Electronic Supplementary Information

A Phosphonium Ylide as a Visible Light Organophotoredox Catalyst

Yasunori Toda, Katsumi Tanaka, Riki Matsuda, Tomoyuki Sakamoto, Shiho Katsumi, Masahiro Shimizu, Fuyuki Ito, and Hiroyuki Suga

Department of Materials Chemistry, Faculty of Engineering
Shinshu University, 4-17-1 Wakasato, Nagano 380-8553, Japan

E-mail: ytoda@shinshu-u.ac.jp

General Information

All reagents and solvents were commercial grade and purified prior to use when necessary. Thin layer chromatography (TLC) was performed using TLC aluminum sheets from Merck (silica gel 60 F_{254}, 200 μm), and flash chromatography utilized silica gel from Fuji Silysia Chemical (PSQ60B, 60 μm). Products were visualized by ultraviolet (UV) light and/or TLC stains. Melting points were measured on a Yanaco micro melting point apparatus and were not corrected. Nuclear magnetic resonance (NMR) spectra were acquired on a Bruker Fourier 300 (300 MHz). Chemical shifts are measured relative to residual solvent peaks as an internal standard set to 0.00 (^{1}H) for TMS and 77.0 (^{13}C{^{1}H}) for $CDCl_3$. ^{13}C{^{1}H} NMR peak assignments were confirmed by DEPT135. Data are reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sep = septet, br = broad, m = multiplet), coupling constants (Hz), and integration. Infrared (IR) spectra were recorded on a Jasco FT/IR-4200 spectrophotometer and are reported in wavenumbers (cm^{-1}). All compounds were analyzed as neat films on a potassium bromide (KBr) plate. Mass spectra were recorded on a Bruker micrOTOF II mass spectrometer by the ionization method noted. A post-acquisition gain correction was applied using sodium formate (HCO_2Na) as the lock mass. UV-vis absorption spectra were recorded on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF-5300pc spectrophotometer. The irradiation light intensity was measured by a USHIO UIT201 digital UV intensity meter with a visible light detector at 405 nm.

General Procedure for the Halohydrin Synthesis

To an oven-dried 10 mL test tube equipped with a stir bar was added epoxide **2** (0.20 mmol, 1.0 equiv), phosphonium ylide **1** (7.4 mg, 0.02 mmol, 10 mol %), a 99:1 mixture of DMF/H_2O (v/v, 2.0 mL, 0.1 M), and trichloroacetonitrile (60 μL, 0.60 mmol, 3.0 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 6 h, the mixture was treated with H_2O (3 mL). The aqueous layer was extracted with Et_2O (5 mL x 3). The organic layers were combined, washed with H_2O (15 mL x 2), dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography (SiO_2: 8 g) yielded halohydrin **3**.

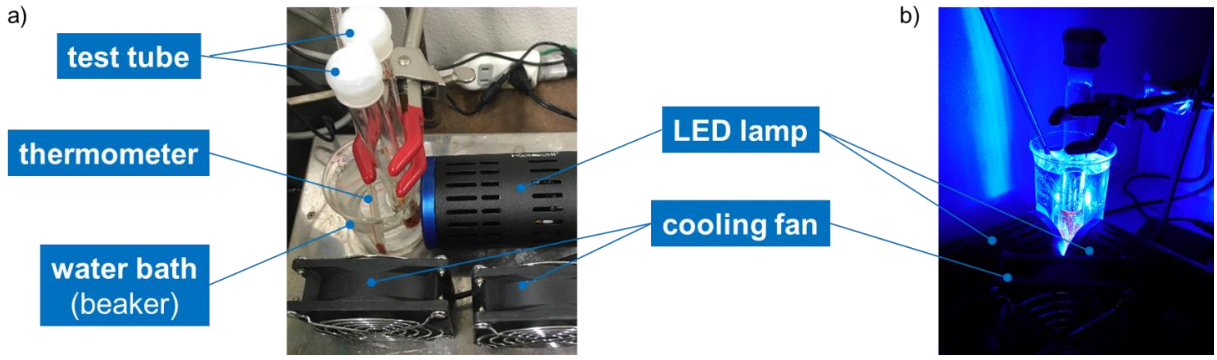
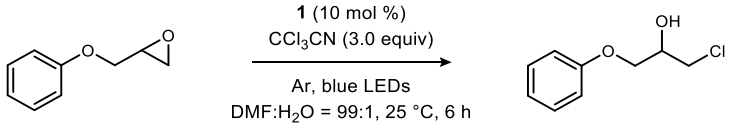


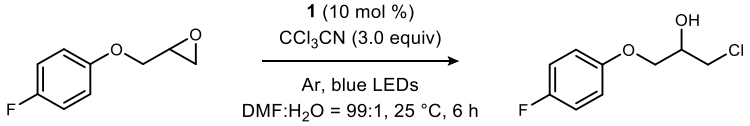
Figure S1. Equipment for photoredox reactions by **1** (a: 0.2 mmol scale, b: 1.0 mmol scale)



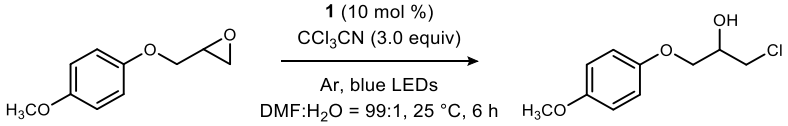
1-Chloro-3-phenoxypropan-2-ol (3a).[1] Prepared according to the general procedure using epoxide **2a** (30.0 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 20:1-10:1) yielded a colorless oil (33.9 mg, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.01-6.95 (m, 1H), 6.94-6.89 (m, 2H), 4.25-4.18 (m, 1H), 4.10 (dd, *J* = 9.6, 5.1 Hz, 1H), 4.06 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.78 (dd, *J* = 11.1, 5.1 Hz, 1H), 3.72 (dd, *J*

= 11.1, 5.7 Hz, 1H), 2.66 (br s, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 158.2 (C), 129.6 (CH), 121.4 (CH), 114.5 (CH), 69.9 (CH), 68.4 (CH_2), 45.9 (CH_2).

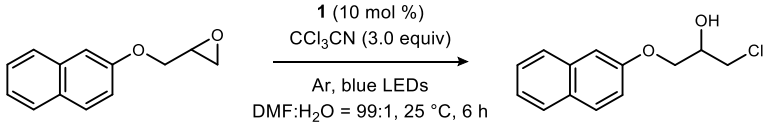
Procedure for larger scale synthesis: To an oven-dried 20 mL test tube equipped with a stir bar was added **2a** (1.0 mmol, 1.0 equiv), **1** (36.8 mg, 0.10 mmol, 10 mol %), a 99:1 mixture of DMF/H_2O (v/v, 10 mL, 0.1 M), and trichloroacetonitrile (300 μL, 0.60 mmol, 3.0 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 1.0 cm from two Kessil A160WE TUNA BLUEs at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 24 h, the mixture was treated with H_2O (10 mL). The aqueous layer was extracted with Et_2O (15 mL x 3). The organic layers were combined, washed with H_2O (50 mL x 2), dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography (SiO_2: 15 g, Hexane:EtOAc = 20:1-10:1) yielded **3a** (158.4 mg, 85%).



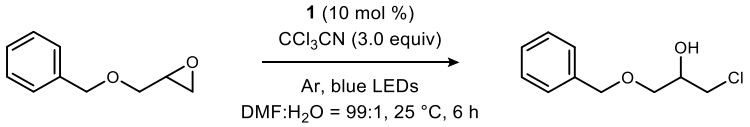
1-Chloro-3-(4-fluorophenoxy)propan-2-ol (3b).[1] Prepared according to the general procedure using epoxide **2b** (33.6 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 20:1-10:1) yielded a colorless oil (36.3 mg, 89%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.03-6.94 (m, 2H), 6.89-6.82 (m, 2H), 4.25-4.16 (m, 1H), 4.07 (dd, *J* = 9.3, 5.1 Hz, 1H), 4.03 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.78 (dd, *J* = 11.1, 5.1 Hz, 1H), 3.72 (dd, *J* = 11.1, 5.7 Hz, 1H), 2.61 (d, *J* = 5.1 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 157.6 (d, $J_{C\text{-}F}$ = 239.3 Hz, C), 154.3 (d, $J_{C\text{-}F}$ = 2.2 Hz, C), 115.9 (d, $J_{C\text{-}F}$ = 23.1 Hz, CH), 115.6 (d, $J_{C\text{-}F}$ = 8.3 Hz, CH), 69.8 (CH), 69.2 (CH_2), 45.9 (CH_2).



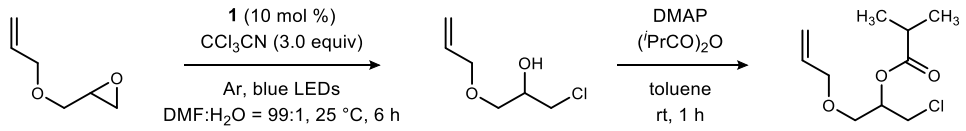
1-Chloro-3-(4-methoxyphenoxy)propan-2-ol (3c).[1] Prepared according to the general procedure using epoxide **2c** (36.0 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 20:1-10:1) yielded a colorless oil (35.0 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.88-6.81 (m, 4H), 4.23-4.14 (m, 1H), 4.05 (dd, *J* = 9.6, 5.1 Hz, 1H), 4.01 (dd, *J* = 9.6, 5.4 Hz, 1H), 3.78 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.77 (s, 3H), 3.72 (dd, *J* = 11.1, 5.7 Hz, 1H), 2.63 (d, *J* = 5.7 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 154.3 (C), 152.3 (C), 115.6 (CH), 114.7 (CH), 69.9 (CH), 69.3 (CH_2), 55.7 (CH_3), 45.9 (CH_2).



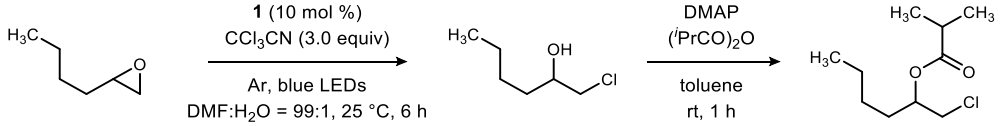
1-Chloro-3-(naphthalen-2-yloxy)propan-2-ol (3d).[1] Prepared according to the general procedure using epoxide **2d** (40.0 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 20:1-10:1) yielded a white solid (38.8 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.70 (m, 3H), 7.44 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.34 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.16-7.12 (m, 2H), 4.31-4.22 (m, 1H), 4.16 (dd, *J* = 9.3, 4.8 Hz, 1H), 4.19 (dd, *J* = 9.3, 5.4 Hz, 1H), 3.81 (dd, *J* = 11.1, 5.1 Hz, 1H), 3.75 (dd, *J* = 11.1, 5.4 Hz, 1H), 2.69 (d, *J* = 5.4 Hz, 1H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 156.1 (C), 134.3 (C), 129.6 (CH), 129.2 (C), 127.6 (CH), 126.8 (CH), 126.5 (CH), 123.9 (CH), 118.5 (CH), 107.0 (CH), 69.8 (CH), 68.5 (CH_2), 46.0 (CH_2).



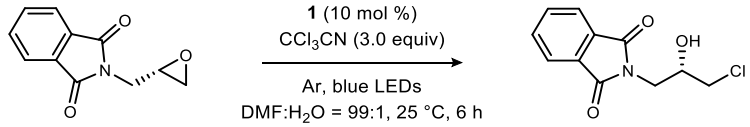
1-Benzyloxy-3-chloropropan-2-ol (3e).[1] Prepared according to the general procedure using epoxide **2e** (33.8 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 20:1-10:1) yielded a colorless oil (32.0 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 4.56 (s, 2H), 4.03-3.96 (m, 1H), 3.65 (dd, *J* = 11.1, 5.4 Hz, 1H), 3.60 (dd, *J* = 11.1, 5.7 Hz, 1H), 3.59 (d, *J* = 5.1 Hz, 2H), 2.62 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 137.6 (C), 128.5 (CH), 127.9 (CH), 127.7 (CH), 73.5 (CH_2), 70.8 (CH_2), 70.3 (CH), 46.0 (CH_2).



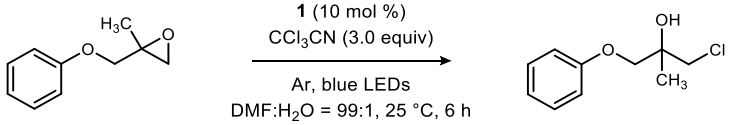
1-Allyloxy-3-chloropropan-2-yl isobutyrate (derived from 3f). To an oven-dried test tube equipped with a stir bar was added epoxide **2f** (22.8 mg, 0.20 mmol), phosphonium ylide **1** (7.4 mg, 0.02 mmol, 10 mol %), a 99:1 mixture of DMF/H_2O (v/v, 2.0 mL, 0.1 M), and trichloroacetonitrile (60 μL, 0.60 mmol, 3.0 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 6 h, the mixture was treated with H_2O (3 mL). The aqueous layer was extracted with Et_2O (5 mL x 3). The organic layers were combined, washed with H_2O (15 mL x 2), dried over Na_2SO_4, filtered, and concentrated. To the crude material was added DMAP (4.9 mg, 40 μmol, 20 mol %), toluene (0.25 mL, 0.8 M), and isobutyric anhydride (166 μL, 1.0 mmol, 5.0 equiv). The reaction mixture was stirred at rt for 1 h, and then directly purified by flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 50:1) to obtain a colorless oil (34.8 mg, 79%, over two steps). R_f = 0.5 (Hexane:EtOAc = 10:1) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.20 (dq, *J* = 10.4, 1.5 Hz, 1H), 5.14 (qui, *J* = 5.2 Hz, 1H), 4.04 (ddt, *J* = 12.9, 5.6, 1.5 Hz, 1H), 4.04 (ddt, *J* = 12.9, 5.6, 1.5 Hz, 1H), 3.76 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.68 (dd, *J* = 11.6, 5.2 Hz, 1H), 3.64 (dd, *J* = 11.4, 5.2 Hz, 1H), 3.60 (dd, *J* = 11.4, 5.2 Hz, 1H), 2.60 (sep, *J* = 6.9 Hz, 1H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.4 (C), 134.2 (CH), 117.4 (CH_2), 72.3 (CH_2), 71.3 (CH), 68.2 (CH_2) 42.9 (CH_2), 34.0 (CH), 19.0 (CH_3), 18.8 (CH_3); IR (KBr) 2979, 2938, 1812, 1740, 1707, 1469, 1244, 1156, 1023, 930 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{17}ClNaO_3$ 243.0758, found 243.0744.



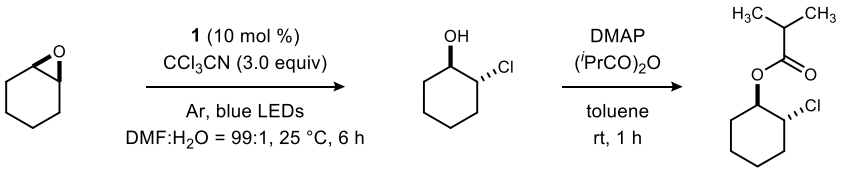
1-Chlorohexan-2-yl isobutyrate (derived from 3g).[1] To an oven-dried test tube equipped with a stir bar was added epoxide **2g** (20.0 mg, 0.20 mmol), phosphonium ylide **1** (7.4 mg, 0.02 mmol, 10 mol %), a 99:1 mixture of DMF/H_2O (v/v, 2.0 mL, 0.1 M), and trichloroacetonitrile (60 μL, 0.60 mmol, 3.0 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 6 h, the mixture was treated with H_2O (3 mL). The aqueous layer was extracted with Et_2O (5 mL x 3). The organic layers were combined, washed with H_2O (15 mL x 2), dried over Na_2SO_4, filtered, and concentrated. To the crude material was added DMAP (4.9 mg, 40 μmol, 20 mol %), toluene (0.25 mL, 0.8 M), and isobutyric anhydride (166 μL, 1.0 mmol, 5.0 equiv). The reaction mixture was stirred at rt for 1 h, and then directly purified by flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 300:1) to obtain a colorless oil (31.0 mg, 75%, over two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.07-4.99 (m, 1H), 3.64 (dd, *J* = 11.7, 4.5 Hz, 1H), 3.56 (dd, *J* = 11.7, 5.7 Hz, 1H), 2.58 (sep, *J* = 6.9 Hz, 1H), 1.71-1.64 (m, 2H), 1.39-1.26 (m, 4H), 1.192 (d, *J* = 6.9 Hz, 3H), 1.186 (d, *J* = 6.9 Hz, 3H), 0.93-0.88 (m, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.5 (C), 72.4 (CH), 45.7 (CH), 34.1 (CH), 31.2 (CH_2), 27.2 (CH_2), 22.4 (CH_2), 18.94 (CH_3), 18.88 (CH_3), 13.82 (CH_3).



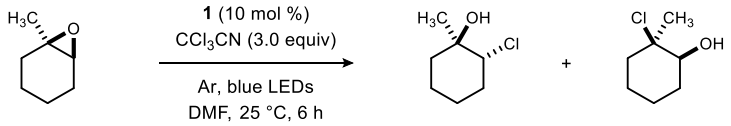
(*S*)-**1-Chloro-3-phthalimidopropan-2-ol (3h).**[1] Prepared according to the general procedure using epoxide (*S*)-**2h** (40.6 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 10:1-6:1) yielded a white solid (37.6 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.83 (m, 2H), 7.77-7.71 (m, 2H), 4.22-4.15 (m, 1H), 3.97 (dd, *J* = 14.4, 7.2 Hz, 1H), 3.88 (dd, *J* = 14.4, 4.5 Hz, 1H), 3.69 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.62 (dd, *J* = 11.4, 5.4 Hz, 1H), 3.05 (br s, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 168.6 (C), 134.2 (CH), 131.8 (C), 123.5 (CH), 69.7 (CH), 47.2 (CH_2), 41.6 (CH_2). The product was determined to be 99% ee by chiral HPLC analysis (Chiralpak AD-3, Hexane:^{i}PrOH = 90:10, 0.5 mL/min, t_r(*major*) = 30.7 min, t_r(*minor*) = 34.0 min, 225 nm, 35 °C); $[\alpha]_D^{20}$ -39.1 (*c* 0.48, EtOH, 99% ee). The absolute configuration was determined by comparison of optical rotation with the reported data.[2]



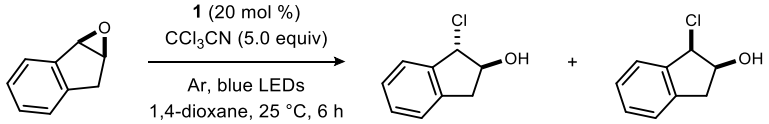
1-Chloro-2-methyl-3-phenoxypropan-2-ol (3i). Prepared according to the general procedure using epoxide **2i** (32.8 mg, 0.20 mmol). Flash column chromatography (Hexane:EtOAc = 20:1) yielded a colorless oil (34.6 mg, 86%). R_f = 0.4 (Hexane:EtOAc = 4:1) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.26 (m, 2H), 7.01-6.95 (m, 1H), 6.94-6.89 (m, 2H), 3.98 (d, *J* = 9.0 Hz, 1H), 3.90 (d, *J* = 9.0 Hz, 1H), 3.71 (d, *J* = 11.1 Hz, 1H), 3.67 (d, *J* = 11.1 Hz, 1H), 2.61 (s, 1H), 1.41 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.2 (C), 129.5 (CH), 121.4 (CH), 114.6 (CH), 71.9 (C), 71.4 (CH_2), 50.1 (CH_2), 22.2 (CH_3); IR (KBr) 3444, 2981, 2936, 1599, 1496, 1244, 1049, 837 cm^{-1}; HRMS (ESI/TOF) m/z: $[M+Na]^+$ calcd for $C_{10}H_{13}ClNaO_2$ 223.0496, found 223.0520.



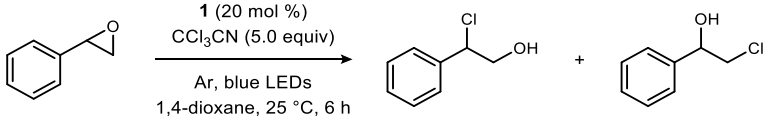
2-Chlorocyclohexyl isobutyrate (derived from 3j).[1] To an oven-dried test tube equipped with a stir bar was added epoxide **2j** (19.6 mg, 0.20 mmol), phosphonium ylide **1** (7.4 mg, 0.02 mmol, 10 mol %), a 99:1 mixture of DMF/H_2O (v/v, 2.0 mL, 0.1 M), and trichloroacetonitrile (60 μL, 0.60 mmol, 3.0 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 6 h, the mixture was treated with H_2O (3 mL). The aqueous layer was extracted with Et_2O (5 mL x 3). The organic layers were combined, washed with H_2O (15 mL x 2), dried over Na_2SO_4, filtered, and concentrated. To the crude material was added DMAP (4.9 mg, 40 μmol, 20 mol %), toluene (0.25 mL, 0.8 M), and isobutyric anhydride (166 μL, 1.0 mmol, 5.0 equiv). The reaction mixture was stirred at rt for 1 h, and then directly purified by flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 300:1) to obtain a colorless oil (31.9 mg, 78%, over two steps). ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84-4.77 (m, 1H), 3.86 (ddd, *J* = 10.5, 9.0, 4.5 Hz, 1H), 2.57 (sep, *J* = 6.9 Hz, 1H), 2.29-2.20 (m, 1H), 2.11-2.03 (m, 1H), 1.82-1.69 (m, 3H), 1.50-1.24 (m, 3H), 1.20 (d, *J* = 6.9 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 176.2 (C), 75.4 (CH), 60.8 (CH), 34.8 (CH_2), 34.1 (CH), 30.7 (CH_2), 24.6 (CH_2), 23.2 (CH_2), 19.1 (CH_3), 18.8 (CH_3).



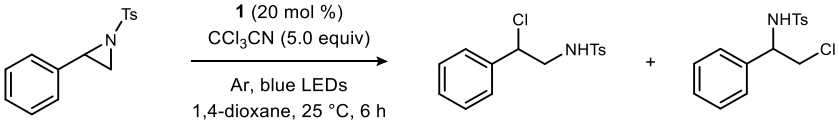
2-Chloro-1-methyl-cyclohexanol & 2-chloro-2-methyl-cyclohexanol (3k/3k').[3] Prepared according to the general procedure using epoxide **2k** (22.4 mg, 0.20 mmol) in DMF (0.4 mL, 0.5 M). Flash column chromatography (Hexane:Et_2O = 20:1) yielded a pale yellow oil (15.1 mg, 51%, **3k**:**3k'** = 68:32). R_f = 0.3 (Hexane:Et_2O = 10:1) visualized with 4-anisaldehyde; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95 (dd, *J* = 10.8, 4.2 Hz, 1H x 68/100), 3.78 (dd, *J* = 9.6, 4.5 Hz, 1H x 32/100), 2.31-2.09 (m, 2H), 1.98-1.60 (m, 4H), 1.57 (d, *J* = 0.3 Hz, 3H x 32/100), 1.53-1.33 (m, 3H), 1.31 (d, *J* = 0.3 Hz, 3H x 68/100); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 77.3 (CH, **3k'**), 77.2 (C, **3k'**), 72.9 (C, **3k**) 70.3 (CH, **3k**), 40.8 (CH_2, **3k'**), 38.1 (CH_2, **3k**), 33.5 (CH_2, **3k**), 30.1 (CH_2, **3k'**), 25.0 (CH_2, **3k**), 23.4 (CH_2, **3k'**), 23.2 (CH_2, **3k'**), 22.7 (CH_2, **3k**), 22.5 (CH_3, **3k'**), 22.0 (CH_3, **3k**).



1-Chloro-2,3-dihydro-1*H*-inden-2-ol (3l).[4] Prepared according to the general procedure using epoxide **2l** (26.4 mg, 0.20 mmol), phosphonium ylide **1** (14.7 mg, 0.04 mmol, 20 mol %), and trichloroacetonitrile (100 μL, 1.0 mmol, 5.0 equiv) in 1,4-dioxane (2.0 mL, 0.1 M). Flash column chromatography (Hexane:EtOAc = 20:1) yielded a pale yellow oil (23.0 mg, 68%, *trans*:*cis* = 92:8). R_f = 0.25 (Hexane:EtOAc = 4:1) visualized with 4-anisaldehyde; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.38 (m, 1H), 7.32-7.22 (m, 3H), 5.36 (d, *J* = 5.1 Hz, 1H x 8/100), 5.12 (d, *J* = 4.2 Hz, 1H x 92/100), 4.67-4.62 (m, 1H x 92/100), 4.58-4.54 (m, 1H x 8/100), 3.39 (dd, *J* = 15.9, 6.6 Hz, 1H x 92/100), 3.16 (dd, *J* = 15.6, 6.3 Hz, 1H x 8/100), 2.97 (dd, *J* = 15.6, 6.9 Hz, 1H x 8/100), 2.90 (dd, *J* = 15.9, 5.1 Hz, 1H x 92/100), 2.54 (br s, 1H x 8/100) 2.34 (br s, 1H x 8/100); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 140.0 (C), 139.6 (C), 129.2 (CH), 127.6 (CH), 125.5 (CH), 125.1 (CH), 81.3 (CH), 67.4 (CH), 38.7 (CH_2); IR (KBr) 3346, 3075, 3026, 2949, 2924, 2850, 1463, 1324, 1259, 1223, 1081, 1043 cm^{-1}.

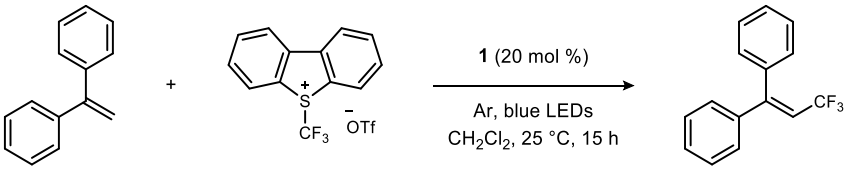


2-Chloro-2-phenylethan-1-ol & 2-chloro-1-phenylethan-1-ol (3m/3m').[5] Prepared according to the general procedure using epoxide **2m** (24.0 mg, 0.20 mmol), phosphonium ylide **1** (14.7 mg, 0.04 mmol, 20 mol %), and trichloroacetonitrile (100 μL, 1.0 mmol, 5.0 equiv) in 1,4-dioxane (2.0 mL, 0.1 M). Flash column chromatography (Hexane:Et_2O = 20:1) yielded a pale yellow oil (21.1 mg, 67%, **3m**:**3m'** = 72:28). R_f = 0.21 (**3m**), 0.36 (**3m'**) (Hexane:Et_2O = 10:1) visualized with PMA; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.29 (m, 5H), 4.98 (dd, *J* = 7.2, 5.7 Hz, 1H x 72/100), 4.90 (dd, *J* = 8.7, 3.3 Hz, 1H x 28/100), 3.95 (dd, *J* = 12.0, 7.2 Hz, 1H x 72/100), 3.90 (dd, *J* = 12.0, 5.7 Hz, 1H x 72/100), 3.75 (dd, *J* = 11.1, 3.3 Hz, 1H x 28/100), 3.65 (dd, *J* = 11.1, 8.7 Hz, 1H x 28/100), 2.72 (br s, 1H x 28/100), 2.20 (br s, 1H x 72/100); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.9 (C, **3m'**), 137.8 (C, **3m**), 128.9 (CH, **3m**) 128.8 (CH, **3m**), 128.6 (CH, **3m'**), 128.4 (CH, **3m'**), 127,4 (CH, **3m**), 126.0 (CH, **3m'**), 74.0 (CH, **3m'**), 67.9 (CH_2, **3m**), 64.8 (CH, **3m**), 50.9 (CH_2, **3m'**).



***N*-(2-Chloro-2-phenylethyl)-4-methylbenzenesulfonamide & *N*-(2-chloro-1-phenylethyl)-4-methylbenzenesulfonamide (3n/3n').**[6] To an oven-dried test tube equipped with a stir bar was added aziridine **2n** (54.6 mg, 0.20 mmol), phosphonium ylide **1** (14.7 mg, 0.04 mmol, 20 mol %), MeCN (2.0 mL, 0.1 M), and trichloroacetonitrile (100 μL, 0.60 mmol, 5.0 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 1 h, the mixture was

treated with satd $NaHCO_3$ aq (3 mL). The aqueous layer was extracted with Et_2O (5 mL x 3). The organic layers were combined, washed with H_2O (15 mL x 2), dried over Na_2SO_4, filtered, and concentrated. Flash column chromatography (Hexane:EtOAc = 10:1-4:1) yielded a white solid (40.6 mg, 65%, **3n**:**3n'** = 86:14). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.75-7.71 (m, 2H x 86/100), 7.64-7.60 (m, 2H x 14/100), 7.38-7.09 (m, 7H), 5.29 (d, *J* = 6.0 Hz, 1H x 14/100), 4.91-4.84 (m, 2H x 86/100), 4.57 (q, *J* = 6.0 Hz, 1H x 14/100), 3.74 (dd, *J* = 11.4, 6.0 Hz, 1H x 14/100), 3.70 (dd, *J* = 11.4, 6.0 Hz, 1H x 14/100), 3.53-3.37 (m, 2H x 86/100), 2.44 (s, 3H x 86/100), 2.39 (s, 3H x 14/100); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 137.8 (C), 136.9 (C), 129.9 (CH), 129.1 (CH), 128.9 (CH), 127.2 (CH), 127.0 (CH), 61.6 (CH), 50.3 (CH_2), 21.5 (CH_3).



1,1'-(3,3,3-trifluoroprop-1-ene-1,1-diyl)dibenzene (10).[7] To an oven-dried test tube equipped with a stir bar was added 1,1-diphenylethylene (**9**: 18.0 mg, 0.10 mmol), trifluoromethylating reagent (**8**: 60.3 mg, 0.15 mmol, 1.5 equiv), phosphonium ylide **1** (7.4 mg, 0.02 mmol, 20 mol %), and CH_2Cl_2 (5.0 mL, 0.02 M). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 15 h, the mixture was filtered through the plug of silica gel with CH_2Cl_2 (50 mL) and then concentrated. The NMR yield of **10** (70%) was determined by ^{1}H NMR analysis of the unpurified material using 1,1,2,2-tetrachloroethane (7.0 μL) as an internal standard. After flash column chromatography (SiO_2: 8 g, Hexane), GPC ($CHCl_3$) was performed to obtain a colorless oil (10.9 mg, 44%, a trace amount of inseparable impurity was contaminated). R_f = 0.7 (Hexane) visualized with $KMnO_4$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.18 (m, 10H), 6.13 (q, *J* = 8.3 Hz, 1H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 152.5 (q, *J* = 5.7 Hz, C), 140.1 (C), 137.3 (C), 129.4 (CH), 129.1 (q, *J* = 1.9 Hz, CH), 128.5 (2CH), 128.02 (CH), 127.95 (CH), 123.1 (q, *J* = 270.7 Hz, C), 115.4 (q, *J* = 33.2 Hz, CH).

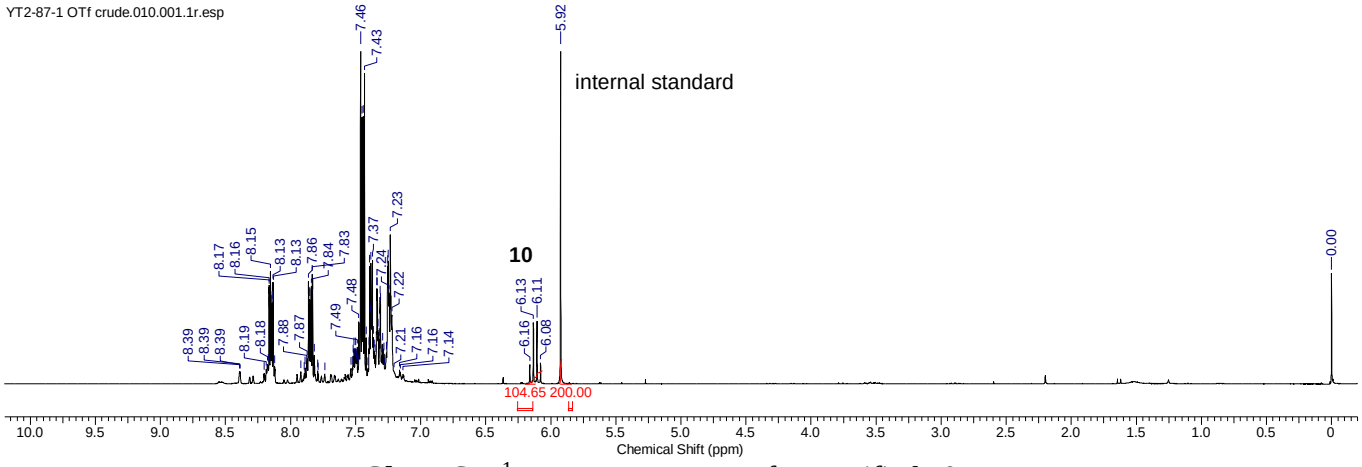
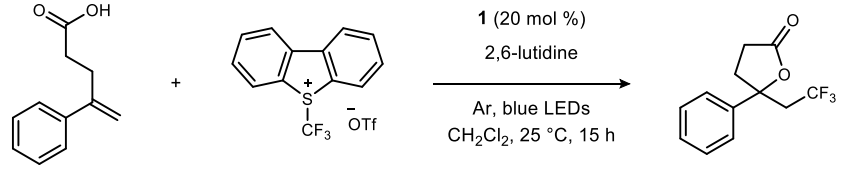


Chart S1. ^{1}H NMR spectrum of *unpurified* **10**



5-Phenyl-5-(2,2,2-trifluoroethyl)dihydrofuran-2(3*H*)-one (12).[8] To an oven-dried test tube equipped with a stir bar was added alkenoic acid **11** (17.6 mg, 0.10 mmol), 2,6-lutidine (29.1 μL, 0.25 mmol, 2.5 equiv), trifluoromethylating reagent (**8**: 60.3 mg, 0.15 mmol, 1.5 equiv), phosphonium ylide **1** (7.4 mg, 0.02 mmol, 20 mol %), and CH_2Cl_2 (5.0 mL, 0.02 M). The atmosphere was replaced with argon (x 3) using a diaphragm

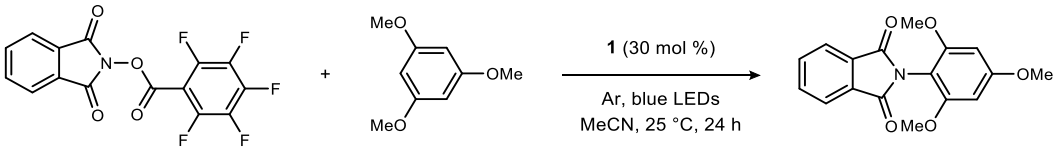
pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 15 h, the mixture was concentrated. Flash column chromatography (SiO_2: 10 g, Hexane:EtOAc = 40:1-4:1) yielded a white solid (15.4 mg, 63%). R_f = 0.4 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; ^1H NMR (300 MHz, $CDCl_3$) δ 7.45-7.33 (m, 5H), 2.95-2.72 (m, 2H), 2.70-2.38 (m, 4H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 175.1 (C), 141.1 (C), 128.8 (CH), 128.5 (CH), 124.64 (CH), 124.58 (q, J = 278.4 Hz, C), 84.2 (q, J = 2.2 Hz, C), 45.3 (q, J = 27.5 Hz, CH_2), 34.1 (q, J = 1.1 Hz, CH_2), 28.0 (CH_2).

2-(2,6-Dimethylpyridin-3-yl)isoindoline-1,3-dione (15a).[9] To an oven-dried test tube equipped with a stir bar was added *N*-acyloxyphthalimide **13** (35.7 mg, 0.10 mmol), phosphonium ylide **1** (3.7 mg, 0.01 mmol, 10 mol %), MeCN (5.0 mL, 0.02 M), and 2,6-lutidine (116 μL, 1.0 mmol, 10 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 24 h, the mixture was concentrated. Flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 7:1-3:1) yielded a white solid (16.6 mg, 63%). R_f = 0.4 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.85-7.79 (m, 2H), 7.42 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 2.60 (s, 3H), 2.42 (s, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.0 (C), 159.0 (C), 155.9 (C), 136.6 (CH), 134.5 (CH), 131.9 (C), 124.2 (C), 123.9 (CH), 121.4 (CH), 24.4 (CH_3), 21.2 (CH_3).

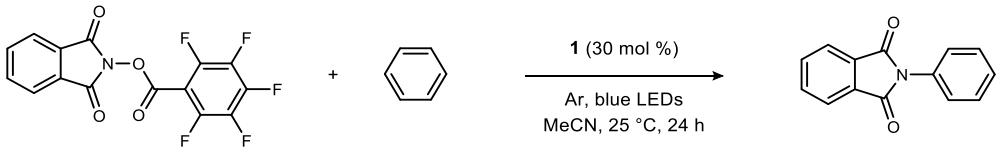
2-(2,4,6-Trimethylpyridin-3-yl)isoindoline-1,3-dione (15b).[9] To an oven-dried test tube equipped with a stir bar was added *N*-acyloxyphthalimide **13** (35.7 mg, 0.10 mmol), phosphonium ylide **1** (3.7 mg, 0.01 mmol, 10 mol %), MeCN (5.0 mL, 0.02 M), and 2,4,6-collidine (132 μL, 1.0 mmol, 10 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 24 h, the mixture was concentrated. Flash column chromatography (SiO_2: 12 g, Hexane:EtOAc = 4:1-2:1) yielded a white solid (18.0 mg, 68%). R_f = 0.2 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; ^1H NMR (300 MHz, $CDCl_3$) δ 8.01-7.94 (m, 2H), 7.86-7.80 (m, 2H), 7.02 (d, J = 0.3 Hz, 1H), 2.55 (s, 3H), 2.36 (s, 3H), 2.14 (d, J = 0.3 Hz, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 166.9 (C), 158.6 (C), 156.2 (C), 146.3 (C), 134.5 (CH), 131.9 (C), 123.90 (CH), 123.87 (C), 123.2 (CH), 24.2 (CH_3), 21.0 (CH_3), 17.6 (CH_3).

2-Mesitylisoindoline-1,3-dione (15c).[9] To an oven-dried test tube equipped with a stir bar was added *N*-acyloxyphthalimide **13** (35.7 mg, 0.10 mmol), phosphonium ylide **1** (3.7 mg, 0.01 mmol, 10 mol %), MeCN (5.0 mL, 0.02 M), and mesitylene (140 μL, 1.0 mmol, 10 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 24 h, the mixture was concentrated. Flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 100:1-3:1) yielded a

white solid (16.6 mg, 63%). R_f = 0.4 (Hexane:EtOAc = 4:1) visualized with $KMnO_4$; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99-7.93 (m, 2H), 7.83-7.76 (m, 2H), 7.01 (d, *J* = 0.6 Hz, 2H), 2.33 (s, 3H), 2.12 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.4 (C), 139.4 (C), 136.4 (C), 134.2 (CH), 132.0 (C), 129.3 (CH), 127.0 (C), 123.7 (CH), 21.1 (CH_3), 17.9 (CH_3).



2-(2,4,6-Trimethoxyphenyl)isoindoline-1,3-dione (15d).[9] To an oven-dried test tube equipped with a stir bar was added *N*-acyloxyphthalimide **13** (35.7 mg, 0.10 mmol), phosphonium ylide **1** (11.1 mg, 0.03 mmol, 30 mol %), MeCN (5.0 mL, 0.02 M), and 1,3,5-trimethoxybenzene (168.2 mg, 1.0 mmol, 10 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 24 h, the mixture was concentrated. Flash column chromatography (SiO_2: 12 g, Hexane:EtOAc = 4:1-2:1) yielded a white solid (17.0 mg, 54%). R_f = 0.3 (Hexane:EtOAc = 2:1) visualized with $KMnO_4$; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95-7.89 (m, 2H), 7.78-7.71 (m, 2H), 6.22 (s, 2H), 3.85 (s, 3H), 3.75 (s, 6H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.7 (C), 162.1 (C), 157.6 (C), 133.8 (CH), 132.6 (C), 123.5 (CH), 101.7 (C), 91.1 (CH), 56.0 (CH_3), 55.5 (CH_3).



2-Phenylisoindoline-1,3-dione (15e).[9] To an oven-dried test tube equipped with a stir bar was added *N*-acyloxyphthalimide **13** (35.7 mg, 0.10 mmol), phosphonium ylide **1** (11.1 mg, 0.03 mmol, 30 mol %), MeCN (5.0 mL, 0.02 M), and benzene (89 μL, 1.0 mmol, 10 equiv). The atmosphere was replaced with argon (x 3) using a diaphragm pump. The mixture was then placed 0.2 cm from a Kessil A160WE TUNA BLUE at maximum blue/brightness, and irradiated with continuous fan cooling. After stirring at 25 °C for 24 h, the mixture was concentrated. Flash column chromatography (SiO_2: 8 g, Hexane:EtOAc = 100:1-3:1) yielded a white solid (9.1 mg, 41%). R_f = 0.3 (Hexane:EtOAc =4:1) visualized with $KMnO_4$; ^1H NMR (300 MHz, $CDCl_3$) δ 7.99-7.92 (m, 2H), 7.82-7.76 (m, 2H), 7.54-7.48 (m, 2H), 7.46-7.38 (m, 3H); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 167.2 (C), 134.4 (CH), 131.73 (C), 131.65 (C), 129.1 (CH), 128.1 (CH), 126.5 (CH), 123.7 (CH).

Phosphonium ylides **1** and **4** were synthesized according to the reported methods.[10]

1: ^1H NMR (300 MHz, $CDCl_3$) δ 7.71-7.60 (m, 9H), 7.54-7.48 (m, 6H), 7.18 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.64 (dd, *J* = 8.7, 6.6 Hz, 1H), 6.29 (dd, *J* = 14.1, 2.1 Hz, 1H), 2.03 (s, 3H).

4: ^1H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.77-7.69 (m, 6H), 7.59-7.53 (m, 2H), 7.50-7.44 (m, 6H), 7.38-7.77 (m, 3H).

Appendix

We performed ON/OFF experiments under the optimal conditions. The reaction proceeded under photo-irradiation (ON) but did not proceeded in dark (OFF). These results indicate that in-situ generated HCl immediately reacts with epoxides. Partial decomposition of **1** was also observed under photo-irradiation.

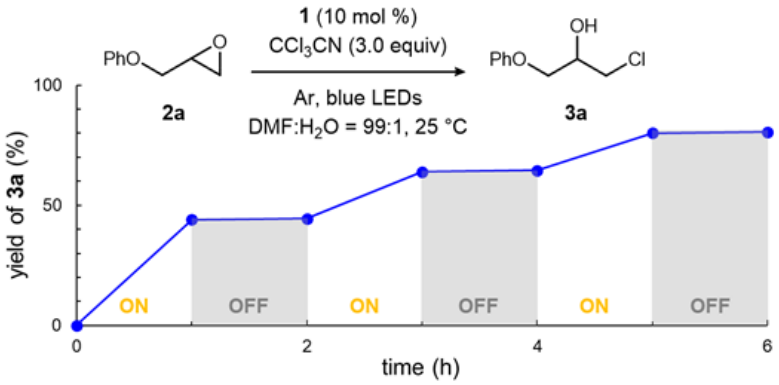
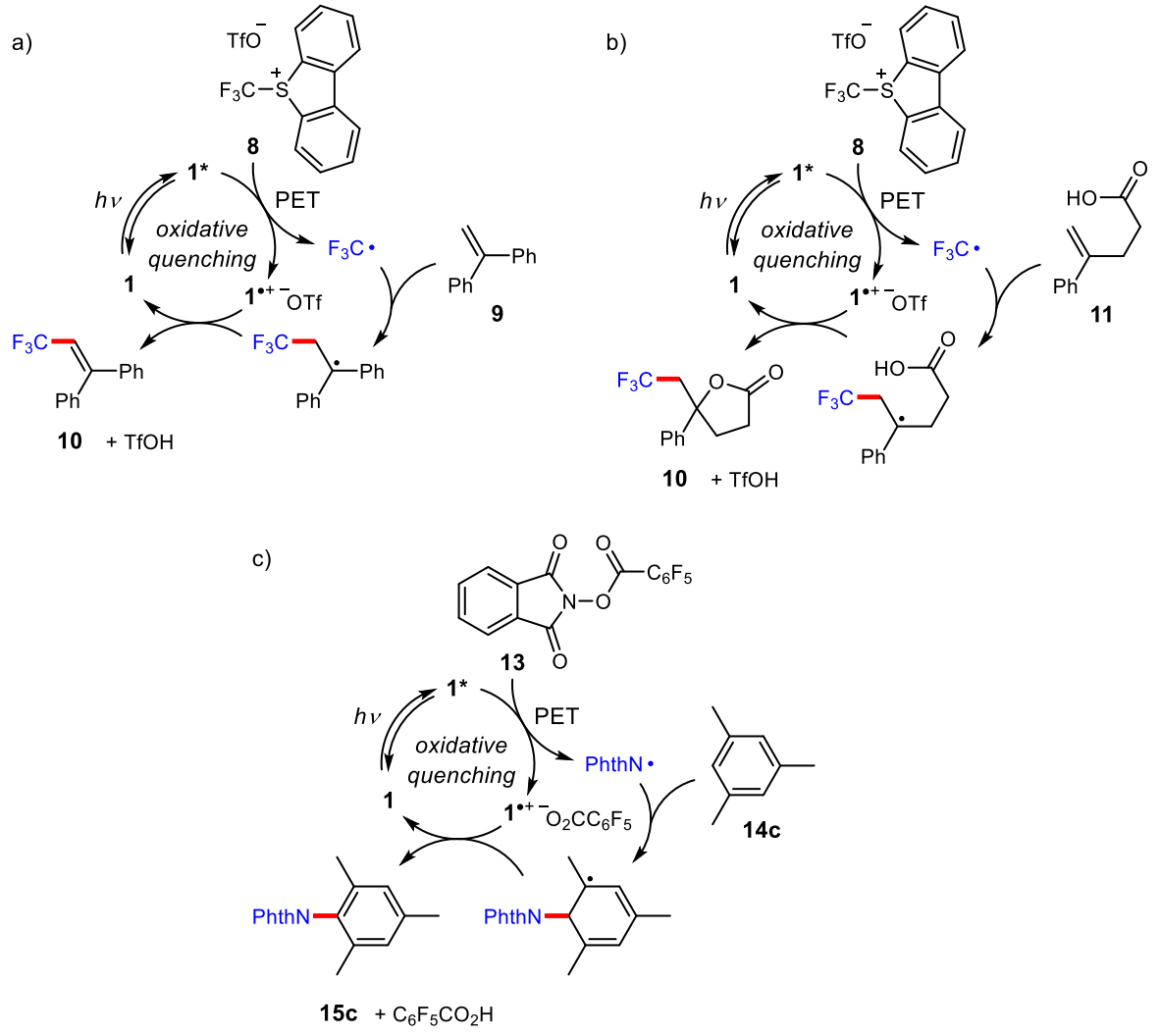


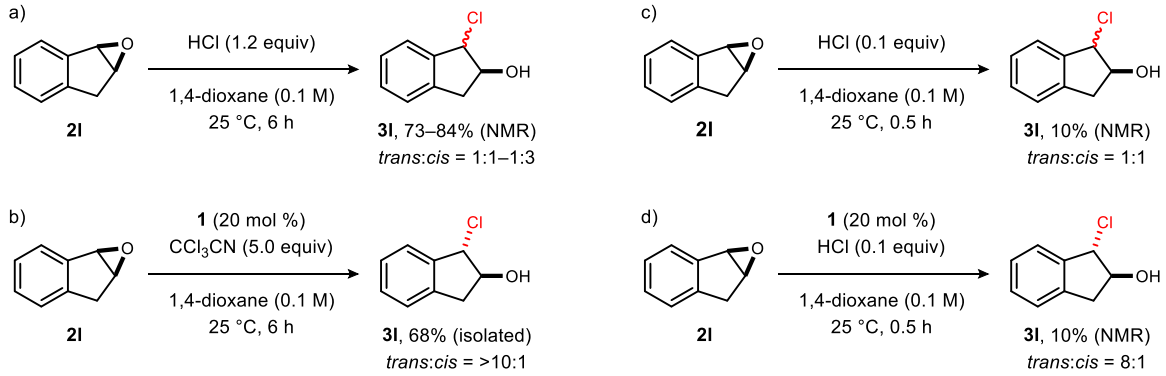
Figure S2. ON/OFF experiments

Possible mechanisms of trifluoromethylation and imidation reactions are shown in Scheme S1. Phosphonium ylide **1** behaves as an excited-state reductant, enabling the oxidative quenching cycles.



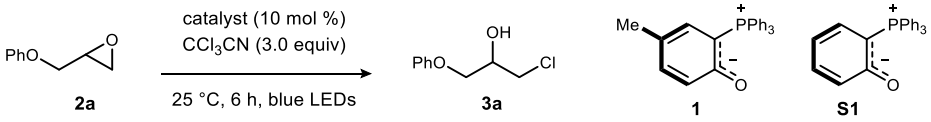
Scheme S1. Possible mechanisms
(a: C(sp^2)–H trifluoromethylation, b: trifluoromethylative lactonization, c: C(sp^2)–H imidation)

a) Surprisingly, a significant *trans*/*cis* mixture of **3l** was afforded with poor reproducibility (73−84%, *trans*:*cis* = 1:1−1:3) by the reaction of indene oxide (**2l**) using 1.2 equiv of HCl. b) It should be emphasized that *in situ* HCl generation enabled the selective formation of *trans*-**3l**. c) Moreover, two additional reactions of **2l** using 0.1 equiv of HCl were carried out. Poor selectivity was observed in the absence of **1**. d) In contrast, HCl addition to **2l** proceeded with high stereoselectivity in the presence of **1**. Thus, **1** seems to serve as not only a photoredox catalyst but also as a ligand of proton.[11]



Scheme S2. HCl addition reactions to indene oxide (**2l**)

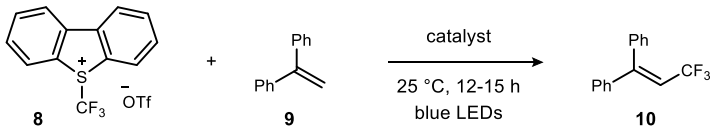
Table S1. Optimization of reaction conditions for HCl addition



Entry	Catalyst (mol %)	Light	Solvent (0.1 M)	**3a** (%)[a]
1	**1** (10)	yes	MeCN:H_2O = 99:1	33
2	**1** (10)	yes	1,4-dioxane:H_2O = 99:1	92
3	**1** (10)	yes	DMF:H_2O = 99:1	95 (91)[b]
4	**1** (10)	yes	DMF	74
5	**1** (10)	yes	DMF:H_2O = 9:1	77
6	**1** (2)	yes	DMF:H_2O = 99:1	39
7[c]	**1** (10)	yes	DMF:H_2O = 99:1	73
8	**S1** (10)	yes	DMF:H_2O = 99:1	89
9	$Ru(bpy)_3Cl_2$	yes	DMF:H_2O = 99:1	66
10	none	yes	DMF:H_2O = 99:1	24
11	**1** (10)	no	DMF:H_2O = 99:1	0

a) NMR yield. b) Isolated yield. c) 1.0 equiv of CCl_3CN was used.

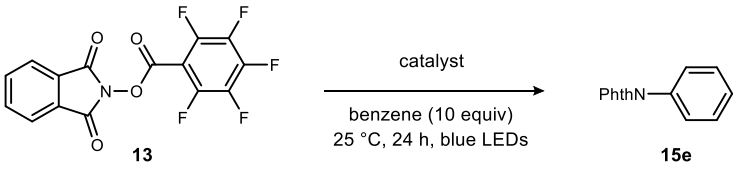
Table S2. Optimization of reaction conditions for trifluoromethylation



Entry	Catalyst (mol %)	**8**:**9**	Solvent (M)	**10** (%)[a]
1	**S1** (20)	1:2	MeCN (0.05)	48
2	**S1** (20)	1:2	MeOH (0.05)	<5
3	**S1** (20)	1:2	CH_2Cl_2 (0.05)	64
4	**1** (20)	1:2	CH_2Cl_2 (0.05)	65
5	**1** (10)	1:2	CH_2Cl_2 (0.05)	50
6	**1** (30)	1:2	CH_2Cl_2 (0.05)	66
7	**1** (20)	1:2	CH_2Cl_2 (0.02)	67
8	**1** (20)	1.5:1	CH_2Cl_2 (0.02)	70 (44)[b]

a) NMR yield. b) Isolated yield.

Table S3. Optimization of reaction conditions for C-H imidation



Entry	Catalyst (mol %)	Solvent (M)	Conv. (%)[a]	**15e** (%)[a]
1	**1** (10)	MeCN (0.1)	58	18
2	**S1** (10)	MeCN (0.1)	47	14
3	**1** (10)	MeCN (0.2)	30	6
4	**1** (10)	MeCN (0.05)	58	28
5	**1** (10)	MeCN (0.02)	71	23
6	**1** (20)	MeCN (0.02)	56	19
7	**1** (30)	MeCN (0.02)	100	41[b]

a) NMR yield. b) Isolated yield.

Electrochemical Studies

Cyclic voltammetry was performed using an ALS/DY2325 bi-potentiostat. The cell was consisted of a glassy carbon working electrode (W.E.), a Pt wire counter electrode (C.E.), and an Ag wire reference electrode (R.E.). The redox potentials were calibrated to the SCE scale with a Fc/Fc^+ couple.[12]

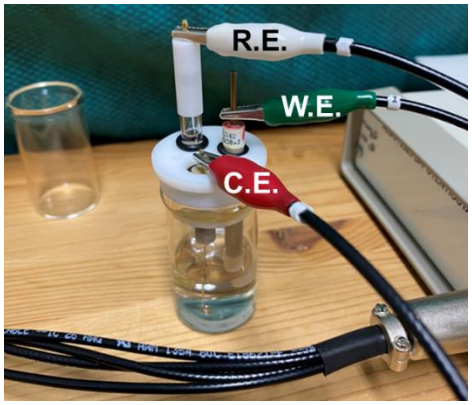


Figure S3. Experimental Setup

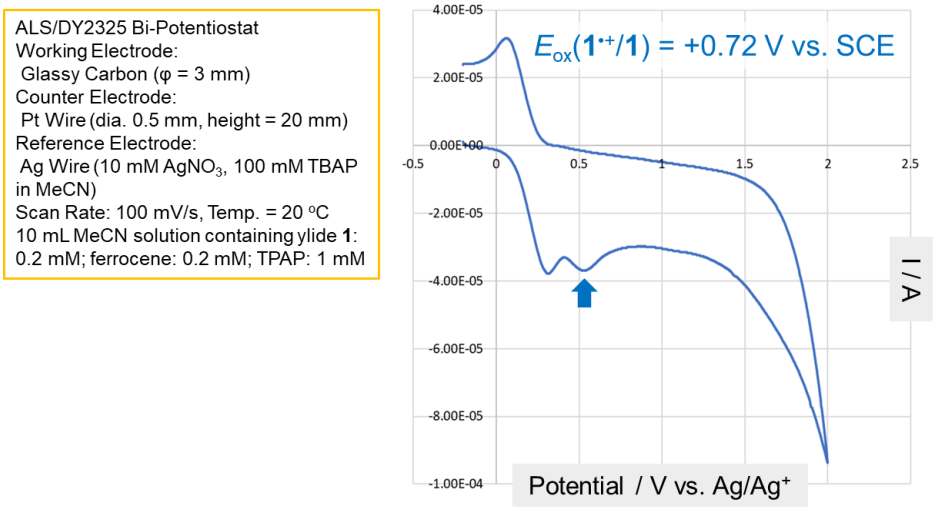


Figure S4. Cyclic voltammogram of **1** in 100 mM TBAP/MeCN

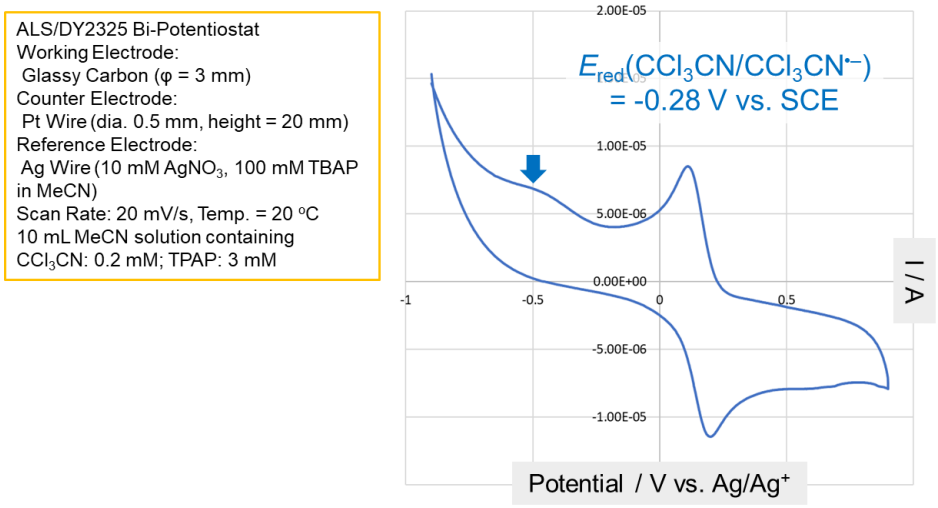


Figure S5. Cyclic voltammogram of CCl_3CN in 100 mM TBAP/MeCN

Fluorescence Spectroscopic Studies

Fluorescence emission spectra were measured at room temperature with a 370 nm longpass filter (excitation wavelength = 340 nm). The signals of the solvents were subtracted for clarity. All solutions were degassed by argon gas bubbling before use. Fluorescence lifetime measurement of **1** was taken at room temperature with a time-correlated single-photon-counting (TCSPC) technique. The excitation light source was a picosecond light pulse of 375 nm (LDB-160C, Tama Electric Inc.) with the repetition frequency of 50 MHz. TCSPC traces were recorded with counting board (SPC-130, Becker & Hickl GmbH). The fluorescence time profiles were analyzed by nonlinear least-squares fitting. Fluorescence quenching experiments of **1** were performed at room temperature in MeCN ([**1**] = 5.0 x 10^{-5} M) with various amount of quenchers ([*Q*]/[**1**] = 200, 400, and 600).

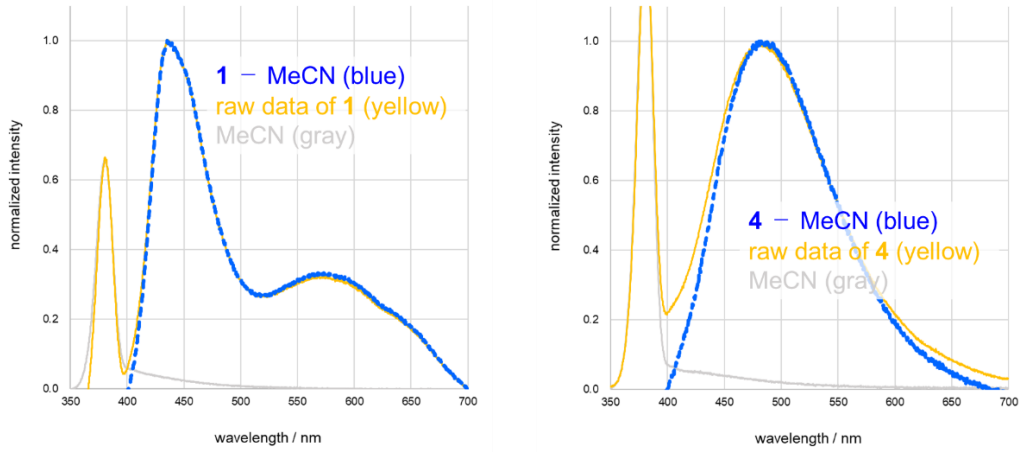


Figure S6. Fluorescence emission spectra of **1** and **4** in MeCN (5.0 x 10^{-4} M) (blue: after removal of background, yellow: raw data, gray: solvent only)

The CT emission was observed (λ_{max} = 563 nm in MeCN) when fluorescence emission spectra of **1** was measured. In order to confirm the CT character of **1**, the dipole moment in the excited state (μ_e) was estimated by the Lippert–Mataga equation (Figure SX). In addition, the dipole moment in the ground state (μ_g) was calculated by DFT using the B3LYP/6-311+G(d,p) level of theory. The $\Delta\mu$ value was therefore determined to be $|\mu_e(3.0) - \mu_g(6.7)|$ = 3.7 D and the relativity large change of dipole moment indicated the CT character.

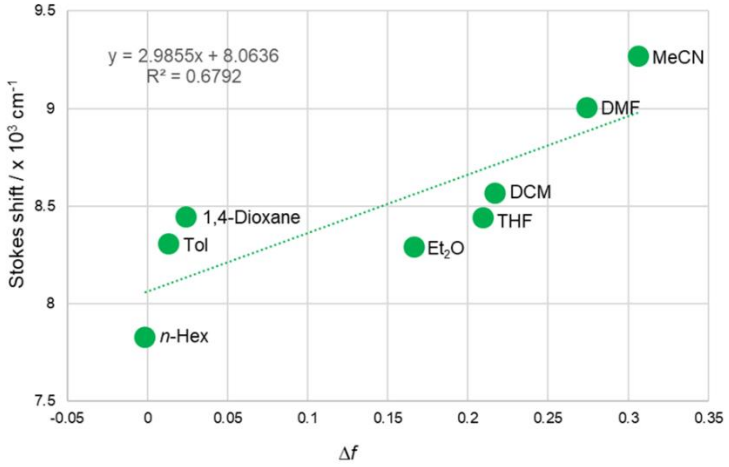


Figure S7. Lippert–Mataga plot of **1**: $\Delta f = [(\varepsilon-1)/(2\varepsilon+1)] - [(n^2-1)/(2n^2+1)]$ (ε: dielectric permittivity of the solvent, n: refractive index of the solvent)

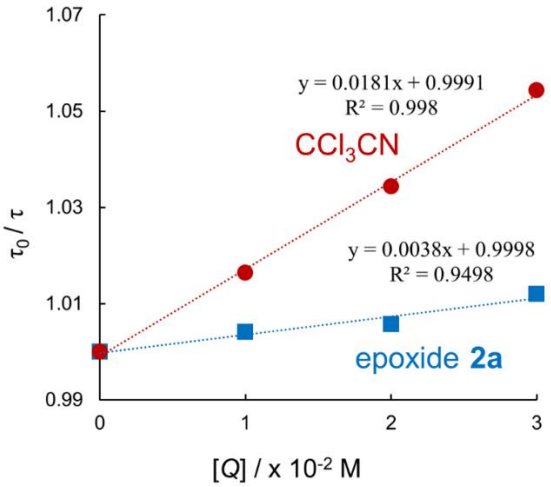


Figure S8. Stern-Volmer analyses by fluorescence quenching
$\tau_0/\tau = 1 + K_{sv}[Q] = 1 + k_q\tau_0[Q]$

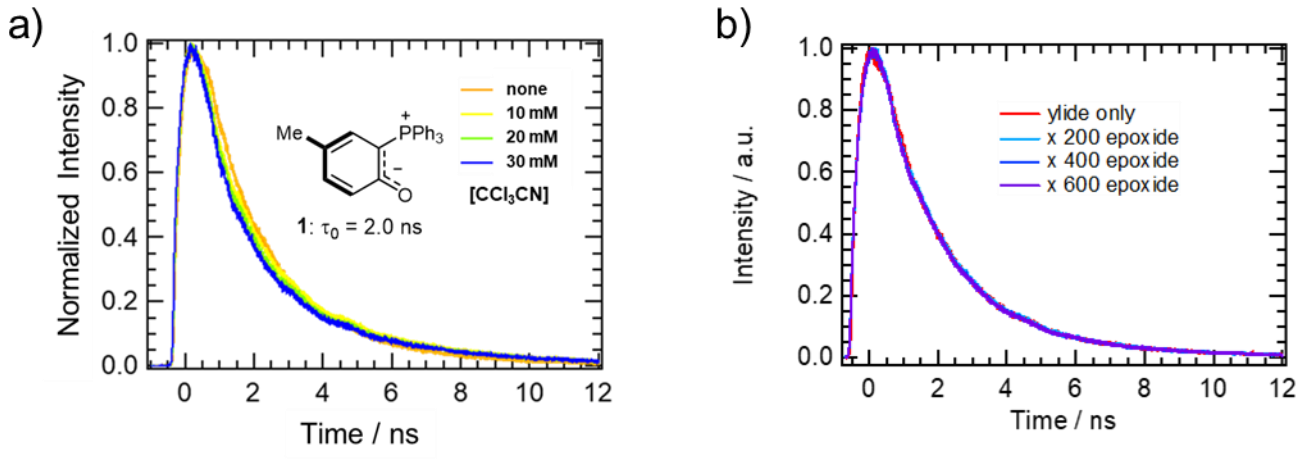


Figure S9. Fluorescence lifetime quenching experiments using **1** (a: Q = CCl_3CN, b: Q = **2a**)

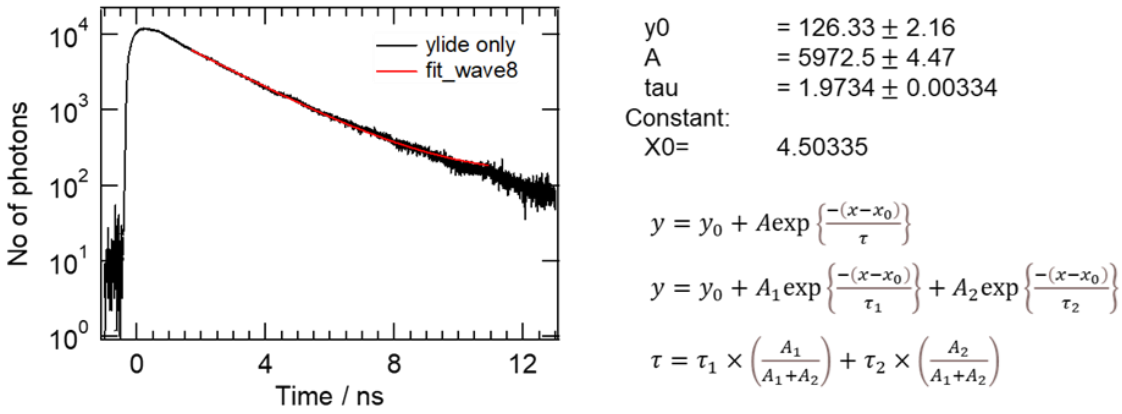


Figure S10. Fluorescence intensity decay profile of phosphonium ylide **1**

Table S4. Quenching experiments using CCl_3CN

CCl_3CN (mM)	τ (ns)	τ_0 / τ
0	1.9734 (τ_0)	1
10	1.9416	1.01638
20	1.9079	1.03433
30	1.8718	1.05428

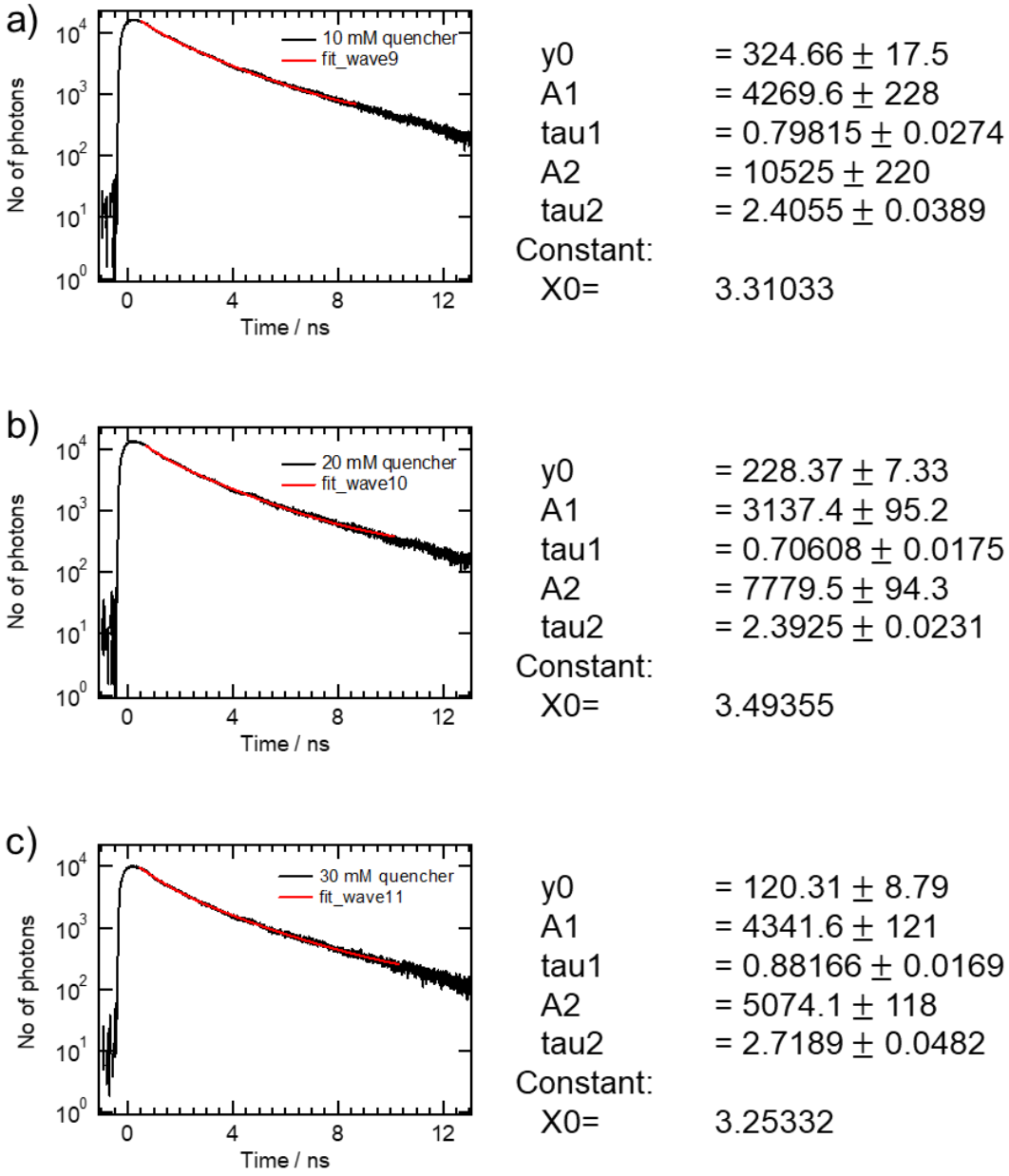


Figure S11. Fluorescence intensity decay profiles
(a: 10 mM of CCl_3CN, b: 20 mM of CCl_3CN, c: 30 mM of CCl_3CN)

Table S5. Quenching experiments using epoxide **2a**

2a (mM)	τ (ns)	τ_0 / τ
0	1.9734 (τ_0)	1
10	1.9654	1.00407
20	1.9622	1.00571
30	1.9500	1.01200

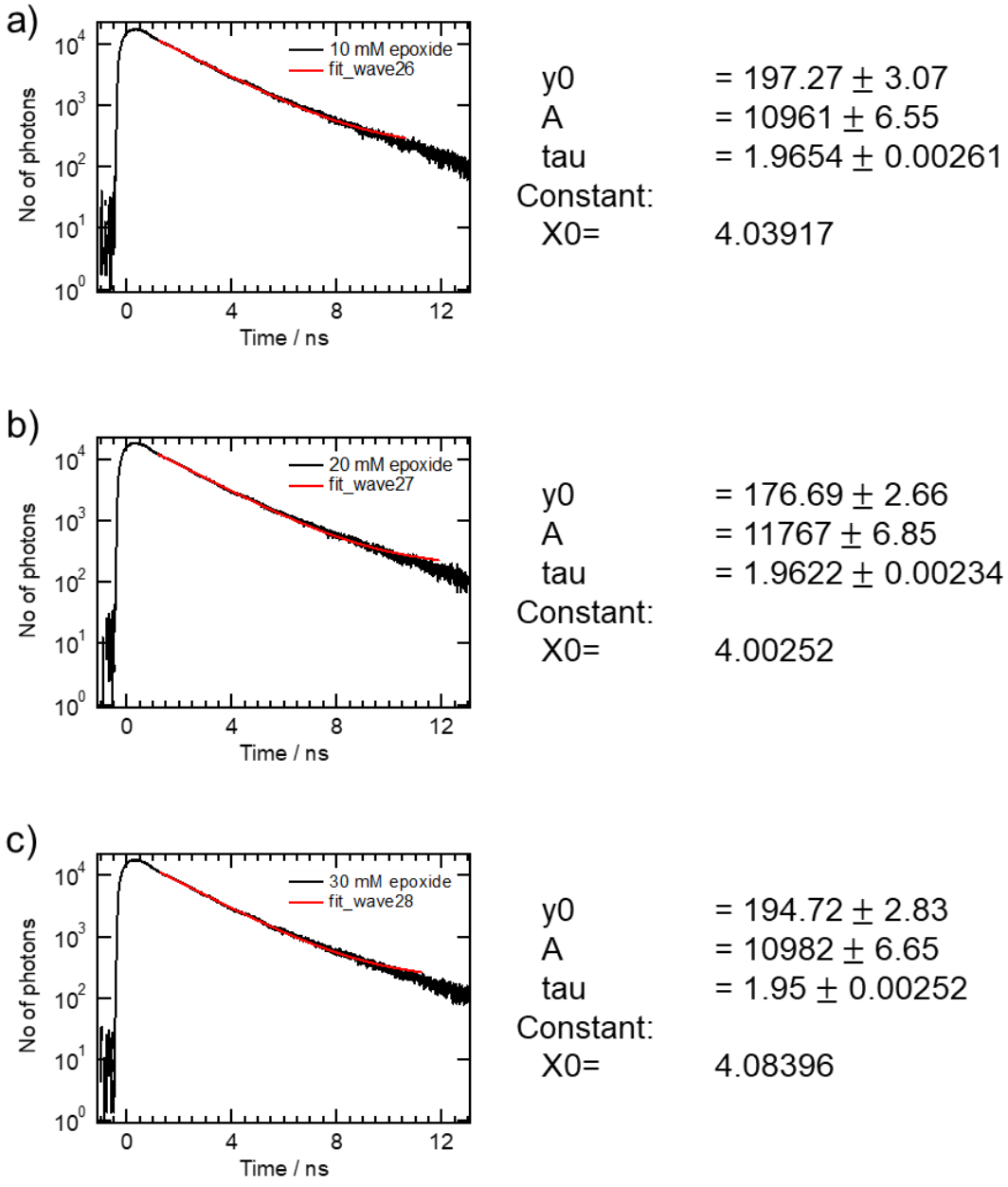


Figure S12. Fluorescence intensity decay profiles
(a: 10 mM of **2a**, b: 20 mM of **2a**, c: 30 mM of **2a**)

Our fluorescence *lifetime* quenching experiments suggested that the electron transfer step is activation-controlled, while the formation of encounter complex [**1*** ••• CCl_3CN] proceeds as a diffusion-controlled process. With this information in hand, the fluorescence quenching experiments were performed as shown below. We observed increasing intensity of fluorescence with increasing amount of CCl_3CN presumably due to the exciplex fluorescence. The formation of exciplex is a key process in photoinduced electron transfer (PET) and the increased fluorescence intensity would be an indirect evidence of the exciplex generation as an intermediate of PET. The *lifetime* studies conducted for evaluating the net rate of quenching of **1** by CCl_3CN, where the influence of the excited complex can be distinguished.

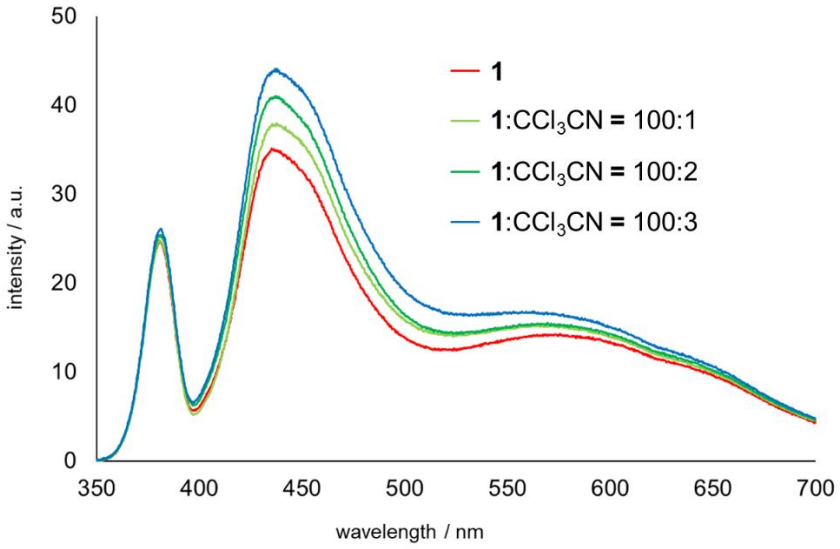


Figure S13. Fluorescence quenching experiments
([**1**] = 50 μM, [CCl_3CN] = 0.5 μM, 1.0 μM, and 1.5 μM)

DFT Studies

All calculations were performed with Gaussian16 B.01 using the B3LYP/6-311+G(d,p) level of theory. For geometry optimization of **1**, $\mathbf{1}^{\bullet+}$, **4**, and $\mathbf{4}^{\bullet+}$, an ultrafine integration grid within the IEFPCM (MeCN) model was used. The full list of authors in the Gaussian16 is as follows:

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

Bond dissociation energies were estimated in accordance with equation (s1),

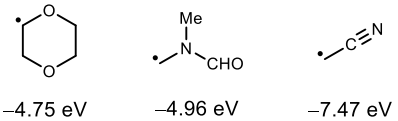
$$\text{BDE (kcal mol}^{-1}) = [(H_X + H_Y) - H_{X\text{-}Y}] \times 627.51 \quad \text{(s1)}$$

where H is the enthalpy (hartree). The results are summarized in Table S3.

Table S6. BDE of halomethanes at the B3LYP/6-311+G(d,p) level of theory

$H_{X\text{-}Y}$ (hartree)		H_X (hartree)		H_Y (hartree)		BDE (kcal mol^{-1})
CCl_3CN	-1511.593803	•Cl	-460.164522	•CCl_2CN	-1051.348984	50.39
CCl_4	-1878.967309	•Cl	-460.164522	•CCl_3	-1418.709230	58.71
$CHCl_3$	-1419.354463	•Cl	-460.164522	•$CHCl_2$	-959.084386	66.24
$[CCl_3CN]^-$	-1511.671733	Cl^-	-460.301367	•CCl_2CN	-1051.348984	13.42

The solvent effects observed in HCl addition reactions would be attributed to how easily the solvent-derived radicals are oxidized. Based on the results of DFT calculations (B3LYP/6-311+G(d,p)), the HOMO levels of DMF radical and dioxane radical are much higher than that of MeCN radical.



–4.75 eV –4.96 eV –7.47 eV

Figure S14. Level of HOMOs

Energies and geometries of halomethanes and the corresponding radicals

CCl_3CN

Zero-point correction=	0.017107
Thermal correction to Energy=	0.023459
Thermal correction to Enthalpy=	0.024404
Thermal correction to Gibbs Free Energy=	-0.014498
Sum of electronic and zero-point Energies=	-1511.601099
Sum of electronic and thermal Energies=	-1511.594747
Sum of electronic and thermal Enthalpies=	-1511.593803
Sum of electronic and thermal Free Energies=	-1511.632704

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.039663	-0.000045	-0.000031
2	6	0	-1.494966	-0.001280	-0.000613
3	7	0	-2.647054	-0.002181	-0.001094
4	17	0	0.540937	0.873995	-1.458707
5	17	0	0.542610	-1.699791	-0.026825
6	17	0	0.539738	0.827148	1.486215

CCl_4

Zero-point correction=	0.009213
Thermal correction to Energy=	0.014873
Thermal correction to Enthalpy=	0.015818
Thermal correction to Gibbs Free Energy=	-0.021758
Sum of electronic and zero-point Energies=	-1878.973914
Sum of electronic and thermal Energies=	-1878.968254
Sum of electronic and thermal Enthalpies=	-1878.967309
Sum of electronic and thermal Free Energies=	-1879.004885

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.653280	0.672121	0.000000
2	17	0	-2.444696	0.672147	0.000000
3	17	0	-0.056116	1.516574	-1.462704
4	17	0	-0.056116	1.516574	1.462704
5	17	0	-0.056123	-1.016865	0.000000

$CHCl_3$

Zero-point correction=	0.019775
Thermal correction to Energy=	0.024255
Thermal correction to Enthalpy=	0.025199
Thermal correction to Gibbs Free Energy=	-0.009450
Sum of electronic and zero-point Energies=	-1419.359887
Sum of electronic and thermal Energies=	-1419.355408
Sum of electronic and thermal Enthalpies=	-1419.354463
Sum of electronic and thermal Free Energies=	-1419.389113

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.666088	0.653868	0.031441
2	17	0	-2.451768	0.685038	-0.021801
3	17	0	-0.042036	1.536956	1.453845
4	17	0	-0.041684	-1.019272	-0.022204
5	1	0	-0.305240	1.163891	-0.852236

$[CCl_3CN]^{\bullet-}$

Zero-point correction=	0.015261
Thermal correction to Energy=	0.022585
Thermal correction to Enthalpy=	0.023529
Thermal correction to Gibbs Free Energy=	-0.019047
Sum of electronic and zero-point Energies=	-1511.680002
Sum of electronic and thermal Energies=	-1511.672677
Sum of electronic and thermal Enthalpies=	-1511.671733
Sum of electronic and thermal Free Energies=	-1511.714310

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.146623	-0.133363	-0.240715
2	6	0	-1.539610	-0.060302	-0.103001
3	7	0	-2.692519	0.014657	0.036760
4	17	0	0.532892	0.838759	-1.540389
5	17	0	0.540224	-1.747146	-0.102359
6	17	0	0.747238	1.085241	1.948648

$\bullet CCl_2CN$

Zero-point correction=	0.014783
Thermal correction to Energy=	0.019949
Thermal correction to Enthalpy=	0.020894
Thermal correction to Gibbs Free Energy=	-0.014990
Sum of electronic and zero-point Energies=	-1051.355095
Sum of electronic and thermal Energies=	-1051.349928
Sum of electronic and thermal Enthalpies=	-1051.348984
Sum of electronic and thermal Free Energies=	-1051.384868

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.064160
2	17	0	0.000000	1.475969	-0.807424
3	17	0	0.000000	-1.475969	-0.807424
4	6	0	0.000000	0.000000	1.448427
5	7	0	0.000000	0.000000	2.613786

$\bullet CCl_3$

Zero-point correction=	0.007035
Thermal correction to Energy=	0.011513
Thermal correction to Enthalpy=	0.012458
Thermal correction to Gibbs Free Energy=	-0.022809
Sum of electronic and zero-point Energies=	-1418.714652
Sum of electronic and thermal Energies=	-1418.710174
Sum of electronic and thermal Enthalpies=	-1418.709230
Sum of electronic and thermal Free Energies=	-1418.744497

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.320586	1.305903	0.000000
2	17	0	1.018839	1.884063	-1.473507
3	17	0	1.018839	1.884063	1.473507
4	17	0	-1.387121	1.032557	0.000000

$\bullet CHCl_2$

Zero-point correction=	0.015610
Thermal correction to Energy=	0.019279
Thermal correction to Enthalpy=	0.020224
Thermal correction to Gibbs Free Energy=	-0.011692
Sum of electronic and zero-point Energies=	-959.088999
Sum of electronic and thermal Energies=	-959.085330
Sum of electronic and thermal Enthalpies=	-959.084386
Sum of electronic and thermal Free Energies=	-959.116302

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.223404	1.607515	0.015040
2	17	0	1.055976	1.811114	-1.474510
3	17	0	-1.366318	0.954738	0.008841
4	1	0	0.828077	1.407954	0.887246

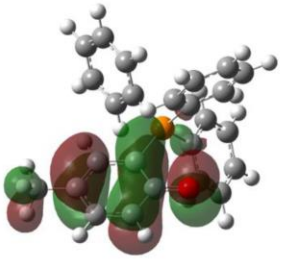
$\bullet Cl$

Zero-point correction=	0.000000
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.015677
Sum of electronic and zero-point Energies=	-460.166882
Sum of electronic and thermal Energies=	-460.165466
Sum of electronic and thermal Enthalpies=	-460.164522
Sum of electronic and thermal Free Energies=	-460.182560

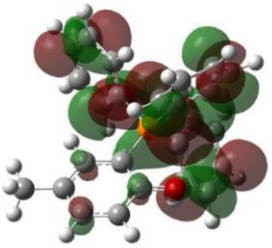
Cl^-

Zero-point correction=	0.000000
Thermal correction to Energy=	0.001416
Thermal correction to Enthalpy=	0.002360
Thermal correction to Gibbs Free Energy=	-0.015023
Sum of electronic and zero-point Energies=	-460.303727
Sum of electronic and thermal Energies=	-460.302311
Sum of electronic and thermal Enthalpies=	-460.301367
Sum of electronic and thermal Free Energies=	-460.318750

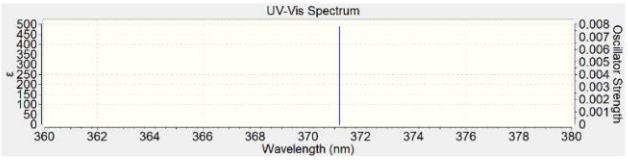
phosphonium ylide **1**



HOMO: -5.23eV



LUMO: -1.57 eV



UV-vis: λ_{calcd} = 371 nm (TD-DFT)

SCF Done: E(RB3LYP) = -1382.17250822
Zero-point correction= 0.383257
Thermal correction to Energy= 0.406956
Thermal correction to Enthalpy= 0.407900
Thermal correction to Gibbs Free Energy= 0.328055
Sum of electronic and zero-point Energies= -1381.789251
Sum of electronic and thermal Energies= -1381.765552
Sum of electronic and thermal Enthalpies= -1381.764608
Sum of electronic and thermal Free Energies= -1381.844453

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.228598	-0.013683	0.002807
2	8	0	-0.506218	-2.738419	-0.855780
3	6	0	-3.951234	-1.570990	-0.917912
4	1	0	-4.944217	-1.962602	-1.125723
5	6	0	-2.869702	-2.419835	-1.014236
6	1	0	-3.008364	-3.460026	-1.292428
7	6	0	-1.525037	-1.977670	-0.761147
8	6	0	-1.414136	-0.587604	-0.392781
9	6	0	0.130373	1.708979	0.610893
10	6	0	0.229460	2.004599	1.974954
11	1	0	0.400196	1.216525	2.697086
12	6	0	0.116674	3.323592	2.413266
13	1	0	0.199206	3.544376	3.470959
14	6	0	-0.096458	4.350937	1.496628
15	1	0	-0.181874	5.375466	1.839862
16	6	0	2.013986	-2.523462	3.447191
17	1	0	2.423332	-3.104980	4.265161
18	6	0	2.853959	-2.042161	2.444182
19	1	0	3.917116	-2.249715	2.477145
20	6	0	2.331476	-1.296095	1.388948
21	1	0	2.995182	-0.939720	0.611808
22	6	0	0.959429	-1.029925	1.334689
23	6	0	1.362646	0.052106	-1.429433
24	6	0	2.528451	0.828981	-1.358064
25	1	0	2.763604	1.393480	-0.463704
26	6	0	3.389492	0.896660	-2.450800
27	1	0	4.289003	1.497645	-2.387785
28	6	0	3.087722	0.202723	-3.622246
29	1	0	3.756189	0.260906	-4.473571
30	6	0	1.923111	-0.559926	-3.699858
31	1	0	1.683216	-1.096126	-4.610622
32	6	0	1.060696	-0.639803	-2.608081
33	1	0	0.168814	-1.247750	-2.663666
34	6	0	-0.081428	2.746756	-0.309128
35	1	0	-0.153444	2.535450	-1.369489
36	6	0	-0.195684	4.060796	0.135292
37	1	0	-0.358855	4.856756	-0.581692
38	6	0	-3.820862	-0.208891	-0.555491
39	6	0	-2.542370	0.255869	-0.293549
40	1	0	-2.410942	1.291771	-0.000956
41	6	0	-5.033460	0.687664	-0.458679
42	1	0	-5.760681	0.307375	0.266820
43	1	0	-5.553726	0.769258	-1.419348
44	1	0	-4.753103	1.696878	-0.148399
45	6	0	0.115916	-1.519991	2.339986
46	1	0	-0.950777	-1.334713	2.294439
47	6	0	0.644863	-2.262239	3.392801
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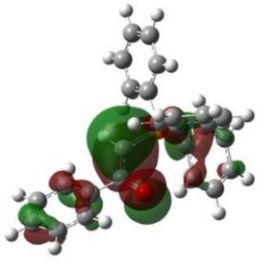
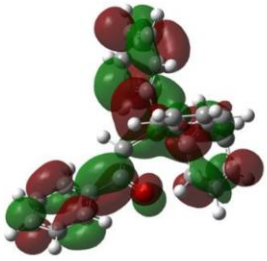
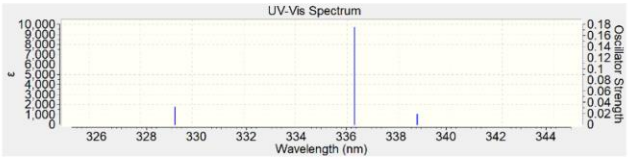
phosphonium ylide **4**



HOMO: -5.79 eV



LUMO: -1.47 eV



UV-vis: λ_{calcd} = 336 nm (TD-DFT)

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Thermal correction to Enthalpy= 0.414661
Thermal correction to Gibbs Free Energy= 0.331874
Sum of electronic and zero-point Energies= -1419.895579
Sum of electronic and thermal Energies= -1419.871502
Sum of electronic and thermal Enthalpies= -1419.870558
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3	6	0	0.213038	1.753118	-0.593796
4	6	0	-0.486095	2.959250	-0.545085
5	6	0	-1.727974	3.024296	0.082830
6	6	0	-2.275661	1.879403	0.663660
7	1	0	-2.020834	-0.211077	1.067347
8	1	0	1.178047	1.714642	-1.083077
9	1	0	-0.056650	3.845359	-0.997713
10	1	0	-2.269138	3.962709	0.120033
11	1	0	-3.242318	1.924814	1.151508
12	15	0	0.557110	-0.993472	-0.041115
13	6	0	-0.342315	-2.069673	-1.226503
14	6	0	-0.129007	-3.456537	-1.197283
15	6	0	-1.239027	-1.526380	-2.155254
16	6	0	-0.809952	-4.281853	-2.088974
17	1	0	0.570671	-3.873077	-0.482568
18	6	0	-1.915029	-2.360504	-3.045695
19	1	0	-1.417338	-0.458715	-2.188081
20	6	0	-1.702398	-3.737289	-3.013584
21	1	0	-0.642744	-5.352612	-2.061237
22	1	0	-2.607650	-1.931532	-3.760609
23	1	0	-2.230102	-4.384108	-3.705241
24	6	0	2.212492	-0.695055	-0.766947
25	6	0	3.248672	-0.275351	0.075670
26	6	0	2.449092	-0.842308	-2.138319
27	6	0	4.507695	0.000729	-0.451393
28	1	0	3.069792	-0.176249	1.140095
29	6	0	3.711710	-0.565356	-2.661114
30	1	0	1.657991	-1.175458	-2.798923
31	6	0	4.740233	-0.143139	-1.819877
32	1	0	5.307333	0.322061	0.205948
33	1	0	3.890248	-0.683023	-3.723639
34	1	0	5.721833	0.068675	-2.228145
35	6	0	0.612183	-1.553911	1.606667
36	6	0	1.354783	-2.685297	1.987305
37	6	0	1.402155	-3.047162	3.457459
38	6	0	2.475348	-3.820786	3.919404
39	6	0	0.412121	-2.663996	4.373099
40	6	0	2.569905	-4.185029	5.260787
41	1	0	3.233126	-4.129993	3.209983
42	6	0	0.497830	-3.037713	5.713525
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44	6	0	1.579758	-3.795112	6.163741
45	1	0	3.413587	-4.775122	5.601819
46	1	0	-0.282803	-2.741027	6.405355
47	1	0	1.647623	-4.082686	7.206999
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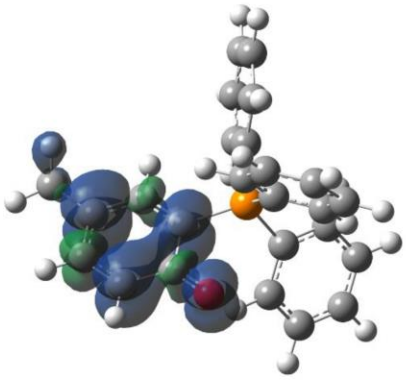
49	1	0	0.117651	-0.917291	2.324832

radical cation **1**$^{\bullet+}$



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Thermal correction to Gibbs Free Energy= 0.328015
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Sum of electronic and thermal Energies= -1381.582340
Sum of electronic and thermal Enthalpies= -1381.581396
Sum of electronic and thermal Free Energies= -1381.661871

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	15	0	0.273685	0.035277	0.024489
2	8	0	-0.566415	-2.760574	-0.780181
3	6	0	-3.976139	-1.608242	-0.885337
4	1	0	-4.973995	-1.983627	-1.080727
5	6	0	-2.901645	-2.460171	-0.951898
6	1	0	-3.021856	-3.508328	-1.198273
7	6	0	-1.552115	-1.995618	-0.704770
8	6	0	-1.397494	-0.578330	-0.369514
9	6	0	0.129368	1.748699	0.619126
10	6	0	0.235669	2.045830	1.983083
11	1	0	0.430860	1.263932	2.705366
12	6	0	0.100512	3.363250	2.416384
13	1	0	0.189014	3.589757	3.472014
14	6	0	-0.141300	4.382001	1.497171
15	1	0	-0.243835	5.405514	1.838109
16	6	0	2.017979	-2.560958	3.404376
17	1	0	2.426367	-3.165653	4.205528
18	6	0	2.847564	-2.112654	2.378031
19	1	0	3.900335	-2.368179	2.375937
20	6	0	2.327318	-1.338257	1.343518
21	1	0	2.979663	-1.006037	0.546371
22	6	0	0.966757	-1.011403	1.339634
23	6	0	1.354803	0.071330	-1.437303
24	6	0	2.494707	0.890166	-1.398036
25	1	0	2.709976	1.501738	-0.530458
26	6	0	3.356442	0.930178	-2.490003
27	1	0	4.236286	1.561035	-2.453144
28	6	0	3.082434	0.169522	-3.626219
29	1	0	3.752191	0.207726	-4.477272
30	6	0	1.945115	-0.634663	-3.670507
31	1	0	1.725704	-1.221637	-4.554172
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39	6	0	-2.496305	0.242361	-0.304860
40	1	0	-2.386789	1.287766	-0.042239
41	6	0	-4.972443	0.691822	-0.479414
42	1	0	-5.908192	0.196803	-0.736913
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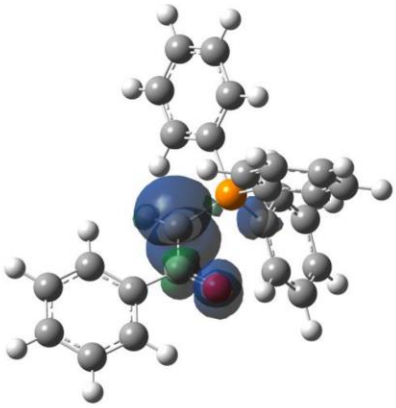
44	1	0	-5.061205	1.099270	0.533739
45	6	0	0.130632	-1.465779	2.369203
46	1	0	-0.927108	-1.230432	2.372597
47	6	0	0.661056	-2.238001	3.398462
48	1	0	0.012380	-2.589787	4.191579

radical cation **4**$^{\bullet+}$



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Sum of electronic and thermal Energies= -1419.672699
Sum of electronic and thermal Enthalpies= -1419.671755
Sum of electronic and thermal Free Energies= -1419.755533

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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4	6	0	-0.562494	2.970005	-0.547287
5	6	0	-1.799071	3.022459	0.092305
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10	1	0	-2.340397	3.959538	0.147327
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14	6	0	-0.038820	-3.439827	-1.346475
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32	1	0	5.103144	0.656699	0.422687
33	1	0	4.178099	-1.008513	-3.429602
34	1	0	5.797780	0.055291	-1.881832
35	6	0	0.474318	-1.642596	1.519358
36	6	0	1.394612	-2.687745	1.956662
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48	8	0	2.060520	-3.285413	1.102698
49	1	0	-0.318248	-1.286721	2.164671

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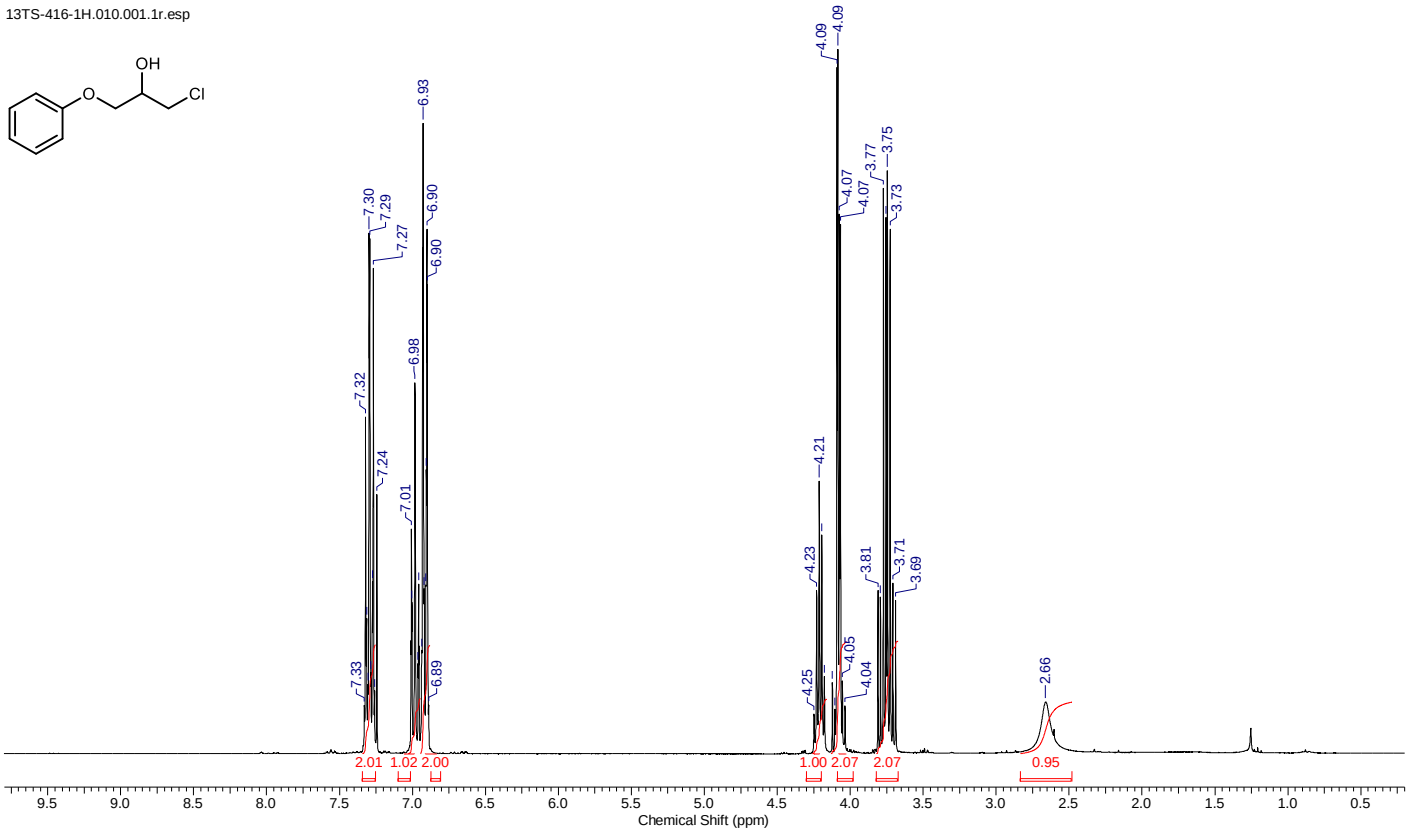

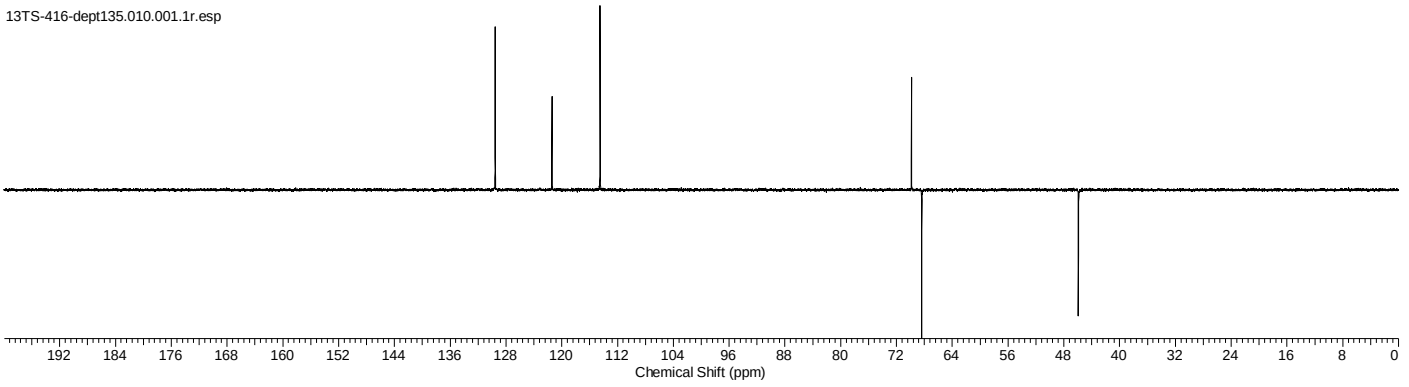

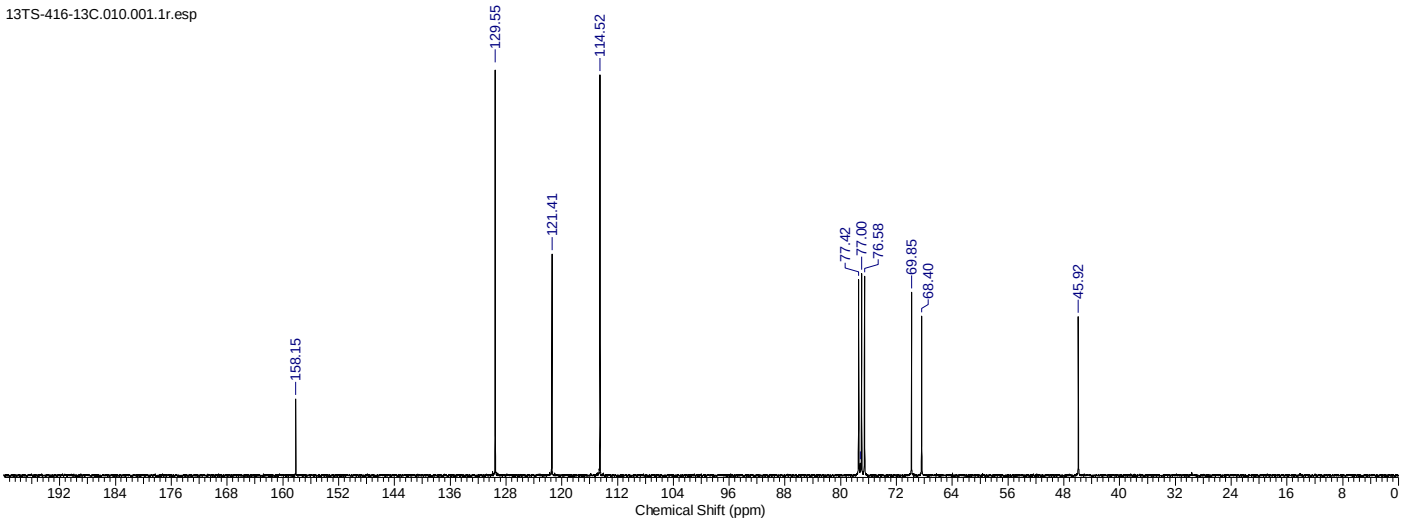

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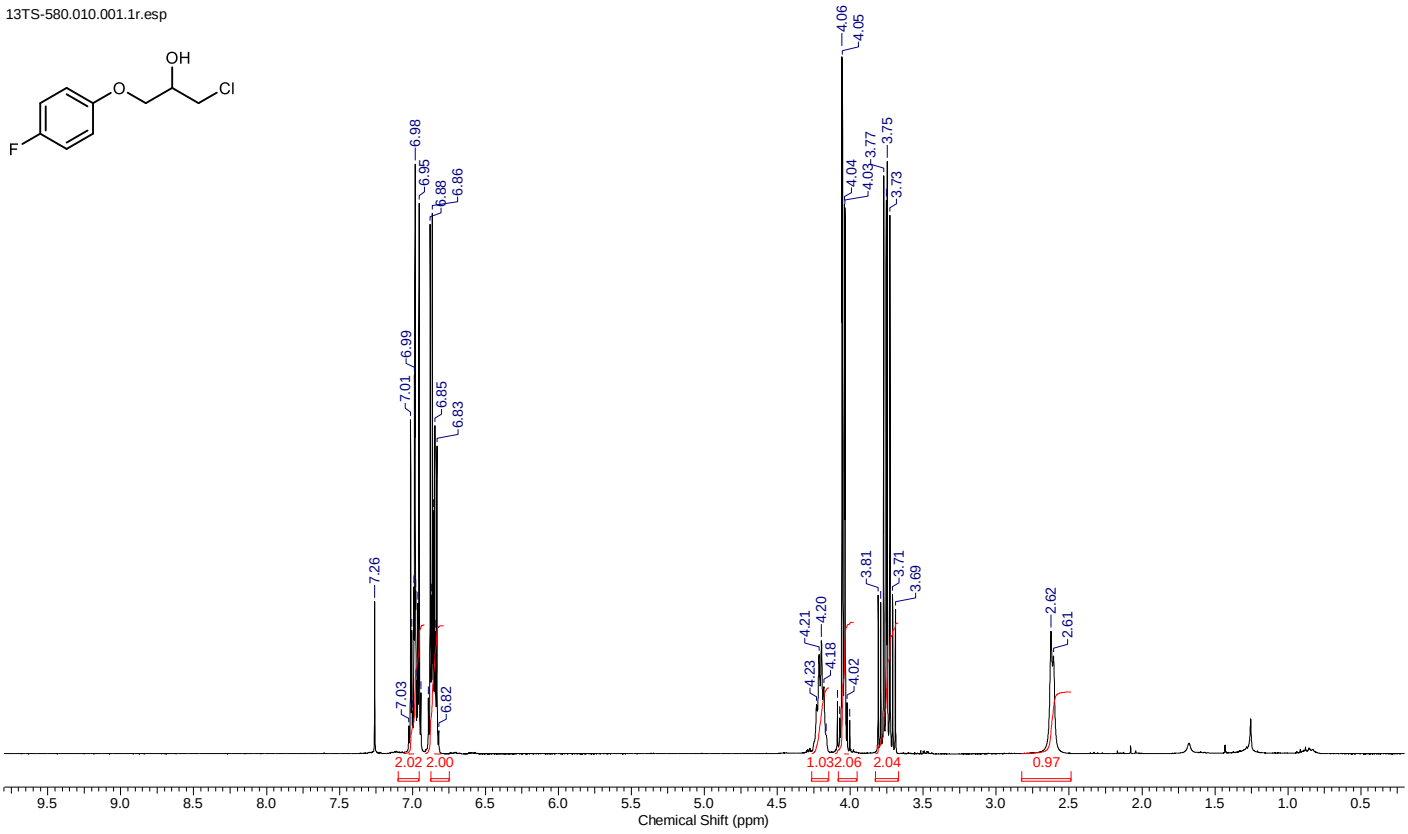

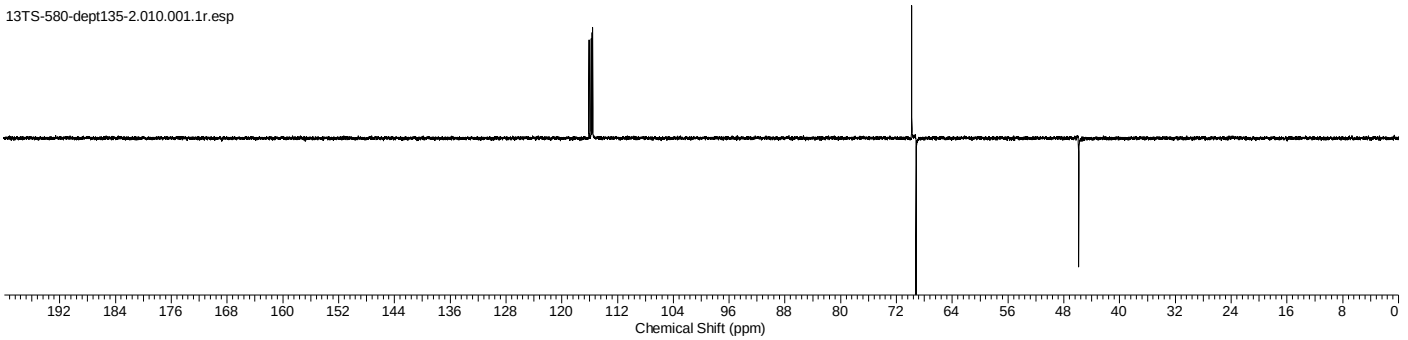

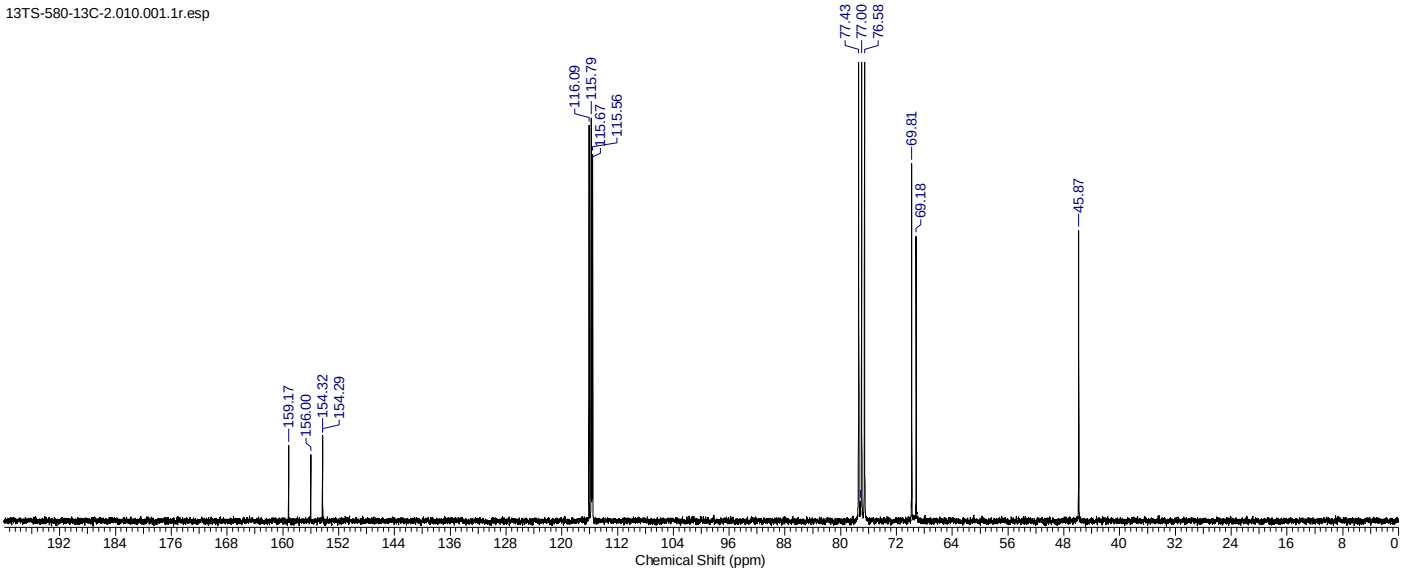

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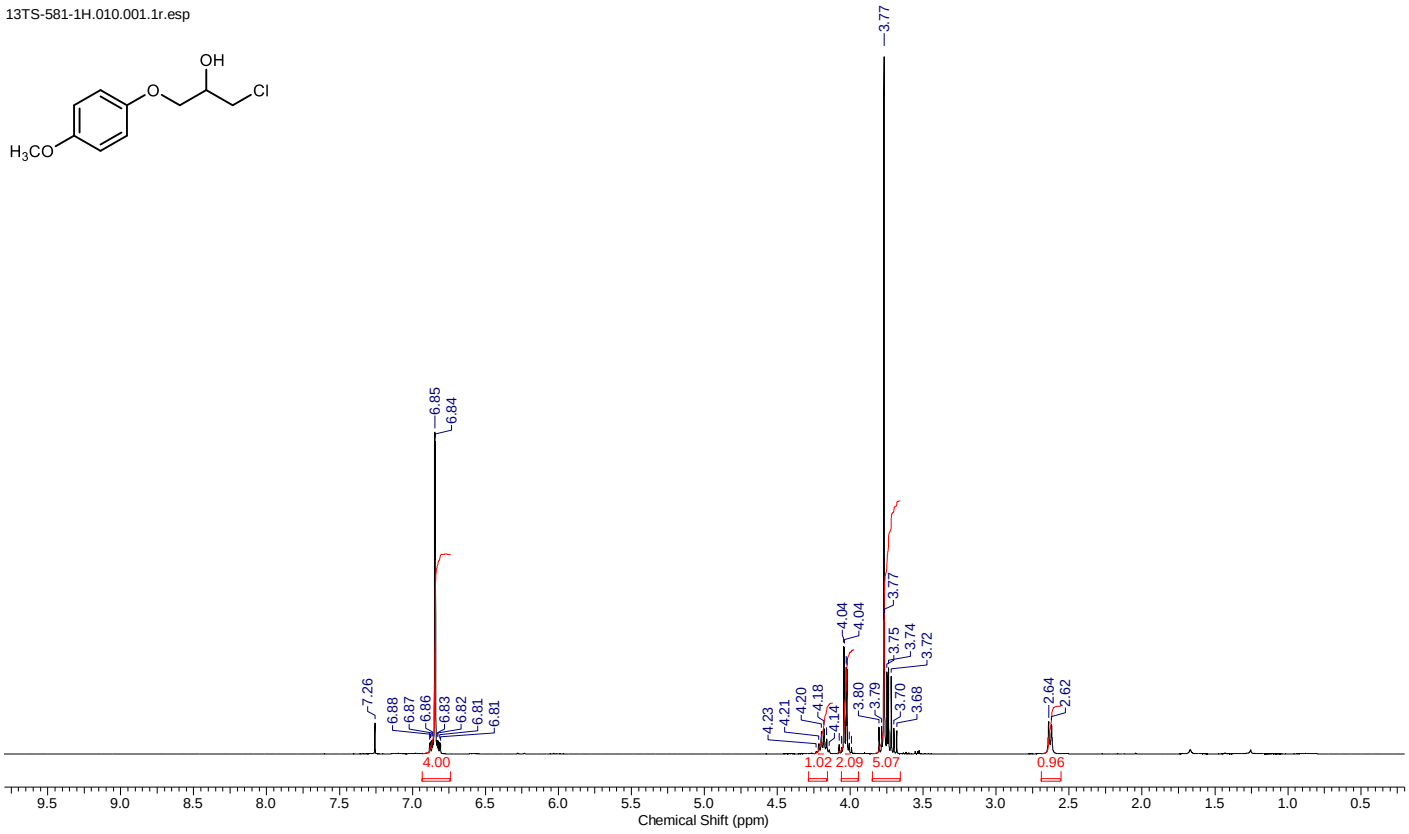
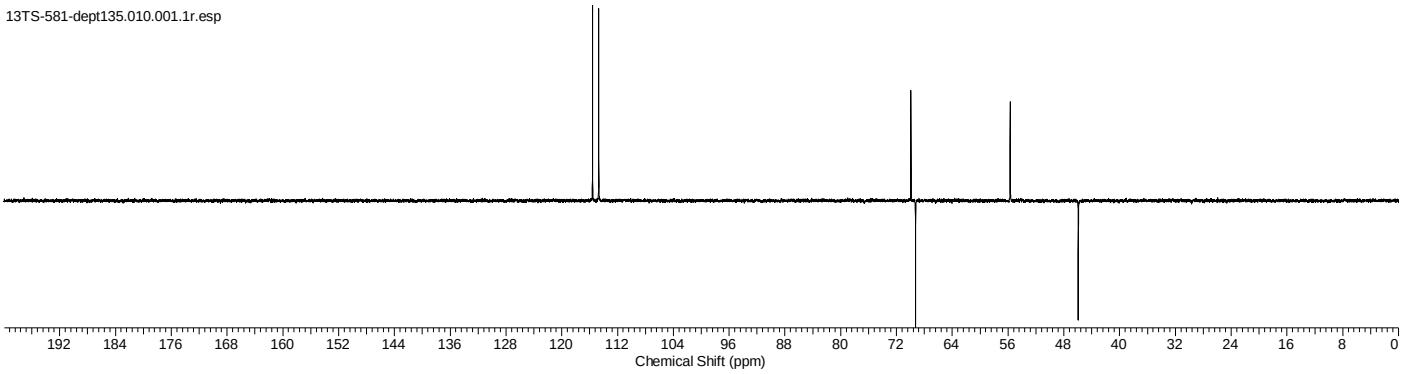
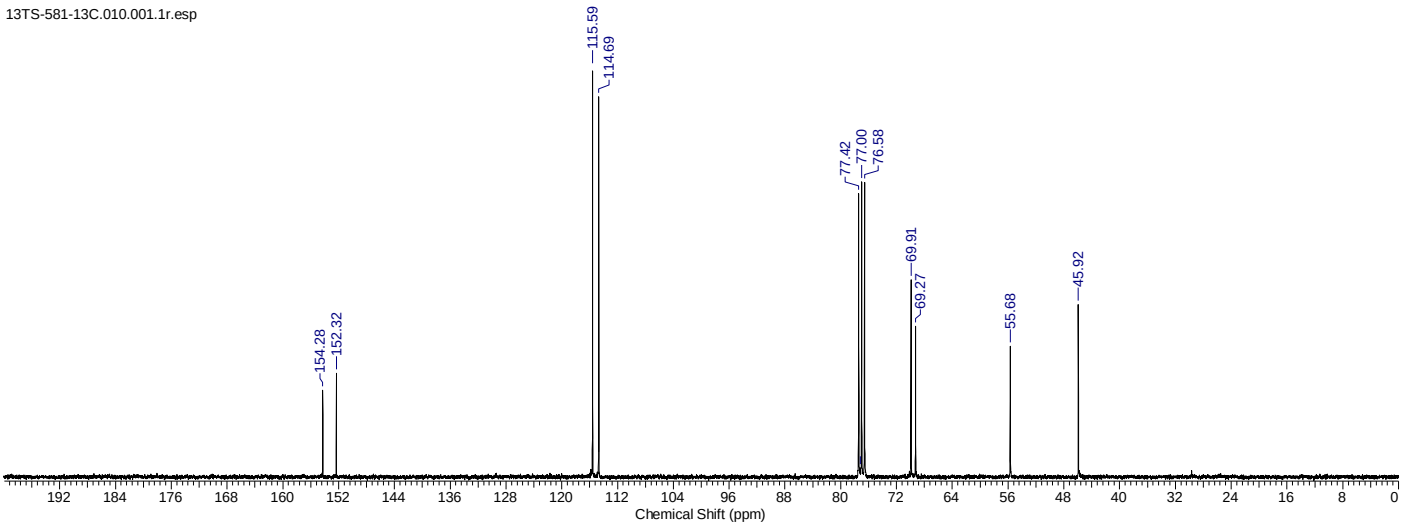
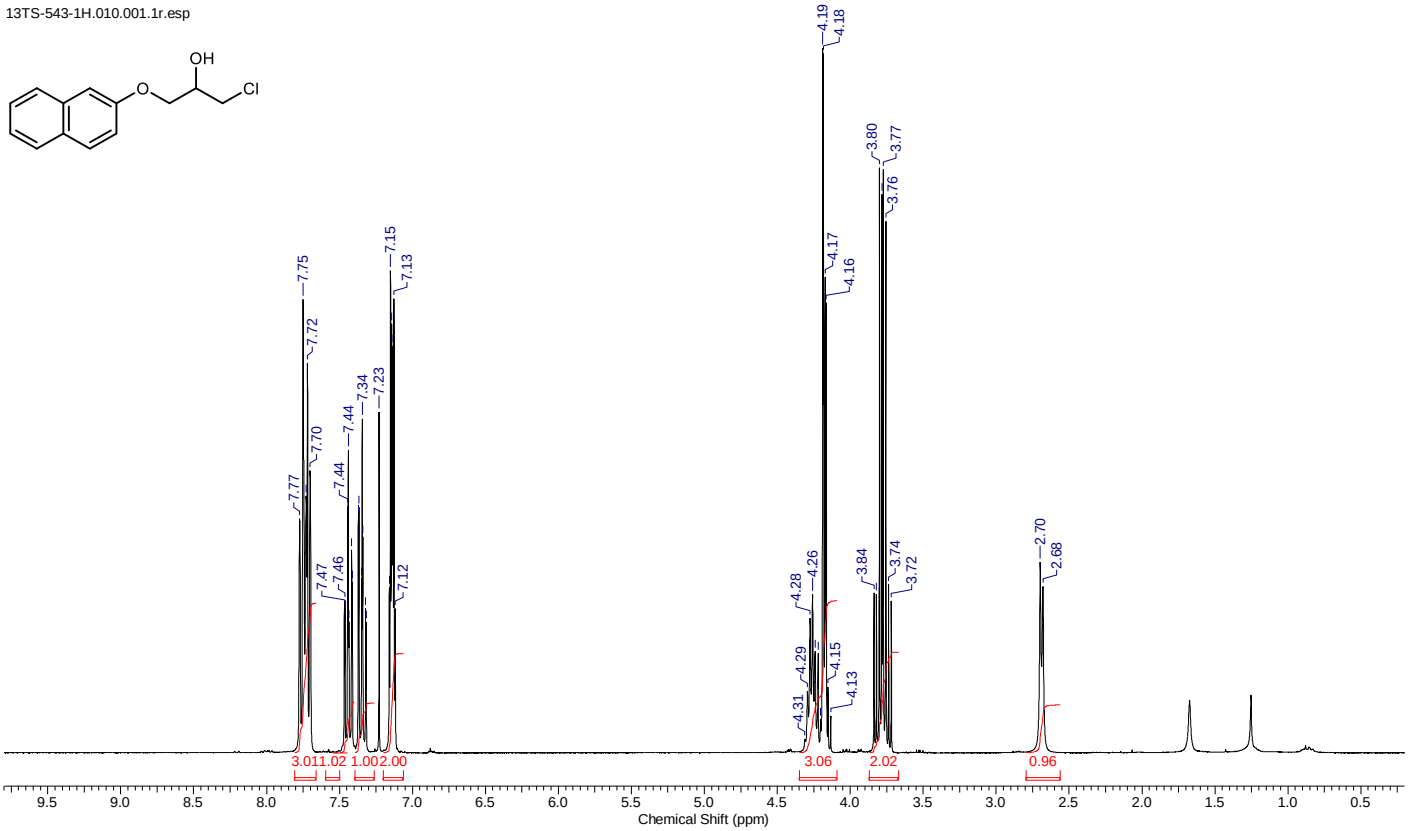
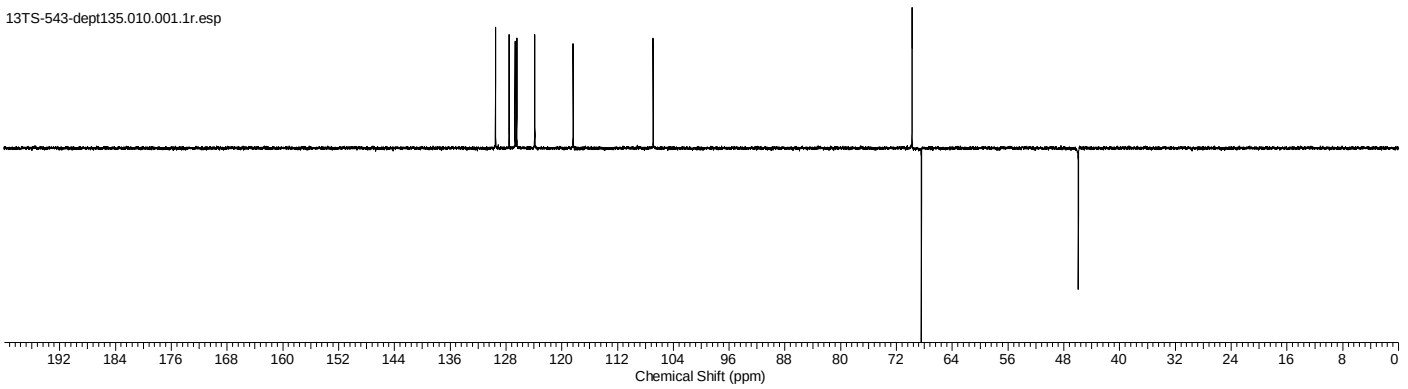


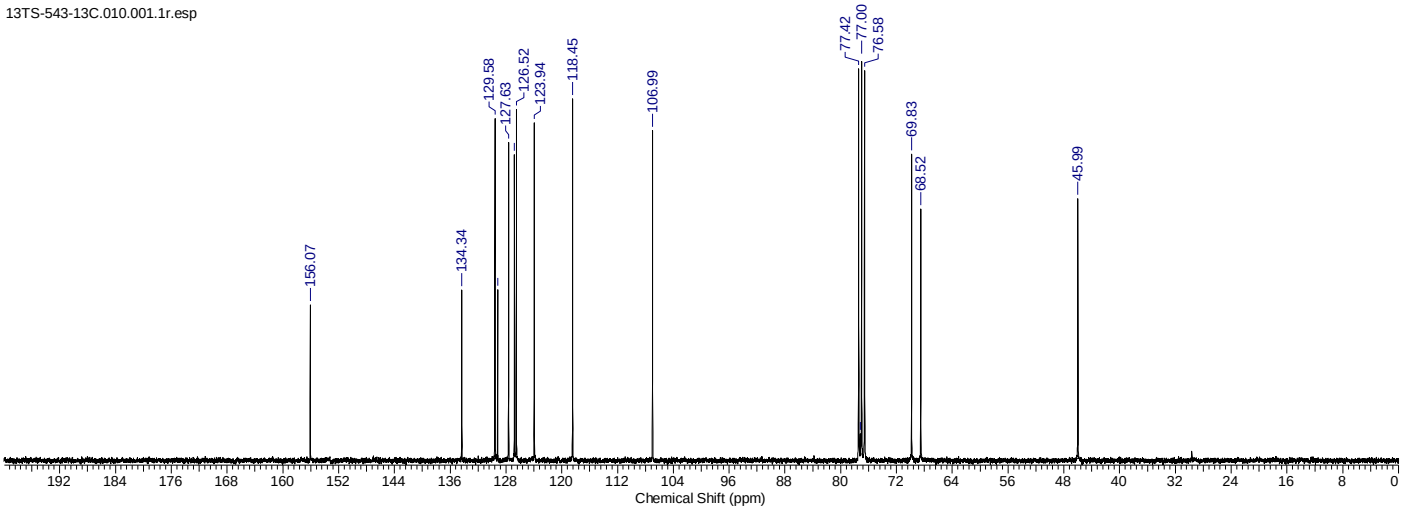




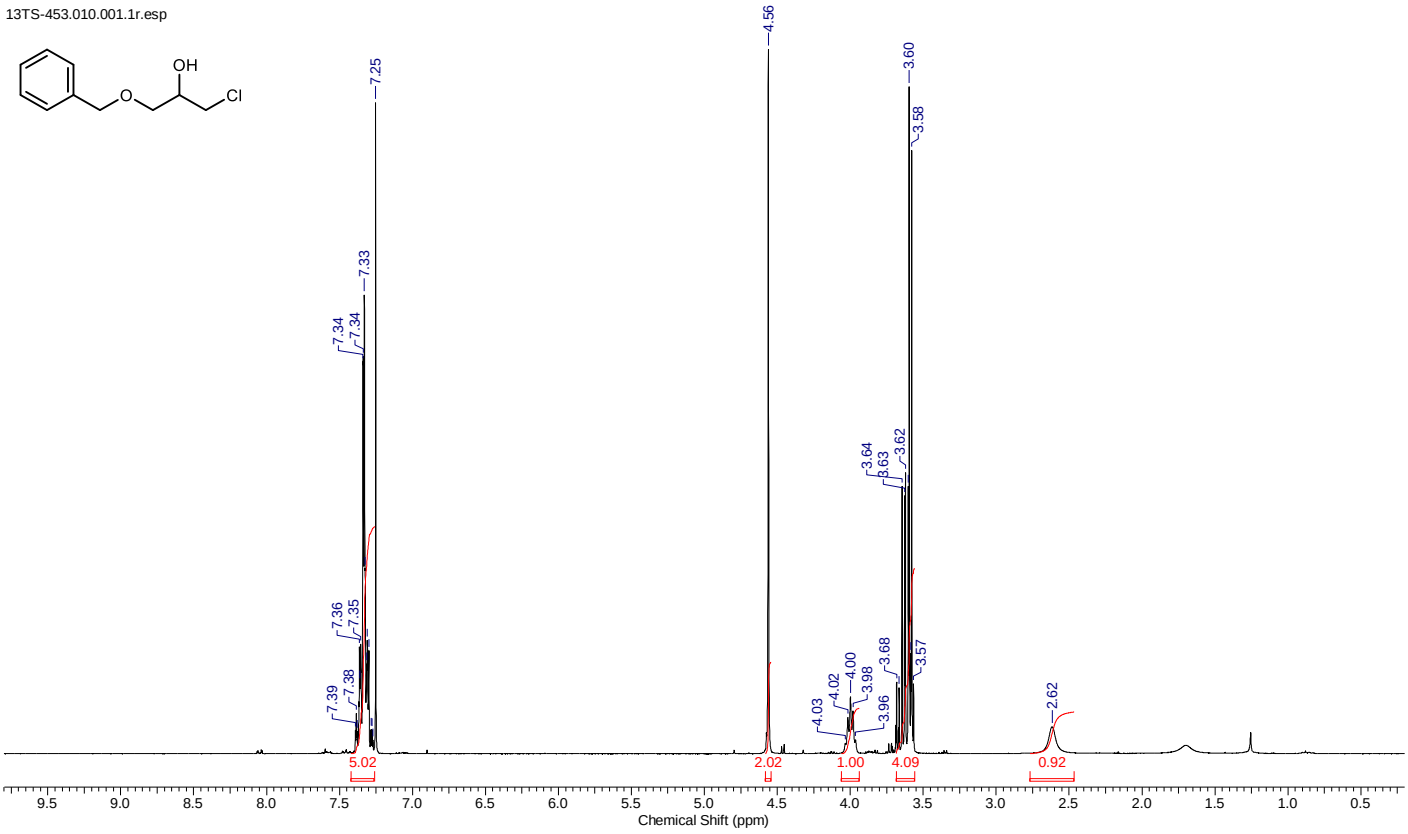
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3d

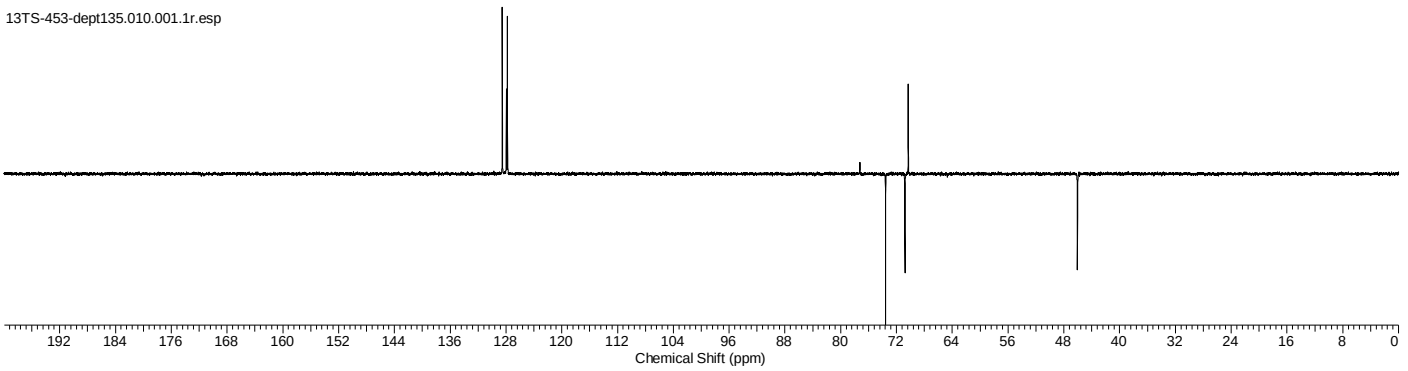


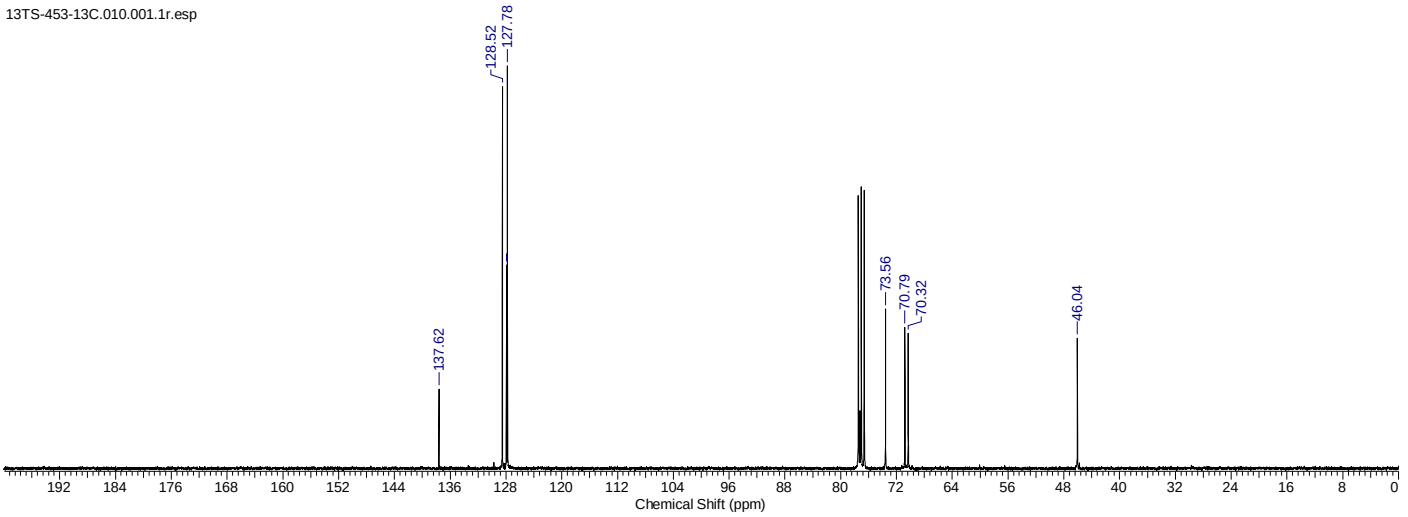




^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3e

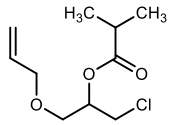






^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1-allyloxy-3-chloropropan-2-yl isobutyrate (3f-Deriv.)

13TS-604.010.001.1r.esp



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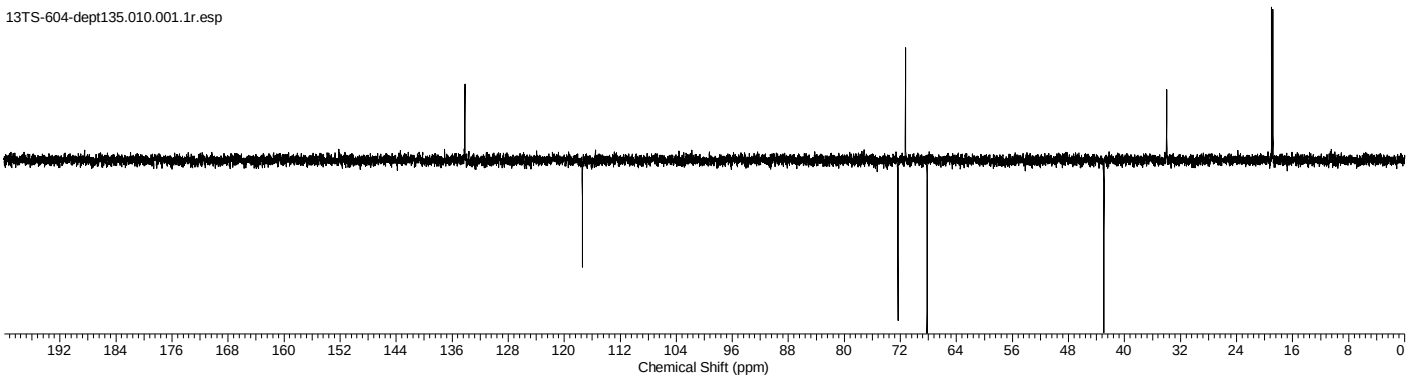

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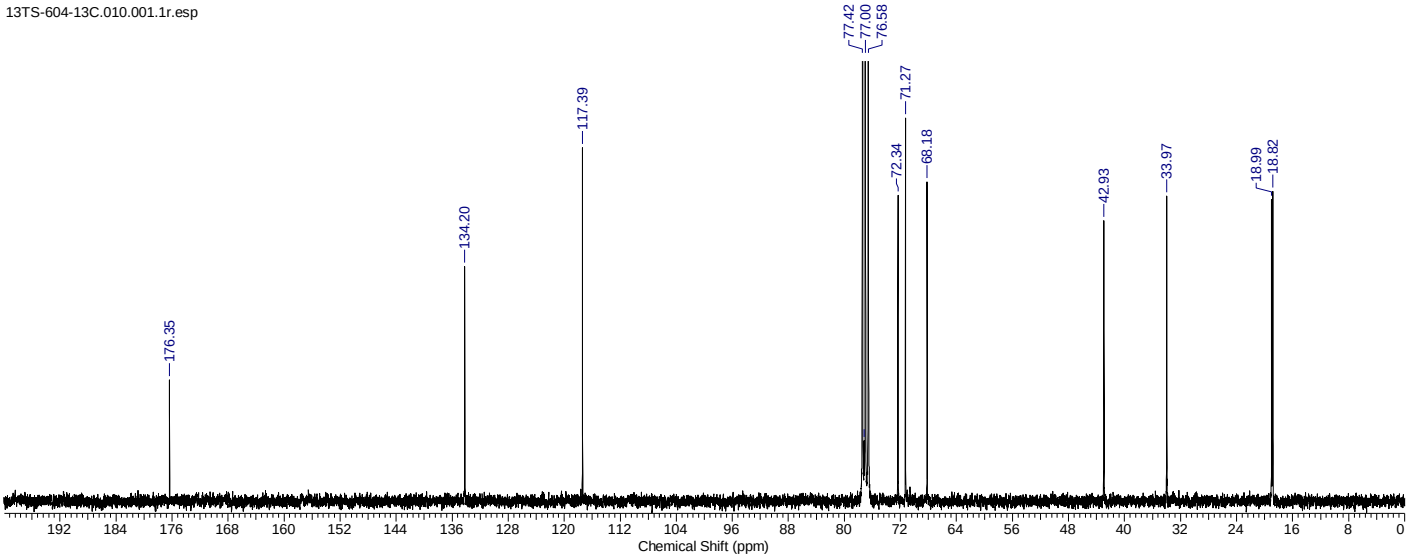
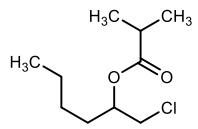


^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 1-chlorohexan-2-yl isobutyrate (3g-Deriv.)

13TS-611-1H.010.001.1r.esp



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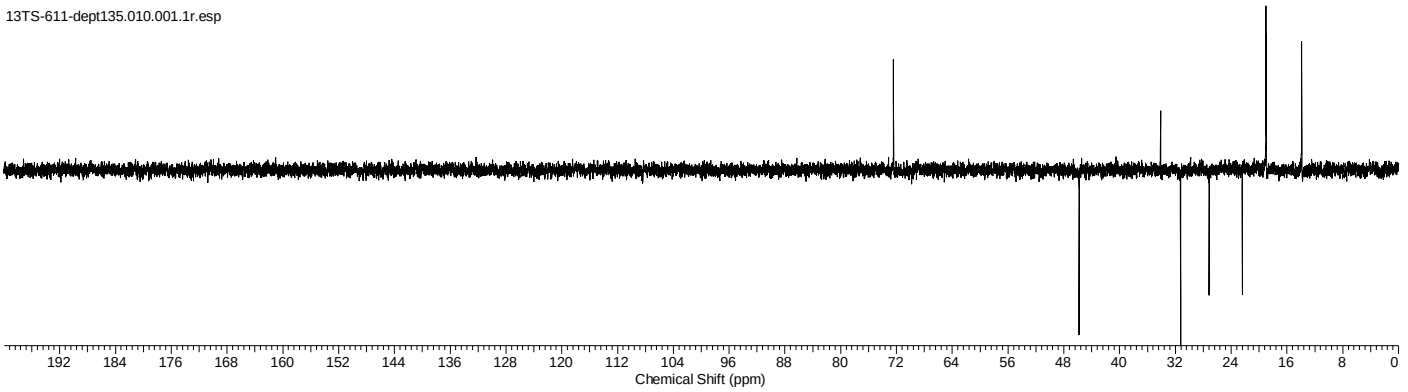

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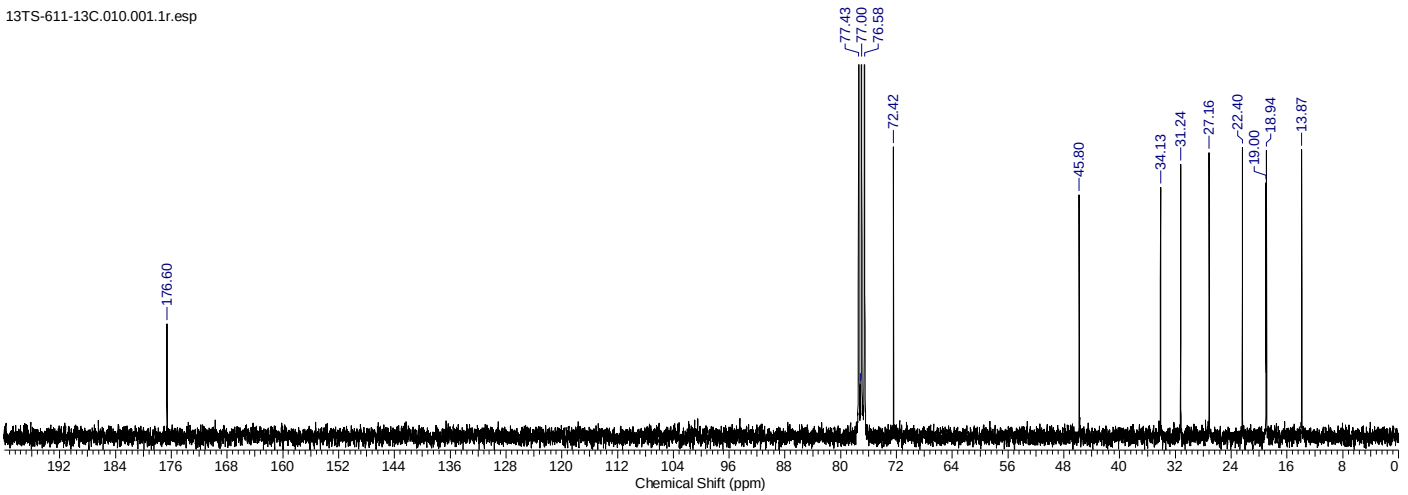
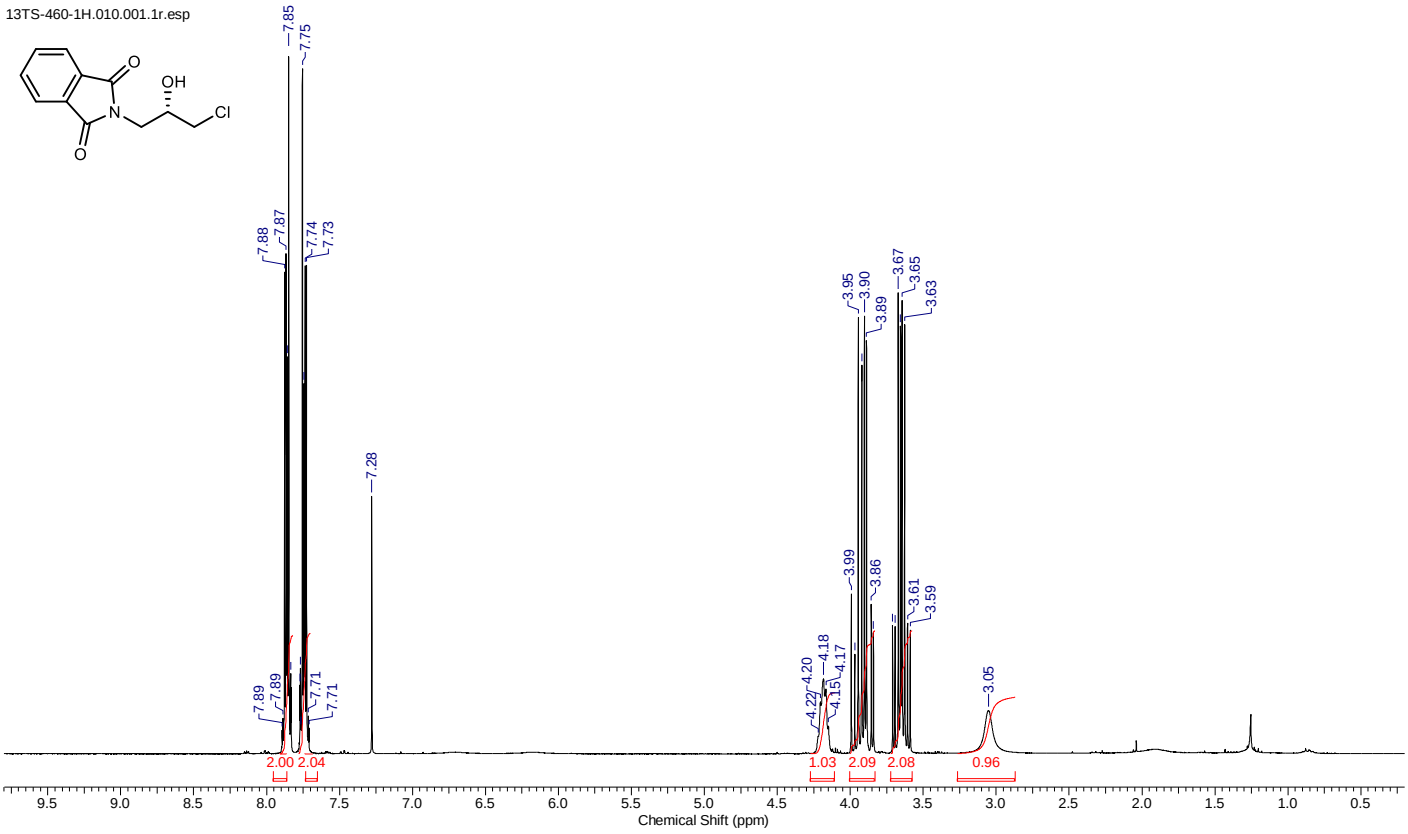
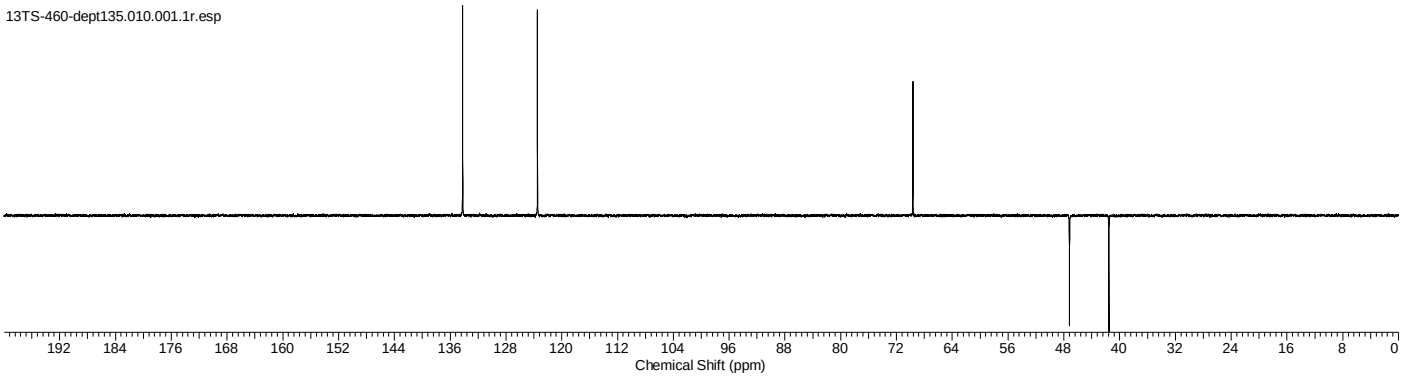
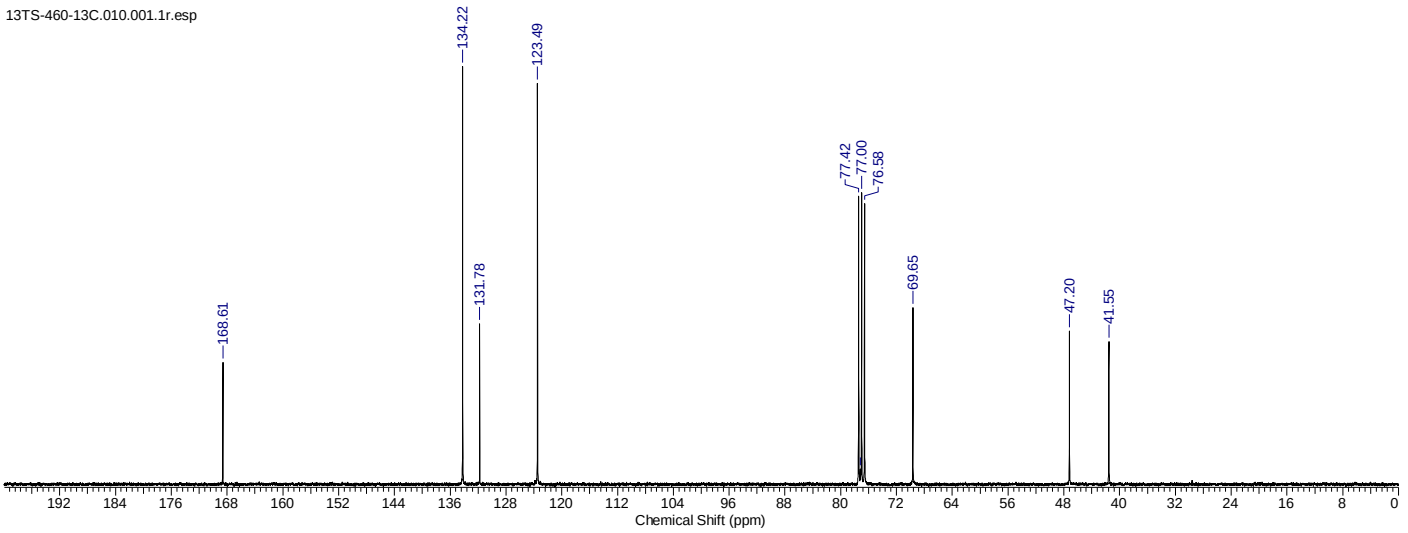


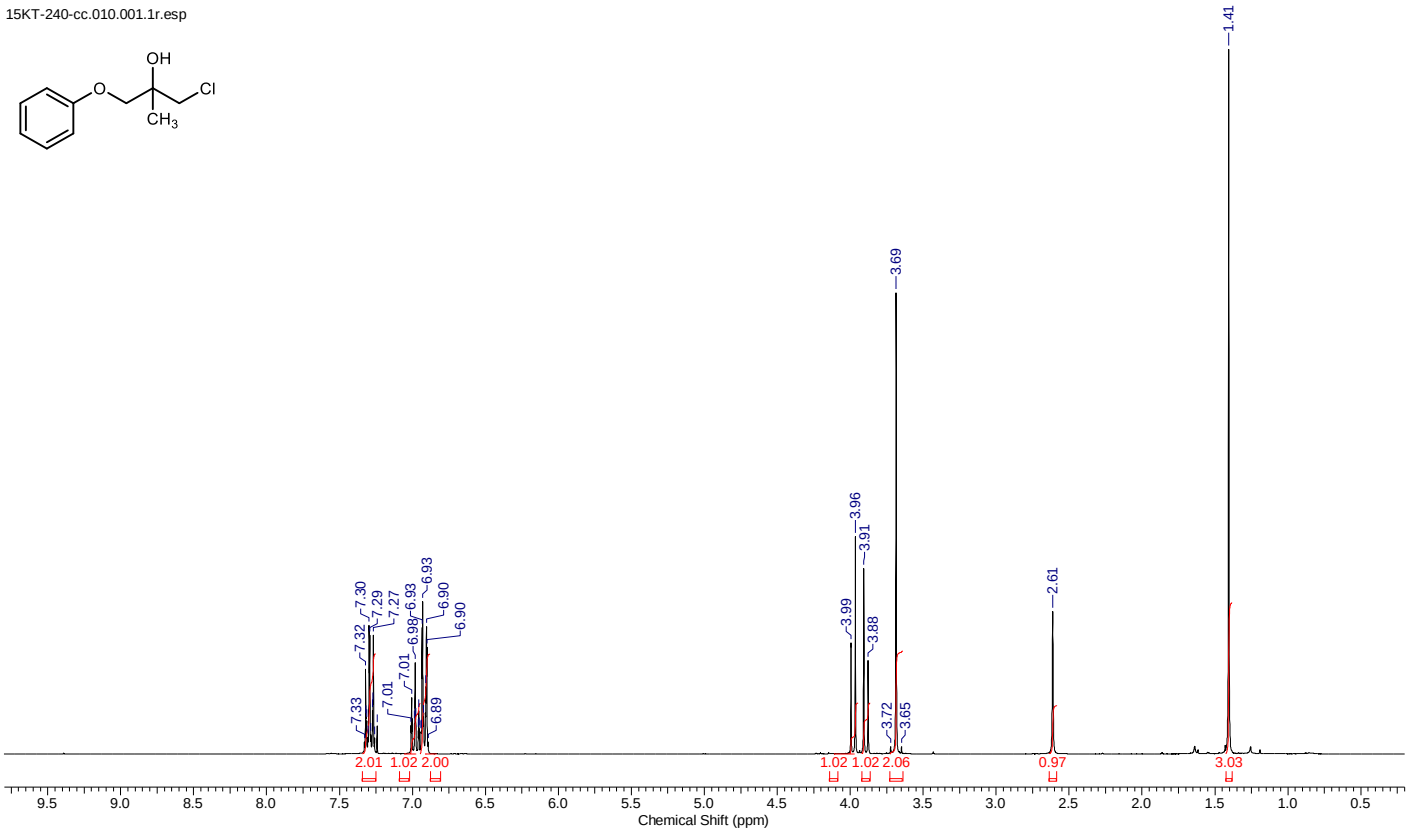
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3h

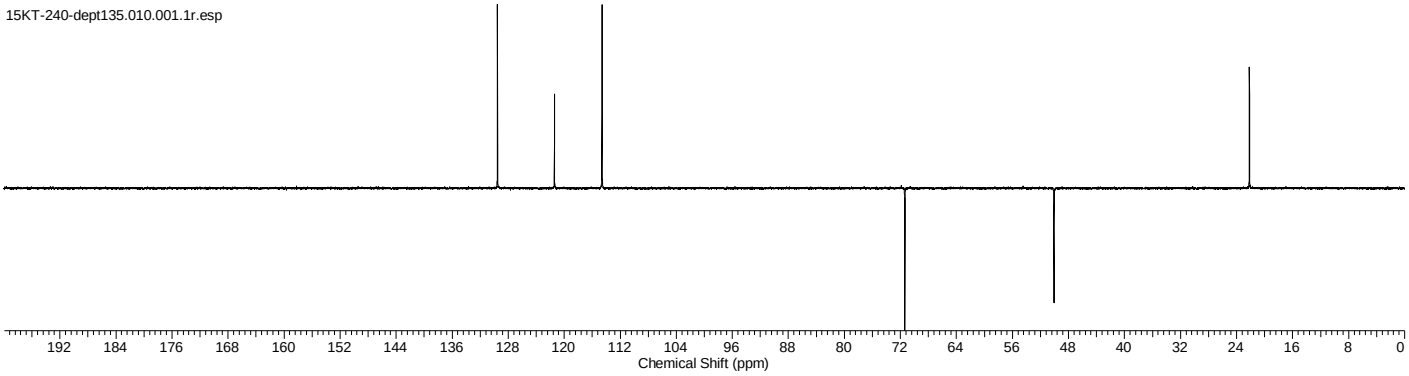


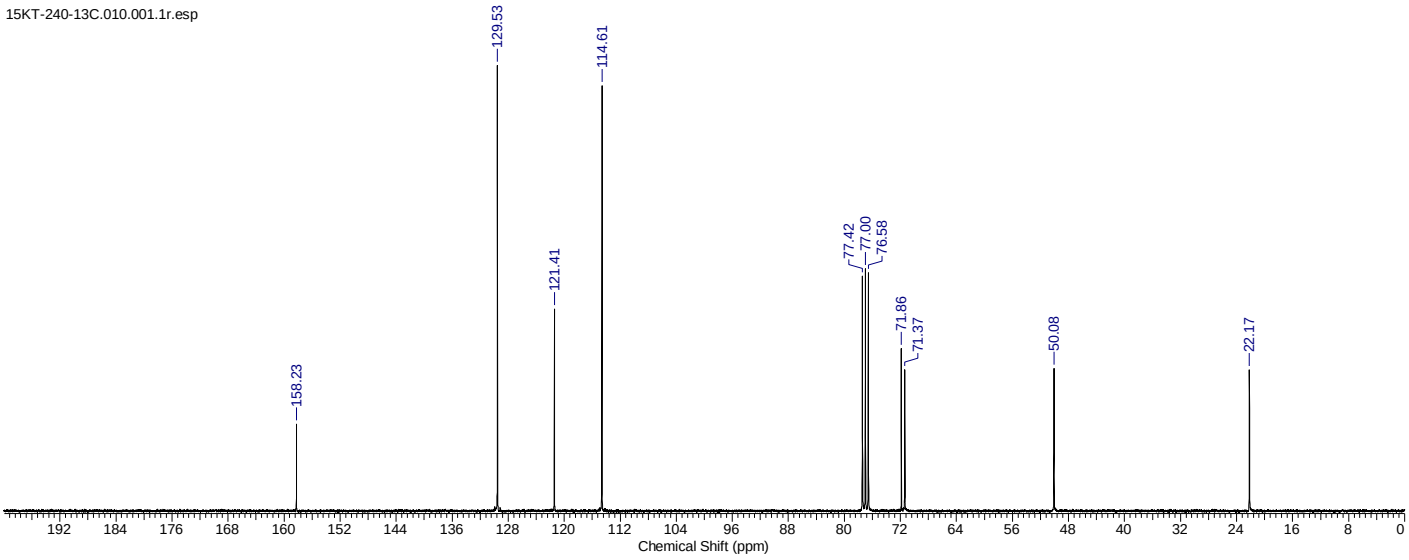




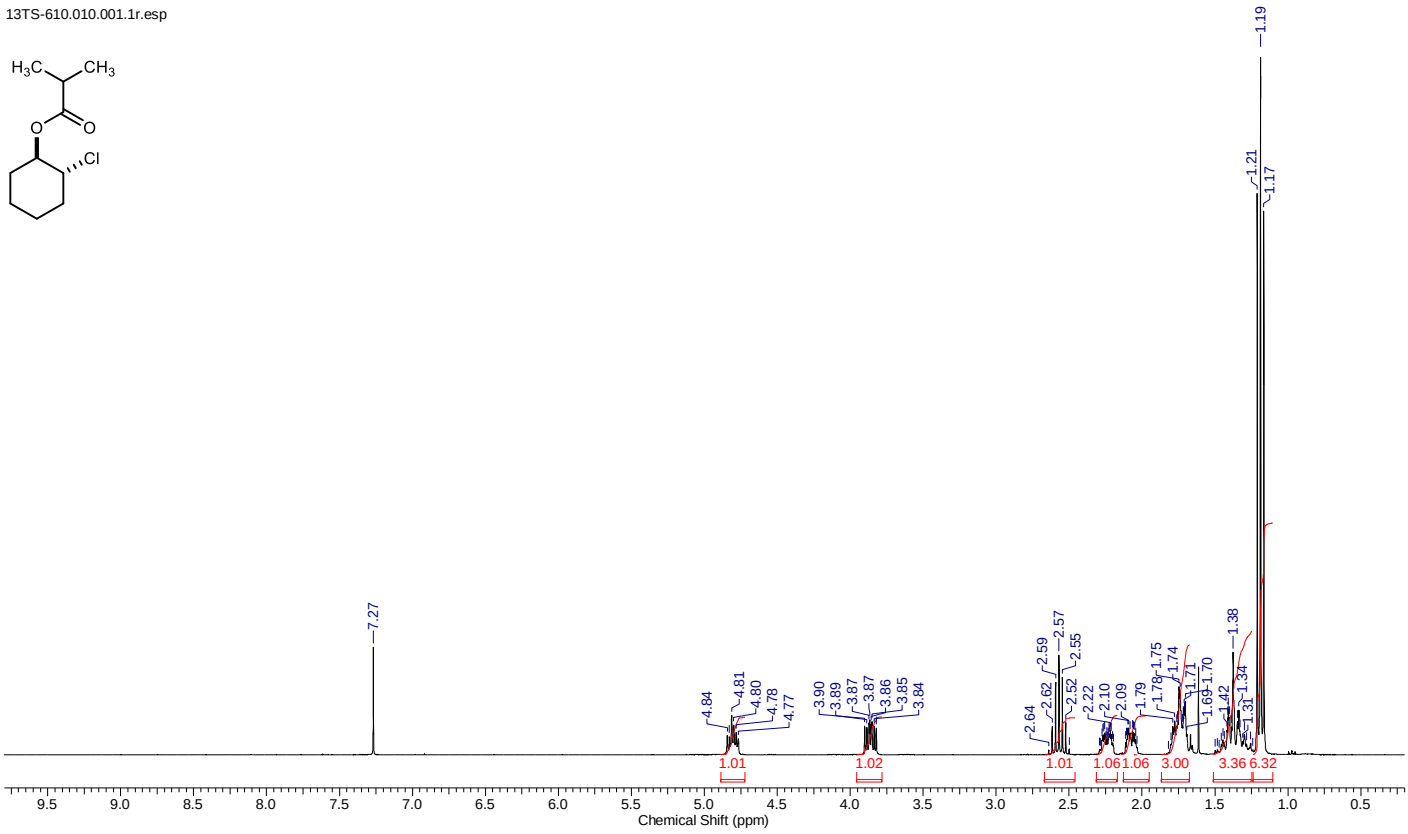
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3i

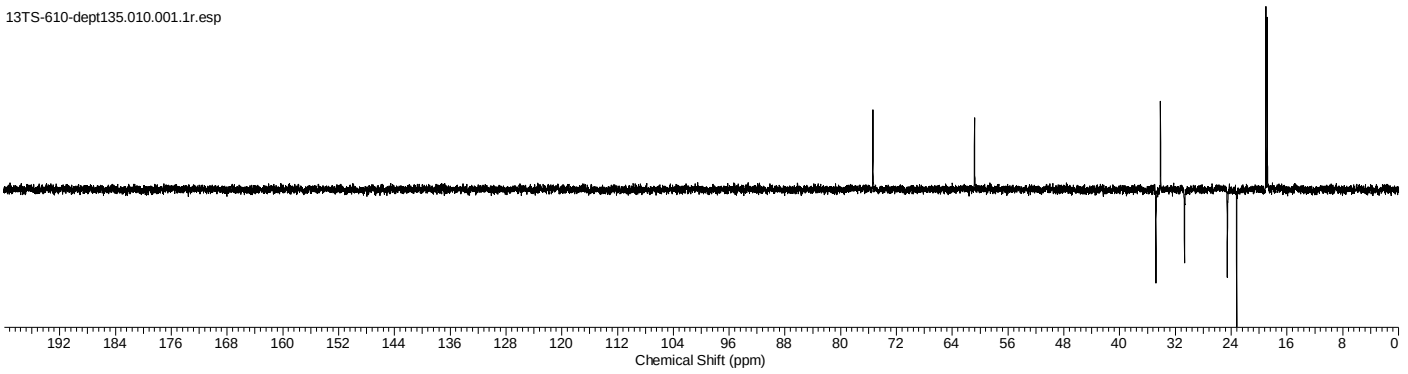


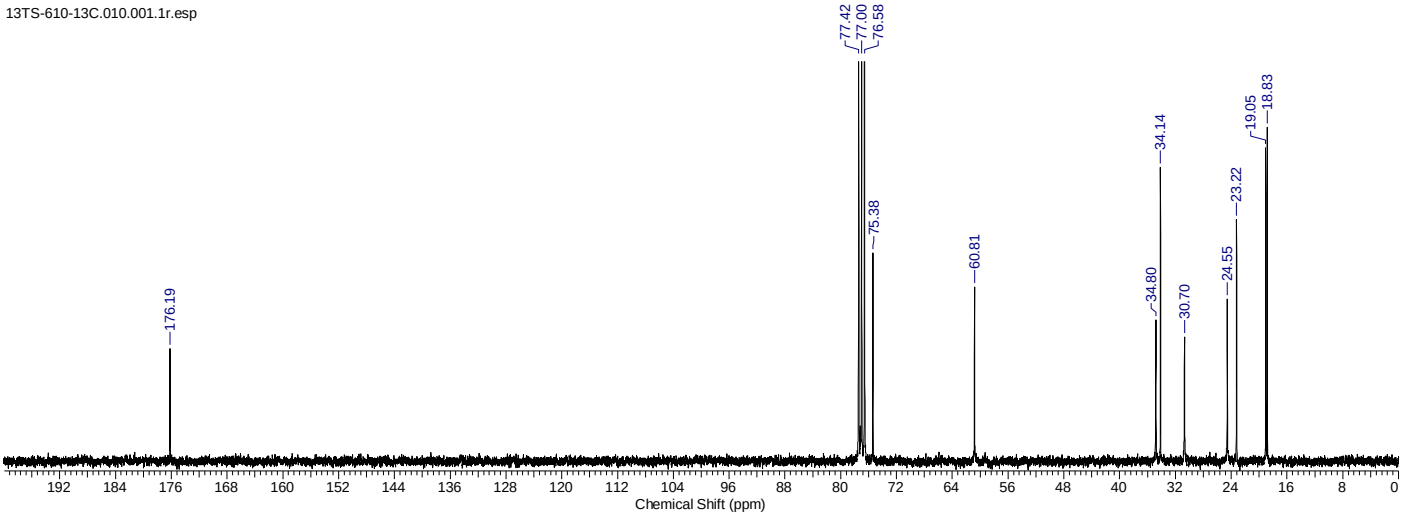




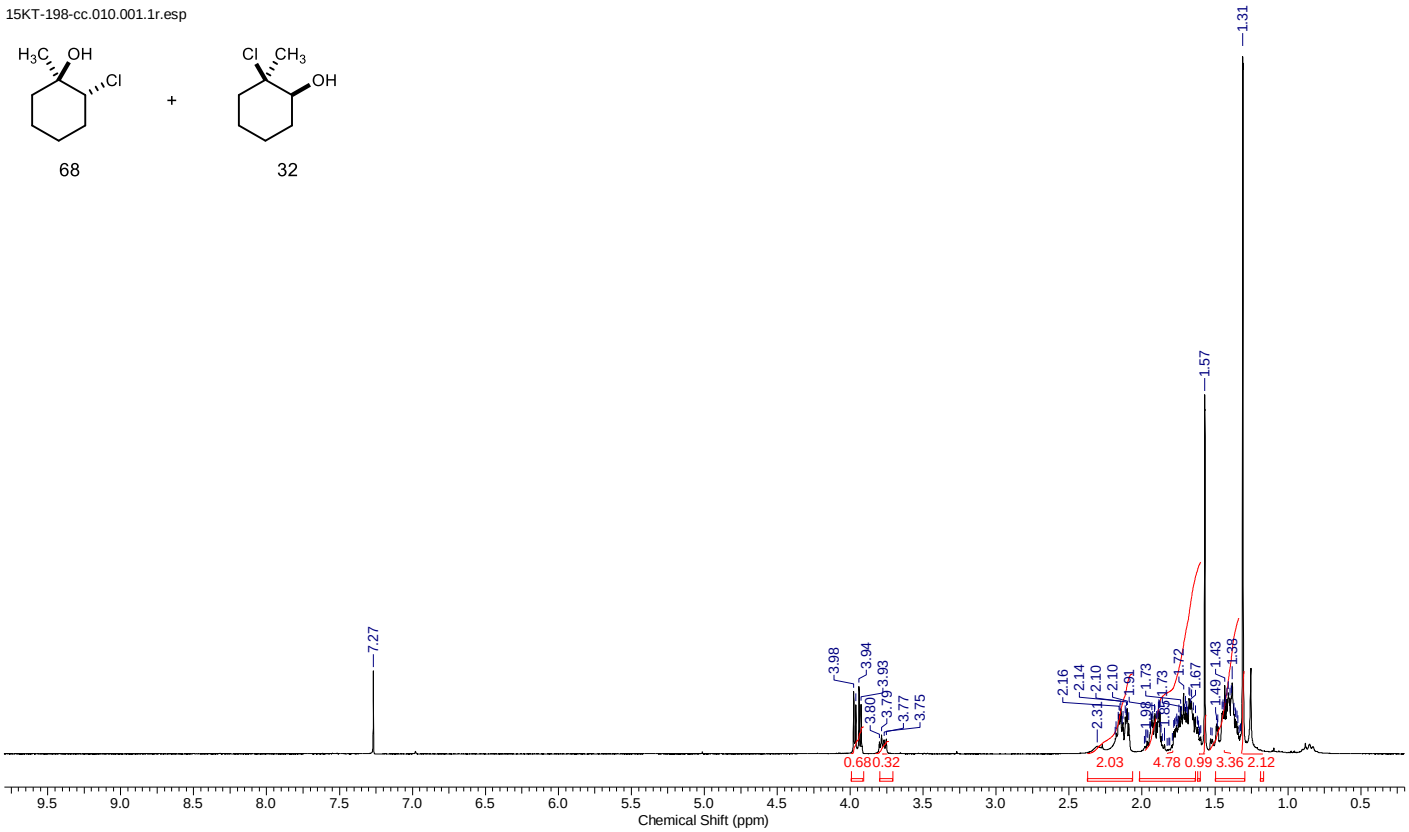
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 2-chlorocyclohexyl isobutyrate (3j-Deriv.)

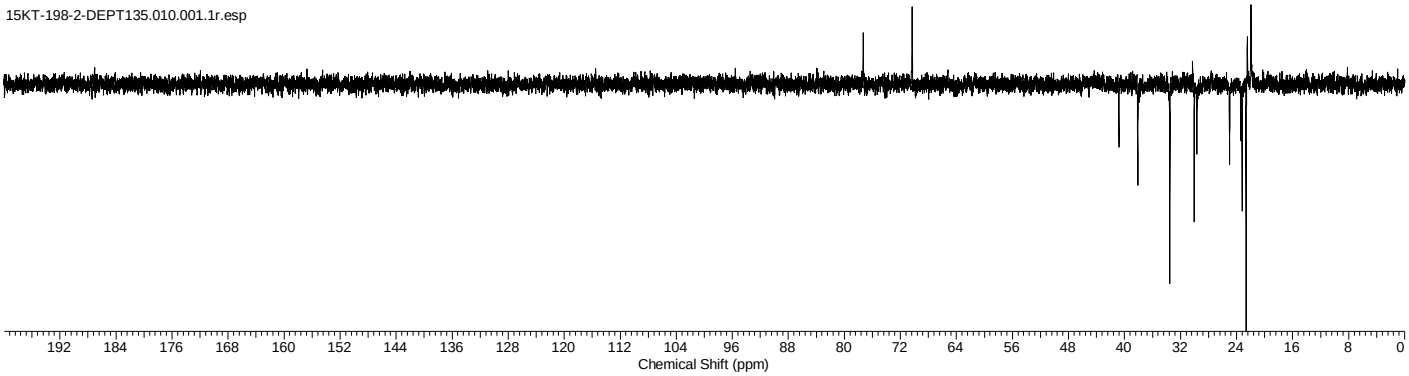


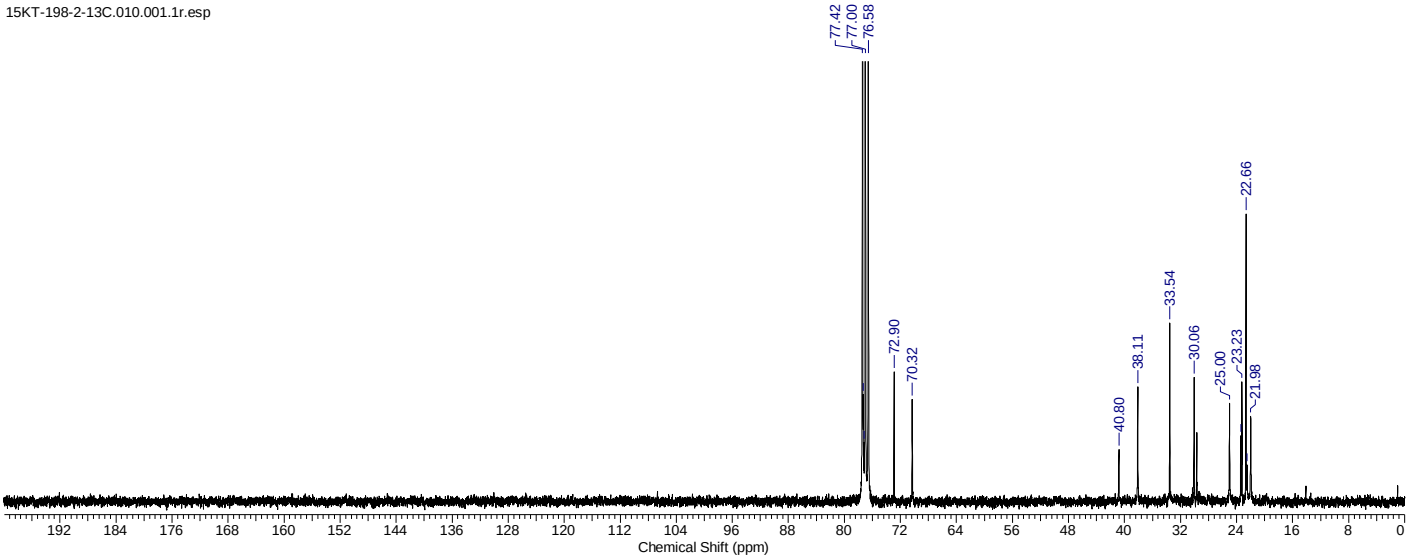




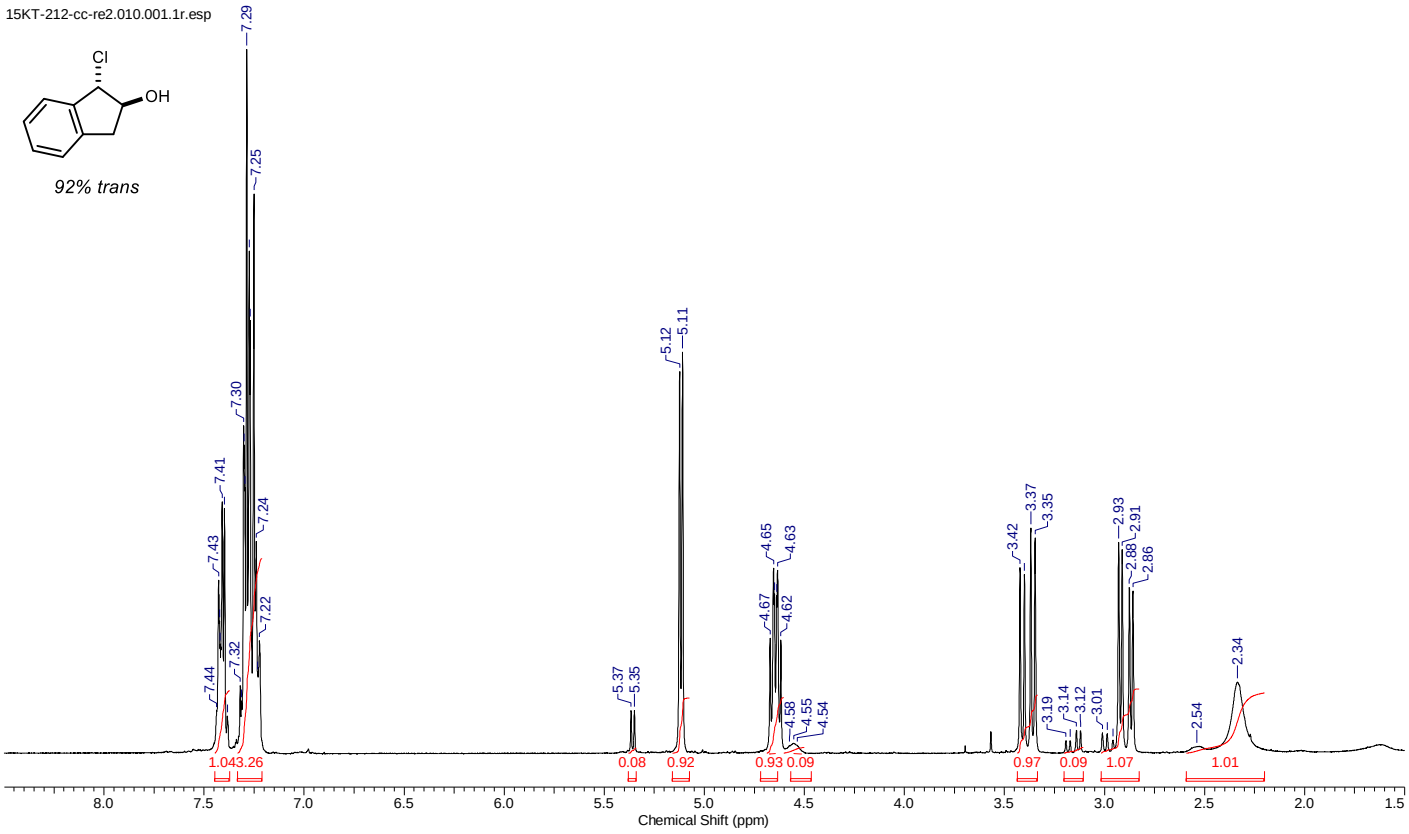
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3k/3k'

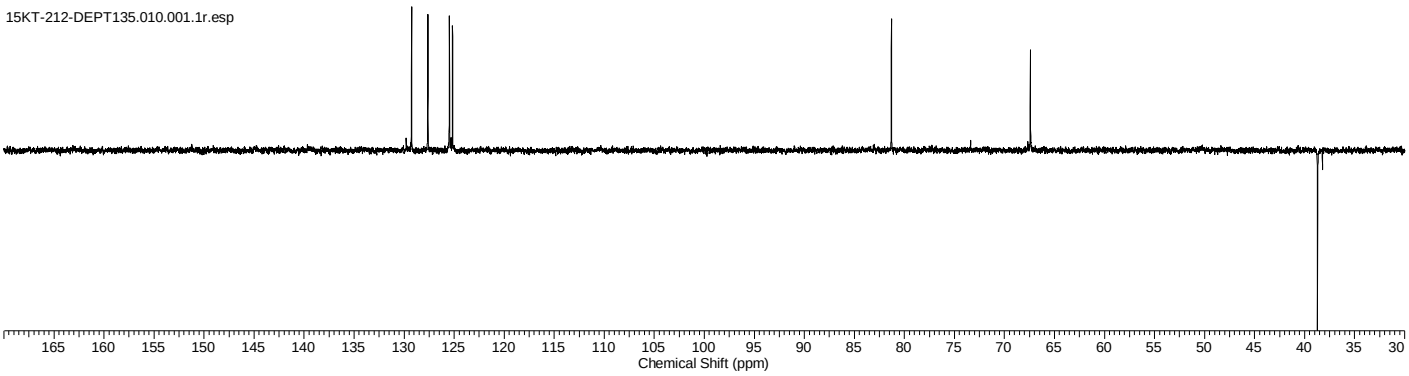


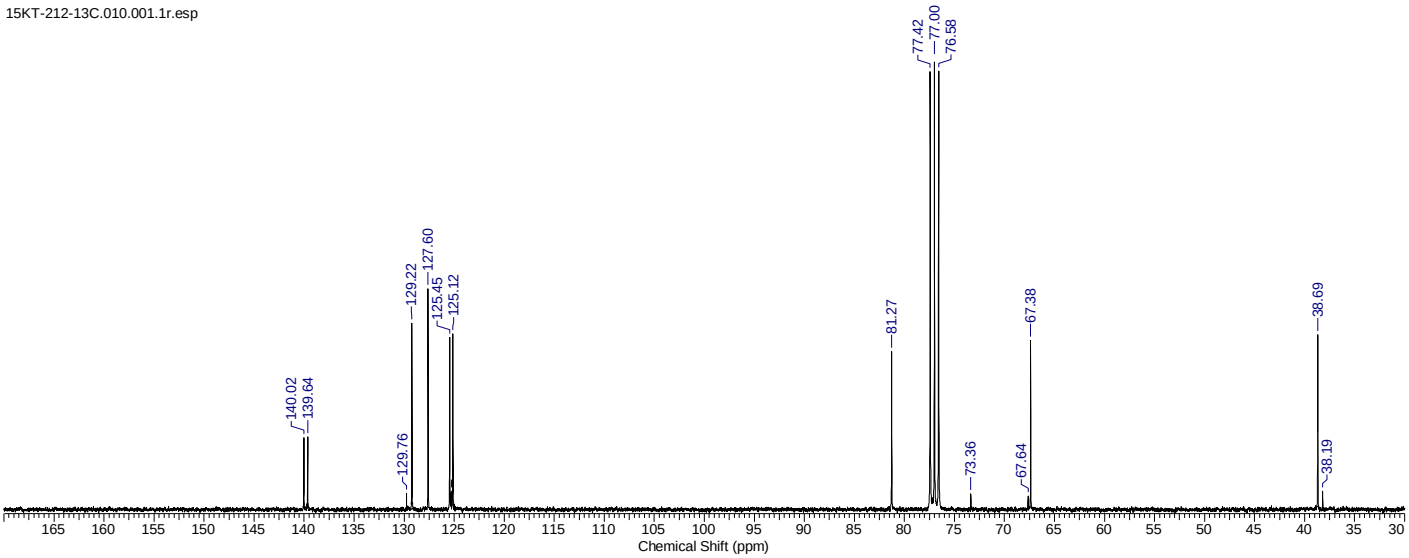




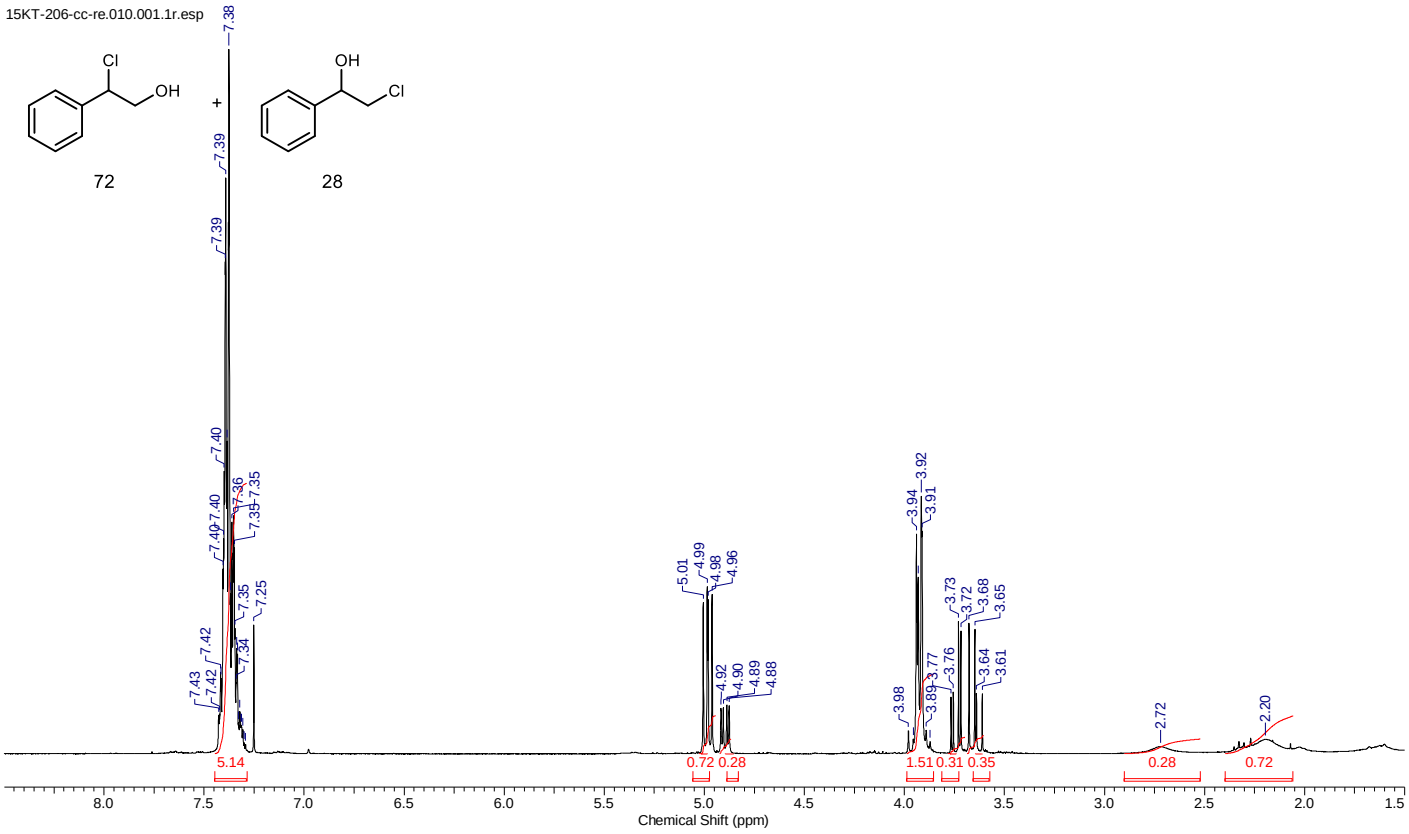
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3l

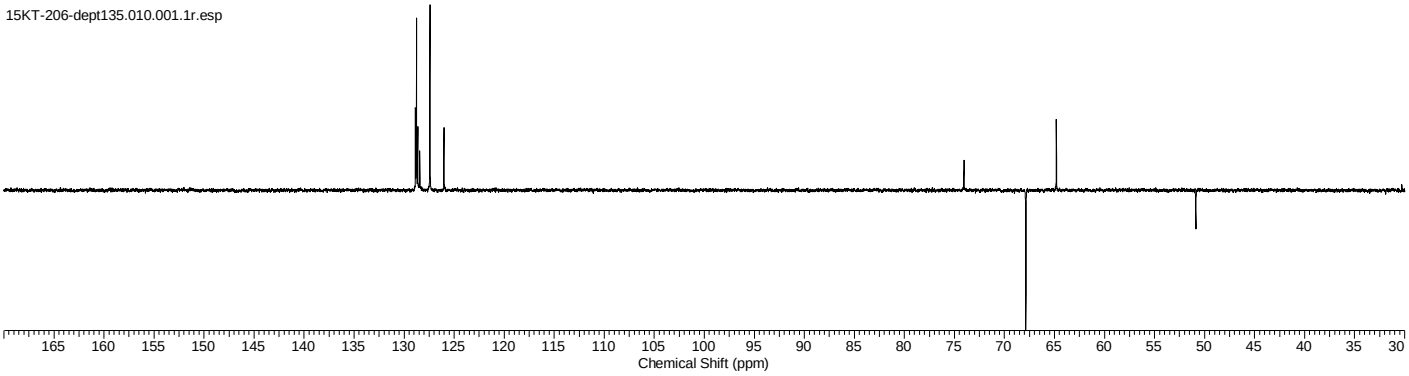


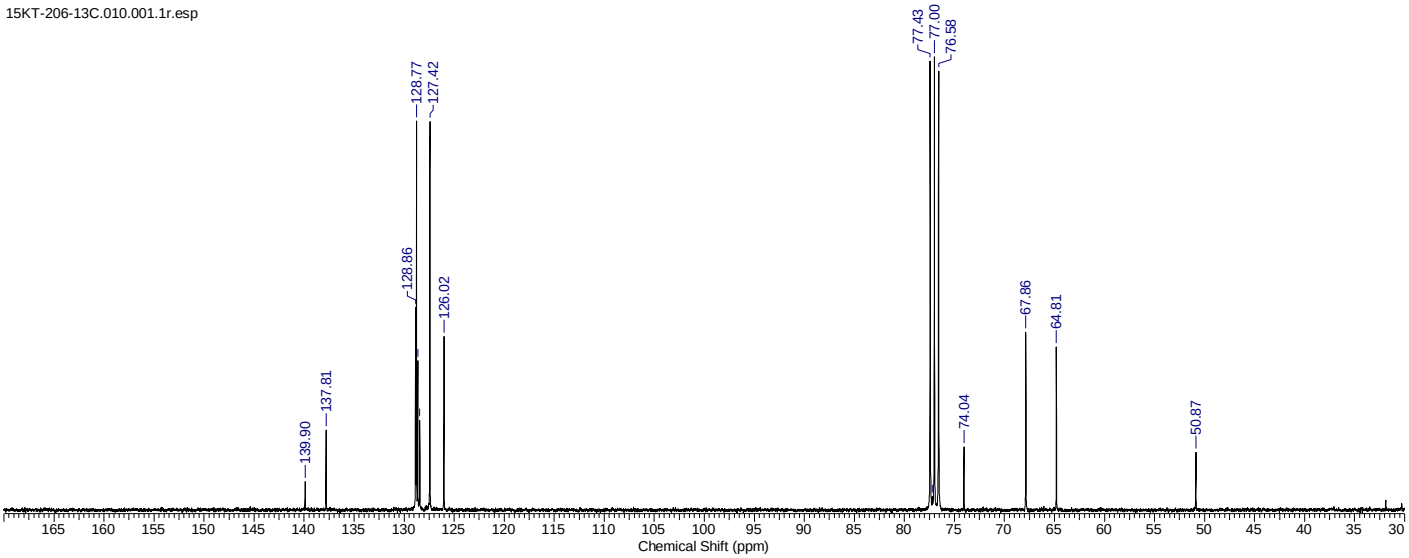




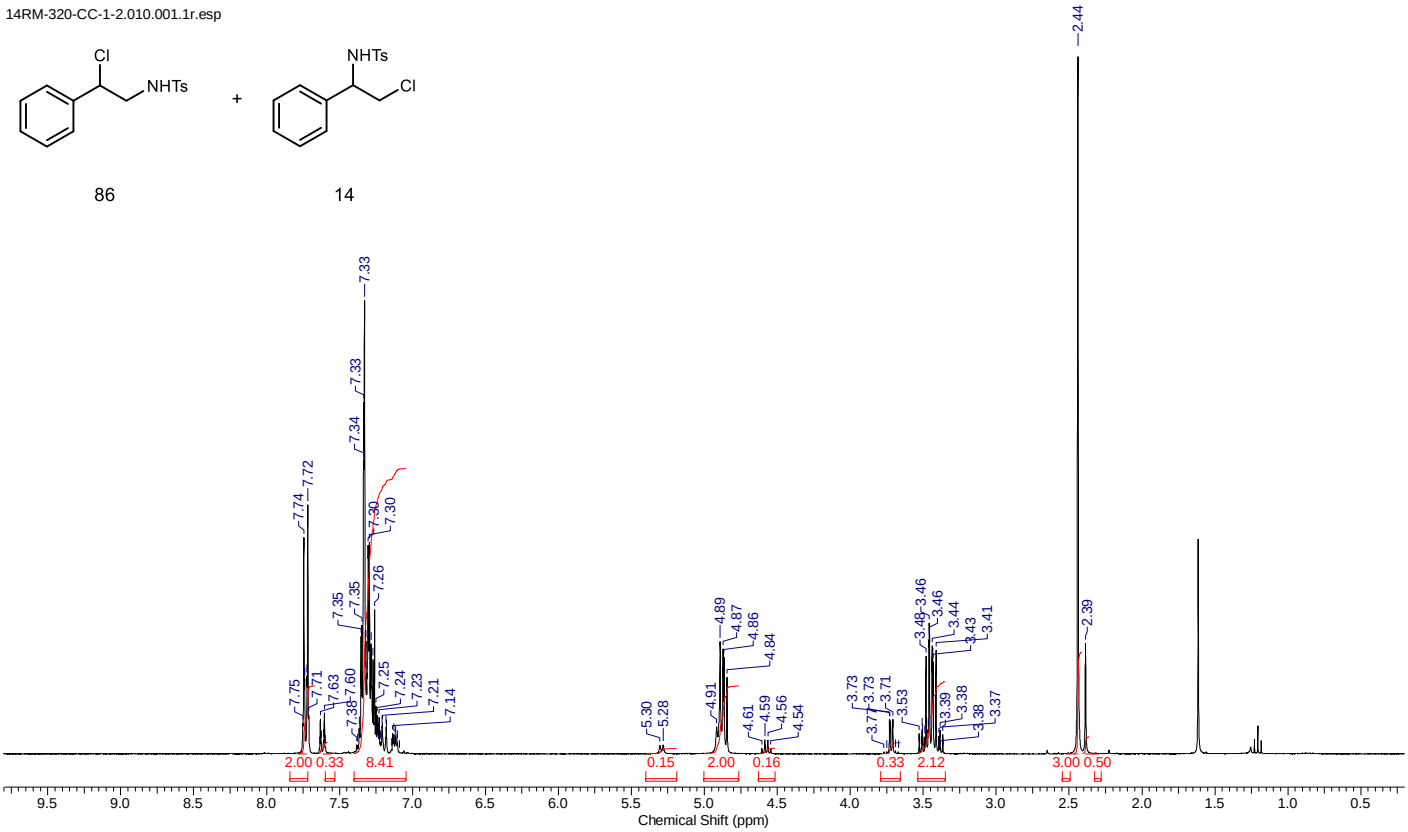
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3m

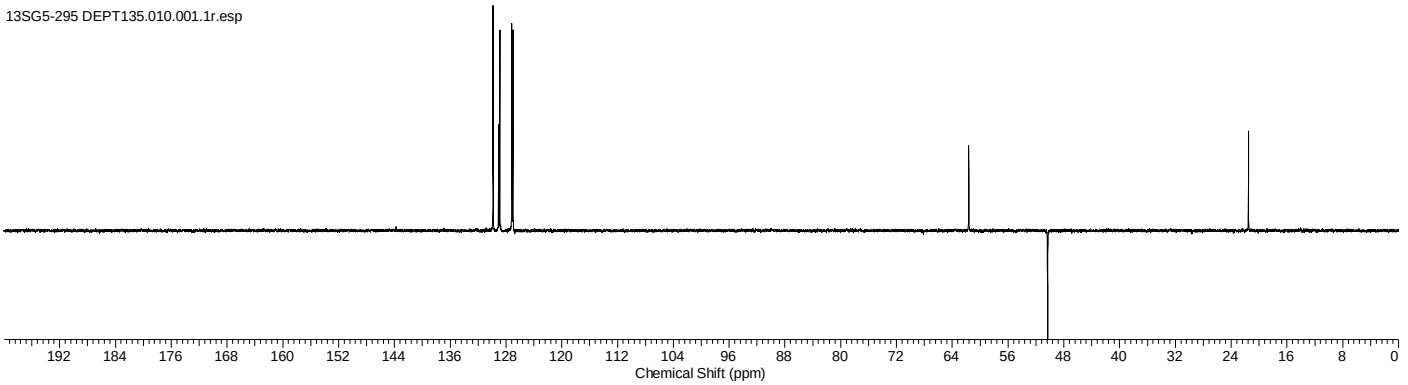


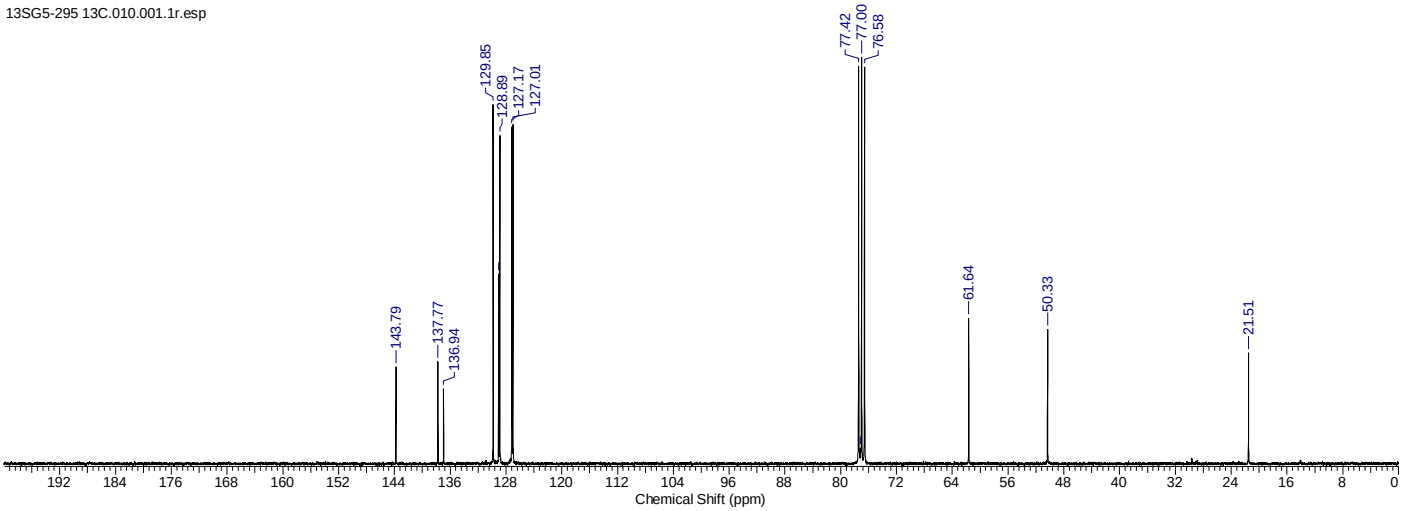




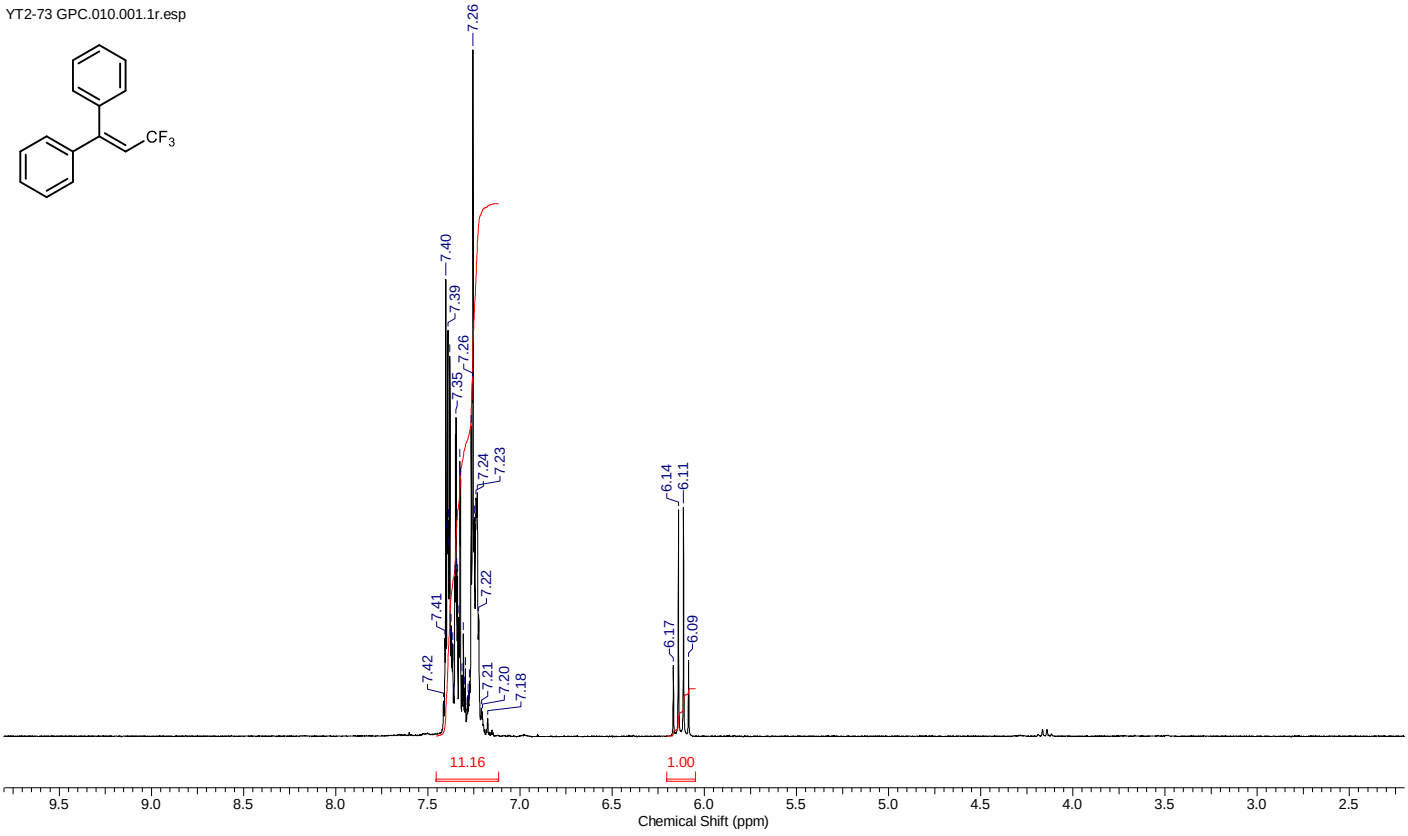
^{1}H NMR (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 3n/3n'

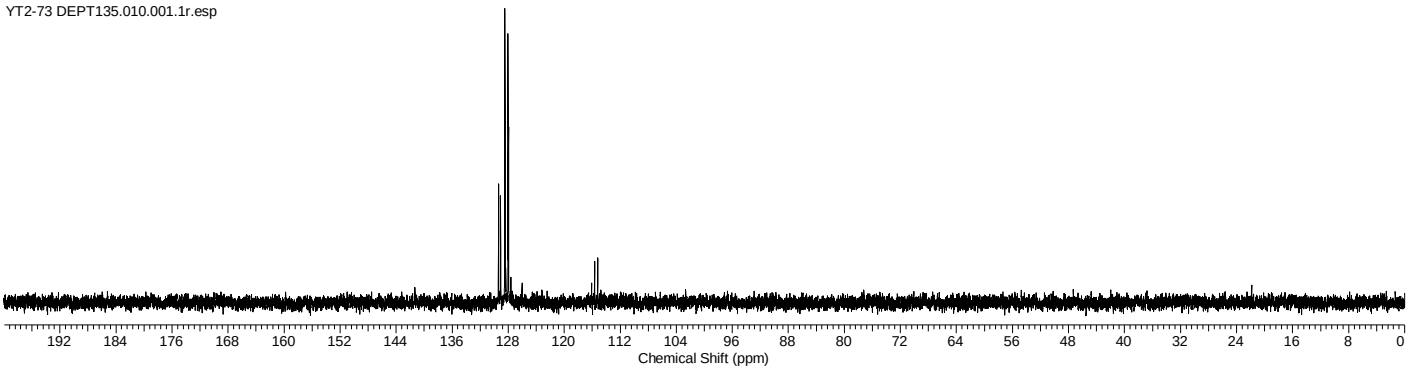


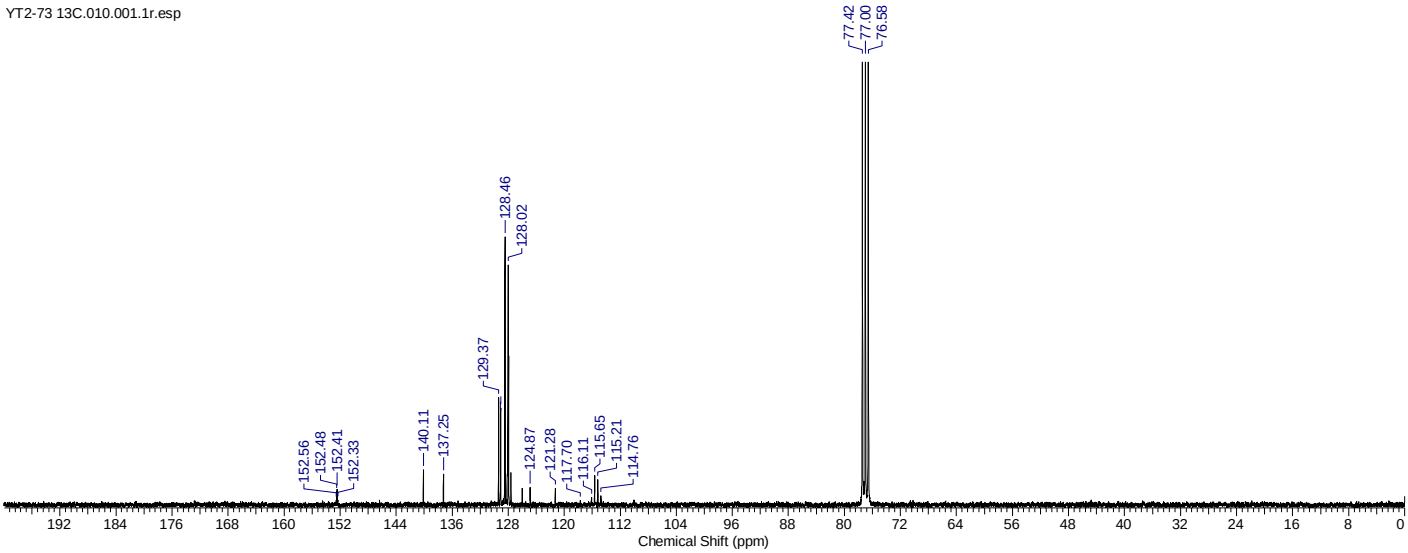




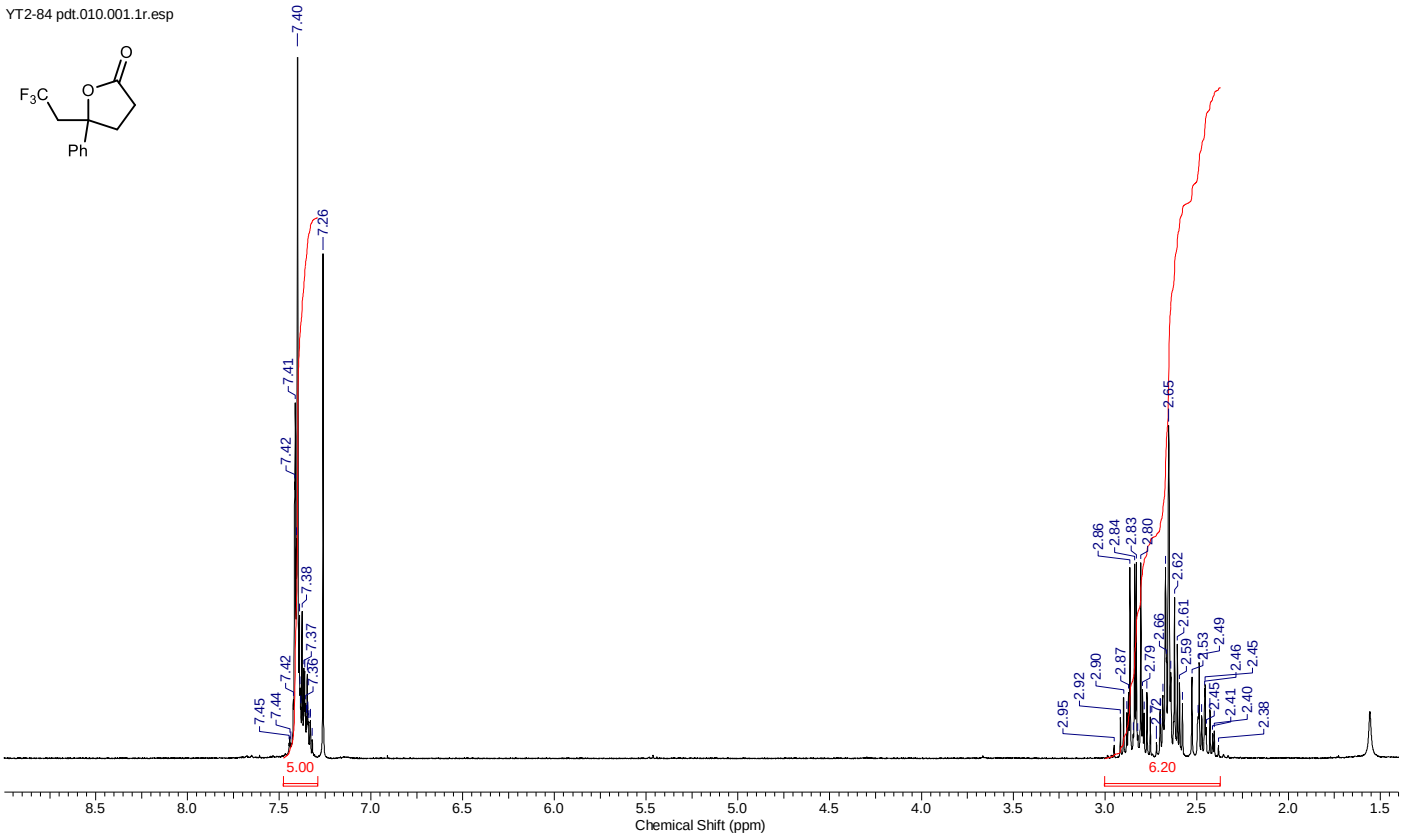
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 10

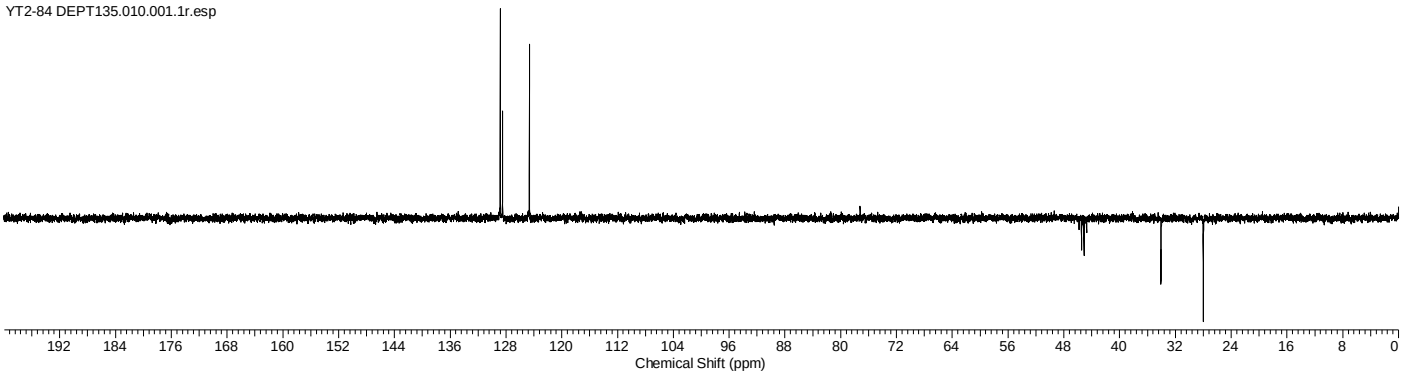


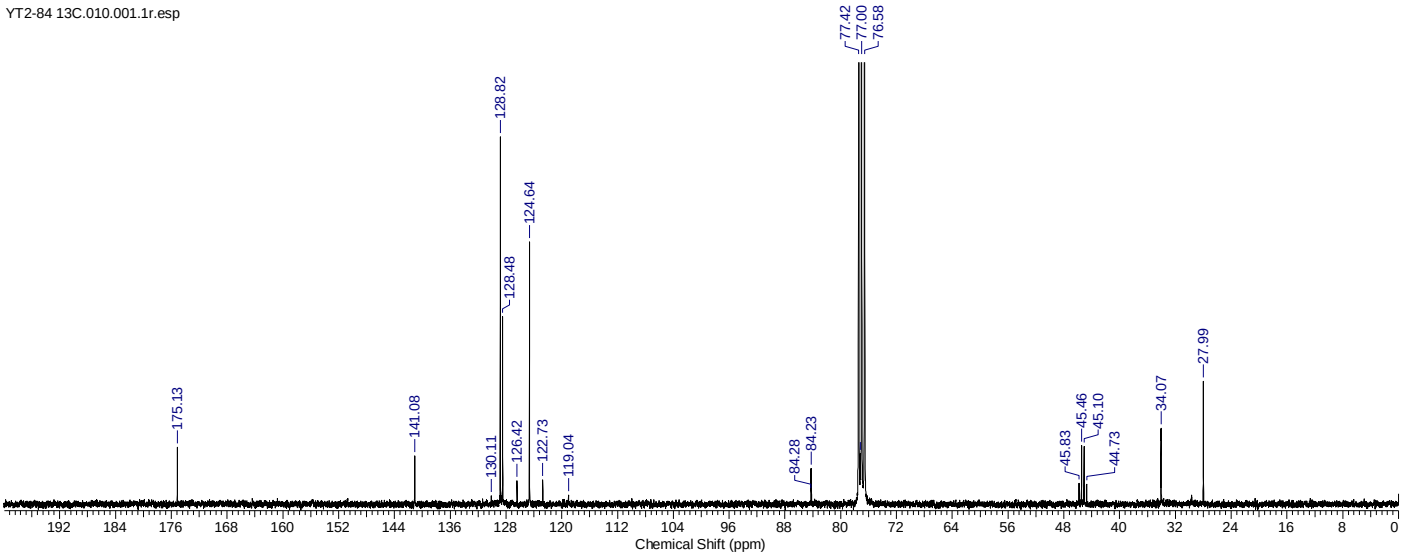




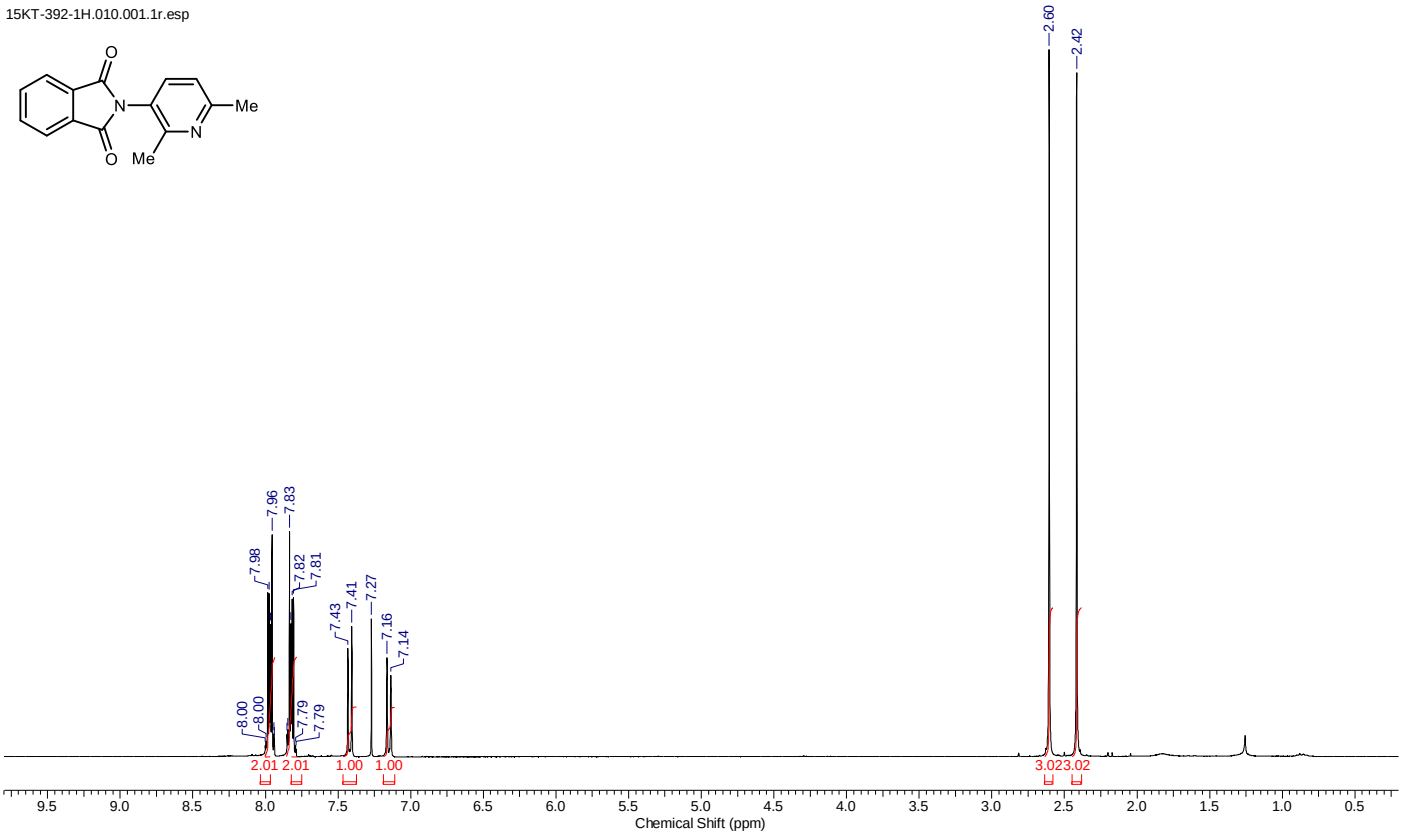
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 12

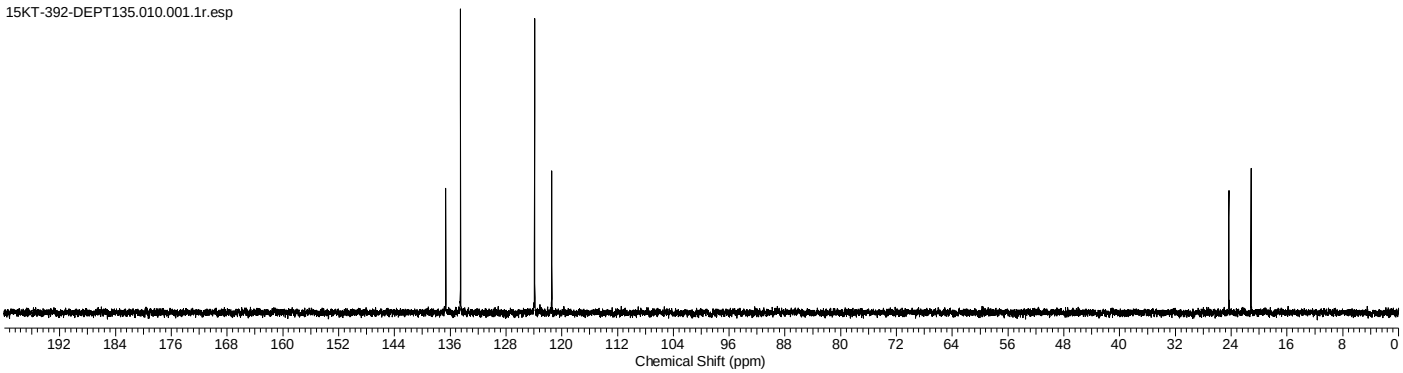


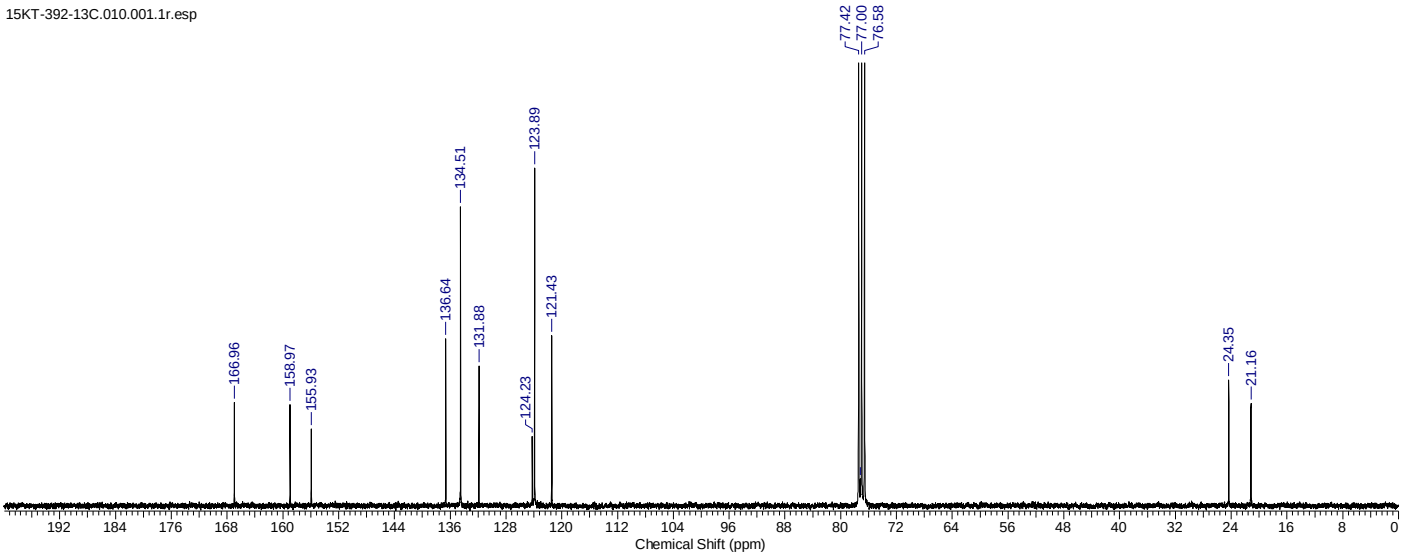




^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 15a

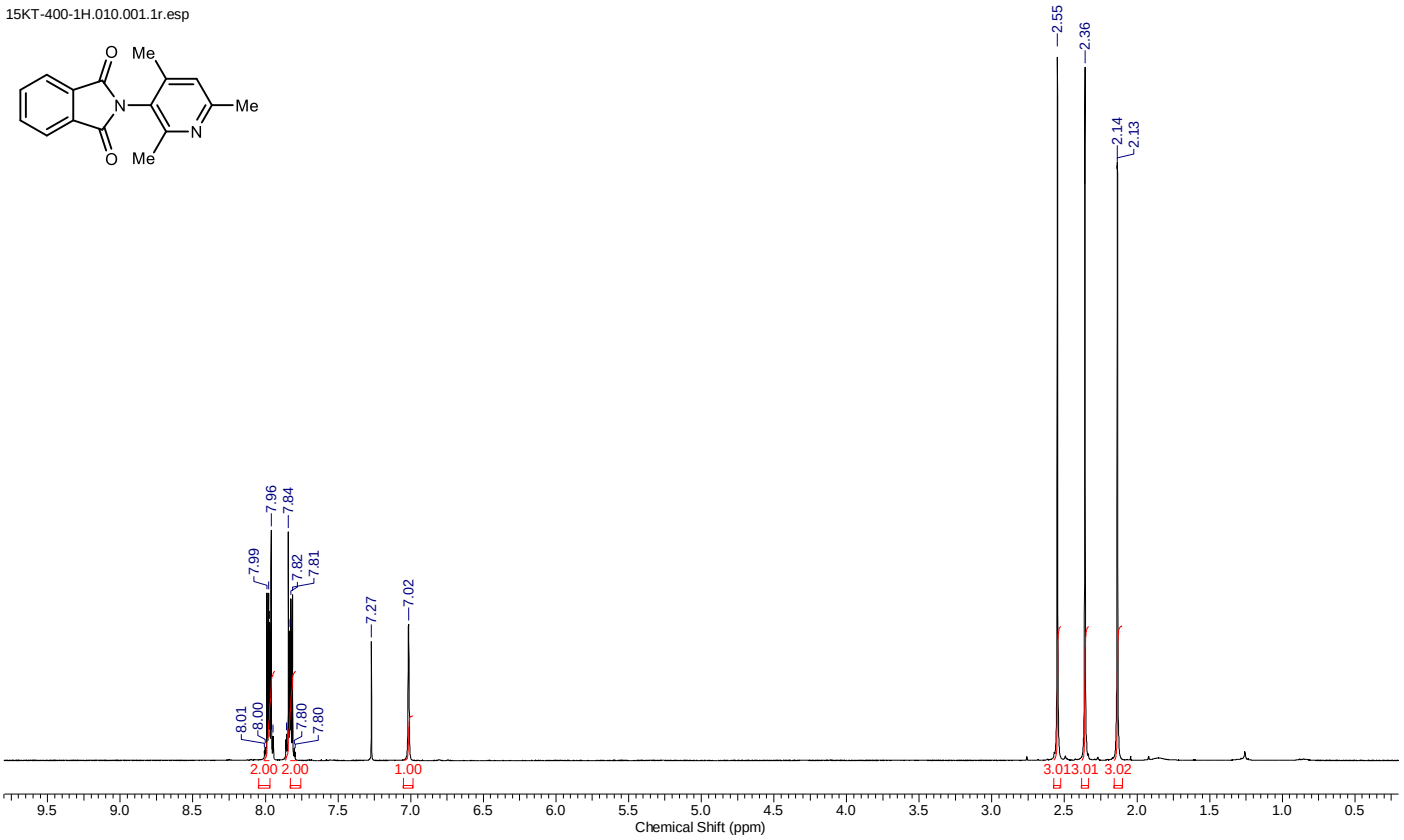






^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 15b

15KT-400-1H.010.001.1r.esp



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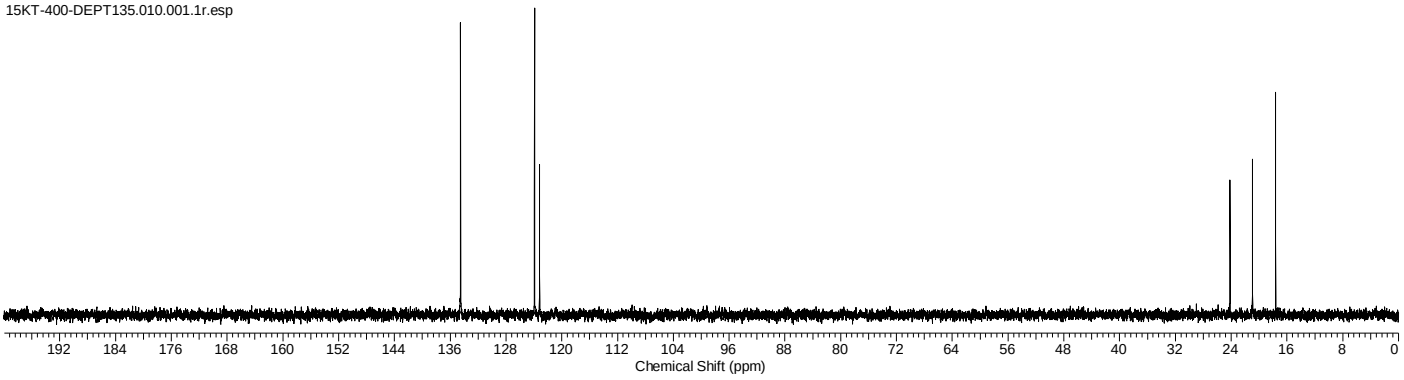

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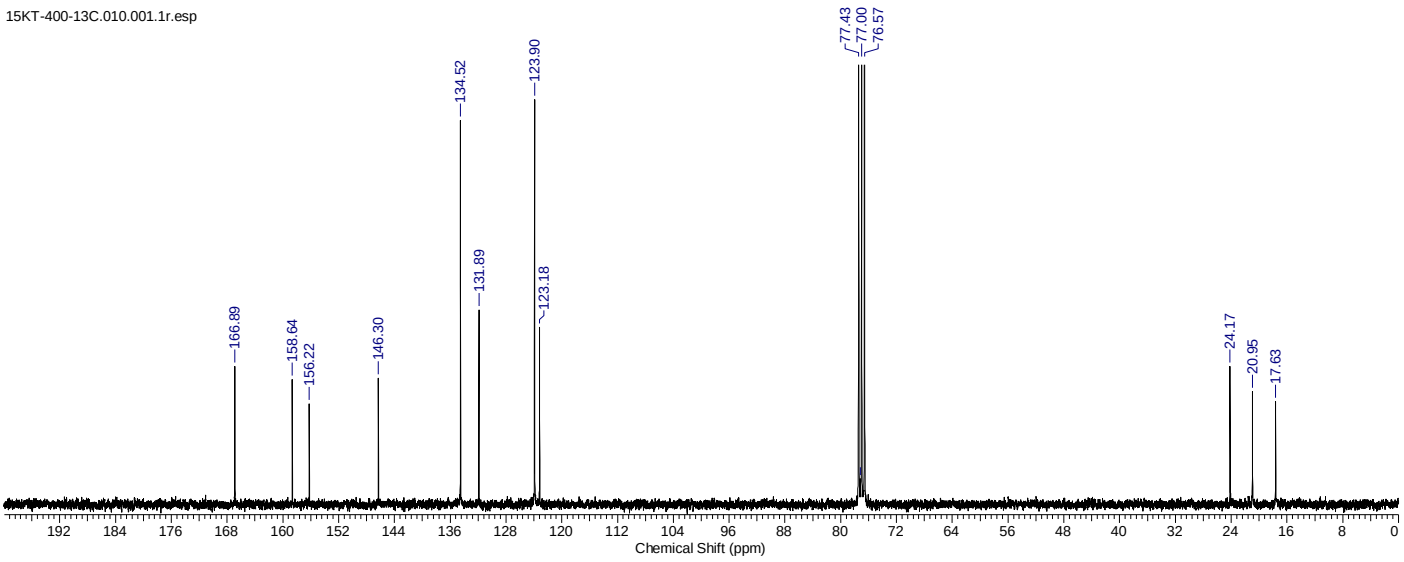

^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 15c

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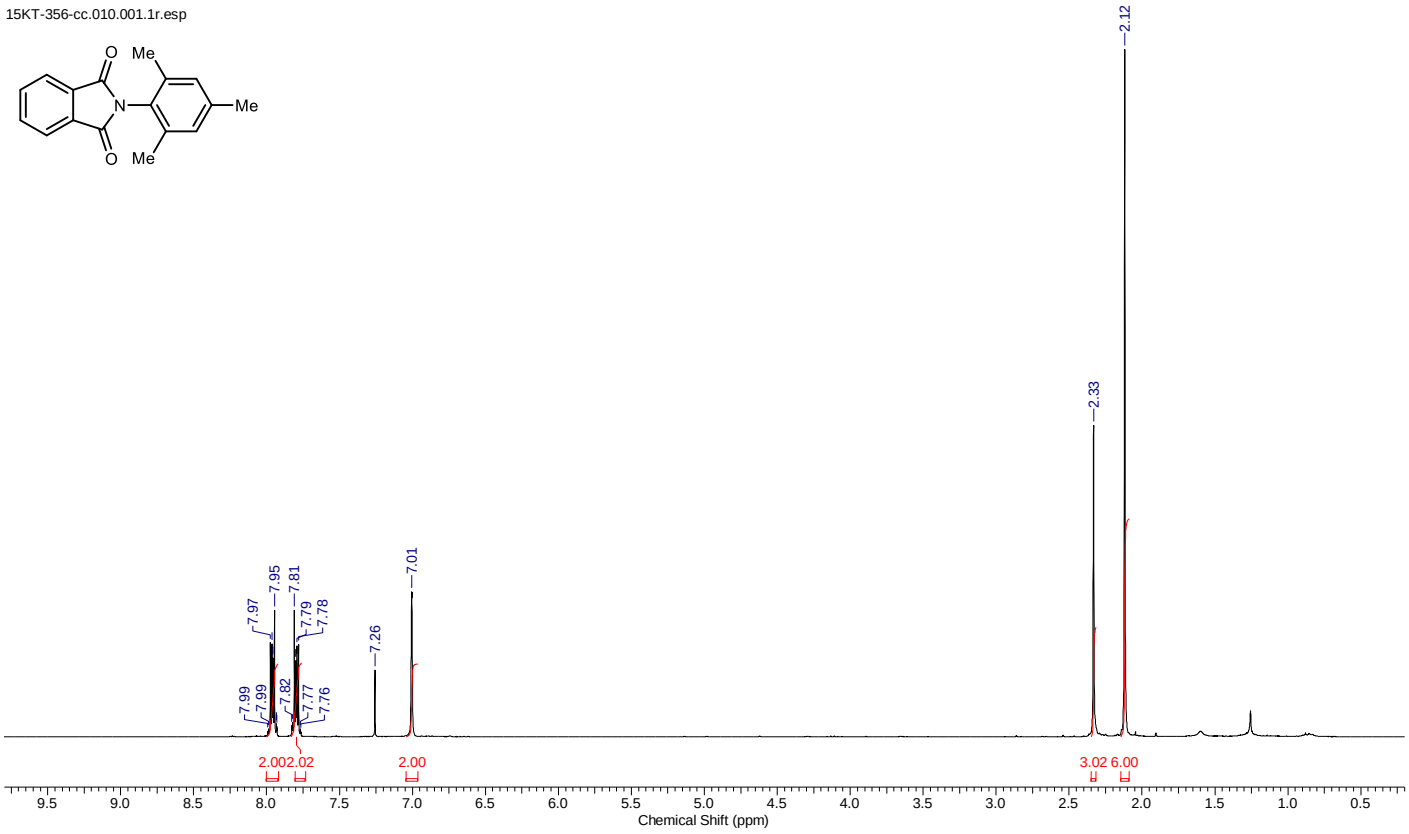

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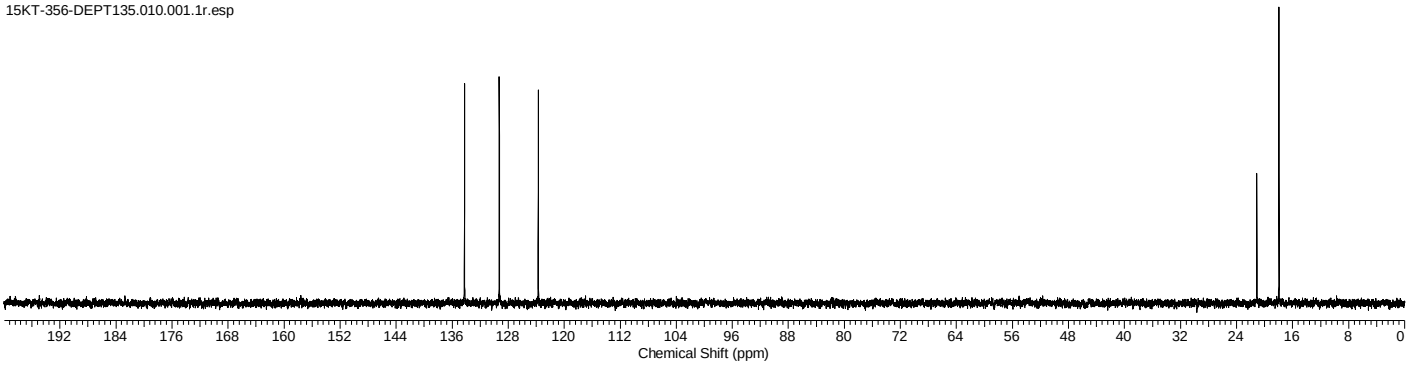

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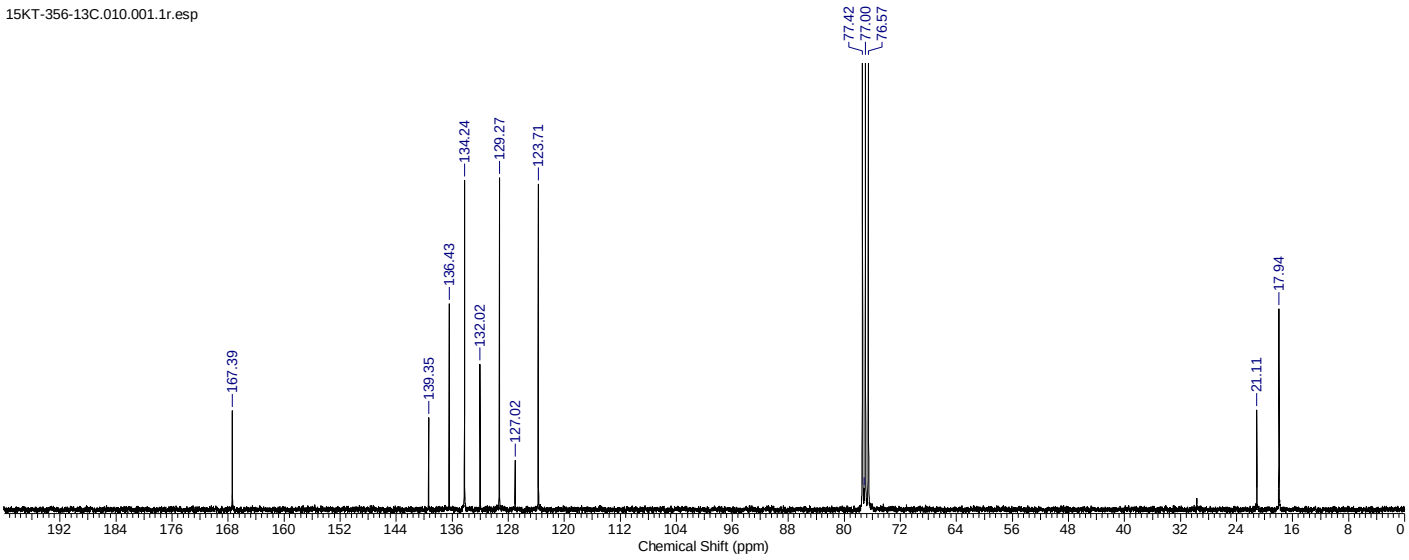
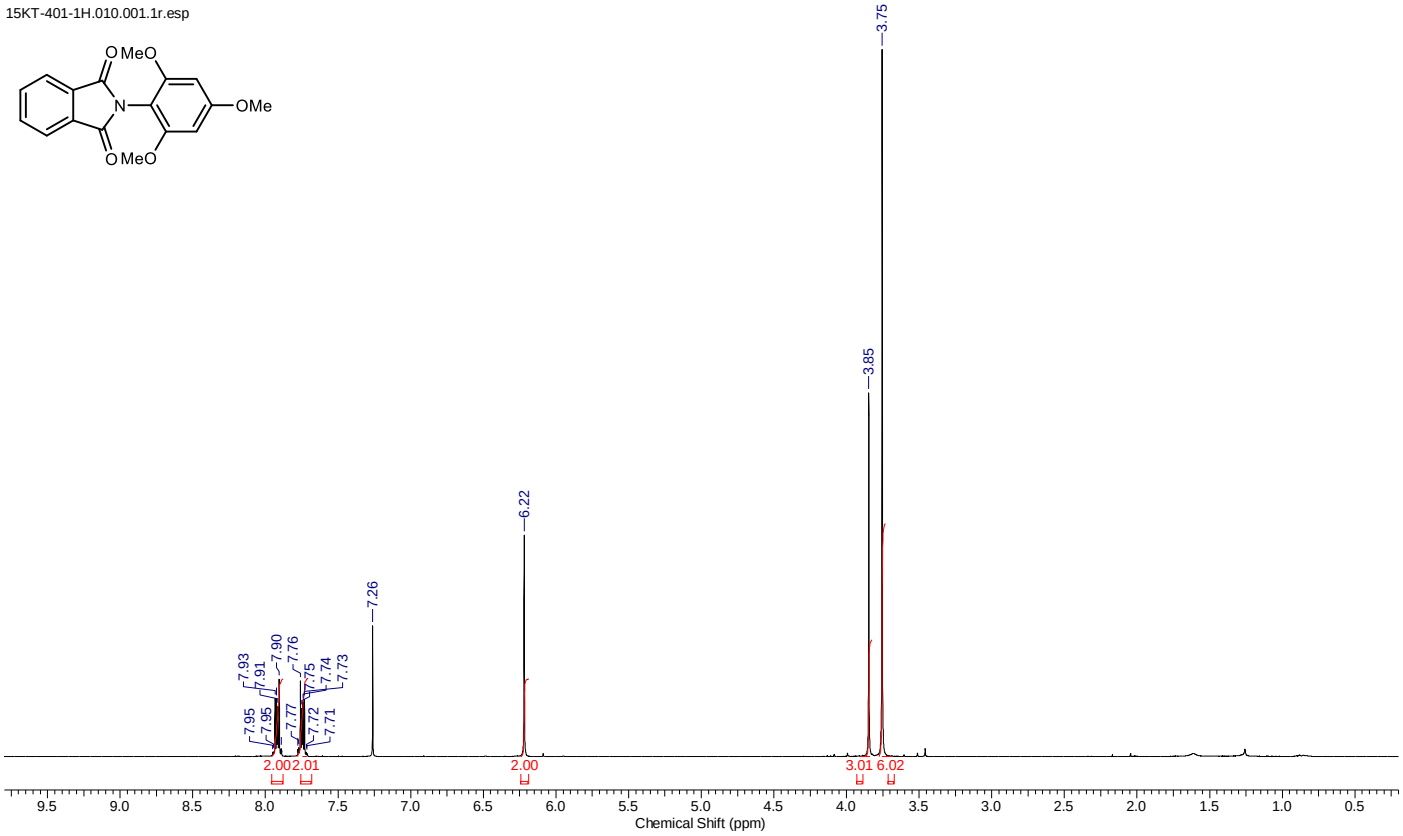
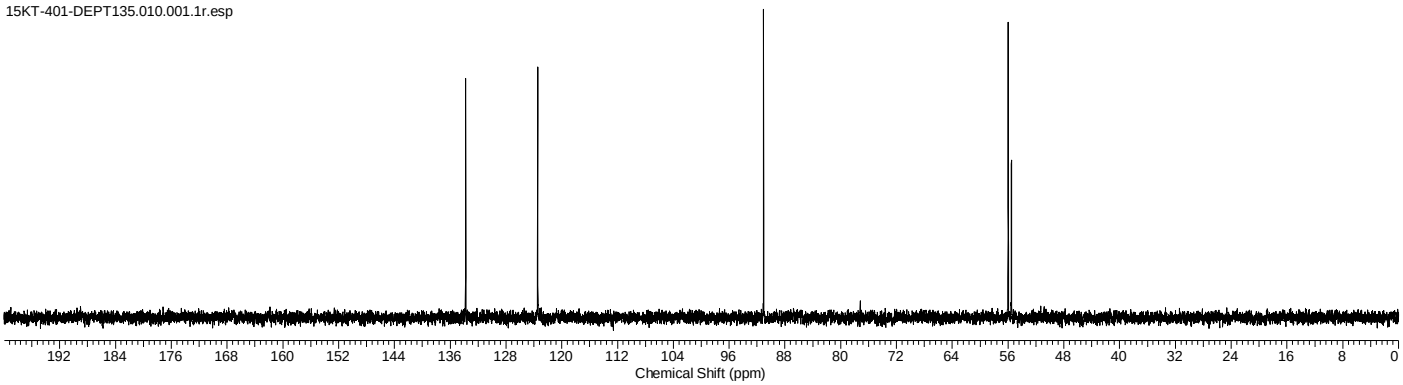
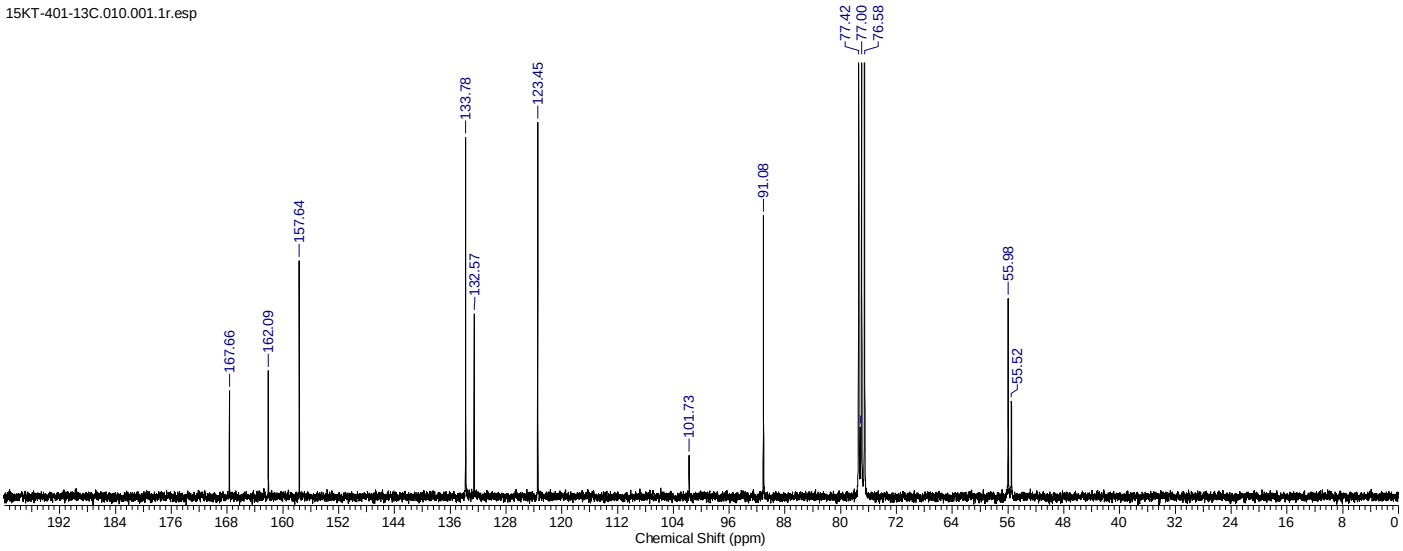


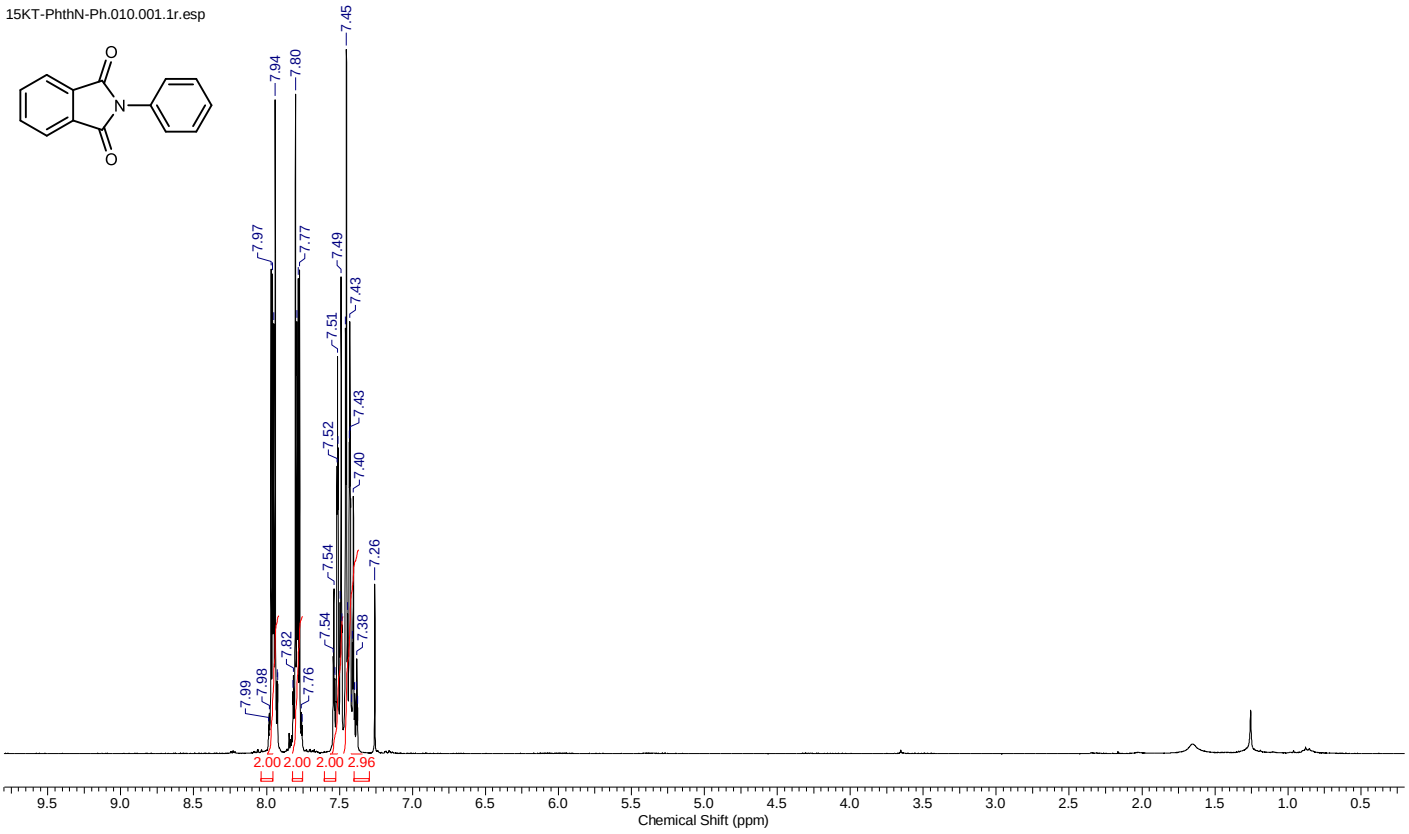
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 15d

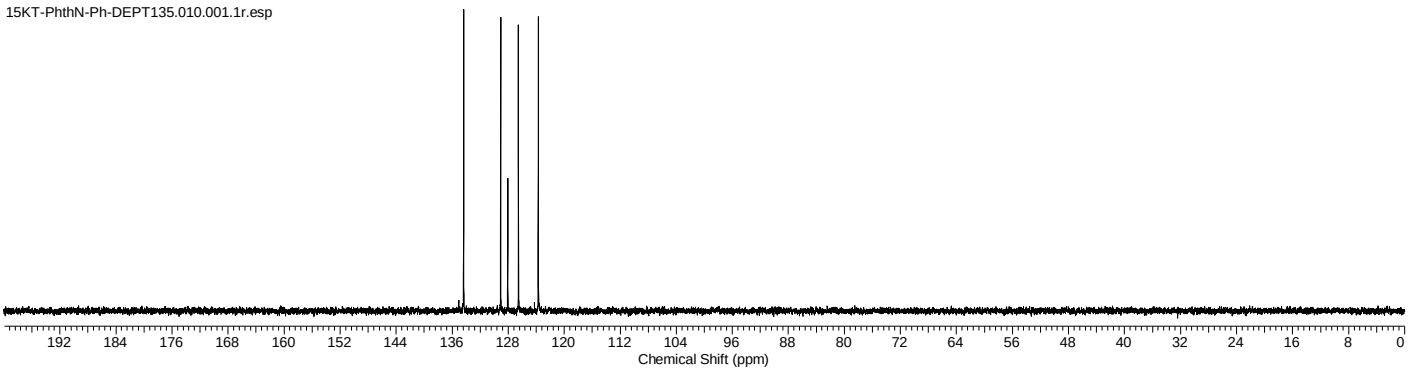


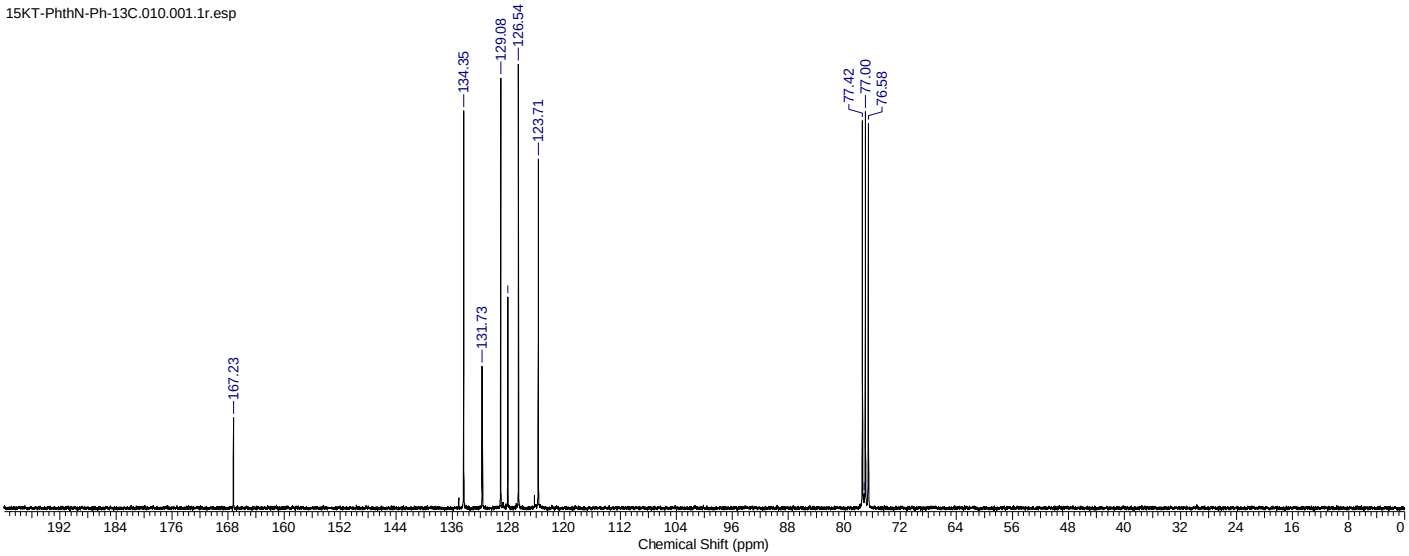




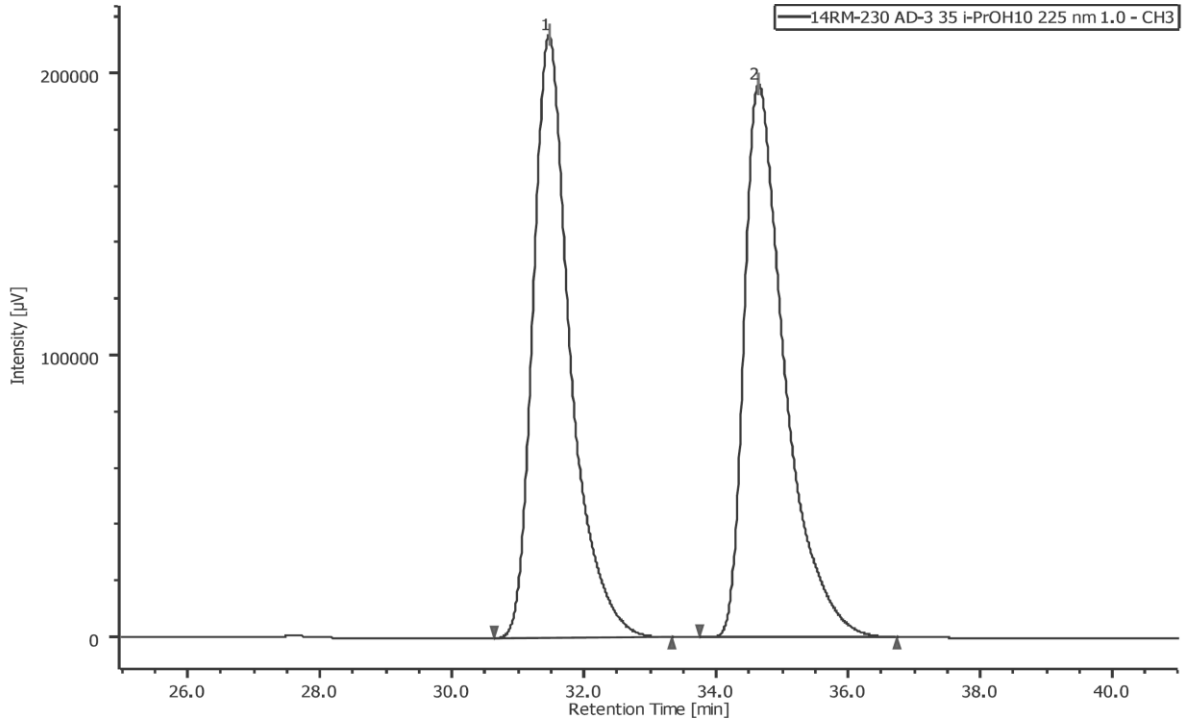
^{1}H (300 MHz, $CDCl_3$) & $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) Spectra of 15e





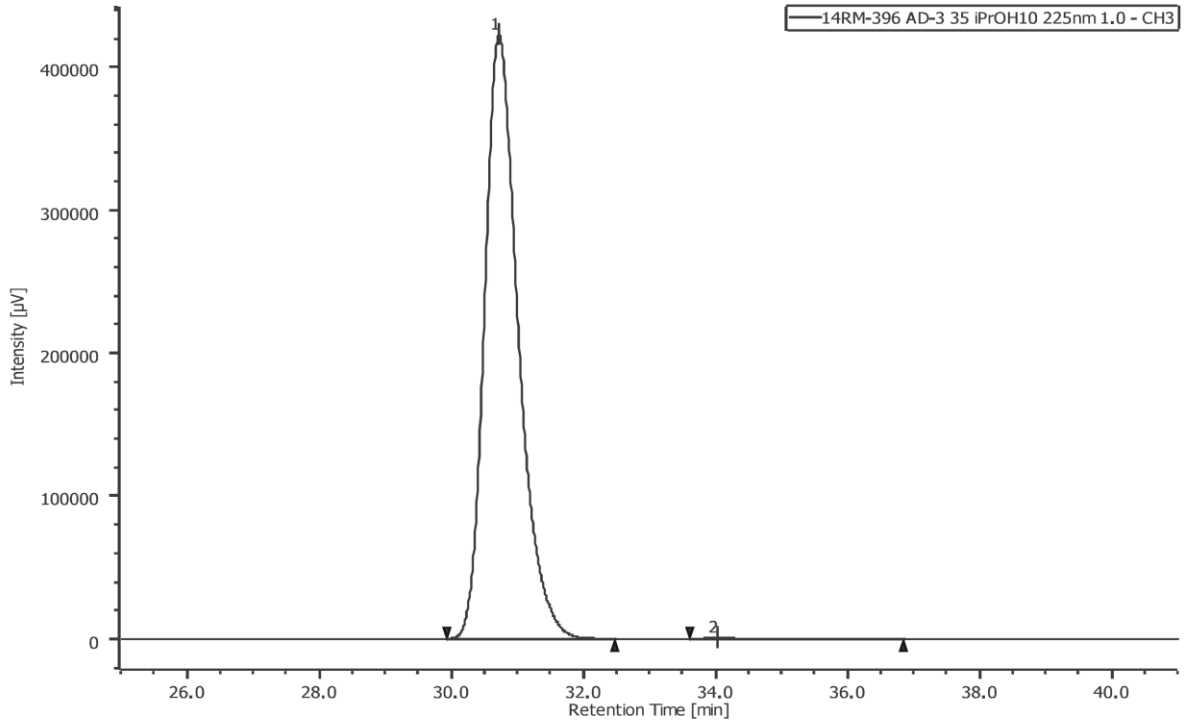


HPLC Trace of 3h



# Peak	CH	tR (min)	Area	Height	Area%
1	3	31.458	8343993	213325	49.895
2	3	34.633	8378962	195719	50.105

Racemate



# Peak	CH	tR (min)	Area	Height	Area%
1	3	30.717	14920466	421681	99.881
2	3	34.008	15443	502	0.103

99% ee

Daicel Chiralpak AD-3, hexane/iPrOH, 90/10, v/v, detector: UV 225 nm, flow rate 1.0 mL/min, 35 °C

HRMS Analysis of 6

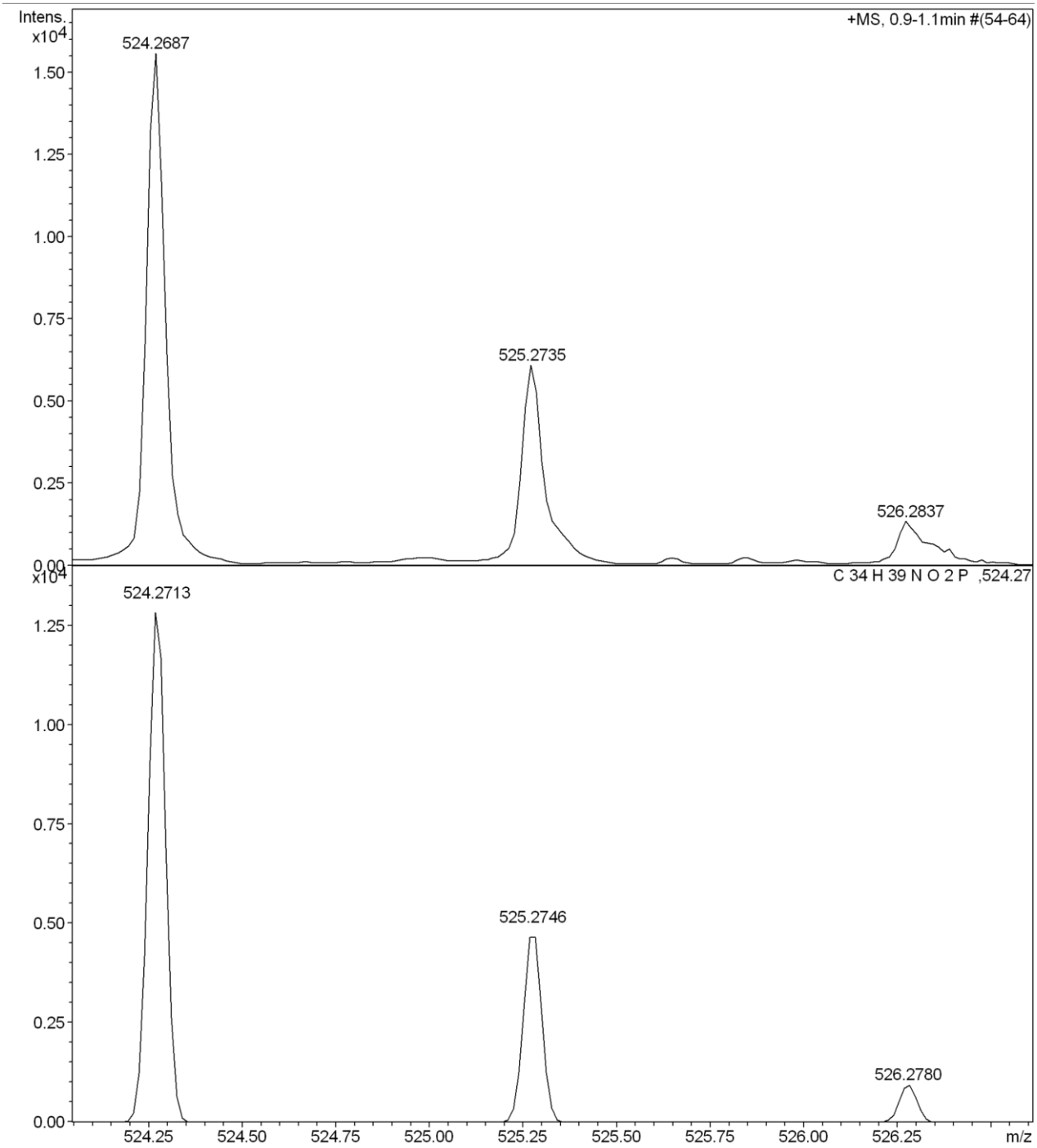
Display Report

Analysis Info

Analysis Name	D:\Data\Suga\14RM\14RM-509-CC-pos_1-1_01_446.d	Acquisition Date	3/5/2020 2:38:32 PM
Method	lcms_esi_pos_low.m	Operator	BDAL
Sample Name	14RM-509-CC-pos	Instrument / Ser#	micrOTOF 10366
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
Focus	Not active			Set Dry Heater	200 °C
Scan Begin	50 m/z	Set Capillary	4500 V	Set Dry Gas	8.0 l/min
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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HRMS Analysis of 7

Display Report

Analysis Info

Analysis Name	D:\Data\Suga\14RM\14RM-509-CC-pos_1-1_01_446.d	Acquisition Date	3/5/2020 2:38:32 PM
Method	lcms_esi_pos_low.m	Operator	BDAL
Sample Name	14RM-509-CC-pos	Instrument / Ser#	micrOTOF 10366
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	1.6 Bar
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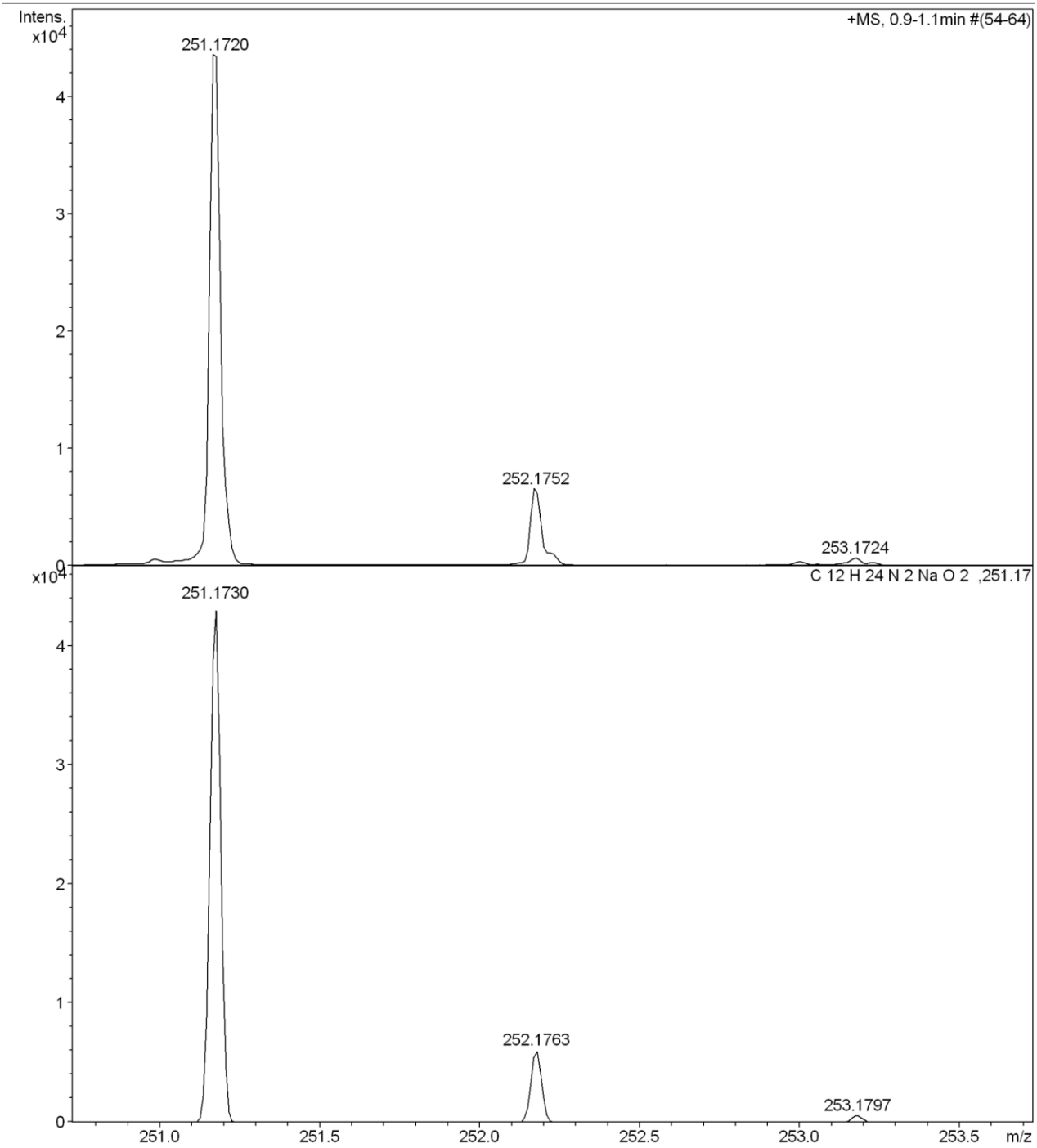
Scan End	3000 m/z	Set End Plate Offset	-500 V	Set Divert Valve	Waste



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