Electronic Supplementary Information

Chiral Brønsted Acid-Catalyzed Intramolecular S_N2' Reaction for Enantioselective Construction of Quaternary Stereogenic Center

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Contents:

1. General Information

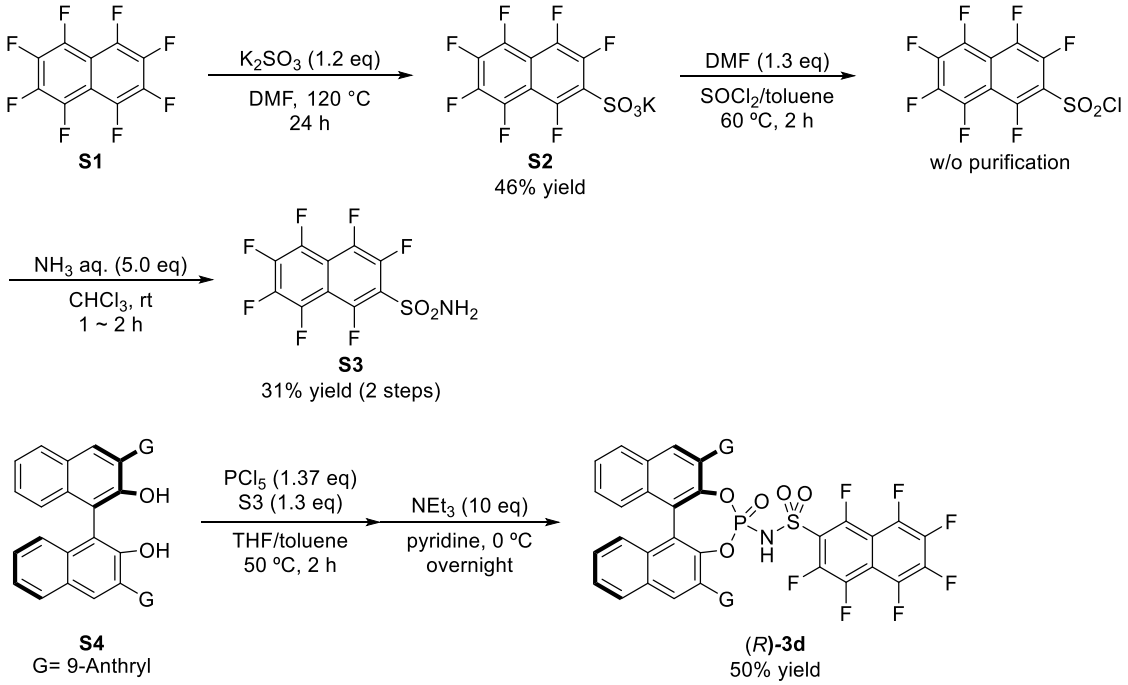
1-1. Instruments and materials

^{1}H NMR spectra were recorded on a JEOL ECA-600 (600 MHz) or JEOL ECA-700 (700 MHz) spectrometer at ambient temperature. ^{2}H NMR spectra were recorded on a JEOL ECA-700 (700 MHz) spectrometer at ambient temperature. Chemical shifts are reported in ppm, with solvent resonance employed as internal standard; $CDCl_3$ (7.26 ppm), C_6D_6 (7.16 ppm), and acetone-d_6 (2.06 ppm). ^{13}C NMR spectra were recorded on a JEOL ECA-600 (151 Hz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard; $CDCl_3$ (77.0 ppm), C_6D_6 (128.0 ppm), and acetone-d_6 (206.7 ppm, 29.9 ppm). ^{19}F NMR spectra were recorded on a JEOL ECA-600 (565 MHz). Chemical shifts are reported in ppm from the $C_6H_5CF_3$ (-67.2 ppm) resonance as the external standard. ^{31}P NMR spectra were recorded on a JEOL ECA600 (243 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the PPh_3 (-6 ppm) resonance as the external standard. Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. Optical rotations were measured on a Jasco P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T\,^{\circ}C}_{D}$ (c = g/100 mL, solvent, % ee). Chiral stationary phase HPLC analysis was performed on a Jasco LC-2000 Plus Series system. High-resolution mass spectra analysis was performed on a Bruker Daltonics solariX 9.4T spectrometer at the Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University.

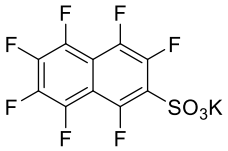
1-2. Material and methods

CH_2Cl_2, toluene, Et_2O and THF were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were dried over activated MS4A and used under nitrogen atmosphere. Reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out in flame-dried glassware with magnetic stirring under nitrogen atmosphere. Analytical thin layer chromatography (TLC) was performed on Merck pre-coated TLC plates (silica gel 60 GF 254, 0.25 mm). Purification of reaction products was carried out by flash column chromatography using silica gel 60 (spherical, neutral, 100-210 μm; KANTO Chemical Co., Inc.), silica gel 60 (230-400 mesh; E. Merk), and DIOL silica gel (45-75 μm; Fuji Silysia Chemical Ltd.). NH silica gel (45-75 μm; Fuji Silysia Chemical Ltd.).

2. Preparation of Catalysts



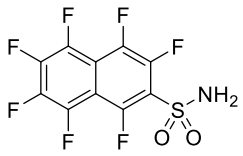
Potassium 1,3,4,5,6,7,8-heptafluoronaphthalene-2-sulfonate (S2): In a flame dried flask with reflux condenser under N_2, perfluoronaphthalene (**S1**) (2.7 g, 10 mmol, 1.0 equiv) and K_2SO_3 (1.9g, 12 mmol, 1.2 equiv) was dissolved in DMF (50 mL, 0.2 M) and H_2O (5 mL, 2.0 M). The mixture was stirred at 120 °C for 24 h, then the reaction mixture was concentrated. The residual mixture was dissolved in H_2O (40 mL) and Acetone (20 mL) after cooled to room temperature. Then acetone in the residual mixture was removed under reduced pressure. To the residual suspension was added CH_2Cl_2 (20 mL) and filtered to give the crude of **S2** (1.7g, 46% yield) as a brown solid. The crude was used without further purification.



S2

^{13}C NMR could not be measured due to low solubility in any solvent.^{19}F NMR (565 MHz, Acetone-d_6): δ -115.4 (dd, *J* = 77.5, 16.7 Hz, 1F), -134.1 (d, *J* = 16.7 Hz, 1F), -145.69 (dt, *J* = 76.3, 16.7 Hz, 1F), -149.3 (dt, *J* = 57.2, 16.7 Hz, 1F), -152.3 (dt, *J* = 57.2, 16.7 Hz, 1F), -156.7 (t, *J* = 16.7 Hz, 1F), -159.5 (m, 1F); IR(neat, cm^{-1}): 3282, 3056, 2924, 1644, 1603, 1490, 1418, 1316, 1228, 1184, 1102, 959, 912; HRMS(ESI+): Calcd for $C_{10}F_7K_2O_3S$, ($[M + K]^+$) 410.8731, Found, 410.8725.

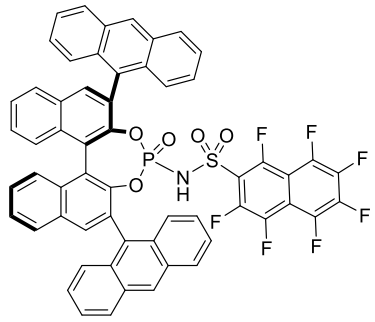
1,3,4,5,6,7,8-heptafluoronaphthalene-2-sulfonamide (S3): To a suspension of **S2** (856 mg, 2.3 mmol, 1.0 equiv) in $SOCl_2$ (2.3 mL, 1.0 M) and toluene (2.3 mL, 1.0 M) was added DMF (230 µl, 3.0 mmol, 1.3 equiv) at 0°C. After stirring at 60 °C for 2 h, the mixture was cooled to 0°C and carefully poured the ice cold water. Then the mixture was extracted with Et_2O to give the crude of sulfonylchloride as a brown solid. The crude of sulfonylchloride was dissolved in CH_2Cl_2 (9.2 mL, 0.25M) and added 30% NH_3 aq (767 µL, 11.5 mmol 5 equiv). After stirring at room temperature for 30 min, the mixture was directly purified by column chromatography on silica gel (Hexane/EtOAc = 7/1) to provide **S3** (239 mg, 0.72 mmol) in 31% yield (2 steps) as a colorless solid.



S3

^{1}H NMR (600 MHz, Acetone-d_6): δ 7.56 (brs, 2H); ^{19}F NMR (565 MHz, Acetone-d_6): δ -114.8 (dd, *J* = 76.3, 16.7 Hz, 1F), 138.2 (m, 1F), -144.1 (dm, *J* = 73.9 Hz, 1F), -147.6 (dm, *J* = 59.6 Hz, 1F), -149.1 (dm, *J* = 59.6 Hz, 1F), -152, 3 (m, 1F), -156.4 (m, 1F); ^{13}C NMR (151 MHz, Acetone-d_6): δ 150.8 (dm, *J* = 266 Hz, 1C), 144.6 (ddm, *J* = 262, 13.7 Hz, 1C), 144.8 (dm, *J* = 252 Hz, 1C), 142.0 (dm, *J* = 250 Hz, 3C), 140.3 (dm, *J* = 254 Hz, 1C), 122.5 (m, 1C), 113.7 (m, 1C), 109.1 (m, 1C); IR(neat, cm^{-1}): 3407, 3291, 1653, 1605, 1532, 1497, 1407, 1365, 1265, 1175, 1115, 963, 904; HRMS(ESI+): Calcd for $C_{10}H_2F_7NNaO_2S$, ([M + Na]$^+$) 335.9592, Found, 335.9587.

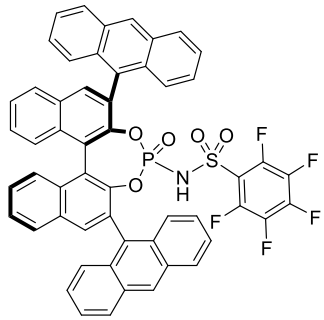
***N*-((*2r*,11b*R*)-2,6-di(anthracen-9-yl)-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-1,3,4,5,6,7,8-heptafluoronaphthalene-2-sulfonamide ((*R*)-3d):** In a flame dried flask under N_2, PCl_5 (83 mg, 0.4 mmol, 1.37 equiv) and **S3** (127 mg, 0.38 mmol, 1.3 equiv) were dissolved in toluene (1.9 mL, 0.25 M) and THF (76 μL, 5.0 M). The mixture was stirred at 50 °C for 2 h and concentrated. To the resulting mixture were added pyridine (2.9 mL), **S4** (185 mg, 0.29 mmol, 1.0 equiv) and NEt_3 (407 μL, 0.29 mmol, 10 equiv) at 0°C. After the reaction mixture was stirred for 2 h, quenched with 1 N HCl aq and extracted with CH_2Cl_2. The combined CH_2Cl_2 extracts were washed with brine and concentrated. Then the residual crude was purified by flash column chromatography on silica gel (Hexane/Acetone = 5/1 to 2/1), acidified with 6 N HCl (2 mL) in CH_2Cl_2 (2 mL), followed by drying under reduced pressure afforded compound (*R*)-**3d** (180 mg, 61%) as a yellow powder.



(*R*)-**3d**

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (s, 1H), 8.24-7.95 (m, 8H), 7.75-7.30 (m, 17H), 7.22-7.09 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 150.1 (dm, *J* = 279 Hz, 1C), 149.2, 146.0, 145.9, 144.5, 144.4-138.1 (m, 6C), 134.44, 134.40, 132.6, 132.4, 132.0, 131.8, 131.6, 131.3, 131.0, 130.9, 130.8, 130.5, 130.4, 129.9, 129.8, 129.7, 129.6, 129.4, 128.8, 128.7, 128.5, 128.4, 127.74, 127.71, 127.52, 127.46, 127.42, 127.36, 126.9, 126.8, 126.7, 126.5, 126.0, 125.8, 125.41, 125.39, 125.2, 124.98, 124.95, 124.8, 124.4, 122.4, 122.0, 117.5 (m), 113.0 (m), 106.7 (m); ^{19}F NMR (565 MHz, $CDCl_3$): δ -110.7 (dd, *J* = 77.5, 16.7 Hz, 1F), -136.7 (dm, *J* = 11.9 Hz, 1F), -140.0 (dm, *J* = 76.3 Hz, 1F), -144.7 (dt, *J* = 57.2, 16.7 Hz, 1F), -145.8 (dt, *J* = 59.6, 16.7 Hz, 1F), -148.7 (m, 1F), -153.8 (m, 1F); ^{31}P NMR (243 MHz, $CDCl_3$): δ -5.63; IR(neat, cm^{-1}): 3282, 3056, 2924, 1644, 1603, 1490, 1418, 1316, 1228, 1184, 1102, 959, 912; HRMS(ESI-): Calcd for $C_{58}H_{28}F_7NO_5PS$, [M - H]$^-$, 1014.1314; found, 1014.1317.

***N*-((*2r*,11b*R*)-2,6-di(anthracen-9-yl)-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-2,3,4,5,6-pentafluorobenzenesulfonamide ((*R*)-3c):** (*R*)-**3c** was synthesized according to the same procedure of (*R*)-**3d** :^{1}H NMR (600 MHz, $CDCl_3$): δ 8.61 (s, 1H), 8.47 (s, 1H), 8.22 (s, 1H), 8.11-8.02 (m, 6H), 7.92 (d, *J* = 8.6 Hz, 1H), 7.74-7.30 (m, 17H), 7.19 (t, *J* = 7.6 Hz, 1H);^{13}C NMR (151 MHz, $CDCl_3$): δ 145.93, 145.86, 144.4, 144.3, 143.7 (dm, *J* = 262 Hz, 4C), 136.7 (dm, *J* = 254 Hz, 1C), 134.5, 134.3, 132.6, 132.4, 132.1, 131.8, 131.6, 131.24, 131.24, 130.9, 130.8, 130.7, 130.6, 130.5, 130.1, 129.8, 129.5, 129.4, 128.8, 128.7, 128.6, 128.5, 127.7, 127.5, 127.42, 127.38, 127.11, 127.09, 126.84, 126.79, 126.5, 126.0, 125.9, 125.4, 125.3, 125.2, 125.1, 125.0, 124.8, 124.5, 122.4, 121.9, 115.2 (m, 1C), two carbons were not found probably due to overlapping.; ^{19}F NMR (565 MHz, $CDCl_3$): δ -136.7 (d, *J* = 19.1 Hz, 2F), -143.9 (m, 1F), -158.9 (t, *J* = 19.1 Hz, 1F); ^{31}P NMR (243 MHz, $CDCl_3$): δ -5.92; IR(neat, cm^{-1}): 3056, 2360, 1723, 1644, 1499, 1403, 1300, 1227, 1180, 1100, 988, 889, 751; HRMS(ESI-): Calcd for $C_{54}H_{28}F_5NO_5PS$, $[M - H]^-$, 928.1346; found, 928.1350.

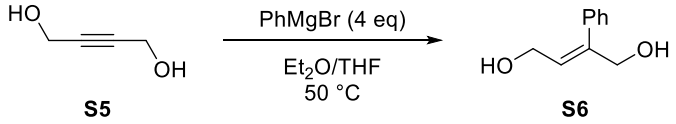


(*R*)-**3c**

3. Preparation of Starting Materials

3-1. General procedure for the preparation of 2-substituted but-2-ene-1,4-diols (S6)

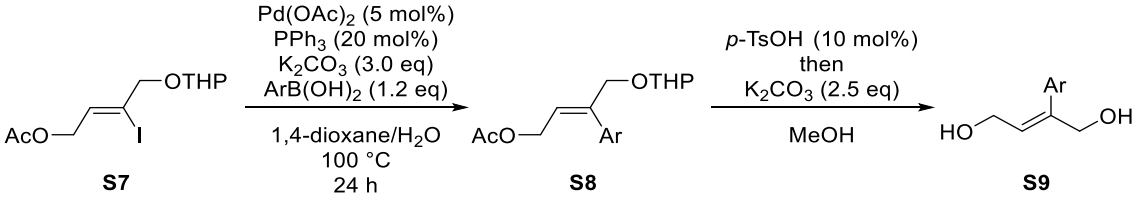
Method A[1]: for the preparation of **1a~1h**, **1j**, **1l~1o**



S5 **S6**

To a solution of PhMgBr (20.0 mL, 1.0 M solution in Et_2O, 20.0 mmol) in Et_2O (20 mL) solution was added but-2-yne-1,4-diol **S5** (1.05 g, 5.0 mmol) in THF (10 mL) dropwise. The reaction mixture was stirred at 50 °C for overnight. Then the reaction mixture was cooled to 0 °C and quenched with H_2O and 3 M HCl aq. Then the resulting mixture was extracted with EtOAc and concentrated. The residual crude was purified by flash column chromatography on silica gel (Hexane/EtOAc = 4/1 to EtOAc only) to provide (*2E*)-2-phenylbut-2-ene-1,4-diol **S6** (608 mg, 3.7 mmol, 74% yield) as a yellow oil.

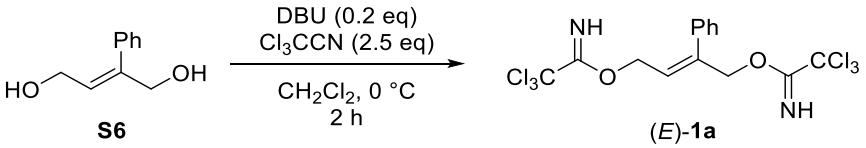
Method B[2]: for the preparation of **1i**, **1k**



S7 **S8** **S9**

S9 was synthesized according to the reported procedure.[2]

3-2. General procedure for the synthesis of bis-imidates: preparation of (*E*)-2-phenylbut-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1a)

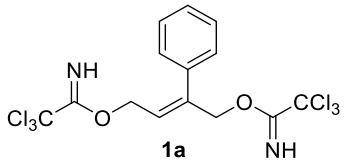


S6 (*E*)-**1a**

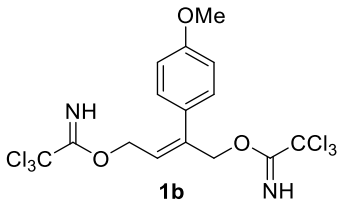
To a solution of **S6** (164 mg, 1.0 mmol) and trichloroacetonitrile (250 μL, 2.5 mmol, 2.5 eq) in CH_2Cl_2 (5 mL) was added DBU (30 μL, 0.2 mmol, 20 mol%) at 0 °C. The resulting solution was stirred for 2 h. Then the residual crude was concentrated and purified by flash column chromatography (Hexane/EtOAc = 20/1) to give the product **1a** (408 mg, 0.9 mmol, 90% yield) as a colorless oil.

3-3. Spectral data of starting materials

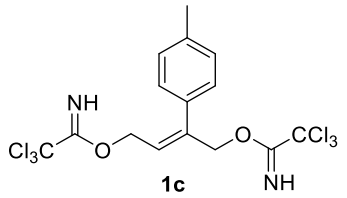
(*E*)-2-phenylbut-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1a): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 8.27 (brs, 1H), 7.38-7.30 (m, 5H), 6.19 (t, *J* = 6.9 Hz, 1H), 5.07 (s, 2H), 4.79 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 162.2, 141.0, 136.0, 128.4 (4C), 128.2, 123.0, 91.3, 91.2, 71.6, 66.2; IR (ATR, cm^{-1}): 3342, 2940, 2878, 1662, 1495, 1443, 1395, 1374, 1340, 1295, 1074, 1013, 984, 826; HRMS (ESI+) Calcd for $C_{14}H_{12}Cl_6N_2NaO_2$, ($[M + Na]^+$) 472.8928, Found, 472.8922.



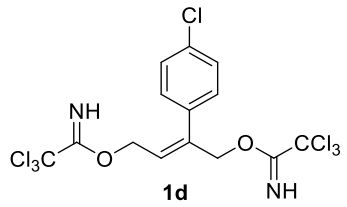
(*E*)-2-(4-methoxyphenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1b): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 8.27 (brs, 1H), 7.26-7.23 (m, 2H), 6.91-6.89 (m, 2H), 6.14 (t, *J* = 6.9 Hz, 1H), 5.05 (s, 2H), 4.80 (d, *J* = 6.6 Hz, 2H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 162.3, 159.5, 140.6, 129.7, 128.2, 122.5, 113.8, 91.3, 91.2, 71.7, 66.4, 55.2; IR (ATR, cm^{-1}): 3342, 2955, 2837, 1663, 1609, 1513, 1291, 1251, 1180, 1073, 984, 830; HRMS (ESI+) Calcd for $C_{15}H_{14}Cl_6N_2NaO_3$, ($[M + Na]^+$) 502.9033, Found, 502.9028.



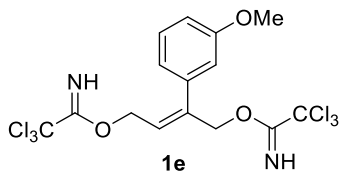
(*E*)-2-(p-tolyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1c): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 8.27 (brs, 1H), 7.21-7.17 (m, 4H), 6.17 (t, *J* = 6.7 Hz, 1H), 5.06 (s, 2H), 4.80 (d, *J* = 6.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 162.3, 140.9, 138.0, 133.0, 129.1, 128.3, 122.6, 91.4, 91.2, 71.6, 66.4, 21.2; IR (ATR, cm^{-1}): 3343, 3027, 2945, 2866, 1662, 1513, 1456, 1297, 1074, 984, 825; HRMS (ESI+) Calcd for $C_{15}H_{14}Cl_6N_2NaO_2$, ($[M + Na]^+$) 486.9084, Found, 486.9079.



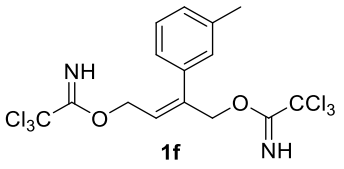
(*E*)-2-(4-chlorophenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1d): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 8.29 (brs, 1H), 7.36-7.34 (m, 2H), 7.27-7.25 (m, 2H), 6.20 (t, *J* = 6.9 Hz, 1H), 5.04 (s, 2H), 4.75 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 162.1, 140.0, 134.4, 134.2, 129.8, 128.7, 124.0, 91.2, 91.1, 71.5, 65.9; IR (ATR, cm^{-1}): 3342, 3036, 2943, 2878, 1664, 1492, 1446, 1292, 1085, 1014, 985, 827; HRMS (ESI+) Calcd for $C_{14}H_{11}Cl_7N_2NaO_2$, ($[M + Na]^+$) 506.8538, Found, 506.8532.



(*E*)-2-(3-methoxyphenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1e): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 8.28 (brs, 1H), 7.29-7.27 (m, 1H), 6.89-6.87 (m, 3H), 6.18 (t, *J* = 6.9Hz, 1H), 5.05 (s, 2H), 4.80 (d, *J* = 6.9 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 162.3, 159.5, 140.8, 137.4, 129.5, 123.2, 120.8, 113.94, 113.90, 91.3, 91.2, 71.6, 66.3, 55.3; IR (ATR, cm^{-1}): 3342, 3001, 2941, 2835, 1662, 1599, 1578, 1488, 1454, 1430, 1288, 1074, 984, 827; HRMS (ESI+) Calcd for $C_{15}H_{14}Cl_6N_2NaO_3$, ($[M + Na]^+$) 502.9033, Found, 502.9028.

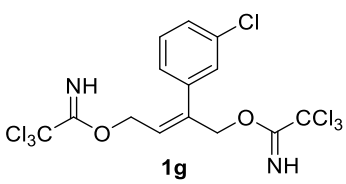


(*E*)-2-(m-tolyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1f): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37 (brs, 1H), 8.26 (brs, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.15-7.09 (m, 3H), 6.16 (tt, *J* = 6.9, 1.4 Hz, 1H), 5.05 (d, *J* = 1.0 Hz, 2H), 4.79 (d, *J* = 6.9 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 162.3, 141.2, 138.0, 136.0, 129.1, 129.0, 128.3, 125.5, 122.6, 91.4, 91.2, 71.6, 66.3, 21.4; IR (ATR, cm^{-1}): 3342, 3033, 2951, 1662, 1450, 1375, 1296, 1073, 984; HRMS (ESI+) Calcd for $C_{15}H_{14}Cl_6N_2NaO_2$, ([M + Na]$^+$) 486.9084, Found,486.9079.



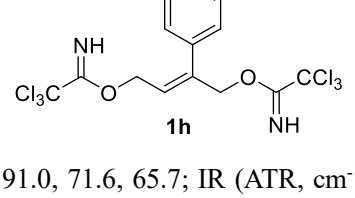
1f

(*E*)-2-(3-chlorophenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1g): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (brs, 1H), 8.30 (brs, 1H), 7.35-7.29 (m, 3H), 7.20-7.19 (m, 1H), 6.21 (t, *J* = 6.9Hz, 1H), 5.03 (s, 2H), 4.76 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 162.1, 139.9, 137.9, 134.4, 129.7, 128.6, 128.4, 126.7, 124.3, 91.2, 91.1, 71.5, 65.9; IR (ATR, cm^{-1}): 3342, 3062, 2946, 2871, 1663, 1595, 1562, 1292, 1072, 985, 826; HRMS (ESI+) Calcd for $C_{14}H_{11}Cl_7N_2NaO_2$, ([M + Na]$^+$) 506.8538, Found, 506.8533.



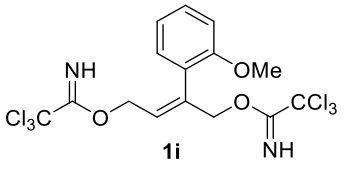
1g

(*E*)-2-(3-(trifluoromethyl)phenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1h): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ8.40 (brs, 1H), 8.31 (brs, 1H), 7.62-7.51 (m, 4H), 6.27 (t, *J* = 6.9 Hz, 1H), 5.06 (s, 2H), 4.74 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ162.3, 162.1, 140.0, 136.9, 131.9, 130.9 (q, *J* = 31.8 Hz, 1C), 129.0, 125.4 (q, *J* = 4.3 Hz, 1C), 125.1 (q, *J* = 2.9 Hz, 1C), 125.0, 123.9 (q, *J* = 273.6 Hz, 1C), 91.1, 91.0, 71.6, 65.7; IR (ATR, cm^{-1}): 3344, 2947, 1665, 1437, 1324, 1299, 1219, 1169, 1131, 1073, 987, 828; HRMS (ESI+) Calcd for $C_{15}H_{11}Cl_6F_3N_2NaO_2$, ([M + Na]$^+$) Exact Mass: 542.8772, Found, 542.8766.



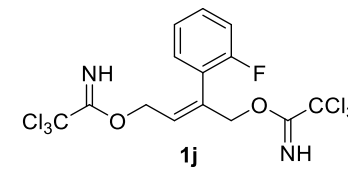
1h

(*E*)-2-(2-methoxyphenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1i): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ8.30 (brs, 1H), 8.22 (brs, 1H), 7.30 (tm, *J* = 7.7 Hz, 1H), 7.18 (dm, *J* = 7,6 Hz, 1H), 6.94(t, *J* = 7,4 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.22 (t, *J* = 6.7 Hz, 1H), 5.01 (s, 2H), 4.70 (d, *J* = 6.0 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 162.3, 156.7, 138.3, 130.8, 129.6, 124.5, 123.5, 120.5, 110.8, 91.38, 91.33, 71.0, 66.7, 55.4; IR (ATR, cm^{-1}): 3343, 2945, 2837, 1662, 1600, 1492, 1457, 1436, 1295, 1248, 1081, 984, 826; HRMS (ESI+) Calcd for $C_{15}H_{14}Cl_6N_2NaO_3$, ([M + Na]$^+$) 504.9004, Found, 504.8998.



1i

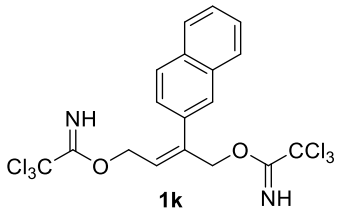
(*E*)-2-(2-fluorophenyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1j): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.35 (brs, 1H), 8.27 (brs, 1H), 7.34-7.28 (m, 2H), 7.15 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 9.3 Hz, 1H), 6.30 (t, *J* = 6.9 Hz, 1H), 5.07 (s, 2H), 4.74 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 162.1, 159.7 (d, *J* = 247 Hz, 1C), 134.8, 131.0 (d, *J* = 2.9 Hz, 1C), 130.2 (d, *J* = 8.7 Hz, 1C), 125.7, 124.1 (d, *J* = 2.9 Hz, 1C), 123.3 (d, *J* = 15.9 Hz, 1C), 115.7 (d, *J* = 21.7 Hz, 1C), 91.2, 91.1, 71.0, 66.2; IR (ATR, cm^{-1}): 3343, 2947, 2869, 1662, 1490, 1450, 1295, 1227, 1077, 986, 827; HRMS (ESI+) Calcd for $C_{14}H_{11}Cl_6FN_2NaO_2$, ([M + Na]$^+$)



1j

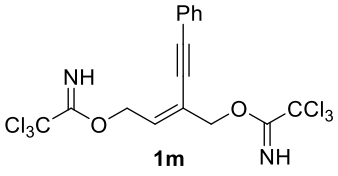
492.8804, Found, 492.8799.

(*E*)-2-(naphthalen-2-yl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1k): colorless solid; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (brs, 1H), 8.26 (brs, 1H), 7.87-7.79 (m, 4H), 7.52-7.48 (m, 2H), 7.44 (dm, *J* = 8.3 Hz, 1H), 6.28 (tm, *J* = 6.9 Hz, 1H), 5.16 (s, 2H), 4.83 (d, *J* = 6.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 162.3, 141.1, 133.5, 133.1, 132.9, 128.2, 128.1, 127.9, 127.7, 126.4 (2C), 126.1, 123.5, 91.3, 91.2, 71.7, 66.3; IR (ATR, cm^{-1}): 3341, 3058, 2946, 1662, 1505, 1454, 1294, 1074, 984, 824; HRMS (ESI+) Calcd for $C_{18}H_{14}Cl_6N_2NaO_2$, ($[M + Na]^+$) 522.9084, Found, 522.9079.



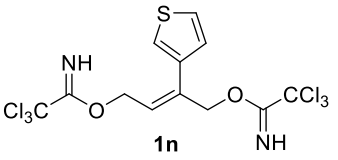
1k

(*E*)-2-(phenylethynyl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1m): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (brs, 1H), 8.39 (brs, 1H), 7.47-7.45 (m, 2H), 7.32-7.33 (m, 3H), 6.36 (tm, *J* = 6.4 Hz, 1H), 5.19 (d, *J* = 6.5 Hz, 1H), 4.95 (d, *J* = 0.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 162.1, 131.6, 131.5, 128.8, 128.3, 122.4, 122.0, 97.3, 91.2, 91.1, 83.2, 69.7, 67.1; IR (ATR, cm^{-1}): 3342, 2926, 2852, 1666, 1491, 1443, 1297, 1072, 991, 827; HRMS (ESI+) Calcd for $C_{16}H_{12}Cl_6N_2NaO_2$, ($[M + Na]^+$) 496.8928, Found, 496.8922.



1m

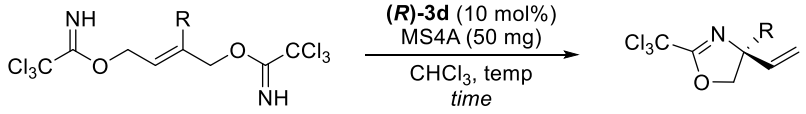
(*E*)-2-(thiophen-3-yl)but-2-ene-1,4-diyl bis(2,2,2-trichloroacetimidate) (1n): colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (brs, 1H), 8.32 (brs, 1H), 7.36-7.32 (m, 2H), 7.16-7.14 (m, 1H), 6.18 (t, *J* = 6.9 Hz, 1H), 5.05 (s, 2H), 4.92 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ162.4, 162.3, 136.3, 135.5, 127.5, 125.8, 124.4, 123.9, 91.3, 91.2, 71.7, 66.3; IR (ATR, cm^{-1}): 3341, 3109, 2949, 1662, 1454, 1375, 1291, 1071, 985, 826; HRMS (ESI+) Calcd for $C_{12}H_{10}Cl_6N_2NaO_2S$, ($[M + Na]^+$) 480.8462, Found, 480.8457.



1n

4. Enantioselective S_N2' Reaction Catalyzed by Chiral Brønsted Acids

4-1. Representative procedure



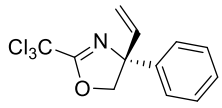
1
0.1 mmol

2

To a $CHCl_3$ (1.0 mL) solution of **1** (0.1 mmol, 1.0 equiv.) and MS4A (50 mg) was added (*R*)-**3d** (10 mg, 0.01 mmol, 10 mol%) at indicated temperature and the reaction mixture was quenched with NEt_3 (10 μL) at indicated time (monitored by TLC). The reaction mixture was directly purified by flash silica gel column chromatography to give **2**. The enantiomeric excess of **2** was determined by chiral stationary phase HPLC analysis.

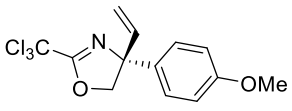
4-2. Spectral data of products

(*R*)-4-phenyl-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2a): Prepared according to the representative procedure over the course of 48 h at -60 °C.; Colorless oil (85% yield).; HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 8.34 (minor), 8.98 (major) min, (95% ee); $[\alpha]^{22.0}_D$ = +53.2 (c = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.35 (m, 4H), 7.31 (tt, *J* = 7.2, 1.8 Hz, 1H), 6.20 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H), 5.27 (d, *J* = 17.4 Hz, 1H), 4.92 (d, *J* = 8.4 Hz, 1H), 4.66 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 142.7, 139.7, 128.8, 127.7, 125.8, 115.2, 86.6, 81.1, 77.9; IR (ATR, cm^{-1}): 3090, 3022, 2959, 2924, 1905, 1728, 1662, 1637, 1513, 1471, 1405, 1379, 1351, 1270, 1186, 1116, 1074, 1039, 996, 938, 899, 842, 821; HRMS (ESI+) Calcd for $C_{12}H_{10}Cl_3NNaO$, ($[M + Na]^+$) 311.9726, Found, 311.9720.



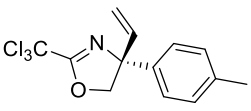
2a

(*R*)-4-(4-methoxyphenyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2b): Prepared according to the representative procedure over the course of 12 h at -60 °C.; White solid (98% yield); HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 14.1 (major), 15.4 (minor) min, (79% ee); $[\alpha]^{21.5}_D$ = +38.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29-7.26 (m, 2H), 6.92-6.89 (m, 2H), 6.18 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 4.88 (d, *J* = 8.4 Hz, 1H), 4.63 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0, 159.1, 139.8, 134.8, 127.1, 115.1, 114.1, 86.7, 81.2, 77. 5, 55.3; IR (ATR, cm^{-1}): 3004, 2957, 2934, 2908, 2837, 2047, 1888, 1728, 1662, 1637, 1711, 1682, 1511, 1465, 1442, 1405, 1351, 1302, 1250, 1179, 1115, 1074, 1034, 996, 944, 888, 832; HRMS (ESI+) Calcd for $C_{13}H_{12}Cl_3NNaO_2$, ($[M + Na]^+$) 341.9831, Found, 341.9826.



2b

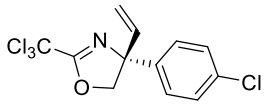
(*R*)-4-(p-tolyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2c): Prepared according to the representative procedure over the course of 12 h at -60 °C.; Colorless oil (96% yield); HPLC analysis Chiralcel OB-H (Only hexane, 1.0 mL/min, 220 nm, 40 °C) 7.38 (minor), 8.83 (major) min, (90% ee); $[\alpha]^{21.9}_D$ = +22.9 (c = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25-7.18 (m, 4H), 6.19 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.29 (d, *J* = 10.2 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 4.89 (d, *J* = 7.8 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0, 139.94, 139.86, 137.5, 129.4, 125.7,



2c

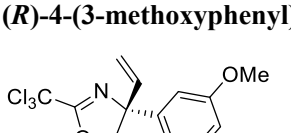
115.1, 86.7, 81.2, 77.8, 21.0; IR (ATR, cm^{-1}): 3568, 3390, 3091, 2959, 2924, 1905, 1728, 1663, 1637, 1513, 1471, 1406, 1351, 1270, 1186, 1116, 1074, 997, 939, 843, 821; HRMS (ESI+) Calcd for $C_{13}H_{12}Cl_3NNaO$, ($[M + Na]^+$) 325.9882, Found, 325.9877.

(*R*)-4-(4-chlorophenyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2d): Prepared according to the representative procedure over the course of 48 h at -50 °C.; Colorless oil (90% yield); HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 8.98 (minor), 9.64 (major) min, (91% ee); $[\alpha]^{21.9}_D$ = +21.5 (c = 1.2, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37-7.33 (m, 2H), 7.32-7.27 (m, 2H), 6.15 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.32 (d, *J* = 10.8 Hz, 1H), 5.26 (d, *J* = 16.8 Hz, 1H), 4.91 (d, *J* = 10.4 Hz, 1H), 4.61 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 141.2, 139.3, 133.7, 128.9, 127.3, 115.7, 86.5, 80.9, 77.6; IR (ATR, cm^{-1}): 3725, 3624, 3095, 2960, 2914, 1724, 1663, 1492, 1402, 1350, 1269, 1094, 1000, 940, 831; HRMS (ESI+) Calcd for $C_{12}H_9Cl_4NNaO$, ($[M + Na]^+$) 345.9336, Found, 345.9331.



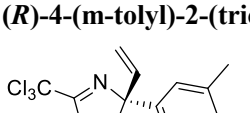
2d

(*R*)-4-(3-methoxyphenyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2e): Prepared according to the representative procedure over the course of 12 h at -50 °C.; White solid (90% yield); HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 16.3 (minor), 21.8 (major) min, (90% ee) $[\alpha]^{25.4}_D$ = +27.4 (c = 1.0, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.8 Hz, 1H), 6.94 (tm, *J* = 1.8 Hz, 1H), 6.92 (dm, *J* = 7.8 Hz, 1H), 6.84 (ddm, *J* = 8.4, 2.4 Hz, 1H), 6.19 (dd, *J* = 16.8, 10.2 Hz, 1H), 5.31 (d, *J* = 10.8 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 4.90 (d, *J* = 8.4 Hz, 1H), 4.64 (d, *J* = 8.4 Hz, 1 H), 3.82 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 159.9, 144.4, 139.6, 129.9, 118.0, 115.3, 112.9, 111.9, 86.6, 81.1, 77.9, 55.3; IR (ATR, cm^{-1}): 2958, 2836, 1663, 1602, 1584, 1487, 1434, 1290, 1259, 1048, 998, 949; HRMS (ESI+) Calcd for $C_{13}H_{12}Cl_3NNaO_2$, ($[M + Na]^+$) 341.9831, Found, 341.9826.



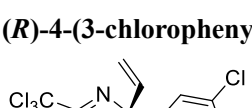
2e

(*R*)-4-(m-tolyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2f): Prepared according to the representative procedure over the course of 48 h at -60 °C.; Colorless oil (97% yield); HPLC analysis Chiralcel OB-H (Only hexane, 1.0 mL/min, 220 nm, 40 °C) 6.58 (minor), 7.78 (major) min, (91% ee); $[\alpha]^{22.7}_D$ = +26.5 (c = 0.6, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.8 Hz, 1H), 7.17 (brs, 1H), 7.14 (dm, *J* = 7.8 Hz, 1H), 7.11 (dm, *J* = 8.4 Hz, 1H), 6.19 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.30 (d, *J* = 10.8 Hz, 1H), 5.26 (d, *J* = 16.8 Hz, 1H), 4.91 (d, *J* = 9.0 Hz, 1H), 4.64 (d, *J* = 7.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.0, 142.7, 139.9, 138.5, 128.7, 128.5, 126.5, 122.8, 115.1, 86.7, 81.1, 77.9, 21.5; IR (ATR, cm^{-1}): 3728, 2958, 2925, 1662, 1607, 1490, 1351, 1273, 1219, 998, 949, 846; HRMS (ESI+) Calcd for $C_{13}H_{12}Cl_3NNaO$, ($[M + Na]^+$) 325.9882, Found, 325.9877.



2f

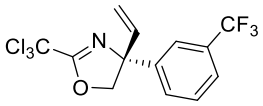
(*R*)-4-(3-chlorophenyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2g): Prepared according to the representative procedure over the course of 36 h at -40 °C.; White solid (87% yield); HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 8.59 (minor), 10.1 (major) min, (88% ee); $[\alpha]^{25.8}_D$ = +33.2 (c = 0.8, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$)



2g

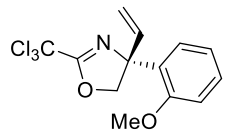
δ 7.36 (t, *J* = 2.4 Hz, 1H), 7.34-7.28 (m, 2H), 7.24 (dt, *J* = 7.8, 1.2 Hz, 1H), 6.15 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.34 (d, *J* = 10.2 Hz, 1H), 5.28 (d, *J* = 17.4 Hz, 1H), 4.92 (d, *J* = 8.4 Hz, 1H), 4.61 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.5, 144.7, 139.2, 134.8, 130.1, 128.0, 126.2, 124.0, 115.8, 86.5, 80.8, 77.7; IR (ATR, cm^{-1}): 3069, 2965, 2904, 1663, 1597, 1574, 1475, 1421, 1353, 1270, 1233, 1083, 999, 949, 845, 821; HRMS (ESI+) Calcd for $C_{12}H_9Cl_4NNaO$, ($[M + Na]^+$) 345.9336, Found, 345.9331.

(*R*)-2-(trichloromethyl)-4-(3-(trifluoromethyl)phenyl)-4-vinyl-4,5-dihydrooxazole (2h): Prepared according to the representative procedure over the course of 48 h at -40 °C.; White solid (86% yield); HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 7.06 (minor), 7.82 (major) min, (89% ee); $[\alpha]^{26.7}_D$ = +33.0 (c = 0.8, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.58 (t, *J* = 7.2 Hz, 2H), 7.52 (t, *J* = 7.8 Hz, 1H), 6.18 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.37 (d, *J* = 10.8 Hz, 1H), 5.29 (d, *J* = 16.8 Hz, 1H), 4.96 (d, *J* = 9.0 Hz, 1H), 4.64 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ162.7, 143.8, 139.0, 131.2 (q, *J* = 32.3 Hz, 1C), 129.4 (2C), 124.7 (q, *J* = 4.3 Hz, 1C), 123.9 (q, *J* = 272.6 Hz, 1C), 122.8 (q, *J* = 4.3 Hz, 1C), 116.1, 86.4, 80.8, 76.8; IR (ATR, cm^{-1}): 2932, 1665, 1332, 1269, 1228, 1169, 1130, 1075, 1001; HRMS (ESI+) Calcd for $C_{13}H_9Cl_3F_3NNaO$, ($[M + Na]^+$) 379.9600, Found, 379.9594.



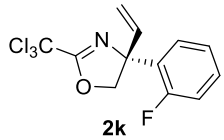
2h

(*R*)-4-(2-methoxyphenyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2i): Prepared according to the representative procedure over the course of 12 h at -40 °C.; Colorless oil (90% yield).; HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 7.16 (minor), 8.86 (major) min, (67% ee); $[\alpha]^{26.4}_D$ = +52.1 (c = 1.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.30 (tm, *J* = 7.7 Hz, 1H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.23 (dd, *J* = 17.2, 10.3 Hz, 1H), 5.16 (d, *J* = 18.2 Hz, 1H), 5.14 (d, *J* = 10.3 Hz, 1H), 5.00 (d, *J* = 8.9 Hz, 1H), 4.61 (d, *J* = 8.9 Hz, 1 H) 3.84 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.6, 155.4, 139.6, 131.3, 128.9, 127.3, 121.0, 114.1, 111.0, 86.9, 81.9, 76.5, 55.3; IR (ATR, cm^{-1}): 3012, 2971, 2944, 2841, 1672, 1583, 1488, 1463, 1403, 1353, 1284, 1242, 1182, 1159, 1119, 1027, 996, 937, 845, 821; HRMS (ESI+) $C_{13}H_{12}Cl_3NNaO_2$, ($[M + Na]^+$) 341.9831, Found, 341.9826.



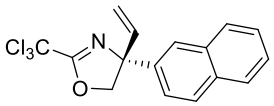
2i

(*R*)-4-(2-fluorophenyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2k): Prepared according to the representative procedure over the course of 12 h at -20 °C.; Colorless oil (87% yield).; HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 5.17 (minor), 5.53 (major) min, (90% ee); $[\alpha]^{26.8}_D$ = +65.1 (c = 0.9, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 7.7, 1.7 Hz, 1H), 7.34-7.29 (m, 1H), 7.18 (tm, *J* = 7.3 Hz, 1H), 7.09 (dd, *J* = 11.0, 8.3 Hz, 1H), 6.17 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.23 (d, *J* = 10.7 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 5.02 (dd, *J* = 8.9, 3.1 Hz, 1H), 4.66 (dd, *J* = 8.9, 2.1 Hz, 1 H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 159.3 (d, *J* = 246 Hz, 1C), 138.6, 130.1 (d, *J* = 14.5 Hz, 1C), 129.6 (d, *J* = 8.7 Hz, 1C), 127.9 (d, *J* = 4.3 Hz, 1C), 124.5, 115.8 (d, *J* = 21.7 Hz, 1C), 115.2, 86.6, 81.4, 75.8; IR (ATR, cm^{-1}): 2959, 2903, 1666, 1488, 1455, 1405, 1356, 1283, 1264, 1219, 998, 943; HRMS (ESI+) Calcd for $C_{12}H_9Cl_3FNNaO$, ($[M + Na]^+$) 329.9631, Found, 329.9626.



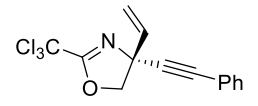
2k

(*R*)-4-(naphthalen-2-yl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2l): Prepared according to the representative procedure over the course of 12 h at -60 °C.; White solid (85% yield); HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.5:0.5, 1.0 mL/min, 220 nm, 40 °C) 10.5 (minor), 11.0 (major) min, (86% ee); $[\alpha]^{23.4}_D$ = -3.6 (c = 1.3, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.51-7.48 (m, 2H), 7.41 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.28 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.35 (d, *J* = 10.3 Hz, 1H), 5.31 (d, *J* = 17.2 Hz, 1H), 4.99 (d, *J* = 8.6 Hz, 1H), 4.75 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 139.9, 139.7, 133.2, 132.7, 128.8, 128.2, 127.6, 126.5, 126.3, 124.7, 123.8, 115.6, 86.7, 81.0, 78.2; IR (ATR, cm^{-1}): 3726, 3344, 3058, 3018, 2921, 1661, 1635, 1601, 1506, 1470, 1405, 1354, 1269, 1221, 1184, 1129, 1080, 998, 938, 901, 845, 820; HRMS (ESI+) Calcd for $C_{16}H_{12}Cl_3NNaO$, ($[M + Na]^+$) 361.9882, Found, 361.9876.



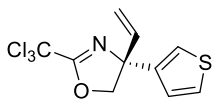
2l

(*R*)-4-(phenylethynyl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2m): Prepared according to the representative procedure over the course of 48 h at -40 °C.; Colorless oil (55% yield).; HPLC analysis Chiralcel OD-3 (Hexane only, 1.0 mL/min, 220 nm, 40 °C) 21.88 (major), 25.08 (minor) min, (62% ee); $[\alpha]^{23.9}_D$ = -31.9 (c = 0.5, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.8 Hz, 1.8 Hz, 2 H), 7.36-7.30 (m, 3H), 5.99 (dd, *J* = 16.8, 10.3 Hz, 1H), 5.70 (d, *J* = 16.8 Hz, 1H), 5.39 (d, *J* = 10.2 Hz, 1H), 4.84 (d, *J* = 8.4 Hz, 1H), 4.64 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 163.7, 136.5, 131.8, 128.9, 128.3, 122.0, 117.4, 88.0, 86.1, 81.6, 70.4, 29.7; IR (ATR, cm^{-1}): 2956, 2925, 2852, 1727, 1657, 1600, 1490, 1407, 1259, 998, 849; HRMS (ESI+) Calcd for $C_{14}H_{10}Cl_3NNaO$, ($[M + Na]^+$) 335.9726, Found, 335.9720.



2m

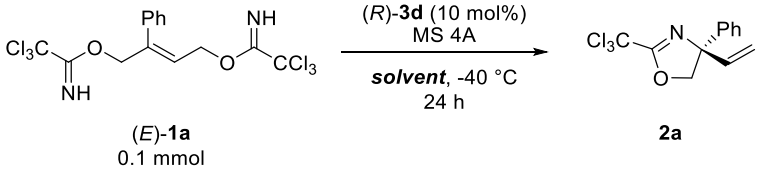
(*R*)-4-(thiophen-3-yl)-2-(trichloromethyl)-4-vinyl-4,5-dihydrooxazole (2n): Prepared according to the representative procedure over the course of 8 h at -60 °C.; Colorless oil (95% yield).; HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 10.36 (minor), 10.83 (major) min, (91% ee); $[\alpha]^{26.1}_D$ = -20.8 (c = 0.9, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.23 (dd, *J* = 3.1, 1.4 Hz, 1H), 7.01 (dd, *J* = 5.2, 1.4 Hz, 1H), 6.23 (dd, *J* = 17.2, 10.7 Hz, 1H), 5.33 (d, *J* = 10.7 Hz, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 4.80 (d, *J* = 8.6 Hz, 1H), 4.68 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 143.4, 139.0, 126.9, 125.5, 121.6, 115.7, 86.6, 81.1, 75.8; IR (ATR, cm^{-1}): 3108, 2962, 2925, 2854, 1740, 1661, 1470, 1409, 1351, 1267, 1219, 998, 950, 849; HRMS (ESI+) Calcd for $C_{10}H_8Cl_3NNaOS$, ($[M + Na]^+$) 317.9290, Found, 317.9284.



2n

5. Additional Screenings

5-1. Screening of solvents



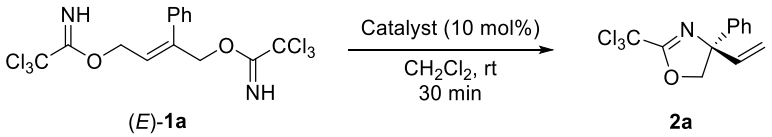
(*E*)-**1a**
0.1 mmol

2a

Table S1

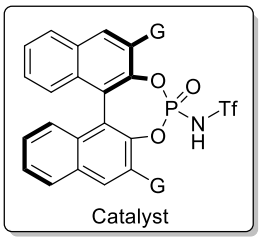
entry	*solvent*	*yield (%)*	*ee (%)*	*note*
1	CH_2Cl_2	96	75	
2	$CHCl_3$	96	89	5 mol% of catalyst was used
3	toluene	94	70	
4	THF	4	1	
5	Et_2O	20	14	
6	MeCN	8	-8	

5-2. Screening of catalyst substituent G

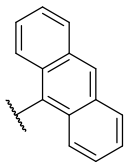


(*E*)-**1a**

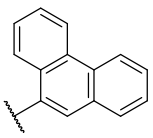
2a



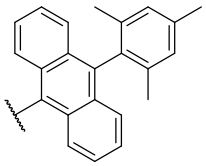
G=



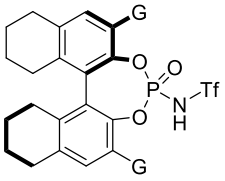
3a



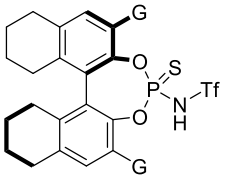
3j



3k



3l

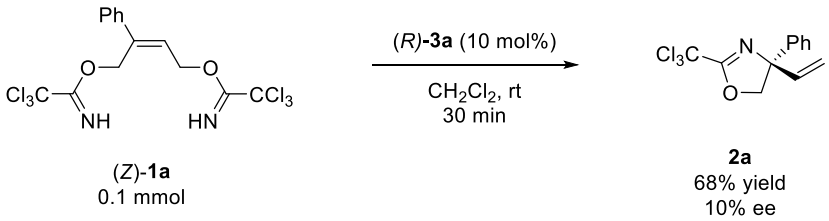


3m

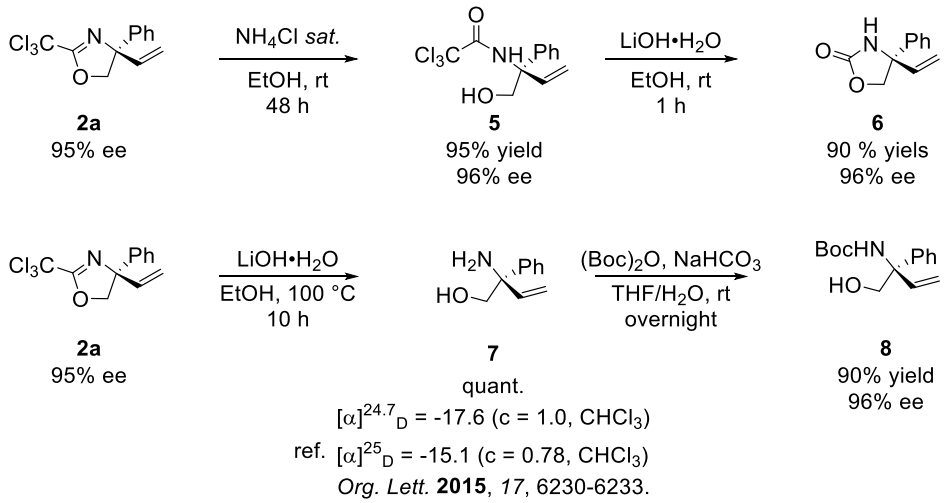
Table S2.

entry	*catalyst*	**G**	*yield (%)*	*%ee*	*note*
1	(*R*)-**3a**	9-Anthryl	92	27	
2	(*R*)-**3e**	Ph	90	-2	
3	(*R*)-**3f**	4-PhC_6H_4	85	-5	
4	(*R*)-**3g**	3,5-(^{t}Bu)$_2C_6H_3$	79	6	1 h
5	(*R*)-**3h**	2,4,6-(^{i}Pr)$_3C_6H_2$	52	6	24 h
6	(*R*)-**3i**	$SiPh_3$	35	5	24 h
7	(*R*)-**3j**	9-Phenanthryl	90	17	
8	(*R*)-**3k**	10-Mesityl-9-Anthryl	95	−8	
9	(*R*)-**3l**	9-Anthryl	90	22	1 h
10	(*R*)-**3m**	9-Anthryl	trace	n.d.	72 h

5-3. The use of (*Z*)-1a as a substrate



6. Derivatization of Product

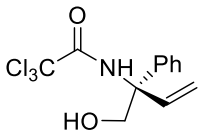


$[\alpha]^{24.7}_D$ = -17.6 (c = 1.0, $CHCl_3$)

ref. $[\alpha]^{25}_D$ = -15.1 (c = 0.78, $CHCl_3$)

Org. Lett. **2015**, *17*, 6230-6233.

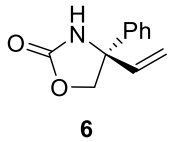
(*R*)-2,2,2-trichloro-N-(1-hydroxy-2-phenylbut-3-en-2-yl)acetamide (5): To a solution of **2a** (29 mg, 0.1 mmol, 95% ee) in EtOH (1 mL) solution was added NH_4Cl (1 ml) at room temperature. The reaction mixture was stirred for 48 h, then H_2O was added and extracted with EtOAc. The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration. The residual crude was purified by silica gel column chromatography (Hexane/EtOAc = 10/1) to give the **5** (29 mg, 95% yield) as a white solid.



5

HPLC analysis Chiralpak IA-3 (Hex:IPA = 98:2, 1.0 mL/min, 220 nm, 40 °C) 24.1 (minor), 26.2 (major) min, (96% ee); $[\alpha]^{24.8}_D$ = -22.2 (c = 1.2, CH_2Cl_2); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 (brs, 1H), 7.42-7.32 (m, 5H), 6.37 (dd, *J* = 17.6, 10.7 Hz, 1H), 5.52 (d, *J* = 10.7 Hz, 1H), 5.36 (d, *J* = 17.5 Hz, 1H), 3.99 (d, *J* = 12.0 Hz, 1H), 3.91 (d, *J* = 12.0 Hz, 1H), 2.51 (brs, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.8, 139.1, 136.0, 128.9, 128.2, 125.9, 117.3, 93.0, 68.5, 65.8; IR (ATR, cm^{-1}): 3387, 2927, 2860, 2371, 2346, 2320, 1720, 1499, 1248, 1044; HRMS (ESI+) Calcd for $C_{12}H_{12}Cl_3NNaO_2$, ($[M + Na]^+$) 329.9831, Found, 329.9826.

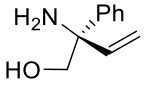
(*R*)-4-phenyl-4-vinyloxazolidin-2-one (6): To a solution of **5** (29 mg, 0.1 mmol) in EtOH (1mL) was added LiOH·H_2O (21 mg, 0.5 mmol, 5 eq.) at room temperature. The reaction mixture was stirred for 1 h, then H_2O was added and extracted with EtOAc. The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration. The residual crude was purified by silica gel column chromatography (Hexane/EtOAc = 10/1) to give the **6** (16 mg, 90% yield) as a white solid.



6

HPLC analysis Chiralcel OD-3 (Hex:IPA = 95:5, 1.0 mL/min, 220 nm, 40 °C) 21.6 (major), 23.7 (minor) min, (96% ee); $[\alpha]^{24.7}_D$ = +24.7 (c = 0.25, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.32 (m, 5H), 6.71 (brs, 1H), 6.21 (dd, *J* = 17.2, 10.3 Hz, 1H), 5.36 (d, *J* = 10.3 Hz, 1H), 5.32 (d, *J* = 17.2 Hz, 1H), 4.56 (d, *J* = 8.6 Hz, 1H), 4.48 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.2, 141.1, 139.2, 129.0, 128.2, 125.3, 115.8, 76.3, 64.6; IR (ATR, cm^{-1}): 3260, 2959, 2927, 2856, 1752, 1449, 1387, 1276, 1125, 1037, 938; HRMS (ESI+) Calcd for $C_{11}H_{11}NNaO_2$, ($[M + Na]^+$) 212.0687, Found, 212.0682.

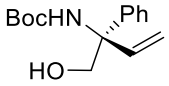
(*R*)-2-amino-2-phenylbut-3-en-1-ol (7): To a solution of **5** (29 mg, 0.1 mmol) in EtOH (1 mL) and H_2O (0.3 mL) was added LiOH-H_2O (21 mg, 0.5 mmol, 5 eq.) at room temperature. The reaction mixture was stirred at 100 °C for 10 h. Then H_2O was added and extracted with EtOAc. The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration. The residual crude was pure **7** as a white solid.



7

$[\alpha]^{24.7}_D$ = -17.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.36 (tt, *J* = 7.2 Hz, 1.8 Hz, 2H), 7.27 (tt, *J* = 7.2 Hz, 1.2 Hz, 1H), 6.17 (dd, *J* = 17.5, 10.7 Hz, 1H), 5.28 (dd, *J* = 5.5, 1.0 Hz, 1H), 5.26 (m, 1H), 3.76 (s, 2H), 1.92 (brs, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.9, 143.0, 128.5, 127.2, 126.0, 114.2, 69.7, 60.9; IR (ATR, cm^{-1}): 3351, 3291, 3086, 2925, 2854, 1639, 1601, 1494, 1446, 1412, 1219, 1060, 923;

tert-butyl (*R*)-(1-hydroxy-2-phenylbut-3-en-2-yl)carbamate (8): To a solution of **7** (16mg, 0.1 mmol) in saturated $NaHCO_3$ solution (1 mL) and THF (1 mL) was added Boc_2O (0.33 g, 1.5 mmol, 3 equiv) at room temperature. The reaction mixture was stirred for overnight. Then H_2O was added and extracted with EtOAc. The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration. The residual crude was purified by silica gel column chromatography (Hexane/EtOAc = 2/1) to give the **8** (23.7 mg, 90% yield) as a white solid.



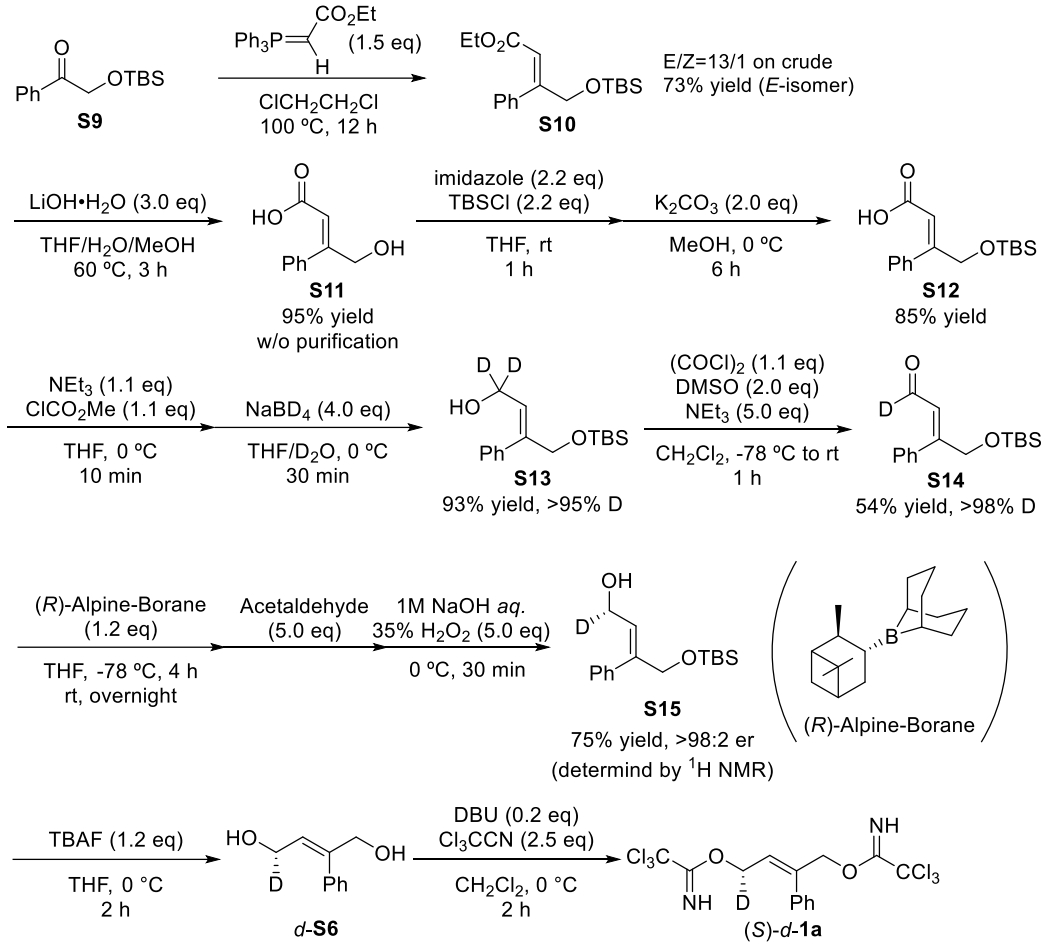
8

HPLC analysis Chiralpak IA-3 (Hex:IPA = 98:2, 1.0 mL/min, 220 nm, 40 °C) 29.4 (major), 32.8 (minor) min, (96% ee); $[\alpha]^{20.8}_D$ = -19.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.27 (m, 5H), 6.25 (dd, *J* = 17.4, 10.6 Hz, 1H), 5.40 (d, *J* = 10.3 Hz, 1H), 5.31-5.23 (m, 2H), 4.04-3.82 (m, 3H), 1.45 (brs, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ155.8, 141.5, 138.7, 128.5, 127.5, 126.2, 115.9, 80.2, 69.4, 28.3, one carbon was not found probably due to overlapping.; IR (ATR, cm^{-1}): 3416, 2978, 2928, 1689, 1493, 1392, 1367, 1253, 1168, 1069, 921; HRMS (ESI+) Calcd for $C_{15}H_{21}NNaO_3$, ($[M + Na]^+$) 286.1419, Found, 286.1414.

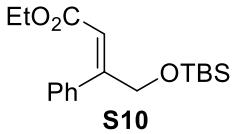
7. Mechanistic Study

7-1. Deuterium experiment

7-1-1. Preparation of deuterated material (*S*)-*d*-**1a**



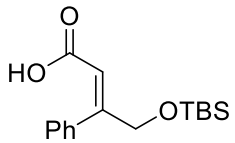
ethyl (*E*)-4-((tert-butyldimethylsilyl)oxy)-3-phenylbut-2-enoate (S10): A 30 mL round bottom flask was charged with **S9** (1.5 g, 6.3 mmol, 1.0 eq), Ethyl (triphenylphosphoranylidene)acetate (3.3 g, 9.5 mmol), and $ClCH_2CH_2Cl$ (6.3 mL). The mixture was allowed to warm to 100 °C for 12 h. The residual crude was directly purified by flash column chromatography on silica gel (Hexane/EtOAc = 40/1 to 20/1) to provide **S10** (1.48 g, 73% yield, 4.6 mmol) as a colorless oil.



^{1}H NMR (600 MHz, $CDCl_3$) δ7.36-7.31 (m, 3H), 7.17-7.16 (m, 2H), 6.20 (s, 1H), 4.33 (s, 2H), 4.00 (q, *J* = 7.2 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.95 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 157.6, 137.5, 127.9, 127.4, 127.3, 115.2, 66.8, 59.8, 25.9, 18.4, 13.9, -5.5; IR (ATR, cm^{-1}): 2955, 2929, 2857, 1725, 1655, 1471, 1444, 1363, 1333, 1255, 1220, 1154, 1130, 1045, 837, 697; HRMS (ESI+) Calcd for $C_{18}H_{28}NaO_3Si$, ([M + Na]$^+$) 343.1705, Found, 343.1700.

(*E*)-4-((tert-butyldimethylsilyl)oxy)-3-phenylbut-2-enoic acid (S12): A 20 mL round bottom flask was charged with **S10** (320 mg, 1.0 mmol, 1.0 eq), LiOH (84 mg, 2.0 mmol, 2.0 eq), THF (8 mL), H_2O (1 mL) and MeOH (1

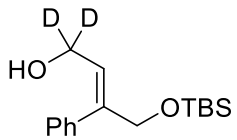
mL). The mixture was allowed to warm to 60 °C for 3 h. Then the solvent was removed under reduced pressure and H_2O and Et_2O were added. Organic layer was extracted with H_2O. The combined aqueous extracts were washed with Et_2O, then acidified with 1 M HCl aq. (pH= ~4) and extract with EtOAc. The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration to give the crude product **S6**. The crude product **S11** was used next step without purification. To an ice bath cooled solution of **S11** in THF (10 mL) was added imidazole (150 mg, 2.2 mmol, 2.2 eq) and TBSCl (332 mg, 2.2 mmol, 2.2 eq). The mixture was stirred at 0 °C for 1 h. Then the reaction mixture was added K_2CO_3 (276 mg, 2.0 mmol, 2.0 eq) and MeOH (5 mL). The mixture was stirred at 0 °C for 30 min (monitored by TLC). Then the solvent was removed under reduced pressure and added H_2O and EtOAc (~15 mL). The combined layer was acidified with 1 M HCl aq. (pH= ~4) and extract with EtOAc (10 mL × 3). The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration to give the crude product **S12** (249 mg, 85% yield, 0.85 mmol) as a white solid. The crude product **S12** was used next step without purification.



S12

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.33 (m, 3H), 7.16-7.14 (m, 2H), 6.19 (t, *J* = 2.1 Hz, 1H), 4.32 (d, *J* = 2.4 Hz, 1H), 0.94 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.4, 160.2, 136.8, 128.2, 128.1, 127.3, 114.2, 66.9, 25.8, 18.4, -5.5; IR (ATR, cm^{-1}): 2955, 2929, 2857, 1698, 1650, 1472, 1418, 1256, 1178, 1135, 1020; HRMS (ESI+) Calcd for $C_{16}H_{24}NaO_3Si$, ([M + Na]$^+$) 315.1392, Found, 315.1387.

(*E*)-4-((tert-butyldimethylsilyl)oxy)-3-phenylbut-2-en-1,1-d$_2$-1-ol (S13): To an ice bath cooled solution of **S12** (205 mg, 0.7 mmol, 1.0 eq), NEt_3 (107 μL, 0.77 mmol, 1.1 eq) in THF (7 mL) was added methyl carbonochloridate (59 μL, 0.77 mmol, 1.1 eq). The mixture was stirred at 0 °C for 10 min. Then $NaBD_4$ (117 mg, 2.8 mmol, 4.0 eq) and D_2O (350 μL) were added to the reaction mixture. The mixture was stirred at 0 °C for 10 min. Then the reaction mixture was quenched with NH_4Cl sat. and extract with EtOAc. The combined EtOAc extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration to give the crude product. The residual crude was purified by silica gel column chromatography (Hexane/EtOAc = 20/1 to 10/1) to give the product **S13** (182 mg, 0.65 mmol, 93% yield, <95% D) as a colorless oil.

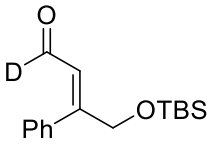


S13

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.28 (m, 3H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.97 (s, 1H), 4.33 (s, 2H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 137.7, 128.3, 128.1, 127.4, 124.4, 66.6, 59.0 (q, *J* = 21.7 Hz, 1C), 25.8, 18.3, -5.5; IR (ATR, cm^{-1}): 3365, 3057, 2954, 2928, 2856, 2206, 2089, 1724, 1471, 1463, 1362, 1255, 1128, 1086, 1000; HRMS (ESI+) Calcd for $C_{16}H_{24}D_2NaO_2Si$, ([M + Na]$^+$) 303.1725, Found, 303.1720.

(*E*)-4-((tert-butyldimethylsilyl)oxy)-3-phenylbut-2-enal-1-*d* (S14): To an acetone bath cooled solution of $(COCl)_2$ (61 μL, 0.72 mmol, 1.1 eq) in CH_2Cl_2 (7 mL) was added DMSO (92 μL, 1.3 mmol, 2.0 eq) in CH_2Cl_2 (1 mL) dropwise. After 10 min, **S13** (182 mg, 0.65 mmol, 1.0 eq) in CH_2Cl_2 (1 mL) was added dropwise. After 15 min, NEt_3 (460 μL, 3.3 mmol, 5.0 eq) was added to the reaction mixture. After 15 min, the mixture was gradually warmed up to room temperature. Then the reaction mixture was quenched with H_2O. The combined CH_2Cl_2 solution were washed with NH_4Cl sat. and brine, dried over Na_2SO_4 and concentrated after filtration to give the crude product. The residual

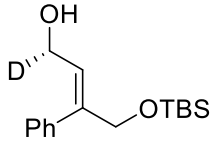
crude was purified by silica gel column chromatography (Hexane/EtOAc = 20/1) to give the product **S14** (95 mg, 0.39 mmol, 54% yield, <98% D) as a yellow oil.



S14

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42-7.41 (m, 3H), 7.27-7.25 (m, 2H), 6.42 (s, 1H), 4.48 (s, 2H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.0 (t, *J* = 26.7 Hz, 1C), 164.8, 134.9, 129.3, 128.6, 128.5, 125.6, 66.1, 25.8, 18.3, -5.5; IR (ATR, cm^{-1}): 3057, 3031, 2954, 2929, 2886, 2856, 2098, 1662, 1471, 1442, 1318, 1256, 1131, 1047, 900, 838, 795, 779, 701; HRMS (ESI+) Calcd for $C_{16}H_{24}DO_2Si$, ([M + H]$^+$) 278.1687, Found, 278.1681.

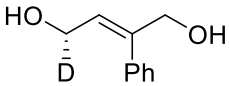
(*S*, *E*)-4-((tert-butyldimethylsilyl)oxy)-3-phenylbut-2-en-1-*d*-1-ol (S15): To a solution of (*R*)-Alpine-Borane (1.1 mL, 0.54 mmol, 1.2 eq, 0.5 M in THF solution) in THF (2.8 mL) was added **S14** (125 mg, 0.45 mmol, 1.0 eq) dropwise at -78 °C. The resulting reaction mixture was stirred for 4 h at the same temperature, then gradually warmed up to room temperature and stirred for 12 h. To the resulting reaction mixture was added acetaldehyde (126 μL, 2.3 mmol, 5.0 eq) at 0 °C. After stirring for 15 min, NaOH aq. (200 μL) and H_2O_2 (126 μL, 2.3 mmol, 5.0 eq) were added. After stirring for 30 min, H_2O was added to the reaction mixture and extract with Et_2O. The combined Et_2O extracts were washed with brine, dried over Na_2SO_4 and concentrated after filtration to give the crude product. The residual crude was purified by silica gel column chromatography (Hexane/EtOAc = 20/1 to 10/1) to give the product **S15** (95 mg, 0.34 mmol, 75% yield) as a colorless oil.



S15

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.8 Hz, 2H), 7.31-7.28 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 6.9 Hz, 1H), 4.33 (s, 2H), 4.09 (d, *J* = 6.9 Hz, 1H), 0.92 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 137.8, 128.4, 128.2, 127.5, 124.4, 66.6, 59.6 (t, *J* = 22.4 Hz), 25.9, 18.4, -5.4; IR (ATR, cm^{-1}): 3349, 3057, 2954, 2928, 2856, 1494, 1471, 1255, 1127, 1006, 837, 795, 777, 696; HRMS (ESI+) Calcd for $C_{16}H_{25}DNaO_2Si$, ([M + Na]$^+$) 302.1663, Found, 302.1657. Enantiomeric purity was determined by ^{1}H NMR analysis of the mosher's ester for **S15**.

(*S*, *E*)-2-phenylbut-2-ene-4-*d*-1,4-diol ((*S*)-*d*-S6): To an ice bath cooled solution of **S15** (84 mg, 0.3 mmol) in THF (1.5 mL) was added TBAF (450 μL, 0.45 mmol, 1.5 eq, 1 M in THF solution). The mixture was stirred at 0 °C for 1 h. Then the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography (Hexane/EtOAc = 4/1 to EtOAc only) to give the product (*S*)-*d*-**S6** (48.6 mg, 0.29 mmol, 98% yield) as a colorless oil.

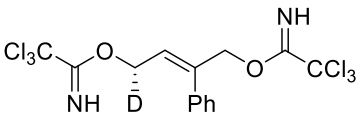


(*S*)-*d*-**S6**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.29 (m, 3H), 7.17 (d, *J* = 7.8 Hz, 2H), 5.93 (d, *J* = 6.6 Hz, 1H), 4.33 (s, 2H), 4.09 (d, *J* = 6.5 Hz, 1H), 2.49 (brs, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 137.3, 128.4, 128.3, 127.8, 125.8, 66.8, 59.4 (t, *J* = 21.7 Hz, 1C); IR (ATR, cm^{-1}): 3330, 2925, 2847, 1751, 1442, 1097, 1020, 991; HRMS (ESI+) Calcd for $C_{10}H_{11}DNaO_2$, ([M + Na]$^+$) 188.0798, Found, 188.0792.

(*E*)-2-phenylbut-2-ene-1,4-diyl-4-*d* bis(2,2,2-trichloroacetimidate) ((*S*)-*d*-1a): To a solution of (*S*)-*d*-**S6** (41 g, 0.25 mmol, 1.0 eq) in CH_2Cl_2 (1.3 mL) was added MS4 Å and DBU (8 μL, 0.05 mmol, 0.2 eq). The reaction mixture was cooled to 0 °C, then trichloroacetonitrile (63 μL, 0.63 mmol, 2.5 eq) was added and stirred for 2 h at the same

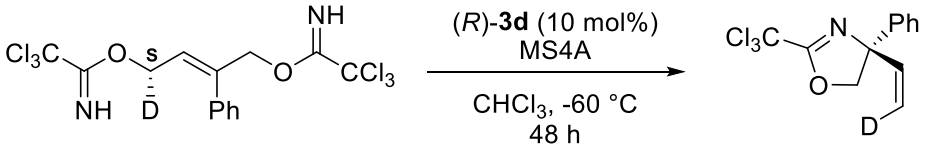
temperature. Then the reaction mixture was warmed to room temperature and concentrated. The residual crude was purified by flash column chromatography (Hexane/EtOAc = 20/1) to provide (*S*)-*d*-**1a** (91 mg, 0.2 mmol, 80% yield) as a colorless oil.



(*S*)-*d*-**1a**

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 8.27 (brs, 1H), 7.38-7.30 (m, 5H), 6.19 (d, *J* = 6.9 Hz, 1H), 5.07 (s, 2H), 4.78 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.4, 162.2, 141.0, 136.0, 128.4 (4C), 128.2, 122.9, 91.3, 91.2, 71.6, 66.0 (t, *J* = 22.4 Hz, 1C); IR (ATR, cm^{-1}): 3343, 3056, 3024, 2941, 1662, 1496, 1444, 1342, 1285, 1078, 986, 826; HRMS (ESI+) Calcd for $C_{14}H_{11}DCl_6N_2NaO_2$, ($[M + Na]^+$) 473.8990, Found, 473.8985.

7-1-2. Reaction of chiral deuterated substrate

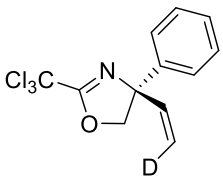


(*S*)-*d*-**1a**
0.05 mmol
>98% D
>98:2 er

(*Z*)-*d*-**2a**
90% yield, 93% ee
E/*Z* = 1/20

To a $CHCl_3$ (0.5 mL) solution of (*S*)-*d*-**1a** (24.3 mg, 0.05 mmol, 1.0 equiv.) and MS4A (25 mg) was added (*R*)-**3d** (5 mg, 0.05 mmol, 10 mol%) at -60 °C for 48 h. The reaction mixture was quenched with NEt_3 (10 μL) and directly purified by flash silica gel column chromatography (Hexane/EtOAc = 30/1 as eluent) to give (*Z*)-*d*-**2a** (14.6 mg, 90%).

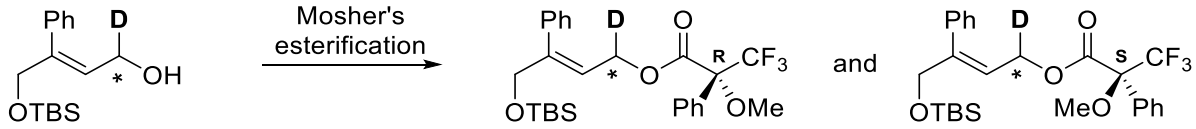
(*R*,*Z*)-4-phenyl-2-(trichloromethyl)-4-(vinyl-2-d)-4,5-dihydrooxazole ((*Z*)-*d*-2a):; HPLC analysis Chiralcel OD-3 (Hex:IPA = 99.8:0.2, 1.0 mL/min, 220 nm, 40 °C) 8.57 (minor), 9.29 (major) min, (93% ee); $[\alpha]^{23.7}_D$ = +29.9 (c = 0.3, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.33 (m, 4H), 7.32-7.28 (m, 1H), 6.20 (dm, *J* = 10.7 Hz, 1H), 5.30 (d, *J* = 10.7 Hz, 1H), 4.93 (d, *J* = 8.3 Hz, 1H), 4.66 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.1, 142.8, 139.7, 128.8, 127.7, 125.8, 115.0, 86.6, 81.1, 77.9; IR (ATR, cm^{-1}): 3057, 3026, 2927, 2859, 1727, 1662, 1494, 1448, 1266, 1220, 998, 814; HRMS (ESI+) Calcd for $C_{12}H_9DCl_3NO$, ($[M + H]^+$) 290.9969, Found, 290.9964.



(*Z*)-*d*-**2a**

7-1.3. Determination of absolute configuration of allylic alcohol **S10** by Mosher ester analysis[3].

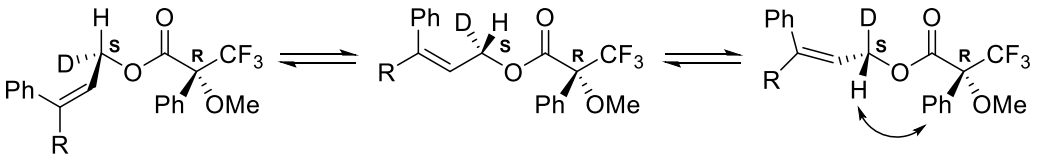
(*R*)- and (*S*)- MTPA esterification



S15

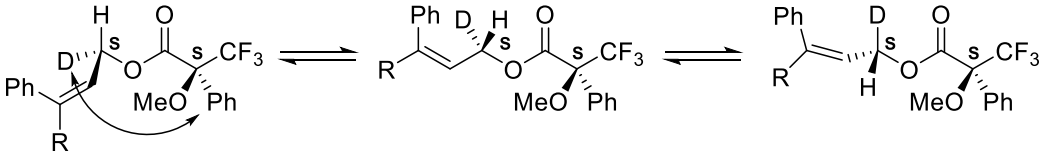
Mosher's conformational model for MTPA ester (The case of (***S***)-alcohol is shown)

(*R*)-MTPA ester



H shielded by Ph Group

(*S*)-MTPA ester



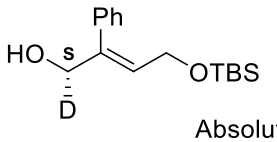
D shielded by Ph Group

R= CH_2OTBS

|| MTPA ester would be expected to exist in 60º rotation about the allylic C-O bond

^{1}H and ^{2}H NMR Chemical Shifts of MTPA Adducts

entry	compound	H δ (ppm)	D δ (ppm)
1	(*R*)-MTPA ester	4.725	4.789
2	(*S*)-MTPA ester	4.757	4.754
		Δ_{R-S} = -0.032	Δ_{R-S} = +0.035



H: $\Delta_{(R)\text{-ester} - (S)\text{-ester}}$ = < 0,

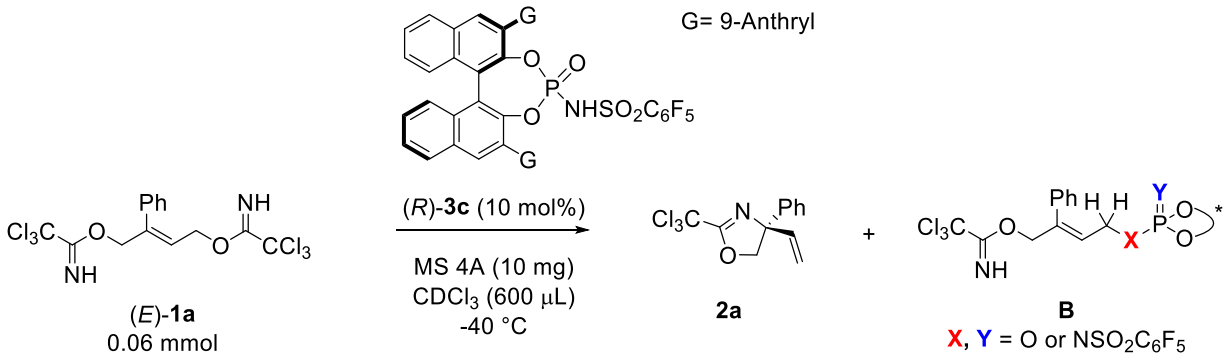
D: $\Delta_{(R)\text{-ester} - (S)\text{-ester}}$ = > 0

Absolute configuration is decided to ***S***-isomer.

|| This configration of the alcohol is in agreement with the absolute configuration derived from the expected stereoselectivity of the Alpine-Brane reduction[4].

7-2. Mechanistic study for phosphorimidate B

7-2-1. ^{31}P NMR monitoring of the reaction of **1a** catalyzed by **3c**



In $CDCl_3$ (0.6 mL), at -40 ºC, the reaction using **1a** (27 mg, 0.06 mmol, 1.0 equiv.) and (*R*)-**3c** (9.3 mg, 0.001 mmol), was monitored for 4 h by ^{31}P NMR. In this reaction, the formation of a new peak **B** was detected.

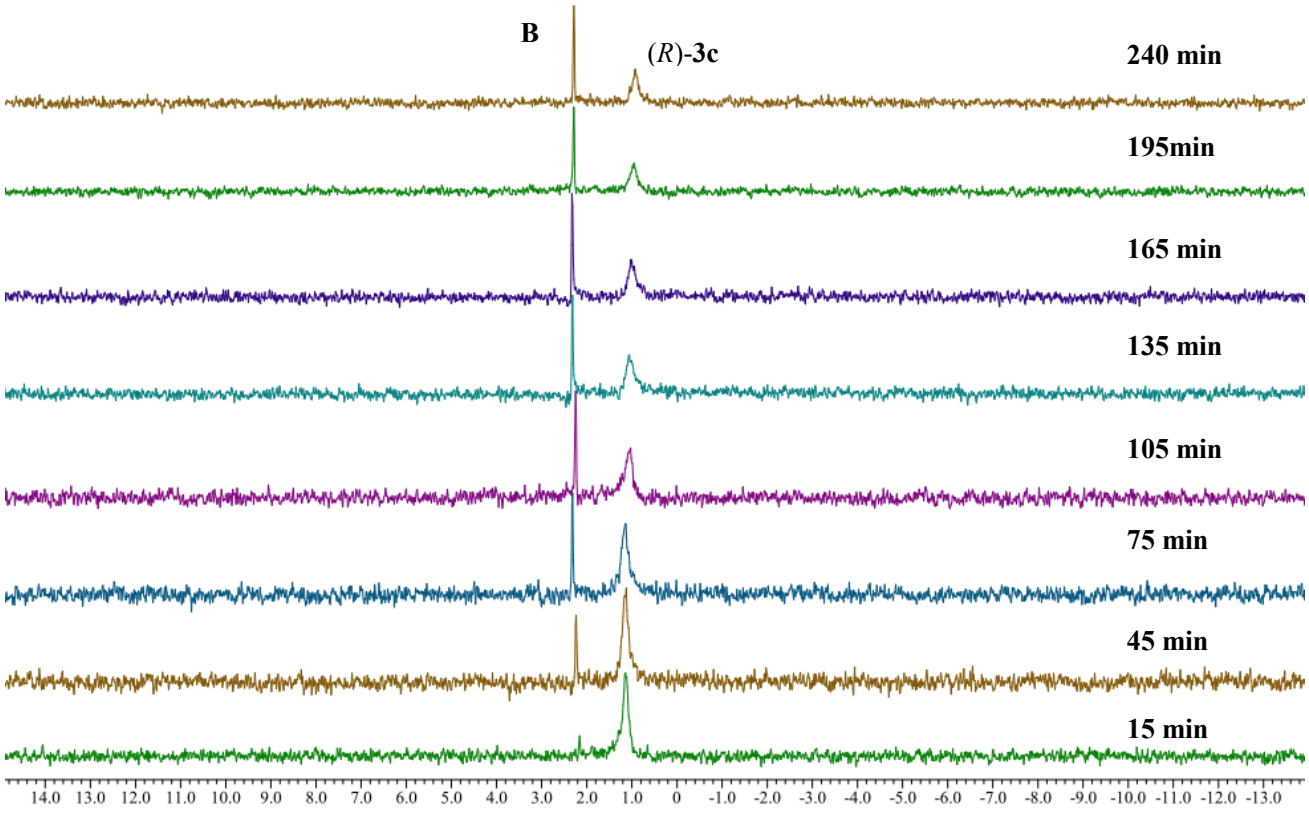


Figure 1. **NMR monitoring of reaction (^{31}P NMR)**

We also measured the ^{31}P NMR spectrum without ^{1}H decoupling in the presence of $PO(OMe)_3$ as an internal standard. As a result, formation of a new peak (dd, J = 16.4, 6.6 Hz)) which couples to two neighboring protons was observed. This result indicates that the S_N2 reaction of catalyst **3c** with **1a** at the terminal allylic position of the far side from Ph group proceeded.

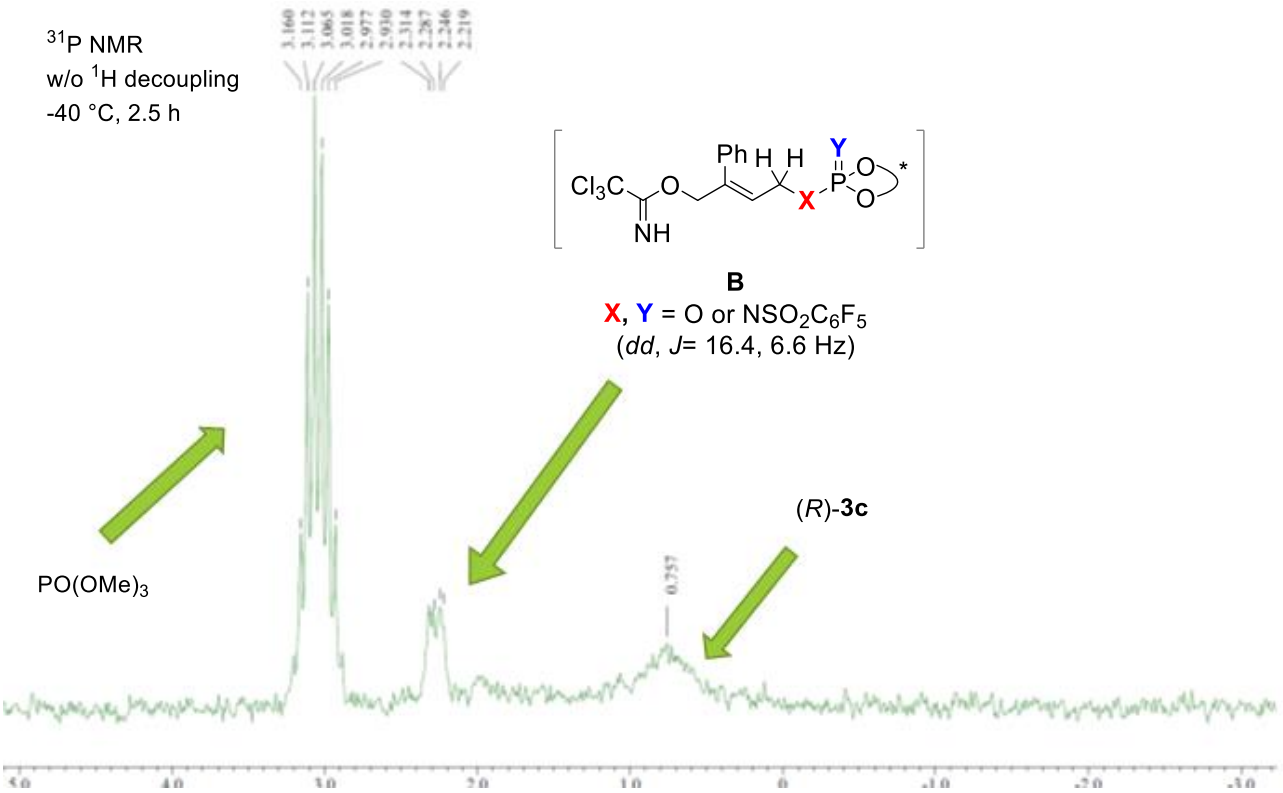
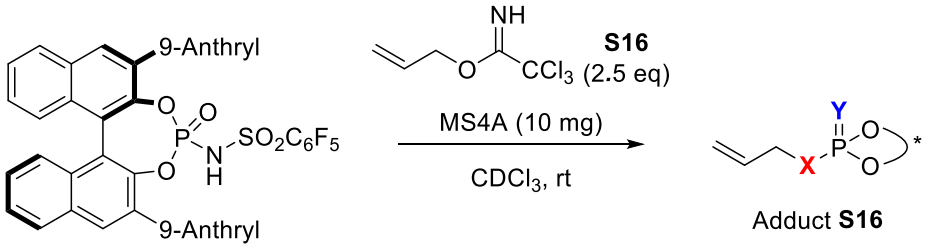


Figure 2. **^{31}P NMR spectrum w/o ^{1}H decoupling.**

7-2-2. Preparation of allyl phosphorimidate

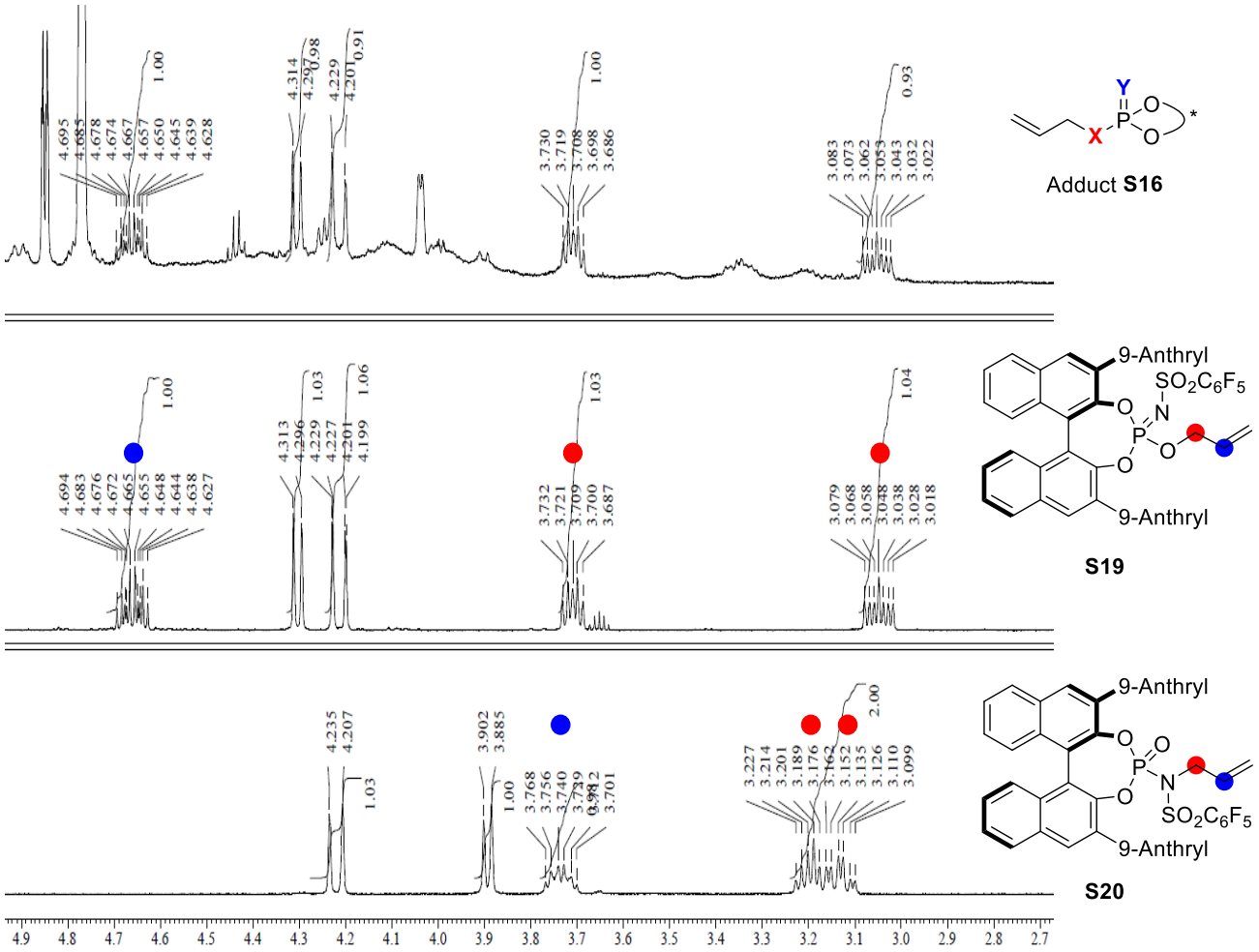


(*R*)-3c
(1.0 eq, 0.01 mmol)

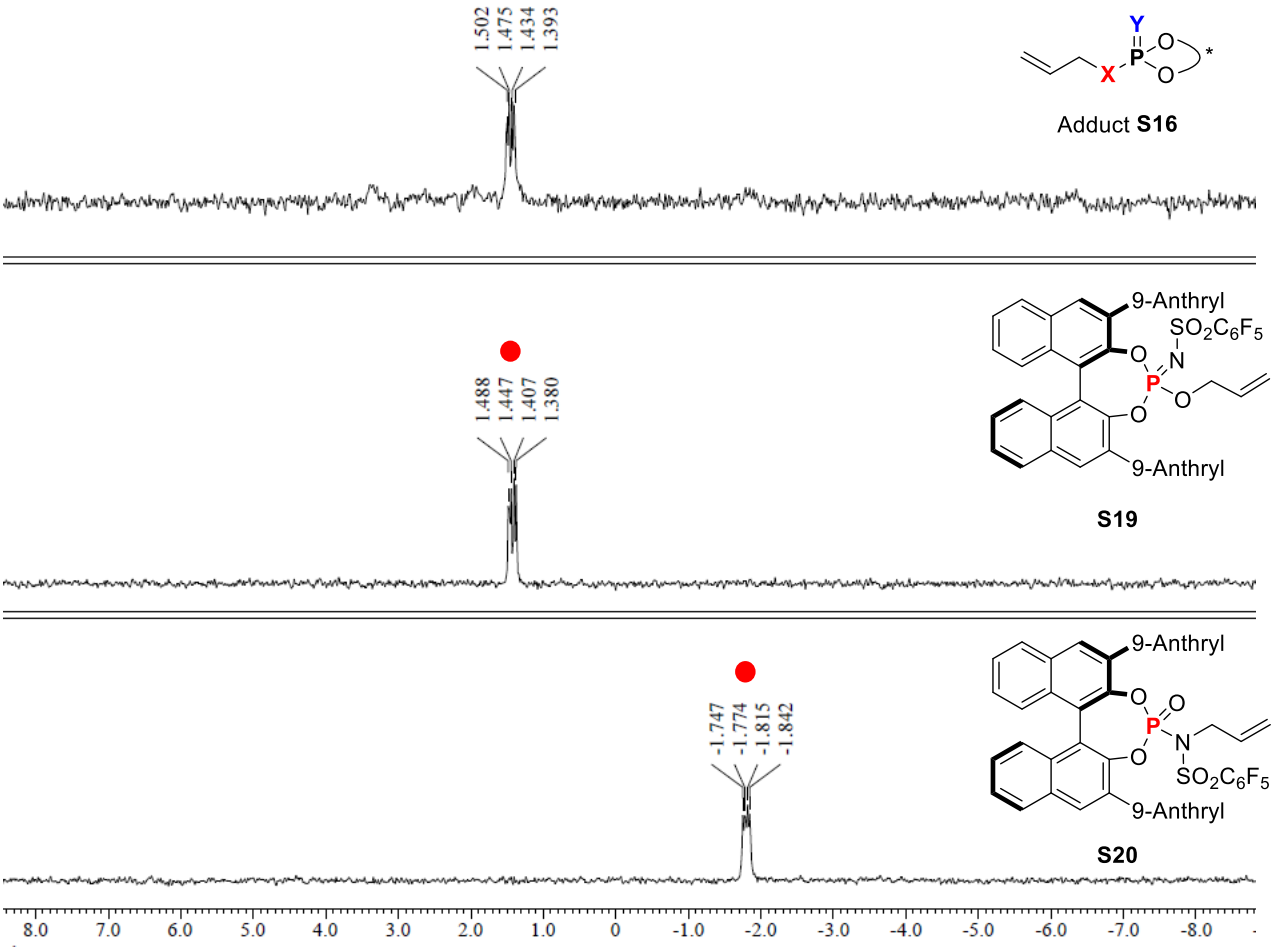
To determine the structure of phosphorimidate **B**, we prepared allyl phosphorimidate from the reaction of catalyst (*R*)-**3c** and allyltrichloroacetimidate **S16**.: **S16** (5 mg, 0.025 mmol, 2.5 equiv.) and dry $CDCl_3$ (0.6 mL) were added to an NMR tube, and then (*R*)-**3c** (9.3 mg, 0.01 mmol, 1.0 equiv.) was added at room temperature. The mixture was shaken for about 30 s and then was analyzed by ^{1}H and/or ^{31}P NMR. The result of the ^{1}H and/or ^{31}P NMR is consistent with the allyl phosphorimidate **S19**. Therefore, it was found that the phosphoryl oxygen attacks at the carbon having the leaving group to generate phosphorimidate in the S_N2 reaction process.

Figure 3. Comparing NMR spectrum of Adduct **S16** with allyl phosphorimidate **S19** and **S20**.

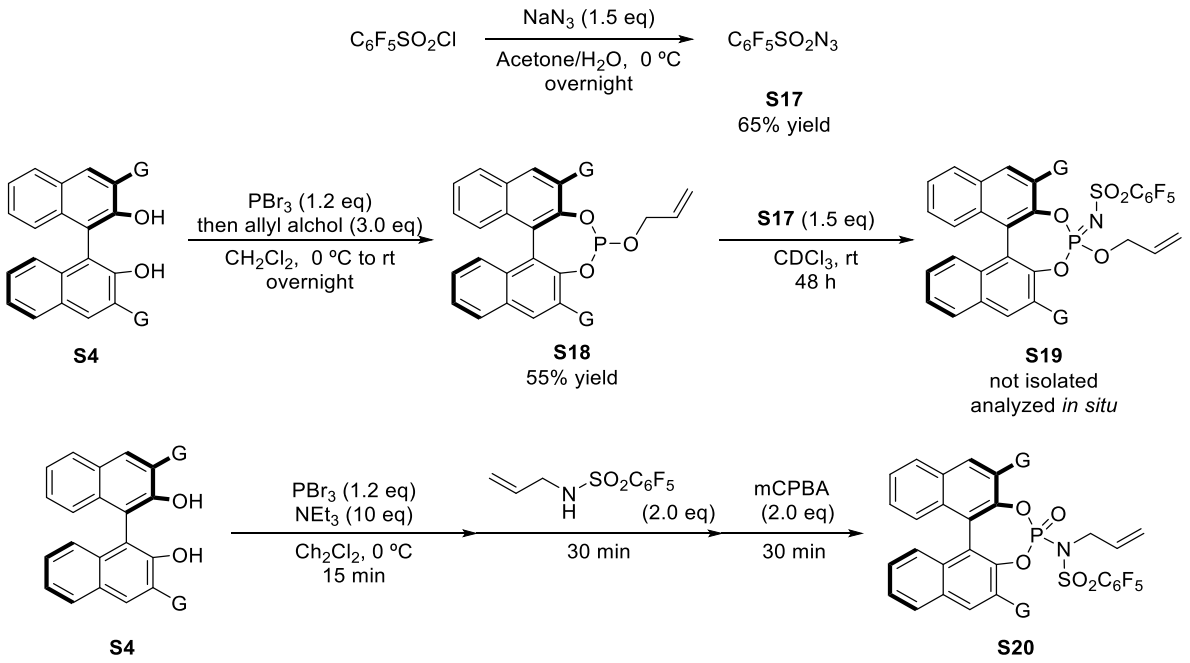
^{1}H NMR Spectra



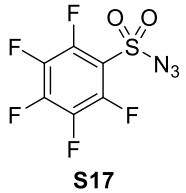
^{31}P NMR Spectra (w/o ^{1}H decoupling)



7-2-3. Procedure for the preparation of allyl phosphorimidate



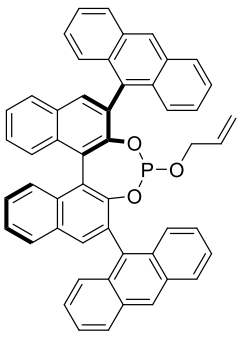
2,3,4,5,6-pentafluorobenzenesulfonyl azide (S17): To an ice bath cooled solution of sodium azide (39 mg, 0.6 mmol, 1.2 eq) in acetone (1 mL) and H_2O (1 mL) was added pentafluorobenzenesulfonyl chloride (74 μL, 0.5 mmol, 1.0 eq) dropwise. After the mixture was stirred at 0 °C for 12 h, sat. $NaHCO_3$ (1 mL) was added and acetone was removed under reduced pressure. Then the resulting aqueous phase was extracted with toluene. The residual crude was purified by silica gel column chromatography (Hexane/EtOAc = 50/1) to give the product **S17** (89 mg, 0.33 mmol, 66% yield) as a colorless oil.


S17

^{13}C NMR (151 MHz, $CDCl_3$): δ 145.5 (dm, J = 266 Hz, 1C), 144.9 (dm, J = 263 Hz, 2C), 138.1 (dm, J = 261 Hz, 2C), 115.1 (m, 1C); ^{19}F NMR (151 MHz, $CDCl_3$): δ -134.0 (m, 2F), -141.2 (m, 1F), -156.8 (m, 2F); IR(neat, cm^{-1}): 2144, 1644, 1501, 1398, 1306, 1178, 1103, 994.

S17 was unstable under the analysis conditions of HRMS

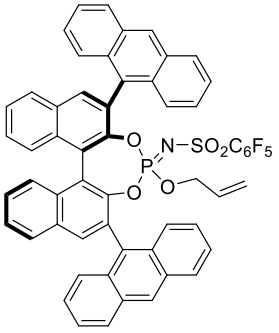
(*6s*,11bR)-4-(allyloxy)-2,6-di(anthracen-9-yl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine (S18): In a flame dried flask under N_2, **S4** (319 mg, 0.5 mmol, 1.0 equiv) and NEt_3 (1.2 mL, 8.5 mmol, 17 equiv) were dissolved in CH_2Cl_2 (10 mL, 0.05 M). The mixture was cooled to -78 °C and added PBr_3 (57 μL, 0.6 mmol, 1.2 equiv) dropwise. The mixture was gradually warmed up to room temperature and allyl alcohol (102 μL, 1.5 mmol, 3.0 equiv) was added. After the reaction mixture was stirred for 12 h, solvent was removed under reduced pressure. Then the residual crude was purified by flash column chromatography on silica gel (Hexane/Acetone = 20/1), to give the product **S18** (200 mg, 0.28 mmol, 55% yield) as a white solid.


S18

^1H NMR (600 MHz, $CDCl_3$): δ 8.47 (s, 2H), 8.06-7.17 (m, 26H), 4.56 (m, 1H), 4.09 (d, J =

10.7 Hz, 1H), 3.78 (d, *J* = 17.2 Hz, 1H), 2.82 (ddt, *J* = 17.0, 10.3, 4.8 Hz, 1H), 2.72 (tdm, *J* = 14.4, 5.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ 147.55, 147.06, 133.11, 132.95, 132.87, 132.84, 132.73, 131.85, 131.44, 131.34, 131.19, 131.09, 131.00, 130.93, 130.86, 130.73, 130.66, 130.43, 128.54, 128.37, 128.24, 128.12, 128.10, 128.07, 127.69, 127.42, 127.36, 127.07, 127.05, 126.98, 126.93, 126.86, 126.49, 126.37, 125.80, 125.75, 125.52, 125.42, 125.39, 125.31, 125.20, 125.09, 125.02, 124.95, 124.79, 123.73, 115.33, 63.91, 63.75, 22.86, one carbon was not found probably due to overlapping; ^{31}P NMR (151 MHz, $CDCl_3$): δ 153.8; IR(neat, cm^{-1}): 3052, 1444, 1402, 1233, 1085, 1014, 937, 866, 795; HRMS(ESI+): Calcd for $C_{51}H_{33}NaO_3P$, $[M+Na]^+$, 747.2065; found, 747.2060.

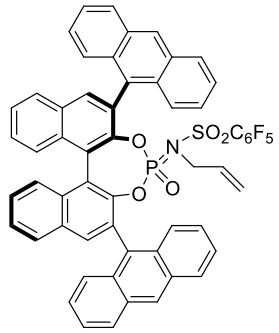
***N*-((*2r*,11b*R*)-4-(allyloxy)-2,6-di(anthracen-9-yl)-4l5-dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-ylidene)-2,3,4,5,6-pentafluorobenzenesulfonamide (S19): S18** (7.2 mg, 0.01 mmol, 1.0 equiv.) and dry $CDCl_3$ (0.6 mL) were added to an NMR tube, and then **S17** (4.1 mg, 0.015 mmol, 1.5 equiv.) was added at room temperature. The mixture was left for 2 days and then was analyzed. **S19** was unstable on the purification conditions.



S19

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.53 (s, 1H), 8.50 (s, 1H), 8.17 (s, 2H), 8.08-7.20 (m, 24H), 4.63 (m, 1H), 4.30 (dm, *J* = 10.3 Hz, 1H), 4.21 (ddm, *J* = 17.5, 1.4 Hz, 1H), 3.71 (m, 1H), 3.05 (dddm, *J* = 18.2, 10.2, 6.2 Hz, 1H); ^{31}P NMR (151 MHz, $CDCl_3$): δ 1.43; IR(neat, cm^{-1}): 3053, 2145, 1494, 1445, 1402, 1329, 1253, 1200, 1164, 1097, 1034, 988, 915, 795, 733.; HRMS(ESI+): Calcd for $C_{57}H_{33}F_5NNaO_5PS$, $[M+Na]^+$, 992.1635; found, 992.1629.

***N*-allyl-*N*-((*2r*,11b*R*)-2,6-di(anthracen-9-yl)-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)-2,3,4,5,6-pentafluorobenzenesulfonamide (S20):** To a solution of **S4** (64 mg, 0.1 mmol, 1.0 equiv) and NEt_3 (70 μL, 0.5 mmol, 5.0 equiv) in CH_2Cl_2 (1.0 mL, 0.1 M) was added PBr_3 (11.4 μL, 0.12 mmol, 1.2 equiv) at 0 °C. After stirring for 30 min, *N*-allyl-pentafluorobenzenesulfonamide (52 mg, 0.2 mmol, 2.0 equiv) was added. After 1 hour, the mixture was filtered through a pad of silica with CH_2Cl_2 and the solvent was removed in vacuo. Then the resulting material was dissolved in CH_2Cl_2 (1.0 mL, 0.1 M) and treated with *m*CPBA (49 mg, 0.2mmol, 2.0 eq). After 15 min, the crude mixture was directly purified by flash column chromatography on silica gel (Hexane/EtOAc = 20/1) to give the product **S20** (9.7 mg, 0.1 mmol, 10% yield) as a white solid.

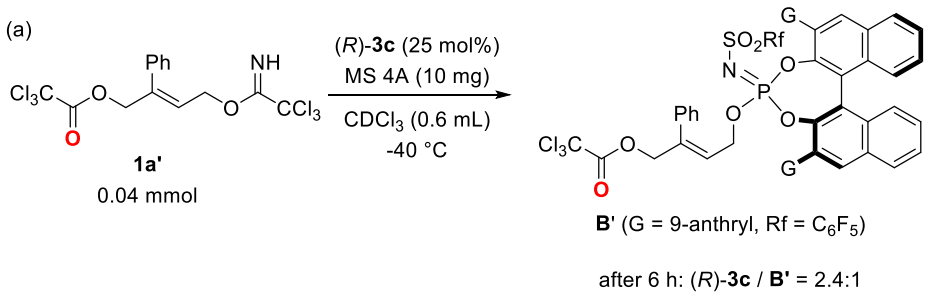


S20

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.56 (s, 1H), 8.51 (s, 1H), 8.20-7.16 (m, 26H), 4.22 (dm, *J* = 16.8. Hz, 1H), 3.89 (d, *J* = 10.0 Hz, 1H), 3.73 (m, 1H), 3.20 (m, 1H), 3.13 (td, *J* = 15.6, 6.2 Hz, 1H); ^{31}P NMR (151 MHz, $CDCl_3$): δ -1.79; IR(neat, cm^{-1}): 3013, 1520, 1497, 1385, 1309, 1228, 1177, 1100, 992, 956, 905, 794; HRMS(ESI+): Calcd for $C_{57}H_{33}F_5NNaO_5PS$, $[M+Na]^+$, 992.1635; found, 992.1629.

7-2-4. Control experiment using substrate **1a'**

In order to further investigate whether phosphorimidate **B** is a reactive intermediate or not, we employed substrate **1a'**, which does not undergo the cyclization reaction but transforms into phosphorimidate **B'** under catalytic conditions. The formation rate of **B'** was monitored by ^{31}P and ^{1}H NMR measurement and compared with that of the actual catalytic reaction. (*R*)-**3c** was partially transformed into phosphorimidate **B'** and still remained in the (*R*)-**3c** / **B'** ratio = 2.4:1 even after 6 h at −40 °C, despite use of a larger amount of (*R*)-**3c** (25 mol%) than that in the optimized reaction conditions (10 mol%). In contrast, in the actual reaction of **1a** catalyzed by (*R*)-**3c** (10 mol%) at −40 °C, most of substrate **1a** was consumed to afford corresponding product **2a** in 88% yield after 2.5 h. Based on the result obtained in the actual reaction (2.5 h, 88% yield), most of (*R*)-**3c** should be transformed into phosphorimidate **B'**, which would accumulate during the NMR monitoring of the reaction of **1a'** catalysed by (*R*)-**3c** for 6 h, because further cyclization, i.e., the consumption of **B'**, does not occur in this case. Consequently, the formation of **B'** is much slower than that of **2a** in the actual reaction. These results also suggest that phosphorimidate **B** is not the active intermediate in the present reaction.



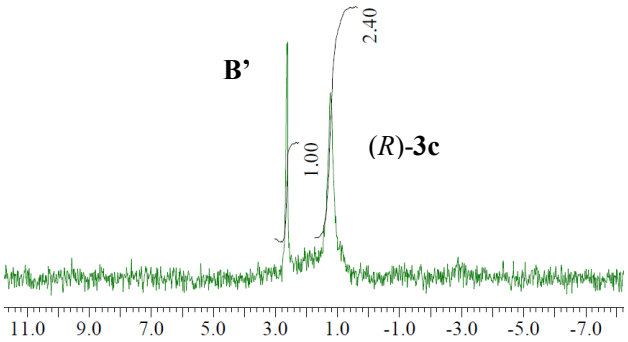
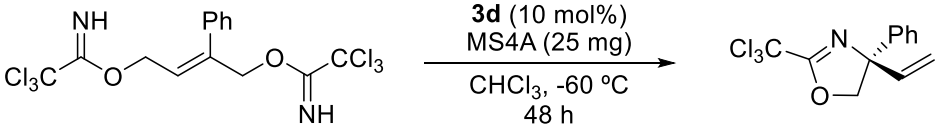


Figure 4. ^{31}P NMR spectrum of **1a'** under the influence of (*R*)-**3c** at −40 ºC after 6 h: Monitoring the formation of phosphorimidate **B'**.

7-3. Non linear effect (NLE) experiments



1a **2a**

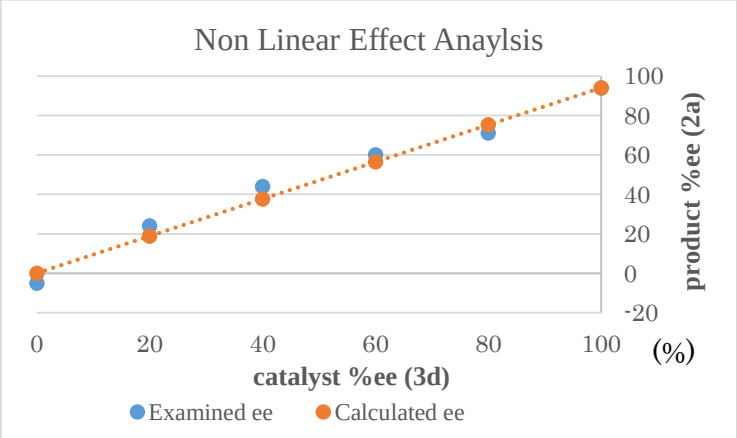
To a $CHCl_3$ (0.5 mL) solution of **1a** (45 mg, 0.05 mmol, 1.0 equiv.) and MS4A (25 mg) was added **3d** (5 mg, 0.005 mmol, 10 mol%, mixtures of two enantiomers determined by weight) at -60 °C and stirred for 48 h. The reaction mixture was quenched with NEt_3 (10 μL) and directly purified by flash silica gel column chromatography to give **2a**. The enantiomeric excess of **2a** was determined by chiral stationary phase HPLC analysis.

As a result, linear relationship between ee of **3d** (%) and ee of **2a** (%) was observed and hence this result strongly suggests that one catalyst molecule is involved in the reaction.

Table S3

entry	ee of **3d** (%)	ee of **2a**	Calculated ee
1	0	-5	0
2	20	24	18.8
3	40	44	37.6
4	60	60	56.4
5	80	71	75.2
6	100	94	94
7	-100	-91	-91

Figure 5



7-4. Effect of additive

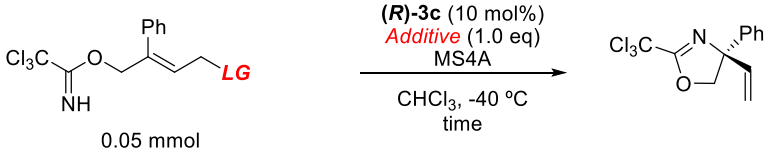
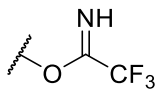
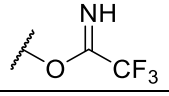
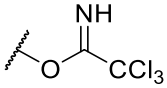
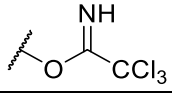
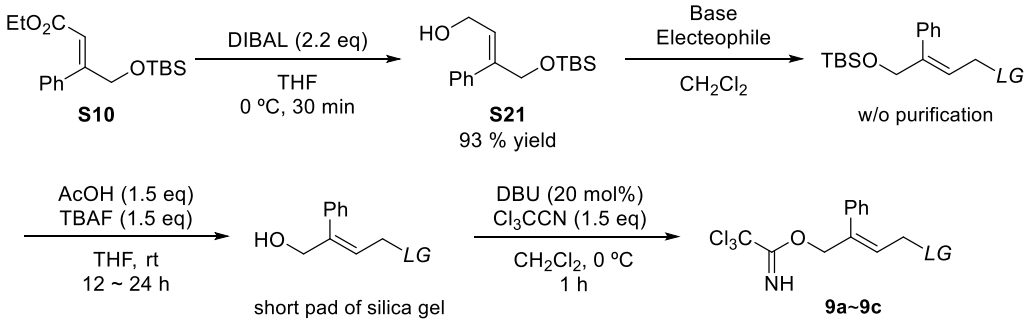


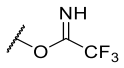
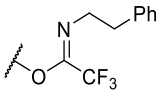
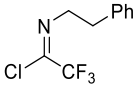
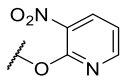
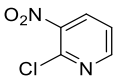
Table S4

entry	***LG***	*time*	***Additive***	*yield*	*ee*	*note*
1		18 h	None	90	60	
2		24 h	Cl_3CCONH_2	92	58	
3		24 h	None	92	83	5 mol% of catalyst
4		24 h	F_3CCONH_2	92	78	5 mol% of catalyst

7-5. Synthesis of the other substrate

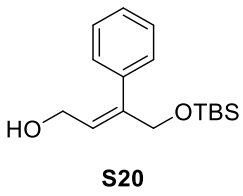
7-5-1. Preparation of substrate having a different leaving group.



entry	***LG***	*Base*	*Electrophile*	*Product* ***9***	*Yield (3 steps from S21)*
1		DBU (2.0 eq)	CF_3CN [a] (5.0 eq)	**9a**	40% yield
2		DBU (2.0 eq) DMAP (0.3 eq)	 (1.4 eq)	**9b**	40% yield
3		NaH (1.2 eq)	 (1.2 eq)	**9c**	75% yield

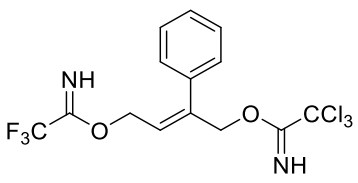
[a] *in situ* generated.

(*E*)-4-((tert-butyldimethylsilyl)oxy)-3-phenylbut-2-en-1-ol (S20) : colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35-7.28 (m, 3H), 7.16-7.15 (m, 2H), 5.98 (t, 6.9 Hz, 1H), 4.34 (s, 2H), 4.10 (d, 6.9 Hz, 2H), 0.92 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (151 MHz, $CDCl_3$) δ143.1, 137.7, 128.4, 128.2, 127.5, 124.4, 66.5, 59.8, 25.9, 18.4, -5.4; IR (ATR, cm^{-1}): 3359, 3058, 2954, 2928, 2856, 1494, 1472, 1256, 1128, 1097, 1054, 1005, 837, 778, 701; HRMS (ESI+) Calcd for $C_{16}H_{26}NaO_2Si$, ([M + Na]$^+$) 301.1600, Found, 301.1594.



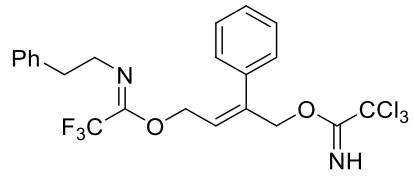
S20

(*E*)-3-phenyl-4-(2,2,2-trichloro-1-iminoethoxy)but-2-en-1-yl 2,2,2-trifluoroacetimidate (9a) : 40% yield (3 steps); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (bs, 1H), 8.14 (bs, 1H), 7.39-7.27 (m, 5H), 6.15 (t, *J* = 6.9 Hz, 1H), 5.06 (s, 2H), 4.76 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 157.6 (q, 38 Hz, 1C), 141.2, 135.9, 128.5, 128.4, 128.3, 122.5, 115.5 (q, 280 Hz, 1C), 91.2, 71.6, 64.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -74.3 (s); IR (ATR, cm^{-1}): 3342, 3060, 2933, 1685, 1663, 1496, 1444, 1300, 1197, 1165, 1071, 1013, 988, 827, 796, 701, 648; HRMS (ESI+) Calcd for $C_{14}H_{12}Cl_3F_3N_2NaO_2$, ([M + Na]$^+$) 424.9814, Found, 424.9809.



9a

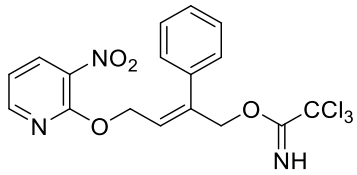
(*E*)-3-phenyl-4-(2,2,2-trichloro-1-iminoethoxy)but-2-en-1-yl-2,2,2-trifluoro-*N*-phenethylacetimidate (9b) :



9b

40% yield (3 steps); yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.39 (bs, 1H), 7.42-7.17 (m, 10H), 6.11 (t, *J* = 6.9 Hz, 1H), 5.06 (s, 2H), 4.62 (d, *J* = 6.9 Hz, 2H), 3.73 (tm, *J* = 7.4 Hz, 2H), 2.84 (t, *J* = 7.2 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.3, 145.8 (q, 35 Hz, 1C), 140.1, 139.6, 136.3, 128.9, 128.45, 128.39, 128.27, 128.1, 126.2, 124.0, 116.0 (q, 286 Hz, 1C), 91.2, 71.9, 63.7, 48.8, 37.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.9 (s); IR (ATR, cm^{-1}): 3344, 3063, 3027, 2947, 1703, 1664, 1496, 1455, 1307, 1195, 1149, 1062, 779, 700; HRMS (ESI+) Calcd for $C_{22}H_{20}Cl_3F_3N_2NaO_2$, ([M + Na]$^+$) 529.0440, Found, 529.0435.

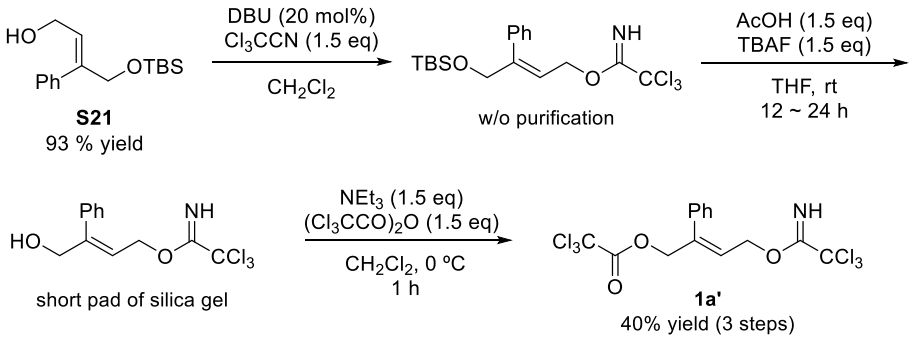
(*E*)-4-((3-nitropyridin-2-yl)oxy)-2-phenylbut-2-en-1-yl 2,2,2-trichloroacetimidate (9c) : 75% yield (3 steps);



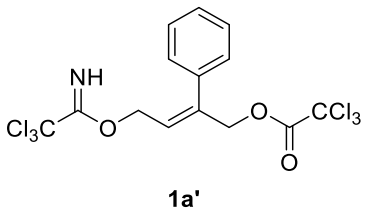
9c

yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (bs, 1H), 8.31 (dd, *J* = 4.8, 1.7 Hz, 1H), 8.24 (dd, *J* = 7.9, 2.1 Hz, 1H), 7.40-7.32 (m, 5H), 7.01 (dd, *J* = 7.9, 4.8 Hz, 1H), 6.26 (tm, *J* = 6.9 Hz, 1H), 5.07 (s, 2H), 5.02 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4, 154.9, 150.5, 139.6, 135.4, 134.1, 133.2, 127.6, 127.5, 127.2, 123.1, 115.6, 90.3, 70.9, 63.6; IR (ATR, cm^{-1}): 3336, 3081, 2955, 1664, 1602, 1571, 1525, 1464, 1438, 1349, 1299, 1247, 1091, 976, 828, 797, 763, 702, 647; HRMS (ESI+) Calcd for $C_{17}H_{14}Cl_3N_3NaO_4$, ([M + Na]$^+$) 451.9948, Found, 451.9942.

7-5-2. Preparation of substrate **1a'**.



(*E*)-2-phenyl-4-(2,2,2-trichloro-1-iminoethoxy)but-2-en-1-yl 2,2,2-trichloroacetate (1a') : 75% yield (3 steps);



1a'

yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (bs, 1H), 7.40-7.26 (m, 5H), 6.18 (t, *J* = 6.7 Hz, 1H), 5.11 (s, 2H), 4.78 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ162.4 161.5, 139.7, 135.3, 128.7, 128.6, 128.3, 125.0, 91.2, 89.6, 71.5, 66.0; IR (ATR, cm^{-1}): 3340, 3058, 3027, 2954, 1766, 1663, 1496, 1444, 1292, 1222, 1073, 980, 826, 796, 701, 680, 671, 650; HRMS (ESI+) Calcd for $C_{14}H_{11}C_{l6}NNaO_3$, ([M + Na]$^+$) 437.8768, Found, 437.8762.

8. DFT Calculation

8-1. Full citation of reference 28.

Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.

8-2. Energy profile of the *syn*-S_N2' pathway

The theoretical calculation of the *syn*-S_N2' mechanism was conducted. As expected, the energy barrier of the *syn*-S_N2' was much higher than that of *anti*-S_N2' mechanism of which pathway was supported by experimental and theoretical studies.

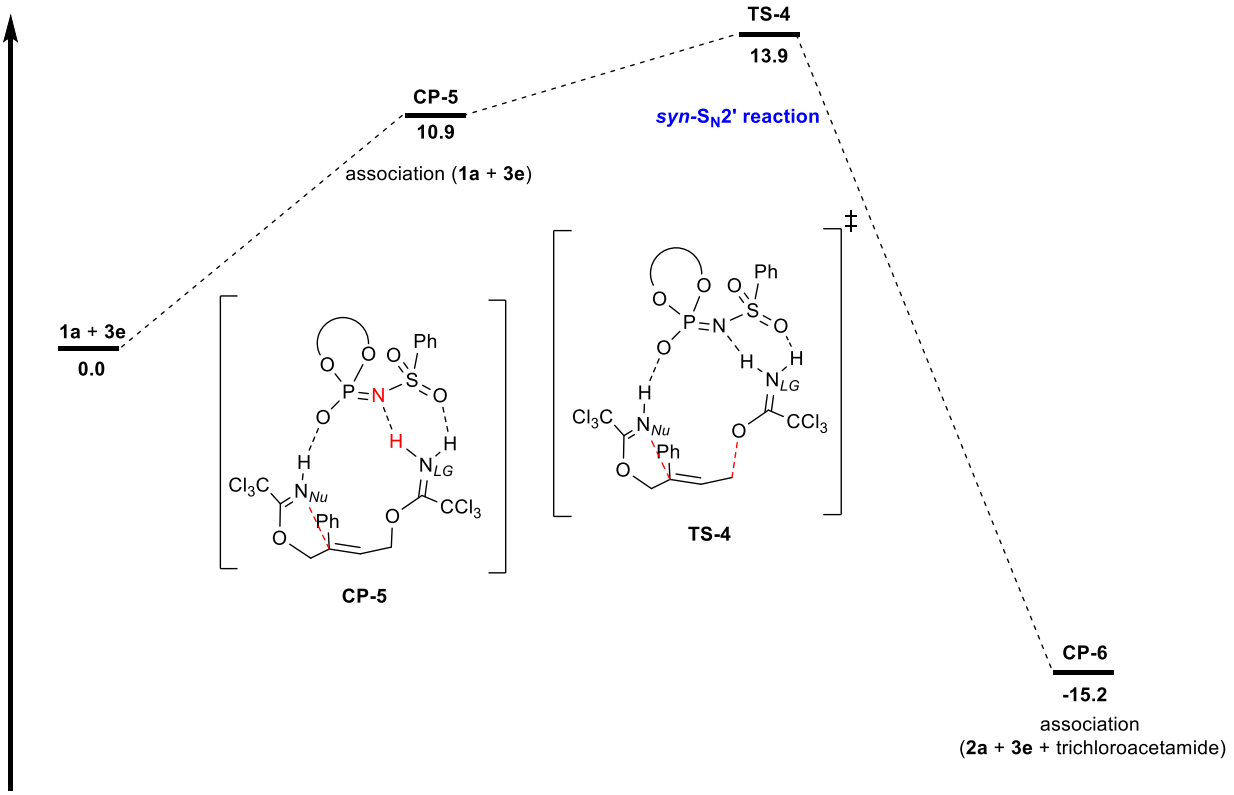


Figure 6. The potential energy for the sum of **1a** and **3e** was set to zero. Geometries were optimized and characterized using frequency calculations at the B97D/6-31G(d) level. Gibbs free energies (kcal/mol) in solution phase were calculated using single-point energy calculations at the same level as those for the optimized structures according to the SCRF method based on PCM ($CHCl_3$).

8-3. 3D structures of the transition states from different angle

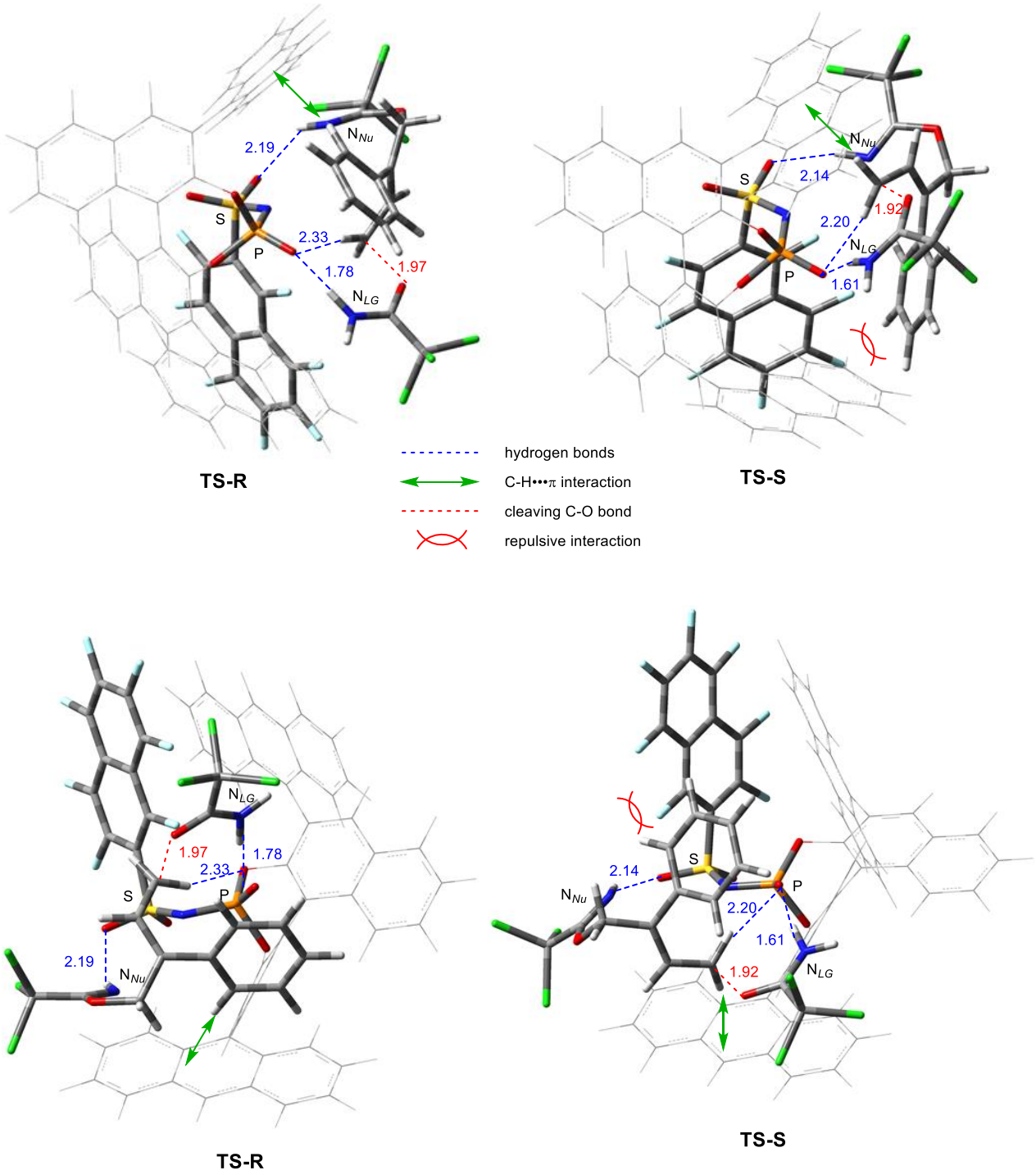


Figure 7. Transition states of synchronous *anti*-S_N2' reaction of **1a** catalyzed by (*R*)-**3d**. Geometries were optimized and characterized using frequency calculations at the B97D/6-31G(d) level.

8-4. Cartesian coordinates

1a

B97D/6-31g(d); E(RB97D) = -3561.263761 hartree
Sum of electronic and thermal Free Energies= -3561.089553 hartree
Thermal correction to Gibbs Free Energy= 0.174208 hartree
pcm(chloroform e)/B97D/6-31g(d); E(RB97D) = -3561.270674 hartree
Gibbs Free Energy in toluene = -3561.096466 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.672131	0.125626	-0.623392
2	1	0	-1.619734	1.222188	-0.585305
3	1	0	-1.641403	-0.177425	-1.683794
4	6	0	-0.620356	-0.547616	0.203201
5	1	0	-0.812833	-1.599715	0.428119
6	6	0	0.502963	0.026015	0.690556
7	8	0	2.794469	-0.699609	1.259432
8	6	0	3.169625	-1.340591	0.136905
9	7	0	2.412837	-2.131851	-0.511662
10	1	0	2.882789	-2.521973	-1.331969
11	6	0	4.639492	-0.908884	-0.196984
12	17	0	5.271480	-1.807223	-1.644037
13	17	0	4.654607	0.865959	-0.559771
14	17	0	5.723687	-1.265403	1.214820
15	6	0	0.948686	1.406733	0.379936
16	6	0	1.502468	2.238030	1.379650
17	6	0	0.875246	1.903070	-0.940325
18	6	0	1.937250	3.532574	1.074025
19	1	0	1.588001	1.869590	2.402938
20	6	0	1.311466	3.199104	-1.247898
21	6	0	1.841732	4.019431	-0.240720
22	1	0	2.355393	4.162271	1.861776
23	1	0	1.249455	3.560992	-2.276006
24	1	0	2.187425	5.027321	-0.478517
25	6	0	1.382614	-0.784884	1.621866
26	1	0	1.375477	-0.372892	2.640556
27	1	0	1.072729	-1.838272	1.644002
28	8	0	-2.960187	-0.308275	-0.078220
29	6	0	-4.048843	0.145160	-0.720023
30	7	0	-3.997416	0.906845	-1.739808
31	1	0	-4.929141	1.144055	-2.088305
32	6	0	-5.316413	-0.422918	0.007449
33	17	0	-6.842327	0.132947	-0.801798
34	17	0	-5.331432	0.156640	1.727424
35	17	0	-5.271313	-2.237778	-0.032881
36	1	0	0.506893	1.249492	-1.732240

(*R*)-3e

B97D/6-31g(d); E(RB97D) = -2325.734857 hartree
Sum of electronic and thermal Free Energies= -2325.355693 hartree
Thermal correction to Gibbs Free Energy= 0.379163 hartree
pcm(chloroform e)/B97D/6-31g(d); E(RB97D) = -2325.747753 hartree
Gibbs Free Energy in toluene = -2325.36859 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.527527	-2.693513	2.284727
2	6	0	2.868988	-2.397171	2.550525
3	6	0	0.938736	-2.324473	1.057873
4	6	0	3.636698	-1.704874	1.605557
5	6	0	3.093819	-1.323056	0.362875
6	6	0	1.755711	-1.681572	0.106044
7	1	0	4.672860	-1.441194	1.822539
8	6	0	-0.496067	-2.594913	0.793129
9	6	0	-1.061898	-3.837025	1.148676
10	6	0	-1.343399	-1.632525	0.197063
11	6	0	-2.412198	-4.107025	0.903212
12	6	0	-2.706622	-1.877202	-0.076743
13	6	0	-3.219360	-3.140053	0.292299
14	1	0	-4.274081	-3.344062	0.102806
15	8	0	1.217979	-1.398911	-1.157928
16	15	0	0.200500	-0.126734	-1.322507
17	8	0	-0.834326	-0.351336	-0.078882
18	8	0	-0.289266	-0.019835	-2.715806
19	7	0	0.940969	1.293149	-0.755020
20	16	0	1.122285	1.972423	0.830547
21	8	0	1.912892	3.189846	0.569405
22	8	0	1.566958	0.959557	1.799541
23	6	0	-0.572946	2.431900	1.250838
24	6	0	-1.218330	3.412157	0.483346
25	6	0	-1.184106	1.834091	2.360913
26	6	0	-2.514836	3.802274	0.844026
27	6	0	-2.482657	2.235109	2.709841
28	6	0	-3.145193	3.216523	1.955366
29	1	0	1.544911	1.773596	-1.422336
30	6	0	-3.592374	-0.888890	-0.749908
31	6	0	-3.624463	0.471774	-0.375233
32	6	0	-4.456863	-1.328811	-1.776328
33	6	0	-4.499872	1.361453	-1.010628
34	1	0	-2.975618	0.829882	0.420233
35	6	0	-5.328550	-0.435708	-2.412955
36	1	0	-4.421837	-2.374085	-2.089027
37	6	0	-5.353680	0.914727	-2.031367
38	1	0	-4.510618	2.408099	-0.701736
39	1	0	-5.979989	-0.793169	-3.213108
40	1	0	-6.029609	1.613407	-2.528946
41	6	0	3.867657	-0.469427	-0.576531
42	6	0	4.511063	0.681254	-0.070818
43	6	0	3.944902	-0.740069	-1.959795
44	6	0	5.206160	1.546072	-0.927410
45	1	0	4.419112	0.915390	0.990143
46	6	0	4.644499	0.123871	-2.813705
47	1	0	3.453057	-1.624673	-2.362113
48	6	0	5.274261	1.270966	-2.302433
49	1	0	5.678646	2.442615	-0.521500
50	1	0	4.695513	-0.099325	-3.881373
51	1	0	5.809787	1.947203	-2.972046
52	1	0	-2.834943	-5.074035	1.181116
53	1	0	-0.417453	-4.592879	1.599766
54	1	0	0.909570	-3.188049	3.035840
55	1	0	3.310696	-2.684086	3.506310
56	1	0	-0.652486	1.068491	2.924000
57	1	0	-0.715954	3.857533	-0.375074
58	1	0	-3.031869	4.563365	0.257429
59	1	0	-4.156886	3.521046	2.228741
60	1	0	-2.977171	1.775379	3.566961

trichloroacetamide

B97D/6-31g(d); E(RB97D) = -1587.869667 hartree
Sum of electronic and thermal Free Energies= -1587.860456 hartree
Thermal correction to Gibbs Free Energy= 0.009211 hartree
pcm(chloroform e)/B97D/6-31g(d); E(RB97D) = -1587.875766 hartree
Gibbs Free Energy in toluene = -1587.866555 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.562369	1.705583	0.002735
2	6	0	-1.298316	0.517199	0.002280
3	6	0	0.214664	-0.000455	0.000362
4	17	0	0.491488	-1.023614	-1.492876
5	17	0	1.344283	1.373714	0.003498
6	17	0	0.494972	-1.033169	1.485673
7	1	0	-1.950273	-1.468087	-0.002364
8	1	0	-3.192708	-0.237774	-0.000168
9	7	0	-2.211254	-0.489586	0.003969

Sequential S_N2/syn-S_N2' pathway

CP-1

B97D/6-31g(d); E(RB97D) = -5887.028597 hartree
Sum of electronic and thermal Free Energies= -5886.448148 hartree
Thermal correction to Gibbs Free Energy= 0.580449 hartree
pcm(chloroform)/B97D/6-31g(d); E(RB97D) = -5887.046014 hartree
Gibbs Free Energy in toluene = -5886.465565 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.140672	-3.704202	-1.066066
2	6	0	6.240441	-2.840109	-1.010435
3	6	0	3.843184	-3.204527	-1.293476
4	6	0	6.057830	-1.460869	-1.169929
5	6	0	4.780354	-0.917019	-1.411145
6	6	0	3.695712	-1.813473	-1.492575
7	1	0	6.910814	-0.782804	-1.111347
8	6	0	2.669483	-4.113848	-1.331608
9	6	0	2.722111	-5.333033	-2.038162
10	6	0	1.459147	-3.782937	-0.681273
11	6	0	1.598175	-6.164079	-2.118650
12	6	0	0.298960	-4.580302	-0.775078
13	6	0	0.396365	-5.781842	-1.507651
14	1	0	-0.487224	-6.418063	-1.582058
15	8	0	2.436793	-1.309111	-1.807859
16	15	0	1.289900	-1.168455	-0.617285
17	8	0	1.415971	-2.638071	0.116754
18	8	0	-0.004423	-0.861620	-1.292126
19	7	0	1.759845	-0.096724	0.545061
20	16	0	2.729015	-0.427275	1.859902
21	8	0	2.950270	0.898873	2.504792
22	8	0	3.909922	-1.264485	1.556927
23	6	0	1.656240	-1.382874	2.967274
24	6	0	0.507544	-0.772085	3.490391
25	6	0	1.990973	-2.706624	3.279499
26	6	0	-0.323229	-1.509410	4.345261
27	6	0	1.150775	-3.435654	4.135922
28	6	0	-0.004022	-2.839651	4.668358
29	1	0	1.746778	1.419767	0.350034
30	6	0	-1.000260	-4.152396	-0.189275
31	6	0	-1.112416	-3.691887	1.140345
32	6	0	-2.162097	-4.203718	-0.988309
33	6	0	-2.354801	-3.290827	1.648830
34	1	0	-0.229832	-3.650324	1.775657
35	6	0	-3.401488	-3.791102	-0.479823
36	1	0	-2.078815	-4.541486	-2.023089
37	6	0	-3.503163	-3.326615	0.840896
38	1	0	-2.419630	-2.950958	2.684155

39	1	0	-4.288049	-3.830020	-1.115943
40	1	0	-4.466078	-2.995043	1.233583
41	6	0	4.598066	0.556066	-1.504702
42	6	0	5.227208	1.387061	-0.551230
43	6	0	3.834838	1.161293	-2.528002
44	6	0	5.121558	2.782337	-0.634214
45	1	0	5.775780	0.923395	0.269242
46	6	0	3.724138	2.557466	-2.604923
47	1	0	3.343478	0.532461	-3.269255
48	6	0	4.374905	3.374564	-1.665081
49	1	0	5.617427	3.407023	0.111603
50	1	0	3.142697	3.009713	-3.411825
51	1	0	4.299603	4.460955	-1.735548
52	1	0	1.652838	-7.102397	-2.673662
53	1	0	3.648546	-5.602352	-2.548184
54	1	0	5.269598	-4.776188	-0.906595
55	1	0	7.239316	-3.239643	-0.826806
56	1	0	2.886601	-3.148823	2.845399
57	1	0	0.263487	0.255694	3.224176
58	1	0	-1.219620	-1.043916	4.760181
59	1	0	-0.655298	-3.410639	5.332995
60	1	0	1.396962	-4.470048	4.382951
61	6	0	-0.104642	2.007406	-1.382270
62	1	0	-0.169358	1.468525	-0.436372
63	1	0	0.650777	1.551453	-2.029494
64	6	0	-1.436813	2.186772	-2.019334
65	1	0	-1.458801	2.374664	-3.095407
66	6	0	-2.595316	2.162643	-1.323860
67	8	0	-5.052713	1.823166	-1.492846
68	6	0	-5.067900	0.476819	-1.592896
69	7	0	-4.177325	-0.183553	-2.212091
70	1	0	-4.313999	-1.194868	-2.154349
71	6	0	-6.303970	-0.054192	-0.791674
72	17	0	-6.560101	-1.826620	-1.091848
73	17	0	-5.997136	0.209639	0.972194
74	17	0	-7.812107	0.822978	-1.299269
75	6	0	-2.691736	1.866422	0.131945
76	6	0	-3.225265	2.819460	1.024120
77	6	0	-2.287250	0.607361	0.620413
78	6	0	-3.321802	2.530205	2.391492
79	1	0	-3.554858	3.789845	0.646854
80	6	0	-2.393753	0.319973	1.988170
81	6	0	-2.905044	1.278459	2.876476
82	1	0	-3.726534	3.277970	3.076625
83	1	0	-2.077809	-0.658376	2.346416
84	1	0	-2.987338	1.052330	3.942259
85	6	0	-3.892491	2.501984	-2.040194
86	1	0	-4.149608	3.561880	-1.896851
87	1	0	-3.809870	2.281169	-3.114350
88	8	0	0.430318	3.400291	-1.062227
89	6	0	1.328738	3.509547	-0.126838
90	7	0	1.899325	2.528678	0.492165
91	1	0	2.576061	2.698597	1.237163
92	6	0	1.563464	4.999917	0.273790
93	17	0	3.025736	5.208696	1.309034
94	17	0	0.088669	5.490190	1.211462
95	17	0	1.733060	6.019986	-1.201925
96	1	0	-1.891408	-0.135078	-0.071645

TS-1

B97D/6-31g(d); E(RB97D) = -5887.019790 hartree
Sum of electronic and thermal Free Energies= -5886.437820 hartree
Thermal correction to Gibbs Free Energy= 0.581970 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.037161 hartree
Gibbs Free Energy in toluene = -5886.455191 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.850797	-4.120996	-0.982667
2	6	0	6.024889	-3.362633	-0.909596
3	6	0	3.608387	-3.502321	-1.227543
4	6	0	5.974462	-1.972308	-1.073353
5	6	0	4.757479	-1.311842	-1.332439
6	6	0	3.595046	-2.103233	-1.423192
7	1	0	6.885544	-1.375989	-1.002095
8	6	0	2.357144	-4.300723	-1.292973
9	6	0	2.314495	-5.517738	-2.004156
10	6	0	1.167282	-3.864943	-0.666934
11	6	0	1.122916	-6.244996	-2.111370
12	6	0	-0.058474	-4.553937	-0.789729
13	6	0	-0.052687	-5.758339	-1.524558
14	1	0	-0.986814	-6.314652	-1.618955
15	8	0	2.390239	-1.481911	-1.748263
16	15	0	1.246879	-1.241581	-0.572986
17	8	0	1.211155	-2.726724	0.140291
18	8	0	-0.015614	-0.862269	-1.305280
19	7	0	1.711172	-0.186036	0.576315
20	16	0	2.673734	-0.511037	1.884244
21	8	0	2.972289	0.814999	2.490419
22	8	0	3.802365	-1.427797	1.601310
23	6	0	1.567912	-1.375237	3.038702
24	6	0	0.584565	-0.641177	3.717322
25	6	0	1.703306	-2.758315	3.220228
26	6	0	-0.288581	-1.312255	4.586127
27	6	0	0.823431	-3.420368	4.090897
28	6	0	-0.174113	-2.701156	4.769913
29	1	0	1.904449	1.621545	0.325990
30	6	0	-1.328485	-4.016162	-0.230112
31	6	0	-1.423644	-3.521018	1.089255
32	6	0	-2.483443	-4.001348	-1.040778
33	6	0	-2.638224	-3.019112	1.574656
34	1	0	-0.548515	-3.532106	1.735714
35	6	0	-3.697117	-3.496459	-0.552800
36	1	0	-2.415478	-4.366457	-2.067220
37	6	0	-3.779294	-2.994756	0.755954
38	1	0	-2.689856	-2.651817	2.601352
39	1	0	-4.581283	-3.500209	-1.194450
40	1	0	-4.721441	-2.592798	1.132451
41	6	0	4.710278	0.171585	-1.431904
42	6	0	5.367215	0.947477	-0.452528
43	6	0	4.039587	0.834865	-2.483265
44	6	0	5.369194	2.347217	-0.531429
45	1	0	5.841844	0.440932	0.388135
46	6	0	4.038529	2.235254	-2.557526
47	1	0	3.531228	0.246074	-3.246314
48	6	0	4.708526	2.996977	-1.585681
49	1	0	5.876394	2.930953	0.239647
50	1	0	3.520825	2.733824	-3.380082
51	1	0	4.707045	4.086882	-1.645723
52	1	0	1.105492	-7.183649	-2.668180
53	1	0	3.223731	-5.867937	-2.495530
54	1	0	4.877470	-5.200527	-0.823990
55	1	0	6.979194	-3.853404	-0.710572
56	1	0	2.481621	-3.294515	2.679648
57	1	0	0.509910	0.435094	3.564330
58	1	0	-1.054472	-0.749616	5.124732
59	1	0	-0.855407	-3.219991	5.447262
60	1	0	0.917069	-4.498151	4.237537
61	6	0	-0.023966	1.573220	-1.455427
62	1	0	0.014646	1.403891	-0.387384
63	1	0	0.848314	1.319577	-2.047803
64	6	0	-1.281455	1.810414	-2.075872
65	1	0	-1.314421	1.883908	-3.164477
66	6	0	-2.442258	2.000312	-1.365475
67	8	0	-4.918060	1.957023	-1.565297
68	6	0	-5.049750	0.610155	-1.532330
69	7	0	-4.177380	-0.172970	-2.017871
70	1	0	-4.372852	-1.164459	-1.863330
71	6	0	-6.352957	0.254926	-0.746139
72	17	0	-6.820239	-1.474888	-1.027920
73	17	0	-6.009226	0.503646	1.016735
74	17	0	-7.738746	1.302449	-1.262176
75	6	0	-2.566553	1.844779	0.094543
76	6	0	-3.186648	2.852044	0.869838
77	6	0	-2.111223	0.663012	0.722267
78	6	0	-3.298835	2.702522	2.255630
79	1	0	-3.557030	3.757793	0.387485
80	6	0	-2.251314	0.510529	2.106246
81	6	0	-2.832368	1.530014	2.876481
82	1	0	-3.757382	3.494584	2.850327
83	1	0	-1.900594	-0.407363	2.574302
84	1	0	-2.931793	1.410673	3.957666
85	6	0	-3.677395	2.451742	-2.124805
86	1	0	-3.791227	3.544173	-2.056266
87	1	0	-3.604369	2.154620	-3.180865
88	8	0	0.755359	3.478285	-1.200551
89	6	0	1.575115	3.602360	-0.256319
90	7	0	2.098445	2.639108	0.476242
91	1	0	2.760169	2.812981	1.226416
92	6	0	1.921830	5.098482	0.121497
93	17	0	3.364596	5.265314	1.213743
94	17	0	0.456181	5.744981	0.978406
95	17	0	2.228723	6.038195	-1.383823
96	1	0	-1.675988	-0.131056	0.116968

INT-1

B97D/6-31g(d); E(RB97D) = -5887.043652 hartree
Sum of electronic and thermal Free Energies= -5886.464547 hartree
Thermal correction to Gibbs Free Energy= 0.579105 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.058441 hartree
Gibbs Free Energy in toluene = -5886.479336 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.557626	-3.364805	-0.845077
2	6	0	6.601680	-2.431885	-0.867452
3	6	0	4.233946	-2.965369	-1.123072
4	6	0	6.344357	-1.083645	-1.152024
5	6	0	5.041574	-0.638284	-1.450016
6	6	0	4.026087	-1.612002	-1.455264
7	1	0	7.153409	-0.352074	-1.137950
8	6	0	3.106883	-3.934587	-1.066461
9	6	0	3.244782	-5.221010	-1.629042
10	6	0	1.866694	-3.624201	-0.463203
11	6	0	2.185323	-6.135273	-1.602779
12	6	0	0.768898	-4.509278	-0.436949
13	6	0	0.961008	-5.778802	-1.023586
14	1	0	0.133569	-6.489365	-1.004205
15	8	0	2.716366	-1.215186	-1.800642
16	15	0	1.704649	-0.974490	-0.547144
17	8	0	1.715520	-2.398781	0.214958
18	8	0	0.312678	-0.817335	-1.297887
19	7	0	1.982347	0.225930	0.442889
20	16	0	2.950243	0.208265	1.802937

21	8	0	2.972457	1.608392	2.281810
22	8	0	4.226124	-0.509576	1.587396
23	6	0	1.974899	-0.763733	2.983534
24	6	0	0.796411	-0.210533	3.504639
25	6	0	2.410807	-2.045600	3.344603
26	6	0	0.038120	-0.967032	4.409475
27	6	0	1.640715	-2.793490	4.249011
28	6	0	0.456690	-2.256618	4.780349
29	1	0	1.669617	2.246072	0.062954
30	6	0	-0.555802	-4.130572	0.129557
31	6	0	-0.689656	-3.463536	1.368430
32	6	0	-1.726100	-4.456587	-0.590298
33	6	0	-1.956771	-3.118595	1.856628
34	1	0	0.193040	-3.222474	1.956698
35	6	0	-2.991752	-4.116416	-0.093985
36	1	0	-1.635006	-4.957506	-1.555840
37	6	0	-3.113826	-3.435643	1.127173
38	1	0	-2.033536	-2.603512	2.815621
39	1	0	-3.885409	-4.384051	-0.661856
40	1	0	-4.098751	-3.154880	1.502701
41	6	0	4.725238	0.804236	-1.626650
42	6	0	5.184522	1.724148	-0.660922
43	6	0	3.916410	1.272882	-2.684816
44	6	0	4.822193	3.076016	-0.737649
45	1	0	5.768026	1.358134	0.183573
46	6	0	3.554733	2.624947	-2.758412
47	1	0	3.566031	0.571937	-3.442578
48	6	0	4.001107	3.529713	-1.781137
49	1	0	5.157482	3.768203	0.036786
50	1	0	2.914503	2.972682	-3.571128
51	1	0	3.695808	4.576120	-1.825332
52	1	0	2.310232	-7.125167	-2.044693
53	1	0	4.189947	-5.481355	-2.107418
54	1	0	5.749433	-4.405811	-0.580611
55	1	0	7.619410	-2.753171	-0.639837
56	1	0	3.331749	-2.440231	2.917402
57	1	0	0.479694	0.786947	3.201640
58	1	0	-0.877082	-0.546418	4.830979
59	1	0	-0.138382	-2.840859	5.484704
60	1	0	1.966261	-3.794563	4.537541
61	6	0	-0.063140	0.572046	-1.742417
62	1	0	-0.058386	1.204126	-0.852957
63	1	0	0.711037	0.908533	-2.445249
64	6	0	-1.410532	0.529141	-2.376052
65	1	0	-1.474654	0.172788	-3.406745
66	6	0	-2.523297	0.981012	-1.757728
67	8	0	-4.974072	0.658800	-1.812617
68	6	0	-5.038513	-0.668161	-1.591771
69	7	0	-4.229979	-1.505278	-2.103739
70	1	0	-4.411230	-2.463107	-1.798751
71	6	0	-6.219959	-0.935669	-0.597043
72	17	0	-6.531251	-2.720705	-0.417585
73	17	0	-5.776560	-0.251857	1.019948
74	17	0	-7.743906	-0.161269	-1.203472
75	6	0	-2.567537	1.354086	-0.321265
76	6	0	-3.051904	2.610490	0.098428
77	6	0	-2.153797	0.416275	0.647497
78	6	0	-3.098553	2.931745	1.460226
79	1	0	-3.365166	3.345088	-0.644658
80	6	0	-2.221069	0.733502	2.010728
81	6	0	-2.687313	1.991680	2.421095
82	1	0	-3.451952	3.915788	1.772065
83	1	0	-1.911616	-0.009994	2.744981
84	1	0	-2.734664	2.241653	3.483290
85	6	0	-3.806678	1.137976	-2.544915
86	1	0	-4.044087	2.200075	-2.699806
87	1	0	-3.743639	0.621569	-3.513015
88	8	0	0.182351	3.612627	-1.560081
89	6	0	0.568157	3.911751	-0.435607
90	7	0	1.349764	3.169095	0.363872
91	1	0	1.639141	3.447113	1.294038
92	6	0	0.199100	5.350159	0.161916
93	17	0	1.655563	6.422639	-0.096149
94	17	0	-0.175989	5.288892	1.953487
95	17	0	-1.215415	6.037322	-0.697922
96	1	0	-1.806875	-0.565193	0.325761

12	6	0	-0.698077	3.323667	-0.911991
13	6	0	-0.871957	4.500881	-1.671957
14	1	0	-0.029139	5.187304	-1.762918
15	8	0	-2.845099	-0.094830	-1.708545
16	15	0	-1.781374	-0.191720	-0.471251
17	8	0	-1.675914	1.345366	0.041329
18	8	0	-0.433462	-0.513896	-1.264462
19	7	0	-2.009929	-1.210169	0.702308
20	16	0	-3.000389	-1.017805	2.031995
21	8	0	-3.007339	-2.314833	2.732132
22	8	0	-4.282734	-0.357992	1.686099
23	6	0	-2.058406	0.159863	3.047187
24	6	0	-0.926749	-0.294599	3.739364
25	6	0	-2.466528	1.499525	3.106637
26	6	0	-0.185043	0.620226	4.501645
27	6	0	-1.715698	2.405802	3.871524
28	6	0	-0.575347	1.969012	4.565906
29	6	0	0.622885	3.033748	-0.289345
30	6	0	0.747763	2.572342	1.040832
31	6	0	1.799472	3.277924	-1.031018
32	6	0	2.013581	2.357746	1.601820
33	1	0	-0.141222	2.396677	1.642863
34	6	0	3.062772	3.067736	-0.463061
35	1	0	1.715752	3.620319	-2.064093
36	6	0	3.177309	2.597665	0.854231
37	1	0	2.084849	2.007437	2.632677
38	1	0	3.960814	3.275986	-1.048217
39	1	0	4.161466	2.419710	1.289763
40	6	0	-5.015057	-1.922809	-1.350600
41	6	0	-5.483281	-2.734044	-0.297070
42	6	0	-4.371730	-2.528655	-2.450356
43	6	0	-5.305885	-4.123895	-0.340290
44	1	0	-5.933672	-2.259948	0.574626
45	6	0	-4.202154	-3.919056	-2.494157
46	1	0	-4.011711	-1.905308	-3.269625
47	6	0	-4.666983	-4.720548	-1.438184
48	1	0	-5.651322	-4.737357	0.493879
49	1	0	-3.709852	-4.377675	-3.354850
50	1	0	-4.525456	-5.802983	-1.468619
51	1	0	-2.206470	5.723881	-2.855392
52	1	0	-4.134952	4.151762	-2.620810
53	1	0	-5.634284	3.430637	-0.874849
54	1	0	-7.606045	1.914962	-0.651290
55	1	0	-3.353108	1.815143	2.558198
56	1	0	-0.638287	-1.343624	3.677744
57	1	0	0.693746	0.277822	5.052387
58	1	0	0.005340	2.677071	5.160362
59	1	0	-2.021333	3.452513	3.924130
60	6	0	-0.010299	-1.942110	-1.394198
61	1	0	-0.000839	-2.377309	-0.388437
62	1	0	-0.771904	-2.443030	-2.010620
63	6	0	1.333836	-1.981639	-2.044784
64	1	0	1.358777	-1.872745	-3.132175
65	6	0	2.494638	-2.191352	-1.381438
66	8	0	4.943611	-1.847826	-1.596855
67	6	0	4.985199	-0.500416	-1.579559
68	7	0	4.127662	0.232040	-2.165071
69	1	0	4.290021	1.229028	-2.013374
70	6	0	6.199499	-0.063177	-0.691356
71	17	0	6.531509	1.716310	-0.871735
72	17	0	5.790495	-0.417250	1.036638
73	17	0	7.702519	-0.960335	-1.169762
74	6	0	2.619302	-2.216503	0.096170
75	6	0	3.358945	-3.224859	0.752323
76	6	0	2.041962	-1.182730	0.864446
77	6	0	3.487021	-3.219629	2.145888
78	1	0	3.829501	-4.017590	0.168114
79	6	0	2.179450	-1.174781	2.258280
80	6	0	2.896001	-2.193862	2.903762
81	1	0	4.052340	-4.011494	2.641130
82	1	0	1.726534	-0.366656	2.831227
83	1	0	3.002541	-2.187591	3.990818
84	6	0	3.756689	-2.450084	-2.185577
85	1	0	4.011586	-3.519782	-2.185857
86	1	0	3.639327	-2.095930	-3.219469
87	1	0	1.517092	-0.372837	0.360476

INT-2

B97D/6-31g(d); E(RB97D) = -4299.140597 hartree
Sum of electronic and thermal Free Energies= -4298.591450 hartree
Thermal correction to Gibbs Free Energy= 0.549147 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -4299.156606 hartree
Gibbs Free Energy in toluene = -4298.607459 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-5.519259	2.352926	-1.000325
2	6	0	-6.620355	1.499617	-0.867610
3	6	0	-4.233778	1.833401	-1.261896
4	6	0	-6.459238	0.113580	-0.996851
5	6	0	-5.198623	-0.449948	-1.272086
6	6	0	-4.115371	0.437007	-1.404990
7	1	0	-7.312781	-0.556021	-0.882326
8	6	0	-3.063146	2.738834	-1.395227
9	6	0	-3.181359	3.932312	-2.138749
10	6	0	-1.813586	2.466795	-0.793728
11	6	0	-2.097416	4.805582	-2.275993

INT-2'

B97D/6-31g(d); E(RB97D) = -4299.140505 hartree
Sum of electronic and thermal Free Energies= -4298.592098 hartree
Thermal correction to Gibbs Free Energy= 0.548407 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -4299.154222 hartree
Gibbs Free Energy in toluene = -4298.605815 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.683710	-2.735982	0.125447
2	6	0	5.622930	-1.786849	0.539318
3	6	0	3.508266	-2.336120	-0.541534
4	6	0	5.400003	-0.427891	0.295196
5	6	0	4.244105	0.025633	-0.378066
6	6	0	3.324025	-0.959667	-0.793793
7	1	0	6.134456	0.312184	0.613696
8	6	0	2.516033	-3.351182	-0.976942
9	6	0	2.960073	-4.542700	-1.587202
10	6	0	1.125290	-3.182071	-0.793516
11	6	0	2.047574	-5.518913	-1.998701

12	6	0	0.175145	-4.141995	-1.202844
13	6	0	0.676466	-5.316563	-1.808737
14	1	0	-0.036723	-6.083913	-2.111649
15	8	0	2.189562	-0.582671	-1.539717
16	15	0	0.773353	-0.551360	-0.717008
17	8	0	0.663290	-2.048062	-0.094295
18	8	0	-0.272113	-0.539098	-1.922964
19	7	0	0.709141	0.623246	0.313366
20	16	0	0.376150	0.619271	1.936701
21	8	0	-0.649710	-0.397526	2.284520
22	8	0	0.172213	2.024396	2.340083
23	6	0	1.942410	0.073937	2.677578
24	6	0	2.823471	1.037521	3.185994
25	6	0	2.242848	-1.295608	2.727958
26	6	0	4.036498	0.616291	3.752790
27	6	0	3.461243	-1.701975	3.287907
28	6	0	4.357622	-0.749160	3.799248
29	6	0	-0.685714	0.737413	-2.572227
30	1	0	-0.846736	0.424523	-3.613969
31	1	0	0.138899	1.461856	-2.533137
32	6	0	-1.930372	1.265739	-1.934494
33	1	0	-2.756669	0.559316	-1.828315
34	6	0	-2.059302	2.521472	-1.468186
35	8	0	-4.275403	2.026956	-0.410772
36	6	0	-3.947895	1.354170	0.721416
37	7	0	-2.860942	1.545315	1.340633
38	1	0	-2.705392	0.948926	2.154599
39	6	0	-5.139864	0.416134	1.089248
40	17	0	-4.740898	-0.612644	2.520752
41	17	0	-6.581628	1.452800	1.505010
42	17	0	-5.551814	-0.659699	-0.314310
43	6	0	-1.014863	3.578570	-1.578778
44	6	0	-0.400503	4.076274	-0.409176
45	6	0	-0.687425	4.139377	-2.829252
46	6	0	0.516293	5.130803	-0.499187
47	1	0	-0.616994	3.603890	0.549501
48	6	0	0.224977	5.203122	-2.912253
49	6	0	0.817738	5.706755	-1.744928
50	1	0	1.005835	5.495338	0.405422
51	1	0	0.462074	5.642288	-3.883897
52	1	0	1.522178	6.539047	-1.806900
53	6	0	-3.329868	3.040909	-0.818382
54	1	0	-3.062092	3.660151	0.051186
55	1	0	-3.894120	3.659630	-1.533147
56	1	0	-1.170834	3.753532	-3.729790
57	6	0	-1.293820	-3.978727	-1.035529
58	6	0	-1.872442	-3.478845	0.152682
59	6	0	-2.148613	-4.394246	-2.081435
60	6	0	-3.264930	-3.420352	0.290075
61	1	0	-1.239809	-3.140376	0.970942
62	6	0	-3.540753	-4.329691	-1.942167
63	1	0	-1.711033	-4.754496	-3.014501
64	6	0	-4.103878	-3.848960	-0.750511
65	1	0	-3.695316	-3.033571	1.213752
66	1	0	-4.182852	-4.650743	-2.765215
67	1	0	-5.187880	-3.797183	-0.634564
68	6	0	4.046548	1.480338	-0.604206
69	6	0	4.388849	2.385772	0.423189
70	6	0	3.568328	1.996248	-1.828879
71	6	0	4.259256	3.767392	0.234281
72	1	0	4.728791	1.993638	1.381754
73	6	0	3.436382	3.377396	-2.014364
74	1	0	3.315226	1.313208	-2.638283
75	6	0	3.783665	4.267418	-0.986291
76	1	0	4.520798	4.451497	1.044555
77	1	0	3.051192	3.762204	-2.959767
78	1	0	3.672604	5.342224	-1.134330
79	1	0	2.403807	-6.437417	-2.468112
80	1	0	4.030448	-4.678671	-1.747430
81	1	0	4.834253	-3.796373	0.332748
82	1	0	6.526963	-2.104472	1.061426
83	1	0	1.531533	-2.022903	2.340718
84	1	0	2.552797	2.091278	3.136483
85	1	0	4.728394	1.356602	4.160342
86	1	0	5.304311	-1.072182	4.236970
87	1	0	3.709838	-2.763764	3.324790

12	6	0	2.043973	-3.386845	-1.296159
13	6	0	2.893195	-4.127380	-2.145308
14	1	0	2.663517	-5.180664	-2.314206
15	8	0	1.766813	0.794249	-1.743818
16	15	0	0.726843	0.084066	-0.667677
17	8	0	1.536925	-1.294176	-0.233248
18	8	0	-0.541316	-0.202987	-1.451422
19	7	0	0.715469	1.054031	0.616840
20	16	0	0.357441	0.587196	2.134058
21	8	0	-0.807098	-0.357804	2.203335
22	8	0	0.286775	1.816068	2.958985
23	6	0	1.801349	-0.381401	2.663475
24	6	0	3.082332	0.024568	2.260104
25	6	0	1.612361	-1.521906	3.455665
26	6	0	4.191810	-0.737685	2.649225
27	6	0	2.731670	-2.274936	3.844775
28	6	0	4.018952	-1.886597	3.439647
29	6	0	-1.400523	1.778906	-2.312625
30	1	0	-0.991803	1.340014	-3.219677
31	1	0	-0.766734	2.487319	-1.779947
32	6	0	-2.730157	1.590803	-1.995073
33	1	0	-3.278145	0.842619	-2.571685
34	6	0	-3.415707	2.147673	-0.893626
35	8	0	-4.964723	0.244474	-0.798493
36	6	0	-4.021930	-0.375119	-0.034559
37	7	0	-3.178871	0.315633	0.605648
38	1	0	-2.391680	-0.109128	1.124608
39	6	0	-4.152233	-1.913300	-0.150079
40	17	0	-2.845838	-2.740459	0.731178
41	17	0	-5.775147	-2.398359	0.535046
42	17	0	-4.070190	-2.377606	-1.911777
43	6	0	-2.963256	3.273410	-0.071519
44	6	0	-1.682089	3.286418	0.521816
45	6	0	-3.857472	4.343684	0.187685
46	6	0	-1.309928	4.333741	1.368827
47	1	0	-1.006715	2.444158	0.392075
48	6	0	-3.457880	5.415269	0.992475
49	6	0	-2.187166	5.406163	1.595241
50	1	0	-0.342123	4.278796	1.863062
51	1	0	-4.144253	6.246127	1.166184
52	1	0	-1.893028	6.225242	2.254805
53	6	0	-4.863081	1.687431	-0.714264
54	1	0	-5.244589	2.018940	0.260402
55	1	0	-5.511133	2.049845	-1.525617
56	1	0	-4.850350	4.349925	-0.267234
57	6	0	0.925490	-4.077673	-0.599641
58	6	0	0.740570	-3.928659	0.792675
59	6	0	0.101423	-4.984234	-1.299734
60	6	0	-0.225632	-4.688310	1.465287
61	1	0	1.368845	-3.235690	1.349406
62	6	0	-0.871672	-5.735801	-0.626680
63	1	0	0.224847	-5.089428	-2.379553
64	6	0	-1.031902	-5.598443	0.760866
65	1	0	-0.344760	-4.570115	2.544586
66	1	0	-1.505923	-6.426421	-1.186348
67	1	0	-1.787314	-6.185473	1.287122
68	6	0	2.491894	3.483034	-0.943563
69	6	0	2.439611	4.385922	0.139096
70	6	0	1.667911	3.724668	-2.063888
71	6	0	1.588942	5.498484	0.104153
72	1	0	3.050624	4.191712	1.021995
73	6	0	0.812710	4.835392	-2.095106
74	1	0	1.709015	3.041713	-2.911814
75	6	0	0.768550	5.726411	-1.011316
76	1	0	1.553866	6.178469	0.957724
77	1	0	0.185392	5.009562	-2.972462
78	1	0	0.093283	6.583697	-1.030916
79	1	0	4.674315	-4.146159	-3.375187
80	1	0	5.260891	-1.770624	-2.852229
81	1	0	5.974040	-0.654495	-0.760547
82	1	0	6.699144	1.641708	-0.078871
83	1	0	0.602133	-1.820589	3.734624
84	1	0	3.201364	0.898744	1.621147
85	1	0	5.188138	-0.438648	2.319123
86	1	0	4.885543	-2.482325	3.733893
87	1	0	2.595630	-3.170831	4.454231

TS-2

B97D/6-31g(d); E(RB97D) = -4299.113791 hartree
Sum of electronic and thermal Free Energies= -4298.566579 hartree
Thermal correction to Gibbs Free Energy= 0.547213 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -4299.131221 hartree
Gibbs Free Energy in toluene = -4298.584008 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.278056	0.184182	-0.811259
2	6	0	5.676804	1.467117	-0.419025
3	6	0	3.956749	-0.058704	-1.240650
4	6	0	4.763121	2.528980	-0.462701
5	6	0	3.436892	2.337131	-0.904255
6	6	0	3.063138	1.030325	-1.286676
7	1	0	5.073418	3.533363	-0.170259
8	6	0	3.535011	-1.436702	-1.604621
9	6	0	4.360525	-2.223522	-2.433588
10	6	0	2.357269	-2.024368	-1.082728
11	6	0	4.031587	-3.552218	-2.723025

CP-2

B97D/6-31g(d); E(RB97D) = -4299.143660 hartree
Sum of electronic and thermal Free Energies= -4298.595050 hartree
Thermal correction to Gibbs Free Energy= 0.548610 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -4299.161098 hartree
Gibbs Free Energy in toluene = -4298.612488 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.311272	4.923654	-0.897145
2	6	0	1.361892	5.863287	-0.478702
3	6	0	1.921620	3.616640	-1.254995
4	6	0	0.008169	5.505542	-0.411641
5	6	0	-0.427190	4.219096	-0.789254
6	6	0	0.546534	3.296179	-1.222043
7	1	0	-0.738633	6.226801	-0.074810
8	6	0	2.948563	2.596715	-1.587185
9	6	0	4.007514	2.896790	-2.465942
10	6	0	2.930811	1.327406	-0.959758
11	6	0	5.017882	1.959705	-2.712136

12	6	0	3.966180	0.384649	-1.150742
13	6	0	4.998340	0.724606	-2.052470
14	1	0	5.810006	0.010709	-2.202665
15	8	0	0.149955	2.029436	-1.652132
16	15	0	0.355847	0.773893	-0.592541
17	8	0	1.916295	1.043645	-0.056206
18	8	0	0.209232	-0.522795	-1.325621
19	7	0	-0.586090	1.200973	0.662364
20	16	0	-0.738031	0.440270	2.061084
21	8	0	-0.947210	-1.057202	1.898043
22	8	0	-1.763955	1.136926	2.869686
23	6	0	0.849543	0.594431	2.926423
24	6	0	1.551592	1.805983	2.830950
25	6	0	1.328942	-0.468766	3.703581
26	6	0	2.764989	1.945018	3.518027
27	6	0	2.539240	-0.313606	4.397607
28	6	0	3.259482	0.887786	4.301624
29	6	0	-3.487484	0.147787	-2.491538
30	1	0	-3.179685	0.793754	-3.314045
31	1	0	-4.418225	0.393896	-1.980864
32	6	0	-2.711819	-0.876102	-2.117020
33	1	0	-1.761058	-1.068320	-2.614590
34	6	0	-3.084663	-1.890611	-1.039492
35	8	0	-2.011387	-3.862508	-1.847897
36	6	0	-1.261269	-3.292639	-0.910997
37	7	0	-1.795501	-2.276604	-0.315119
38	1	0	-1.364900	-1.689963	0.476239
39	6	0	0.112771	-3.927043	-0.680158
40	17	0	1.043232	-3.127346	0.582681
41	17	0	-0.211870	-5.672777	-0.209202
42	17	0	0.989217	-3.867137	-2.260638
43	6	0	-4.136042	-1.406953	-0.049241
44	6	0	-3.881886	-0.197656	0.627034
45	6	0	-5.330667	-2.103485	0.211379
46	6	0	-4.781727	0.281876	1.584777
47	1	0	-2.986629	0.377408	0.399190
48	6	0	-6.246661	-1.605104	1.150796
49	6	0	-5.967909	-0.420100	1.848487
50	1	0	-4.533545	1.197332	2.119261
51	1	0	-7.173135	-2.150925	1.339305
52	1	0	-6.673864	-0.046680	2.593110
53	6	0	-3.351197	-3.264195	-1.716038
54	1	0	-3.924260	-3.958741	-1.087617
55	1	0	-3.774318	-3.183425	-2.720860
56	1	0	-5.577275	-3.027176	-0.314297
57	6	0	4.044499	-0.898926	-0.402555
58	6	0	3.837950	-0.949622	0.994378
59	6	0	4.433186	-2.080693	-1.069675
60	6	0	4.048789	-2.142474	1.700037
61	1	0	3.535113	-0.052350	1.530988
62	6	0	4.633999	-3.274939	-0.363231
63	1	0	4.570852	-2.056258	-2.152444
64	6	0	4.453509	-3.307684	1.027802
65	1	0	3.898522	-2.151713	2.780769
66	1	0	4.929680	-4.178641	-0.900657
67	1	0	4.614265	-4.235229	1.581548
68	6	0	-1.872898	3.875519	-0.702296
69	6	0	-2.538924	3.975852	0.535349
70	6	0	-2.605461	3.498402	-1.843825
71	6	0	-3.910938	3.708966	0.629666
72	1	0	-1.965495	4.225803	1.428311
73	6	0	-3.982643	3.249160	-1.751622
74	1	0	-2.091762	3.414297	-2.802439
75	6	0	-4.639712	3.349151	-0.515023
76	1	0	-4.408081	3.775355	1.599487
77	1	0	-4.544439	2.978458	-2.648127
78	1	0	-5.709659	3.142736	-0.442839
79	1	0	5.830145	2.197902	-3.401331
80	1	0	4.019338	3.871078	-2.957906
81	1	0	3.373125	5.175784	-0.914099
82	1	0	1.676833	6.867862	-0.190086
83	1	0	0.764333	-1.399491	3.749802
84	1	0	1.166374	2.605962	2.199698
85	1	0	3.327948	2.876745	3.435956
86	1	0	4.206500	0.999784	4.833300
87	1	0	2.921522	-1.134289	5.008331

anti-S$_N$2' pathway

CP-3

B97D/6-31g(d); E(RB97D) = -5887.024689 hartree
Sum of electronic and thermal Free Energies= -5886.441084 hartree
Thermal correction to Gibbs Free Energy= 0.583605 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.042640 hartree
Gibbs Free Energy in toluene = -5886.459035 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.126011	5.725869	1.113917
2	6	0	1.048344	6.599493	0.945154
3	6	0	2.132251	4.450550	0.511145
4	6	0	-0.040512	6.211171	0.154932
5	6	0	-0.089899	4.938706	-0.447209
6	6	0	0.998258	4.065418	-0.243948
7	1	0	-0.883473	6.887208	0.002707
8	6	0	3.348864	3.604580	0.612762
9	6	0	4.622313	4.195834	0.473833
10	6	0	3.287692	2.213825	0.855708
11	6	0	5.788316	3.430353	0.576432
12	6	0	4.449590	1.408686	0.943676
13	6	0	5.699212	2.053441	0.805941
14	1	0	6.608574	1.459187	0.906318
15	8	0	1.013009	2.855608	-0.939056
16	15	0	0.978604	1.402999	-0.156750
17	8	0	2.049130	1.633775	1.089767
18	8	0	1.521405	0.411285	-1.172781
19	7	0	-0.442045	1.014915	0.477688
20	16	0	-1.001695	1.475957	1.948478
21	8	0	-2.488165	1.508259	1.875879
22	8	0	-0.321916	2.654896	2.536928
23	6	0	-0.572368	0.025158	2.954700
24	6	0	0.457137	0.113582	3.899767
25	6	0	-1.253938	-1.181349	2.727421
26	6	0	0.822450	-1.036578	4.620443
27	6	0	-0.880761	-2.323884	3.448026
28	6	0	0.160720	-2.254087	4.391861
29	1	0	2.004479	-0.990749	-0.869343
30	6	0	4.412161	-0.062018	1.170397
31	6	0	3.497320	-0.676662	2.056502
32	6	0	5.362079	-0.888902	0.521481
33	6	0	3.537091	-2.058324	2.289759
34	1	0	2.757329	-0.073462	2.574827
35	6	0	5.416537	-2.268412	0.773668
36	1	0	6.063123	-0.440020	-0.184318
37	6	0	4.500853	-2.861471	1.659756
38	1	0	2.810866	-2.497221	2.976636
39	1	0	6.169886	-2.879510	0.273186
40	1	0	4.539235	-3.934726	1.851566
41	6	0	-1.254577	4.608830	-1.322927
42	6	0	-2.228685	3.666527	-0.942808
43	6	0	-1.429826	5.327173	-2.524434
44	6	0	-3.361531	3.459224	-1.743374
45	1	0	-2.119645	3.107922	-0.017476
46	6	0	-2.553349	5.103739	-3.334630
47	1	0	-0.675217	6.059303	-2.819911
48	6	0	-3.525774	4.169023	-2.943005
49	1	0	-4.108103	2.728528	-1.426297
50	1	0	-2.670498	5.661757	-4.266388
51	1	0	-4.404934	3.997565	-3.568049
52	1	0	6.765811	3.904926	0.475233
53	1	0	4.680501	5.266083	0.271278
54	1	0	2.981723	6.016996	1.725201
55	1	0	1.056427	7.579038	1.426224
56	1	0	-2.065943	-1.215818	2.002258
57	1	0	0.954167	1.070628	4.058043
58	1	0	1.621969	-0.978641	5.361987
59	1	0	0.443859	-3.143822	4.958345
60	1	0	-1.413662	-3.262748	3.284292
61	6	0	-0.385127	-2.109413	-0.612149
62	1	0	-0.013994	-1.155813	-0.988231
63	1	0	-0.210984	-2.207038	0.467193
64	6	0	-1.782839	-2.362885	-1.019809
65	1	0	-2.386934	-3.035799	-0.410766
66	6	0	-2.364366	-1.633304	-2.003663
67	8	0	-4.626331	-1.997543	-1.039872
68	6	0	-4.555642	-1.071882	-0.047118
69	7	0	-4.002120	0.056190	-0.200701
70	1	0	-3.896482	0.631266	0.640845
71	6	0	-5.241918	-1.662345	1.226632
72	17	0	-5.198120	-0.506777	2.594518
73	17	0	-6.971965	-2.068046	0.838217
74	17	0	-4.367949	-3.199135	1.730579
75	6	0	-1.589817	-0.731816	-2.889650
76	6	0	-1.876583	0.648523	-2.901561
77	6	0	-0.515749	-1.225286	-3.660765
78	6	0	-1.083955	1.527388	-3.648599
79	1	0	-2.672246	1.025868	-2.263595
80	6	0	0.261620	-0.345905	-4.426023
81	6	0	-0.016371	1.030234	-4.413820
82	1	0	-1.290187	2.596963	-3.608669
83	1	0	1.090433	-0.732822	-5.022994
84	1	0	0.606413	1.716676	-4.990877
85	6	0	-3.867516	-1.668361	-2.229965
86	1	0	-4.201309	-0.698361	-2.624660
87	1	0	-4.141129	-2.459342	-2.943894
88	8	0	0.525135	-3.217253	-1.209248
89	6	0	1.810082	-3.075901	-1.193334
90	7	0	2.461178	-1.986185	-0.906822
91	1	0	3.479169	-2.011488	-0.817134
92	6	0	2.540513	-4.423793	-1.508160
93	17	0	4.271975	-4.177697	-1.960230
94	17	0	1.708464	-5.253236	-2.872164
95	17	0	2.429743	-5.422847	-0.000818
96	1	0	-0.304762	-2.296433	-3.655550

TS-3

B97D/6-31g(d); E(RB97D) = -5887.020028 hartree
Sum of electronic and thermal Free Energies= -5886.437447 hartree
Thermal correction to Gibbs Free Energy= 0.582581 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.036921 hartree
Gibbs Free Energy in toluene = -5886.454374 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.117556	6.072411	0.533555
2	6	0	-1.434812	6.516385	0.404395
3	6	0	0.278181	4.797448	0.071983
4	6	0	-2.381375	5.686205	-0.206567
5	6	0	-2.044483	4.393712	-0.653470
6	6	0	-0.713197	3.949861	-0.482766
7	1	0	-3.413009	6.020097	-0.329055
8	6	0	1.723215	4.452984	0.107599
9	6	0	2.677303	5.434530	-0.237305
10	6	0	2.194179	3.181611	0.501539
11	6	0	4.046522	5.160714	-0.173645
12	6	0	3.574363	2.865463	0.556740
13	6	0	4.485093	3.893103	0.221772
14	1	0	5.554047	3.690109	0.297141
15	8	0	-0.365147	2.722821	-1.038440
16	15	0	0.335950	1.461223	-0.224950
17	8	0	1.261806	2.237103	0.914593
18	8	0	1.174695	0.733376	-1.251002
19	7	0	-0.694322	0.508347	0.572755
20	16	0	-1.426594	0.929490	1.976447
21	8	0	-2.577428	0.003958	2.170705
22	8	0	-1.684010	2.388137	2.101990
23	6	0	-0.217018	0.480031	3.254203
24	6	0	0.436483	1.488886	3.973487
25	6	0	0.057531	-0.877713	3.481202
26	6	0	1.393206	1.127882	4.936129
27	6	0	1.014687	-1.227044	4.443905
28	6	0	1.684936	-0.225639	5.169625
29	1	0	2.288197	-0.481214	-0.958176
30	6	0	4.104506	1.529261	0.945655
31	6	0	3.519675	0.736460	1.960485
32	6	0	5.281688	1.044802	0.322691
33	6	0	4.095064	-0.485096	2.338156
34	1	0	2.625275	1.079906	2.471889
35	6	0	5.867639	-0.167740	0.716856
36	1	0	5.735415	1.624211	-0.482997
37	6	0	5.272843	-0.942262	1.727489
38	1	0	3.616148	-1.068137	3.125989
39	1	0	6.779799	-0.511669	0.226320
40	1	0	5.722155	-1.889689	2.028779
41	6	0	-3.105972	3.594770	-1.331966
42	6	0	-3.570197	2.372093	-0.811585
43	6	0	-3.735724	4.130834	-2.476254
44	6	0	-4.652479	1.712412	-1.410710
45	1	0	-3.108207	1.964095	0.081315
46	6	0	-4.805336	3.460140	-3.087905
47	1	0	-3.376553	5.078654	-2.882944
48	6	0	-5.269766	2.247133	-2.552752
49	1	0	-5.002586	0.770421	-0.984741
50	1	0	-5.277804	3.886742	-3.975697
51	1	0	-6.109269	1.726975	-3.019605
52	1	0	4.772570	5.933790	-0.431188
53	1	0	2.324745	6.413578	-0.563945
54	1	0	0.634495	6.710699	0.999989
55	1	0	-1.722387	7.501746	0.774958
56	1	0	-0.488082	-1.640199	2.924381
57	1	0	0.196018	2.531319	3.768718
58	1	0	1.911133	1.904783	5.501954
59	1	0	2.428756	-0.501457	5.919920
60	1	0	1.231043	-2.280239	4.636436
61	6	0	0.198294	-2.250026	-0.674957
62	1	0	0.314968	-1.222580	-1.007097
63	1	0	0.641338	-2.500431	0.289825
64	6	0	-0.939784	-2.974489	-1.103034
65	1	0	-1.218580	-3.882825	-0.569557
66	6	0	-1.834204	-2.434309	-2.009525
67	8	0	-3.703333	-3.618598	-0.886143
68	6	0	-3.868700	-2.711444	0.118876
69	7	0	-3.736379	-1.467438	-0.066280
70	1	0	-3.719705	-0.888587	0.782843
71	6	0	-4.130956	-3.471498	1.456063
72	17	0	-4.832159	-2.383439	2.692614
73	17	0	-5.257876	-4.875553	1.206116
74	17	0	-2.513617	-4.105444	2.052585
75	6	0	-1.521732	-1.301313	-2.880224
76	6	0	-2.435149	-0.225903	-2.997606
77	6	0	-0.282853	-1.237427	-3.565662
78	6	0	-2.097713	0.906329	-3.741870
79	1	0	-3.354783	-0.243612	-2.419068
80	6	0	0.031777	-0.117960	-4.339575
81	6	0	-0.866999	0.959146	-4.418052
82	1	0	-2.784240	1.752332	-3.765509
83	1	0	0.987132	-0.074305	-4.864988
84	1	0	-0.601787	1.846971	-4.995107
85	6	0	-3.220021	-3.049194	-2.122229
86	1	0	-3.938457	-2.311993	-2.503782
87	1	0	-3.187064	-3.905026	-2.814235
88	8	0	1.770744	-2.981245	-1.607484
89	6	0	2.881730	-2.426796	-1.385761
90	7	0	3.071454	-1.188730	-0.972681
91	1	0	4.001754	-0.845890	-0.734106
92	6	0	4.141810	-3.367344	-1.549865
93	17	0	5.627906	-2.454366	-2.051121
94	17	0	3.814376	-4.639690	-2.772044
95	17	0	4.403795	-4.127548	0.081612
96	1	0	0.410507	-2.074199	-3.488557

B97D/6-31g(d); E(RB97D) = -5887.048353 hartree
Sum of electronic and thermal Free Energies= -5886.466699 hartree
Thermal correction to Gibbs Free Energy= 0.581654 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.065822 hartree
Gibbs Free Energy in toluene = -5886.484168 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.137460	5.767534	0.565651
2	6	0	-1.505099	5.960536	0.782256
3	6	0	0.337007	4.643581	-0.142107
4	6	0	-2.423227	5.038341	0.264617
5	6	0	-1.993942	3.914498	-0.465683
6	6	0	-0.608454	3.713826	-0.638406
7	1	0	-3.495429	5.186012	0.405402
8	6	0	1.796460	4.479163	-0.354469
9	6	0	2.592856	5.562851	-0.777678
10	6	0	2.430641	3.244054	-0.110817
11	6	0	3.970780	5.404048	-0.966946
12	6	0	3.818582	3.056497	-0.280440
13	6	0	4.573892	4.163215	-0.722075
14	1	0	5.650624	4.039537	-0.849917
15	8	0	-0.189664	2.618361	-1.389217
16	15	0	0.714334	1.374806	-0.746635
17	8	0	1.654435	2.188060	0.358926
18	8	0	1.483408	0.745064	-1.863639
19	7	0	-0.167703	0.340184	0.154071
20	16	0	-0.739730	0.619468	1.627801
21	8	0	-1.582306	-0.608714	1.942558
22	8	0	-1.399400	1.928985	1.860127
23	6	0	0.645821	0.497663	2.789562
24	6	0	1.091131	1.653519	3.443976
25	6	0	1.270842	-0.743437	2.979490
26	6	0	2.187010	1.558899	4.315682
27	6	0	2.360017	-0.826474	3.857610
28	6	0	2.819506	0.322305	4.524375
29	1	0	2.408871	-0.837069	-1.476286
30	6	0	4.491636	1.762275	0.005446
31	6	0	4.254594	1.059907	1.207743
32	6	0	5.436817	1.245196	-0.906135
33	6	0	4.968441	-0.111303	1.497087
34	1	0	3.526600	1.438775	1.922467
35	6	0	6.136708	0.064357	-0.622521
36	1	0	5.602139	1.767526	-1.850143
37	6	0	5.912345	-0.614276	0.585482
38	1	0	4.779267	-0.630474	2.436851
39	1	0	6.850323	-0.330821	-1.348043
40	1	0	6.453680	-1.534430	0.808098
41	6	0	-3.021319	3.014717	-1.060976
42	6	0	-3.945577	2.341056	-0.238065
43	6	0	-3.158680	2.918721	-2.459929
44	6	0	-4.988772	1.593483	-0.806378
45	1	0	-3.822908	2.399650	0.843053
46	6	0	-4.199700	2.170790	-3.027301
47	1	0	-2.446838	3.443999	-3.098277
48	6	0	-5.120333	1.505615	-2.201469
49	1	0	-5.708806	1.091291	-0.158940
50	1	0	-4.291834	2.107009	-4.113483
51	1	0	-5.936367	0.927946	-2.641577
52	1	0	4.576445	6.247287	-1.303870
53	1	0	2.110952	6.521564	-0.976514
54	1	0	0.591855	6.475906	0.962658
55	1	0	-1.855076	6.827054	1.346038
56	1	0	0.900757	-1.625400	2.458311
57	1	0	0.585979	2.601225	3.262370
58	1	0	2.546370	2.451698	4.830850
59	1	0	3.670797	0.253506	5.204395
60	1	0	2.848680	-1.788657	4.022619
61	6	0	-0.122144	-3.132771	0.232318
62	1	0	0.346719	-2.192405	-0.061110
63	1	0	0.446987	-3.813958	0.867309
64	6	0	-1.359539	-3.448608	-0.173765
65	1	0	-1.846077	-4.371880	0.156759
66	6	0	-2.228479	-2.513846	-1.004113
67	8	0	-4.564430	-3.067715	-0.692318
68	6	0	-4.180284	-2.134339	0.163519
69	7	0	-2.975279	-1.677162	0.024848
70	1	0	-2.411335	-1.098815	0.774875
71	6	0	-5.181688	-1.809898	1.279859
72	17	0	-4.719197	-0.368410	2.204442
73	17	0	-6.822108	-1.585401	0.541298
74	17	0	-5.182530	-3.277454	2.361330
75	6	0	-1.512974	-1.700572	-2.075695
76	6	0	-1.984246	-0.432078	-2.460668
77	6	0	-0.471649	-2.307971	-2.797975
78	6	0	-1.395649	0.221352	-3.549919
79	1	0	-2.778398	0.063042	-1.902075
80	6	0	0.110397	-1.646879	-3.888322
81	6	0	-0.353158	-0.382703	-4.267941
82	1	0	-1.738288	1.218299	-3.816908
83	1	0	0.946716	-2.118338	-4.403062
84	1	0	0.113389	0.147121	-5.100166
85	6	0	-3.448044	-3.245102	-1.648210
86	1	0	-3.765123	-2.770606	-2.584204
87	1	0	-3.300648	-4.323583	-1.775050
88	8	0	2.438519	-3.266484	-2.419954
89	6	0	2.908021	-2.839279	-1.372372
90	7	0	2.895130	-1.570760	-0.935503

91	1	0	3.388142	-1.271558	-0.098827
92	6	0	3.666942	-3.888270	-0.420900
93	17	0	5.411248	-3.911559	-0.930985
94	17	0	2.952566	-5.526014	-0.634077
95	17	0	3.573417	-3.466584	1.370595
96	1	0	-0.084911	-3.279316	-2.499269

syn-S$_N$2' pathway

CP-5

B97D/6-31g(d); E(RB97D) = -5887.014319 hartree
Sum of electronic and thermal Free Energies= -5886.428353 hartree
Thermal correction to Gibbs Free Energy= 0.585966 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.033700 hartree
Gibbs Free Energy in toluene = -5886.447734 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.417643	-5.465299	0.096123
2	6	0	-1.252183	-6.209681	0.300310
3	6	0	-2.364669	-4.206343	-0.532280
4	6	0	-0.020486	-5.704797	-0.125709
5	6	0	0.089524	-4.442412	-0.751832
6	6	0	-1.108251	-3.713691	-0.944794
7	1	0	0.880618	-6.305589	0.002087
8	6	0	-3.619763	-3.455981	-0.788499
9	6	0	-4.736857	-4.148313	-1.301438
10	6	0	-3.753477	-2.072227	-0.525202
11	6	0	-5.945476	-3.489016	-1.542930
12	6	0	-4.971132	-1.386080	-0.738992
13	6	0	-6.056572	-2.123563	-1.259850
14	1	0	-7.003996	-1.605443	-1.415700
15	8	0	-1.072695	-2.498819	-1.622564
16	15	0	-1.284117	-1.083345	-0.780640
17	8	0	-2.690505	-1.372462	0.042638
18	8	0	-1.333692	0.021251	-1.781118
19	7	0	-0.130115	-0.954571	0.384215
20	16	0	-0.292470	-1.493574	1.932340
21	8	0	1.060477	-1.293394	2.560675
22	8	0	-0.896141	-2.836324	2.086461
23	6	0	-1.402520	-0.298502	2.725966
24	6	0	-1.390298	1.046108	2.327642
25	6	0	-2.224230	-0.745810	3.770325
26	6	0	-2.197150	1.965894	3.011111
27	6	0	-3.035136	0.182218	4.441424
28	6	0	-3.013403	1.536969	4.070641
29	1	0	1.588046	-0.985251	-0.011710
30	6	0	-5.178227	0.051497	-0.416368
31	6	0	-4.797854	0.600418	0.827725
32	6	0	-5.866570	0.872689	-1.336780
33	6	0	-5.132615	1.923495	1.147318
34	1	0	-4.258779	-0.011269	1.549547
35	6	0	-6.185686	2.199590	-1.020413
36	1	0	-6.139923	0.461597	-2.310422
37	6	0	-5.828819	2.727030	0.230159
38	1	0	-4.839181	2.324858	2.117351
39	1	0	-6.708251	2.820836	-1.750878
40	1	0	-6.076431	3.760180	0.482320
41	6	0	1.430039	-3.970566	-1.193488
42	6	0	2.576209	-4.319306	-0.439213
43	6	0	1.625169	-3.249415	-2.397002
44	6	0	3.865274	-4.003411	-0.887605
45	1	0	2.448163	-4.839638	0.511115
46	6	0	2.913850	-2.918237	-2.833234
47	1	0	0.765482	-2.968257	-3.000190
48	6	0	4.041943	-3.301924	-2.090182
49	1	0	4.731224	-4.301008	-0.293732
50	1	0	3.035240	-2.367847	-3.768516
51	1	0	5.045420	-3.060892	-2.445011
52	1	0	-6.799482	-4.037419	-1.944488
53	1	0	-4.631852	-5.211526	-1.522955
54	1	0	-3.384363	-5.843109	0.432061
55	1	0	-1.302677	-7.186057	0.785183
56	1	0	-2.232545	-1.803192	4.034056
57	1	0	-0.778312	1.362212	1.485396
58	1	0	-2.196746	3.010462	2.698028
59	1	0	-3.643899	2.255676	4.598399
60	1	0	-3.684211	-0.154148	5.252312
61	6	0	4.408377	1.100296	-1.815460
62	1	0	4.925355	1.521913	-0.950867
63	1	0	5.120700	0.644452	-2.510533
64	6	0	3.518235	2.099211	-2.472148
65	1	0	3.429168	2.054535	-3.559654
66	6	0	2.851684	3.054205	-1.785176
67	8	0	0.938867	4.623422	-1.882896
68	6	0	-0.037956	3.681769	-1.759893
69	7	0	0.065172	2.530124	-2.271235
70	1	0	-0.686895	1.855890	-2.075805
71	6	0	-1.191028	4.288613	-0.903621
72	17	0	-0.527517	4.756882	0.738621
73	17	0	-1.831216	5.784612	-1.738319
74	17	0	-2.527238	3.127904	-0.677563
75	6	0	2.785718	3.078958	-0.298080
76	6	0	2.054042	2.075722	0.372064
77	6	0	3.405084	4.098489	0.450534
78	6	0	1.974163	2.068372	1.771695
79	1	0	1.519481	1.329793	-0.213462
80	6	0	3.322910	4.091540	1.850671
81	6	0	2.610813	3.076182	2.512033
82	1	0	1.431854	1.267948	2.274915
83	1	0	3.812438	4.881088	2.424559
84	1	0	2.550443	3.072585	3.602094
85	6	0	2.144985	4.173619	-2.532120
86	1	0	2.773752	5.077366	-2.538480
87	1	0	1.926333	3.864331	-3.565291
88	8	0	3.560761	-0.062335	-1.323043
89	6	0	3.654366	-0.644648	-0.156622
90	7	0	2.577045	-1.147560	0.351984
91	1	0	2.523262	-1.571822	1.287477
92	6	0	4.997466	-0.734086	0.650078
93	17	0	4.961241	-2.059670	1.874652
94	17	0	5.219711	0.838576	1.518245
95	17	0	6.379749	-1.038765	-0.476937
96	1	0	3.959015	4.887796	-0.062215

TS-4

B97D/6-31g(d); E(RB97D) = -5887.008299 hartree
Sum of electronic and thermal Free Energies= -5886.423253 hartree
Thermal correction to Gibbs Free Energy= 0.585045 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.027945 hartree
Gibbs Free Energy in toluene = -5886.44290 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.167234	-5.835114	-0.088388
2	6	0	0.117253	-6.365743	0.061447
3	6	0	-1.353817	-4.555566	-0.646143
4	6	0	1.229040	-5.624587	-0.348654
5	6	0	1.099432	-4.329444	-0.900056
6	6	0	-0.214494	-3.821139	-1.036797
7	1	0	2.225171	-6.060451	-0.266152
8	6	0	-2.729983	-4.039993	-0.861501
9	6	0	-3.699213	-4.908644	-1.406472
10	6	0	-3.124569	-2.722237	-0.526256
11	6	0	-5.017205	-4.488352	-1.603546
12	6	0	-4.460250	-2.282143	-0.684557
13	6	0	-5.389152	-3.190856	-1.237812
14	1	0	-6.424624	-2.865895	-1.349139
15	8	0	-0.414476	-2.587012	-1.646484
16	15	0	-0.878457	-1.277611	-0.741960
17	8	0	-2.208682	-1.853635	0.062343
18	8	0	-1.147852	-0.173502	-1.711708
19	7	0	0.227611	-0.959714	0.423856
20	16	0	0.202399	-1.587310	1.943486
21	8	0	1.479829	-1.128516	2.585371
22	8	0	-0.101269	-3.034237	2.034277
23	6	0	-1.129185	-0.696636	2.798167
24	6	0	-1.444785	0.621458	2.438061
25	6	0	-1.772894	-1.336200	3.867371
26	6	0	-2.400002	1.321623	3.187399
27	6	0	-2.735458	-0.629285	4.604039
28	6	0	-3.039408	0.701642	4.273418
29	1	0	2.000561	-0.680225	0.025387
30	6	0	-4.957614	-0.946332	-0.254523
31	6	0	-4.664679	-0.414062	1.020129
32	6	0	-5.855896	-0.242097	-1.089358
33	6	0	-5.288572	0.763781	1.454403
34	1	0	-3.968697	-0.932366	1.677770
35	6	0	-6.471423	0.939165	-0.654369
36	1	0	-6.067755	-0.633306	-2.086306
37	6	0	-6.197584	1.440754	0.627309
38	1	0	-5.059191	1.147926	2.448136
39	1	0	-7.157113	1.469267	-1.318793
40	1	0	-6.676553	2.359622	0.972011
41	6	0	2.324298	-3.596059	-1.322394
42	6	0	3.531135	-3.787670	-0.607386
43	6	0	2.361054	-2.762386	-2.466648
44	6	0	4.730816	-3.206720	-1.036800
45	1	0	3.521377	-4.393879	0.299620
46	6	0	3.556798	-2.159896	-2.877159
47	1	0	1.454094	-2.600104	-3.043567
48	6	0	4.750749	-2.384257	-2.173289
49	1	0	5.648384	-3.387338	-0.474818
50	1	0	3.555070	-1.517373	-3.759721
51	1	0	5.683039	-1.923629	-2.505146
52	1	0	-5.754182	-5.171268	-2.029950
53	1	0	-3.392204	-5.917610	-1.685917
54	1	0	-2.043215	-6.400217	0.233281
55	1	0	0.253361	-7.360189	0.489966
56	1	0	-1.526661	-2.371742	4.101799
57	1	0	-0.962356	1.081842	1.578041
58	1	0	-2.657637	2.342785	2.903947
59	1	0	-3.786451	1.249427	4.851918
60	1	0	-3.247325	-1.118539	5.435140
61	6	0	4.002234	2.589089	-1.561259
62	1	0	4.173614	2.853009	-0.519859
63	1	0	4.893572	2.413288	-2.160574
64	6	0	2.869389	3.155248	-2.202709
65	1	0	2.833069	3.142258	-3.293808
66	6	0	1.859153	3.811087	-1.520478
67	8	0	-0.381918	4.824482	-1.814159
68	6	0	-1.000444	3.607776	-1.768894
69	7	0	-0.402512	2.553962	-2.125812
70	1	0	-0.871584	1.641236	-1.996601

71	6	0	-2.423242	3.780610	-1.166578
72	17	0	-2.212079	4.270200	0.591572
73	17	0	-3.318527	5.105506	-2.050066
74	17	0	-3.358779	2.275386	-1.256610
75	6	0	1.673906	3.726163	-0.066629
76	6	0	1.633304	2.453353	0.548484
77	6	0	1.474813	4.882919	0.722418
78	6	0	1.447954	2.334040	1.929811
79	1	0	1.668219	1.570814	-0.082921
80	6	0	1.306296	4.762486	2.105740
81	6	0	1.295549	3.491932	2.710365
82	1	0	1.411234	1.342395	2.381739
83	1	0	1.172002	5.659289	2.713137
84	1	0	1.146357	3.403441	3.788068
85	6	0	0.970757	4.765255	-2.299122
86	1	0	1.334246	5.798101	-2.181788
87	1	0	0.977136	4.493307	-3.365382
88	8	0	3.691311	0.728818	-1.305935
89	6	0	3.906750	0.122644	-0.207954
90	7	0	2.997858	-0.633717	0.354196
91	1	0	3.122226	-1.110842	1.248392
92	6	0	5.275252	0.302012	0.565137
93	17	0	5.714957	-1.132221	1.572141
94	17	0	5.075638	1.731844	1.680787
95	17	0	6.605833	0.616901	-0.610268
96	1	0	1.472338	5.868016	0.254155

CP-6

B97D/6-31g(d); E(RB97D) = -5887.052481 hartree
Sum of electronic and thermal Free Energies= -5886.474044 hartree
Thermal correction to Gibbs Free Energy= 0.578437 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -5887.067698 hartree
Gibbs Free Energy in toluene = -5886.489261 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.730685	-5.658328	-1.009454
2	6	0	0.604464	-6.025626	-1.204975
3	6	0	-1.148627	-4.325841	-1.212787
4	6	0	1.543164	-5.070110	-1.613076
5	6	0	1.175709	-3.727402	-1.834695
6	6	0	-0.176335	-3.392333	-1.625079
7	1	0	2.584195	-5.353904	-1.772212
8	6	0	-2.573784	-3.955334	-1.013117
9	6	0	-3.591531	-4.804725	-1.496264
10	6	0	-2.968421	-2.785950	-0.326208
11	6	0	-4.940430	-4.495639	-1.294827
12	6	0	-4.320371	-2.442892	-0.100476
13	6	0	-5.296164	-3.331242	-0.604977
14	1	0	-6.347286	-3.102988	-0.424799
15	8	0	-0.582746	-2.070075	-1.883532
16	15	0	-0.925197	-1.090318	-0.626980
17	8	0	-1.982765	-1.968655	0.246211
18	8	0	-1.648178	0.061154	-1.414344
19	7	0	0.231547	-0.545854	0.316325
20	16	0	0.923979	-1.443207	1.542118
21	8	0	2.009175	-0.596085	2.099031
22	8	0	1.240491	-2.828243	1.122690
23	6	0	-0.349243	-1.537391	2.828949
24	6	0	-0.672006	-0.374868	3.542645
25	6	0	-0.974950	-2.763538	3.089295
26	6	0	-1.651887	-0.447697	4.542661
27	6	0	-1.955161	-2.821939	4.091978
28	6	0	-2.294263	-1.667551	4.816701
29	1	0	2.795095	0.885271	-0.495560
30	6	0	-4.749902	-1.219056	0.631434
31	6	0	-4.104814	-0.772452	1.806922
32	6	0	-5.883696	-0.506111	0.175987
33	6	0	-4.583336	0.348368	2.498721
34	1	0	-3.244971	-1.310586	2.196379
35	6	0	-6.365494	0.608049	0.876727
36	1	0	-6.379902	-0.825433	-0.742325
37	6	0	-5.714072	1.042443	2.041906
38	1	0	-4.067314	0.667317	3.405951
39	1	0	-7.238390	1.145894	0.501632
40	1	0	-6.082149	1.916245	2.583292
41	6	0	2.202538	-2.730421	-2.236513
42	6	0	3.447014	-2.714894	-1.570189
43	6	0	1.988545	-1.822741	-3.296474
44	6	0	4.454080	-1.822099	-1.958224
45	1	0	3.600036	-3.381662	-0.721050
46	6	0	3.000139	-0.931620	-3.682642
47	1	0	1.036163	-1.829077	-3.825806
48	6	0	4.237147	-0.927032	-3.017299
49	1	0	5.403168	-1.810849	-1.420309
50	1	0	2.822874	-0.246102	-4.514529
51	1	0	5.014582	-0.216146	-3.298829
52	1	0	-5.716124	-5.163600	-1.672877
53	1	0	-3.303761	-5.703584	-2.042993
54	1	0	-1.465358	-6.392734	-0.676084
55	1	0	0.915761	-7.057874	-1.036572
56	1	0	-0.697316	-3.643605	2.510560
57	1	0	-0.156467	0.558343	3.320390
58	1	0	-1.909589	0.447297	5.113087
59	1	0	-3.059482	-1.717972	5.593532
60	1	0	-2.455056	-3.768646	4.304619
61	6	0	2.153149	2.477894	-2.526475
62	1	0	2.475796	3.516413	-2.633813
63	1	0	2.756260	1.724766	-3.031449
64	6	0	1.105617	2.117867	-1.772505
65	1	0	0.851343	1.062914	-1.662295
66	6	0	0.254583	3.054366	-0.935254
67	8	0	-1.219413	4.864597	-1.445388
68	6	0	-1.857673	3.693558	-1.281085
69	7	0	-1.174569	2.633302	-1.047956
70	1	0	-1.492224	1.039599	-1.118124
71	6	0	-3.379279	3.773181	-1.403813
72	17	0	-3.971948	5.016519	-0.211780
73	17	0	-3.774479	4.306708	-3.096556
74	17	0	-4.151763	2.203759	-1.056467
75	6	0	0.685646	3.046126	0.548849
76	6	0	2.049292	3.206909	0.857567
77	6	0	-0.253073	2.986280	1.593642
78	6	0	2.471513	3.288281	2.190841
79	1	0	2.786721	3.247950	0.055287
80	6	0	0.171324	3.083205	2.928198
81	6	0	1.533147	3.225667	3.232229
82	1	0	3.535539	3.385362	2.410190
83	1	0	-0.569127	3.040669	3.730241
84	1	0	1.861540	3.284583	4.271515
85	6	0	0.206193	4.526232	-1.472638
86	1	0	0.729973	5.246642	-0.836046
87	1	0	0.534246	4.607277	-2.518016
88	8	0	5.010435	1.813464	-1.259770
89	6	0	4.787785	1.071236	-0.306297
90	7	0	3.592357	0.591723	0.058469
91	1	0	3.374828	0.041925	0.891642
92	6	0	6.009811	0.668848	0.637522
93	17	0	5.718627	-0.801906	1.670765
94	17	0	6.304366	2.105017	1.727683
95	17	0	7.468013	0.374103	-0.381905
96	1	0	-1.312522	2.855479	1.374939

Real System

TS-R

B97D/6-31g(d); E(RB97D) = -7655.963068 hartree
Sum of electronic and thermal Free Energies= -7655.141952 hartree
Thermal correction to Gibbs Free Energy= 0.821116 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -7655.981163 hartree
Gibbs Free Energy in toluene = -7655.160047 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.144522	4.603647	1.434229
2	6	0	-3.466170	4.302267	1.923455
3	6	0	-1.601414	3.808737	0.366334
4	6	0	-4.197463	3.239977	1.331374
5	6	0	-3.651817	2.427563	0.346570
6	6	0	-2.318664	2.699399	-0.081992
7	1	0	-5.218335	3.048550	1.666764
8	6	0	-0.290737	4.141096	-0.251905
9	6	0	-0.056826	5.417078	-0.876337
10	6	0	0.731566	3.193433	-0.267816
11	6	0	1.254162	5.707839	-1.405080
12	6	0	2.038501	3.476045	-0.753260
13	6	0	2.277523	4.727413	-1.305152
14	1	0	3.276255	4.961904	-1.678807
15	8	0	-1.746714	1.860215	-1.041403
16	15	0	-0.481526	0.881476	-0.578720
17	8	0	0.505709	1.928648	0.260380
18	8	0	0.144242	0.367119	-1.848032
19	7	0	-0.942708	-0.256387	0.477980
20	16	0	-0.931683	-0.106173	2.079287
21	8	0	-1.586795	-1.307018	2.656094
22	8	0	-1.342040	1.223888	2.585747
23	1	0	1.510409	-0.726187	-2.149659
24	6	0	0.134392	-2.904788	-0.902925
25	1	0	0.050532	-1.868632	-1.213048
26	1	0	0.758056	-3.098089	-0.033108
27	6	0	-0.962373	-3.765406	-1.148438
28	1	0	-1.059199	-4.680024	-0.562821
29	6	0	-2.044744	-3.313347	-1.878785
30	8	0	-3.588333	-4.706421	-0.518120
31	6	0	-3.502508	-3.951540	0.621010
32	7	0	-3.325816	-2.703810	0.577113
33	1	0	-3.196392	-2.216534	1.467269
34	6	0	-3.638520	-4.898291	1.847508
35	17	0	-3.450138	-4.011963	3.389744
36	17	0	-5.287856	-5.682169	1.799956
37	17	0	-2.351451	-6.197314	1.758683
38	6	0	-1.942092	-2.216704	-2.842872
39	6	0	-2.860371	-1.141105	-2.832915
40	6	0	-0.895153	-2.234682	-3.797507
41	6	0	-2.714595	-0.098207	-3.751087
42	1	0	-3.627081	-1.090118	-2.061239
43	6	0	-0.773611	-1.200185	-4.728256
44	6	0	-1.680359	-0.129009	-4.700492
45	1	0	-3.393425	0.748694	-3.713987
46	1	0	0.030678	-1.226318	-5.465874
47	1	0	-1.577283	0.691933	-5.412824
48	6	0	-3.407395	-3.960349	-1.732993
49	1	0	-4.185413	-3.187117	-1.821327

50	1	0	-3.553975	-4.701807	-2.534244
51	8	0	1.630678	-3.403091	-2.077462
52	6	0	2.373485	-2.564618	-2.644889
53	7	0	2.297834	-1.245325	-2.598382
54	1	0	2.974178	-0.670312	-3.099728
55	6	0	3.546614	-3.184504	-3.519082
56	17	0	3.547328	-2.408142	-5.172038
57	17	0	3.328698	-4.951231	-3.722946
58	17	0	5.109225	-2.861587	-2.672613
59	1	0	-0.209914	-3.081514	-3.810829
60	6	0	3.163091	2.501073	-0.645925
61	6	0	3.696697	1.921783	-1.825694
62	6	0	3.779395	2.267682	0.612306
63	6	0	3.056513	2.059831	-3.103943
64	6	0	4.923927	1.144555	-1.752109
65	6	0	5.020548	1.511620	0.667930
66	6	0	3.243120	2.773861	1.843808
67	6	0	3.606919	1.500850	-4.241396
68	1	0	2.110749	2.596578	-3.158612
69	6	0	5.468484	0.594238	-2.957848
70	6	0	5.558262	0.969933	-0.511409
71	6	0	5.679237	1.347814	1.930274
72	1	0	2.305233	3.326707	1.824894
73	6	0	3.889111	2.559267	3.044097
74	6	0	4.836737	0.771330	-4.172580
75	1	0	3.096818	1.608194	-5.200545
76	1	0	6.398413	0.026247	-2.893275
77	1	0	6.483492	0.390736	-0.458729
78	6	0	5.130466	1.852269	3.089321
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TS-S

B97D/6-31g(d); E(RB97D) = -7655.960528 hartree
Sum of electronic and thermal Free Energies= -7655.139687 hartree
Thermal correction to Gibbs Free Energy= 0.820842 hartree
pcm(chloroform)/RB97D/6-31g(d); E(RB97D) = -7655.978448 hartree
Gibbs Free Energy in toluene = -7655.157606 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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138	1	0	-4.783336	-6.436020	0.017012

9. Reference

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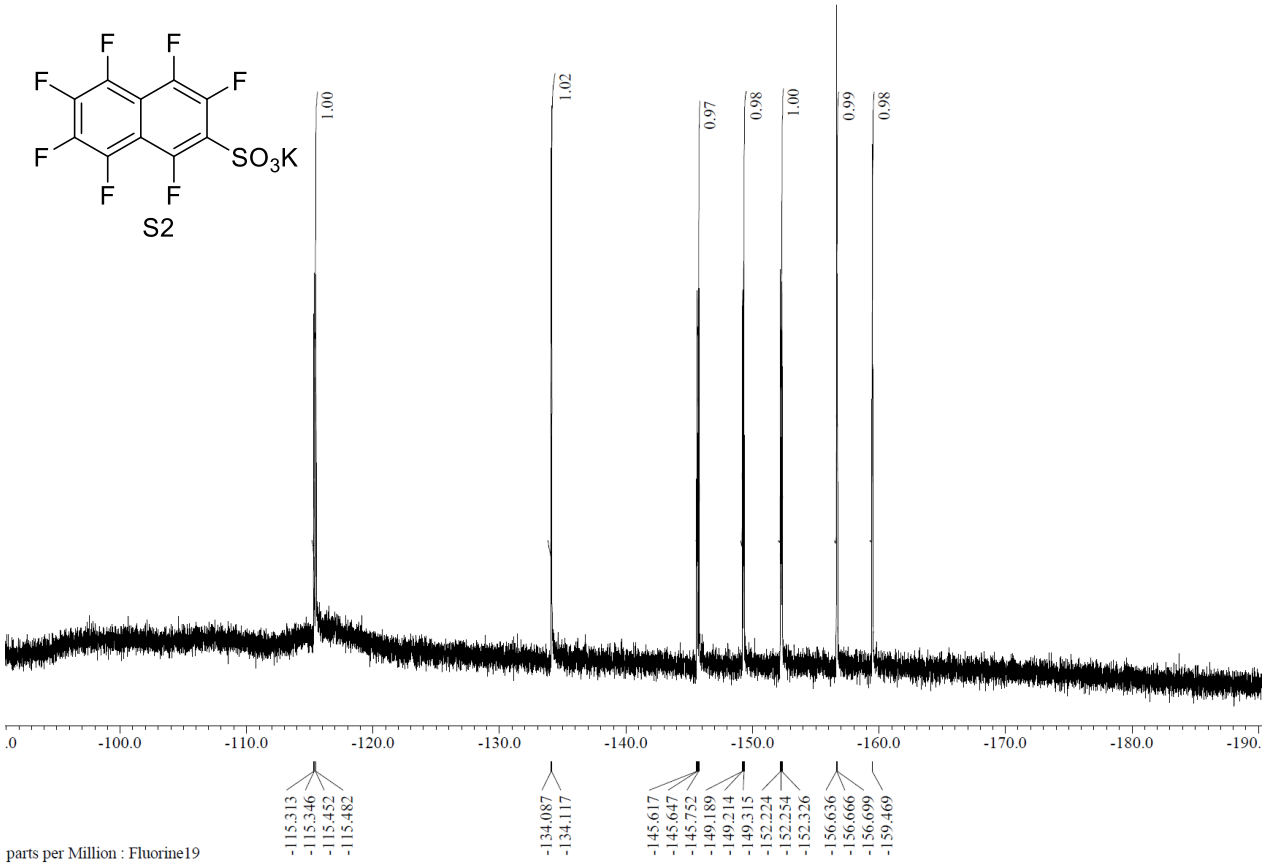
(2) Joel A. Bergman; Kalub Hahne; Christine A. Hrycyna; Richard A. Gibbs, *Bioorg. Med. Chem. Lett.*, **2011**, *21*, 5616-5619.

(3) (a) Cannon, J. S.; Kirsch, S. F.; Overman, L. E.; Sneddon, H. F. *J. Am. Chem. Soc.* **2010**, *132*, 15192-15203. (b) Cannon, J. S.; Olson, A. C.; Overman, L. E.; Solomon, N. S. *J. Org. Chem.* **2012**, *77*, 1961−1973.

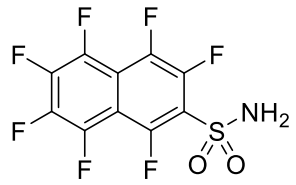
(4) (a) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352-2355. (b) Midland, M. M. B-3-Pinanyl-9-borabicyclo[3.3.1]nonane, *e-EROS Encyclopedia of Reagents for Organic Synthesis* **2001**.

10. NMR spectra

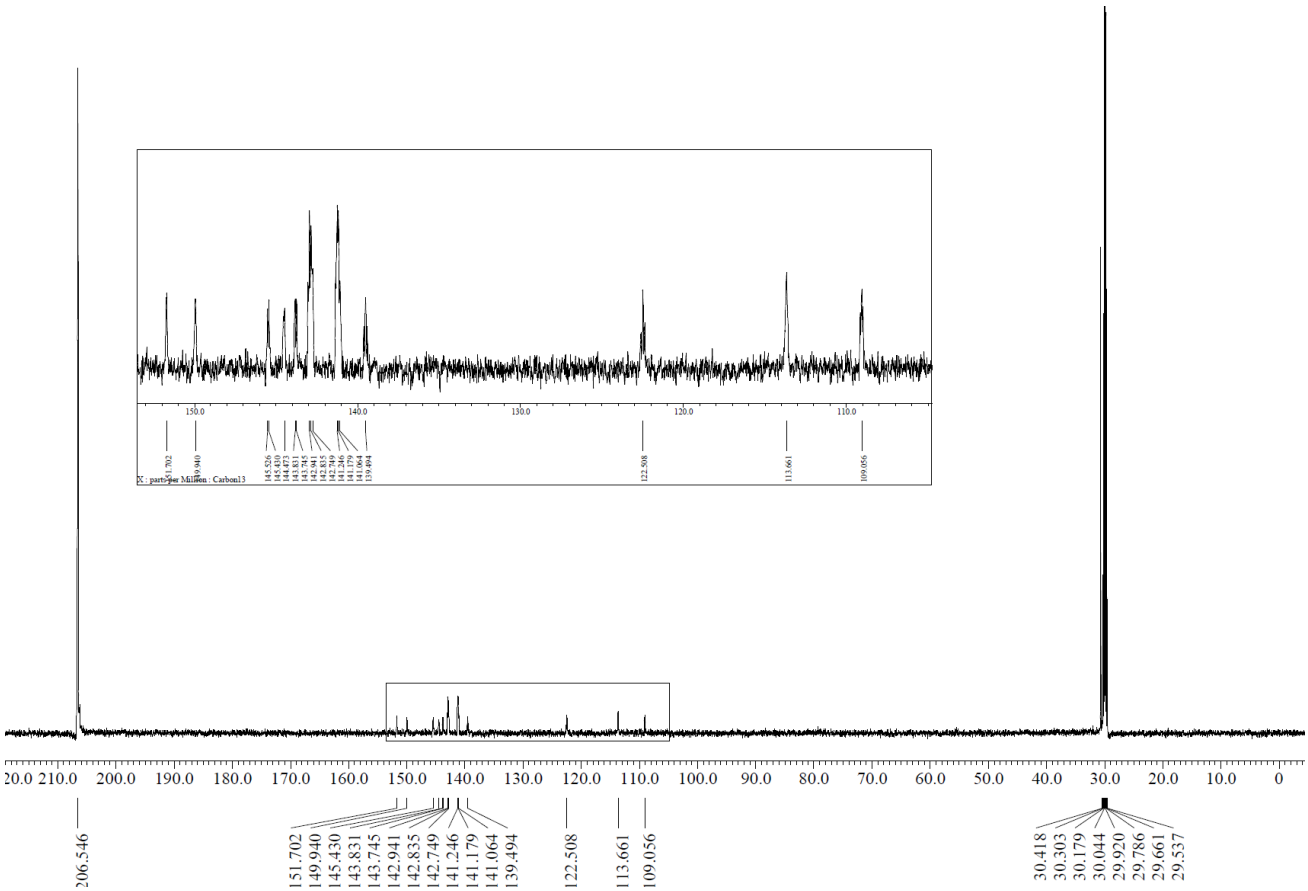
^{19}F NMR (565 MHz) spectra of **S2**



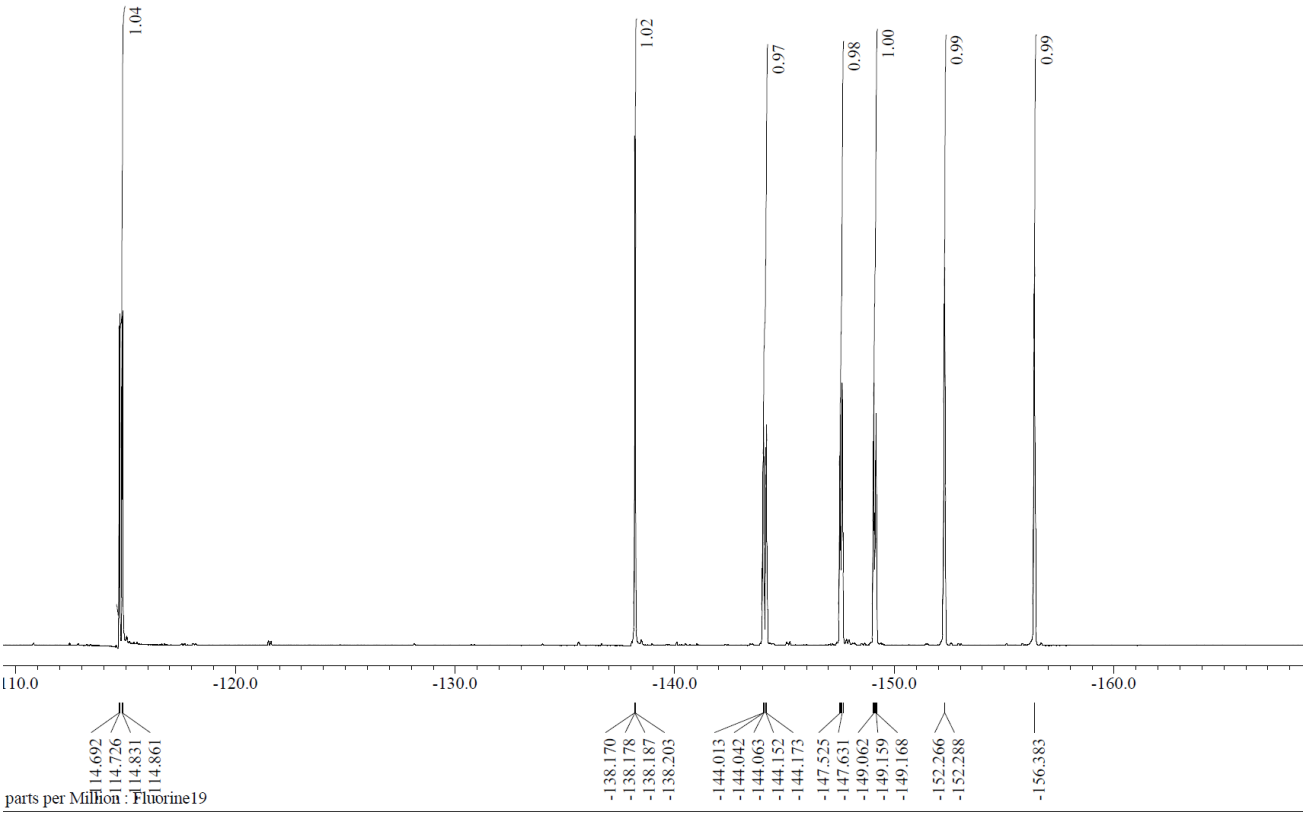
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S3**



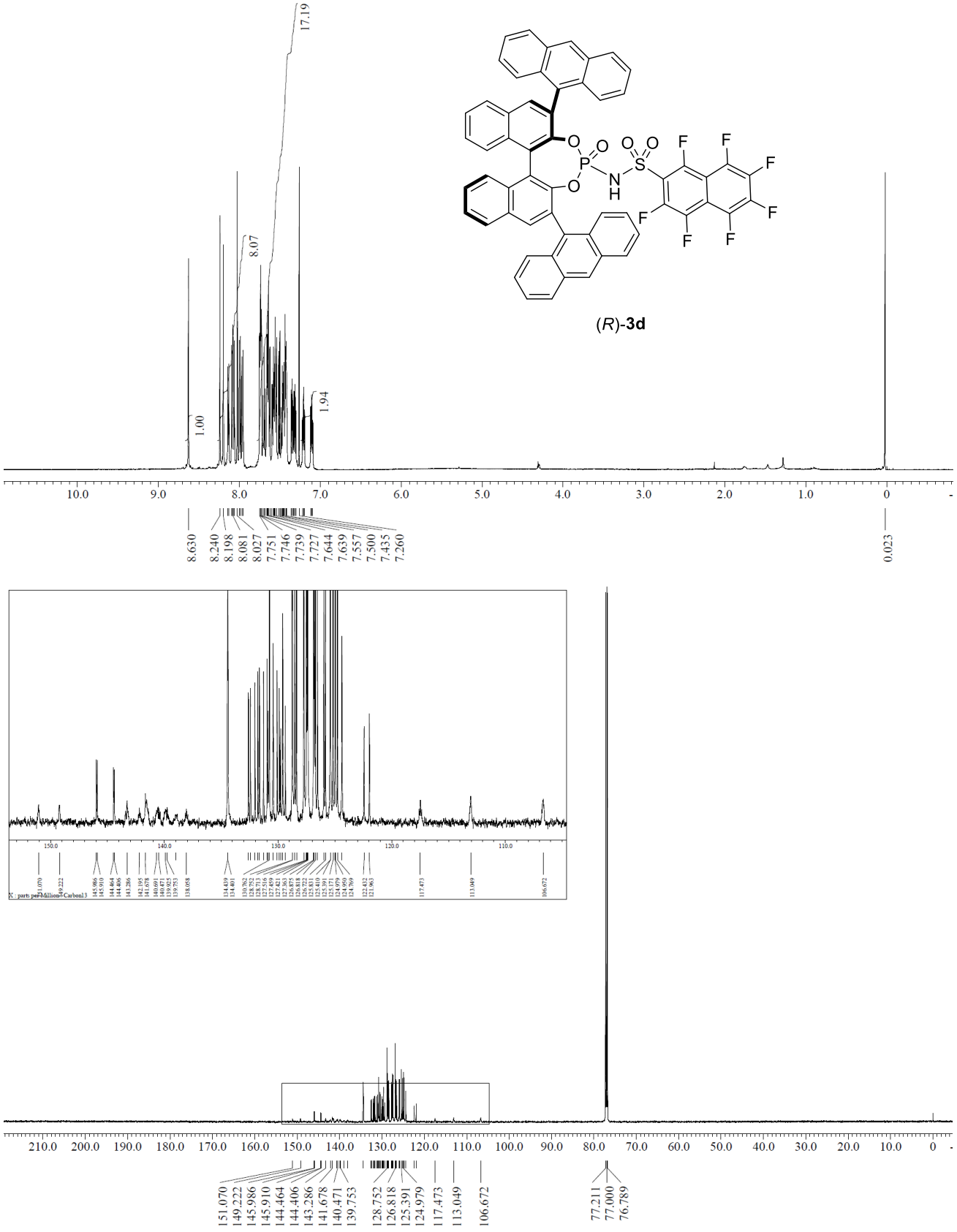
S3



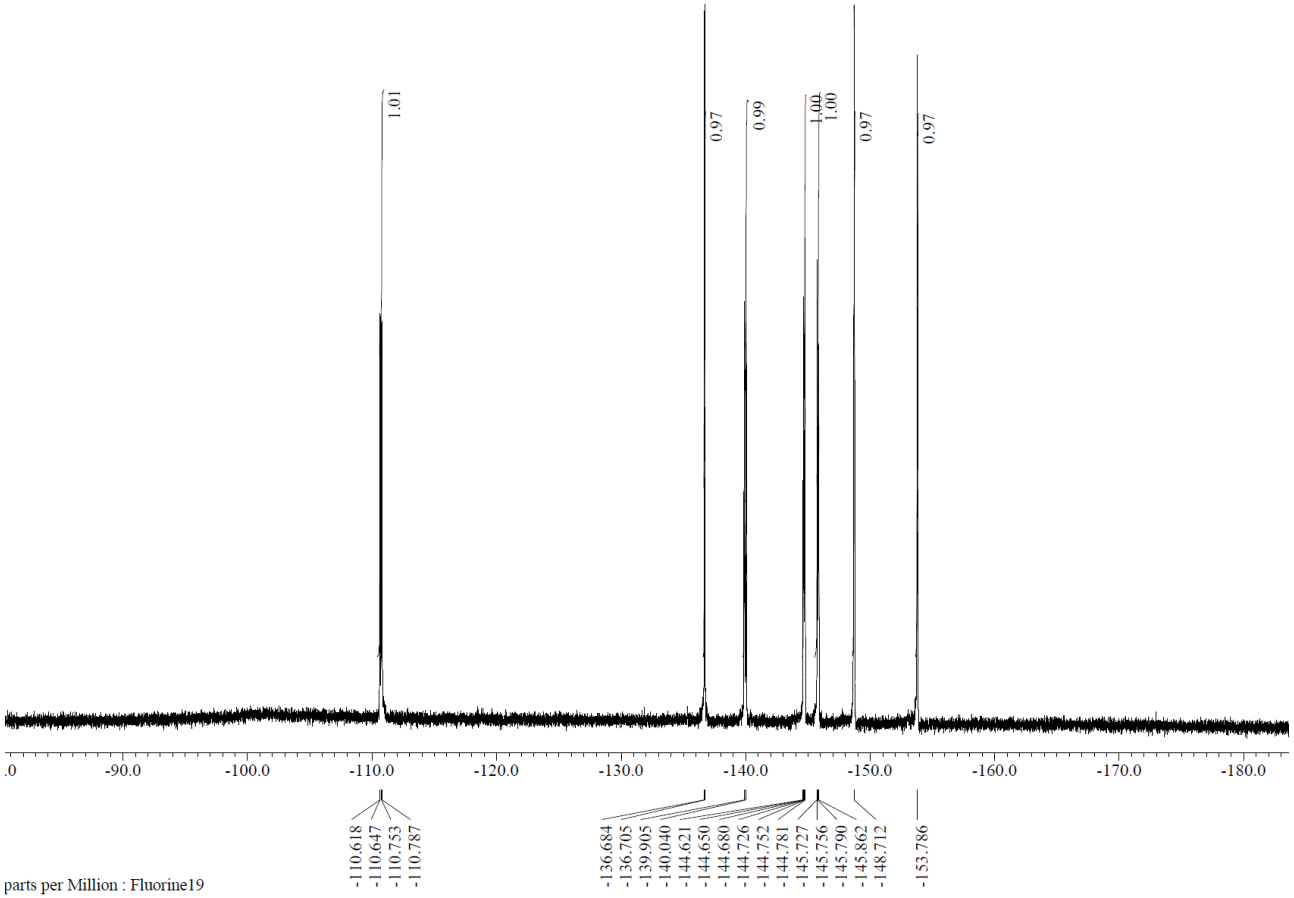
^{19}F NMR (565 MHz) spectra of **S3**

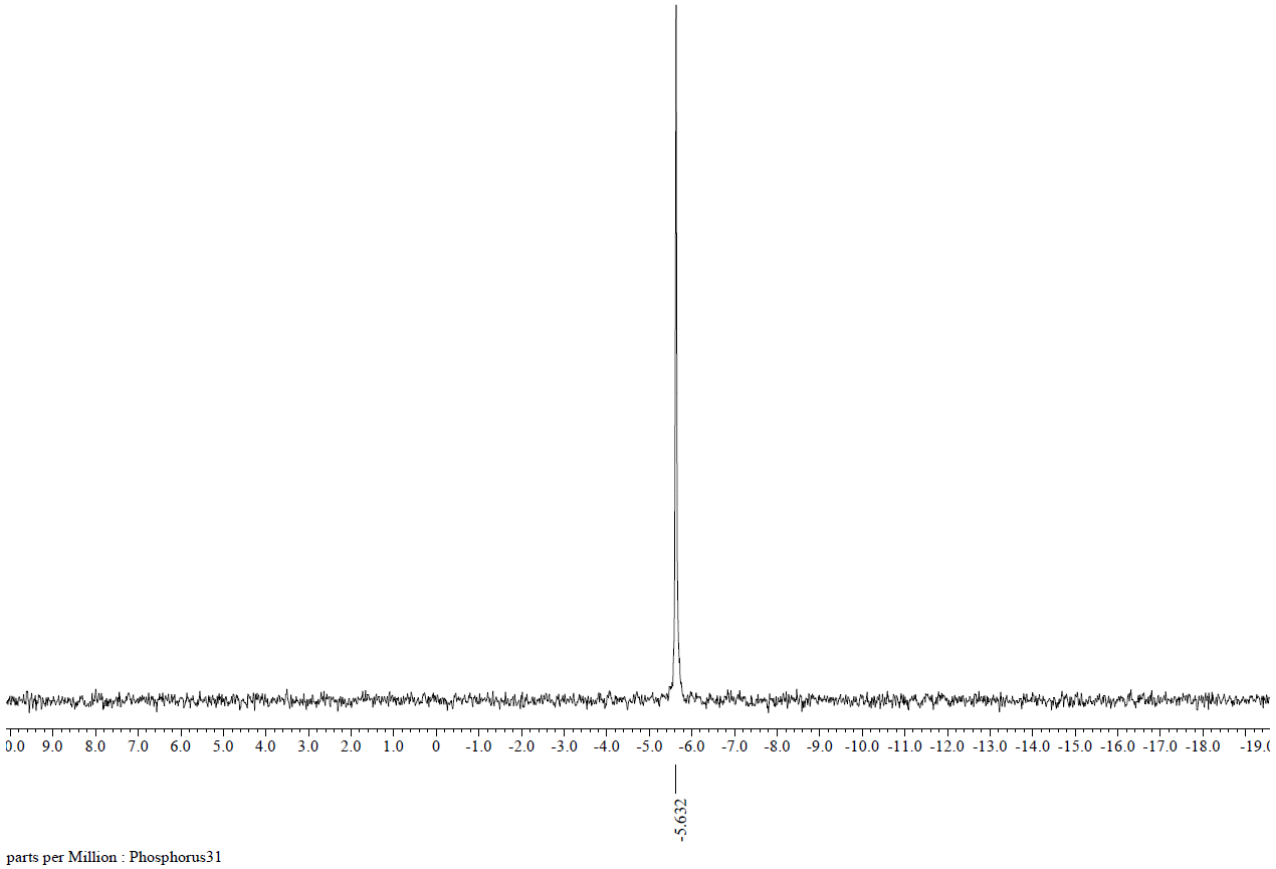


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*R*)-**3d**



^{19}F NMR (565 MHz) and ^{31}P NMR (243 MHz) spectra of (*R*)-**3d**





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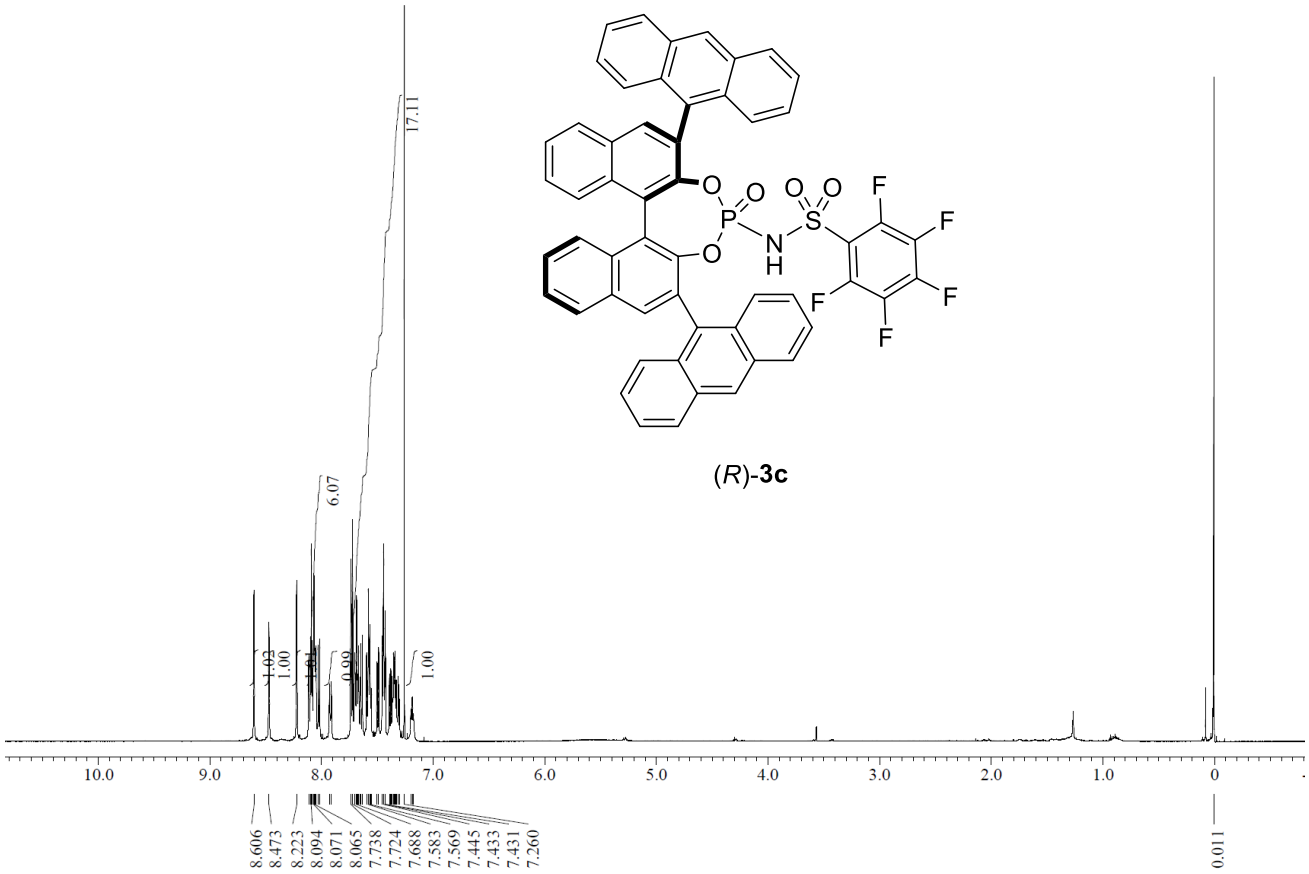

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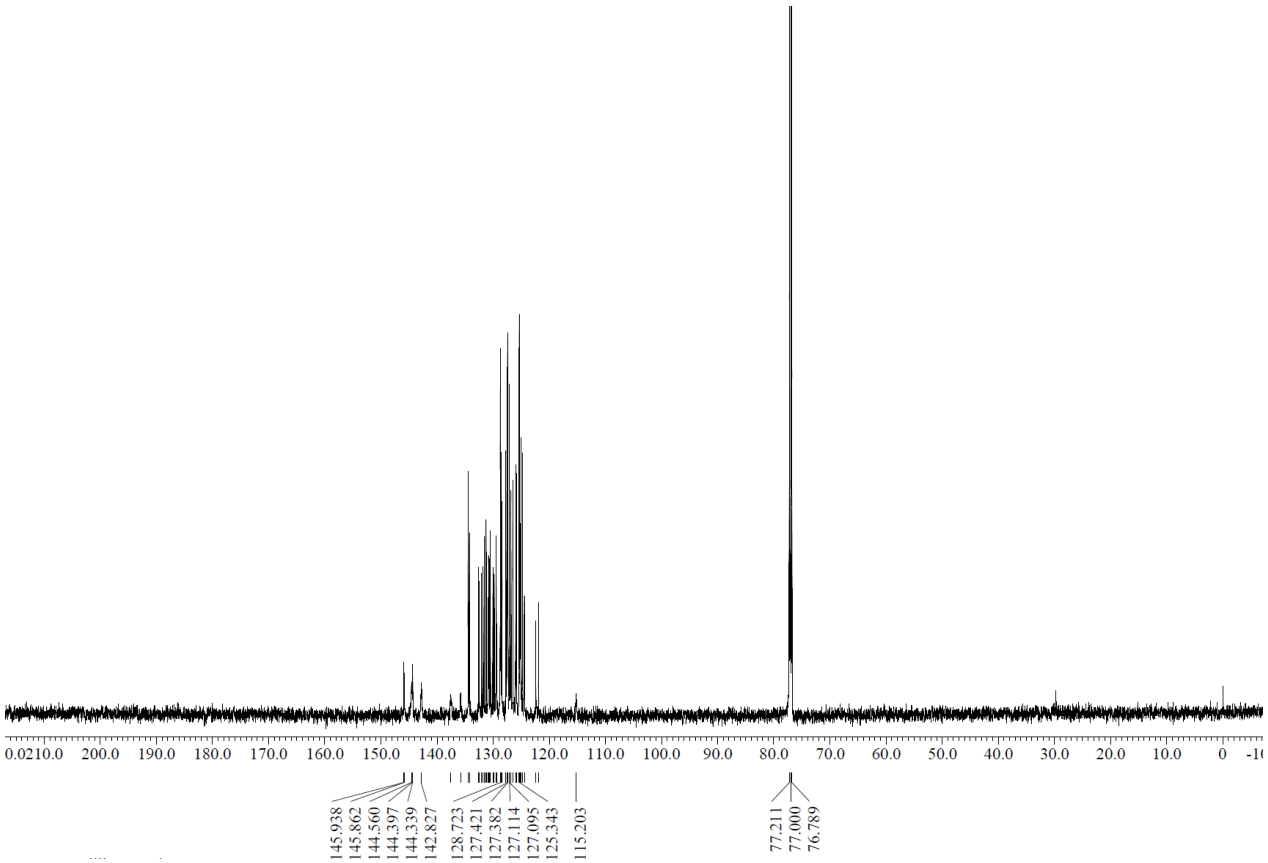
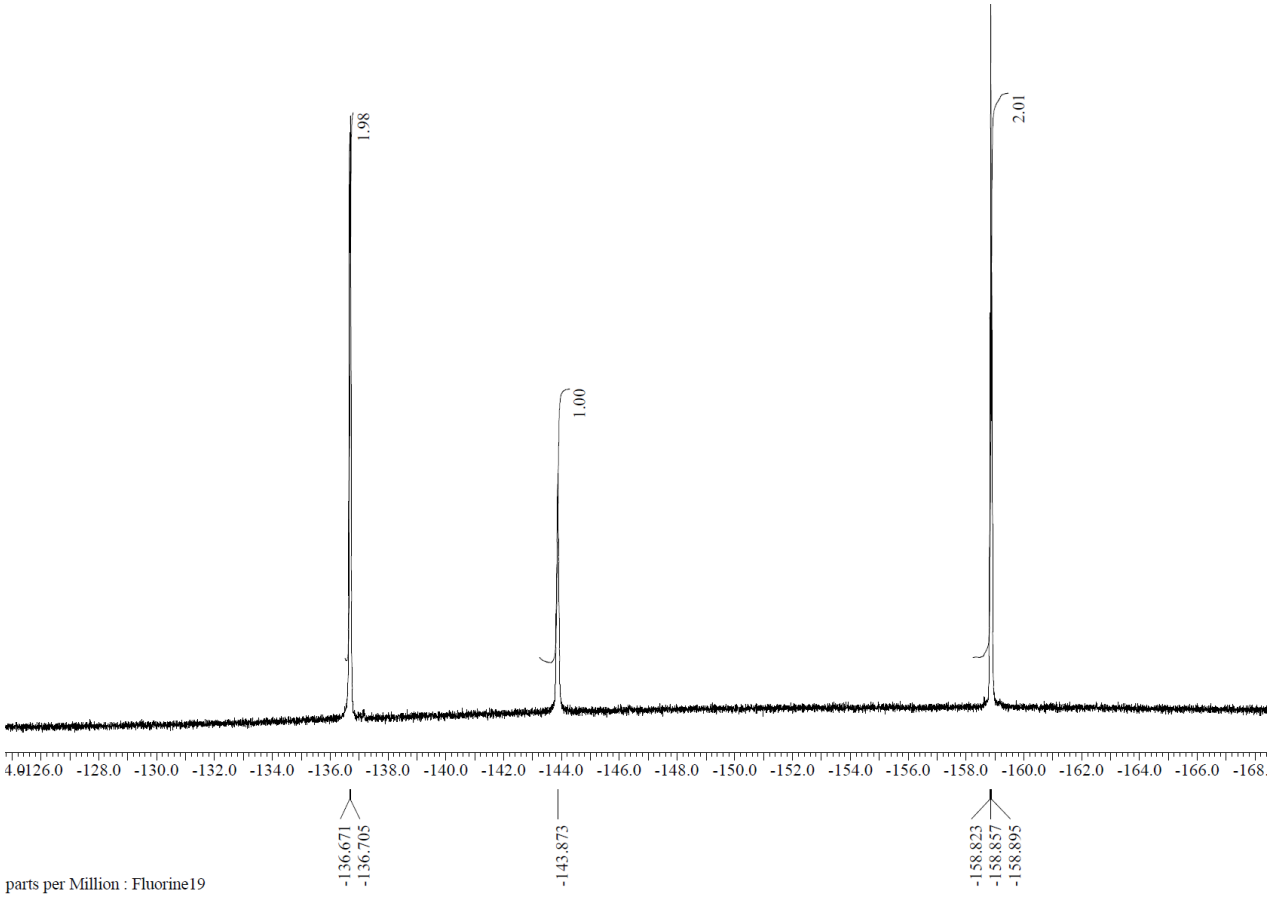
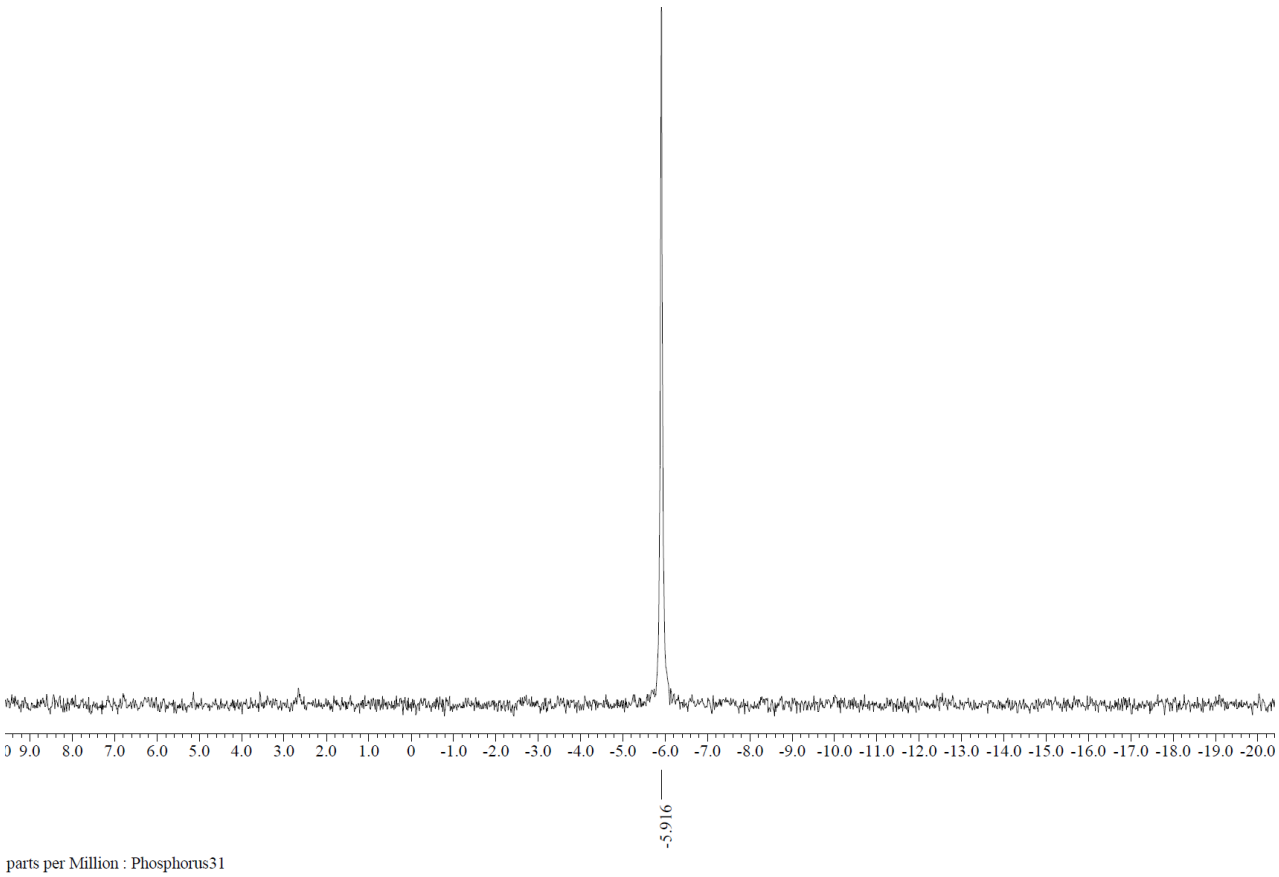


^{19}F NMR (565 MHz) and ^{31}P NMR (243 MHz) spectra of (*R*)-**3c**





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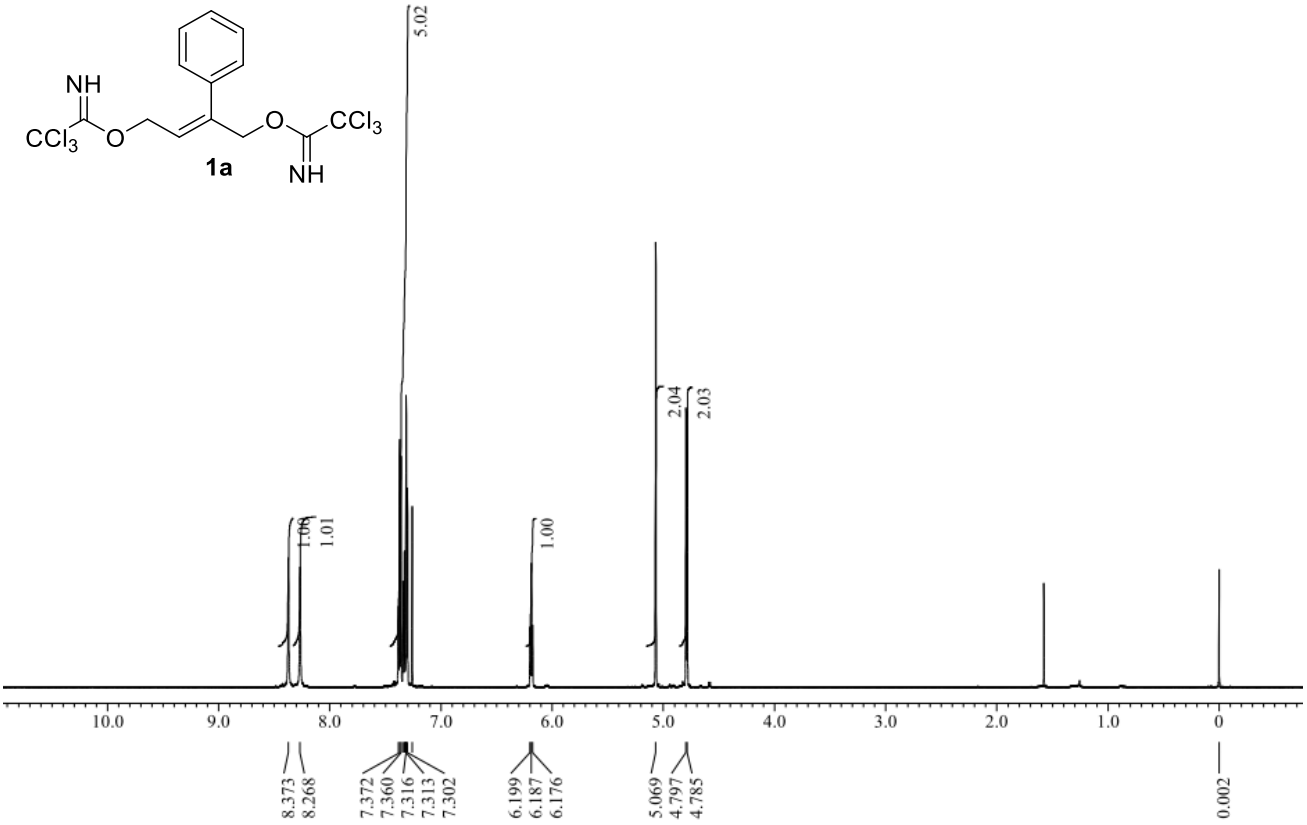

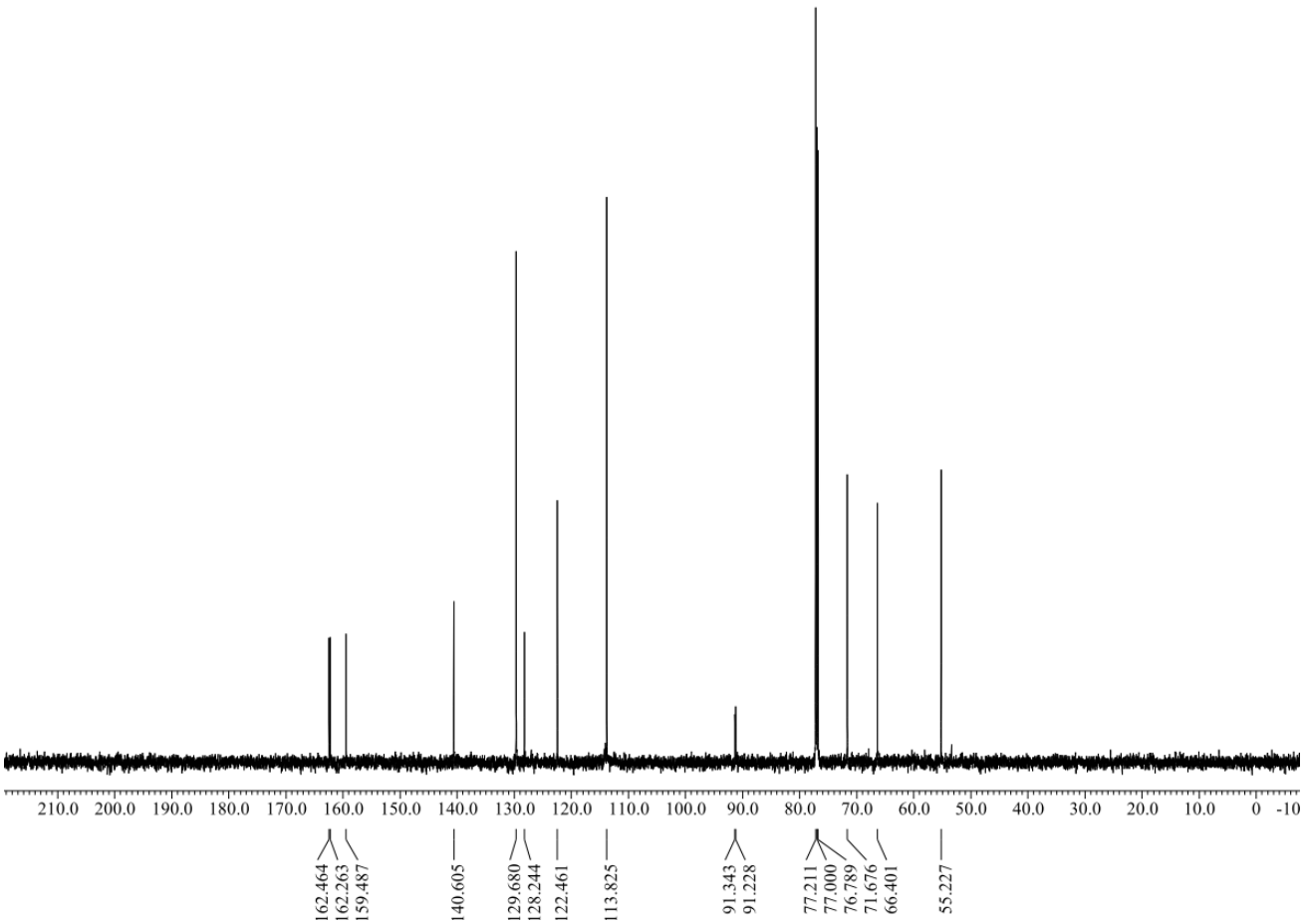

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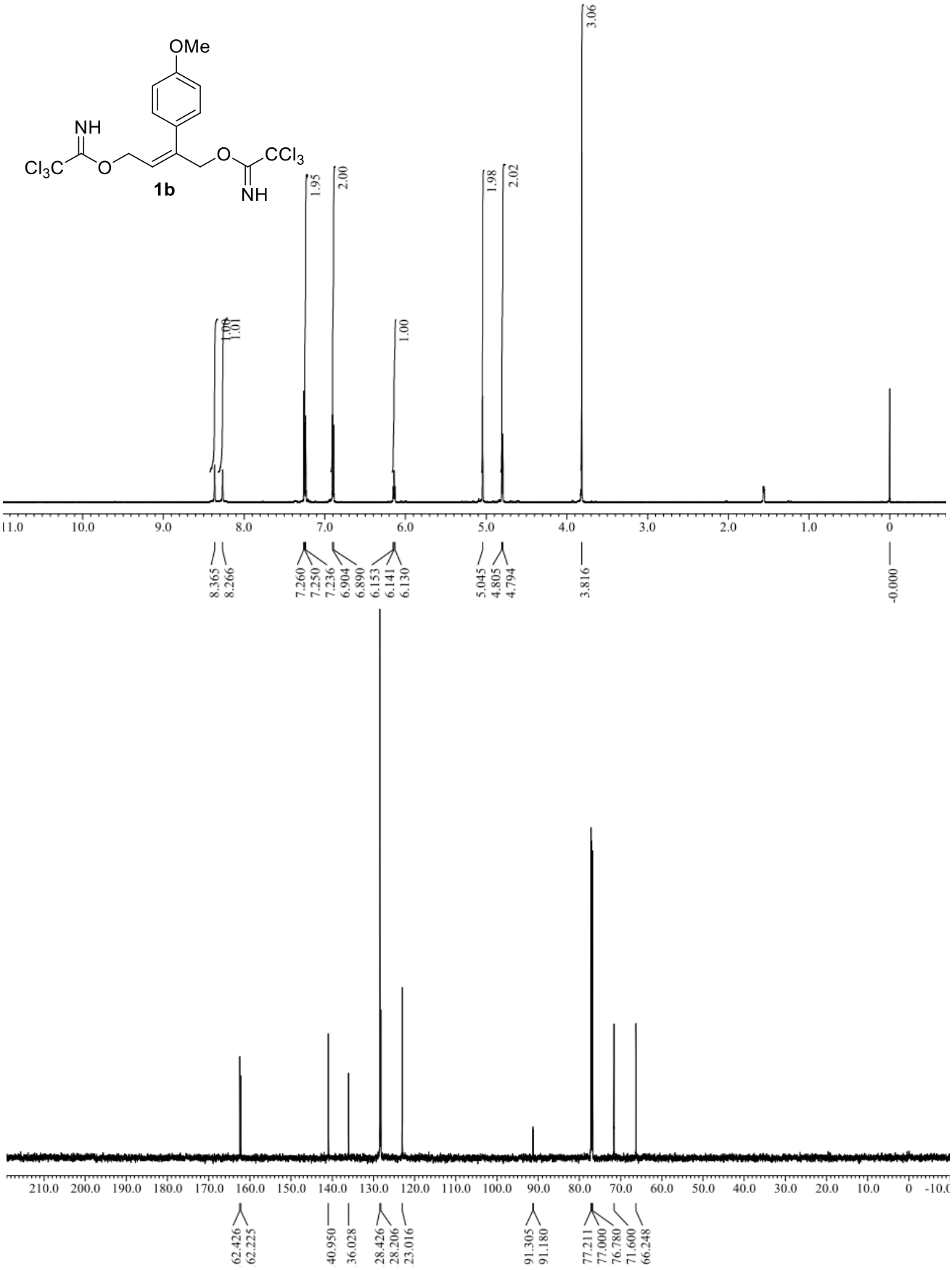

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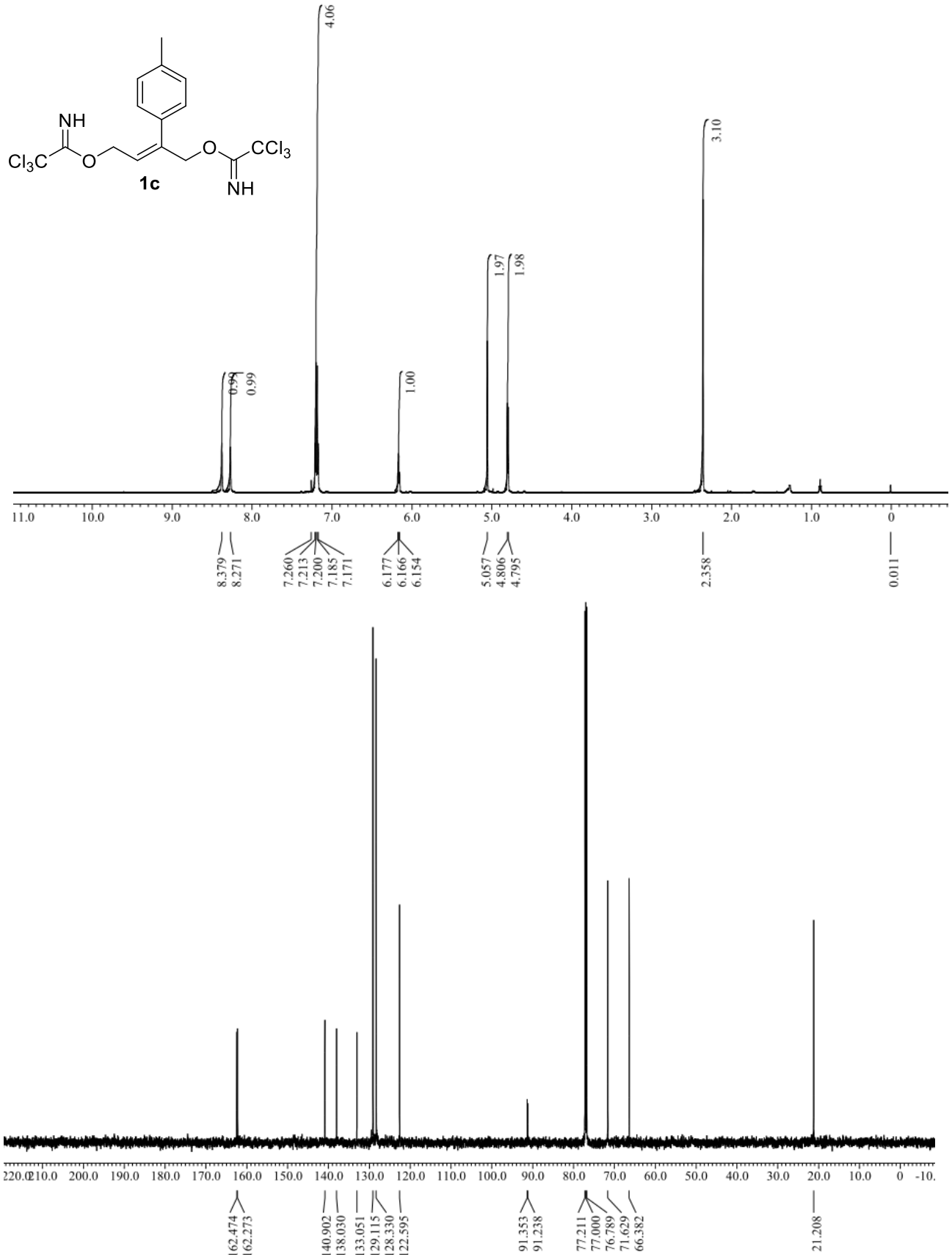

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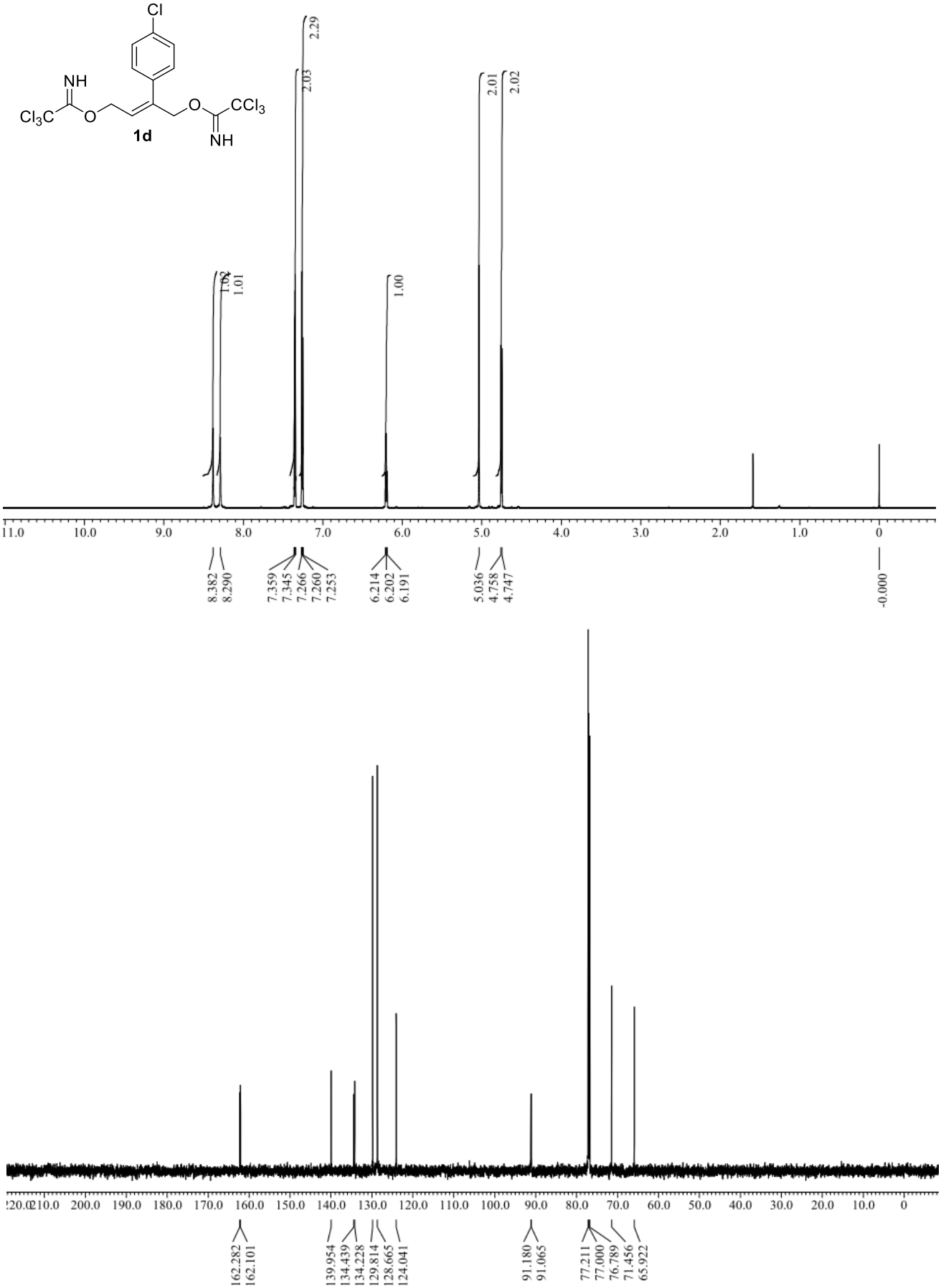
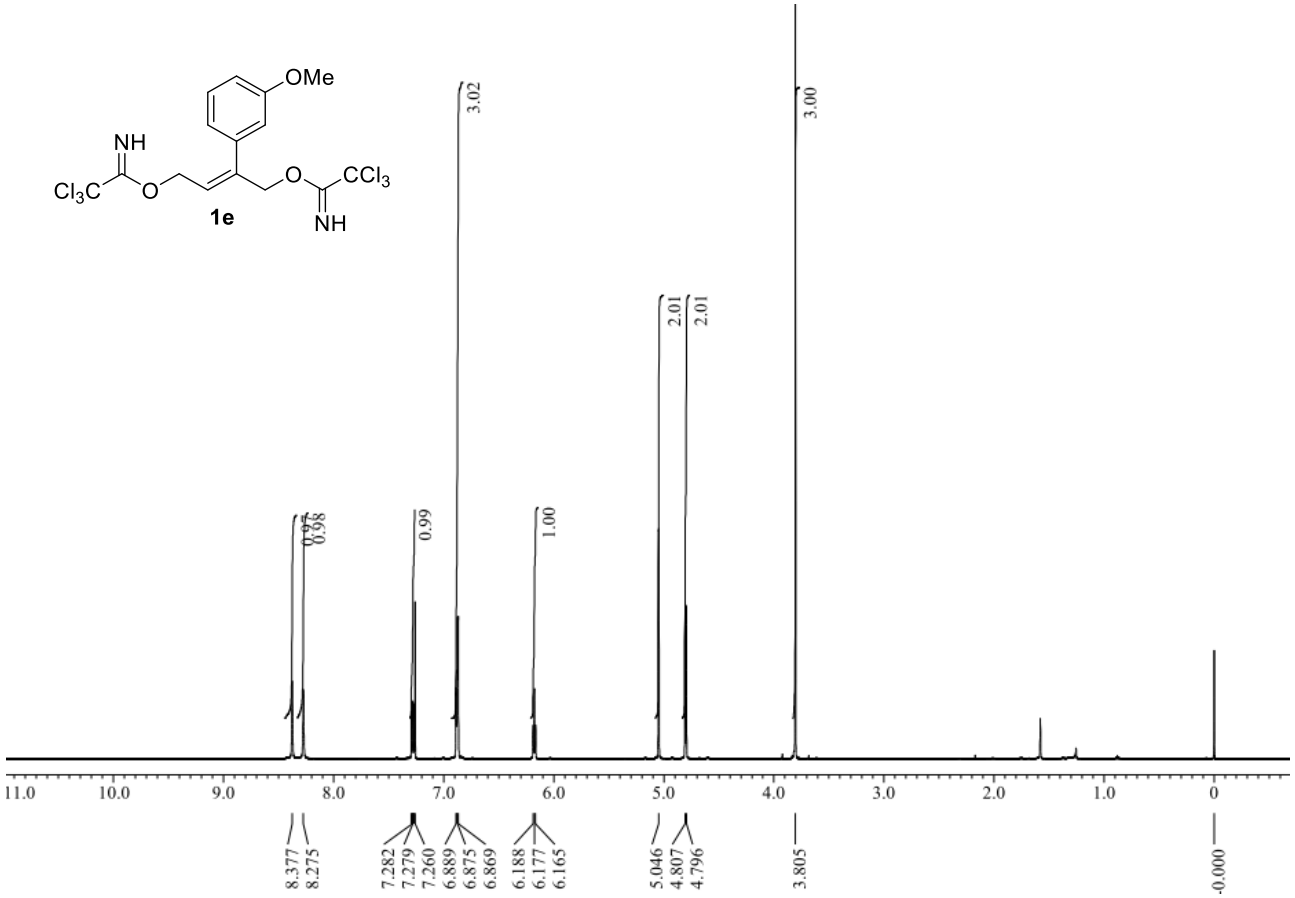
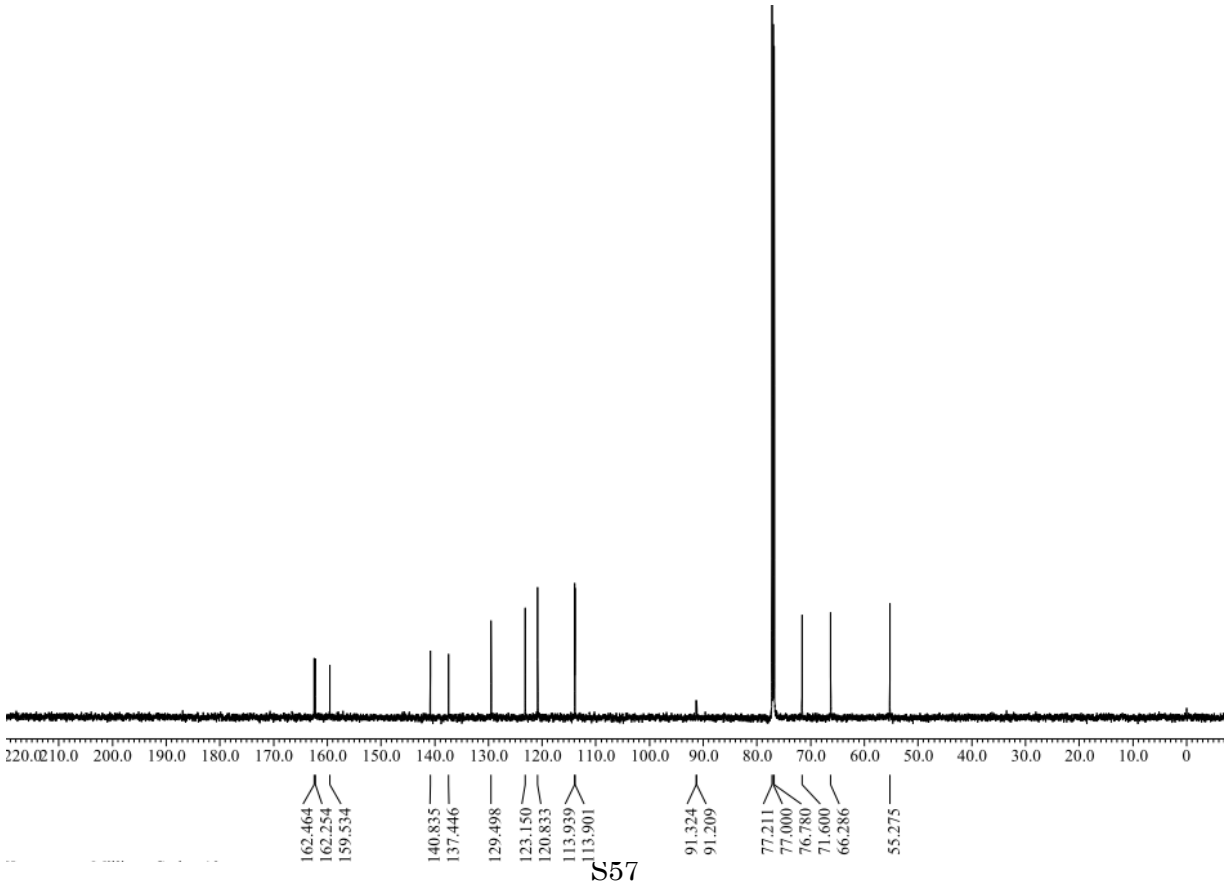
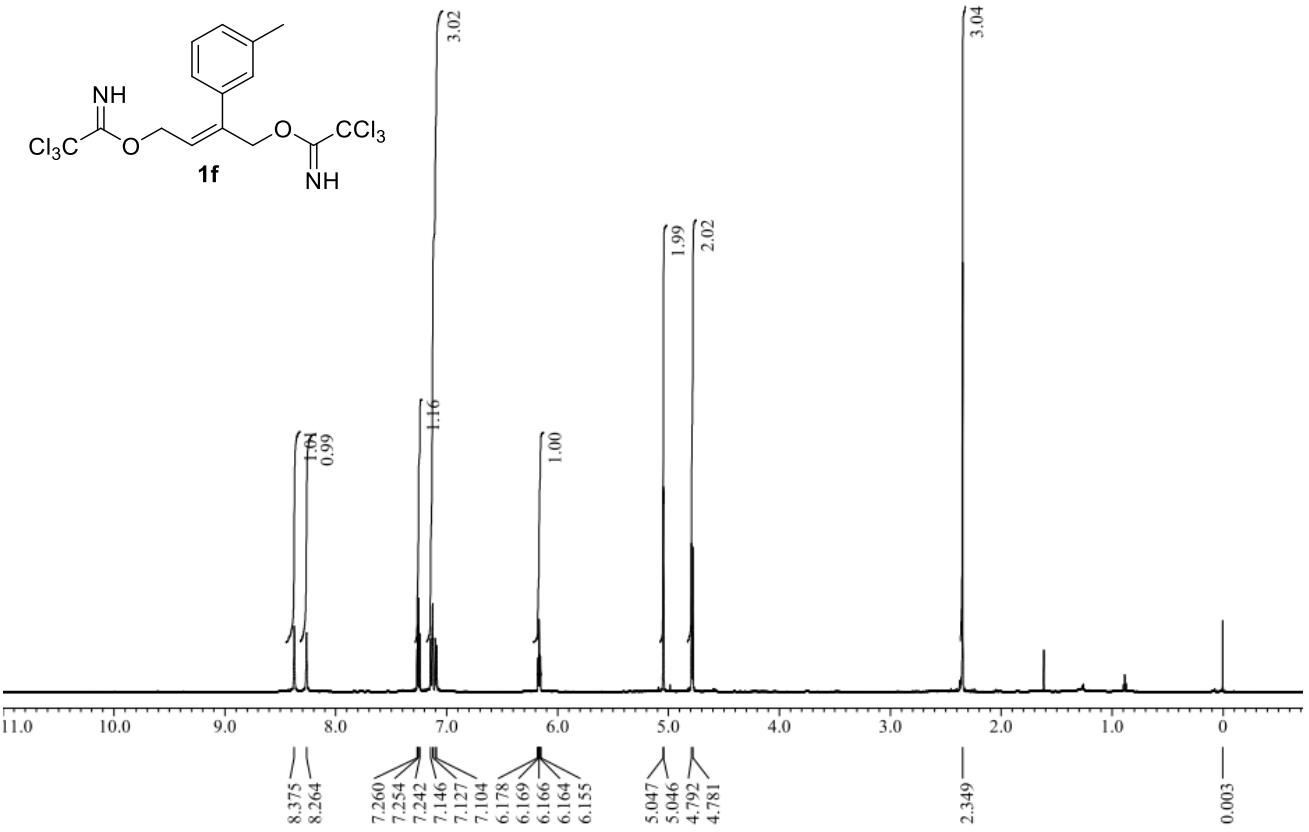


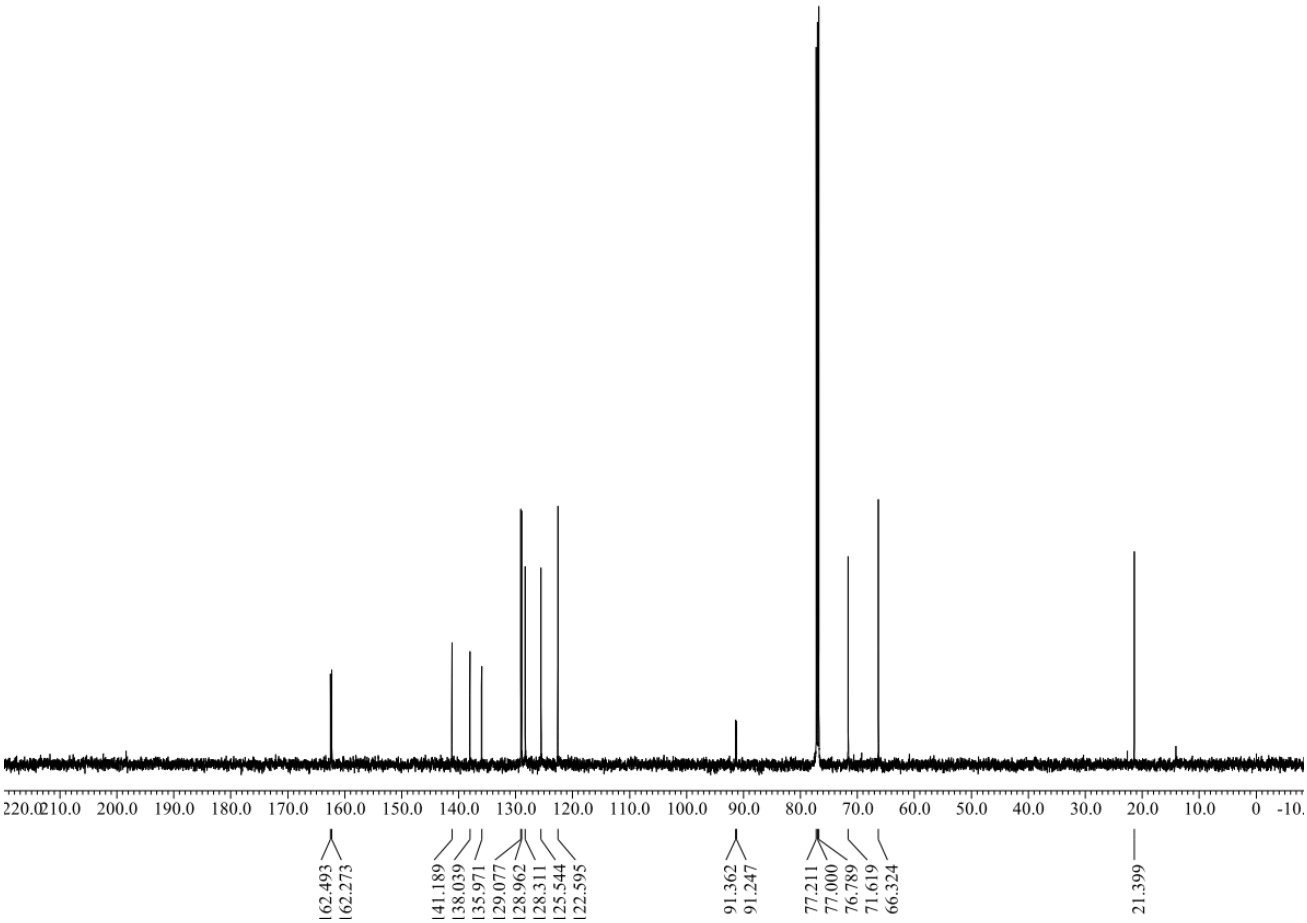
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1e**



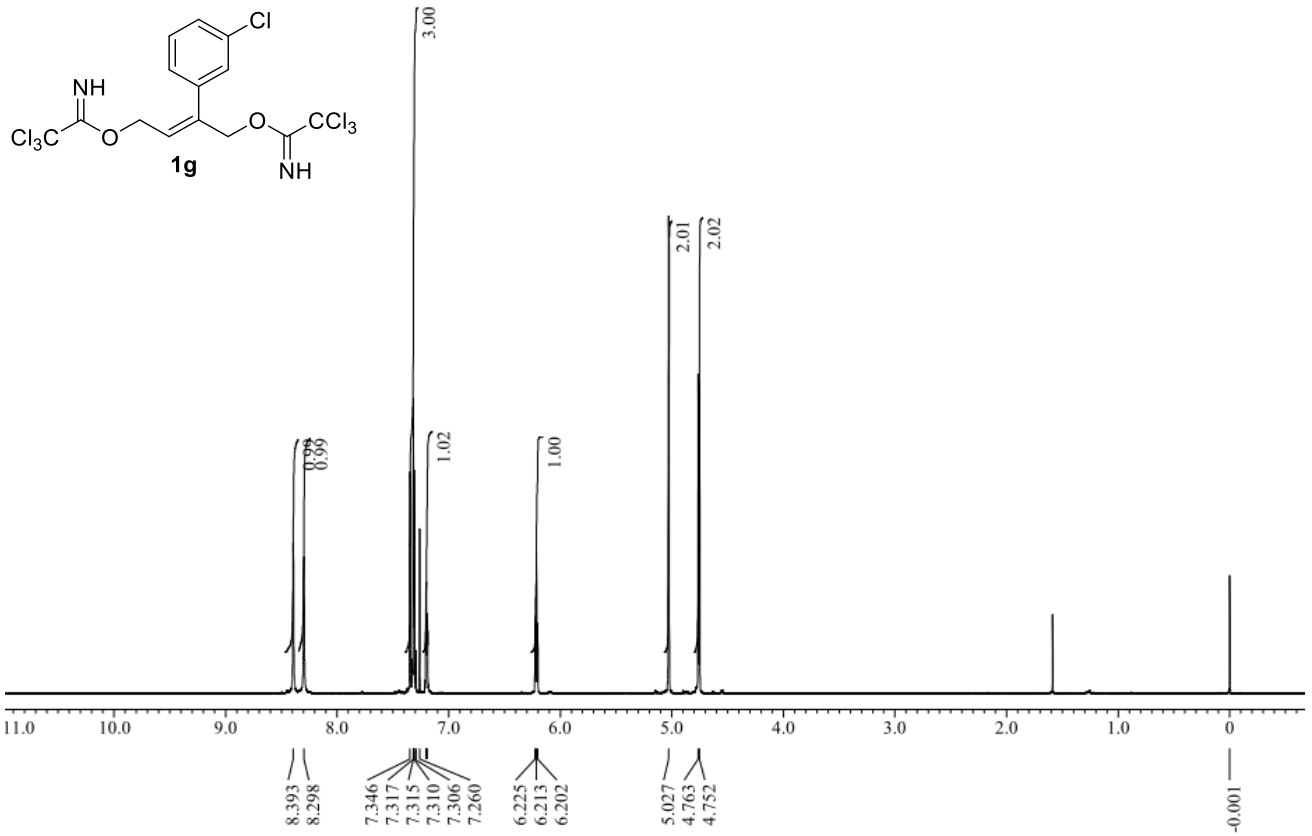


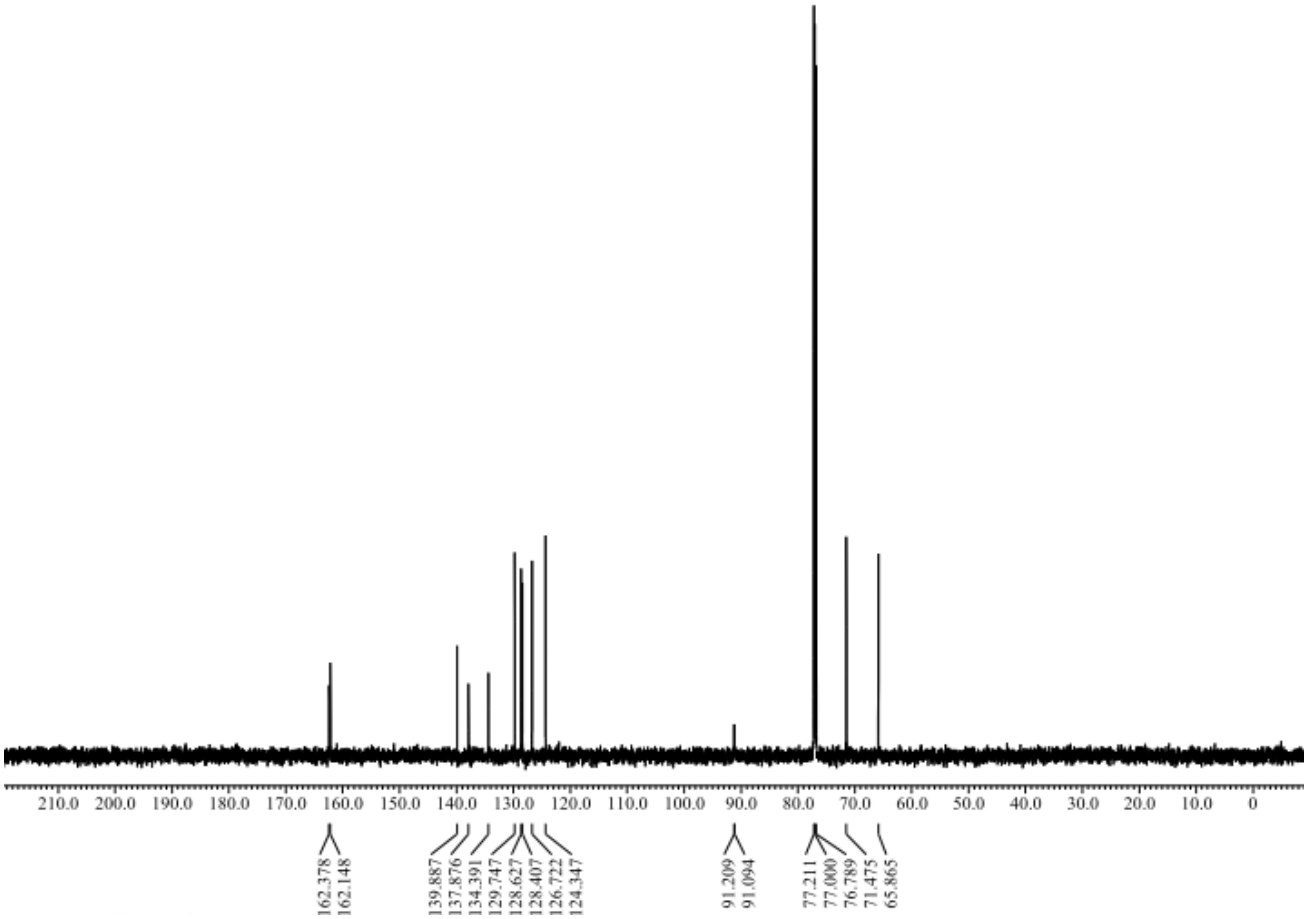
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1f**



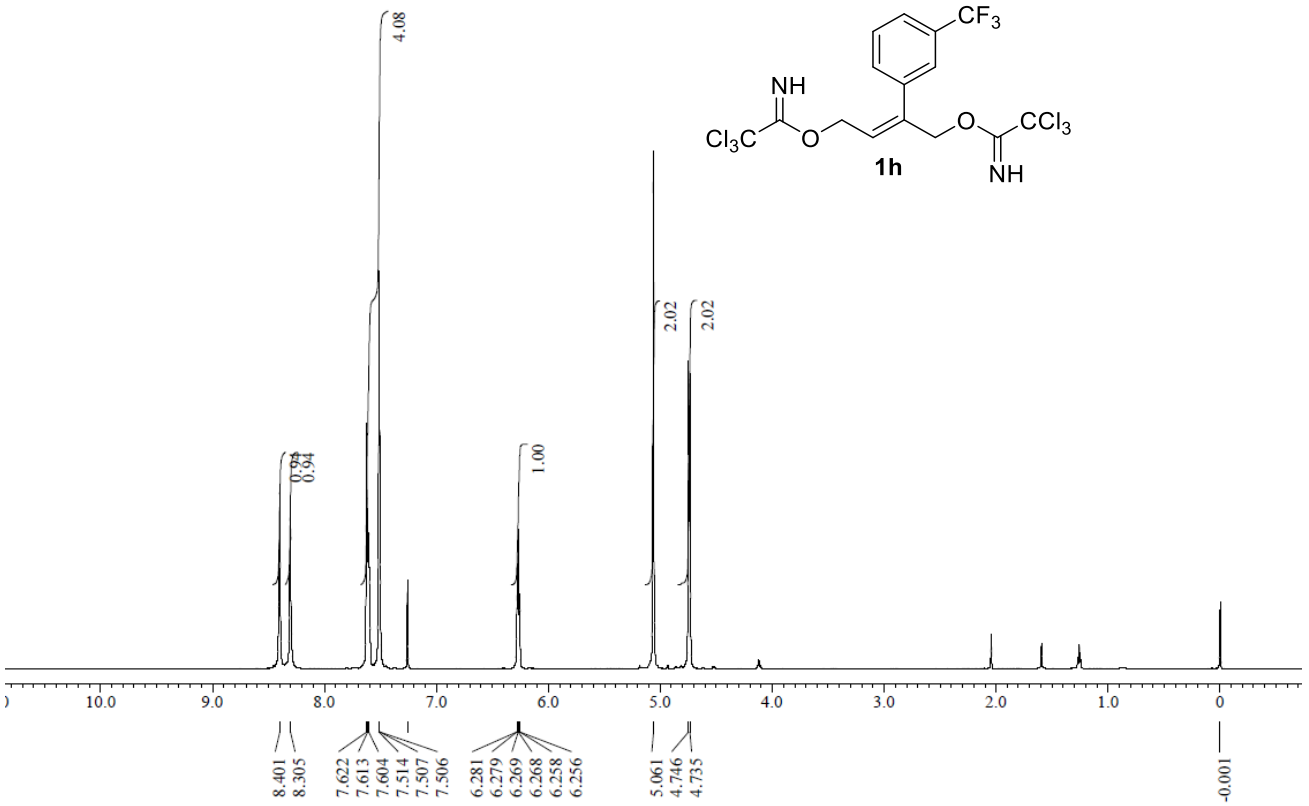


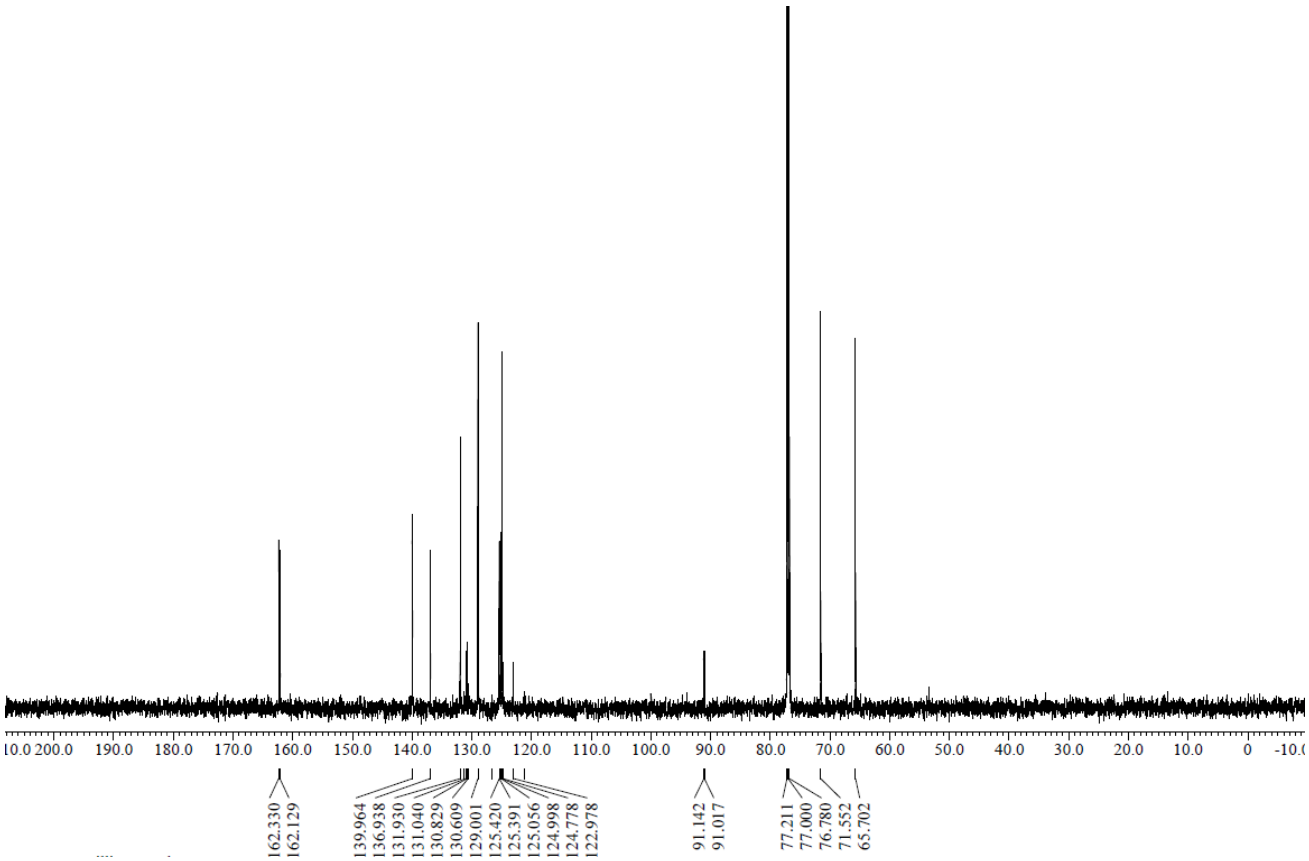
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1g**



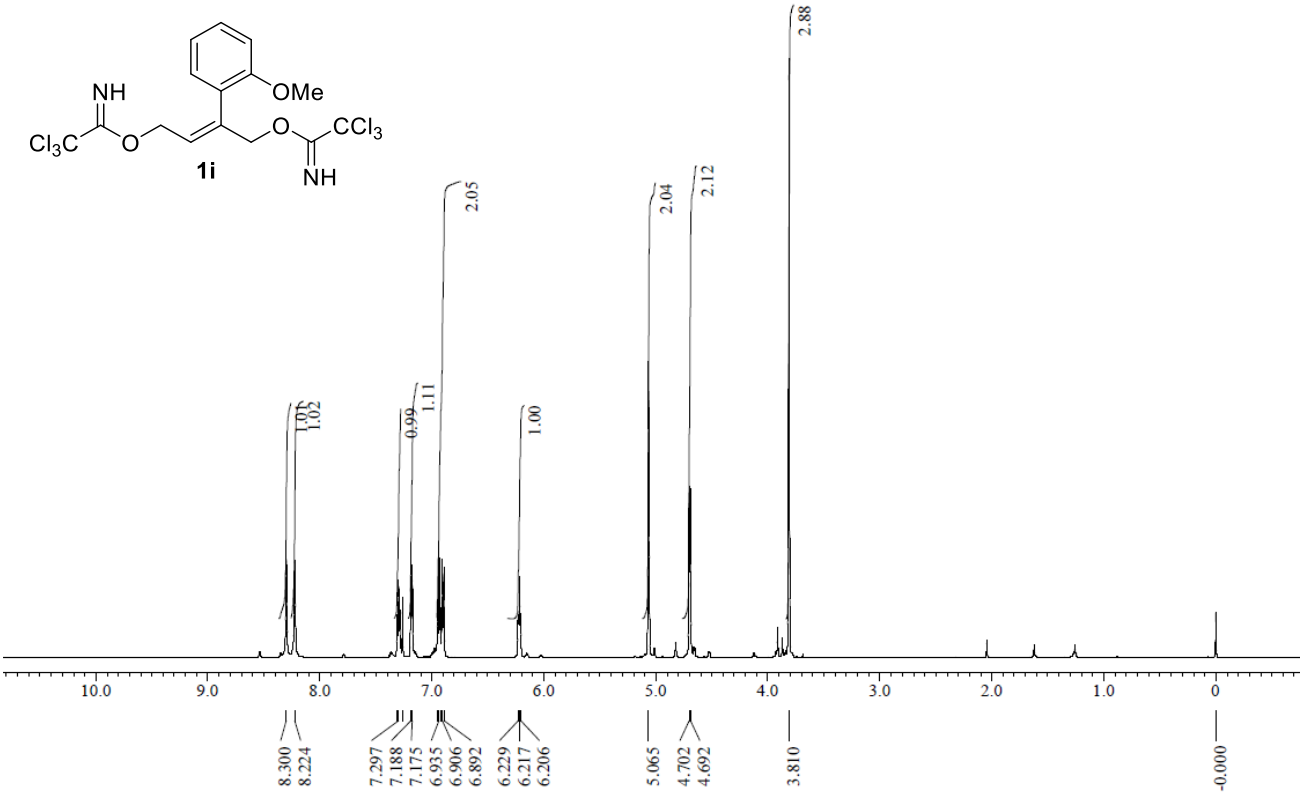


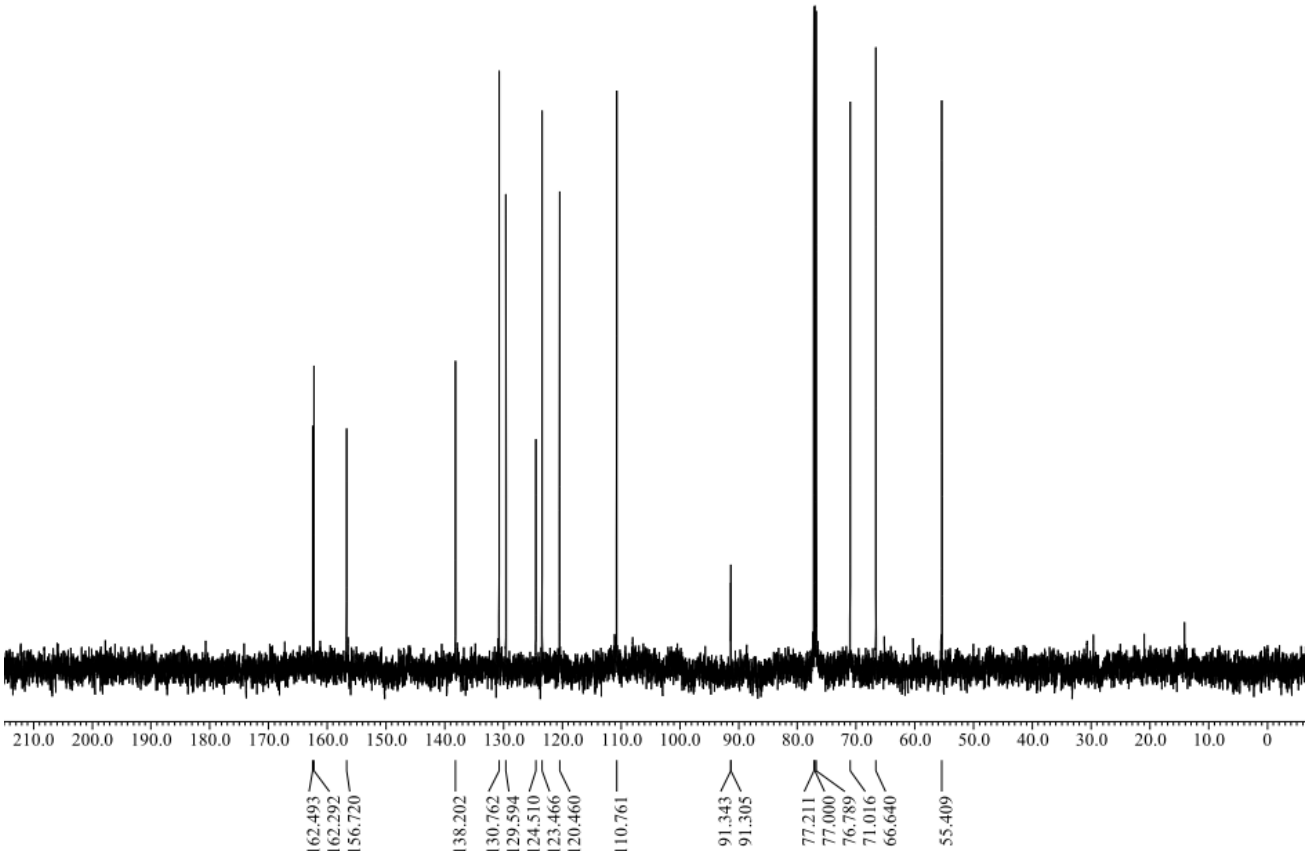
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1h**



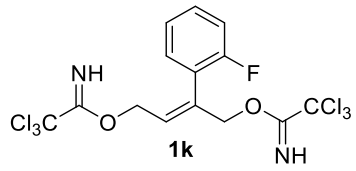


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1i**

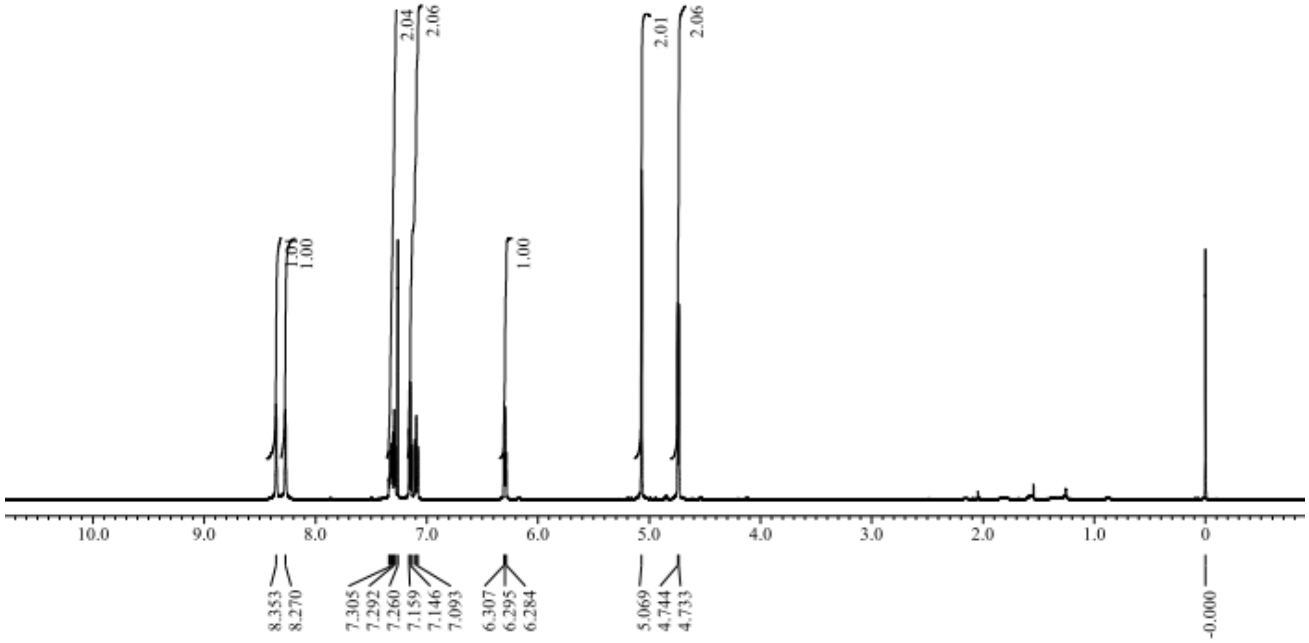


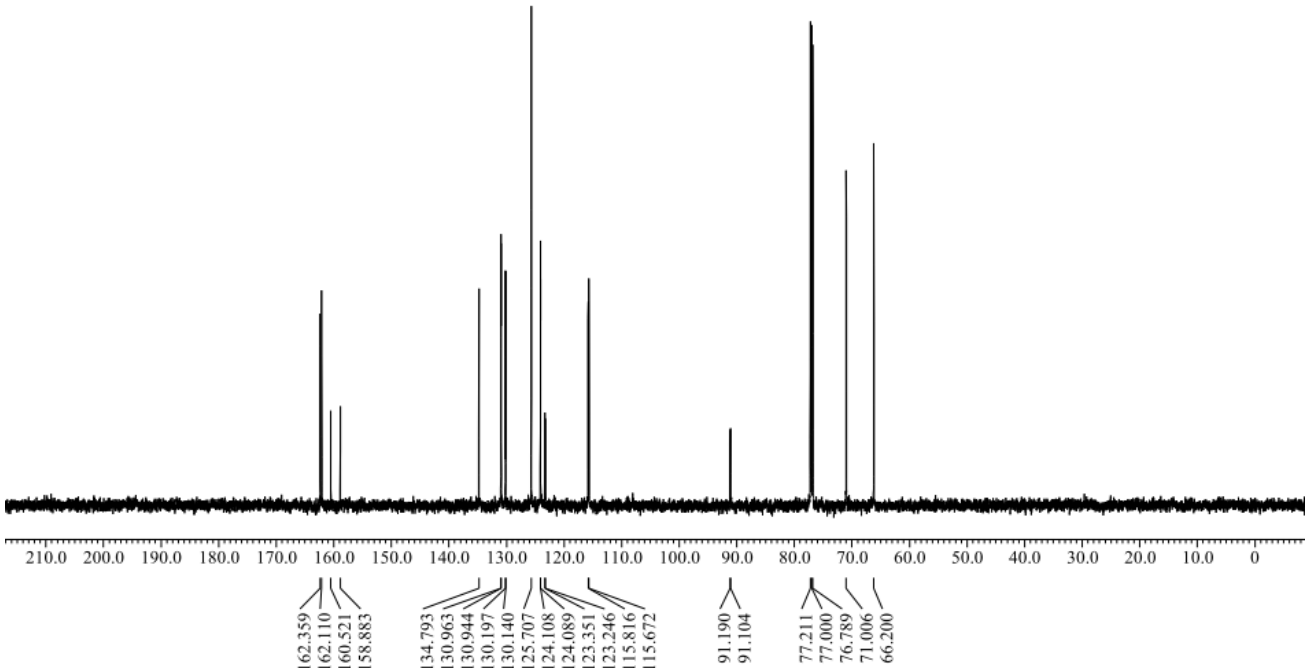


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1k**

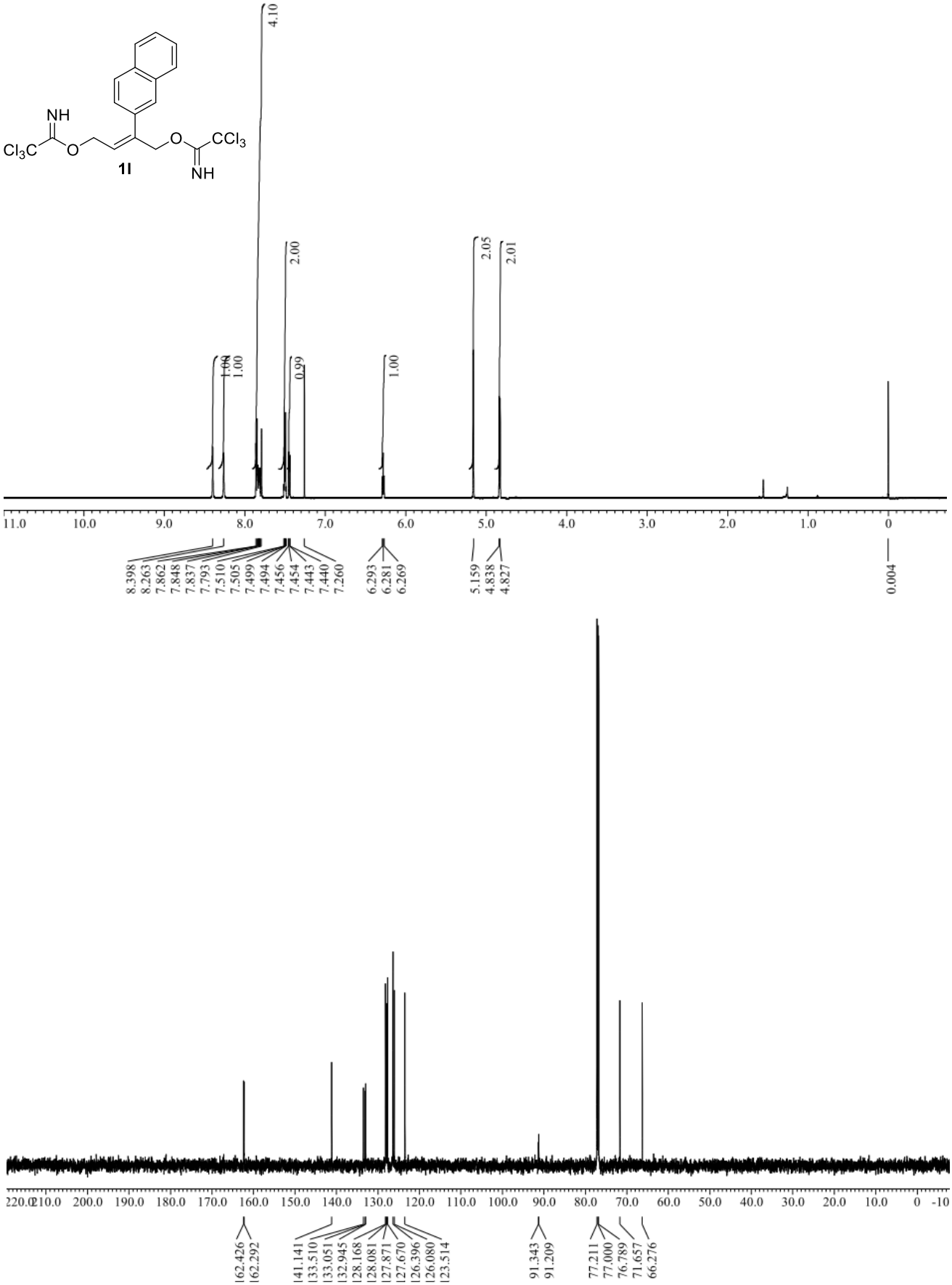


1k

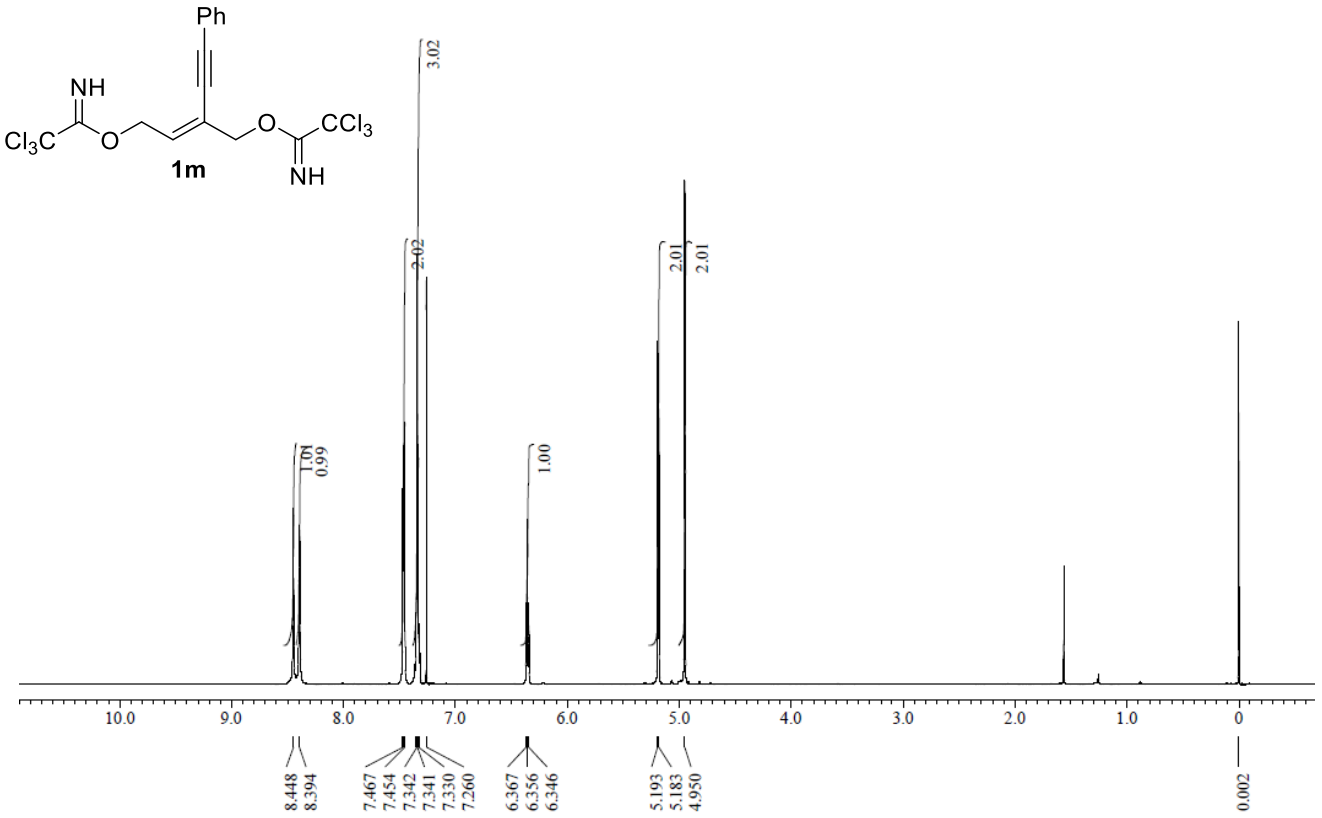


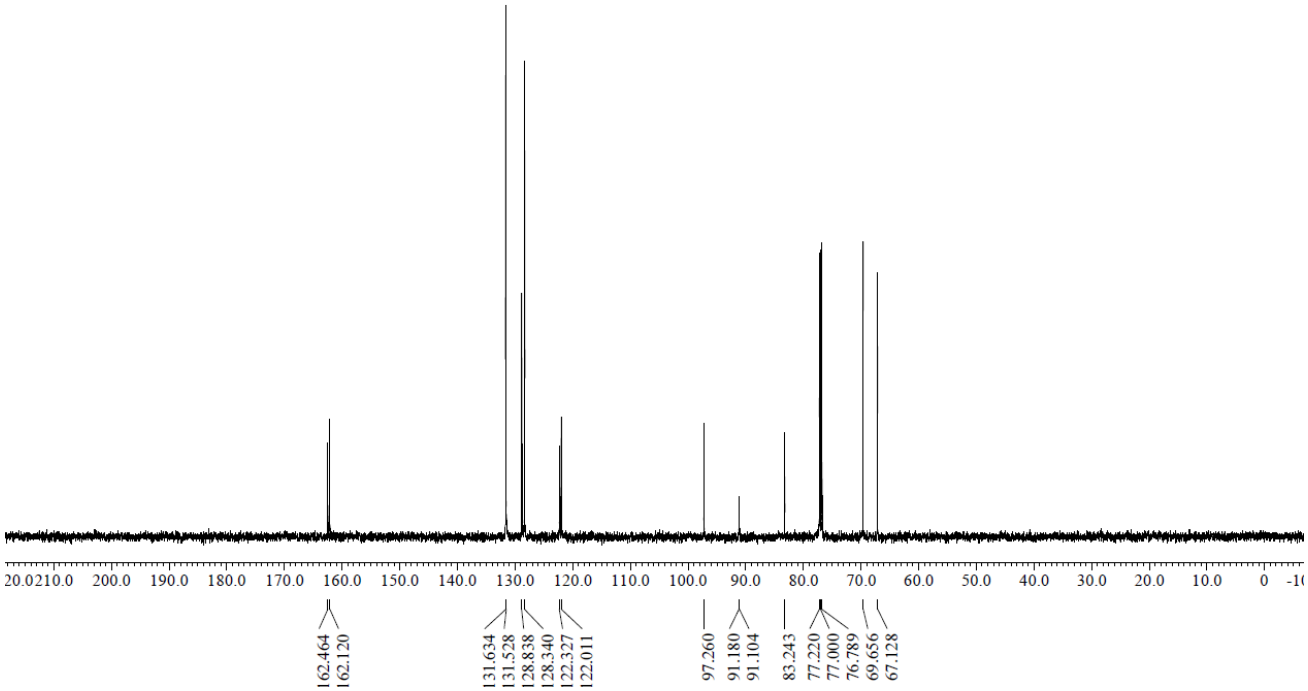


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1l**

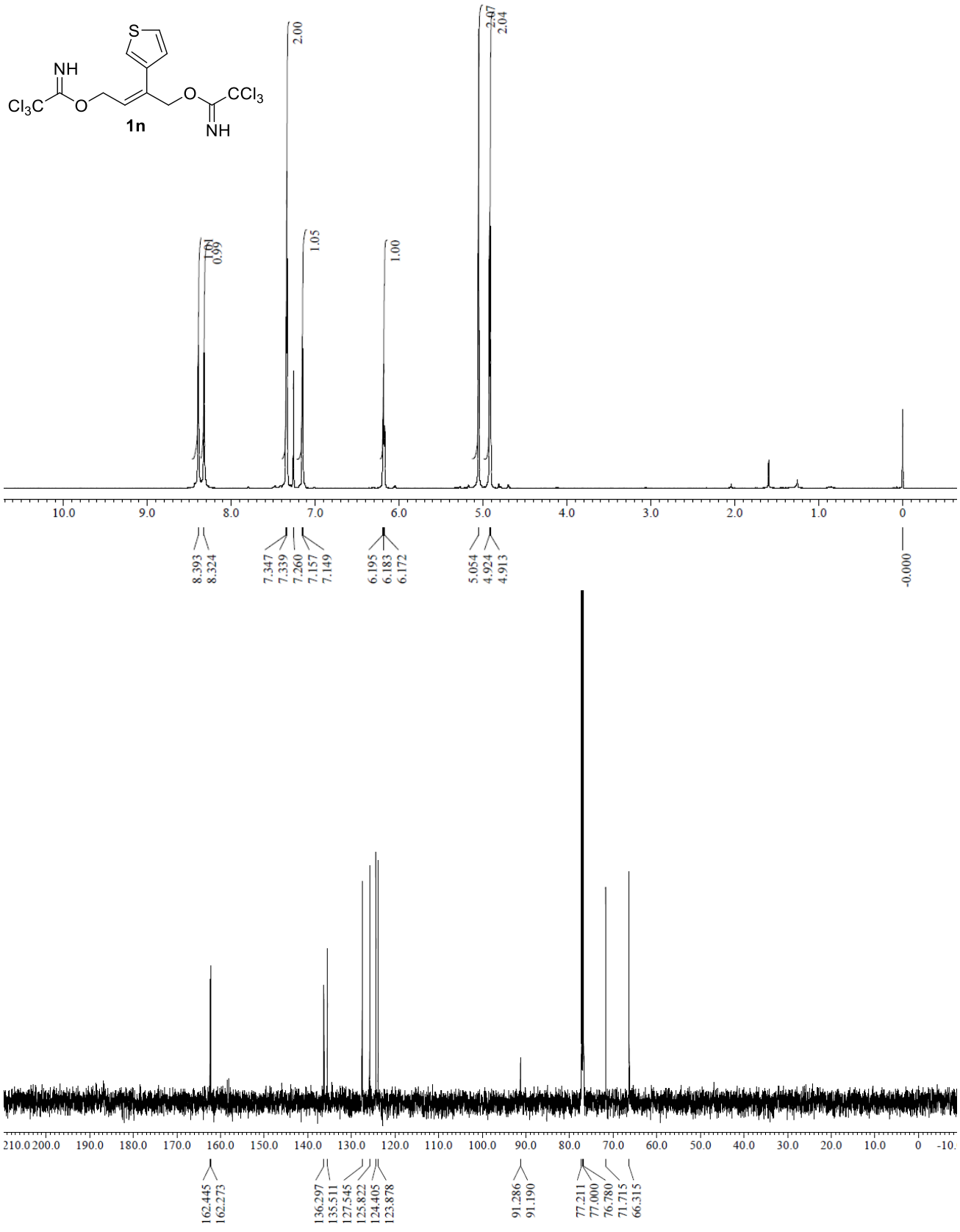


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1m**

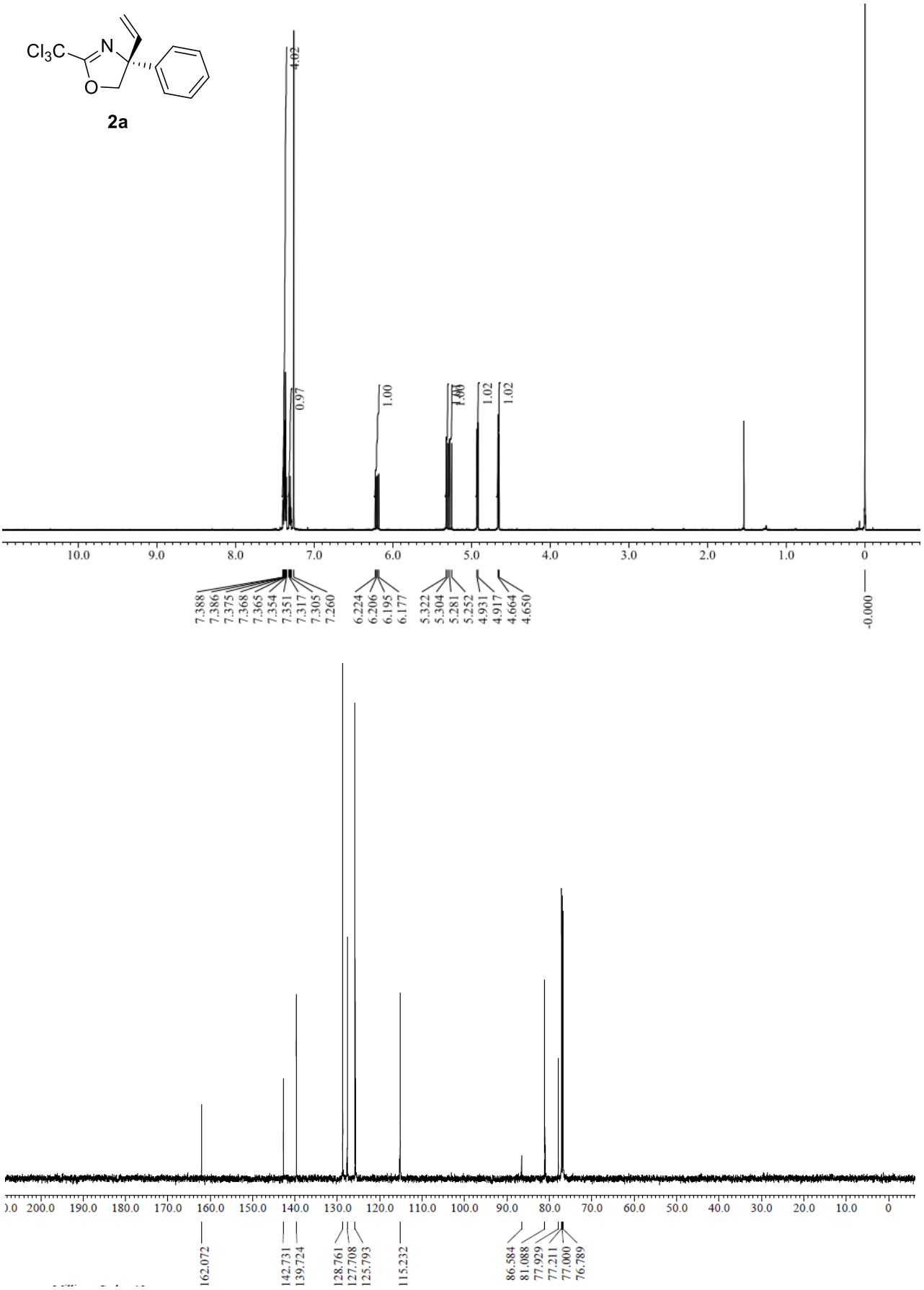




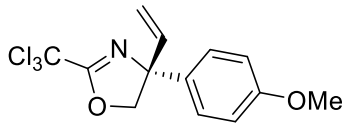
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1n**



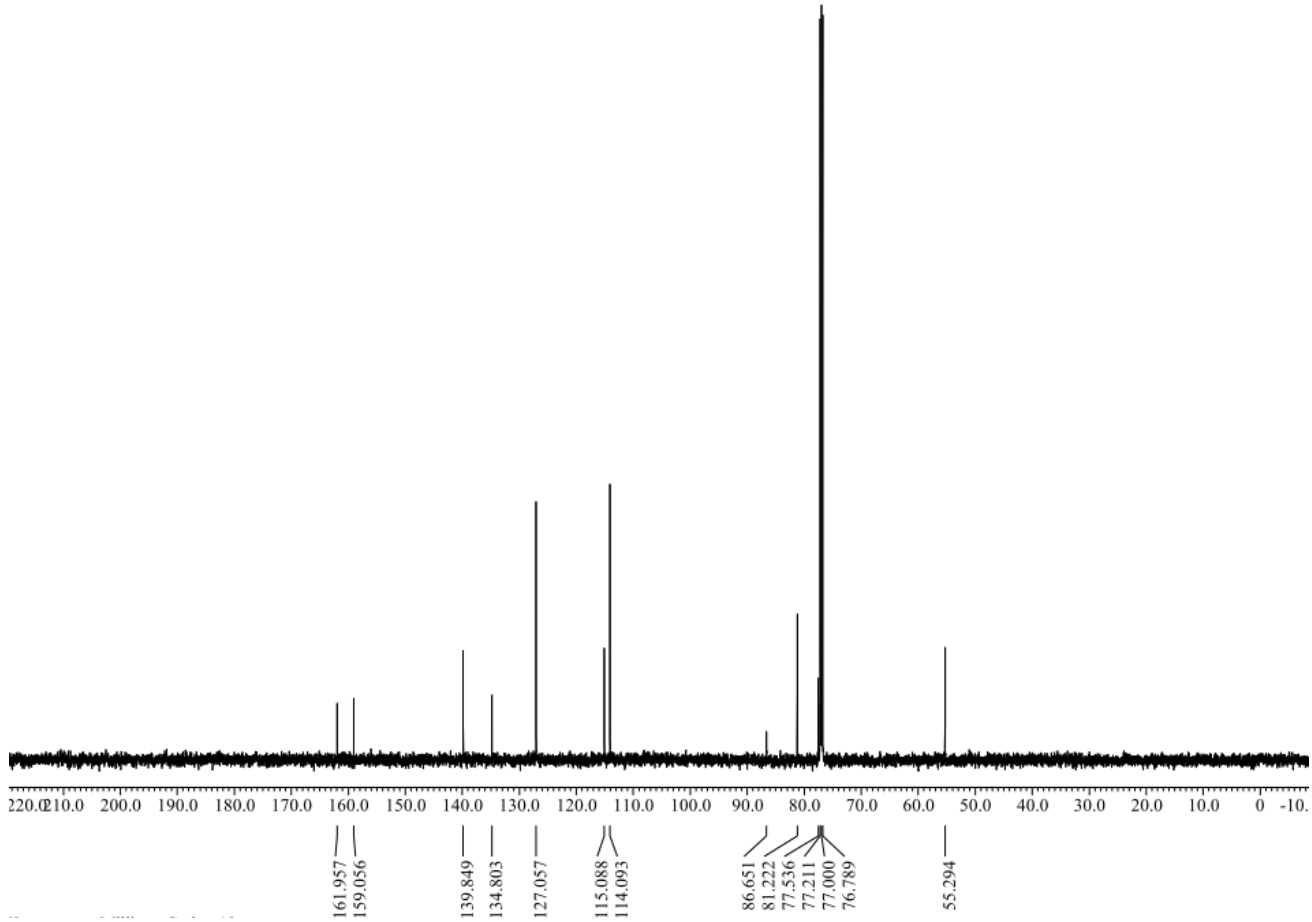
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2a**



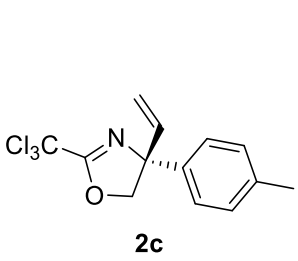
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2b**



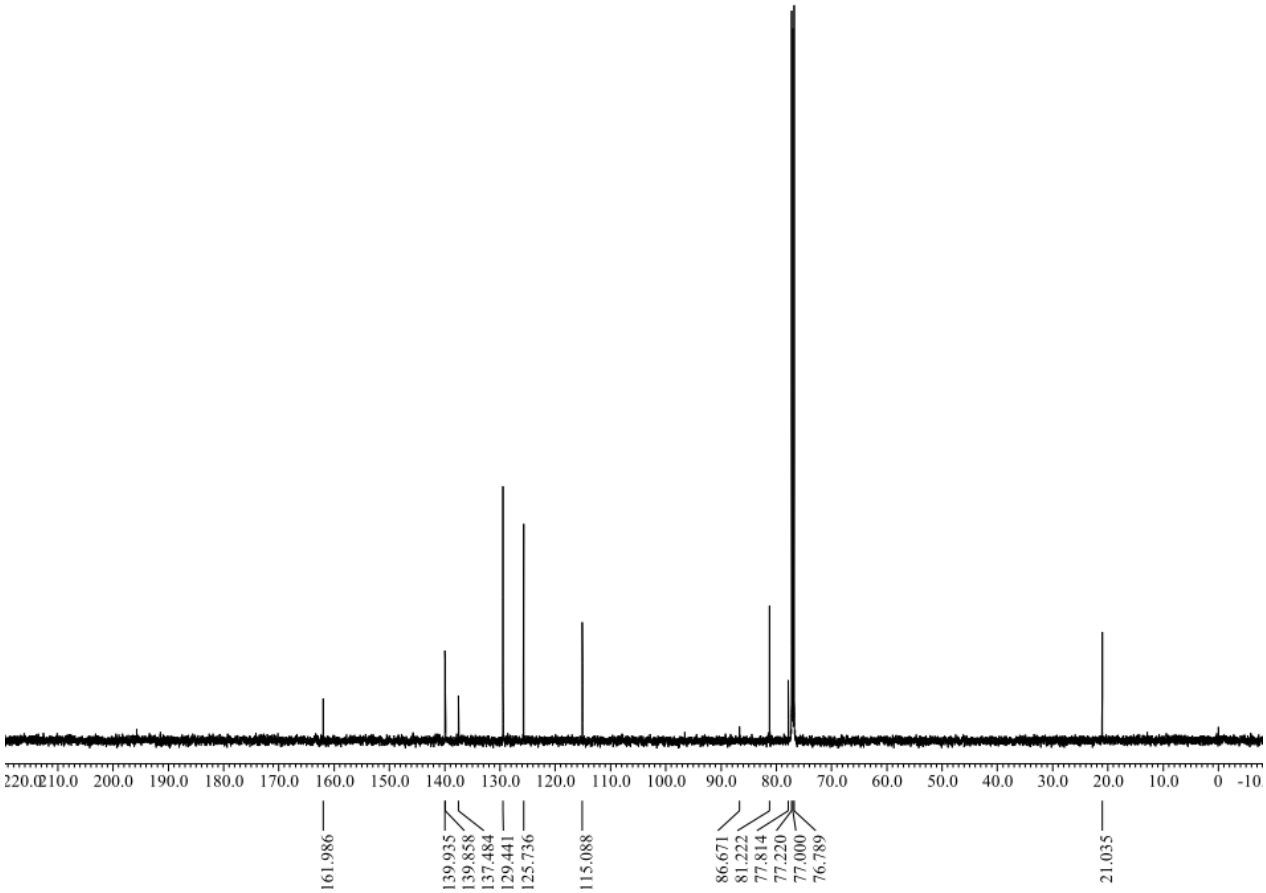
2b



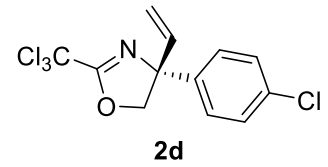
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2c**



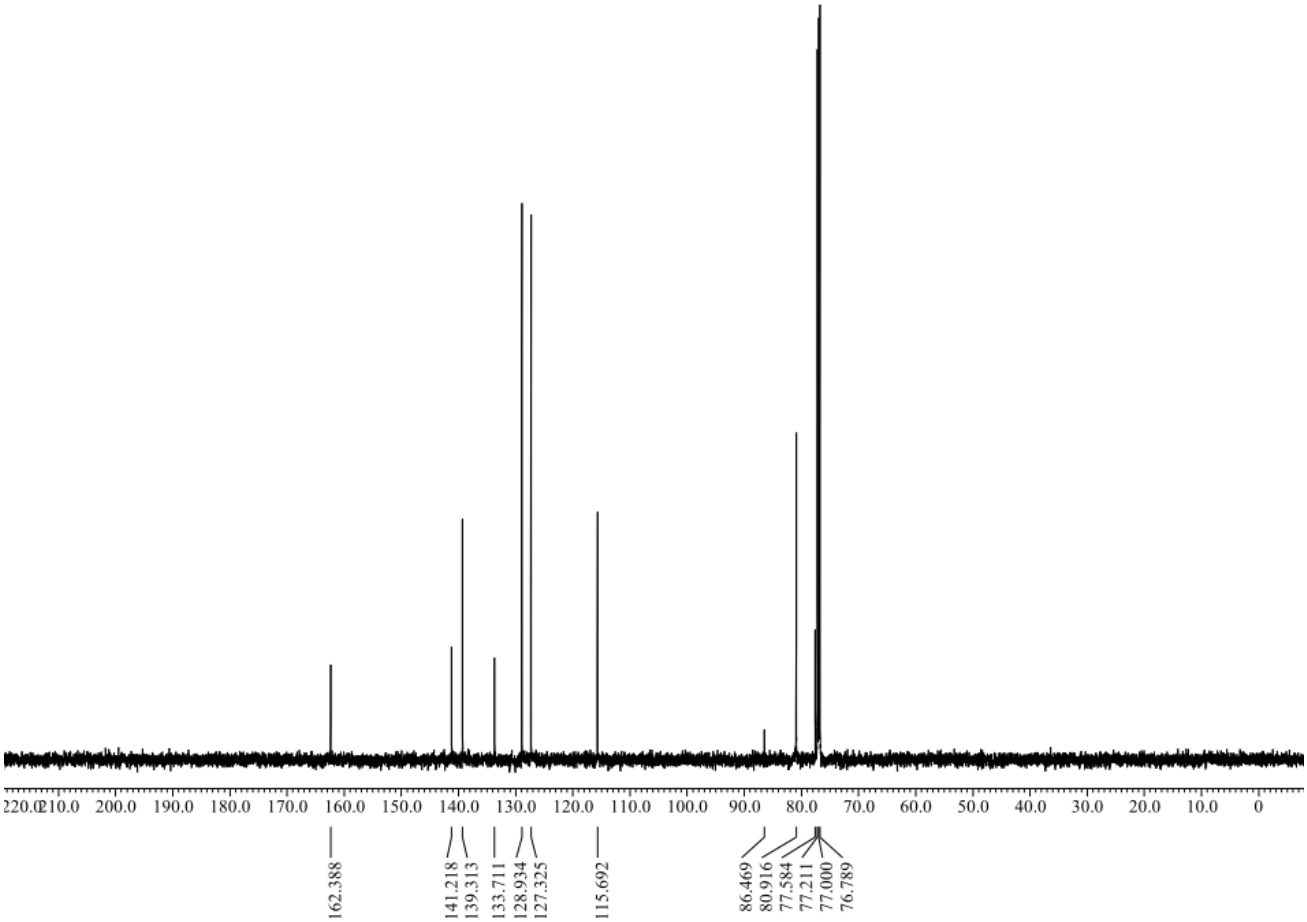
2c



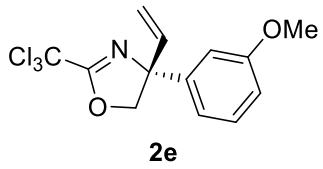
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2d**



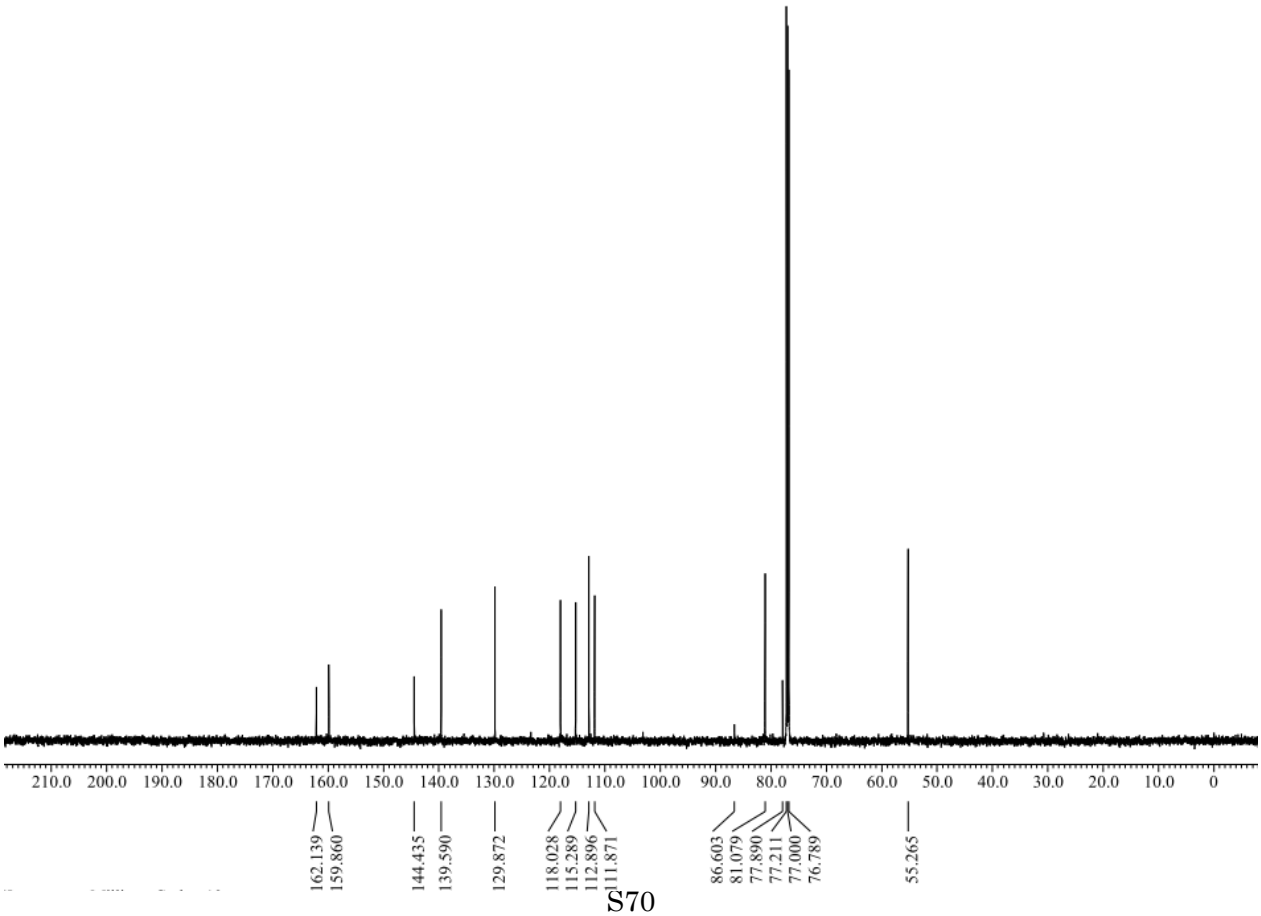
2d



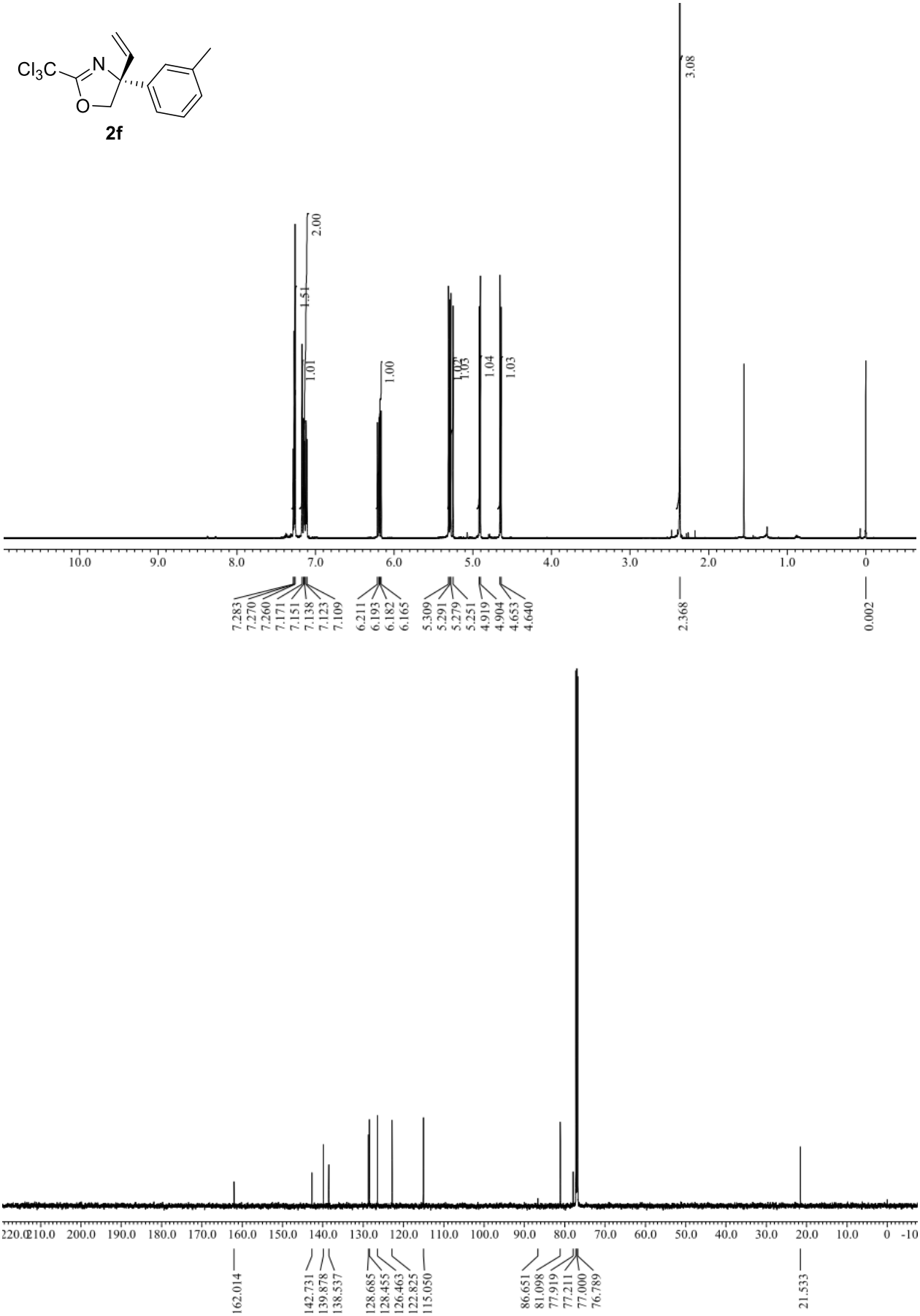
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2e**



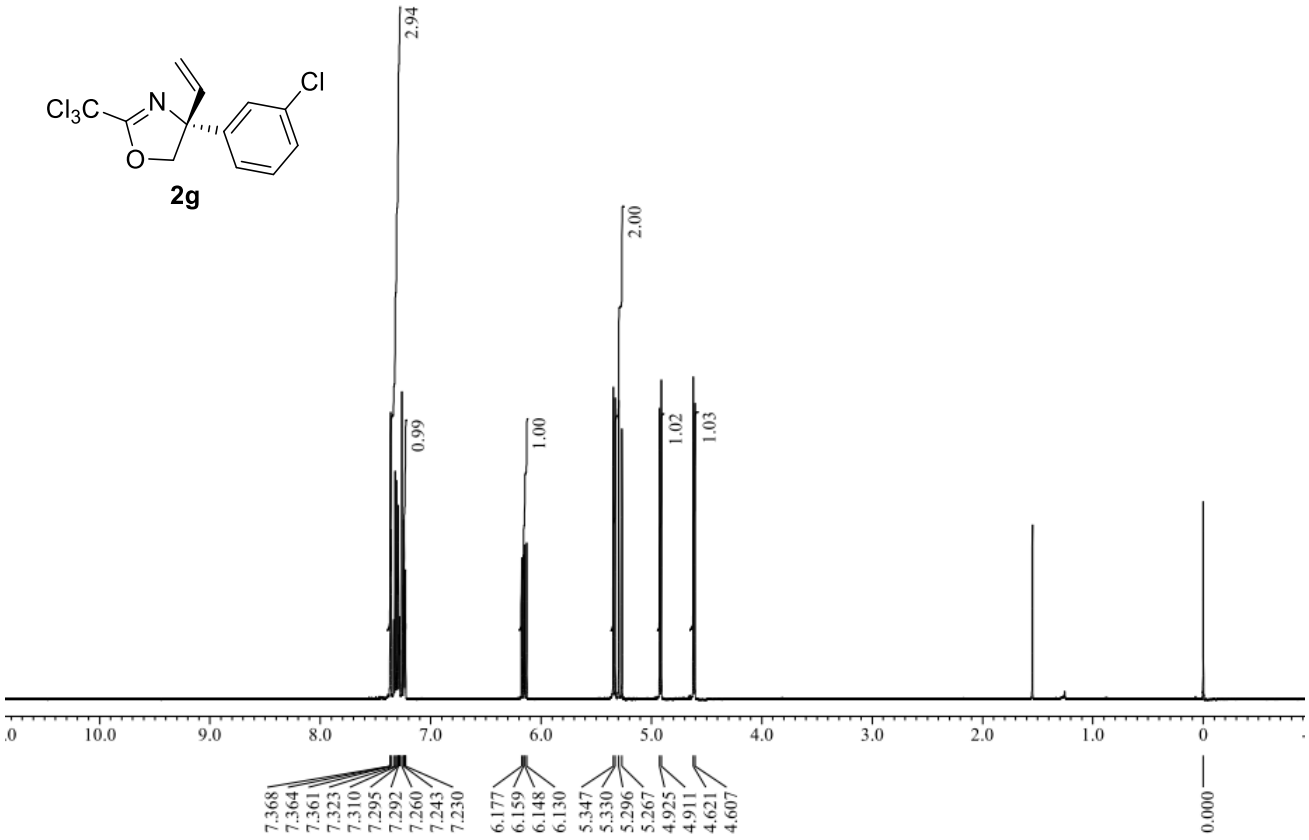
2e

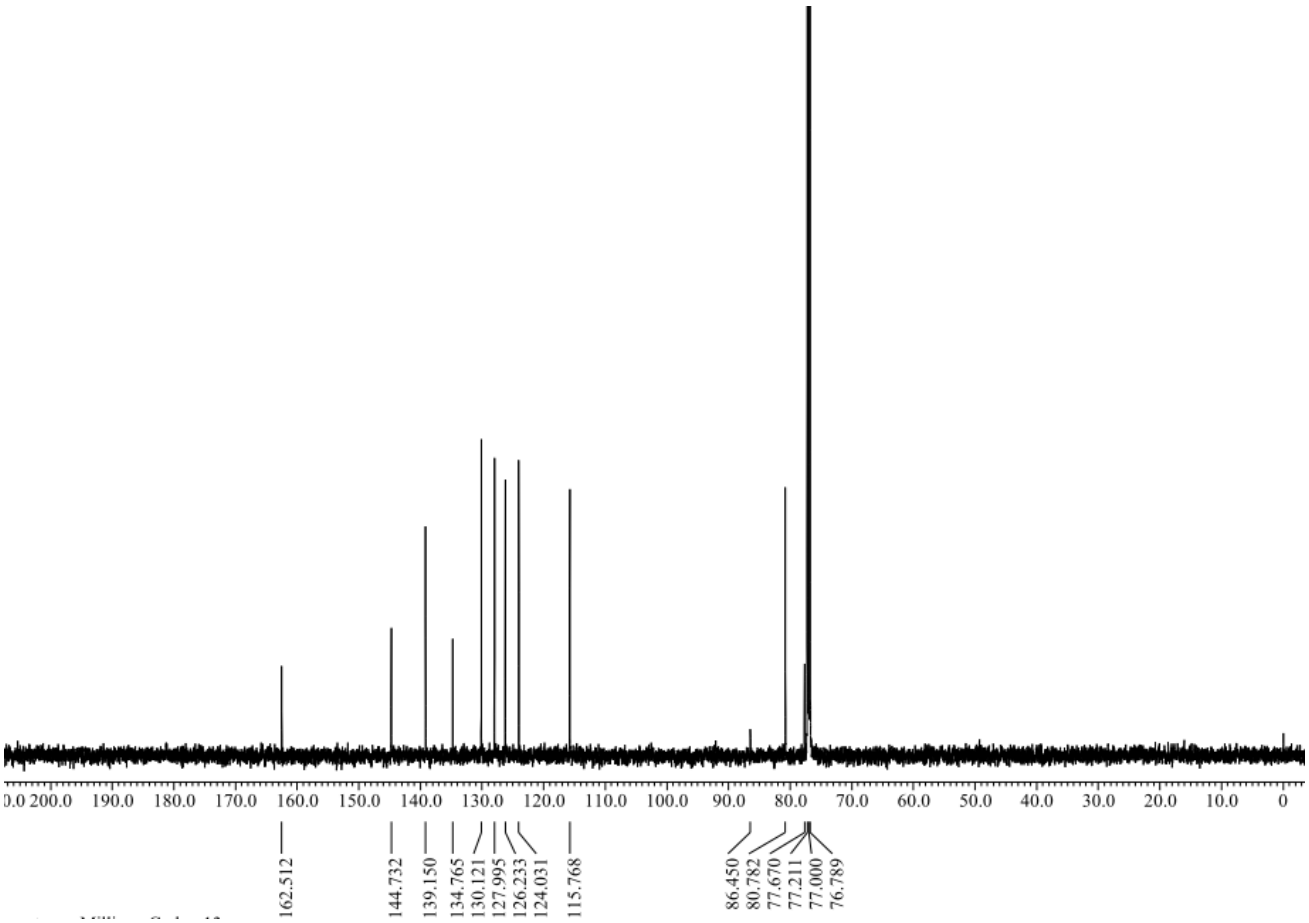


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2f**

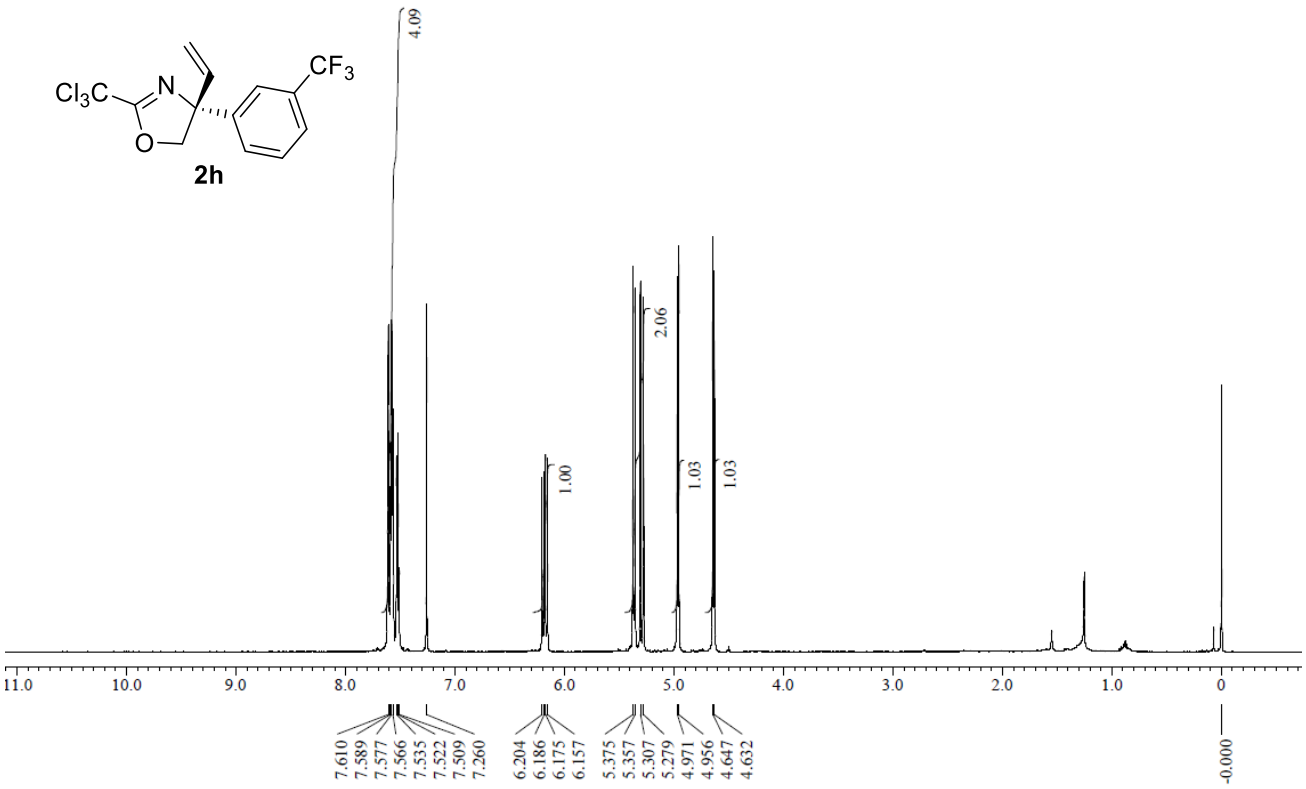


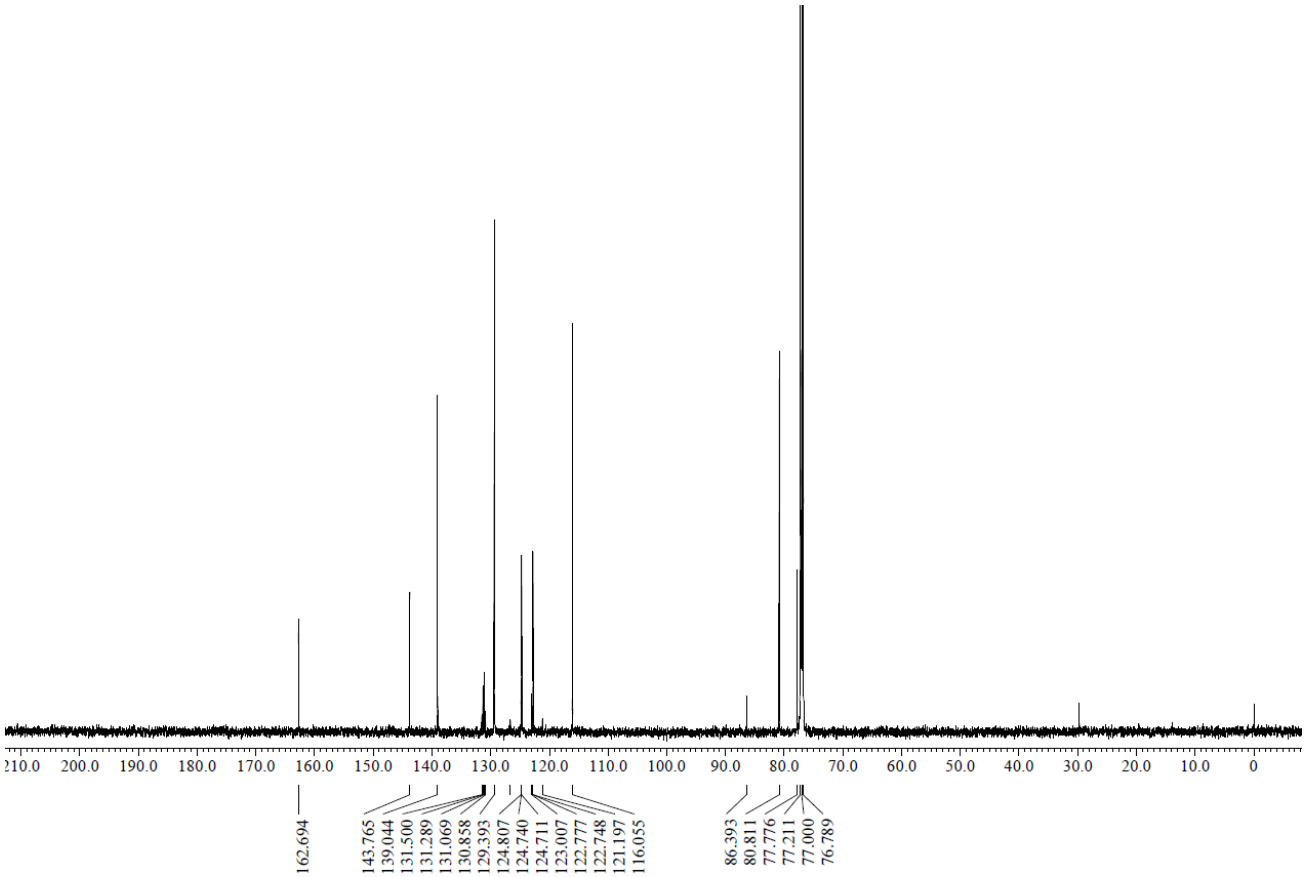
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2g**



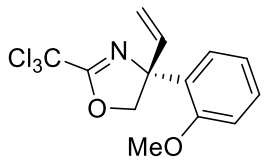


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2h**

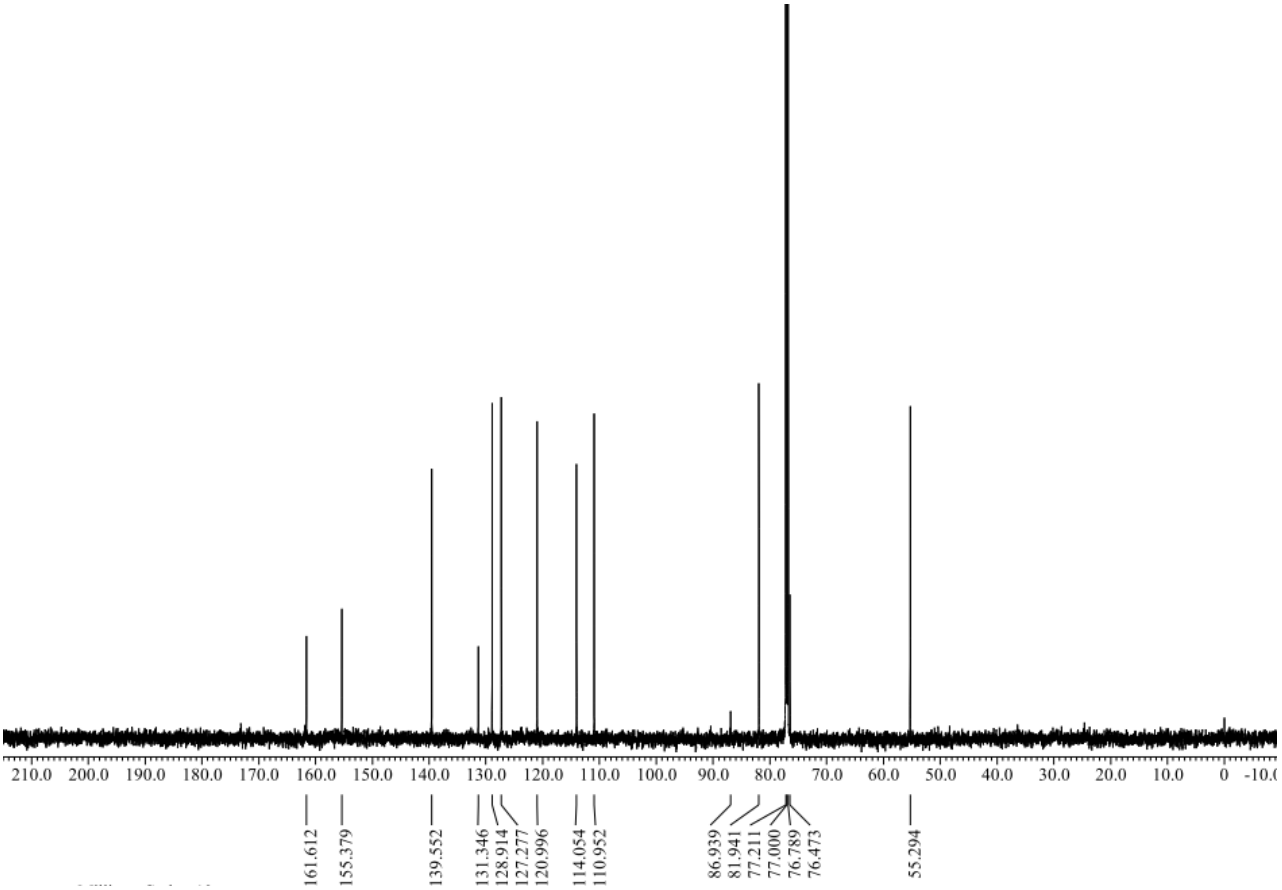




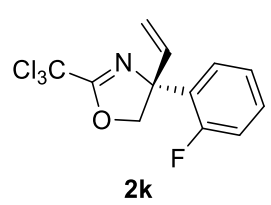
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2i**



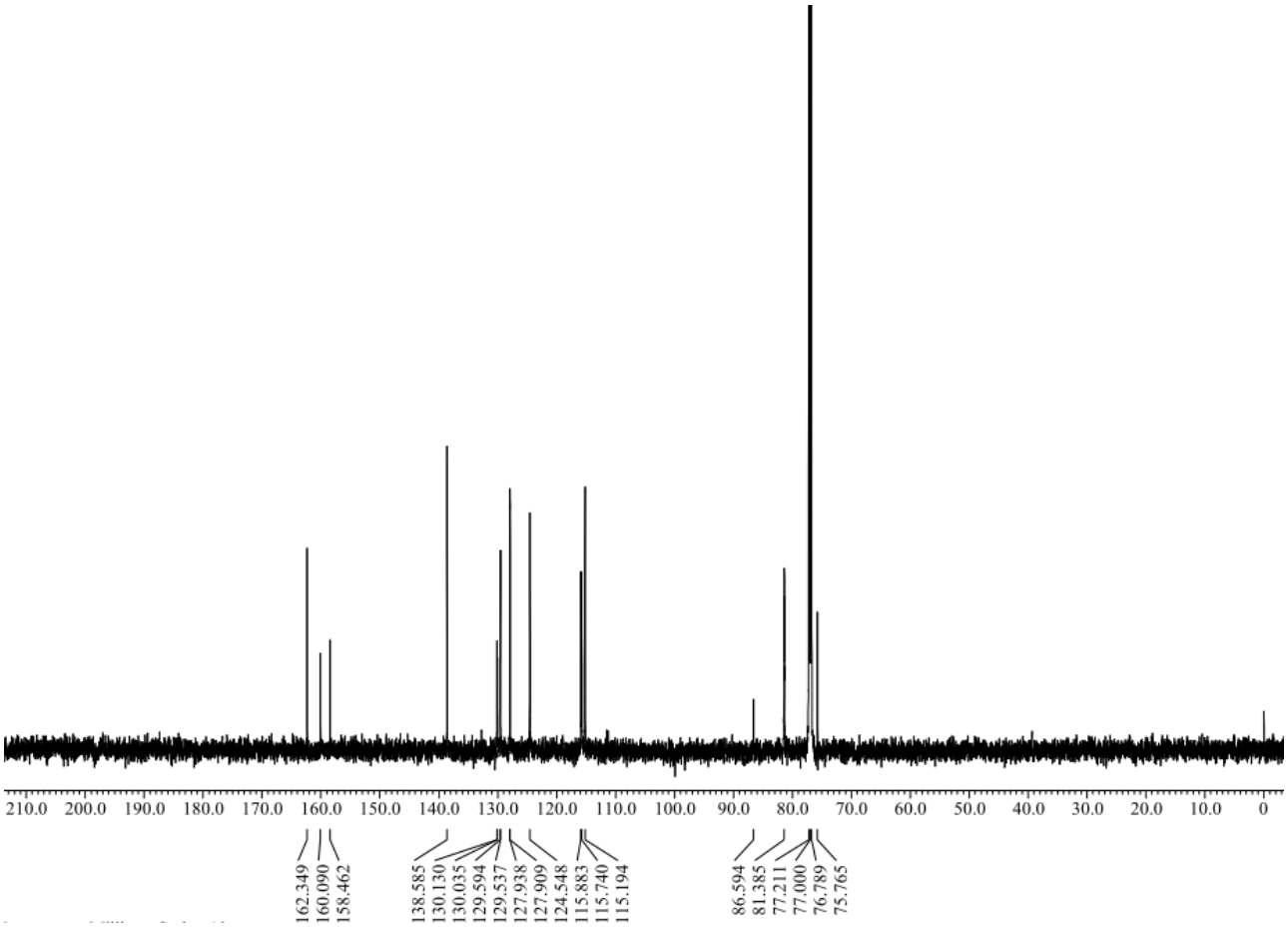
2i



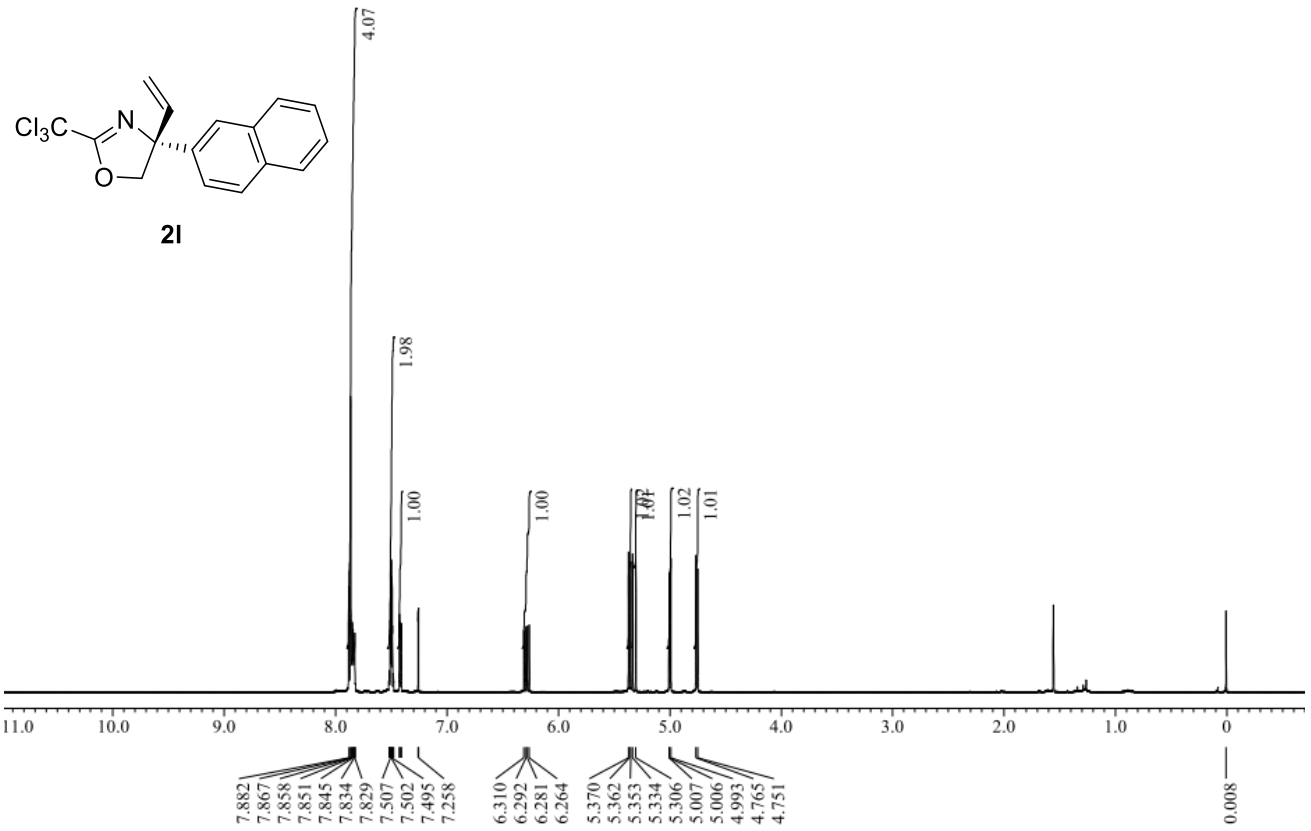
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2k**

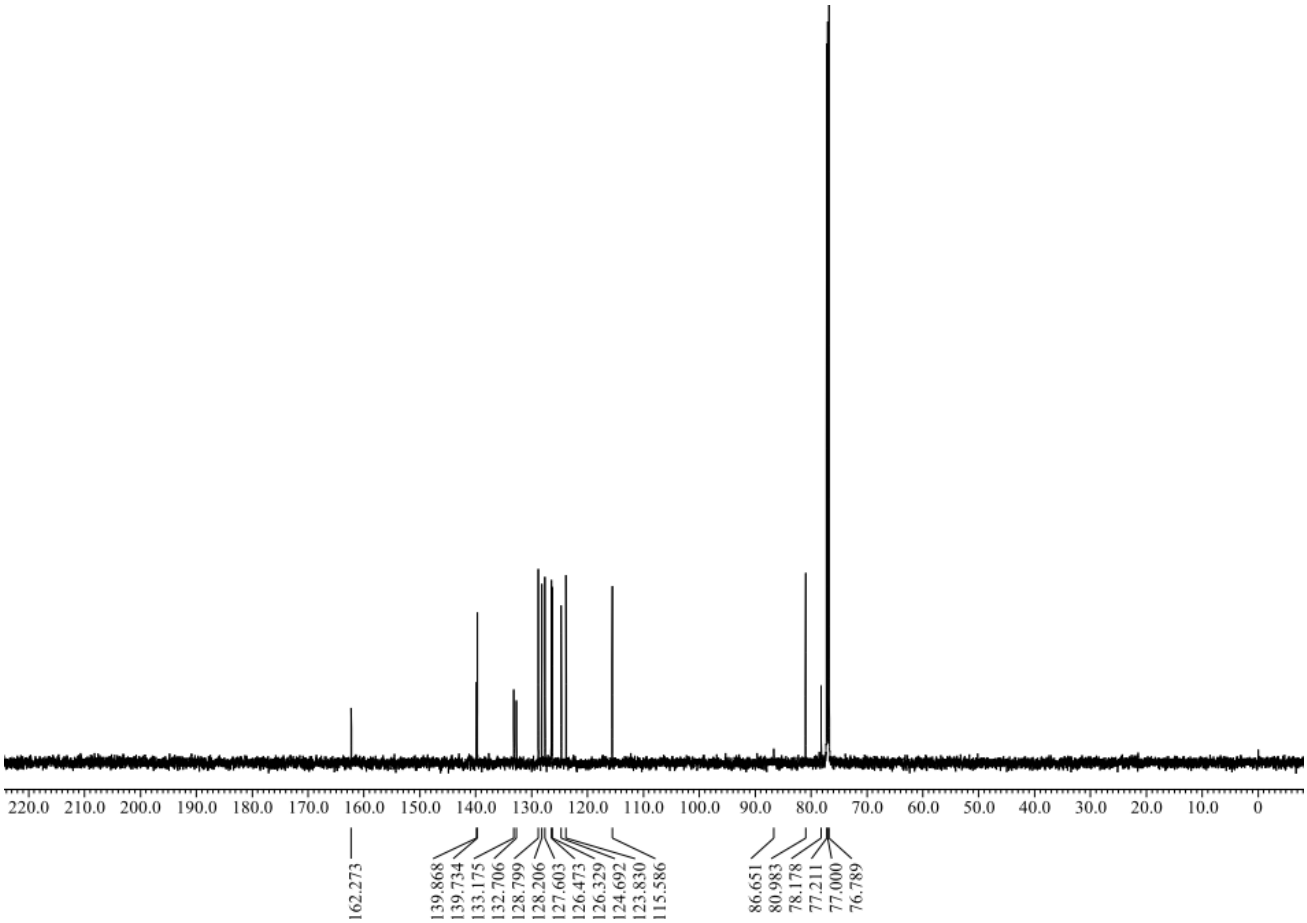


2k

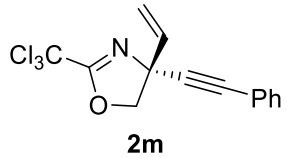


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2l**

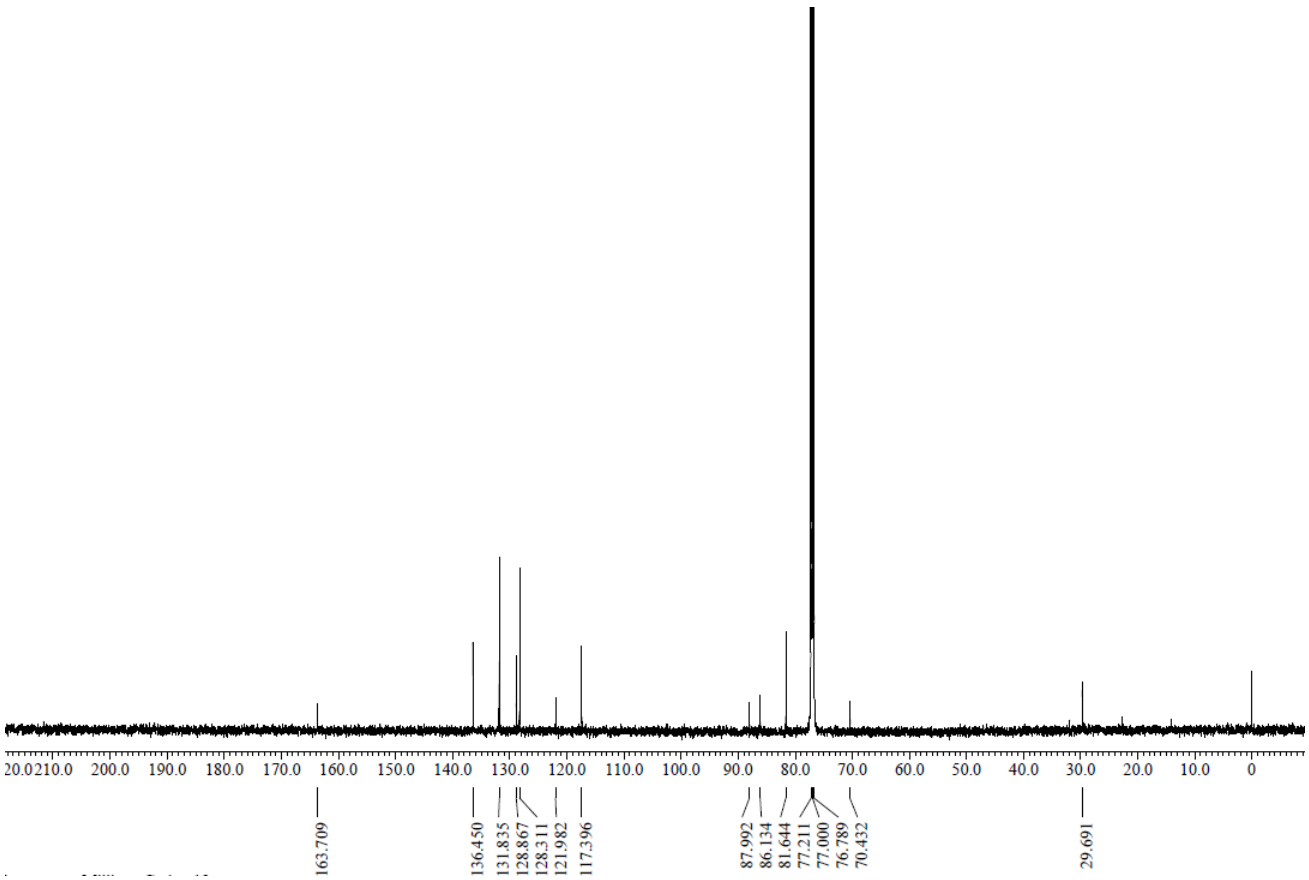




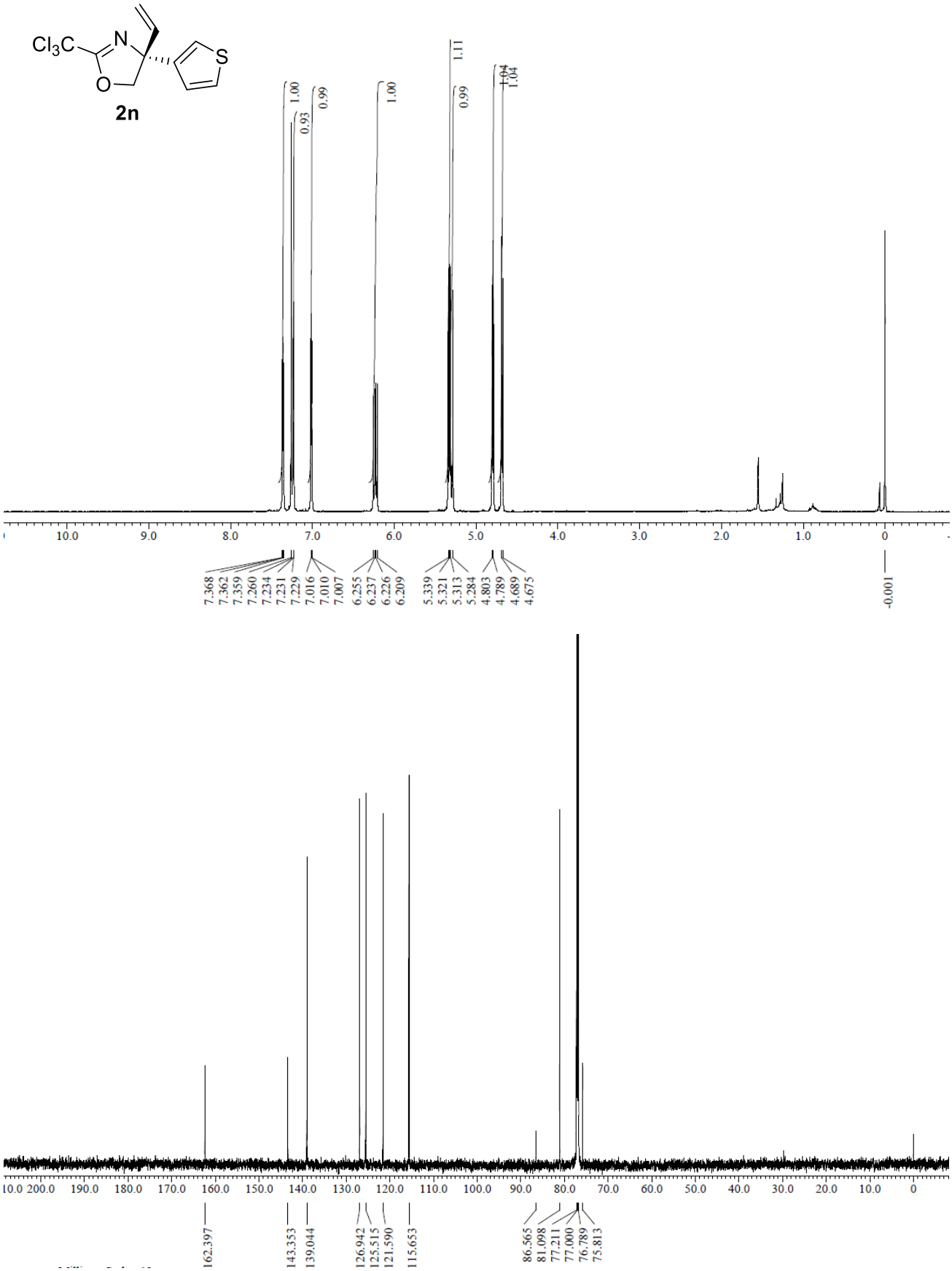
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2m**



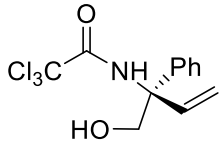
2m



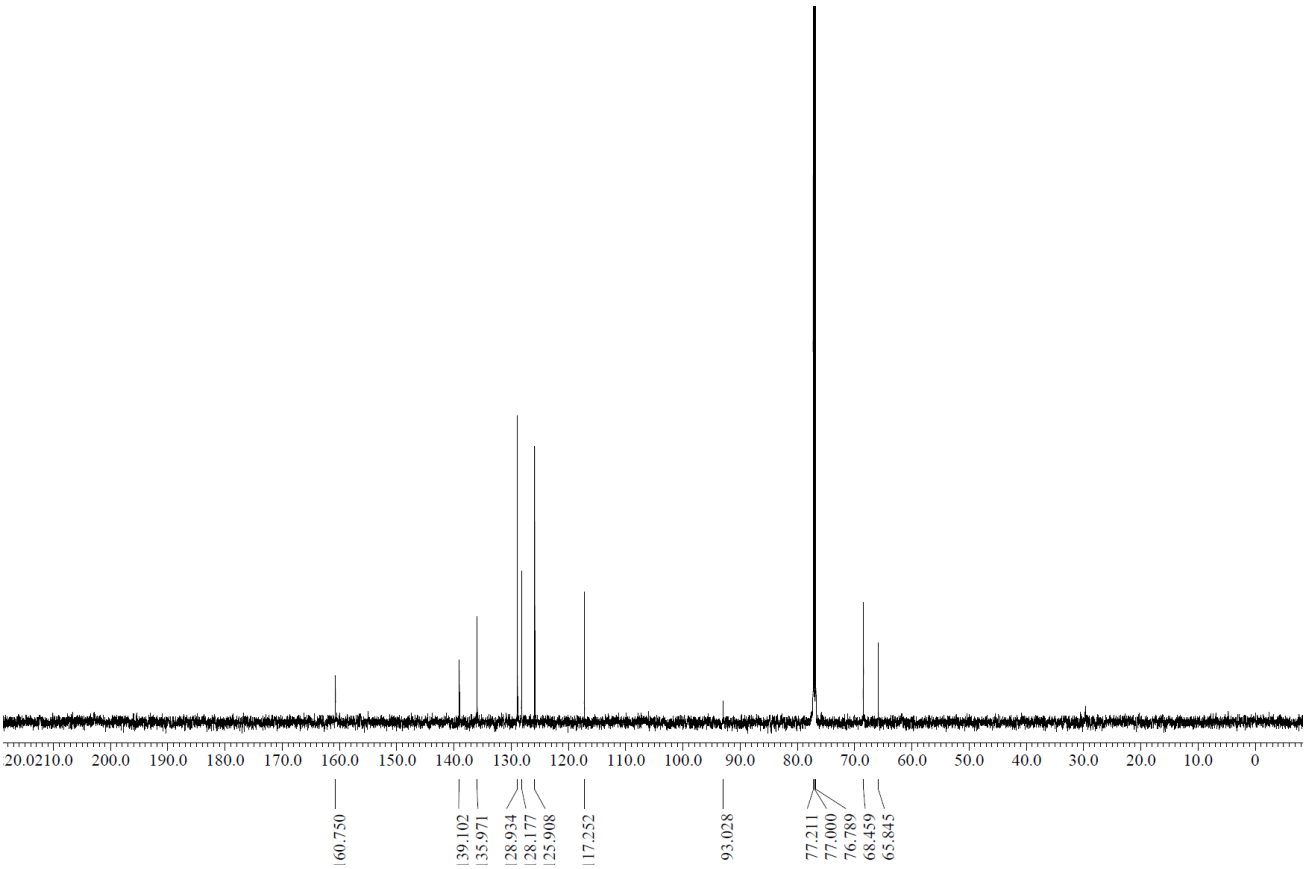
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **2n**



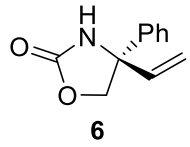
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **5**



5



^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **6**



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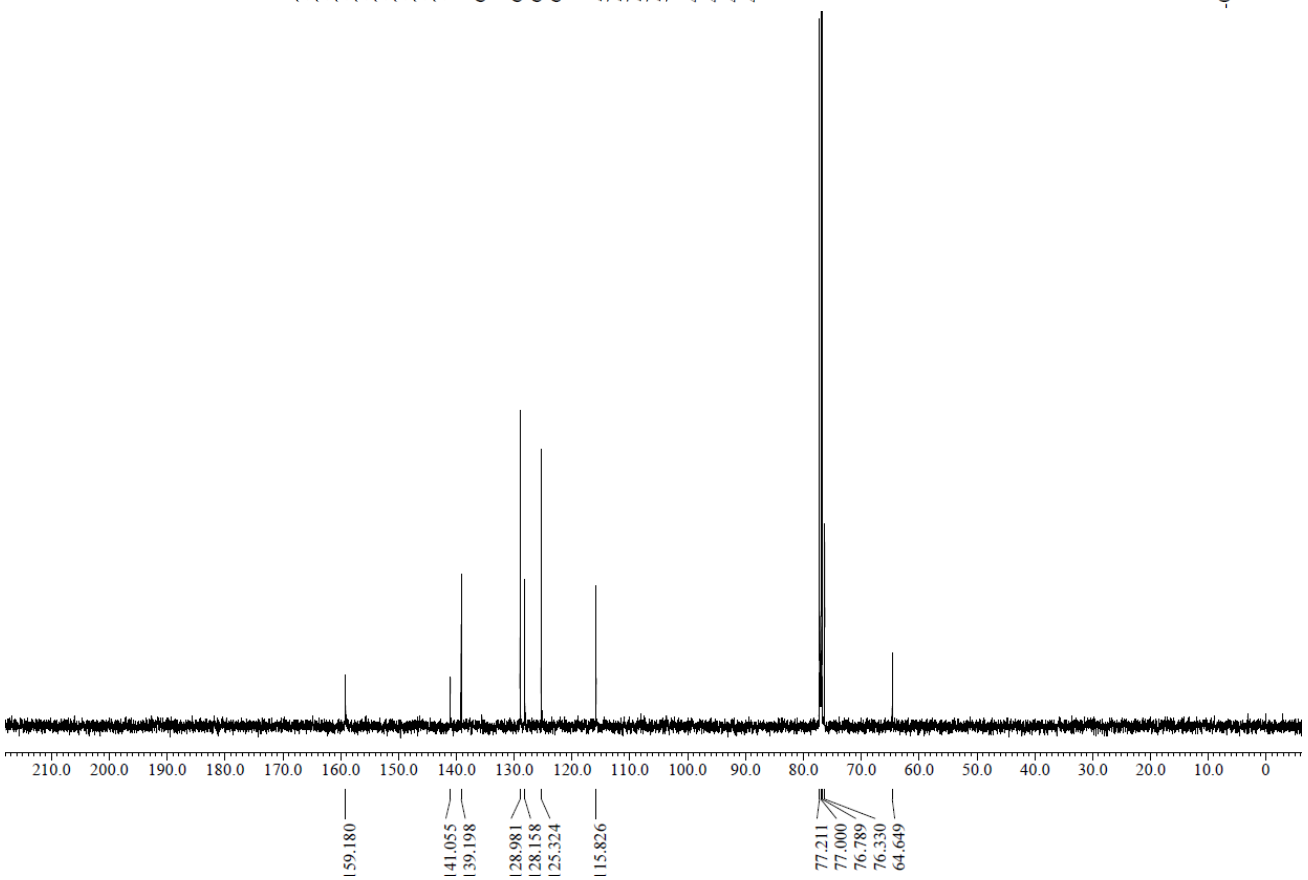
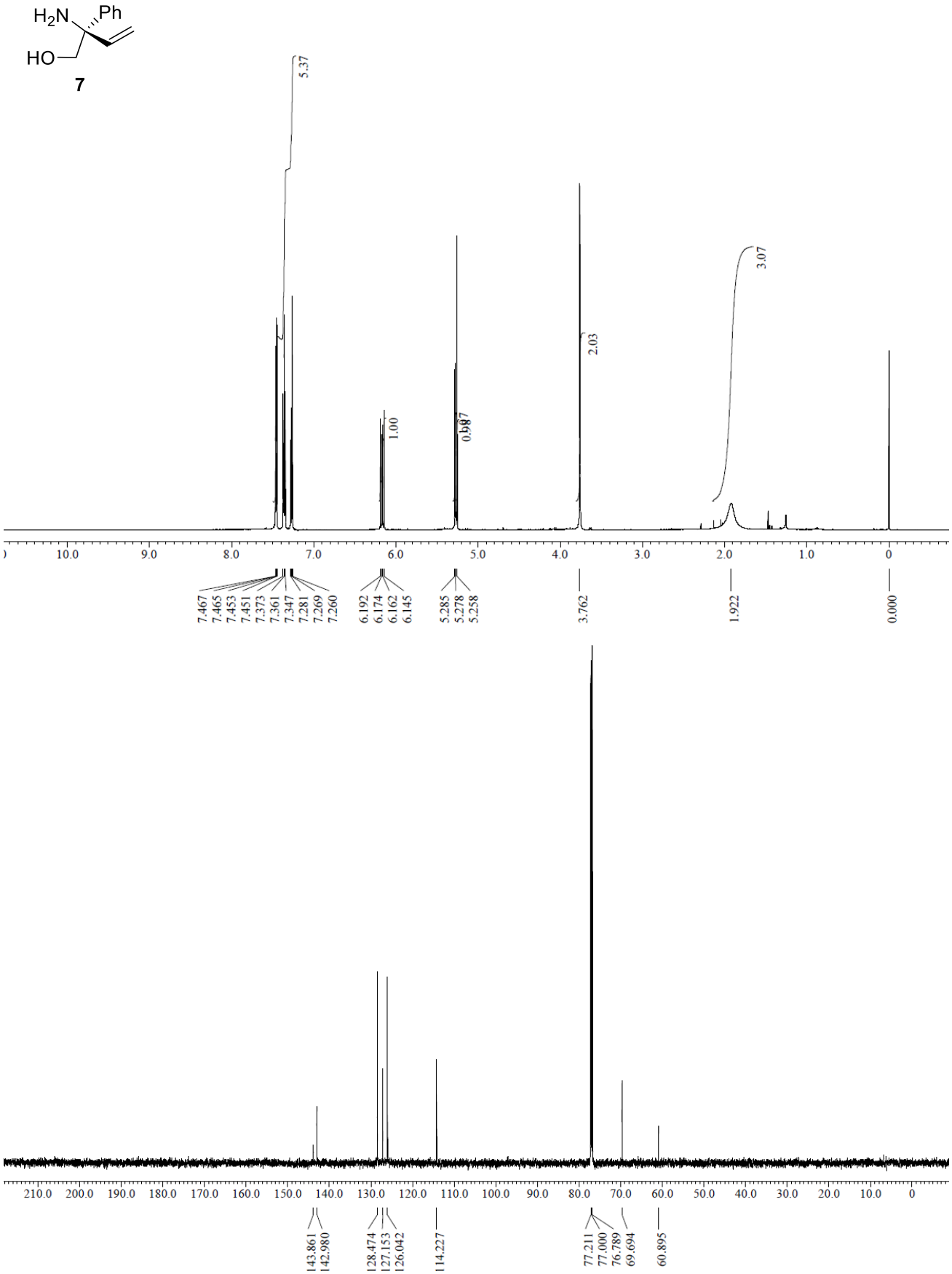
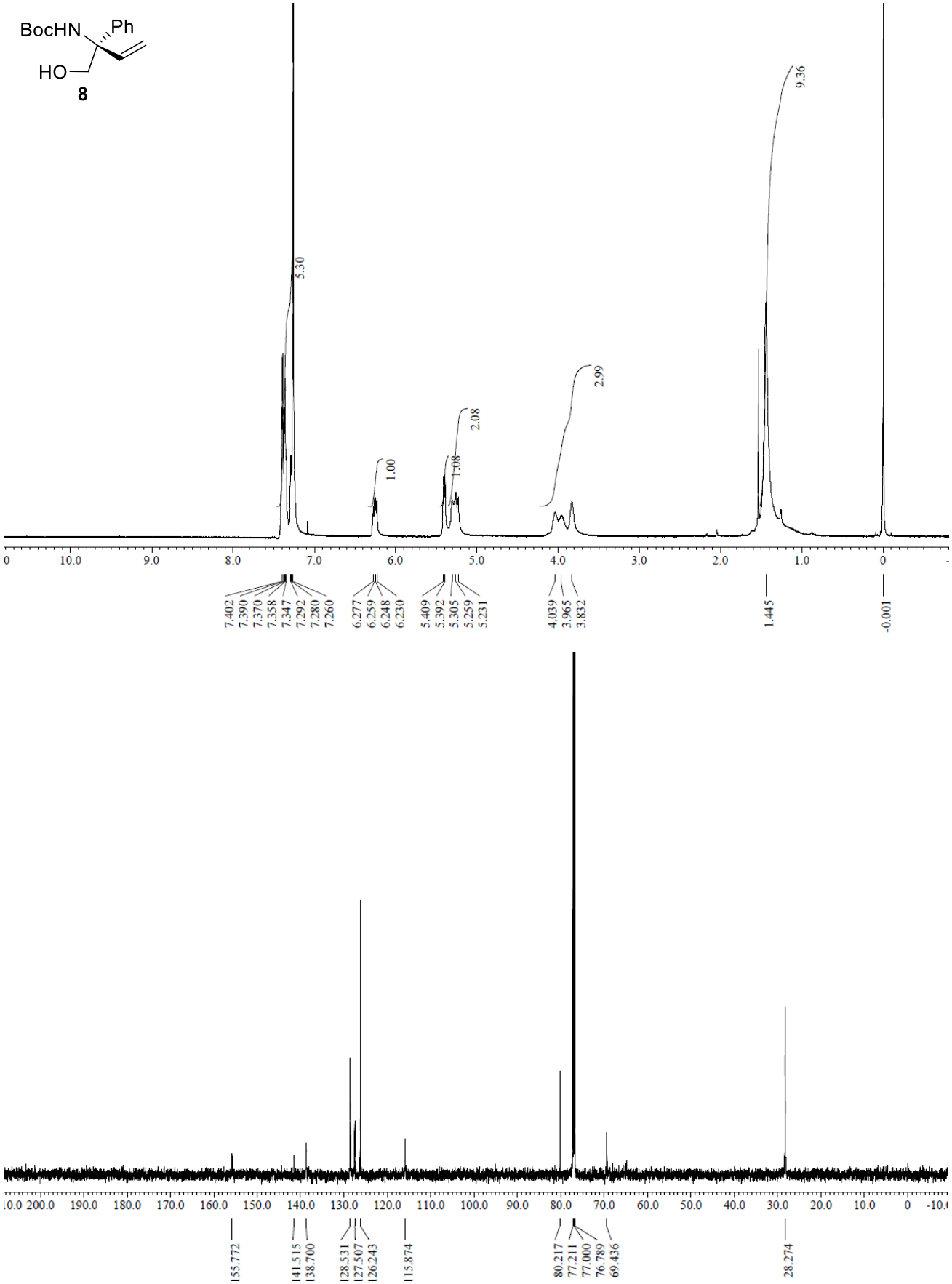


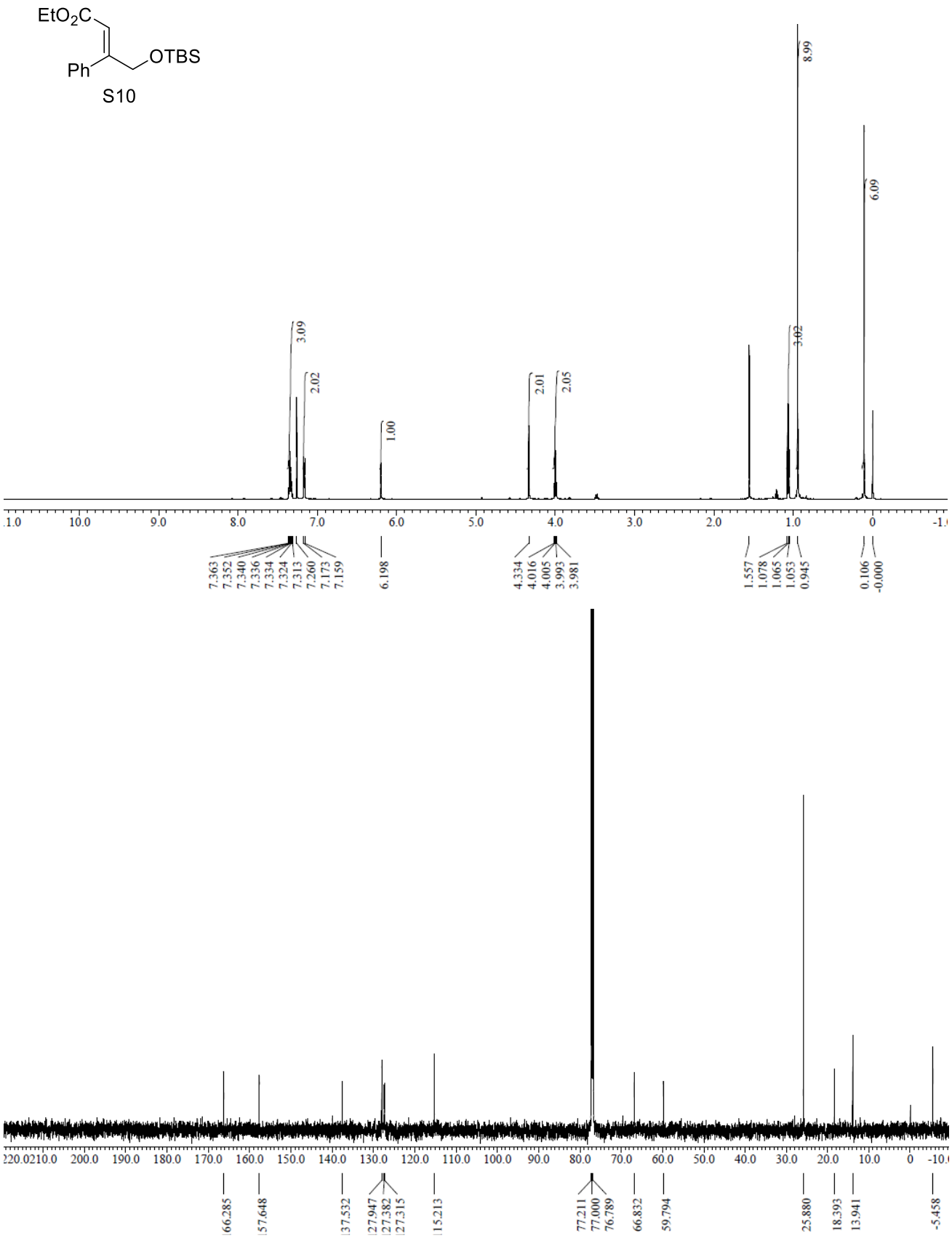
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **7**



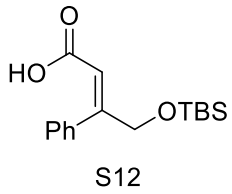
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **8**



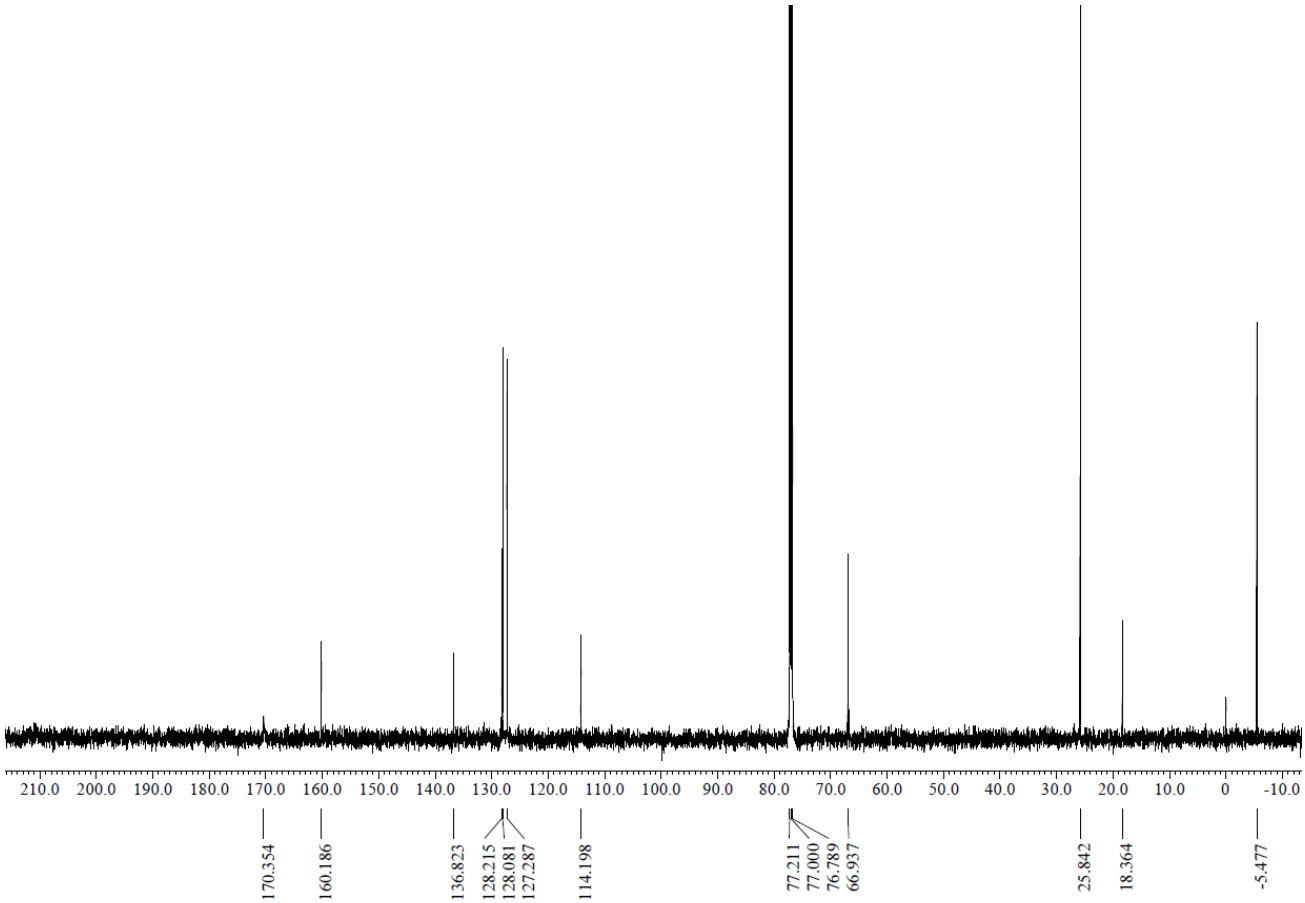
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S10**



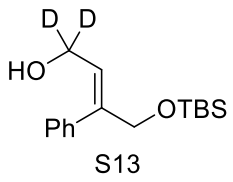
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S12**



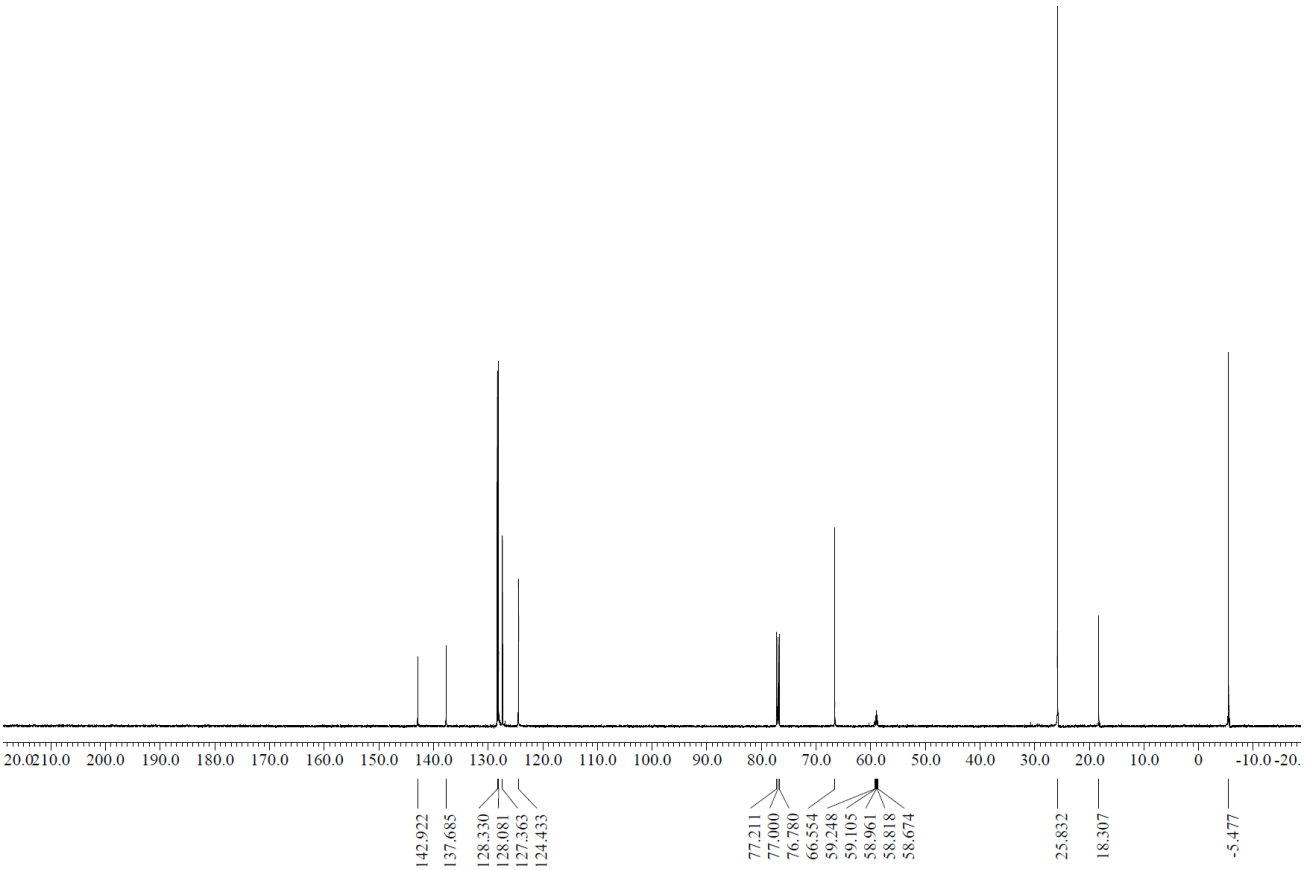
S12



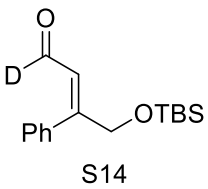
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S13**



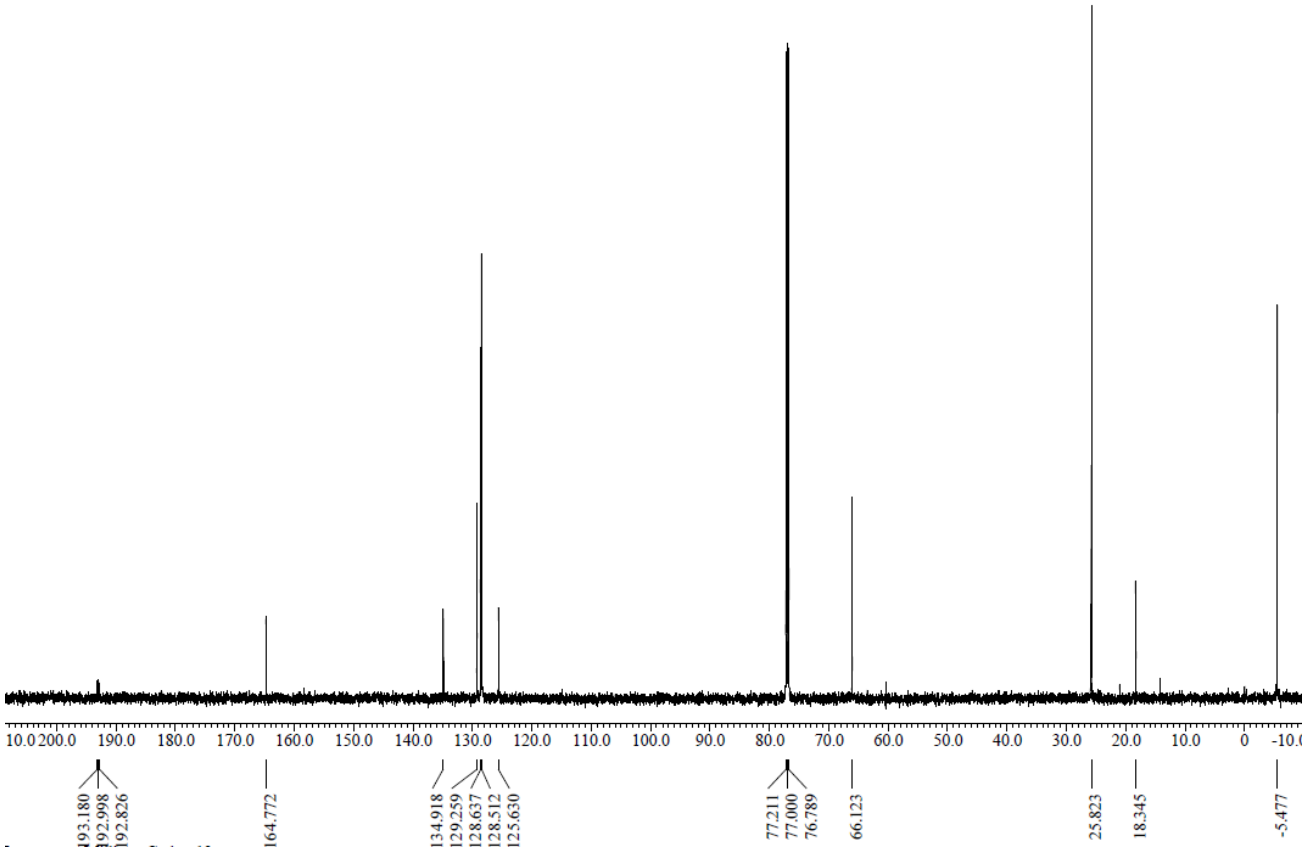
S13



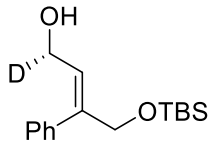
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S14**



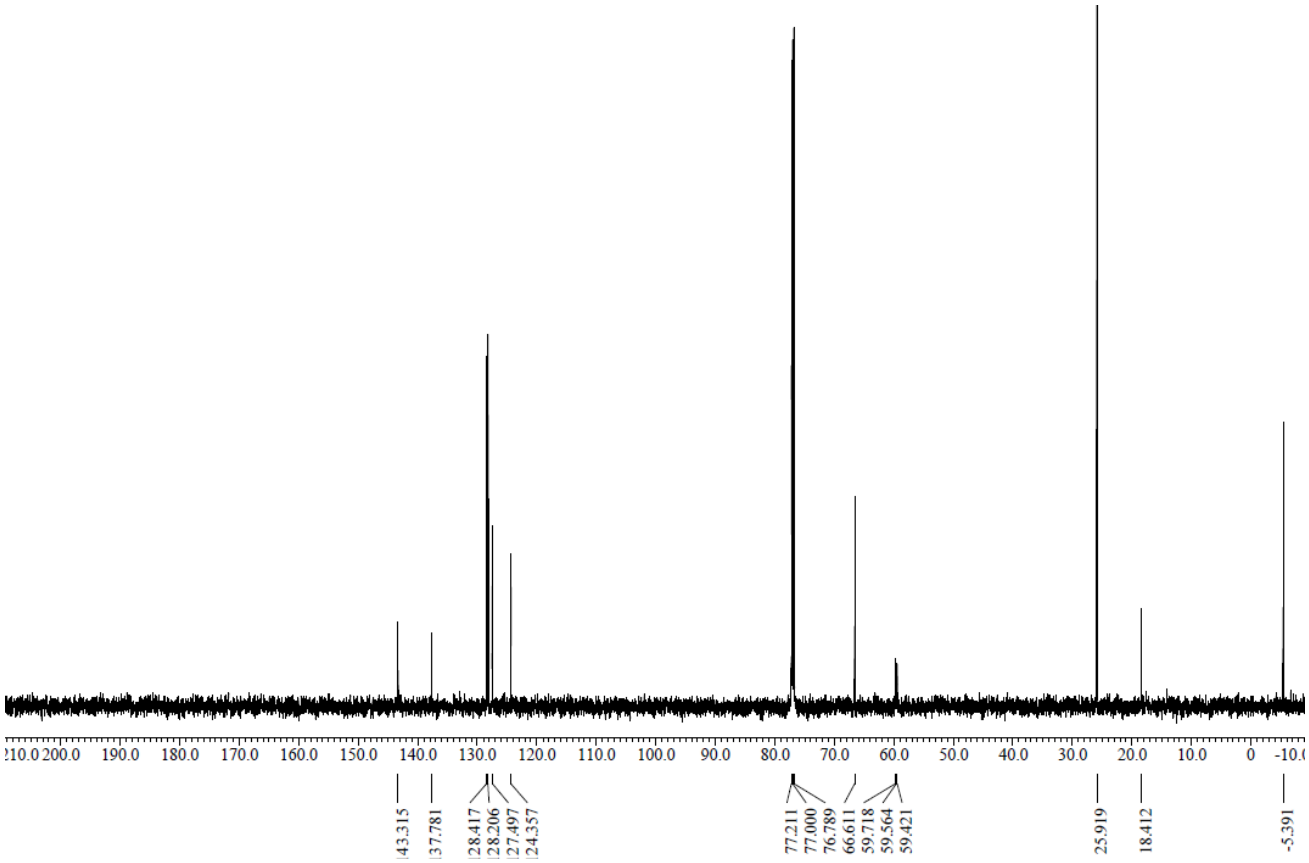
S14



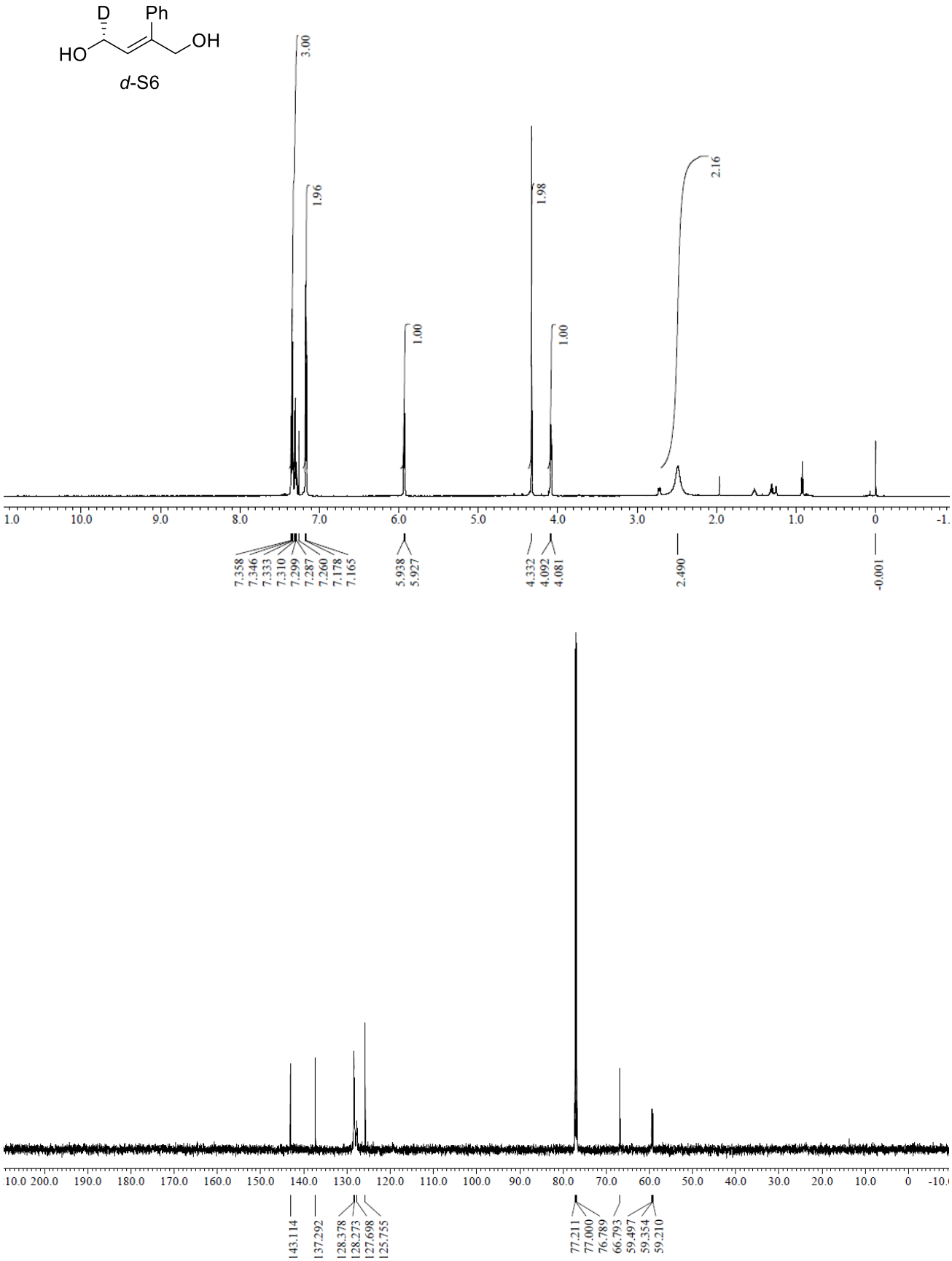
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S15**



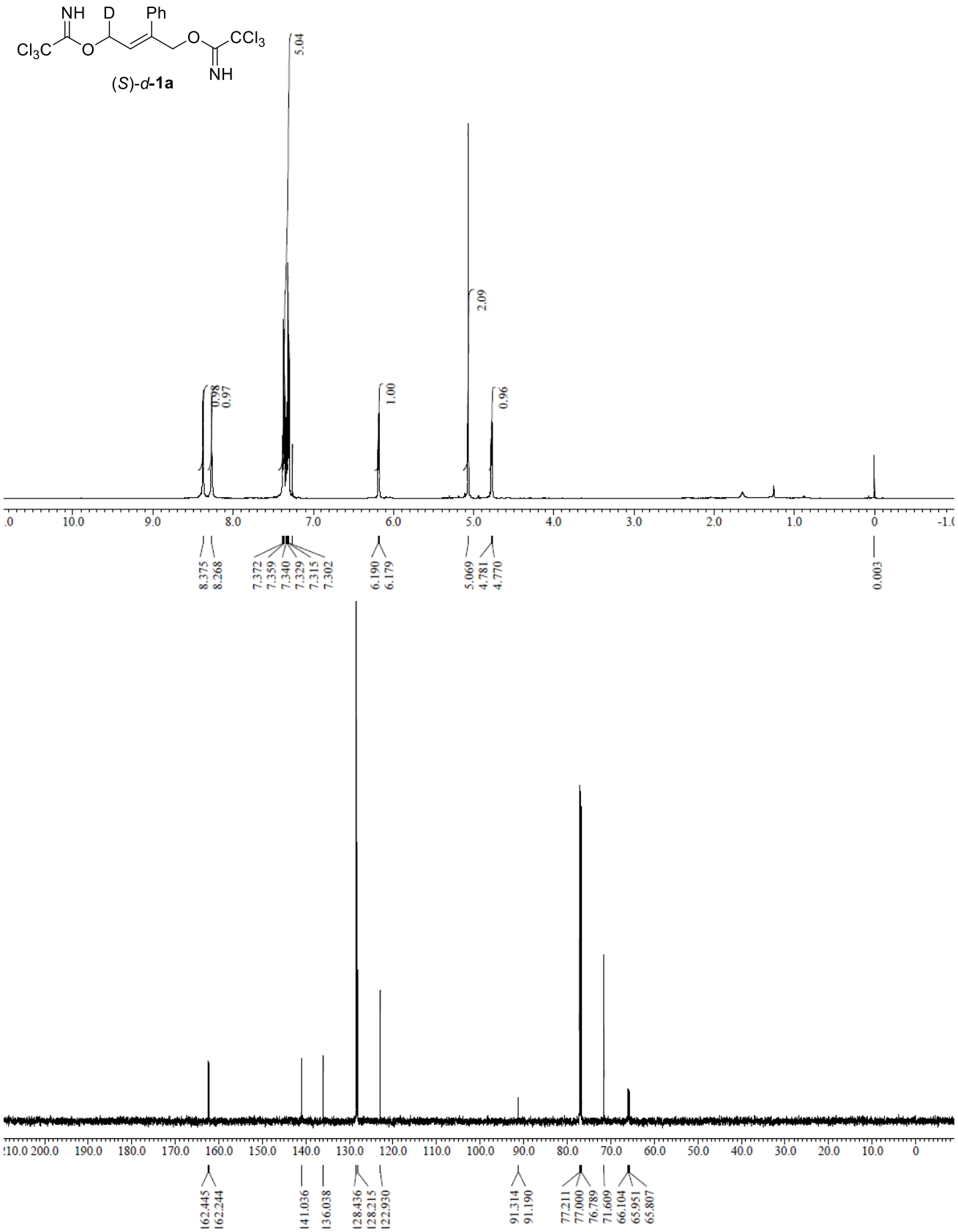
S15



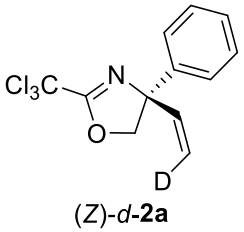
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of *d*-**S6**



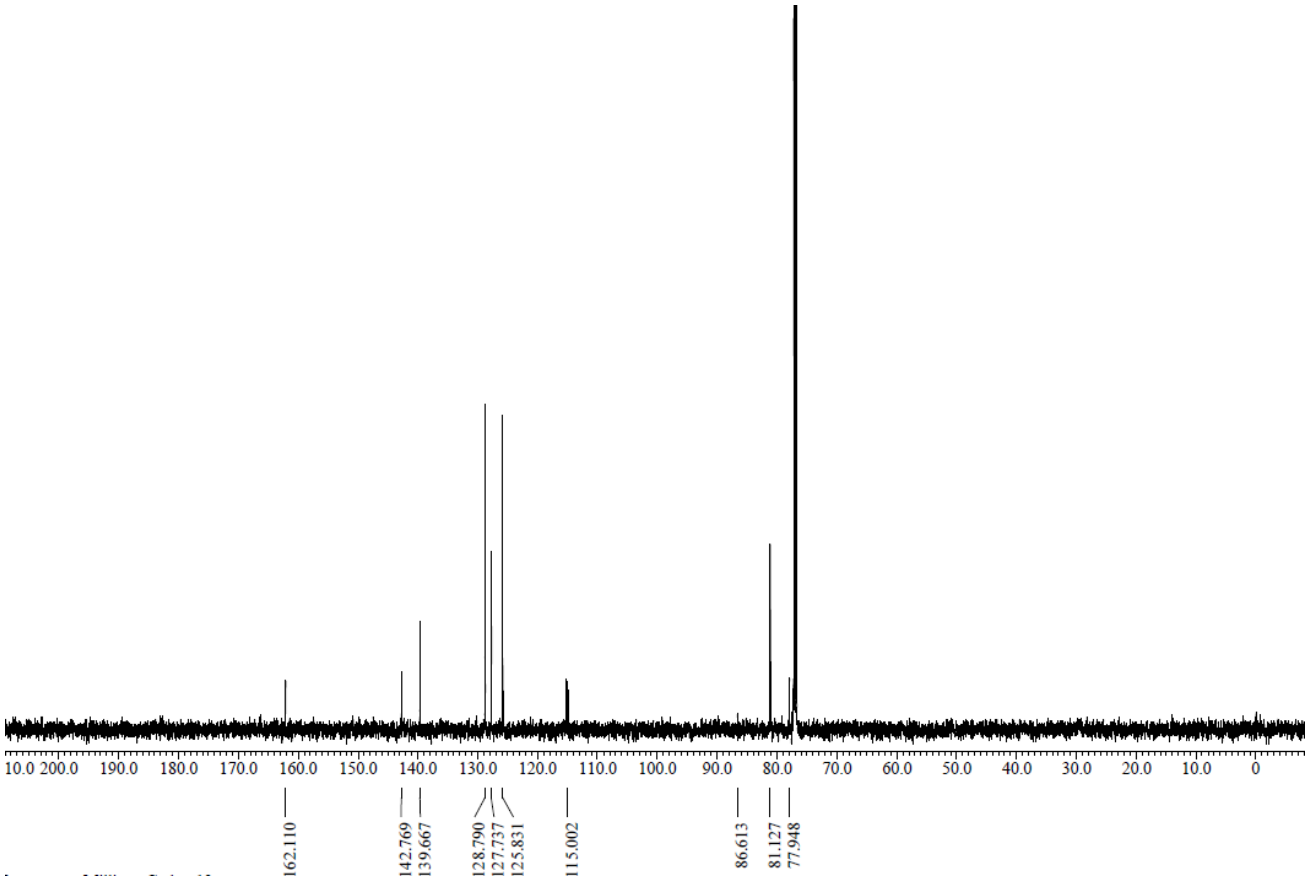
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*S*)-*d*-**1a**



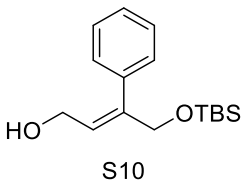
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of (*Z*)-*d*-**2a**



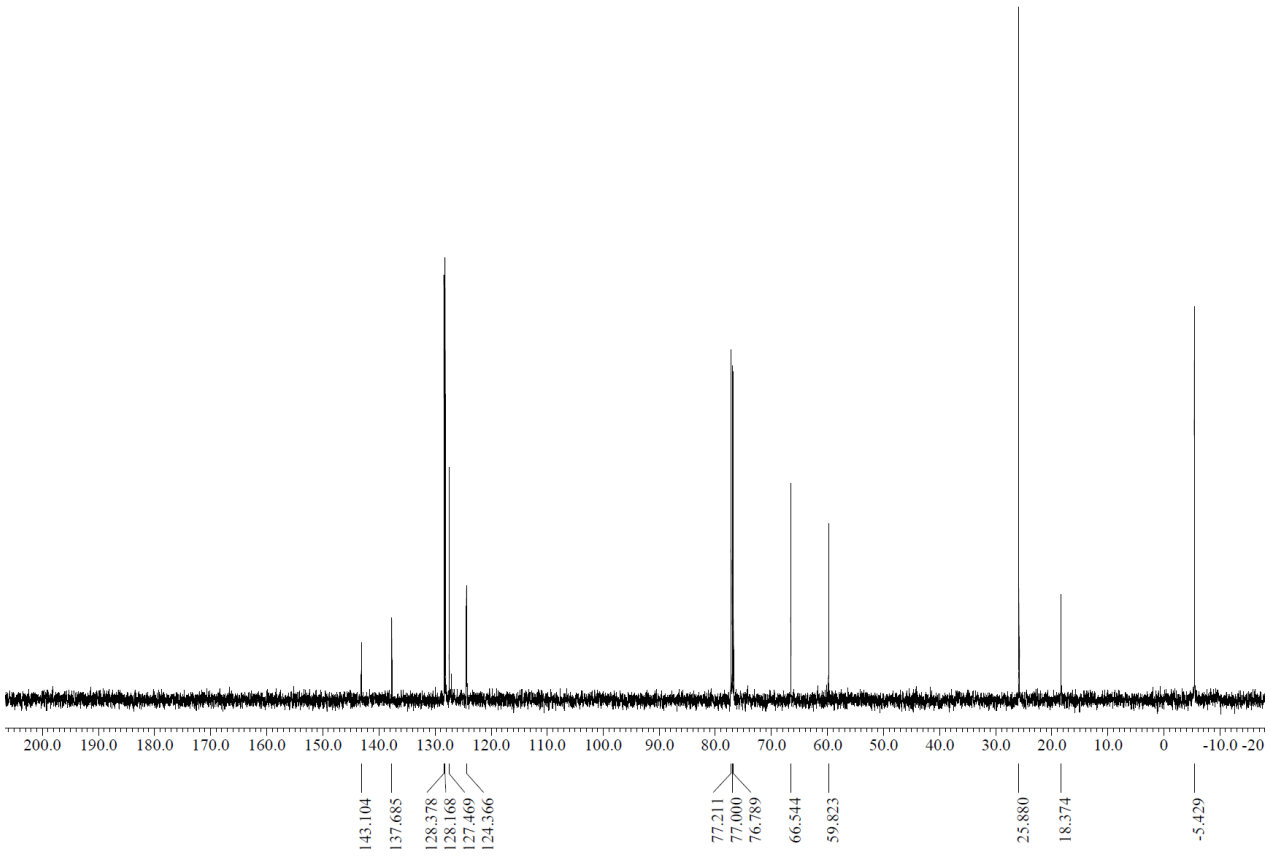
(*Z*)-*d*-**2a**



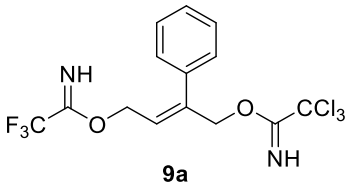
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **S10**



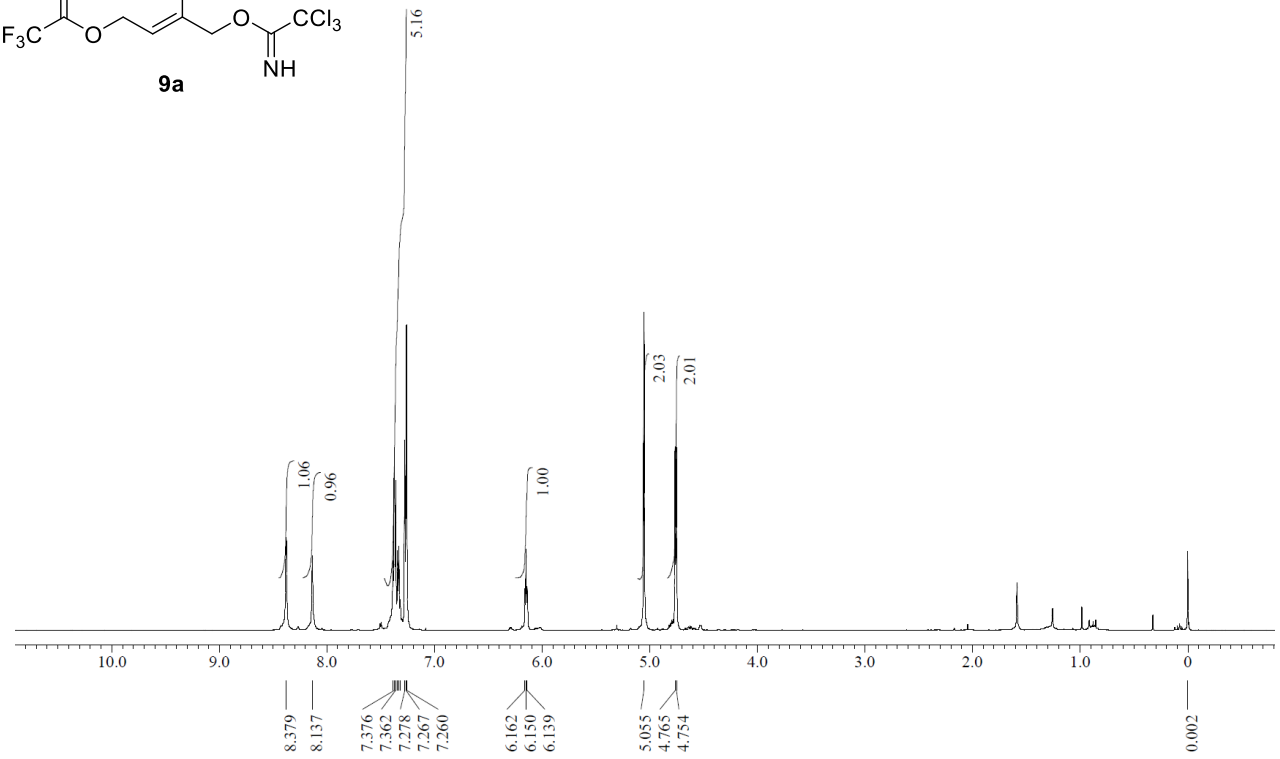
S10

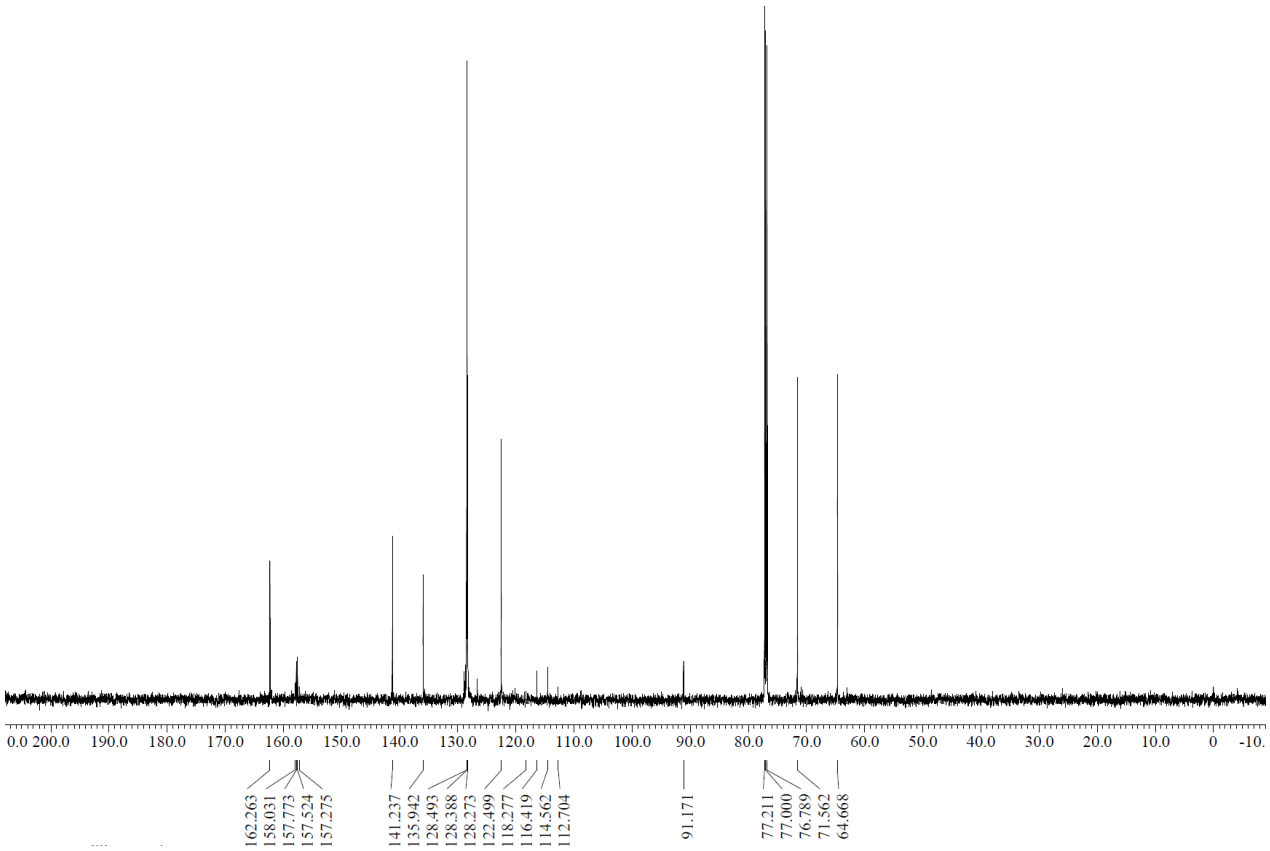


^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **9a**

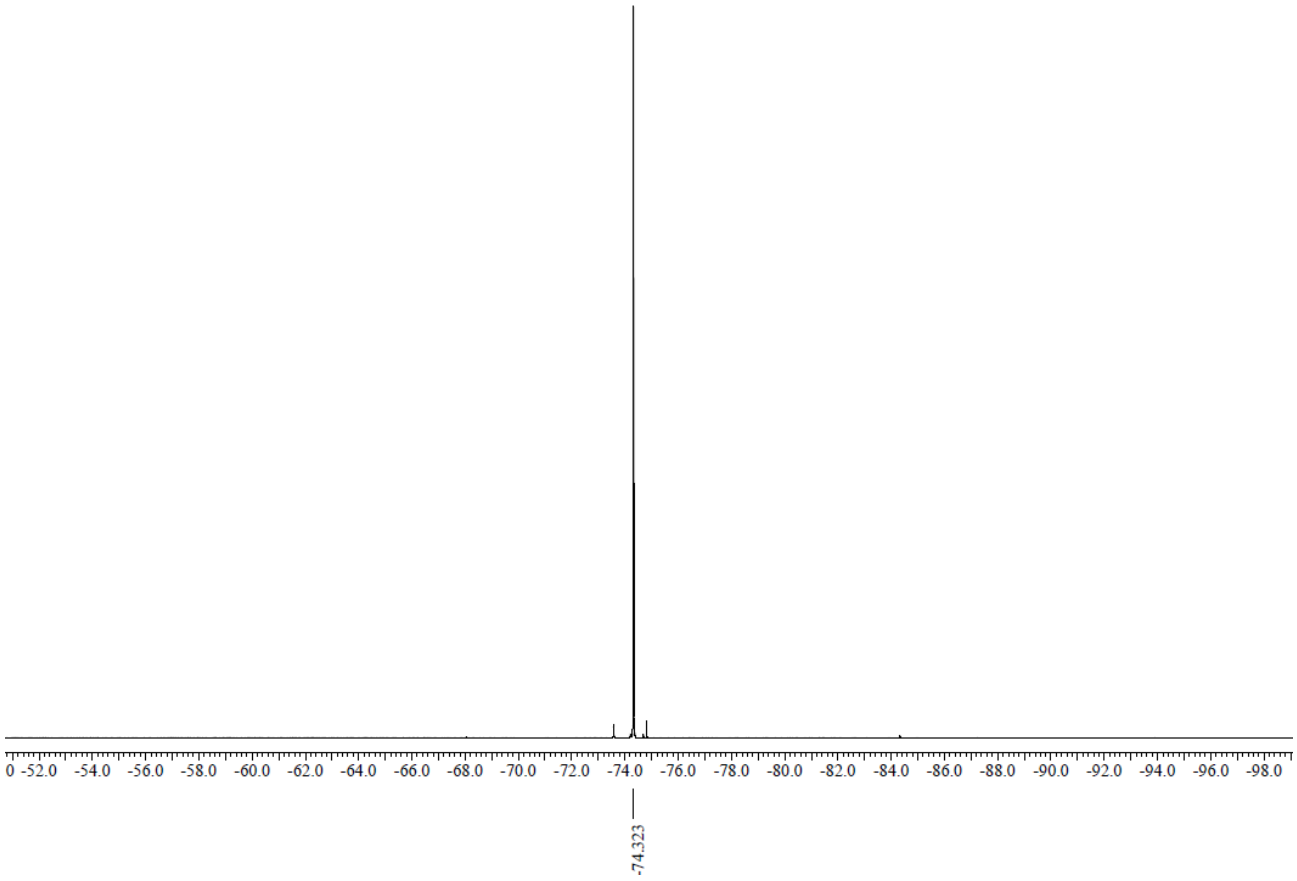


9a

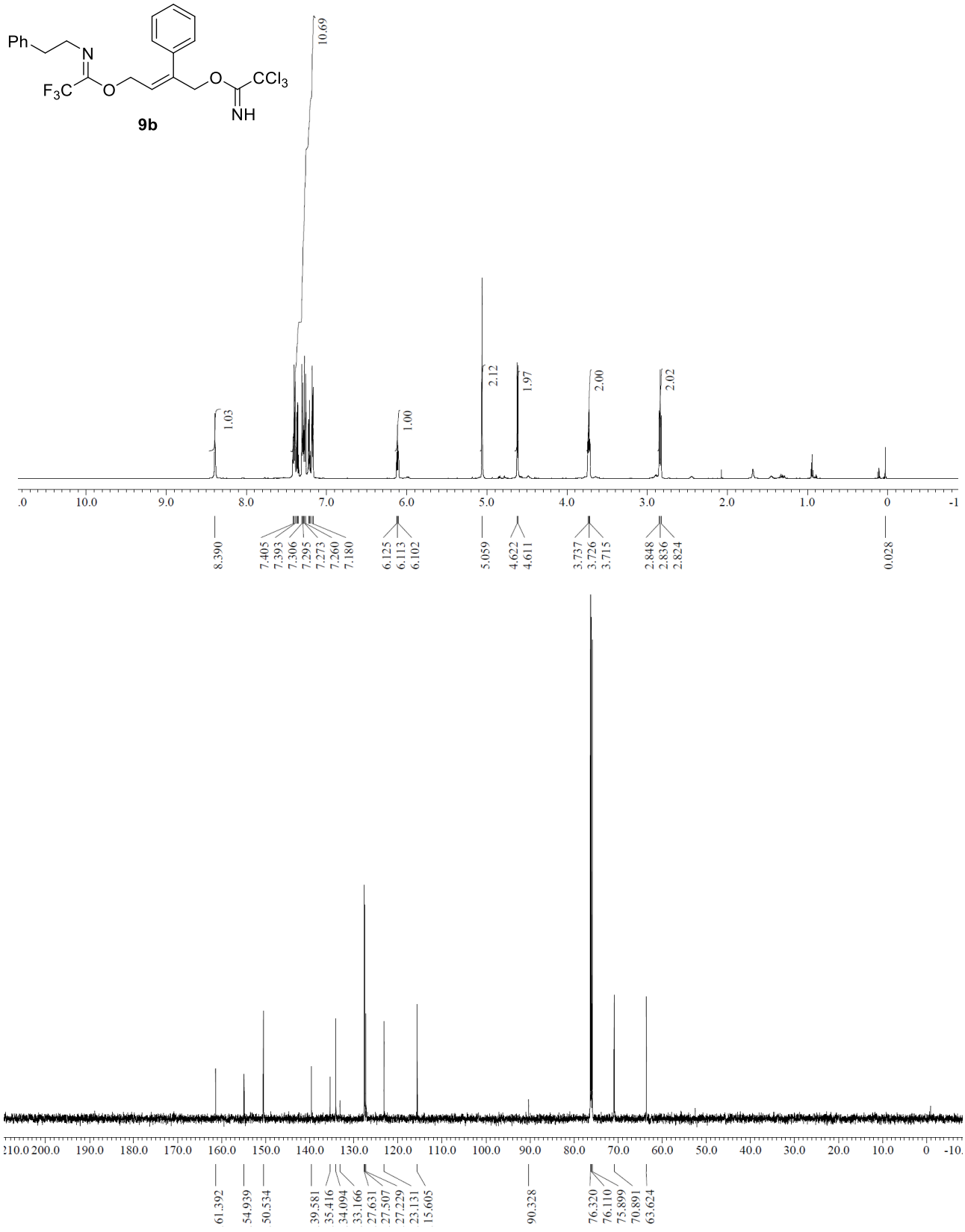




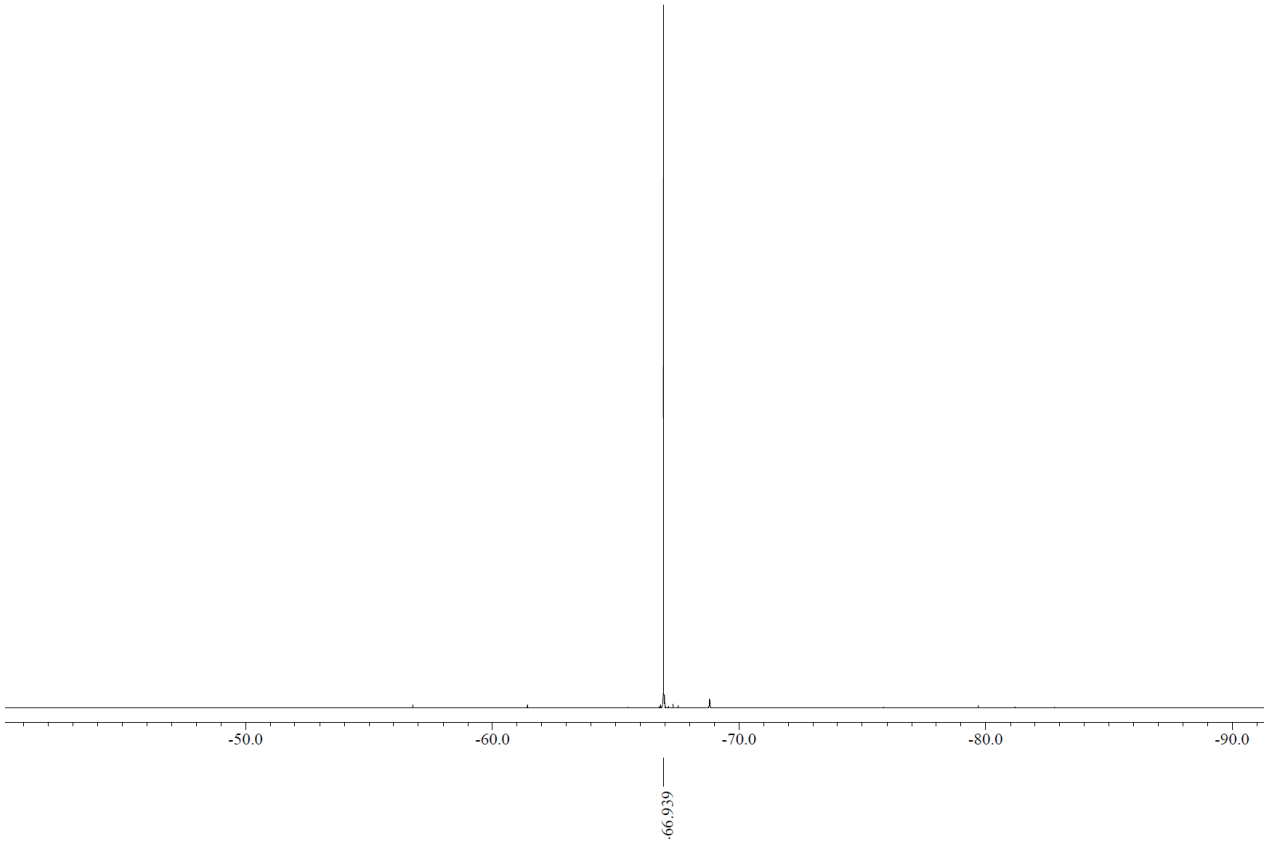
^{19}F NMR (565 MHz) spectra of **9a**



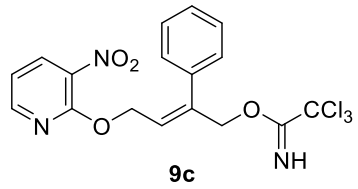
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **9b**



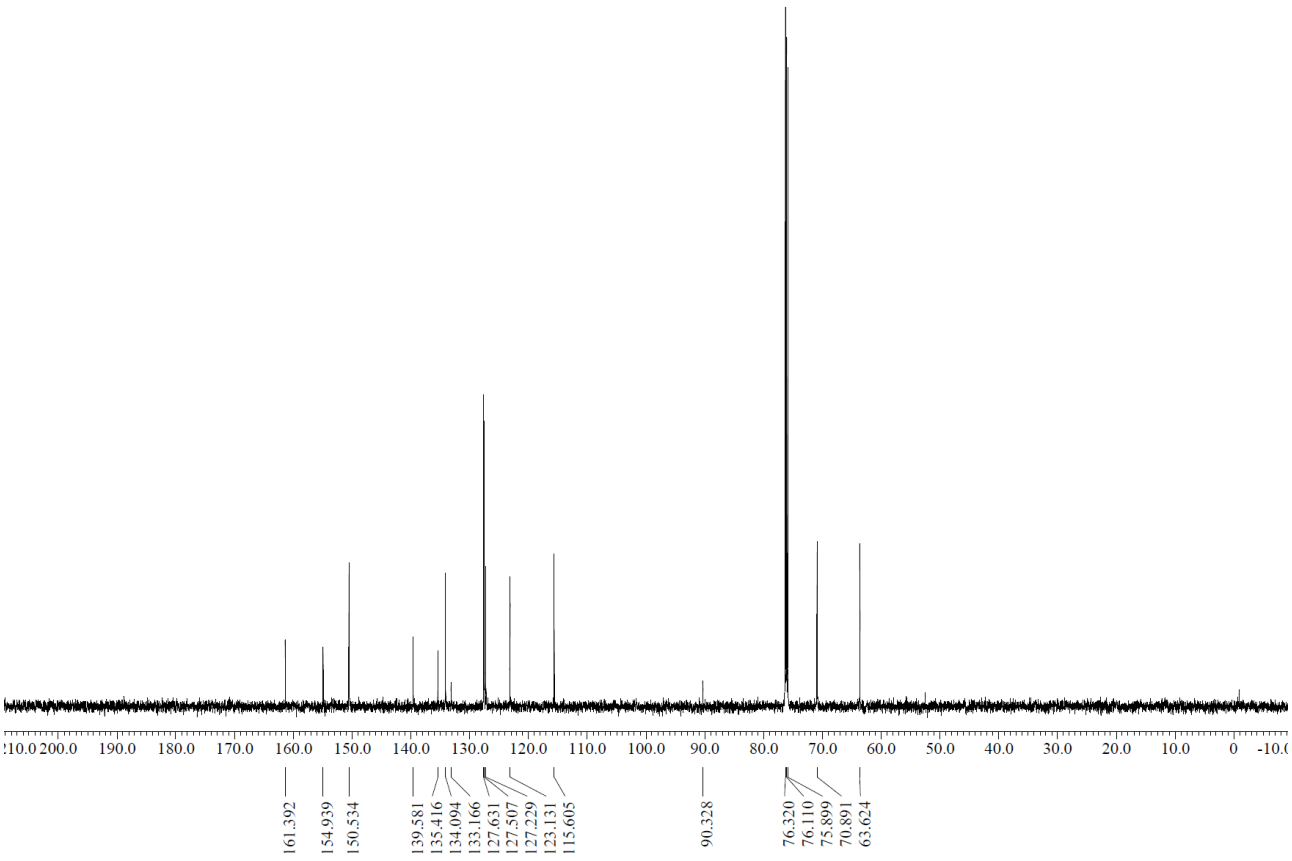
^{19}F NMR (565 MHz) spectra of **9b**



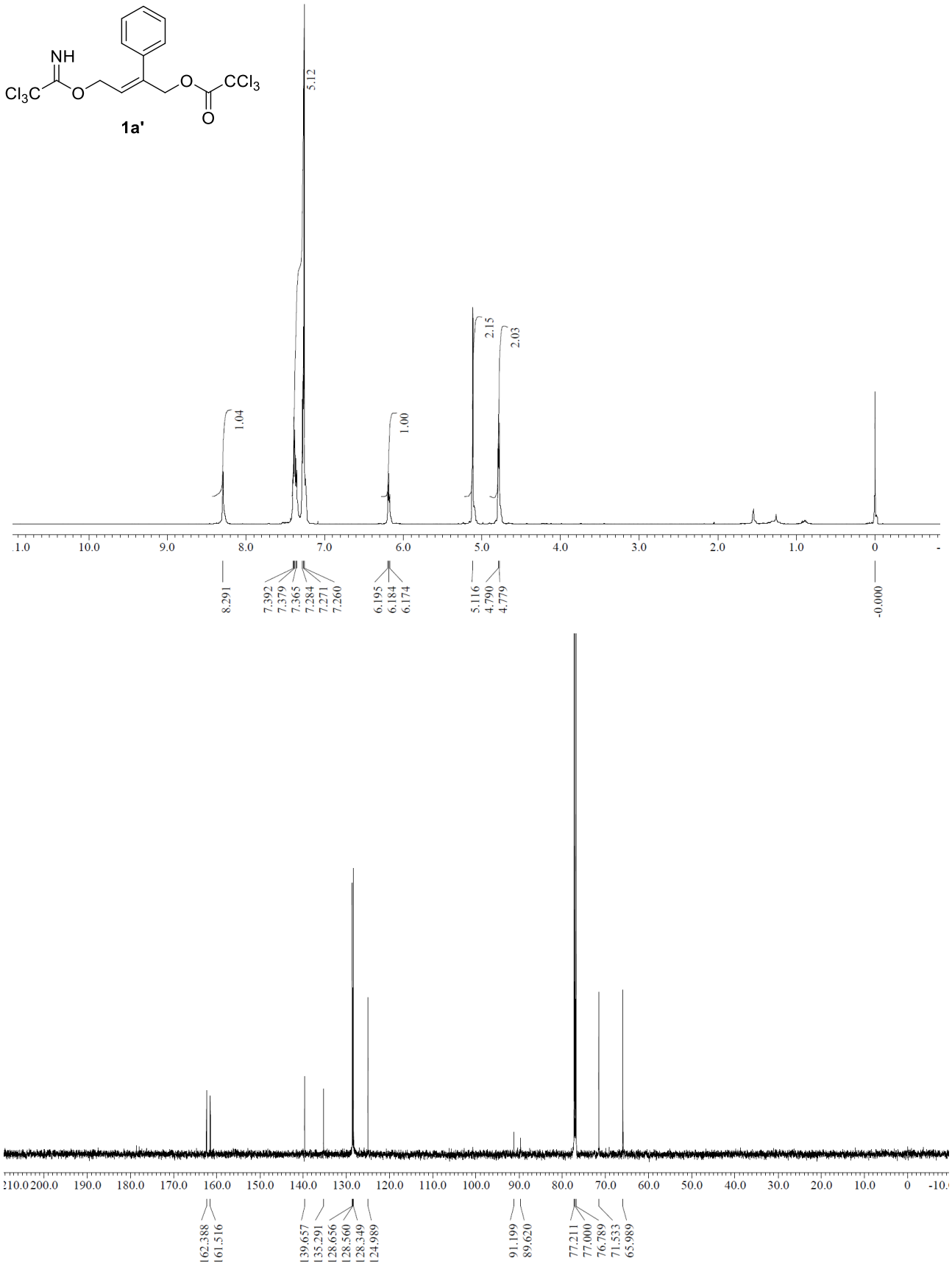
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **9c**



9c

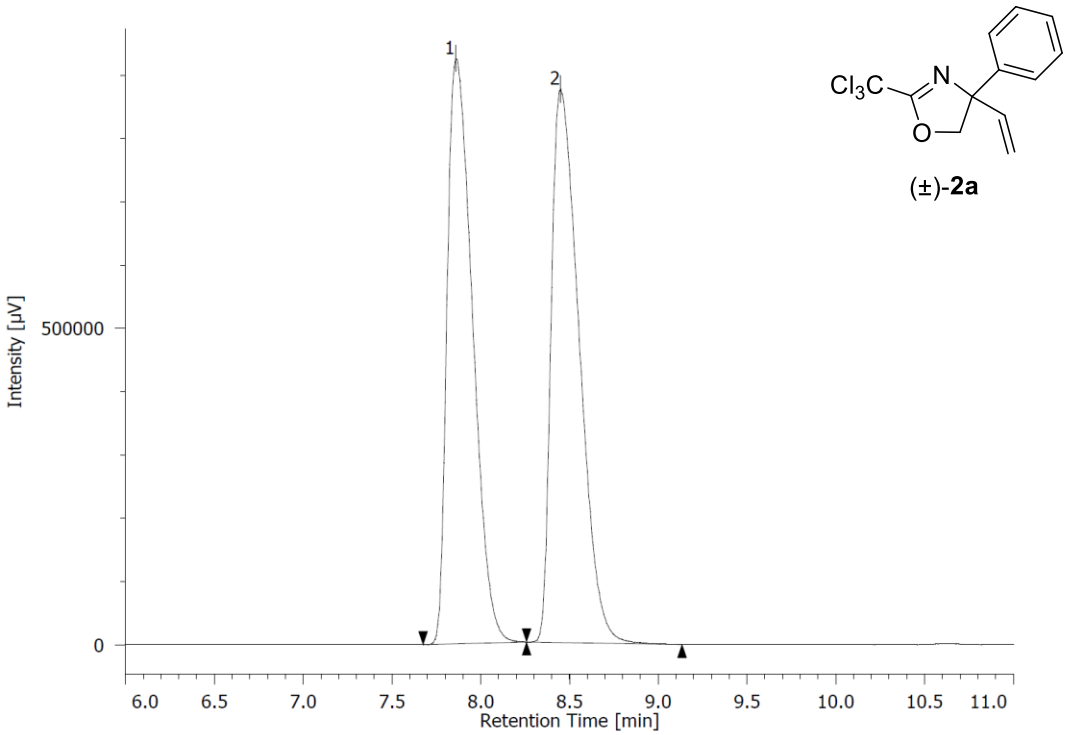


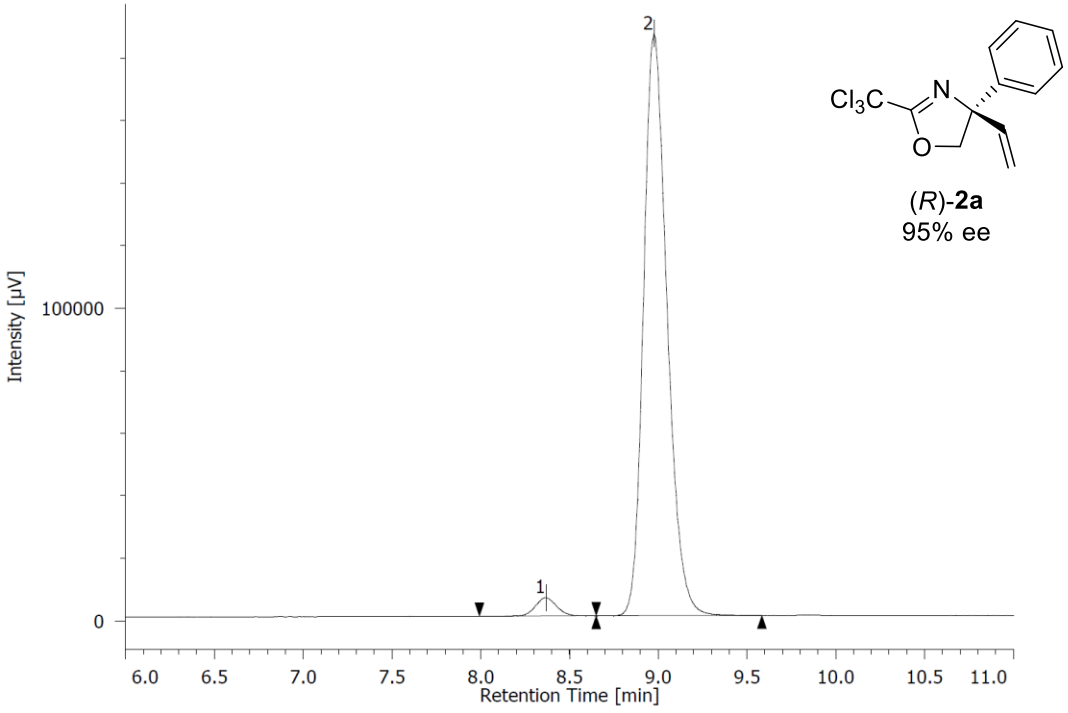
^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra of **1a'**



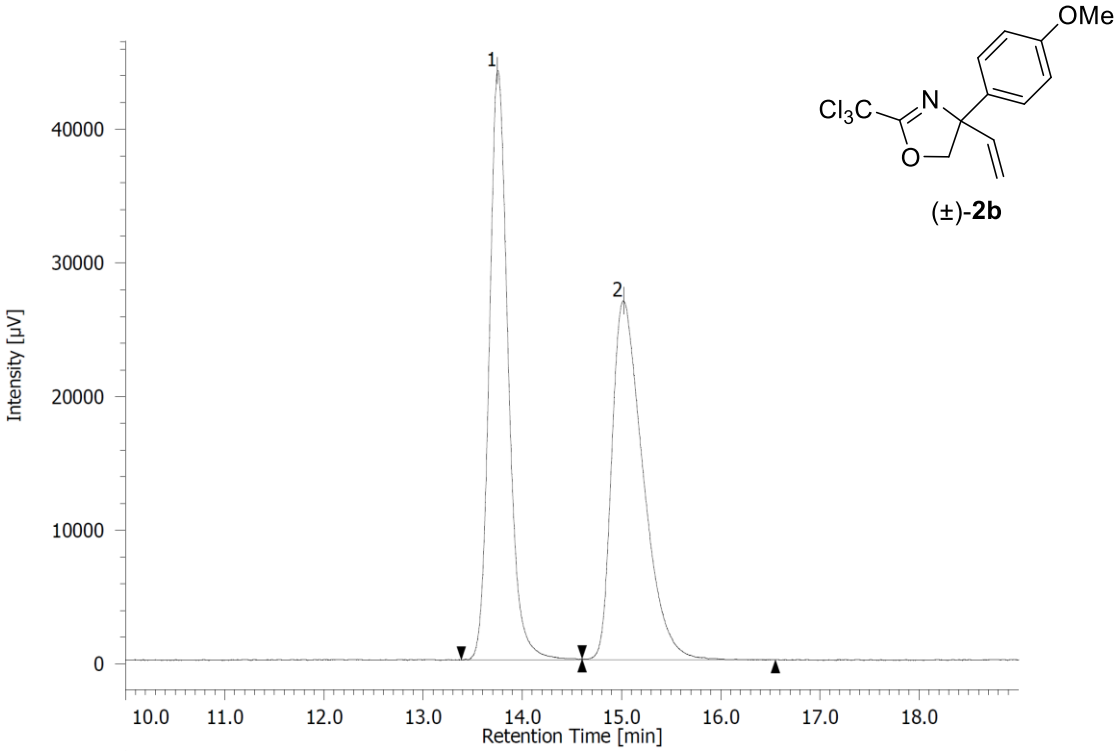
11. HPLC charts

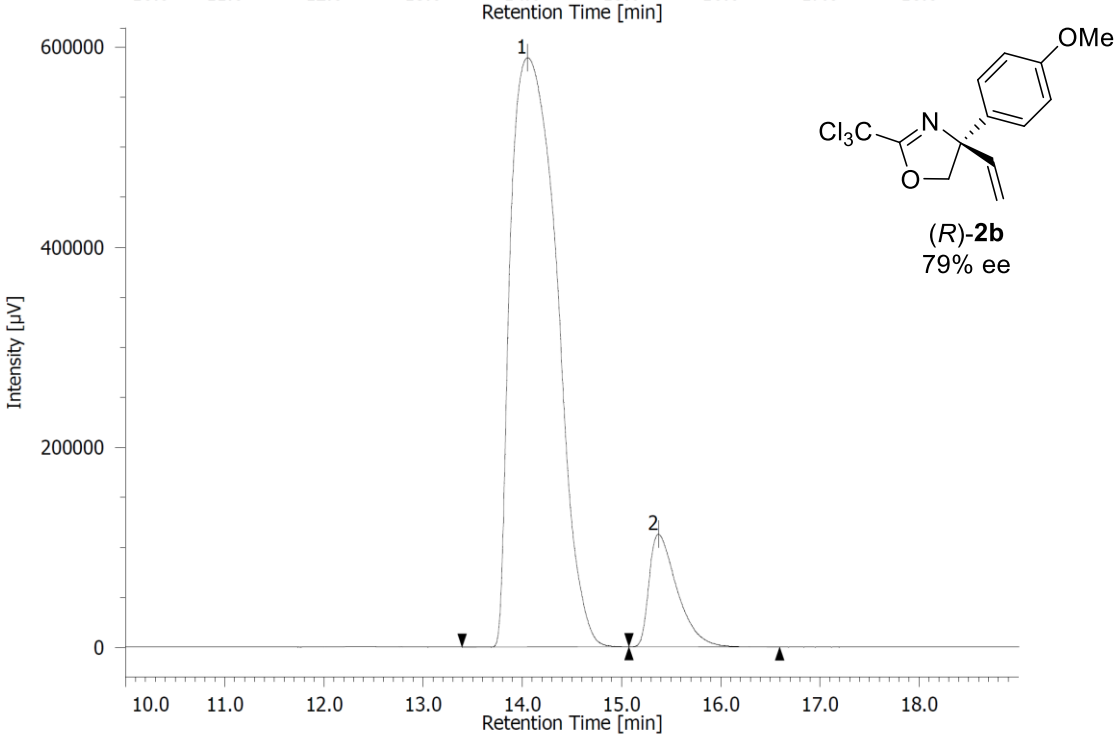
HPLC charts of **2a** (Table 1, entry 12)



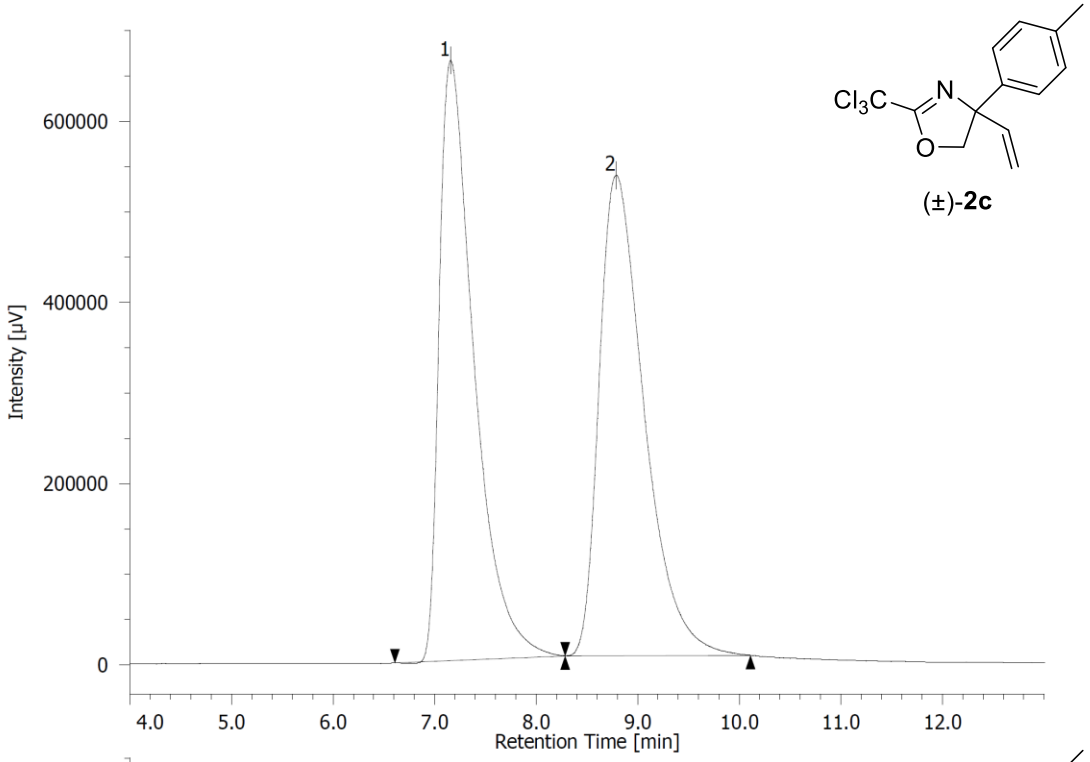


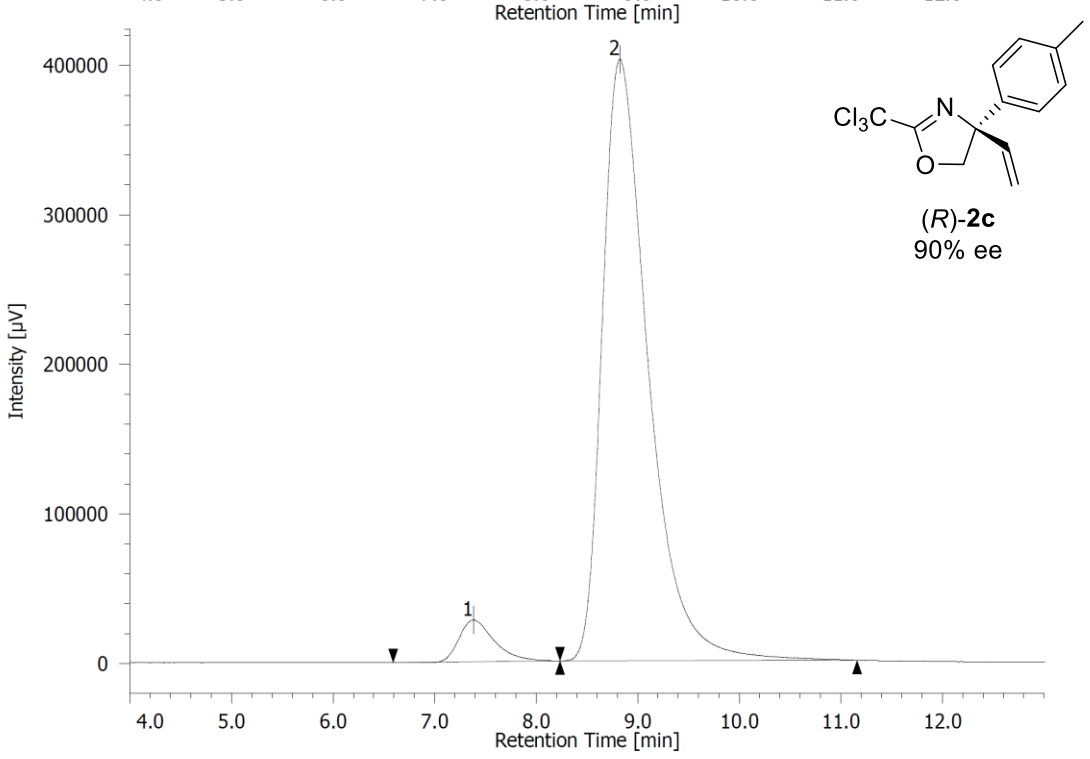
HPLC charts of **2b** (Table 2, entry 1)



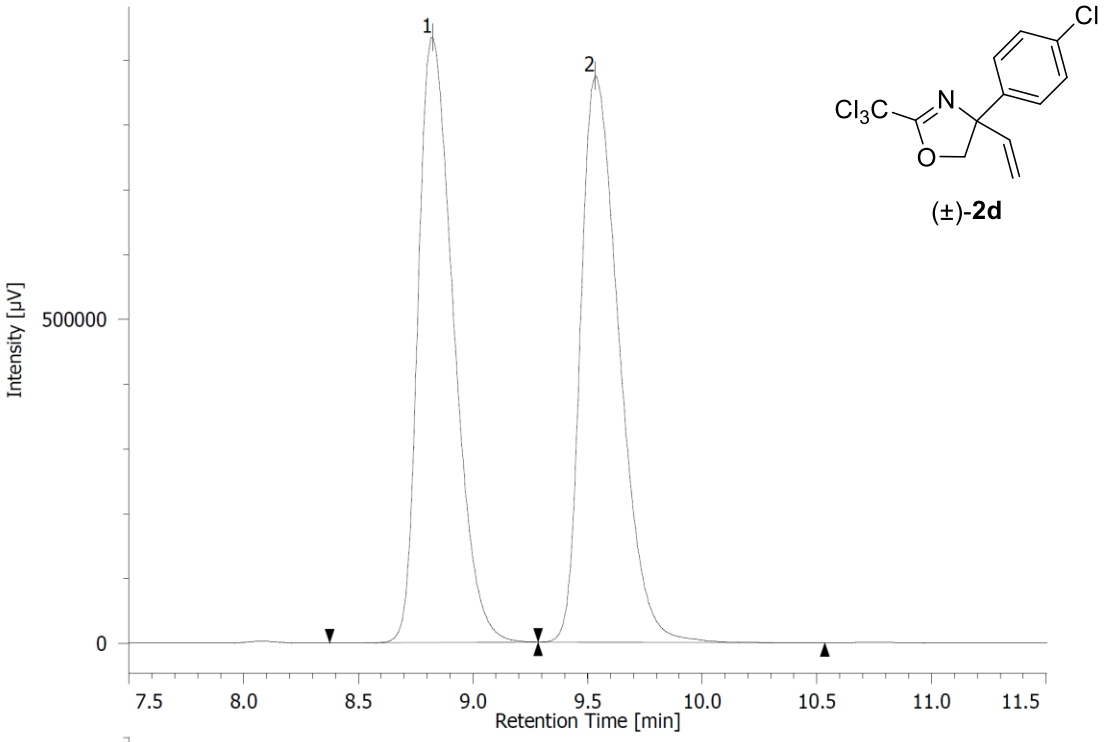


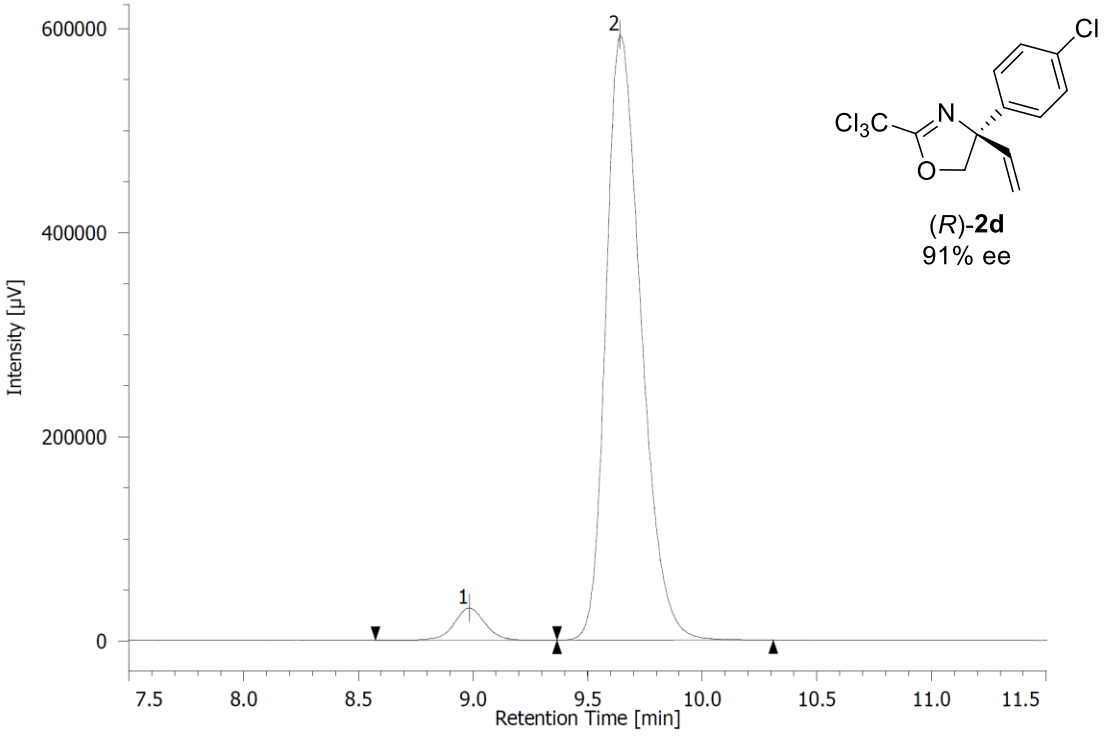
HPLC charts of **2c** (Table 2, entry 3)



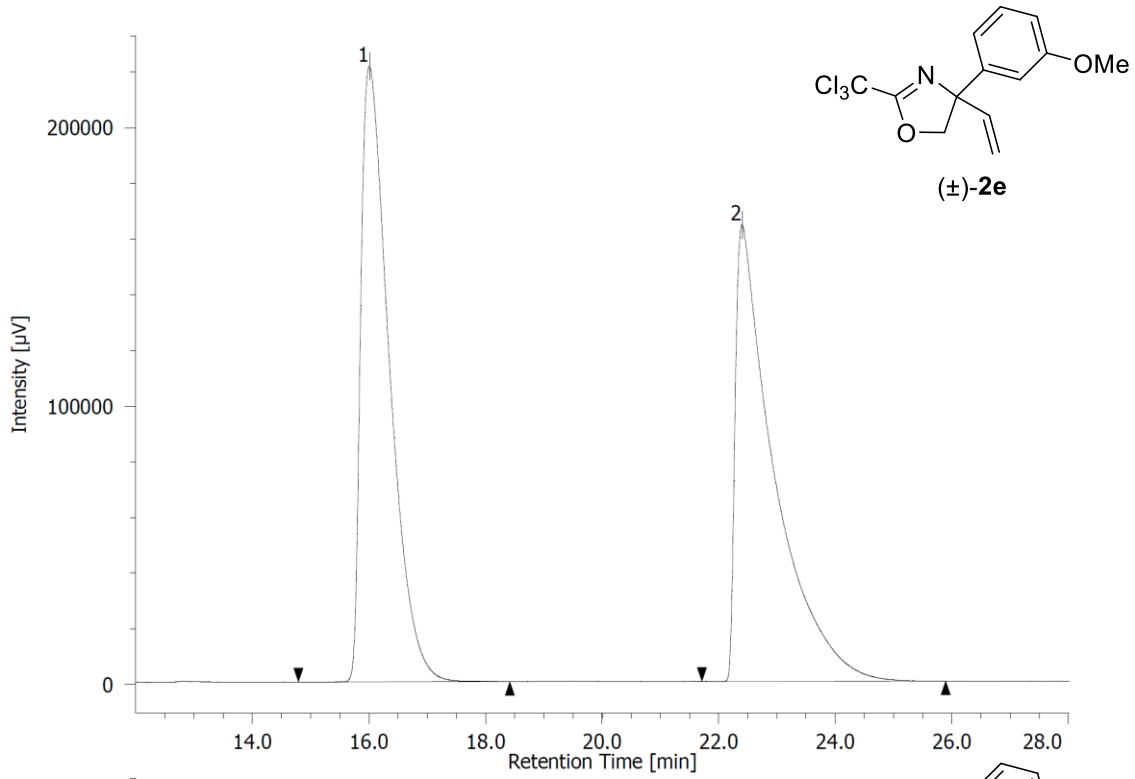


HPLC charts of **2d** (Table 2, entry 4)

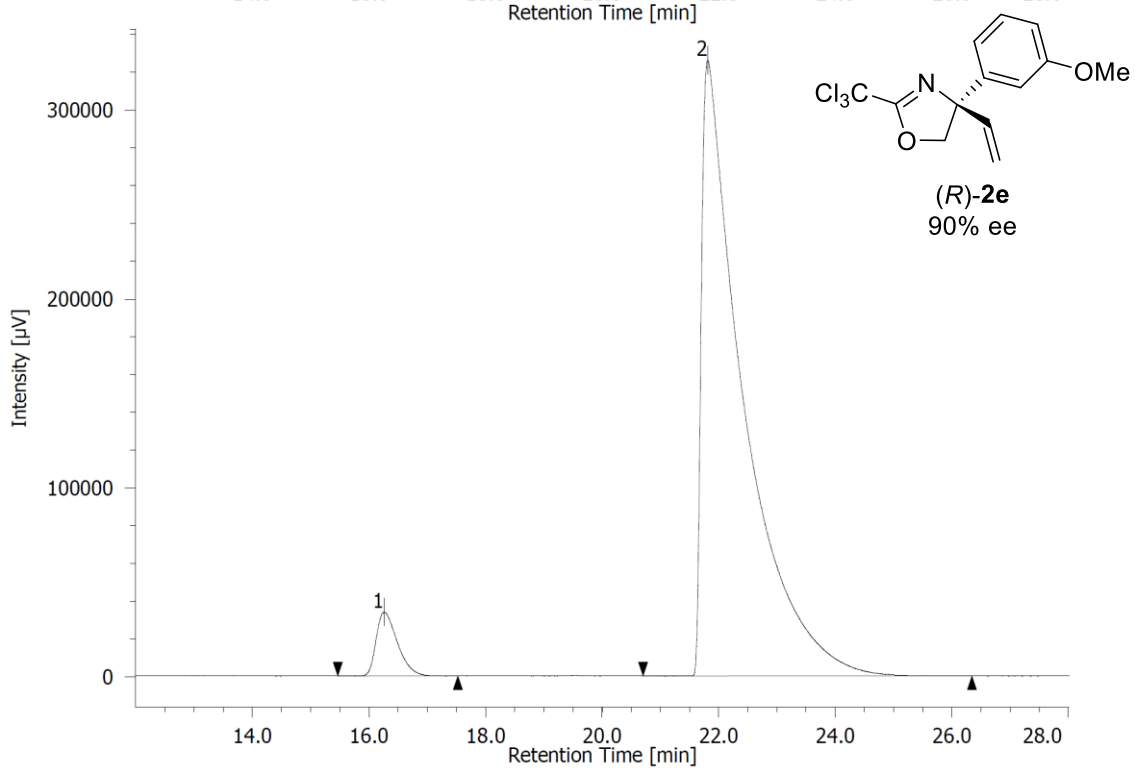




HPLC charts of **2e** (Table 2, entry 4)

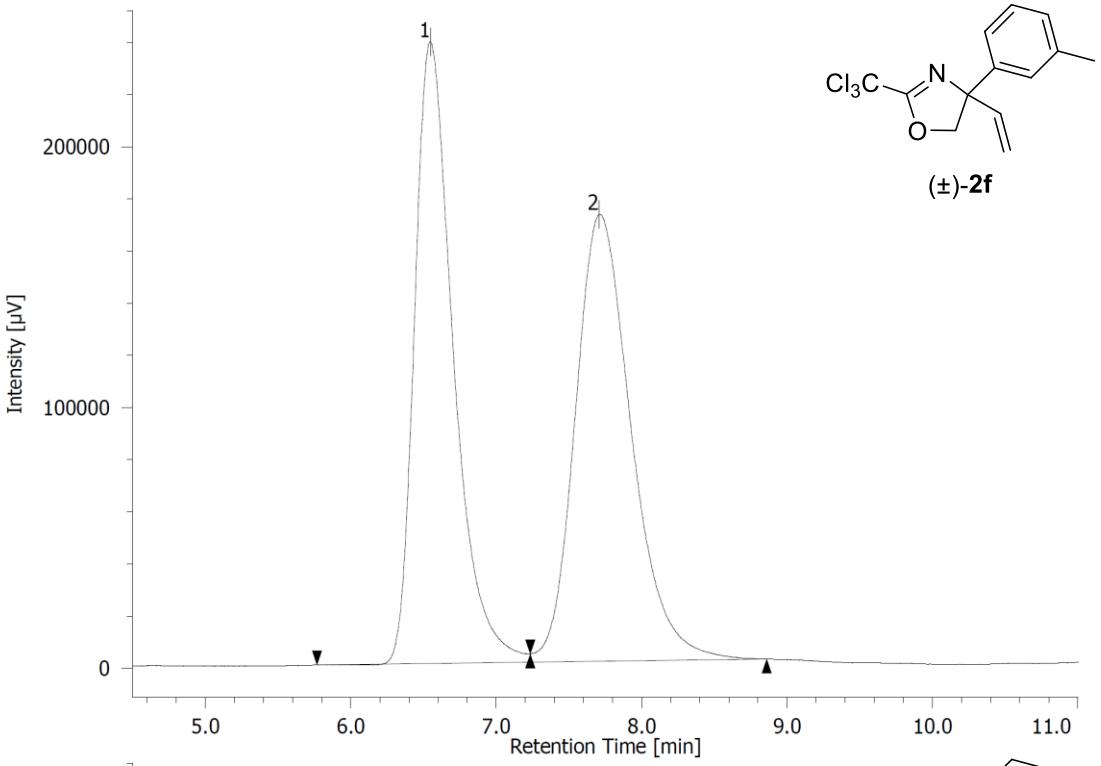


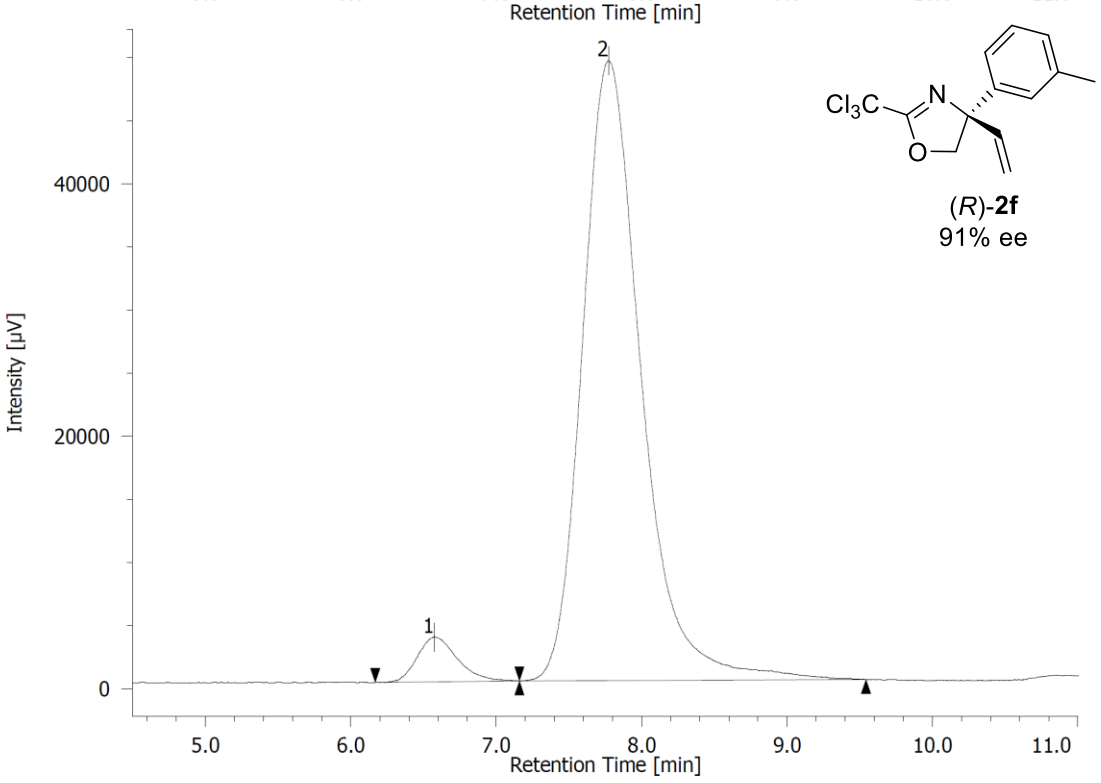
(±)-**2e**



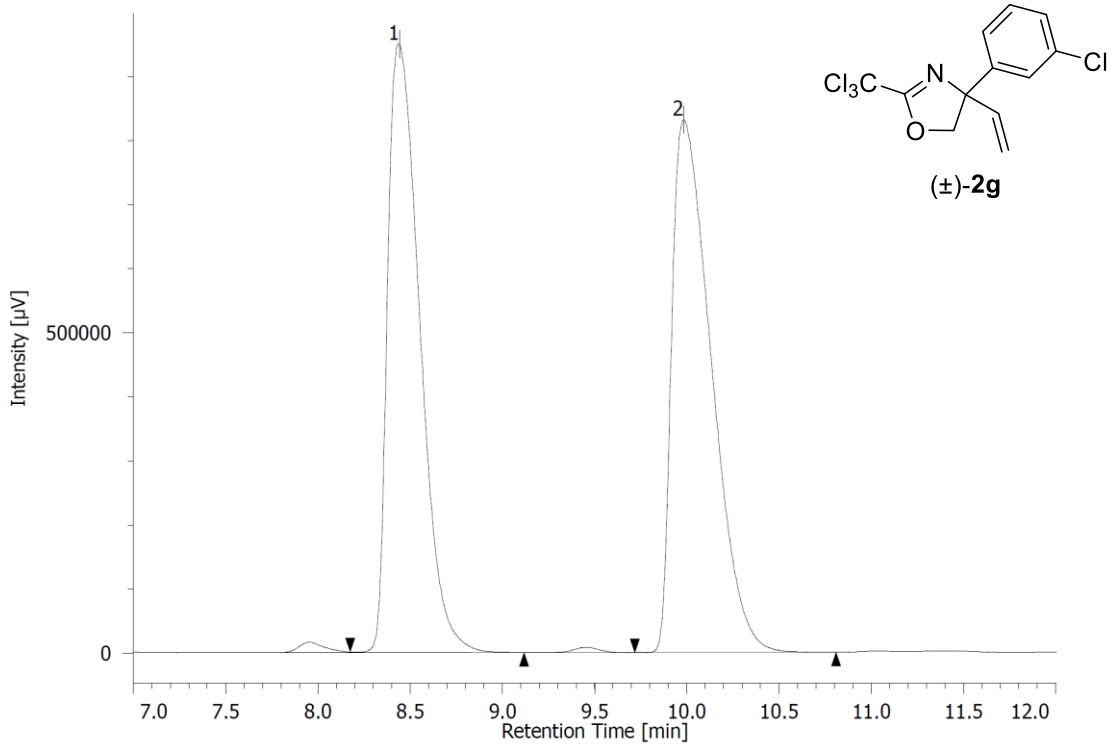
(*R*)-**2e**
90% ee

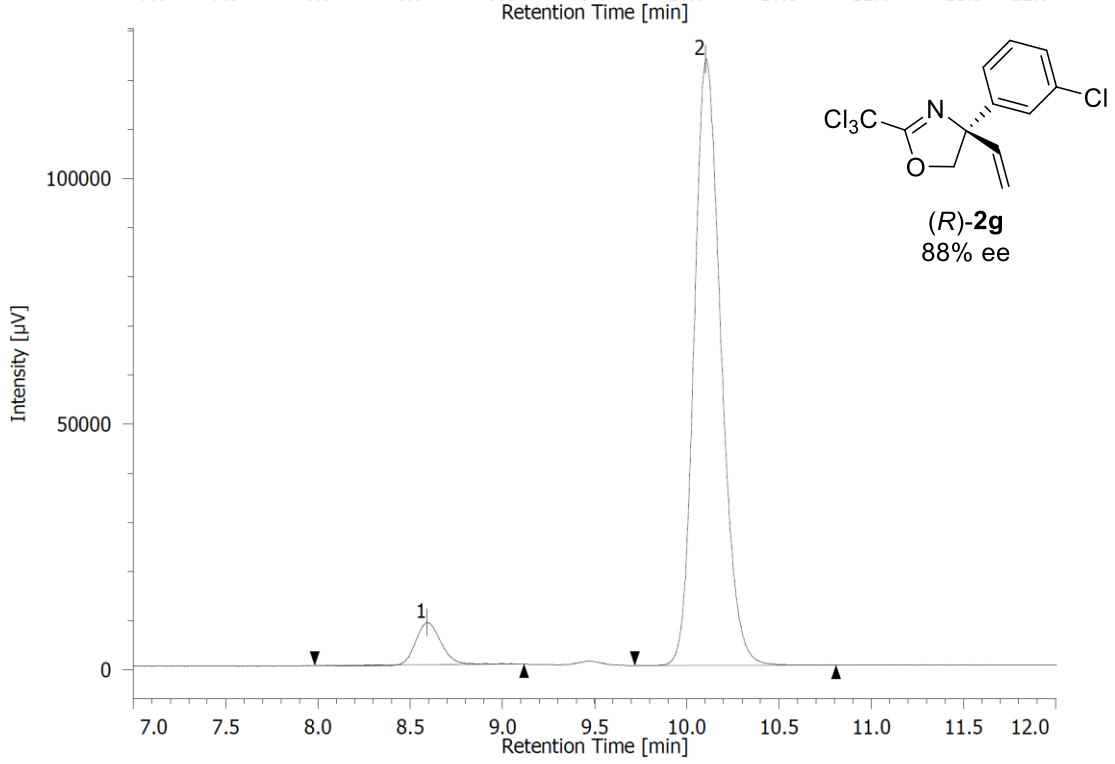
HPLC charts of **2f** (Table 2, entry 5)



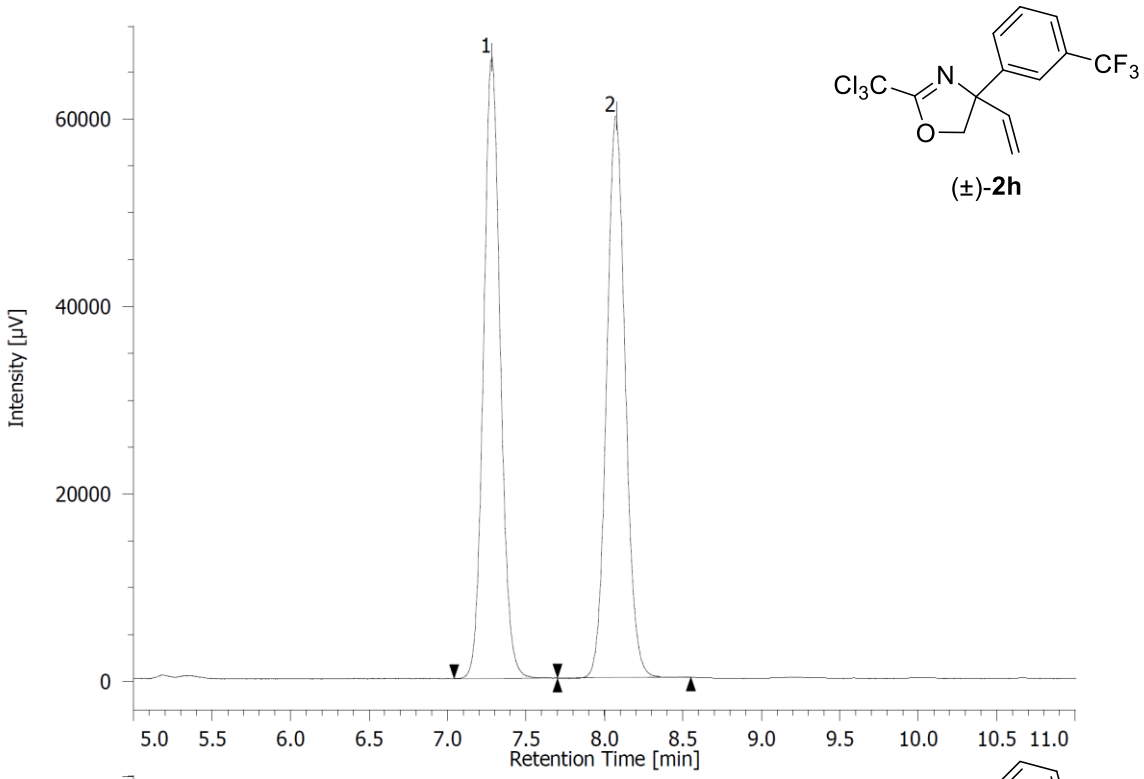


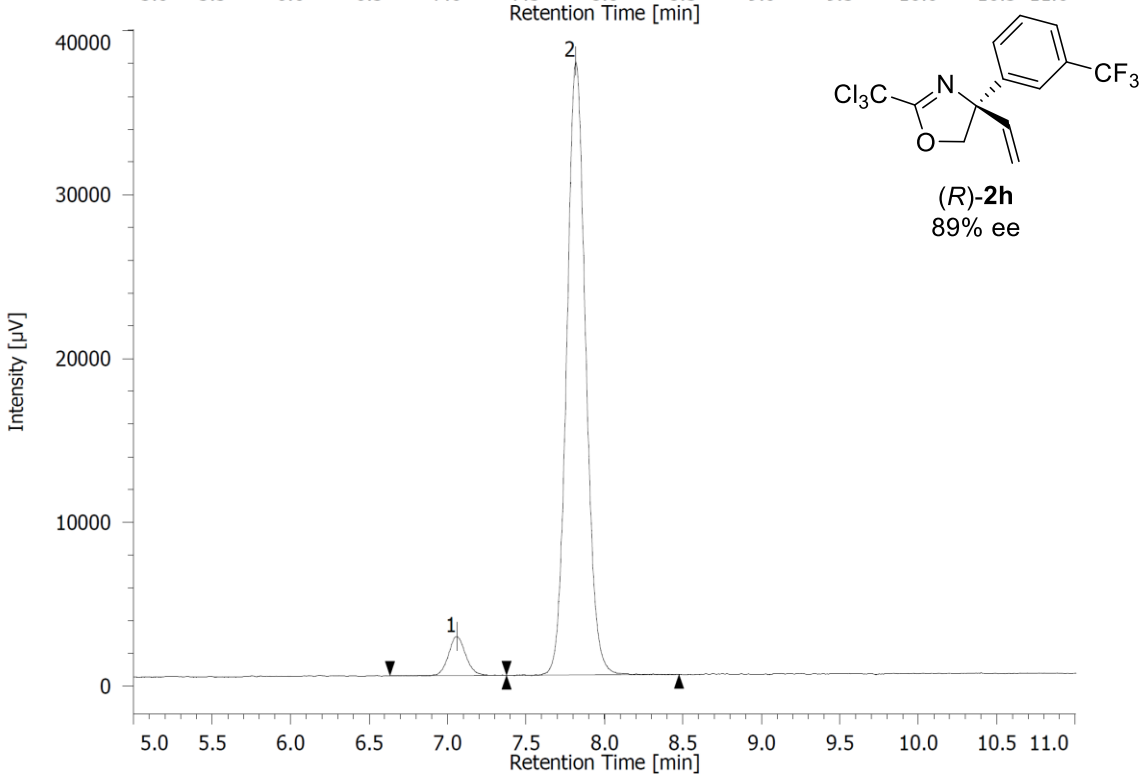
HPLC charts of **2g** (Table 2, entry 6)



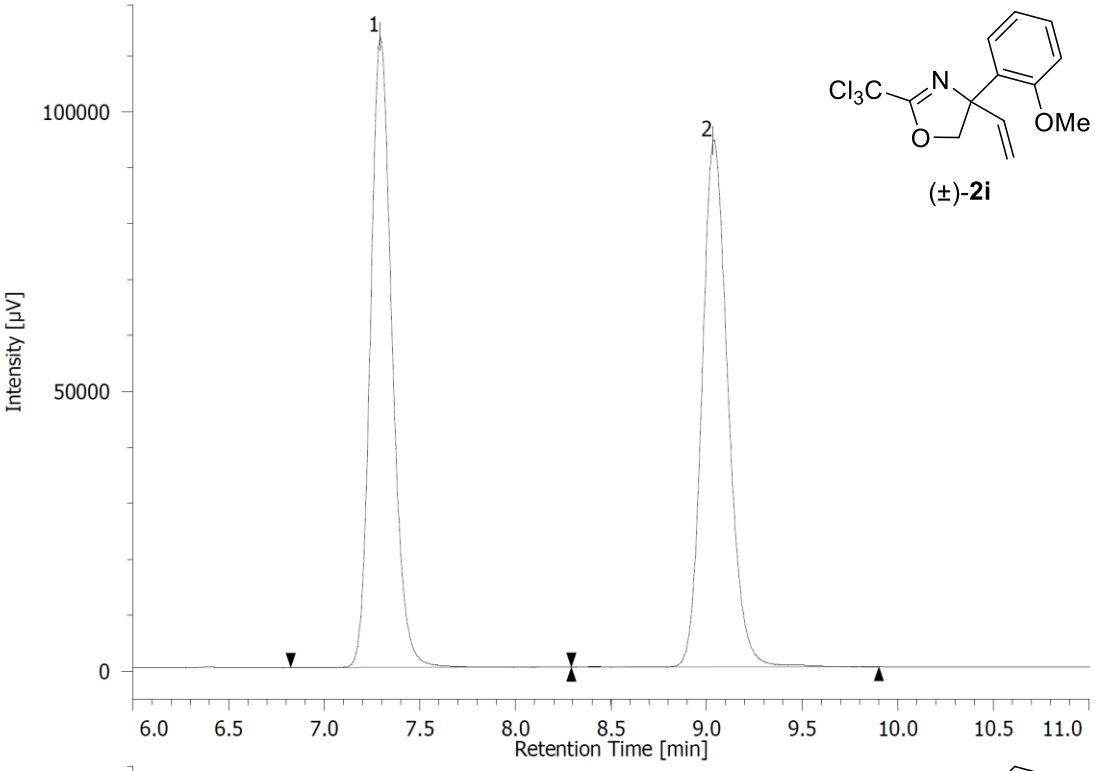


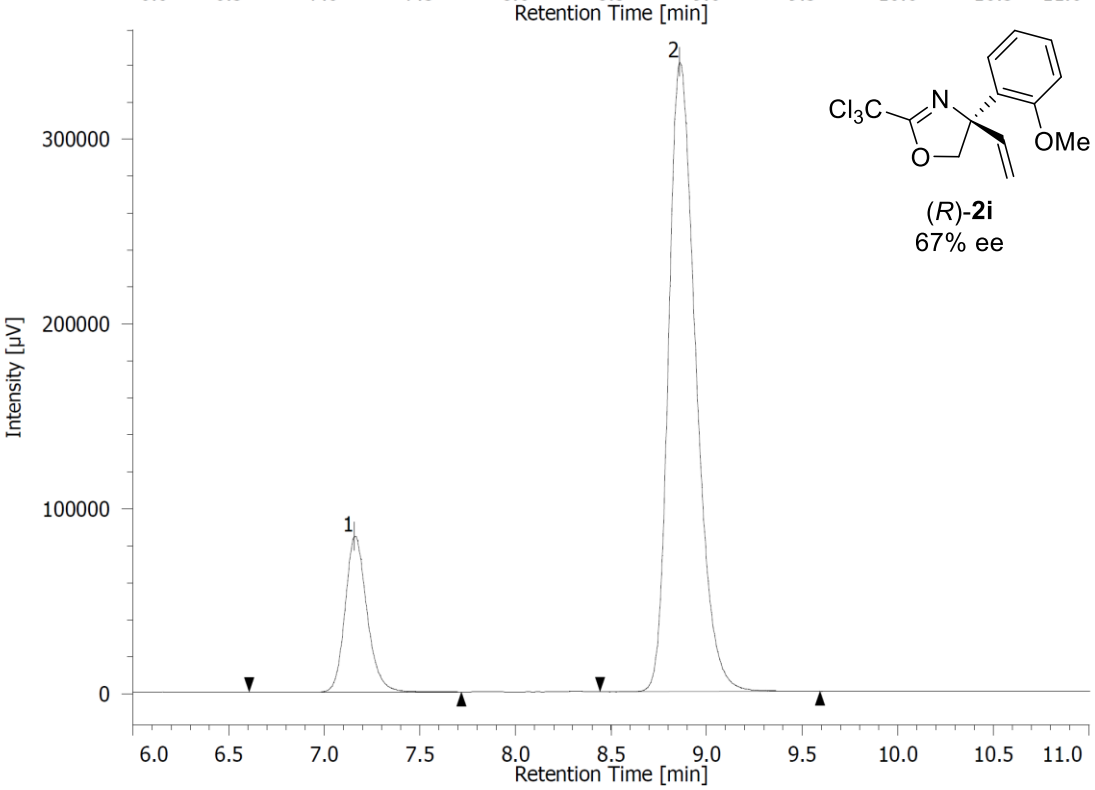
HPLC charts of **2h** (Table 2, entry 7)



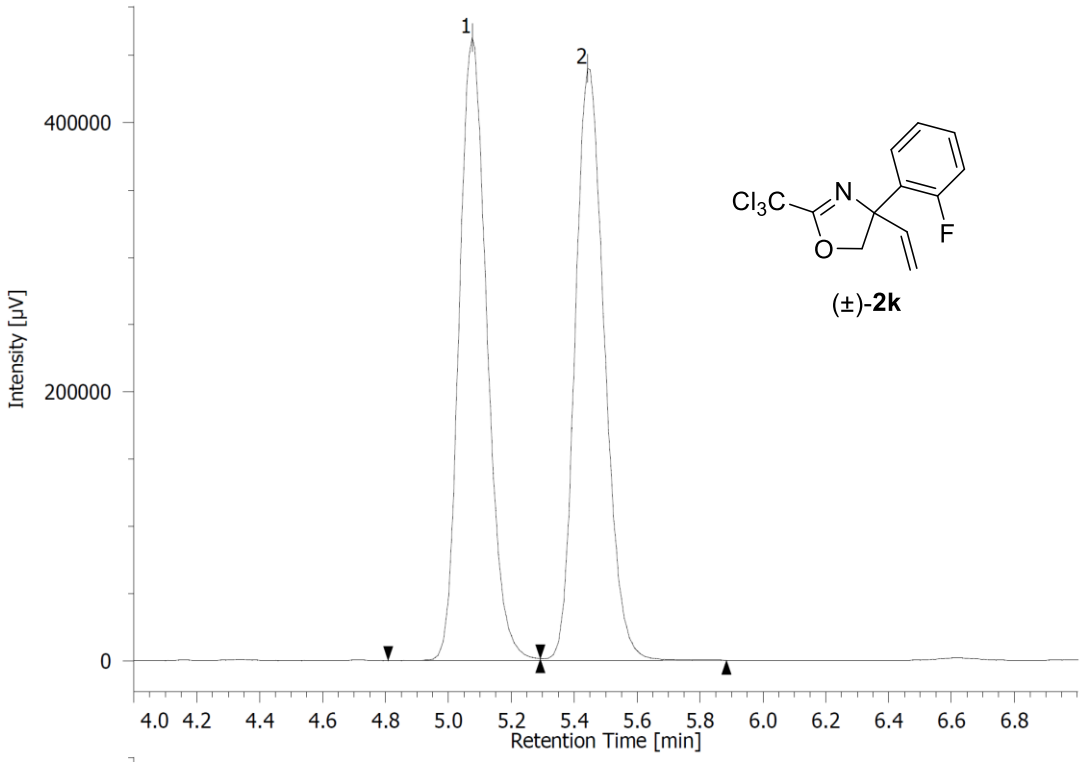


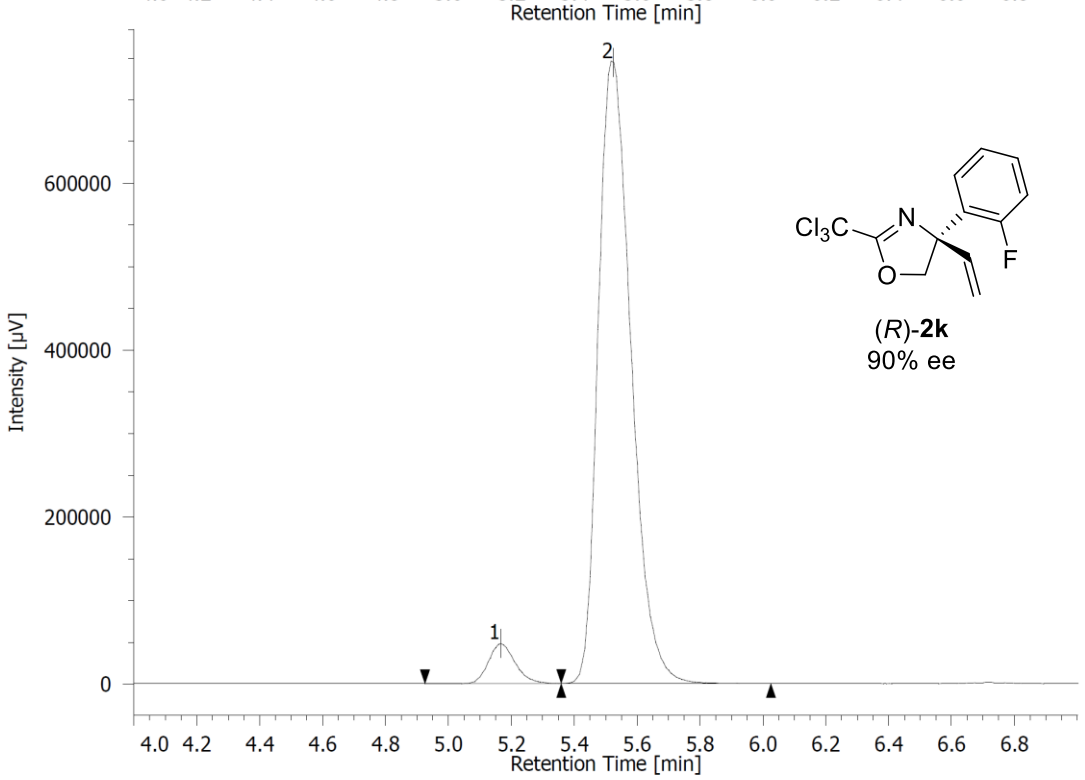
HPLC charts of **2i** (Table 2, entry 8)



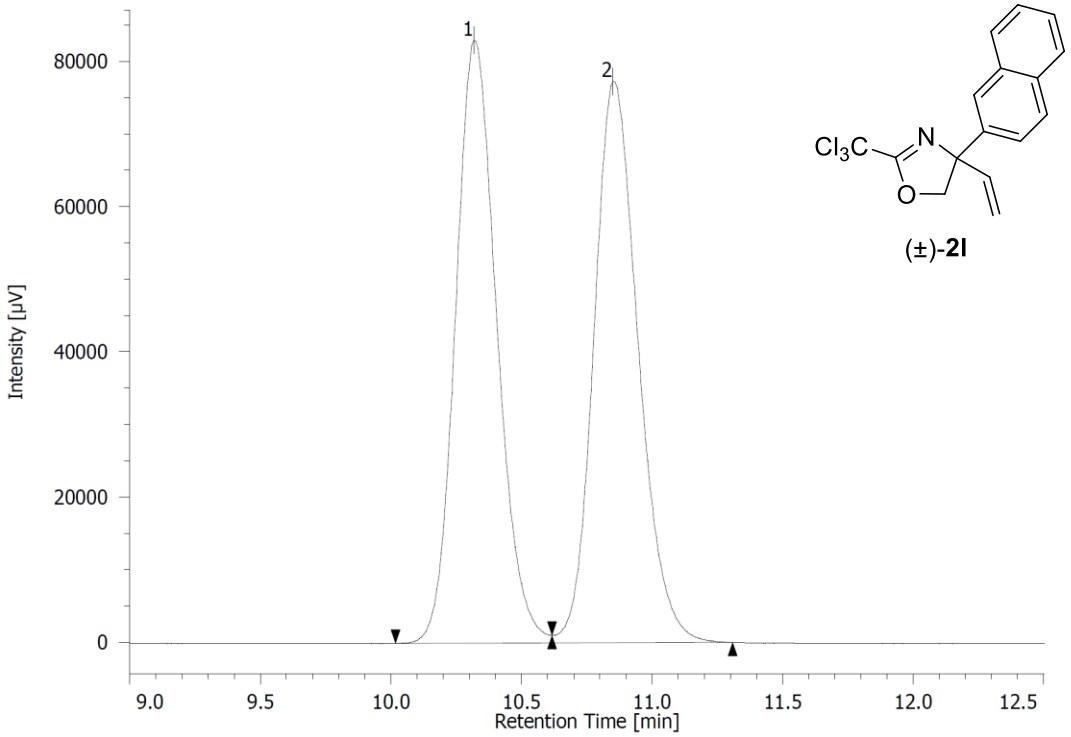


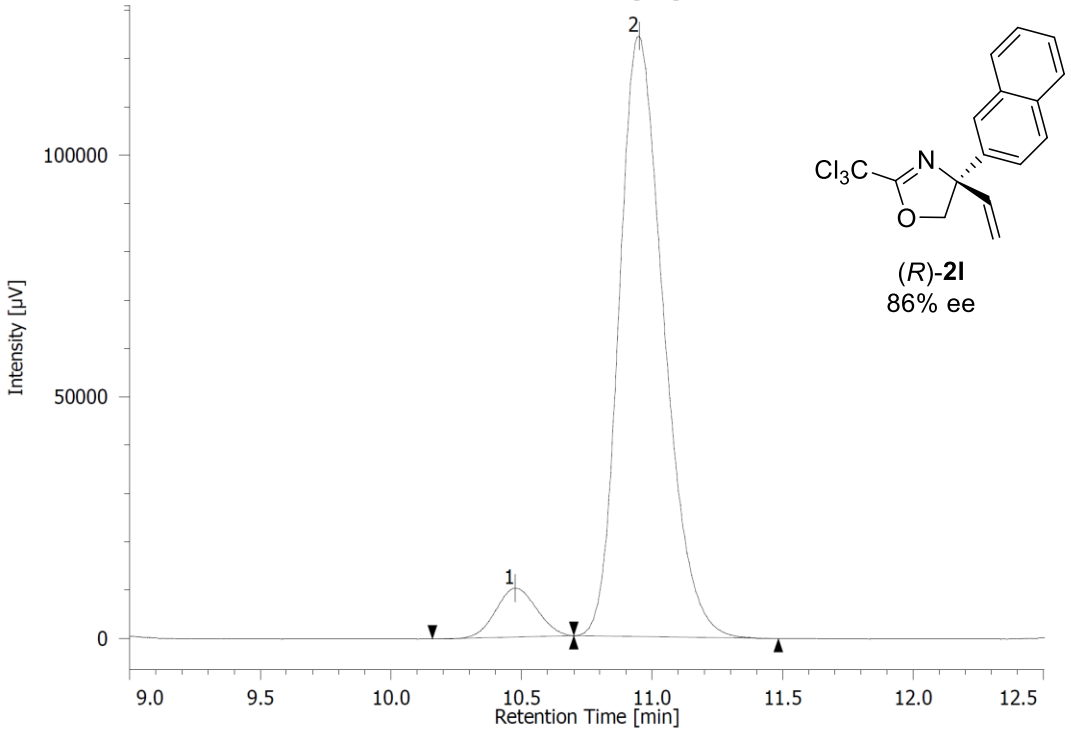
HPLC charts of **2k** (Table 2, entry 10)



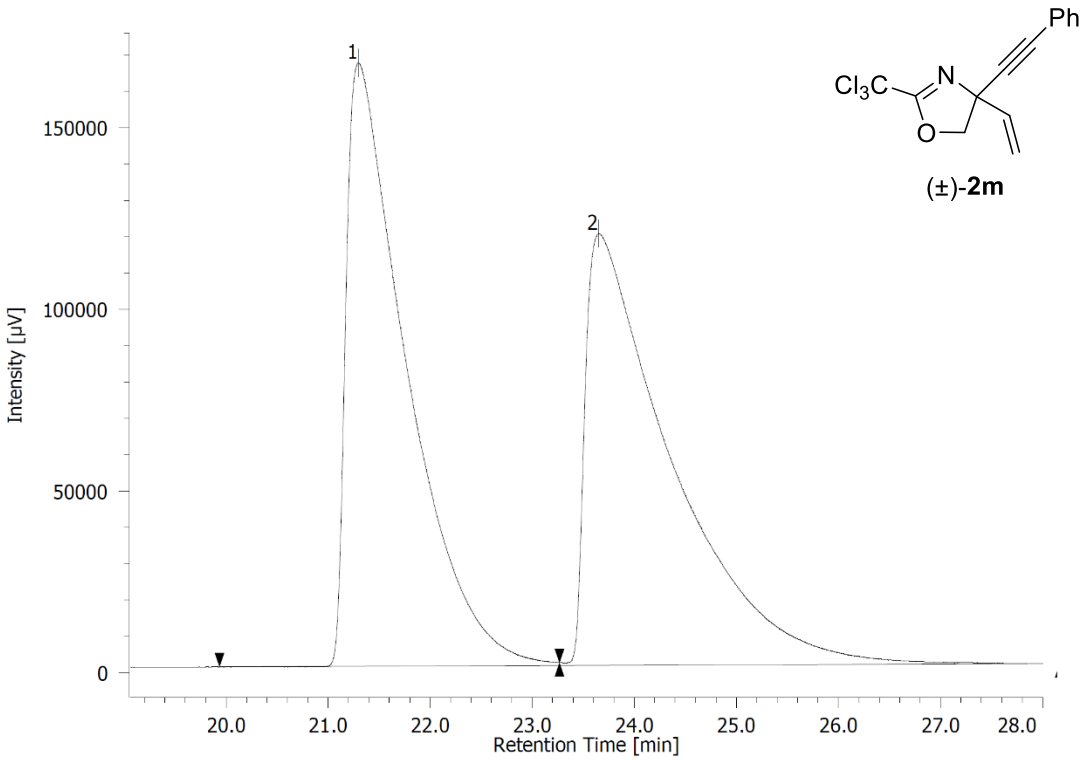


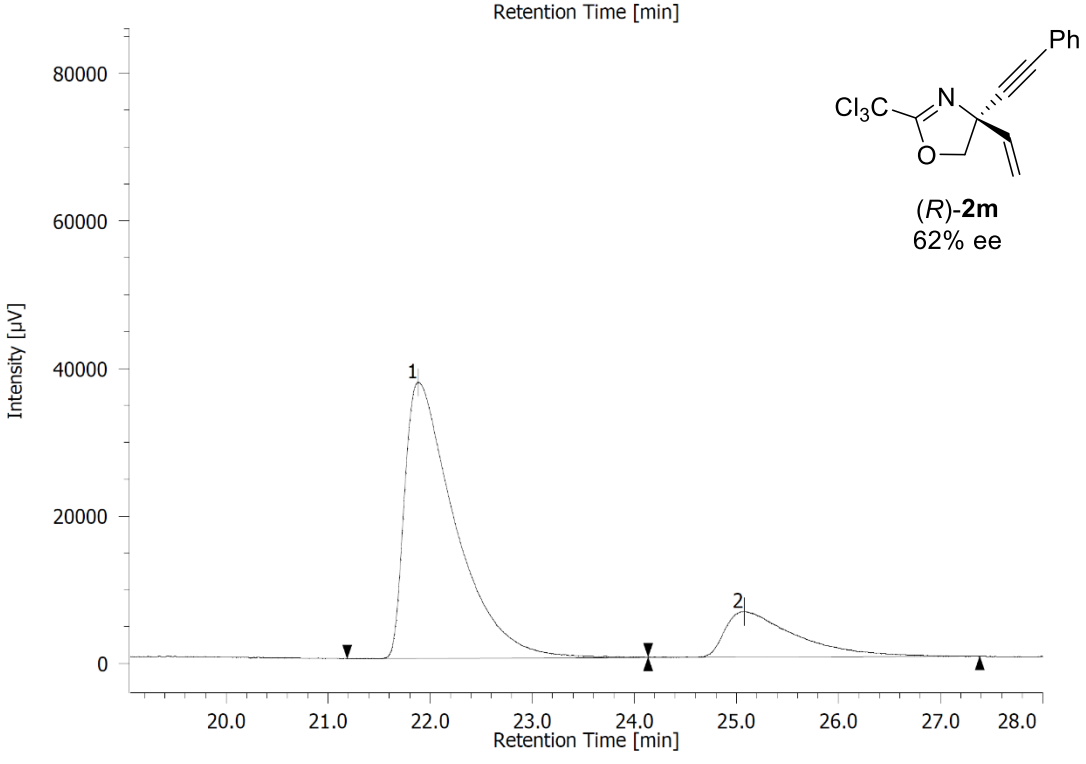
HPLC charts of **2l** (Table 2, entry 11)



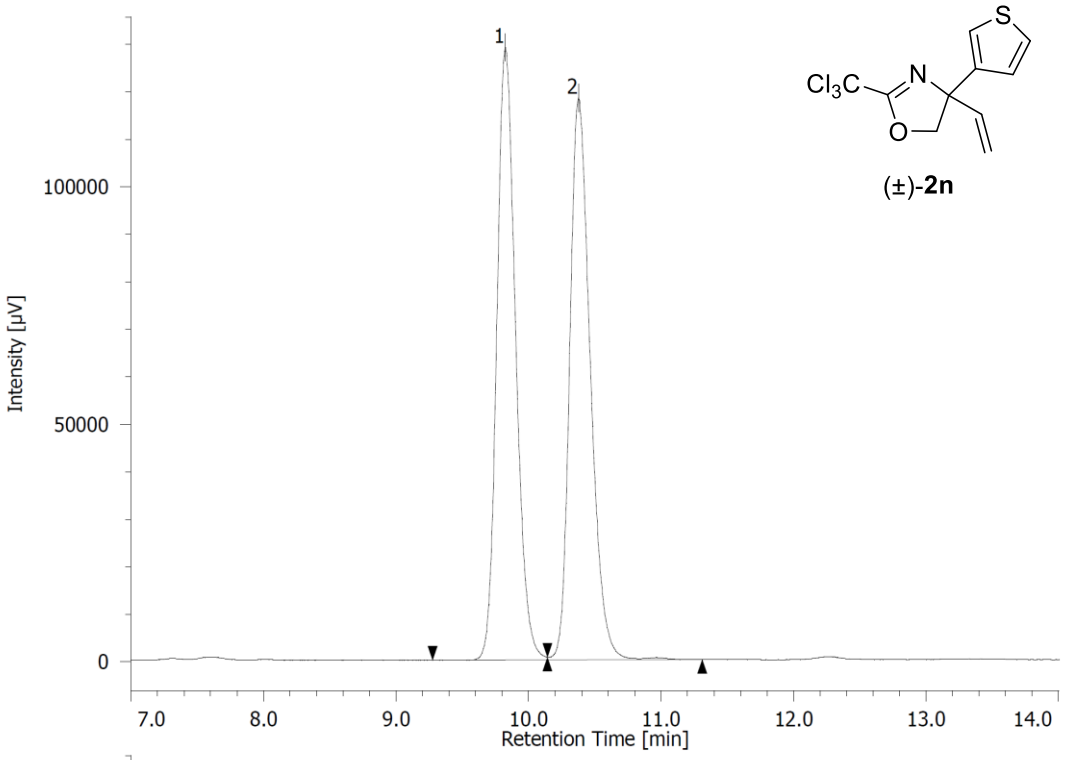


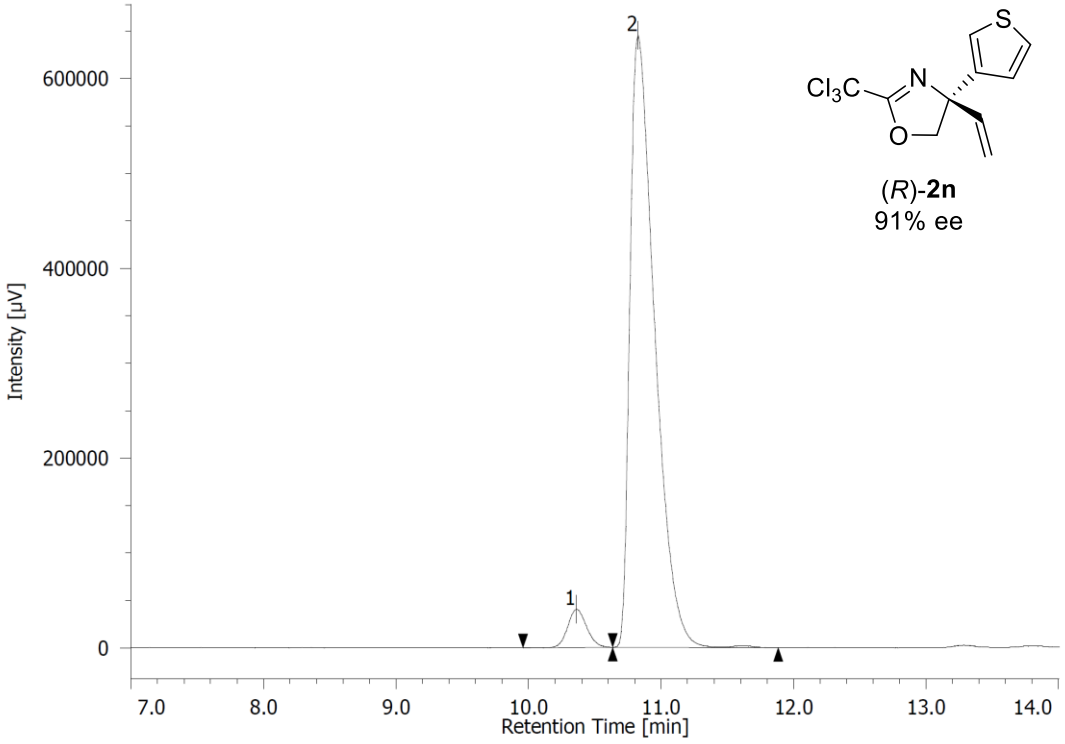
HPLC charts of **2m** (Table 2, entry 12)



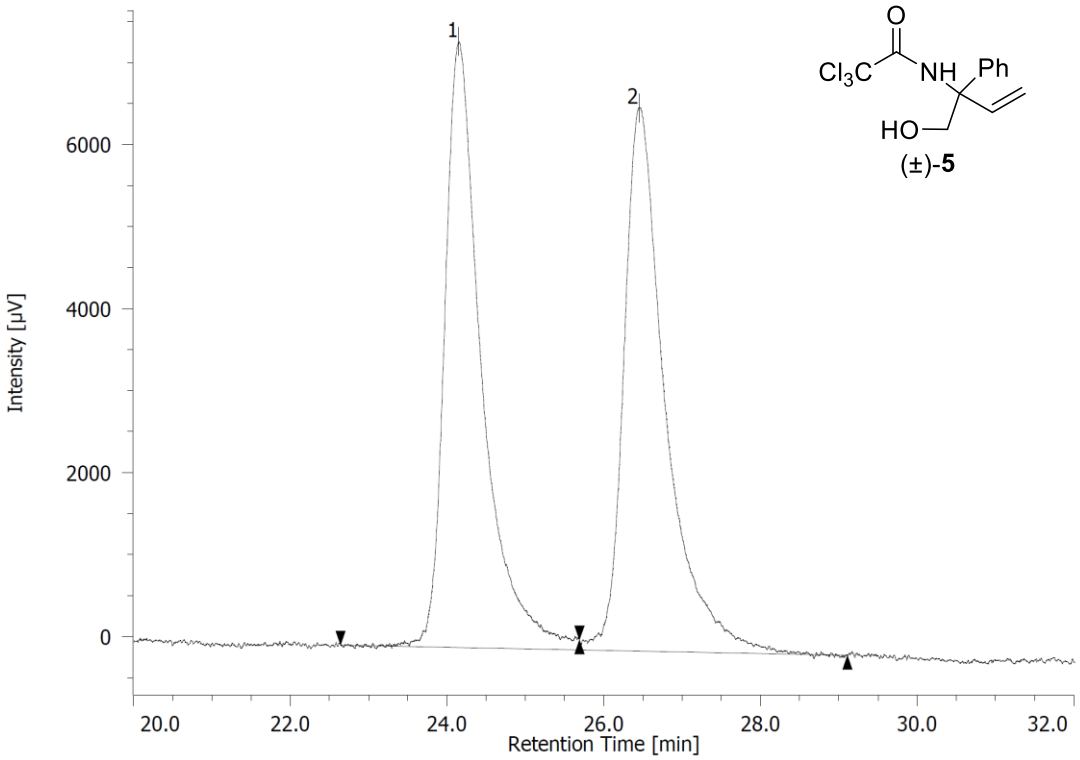


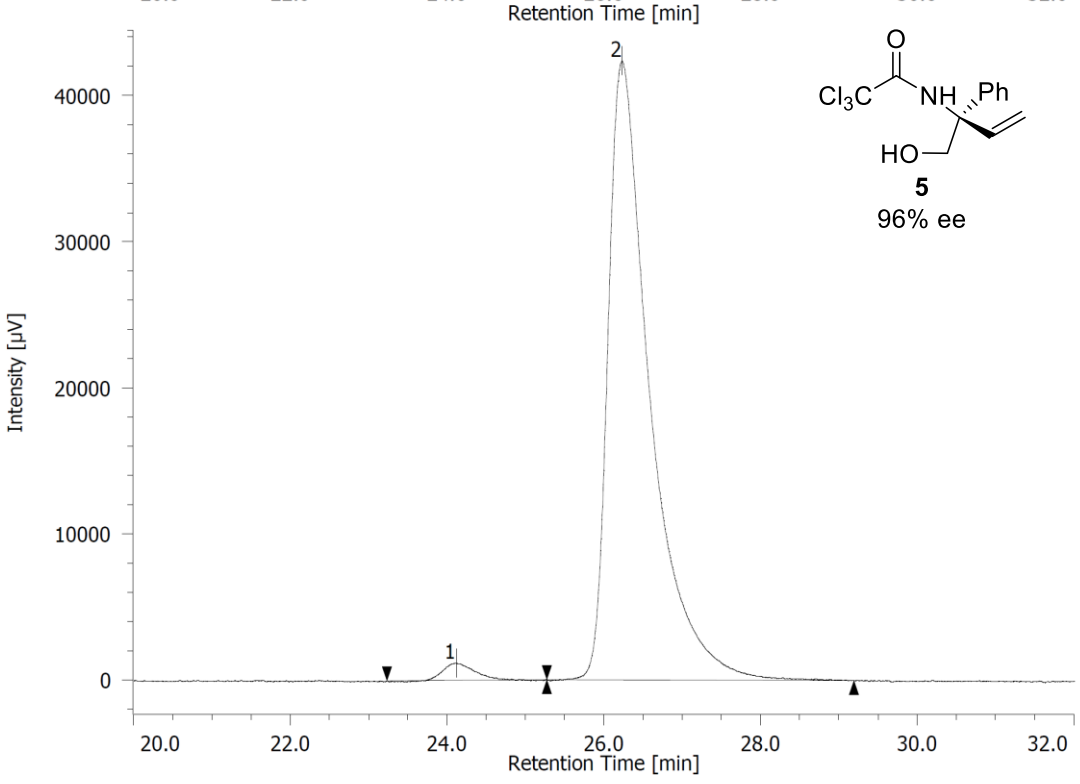
HPLC charts of **2n** (Table 2, entry 13)



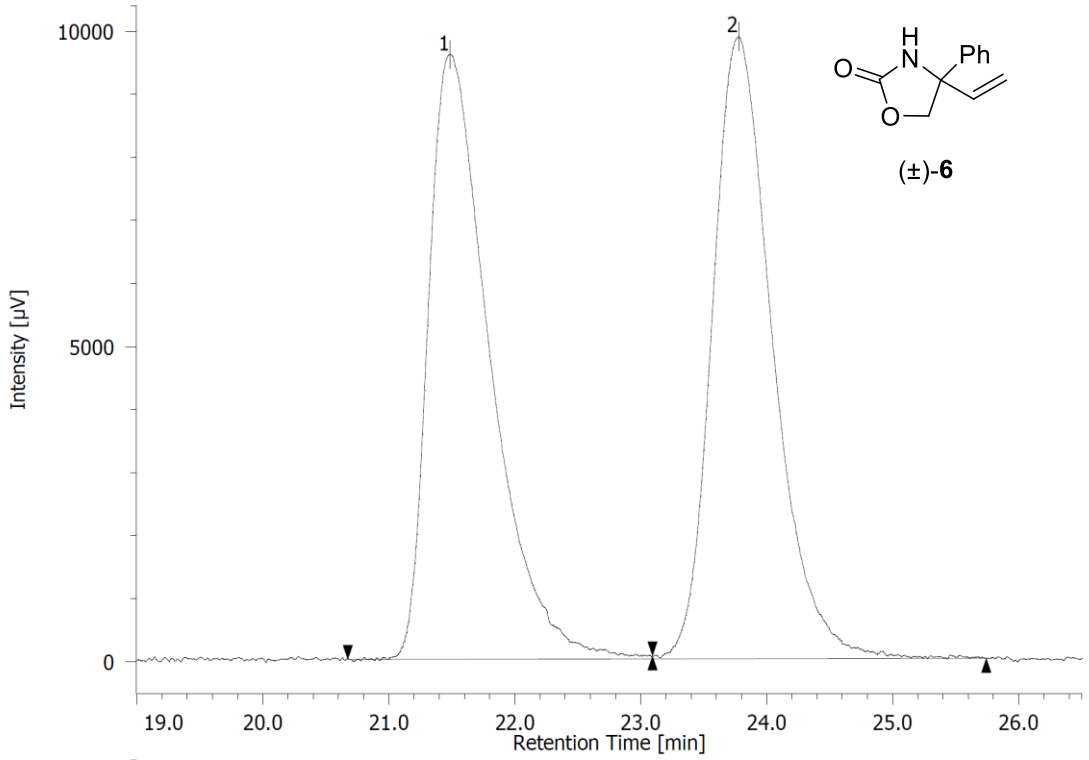


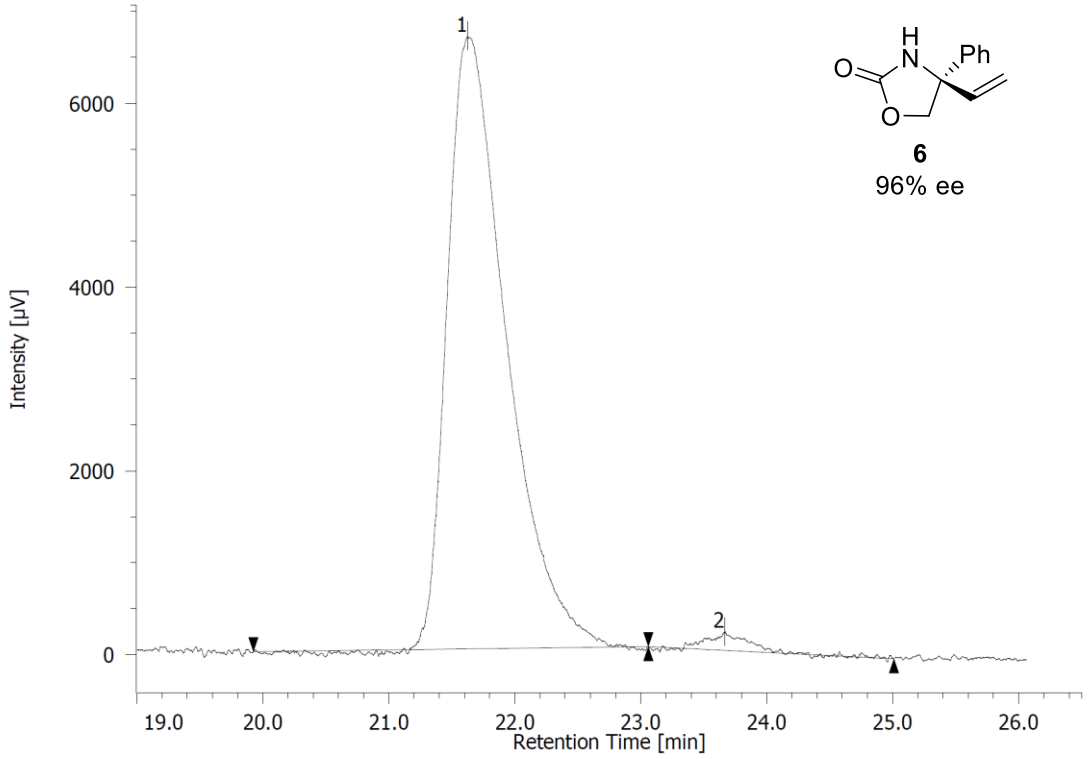
HPLC charts of **5** (Scheme 2)



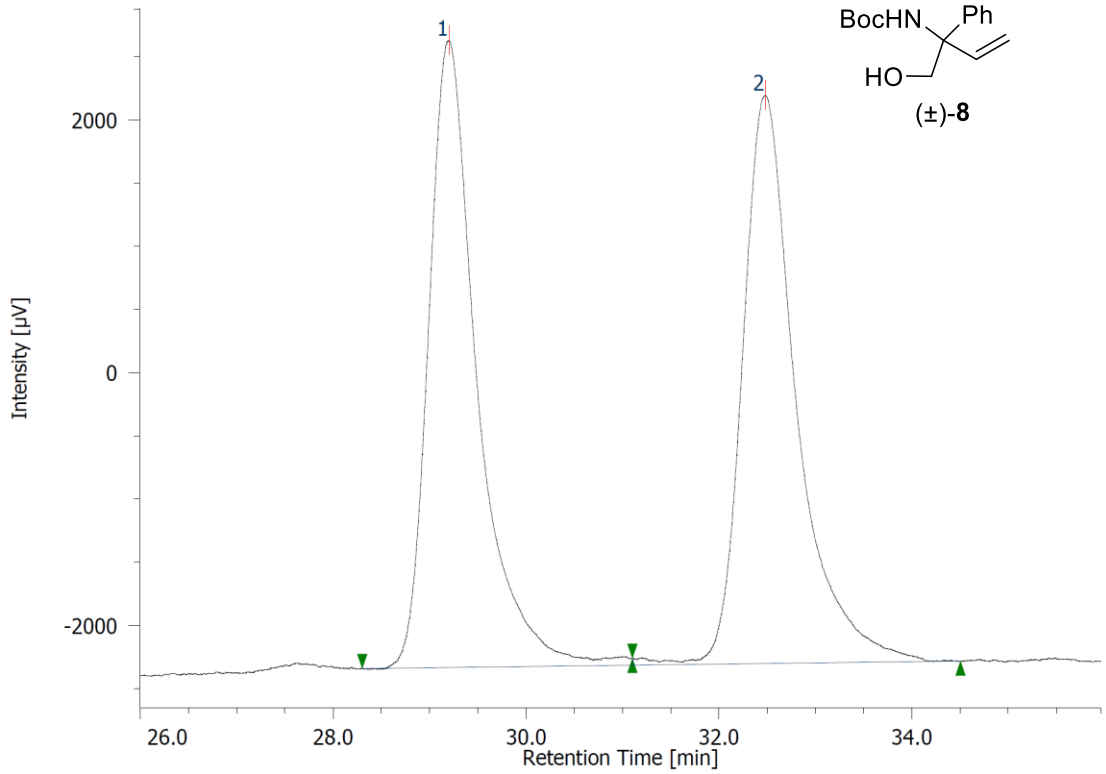


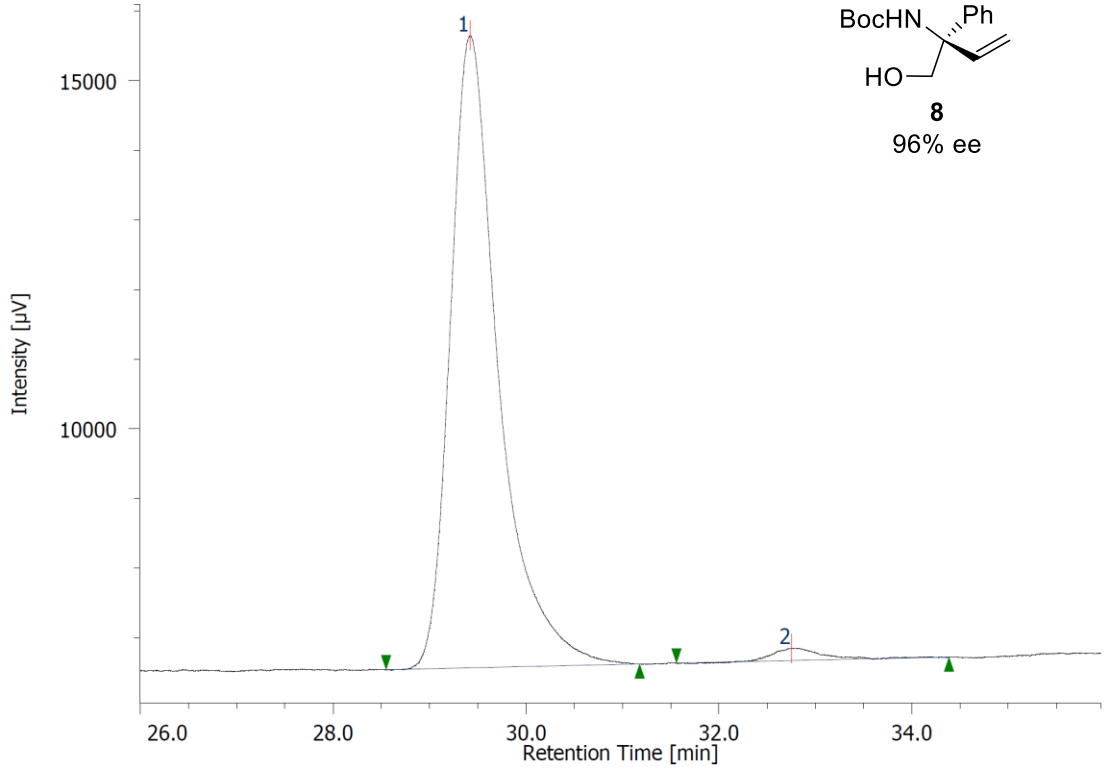
HPLC charts of **6** (Scheme 2)





HPLC charts of **8** (Scheme 2)





HPLC charts of (*R*)-(*Z*)-*d*-**2a** (Scheme 3)