosyl-2,2-dimthyl-5-phenyl-4-pentenamine (**1a**) (43.6, 0.127 mmol), Bu_4NBF_4 (180 mg, 1.5 mmol), DMSO (0.5 mL) and CH_2Cl_2 (4.5 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (25 μL, 0.3 mmol), Bu_4NBF_4 (180 mg, 1.5 mmol), and CH_2Cl_2 (5 mL). The constant current electrolysis (4.0 mA) was carried out at 0 °C with magnetic stirring until TLC analysis indicated that the starting material was consumed (2.1 F mol^{-1} of electricity). Then 0.5 mL of aqueous sodium hydroxide was added to both the anodic and the cathodic chambers, and the resulting mixture was stirred for 5 minutes at 0 °C. The mixture was poured into water, extracted with diethyl ether (10 mL x 3), and dried over Na_2SO_4. After removal of solvent under reduced pressure, the residue was quickly filtered through a short column (2 x 4 cm) of silica gel to remove Bu_4NBF_4 using hexane/EtOAc (1:1) as an eluent. Purification of the crude product by flash chromatography (hexane/EtOAc 4:1) gave **(*S**)-phenyl-[(*R**)-*N*-tosyl-4,4-dimethylpyrrolidin-2-yl]methanol** (**4a**) (36.1 mg, 79%): TLC R_f 0.10 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.32 (s, 3 H), 0.95 (s, 3 H), 1.04 (dd, *J* = 6.8, 12.4 Hz, 1 H), 1.88 (dd, *J* = 10.4, 10.4 Hz, 1 H), 2.44 (s, 3 H), 2.70 (d, *J* = 3.2 Hz, 1 H), 3.16 (d, *J* = 11.2 Hz, 1 H), 3.28 (d, *J* = 10.8 Hz, 1 H), 5.48 (m, 1 H), 7.26 (m, 1 H), 7.36 (m, 6 H), 7.81 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 25.6, 25.9, 36.9, 38.7, 62.5, 66.1, 72.7, 125.7, 127.3, 127.5, 128.2, 129.8, 135.0, 140.2, 143.8; HRMS (ESI) calcd for $C_{20}H_{25}O_3NS$ [M+H$^+$]: 360.1628, found 360.1623. The stereochemistry was determined by the X-ray analysis. The spectral data were reported in the preliminary communication.[8]

Oxidative cyclization of 1,6-dienes

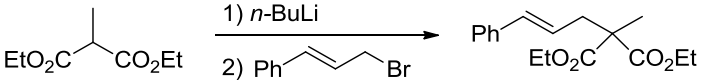
Preparation of *N*-cinnamyl-*N*-((*E*)-4-phenyl-3-buten-1-yl)tosylamide (6f)



To a round-bottom flask was added sodium hydride (55% with oil, 310 mg, 7.1 mmol), and was washed with dry hexane three times. After removal of hexane by vacuum, were added DMF (15 mL), *N*-cinnamyltosylamide (849 mg, 2.96 mmol), and 4-bromo-1-bunene (700 mg, 5.19 mmol), at 0 ^{o}C. Then the mixture was stirred for 12 hours at room temperature. Water was added to the reaction mixture, and the resulting solution was extracted by EtOAc (10 mL x 3) and washed with brine (15 mL x 3). The resulting crude product was purified with flash chromatography (hexane/EtOAc 5:1) to obtain ***N*-cinnamyl-*N*-(3-butenyl)tosylamide** (540 mg, 53%): TLC R_f 0.33 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (q, *J* = 7.2 Hz, 2 H), 2.43 (s, 3 H), 3.24 (dd, *J* = 7.6, 7.6 Hz, 2 H), 3.97 (dd, *J* = 1.2, 6.8 Hz, 2 H), 5.02 (m, 2 H), 5.71 (m, 1 H), 5.97 (dt, *J* = 6.8, 16.0 Hz, 1 H), 6.45 (d, *J* = 15.6 Hz, 1 H), 7.23-7.29 (m, 7 H), 7.73 (d, *J* = 8.4 Hz, 2 H).

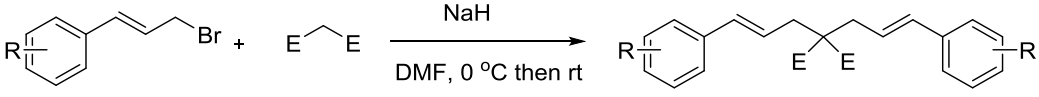
To a 10 mL schlenk flask were added *N*-cinnamyl-*N*-(3-butenyl)tosylamide (500mg, 1.46 mmol), iodobenzene (420 mg, 2.06 mmol), palladium diacetate (43 mg, 0.19 mmol), tri-(*o*-tolyl)phosphine (90 mg, 0.3 mmol), potassium carbonate (400 mg, 2.89 mmol), and DMF (5 mL), and the mixture was stirred for 20 hours at 100 ^{o}C. After cooling to room temperature, the reaction mixture was filtered through a short column (2 x 4 cm) of silica gel by using EtOAc as an eluent. The resulting crude product was purified with flash chromatography (hexane/EtOAc 5:1) to obtain the title compound (150 mg, 25%): TLC R_f 0.32 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3 H), 2.48 (ddt, *J* = 1.2, 7.2, 7.6 Hz, 2 H), 3.30 (dd, *J* = 6.4, 8.0 Hz, 2 H), 3.99 (dd, *J* = 1.2, 6.8 Hz, 2 H), 6.01 (dt, *J* = 6.8, 15.6 Hz,1 H), 6.07 (dt, *J* = 6.8, 16.0 Hz, 1 H), 6.36, (dd, *J* = 1.2, 16.8 Hz, 1 H), 6.47 (d, *J* 15.6 Hz, 1 H), 7.18-7.29 (m, 12 H), 7.73 (d, *J* = 8.4 Hz, 2 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.5, 32.5, 47.1, 50.4, 124.4, 126.4, 126.5, 127.2, 127.9, 128.5, 128.6, 129.7, 132.3, 133.7, 136.1, 137.1, 137.2, 143.2; IR (neat) 1153.4, 1319.3, 1446.5 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{27}NO_2S$ [M+H^{+}]: 418.1833, found: 418.1824.

Preparation of (*E*)-diethyl 1-phenyl-1-penten-4,4-dicarboxylate



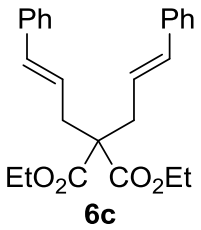
To a round-bottom flask were added diethyl 2-methylmalonate (520 mg, 2.99 mmol) and THF (10 mL). At 0 ^{o}C, was added *n*-BuLi/THF (1.62 M, 2.0 mL). After stirring for 1 hour at room temperature, cinnamyl bromide (700 mg, 3.55 mmol) was added, and the mixture was stirred at room temperature. After 7 hours, water was added to the reaction mixture, and the resulting solution was extracted by EtOAc (20 mL x 3). The resulting crude mixture was purified with flash chromatography (hexane/EtOAc 20:1 – 5:1) to obtain the title compound (700 mg, 81%): TLC R_f 0.47 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1,25 (t, *J* = 7.2 Hz, 6 H), 1.44 (s, 3 H), 2.76 (dd, *J* = 1.6, 7.6 Hz, 2 H), 4.20 (q, *J* = 7.2 Hz, 4 H), 6.10 (dt, *J* = 7.6, 15.6 Hz, 1 H), 6.44 (d, *J* = 16.0 Hz, 1 H), 7.23 (m, 1 H), 7.31 (m, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 20.0, 39.4, 53.8, 61.3, 124.3, 126.2, 127.3, 128.5, 134.0, 137.1, 171.9; HRMS (ESI) calcd for $C_{17}H_{23}O_4$ [M+H^{+}]: 291.1591, found: 291.1582.

Typical procedure for preparation of (*E*,*E*)-diethyl 1,7-diphenyl-1,6-heptadien-4,4-dicarboxylate (6c), (*E*,*E*)-diethyl 1,7-di(4-chlorophenyl)-1,6-heptadien-4,4-dicarboxylate (6d), and 9,9-dicinnamylfluorene (6e)



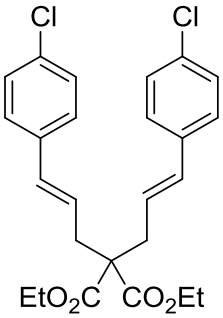
To a round-bottom flask was added sodium hydride (3 equiv.) and washed by hexane three times. After removal of hexane by vacuum, were added DMF, cinnamyl bromide or 4-

chlorocinnamyl chloride (2.2 equiv.), and substrate at 0 °C. Then, the mixture was allowed to warm to room temperature and stirred for 4 hours. Water was added to the reaction mixture at 0 °C, and the solution was extracted with hexane/EtOAc (1:1) and washed with brine. Purification of the crude product by flash chromatography or preparative GPC gave the 1,6-diene starting materials.



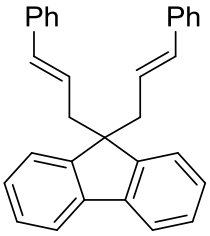
6c

(*E*,*E*)-Diethyl 1,7-diphenyl-1,6-heptadien-4,4-dicarboxylate (6c): Reaction of diethyl malonate (720 mg, 4.4 mmol) with cinnamyl bromide (2.2 g, 11.2 mmol) followed by flash chromatography (hexane/ EtOAc 9:1) and preparative GPC gave the title compound (900 mg, 52%): TLC R_f 0.48 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (t, *J* = 7.2 Hz, 3 H), 1.25 (t, *J* = 7.2 Hz, 3 H), 2.84 (d, *J* = 7.6 Hz, 4 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 4.21 (q, *J* = 7.2 Hz, 2 H) 6.09 (dt, *J* = 7.6, 15.6 Hz, 1 H), 6.09 (dt, *J* = 7.6, 15.6 Hz, 1 H), 6.47 (d, *J* = 15.6 Hz, 2 H), 7.22-7.34 (m, 10 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 36.6, 57.9, 61.3, 124.0, 126.2, 127.4, 128.5, 134.0, 137.1, 170.8; HRMS (ESI) calcd for $C_{25}H_{28}O_4$ [M+H$^+$]: 393.2060, found: 393.2054.



6d

(*E*,*E*)-Diethyl 1,7-di(4-chlorophenyl)-1,6-heptadien-4,4-dicarboxylate (6d): Reaction of diethyl malonate (370 mg, 2.31 mmol) with 4-chlorocinnamyl chloride (900 mg, 4.81 mmol) followed by flash chromatography (hexane/ EtOAc 9:1) and preparative GPC gave the title compound (130 mg, 12%): TLC R_f 0.38 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 3 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 2.81 (d, *J* = 7.6 Hz, 4 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 6.06 (dt, *J* = 7.2, 14.8 Hz, 2 H), 6.40 (d, *J* = 14.8 Hz, 2 H), 7.25 (m, 8 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.2, 36.7, 57.9, 61.4, 124.7, 127.4, 128.7, 132.8, 133.1, 135.5, 170.7; HRMS (ESI) calcd for $C_{25}H_{26}Cl_2O_4$ [M+H$^+$]: 461.1281, found: 461.1273.

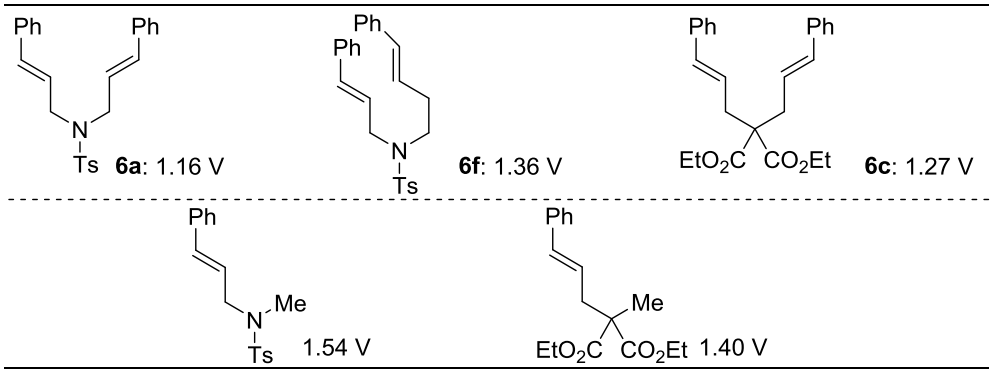


6e

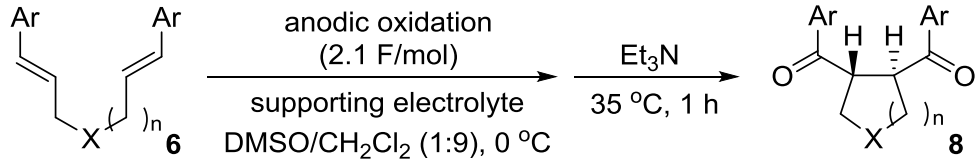
9,9-Dicinnamylfluorene (6e): Reaction of fluorene (890 mg, 5.4 mmol) with cinnamyl bromide (2.2 g, 11.2 mmol) followed by preparative GPC separation gave the title compound (1.3 g, 60%): TLC R_f 0.53 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83 (dd, *J* = 1.2, 7.2 Hz, 4 H), 5.79 (dt, *J* = 7.2, 16.0 Hz, 2 H), 6.22 (d, *J* = 16.0 Hz, 2 H), 7.07 (m, 6 H), 7.15 (m, 4 H), 7.29 (m, 4 H), 7.44 (d, *J* = 8.0 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 42.3, 54.7, 119.9, 123.7, 125.8, 126.0, 126.87, 126.93, 127.2, 128.3, 132.8, 137.4, 140.5, 149.3; HRMS (ESI) calcd for $C_{31}H_{26}$ [M$^+$]: 398.2035, found: 398.2029.

Oxidation potentials of deiens and monoenes

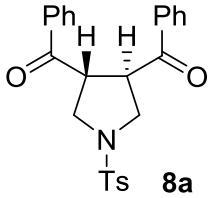
Table S2. Oxidation potentials (V vs. SCE) of **6a**, **6c**, **6f**, *N*-methyl-*N*-tosylcinnamylamine, and (*E*)-diethyl 1-phenyl-1-penten-4,4-dicarboxylate.



Typical procedure for oxidation of dienes

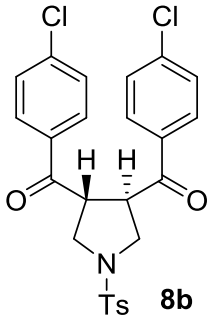


The anodic oxidation was carried out using an H-type divided cell (4G glass filter) equipped with a carbon felt anode (Nippon Carbon JF-20-P7, ca. 80 mg, dried at 300 °C/1 mmHg for 4 h before use) and a platinum plate cathode (10 mm x 10 mm). In the anodic chamber were placed 0.125 mmol of 1,6-dienes **6**, a supporting electrolyte ($Bu_4NB(C_6F_5)_4$ (460 mg, 0.50 mmol) or Bu_4NBF_4 (490 mg, 0.50 mmol)), DMSO (0.5 mL) and CH_2Cl_2 (4.5 mL). In the cathodic chamber were placed trifluoromethanesulfonic acid (30 μL, 0.34 mmol), a supporting electrolyte ($Bu_4NB(C_6F_5)_4$ (460 mg, 0.50 mmol) or Bu_4NBF_4 (490 mg, 0.50 mmol)) and CH_2Cl_2 (5 mL). The constant current electrolysis (4.0 mA) was carried out at 0 °C with magnetic stirring until TLC analysis indicated that the alkene was consumed. Then 0.3 mL of Et_3N was added to both the anodic and the cathodic chambers, and the resulting mixture was heated at 35 °C with stirring for 1 h. After removal of solvent under reduced pressure, the residue was quickly filtered through a short column (2 x 4 cm) of silica gel to remove the supporting electrolyte by using hexane/EtOAc 1:1 containing 1 vol% of triethylamine as an eluent. Purification of the crude product by flash chromatography gave the cyclized carbonyl compounds.



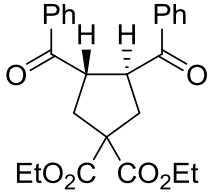
8a

***trans*-3,4-Dibenzoyl-*N*-tosylpyrroridine (8a):** Electrochemical oxidation (2.1 F mol^{-1}, using $Bu_4NB(C_6F_5)_4$) of *N*,*N*-dicinnamyltosylamine (**6a**) (45.6 mg, 0.113 mmol) followed by flash chromatography (hexane/EtOAc 3:1) gave the title compound (36.4 mg, 72%): TLC R_f 0.38 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3 H), 3.40 (m, 2 H), 3.81 (m, 2 H), 4.50 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 7.58 (tt, *J* = 1.2 7.6 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 47.1, 50.8, 127.7, 128.6, 128.8, 129.8, 132.7, 133.8, 135.3, 144.0, 197.3; IR (neat) 1342.5, 1674.2 cm^{-1}; LRMS (ESI) m/z 434 [M+H^+], 451 [M+NH_4^+]; HRMS (ESI) calcd for $C_{25}H_{24}O_4NS$ [M+H^+]: 434.1421, found 434.1408. The stereochemistry was determined by the X-ray analysis. The spectral data were reported in the preliminary communication.[1]



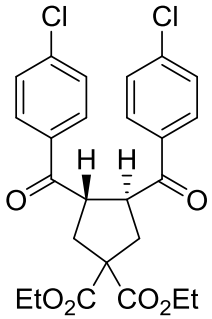
8b

***trans*-3,4-Di(4-chlorobenzoyl)-*N*-tosyl-pyrrolidine (8b):** Electrochemical oxidation (2.1 F mol^{-1}, using $Bu_4NB(C_6F_5)_4$) of *N*,*N*-di-4-chlorocinnamyl-*N*-tosylamine (**6b**) (59.2 mg, 0.125 mmol), followed by flash chromatography (hexane/EtOAc 5:1 with 1 vol% of Et_3N) gave the title compound (56.4 mg, 90%): TLC R_f 0.17 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 3.36 (m, 2 H), 3.79 (m, 2 H), 4.43 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.44 (dt, *J* = 2.0, 8.8 Hz, 4 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 7.81 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 47.2, 50.7, 127.7, 129.3, 129.9, 130.0, 132.7, 133.6, 140.6, 144.1, 196.1; IR (neat) 1670.4, 1685.8 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{22}NO_4SCl_2$ (M+H^+): 502.0641, found: 502.0638. The spectral data were reported in the preliminary communication.[1]



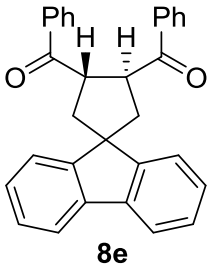
8c

***trans*-Diethyl 3,4-dibenzoylcyclopentane-1,1-dicarboxylate (8c):** Electrochemical oxidation (2.1 F mol^{-1} using Bu_4NBF_4) of (*E*,*E*)-diethyl 1,7-diphenyl-1,6-heptadien-5,5-dicarboxylate (**6c**) (48.8 mg, 0.124 mmol) followed by flash chromatography (hexane/EtOAc 5:1) gave the title compound (28.2 mg, 54%): TLC R_f 0.15 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 6 H), 2.33 (dd, *J* = 9.2, 13.2 Hz, 2 H), 3.01 (dd, *J* = 8.4, 13.2 Hz, 2 H), 4.20 (t, *J* = 7.2 Hz, 4 H), 4.20 (m, 2 H), 4.53 (m, 2 H), 7.46 (m, 4 H), 7.55 (t, *J* = 7.2 Hz, 2 H), 8.00 (d, *J* = 7.2 Hz, 4 H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.0, 38.2, 48.2, 60.2, 61.9, 128.7, 128.7, 133.3, 136.0, 170.9, 200.0; IR (neat) 1246.0, 1678.1, 1728.2 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{27}O_6$ [M+H^+]: 423.1802, found: 423.1789.



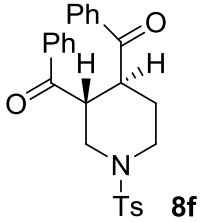
8d

***trans*-Diethyl 3,4-di(4-chlorobenzoyl)cyclopentane-1,1-dicarboxylate (8d):** Electrochemical oxidation (2.1 F mol^{-1} using Bu_4NBF_4) of (*E*,*E*)-diethyl 1,7-di(4-chlorophenyl)-1,6-heptadien-5,5-dicarboxylate (**6d**) (56.6 mg, 0.123 mmol) followed by flash chromatography (hexane/EtOAc 7:1 with 1 vol% of Et_3N) gave the title compound (43.1 mg, 71%): TLC R_f 0.29 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 (t, *J* = 7.2 Hz, 6 H), 2.28 (dd, *J* = 9.2, 13.2 Hz, 2 H), 2.97 (dd, *J* = 8.4, 13.2 Hz, 2 H), 4.20 (m, 4 H), 4.43 (m, 2 H), 7.43 (dd, *J* = 2.0, 6.4 Hz, 4 H), 7.93 (dd, *J* = 2.0, 6.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 38.6, 48.2, 60.1, 62.0, 129.0, 130.1, 134.3, 140.0, 170.8, 198.5; IR (neat) 1246.0, 1678.1, 1728.2 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{25}O_6Cl_2$ [M+H^+]: 491.1023, found: 491.1020.



8e

***trans*-3,4-Dibenzoyl-spiro[cyclopentane-1,9'-fluorene] (8e):** Electrochemical oxidation (2.1 F mol^{-1} using Bu_4NBF_4) of 9,9-dicinnamylfulorene (**6e**) (99.8 mg, 0.250 mmol) followed by flash chromatography (hexane/EtOAc 5:1) gave the title compound (77.1 mg, 72%): TLC R_f 0.32 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (m, 2 H), 2.72 (m, 2 H), 5.12 (m, 2 H), 7.36 (m, 4 H), 7.45 (m, 4 H), 7.54 (m, 2 H), 7.70 (m, 4 H), 8.07 (d, *J* = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.2, 49.9, 57.8, 119.8, 123.2, 127.4, 128.0, 128.7, 128.8, 133.4, 136.4, 139.4, 152.3, 200.8; HRMS (ESI) calcd for $C_{31}H_{24}O_2$ [M+H^+]: 429.1849, found: 429.1847.



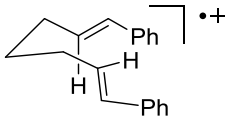
8f

***trans*-3,4-Dibenzoyl-*N*-tosyl-piperidine (8f):** Electrochemical oxidation (2.1 F mol^{-1}, using $Bu_4NB(C_6F_5)_4$) of *N*-cinnamyl-*N*-((*E*)-4-phenyl-3-buten-1-yl)tosylamide (**6f**) (52.3 mg, 0.125 mmol) followed by flash chromatography (hexane/EtOAc 5:1) gave the title compound (25.2 mg, 45%): TLC R_f 0.54 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (dq, *J* = 4.0, 12.8 Hz, 1 H), 2.17 (dd, *J* = 3.2, 13.2 Hz, 1 H), 2.30 (t, *J* = 11.6 Hz, 1H), 2.45 (s, 3 H), 2.46 (m, 1 H), 3.83 (dt, *J* = 3.2, 13.6 Hz, 1 H), 3.99 (d, *J* = 13.6 Hz, 1 H), 4.16 (dd, *J* = 3.6, 11.6 Hz, 1 H), 4.26 (dt, *J* = 3.6, 11.2 Hz, 1 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 7.43 (m, 2 H), 7.55 (m, 3 H), 7.63 (m, 3 H), 7.89 (d, *J* = 8.0 Hz, 2 H), 8.05 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 28.7, 45.2, 45.5, 46.1, 48.2, 127.6, 128.4, 128.68, 128.73, 128.9, 129.8, 132.7, 133.4, 133.9, 135.3, 144.0, 200.0, 200.9; HRMS (ESI) calcd for $C_{26}H_{26}NO_4$ [M+H^+]: 448.1577, found: 448.1580.

Theoretical calculation of cation radicals and transition state

Table S3. Cartesian coordinates (Å) of the optimized structure of the cation radical of (*E*,*E*)-1,7-diphenyl-1,6-heptadiene conformer A (C_1 symmetry) calculated at UB3LYP/6-31+G(d)

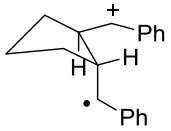
level.



conformer A

Atom	X	Y	Z	Atom	X	Y	Z
C	0.659156	1.616821	-0.74536	H	1.457974	3.343391	-1.79535
C	0.944392	3.150389	-0.84827	H	0.004269	3.711207	-0.88287
C	1.793358	3.560301	0.380129	H	1.204038	4.189399	1.056232
C	2.175095	2.249284	1.07959	H	2.677587	4.139235	0.097359
C	0.969441	1.304314	0.851957	H	3.071233	1.806958	0.625235
C	1.254862	-0.10209	1.105681	H	2.376334	2.373473	2.148622
C	-0.69437	1.240084	-1.13435	H	0.103462	1.666411	1.413753
C	-1.10333	0.10278	-1.86377	H	2.220182	-0.46139	0.745752
C	0.426985	-1.05803	1.732967	H	-1.48918	1.90274	-0.78914
C	0.899859	-2.40134	1.856292	H	1.882794	-2.65047	1.464258
C	0.127834	-3.37559	2.466271	H	0.50254	-4.39075	2.556485
C	-1.14053	-3.04701	2.971509	H	-1.74429	-3.81031	3.454137
C	-1.6296	-1.73468	2.866356	H	-2.60766	-1.48883	3.269332
C	-0.86292	-0.75022	2.263096	H	-1.24634	0.263252	2.208011
C	-0.18915	-0.85795	-2.3933	H	0.879261	-0.72313	-2.2617
C	-0.65336	-1.95894	-3.09599	H	0.050694	-2.68147	-3.4981
C	-2.03084	-2.13577	-3.30342	H	-2.3855	-2.99651	-3.8633
C	-2.95155	-1.20121	-2.80215	H	-4.01485	-1.34074	-2.97237
C	-2.49933	-0.10088	-2.09375	H	-3.20777	0.625605	-1.70358
H	1.417437	1.057509	-1.29915				

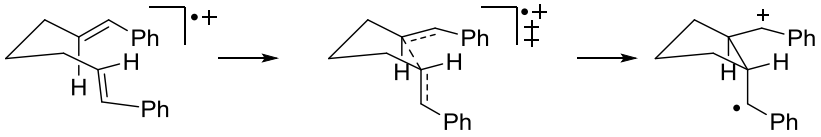
Table S4. Cartesian coordinates of the optimized structure of the cation radical of *trans*-cyclized cation radical (C_1 symmetry) calculated at UB3LYP/6-31+G(d) level.



Atom	X	Y	Z	Atom	X	Y	Z
C	-2.02898	0.291167	0.586203	H	-3.84807	-0.14017	1.68644
C	-3.58291	0.30794	0.721687	H	-3.97119	1.33172	0.727061
C	-4.13504	-0.5452	-0.42424	H	-4.12934	0.015032	-1.36881
C	-3.1551	-1.71844	-0.49136	H	-5.16599	-0.86739	-0.24668
C	-1.74374	-1.08916	-0.37402	H	-3.32885	-2.40075	0.350581
C	-0.74026	-1.91415	0.278755	H	-3.23277	-2.30545	-1.41218

C	-1.4746	1.433348	-0.12419	H	-1.4155	-0.73104	-1.35177
C	-0.26011	2.114597	0.121311	H	-1.0734	-2.43006	1.180604
C	0.623347	-2.07574	-0.05932	H	-2.04566	1.773397	-0.98946
C	1.444624	-2.87898	0.789485	H	0.997623	-3.35106	1.660685
C	2.791195	-3.05863	0.516403	H	3.402056	-3.67261	1.170307
C	3.362618	-2.44578	-0.60952	H	4.417902	-2.58637	-0.82394
C	2.574962	-1.65955	-1.4672	H	3.024398	-1.19884	-2.34216
C	1.226472	-1.47757	-1.2062	H	0.628855	-0.8763	-1.88406
C	0.611175	1.80061	1.207101	H	0.348017	1.012985	1.906205
C	1.795636	2.497626	1.3821	H	2.452367	2.250701	2.211746
C	2.146478	3.530883	0.497043	H	3.074672	4.076345	0.645172
C	1.301014	3.86921	-0.57083	H	1.573559	4.674372	-1.24697
C	0.117233	3.174155	-0.75912	H	-0.54089	3.431564	-1.58541
H	-1.54702	0.133612	1.551532				

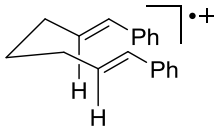
Table S5. Cartesian coordinates of the optimized structure of transition state from the conformer A to the cation radical of *trans*-cyclized cation radical (C_1 symmetry) calculated at UB3LYP/6-31+G(d) level.



Atom	X	Y	Z	Atom	X	Y	Z
C	-2.05448	0.220629	0.682371	H	-3.75784	-0.58958	1.71732
C	-3.56549	-0.02143	0.800284	H	-4.09477	0.93352	0.898231
C	-4.0383	-0.82539	-0.41566	H	-4.04739	-0.19885	-1.31754
C	-3.00215	-1.94421	-0.55403	H	-5.05327	-1.21357	-0.28455
C	-1.60826	-1.32808	-0.46589	H	-3.13505	-2.67878	0.250236
C	-0.58703	-2.02127	0.234948	H	-3.09515	-2.4827	-1.5052
C	-1.60983	1.333882	-0.07856	H	-1.29521	-0.8372	-1.38544
C	-0.39464	2.067576	0.059283	H	-0.91447	-2.63097	1.078156
C	0.820086	-1.9888	0.003661	H	-2.26346	1.655606	-0.89073
C	1.669399	-2.69947	0.898214	H	1.226751	-3.23087	1.737178
C	3.043929	-2.72387	0.709258	H	3.67829	-3.27245	1.399049
C	3.610259	-2.04411	-0.37845	H	4.685462	-2.06844	-0.53164
C	2.792427	-1.34188	-1.27863	H	3.237257	-0.82852	-2.12603
C	1.418245	-1.31246	-1.0967	H	0.799238	-0.77877	-1.81067
C	0.550154	1.832146	1.097553	H	0.369241	1.054742	1.832683
C	1.700551	2.600489	1.189457	H	2.411255	2.417024	1.989893

C	1.944092	3.623921	0.258861	H	2.844035	4.226624	0.342384
C	1.025994	3.878087	-0.76981	H	1.214142	4.674498	-1.48358
C	-0.12742	3.113138	-0.86922	H	-0.84416	3.311949	-1.66229
H	-1.49016	0.023243	1.590815				

Table S6. Cartesian coordinates (Å) of the optimized structure of the cation radical of (*E*,*E*)-1,7-diphenyl-1,6-heptadiene conformer B (C_1 symmetry) calculated at UB3LYP/6-31+G(d) level.



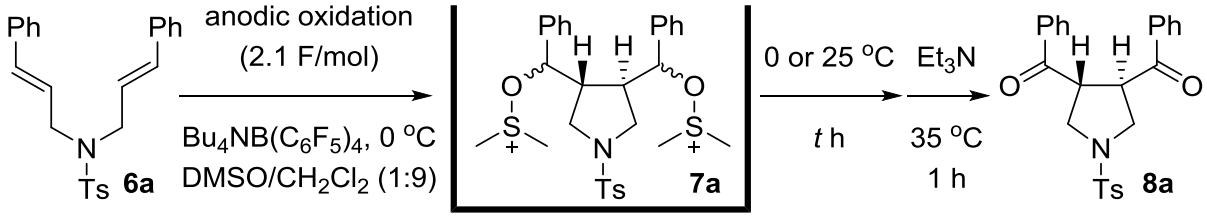
conformer B

Atom	X	Y	Z	Atom	X	Y	Z
C	4.3505	0.00008	0.252852	H	4.567696	-0.00028	1.328907
C	3.469988	1.207416	-0.11469	H	3.490612	1.36456	-1.20147
C	2.047088	0.78904	0.343284	H	3.789679	2.143479	0.354132
C	2.047275	-0.78933	0.342915	H	1.858015	1.153531	1.35646
C	3.470172	-1.20713	-0.11552	H	1.858522	-1.15432	1.355976
C	0.933052	-1.19296	-0.58946	H	3.790075	-2.1435	0.352554
C	0.93297	1.192812	-0.58915	H	3.490708	-1.36343	-1.20243
C	-0.31472	-1.76808	-0.24835	H	1.187162	-1.20859	-1.64886
C	-1.1805	-2.20094	-1.29773	H	1.187196	1.208506	-1.64852
C	-0.75388	-1.93511	1.097584	H	-0.85792	-2.08423	-2.32944
C	-2.40841	-2.77729	-1.01544	H	-0.11964	-1.62019	1.919568
C	-1.98396	-2.51428	1.369961	H	-3.05254	-3.11139	-1.82322
C	-2.81381	-2.93649	0.319022	H	-2.30484	-2.6463	2.399005
C	-0.3148	1.768002	-0.24814	H	-3.7741	-3.39346	0.540805
C	-1.18043	2.200991	-1.29759	H	-0.85774	2.084318	-2.32927
C	-0.75409	1.934984	1.097758	H	-0.11997	1.61998	1.919795
C	-2.40834	2.777402	-1.0154	H	-3.05235	3.111592	-1.82323
C	-1.98416	2.514218	1.37003	H	-2.30515	2.646202	2.399046
C	-2.81387	2.936545	0.319025	H	-3.77416	3.393563	0.540728
H	5.310118	0.000334	-0.2735				

Thermal stability of alkoxysulfonium ion 7a.

After electrochemical oxidation of **6a**, the reaction mixture was stirred at 0 ^{o}C or 25 ^{o}C for pre-set hours. Then 0.5 mL of Et_3N was added to both the anodic and the cathodic chambers, and the resulting mixture was heated at 35 ^{o}C with stirring for 1 h. After removal of solvent of anodic solution under reduced pressure, the residue was quickly filtered through a short column (2 x 4 cm) of silica gel to remove Bu_4NBF_4 using hexane/EtOAc 1:1 containing 1 vol% of triethylamine as an eluent. The reaction yield was determined by ^{1}H NMR analysis

using tetrachloroethane as an internal standard (Figure S2).



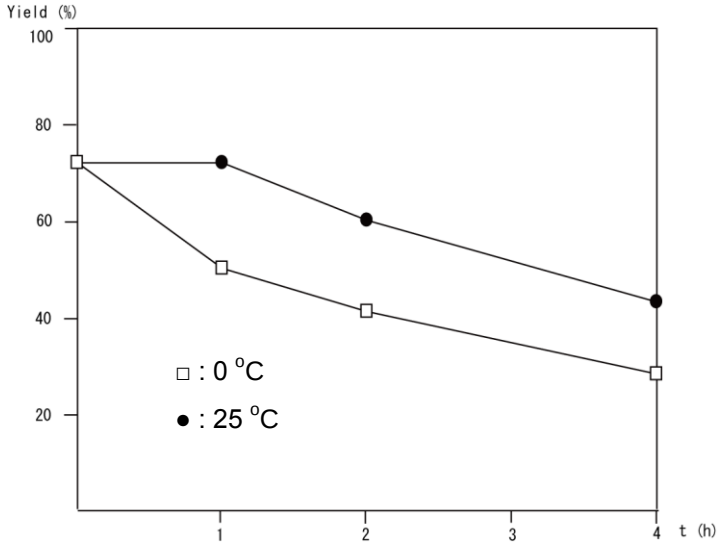
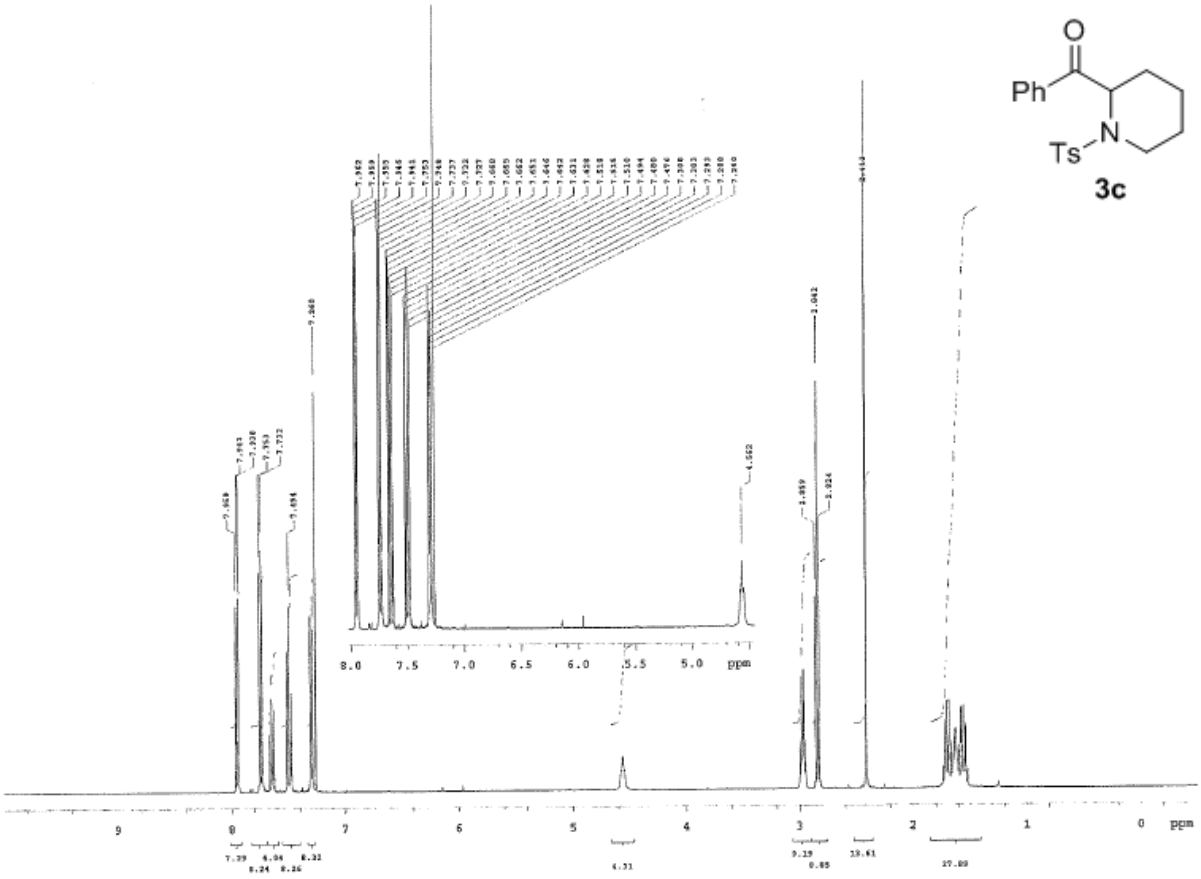


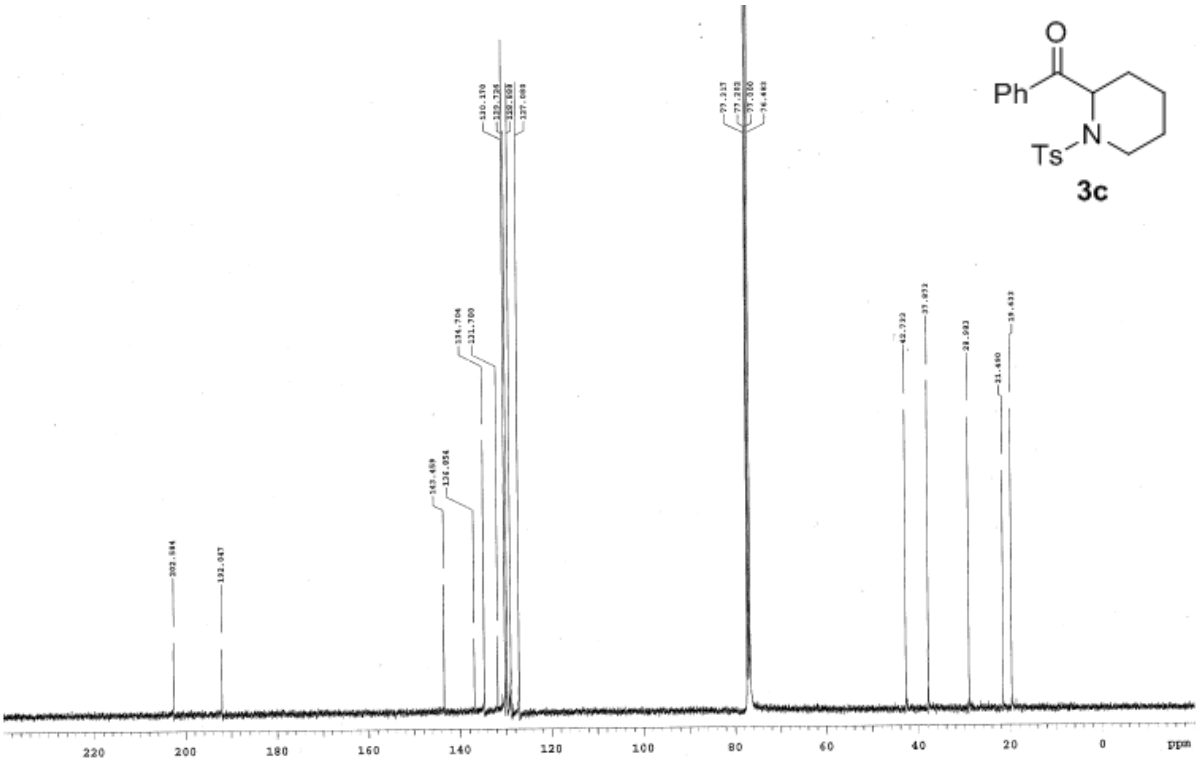
Figure S2. Thermal Stability of Alkoxysulfonium Ion **7a**.

Reference

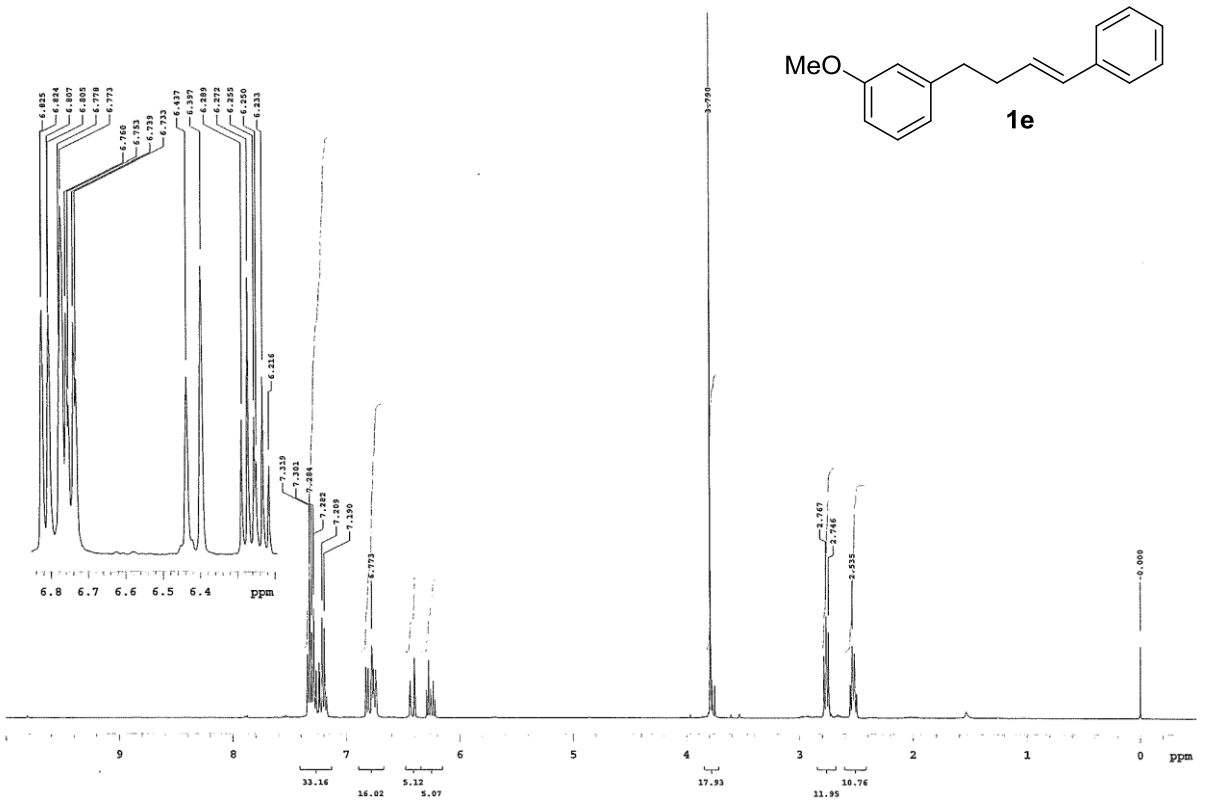
[1] Y. Ashikari, T. Nokami and J. Yoshida, *J. Am. Chem. Soc.*, 2011, **133**, 11840.
[2] B. Schlummer and J. F. Hartwig, *Org. Lett.*, 2002, **4**, 1471.
[3] S. G. Jarboe and P. Beak, *Org. Lett.*, 2000, **2**, 357.
[4] D. G. New, Z. Tesfai and K. D. Moeller, *J. Org. Chem.*, 1996, **61**, 1578.
[5] S. E. Gibson, K. A. C. Kaufmann, P. R. Haycock, A. J. P. White, D. J. Hardick and M. J. Tozer, *Organometallics*, 2007, **26**, 1578.
[6] K. Matsuomoto, S. Fujie, K. Ueoka, S. Suga and J. Yoshida, *Angew. Chem., Int. Ed.*, 2008, **47**, 2506.
[7] Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.
[8] Y. Ashikari, T. Nokami and J. Yoshida, *Org. Lett.*, 2012, **14**, 938.

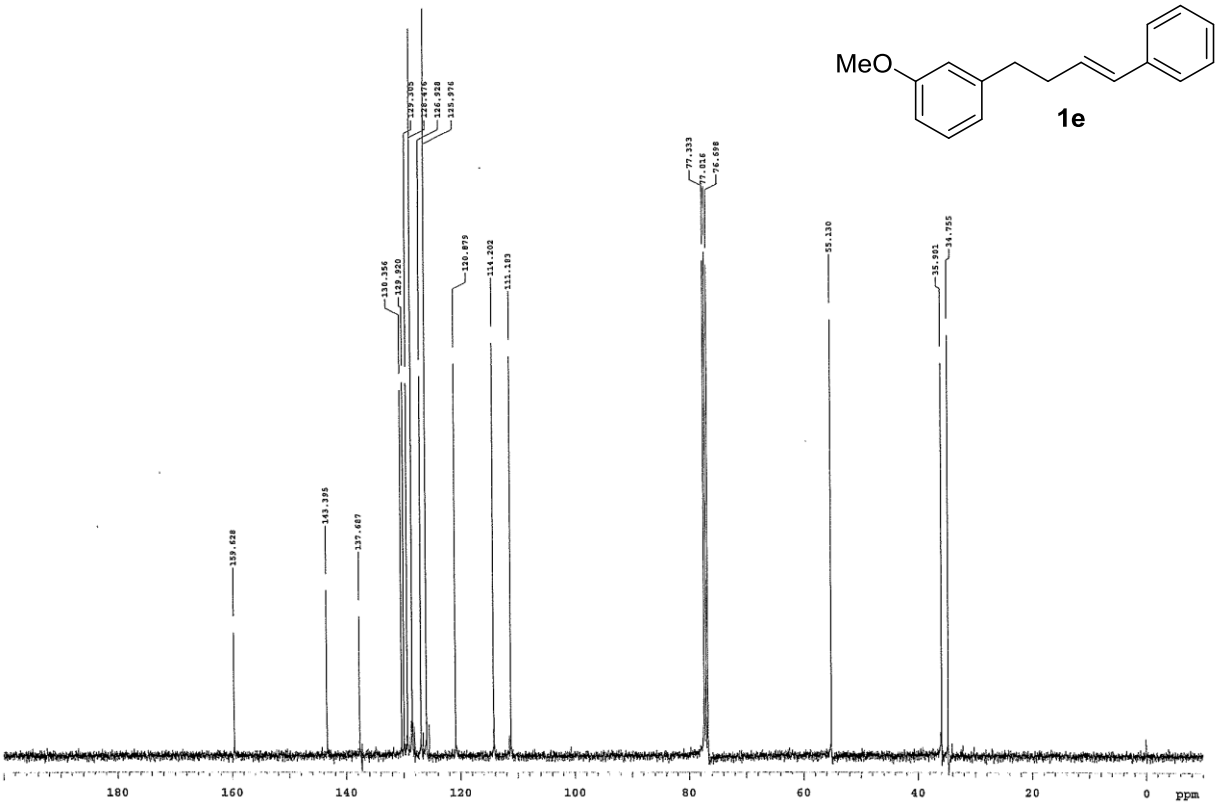
^{1}H NMR and ^{13}C NMR spectra of 3c





^{1}H NMR and ^{13}C NMR spectra of 1e





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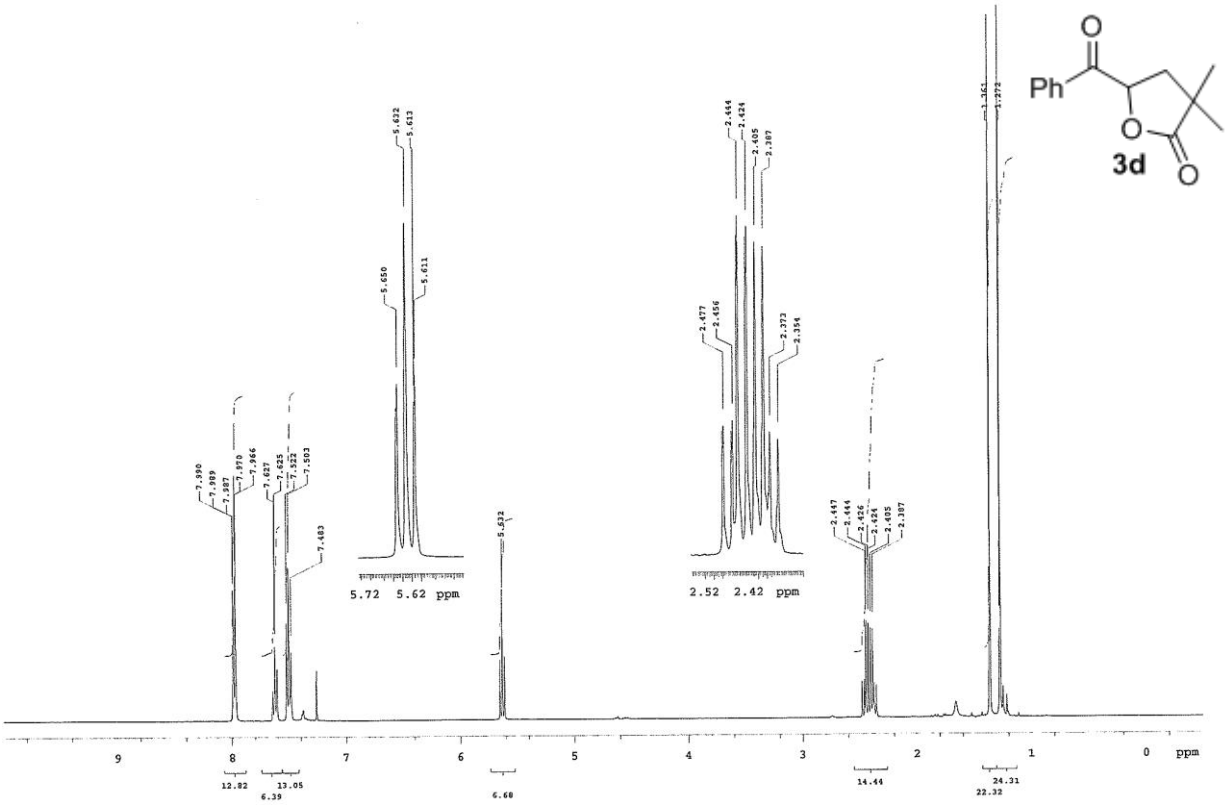
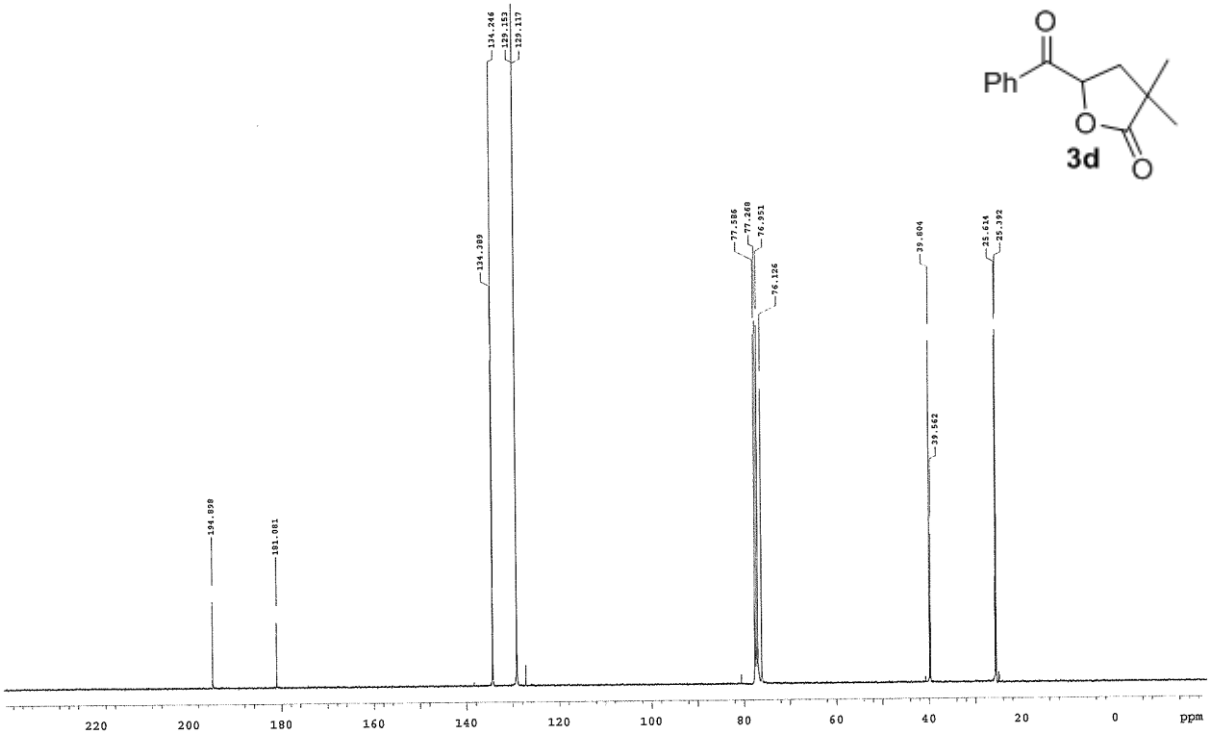
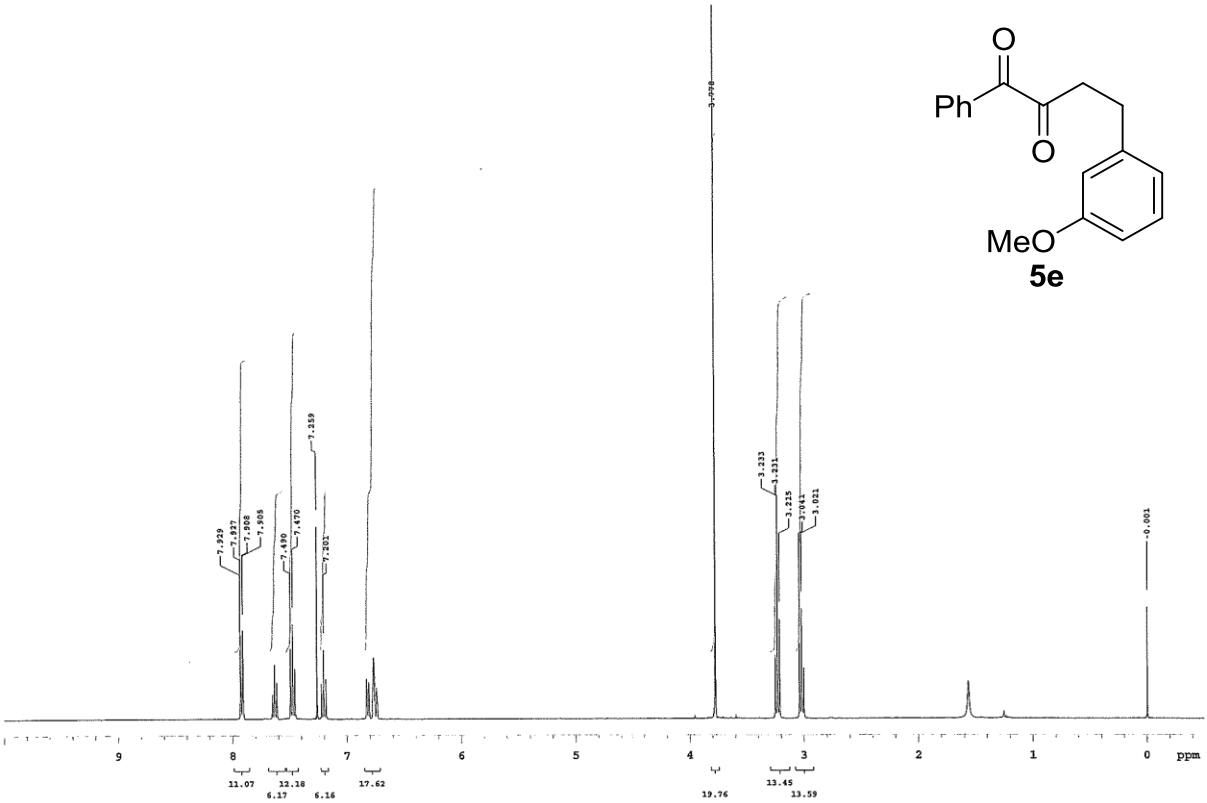
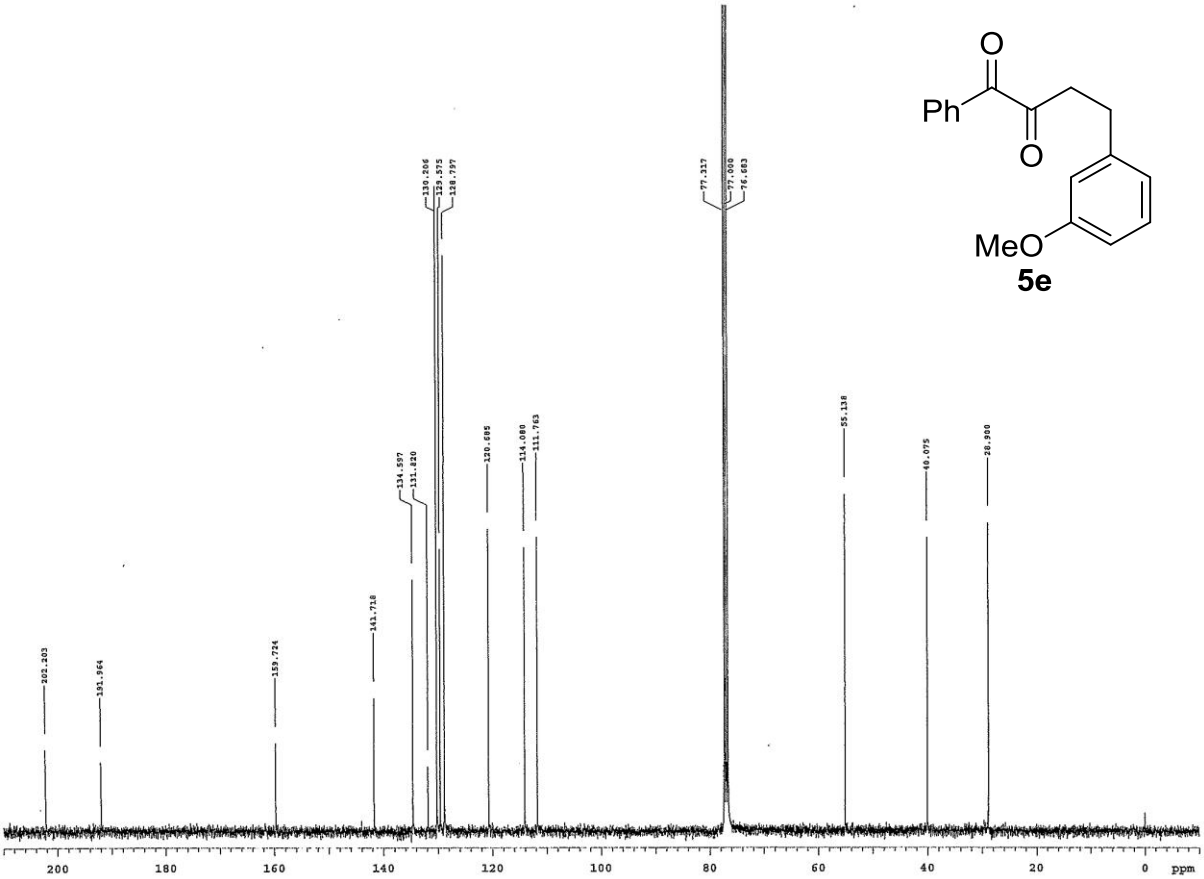


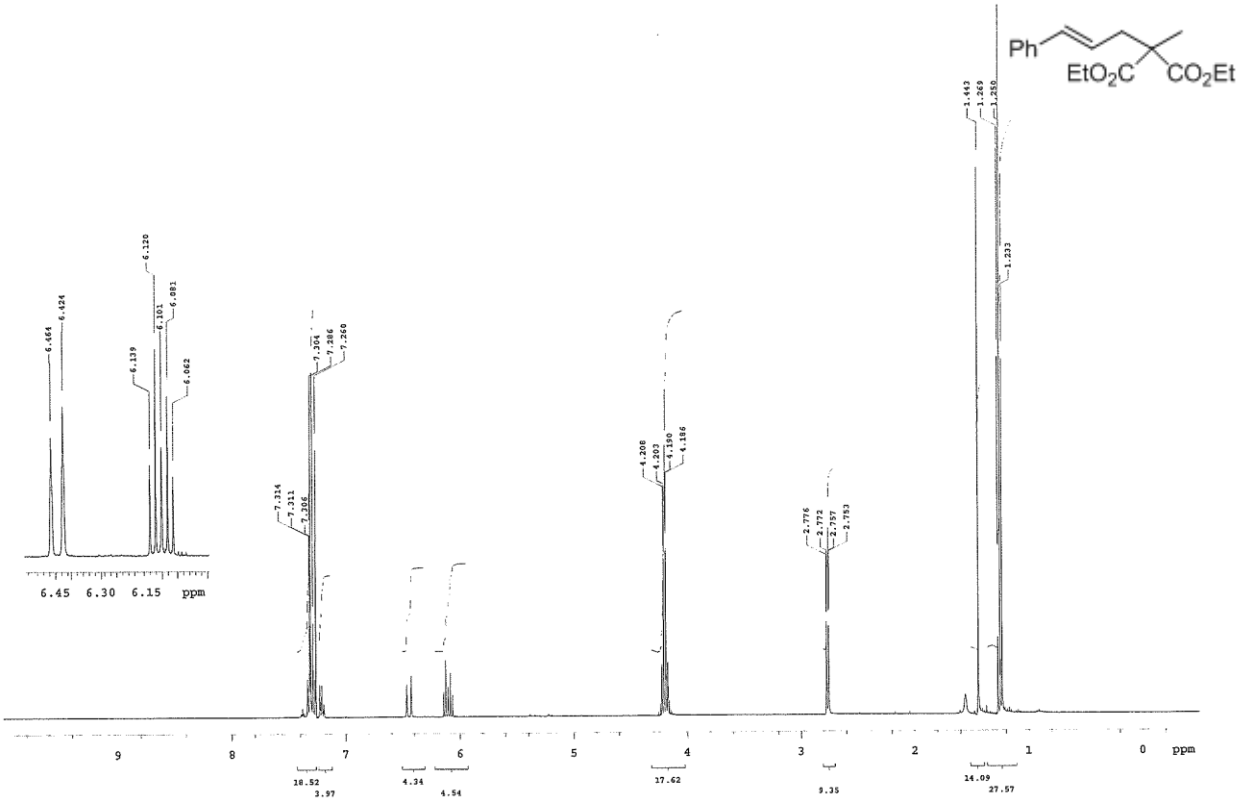


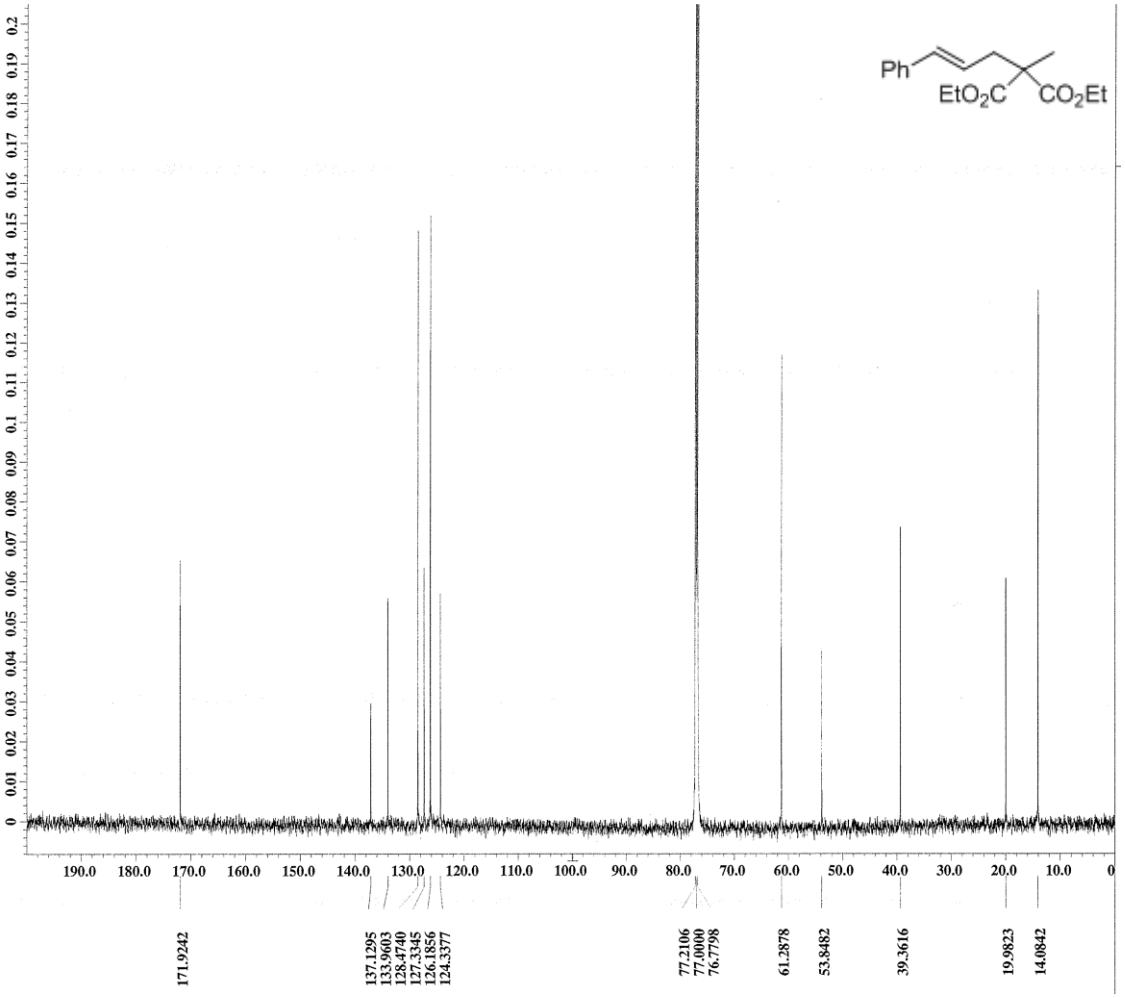
^{1}H NMR and ^{13}C NMR spectra of 5e



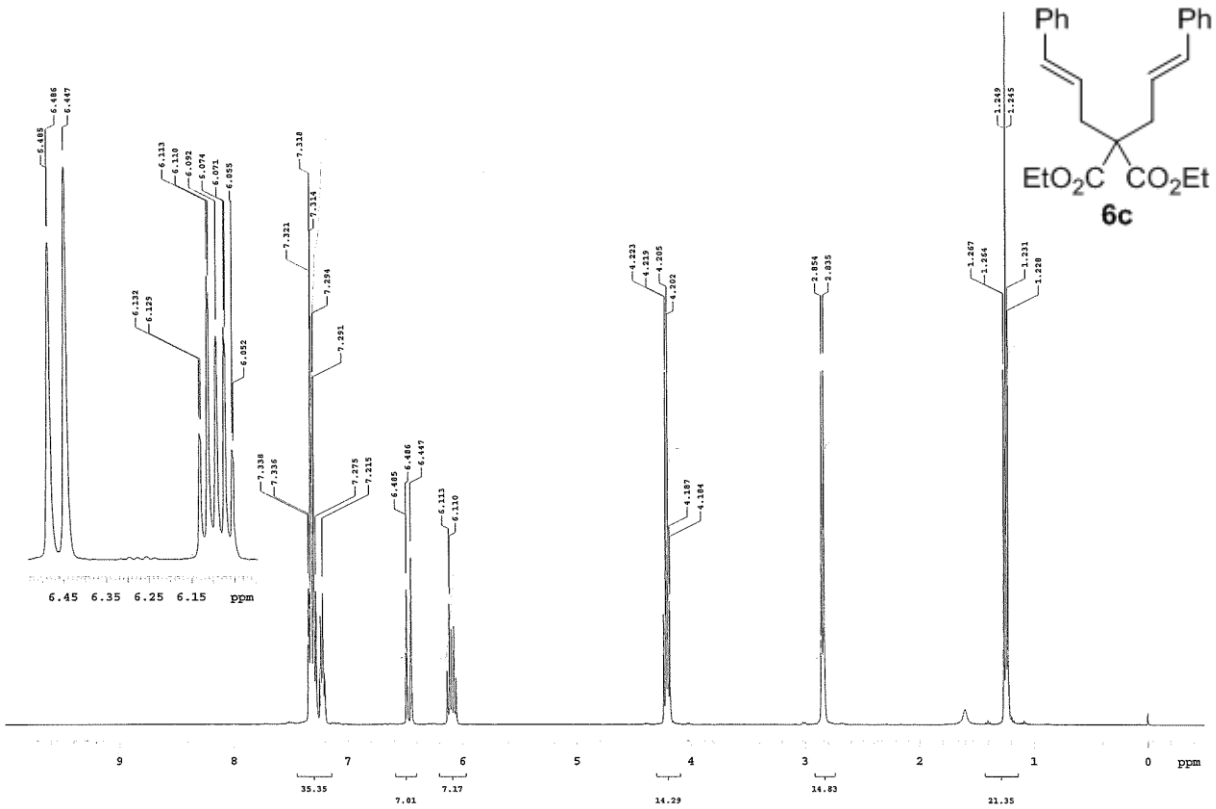


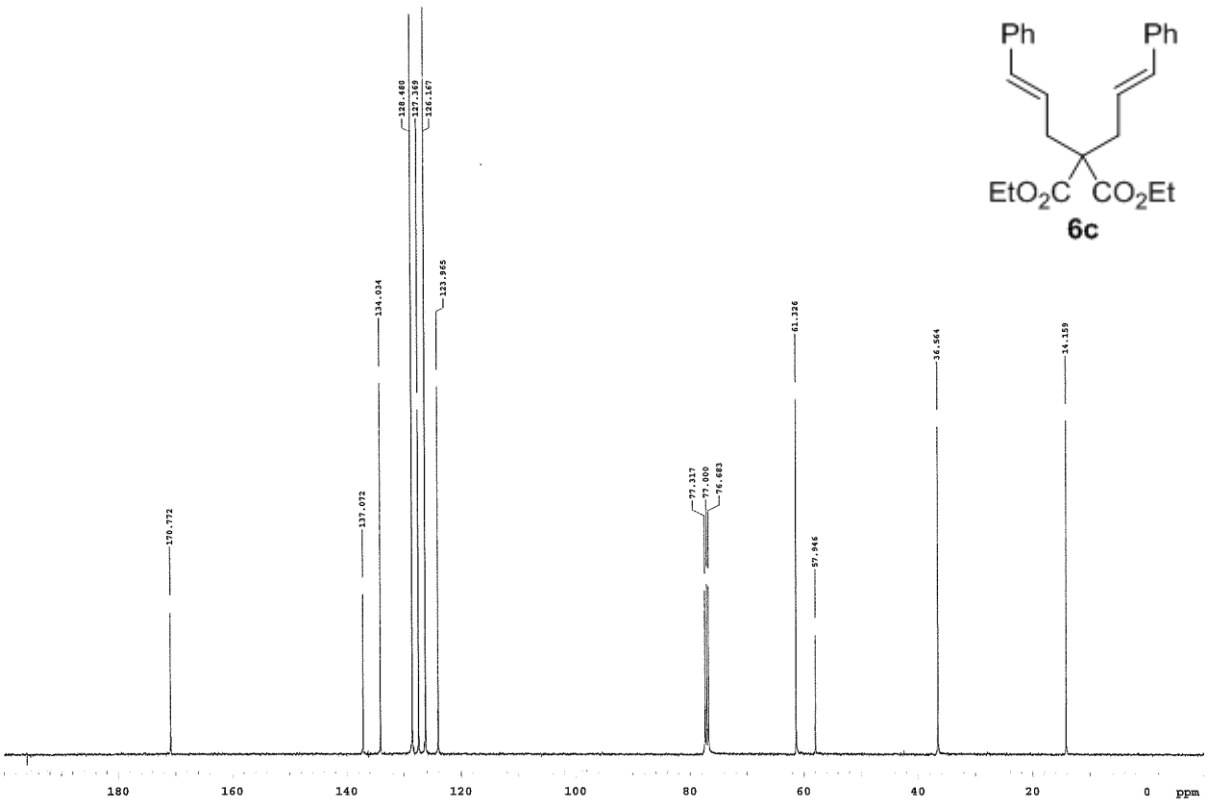
^{1}H NMR and ^{13}C NMR spectra of (*E*)-diethyl 1-phenyl-1-penten-4,4-dicarboxylate





^{1}H NMR and ^{13}C NMR spectra of 6c





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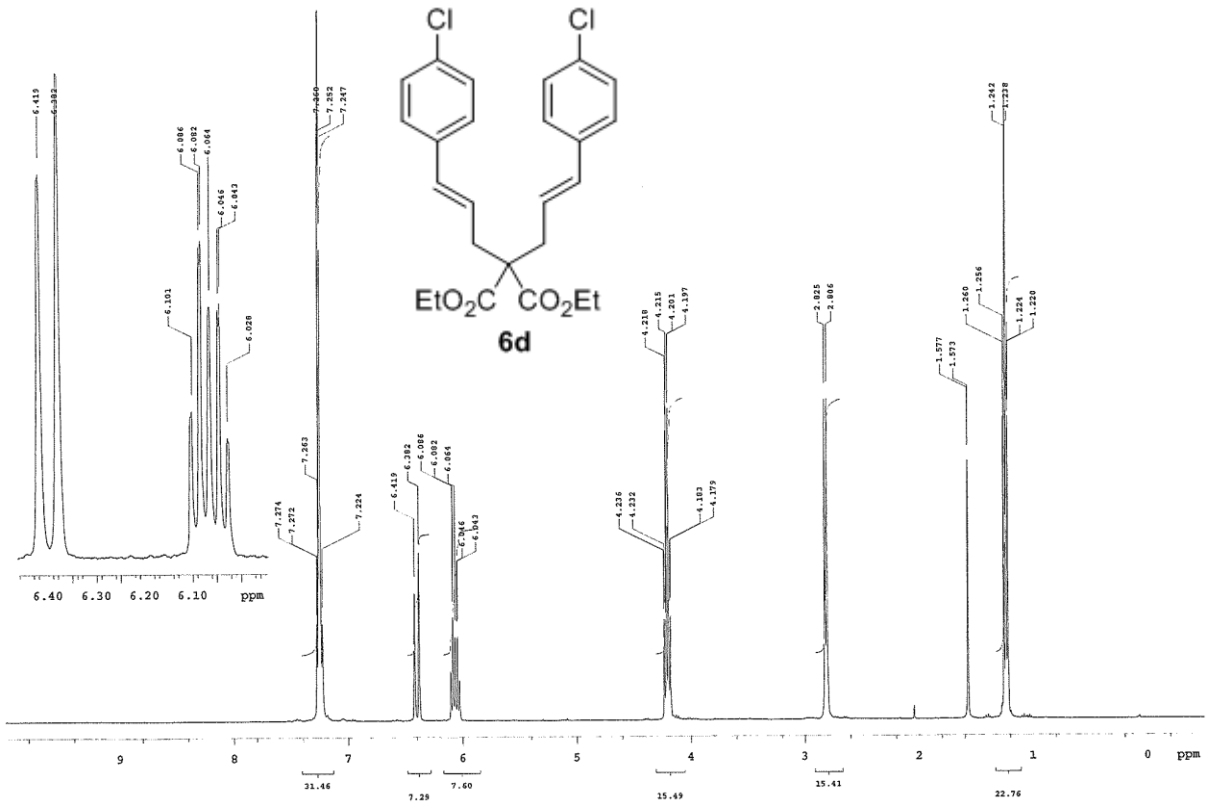
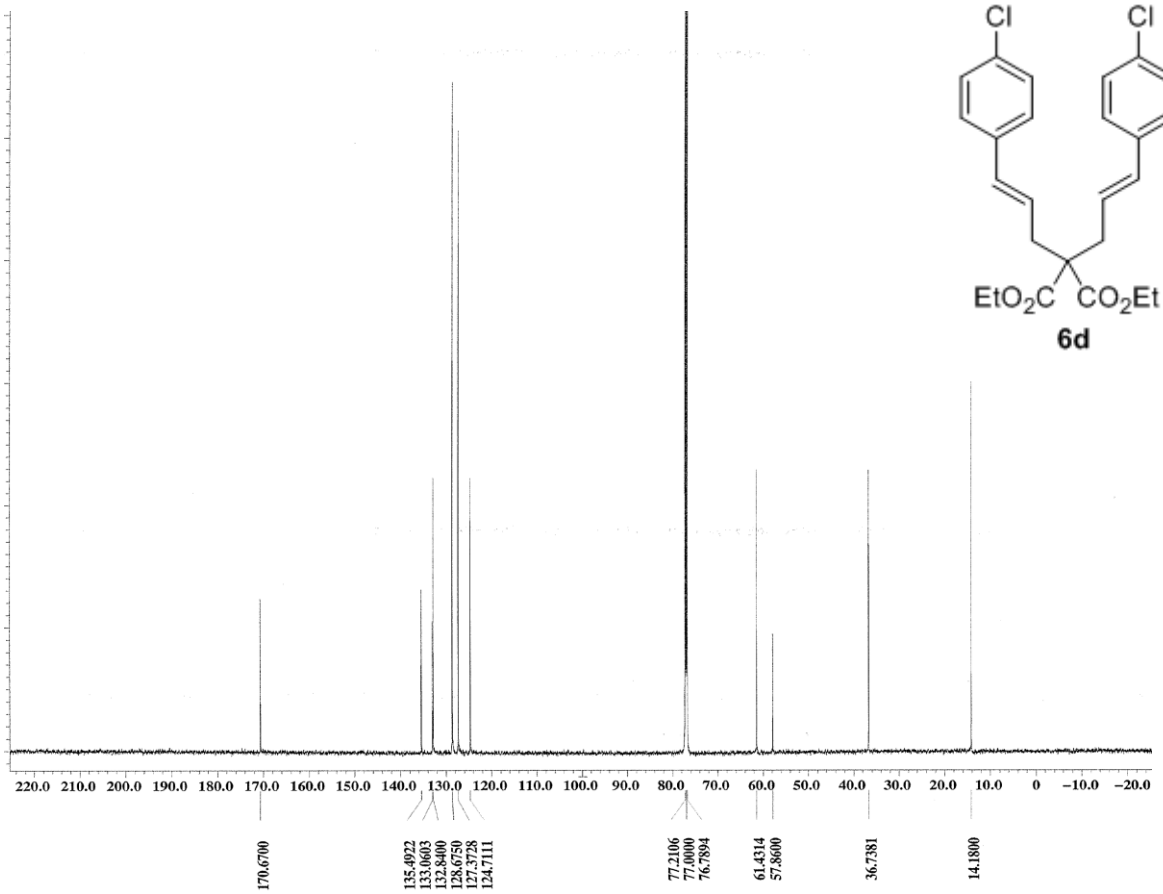
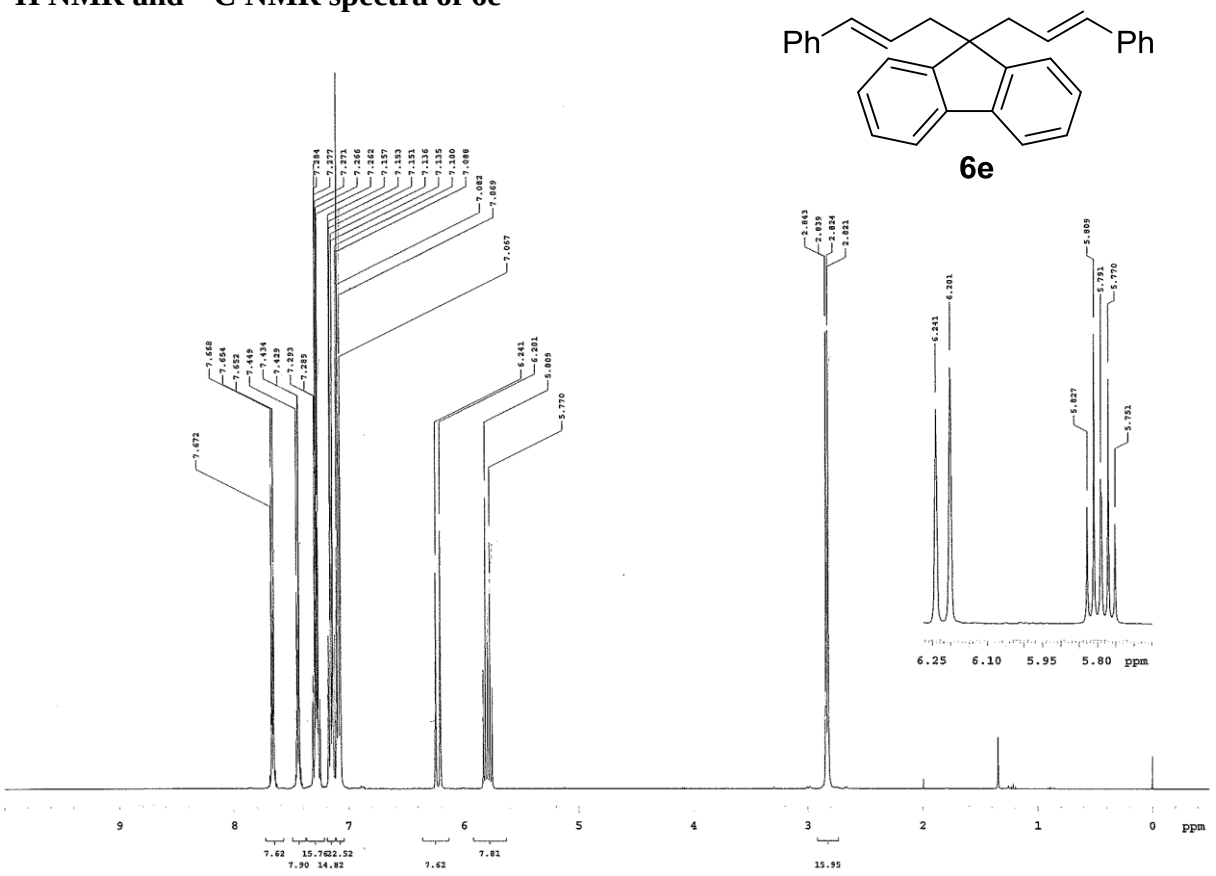
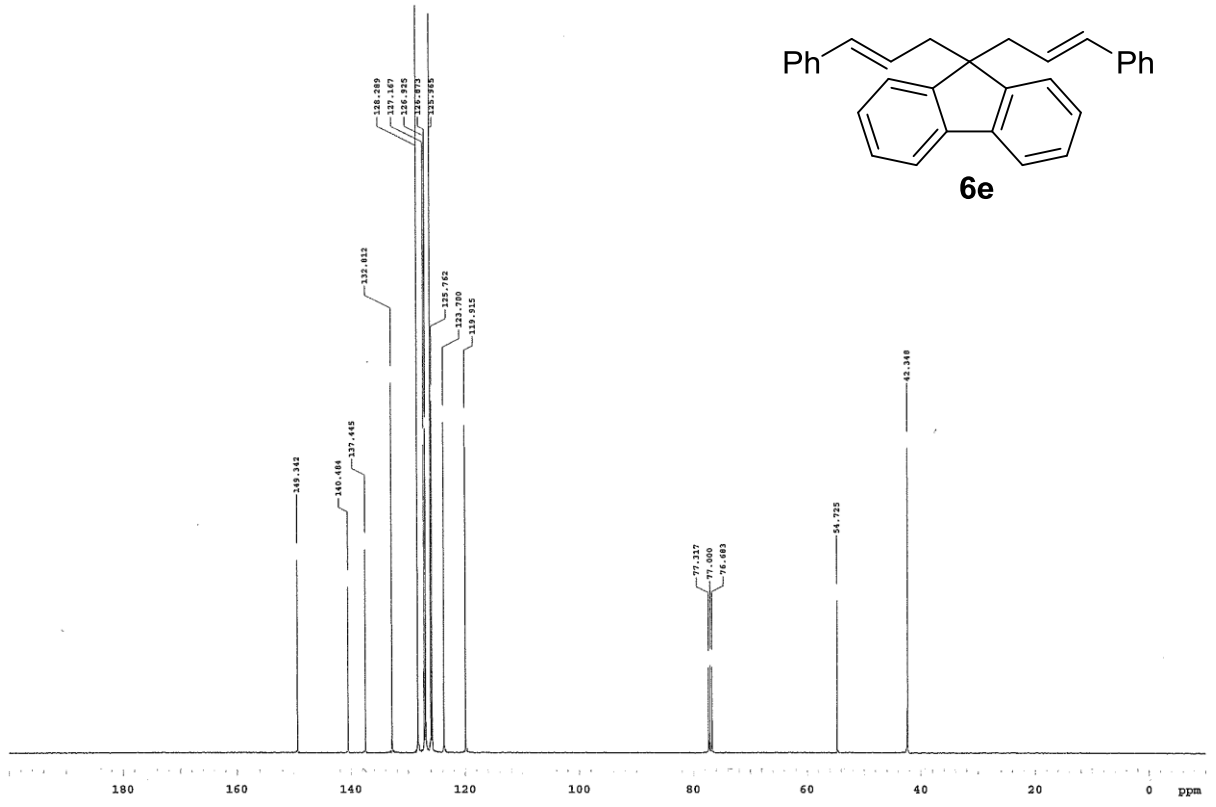


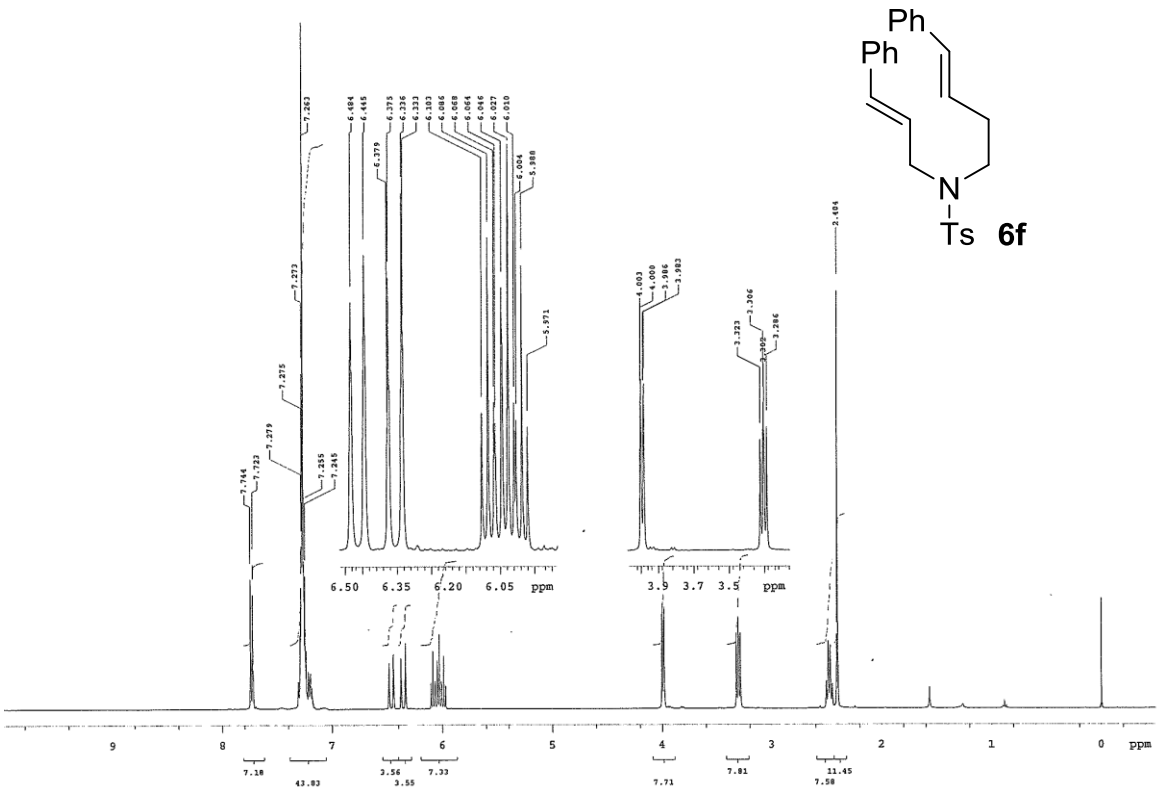


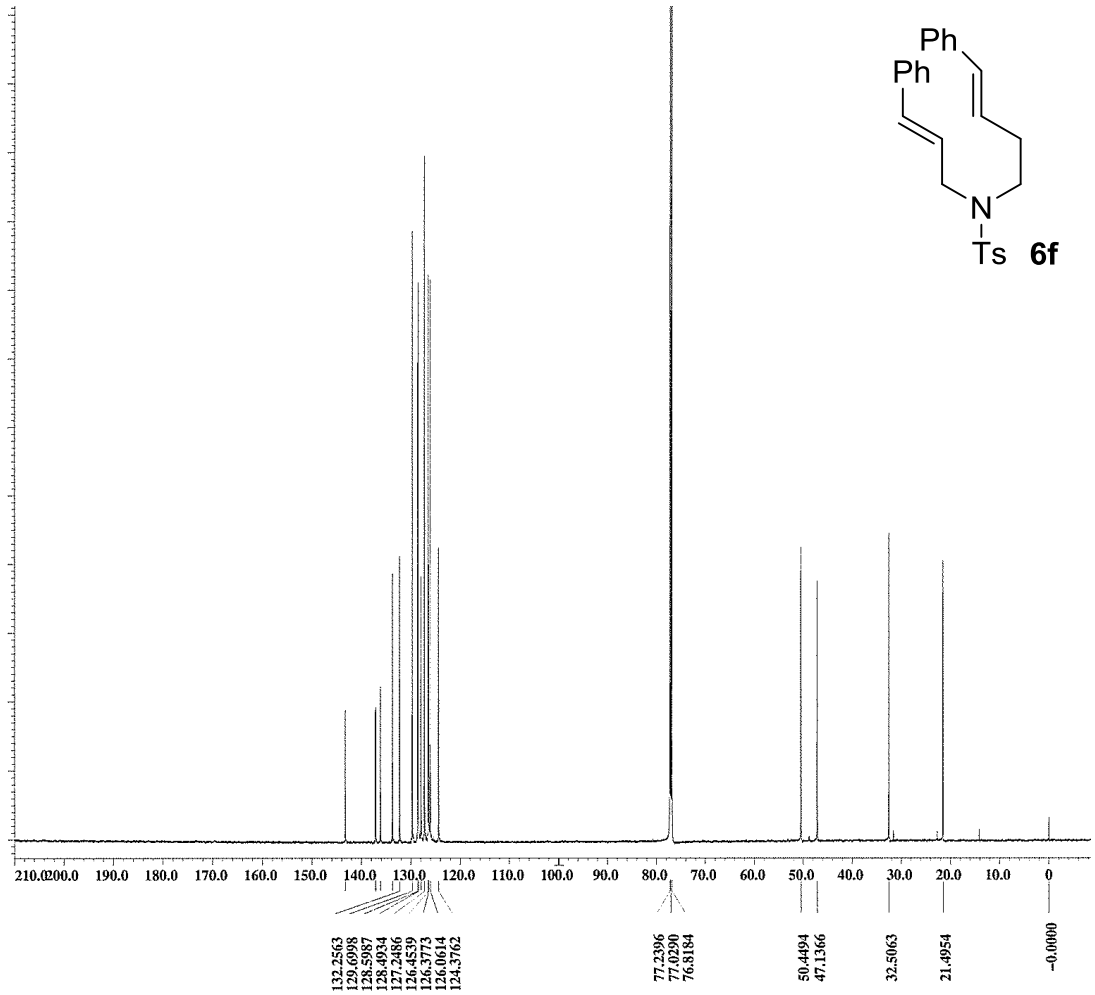
^{1}H NMR and ^{13}C NMR spectra of 6e



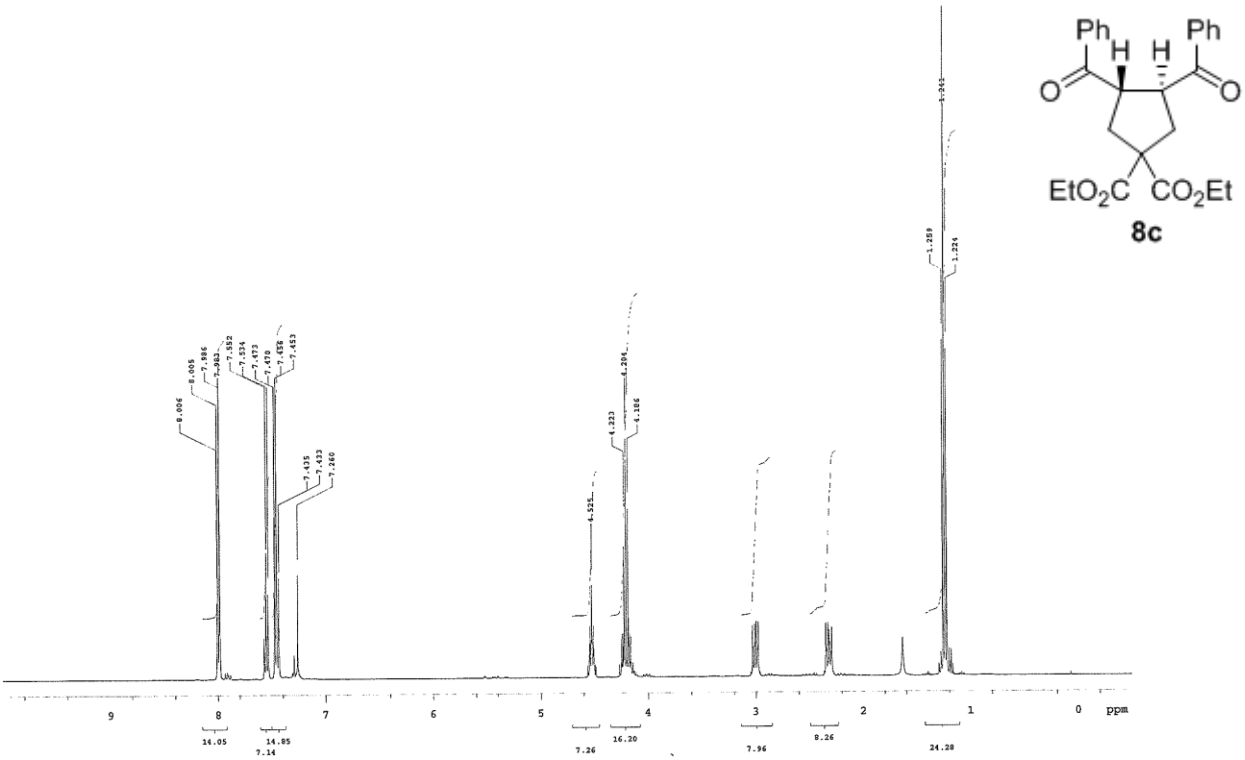


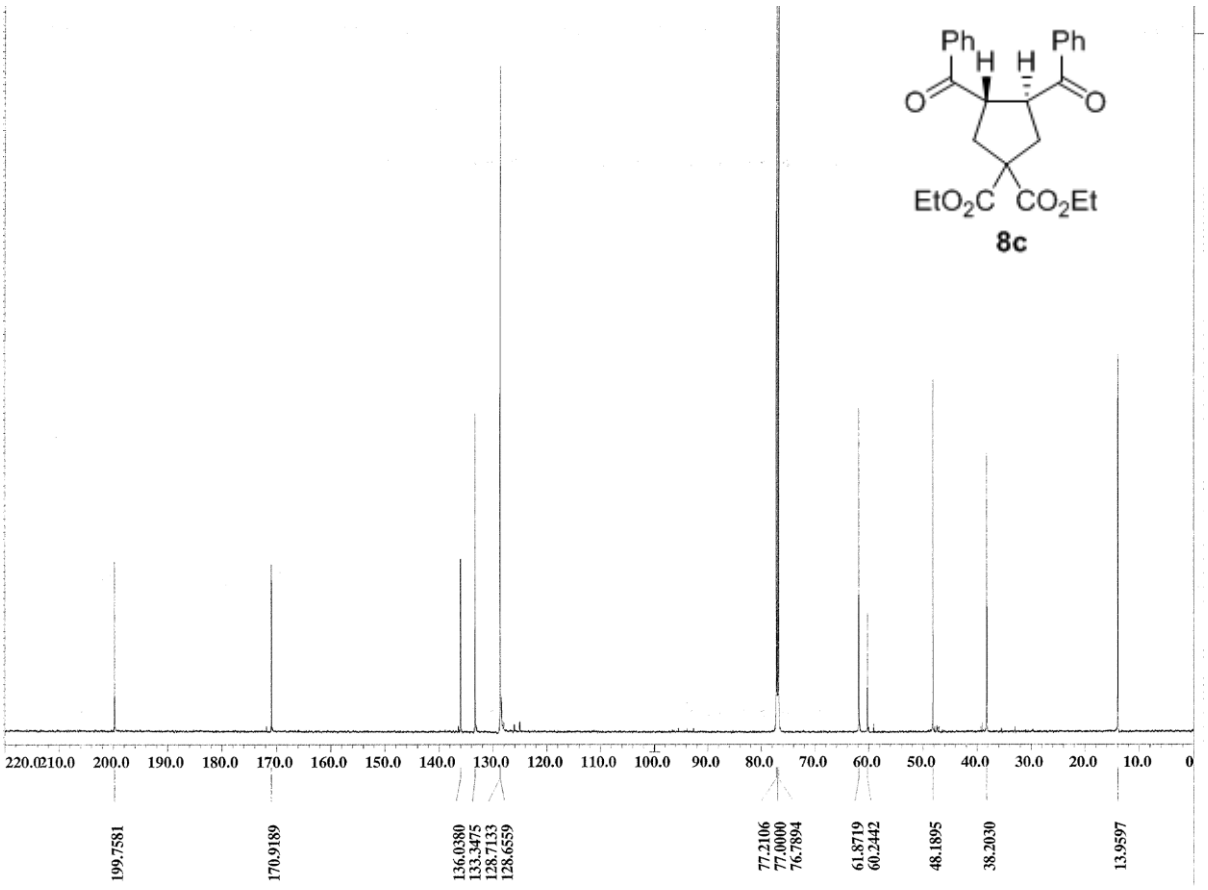
^{1}H NMR and ^{13}C NMR spectra of 6f





^{1}H NMR and ^{13}C NMR spectra of 8c





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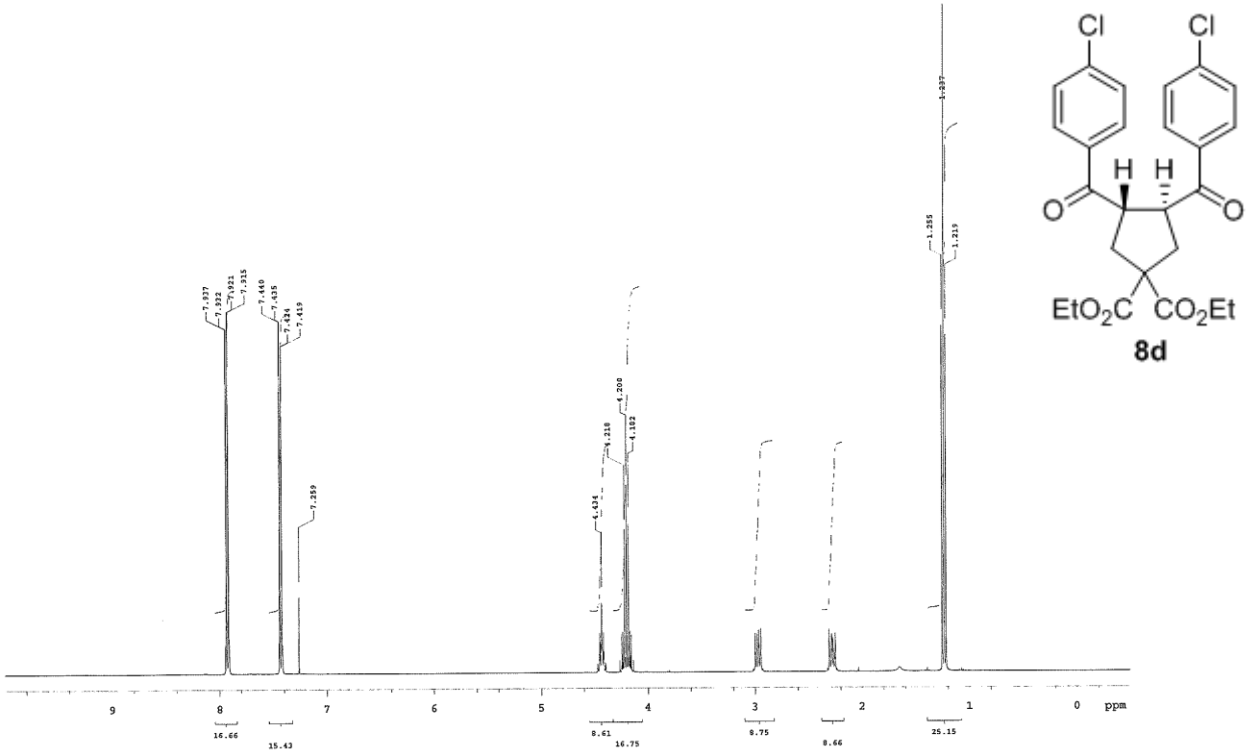

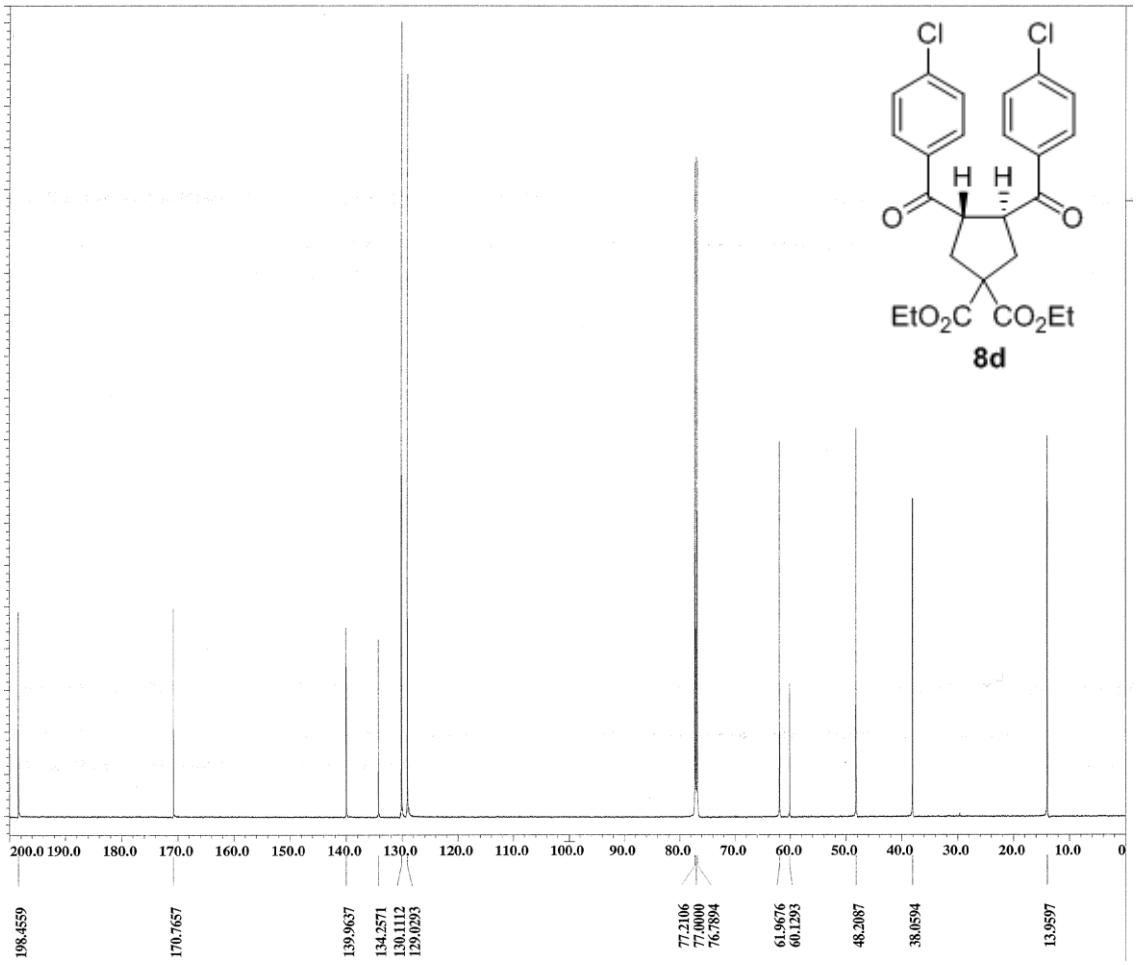

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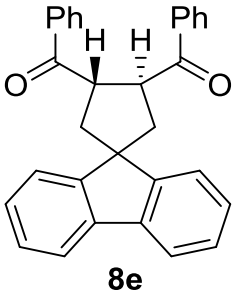
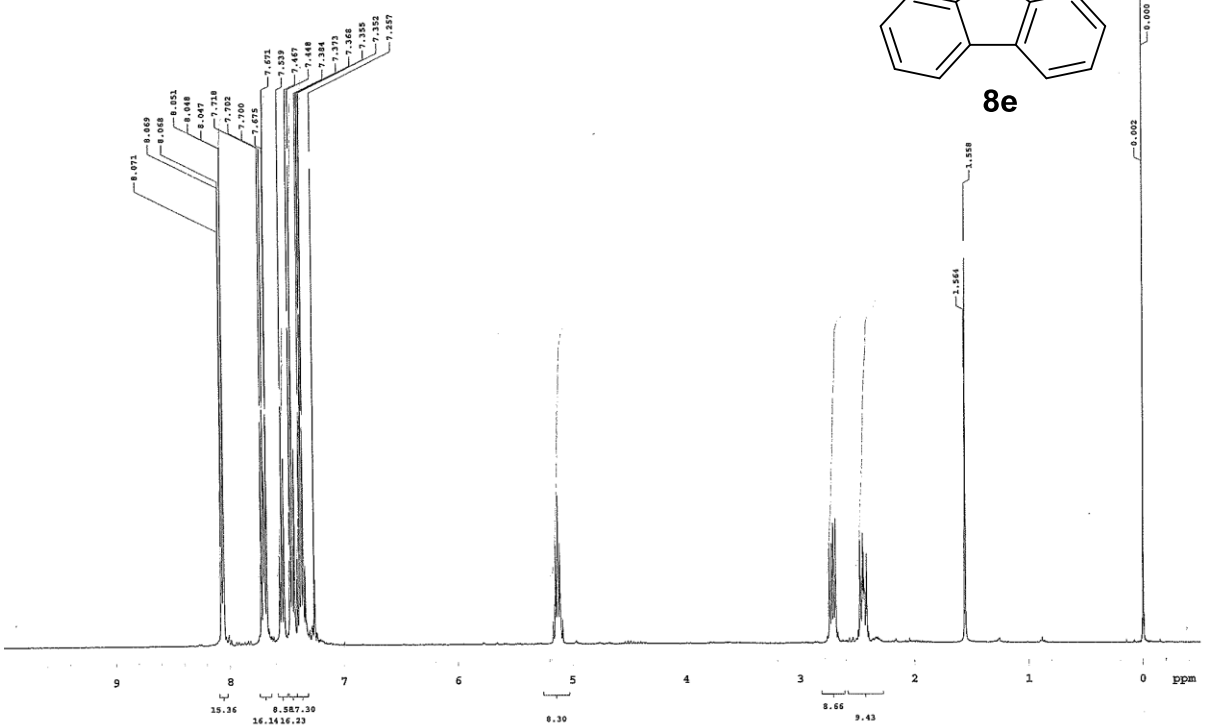
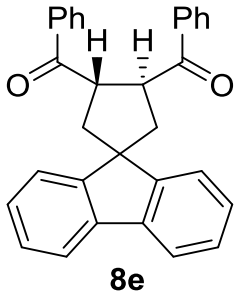


8e





8e

^{1}H NMR and ^{13}C NMR spectra of 8f