Visible Light-Promoted Metal-Free sp^3-C–H Fluorination

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Supplementary Information

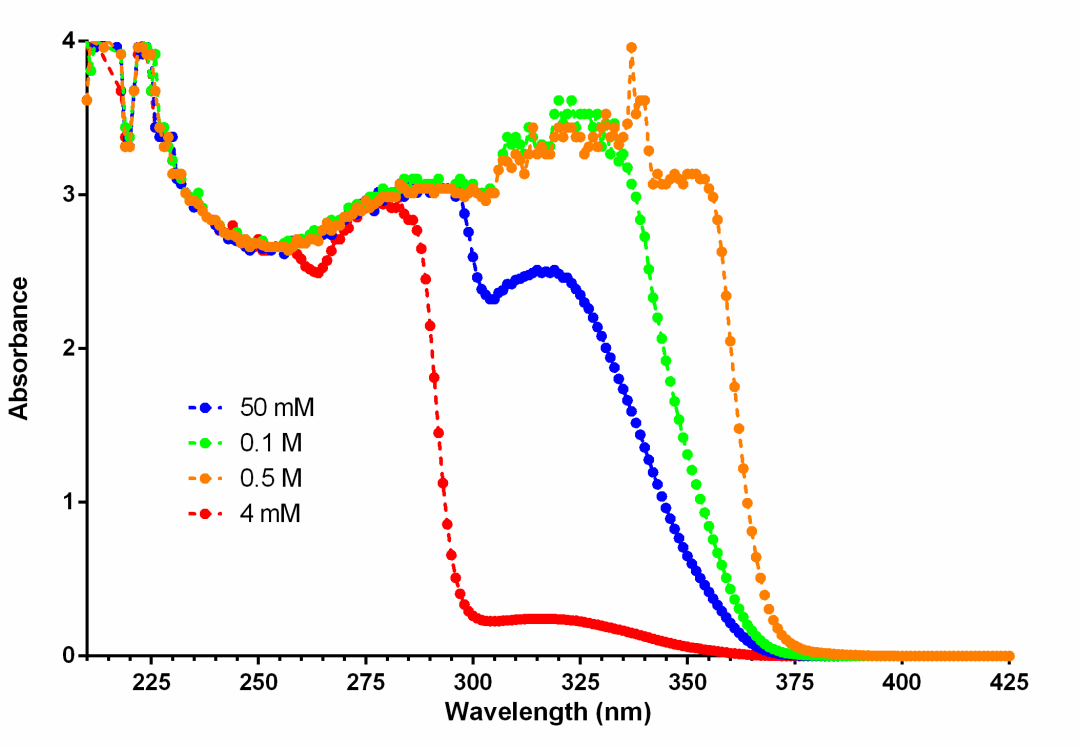


Figure S1. The UV-vis spectra of acetophenone in acetonitrile at different concentrations.

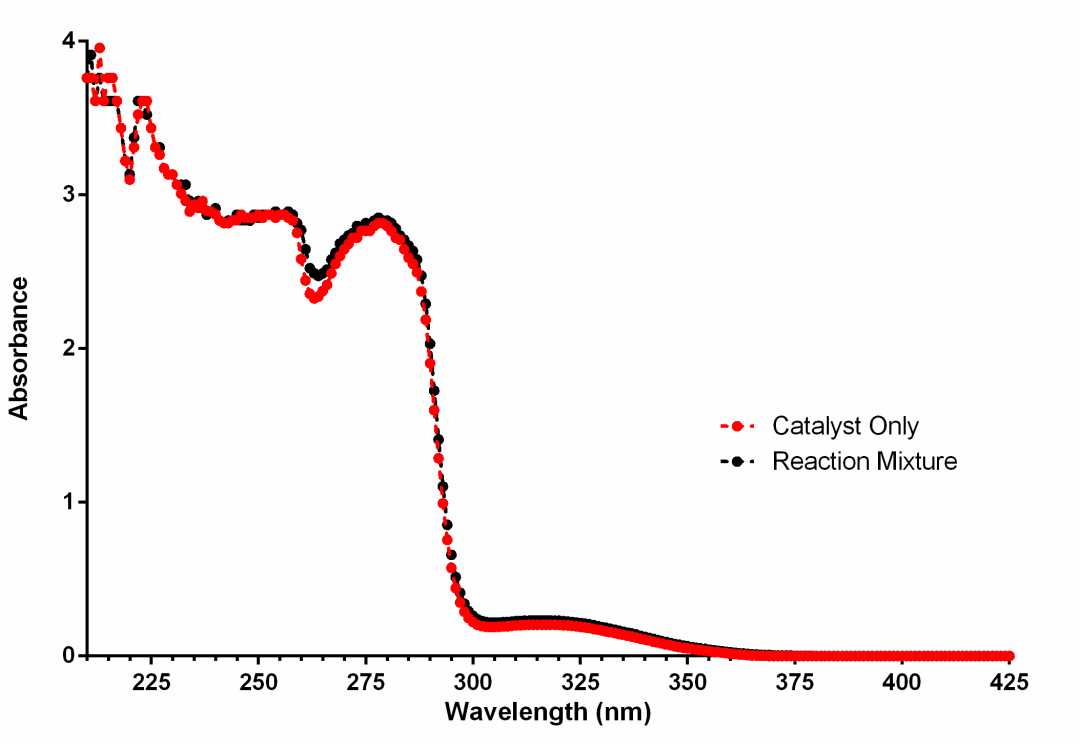


Figure S2. The UV-vis spectra of 5 mol % acetophenone catalyst alone in acetonitrile (4 mM) (red), and of the reaction mixture (5 mol % acetophenone, 1.0 equiv ethylbenzene, 2.0 equiv Selectfluor) in acetonitrile (blue).

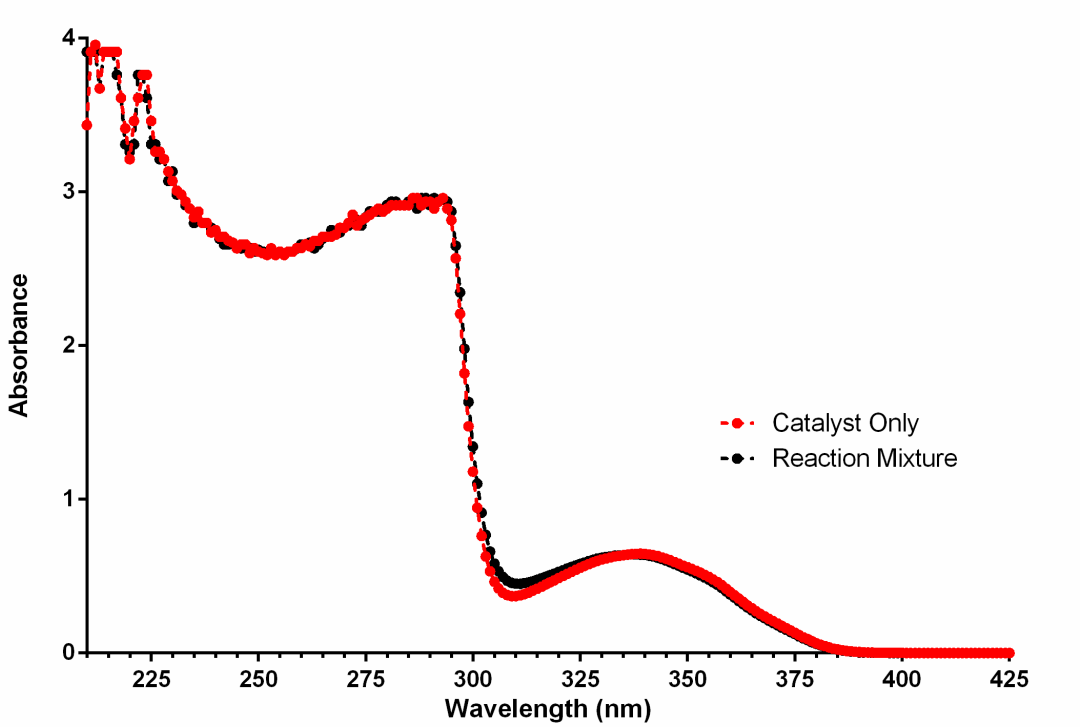


Figure S2. The UV-vis spectra of 5 mol % benzophenone catalyst alone in acetonitrile (4 mM) (red), and of the reaction mixture (5 mol % benzophenone, 1.0 equiv ethylbenzene, 2.0 equiv Selectfluor) in acetonitrile (blue).

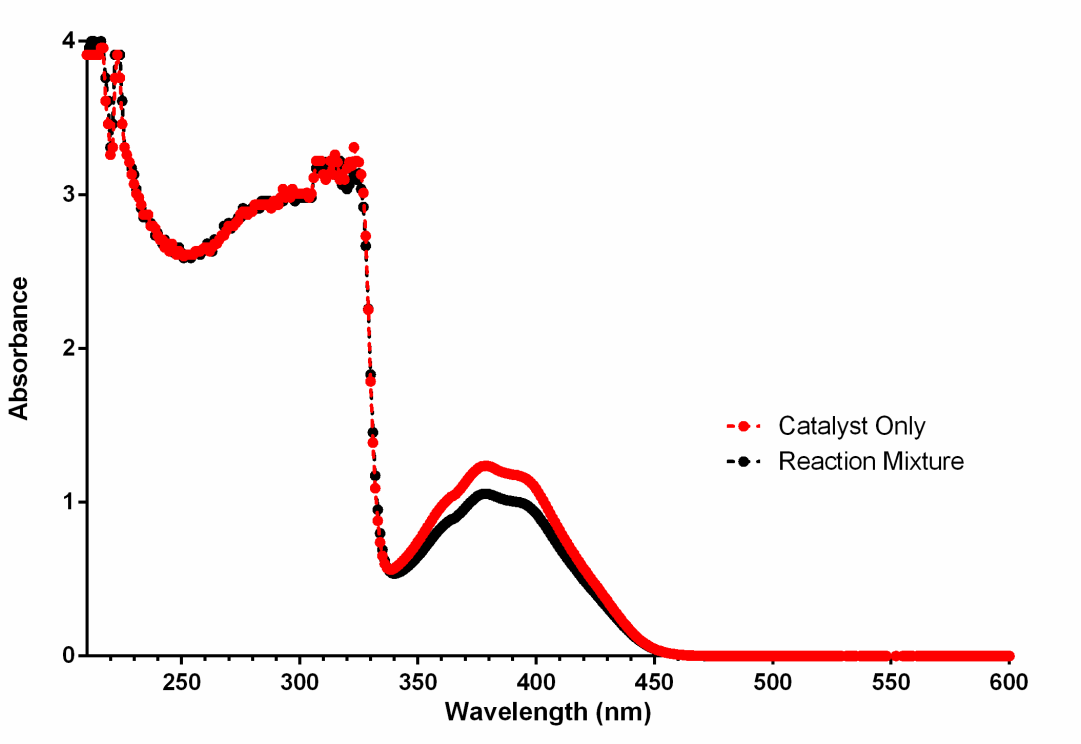


Figure S3. The UV-vis spectra of 5 mol % 9-fluorenone catalyst alone in acetonitrile (4 mM) (red), and of the reaction mixture (5 mol % 9-fluorenone, 1.0 equiv ethylbenzene, 2.0 equiv Selectfluor) in acetonitrile (blue).

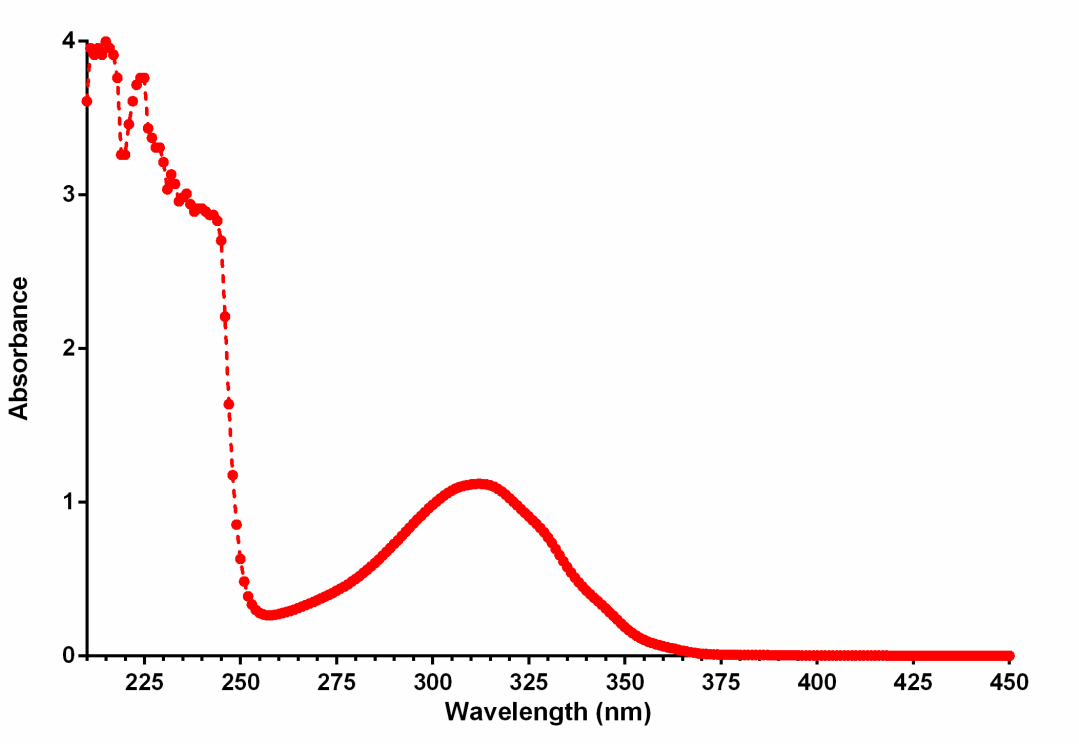


Figure S5. The UV-vis spectrum of cyclopentenone (**27**) in 2-propanol (50 mM).

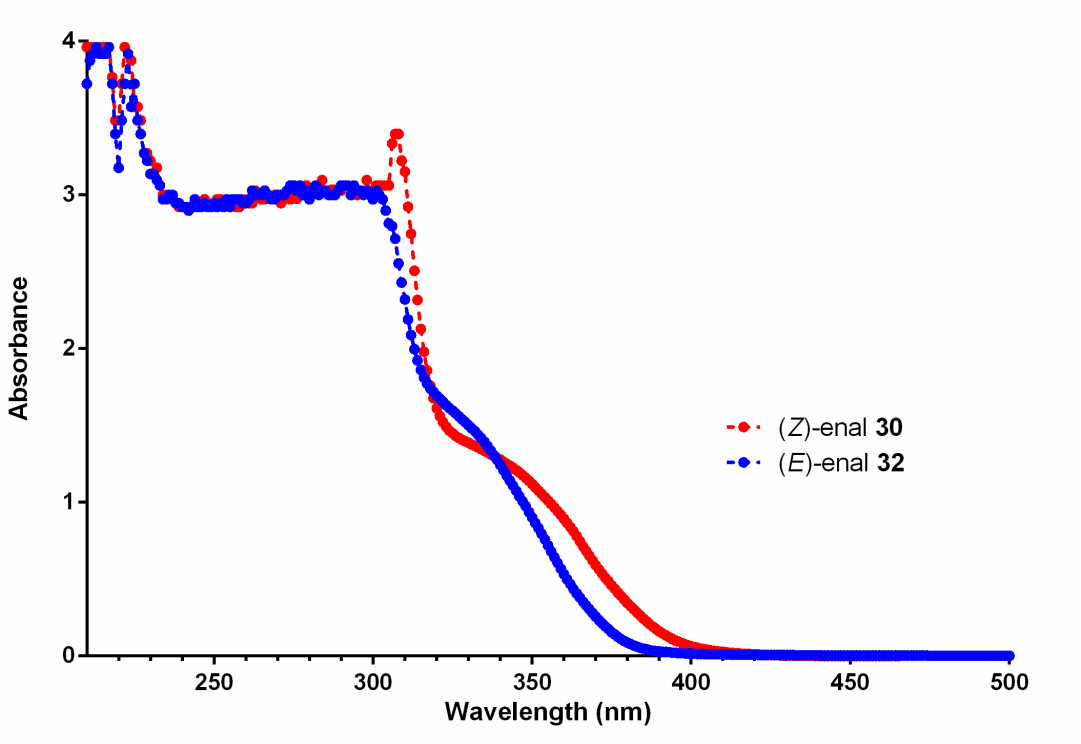


Figure S6. The UV-vis spectra of (*Z*)-enal **30** in methylene chloride (50 mM) (red), and (*E*)-enal **32** in methylene chloride (50 mM) (blue).

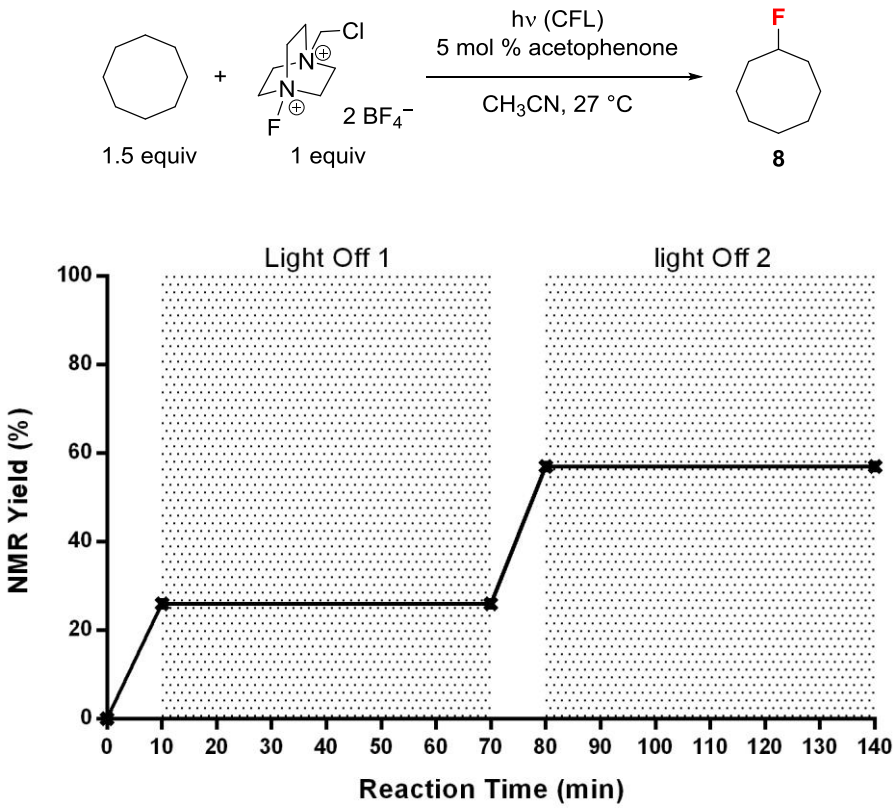


Figure S7. Acetophenone-catalyzed fluorination of cyclooctane under CFL-irradiation is a light-dependent reaction.

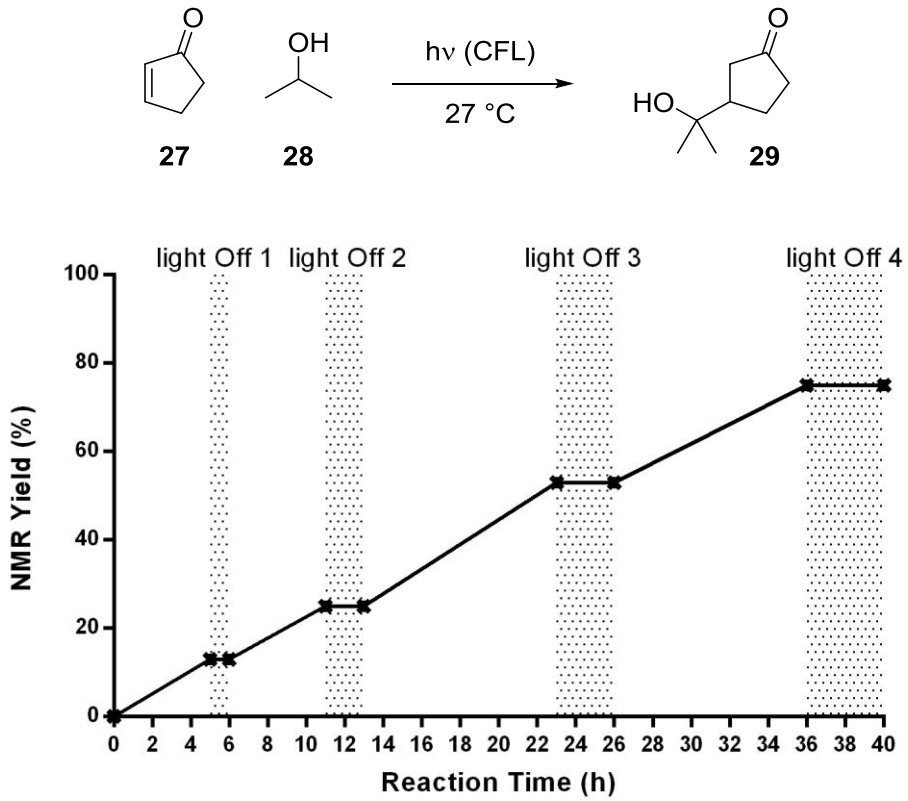


Figure S8. C–H abstraction/conjugate addition of cyclopentenone (**27**) under CFL-irradiation is a light-dependent reaction.

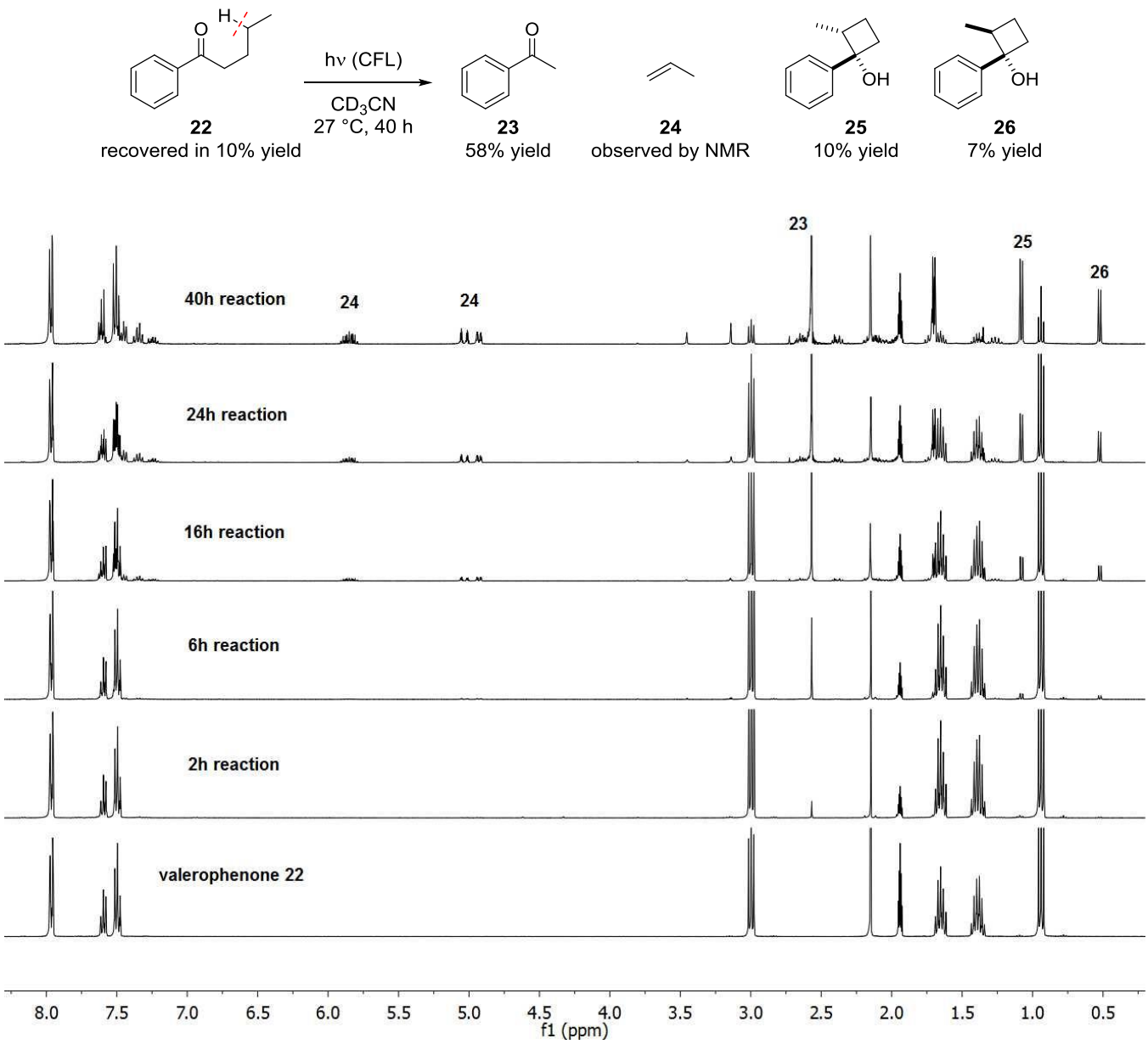


Figure S9. Time-course NMR spectra of the Norrish type II cleavage and the Norrish–Yang cyclization of valerophenone (**22**) under CFL-irradiation.

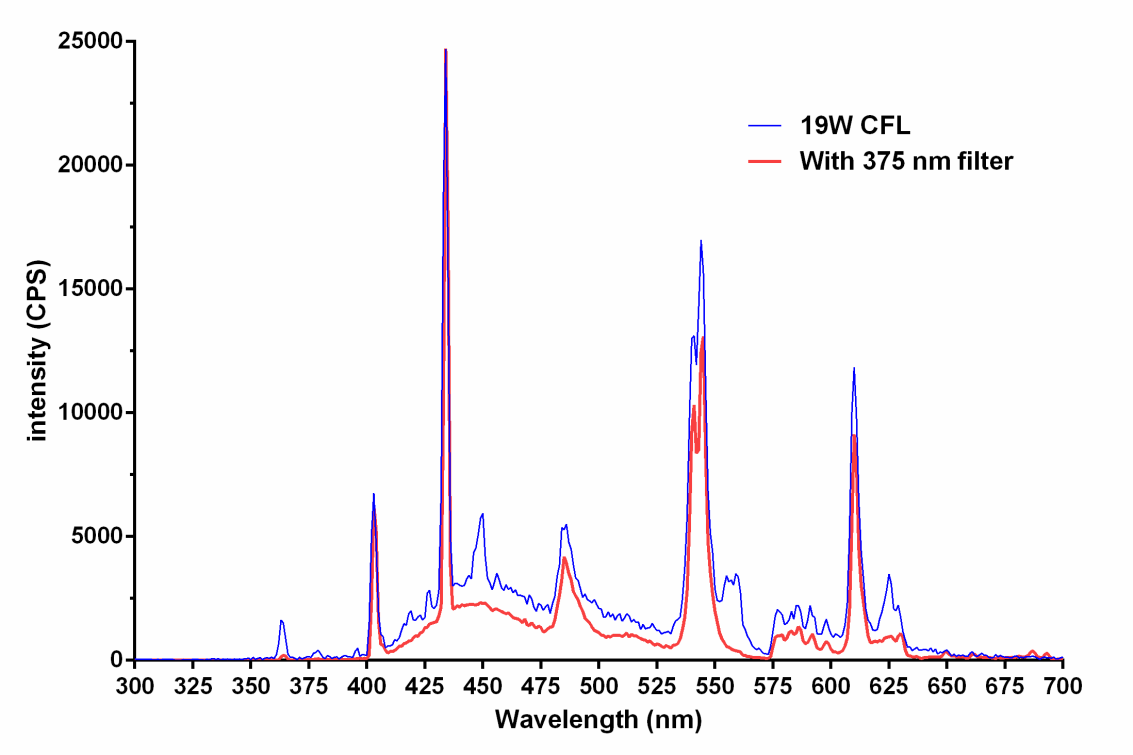


Figure S10. The emission spectra of the 19 W CFL used.

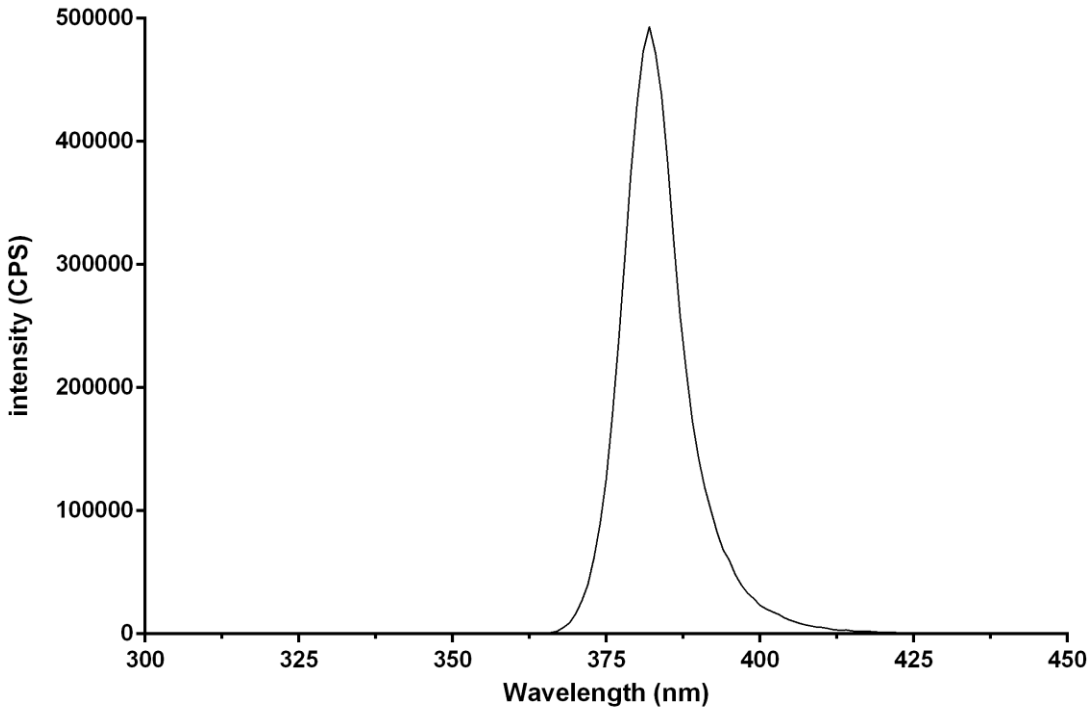


Figure S10. The emission spectra of the 9 W violet LED bulb used.

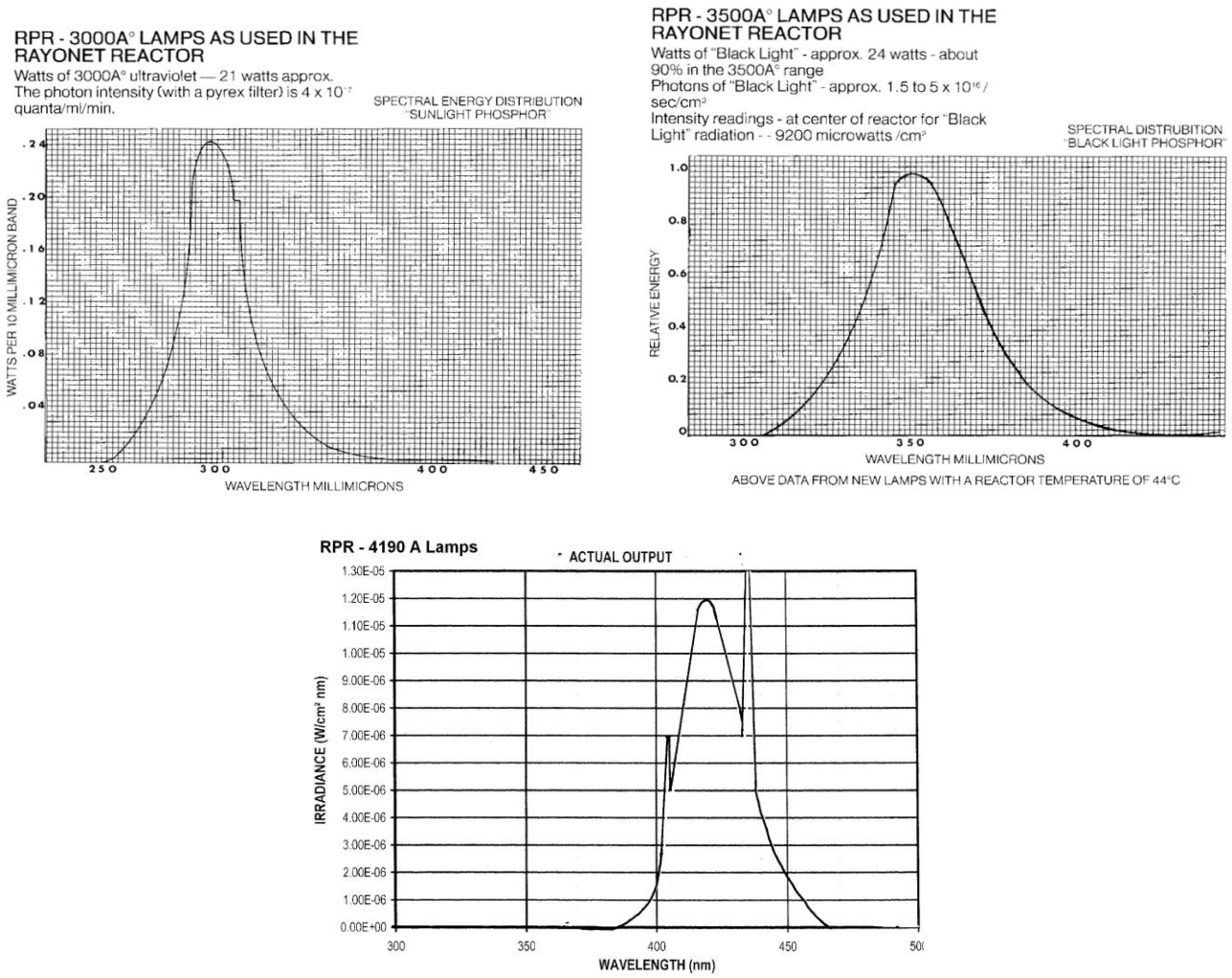
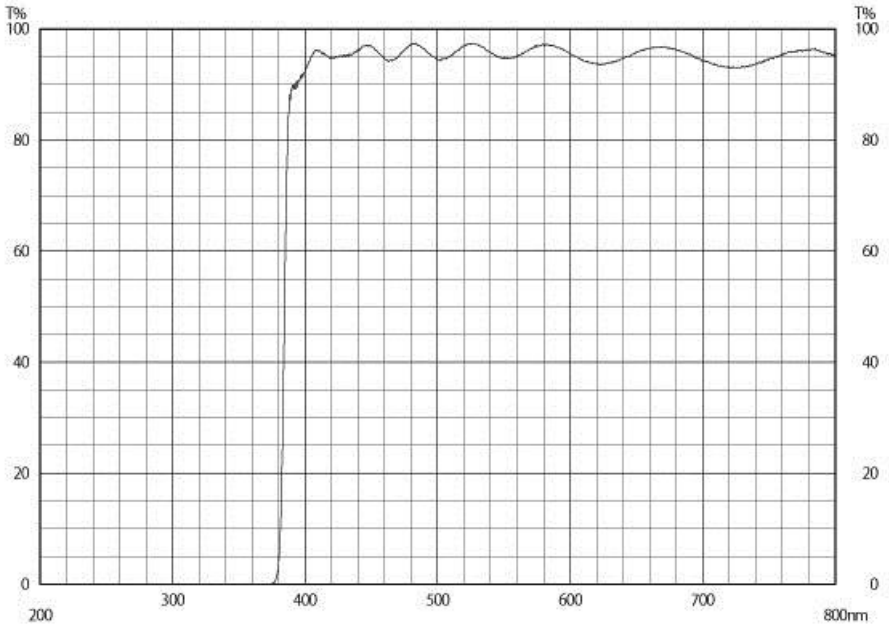


Figure S12. The emission spectra of the RPR lamps used in Table 1 (provided by Southern New England Ultraviolet Company).

XUL0385 Longpass Filter



XUL0400 Longpass Filter

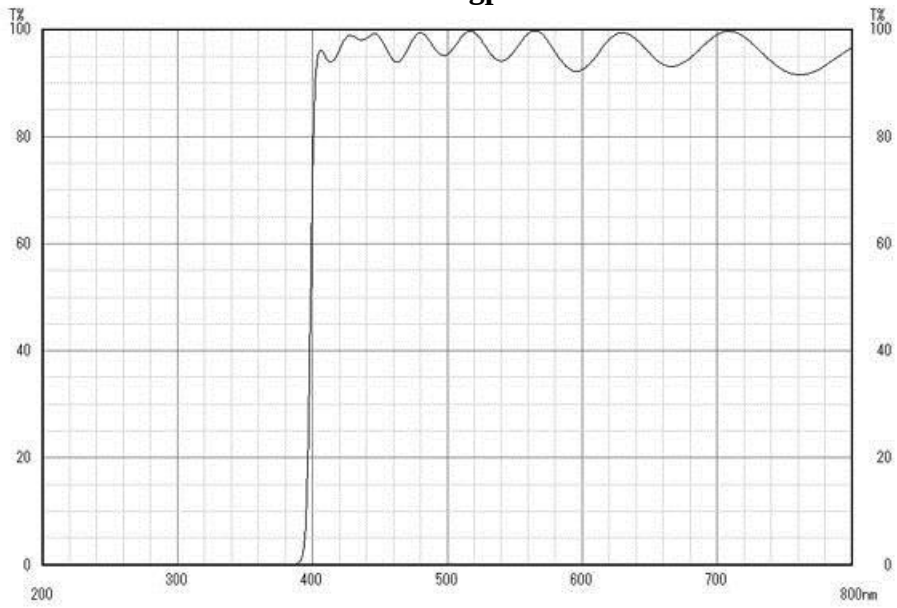


Figure S13. The transmission spectra of the Asahi longpass filters used in Table 1 (provided by Asahi Spectra).

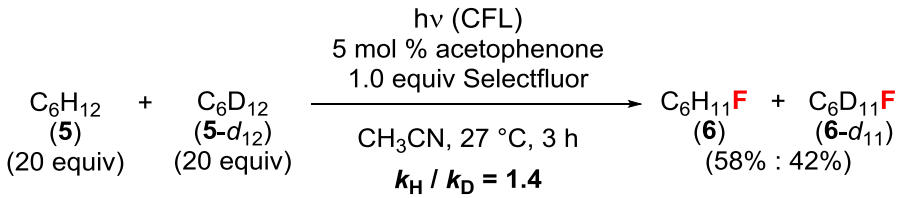
Materials and Methods

General Information. All reactions were performed in glassware under argon. Organic solutions were concentrated by rotary evaporator at ca. 30 mmHg unless otherwise noted. Flash column chromatography was performed as described by Still[S1], employing EMD silica gel 60 (230–400 mesh ASTM). TLC analyses were performed on EMD 250 μm Silica Gel 60 F_{254} plates and visualized by quenching of UV fluorescence (λ_{max} 254 nm), or by staining ceric ammonium molybdate. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Inova-600, Inova-500, or Inova-400. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to the ^{1}H and ^{13}C signals in the solvent ($CDCl_3$: 7.26, 77.00 ppm; C_6D_6: δ 7.16, 128.06 ppm; CD_3CN: δ 1.94, 1.32 ppm) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet. Crude ^{1}H and ^{19}F NMR spectra were recorded on an Inova-400 in CD_3CN using fluorobenzene (^{19}F NMR δ –114.930) as an external standard. Mass spectra were acquired on an Agilent 6120 Single Quadrupole LC/MS or Agilent 7820A GC/5975 MSD. UV-vis spectra was collected on Shimadzu UV-Visible Spectrophotometer (UV-1601).

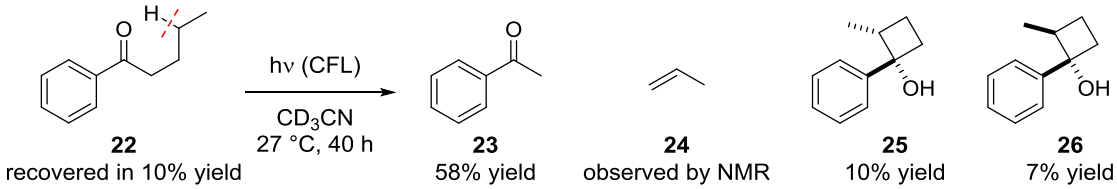
Materials. Acetophenone (analytical standard, ≥99.5% GC), and acetonitrile (anhydrous, 99.8%) was purchased from Sigma-Aldrich. Selectfluor (98+%) was purchased from Alfa Aesar. Fluorobenzene (≥99.5%) was purchased from Fluka. Acetonitrile-*d*3 (D, 99.8%) was purchased from Cambridge Isotope Laboratories, Inc. A 19 W EcoSmart Daylight CFL Bulb was used for the photoreaction. RPR-3000Å, RPR-3500Å, RPR-4190Å, Rayonet RMR-200 chamber reactor, and RMA-500 Merry-Go-Round were purchased from Southern New England Ultraviolet Company. 9-W (3 × 3W) 380–385nm violet LED flashlight was purchased from LED wholesalers. The 385 nm, and 400 nm longpass filters were purchased from Asahi Spectra USA Inc.

General procedure for the acetophenone-catalyzed C(sp^3)–H fluorination. To a 4 mL clear vial charged with Selectfluor (70.9 mg, 0.2 mmol, 1.0 equiv) were added anhydrous acetonitrile (2.0 mL), acetophenone (1.2 mg, 0.01 mmol), and the reaction substrate (0.3 mmol, 1.5 equiv). The reaction mixture was degassed by *Freeze-Pump-Thaw* cycles for three times and irradiated with a 19 W CFL 2–5 cm away from the reaction at room temperature (27±2 °C). The crude yield was determined by NMR using fluorobenzene as an external standard. The reaction mixture was then poured into diethyl ether (20 mL), filtrated, concentrated and purified by silica gel flash column chromatography using diethyl ether/pentane as the eluent.

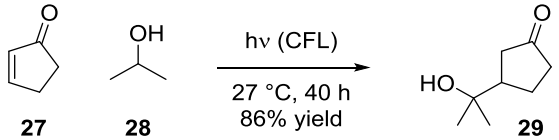
[S1] W. C. Still, M. Kahn and A. Mitra, *J. Org. Chem.* **1978**, *43*, 2923.



The intermolecular kinetic isotope effect study. To a 4 mL clear vial charged with Selectfluor (35.4 mg, 0.1 mmol, 1.0 equiv) were added anhydrous acetonitrile (1.0 mL), acetopheneone (0.6 mg, 0.005 mmol) cyclohexane (168.4 mg, 20.0 mmol, 20.0 equiv), and cyclohexane-d_{12} (192.5 mg, 1.0 mmol, 20.0 equiv). The reaction mixture was degassed by *Freeze-Pump-Thaw* cycles for three times and irradiated with a 19 W CFL 2–5 cm away from the reaction at room temperature for 3 h. The ratio of **6**:**6**-d_{11} was determined by ^{19}F NMR on a Varian Inova-400 NMR instrument to be 58:42.



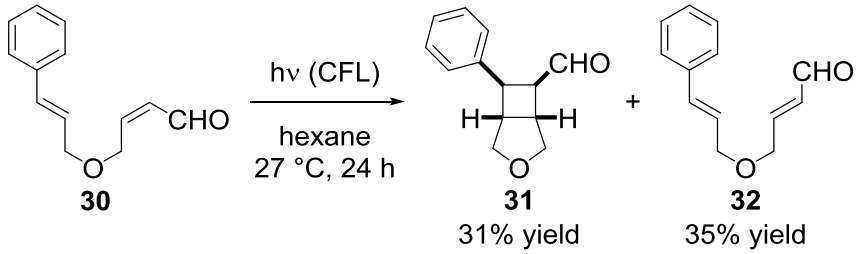
Norrish type II cleavage and Norrish–Yang cyclization reaction of valerophenone (22) under CFL irradiation. To a 4 mL clear vial charged with valerophenone (**22**) (8.1 mg, 0.05 mmol) was added acetonitrile-*d*3 (0.5 mL, redistilled from calcium hydride and degassed by *freeze-pump-thaw* cycles for three times) in glovebox. The reaction solution was transfer to a NMR tube (Wilmad-Lab Glass, 527PP, 5mm OD). The NMR tube was taken out from the glovebox, irradiated with a 19 W CFL at room temperature, and monitored by a Varian Inova-400 NMR instrument. After 40 h, the solution was concentrated and the residue was purified by silica gel chromatography (3% diethyl ether/pentane) to recover valerophenone (**22**) (0.8 mg, 10% yield) and give acetophenone (**23**) (3.5 mg, 58% yield), *trans*-2-methyl-1-phenylcyclobutanol (**25**) (0.8 mg, 10% yield), and *cis*-2-methyl-1-phenylcyclobutanol (**26**) (0.6 mg, 7% yield).[S2] **23**: ^{1}H NMR (400 MHz, CD_3CN) δ 7.96–7.98 (m, 2H), 7.59–7.63 (m, 1H), 7.48–7.53 (m, 2H), 2.57 (s, 3H); **25**: ^{1}H NMR (400 MHz, CD_3CN) δ 7.43–7.45 (m, 2H), 7.32–7.36 (m, 2H), 7.20–7.25 (m, 1H), 3.14 (s, 1H), 2.60–2.69 (m, 1H), 2.35–2.42 (m, 1H), 2.08–2.13 (m, 1H), 1.96–2.00 (m, 1H), 1.67–1.76 (m, 1H), 1.08 (d, *J* = 7.0 Hz, 3H). **26**: ^{1}H NMR (400 MHz, CD_3CN) δ 7.45 (d, *J* = 7.8 Hz, 2H), 7.37 (dd, *J* = 7.4, 7.9 Hz, 2H), 7.25 (d, *J* = 7.3 Hz,1H), 3.46 (s, 1H), 2.65 (ddd, *J* = 11.7, 9.0, 3.1 Hz, 1H), 2.53–2.59 (m, 1H), 2.12–2.22 (m, 1H), 2.01–2.09 (m, 1H), 1.22–1.31 (m, 1H), 0.52 (d, *J* = 7.0 Hz, 3H).



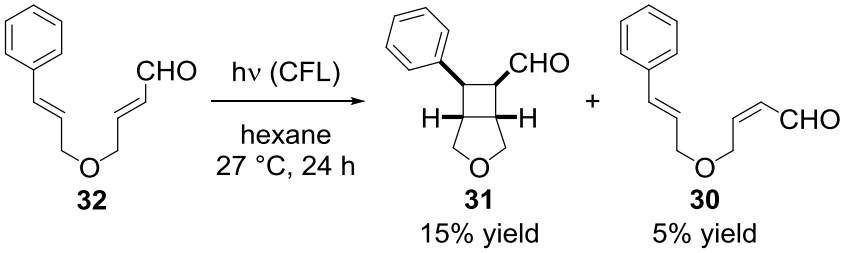
Photolytic C–H abstraction/conjugate addition of 2-cyclopentenone 27 under CFL-irradiaion. To a 4 mL clear vial charged with 2-cyclopentenone **27** (8.2 mg, 0.1 mmol) was added anhydrous 2-propanol (2.0 mL), and the reaction mixture was degassed three times by *Freeze-Pump-Thaw* cycles and stirred at room temperature under CFL for 40 h. After remove the 2-propanol, the residue was purified by flash column chromatography (30% ethyl acetate/hexanes) to give **29** (12.2 mg, 86% yield) as a colorless oil:

[S2] F. D. Lewis and T. A. Hilliard, *J. Am. Chem. Soc.* **1972**, *94*, 3852.

R_f = 0.3 (60% ethyl acetate/hexanes).[S3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (dd, *J* = 18.7, 8.6 Hz, 1H), 2.13–2.31 (m, 4H), 2.03–2.10 (m, 1H), 1.71–1.82 (m, 1H), 1.47 (brs, 1H), 1.25 (d, *J* = 11.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 219.3, 70.8, 47.7, 40.0, 39.0, 28.6, 27.8, 23.8; MS(ESI) calcd for $C_8H_{14}O_2Na$ $(M+Na)^+$ 165.1, found 165.1.



Photolytic [2+2] cycloaddition and *E*/*Z* isomerization of enal 30 under CFL-irradiation. To a 4 mL clear vial charged with (*Z*)-4-(cinnamyloxy)but-2-enal **30** (20.4 mg, 0.1 mmol) was added anhydrous DCM (2.0 mL), and the reaction mixture was degassed three times by *Freeze-Pump-Thaw* cycles and stirred at room temperature under CFL for 24h. After remove the DCM, the residue was purified by flash column chromatography (10% ethyl acetate/hexanes) to give **31** (6.2 mg, 31% yield) and **32** (7.1 mg, 35% yield).[S4] **30**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.09 (d, *J* = 6.7 Hz, 1H), 7.38–7.41 (m, 2H), 7.31–7.35 (m, 2H), 7.24–7.28 (m, 1H), 6.66 (t, *J* = 5.7 Hz, 2H), 6.29 (dt, *J* = 16.0, 6.2 Hz, 1H), 6.64–6.51 (m, 1H), 4.23 (dd, *J* = 6.1, 1.2 Hz, 4H), 6.62–6.67 (m, 2H), 6.62 (d, *J* = 5.5 Hz, 1H), 6.08 (ddt, *J* = 10.8, 6.7, 1.8 Hz, 1H), 4.55 (dd, *J* = 5.5, 2.0 Hz, 3H), 4.23 (dd, *J* = 6.1, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4, 147.6, 136.3, 133.3, 129.7, 128.6, 127.9, 126.5, 125.0, 71.6, 66.8; MS(ESI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$ 203.1, found 203.1. **31**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.26 (s, 1H), 7.31–7.33 (m, 2H), 7.21–7.24 (m, 3H), 4.03 (d, *J* = 9.8 Hz, 1H), 3.96 (d, *J* = 9.5 Hz, 1H), 3.69 (dd, *J* = 10.7, 5.0 Hz, 1H), 3.63 (dd, *J* = 9.4, 5.5 Hz, 1H), 3.58 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.55 (dd, *J* = 5.5, 5.6 Hz, 1H), 3.27 (dd, *J* = 10.7, 4.9 Hz, 1H), 3.13 (dd, *J* = 5.5, 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 139.2, 128.8, 127.7, 127.0, 73.7, 73.2, 52.6, 45.4, 43.7, 36.1; MS(ESI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$ 203.1, found 203.1. **32**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (d, *J* = 7.9 Hz, 1H), 7.37–7.40 (m, 2H), 7.30–7.33 (m, 2H), 7.22–7.26 (m, 1H), 6.84 (dt, *J* = 15.8, 4.1 Hz, 1H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.38 (ddt, *J* = 15.7, 7.9, 1.9 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.29 (dd, *J* = 4.1, 1.9 Hz, 2H), 4.21 (dd, *J* = 6.1, 1.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.2, 153.0, 136.3, 133.0, 131.7, 128.6, 127.8, 126.5, 125.0, 71.5, 68.4; MS(ESI) calcd for $C_{13}H_{15}O_2$ $(M+H)^+$ 203.1, found 203.1.

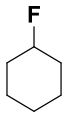


When (*E*)-4-(cinnamyloxy)but-2-enal **32** was used as the starting material under the same conditions, The reaction was slow and most of the **32** (65% yield) was recovered after 1d.

[S3] J. F. Gil, D. J. Ramón and M. Yus, *Tetrahedron*, **1994**, *50*, 3437.

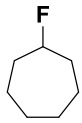
[S4] C. Ko, J. B. Feltenberger, S. K. Ghosh and R. P. Hsung, *Org. Lett.* **2008**, *10*, 1971.

Characterization Data



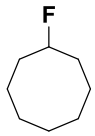
6

1-Fluorocyclohexane (6).[S5] Prepared from cyclohexane (25.3 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (15 h) to give **6** (76% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ –172.38 (brs, 1F).



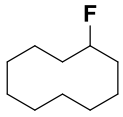
7

1-Fluorocycloheptane (7).[S6] Prepared from cycloheptane (29.5 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (6 h) to give **7** (85% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ –163.78 (m, 1F).



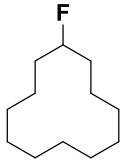
8

1-Fluorocyclooctane (8).[S6] Prepared from cyclooctane (33.7 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (3 h) to give **8** (82 % NMR yield). ^{19}F NMR (376 MHz, C_6D_6) δ –159.23 (brs, 1F).



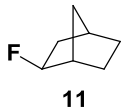
9

1-Fluorocyclodecane (9).[S7] Prepared from cyclodecane (42.1 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (15 h), purified by flash column chromatography (pentane), and concentrated by rotary evaporator at ca. 100 mm Hg to give **9** (23.1 mg, 73% yield) as a colorless oil: R_f = 0.5 (pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 4.65 (dtt, J = 46.6, 7.8, 4.1 Hz, 1H), 1.63–1.89 (m, 4H), 1.42–1.51 (m, 2H), 1.27–1.38 (m, 12H); ^{13}C NMR (100 MHz, C_6D_6) δ 93.5 (d, J = 165.8 Hz), 31.1 (d, J = 21.9 Hz), 25.4, 25.1, 24.0, 21.8 (d, J = 7.7 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ –165.63 (dtt, J = 46.5, 26.5, 13.7 Hz, 1F); MS(EI) calcd for $C_{10}H_{19}F$ $(M)^+$ 158.1, found 158.1.



10

1-Fluorocyclododecane (10).[S8] Prepared from cyclododecane (50.5 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (15 h), purified by flash column chromatography (pentane), and concentrated by rotary evaporator at ca. 100 mm Hg to give **10** (27.9 mg, 75% yield) as a colorless oil: R_f = 0.5 (pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 4.59 (dddd, J = 47.3, 11.5, 7.2, 4.7 Hz, 1H), 1.55–1.73 (m, 4H), 1.31–1.38 (m, 2H), 1.19 (brs, 16H); ^{13}C NMR (100 MHz, C_6D_6) δ 91.8 (d, J = 167.0 Hz), 30.3 (d, J = 21.2 Hz), 24.4, 24.2, 23.6, 23.5, 20.9 (d, J = 6.7 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ –176.13 (dddd, J = 47.3, 23.6, 15.4, 8.2 Hz, 1F); MS(EI) calcd for $C_{12}H_{23}F$ $(M)^+$ 186.2, found 186.1.



11

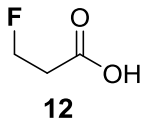
***exo*-2-Fluoronorbornane (11).**[S6] Prepared from norborane (28.9 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (24 h) to give *exo*-2-fluoronorbornane **11** (58% NMR yield) and *endo*-2-fluoronorbornane (4% NMR yield). *exo*-2-fluoronorbornane **11**: ^{19}F NMR (376 MHz, CD_3CN) δ –160.29 (m, 1F); *endo*-2-fluoronorbornane: ^{19}F NMR (376 MHz, CD_3CN) δ –190.00 (m, 1F).

[S5] R. D. Chambers, A. M. Kenwright, M. Parsons, G. Sandford and J. S. Moilliet, *J. Chem. Soc., Perkin Trans. 1*, **2002**, 2190.

[S6] H.-J. Schneider, W. Gschwendtner, D. Heiske, V. Hoppen and F. Thomas, *Tetrahedron*, **1977**, *33*, 1769.

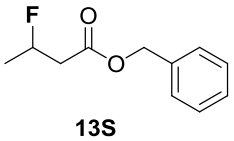
[S7] S. Bloom, C. R. Pitts, D. C. Miller, N. Haselton, M. G. Holl, E. Urheim and T. Lectka, *Angew. Chem. Int. Ed.* **2012**, *51*, 10580.

[S8] Y. Amaoka, M. Nagatomo and M. Inoue, *Org. Lett.* **2013**, *15*, 2160.



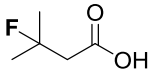
12

3-Fluoropropanoic acid (12). Prepared from propanoic acid (22.2 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (40 h) to give **12** (<5% NMR yield). ^{19}F NMR (376 MHz, CD_3CN) δ –219.68 (tt, *J* = 47.6, 26.8 Hz, 1F).



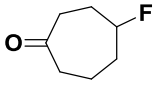
13S

Benzyl 3-fluorobutanoate (13S).[S9] Prepared from butyric acid (26.4 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (15 h) to give 3-fluorobutyric acid (70% NMR yield). To the reaction mixture were added *N*,*N*-diisopropylethylamine (77.5 mg, 3.0 equiv) and benzyl bromide (68.4 mg, 2.0 equiv). The reaction mixture was stirred at room temperature for 12 h, then poured into diethyl ether (20 mL), filtrated, concentrated and purified by silica gel flash column chromatography (10% ethyl acetate/hexanes) to give **13S** (21.7 mg, 55% yield) as a colorless oil: R_f = 0.3 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.39 (m, 5H), 5.02–5.22 (m, 1H), 5.16 (s, 2H), 2.78 (ddd, *J* = 15.8, 14.2, 7.9 Hz, 1H), 2.59 (ddd, *J* = 28.3, 15.8, 4.8 Hz, 1H), 1.40 (dd, *J* = 23.8, 6.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 135.6, 128.6, 128.3, 128.2, 87.0 (d, *J* = 167.2 Hz), 66.6, 41.9 (d, *J* = 24.0 Hz), 20.8 (d, *J* = 22.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –172.54 (ddqd, *J* = 47.6, 28.3, 23.7, 14.2 Hz); MS(ESI) calcd for $C_{11}H_{13}FO_2Na$ $(M+Na)^+$ 219.1, found 219.1.



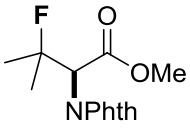
14

3-Fluoro-3-methylbutanoic acid (14).[S10] Prepared from isovaleric acid (30.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (15 h), purified by flash column chromatography (20% ethyl acetate/hexanes), and concentrated by rotary evaporator at ca. 100 mm Hg to give **14** (19.5 mg, 81% yield) as a colorless oil: R_f = 0.2 (30% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, C_6D_6) δ 10.68 (brs, 1H), 2.36 (d, *J* = 15.8 Hz, 2H), 1.23 (d, *J* = 21.3 Hz, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ 176.6 (d, *J* = 8.9 Hz), 92.6 (d, *J* = 170.1 Hz), 45.8 (d, *J* = 26.6 Hz), 26.7 (d, *J* = 24.0 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ –134.48 (heptt, *J* = 21.3, 15.8 Hz, 1F); MS(ESI) calcd for $C_5H_9FO_2Na$ $(M+Na)^+$ 143.1, found 143.1.



15a

4-Fluorocycloheptan-1-one (15a).[S11] Prepared from cycloheptanone (33.6 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (18 h) to give **15** (72% NMR yield, β:γ = 3:4). Purified by preparative TLC (plate pretreated with ammonium (7.0 M in methanol, 1 mL) in hexane (50 mL)) (20% ethyl acetate/hexanes), and concentrated by rotary evaporator at ca. 100 mm Hg to give **15a** (9.1 mg, 35% yield). ^{1}H NMR (400 MHz, C_6D_6) δ 4.13 (ddddd, *J* = 46.1, 7.8, 5.5, 2.8, 2.8 Hz, 1H), 2.37 (ddt, *J* = 15.3, 10.1, 1.9 Hz, 1H), 1.98 (dt, *J* = 8.6, 4.0 Hz, 2H), 1.88 (ddd, *J* = 15.3, 9.6, 2.6 Hz, 1H), 1.22–1.56 (m, 5H), 0.85–0.93 (m, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 210.3, 91.7 (d, *J* = 170.3 Hz), 43.2, 36.3 (d, *J* = 8.7 Hz), 35.4 (d, *J* = 21.7 Hz), 29.7 (d, *J* = 22.6 Hz), 17.6 (d, *J* = 8.2 Hz); ^{19}F NMR (376 MHz, C_6D_6) δ –172.87 (dddd, *J* = 43.1, 27.1, 21.4, 7.8 Hz, 1F); MS(ESI) calcd for $C_7H_{12}FO$ $(M+H)^+$ 131.1, found 131.1.

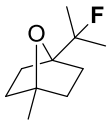


16

(2*R*)-*N*-Phthaloyl-3-fluorovaline methyl ester (16).[S12] Prepared from (*S*)-*N*-phthaloylvaline methyl ester (52.2 mg, 0.2 mmol, 1.0 equiv) with selectfluor (106.5 mg, 0.3 mmol, 1.5 equiv) catalyzed by acetophenone (4.8 mg, 0.02 mmol, 20 mol%) according to the general procedure (48 h) and purified by flash column chromatography (10% ethyl acetate/hexanes) to give **16** (47.6 mg, 85% yield) as a colorless oil: R_f = 0.2 (20% ethyl acetate/hexanes). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.76 (dd, *J* = 5.4, 3.1 Hz, 2H), 4.98 (d, *J* = 10.2 Hz, 1H), 3.72 (s, 3H), 1.69 (d, *J* = 22.9 Hz, 3H), 1.55 (d, *J* = 22.4 Hz,

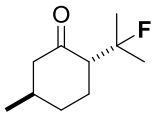
[S9] K.-Y. Kim, B. C. Kim, H. B. Lee and H. Shin, *J. Org. Chem.* **2008**, *73*, 8106.
[S10] R. Keck and J. Rétey, *Helv Chim Acta* **1980**, *63*, 769.
[S11] W. Liu, X. Huang, M.-J. Cheng, R. J. Nielsen, W. A. Goddard III and J. T. Groves, *Science* **2012**, *337*, 1322.
[S12] J.-B. Xia, Y. Ma and C. Chen, *Org. Chem. Front*. **2014**, *1*, 468.

3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.6 (d, *J* = 10.5 Hz), 134.3, 131.6, 123.7, 95.6 (d, *J* = 172.9 Hz), 57.7 (d, *J* = 25.9 Hz), 52.5, 26.3 (d, *J* = 22.8 Hz), 23.7 (d, *J* = 23.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –136.53 (dqq, *J* = 10.2, 22.6, 22.6 Hz, 1F); MS(ESI)$^+$ calcd for $C_{14}H_{14}FNO_4Na$ $(M+Na)^+$ 302.1, found 302.1.



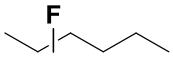
17

1-(2-Fluoropropan-2-yl)-4-methyl-7-oxabicyclo[2.2.1]heptane (17).[S12] Prepared from 1,4-Cineole (30.9 mg, 0.2 mmol, 1.0 equiv) with selectfluor (106.5 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (20 h), purified by flash column chromatography (2% diethyl ether/pentane), and concentrated by rotary evaporator at ca. 100 mm Hg to give **17** (25.1 mg, 73% yield) as a colorless oil: R_f = 0.4 (5% diethyl ether/pentane). ^{1}H NMR (400 MHz, C_6D_6) δ 1.80 (ddd, *J* = 12.9, 10.6, 4.0 Hz, 2H), 1.24–1.43 (m, 15H); ^{13}C NMR (100 MHz, C_6D_6) δ 94.9 (d, *J* = 172.0 Hz), 89.7 (d, *J* = 21.1 Hz), 83.7, 37.2, 32.5 (d, *J* = 5.3 Hz), 23.5 (d, *J* = 25.6 Hz), 21.3; ^{19}F NMR (376 MHz, C_6D_6) δ –146.22 (hept, *J* = 21.4 Hz, 1F); MS(EI) calcd for $C_{10}H_{17}FO$ $(M)^+$ 172.1, found 172.1.



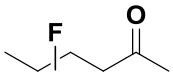
18

(2*R*,5*R*)-2-(2-Fluoropropan-2-yl)-5-methylcyclohexanone (18).[S12] Prepared from L-menthone (15.4 mg, 0.1 mmol, 1.0 equiv) with selectfluor (53.1 mg, 0.15 mmol, 1.5 equiv) in CH_3CN (1.5 mL) according to the general procedure (30 h), purified by preparative TLC (plate pretreated with ammonium (7.0 M in methanol, 1 mL) in hexane (50 mL)) (5% ethyl acetate/hexanes), and concentrated by rotary evaporator at ca. 100 mm Hg to give **18** (12.3 mg, 71% yield). ^{1}H NMR (400 MHz, C_6D_6) δ 2.30 (dt, *J* = 12.8, 6.3 Hz, 1H), 2.09–2.18 (m, 2H), 1.55 (d, *J* = 23.2 Hz, 3H), 1.45 (d, *J* = 22.8 Hz, 3H), 1.32–1.47 (m, 3H), 1.18–1.28 (m, 1H), 0.77–0.89 (m, 1H), 0.61 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ 207.9 (d, *J* = 11.0 Hz), 95.3 (d, *J* = 165.5 Hz), 58.9 (d, *J* = 22.5 Hz), 51.2 (d, *J* = 4.3 Hz), 35.8, 33.7, 27.8 (d, *J* = 4.7 Hz), 27.6 (d, *J* = 23.3 Hz), 22.3 (d, *J* = 23.4 Hz), 22.2; ^{19}F NMR (376 MHz, C_6D_6) δ –133.73 (heptd, *J* = 23.0, 7.4 Hz, 1F); MS(EI) calcd for $C_{10}H_{17}FO$ $(M)^+$ 172.1, found 172.1.



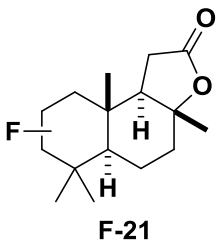
F-19

Fluorohexanes (F-19).[S 13] Prepared from hexane (86.2 mg, 1.0 mmol, 5.0 equiv) according to the general procedure (15 h) to give 2-fluorohexane **F-19a** (50% NMR yield), 3-fluorohexane **F-19b** (22% NMR yield), and 1-fluorohexane **F-19c** (3% NMR yield). **F-19a**: ^{19}F NMR (376 MHz, CD_3CN) δ –172.17 (ddqd, *J* = 48.3, 27.9, 24.1, 17.1 Hz, 1F); **F-19b**: ^{19}F NMR (376 MHz, CD_3CN) δ –181.79 (m, 1F); **F-19c**: ^{19}F NMR (376 MHz, CD_3CN) δ –218.46 (tt, *J* = 47.6, 25.1 Hz, 1F).



F-20

Fluorohexan-2-ones (F-20). Prepared from 2-hexanone (30.0 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (48 h) to give 5-fluorohexan-2-one **F-20a** (34% NMR yield), and 4-fluorohexan-2-one **F-20b** (26% NMR yield). **F-20a**: ^{19}F NMR (376 MHz, CD_3CN) δ –174.13 (m, 1F); **F-20b**: ^{19}F NMR (376 MHz, CD_3CN) δ –181.77 (m, 1F).

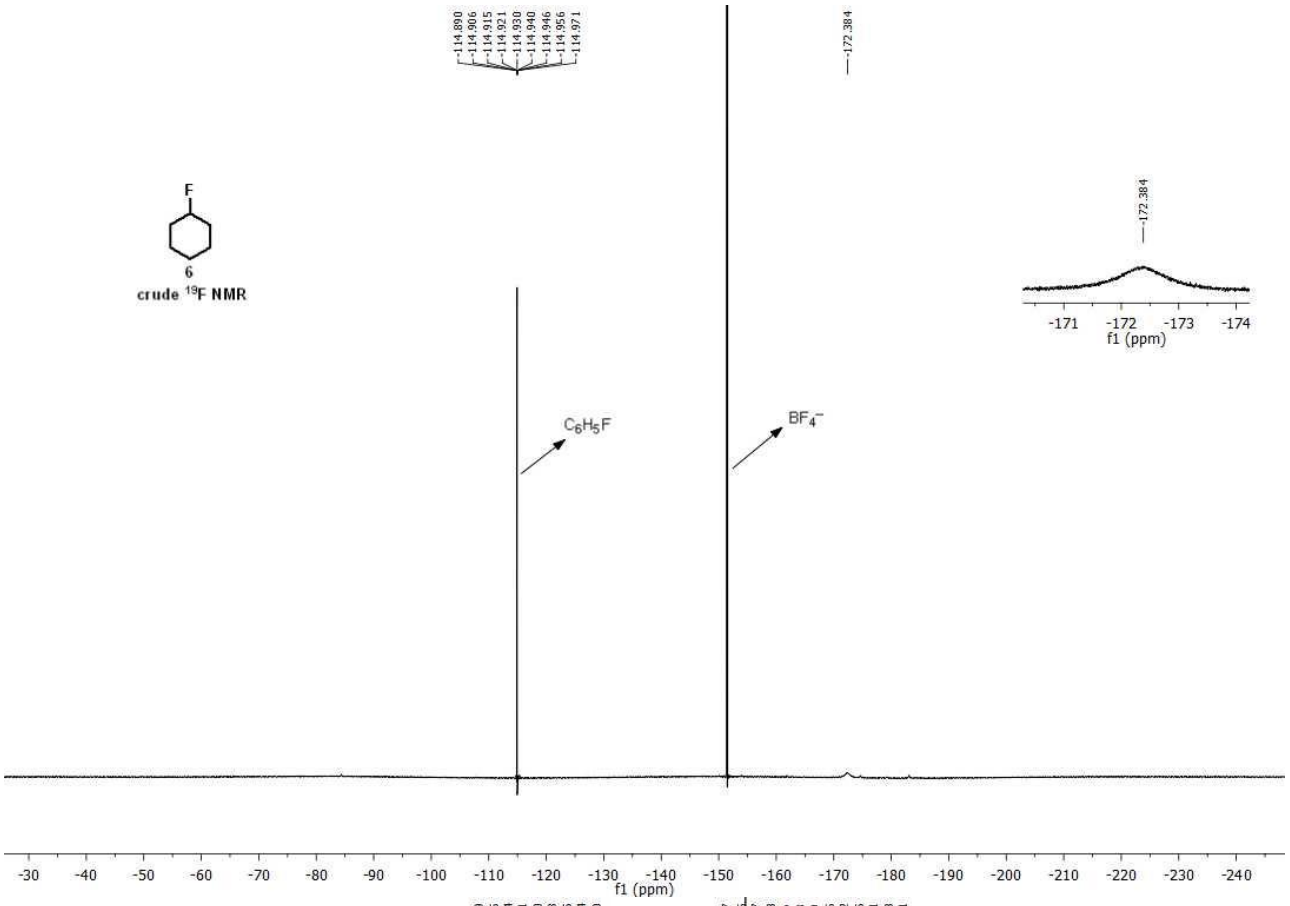


F-21

Fluorosclareolides (F-21).[S11] Prepared from sclareolide (30.0 mg, 0.3 mmol, 1.5 equiv) according to the general procedure (24 h) to give 2α-fluorosclareolide **F-21a** (59% NMR yield), 2β-fluorosclareolide **F-21b** (6% NMR yield) and 3α-fluorosclareolide **F-21c** (18% NMR yield). Purified by flash column chromatography (10% ethyl acetate/hexanes) to give a mixture of all three isomers (43.0 mg, 80% yield) as a colorless solid: R_f = 0.3 (20% ethyl acetate/hexanes). **F-21a**: ^{19}F NMR (376 MHz, $CDCl_3$) δ –179.85 (ddddd, *J* = 48.0, 11.0, 11.0, 5.5, 5.5 Hz, 1F); **F-21b**:

[S13] I. Bucsi, B. Török, A. I. Marco, G. Rasul, G. K. S. Prakash and G. A. Olah, *J. Am. Chem. Soc.*, **2002**, *124*, 7728.

^{19}F NMR (376 MHz, $CDCl_3$) δ –171.12 (m, 1F); **F-21c**: ^{19}F NMR (376 MHz, $CDCl_3$) δ –187.33 (ddd, *J* = 46.3, 46.5, 14.6 Hz, 1F).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-114.946
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-114.971
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F
6
crude ^{19}F NMR
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-171
-172
-173
-174
f1 (ppm)
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BF_4^-
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-40
-50
-60
-70
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-200
-210
-220
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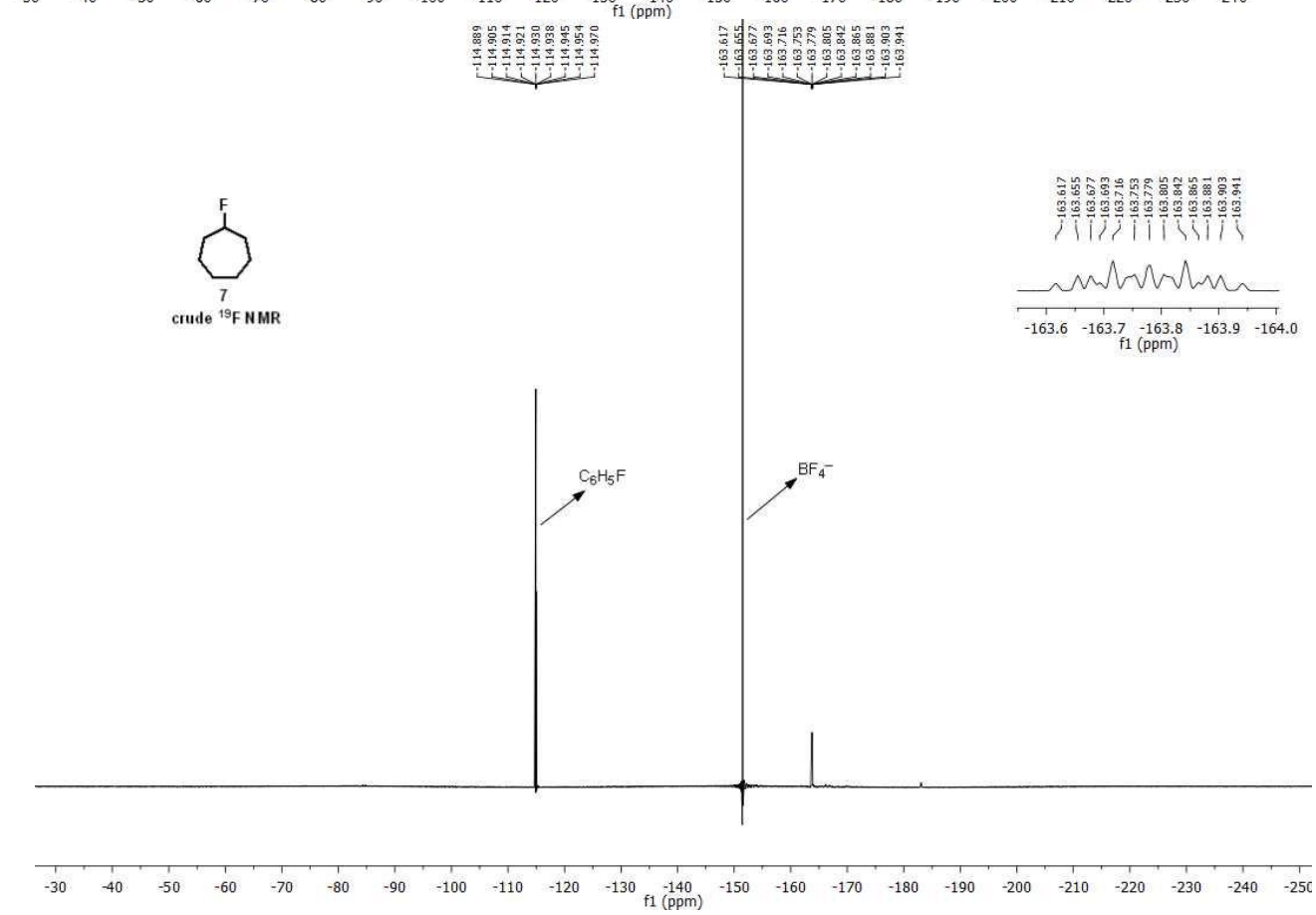
-240
f1 (ppm)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-163.903
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BF_4^-
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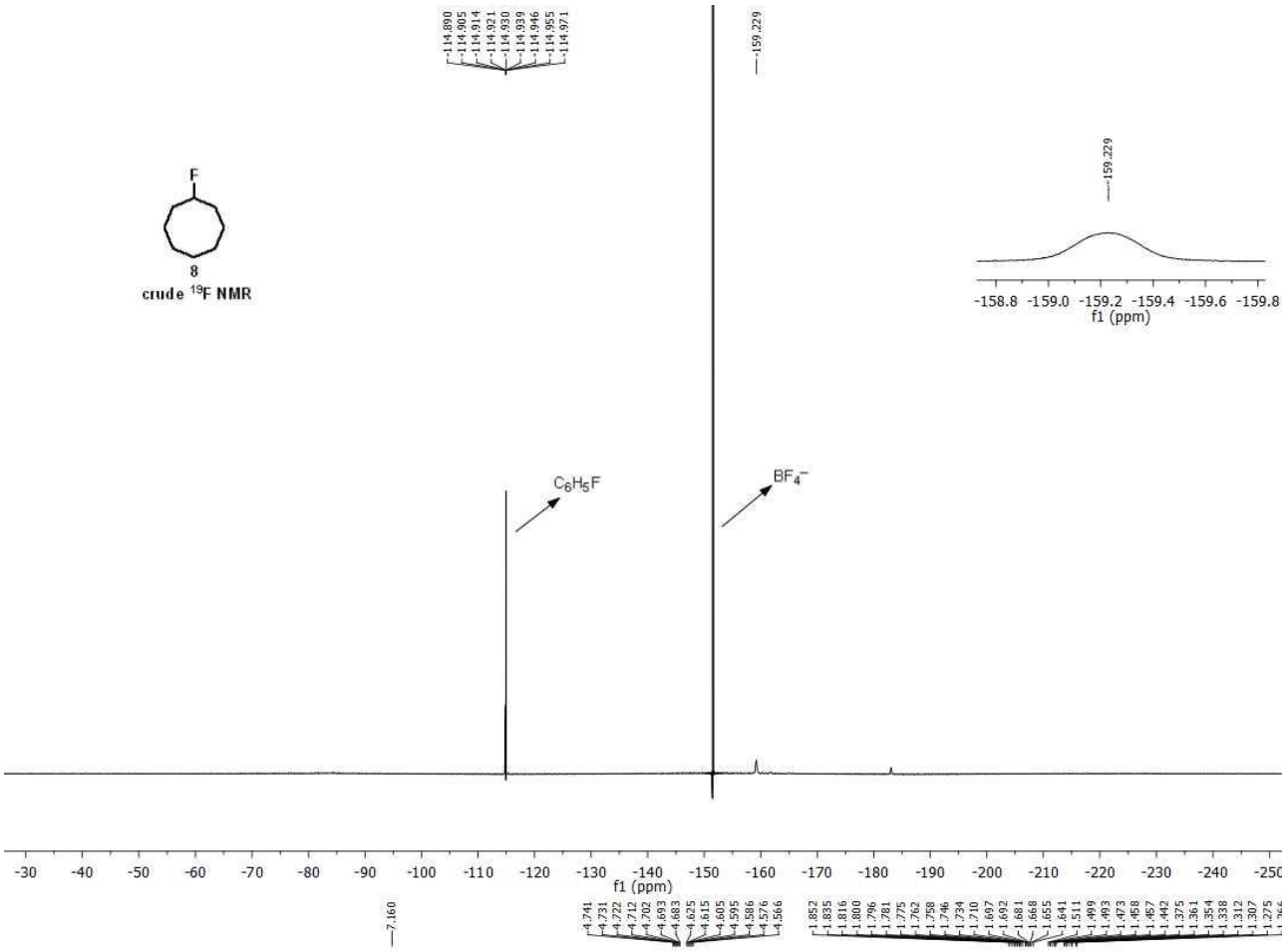
f1 (ppm)


F
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crude ^{19}F NMR
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-159.229
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f1 (ppm)
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BF_4^-
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f1 (ppm)
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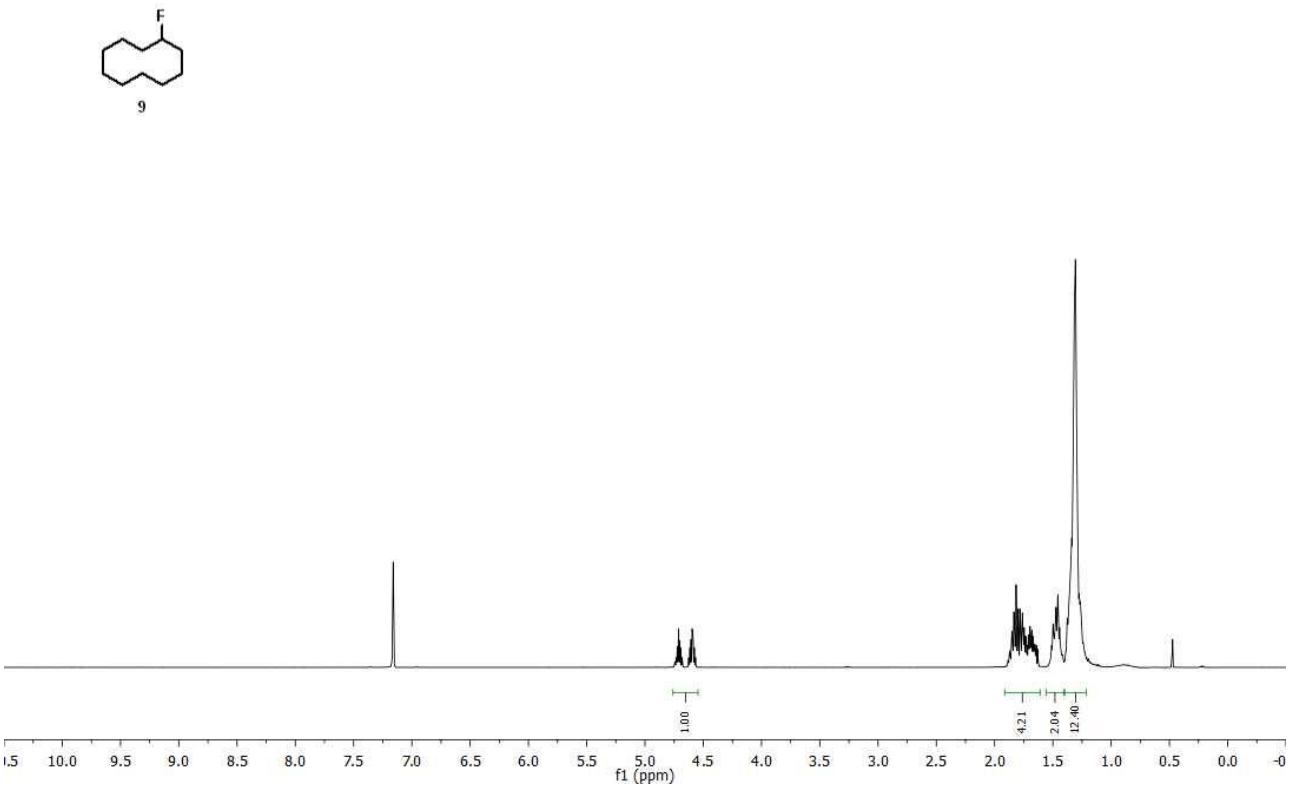
F
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12.40
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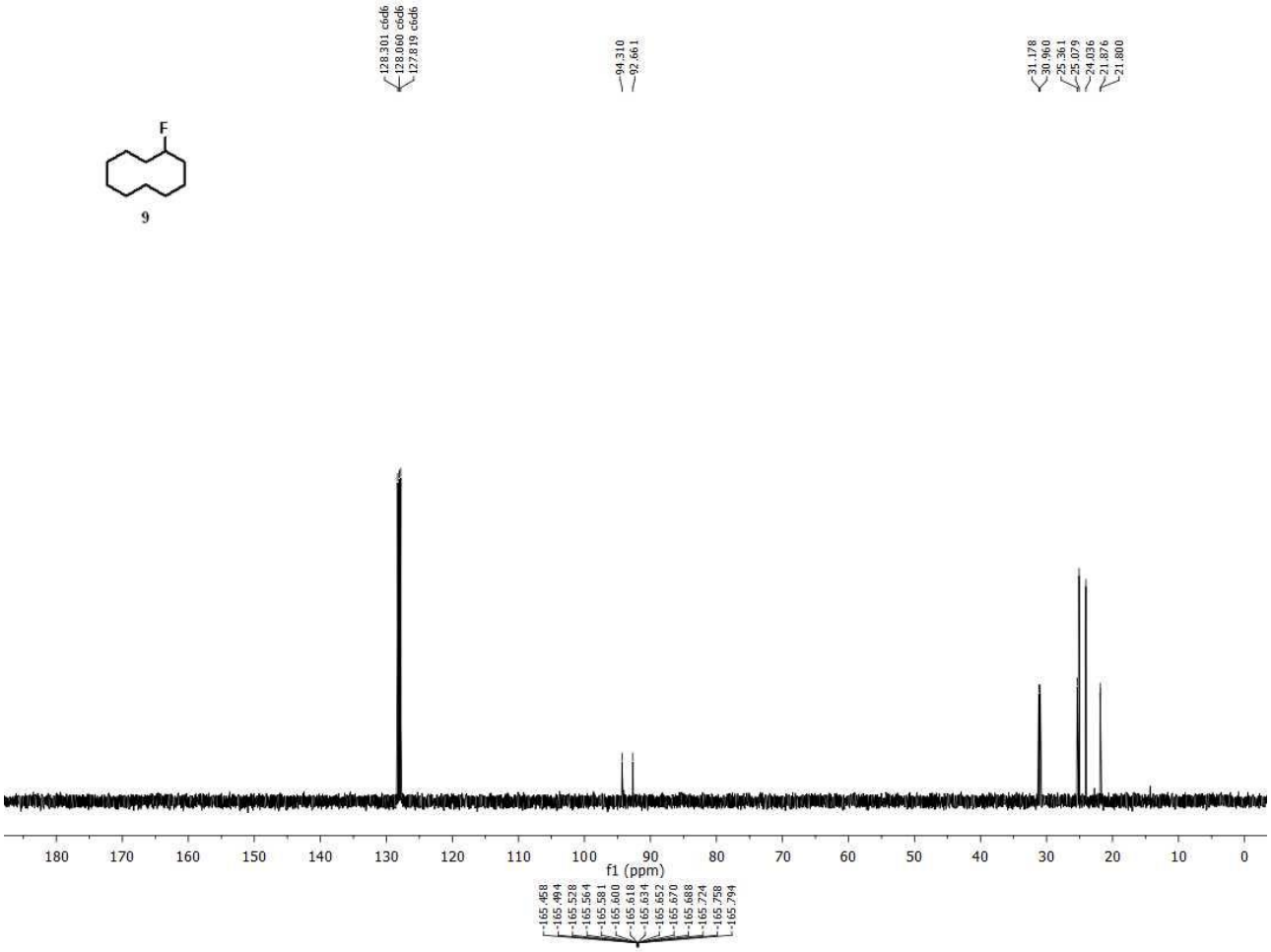
f1 (ppm)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21.800
F
9
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-165.670
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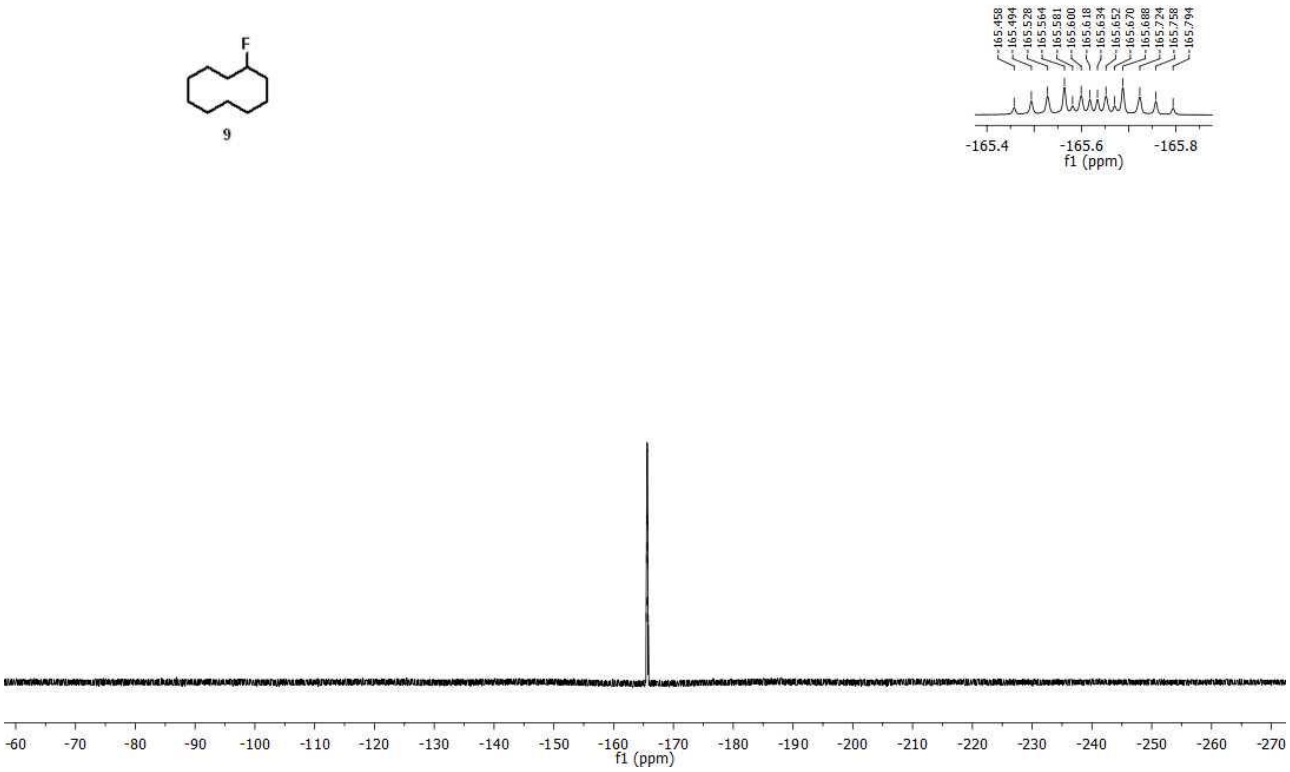
F
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-165.758
-165.794
-165.4
-165.6
-165.8
f1 (ppm)
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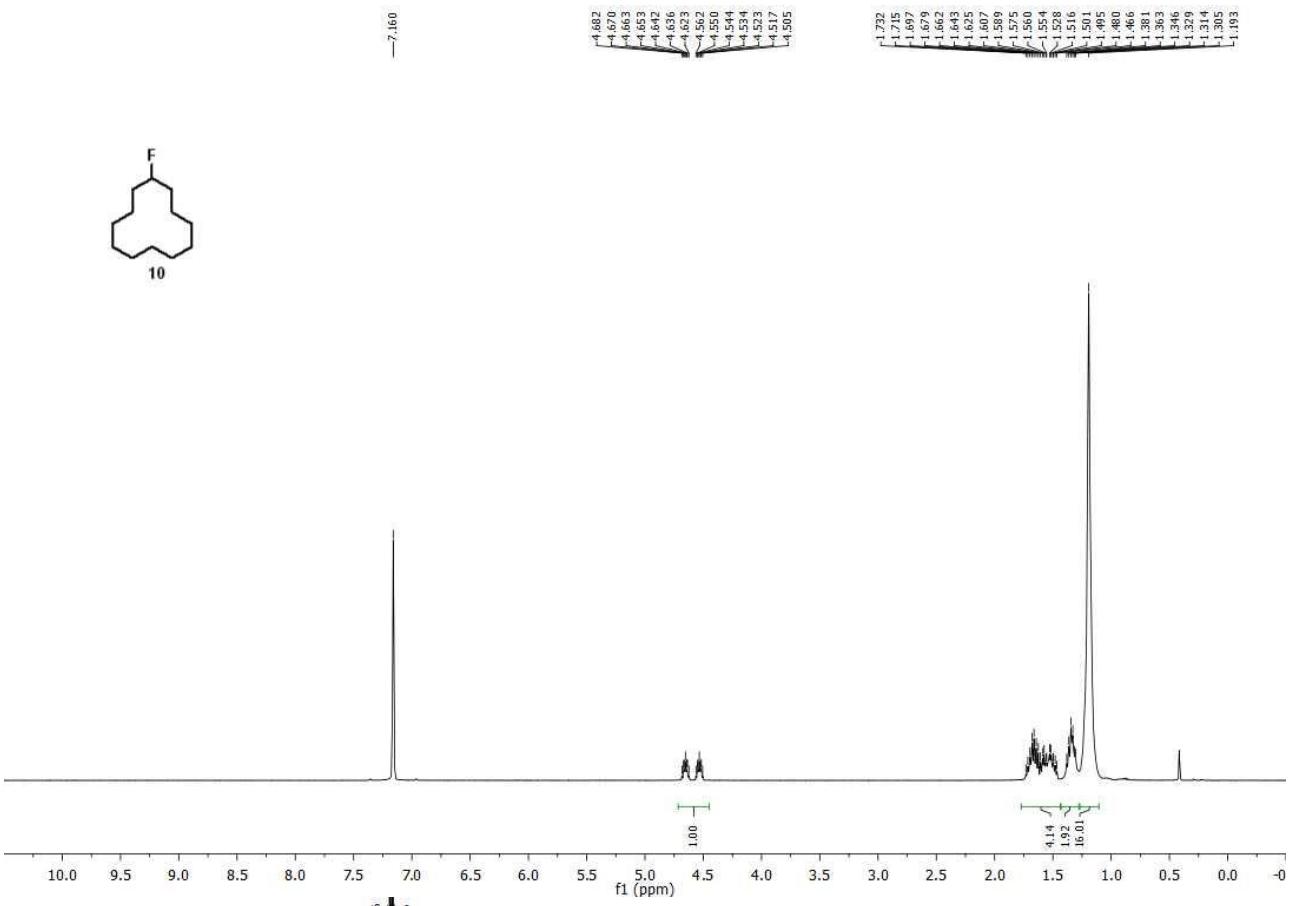
f1 (ppm)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1.305
1.193
F
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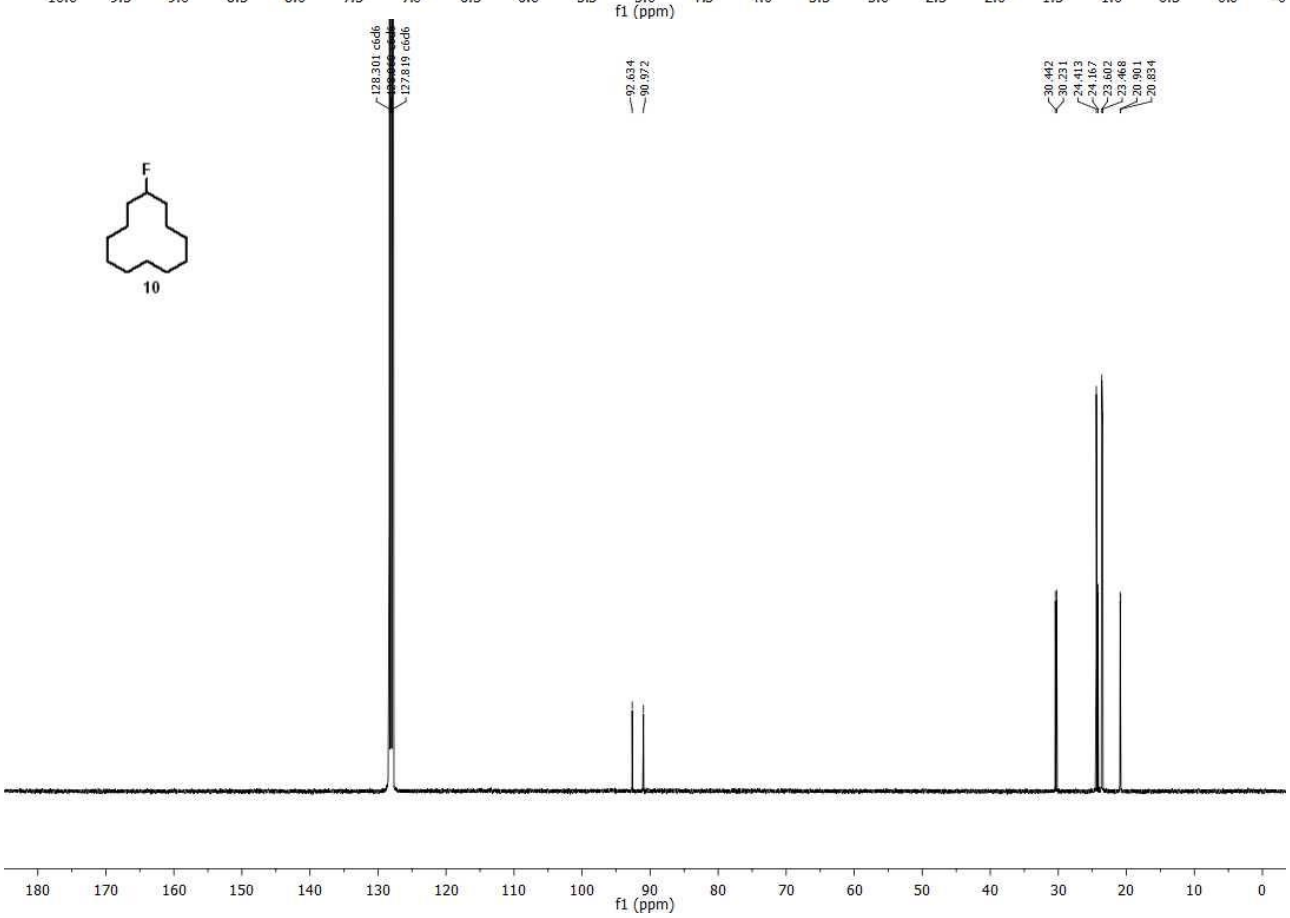
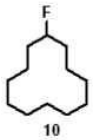
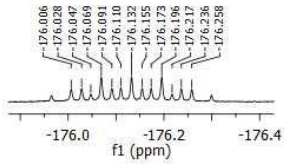
4.14
1.92
16.01
f1 (ppm)


128.301 c6d6
127.819 c6d6
92.634
90.972
30.442
30.231
24.413
24.167
23.602
23.468
20.901
20.834
F
10
f1 (ppm)


F
10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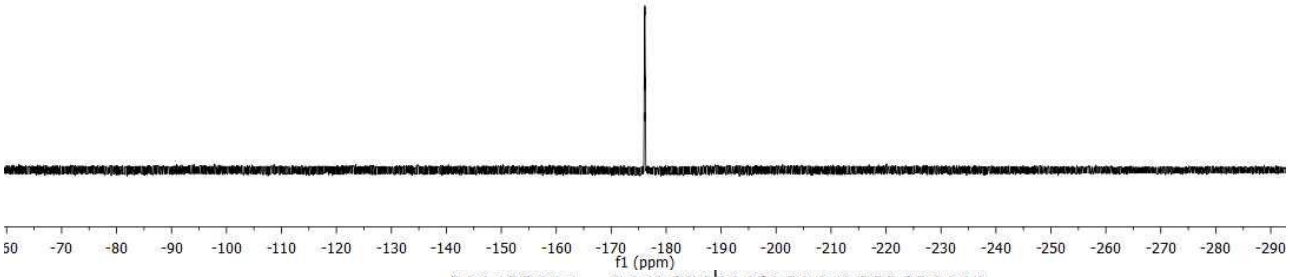
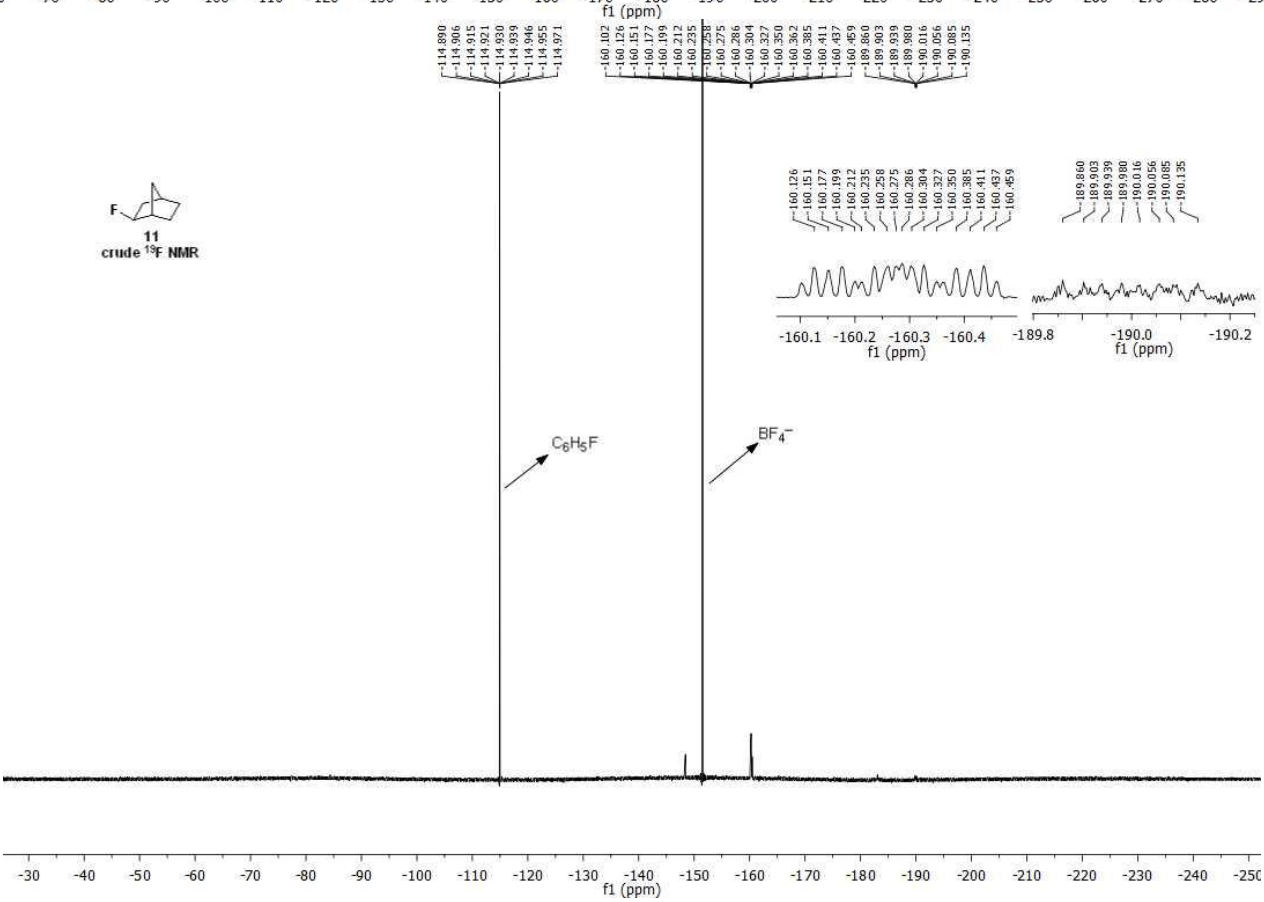
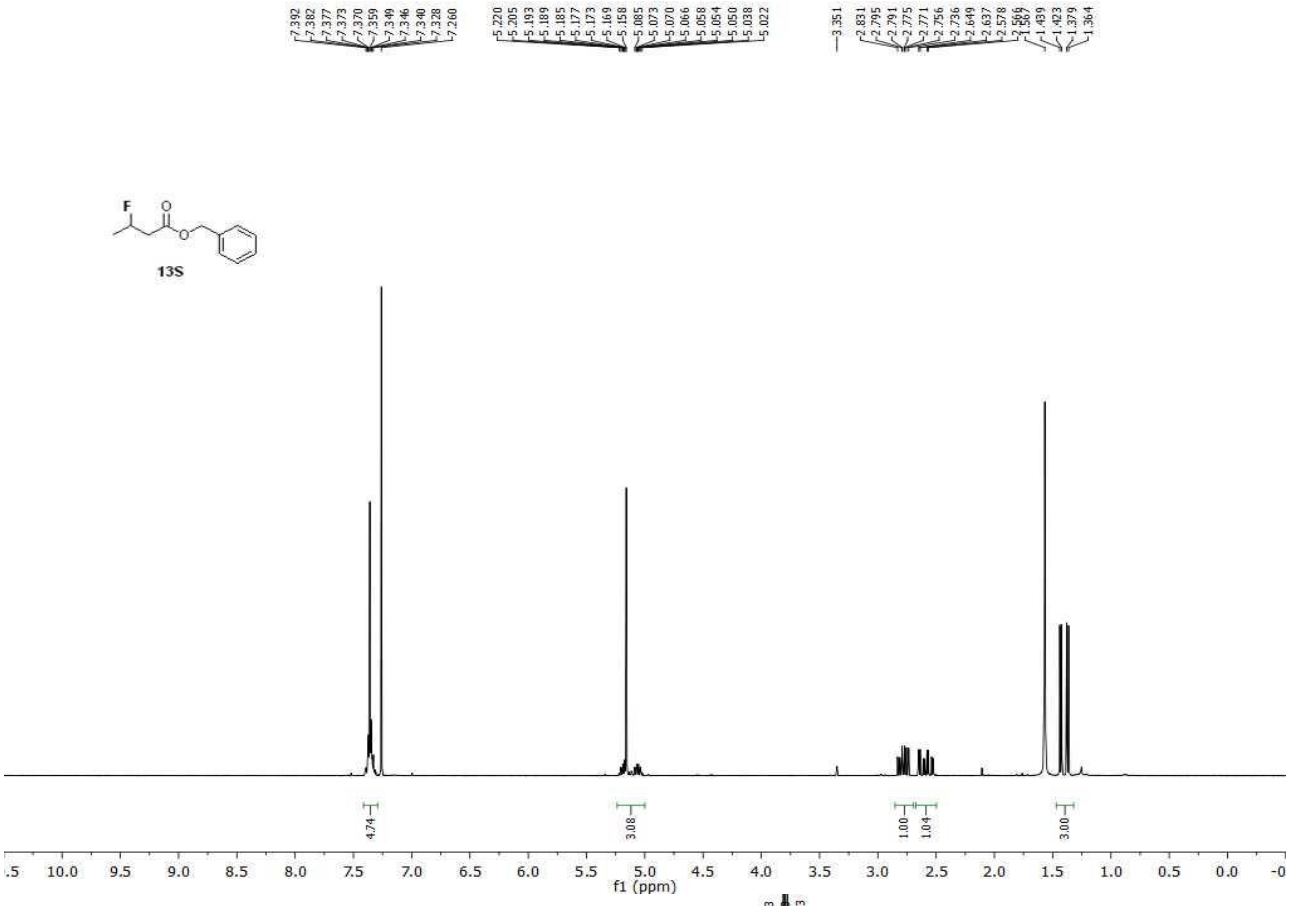
-176.028
-176.047
-176.069
-176.091
-176.110
-176.132
-176.155
-176.173
-176.196
-176.217
-176.236
-176.258
-176.0
-176.2
-176.4
f1 (ppm)


f1 (ppm)


F
11
crude ^{19}F NMR
C_6H_5F
BF_4^-
f1 (ppm)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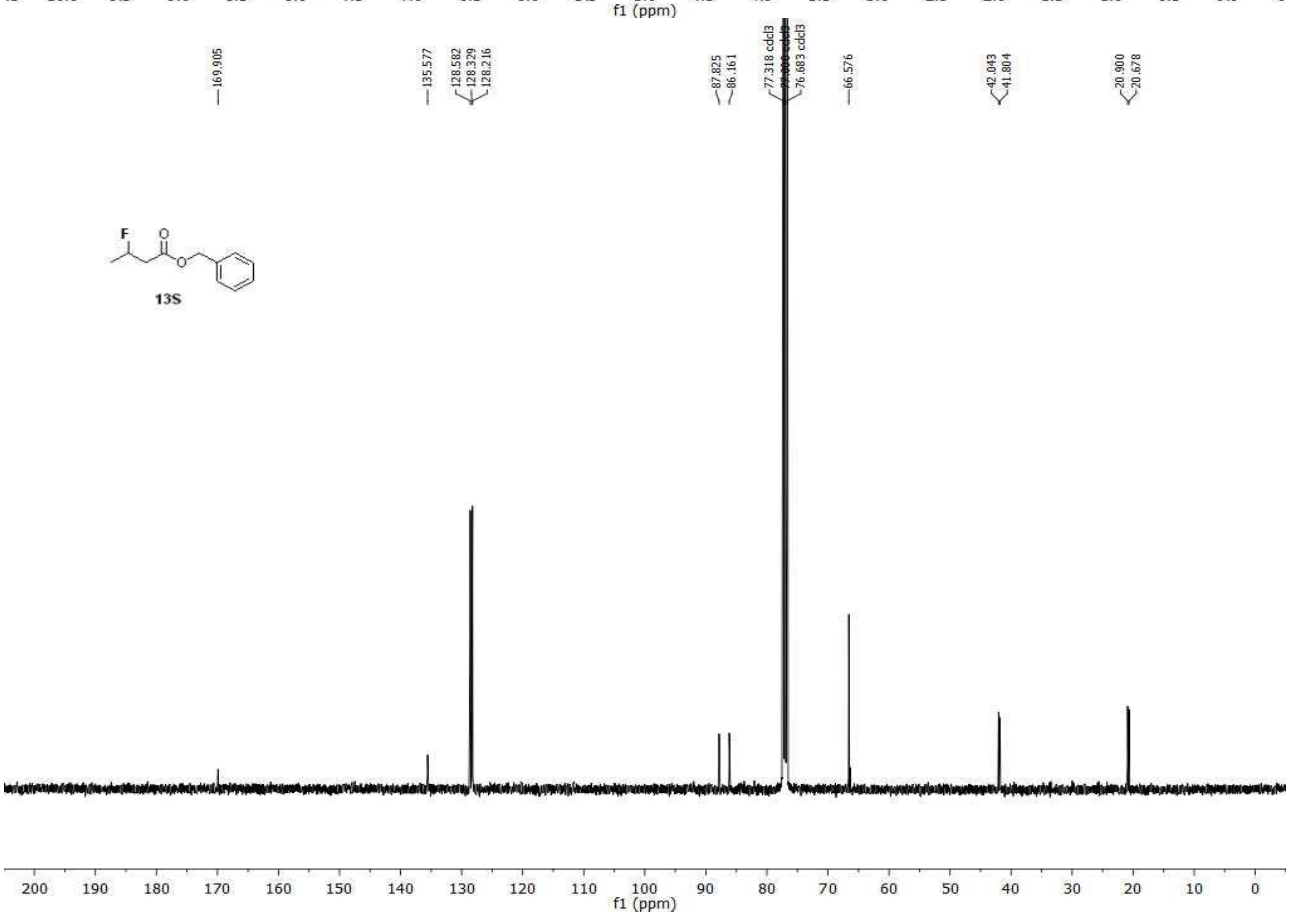
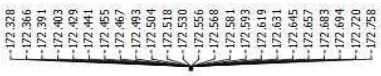
7.377
7.373
7.370
7.359
7.349
7.346
7.340
7.328
7.260
5.220
5.205
5.193
5.189
5.185
5.177
5.173
5.169
5.158
5.085
5.073
5.070
5.066
5.058
5.054
5.050
5.038
5.022
3.351
2.831
2.795
2.791
2.775
2.771
2.756
2.736
2.649
2.637
2.578
1.566
1.567
1.459
1.423
1.379
1.364
F
O
O
13S
4.74
3.08
1.00
1.04
3.00
f1 (ppm)


169.905
135.577
128.582
128.329
128.216
87.825
86.161
77.318 cdcl3
76.683 cdcl3
66.576
42.043
41.804
20.900
20.678
F
O
O
13S
f1 (ppm)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172.366
172.391
172.403
172.429
172.441
172.455
172.467
172.493
172.504
172.518
172.530
172.556
172.568
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172.593
172.619
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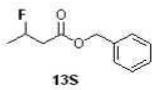
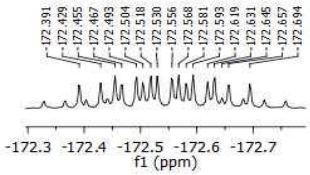
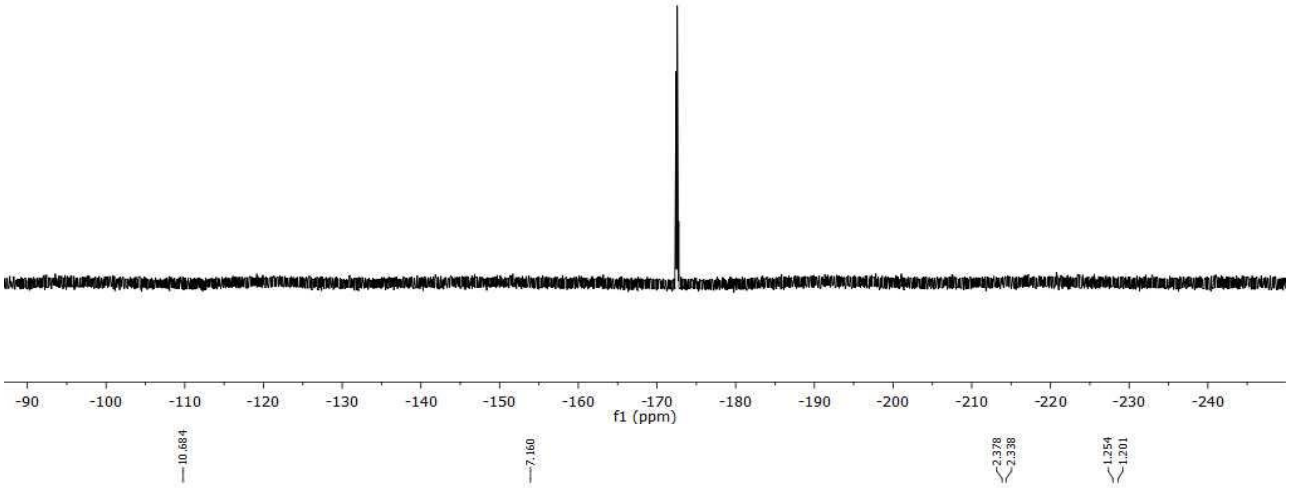
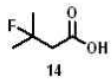
172.645
172.657
172.683
172.694
172.720
172.758


F
O
O

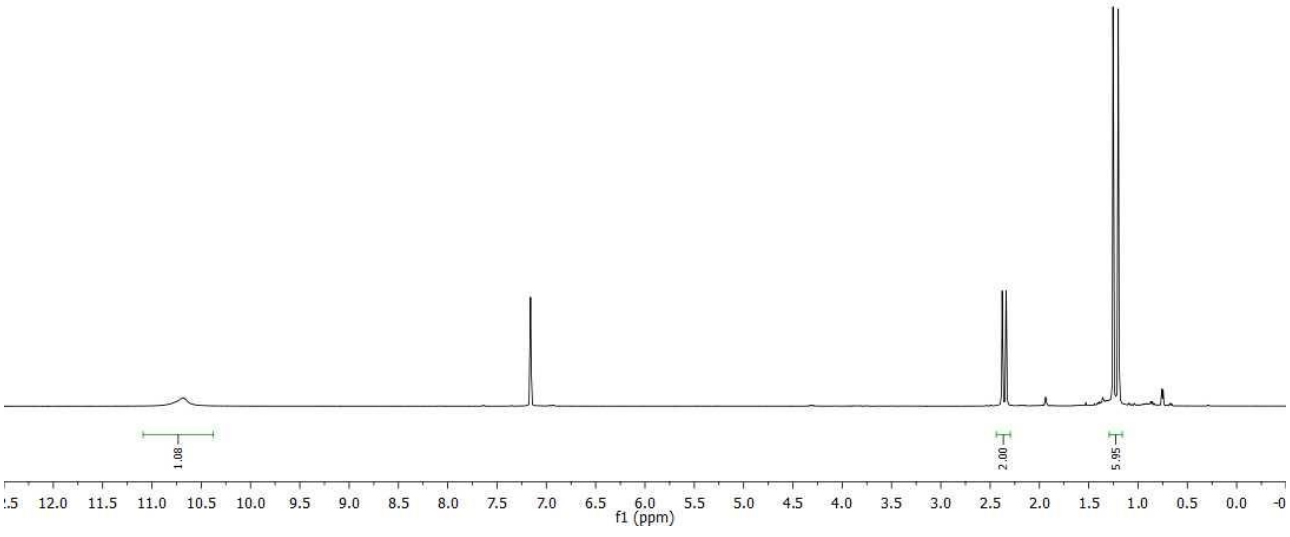
13S

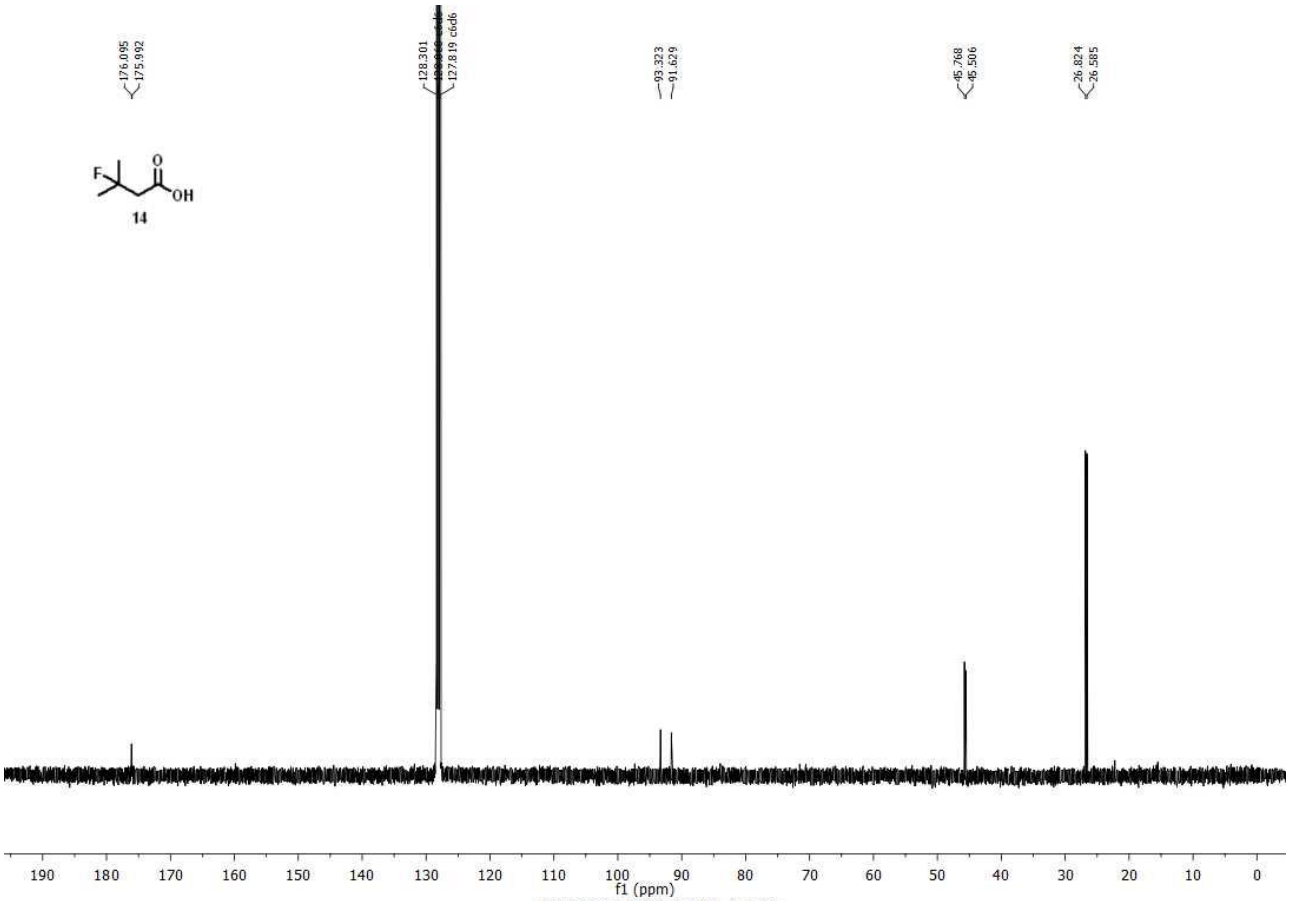

172.391
172.429
172.455
172.467
172.493
172.504
172.518
172.530
172.556
172.568
172.581
172.593
172.619
172.631
172.645
172.657
172.694
-172.3 -172.4 -172.5 -172.6 -172.7
f1 (ppm)

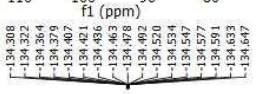

-90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240
f1 (ppm)
10.684
7.160
2.378
2.338
1.254
1.201

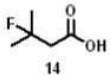

F
O
OH

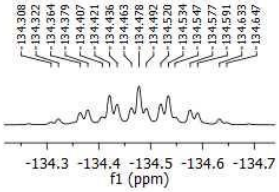
14


1.08
2.00
5.95
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)


176.095
175.992
128.301
93.323
91.629
45.768
45.506
26.824
26.585
F
O
OH
14
f1 (ppm)


-134.308
-134.322
-134.364
-134.379
-134.407
-134.421
-134.436
-134.463
-134.478
-134.492
-134.520
-134.534
-134.547
-134.577
-134.591
-134.633
-134.647


F
O
OH
14


-134.308
-134.322
-134.364
-134.379
-134.407
-134.421
-134.436
-134.463
-134.478
-134.492
-134.520
-134.534
-134.547
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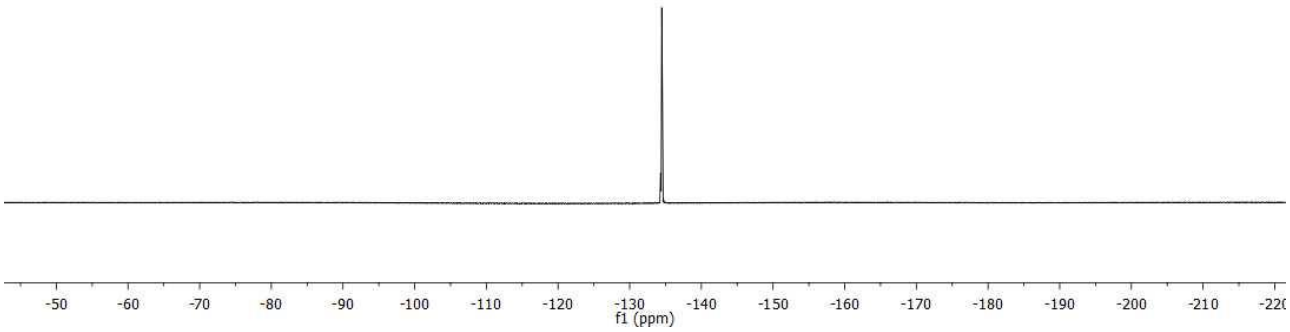
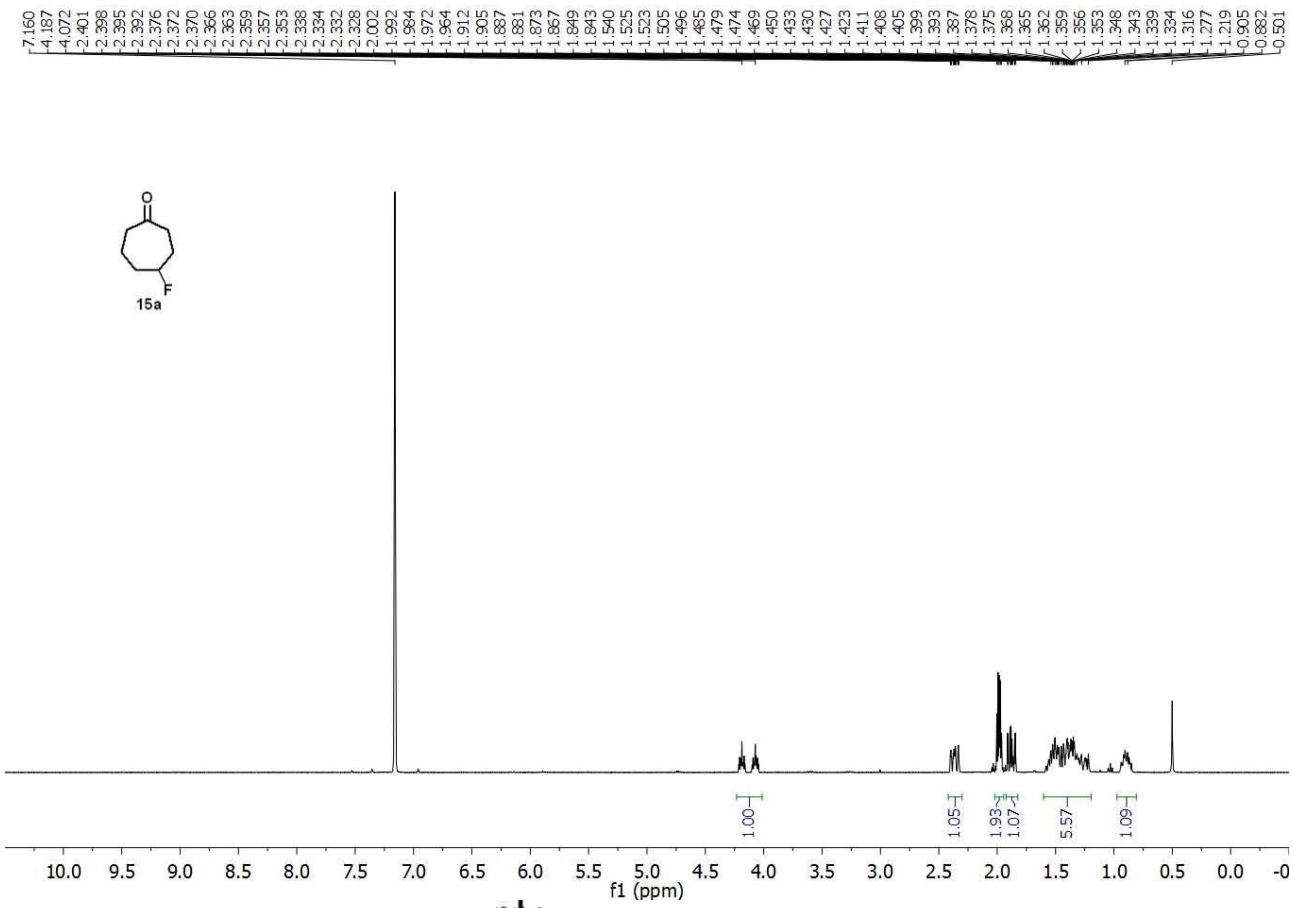
-134.591
-134.633
-134.647
-134.3 -134.4 -134.5 -134.6 -134.7
f1 (ppm)


f1 (ppm)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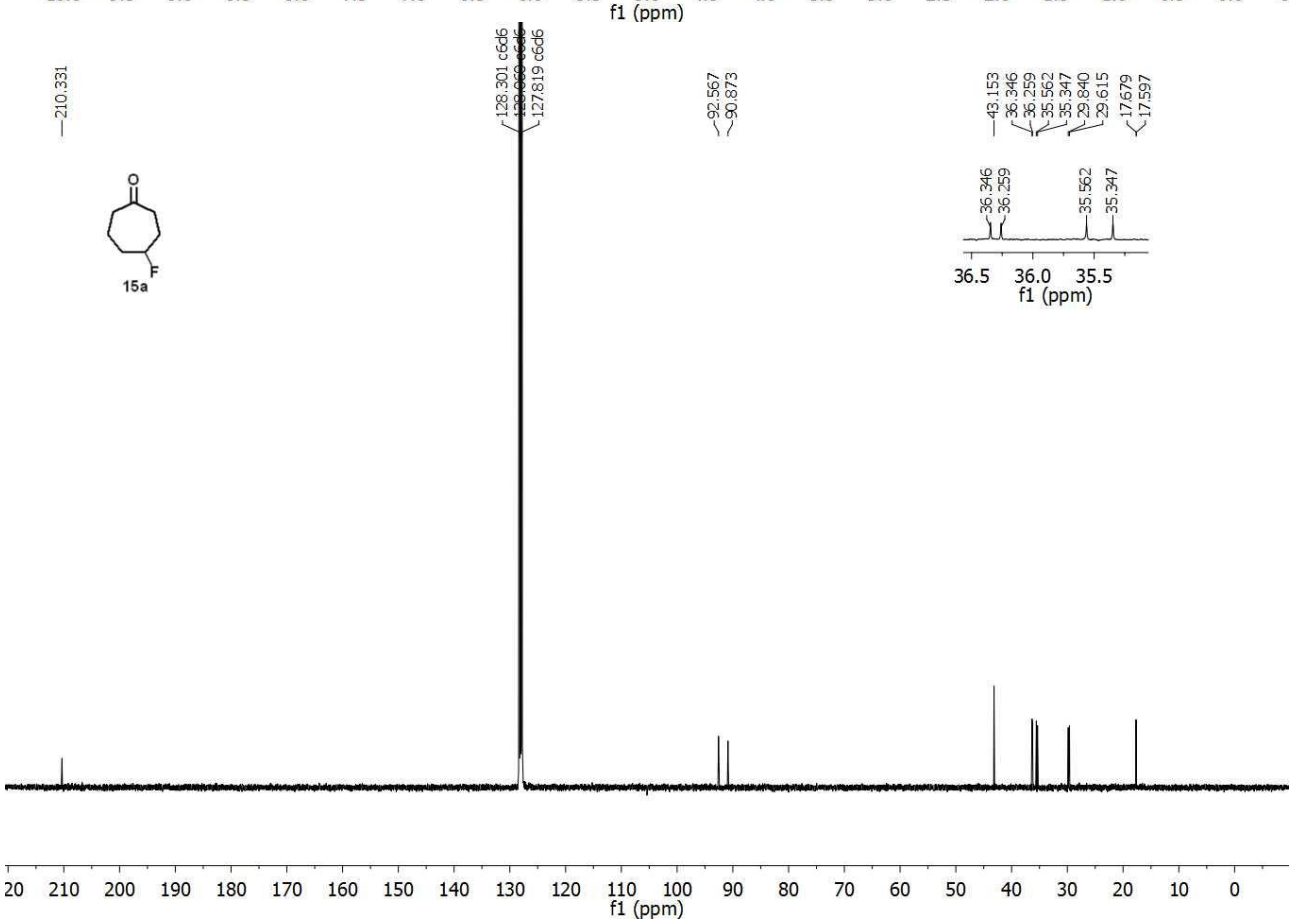
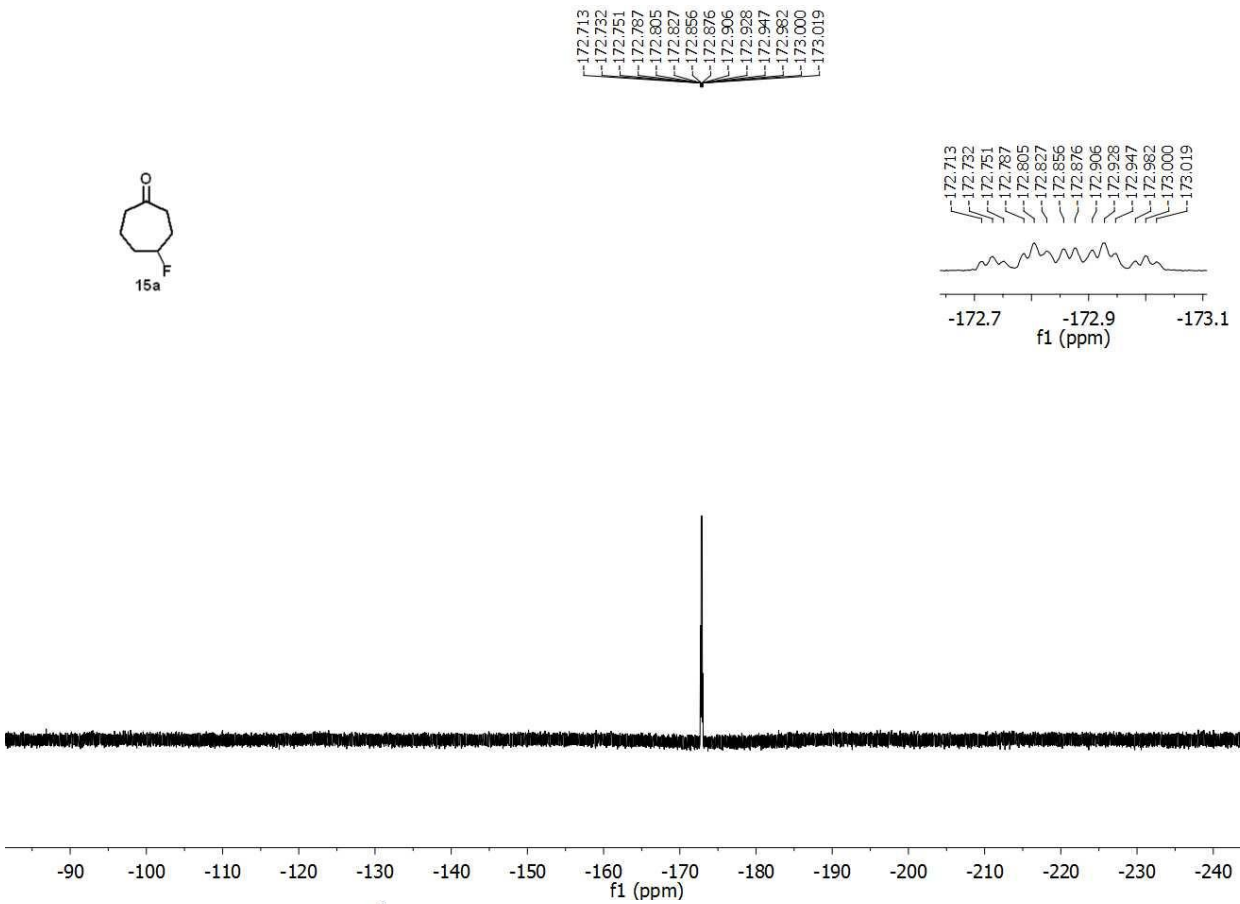
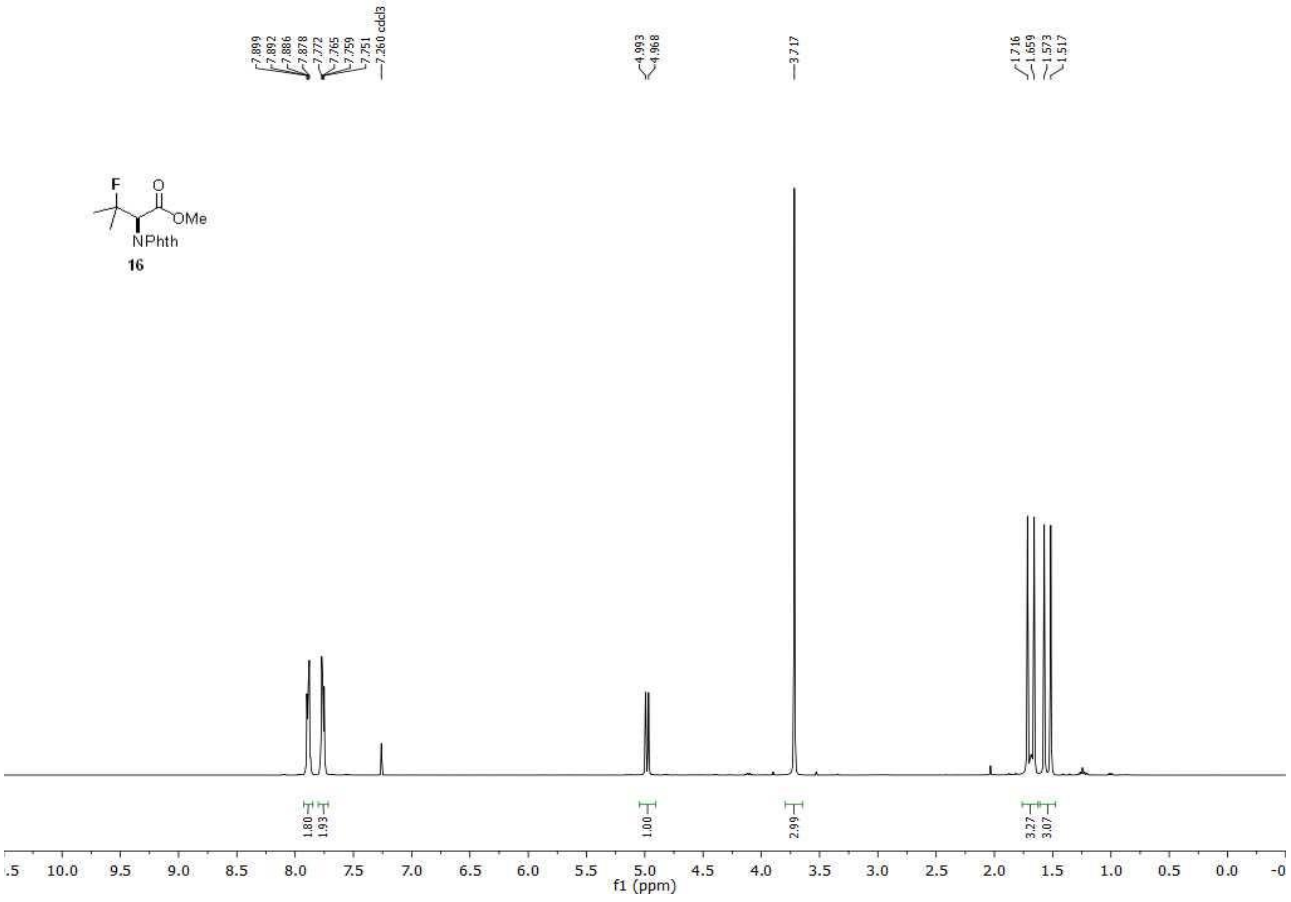
4.187
4.072
2.401
2.398
2.395
2.392
2.376
2.372
2.370
2.366
2.363
2.359
2.357
2.353
2.338
2.334
2.332
2.328
2.002
1.992
1.984
1.972
1.964
1.912
1.905
1.887
1.881
1.873
1.867
1.849
1.843
1.540
1.525
1.523
1.505
1.496
1.485
1.479
1.474
1.469
1.450
1.433
1.430
1.427
1.423
1.411
1.408
1.405
1.399
1.393
1.387
1.378
1.375
1.368
1.365
1.362
1.359
1.356
1.353
1.348
1.343
1.339
1.334
1.316
1.277
1.219
0.905
0.882
0.501
O
F
15a
1.00
1.05
1.93
1.07
5.57
1.09
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 -0
f1 (ppm)


210.331
128.301 c6d6
128.080 c6d6
127.819 c6d6
92.567
90.873
43.153
36.346
36.259
35.562
35.347
29.840
29.615
17.679
17.597
O
F
15a
36.346
36.259
35.562
35.347
36.5 36.0 35.5
f1 (ppm)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


172.713
172.732
172.751
172.787
172.805
172.827
172.856
172.876
172.906
172.928
172.947
172.982
173.000
173.019
O
F
15a
-172.7
-172.9
-173.1
f1 (ppm)
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
-230
-240
f1 (ppm)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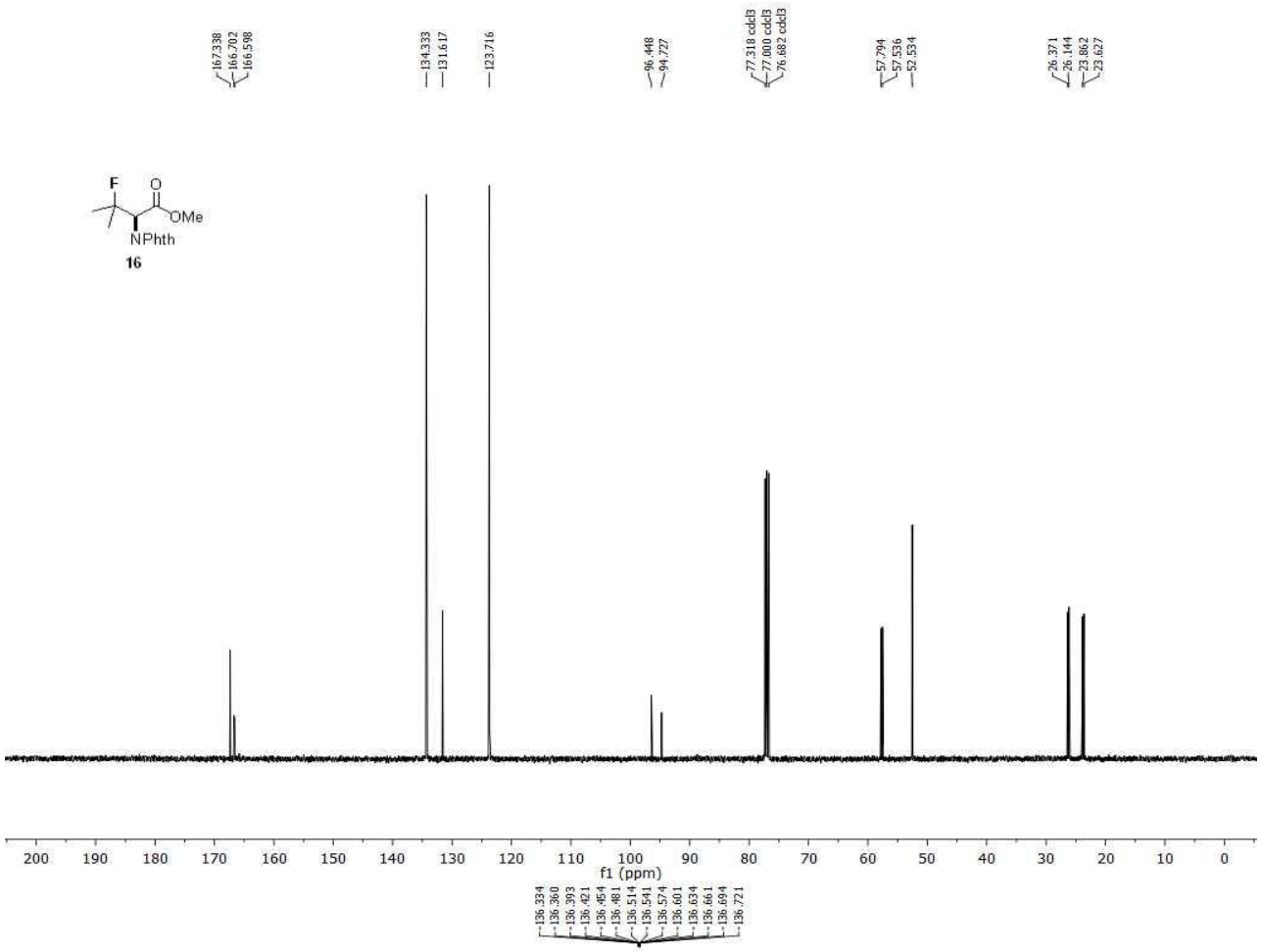
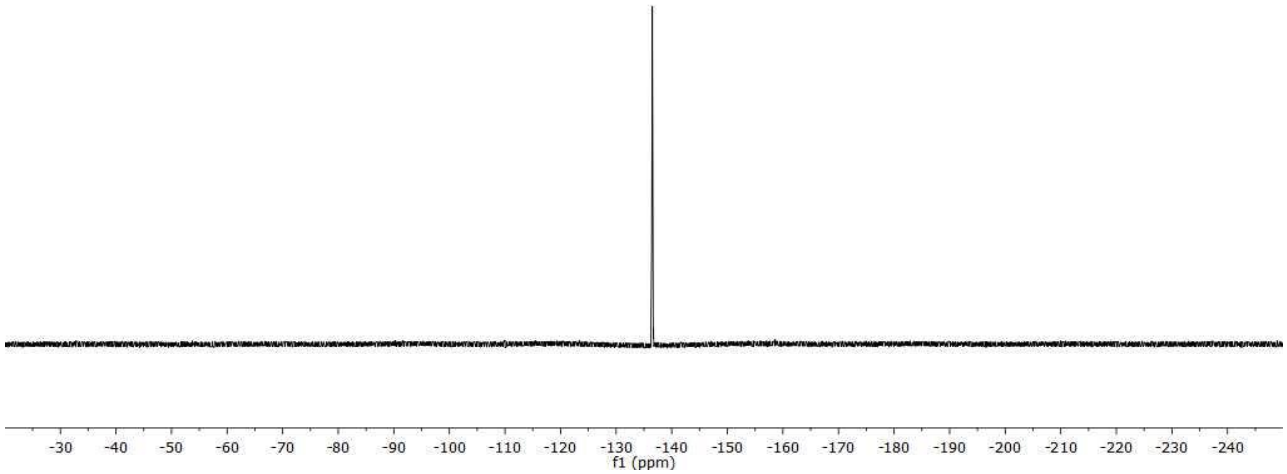
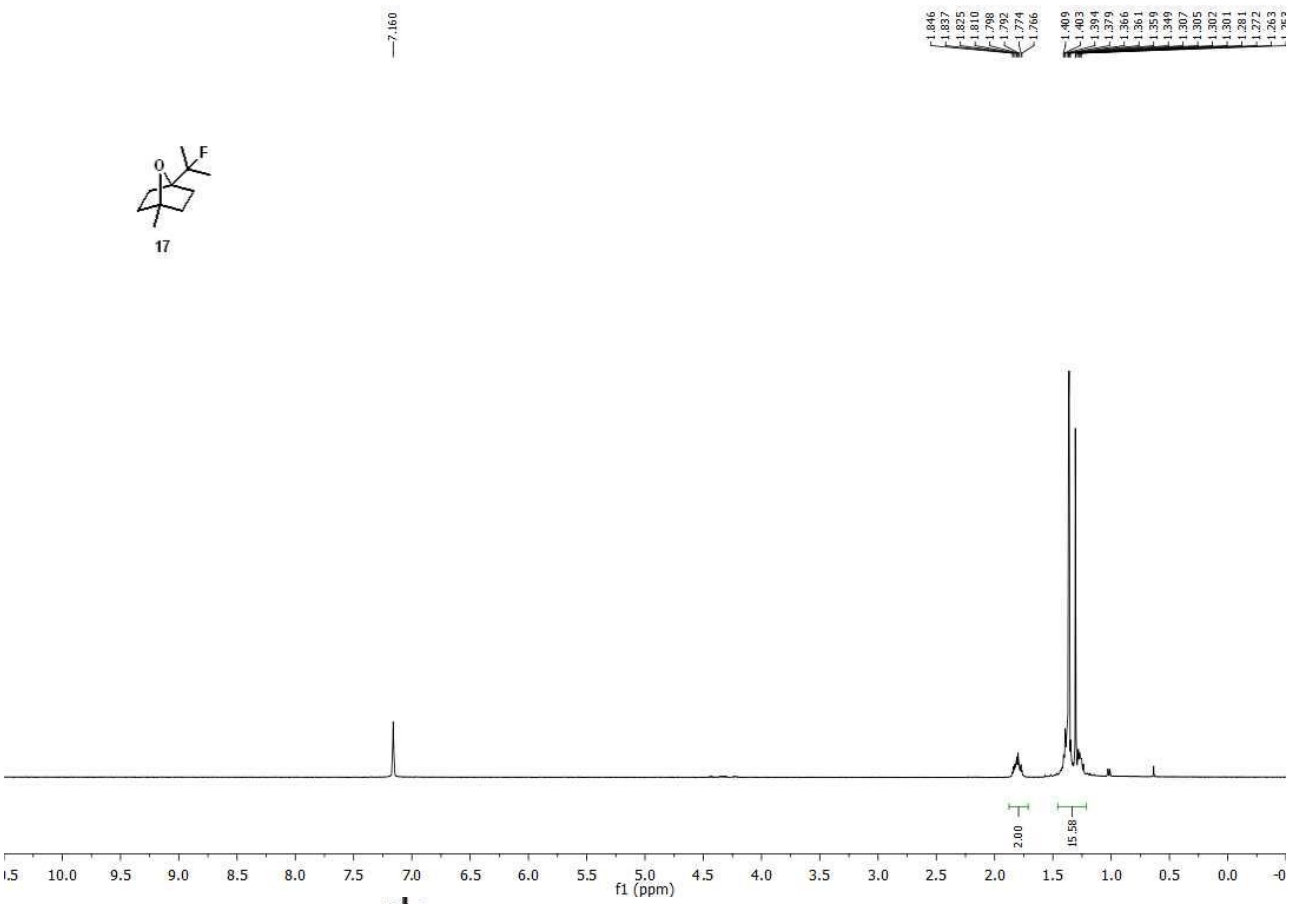
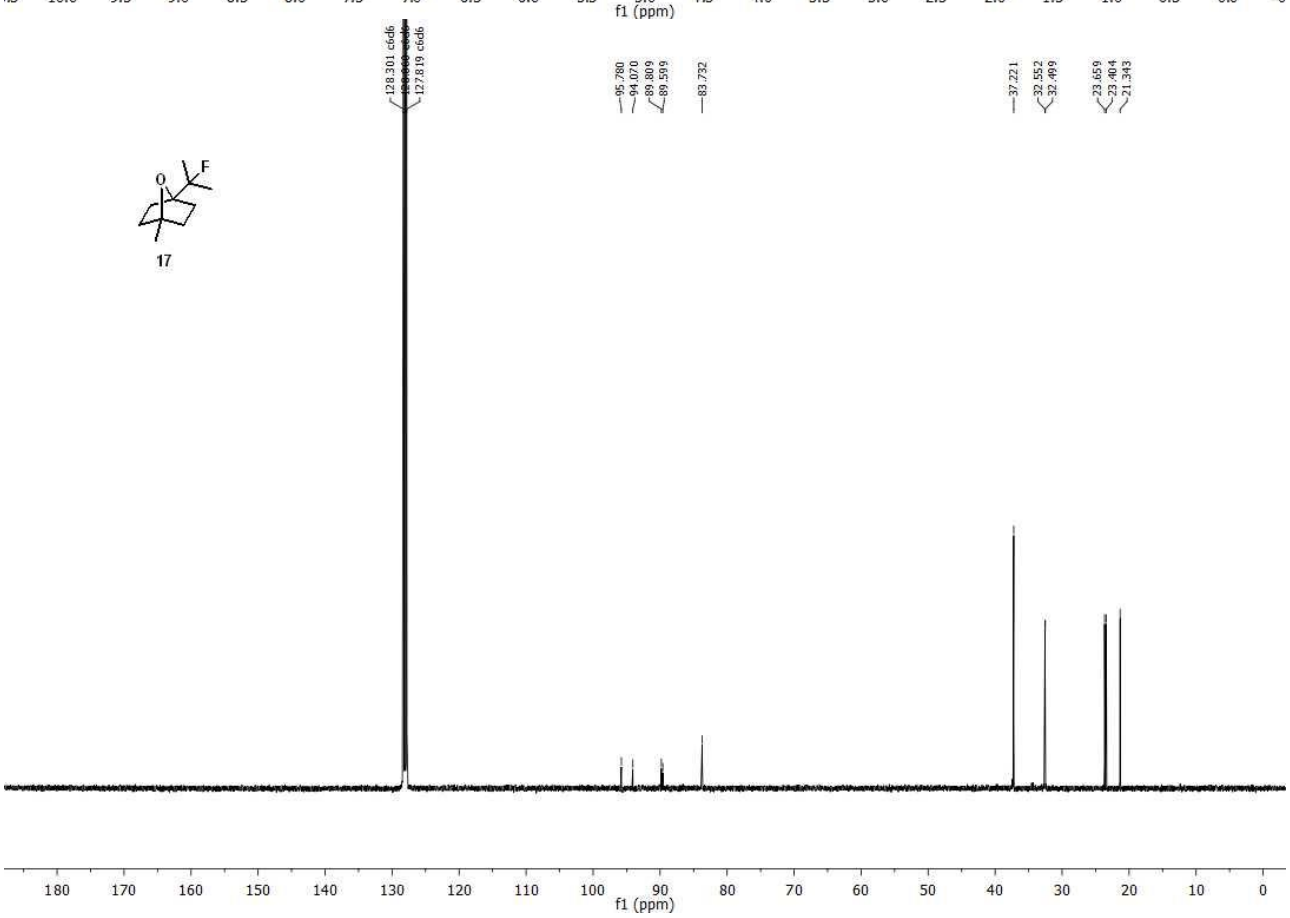
7.886
7.878
7.772
7.765
7.759
7.751
7.260 cdcl3
4.993
4.968
3.717
1.716
1.659
1.573
1.517
F
O
OMe
NPhth
16
1.80
1.93
1.00
2.99
3.27
3.07
f1 (ppm)

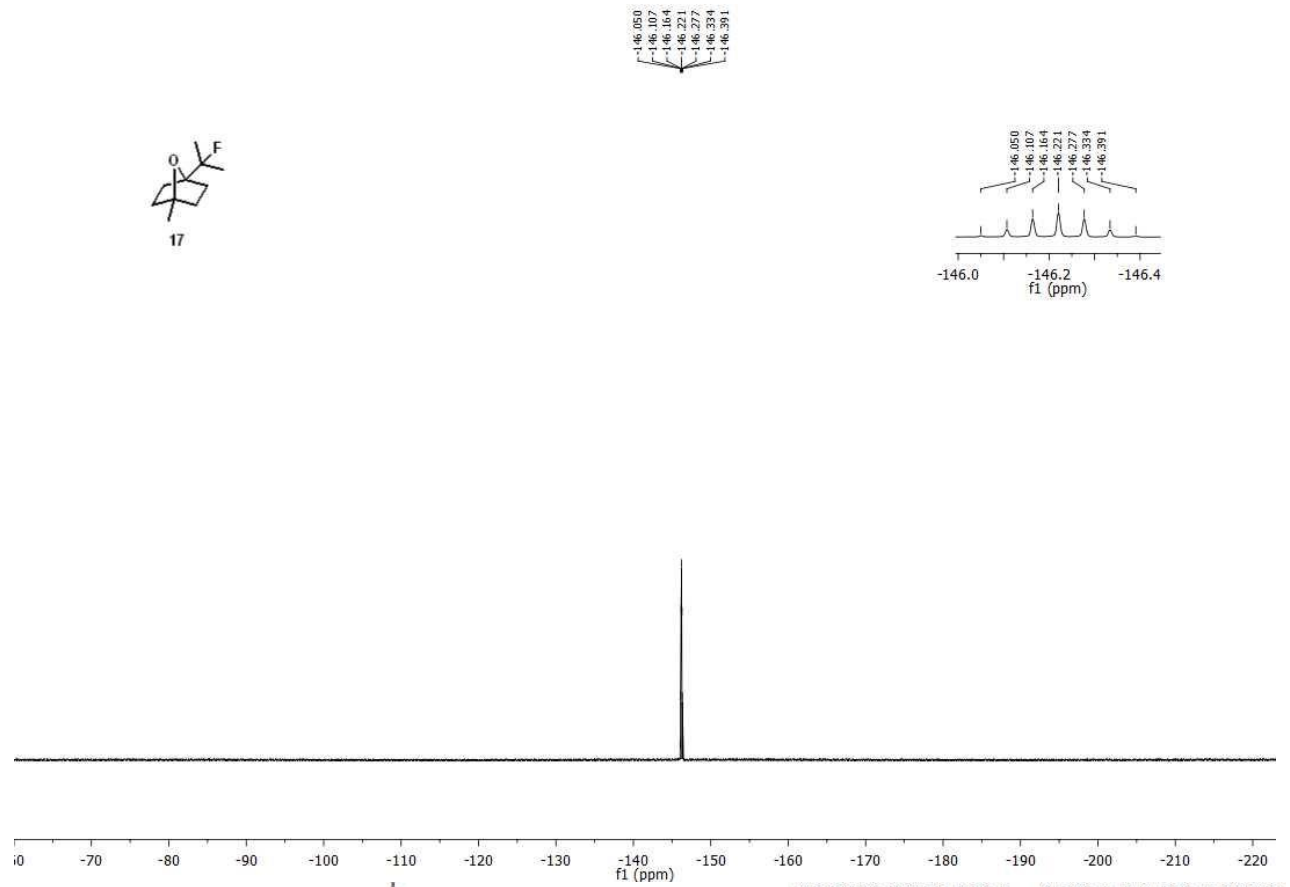

167.338
166.702
166.598
134.333
131.617
123.716
96.448
94.727
77.318 cdcl3
77.000 cdcl3
76.682 cdcl3
57.794
57.536
52.534
26.371
26.144
23.862
23.627
F
O
OMe
NPhth
16
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
136.334
136.360
136.393
136.421
136.454
136.481
136.514
136.541
136.574
136.601
136.634
136.661
136.694
136.721


F
O
OMe
NPhth
16
136.334
136.360
136.393
136.421
136.454
136.481
136.514
136.541
136.574
136.601
136.634
136.661
136.694
136.721
-136.3 -136.4 -136.5 -136.6 -136.7
f1 (ppm)


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


7.160
1.846
1.837
1.825
1.810
1.798
1.792
1.774
1.766
1.409
1.403
1.394
1.379
1.366
1.361
1.359
1.349
1.307
1.305
1.302
1.301
1.281
1.272
1.263
O
F
17
2.00
15.58
f1 (ppm)


128.301 c6d6
127.819 c6d6
95.780
94.070
89.809
89.599
83.732
37.221
32.552
32.499
23.659
23.404
21.343
O
F
17
f1 (ppm)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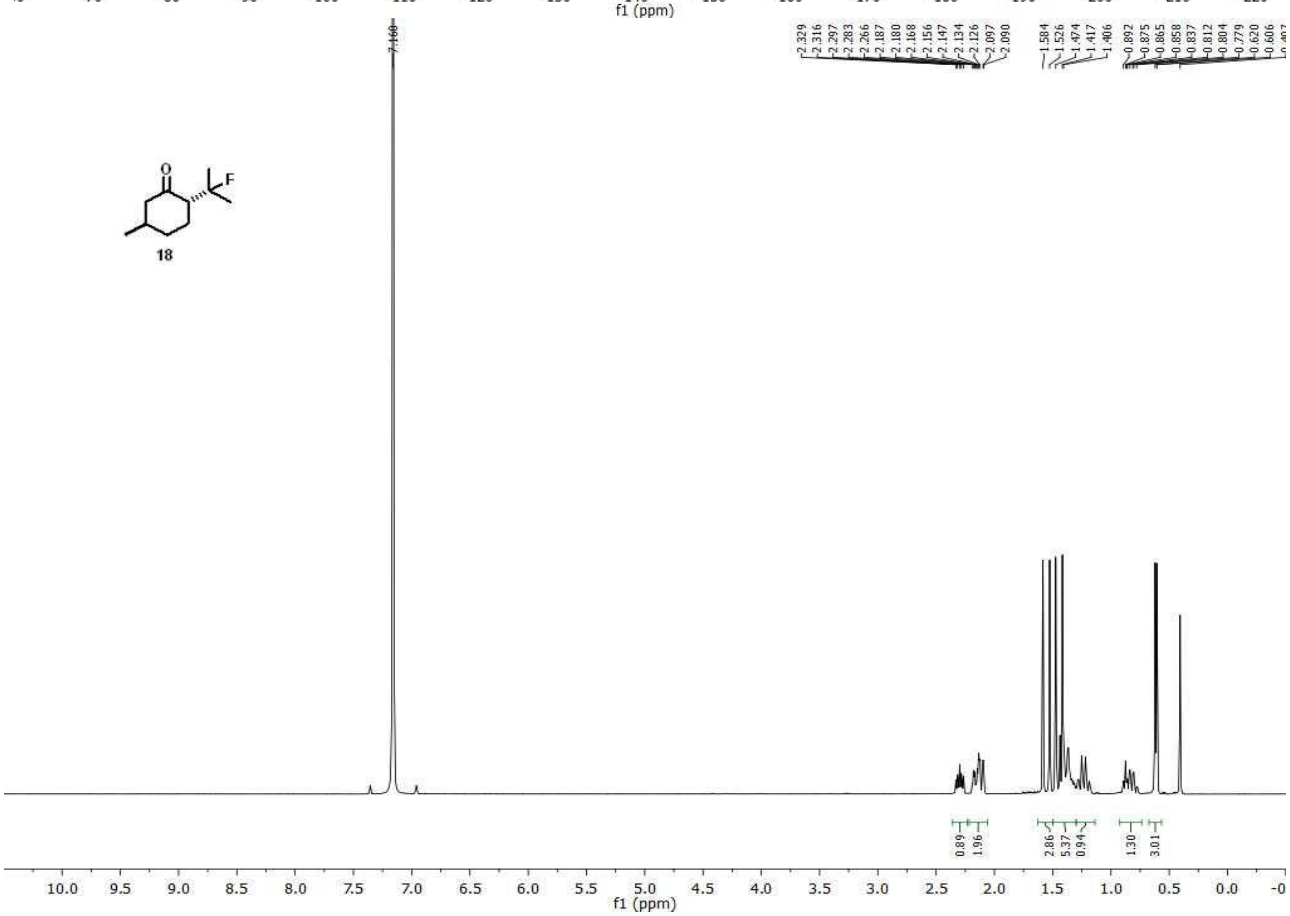
-146.107
-146.164
-146.221
-146.277
-146.334
-146.391
F
O
17
-146.0
-146.2
-146.4
f1 (ppm)
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)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2.329
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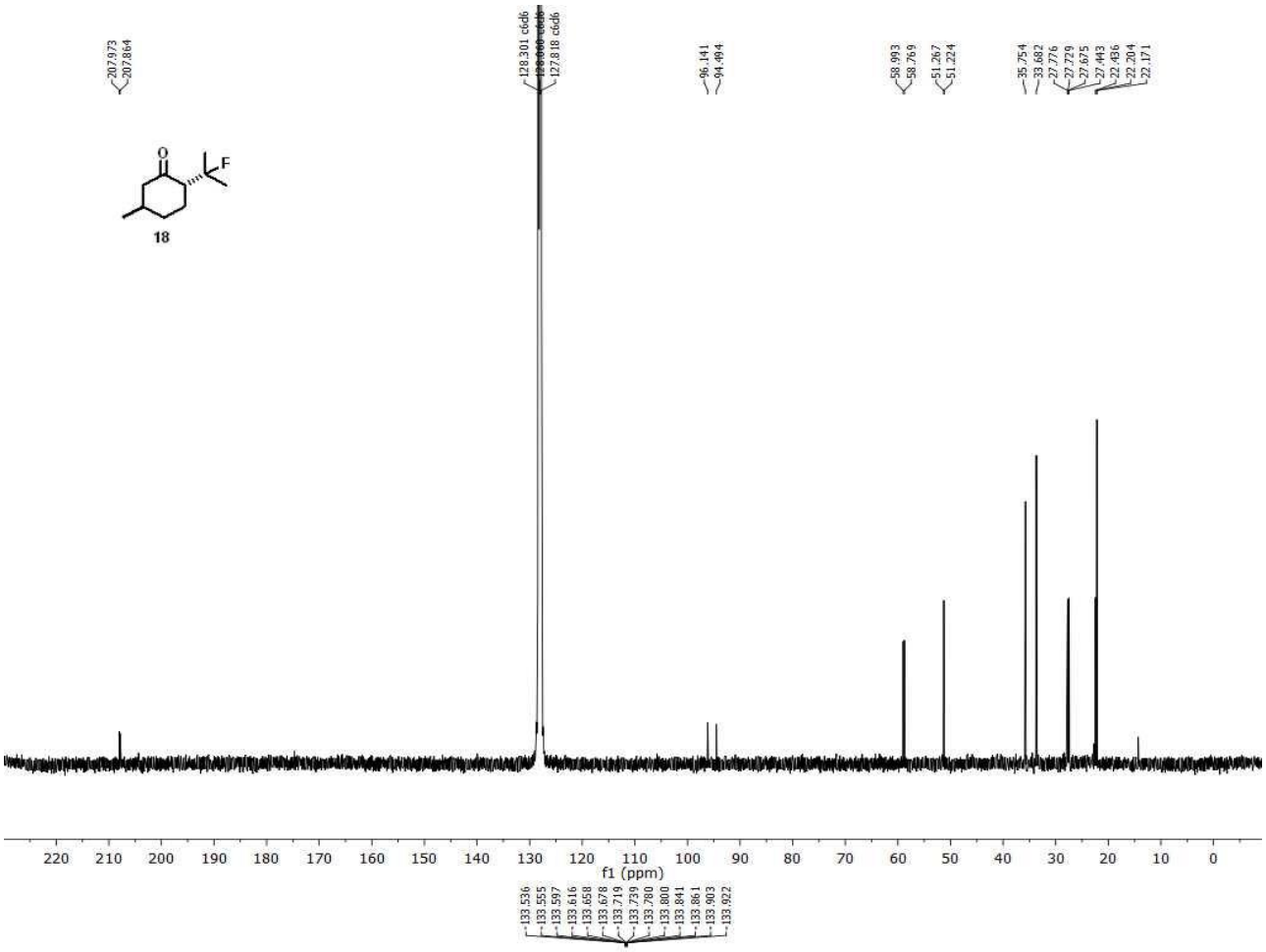
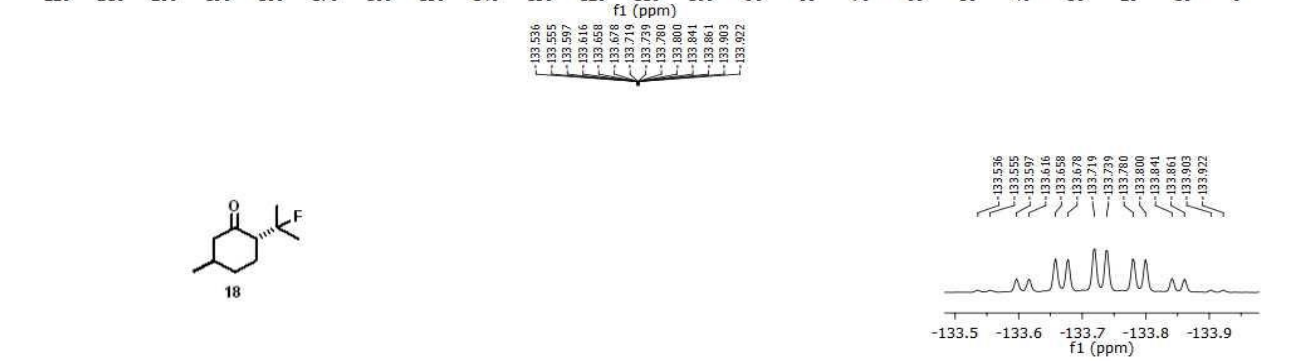
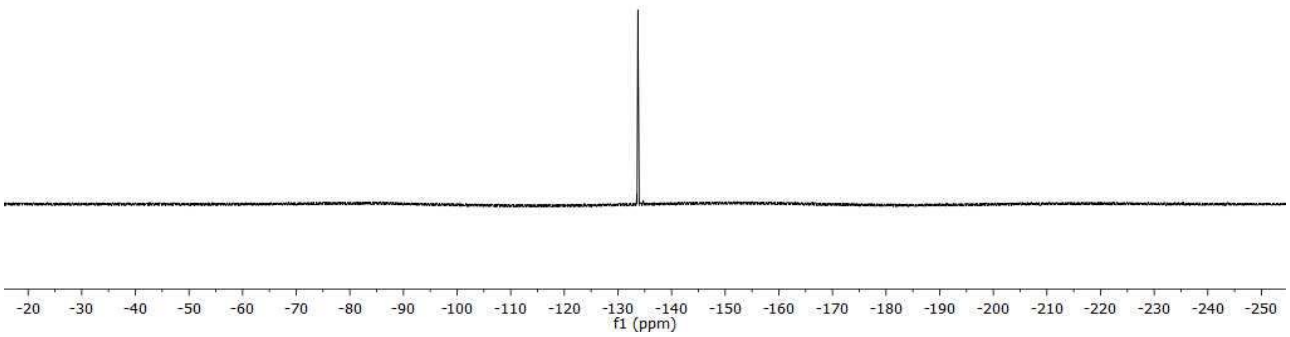
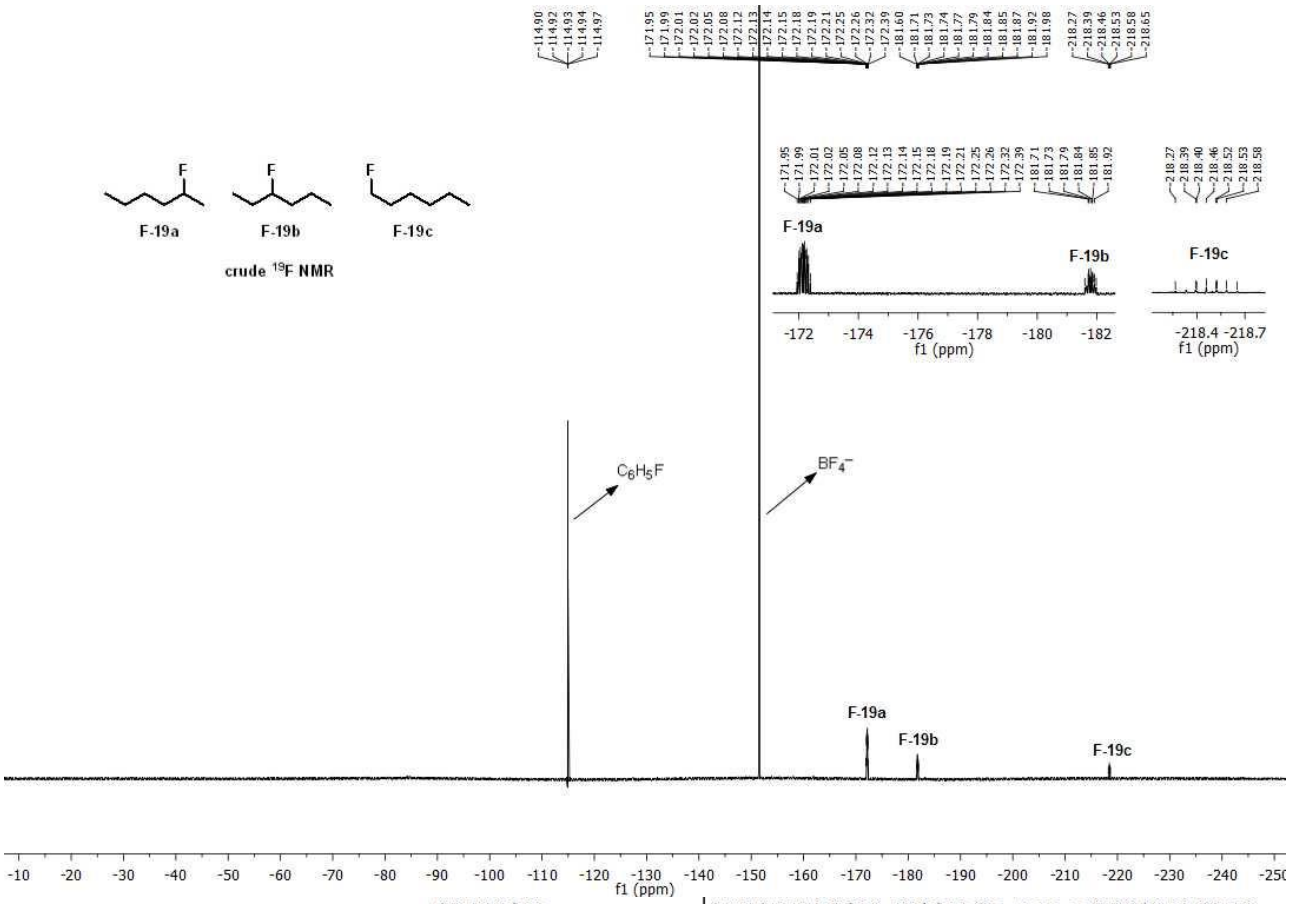
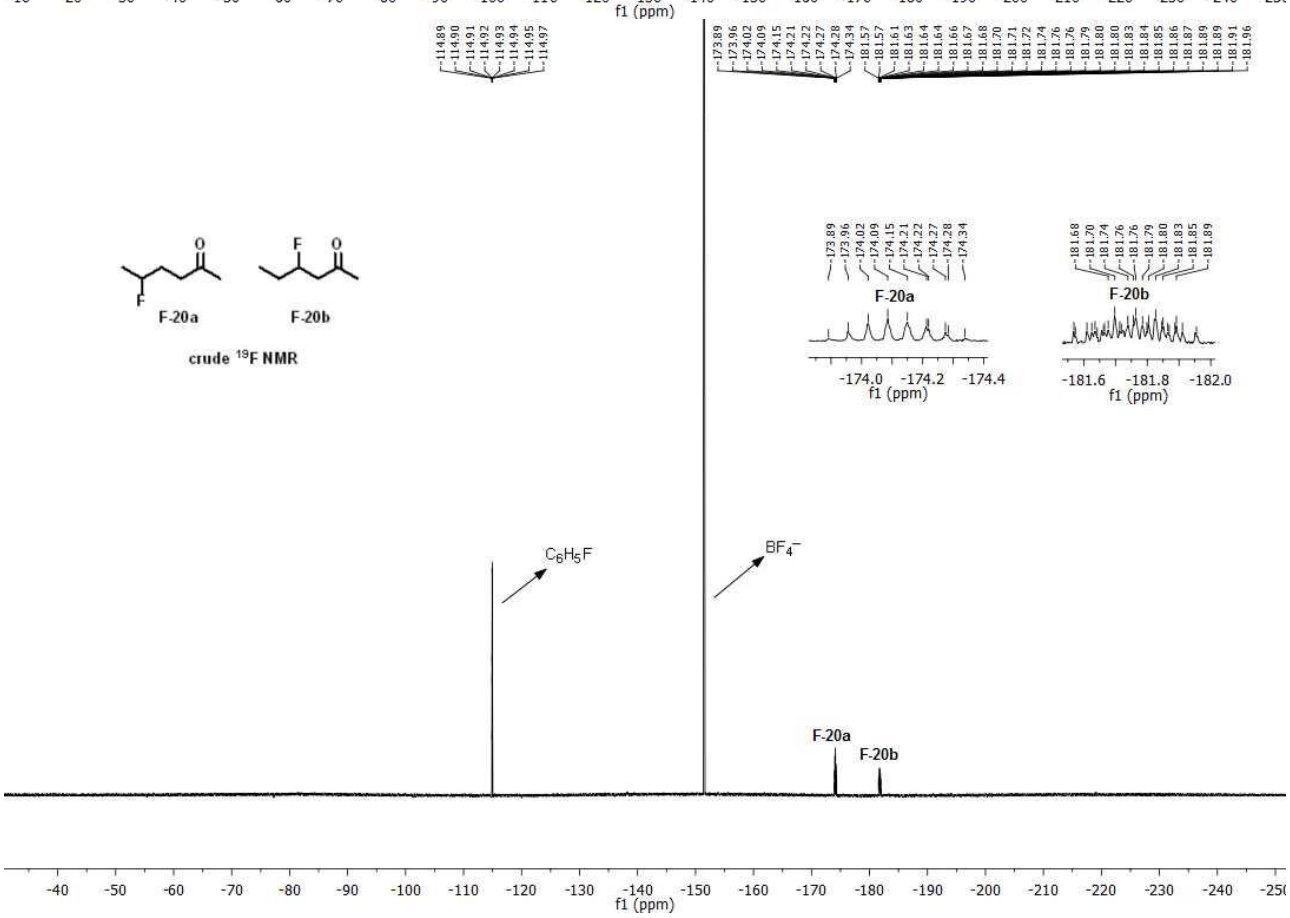
2.187
2.180
2.168
2.156
2.147
2.134
2.126
2.097
2.090
1.584
1.526
1.474
1.417
1.406
0.892
0.875
0.865
0.858
0.837
0.812
0.804
0.779
0.620
0.606
O
F
18
0.89
1.96
2.86
5.37
0.94
1.30
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

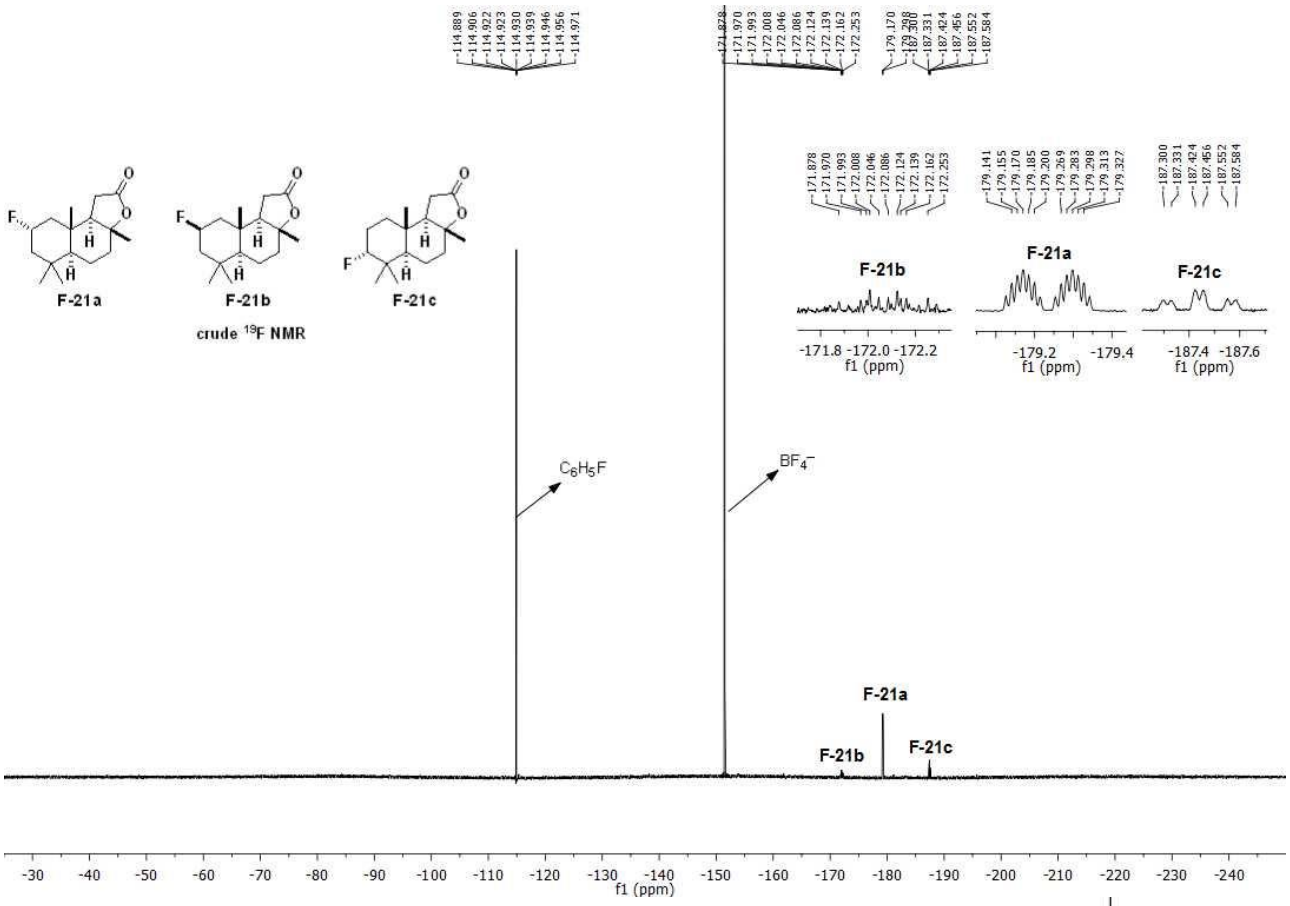

207.973
207.864
128.301 cdcl3
128.060 cdcl3
127.818 cdcl3
96.141
94.494
58.993
58.769
51.267
51.224
35.754
33.682
27.776
27.729
27.675
27.443
22.436
22.204
22.171
O
F
18
f1 (ppm)

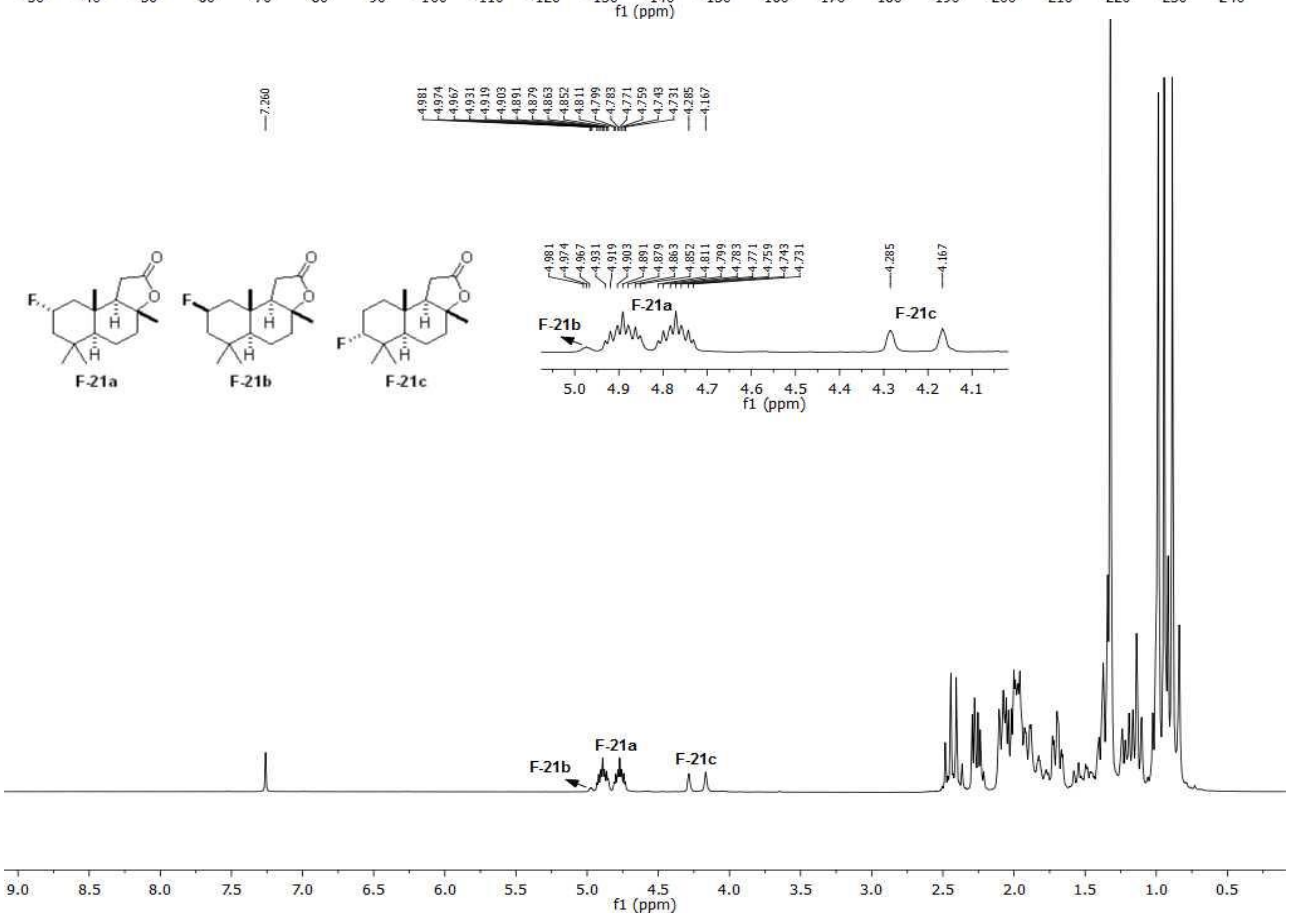

-133.536
-133.555
-133.597
-133.616
-133.658
-133.678
-133.719
-133.739
-133.780
-133.800
-133.841
-133.861
-133.903
-133.922
O
F
18
-133.5
-133.6
-133.7
-133.8
-133.9
f1 (ppm)

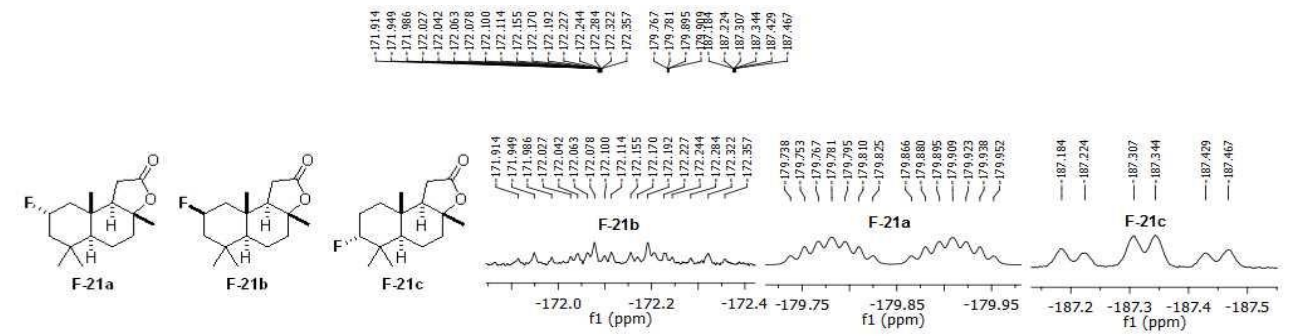

f1 (ppm)

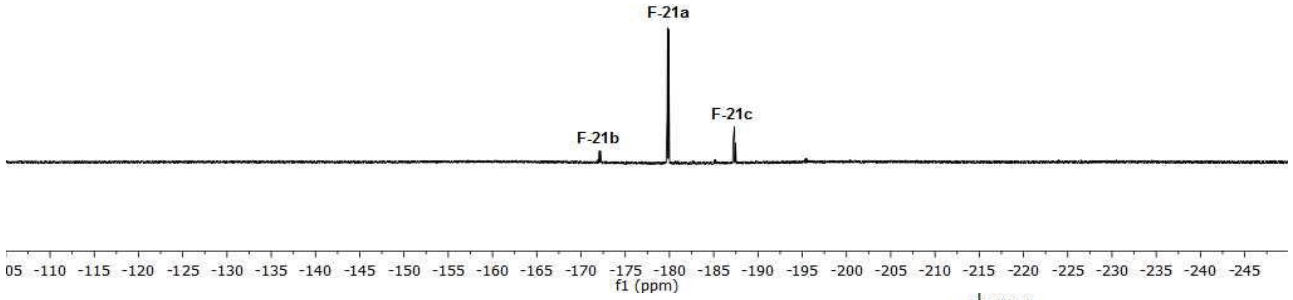

F-19a
F-19b
F-19c
crude ^{19}F NMR
C_6H_5F
BF_4^-
f1 (ppm)

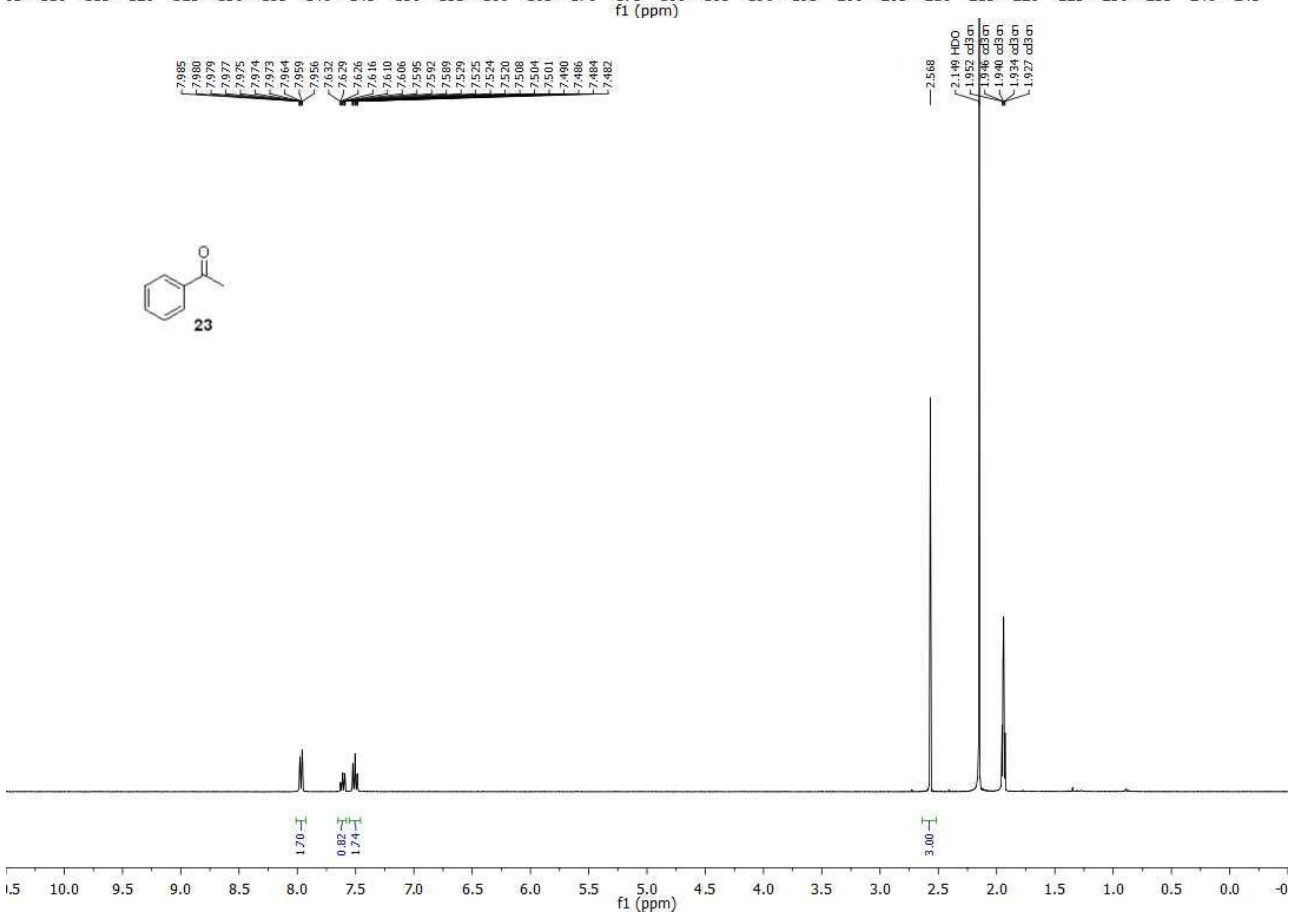

F-20a
F-20b
crude ^{19}F NMR
C_6H_5F
BF_4^-
f1 (ppm)

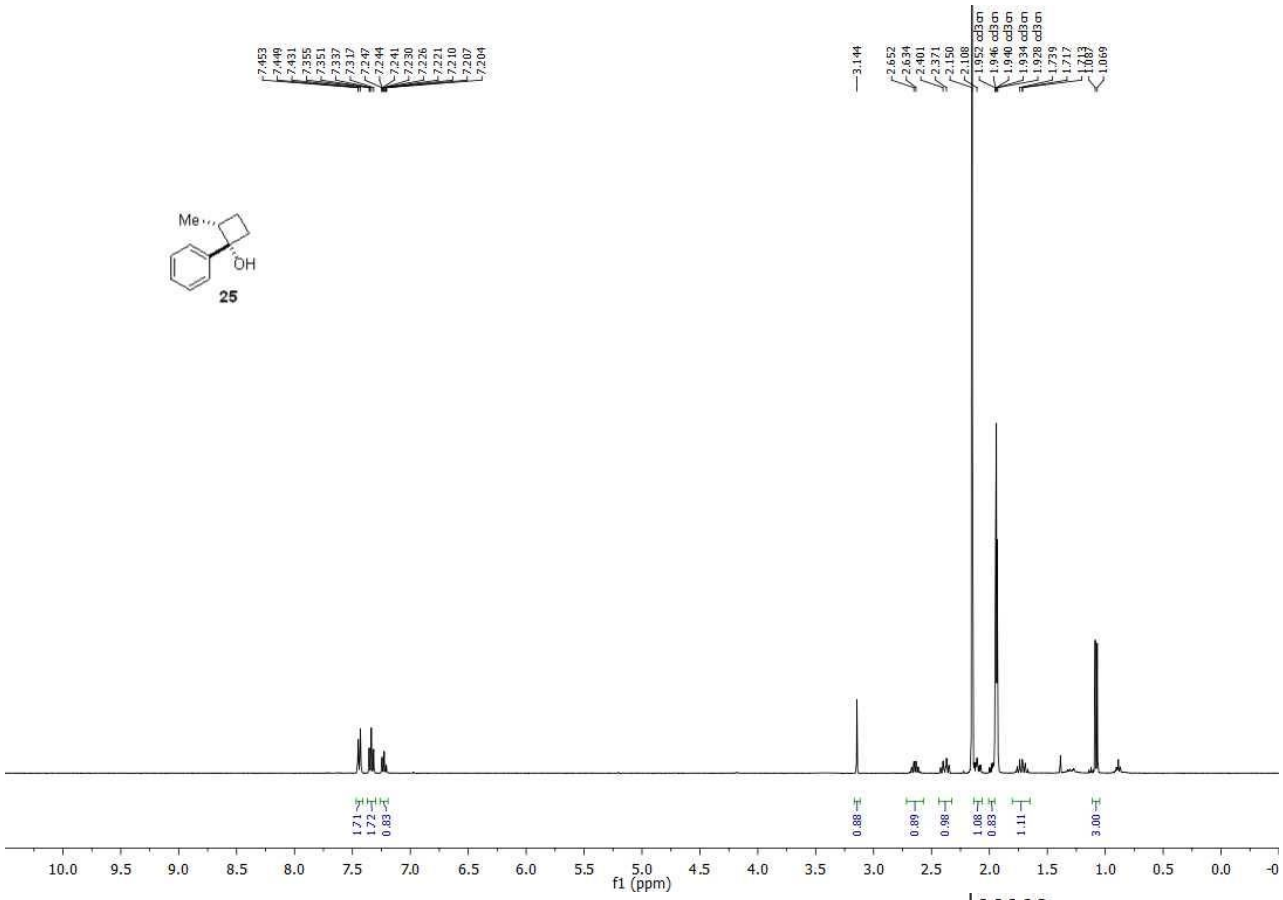

F-21a
F-21b
F-21c
crude ^{19}F NMR
C_6H_5F
BF_4^-
F-21a
F-21b
F-21c
f1 (ppm)

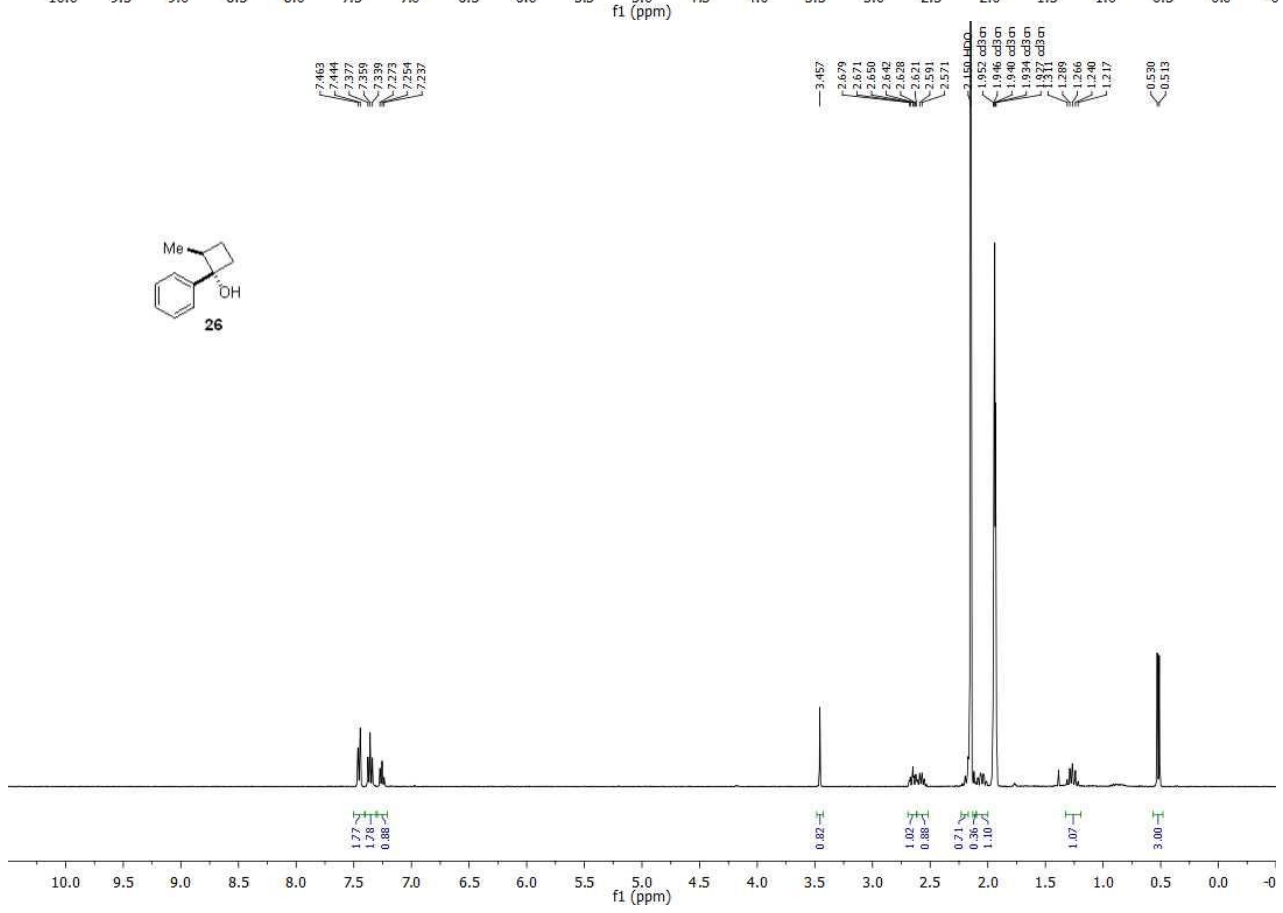

F-21a
F-21b
F-21c
F-21b
F-21a
F-21c
f1 (ppm)

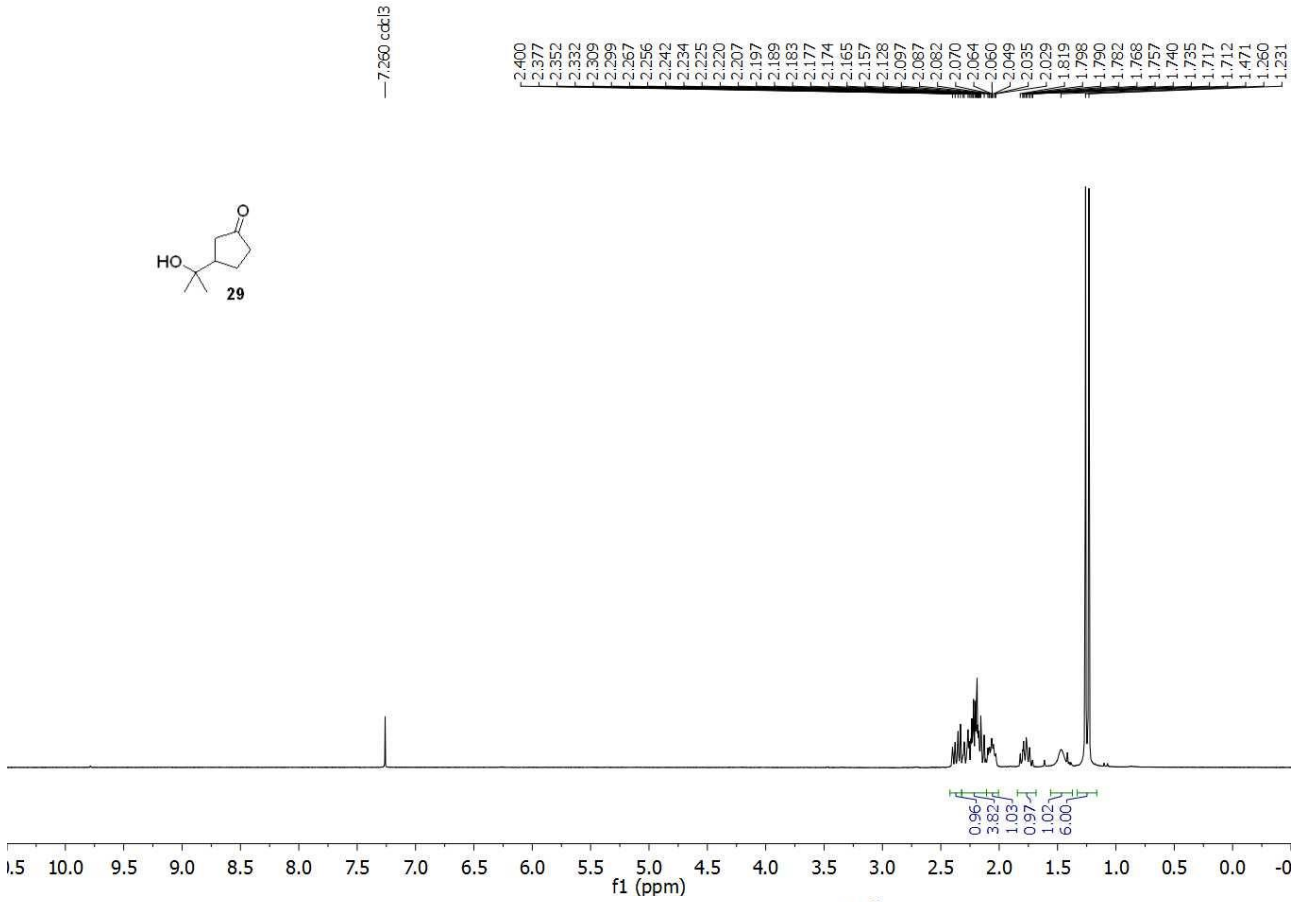

F-21a
F-21b
F-21c
F-21b
F-21a
F-21c
f1 (ppm)
f1 (ppm)
f1 (ppm)

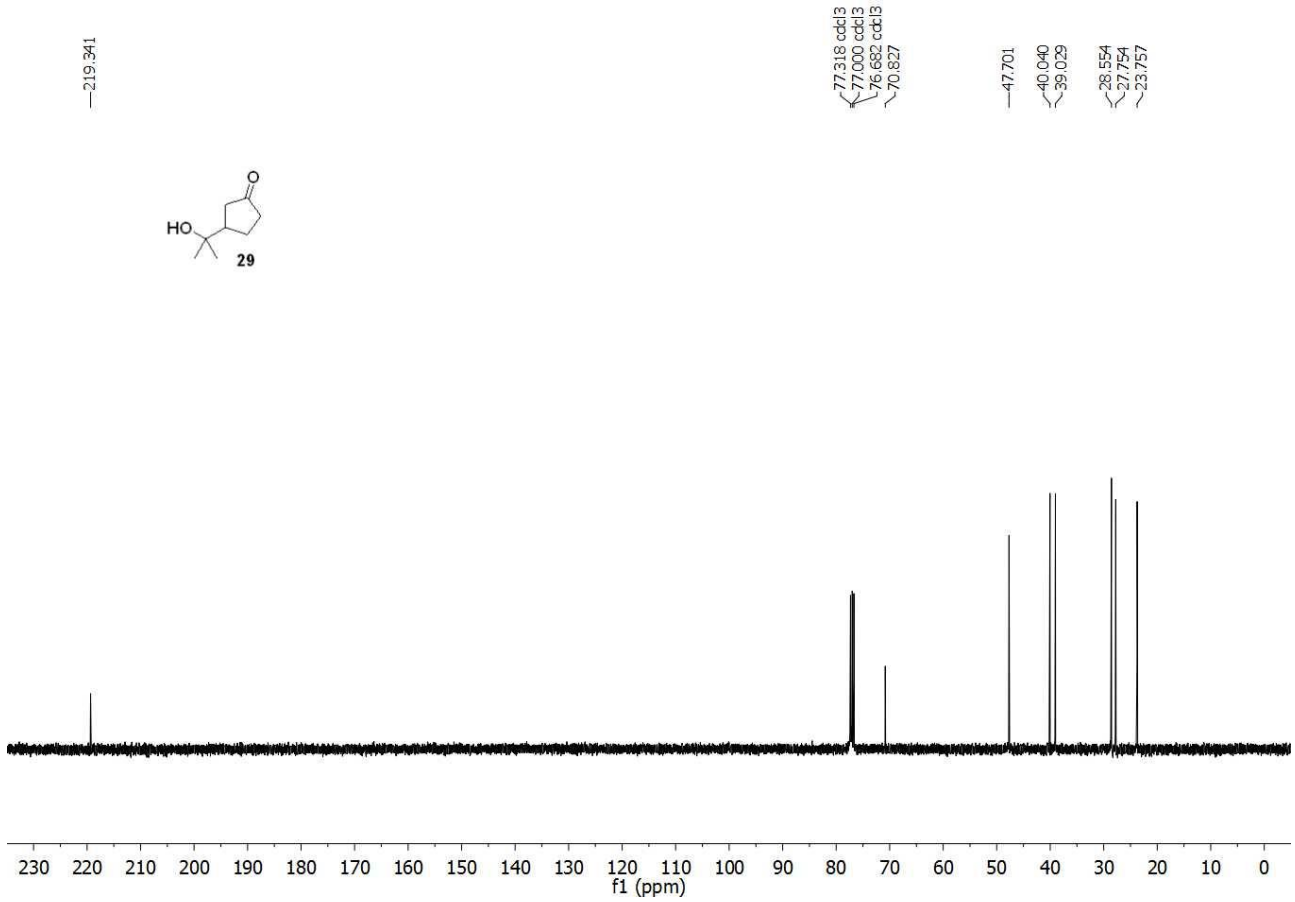

F-21a
F-21b
F-21c
f1 (ppm)


23
1.70
0.82
1.74
3.00
f1 (ppm)


Me
OH
25
f1 (ppm)


Me
OH
26
f1 (ppm)

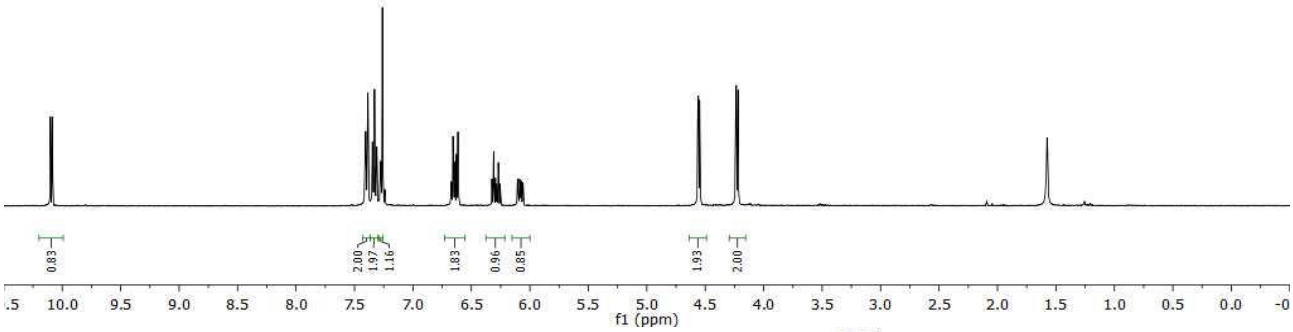

7.260 cdcl3
2.400
2.377
2.352
2.332
2.309
2.299
2.267
2.256
2.242
2.234
2.225
2.220
2.207
2.197
2.189
2.183
2.177
2.174
2.165
2.157
2.128
2.097
2.087
2.082
2.070
2.064
2.060
2.049
2.035
2.029
1.819
1.798
1.790
1.782
1.768
1.757
1.740
1.735
1.717
1.712
1.471
1.260
1.231
HO
O
29
0.96
3.82
1.03
0.97
1.02
6.00
f1 (ppm)


219.341
77.318 cdcl3
77.000 cdcl3
76.682 cdcl3
70.827
47.701
40.040
39.029
28.554
27.754
23.757
HO
O
29
f1 (ppm)

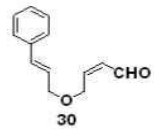

10.101
10.084
7.408
7.405
7.385
7.347
7.329
7.309
7.277
7.261
7.260 cdcl3
7.241
6.658
6.629
6.615
6.325
6.310
6.294
6.285
6.270
6.254
6.105
6.088
6.081
6.076
6.059
4.562
4.558
4.549
4.544
4.238
4.235
4.222
4.219

CHO
O

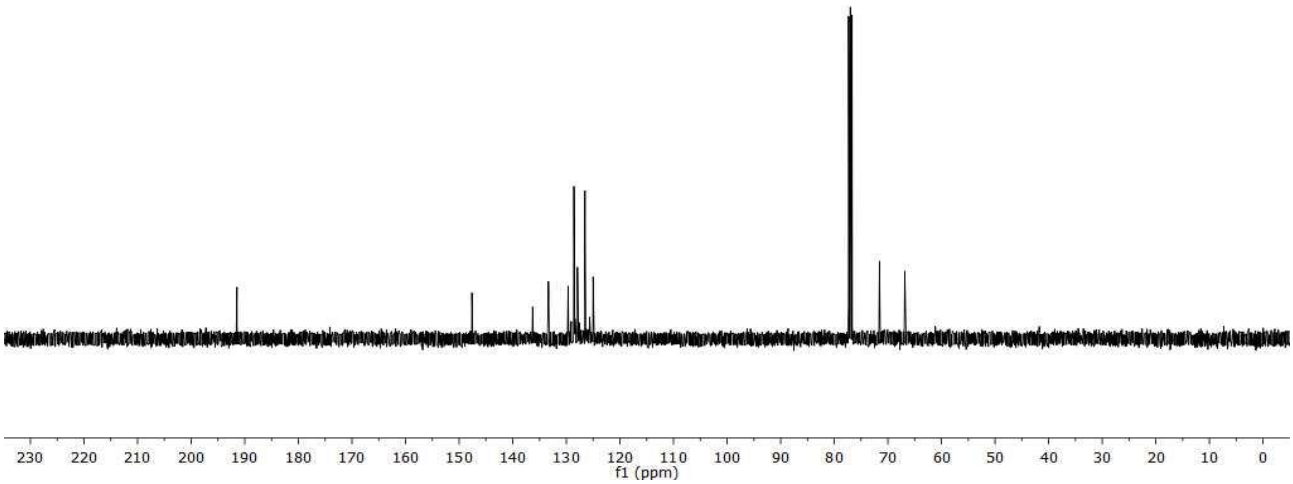
30

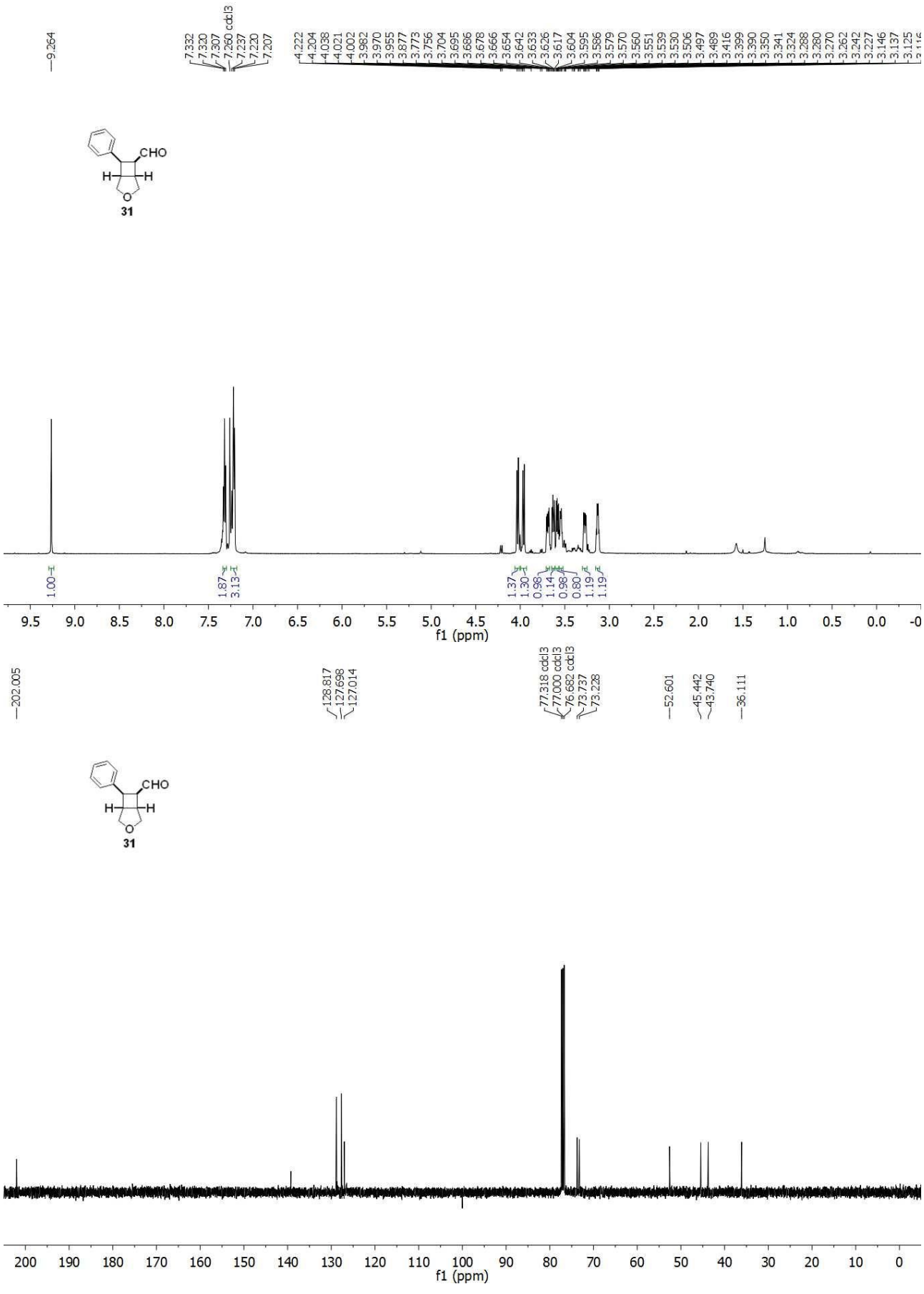

0.83
2.00
1.97
1.16
1.83
0.96
0.85
1.93
2.00
f1 (ppm)

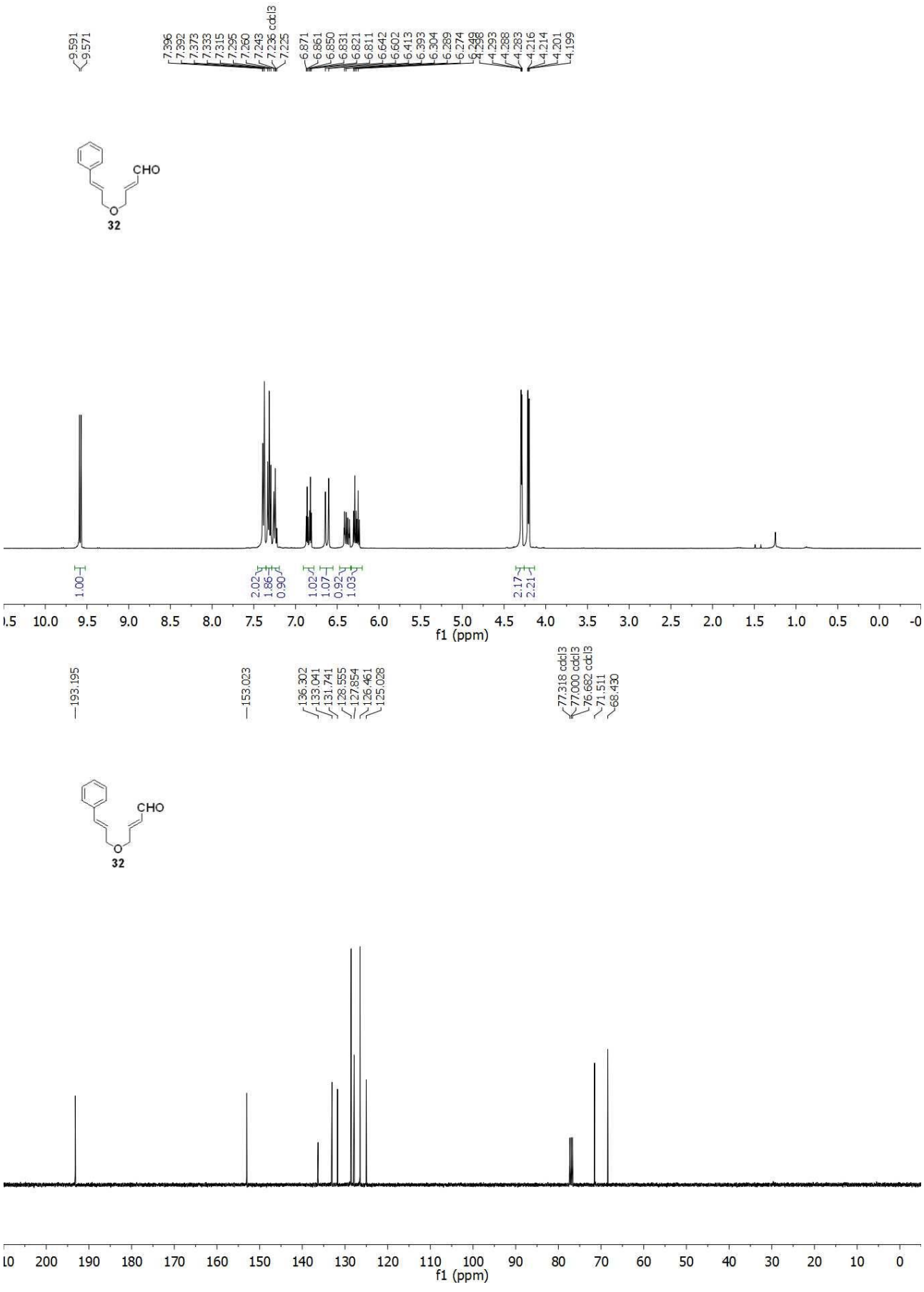

191.453
147.623
136.287
133.336
129.664
128.585
127.919
126.513
125.005
77.318 cdcl3
77.000 cdcl3
76.682 cdcl3
71.561
66.837


CHO
O

30


f1 (ppm)


9.264
7.332
7.320
7.307
7.260 cdcl3
7.237
7.220
7.207
4.222
4.204
4.038
4.021
4.002
3.982
3.970
3.955
3.877
3.773
3.756
3.704
3.695
3.686
3.678
3.666
3.654
3.642
3.633
3.626
3.617
3.604
3.595
3.586
3.579
3.570
3.560
3.551
3.539
3.530
3.506
3.497
3.489
3.416
3.399
3.390
3.350
3.341
3.324
3.288
3.280
3.270
3.262
3.242
3.227
3.146
3.137
3.125
CHO
H
H
O
31
1.00
1.87
3.13
1.37
1.30
0.98
1.14
0.98
0.80
1.19
1.19
f1 (ppm)
202.005
128.817
127.698
127.014
77.318 cdcl3
77.000 cdcl3
76.682 cdcl3
73.737
73.228
52.601
45.442
43.740
36.111
CHO
H
H
O
31
f1 (ppm)


9.591
9.571
7.396
7.392
7.373
7.333
7.315
7.295
7.260
7.243
7.236 cdcl3
7.225
6.871
6.861
6.850
6.831
6.821
6.811
6.642
6.602
6.413
6.393
6.304
6.289
6.274
6.249
6.238
4.293
4.288
4.283
4.216
4.214
4.201
4.199
CHO
O
32
1.00
2.02
1.86
0.90
1.02
1.07
0.92
1.03
2.17
2.21
f1 (ppm)
193.195
153.023
136.302
133.041
131.741
128.555
127.854
126.461
125.028
77.318 cdcl3
77.000 cdcl3
76.682 cdcl3
71.511
68.430
CHO
O
32
f1 (ppm)