Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

Palladium-Catalyzed Decarboxylative Cyclization of α-Acyloxyketones Having an Allene Moiety in the Tether

Akimasa Yabuta, Yoshihiro Oonishi, Ryohei Doi, Kazuhiro Morisaki and Yoshihiro Sato*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060-0812, Japan

Tel &Fax: +81 11 7063722

Email: biyo@pharm.hokudai.ac.jp

General Information

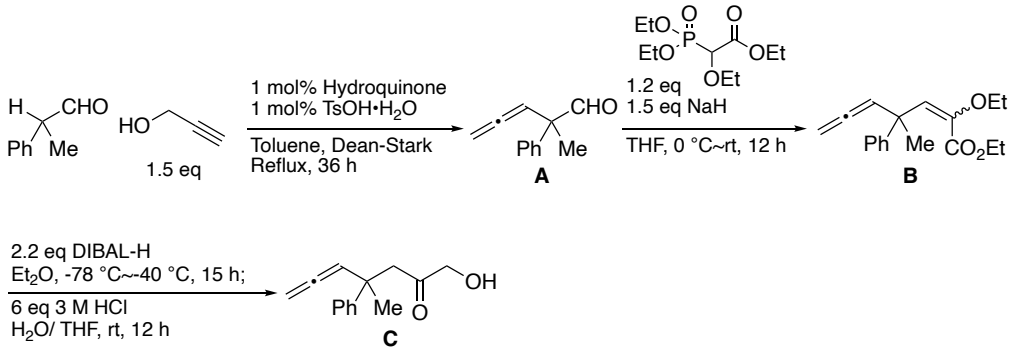
All reactions were performed under an atmosphere of argon or nitrogen (1 atm) unless otherwise stated. Solvents were purified under argon using The Ultimate Solvent System (Glass Counter Inc.) (THF, toluene, and DMF), and were distilled from CaH_2 (DMF). 1,4-dioxane and 1,2-dimethoxy ethane were distilled from Na/benzophenone ketyl and stored under nitrogen. All other reagents were purified by standard procedures. Column chromatography was performed on silica gel 60 N (spherical, neutral, Kanto Chemical, Co. Inc., 45-50 μm) with the indicated solvent as an eluent. Analytical thin-layer chromatography was performed on Silica gel 60 $PF_{254\alpha}$ (Merck).

Infrared (IR) spectra were recorded on a JASCO FT/IR 4100 infrared spectrometer. ^{1}H NMR spectroscopy was recorded on JEOL ECZ500R (500 MHz) or ECX400P (400 MHz) NMR spectrometer. Chemical shifts are reported in ppm from the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. ^{13}C NMR spectroscopy was recorded on JEOL ECA500 (125 MHz), ECX400P, ECS400, or ECP400 (100 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the internal reference ($CDCl_3$: δ = 77.00 ppm). Mass spectra were obtained on JEOL JMS-T100GCv mass spectrometer.

Experimental Details

Synthesis of Starting Material

Synthesis of α-Hydroxy Ketone

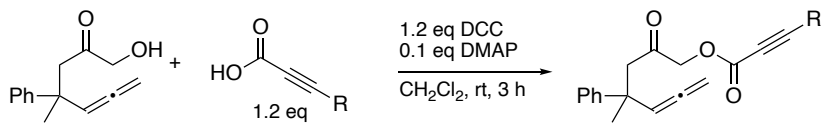


A 300-ml round bottomed flask was charged 2-phenylpropionaldehyde (6.71 g, 50 mmol), 2-butyn-l-ol (4.2 g, 75 mmol), TsOH•H_2O (95 mg, 0.5 mmol) and hydroquinone (55 mg, 0.5 mmol). The flask was equipped with a condenser, a Dean-Stark water separator and nitrogen balloon. Then, anhydrous toluene (50 mL) was loaded. The solution was heated under reflux for 36 h and then evaporated. The residue was purified by column chromatography (eluent: Hexane/EtOAc = 50:1), affording 3.05 g of β-allenyl aldehyde **A**[1] as a brown oil (35%). IR (neat): 1725, 1445, 699 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 9.55 (s, 1H), 7.41-7.38 (m, 2H), 7.32-7.29 (m, 3H), 5.58 (t, J = 6.9 Hz, 1H), 4.95-4.93 (m, 2H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.4, 198.9, 140.1, 128.9, 127.5, 127.3, 92.6, 78.5, 54.3, 20.9. LRMS (EI) *m/z* 172 [M$^+$], 153, 143.

To a suspension of 60% sodium hydride (702 mg, 17.6 mmol) in anhydrous THF (30 mL), phosphonoacetate (3.78 g, 14.1 mmol) in THF (60 mL) was added at 0 °C, and the reaction mixture was stirred at 0 °C for 1 h. To the solution was added aldehyde **A** (2.02 g, 11.7 mmol) in dry THF (30 mL) at 0 °C. The reaction mixture was stirred at roo for 12 h. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $NaSO_4$, and evaporated under reduced pressure. The residue was then purified by silica gel column chromatography (hexane/AcOEt, 30:1) to yield 2.064 g of desired compound **B** as a yellow oil, which was the mixture of *E*/*Z* isomers (73%). IR (neat): 2978, 1954, 1719, 1642, 847, 764, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.41-7.36 (m, 2H), 7.31-7.24 (m, 2H), 7.21-7.13 (m, 1H), 6.50 (s, 0.3H), 5.69 (td, J = 6.6, 2.3 Hz, 1H), 5.27 (s, 0.7H), 4.90-4.86 (m, 2H), 4.23 (q, J = 7.2 Hz, 0.7H), 3.83-3.72 (m, 2H), 3.62-3.42 (m, 1.3H), 1.60 (s, 1H), 1.55 (s, 2H), 1.37-1.30 (m, 3H), 1.05 (t, J = 7.1 Hz, 2H), 0.95 (t, J = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 207.1, 207.0, 164.4, 164.3, 147.8, 147.6, 145.0, 132.9, 128.0, 127.9, 126.5, 126.2, 125.9, 116.1, 99.8, 98.6, 78.1, 77.9, 66.9, 64.1, 61.0, 61.0, 43.0, 42.3, 30.5, 27.6, 14.9, 14.5, 14.2, 13.6 (two carbons missing). LRMS(EI) *m/z* 285 [$(M-H)^+$], 271, 143.

To a stirred solution of ester **B** (2.06 g, 7.19 mmol) in dry Et_2O (22 mL), DIBAL-H (15.8 mL of a 1 M solution in toluene, 15.8 mmol) was added under N_2 at -78 °C. The reaction mixture was stirred at -40 °C for 12 h. A saturated aqueous solution of potassium sodium tartrate tetrahydrate (30 mL) was added to the reaction mixture, and it was left to stir for several hours until the organic and aqueous layers had completely separated. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude as a yellow oil, which was used without further purification in the next step. To a stirred solution of the crude alcohol in THF (32 mL) was added HCl (16 mL of a 3 M solution in H_2O, 48 mmol) at room temperature. After 24 h, the reaction mixture was quenched by saturated solution of $NaHCO_3$ (30 mL). The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. The residue was then purified by silica gel column chromatography (hexane/AcOEt, 5:1) to yield 1.192 g of desired compound **C** as a yellow oil (77%). IR (neat): 3469, 3057, 2969, 1955, 1719, 1038, 835 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.37-7.31 (m, 4H), 7.25-7.21 (m, 1H), 5.49 (t, J = 6.6 Hz, 1H), 4.95-4.89 (m, 2H), 3.99 (dd, J = 19.2, 4.6 Hz, 1H), 3.75 (dd, J = 19.2, 4.6 Hz, 1H), 2.94 (t, J = 4.8 Hz, 1H), 2.88 (d, J = 15.1 Hz, 1H), 2.82 (d, J = 15.1 Hz, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.0, 206.6, 145.8, 128.5, 126.7, 126.0, 99.4, 78.4, 69.3, 49.8, 40.9, 26.7. LRMS(EI) *m/z* 216 [M^+], 201, 185.

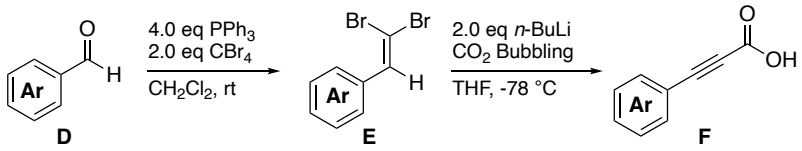
General Procedure A: Synthesis of α-Acyloxy Ketones



α-Hydroxy ketone (1 eq) and 3-(triisoprosilyl)propiolic acid (1.2 eq) were dissolved in CH_2Cl_2 (0.25 M). To the solution were added *N*,*N*'-dicyclohexylcarbodiimide (1.2 eq) and 4-dimethylaminopyridine (10 mol%) with stirring at 0 °C. After a further 5 min at 0 °C, the ice bath was removed, and the reaction mixture

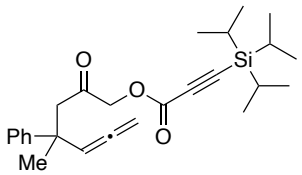
was stirred for 3 h at room temperature (monitored by TLC). The precipitate was removed by filtration over a pad of Celite. Then the filtrate was evaporated. The residue was purified by column chromatography to afford desired product.

General Procedure B: Synthesis of Aryl Propiolic acids[2]



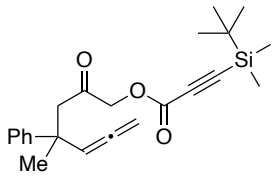
Triphenylphosphine (20 mmol) was added to a solution of carbon tetrabromide (10 mmol) in dry dichloromethane (50 mL). Upon addition of aldehyde (5 mmol), the solution slowly faded away. The reaction mixture was stirred at ambient temperature until the completion of the reaction. After removal of solvent, the residue was repeatedly triturated with hexane and hexane solution was concentrated. Finally, the mixture was subjected to column chromatography to afford the (2,2-dibromovinyl) arene. A solution of (2,2-dibromovinyl)arene (6 mmol) in10 mL of dry THF at −78 °C was treated with a solution of *n*-BuLi in hexane (1.56 M, 7.5 mL, 12 mmol) under nitrogen atmosphere. After stirring for 1 h at −78 °C, the reaction mixture was warmed to 25 °C during 1 h, and cooled to −78 °C. Carbon dioxide was bubbled through the solution for 30 min at −78 °C, and the mixture was allowed to warm gradually to room temperature. The mixture was poured into water, and diethyl ether was added to it. The aqueous layer was separated and washed further with ethyl acetate. The aqueous part was acidified with 3 M HCl and extracted with diethyl ether three times. The organic layer was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of solvent afforded pure arylpropiolic acid.

1a



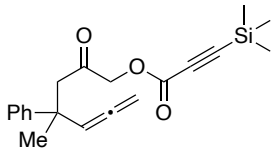
By following general procedure **A**, the reaction of α-hydroxy ketone (1.08 mg, 5.0 mmol) with the corresponding propiolic acid[3] (1.36 g, 6.0 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (1.24 g, 6.0 mmmol) and 4-dimethylaminopyridine (61 mg, 0.5 mmol) in 20 mL CH_2Cl_2 delivered 2.14 g of compound **1a** as a colorless liquid (100%). IR (neat): 2944, 2866, 2173, 1956, 1717, 1221 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39-7.31 (m, 4H), 7.24-7.21 (m, 1H), 5.49 (t, J = 6.6 Hz, 1H), 4.96-4.88 (m, 2H), 4.48 (d, J = 16.5 Hz, 1H), 4.25 (d, J = 16.9 Hz, 1H), 2.92 (d, J = 15.1 Hz, 1H), 2.86 (d, J = 15.1 Hz, 1H), 1.57 (s, 3H), 1.16-1.07 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.6, 200.6, 151.8, 146.0, 128.4, 126.7, 126.1, 99.4, 95.7, 93.2, 78.4, 69.4, 50.1, 40.8, 26.5, 18.4, 10.9. HRMS (EI) calcd. for $C_{26}H_{36}O_3Si$ [M^+] *m/z* 424.2434, found 424.2437.

1b



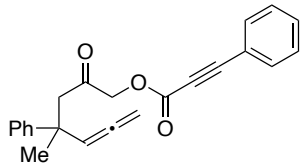
By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[4] (221 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 355 mg of compound **1b** as a colorless liquid (93%). IR (neat): 3059, 2930, 2176, 1955, 1715, 1223 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39-7.31 (m, 4H), 7.24-7.22 (m, 1H), 5.48 (t, J = 6.6 Hz, 1H), 4.91 (dd, J = 6.4, 5.0 Hz, 2H), 4.49 (d, J = 16.9 Hz, 1H), 4.24 (d, J = 16.5 Hz, 1H), 2.91 (d, J = 15.1 Hz, 1H), 2.84 (d, J = 15.1 Hz, 1H), 1.57 (s, 3H), 0.96 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.6, 200.4, 151.8, 145.9, 128.5, 126.7, 126.1, 99.4, 94.6, 94.4, 78.4, 69.5, 50.1, 40.8, 26.4, 25.9, 16.5, -5.3. HRMS (ESI) calcd. for $C_{23}H_{30}NaO_3Si$ [$(M+Na)^+$] *m/z* 405.1862, found 406.1867.

1c



By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[5] (170 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 102 mg of compound **1c** as a colorless liquid (30%). IR (neat): 2965, 2177, 1955, 1715, 1223 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39-7.31 (m, 4H), 7.22 (tt, J = 7.1, 1.7 Hz, 1H), 5.48 (t, J = 6.8 Hz, 1H), 4.96-4.87 (m, 2H), 4.50 (d, J = 16.8 Hz, 1H), 4.23 (d, J = 16.8 Hz, 1H), 2.90 (d, J = 15.0 Hz, 1H), 2.84 (d, J = 15.4 Hz, 1H), 1.57 (s, 3H), 0.23 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.6, 200.3, 151.8, 145.9, 128.5, 126.7, 126.1, 99.4, 95.9, 93.6, 78.4, 69.5, 50.1, 40.9, 26.4, -1.0. HRMS (EI) calcd. $C_{20}H_{24}NaO_3Si$ for [M^+] *m/z* 363.1392, found 364.1403.

1d

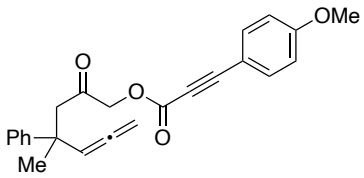


Corresponding propiolic acid was purchased from commercial source (TCI).

By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid (175 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 273 mg of

compound **1d** as a colorless liquid (79%). IR (nujol): 2923, 2853, 2220, 1735, 1694, 1172 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.46-7.44 (m, 2H), 7.34-7.30 (m, 1H), 7.28-7.19 (m, 6H), 7.13-7.09 (m, 1H), 5.38 (t, J = 6.6 Hz, 1H), 4.84-4.76 (m, 2H), 4.44 (d, J = 16.9 Hz, 1H), 4.17 (d, J = 16.5 Hz, 1H), 2.81 (d, J = 15.1 Hz, 1H), 2.75 (d, J = 15.1 Hz, 1H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.6, 200.5, 152.9, 145.9, 133.0, 130.8, 128.6, 128.5, 126.7, 126.1, 119.3, 99.4, 87.8, 79.8, 78.4, 69.6, 50.1, 40.9, 26.5. HRMS (EI) calcd. for $C_{22}H_{17}O_3$ $[(M\text{-}Me)^+]$ *m/z* 329.1178, found 329.1170.

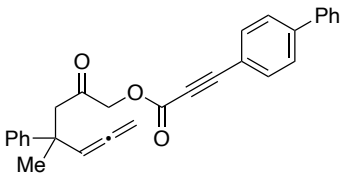
1e



Corresponding propiolic acid was prepared according to general procedure **B**. The spectrum data of the propiolic acid matched to that of literature.[6]

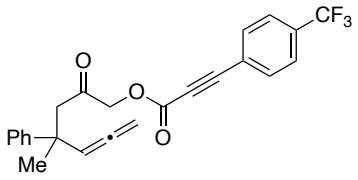
By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid (211 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 230 mg of compound **1e** as a white solid (61%). IR (nujol): 2923, 2214, 1715, 1602, 1291, 1157 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.53 (d, J = 8.2 Hz, 2H), 7.40-7.32 (m, 4H), 7.23 (t, J = 7.3 Hz, 1H), 6.88 (d, J = 8.2 Hz, 2H), 5.51 (t, J = 6.6 Hz, 1H), 4.96-4.88 (m, 2H), 4.56 (d, J = 16.9 Hz, 1H), 4.29 (d, J = 16.9 Hz, 1H), 3.84 (s, 3H), 2.93 (d, J = 15.1 Hz, 1H), 2.88 (d, J = 15.1 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.8, 161.7, 153.2, 146.0, 135.1, 128.5, 126.7, 126.1, 114.3, 111.1, 99.4, 88.8, 79.3, 78.4, 69.5, 55.4, 50.1, 40.9, 26.5. HRMS (EI) calcd. for $C_{23}H_{19}O_4$ $[(M\text{-}Me)^+]$ *m/z* 359.1283, found 359.1274.

1f



By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[7] (211 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 161 mg of compound **1f** as a white solid (38%). IR (nujol): 2928, 2222, 1952, 1739, 1702, 1292, 1171 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.66-7.58 (m, 6H), 7.48-7.33 (m, 7H), 7.31-7.22 (m, 1H), 5.51 (t, J = 6.8 Hz, 1H), 4.98-4.89 (m, 2H), 4.58 (d, J = 16.8 Hz, 1H), 4.31 (d, J = 16.8 Hz, 1H), 2.94 (d, J = 15.0 Hz, 1H), 2.88 (d, J = 15.0 Hz, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.6, 152.9, 146.0, 143.7, 139.8, 133.6, 129.0, 128.5, 128.2, 127.3, 127.1, 126.7, 126.2, 118.1, 99.4, 87.9, 80.4, 78.5, 69.6, 50.2, 40.9, 26.5. HRMS (EI) calcd. for $C_{29}H_{24}O_3$ $[M^+]$ *m/z* 420.1725, found 420.1717.

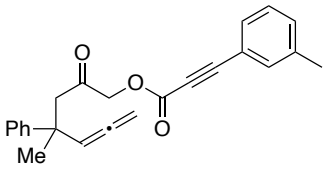
1g



Corresponding propiolic acid was prepared according to general procedure **B**. The spectrum data of the propiolic acid matched to that of literature.[6]

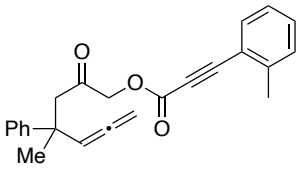
By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid (221 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 324 mg of compound **1g** as a pale yellow oil (79%). IR (neat): 3250, 2971, 2933, 2233, 1955, 1715, 1616, 1290, 1174 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.68 (d, J = 8.2 Hz, 2H), 7.64 (d, J = 8.2 Hz, 2H), 7.41-7.33 (m, 4H), 7.26-7.22 (m, 1H), 5.51 (t, J = 6.6 Hz, 1H), 4.98-4.89 (m, 2H), 4.59 (d, J = 16.5 Hz, 1H), 4.31 (d, J = 16.9 Hz, 1H), 2.93 (d, J = 14.6 Hz, 1H), 2.87 (d, J = 14.6 Hz, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.2, 152.4, 145.9, 133.2, 132.4, 128.5, 126.7, 126.1, 125.5, 123.5, 123.2, 99.4, 85.4, 81.4, 78.5, 69.7, 50.2, 40.9, 26.4. ^{19}F NMR (376 MHz, $CDCl_3$, rt, δ/ppm): δ -63.1. HRMS (ESI) calcd. for $C_{24}H_{19}F_3NaO_3$ [$(M+Na)^+$] *m/z* 435.1184, found 435.1171.

1h



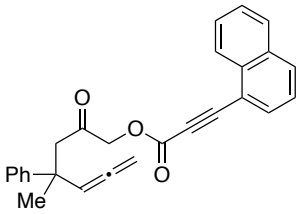
By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[5] (192 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 324 mg of compound **1h** as a colorless oil (90%). IR (neat): 3057, 2928, 2211, 1955, 1714, 1298, 1213, 1156 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.41-7.32 (m, 6H), 7.27-7.21 (m, 4H), 5.51 (t, J = 6.6 Hz, 1H), 4.93 (ddd, J = 16.6, 10.1, 6.2 Hz, 2H), 4.56 (d, J = 16.9 Hz, 1H), 4.30 (d, J = 16.5 Hz, 1H), 2.93 (d, J = 15.1 Hz, 1H), 2.94 (d, J = 15.1 Hz, 1H), 2.88 (d, J = 15.1 Hz, 1H), 2.34 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.6, 153.0, 146.0, 138.4, 133.6, 131.8, 130.2, 128.5, 126.7, 126.1, 119.1, 99.4, 88.2, 79.5, 78.4, 69.6, 50.2, 40.9, 26.5, 21.1 One aromatic carbon is missing probably due to overlapping. HRMS (ESI) calcd. for $C_{24}H_{22}NaO_3$ [$(M+Na)^+$] *m/z* 381.1467, found 381.1449.

1i



By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[6] (192 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 331 mg of compound **1i** as a colorless oil (92%). IR (neat): 3059, 2928, 2221, 1955, 1714, 1182 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.53 (d, J = 7.8 Hz, 1H), 7.41-7.39 (m, 2H), 7.36-7.32 (m, 3H), 7.25-7.22 (m, 2H), 7.18 (t, J = 7.5 Hz, 1H), 5.51 (t, J = 6.6 Hz, 1H), 4.95-4.91 (m, 2H), 4.57 (d, J = 16.9 Hz, 1H), 4.31 (d, J = 16.9 Hz, 1H), 2.94 (d, J = 15.1 Hz, 1H), 2.89 (d, J = 15.1 Hz, 1H), 2.48 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.7, 153.0, 146.0, 142.4, 133.5, 130.8, 129.8, 128.5, 126.7, 126.1, 125.8, 119.2, 99.4, 86.9, 83.5, 78.4, 69.6, 50.2, 40.9, 26.5, 20.5. HRMS (EI) calcd. for $C_{24}H_{22}O_3$ [M^+] *m/z* 358.1569, found 358.1558.

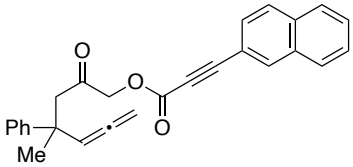
1j



Corresponding propiolic acid was prepared according to general procedure **B**. The spectrum data of the propiolic acid matched to that of literature.[11]

By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid (235 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 291 mg of compound **1j** as a colorless liquid (74%). IR (neat): 3058, 2929, 2217, 1955, 1714, 1253 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt, δ/ppm):δ 8.32 (d, J = 7.8 Hz, 1H), 7.96 (d, J = 8.7 Hz, 1H), 7.89-7.84 (m, 2H), 7.62-7.56 (m, 2H), 7.49-7.41 (m, 3H), 7.38-7.34 (m, 2H), 7.26-7.25 (m, 1H), 5.52 (t, J = 6.6 Hz, 1H), 4.96-4.93 (m, 2H), 4.62 (d, J = 16.9 Hz, 1H), 4.36 (d, J = 16.5 Hz, 1H), 2.97 (d, J = 15.1 Hz, 1H), 2.91 (d, J = 15.1 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.6, 153.0, 146.0, 133.6, 133.3, 133.0, 131.6, 128.5, 128.5, 127.7, 126.9, 126.7, 126.2, 125.7, 125.1, 116.9, 99.4, 86.2, 84.4, 78.5, 69.7, 50.2, 40.9, 26.5. HRMS (EI) calcd. for $C_{27}H_{22}O_3$ [M^+] *m/z* 394.1569, found 394.1562.

1k



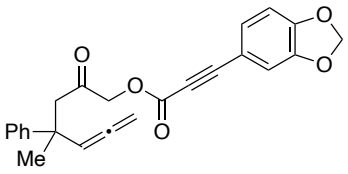
Corresponding propiolic acid was prepared according to general procedure **B**. The spectrum data of the propiolic acid matched to that of literature.[9]

By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid (235 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248

mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 331 mg of compound **1k** as a yellow oil (84%).

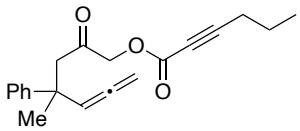
IR (neat): 3057, 2931, 2220, 1955, 1713, 1236, 1202 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 8.15 (s, 1H), 7.85-7.81 (m, 3H), 7.58-7.53 (m, 3H), 7.42-7.39 (m, 2H), 7.35 (td, J = 6.7, 2.0 Hz, 2H), 7.27-7.23 (m, 1H), 5.52 (t, J = 6.6 Hz, 1H), 4.98-4.90 (m, 2H), 4.60 (d, J = 16.9 Hz, 1H), 4.32 (d, J = 16.5 Hz, 1H), 2.95 (d, J = 14.6 Hz, 1H), 2.89 (d, J = 15.1 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.6, 152.9, 146.0, 134.5, 133.9, 132.6, 128.5, 128.4, 128.2, 128.2, 128.0, 127.9, 127.0, 126.7, 126.1, 116.5, 99.4, 88.3, 80.0, 78.4, 69.7, 50.2, 40.9, 26.5. HRMS (ESI) calcd. for $C_{27}H_{22}NaO_3$ [$(M+Na)^+$] *m/z* 417.1467, found 417.1450.

1l



By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[7] (229 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 200 mg of compound **1l** as a colorless oil (59%). IR (neat): 2969, 2925, 2211, 1955, 1714, 1233 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.40-7.38 (m, 2H), 7.36-7.32 (m, 2H), 7.25-7.21 (m, 1H), 7.15 (dd, J = 8.0, 1.6 Hz, 1H), 6.99 (d, J = 1.4 Hz, 1H), 6.79 (d, J = 8.2 Hz, 1H), 6.01 (s, 2H), 5.50 (t, J = 6.6 Hz, 1H), 4.97-4.88 (m, 2H), 4.55 (d, J = 16.5 Hz, 1H), 4.29 (d, J = 16.9 Hz, 1H), 2.93 (d, J = 15.1 Hz, 1H), 2.87 (d, J = 15.1 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm):δ 206.6, 200.6, 153.0, 150.2, 147.6, 146.0, 129.0, 128.5, 126.7, 126.1, 112.5, 112.3, 108.7, 101.8, 99.4, 88.4, 78.8, 78.4, 69.5, 50.1, 40.9, 26.5. HRMS (EI) calcd. for $C_{24}H_{20}O_5$ [M^+] *m/z* 388.1311, found 388.1306.

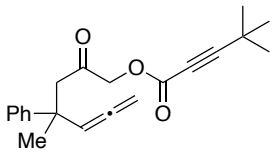
1m



By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[11,12] (135 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol,) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 288 mg of compound **1m** as a colorless liquid (93%). IR (neat): 2967, 2875, 2239, 1955, 1717, 1635, 1246 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39-7.31 (m, 4H), 7.24-7.21 (m, 1H), 5.49 (t, J = 6.6 Hz, 1H), 4.95-4.87 (m, 2H), 4.49 (d, J = 16.5 Hz, 1H), 4.23 (d, J = 16.9 Hz, 1H), 2.90 (d, J = 15.1 Hz, 1H), 2.84 (d, J = 15.1 Hz, 1H), 2.31 (t, J = 7.1 Hz, 2H), 1.65-1.58 (m, 2H), 1.57 (s, 3H), 1.00 (t, J = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.7, 152.7, 146.0, 128.5, 126.7, 126.1, 99.4, 91.3, 78.4, 72.4, 69.4, 50.1, 40.9, 26.5, 21.0, 20.7, 13.4. HRMS (EI) calcd. for $C_{19}H_{19}O_3$ [$(M-Me)^+$] *m/z* 295.1334,

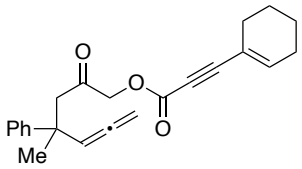
found 295.1333.

1n



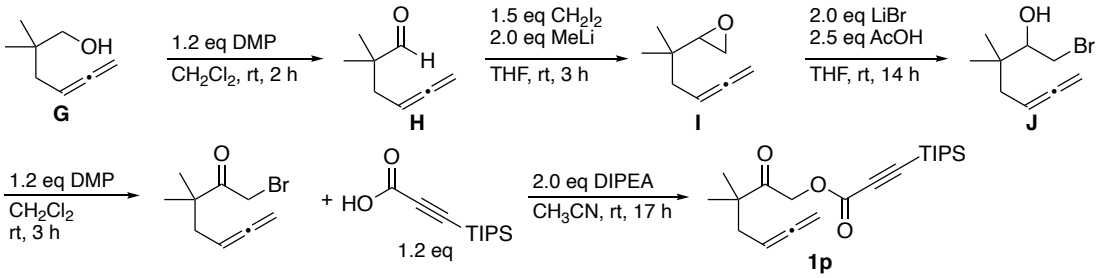
By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[11] (144 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol,) and 4-dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 299 mg of compound **1n** as a pale yellow liquid (92%). IR (neat): 2972, 2932, 2241, 1955, 1715, 1221 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39-7.31 (m, 4H), 7.24-7.22 (m, 1H), 5.49 (t, J = 6.6 Hz, 1H), 4.93-4.90 (m, 2H), 4.49 (d, J = 16.9 Hz, 1H), 4.23 (d, J = 16.9 Hz, 1H), 2.90 (d, J = 15.1 Hz, 1H), 2.84 (d, J = 15.1 Hz, 1H), 1.57 (s, 3H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.7, 200.7, 152.9, 146.0, 128.5, 126.7, 126.1, 99.4, 98.3, 78.4, 77.3, 77.0, 76.7, 71.0, 69.4, 50.1, 40.8, 29.9, 27.6, 26.5. HRMS (EI) calcd. for $C_{20}H_{21}O_3$ [M^+-Me] *m/z* 309.1491, found 309.1485.

1o



By following general procedure **A**, the reaction of α-hydroxy ketone (216 mg, 1.0 mmol) with the corresponding propiolic acid[10]. (180 mg, 1.2 mmol) in the presence of *N*,*N*'-dicyclohexylcarbodiimide (248 mg, 1.2 mmol,) and 4-Dimethylaminopyridine (12 mg, 0.1 mmol) in 4 mL CH_2Cl_2 delivered 292 mg of compound **1o** as pale yellow liquid (84%). IR (neat): 2933, 2207, 1955, 1714, 1257cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39-7.31 (m, 4H), 7.24-7.20 (m, 1H), 6.47-6.45 (m, 1H), 5.49 (t, J = 6.6 Hz, 1H), 4.95-4.87 (m, 2H), 4.50 (d, J = 16.9 Hz, 1H), 4.24 (d, J = 16.9 Hz, 1H), 2.90 (d, J = 15.1 Hz, 1H), 2.85 (d, J = 15.1 Hz, 1H), 2.16-2.14 (m, 4H), 1.66-1.58 (m, 4H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 206.6, 200.8, 153.2, 146.0, 142.8, 128.4, 126.6, 126.1, 118.3, 99.4, 90.2, 78.4, 77.8, 69.5, 50.1, 40.8, 28.0, 26.5, 26.0, 21.8, 21.0. HRMS (EI) calcd. for $C_{23}H_{24}O_3$ [M^+] *m/z* 348.1725, found 348.1729.

Synthesis of 1p from ε-allyl alchol

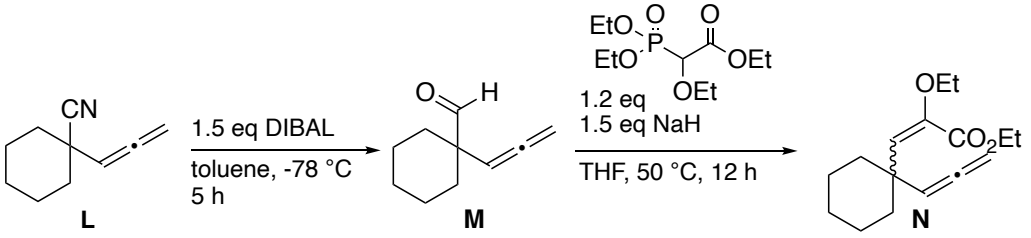


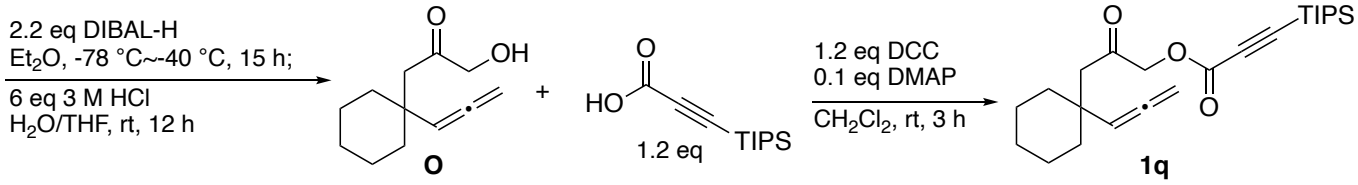
The alcohol **G**[12] (402 mg, 3.18 mmol) was dissolved in in anhydrous CH_2Cl_2 (30 mL) under N_2. To the solution was added DMP (1.62 g, 3.82 mmol) at 0 °C. The ice bath was removed. The reaction mixture was stirred for 2 h at room temperature. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude as a yellow oil, which was used without further purification in the next step. To a solution of the crude aldehyde **H** and CH_2I_2 (0.36 mL, 4.29 mmol) in THF (12 mL), methyllithium (1.15 M in Et_2O, 5.0 mL, 5.72 mmol) was added at 0 ° C under Ar. After 30 min, the reaction mixture was stirred for 3 h at room temperature. The reaction mixture was quenched by H_2O. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude as a yellow oil, which was used without further purification in the next step. To a solution of the crude epoxide **I** and LiBr (392 mg, 4.51 mmol) in THF (23 mL), acetic acid (0.32 mL, 5.65 mmol) was added at room temperature. The reaction mixture was stirred for 14 h at the same temperature. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$. The mixture was extracted with AcOEt three times. The combined organic layer was washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was then purified by silica gel column chromatography (hexane/AcOEt, 1:20) to yield 154 mg of desired compound **J** as a colorless oil (22%, 3 steps). IR (neat): 3466, 2962, 1954, 1469, 1073, 842 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, rt, δ/ppm):δ 5.10-5.04 (m, 1H), 4.67-4.65 (m, 2H), 3.69 (dd, J = 10.3, 1.8 Hz, 1H), 3.64 (d, J = 10.3 Hz, 1H), 3.39 (t, J = 10.3 Hz, 1H), 2.26 (d, J = 3.0 Hz, 1H), 2.19-2.14 (m, 1H), 2.01-1.95 (m, 1H), 0.96 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (126 MHz,, $CDCl_3$, rt, δ/ppm): δ 209.8, 85.5, 77.5, 73.9, 38.9, 38.6, 38.2, 23.1, 22.5. LRMS (CI) *m/z* 218 [M^+], 125, 139.

The alcohol **J** (154 mg, 0.70 mmol) was dissolved in in anhydrous CH_2Cl_2 (7 mL) under N_2. To the solution was added DMP (357 g, 0.84 mmol) at 0 °C. The ice bath was removed. The reaction mixture was stirred for 3 h at room temperature. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ and $Na_2S_2O_3$. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude as a yellow oil, which was used without further purification in the next step. The crude acyl bromide **K** and 3-(triisoprosilyl)propiolic acid (179 mg, 0.66 mmol) were dissolved in MeCN (2.6 mL). To the solution was added *N*,*N*-diisopropylethylamine (0.23 mL, 1.32 mmol). The solution was stirred for 17 h at room temperature and then evaporated. The residue was then purified by silica gel column chromatography (hexane/AcOEt, 50:1) to yield 198 mg of desired compound **1p** as a colorless oil (78%, 2 steps). IR (neat): 2945, 2867, 2173, 1956, 1715, 1220 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 5.02-4.97 (m, 1H),

4.94 (s, 2H), 4.69 (td, J = 4.5, 2.1 Hz, 2H), 2.26 (td, J = 5.1, 2.6 Hz, 2H), 1.21 (s, 6H), 1.18-1.07 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 209.9, 205.7, 152.1, 95.9, 93.0, 85.1, 74.7, 66.0, 46.7, 38.7, 23.9, 18.4, 10.9. HRMS (ESI) calcd. for $C_{21}H_{34}NaO_3Si$ [$(M+Na)^+$] *m/z* 385.2175, found 386.2182.

Synthesis of 1q from β-allenyl nitrile



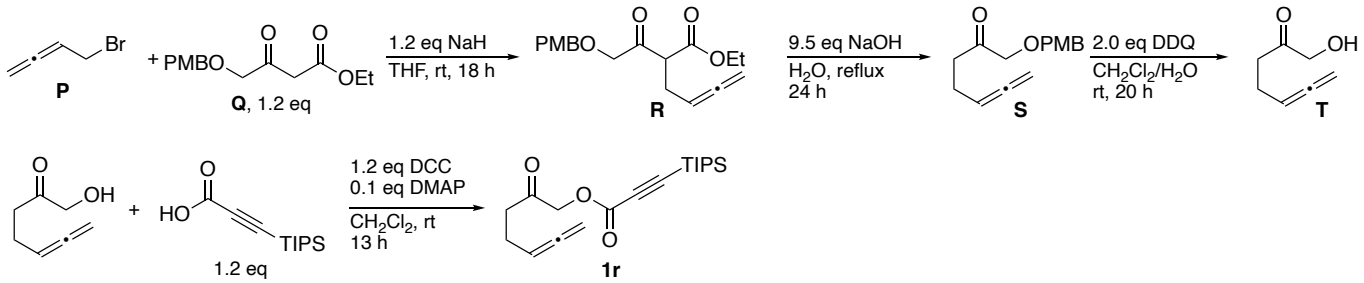


To a stirred solution of allenyl nitrile **L**[13] (155 mg, 1.05 mmol) in dry toluene (3.5 mL), DIBAL-H (1.58 mL of a 1 M solution in toluene, 1.58 mmol) was added under N_2 at -78 °C. After 5 h, a saturated aqueous solution of potassium sodium tartrate tetrahydrate was added to the reaction mixture, and it was left to stir for several hours until the organic and aqueous layers had completely separated. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Then, the residue was purified by silica gel column chromatography (hexane/AcOEt, 20:1) to yield 84 mg of desired compound **M** as a brown oil (53%). IR (neat): 2927, 2853, 1725, 1449, 841 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 9.32 (s, 1H), 4.95-4.92 (m, 1H), 4.88-4.86 (m, 2H), 1.87-0.83 (m, 10H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 209.1, 202.4, 92.3, 77.8, 50.0, 30.7, 25.7, 22.3. LRMS (EI) *m/z* 150 [M^+], 149, 121, 111.

To a suspension of 60% sodium hydride (238 mg, 5.96 mmol) in anhydrous THF (13 mL), phosphonoacetate (1.28 g, 4.76 mmol) in THF (26 mL) was added at 0 °C and the reaction mixture was stirred at the same temperature for 1 h. To the solution was added aldehyde **M** (596 mg, 3.97 mmol) in dry THF (13 mL) at the same temperature. The reaction mixture was stirred at 50 °C for 3 h. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $NaSO_4$, and evaporated under reduced pressure. Then, the resideu was roughly purified by silica gel column chromatography (hexane/AcOEt, 20:1) to the desired compound **N** as a yellow oil, which was used without further purification in the next step. To a stirred solution of the crude ester **N** in dry Et_2O (6.8 mL), DIBAL-H (2.91 mL of a 1 M solution in toluene, 2.97 mmol) was added under N_2 at -78 °C. After 8 h, a saturated aqueous solution of potassium sodium tartrate tetrahydrate was added to the mixture, and it was left to stir for several hours until the organic and aqueous layers had completely separated. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure to give the crude product as a yellow oil, which was used without further

purification in the next step. To a stirred solution of the crude alcohol in THF (6.8 mL) was added HCl (2.7 mL of a 3 M solution in H_2O, 8.1 mmol) at room temperature. After 4 h, the reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$ (30 mL). The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Then, the residue was roughly purified by silica gel column chromatography (hexane/AcOEt, 5:1) to yield desired compound **O** as a pale-yellow oil. It was used without further purification in the next step. The crude α-hydroxy ketone **O** and 3-(triisoprosilyl)propiolic acid (139 mg, 0.61 mmol) were dissolved in CH_2Cl_2 (2.0 mL). To the solution were added *N*,*N*'-dicyclohexylcarbodiimide (126 mg, 0.61 mmol) and 4-dimethylaminopyridine (6.1 mg, 0.05 mmol) with stirring at 0 °C. After a further 5 min at 0 °C, the ice bath was removed, and the reaction mixture was stirred for 52 h at room temperature. The precipitate was removed by filtration over a pad of Celite. Then the filtrate was evaporated. The residue was then purified by silica gel column chromatography (hexane/AcOEt, 20:1) to yield 193 mg of desired compound **1q** as a yellow oil (3%, 3steps). IR (neat): 2930, 2865, 2172, 2119, 1954, 1716, 1662, 1212 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 5.15 (t, J = 6.8 Hz, 1H), 4.79 (d, J = 6.8 Hz, 2H), 4.69 (s, 2H), 2.45 (s, 2H), 1.71-1.63 (m, 2H), 1.53-1.39 (m, 6H), 1.28-1.21 (m, 1H), 1.13-1.09 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm):δ 207.4, 201.1, 151.9, 97.1, 95.8, 93.2, 77.2, 70.0, 37.7, 36.5, 33.1, 25.8, 22.2, 18.4, 10.9. HRMS (ESI) calcd. $C_{24}H_{38}NaO_3Si$ for [$(M+Na)^+$] *m/z* 425.2488, found 425.2474.

Synthesis of 1r from β-allenyl bromide

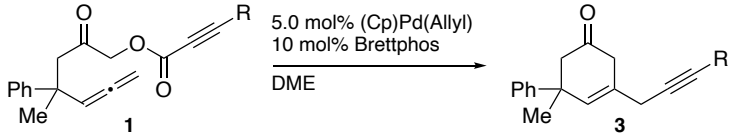


To a suspension of 55% sodium hydride (160 mg, 3.6 mmol) in anhydrous THF (3 mL), β-keto ester **Q** (960 mg, 3.60 mmol) in THF (3 mL) was added at 0 °C, and the reaction mixture was stirred at 0 °C for 30 min. To the solution was added allenyl bromide **P**[14] (400 mg, 3.0 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 18 h. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Then, the residue was roughly purified by silica gel column chromatography (hexane/AcOEt, 10:1~5:1) to yield 281 mg of desired compound as a yellow oil, which was used without further purification in the next step. To a solution of the crude β-keto ester **R** in H_2O (9.0 mL) was added NaOH (334 mg, 8.36 mmol) at room temperature. The reaction mixture was heated under reflux for 24 h. The mixture was extracted with Et_2O three times. The combined organic layer was washed with brine, dried over $MgSO_4$, and evaporated under reduced pressure. Then, the residue was roughly purified by silica gel column chromatography (hexane/AcOEt, 5:1) to yield 84 mg of desired compound as a pale yellow oil, which was used without further purification in the next step. To a solution of the crude PMB ether **S** in CH_2Cl_2/H_2O (10:1, 3.7 mL), DDQ (154 mg, 0.68 mmol) was added at 0 ° C. The reaction mixture was stirred at room temperature for

20 h. The reaction mixture was quenched by saturated aqueous solution of $NaHCO_3$. The mixture was extracted with CH_2Cl_2 three times. The combined organic layer was dried over $MgSO_4$ and evaporated under reduced pressure to give the crude as a pale yellow oil. Then, the residue was roughly purified by silica gel column chromatography (hexane/AcOEt, 4:1) to yield 51 mg of desired compound as pale yellow oil, which was used without further purification in the next step. The crude α-hydroxy ketone **T** and 3-(triisoprosilyl)propiolic acid (109 mg, 0.48 mmol) were dissolved in CH_2Cl_2 (1.6 mL). To the solution were added *N*,*N*'-dicyclohexylcarbodiimide (99 mg, 0.48 mmol) and 4-dimethylaminopyridine (5 mg, 0.04 mmol) with stirring at 0 °C. After a further 5 min at 0 °C, the ice bath was removed. The reaction mixture was stirred for 11 h at room temperature. The precipitate was removed by filtration over a pad of Celite. Then the filtrate was evaporated, and the residue was then purified by silica gel column chromatography (hexane/AcOEt, 50:1) to yield 59 mg of desired compound **1r** as a yellow oil (6%, 4 steps). IR (neat): 2945, 2867, 2173, 1956, 1718, 1219 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 5.21-5.15 (m, 1H), 4.75-4.69 (m, 4H), 2.59 (t, J = 7.1 Hz, 2H), 2.35-2.28 (m, 2H), 1.15-1.05 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.3, 202.0, 152.0, 95.7, 93.5, 88.7, 76.5, 68.8, 37.4, 21.1, 18.4, 10.9. HRMS (ESI) calcd. for $C_{19}H_{30}NaO_3Si$ [$(M+Na)^+$] *m/z* 357.1862, found 357.1865.

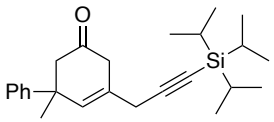
Palladium-Catalyzed Decarboxylative Cyclization of α-Acyloxyketones Having an Allene Moiety in the Tether

General Procedure C: Palladium-Catalyzed Decarboxylative Cyclization



In a sealed tube, starting material **1**, (Cp)Pd(Allyl) (5.0 mol%) and Brettphos (10 mol%) were dissolved in 1,2-dimethoxymethane (0.01 M). The solution was heated at 100 °C or 120 °C for 15~36 h under nitrogen and then evaporated. The residue was purified by column chromatography to afford desired product.

3a

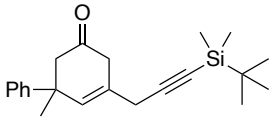


By following general procedure **C**, the reaction of the corresponding propionate (41.1mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 100 °C delivered 27 mg of compound **3a** as a yellow oil (71%). IR (neat): 2942, 2864 2173, 1719, 1683, 1233 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.31-7.29 (m, 4H), 7.22-7.19 (m, 1H), 6.15 (s, 1H), 3.08 (s, 2H), 2.88 (s, 2H), 2.81 (d, J = 13.9 Hz, 1H), 2.58 (d, J = 13.9 Hz, 1H), 1.48 (s, 3H), 1.10-1.05 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.7, 146.7, 132.4, 130.1, 128.5, 126.5, 125.6, 104.0, 83.9, 53.9, 43.1, 41.9, 29.0, 27.5, 18.6, 11.2. HRMS (EI) calcd. for $C_{25}H_{36}OSi$ [M^+] *m/z* 380.2535, found 380.2528.

1 mmol Scale Reaction of 3a

By following general procedure **C**, the reaction of the corresponding propionate (424.7 mg, 1.0 mmol) in the presence of (Cp)Pd(Allyl) (10.6 mg, 0.05 mmol) and Brettphos (53.7 mg, 0.1 mmol) in 100 mL 1,2-dimethoxyethane at 100 °C delivered 247 mg of compound **3a** as a yellow oil (68%).

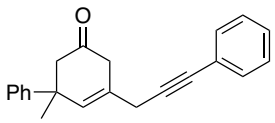
3b



By following general procedure **C**, the reaction of the corresponding propionate (38.3 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 100 °C delivered 18 mg of compound **3b** as a yellow oil (53%). IR (neat): 2928, 2856, 2173, 1941, 1868, 1718, 1250 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.31-7.30 (m, 4H), 7.23-7.18 (m, 1H), 6.11 (s, 1H), 3.06 (s, 2H), 2.88 (s, 2H), 2.81 (d, J = 14.2 Hz, 1H), 2.58 (d, J = 14.2 Hz, 1H), 1.48 (s, 3H), 0.94 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.5, 146.8, 132.4, 129.9, 128.6, 126.5, 125.6, 103.0, 86.2, 53.9, 43.1, 41.8, 28.9, 27.4, 26.1, 16.5, -4.5. HRMS (EI) calcd. for

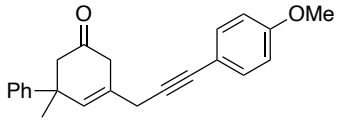
$C_{22}H_{30}OSi$ [M^+] *m/z* 338.2066, found 380.2064.

3d



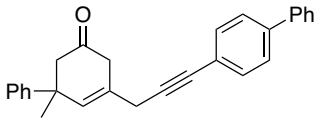
By following general procedure **C**, the reaction of the corresponding propionate (34.4 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 20 mg of compound **3d** as a yellow oil (67%). IR (neat): 3057, 2964, 1716, 1277 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.43-7.41 (m, 2H), 7.33-7.29 (m, 7H), 7.22-7.21 (m, 1H), 6.12 (s, 1H), 3.26 (s, 2H), 2.97 (s, 2H), 2.83 (d, J = 13.7 Hz, 1H), 2.60 (d, J = 13.7 Hz, 1H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.7, 146.8, 132.4, 131.6, 130.1, 128.6, 128.3, 128.0, 126.5, 125.6, 123.3, 85.6, 83.5, 54.0, 43.2, 41.9, 28.8, 27.1. HRMS (EI) calcd. for $C_{22}H_{20}O$ [M^+] *m/z* 300.1514, found 300.1509.

3e



By following general procedure **C**, the reaction of the corresponding propionate (37.4 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 15 mg of compound **3e** as a yellow oil (45%). IR (neat): 2963, 2930, 1716, 1604, 1248 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.37-7.32 (m, 6H), 7.22 (q, J = 4.6 Hz, 1H), 6.83 (d, J = 7.6 Hz, 2H), 6.11 (s, 1H), 3.81 (s, 3H), 3.24 (s, 2H), 2.96 (s, 2H), 2.83 (d, J = 13.9 Hz, 1H), 2.59 (d, J = 13.9 Hz, 1H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.8, 159.3, 146.8, 133.0, 132.2, 130.3, 128.6, 126.5, 125.7, 115.4, 113.9, 84.0, 83.2, 55.3, 54.0, 43.3, 41.9, 28.8, 27.1. HRMS (EI) calcd. for $C_{23}H_{22}O_2$ [M^+] *m/z* 330.1620, found 330.1626.

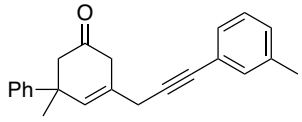
3f



By following general procedure **C**, the reaction of the corresponding propionate (42.0 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 17 mg of compound **3f** as a yellow oil (45%). IR (neat): 3057, 3029, 2964, 1715, 1233 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.60-7.54 (m, 4H), 7.51-7.43 (m, 5H), 7.38-7.30 (m, 4H), 7.24-7.21 (m, 1H), 6.15 (s, 1H), 3.28 (s, 2H), 2.99 (s, 2H), 2.85 (d, J = 14.2 Hz, 1H), 2.61 (d, J = 14.2 Hz, 1H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.5, 146.8, 140.8,

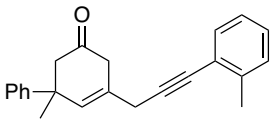
140.4, 132.4, 132.0, 130.1, 128.8, 128.6, 127.6, 127.0, 127.0, 126.5, 125.7, 122.2, 86.3, 83.3, 54.0, 43.3, 41.9, 28.9, 27.2. HRMS (EI) calcd. for $C_{28}H_{24}O$ [M^+] *m/z* 376.1827, found 376.1810.

3h



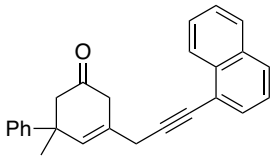
By following general procedure **C**, the reaction of the corresponding propionate (35.8 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 17 mg of compound **3h** as a yellow oil (54%). IR (neat): 3056, 2964, 2920, 1716, 1601, 1279 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.33-7.29 (m, 4H), 7.25-7.17 (m, 4H), 7.11 (d, J = 6.8 Hz, 1H), 6.12 (s, 1H), 3.25 (s, 2H), 2.97 (s, 2H), 2.83 (d, J = 13.6 Hz, 1H), 2.60 (d, J = 13.6 Hz, 1H), 2.33 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.6, 146.8, 137.9, 132.4, 132.2, 130.1, 128.9, 128.6, 128.6, 128.2, 126.5, 125.7, 123.1, 85.2, 83.6, 54.0, 43.3, 41.8, 28.8, 27.1, 21.2. HRMS (EI) calcd. for $C_{23}H_{22}O$ [M^+] *m/z* 314.1671, found 314.1662.

3i



By following general procedure **C**, the reaction of the corresponding propionate (35.8 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 15 mg of compound **3i** as a yellow oil (48%). IR (neat): 3059, 2965, 1717, 1276 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.39 (d, J = 7.3 Hz, 1H), 7.33-7.32 (m, 4H), 7.23-7.19 (m, 3H), 7.13 (dd, J = 8.0, 3.0 Hz, 1H), 6.17 (s, 1H), 3.30 (s, 2H), 2.97 (s, 2H), 2.84 (d, J = 14.2 Hz, 1H), 2.60 (d, J = 14.2 Hz, 1H), 2.42 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.5, 146.8, 140.0, 132.4, 131.9, 130.2, 129.4, 128.6, 128.0, 126.5, 125.6, 125.5, 123.1, 89.5, 82.4, 54.0, 43.2, 41.9, 28.9, 27.2, 20.8. HRMS (EI) calcd. for $C_{23}H_{22}O$ [M^+] *m/z* 314.1671, found 314.1667.

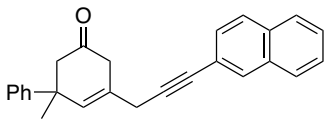
3j



By following general procedure **C**, the reaction of the corresponding propionate (39.4 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 20 mg of compound **3j** as a yellow oil (57%). IR (neat): 3061, 2964, 2250, 1932, 1715, 1231 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm):δ 8.34-8.31 (m, 1H), 7.86-7.81 (m, 2H), 7.67-7.65 (m, 1H), 7.56-7.49 (m, 2H), 7.44-7.40 (m, 1H), 7.38-7.31 (m, 4H), 7.25-7.21 (m, 1H), 6.26

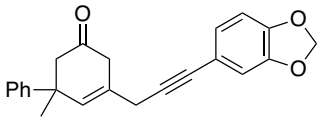
(s, 1H), 3.42 (s, 2H), 3.04 (s, 2H), 2.87 (d, J = 14.2 Hz, 1H), 2.63 (d, J = 13.7 Hz, 1H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.5, 146.8, 133.4, 133.2, 132.6, 130.3, 130.1, 128.6, 128.4, 128.3, 126.7, 126.5, 126.3, 126.0, 125.7, 125.2, 121.0, 90.6, 81.6, 53.9, 43.3, 42.0, 28.9, 27.4. HRMS (ESI) calcd. $C_{26}H_{22}NaO$ for [M^+] *m/z* 373.1568, found 373.1557.

3k



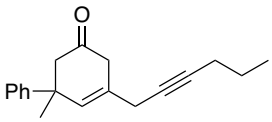
By following general procedure **C**, the reaction of the corresponding propionate (39.4 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 20 mg of compound **3k** as a yellow oil (57%). IR (neat): 3056, 2964, 1715, 1234 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.94 (s, 1H), 7.82-7.76 (m, 3H), 7.51-7.46 (m, 3H), 7.36-7.31 (m, 4H), 7.23 (td, J = 5.7, 2.9 Hz, 1H), 6.16 (s, 1H), 3.31 (s, 2H), 3.01 (s, 2H), 2.85 (d, J = 14.0 Hz, 1H), 2.62 (d, J = 14.0 Hz, 1H), 1.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.5, 146.8, 133.0, 132.7, 132.5, 131.3, 130.1, 128.6, 128.5, 127.9, 127.7, 127.6, 126.5, 126.5, 125.7, 120.6, 86.0, 83.8, 54.0, 43.3, 41.9, 28.9, 27.2(one aromatic carbon missing). HRMS (EI) calcd. for $C_{26}H_{22}O$ [M^+] *m/z* 350.1671, found 350.1661.

3l



By following general procedure **C**, the reaction of the corresponding propionate (38.8 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 20 mg of compound **3l** as a yellow oil (58%). IR (neat): 2965, 2899, 1717, 1601, 1213 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.33-7.30 (m, 4H), 7.22 (q, J = 4.3 Hz, 1H), 6.94 (dd, J = 8.0, 1.6 Hz, 1H), 6.87 (d, J = 1.8 Hz, 1H), 6.74 (d, J = 7.8 Hz, 1H), 6.10 (s, 1H), 5.96 (s, 2H), 3.22 (s, 2H), 2.95 (s, 2H), 2.83 (d, J = 13.7 Hz, 1H), 2.59 (d, J = 13.7 Hz, 1H), 1.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm):δ 208.6, 147.6, 147.4, 146.8, 132.3, 130.2, 128.6, 126.5, 126.0, 125.7, 116.6, 111.6, 108.4, 101.2, 83.9, 83.2, 54.0, 43.3, 41.9, 28.8, 27.0. HRMS (EI) calcd. for $C_{23}H_{20}O_3$ [M^+] *m/z* 344.1412, found 344.1402.

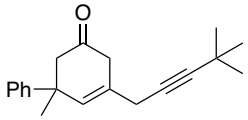
3m



By following general procedure **C**, the reaction of the corresponding propionate (31.0 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-

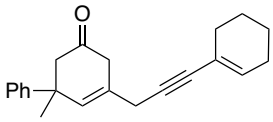
dimethoxyethane at 120 °C delivered 4 mg of compound **3m** as a yellow oil (15%). IR (neat): 2963, 2930, 2872, 1716, 1275 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.32-7.29 (m, 4H), 7.21 (q, J = 4.6 Hz, 1H), 6.04 (s, 1H), 2.99 (d, J = 1.4 Hz, 2H), 2.89 (s, 2H), 2.80 (d, J = 13.7 Hz, 1H), 2.57 (d, J = 14.2 Hz, 1H), 2.19-2.15 (m, 2H), 1.54-1.50 (m, 2H), 1.48 (s, 3H), 0.98 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.9, 146.9, 131.7, 130.9, 128.5, 126.5, 125.7, 83.4, 75.9, 54.0, 43.2, 41.8, 28.9, 26.5, 22.4, 20.8, 13.5. HRMS (EI) calcd. for $C_{19}H_{22}O$ [M^+] *m/z* 266.1671, found 266.1662.

3n



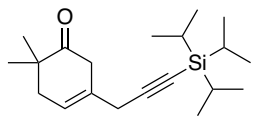
By following general procedure **C**, the reaction of the corresponding propionate (31.0 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 5 mg of compound **3n** as a yellow oil (17%). IR (neat): 2955, 2917, 1659, 1592, 1070 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.32-7.30 (m, 4H), 7.23-7.20 (m, 1H), 6.05 (s, 1H), 2.98 (s, 2H), 2.87 (s, 2H), 2.80 (d, J = 13.7 Hz, 1H), 2.58 (d, J = 13.7 Hz, 1H), 1.49 (s, 3H), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 209.0, 147.0, 131.7, 131.0, 128.5, 126.5, 125.6, 92.3, 74.3, 54.0, 43.1, 41.8, 31.2, 28.9, 27.5, 26.3. HRMS (ESI) calcd. for $C_{20}H_{24}NaO$ [$(M+Na)^+$] *m/z* 303.1725, found 303.1712.

3o



By following general procedure **C**, the reaction of the corresponding propionate (31.0 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 100 °C delivered 11 mg of compound **3o** as a yellow oil (36%). IR (neat): 3055, 3024, 2930, 2861, 1716, 1268 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 7.35-7.29 (m, 4H), 7.23-7.19 (m, 1H), 6.07-6.06 (m, 1H), 6.04 (s, 1H), 3.13 (s, 2H), 2.90 (s, 2H), 2.80 (d, J = 14.2 Hz, 1H), 2.57 (d, J = 14.2 Hz, 1H), 2.13-2.07 (m, 4H), 1.65-1.57 (m, 4H), 1.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 208.7, 146.9, 134.2, 132.0, 130.5, 128.6, 126.5, 125.7, 120.6, 85.3, 82.6, 54.0, 43.2, 41.8, 29.4, 28.8, 27.0, 25.6, 22.3, 21.5. HRMS (ESI) calcd. for $C_{22}H_{24}NaO$ [$(M+Na)^+$] *m/z* 327.1725, found 327.1715.

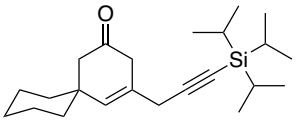
3p



By following general procedure **C**, the reaction of the corresponding propionate (36.3 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-

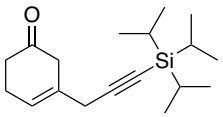
dimethoxyethane at 100 °C delivered 23 mg of compound **3p** as a yellow oil (71%). IR (neat): 2942, 2865, 2172, 1717 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$, rt, δ/ppm): δ 5.76 (br, 1H), 2.98 (s, 2H), 2.93 (s, 2H), 2.28-2.27 (m, 2H), 1.13 (s, 6H), 1.07-1.05 (m, 21H). ^{13}C NMR (126 MHz, $CDCl_3$, rt, δ/ppm): δ 213.4, 130.6, 121.1, 104.3, 83.2, 43.4, 40.7, 40.3, 27.4, 24.2, 18.6, 11.2. HRMS (ESI) calcd. for $C_{20}H_{34}NaOSi$ [$(M+Na)^+$] *m/z* 341.2277, found 341.2272.

3q



By following general procedure **C**, the reaction of the corresponding propionate (33.4 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 120 °C delivered 24 mg of compound **3q** as a yellow oil (63%). IR (neat): 2927, 2863, 2174, 1719, 1462, 1020 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 6.06 (s, 1H), 2.99 (s, 2H), 2.83 (s, 2H), 2.37 (s, 2H), 1.56-1.37 (m, 8H), 1.34-1.22 (m, 2H), 1.11-1.03 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 210.0, 131.9, 128.7, 104.3, 83.7, 51.5, 42.5, 39.0, 37.8, 27.4, 25.6, 21.7, 18.6, 11.3. HRMS (ESI) calcd. for $C_{23}H_{38}NaOSi$ [$(M+Na)^+$] *m/z* 381.2590, found 381.2578.

3r



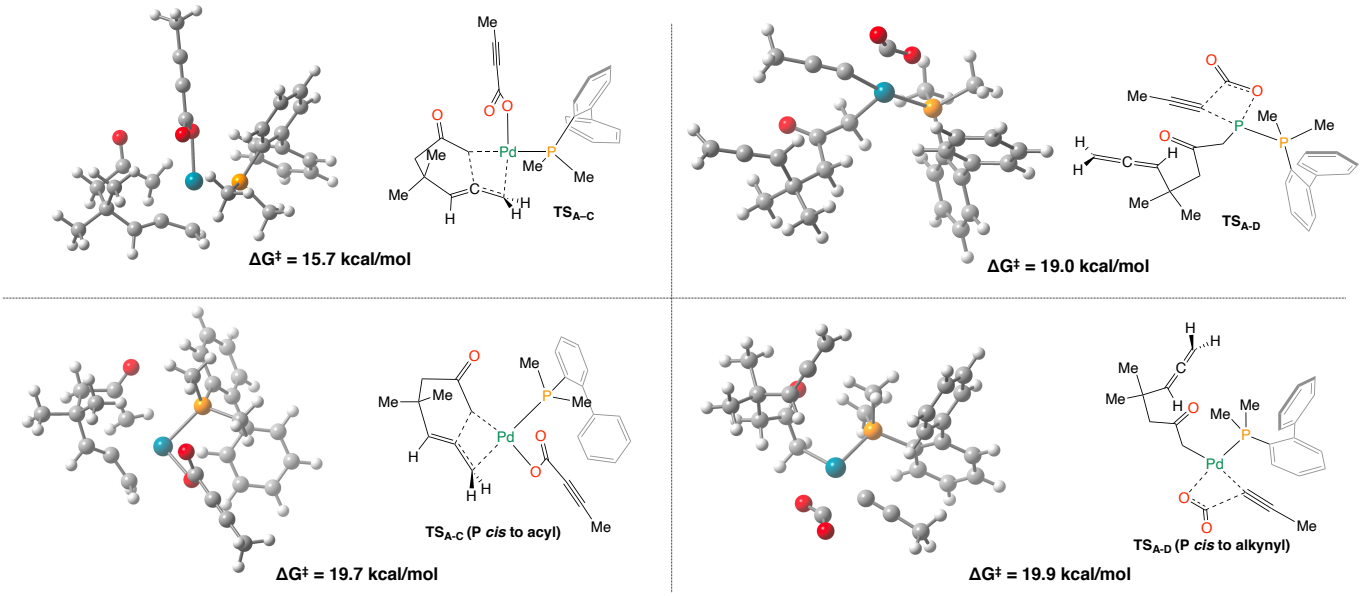
By following general procedure **C**, the reaction of the corresponding propionate (33.4 mg, 0.1 mmol) in the presence of (Cp)Pd(Allyl) (1.1 mg, 0.005 mmol) and Brettphos (5.4 mg, 0.01 mmol) in 10 mL 1,2-dimethoxyethane at 100 °C delivered 5 mg of compound **3r** as a yellow oil (17%). IR (neat): 2942, 2864, 2173, 1720, 1463, 1019 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, rt, δ/ppm): δ 5.94 (t, J = 1.6 Hz, 1H), 3.00 (s, 2H), 2.88 (s, 2H), 2.47 (br, 4H), 1.09-1.07 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, rt, δ/ppm): δ 209.9, 131.2, 122.3, 104.1, 83.5, 42.6, 38.3, 27.5, 24.8, 18.6, 11.3. HRMS (ESI) calcd. for $C_{18}H_{30}NaOSi$ [$(M+Na)^+$] *m/z* 313.1964, found 313.1956.

Computational Studies of the Reaction

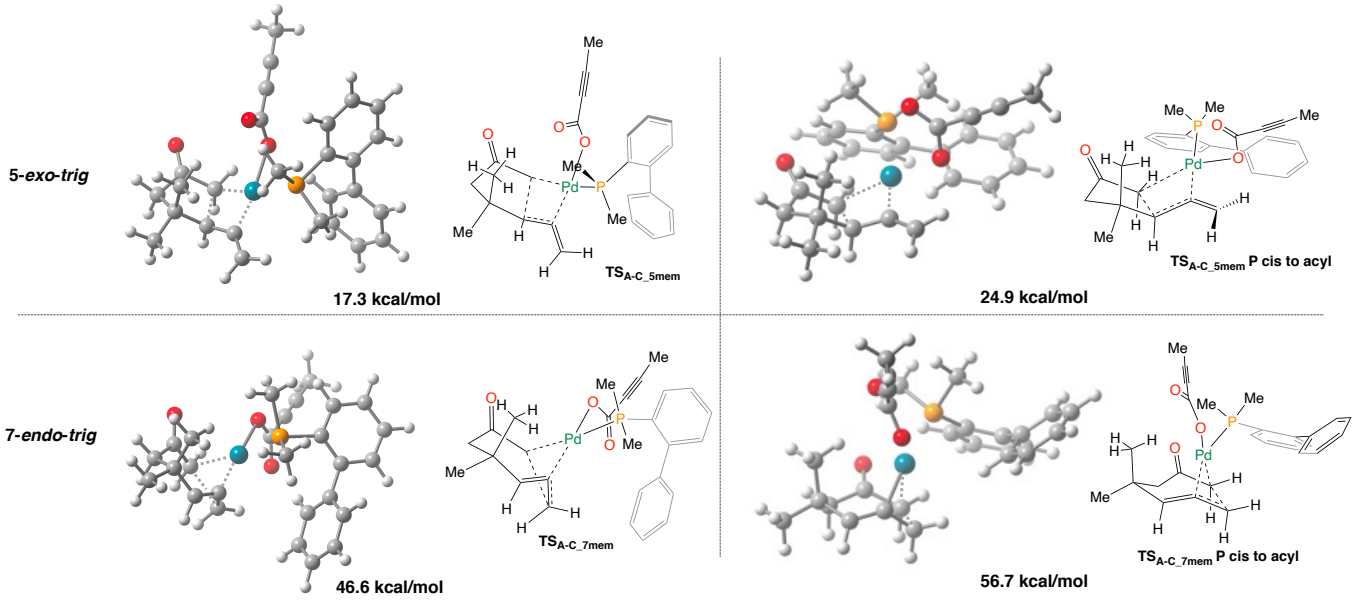
General computational details

All calculation reported in the present study were carried out using density functional theory with the B3LYP or M06-2x functional, as implemented in the Gaussian 16, Revision C. 01. For ease, a model complexes X were used instead of Y and the structures of them are described in Figure SX. Geometry optimization calculations were performed at the B3LYP/BS1 level of the theory under the condition of tight SCF convergence criteria (scf=tight) with an ultrafine integration grid (int=(grid=ultrafine)). BS1 refers to the basis sets employed, which were LANL2DZ for Pd atom and 6-31G(d) basis sets for all other atoms. After optimization of structures, frequency calculations were performed at the same level of the theory to confirm that the obtained structure were either a stationary point (no imaginary frequencies) or a transition state (one imaginary frequency). The IRC calculations were performed for each transition state structure to confirm the transition state connects the reaction pathway between the starting materials and the products. Thermal corrections to the Gibbs energy at 373K (100 °C) were calculated by frequency calculation. Single-point energy calculation were performed for all optimized geometries at the M06-2x/BS2 level of theory with solvents effects simulated by a polarizable continuum model (PCM) solvation model (THF). BS2 refers to the basis sets employed, which were SDD pseudopotential for Pd atom and 6-311+G(d,p) basis sets for all other atoms.

Key transition structures (insertion vs. decarboxylation) and their energies

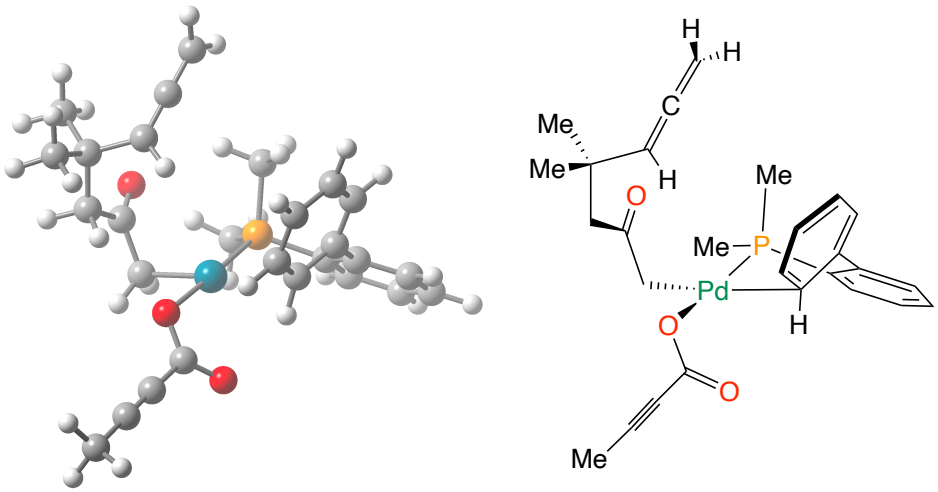


Key transition structures (regioselectivity) and their energies



Detailed information for calculated structures

A



M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.85097703

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.77

Entropy [cal/mol•K]: 233.737

Pd	0.08754400	0.52511800	-0.62803400
P	-1.59836600	-0.97486100	-1.08771700
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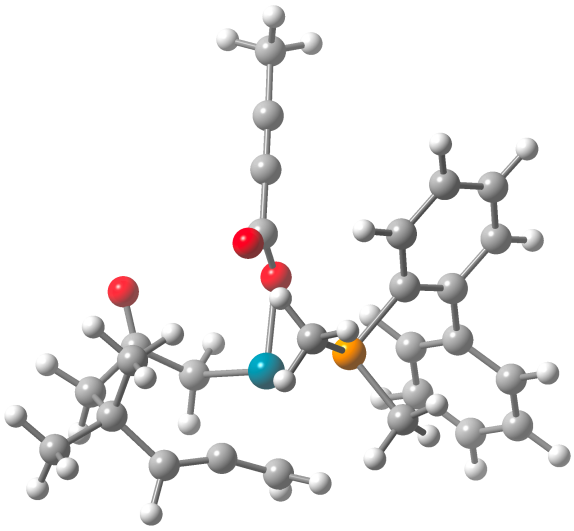
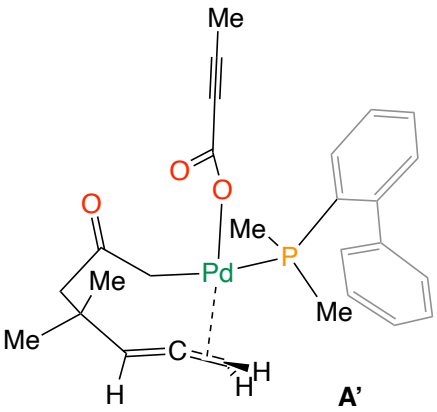
C	-1.72876900	-1.63161300	-2.80064500

C	-1.48549000	-2.52328300	-0.09241600
C	-3.24815500	-0.25036900	-0.69519500
C	3.17902300	-1.25223600	-0.92757600
O	1.36815200	-2.51980900	-1.93577800
H	-0.79369100	-2.16595700	-2.99270500
H	-1.83836500	-0.82124300	-3.52679800
H	-2.56736900	-2.32872700	-2.89630300
H	-2.32449400	-3.19037500	-0.31823600
H	-0.54041100	-3.00889100	-0.35355100
H	-1.47999300	-2.28631700	0.97336800
C	-4.29615300	-0.29341100	-1.62754700
C	-3.47922100	0.33727600	0.57183900
C	3.52946300	-2.30649600	0.15728800
H	3.98489000	-1.24499800	-1.67939500
H	3.17827200	-0.24921900	-0.48365500
C	-5.55888900	0.21125100	-1.31617800
H	-4.13536000	-0.72714000	-2.60849200
C	-4.76032600	0.81763900	0.87667900
C	-2.40521300	0.45440600	1.60191800
C	2.41062900	-2.33585800	1.19751000
C	-5.79434800	0.76078000	-0.05713200
H	-6.35365200	0.16924000	-2.05558800
H	-4.93261600	1.26257200	1.85268800
C	-1.32083300	1.33989600	1.42418000
C	-2.47905700	-0.29676000	2.78355100
C	1.82514600	-3.40149100	1.68203200
H	2.10969200	-1.36013800	1.58710700
H	-6.77512100	1.15334100	0.19627400
C	-0.32233100	1.43581400	2.40537400
H	-1.30878700	2.05075900	0.59173900
C	-1.48002400	-0.19618800	3.75457500
H	-3.31662400	-0.97294500	2.93334300
C	1.23895800	-4.46267900	2.17575900
C	-0.39514900	0.66250000	3.56443000
H	0.50373800	2.12136500	2.25184700
H	-1.54853100	-0.79488700	4.65895500
H	0.33532500	-4.87747200	1.73169500
H	1.63416400	-4.98225800	3.04745500
H	0.38122400	0.73746000	4.32037900

C	2.34478300	4.07089800	-0.20348100
C	1.27770900	3.08504300	-0.35346500
C	3.20567300	4.91490600	-0.08437200
O	1.67083900	1.85199000	-0.22443600
O	0.11443000	3.45165800	-0.57010200
C	4.23992000	5.93462300	0.05356300
H	5.15641400	5.52372100	0.49438700
H	4.50168100	6.35873700	-0.92380500
H	3.90037500	6.76107900	0.68999800
C	1.25299300	-0.15937800	-2.20236100
H	1.94622800	0.67463000	-2.31276900
H	0.63570800	-0.31022300	-3.08720800
C	4.81260600	-1.81766900	0.87284500
H	5.63798800	-1.71161100	0.15752700
H	4.65825900	-0.84490000	1.35485600
H	5.11843900	-2.53414700	1.64333000
C	3.79018700	-3.69360200	-0.45286800
H	2.90689600	-4.06391700	-0.97477800
H	4.61806200	-3.63770200	-1.17060500
H	4.06898400	-4.41154100	0.32666200

A’





A’

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.85039166

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.703

Entropy [cal/mol•K]: 223.642

Pd	0.98156100	-0.12563900	-0.50956200
P	-0.27187800	1.95729600	-0.16248200
C	2.43863600	-2.74279500	0.20589500
C	0.60654400	2.96595900	1.10667500
C	-0.37651400	3.14610300	-1.58443900
C	-2.02073900	1.84504100	0.41895400
C	3.94527900	-2.56785200	0.44641400
O	1.80713100	-3.48890500	0.94075200
H	1.60355800	3.19440300	0.71467400
H	0.72441000	2.35685700	2.00518000
H	0.09034100	3.90464800	1.33375400
H	-0.92604100	4.04727600	-1.29325900
H	0.63290500	3.43787800	-1.89094300
H	-0.87896100	2.68034900	-2.43435200
C	-2.31814500	2.22580600	1.73714800
C	-3.07573000	1.42272600	-0.42848300
C	4.44652100	-1.14861800	0.85145800
H	4.20397400	-3.26922900	1.24688800
H	4.48435800	-2.87876100	-0.46009100
C	-3.62997200	2.24221400	2.20920600
H	-1.51888800	2.50260500	2.41371700
C	-4.39084800	1.47186800	0.05883800
C	-2.87389900	0.89054200	-1.81144500
C	4.21949200	-0.17959000	-0.30656300
C	-4.67385900	1.88078200	1.36093100
H	-3.82842400	2.53785600	3.23549600
H	-5.19674800	1.15228600	-0.59605600
C	-2.20964600	-0.33093100	-2.01403700
C	-3.41479600	1.56081000	-2.92097200
C	3.11888800	0.23407000	-0.89994600
H	5.12821100	0.21189500	-0.77273100
H	-5.70171400	1.89688500	1.71309000
C	-2.07476800	-0.85302300	-3.30310700
H	-1.82780400	-0.87737900	-1.15612100
C	-3.27183200	1.03904800	-4.20795700
H	-3.94194200	2.49981900	-2.77093900
C	2.37034100	0.87002800	-1.85430800
C	-2.59792200	-0.16912300	-4.40263400

H	-1.57004700	-1.80547100	-3.44306100
H	-3.69039200	1.57396100	-5.05659300
H	2.22151700	0.41050000	-2.83169100
H	2.22492000	1.94555700	-1.81460300
H	-2.49188500	-0.57950800	-5.40340100
C	-1.36481100	-1.67528000	2.70280700
C	-0.45578200	-0.86411900	1.89944600
C	-2.09673700	-2.33334400	3.40894300
O	0.21950100	0.02683200	2.43631600
O	-0.45164800	-1.16728400	0.63590700
C	-2.97586200	-3.13856100	4.25032600
H	-3.98821200	-3.19000500	3.83060600
H	-2.60122300	-4.16641000	4.33188200
H	-3.05233700	-2.72919700	5.26518100
C	1.77862600	-2.06326400	-0.94995200
H	2.41387700	-1.98613900	-1.83461200
H	0.82341100	-2.54540500	-1.16672600
C	5.97013700	-1.23528000	1.09923500
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H	2.67447500	-0.57713600	2.04254200
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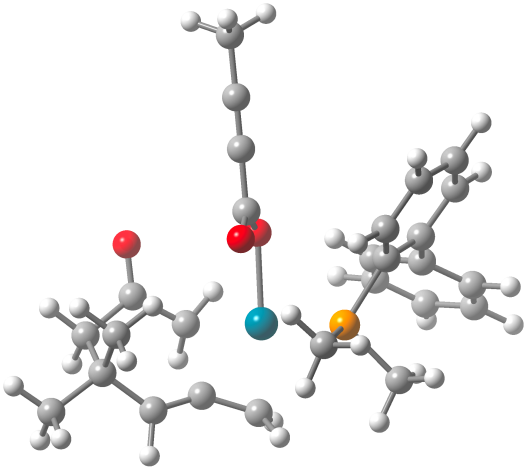
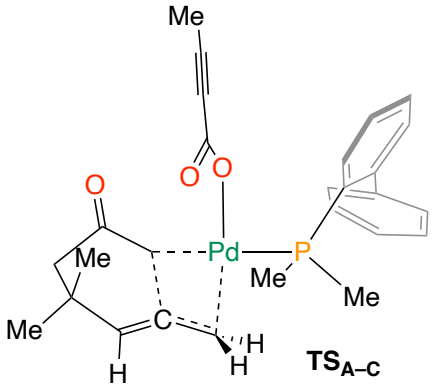
$TS_{A\text{-}C}$





TS_{A-C}

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.82270374

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 341.795

Entropy [cal/mol•K]: 222.707

Pd	-0.77227700	-0.73878200	-0.02809300
P	0.97525300	-0.69581700	1.56067200
C	-3.32349300	0.24156100	-1.70117900
C	0.27588800	-0.12775100	3.16826700
C	1.73510000	-2.31868700	2.02743200
C	2.42880900	0.39507400	1.24194500
C	-4.69996000	0.04993000	-1.08067700
O	-3.02636900	1.28607300	-2.25661200
H	-0.48319400	-0.85484300	3.47489700
H	-0.21280400	0.83532600	3.00808200
H	1.03900000	-0.05783300	3.95055700
H	2.48326500	-2.17966400	2.81498500
H	0.94909200	-2.98450300	2.39674100
H	2.20832800	-2.78295700	1.16047300
C	2.58815400	1.55290100	2.02009500
C	3.40805200	0.08156200	0.26702900
C	-4.69566700	-0.21087100	0.45201600
H	-5.28097800	0.95200000	-1.29821900
H	-5.19098600	-0.80075600	-1.57495400
C	3.71120200	2.36807000	1.88383600
H	1.82377900	1.83614100	2.73320000
C	4.54164900	0.90182600	0.16385300
C	3.29241300	-1.05978300	-0.69154500
C	-3.87364500	-1.45155300	0.76129100
C	4.70130500	2.03216500	0.96357600
H	3.80546500	3.26007600	2.49655900
H	5.29194300	0.65498100	-0.58218200
C	2.29079700	-1.06093000	-1.67666300
C	4.22799000	-2.10687300	-0.67208600
C	-2.66418200	-1.77839000	0.32191400
H	-4.34130500	-2.19730900	1.40838000
H	5.58502300	2.65463200	0.85247700
C	2.22033600	-2.10226000	-2.60533600
H	1.58990900	-0.23195900	-1.72282300

C	4.14971600	-3.14889700	-1.59782000
H	5.01398000	-2.10512100	0.07916300
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O	-0.11469700	1.07825700	-0.90576400
C	0.84523100	5.69982200	-1.90188600
H	1.83339000	5.63745700	-2.37459600
H	0.12583800	5.98056600	-2.68118900
H	0.87487200	6.51343800	-1.16654800
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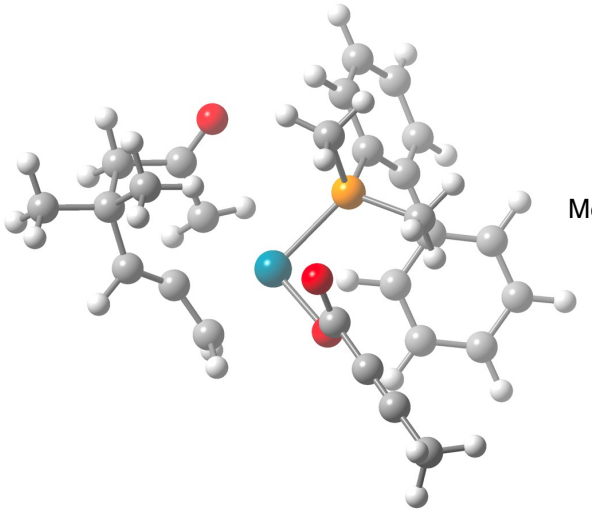
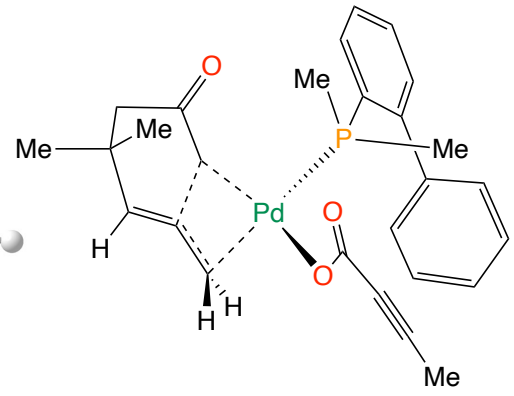
H	-2.78797800	-1.86589100	-1.92893700
H	-1.47935600	-0.68957500	-2.24231700
C	-6.15042200	-0.45580000	0.90136000
H	-6.77471500	0.41654500	0.67893400
H	-6.58705300	-1.32395700	0.39253200
H	-6.19984400	-0.63552000	1.98228300
C	-4.13264100	1.01528400	1.20769100
H	-3.09505400	1.23513100	0.93859800
H	-4.73872100	1.90353800	0.99002000
H	-4.16455800	0.84279400	2.29008900

$TS_{A\text{-}C}$ P cis to acyl





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.82270374

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 341.751

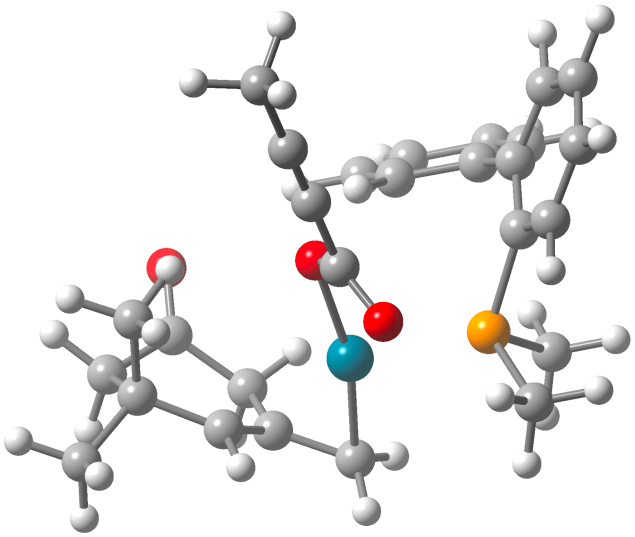
Entropy [cal/mol•K]: 225.851

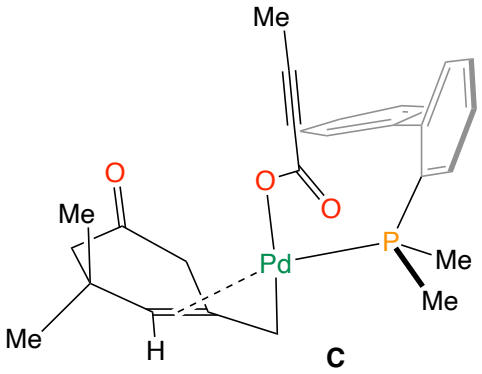
Pd	0.66535300	0.48543000	-0.60584300
P	-0.63911600	-0.55563500	1.18696500
C	2.73593100	-1.97797400	-0.25225500
C	0.35507000	-0.86929900	2.70784600
C	-1.99072900	0.50644200	1.86741700
C	-1.44941400	-2.17513700	0.78572100
C	4.23712100	-1.82361800	-0.39137300
O	2.25146300	-2.57286300	0.70361100
H	0.70104200	0.11395000	3.04041500
H	1.22336600	-1.48946900	2.47840700
H	-0.24373200	-1.33973400	3.49503600
H	-2.62666000	-0.07091100	2.54590400
H	-1.50882100	1.31972400	2.41516500
H	-2.59598100	0.93195200	1.06736300
C	-0.84950200	-3.35219800	1.26716200
C	-2.63722300	-2.28433400	0.01482500
C	4.70258800	-0.35070000	-0.19081400
H	4.71380900	-2.46729300	0.35452000
H	4.55010400	-2.15355400	-1.39096700
C	-1.40945200	-4.60760600	1.03385400
H	0.07749500	-3.29326300	1.82249200

C	-3.19169000	-3.55860500	-0.19392400
C	-3.35638300	-1.12662700	-0.59665300
C	3.99435000	0.54845800	-1.18746200
C	-2.59347100	-4.71225300	0.30755800
H	-0.91874000	-5.49561100	1.42277500
H	-4.10127200	-3.63454000	-0.78333700
C	-2.73078700	-0.26725400	-1.51286700
C	-4.71185900	-0.90885100	-0.29616300
C	2.72203500	0.54461000	-1.57369300
H	4.61026500	1.30131600	-1.68265500
H	-3.04438900	-5.68316900	0.12047500
C	-3.42908100	0.79390400	-2.09049600
H	-1.68864100	-0.42664600	-1.77584700
C	-5.41245000	0.14852600	-0.87629100
H	-5.20962400	-1.56485200	0.41315000
C	1.75448000	1.33844200	-2.20016800
C	-4.77164500	1.00649700	-1.77315100
H	-2.91917000	1.45484300	-2.78534200
H	-6.45740600	0.30605500	-0.62206700
H	1.29474300	1.00776200	-3.13234200
H	1.75046800	2.41054800	-2.01836300
H	-5.31426900	1.83487500	-2.22034300
C	-0.64584900	4.24580000	0.84460400
C	-0.04717900	2.91666100	0.73365000
C	-1.12152700	5.35273400	0.97121400
O	0.65884800	2.47386100	1.64908800
O	-0.35302400	2.30556900	-0.37090300
C	-1.69622600	6.68495000	1.12511200
H	-2.72552100	6.62508200	1.50034000
H	-1.11986000	7.29158700	1.83435300
H	-1.72501200	7.22091500	0.16840100
C	1.88891100	-1.33572200	-1.30094400
H	2.24396600	-1.48263700	-2.32116000
H	0.86072600	-1.71744500	-1.24581800
C	6.22177800	-0.28643200	-0.44487800
H	6.75855400	-0.93810900	0.25352100
H	6.47050900	-0.60233800	-1.46504600
H	6.59613300	0.73469900	-0.30509400
C	4.40791600	0.12047900	1.25199800

H	3.33624100	0.11012300	1.47010700
H	4.91851900	-0.52406600	1.97844800
H	4.76109300	1.14704500	1.39849500

C





C

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.91488651

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 344.095

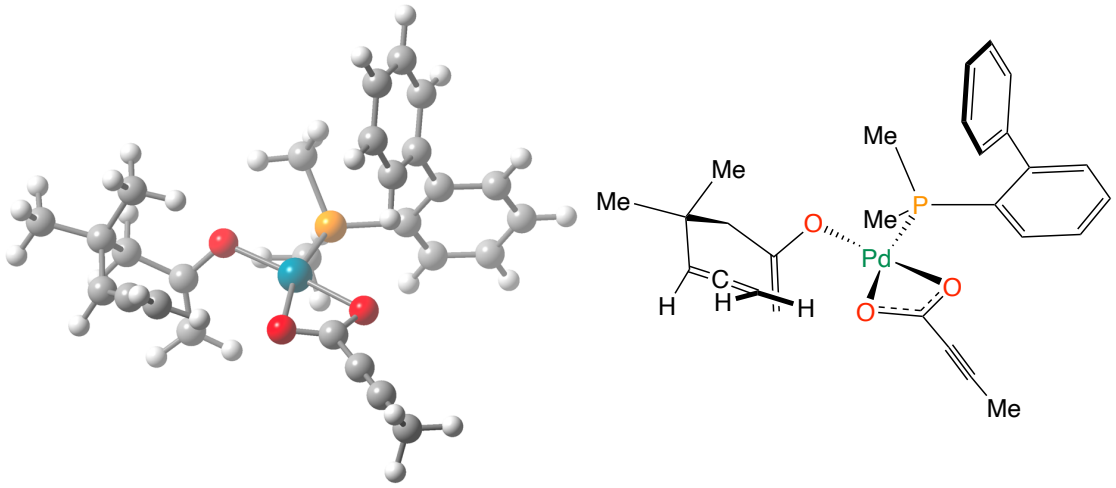
Entropy [cal/mol•K]: 225.057

Pd	0.87247200	-0.01387900	-0.50300600
P	-0.26920300	1.94431200	-0.18222700
C	2.61643400	-2.72235700	0.17613300
C	0.61605300	2.93483800	1.09325100
C	-0.35612300	3.12459200	-1.60077200
C	-2.01648600	1.82971500	0.41231500
C	4.07052900	-2.65198000	0.56050400
O	1.79903800	-3.40072700	0.76447400
H	1.61002700	3.16666600	0.69797700
H	0.73131300	2.31925400	1.98757600
H	0.09397500	3.86993700	1.32229500
H	-0.87520100	4.04268500	-1.30483300
H	0.66446800	3.36941000	-1.91073300
H	-0.87906100	2.67022400	-2.44387700
C	-2.30869600	2.21550700	1.73112100

C	-3.07721100	1.41716300	-0.43216400
C	4.51875100	-1.20414000	0.88281000
H	4.25106600	-3.31523900	1.41172100
H	4.66089200	-3.01558700	-0.29398700
C	-3.62029400	2.24229700	2.20516000
H	-1.50665200	2.48362700	2.40764700
C	-4.39083100	1.47375400	0.05794100
C	-2.87984900	0.88575600	-1.81492500
C	4.11824600	-0.27067300	-0.23560700
C	-4.66846900	1.88462000	1.36048600
H	-3.81434400	2.54006700	3.23164800
H	-5.19947800	1.15830700	-0.59549800
C	-2.21990900	-0.33769700	-2.01586300
C	-3.41607000	1.56022100	-2.92351200
C	3.05555700	-0.46080400	-1.05048500
H	4.64504300	0.68264800	-0.28841500
H	-5.69527600	1.90634500	1.71546600
C	-2.08250600	-0.85712700	-3.30505000
H	-1.83989700	-0.88361800	-1.15706100
C	-3.27131700	1.04013400	-4.21096700
H	-3.94066400	2.50061200	-2.77284700
C	2.36575000	0.62873300	-1.76789400
C	-2.59962600	-0.16927600	-4.40496700
H	-1.58034300	-1.81091200	-3.44610100
H	-3.68606200	1.57717900	-5.06007800
H	2.04969100	0.45390700	-2.79953300
H	2.78544500	1.62401400	-1.61896200
H	-2.49094500	-0.57794600	-5.40618700
C	-1.36338900	-1.68130400	2.73886000
C	-0.46154500	-0.86883100	1.93075800
C	-2.10463200	-2.34341500	3.43011300
O	0.21173600	0.03013500	2.46334800
O	-0.46284200	-1.16873000	0.67505300
C	-2.98988800	-3.14964600	4.26173900
H	-4.00017700	-3.19849000	3.83655400
H	-2.61823800	-4.17880400	4.34254800
H	-3.07203700	-2.74443700	5.27798100
C	2.31779800	-1.86358000	-1.06140200
H	2.68330800	-2.39879500	-1.95197400

H	1.22032100	-1.87598900	-1.23556200
C	6.04127300	-1.21231000	1.09469300
H	6.30946500	-1.88613300	1.91686400
H	6.56900900	-1.54769200	0.19393100
H	6.40939100	-0.21123200	1.35023200
C	3.82406700	-0.70846000	2.17990000
H	2.73435000	-0.67335100	2.08503900
H	4.07644300	-1.36528200	3.02235600
H	4.16476500	0.30328600	2.43084800

B



M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.81560729

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.52

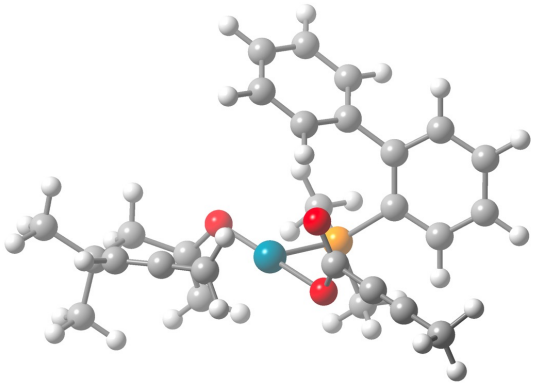
Entropy [cal/mol•K]: 234.039

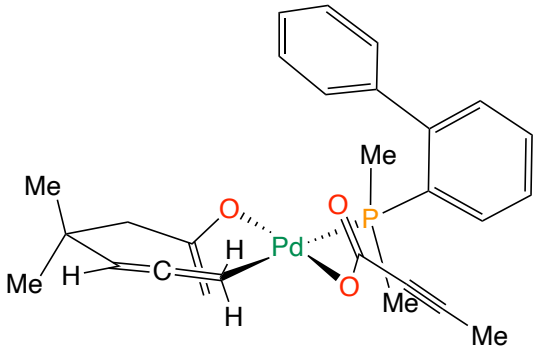
Pd	0.34848800	0.27749000	-0.57516800
P	-1.13004400	-1.40098300	-0.95729500
C	2.69357700	-1.27193000	-1.28232800
C	-0.72899200	-2.18116200	-2.57584700
C	-0.92328500	-2.78937800	0.22692900
C	-2.91567500	-0.95481300	-1.03005700
C	3.84747000	-2.11835500	-0.76979000
O	1.64874000	-1.25725900	-0.43594600
H	0.31124500	-2.51164800	-2.51226000
H	-0.79332500	-1.45485400	-3.38910200
H	-1.38443200	-3.03298600	-2.78609700

H	-1.48117800	-3.66867700	-0.11189200
H	0.14907900	-2.99909800	0.25446900
H	-1.25857200	-2.50320700	1.22375100
C	-3.52474100	-0.88675300	-2.29544200
C	-3.69884000	-0.69057400	0.12274500
C	4.63852000	-1.56326100	0.46016000
H	3.46456700	-3.11312700	-0.49880300
H	4.55075700	-2.26228100	-1.59893100
C	-4.87991600	-0.59509400	-2.43786600
H	-2.94110100	-1.07051400	-3.19017800
C	-5.06638700	-0.42149500	-0.04376300
C	-3.16362500	-0.67863800	1.51799400
C	5.10850500	-0.14637900	0.14651800
C	-5.65798800	-0.37122500	-1.30422000
H	-5.32054300	-0.54987500	-3.42967900
H	-5.66333100	-0.22528200	0.84230600
C	-2.23048900	0.28663800	1.92812500
C	-3.63925300	-1.60716900	2.45880600
C	4.77523000	0.94168500	0.79233400
H	5.77005700	-0.05271900	-0.71806200
H	-6.71724600	-0.14839700	-1.39780300
C	-1.76438600	0.29975100	3.24493400
H	-1.88798800	1.03678800	1.22195400
C	-3.16982700	-1.59197500	3.77280300
H	-4.36850400	-2.35229400	2.15086600
C	4.41840900	2.03539500	1.41537200
C	-2.22611000	-0.64059200	4.16781600
H	-1.04216300	1.05284900	3.54815600
H	-3.53994000	-2.32347000	4.48630000
H	3.52970300	2.58308000	1.10607500
H	4.98628500	2.42854600	2.25767800
H	-1.85838500	-0.62886000	5.19022100
C	0.02693600	4.21297100	-0.24393200
C	0.21637800	2.78940400	-0.36082500
C	-0.12226800	5.41063800	-0.14432000
O	1.36435900	2.27200800	-0.26095600
O	-0.81299600	2.03993200	-0.56755100
C	-0.29344500	6.85283200	-0.02573900
H	0.12800700	7.22003800	0.91768100

H	0.21997700	7.37310400	-0.84326600
H	-1.35257900	7.13380700	-0.05746300
C	2.74714000	-0.65610900	-2.48165200
H	3.63974500	-0.71278500	-3.09424100
H	1.93388300	-0.03072400	-2.84012200
C	5.88669300	-2.45639000	0.64821400
H	5.59705200	-3.50382600	0.80243000
H	6.54522900	-2.41510300	-0.22834200
H	6.46648500	-2.13225300	1.51989800
C	3.79344100	-1.61223700	1.74356500
H	2.89989900	-0.99233500	1.65687700
H	3.47433900	-2.64224300	1.94575200
H	4.37995300	-1.26359200	2.60137300

B’





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.81599972

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.339

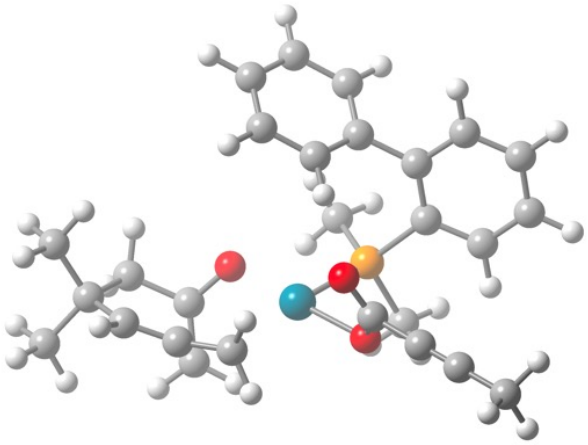
Entropy [cal/mol•K]: 229.684

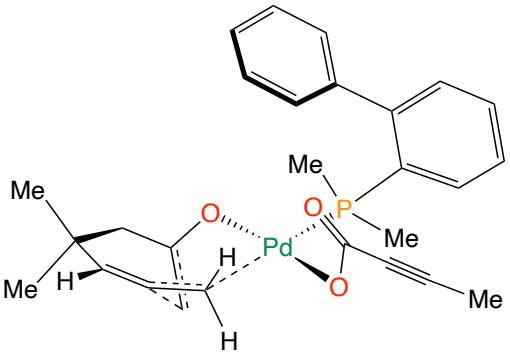
Pd	0.53432400	-0.72457400	0.24418400
P	-0.84720500	0.49329600	1.58268700
C	3.04712200	0.40868600	1.14192300
C	-1.11017300	-0.44310200	3.14632000
C	-0.12601300	2.09157100	2.12956900
C	-2.53453000	0.83425000	0.93100600
C	4.34979200	0.75224200	0.43844100
O	1.99200500	0.65290100	0.36073500
H	-0.14626600	-0.51087700	3.65824400

H	-1.44349700	-1.45674400	2.91080000
H	-1.83279300	0.05082800	3.80423400
H	-0.83103900	2.63230800	2.76975300
H	0.79502000	1.87126500	2.67612600
H	0.13062900	2.69719100	1.26046600
C	-3.61627600	0.11820700	1.47228600
C	-2.78365700	1.80232800	-0.07412900
C	5.08828200	-0.42076000	-0.27562800
H	4.12495300	1.52691100	-0.30269000
H	5.06166700	1.18027000	1.15591400
C	-4.92677800	0.37006300	1.07068300
H	-3.44383700	-0.64773000	2.21893000
C	-4.11330500	2.05621200	-0.44392500
C	-1.71263400	2.56327700	-0.78513200
C	4.23359000	-1.27131400	-1.21964400
C	-5.17809800	1.35437800	0.11743000
H	-5.74242400	-0.20048900	1.50558100
H	-4.30010000	2.80285200	-1.21039400
C	-0.81941300	1.90475800	-1.64494200
C	-1.63373900	3.95960100	-0.65539300
C	2.97918600	-1.63459700	-1.23852600
H	4.82205300	-1.75864300	-2.00394200
H	-6.19515400	1.56629800	-0.20081500
C	0.14992800	2.63366500	-2.33754900
H	-0.90328000	0.83046600	-1.78897100
C	-0.66192500	4.68237500	-1.34791400
H	-2.33057500	4.47502500	0.00109100
C	1.75300300	-2.11757200	-1.37876700
C	0.23563800	4.01873900	-2.18827600
H	0.83641800	2.11259700	-2.99888900
H	-0.60618300	5.76160800	-1.23132800
H	1.48067600	-3.06800200	-0.92042500
H	1.03916500	-1.69504700	-2.08759800
H	0.99356300	4.58050600	-2.72780100
C	-2.66243900	-3.20935100	-0.99197700
C	-1.61038700	-2.19786300	-0.96973400
C	-3.53769500	-4.04457500	-1.05256700
O	-1.38414200	-1.50416200	-1.96625500
O	-0.97491400	-2.13907700	0.16923700

C	-4.59178600	-5.04981100	-1.13398200
H	-5.54285300	-4.59944100	-1.44398000
H	-4.33924200	-5.82234100	-1.87075700
H	-4.75282400	-5.54719900	-0.16976400
C	3.01982400	-0.06807000	2.40841800
H	3.93414200	-0.19107600	2.97802000
H	2.09379900	-0.38038200	2.88114500
C	5.70650200	-1.38807500	0.76060700
H	6.42662100	-0.85545600	1.39520100
H	4.93136400	-1.81752700	1.40089000
H	6.23829600	-2.20808300	0.26384500
C	6.22566800	0.20166600	-1.11665400
H	5.82667600	0.85549400	-1.90063200
H	6.88648600	0.80050200	-0.47939300
H	6.83598500	-0.57298300	-1.59701100

$TS_{B\text{-}F}$





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.79603584

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 341.269

Entropy [cal/mol•K]: 226.281

Pd	0.42409900	-0.78570900	0.43310800
P	-1.03366300	0.50440700	1.65981700
C	3.09667800	-0.01038100	1.14348700
C	-1.46983500	-0.43755600	3.18170700
C	-0.29707200	2.05923900	2.31308900

C	-2.64068300	0.96173900	0.88612400
C	4.35542400	0.68625200	0.66573000
O	1.98024700	0.51537300	0.70416000
H	-0.54521600	-0.58916400	3.74684800
H	-1.86126600	-1.41892100	2.90178100
H	-2.19241600	0.09315000	3.81049500
H	-1.00709100	2.58892400	2.95687200
H	0.59868100	1.79234000	2.88021600
H	0.00450800	2.70206800	1.48532600
C	-3.81638100	0.35805400	1.36356500
C	-2.73198200	1.91021000	-0.16348500
C	5.12936900	-0.19038000	-0.39366500
H	4.05567900	1.63334200	0.20886500
H	5.02973500	0.91456300	1.49944200
C	-5.06744300	0.69907000	0.85214100
H	-3.76539800	-0.38908300	2.14680300
C	-4.00364800	2.25513600	-0.64625800
C	-1.55083400	2.56622100	-0.80335000
C	4.23977800	-1.27352100	-1.00064900
C	-5.16290200	1.66208500	-0.14979800
H	-5.95865400	0.21383300	1.24000100
H	-4.06908800	2.98633500	-1.44690700
C	-0.65465200	1.82494400	-1.59012500
C	-1.36863200	3.95415300	-0.68395400
C	3.09641500	-1.76785600	-0.57481500
H	4.62034100	-1.71840600	-1.92456700
H	-6.13159600	1.94226000	-0.55450300
C	0.41408200	2.46494100	-2.22238600
H	-0.80612200	0.75739300	-1.73054500
C	-0.29723100	4.58714600	-1.31499500
H	-2.06713200	4.53412500	-0.08556000
C	1.82668100	-2.25942900	-0.68404900
C	0.59940100	3.84126500	-2.08425800
H	1.09835100	1.87930300	-2.82993500
H	-0.16492100	5.66071000	-1.20762500
H	1.56379700	-3.19131900	-0.18521500
H	1.28421400	-2.03478100	-1.60563200
H	1.43322700	4.33319800	-2.57833400
C	-2.66823500	-3.15445300	-1.19811300

C	-1.58729300	-2.18334700	-1.05356400
C	-3.56163400	-3.95597300	-1.36144400
O	-1.17678500	-1.54838400	-2.02853400
O	-1.14116600	-2.09528600	0.17059700
C	-4.63659200	-4.92078900	-1.56626600
H	-5.54134200	-4.42757700	-1.94278300
H	-4.34683700	-5.68065800	-2.30253100
H	-4.89894000	-5.43885100	-0.63570300
C	3.21501700	-1.20889200	1.80446400
H	4.17718700	-1.53800500	2.17957800
H	2.34194900	-1.78123400	2.09836900
C	6.36577000	-0.87034700	0.24031700
H	7.06496000	-0.11776500	0.62552900
H	6.08215800	-1.53058900	1.06554100
H	6.89908700	-1.47653900	-0.50152100
C	5.60949100	0.73423200	-1.53414000
H	4.76004200	1.19618800	-2.04905000
H	6.24168300	1.53499200	-1.13160700
H	6.20010500	0.18248200	-2.27549700

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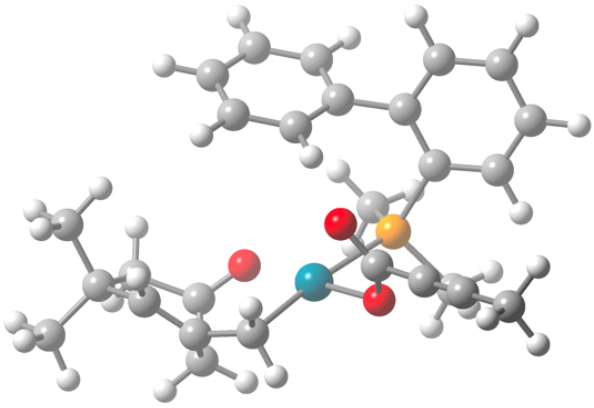

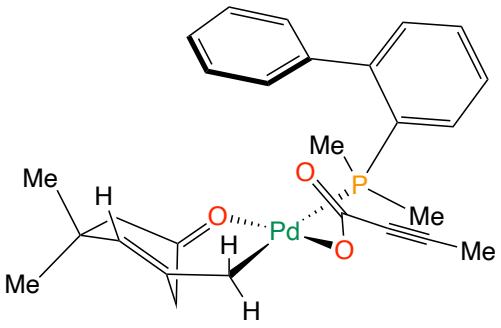

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.85874291

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 343.729

Entropy [cal/mol•K]: 225.63

Pd	0.35610200	-0.90170500	0.66439200
P	-1.30762800	0.56317700	1.67459200
C	3.15492600	0.00876200	1.22246400
C	-2.10385600	-0.40343600	3.03244800
C	-0.68010000	2.05535200	2.57499300
C	-2.71974000	1.21313400	0.67523900
C	4.36379600	0.68785000	0.63435200
O	2.02329300	0.51785000	1.21814500
H	-1.31477100	-0.68134500	3.73866000
H	-2.52034400	-1.32600100	2.61859700
H	-2.87793500	0.15569600	3.56855900
H	-1.48388000	2.57379700	3.10843800
H	0.08258500	1.72957400	3.28943900
H	-0.21171600	2.74100000	1.86560700
C	-4.03327300	0.81658900	0.97517000
C	-2.50911600	2.12614600	-0.38807600
C	4.87690800	-0.20765300	-0.58755300
H	4.08039300	1.68559800	0.29112000
H	5.15288300	0.78600800	1.39046300
C	-5.12646100	1.32345500	0.27262800
H	-4.21719100	0.10256300	1.76976800
C	-3.62323000	2.64334200	-1.06597100

C	-1.15642500	2.56786900	-0.85067800
C	3.80473600	-1.24734100	-0.92728800
C	-4.92203700	2.25176800	-0.74525300
H	-6.13030300	0.99407000	0.52661800
H	-3.45391400	3.34660400	-1.87664600
C	-0.30327100	1.67617000	-1.52171600
C	-0.76086100	3.90718000	-0.70009900
C	3.01479900	-1.82157300	0.01119600
H	3.59306100	-1.41682900	-1.98157600
H	-5.76430300	2.65989200	-1.29738200
C	0.92287700	2.12425000	-2.01937300
H	-0.60706600	0.64383100	-1.67918500
C	0.46939000	4.34677200	-1.19186800
H	-1.42379100	4.60456800	-0.19347900
C	1.66796200	-2.37369400	-0.16968100
C	1.31497200	3.45414100	-1.85471600
H	1.56411800	1.42539800	-2.55030600
H	0.76196500	5.38594200	-1.06423400
H	1.44296700	-3.25281600	0.44005800
H	1.35692400	-2.50518100	-1.20693100
H	2.26797500	3.79783900	-2.24947100
C	-2.64120200	-3.20144800	-1.23133600
C	-1.56310300	-2.23988600	-1.00498600
C	-3.53215200	-3.98942600	-1.46088200
O	-1.12540600	-1.55898800	-1.93433000
O	-1.16743200	-2.21904900	0.23833400
C	-4.60354200	-4.93830000	-1.74457300
H	-5.49272300	-4.42481200	-2.13113900
H	-4.29153000	-5.66821900	-2.50188200
H	-4.90098300	-5.49422000	-0.84688200
C	3.33922200	-1.45264700	1.46919800
H	4.35161900	-1.71911000	1.77909600
H	2.59584700	-1.85573900	2.15937600
C	6.23504100	-0.86938500	-0.25778800
H	7.00145100	-0.11188200	-0.04926600
H	6.17221300	-1.53546300	0.60901300
H	6.57649800	-1.47025400	-1.10789700
C	5.06801100	0.72177000	-1.80271800
H	4.12478400	1.20557500	-2.08000000

H	5.80458300	1.50451000	-1.58597700
H	5.42502700	0.15309900	-2.66950600

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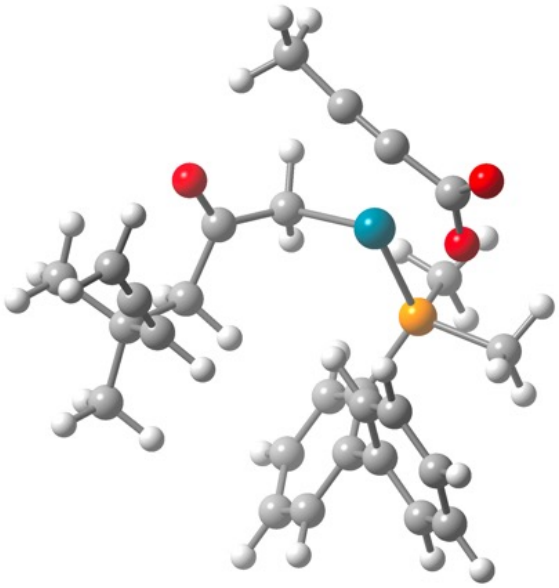

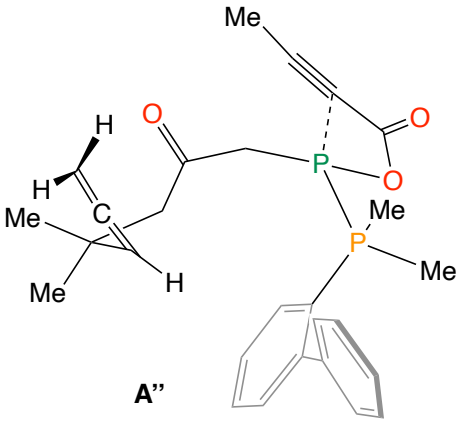

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M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.84718493

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.333

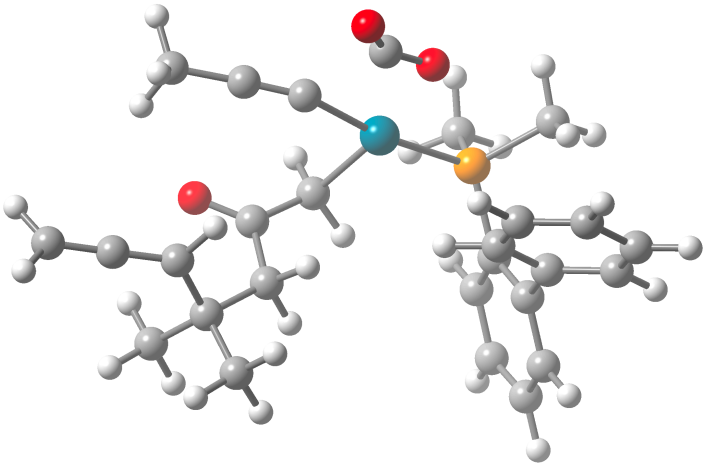
Entropy [cal/mol•K]: 230.228

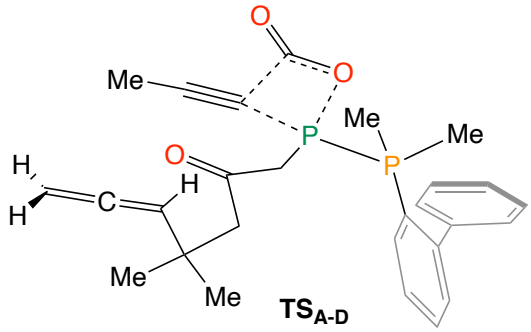
Pd	0.84045400	-1.36808300	-0.75192900
P	-1.32941600	-1.20293000	-1.45315500
C	1.95910500	1.34905400	-1.13899100
C	-1.44081500	-1.59161600	-3.25543400
C	-2.35938800	-2.53799600	-0.71629000
C	-2.25354200	0.38095400	-1.24770500
C	0.96711200	2.47472500	-0.83125600
O	3.12130600	1.38689600	-0.74463800
H	-1.06916500	-2.61274800	-3.38313600
H	-0.80567600	-0.93004800	-3.84856700
H	-2.47269000	-1.53614900	-3.61777700
H	-3.39902300	-2.43963200	-1.04494900
H	-1.94641700	-3.49365600	-1.04948300
H	-2.29870500	-2.51397300	0.37046300
C	-2.42193000	1.19377600	-2.38346600

C	-2.80087700	0.81018200	-0.00936800
C	1.30376500	3.47513600	0.30722200
H	0.84341900	3.03962700	-1.76967500
H	-0.01441900	2.02143700	-0.64365000
C	-3.12446100	2.39612300	-2.32626900
H	-2.00965700	0.88532800	-3.33760600
C	-3.51964700	2.01795200	0.01808800
C	-2.68388700	0.05640700	1.27398300
C	1.39859600	2.71636400	1.62925200
C	-3.68285300	2.80749000	-1.11813500
H	-3.23669300	2.99924300	-3.22263500
H	-3.93909900	2.34354400	0.96553100
C	-1.43802800	-0.27807300	1.82645100
C	-3.84812700	-0.29616200	1.97831700
C	2.43644800	2.65685600	2.42364600
H	0.48815600	2.19313200	1.93253200
H	-4.23662500	3.73998300	-1.05536000
C	-1.35709800	-0.97030300	3.03566000
H	-0.52424800	-0.00298300	1.30857200
C	-3.76698200	-0.98389700	3.18873100
H	-4.82003400	-0.04604100	1.56083600
C	3.46904600	2.59150900	3.22368500
C	-2.52060200	-1.32656900	3.71890500
H	-0.38339000	-1.23582200	3.43557600
H	-4.67785600	-1.25907000	3.71364100
H	4.21556200	1.80558700	3.12423400
H	3.62680300	3.31976400	4.01766200
H	-2.45661400	-1.87062400	4.65692300
C	2.56736100	-2.59261400	0.33543300
C	1.48167000	-3.38322700	0.99010800
C	3.44272600	-2.00314300	-0.28591500
O	0.32599300	-3.00517800	0.52693800
O	1.72637900	-4.23972200	1.81893700
C	4.59948500	-1.39186800	-0.93199400
H	4.71347100	-1.76452900	-1.95729200
H	4.47196600	-0.30470500	-0.96292200
H	5.51194200	-1.63683400	-0.37588800
C	1.44599900	0.22943600	-1.98716900
H	0.63222000	0.56087900	-2.63785800

H	2.25167600	-0.20807400	-2.58499600
C	0.11394800	4.45849800	0.42090700
H	-0.02788200	5.00783800	-0.51857800
H	-0.82254900	3.93431400	0.64766900
H	0.29530000	5.18852000	1.21758300
C	2.58215200	4.27534400	0.00441000
H	3.45175300	3.62080900	-0.05595600
H	2.47703500	4.80489500	-0.95104600
H	2.75729300	5.02376700	0.78548100

$TS_{A\text{-}D}$





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.81587804

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 340.869

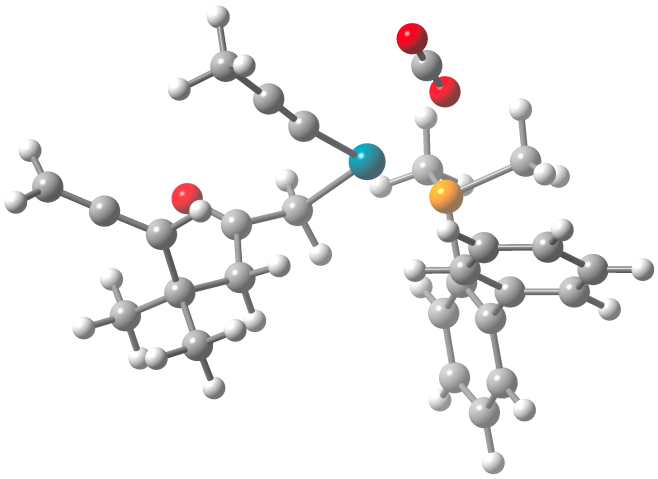
Entropy [cal/mol•K]: 236.77

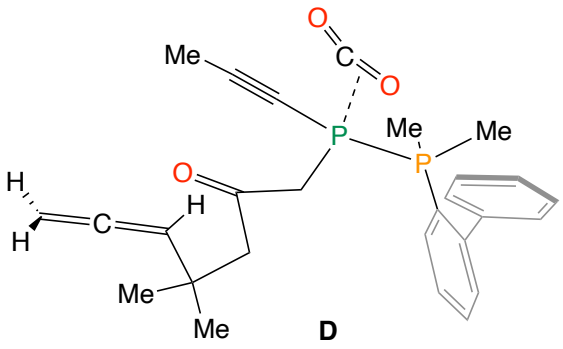
Pd	-0.02100900	-1.10536900	0.90541500
P	2.12393700	-0.35770200	1.52071600
C	-2.16469100	1.02061100	1.09142900
C	2.26432300	-0.21972100	3.35870800
C	3.44557300	-1.59450800	1.14781000
C	2.74172800	1.26635700	0.88643400
C	-2.03557500	1.69971100	-0.27544100
O	-3.24000700	0.86941100	1.65339500
H	2.08959400	-1.21906900	3.76934100
H	1.49168600	0.44104000	3.75977200
H	3.25180100	0.13129700	3.67593500

H	4.42372300	-1.24093200	1.48985700
H	3.18944900	-2.52261700	1.66838100
H	3.48456300	-1.80262500	0.07816200
C	2.77524500	2.36043700	1.76852900
C	3.16588100	1.45866600	-0.45413200
C	-3.32595800	2.15146200	-1.00114000
H	-1.37673900	2.57205000	-0.14515700
H	-1.47324000	1.01032700	-0.92061500
C	3.23139700	3.61479300	1.36334300
H	2.45133600	2.23961300	2.79613400
C	3.64219600	2.72371300	-0.83388700
C	3.14873700	0.39201600	-1.50026800
C	-4.20678300	0.93527300	-1.28712700
C	3.67632400	3.79549000	0.05629600
H	3.24305300	4.43877700	2.07117900
H	3.96995900	2.86347900	-1.86011500
C	1.95111500	-0.21357200	-1.91089700
C	4.34478300	0.01482800	-2.13382700
C	-5.51320100	0.89557300	-1.23073700
H	-3.67654800	0.03634800	-1.60952000
H	4.04046700	4.76426300	-0.27416600
C	1.95274300	-1.18880900	-2.90972400
H	1.01363700	0.08246600	-1.44912700
C	4.34588500	-0.95900800	-3.13288400
H	5.27855900	0.47876600	-1.82671800
C	-6.81977100	0.84517000	-1.16964300
C	3.14942800	-1.56672000	-3.52104700
H	1.01629100	-1.65025200	-3.20991700
H	5.28182500	-1.24523600	-3.60523100
H	-7.33886900	0.54008800	-0.26214200
H	-7.44504300	1.10913000	-2.02148300
H	3.14958800	-2.32785300	-4.29627600
C	-1.81188000	-2.02173200	0.45032700
C	-0.61740300	-3.46203200	-0.38612900
C	-3.02916200	-2.13245700	0.61272800
O	0.48863800	-3.09847700	-0.00461100
O	-1.25189500	-4.23995100	-1.01077000
C	-4.46743300	-2.22100300	0.79578500
H	-4.74086900	-2.94929700	1.56864900

H	-4.83312900	-1.23192700	1.10356700
H	-4.97971900	-2.48992200	-0.13621800
C	-0.87124900	0.59998100	1.73739900
H	-0.13422600	1.40694400	1.65706900
H	-1.05454400	0.34442800	2.78521200
C	-2.90162800	2.74527200	-2.36759000
H	-2.21762600	3.59288100	-2.23006400
H	-2.39217000	1.99873800	-2.98929800
H	-3.77921500	3.09912800	-2.91930700
C	-4.07423900	3.22638500	-0.19432600
H	-4.38633800	2.83430700	0.77531100
H	-3.42747700	4.09798500	-0.03204100
H	-4.96462700	3.56526800	-0.73506200

D





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.83829351

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.007

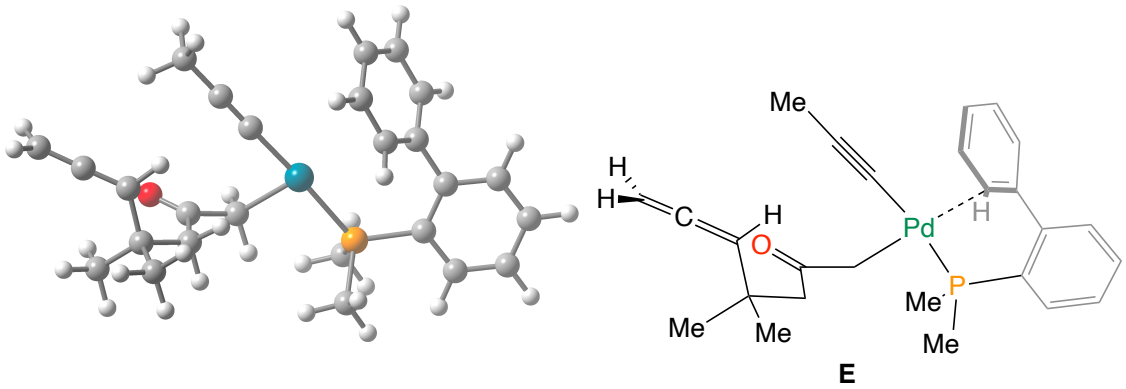
Entropy [cal/mol•K]: 245.464

Pd	0.01698100	-0.79093900	-0.99997900
P	-2.16615700	0.04655700	-1.57220700
C	2.25865500	1.31761100	-0.92523800
C	-2.23507600	0.57604400	-3.34320400
C	-3.51930000	-1.21811300	-1.53263200
C	-2.85074200	1.48976400	-0.63550700

C	2.31673900	1.66827200	0.56384700
O	3.23013200	1.36481200	-1.66076100
H	-2.00055000	-0.30395500	-3.95039700
H	-1.47249000	1.33136300	-3.55118100
H	-3.21991400	0.95761100	-3.63213600
H	-4.46930200	-0.79029700	-1.86917600
H	-3.23619300	-2.04129300	-2.19627900
H	-3.63754900	-1.61485300	-0.52292700
C	-2.98530900	2.72884300	-1.28415000
C	-3.23464600	1.39015200	0.72677200
C	3.70343100	1.91957300	1.20694200
H	1.69441900	2.56668200	0.70481500
H	1.79990500	0.86526300	1.10407500
C	-3.50311800	3.84635500	-0.62852400
H	-2.69199500	2.83273900	-2.32273400
C	-3.77510400	2.51958000	1.36071000
C	-3.10251400	0.14471300	1.54480700
C	4.54173000	0.64807800	1.10244800
C	-3.90979700	3.73910400	0.69878100
H	-3.59170100	4.78996300	-1.15958300
H	-4.07275400	2.43402800	2.40208100
C	-1.84326000	-0.38401600	1.86944800
C	-4.24835900	-0.47871500	2.06637600
C	5.79664000	0.56825800	0.74387800
H	4.02178500	-0.27223900	1.37468300
H	-4.32127100	4.59807300	1.22148700
C	-1.73505700	-1.51697300	2.67888400
H	-0.94476600	0.09852900	1.49654400
C	-4.13975200	-1.61335600	2.87186700
H	-5.22862000	-0.07342000	1.82879600
C	7.04933900	0.47340100	0.37513500
C	-2.88157500	-2.13699100	3.17905600
H	-0.75029900	-1.90509400	2.92524900
H	-5.03768800	-2.08589900	3.26107300
H	7.32456400	0.31203900	-0.66599700
H	7.86765500	0.55779100	1.08905800
H	-2.79591200	-3.01723300	3.81042100
C	1.79508700	-1.59519600	-0.61724100
C	-0.10628600	-3.92756500	-0.17644300

C	2.83511400	-2.21481900	-0.43085600
O	-0.86604300	-3.12353400	-0.57944900
O	0.58585800	-4.76931400	0.23111100
C	4.09147100	-2.93684500	-0.22823800
H	4.33163100	-3.57381100	-1.08946800
H	4.92782900	-2.23872200	-0.09356000
H	4.05256100	-3.58489000	0.65718600
C	0.88511600	1.02379300	-1.47932600
H	0.16311200	1.76607700	-1.11811100
H	0.93342100	1.01650800	-2.57159000
C	3.46947900	2.19723000	2.71251700
H	2.81885200	3.07037500	2.85281000
H	2.99651100	1.34132500	3.20986100
H	4.42117600	2.39571400	3.21763200
C	4.40758000	3.13205200	0.57518400
H	4.59035000	2.96306700	-0.48711000
H	3.78859800	4.03132700	0.68876100
H	5.36736600	3.32097200	1.06890100

E



M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1553.27433073

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 331.440

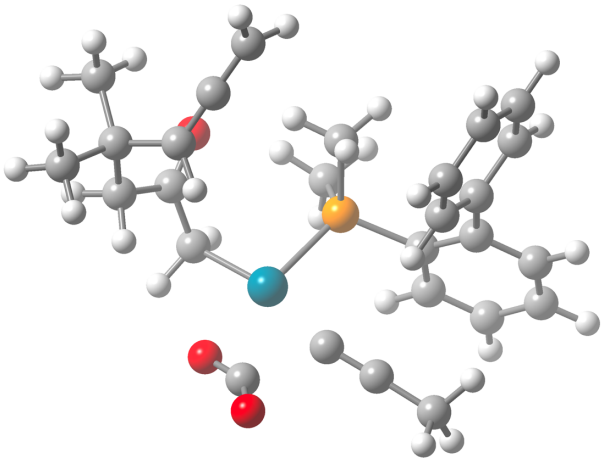
Entropy [cal/mol•K]: 219.911

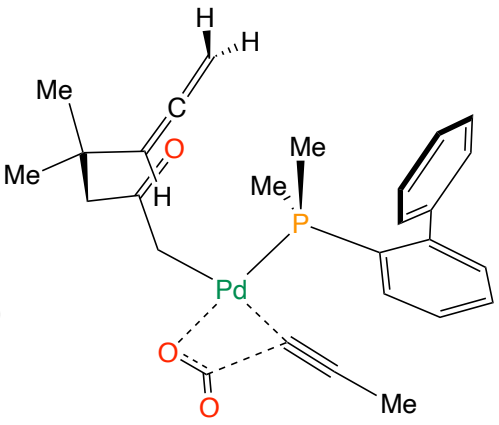
Pd	0.19998500	0.20354400	-0.29905600
P	1.89755600	-1.49916200	-0.37635600

C	-2.59015600	-0.94650700	-0.98754000
C	1.46031100	-2.97771000	0.65311500
C	2.15850400	-2.24475500	-2.05246300
C	3.63109100	-1.11747200	0.14988700
C	-2.96154900	-1.42520000	0.41850500
O	-3.42006100	-0.62052600	-1.81928400
H	0.45936900	-3.31840300	0.37112100
H	1.43480100	-2.68838000	1.70782900
H	2.16126800	-3.80907900	0.52766300
H	2.85441700	-3.08949200	-2.02365300
H	1.19713400	-2.58350500	-2.45034900
H	2.55460600	-1.47838800	-2.72504000
C	4.56277700	-2.16635000	0.23495500
C	4.06897400	0.20637900	0.38581300
C	-4.44801100	-1.35435000	0.84643300
H	-2.61700900	-2.46858100	0.50655100
H	-2.34630800	-0.85301500	1.12331500
C	5.90079100	-1.93286900	0.54209300
H	4.24417200	-3.18756500	0.04555900
C	5.42685800	0.42609400	0.68199500
C	3.17280700	1.39584700	0.34074200
C	-4.90987700	0.10132000	0.81290500
C	6.33508100	-0.62523700	0.76281600
H	6.59769600	-2.76404500	0.60320200
H	5.75845100	1.44288000	0.87159900
C	2.04060200	1.49462300	1.18087600
C	3.49075300	2.48110300	-0.48522100
C	-6.05882500	0.54198100	0.37035600
H	-4.20092700	0.82282400	1.22354900
H	7.37558800	-0.42489500	1.00305600
C	1.25593000	2.65453300	1.17892600
H	1.84125500	0.71146900	1.90815800
C	2.70289900	3.63630000	-0.48263300
H	4.35588900	2.41623000	-1.13944800
C	-7.20150800	0.99422300	-0.08116500
C	1.58512000	3.72557600	0.34304800
H	0.39095400	2.71644300	1.82877400
H	2.96410800	4.46360700	-1.13702200
H	-7.31919600	1.31056200	-1.11649200

H	-8.08246500	1.06977400	0.55501700
H	0.96453500	4.61594400	0.33537800
C	-1.27335400	1.54291400	-0.26870800
C	-2.16570700	2.37963600	-0.28652000
C	-3.23731100	3.37482500	-0.33425400
H	-3.12053200	4.04859200	-1.19352000
H	-4.21944000	2.89345500	-0.42811200
H	-3.26170300	4.00009900	0.56885400
C	-1.12384900	-1.01372000	-1.34690600
H	-0.76507400	-2.03651200	-1.17720500
H	-0.99377500	-0.73208600	-2.39437300
C	-4.52790500	-1.83159300	2.31773700
H	-4.15045900	-2.85794700	2.41726300
H	-3.93544100	-1.18886500	2.98060700
H	-5.56498400	-1.81346300	2.67041500
C	-5.33133100	-2.26161500	-0.02633900
H	-5.29499400	-1.94643700	-1.07043000
H	-4.98975700	-3.30261000	0.04159600
H	-6.37304300	-2.22787700	0.31162200

$TS_{A\text{-}D}$ P cis to acyl





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.81785805

B3LYP/6-31G(d)

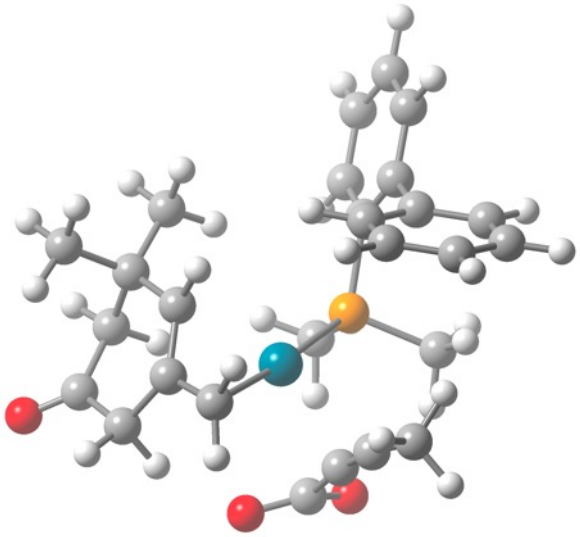
Total thermal energy [kcal/mol]: 341.307

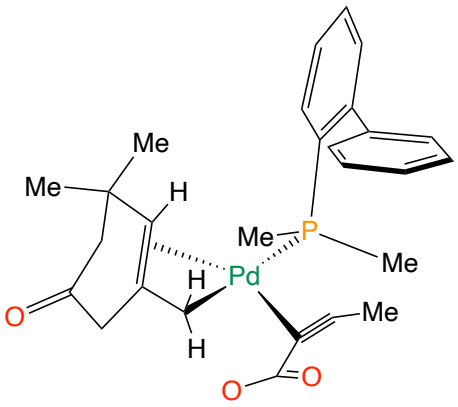
Entropy [cal/mol•K]: 232.144

Pd	-0.54814700	-1.54637600	-0.14555600
P	0.63934600	-0.04791300	-1.38496000
C	-2.92098000	-0.46283100	-1.53148600
C	0.40896100	-0.12564400	-3.21623500
C	0.11613100	1.68230000	-1.05772000
C	2.46961100	-0.25139400	-1.20324800
C	-4.07820500	-0.51840900	-0.52773200
O	-2.72041800	0.52285600	-2.24741300
H	-0.63185800	0.14322500	-3.41753500
H	0.60491000	-1.12709000	-3.60571300
H	1.08204600	0.58816200	-3.70265700
H	0.75744600	2.38873800	-1.59386000
H	-0.91064000	1.75185300	-1.43003300
H	0.12758700	1.91517900	0.00548400
C	2.97972500	-1.38857900	-1.85813700
C	3.36988300	0.60950200	-0.53221400
C	-4.58744400	0.80703300	0.10019500
H	-4.91777700	-0.99763900	-1.05660000
H	-3.79997200	-1.21564400	0.27303600
C	4.34279500	-1.66348800	-1.90054700
H	2.29552100	-2.07852600	-2.34393500
C	4.74687300	0.32369500	-0.60553500
C	2.98361800	1.79669000	0.29010400
C	-3.43765700	1.46941600	0.85676300
C	5.23646600	-0.79026900	-1.28026400
H	4.70093500	-2.54999700	-2.41617500
H	5.43553700	0.98987700	-0.09347300
C	2.23518200	1.64954500	1.46908100
C	3.44696500	3.07487500	-0.06009700
C	-3.05441600	2.71703400	0.76106400
H	-2.91924600	0.82514800	1.57185100
H	6.30560300	-0.98196500	-1.30832500
C	1.94626800	2.75844900	2.26666200
H	1.87669400	0.66517600	1.75801400
C	3.15089300	4.18329200	0.73473400
H	4.03341400	3.19873200	-0.96703900
C	-2.66616500	3.96382100	0.67415400
C	2.39900800	4.02809000	1.90100500
H	1.36674100	2.62752700	3.17655400

H	3.50825100	5.16709200	0.44221100
H	-1.89504500	4.27553900	-0.02850300
H	-3.10130900	4.74399900	1.29694000
H	2.16988100	4.88974200	2.52202200
C	0.78176200	-1.87674600	1.46734900
C	-0.82357600	-2.74487500	2.27307000
C	1.89638000	-2.03003600	1.97332900
O	-1.57361300	-2.85666200	1.30285400
O	-0.69498300	-2.93100900	3.43562200
C	3.17982700	-2.21514600	2.63462600
H	3.80890900	-2.94650400	2.11343500
H	3.73396400	-1.27021900	2.70035100
H	3.02115100	-2.57651400	3.65986500
C	-2.07291700	-1.67361300	-1.60711300
H	-2.56951900	-2.58169200	-1.25131300
H	-1.64539000	-1.81694600	-2.59970500
C	-5.67068700	0.43538800	1.14239500
H	-6.49786000	-0.10542400	0.66547700
H	-5.26446500	-0.20322800	1.93623900
H	-6.07818300	1.33833600	1.61039200
C	-5.20459900	1.74208400	-0.95305900
H	-4.46942400	2.01943000	-1.70909200
H	-6.04265300	1.24107400	-1.45340000
H	-5.59078700	2.65197200	-0.47992600

C’





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.90632517

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 343.393

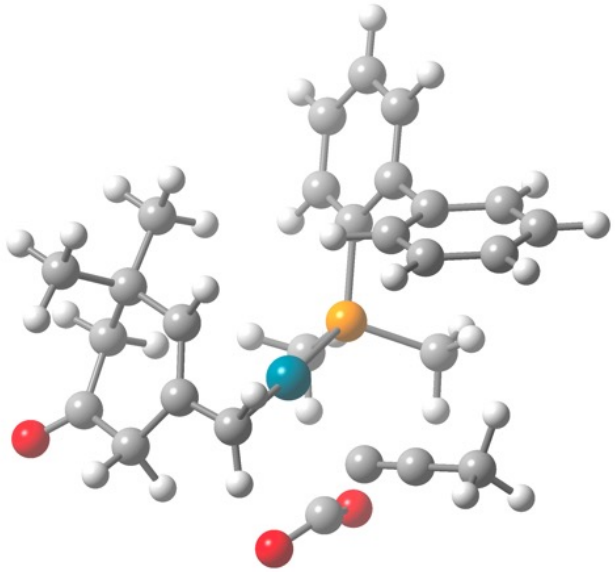
Entropy [cal/mol•K]: 219.132

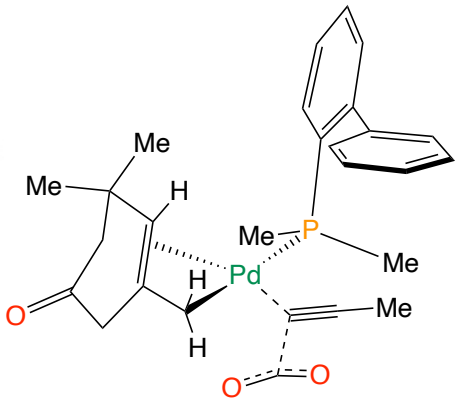
Pd	0.66173200	-0.79501700	-0.21690600
P	-0.76808200	0.24618600	1.44885600
C	4.27232000	1.11176200	-0.31217500
C	-1.77474400	-1.00909800	2.35870500
C	0.21054900	0.96230700	2.83969100
C	-2.00274600	1.55677000	1.00138400
C	3.14929000	2.08741800	0.00176200
O	5.44658300	1.41162600	-0.22285600
H	-1.06280700	-1.67662400	2.85649500
H	-2.39985600	-1.57939800	1.66842100
H	-2.40802900	-0.51442500	3.10268300
H	-0.43962900	1.31979800	3.64528900
H	0.82812300	0.14221000	3.22453200
H	0.85697300	1.77717500	2.50317000
C	-1.96130700	2.79869000	1.65848600
C	-3.02406800	1.33449800	0.04542500
C	2.13856100	2.19206400	-1.16829300
H	2.62516600	1.72084600	0.89559800
H	3.58841200	3.06275300	0.23284800
C	-2.89790400	3.79895100	1.39765300

H	-1.18991700	2.99538100	2.39412400
C	-3.96838400	2.34554400	-0.19180900
C	-3.17546100	0.07686600	-0.75482100
C	1.64526100	0.80294900	-1.54069100
C	-3.91255400	3.57007500	0.47182300
H	-2.83394000	4.74719400	1.92415000
H	-4.75134500	2.16174500	-0.92246200
C	-4.20709900	-0.82978900	-0.46666600
C	-2.37118100	-0.15748600	-1.88114500
C	2.49558500	-0.32916000	-1.45317900
H	0.86230600	0.77817700	-2.30073100
H	-4.65386500	4.33625600	0.26255900
C	-4.42513600	-1.94550000	-1.27836700
H	-4.84596700	-0.65177300	0.39418900
C	-2.59265500	-1.26820200	-2.69778800
H	-1.59296600	0.55666900	-2.13194900
C	1.93353600	-1.57194200	-1.81229300
C	-3.62056100	-2.16567500	-2.39874300
H	-5.23131900	-2.63462300	-1.04156900
H	-1.97241500	-1.42377400	-3.57685800
H	2.47058100	-2.48939900	-1.59070000
H	1.18308500	-1.62857700	-2.59975400
H	-3.79902100	-3.02521800	-3.03915500
C	0.83984400	-2.68048400	1.07456600
C	1.79390100	-2.19233400	2.18033400
C	0.05818600	-3.21873600	0.28891500
O	1.23462700	-2.06655600	3.28732100
O	2.95501200	-1.95708400	1.79299400
C	-0.84263400	-4.01782700	-0.54179000
H	-0.97212500	-5.00827800	-0.08746200
H	-1.83104100	-3.55517800	-0.63081900
H	-0.44564200	-4.16319100	-1.55380600
C	3.83359400	-0.27884000	-0.74127100
H	4.61513900	-0.70913200	-1.37769300
H	3.76729100	-0.91326700	0.16211300
C	2.84846200	2.78203400	-2.41728100
H	3.22221600	3.78909500	-2.19778200
H	3.70142200	2.17037800	-2.73082100
H	2.15533700	2.85522900	-3.26343600

C	0.97531500	3.12002900	-0.78760600
H	0.45213200	2.76526300	0.10314900
H	1.34440800	4.13269700	-0.58780400
H	0.24125400	3.18679100	-1.60028400

$TS_{C\text{-}G}$





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.89532991

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.423

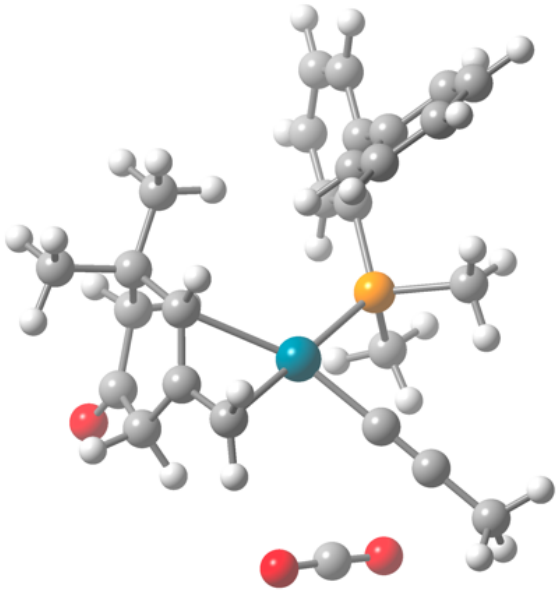
Entropy [cal/mol•K]: 216.521

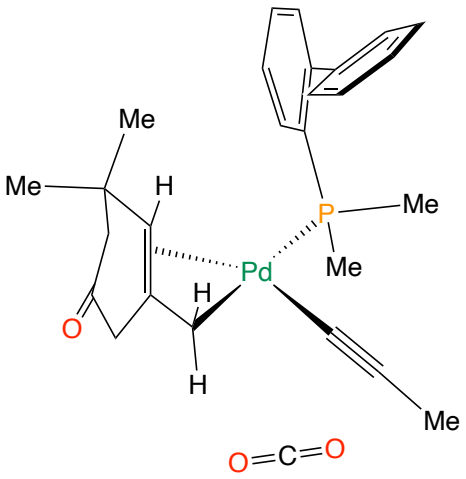
Pd	0.72388600	-0.75852700	-0.22486000
P	-0.74419300	0.27056600	1.39990600
C	4.27954700	1.10253600	-0.00939600
C	-1.86704800	-0.95579200	2.20585500
C	0.23114100	0.83407900	2.86325800
C	-1.87160700	1.68867600	0.99876900
C	3.15340300	2.11956800	0.08667400
O	5.42042200	1.36077300	0.32029100
H	-1.22296800	-1.72131900	2.64868400
H	-2.52817200	-1.41656500	1.46986300
H	-2.46482300	-0.46724500	2.98262200
H	-0.41554100	1.18008700	3.67676400
H	0.79023100	-0.04690300	3.19599100
H	0.93860400	1.62455300	2.59906400

C	-1.69183900	2.91895800	1.65363400
C	-2.94544000	1.56267300	0.08103000
C	2.30481000	2.18805200	-1.20600200
H	2.50180800	1.81500500	0.91808500
H	3.58848900	3.09322800	0.33296500
C	-2.54220500	4.00208500	1.42887700
H	-0.88071900	3.03952700	2.36294500
C	-3.80235600	2.65682400	-0.11677500
C	-3.23987000	0.32120000	-0.70007100
C	1.82316200	0.79356100	-1.56654900
C	-3.60878800	3.86905900	0.54365100
H	-2.37226000	4.93865900	1.95276200
H	-4.62516400	2.54914600	-0.81825100
C	-4.44549900	-0.36964300	-0.49505000
C	-2.37161200	-0.13055400	-1.70570200
C	2.62532800	-0.34898900	-1.34329900
H	1.09518900	0.74510700	-2.37790100
H	-4.28440000	4.70047600	0.36278400
C	-4.76739800	-1.48988800	-1.26269100
H	-5.12922800	-0.02584700	0.27657300
C	-2.69551300	-1.24734900	-2.47875400
H	-1.45020100	0.41115700	-1.89433800
C	2.07728700	-1.60722500	-1.68730000
C	-3.89295600	-1.93207900	-2.25858900
H	-5.70354100	-2.01292400	-1.08665400
H	-2.01630500	-1.57485300	-3.26146000
H	2.56912300	-2.51458900	-1.35123000
H	1.40916600	-1.69800900	-2.54219900
H	-4.14880200	-2.79575800	-2.86664000
C	0.42687500	-2.72798600	0.60383900
C	1.59694900	-2.61920300	1.80142600
C	-0.36359000	-3.55796800	0.13942500
O	1.08741400	-2.35292700	2.88941900
O	2.72383800	-2.81965000	1.35662100
C	-1.31479700	-4.52695600	-0.38513900
H	-1.69903900	-5.16238900	0.42392000
H	-2.17727600	-4.01172500	-0.82774900
H	-0.87322100	-5.17720600	-1.15023100
C	3.90879500	-0.27941500	-0.53707100

H	4.74631600	-0.63414700	-1.15084800
H	3.84311700	-0.98151000	0.30841400
C	3.18079800	2.70829100	-2.37738900
H	3.54150600	3.72097900	-2.16088800
H	4.05535400	2.07089600	-2.54916100
H	2.60452500	2.74662700	-3.30900300
C	1.12170100	3.15015200	-1.01541200
H	0.47011300	2.83005900	-0.19834700
H	1.48092500	4.16195200	-0.79357100
H	0.51225600	3.20572200	-1.92613100

G





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.9188206

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 343.486

Entropy [cal/mol•K]: 234.017

Pd	0.95552500	-0.44555800	-0.64338100
P	-0.62574200	-0.86702300	1.10732500
C	2.71039900	2.92759600	0.25527000
C	-1.39030000	-2.54953600	1.06076800
C	0.36215400	-1.00046000	2.66693000
C	-2.03002700	0.26258100	1.55947400

C	1.21781200	3.20640300	0.34565900
O	3.51225800	3.47281000	0.98931000
H	-0.56714900	-3.25989800	0.95193700
H	-2.05365200	-2.65409100	0.20189900
H	-1.94910000	-2.74682400	1.98156800
H	-0.25802300	-1.26349200	3.53044000
H	1.10207900	-1.78622300	2.48980100
H	0.90584800	-0.07500800	2.87486500
C	-1.86475800	1.12213200	2.66021500
C	-3.25513300	0.31311200	0.84220000
C	0.46172400	3.07113200	-0.99377800
H	0.80366900	2.47218100	1.05310000
H	1.08500600	4.19720500	0.79393700
C	-2.86792600	2.00077200	3.06852000
H	-0.93931200	1.10315800	3.22508800
C	-4.25884900	1.19323500	1.28105700
C	-3.56376900	-0.51885700	-0.35985300
C	0.80653100	1.72989700	-1.62326100
C	-4.07711600	2.03219100	2.37838700
H	-2.70231200	2.64811600	3.92528100
H	-5.19263900	1.22680000	0.72675500
C	-4.71166200	-1.32944000	-0.37001100
C	-2.76318400	-0.48079600	-1.51238300
C	2.11592200	1.22913900	-1.60909500
H	0.14080700	1.39000900	-2.41776100
H	-4.87155200	2.70750600	2.68382600
C	-5.03857500	-2.09374000	-1.49037400
H	-5.33889200	-1.37240300	0.51646300
C	-3.08989900	-1.24578700	-2.63313500
H	-1.88158800	0.15127100	-1.53131700
C	2.38146000	-0.04134500	-2.19838300
C	-4.22644200	-2.05664000	-2.62590800
H	-5.92510500	-2.72215400	-1.47360000
H	-2.45474500	-1.20482600	-3.51391100
H	3.36387200	-0.48716000	-2.08259500
H	1.82899600	-0.35181300	-3.08354100
H	-4.47765700	-2.65418400	-3.49792300
C	1.60462300	-2.33421800	-0.40917700
C	4.34973000	-1.78832600	1.33175500

C	2.01114500	-3.48030400	-0.26303500
O	3.96263200	-2.42416300	2.23405600
O	4.78623000	-1.13601700	0.46395200
C	2.49645600	-4.85118800	-0.08371400
H	2.99442700	-4.97464500	0.88737600
H	1.67777100	-5.58201700	-0.12451900
H	3.22001800	-5.13316800	-0.86008000
C	3.18869100	1.91439900	-0.78714500
H	3.85633300	2.46313000	-1.46870000
H	3.82827900	1.17902800	-0.28656800
C	0.89380900	4.20520100	-1.95991900
H	0.64308000	5.18672700	-1.53868500
H	1.97203700	4.18968100	-2.15617800
H	0.38017400	4.11097000	-2.92360900
C	-1.05185600	3.19016300	-0.75074300
H	-1.40793000	2.41969900	-0.06209900
H	-1.29936900	4.16945100	-0.32379100
H	-1.60613100	3.08903400	-1.69225900

CO_2 (carbon dioxide)

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -188.560829811

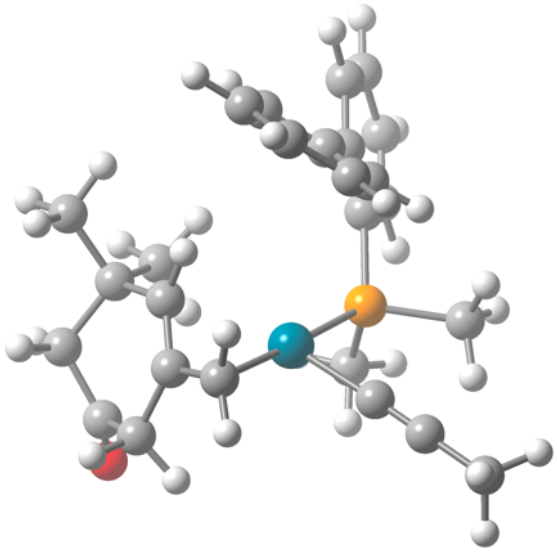
B3LYP/6-31G(d)

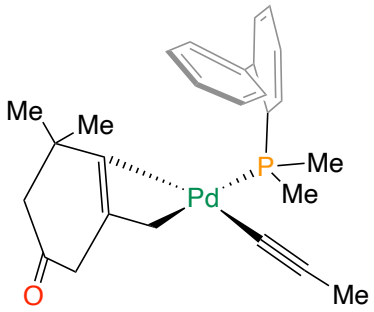
Total thermal energy [kcal/mol]: 8.933

Entropy [cal/mol•K]: 51.165

C	0.00000000	0.00000000	0.00000000
O	0.00000000	0.00000000	1.16930900
O	0.00000000	0.00000000	-1.16930900

H





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1553.34777834

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 333.104

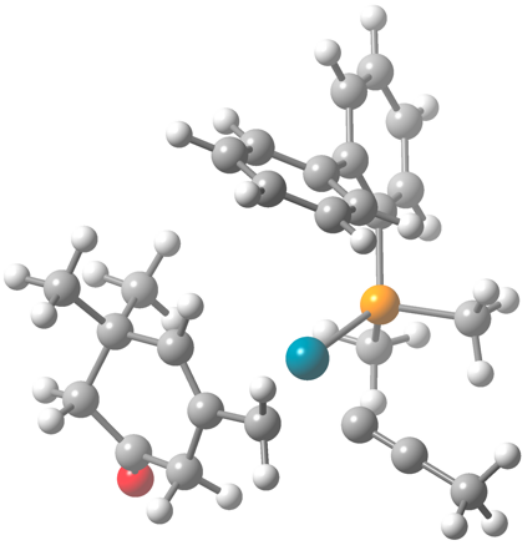
Entropy [cal/mol•K]: 208.268

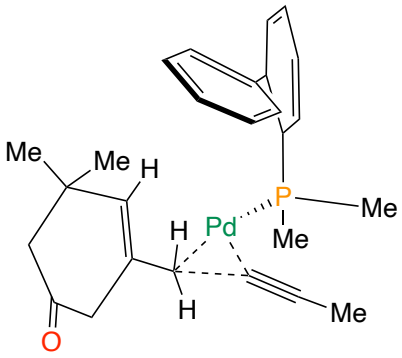
Pd	1.01188000	0.86675900	0.07514700
P	-0.86050100	0.92905200	-1.41944100
C	3.40671000	-2.09356500	-1.14934100
C	-1.52805000	2.63006800	-1.72441200
C	-0.29712300	0.49191700	-3.13217800
C	-2.42360000	-0.05365800	-1.17540200
C	2.73985700	-3.22694000	-0.39697000
O	3.64870200	-2.12597100	-2.34083300
H	-0.68864500	3.28165200	-1.97826600
H	-1.99147200	3.02983000	-0.81942200
H	-2.26872800	2.61685100	-2.53120300
H	-1.00207900	0.79651200	-3.91256100
H	0.64842400	1.01786500	-3.29544100
H	-0.10791900	-0.58143600	-3.21341200
C	-3.15075400	-0.43064800	-2.31876300
C	-2.91356500	-0.45001200	0.09779400
C	1.38155700	-2.77942500	0.22048100
H	2.60246800	-4.07998400	-1.06810800
H	3.41272500	-3.53200400	0.41774100

C	-4.32240600	-1.18005100	-2.24058600
H	-2.79493200	-0.13983800	-3.30130900
C	-4.09979800	-1.20754500	0.15315600
C	-2.26716400	-0.13225600	1.40532000
C	1.52383800	-1.39640800	0.85779600
C	-4.79980100	-1.57350300	-0.99202400
H	-4.85424400	-1.45106100	-3.14850300
H	-4.48446800	-1.49179000	1.12826500
C	-1.90576300	1.17319500	1.77224000
C	-2.07255300	-1.16064800	2.34642600
C	2.65118600	-0.58133600	0.73776900
H	0.85216000	-1.20334100	1.69395500
H	-5.71458900	-2.15370300	-0.90694600
C	-1.35790800	1.44182000	3.02836600
H	-2.07987200	1.99564200	1.08829400
C	-1.52451700	-0.89524200	3.60112000
H	-2.34512000	-2.17915400	2.08287700
C	2.67055700	0.69140800	1.39433000
C	-1.16318600	0.40994100	3.94670700
H	-1.08470400	2.46169000	3.28253700
H	-1.38131500	-1.70759400	4.30893700
H	3.50887200	1.35915700	1.22215400
H	2.19176600	0.79452400	2.36667100
H	-0.73952000	0.62016900	4.92499300
C	1.23584500	2.85257900	-0.02402500
C	1.41196900	4.06178300	-0.08402800
C	1.62236500	5.50953900	-0.15578500
H	2.34578400	5.77475400	-0.93883000
H	0.69276100	6.05150200	-0.37877900
H	2.01114400	5.91171200	0.78955800
C	3.74494300	-0.89893500	-0.27243100
H	4.66736300	-1.13991200	0.27993100
H	3.96716700	-0.03224300	-0.90166000
C	0.98473500	-3.78619300	1.32314700
H	0.92045100	-4.80249000	0.91584400
H	1.71726500	-3.79117700	2.13882800
H	0.00769500	-3.52970400	1.74881300
C	0.29906900	-2.79668600	-0.87894900
H	0.60019800	-2.17936500	-1.73082000

H	0.13589000	-3.81942500	-1.24230400
H	-0.65175700	-2.41177100	-0.49887200

$TS_{H\text{-}I}$





M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1553.30990001

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 332.21

Entropy [cal/mol•K]: 211.885

Pd	0.65355700	0.85761800	-0.02660700
P	-1.35498800	1.14046500	-1.15401600
C	3.73935600	-1.09818100	-1.75209000
C	-2.10439200	2.81882100	-0.88580700
C	-1.06716000	1.18860900	-2.98944500
C	-2.84458800	0.03196600	-0.97843500
C	3.64442800	-2.42811600	-1.03140900
O	3.83285400	-0.99716700	-2.96073800
H	-1.32801700	3.56888100	-1.06533700
H	-2.42995000	2.92101800	0.15336400
H	-2.95998900	2.99855500	-1.54651100
H	-1.90072600	1.61039900	-3.56120900
H	-0.18191900	1.80918400	-3.15852400
H	-0.84915400	0.18157500	-3.35671400

C	-3.77439000	-0.00456000	-2.03313600
C	-3.06887200	-0.80704300	0.14420000
C	2.34958500	-2.52883200	-0.17707800
H	3.70071400	-3.24027100	-1.76262200
H	4.51309500	-2.50665400	-0.36076500
C	-4.88675100	-0.84272600	-2.01616900
H	-3.62777900	0.63267900	-2.89903800
C	-4.19622000	-1.65118700	0.14013000
C	-2.20653500	-0.86240000	1.36107600
C	2.13137100	-1.23471500	0.59267600
C	-5.09570300	-1.67874100	-0.92074800
H	-5.58085700	-0.84067400	-2.85231700
H	-4.37301600	-2.27981700	1.00820000
C	-1.88372200	0.28628100	2.10057700
C	-1.77199500	-2.10786100	1.84887900
C	2.77378000	-0.04645900	0.35138200
H	1.51189300	-1.31682300	1.48509100
H	-5.95740800	-2.33987200	-0.88541100
C	-1.15048000	0.19491700	3.28544400
H	-2.23832900	1.25659400	1.76965900
C	-1.03572600	-2.20143300	3.03005300
H	-2.01014900	-3.00826800	1.28889900
C	2.55535800	1.16706400	1.18045500
C	-0.72256200	-1.04802500	3.75450900
H	-0.92005200	1.09916900	3.84179000
H	-0.71240400	-3.17576300	3.38764700
H	3.39396000	1.85381600	1.12883800
H	2.25459300	0.96686100	2.20680600
H	-0.15757700	-1.11913100	4.68016600
C	1.35656100	2.62743200	0.72259200
C	1.36433900	3.82757400	0.97631800
C	1.36695500	5.25922300	1.27389600
H	1.36249100	5.86205400	0.35587700
H	0.48741800	5.55630700	1.86074500
H	2.25527300	5.55767100	1.84943600
C	3.71823700	0.11299200	-0.83207200
H	4.74370600	0.26622300	-0.45504800
H	3.46793700	1.00071200	-1.42192500
C	2.50082100	-3.68966100	0.83019800

H	2.68652800	-4.63628700	0.30836900
H	3.33389100	-3.51134600	1.52031500
H	1.58762000	-3.80629800	1.42596100
C	1.14303800	-2.82542200	-1.09935700
H	1.04916600	-2.06333600	-1.87961000
H	1.25684600	-3.80471500	-1.58283800
H	0.21214200	-2.82964300	-0.52306600

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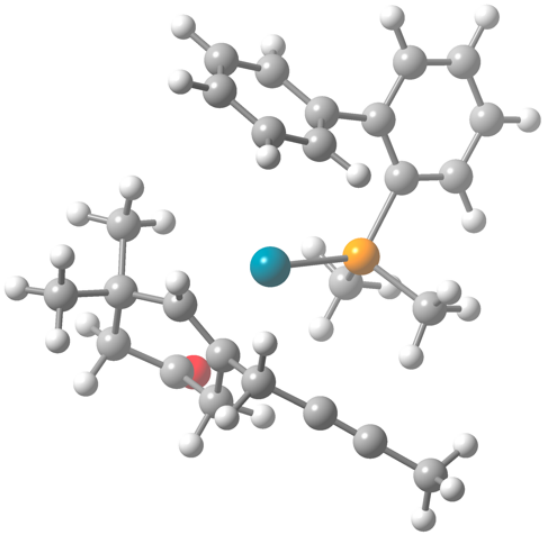

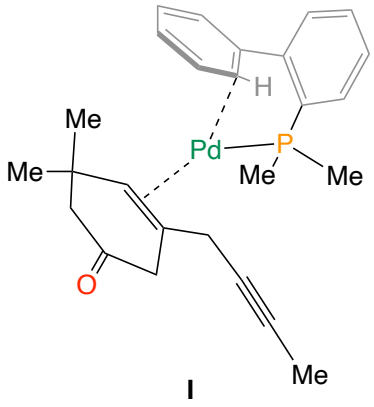

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M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1553.36620059

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 333.522

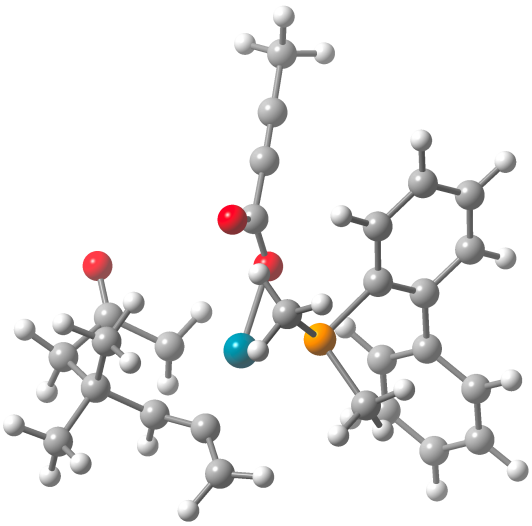
Entropy [cal/mol•K]: 211.653

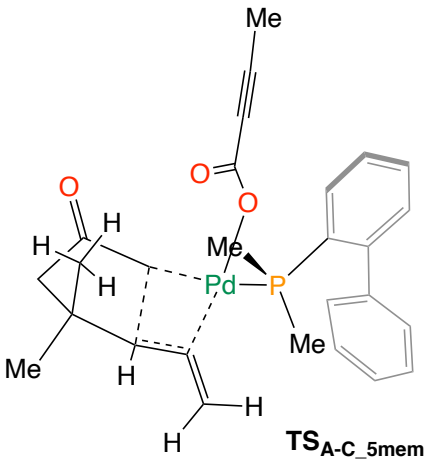
Pd	0.52907700	-0.11700700	0.21944500
P	-1.14140200	1.32127500	-0.57473300
C	2.97628800	0.07309000	-2.03229600
C	-1.09419300	3.03620400	0.13777700
C	-0.96609200	1.66692500	-2.39178700
C	-2.95561400	0.90732500	-0.45732600
C	3.47044400	-1.35127400	-1.85599500
O	2.47693400	0.48772300	-3.06316000
H	-0.06584400	3.40035000	0.06059700
H	-1.35521500	2.99478400	1.19964000
H	-1.76872800	3.73474000	-0.37003300
H	-1.61847700	2.47631700	-2.73909700

H	0.07853100	1.91618400	-2.60148100
H	-1.20307600	0.75598600	-2.94981500
C	-3.88702800	1.82799700	-0.96880600
C	-3.43536000	-0.32296300	0.05618500
C	2.85038000	-2.09380000	-0.62880800
H	3.29612900	-1.90976700	-2.78052900
H	4.55888300	-1.28086100	-1.70967200
C	-5.25485300	1.56785300	-0.98603200
H	-3.53572800	2.77200200	-1.37634600
C	-4.82101300	-0.57440300	0.02180300
C	-2.58108600	-1.39867000	0.64413700
C	2.49961900	-1.10787500	0.49576700
C	-5.72448100	0.35233700	-0.48853400
H	-5.94502700	2.30543800	-1.38694100
H	-5.18610200	-1.51402200	0.42689300
C	-1.74884000	-1.16534400	1.75497600
C	-2.67934200	-2.70997700	0.15068500
C	2.69535200	0.27537400	0.44554600
H	2.43903500	-1.56687300	1.48443500
H	-6.78796200	0.12856000	-0.49145400
C	-1.05341000	-2.21824900	2.35828600
H	-1.69851600	-0.17166500	2.18833900
C	-1.97869900	-3.75913800	0.74857000
H	-3.31230500	-2.90502200	-0.71096500
C	2.95529400	1.04032300	1.74738400
C	-1.16702300	-3.51742500	1.85845500
H	-0.43597500	-2.01905100	3.22990500
H	-2.07279800	-4.76550300	0.34913700
H	4.03869300	0.97938500	1.95555000
H	2.45819100	0.52025400	2.57524100
H	-0.63138900	-4.33478900	2.33398400
C	2.57872200	2.45800500	1.75107300
C	2.33009300	3.64223000	1.78073300
C	2.02871200	5.07198400	1.82927900
H	0.98144400	5.27224000	1.57082200
H	2.20410600	5.48033300	2.83235600
H	2.65622000	5.63753800	1.12919200
C	3.21164500	0.94949600	-0.81522200
H	4.30061900	1.12143500	-0.71944100

H	2.74656400	1.92650100	-0.96536500
C	3.89278500	-3.09655900	-0.08251100
H	4.21233900	-3.79379900	-0.86729100
H	4.78294400	-2.57912400	0.29540800
H	3.47196200	-3.68866600	0.73950100
C	1.60568500	-2.88381000	-1.08547000
H	0.87286800	-2.22032800	-1.55776400
H	1.88488000	-3.66354200	-1.80695900
H	1.11384800	-3.36553200	-0.23326600

$TS_{A\text{-}C\text{-}5mem}$





$TS_{A\text{-}C\_5mem}$

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.82768663

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.180

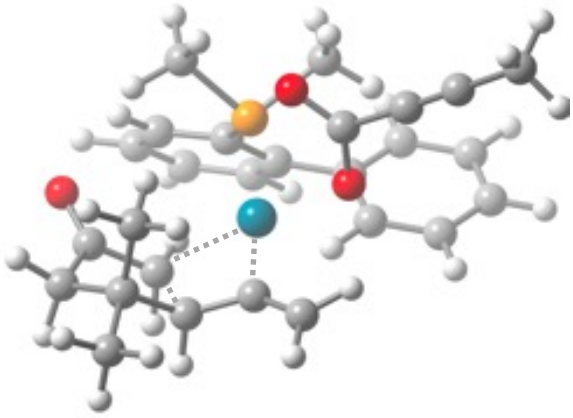
Entropy [cal/mol•K]: 224.857

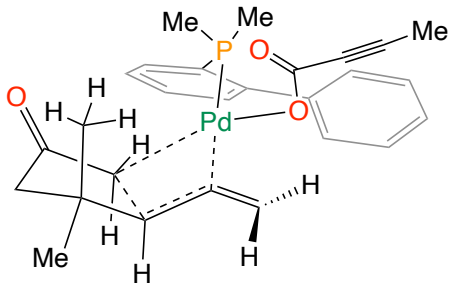
Pd	-0.94875100	-0.40763500	-0.11297700
P	0.77321000	-0.81532400	1.44983500
C	-3.55672300	1.23462600	-1.43848700
C	0.18883800	-0.28439000	3.11543800
C	1.36461000	-2.53867400	1.79140000
C	2.35222300	0.10454000	1.17173600
C	-4.76776000	0.57622100	-0.79642600
O	-3.49318500	2.42848100	-1.66413900
H	-0.65205000	-0.93113200	3.38496200
H	-0.17243200	0.74345700	3.04346300

H	0.97144400	-0.37106500	3.87635300
H	2.26148600	-2.50269500	2.41800000
H	0.58856700	-3.08781000	2.32978800
H	1.59655600	-3.06317300	0.86343900
C	2.65165100	1.19426000	2.00421200
C	3.29422000	-0.28971300	0.18960100
C	-4.27872200	-0.39963400	0.29248800
H	-5.44303900	1.34100900	-0.40276300
H	-5.30924500	0.02012200	-1.57771900
C	3.87096200	1.86469800	1.90940300
H	1.92284400	1.54069300	2.72641700
C	4.52384700	0.38320600	0.12766400
C	3.04620900	-1.37062400	-0.81190700
C	-3.16233900	-1.24148200	-0.34134300
C	4.81847500	1.44766400	0.97785300
H	4.07244000	2.70818400	2.56359100
H	5.24397900	0.07525100	-0.62538200
C	2.03821500	-1.22773400	-1.77958600
C	3.86137000	-2.51370700	-0.84432200
C	-2.17159400	-1.92382800	0.41435500
H	-3.47470000	-1.75292300	-1.25001500
H	5.77527000	1.95663400	0.89830700
C	1.83860100	-2.22270000	-2.73940100
H	1.43705700	-0.32349900	-1.78573800
C	3.65625700	-3.50759100	-1.80253900
H	4.65119100	-2.62572700	-0.10559500
C	-2.13873300	-3.06168500	1.10453300
C	2.63991300	-3.36632200	-2.75063400
H	1.06005900	-2.09571700	-3.48720400
H	4.29065200	-4.39020100	-1.80924800
H	-1.24119600	-3.44076200	1.57773600
H	-3.02984200	-3.68085800	1.21092100
H	2.48089800	-4.13841800	-3.49880500
C	0.66188800	3.55283200	-0.49945300
C	0.08178300	2.31735700	0.01903200
C	1.12514800	4.59530300	-0.90644900
O	-0.39591500	2.28918700	1.16394700
O	0.13327500	1.31643100	-0.80503000
C	1.67587400	5.85163500	-1.40285300

H	0.95676900	6.35820500	-2.05859200
H	1.91763100	6.53872200	-0.58252100
H	2.59109200	5.68484400	-1.98434400
C	-2.42345600	0.29751600	-1.76350600
H	-2.66572300	-0.40880800	-2.55806700
H	-1.53649600	0.87527300	-2.03018600
C	-5.40362400	-1.37939000	0.69542600
H	-6.25672100	-0.82088800	1.09779500
H	-5.75964600	-1.96392500	-0.16171200
H	-5.06162600	-2.07497000	1.46947300
C	-3.79887700	0.37743500	1.53068900
H	-2.98922800	1.07690100	1.29300600
H	-4.63189900	0.95105600	1.95310400
H	-3.43266300	-0.30840700	2.30119300

$TS_{A\text{-}C\text{-}5mem}$ P cis to acyl





$TS_{A\text{-}C\_5mem}$ P cis to acyl

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.81642847

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 342.035

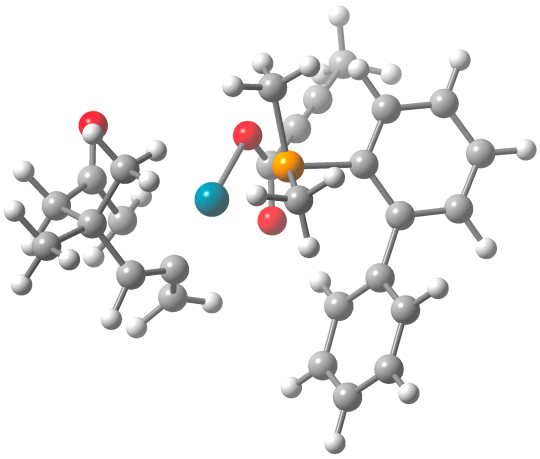
Entropy [cal/mol•K]: 226.767

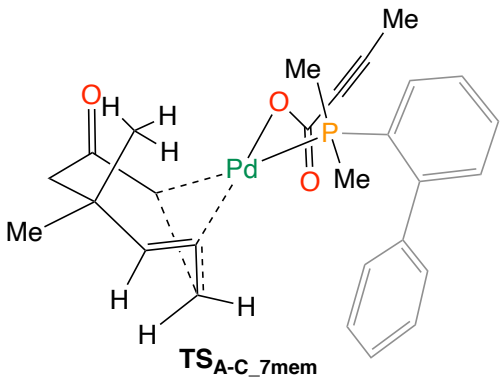
Pd	0.88956300	0.10839000	-0.37072000
P	-0.93428000	-0.29687100	1.24930200
C	2.03181800	-2.94973300	0.19268700
C	-0.21640700	-0.88316300	2.84578000
C	-1.93790900	1.14785500	1.81629200
C	-2.15536500	-1.61053300	0.77461600
C	3.50201900	-3.01448800	-0.18202600

O	1.57406100	-3.38988200	1.23474600
H	0.39313300	-0.05304100	3.21347300
H	0.43585100	-1.74437300	2.68177600
H	-0.99014200	-1.13675000	3.57839400
H	-2.74856900	0.82143900	2.47554100
H	-1.25693100	1.80331000	2.36499900
H	-2.35173600	1.69627400	0.96991200
C	-1.97011800	-2.90689600	1.28923800
C	-3.24075100	-1.38253300	-0.11337000
C	3.91847700	-1.57659200	-0.57401100
H	4.09720200	-3.41397000	0.64328200
H	3.61509600	-3.68855300	-1.04463900
C	-2.84492000	-3.94954700	0.98191300
H	-1.12509100	-3.11556400	1.93473000
C	-4.12117100	-2.44109900	-0.39030200
C	-3.51200800	-0.07719600	-0.78681700
C	2.81552500	-1.02522200	-1.50549500
C	-3.93563900	-3.71275200	0.14917400
H	-2.67116300	-4.93763500	1.39913900
H	-4.95244300	-2.25755400	-1.06552100
C	-2.55957900	0.53247600	-1.61877100
C	-4.76361200	0.54342500	-0.63673100
C	2.50527000	0.35755100	-1.55750800
H	2.76946100	-1.54506100	-2.46152800
H	-4.63066200	-4.51212700	-0.09346400
C	-2.84081000	1.73848700	-2.26200300
H	-1.58951100	0.06455100	-1.76251600
C	-5.04663800	1.74753800	-1.28177100
H	-5.50982500	0.08442000	0.00656300
C	2.97238100	1.47923600	-2.09112800
C	-4.08415100	2.35114500	-2.09428700
H	-2.08405000	2.19718400	-2.89200400
H	-6.01713900	2.21715700	-1.14411200
H	2.46122200	2.42328900	-1.92793800
H	3.88670000	1.49479800	-2.68612200
H	-4.30141400	3.29194500	-2.59268500
C	0.97793300	4.12765400	0.98519600
C	0.99758400	2.66657100	0.93918800
C	0.97456100	5.33663600	1.06201100

O	1.26253900	2.01705000	1.95902100
O	0.70415100	2.18541100	-0.23079400
C	0.97078500	6.79249900	1.15811100
H	0.14851200	7.14123200	1.79526800
H	1.90556400	7.16164800	1.59794400
H	0.85337300	7.26287300	0.17417500
C	1.22534500	-2.20322600	-0.82633800
H	1.24293500	-2.67399000	-1.80800200
H	0.17656800	-2.13930400	-0.53285500
C	5.23209600	-1.57750800	-1.38307200
H	6.04536300	-1.99314600	-0.77715700
H	5.14758100	-2.18289200	-2.29376700
H	5.51586800	-0.55924500	-1.67127700
C	4.08789500	-0.71743300	0.69080000
H	3.16591500	-0.66364700	1.28030600
H	4.87370900	-1.14373600	1.32470200
H	4.36723600	0.30805900	0.43496100

$TS_{A\text{-}C\text{-}7mem}$





$TS_{A\text{-}C\_7mem}$

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.77999368

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 341.624

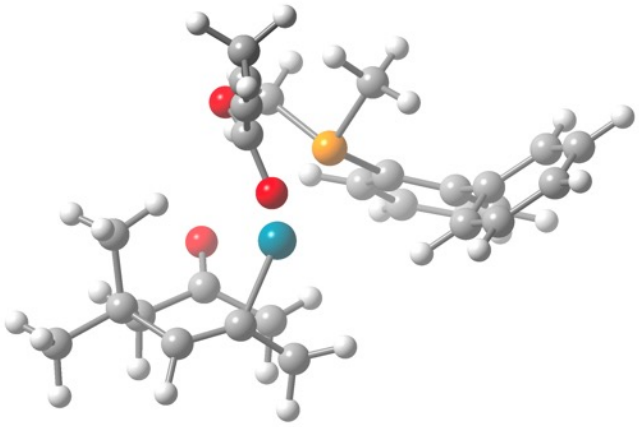
Entropy [cal/mol•K]: 225.037

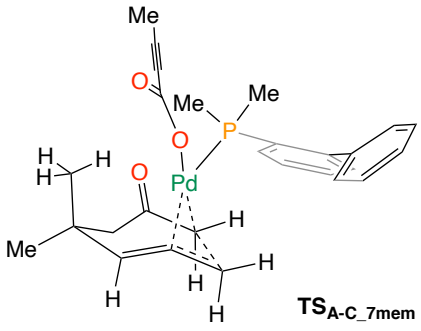
Pd	0.88097100	-0.56660800	-0.17526900
P	-0.32374900	0.50834700	1.50268200
C	3.24928600	-1.91566500	-0.29410200
C	-0.10590200	-0.48095700	3.04664600

C	0.16046000	2.20461600	2.04888600
C	-2.15783900	0.58306600	1.27669600
C	4.49020200	-1.03309400	-0.07338000
O	2.99307100	-2.79990300	0.51390900
H	0.93654400	-0.39056800	3.36400900
H	-0.30312200	-1.53341200	2.82837700
H	-0.75644400	-0.13152500	3.85512200
H	-0.46090700	2.53687100	2.88724100
H	1.20821700	2.17726400	2.36138800
H	0.06257700	2.91099400	1.22321000
C	-2.95547700	-0.32634500	1.99244300
C	-2.79315100	1.53001300	0.43648700
C	4.26895700	0.40022500	0.58094600
H	5.15018900	-1.60580000	0.58893400
H	5.01044300	-0.88398000	-1.02840800
C	-4.34714300	-0.28251900	1.92894200
H	-2.49265100	-1.08728600	2.60827000
C	-4.19571500	1.57461600	0.40779700
C	-2.06751900	2.47204900	-0.46995200
C	3.46073700	1.13156300	-0.47354200
C	-4.97267000	0.68463900	1.14606800
H	-4.93363200	-1.00270500	2.49237400
H	-4.67451700	2.30869500	-0.23417900
C	-1.41310100	1.98497400	-1.61259300
C	-2.11581300	3.85779800	-0.24931600
C	2.21848200	0.78379300	-0.85014900
H	4.06166100	1.71050300	-1.18286100
H	-6.05672100	0.73679500	1.09345400
C	-0.80671900	2.87432000	-2.50319500
H	-1.40799700	0.91483500	-1.80875300
C	-1.49921400	4.74128700	-1.13679500
H	-2.63546300	4.24028500	0.62579100
C	1.88837300	0.30554500	-2.15465700
C	-0.84122100	4.25015700	-2.26666200
H	-0.31725500	2.48978800	-3.39438100
H	-1.53892900	5.81118300	-0.94918600
H	2.65415600	0.28377100	-2.92809500
H	0.87185400	0.27082100	-2.53907500
H	-0.36786500	4.93684200	-2.96353900

C	-2.32159600	-3.24543200	-0.97990900
C	-1.29393800	-2.20480100	-0.98279300
C	-3.17543700	-4.10439400	-1.00813200
O	-1.17945600	-1.46012500	-1.97416000
O	-0.56639000	-2.15892000	0.08411300
C	-4.20311500	-5.13957400	-1.04613800
H	-4.20282700	-5.74586400	-0.13179900
H	-5.20250500	-4.70014100	-1.15649400
H	-4.04834600	-5.81677400	-1.89544300
C	2.39782400	-1.76209300	-1.54145500
H	2.99435100	-1.69471200	-2.44726500
H	1.63012200	-2.53070600	-1.62932700
C	5.65084000	1.06046300	0.74615500
H	6.29305700	0.46836900	1.40767000
H	6.16433200	1.16559100	-0.21723100
H	5.54694800	2.06086100	1.18272700
C	3.61341200	0.25904200	1.96168800
H	2.64570900	-0.24112800	1.89528700
H	4.25306200	-0.33392700	2.62556200
H	3.47169600	1.24566100	2.41795000

$TS_{A\text{-}C\text{-}7mem}$ P cis to acyl





$TS_{A\text{-}C\_7mem}$

M06/6-311+G(d,p) (PCM, solvent = THF)

Electronic energy [Hartree]: -1741.76787402

B3LYP/6-31G(d)

Total thermal energy [kcal/mol]: 341.613

Entropy [cal/mol•K]: 224.210

Pd	0.83427900	-0.21931100	-0.42143700

P	-0.97488400	-0.05347900	1.28086000
C	1.59981100	-2.69002500	0.09830200
C	-0.39941600	-0.61834300	2.94258800
C	-1.66205400	1.60942500	1.71500000
C	-2.44065600	-1.13972100	0.92240100
C	3.11419100	-2.82625200	-0.14503500
O	1.15173600	-2.90946800	1.21913000
H	0.33825200	0.12186600	3.26174200
H	0.10097500	-1.58492400	2.86542700
H	-1.22331400	-0.67142200	3.66214000
H	-2.51088000	1.51551700	2.40005100
H	-0.84891400	2.15140900	2.20459200
H	-1.97030600	2.16145500	0.82722200
C	-2.43791600	-2.43100500	1.48318100
C	-3.53007100	-0.77138300	0.08887900
C	3.99489500	-1.55349400	-0.49907900
H	3.51254100	-3.26658800	0.77583600
H	3.25640400	-3.55674300	-0.95434100
C	-3.48634500	-3.32725400	1.27554800
H	-1.59956400	-2.74705400	2.09318400
C	-4.58571800	-1.68209500	-0.08986500
C	-3.63433300	0.53128700	-0.63415000
C	3.40560700	-1.05179100	-1.80737200
C	-4.57565100	-2.94619900	0.49541500
H	-3.44921300	-4.31382600	1.72965900
H	-5.41731200	-1.38938900	-0.72512900
C	-2.64298400	0.95308900	-1.53403400
C	-4.76910200	1.34209000	-0.46635900
C	2.14533600	-0.62085700	-1.91659800
H	3.94963400	-1.32910700	-2.71624700
H	-5.40496900	-3.62866800	0.33004300
C	-2.76979900	2.15637500	-2.22878200
H	-1.76108700	0.33700300	-1.68289200
C	-4.89923500	2.54459900	-1.16178400
H	-5.54367000	1.03256500	0.23032800
C	1.06535200	-1.20847300	-2.63270700
C	-3.89853500	2.95761100	-2.04394100
H	-1.98456500	2.46700700	-2.91262500
H	-5.78024500	3.16236800	-1.00863600

H	1.26451100	-2.01290400	-3.33954900
H	0.17771200	-0.63551300	-2.89564200
H	-3.99654400	3.89642300	-2.58207600
C	2.10914400	3.70135800	0.79346600
C	1.69441700	2.29880400	0.84437300
C	2.45646900	4.86194200	0.78641700
O	1.59304400	1.72648000	1.93910800
O	1.46496900	1.79104500	-0.32347000
C	2.87352300	6.26013900	0.77808500
H	3.25482300	6.56128100	-0.20546400
H	2.03257100	6.92059800	1.02415700
H	3.66344600	6.44512200	1.51658400
C	0.61375500	-2.49497600	-1.05747300
H	0.79267000	-3.26229100	-1.80673300
H	-0.42265800	-2.54648200	-0.72227700
C	5.43685400	-2.04388000	-0.73776900
H	5.83809900	-2.53038500	0.15802600
H	5.49057900	-2.76199500	-1.56547800
H	6.08918600	-1.19744900	-0.98138500
C	4.00054600	-0.54911500	0.66687900
H	3.00296800	-0.21079300	0.95518400
H	4.46452800	-1.00995600	1.54734400
H	4.58425400	0.33780000	0.39848900

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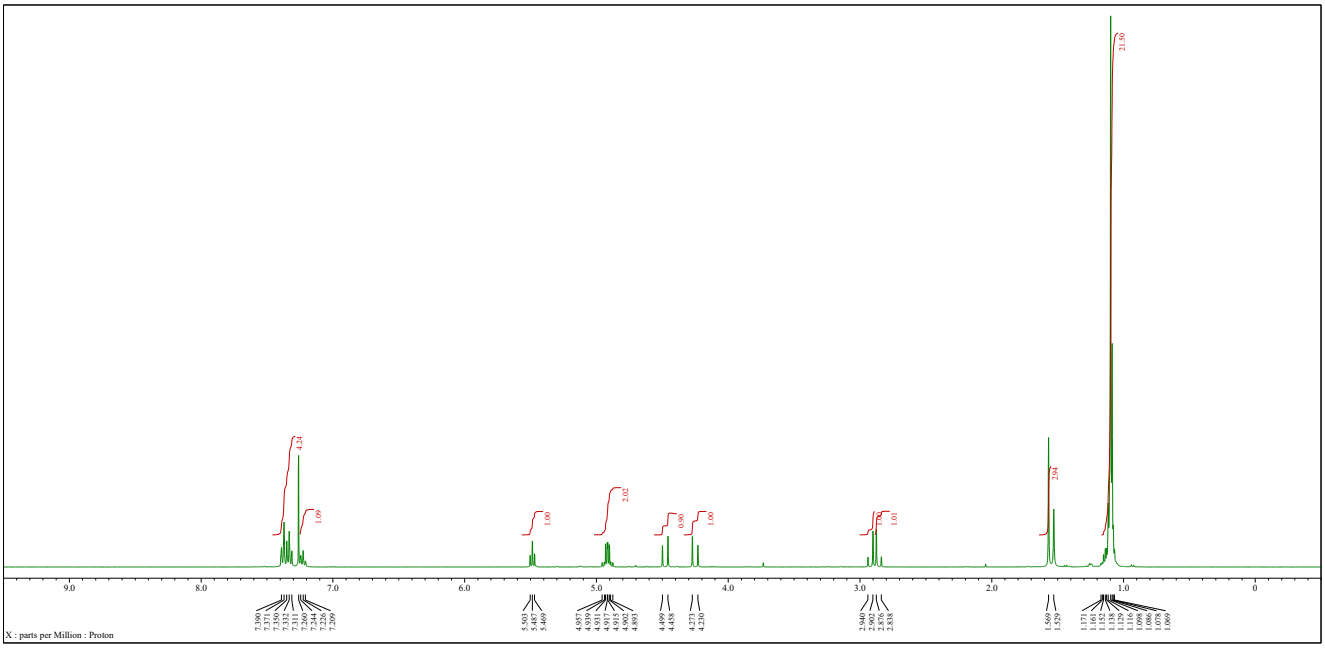
Spectrum Data

1a

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



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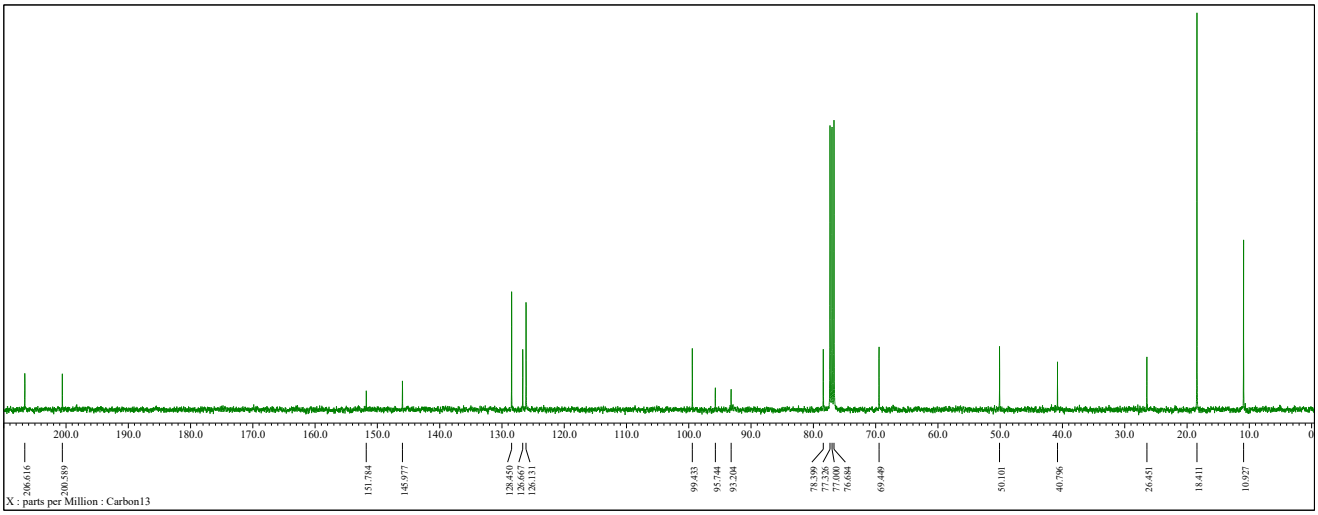
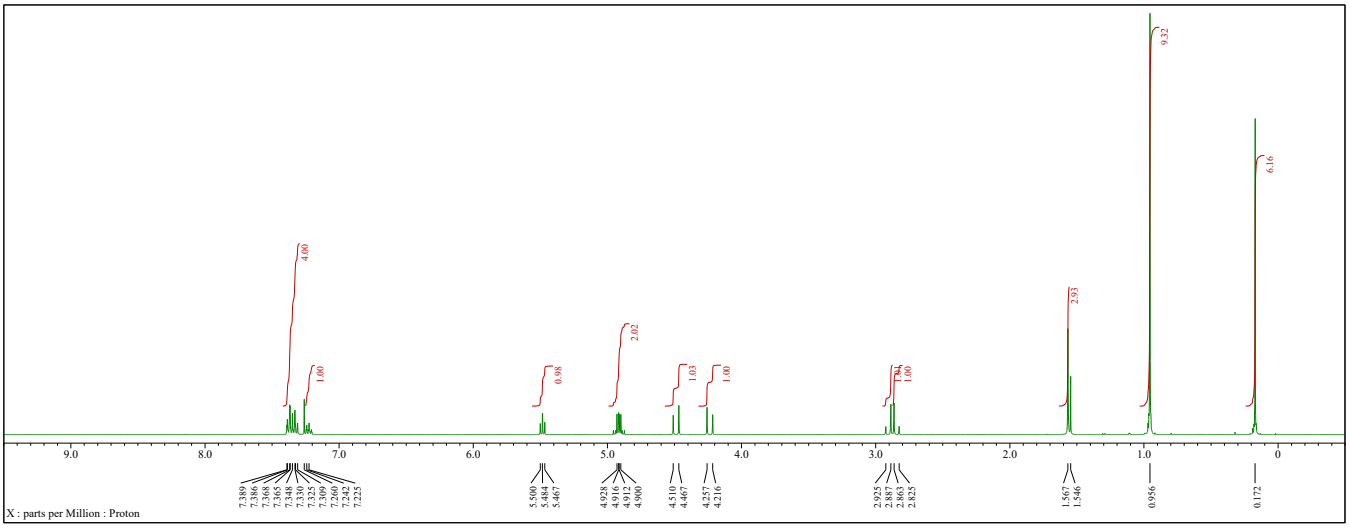


1b

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



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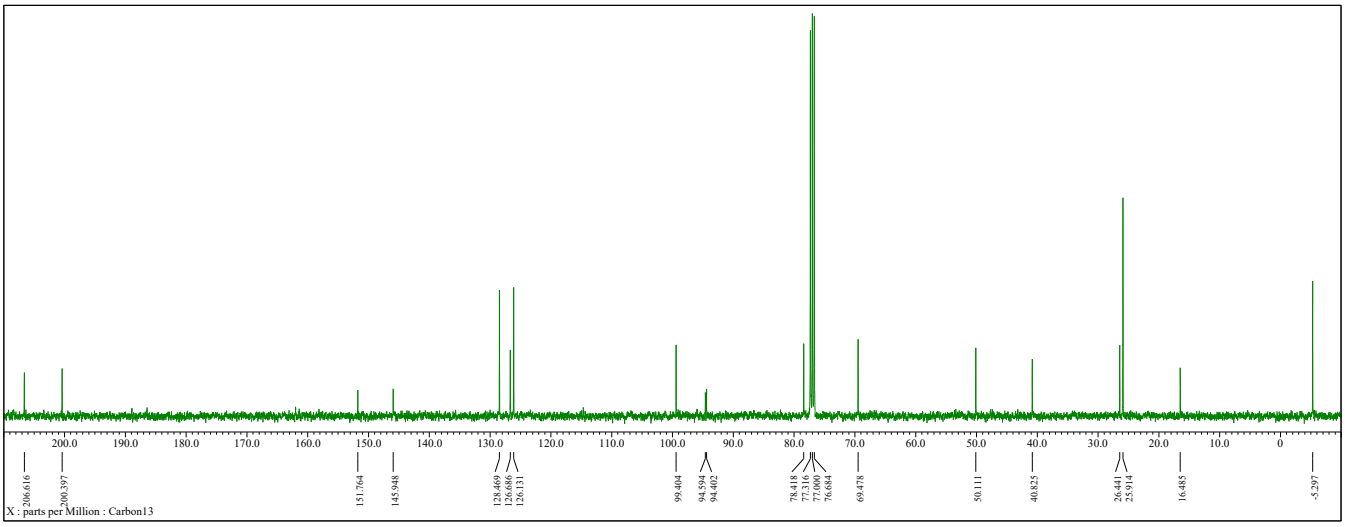
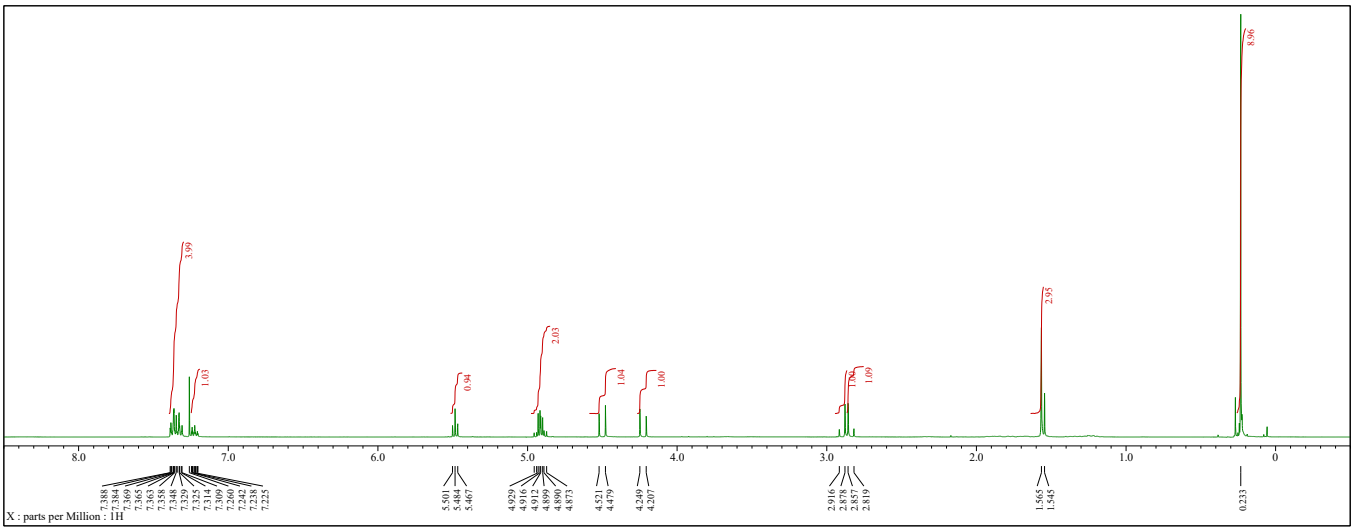


1c

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



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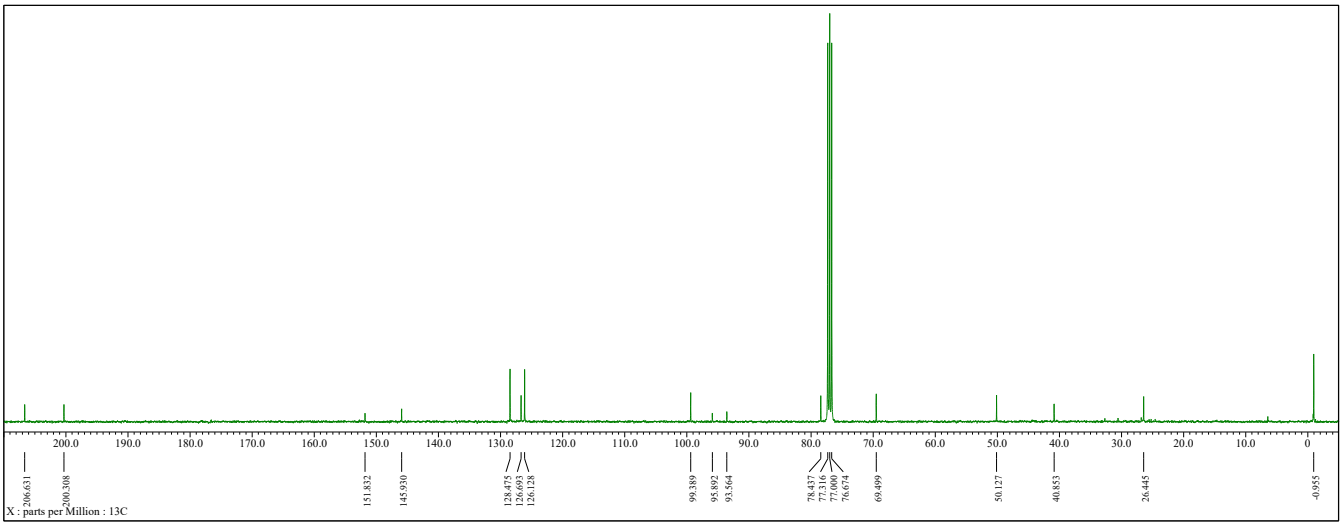
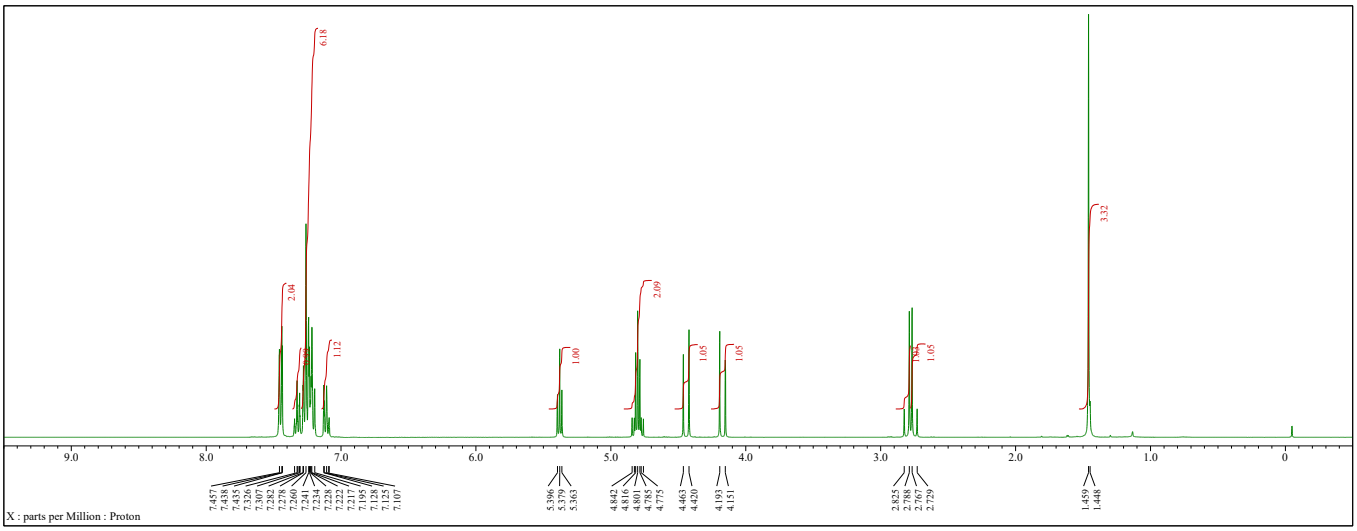


1d

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



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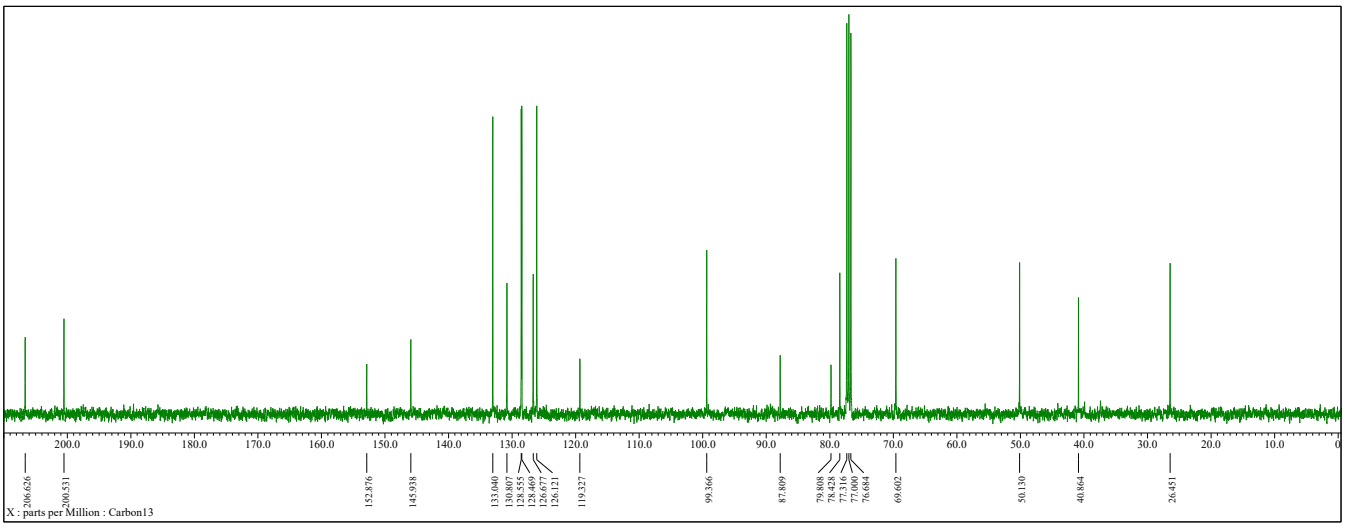

1e

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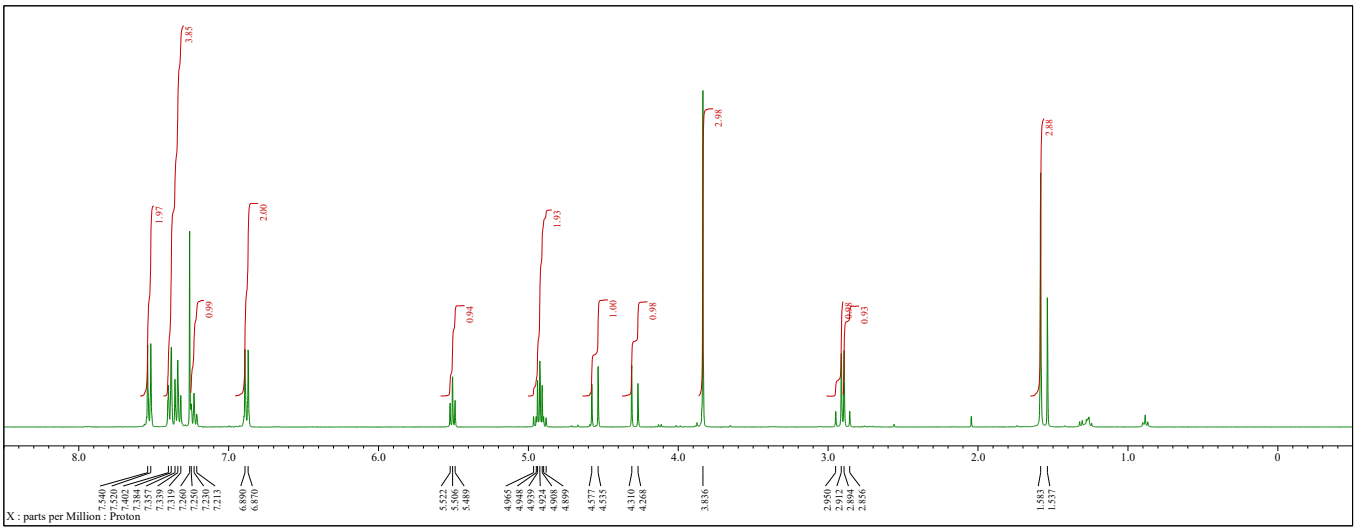

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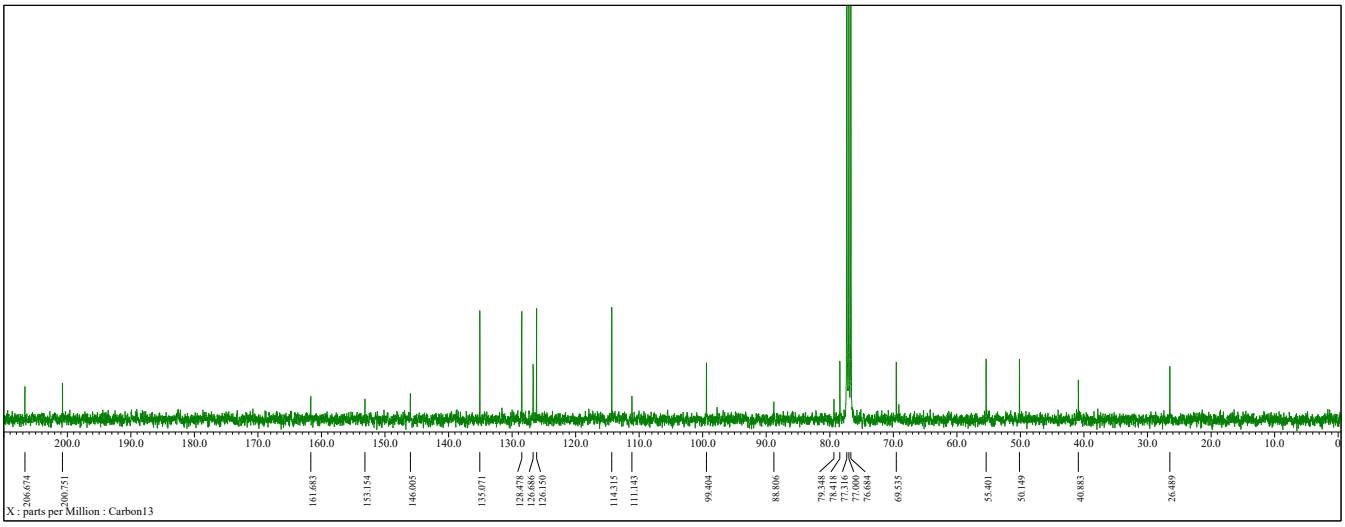

1f

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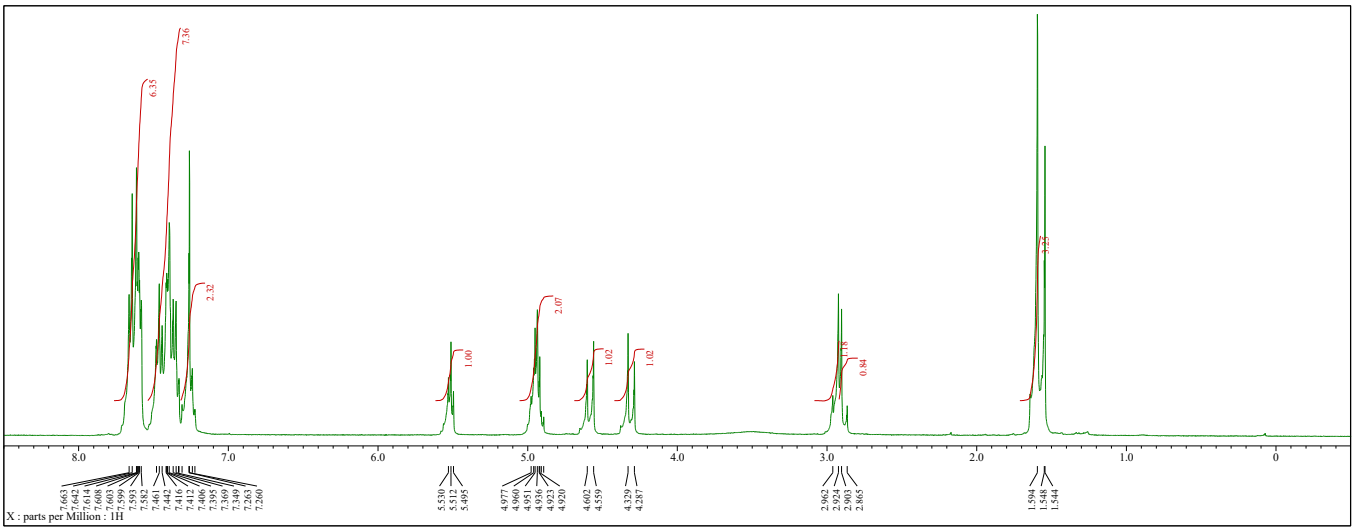
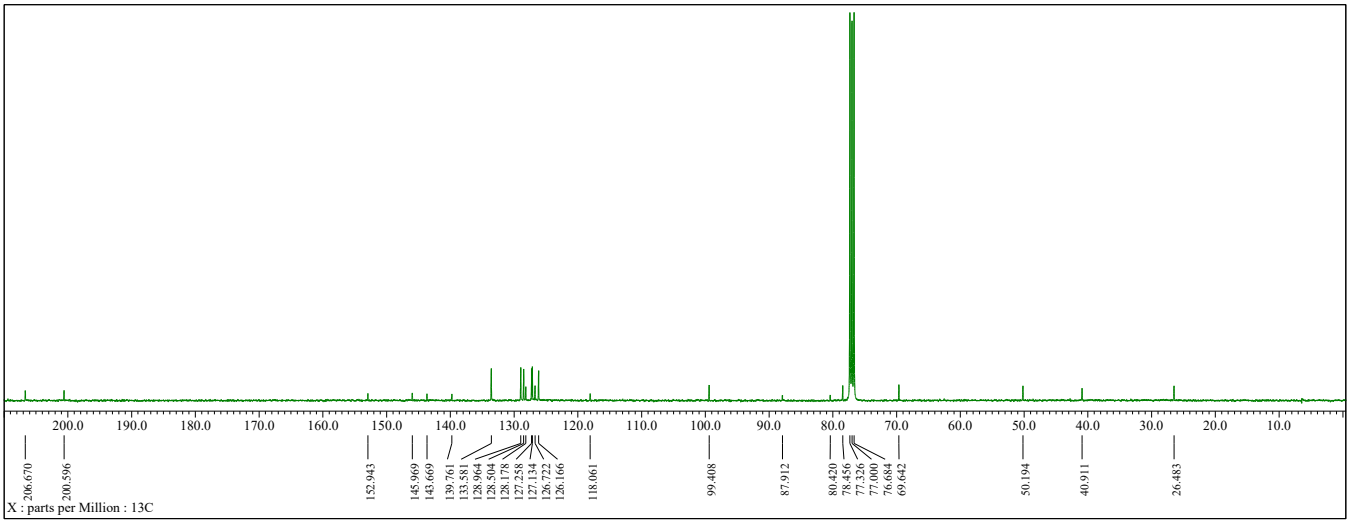
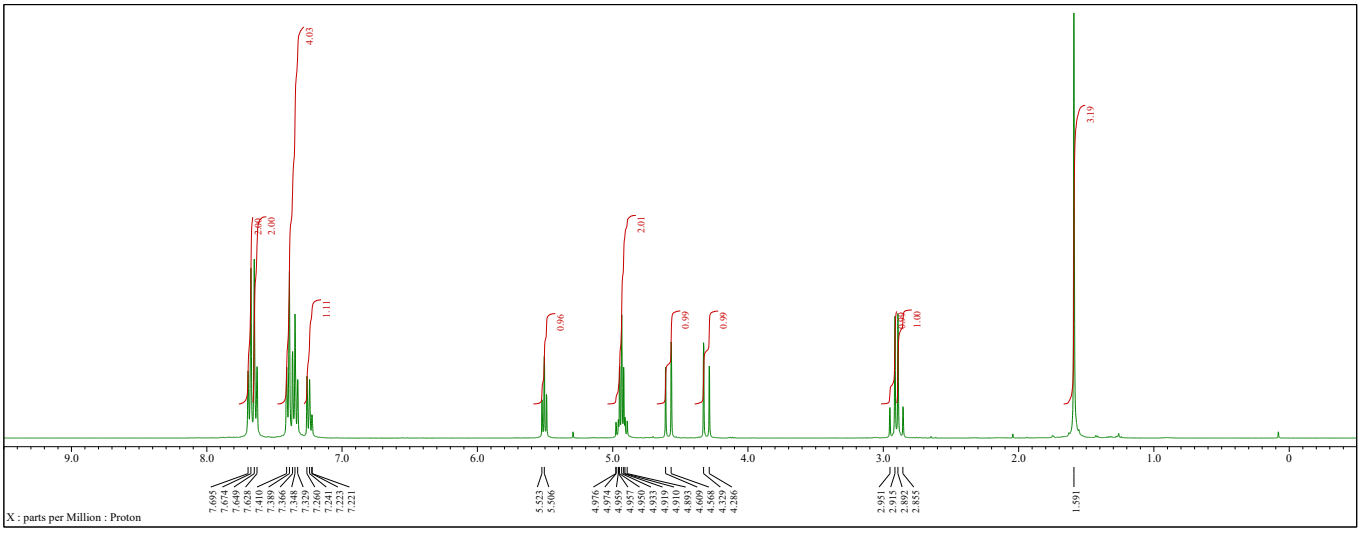


^{13}C NMR (100 MHz, $CDCl_3$)

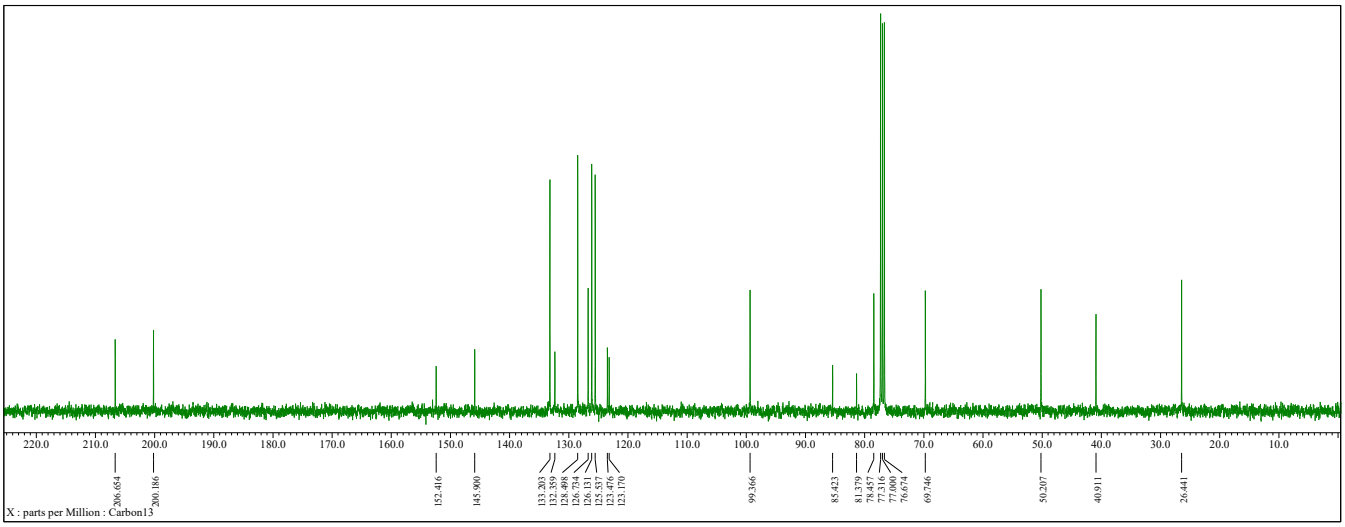


1g

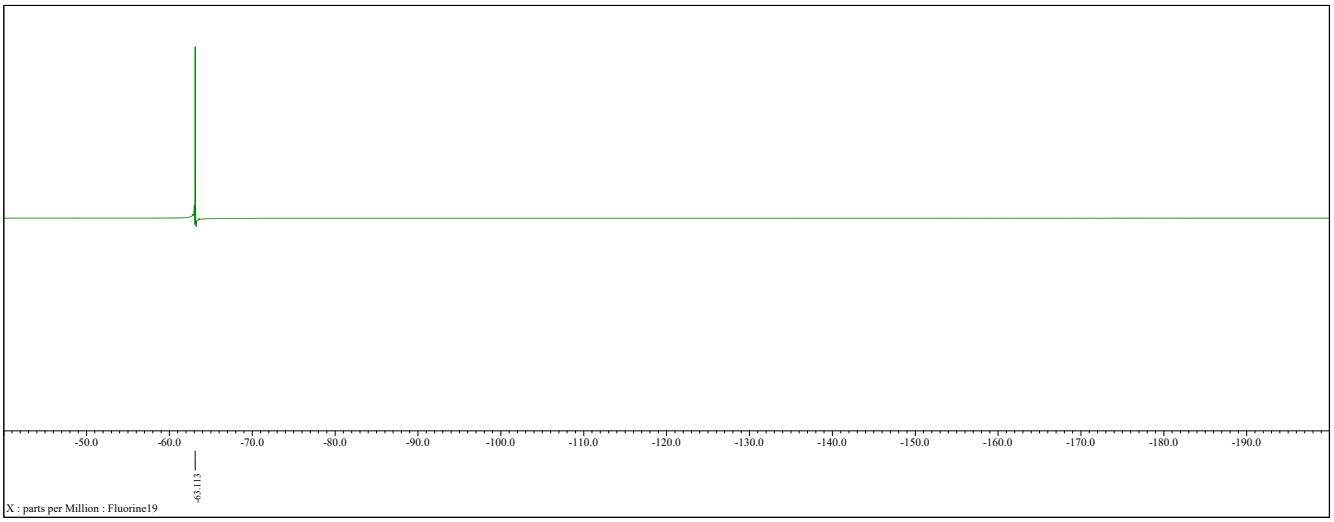
^{1}H NMR (400 MHz, $CDCl_3$)



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

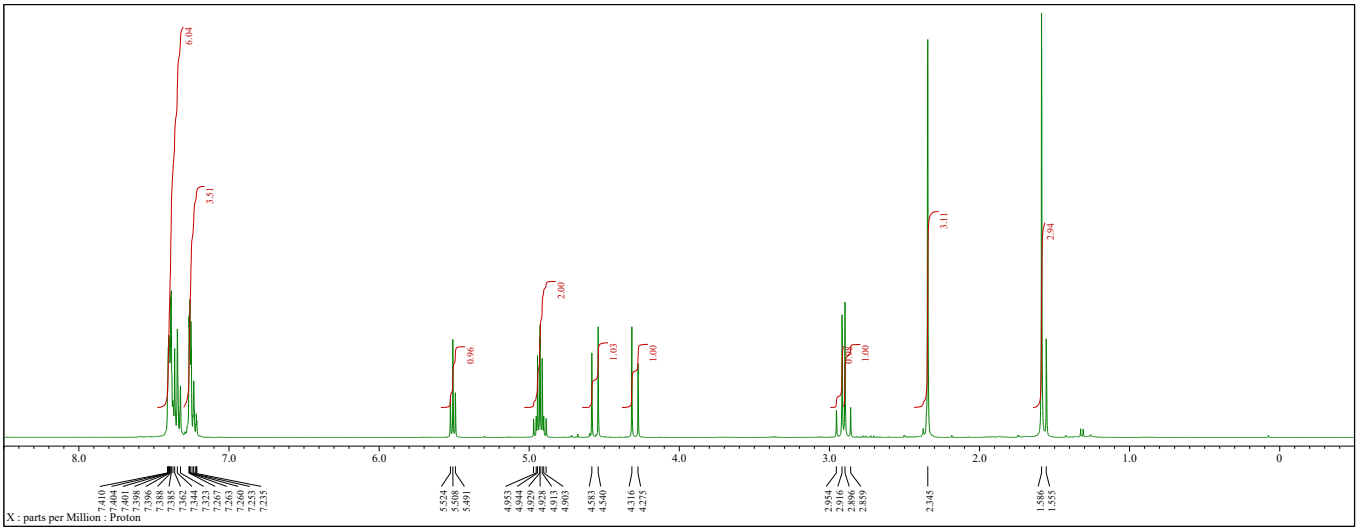


^{19}F NMR (376 MHz, $CDCl_3$)

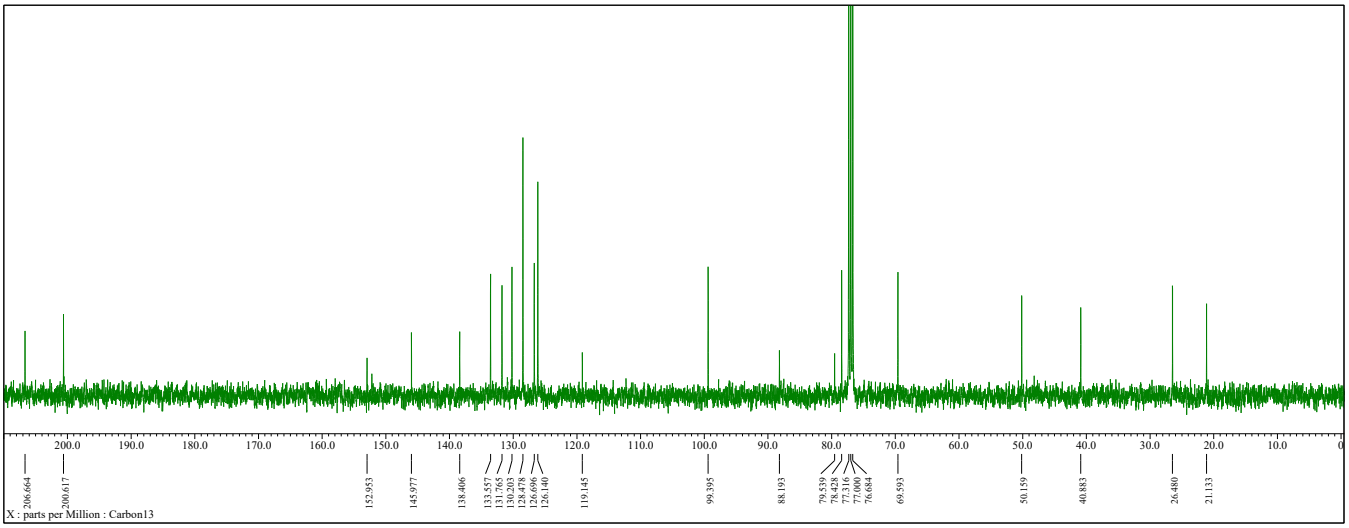


1h

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

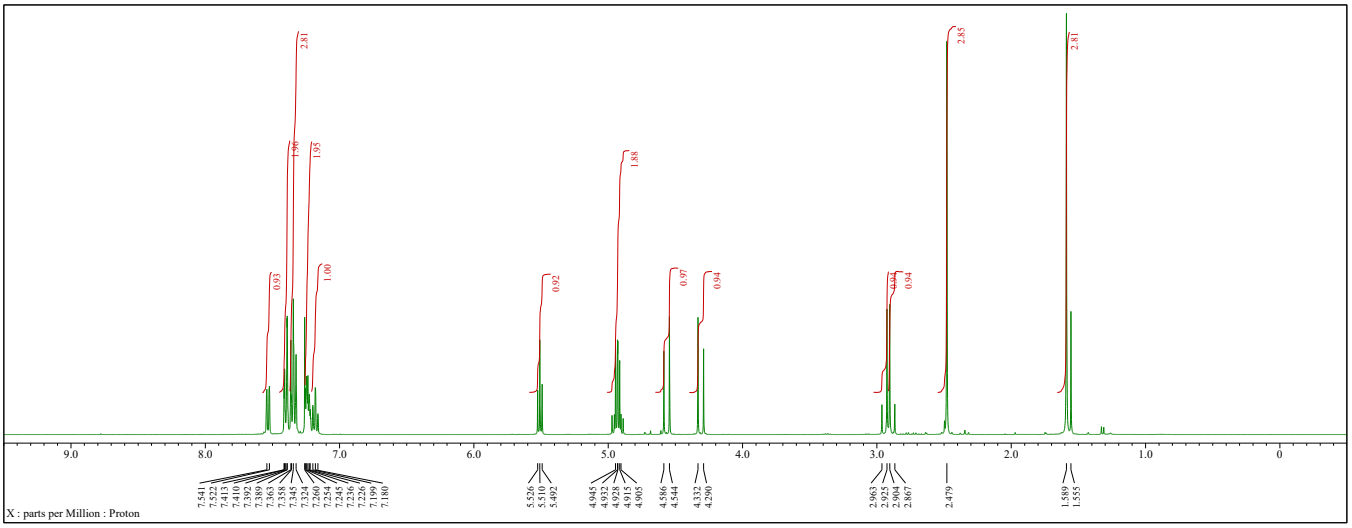


^{13}C NMR (100 MHz, $CDCl_3$)

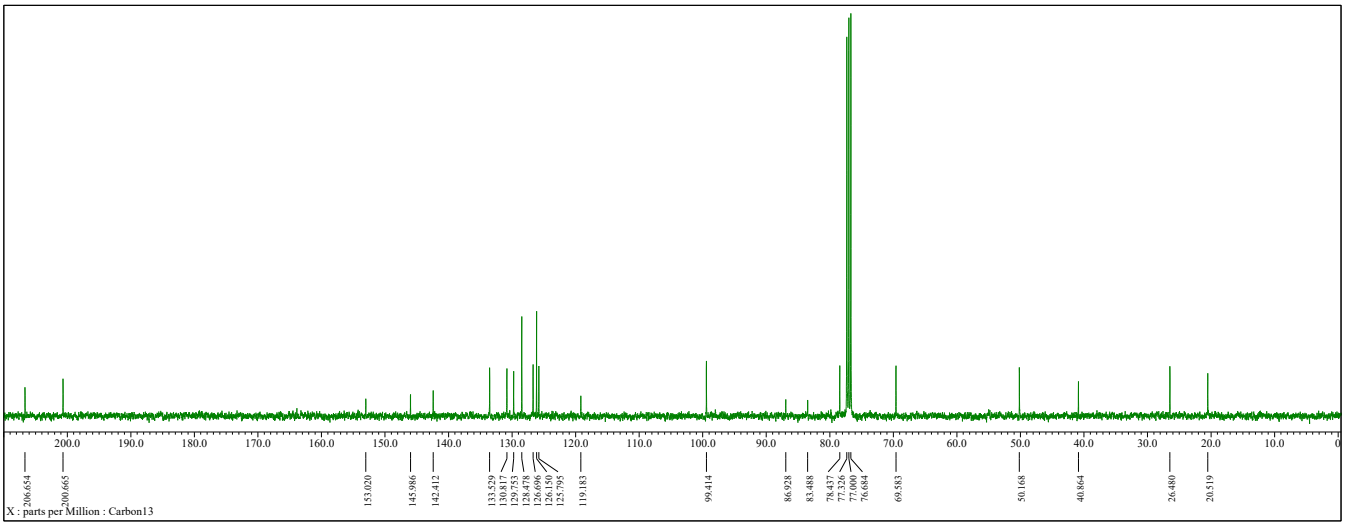


1i

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

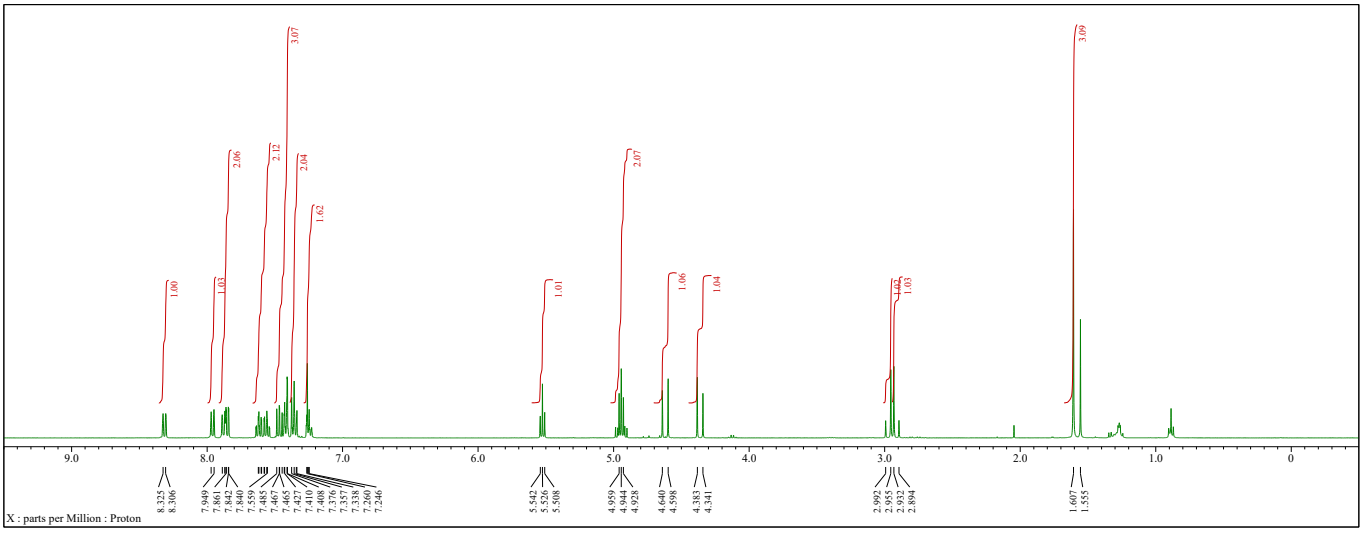


^{13}C NMR (100 MHz, $CDCl_3$)

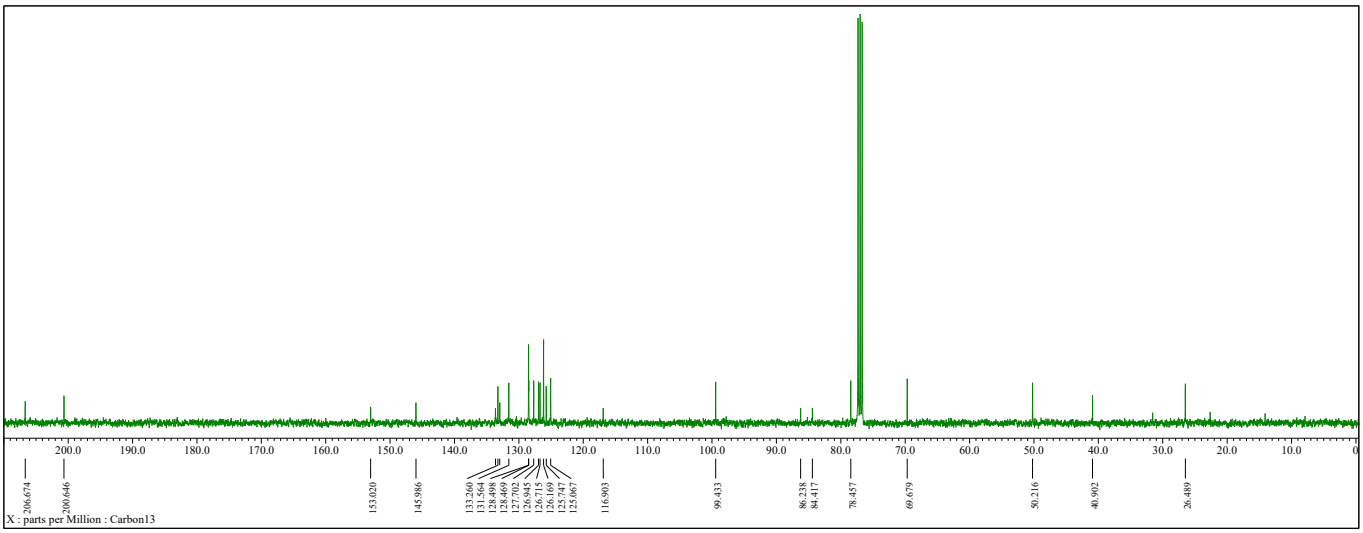


1j

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

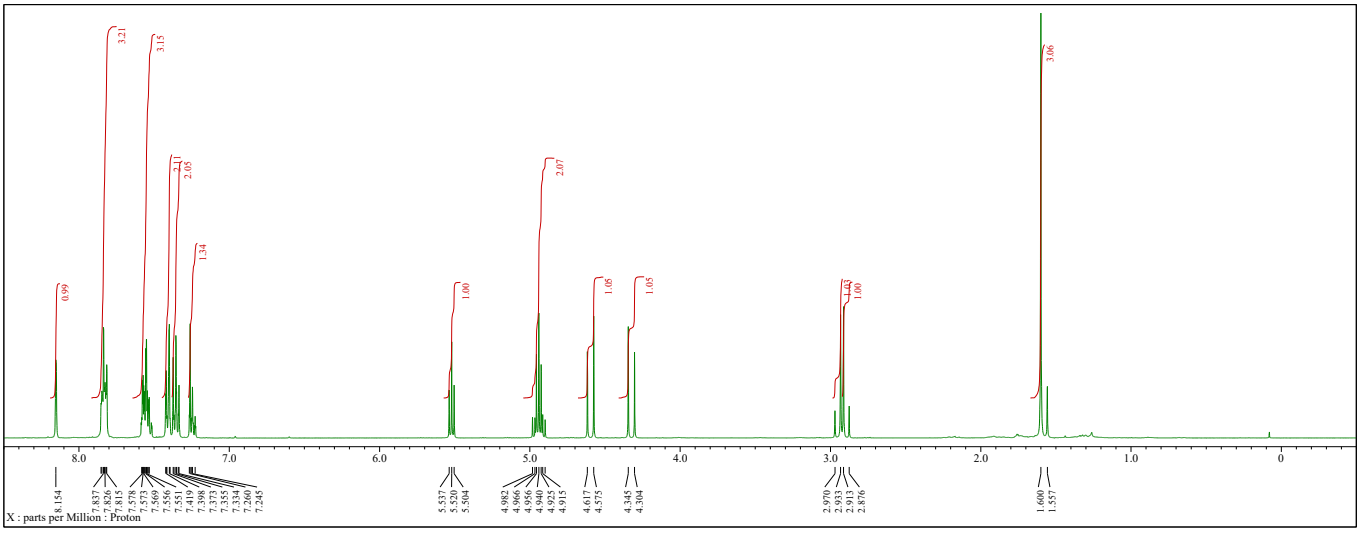


^{13}C NMR (100 MHz, $CDCl_3$)

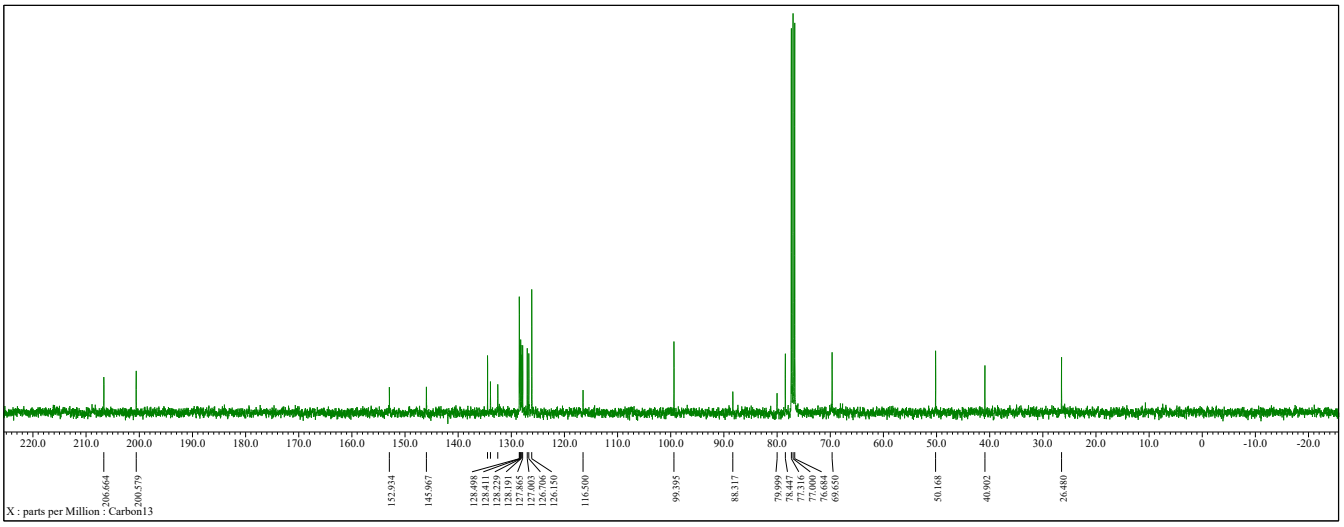


1k

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

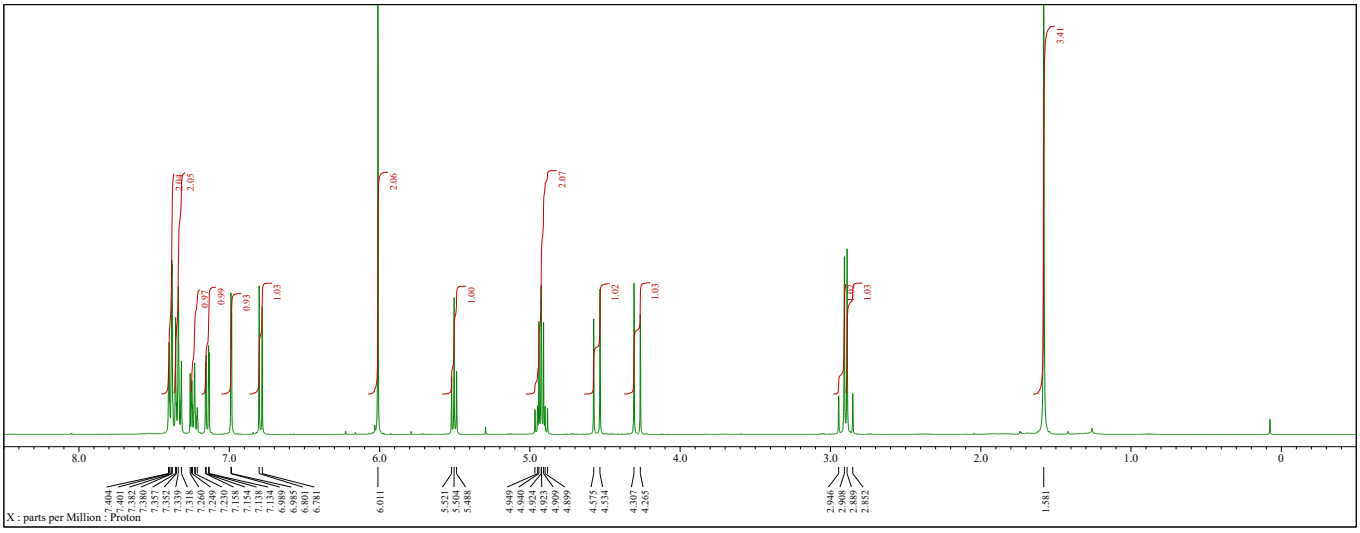


^{13}C NMR (100 MHz, $CDCl_3$)

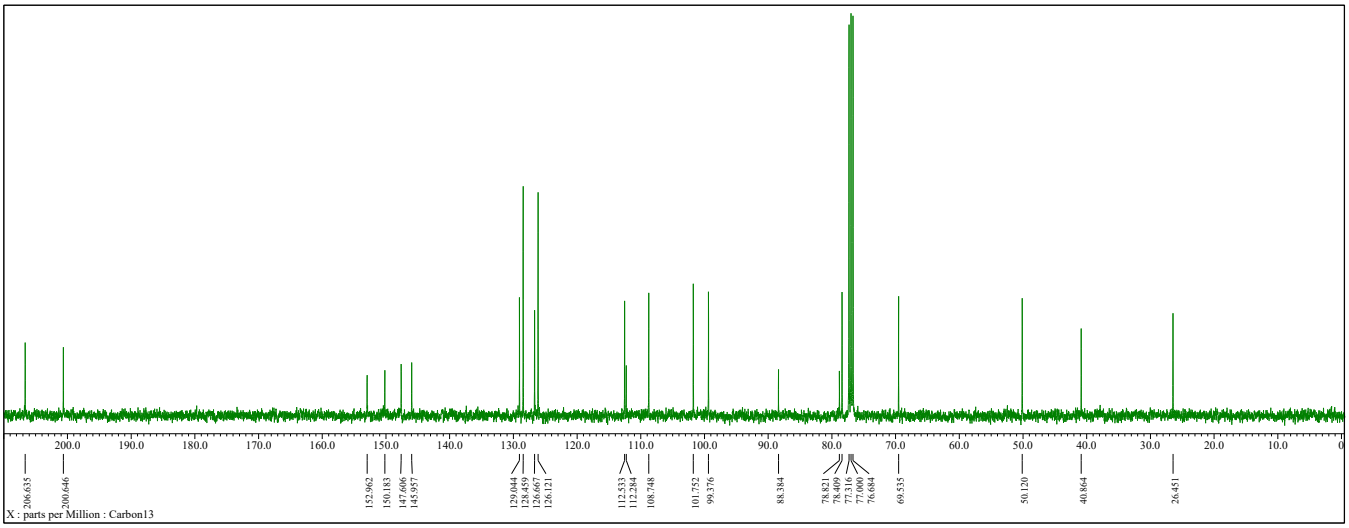


1l

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

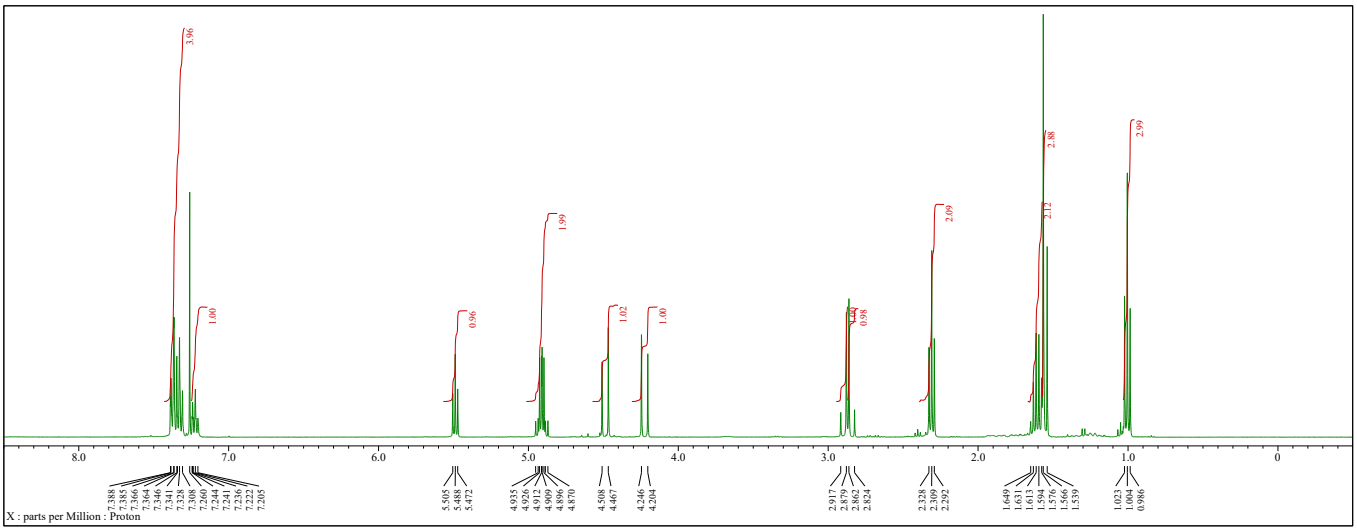


^{13}C NMR (100 MHz, $CDCl_3$)

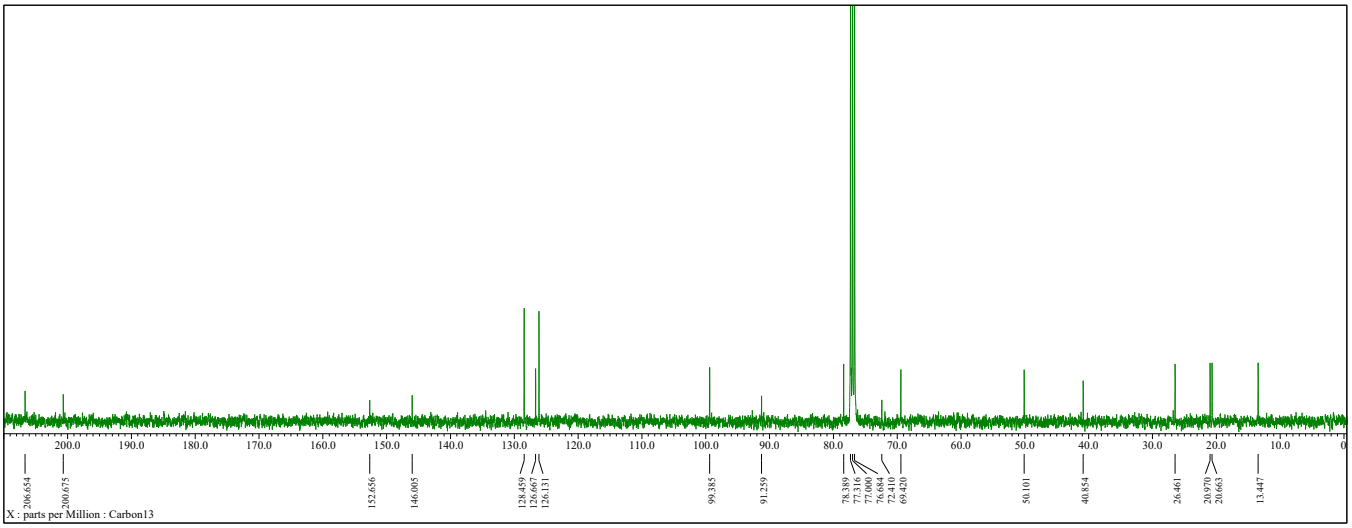


1m

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

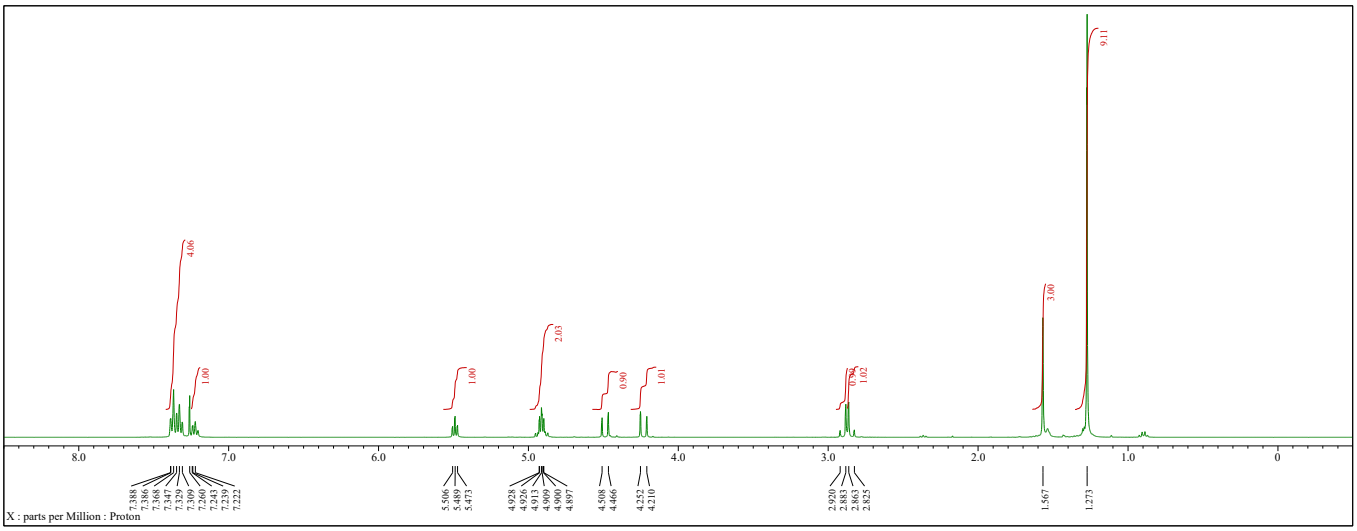


^{13}C NMR (100 MHz, $CDCl_3$)

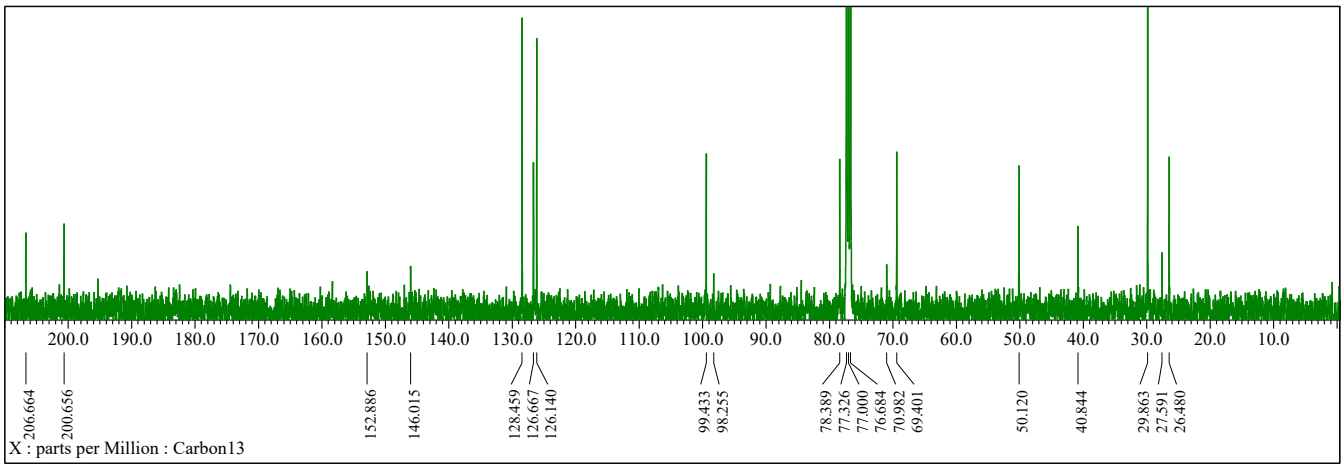


1n

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

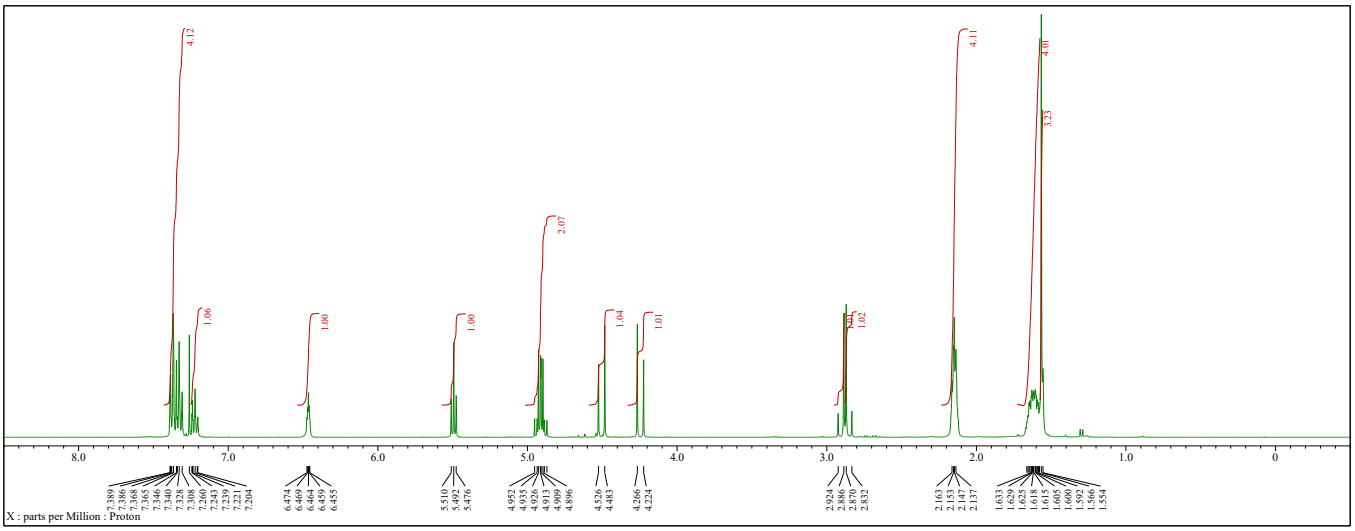


^{13}C NMR (100 MHz, $CDCl_3$)

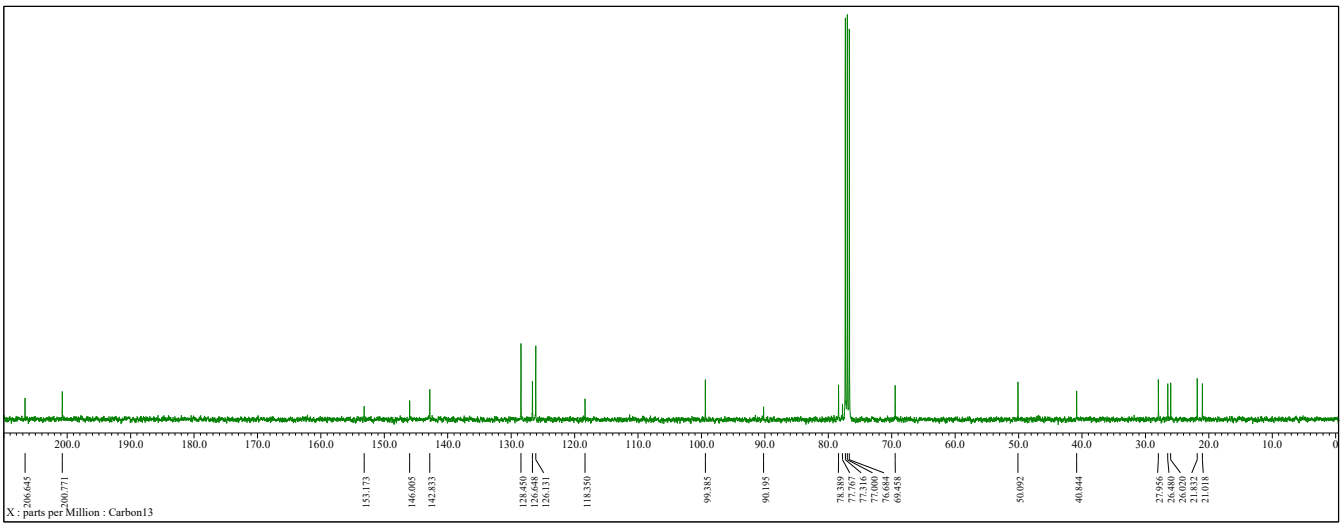


1o

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

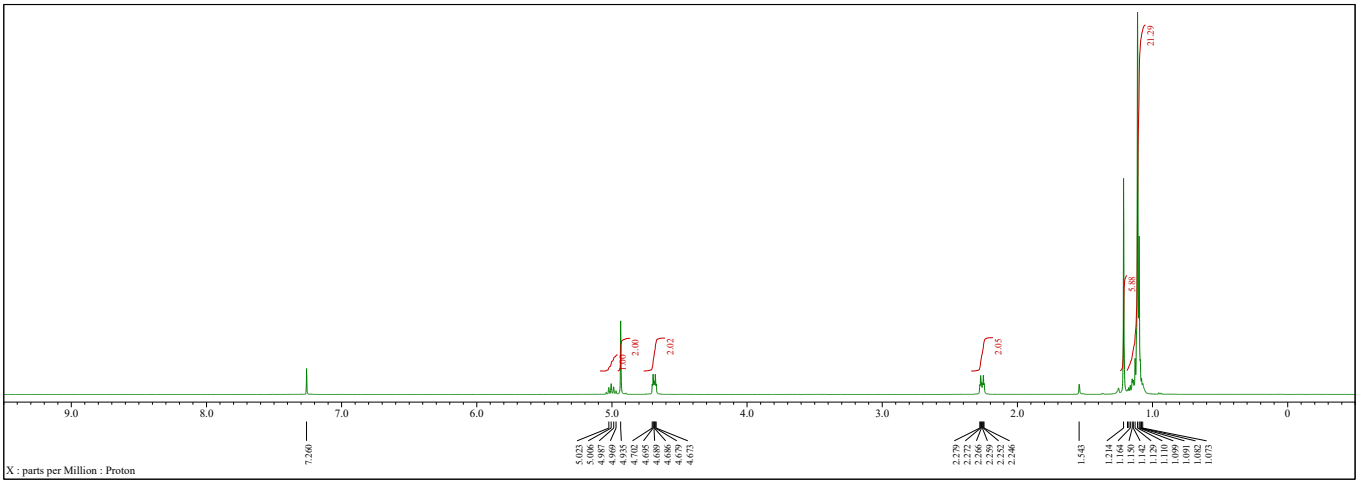


^{13}C NMR (100 MHz, $CDCl_3$)

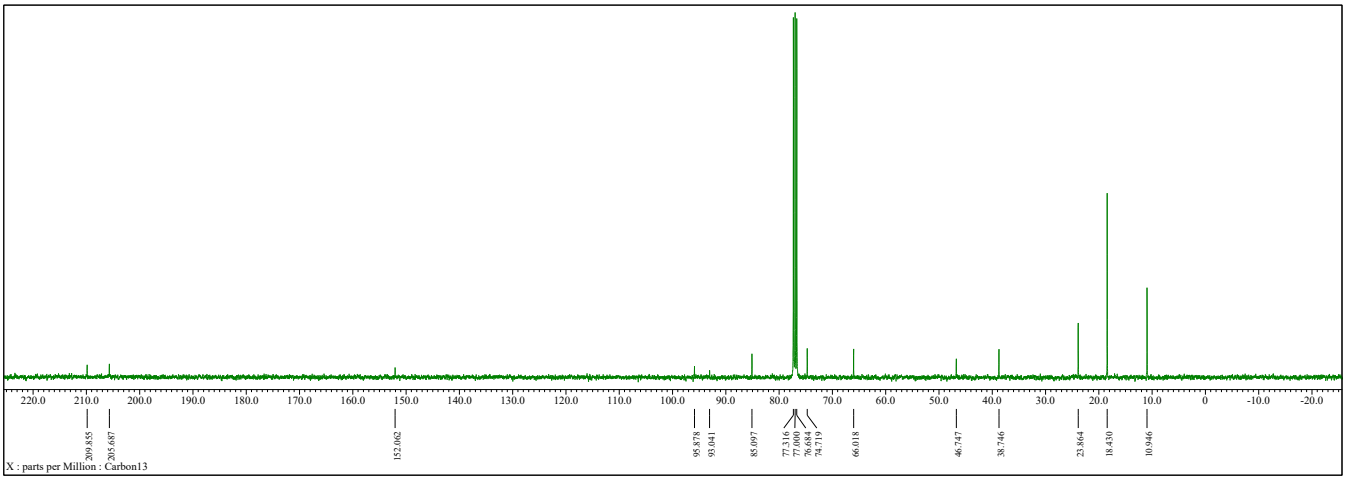


1p

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

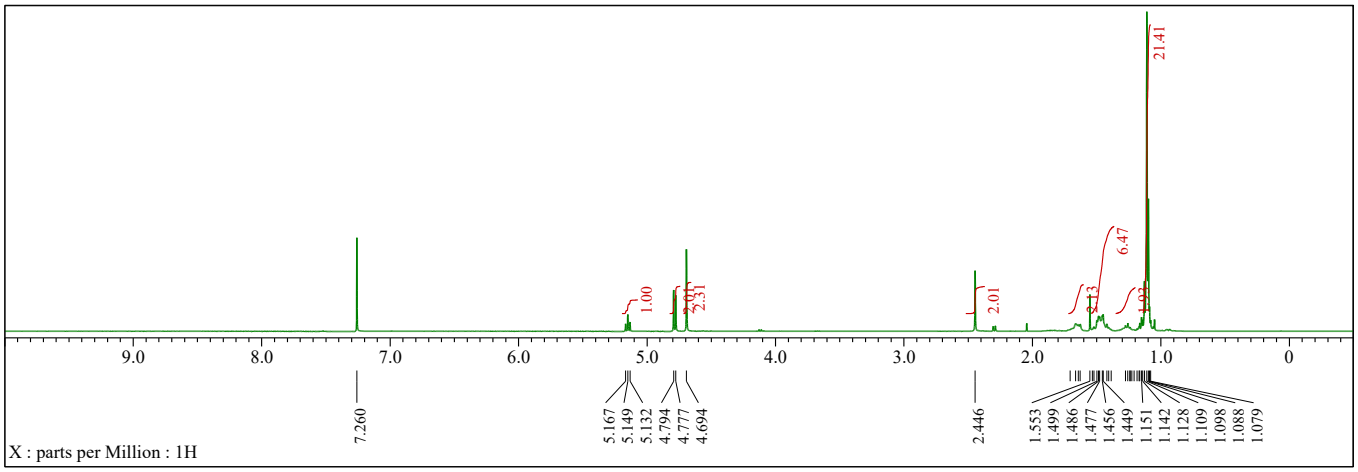


^{13}C NMR (100 MHz, $CDCl_3$)

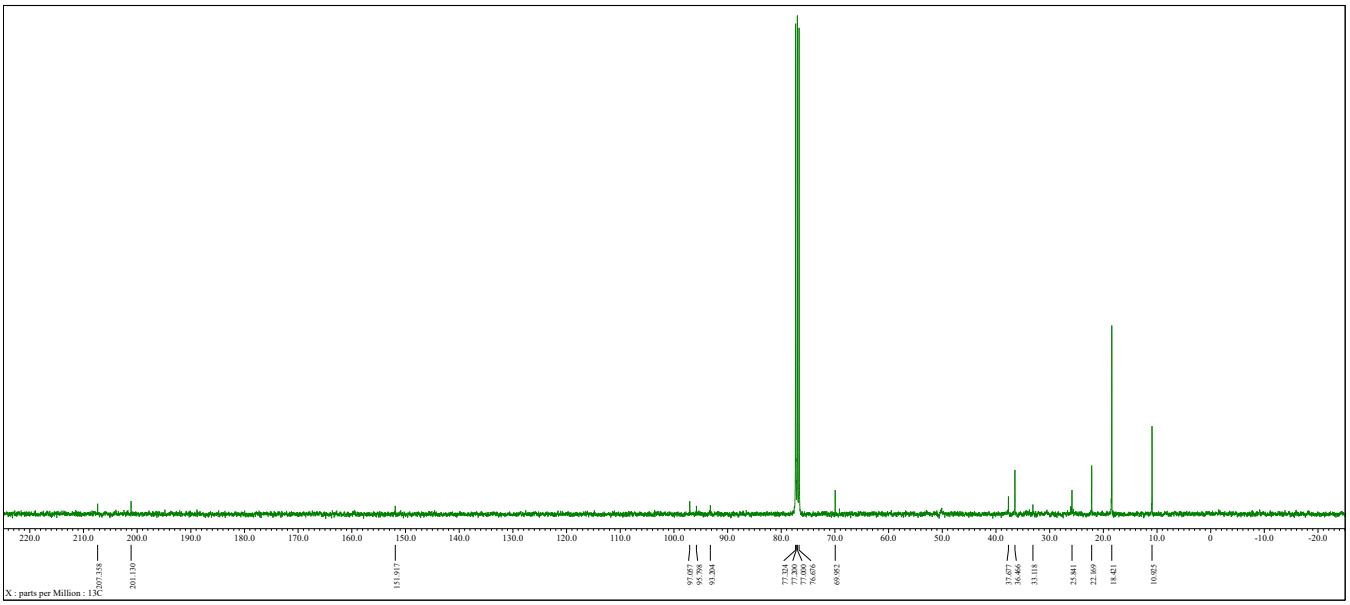


1r

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

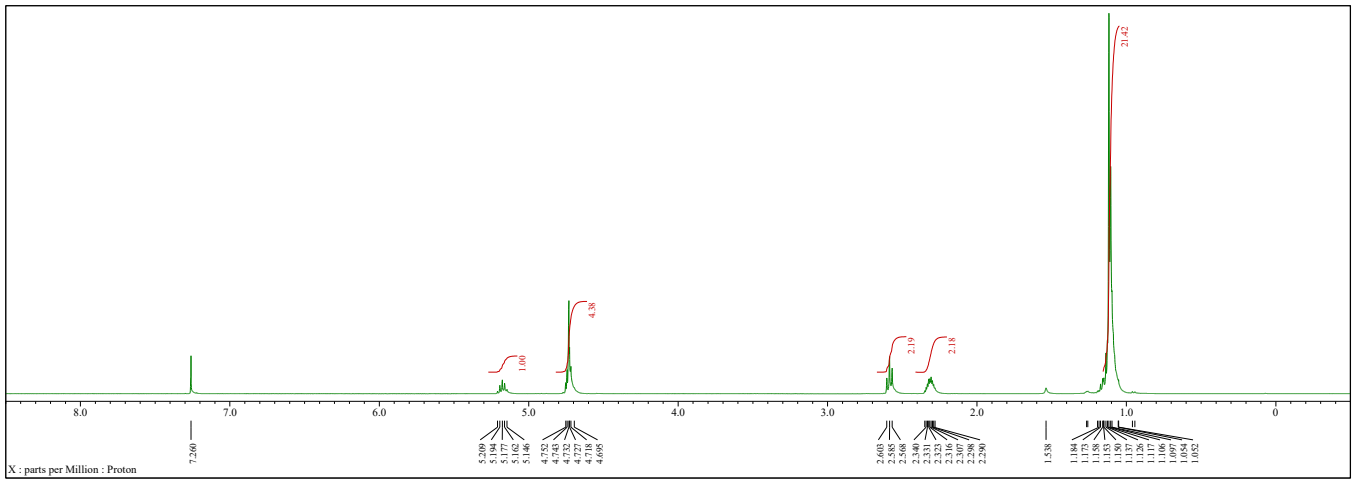


^{13}C NMR (100 MHz, $CDCl_3$)

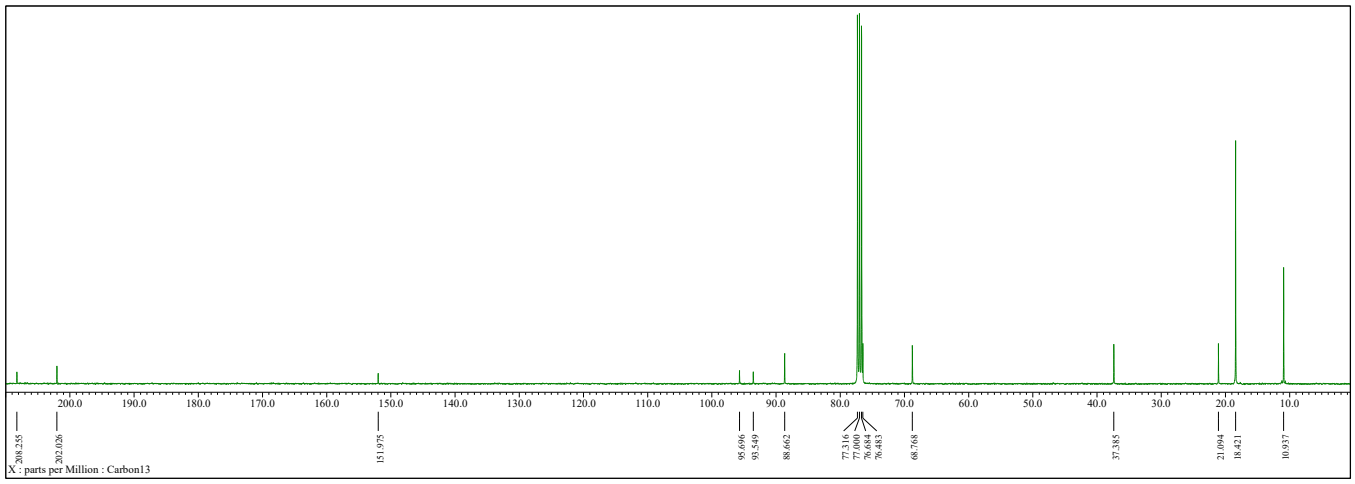


1q

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

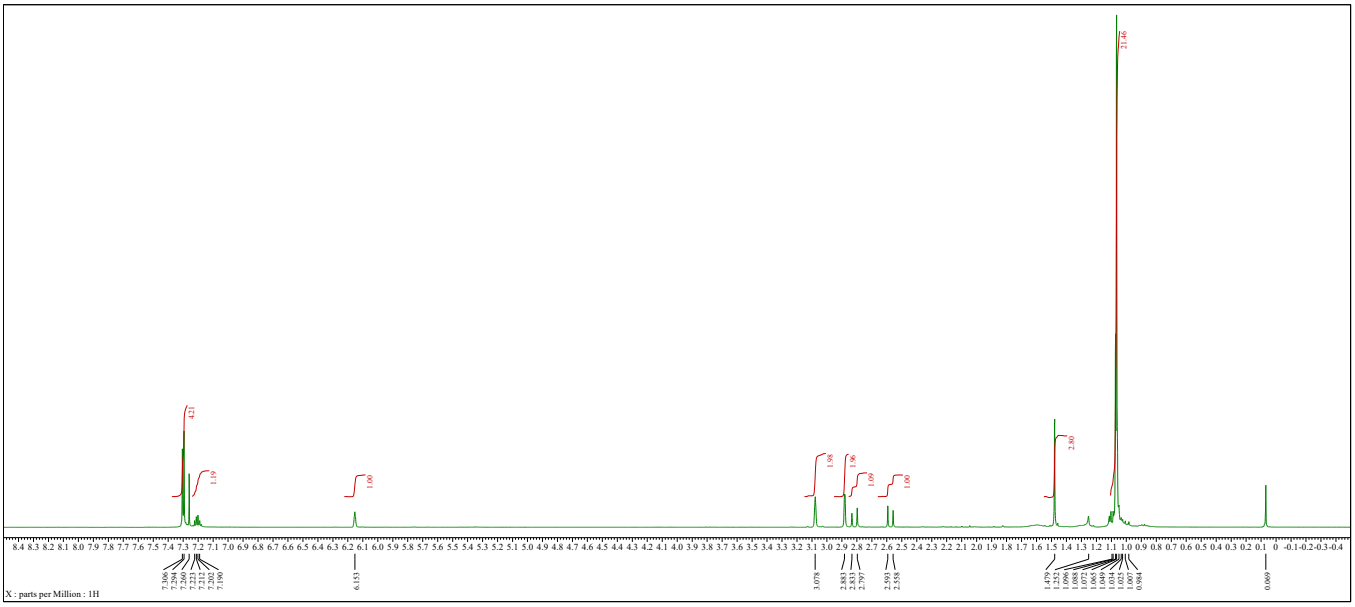


^{13}C NMR (100 MHz, $CDCl_3$)

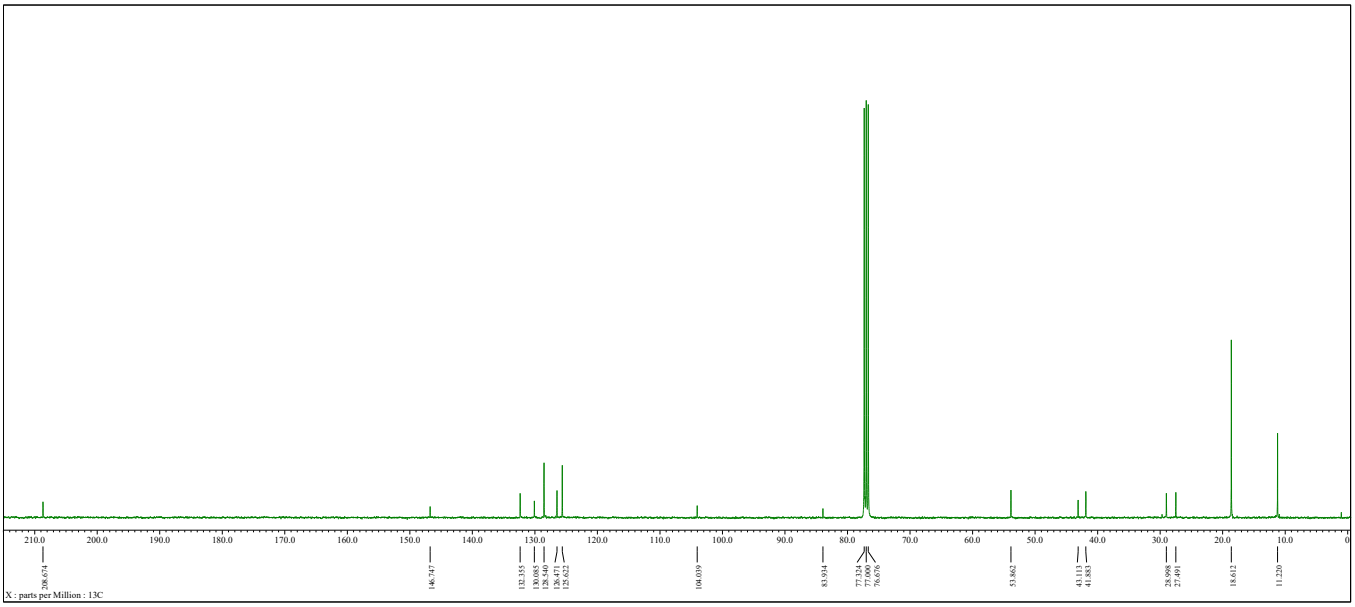


3a

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

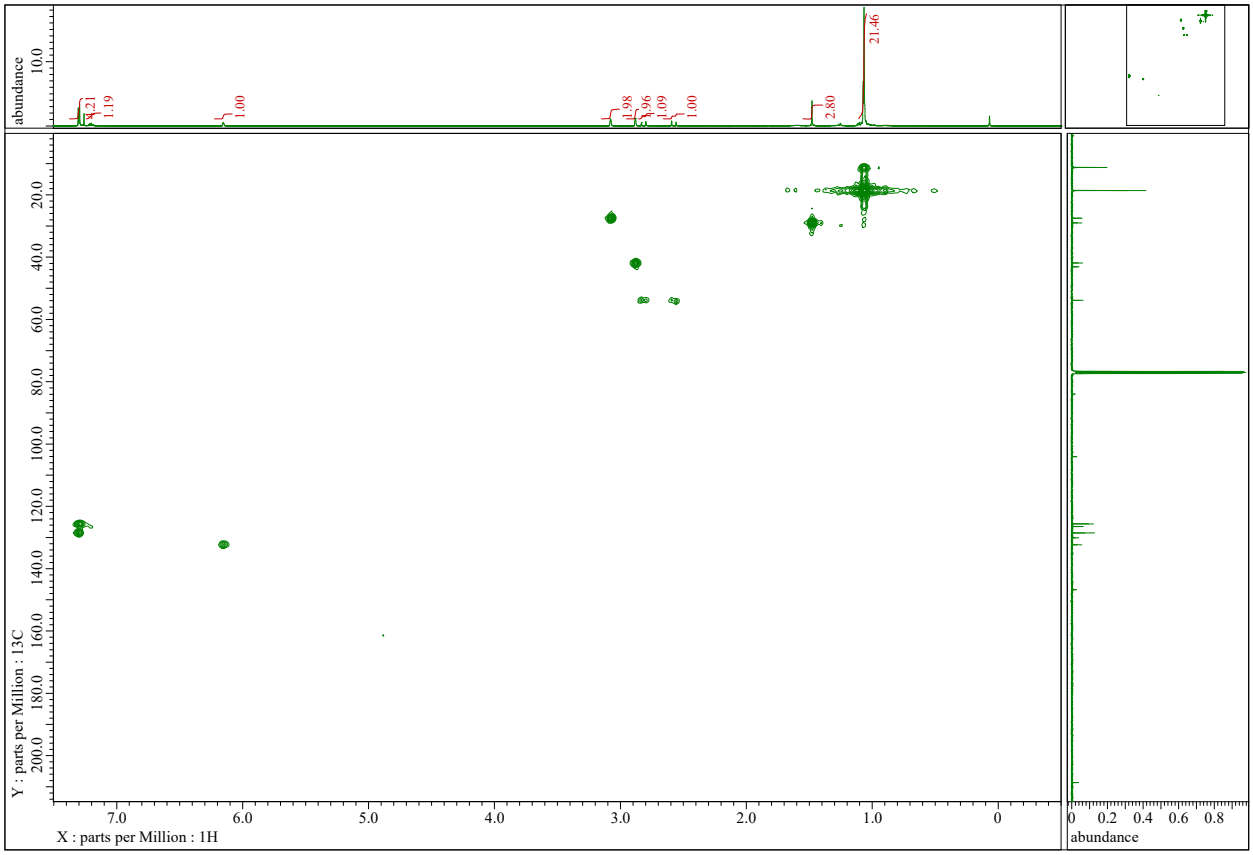


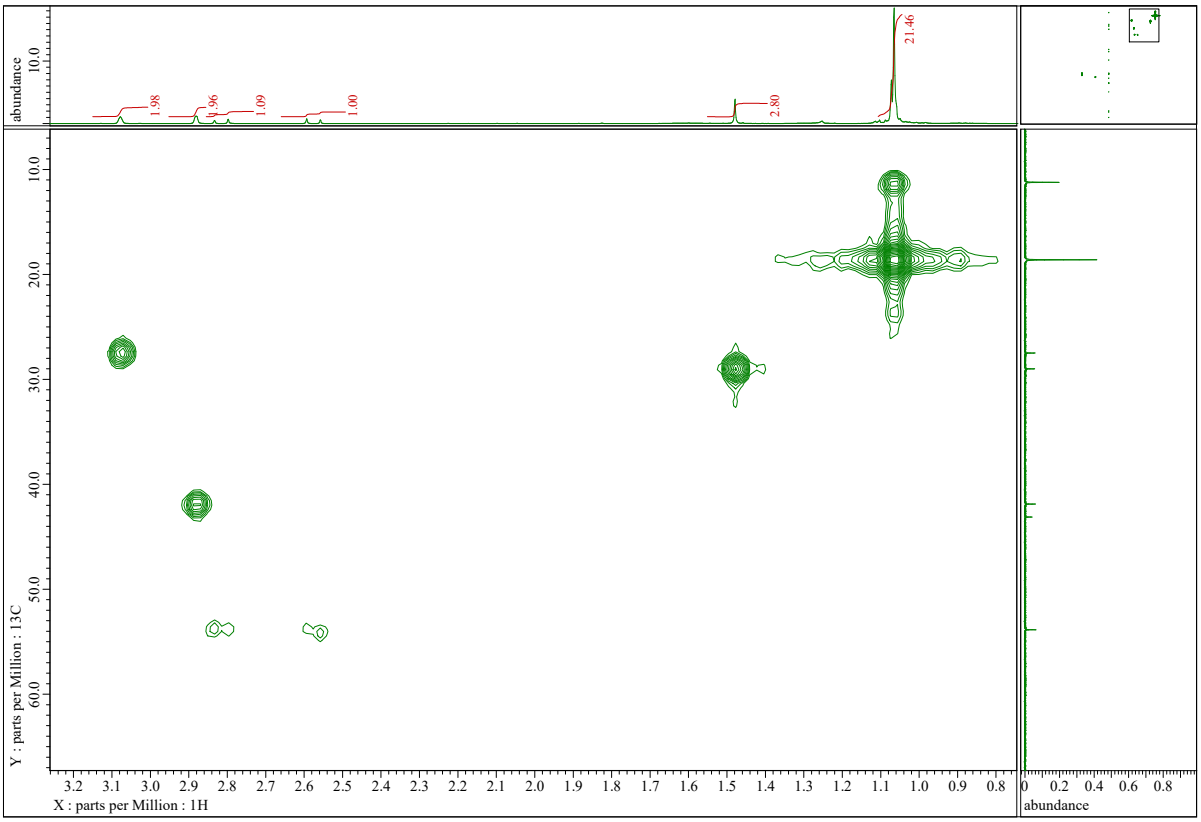
^{13}C NMR (100 MHz, $CDCl_3$)

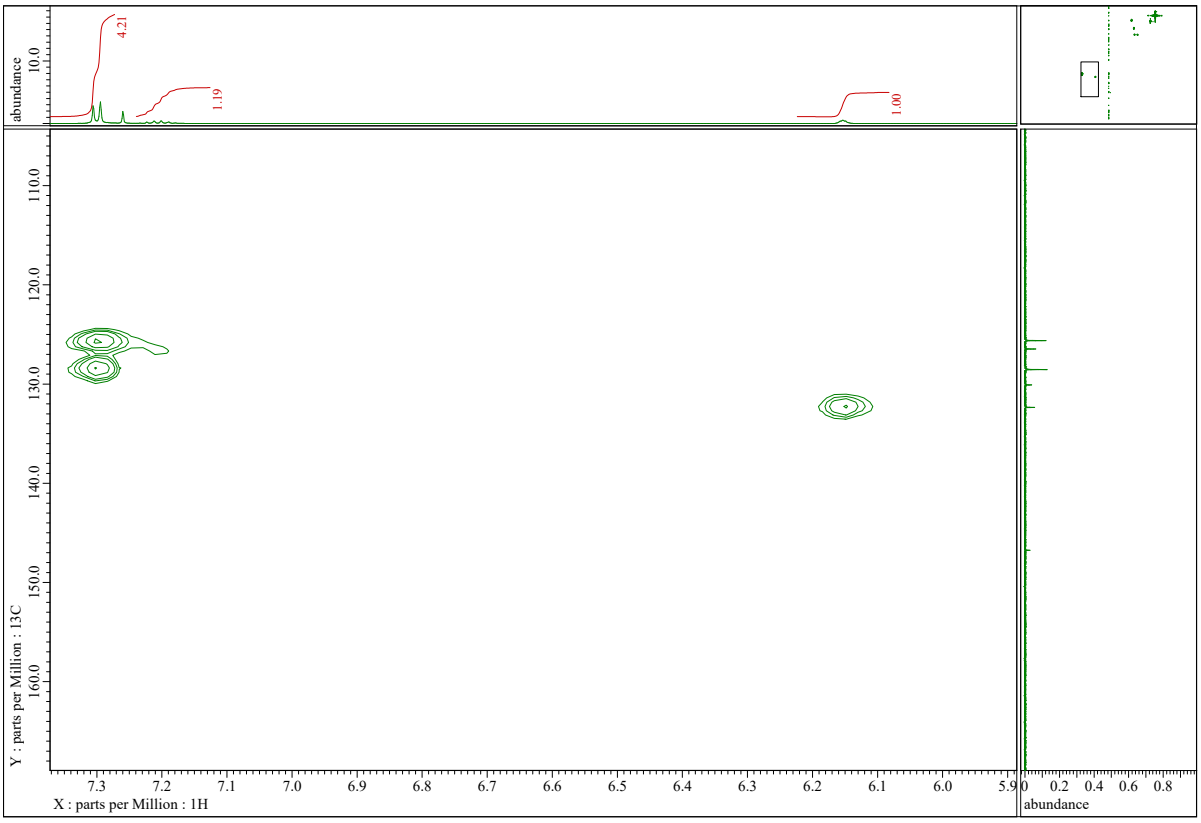


3a

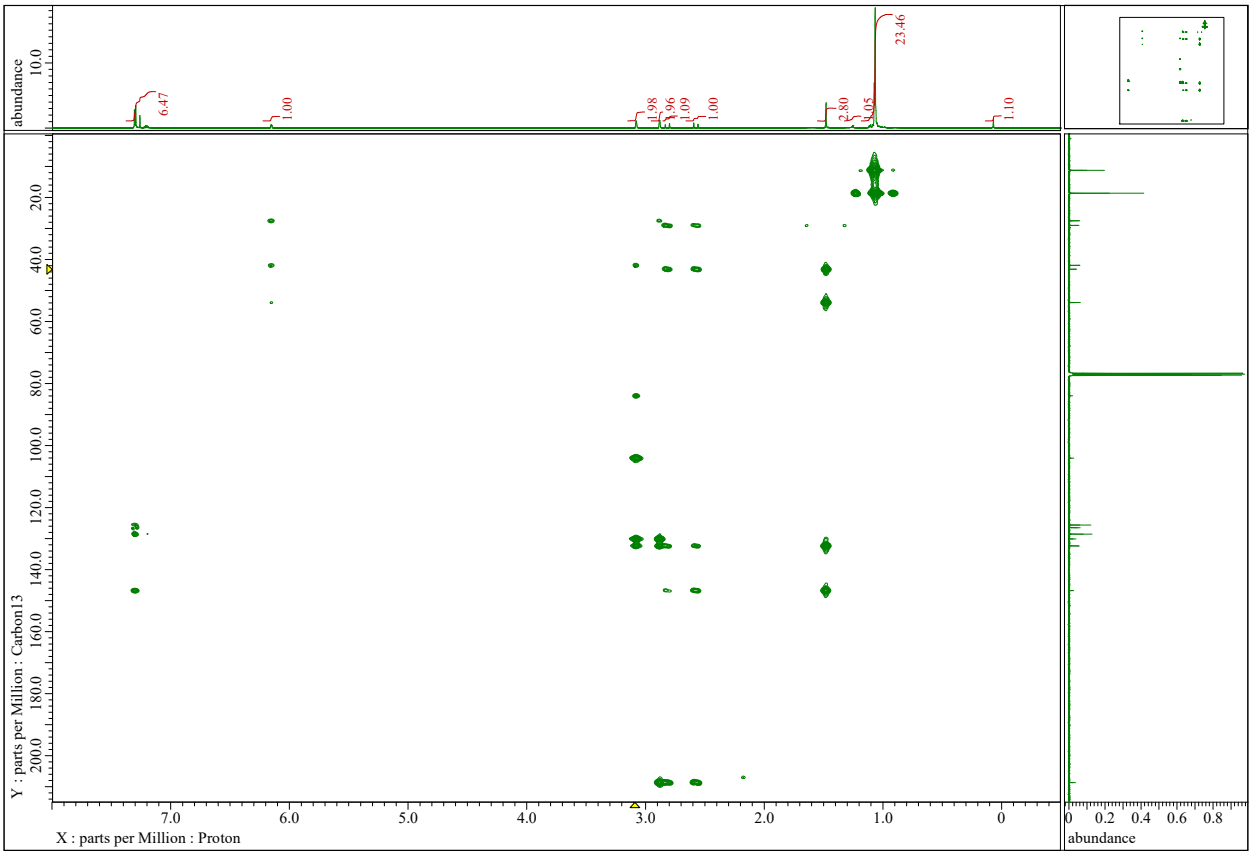
HMQC

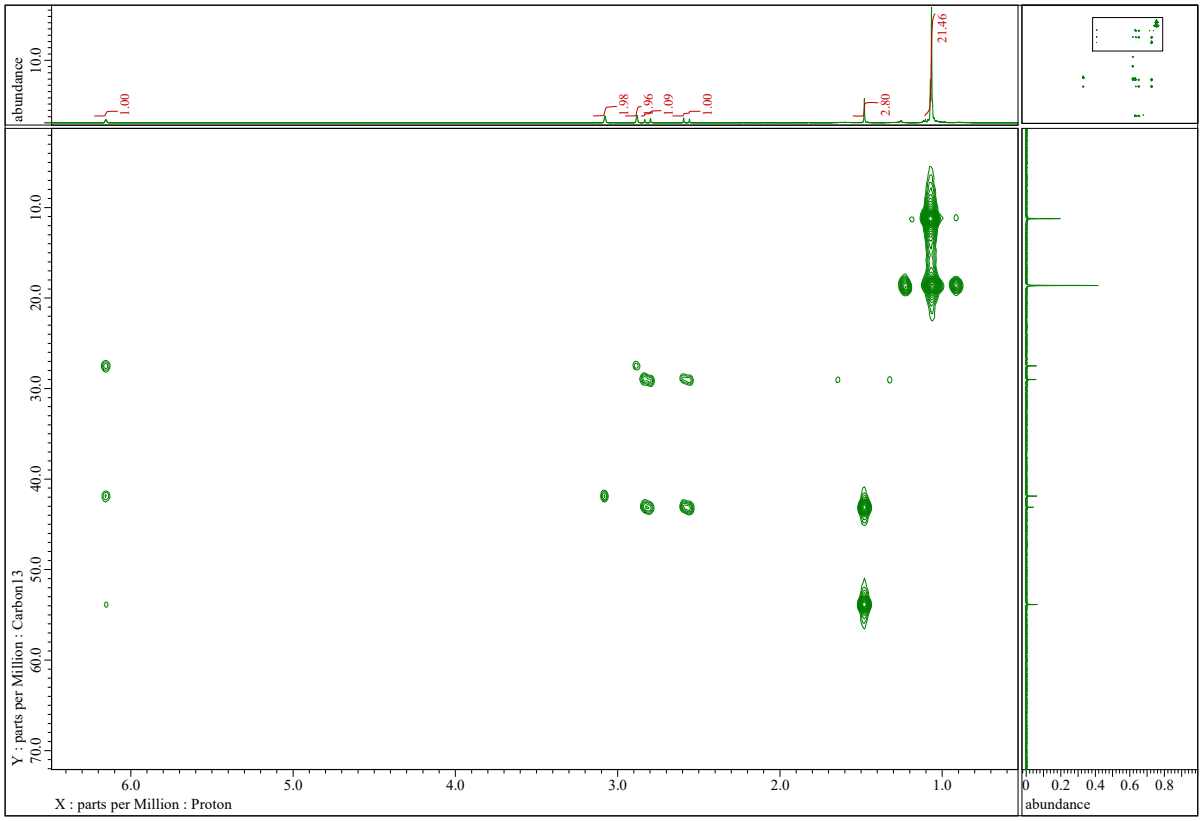

abundance
21.46
1.21
1.19
1.00
1.98
1.96
1.09
1.00
2.80
Y : parts per Million : 13C
X : parts per Million : 1H
abundance

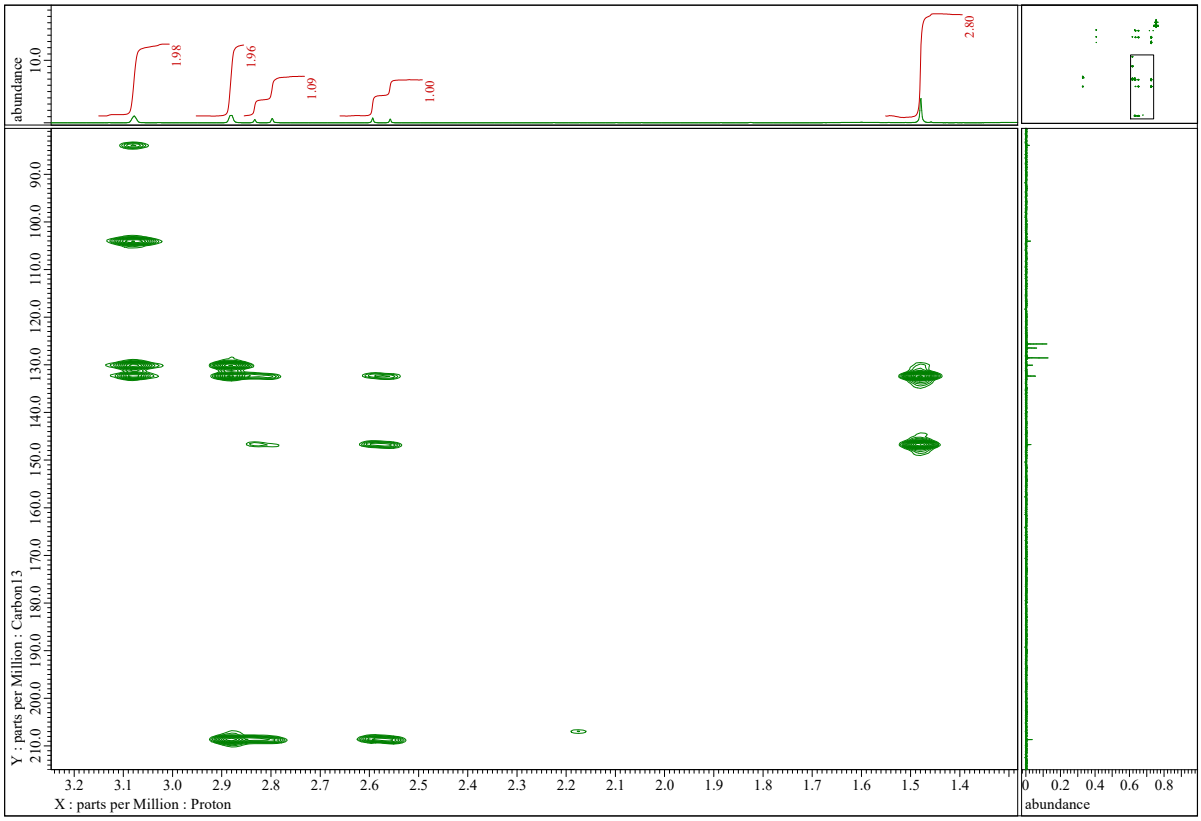

abundance
21.46
1.98
1.96
1.09
1.00
2.80
Y : parts per Million : 13C
X : parts per Million : 1H
abundance


abundance
4.21
1.19
1.00
Y : parts per Million : 13C
X : parts per Million : 1H
abundance

HMBC

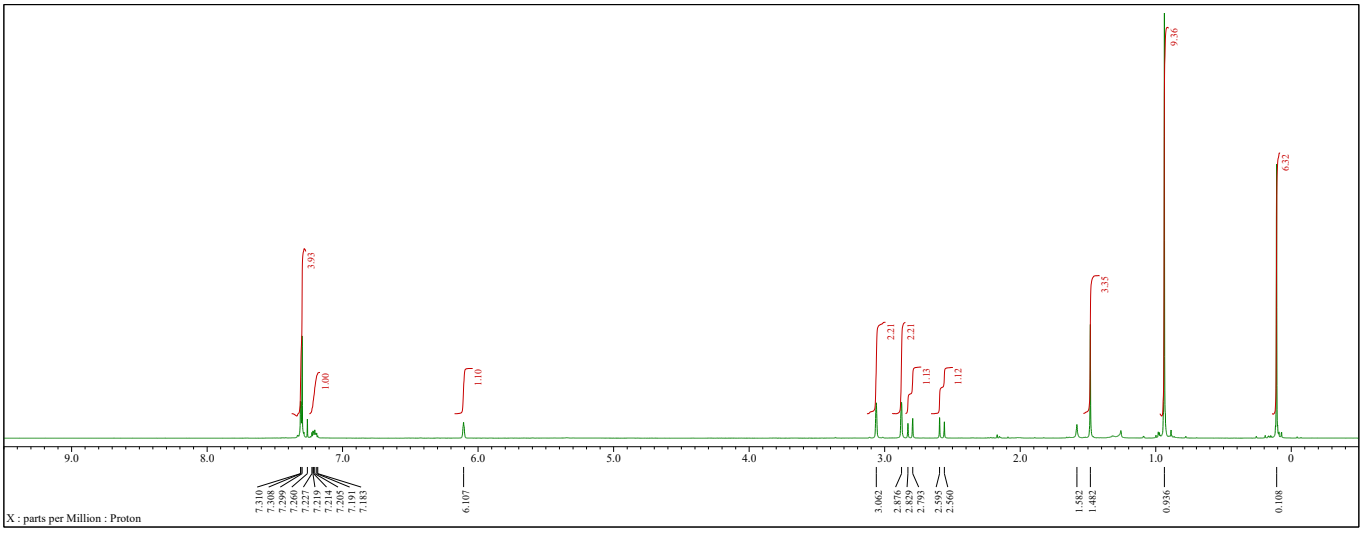

abundance
6.47
1.00
1.98
3.96
1.09
1.00
2.80
5.05
23.46
1.10
Y : parts per Million : Carbon13
X : parts per Million : Proton
abundance


abundance
1.00
1.98
1.96
1.09
1.00
2.80
21.46
Y : parts per Million : Carbon13
X : parts per Million : Proton
abundance

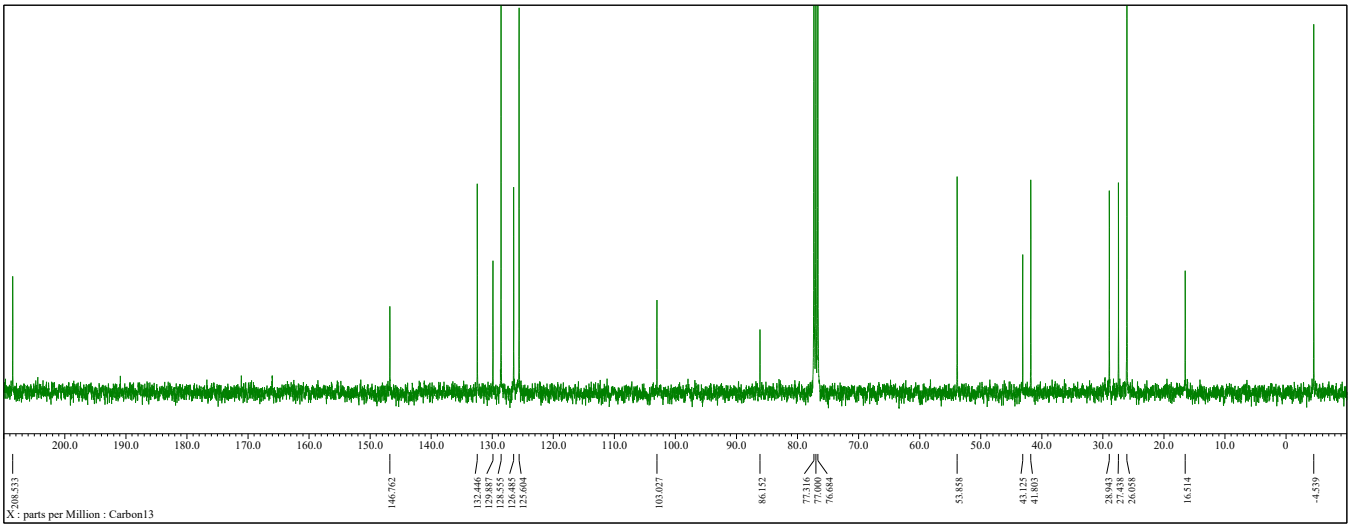

abundance
1.98
1.96
1.09
1.00
2.80
Y : parts per Million : Carbon13
X : parts per Million : Proton
abundance

3b

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

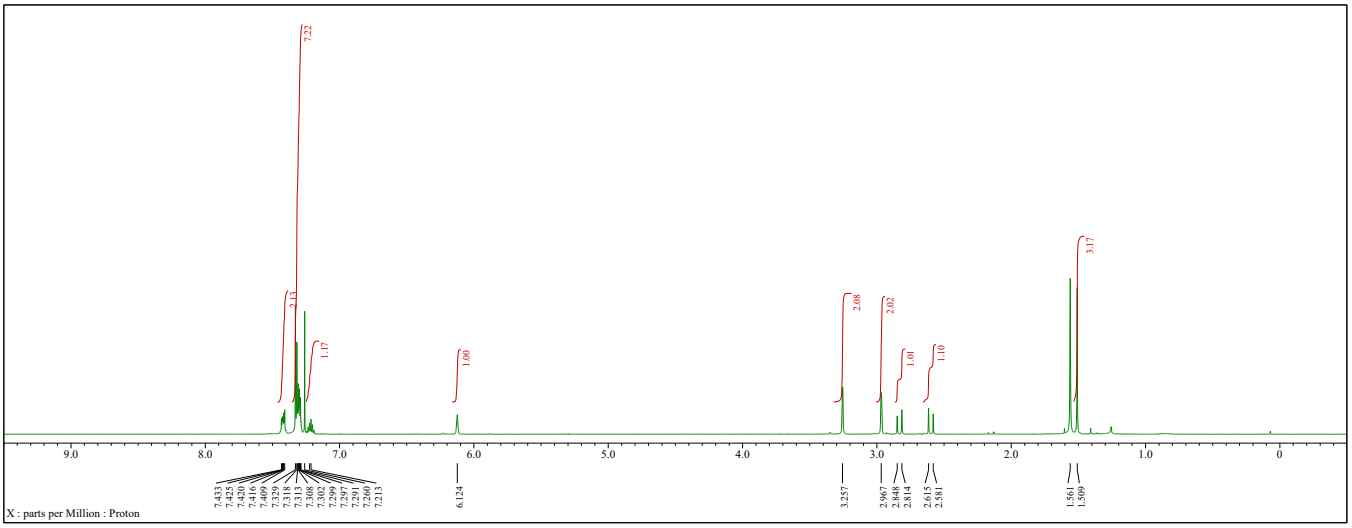


^{13}C NMR (100 MHz, $CDCl_3$)

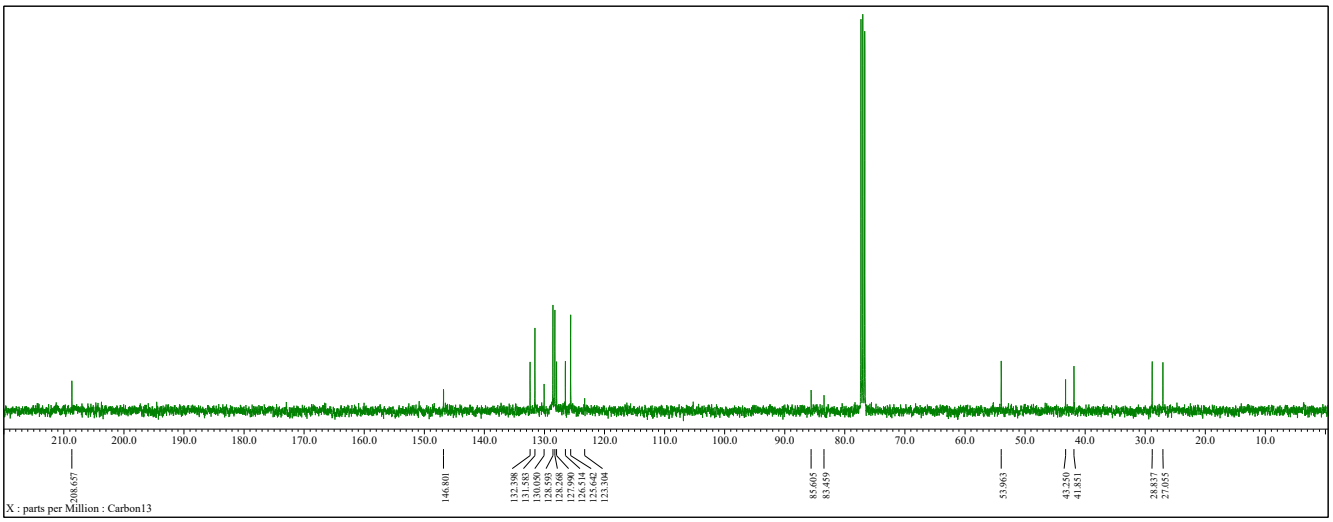


3d

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

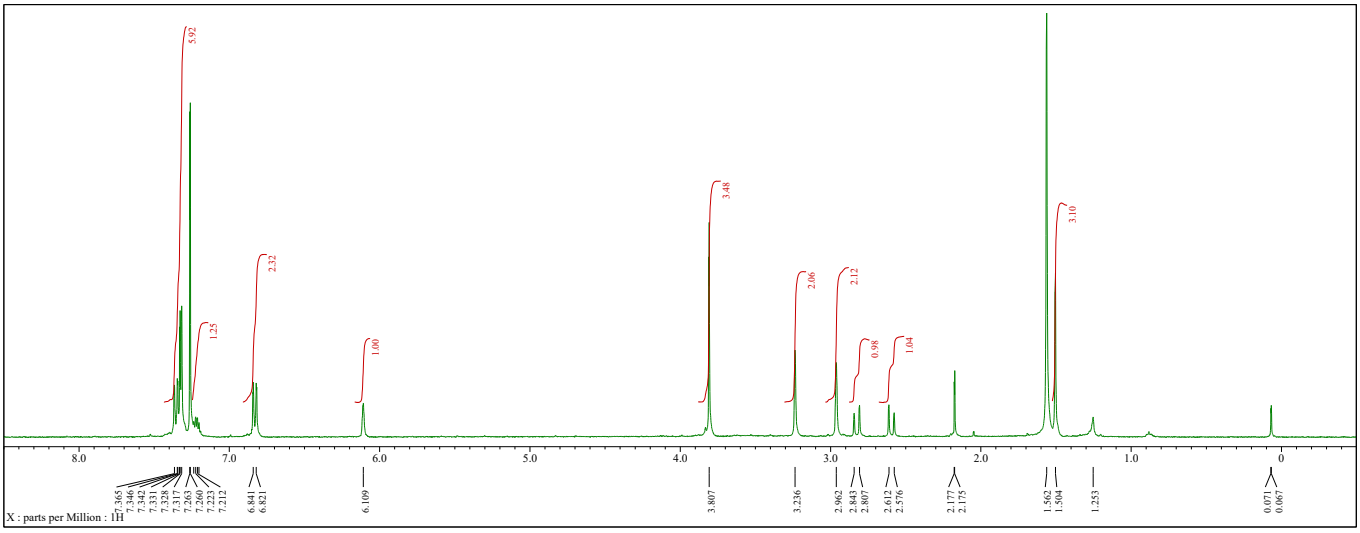


^{13}C NMR (100 MHz, $CDCl_3$)

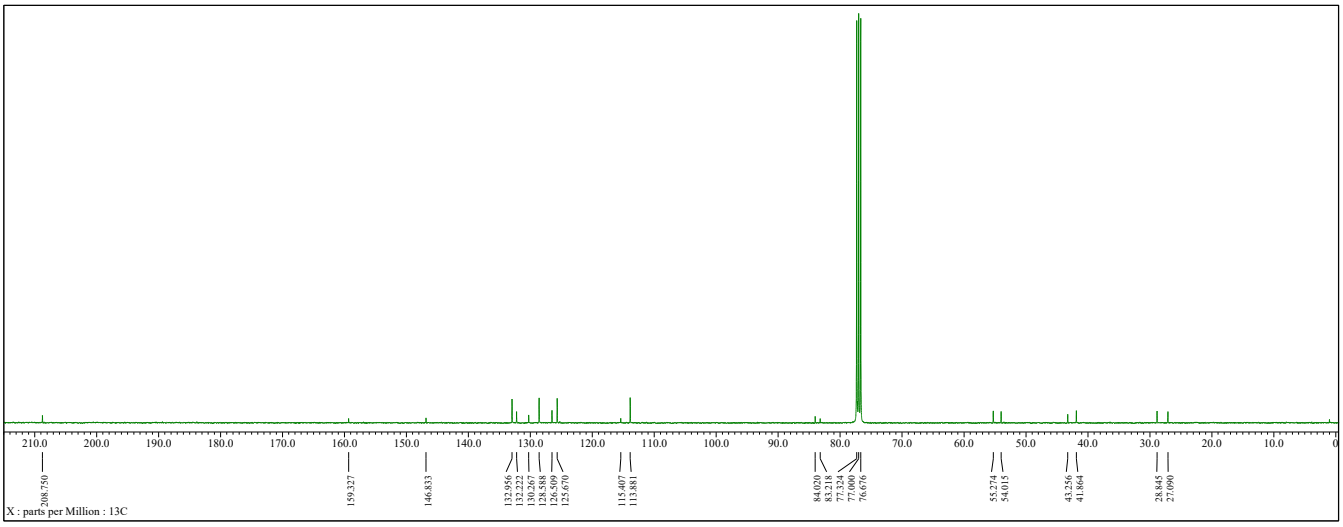


3e

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

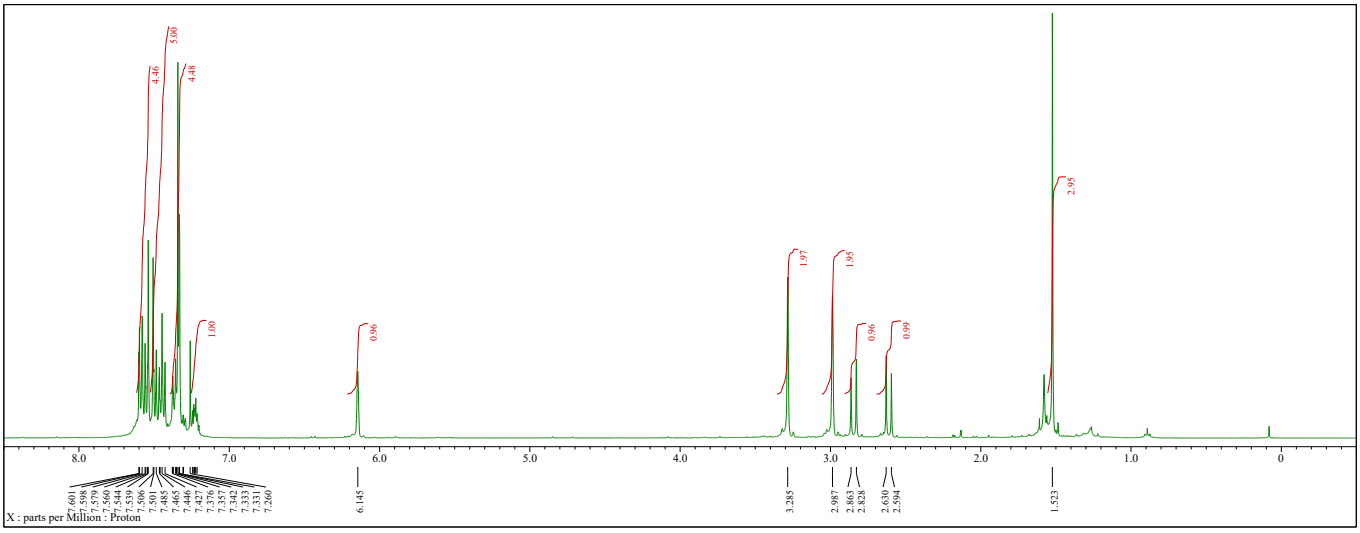


^{13}C NMR (100 MHz, $CDCl_3$)

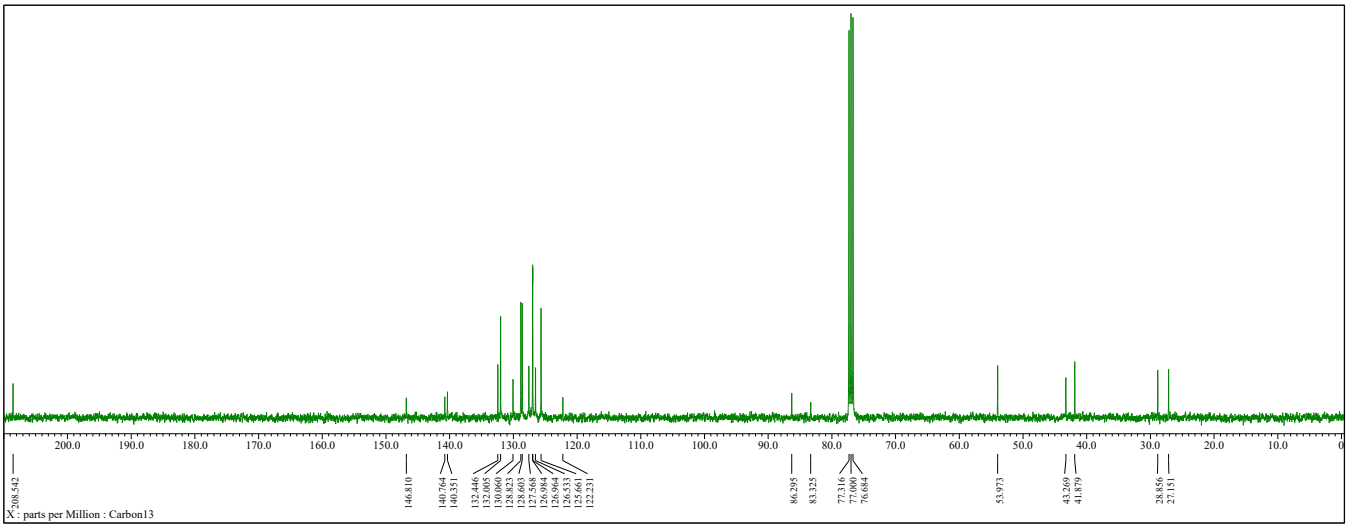


3f

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

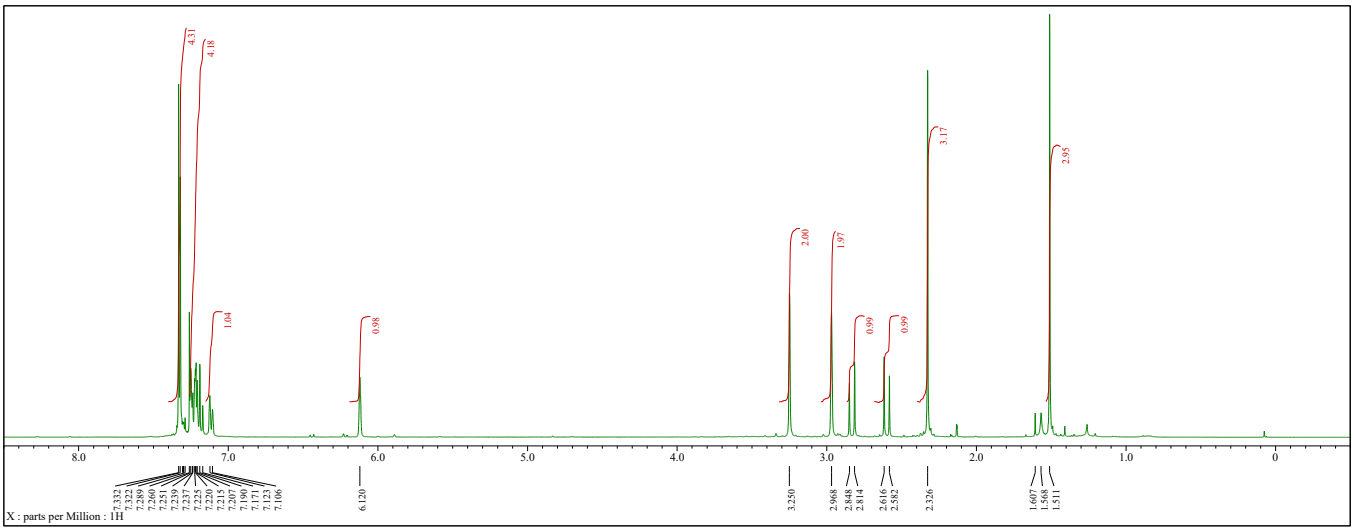


^{13}C NMR (100 MHz, $CDCl_3$)

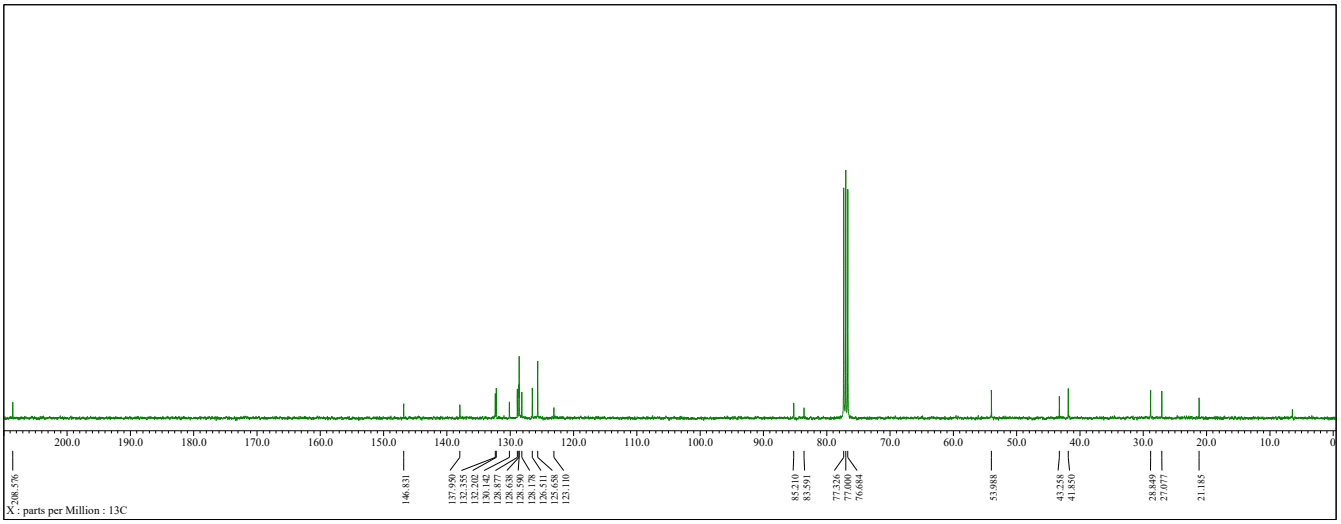


3h

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

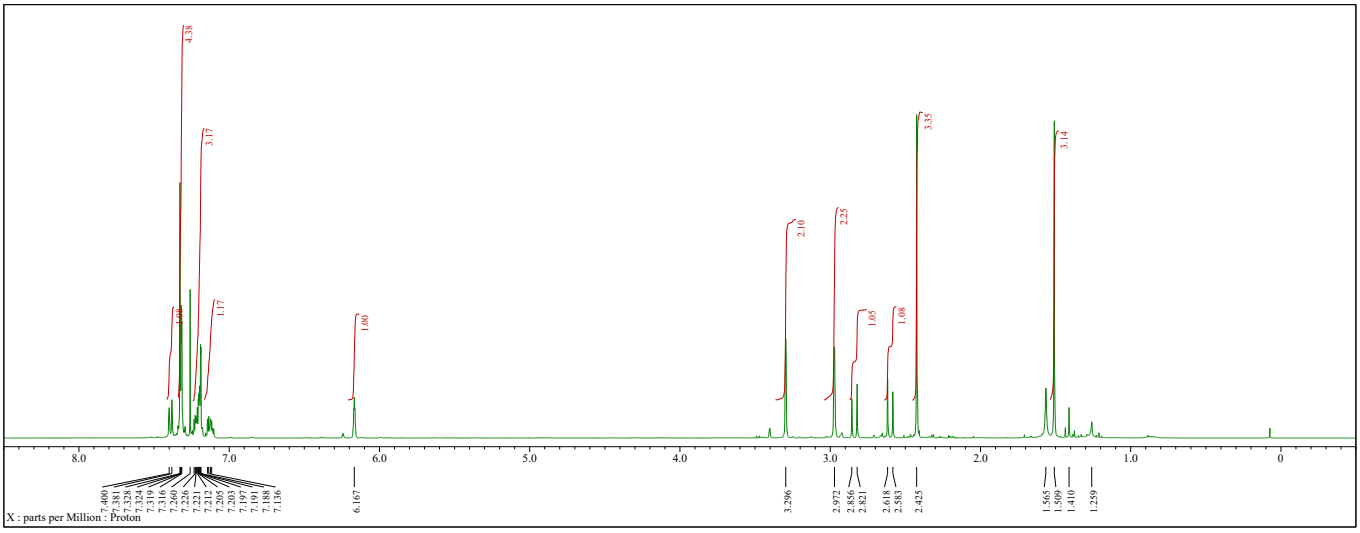


^{13}C NMR (100 MHz, $CDCl_3$)

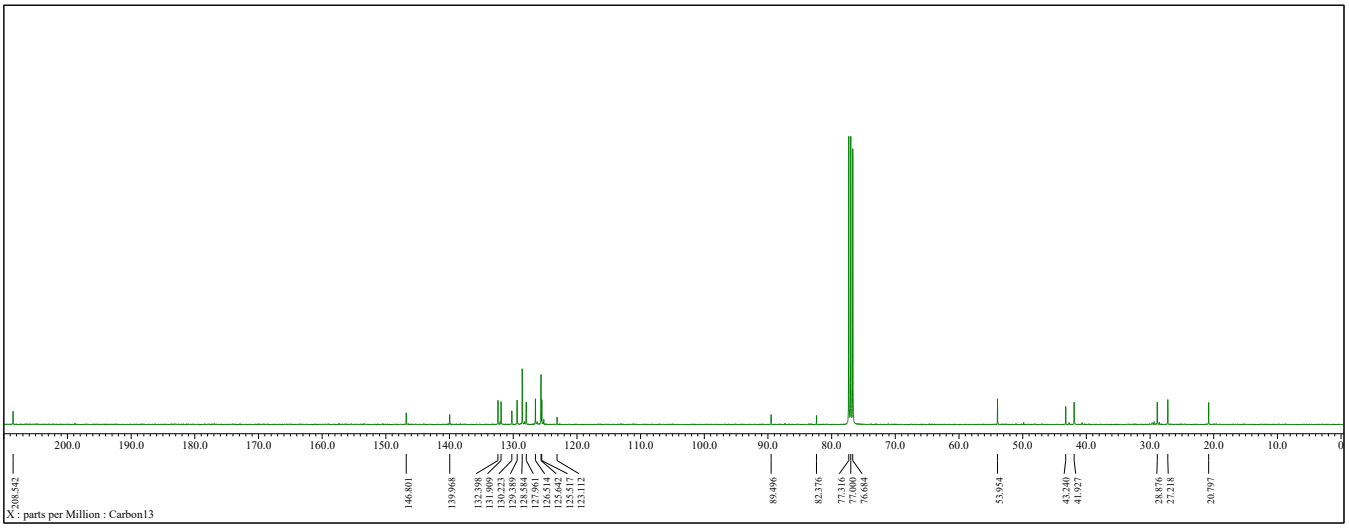


3i

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

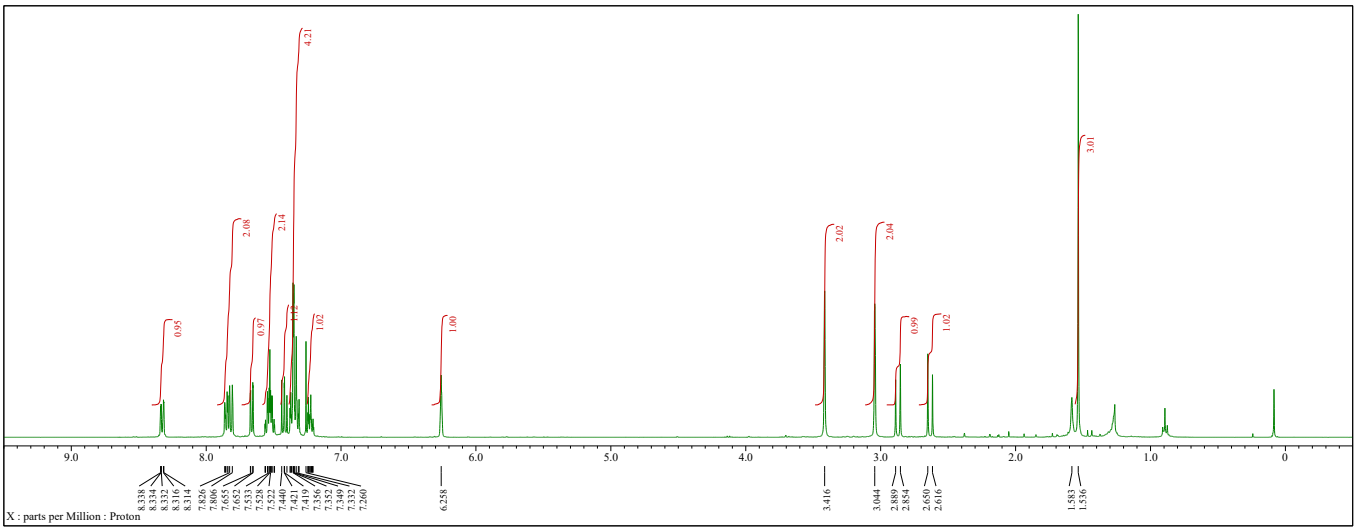


^{13}C NMR (100 MHz, $CDCl_3$)

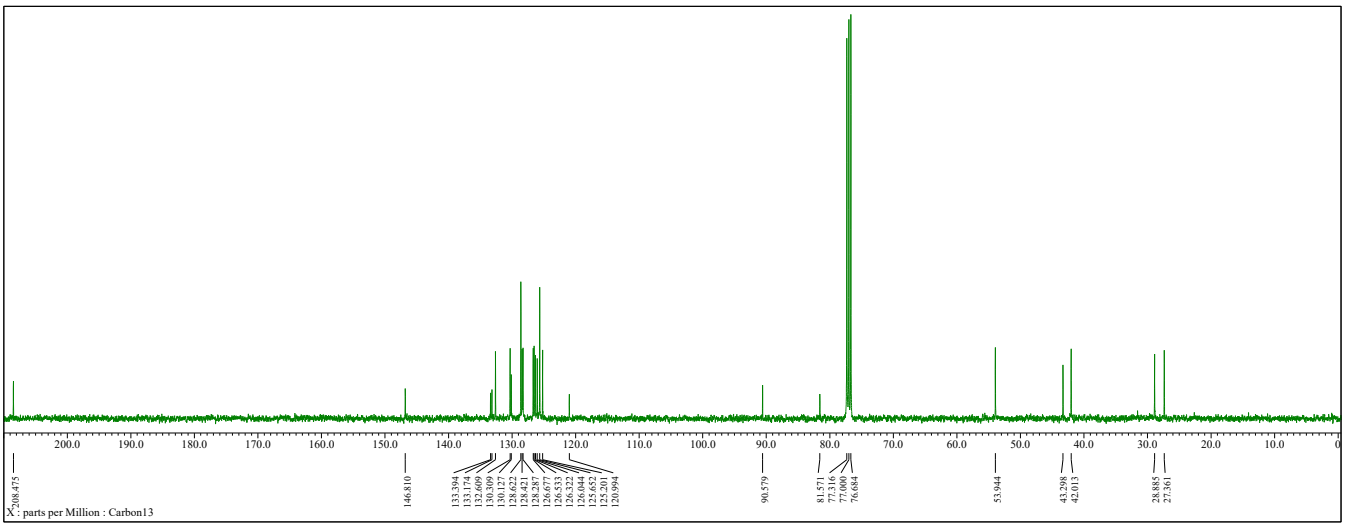


3j

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

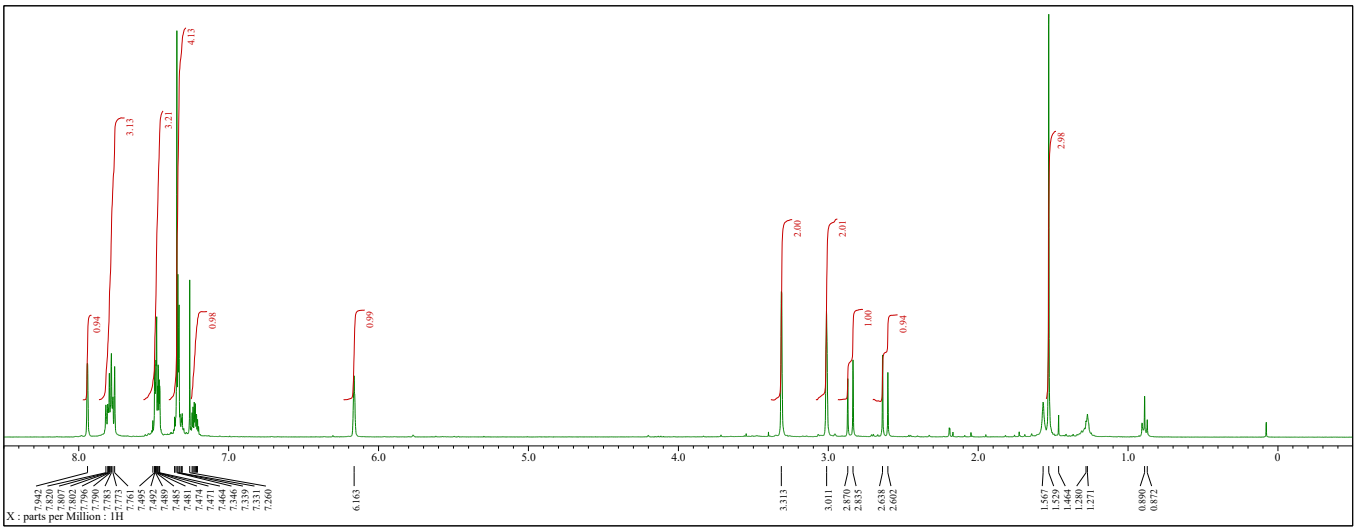


^{13}C NMR (100 MHz, $CDCl_3$)

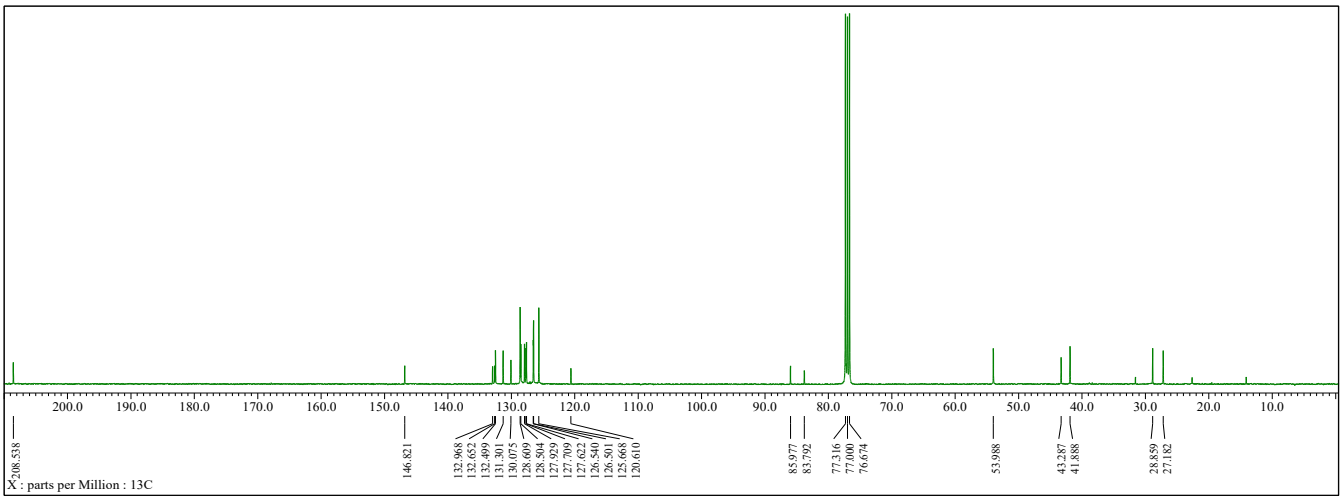


3k

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

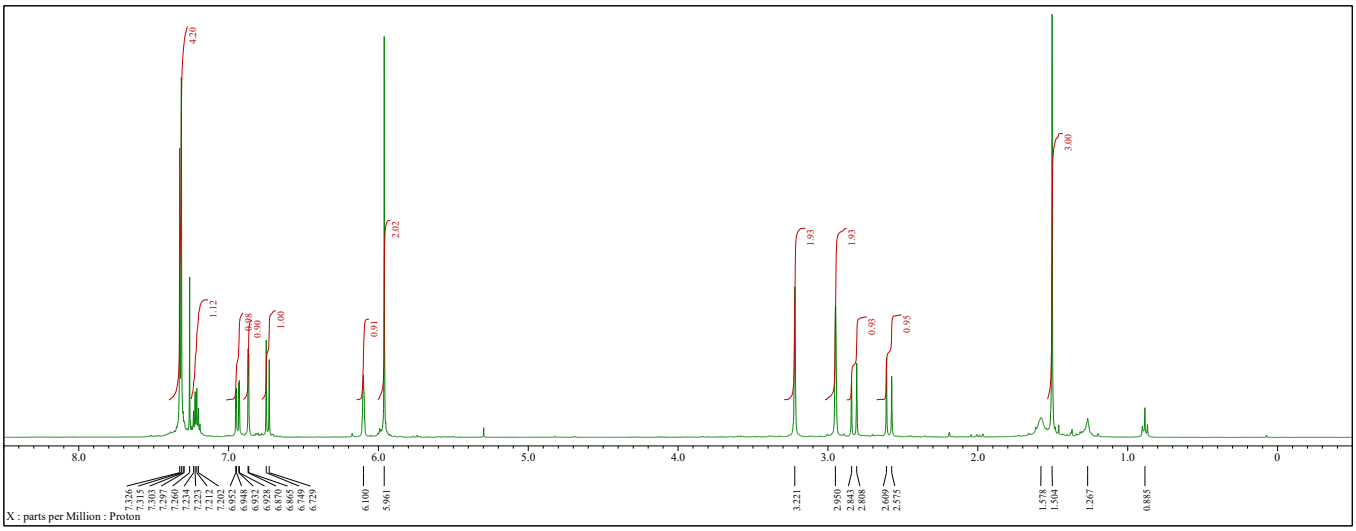


^{13}C NMR (100 MHz, $CDCl_3$)

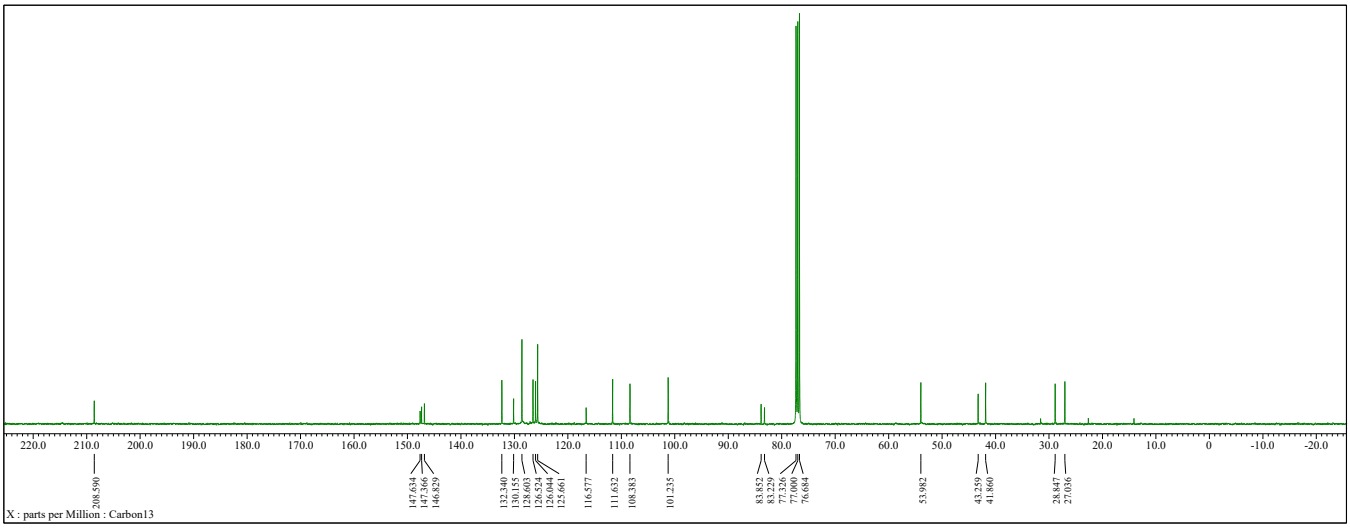


3l

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

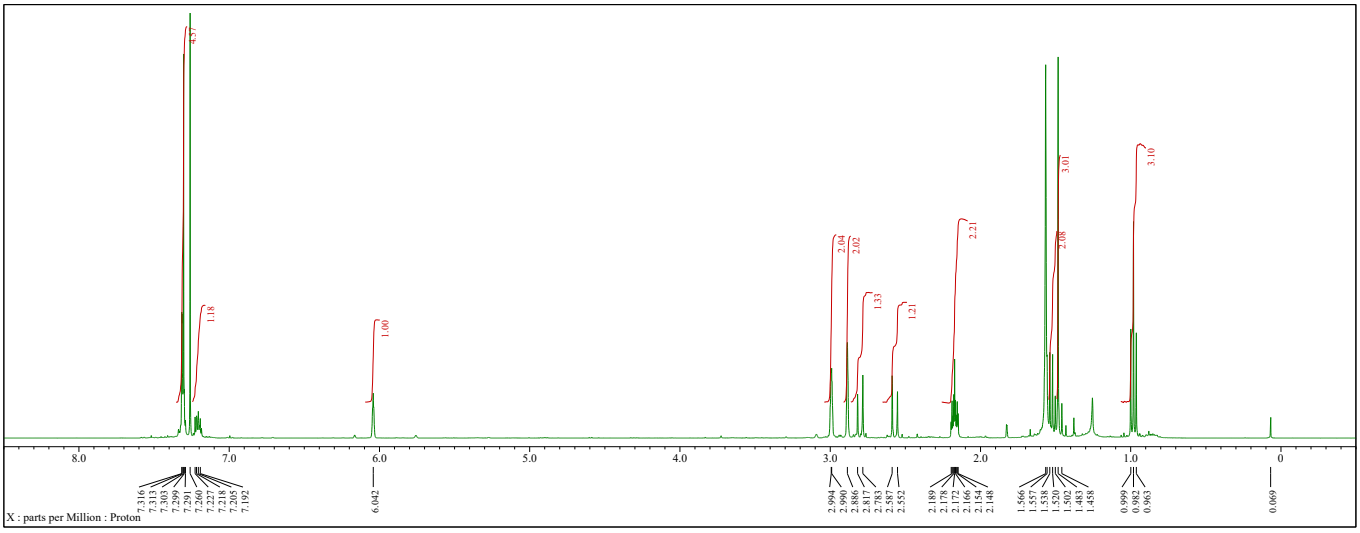


^{13}C NMR (100 MHz, $CDCl_3$)

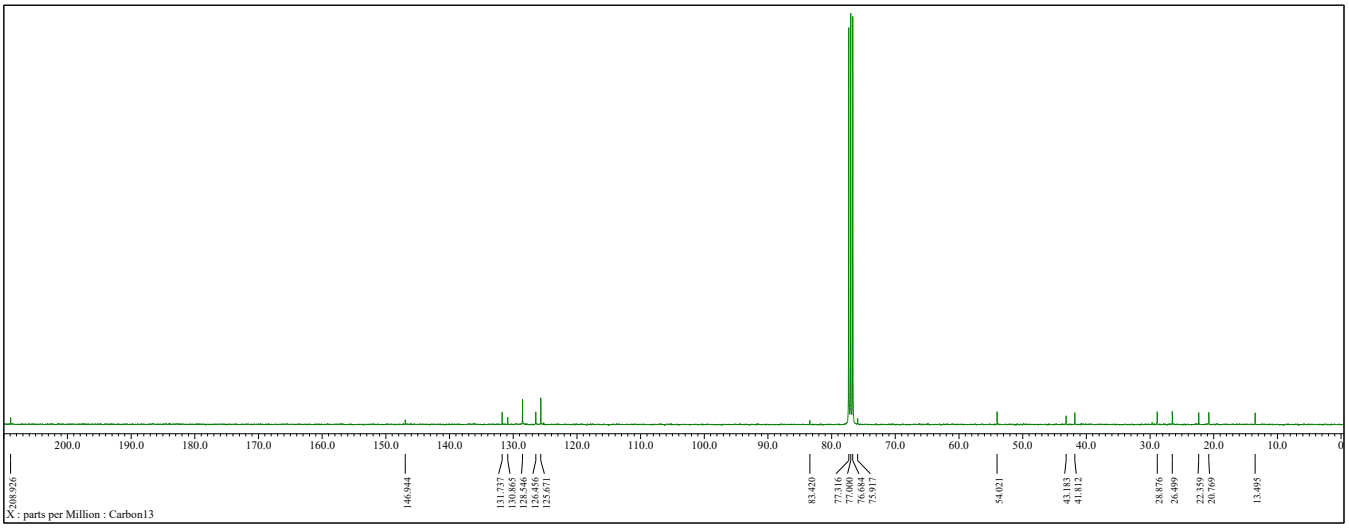


3m

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

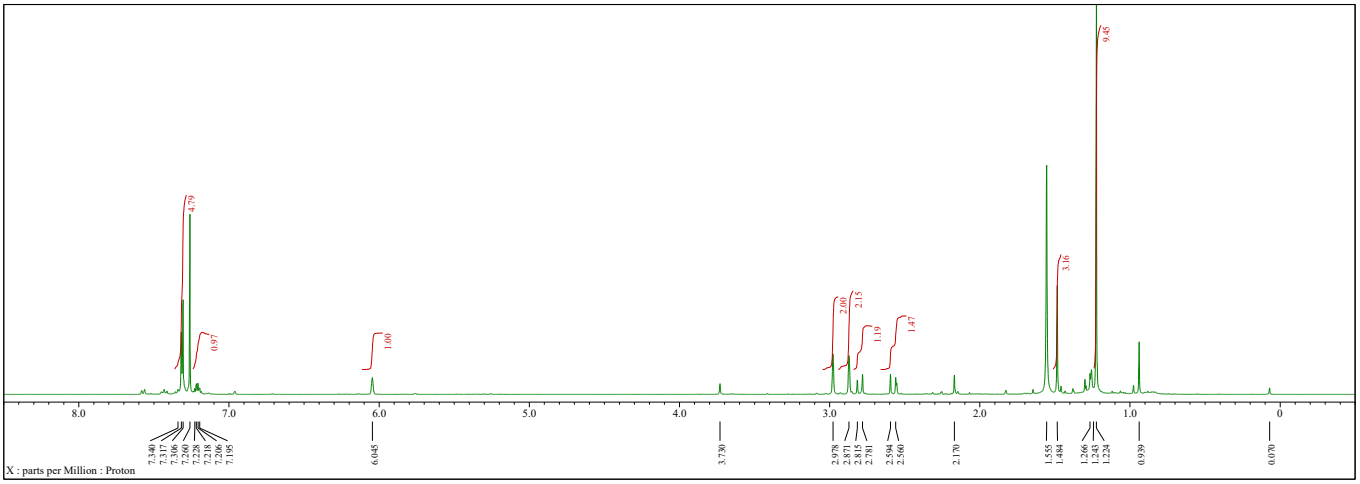


^{13}C NMR (100 MHz, $CDCl_3$)

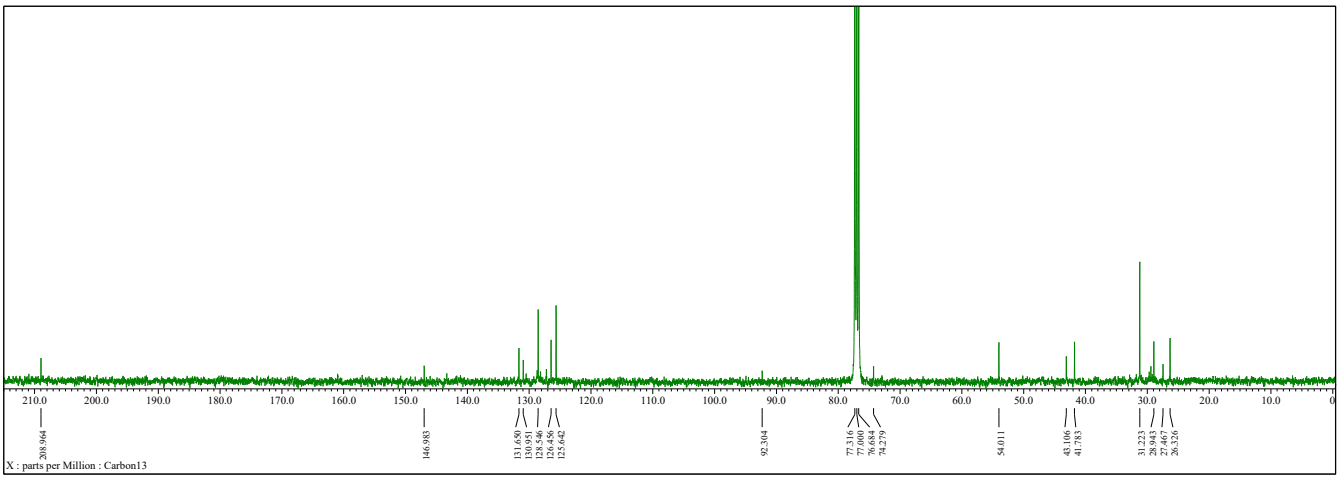


3n

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

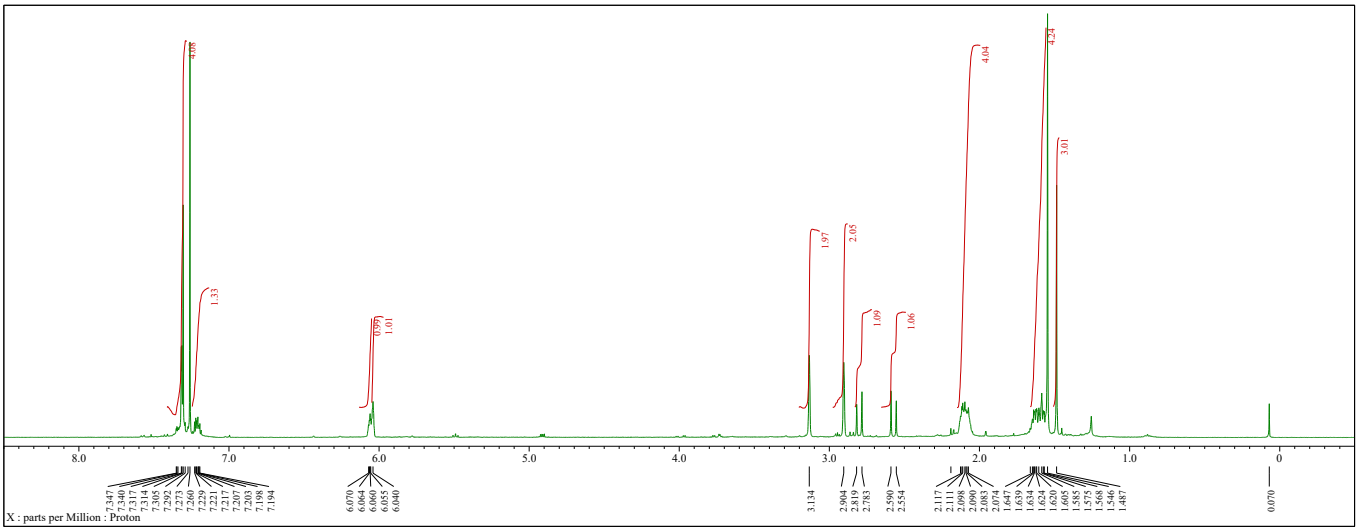


^{13}C NMR (100 MHz, $CDCl_3$)

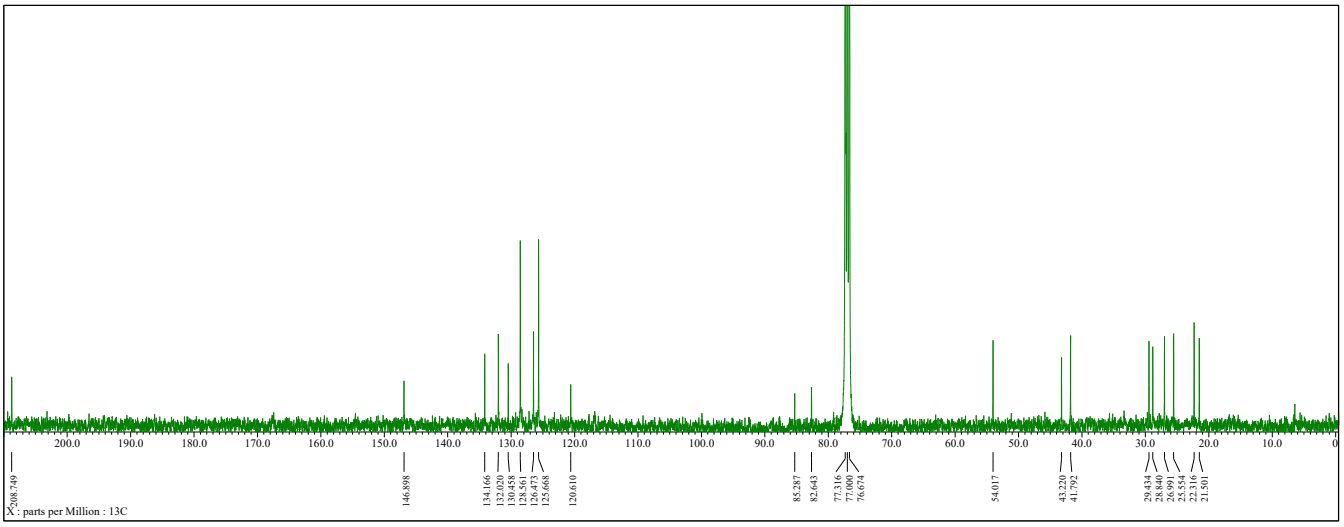


3o

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

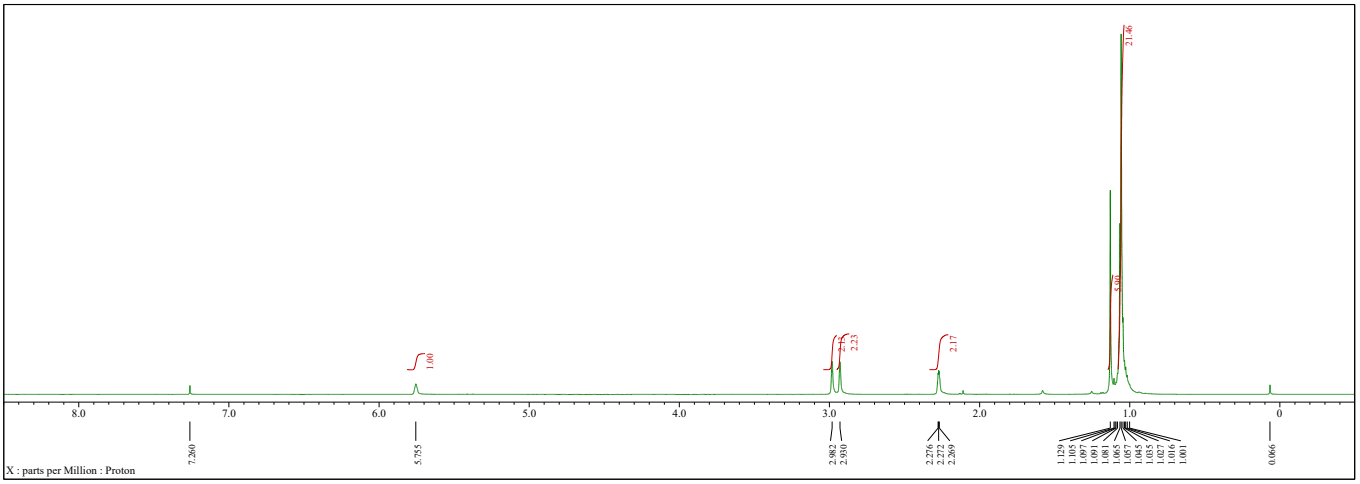


^{13}C NMR (100 MHz, $CDCl_3$)

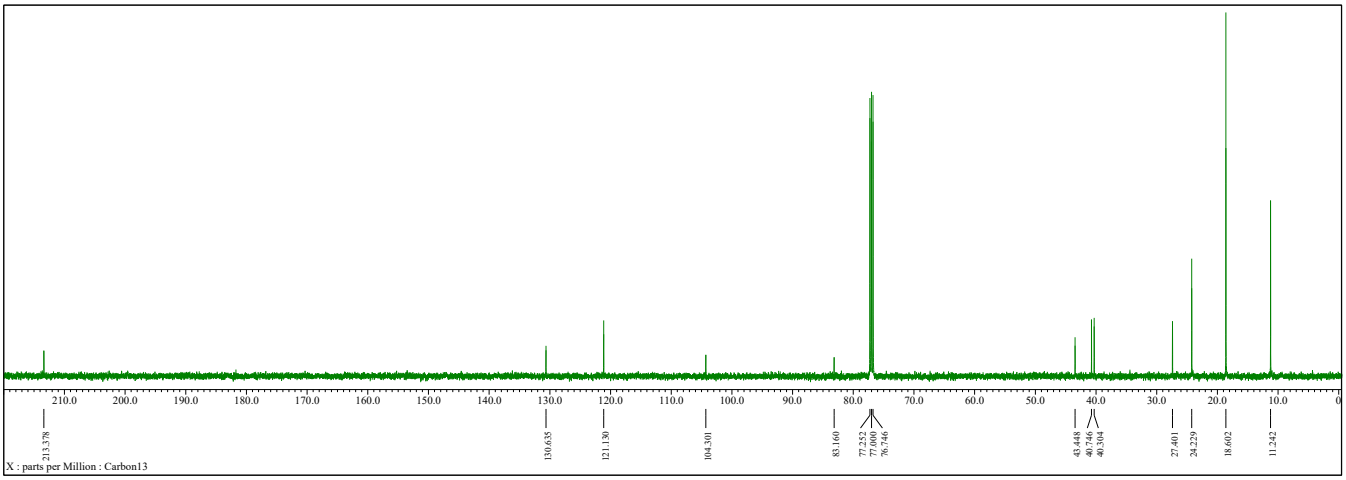


3p

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

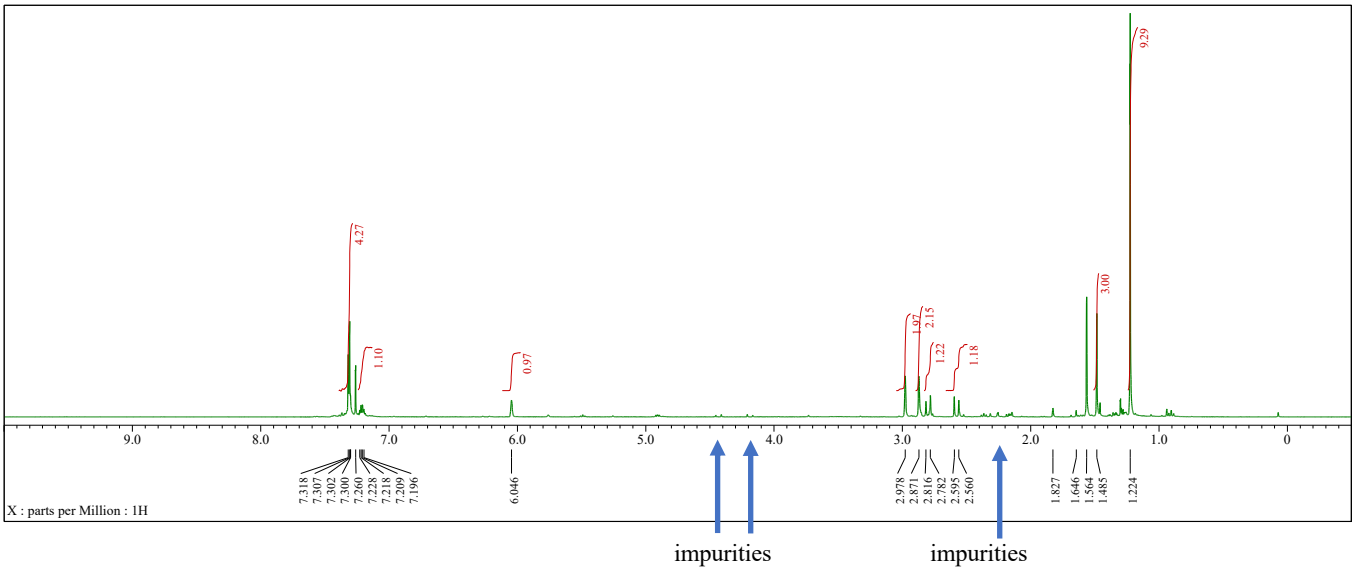


^{13}C NMR (100 MHz, $CDCl_3$)

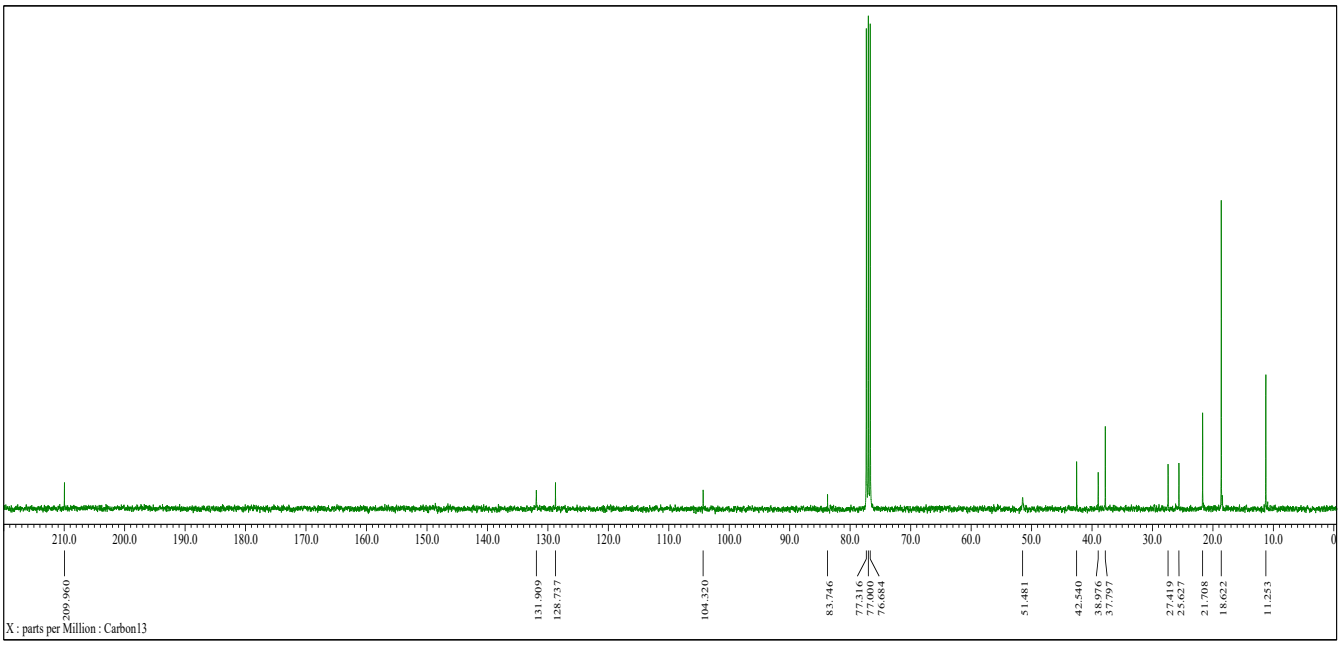


3q

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

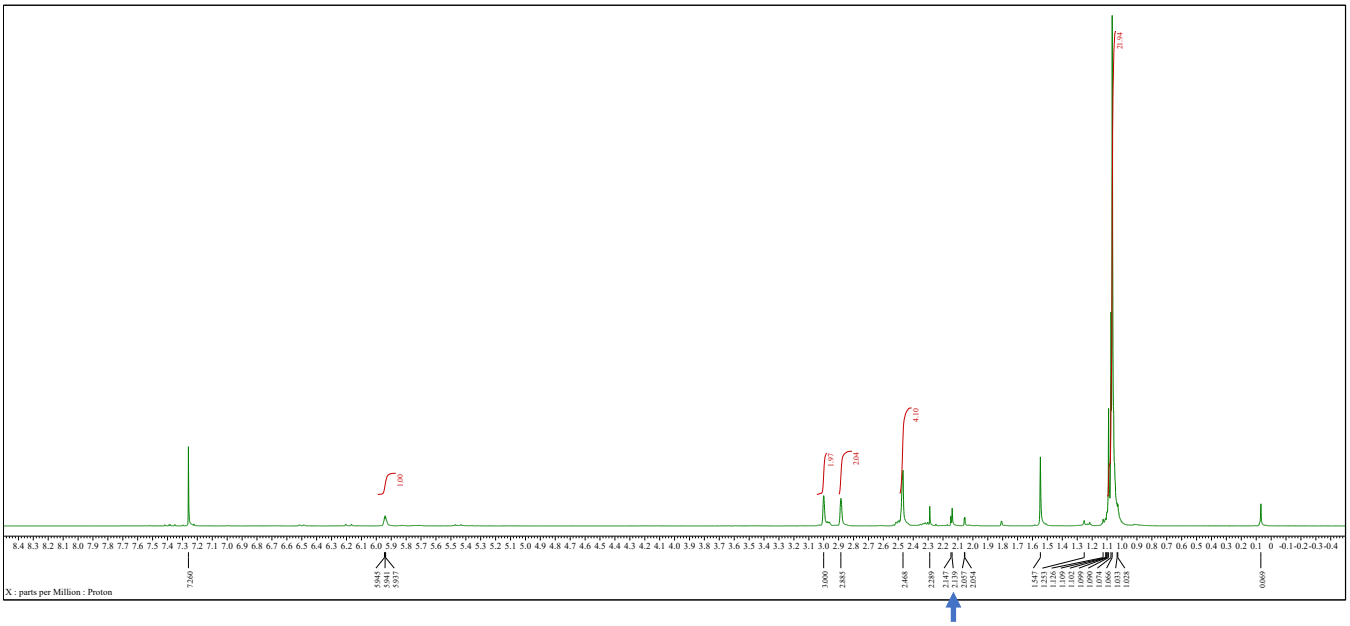


^{13}C NMR (100 MHz, $CDCl_3$)



3r

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



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