Electronic Supplementary Material (ESI) for ChemComm.

Application of Coumarin Dyes for Organic Photoredox Catalysis.

Andrea Gualandi,*[a] Giacomo Rodeghiero,[a,b] Francesco Bertoni,[a] Emanuele Della Rocca,[a] Rossana Pierciaccante,[b] Thomas Paul Jansen,[b] Marianna Marchini,[a,c] Paola Ceroni,[a,c] and Pier Giorgio Cozzi*[b]

Table of Content

Experimental Procedures

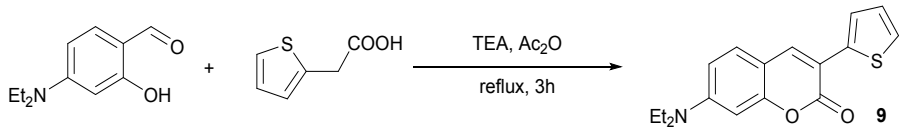
General methods and materials

^{1}H NMR spectra were recorded on Varian Mercury 400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent resonance as the internal standard (deuterochloroform: δ = 7.27 ppm; dimethyl sulfoxide-d_6: δ = 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = duplet, t = triplet, q = quartet, dd = double duplet, dt = double triplet, bs = broad signal, m = multiplet, quint = quintet), coupling constants (Hz). ^{13}C NMR spectra were recorded on Varian MR400 spectrometer. Chemical shifts are reported in ppm from TMS with the solvent as the internal standard (deuterochloroform: δ = 77.0 ppm; dimethyl sulfoxide-d_6: δ = 39.5 ppm). LC-electrospray ionization mass spectra (ESI-MS) were obtained with Agilent Technologies MSD1100 single-quadrupole mass spectrometer. Chromatographic purification was done with 240-400 mesh silica gel. Purification on preparative thin layer chromatography was done on Merck TLC silica gel 60 F_{254}.

All reactions were set up under an argon atmosphere in oven-dried glassware using standard Schlenk techniques. Synthesis grade solvents were used as purchased and the reaction mixtures were degassed by four cycles of freeze-pump-thaw.

Coumarins **8** was prepared according to literature procedure.[1]

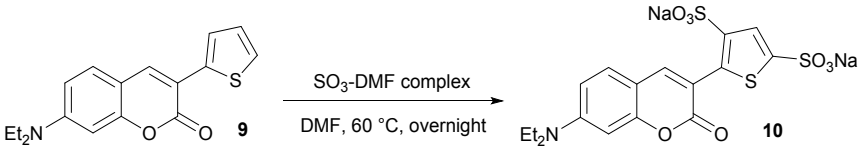
Synthesis of coumarin 9



In a one necked round bottom flask (50 mL) equipped with magnetic stirring bar, condenser and glass stoppers, thiophene acetic acid (5.5 mmol, 0.780 mg), 4-(diethylamino)-salicylaldehyde (8.5 mmol, 1.64 g) were dissolved in acetic anhydride (20 mL). Triethylamine (10.5 mmol, 1.46 mL) was added and the mixture was stirred at reflux for three hours. The reaction was cooled down at room temperature, water was added, the organic material was extracted with AcOEt (3 x 50 mL) and the organic layers were dried over Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, cyclohexane to cyclohexane/ethyl acetate, 7/3) to afford **9** as yellow solid (46%, 2.5 mmol, 0.760 g). Spectroscopic properties were according to those reported in literature.[2]

^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.85 (s, 1H), 7.64 (dd, *J* = 1.1, 3.7 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.07 (dd, *J* = 3.7, 5.1 Hz, 1H), 6.58 (dd, *J* = 2.5, 8.9 Hz, 1H), 6.50 (d, *J* = 2.3 Hz, 1H), 3.40 (q, *J* = 7.1 Hz, 4H), 1.20 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 160.6, 155.6, 150.6, 137.6, 136.9, 128.9, 127.3, 125.6, 124.8, 114.8, 109.3, 108.8, 97.1, 44.9 (2C), 12.6 (2C).

Synthesis of coumarin 10

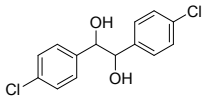


Coumarin **10** was prepared following reported procedure on coumarin **9**.[3] A two necked round bottom flask (100 mL) equipped with stirring bar, glass stopper and vacuum adapter was flame dried under an Argon atmosphere. The flask was charged with **9** (1.2 mmol, 0.360 g) and dissolved in anhydrous N,N-dimethylformamide (30 mL). Sulfur trioxide N,N-dimethylformamide complex (48 mmol, 7.3 g) was added and the reaction mixture was stirred overnight at 60°C under Argon, then cooled to room temperature. Diethyl ether (400 mL) was slowly added under stirring. Two phases were formed: the viscous oil was decanted, and the upper layer was removed. The viscous oil was taken up in aqueous saturated $NaHCO_3$ (10 mL) and purified by reverse phase chromatography (elution gradient: water to water/acetonitrile 8/2) to give the product as a yellow solid (33%, 0.4 mmol, 0.200 g).

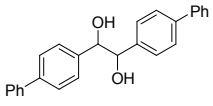
^{1}H NMR (400 MHz, D_2O, 25°C): δ = 8.10 (s, 1H), 7.69 (s, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.46 (s, 1H), 3.38 (q, *J* = 6.9 Hz, 5H), 1.14 (t, *J* = 7.0 Hz, 7H); ^{13}C NMR (100 MHz, D_2O, 25°C): δ = 162.8, 155.7, 152.0, 146.5, 142.6, 139.5, 139.1, 130.3, 128.4, 110.3, 108.0, 107.6, 96.0, 44.6 (2C), 11.7 (2C).

General procedure for photoredox pinacol coupling of aldehyde, ketones and imines.

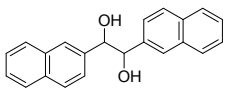
A dry 10 mL Schlenk tube, equipped with a Rotaflo stopcock, magnetic stirring bar and an argon supply tube, was charged in order and under argon with the photocatalyst **10** (5 mol%, 0.01 mmol, 5.0 mg), substrate (0.2 mmol) and DMF (1.0 mL). The reaction mixture was then subjected to a freeze-pump-thaw procedure (three cycles) and the vessel refilled with argon. Then Et_3N was added (0.8 mmol, 4 equiv., 112 µL). The reaction was irradiated with 16W blue LEDs (approx. 10 cm distance) and stirred for 36 h. After that the reaction mixture was diluted with H_2O (5 mL) extracted with AcOEt (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and the solvent was removed under reduced pressure. Two identical reactions were performed for each substrate and the crudes were reunite before purification. The residue was purified by flash column chromatography (SiO_2) to afford the title compounds in the stated yields.



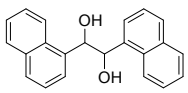
(**7a**): brown oil; 66% (0.07 mmol, 0.019 g); d.r. = 1.1:1 (*d/l*-**7a**:*meso*-**7a**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6a** (0.2 mmol, 0.028 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2) as mixture of diastereoisomers in 1.1:1 ratio (*d/l*-**7a**:*meso*-**7a**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.24 (*meso*, m, 4H), 7.22–7.17 (*d/l*, m, 4H), 7.11–7.06 (*meso*, m, 4H), 7.03–6.98 (*d/l*, m, 4H), 4.82 (*meso*, s, 2H), 4.60 (*d/l*, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{d/l,meso}$ = 137.9 (*meso*, 2C), 137.8 (*d/l*, 2C), 133.8 (4C), 128.4 (*meso*, 4C), 128.3 (*d/l*, 4C), 128.3 (8C), 78.5 (2C), 77.1 (2C); ESI-MS *m/z*: 265.0 $[M\text{-}OH]^+$, 305.1 $[M+Na]^+$.



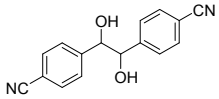
(**7b**): yellowish solid; 50% (0.05 mmol, 0.018 g); d.r. = 1:1 (*d/l*-**7b**:*meso*-**7b**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6b** (0.2 mmol, 0.036 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2) as mixture of diastereoisomers in 1:1.7 ratio (*d/l*-**7b**:*meso*-**7b**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 7.66–7.57 (m, 8H), 7.55 (d, *J* = 8.2 Hz, 4H), 7.49 (d, *J* = 8.3 Hz, 6H), 7.46 – 7.34 (m, 10H), 7.34–7.27 (m, 4H), 7.24 (d, *J* = 8.2 Hz, 4H), 5.40–5.35 (*meso*, m, 2H), 5.29–5.24 (*d/l*, m, 2H), 4.69–4.65 (*meso*, m, 2H), 4.62–4.58 (*d/l*, m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta_{d/l,meso}$ = 142.2 (4C), 140.3 (4C), 138.8 (4C), 129.3 (*meso,* 2C), 129.2 (*d/l,* 2C), 128.4 (*meso,* 2C), 128.2 (*d/l,* 2C), 127.6 (4C), 126.9 (*meso,* 2C), 126.8 (*d/l,* 2C), 126.1 (*meso,* 2C), 126.0 (*d/l,* 2C), 77.4 (*meso,* 2C), 77.2 (*d/l,* 2C); ESI-MS m/z: 349.1 $[M\text{-}OH]^+$, 367.3 $[M+H]^+$.



(**7c**): white solid; 95% (0.095 mmol, 0.029 g); d.r. = 1:2.46 (*d/l*-**7c**:*meso*-**7c**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6c** (0.2 mmol, 0.031 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2) as mixture of diastereoisomers in 1:2.46 ratio (*d/l*-**7c**:*meso*-**7c**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 7.89–7.77 (m, 8H), 7.77–7.71 (m, 3H), 7.71–7.64 (m, 6H), 7.52–7.44 (m, 3H), 7.44–7.37 (m, 6H), 7.32 (dd, *J* = 8.4, 1.6 Hz, 2H), 5.58–5.53 (*meso*, m, 2H), 5.43–5.40 (*d/l*, m, 2H), 4.93–4.88 (*meso*, m, 2H), 4.85–4.82 (*d/l*, m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta_{d/l,meso}$ = 141.1 (*meso,* 2C), 140.1 (*d/l*, 2C), 132.5 (*meso*, 2C), 132.4 (*d/l*, 2C), 132.2 (*meso*, 2C), 132.1 (*d/l*, 2C), 127.6 (*meso*, 2C), 127.6 (*d/l*, 2C), 127.4 (*meso*, 2C), 127.3 (*d/l*, 2C), 126.6 (*meso*, 2C), 126.5 (*d/l*, 2C), 126.0 (*meso*, 2C), 125.8 (*d/l*, 2C), 125.7 (*meso*, 2C), 125.7 (*d/l*, 2C), 125.6 (*meso*, 4C), 125.3 (*d/l*, 4C), 77.4 (*meso*, 2C), 77.1 (*d/l*, 2C); ESI-MS m/z: 297.1 $[M\text{-}OH]^+$, 337.1 $[M+Na]^+$.

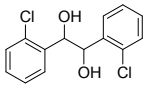


(**7d**): yellow solid; 60% (0.06 mmol, 0.019 g); d.r. = 1:1 (*d/l*-**7d**:*meso*-**7d**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6d** (0.2 mmol, 27 µL), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 3/1) as mixture of diastereoisomers in 1:2.6 ratio (*d/l*-**7d**:*meso*-**7d**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 8.13 (*d/l*, d, *J* = 8.2 Hz, 2H), 8.04 (*meso*, d, *J* = 8.4 Hz, 2H), 7.89 (*d/l*, d, *J* = 8.0 Hz, 2H), 7.79-7.74 (m, 4H), 7.64-7.59 (m, 4H), 7.48-7.26 (m, 14H), 5.67 (*meso*, s, 2H), 5.63 (*d/l*, s, 2H); 5.57 (*meso*, s, 2H), 5.42 (*d/l*, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 136.0 (*meso,* 2C), 135.8 (*d/l*, 2C), 133.6 (*meso,* 2C), 133.5 (*d/l*, 2C), 131.4 (*d/l,* 2C), 130.8 (*meso*, 2C), 128.7 (*d/l,* 2C), 128.6 (*meso*, 2C), 128.5 (4C), 125.9 (*d/l,* 2C), 125.7 (*meso*, 2C), 125.4 (*d/l,* 2C), 125.3 (*meso*, 2C), 125.1 (d/l*,* 2C), 125.0 (*meso*, 2C), 124.9 (*d/l,* 2C), 124.8 (*meso*, 2C), 123.1 (*d/l,* 2C), 123.0 (*meso*, 2C), 74.4 (*meso*, 2C), 74.2 (*d/l*, 2C); ESI-MS m/z: 297.1 $[M\text{-}OH]^+$, 337.1 $[M+Na]^+$.

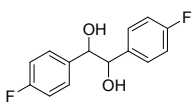


(**7e**): yellowish sticky solid; 31% (0.03 mmol, 0.008 g); d.r. = 1.1:1 (*d/l*-**7e**:*meso*-**7e**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6e** (0.2 mmol, 0.026 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2) as mixture of diastereoisomers in 1.5:1 ratio (*d/l*-**7e**:*meso*-**7e**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 7.75–7.70 (*d/l*, m, 4H), 7.70–7.64 (*meso*, m, 4H), 7.44–7.39 (*d/l*, m, 4H), 7.35–7.31 (*meso*, m, 4H), 5.74–5.69 (*meso*, m, 2H), 5.69-5.71 (*d/l*, m, 2H), 4.81 (*meso*, d, *J* = 3.6, 2H), 4.67 (*d/l*, d, *J* = 3.3, 2H).

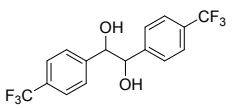
^{13}C NMR (100 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 157.9 (*d/l,* 2C), 157.2 (*meso,* 2C), 140.8 (*d/l,* 4C), 140.7 (*meso,* 4C), 137.7 (*d/l,* 4C), 137.4 (*meso,* 4C), 128.5 (2C), 119.1 (*d/l,* 2C), 118.9 (*meso,* 2C), 85.6 (*d/l,* 2C), 85.4 (*meso,* 2C); ESI-MS *m/z*: 247.0 $[M\text{-}OH]^+$, 265.1 $[M+H]^+$.



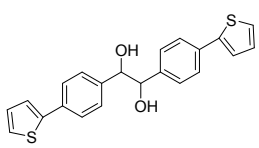
(**7f**): brown oil; 46% (0.046 mmol, 0.013 g); d.r. = 1.2:1 (*d/l*-**7f**:*meso*-**7f**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6f** (0.2 mmol, 22.5 µL), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 7/3) as mixture of diastereoisomers in 1.1:1 ratio (*d/l*-**7f**:*meso*-**7f**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.67 (*d/l,* d, J= 1.6Hz, 2H), 7.65 (*meso*, d, J = 1.7 Hz, 2H), 7.29-7.24 (m, 6H), 7.22-7.14 (m, 6H), 5.59 (*d/l,* s, 2H), 5.35 (*meso,* s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 137.2 (2C), 136.4 (2C), 133.3 (2C), 132.6 (2C), 129.5 (2C), 129.2 (2C), 129.1 (2C), 128.9 (2C), 128.8 (*d/l,* 2C), 128.7 (*meso,* 2C), 126.8 (*d/l,* 2C), 126.4 (*meso,* 2C), 73.0 (*meso,* 2C), 72.2 (*d/l,* 2C); ESI-MS *m/z*: 265.0 $[M\text{-}OH]^+$, 305.1 $[M+Na]^+$.



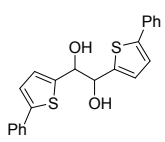
(**7g**): yellowish sticky solid; 45% (0.045 mmol, 0.012 g); d.r. = 1:1 (*d/l*-**7g**:*meso*-**7g**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6g** (0.2 mmol, 21 µL), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 9/1) as mixture of diastereoisomers in 2:1 ratio (*d/l*-**7g**:*meso*-**7g**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.17–7.12 (m, 4H), 7.07–7.01 (m, 4H), 6.99–6.87 (m, 8H), 4.81 (*meso,* s, 2H), 4.61 (*d/l,* s, 2H), 2.90 (*d/l,* bs, 2H), 2.30 (*meso,* s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 162.5 (*meso*, d, *J* = 246.4 Hz, 2C), 162.4 (*d/l*, d, *J* = 246.4 Hz, 2C), 135.3 (*d/l*, d, *J* = 3.14 Hz, 2C), 135.2 (*meso*, d, *J* = 3.12 Hz, 2C), 128.7 (*meso*, d, *J* = 8.04 Hz, 4C), 128.6 (*d/l*, d, *J* = 8.11 Hz, 4C), 115.1 (*d/l*, d, *J* = 21.40 Hz, 4C), 115.0 (*meso*, d, *J* = 21.43 Hz, 4C), 78.7 (2C); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta_{d,l/meso}$ = -112.84 (*d/l*, td, *J* = 8.6, 4.5 Hz, 2F), -112.92 (*meso*, td, J = 8.5, 4.3 Hz, 2F); ESI-MS *m/z*: 233.0 $[M\text{-}OH]^+$, 273.0 $[M+Na]^+$.



(**7h**): pale yellow sticky solid; 61% (0.06 mmol, 0.021 g); d.r. = 1.2:1 (*d/l*-**7h**:*meso*-**7h**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6h** (0.2 mmol, 28 µL), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 6/4) as mixture of diastereoisomers in 1.3:1 ratio (*d/l*-**7h**:*meso*-**7h**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.54–7.48 (m, 8H), 7.27–7.21 (m, 8H), 4.94 (*meso*, s, 2H), 4.73 (*d/l*, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 143.3 (*meso*, q, *J* = 1Hz, 2C), 143.1 (*d/l*, q, *J* = 1Hz, 2C), 130.4 (*meso*, q, *J* = 32Hz, 4C), 130.3 (*d/l*, q, *J* = 32Hz, 4C), 127.3 (*meso*, 2C), 127.2 (*d/l*, 2C), 125.2 (*meso*, q, *J* = 4 Hz, 2C), 125.0 (*d/l*, q, *J* = 3 Hz, 2C), 124.0 (*meso*, q, *J* = 270 Hz, 2C), 123.9 (*d/l*, q, *J* = 270 Hz, 2C), 78.3 (*meso*, 2C) 77.1 (*d/l*, 2C); ^{19}F NMR (377 MHz, $CDCl_3$): $\delta_{d,l/meso}$ = -61.4 (6F), -61.4 (6F); ESI-MS *m/z*: 333.0 $[M\text{-}OH]^+$, 351.1 $[M+H]^+$.

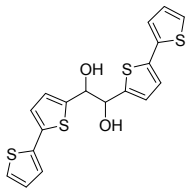


(**7i**): brownish solid; 61% (0.06 mmol, 0.023 g); d.r. = 1:1.5 (*d/l*-**7i**:*meso*-**7i**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6i** (0.2 mmol, 0.037 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2) as mixture of diastereoisomers in 1:1.5 ratio (*d/l*-**7i**:*meso*-**7i**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 7.58–7.42 (m, 16H), 7.29 (d, J = 8.3 Hz, 4H), 7.19–7.07 (m, 8H), 5.48–5.43 (*meso*, m, 2H), 5.36–5.32 (*d/l*, m, 2H), 4.66–4.62 (*meso*, m, 2H), 4.62–4.59 (*d/l*, m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): $\delta_{d/l,meso}$ = 143.9 (*meso*, 2C), 143.8 (*d/l*, 2C), 143.1 (*meso*, 2C), 142.2 (*d/l*, 2C), 132.6 (4C), 128.84 (4C), 128.5 (*meso*, 4C), 128.3 (*d/l*, 4C), 125.6 (4C), 124.8 (*meso*, 4C), 124.7 (*d/l*, 4C), 123.7 (*meso,* 2C), 123.7 (*d/l*, 2C), 77.5 (*meso*, 2C), 77.1 (*d/l*, 2C); ESI-MS *m/z*: 361.1 $[M\text{-}OH]^+$, 401.3 $[M+Na]^+$.

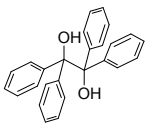


(**7j**): brownish solid; 50% (0.05 mmol, 0.019 g); d.r. = 1:1.3 (*d/l*-**7j**:*meso*-**7j**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **6j** (0.2 mmol, 0.037 g), **10** (0.01

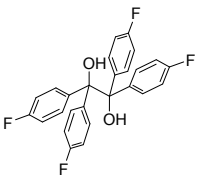
mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (dichloromethane/ethyl acetate, 97/3) as mixture of diastereoisomers in 1:1.3 ratio (*d/l*-**7j**:*meso*-**7j**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 7.62–7.55 (m, 10H), 7.42–7.34 (m, 8H), 7.31 (*d/l*, d, *J* = 3.6, 2H), 7.29–7.22 (m, 4H), 6.97 (*d/l*, d, *J* = 3.7, 2H), 6.82 (*meso*, d, *J* = 3.7, 2H), 6.01–5.98 (*meso*, m, 2H), 5.98–5.96 (*d/l*, m, 2H), 4.93 –4.89 (*meso*, m, 2H), 4.89–4.84 (*d/l*, m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 146.4 (4C), 145.4 (4C), 141.8 (4C), 134.1 (4C), 134.0 (4C), 129.0 (4C), 127.2 (4C), 125.8 (*meso*, 2C), 125.7 (*d/l*, 2C), 124.9 (4C), 122.6 (4C), 73.5 (*meso*, 2C), 73.2 (*d/l*, 2C); ESI-MS *m/z*: 361.0 [M-OH]$^+$.



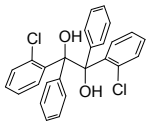
(**7k**): brownish solid; 50% (0.05 mmol, 0.019 g); d.r. = 1:3.7 (*d/l*-**7k**:*meso*-**7k**) was determined by integration of benzylic CH ^{1}H NMR signal. The general procedure was applied using **6k** (0.2 mmol, 0.039 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (dichloromethane/ethyl acetate, 6/1) as mixture of diastereoisomers in 1:3.7 ratio (*d/l*-**7k**:*meso*-**7k**). ^{1}H NMR (400 MHz, DMSO-d_6, 25°C): $\delta_{d/l,meso}$ = 7.45–7.43 (*d/l,* m, 2H), 7.43 (*meso,* dd, *J* = 5.1 Hz, *J* = 1.1 Hz, 2H), 7.22 (*d/l,* dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 2H), 7.19 (*meso,* dd, *J* = 3.6 Hz, *J* = 1.2 Hz, 2H), 7.10 (*d/l,* d, *J* = 3.6 Hz, 2H), 7.07–7.02 (m, 6H), 6.91 (*d/l,* d, *J* = 3.7 Hz, 2H), 6.77 (*meso,* d, *J* = 3.7 Hz, 2H), 6.06 (m, 4H), 4.89 (*meso,* d, *J*= 4.2 Hz 2H), 4.83 (*d/l,* d, *J*= 4.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): 146.4 (*d/l*, 2C), 145.4 (*meso*, 2C), 137.5 (*meso*, 2C), 137.4 (*d/l*, 2C), 135.7 (*meso*, 2C), 135.6 (*d/l*, 2C), 128.6 (*meso*, 2C), 128.6 (*d/l*, 2C), 126.0 (*d/l*, 2C), 125.9 (*meso*, 2C), 125.3 (*meso*, 2C), 125.3 (*d/l*, 2C), 123.8 (*meso*, 2C), 123.8 (*d/l*, 2C), 123.3 (*meso*, 2C), 123.3 (*d/l*, 2C), 73.7 (*meso*, 2C), 73.5 (*d/l*, 2C); ESI-MS *m/z*: 373.0 [M-OH]$^+$.



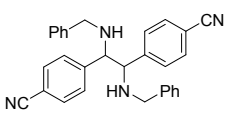
(**12a**): white solid; 58% (0.06 mmol, 0.021 g). The general procedure was applied using **11a** (0.2 mmol, 0.036 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 99/1). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.32–7.25 (m, 8H), 7.20–7.11 (m, 12H), 3.00 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.1 (4C), 128.5 (8C), 127.2 (8C), 126.9 (4C), 83.0 (2C); ESI-MS *m/z*: 349.3 [M-OH]$^+$.



(**12b**): yellowish solid; 55% (0.05 mmol, 0.024 g). The general procedure was applied using **12b** (0.2 mmol, 0.044 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 7.24-7.20 (m, 8H), 6.89-6.83 (m, 8H), 2.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7 (d, *J* = 247.4 Hz, 4C), 139.6 (d, *J* = 3.2 Hz, 4C), 130.2 (d, *J* = 8.0 Hz, 8C), 114.2 (d, *J* = 21.1 Hz, 8C), 82.5 (2C); ^{19}F NMR (377 MHz, $CDCl_3$, 25°C) δ = -113.8 (4F); ESI-MS *m/z*: 421.1 [M-OH]$^+$.

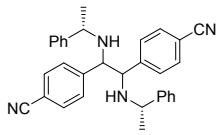


(**12c**): yellowish oil; 37% (0.04 mmol, 0.016 g); The two diastereoisomer present very similar NMR signal avoiding the determination of the d.r.. The general procedure was applied using **12c** (0.2 mmol, 0.043 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (n-hexane/diethyl ether, 95/5) as mixture of diastereoisomers. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.61 (d, *J* = 1.6 Hz, 2H), 7.59 (d, *J* = 1.6 Hz, 2H), 7.40-7.36 (m, 4H), 7.34-7.19 (m, 10 H), 6.22 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{d/l,meso}$ = 142.2 (2C), 140.9 (2C), 132.5 (2C), 129.5 (2C), 128.7 (2C), 128.4 (4C), 128.0 (2C), 127.7 (2C), 127.1 (2C), 126.9 (4C), 72.7 (2C); ESI-MS *m/z*: 417.3 [M-OH]$^+$.

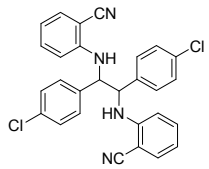


(**14a**): yellowish oil; 50% (0.05 mmol, 0.022 g); d.r. = 1:1.4 (*d/l*-**14a**:*meso*-**14a**) was determined by integration of benzylic CH ^{1}H NMR signals at δ = 3.43, 3.32. The general procedure was applied using **13a** (0.2 mmol, 0.044 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/diethyl ether, 7/3) as mixture of diastereoisomers in 1:1.1 ratio (*d/l*-**11a**:*meso*-**11a**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.57 – 7.51 (m, 4H), 7.47–7.42 (m, 4H), 7.30– 7.25 (m, 6H), 7.24– 7.19 (m, 8H), 7.18–7.13 (m, 4H), 7.12–7.06 (m, 4H), 7.04–6.99 (m, 6H), 3.84 (*meso*, s, 2H), 3.69 (*d/l*, s, 2H), 3.61 (*d/l*, d, *J* = 13.2 Hz, 2H), 3.56 (*meso*, d, *J* = 13.6 Hz, 2H), 3.43 (*d/l*, d, *J* = 13.3 Hz, 2H), 3.32 (*meso*, d, *J* = 13.6 Hz, 2H);

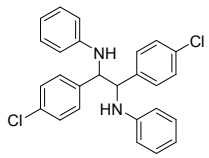
^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{d/l,meso}$ = 146.3 (*meso*, 2C), 145.5 (*d/l*, 2C), 139.5 (*meso*, 2C), 139.3 (*d/l*, 2C), 132.0 (8C), 129.1 (4C), 128.6 (4C), 128.5 (4C), 128.4 (4C), 128.0 (4C), 127.9 (4C), 127.0 (4C), 118.6 (*meso*, 2C), 118.5 (*d/l*, 2C), 111.6 (*meso*, 2C), 111.3 (*d/l*, 2C), 67.8 (*meso*, 2C), 66.3 (*d/l*, 2C), 51.3 (*meso*, 2C), 51.1 (*d/l*, 2C); ESI-MS *m/z*: 336.2 [M-BnNH]$^+$.



(**14b**): yellowish oil; 50% (0.05 mmol, 0.024 g); d.r. = 2.15:3.5:2:1 (*syn*-**14b**:*anti*-**14b**:*syn*-**14b**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signals at δ = 5.04, 4.09, 4.27. The general procedure was applied using **13b** (0.2 mmol, 0.047 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (cyclohexane/diethyl ether, 6/4) as mixture of diastereoisomers in 2.15:3.5:2:1 ratio (*syn*-**14b**:*anti*-**14b**:*syn*-**1b**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{syn,anti}$ = 7.67–7.59 (m, 4H), 7.58–7.49 (m, 4H), 7.49–7.37 (m, 12H), 7.37–7.26 (m, 18H), 7.24–7.17 (m, 2H), 7.05–6.88 (m, 8H), 6.86–6.74 (m, 6H), 5.04 (*syn*, s, 2H), 4.27 (*syn*, s, 2H), 4.09 (*anti*, d, 1H), 3.97 (d, *J* = 4.01 Hz,1H), 3.92 (*syn*, q, *J* = 6.6 Hz, 2H), 3.75 (*syn*, q, *J* = 6.7 Hz, 2H), 3.62 (*anti*, q, *J* = 6.5Hz, 1H), 3.36 (*anti*, q, *J* = 6.3 Hz, 1H), 1.72 (d, *J* = 6.8 Hz, 3H), 1.56 (d, *J* = 6.5 Hz, 6H), 1.45 (d, *J* = 6.8 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{syn,anti}$ = 146.8 (2C), 146.8 (2C), 146.7 (2C), 145.6 (2C), 145.3 (2C), 144.6, 144.5, 132.0 (4C), 131.9 (4C), 131.7 (2C), 131.6 (2C), 129.1 (4C), 128.7 (4C), 128.5 (2C), 128.5 (2C), 128.5 (4C), 128.4 (4C), 128.4 (2C), 128.3 (2C), 127.3 (2C), 127.0 (4C), 126.5 (4C), 126.4 (4C), 126.3 (4C), 118.7 (4C), 118.6 (2C), 111.2 (2C), 111.2 (2C), 111.0, 110.8, 66.8 (2C), 65.4 (2C), 65.1, 62.5, 56.0 (2C), 55.0 (2C), 54.9 (2C), 24.1 (2C), 23.2 (2C), 22.4 (2C); ESI-MS *m/z*: 350.2 [M-PhCH(Me)NH]$^+$.



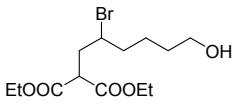
(**14c**): brownish solid; 54% (0.05 mmol, 0.026 g); d.r. = 1:1.1 (*d/l*-**14c**:*meso*-**14c**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **13c** (0.2 mmol, 0.048 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (n-hexane/diethyl ether, 9/1) as mixture of diastereoisomers in 1:1.1 ratio (*d/l*-**14c**:*meso*-**14c**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.40-7.38 (m, 4H), 7.30-7.18 (m, 12H), 7.04-6.97 (m, 8H), 6.71-6.68 (m, 4H), 6.36-6.34 (m, 4H), 5.26 (*meso,* m, 4H), 4.94 (*d/l* m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{d/l,meso}$ = 148.4 (4C), 148.0 (4C), 134.8 (4C), 134.5 (4C), 134.2 (4C), 132.8 (4C), 129.2 (8C), 128.5 (8C), 118.2 (4C), 112.4 (4C), 97.4 (4C), 61.3 (4C); ESI-MS *m/z*: 483.1 [M+H]$^+$.



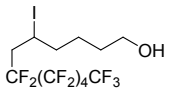
(**14d**): yellowish oil; 40% (0.04 mmol, 0.018 g); d.r. = 1:1 (*d/l*-**14d**:*meso*-**14d**) was determined by integration of benzylic C<u>H</u> ^{1}H NMR signal. The general procedure was applied using **13d** (0.2 mmol, 0.045 g), **10** (0.01 mmol, 0.005 g) and TEA (0.8 mmol, 112 µL, 4 eq). The title compound was isolated by flash column chromatography (n-hexane/diethyl ether, 9/1) as mixture of diastereoisomers in 1:1.3 ratio (*d/l*-**14d**:*meso*-**14d**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 7.26–7.14 (m, 8H), 7.1 –6.98 (m, 12H), 6.89 (d, *J* = 8.3 Hz, 4H), 6.73–6.66 (m, 4H), 6.49 (d, *J* = 8.0 Hz, 8H), 4.92 (*meso*, s, 2H), 4.53 (*d/l*, s, 2H), 4.47 (*meso*, s, 2H), 4.45 (*d/l*, s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): $\delta_{d/l,meso}$ = 146.5 (2C), 145.9 (2C), 138.2 (2C), 136.5 (2C), 133.6 (2C), 133.4 (2C), 129.3 (4C), 129.5 (4C), 128.8 (4C), 128.7 (4C), 128.7 (4C), 128.6 (4C), 118.6 (2C), 118.3 (2C), 114.1 (4C), 113.8 (4C), 63.5 (2C), 61.4 (2C); ESI-MS *m/z*: 447.2 [M+H]$^+$.

General procedure for photoredox ATRA reaction

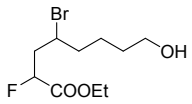
A dry 10 mL Schlenk tube, equipped with a Rotaflo Stopcock, magnetic stirring bar and an argon supply tube, was charged in order and under argon with the photocatalyst **9** (2.5 mol%, 0.005 mmol, 1.5 mg), EtOH (500 µL), H_2O (500 µL), alkyl halide (0.2 mmol, 1 equiv., or different if specified), olefin (0.4 mmol, 2 equiv., or different if specified). The reaction mixture was degassed *via* freeze pump thaw (x4), and the vessel refilled with argon. The reaction mixture was positioned approximately 10 cm from the light source (16 W blue LEDs). After vigorous stirring for 36 h, the mixture was transferred in a separator funnel and extracted with AcOEt (3 x 5 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4 and concentrated under reduced pressure to give the crude products. The residue was purified by flash column chromatography (SiO_2) to afford the title compounds in the stated yields.



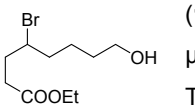
(**17a**): colorless oil; 85% (0.17 mmol, 0.058 g). The general procedure was applied using **16a** (0.2 mmol, 34 µL), **15** (0.4 mmol, 48 µL, 2 equiv.) and **9** (0.005 mmol, 0.0015 g). The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 7/3). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.29–4.09 (m, 4H), 4.03–3.93 (m, 1H), 3.75 (dd, *J* = 10.2, 4.2 Hz, 1H), 3.63 (t, *J* = 6.0 Hz, 2H), 2.44 (ddd, *J* = 14.7, 10.2, 3.1 Hz, 1H), 2.23 (ddd, *J* = 14.8, 10.6, 4.2 Hz, 1H), 1.92–1.79 (m, 2H), 1.71–1.41 (m, 4H), 1.32–1.19 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 168.9, 168.8, 62.5, 61.7, 61.6, 54.6, 50.5, 39.1, 37.8, 31.9, 23.7, 14.01, 13.98; HRMS (ESI): calculated for $C_{13}H_{23}BrNaO_5^+$ $[M+Na]^+$ 361.0621, found 361.0624.



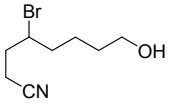
(**17b**): colorless oil; 35% (0.09 mmol, 0.049 g). The general procedure was applied using **16b** (0.4 mmol, 86 µL, 2 equiv.), **15** (0.2 mmol, 24 µL), **9** (0.005 mmol, 0.0015 g) and DMF/H_2O (1/1) mixture as reaction solvent. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 85/15). Spectroscopic properties were according to those reported in literature.[4] ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.39–4.32 (m, 1H), 3.69 (t, *J* = 5.9 Hz, 2H), 2.98–2.74 (m, 2H), 1.87–1.83 (m, 2H), 1.69–1.50 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 62.5 , 41.7 (t, J = 20.9 Hz), 40.0 (d, J = 2.1 Hz), 31.5, 29.7, 26.0, 20.4. ^{19}F NMR (377 MHz, $CDCl_3$, 25°C): δ = -79.59 (t, J = 10.0 Hz, 3F), -109.21– -114.58 (m, 2F), -120.56 (s, 2F), -121.63 (s, 2F), -122.40 (s, 2F), -124.56– -125.16 (m, 2F); Elemental Analysis: Found C, 26.3; H, 2.1%; Calc. for $C_{12}H_{12}F_{13}IO$; C, 26.4; H, 2.2%.



(**17c**): colorless oil; 65% (0.13 mmol, 0.037 g). The general procedure was applied using **16c** (0.6 mmol, 72 µL, 3 eq.), **15** (0.2 mmol, 24 µL), **9** (0.005 mmol, 0.0015 g) and DMF/H_2O (1/1) mixture as reaction solvent. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 85/15) and obtained as mixture of diastereoisomers A and B. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 5.32–4.99 (m), 4.31–4.21 (m, 2H), 4.20–4.12 (m), 3.64 (t, *J* = 5.8 Hz, 2H), 2.52–2.19 (m, 2H), 1.96–1.79 (m, 2H), 1.70–1.44 (m, 4H), 1.35–1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 169.4 (d, J = 22.8 Hz, A), 169.1 (d, J = 23.4 Hz, B), 87.3 (d, J = 184.7 Hz, A), 86.7 (d, J = 185.2 Hz, B), 62.5 (s, A+B), 61.9 (s, B), 61.8 (s, B), 51.6 (d, J = 1.9, A), 50.6 (d, J = 4.0, B), 41.7 (d, J = 20.6, A), 41.3 (d, J = 21.1, B), 39.0 (s, A+B), 38.0 (s, A+B), 31.8 (s, A), 31.8 (s, B), 23.8 (s, B), 23.7 (s, A), 14.1 (s, B), 14.1 (s, A); ^{19}F NMR (377 MHz, $CDCl_3$, 25°C): δ = -190.5 – -190.8 (m), -194.7 – -195.0 (m); HRMS (ESI): calculated for $C_{10}H_{18}BrFNaO_3^+$ $[M+Na]^+$ 307.0316, found 307.0313.



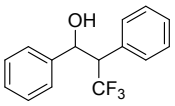
(**17d**): colorless oil; 47% (0.09 mmol, 0.025 g). The general procedure was applied using **16d** (0.6 mmol, 67 µL, 3 eq.), **15** (0.2 mmol, 24 µL), **9** (0.005 mmol, 0.0015 g) and DMF/H_2O (1/1) mixture as reaction solvent. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.12 (q, *J* = 7.1 Hz, 2H), 4.08–4.00 (m), 3.64 (t, *J* = 6.1 Hz, 2H), 2.62–2.44 (m, 2H), 2.23–2.12 (m), 2.10–1.97 (m), 1.90–1.79 (m, 2H), 1.66–1.46 (m, 4H), 1.24 (t, *J* = 8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 172.8, 62.6, 60.5, 56.8, 38.9, 33.9, 32.3, 31.9, 23.8, 14.2; HRMS (ESI): calculated for $C_{10}H_{19}BrNaO_3^+$ $[M+Na]^+$ 289.0410, found 289.0416.



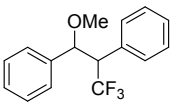
(**17e**): colorless oil; 89% (0.18 mmol, 0.039 g). The general procedure was applied using **16e** (0.6 mmol, 67 µL, 3 eq.), **15** (0.2 mmol, 42 µL), and **9** (0.005 mmol, 0.0015 g) and DMF/H_2O (1/1) mixture as reaction solvent. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 8/2). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 4.05 (m, 1H), 3.64 (m, 2H), 2.59 (m, 2H), 2.16 (m, 1H), 2.06 (m 1H), 1.87 (m, 2H), 1.59 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 118.7, 62.4, 54.67, 38.6, 34.5, 31.8, 23.8, 16.0; HRMS (ESI): calculated for $C_8H_{15}BrNO^+$ $[M+H]^+$ 220.0332, found 220.0323.

General procedure for trifluoromethylation reaction

In a Schlenk tube with rotaflo stopcock under argon atmosphere at r.t., coumarin **9** (0.05 mmol, 1.5 mg) was dissolved in 2.0 mL of a mixture of DCM and ROH (9/1, water or methanol). Stilbene **18** (0.1 mmol, 0.018 g), Umemoto reagents **19** (0.14 mmol, 0.052g) were added. The reaction mixture was carefully degassed via freeze-pump thaw (three times), and the vessel refilled with argon. The Schlenk tube was stirred and irradiated with 16 W blue LEDs positioned approximately at 10 cm distance from the reaction vessel. After 18 h of irradiation, 10% aq. Na_2SO_3 (5 mL) was added and the mixture was extracted with DCM (4 x 5 mL). The collected organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Products **20a-b** were purified by column flash chromatography on SiO_2.



(**20a**): colorless oil; 49% (0.05 mmol, 0.012 g); d.r. = 4.45:1 (*syn*-**20a**:*anti*-**20a**) was determined by integration of benzylic C<u>H</u>OH ^{1}H NMR signal. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 9/1) as mixture of diastereoisomers in 7:1 ratio (*syn*-**20a**:*anti*-**20a**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{syn,anti}$ = 7.35–7.25 (m, 2H), 7.21–7.11 (m, 11H), 7.10–6.98 (m, 7H), 5.38–5.33 (*anti,* m, 1H), 5.21 (*syn*, dd, *J* = 9.2, 2.9 Hz, 1H), 3.67 (*syn*, p, *J* = 9.2 Hz, 1H), 3.56 (*anti,* ddd, *J*=19.3, 9.7, 5.4 Hz, 1H), 2.27 (*syn,* d, *J* = 3.3 Hz, 1H), 1.98 (*anti,* d, *J* = 3.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{syn,anti}$ = 140.7, 132.7, 130.2, 129.3 (2C), 128.5, 128.4 (2C), 128.3, 128.2 (2C), 128.1 (2C), 128.0 (2C), 127.9, 126.8 (2C), 126.3, 125.1, 74.7 (*syn*), 72.3 (*anti*), 57.4 (quin, *J* = 25.0, 2C); ^{19}F NMR (377 MHz, $CDCl_3$, 25°C): $\delta_{syn,anti}$ =-62.02 (d, *J* = 9.2 Hz, 3F, *syn*), -63.77 (d, *J* = 9.2 Hx, 3F, *anti*); HRMS (ESI): calculated for $C_{15}H_{14}F_3O^+$ $[M+H]^+$ 267.0991, found 267.0993.

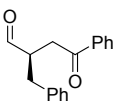


(**20b**): pale yellow oil; 41% (0.04 mmol, 0.011 g); d.r. = 3.9:1 (*syn*-**20b**:*anti*-**20b**) was determined by integration of benzylic C<u>H</u>OH ^{1}H NMR signal. The title compound was isolated by flash column chromatography (cyclohexane/ethyl acetate, 95/5) as mixture of diastereoisomers in 5.8:1 ratio (*syn*-**20b**:*anti*-**20b**). ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): $\delta_{syn,anti}$ =7.20–7.09 (m, 6H *syn* + 6H *ant*i), 7.02-6.96 (m, 4H *syn* + 4H *anti*), 4.78 (d, *J* = 4.9 Hz, 1H *anti*), 4.59 (d, *J* = 9.3 Hz, 1H *syn*), 3.63 (m, 1H *syn*), 3.45 (m, 1H *anti*), 3.23 (s, 3H *syn*), 3.19 (s, 3H *anti*); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta_{syn,anti}$ = 138.7 (*anti*), 138.1 (*syn*), 132.9, 130.5, 129.3 (2C), 128.3 (2C), 128.2 (2C), 128.1, 128.0, 127.8, 127.6 (2C), 127.05, 124.9, 83.5, 81.3, 57.4-56.8 (m), 56.6; ^{19}F NMR (377 MHz, $CDCl_3$, 25°C): $\delta_{syn,anti}$ =-62.07 (3F, *syn*), -64.28 (3F, *anti*); HRMS (ESI): calculated for $C_{16}H_{16}F_3O^+$ $[M+H]^+$ 281.1148, found 281.1149.

General procedure for enantioselective α-alkylation of aldehydes

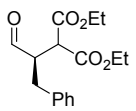
In a Schlenk tube with rotaflo stopcock under argon atmosphere at r.t., coumarin **10** (0.01 mmol, 0.005 mg) and the Macmillan catalyst **23** (0.04 mmol, 0.013 g) were dissolved in 1.0 mL DMF. Aldehyde **21** (0.6 mmol, 3 equiv., 79 µL), bromo derivatives **22a-b** (0.2 mmol, 1 equiv.) and 2,6-lutidine (0.3 mmol, 35 µL) were then added.

The reaction mixture was carefully degassed via freeze-pump thaw (three times), and the vessel refilled with argon. The Schlenk tube was stirred and irradiated with 16 W blue LEDs positioned approximately at 10 cm distance from the reaction vessel. After 18 h of irradiation, aq. HCl 1M (5 mL) was added and the mixture was extracted with AcOEt (4 x 5 mL). The collected organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Products **24a-b** were purified by column flash chromatography on SiO_2.



(**24a**): the title compound was isolated by flash column chromatography (SiO_2, cyclohexane/EtOAc, 9/1) as colorless oil (28 mg, 0.11 mmol, 56% yield, 83% ee). Ee was determined by chiral HPLC analysis using Daicel Chiralpak®IC column, hexane/*i*-PrOH 90:10, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major}= 18.4 min., τ_{minor} = 15.3 min.; ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ = 9.89 (s, 1H), 7.94–7.80 (m, 2H), 7.58– 7.51(m, 1H), 7.47–7.39 (m, 2H), 7.32–7.25 (m, 2H), 7.21 (ddd, *J* = 12.3, 6.7, 4.1 Hz, 3H), 3.52–3.30 (m, 2H), 3.26–3.08 (m, 1H), 3.05–2.93 (m, 1H), 2.87–2.76 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ =203.0, 197.8, 138.1, 136.4, 133.3, 129.0 (2C), 128.7 (2C), 128.6(2C), 128.0 (2C), 126.7, 48.3, 37.2, 34.7.



(24b): the title compound was isolated by flash column chromatography (SiO_2, cyclohexane/EtOAc, 95/5) as colorless oil (36 mg, 0.12 mmol, 62% yield, 89% ee). Ee was determined by chiral HPLC analysis using Daicel Chiralpak®IC column: hexane/*i*-PrOH 90:10, flow rate 1.00 mL/min, 30°C, λ = 210 nm: τ_{major}= 17.8 min., τ_{minor} = 14.1 min. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ =9.76 (d, *J* = 0.5 Hz, 1H), 7.32–7.26 (m, 2H), 7.24–7.15 (m, 3H), 4.33–4.06 (m, 4H), 3.66 (d, *J* = 7.0 Hz, 1H), 3.47–3.28 (m, 1H), 3.10 (dd, *J* = 14.3, 7.5 Hz, 1H), 2.81 (dd, *J* = 14.3, 7.3 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ = 201.1, 168.1, 167.9, 137.4, 129.1 (2C), 128.8 (2C), 126.9, 61.9 (2C), 51.8, 51.5, 33.2, 14.0 (2C).

Procedure for reductive protonation of α-bromoketones.

A Schlenk tube with rotaflo stopcock under argon atmosphere at r.t. was charged with coumarin **10** (0.01 mmol, 0.005 mg), 2-bromoacetophenone **25** (0.2 mmol, 0.040 g), Hantzsch ester 26 (0.3 mmol, 1.5 equiv., 0.068 g) and DMF (1 mL). The reaction mixture was carefully degassed via freeze-pump thaw (three times), and the vessel refilled with argon. The Schlenk tube was stirred and irradiated with 16 W blue LEDs positioned approximately at 10 cm distance from the reaction vessel. After 36 h of irradiation, reaction mixture was injected in GC to confirm the complete conversion of the 2-bromoacetophenone to acetophenone.

Results and Discussion

Scheme S1. Poor reactive (a) and inactive (b) substrates tested in the photocatalytic pinacol coupling reaction.

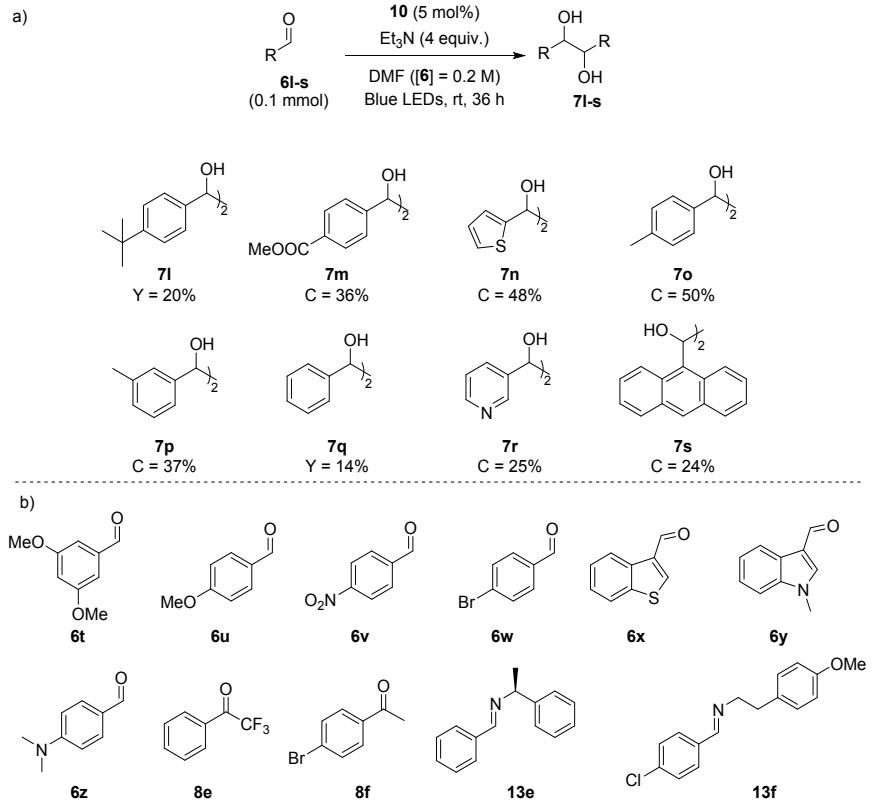
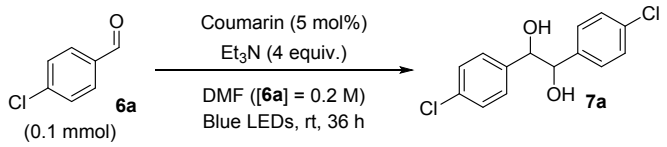
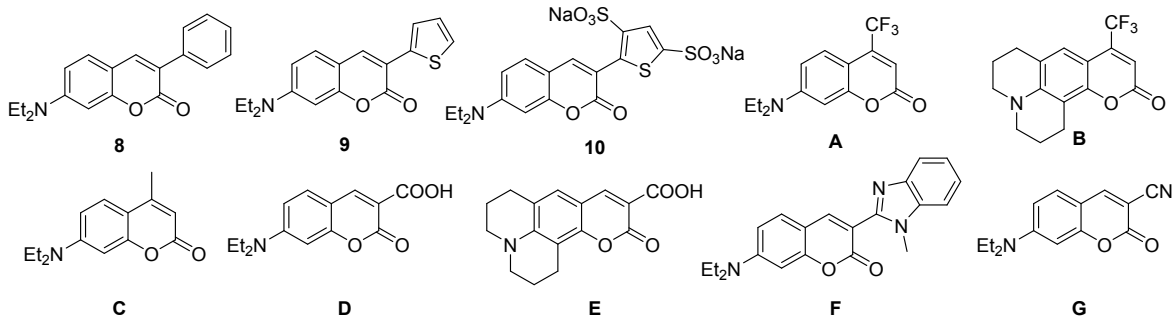


Table S1. Screening of coumarin derivatives in the photocatalytic pinacol coupling reaction.

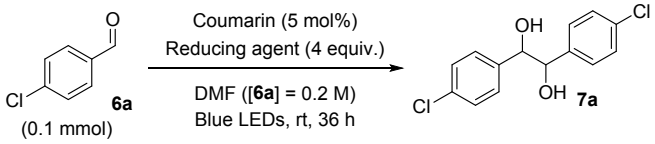


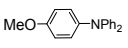


Entry[a]	Coumarin	Conversion (%)[b]
1	**8**	80
2	**9**	50
3	**10**	89
4	**A**	0
5	**B**	31
6[c]	**C**	24
7[c]	**D**	0
8	**E**	0
9	**F**	0
10	**G**	0

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis. [c] The reaction was irradiated with 23W CFL.

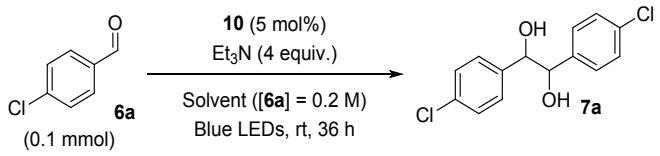
Table S2. Screening of reducing agent in the photocatalytic pinacol coupling reaction.



Entry[a]	Coumarin	Solvent	Reducing agent	Conversion (%)[b]
1	**9**	DMF	-	0
2	**9**	DMF	Et_3N	50
3	**9**	DMF	Bu_3N	38
4	**9**	DMF	*N*,*N*-Dimethylaniline	6
5	**10**	DMF/H_2O (1/1)	Sodium ascorbate	0
6	**10**	DMF	Et_3N	89
7	**10**	DMF		0
8	**10**	DMF	Bu_3N	67

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

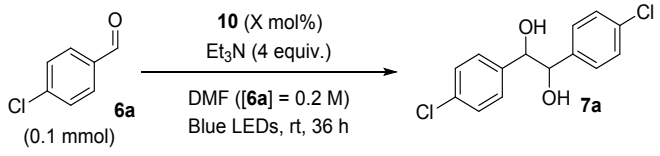
Table S3. Solvent screening of reducing agent in the photocatalytic pinacol coupling reaction.



Entry[a]	Solvent	Conversion (%)[b]
1	DMF/H_2O (1/1)	0
2	DMF	89
3	CH_3CN	37
4	1,2-DCE	0
5	THF	0
6	DMSO	66
7	EtOH	0

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

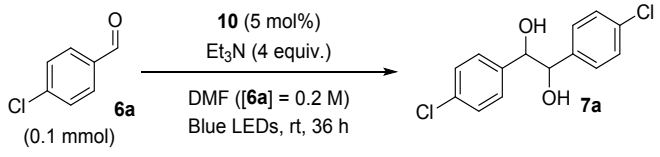
Table S4. Effect of coumarin loading in the photocatalytic pinacol coupling reaction.



Entry[a]	Coumarin loading (mol%)	Conversion (%)[b]
1	1	65
2	2.5	69
3	5	89

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

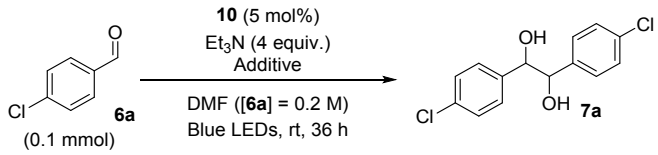
Table S5. Effect of air, light and catalyst in the photocatalytic pinacol coupling reaction.



Entry[a]	Air	Light	**10**	Conversion (%)[b]
1				0
2				89
3				0
4				0
5				0

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

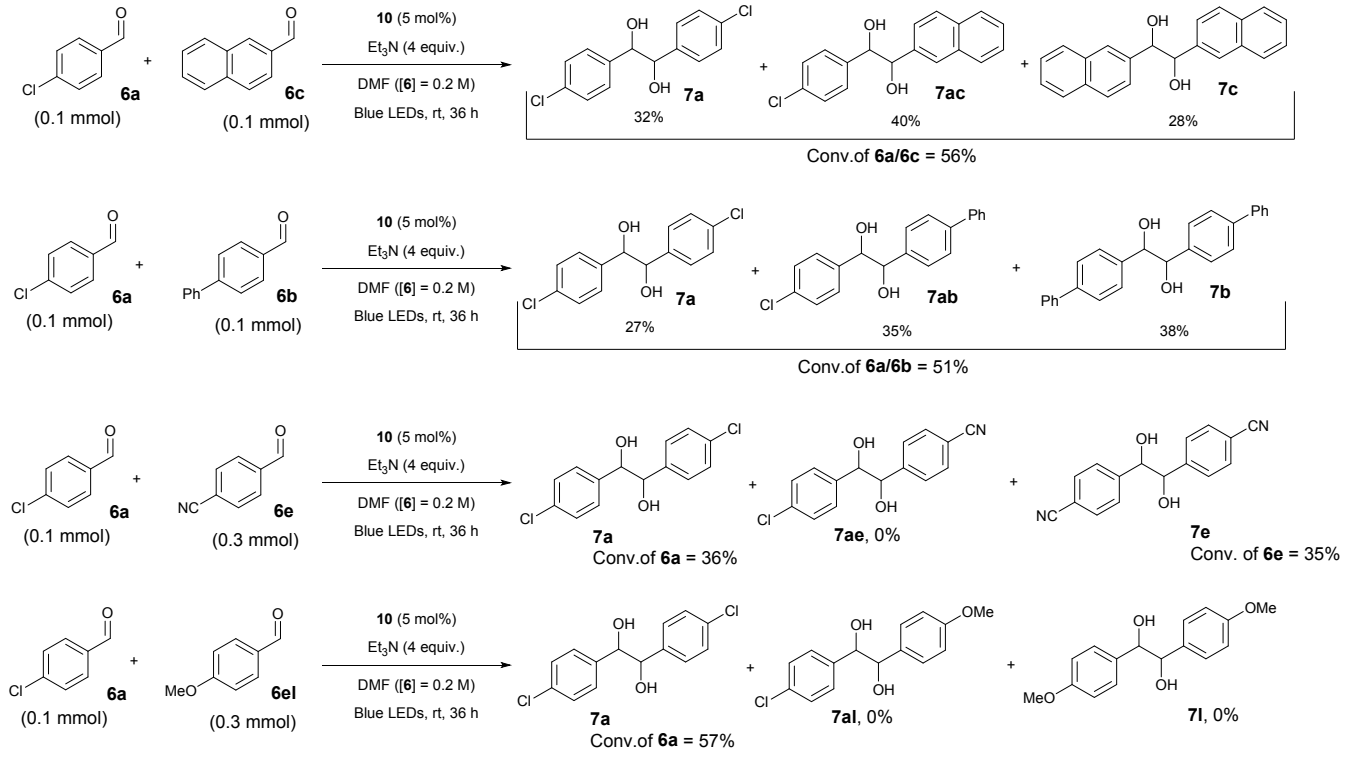
Table S6. Effect of additives in the photocatalytic pinacol coupling reaction.



Entry[a]	Additive	Conversion (%)[b]
1	TMSCl (1 equiv.)	29
2	Colloidine*HCl (1 equiv.)	30
3	Oxalic Acid (20 mol%)	49
4	K_3PO_4 (20 mol%)	12
5	K_2CO_3 (20 mol%)	16
6	-	89

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

Scheme S2. Attempts to perform cross pinacol coupling reaction; Conversions and ratios determined by ^{1}H NMR analysis.



Scheme S3. Different bromides and alkenes tested in the ATRA reaction.

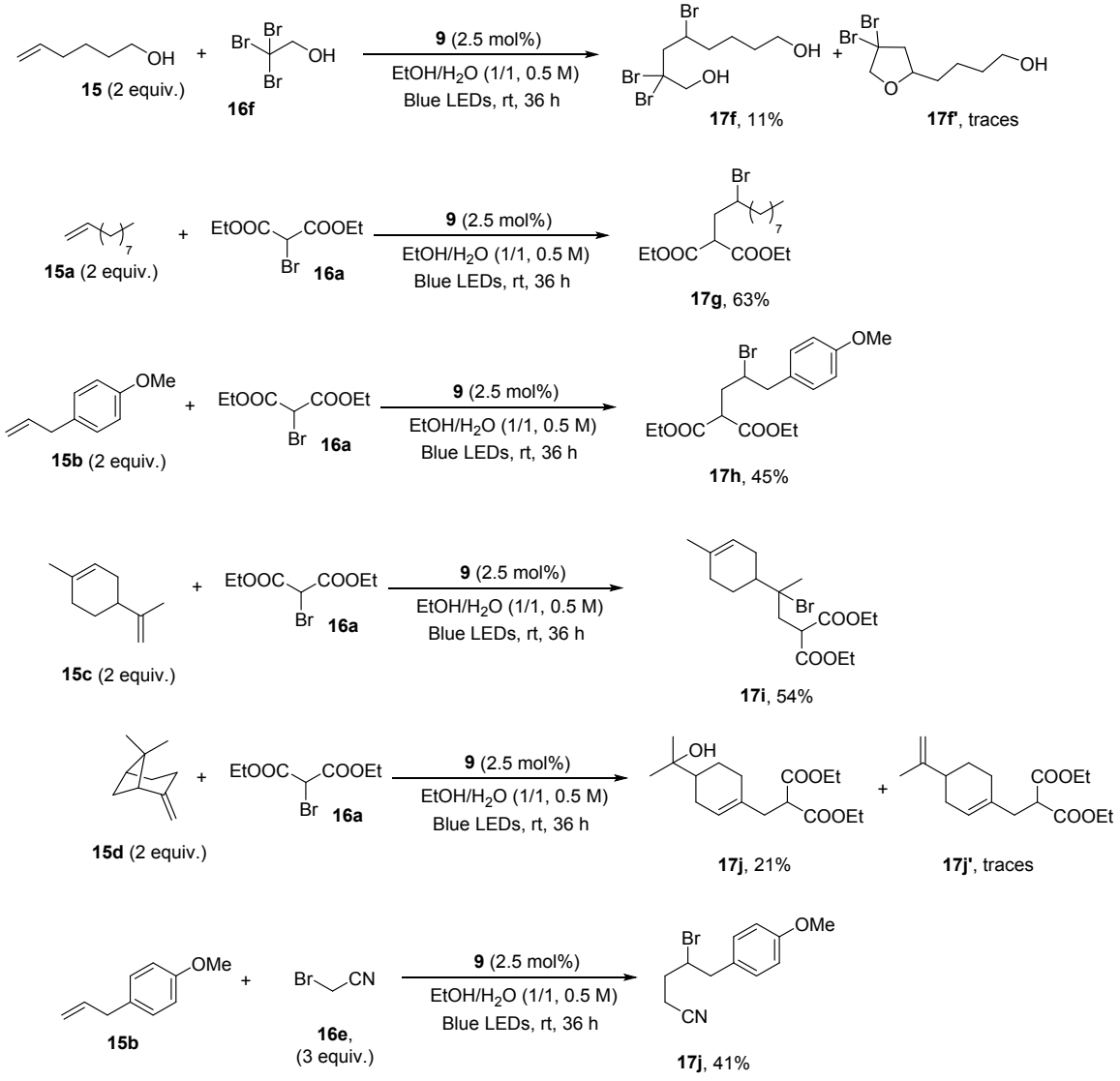
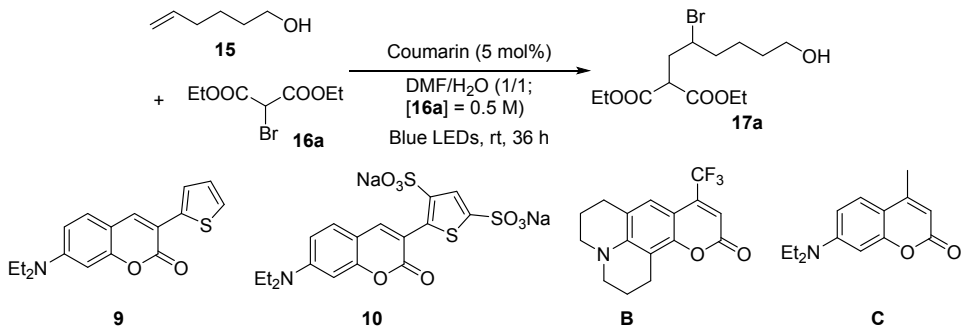


Table S7. Screening of coumarin derivatives in the ATRA reaction.

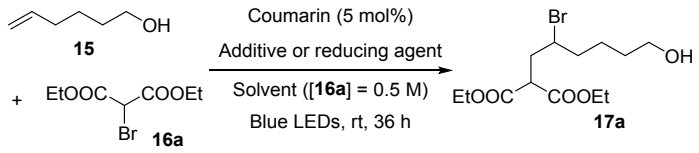


Entry[a]	Coumarin	Conversion (%)[b]
1	**9**	96
2	**10**	96

3	**B**	0
4	**C**	74

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

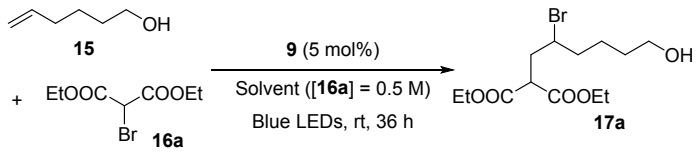
Table S8. Effect of additives, solvent and reducing agent in the ATRA reaction.



Entry[a]	Coumarin	Solvent	Additive	Reducing agent	Conversion (%)[b]
1	**9**	DMF	-	-	33
2	**9**	DMF	-	Et_3N (4 equiv.)	0
3	**9**	DMF/H_2O (1/1)	LiBr (2 equiv.)	-	96
4	**9**	DMF/H_2O (1/1)	-	-	96
5	**10**	DMF	-	Et_3N (20 mol%)	33
6	**10**	DMF	-	-	3
7	**10**	DMF/H_2O (1/1)	LiBr (2 equiv.)	-	96
8	**10**	DMF/H_2O (1/1)	-	-	96

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

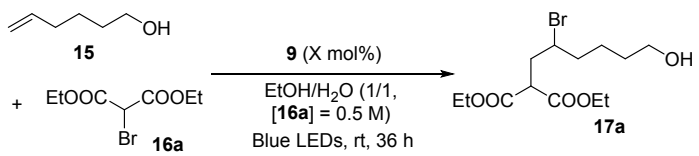
Table S9. Solvent effect in the ATRA reaction.



Entry[a]	Solvent	Conversion (%)[b]
1	DMF	33
2	DMF/H_2O (1/1)	96
3	CH_3CN/H_2O (1/1)	93
4	EtOH/H_2O (1/1)	98
5	DMSO/H_2O (1/1)	98

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

Table S10. Effect of coumarin loading in the ATRA reaction.

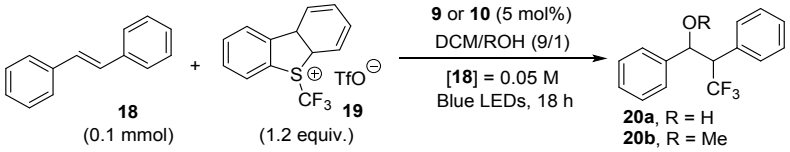


Entry[a]	Coumarin loading (mol%)	Conversion (%)[b]
1	1	94
2	2.5	96

3	5	86

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

Table S11. Screening of coumarin in the photocatalytic trifluoromethylation reaction.



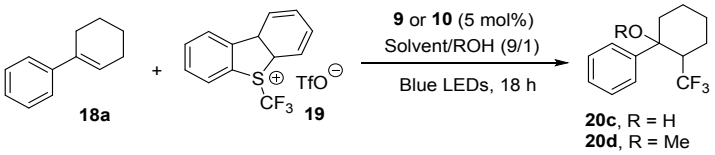
18 (0.1 mmol) + **19** (1.2 equiv.)

20a, R = H
20b, R = Me

Entry[a]	Coumarin	Solvent	Conversion (%)[b]
1	**9**	DCM/MeOH (9/1)	67(45)[c]
2	**9**	DCM/H_2O (9/1)	68(41)[c]
3	**10**	DCM/MeOH (9/1)	56
4	**10**	DCM/H_2O (9/1)	53

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis. [c] Yield determined after chromatographic purification.

Table S12. Miscellaneous tests in the photocatalytic trifluoromethylation reaction.



18a + **19**

20c, R = H
20d, R = Me

Entry[a]	**18a**	**19**	Coumarin	Solvent	Conversion (%)[b]
1	0.1 mmol	0.12 mmol	**9**	Acetone/H_2O (9/1)	50
2	0.1 mmol	0.12 mmol	**10**	Acetone/H_2O (9/1)	46
3	0.2 mmol	0.1mmol	**9**	Acetone/H_2O (9/1)	45
4	0.2 mmol	0.1mmol	**10**	DCM/MeOH (9/1)	34

[a] Reaction condition reported in the above figure. [b] Determined by ^{1}H NMR analysis.

Photophysical studies

Figure S1. Absorption (left, solid lines) and emission spectra (right, dashed lines) of **8** (red line), **9** (black line) and **10** (gray line) in DMF solution at 298 K. λ_{ex} = 400 nm.

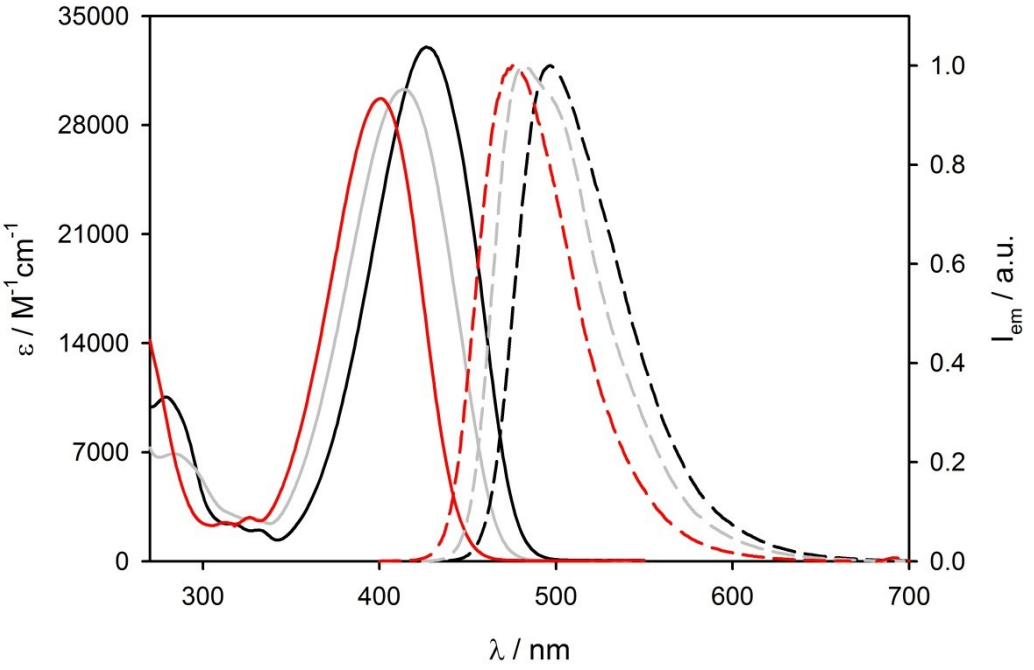


Figure S2. Cyclic Voltammetry of an argon-purged solution of **8** (1mM) in CH_3CN in the presence of 0.1M tetraethylammonium hexafluorophosphate ($TEAPF_6$). Scan rate=0.1Vs^{-1}; working electrode: glassy carbon.

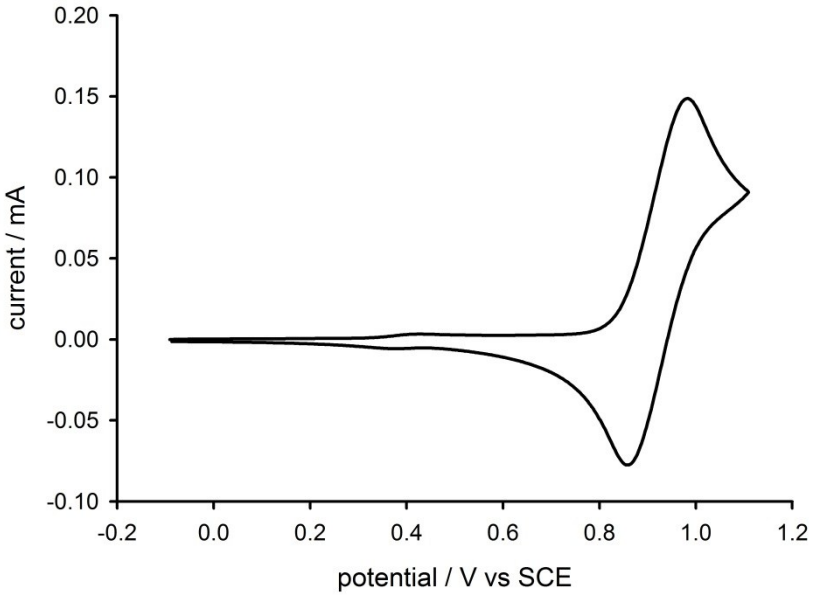


Figure S3. Cyclic Voltammetry of an argon-purged solution of **9** (1mM) in CH_3CN in the presence of 0.1M tetraethylammonium hexafluorophosphate ($TEAPF_6$). Scan rate=0.2Vs^{-1}; working electrode: glassy carbon; two scans.

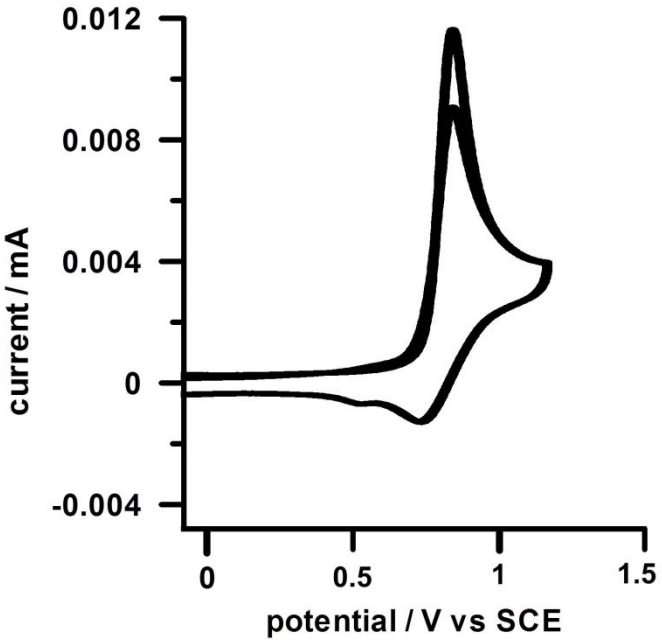


Figure S4. Cyclic Voltammetry of an argon-purged solution of **10** (1.4mM) in CH_3CN in the presence of 0.1M tetraethylammonium hexafluorophosphate ($TEAPF_6$). Scan rate=0.2Vs^{-1}; working electrode: glassy carbon.

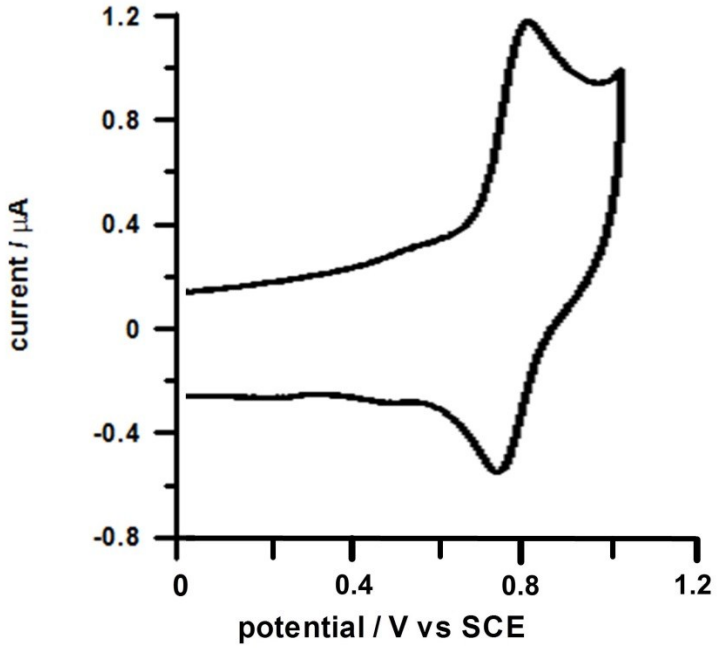
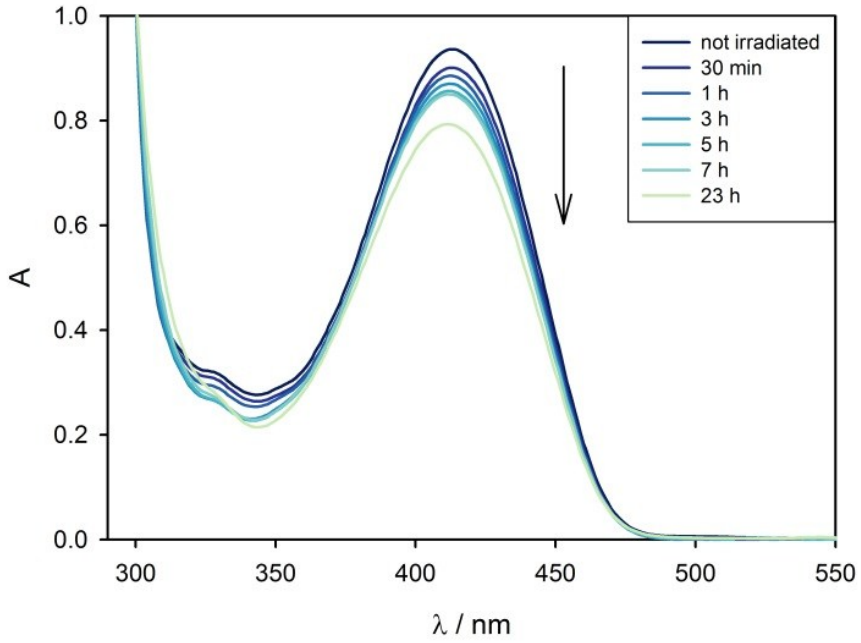
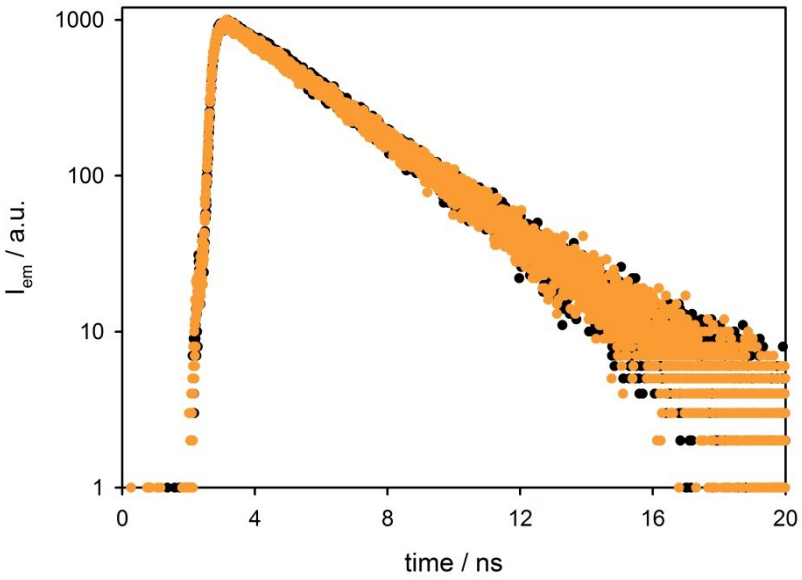


Figure S5. Absorption spectra of coumarin **10** 3.1 x 10^{-4} M (0.15 mol%) in degassed DMF solution in the presence of aldehyde **6a** 0.21 M and Et_3N 0.8 M upon irradiation at 450 in the time interval 0 – 23 h (left). Optical pathlength = 0.1 cm.



The reaction was performed under the same experimental conditions reported in the text (Scheme 2), apart from coumarin **10** that was 0.15 mol% instead of 5 mol% in order to record its absorption spectrum (optical pathlength = 0.1 cm). Under the present experimental conditions, a slight decrease of the absorption band (λ_{max} = 413 nm) of the coumarin is observed during the irradiation (Figure S2). By taking into account the photocatalyst amount (5 mol%) reported in Scheme 2, a degradation of ca. 1% of coumarin **10** is estimated.

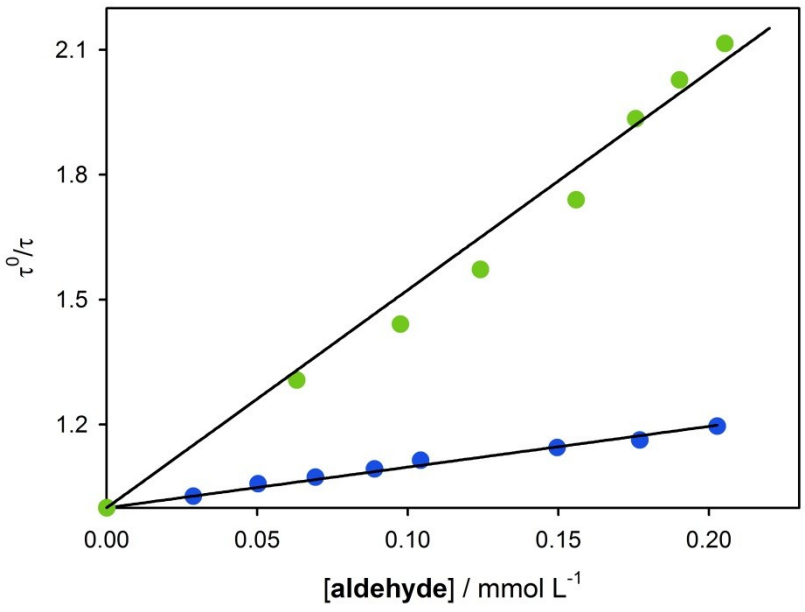
Figure S6. Emission intensity decays of **10** in DMF solution in absence (black dots) and in presence of Et_3N 0.8 M (orange dots) upon excitation at 405 nm.



Since the emission intensity decay of **10** does not change upon the addition of Et_3N 0.8 M (same concentration used to perform the reaction), Et_3N does not quench the fluorescence of the coumarin **10**.

In order to simulate the reaction condition, the Stern-Volmer analysis was conducted at different concentrations of selected aldehyde, in the presence of tertiary amine, as the amine is not able to quench the excited state of the coumarin catalyst.

Figure S7. Emission intensity decays of **10** in DMF solution containing Et_3N 0.8M in the absence (τ^0) and in the presence (τ) of increasing amount of aldehyde **6a** (blue dots) and **6c** (green dots). The slopes represent the Stern-Volmer constant (K_{SV}), i.e. the product of the quenching constant (k_q) and τ^0.



The Stern-Volmer plots show a linear correlation between the ratio τ^0/τ and the aldehyde concentration, as expected for a dynamic quenching process according to the Stern-Volmer equation:

$$\tau^0/\tau = 1 + K_{SV}[Q] = 1 + k_q\tau^0[Q] \qquad (S1)$$

where τ^0 and τ are the lifetimes in the absence and in the presence of the quencher Q (i.e. aldehydes), respectively, K_{SV} is the Stern-Volmer constant and k_q is the quenching constant.
The analysis of the plots reported above yields the following quenching constants:

$k_q = 3.1 \times 10^8\ M^{-1}s^{-1}$ for aldehyde **6a**
$k_q = 1.8 \times 10^9\ M^{-1}s^{-1}$ for aldehyde **6c**

Quenching by energy transfer from the lowest excited state of coumarin to populate the lowest triplet excited state of benzaldehyde is ruled out, being endoergonic. Indeed, the S_1 fluorescent excited states of coumarins **9** and **10** (Table 1) lye at lower energy than the T_1 excited states of the investigated aldehydes.[5]
The most plausible quenching mechanism is photoinduced electron transfer from the S_1 excited state of coumarin to aldehydes, yielding the corresponding ketyl radicals.
To discuss thermodynamic aspects of the photoinduced electron transfer we need to consider the reduction potentials of aldehydes (Table S13) and of the S_1 excited state of coumarins, which can be evaluated as follows:

$E(\mathbf{9}^+/^*\mathbf{9}) = E(\mathbf{9}^+/\mathbf{9}) - E_{00}(\mathbf{9}/^*\mathbf{9}) = 0.79 - 2.66 = -1.87$ V (vs SCE)
$E(\mathbf{10}^+/^*\mathbf{10}) = E(\mathbf{10}^+/\mathbf{10}) - E_{00}(\mathbf{10}/^*\mathbf{10}) = 0.83 - 2.72 = -1.89$ V (vs SCE)

Where the energy difference between the ground and the S_1 excited state (E_{00}) was estimated from the fluorescence spectrum (wavelength corresponding to the 20% of the maximum emission intensity).

Table S13. Half-wave reduction potentials ($E_{1/2}$ in V vs SCE) of selected aldehydes in different environments.

	EtOH/H_2O	0.5 M TBAP/ THF[6]	0.5 M $LiClO_4$/THF[a]
6a		-1.96	-1.71
6c	-1.34[7]		

The oxidative quenching of coumarins **9** and **10** by the investigated aldehydes is exoergonic, apart from **6a** in which it is slightly endoergonic if the reduction potential of -1.96 V is considered. However, as evident from data reported in Table S13, the presence of Lewis acids can greatly affect the reduction potentials of aldehydes. In particular, **6a** become much easier to be reduced in the presence of $LiClO_4$ supporting electrolyte. Indeed, lithium ion interaction with the carbonyl withdraws electrons from the carbonyl compound and makes the carbonyl easier to be reduced than if the lithium were not present.[8] Under the conditions reported in Scheme 2, the radical cation $Et_3N^{\bullet+}$ can act as Lewis acid, as previously discussed by Rueping[9] making the photoinduced electron transfer exoergonic also in the case of **6a**.

References

[1] F. Jafarpour, S. Zarei, M. Barzegar Amiri Olia, N. Jalalimanesh and S. Rahiminejadan, *J. Org. Chem.* 2013, **78**, 2957-2964.

[2] a) K. Palita, P. Narid, S. Thitiya, N. Supawadee, S. Taweesak, K. Tinnagon, J. Siriporn and P. Vinich, *Eur. J. Org. Chem.*, 2015, 496-505; b) P. Kochapradist, T. Sunonnam, N. Prachumrak, S. Namuangruk, T. Keawin, S. Jungsuttiwong, T. Sudyoadsuk and V. Promarak, *Tetrahedron Lett.*, 2014, **55**, 6689-6693; c) L. Liu, D. Huang, S. M. Draper, X. Yi, W. Wu and J. Zhao, *Dalton Transactions*, 2013, **42**, 10694-10706.

[3] T. P. Jansen, G. Rodeghiero, D. Foglietta, R. Perciaccante, L. Della Ciana (Cynagen srl), EP3219712 (A1), **2017**.

[4] a) G. Foulard, T. Brigaud and C. Portella, *Tetrahedron*, 1996, **52**, 6187-6200; A. Elena, M. Elisa and M. Paolo, *Angew. Chem. Int. Ed.*, 2014, **53**, 12064-12068; b) G. Magagnano, A. Gualandi, M. Marchini, L. Mengozzi, P. Ceroni and P. G. Cozzi, *Chem. Commun.*, 2017, **53**, 1591-1594.; c) C.-J. Wallentin, J. D. Nguyen, P. Finkbeiner and C. R. J. Stephenson, *J. Am. Chem. Soc.*, 2012, **134**, 8875-8884.

[5] H. Gorner, H. J. Kuhn, *J. Phys. Chem.* **1986**, *90,* 5946-5955; M. J. van der Burgt, J. Jansen, A. H. Huizer, C. A.G.O. Varma, *J. Mol. Struct.* 1996, **385**, 175-183.

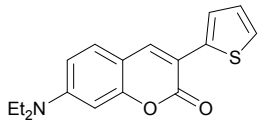
[6] E. M. Arnett, C. A. Palmer, *J. Am. Chem. Soc.* 1990, **112**, 1354-1360.

[7] A. J. G. Barwise, A. A. Gorman, R. L. Leyland, P. G. Smith, M. A. J. Rodgers, *J. Am. Chem. Soc.* 1968, **100**, 1814-1820.

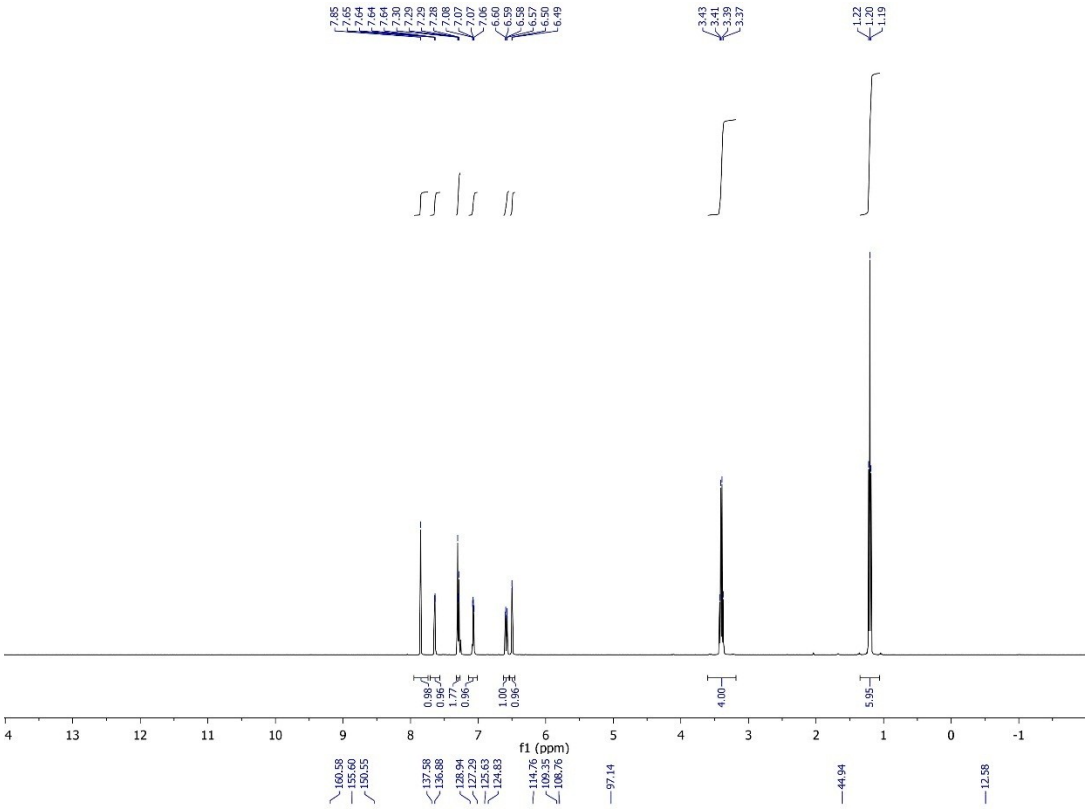
[8] . E. M. Arnett, C. A. Palmer, *J. Am. Chem. Soc.* **1990**, *112*, 1354-1360.

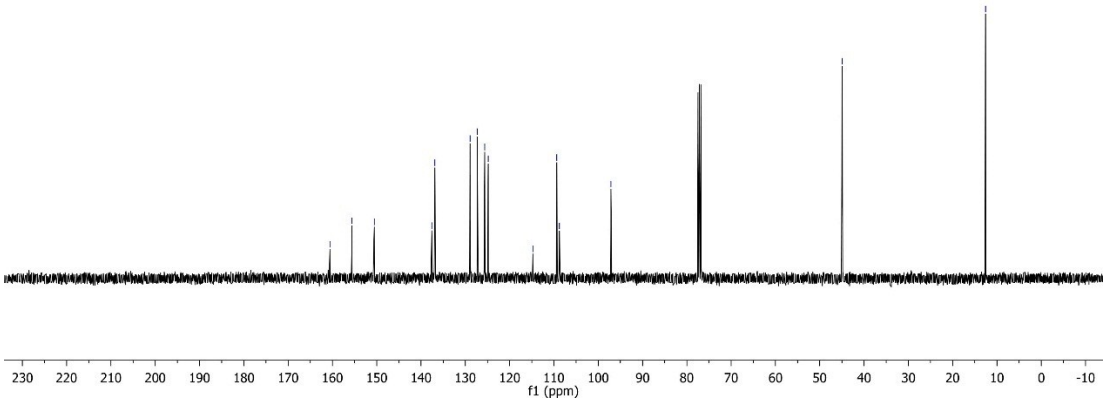
[9] E. Fava, S. Loescher, Z. Jiang, M. Rueping, *Angew. Chem.* **2015**, *127*, 8952-8954; *Angew. Chem. Int. Ed.* 2015, **54**, 8828-8832.

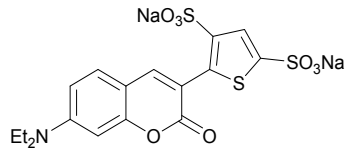
Copies of NMR spectra



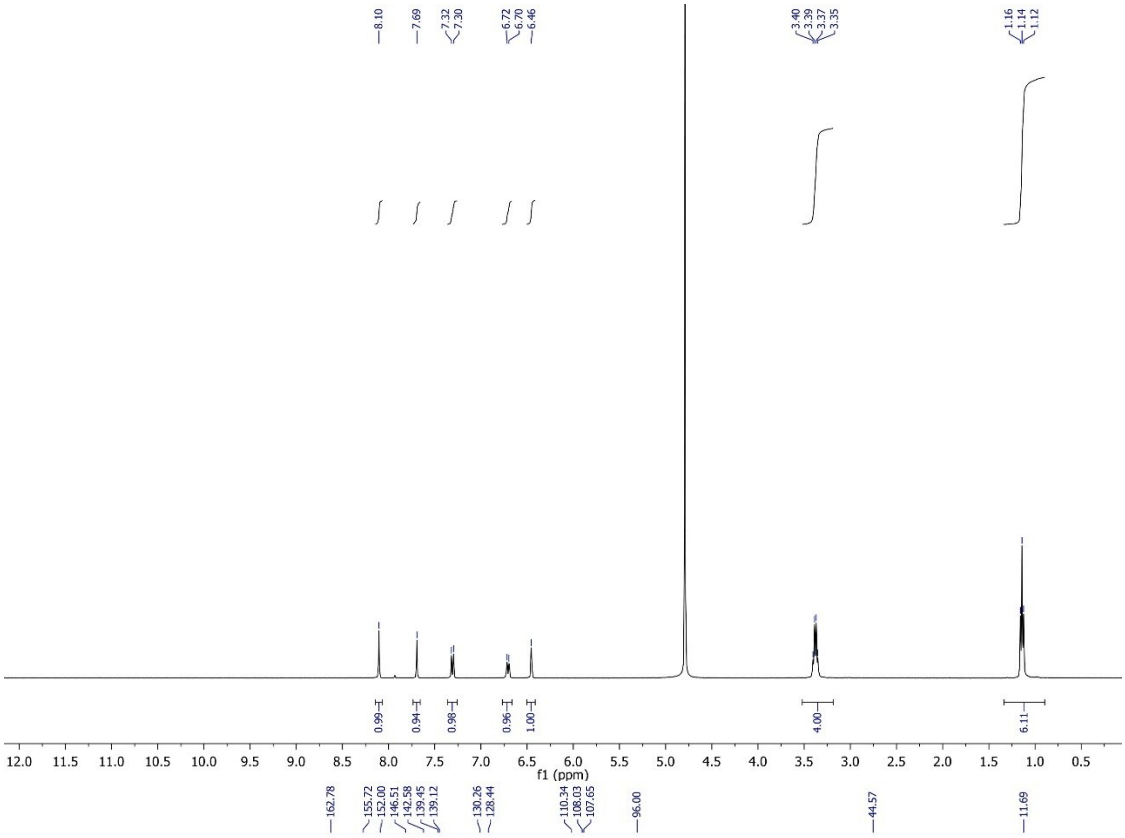
9

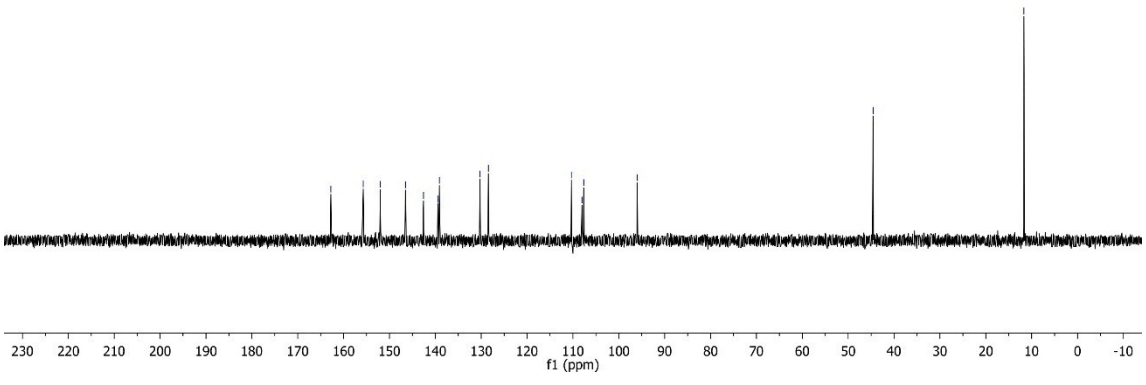


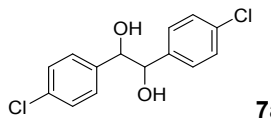



NaO3S
SO3Na
S
Et2N
O
O

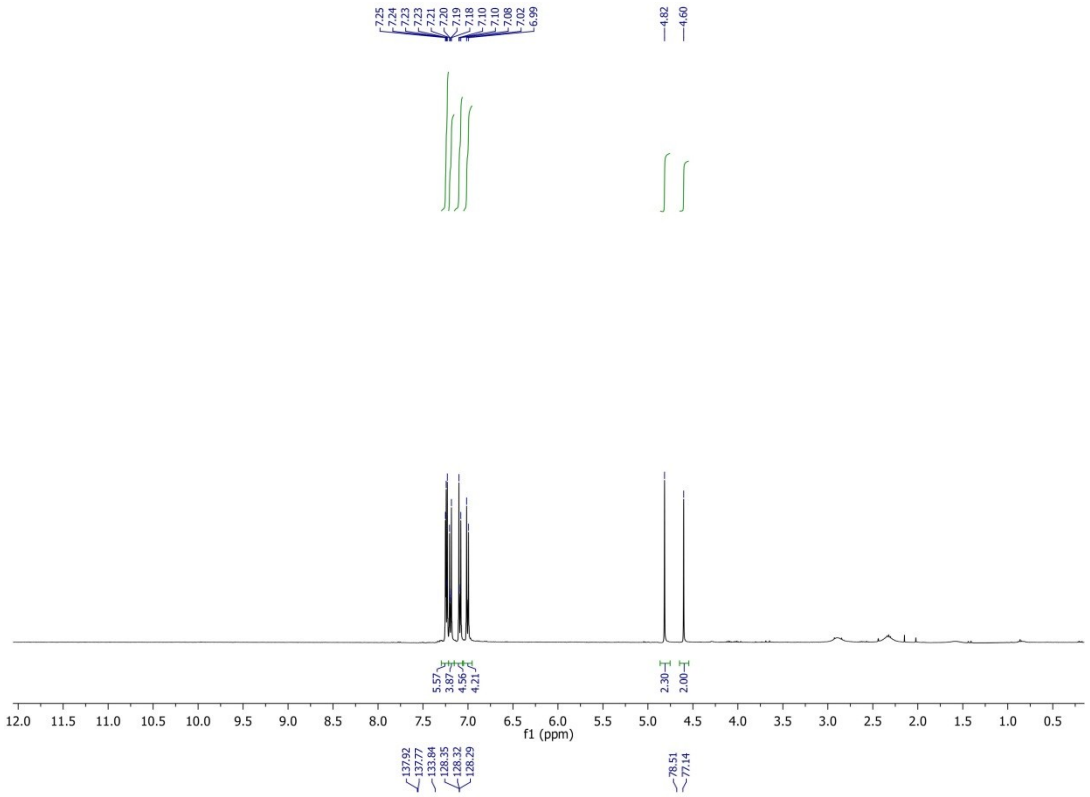
10

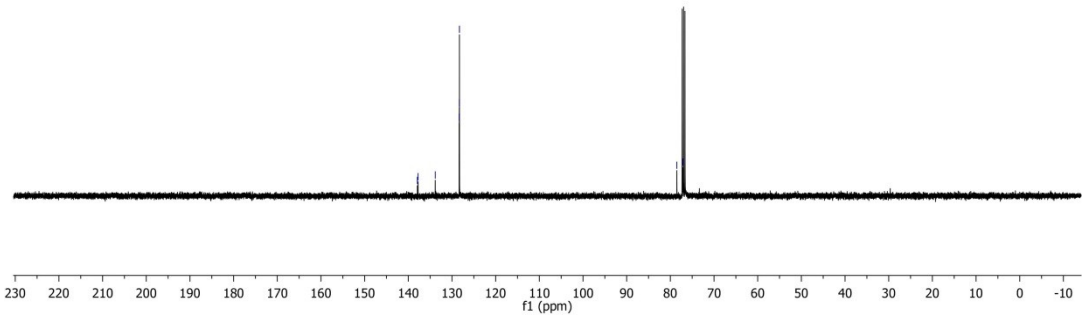

8.10
7.69
7.32
7.30
6.72
6.70
6.46
3.40
3.39
3.37
3.35
1.16
1.14
1.12
0.99
0.94
0.98
0.96
1.00
4.00
6.11
f1 (ppm)

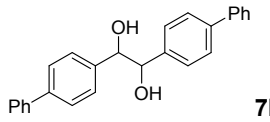

162.78
155.72
152.00
146.51
142.58
139.45
139.12
130.26
128.44
110.34
108.03
107.65
96.00
44.57
11.69
f1 (ppm)


OH
Cl
OH
Cl

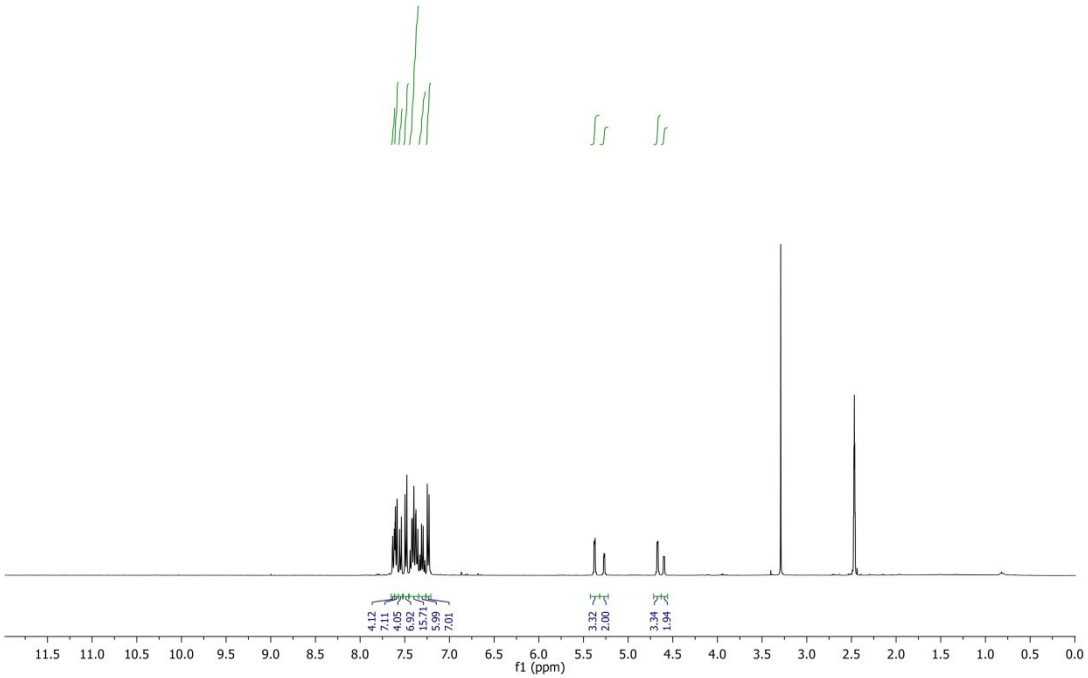
7a

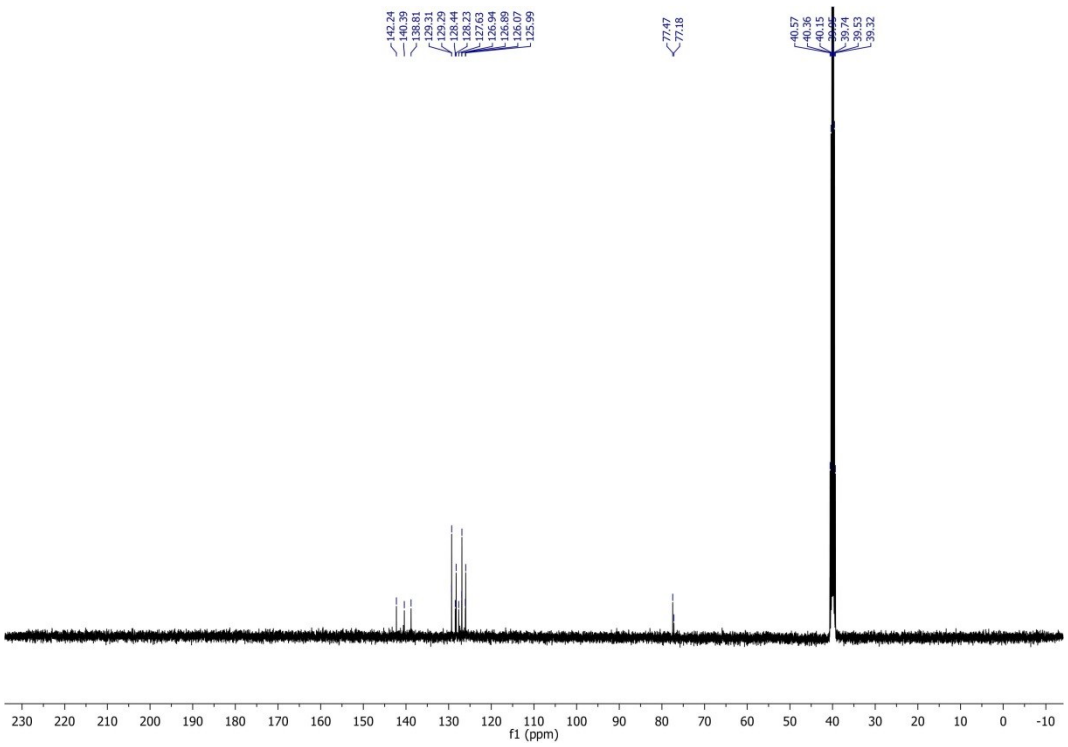

7.25
7.24
7.23
7.23
7.21
7.20
7.19
7.18
7.10
7.10
7.08
7.02
6.99
4.82
4.60
5.57
3.87
4.56
4.21
2.30
2.00
f1 (ppm)
137.92
137.77
133.84
128.35
128.32
128.29
78.51
77.14

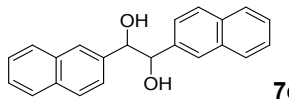

f1 (ppm)


OH
Ph
OH
Ph

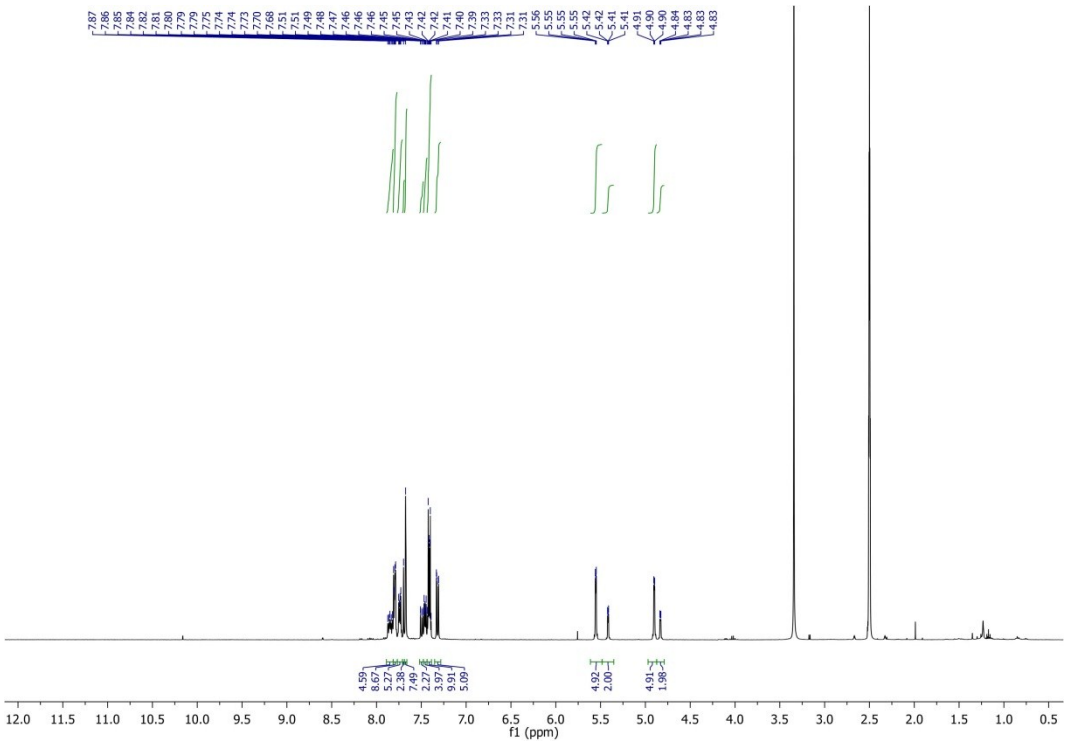
7b

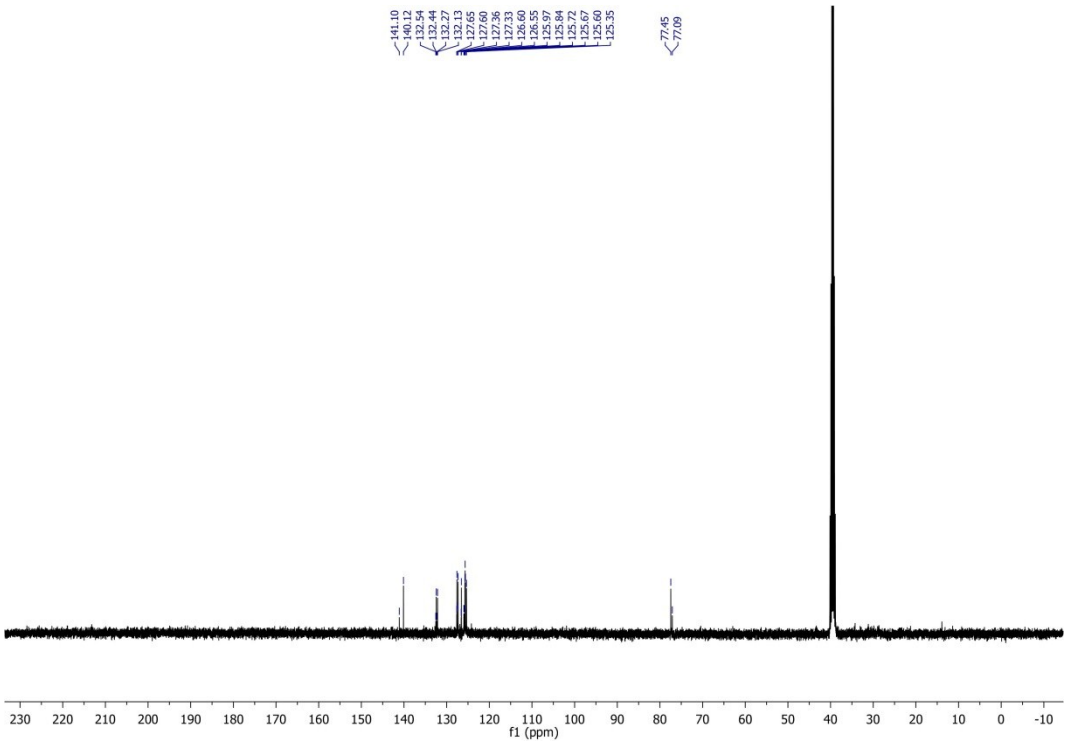

4.12
7.11
4.05
6.92
15.71
5.99
7.01
3.32
2.00
3.34
1.94
f1 (ppm)

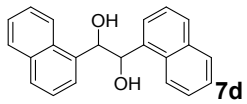

142.24
140.39
138.81
129.31
129.29
128.44
128.23
127.63
126.94
126.89
126.07
125.99
77.47
77.18
40.57
40.36
40.15
39.74
39.53
39.32
f1 (ppm)


OH
OH

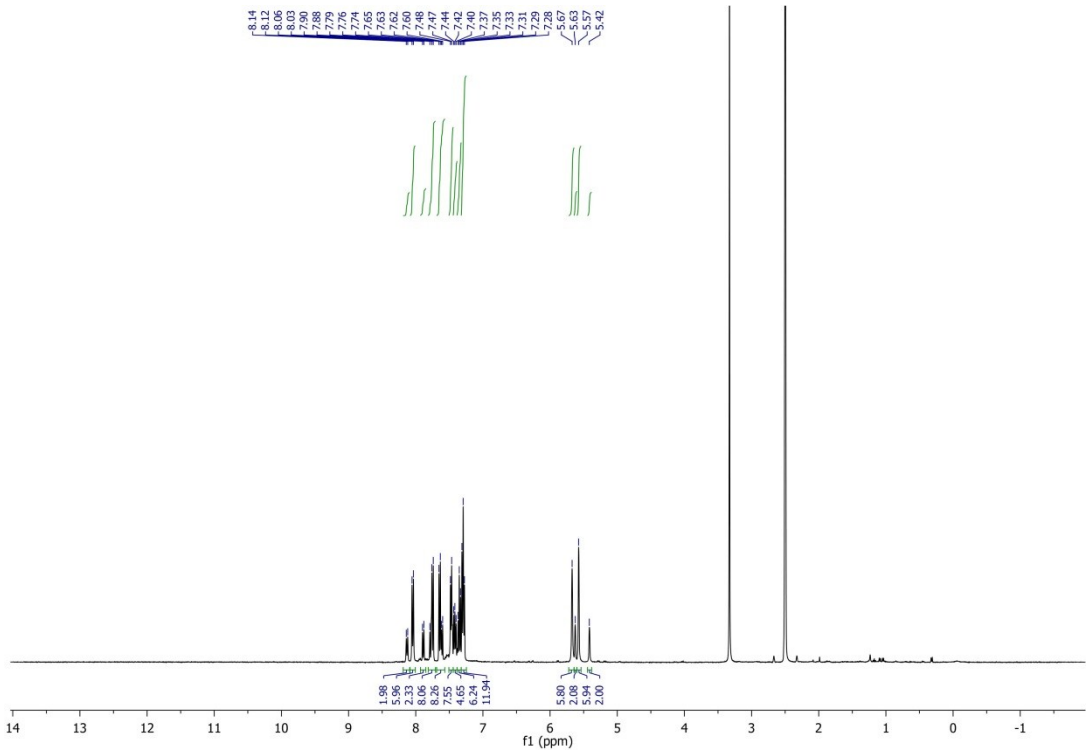
7c

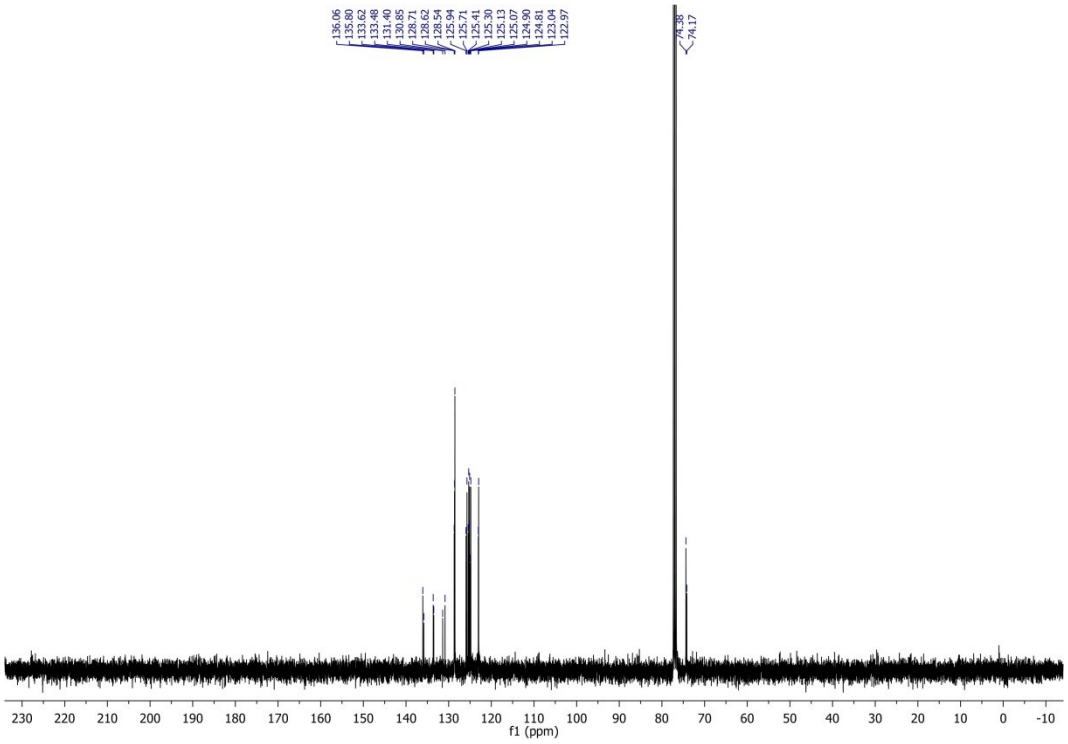

7.87
7.86
7.85
7.84
7.82
7.81
7.80
7.79
7.79
7.75
7.74
7.74
7.73
7.70
7.68
7.51
7.51
7.49
7.48
7.47
7.46
7.46
7.46
7.45
7.43
7.42
7.42
7.41
7.40
7.39
7.33
7.33
7.31
7.31
5.56
5.55
5.55
5.55
5.42
5.42
5.41
5.41
4.91
4.91
4.90
4.90
4.84
4.83
4.83
4.83
4.59
8.67
5.27
2.38
7.49
2.77
3.97
9.91
5.09
4.92
2.00
4.91
1.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

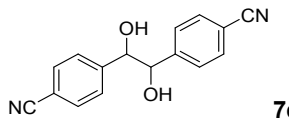

141.10
140.12
132.54
132.44
132.27
132.13
127.65
127.60
127.36
127.33
126.60
126.55
125.97
125.84
125.72
125.67
125.60
125.35
77.45
77.09
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


OH
OH

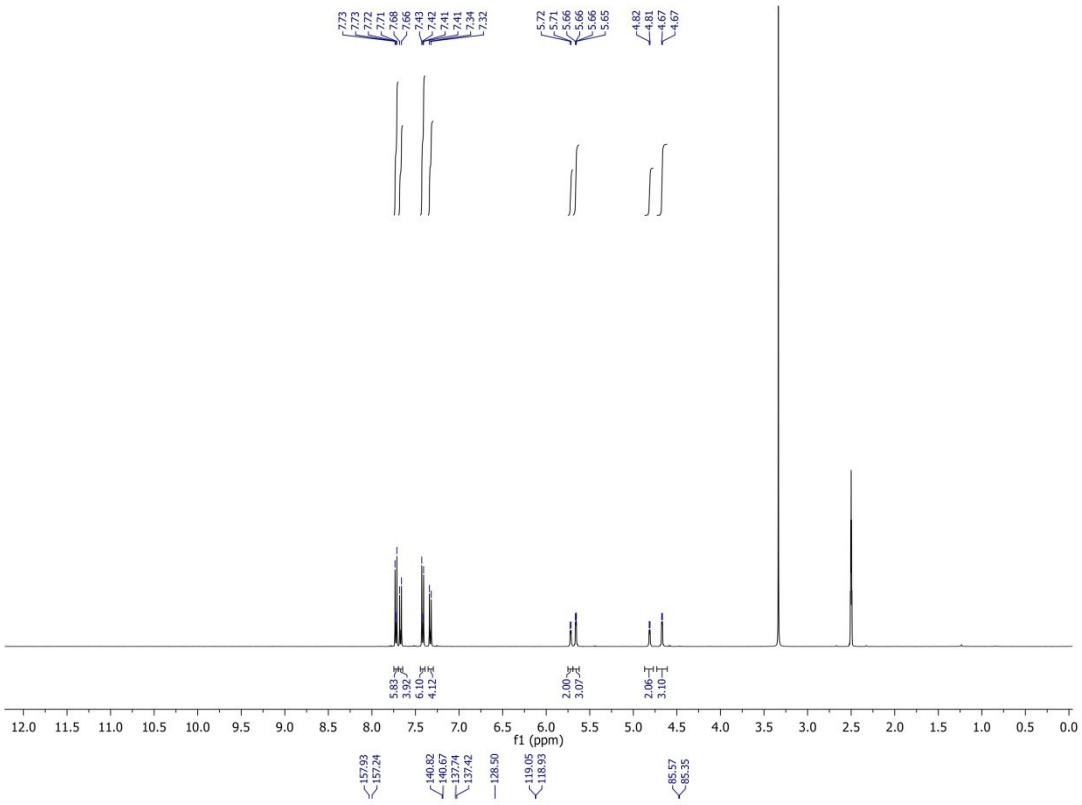
7d

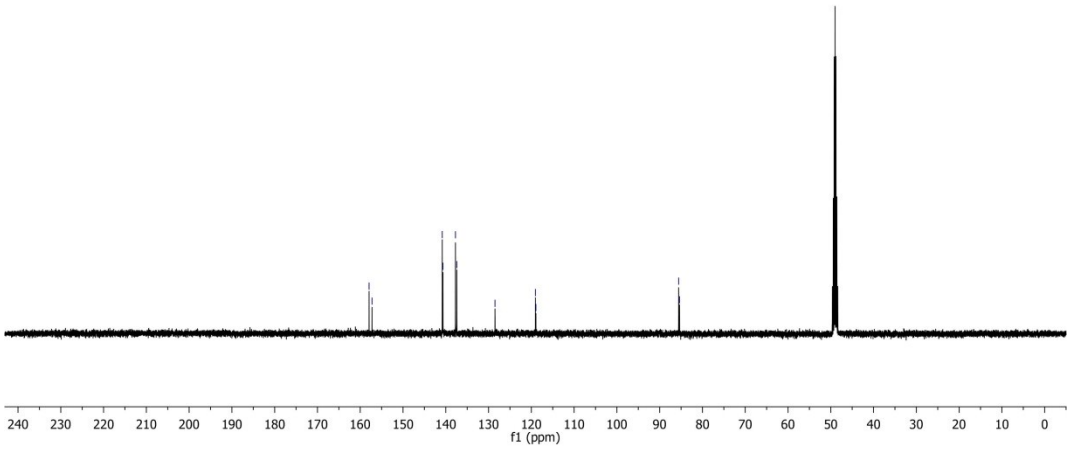

8.14
8.12
8.06
8.03
7.90
7.88
7.79
7.76
7.74
7.65
7.63
7.62
7.60
7.48
7.47
7.44
7.42
7.40
7.37
7.35
7.33
7.31
7.29
7.28
5.67
5.63
5.57
5.42
1.98
5.96
2.33
8.06
8.26
7.55
4.65
6.24
11.94
5.80
2.08
5.94
2.00
f1 (ppm)

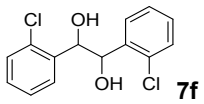

136.06
135.80
133.62
133.48
131.40
130.85
128.71
128.62
128.54
125.94
125.71
125.41
125.30
125.13
125.07
124.90
124.61
123.64
122.97
74.38
74.17
f1 (ppm)


OH
CN
NC
OH

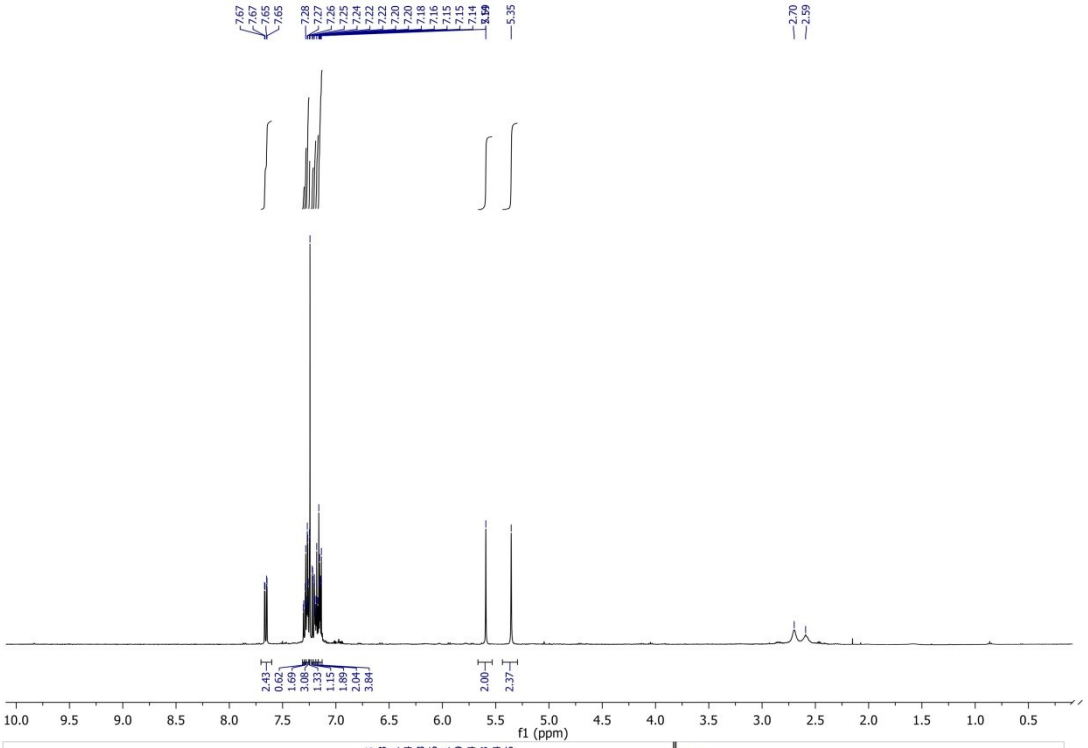
7e

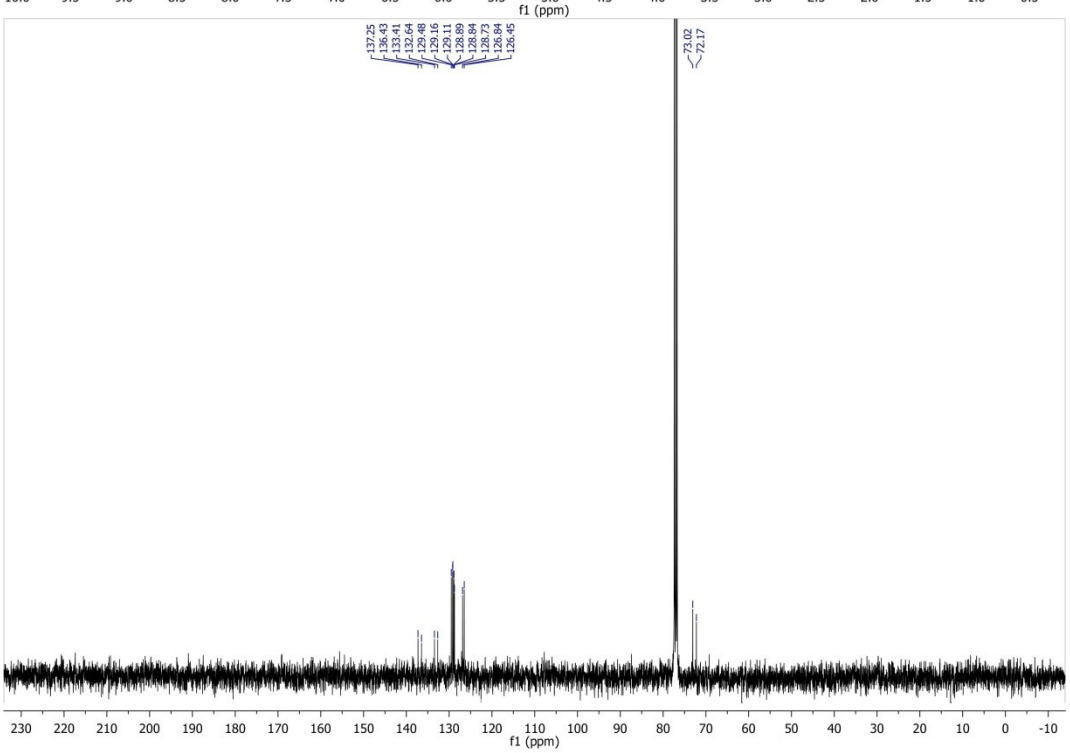

7.73
7.73
7.72
7.71
7.68
7.66
7.43
7.42
7.41
7.41
7.34
7.32
5.72
5.71
5.66
5.66
5.66
5.65
4.82
4.81
4.67
4.67
5.83
3.92
6.10
4.12
2.00
3.07
2.06
3.10
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
157.93
157.24
140.82
140.67
137.74
137.42
128.50
119.05
118.93
85.57
85.35

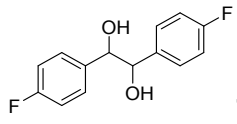

240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
OH
OH
Cl

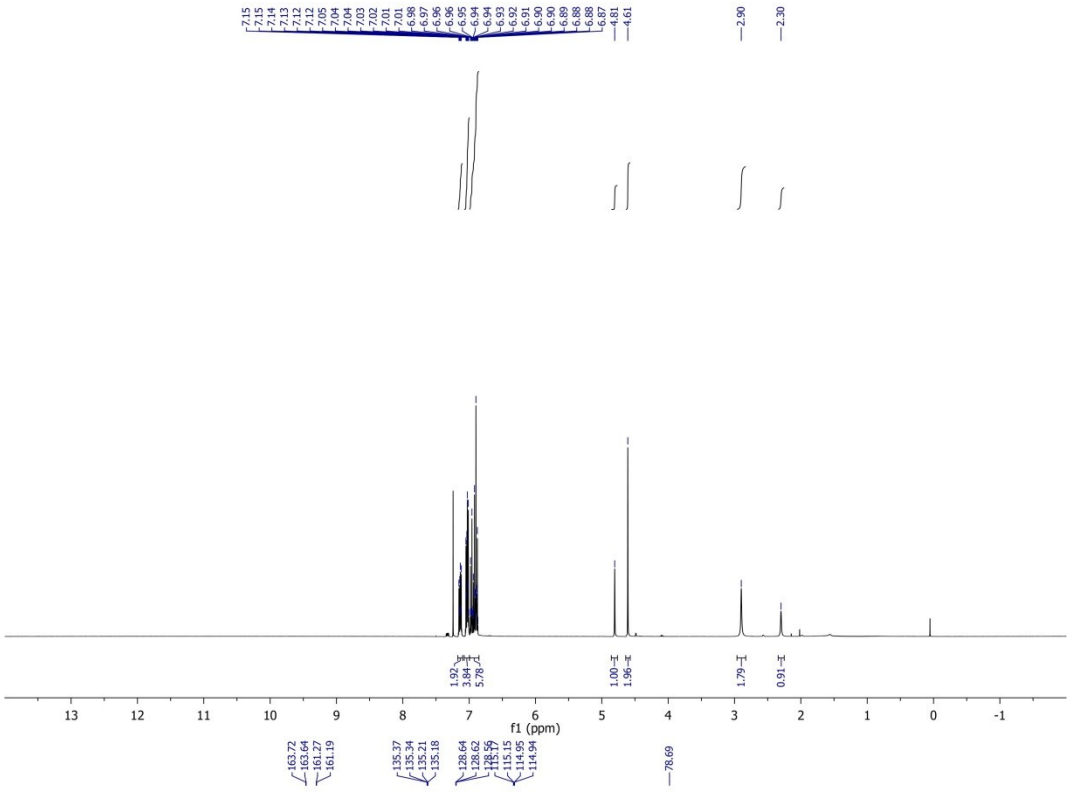
7f


7.67
7.67
7.65
7.65
7.28
7.27
7.26
7.25
7.24
7.22
7.22
7.20
7.20
7.18
7.16
7.15
7.15
7.14
5.39
5.35
2.70
2.59
2.43
0.62
1.69
3.08
1.33
1.15
1.89
2.04
3.84
2.00
2.37
f1 (ppm)

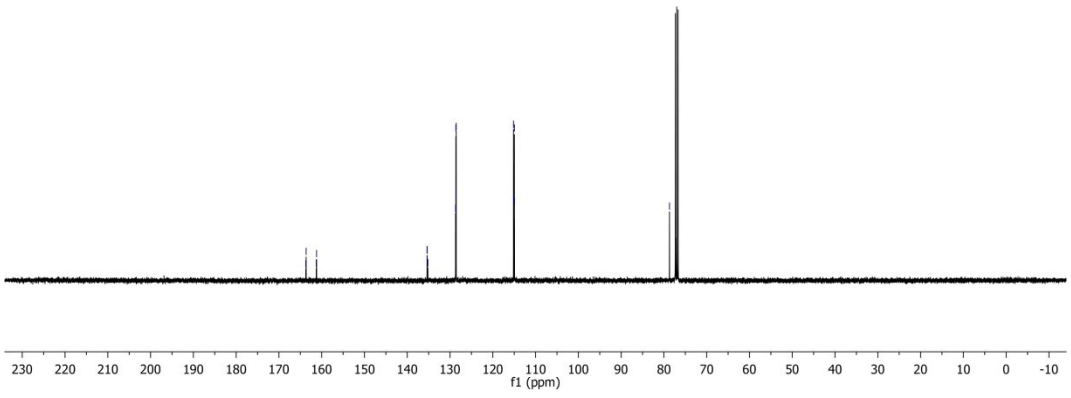

137.25
136.43
133.41
132.64
129.48
129.16
129.11
128.89
128.84
128.73
126.84
126.45
73.02
72.17
f1 (ppm)

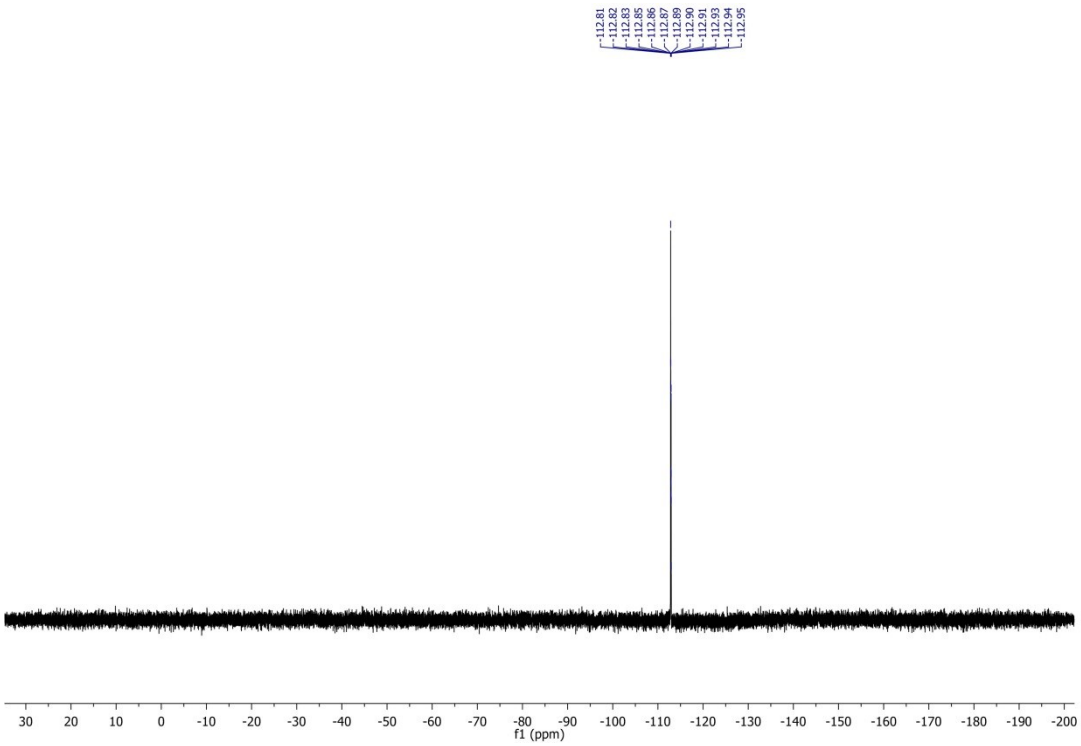

OH
F
F
OH

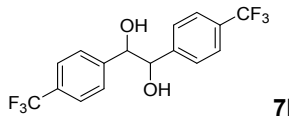
7g


7.15
7.15
7.14
7.13
7.12
7.12
7.05
7.04
7.04
7.03
7.02
7.01
7.01
6.98
6.97
6.96
6.96
6.95
6.94
6.94
6.93
6.92
6.91
6.90
6.90
6.89
6.88
6.88
6.87
4.81
4.61
2.90
2.30
1.92
3.84
5.78
1.00
1.96
1.79
0.91
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

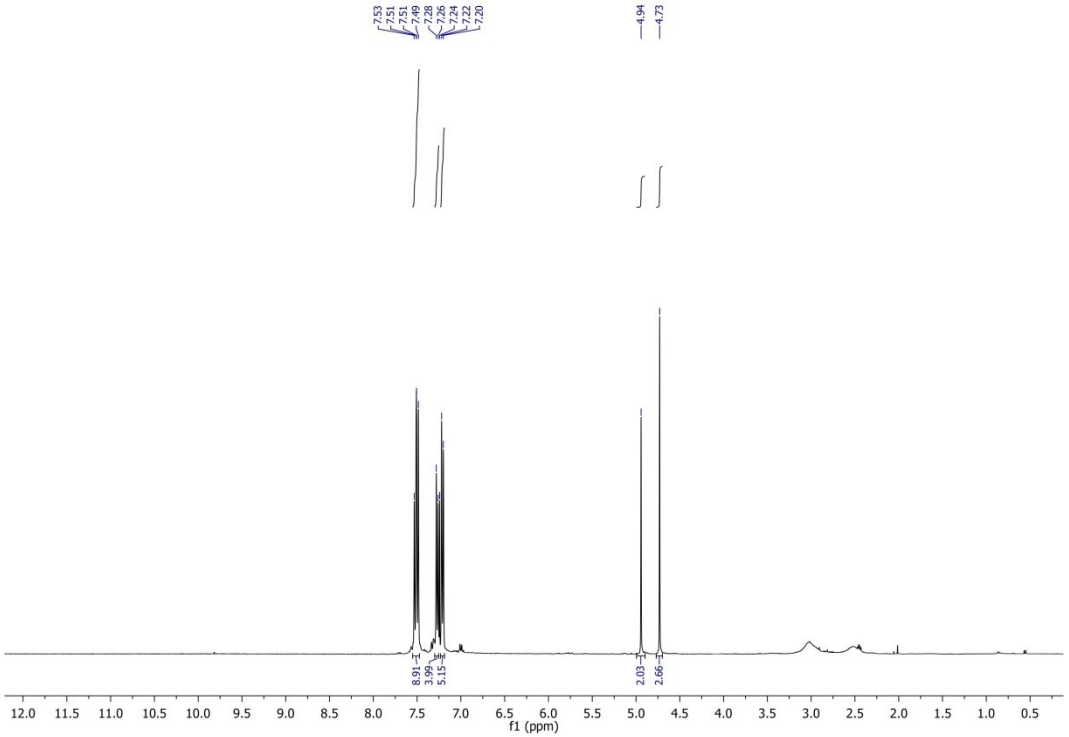
163.72
163.64
161.27
161.19
135.37
135.34
135.21
135.18
128.64
128.62
115.15
114.95
114.94
78.69

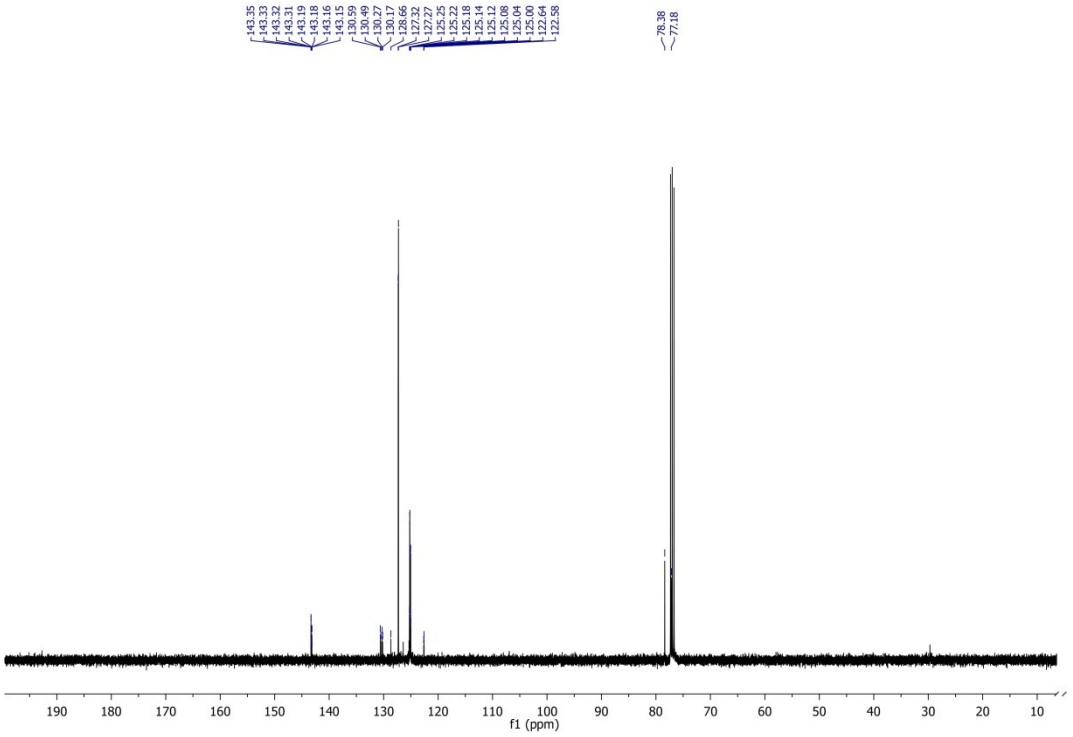

230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

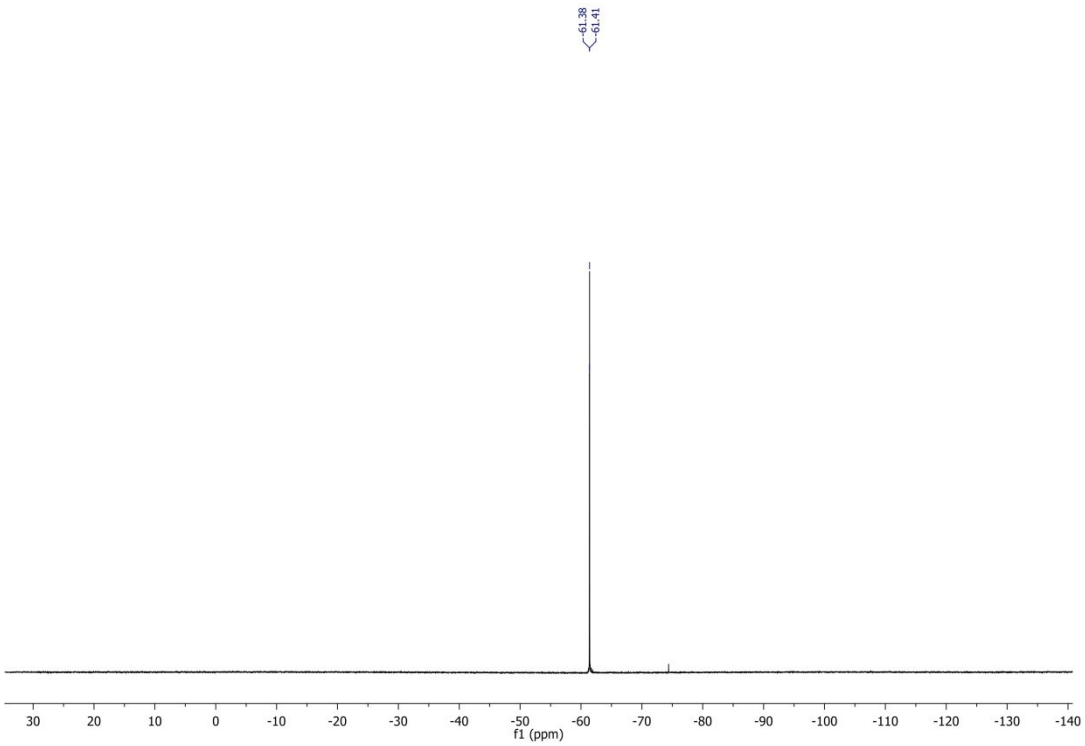

-112.81
-112.82
-112.83
-112.85
-112.86
-112.87
-112.89
-112.90
-112.91
-112.93
-112.94
-112.95
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

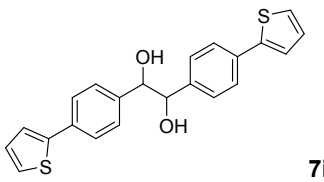

OH
CF3
F3C
OH

7h

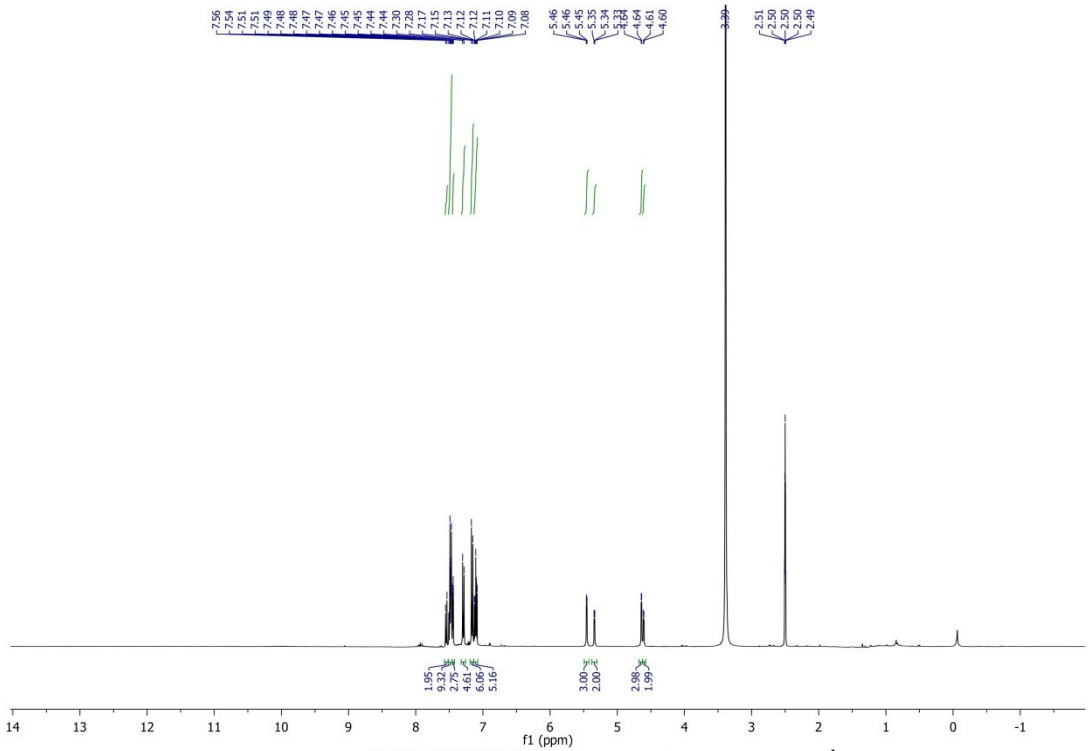

7.53
7.51
7.51
7.49
7.28
7.26
7.24
7.22
7.20
4.94
4.73
8.91
3.99
5.15
2.03
2.66
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

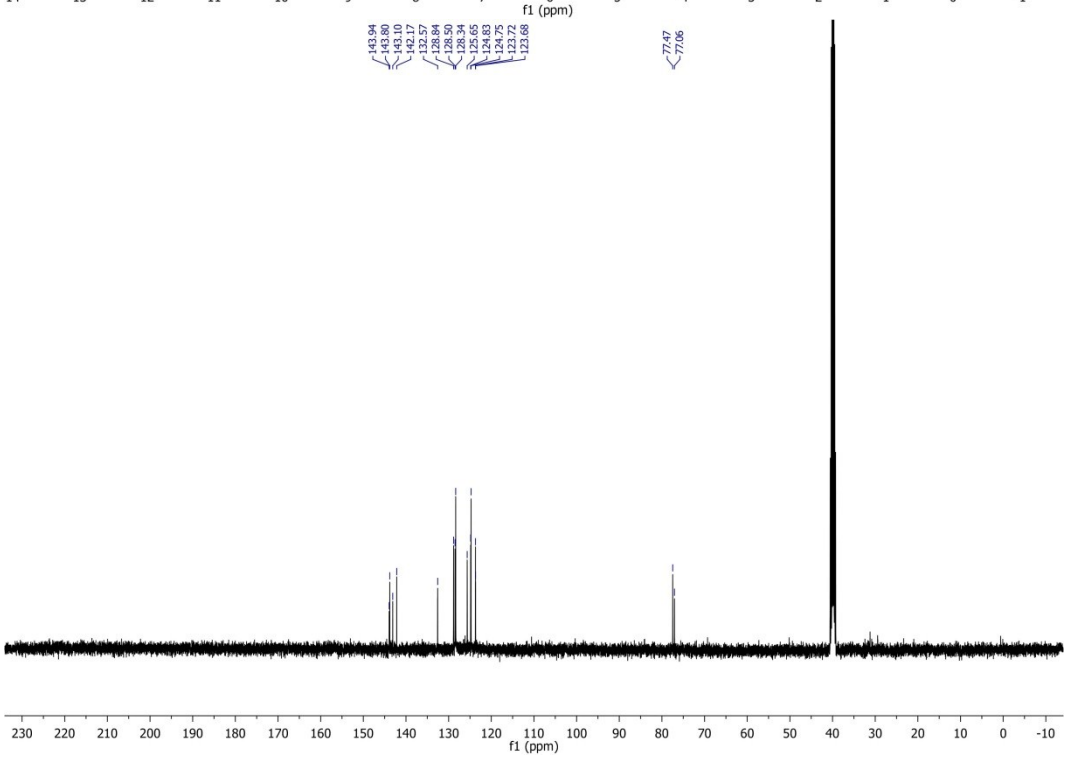

143.35
143.33
143.32
143.31
143.19
143.18
143.16
143.15
130.59
130.49
130.27
130.17
128.66
127.32
127.27
125.25
125.22
125.18
125.14
125.12
125.08
125.04
125.00
122.64
122.58
78.38
77.18
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

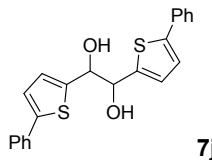

-61.38
-61.41
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)


S
OH
OH
S

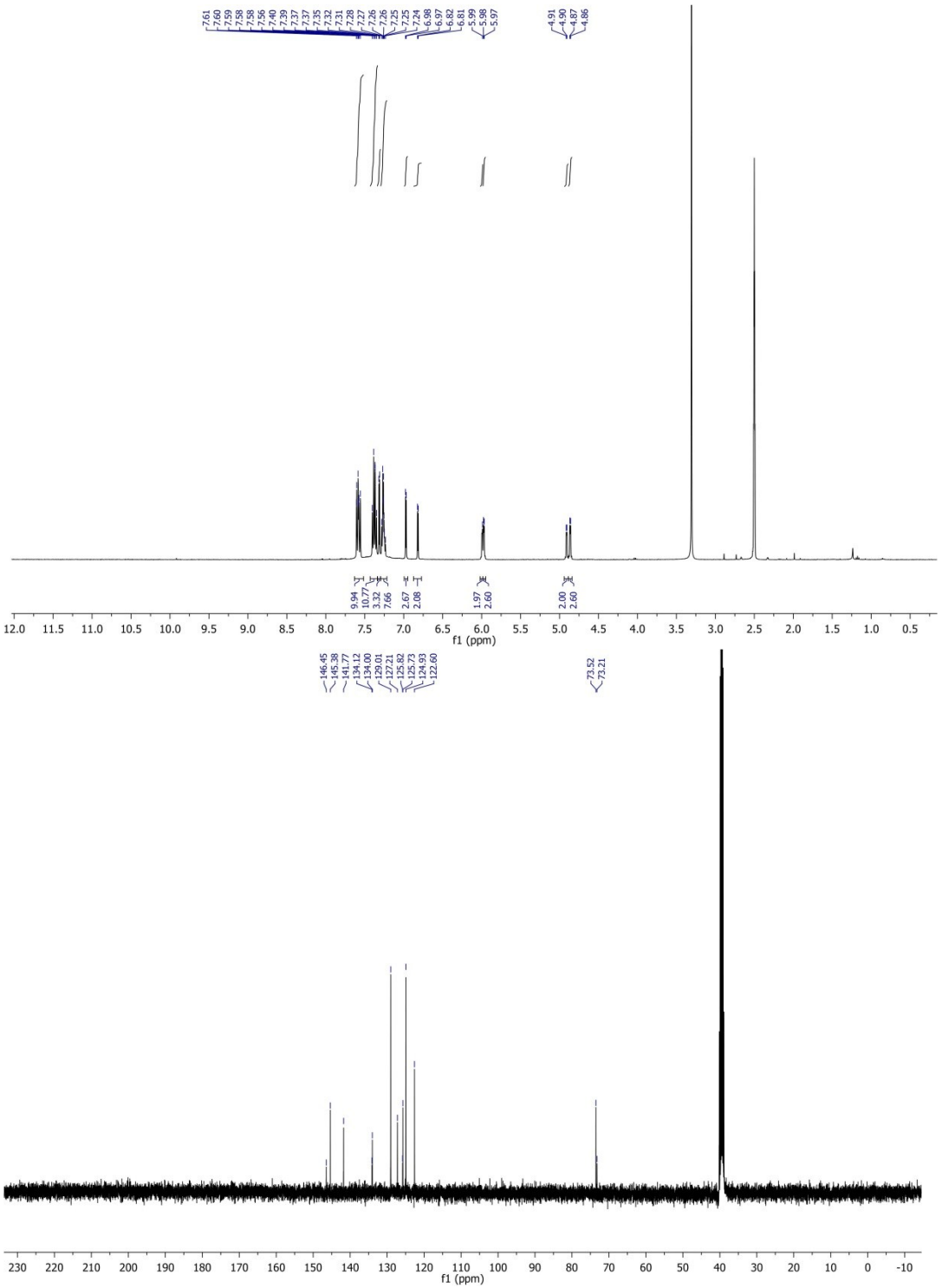
7i

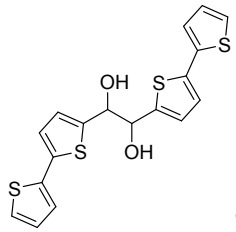

7.56
7.54
7.51
7.51
7.49
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.44
7.30
7.28
7.17
7.15
7.13
7.12
7.12
7.11
7.10
7.09
7.08
5.46
5.46
5.45
5.35
5.34
4.64
4.61
4.60
3.99
2.51
2.50
2.50
2.50
2.49
1.95
9.32
7.73
4.61
6.06
5.16
3.00
2.00
2.98
1.99
f1 (ppm)


143.94
143.80
143.10
142.17
132.57
128.84
128.50
128.34
125.65
124.83
124.75
123.72
123.68
77.47
77.06
f1 (ppm)

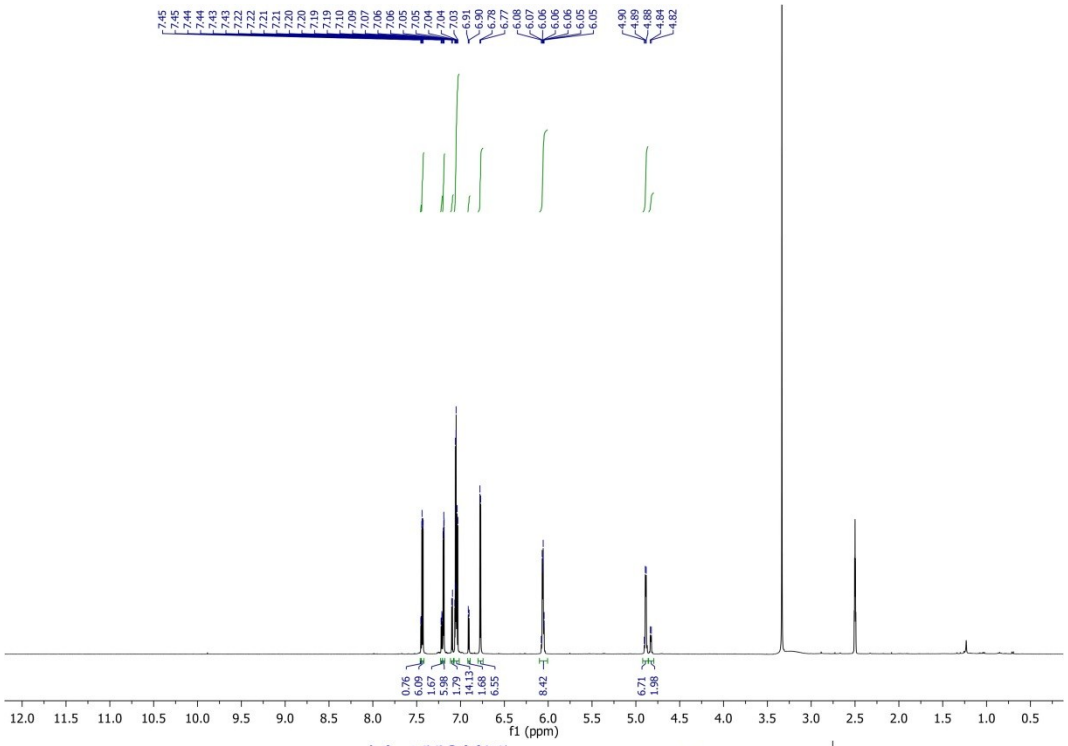

Ph
OH
S
S
OH
Ph

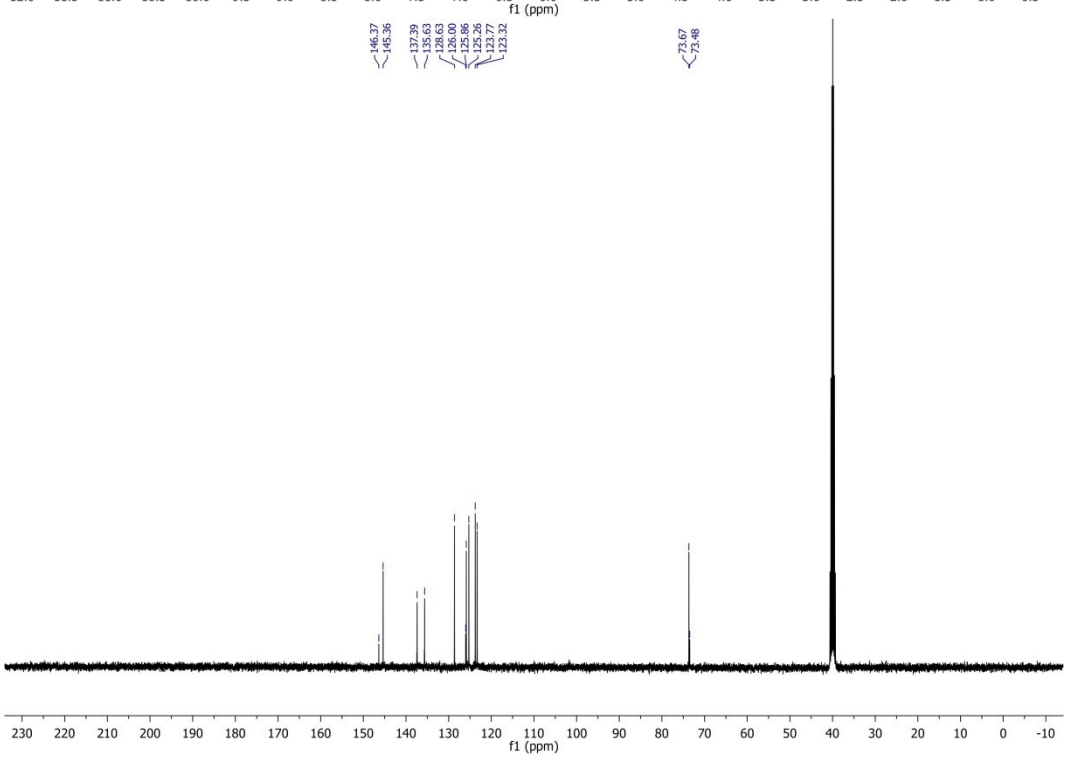
7j

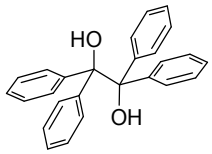

7.61
7.60
7.59
7.58
7.58
7.56
7.40
7.39
7.37
7.37
7.35
7.32
7.31
7.28
7.27
7.26
7.26
7.25
7.25
7.24
6.98
6.97
6.82
6.81
5.99
5.98
5.97
4.91
4.90
4.87
4.86
9.94
10.77
3.32
7.66
2.67
2.08
1.97
2.60
2.00
2.60
f1 (ppm)
146.45
145.38
141.77
134.12
134.00
129.01
127.21
125.82
125.73
124.93
122.60
73.52
73.21
f1 (ppm)


OH
OH
S
S
S
S

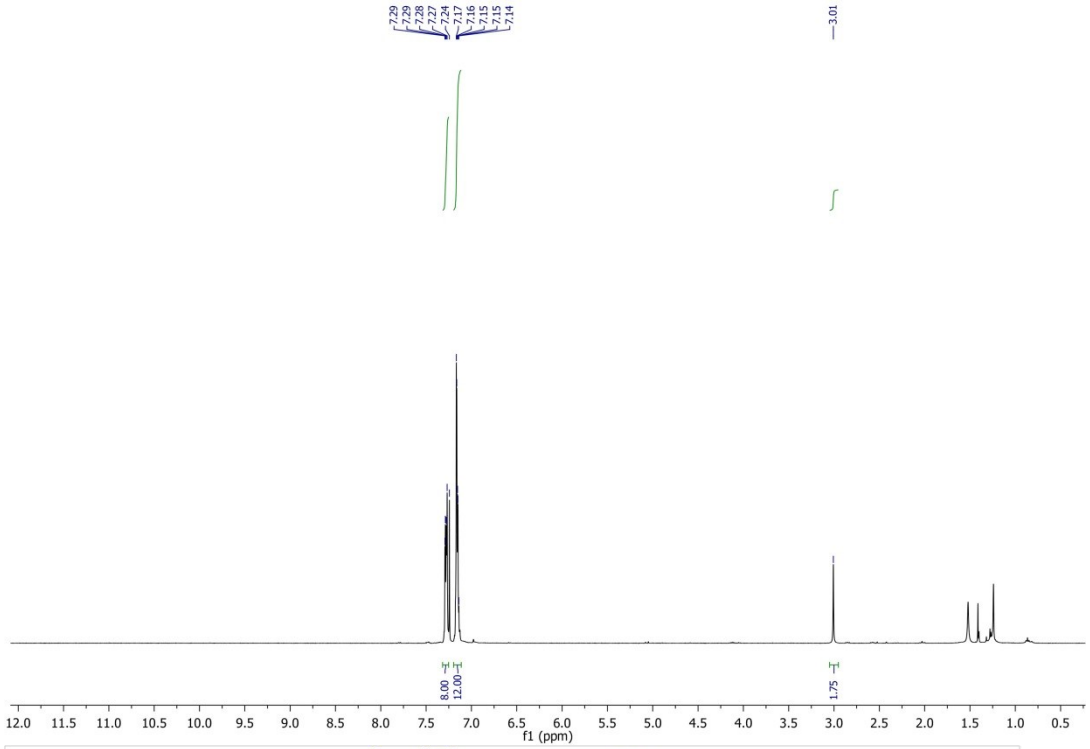
7k

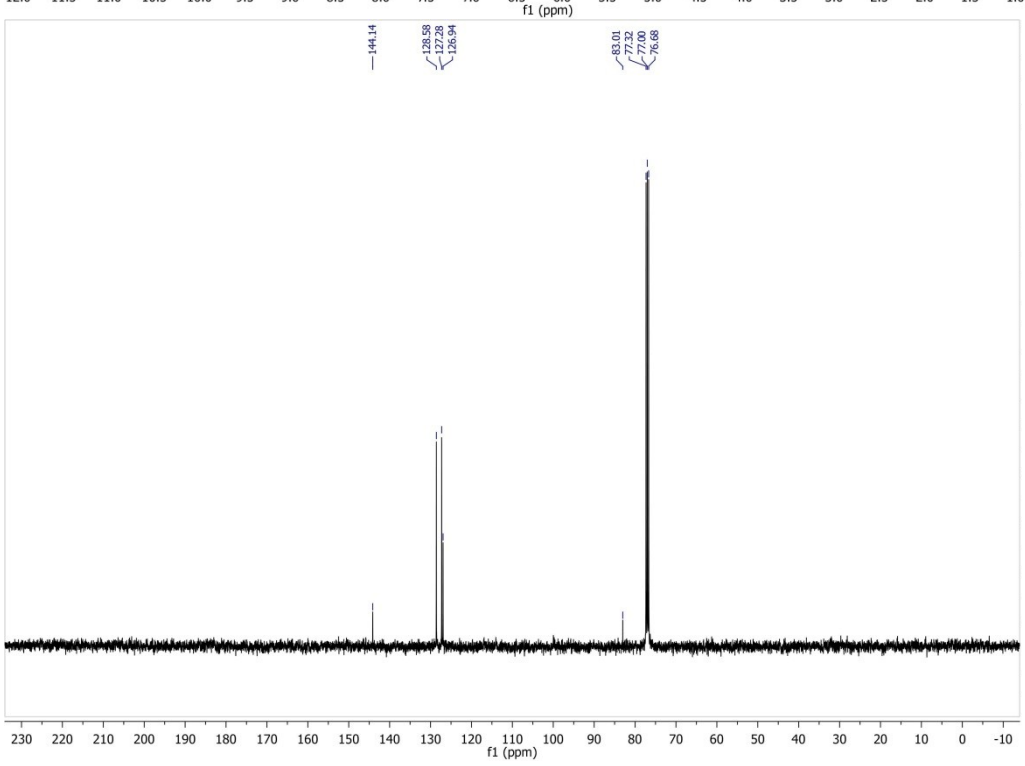

7.45
7.45
7.44
7.44
7.43
7.43
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.10
7.09
7.07
7.06
7.06
7.05
7.05
7.04
7.04
7.03
6.91
6.90
6.78
6.77
6.08
6.07
6.06
6.06
6.06
6.06
6.05
6.05
4.90
4.89
4.88
4.84
4.82
0.76
6.09
1.67
5.98
1.79
14.13
1.68
6.55
8.42
6.71
1.98
f1 (ppm)

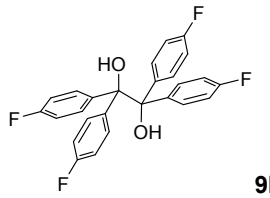

146.37
145.36
137.39
135.63
128.63
126.00
125.86
125.26
123.77
123.32
73.67
73.48
f1 (ppm)


HO
OH

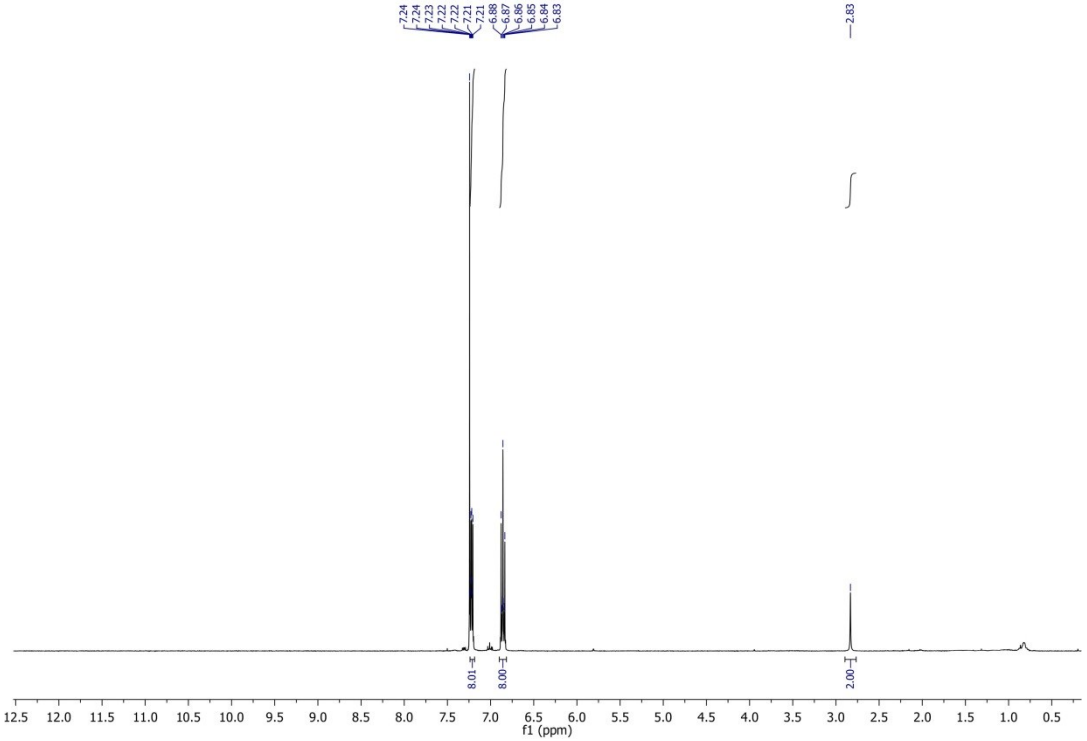
9a

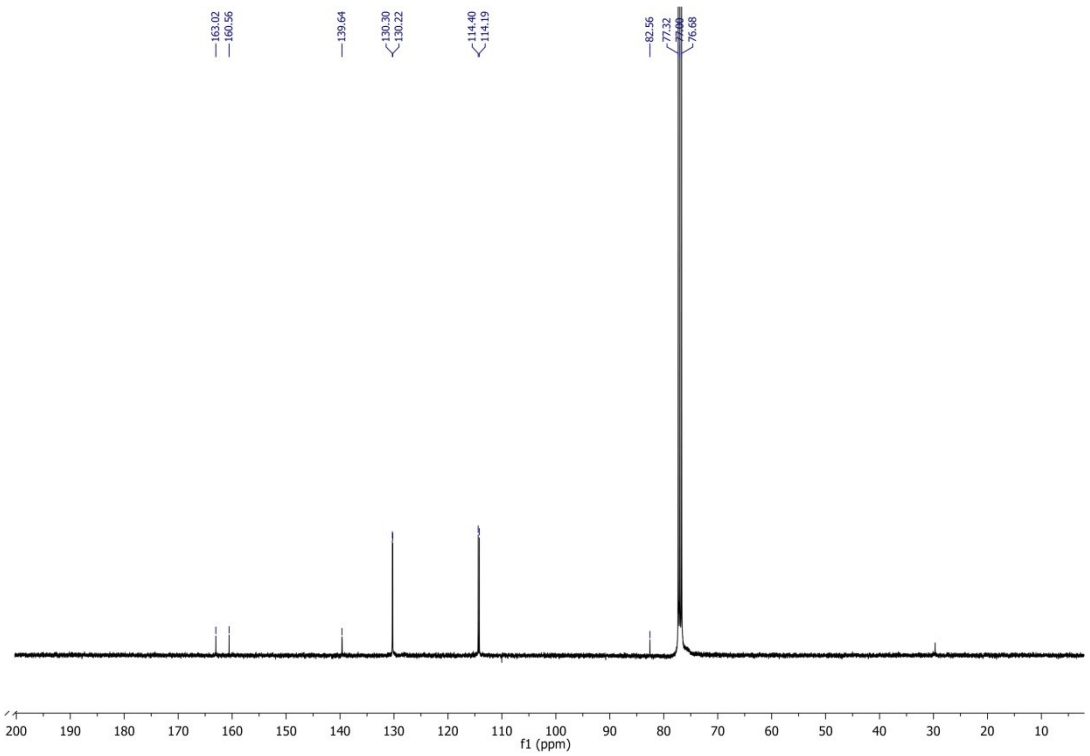

7.29
7.29
7.28
7.27
7.24
7.17
7.16
7.15
7.15
7.15
7.14
3.01
8.00
12.00
1.75
f1 (ppm)

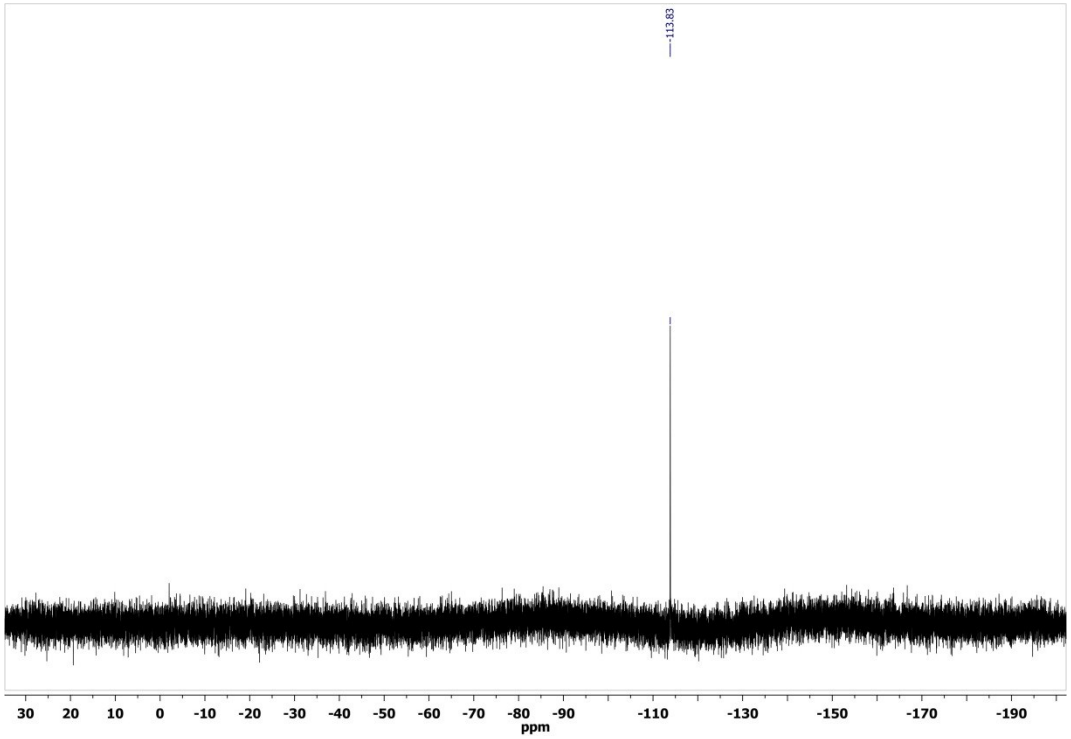

144.14
128.58
127.28
126.94
83.01
77.32
77.00
76.68
f1 (ppm)

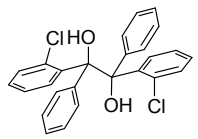

F
HO
F
F
OH
F

9b

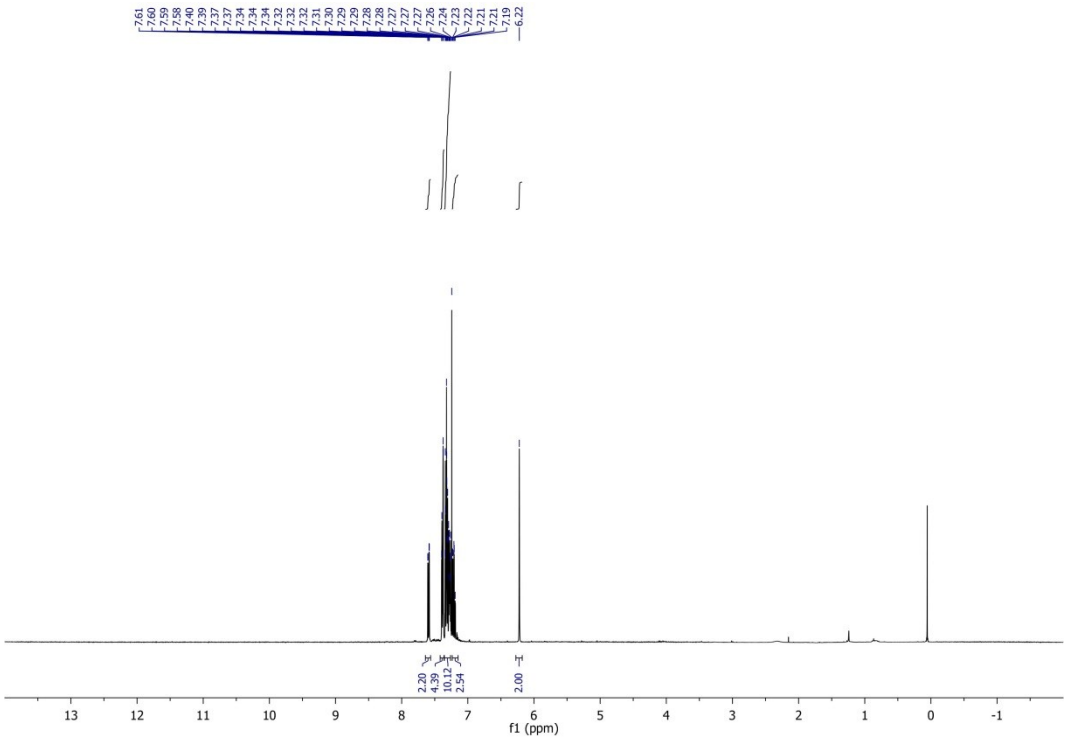

7.24
7.24
7.23
7.22
7.22
7.21
7.21
6.88
6.87
6.86
6.85
6.84
6.83
2.83
8.01
8.00
2.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

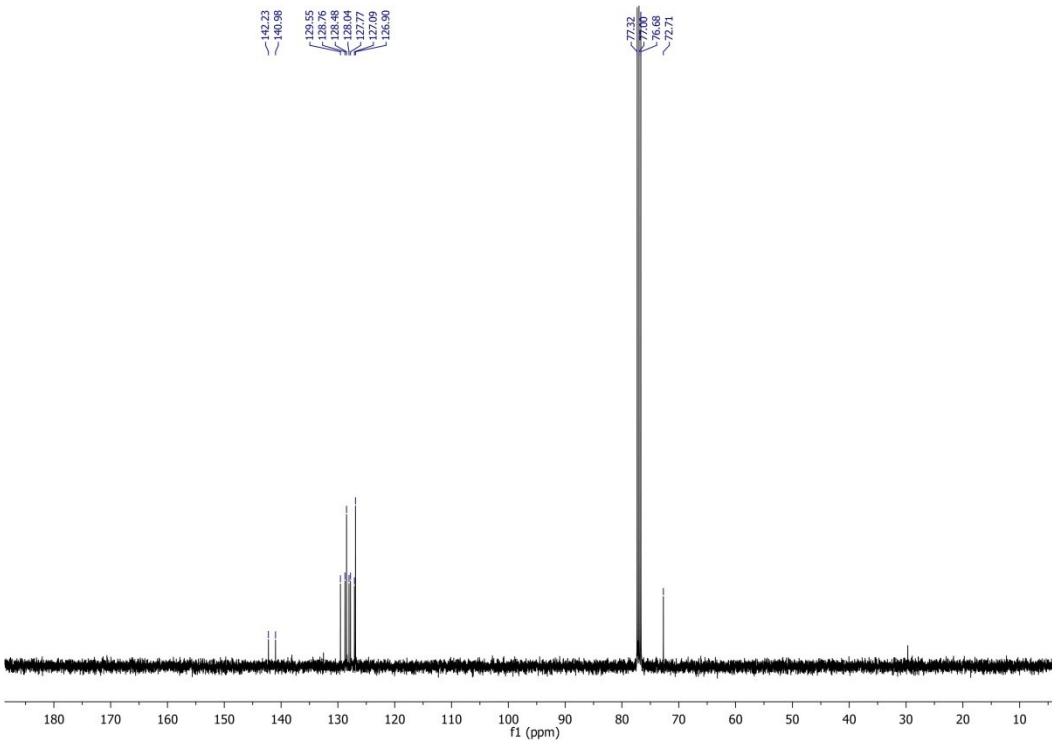

163.02
160.56
139.64
130.30
130.22
114.40
114.19
82.56
77.32
77.00
76.68
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

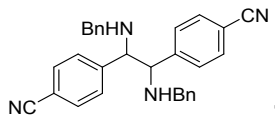

-113.83
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -130 -150 -170 -190
ppm


Cl
HO
OH
Cl

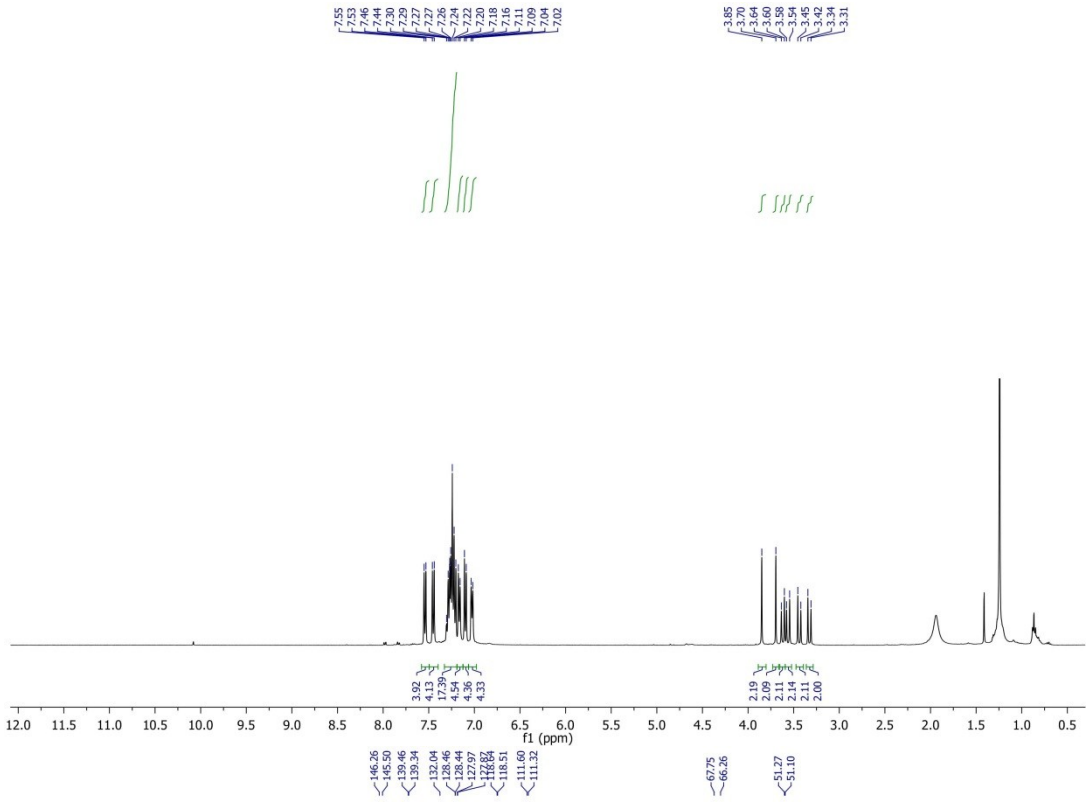
12c

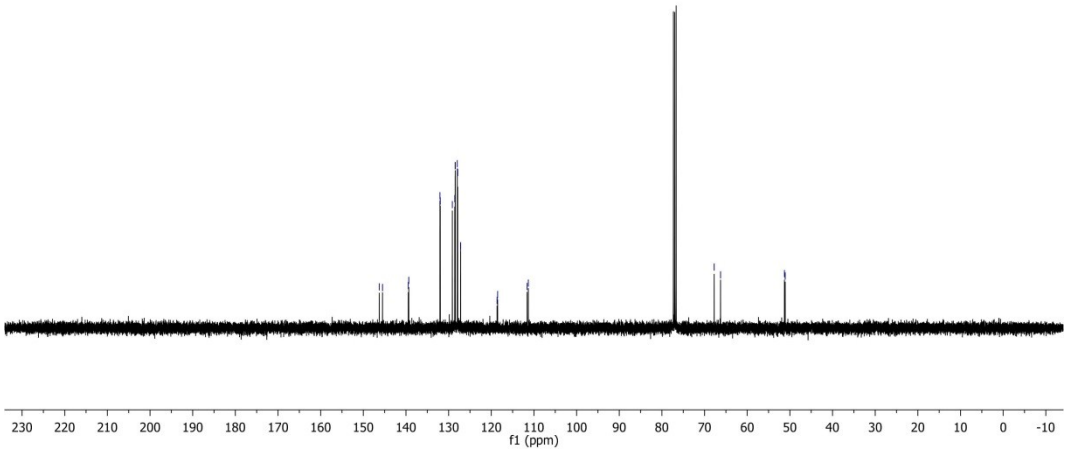

7.61
7.60
7.59
7.58
7.40
7.39
7.37
7.37
7.34
7.34
7.32
7.32
7.32
7.31
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.27
7.26
7.24
7.23
7.22
7.21
7.21
7.19
6.22
2.20
4.39
10.12
2.54
2.00
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
f1 (ppm)

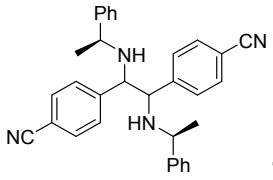

142.23
140.98
129.55
128.76
128.48
128.04
127.77
127.09
126.90
77.32
77.00
76.68
72.71
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


BnHN
CN
NC
NHBn

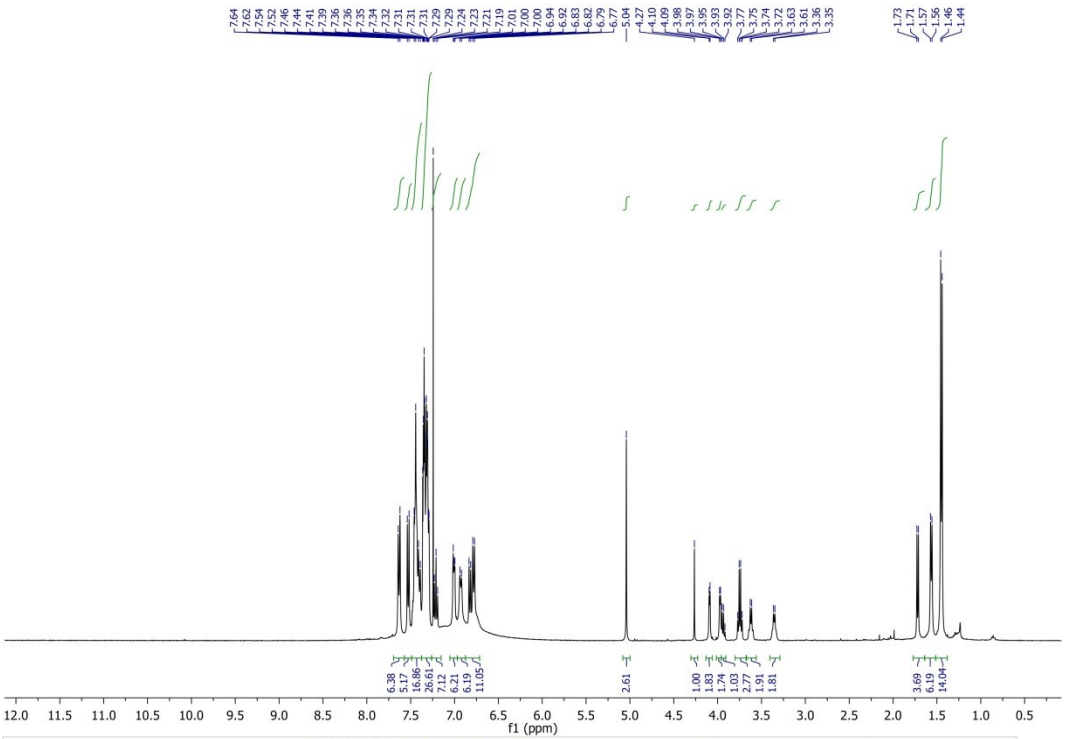
13a

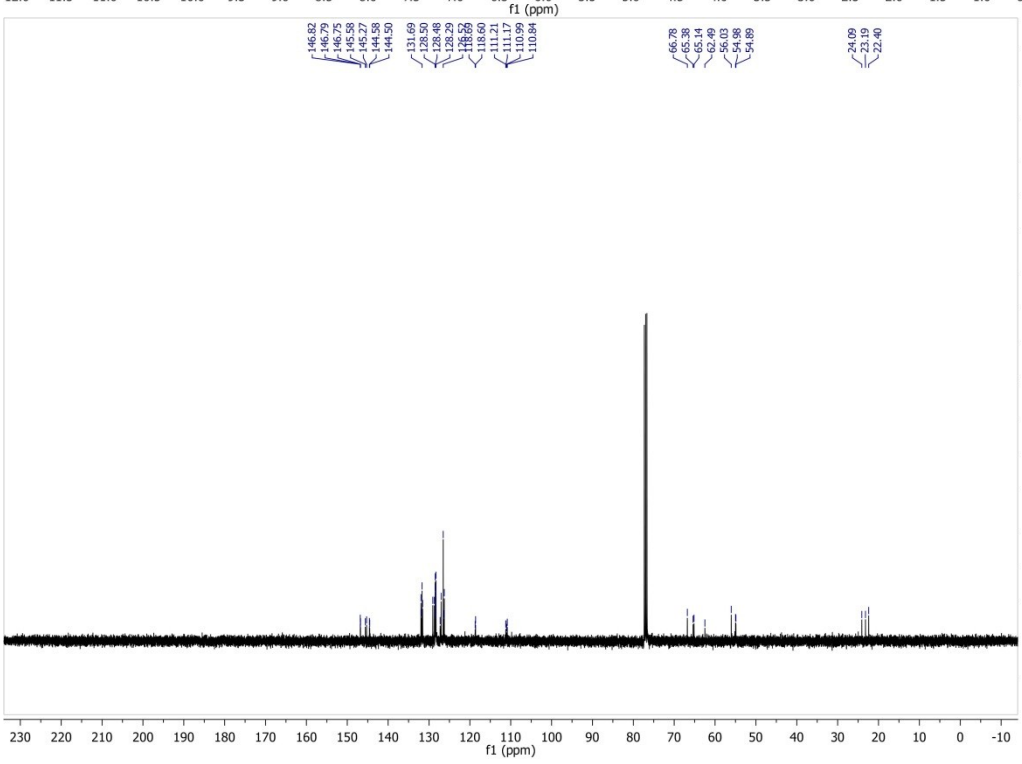

7.55
7.53
7.46
7.44
7.30
7.29
7.27
7.27
7.26
7.24
7.22
7.20
7.18
7.16
7.11
7.09
7.04
7.02
3.85
3.70
3.64
3.60
3.58
3.54
3.45
3.42
3.34
3.31
3.92
4.13
17.39
4.54
4.36
4.33
2.19
2.09
2.11
2.14
2.11
2.00
f1 (ppm)
146.26
145.50
139.46
139.34
132.04
128.46
128.44
127.97
118.51
111.60
111.32
67.75
66.26
51.27
51.10

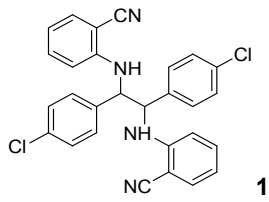

f1 (ppm)



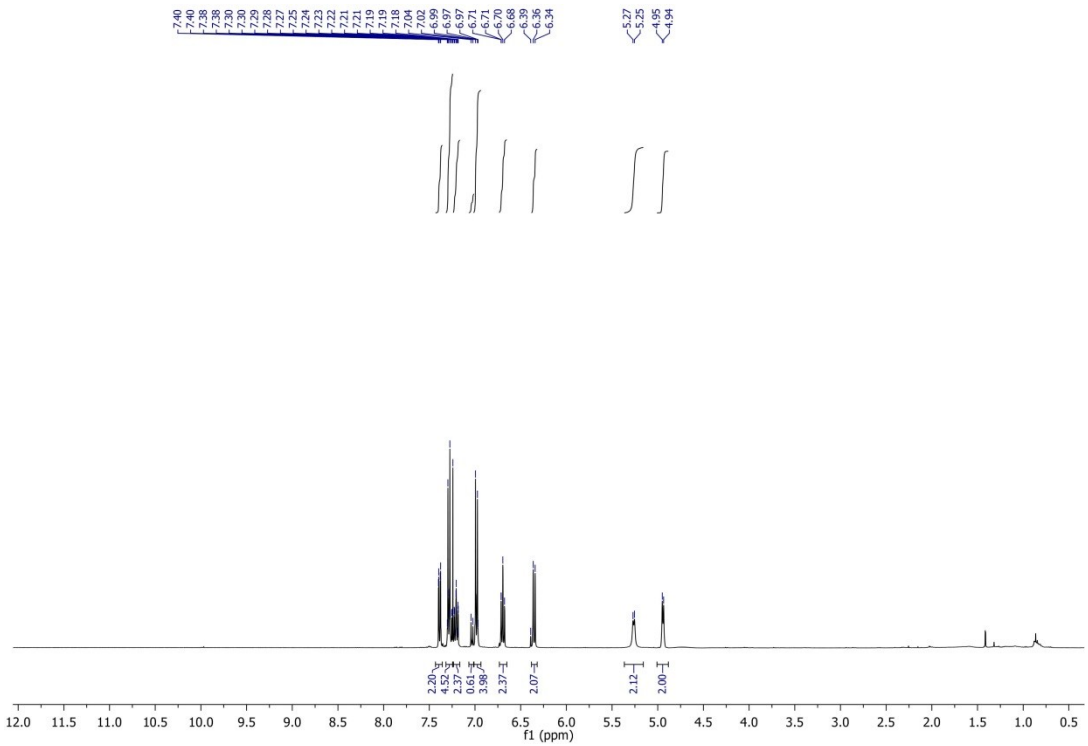
13b1

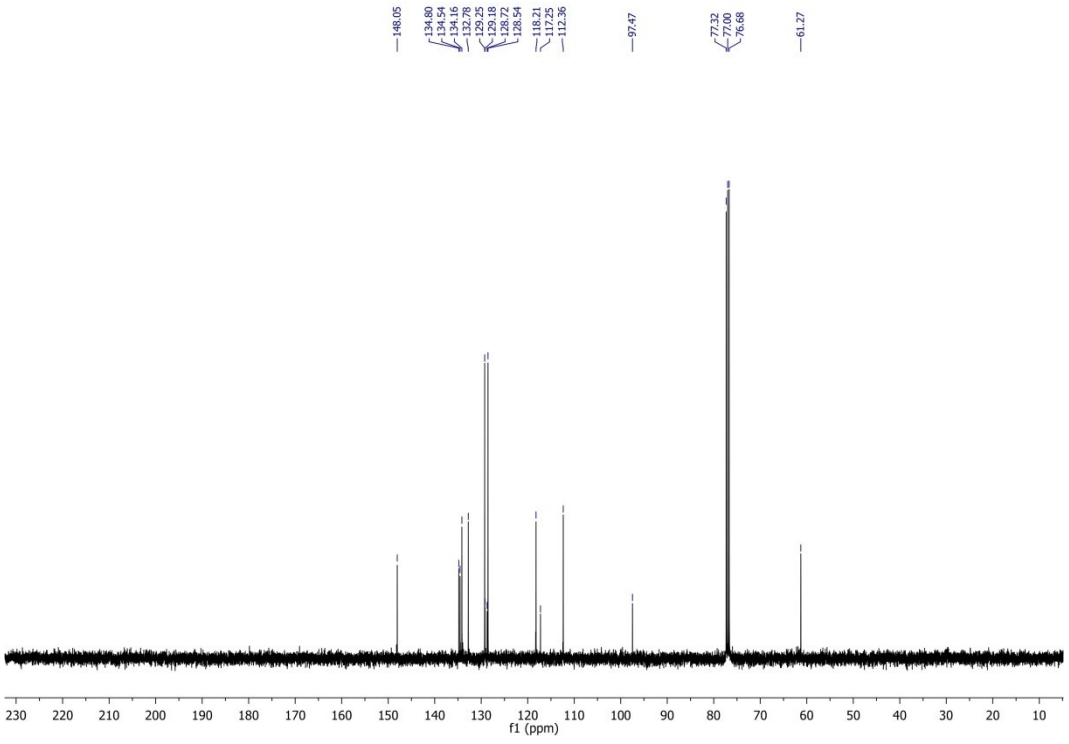


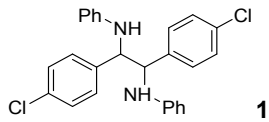



CN
NH
Cl
Cl
NH
NC

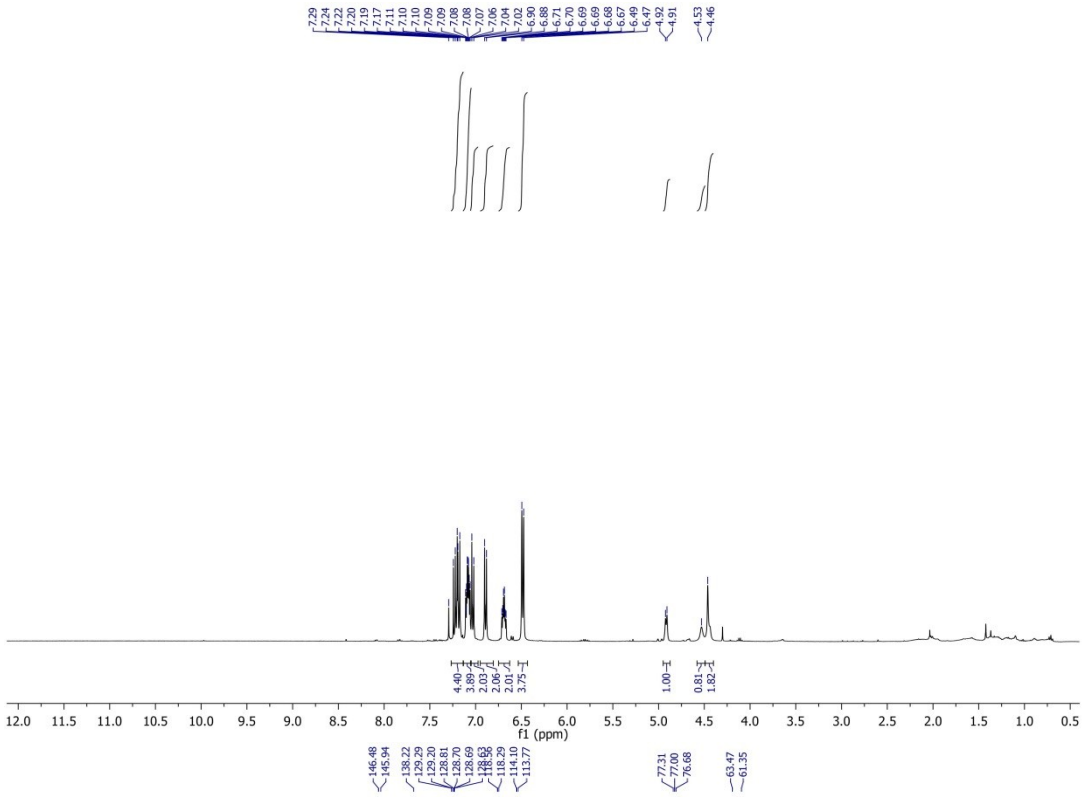
13c

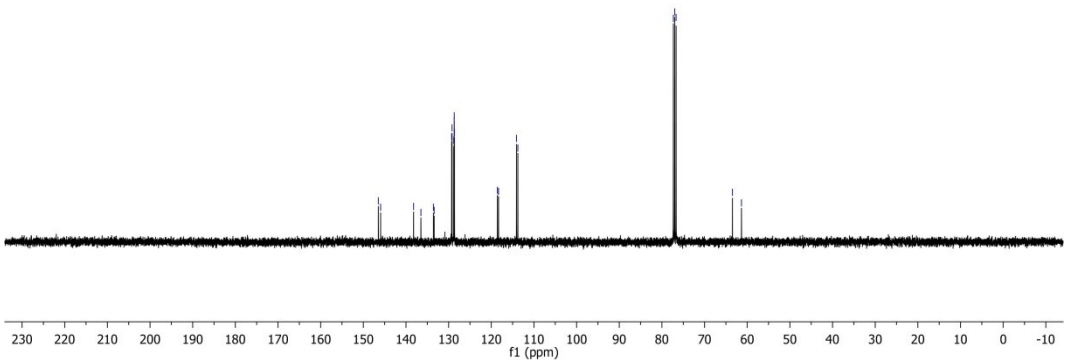

7.40
7.40
7.38
7.38
7.30
7.29
7.28
7.27
7.25
7.24
7.23
7.22
7.21
7.21
7.19
7.18
7.04
7.02
6.99
6.97
6.97
6.71
6.71
6.70
6.68
6.39
6.36
6.34
5.27
5.25
4.95
4.94
2.20
4.52
2.37
0.61
3.98
2.37
2.07
2.12
2.00
f1 (ppm)

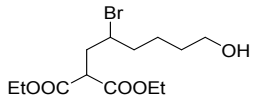

148.05
134.80
134.54
134.16
132.78
129.25
129.18
128.72
128.54
118.21
117.25
112.36
97.47
77.32
77.00
76.68
61.27
f1 (ppm)


Ph
NH
Cl
Cl
NH
Ph

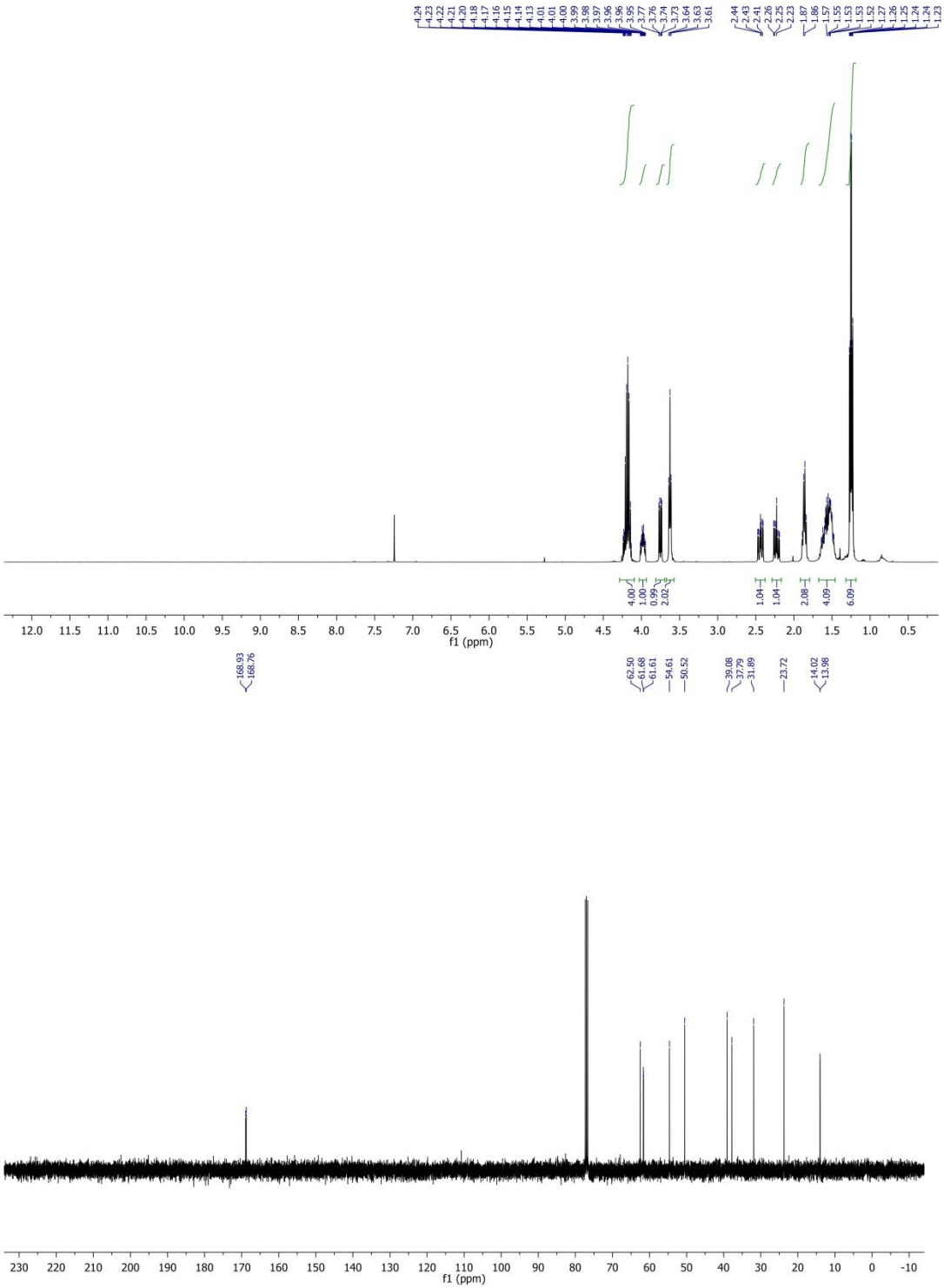
13d

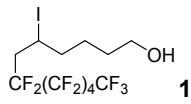

7.29
7.24
7.22
7.20
7.19
7.17
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.07
7.06
7.04
7.02
6.90
6.88
6.71
6.70
6.69
6.69
6.68
6.67
6.49
6.47
4.92
4.91
4.53
4.46
4.40
3.89
2.03
2.00
2.00
3.75
1.00
0.81
1.82
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)
146.48
145.94
138.22
129.29
129.20
128.81
128.70
128.69
118.56
118.29
114.10
113.77
77.31
77.00
76.68
63.47
61.35


230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

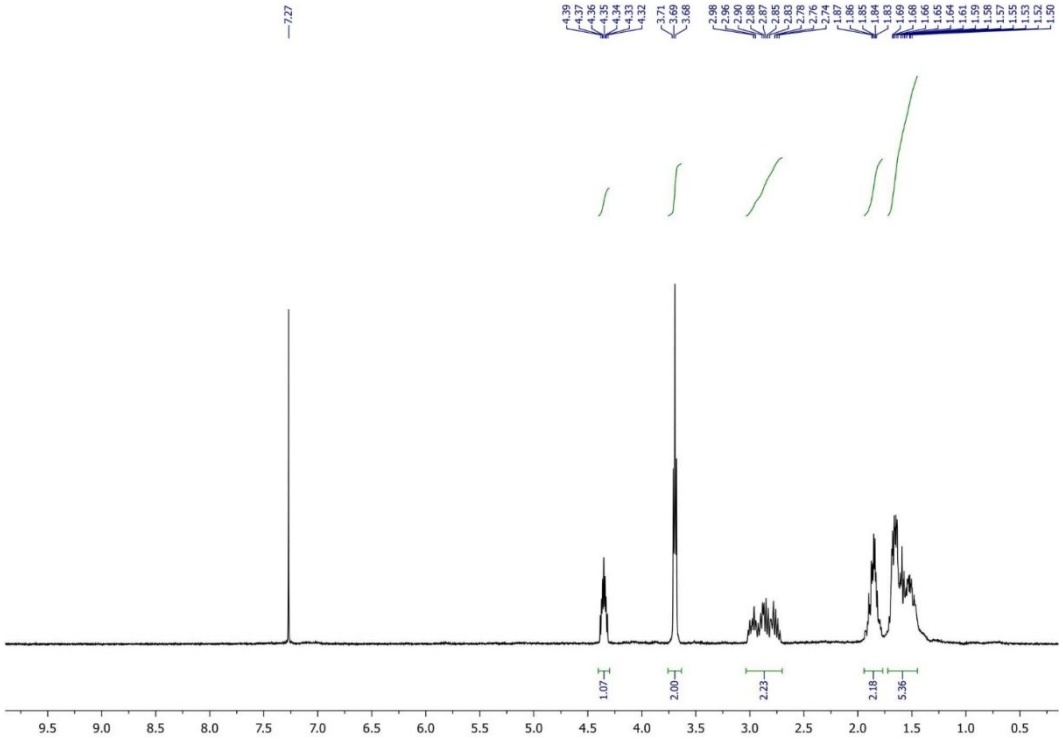


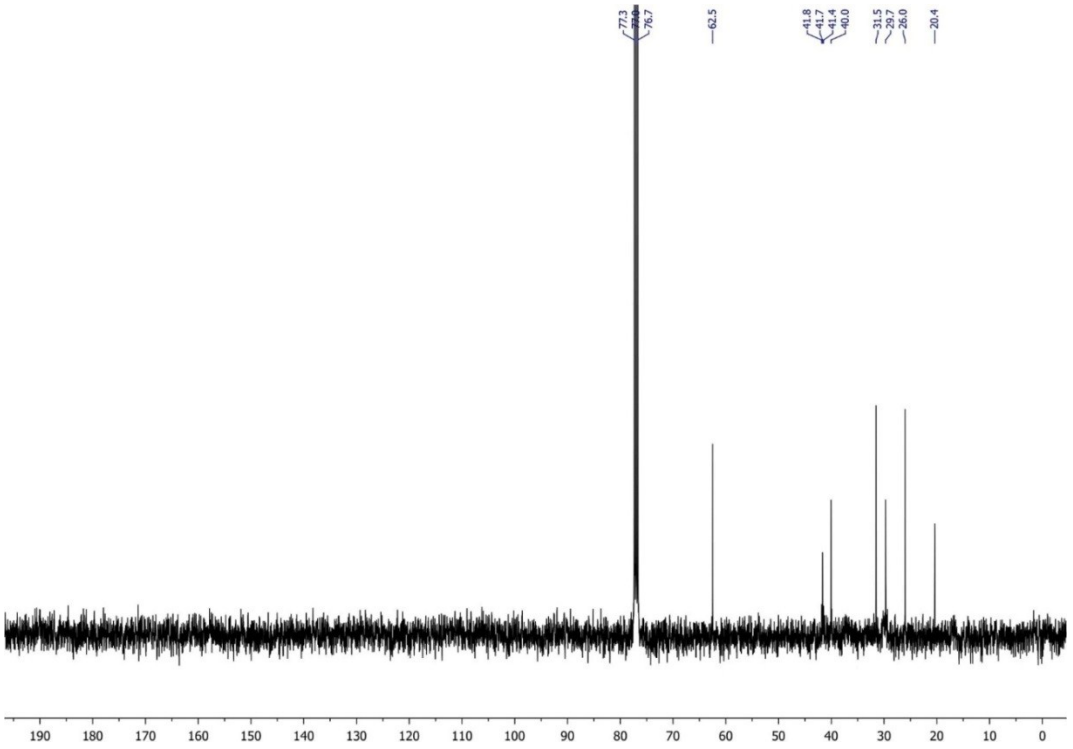
17a

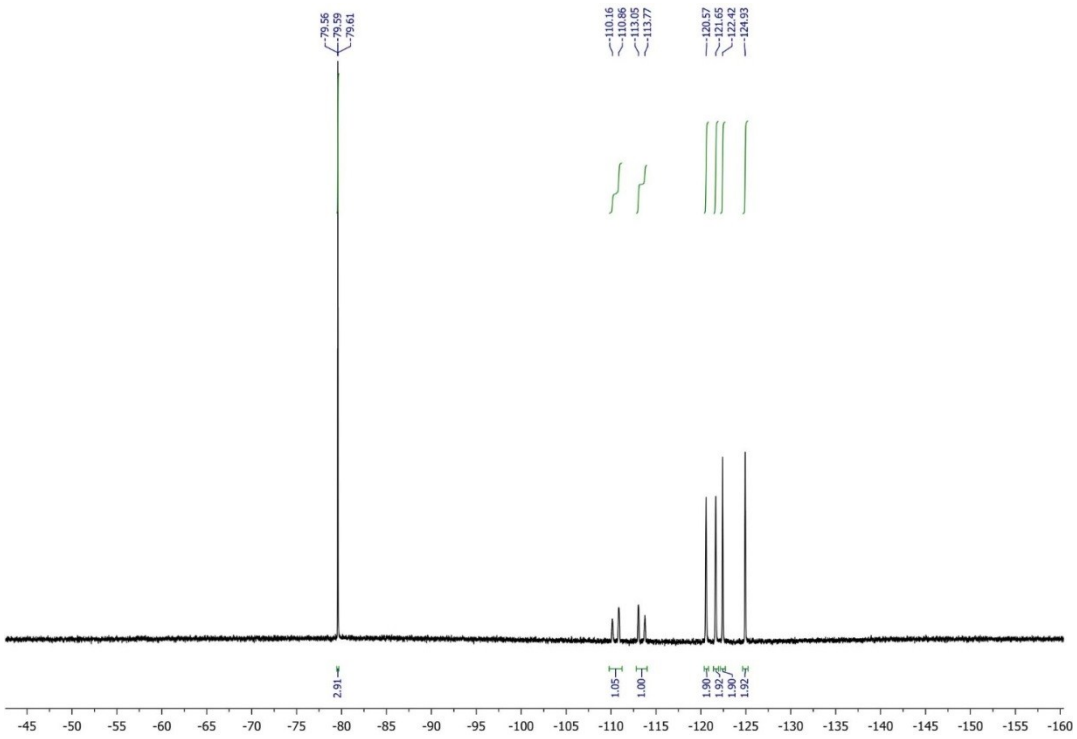


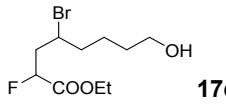

I
OH
CF2(CF2)4CF3

17b

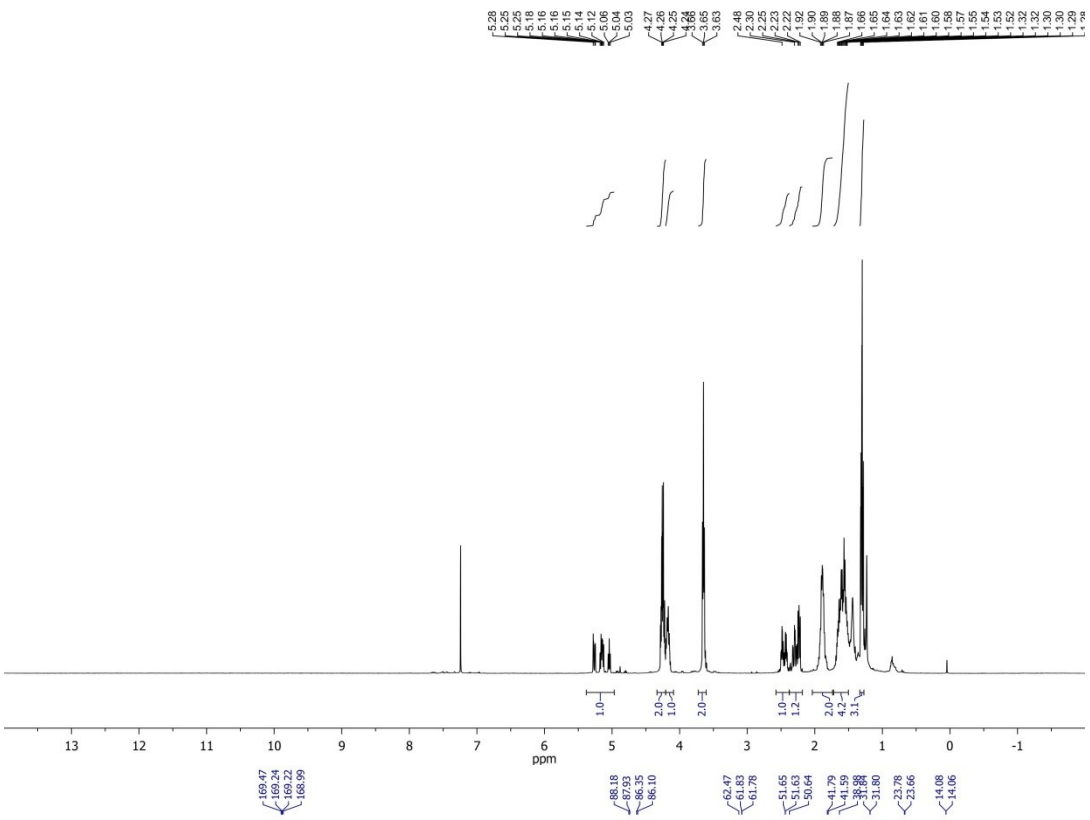

7.27
4.39
4.37
4.36
4.35
4.34
4.33
4.32
3.71
3.69
3.68
2.98
2.96
2.90
2.88
2.87
2.85
2.83
2.78
2.76
2.74
1.87
1.86
1.85
1.84
1.83
1.69
1.68
1.66
1.65
1.64
1.61
1.59
1.58
1.57
1.55
1.53
1.52
1.50
1.07
2.00
2.23
2.18
5.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5

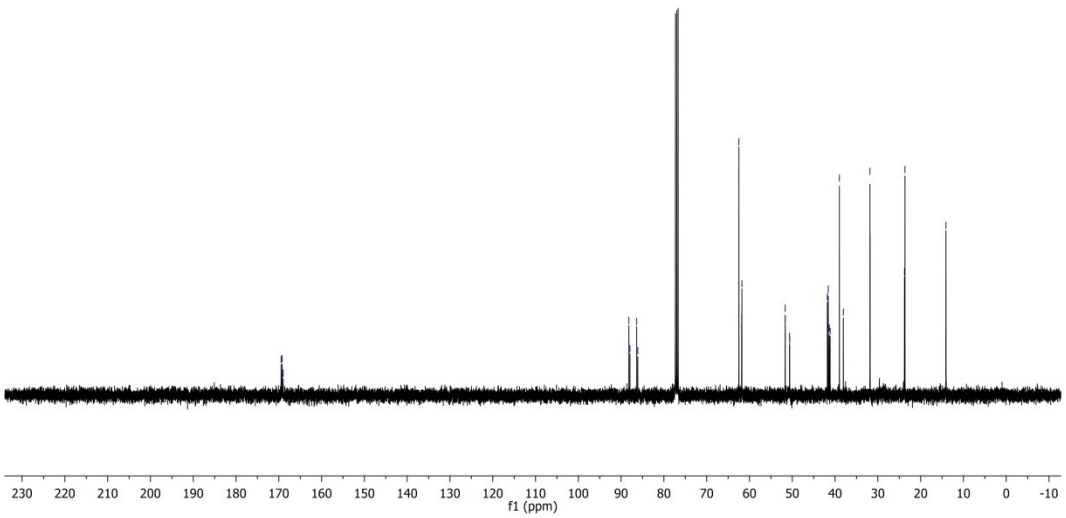

77.3
76.7
62.5
41.8
41.7
41.4
40.0
31.5
29.7
26.0
20.4
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

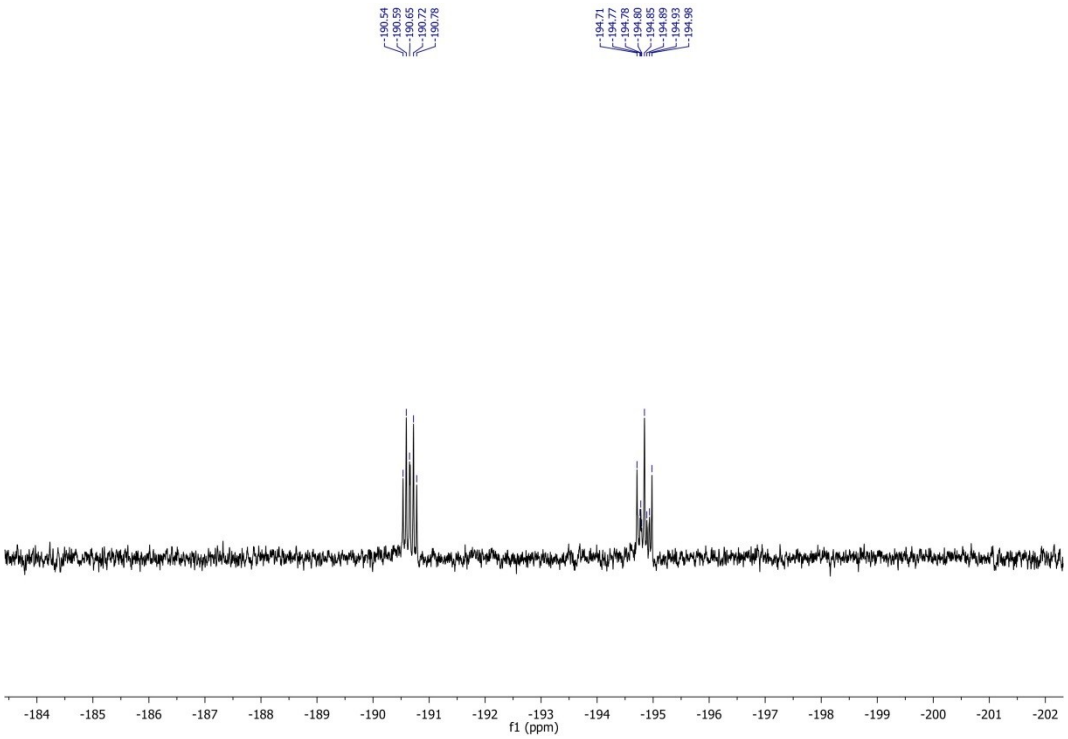

-79.56
-79.59
-79.61
-110.16
-110.96
-113.05
-113.77
-120.57
-121.65
-122.42
-124.93
2.91
1.05
1.00
1.90
1.92
1.90
1.92
-45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160

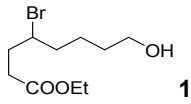


17c

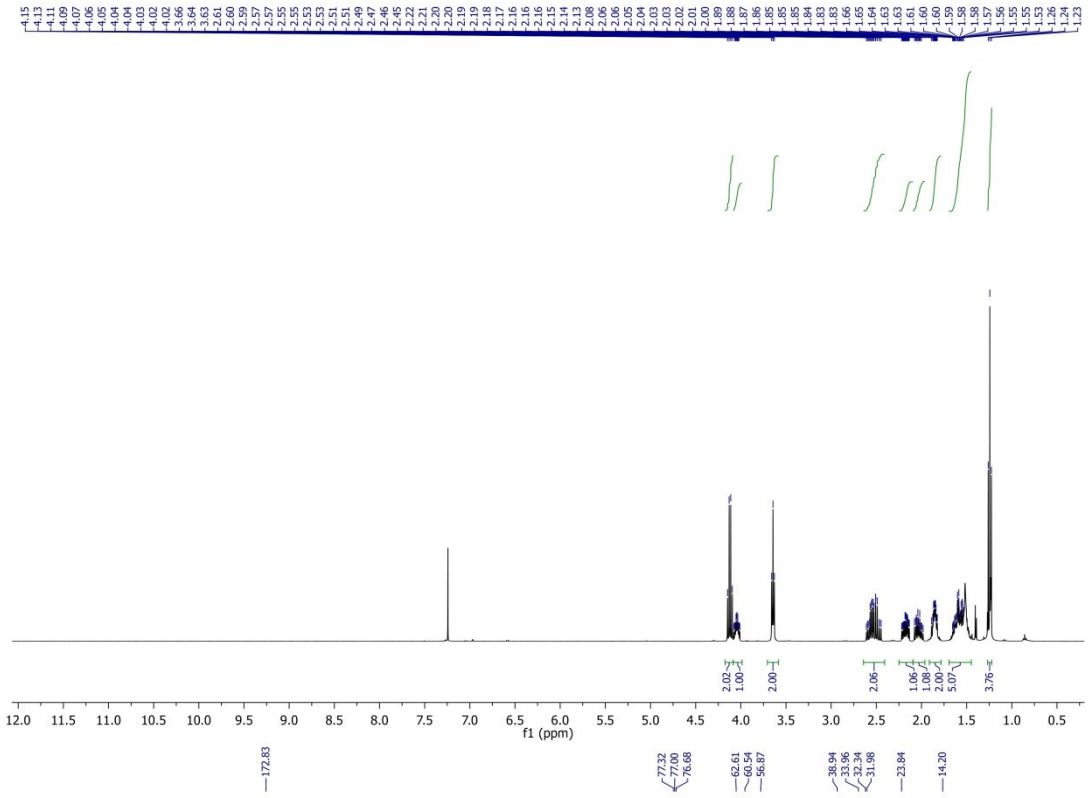


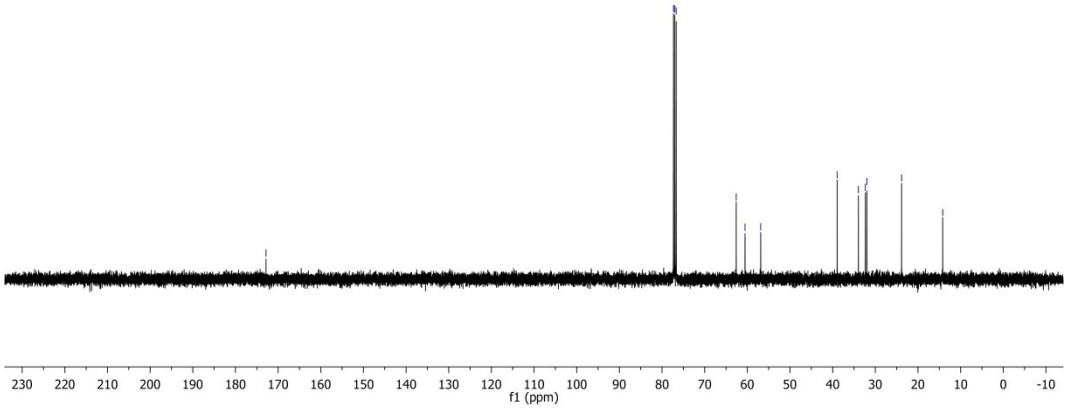


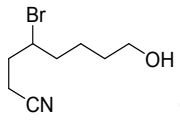

-190.54
-190.59
-190.65
-190.72
-190.78
-194.71
-194.77
-194.78
-194.80
-194.85
-194.89
-194.93
-194.98
-184
-185
-186
-187
-188
-189
-190
-191
-192
-193
-194
-195
-196
-197
-198
-199
-200
-201
-202
f1 (ppm)



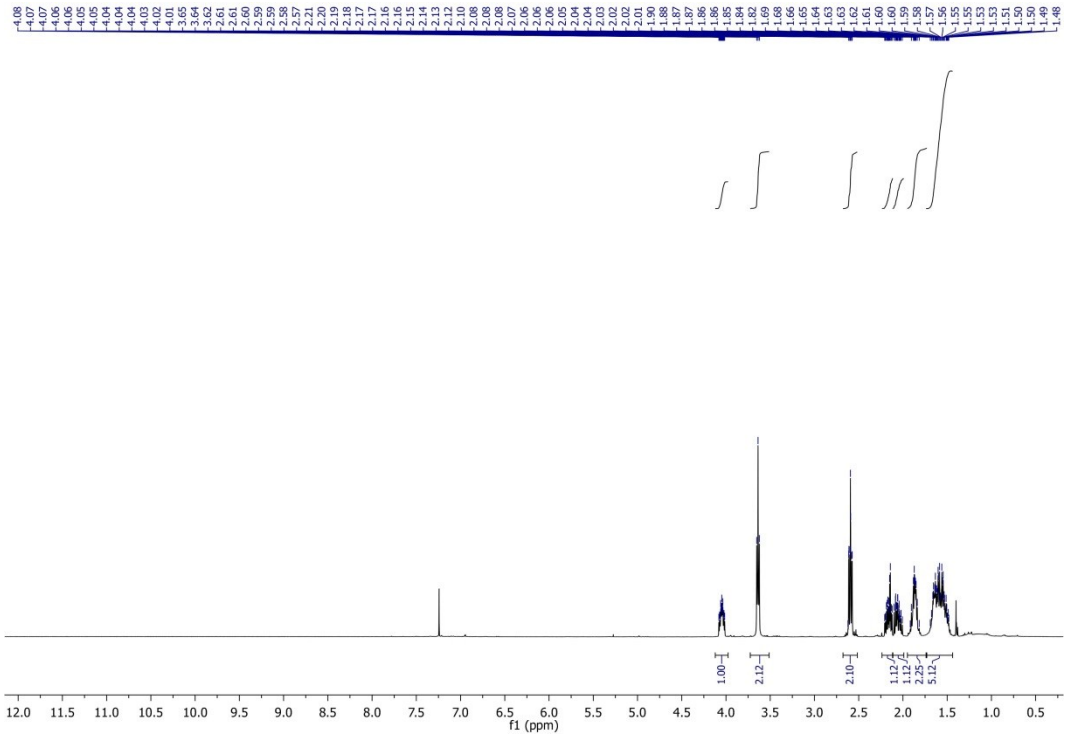
17d

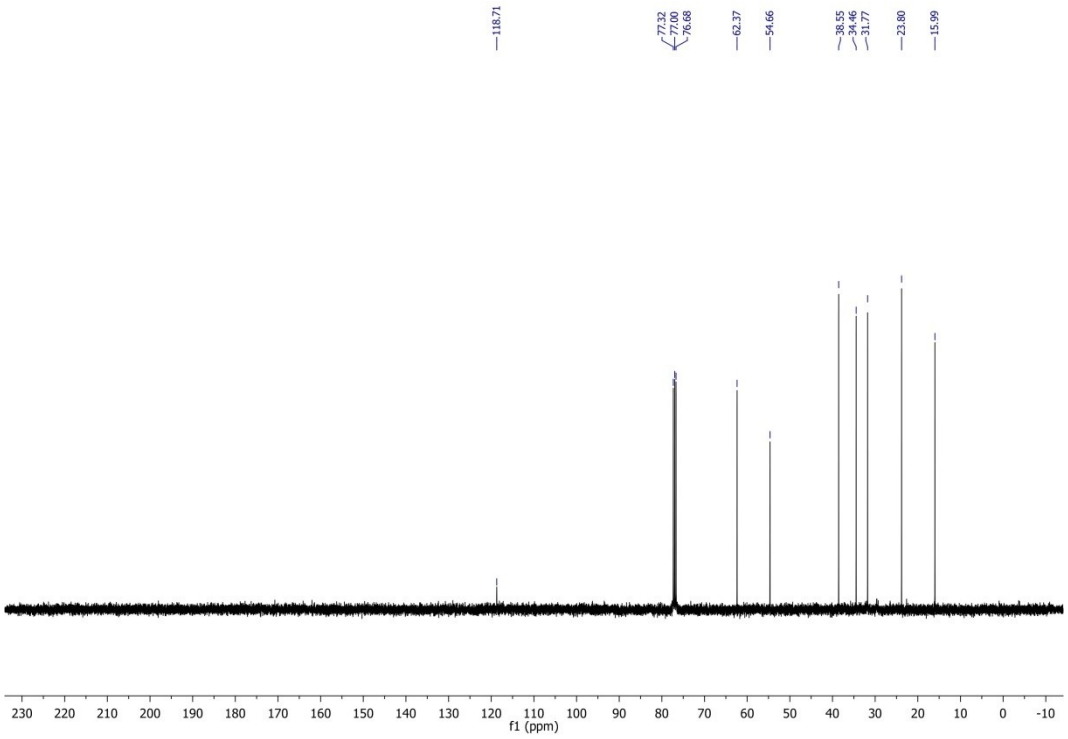


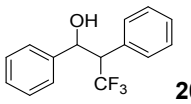



Br
OH
CN

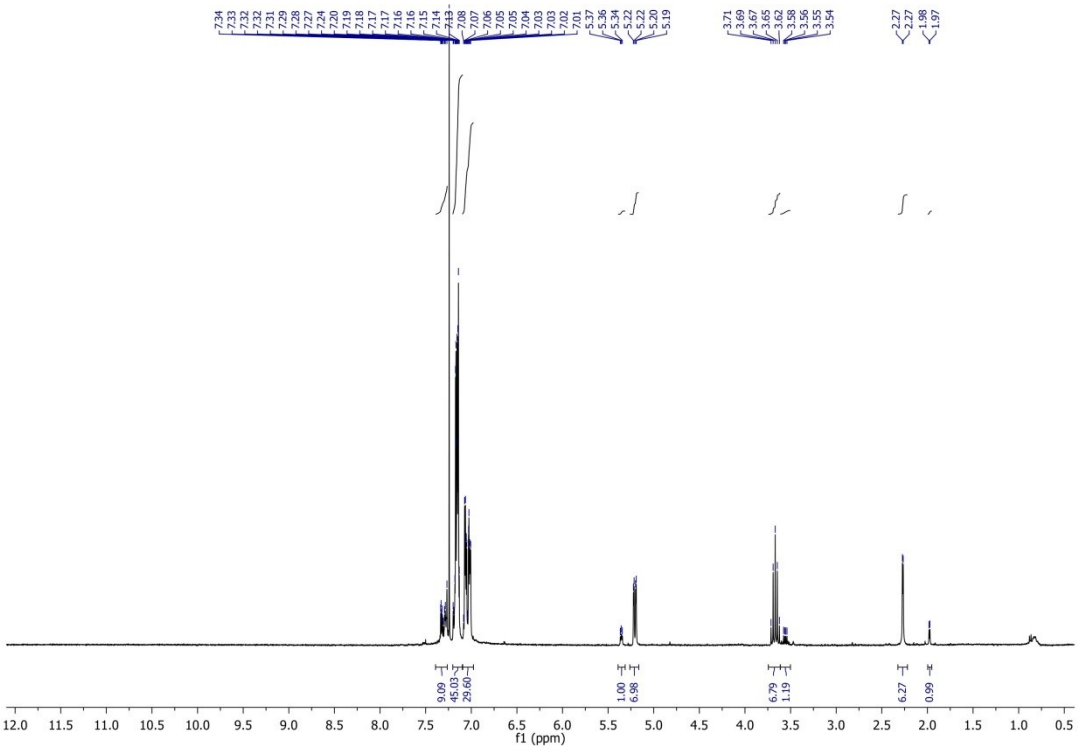
17e

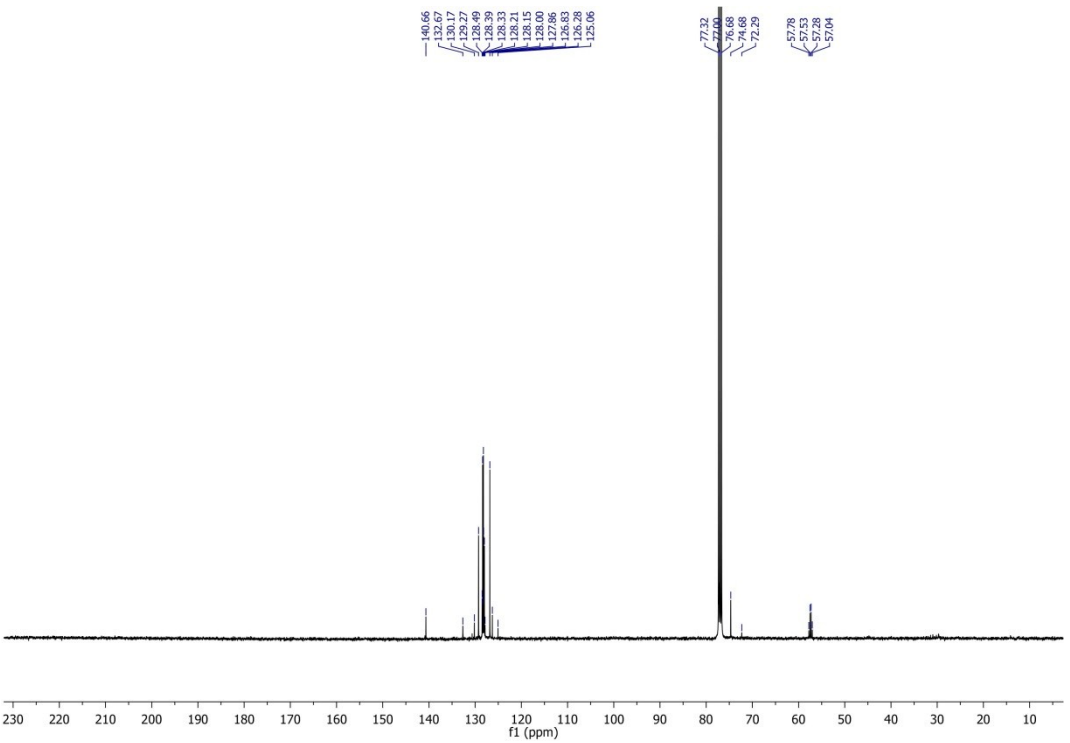

1.00
2.12
2.10
1.12
1.12
2.25
5.12
f1 (ppm)

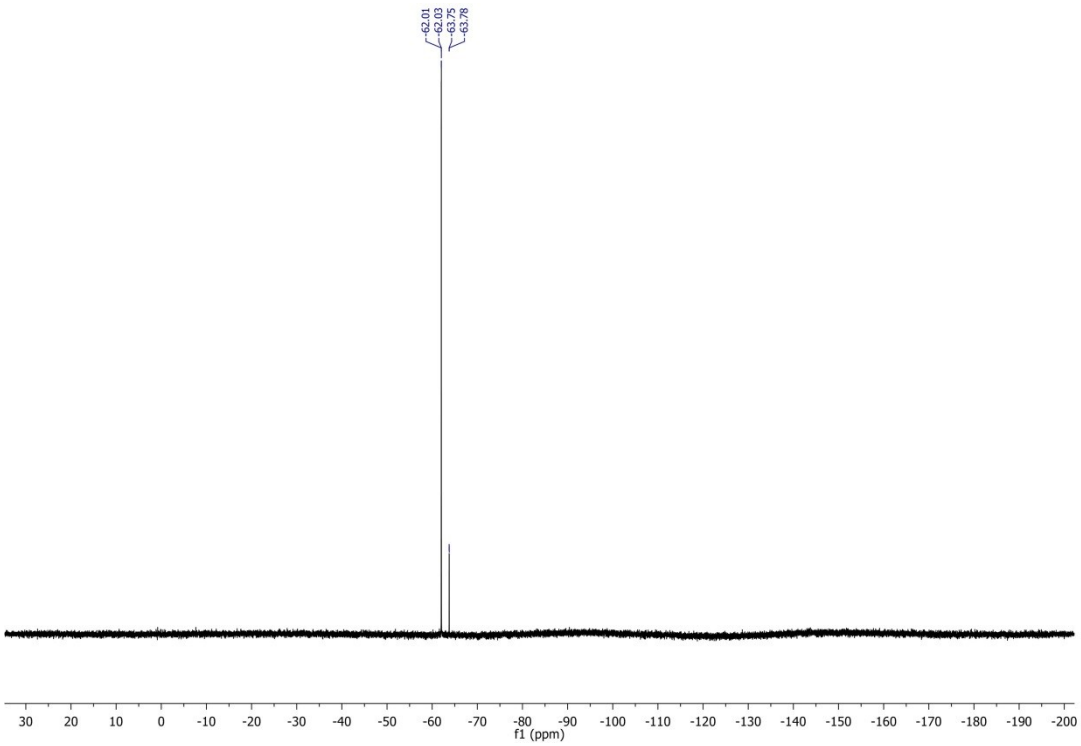

118.71
77.32
77.00
76.68
62.37
54.66
38.55
34.46
31.77
23.80
15.99
f1 (ppm)

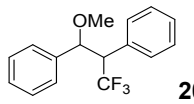

OH
CF3

20e

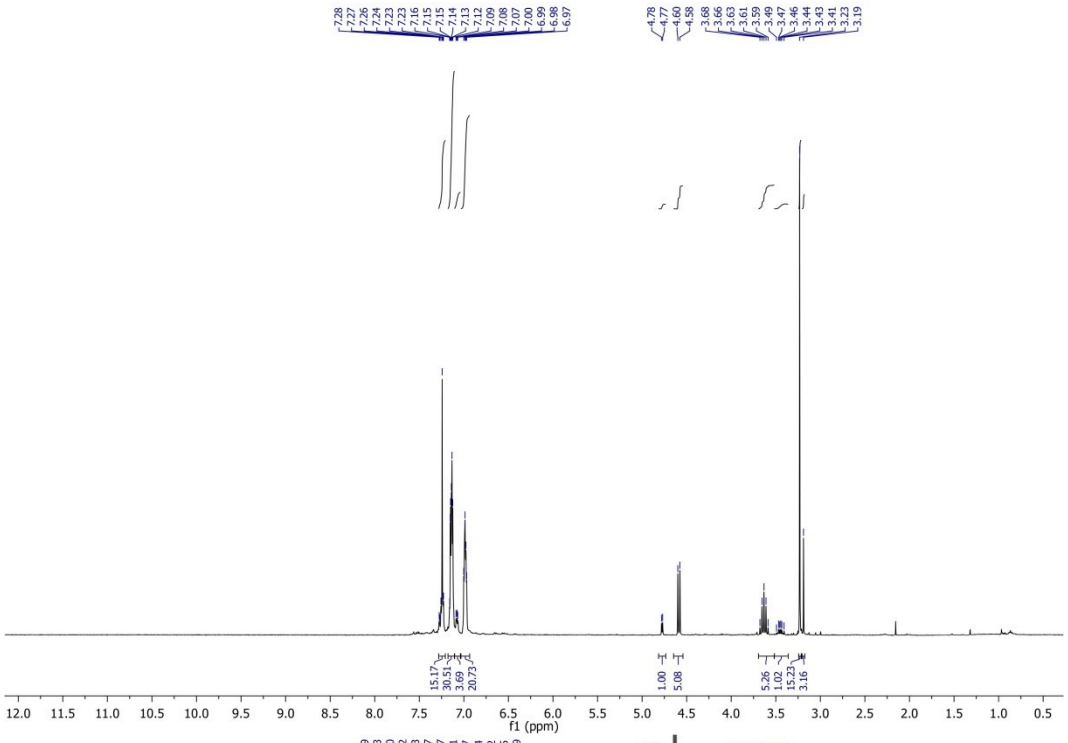

7.34
7.33
7.32
7.32
7.31
7.29
7.28
7.27
7.24
7.20
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.13
7.08
7.07
7.06
7.05
7.05
7.04
7.03
7.03
7.02
7.01
5.37
5.36
5.34
5.22
5.22
5.20
5.19
3.71
3.69
3.67
3.65
3.62
3.58
3.56
3.55
3.54
2.27
2.27
1.98
1.97
9.09
45.03
29.60
1.00
6.98
6.79
1.19
6.27
0.99
f1 (ppm)

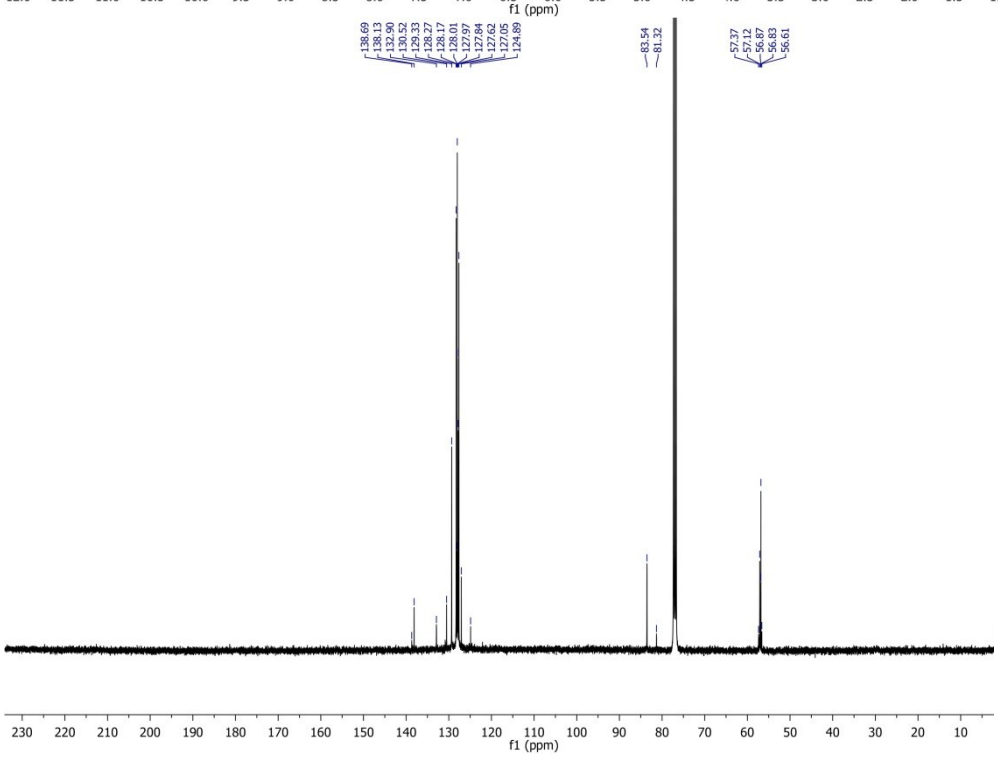

140.66
132.67
130.17
129.27
128.49
128.39
128.33
128.21
128.15
128.00
127.86
126.83
126.28
125.06
77.32
77.00
76.68
74.68
72.29
57.78
57.53
57.28
57.04
f1 (ppm)

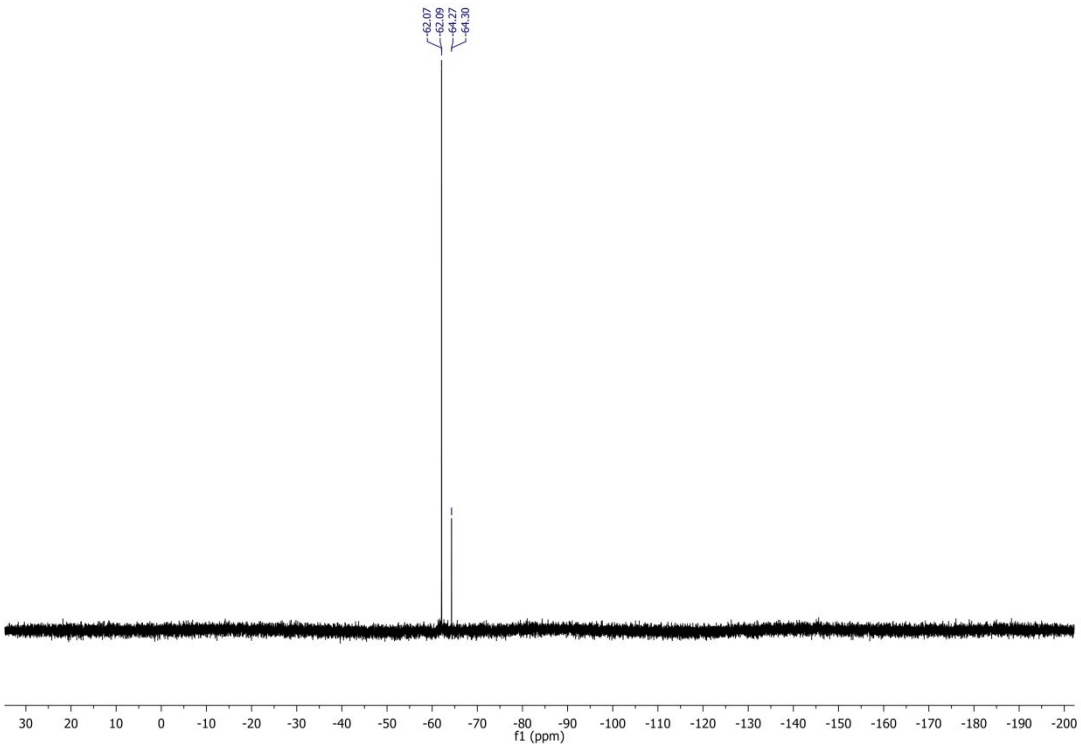

62.01
62.03
63.75
63.78
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

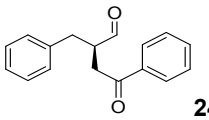

OMe
CF3

20e

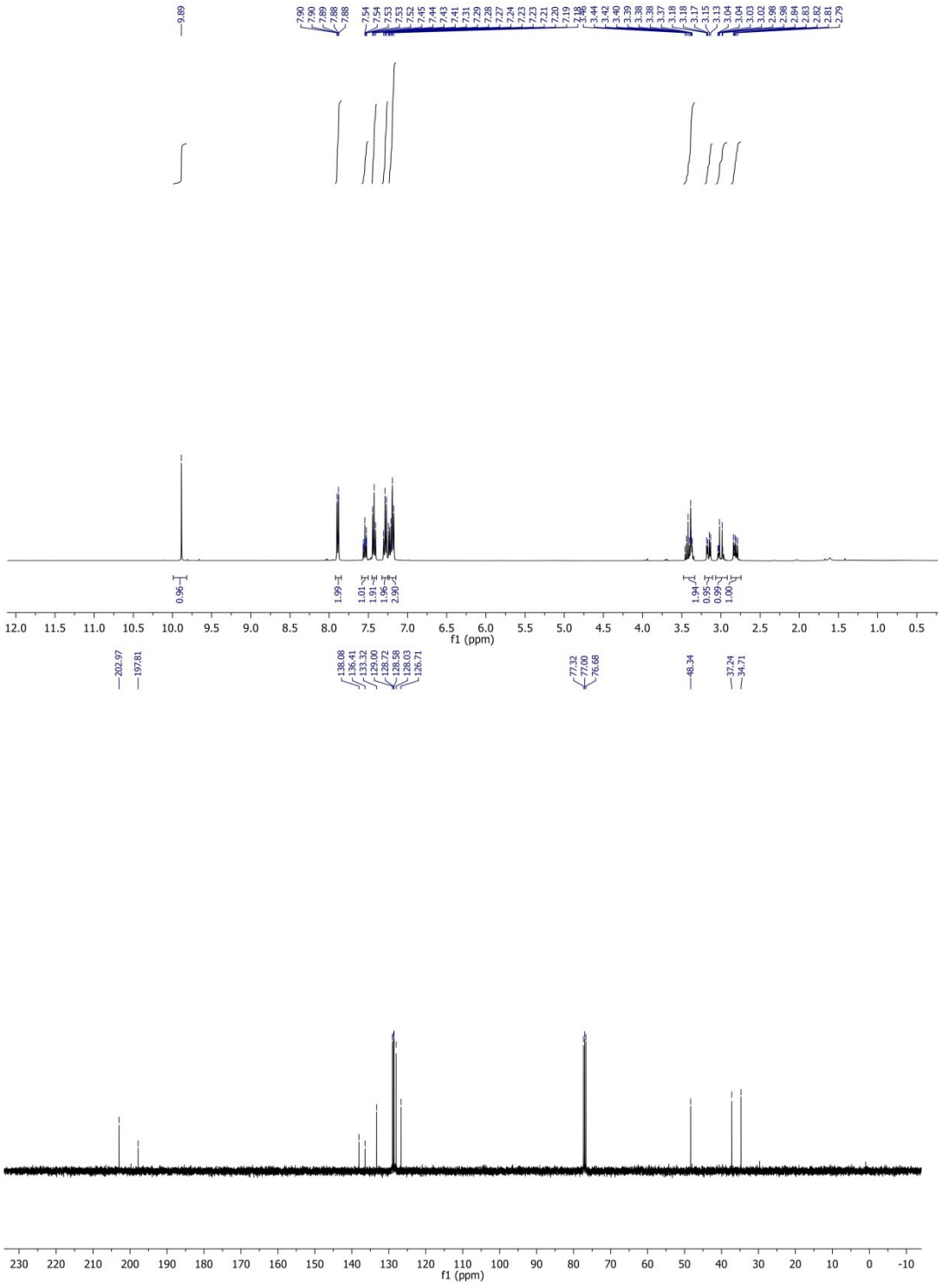

7.28
7.27
7.26
7.24
7.23
7.23
7.16
7.15
7.15
7.14
7.13
7.12
7.09
7.08
7.07
7.00
6.99
6.98
6.97
4.78
4.77
4.60
4.58
3.68
3.66
3.63
3.61
3.59
3.49
3.47
3.46
3.44
3.43
3.41
3.23
3.19
15.17
30.51
3.69
20.73
1.00
5.08
5.26
1.02
15.23
3.16
f1 (ppm)

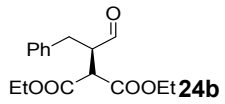

138.69
138.13
132.90
130.52
129.33
128.27
128.17
128.01
127.97
127.84
127.62
127.05
124.89
83.54
81.32
57.37
57.12
56.87
56.83
56.61
f1 (ppm)


-62.07
-62.09
-64.27
-64.30
30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

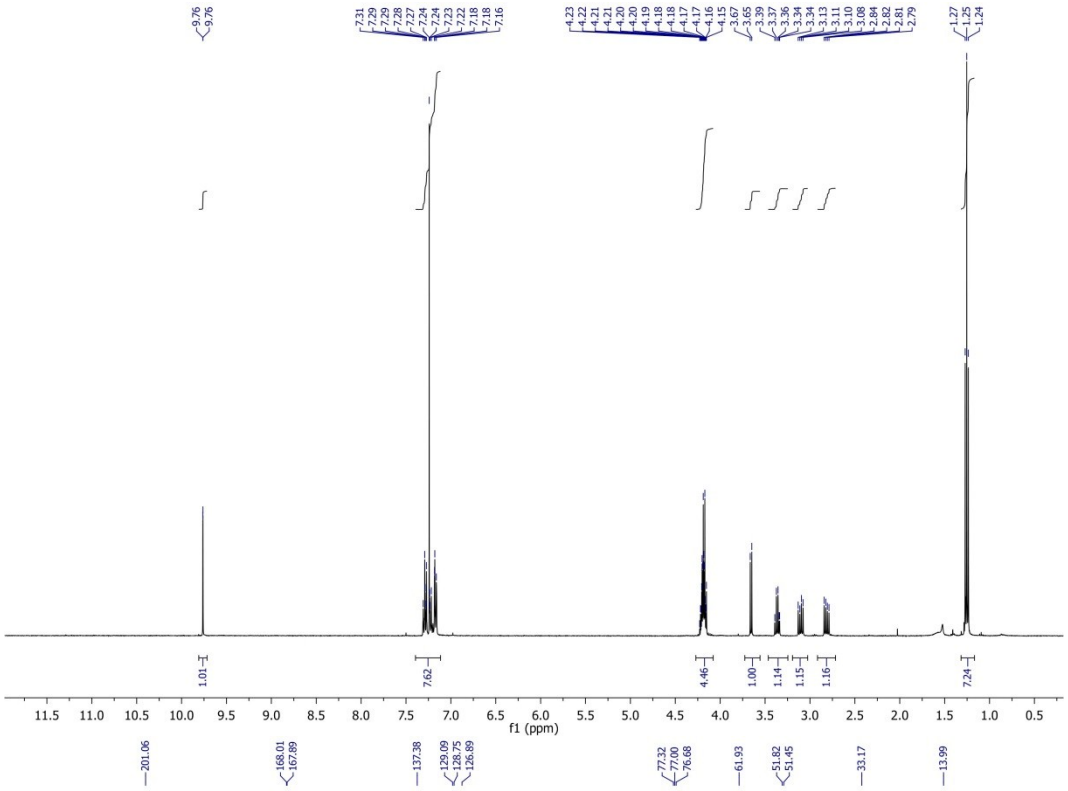


24a

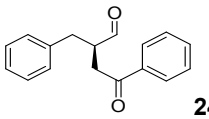

9.89
7.90
7.90
7.89
7.88
7.88
7.54
7.54
7.53
7.53
7.52
7.45
7.44
7.43
7.41
7.31
7.29
7.28
7.27
7.24
7.23
7.23
7.21
7.20
7.19
3.48
3.44
3.42
3.40
3.39
3.38
3.38
3.37
3.18
3.17
3.15
3.13
3.04
3.04
3.03
3.02
2.98
2.98
2.84
2.83
2.82
2.81
2.79
0.96
1.99
1.01
1.91
1.96
2.90
1.94
0.95
0.99
1.00
f1 (ppm)
202.97
197.81
138.08
136.41
133.32
129.00
128.72
128.58
128.03
126.71
77.32
77.00
76.68
48.34
37.24
34.71
f1 (ppm)


O
Ph
EtOOC
COOEt

24b

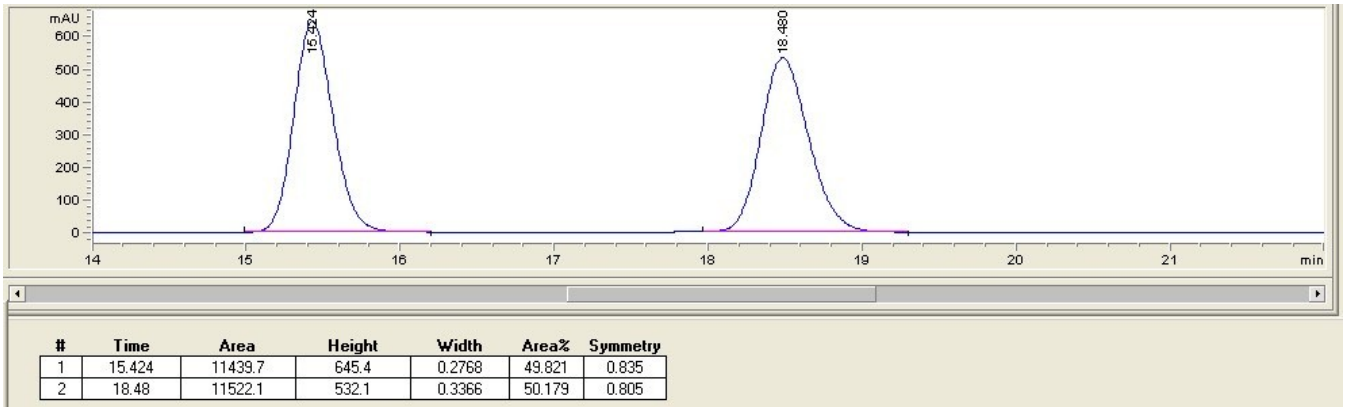

9.76
9.76
7.31
7.29
7.29
7.28
7.27
7.24
7.24
7.23
7.22
7.18
7.18
7.16
4.23
4.22
4.21
4.21
4.20
4.20
4.19
4.18
4.18
4.17
4.17
4.16
4.15
3.67
3.65
3.39
3.37
3.36
3.34
3.34
3.13
3.11
3.10
3.08
2.84
2.82
2.81
2.79
1.27
1.25
1.24
1.01
7.62
4.46
1.00
1.14
1.15
1.16
7.24
f1 (ppm)
201.06
168.01
167.89
137.38
129.09
128.75
126.89
77.32
77.00
76.68
61.93
51.82
51.45
33.17
13.99
f1 (ppm)

HPLC Traces



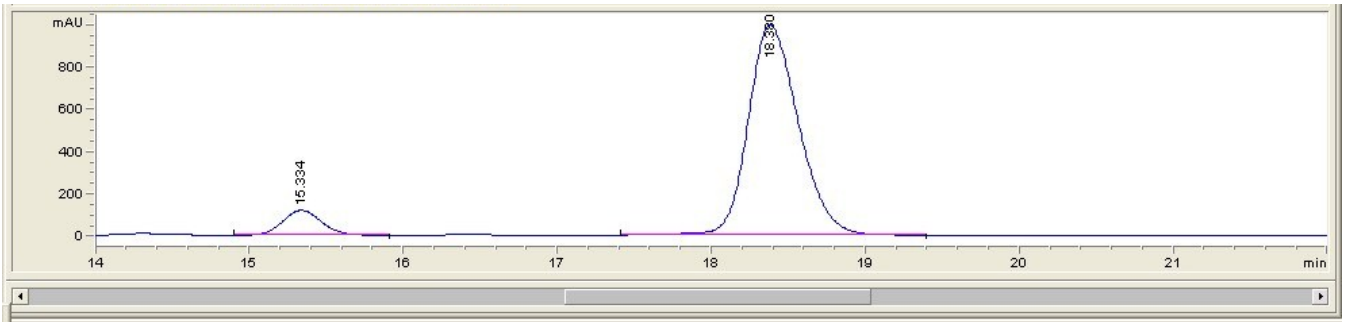
24a

Racemic

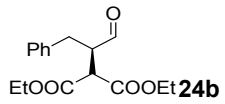


#	Time	Area	Height	Width	Area%	Symmetry
1	15.424	11439.7	645.4	0.2768	49.821	0.835
2	18.48	11522.1	532.1	0.3366	50.179	0.805

Active

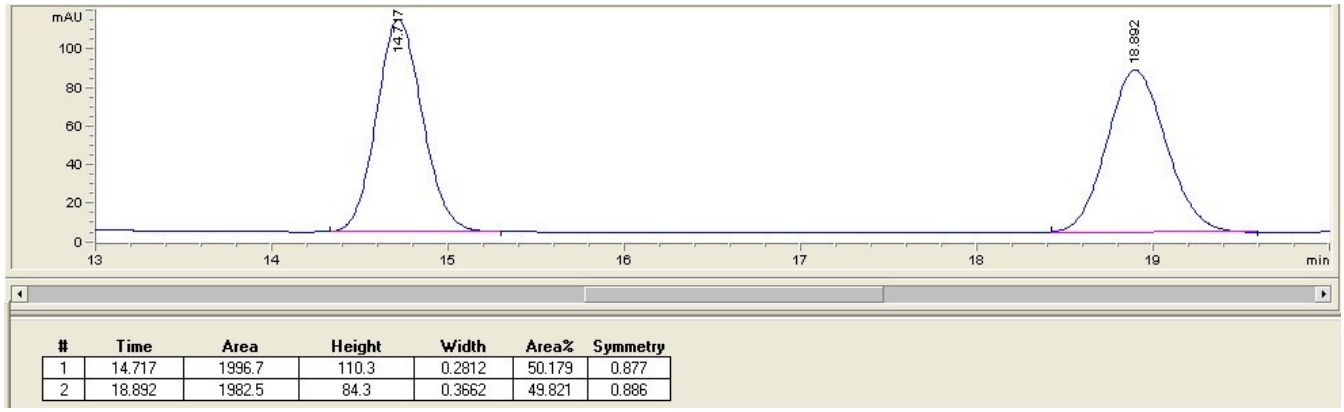


#	Time	Area	Height	Width	Area%	Symmetry
1	15.334	2118.9	119	0.2736	8.533	0.898
2	18.38	22712.2	995.5	0.3502	91.467	0.766



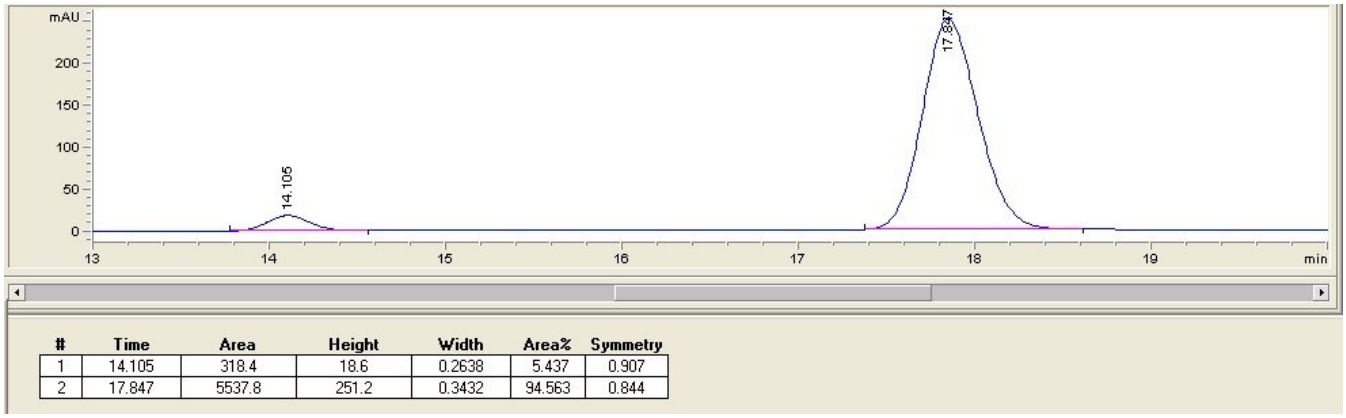
24b

Racemic



#	Time	Area	Height	Width	Area%	Symmetry
1	14.717	1996.7	110.3	0.2812	50.179	0.877
2	18.892	1982.5	84.3	0.3662	49.821	0.886

Active



#	Time	Area	Height	Width	Area%	Symmetry
1	14.105	318.4	18.6	0.2638	5.437	0.907
2	17.847	5537.8	251.2	0.3432	94.563	0.844

GC-MS analysis of reductive protonation of bromoketones