Supplementary Material (ESI) for Green Chemistry

Organic dye photocatalyzed α-oxyamination through irradiation with visible light

Hongjun Liu, Wei Feng, Choon Wee Kee, Yujun Zhao, Dasheng Leow, Yuanhang Pan, Choon-Hong Tan*

Department of Chemistry, 3 Science Drive 3, National University of Singapore, Singapore 117543

E-mail: chmtanch@nus.edu.sg

Supporting Information

General Information

General procedures and methods

Experiments involving moisture and/or air sensitive components were performed under a positive pressure of nitrogen in oven-dried glassware equipped with a rubber septum inlet. Air sensitive reagents were weighed in a glovebox. Dried solvents and liquid reagents were transferred by oven-dried syringes or hypodermic syringe cooled to ambient temperature in a desiccator. Reactions mixtures were stirred in 50 mL round bottle flasks or clear and dry vials with Teflon-coated magnetic stirring bars under an 11W house hold fluorescent bulb unless otherwise stated. Moisture in non-volatile reagents/compounds was removed in high *vacuo* by means of an oil pump and subsequent purging with nitrogen. Solvents were removed in vacuo under ~30 mmHg and heated with a water bath at 33 °C using Heidolph or Büchi rotary evaporator with Eyela A-3S aspirator. The condenser was cooled with running water at 0 °C.

All experiments were monitored by analytical thin layer chromatography (TLC). TLC was performed on pre-coated plates, Merck 60 F_{254}. After elution, plate was visualized under UV illumination at 254 nm for UV active material. Further visualization was achieved by staining $KMnO_4$, ceric molybdate, or anisaldehyde solution. For those using the aqueous stains, the TLC plates were heated on a hot plate.

Columns for flash chromatography (FC) contained silica gel 60 (0.040 mm - 0.063 mm, Merck). Columns were packed as slurry of silica gel in hexane and equilibrated with the appropriate solvent/solvent mixture prior to use. The analyte was loaded neat or as a concentrated solution using the appropriate solvent system. The elution was assisted by applying pressure of about 2 atm with an air pump.

Instrumentations

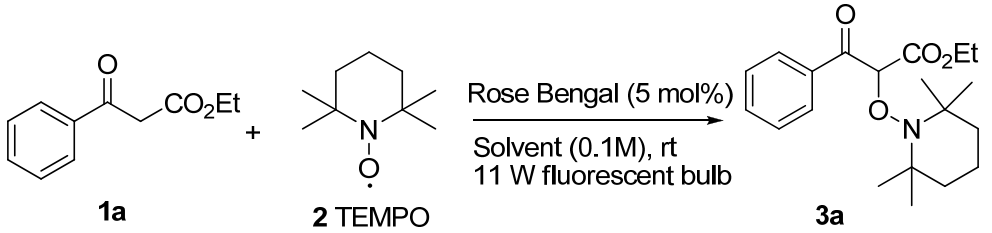
Proton nuclear magnetic resonance (^{1}H NMR), carbon NMR (^{13}C NMR), phosphorous NMR (^{31}P NMR), and fluorine NMR (^{19}F NMR) spectra were recorded in $CDCl_3$ otherwise stated. ^{1}H (300 MHz), ^{13}C (75 MHz) with complete proton decoupling, and ^{1}H Nuclear Overhauser Effect (NOE) NMRs were performed on a 500 MHz Bruker AMX NMR spectrometer. ^{19}F NMR (282 MHz) was performed on a 300 MHz Bruker ACF spectrometer. Chemical shifts were reported as δ in units of parts per million (ppm) downfield from tetramethylsilane (δ 0.00), using the residual solvent signal as an internal standard: $CDCl_3$ (^{1}H NMR: δ 7.26, singlet; ^{13}C NMR: δ 77.0, triplet). Multiplicities were given as: *s* (singlet), *d* (doublet), *t* (triplet), *q* (quartet), *quintet*, *m* (multiplets), *dd* (doublet of doublets), *ddd* (doublet of doublet of doublets), *dt* (doublet of triplets), *dq* (doublet of quartets), *dm* (doublet of multiplets), and *br* (broad). Coupling constants (*J*) were recorded in Hertz (Hz). The number of proton atoms (*n*) for a given resonance was indicated by *n*H. The number of fluorine atoms (*n*) for a given resonance was indicated by *n*F. The number of carbon atoms (*n*) for a given

resonance was indicated by *n*C. High resolution Fast Atom Bombardment (FAB) and Electron Impact (EI) mass spectra were performed by Chemical and Molecular Analysis Centre (CMAC) of the National University of Singapore. They were obtained on a Finnigan/MAT 95XL-T and Micromass VG7035 double focusing mass spectrometer of high resolution. High resolution Electrospray Ionization (ESI) mass spectra were obtained on a Shimadzu LCMS-IT-TOF spectrometer including an SPD-M20A prominence PDA detector, CBM-20A prominence communication bus module, CTO-20A prominence column oven, SIL-20AC prominence auto sampler, DGU-20A3 prominence degasser and LC-20AD prominence liquid chromatograph. Shimadzu Formula Predictor Software was used to process the data. MS and HRMS were reported in units of mass of charge ratio (m/z). Mass samples were dissolved in CH_3CN (HPLC Grade) unless otherwise stated. Infrared spectra (IR) were recorded by dissolving samples in $CHCl_3$ and spread as a thin film on NaCl cells unless otherwise stated. BIO-RAD Excalibur FTS3000 FTIR spectrometer was used to record the IR spectra. Melting points were determined on a BÜCHI B-540 melting point apparatus.

Materials

All commercial reagents were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, Merck, TCI, and Acros of the highest purity grade. They were used without further purification unless specified. All solvents used, mainly hexane (Hex) and ethyl acetate (EtOAc), were distilled. Anhydrous DCM was freshly distilled from CaH_2. Anhydrous THF was freshly distilled from Na/benzophenone. MeCN and $CHCl_3$ were distilled from CaH_2. All compounds synthesized were stored in a −20 °C freezer and light-sensitive compounds were protected with aluminium foil.

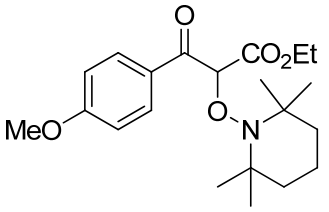
Representative procedure for organic dye photocatalyzed α-oxyamination through irradiation with visible light



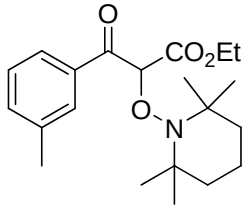
1a 2 TEMPO 3a

To a clear vial, **2** TEMPO (7.8mg, 0.05mmol), Rose Bengal (2.5mg, 0.00025mmol), a stirring bar and distilled CH_3CN (0.5mL) were added in this sequence. After stirring at room temperature for a while, ethyl benzoylacetate **1a** (9.0μL, 0.05mmol) were added to the mixture in one portion. Subsequently, the vial was put under an 11W house hold fluorescent bulb. After the reaction was completed in 24 hours, the reaction mixture was concentrated and loaded onto a short silica gel column, followed by flash chromatography. Product **3a** (16.8mg) was obtained as colorless oil in 97% yield.

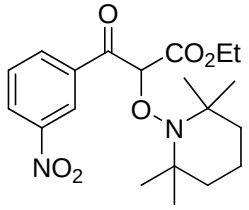
Ethyl 3-oxo-3-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (3a) Colorless oil; 97% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16–8.13 (*m*, 2H), 7.60–7.55 (*m*, 1H), 7.49–7.44 (*m*, 2H), 5.41 (*s*, 1H), 4.17 (*q*, *J* = 7.2 Hz, 2H), 1.59–1.40 (*m*, 6H), 1.29 (*s*, 3H), 1.18–1.14 (*m*, 6H), 0.99 (*s*, 3H), 0.83 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 168.1, 134.5, 133.5, 129.8, 128.4, 92.8, 61.6, 60.4, 59.9, 40.1, 40.0, 33.1, 32.4, 20.2, 16.9, 13.9 ppm; IR (film): 3020, 2977, 1745, 1686, 1524, 1216, 1090, 928 cm^{-1}; LRMS (ESI) *m/z*: 370.0; HRMS (ESI) *m/z*: $C_{20}H_{29}O_4N_1{}^{23}Na_1{}^+$ ([M+Na]$^+$), Calc. 370.1989, Found 370.1982.



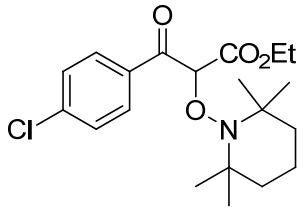
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (3b) Colorless oil; 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16–8.13 (*m*, 2H), 7.60–7.55 (*m*, 1H), 6.95–6.92 (*m*, 2H), 5.35 (*s*, 1H), 4.21–4.11 (*m*, 2H), 3.87 (*s*, 3H), 1.48–1.36 (*m*, 6H), 1.28 (*s*, 3H), 1.19–1.14 (*m*, 6H), 1.00 (*s*, 3H), 0.84 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 168.5, 163.9, 132.3, 127.5, 113.7, 93.1, 61.6, 60.4, 55.4, 40.1, 40.0, 39.1, 33.1, 32.5, 20.2, 17.0, 14.0 ppm; IR (film): 3020, 2977, 1746, 1601, 1514, 1423, 1213, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 400.0; HRMS (ESI) *m/z*: $C_{21}H_{31}O_5N_1{}^{23}Na_1{}^+$ ([M+Na]$^+$), Calc. 400.2094, Found 400.2093.



Ethyl 3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)-3-*m*-tolylpropanoate (3c) White solid; mp: 64.5 – 65.9 °C; 84% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97–7.93 (*m*, 2H), 7.37–7.32 (*m*, 2H), 5.42 (*s*, 1H), 4.16 (*q*, *J* = 7.0 Hz, 2H), 2.41 (*s*, 1H), 1.61–1.40 (*m*, 6H), 1.29 (*s*, 3H), 1.19–1.14 (*m*, 6H), 1.01 (*s*, 3H), 0.83 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.8, 168.2, 138.3, 134.4, 130.0, 128.3, 127.2, 92.7, 61.6, 60.4, 60.0, 40.2, 40.0, 33.1, 32.5, 21.3, 20.2, 17.0, 14.0 ppm; IR (film): 3020, 2977, 1746, 1603, 1523, 1424, 1212, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 384.0; HRMS (ESI) *m/z*: $C_{21}H_{31}O_4N_1{}^{23}Na_1{}^{+}$ ([M+Na]$^{+}$), Calc. 384.2145, Found 384.2146.

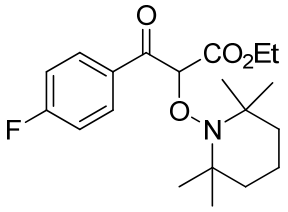


Ethyl 3-(3-nitrophenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (3d) White solid; mp: 99.9 –101.5 °C; 64% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.07 (*s*, 1H), 8.52 (*d*, *J* = 7.6 Hz, 1H), 8.44 (*d*, *J* = 7.3 Hz, 1H), 8.70 (*t*, *J* = 7.9 Hz, 1H), 5.40 (*s*, 1H), 4.27–4.16 (*m*, 2H), 1.50–1.40 (*m*, 6H), 1.20 (*s*, 3H), 1.26–1.23 (*m*, 6H), 0.93 (*s*, 3H), 0.81 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 167.5, 148.2, 135.4, 129.6, 127.6, 124.8, 93.2, 62.0, 60.4, 60.0, 40.0, 39.8, 33.1, 32.3, 20.1, 16.8, 13.8 ppm; IR (film): 3020, 2977, 1744, 1603, 1524, 1424, 1214, 1046, 929 cm^{-1}; LRMS (FAB) *m/z*: 393.1; HRMS (FAB) *m/z*: $C_{20}H_{29}O_6N_2{}^{+}$ ([M+1]$^{+}$), Calc. 393.2020, Found 393.2036.

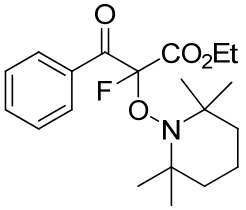


Ethyl 3-(4-chlorophenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (3e) White solid; mp: 67.5 –68.8 °C; 64% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (*d*, *J* = 8.7 Hz, 2H), 7.44 (*d*, *J* = 8.6 Hz, 2H), 5.34 (*s*, 1H), 4.22–4.13 (*m*, 2H), 1.59–1.40 (*m*, 6H), 1.28 (*s*, 3H), 1.20–1.15 (*m*, 6H), 0.97 (*s*, 3H), 0.81 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 168.1, 140.2, 132.7, 131.3, 128.9, 93.2, 61.8, 60.5, 60.0, 40.1, 40.0, 33.2, 32.4, 20.2, 16.9, 14.0 ppm; IR (film): 3020, 2977, 1746, 1602, 1523, 1424, 1214, 1046, 929

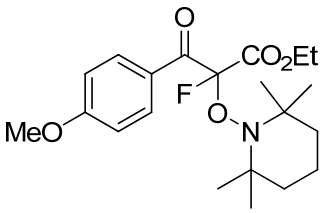
cm^{-1}; LRMS (ESI) *m/z*: 403.9; HRMS (ESI) *m/z*: $C_{20}H_{28}O_4N_1{}^{35}Cl_1{}^{23}Na_1{}^+$ ($[M+Na]^+$), Calc. 404.1599, Found 404.1602; LRMS (ESI) *m/z*: 405.9; HRMS (ESI) *m/z*: $C_{20}H_{28}O_4N_1{}^{37}Cl_1{}^{23}Na_1{}^+$ ($[M+Na]^+$), Calc. 406.1566, Found 406.1562.



Ethyl 3-(4-fluorophenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (3f) Slight yellow solid; mp: 65.8 –66.9 °C; 67% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.23–8.18 (*m*, 2H), 7.14 (*d*, *J* = 8.6 Hz, 2H), 5.35 (*s*, 1H), 4.25–4.10 (*m*, 2H), 1.58–1.40 (*m*, 6H), 1.28 (*s*, 3H), 1.20–1.11 (*m*, 6H), 0.97 (*s*, 3H), 0.81 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 168.2, 166.0 (*d*, *J* = 254.3 Hz, 1C), 132.7 (*d*, *J* = 9.7 Hz, 2C), 130.8, 115.7 (*d*, *J* = 21.5 Hz, 2C), 93.2, 61.8, 60.5, 60.0, 40.1, 40.0, 33.1, 32.4, 20.2, 16.9, 14.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ −27.79-−27.89 (*m*, 1F) ppm; IR (film): 3020, 2977, 1600, 1530, 1426, 1216, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 387.9; HRMS (ESI) *m/z*: $C_{20}H_{28}O_4N_1F_1{}^{23}Na_1{}^+$ ($[M+Na]^+$), Calc. 388.1895, Found 388.1910.

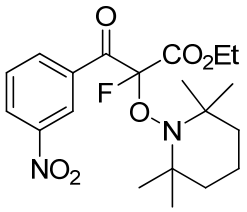


Ethyl 2-fluoro-3-oxo-3-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (5a) Colorless oil; 88% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (*d*, *J* = 8.2 Hz, 2H), 7.57 (*t*, *J* = 7.4 Hz, 1H), 7.44 (*t*, *J* = 7.6 Hz, 2H), 4.41–4.13 (*m*, 2H), 1.62–1.30 (*m*, 9H), 1.25–1.17 (*m*, 9H), 1.11 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.7 (*d*, *J* = 37.1 Hz, 1C), 163.2 (*d*, *J* = 34.4 Hz, 1C), 133.5, 129.7, 129.6, 128.4, 110.7 (*d*, *J* = 235.5 Hz, 1C), 62.4, 62.1, 61.3, 40.8, 40.4, 33.2, 33.0, 21.3, 21.2, 16.9, 13.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ −13.98 (*s*, 1F) ppm; IR (film): 3020, 2977, 1765, 1601, 1523, 1424, 1219, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 388.0; HRMS (ESI) *m/z*: $C_{20}H_{28}O_4N_1F_1{}^{23}Na_1{}^+$ ($[M+Na]^+$), Calc. 388.1895, Found 388.1912.



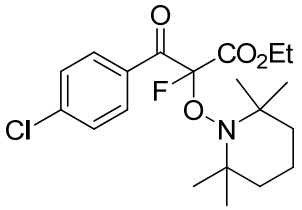
Ethyl 2-fluoro-3-(4-methoxyphenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (5b)

Slight yellow oil; 88% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (*d*, *J* = 8.4 Hz, 2H), 7.44 (*d*, *J* = 8.7 Hz, 2H), 4.44–4.18 (*m*, 2H), 3.91 (*s*, 3H), 1.68–1.43 (*m*, 6H), 1.40 (*s*, 3H), 1.29–1.23 (*m*, 9H), 1.17 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 185.3 (*d*, *J* = 37.1 Hz, 1C), 163.1, 162.6 (*d*, *J* = 34.4 Hz, 1C), 131.5, 131.4, 125.3, 113.0, 110.1 (*d*, *J* = 235.5 Hz, 1C), 61.6, 61.3, 60.5, 54.8, 40.1, 39.7, 32.4, 32.3, 20.6, 20.5, 16.2, 13.0 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ −13.78 (*s*, 1F) ppm; IR (film): 3020, 2977, 1765, 1602, 1514, 1425, 1216, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 417.9; HRMS (ESI) *m/z*: $C_{21}H_{30}O_5N_1F_1{}^{23}Na_1{}^{+}$ ([M+Na]$^{+}$), Calc. 418.2000, Found 418.2021.



Ethyl 2-fluoro-3-(3-nitrophenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (5c)

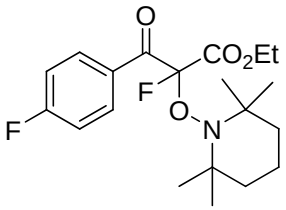
Colorless oil; 95% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.91 (*s*, 1H), 8.45–8.42 (*m*, 1H), 8.32 (*d*, *J* = 7.9 Hz, 1H), 4.45–4.21 (*m*, 2H), 1.60–1.39 (*m*, 6H), 1.35 (*s*, 3H), 1.31–1.27 (*m*, 6H), 1.19 (*s*, 3H), 1.08 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.1 (*d*, *J* = 39.2 Hz, 1C), 162.7 (*d*, *J* = 33.3 Hz, 1C), 148.1, 135.1 (*d*, *J* = 3.2 Hz, 1C), 134.6, 129.7, 127.6, 124.7 (*d*, *J* = 3.8 Hz, 1C), 110.6 (*d*, *J* = 236.6 Hz, 1C), 62.4, 61.5, 40.7, 40.3, 33.1, 32.9, 21.3, 21.2, 16.8, 13.8 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ −14.30 (*s*, 1F) ppm; IR (film): 3020, 2978, 1724, 1536, 1424, 1352, 1215, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 432.9; HRMS (ESI) *m/z*: $C_{20}H_{27}O_6N_2F_1{}^{23}Na_1{}^{+}$ ([M+Na]$^{+}$), Calc. 433.1745, Found 433.1758.



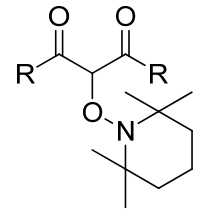
Ethyl 3-(4-chlorophenyl)-2-fluoro-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (5d)

Colorless oil; 91% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (*d*, *J* = 7.6 Hz, 2H), 7.42 (*d*, *J* = 8.7 Hz, 2H), 4.41–4.14 (*m*, 2H), 1.63–1.40 (*m*, 6H), 1.35 (*s*, 3H), 1.25–1.20 (*m*, 9H), 1.10 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.3, 163.0 (*d*, *J* = 34.4 Hz, 1C), 140.1, 131.6, 131.1, 128.8, 110.7 (*d*, *J* = 235.5 Hz, 1C), 62.5, 62.2, 61.4, 40.8, 40.4, 33.1, 33.0, 21.4, 21.3, 16.9, 13.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ −14.07 (*s*, 1F) ppm; IR (film): 3019, 2977, 1766, 1590, 1524, 1423, 1212, 1045, 929 cm^{-1}; LRMS (ESI) *m/z*: 421.9; HRMS (ESI) *m/z*: $C_{20}H_{27}O_4N_1{}^{35}Cl_1F_1{}^{23}Na_1{}^{+}$ ([M+Na]$^{+}$), Calc. 422.1505, Found 422.1491; LRMS (ESI) *m/z*:

423.9; HRMS (ESI) *m/z*: $C_{20}H_{27}O_4N_1{}^{37}Cl_1F_1{}^{23}Na_1{}^+$ ([M+Na]$^+$), Calc. 424.1475, Found 424.1483.

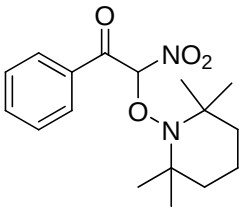


Ethyl 2-fluoro-3-(4-fluorophenyl)-3-oxo-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanoate (5e) Colorless oil; 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (*dd*, *J* = 5.5, 7.9 Hz, 2H), 7.12 (*t*, *J* = 8.8 Hz, 2H), 4.41–4.14 (*m*, 2H), 1.62–1.40 (*m*, 6H), 1.35 (*s*, 3H), 1.24–1.19 (*m*, 9H), 1.10 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 184.7 (*d*, *J* = 38.2 Hz, 1C), 165.9 (*d*, *J* = 254.9 Hz, 1C), 163.1 (*d*, *J* = 34.4 Hz, 1C), 132.5 (*dd*, *J* = 3.8, 9.1 Hz, 2C), 129.7, 115.7 (*d*, *J* = 21.5 Hz, 2C), 110.7 (*d*, *J* = 235.5 Hz, 1C), 62.5, 62.2, 61.4, 40.8, 40.4, 33.1, 33.0, 21.4, 21.3, 16.9, 13.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): δ −13.92 (*s*, 1F), −27.79--27.89 (*m*, 1F) ppm; IR (film): 3020, 2977, 1765, 1601, 1523, 1424, 1214, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 405.9; HRMS (ESI) *m/z*: $C_{20}H_{27}O_4N_1F_2{}^{23}Na_1{}^+$ ([M+Na]$^+$), Calc. 406.1800, Found 406.1809.



R = 4-MeOPh

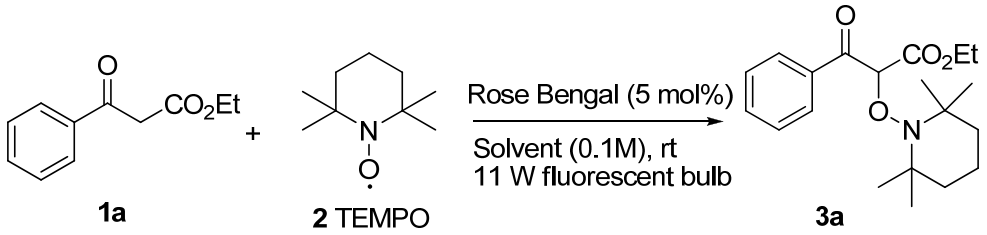
1,3-Bis(4-methoxyphenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propane-1,3-dione (7) Colorless oil; 67% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (*d*, *J* = 8.8 Hz, 4H), 6.91 (*d*, *J* = 8.8 Hz, 4H), 6.18 (*s*, 1H), 3.85 (*s*, 6H), 1.60–1.26 (*m*, 6H), 1.14 (*s*, 6H), 0.95 (*s*, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 193.6, 163.9, 132.7, 127.9, 113.6, 99.0, 60.1, 55.4, 40.1, 32.9, 20.3, 17.0 ppm; IR (film): 3020, 2977, 1661, 1600, 1513, 1424, 1219, 1046, 929 cm^{-1}; LRMS (ESI) *m/z*: 462.0; HRMS (ESI) *m/z*: $C_{26}H_{33}O_5N_1{}^{23}Na_1{}^+$ ([M+Na]$^+$), Calc. 462.2251, Found 462.2270.



2-Nitro-1-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanone (9) Slight yellow oil; 72% yield; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.16 (*d*, *J* = 7.9 Hz, 2H), 7.65 (*t*, *J* = 7.3 Hz, 1H), 7.51 (*t*, *J* = 7.6 Hz, 2H), 6.52

(*s*, 1H), 1.67–1.48 (*m*, 6H), 1.33 (*s*, 3H), 1.09 (*s*, 6H), 0.90 (*s*, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.1, 134.7, 132.4, 130.1, 128.9, 115.1, 40.2, 39.8, 33.0, 32.2, 27.5, 20.4, 16.8 ppm; IR (film): 3020, 2977, 1661, 1600, 1513, 1424, 1219, 1046, 929 cm^{-1}; LRMS (FAB) *m/z*: 321.1; HRMS (FAB) *m/z*: $C_{17}H_{25}O_4N_2^+$ ($[M+1]^+$), Calc. 321.1809, Found 321.1817.

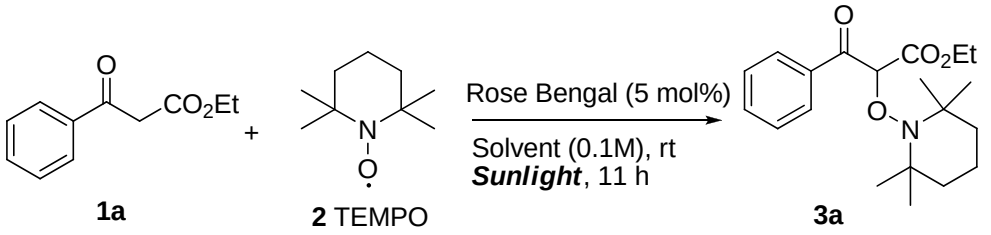
Procedure for organic dye photocatalyzed α-oxyamination through irradiation with visible light under inert condition



1a **2** TEMPO **3a**

To a clear and dry vial, **2** TEMPO (7.8mg, 0.05mmol), Rose Bengal (2.5mg, 0.00025mmol), a stirring bar and anhydrous and degassed CH_3CN (0.5mL) were added in this sequence in an Innovative Technology glove box (O_2<0.5ppm and H_2O<0.2ppm). After stirring at room temperature for a while, ethyl benzoylacetate **1a** (9.0μL, 0.05mmol) were added to the mixture in one portion. Subsequently, the vial was put under an 11W house hold fluorescent bulb. After the reaction was completed in 24 hours, the sample was wrapped in aluminium foil and removed from the glovebox and TLC showed full conversion.

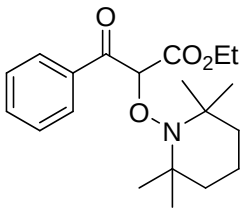
Procedure for organic dye photocatalyzed α-oxyamination through irradiation with sunlight



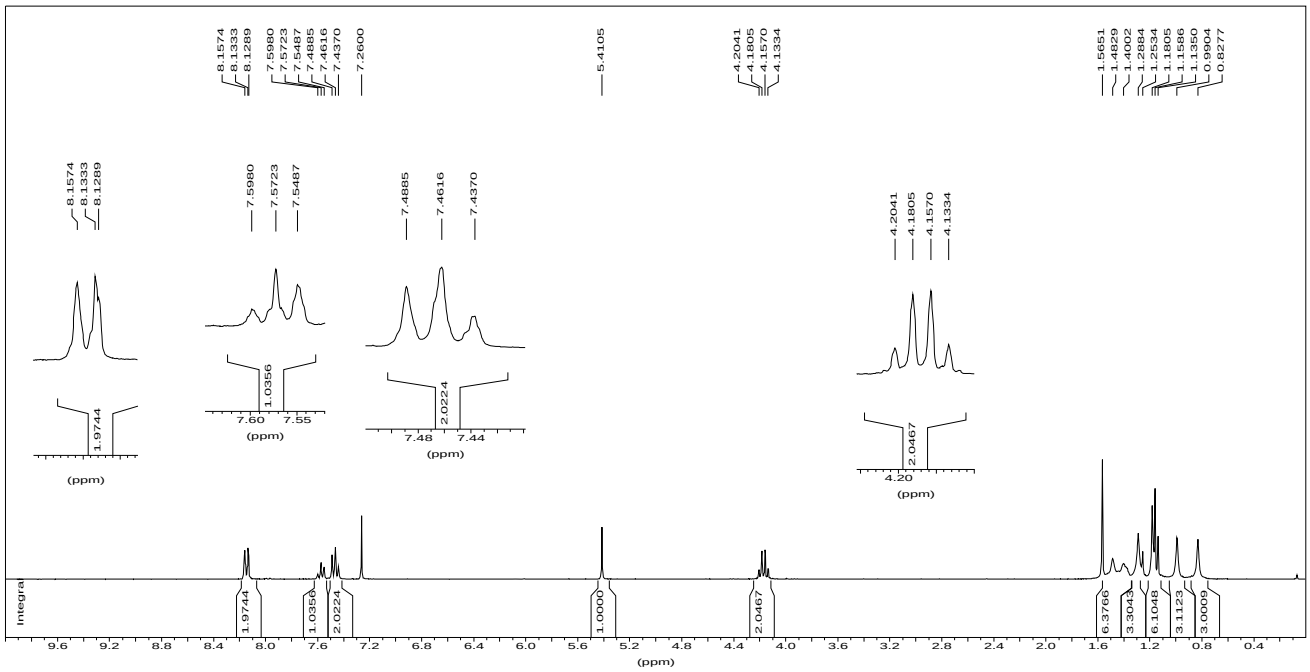
1a **2** TEMPO **3a**

To a clear r.b.f., **2** TEMPO (78mg, 0.5mmol), Rose Bengal (25mg, 0.0025mmol), a stirring bar and distilled CH_3CN (0.5mL) were added in this sequence. After stirring at room temperature for a while, ethyl benzoylacetate **1a** (90μL, 0.5mmol) were added to the mixture in one portion. Subsequently, the r.b.f. was put under ambient sunlight on the roof of our laboratory building. After the reaction was completed in 11 hours (12am – 5pm March 5th, 2010 and 10am – 5pm March 5th, 2010), the reaction mixture was concentrated and loaded onto a short silica gel column, followed by flash chromatography. Product **3a** (148mg) was obtained as colorless oil in 85% yield.

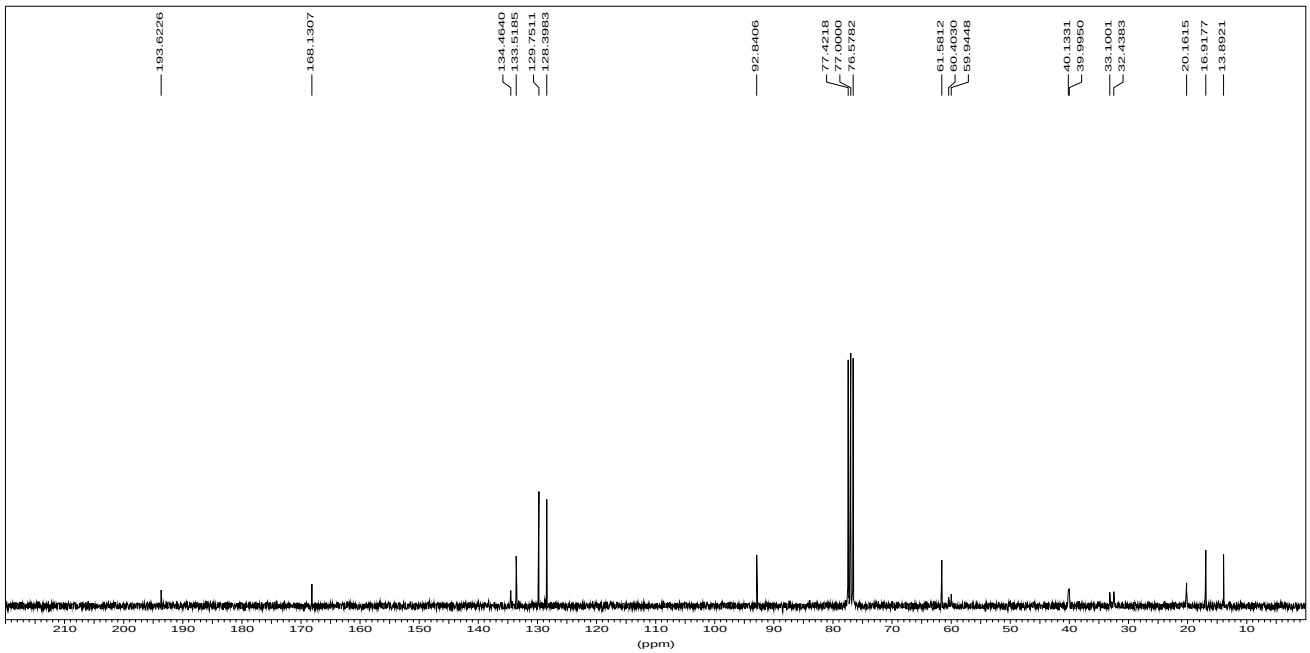
NMR Spectra

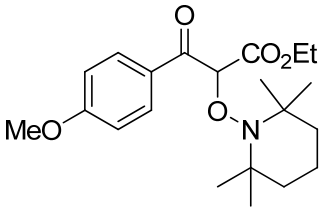


ag20lhj2 2.4 lhj6121-1 HNMR

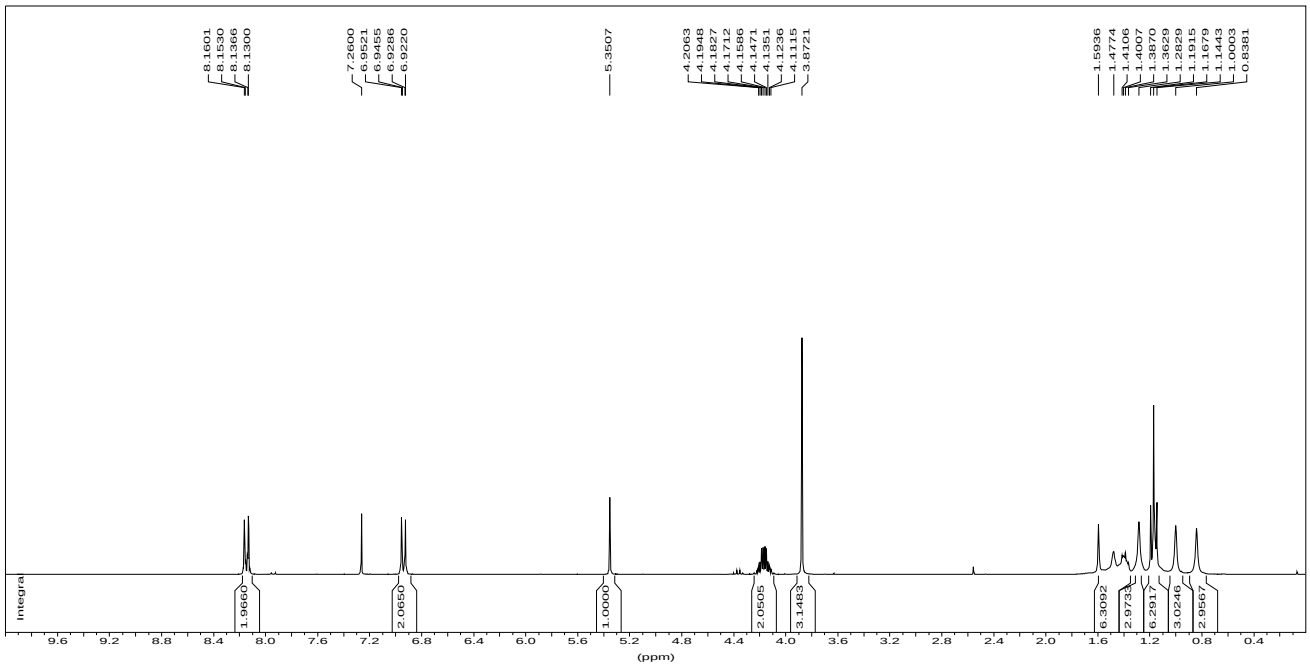


13C Standard AC300 ag20lhj2 2.3 lhj6121-2





ag20lhj2 2.1 lhj6121A



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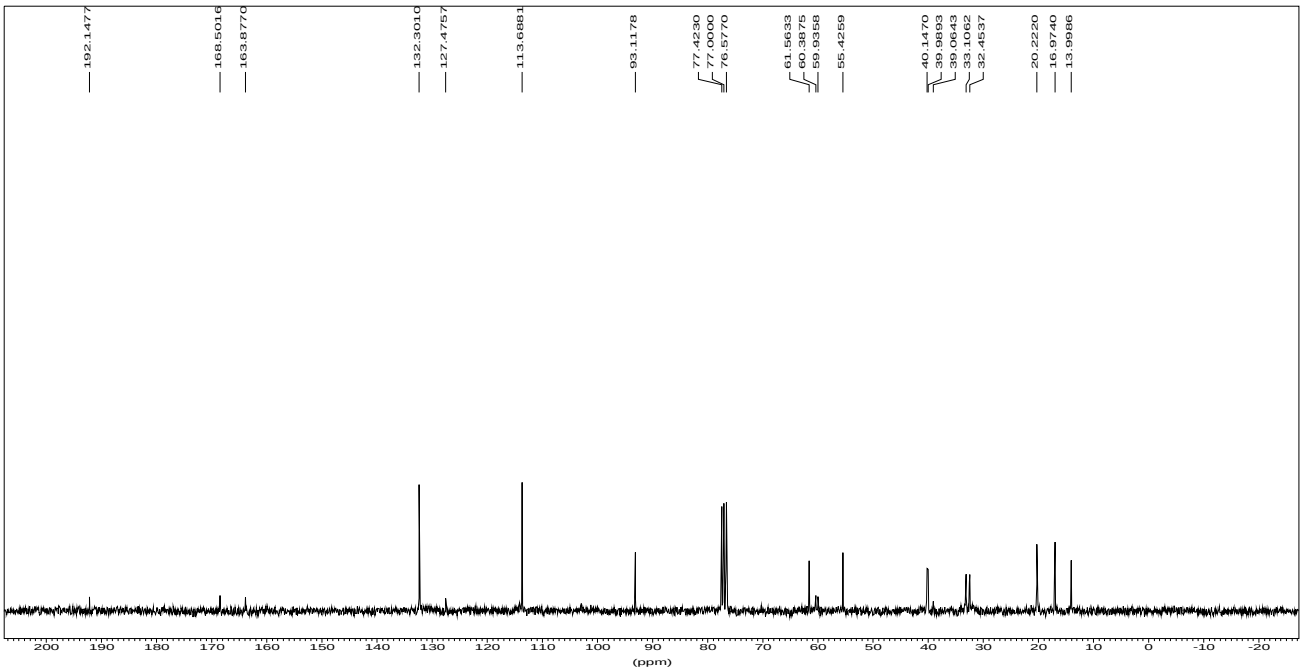

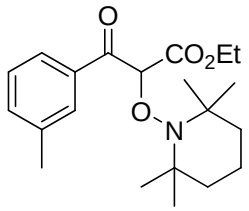

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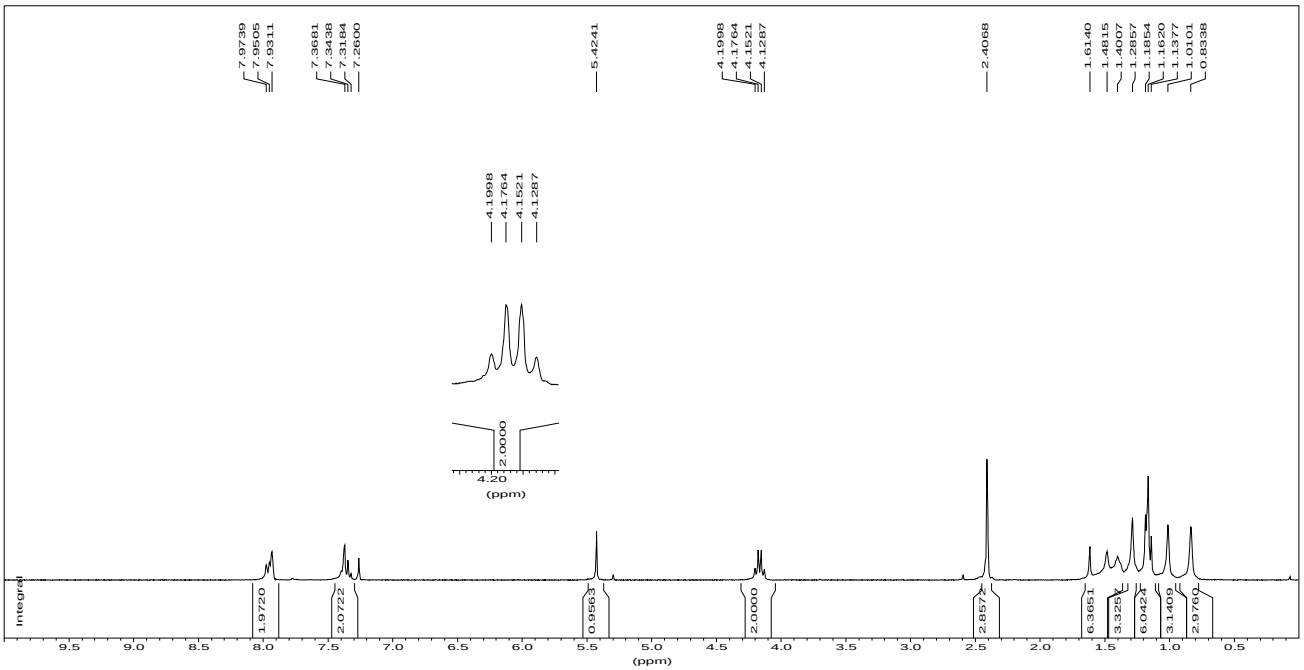

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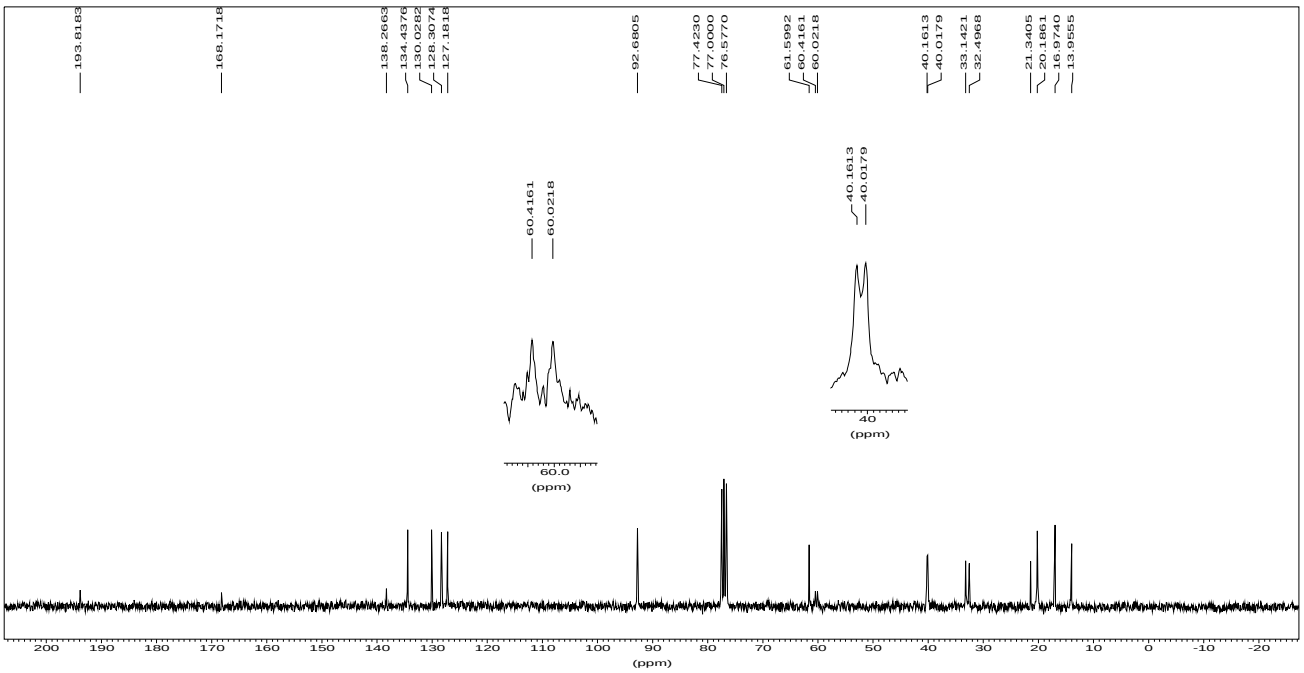

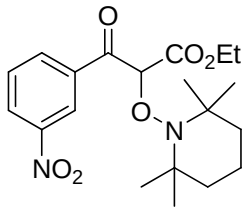

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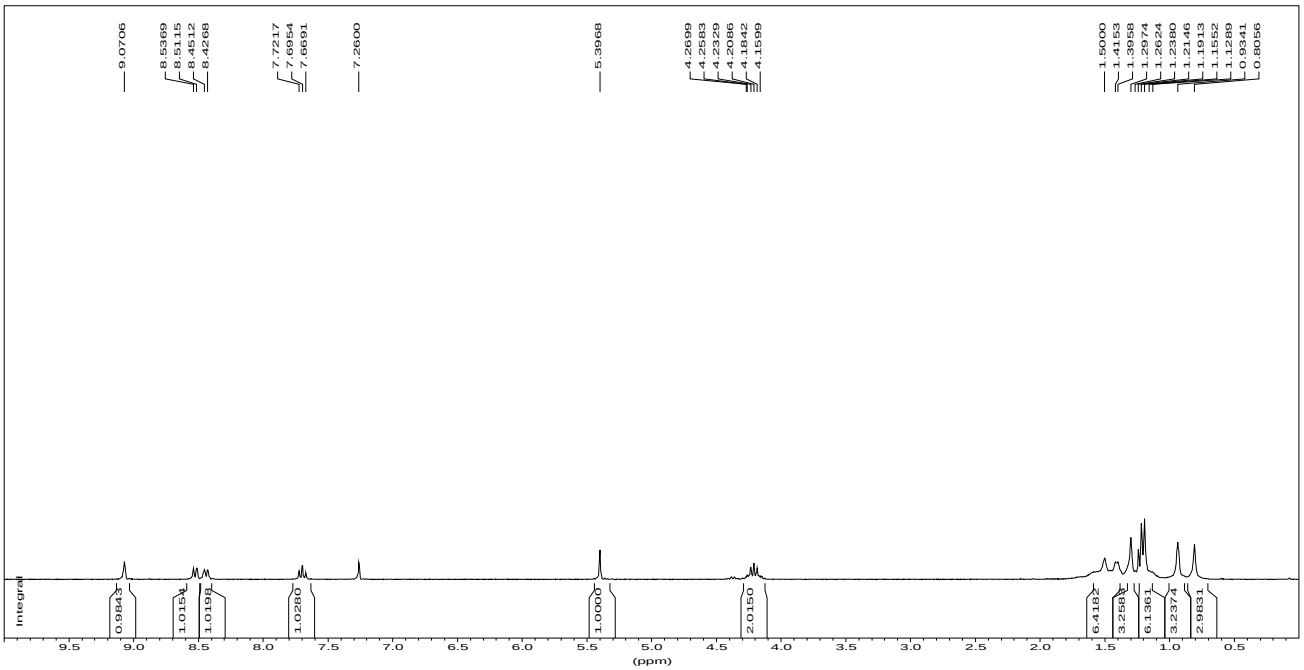
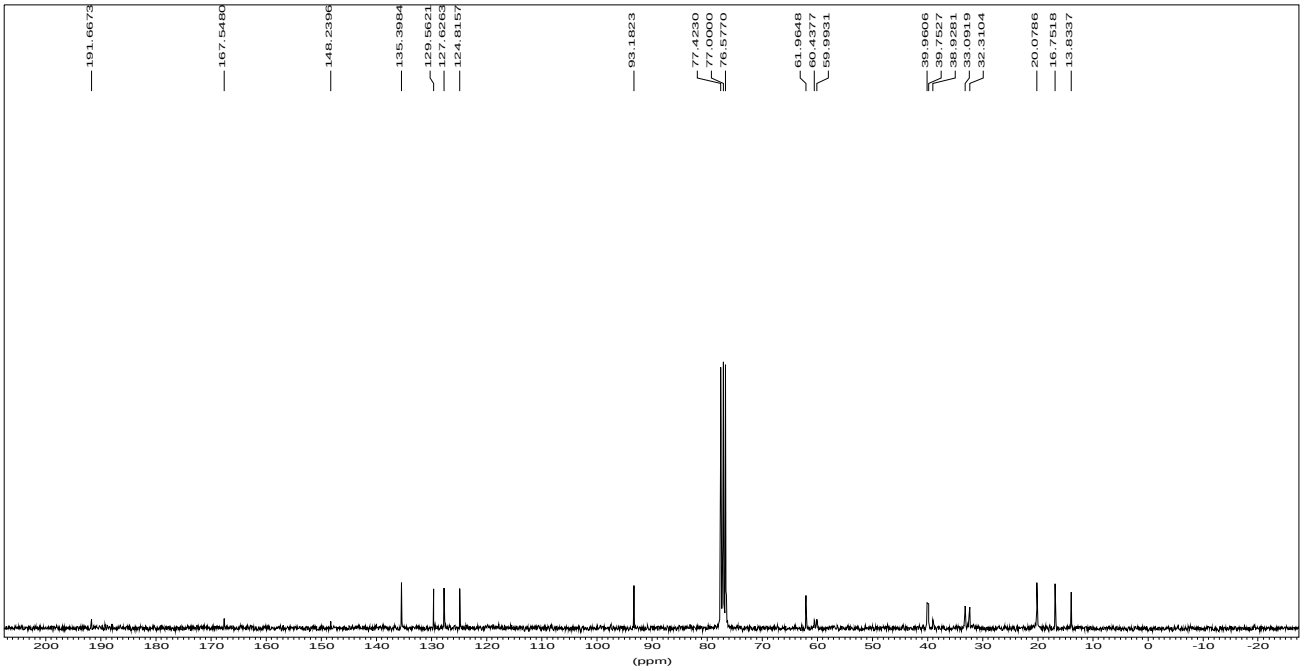
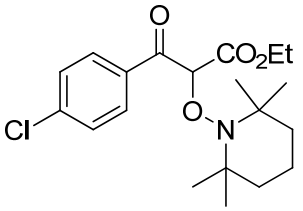
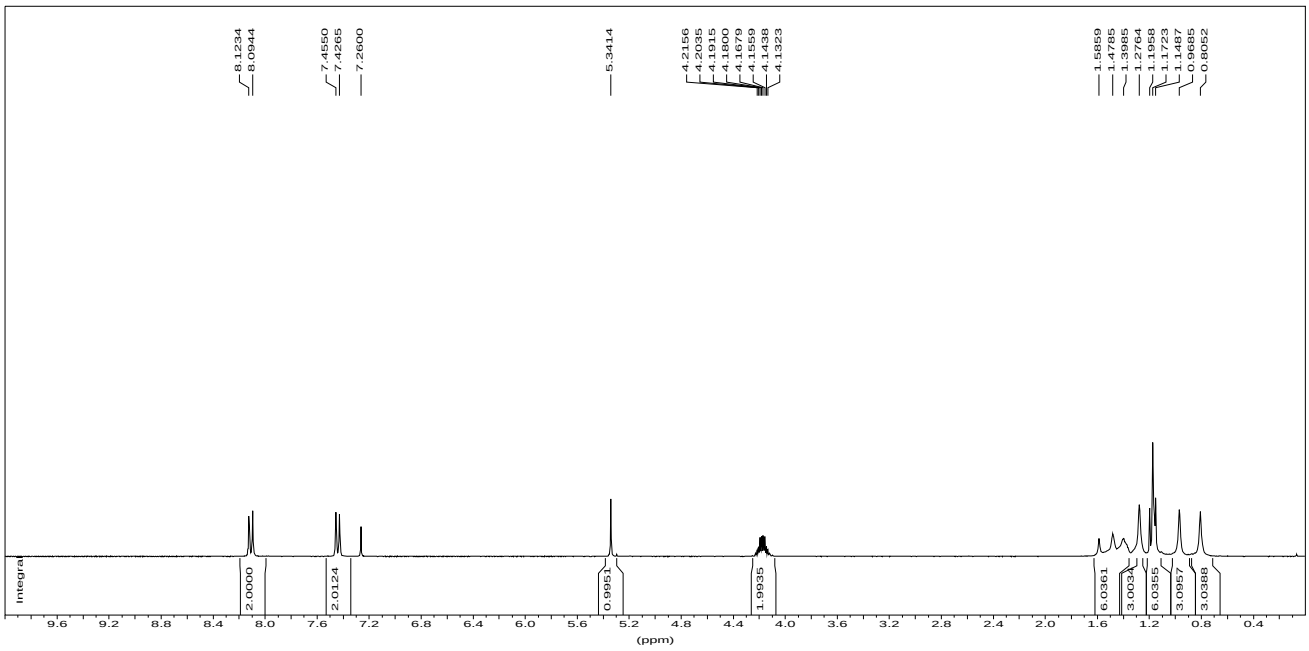


DPX300 ag31lhj 1.2 lhj6127A CNMR





AC300 oc17lhj2 2.1 lhj6146A HNMR



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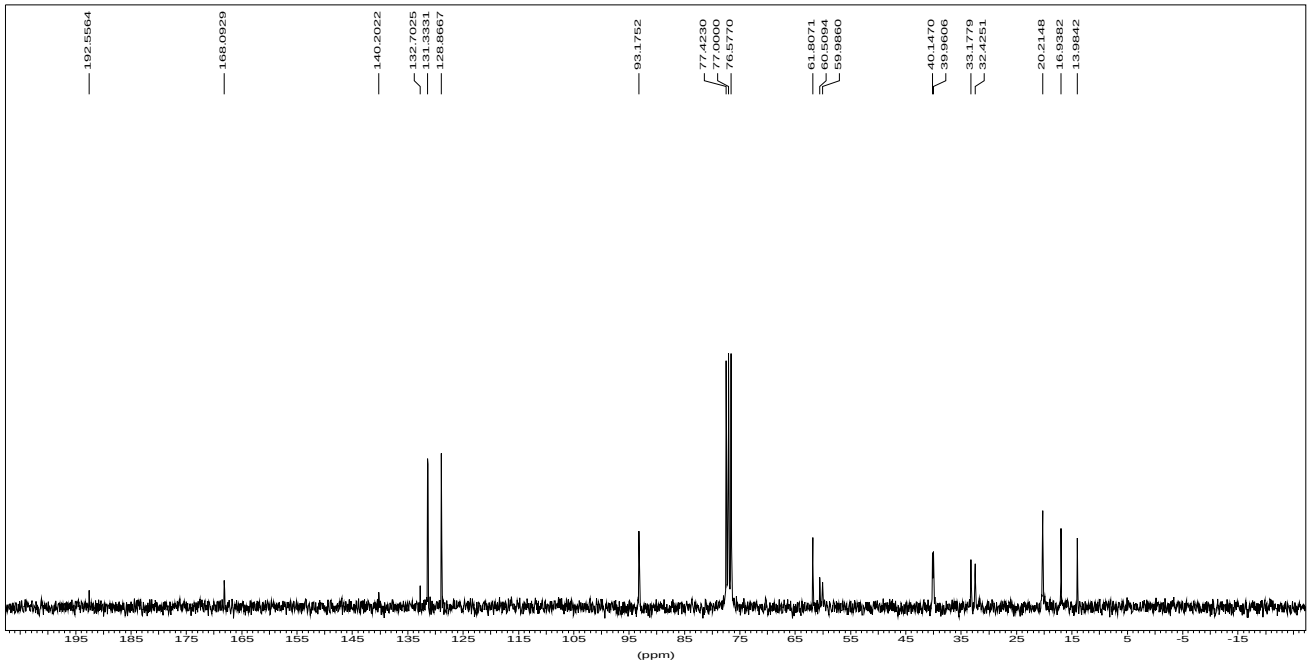

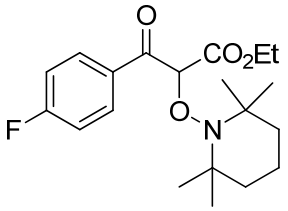

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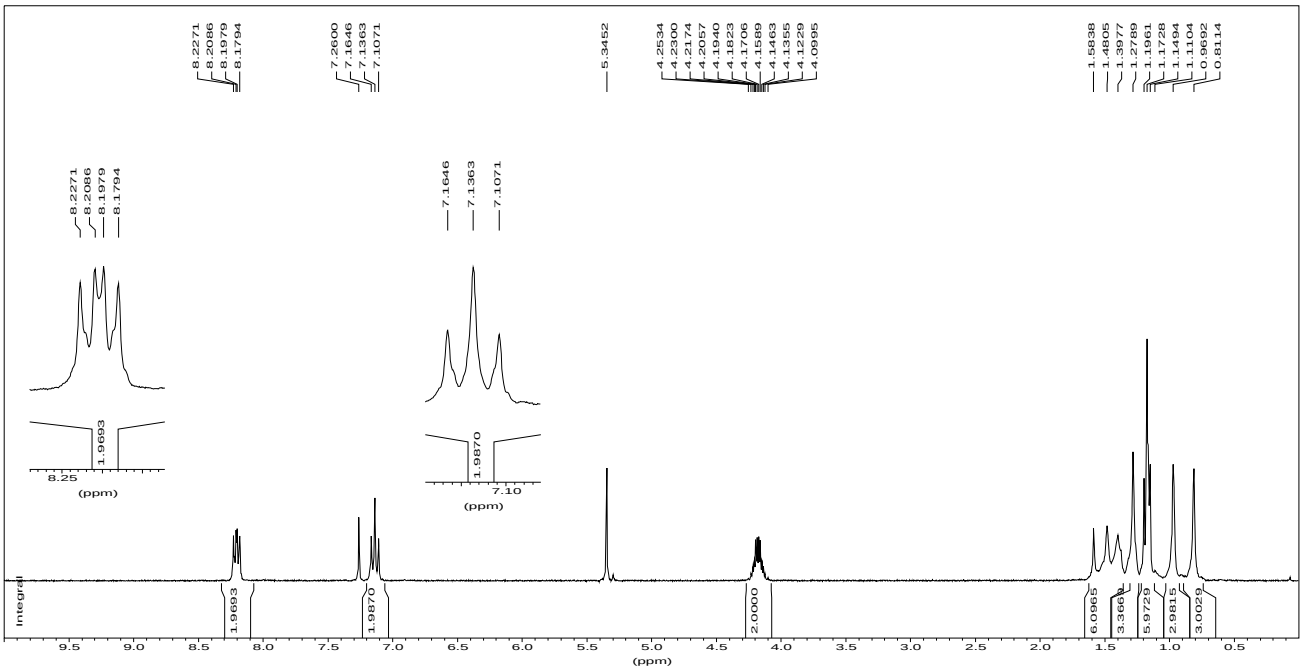

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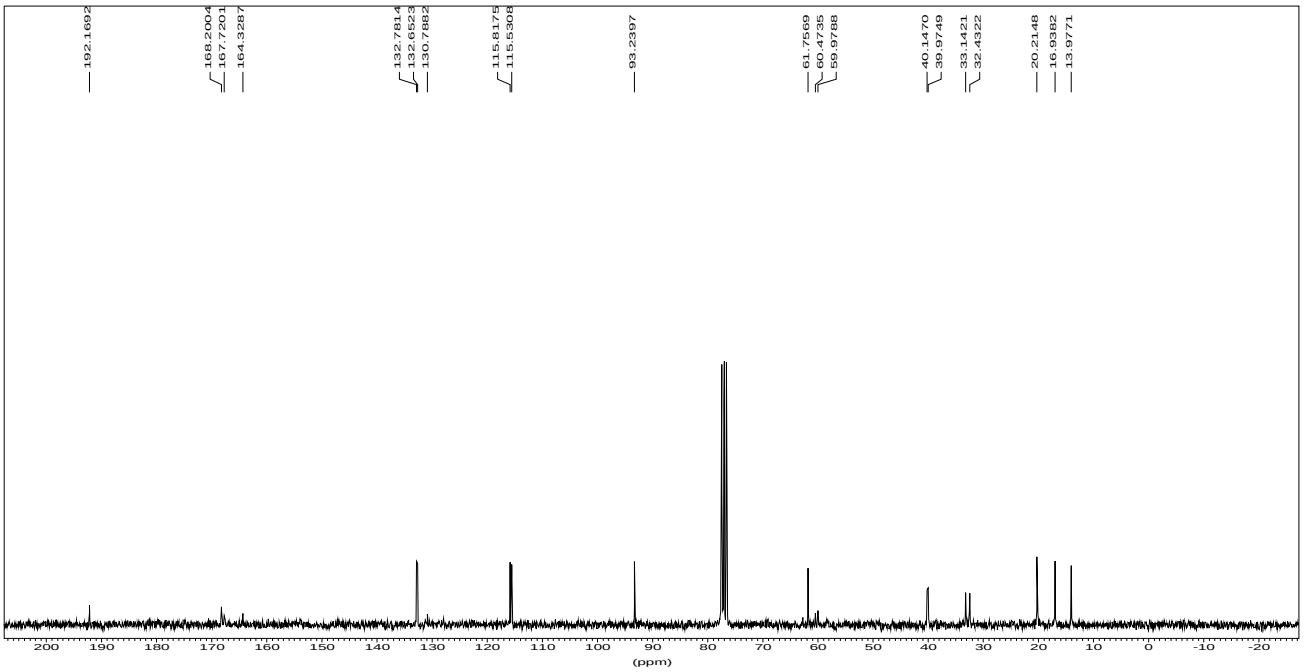
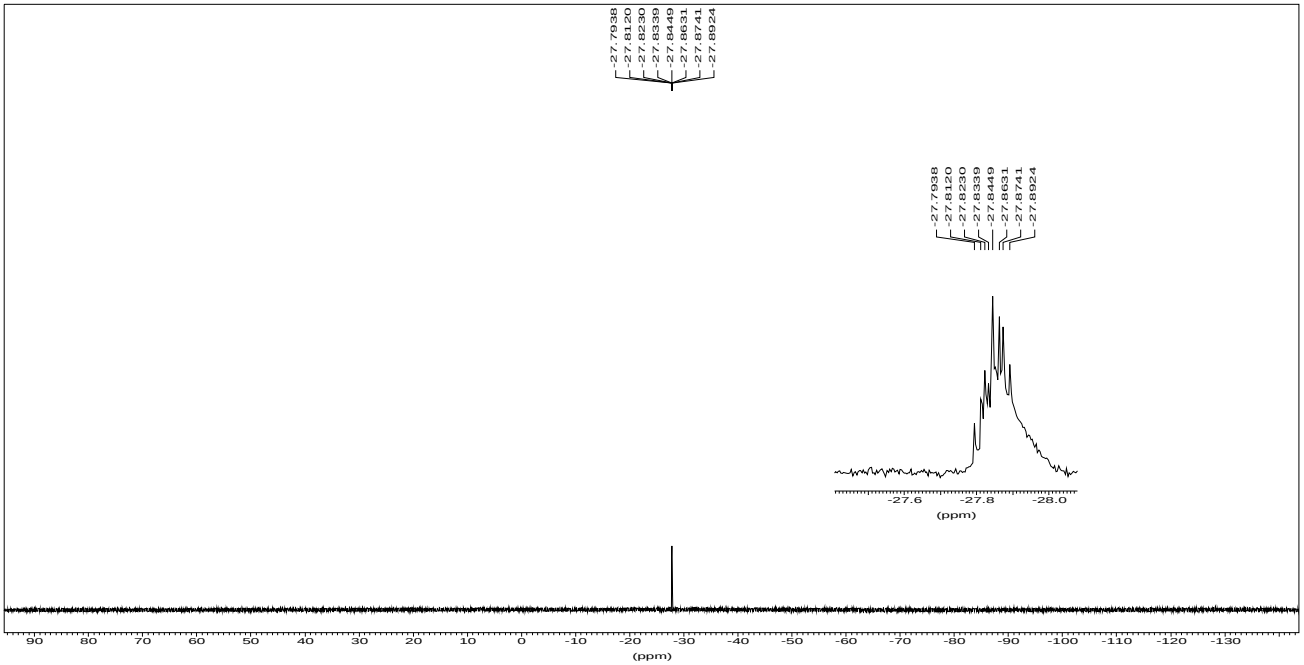
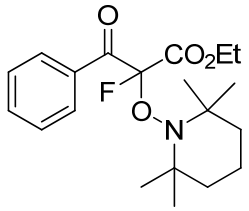
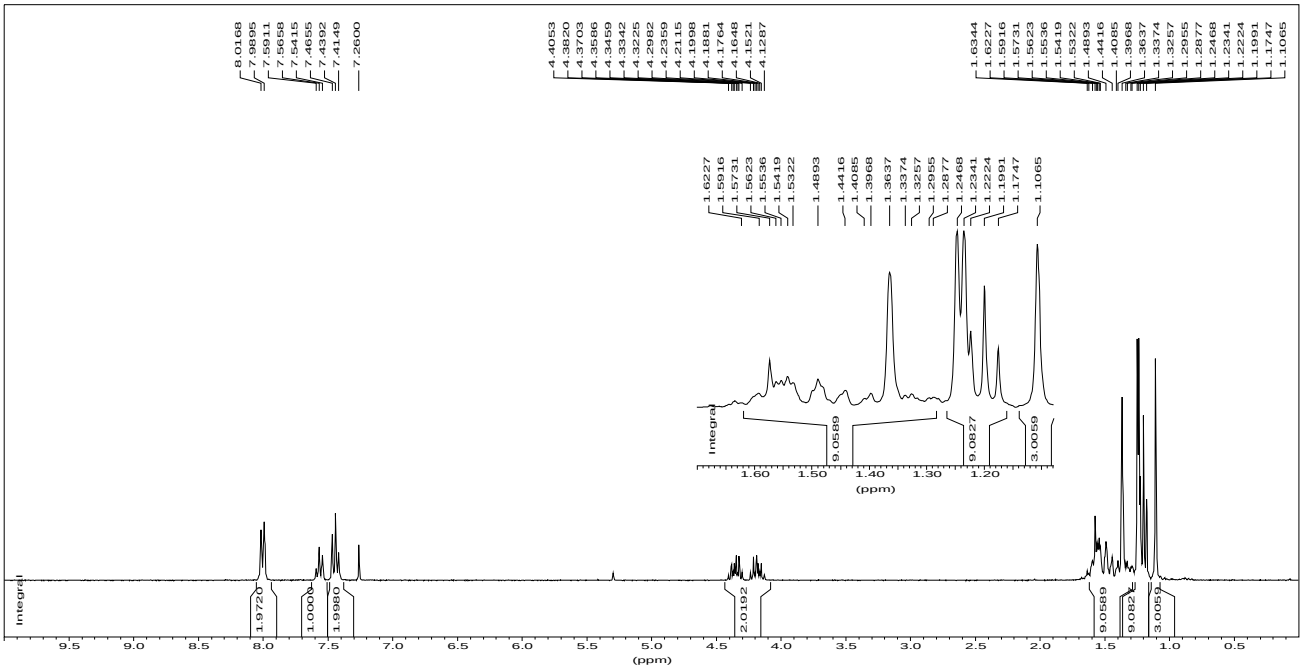


F19(no decoupled) oc28lhj 1.2 lhj6149A FNMR





dpx300 se23lhj 1.1 lhj6133A HNMR



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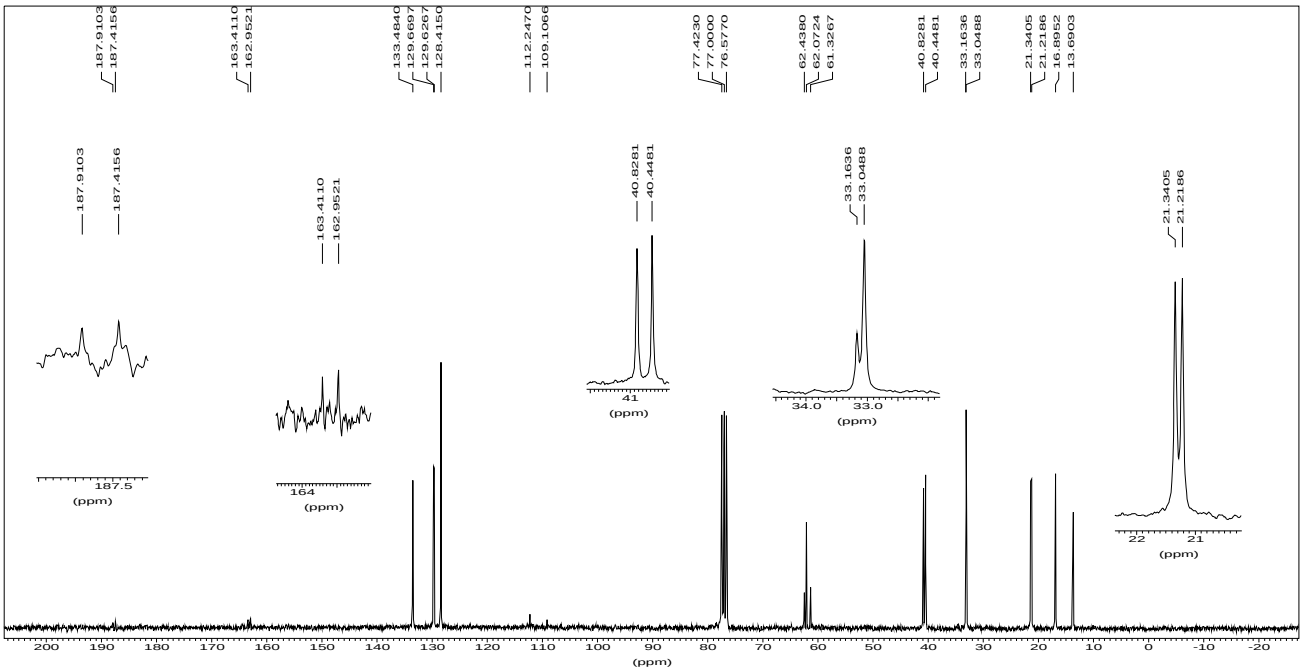

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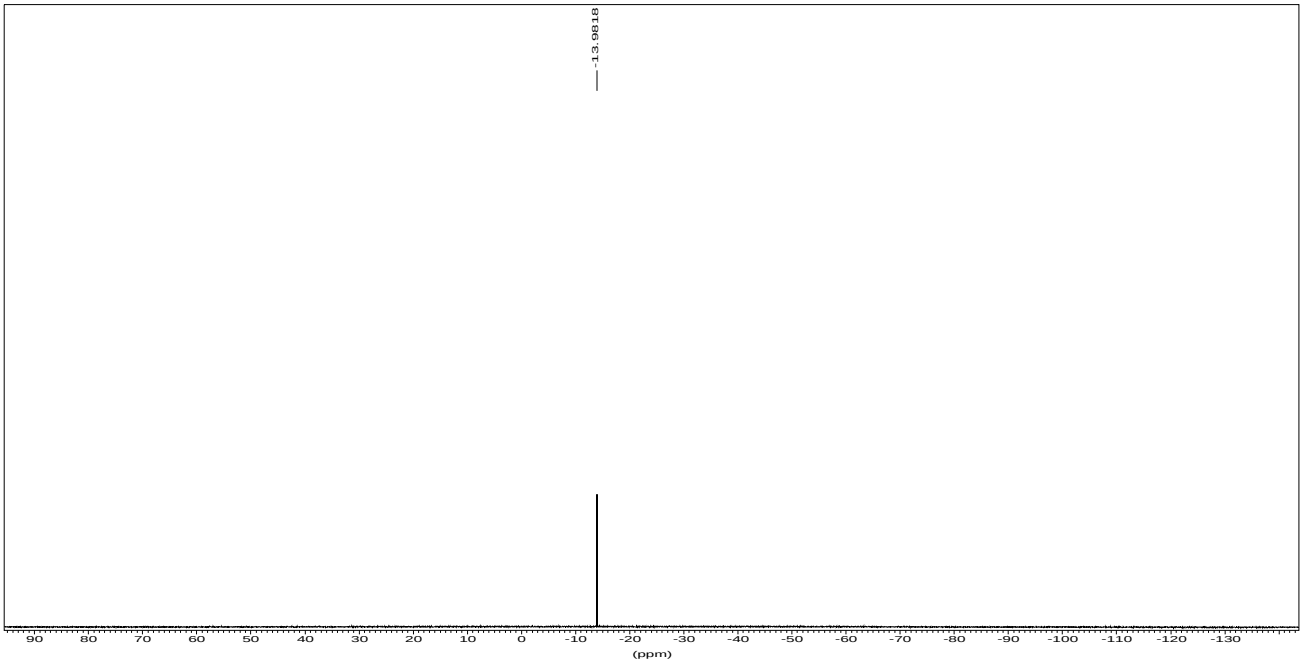

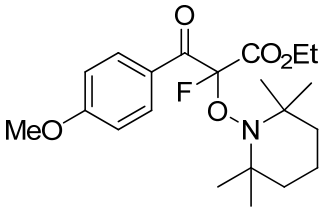

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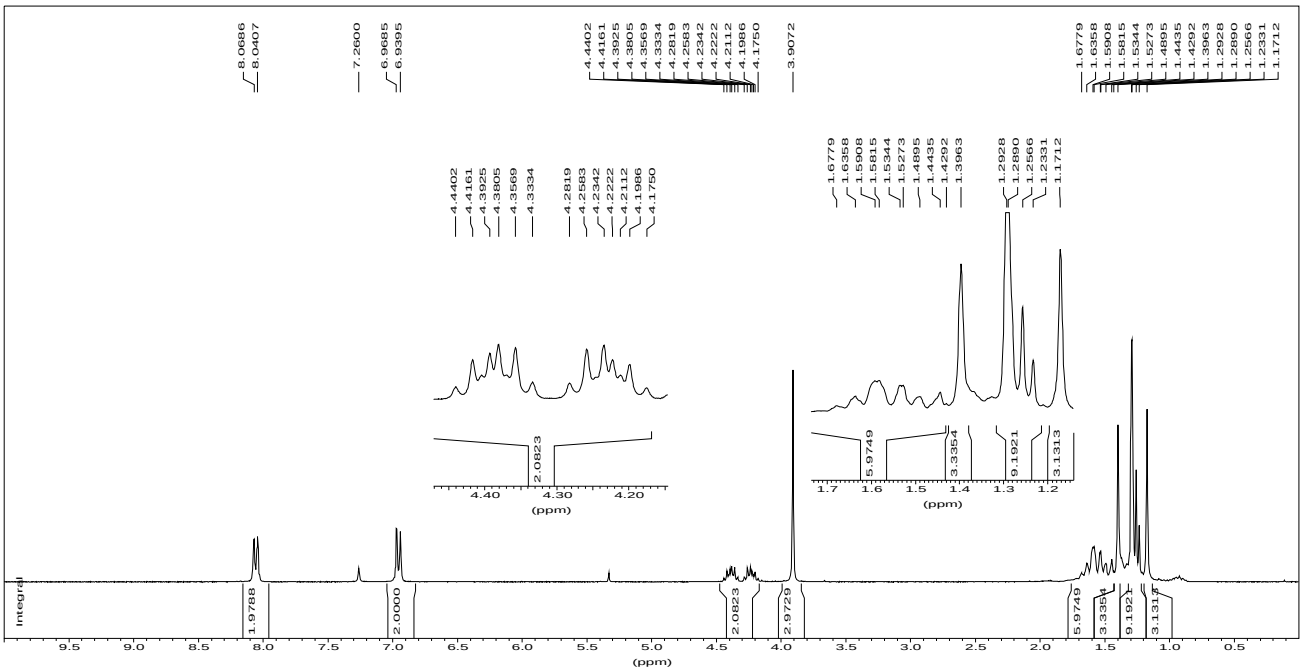

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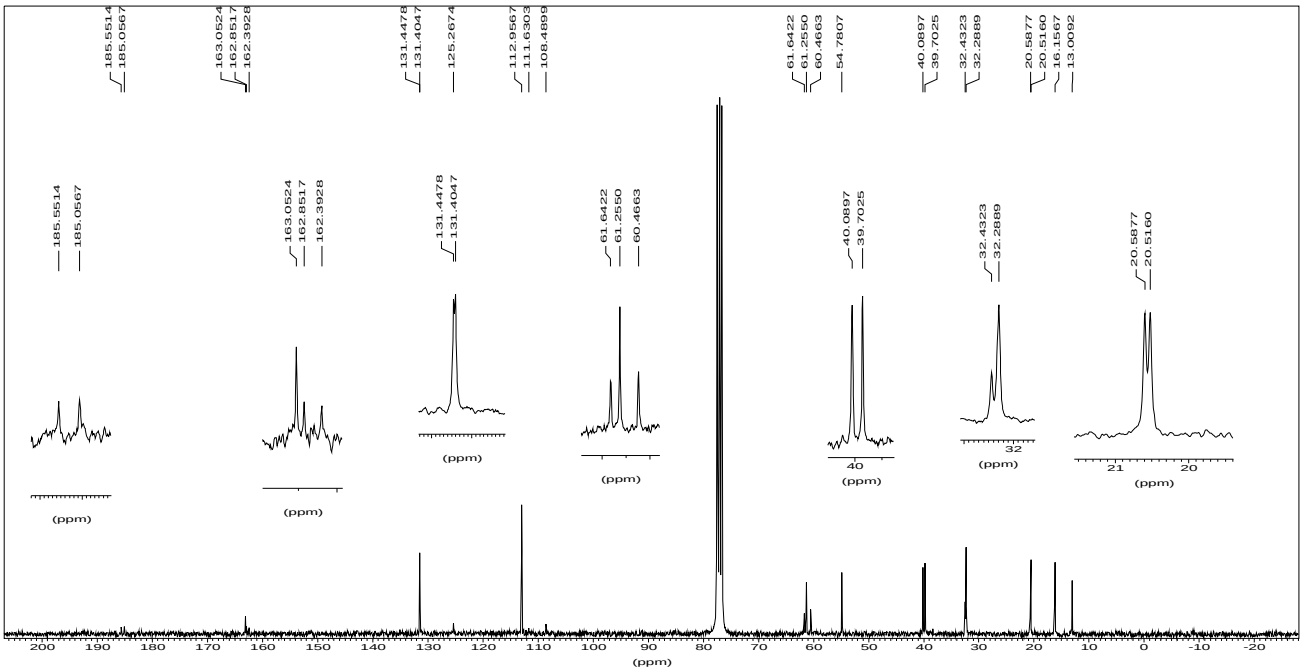

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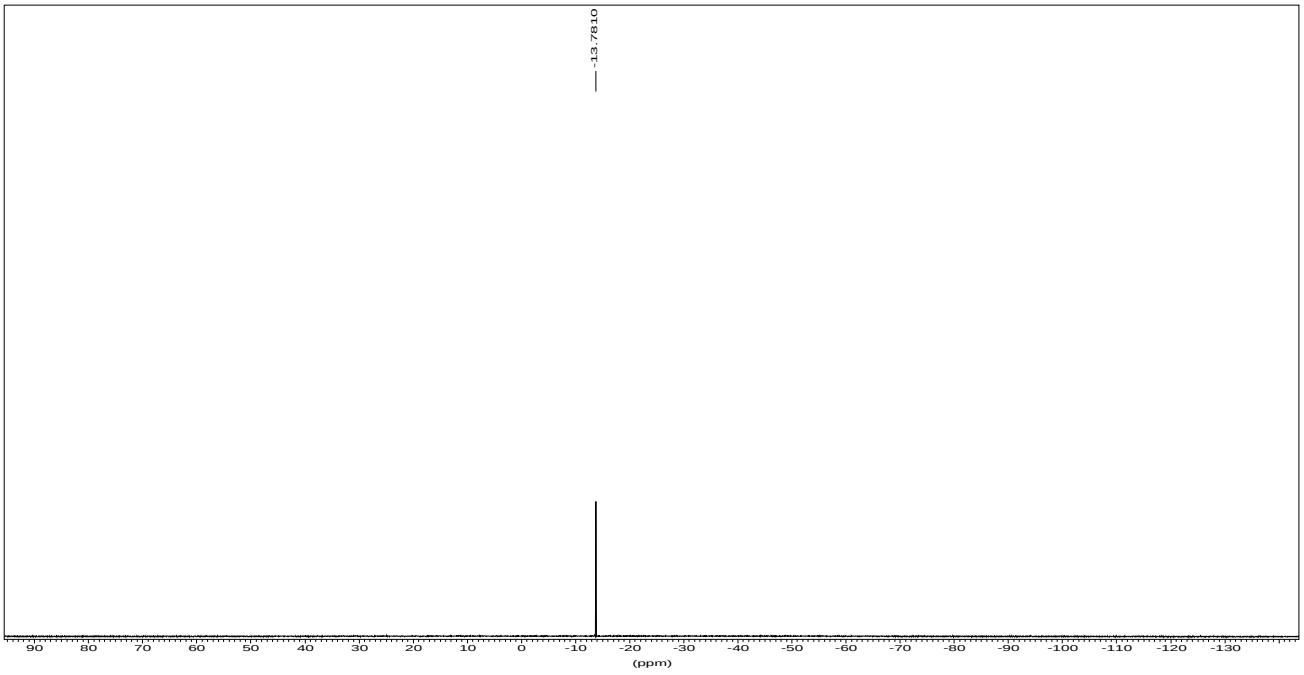

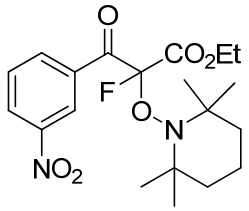

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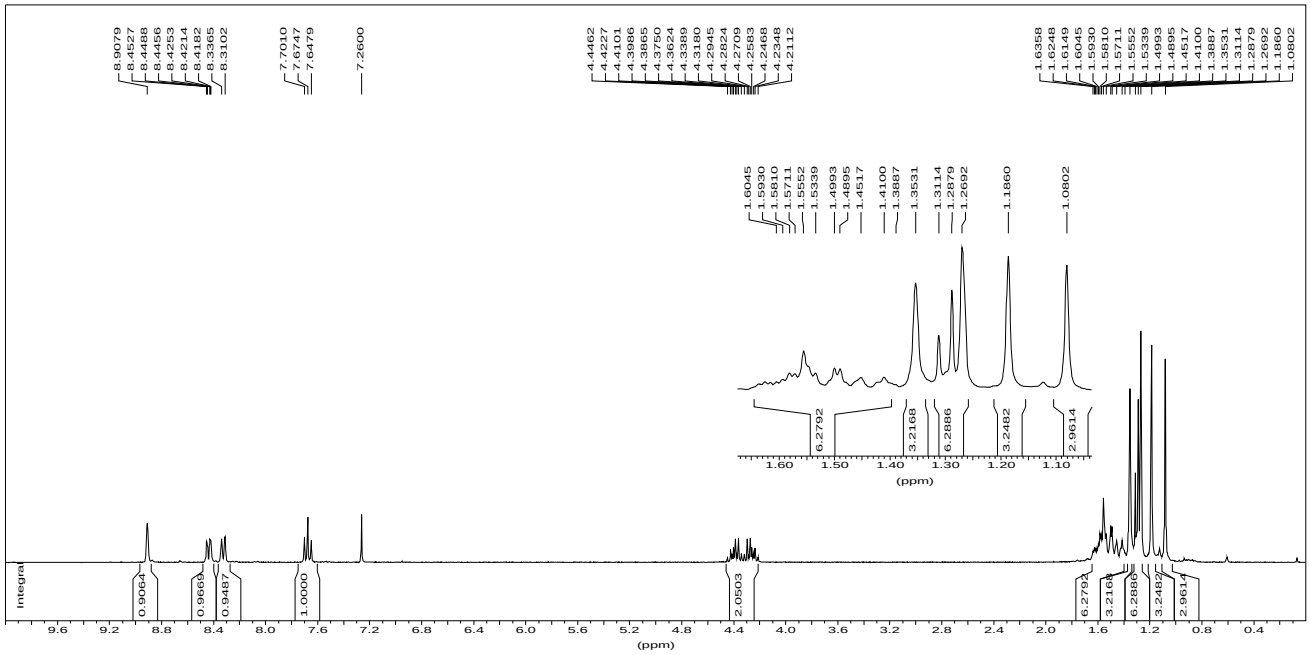

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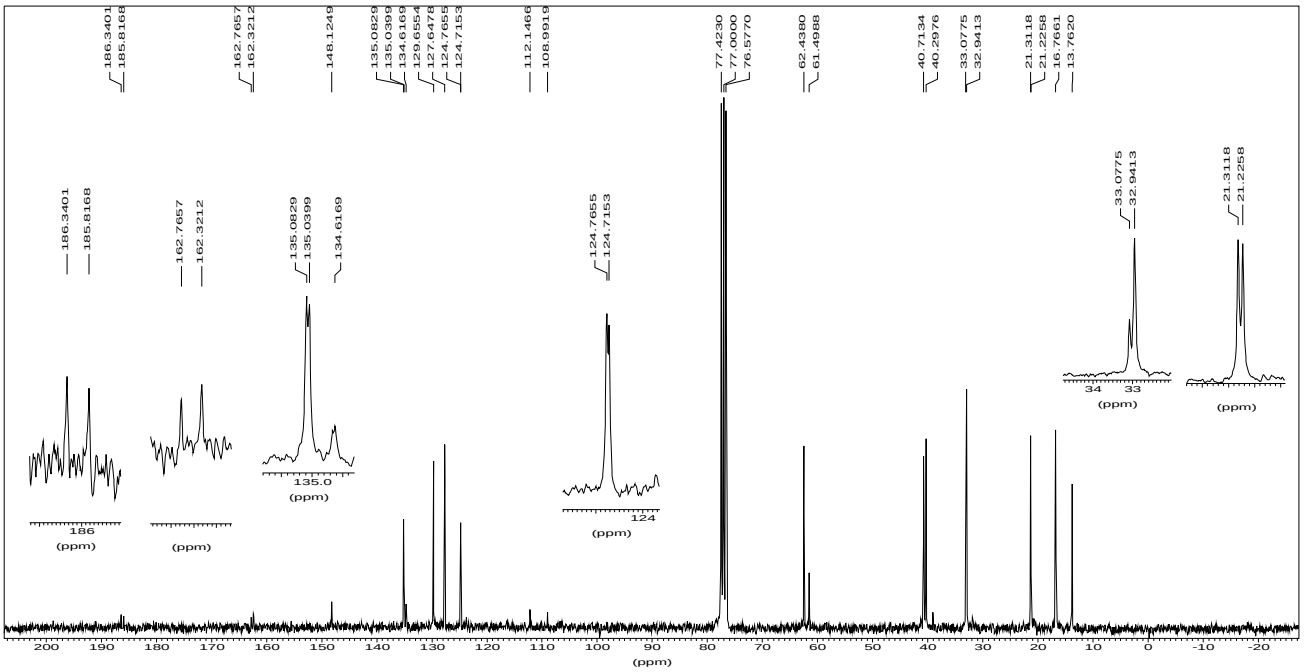
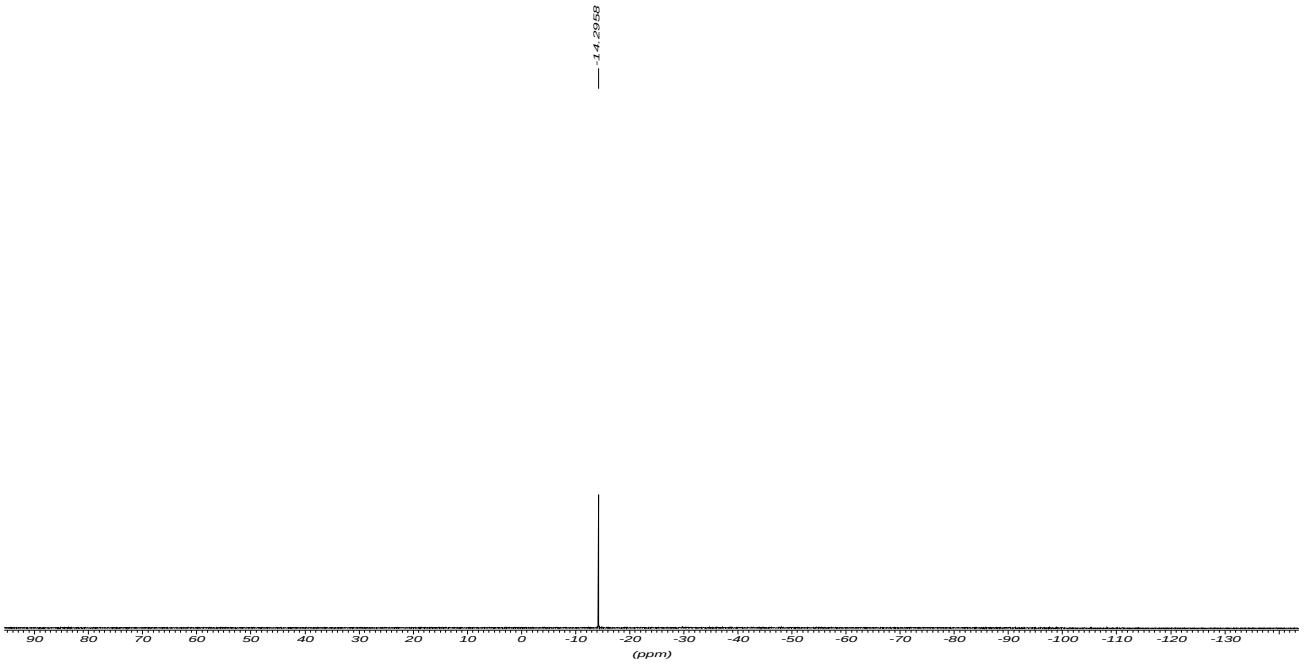
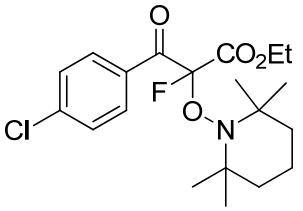
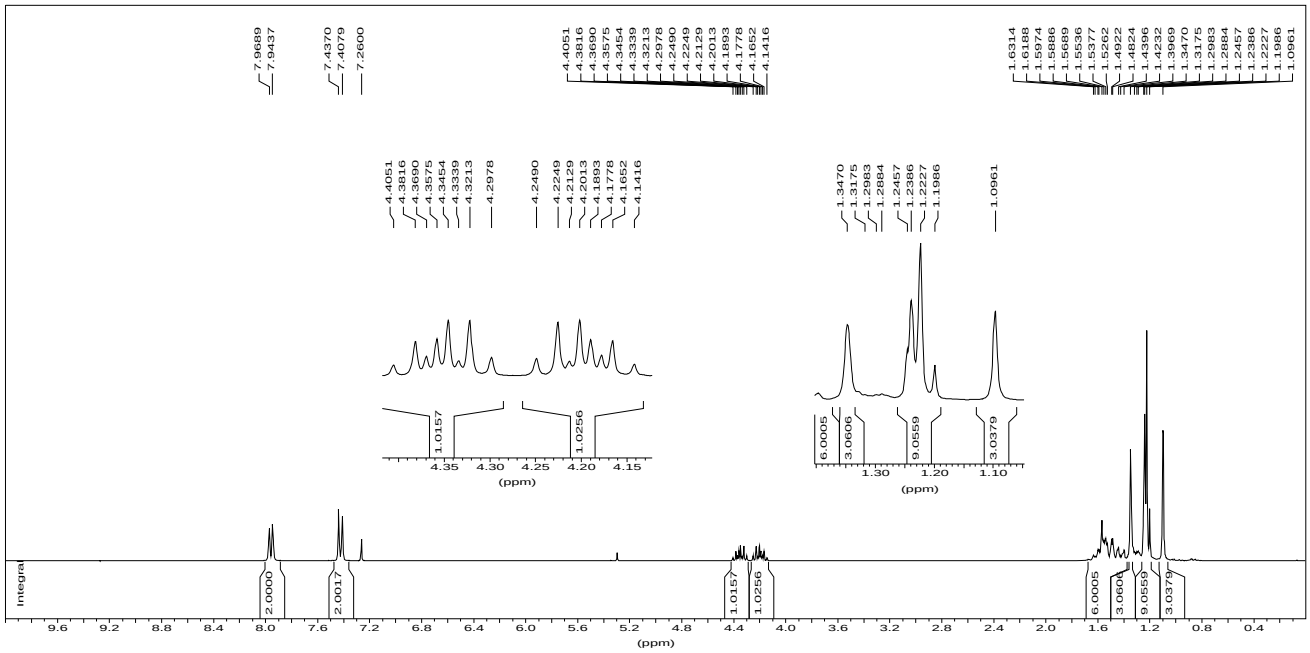


F19(no decoupled) se22lhj 1.2 lhj6133C F





AC300 oc17lhj2 2.2 lhj6146B HNMR



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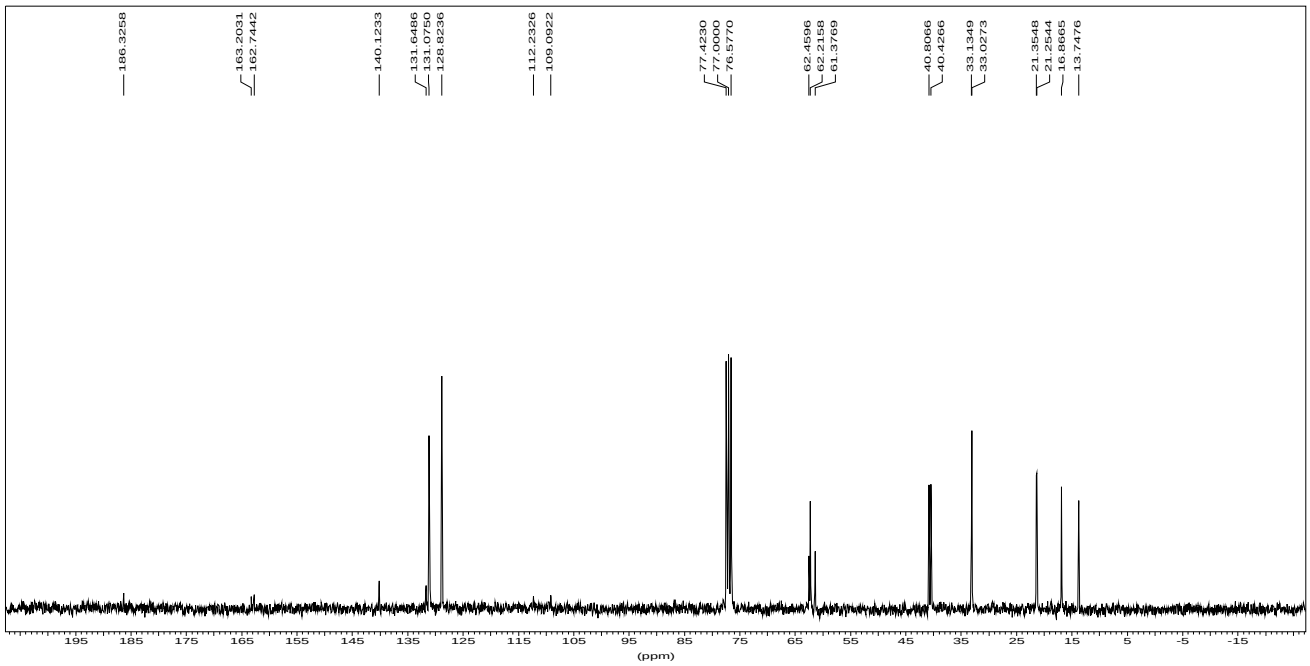
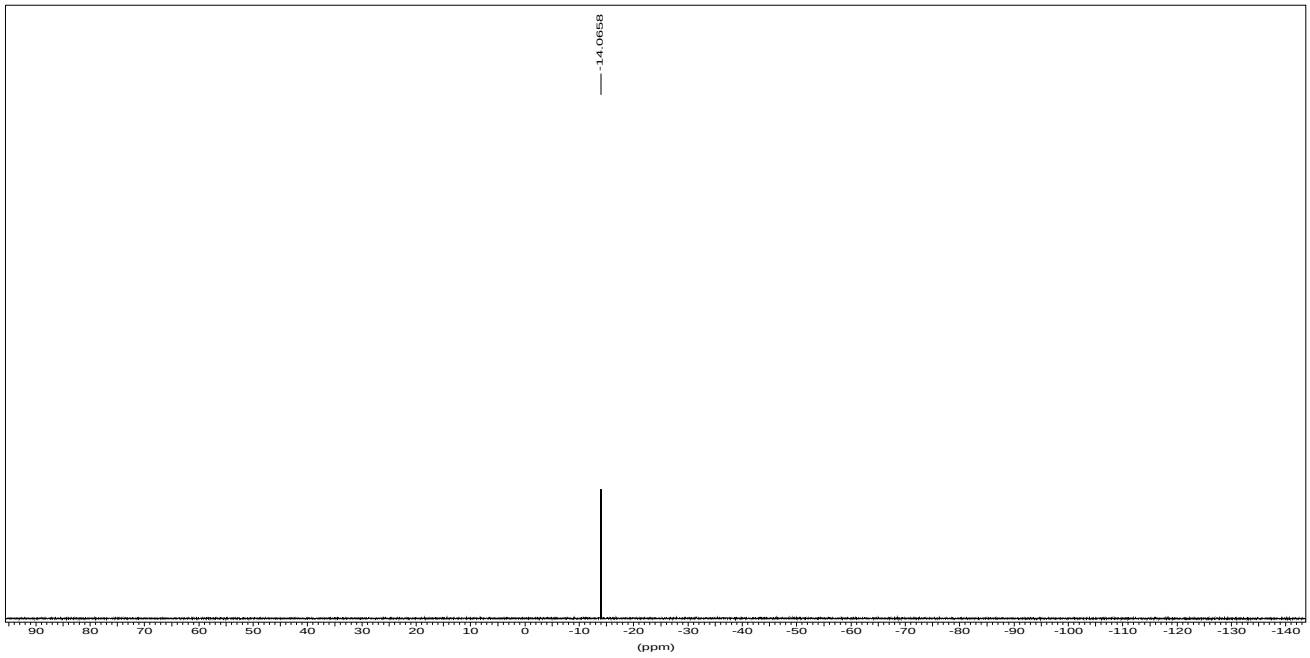
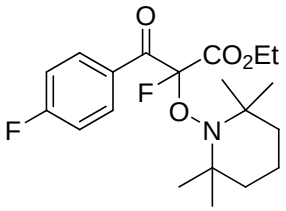
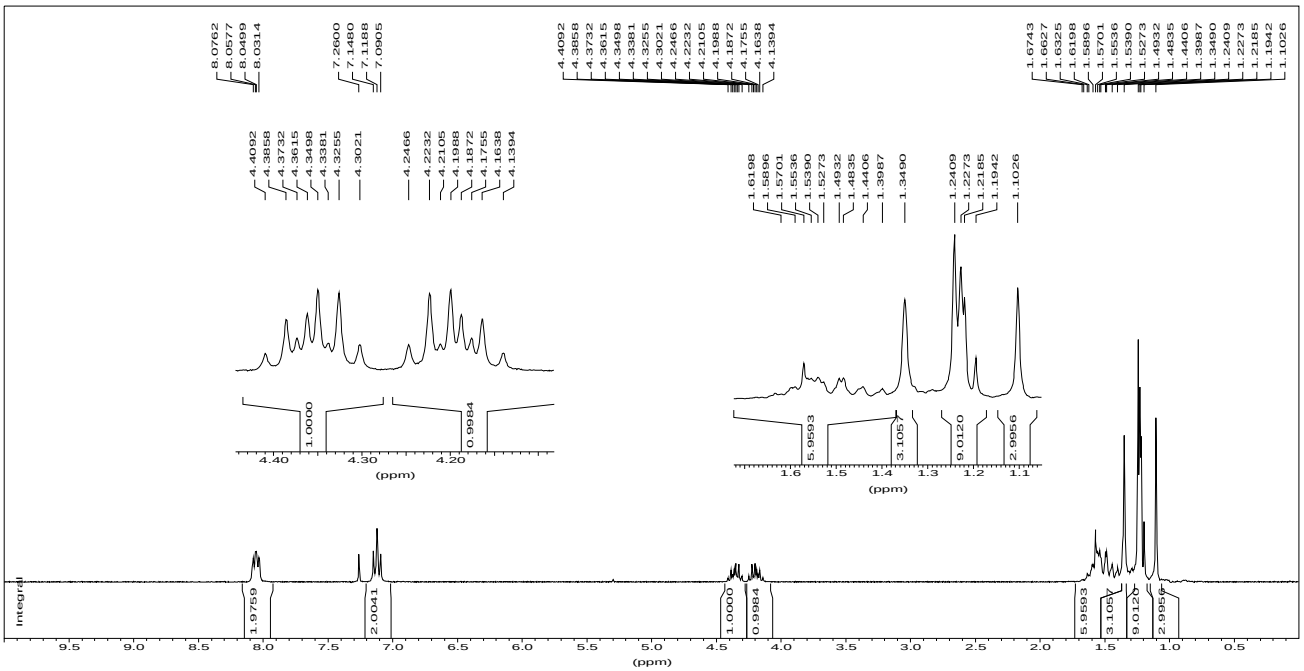


F19(no decoupled) AC300 oc17lhj 3.1 lhj6146B FNMR





DPX300 oc28lhj2 2.1 lhj6149B HNMR



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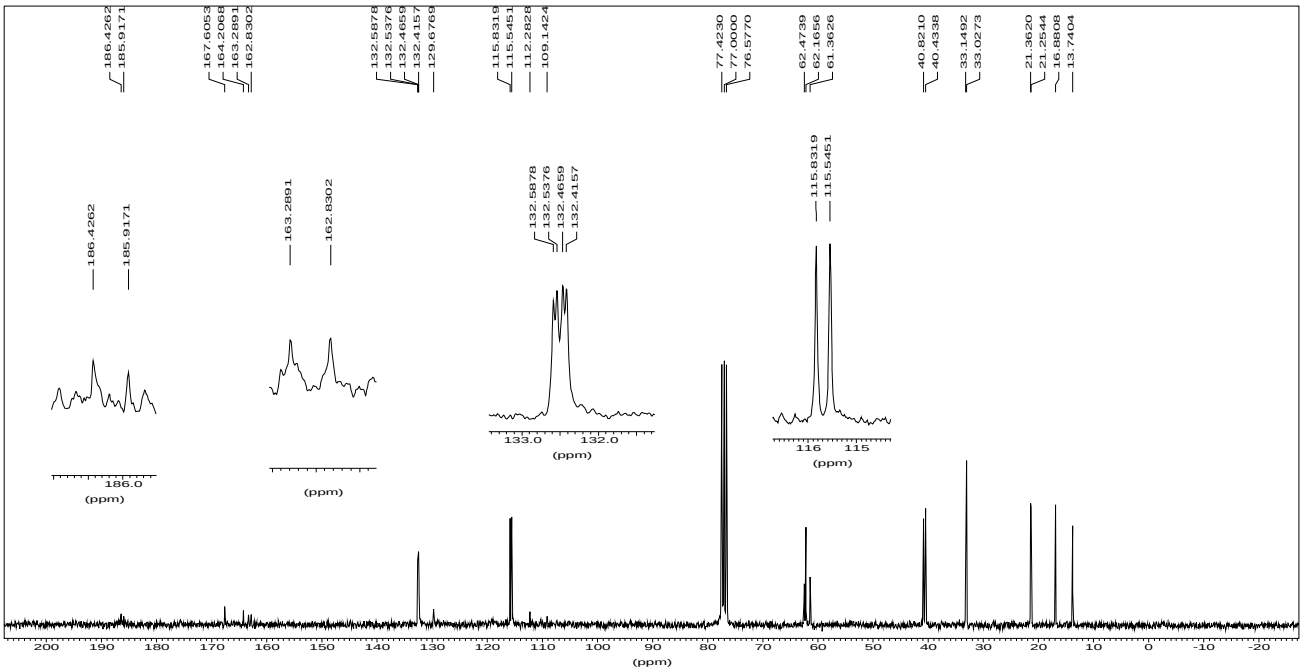
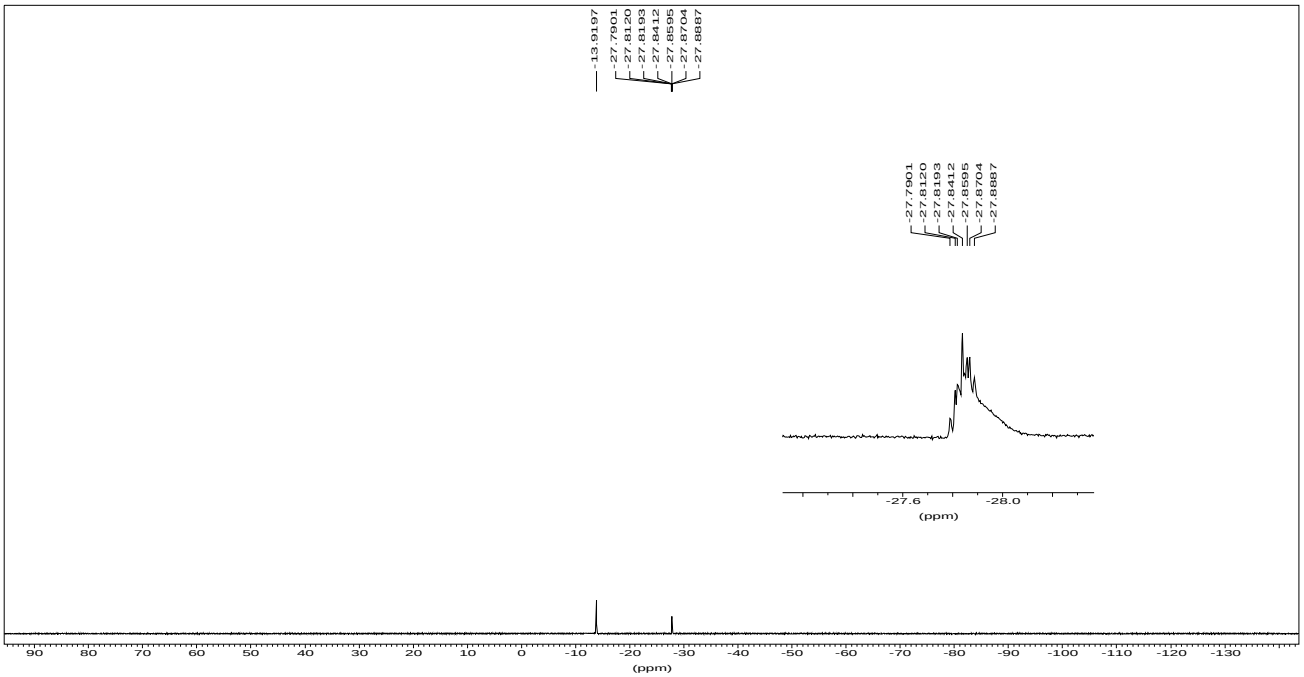
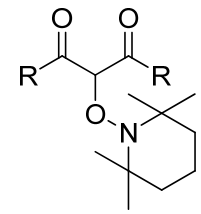


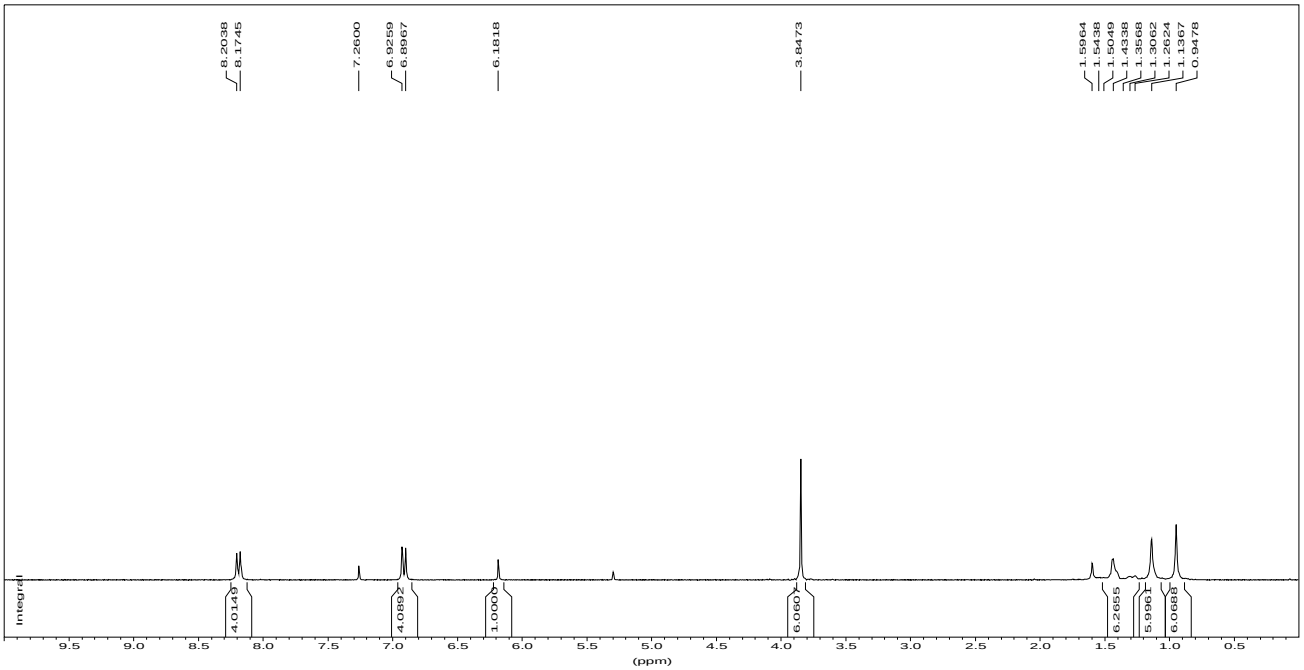
F19(no decoupled) oc28lhj 1.4 lhj6149B FNMR



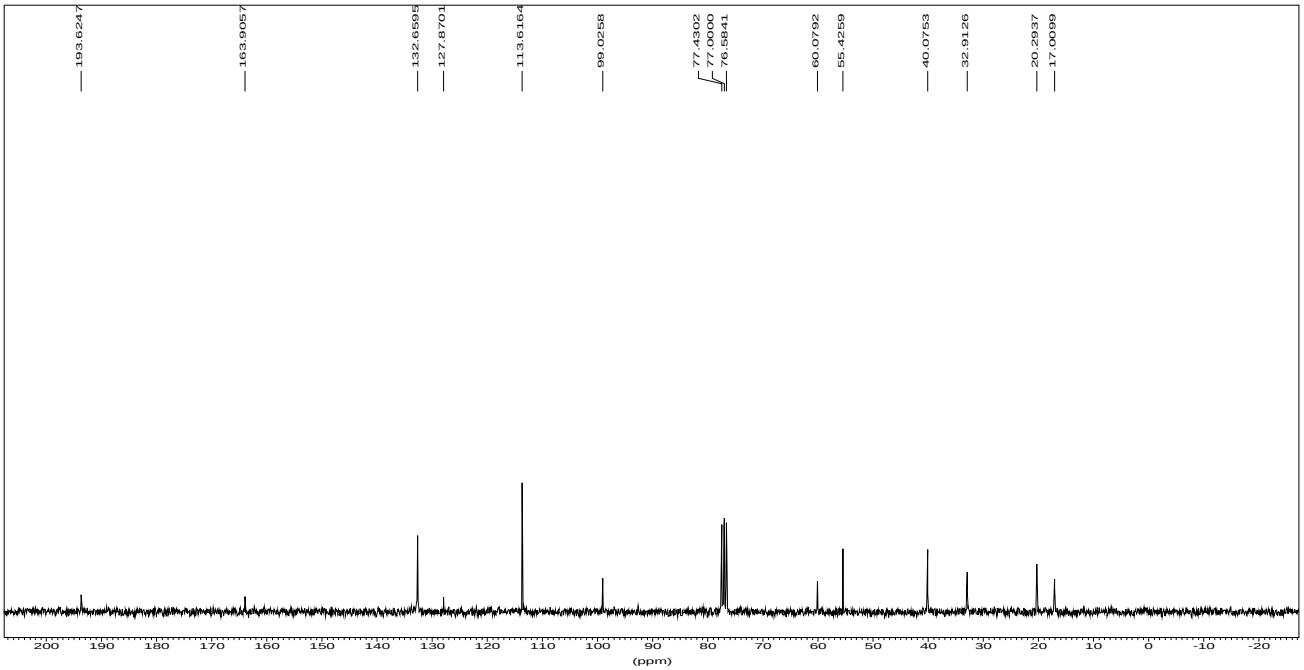


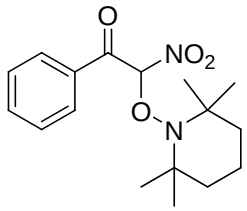
R = 4-MeOPh

DPX300 ag28lhj 3.1 lhj6126B HNMR

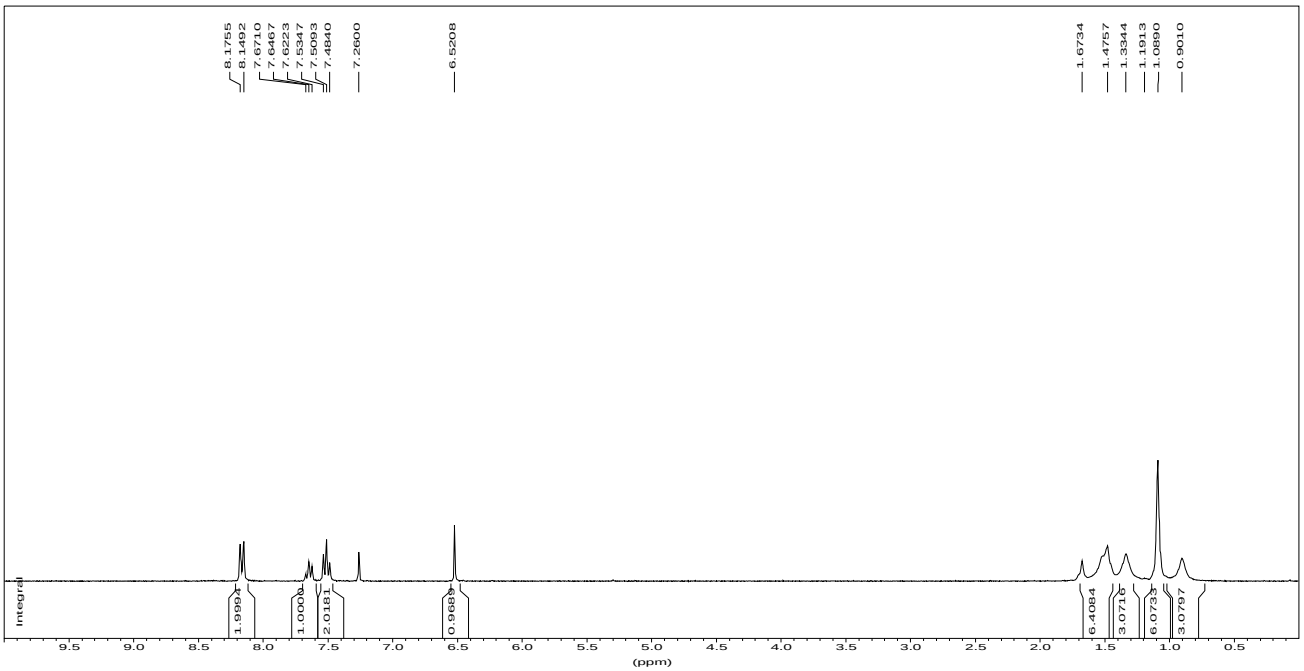


DPX300 ag28lhj 4.1 lhj6126B CNMR





DPX300 ag31lhj 1.3 lhj6127B HNMR



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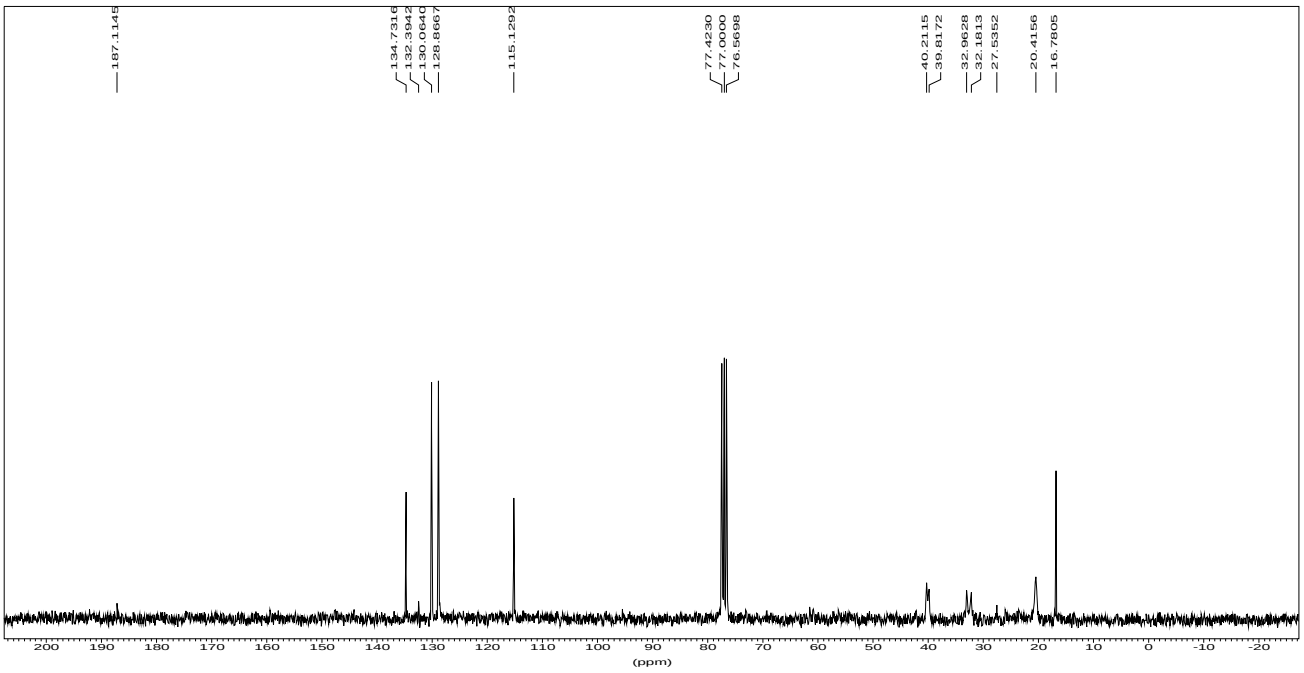


Computational Study

Computational Detail: DFT calculations were performed at M06-2X level of theory using Gaussian 09 program (Revision A.02).[1,2] The double-zeta basis set 6-31+G(d,p) was used for all atoms using the keyword: "6-31+g(d,p)"in the route section.[3] Geometry optimization was performed in the gas phase using "tight" convergence criteria without any constraint using the keyword "opt=tight" in the route section. The integration grid used was specified using "int=ultrafine" in the route section. The conformations were confirmed to be true minima using vibrational frequency analysis: no imaginary frequency.

Electron affinities (Ea) were calculated using the following formula:

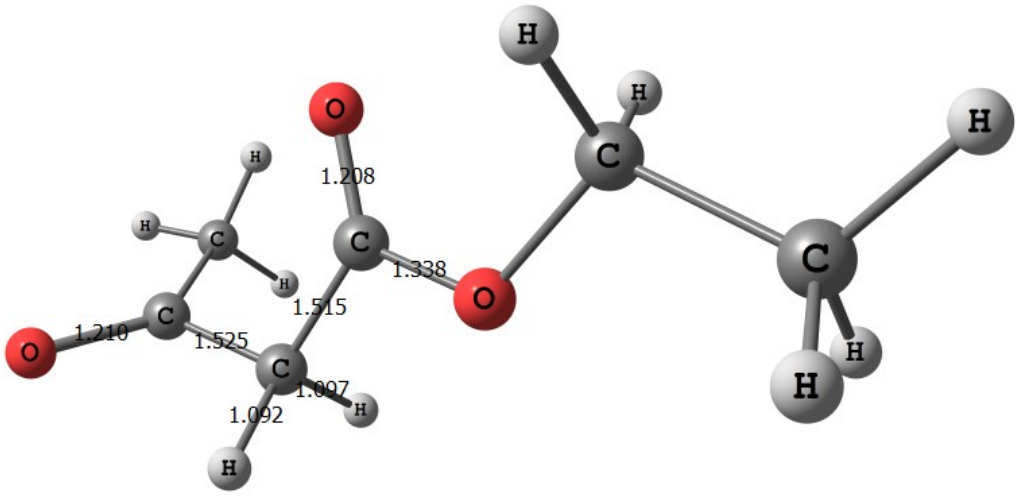
$$E_a = [E_{(neutral)} + ZPE_{(neutral)}] - [(E_{(anionic\ radical)} + ZPE_{(anionic\ radical)}]$$

Where ZPE = Zero-point Correction

Table 1: Electron Affinity and LUMO energy

	Electron Affinity (eV)	LUMO (eV)
Compound 1a	0.59	0.23
Compound 2a	-0.38	-0.93

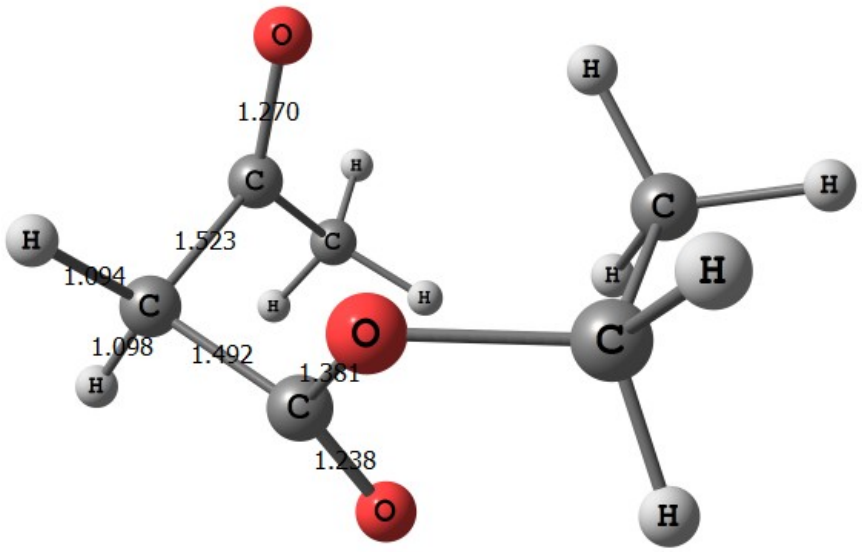
Compound 1a



Calculation Method = RM062X
Basis Set = 6-31+G(d,p)
Charge = 0
Spin = Singlet
E(RM062X) = -460.16695536 a.u.
RMS Gradient Norm = 0.00000024 a.u.
Imaginary Freq = 0
Dipole Moment = 3.9267 Debye
Point Group = C1
Zero-point correction= 0.157457 (Hartree/Particle)

	X	Y	Z
C	2.25979500	-0.33081700	0.01740700
O	2.89448100	-1.02703600	-0.74261500
C	0.87066300	-0.77057900	0.46800700
H	0.68548400	-1.78763900	0.11521500
H	0.80782000	-0.77596900	1.56294200
C	-0.22760400	0.13721400	-0.04586300
O	-0.06124300	1.18876800	-0.61730400
O	-1.43322400	-0.38011200	0.21825000
C	-2.56128400	0.39647100	-0.22818500
C	-3.81005600	-0.36489900	0.15685100
H	-2.47839800	0.53776300	-1.30942500
H	-2.51383600	1.38159100	0.24475200
H	-4.69472300	0.19073200	-0.16433200
H	-3.82545100	-1.34773900	-0.31997100
H	-3.86087200	-0.50239700	1.23956300
C	2.79288200	0.96577100	0.57137200
H	3.81665800	1.11522900	0.22928600
H	2.15522200	1.78701200	0.23192900
H	2.76160400	0.94948900	1.66585400

Compound 1b

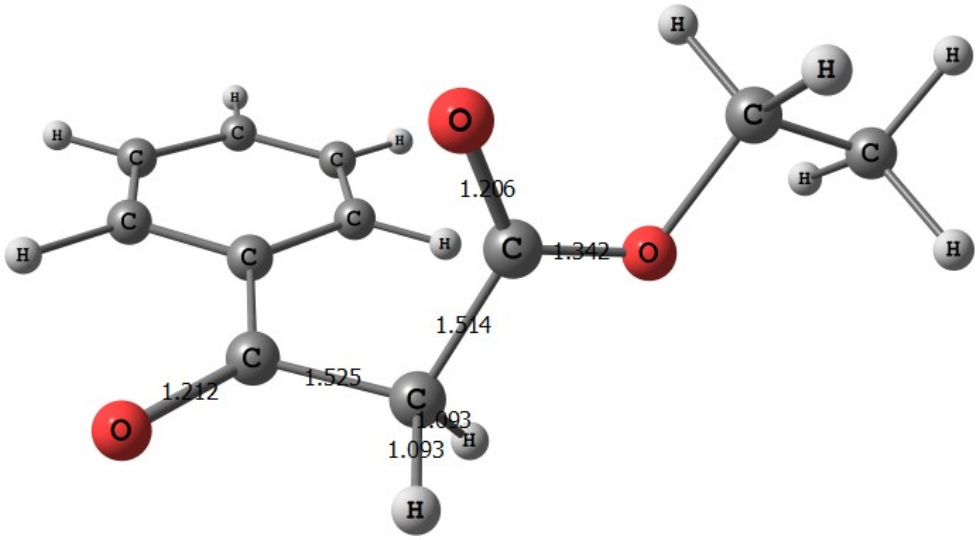


Calculation Method = UM062X
Basis Set = 6-31+G(d,p)
Charge = -1
Spin = Doublet
E(UM062X) = -460.14899375 a.u.
RMS Gradient Norm = 0.00000116 a.u.
Imaginary Freq = 0
Dipole Moment = 2.7547 Debye
Point Group = C1

Zero-point correction= 0.153372 (Hartree/Particle)

	X	Y	Z
C	1.57014600	0.30262100	-0.30570800
O	1.35448900	1.35318100	-0.98626400
C	1.08690800	-1.06124500	-0.78076900
H	1.00393500	-1.06546400	-1.87154800
H	1.70566000	-1.88796200	-0.40815000
C	-0.24830200	-1.09758400	-0.11612400
O	-0.47788100	-1.46459100	1.04380600
O	-1.21441500	-0.46782200	-0.87656500
C	-2.20350500	0.22834700	-0.13350900
C	-1.60199800	1.43457300	0.57647800
H	-2.67723300	-0.45159600	0.58499800
H	-2.94646800	0.53844100	-0.87600000
H	-2.39454700	2.07618600	0.98117900
H	-0.96577300	1.09985700	1.40102200
H	-0.97497900	1.99904500	-0.12076300
C	2.00017600	0.37995500	1.14197600
H	2.55826900	1.30928400	1.29219200
H	1.14400300	0.37063400	1.84515400
H	2.62904500	-0.47457500	1.43003400

Compound 2a

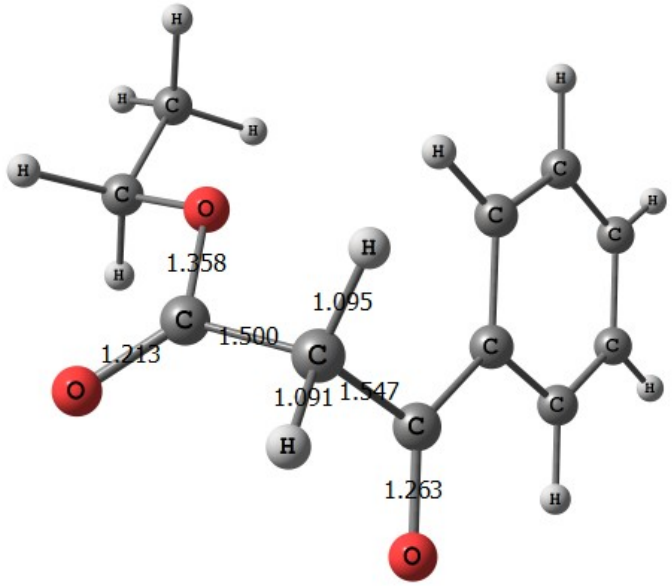


Calculation Method = RM062X
Basis Set = 6-31+G(d,p)
Charge = 0
Spin = Singlet
E(RM062X) = -651.83824794 a.u.
RMS Gradient Norm = 0.00000064 a.u.
Imaginary Freq = 0
Dipole Moment = 4.3809 Debye
Point Group = C1

Zero-point correction= 0.211879 (Hartree/Particle)

	X	Y	Z
C	3.58197400	-0.80795200	0.45877700
C	2.85306900	0.36448600	0.29853400
C	1.54757000	0.31749300	-0.20153500
C	0.98048800	-0.91436600	-0.54352400
C	1.71418200	-2.08830900	-0.38667100
C	3.01291500	-2.03575300	0.11556400
H	4.59291000	-0.76845700	0.85142700
H	3.27270200	1.33125100	0.55712400
H	-0.03034000	-0.97054500	-0.93902200
H	1.27215900	-3.04206100	-0.65605800
H	3.58250700	-2.95150500	0.24006200
C	0.80664800	1.60875200	-0.36153600
O	1.35312200	2.67663300	-0.18802500
C	-0.65991700	1.55703300	-0.77743800
H	-1.01615700	2.58911200	-0.82369700
H	-0.77262400	1.10209900	-1.76519300
C	-1.49747800	0.80855600	0.23694900
O	-1.34872000	0.88777600	1.43128700
O	-2.43716800	0.05035600	-0.34927200
C	-3.29426900	-0.67954500	0.54859200
C	-4.27763800	-1.45549100	-0.29908900
H	-3.79113600	0.03408200	1.21185600
H	-2.67074900	-1.33308400	1.16603400
H	-4.95009100	-2.02717700	0.34547900
H	-4.87719100	-0.77891600	-0.91267600
H	-3.75512600	-2.15234900	-0.95900000

Compound 2b



Calculation Method = UM062X
Basis Set = 6-31+G(d,p)

Charge = -1
Spin = Doublet
E(UM062X) = -651.85649174 a.u.
RMS Gradient Norm = 0.00000200 a.u.
Imaginary Freq = 0
Dipole Moment = 7.3821 Debye
Point Group = C1
Zero-point correction= 0.208410 (Hartree/Particle)

	X	Y	Z
C	3.44004100	0.19975700	-0.73063900
C	2.44604000	-0.75765000	-0.68085800
C	1.26783200	-0.57746300	0.11593200
C	1.17851100	0.65434900	0.84099100
C	2.18926300	1.60002300	0.78135000
C	3.34023400	1.40096400	-0.00074300
H	4.31894000	0.01951200	-1.34825500
H	2.52761800	-1.68327300	-1.24195300
H	0.29466000	0.87221600	1.43178900
H	2.07926200	2.52234200	1.35023400
H	4.12337500	2.15189200	-0.04559100
C	0.29636600	-1.63128300	0.14579500
O	0.40108400	-2.70059400	-0.51848000
C	-0.95658300	-1.48670500	1.04132200
H	-1.29660400	-2.49608400	1.27794100
H	-0.74459400	-0.92446400	1.95717300
C	-2.04402800	-0.79615700	0.27313200
O	-2.93444800	-1.32191100	-0.36050700
O	-1.90152500	0.55331400	0.31676700
C	-2.72602900	1.30155300	-0.57016700
C	-2.26362500	2.74264400	-0.48750900
H	-3.77679200	1.18757000	-0.27863000
H	-2.61800800	0.89735500	-1.58184100
H	-2.84509900	3.36903100	-1.17118000
H	-2.38647000	3.12716100	0.52901400
H	-1.20530600	2.81008200	-0.75257900

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3. R. Ditchfie, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.* 1971, **54**, 724-728 (b) W. J. Hehre, R. Ditchfie, and J. A. Pople, *J. Chem. Phys.* 1972, **56**, 2257-2261 (c) P. Harihara, and J. A. Pople, *Theor. Chim. Acta.* 1973, **28**, 213-222.