Supporting Information

Visible-light Photoredox-Catalyzed Three-Component Radical Alkyl-Acylation of [1.1.1]Propellane

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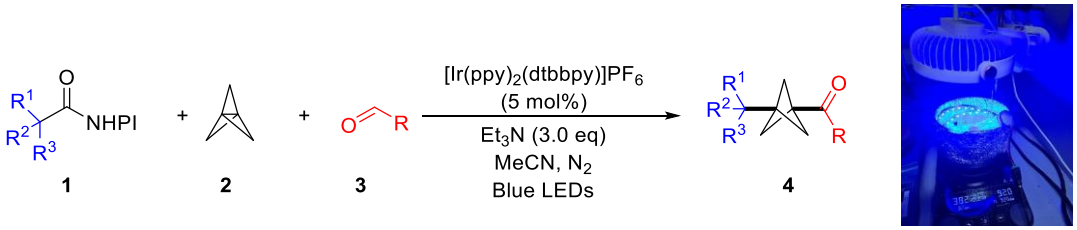
1. General information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents used in reactions were p.A. grade and dried only if indicated. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063-0.2 mm). Melting points were measured on a Yanaco Micro Melting Point Apparatus. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR were recorded on a Variance VNMR 400 or Bruker AV-600 spectro meter in $CDCl_3$. For ^{1}H NMR spectra, data are quoted in the following order: using residual protonated solvent as internal standard ($CDCl_3$ at 7.26 ppm). Multiplicities are indicated s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), coupling constants (*J*) are in Hertz (Hz). For proton-decoupled $^{13}C\{^{1}H\}$ NMR spectra, using deuterated solvent as internal standard ($CDCl_3$ at 77.0 ppm). High resolution mass spectra (HRMS) were obtained on AB 5800 MALDI-TOF/TOF and are recorded using electrospray ionization (ESI). X-ray crystallographic data were collected using the D8 quest X-ray diffractometer.

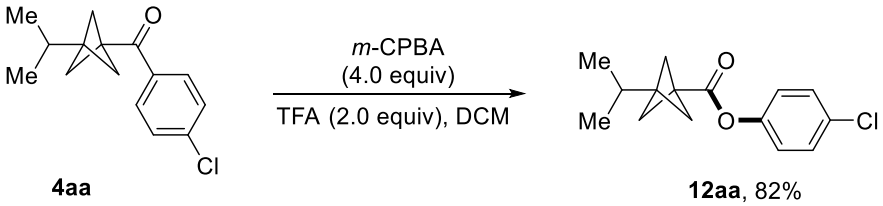
2. General procedure



An over-dried 10 mL reaction tube equipped with a magnetic stir bar was charged with **1** (0.5 mmol, 2.5 equiv.), **2** (0.4 mmol, 2.0 equiv), $[Ir(ppy)_2(dtbbpy)]PF_6$ (9.15 mg, 0.01 mol, 5.0 mmol%), Et_3N (82.0 μL, 0.6 mmol, 3.0 equiv), anhydrous MeCN (3.0 mL) and **3** (0.2 mmol, 1.0 equiv.) under nitrogen atmosphere and the mixture was reacted under the irradiation of blue LEDs (12 W) at room temperature for 24 hours. After **3** was completely consumed (monitored by TLC), the pure product **4** was obtained by flash column chromatography on silica gel.

Light Source, Material of the Irradiation Vessel: The light source used for photochemical experiments was a household Blue LEDs (12V, 12W, 1.0 Meter, 120 dots,) purchased from Alibaba.com; Manufacturer: Philips, China; Broadband source: λ = 450-465 nm; Material of the irradiation vessel: borosilicate reaction tube. Distance from the light source to the irradiation vessel: 5.0 cm (Not use any filters)

3. Product derivation

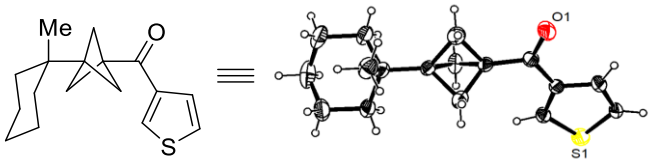


To a 10.0 mL reaction vial equipped with a stir bar was added **4aa** (49.6 mg, 0.20 mmol, 1.0 equiv), *m*-CPBA (140 mg, 0.8 mmol, 4.0 equiv), TFA (30.8 μL, 0.4 mmol, 2.0 equiv), and dry CH_2Cl_2 (2.0 mL). The reaction mixture was allowed to stir at rt for 48 h. After this time, the reaction was quenched with sat aq. $NaHCO_3$ (5.0 mL), and extracted with Et_2O (10.0 mL, 3 times). The combined organic layers were dried (Na_2SO_4), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by silica gel flash column chromatography (gradient hexane/EtOAc) to give the desired product **12aa** as a colorless oil (43.3 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.6 Hz, 2H), 2.05 (s, 6H), 1.94–1.85 (m, 1H), 0.89 (d, J = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.2, 139.3, 131.0, 129.0, 128.6, 64.2, 51.1, 39.1, 26.7, 19.5. HRMS (ESI) Exact mass calculated for $[C_{15}H_{17}ClO_2Na]^+$: 287.0809; found: 287.0812.

4. X-ray Structure of products 4b

Single crystal of **4b** was obtained by recrystallization from dichloromethane/n-hexane solution. The crystal structure was determined by standard crystallographic methods. A colorless light-blocked crystal (0.12 × 0.11 × 0.1 mm^3) was used for single-crystal X-ray diffraction. The data were collected at 273.15 K using a Bruker D8 QUEST X-ray diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Methods and refined by full-matrix least-squares techniques on F_2 with anisotropic displacement parameters for all atoms using SHELX-2014. All the processes were performed within Olex2. The final refinements included anisotropic displacements parameters for all atoms and a secondary extinction correction. The crystallographic parameter data is listed in **Table S1**. Crystal Structure of **4b** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clearity and Crystallographic data for **4b** have been deposited with the Cambridge Crystallographic Data Center as CCDC: 2314777**,** and the crystal data and details of the data collection are given in **Table S1**.

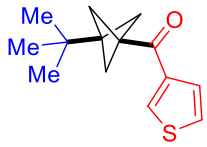
Table S1. Crystal data of **4b**



Empirical formula	$C_{17}H_{22}OS$	
CCDC	2314777	
Formula weight	274.40	
Temperature(K)	273.15	
Wavelength(Å)	0.71073	
Crystal system	monoclinic	
space group	$P2_1/n$	
Unit cell dimensions	a = 6.4888(10) Å b = 17.779(3) Å c = 13.5432(19) Å	α =90° β=101.669(4)° γ = 90°
Volume(Å^3)	1530.1(4)	
Z	4	
Calculated density(g·cm^{-3})	1.191	
μ/mm^{-1}	0.202	
F(000)	592.0	
Crystal size(mm)	0.13 × 0.12 × 0.1	
Radiation	MoKα (λ = 0.71073)	
2θ range for data collection/°	4.582 to 55.024	
h, k, l ranges	-8 ≤ h ≤ 8, -23 ≤ k ≤ 23, -17 ≤ l ≤ 17	
Reflections collected	23519	
Independent reflections	3512 [R_{int} = 0.0480, R_{sigma} = 0.0384]	
Completeness	99.9%	
Absorption correction	multi-scan	
Data / restraints / parameters	3512/0/173	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2σ (I)]	R_1 = 0.0587, wR_2 = 0.1443	
R indices (all data)	R_1 = 0.1067, wR_2 = 0.1666	
Largest diff. peak and hole	0.26/-0.25 e·Å^{-3}	

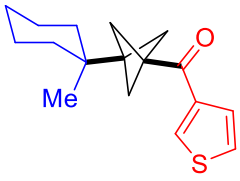
5. Characterization data of products

(3-(tert-butyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-3-yl)methanone (4a)



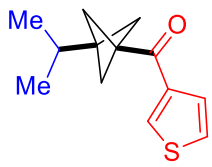
White Solid (35.1 mg, 75% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 72–73 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.12 (m, 1H), 7.58-7.55 (m, 1H), 7.28–7.25 (m, 1H), 2.02 (s, 6H), 0.88 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.6, 141.0, 132.6, 127.6, 125.6, 49.3, 48.1, 41.5, 29.3, 25.7. HRMS (ESI) Exact mass calculated for $[C_{14}H_{18}OSNa]^+$: 257.0971; found: 257.0976

(3-(1-methylcyclohexyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-3-yl)methanone (4b)



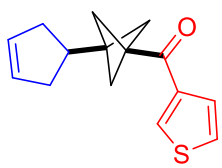
White Solid (40.1 mg, 73% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 74–75 ℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.04 (s, 6H), 1.63–1.59 (m, 1H), 1.55–1.50 (m, 2H), 1.39 (d, *J* = 12.9 Hz, 2H), 1.23 (d, *J* = 4.2 Hz, 4H), 1.11 (d, *J* = 12.1 Hz, 1H), 0.86 (s, 3H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.8, 141.1, 132.7, 127.6, 125.7, 49.1, 48.8, 41.9, 33.3, 31.4, 26.3, 21.9, 19.4. HRMS (ESI) Exact mass calculated for $[C_{17}H_{22}OSNa]^+$: 297.1284; found: 297.1285

(3-isopropylbicyclo[1.1.1]pentan-1-yl)(thiophen-3-yl)methanone (4c)



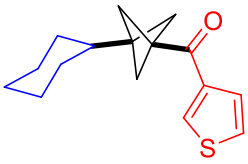
White Solid (22.5 mg, 51% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 70–71 ℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 2.9, 1.2 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.28 (dd, *J* = 5.1, 2.8 Hz, 1H), 2.03 (s, 6H), 1.79–1.70 (m, 1H), 0.87 (d, *J* = 6.8 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.5, 141.1, 132.7, 127.6, 125.7, 50.5, 44.9, 42.9, 28.2, 18.6. HRMS (ESI) Exact mass calculated for $[C_{13}H_{16}OSNa]^+$: 243.0814; found: 243.0816

(3-(cyclopent-3-en-1-yl)bicyclo[1.1.1]pentan-1-yl)(thiophen-3-yl)methanone (4d)



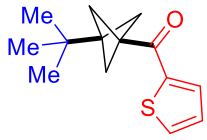
White Solid (30.3 mg, 62% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 65–68 ℃ ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.28 (dd, *J* = 5.1, 2.9 Hz, 1H), 5.64 (s, 2H), 2.44–2.37 (m, 3H), 2.22–2.13 (m, 2H), 2.04 (s, 6H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 192.3, 141.0, 134.0, 130.0, 128.2, 125.8, 50.9, 43.7, 43.0, 37.4, 35.1. HRMS (ESI) Exact mass calculated for $[C_{15}H_{16}OSNa]^+$: 267.0814; found: 267.0817

(3-cyclohexylbicyclo[1.1.1]pentan-1-yl)(thiophen-3-yl)methanone (4e)



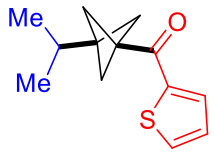
White Solid (35.4 mg, 68% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 70–73 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 2.8, 1.3 Hz, 1H), 7.58 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.28 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.03 (s, 6H), 1.76–1.71 (m, 2H), 1.68–1.63 (m, 3H), 1.38–1.33 (m, 1H), 1.26–1.14 (m, 3H), 0.88 (dd, *J* = 12.3, 3.4 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 192.5, 141.0, 132.7, 127.6, 125.7, 50.7, 44.0, 43.2, 37.7, 29.0, 26.1, 25.9. HRMS (ESI) Exact mass calculated for $[C_{16}H_{20}OSNa]^+$: 283.1127; found: 283.1130

(3-(tert-butyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (4f)



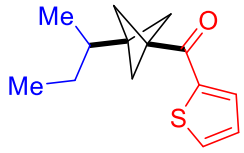
White Solid (36.6 mg, 78% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 70–71 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.61 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.11 (dd, *J* = 5.0, 3.8 Hz, 1H), 2.04 (s, 6H), 0.89 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 191.0, 142.9, 133.3, 132.8, 127.9, 49.4, 48.0, 41.1, 29.4, 25.7. HRMS (ESI) Exact mass calculated for $[C_{14}H_{18}OSNa]^+$: 257.0971; found: 257.0973

(3-isopropylbicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (4g)



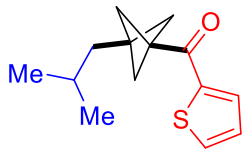
White Solid (25.6 mg, 58% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 78–80 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.61 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.05 (s, 6H), 1.75 (p, *J* = 6.8 Hz, 1H), 0.88 (d, *J* = 6.8 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.8, 142.9, 133.3, 132.8, 127.9, 50.6, 44.8, 42.5, 28.2, 18.6. HRMS (ESI) Exact mass calculated for $[C_{13}H_{16}OSNa]^+$: 243.0814; found: 243.0815

(3-(sec-butyl)bicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (4h)



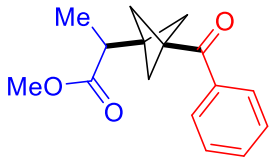
White Solid (29.9 mg, 58% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 71–72 °C ^{1}H NMR (400 MHz, $CDCl_3$) 1H NMR (400 MHz, Chloroform-d) δ 7.82 (dd, J = 3.8, 1.1 Hz, 1H), 7.61 (dd, J = 4.9, 1.1 Hz, 1H), 7.11 (dd, J = 4.9, 3.8 Hz, 1H), 2.06 (s, 6H), 1.50–1.42 (m, 2H), 1.07–0.98 (m, 1H), 0.90 (t, J = 7.1 Hz, 3H), 0.84 (d, J = 6.6 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.8, 142.9, 133.3, 132.8, 127.9, 51.0, 44.5, 42.8, 34.9, 25.9, 15.3, 12.1. HRMS (ESI) Exact mass calculated for $[C_{14}H_{18}OSNa]^+$: 257.0971; found: 257.0968

(3-isobutylbicyclo[1.1.1]pentan-1-yl)(thiophen-2-yl)methanone (4i)



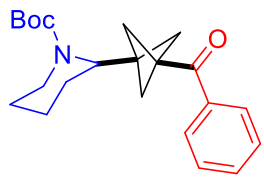
White Solid (25.8 mg, 55% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 82–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.61 (dd, *J* = 4.9, 1.1 Hz, 1H), 7.12 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.15 (s, 6H), 1.68–1.64 (m, 1H), 1.42 (d, *J* = 6.5 Hz, 2H), 0.93 (s, 3H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 190.4, 142.9, 133.3, 132.8, 128.0, 53.9, 44.0, 40.5, 39.8, 26.5, 23.4. HRMS (ESI) Exact mass calculated for $[C_{14}H_{18}OSNa]^+$: 257.0971; found: 257.0970

methyl 2-(3-benzoylbicyclo[1.1.1]pentan-1-yl)propanoate (4j)



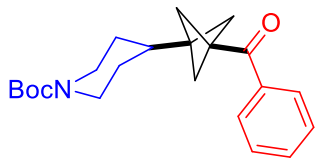
Yellow oily (31.0 mg, 60% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.93 (m, 2H), 7.57–7.51 (m, 1H), 7.48–7.41 (m, 2H), 3.70 (s, 3H), 2.68 (q, *J* = 7.1 Hz, 1H), 2.20 (s, 6H), 1.16 (d, *J* = 7.2 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.6, 174.4, 136.5, 132.2, 128.9, 128.4, 53.0, 51.5, 43.4, 41.3, 40.5, 12.1. HRMS (ESI) Exact mass calculated for $[C_{16}H_{18}O_3Na]^+$: 281.1148; found: 281.1146

tert-butyl 2-(3-benzoylbicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4k)



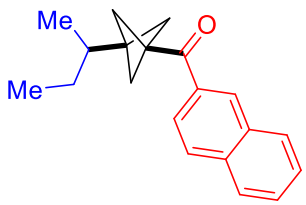
Yellow oily (56.8 mg, 80% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8) ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.1 Hz, 2H), 7.56–7.50 (m, 1H), 7.46–7.38 (m, 2H), 4.37–3.95 (m, 2H), 2.93–2.76 (m, 1H), 2.26 (s, 6H), 1.81–1.71 (m, 1H), 1.67–1.59 (m, 2H), 1.59–1.49 (m, 2H), 1.45 (s, 9H), 1.41–1.29 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 155.4, 136.5, 132.9, 128.9, 128.4, 79.3, 54.2, 44.0, 42.7, 28.4, 25.7, 25.2, 19.9. HRMS (ESI) Exact mass calculated for $[C_{22}H_{29}NO_3Na]^+$: 378.2040 found: 378.2042

tert-butyl 4-(3-benzoylbicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4l)



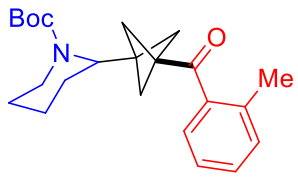
White Solid (51.2 mg, 72% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2, 2H), 7.53–7.47 (m, 1H), 7.42–7.37 (m, 2H), 4.13 (s, 2H), 2.72–2.53 (m, 2H), 2.07 (s, 6H), 1.57 (d, *J* = 12.6 Hz, 2H), 1.53-1.48 (m, 1H),, 1.43 (s, 9H), 1.15–0.99 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.9, 154.8, 136.6, 132.8, 128.8, 128.4, 79.3, 51.2, 43.5, 43.4, 36.2, 28.4, 28.2. HRMS (ESI) Exact mass calculated for $[C_{22}H_{29}NO_3Na]^+$: 378.2040 found: 378.2045

(3-(sec-butyl)bicyclo[1.1.1]pentan-1-yl)(naphthalen-2-yl)methanone (4m)



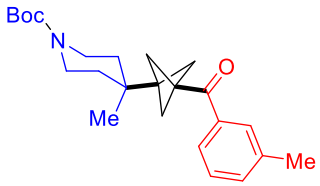
White Solid (37.8 mg, 68% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 75–76 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.8 Hz, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.89–7.82 (m, 2H), 7.61–7.50 (m, 2H), 2.18 (s, 6H), 1.55–1.47 (m, 2H), 1.12–1.03 (m, 1H), 0.94 (t, *J* = 7.2 Hz, 3H), 0.89 (d, *J* = 6.7 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 135.3, 134.1, 132.4, 130.7, 129.6, 128.4, 128.2, 127.8, 126.7, 124.6, 51.7, 45.1, 43.6, 35.1, 26.1, 15.4, 12.2. HRMS (ESI) Exact mass calculated for $[C_{20}H_{22}ONa]^+$: 301.1563 found: 301.1568

tert-butyl 2-(3-(2-methylbenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4n)



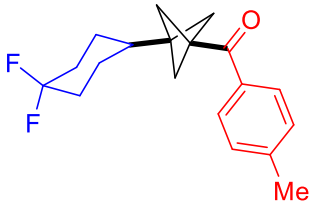
White Solid (49.5 mg, 67% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 90–92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.34–7.28 (m, 1H), 7.23–7.16 (m, 2H), 4.30–3.92 (m, 2H), 2.88–2.74 (m, 1H), 2.37 (s, 3H), 2.13 (s, 6H), 1.75–1.67 (m, 1H), 1.64–1.52 (m, 3H), 1.50–1.46 (m, 1H), 1.43 (s, 9H), 1.38–1.28 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.9, 155.3, 137.3, 137.2, 131.5, 130.6, 127.8, 125.0, 79.2, 53.2, 44.7, 42.3, 28.3, 25.6, 25.1, 20.4, 19.8. HRMS (ESI) Exact mass calculated for $[C_{23}H_{31}NO_3Na]^+$: 392.2196 found: 392.2201

tert-butyl 4-methyl-4-(3-(3-methylbenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4o)



White Solid (53.7 mg, 70% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 101–102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.73 (m, 2H), 7.35–7.27 (m, 2H), 3.86 (s, 2H), 2.91 (t, *J* = 12.6 Hz, 2H), 2.38 (s, 3H), 2.06 (s, 6H), 1.44 (s, 9H), 1.41–1.38 (m, 1H), 1.36–1.22 (m, 1H), 1.23–1.15 (m, 2H), 0.92 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.3, 154.9, 138.2, 136.7, 133.5, 129.2, 128.2, 126.1, 79.3, 49.6, 48.4, 42.2, 39.9, 32.6, 30.4, 28.4, 21.4, 18.4. HRMS (ESI) Exact mass calculated for $[C_{24}H_{33}NO_3Na]^+$: 406.2353 found: 406.2359

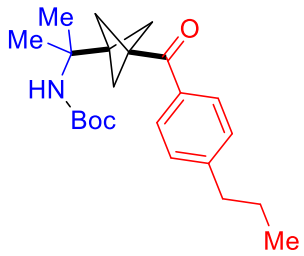
(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)(p-tolyl)methanone (4p)



White Solid (40.8 mg, 67% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:20); m. p. 87–89 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.18–2.12 (m, 1H), 2.11 (s, 6H), 2.09–2.01(m, 1H), 1.79–1.70 (m, 3H), 1.67–1.60 (m, 1H), 1.55–1.45 (m, 1H), 1.36–1.23 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 143.6,

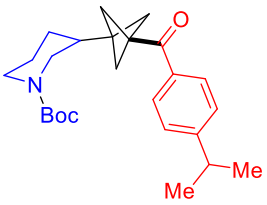
134.0, 129.1, 129.0, 51.4, 43.2, 43.1, 36.0 (d, J = 2.2 Hz), 33.2 (dd, J = 23.2, 26.3 Hz), 25.4(d, J = 10.1 Hz), 21.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -91.39 (d, J = 233.1 Hz), -102.4 (d, J = 267.0 Hz). HRMS (ESI) Exact mass calculated for $[C_{19}H_{22}F_2ONa]^+$: 327.1531 found: 327.1535

tert-butyl (2-(3-(4-propylbenzoyl)bicyclo[1.1.1]pentan-1-yl)propan-2-yl)carbamate (4q)



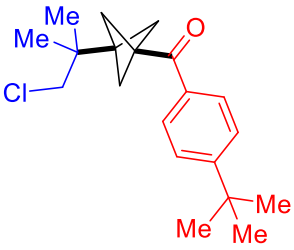
White Solid (46.8 mg, 63% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:6); m. p. 75–78 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 4.46 (s, 1H), 2.65–2.59 (m, 2H), 2.17 (s, 6H), 1.64 (q, J = 7.5 Hz, 2H), 1.42 (d, J = 4.8 Hz, 9H), 1.29 (s, 6H), 0.93 (t, J = 7.3 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.4, 148.3, 134.2, 129.0, 128.5, 115.0, 51.0, 50.7, 47.0, 41.6, 38.0, 28.3, 28.3, 24.1, 23.5, 13.7. HRMS (ESI) Exact mass calculated for $[C_{23}H_{33}NO_3Na]^+$: 394.2353 found: 394.2359

tert-butyl 3-(3-(4-isopropylbenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4r)



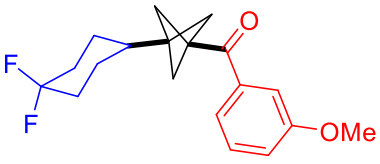
White Solid (57.2 mg, 72% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 80–82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 3.95 (d, J = 28.3 Hz, 2H), 2.93 (p, J = 6.9 Hz, 1H), 2.67 (t, J = 12.5 Hz, 1H), 2.46 (d, J = 28.6 Hz, 1H), 2.11 (s, 6H), 1.76 (d, J = 12.9 Hz, 1H), 1.69–1.53 (m, 2H), 1.44 (s, 9H), 1.41–1.28 (m, 1H), 1.24 (d, J = 6.9 Hz, 6H), 1.17–1.04 (m, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.2, 154.9, 154.3, 134.4, 129.2, 126.5, 79.4, 51.7, 43.6, 42.1, 35.8, 34.2, 28.4, 27.2, 24.5, 23.7. HRMS (ESI) Exact mass calculated for $[C_{25}H_{35}NO_3Na]^+$: 420.2509 found: 420.2506

(4-(tert-butyl)phenyl)(3-(1-chloro-2-methylpropan-2-yl)bicyclo[1.1.1]pentan-1-yl)methanone (4s)



White Solid (47.7 mg, 75% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 102–103 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 3.41 (s, 2H), 2.17 (s, 6H), 1.34 (s, 9H), 1.00 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.3, 156.6, 133.9, 128.9, 125.4, 53.5, 50.7, 46.5, 42.4, 35.1, 34.4, 31.1, 21.7. HRMS (ESI) Exact mass calculated for $[C_{20}H_{27}ClONa]^+$: 341.1643 found: 341.1648

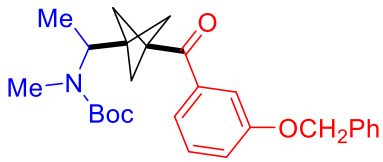
(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)(3-methoxyphenyl)methanone (4t)



White Solid (42.9 mg, 67% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:15); m. p. 78–80 ℃; ^{1}H NMR (400

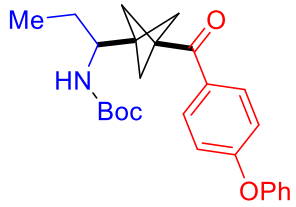
MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6, 1H), 7.48–7.47 (m, 1H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.08 (dd, *J* = 8.3, 2.7 Hz, 1H), 3.84 (s, 3H), 2.18–2.12 (m, 1H), 2.11 (s, 6H), 2.10–2.04 (m, 1H), 1.78–1.69 (m, 3H), 1.67–1.60 (m, 1H), 1.55–1.45 (m, 1H), 1.35–1.22 (m, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.6, 159.6, 137.8, 129.4, 121.6, 119.2, 113.2, 55.4, 51.5, 43.2, 43.1 (d, *J* = 3.0 Hz)), 43.17, 36.0 (d, *J* = 2.0 Hz), 33.2 (dd, *J* = 22.2, 25.3 Hz), 25.4 (d, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -91.2 (d, *J* = 236.9 Hz), -102.3 (d, *J* = 327.1 Hz). HRMS (ESI) Exact mass calculated for $[C_{19}H_{22}F_2O_2Na]^+$: 343.1480 found: 343.1485

tert-butyl (1-(3-(4-(benzyloxy)benzoyl)bicyclo[1.1.1]pentan-1-yl)ethyl)(methyl)carbamate (4u)



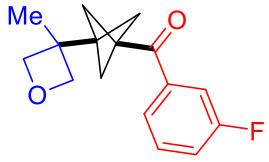
White Solid (37.9 mg, 63% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 102–104 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 1H), 7.53 (d, *J* = 2.7 Hz, 1H), 7.45–7.41 (m, 2H), 7.40–7.24 (m, 4H), 7.20–7.11 (m, 1H), 5.10 (s, 2H), 4.45–4.08 (m, 1H), 2.75 (d, *J* = 17.9 Hz, 3H), 2.24–1.99 (m, 6H), 1.46 (d, *J* = 2.1 Hz, 9H), 1.17–1.07 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.1, 158.8, 155.8, 137.7, 136.5, 129.5, 128.7, 128.1, 127.5, 121.8, 120.2, 114.2, 79.5, 70.2, 52.0, 50.3, 43.6, 43.0, 28.5, 28.3, 14.7. HRMS (ESI) Exact mass calculated for $[C_{27}H_{33}NO_4Na]^+$: 458.2302 found: 458.2309

tert-butyl (1-(3-(4-phenoxybenzoyl)bicyclo[1.1.1]pentan-1-yl)propyl)carbamate (4v)



White Solid (37.9 mg, 45% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 95–96 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.38 (t, *J* = 7.0 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 9.9 Hz, 2H), 6.97 (d, *J* = 6.8 Hz, 2H), 4.33 (s, 1H), 3.60 (d, *J* = 23.4 Hz, 1H), 2.14 (s, 6H), 1.60–1.53 (m, 1H), 1.44 (s, 9H), 1.25–1.18 (m, 1H), 0.96 (d, *J* = 7.3 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.0, 161.8, 155.9, 155.3, 131.1, 130.0, 124.6, 123.4, 120.1, 117.1, 79.0, 51.7, 51.5, 43.4, 42.9, 28.3, 24.8, 10.6. HRMS (ESI) Exact mass calculated for $[C_{26}H_{31}NO_4Na]^+$: 444.2145 found: 444.2149

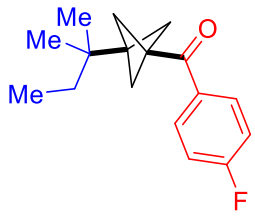
(3-fluorophenyl)(3-(3-methyloxetan-3-yl)bicyclo[1.1.1]pentan-1-yl)methanone (4w)



White Solid (42.7 mg, 82% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 79–81 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.67–7.61 (m, 1H), 7.46–7.38 (m, 1H), 7.28–7.20 (m, 1H), 4.54 (d, J = 5.8 Hz, 2H), 4.34 (d, *J* = 5.8 Hz, 2H), 2.22 (s, 6H), 1.27 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.3, 162.5 (d, *J* = 249.5 Hz), 138.4 (d, *J* = 6.1 Hz), 130.1 (d, *J* = 8.1 Hz), 124.6 (d, *J* = 3.0 Hz), 119.1 (d, *J* = 21.2 Hz), 115.4 (d, *J* = 22.2 Hz), 78.9, 50.0, 44.3, 42.1, 38.5, 20.3. ^{19}F NMR (376

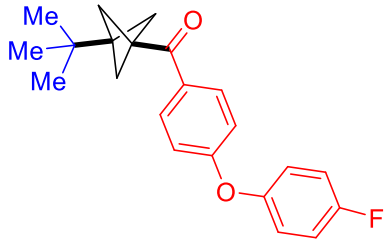
MHz, $CDCl_3$): δ -111.5. HRMS (ESI) Exact mass calculated for $[C_{17}H_{17}FO_2Na]^+$: 283.1105 found: 283.1110

(4-fluorophenyl)(3-(tert-pentyl)bicyclo[1.1.1]pentan-1-yl)methanone (4x)



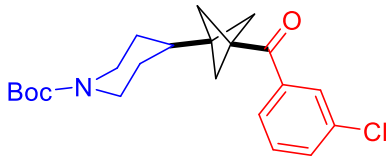
White Solid (44.8 mg, 86% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 82-84 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.99 (m, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 2.07 (s, 6H), 1.26 (q, *J* = 7.6 Hz, 2H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.81 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.8, 165.4 (d, *J* = 255.5 Hz, 1C),133.1 (d, *J* = 3.0 Hz, 1C), 131.5 (d, *J* = 10.1 Hz, 1C), 115.4 (d, *J* = 22.2 Hz, 1C), 50.1, 48.9, 41.9, 31.8, 30.8, 22.1, 8.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -105.5. HRMS (ESI) Exact mass calculated for $[C_{17}H_{21}FONa]^+$: 283.1469; found: 283.1472

(3-(tert-butyl)bicyclo[1.1.1]pentan-1-yl)(4-(4-fluorophenoxy)phenyl)methanone (4y)



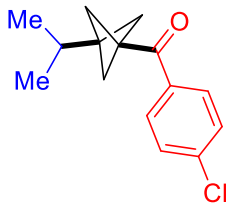
White Solid (37.2 mg, 55% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 105–106 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.9 Hz, 2H), 7.11–7.01 (m, 4H), 6.94 (d, *J* = 8.5 Hz, 2H), 2.06 (s, 6H), 0.89 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.0, 161.8, 159.5 (d, *J* = 244.4 Hz), 151.2 (d, *J* = 2.0 Hz), 131.4, 131.2, 121.8(d, *J* = 5.1 Hz), 116.8 (d, *J* = 23.2 Hz), 116.7, 49.8, 48.6, 41.5, 29.4, 25.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ -118.1. HRMS (ESI) Exact mass calculated for $[C_{22}H_{23}FO_2Na]^+$: 361.1574; found: 361.1575

tert-butyl 4-(3-(3-chlorobenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4z)



White Solid (52.9 mg, 68% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 98–99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (t, *J* = 1.9 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.47 (d, *J* = 9.1 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 4.12 (s, 2H), 2.62 (t, *J* = 12.9 Hz, 2H), 2.06 (s, 6H), 1.58 (s, 1H), 1.55 (s, 2H), 1.42 (s, 9H), 1.15–1.02 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.5, 154.8, 138.1, 134.6, 132.7, 129.8, 128.8, 126.9, 79.3, 51.2, 43.6, 43.3, 36.2, 28.4, 28.1. HRMS (ESI) Exact mass calculated for $[C_{22}H_{28}ClNO_3Na]^+$: 412.1650 found: 412.1655

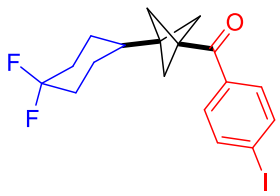
(4-chlorophenyl)(3-isopropylbicyclo[1.1.1]pentan-1-yl)methanone (4aa)



White Solid (37.2 mg, 75% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:40); m. p. 84–86 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.6 Hz, 2H), 2.04 (s, 6H), 1.80–1.63 (m, 1H), 0.85 (d, *J* = 6.9 Hz, 6H).

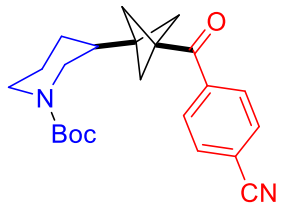
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 197.0, 139.1, 135.0, 130.3, 128.7, 50.9, 45.4, 42.9, 28.2, 18.6. HRMS (ESI) Exact mass calculated for $[C_{15}H_{17}ClONa]^+$: 271.0860 found: 271.0856

(3-(4,4-difluorocyclohexyl)bicyclo[1.1.1]pentan-1-yl)(4-iodophenyl)methanone (4ab)



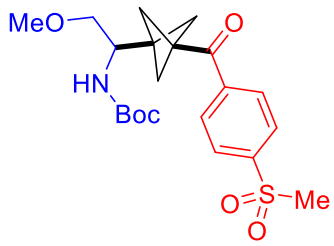
White Solid (35.6 mg, 43% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:20); m. p. 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2H), 7.71–7.65 (m, 2H), 2.63 (s, 1H), 2.12 (s, 1H), 2.10 (s, 6H), 1.76–1.68 (m, 3H), 1.66–1.61 (m, 1H), 1.54–1.46 (m, 1H), 1.32–1.24 (m, 2H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 198.6, 137.8, 135.8, 130.2, 100.8, 61.8, 51.5, 43.4 (d, *J* = 3.0 Hz), 43.1, 36.0 (d, *J* = 2.0 Hz), 33.2 (dd, *J* = 22.2, 26.3 Hz), 25.3 (d, *J* = 10.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ -91.2 (d, *J* = 240.6), -102.0 (d, *J* = 236.9). HRMS (ESI) Exact mass calculated for $[C_{18}H_{19}F_2IONa]^+$: 439.0341 found: 439.0342

tert-butyl 3-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (4ac)



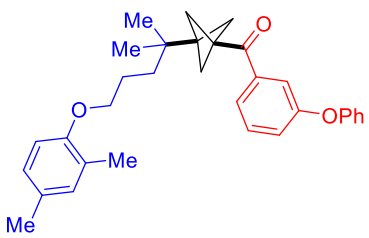
White Solid (44.1 mg, 58% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:8); m. p. 107–109 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.96 (m, 2H), 7.70–7.66 (m, 2H), 4.08–3.57 (m, 2H), 2.70–2.61 (m, 1H), 2.6–2.3 (s, 1H), 2.09 (s, 6H), 1.74–1.67 (m, 1H), 1.61–1.50 (m, 2H), 1.39 (s, 9H),1.36–1.34(m, 1H) 1.13–0.95 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 196.2, 154.6, 139.3, 133.9, 132.1, 129.0, 123.1, 117.7, 115.8, 79.2, 51.5, 43.3, 42.3, 35.5, 28.2, 26.9, 24.3. HRMS (ESI) Exact mass calculated for $[C_{23}H_{28}N_2O_3Na]^+$: 403.1992 found: 403.1996

tert-butyl (2-methoxy-1-(3-(4-(methylsulfonyl)benzoyl)bicyclo[1.1.1]pentan-1-yl)ethyl)carbamate (4ad)



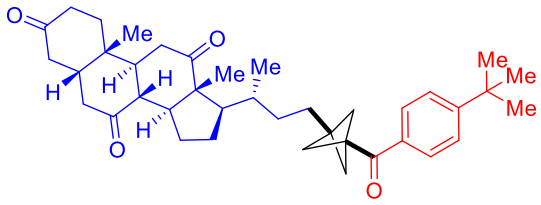
White Solid (44.0 mg, 52% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:3); m. p. 110–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.95 (d, *J* = 8.3 Hz, 2H), 4.89 (d, *J* = 8.9 Hz, 1H), 3.83–3.75 (m, 1H), 3.42–3.37 (m, 2H), 3.28 (s, 3H), 3.03 (s, 3H), 2.17 (s, 6H), 1.39 (s, 9H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 196.5, 155.6, 143.7, 140.5, 129.5, 127.6, 79.4, 72.3, 59.0, 52.4, 44.2, 43.4, 41.6, 29.5, 23.4. HRMS (ESI) Exact mass calculated for $[C_{21}H_{29}NO_6SNa]^+$: 446.1068 found: 446.1074

(3-(5-(2,4-dimethylphenoxy)-2-methylpentan-2-yl)bicyclo[1.1.1]pentan-1-yl)(3-phenoxyphenyl)methanone (4ae)



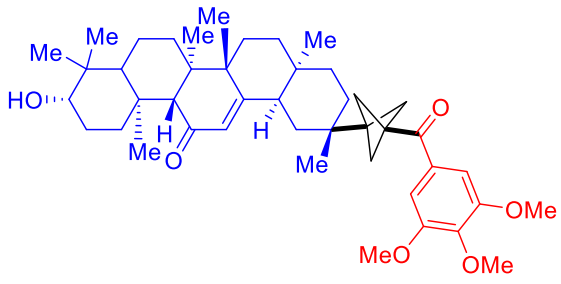
White Solid (65.6 mg, 70% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:15); m. p. 114-116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 1H), 7.65 (dd, *J* = 2.6, 1.5 Hz, 1H), 7.48–7.37 (m, 3H), 7.25–7.16 (m, 2H), 7.12–7.03 (m, 3H), 6.74–6.67 (m, 2H), 3.98 (t, *J* = 6.3 Hz, 2H), 2.37 (s, 3H), 2.25 (s, 3H), 2.12 (s, 6H), 1.85–1.79 (m, 2H), 1.47–1.41 (m, 2H), 0.93 (s, 6H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.7, 157.8, 157.1, 156.4, 138.3, 136.5, 130.4, 130.0, 129.9, 124.0, 123.6, 123.4, 122.8, 120.7, 119.5, 118.4, 112.0, 68.5, 50.2, 48.8, 42.1, 35.0, 31.7, 24.7, 22.9, 21.5, 15.9. HRMS (ESI) Exact mass calculated for $[C_{32}H_{36}O_3Na^+]^+$: 491.2557 found: 491.2560

(5S,8R,9S,10S,13R,14S,17R)-17-((R)-4-(3-(4-(tert-butyl)benzoyl)bicyclo[1.1.1]pentan-1-yl)butan-2-yl)-10,13-dimethyldodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione compound with methane (4af)



White Solid (58.8 mg, 49% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:1); m. p. 120–123 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), δ 2.94–2.77 (m, 4H), 2.38–2.25 (m, 5H), 2.24–2.12 (m, 5H), 2.08 (s, 6H), 2.03–1.90 (m, 5H), 1.65–1.52 (m, 3H), δ 1.41–1.34 (m, 5H), 1.31 (s, 9H), 1.28 (s, 2H), 1.05 (s, 4H), 0.84–0.78 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.0, 209.0, 208.7, 197.4, 156.3, 134.0, 128.8, 125.2, 56.8, 53.1, 51.7, 50.0, 48.9, 47.6, 46.7, 45.6, 45.4, 44.9, 44.1, 42.7, 40.7, 38.5, 36.4, 35.9, 35.7, 35.1, 35.0, 31.7, 31.0, 28.0, 27.7, 25.0, 21.8, 18.8, 11.7. HRMS (ESI) Exact mass calculated for $[C_{40}H_{56}O_4Na]^+$: 623.4071 found: 623.4078

(4aR,6aS,6bR,10S,12aS,12bR,14bR)-10-hydroxy-2,4a,6a,6b,9,9,12a-heptamethyl-2-(3-(3,4,5-trimethoxybenzoyl)bicyclo[1.1.1]pentan-1-yl)-1,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,14b-octadecahydropicen-13(2H)-one (4ag)



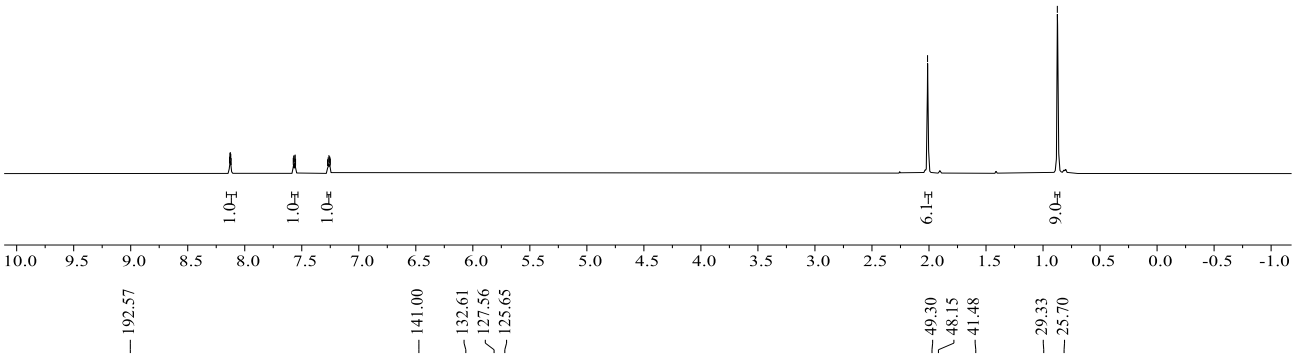
White Solid (76.9 mg, 45% yield) was obtained by the purification with flash column chromatography on silica gel (EtOAc/petroleum ether 1:2); m. p. 115–116 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 3.3 Hz, 2H). 5.55 (s, 1H), 4.06 (q, *J* = 7.2 Hz, 1H), 3.89–3.82 (m, 9H), 3.17 (dd, *J* = 11.0, 5.2 Hz, 1H), 2.78–2.67 (m, 1H), 2.30 (s, 1H), 2.16 (s, 4H), 2.01 (s, 2H), 1.99 (s, 2H), 1.70–1.51 (m, 6H), 1.48–1.34 (m, 5H), 1.31 (s, 4H), 1.20 (t, *J* =

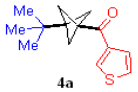
7.2 Hz, 3H), 1.08 (d, *J* = 4.0 Hz, 6H), 0.95 (s, 4H), 0.84 (d, *J* = 5.8 Hz, 2H), 0.80 (d, *J* = 4.9 Hz, 4H), 0.75 (s, 3H), 0.67–0.61 (m, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 200.0, 196.3, 169.7, 152.7, 142.3, 131.6, 128.1, 106.3, 61.6, 60.8, 60.2, 56.1, 54.8, 52.2, 49.3, 48.7, 47.5, 46.6, 45.1, 43.3, 42.4, 41.5, 41.0, 39.0, 36.9, 36.6, 32.3, 31.9, 28.0, 27.1, 26.1, 23.2, 23.0, 20.9, 18.5, 17.7, 17.3, 16.2, 15.5, 14.0. HRMS (ESI) Exact mass calculated for $[C_{44}H_{62}O_6\ Na]^+$: 709.4439 found: 709.4445.

6. ^{1}H NMR, ^{13}C{1H} NMR, ^{19}F NMR spectra of products

4a

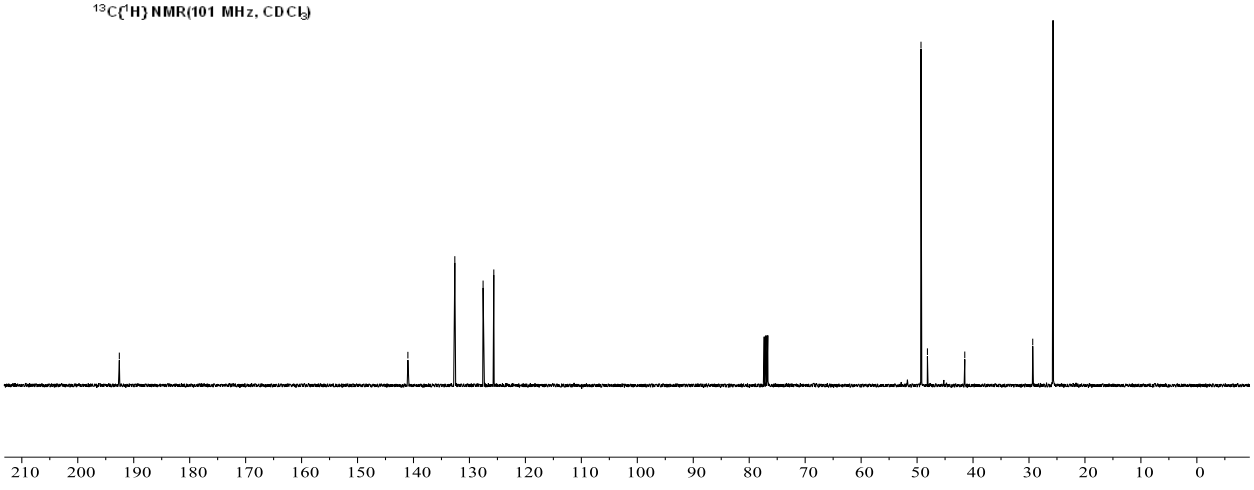
^{1}H NMR(400 MHz, $CDCl_3$)

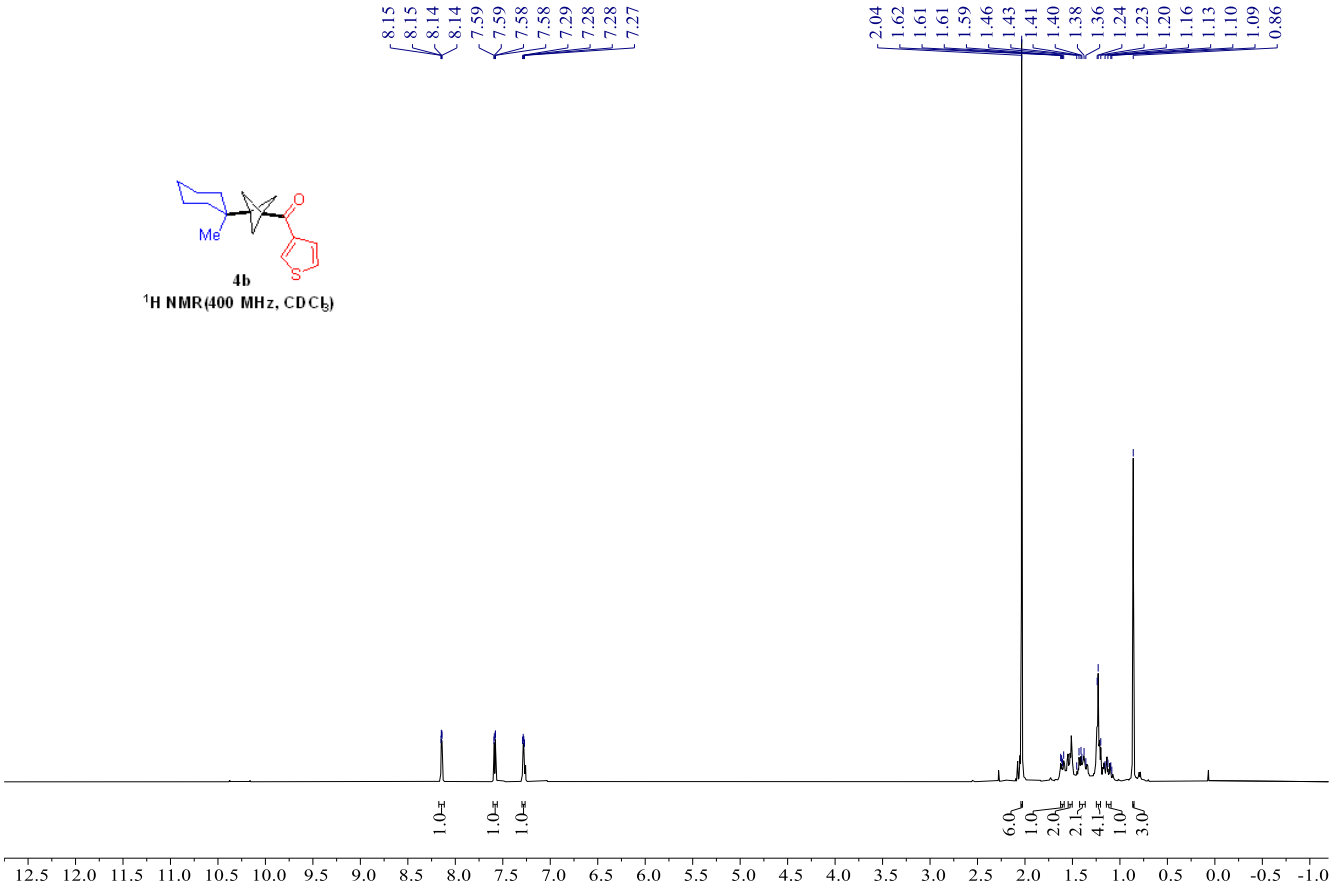


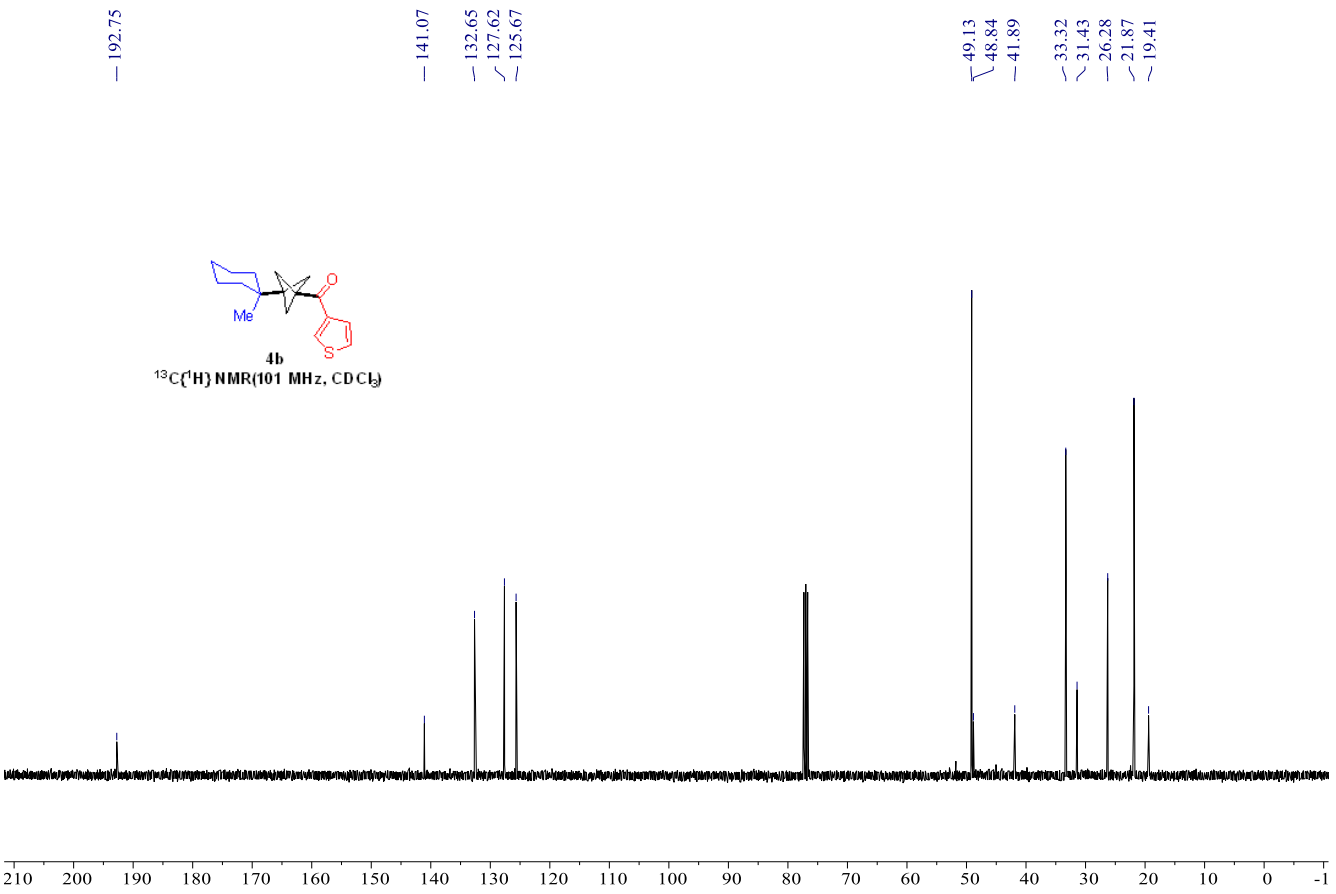


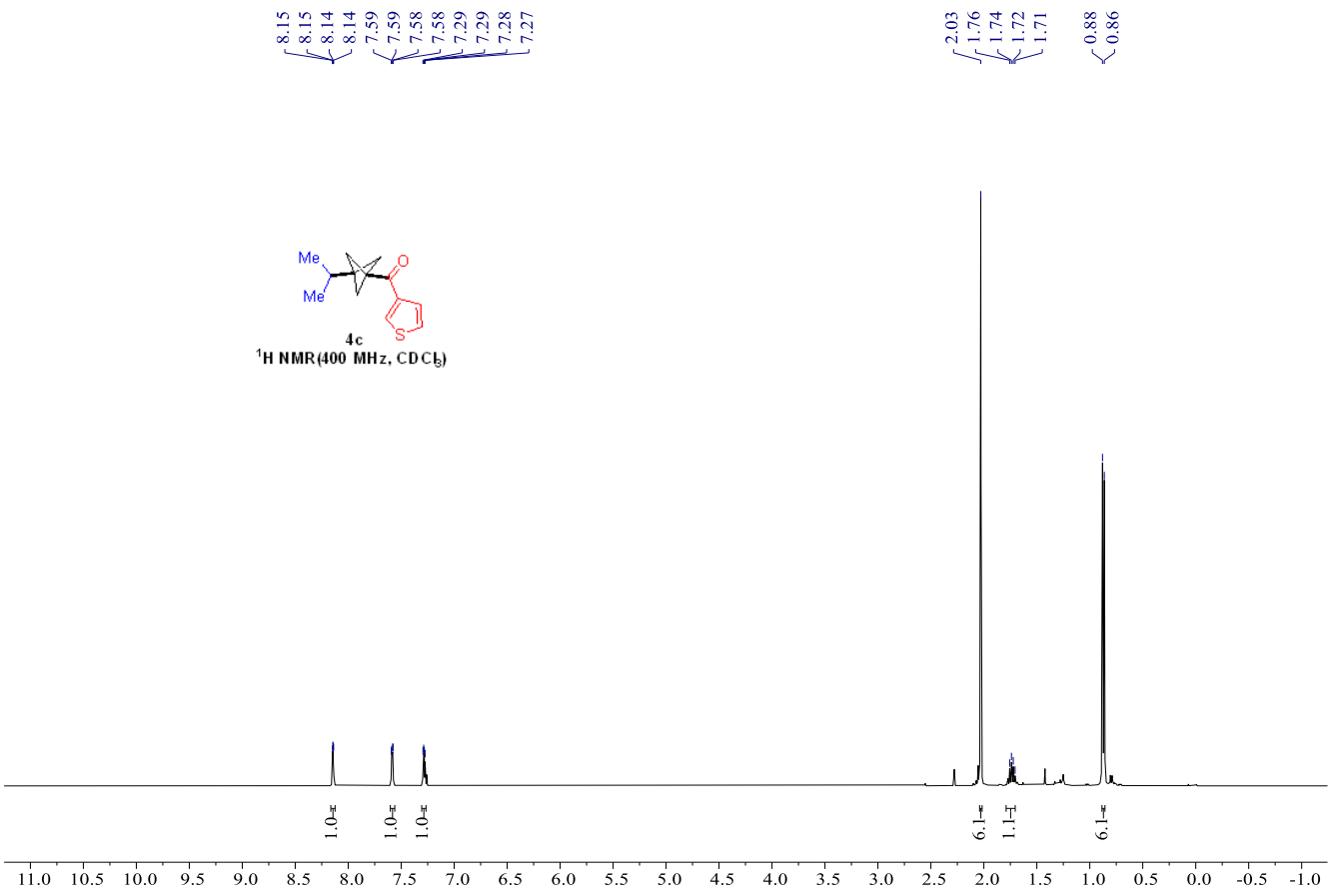
4a

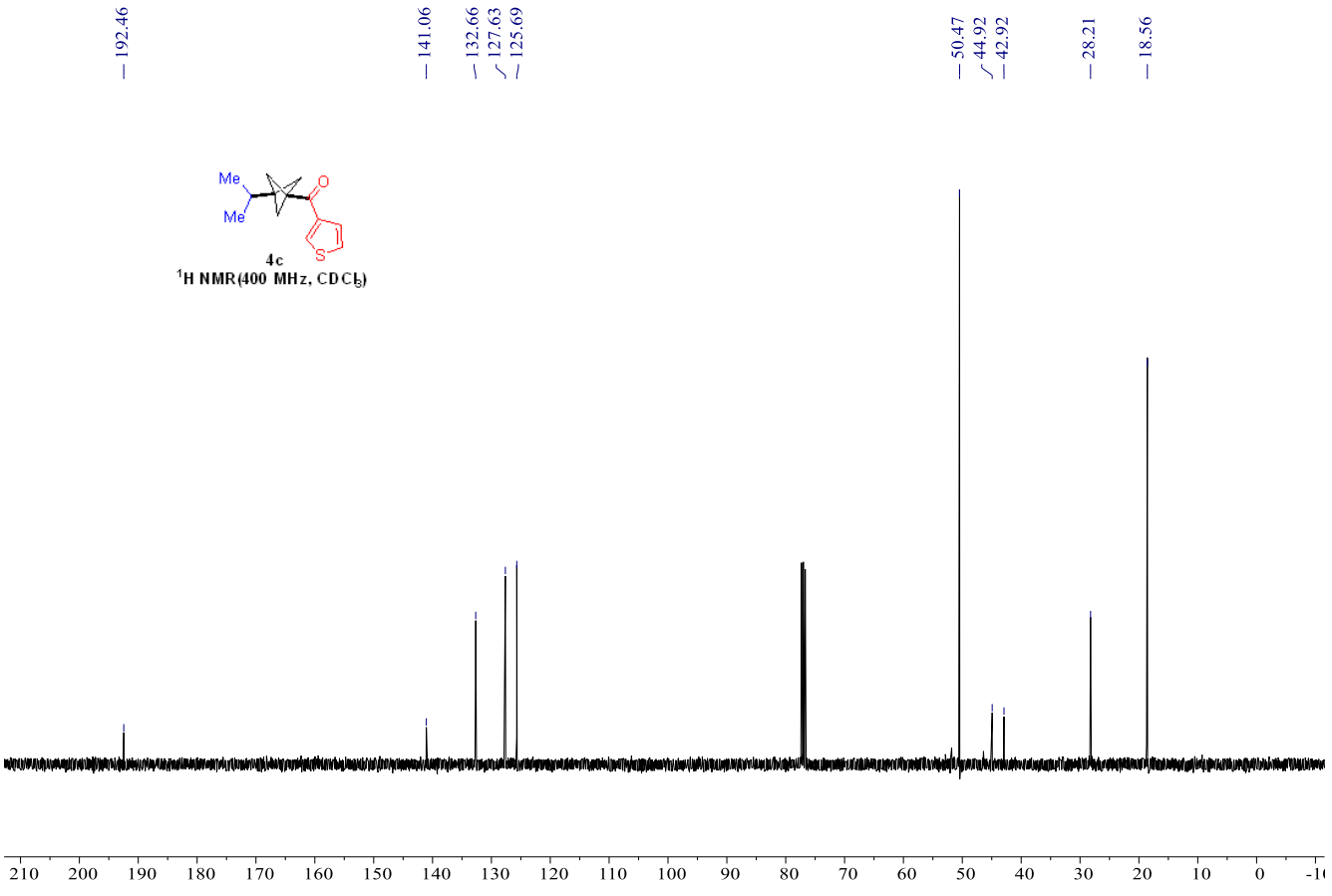
^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$)

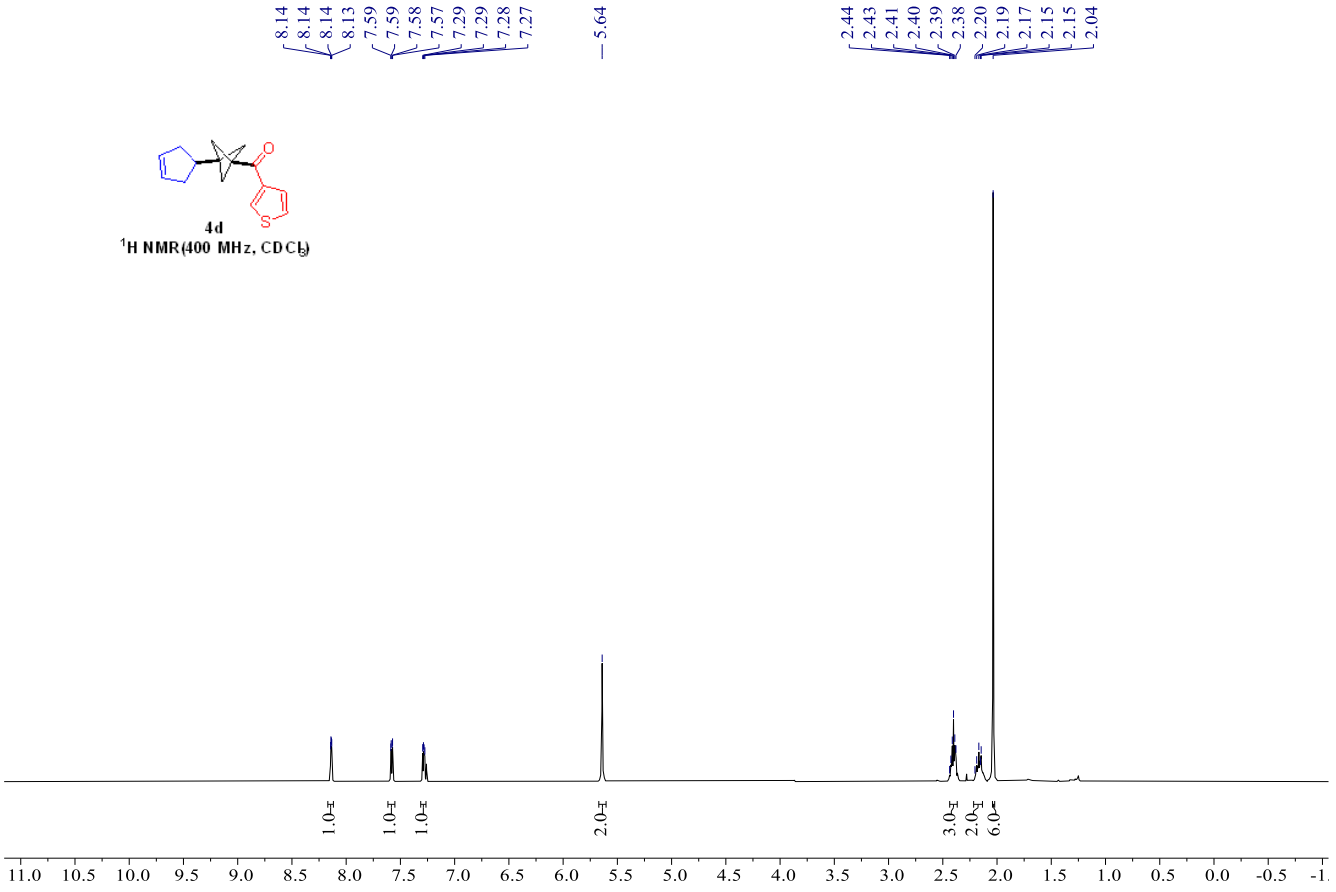


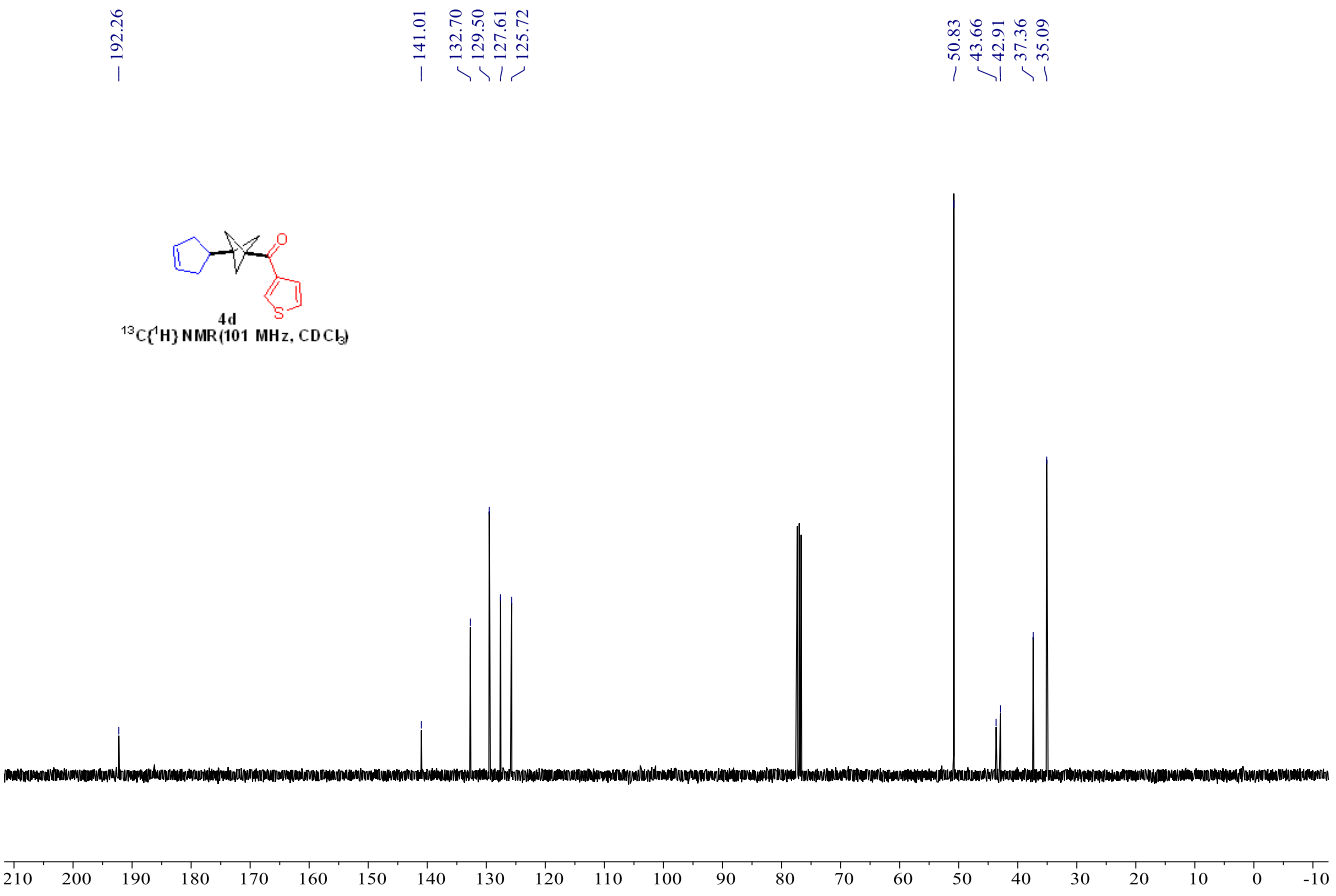

8.15
8.15
8.14
8.14
7.59
7.59
7.58
7.58
7.29
7.28
7.28
7.27
2.04
1.62
1.61
1.61
1.59
1.46
1.43
1.41
1.40
1.38
1.36
1.24
1.23
1.20
1.16
1.13
1.10
1.09
0.86
Me
O
S
4b
1H NMR(400 MHz, CDCl3)
1.0
1.0
1.0
6.0
1.0
2.0
2.1
4.1
1.0
3.0
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

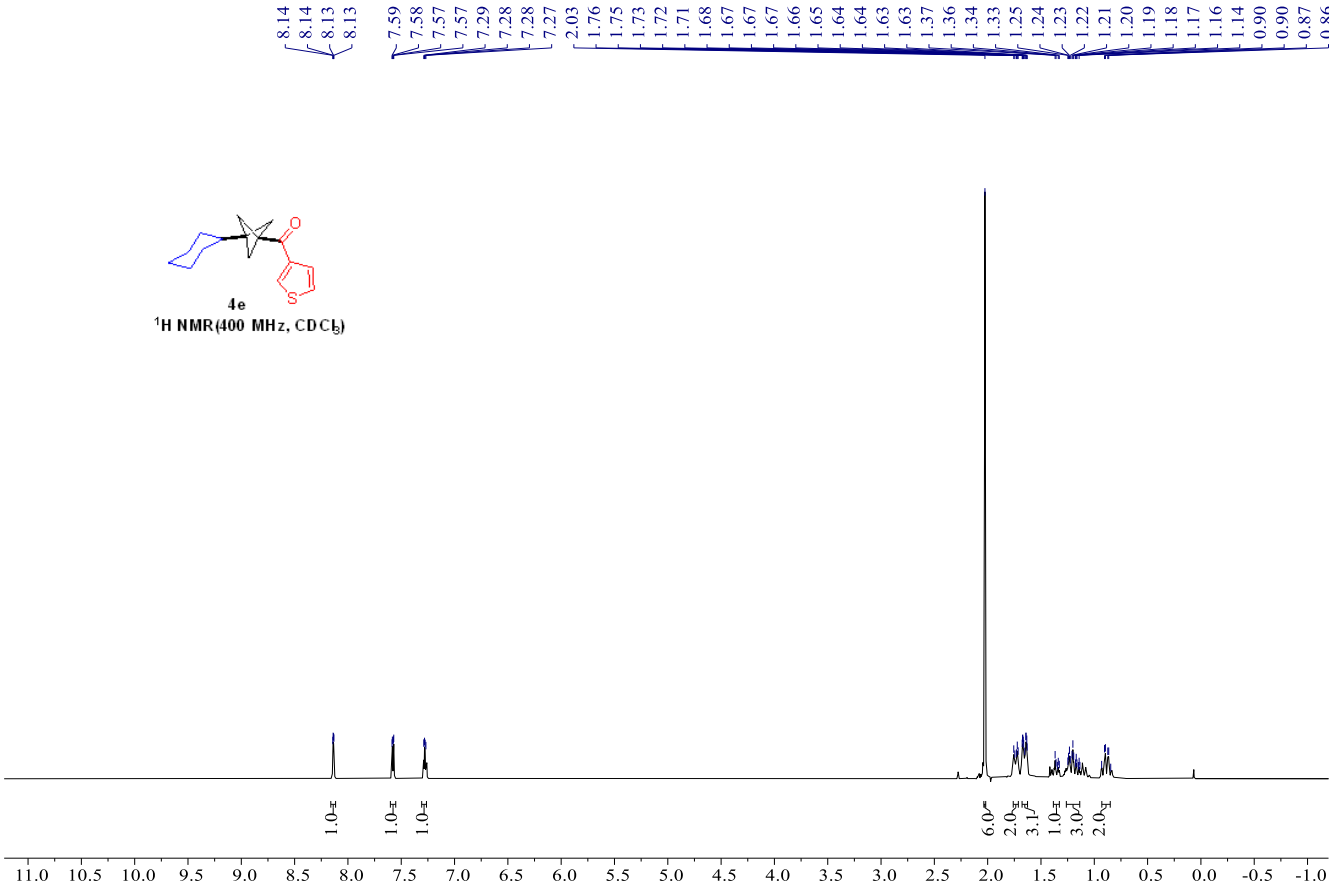

192.75
141.07
132.65
127.62
125.67
49.13
48.84
41.89
33.32
31.43
26.28
21.87
19.41
Me
O
S
4b
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

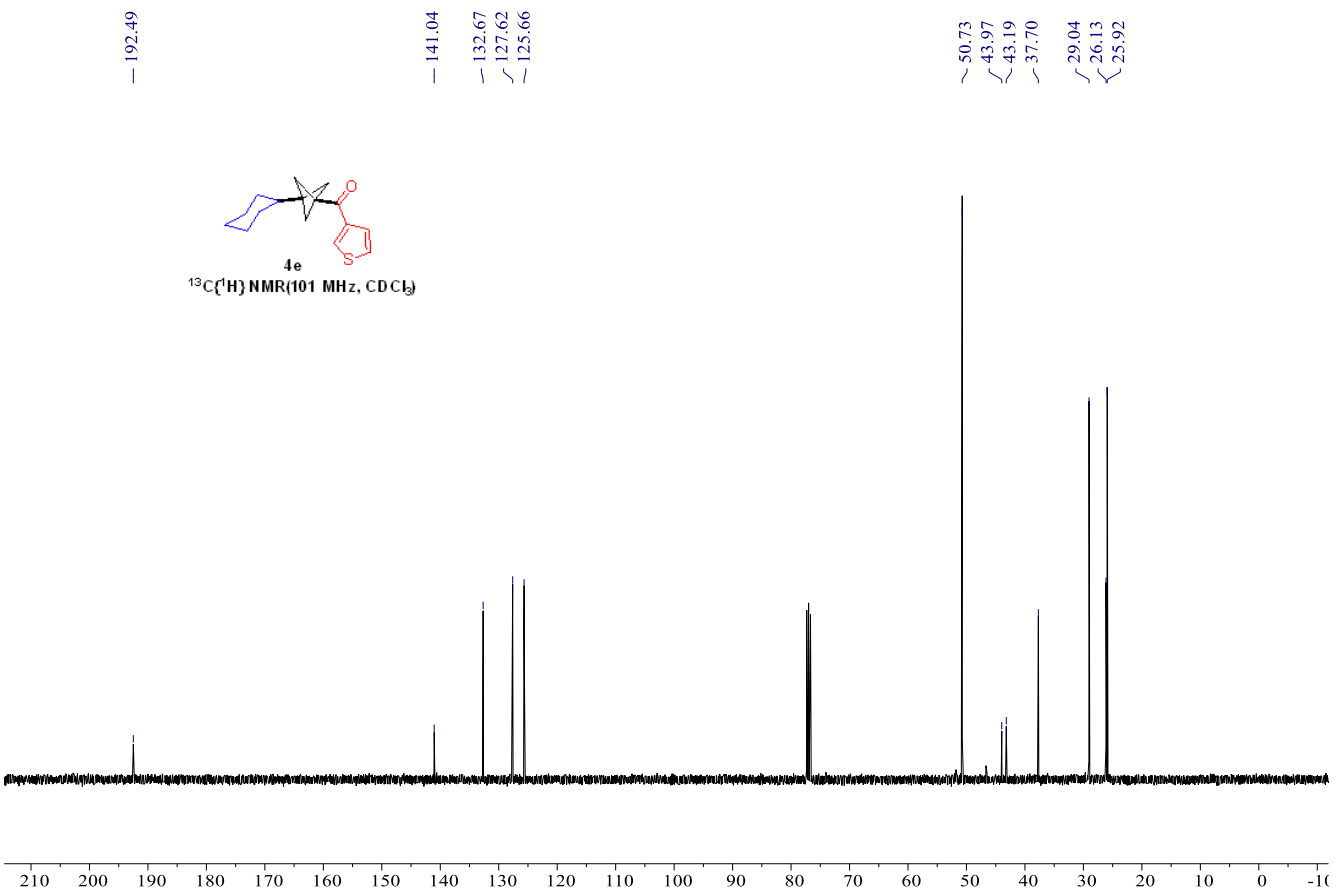

8.15
8.15
8.14
8.14
7.59
7.59
7.58
7.58
7.29
7.29
7.28
7.27
2.03
1.76
1.74
1.72
1.71
0.88
0.86
Me
Me
O
S
4c
^{1}H NMR(400 MHz, CDCl$_3$)
1.0
1.0
1.0
6.1
1.1
6.1
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

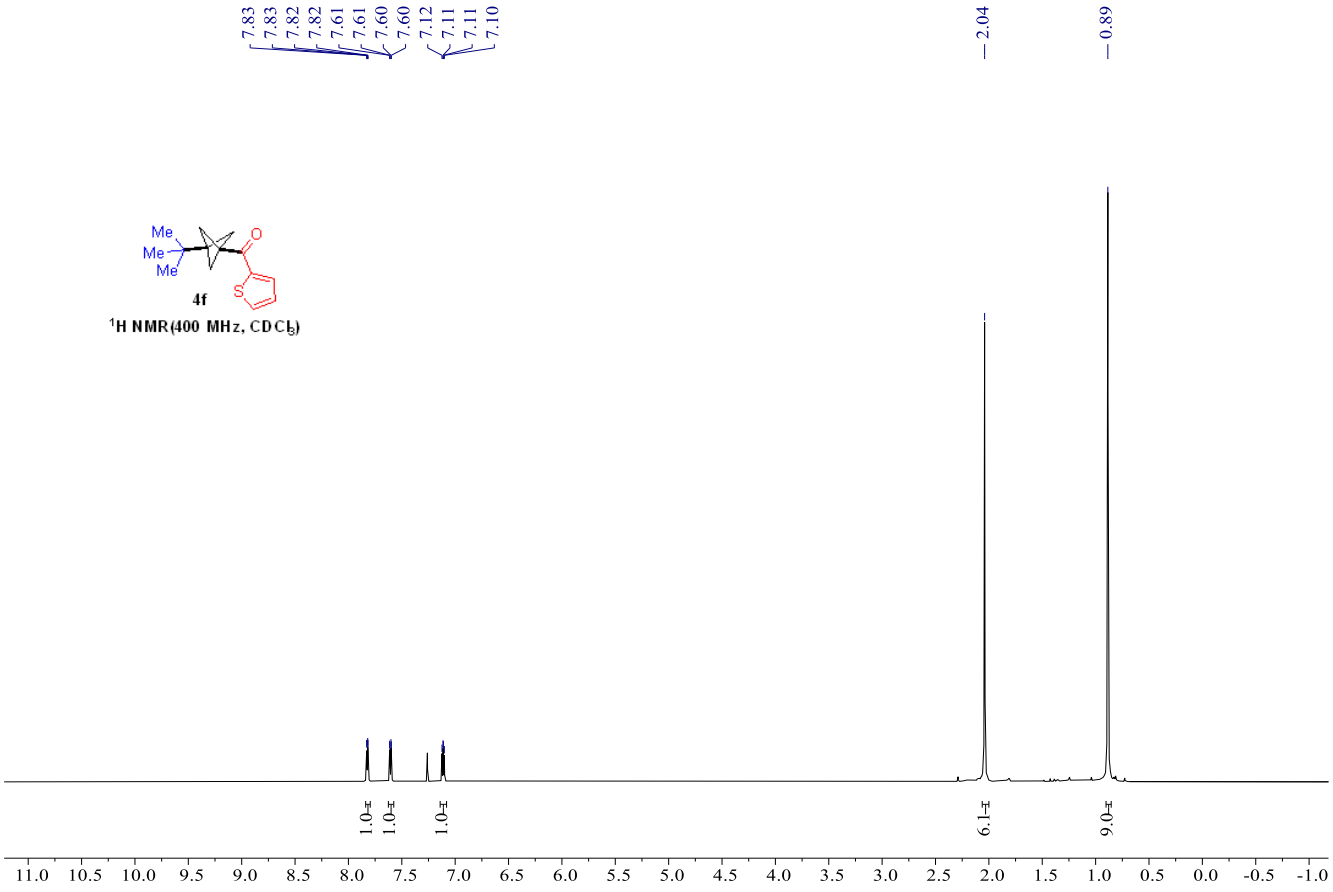

192.46
141.06
132.66
127.63
125.69
50.47
44.92
42.92
28.21
18.56
Me
Me
O
S
4c
^{1}H NMR(400 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

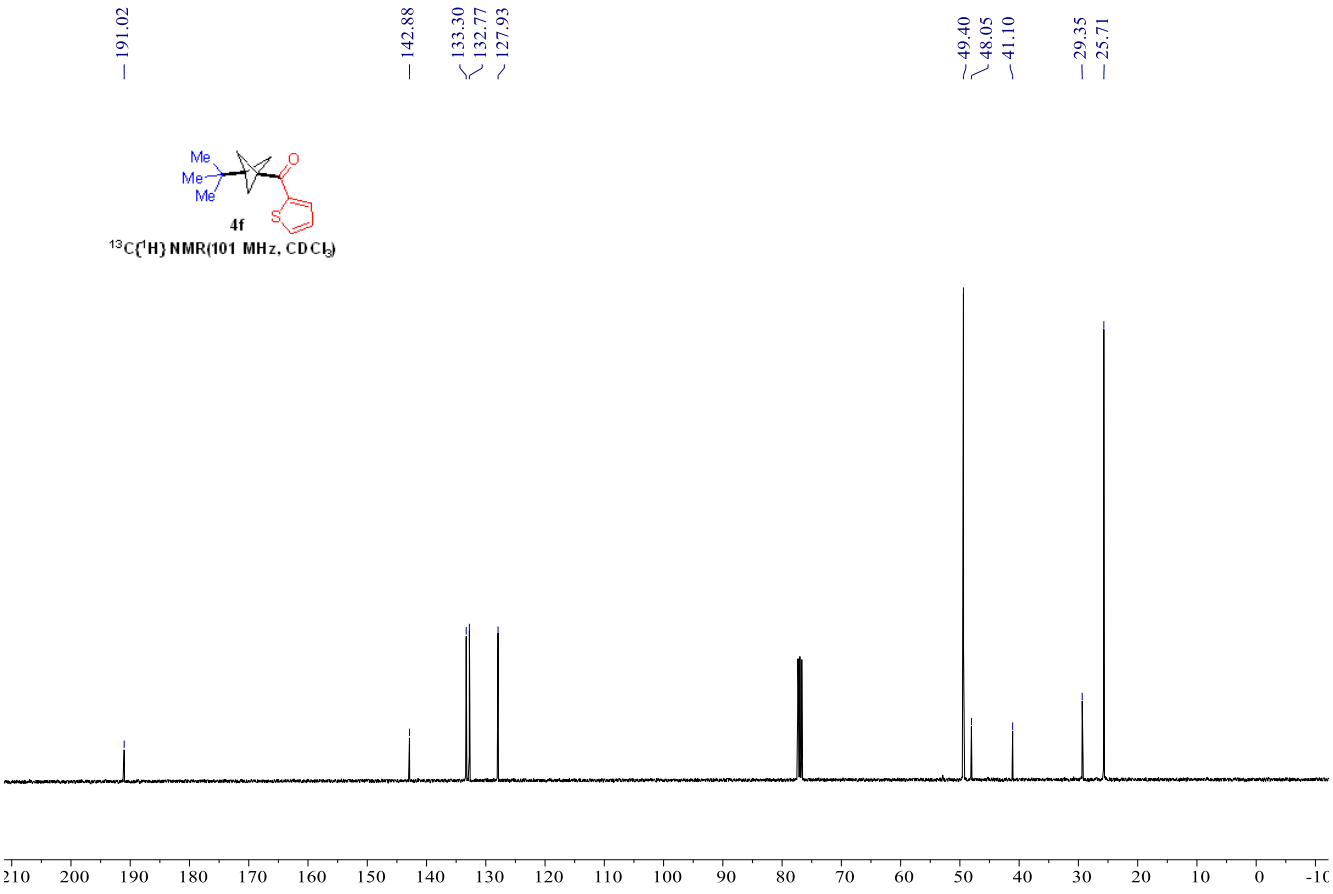

8.14
8.14
8.14
8.13
7.59
7.59
7.58
7.57
7.29
7.29
7.28
7.27
5.64
2.44
2.43
2.41
2.40
2.39
2.38
2.20
2.19
2.17
2.15
2.15
2.04
4d
1H NMR(400 MHz, CDCl3)
1.0
1.0
1.0
2.0
3.0
2.0
6.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5

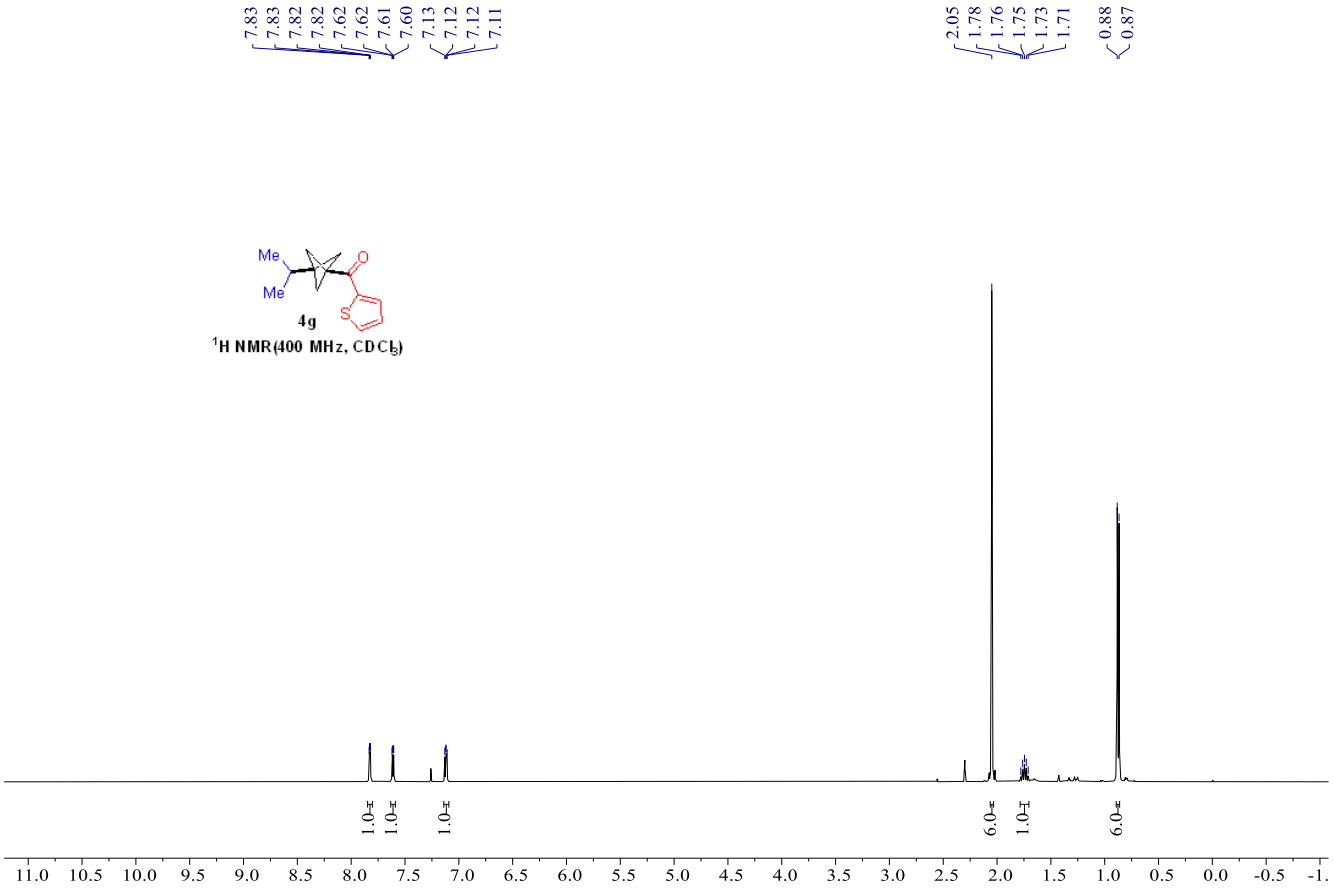

192.26
141.01
132.70
129.50
127.61
125.72
50.83
43.66
42.91
37.36
35.09
4d
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

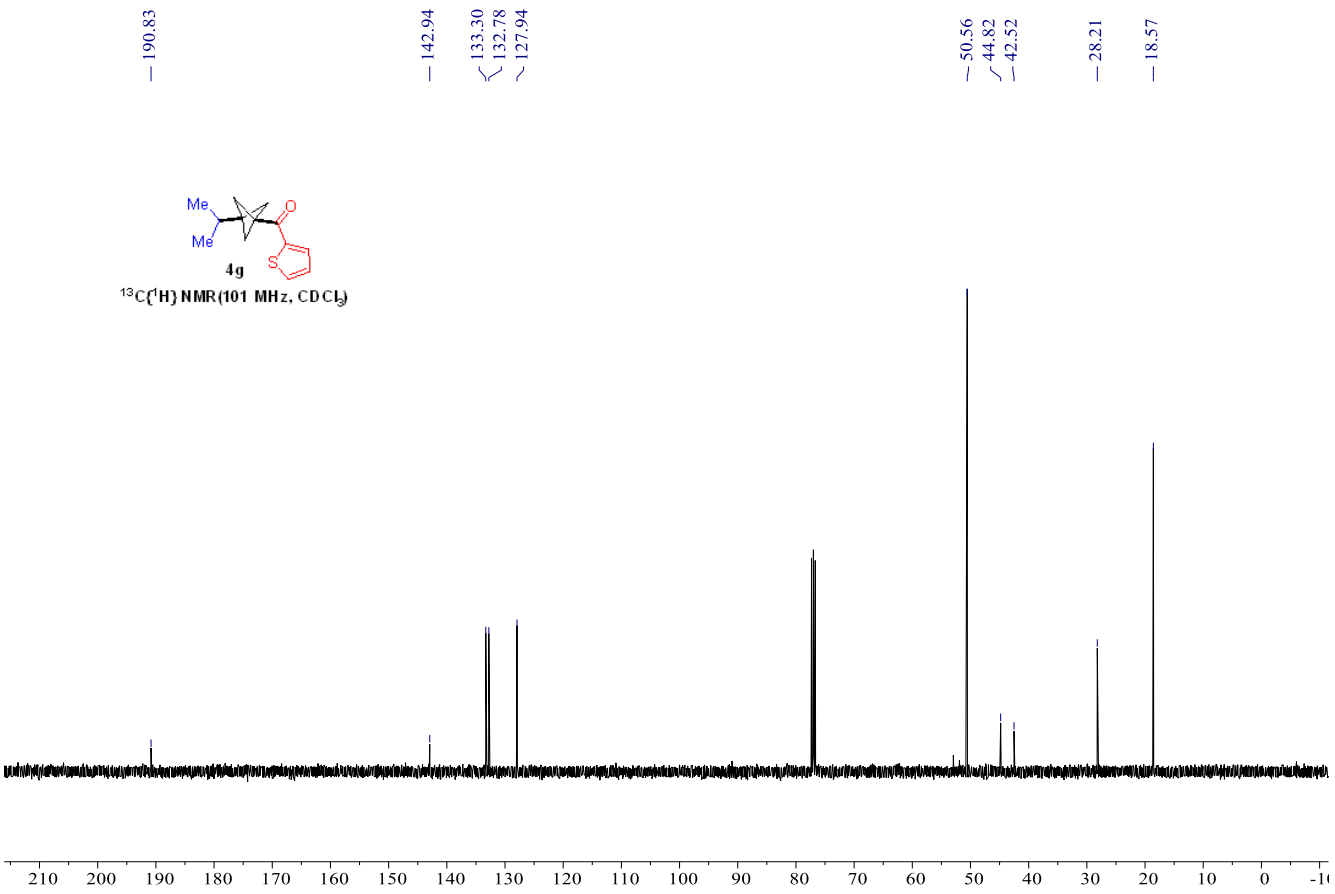

8.14
8.14
8.13
8.13
7.59
7.58
7.57
7.57
7.29
7.28
7.28
7.27
2.03
1.76
1.75
1.73
1.72
1.71
1.68
1.67
1.67
1.67
1.66
1.65
1.64
1.64
1.63
1.63
1.37
1.36
1.34
1.33
1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.18
1.17
1.16
1.14
0.90
0.90
0.87
O
S
4e
^{1}H NMR(400 MHz, CDCl$_3$)
1.0
1.0
1.0
6.0
2.0
3.1
1.0
3.0
2.0
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 -0.5 -1.0

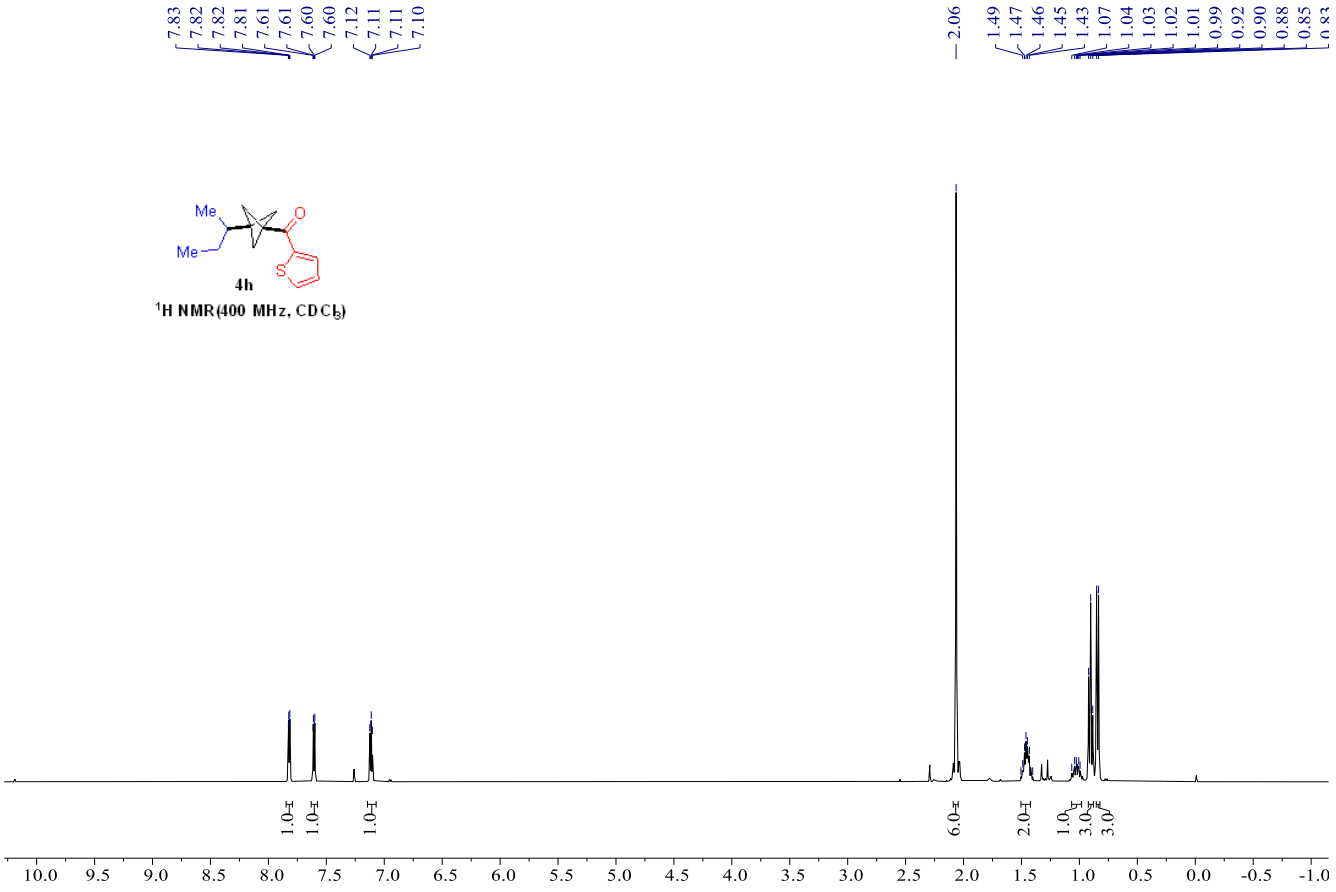

192.49
141.04
132.67
127.62
125.66
50.73
43.97
43.19
37.70
29.04
26.13
25.92
O
S
4e
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

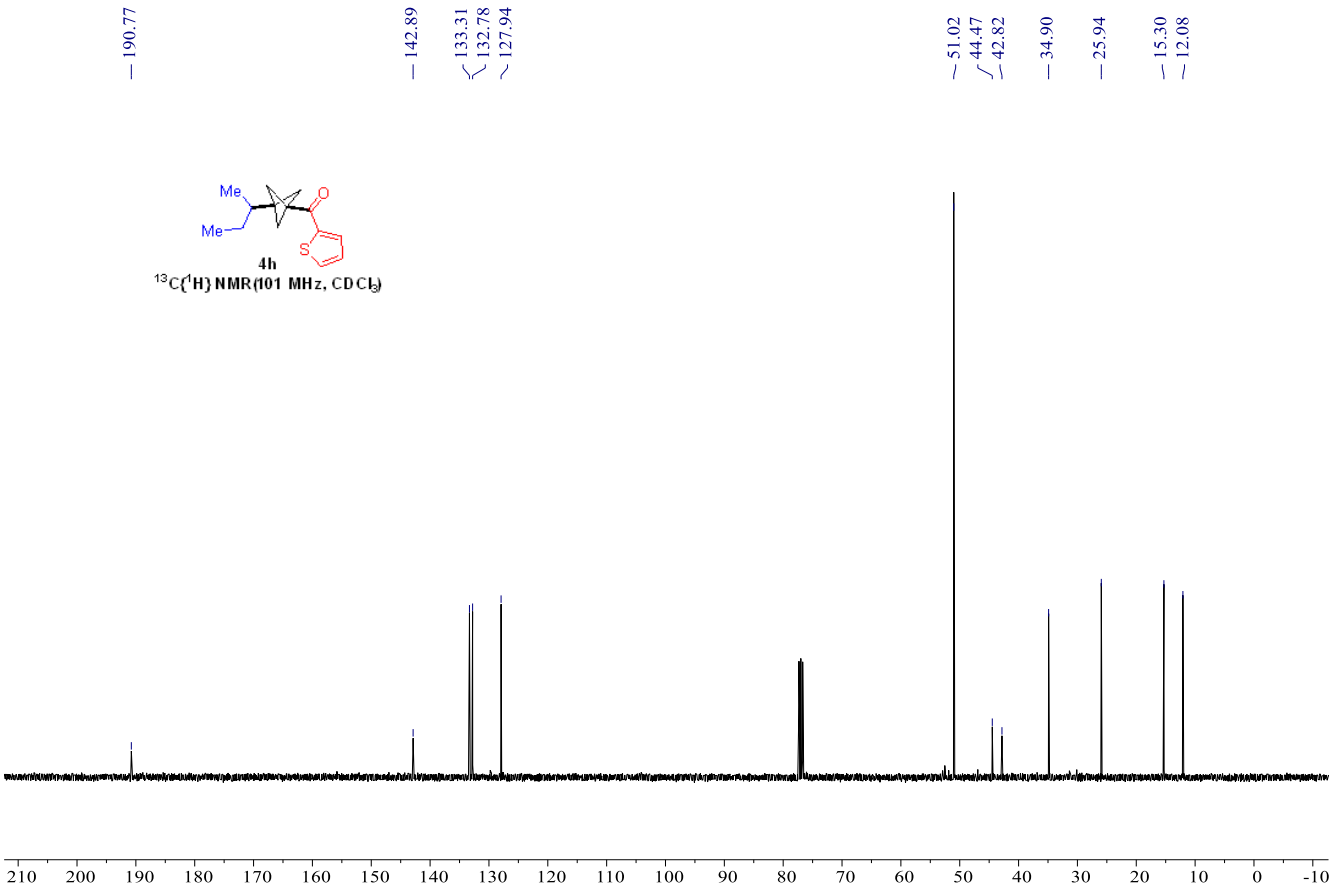

7.83
7.83
7.82
7.82
7.61
7.61
7.60
7.60
7.12
7.11
7.11
7.10
2.04
0.89
Me
Me
Me
O
S
4f
1H NMR(400 MHz, CDCl3)
1.0
1.0
1.0
6.1
9.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

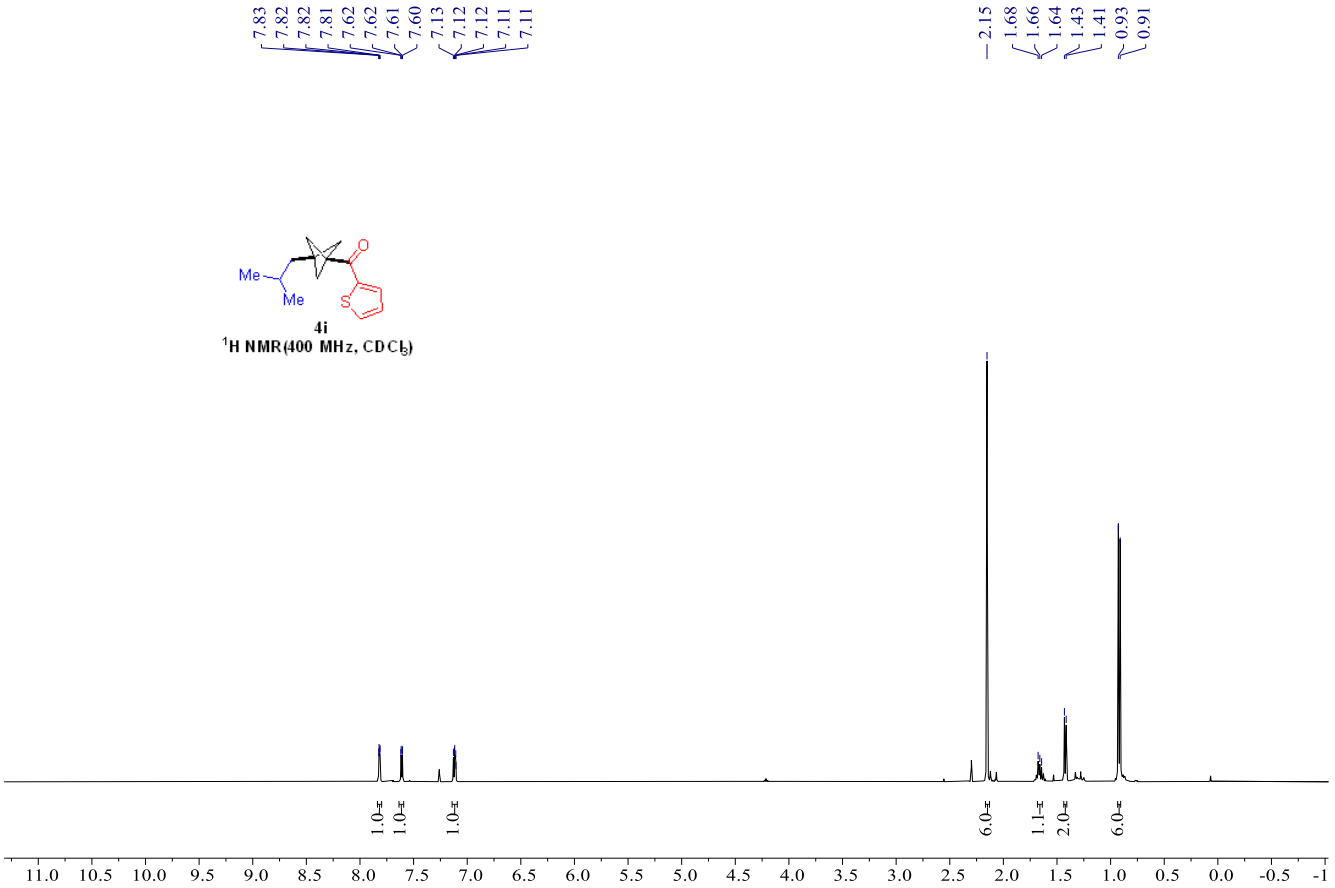

191.02
142.88
133.30
132.77
127.93
49.40
48.05
41.10
29.35
25.71
Me
Me
Me
O
S
4f
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

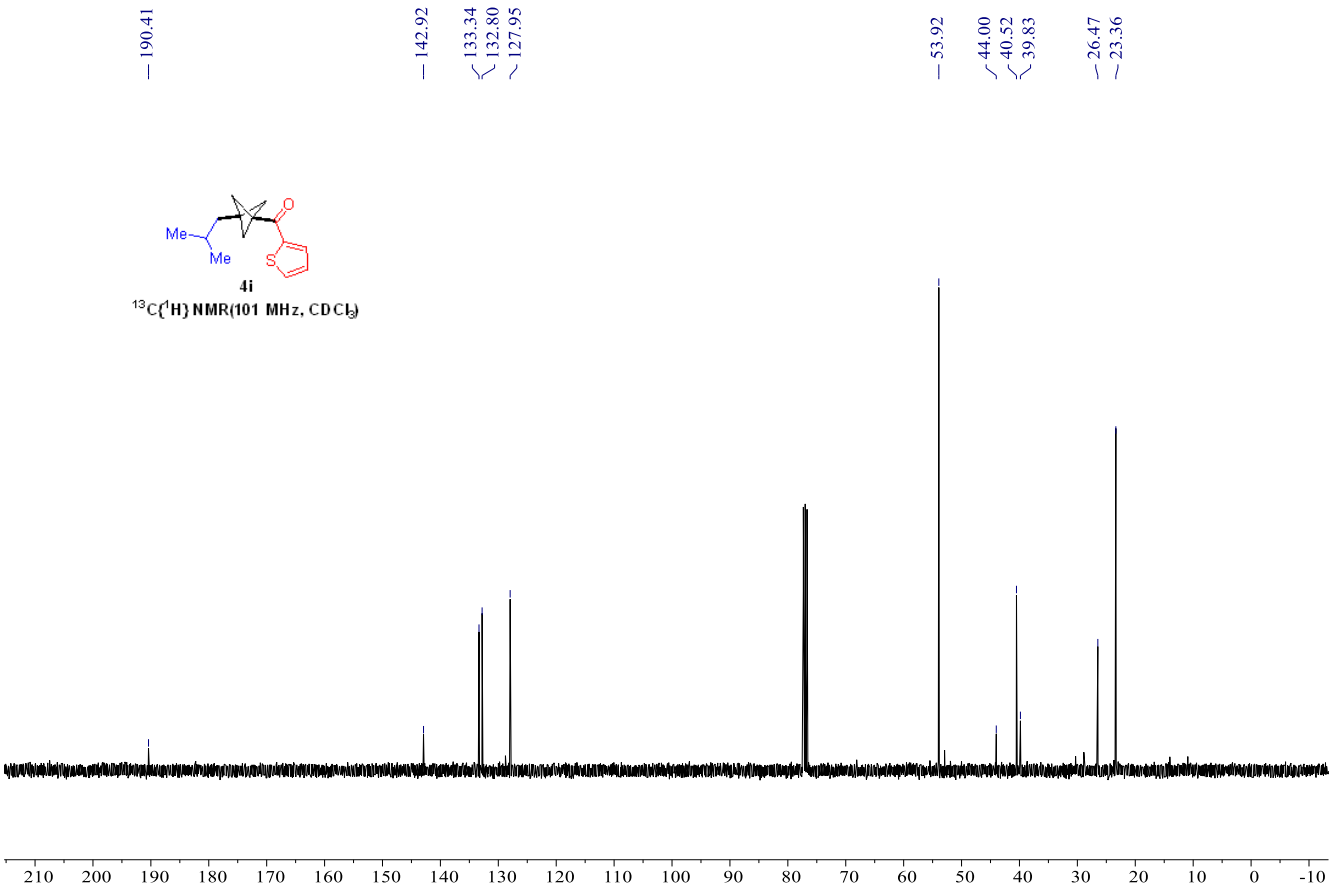

7.83
7.83
7.82
7.82
7.62
7.62
7.61
7.60
7.13
7.12
7.12
7.11
2.05
1.78
1.76
1.75
1.73
1.71
0.88
0.87
Me
Me
O
S
4g
^{1}H NMR(400 MHz, CDCl$_3$)
1.0
1.0
1.0
6.0
1.0
6.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.

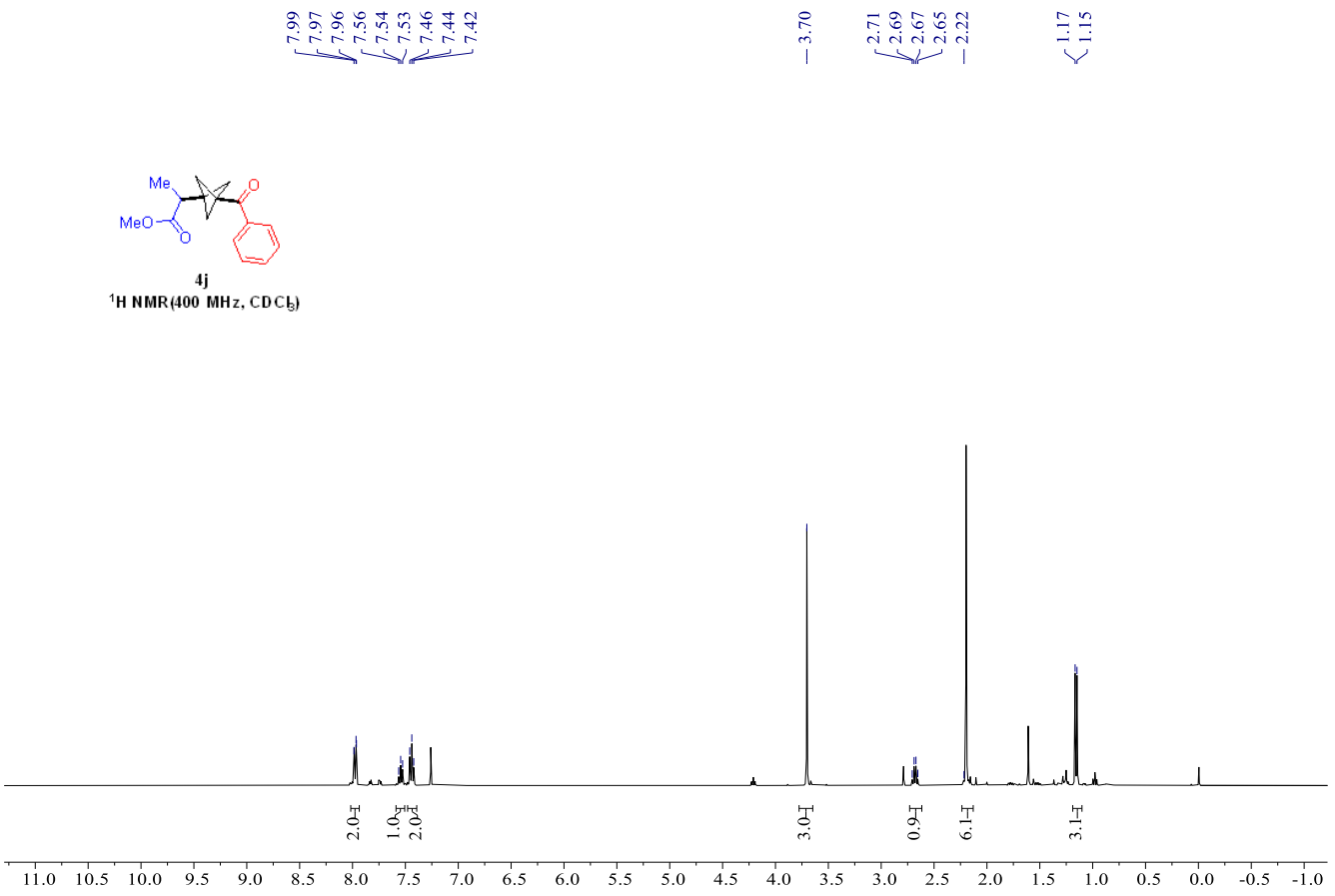

190.83
142.94
133.30
132.78
127.94
50.56
44.82
42.52
28.21
18.57
Me
Me
O
S
4g
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.83
7.82
7.82
7.81
7.61
7.61
7.60
7.60
7.12
7.11
7.11
7.10
2.06
1.49
1.47
1.46
1.45
1.43
1.07
1.04
1.03
1.02
1.01
0.99
0.92
0.90
0.88
0.85
Me
Me
O
S
4h
1H NMR(400 MHz, CDCl3)
1.0
1.0
1.0
6.0
2.0
1.0
3.0
3.0
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 -0.5 -1.0


190.77
142.89
133.31
132.78
127.94
51.02
44.47
42.82
34.90
25.94
15.30
12.08
Me
Me
O
S
4h
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

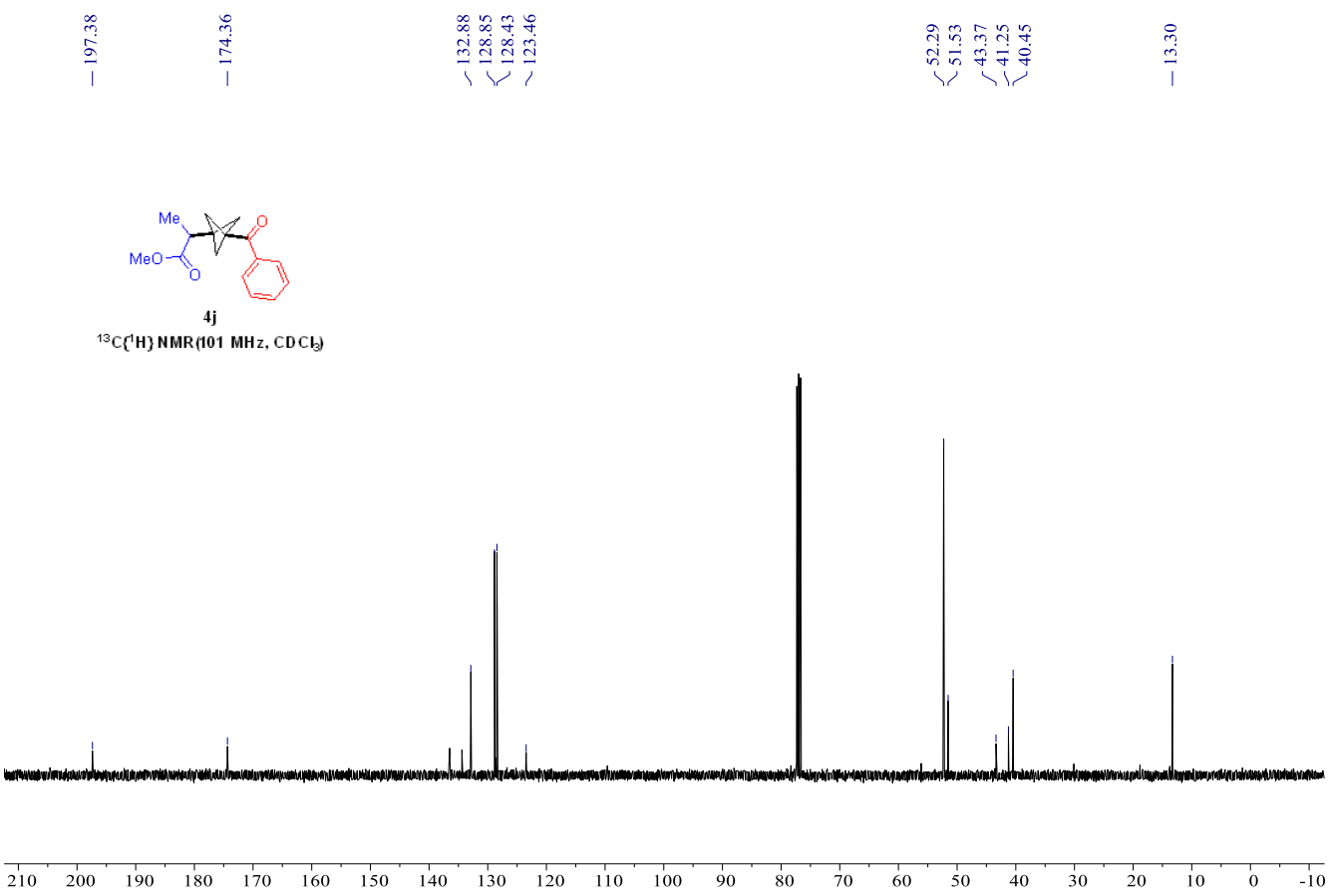

7.83
7.82
7.82
7.81
7.62
7.62
7.61
7.60
7.13
7.12
7.12
7.11
7.11
2.15
1.68
1.66
1.64
1.43
1.41
0.93
0.91
Me
Me
O
S
4i
1H NMR(400 MHz, CDCl3)
1.0
1.0
1.0
6.0
1.1
2.0
6.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1


190.41
142.92
133.34
132.80
127.95
53.92
44.00
40.52
39.83
26.47
23.36
Me
Me
O
S
4i
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



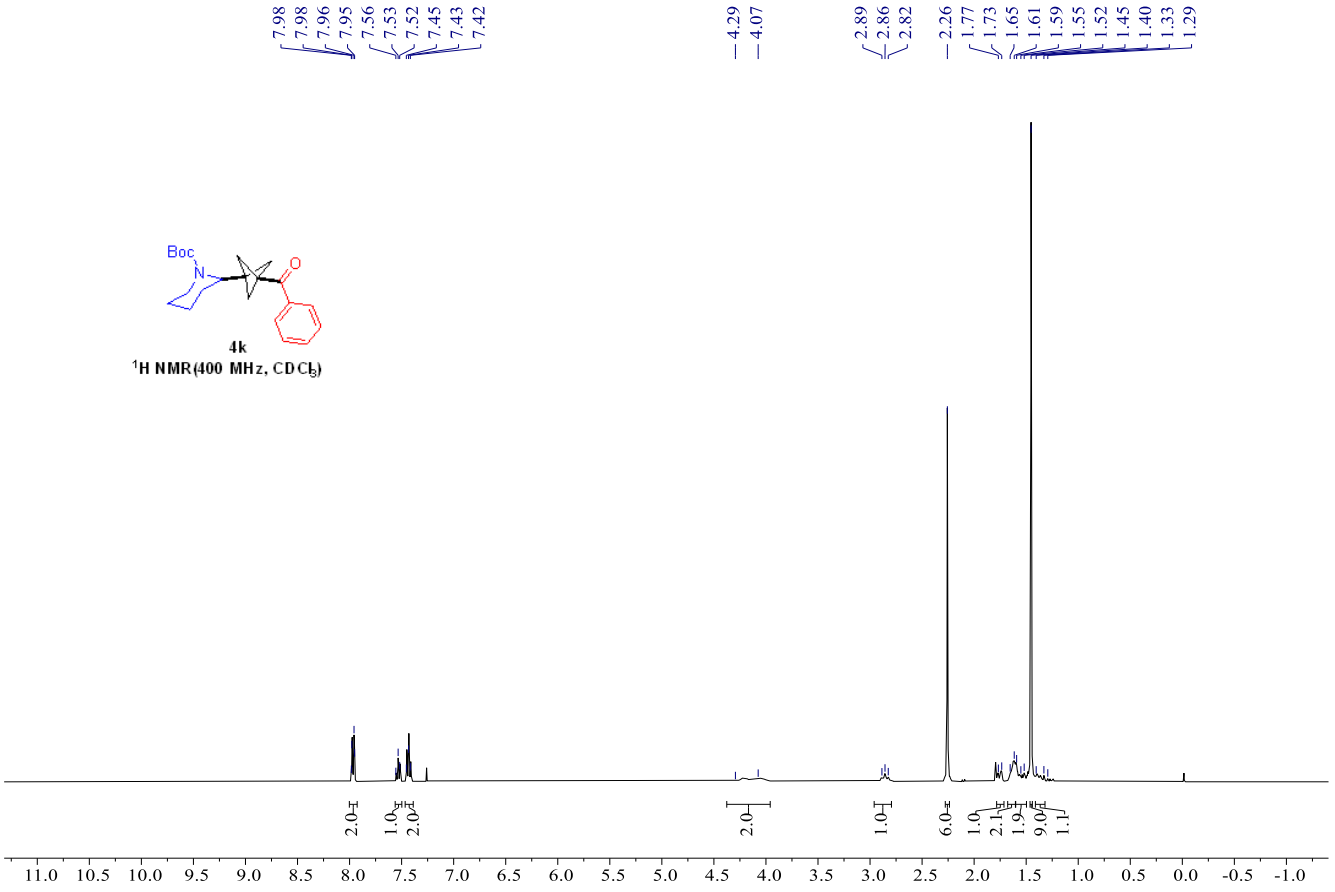
4j

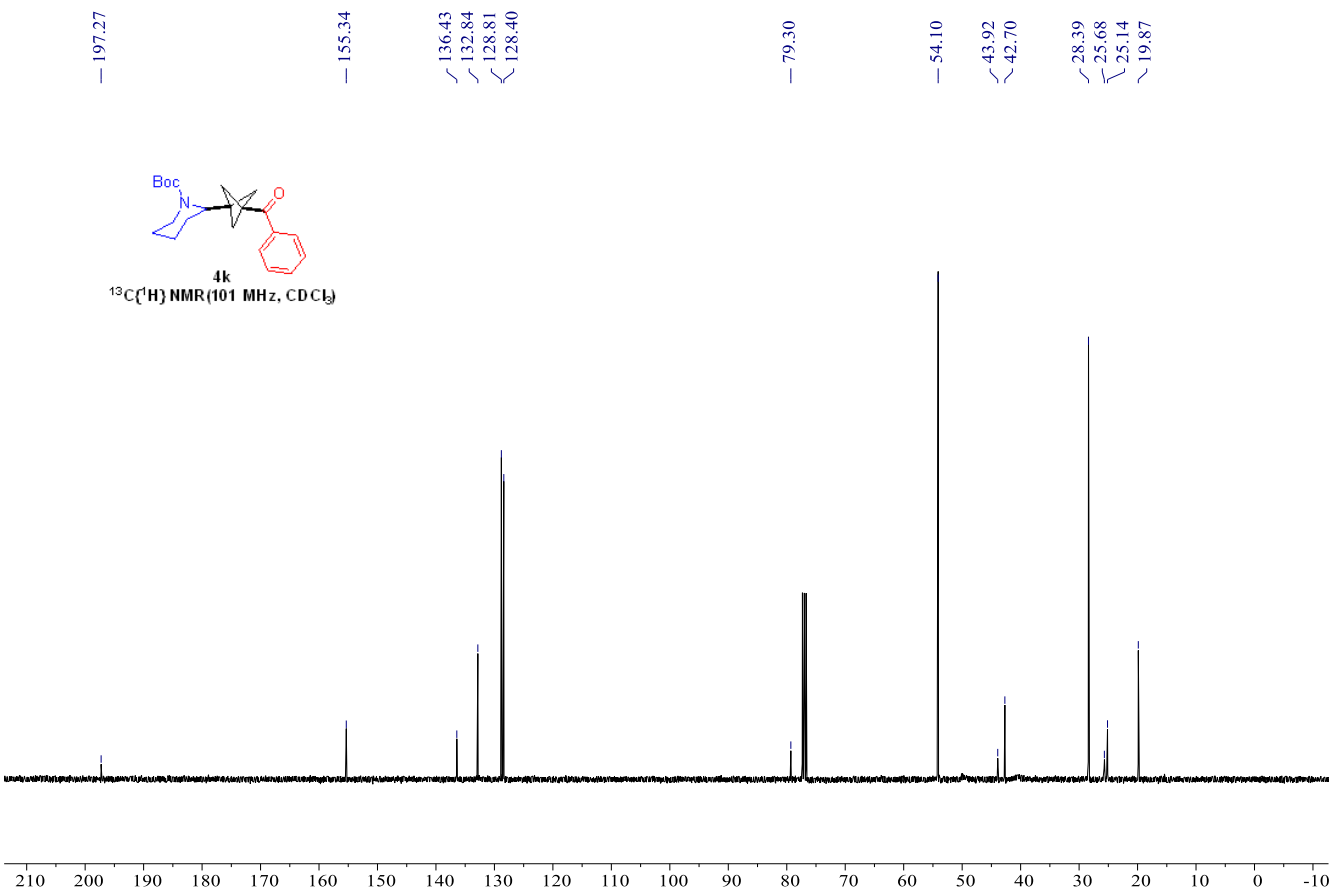
^{1}H NMR(400 MHz, $CDCl_3$)

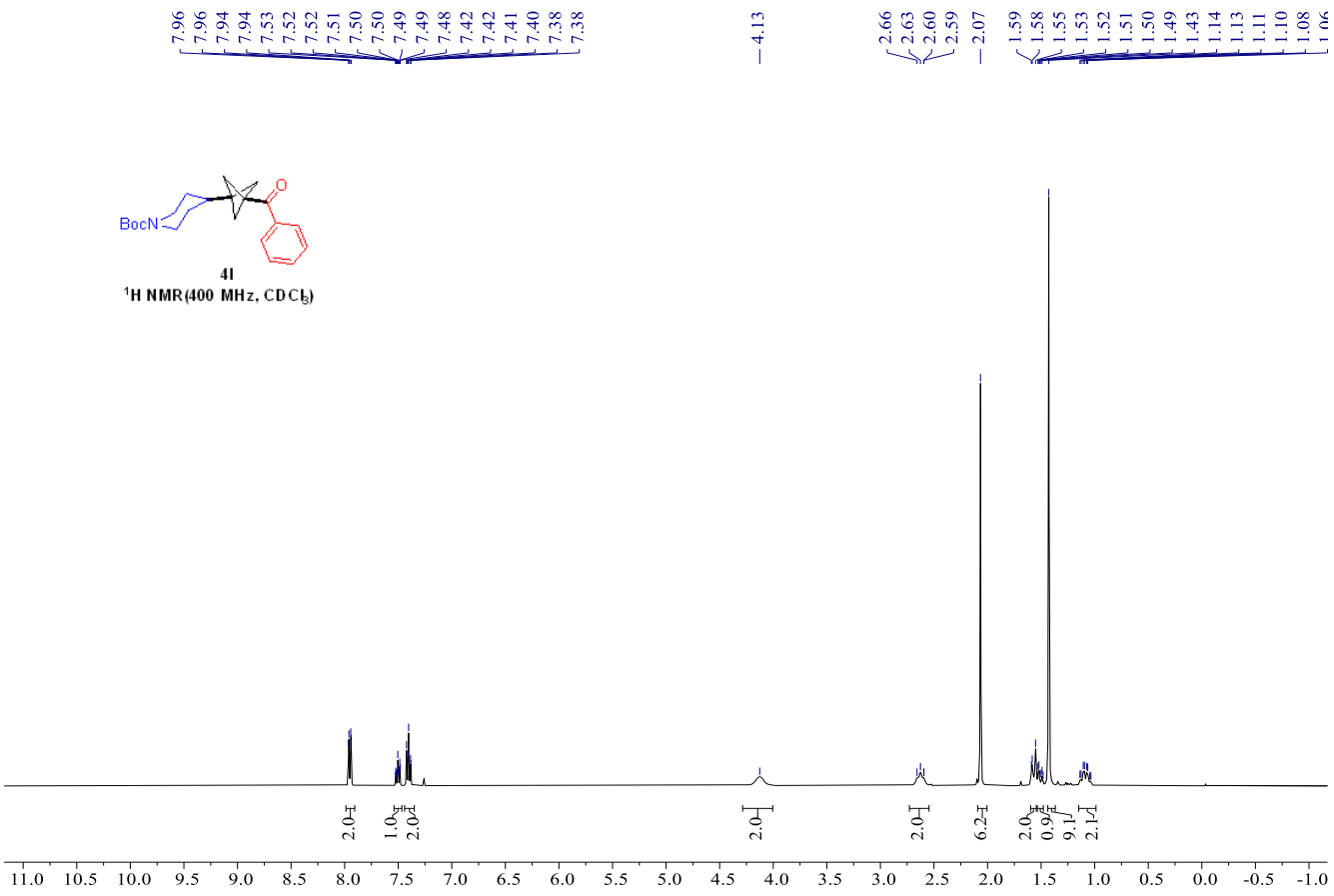


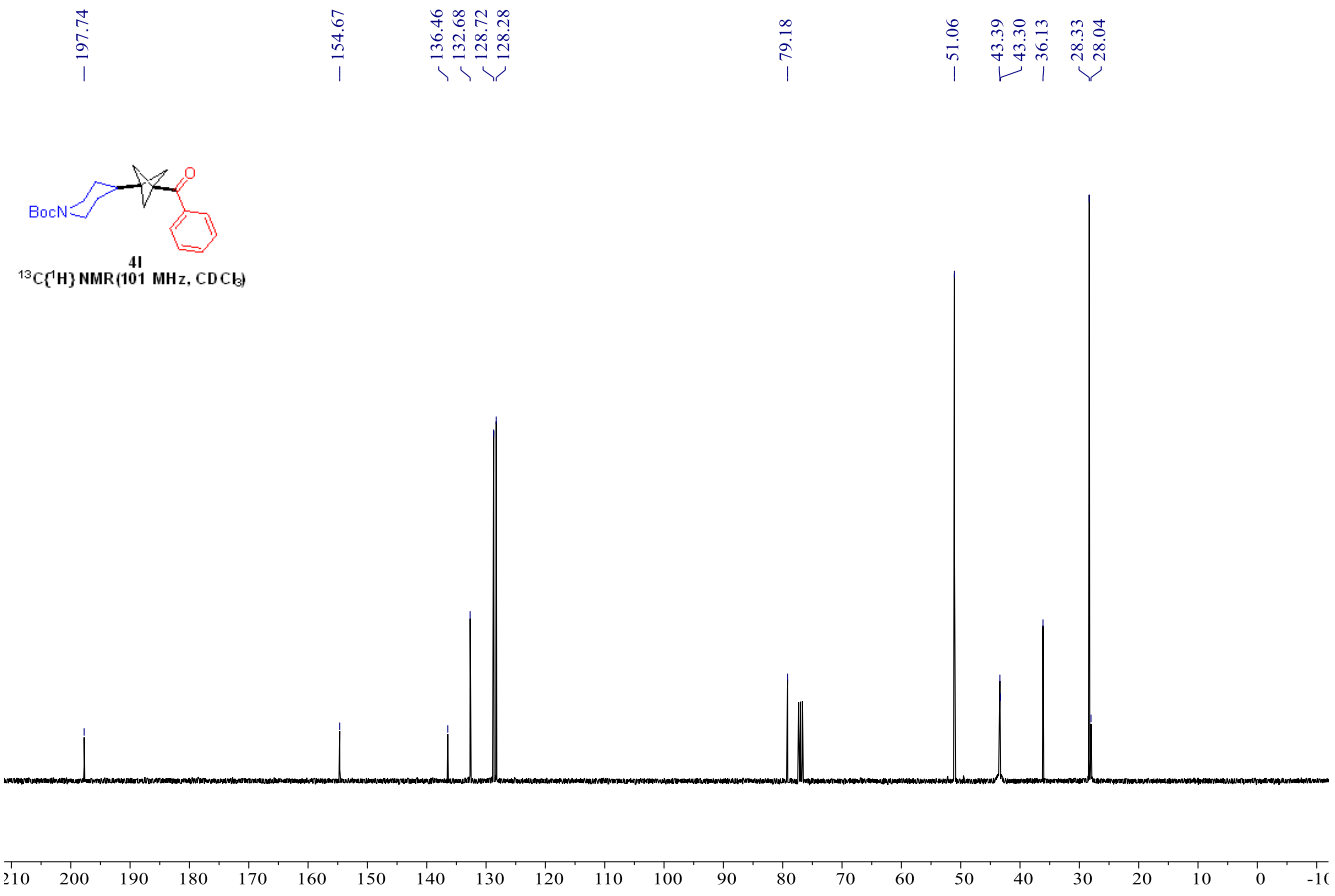
4j

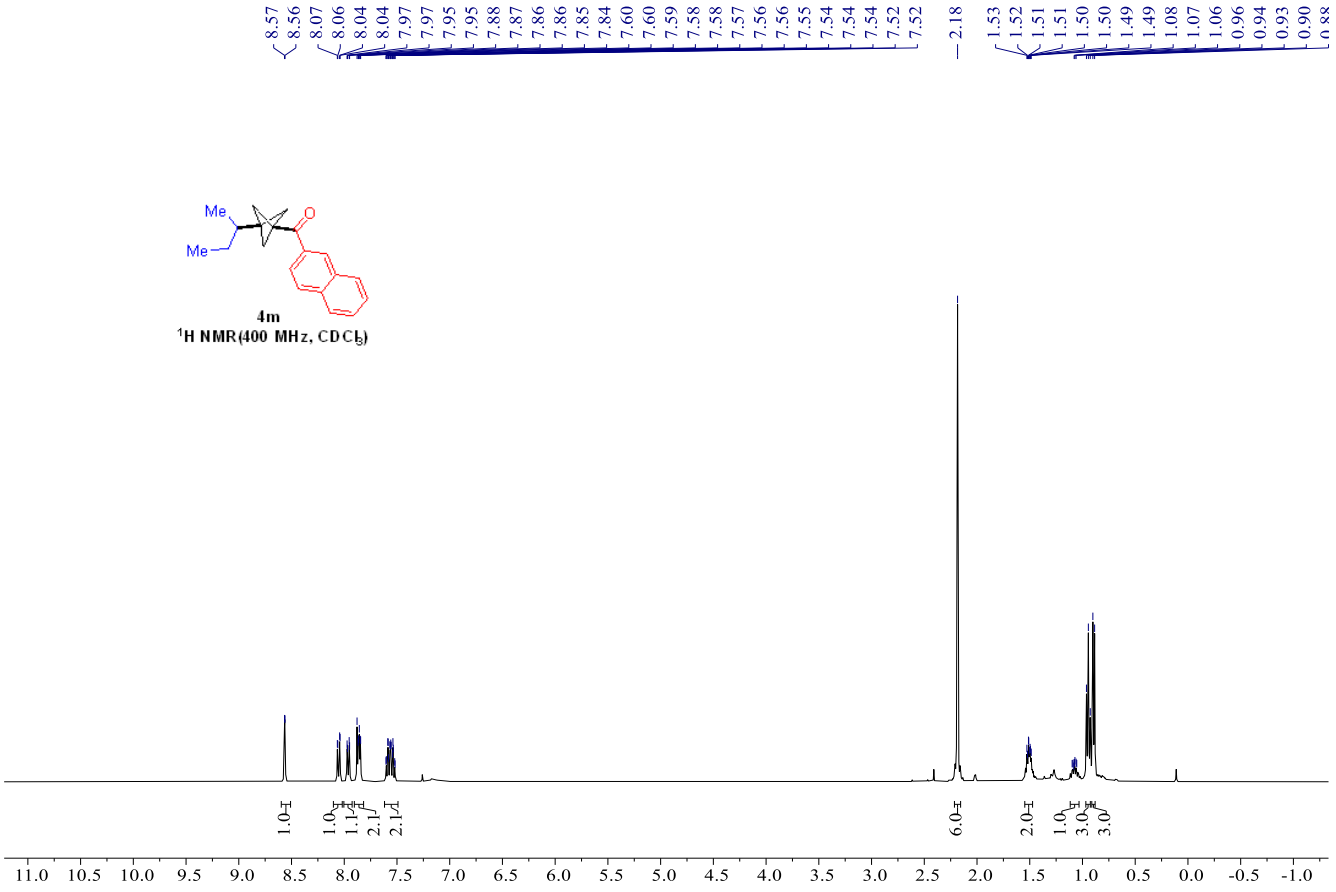
^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$)

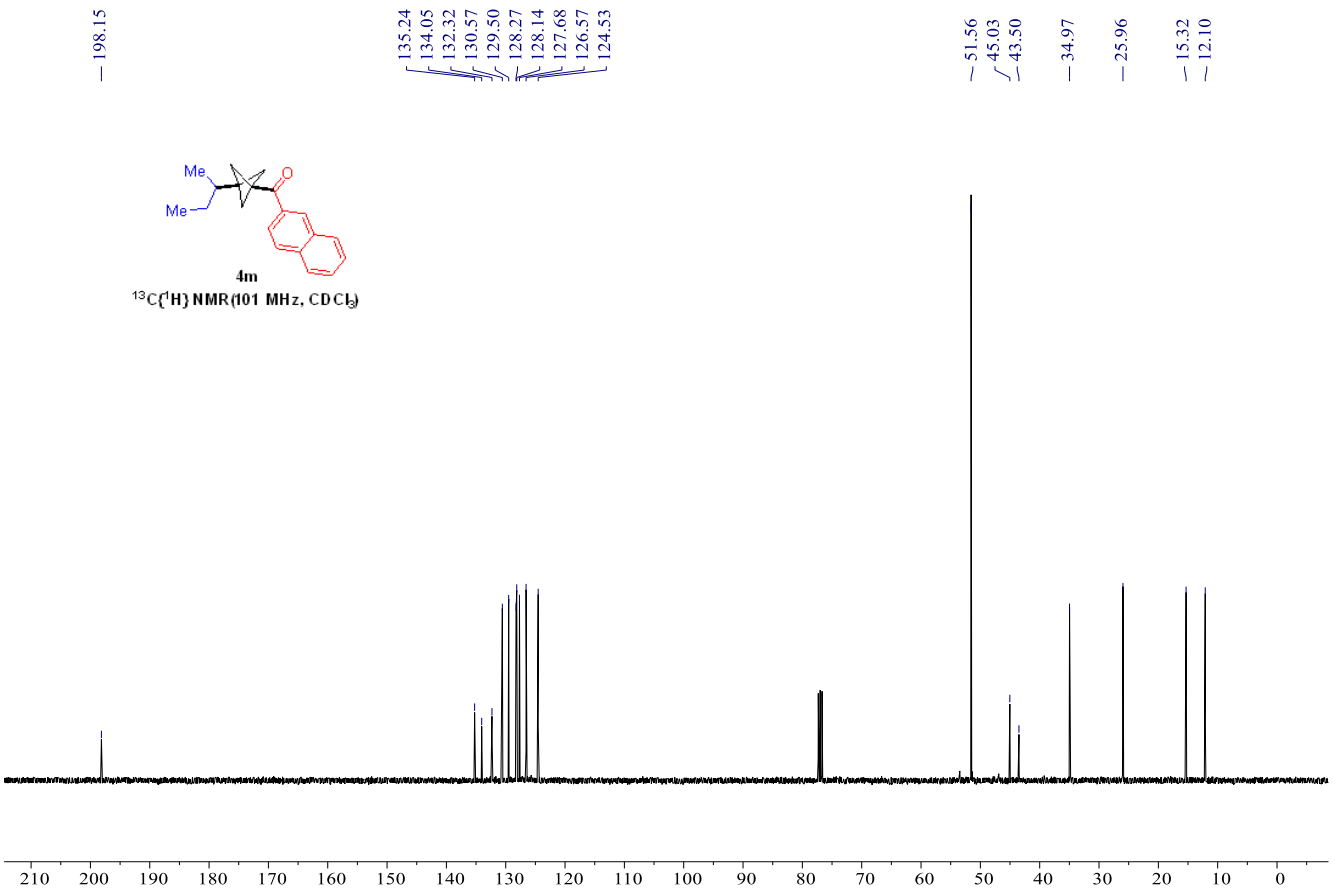

7.98
7.98
7.96
7.95
7.56
7.53
7.52
7.45
7.43
7.42
4.29
4.07
2.89
2.86
2.82
2.26
1.77
1.73
1.65
1.61
1.59
1.55
1.52
1.45
1.40
1.33
1.29
Boc
N
O
4k
^{1}H NMR(400 MHz, CDCl$_3$)
2.0
1.0
2.0
2.0
1.0
6.0
1.0
2.1
1.9
9.0
1.1
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0

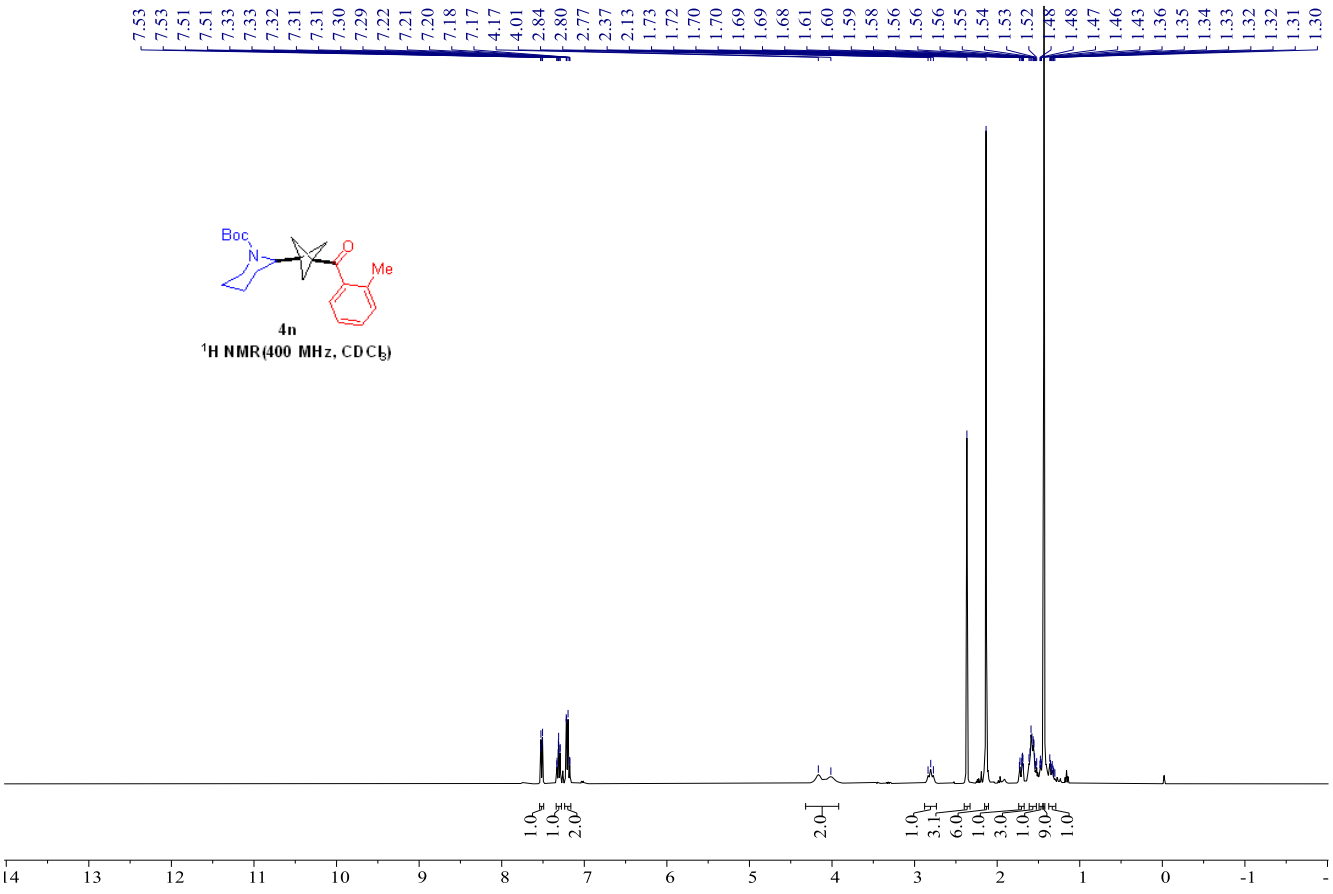

197.27
155.34
136.43
132.84
128.81
128.40
79.30
54.10
43.92
42.70
28.39
25.68
25.14
19.87
Boc
N
O
4k
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

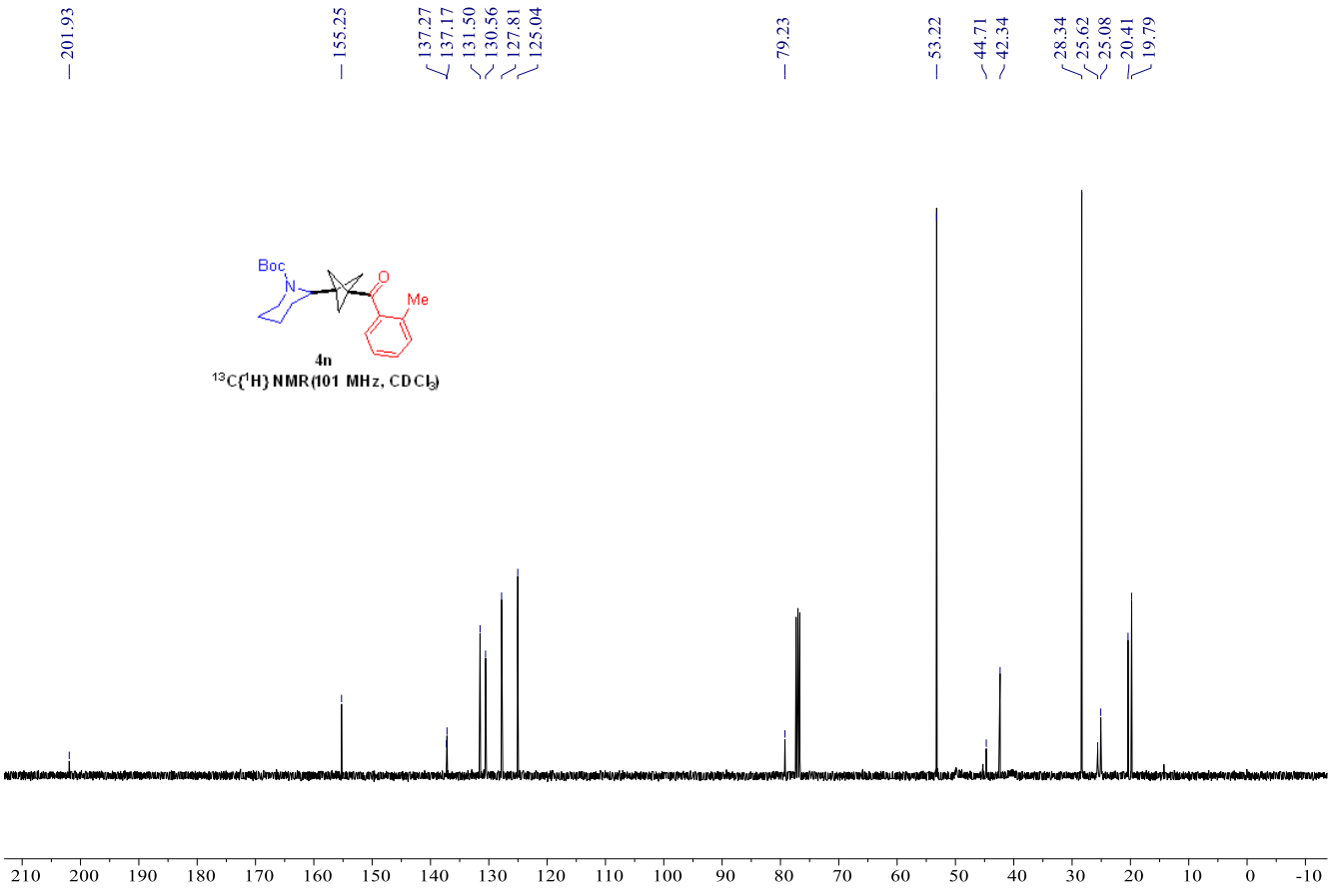

7.96
7.96
7.94
7.94
7.53
7.52
7.52
7.51
7.50
7.50
7.49
7.49
7.48
7.42
7.42
7.41
7.40
7.38
7.38
4.13
2.66
2.63
2.60
2.59
2.07
1.59
1.58
1.55
1.53
1.52
1.51
1.50
1.49
1.43
1.14
1.13
1.11
1.10
1.08
BocN
O
4l
^{1}H NMR(400 MHz, CDCl$_3$)
2.0
1.0
2.0
2.0
2.0
6.2
2.0
0.9
9.1
2.1
11.0 10.5 10.0 9.5 9.0 8.5 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 -0.5 -1.0

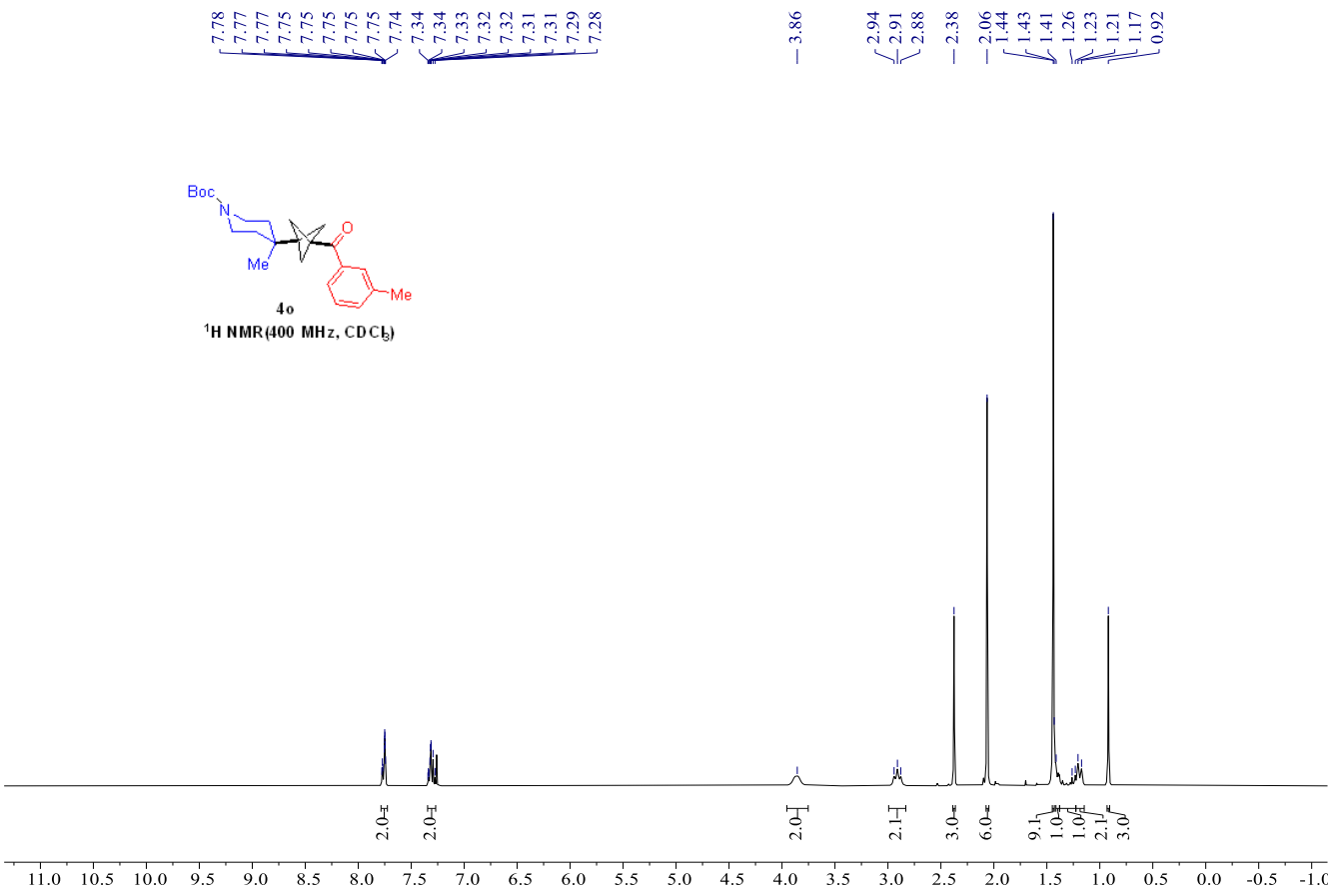

197.74
154.67
136.46
132.68
128.72
128.28
79.18
51.06
43.39
43.30
36.13
28.33
28.04
BocN
O
4l
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

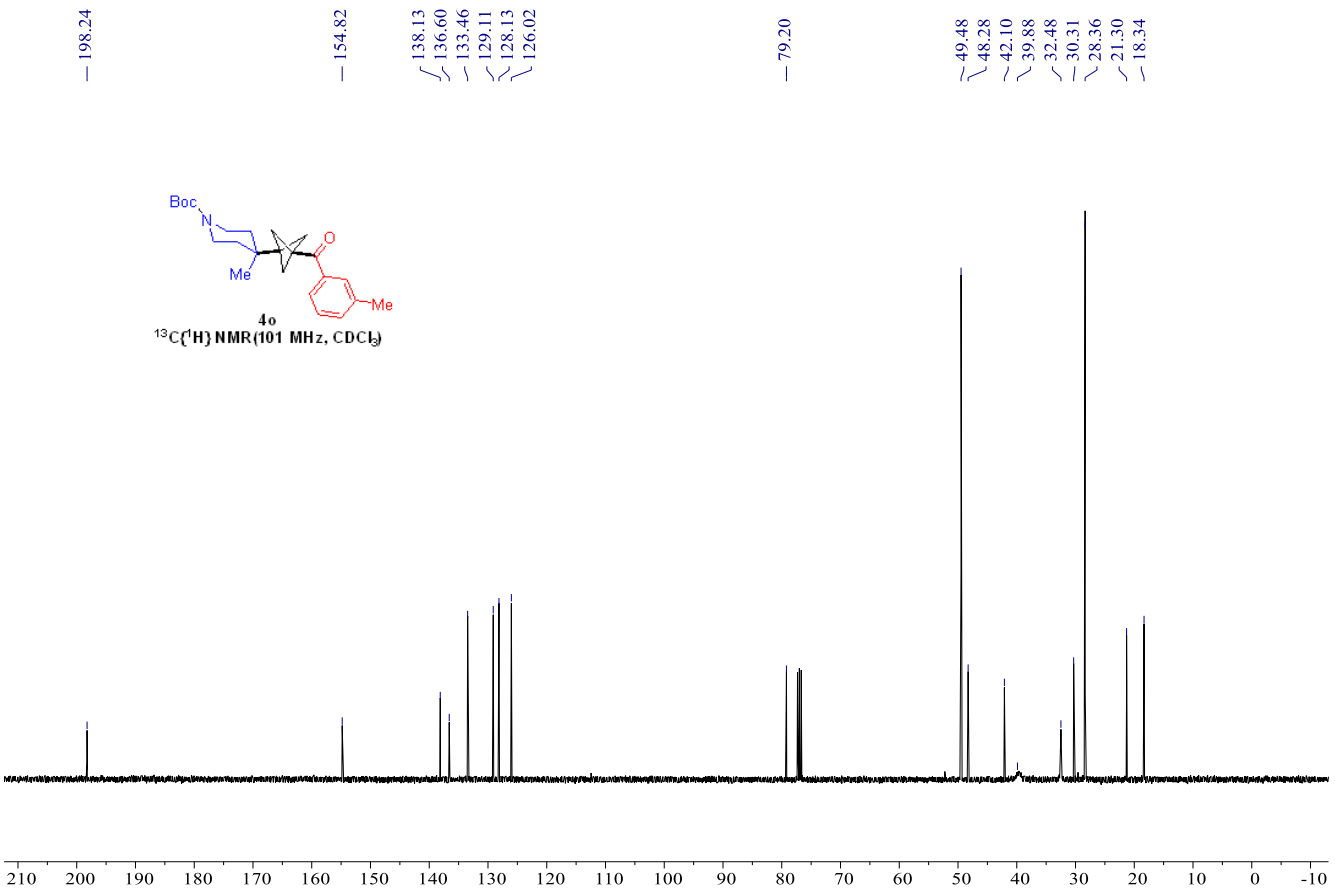

8.57
8.56
8.07
8.06
8.04
8.04
7.97
7.97
7.95
7.95
7.88
7.87
7.86
7.86
7.85
7.84
7.60
7.60
7.59
7.58
7.58
7.57
7.56
7.56
7.55
7.54
7.54
7.54
7.52
7.52
2.18
1.53
1.52
1.51
1.51
1.50
1.50
1.49
1.49
1.08
1.07
1.06
0.96
0.94
0.93
0.90
Me
Me
O
4m
^{1}H NMR(400 MHz, CDCl$_3$)
1.0
1.0
1.1
2.1
2.1
6.0
2.0
1.0
3.0
3.0
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 -0.5 -1.0

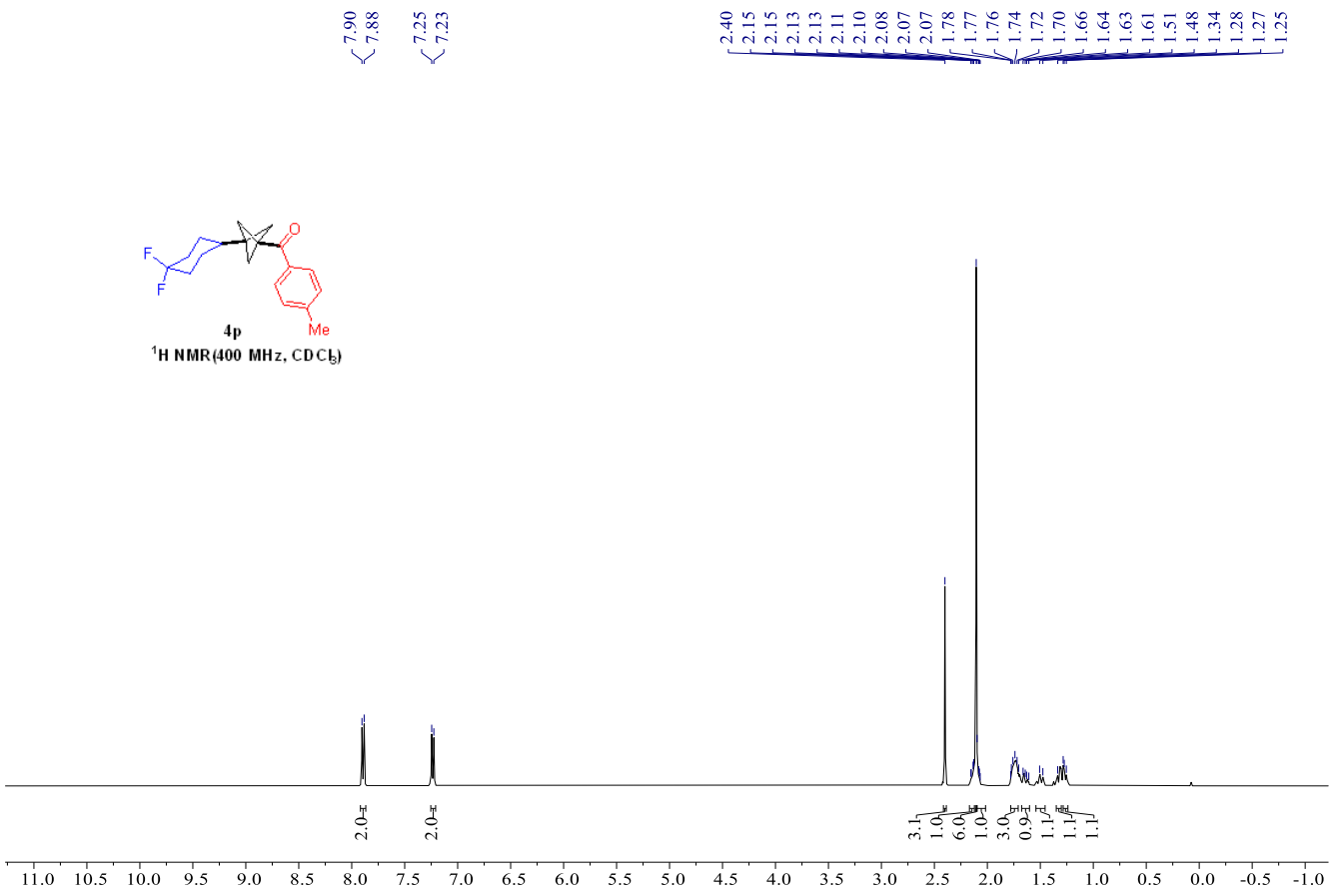

198.15
135.24
134.05
132.32
130.57
129.50
128.27
128.14
127.68
126.57
124.53
51.56
45.03
43.50
34.97
25.96
15.32
12.10
Me
Me
O
4m
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

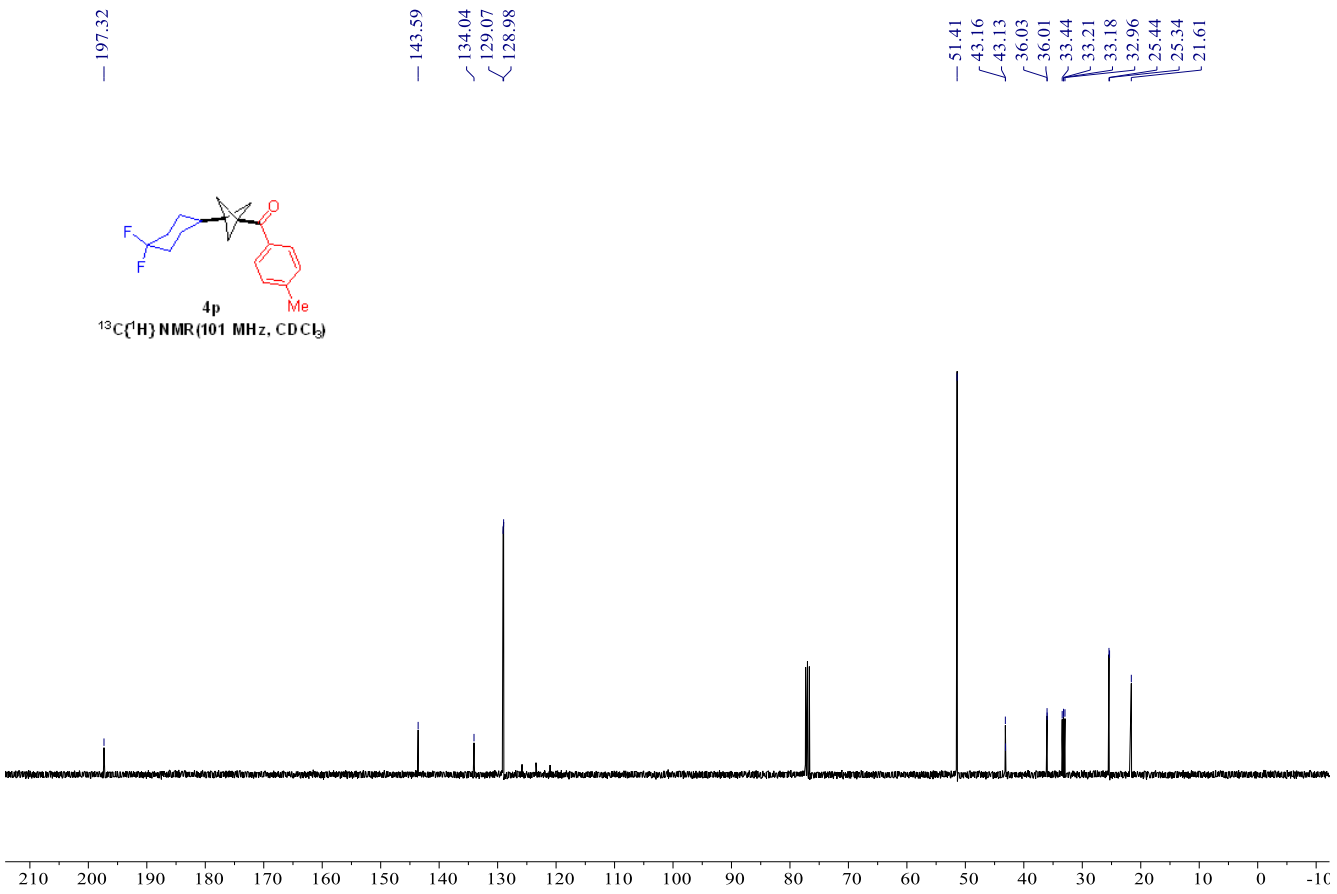

Boc
N
O
Me
4n
^{1}H NMR(400 MHz, CDCl$_3$)

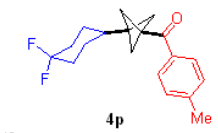

Boc
N
O
Me
4n
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)


7.78
7.77
7.77
7.75
7.75
7.75
7.75
7.75
7.74
7.34
7.34
7.33
7.32
7.32
7.31
7.31
7.29
7.28
3.86
2.94
2.91
2.88
2.38
2.06
1.44
1.43
1.41
1.26
1.23
1.21
1.17
0.92
Boc
N
Me
O
Me
4o
1H NMR(400 MHz, CDCl3)
2.0
2.0
2.0
2.1
3.0
6.0
9.1
1.0
1.0
2.1
3.0
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 -0.5 -1.0


198.24
154.82
138.13
136.60
133.46
129.11
128.13
126.02
79.20
49.48
48.28
42.10
39.88
32.48
30.31
28.36
21.30
18.34
Boc
N
Me
O
Me
4o
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

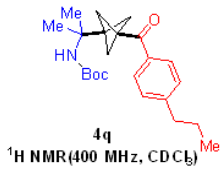

7.90
7.88
7.25
7.23
2.40
2.15
2.15
2.13
2.13
2.11
2.10
2.08
2.07
2.07
1.78
1.77
1.76
1.74
1.72
1.70
1.66
1.64
1.63
1.61
1.51
1.48
1.34
1.28
1.27
1.25
F
F
O
Me
4p
^{1}H NMR(400 MHz, CDCl$_3$)
2.0
2.0
3.1
1.0
6.0
1.0
3.0
0.9
1.1
1.1
1.1
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


197.32
143.59
134.04
129.07
128.98
51.41
43.16
43.13
36.03
36.01
33.44
33.21
33.18
32.96
25.44
25.34
21.61
F
F
O
Me
4p
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



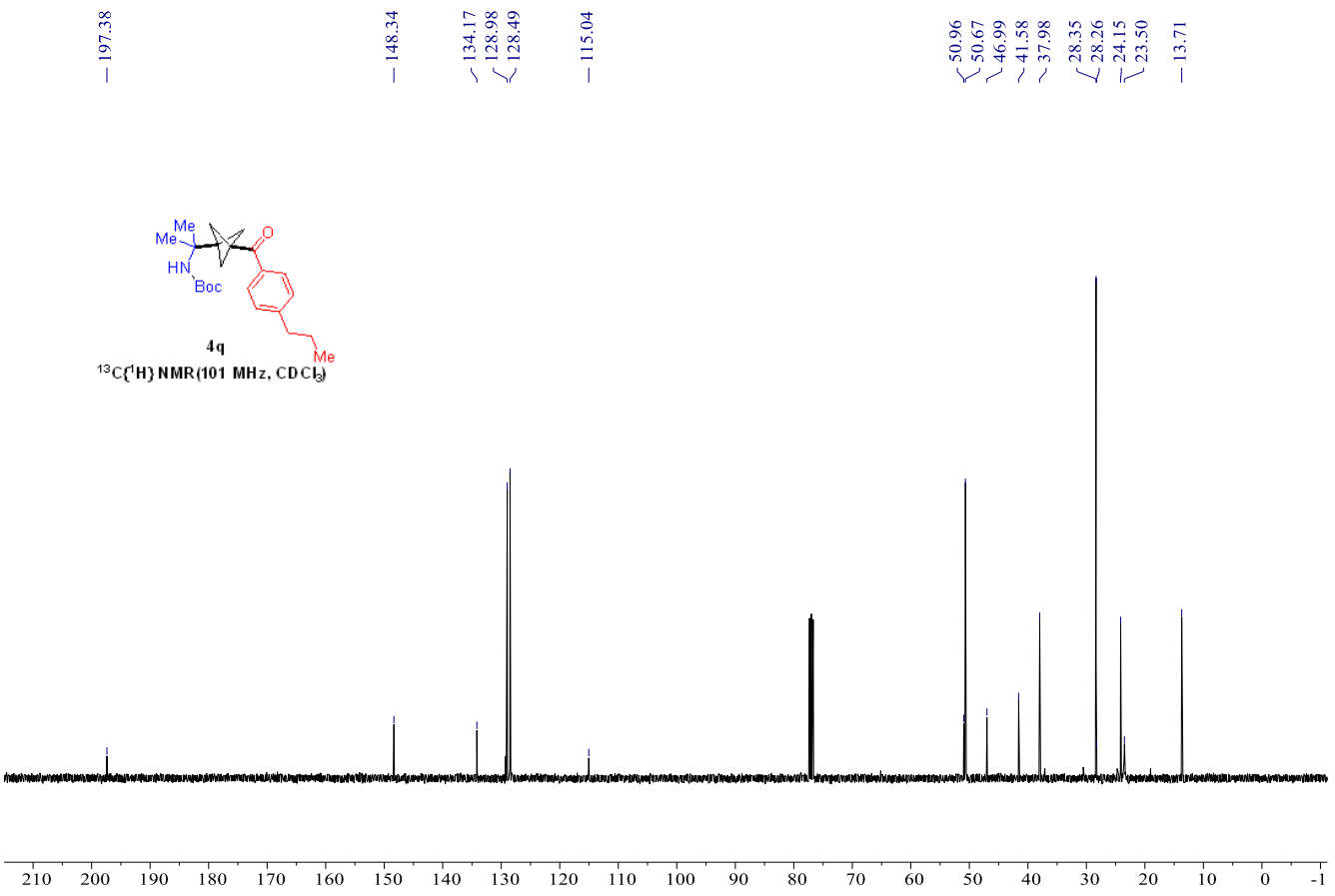
4p

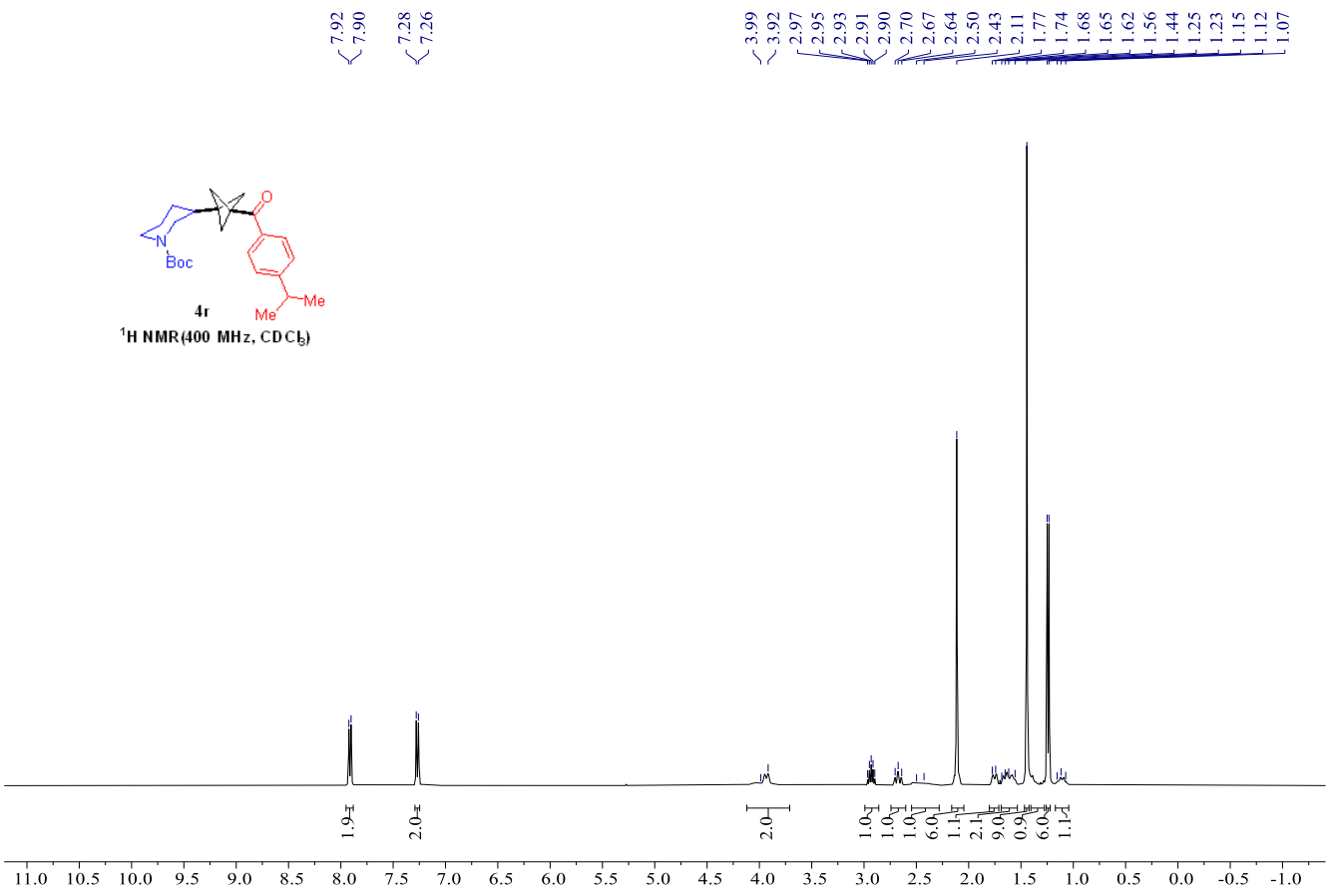
^{19}F NMR(376 MHz, $CDCl_3$)

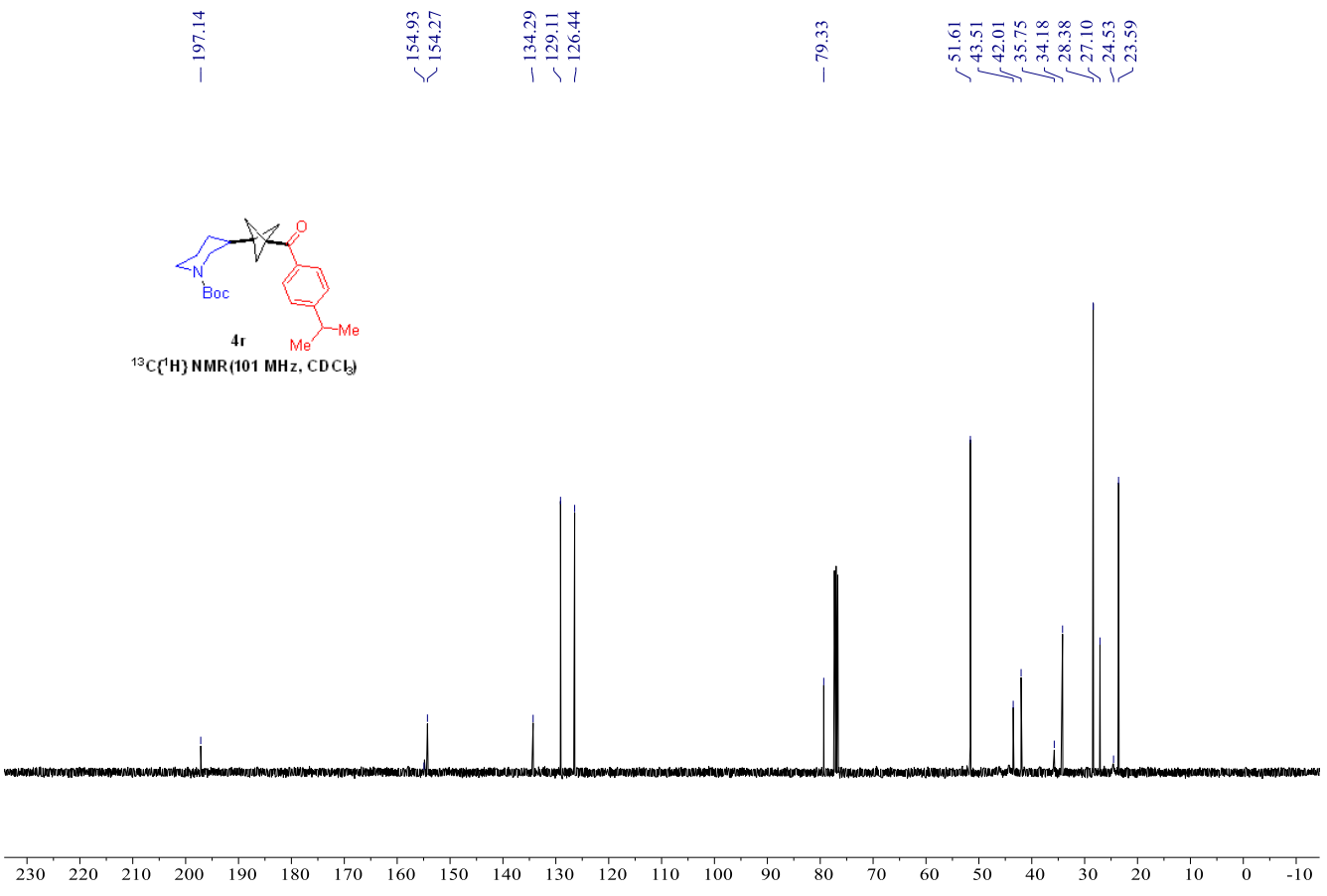


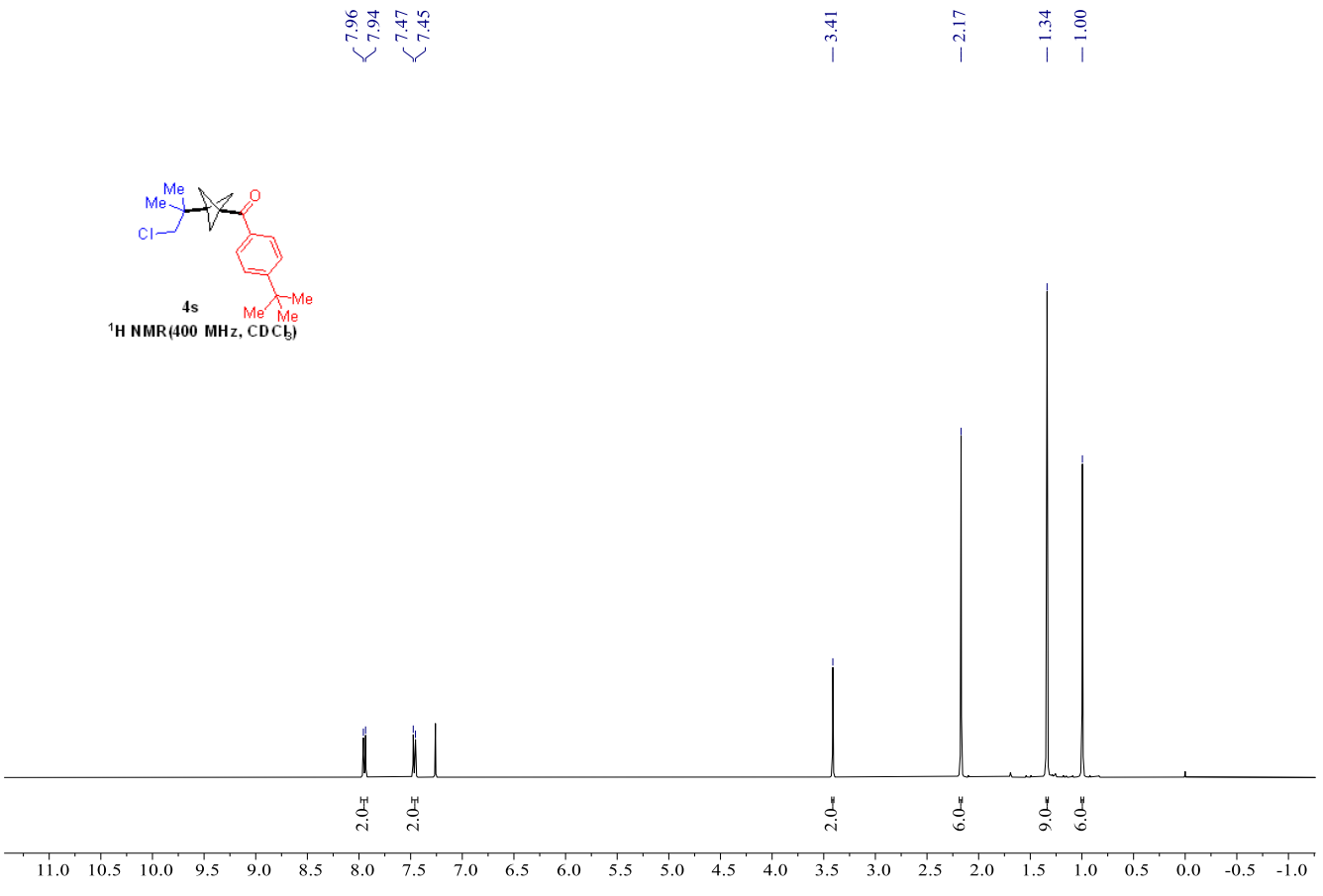
4q

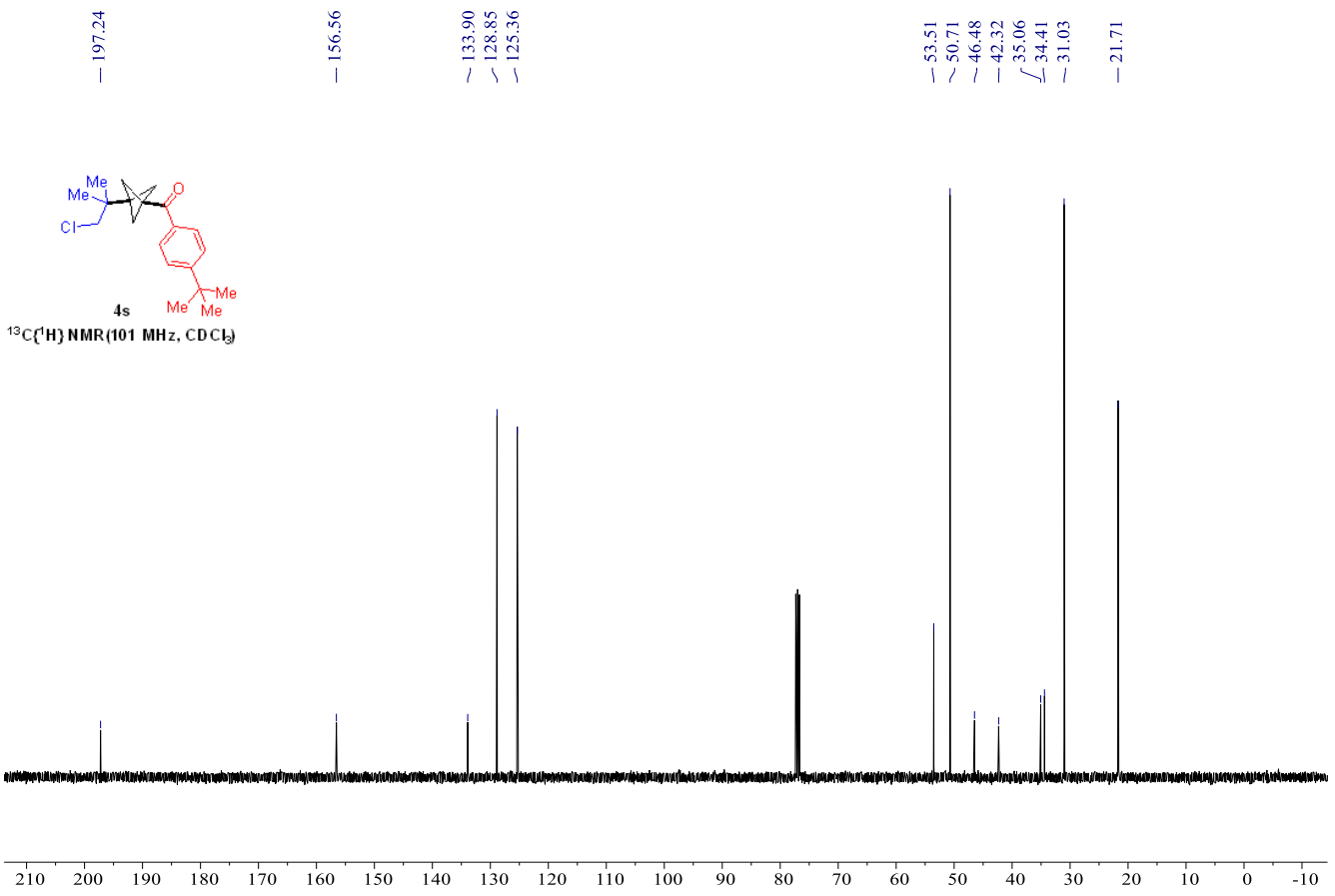
^{1}H NMR(400 MHz, $CDCl_3$)

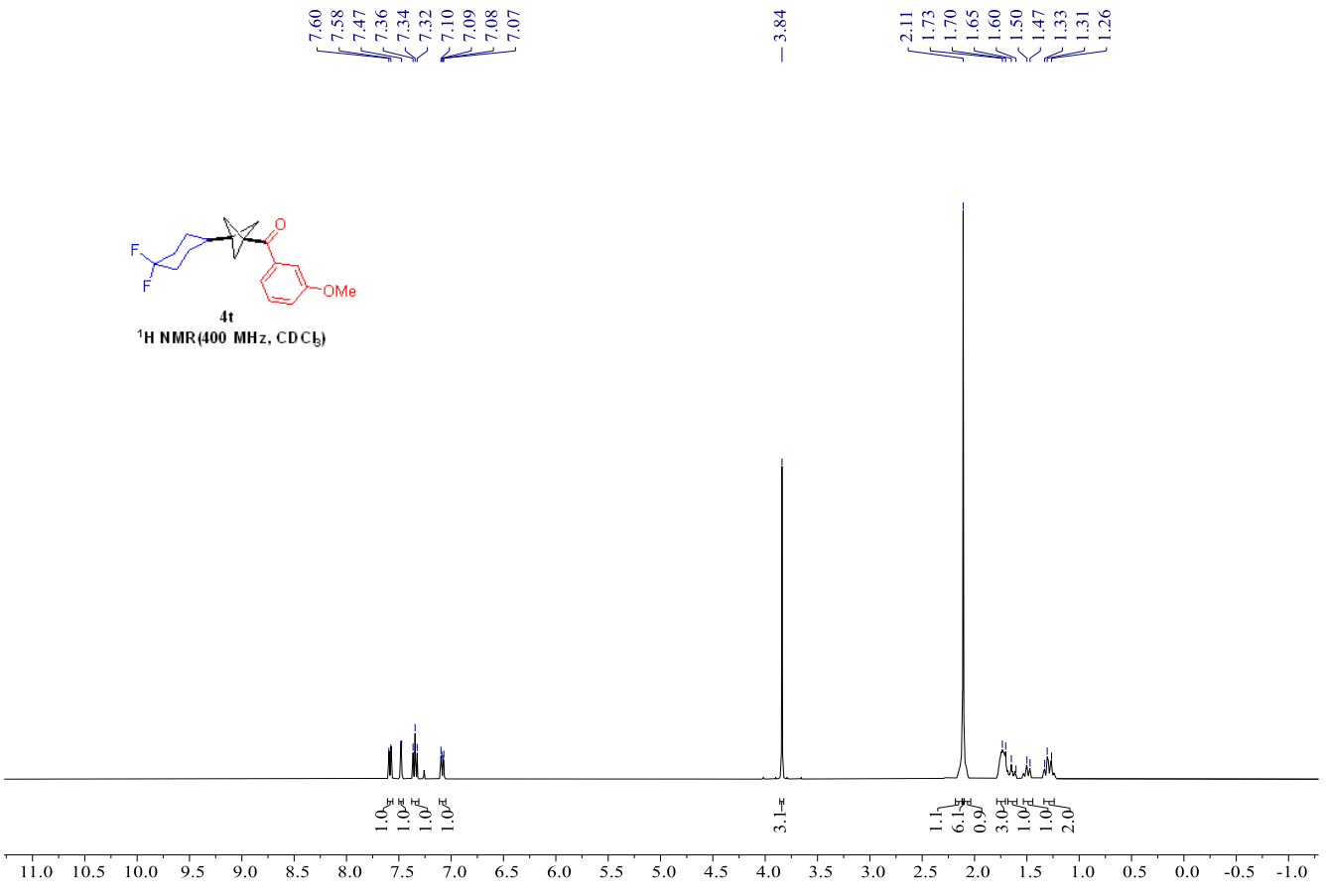

197.38
148.34
134.17
128.98
128.49
115.04
50.96
50.67
46.99
41.58
37.98
28.35
28.26
24.15
23.50
13.71
Me
Me
HN
Boc
O
Me
4q
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

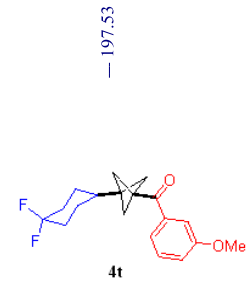

7.92
7.90
7.28
7.26
3.99
3.92
2.97
2.95
2.93
2.91
2.90
2.70
2.67
2.64
2.50
2.43
2.11
1.77
1.74
1.68
1.65
1.62
1.56
1.44
1.25
1.23
1.15
1.12
1.07
N
Boc
O
Me
Me
4r
1H NMR(400 MHz, CDCl3)
1.9
2.0
2.0
1.0
1.0
1.0
6.0
1.1
2.1
9.0
0.9
6.0
1.1
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


197.14
154.93
154.27
134.29
129.11
126.44
79.33
51.61
43.51
42.01
35.75
34.18
28.38
27.10
24.53
23.59
O
N
Boc
Me
Me
4r
$^{13}C\{^{1}H\}$ NMR(101 MHz, $CDCl_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.96
7.94
7.47
7.45
3.41
2.17
1.34
1.00
Me
Me
Cl
O
Me
Me
Me
4s
^{1}H NMR(400 MHz, $CDCl_3$)
2.0
2.0
2.0
6.0
9.0
6.0
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 -0.5 -1.0

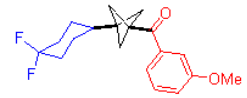

197.24
156.56
133.90
128.85
125.36
53.51
50.71
46.48
42.32
35.06
34.41
31.03
21.71
Me
Me
Cl
O
Me
Me
Me
4s
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


7.60
7.58
7.47
7.36
7.34
7.32
7.10
7.09
7.08
7.07
3.84
2.11
1.73
1.70
1.65
1.60
1.50
1.47
1.33
1.31
1.26
F
F
O
OMe
4t
1H NMR(400 MHz, CDCl3)
1.0
1.0
1.0
1.0
3.1
1.1
6.1
0.9
3.0
1.0
1.0
2.0
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 -0.5 -1.0



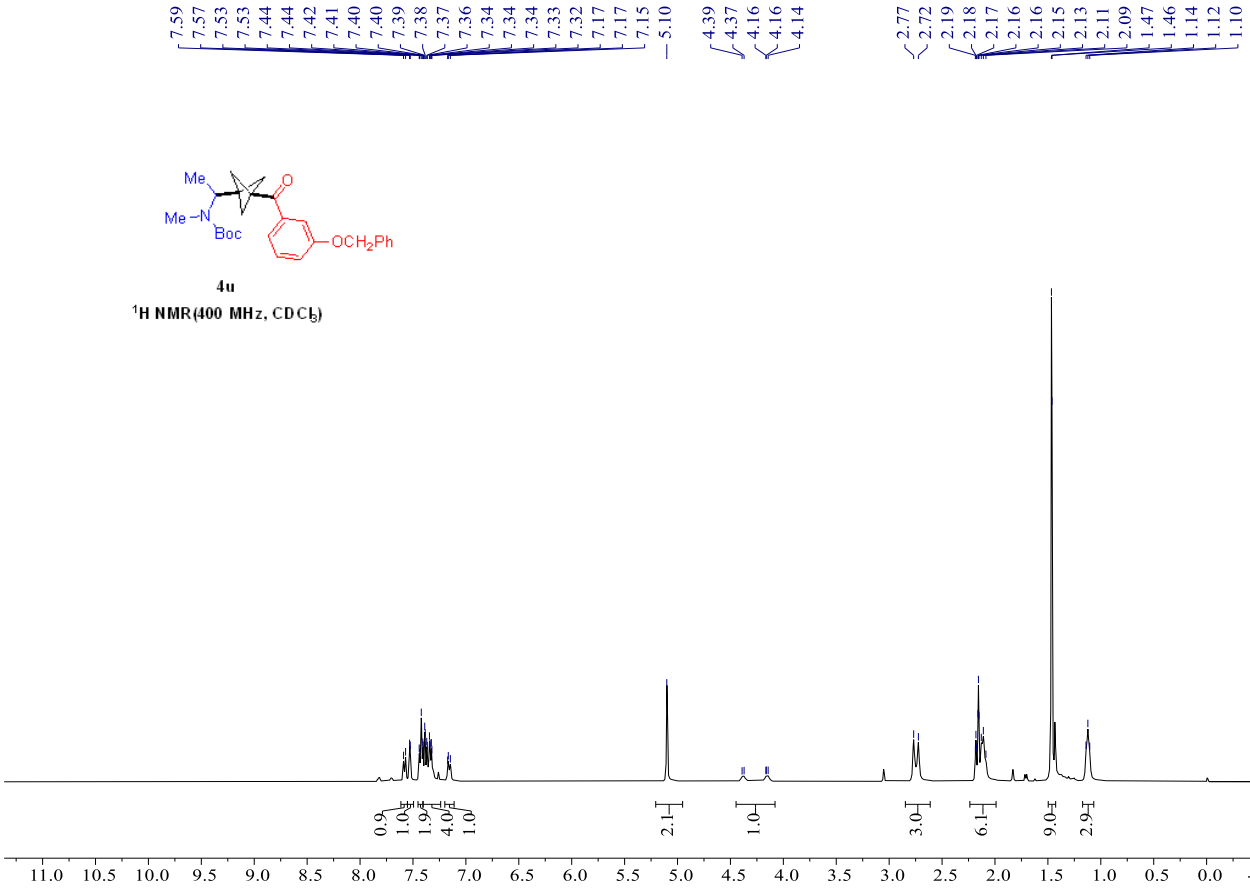
4t

$^{13}C\{^{1}H\}$ NMR(101 MHz, $CDCl_3$)



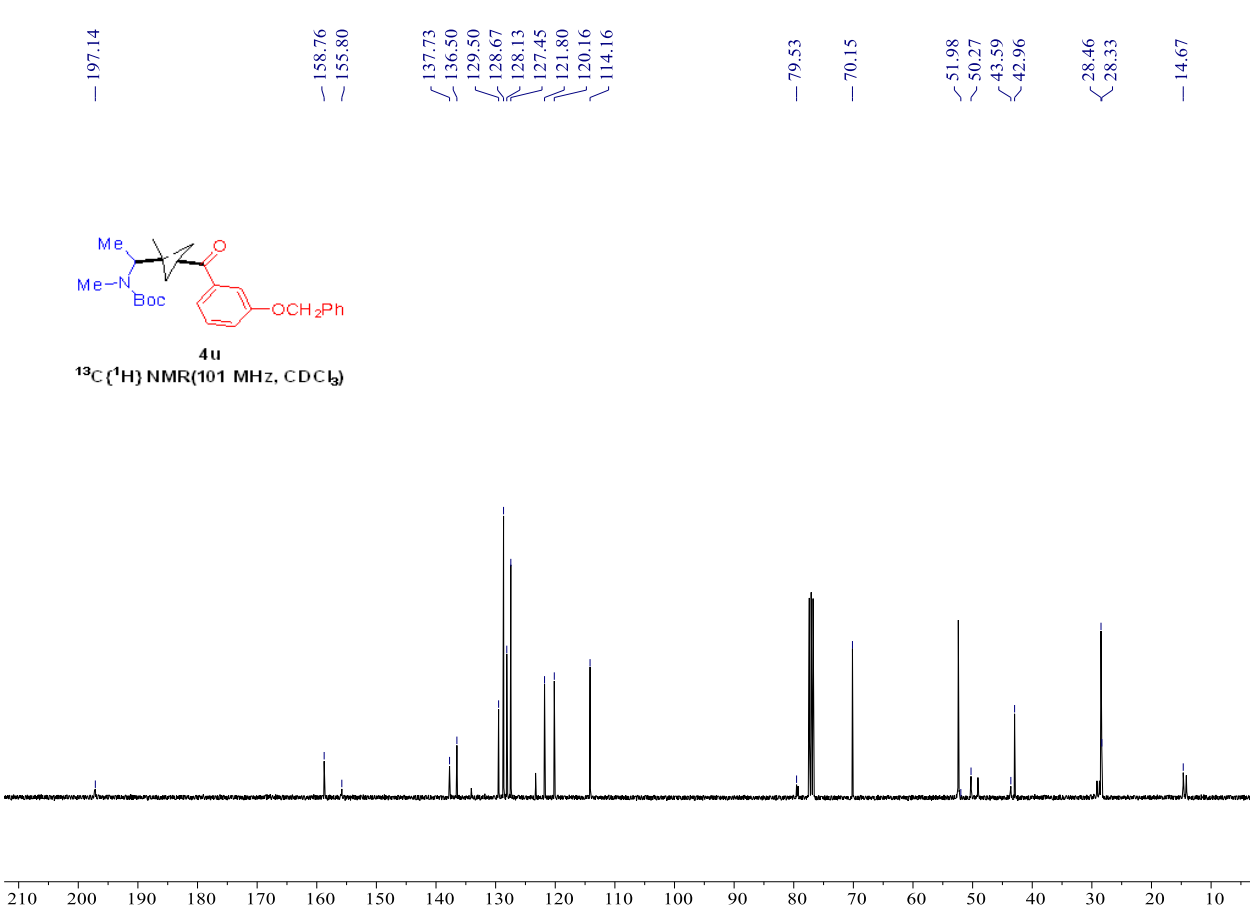
4t

^{19}F NMR(376 MHz, $CDCl_3$)



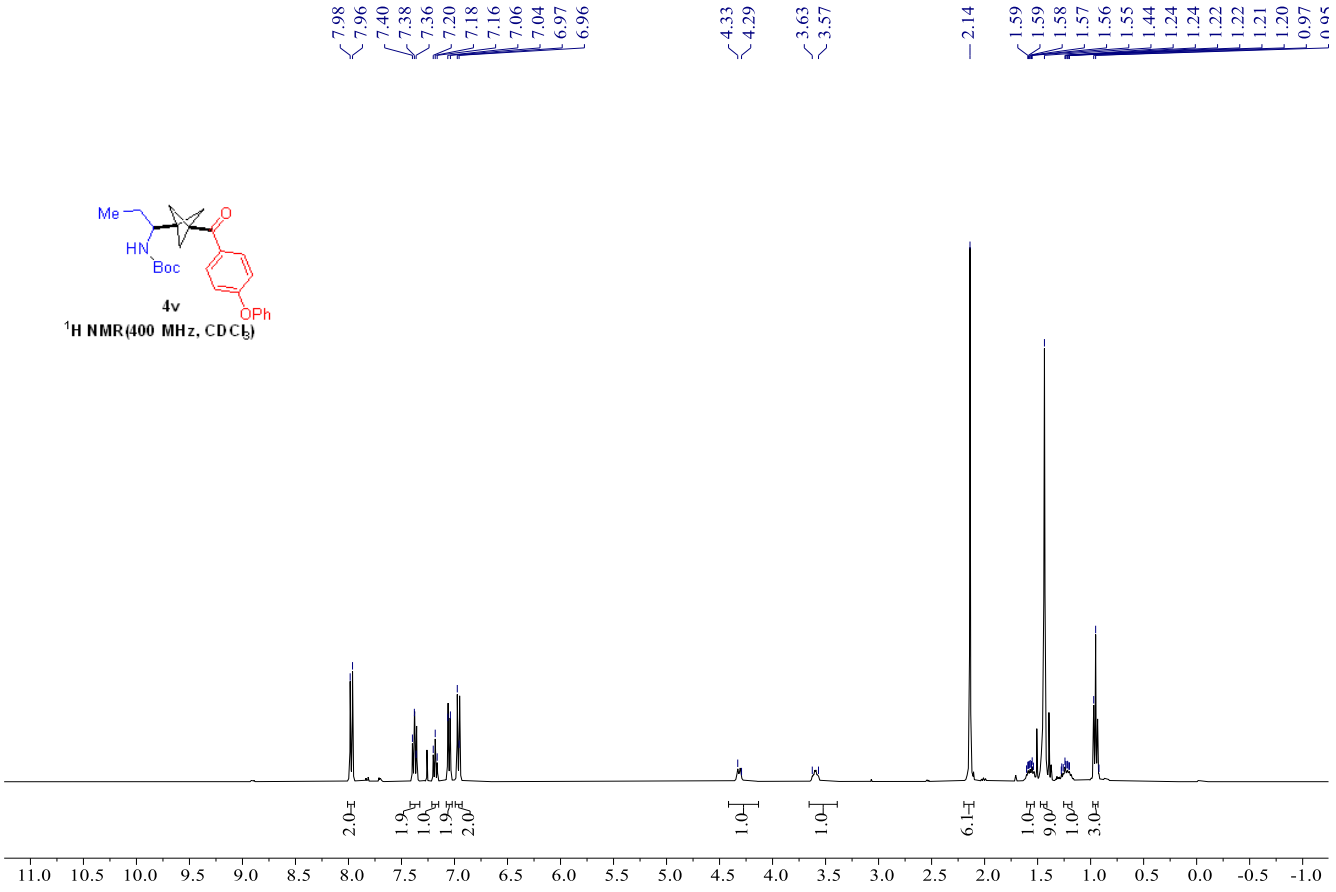
4u

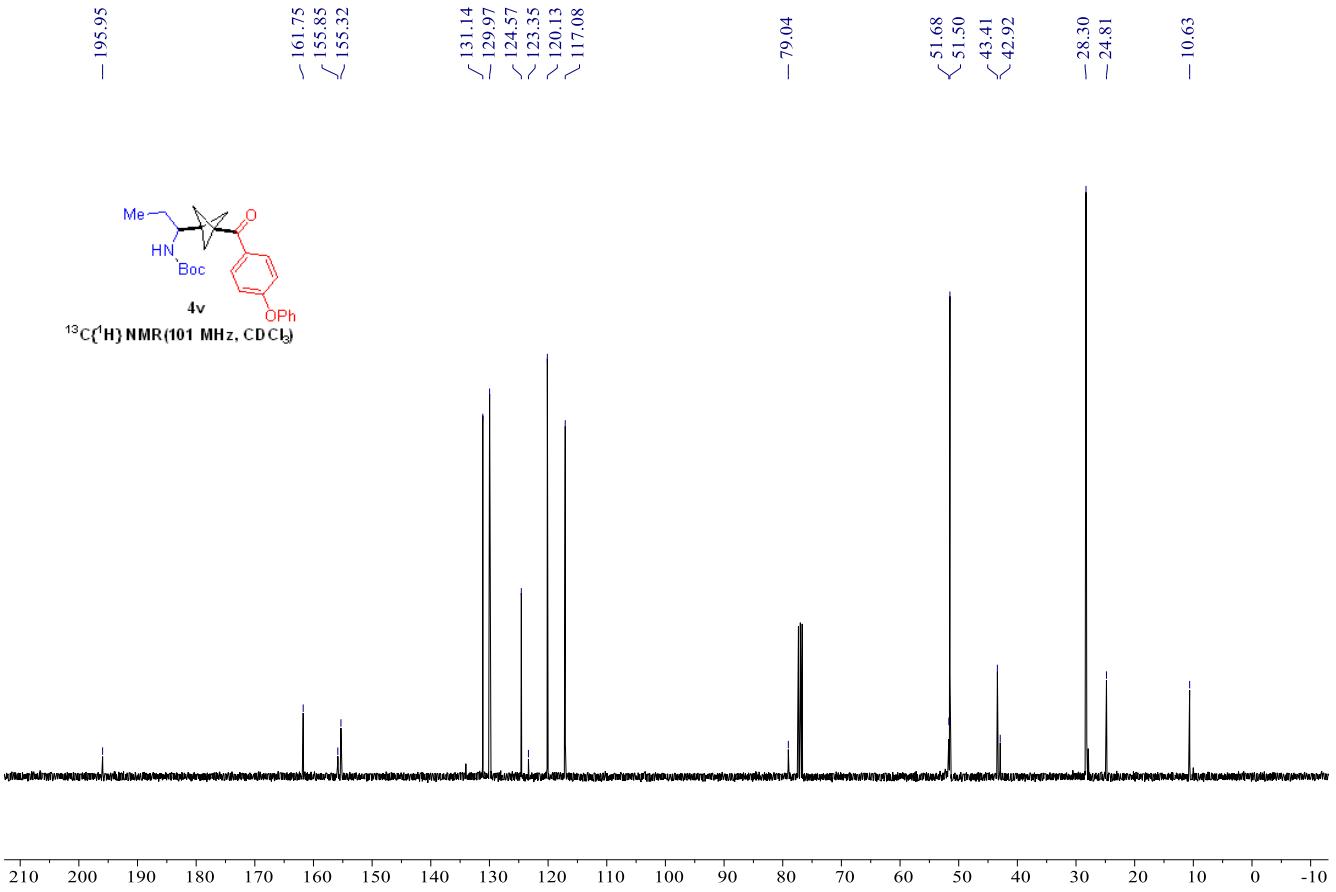
^{1}H NMR(400 MHz, $CDCl_3$)

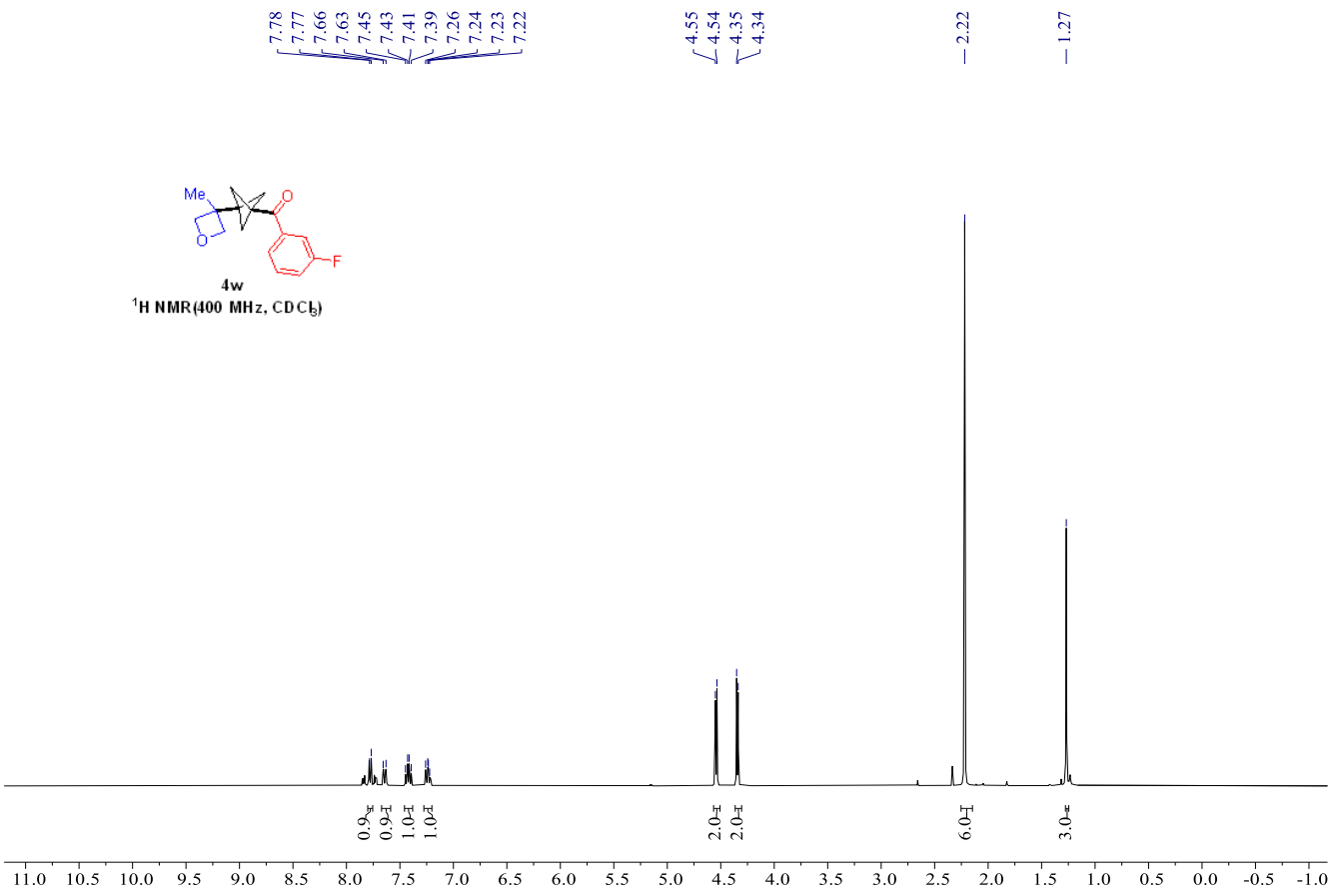


4u

^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$)

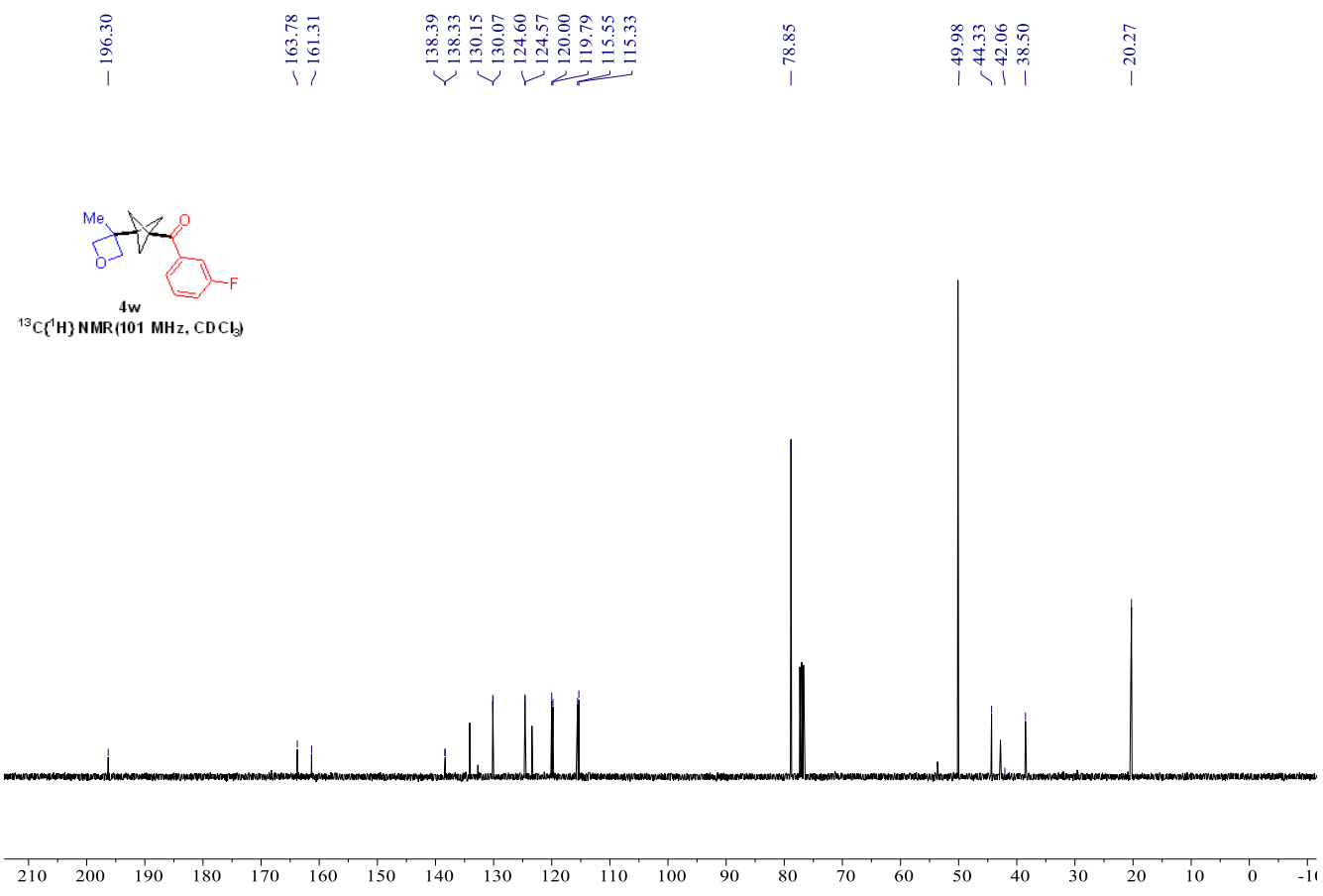

7.98
7.96
7.40
7.38
7.36
7.20
7.18
7.16
7.06
7.04
6.97
6.96
4.33
4.29
3.63
3.57
2.14
1.59
1.59
1.58
1.57
1.56
1.55
1.44
1.24
1.24
1.22
1.22
1.21
1.20
0.97
Me
HN
Boc
O
OPh
4v
^{1}H NMR(400 MHz, CDCl$_3$)
2.0
1.9
1.0
1.9
2.0
1.0
1.0
6.1
1.0
9.0
1.0
3.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


195.95
161.75
155.85
155.32
131.14
129.97
124.57
123.35
120.13
117.08
79.04
51.68
51.50
43.41
42.92
28.30
24.81
10.63
Me
HN
Boc
O
OPh
4v
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



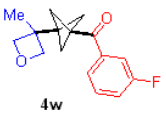
4w

^{1}H NMR (400 MHz, $CDCl_3$)



4w

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$)

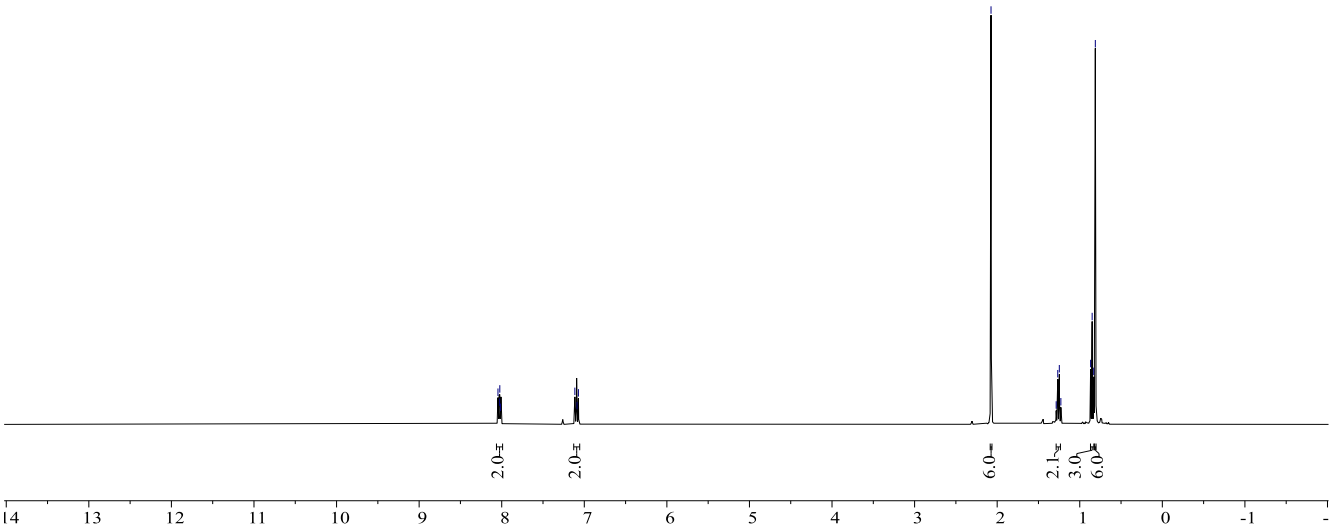


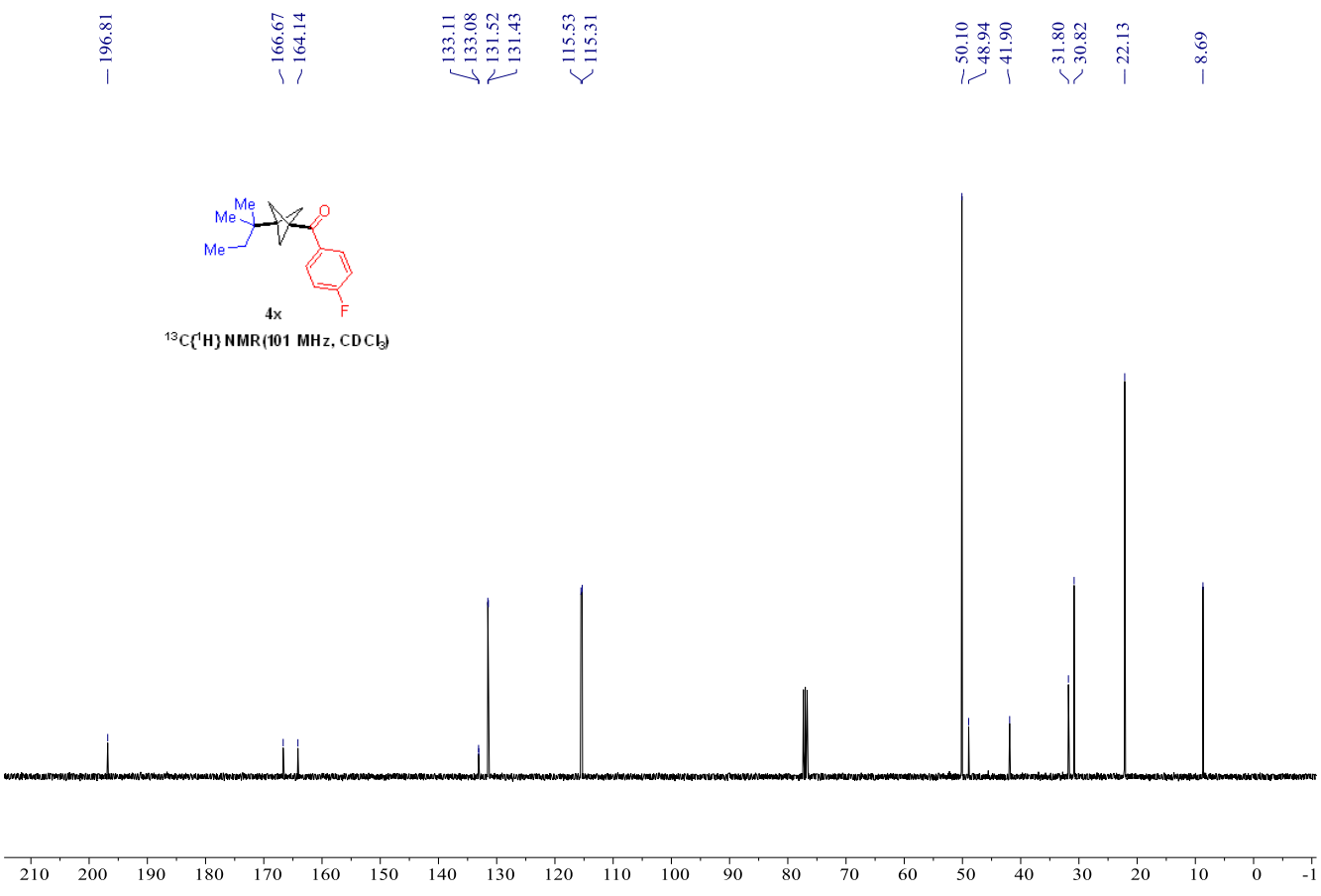
4w

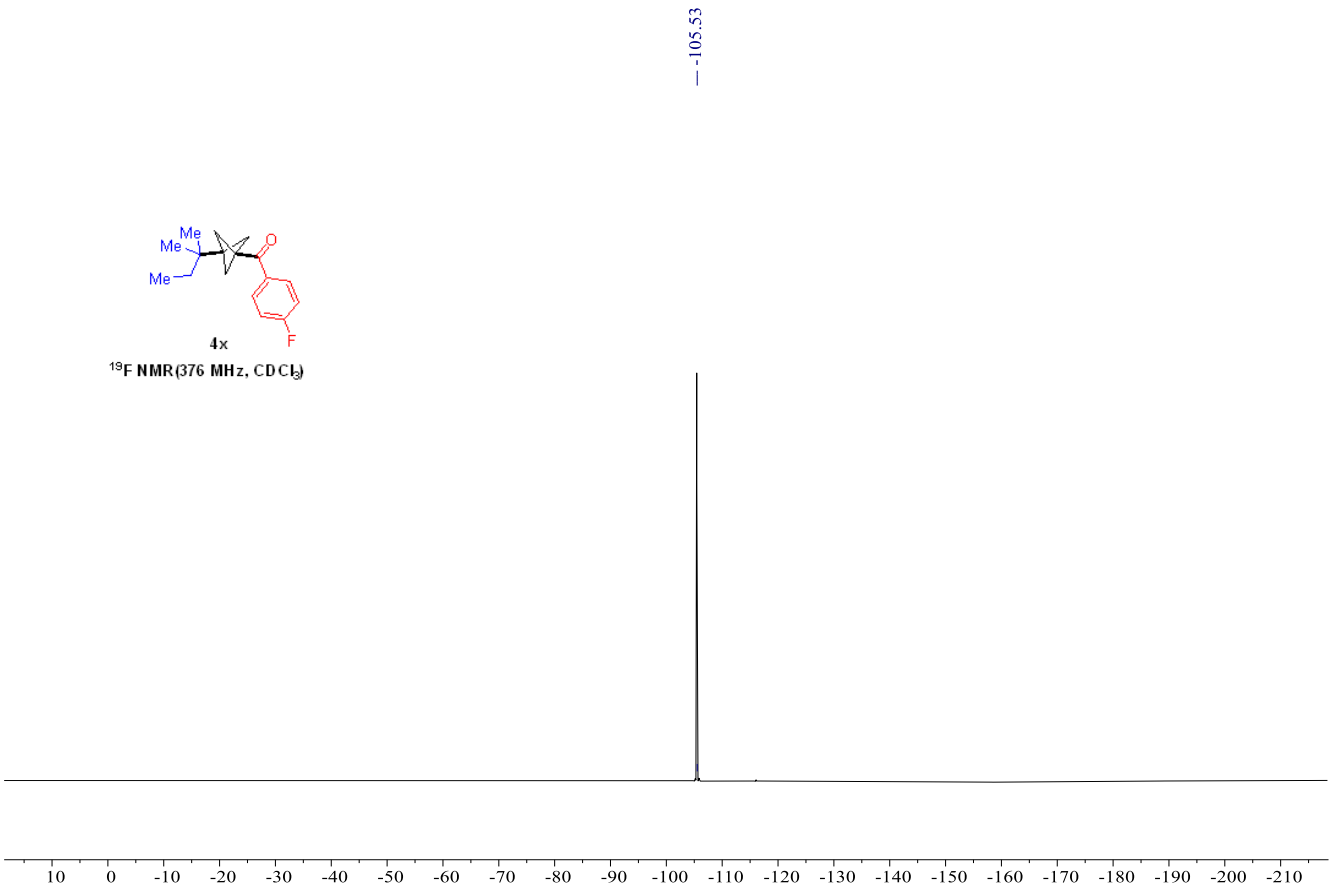
^{19}F NMR(376 MHz, $CDCl_3$)

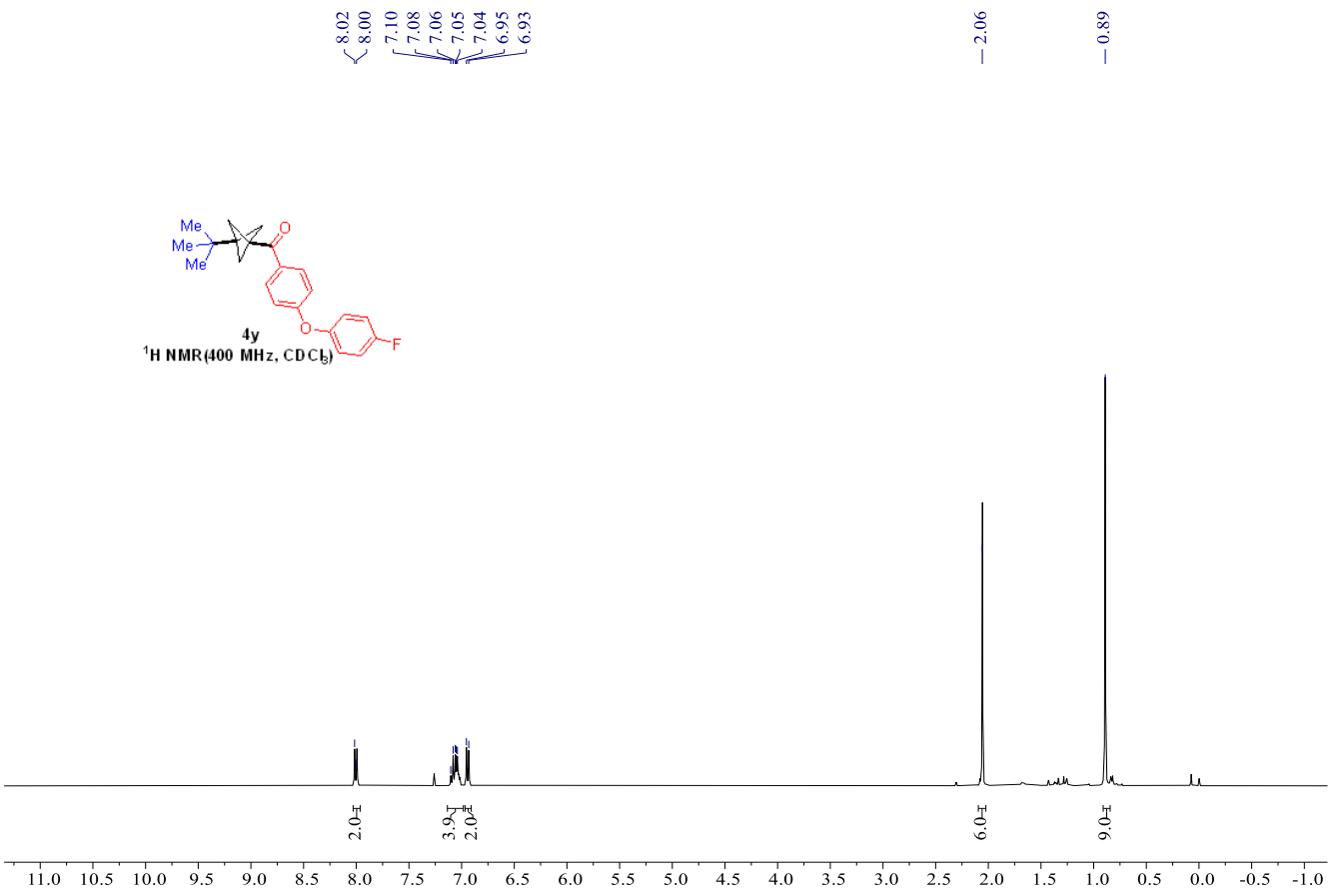
4x

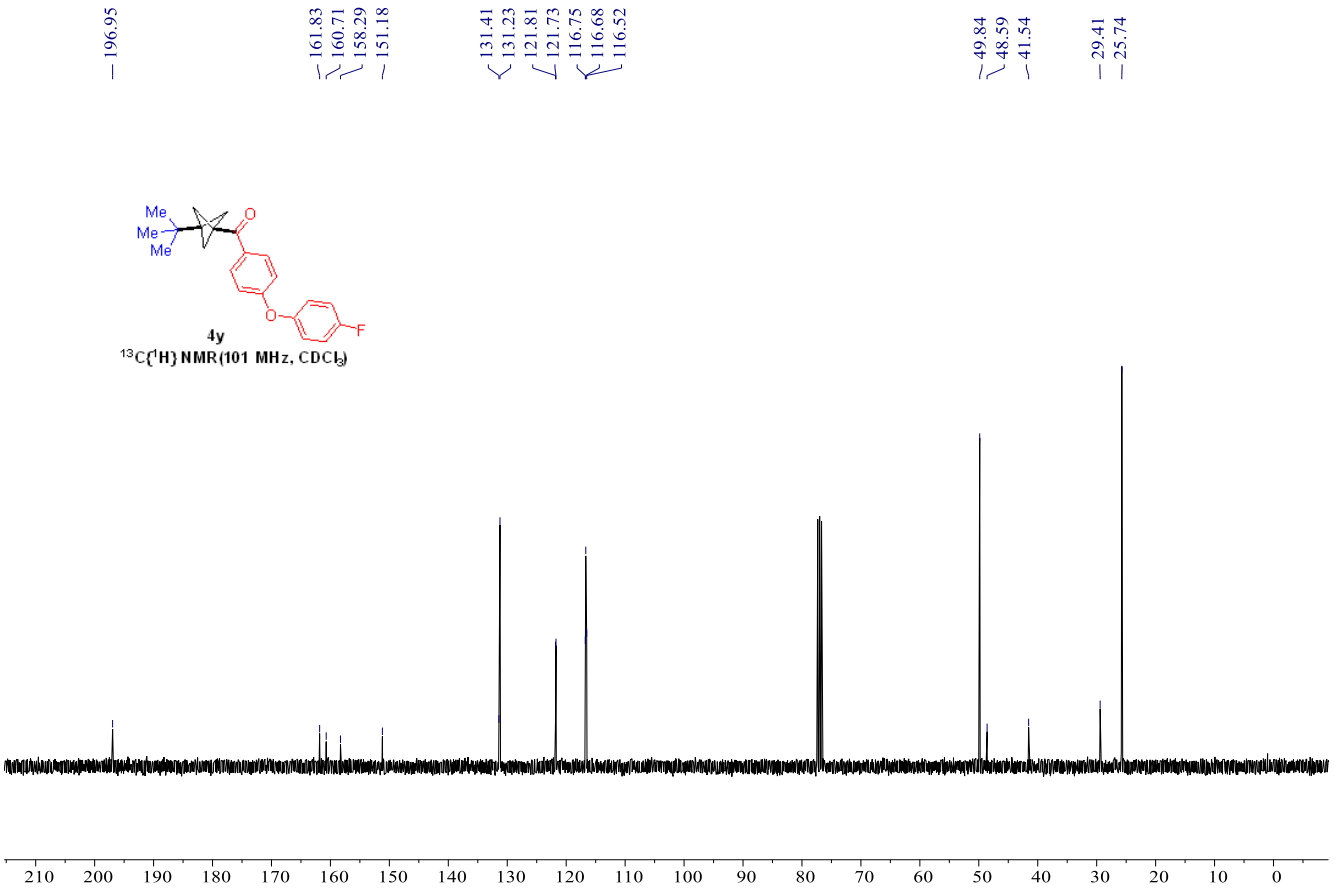
^{1}H NMR(400 MHz, $CDCl_3$)

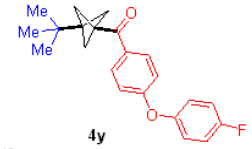



196.81
166.67
164.14
133.11
133.08
131.52
131.43
115.53
115.31
50.10
48.94
41.90
31.80
30.82
22.13
8.69
Me
Me
Me
O
F
4x
13C{1H} NMR (101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1


-105.53
Me
Me
Me
O
F
4x
19F NMR (376 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210


8.02
8.00
7.10
7.08
7.06
7.05
7.04
6.95
6.93
2.06
0.89
Me
Me
Me
O
O
F
4y
^{1}H NMR(400 MHz, CDCl$_3$)
2.0
3.9
2.0
6.0
9.0
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 -0.5 -1.0


196.95
161.83
160.71
158.29
151.18
131.41
131.23
121.81
121.73
116.75
116.68
116.52
49.84
48.59
41.54
29.41
25.74
Me
Me
Me
O
O
F
4y
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

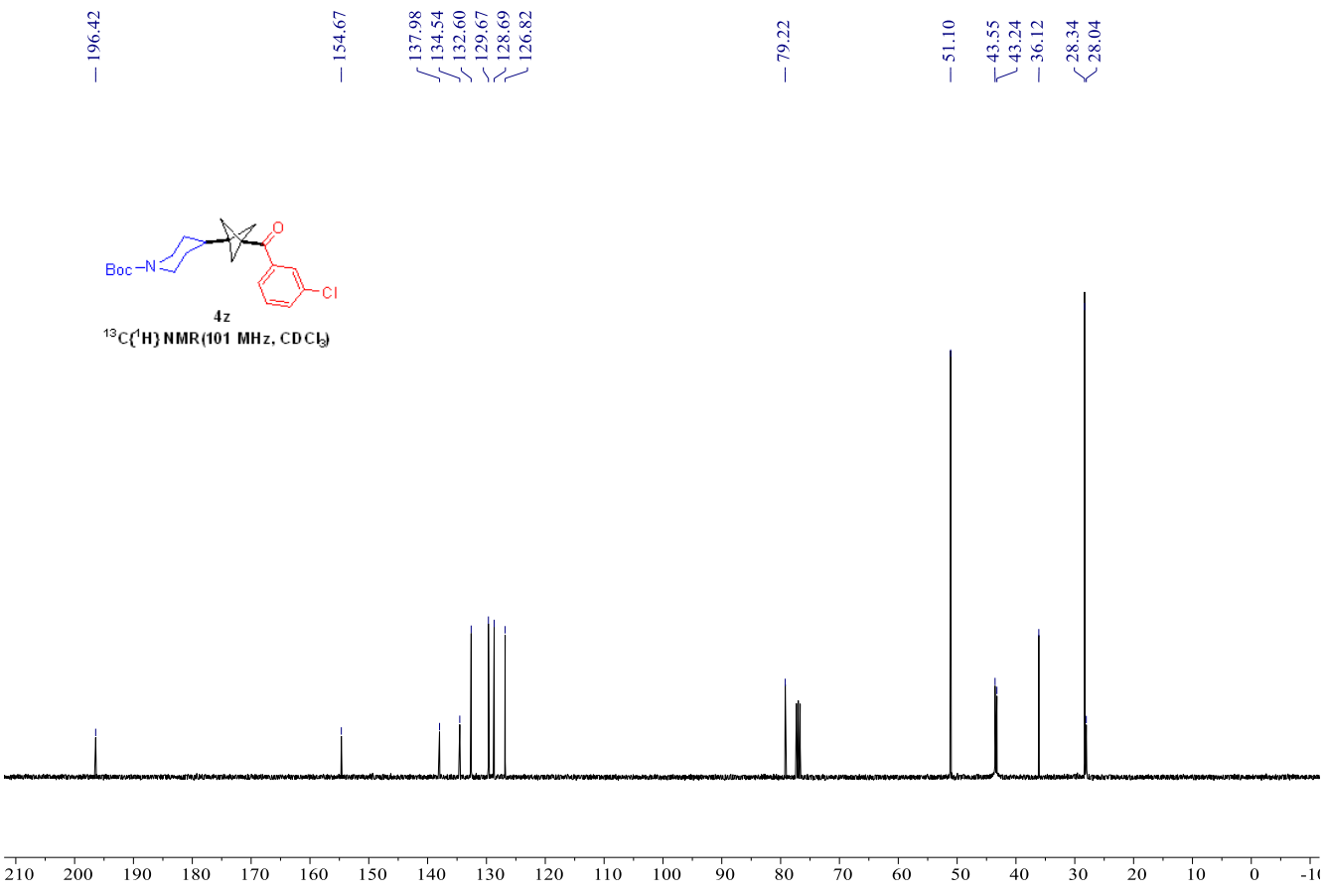


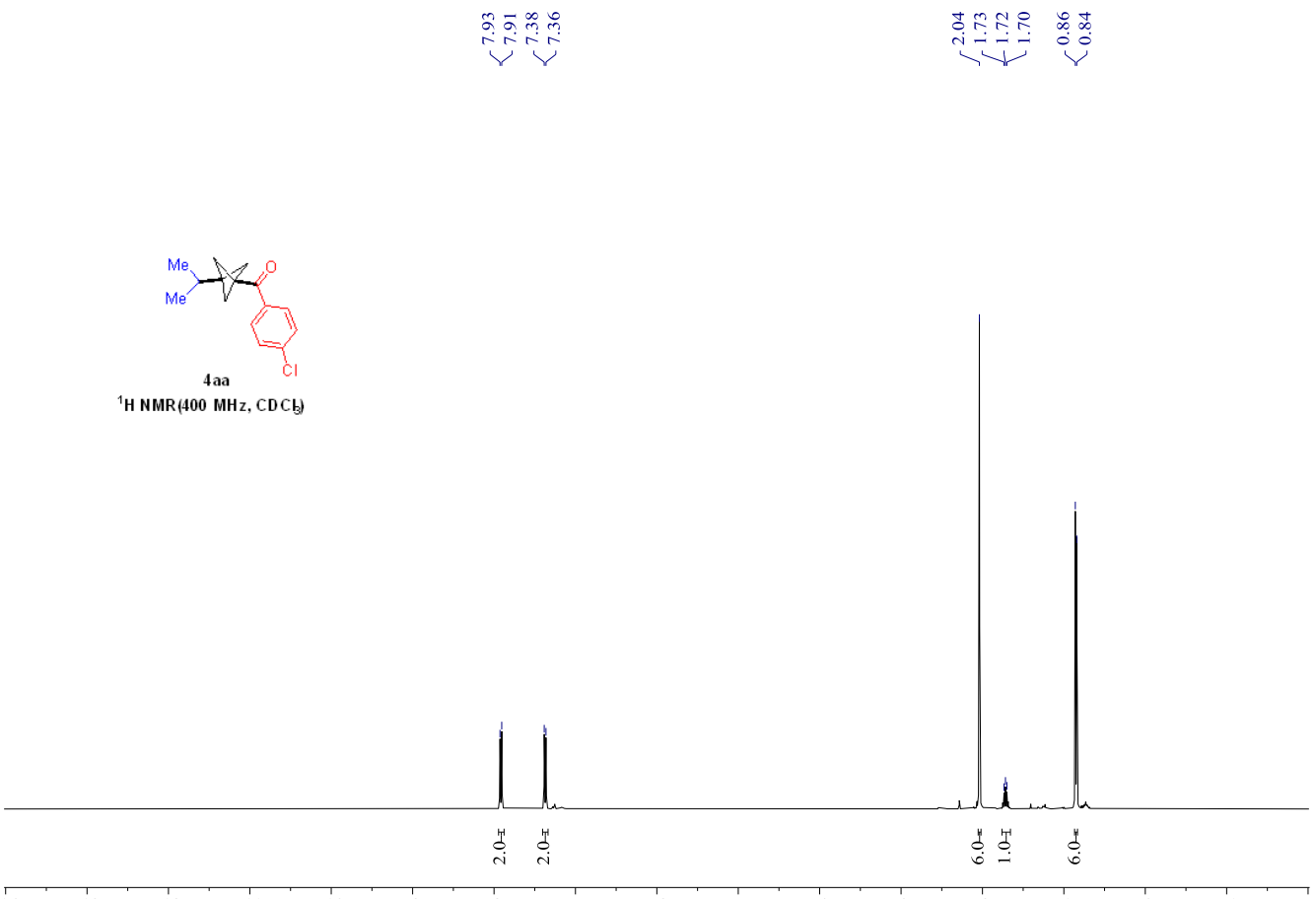
4y

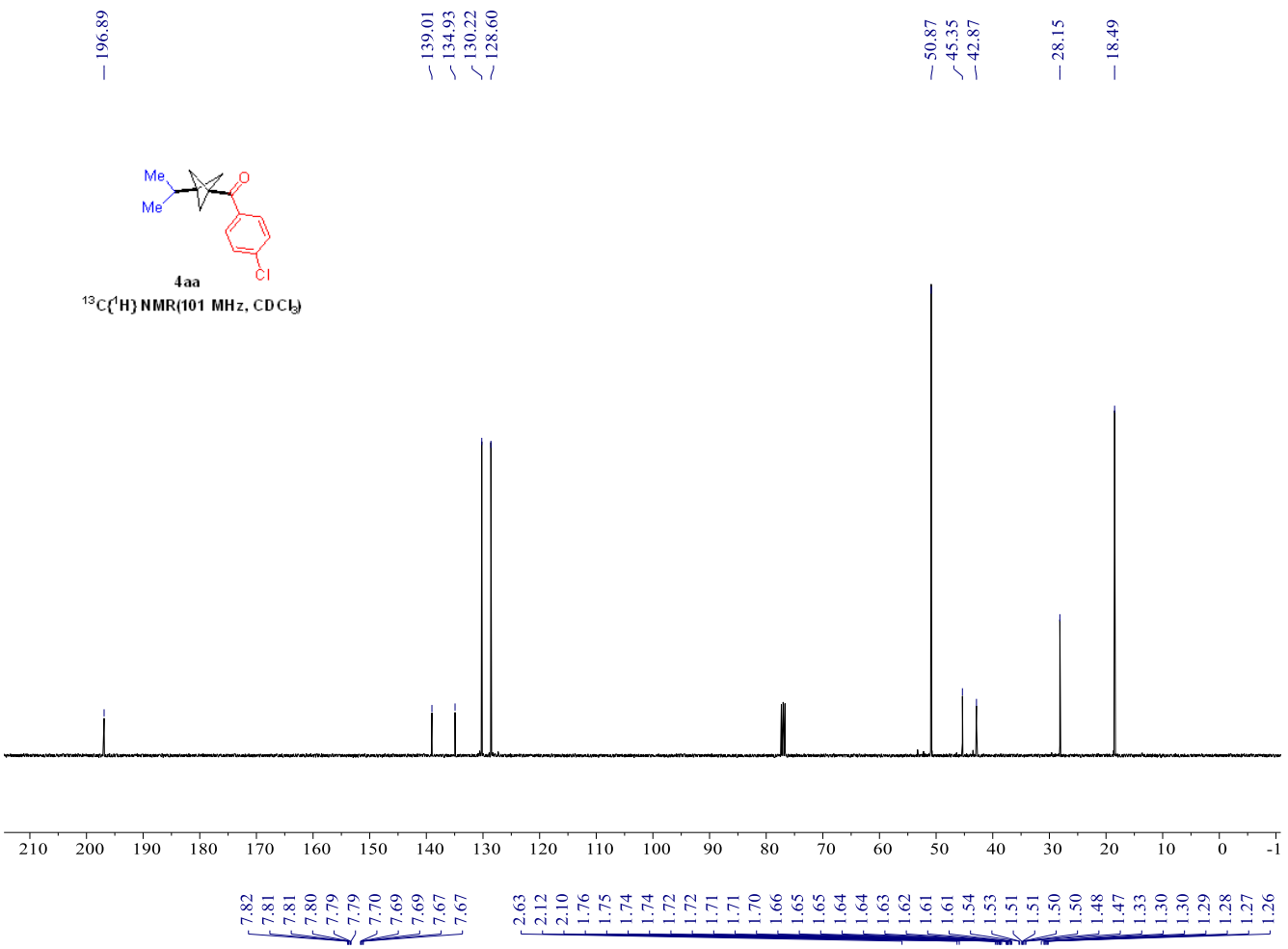
^{19}F NMR(376 MHz, $CDCl_3$)

4z

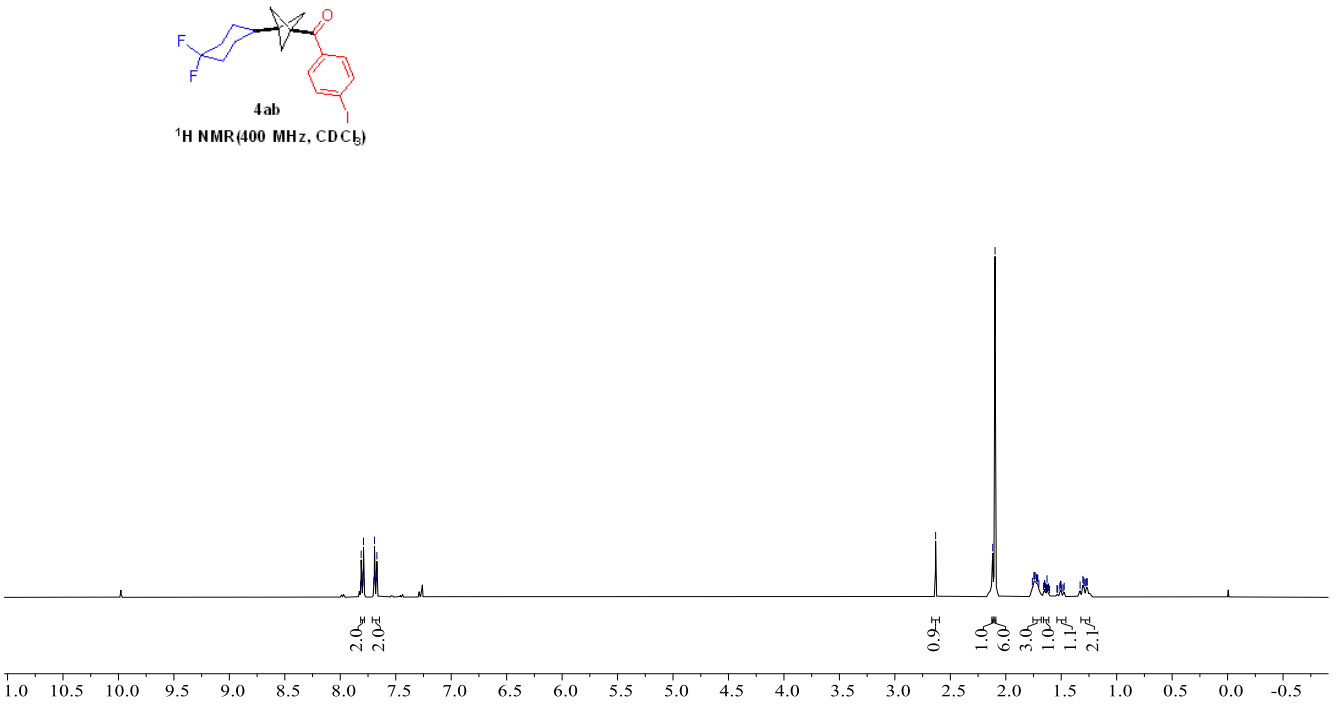
^{1}H NMR(400 MHz, $CDCl_3$)

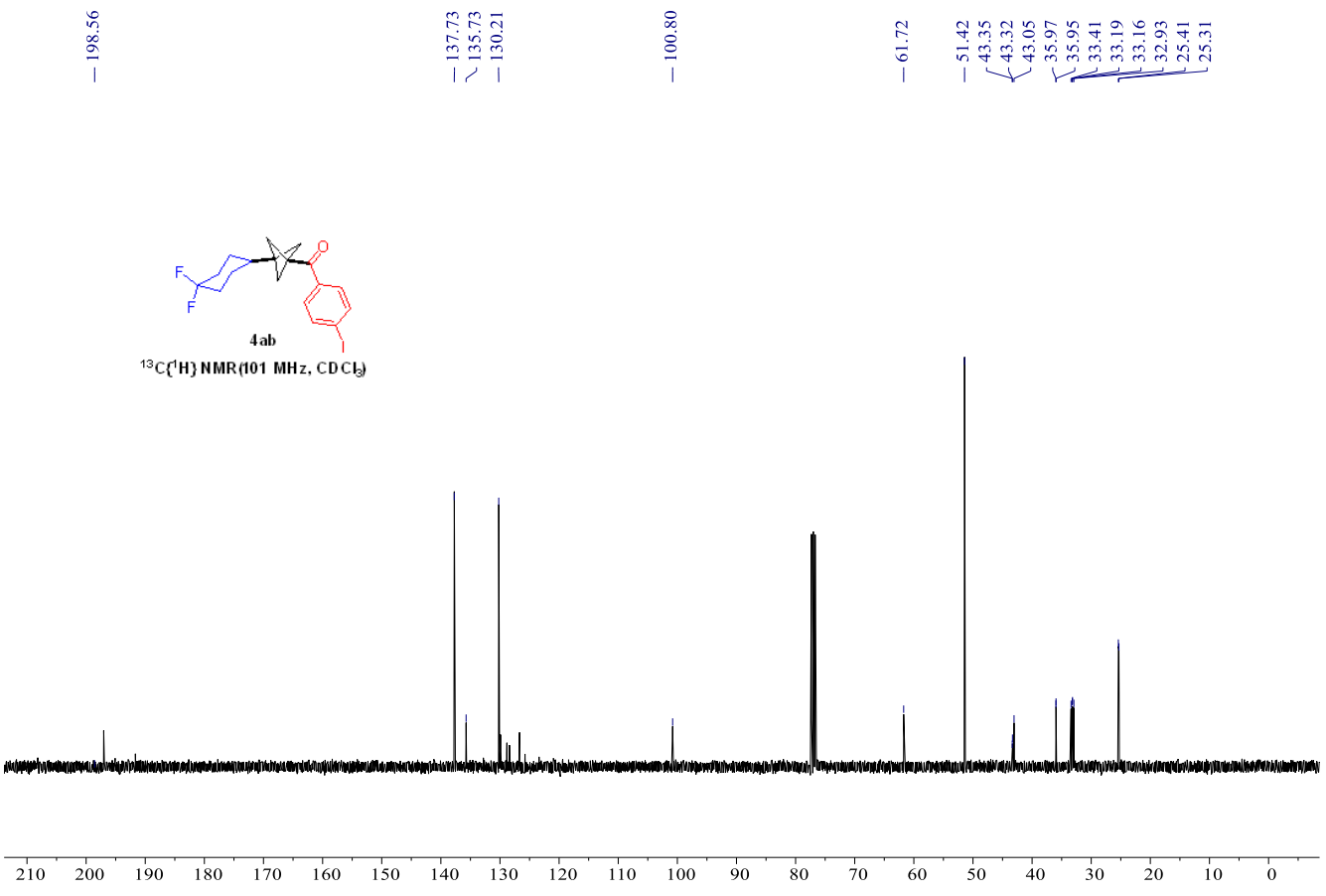

196.42
154.67
137.98
134.54
132.60
129.67
128.69
126.82
79.22
51.10
43.55
43.24
36.12
28.34
28.04
Boc
N
O
Cl
4z
13C{1H} NMR (101 MHz, CDCl3)

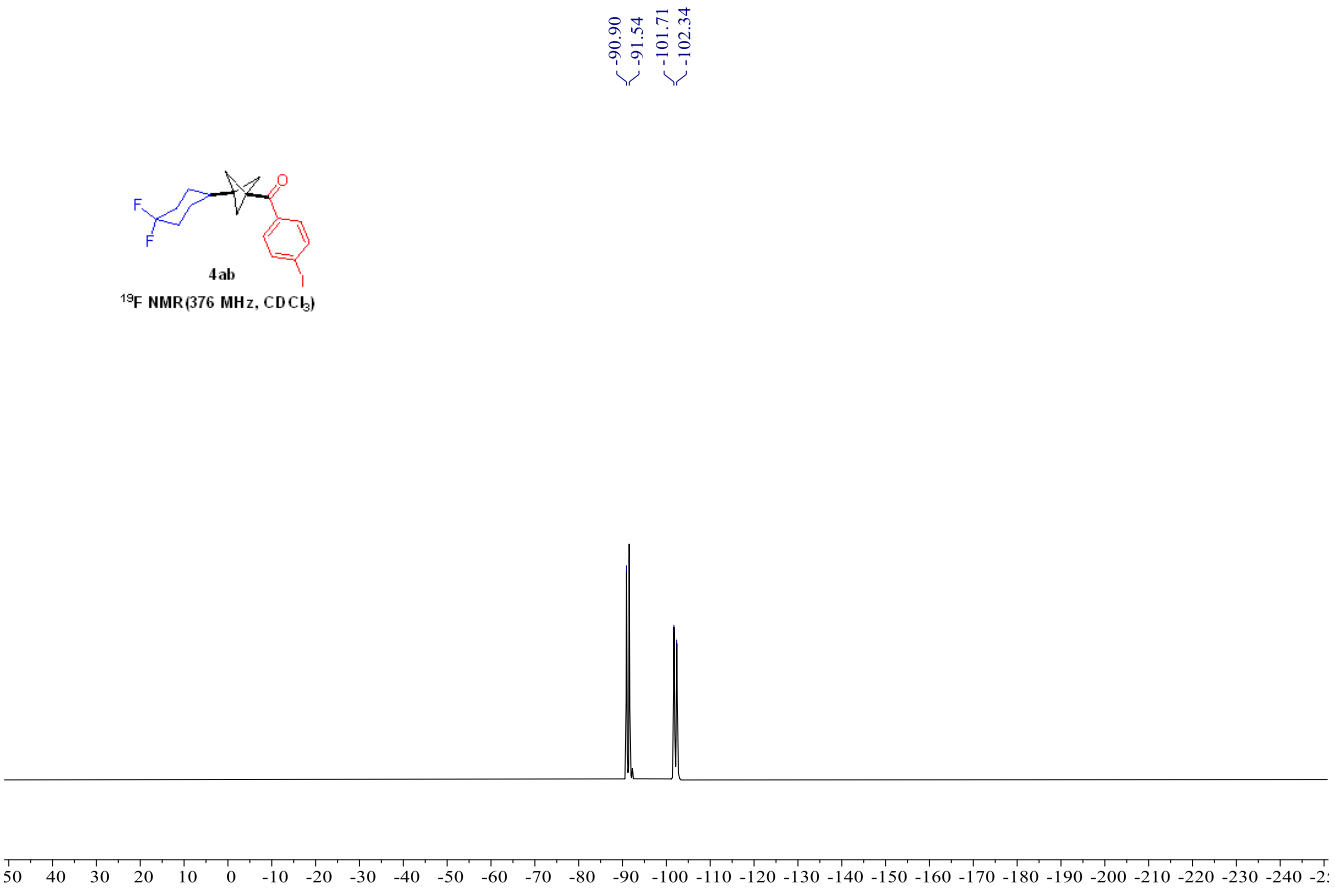

7.93
7.91
7.38
7.36
2.04
1.73
1.72
1.70
0.86
0.84
Me
Me
O
Cl
4aa
1H NMR (400 MHz, CDCl3)
2.0
2.0
6.0
1.0
6.0

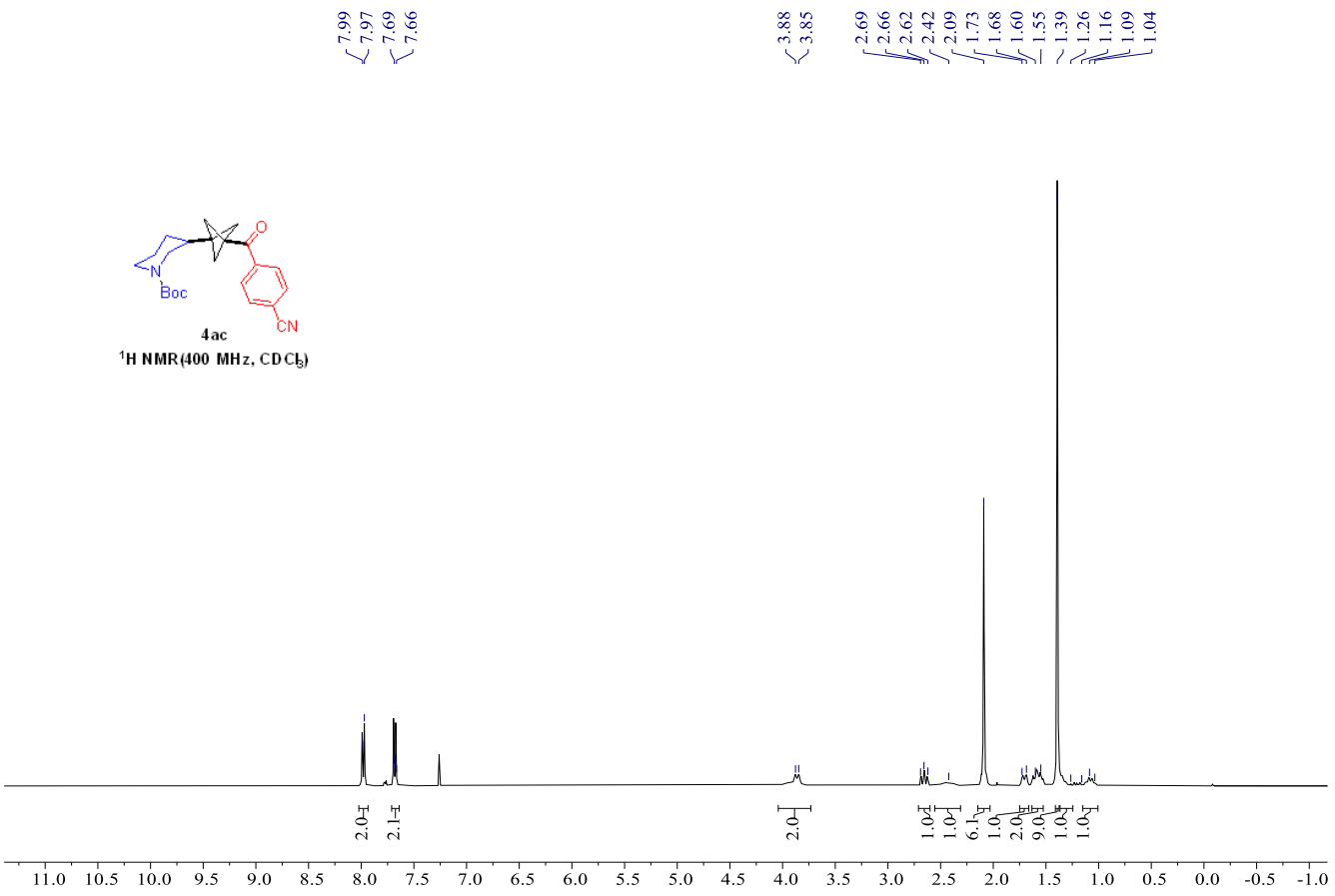

196.89
139.01
134.93
130.22
128.60
50.87
45.35
42.87
28.15
18.49
Me
Me
O
Cl
4aa
$^{13}C\{^{1}H\}$ NMR(101 MHz, $CDCl_3$)

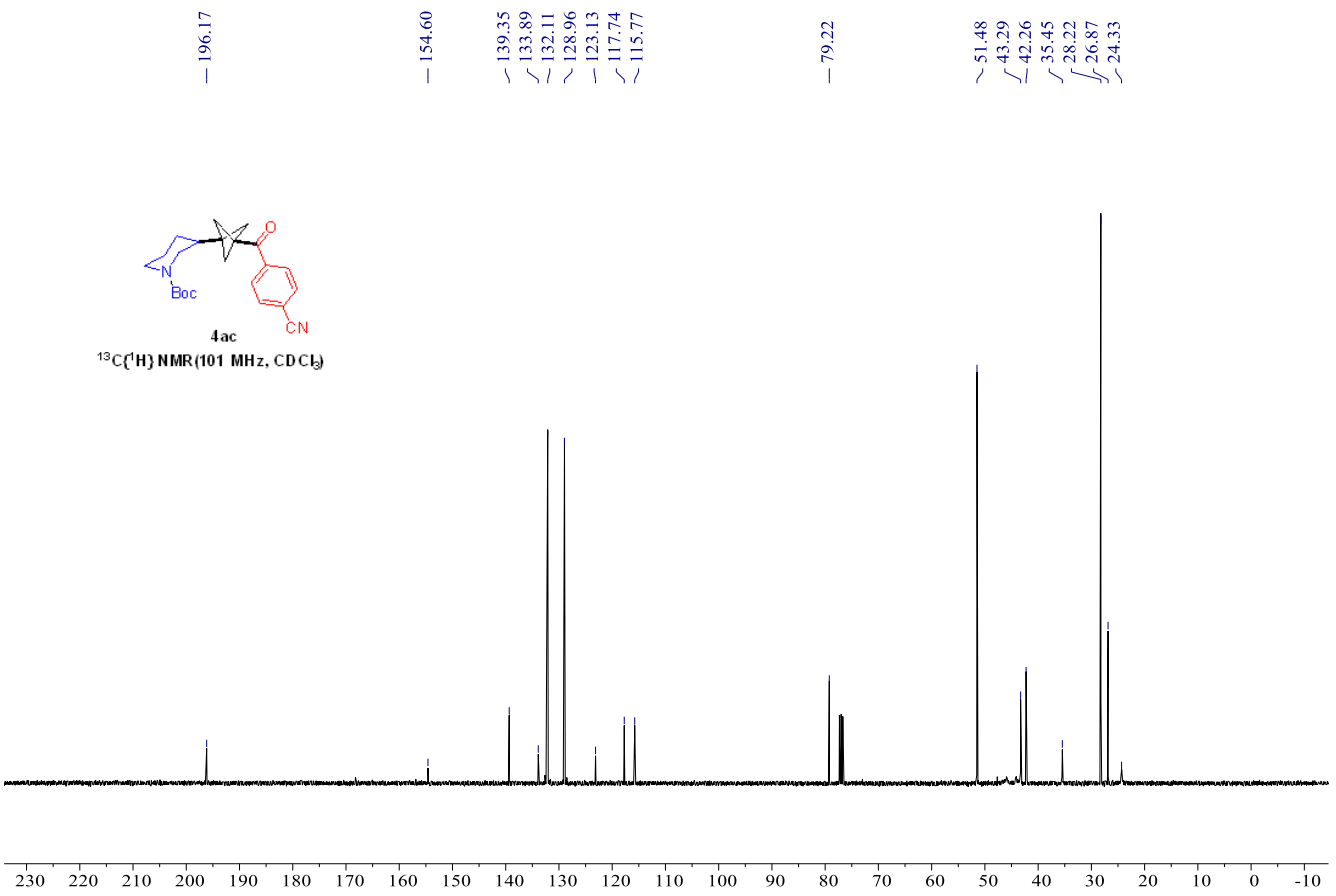
7.82
7.81
7.81
7.80
7.79
7.79
7.70
7.69
7.69
7.67
7.67
2.63
2.12
2.10
1.76
1.75
1.74
1.74
1.72
1.72
1.71
1.71
1.70
1.66
1.65
1.65
1.64
1.64
1.63
1.62
1.61
1.61
1.54
1.53
1.51
1.51
1.50
1.50
1.48
1.47
1.33
1.30
1.30
1.29
1.28
1.27
1.26

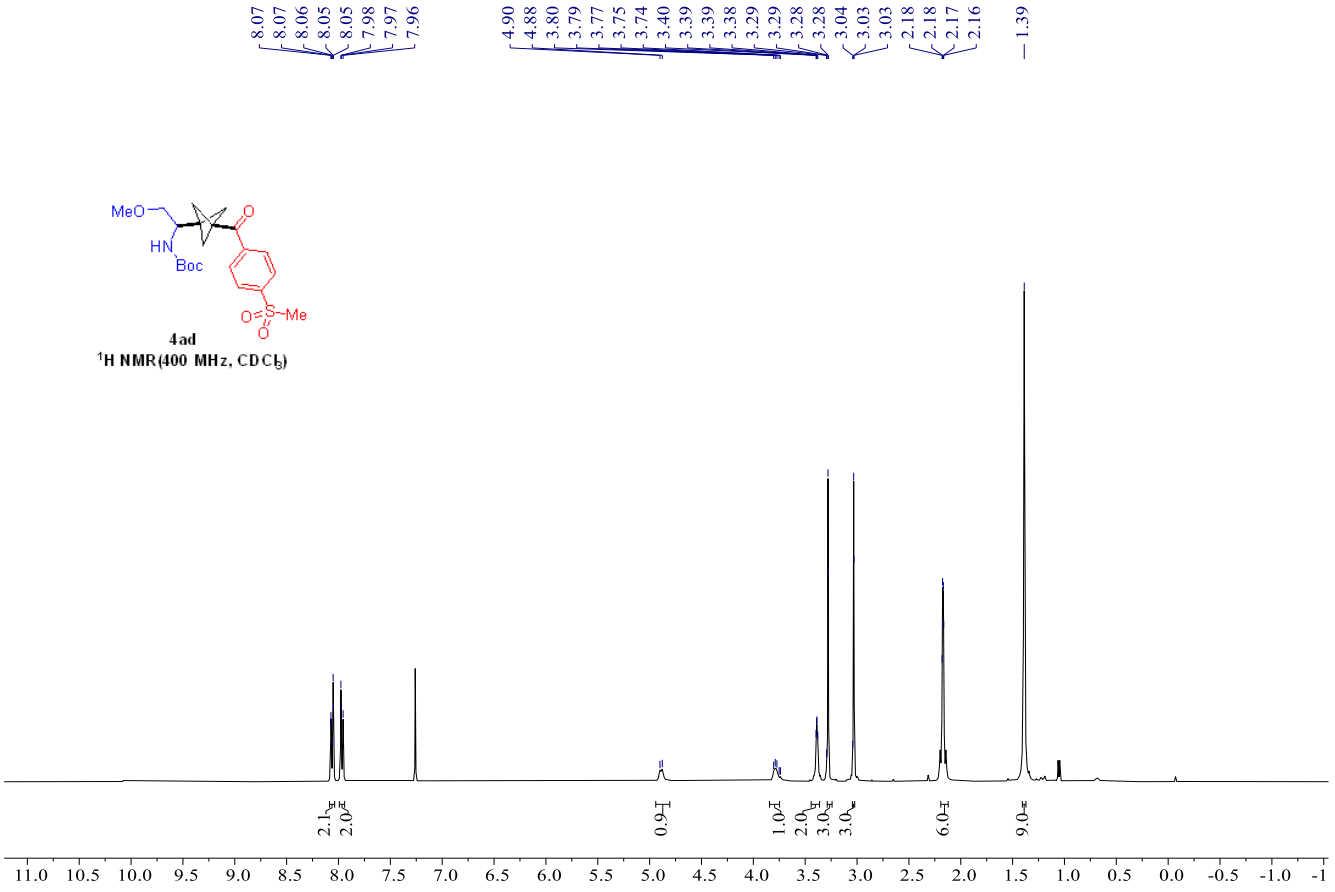

F
F
O
4ab
^{1}H NMR(400 MHz, $CDCl_3$)
2.0
2.0
0.9
1.0
6.0
3.0
1.0
1.1
2.1


198.56
137.73
135.73
130.21
100.80
61.72
51.42
43.35
43.32
43.05
35.97
35.95
33.41
33.19
33.16
32.93
25.41
25.31
F
F
O
4ab
13C{1H} NMR(101 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


-90.90
-91.54
-101.71
-102.34
F
F
O
4ab
19F NMR(376 MHz, CDCl3)
50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220 -230 -240

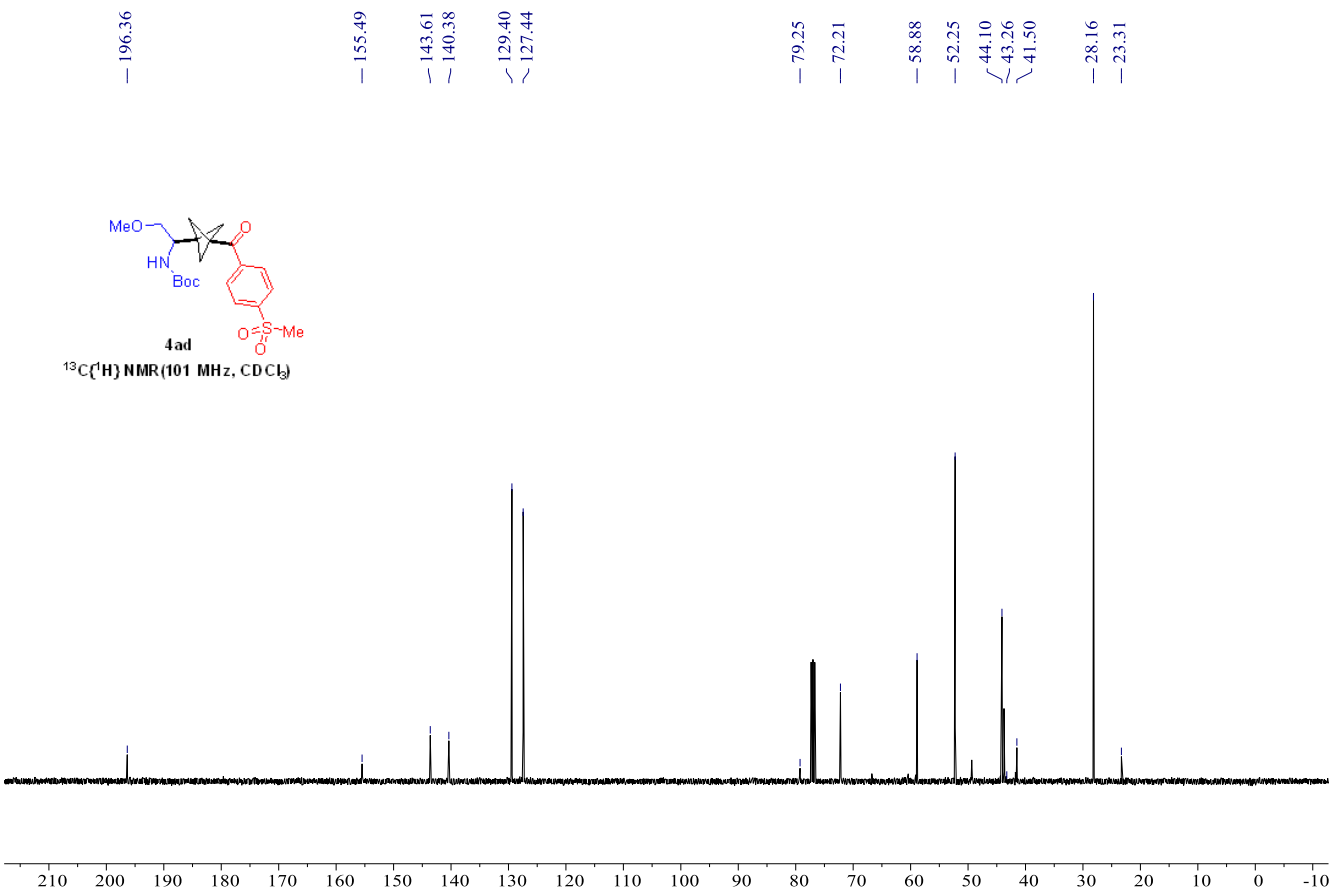

7.99
7.97
7.69
7.66
3.88
3.85
2.69
2.66
2.62
2.42
2.09
1.73
1.68
1.60
1.55
1.39
1.26
1.16
1.09
1.04
O
N
Boc
CN
4ac
^{1}H NMR(400 MHz, CDCl$_3$)
2.0
2.1
2.0
1.0
1.0
6.1
1.0
2.0
9.0
1.0
1.0
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0


196.17
154.60
139.35
133.89
132.11
128.96
123.13
117.74
115.77
79.22
51.48
43.29
42.26
35.45
28.22
26.87
24.33
O
N
Boc
CN
4ac
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10



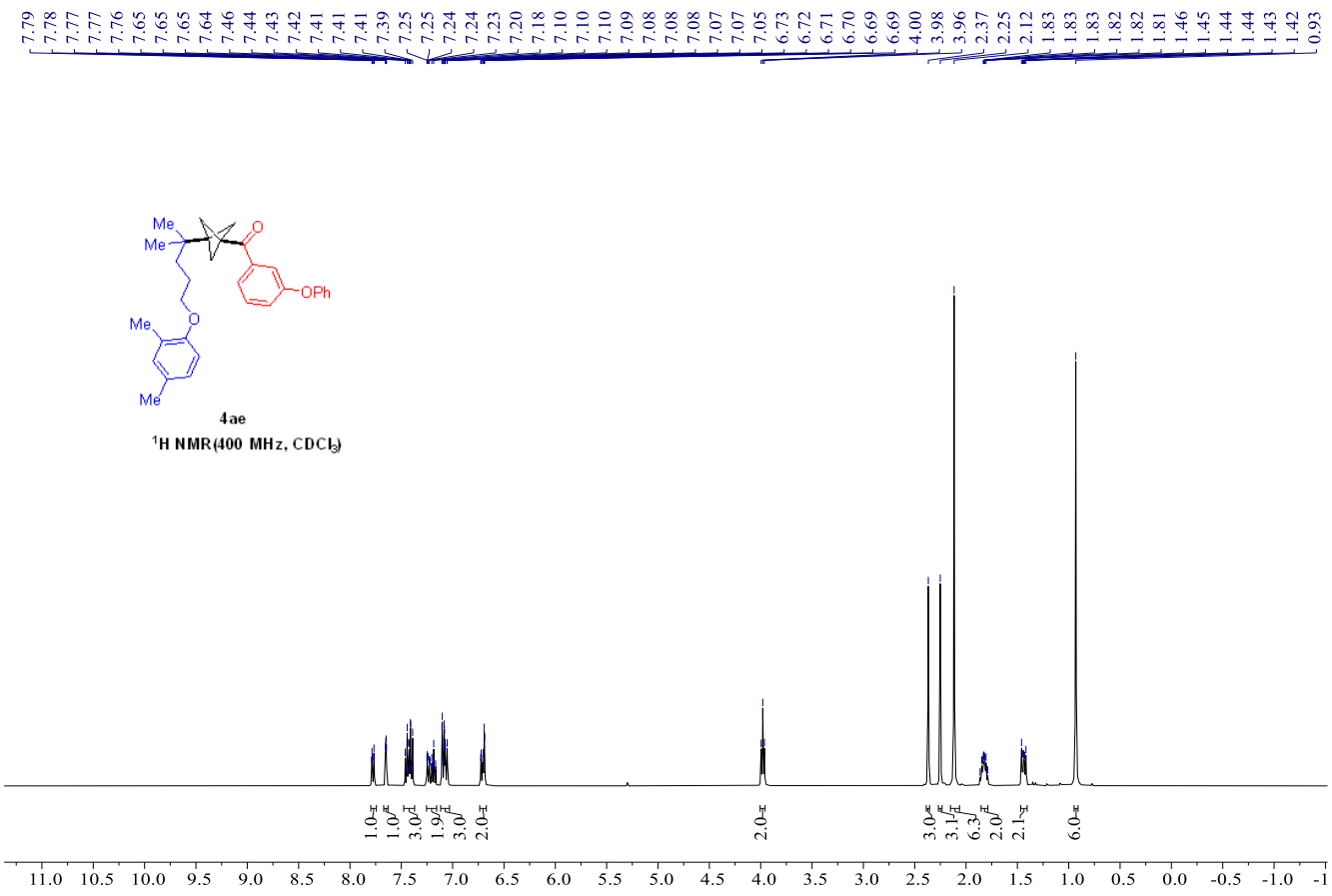
4ad

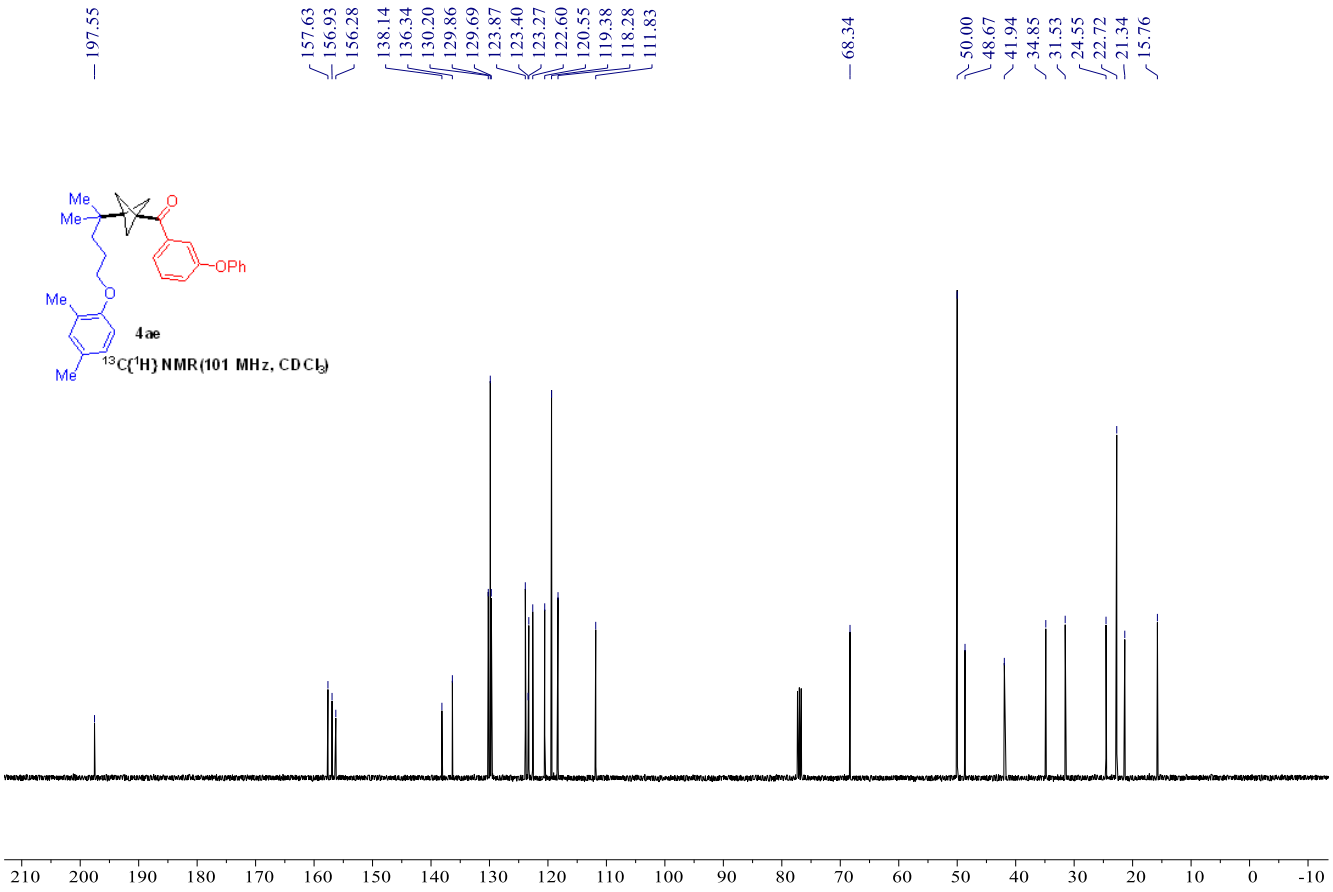
^{1}H NMR(400 MHz, $CDCl_3$)

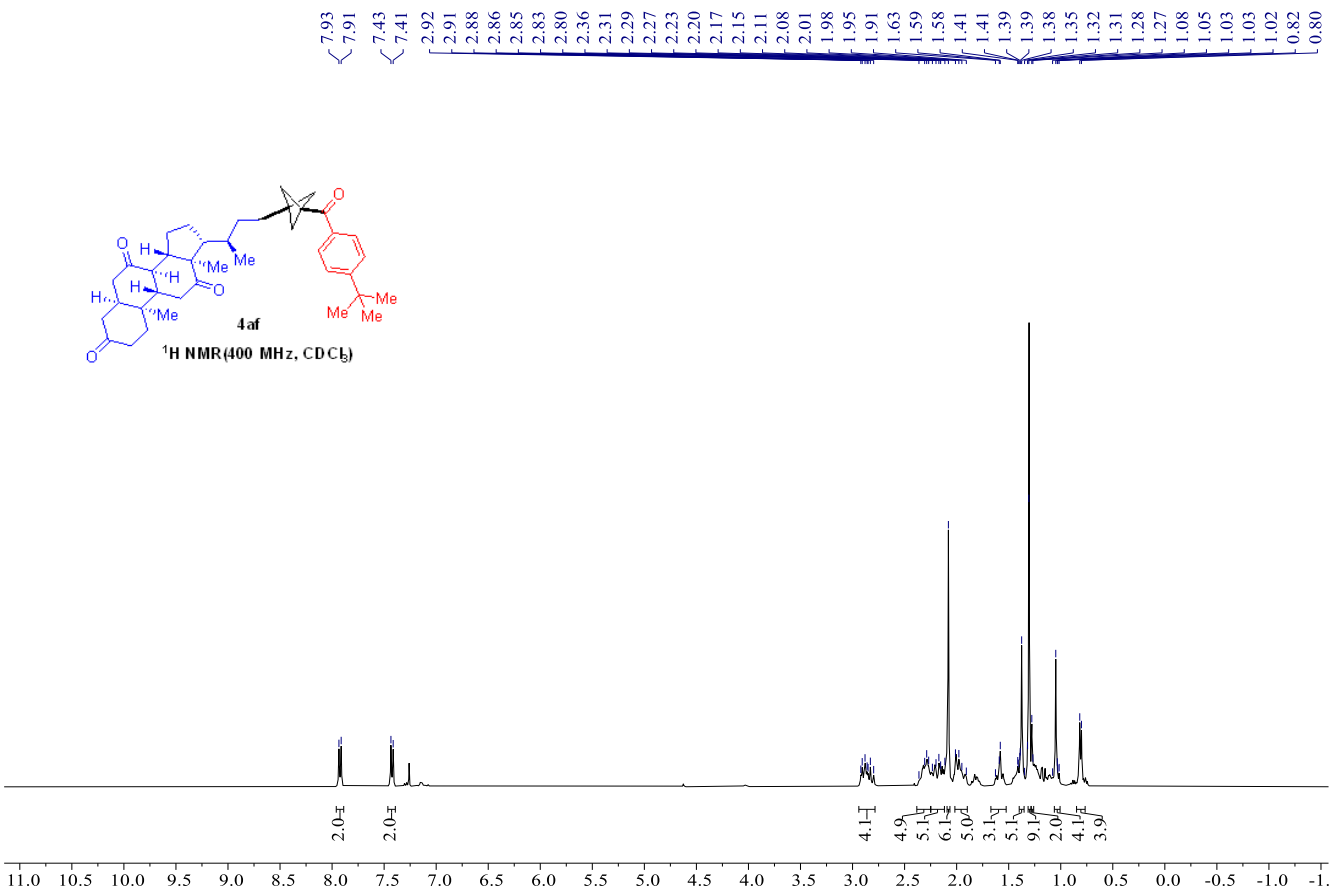


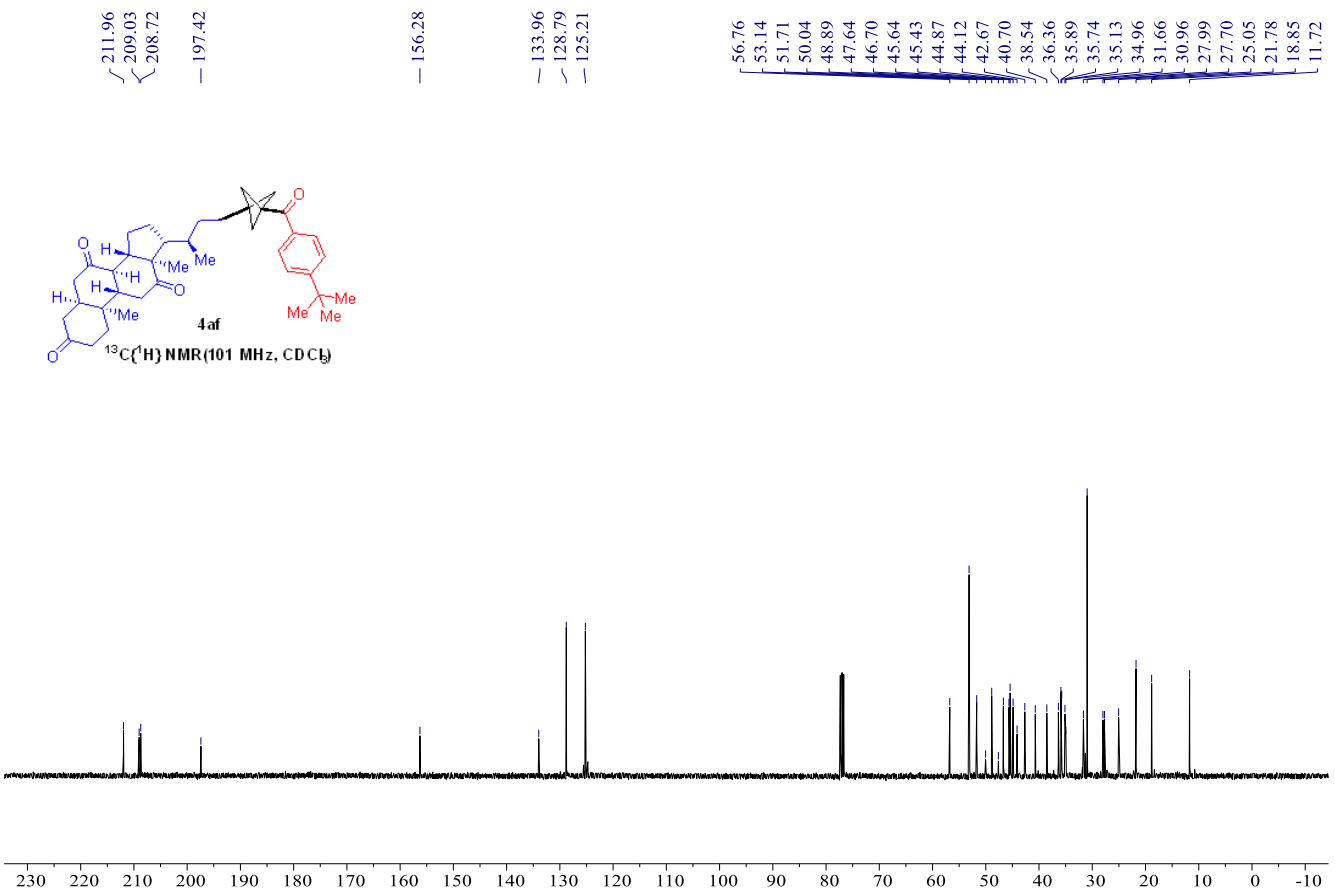
4ad

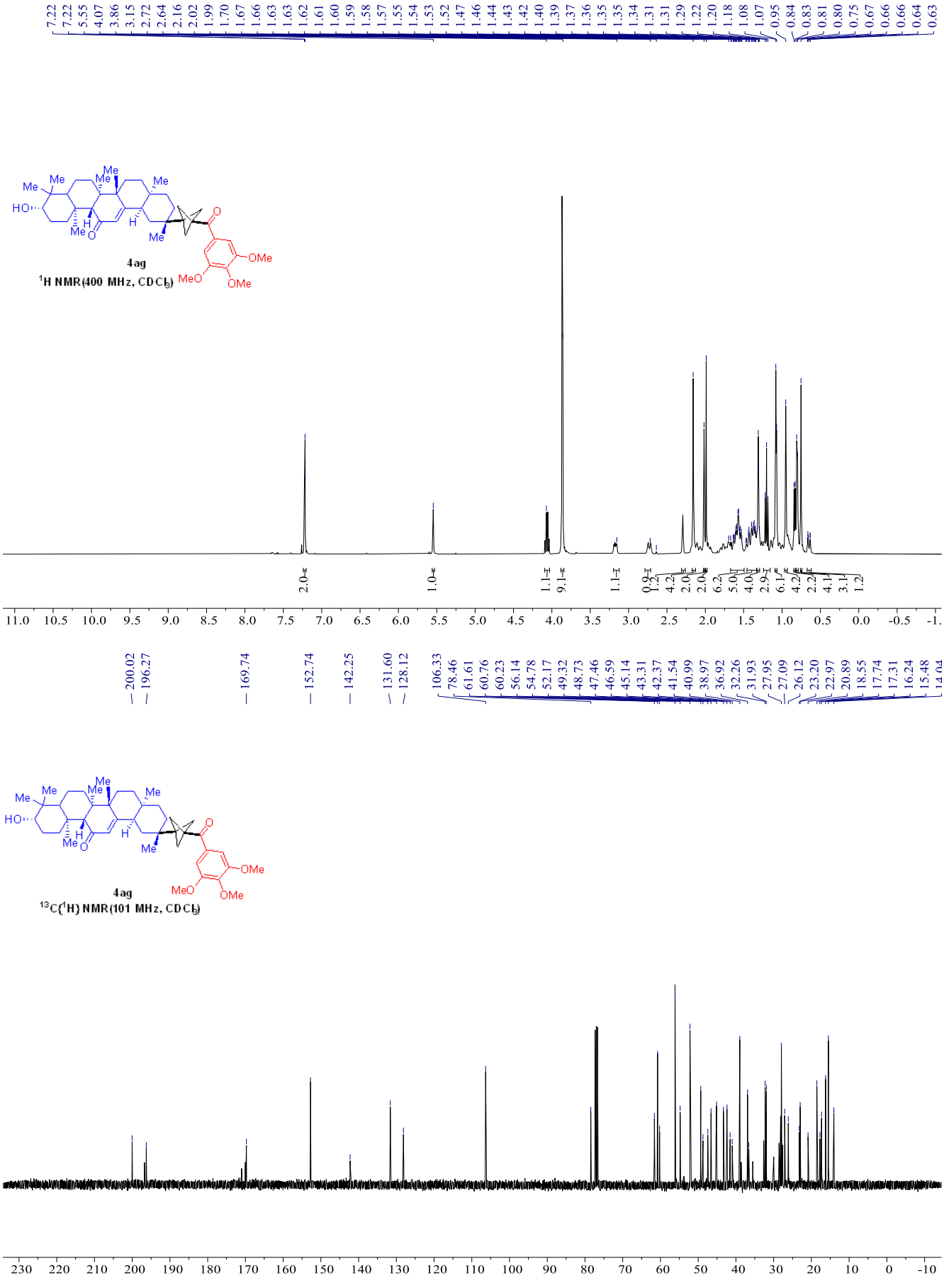
$^{13}C\{^{1}H\}$ NMR(101 MHz, $CDCl_3$)

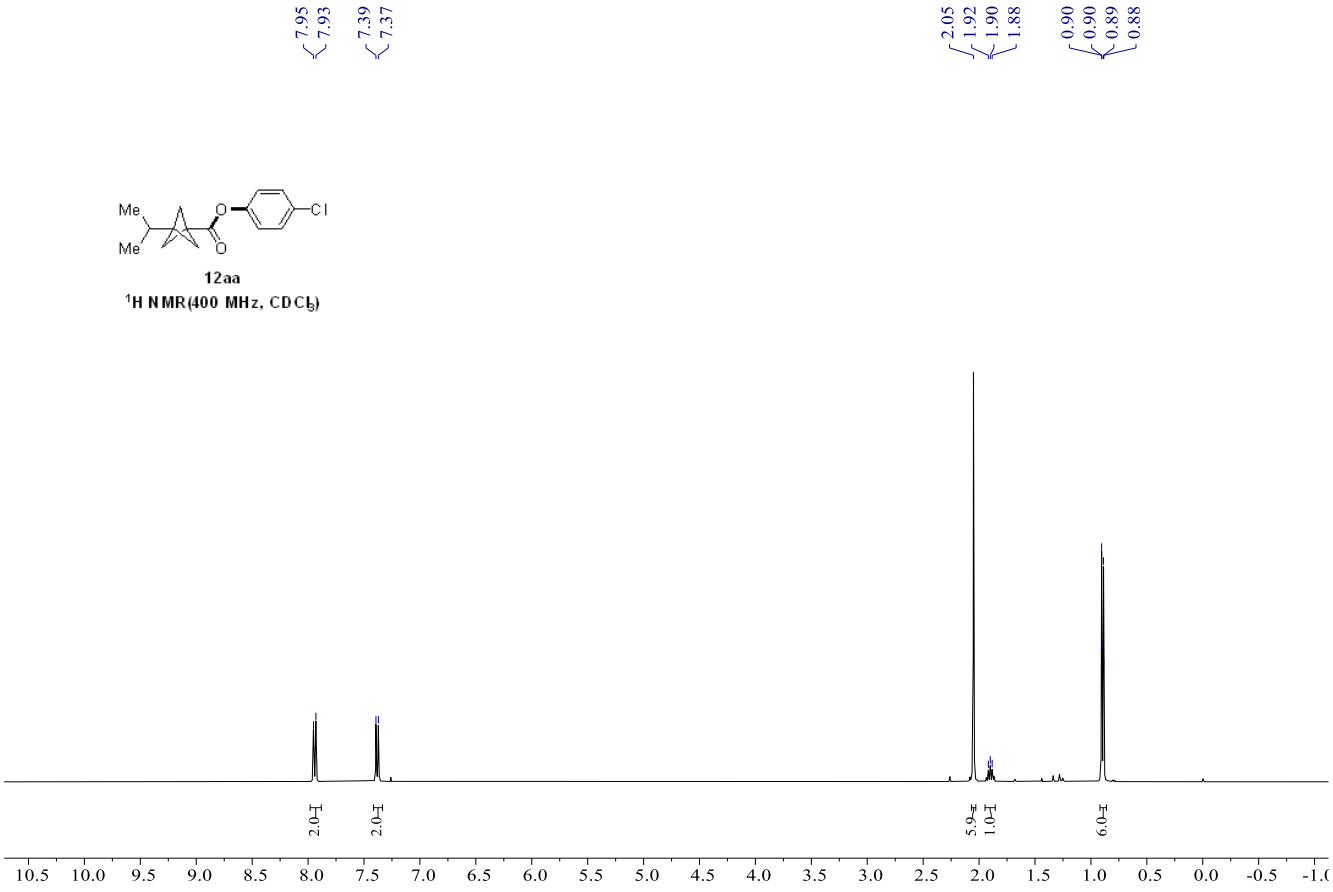

7.79 7.78 7.77 7.77 7.76 7.65 7.65 7.64 7.46 7.44 7.43 7.42 7.41 7.41 7.41 7.39 7.25 7.25 7.24 7.24 7.23 7.20 7.18 7.10 7.10 7.10 7.09 7.08 7.08 7.08 7.07 7.07 7.05 6.73 6.72 6.71 6.70 6.69 6.69 4.00 3.98 3.96 2.37 2.25 2.12 1.83 1.83 1.83 1.82 1.82 1.81 1.46 1.45 1.44 1.44 1.43 1.42 0.93
Me
Me
O
OPh
Me
O
Me
4ae
^{1}H NMR(400 MHz, CDCl$_3$)
1.0 1.0 3.0 1.9 3.0 2.0 2.0 3.0 3.1 6.3 2.0 2.1 6.0
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 -0.5 -1.0 -1


197.55
157.63 156.93 156.28 138.14 136.34 130.20 129.86 129.69 123.87 123.40 123.27 122.60 120.55 119.38 118.28 111.83
68.34
50.00 48.67 41.94 34.85 31.53 24.55 22.72 21.34 15.76
Me
Me
O
OPh
Me
O
Me
4ae
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


4af
^{1}H NMR(400 MHz, CDCl$_3$)

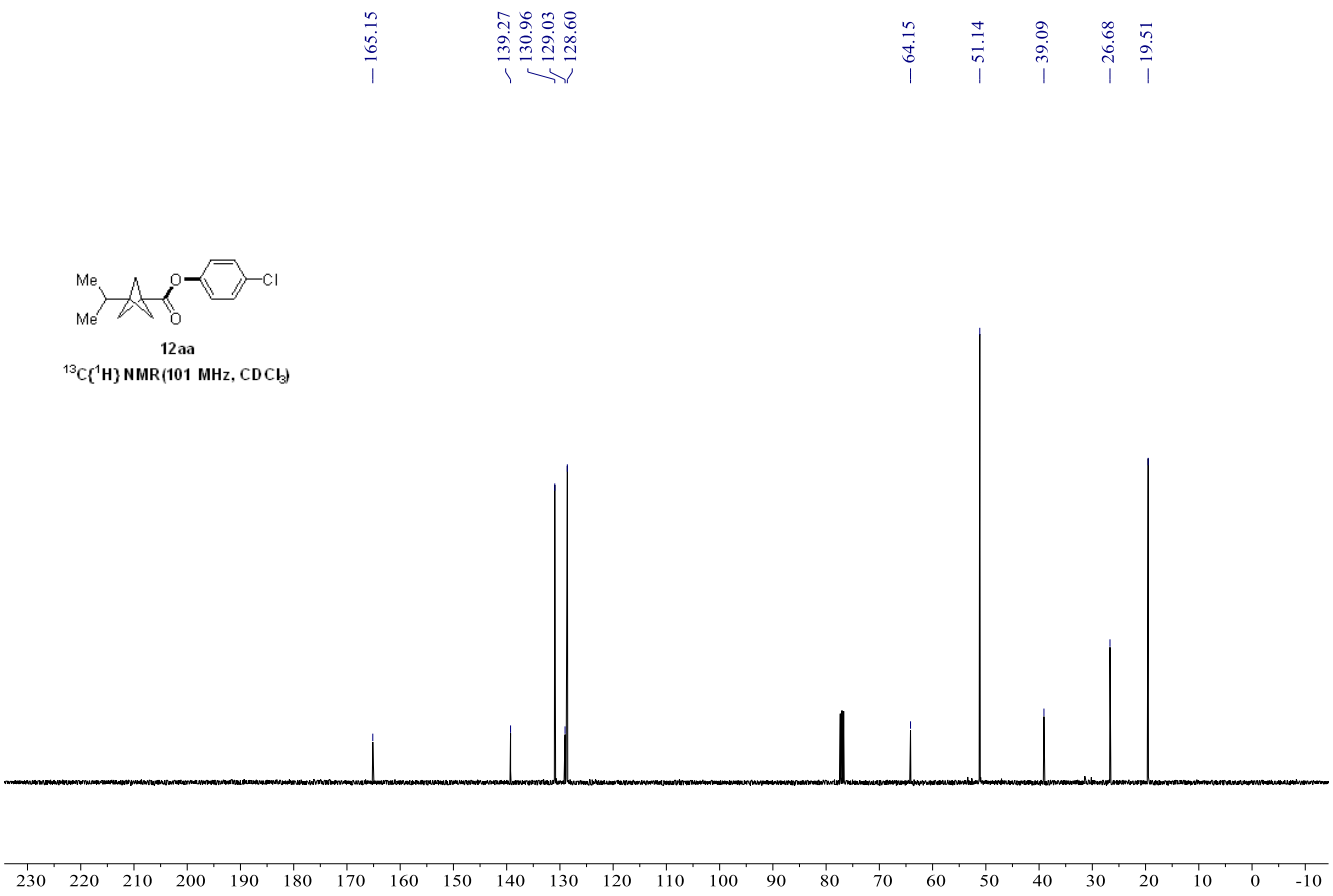

4af
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)


4ag
^{1}H NMR(400 MHz, CDCl$_3$)
4ag
^{13}C{^{1}H} NMR(101 MHz, CDCl$_3$)



12aa

^{1}H NMR(400 MHz, $CDCl_3$)



12aa

^{13}C{^{1}H} NMR(101 MHz, $CDCl_3$)