HAT Process of *N*-Pyridyl Radical Cation for the Synthesis of Benzophenone-Type Bioisosteres

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Supporting Information

Contents

1. General Information

All reactions were performed under argon atmosphere with glass storage tube unless otherwise stated. Reagents were purchased from commercial sources and were used as received. Solvents were purified by VG-P7 solvent drying system or commercial dry solvent. Thin layer chromatography (TLC) was performed to monitor reactions by UV light (254 nm) or phosphomolybdate chromogenic agent. Silica gel column chromatography was performed using 200-300 Mesh silica gel.

The reaction tube used in the experiment was a 10 mL liquid storage sealed tube with a polytetrafluoroethylene thread plug. The photoreactor was an optical parallel reaction instrument produced by WATTCAS (www.wattcas.com), and a 10 W purple LED lamp was used. (Figure S1).

^{1}H NMR spectra and ^{13}C NMR spectra were recorded at 400 MHz, 100 MHz on a Bruker Avance 400 spectrometer. All chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm) relative to residual $CDCl_3$ (7.26 ppm) as internal standards. ^{1}H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, br = broad), the number of protons (n) for a given resonance was indicated by *n*H. Coupling constants were reported as a *J* value in Hz. ^{19}F NMR chemical shifts were reported in ppm. ^{13}C NMR chemical shifts are reported in ppm relative to the central peak of $CDCl_3$ (77.16 ppm) as internal standards. HRMS data were obtained by ESI or APCI method with Bruker mass spectrometer (MAXIS). EPR were recorded with Bruker E500 electron paramagnetic spectrometer.

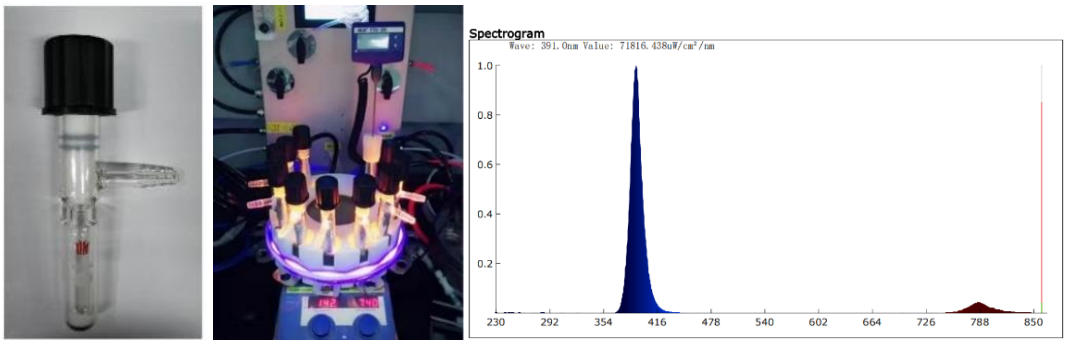
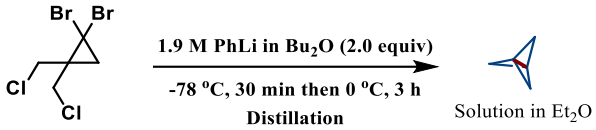


Figure S1. Pictures of photoreactors

(Note: The temperature of the reaction mixture is room temperature due to return water, and the reactor has no external heating devices)

2. Preparation of [1.1.1]propellane (solution in Et_2O) and Katritzky Salts.

2.1 Preparation of [1.1.1]propellane (solution in Et_2O).



1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (10.0 g, 34.1 mmol) was added to 15 mL of Et_2O. The solvent was cooled to -78 °C under Argon atmosphere. Then 42 mL PhLi (42.0 mL, 80.0 mmol, 2.35 equiv, 1.9 M solvent in *n*-Bu_2O) was added slowly dropwise. The mixture was stirred at -78 °C for 30 min, then warmed to 0 °C and stirred for another 3 h. The reaction flask was fitted with a diaphragm vacuum pump refluxed alcohol at -20 °C. A pump was used to evacuate the system down slowly from 200 mbar to 30 mbar, and the solvent was held at this pressure for 5 min. This resulted in the distillation of the Et_2O/[1.1.1]propellane solvent. The concentration was checked by H NMR by taking a 100 µL aliquot of the stock solvent and determining the ratio of [1.1.1]propellane to an added standard, such as 1,3,5-Trimethylbenzene (50%-60% yield, typically concentrations are 0.9-1.1 M with this protocol). This solvent should be kept in a -24 °C freezer with argon atmosphere.

Determination of [1.1.1]propellane concentration (Figure S2): 0.1 mmol of 1,3,5-trimethoxybenzene (16.8 mg) and 100 µL of [1.1.1]propane solution was added to a NMR tube containing an appropriate amount of $CDCl_3$. The concentration of [1.1.1]propellane was calculated based on the ratio of 1,3,5-trimethoxybenzene to [1.1.1]propellane.

c([1.1.1]propellane) = *Int* ([1.1.1]propellane) × 0.5 M = 2.19 × 0.5 M = 1.095 M

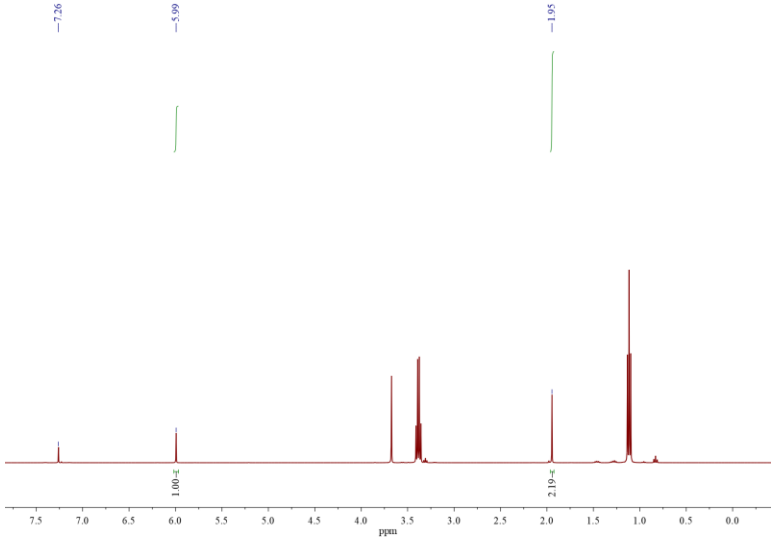
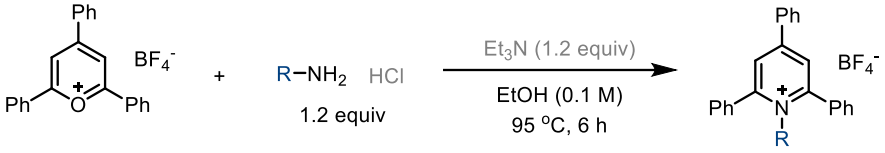


Figure S2. ^{1}H NMR spectrum for the [1.1.1]propellane solution with 1,3,5-trimethoxybenzene in $CDCl_3$

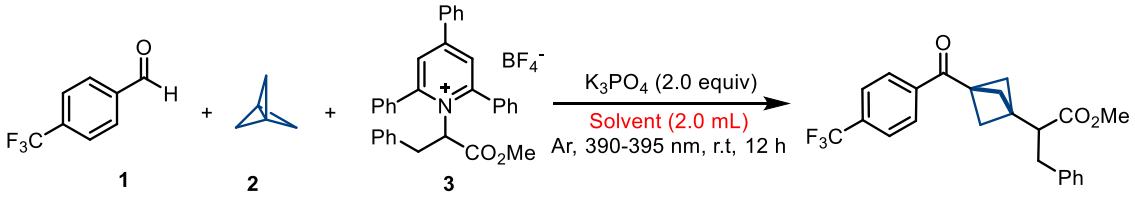
2.2 Preparation of Katritzky salts.



All pyridinium salts used in this study were prepared following a procedure by Hong *et al*.[1-3] A Schlenk tube equipped with a magnetic stirrer bar was charged with amine hydrochloride (1.0 equiv). Ethanol (1.0 M) and triethyl amine (1.2 equiv) was added to the reaction vessel and the tube sealed. The resulting suspension was stirred for 30 min at room temperature. Triphenylpyrylium tetrafluoroborate (1.0 equiv) was added, the tube sealed and stirred for overnight at 96 °C. The mixture was then allowed to cool to room temperature. If product precipitation occurred during reflux, the solid was filtered, washed with EtOH and then Et_2O, and dried under high vacuum. If product precipitation did not occur during reflux, the solution was diluted with Et_2O, and vigorously stirred for 1 h to induce trituration. The resulting solid pyridinium salt was filtered and washed with Et_2O. If the solid did not precipitate, it was purified by flash column chromatography with DCM : acetone (10:1).

3. Optimization of Bicyclo[1.1.1]pentane Ketones Conditions

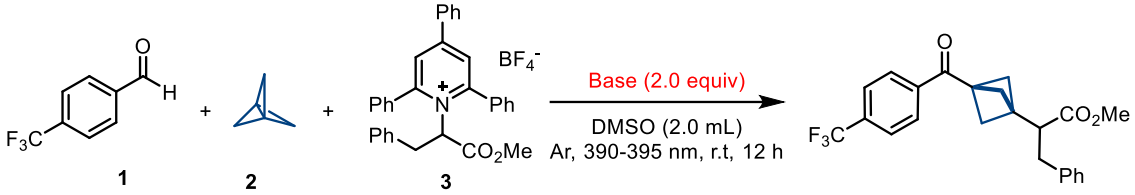
Table S1. Screening of solvent.



Entry	Solvent	Yield (%)
1	**DMSO**	**90**
2	DMF	trace
3	Acetone	42
4	CH_3CN	72
5	DMSO:CH_3CN (1:1)	56

Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol), **3** (0.2 mmol, 2.0 equiv), K_3PO_4 (0.2 mmol, 2.0 equiv), solvent (2.0 mL), Ar, 390-395 nm, r.t, 12 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

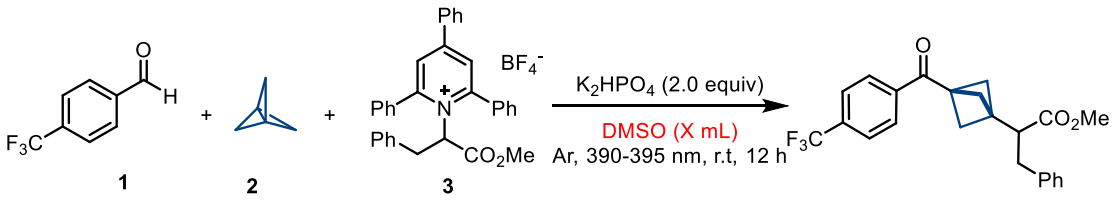
Table S2. Screening of base.



Entry	Base	Yield (%)
1	Na_2CO_3	N.D.
2	K_2CO_3	trace
3	Cs_2CO_3	38
4	**K_2HPO_4**	**90**
5	**K_3PO_4**	**90**
6	$Na_3PO_4•H_2O$	N.D.
7	Et_3N	62
8	DBU	56
9	DIPEA	66
10	DIPA	38

Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol), **3** (0.2 mmol, 2.0 equiv), Base (0.2 mmol, 2.0 equiv), DMSO (2.0 mL), Ar, 390-395 nm, r.t, 12 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

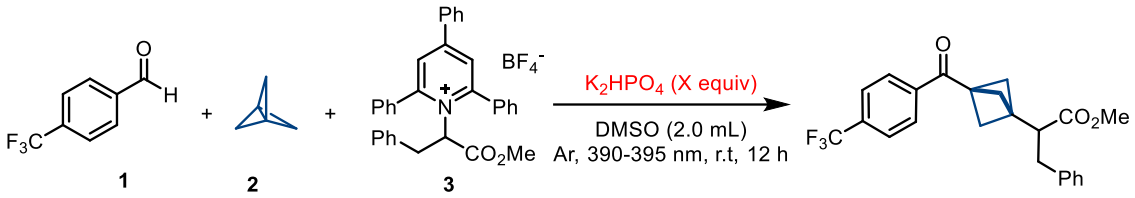
Table S3. Screening of amount of solvent.



Entry	DMSO (X mL)	Yield (%)
1	1	85
2	**2**	**90**
3	3	85
4	4	84

Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol), **3** (0.2 mmol, 2.0 equiv), K_2HPO_4 (0.2 mmol, 2.0 equiv), DMSO (X mL), r.t, Ar, 390-395 nm, 12 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

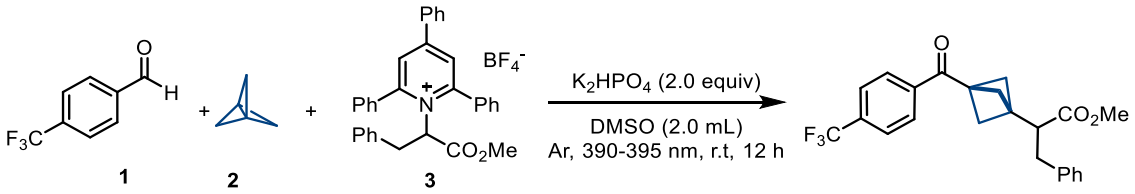
Table S4. Screening of equivalent of base.



Entry	K_2HPO_4	Yield (%)
1	**2.0**	**90**
2	1.5	84
3	1.0	70
4	0.5	58
5	0.2	40

Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol), **3** (0.2 mmol, 2.0 equiv), K_2HPO_4 (X equiv), DMSO (2.0 mL), r.t, Ar, 390-395 nm, 12 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

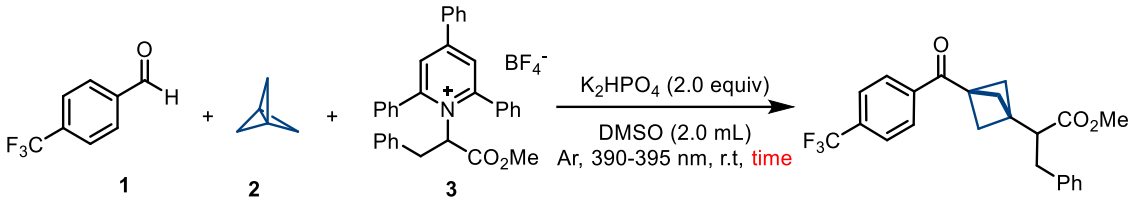
Table S5. Screening of the amount of the substrates.



Entry	**1 : 2 : 3**	Yield (%)
1	1 : 1 : 1	58
2	1.5 : 1 : 1.5	66
3	**2 : 1 : 2**	**90**
4	2.5 : 1 : 2.5	91
5	3 : 1 : 3	92
6	1 : 1.5 : 1	35
7	1 : 2 : 1	34

Reaction conditions: **1** (*x* mmol), **2** (*y* mmol), **3** (*z* mmol), K_2HPO_4 (2.0 equiv), DMSO (2.0 mL), r.t, Ar, 390-395 nm, 12 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

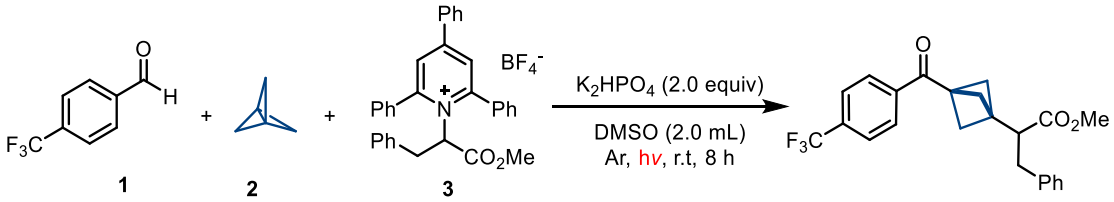
Table S6. Screening of reaction time.



Entry	time	Yield (%)
1	2 h	70
2	4 h	81
3	6 h	90
4	**8 h**	**91**
5	10 h	90
6	12 h	90

Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol.), **3** (0.2 mmol, 2.0 equiv), K_2HPO_4 (0.2 mmol, 2.0 equiv), DMSO (2.0 mL), r.t, Ar, 390-395 nm. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

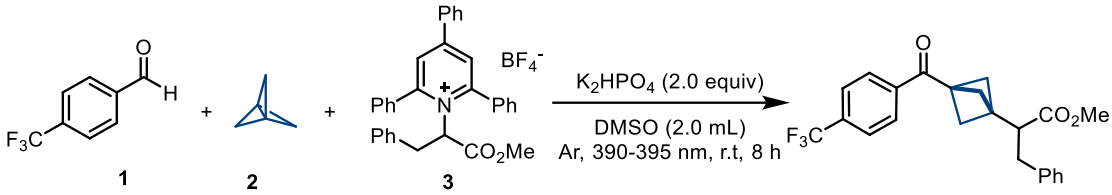
Table S7. Screening of different light sources.



Entry	hν	Yield (%)
1	360-365 nm	61
2	390-395 nm	**90**
3	460-465 nm	80
4	530-535 nm	75
5	620-630 nm	N.D.
6	6000K	74

Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol), **3** (0.2 mmol, 2.0 equiv), K_2HPO_4 (0.2 mmol, 2.0 equiv), DMSO (2.0 mL), r.t, Ar, 8 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

Table S8. Control experiments.



Entry	Deviation from the standard conditions	Yield (%)
1	standard conditions	90
2	standard conditions, no light, r.t.	N.D.
3	standard conditions, no light, 80 ^{o}C.	30
4	standard conditions, no base	24
5	standard conditions, Air instead of Ar	80

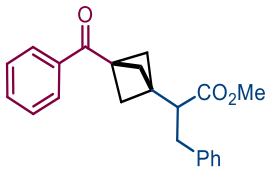
Reaction conditions: **1** (0.2 mmol, 2.0 equiv), **2** (0.1 mmol), **3** (0.2 mmol, 2.0 equiv), K_2HPO_4 (2.0 equiv), DMSO (2 mL), r.t, Ar, 8 h. Yields were determined by ^{19}F NMR analysis using benzotrifluoride as internal standard.

4. General Procedure for bicyclo[1.1.1]pentane Ketones Synthesis.

4.1 Standard procedure for bicyclo[1.1.1]pentane ketones synthesis.

To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.4 mmol, 2.0 equiv), aryl aldehyde (0.4 mmol, 2.0 equiv), Katritzky salt (0.4 mmol, 2.0 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then [1.1.1]propellane (0.1 mmol), DMSO (4.0 mL) were added via a syringe, respectively. The reaction mixture was placed in a photoparallel reactor. The mixture was then stirred rapidly and irradiated for 8 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. Purification of the crude product by flash chromatography on silica gel using the indicated solvent system afforded the desired product.

4.2 Spectra of synthesized compounds

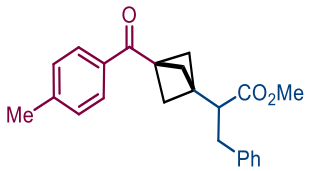


Methyl 2-(3-benzoylbicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (5): The product **5** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow oil (35.8 mg, 54% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 6.3 Hz, 2H), 7.23 – 7.16 (m, 3H), 3.63 (s, 3H), 3.04 – 2.92 (m, 2H), 2.86 – 2.73 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 173.2, 139.1, 136.6, 133.0, 129.0, 128.7, 128.6, 126.5, 52.9, 51.6, 48.7, 43.7, 40.9, 35.0.

HRMS(APCI) m/z calcd. for $C_{22}H_{22}O_3$ $[M+H]^+$: 335.1642, found: 335.1649.



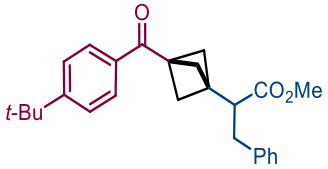
Methyl 2-(3-(4-methylbenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (6): The product **6** was purified by silica gel column chromatography (DCM/Petroleum

ether = 1:1) as a yellow oil (30.1 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.29 – 7.15 (m, 7H), 3.62 (s, 3H), 3.06 – 2.89 (m, 2H), 2.85 – 2.74 (m, 1H), 2.41 (s, 3H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 173.2, 143.8, 139.2, 134.0, 129.2, 129.1, 128.7, 128.5, 126.5, 52.9, 51.5, 48.7, 43.6, 40.8, 35.1, 21.7.

HRMS(APCI) m/z calcd. for $C_{23}H_{24}O_3$ $[M+H]^+$: 349.1798, found: 349.1806.

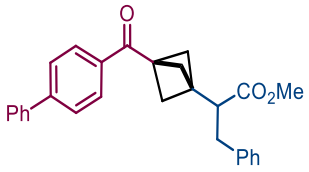


Methyl 2-(3-(4-(*tert*-butyl)benzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (7): The product **7** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a white solid (39.6 mg, 51% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 6.6 Hz, 2H), 7.20 – 7.13 (m, 3H), 3.59 (s, 3H), 3.04 – 2.86 (m, 2H), 2.80 – 2.68 (m, 1H), 2.17 (s, 6H), 1.31 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 173.24, 156.8, 139.2, 133.9, 129.0, 128.7, 128.5, 126.5, 125.5, 52.9, 51.6, 48.7, 43.7, 40.8, 35.2, 35.0, 31.2.

HRMS(APCI) m/z calcd. for $C_{26}H_{30}O_3$ $[M+H]^+$: 391.2268, found: 391.2275.

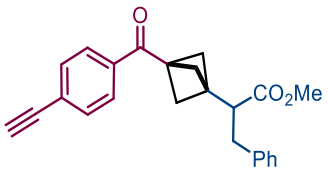


Methyl 2-(3-([1,1'-biphenyl]-4-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (8): The product **8** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow solid (56.8 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.0 Hz, 2H), 7.66 (d, *J* = 7.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.41 (d, *J* = 6.1 Hz, 1H), 7.32 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 3.63 (s, 3H), 3.06 – 2.93 (m, 2H), 2.87 – 2.73 (m, 1H), 2.24 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 173.2, 145.7, 140.0, 139.1, 135.2, 129.6, 129.0, 128.7, 128.5, 128.3, 127.3, 127.2, 126.5, 52.9, 51.6, 48.7, 43.7, 40.9, 35.0.

HRMS(APCI) m/z calcd. for $C_{28}H_{26}O_3$ $[M+H]^+$: 411.1955, found: 411.1961.

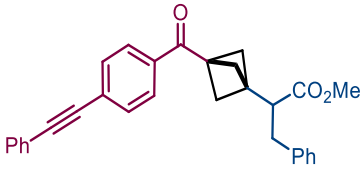


Methyl 2-(3-(4-ethynylbenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (9): The product **9** was purified by silica gel column chromatography (DCM) as a yellow solid (47.6 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 6.4 Hz, 2H), 7.23 – 7.15 (m, 3H), 3.63 (s, 3H), 3.25 (s, 1H), 3.04 – 2.92 (m, 2H), 2.84 – 2.74 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 173.2, 139.1, 136.3, 132.3, 128.8, 128.8, 128.6, 126.9, 126.2, 82.9, 80. 5, 52.9, 51.6, 48.6, 43.7, 41.0, 35.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{22}O_3$ $[M+H]^+$: 359.1642, found: 359.1649.

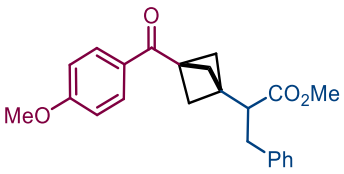


Methyl 3-phenyl-2-(3-(4-(phenylethynyl)benzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (10): The product **10** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a white solid (82.5 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.61 – 7.53 (m, 4H), 7.39 – 7.34 (m, 3H), 7.30 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 3.63 (s, 3H), 3.05 – 2.93 (m, 2H), 2.85 – 2.74 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 173.2, 139.1, 135.6, 131.9, 131.7, 128.9, 128.8, 128.6, 128.6, 128.2, 126.5, 122.7, 92.9, 88.8, 52.9, 51.6, 48.6, 43.7, 40.9, 35.0.

HRMS(APCI) m/z calcd. for $C_{30}H_{26}O_3$ $[M+H]^+$: 435.1955, found: 435.1961.



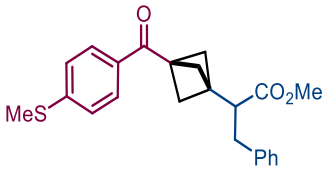
Methyl 2-(3-(4-methoxybenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (11) : The product **11** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a yellow solid (29.8 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 5.4 Hz, 2H), 7.29 – 7.23 (m, 3H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.93 (s, 3H), 3.69 (s, 3H), 3.11 – 2.95 (m, 2H), 2.92 –

2.81 (m, 1H), 2.26 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 173.3, 163.5, 139.2, 131.4, 129.7, 128.8, 128.6, 126.5, 113.8, 55.6, 53.0, 51.6, 48.8, 43.6, 40.8, 35.1.

HRMS(APCI) m/z calcd. for $C_{23}H_{24}O_4$ $[M+H]^+$: 365.1747, found: 365.1756.

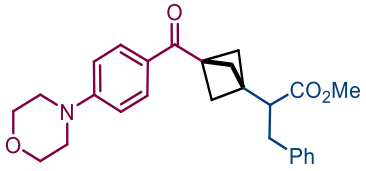


Methyl 2-(3-(4-(methylthio)benzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (12): The product **12** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a yellow solid (42.3 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.24 – 7.13 (m, 7H), 3.59 (s, 3H), 3.00 – 2.89 (m, 2H), 2.79 – 2.72 (m, 1H), 2.48 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.2, 146.0, 139.1, 132.8, 129.4, 128.8, 128.6, 126.5, 125.0, 52.9, 51.6, 48.7, 43.6, 40.9, 35.0, 14.9.

HRMS(APCI) m/z calcd. for $C_{23}H_{24}O_3S$ $[M+H]^+$: 381.1519, found: 381.1521.

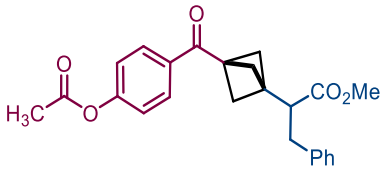


Methyl 2-(3-(4-morpholinobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (13): The product **13** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a yellow solid (14.3 mg, 17% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.25 – 7.21 (m, 2H), 7.19 – 7.13 (m, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 3.87 – 3.80 (m, 4H), 3.59 (s, 3H), 3.32 – 3.24 (m, 4H), 3.00 – 2.89 (m, 2H), 2.79 – 2.70 (m, 1H), 2.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 173.3, 154.2, 139.3, 131.2, 128.8, 128.6, 127.3, 126.5, 113.3, 66.7, 52.9, 51.6, 48.8, 47.6, 43.6, 40.8, 35.1.

HRMS(APCI) m/z calcd. for $C_{26}H_{29}NO_4$ $[M+H]^+$: 420.2169, found: 420.2179.



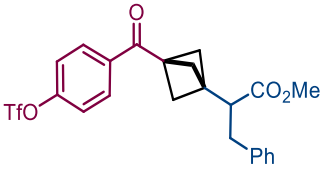
Methyl 2-(3-(4-acetoxybenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (14): The product **14** was purified by silica gel column chromatography (DCM) as a yellow

oil (32.9 mg, 42% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.12 (m, 7H), 3.59 (s, 3H), 3.01 – 2.88 (m, 2H), 2.82 – 2.70 (m, 1H), 2.29 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 173.2, 168.9, 154.3, 139.1, 134.1, 130.6, 128.78, 128.6, 126.5, 121.8, 52.9, 51.6, 48.6, 43.6, 40.9, 35.0, 21.3.

HRMS(APCI) m/z calcd. for $C_{24}H_{24}O_5$ $[M+H]^+$: 393.1697, found: 393.1705.



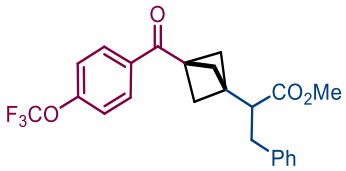
Methyl 3-phenyl-2-(3-(4-(((trifluoromethyl)sulfonyl)oxy)benzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (15): The product **15** was purified by silica gel column chromatography (DCM/Petroleum ether = 3:1) as a white solid (48.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.23 (d, *J* = 7.7 Hz, 2H), 7.20 – 7.11 (m, 3H), 3.59 (s, 3H), 3.02 – 2.89 (m, 2H), 2.81 – 2.69 (m, 1H), 2.18 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ195.4, 173.1, 152.4, 139.0, 136.3, 131.3, 128.8, 128.6, 126.6, 121.7, 118.8 (q, *J* = 318.8 Hz), 52.9, 51.7, 48.6, 43.7, 41.1, 35.0.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -72.6 (s).

HRMS(APCI) m/z calcd. for $C_{23}H_{21}F_3O_6S$ $[M+H]^+$: 483.1084, found: 483.1083.



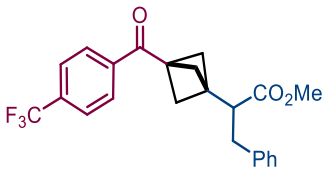
Methyl 3-phenyl-2-(3-(4-(trifluoromethoxy)benzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (16): The product **16** was purified by silica gel column chromatography (DCM/Petroleum ether = 3:1) as a yellow solid (65.5 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 7.33 – 7.24 (m, 4H), 7.23 – 7.13 (m, 3H), 3.63 (s, 3H), 3.06 – 2.92 (m, 2H), 2.87 – 2.72 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 173.1, 152.6, 139.0, 134.8, 131.0, 128.8, 128.6, 126.6, 120.4, 120.4 (q, *J* = 257.1 Hz), 52.9, 51.6, 48.6, 43.6, 41.0, 35.0.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -57.5 (s).

HRMS(APCI) m/z calcd. for $C_{23}H_{21}F_3O_4$ $[M+H]^+$: 419.1465, found: 419.1471.



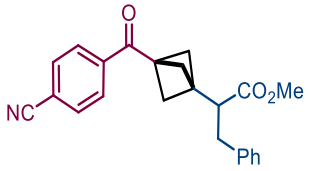
Methyl 3-phenyl-2-(3-(4-(trifluoromethyl)benzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (4): The product **4** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow solid (71.6 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.23 – 7.14 (m, 3H), 3.63 (s, 3H), 3.09 – 2.93 (m, 2H), 2.87 – 2.72 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 173.1, 139.3, 139.0, 134.2 (q, *J* = 32.6 Hz),129.2, 128.7, 128.6, 126.6, 125.6 (q, *J* = 3.7 Hz), 123.7 (q, *J* = 271.0 Hz), 52.9, 51.6, 48.6, 43.7, 41.0, 35.0.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -72.6 (s).

HRMS(APCI) m/z calcd. for $C_{23}H_{21}F_3O_3$ $[M+H]^+$: 403.1516, found: 403.1524.

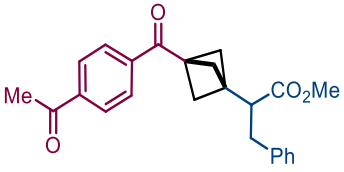


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (17): The product **17** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a yellow oil (64.6 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.23 – 7.15 (m, 3H), 3.63 (s, 3H), 3.09 – 2.93 (m, 2H), 2.87 – 2.72 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 173.0, 139.5, 138.9, 132. 4, 129.2, 128.7, 128.6, 126.6, 118.0, 116.2, 52.86, 51.6, 48.4, 43.6, 41.1, 35.0.

HRMS(APCI) m/z calcd. for $C_{23}H_{21}NO_3$ $[M+H]^+$: 360.1594, found: 360.1593.

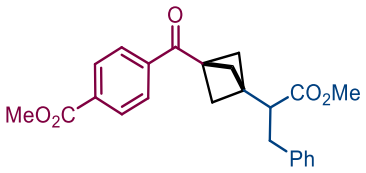


Methyl 2-(3-(4-acetylbenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (18): The product **18** was purified by silica gel column chromatography (DCM) as a yellow oil (49.1 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.95 (m, 4H), 7.30 – 7.25 (m, 2H), 7.23 – 7.16 (m, 3H), 3.63 (s, 3H), 3.07 – 2.92 (m, 2H), 2.89 – 2.74 (m, 1H), 2.64 (s, 3H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 196.8, 173.1, 140.0, 139.8, 139.0, 129.1, 128.7, 128.6, 128.4, 126.6, 52.8, 51.7, 48.6, 43.8, 41.0, 35.0, 27.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{24}O_4$ $[M+H]^+$: 377.1747, found: 377.1755.

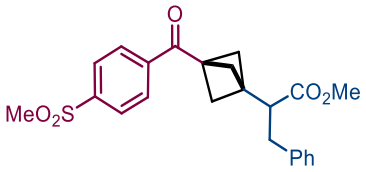


Methyl 4-(3-(1-methoxy-1-oxo-3-phenylpropan-2-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzoate (19): The product **19** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow solid (69.6 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.4 Hz, 2H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 3.95 (s, 3H), 3.63 (s, 3H), 3.05 – 2.92 (m, 2H), 2.85 – 2.74 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 173.1, 166.3, 139.9, 139.0, 133.8, 129.8, 128.8, 128.8, 128.6, 126.6, 52.9, 52.6, 51.7, 48.6, 43.8, 41.0, 35.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{24}O_5$ $[M+H]^+$: 393.1697, found: 393.1704.

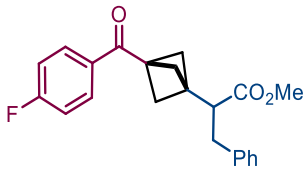


Methyl 2-(3-(4-((methylsulfinyl)oxy)benzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (20): The product **20** was purified by silica gel column chromatography (DCM) as a gray solid (70.8 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 2H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.28 (t, *J* = 6.2 Hz, 2H), 7.24 – 7.13 (m, 3H), 3.63 (s, 3H), 3.08 (s, 3H), 3.04 – 2.90 (m, 2H), 2.86 – 2.72 (m, 1H), 2.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.0, 144.0, 140.6, 138.9, 129.7, 128.7, 128.6, 127.8, 126.6, 52.9, 51.7, 48.5, 44.4, 43.8, 41.1, 35.0.

HRMS(APCI) m/z calcd. for $C_{23}H_{24}O_5S$ $[M+H]^+$: 413.1417, found: 413.1417.



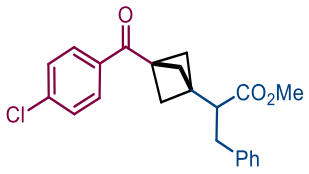
Methyl 2-(3-(4-fluorobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (21): The product **21** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow solid (49.0 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.92 (m, 2H), 7.31 – 7.08 (m, 7H), 3.63 (s, 3H), 3.08 – 2.92 (m, 2H), 2.85 – 2.74 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 173.2, 165.7 (d, *J* = 255.1 Hz), 139.1, 132.9 (d, *J* = 2.9 Hz), 131.6 (d, *J* = 9.3 Hz), 128.8, 128.6, 126.6, 115.7 (d, *J* = 21.8 Hz), 52.9, 51.6, 48.6, 43.6, 40.94, 35.06.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -104.8.

HRMS(APCI) m/z calcd. for $C_{22}H_{21}FO_3$ $[M+H]^+$: 353.1547, found: 353.1547.

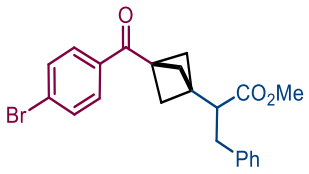


Methyl 2-(3-(4-chlorobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (22): The product **22** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow solid (47.1 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 3.63 (s, 3H), 3.05 – 2.91 (m, 2H), 2.86 – 2.71 (m, 1H), 2.20 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 173.2, 139.5 139.1, 134.9, 130.4, 128.9, 128.8, 128.6, 126.6, 52.9, 51.6, 48.6, 43.6, 41.0, 35.1.

HRMS(APCI) m/z calcd. for $C_{22}H_{21}ClO_3$ $[M+H]^+$: 369.1252 and 371.1222, found: 369.1257 and 371.1234.



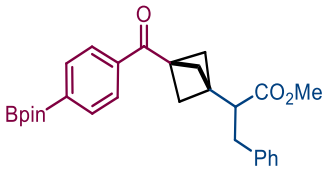
Methyl 2-(3-(4-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (23): The product **23** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow oil (75.4 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.24 (m, 2H), 7.23 – 7.16 (m, 3H), 3.63 (s, 3H), 3.06 – 2.93 (m, 2H), 2.86 – 2.73 (m, 1H), 2.20 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.1, 139.0, 135.2, 131.9, 130.5, 128.7, 128.6,

128.3, 126.6, 52.9, 51.6, 48.6, 43.6, 41.0, 35.0.

HRMS(APCI) m/z calcd. for $C_{22}H_{21}BrO_3$ $[M+H]^+$: 413.0747 and 415.0726, found: 413.0753 and 415.0735.

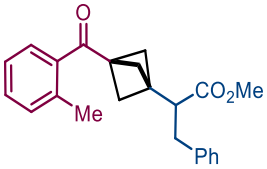


Methyl 3-phenyl-2-(3-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (24): The product **24** was purified by silica gel column chromatography (DCM) as a yellow oil (31.2 mg, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.25 (m, 2H), 7.22 – 7.16 (m, 3H), 3.62 (s, 3H), 3.04 – 2.91 (m, 2H), 2.85 – 2.74 (m, 1H), 2.20 (s, 6H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 173.2, 139.1, 138.6, 134.9, 128.8, 128.6, 127.9, 126.5, 84.3, 52.9, 51.6, 48.7, 43.8, 40.9, 35.0, 25.0.

HRMS(APCI) m/z calcd. for $=C_{28}H_{33}BO_5$ $[M+H]^+$: 461.2494, found: 461.2504.

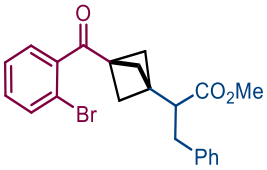


Methyl 2-(3-(2-methylbenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (25): The product **25** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a colorless oil (43.4 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.13 (m, 7H), 3.60 (s, 3H), 3.02 – 2.87 (m, 2H), 2.83 – 2.69 (m, 1H), 2.39 (s, 3H), 2.10 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 173.2, 139.1, 137.5, 137.4, 131.8, 130.9, 128.8, 128.6, 128.1, 126.5, 125.3, 52.1, 51.6, 48.7, 44.6, 40.7, 35.0, 20.7.

HRMS(APCI) m/z calcd. for $C_{23}H_{24}O_3$ $[M+H]^+$: 349.1798, found: 349.1806.

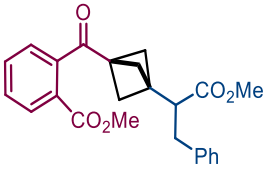


Methyl 2-(3-(2-bromobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (26): The product **26** was purified by silica gel column chromatography (DCM/Petroleum ether = 2:1) as a white solid (49.2 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 8.14 (m, 1H), 7.96 – 7.88 (m, 1H), 7.33 – 7.14 (m, 7H), 3.63 (s, 3H), 3.04 – 2.93 (m, 2H), 2.84 – 2.75 (m, 1H), 2.20 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 173.0, 140.7, 139.0, 133.4, 131.1, 128.7, 128.6, 127.4, 127.1, 126.5, 118.2, 51.6, 51.6, 48.7, 44.1, 41.0, 35.0.

HRMS(APCI) m/z calcd. for $C_{22}H_{21}BrO_3$ $[M+H]^+$: 413.0747 and 415.0726, found: 413.0756 and 415.0733.

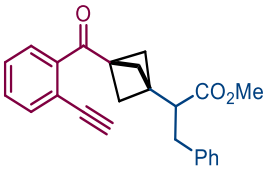


Methyl 2-(3-(1-methoxy-1-oxo-3-phenylpropan-2-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzoate (27): The product **27** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a white solid (46.4 mg, 59% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 1H), 7.56 (t, *J* = 7.5, 1.1 Hz, 1H), 7.48 (t, *J* = 7.7, 1.1 Hz, 1H), 7.26 – 7.09 (m, 6H), 3.87 (s, 3H), 3.57 (s, 3H), 2.99 – 2.84 (m, 2H), 2.77 – 2.66 (m, 1H), 1.97 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 173.1, 166.5, 142.0, 139.2, 132.6, 130.2, 129.5, 128.7, 128.6, 128.0, 126.5, 126.2, 52.7, 51.6, 51.4, 48.8, 44.4, 40.7, 35.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{24}O_5$ $[M+H]^+$: 393.1697, found: 393.1707.

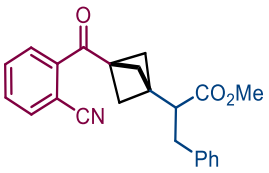


Methyl 2-(3-(2-ethynylbenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (28): The product **28** was purified by silica gel column chromatography (DCM) as a yellow solid (33.3 mg, 47% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.21 – 7.13 (m, 3H), 3.59 (s, 3H), 3.23 (s, 1H), 3.02 – 2.87 (m, 2H), 2.82 – 2.68 (m, 1H), 2.11 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 173.1, 141.5, 139.1, 134.4, 130.4, 128.7, 128.6, 128.4, 127.1, 126.5, 119.9, 81.7, 81.5, 52.1, 51.6, 48.7, 44.2, 40.8, 35.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{22}O_3$ $[M+H]^+$: 359.1642, found: 359.1647.

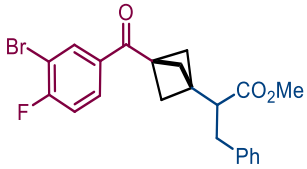


Methyl 2-(3-(2-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (29): The product **29** was purified by silica gel column chromatography (DCM) as a yellow solid (60.2 mg, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 1H), 7.70 – 7.56 (m, 2H), 7.30 – 7.22 (m, 2H), 7.22 – 7.10 (m, 3H), 3.60 (s, 3H), 3.10 – 2.86 (m, 2H), 2.82 – 2.68 (m, 1H), 2.19 (s, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 172.9, 139.6, 138.8, 135.3, 132.2, 132.0, 129.4, 128.7, 128.5, 126.5, 117.7, 111.2, 52.6, 51.6, 48.4, 43.7, 41.0, 34.9.

HRMS(APCI) m/z calcd. for $C_{23}H_{21}NO_3$ $[M+H]^+$: 360.1594, found: 360.1603.



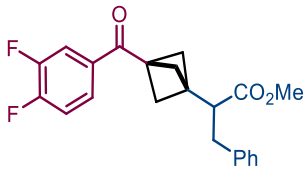
Methyl 2-(3-(3-bromo-4-fluorobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (30): The product **30** was purified by silica gel column chromatography (DCM/Petroleum ether = 2:1) as a white solid (62.8 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.26 – 7.12 (m,6H), 3.59 (s, 3H), 2.99 – 2.87 (m, 2H), 3.59 (2.78 – 2.68 (m, 1H), 2.07 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 173.1, 162.0 (d, *J* = 255.6 Hz),139.0, 134.8 (d, *J* = 1.5 Hz), 134.0 (d, *J* = 3.6 Hz), 130.2 (d, *J* = 8.5 Hz),128.8, 128.6, 126.6, 116.7 (d, *J* = 22.8 Hz), 109.8 (d, *J* = 21.6 Hz), 53.0, 51.7, 48.5, 43.5, 41.0, 35.1.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -99.17 – -99.22(m).

HRMS(APCI) m/z calcd. for $C_{22}H_{20}BrFO_3$ $[M+H]^+$: 431.0653 and 433.0632, found: 431.0649 and 433.0632.



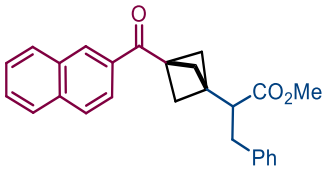
Methyl 2-(3-(3,4-difluorobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (31): The product **31** was purified by silica gel column chromatography (DCM/Petroleum ether = 2:1) as a white solid (59.2 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.66 (m, 2H), 7.32 – 7.16 (m, 6H), 3.63 (s, 3H), 3.05 – 2.89 (m, 2H), 2.86 – 2.74 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.5, 173.1, 153.6 (dd, *J* = 257.2, 12.8 Hz), 150.3 (dd, *J* = 250.9, 13.0 Hz),139.0, 133.4 (t, *J* = 4.0 Hz), 126.6, 126.1 (dd, *J* = 7.4, 3.7 Hz), 118.2 (dd, *J* = 17.9, 1.6 Hz), 117.5 (d, *J* = 17.7 Hz), 53.0, 51.7, 48.5, 43.5, 41.0, 35.0.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -129.36 – -129.47 (m), -135.62 – 135.73(m).

HRMS(APCI) m/z calcd. for $C_{22}H_{20}F_2O_3$ $[M+H]^+$: 371.1453, found: 371.1455.

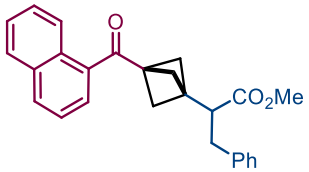


Methyl 2-(3-(2-naphthoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (32): The product **32** was purified by silica gel column chromatography (DCM/Petroleum ether = 1:1) as a yellow solid (47.6 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.03 – 7.98 (m, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.83 (m, 2H), 7.63 – 7.51 (m, 2H), 7.27 (q, 2H), 7.23 – 7.16 (m, 3H), 3.63 (s, 3H), 3.08 – 2.94 (m, 2H), 2.88 – 2.76 (m, 1H), 2.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 173.3, 139.2, 135.56, 134.0, 132.5, 130.8, 129.7, 128.8, 128.6, 128.6, 128.5, 127.9, 126.9, 126.6, 124.6, 53.1, 51.7, 48.7, 43.9, 41.0, 35.1.

HRMS(APCI) m/z calcd. for $C_{26}H_{24}O_3$ $[M+H]^+$: 385.1798, found: 385.1807.

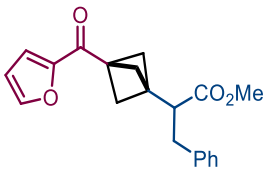


Methyl 2-(3-(1-naphthoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (33): The product **33** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a colorless solid (47.0 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* =7.1 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.51 – 7.44 (m, 1H), 7.30 – 7.25 (m, 2H), 7.22 –7.13 (m, 3H), 3.60 (s, 3H), 3.04 – 2.89 (m, 2H), 2.81 – 2.72 (m, 1H), 2.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 173.2, 139.1, 135.3, 134.0, 132.0, 130.3, 128.8, 128.6, 128.5, 127.8, 127.1, 126.6, 126.6, 125.7, 124.3, 52.3, 51.6, 48.7, 44.9, 40.5, 35.0, 29.8.

HRMS(APCI) m/z calcd. for $C_{26}H_{24}O_3$ $[M+H]^+$: 385.1798, found: 385.1806

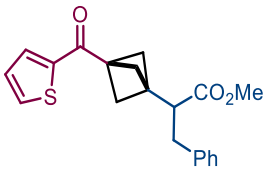


Methyl 2-(3-(furan-2-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (34): The product **34** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a colorless oil (29.7 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 1.7 Hz, 1H), 7.28 – 7.20 (m, 3H), 7.20 – 7.14 (m, 4H), 6.50 (d, J = 3.5, 1.6 Hz, 1H), 3.59 (s, 3H), 2.99 – 2.88 (m, 2H), 2.80 – 2.71 (m, 1H), 2.13 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 185.7, 173.2, 152.4, 146.7, 139.2 128.8, 128.6 126.5, 118.4, 112.2, 52.1, 51.6, 48.7, 42.4, 40.6, 35.0.

HRMS(APCI) m/z calcd. for $C_{20}H_{20}O_4$ $[M+H]^+$: 325.1434, found: 325.1441.

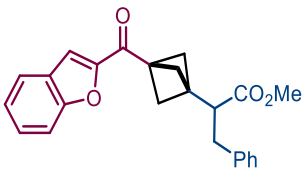


Methyl 3-phenyl-2-(3-(thiophene-2-carbonyl)bicyclo[1.1.1]pentan-1-yl)propanoate (35): The product **35** was purified by silica gel column chromatography (DCM/Petroleum ether = 4:1) as a white solid (20.0 mg, 30% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.68 – 7.59 (m, 1H), 7.31 – 7.26 (m, 2H), 7.19 (t, *J* = 8.3 Hz, 3H), 7.15 – 7.09 (m, 1H), 3.62 (s, 3H), 3.05 – 2.92 (m, 2H), 2.85 – 2.73 (m, 1H), 2.19 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.7, 173.2, 142.7, 139.1, 133.9, 133.1, 128.8, 128.6, 128.2, 126.6, 52.5, 51.7, 48.6, 43.2, 40.4, 35.0.

HRMS(APCI) m/z calcd. for $C_{20}H_{20}O_3S$ $[M+H]^+$: 341.1206, found: 341.1215.



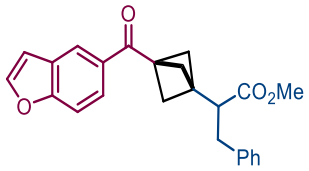
Methyl 2-(3-(benzofuran-2-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (36): The product **36** was purified by silica gel column chromatography (DCM) as a yellow oil (46.7 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 1H), 7.44 (s, 1H), 7.43 – 7.35 (m, 1H), 7.26 – 7.18 (m, 3H), 7.15 – 7.09 (m, 3H), 3.55 (s, 3H), 3.00 – 2.85

(m, 2H), 2.80 – 2.65 (m, 1H), 2.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 187.5, 173.1, 155.6, 152.0, 139.1, 128.8, 128.6, 128.5, 127.0, 126.5, 124.0, 123.4, 114.3, 112.6, 52.2, 51.6, 48.7, 42.7, 40.7, 35.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{22}O_4$ $[M+H]^+$: 375.1591, found: 375.1589.

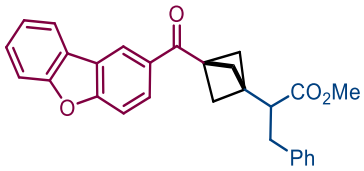


Methyl 2-(3-(benzofuran-5-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (37): The product **37** was purified by silica gel column chromatography (DCM) as a yellow solid (23.9 mg, 32% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.98 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 2.0 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.33 – 7.26 (m, 2H), 7.20 (t, *J* = 6.8 Hz, 3H), 6.86 (d, *J* = 1.6 Hz, 1H), 3.63 (s, 3H), 3.04 – 2.95 (m, 2H), 2.88 – 2.78 (m, 1H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 173.3, 157.5, 146.5, 139.2, 132.1, 128.8, 128.6, 127.5, 126.6, 125.7, 123.3, 111.6, 107.5, 53.1, 51.7, 48.8, 43.8, 40.9, 35.1.

HRMS(APCI) m/z calcd. for $C_{24}H_{22}O_4$ $[M+H]^+$: 375.1591, found: 375.1599.

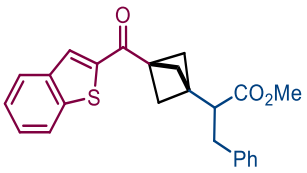


Methyl 2-(3-(dibenzo[*b,d*]furan-2-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (38): The product **38** was purified by silica gel column chromatography (DCM) as a yellow solid (31.4 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 1.3 Hz, 1H), 8.12 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.58 (dd, *J* = 8.4, 4.3 Hz, 2H), 7.52 – 7.46 (m, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.27 (q, *J* = 7.1, 6.6 Hz, 2H), 7.24 – 7.14 (m, 3H), 3.64 (s, 3H), 3.09 – 2.93 (m, 2H), 2.89 – 2.75 (m, 1H), 2.28 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 173.2, 158.8, 156.9, 139.1, 131.9, 128.8, 128.7, 128.6, 128.1, 126.6, 124.7, 123.8, 123.5, 122.2, 121.1, 112.6, 111.6, 53.1, 51.7, 48.7, 43.8, 40.9, 35.1.

HRMS(APCI) m/z calcd. for $C_{28}H_{24}O_4$ $[M+H]^+$: 425.1747, found: 425.1756.

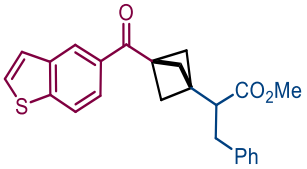


Methyl 2-(3-(benzo[b]thiophene-2-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (39): The product **39** was purified by silica gel column chromatography (DCM/Petroleum ether = 3:1) as a colorless oil (50.0 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.93 – 7.82 (m, 2H), 7.50 – 7.38 (m, 2H), 7.33 – 7.26 (m, 2H), 7.25 – 7.15 (m, 3H), 3.65 (s, 3H), 3.11 – 2.94 (m, 2H), 2.91 – 2.77 (m, 1H), 2.26 (s, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 191.2, 173.2 142.4, 142.4, 139.2, 139.1, 130.3, 128.8, 128.6, 127.7, 126.6, 126.2, 125.2, 123.0, 52.7, 51.7, 48.6, 43.2, 40.6, 35.01.

HRMS(APCI) m/z calcd. for $C_{24}H_{22}O_3S$ $[M+H]^+$: 391.1362, found: 391.1359.

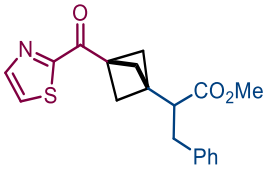


Methyl 2-(3-(benzo[*b*]thiophene-5-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (40): The product **40** was purified by silica gel column chromatography (DCM) as a yellow solid (35.3 mg, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.98 – 7.88 (m, 2H), 7.52 (d, *J* = 5.4 Hz, 1H), 7.44 (d, *J* = 5.4 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23 – 7.18 (m, 3H), 3.64 (s, 3H), 3.08 – 2.96 (m, 2H), 2.88 – 2.78 (m, 1H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.0, 173.3, 144.3, 139.3, 139.1, 133.1, 128.8, 128.6, 127.9, 126.6, 125.0, 124.7, 124.1, 122.7, 53.0, 51.7, 48.7, 43.8, 40.9, 35.1.

HRMS(APCI) m/z calcd. for $C_{24}H_{22}O_3S$ $[M+H]^+$: 391.1362, found: 391.1368.



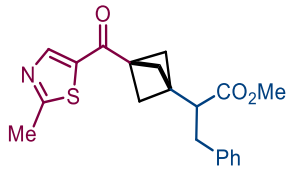
Methyl 3-phenyl-2-(3-(thiazole-2-carbonyl)bicyclo[1.1.1]pentan-1-yl)propanoate (41): The product **41** was purified by silica gel column chromatography (DCM) as a yellow oil (56.4 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 3.0 Hz, 1H), 7.64 (d, *J* = 3.0 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 – 7.17 (m, 3H), 3.63 (s, 3H), 3.06 – 2.94 (m, 2H), 2.87 – 2.75 (m, 1H), 2.28

(s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.6, 173.1, 166.4, 145.2, 139.3, 128.8, 128.6, 126.5, 125.9, 52.4, 51.6, 48.8, 42.7, 41.2, 35.0.

HRMS(APCI) m/z calcd. for $C_{19}H_{19}NO_3S$ $[M+H]^+$: 342.1158, found: 342.1168.

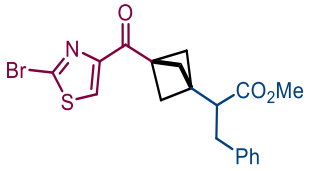


Methyl 2-(3-(2-methylthiazole-5-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (42): The product **42** was purified by silica gel column chromatography (DCM/EtOAc = 10:1) as a yellow solid (30.2 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.31 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 3.63 (s, 3H), 3.04 – 2.93 (m, 2H), 2.85 – 2.72 (m, 4H), 2.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.5, 173.5, 173.1, 147.5, 139.0, 138.4, 128.8, 128.6, 126.6, 52.4, 51.7, 48.5, 43.2, 40.5, 35.1, 20.0.

HRMS(APCI) m/z calcd. for $C_{20}H_{21}NO_3S$ $[M+H]^+$: 356.1315, found: 356.1322.

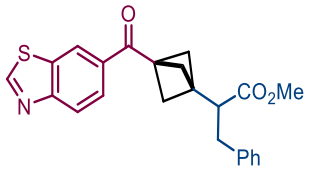


Methyl 2-(3-(2-bromothiazole-4-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (43): The product **43** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a yellow solid (50.8 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.31 – 7.25 (m, 2H), 7.22 – 7.14 (m, 3H), 3.61 (s, 3H), 3.06 – 2.89 (m, 2H), 2.86 – 2.72 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 189.8, 173.2, 153.9, 139.2, 135.8, 129.8, 128.8, 128.5, 126.5, 52.2, 51.6, 48.8, 43.7, 41.1, 35.0.

HRMS(APCI) m/z calcd. for $C_{19}H_{18}BrNO_3S$ $[M+H]^+$: 420.0264 and 422.0243, found: 420.0273 and 422.0257.



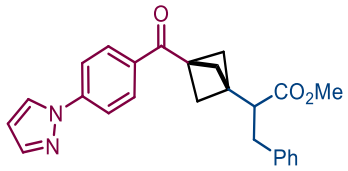
Methyl 2-(3-(benzo[*d*]thiazole-6-carbonyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (44): The product **44** was purified by silica gel column

chromatography (DCM/EtOAc = 50:1) as a yellow solid (35.6 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.61 (s, 1H), 8.22 – 8.08 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.15 (m, 3H), 3.63 (s, 3H), 3.07 – 2.95 (m, 2H), 2.89 – 2.76 (m, 1H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 173.2, 157.7, 155.9, 139.1, 134.1, 133.8, 128.8, 128.6, 126.8, 126.6, 123.7, 123.6, 53.0, 51.7, 48.6, 43.9, 41.0, 35.1.

HRMS(APCI) m/z calcd. for $C_{23}H_{21}NO_3S$ $[M+H]^+$: 392.1315, found: 392.1321.

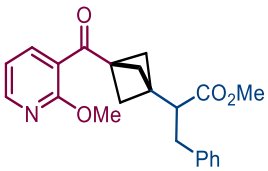


Methyl 2-(3-(4-(1*H*-pyrazol-1-yl)benzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (45): The product **45** was purified by silica gel column chromatography (DCM/EtOAc = 30:1) as a yellow solid (45.7 mg, 57% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.7 Hz, 2H), 8.00 (d, *J* = 2.5 Hz, 1H), 7.84 – 7.73 (m, 3H), 7.32 – 7.26 (m, 2H), 7.23 – 7.14 (m, 3H), 6.52 (t, *J* = 2.0 Hz, 1H), 3.63 (s, 3H), 3.07 – 2.93 (m, 2H), 2.87 – 2.73 (m, 1H), 2.23 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.88, 173.22, 143.3, 142.2, 139.1, 134.2, 130.7, 128.8, 128.6, 127.0, 126.6, 118.4, 108.7, 53.0, 51.7, 48.7, 43.7, 41.0, 35.1.

HRMS(APCI) m/z calcd. for $C_{25}H_{24}BrN_2O_3$ $[M+H]^+$: 401.1864, found: 401.1864.

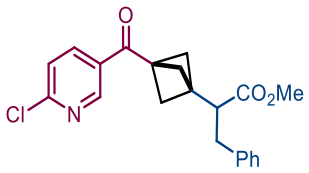


Methyl 2-(3-(2-methoxynicotinoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (46): The product **46** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a yellow solid (52.8 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.74 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 2H), 7.21 – 7.14 (m, 3H), 6.93 (dd, *J* = 7.4, 5.0 Hz, 1H), 3.99 (s, 3H), 3.60 (s, 3H), 3.00 – 2.89 (m, 2H), 2.79 – 2.69 (m, 1H), 2.06 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8, 173.2, 161.0, 149.9, 139.2, 138.8, 128.8, 128.6, 126.5, 122.4, 116.7, 53.5, 51.8, 51.6, 48.7, 44.5, 40.3, 35.0.

HRMS(APCI) m/z calcd. for $C_{22}H_{23}NO_4$ $[M+H]^+$: 366.1700, found: 3366.1707.

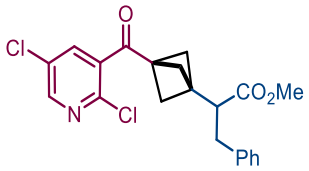


Methyl 2-(3-(6-chloronicotinoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (47): The product **47** was purified by silica gel column chromatography (DCM) as a white solid (36.2 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (s, 1H), 8.17 (d, *J* = 6.2 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.23 – 7.16 (m, 3H), 3.63 (s, 3H), 3.05 – 2.94 (m, 2H), 2.85 – 2.74 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 173.0, 155.6, 150.5, 138.9, 138.8, 130.8, 128.7, 128.6, 126.6, 124.7, 52.8, 51.7, 48.4, 43.6, 41.2, 35.0.

HRMS(APCI) m/z calcd. for $C_{21}H_{20}ClNO_3$ $[M+H]^+$: 370.1204 and 372.1175, found: 370.1210 and 372.1188.

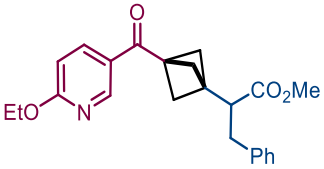


Methyl 2-(3-(2,5-dichloronicotinoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (48): The product **48** was purified by silica gel column chromatography (DCM) as a white solid (65.0 mg, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.54 (s, 1H), 7.30 – 7.24 (m, 2H), 7.22 – 7.12 (m, 3H), 3.59 (s, 3H), 2.99 – 2.88 (m, 2H), 2.80 – 2.66 (m, 1H), 2.08 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.50, 172.81, 149.3, 144.6, 138.8, 135.9, 135.5, 130.9, 128.7, 128.6, 126.6, 51.8, 51.7, 48.4, 44.2, 41.0, 34.9.

HRMS(APCI) m/z calcd. for $C_{21}H_{19}ClNO_3$ $[M+H]^+$: 404.0815 and 406.0785, found: 404.0821 and 406.0796.



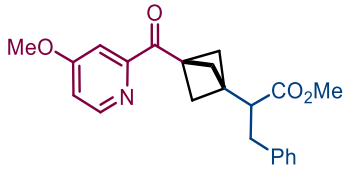
Methyl 2-(3-(6-ethoxynicotinoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (49): The product **49** was purified by silica gel column chromatography (DCM/EtOAc = 30:1) as a yellow solid (42.8 mg, 56% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 8.13 (d, *J* = 11.1 Hz, 1H), 7.31 – 7.26 (m, 2H),

7.24 – 7.14 (m, 3H), 6.76 (d, *J* = 8.7 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 3.63 (s, 3H), 3.06 – 2.93 (m, 2H), 2.83 – 2.73 (m, 1H), 2.20 (s, 6H), 1.42 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 194.8, 173.2, 166.5, 150.0, 139.1, 138.9, 128.8, 128.6, 126.6, 126.3, 111.7, 62.8, 52.8, 51.7, 48.7, 43.5, 41.0, 35.0, 14.7.

HRMS(APCI) m/z calcd. for $C_{23}H_{25}NO_4$ $[M+H]^+$: 380.1856, found: 380.1863.

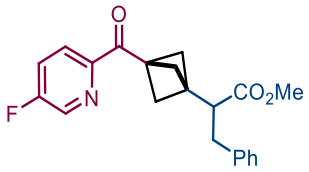


Methyl 2-(3-(4-methoxypicolinoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (50): The product **50** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a white solid (45.9 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 5.6 Hz, 1H), 7.39 (d, *J* = 2.5 Hz, 1H), 7.20 – 7.14 (m, 2H), 7.12 – 7.04 (m, 3H), 6.86 – 6.78 (m, 1H), 3.77 (s, 3H), 3.51 (s, 3H), 2.93 – 2.81 (m, 2H), 2.75 – 2.65 (m, 1H), 2.16 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 173.3, 166.3, 155.8, 150.2, 139.4, 128.8, 128.5, 126.4, 113.6, 107.7, 55.5, 52.7, 51.5, 49.0, 43.5, 41.3, 35.0.

HRMS(APCI) m/z calcd. for $C_{22}H_{23}NO_4$ $[M+H]^+$: 366.1700, found: 366.1706.



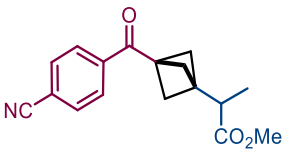
Methyl 2-(3-(5-fluoropicolinoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoate (51): The product **51** was purified by silica gel column chromatography (DCM) as a yellow solid (58.2 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 2.6 Hz, 1H), 8.04 (dd, *J* = 8.7, 4.7 Hz, 1H), 7.46 (td, *J* = 8.4, 2.7 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H), 3.61 (s, 3H), 3.05 – 2.91 (m, 2H), 2.87 – 2.73 (m, 1H), 2.25 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 173.3, 161.2 (d, *J* = 263.7 Hz), 150.4 (d, *J* = 4.4 Hz), 139.3, 137.3 (d, *J* = 24.2 Hz), 128.8, 128.5, 126.4, 124.7 (d, *J* = 5.6 Hz), 123.3 (d, *J* = 18.5 Hz), 52.7, 51.5, 48.9, 43.3, 41.4, 35.0.

^{19}F NMR (JEOL) (376 MHz, $CDCl_3$) δ -119.72 – 119.75 (m).

HRMS(APCI) m/z calcd. for $C_{21}H_{20}FNO_3$ $[M+H]^+$: 354.1500, found: 354.1499.

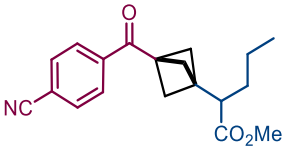


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (52): The product **52** was purified by silica gel column chromatography (DCM) as a yellow oil (49.8 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 3.68 (s, 3H), 2.67 (q, *J* = 7.1 Hz, 1H), 2.19 (s, 6H), 1.14 (d, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 174.2, 139.6, 132.4, 129.2, 118.0, 116.2, 52.4, 51.7, 43.4, 41.6, 40.4, 13.4.

HRMS(APCI) m/z calcd. for $C_{17}H_{17}NO_3$ $[M+H]^+$: 284.1281, found: 284.1285.

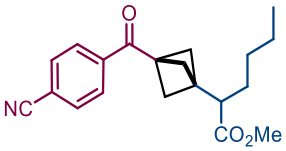


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)pentanoate (53): The product **53** was purified by silica gel column chromatography (DCM) as a yellow oil (56.6 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 3.67 (s, 3H), 2.56 (dd, *J* = 10.4, 4.0 Hz, 1H), 2.17 (q, *J* = 9.5 Hz, 6H), 1.42 – 1.21 (m, 4H), 0.89 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.8, 139.6, 132.4, 129.2, 118.0, 116.2, 77.5, 77.2, 76.8, 52.7, 51.5, 46.5, 43.6, 41.2, 31.1, 21.0, 14.0.

HRMS(APCI) m/z calcd. for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594, found: 312.1601.

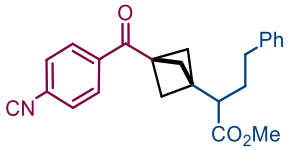


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)hexanoate (54): The product **54** was purified by silica gel column chromatography (DCM) as a yellow oil (48.8 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 3.70 (s, 3H), 2.56 (dd, *J* = 10.3, 4.3 Hz, 1H), 2.19 (q, *J* = 9.4 Hz, 6H), 1.49 – 1.22 (m, 6H), 0.89 (t, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 173.9, 139.6, 132.5, 129.3, 118.1, 116.3, 52.8, 51.6, 46.8, 43.7, 41.3, 30.0, 28.8, 22.8, 14.0.

HRMS(APCI) m/z calcd. for $C_{20}H_{23}NO_3$ $[M+H]^+$: 326.1751, found: 326.1756.

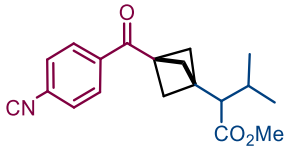


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-4-phenylbutanoate (55): The product **55** was purified by silica gel column chromatography (DCM) as a yellow oil (66.4 mg, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.23 – 7.14 (m, 3H), 3.72 (s, 3H), 2.75 – 2.50 (m, 3H), 2.20 (q, *J* = 9.5 Hz, 6H), 2.07 – 1.96 (m, 1H), 1.80 – 1.69 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 173.5, 141.3, 139.5, 132.4, 129.2, 128.5, 128.5, 126.2, 118.0, 116.2, 52.7, 51.7, 46.2, 43.5, 41.1, 34.0, 30.8.

HRMS(APCI) m/z calcd. for $C_{24}H_{23}NO_3$ $[M+H]^+$: 374.1751, found: 374.1757.

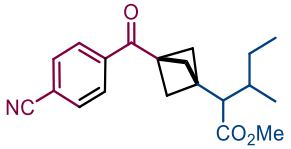


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-methylbutanoate (56): The product **56** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow oil (58.8 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 3.67 (s, 3H), 2.34 (d, *J* = 8.1 Hz, 1H), 2.32 – 2.20 (m, 6H), 2.03 – 1.93 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 3H), 0.90 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.5, 139.6, 132.4, 129.3, 118.0, 116.2, 77.5, 77.1, 76.8, 53.9, 53.6, 51.3, 44.3, 40.7, 29.2, 21.5, 21.0.

HRMS(APCI) m/z calcd. for $C_{19}H_{21}NO_3$ $[M+H]^+$: 312.1594, found: 312.1602.

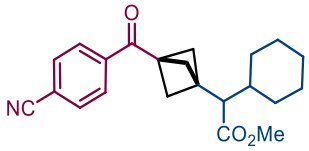


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-methylpentanoate (57): The product **57** was purified by silica gel column chromatography (DCM) as a yellow oil (59.1 mg, 91% yield). d.r. = 1.3:1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 6.7 Hz, 2H), 7.74 (d, *J* = 8.5 Hz, 2H), 3.68 (s, 3H), 2.55 – 2.43 (m, 1H), 2.36 – 2.22 (m, 6H), 1.84 – 1.72 (m, 1H), 1.59 – 1.38 (m, 1H), 1.35 – 1.22 (m, 1H), 1.03 – 0.86 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 196.1, 173.7, 173.4, 139.7, 132.5, 129.3, 118.1, 116.3, 54.2, 53.9, 52.4, 51.4, 51.3, 50.9, 44.6, 44.5, 40.8, 40.7, 35.6, 35.5, 27.8, 27.6, 17.4, 16.9, 11.3, 11.2.

HRMS(APCI) m/z calcd. for $C_{20}H_{23}NO_3$ $[M+H]^+$: 326.1751, found: 326.1755.

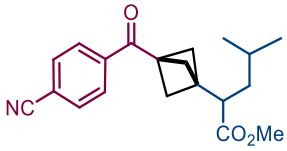


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-2-cyclohexylacetate (58): The product **58** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow solid (40.7 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 3.67 (s, 3H), 2.39 (d, *J* = 8.1 Hz, 1H), 2.34 – 2.21 (m, 6H), 1.88 (d, *J* = 12.6 Hz, 1H), 1.76 – 1.61 (m, 5H), 1.22 – 0.92 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.5, 139.7, 132.5, 129.3, 118.1, 116.2, 54.0, 52.9, 51.3, 44.5, 40.6, 38.8, 31.8, 31.2, 26.2.

HRMS(APCI) m/z calcd. for $C_{22}H_{25}NO_3$ $[M+H]^+$: 352.1907, found: 352.1916.

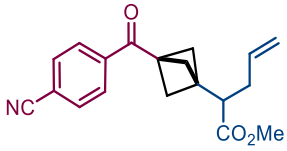


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-4-methylpentanoate (59): The product **59** was purified by silica gel column chromatography (DCM) as a yellow solid (58.4 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.3 Hz, 2H), 3.69 (s, 3H), 2.72 – 2.61 (m, 1H), 2.25 – 2.12 (m, 6H), 1.58 – 1.47 (m, 1H), 1.28 – 1.14 (m, 2H), 0.88 (t, *J* = 6.5 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 174.0, 139.6, 132.5, 129.3, 118.0, 116.2, 52.7, 51.6, 44.8, 43.6, 41.3, 37.9, 26.5, 23.3, 21.9.

HRMS(APCI) m/z calcd. for $C_{20}H_{23}NO_3$ $[M+H]^+$: 326.1751, found: 326.1755.

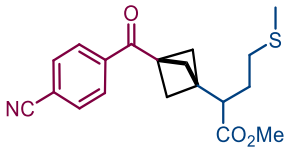


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)pent-4-enoate (60): The product **60** was purified by silica gel column chromatography (DCM) as a yellow solid (57.9 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 5.83 – 5.66 (m, 1H), 5.14 – 4.97 (m, 2H), 3.68 (s, 3H), 2.74 – 2.62 (m, 1H), 2.48 – 2.34 (m, 1H), 2.30 – 2.15 (m, 7H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 173.1, 139.5, 135.2, 132.4, 129.2, 118.0, 117.0, 116.2, 52.9, 51.6, 46.3, 43.7, 41.0, 33.1.

HRMS(APCI) m/z calcd. for $C_{19}H_{19}NO_3$ $[M+H]^+$: 310.1438, found: 310.1442.

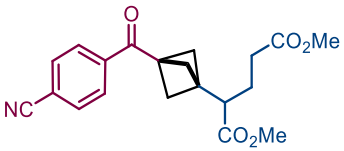


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-4-(methylthio)butanoate (61): The product **61** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a yellow solid (65.7 mg, 94% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 3.70 (s, 3H), 2.80 – 2.70 (m, 1H), 2.55 – 2.38 (m, 2H), 2.26 – 2.14 (m, 6H), 2.07 (s, 3H), 2.02 – 1.94 (m, 1H), 1.74 – 1.64 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 173.1, 139.5, 132.4, 129.2, 118.0, 116.2, 52.8, 51.8, 45.6, 43.5, 41.0, 32.2, 28.2, 15.5.

HRMS(APCI) m/z calcd. for $C_{19}H_{21}NO_3S$ $[M+H]^+$: 344.1315, found: 344.1319.

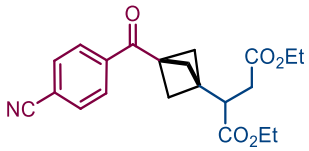


Dimethyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)pentanedioate (62): The product **62** was purified by silica gel column chromatography (DCM/EtOAc = 20:1) as a yellow solid (57.9 mg, 78% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 3.71 (s, 3H), 3.67 (s, 3H), 2.68 – 2.58 (m, 1H), 2.43 – 2.35 (m, 1H), 2.33 – 2.25 (m, 1H), 2.25 – 2.17 (m, 6H), 1.99 – 1.89 (m, 1H), 1.87 – 1.77 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 173.3, 173.0, 139.6, 132.5, 129.3, 118.0, 116.3, 52.8, 51.8, 45.9, 43.6, 41.1, 31.9, 24.0.

HRMS(APCI) m/z calcd. for $C_{20}H_{21}NO_5$ $[M+H]^+$: 356.1492, found: 356.1494.



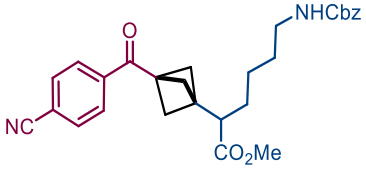
Diethyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)succinate (63): The product

63 was purified by silica gel column chromatography (DCM/EtOAc = 20:1) as a yellow solid (37.2 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 4.23 – 4.12 (m, 4H), 3.13 – 3.03 (m, 1H), 2.78 – 2.69 (m, 1H), 2.47 – 2.38 (m, 1H), 2.20 (s, 6H), 1.29 – 1.23 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 172.0, 171.6, 139.5, 132.5, 129.2, 118.0, 116.3, 61.0, 61.0, 52.8, 43.5, 42.6, 40.5, 33.3, 14.5, 14.3.

HRMS(APCI) m/z calcd. for $C_{21}H_{23}NO_5$ $[M+H]^+$: 370.1649, found: 370.1656.

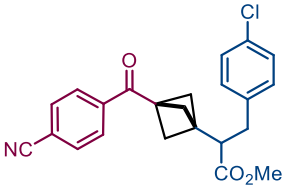


Methyl 6-(((benzyloxy)carbonyl)amino)-2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)hexanoate (64): The product **64** was purified by silica gel column chromatography (DCM/EtOAc = 20:1) as a white solid (76.1 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.29 – 7.20 (m, 5H), 5.01 (s, 2H), 4.84 (s, 1H), 3.62 (s, 3H), 3.18 – 3.05 (m, 2H), 2.58 – 2.42 (m, 1H), 2.25 – 1.99 (m, 6H), 1.66 – 1.22 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 173.6, 156.4, 139.5, 136.7, 132.4, 129.2, 128.5, 128.1, 118.0, 116.1, 66.6, 52.7, 51.60 46.6, 43.5, 41.0, 40.8, 29.8, 28.5, 24.9.

HRMS(APCI) m/z calcd. for $C_{28}H_{30}N_2O_5$ $[M+H]^+$: 475.2227, found: 475.2232.

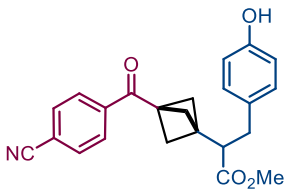


Methyl 3-(4-chlorophenyl)-2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)propanoate (65): The product **65** was purified by silica gel column chromatography (DCM) as a yellow solid (66.8 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 3.61 (s, 3H), 3.01 – 2.88 (m, 2H), 2.82 – 2.69 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 172.7, 139.4, 137.3, 132.4, 132.3, 130.1, 129.2, 128.7, 118.0, 116.2, 52.8, 51.7, 48.4, 43.6, 41.0, 34.3.

HRMS(APCI) m/z calcd. for $C_{23}H_{20}ClNO_3$ $[M+H]^+$: 394.1204 and 396.1175, found: 394.1206 and 396.1186.

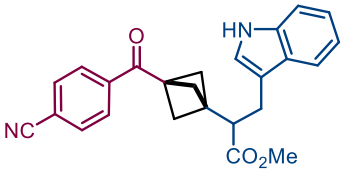


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-(4-hydroxyphenyl)propanoate (66): The product **66** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 4:1) as a white solid (67.5 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.73 (d, *J* = 8.4 Hz, 2H), 6.16 (s, 1H), 3.62 (s, 3H), 2.98 – 2.83 (m, 2H), 2.78 – 2.68 (m, 1H), 2.21 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 173.6, 154.7, 139.5, 132.5, 130.4, 129.8, 129.3, 118.0, 116.2, 115.5, 52.9, 51.8, 48.8, 43.7, 41.0, 34.1.

HRMS(APCI) m/z calcd. for $C_{23}H_{21}NO_4$ $[M+H]^+$: 376.1543, found: 376.1549.

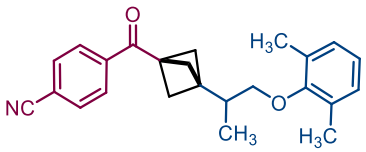


Methyl 2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-(1H-indol-3-yl)propanoate (67): The product **67** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a yellow solid (60.8 mg, 77% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 8.03 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.99 (s, 1H), 3.63 (s, 3H), 3.24 – 3.06 (m, 2H), 3.02 – 2.91 (m, 1H), 2.27 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 173.6, 139.5, 136.3, 132.5, 129.3, 127.2, 122.1, 119.4, 118.6, 118.0, 116.2, 113.1, 111.3, 52.9, 51.7, 47.5, 43.6, 41.2, 24.6.

HRMS(APCI) m/z calcd. for $C_{25}H_{22}N_2O_3$ $[M+H]^+$: 399.1703, found: 399.1694.



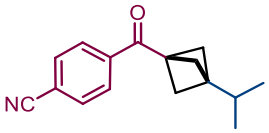
4-(3-(1-(2,6-dimethylphenoxy)propan-2-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (68): The product **68** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow solid (24.4 mg, 34% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 7.4 Hz, 2H), 6.97 – 6.87 (m, 1H), 3.75 (dd, J = 8.9, 5.8 Hz, 1H), 3.58 – 3.49 (m, 1H), 2.29

(s, 6H), 2.24 (s, 7H), 1.11 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 156.1, 139.8, 132.4, 130.9, 129.3, 129.0, 124.0, 118.1, 116.1, 74.7, 52.2, 43.9, 43.1, 34.8, 16.6, 14.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{25}NO_2$ $[M+H]^+$: 360.1958, found: 360.1966.

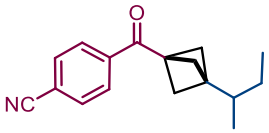


4-(3-isopropylbicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (69): The product **69** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow solid (22.3 mg, 46% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.74 (d, *J* = 8.4 Hz, 2H), 2.08 (s, 6H), 1.82 – 1.70 (m, 1H), 0.88 (d, *J* = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 195.8, 140.0, 132.4, 129.3, 118.2, 116.1, 51.1, 45.9, 43.2, 28.4, 18.7.

HRMS(APCI) m/z calcd. for $C_{16}H_{17}NO$ $[M+H]^+$: 240.1383, found: 240.1391.

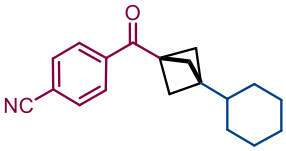


4-(3-(*sec*-butyl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (70): The product **70** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow solid (35.1 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 2.09 (s, 6H), 1.52 – 1.41 (m, 2H), 1.09 – 0.97 (m, 1H), 0.90 (t, *J* = 7.1 Hz, 3H), 0.84 (d, *J* = 6.7 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 139.9, 132.4, 129.3, 118.1, 116.0, 77.5, 77.2, 76.8, 51.6, 45.5, 43.5, 35.0, 26.0, 15.4, 12.2.

HRMS(APCI) m/z calcd. for $C_{17}H_{19}NO$ $[M+H]^+$: 254.1539, found: 254.1554.



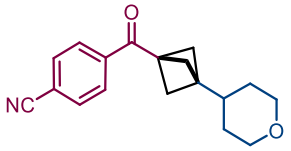
4-(3-cyclohexylbicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (71): The product **71** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow solid (23.3 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 2.08 (s, 6H), 1.75 (d, *J* = 13.0 Hz, 2H), 1.70 – 1.63 (m, 3H), 1.42 – 1.34 (m, 1H), 1.25 – 1.03 (m, 3H),

0.95 – 0.86 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 140.0, 132.4, 129.3, 118.2, 116.1, 51.4, 45.0, 43.5, 37.8, 29.2, 26.3, 26.1.

HRMS(APCI) m/z calcd. for $C_{19}H_{21}NO$ $[M+H]^+$: 280.1696, found: 280.1696.

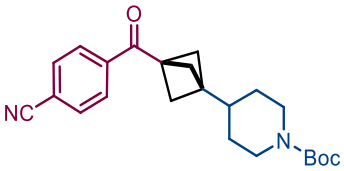


4-(3-(tetrahydro-2*H*-pyran-4-yl)bicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (72): The product **72** was purified by silica gel column chromatography (DCM/EtOAc = 50:1) as a yellow solid (51.3 mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 4.07 – 3.94 (m, 2H), 3.38 (t, *J* = 12.7 Hz, 2H), 2.12 (s, 6H), 1.72 – 1.64 (m, 1H), 1.37 – 1.24 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 139.8, 132.5, 129.3, 118.1, 116.2, 67.8, 51.2, 44.1, 43.6, 35.3, 29.0.

HRMS(APCI) m/z calcd. for $C_{18}H_{19}NO_2$ $[M+H]^+$: 282.1489, found: 282.1489.

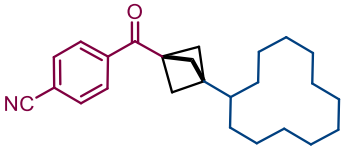


***Tert*-butyl 4-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)piperidine-1-carboxylate (73):** The product **73** was purified by silica gel column chromatography (DCM:EtOAc = 50:1) as a yellow solid (55.9 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 4.23 – 4.04 (m, 2H), 2.64 (t, *J* = 12.0 Hz, 2H), 2.09 (s, 6H), 1.61 – 1.55 (m, 2H), 1.43 (s, 9H), 1.28 – 1.21 (m, 1H), 1.15 – 1.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 154.9, 139.7, 132.4, 129.2, 118.0, 116.1, 79.5, 51.3, 44.0, 43.5, 36.3, 28.5, 28.2.

HRMS(APCI) m/z calcd. for $C_{23}H_{28}N_2O_3$ $[M+H]^+$: 381.2173, found: 381.2177.

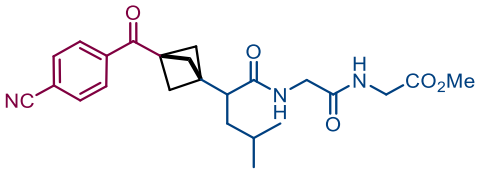


4-(3-cyclododecylbicyclo[1.1.1]pentane-1-carbonyl)benzonitrile (74): The product **74** was purified by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a yellow solid (27.2 mg, 37% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 2.12 (s, 6H), 1.64 – 1.58 (m, 1H), 1.43 – 1.24 (m, 22H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 140.0, 132.4, 129.3, 118.2, 116.1, 52.2, 45.3, 44.0, 33.7, 26.9, 24.3, 24.0, 23.9, 23.4, 23.2.

HRMS(APCI) m/z calcd. for $C_{25}H_{33}NO$ $[M+H]^+$: 364.2635, found: 364.2643.

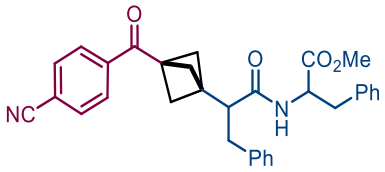


Methyl (2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-4-methylpentanoyl)glycylglycinate (75): The product **75** was purified by silica gel column chromatography (DCM/EtOAc = 2:1) as a yellow solid (53.1 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.15 (s, 1H), 6.76 (s, 1H), 4.10 – 3.94 (m, 4H), 3.71 (s, 3H), 2.50 (d, *J* = 10.4, 3.0 Hz, 1H), 2.17 (s, 6H), 1.73 – 1.63 (m, 1H), 1.57 – 1.45 (m, 1H), 1.20 – 1.13 (m, 1H), 0.87 (t, *J* = 5.6 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 173.5, 170.0, 169.5, 139.6, 132.4, 129.3, 118.1, 116.1, 52.6, 52.5, 46.0, 43.5, 43.1, 41.7, 41.3, 37.8, 26.2, 23.5, 22.0.

HRMS(APCI) m/z calcd. for $C_{24}H_{29}N_3O_5$ $[M+H]^+$: 440.2180, found: 440.2173.

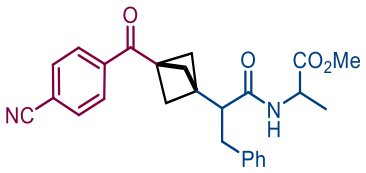


Methyl (2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoyl)phenylalaninate (76): The product **76** was purified by silica gel column chromatography (DCM/EtOAc = 30:1) as a yellow solid (86.0 mg, 85% yield). d.r. = 1:1.1.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 7.95 (m, 2H), 7.81 – 7.66 (m, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.26 – 7.09 (m, 7H), 7.06 (d, *J* = 7.2 Hz, 1H), 6.55 (d, *J* = 7.1 Hz, 1H), 5.76 – 5.59 (m, 1H), 4.94 – 4.76 (m, 1H), 3.73 – 3.60 (m, 3H), 3.17 – 2.68 (m, 4H), 2.62 – 2.53 (m, 1H), 2.35 – 1.95 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 196.1, 171.8, 171.8, 171.4, 170.8, 139.5, 139.4, 139.0, 136.1, 135.4, 132.5, 129.3, 129.3, 129.3, 129.2, 128.8, 128.7, 128.7, 128.6, 127.2, 127.1, 126.7, 126.6, 118.1, 116.3, 116.2, 53.0, 52.7, 52.7, 52.6, 52.5, 52.4, 51.0, 50.2, 43.7, 43.6, 41.4, 41.3, 38.2, 37.9, 35.2, 35.1.

HRMS(APCI) m/z calcd. for $C_{32}H_{30}N_2O_4$ $[M+H]^+$: 507.2278, found: 507.2269.

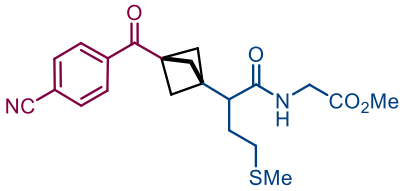


Methyl (2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-3-phenylpropanoyl)alaninate (77): The product **77** was purified by silica gel column chromatography (DCM/EtOAc = 20:1) as a yellow solid (75.2 mg, 87% yield). d.r. = 1:1.2.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.2, 6.6 Hz, 2H), 7.74 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.22 – 7.15 (m, 3H), 5.93 (dd, *J* = 72.4, 7.3 Hz, 1H), 4.61 – 4.43 (m, 1H), 3.70 (d, *J* = 10.3 Hz, 2H), 3.10 – 2.92 (m, 1H), 2.83 – 2.56 (m, 2H), 2.25 (d, *J* = 14.8 Hz, 6H), 1.27 (dd, *J* = 78.0, 7.1 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 196.1, 173.4, 173.2, 171.1, 171.0, 139.5, 139.5, 139.2, 139.1, 132.4, 132.4, 129.3, 129.3, 128.9, 128.8, 128.5, 128.5, 126.5, 118.0, 118.0, 116.2, 116.1, 52.8, 52.7, 52.5, 50.3, 49.9, 48.0, 47.7, 43.8, 43.7, 41.5, 41.4, 35.2, 34.9, 18.8, 18.3.

HRMS(APCI) m/z calcd. for $C_{26}H_{26}N_2O_4$ $[M+H]^+$: 431.1965, found: 431.1956.

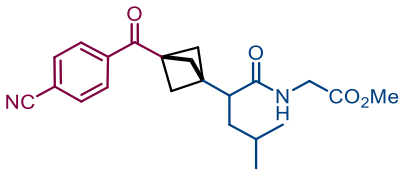


Methyl (2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-4-(methylthio)butanoyl)glycinate (78): The product **78** was purified by silica gel column chromatography (DCM/EtOAc = 10:1) as a yellow solid (67.7mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.72 (d, *J* = 8.3 Hz, 2H), 6.15 (t, *J* = 5.3 Hz, 1H), 4.12 – 3.97 (m, 2H), 3.74 (s, 3H), 2.65 – 2.54 (m, 2H), 2.49 – 2.38 (m, 1H), 2.22 (s, 6H), 2.08 – 1.98 (m, 4H), 1.72 – 1.61 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 172.2, 170.3, 139.5, 132.4, 129.3, 118.0, 116.2, 52.7, 52.5, 46.3, 43.6, 41.3, 41.11 32.0, 27.8, 15.3.

HRMS(APCI) m/z calcd. for $C_{21}H_{24}N_2O_4S$ $[M+H]^+$: 401.1530, found: 401.1533.



Methyl (2-(3-(4-cyanobenzoyl)bicyclo[1.1.1]pentan-1-yl)-4-methylpentanoyl)glycinate (79): The product **79** was purified by silica gel column

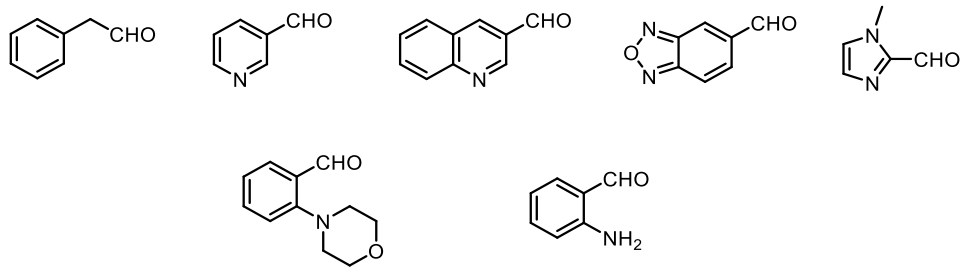
chromatography (DCM/EtOAc = 10:1) as a yellow solid (56.6mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.58 – 7.37 (m, 1H), 5.97 (t, *J* = 5.0 Hz, 1H), 4.11 (dd, *J* = 18.4, 5.4 Hz, 1H), 4.02 (dd, *J* = 18.3, 5.1 Hz, 1H), 3.76 (s, 3H), 2.45 (dd, *J* = 10.7, 3.9 Hz, 1H), 2.21 (s, 6H), 1.74 – 1.66 (m, 1H), 1.21 – 1.16 (m, 1H), 0.90 (t, *J* = 6.9 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 172.8, 170.6, 139.6, 132.5, 129.3, 118.1, 116.2, 77.5, 77.2, 76.8, 52.6, 52.5, 46.3, 43.6, 41.7, 41.1, 37.8, 26.2, 23.5, 22.0.

HRMS(APCI) m/z calcd. for $C_{22}H_{26}N_2O_4$ $[M+H]^+$: 383.1965, found: 383.1959.

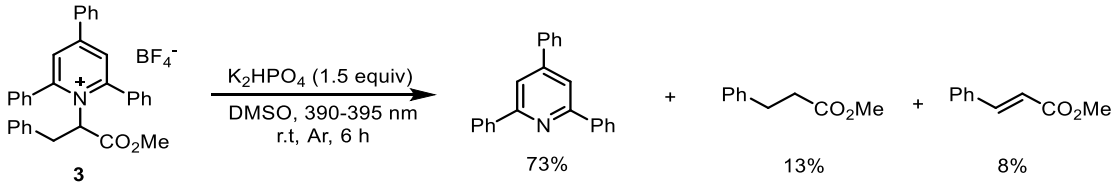
4.3 Limitations of the reaction



5. Mechanistic Investigations.

5.1 Free radical trapping experiment

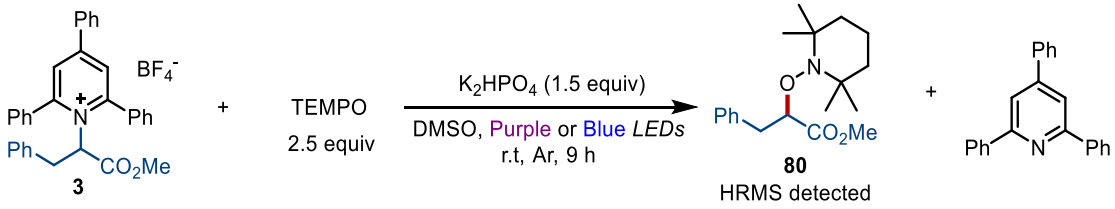
Light-induced homolysis of Katritzky salts



To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol). The mixture was evacuated and backfilled with Ar for 3 times, then DMSO (4.0 mL) were added via a syringe. The reaction mixture was placed in a photoparallel reactor. The mixture was stirred and irradiated for 6 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography. The 2,4,6-triphenylpyridine was obtained by silica gel column chromatography (Petroleum ether/EtOAc = 100:1) as a white solid (44.4

mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.6 Hz, 4H), 7.91 (s, 2H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.58-7.43 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 150.3, 139.7, 139.2, 129.2, 129.1, 129.0, 128.8, 127.3, 127.2, 117.2. The methyl 3-phenylpropanoate (13%) and methyl cinnamate (8%) were isolated as a mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 0.6H), 7.46 (dd, *J* = 6.3, 2.7 Hz, 1.2H), 7.34 – 7.29 (m, 2H), 7.23 – 7.17 (m, 2H), 7.13 (t, *J* = 6.2 Hz, 2.6H), 6.37 (d, *J* = 16.0 Hz, 0.6H), 3.74 (s, 1.8H), 3.60 (s, 3H), 2.88 (t, *J* = 7.8 Hz, 2H), 2.56 (t, *J* = 7.8 Hz, 2H). And unconverted Katritzky salt **3** was obtained by silica gel column chromatography (DCM/ Acetone = 10:1) as a white solid (16.7 mg, 15% yield).

TEMPO-trapping experiment



To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol) and 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (0.5 mmol, 2.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then DMSO (4.0 mL) were added via a syringe. The reaction mixture was placed in a photoparallel reactor (390-395 nm or 460-465 nm). The mixture was stirred and irradiated for 9 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The corresponding product of radical trapping (**80**) was detected by HRMS.

HRMS (ESI-TOF) m/z calcd. for $C_{19}H_{29}NO_3$ $[M+Na]^+$: 342.2045, found: 342.2045.

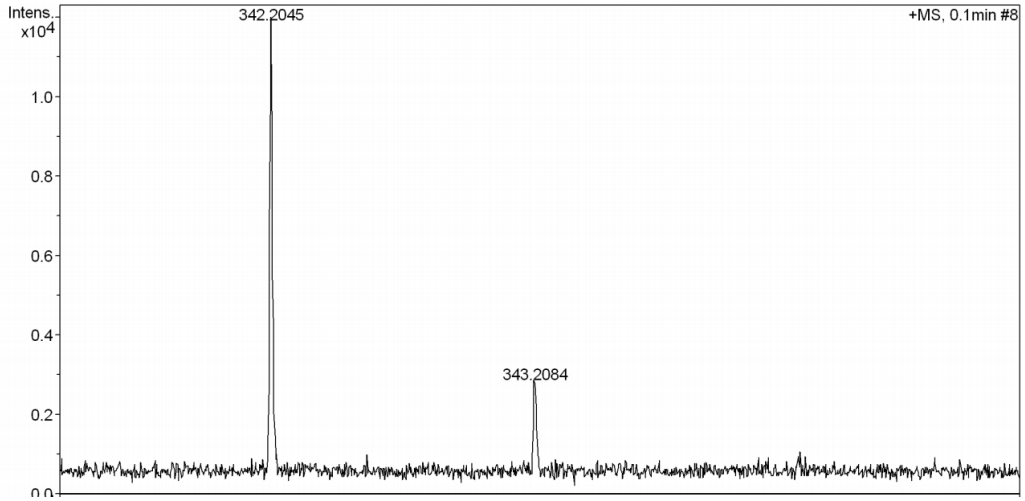
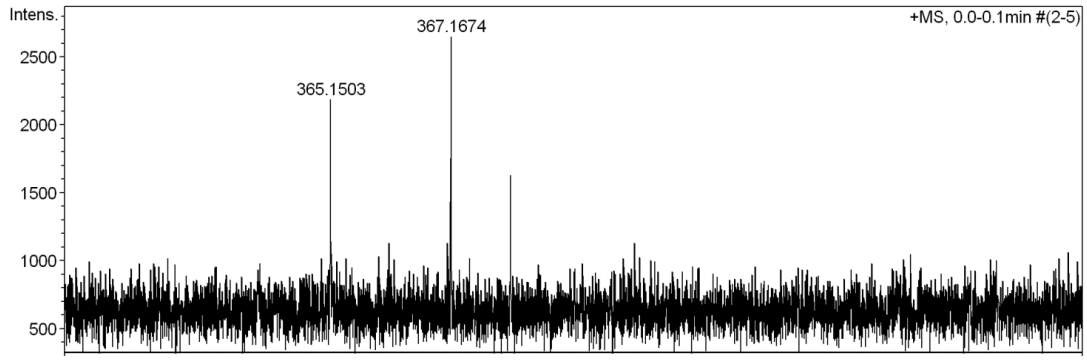


Figure S3. HRMS spectra of **80**

1,1-Diphenylethylene-trapping experiment

To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol). The mixture was evacuated and backfilled with Ar for 3 times, then 1,1-diphenylethylene (0.5 mmol, 2.5 equiv) and DMSO (4.0 mL) were added via a syringe, respectively. The reaction mixture was placed in a photoparallel reactor (390-395 nm or 460-465 nm). The reaction mixture was then stirred and irradiated for 9 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography. The corresponding product of radical trapping (**81**) was obtained by silica gel column chromatography (Petroleum ether/EtOAc = 50:1) as a colourless oil (11.6 mg, 17% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26-7.20 (m, 3H), 7.19-7.06 (m, 8H), 6.93 (d, *J* = 6.5 Hz, 2H), 6.86-6.73 (m, 2H), 6.02 (d, *J* = 10.4 Hz, 1H), 3.57 (s, 3H), 3.45-3.30 (m, 1H), 3.10-2.94 (m, 1H), 2.86-2.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.2, 144.6, 141.7, 139.1, 138.4, 129.6, 129.2, 128.3, 128.2, 128.1, 127.5, 127.3, 127.2, 126.4, 125.6, 51.9, 48.1, 39.3.

HRMS (ESI-TOF) m/z calcd. for $C_{24}H_{24}O_2$ [M+Na]$^+$: 367.1674, found: 367.1674.



HRMS (ESI-TOF) m/z calcd. for $C_{24}H_{22}O_2$ [M+Na]$^+$: 365.1517, found: 365.1512.

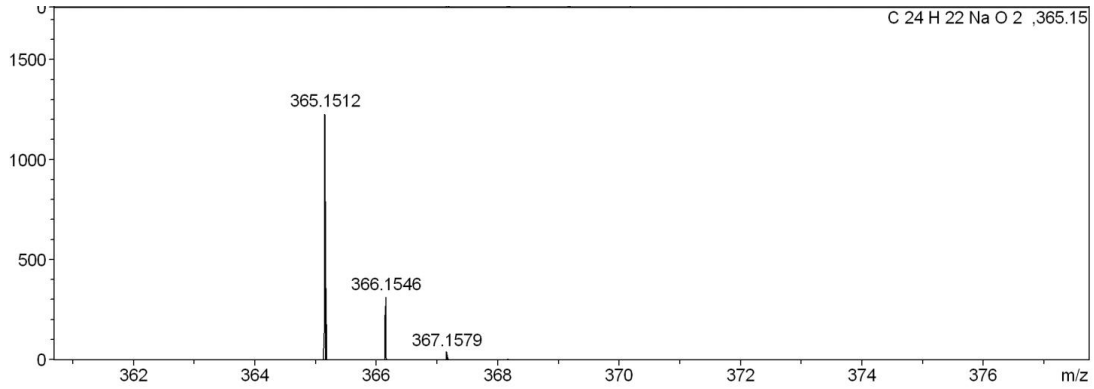
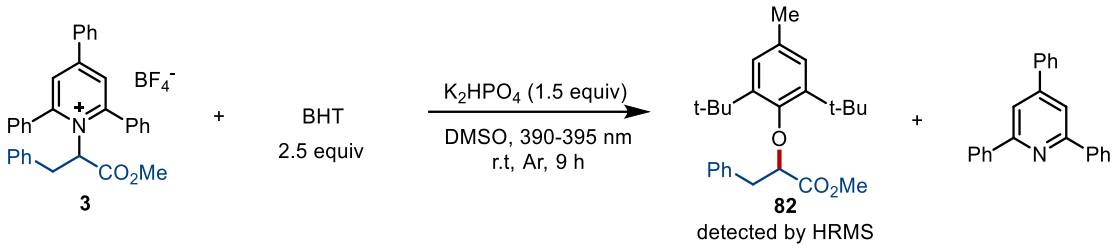


Figure S4. HRMS spectra of **80** and **81**

BHT-trapping experiment



To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol) and butylated hydroxytoluene (BHT) (0.5 mmol, 2.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then DMSO (4.0 mL) were added via a syringe. The reaction mixture was placed in a photoparallel reactor. The reaction mixture was then stirred and irradiated for 9 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The corresponding product of radical trapping

(**82**) was detected by HRMS.

HRMS (ESI-TOF) m/z calcd. for $C_{25}H_{34}O_3$ $[M+Na]^+$: 405.2406, found: 405.2406.

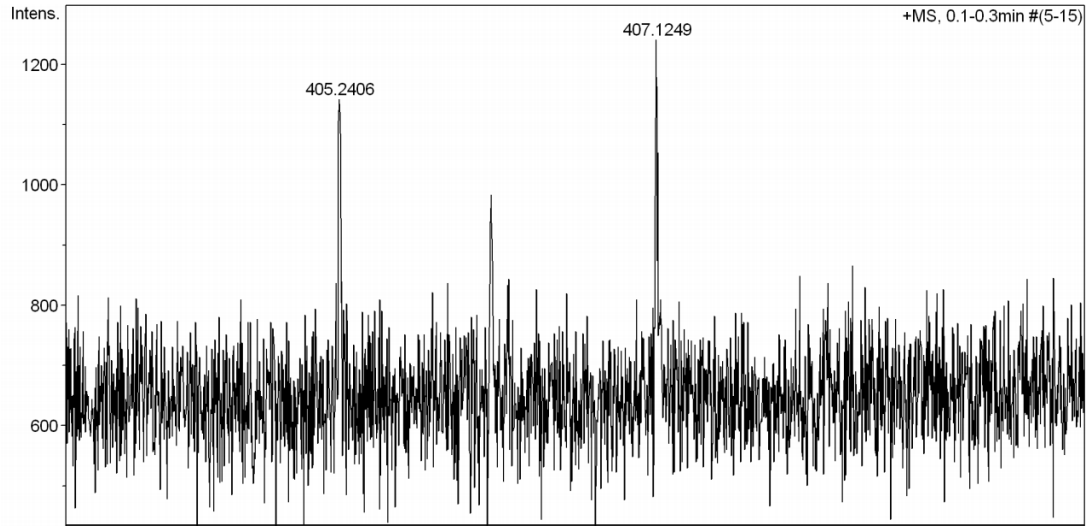
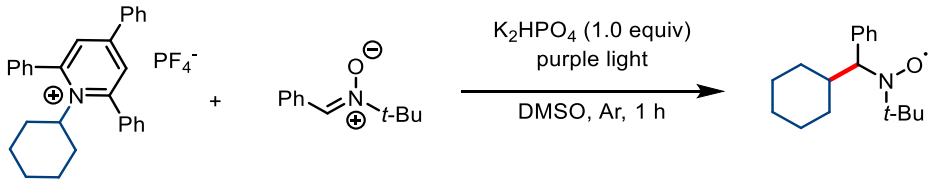


Figure S5. HRMS spectra of **82**

Photoinduced EPR studies



Katritzky salt **PBN** (0.4 equiv) detected by EPR

In a nitrogen-filled glove box, Katritzky salt (0.1 mmol, 49.7 mg), PBN (0.04 mmol, 7.1 mg) were added in an oven-dried 10 mL storage tube with a magnetic stir bar, anhydrous DMSO (2.0 mL) was added subsequently. The tube was sealed with the Teflon screw valve and removed from the glovebox. After the mixture was irradiated with 9 W purple LEDs (390-395 nm) for 1 hour, the tube was moved back to glove box. The reaction solution (approximately 100 uL) was transferred to an oven-dried EPR tube and sealed with a rubber cap, then removed from the glove box. The EPR spectrum was recorded at room temperature.

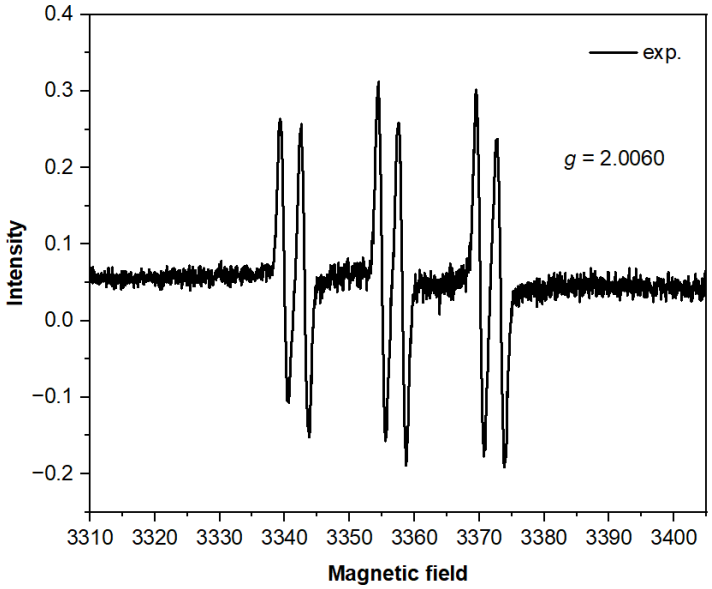
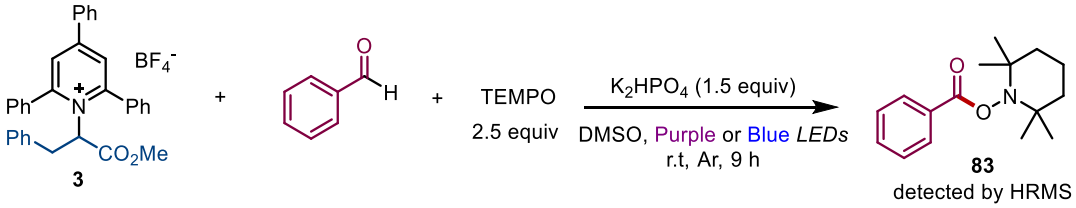


Figure S6. EPR spectrum of carbon radical trapped by PBN

Radical trapping to confirm HAT process between the pyridinium radical cation and aldehyde



To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol) and TEMPO (0.5 mmol, 2.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then benzaldehyde (0.2 mmol) and DMSO (4.0 mL) were added via a syringe. The reaction mixture was placed in a photoparallel reactor (390-395 nm or 460-465 nm). The reaction mixture was then stirred and irradiated for 9 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The corresponding product of radical trapping (**83**) was detected by HRMS.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{25}NO_3$ $[M+H]^+$: 262.1807, found: 262.1808.

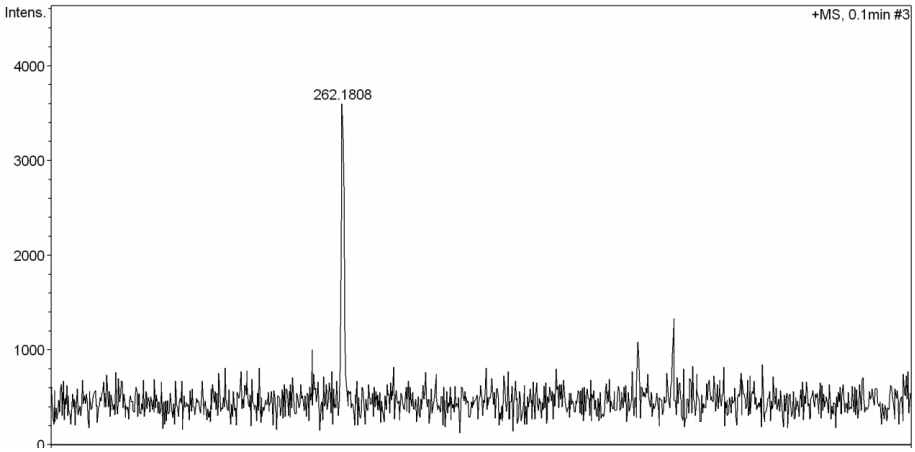
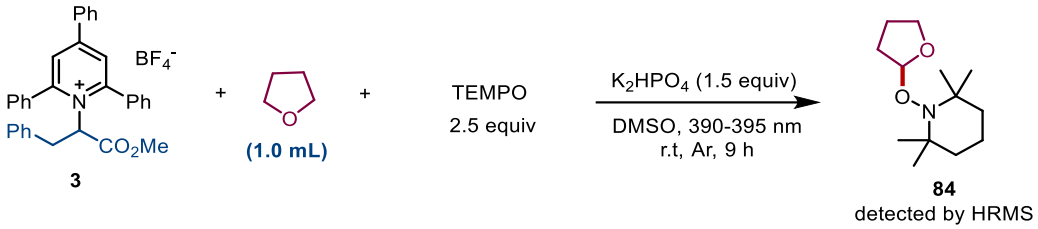


Figure S7. HRMS spectra of **83**

Radical trapping to confirm HAT process between the pyridinium radical cation and THF



To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol) and TEMPO (0.5 mmol, 2.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then DMSO (3.0 mL) and THF (1.0 mL) were added via a syringe. The reaction mixture was placed in a photoparallel reactor. The reaction mixture was then stirred and irradiated for 9 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The corresponding product of radical trapping (**84**) was detected by HRMS.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{25}NO_2$ $[M+H]^+$: 228.1964, found: 228.1966.

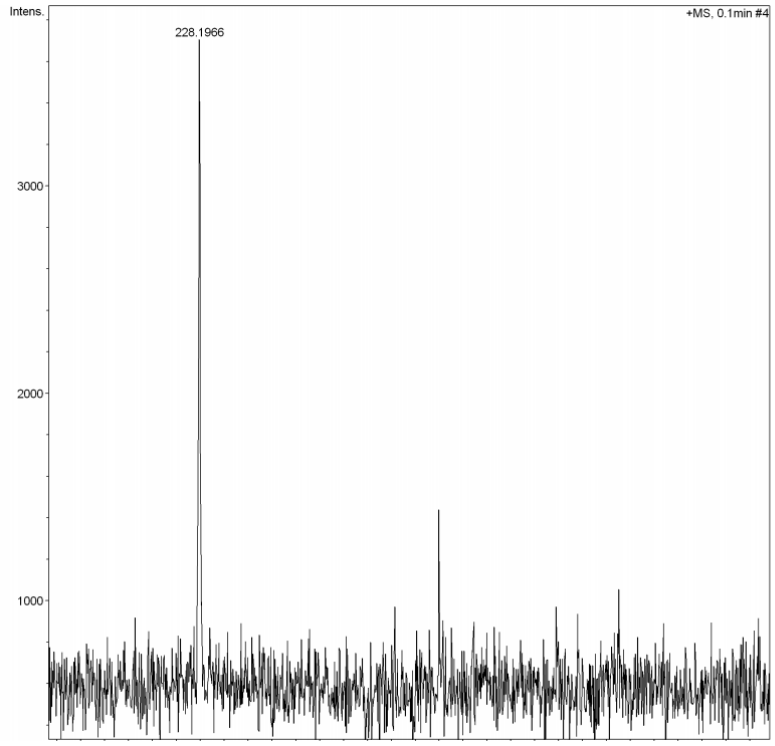


Figure S8. HRMS spectra of **84**

Radical trapping to confirm HAT process between the pyridinium radical cation and 1,4-dioxane

To an oven-dried 10 mL glass storage tube with a stir bar were added K_2HPO_4 (0.3 mmol, 1.5 equiv), Katritzky salt **3** (0.2 mmol) and TEMPO (0.5 mmol, 2.5 equiv). The mixture was evacuated and backfilled with Ar for 3 times, then DMSO (3.0 mL) and 1,4-dioxane (1.0 mL) were added via a syringe. The reaction mixture was placed in a photoparallel reactor. The reaction mixture was then stirred and irradiated for 9 hours. The average temperature of reaction mixture was room temperature without extra heating. The reaction mixture was diluted with EtOAc, and the organic layer was washed with H_2O (3 x 30 mL). The organic layer was dried ($MgSO_4$) and then concentrated under reduced pressure. The corresponding product of radical trapping was detected by HRMS.

HRMS (ESI-TOF) m/z calcd. for $C_{13}H_{25}NO_3$ $[M+H]^+$: 244.1913, found: 244.1905.

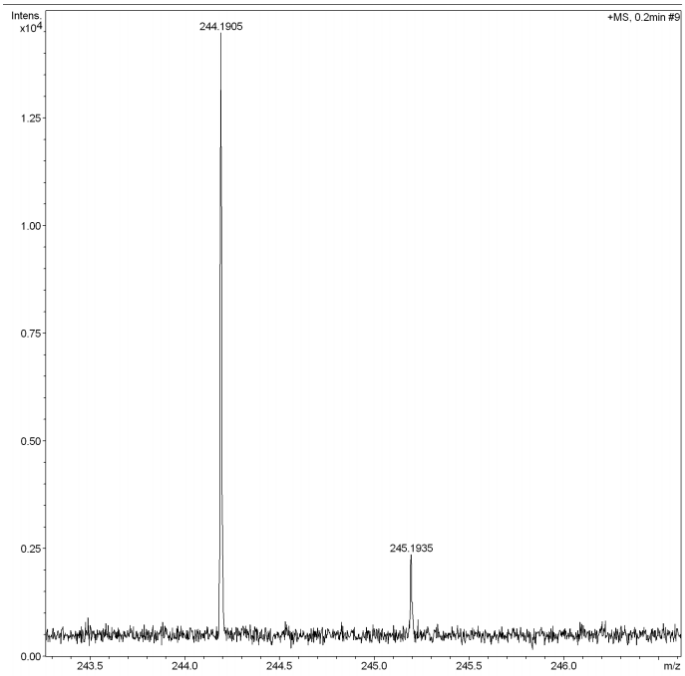
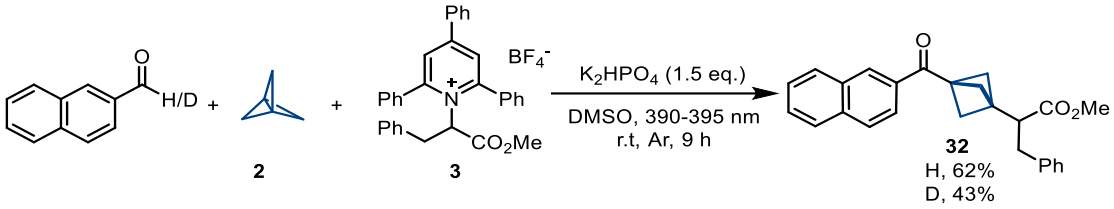


Figure S9. HRMS spectra of **85**

5.2 Experimental comparison of aldehyde and deuterated aldehyde



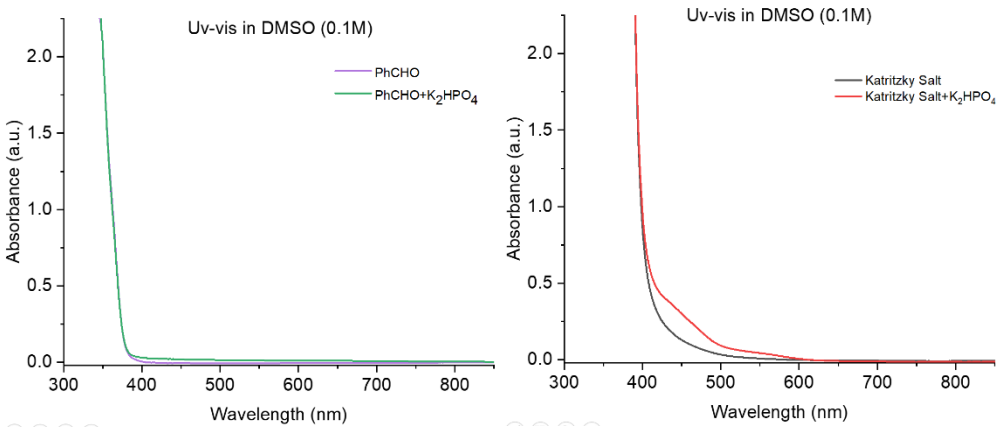
To a 10 mL reaction vial equipped with a magnetic stir bar were added Katritzky salt **3** (0.2 mmol, 2.0 equiv), aldehyde or deuterated aldehyde (0.2 mmol, 2.0 equiv), K_2HPO_4 (0.15 mmol, 1.5 equiv) and the tube was evacuated and backfilled with argon three times. Then [1.1.1]propellane (0.1 mmol, 1.0 equiv, 0.9-1.2 M in Et_2O) and DMSO (2.0 mL) were added under argon atmosphere. The reaction mixture was sealed and placed into the photoparallel reactor, stirred and irradiated 10 W blue LEDs (4390-395 nm) at room temperature for 8 h.The resulting mixture was added 1,3,5-trimethoxybenzene (0.1 mmol) and diluted with 10 mL EtOAc and washed with saturated NaCl (2 × 10 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The reaction yield was determined by ^{1}H NMR.

Deuterated aldehyde was synthesized according to literature procedures.[19]

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.16 (s, 0.09H), 8.34 (s, 11H), 8.05 – 7.85 (m, 4H), 7.69 – 7.52 (m, 2H).

5.3 UV-vis Spectroscopic Analysis.

UV/vis absorption spectra of 0.1 M in 5 mL DMSO solutions of the following freshly prepared sample were recorded in 1.0 cm path quartz cuvettes: (1) PhCHO, PhCHO-K_2HPO_4 (1:1). (2) Katritzky salt **3**, Katritzky salt **3** - K_2HPO_4 (1:1). (3) each species and their mixtures. As K_2HPO_4 could not completely dissolve, the corresponding sample solutions were filtered prior to the measurement.



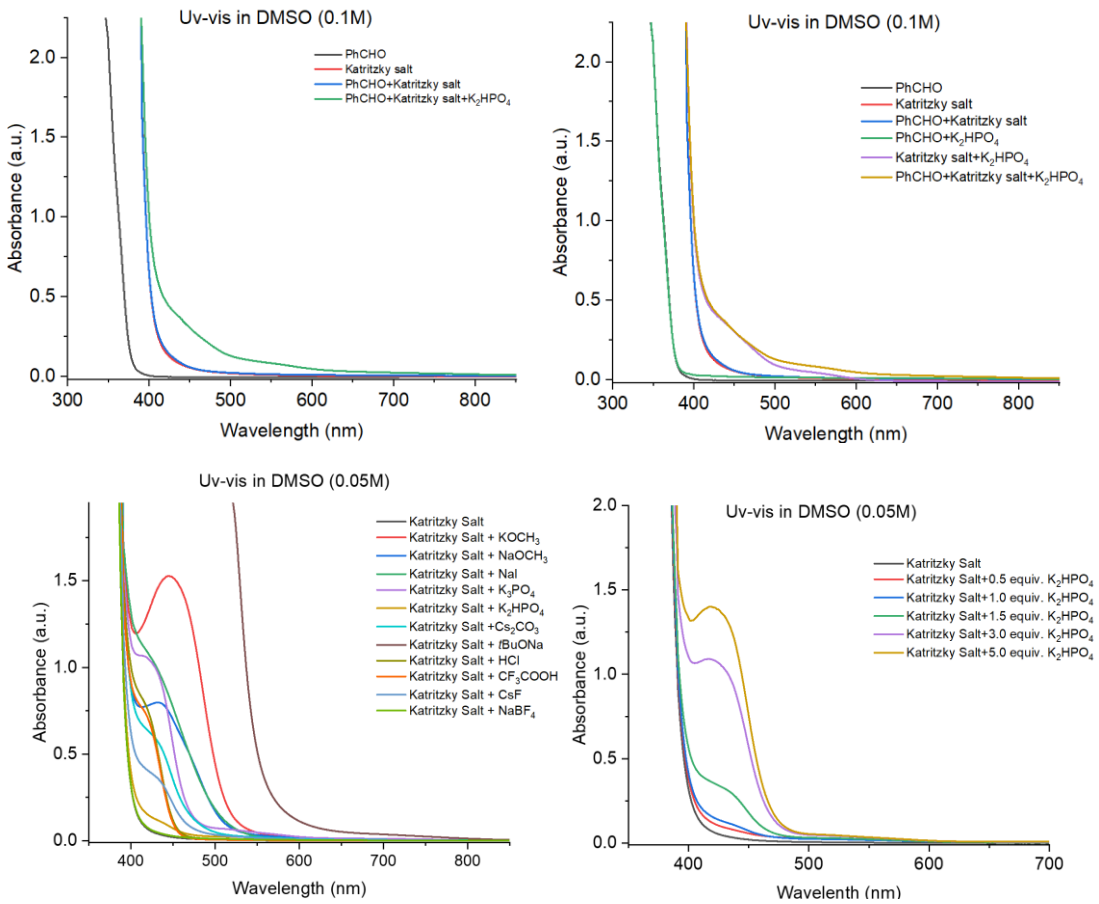


Figure S10. UV−vis absorption spectra of each species and their mixtures

6. References

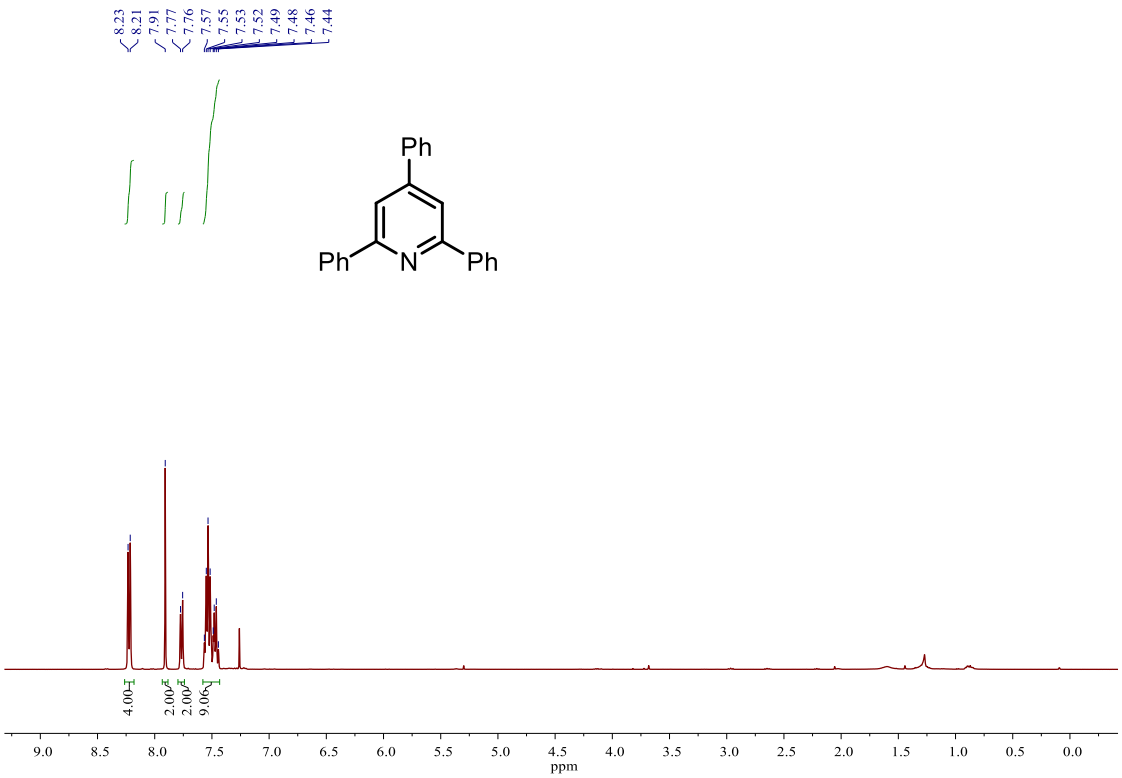
(1) Klauck, F. J. R.; James, M. J.; Glorius, F. *Angew. Chem. Int. Ed.* 2017, **56**, 12336−12339.

(2) Kim, I.; Im, H.; Lee, H.; Hong S. *Chem. Sci.* 2020, **11**, 3192−3197.

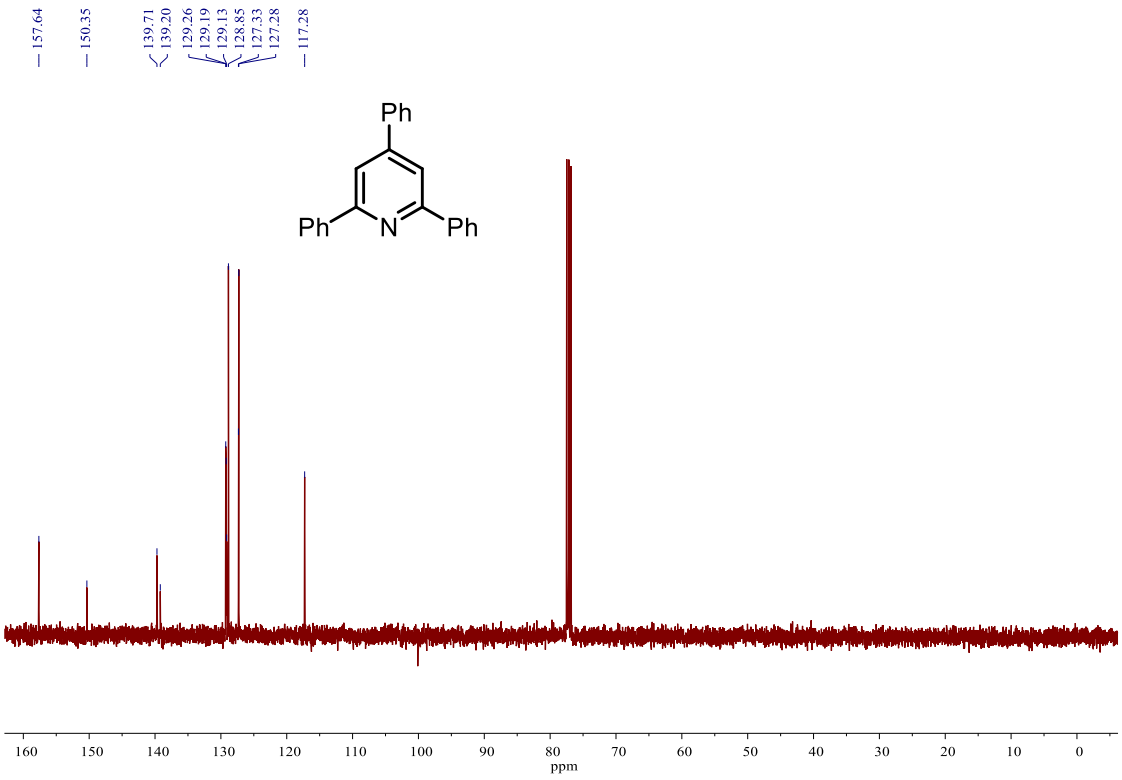
(3) Sun, S.-Z.; Cai, Y.-M.; Zhang, D.-L.; Wang, J.-B.; Yao, H.-Q.; Rui, X.-Y.; Martin, R.; Shang, M. *J. Am. Chem. Soc.* 2022, **144**, 1130−1137.

(4) Hoerrner, M. E.; Baker, K. M.; Basch, C. H.; Bampo, E. M.; Watson, M. P. *Org. Lett.* 2019, **21**, 7356−7360.

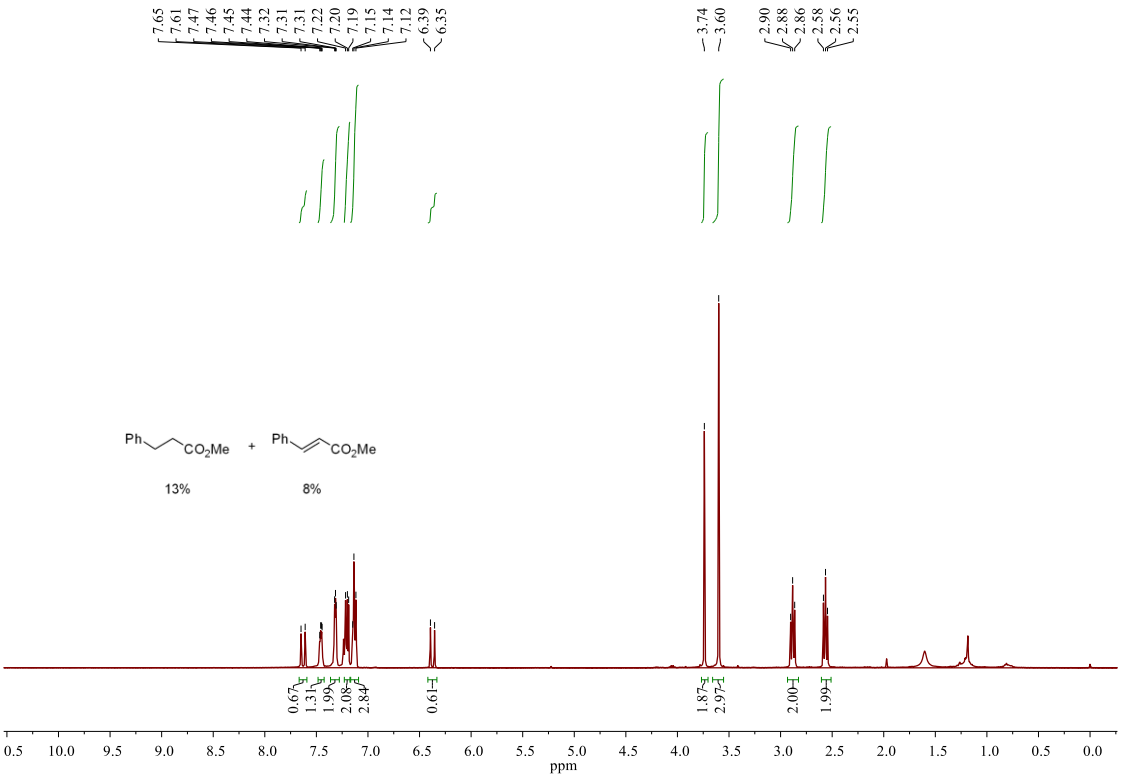
7. Spectra of Synthesized Compounds



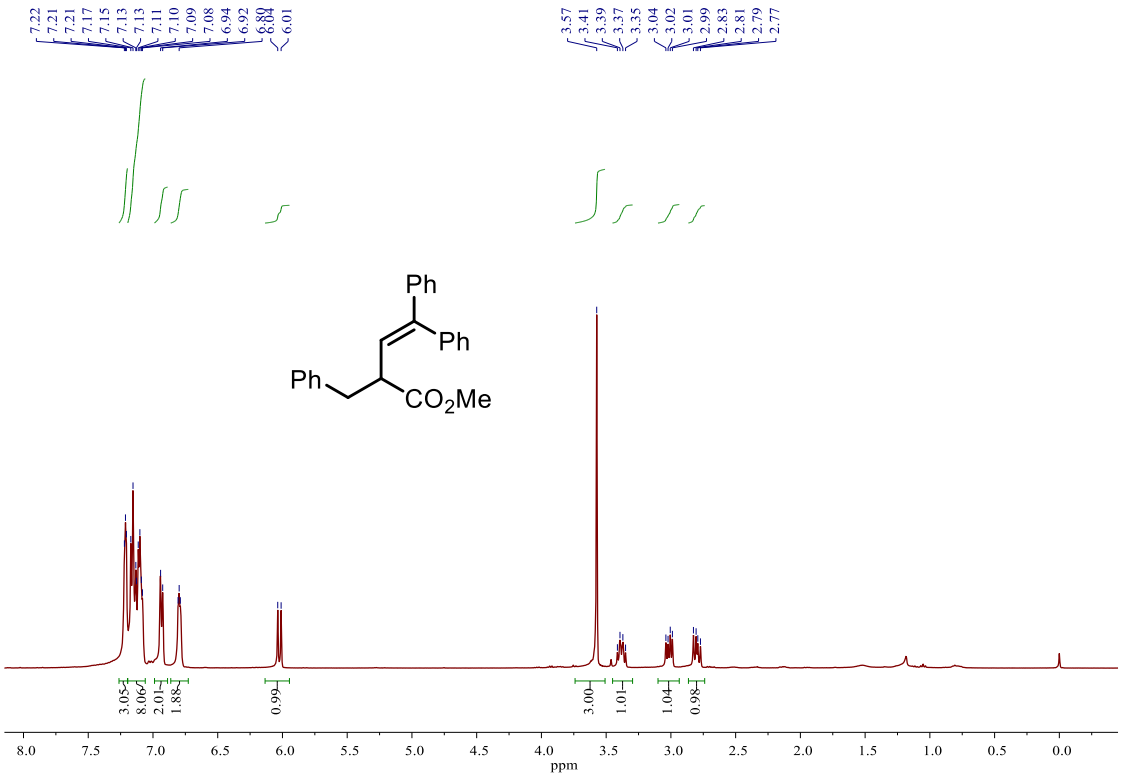
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 2,4,6-triphenylpyridine



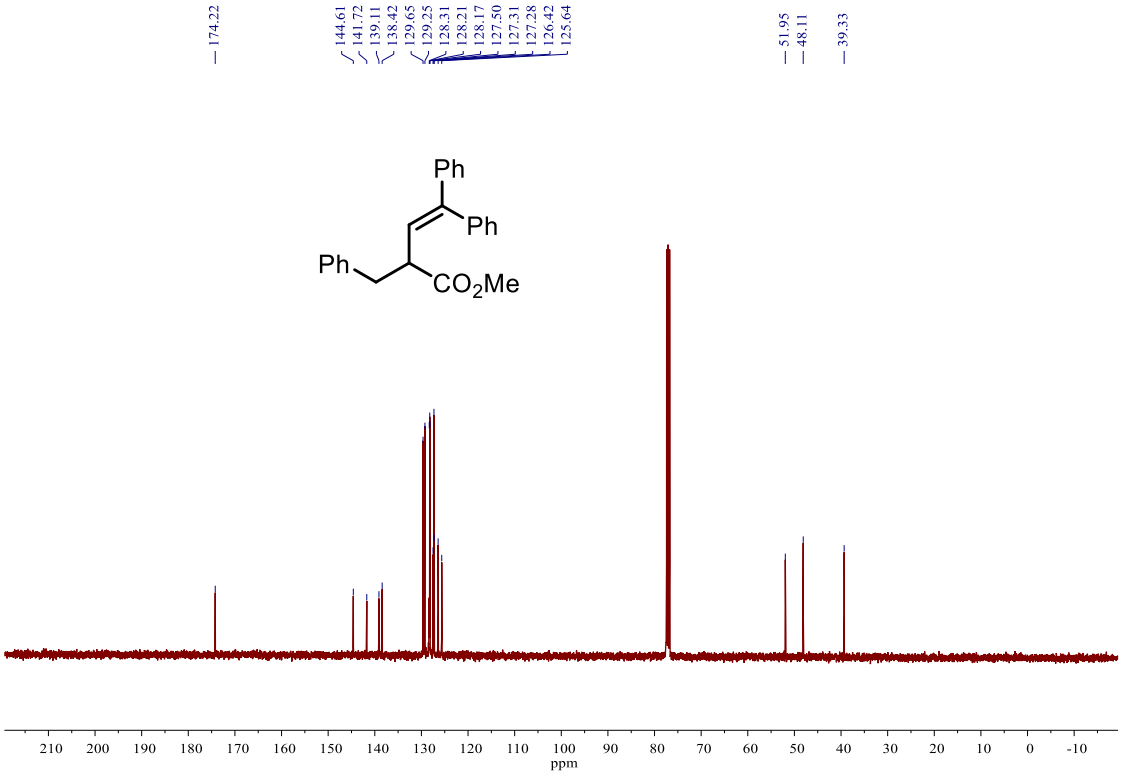
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 2,4,6-triphenylpyridine



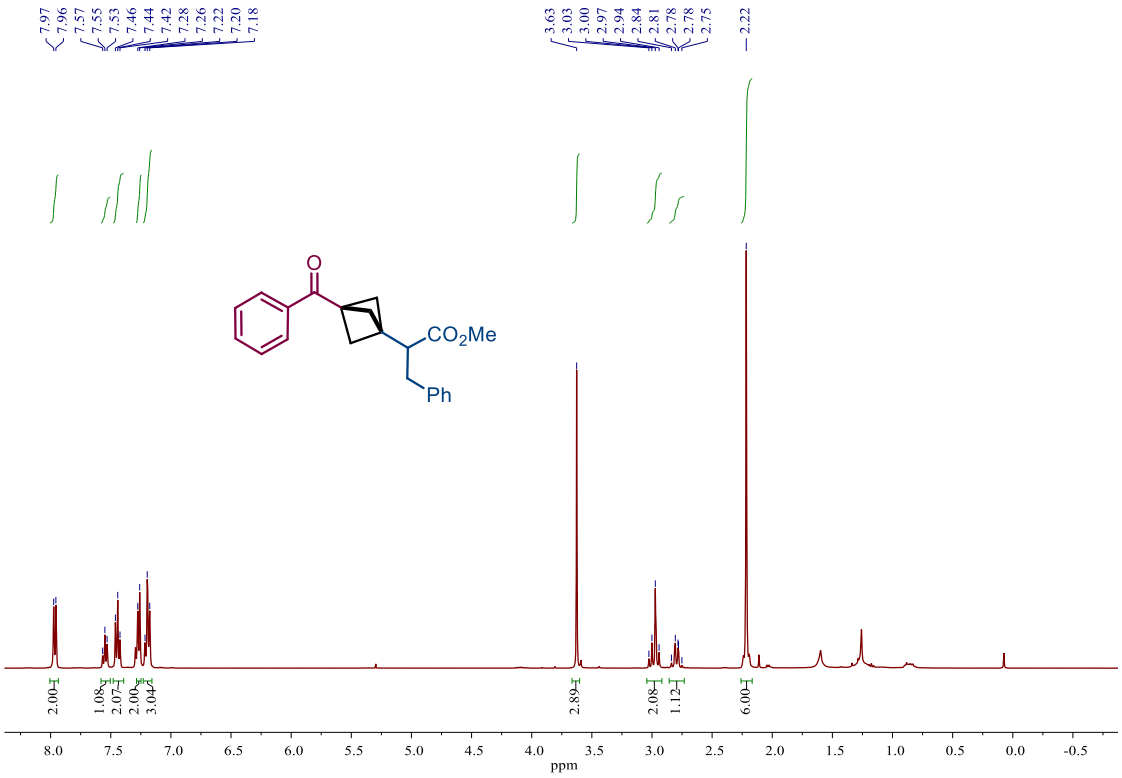
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of mixture of methyl 3-phenylpropanoate and methyl cinnamate



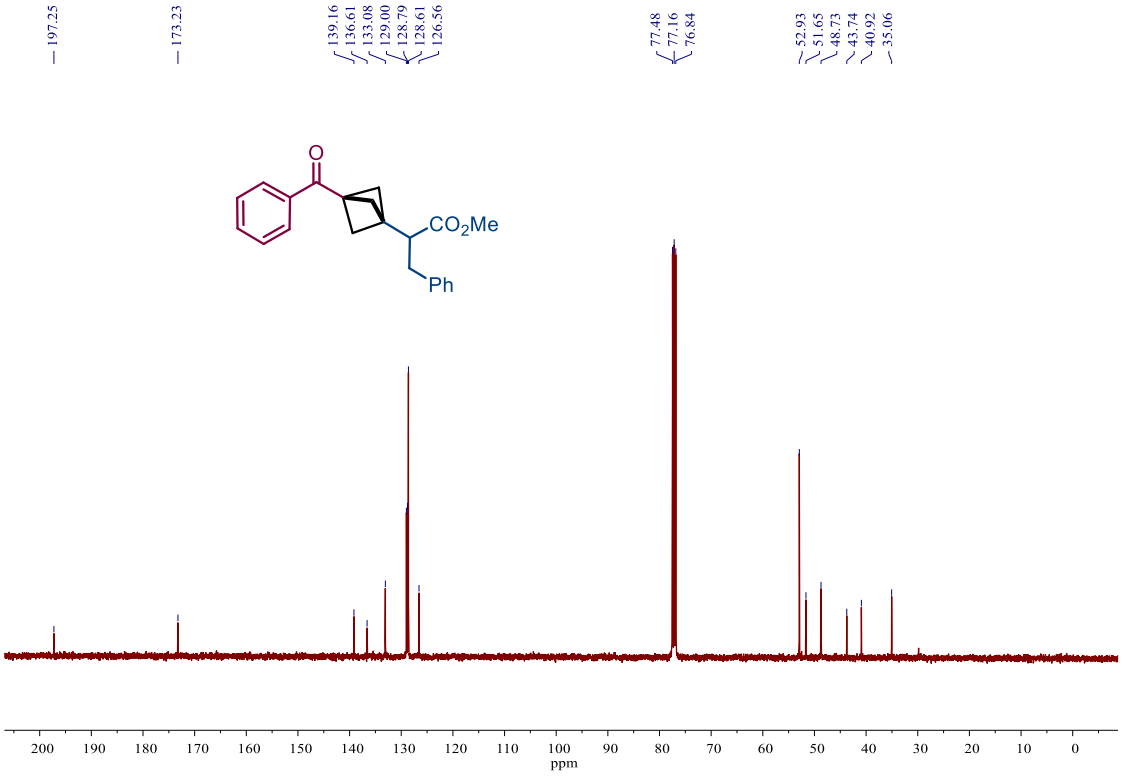
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 81



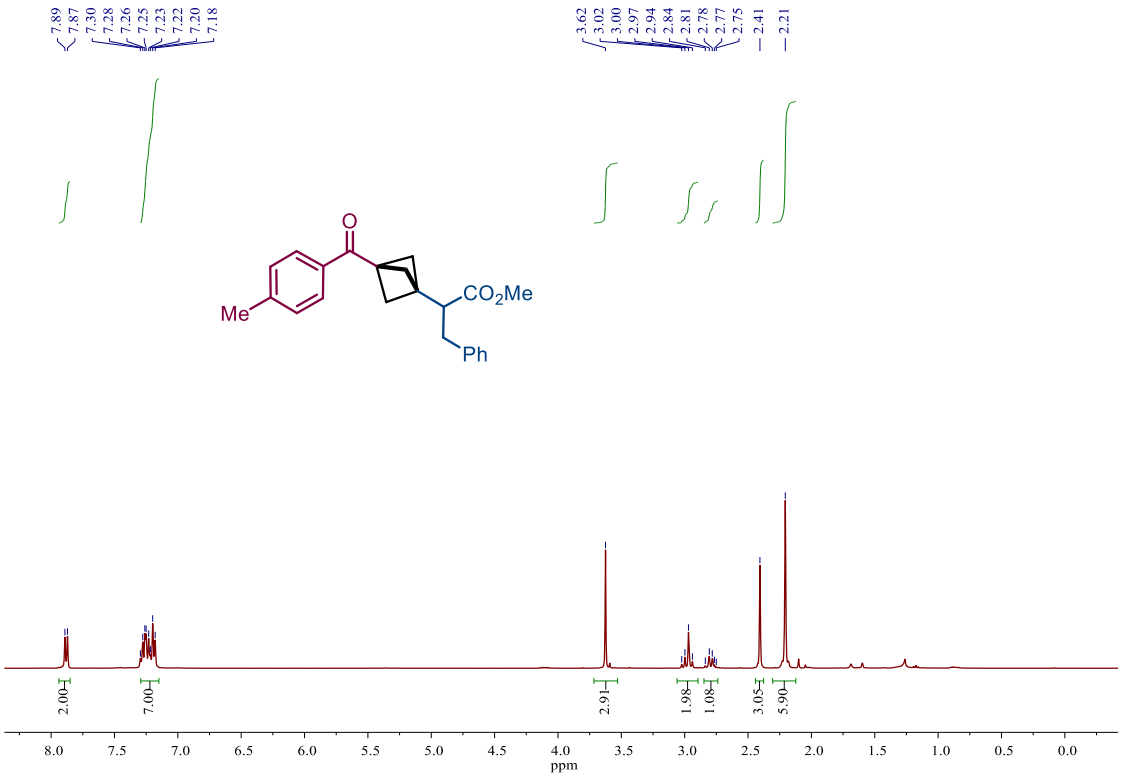
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 81



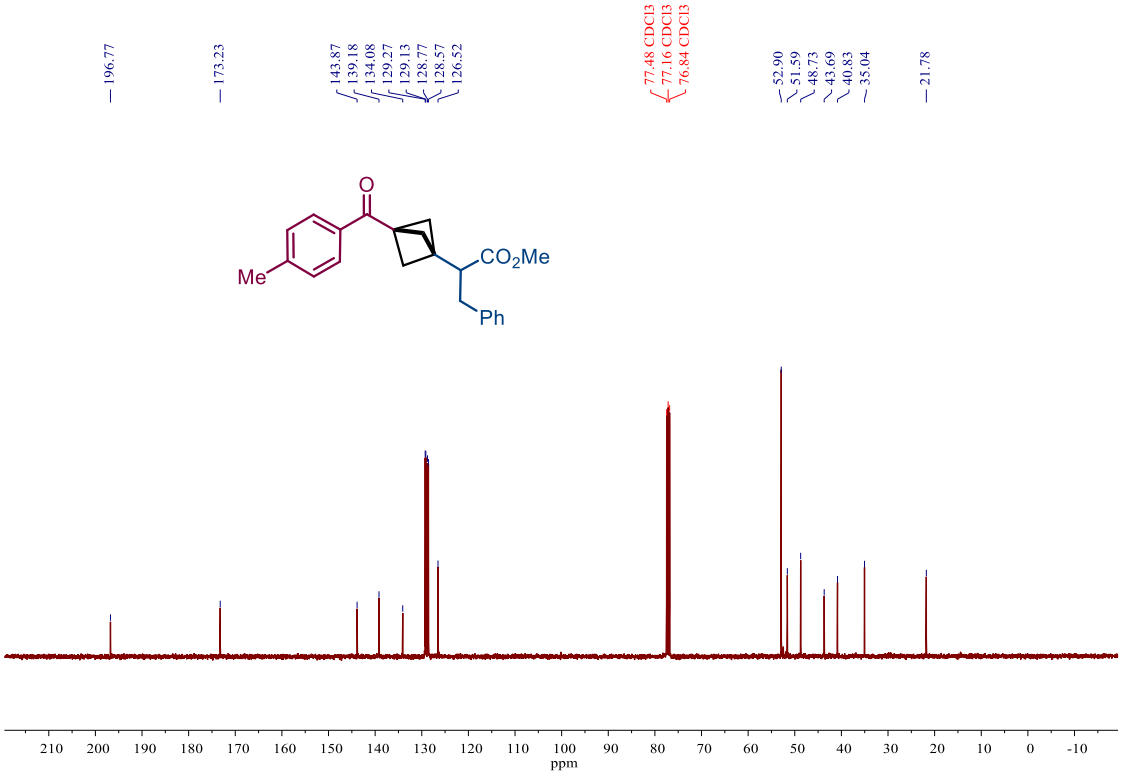
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 5



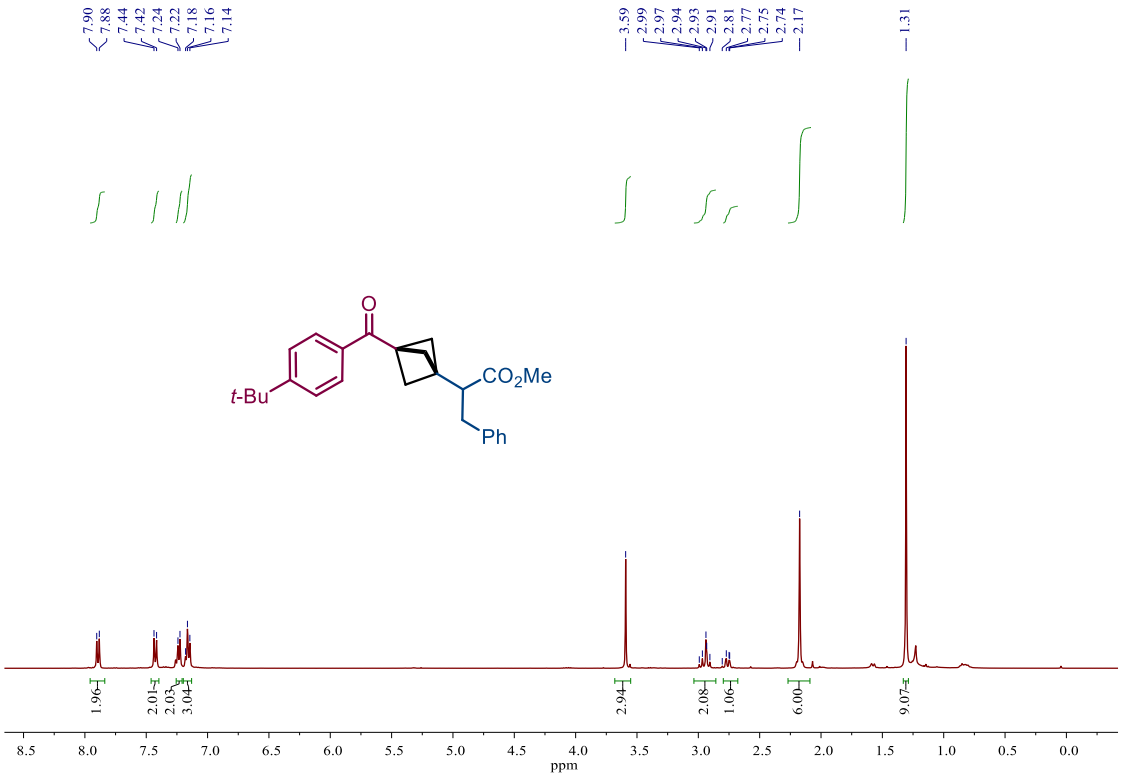
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 5



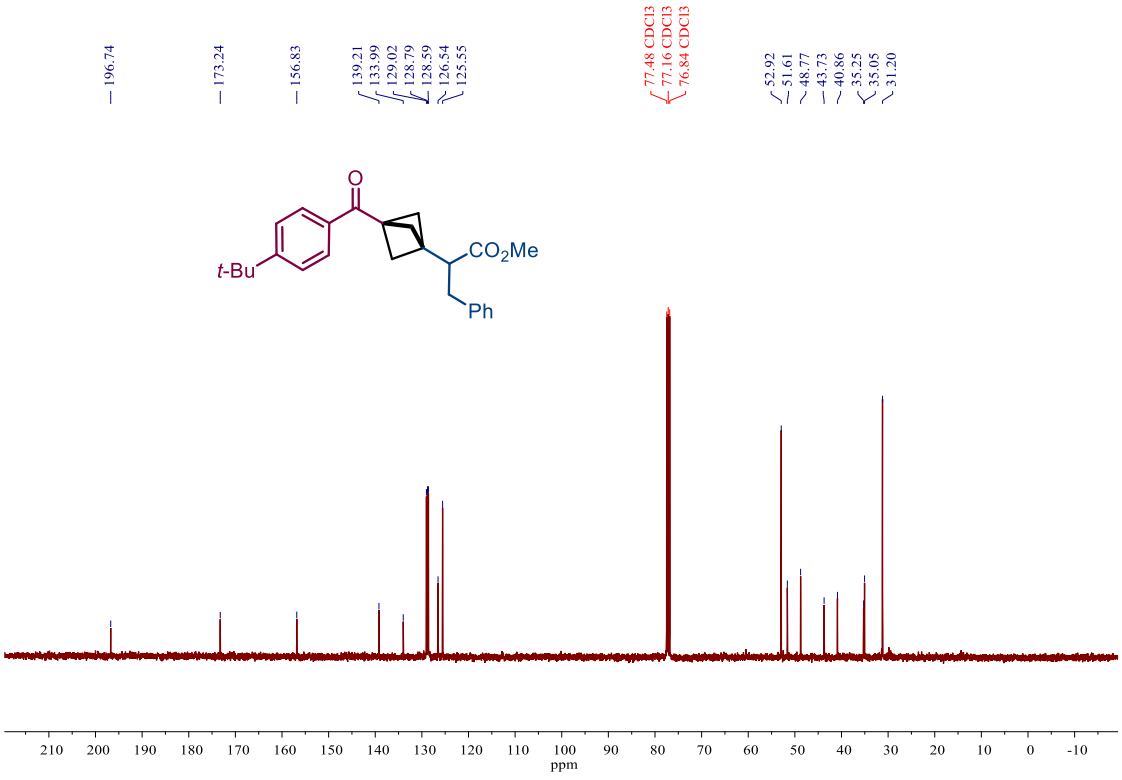
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 6



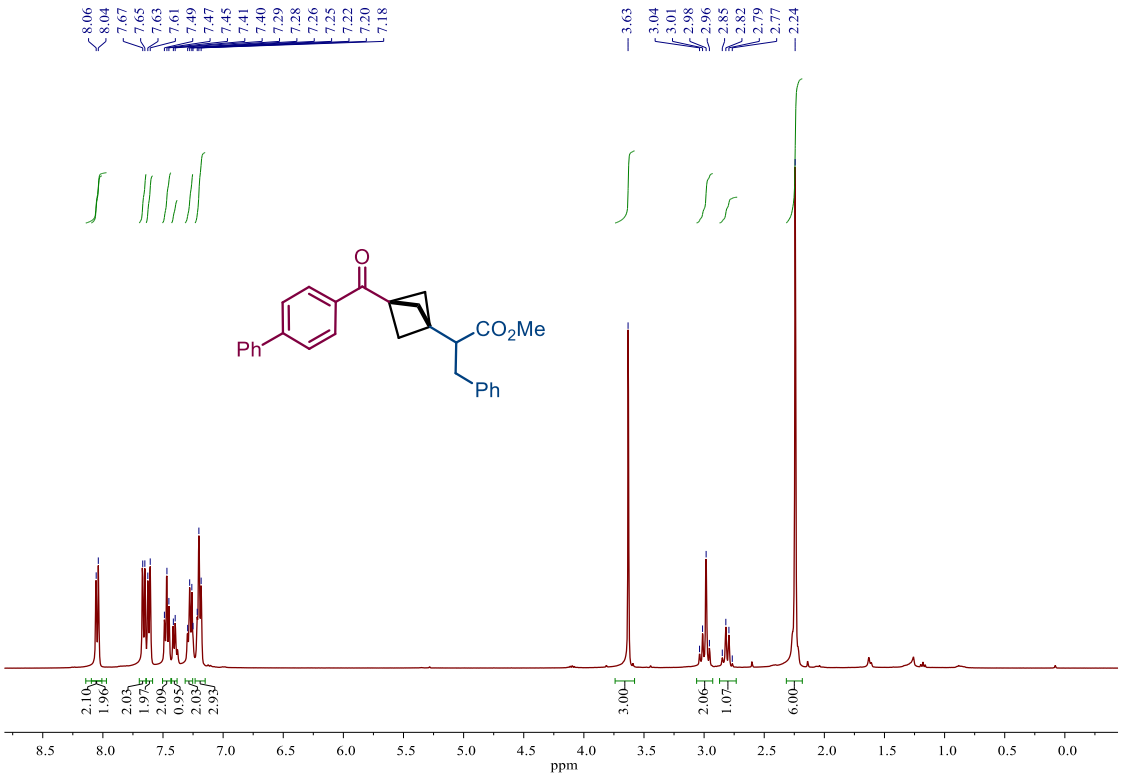
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 6



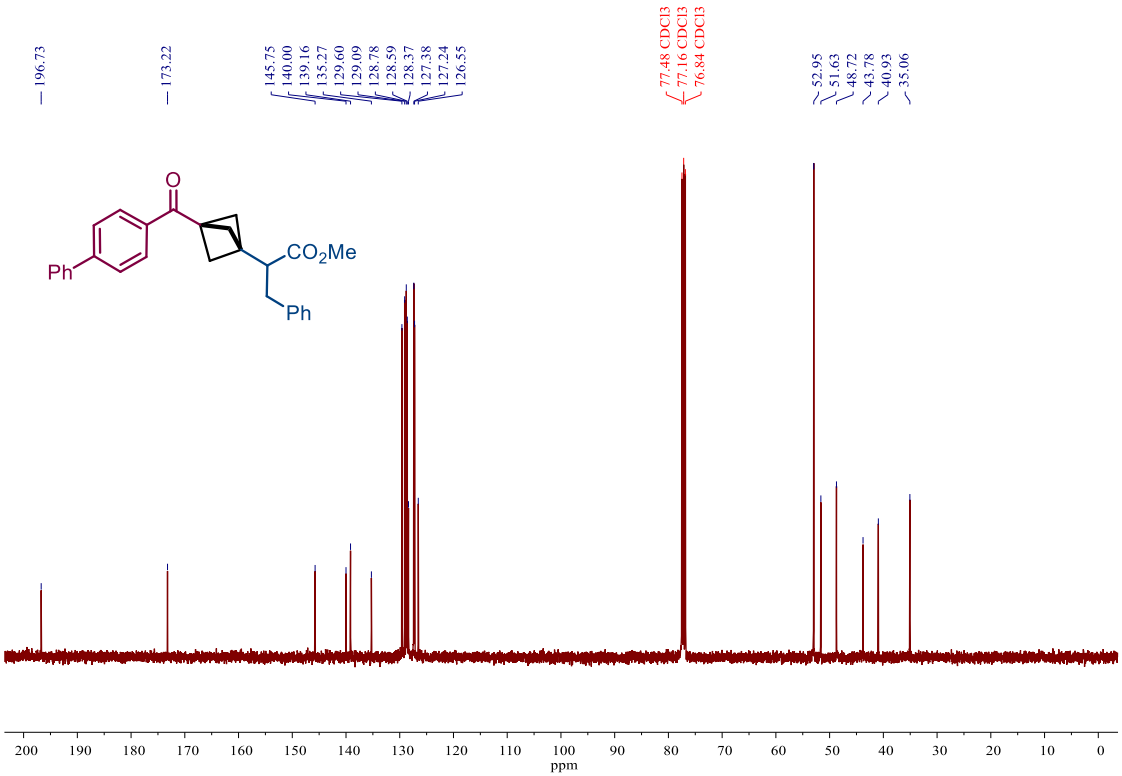
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 7



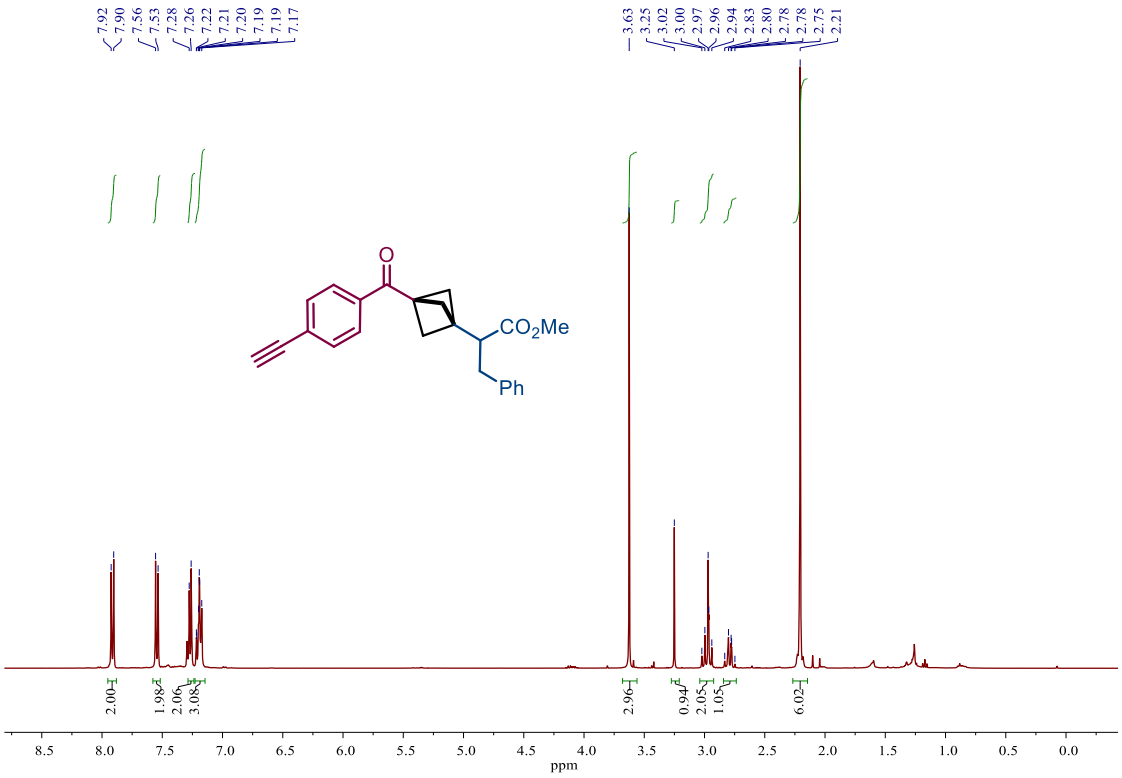
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 7



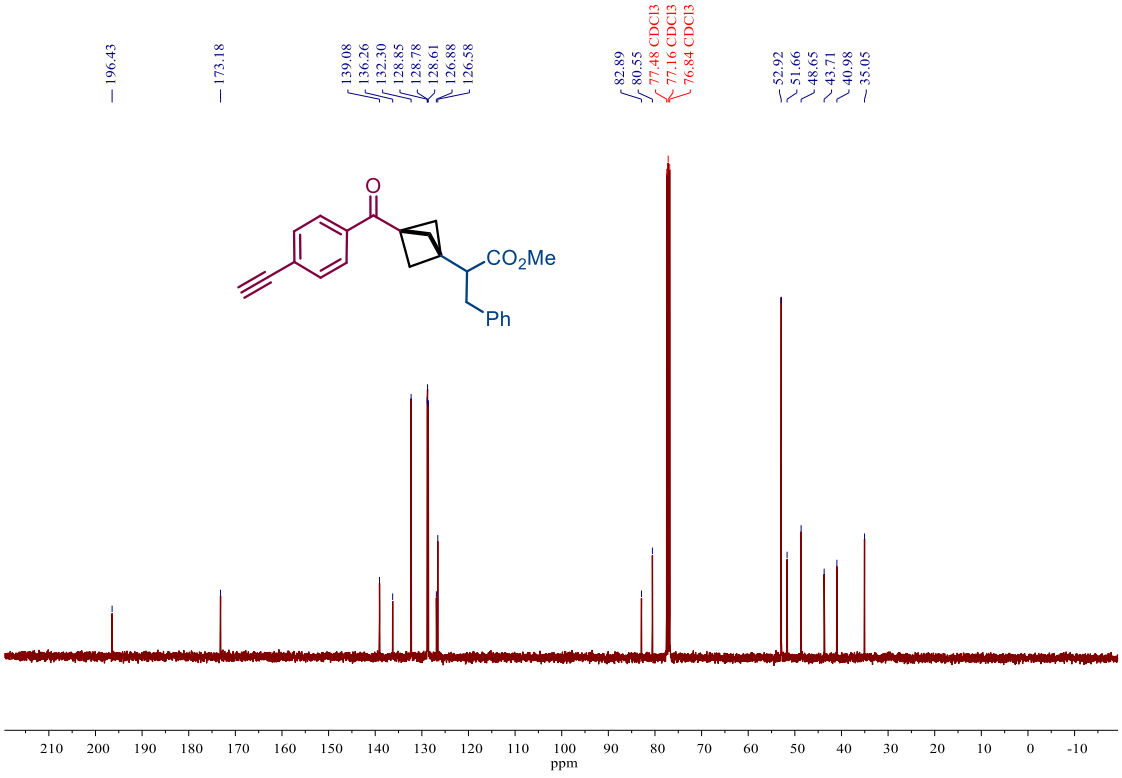
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 8



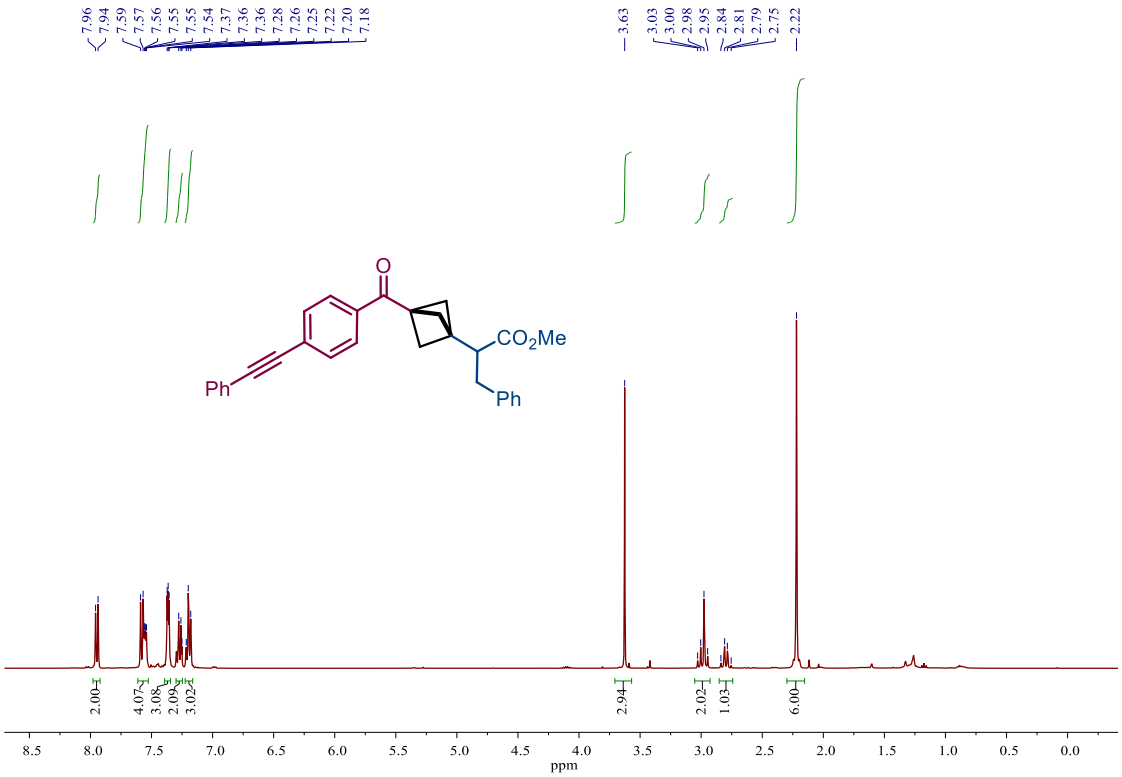
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 8



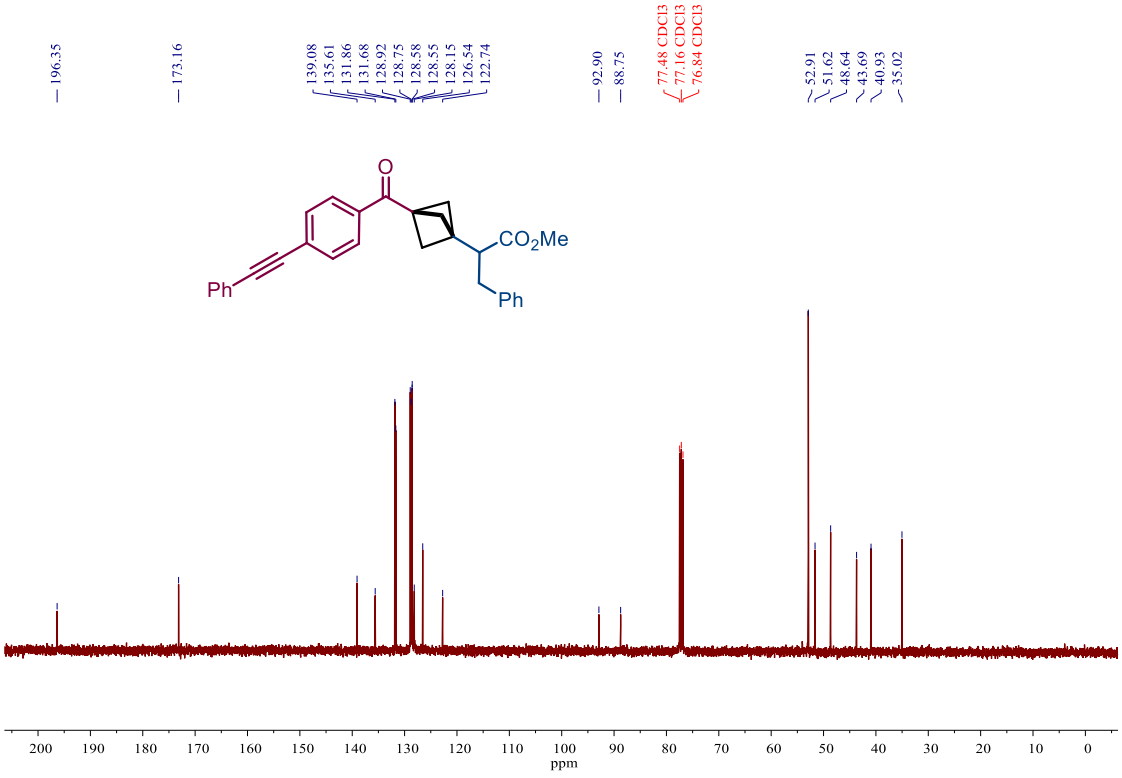
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 9



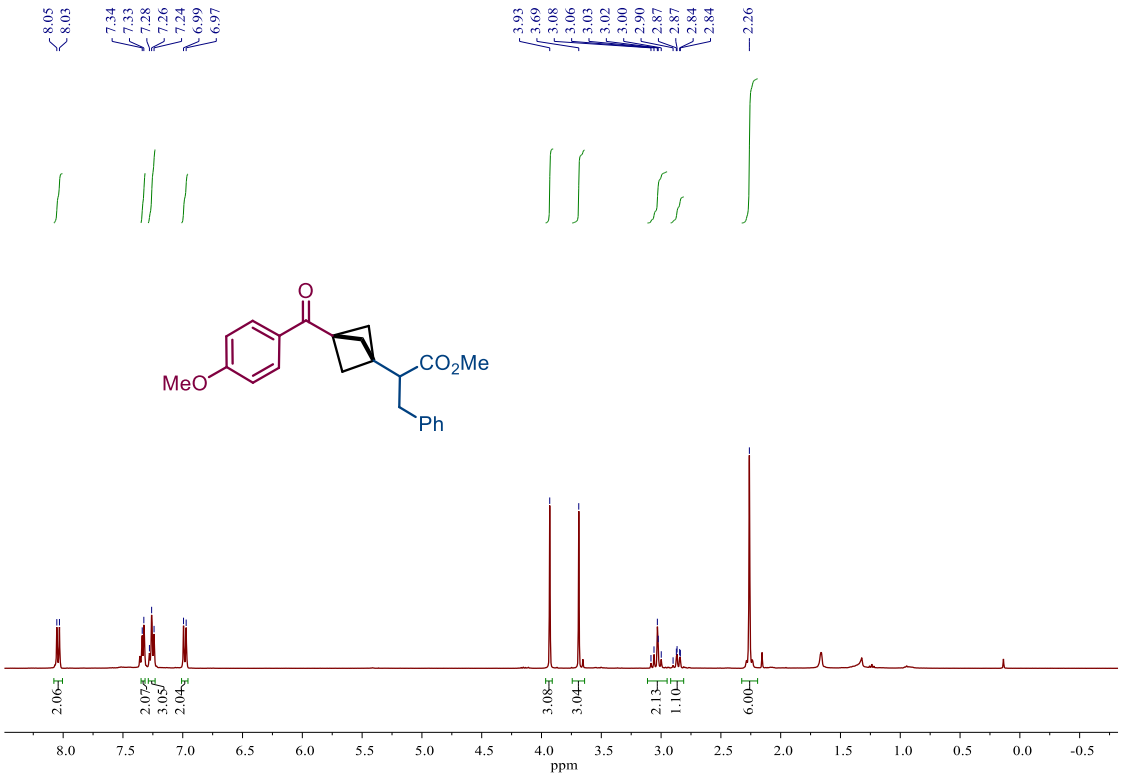
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 9



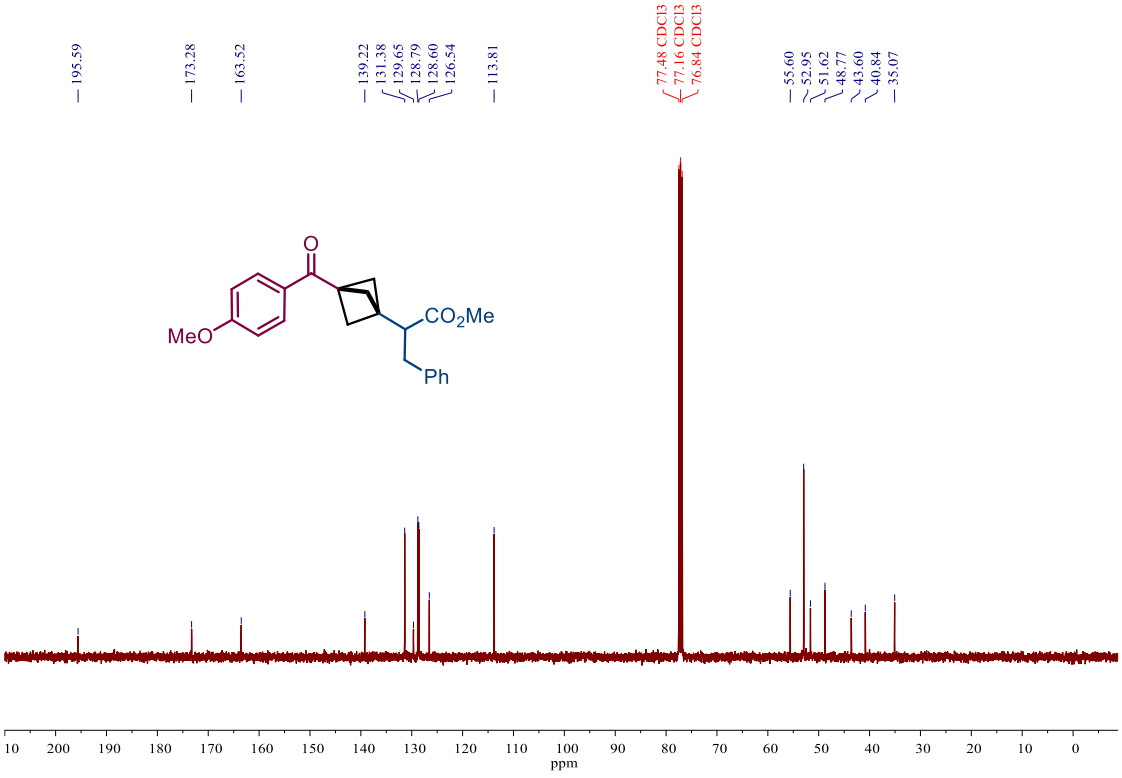
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 10



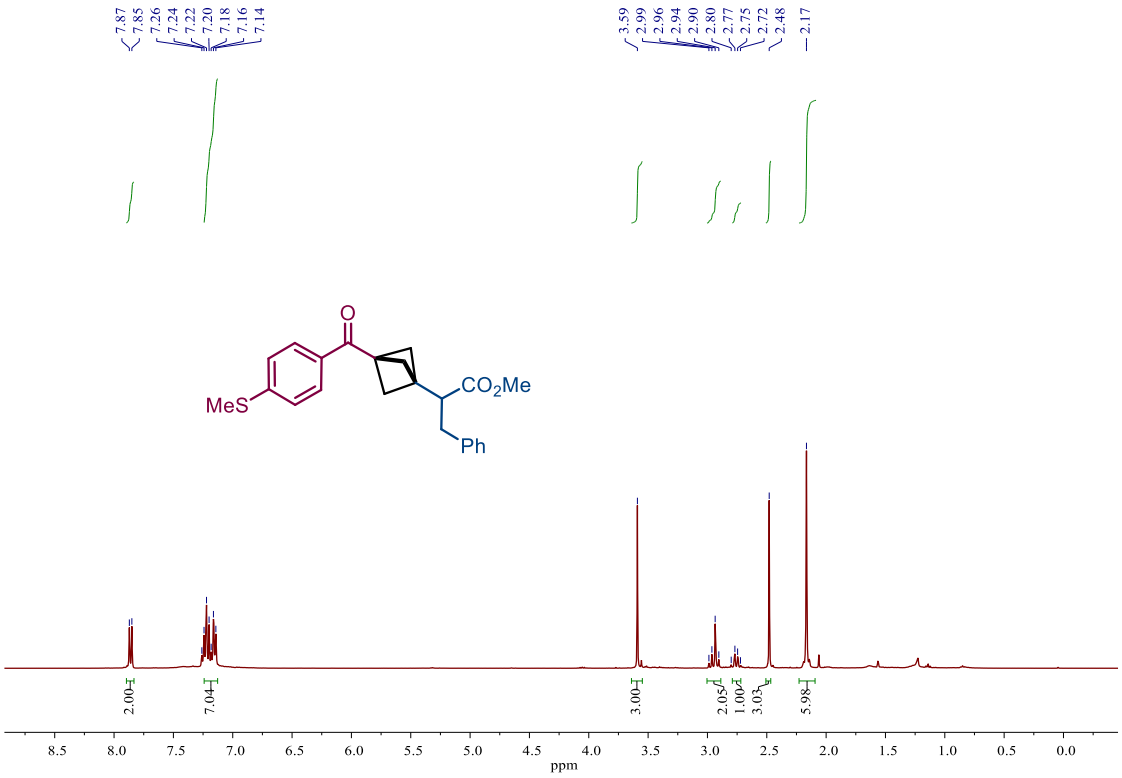
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 10



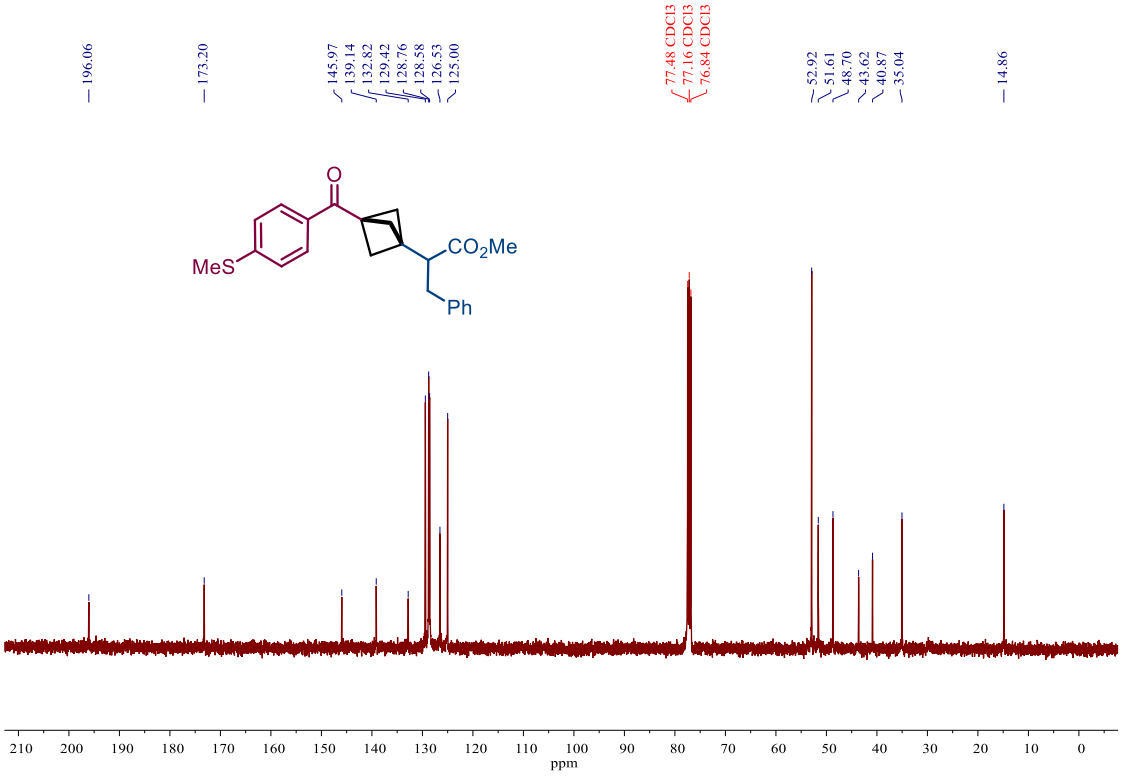
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 11



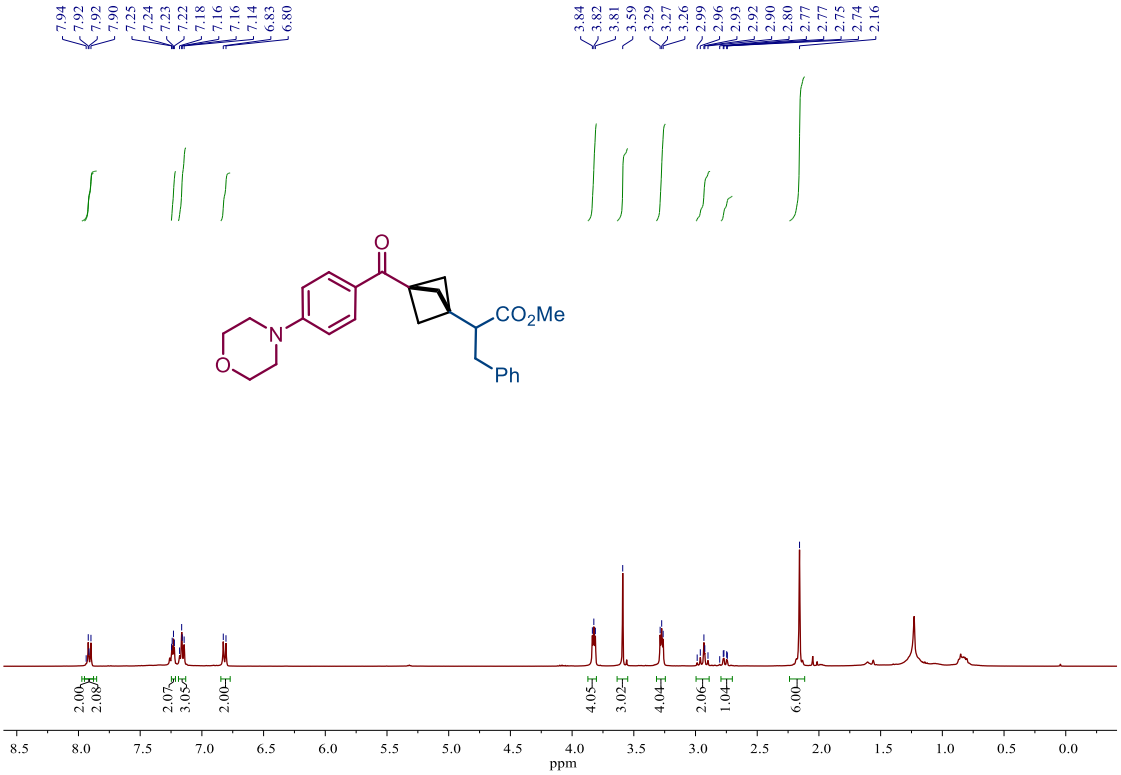
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 11



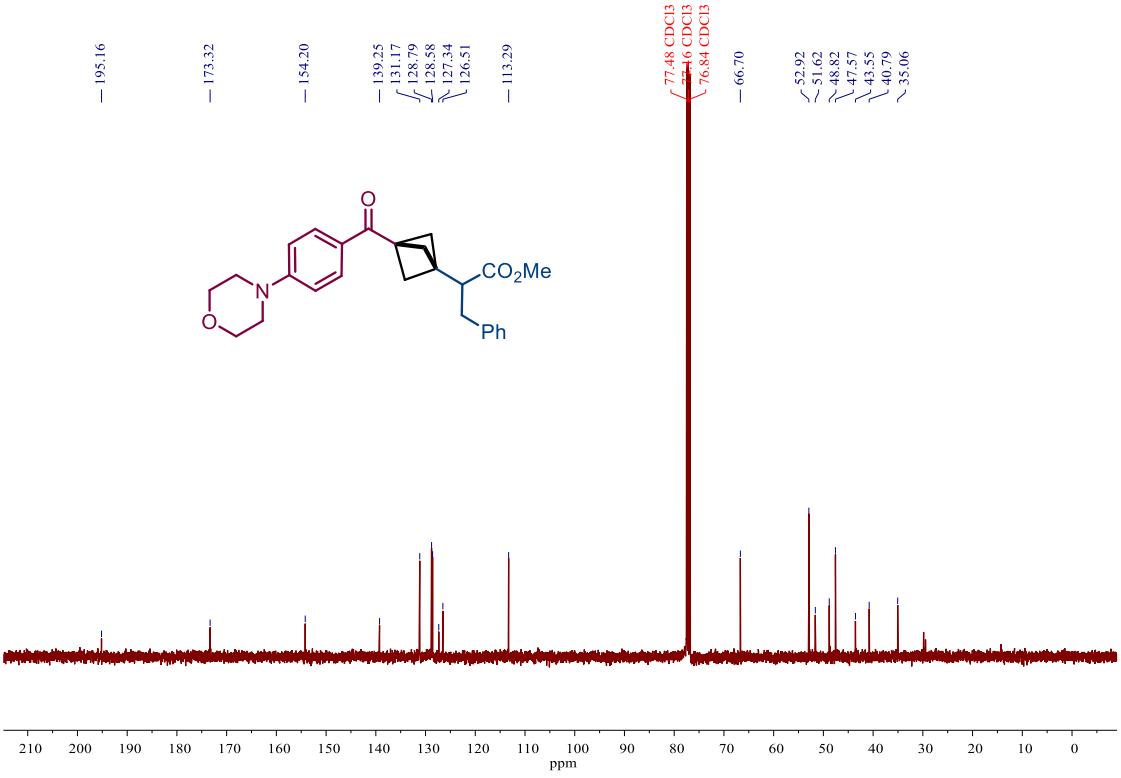
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 12



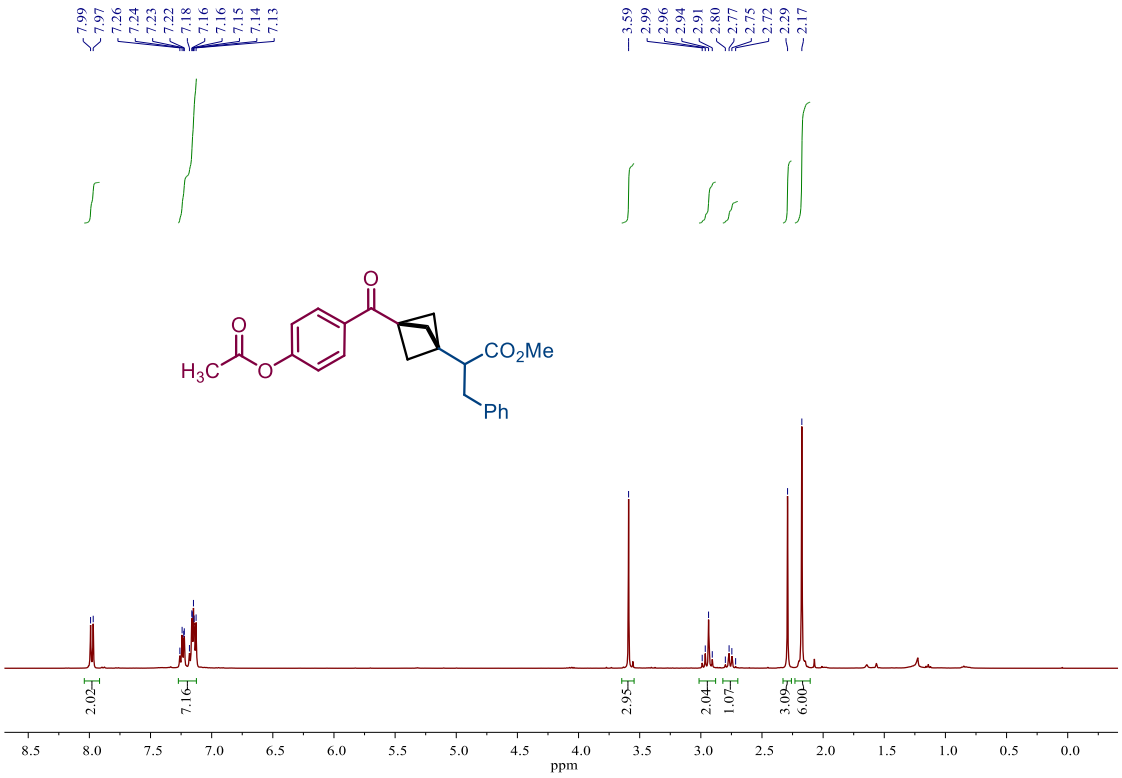
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 12



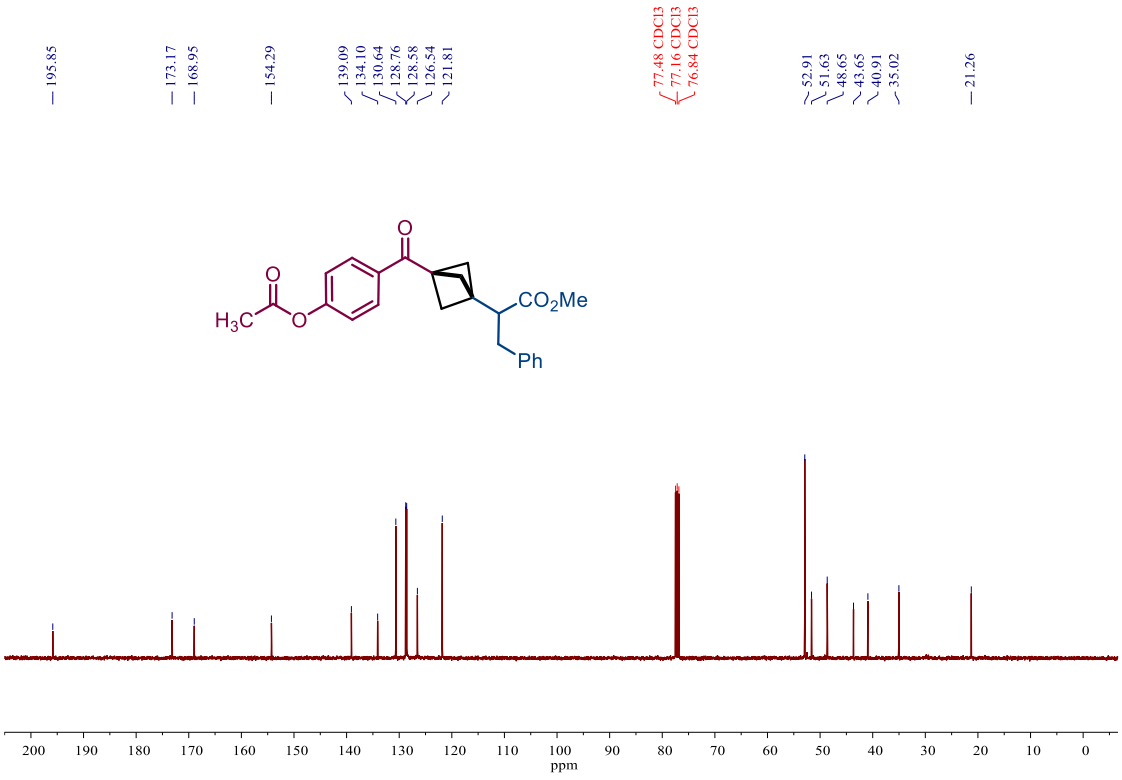
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 13



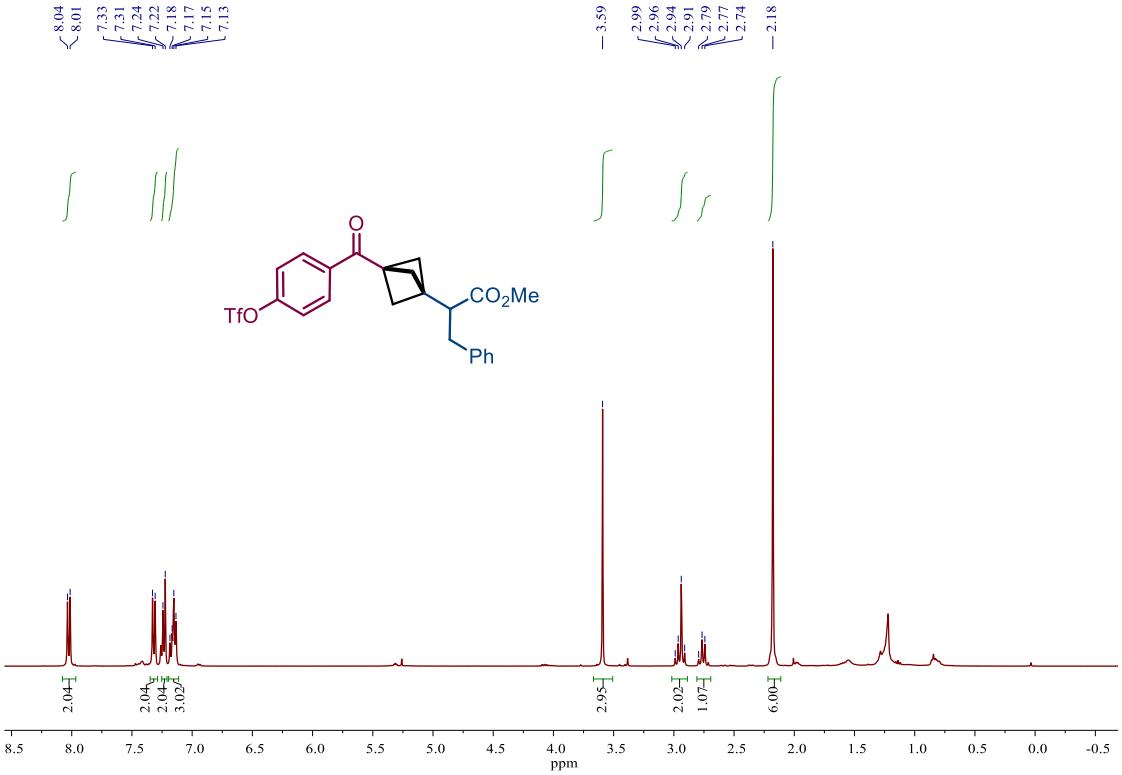
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 13



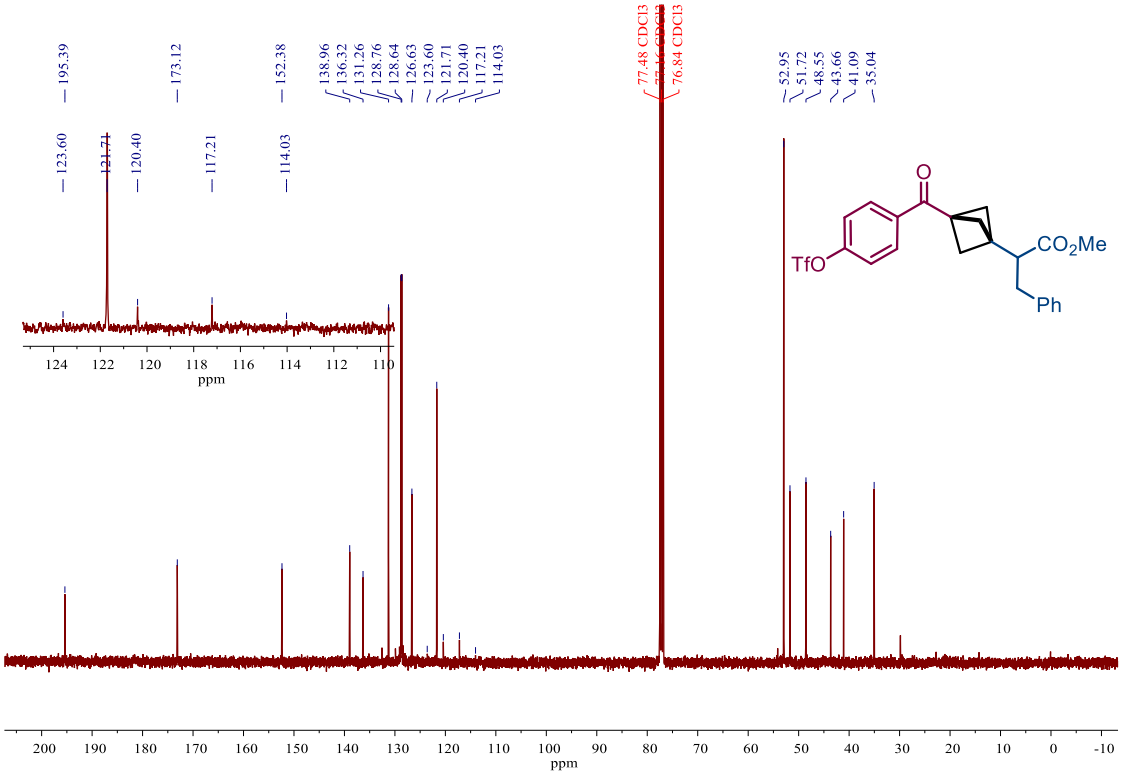
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 14



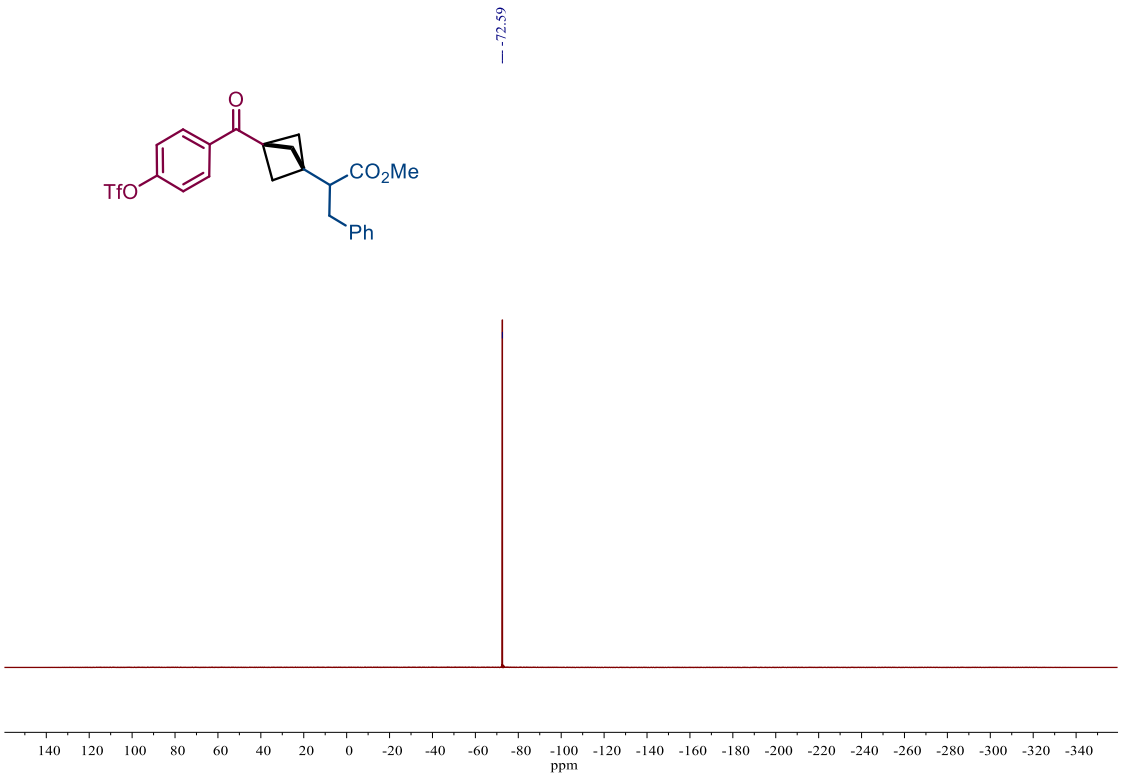
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 14



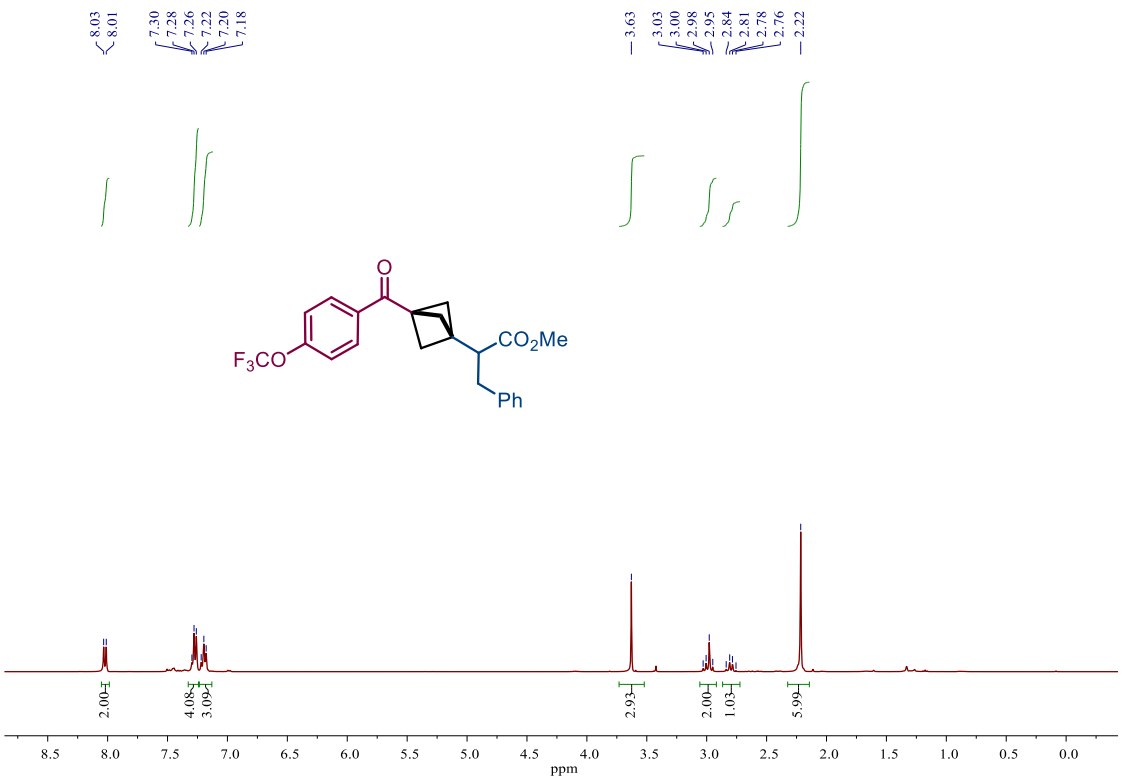
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 15



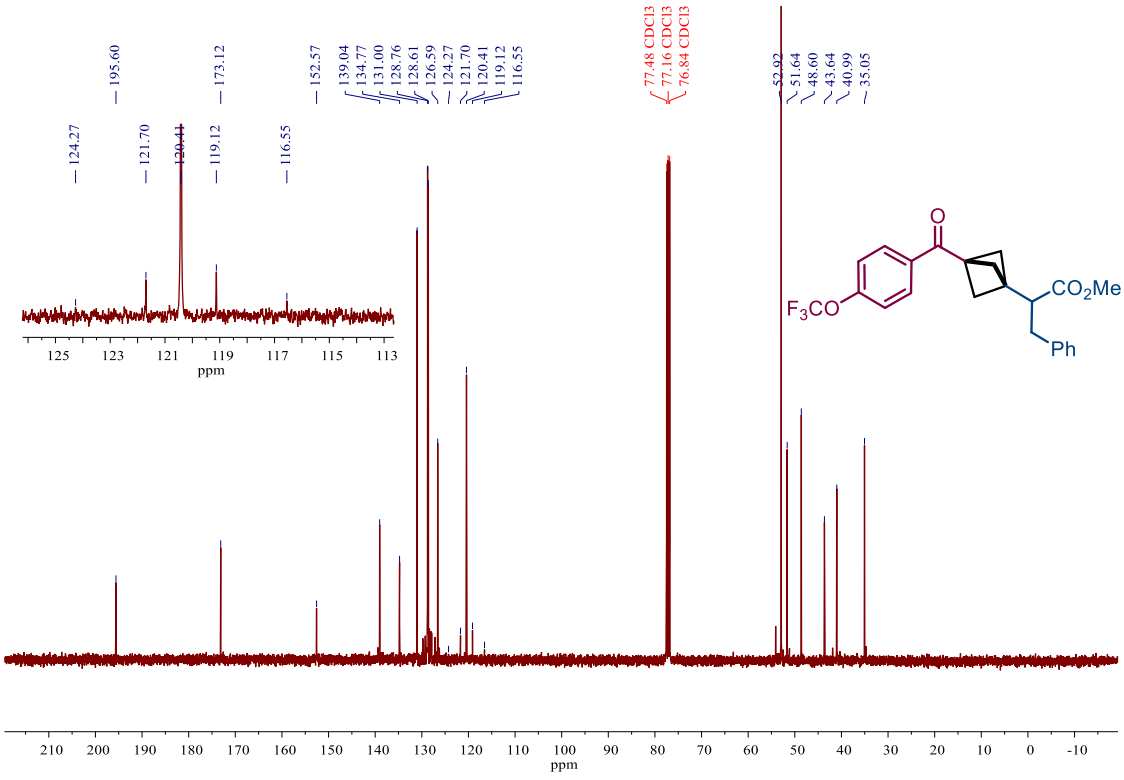
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 15



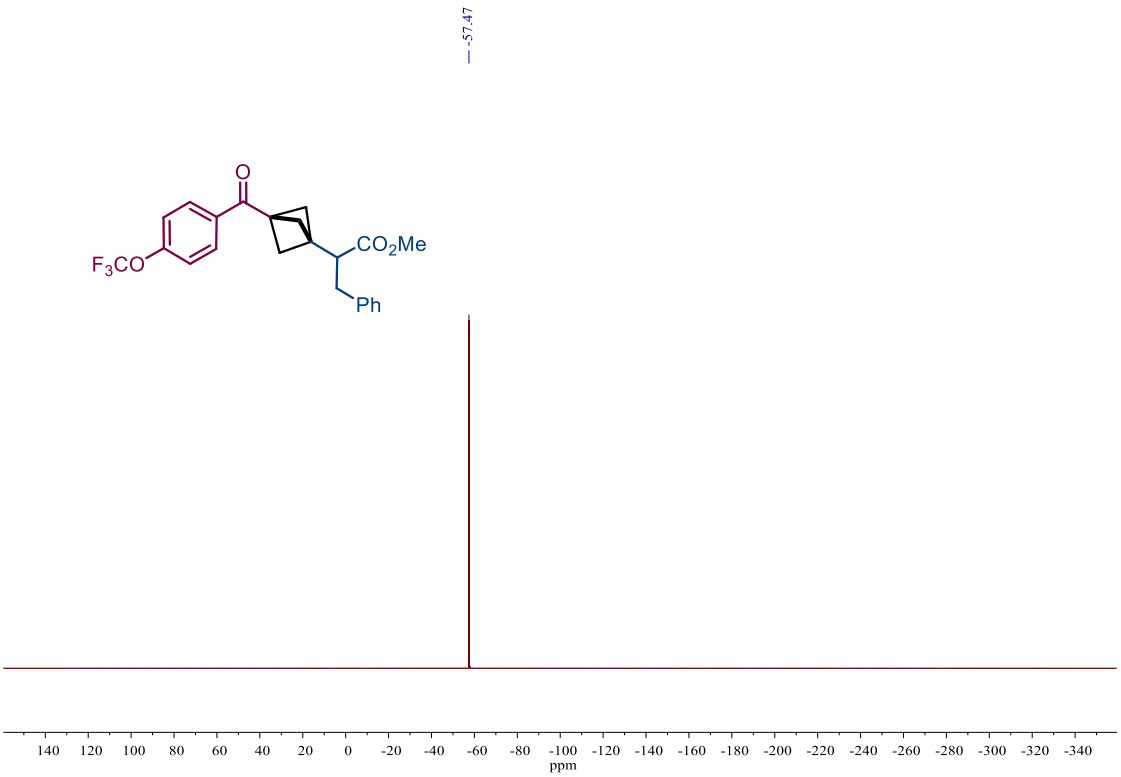
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 15



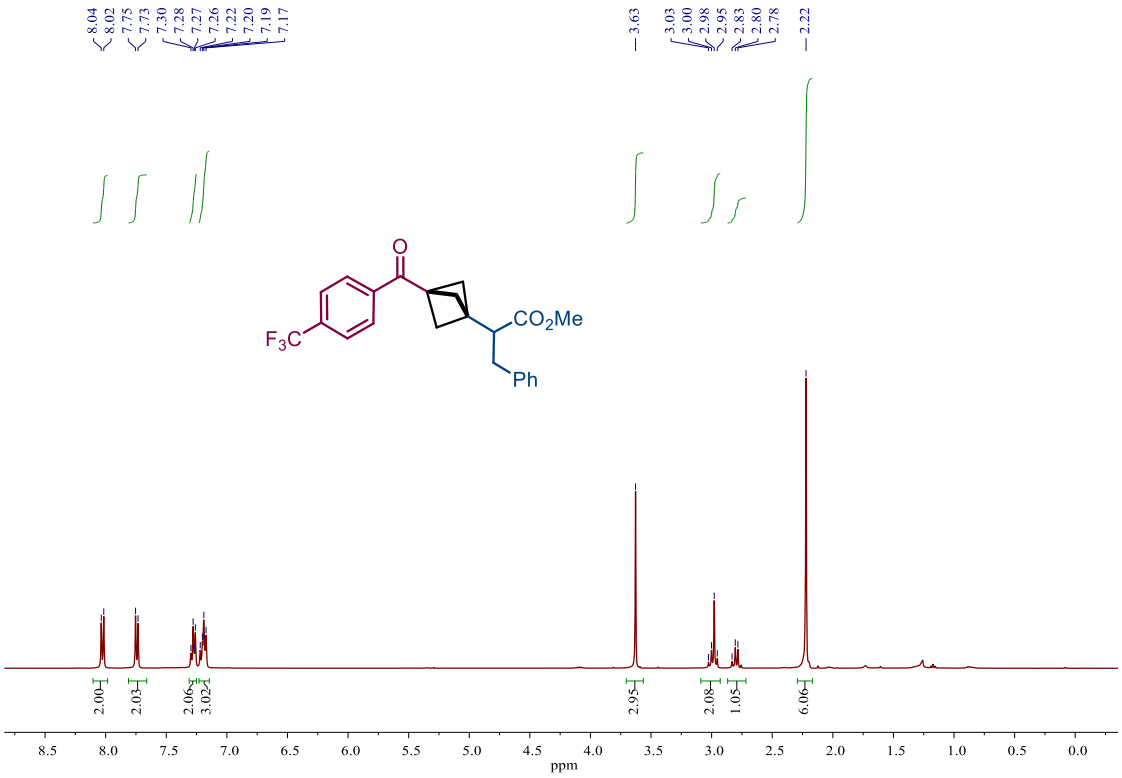
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 16



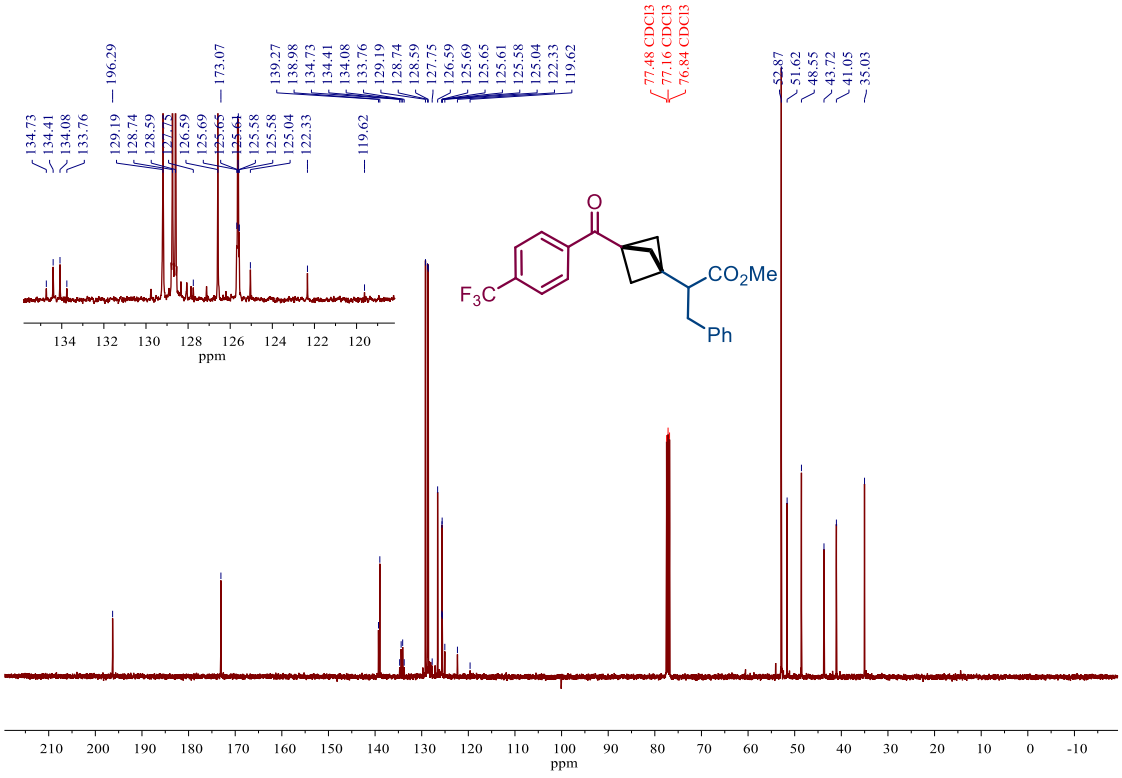
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 16



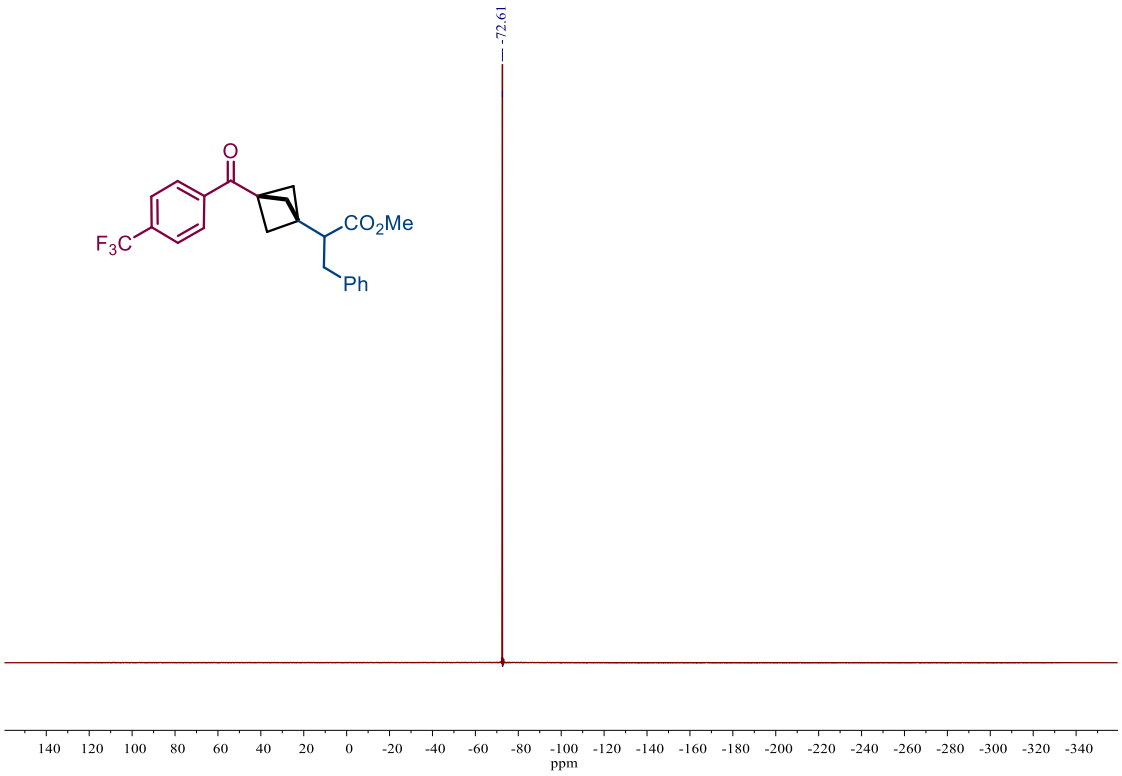
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 16



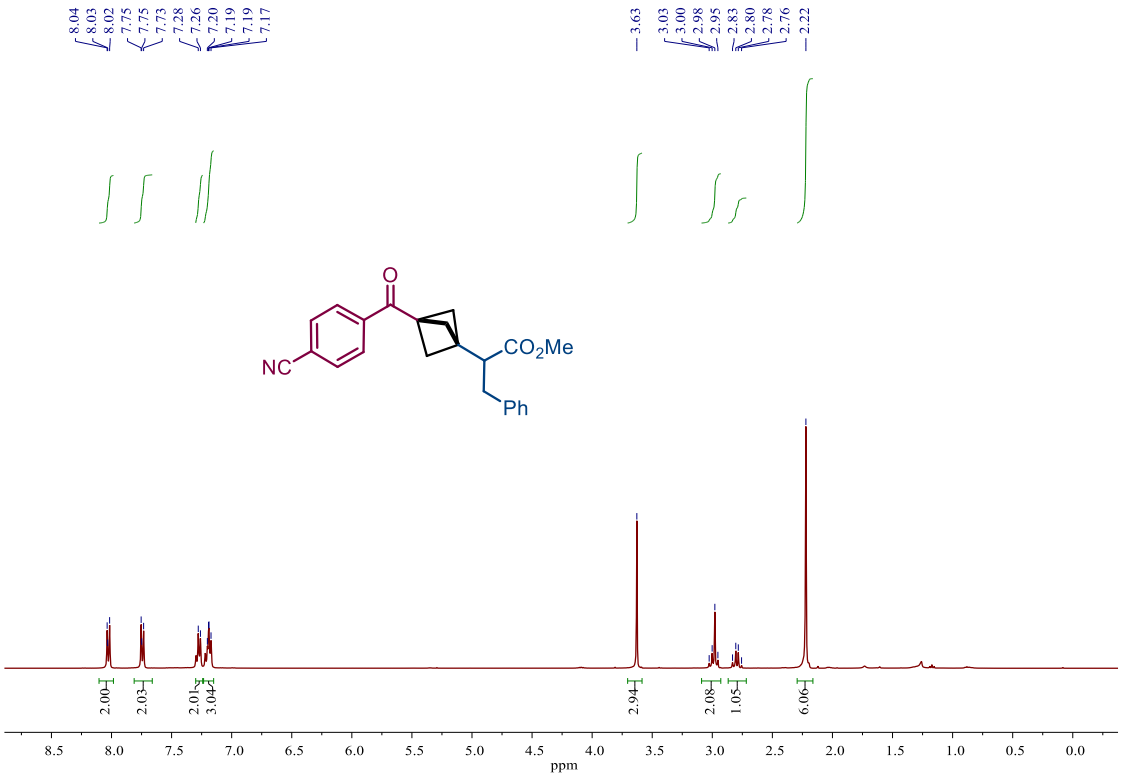
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 4



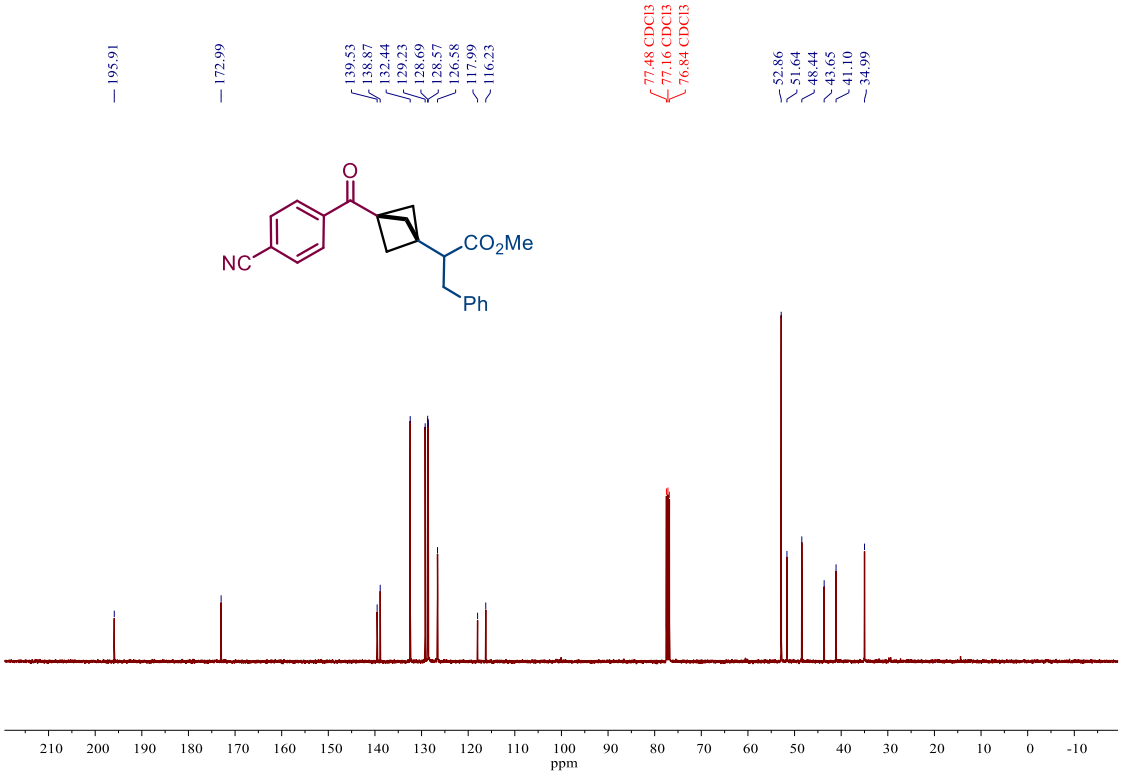
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 4



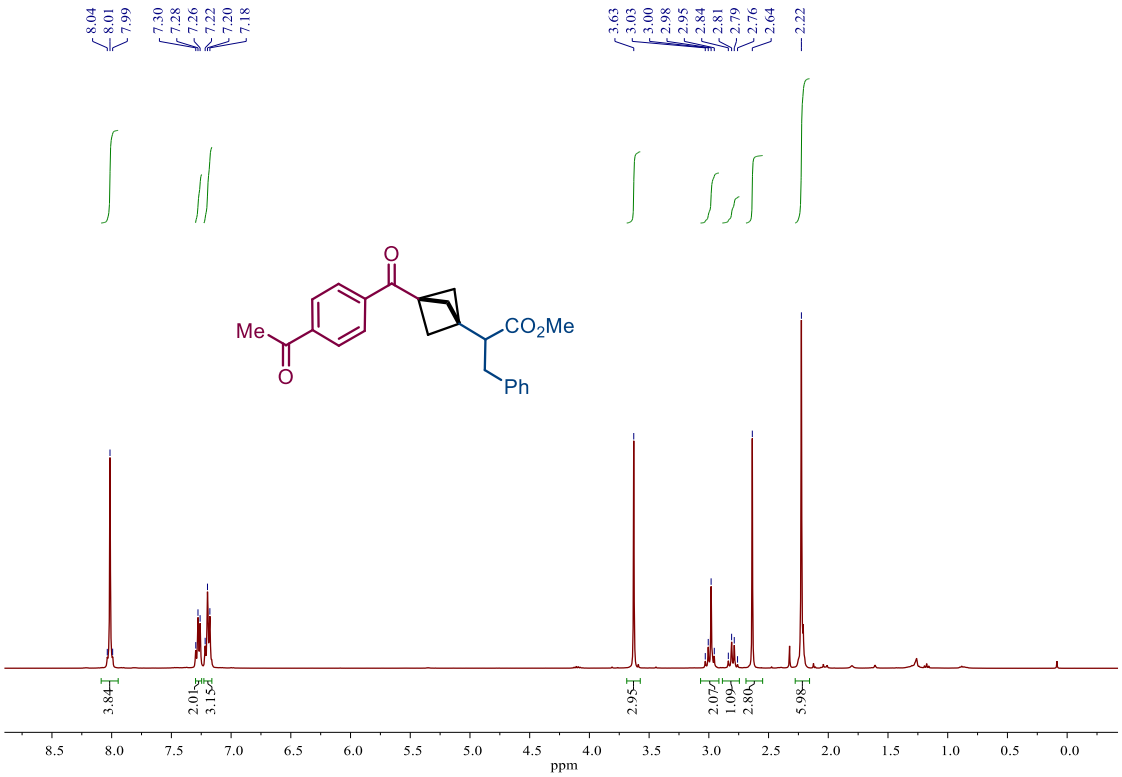
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 4



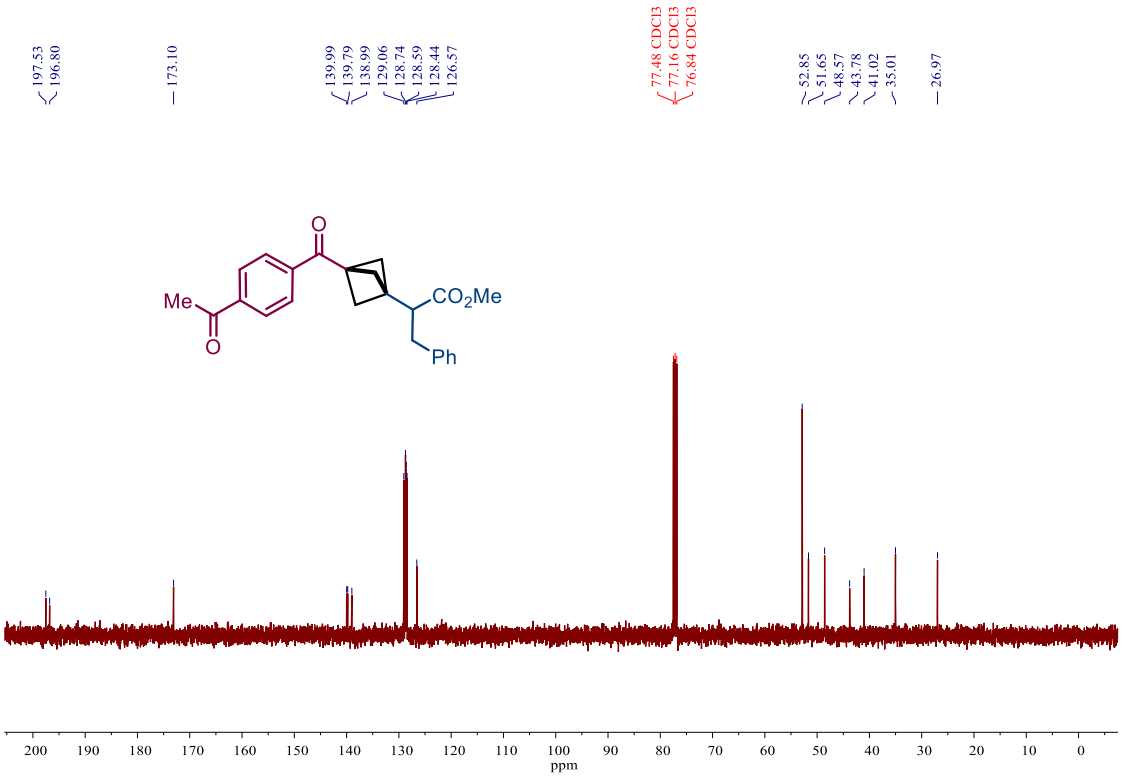
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 17



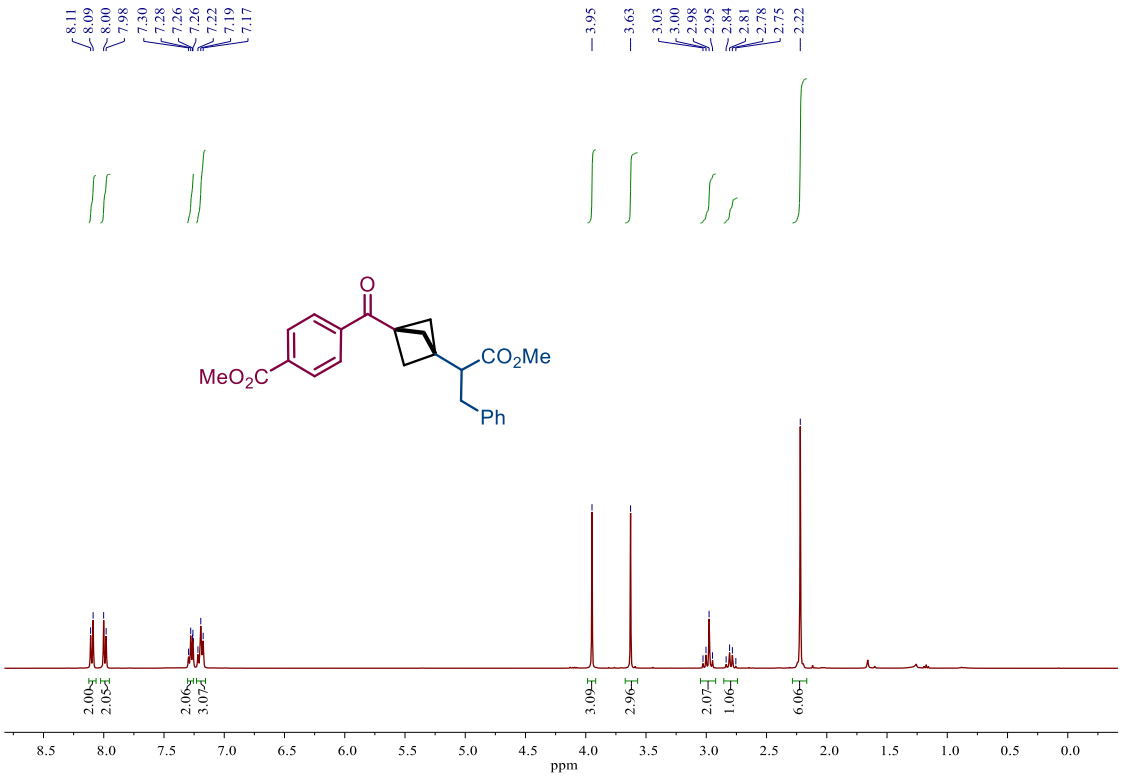
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 17



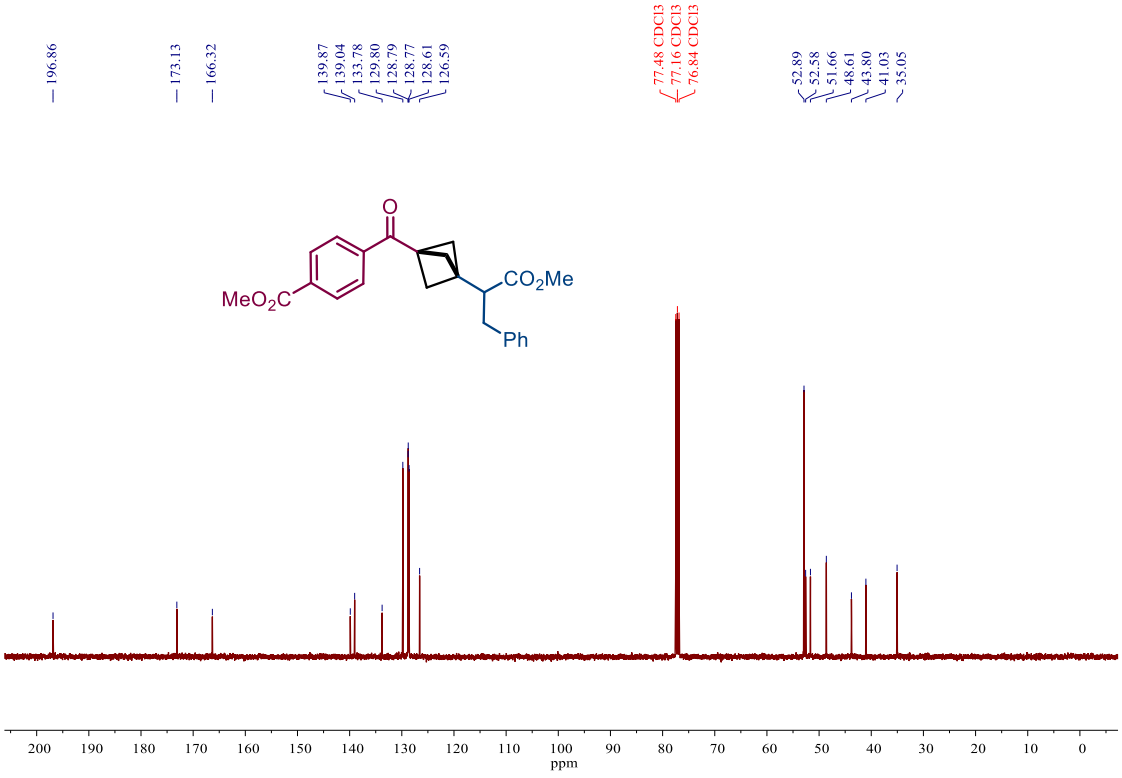
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 18



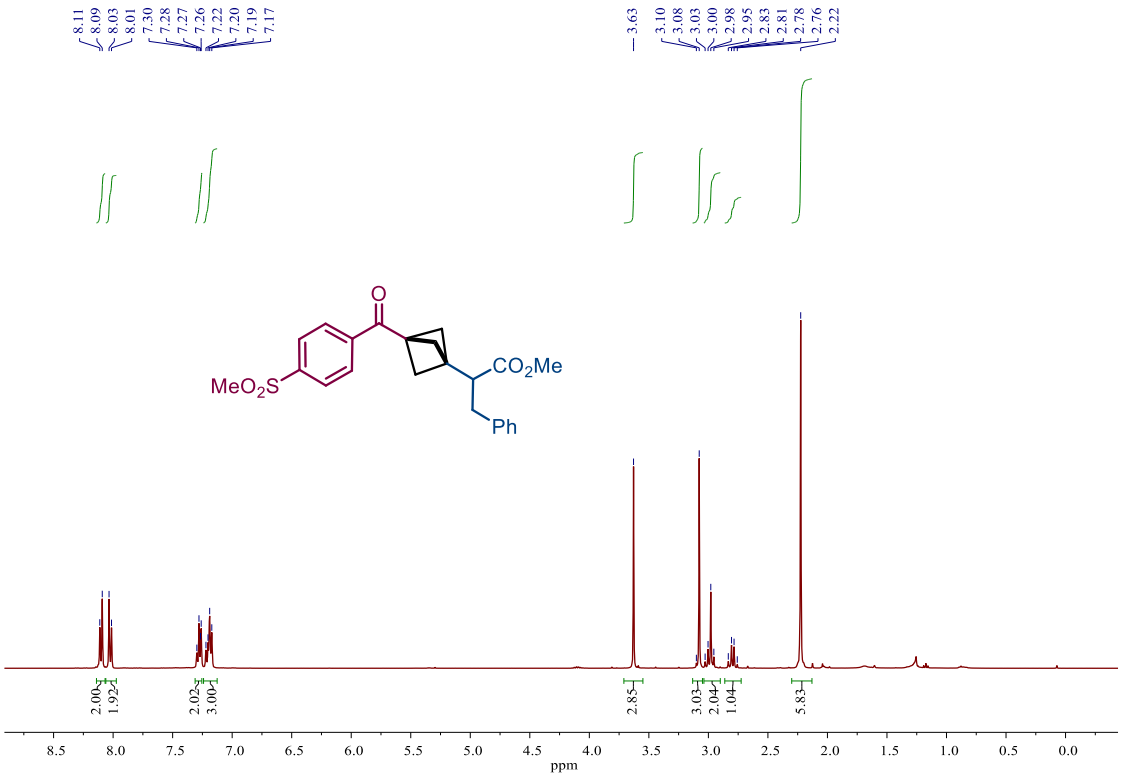
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 18



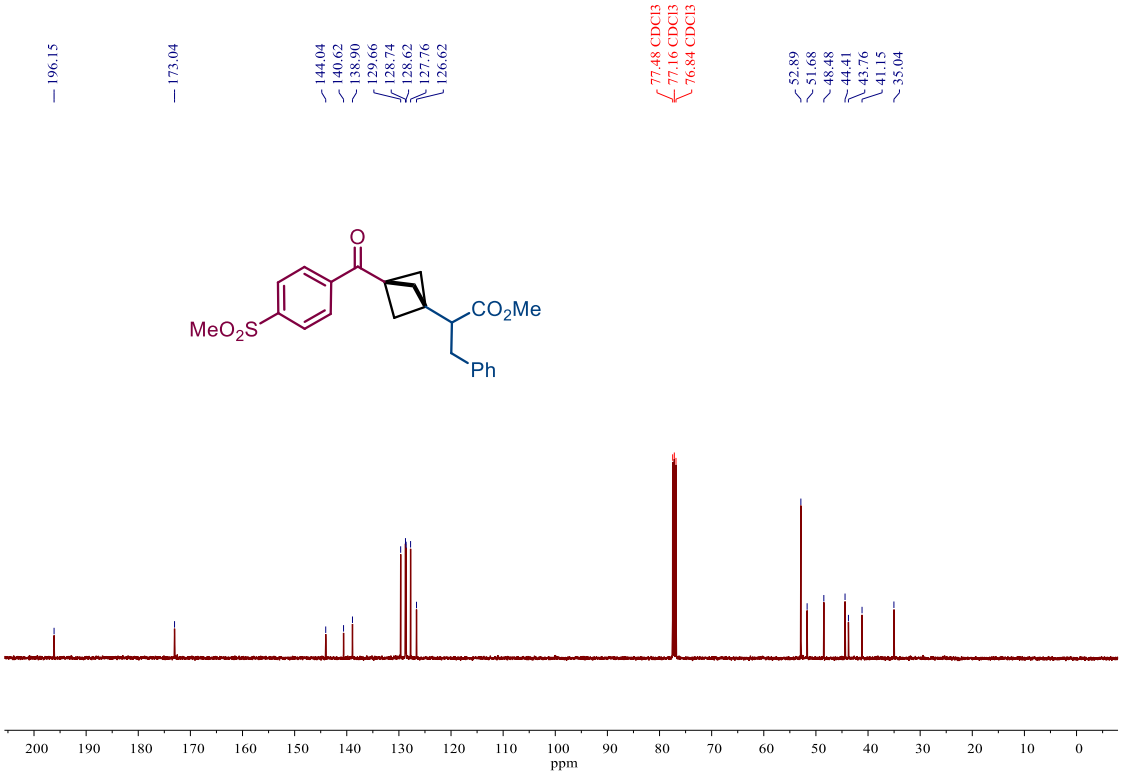
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 19



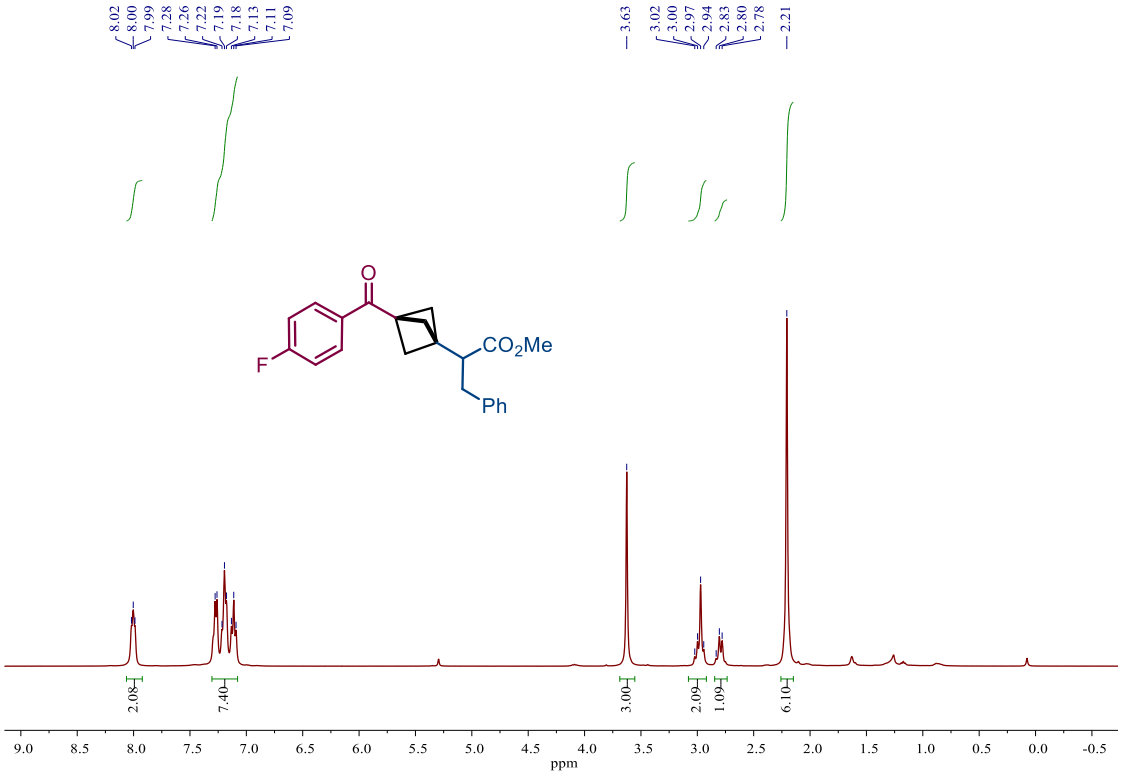
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 19



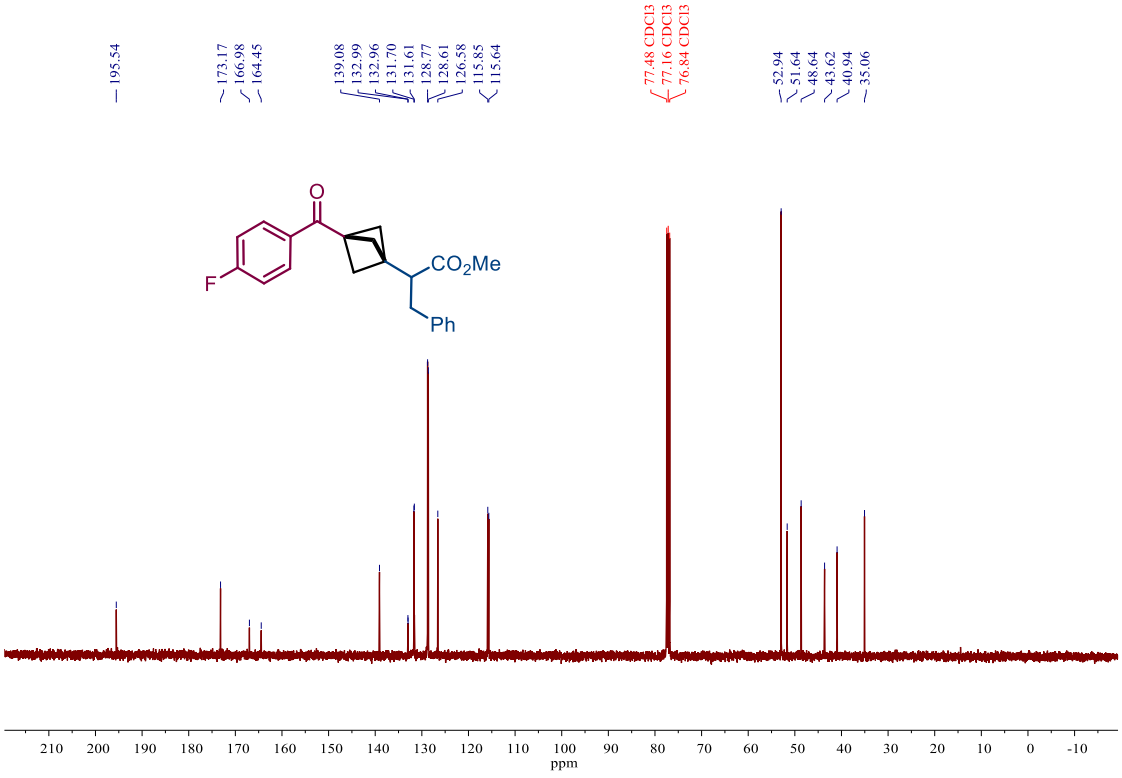
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 20



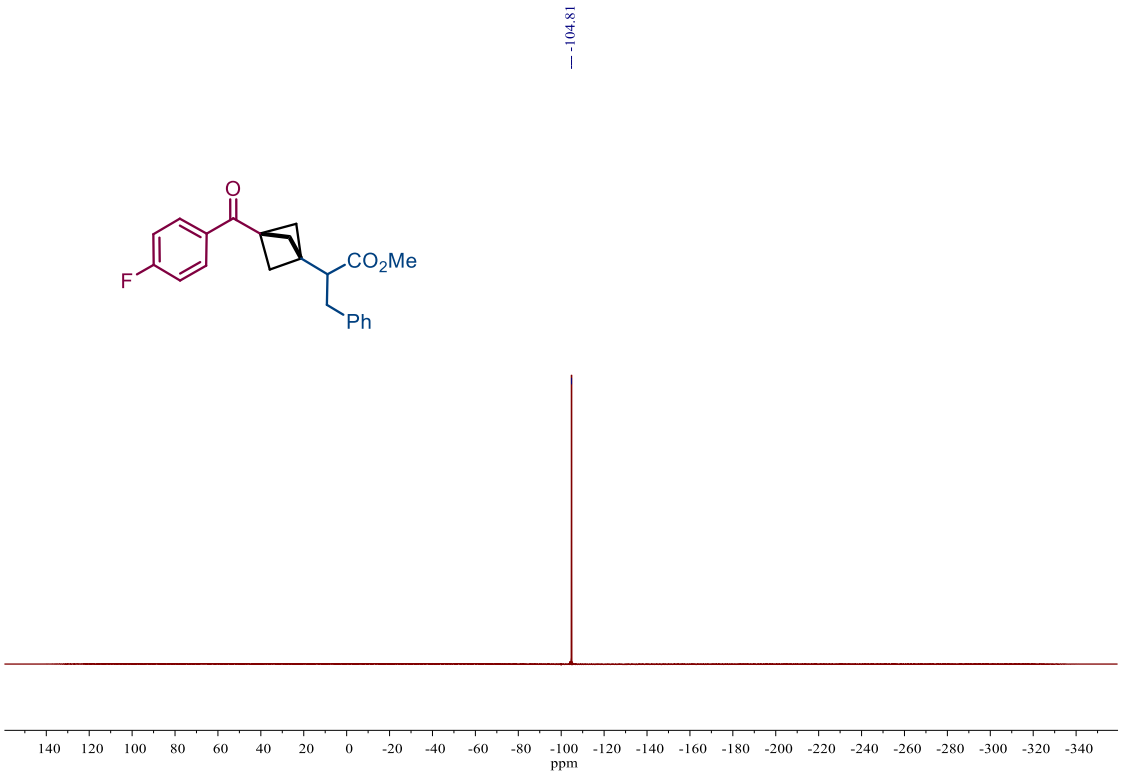
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 20



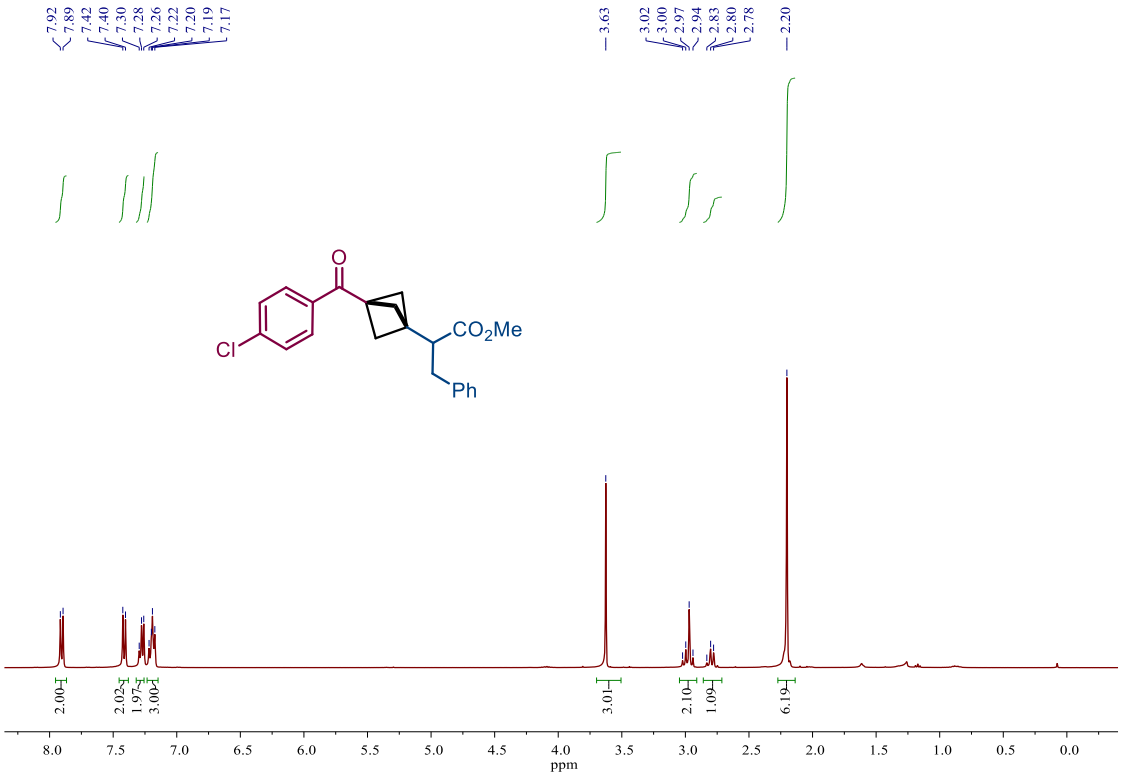
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 21



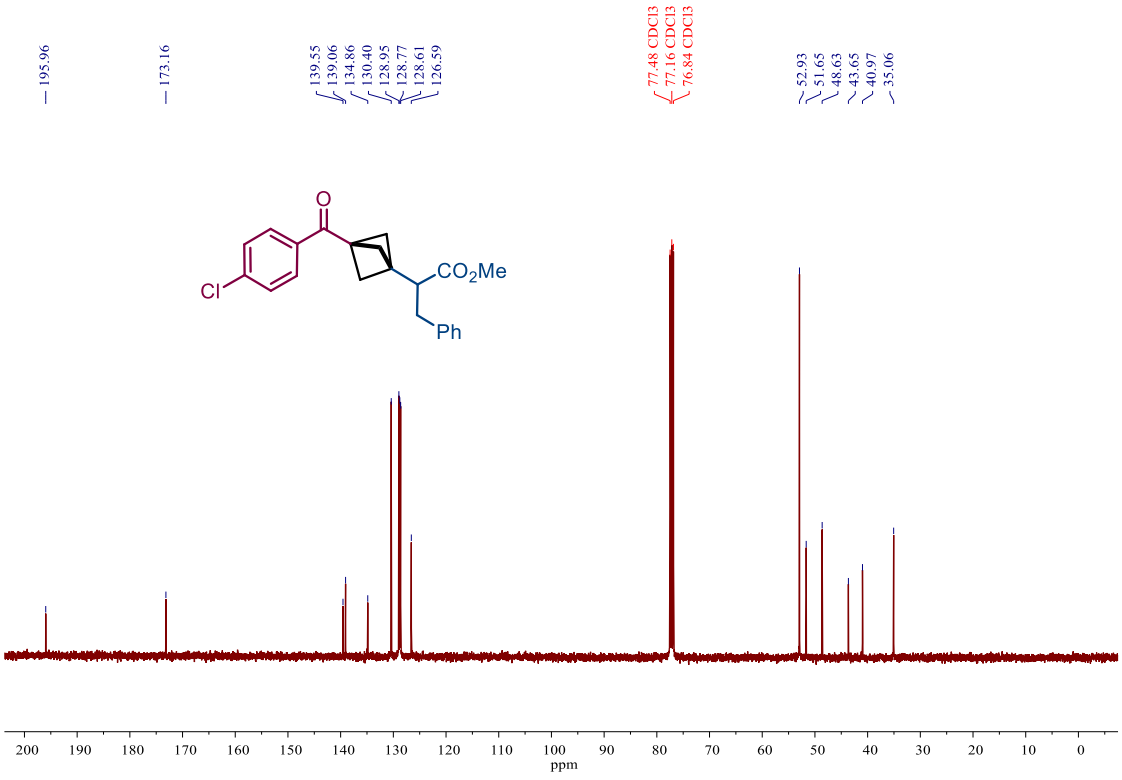
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 21



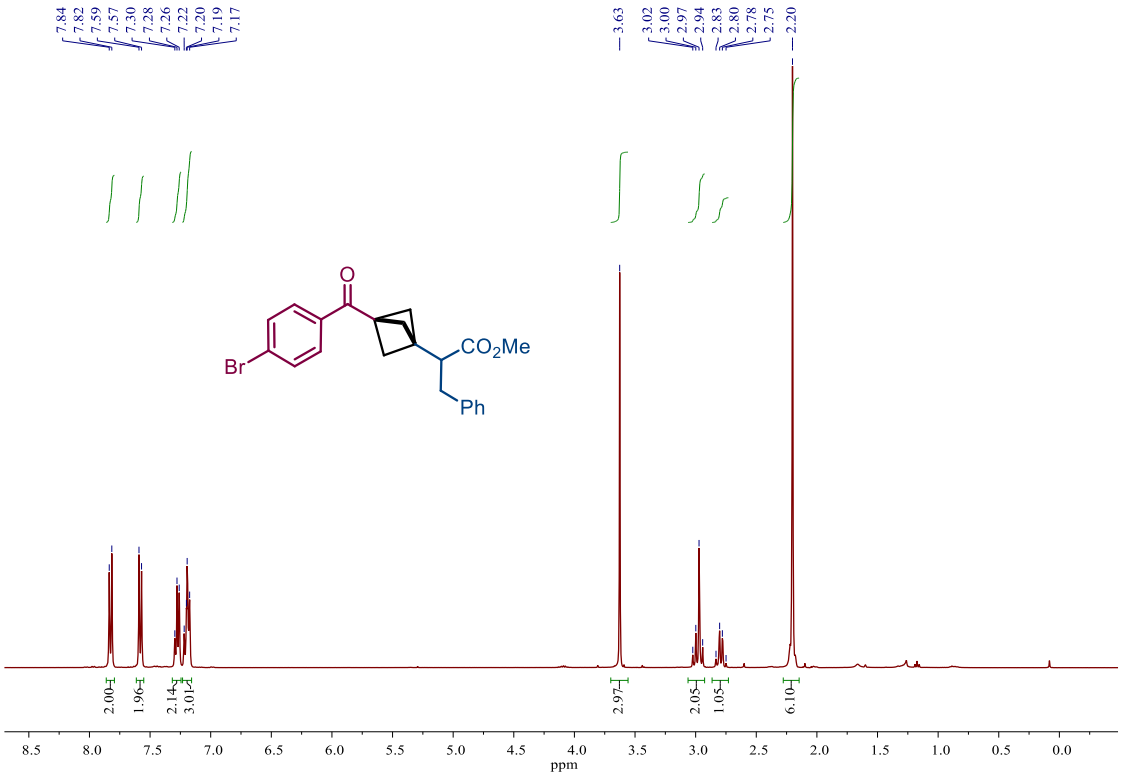
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 21



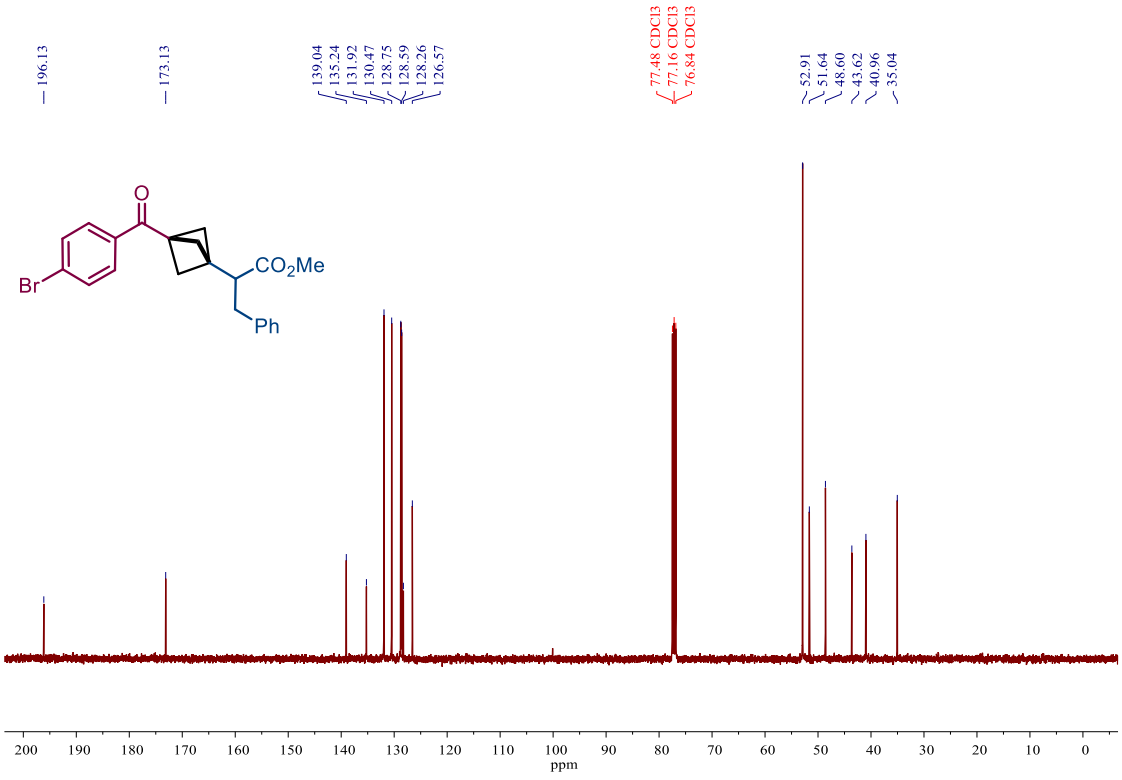
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 22



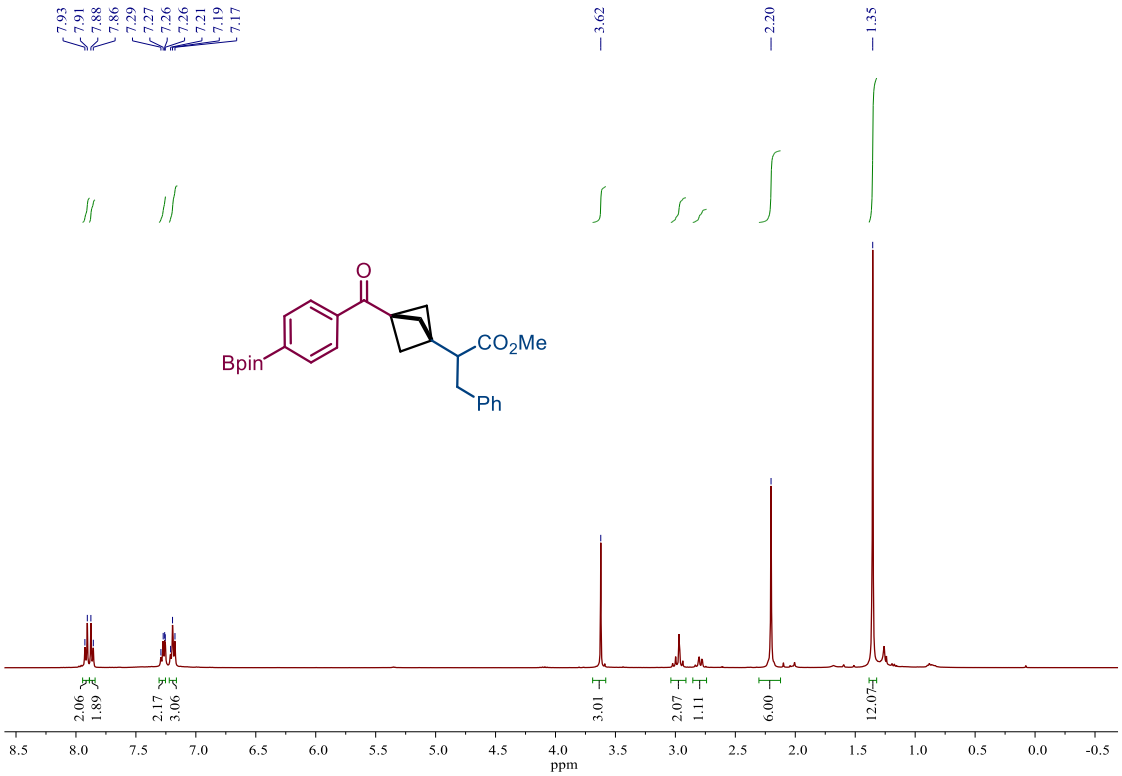
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 22



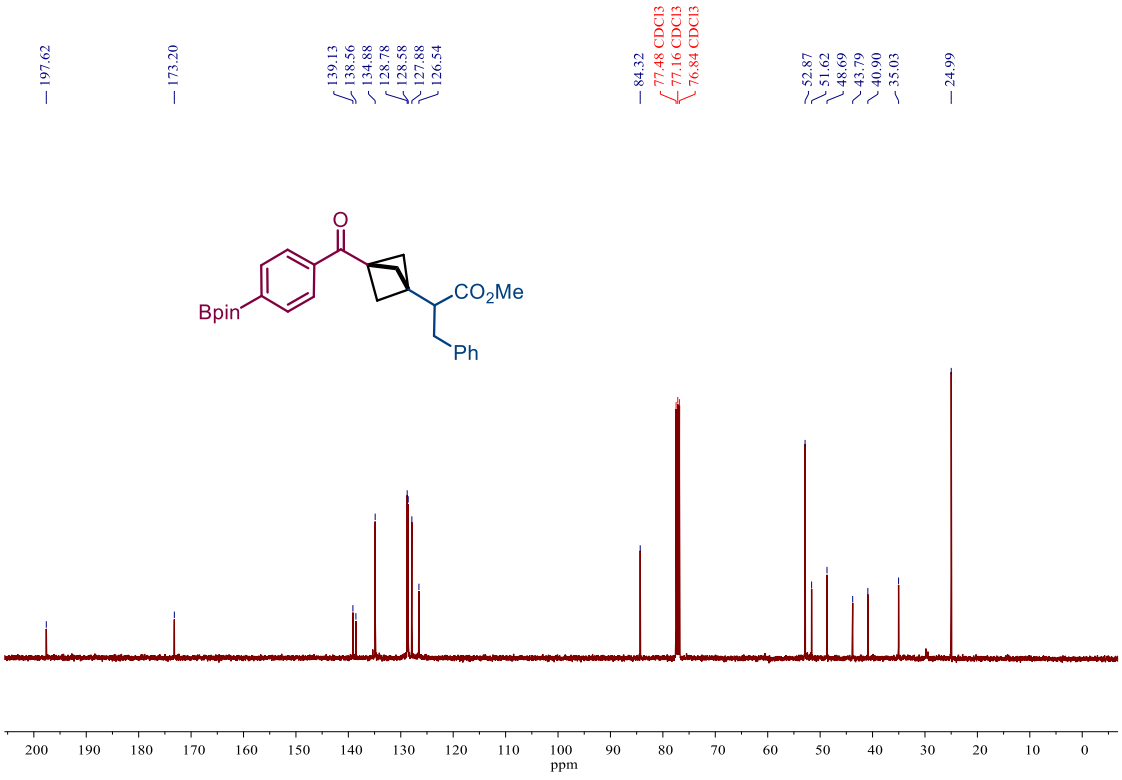
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 23



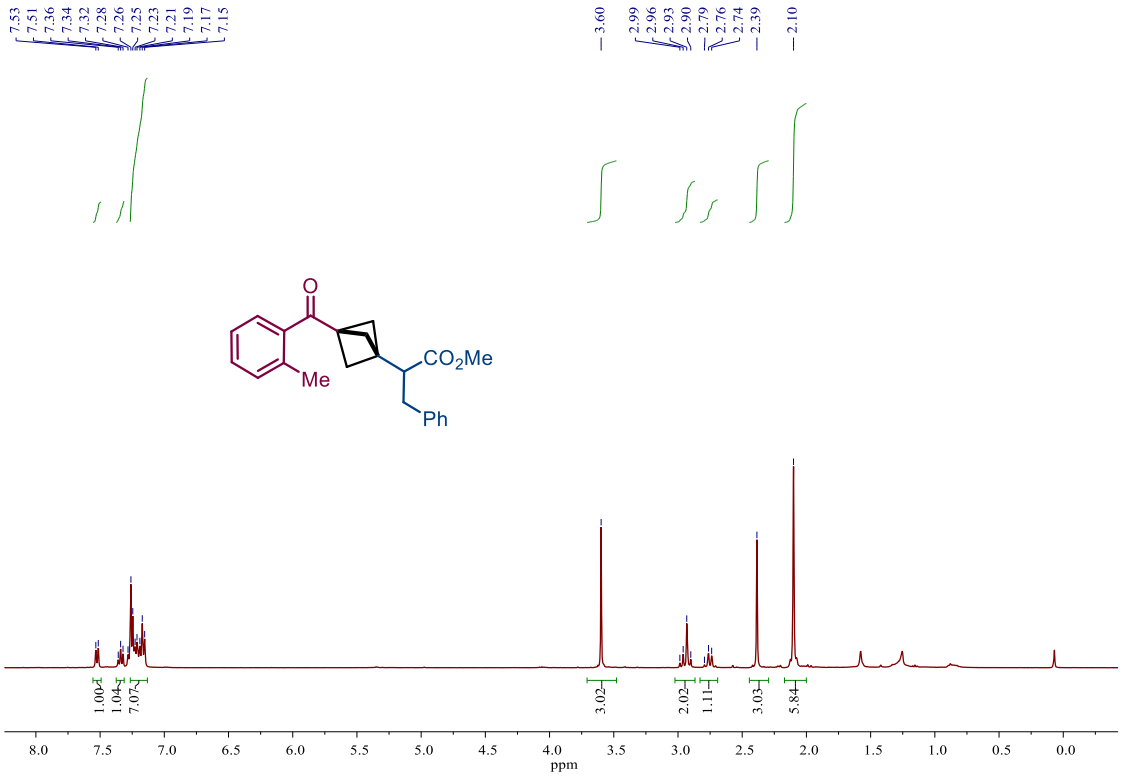
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 23



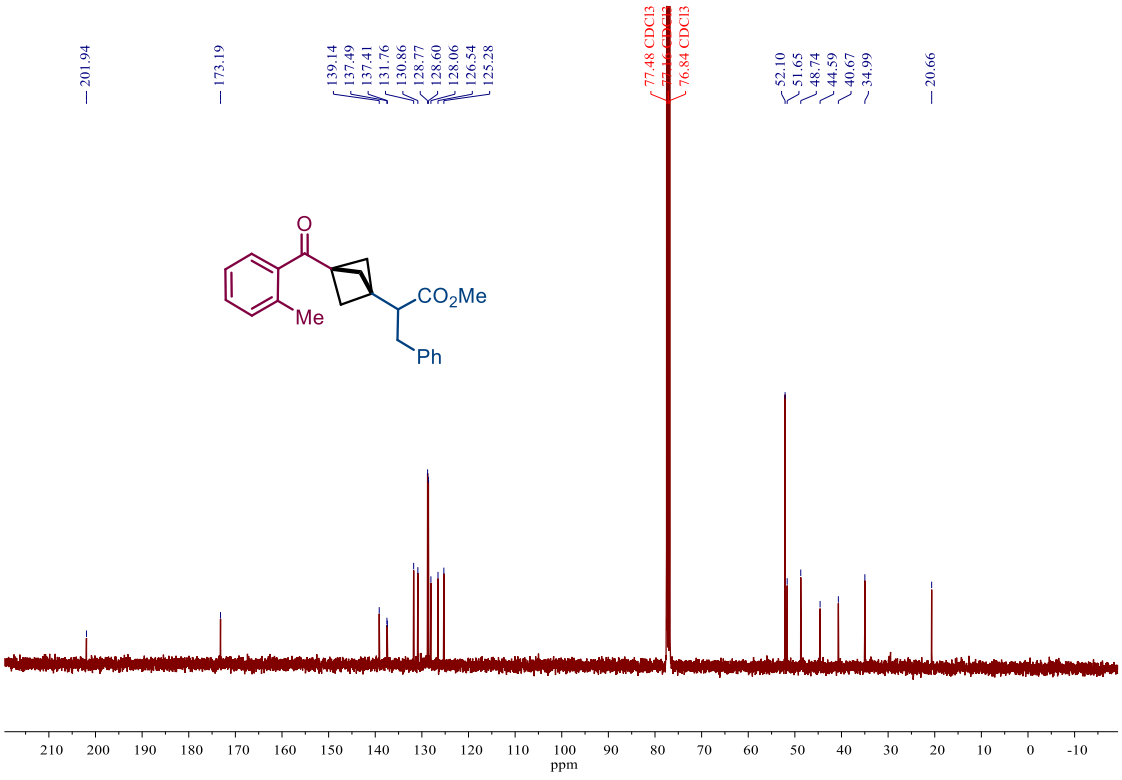
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 24



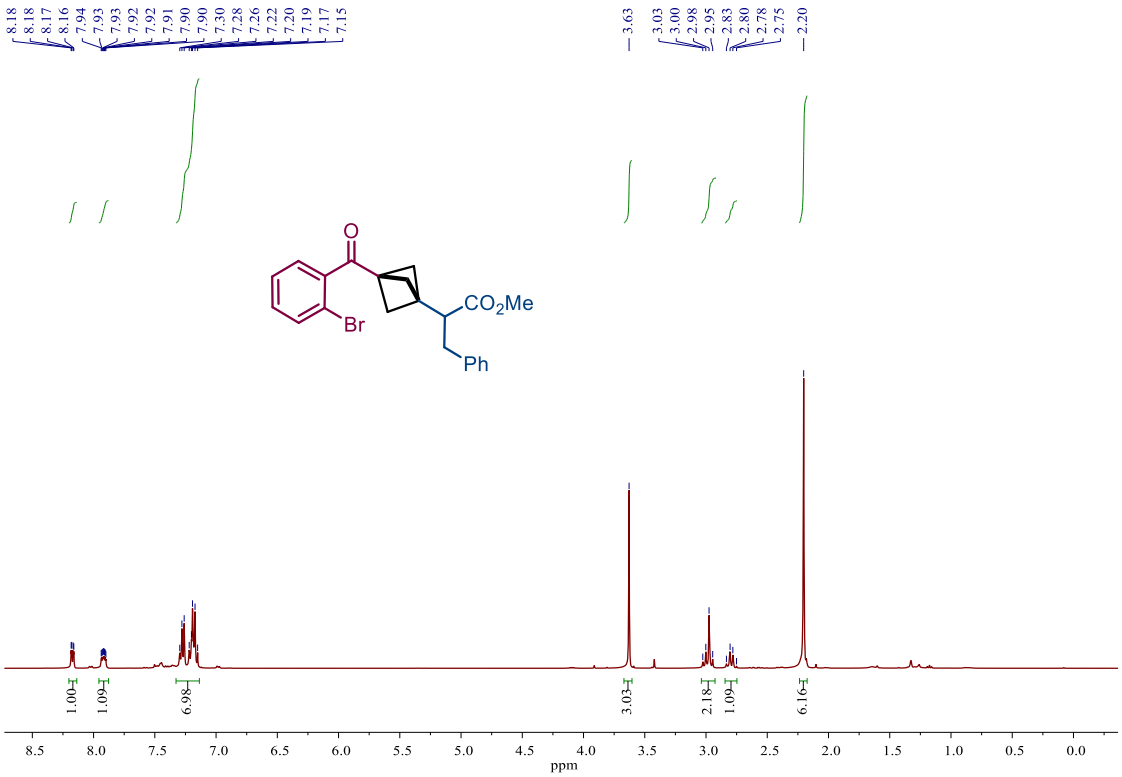
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 24



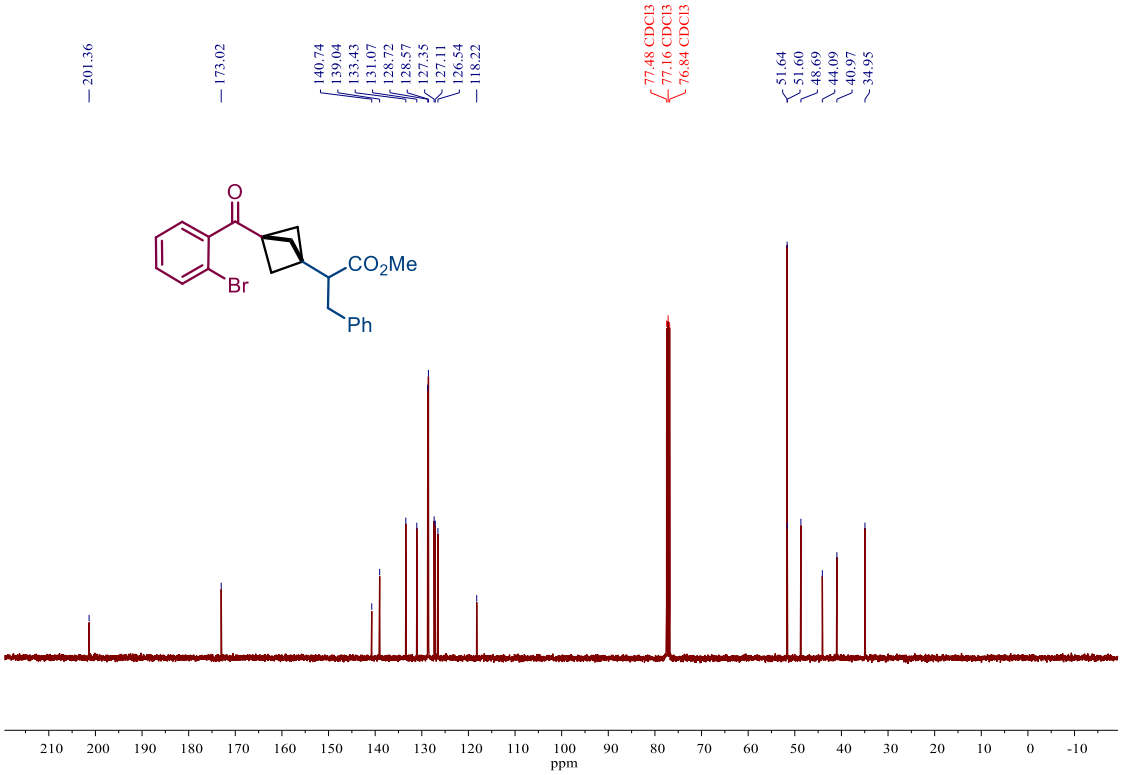
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 25



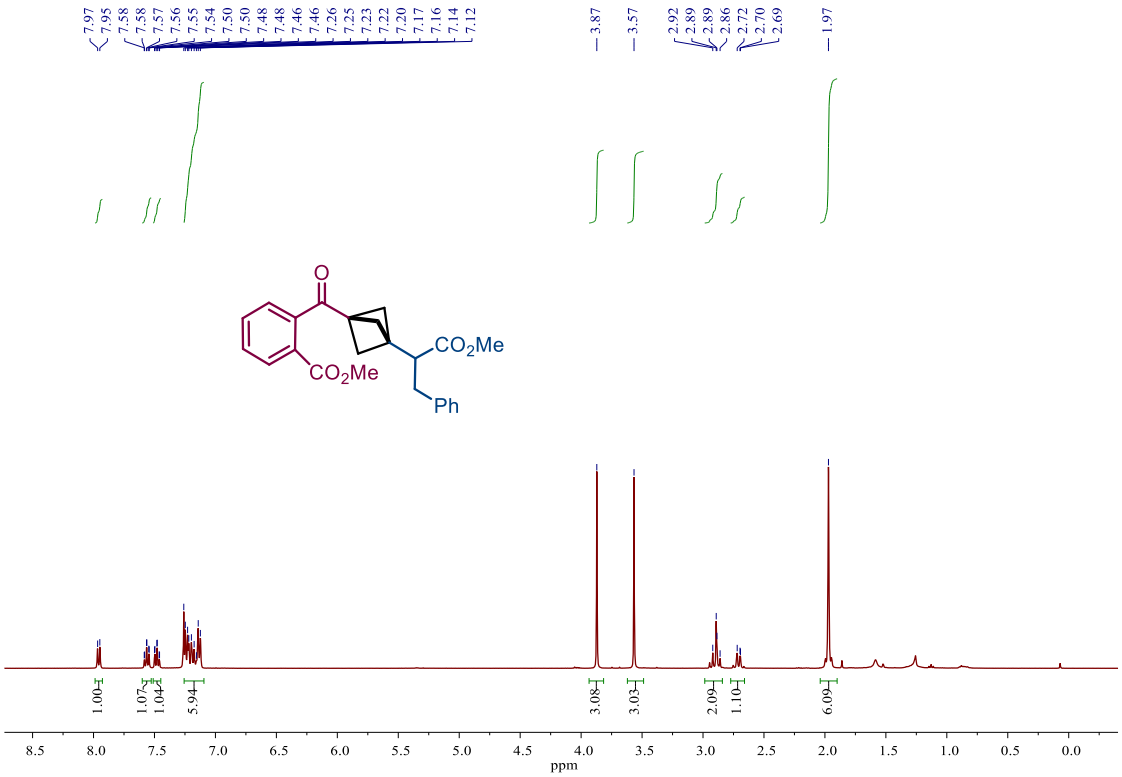
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 25



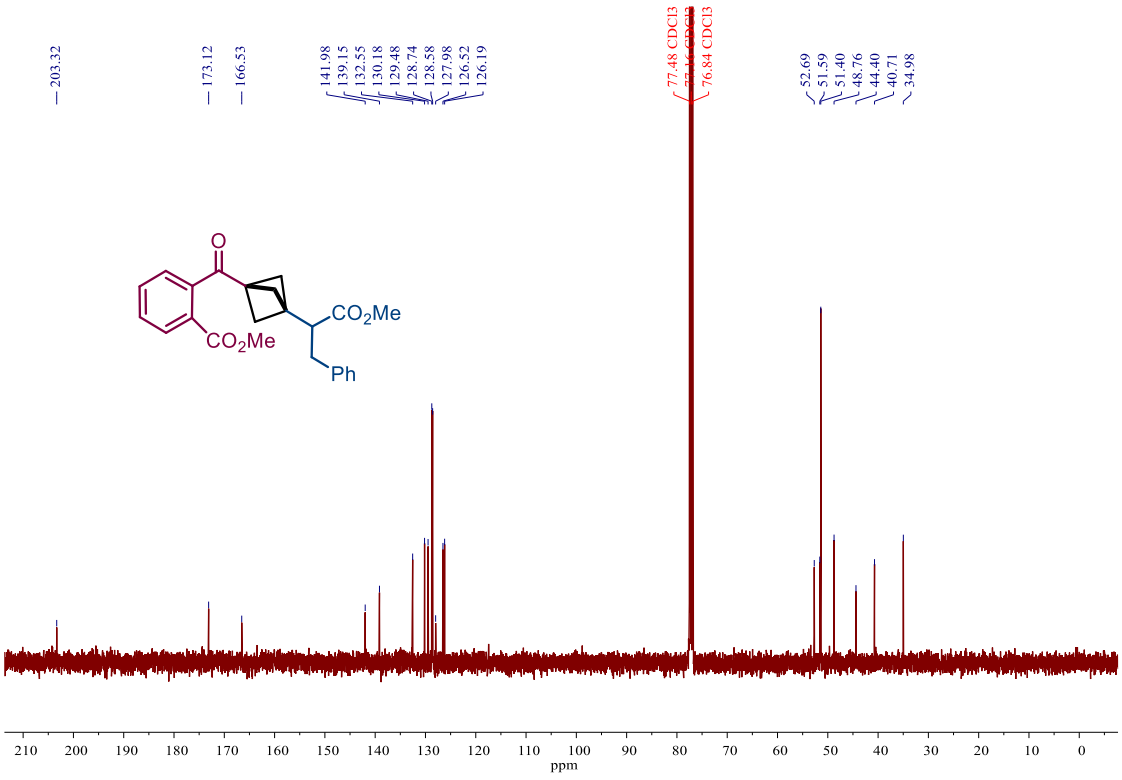
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 26



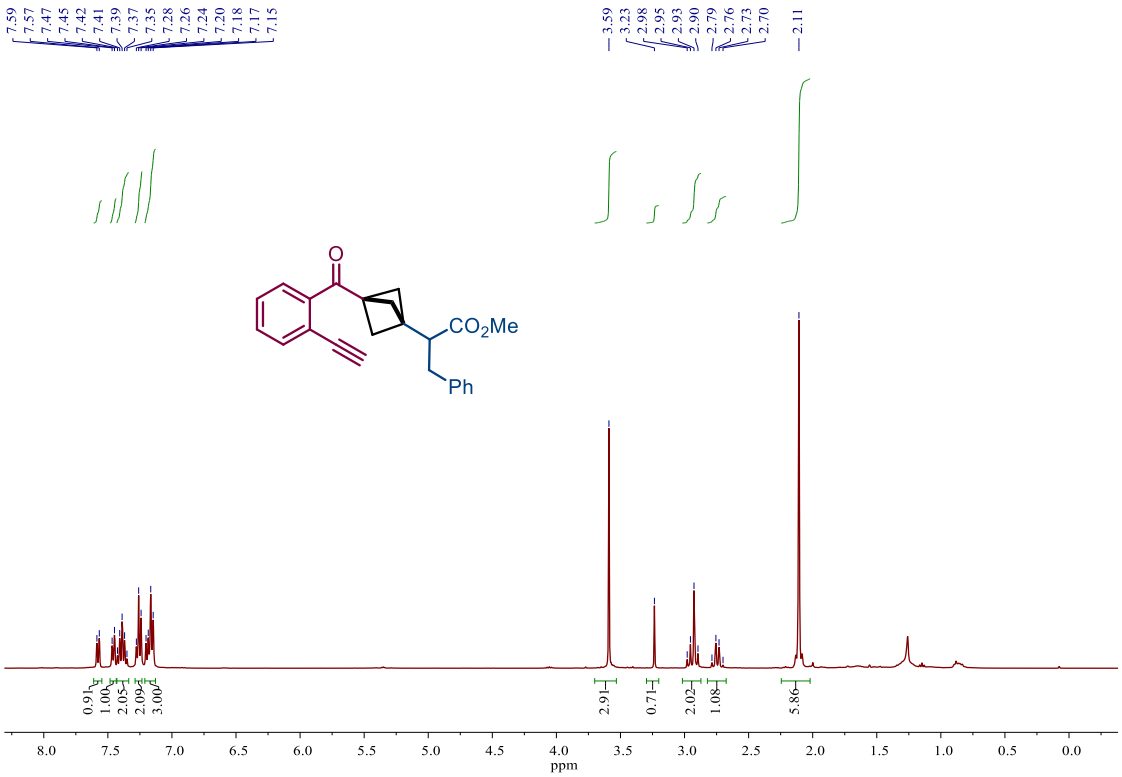
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 26



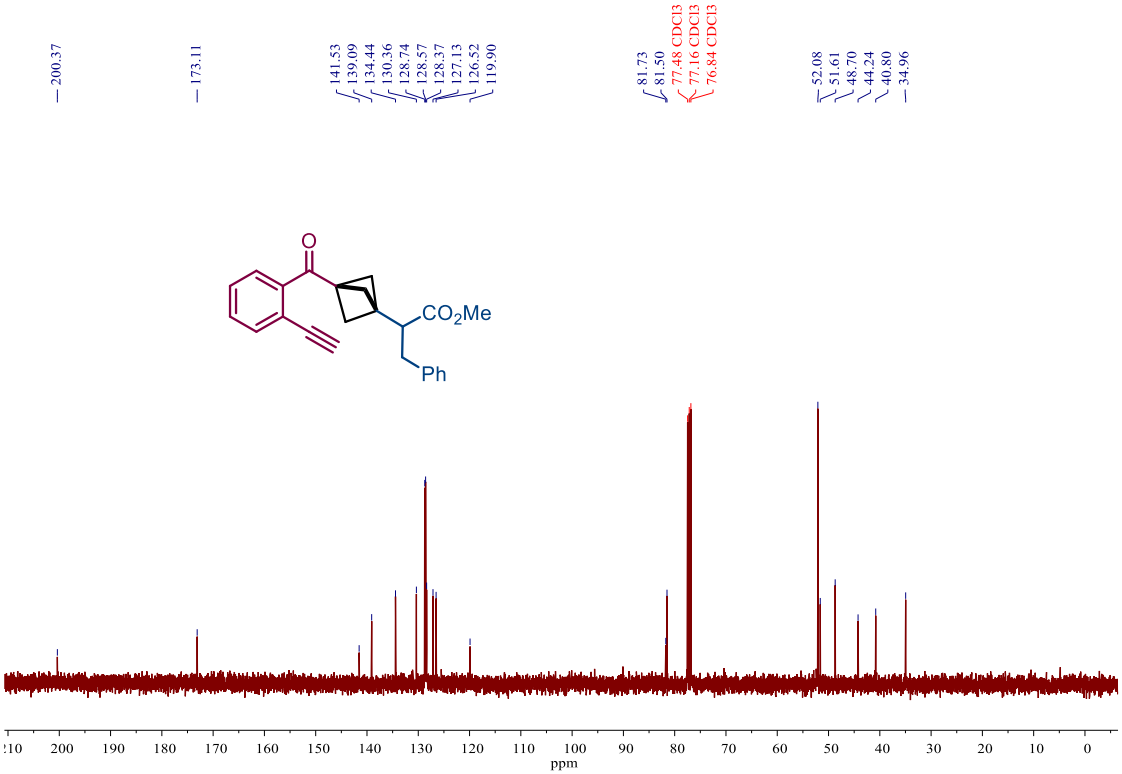
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 27



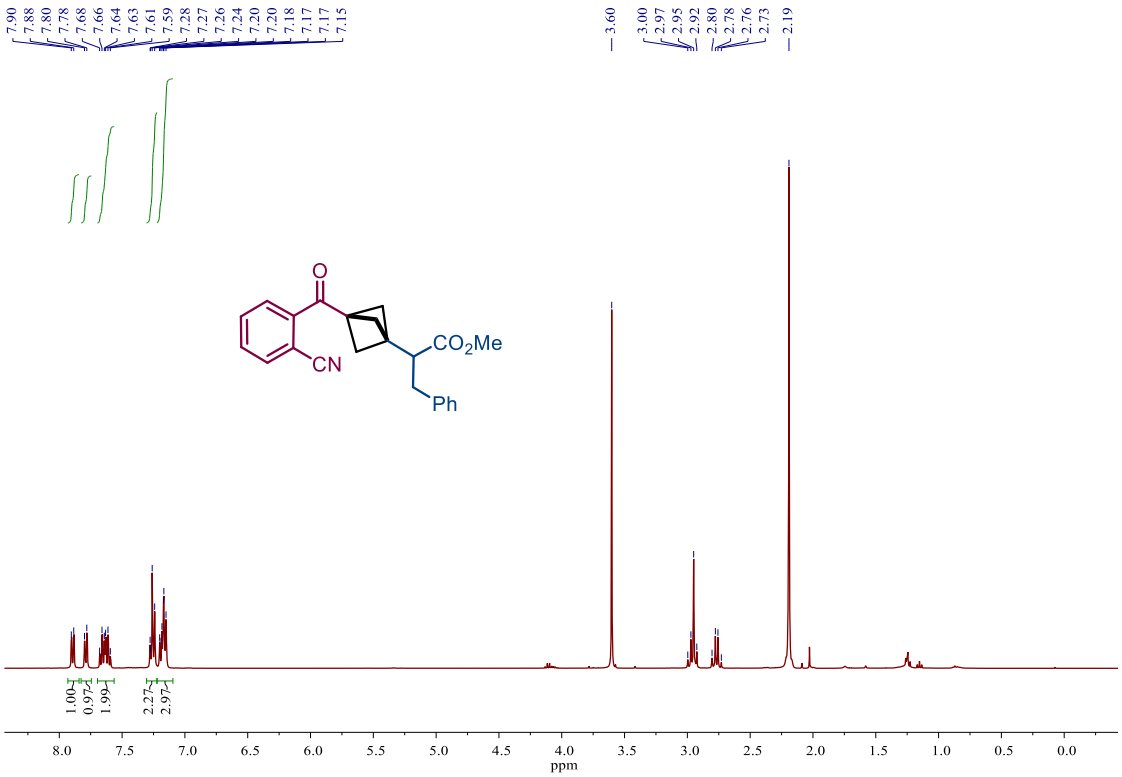
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 27



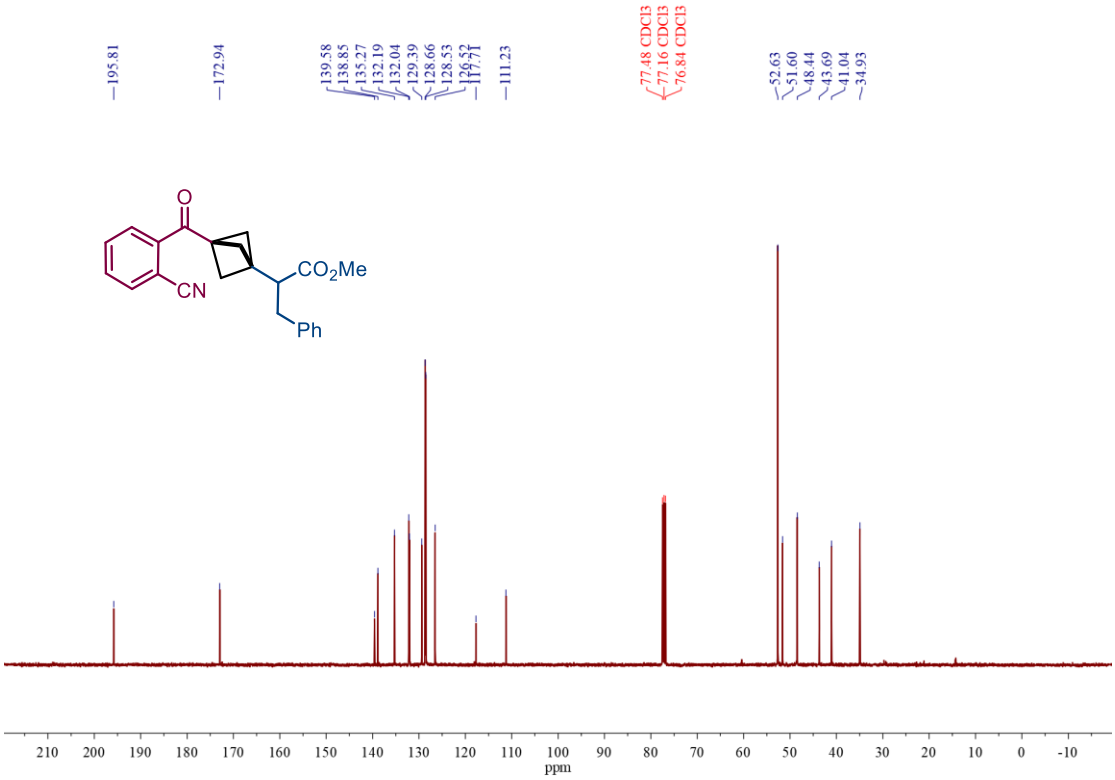
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 28



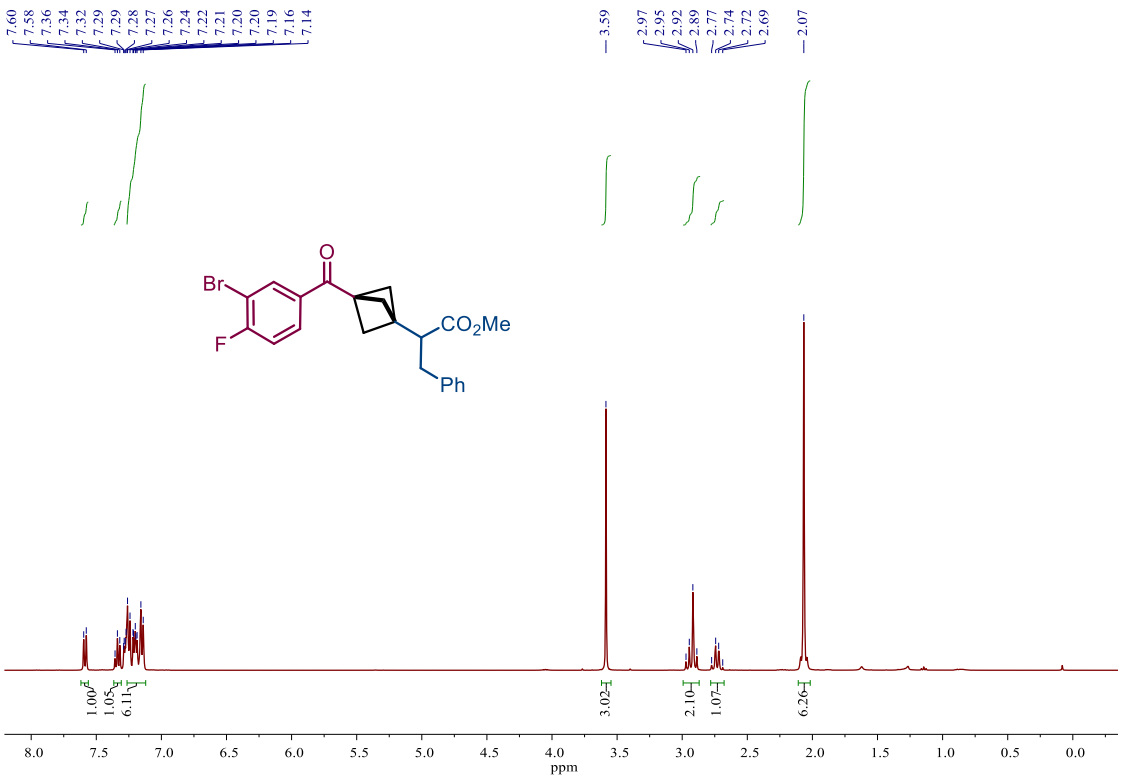
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 28



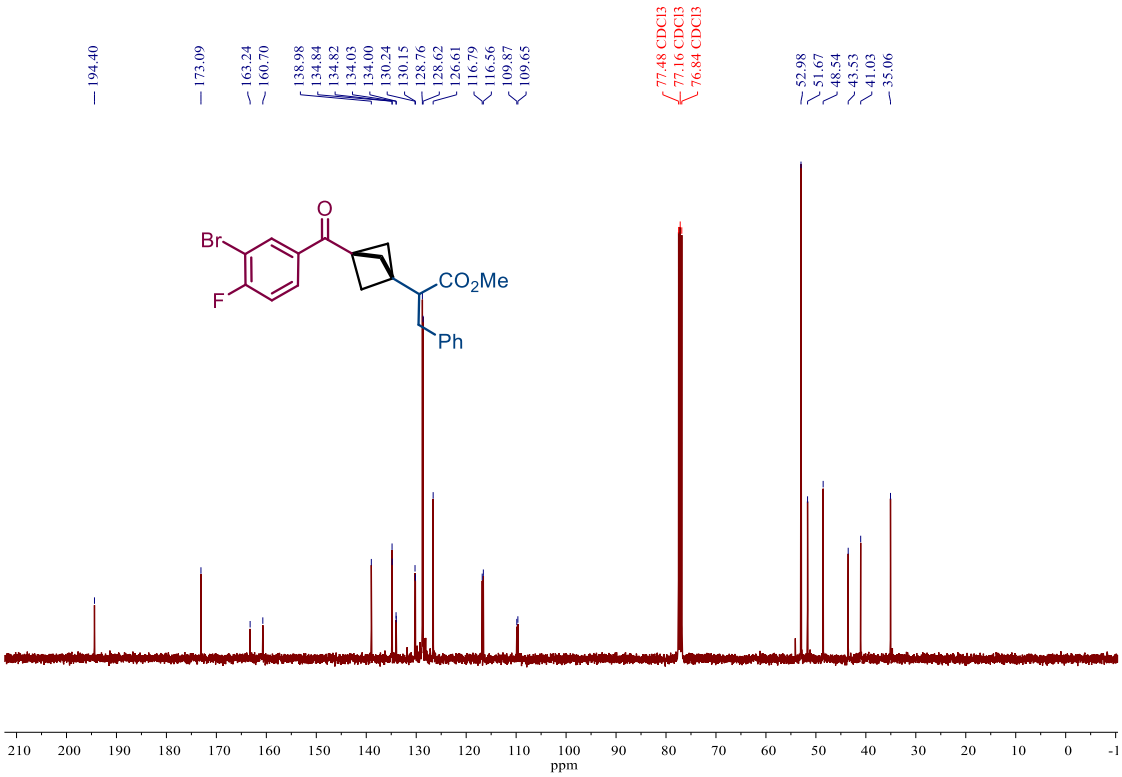
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 29



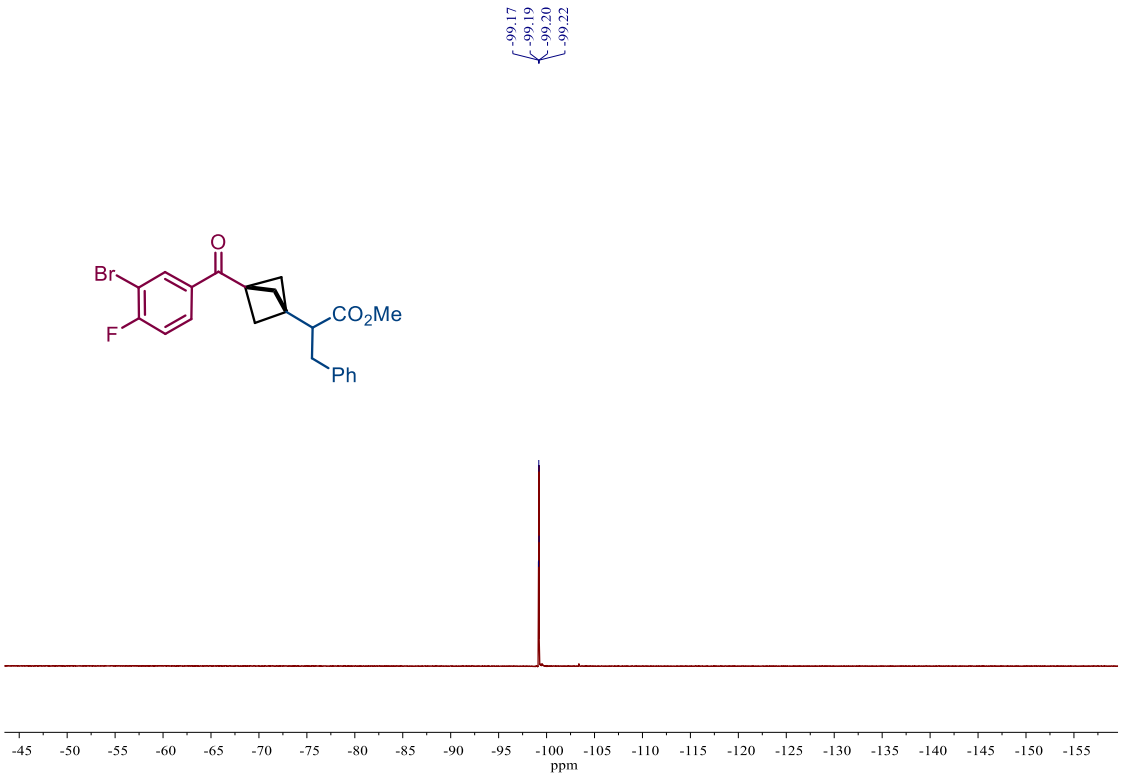
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 29



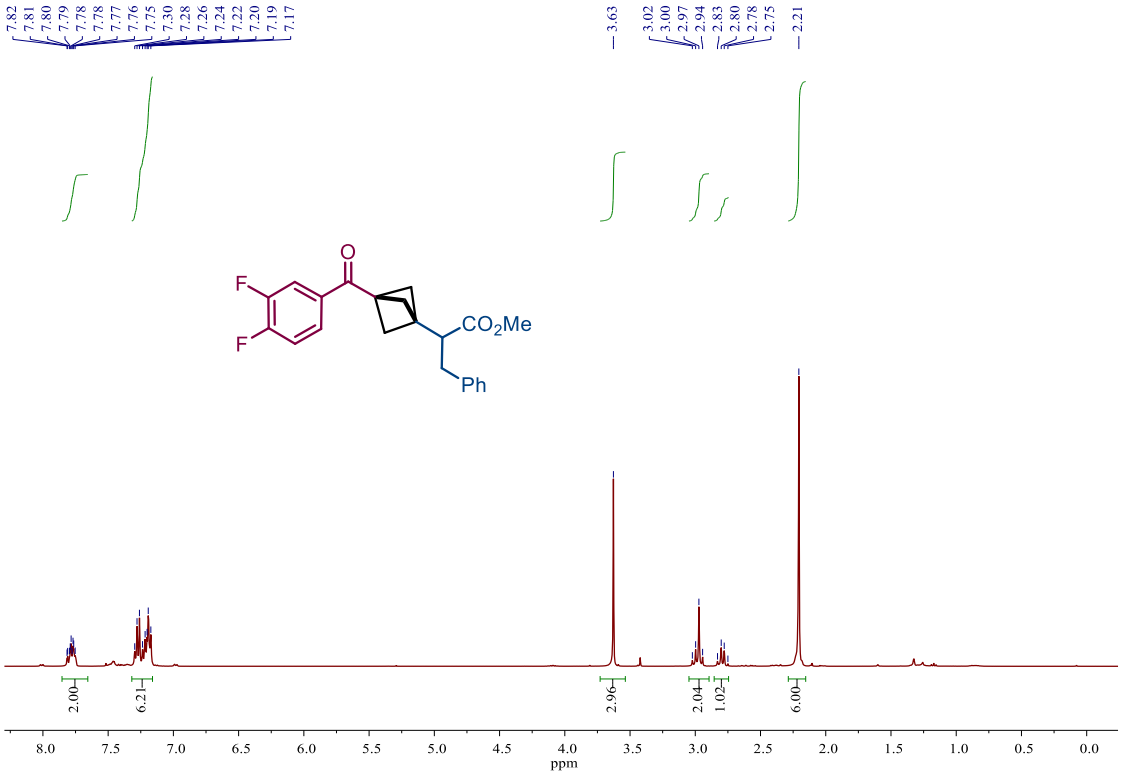
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 30



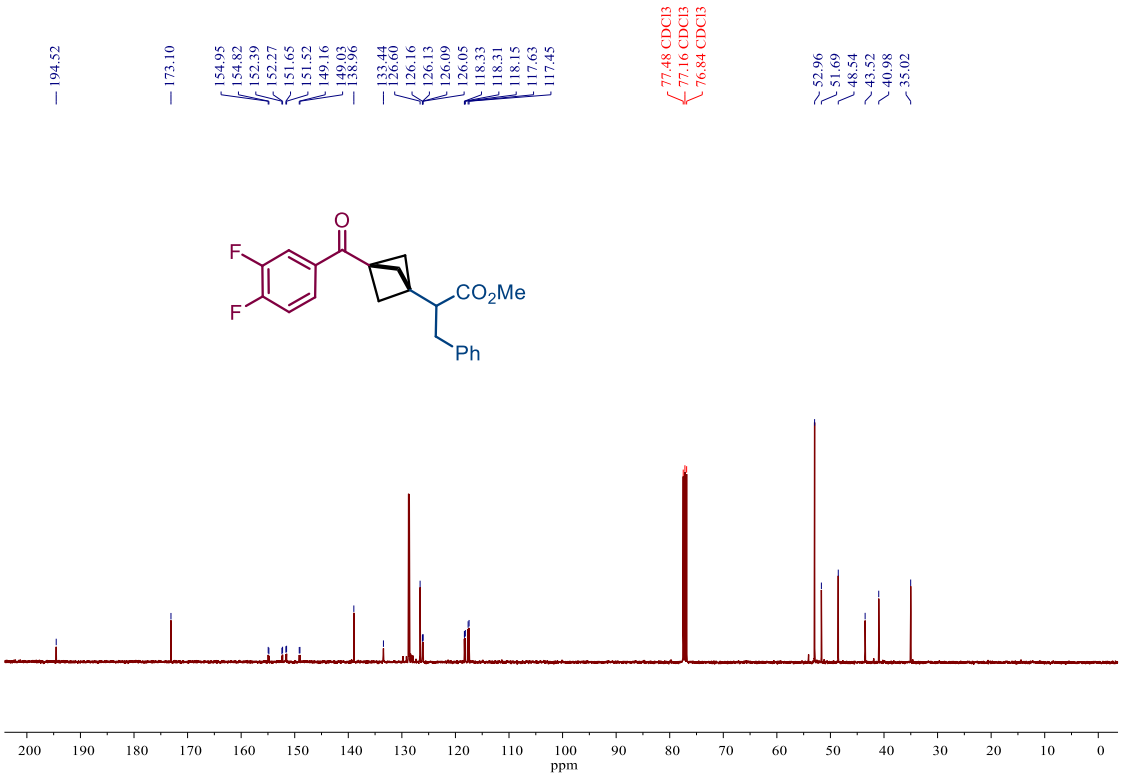
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 30



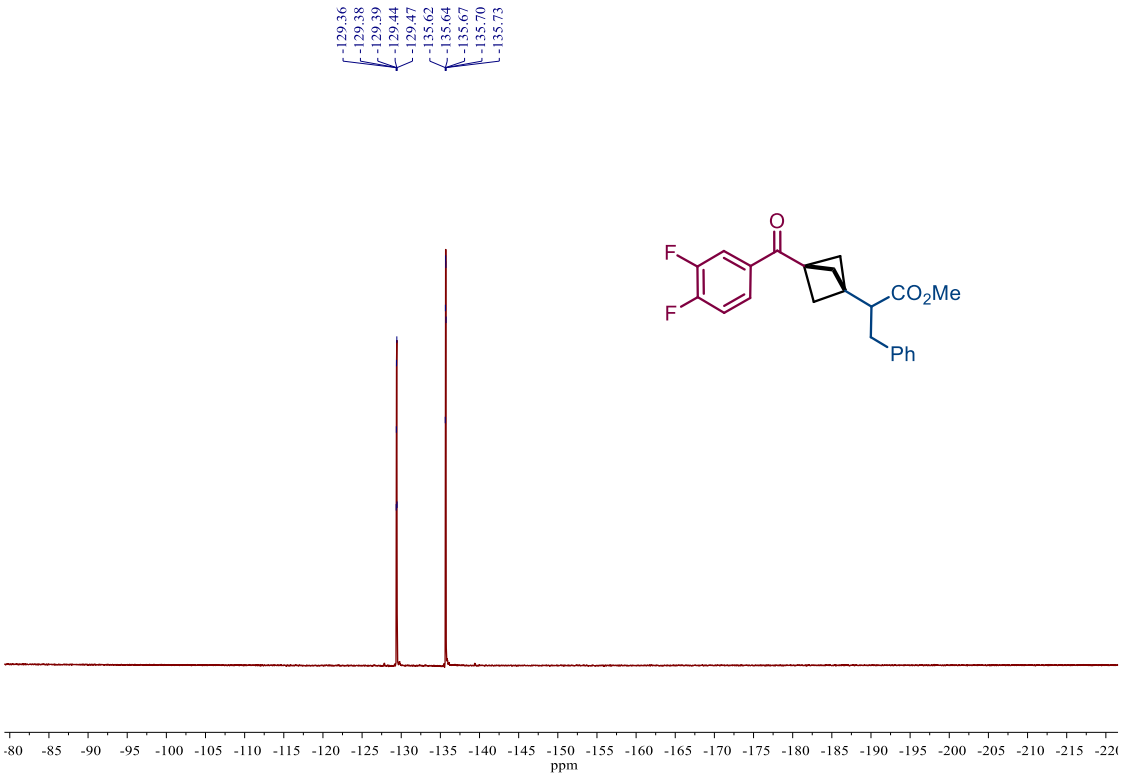
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 30



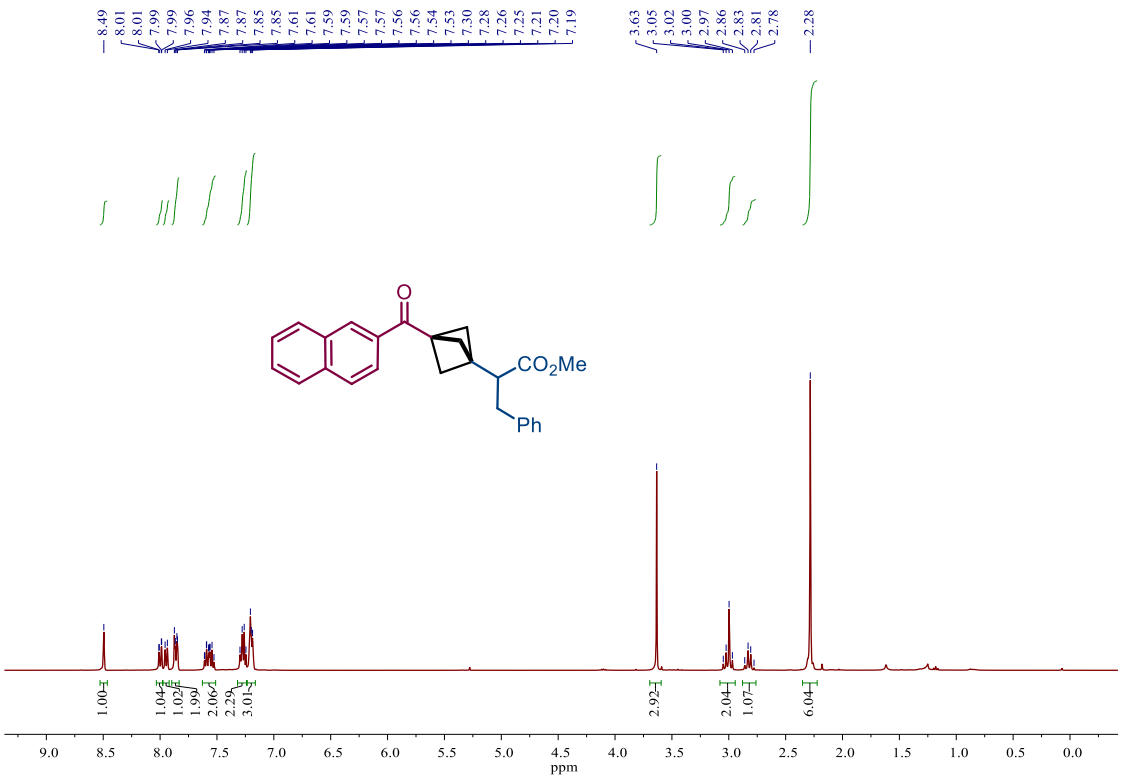
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 31



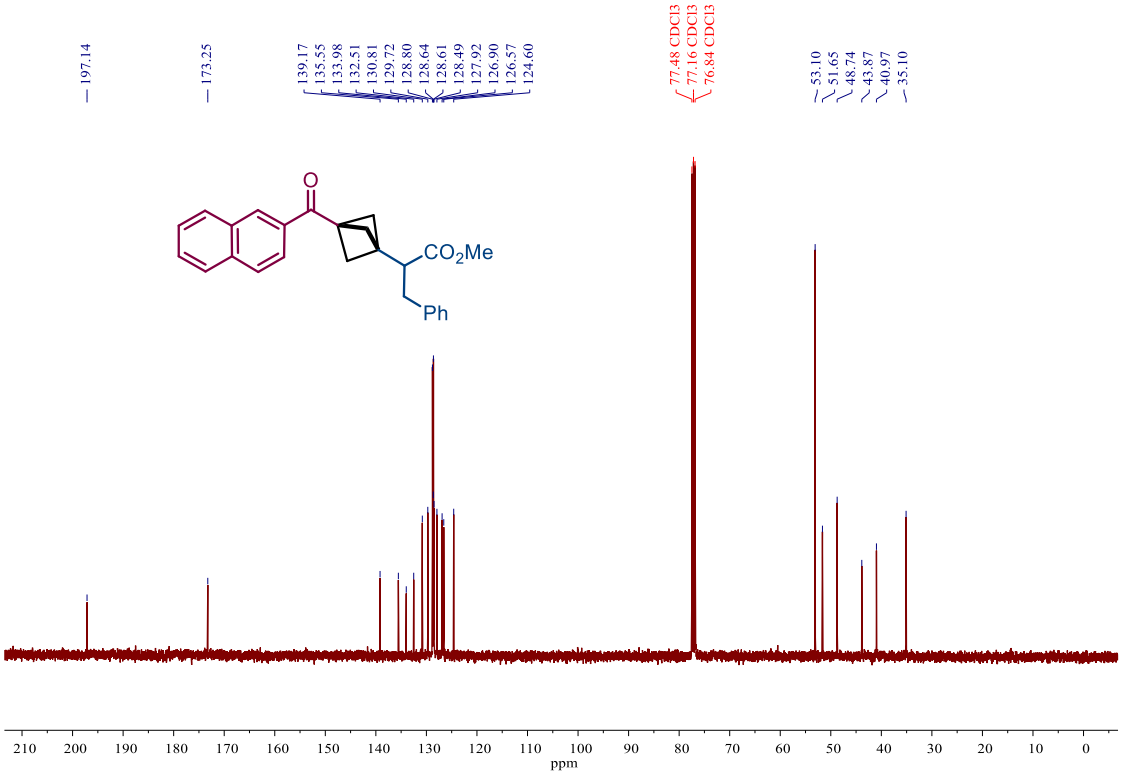
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 31



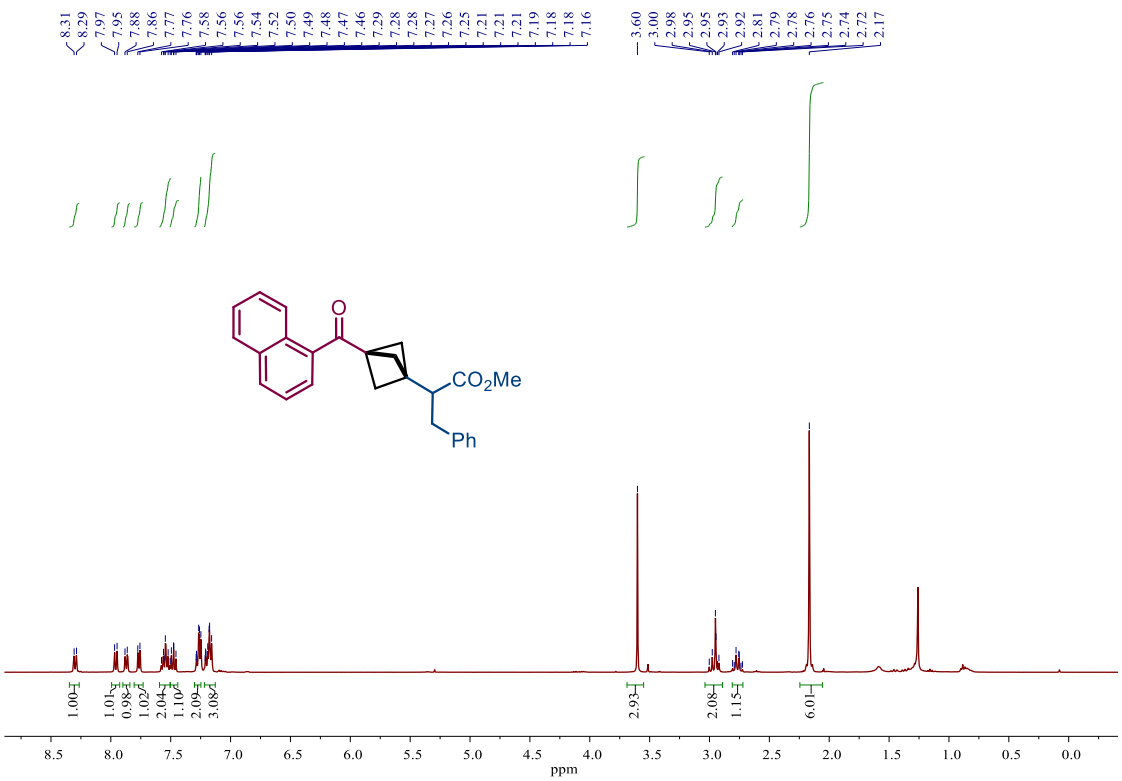
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 31



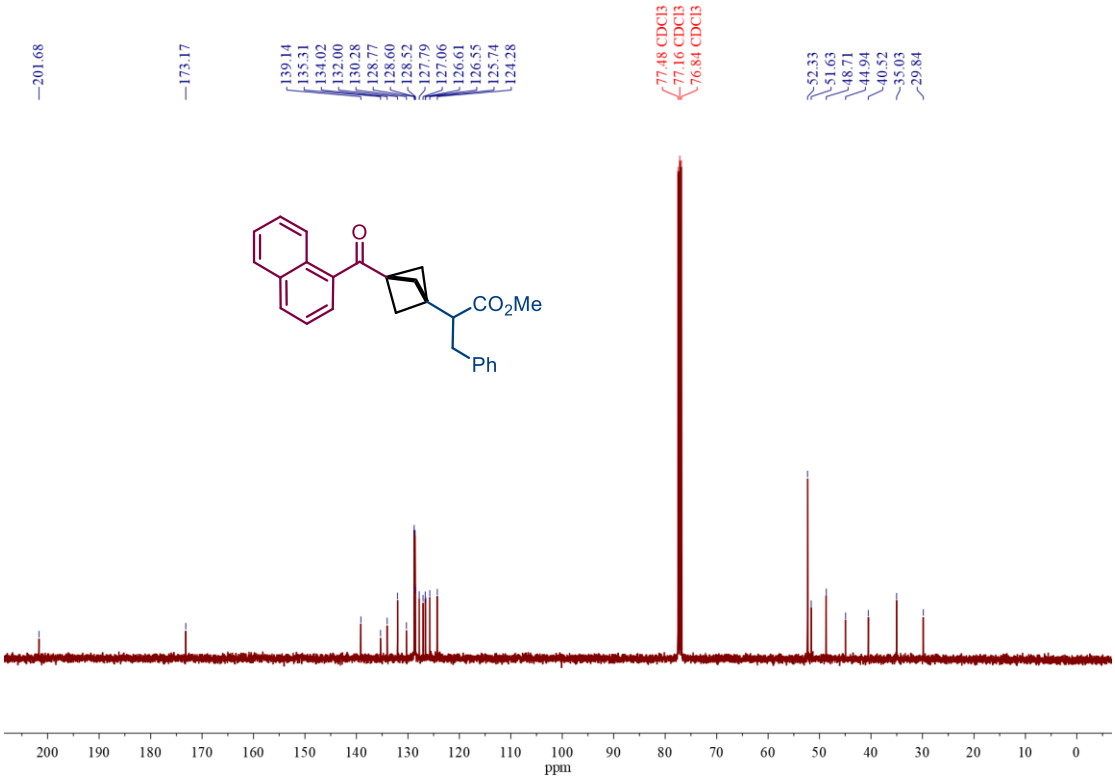
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 32



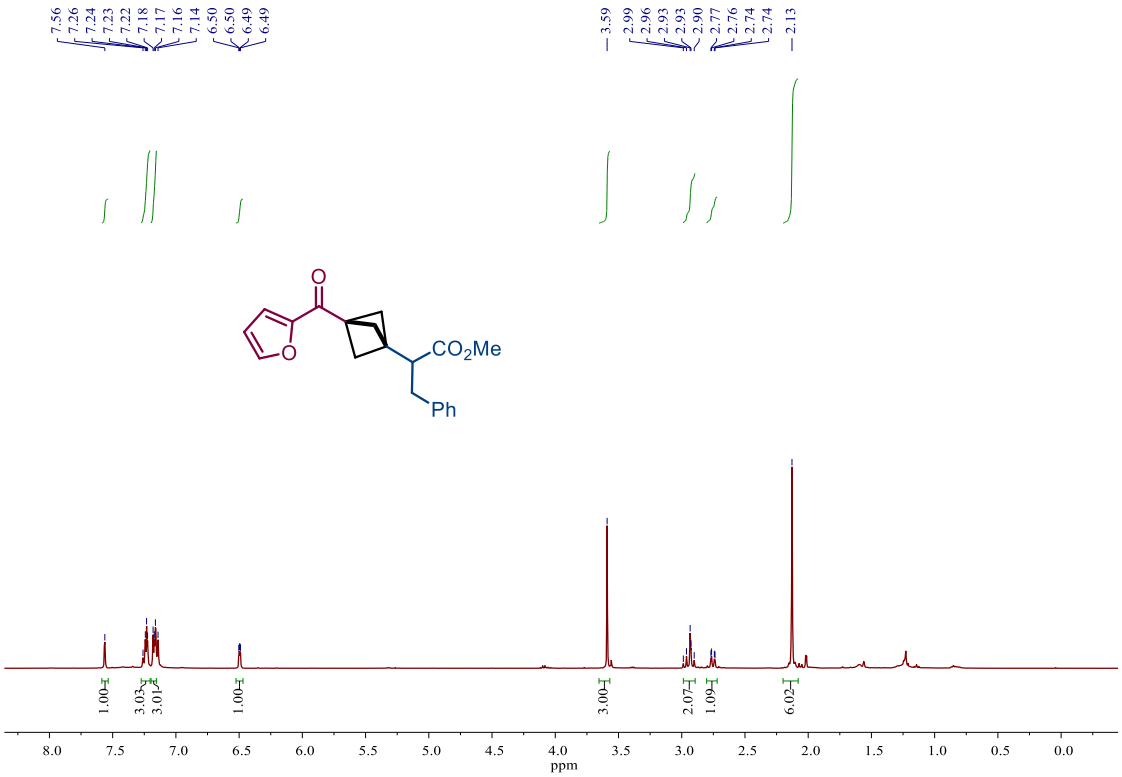
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 32



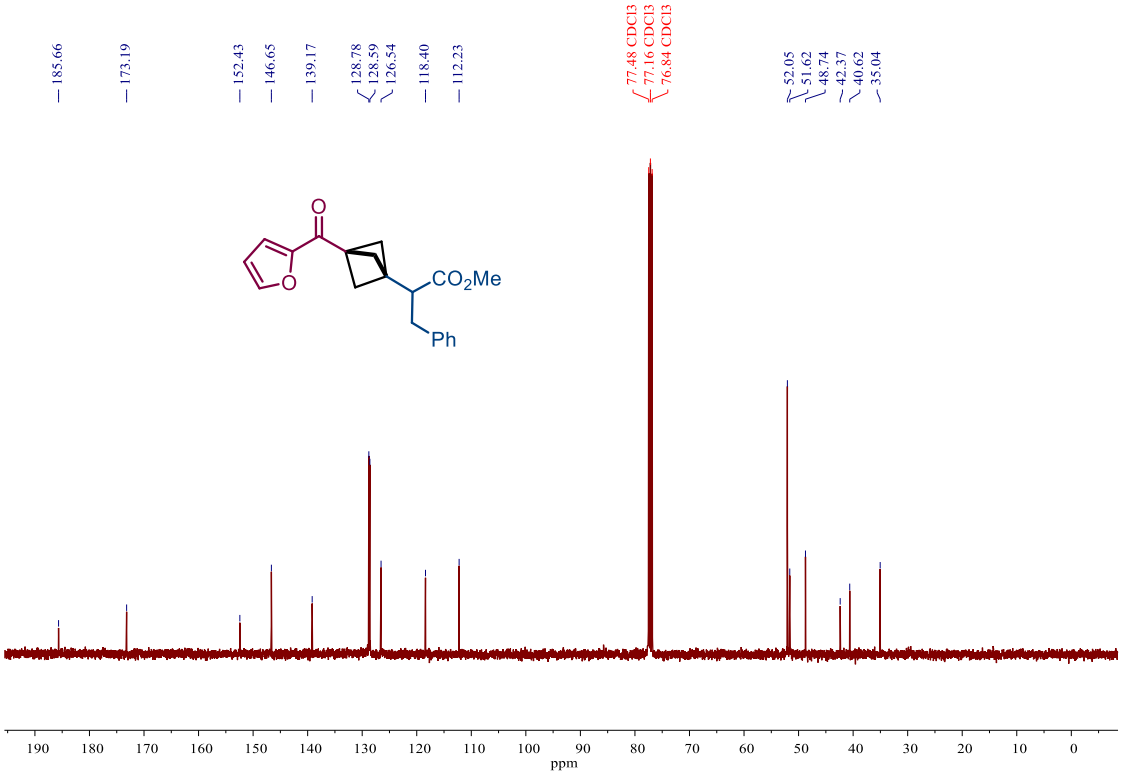
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 33



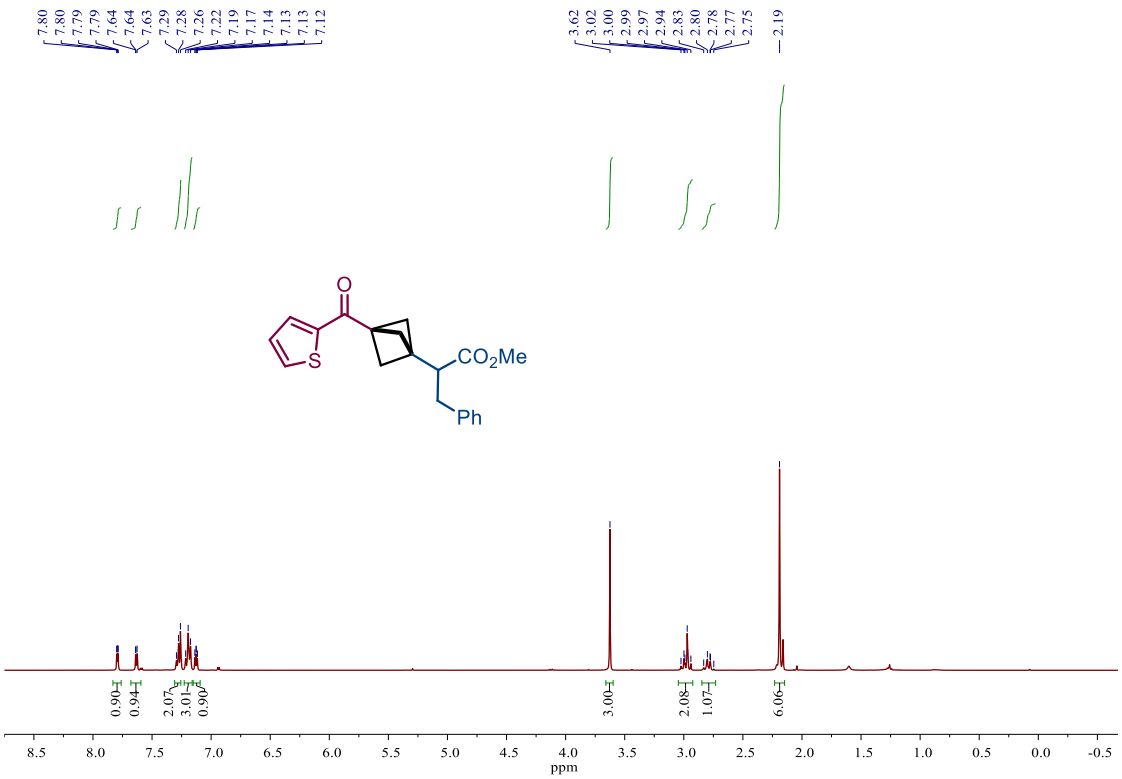
^{1}H NMR (100 MHz, $CDCl_3$) spectrum of compound 33



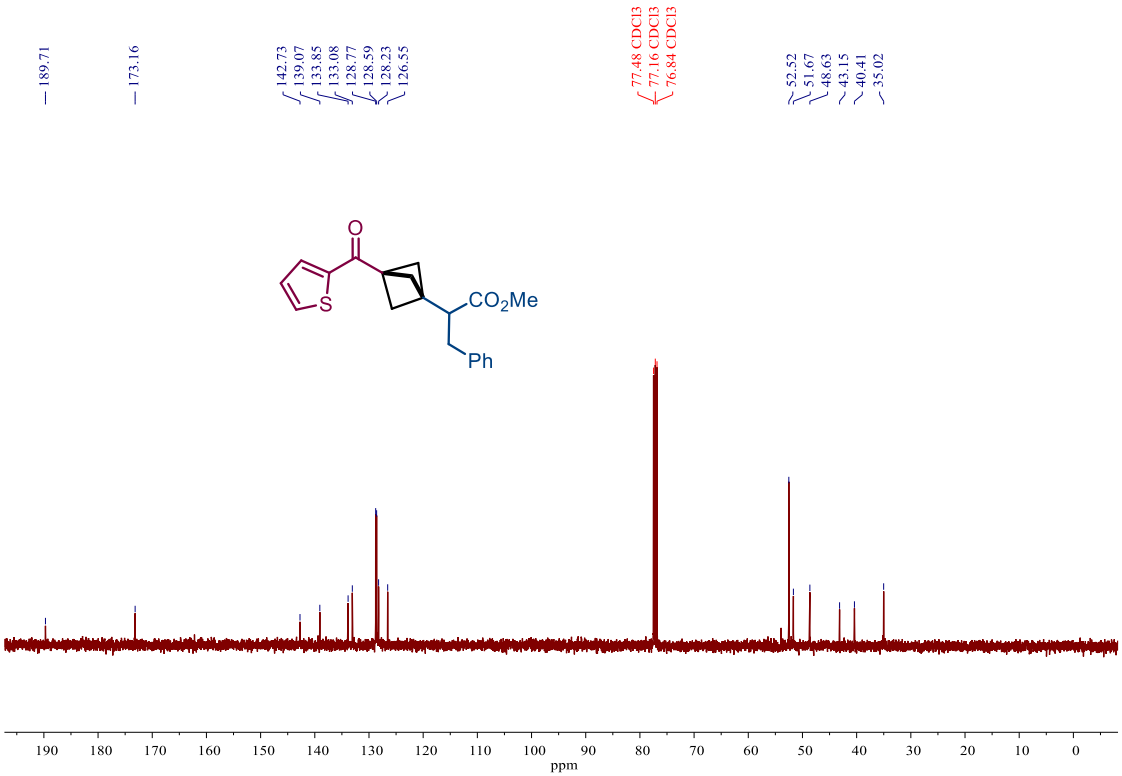
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 34



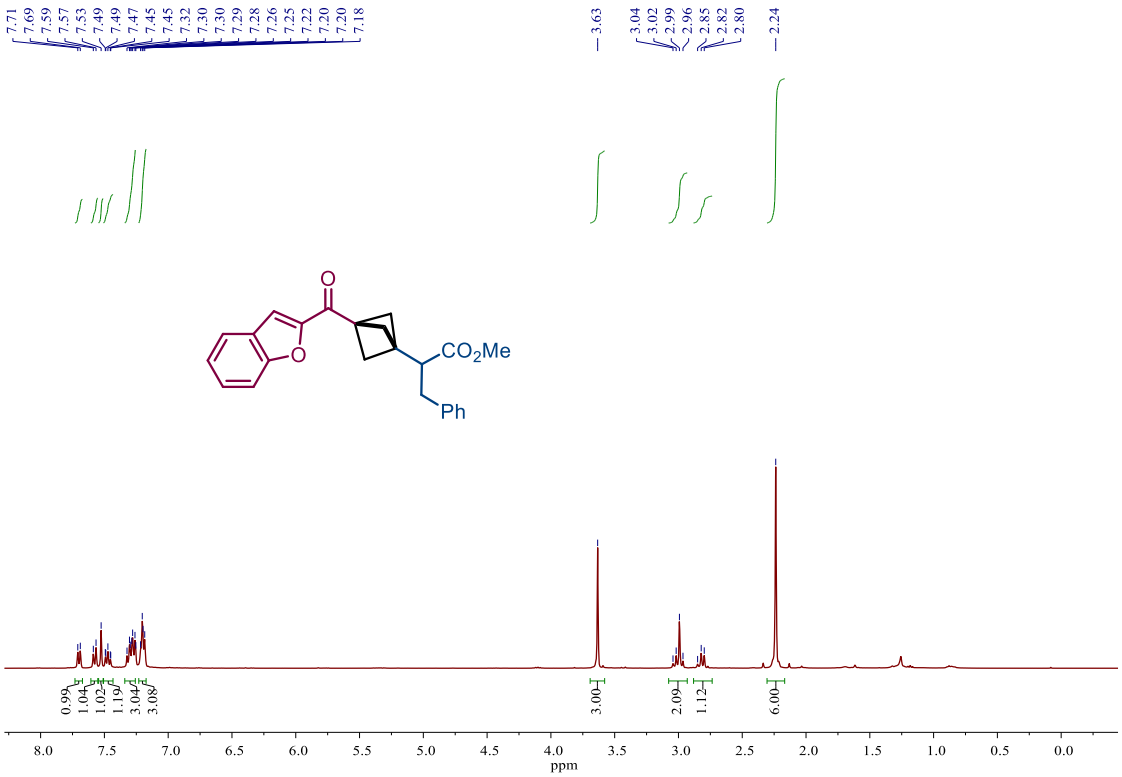
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 34



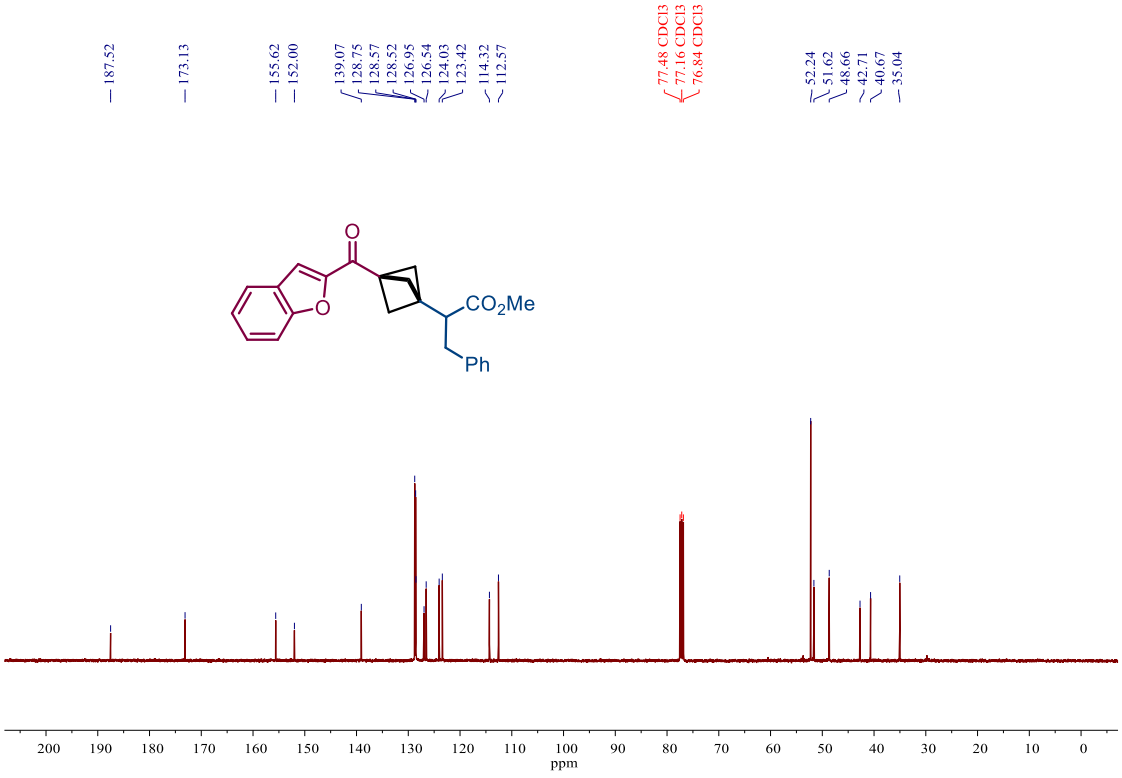
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 35



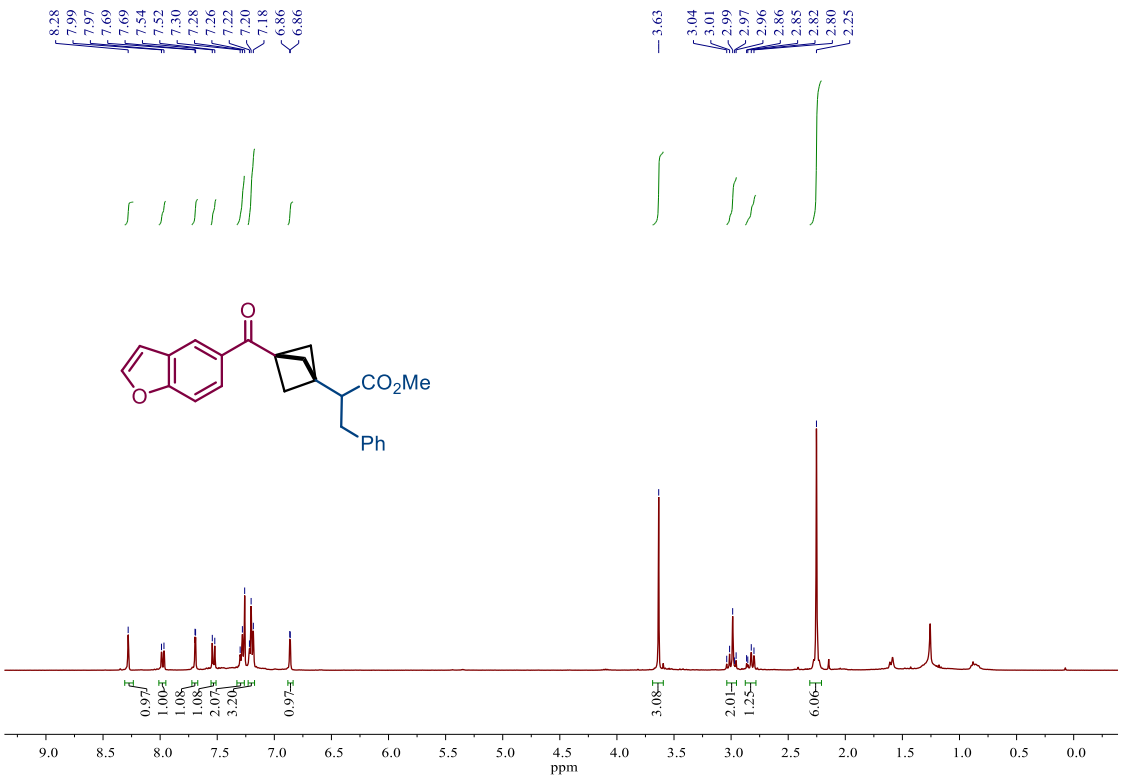
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 35



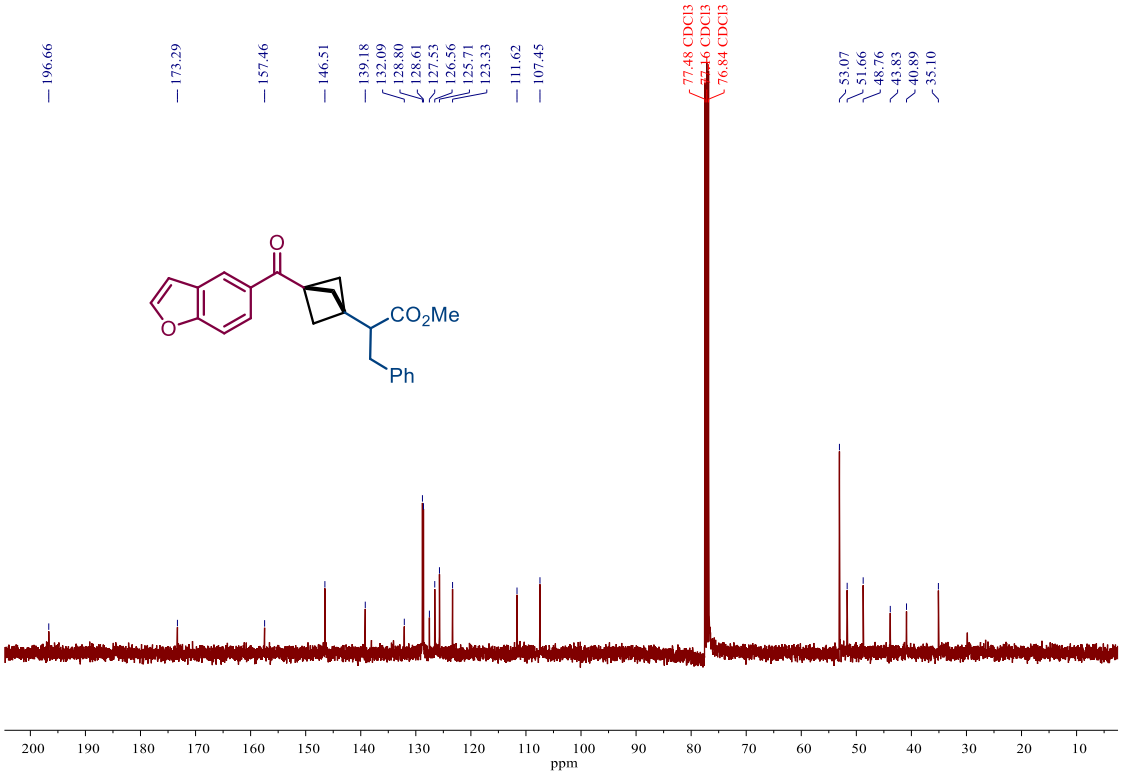
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 36



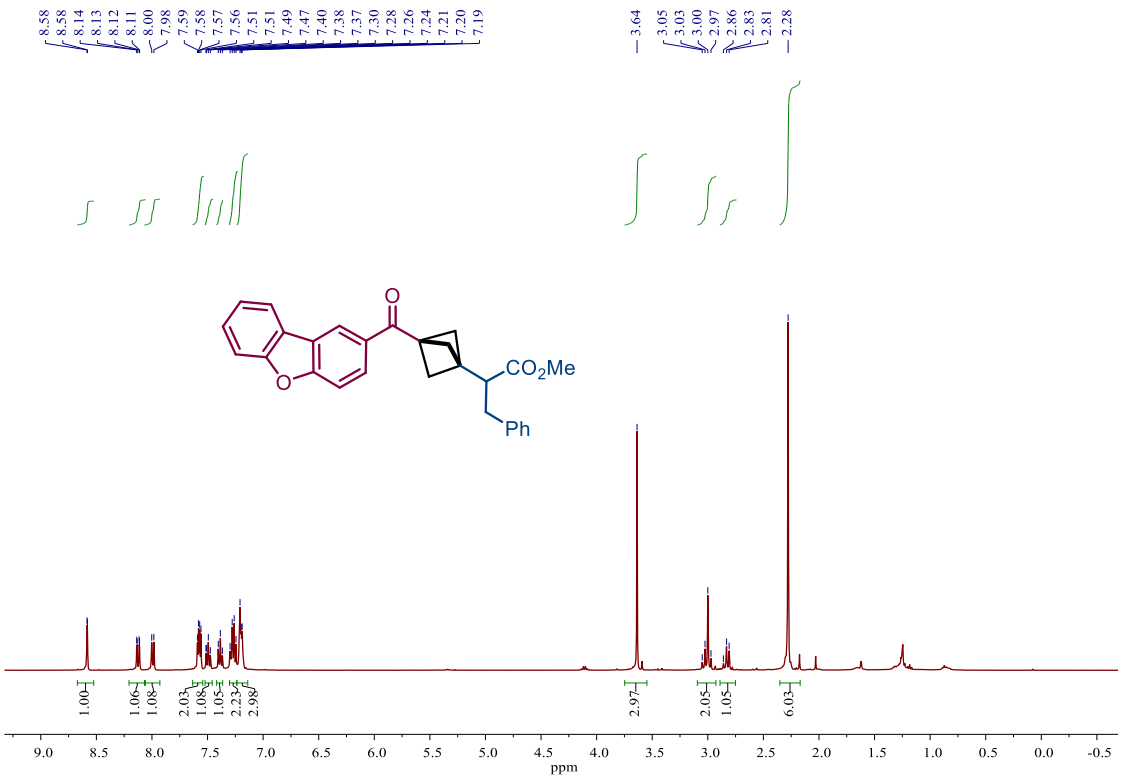
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 36



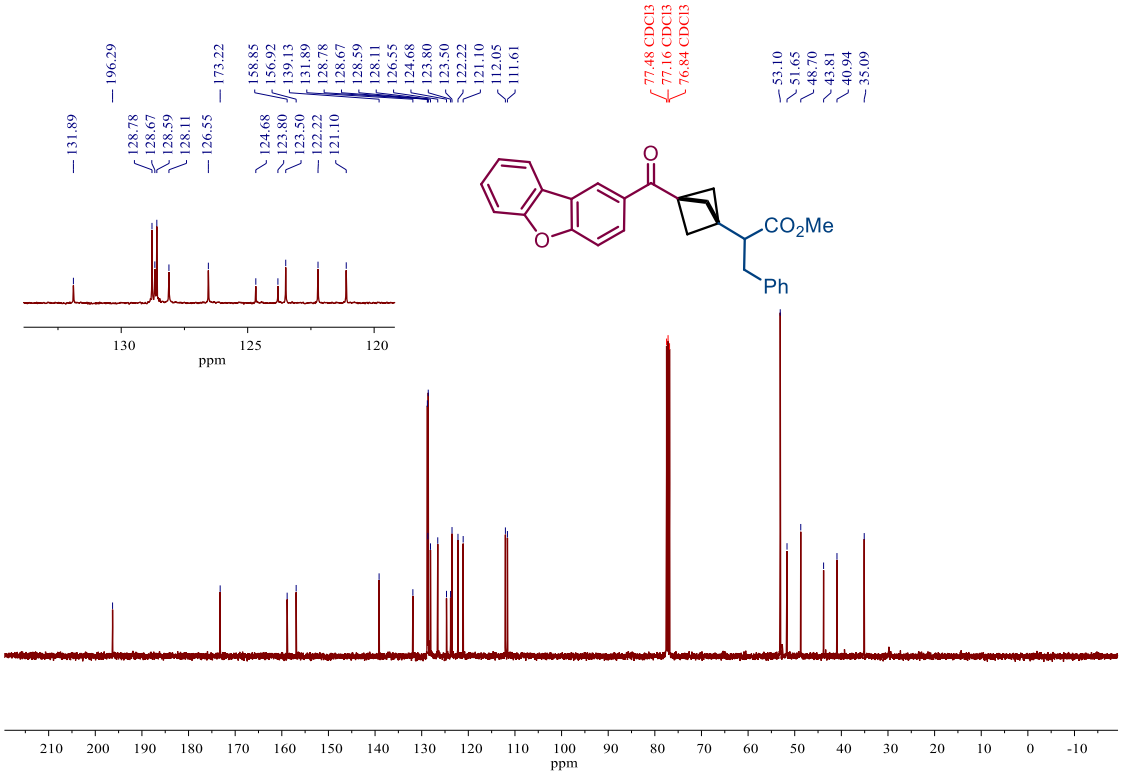
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 37



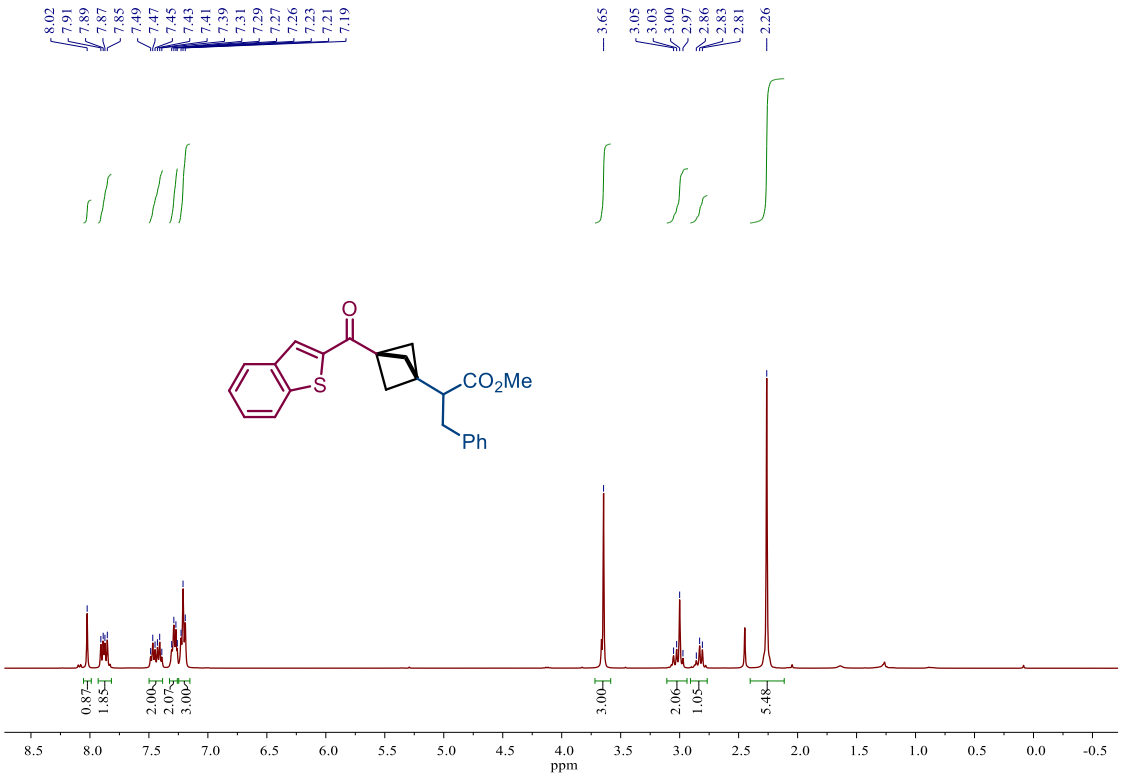
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 37



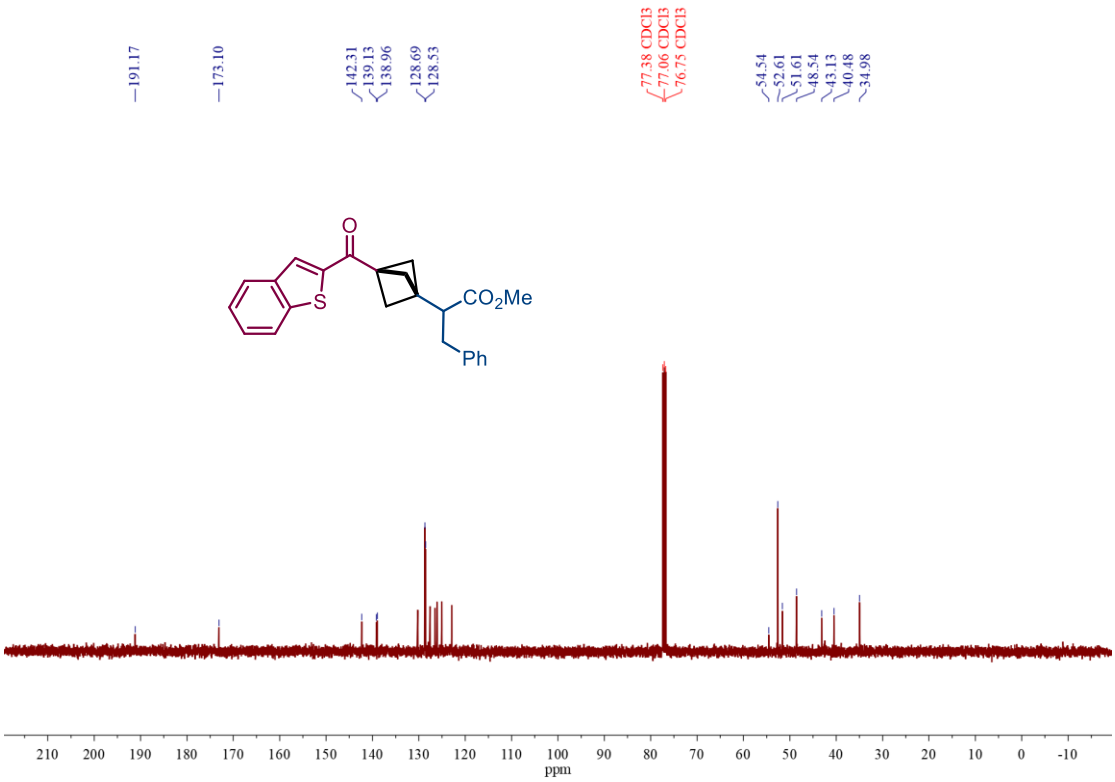
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 38



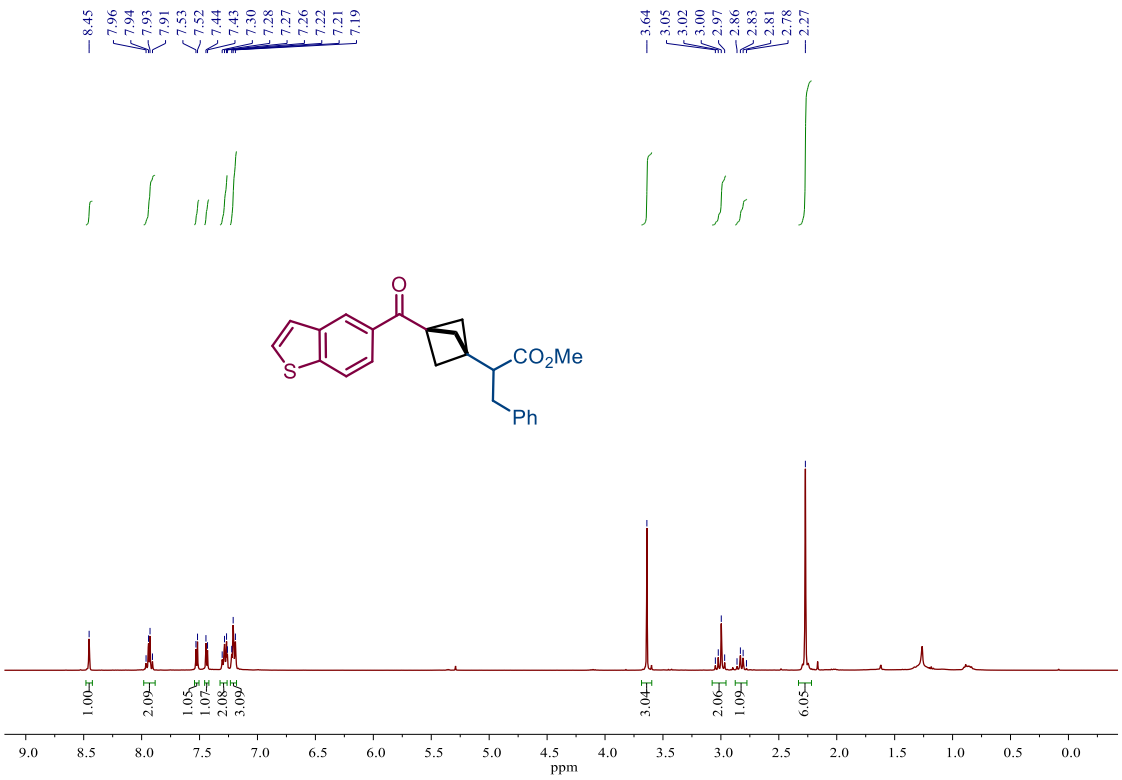
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 38



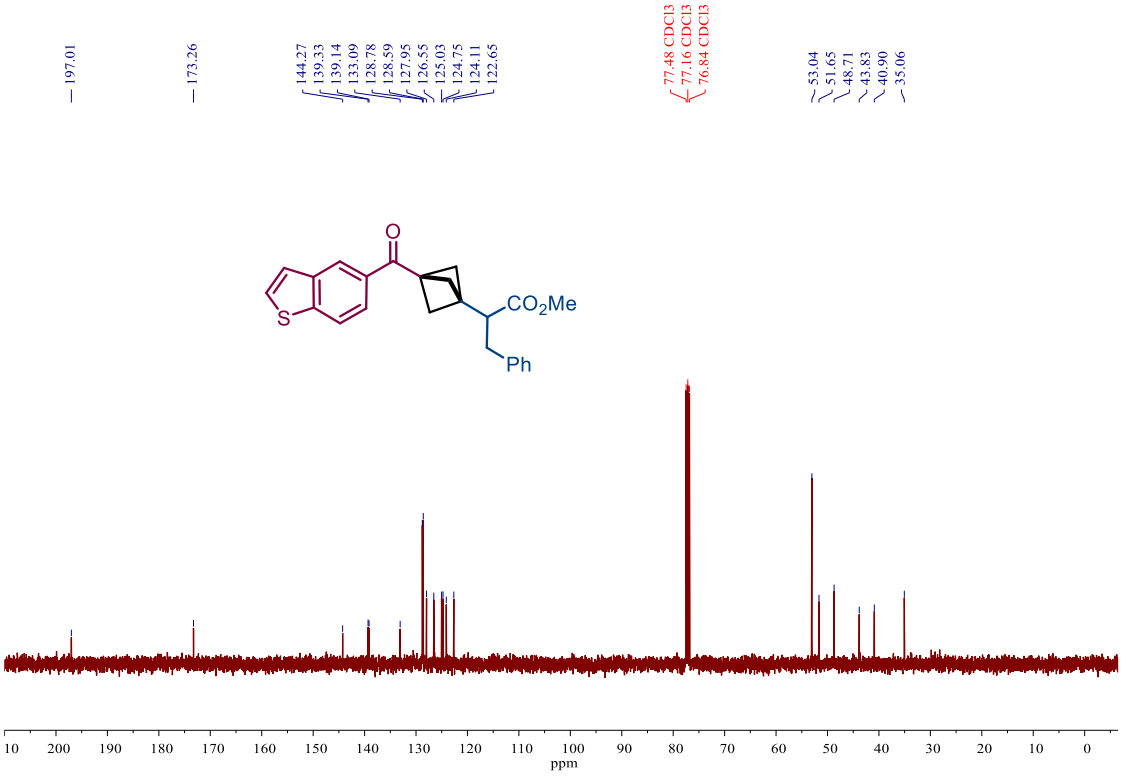
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 39



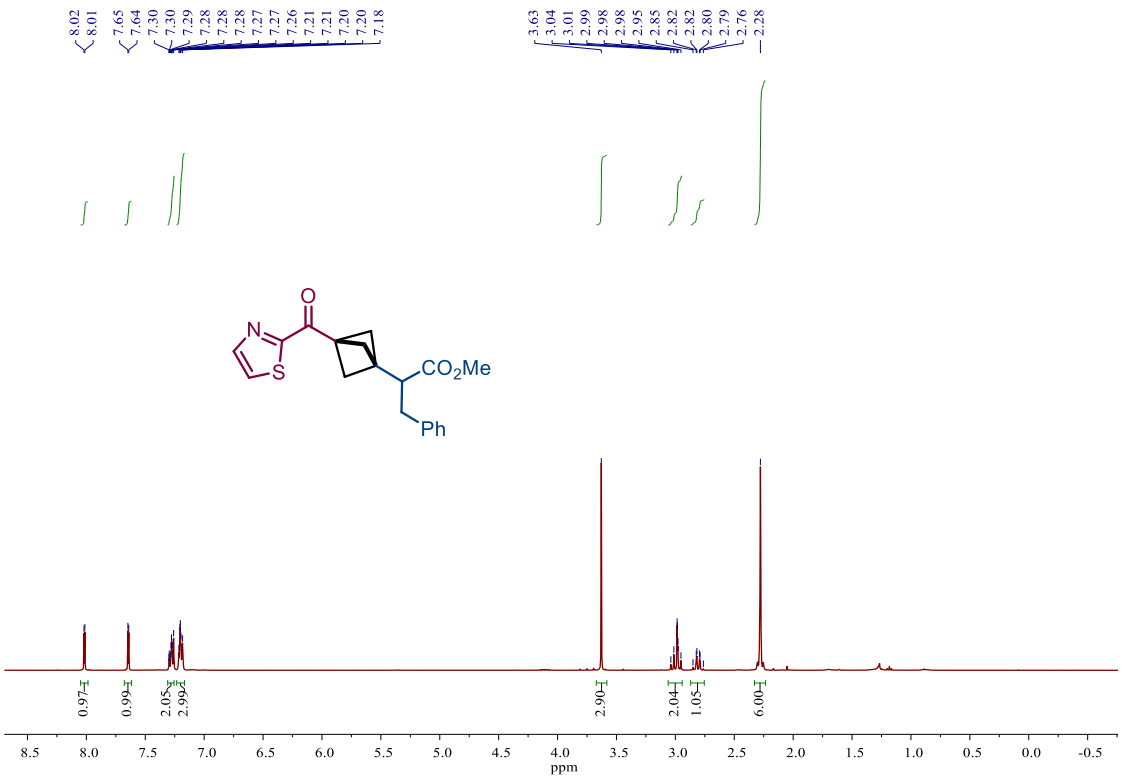
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 39



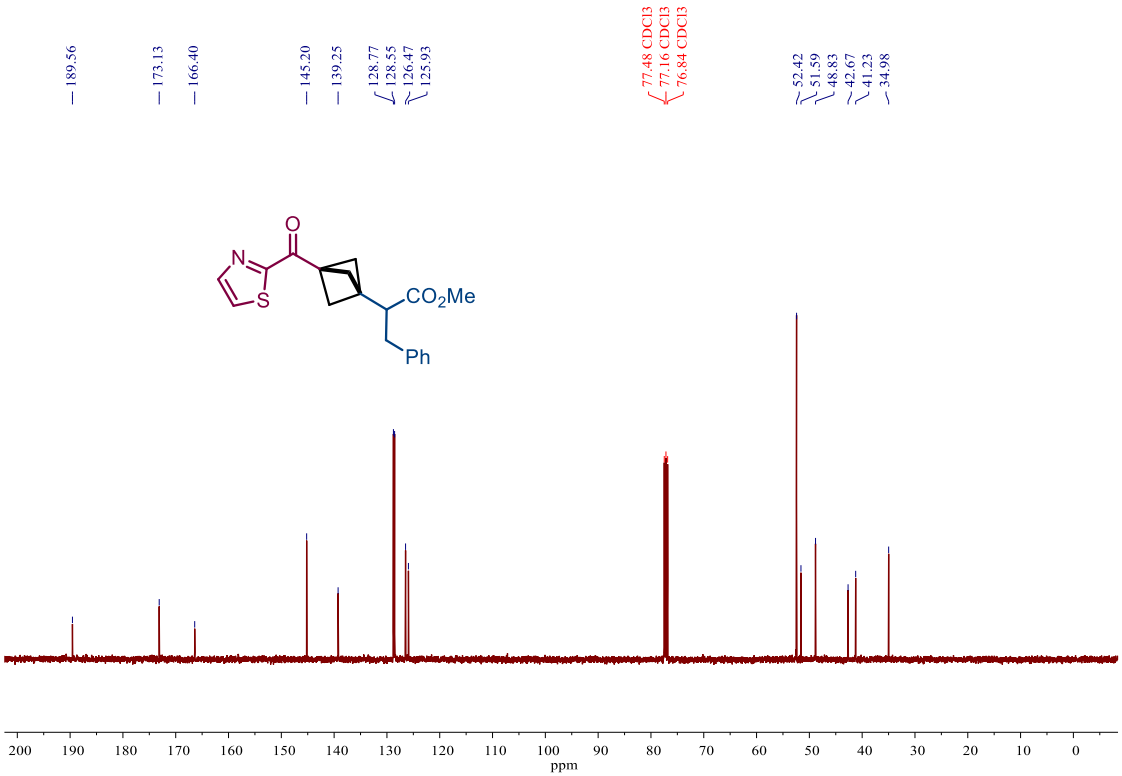
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 40



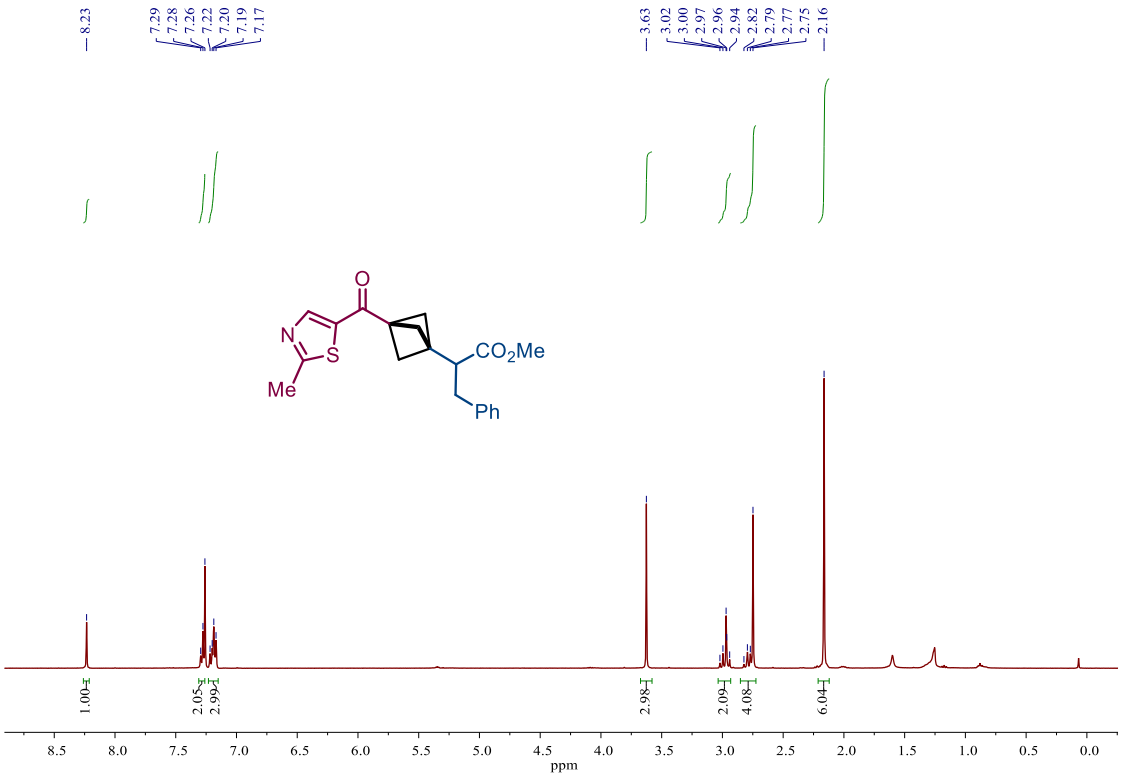
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 40



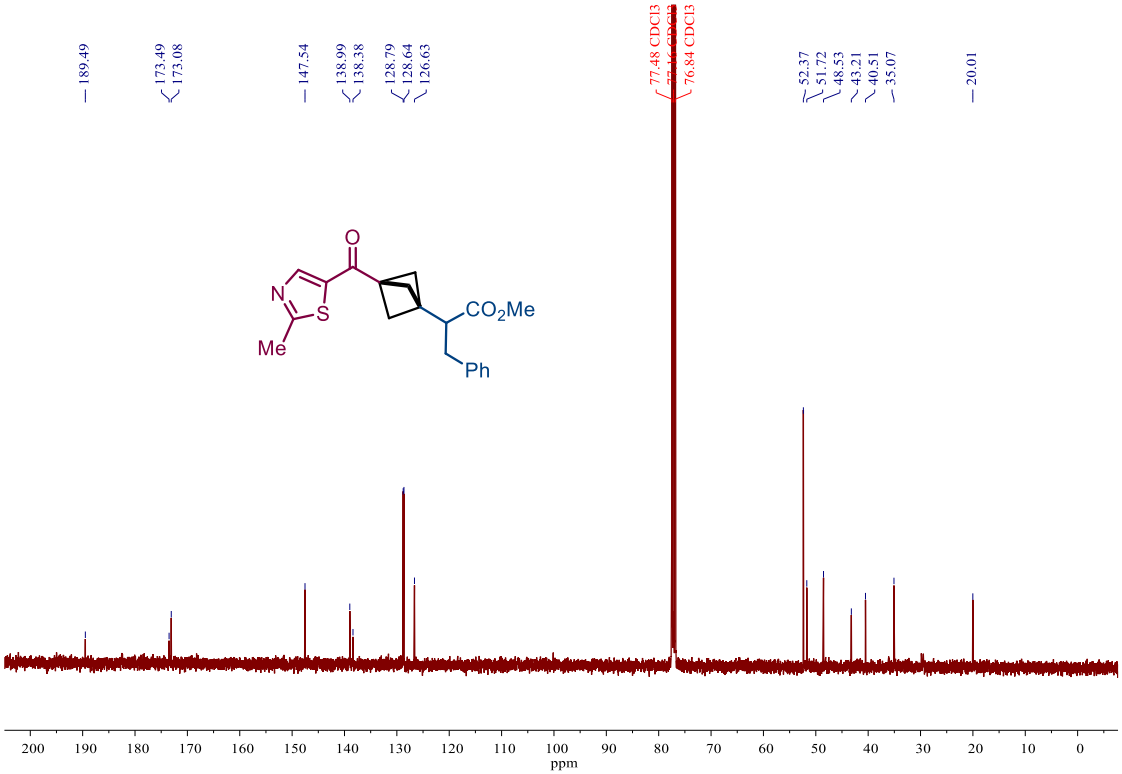
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 41



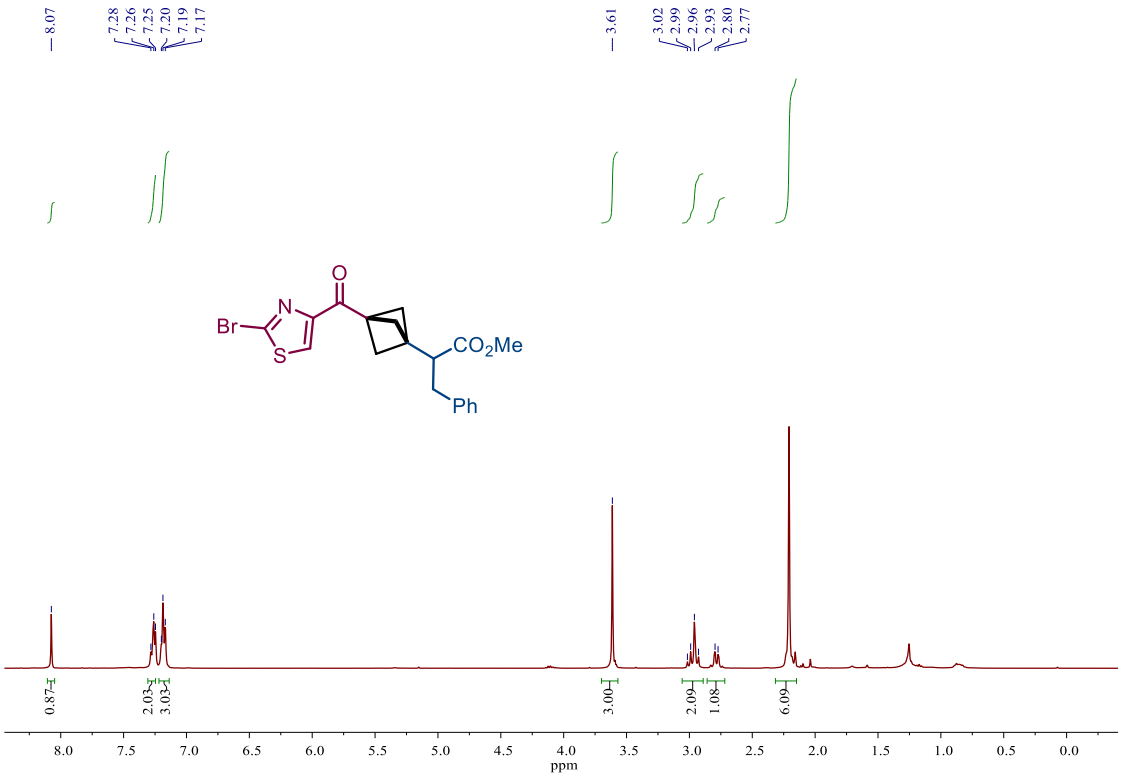
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 41



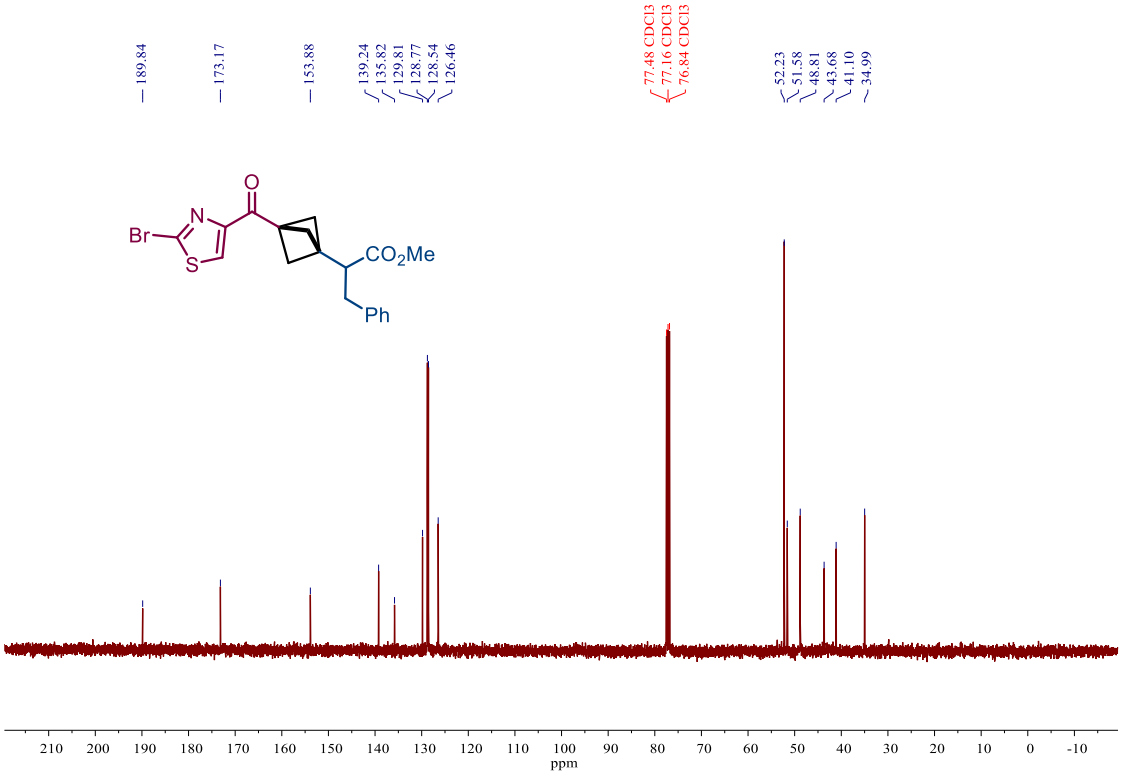
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 42



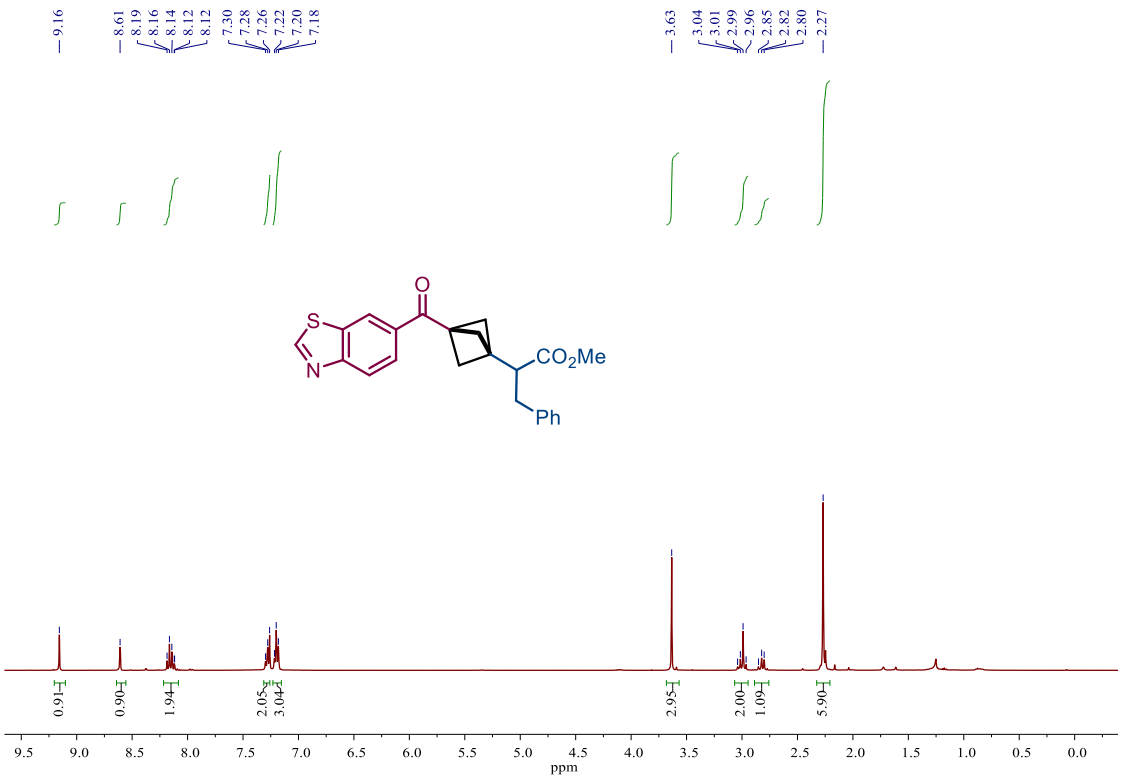
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 42



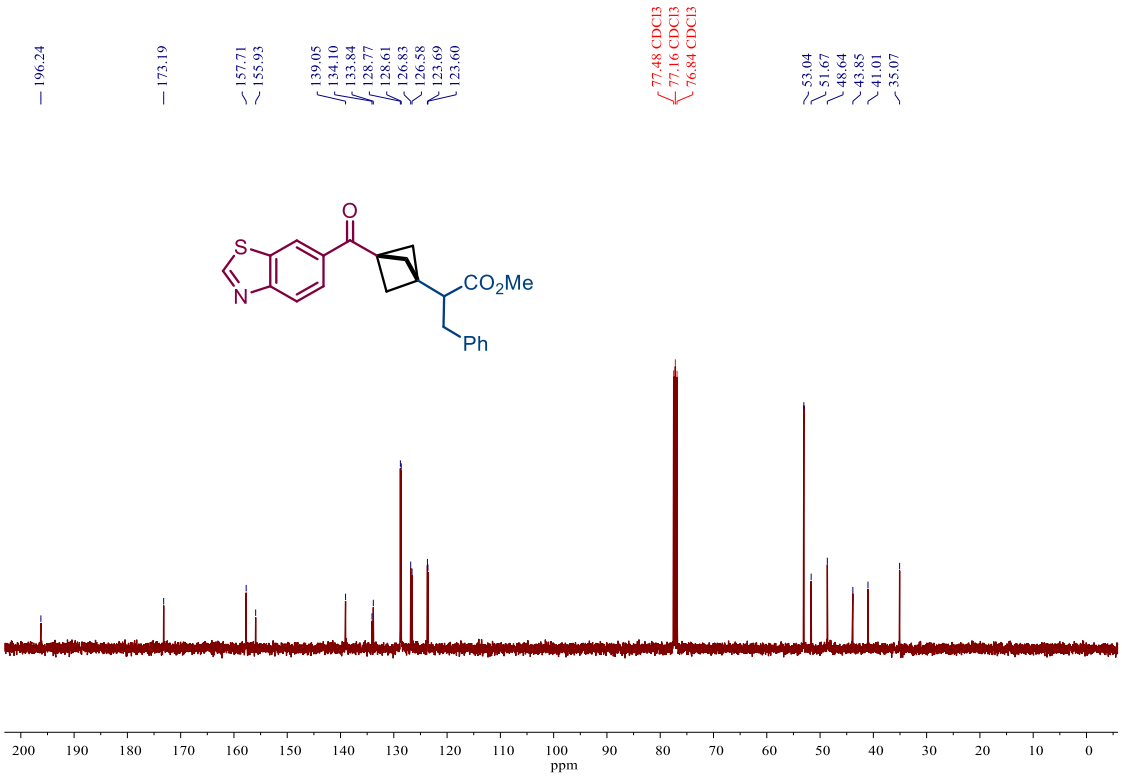
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 43



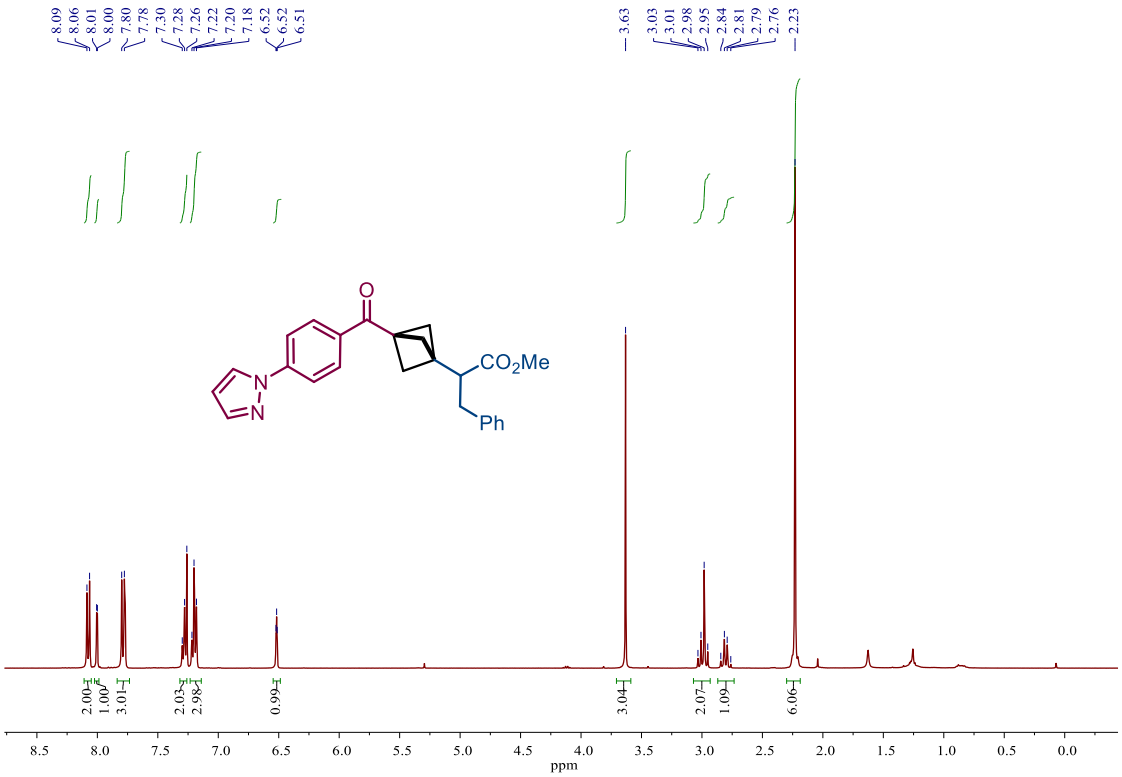
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 43



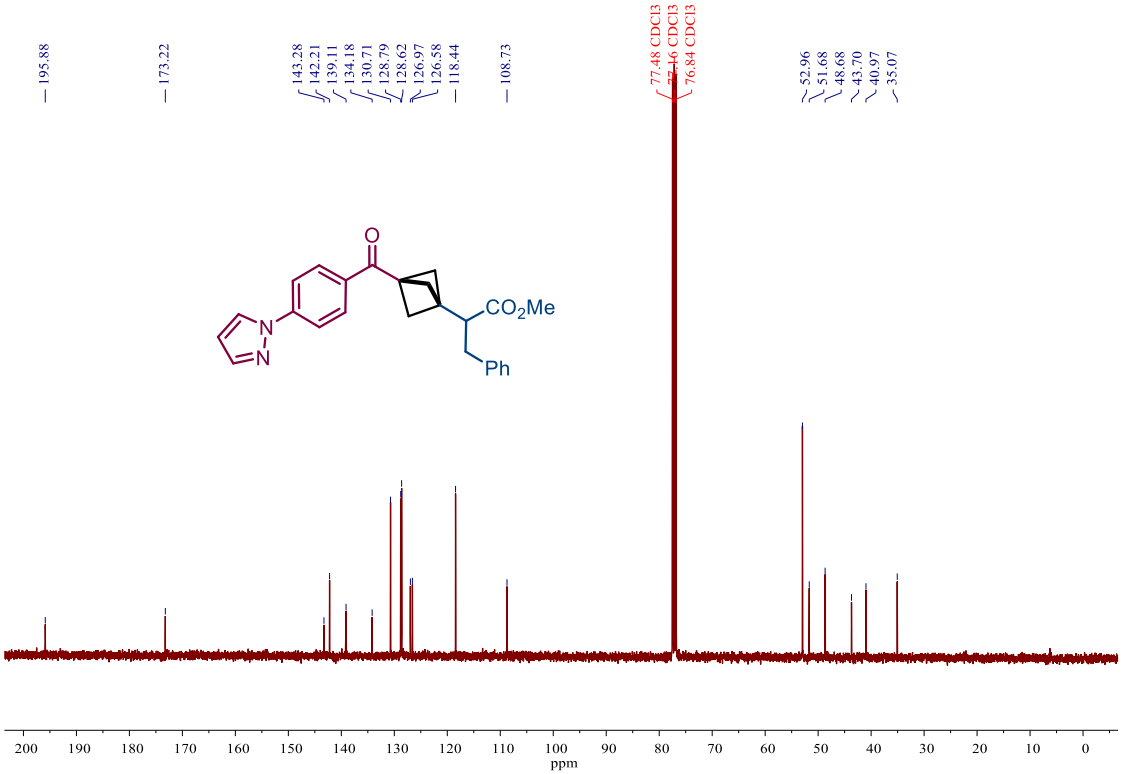
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 44



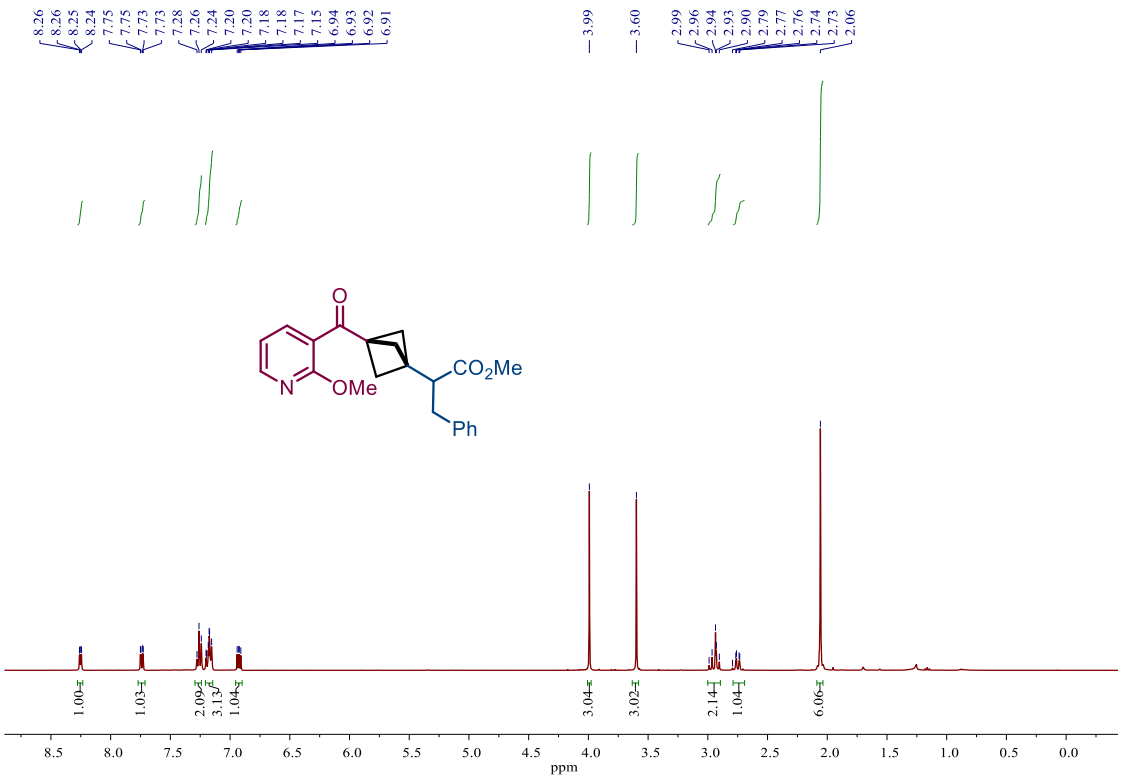
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 44



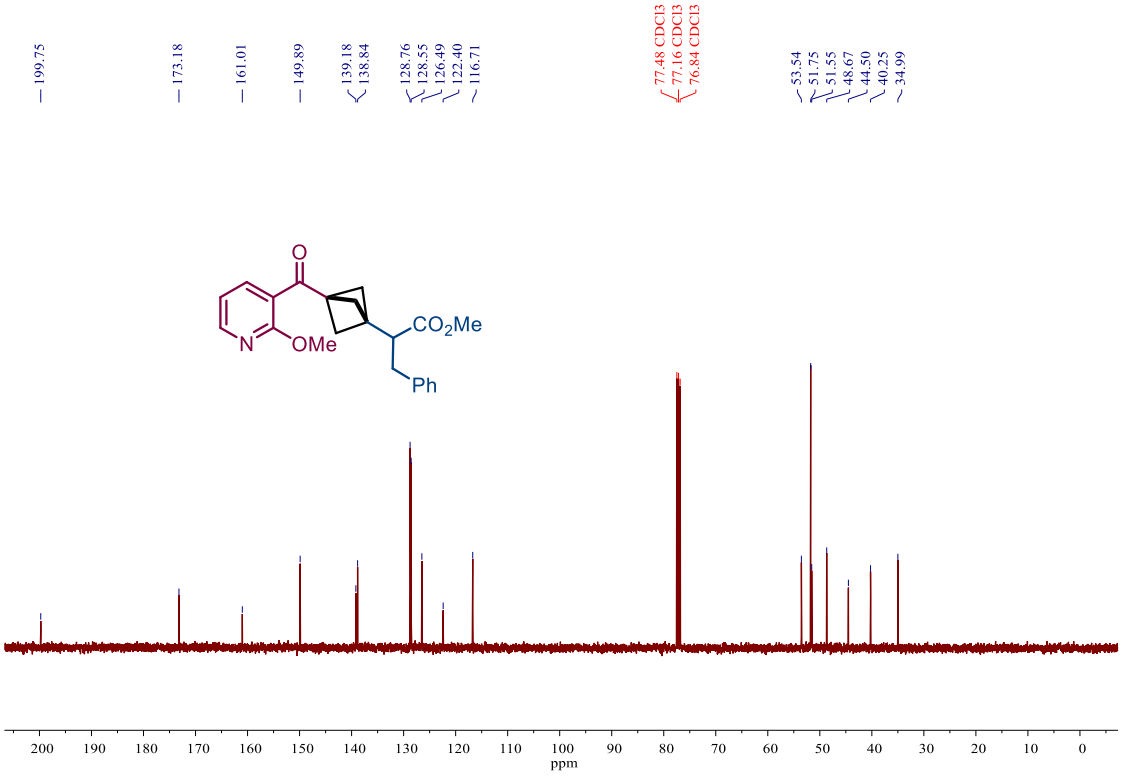
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 45



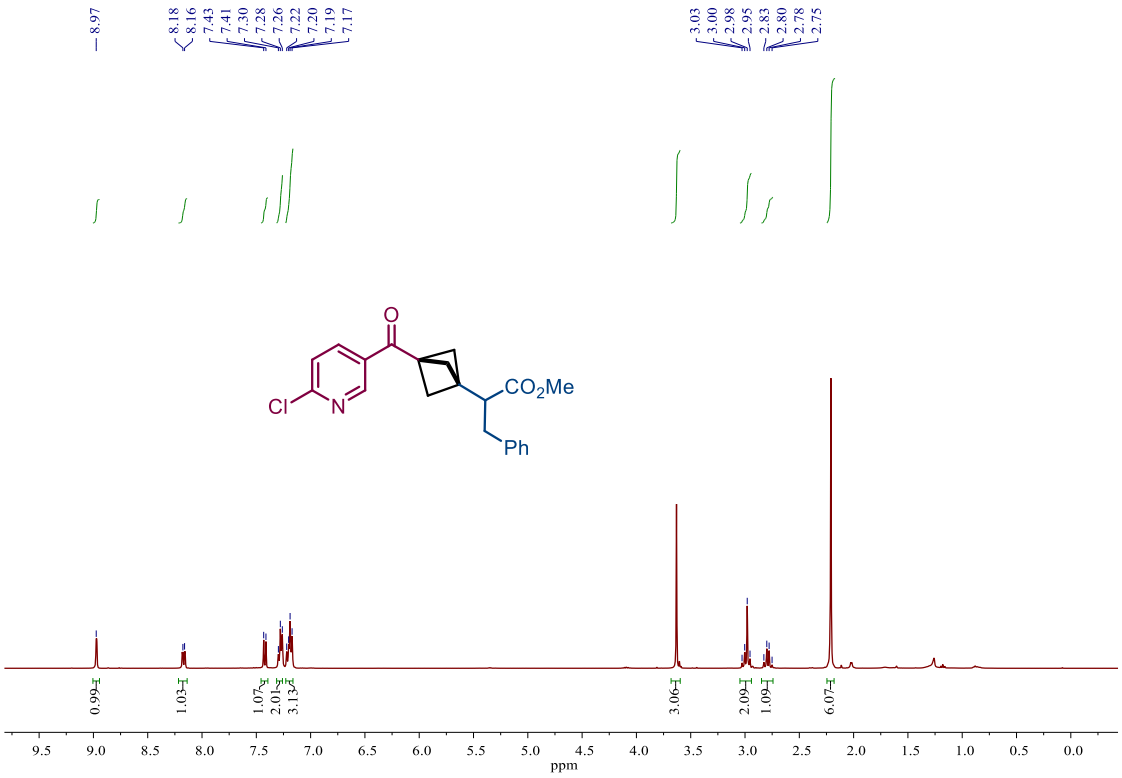
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 45



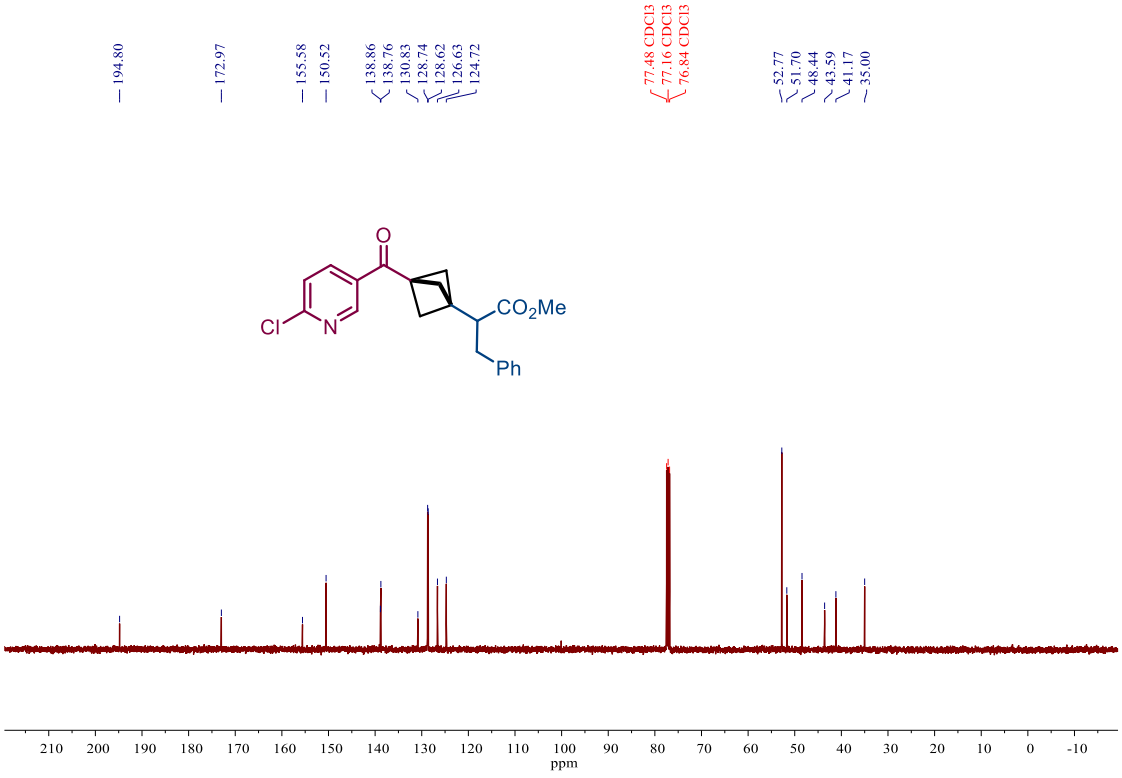
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 46



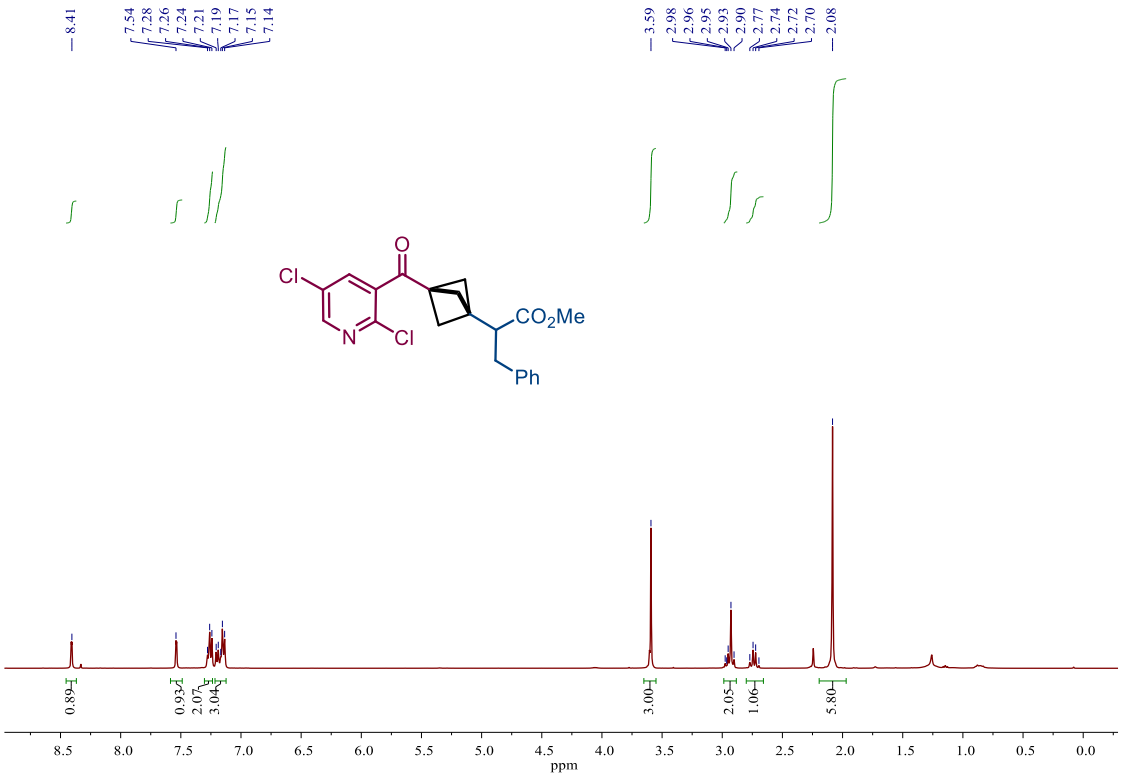
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 46



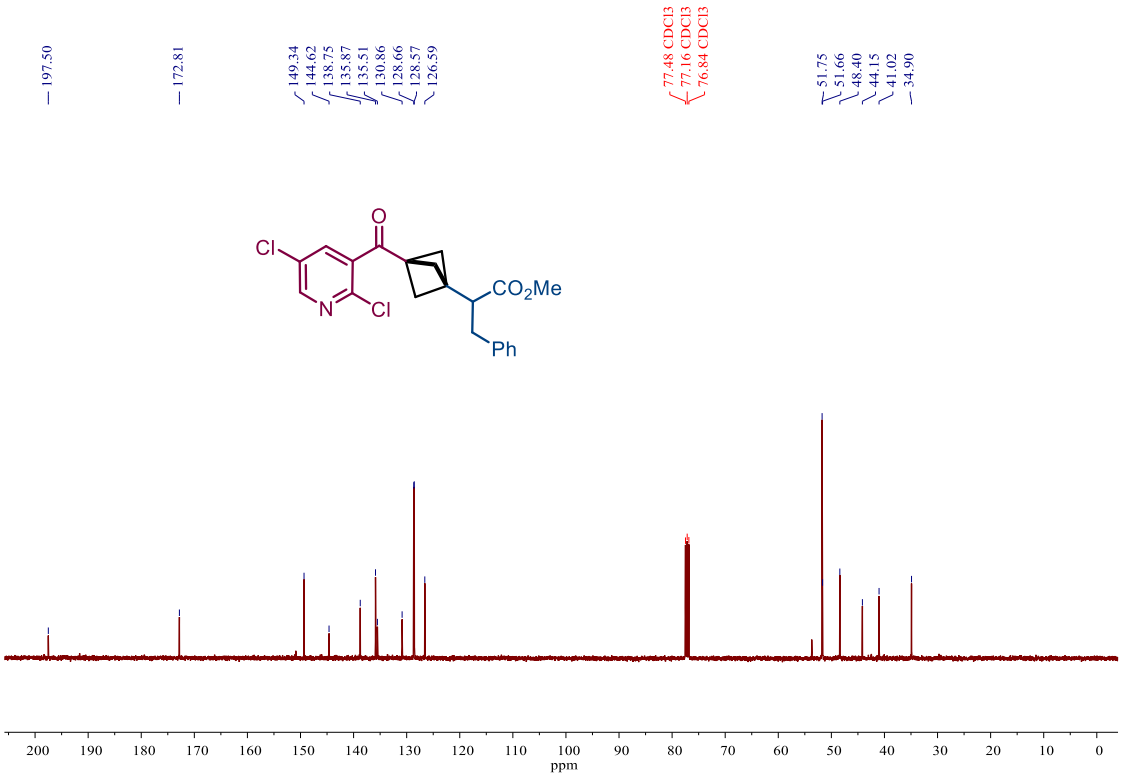
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 47



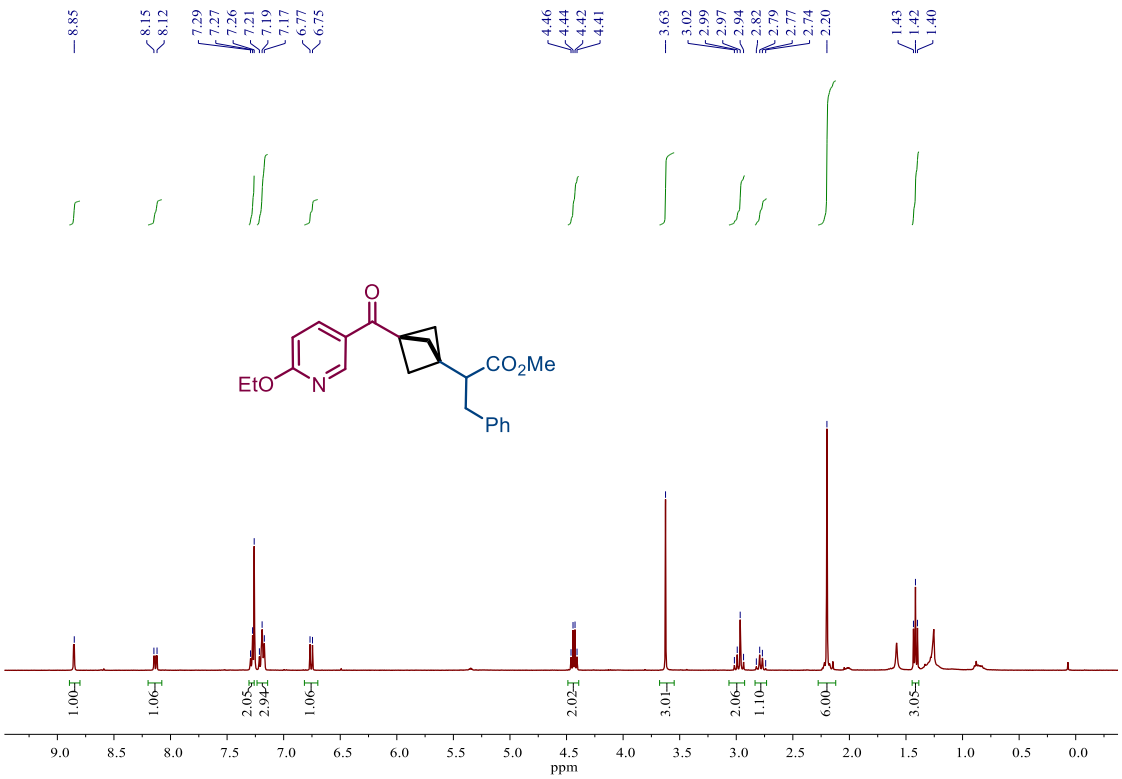
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 47



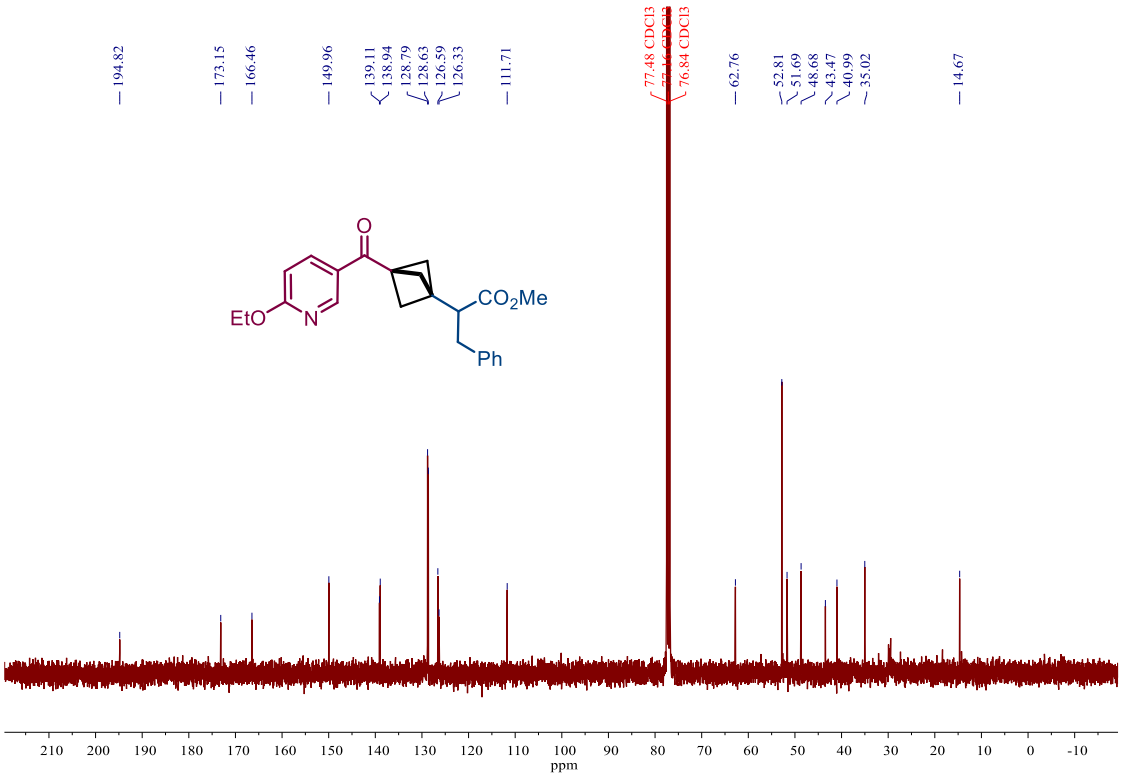
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 48



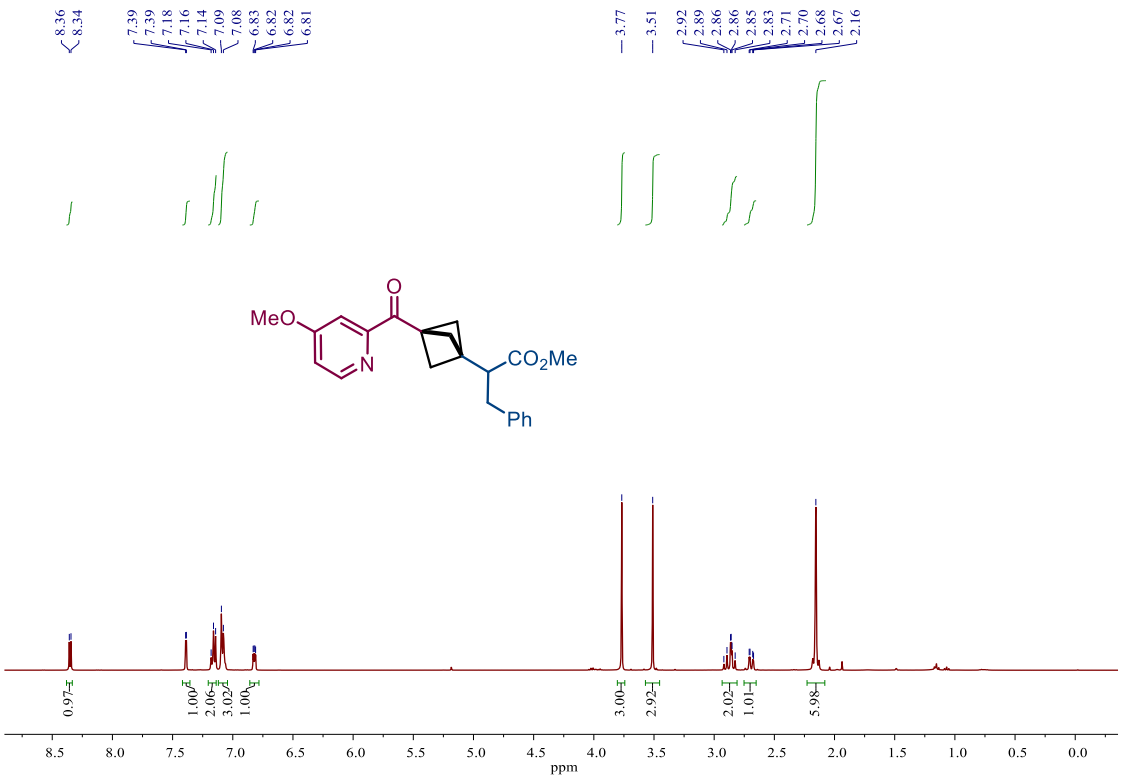
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 48



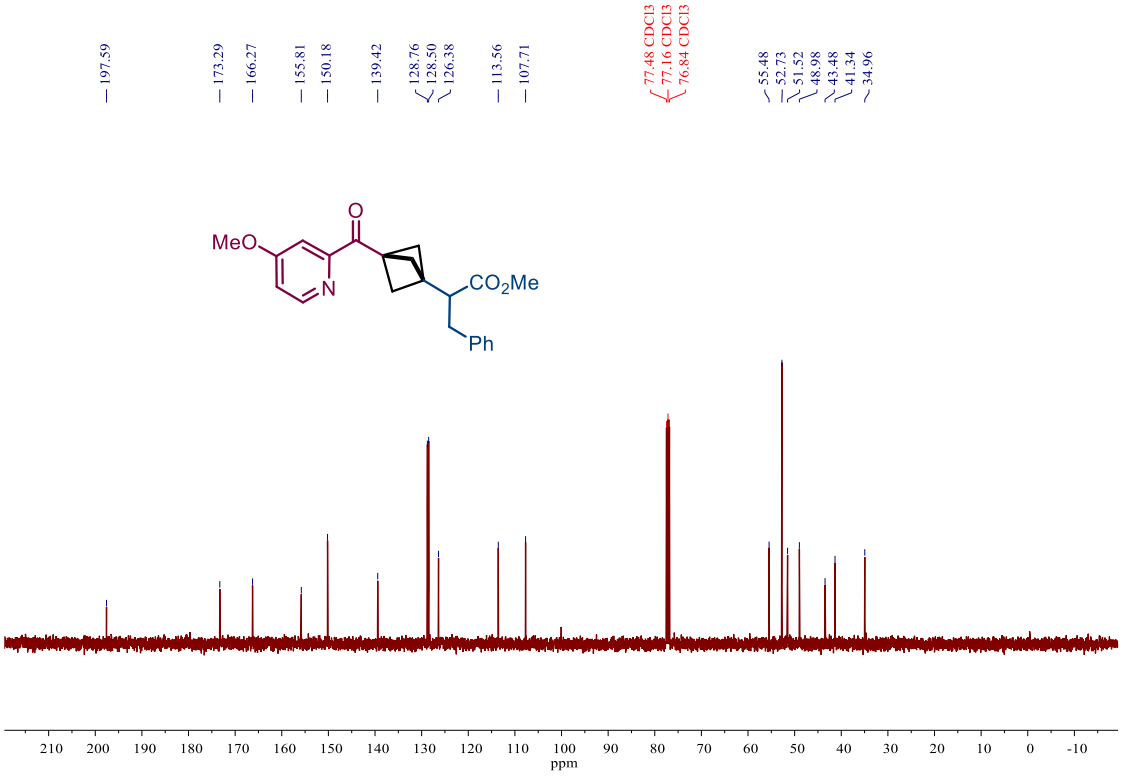
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 49



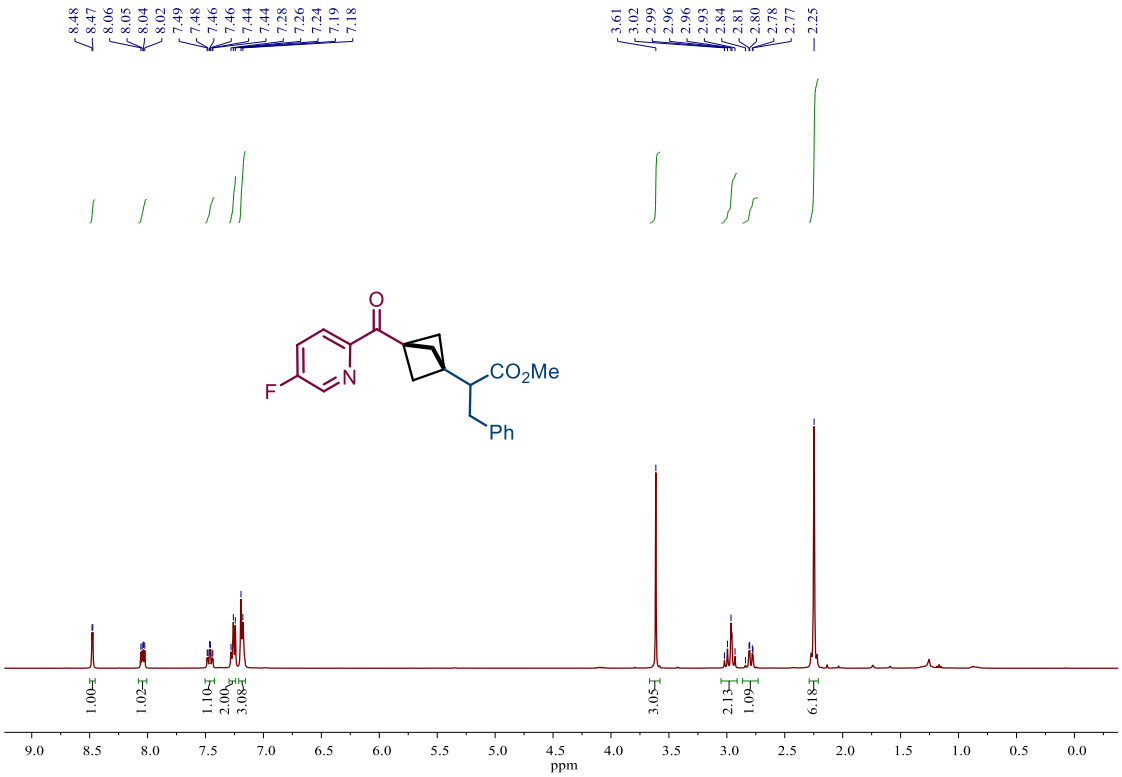
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 49



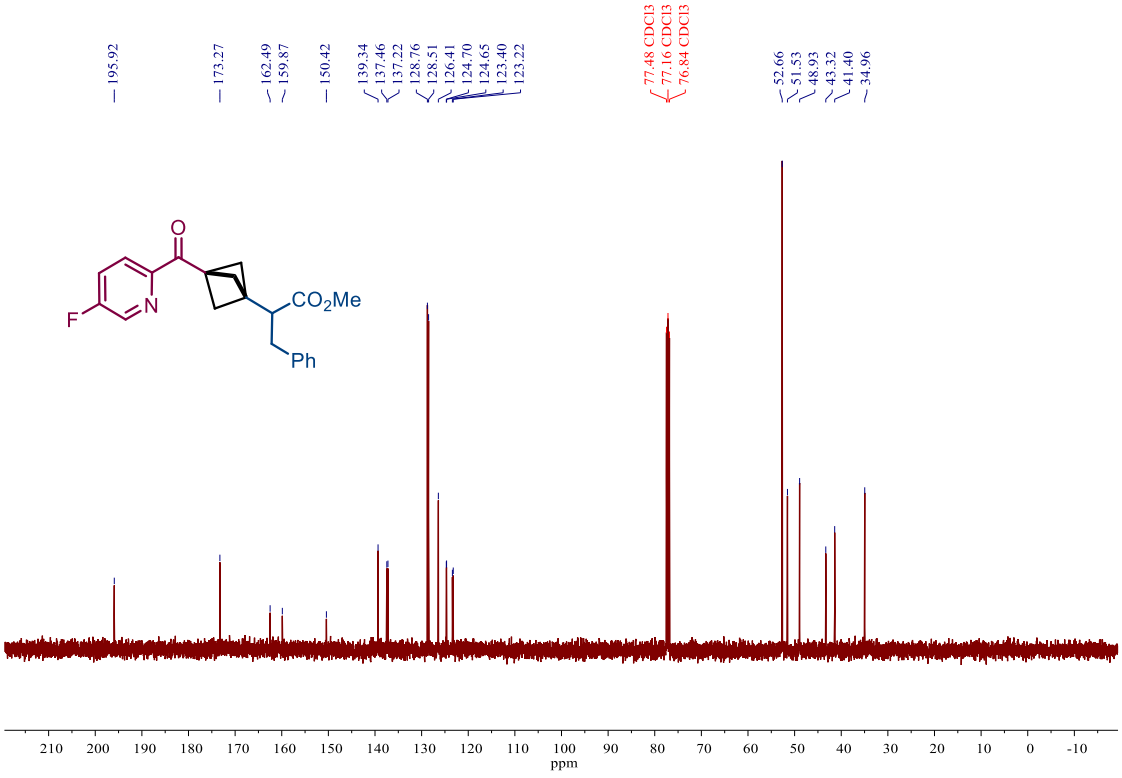
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 50



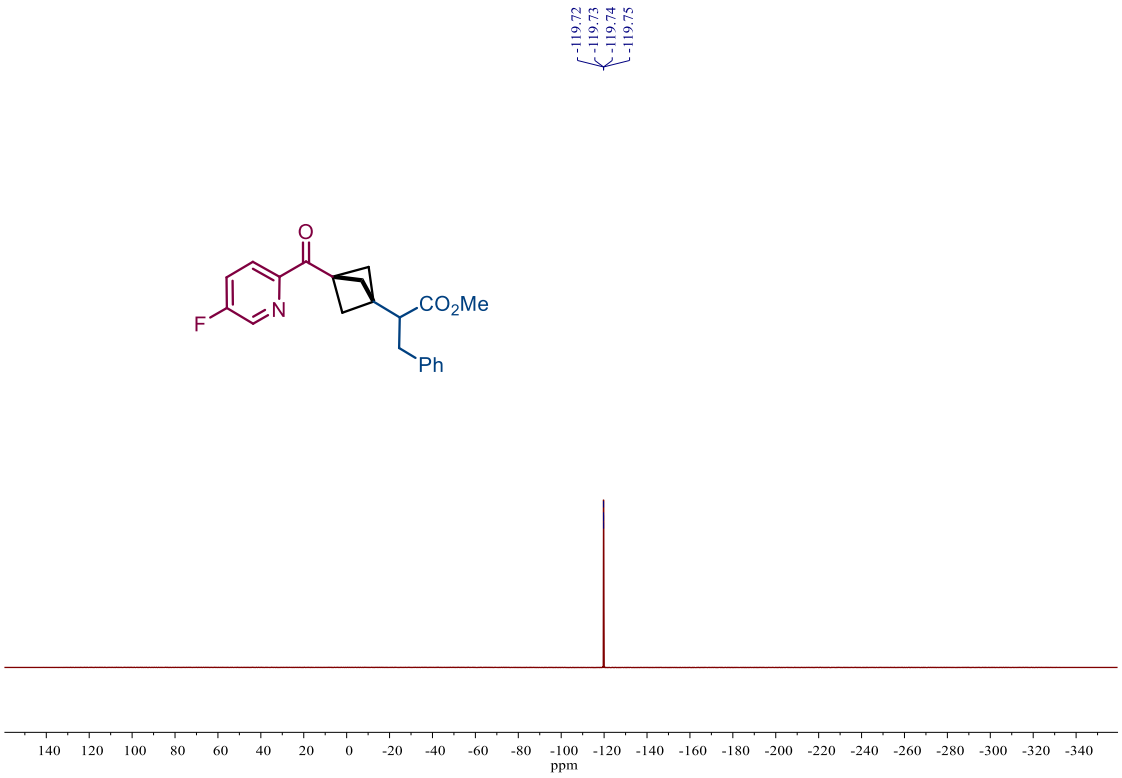
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 50



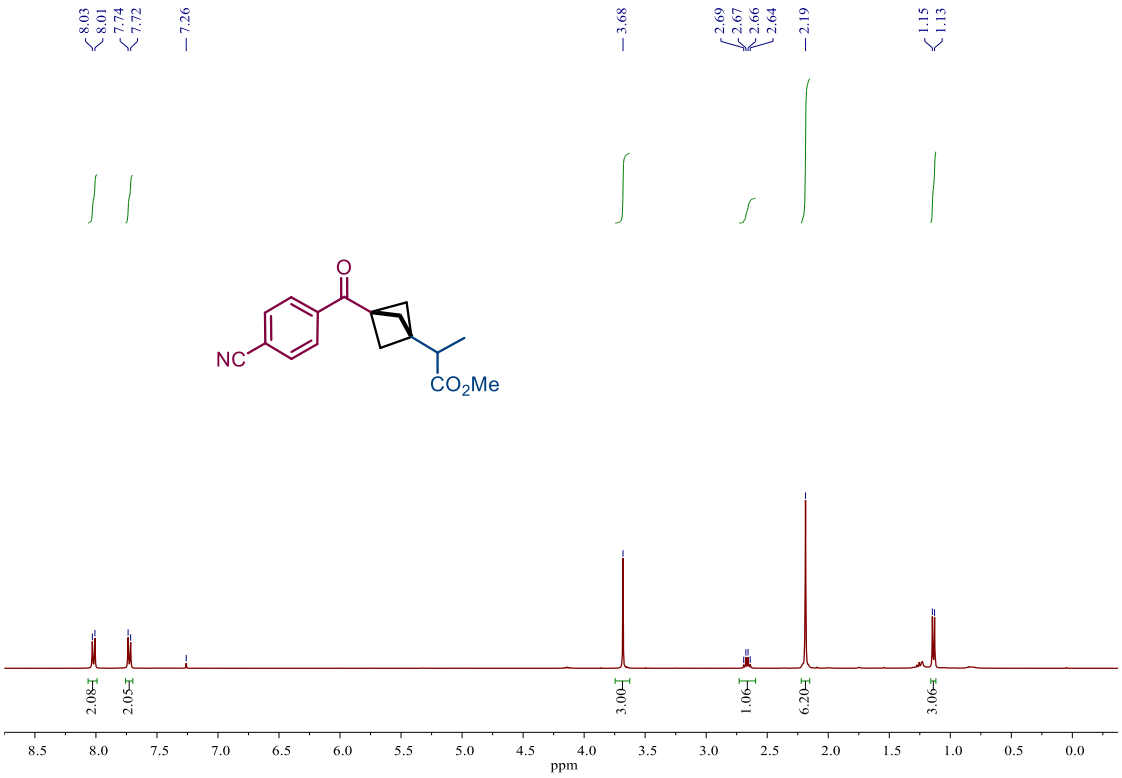
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 51



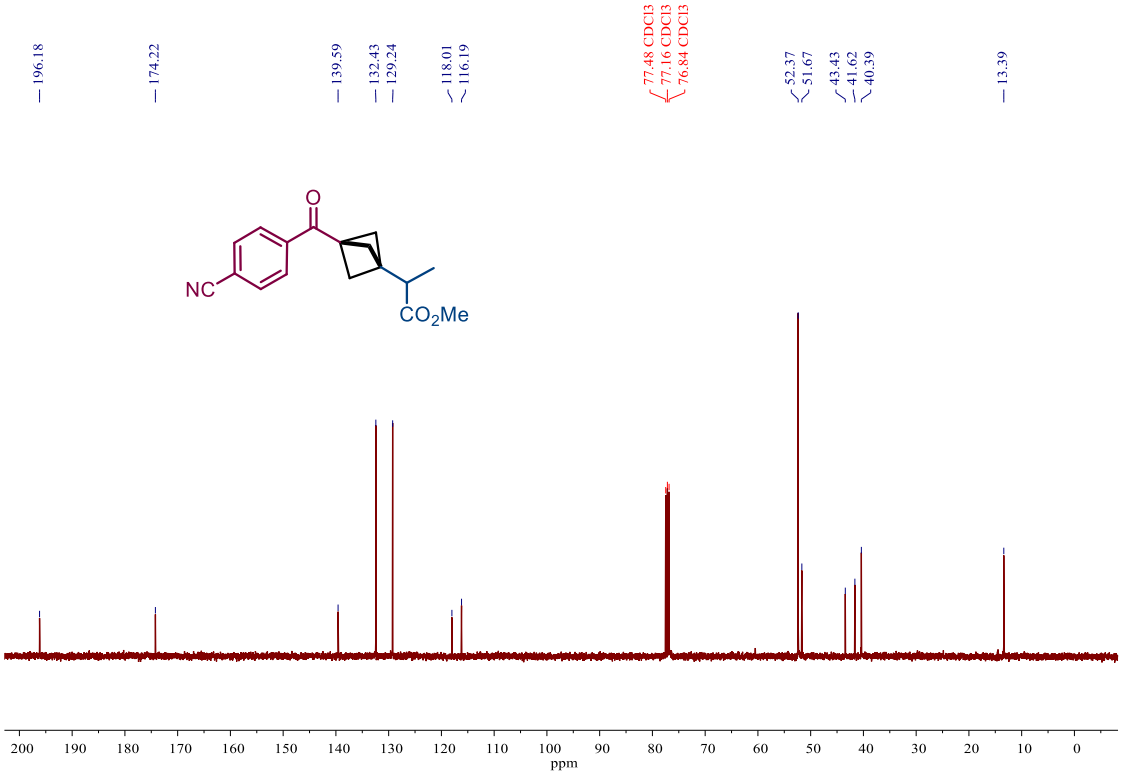
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 51



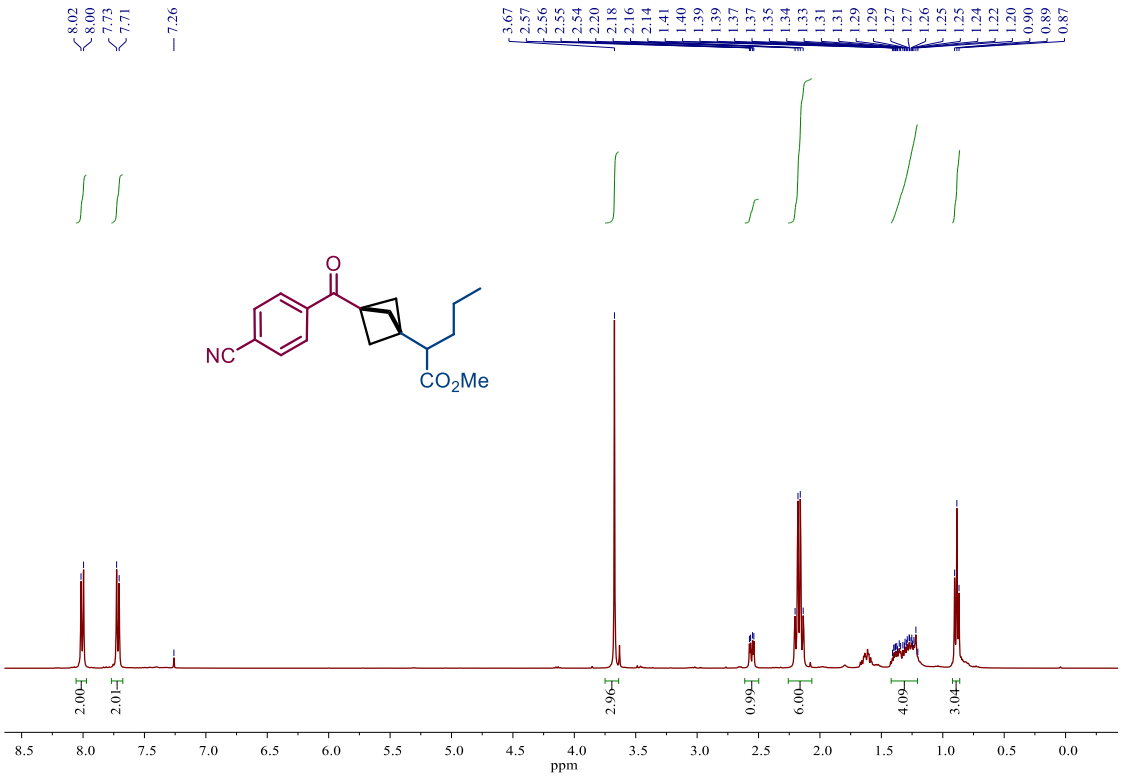
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of compound 51



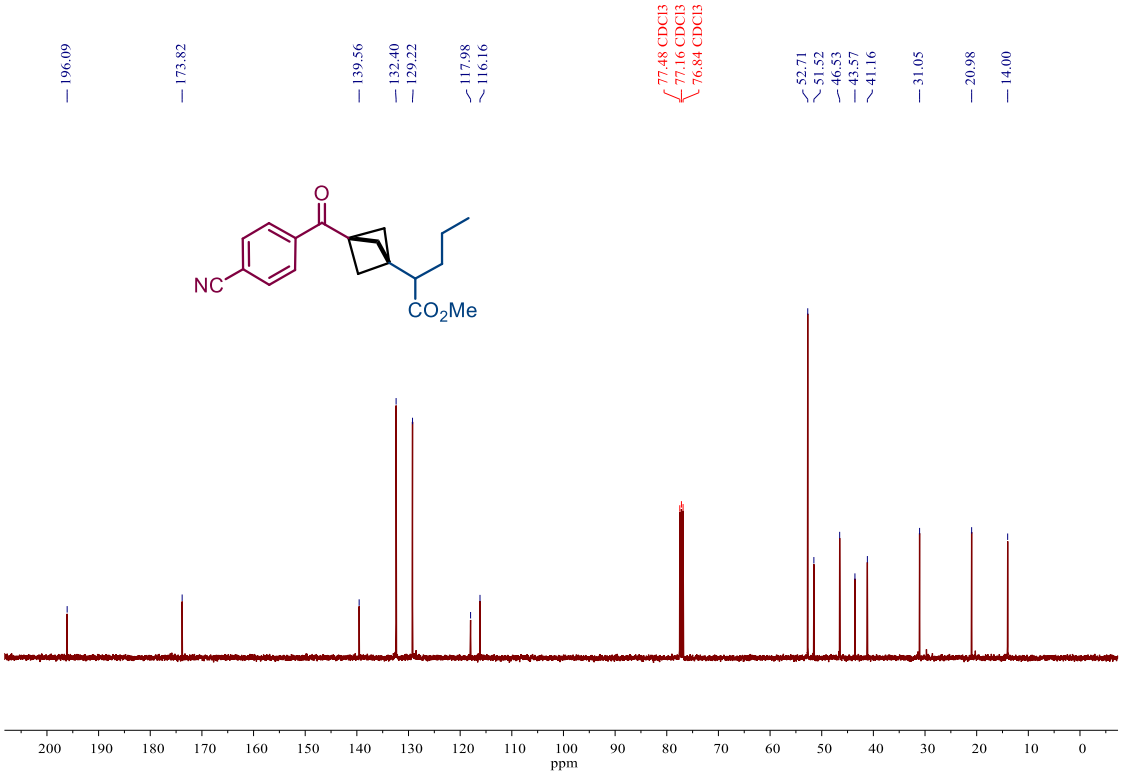
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 52



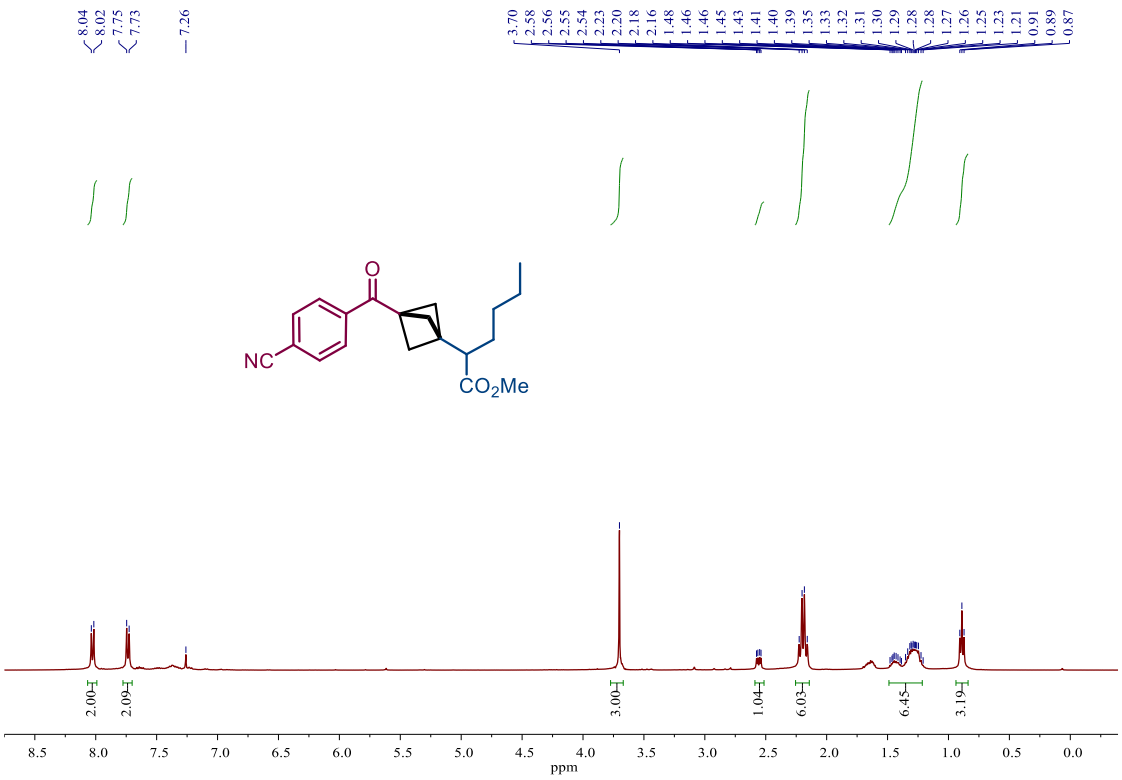
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 52



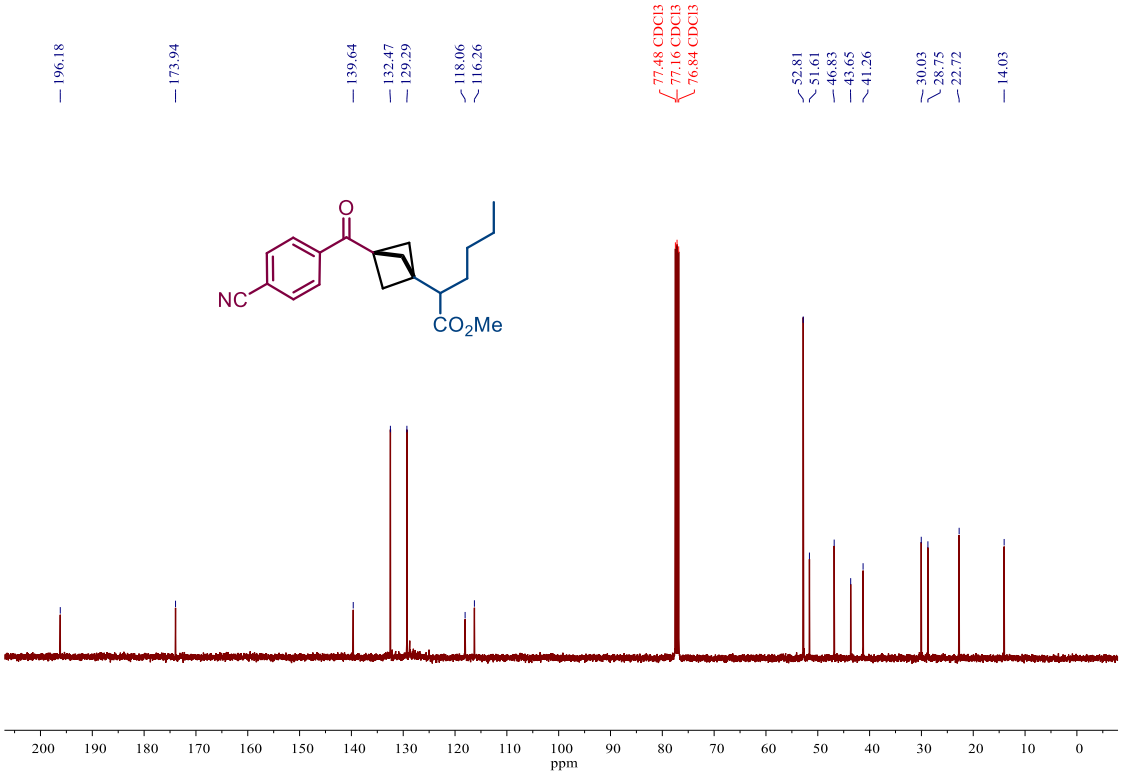
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 53



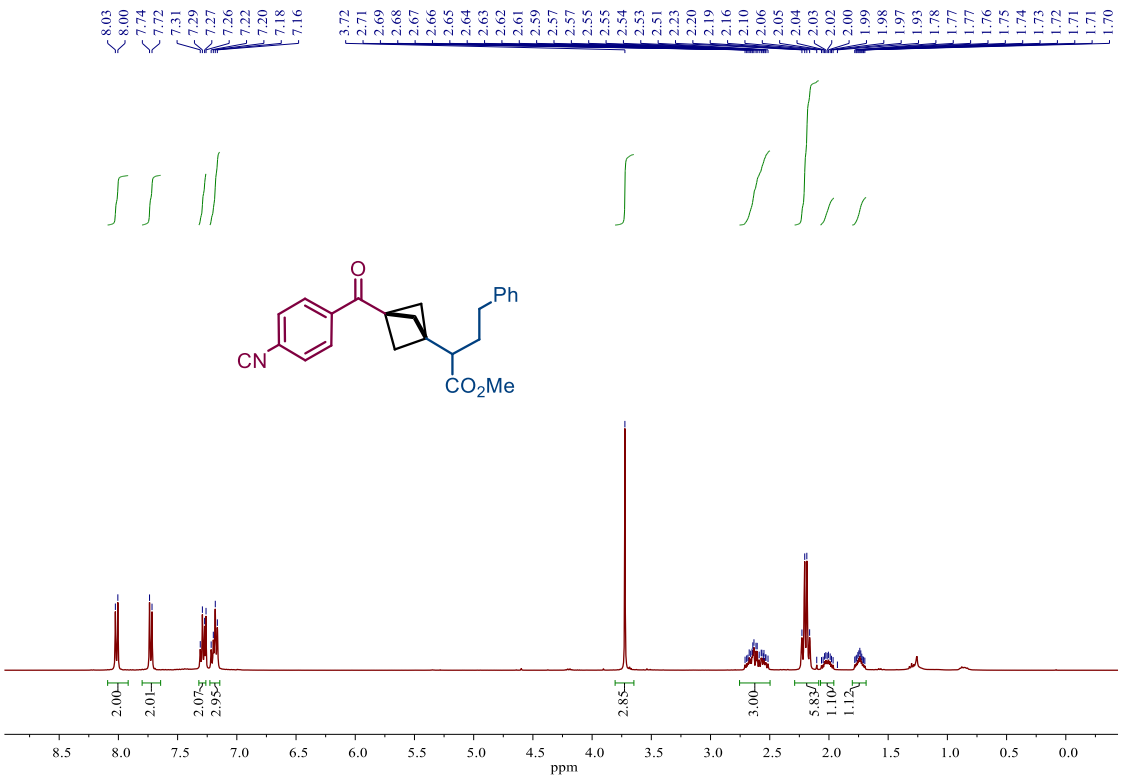
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 53



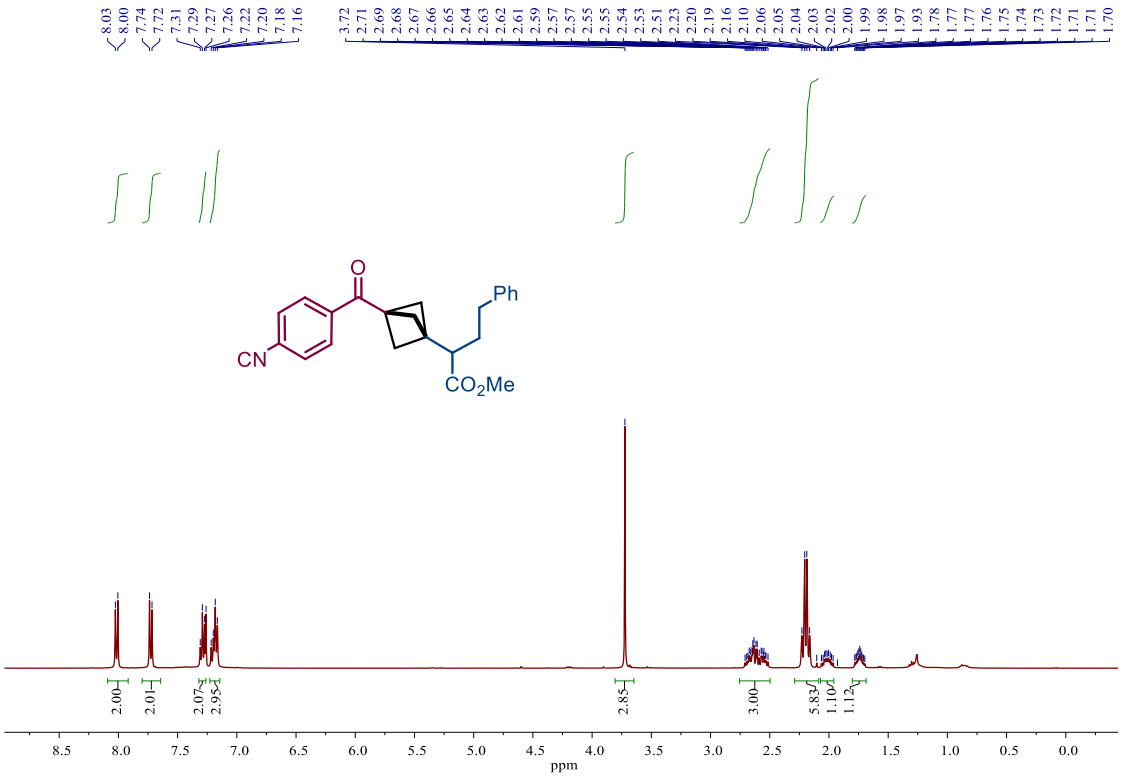
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 54



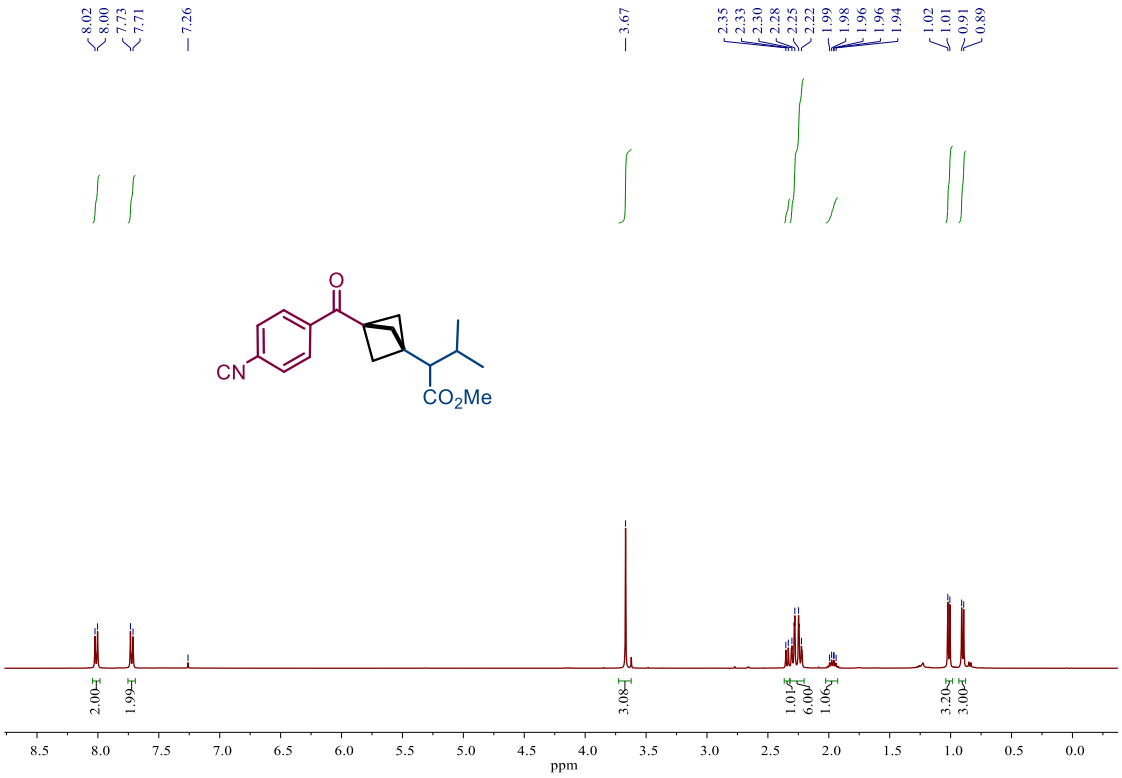
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 54



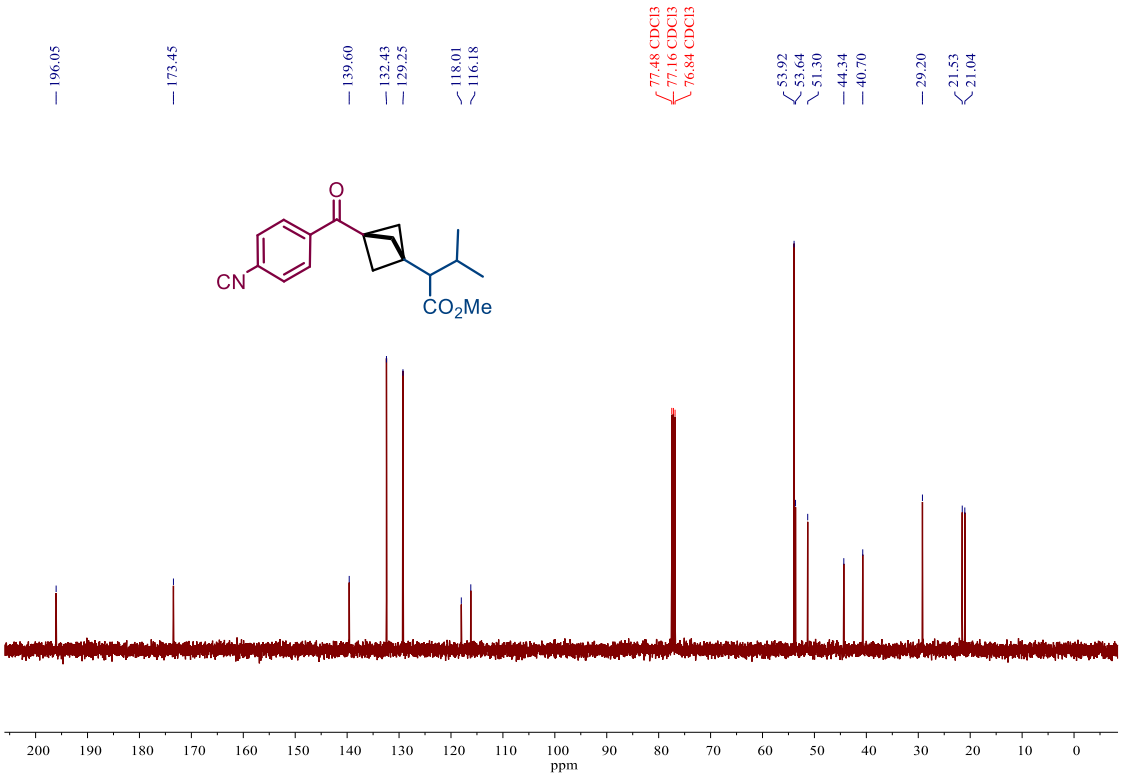
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 55



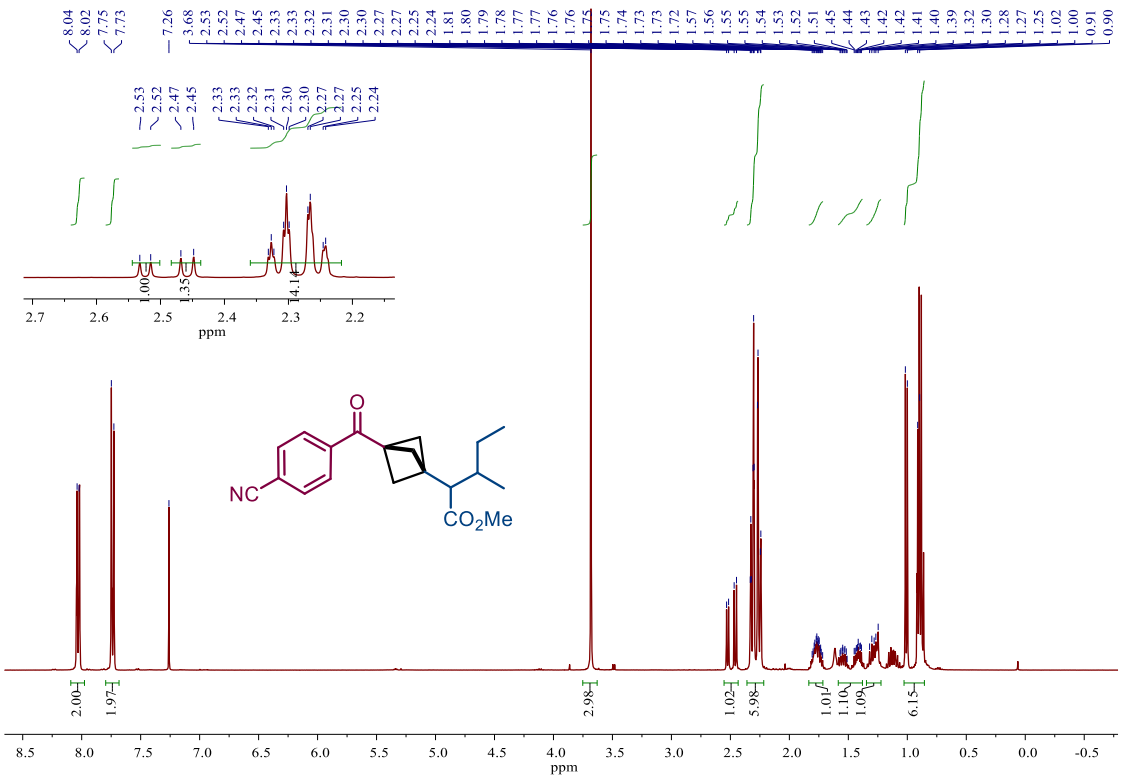
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 55



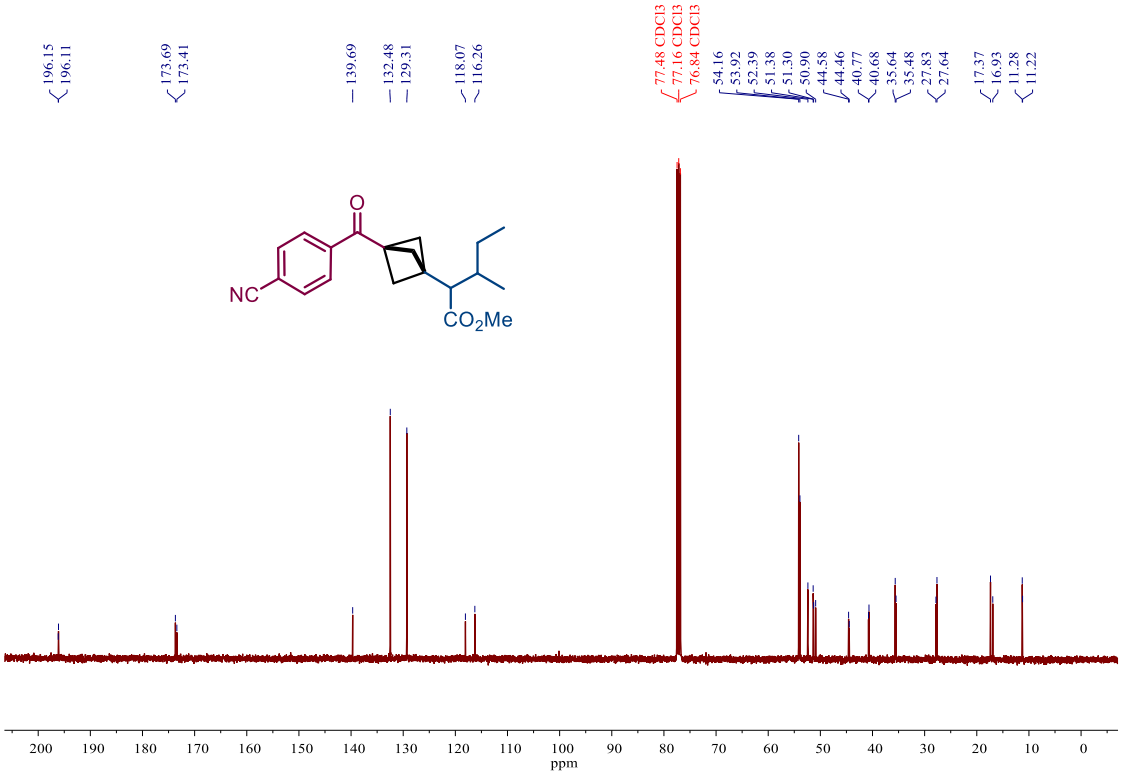
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 56



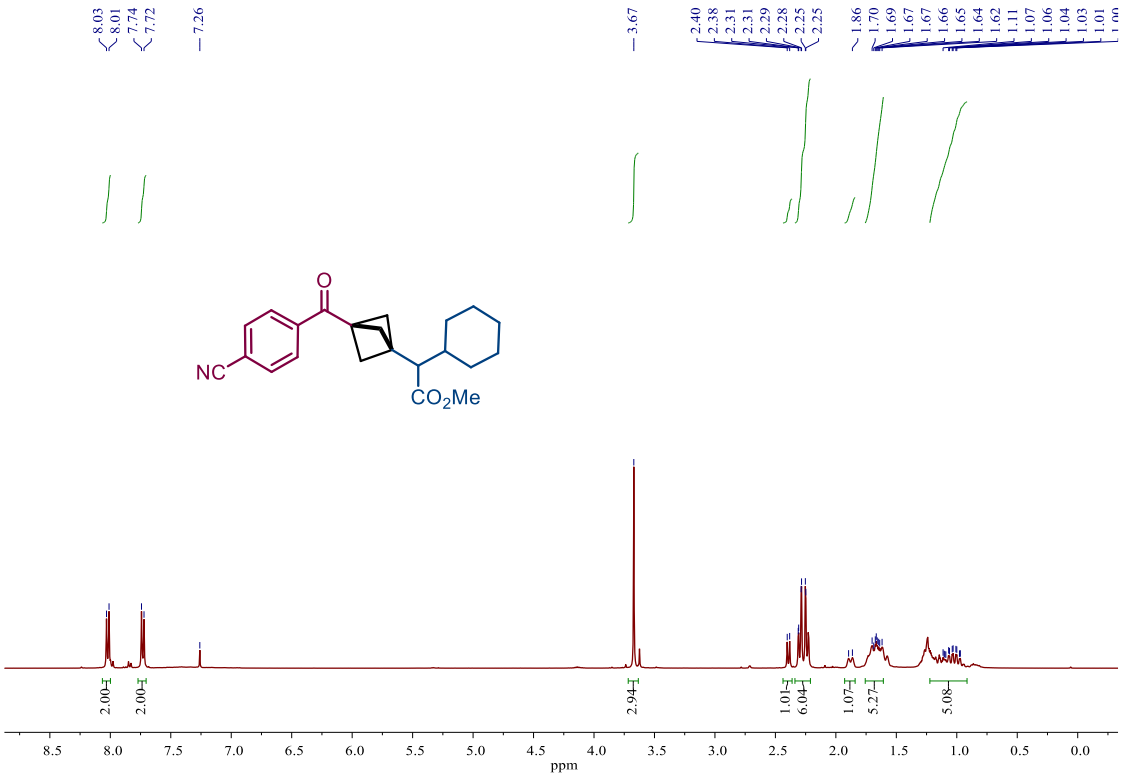
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 56



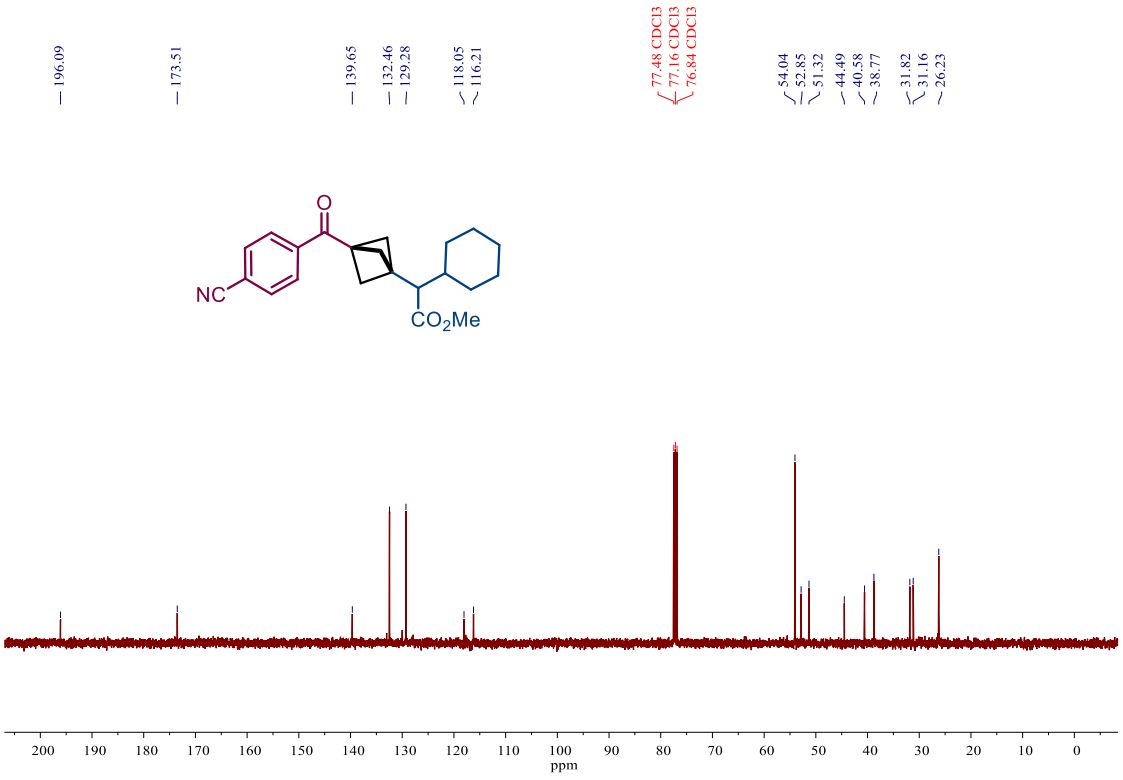
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 57



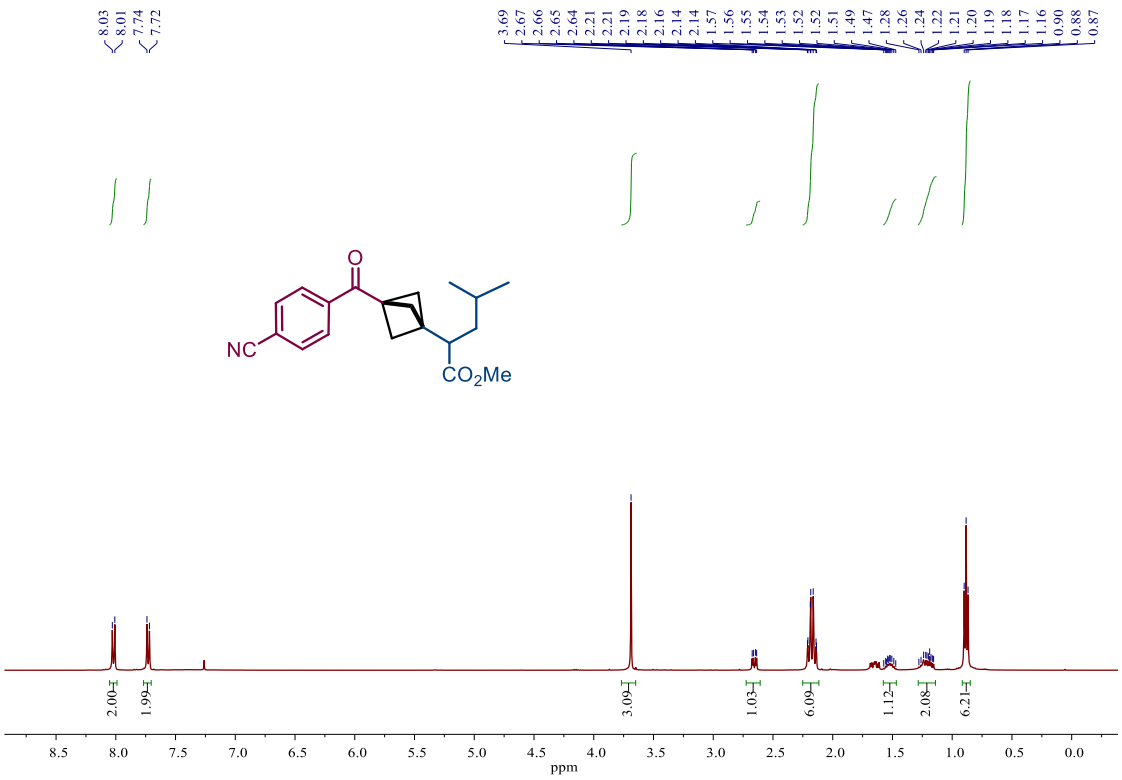
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 57



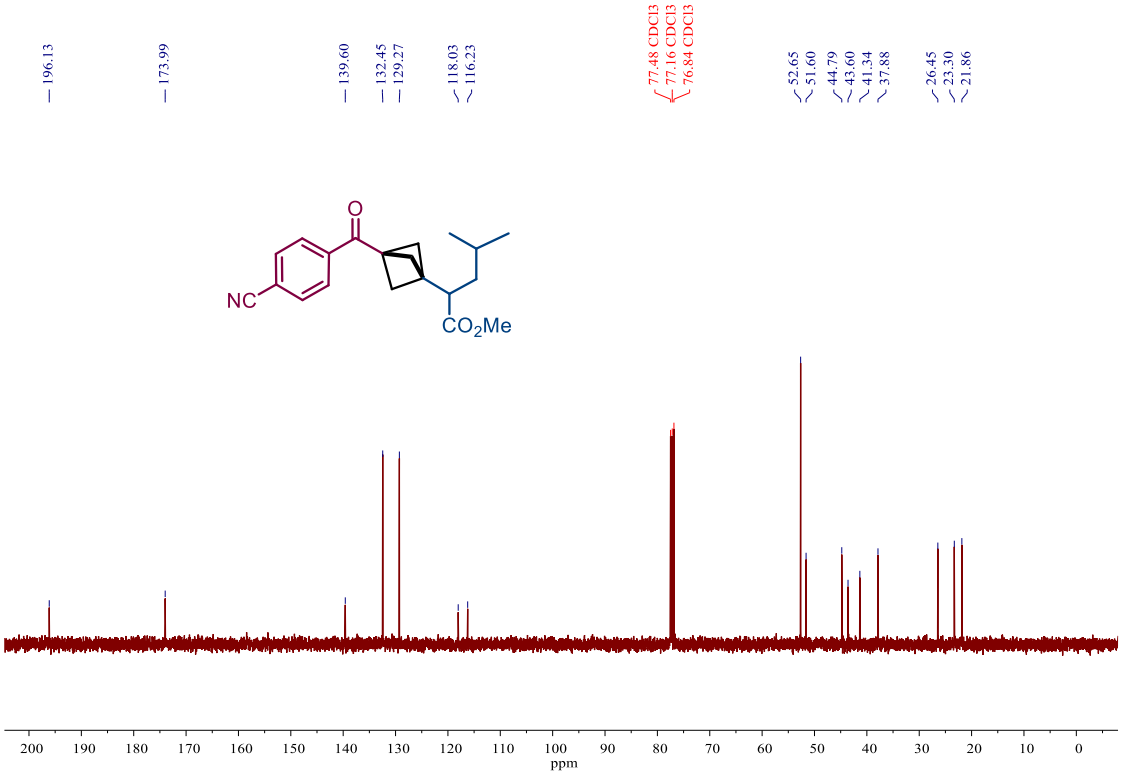
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 58



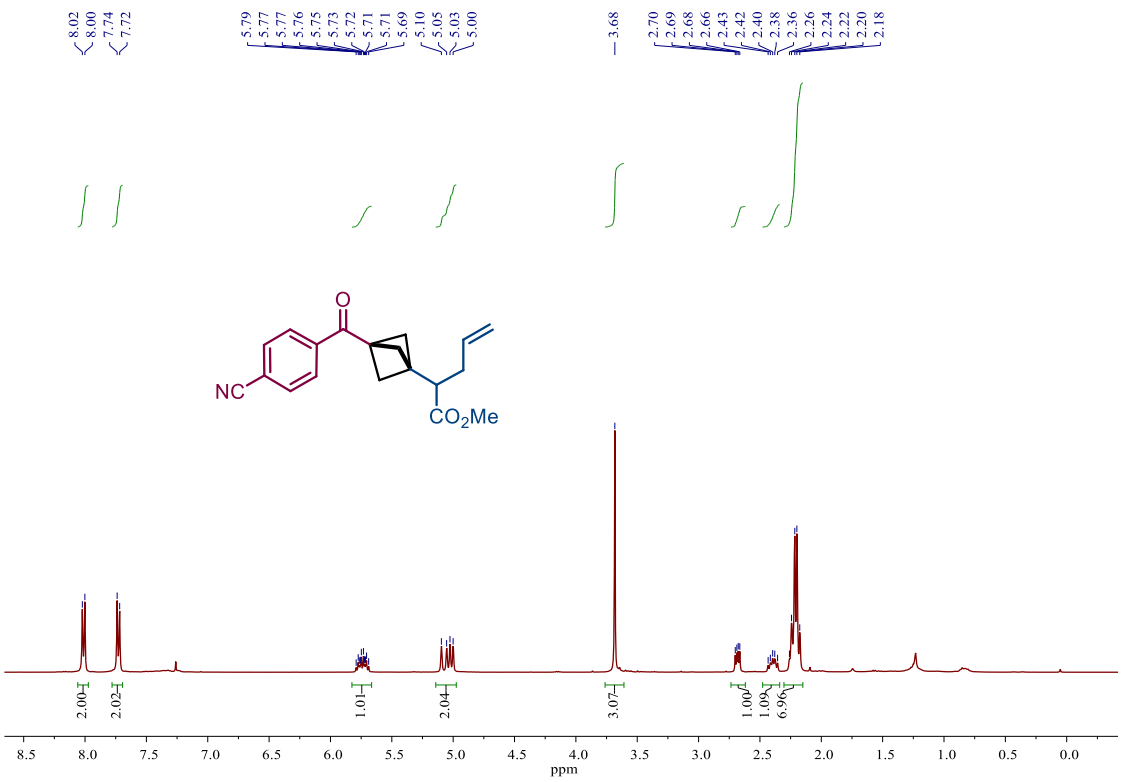
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 58



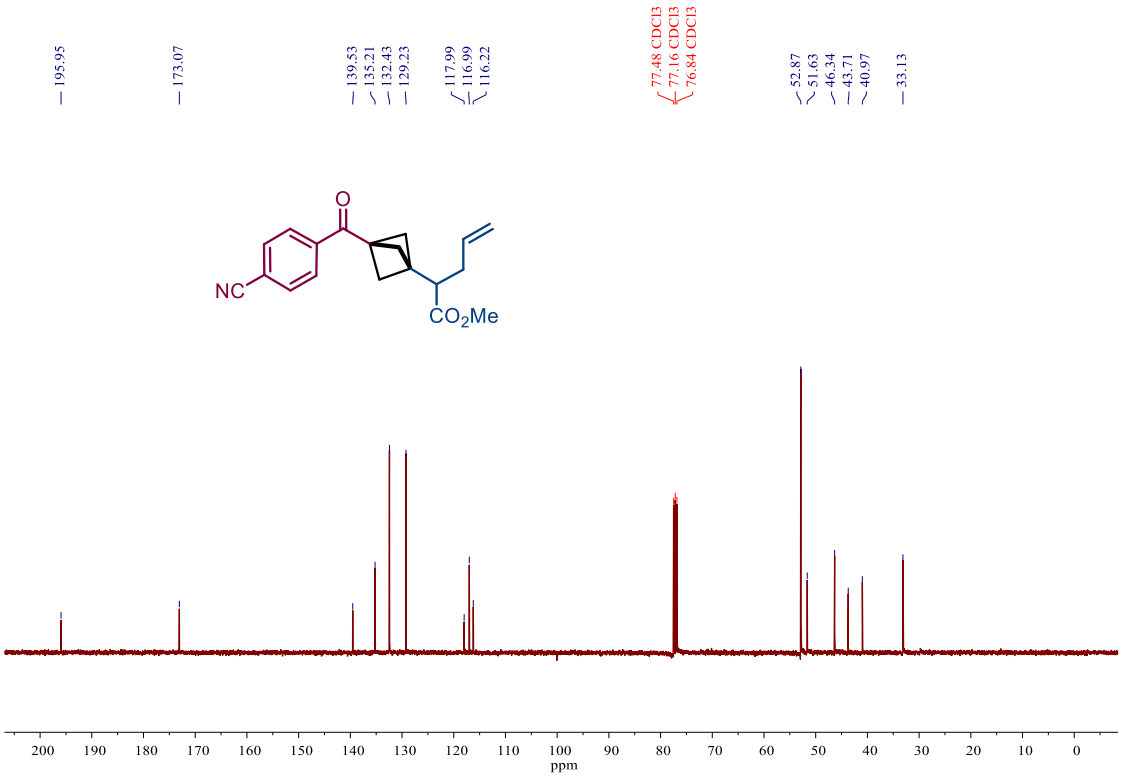
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 59



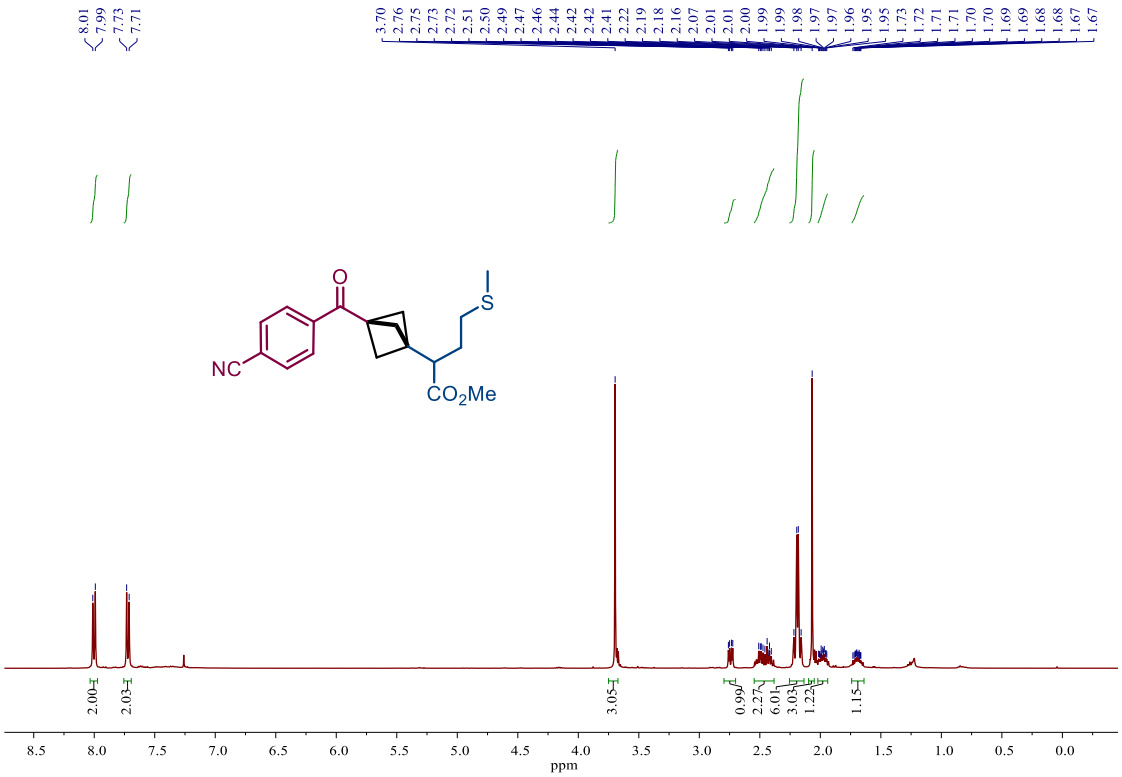
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 59



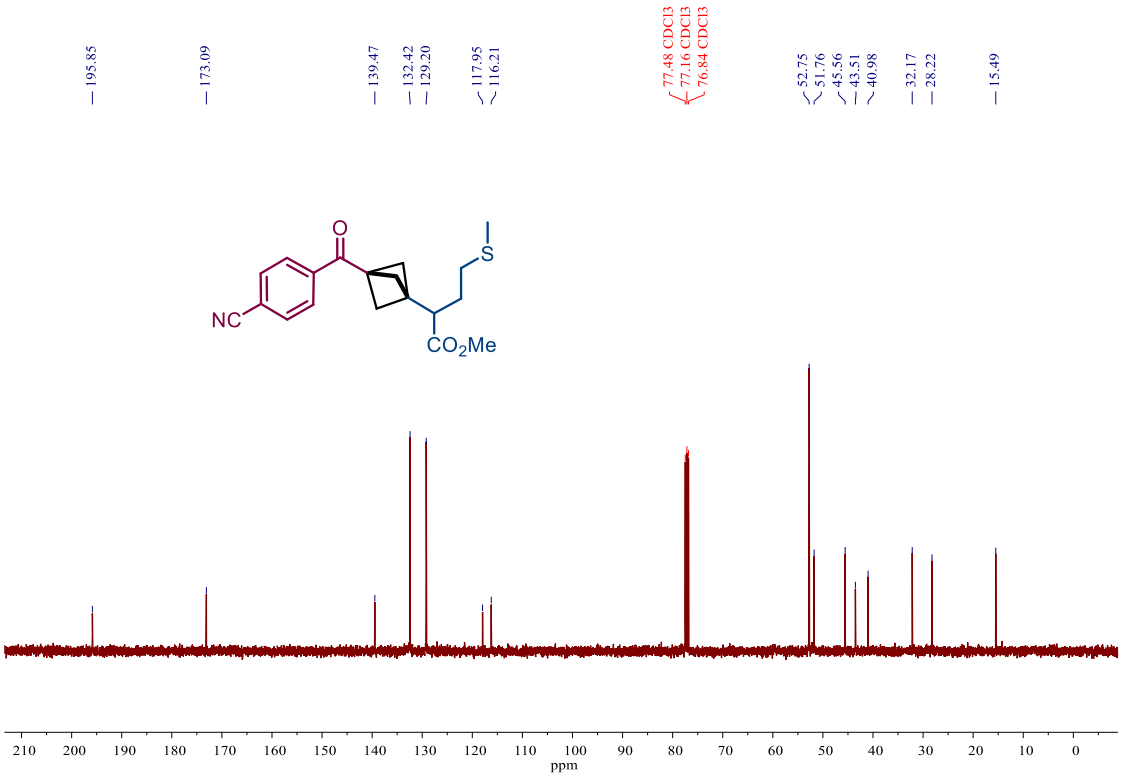
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 60



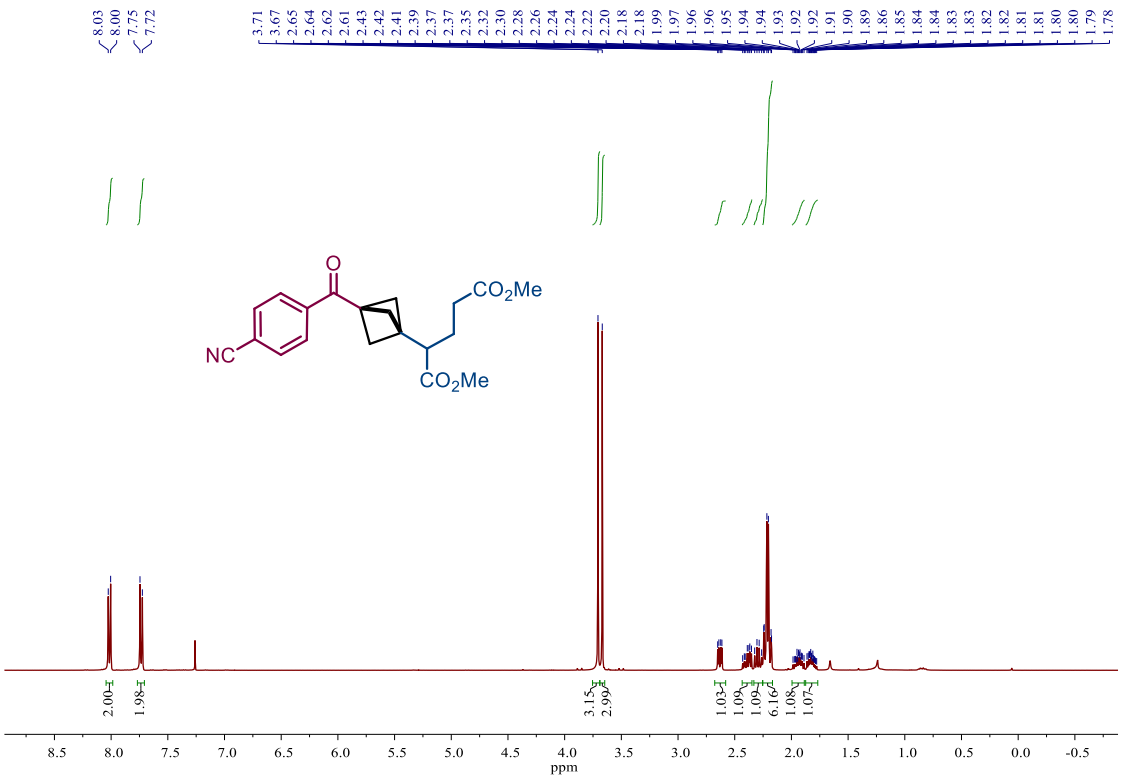
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 60



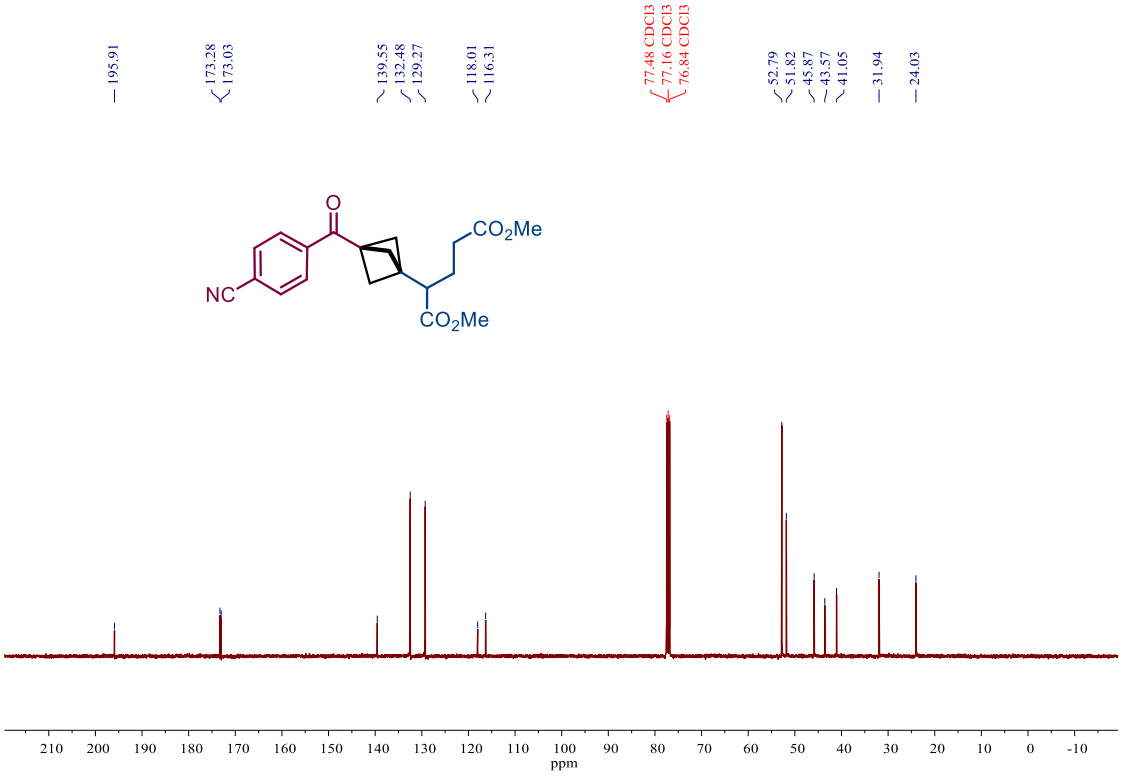
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 61



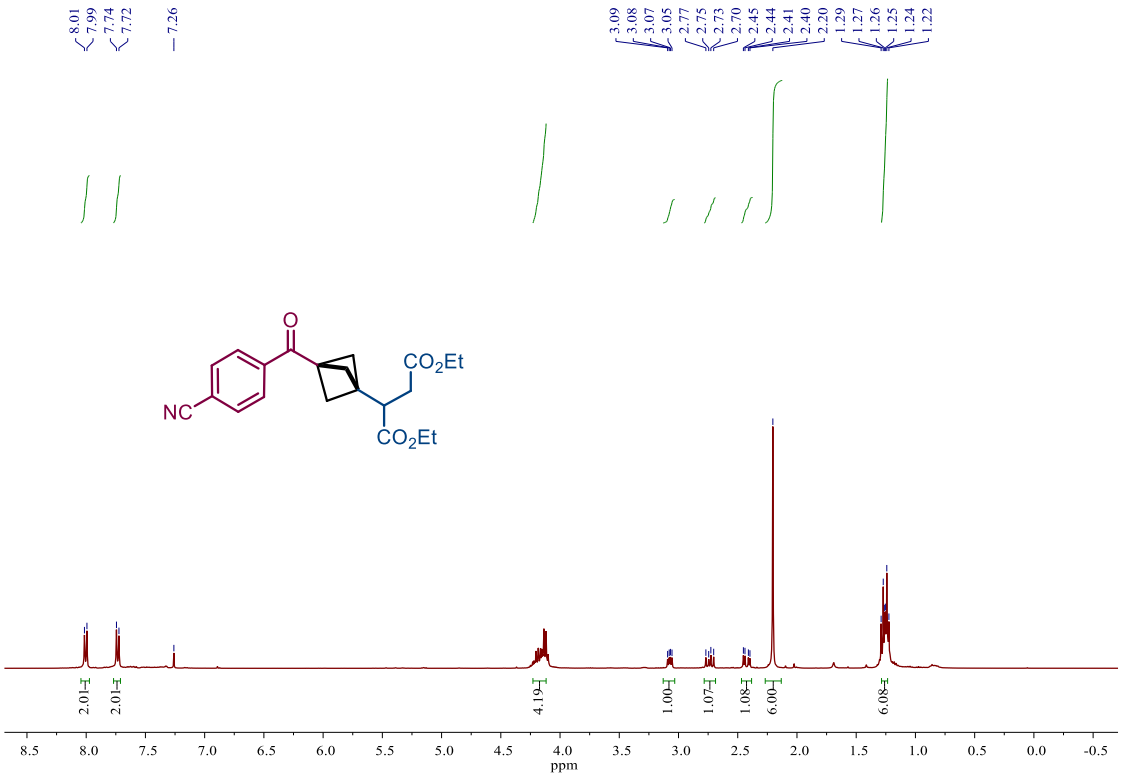
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 61



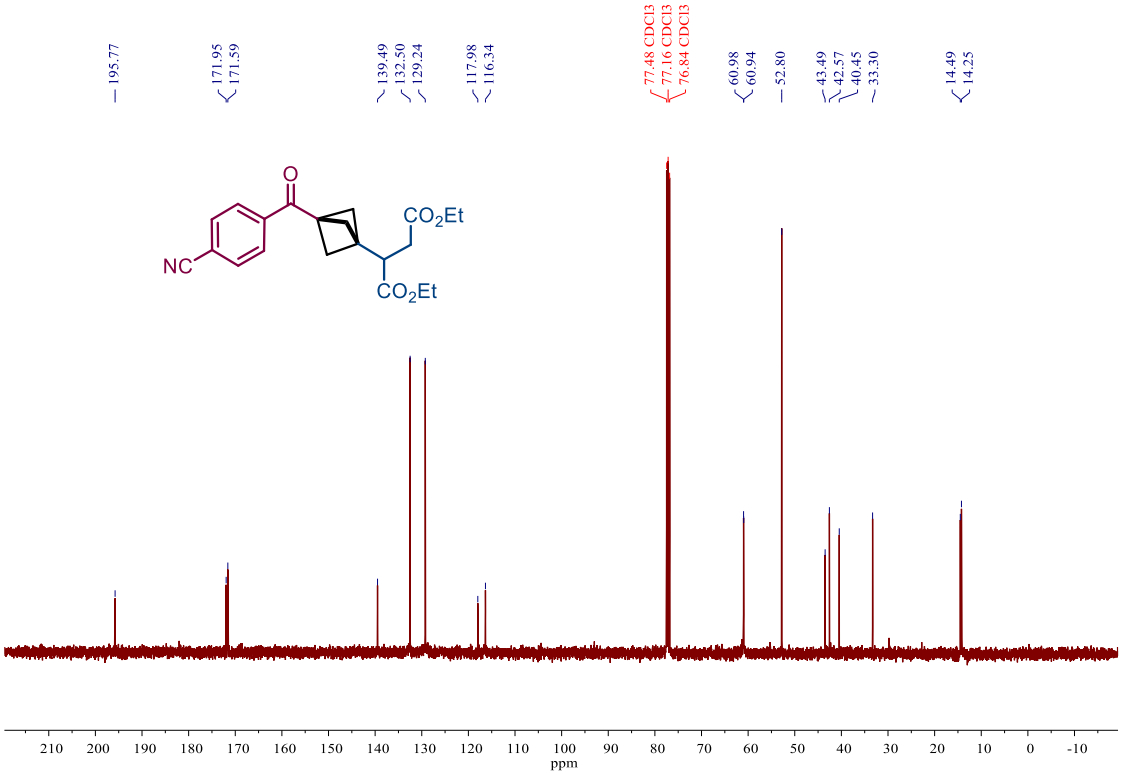
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 62



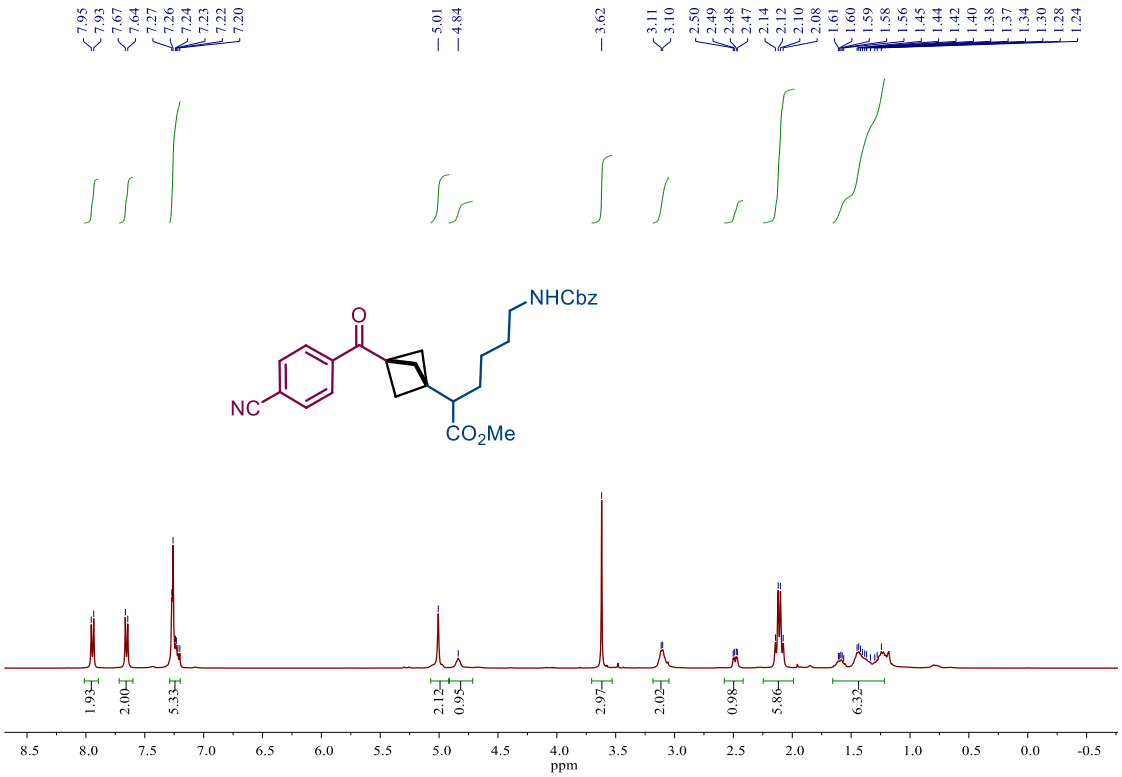
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 62



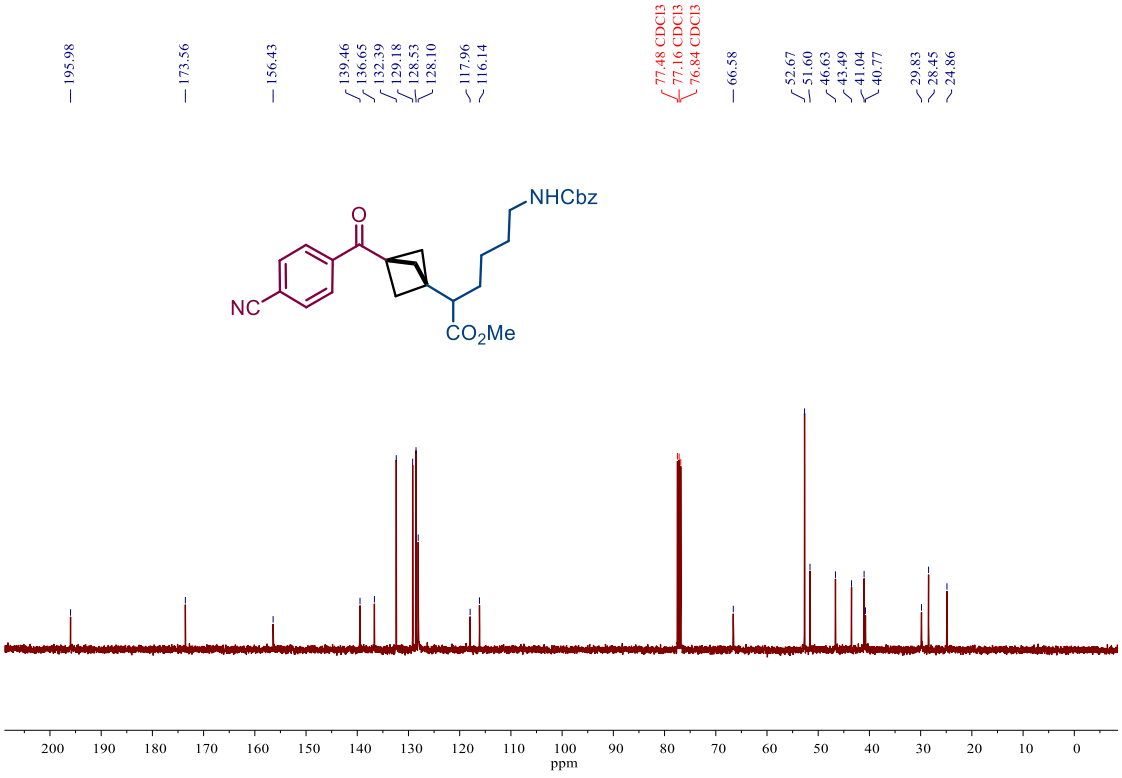
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 63



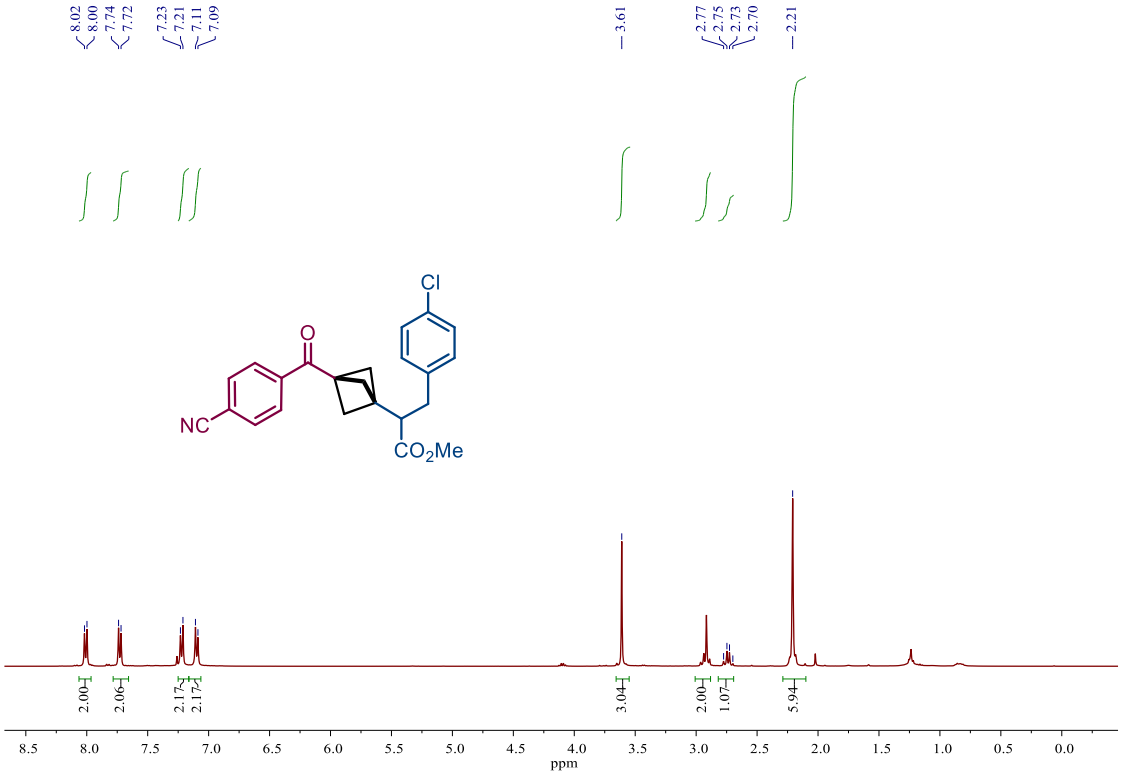
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 63



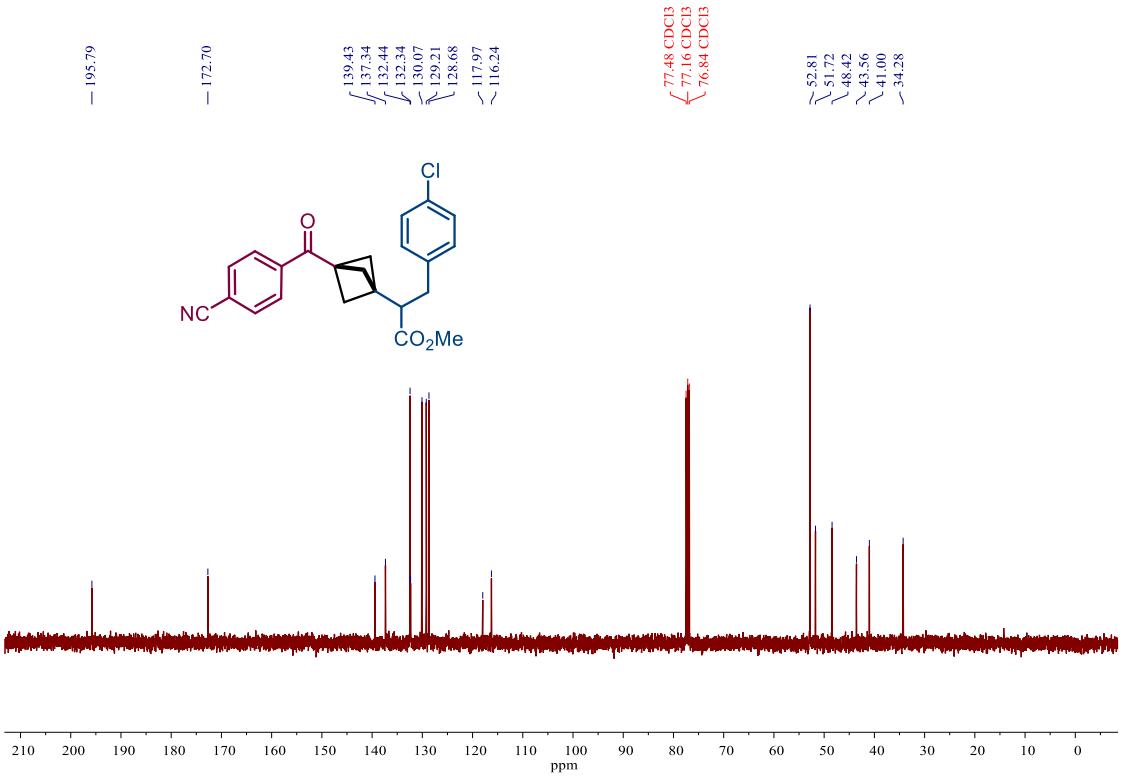
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 64



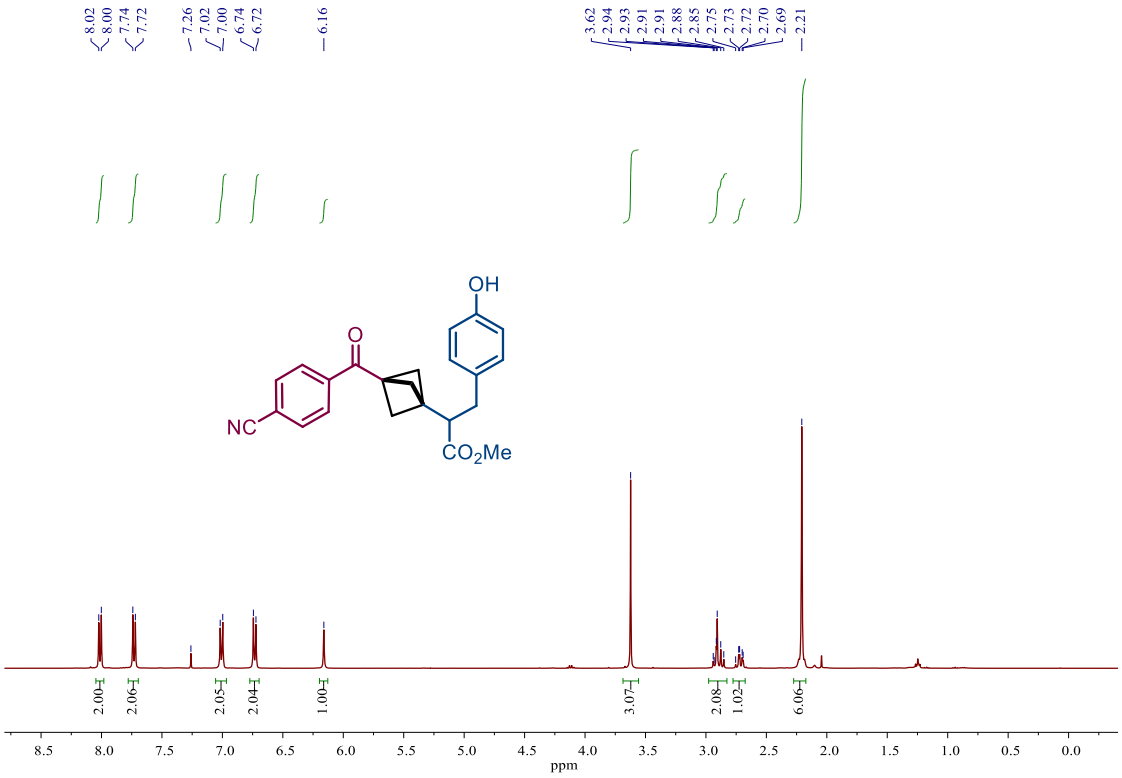
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 64



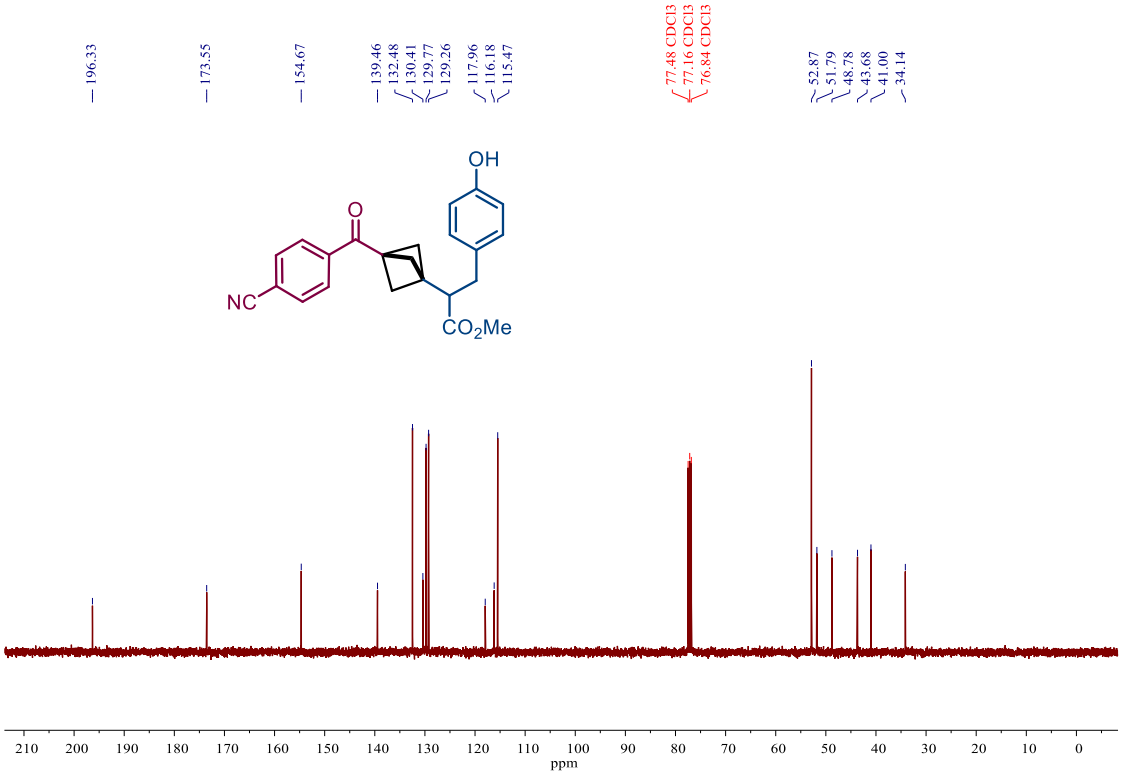
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 65



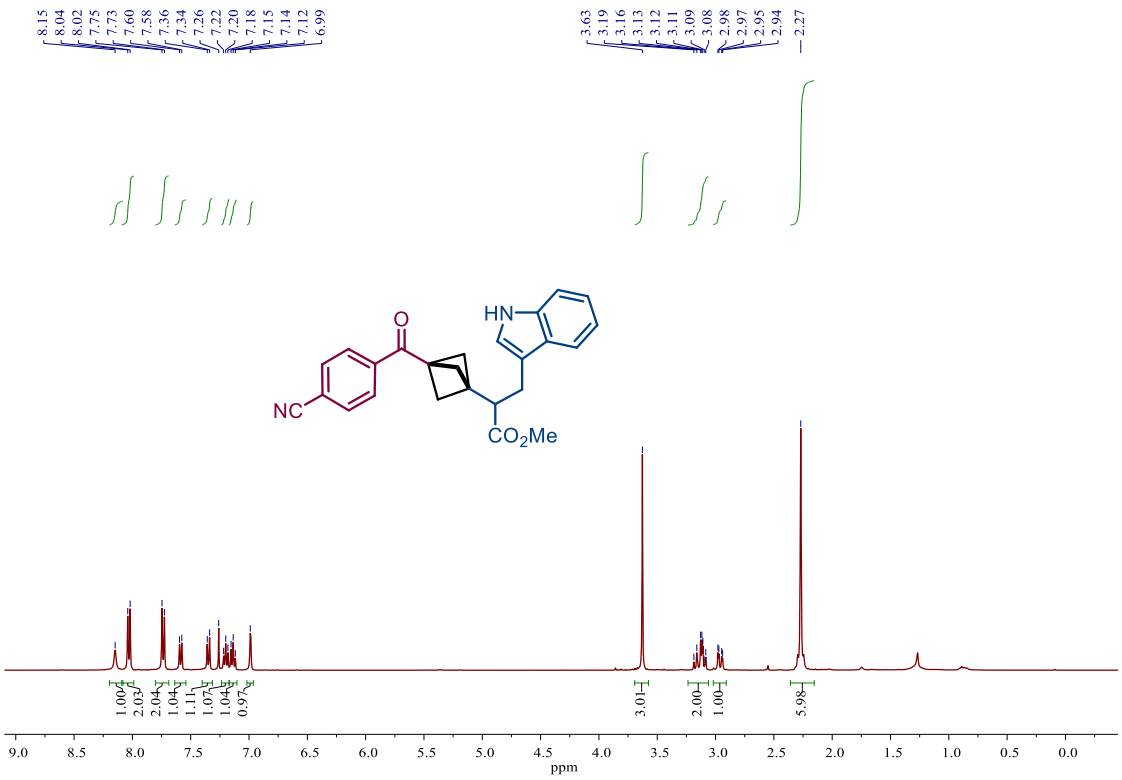
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 65



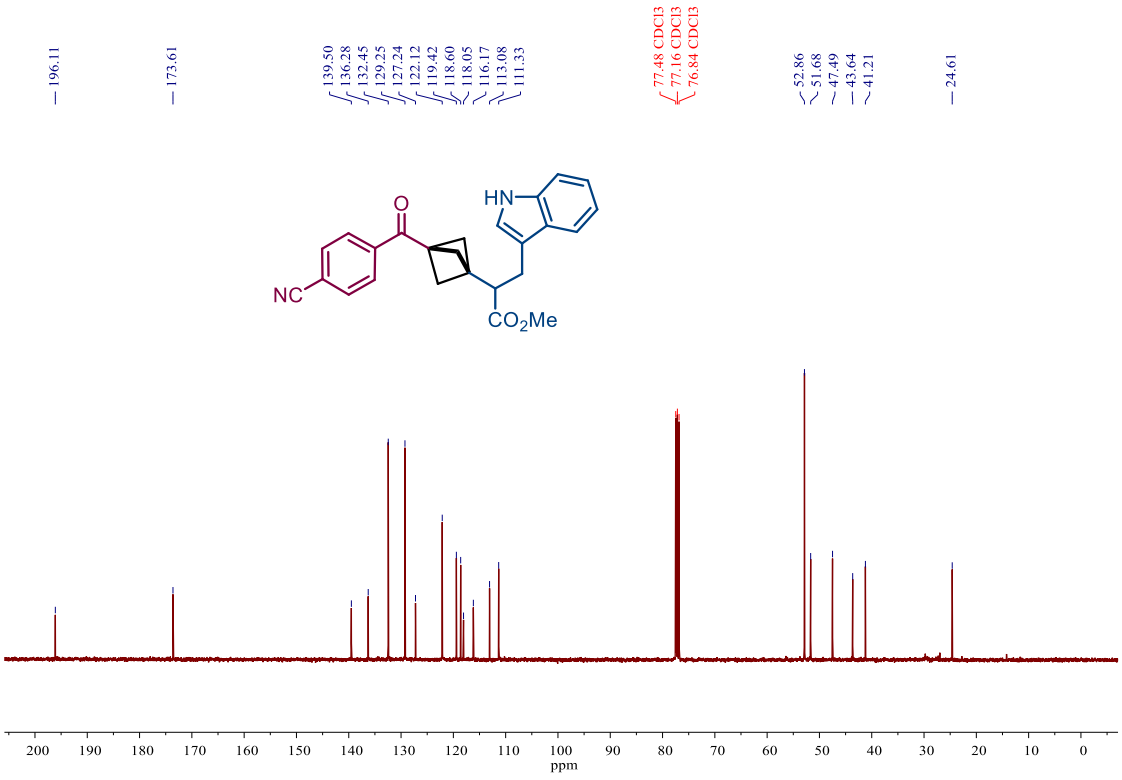
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 66



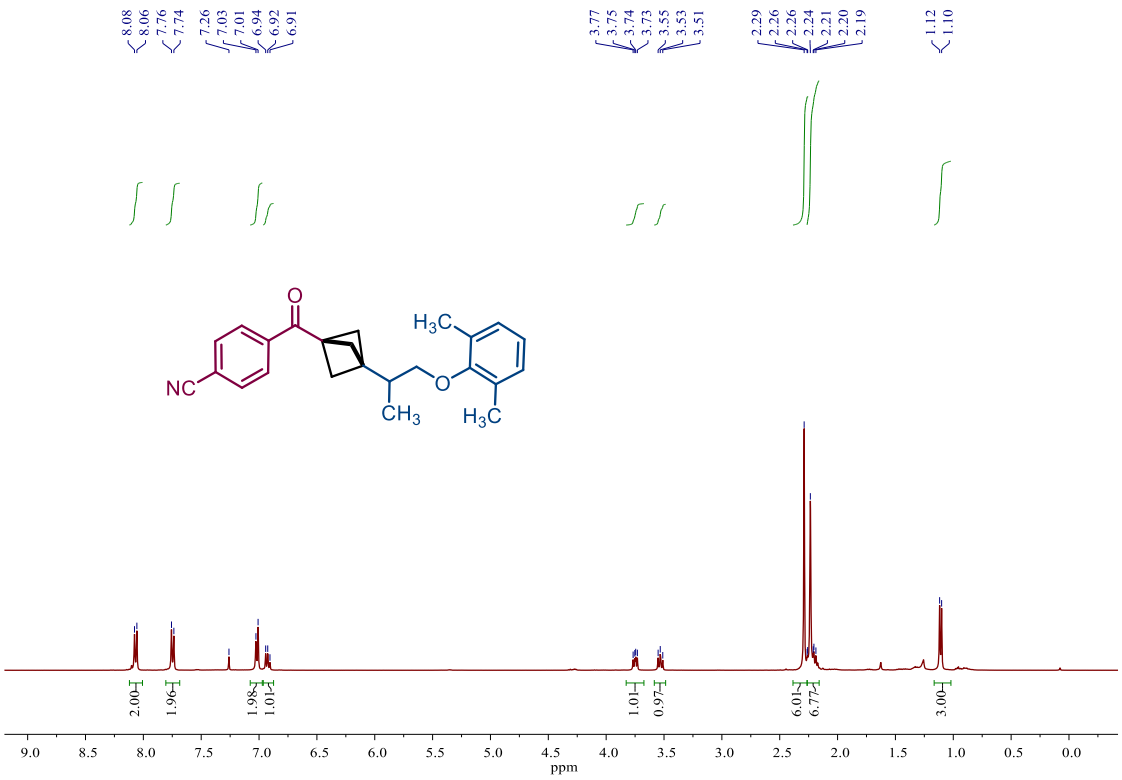
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 66



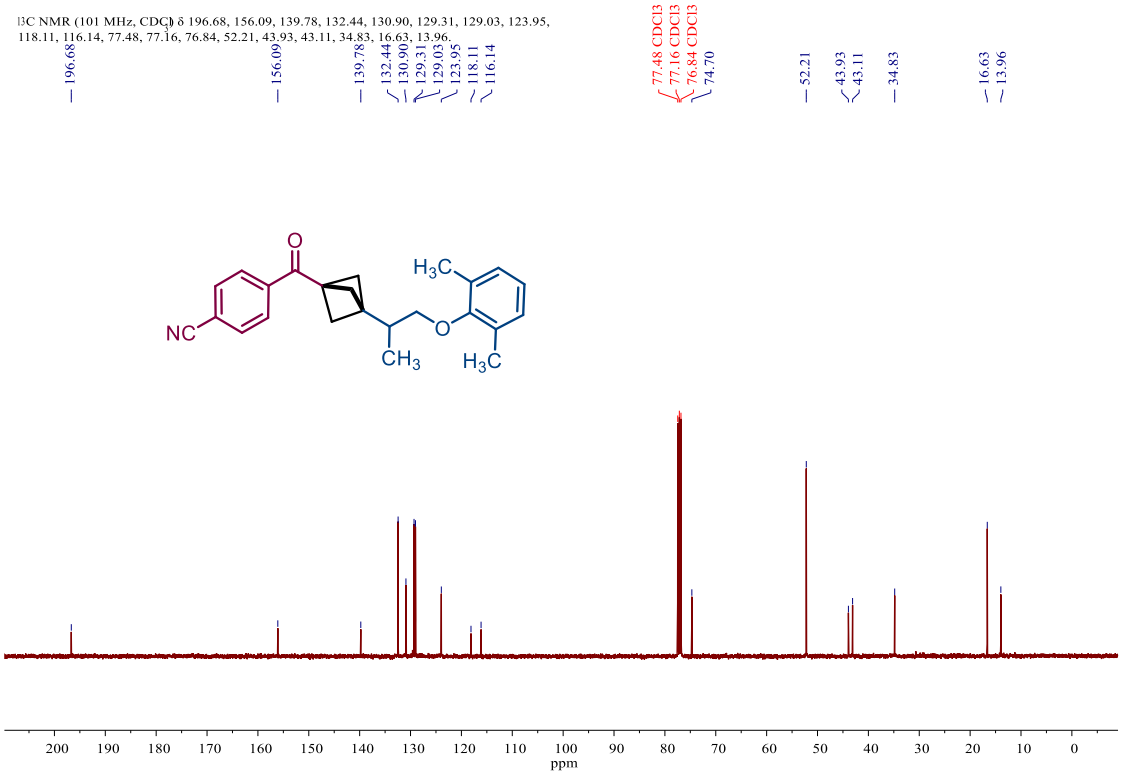
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 67



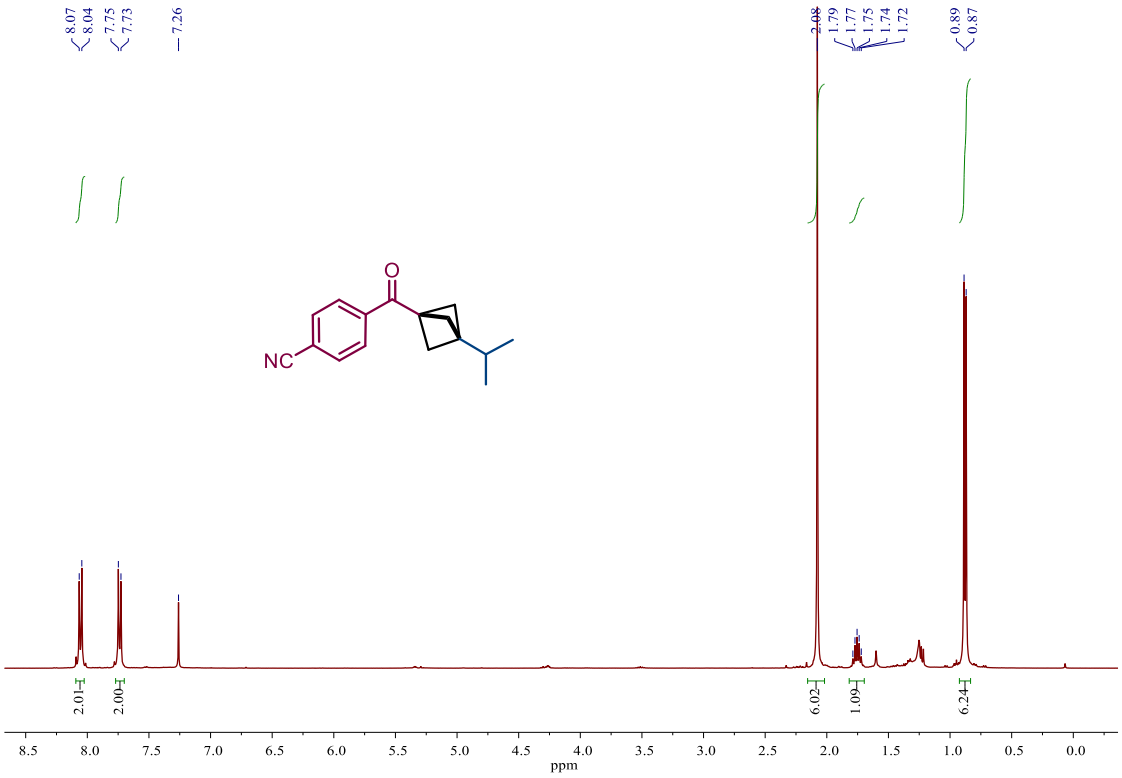
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 67



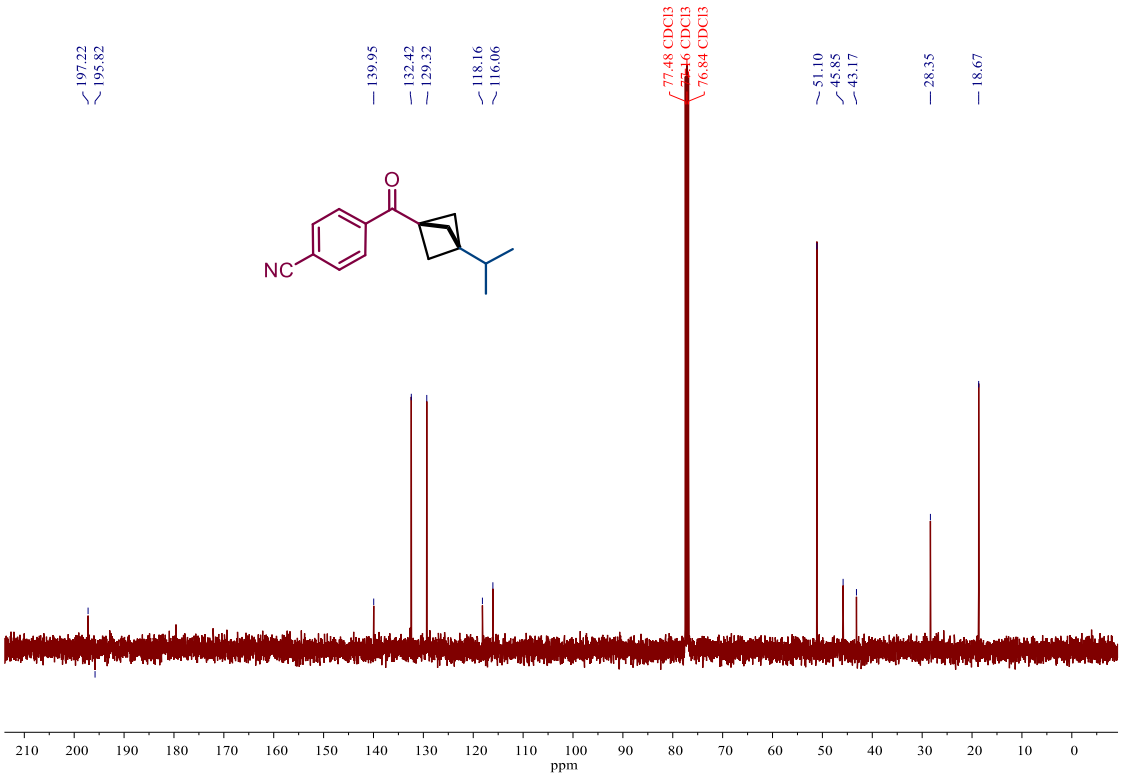
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 68



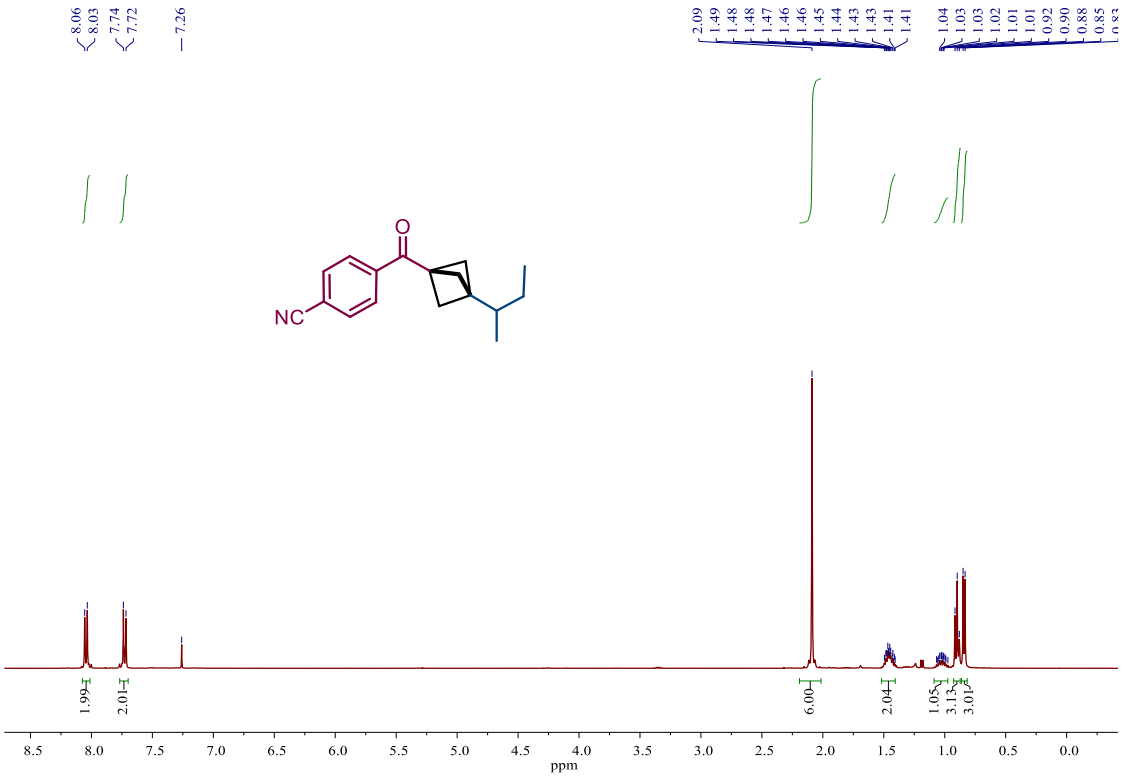
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 68



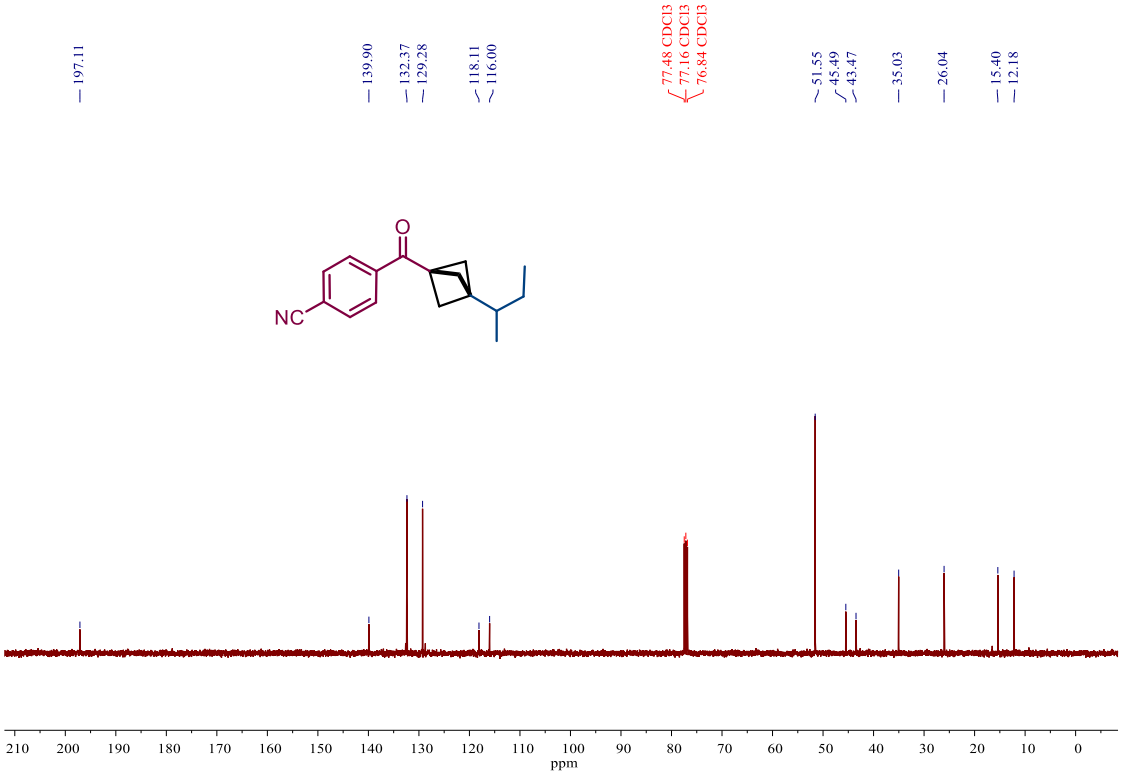
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 69



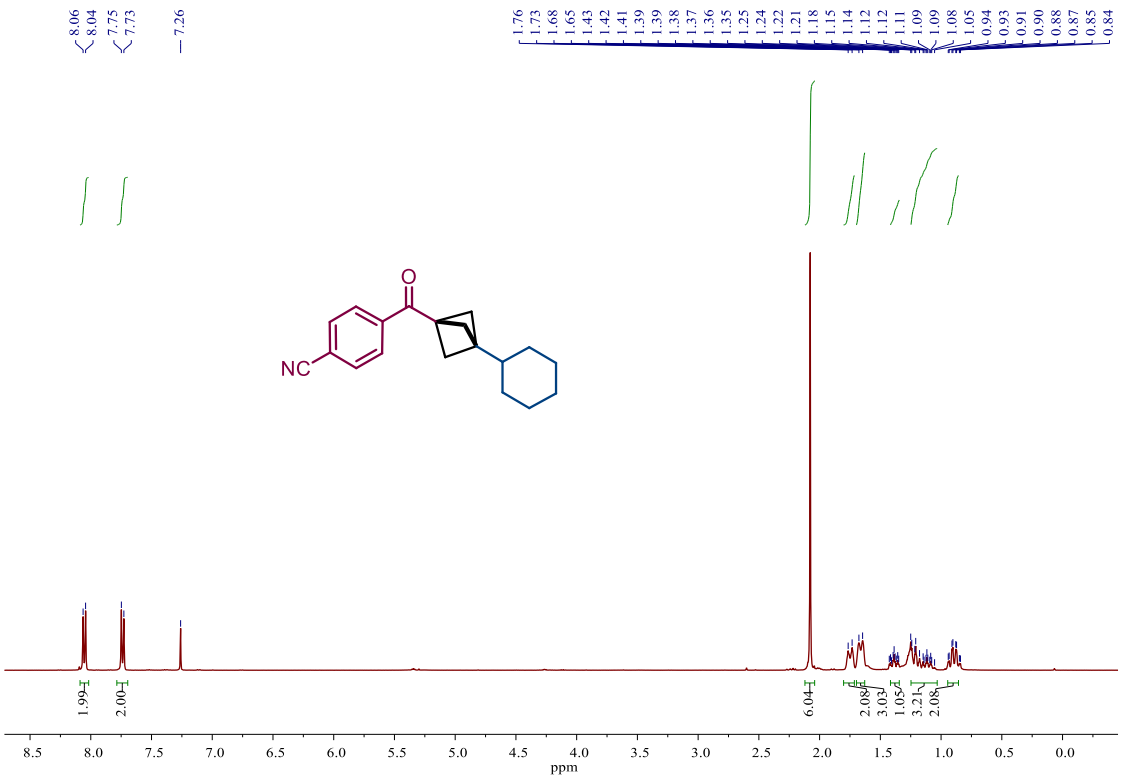
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 69



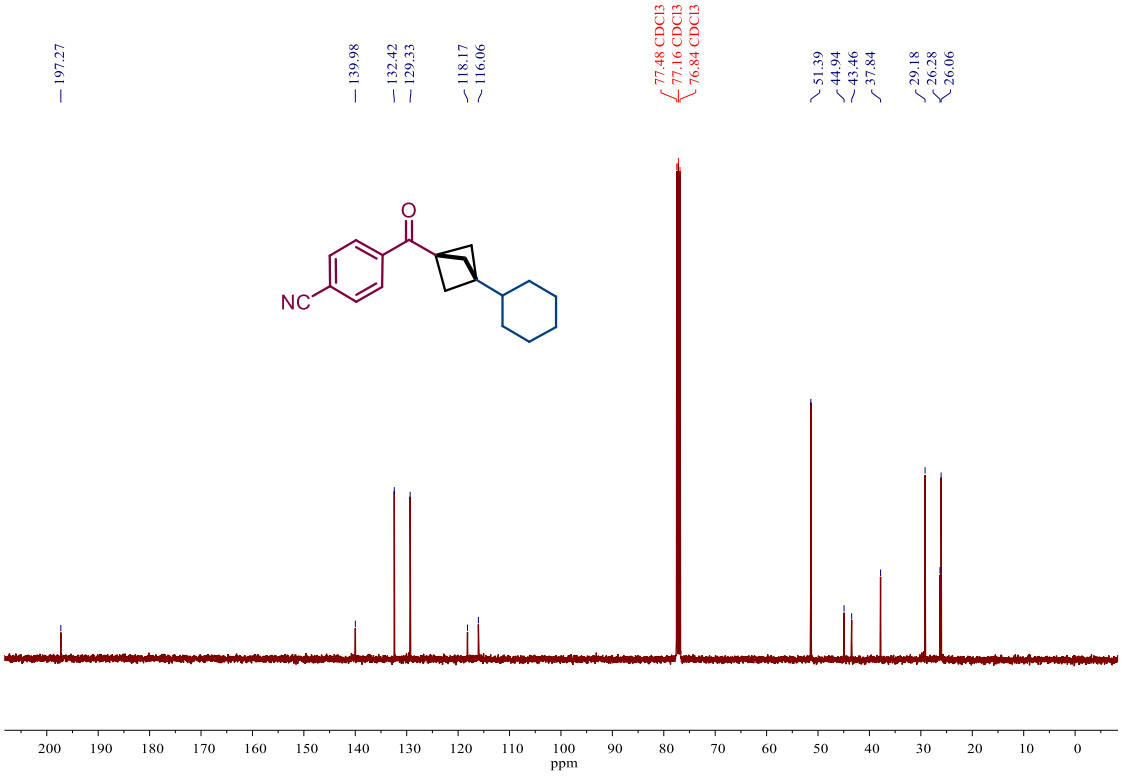
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 70



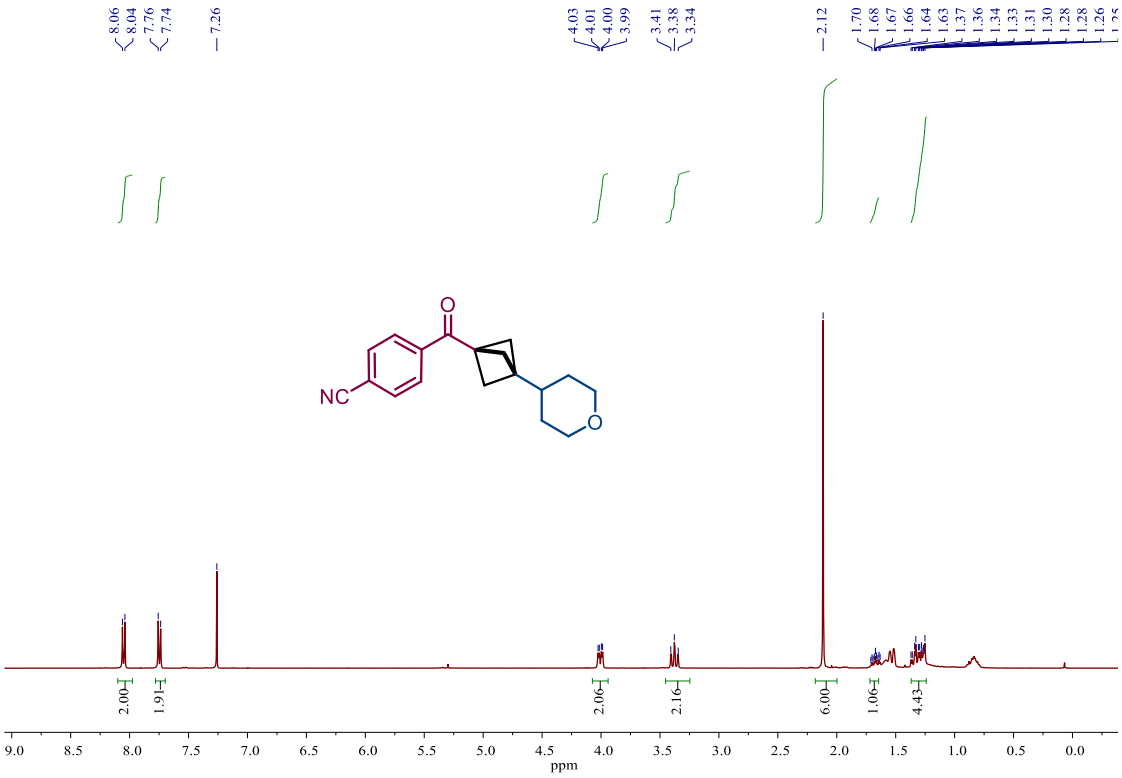
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 70



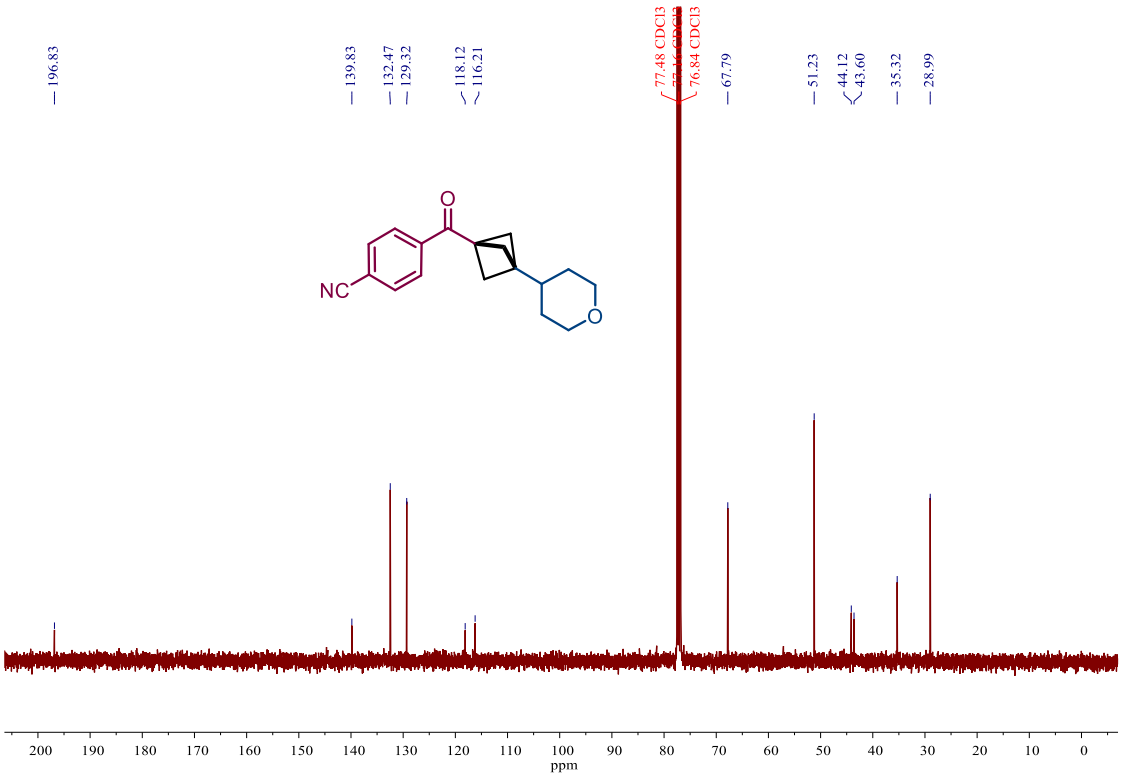
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 71



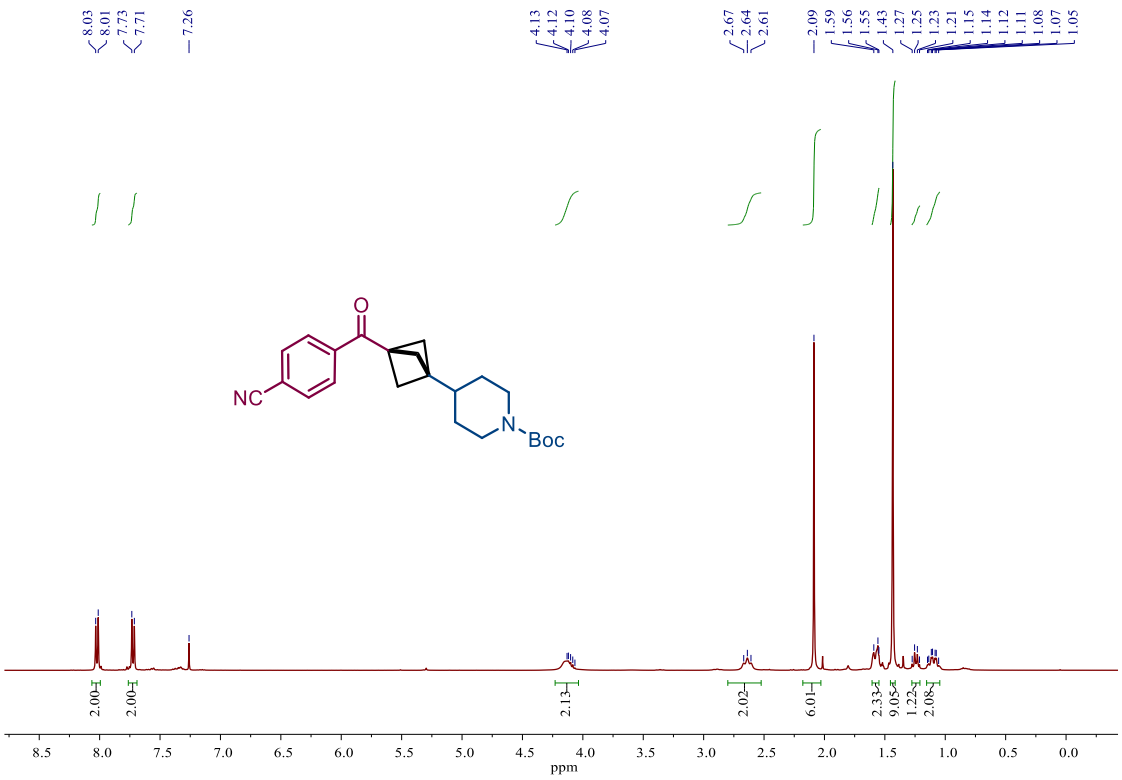
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 71



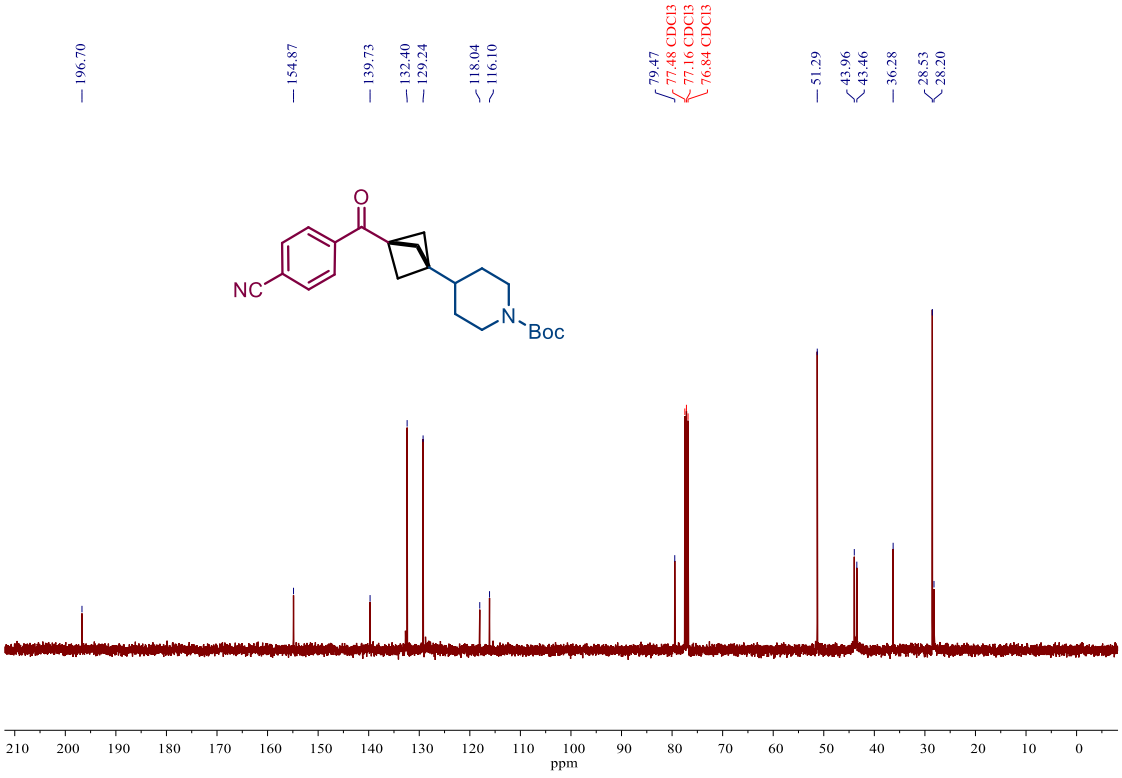
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 72



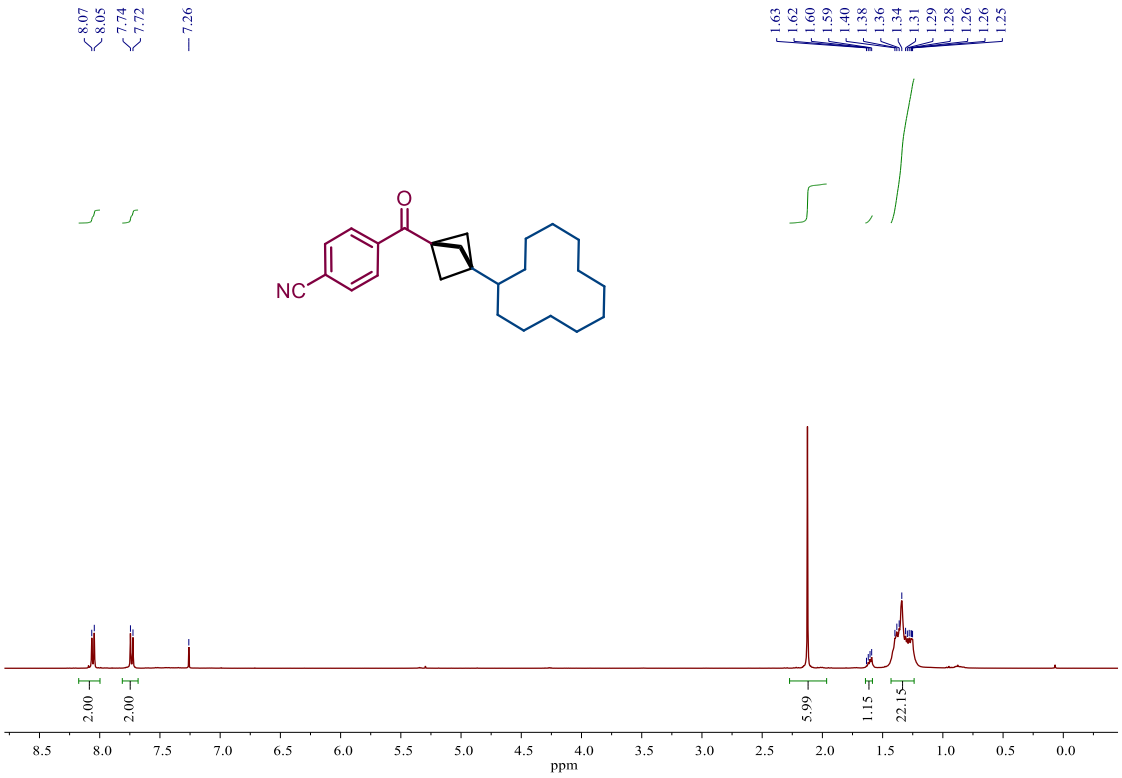
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 72



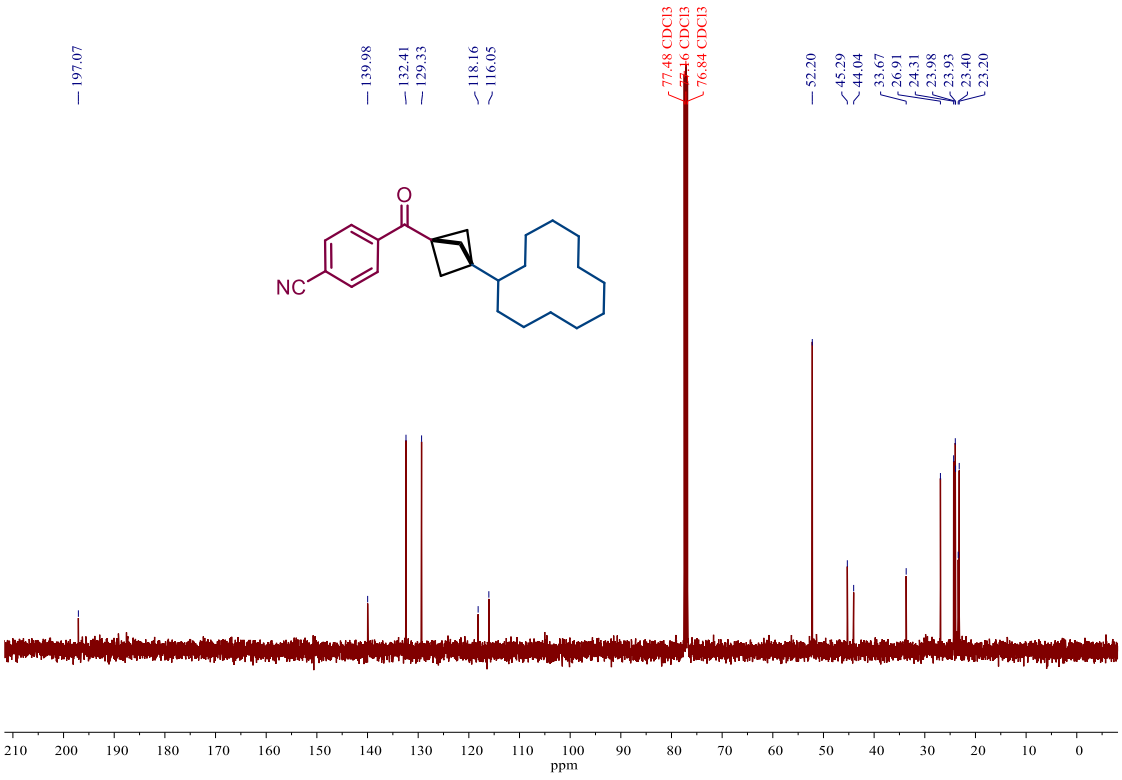
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 73



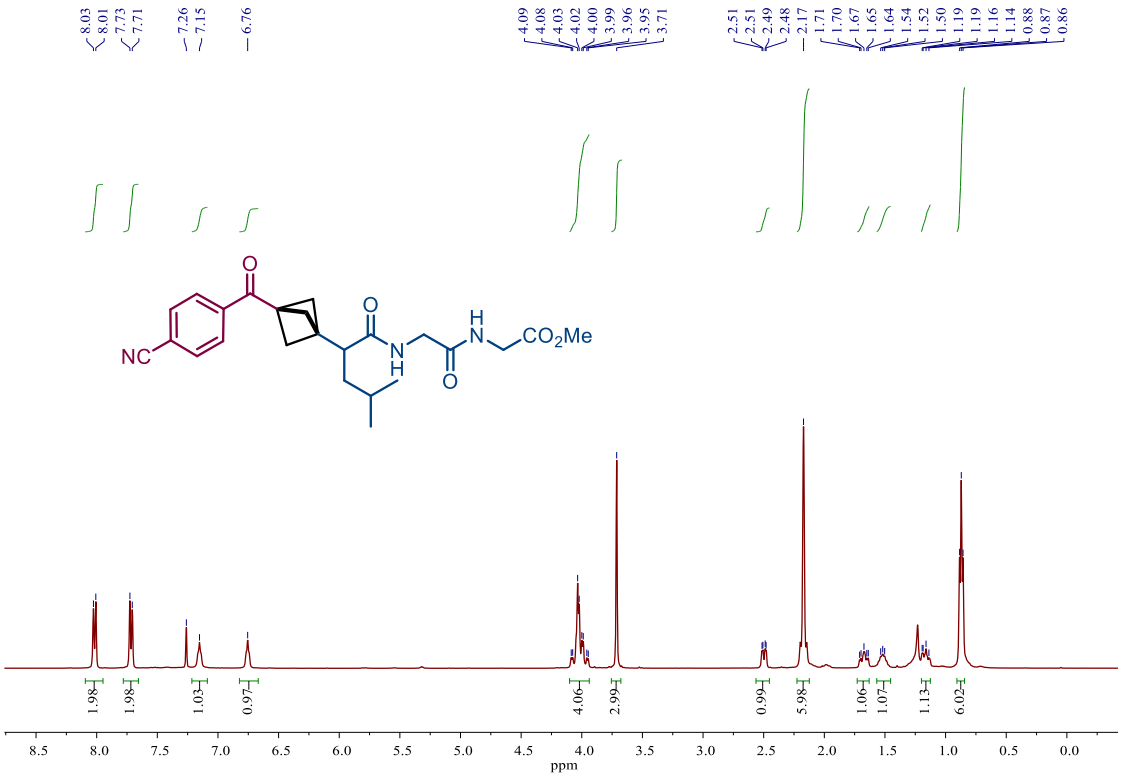
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 73



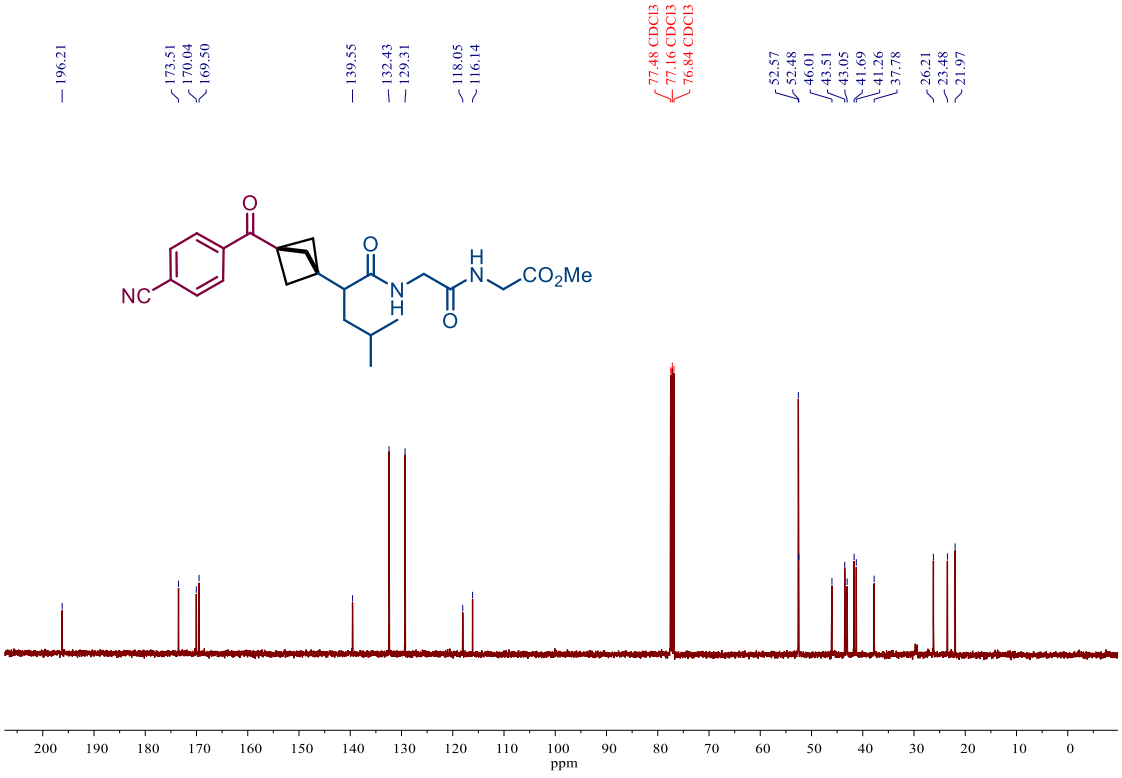
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 74



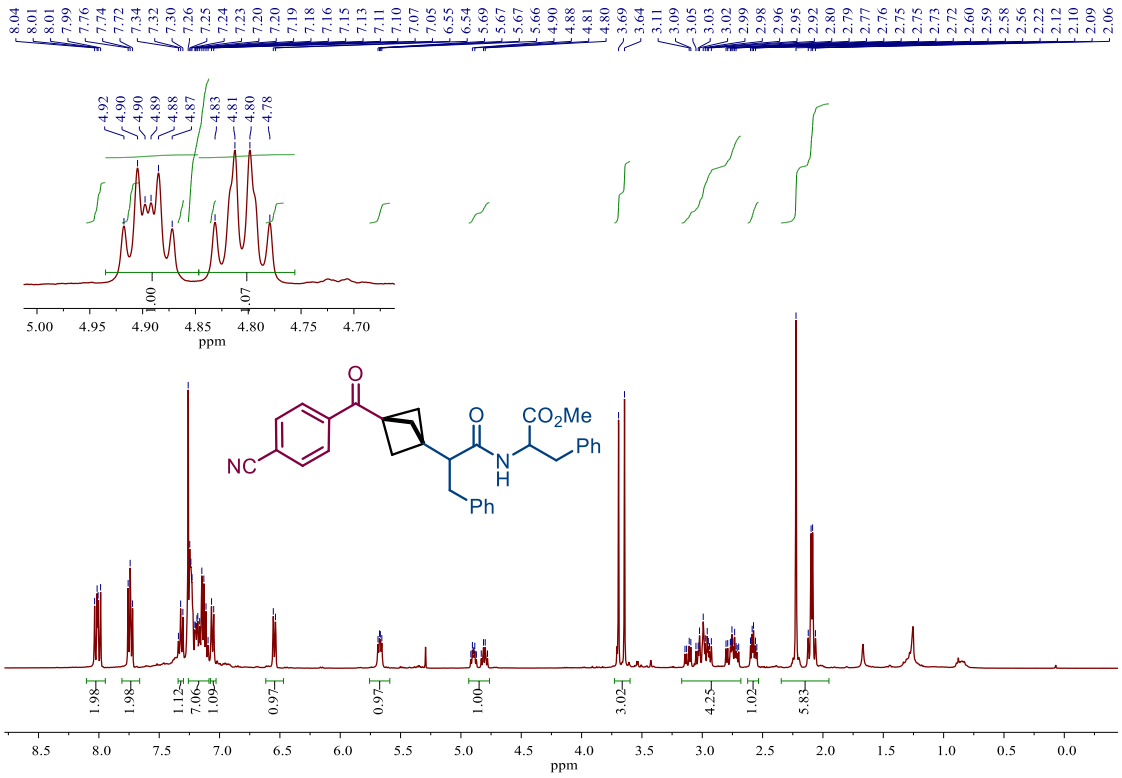
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 74



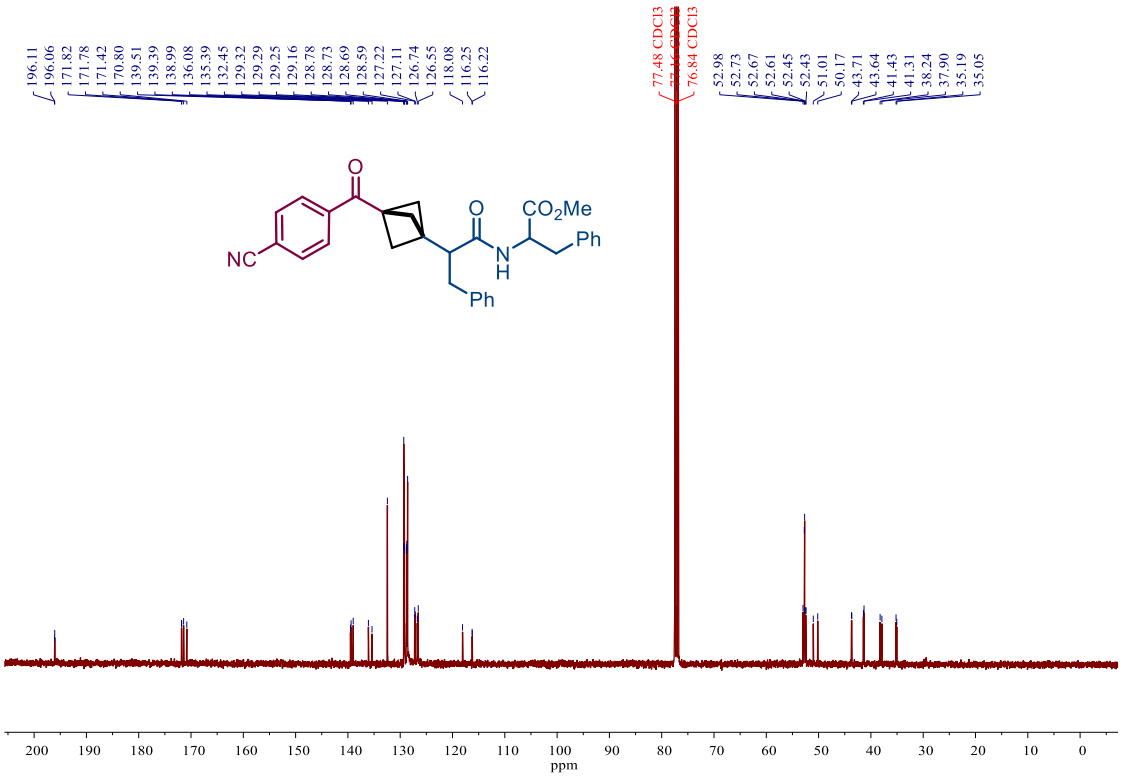
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 75



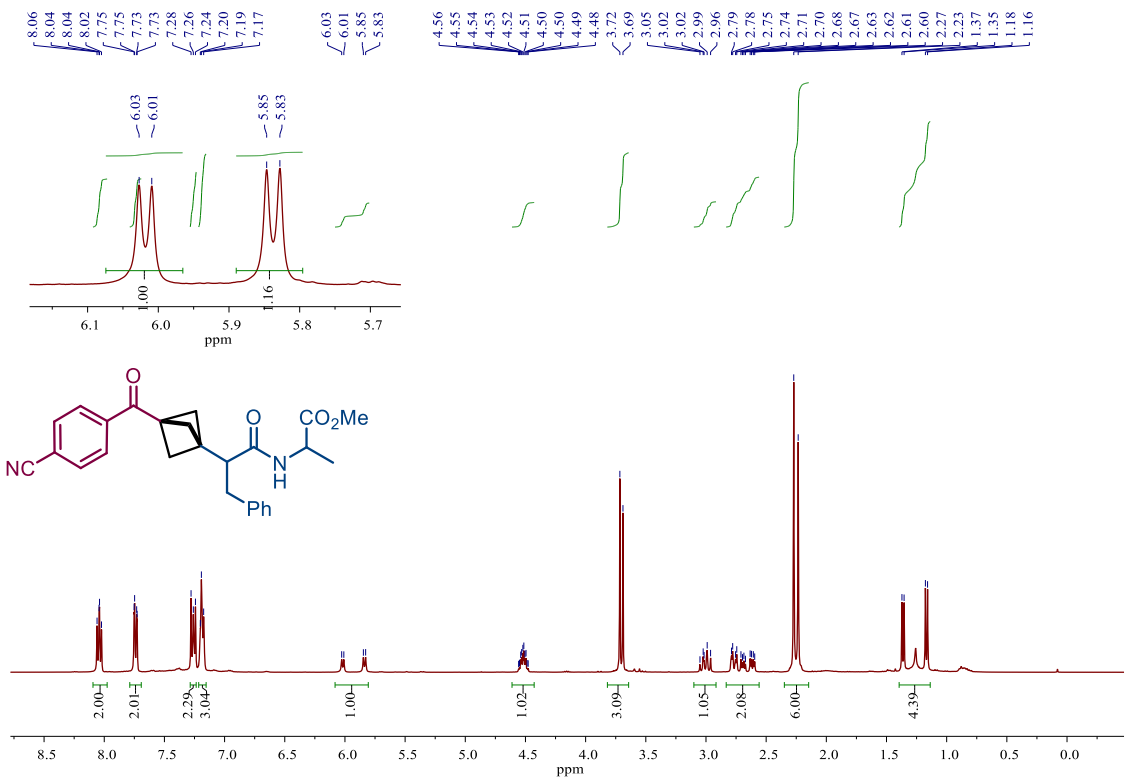
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 75



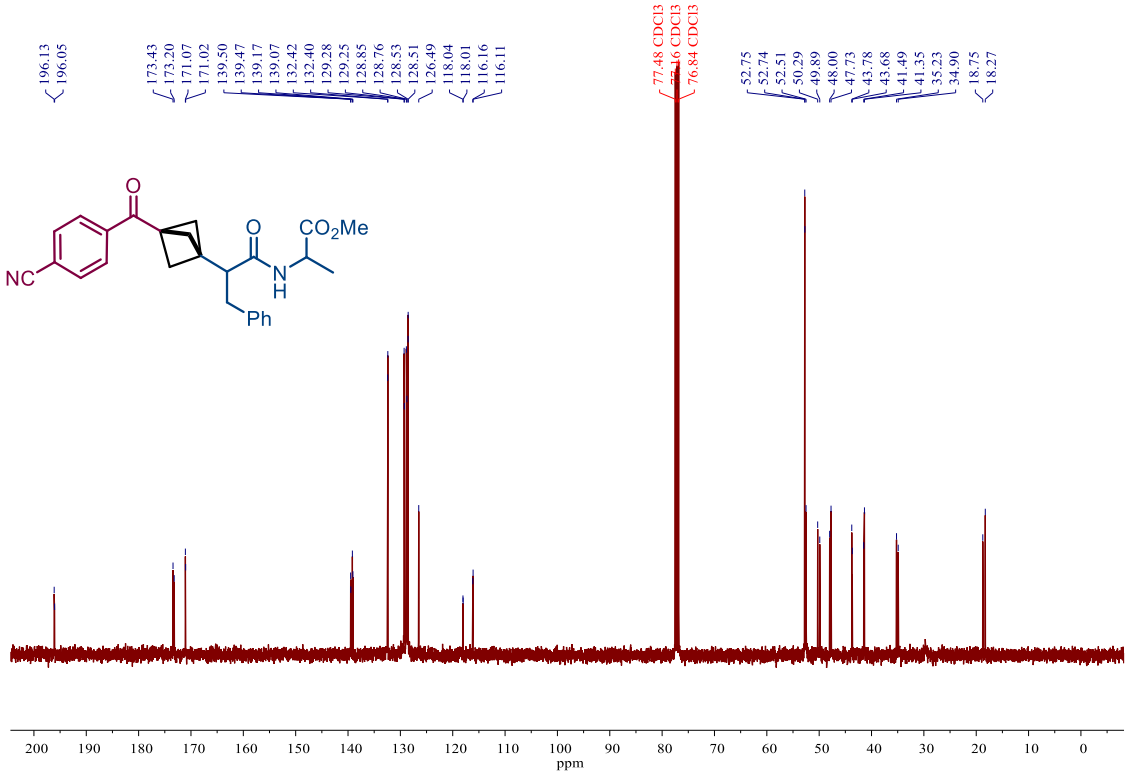
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 76



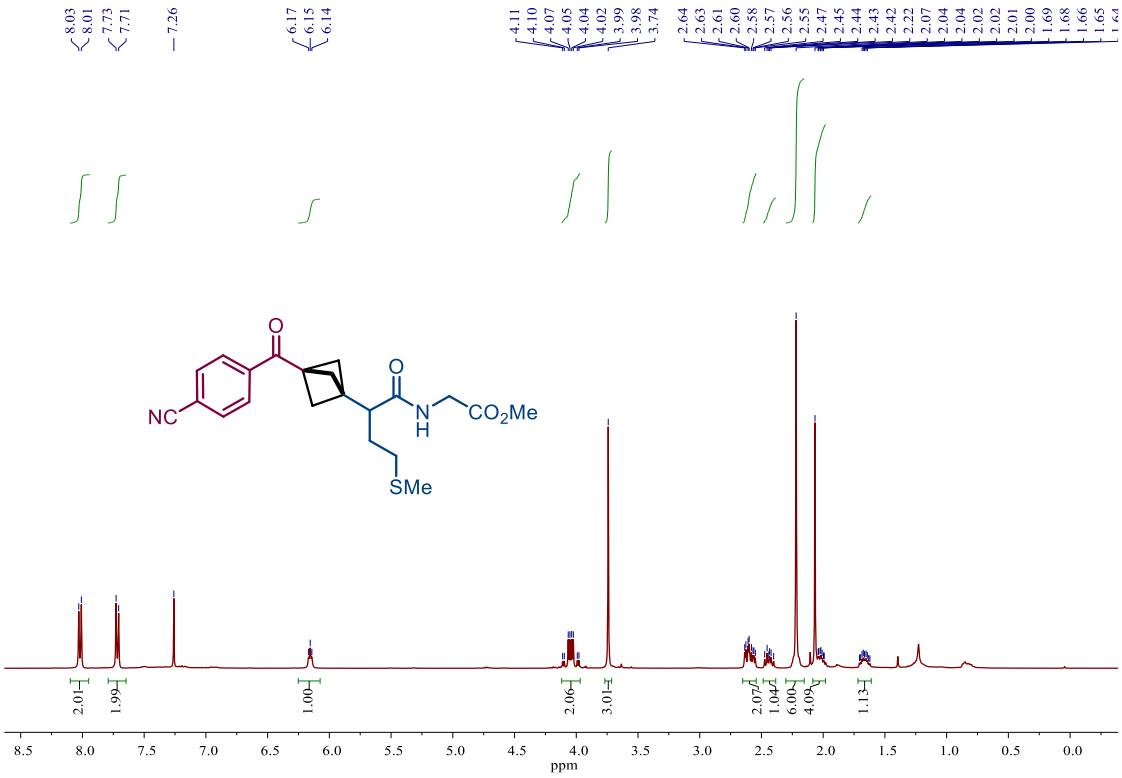
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 76



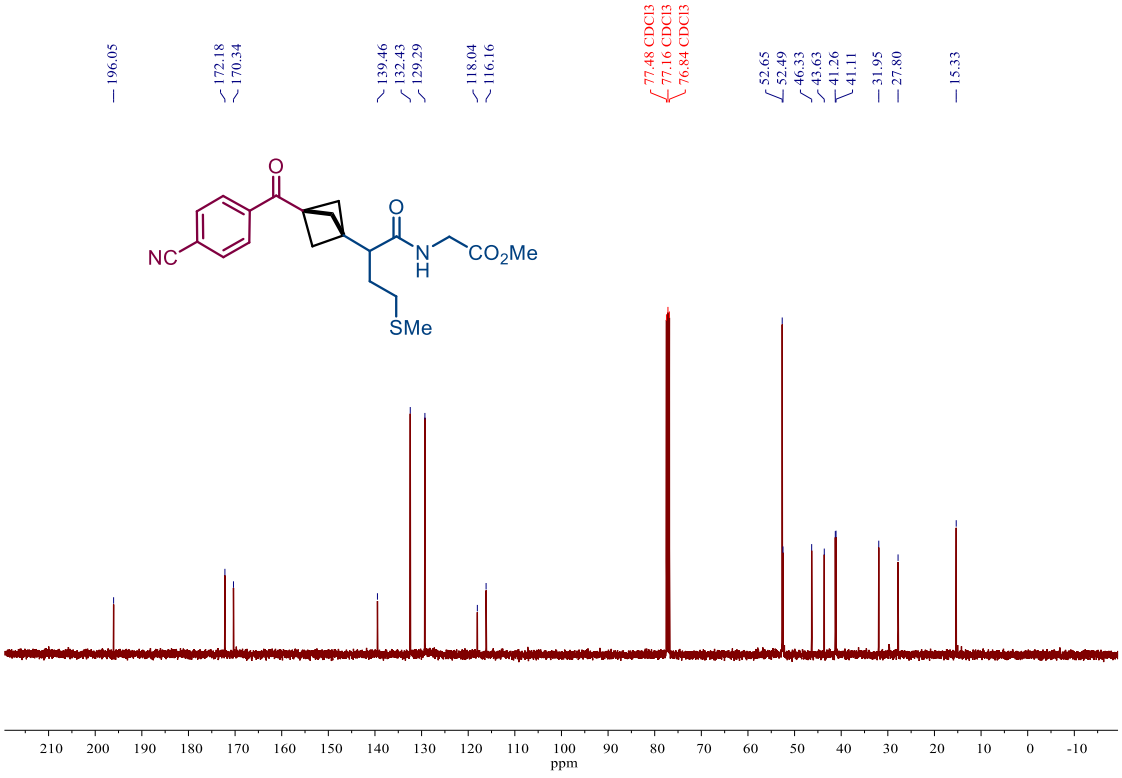
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 77



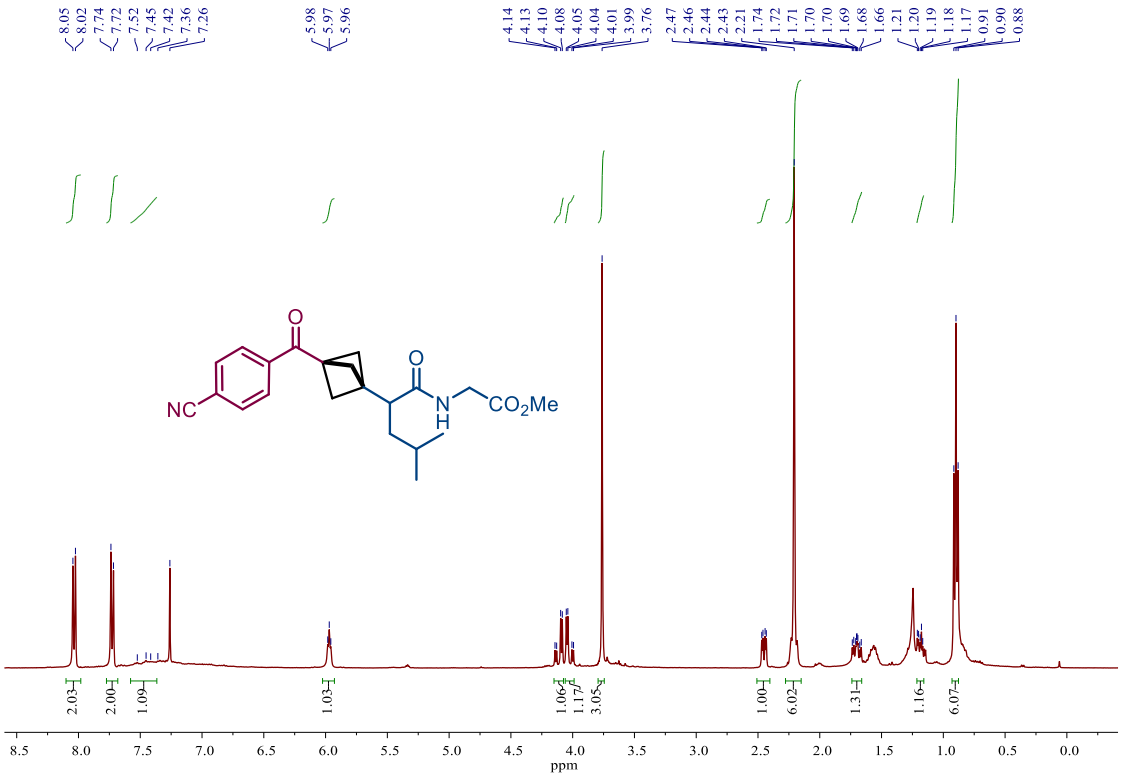
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 77



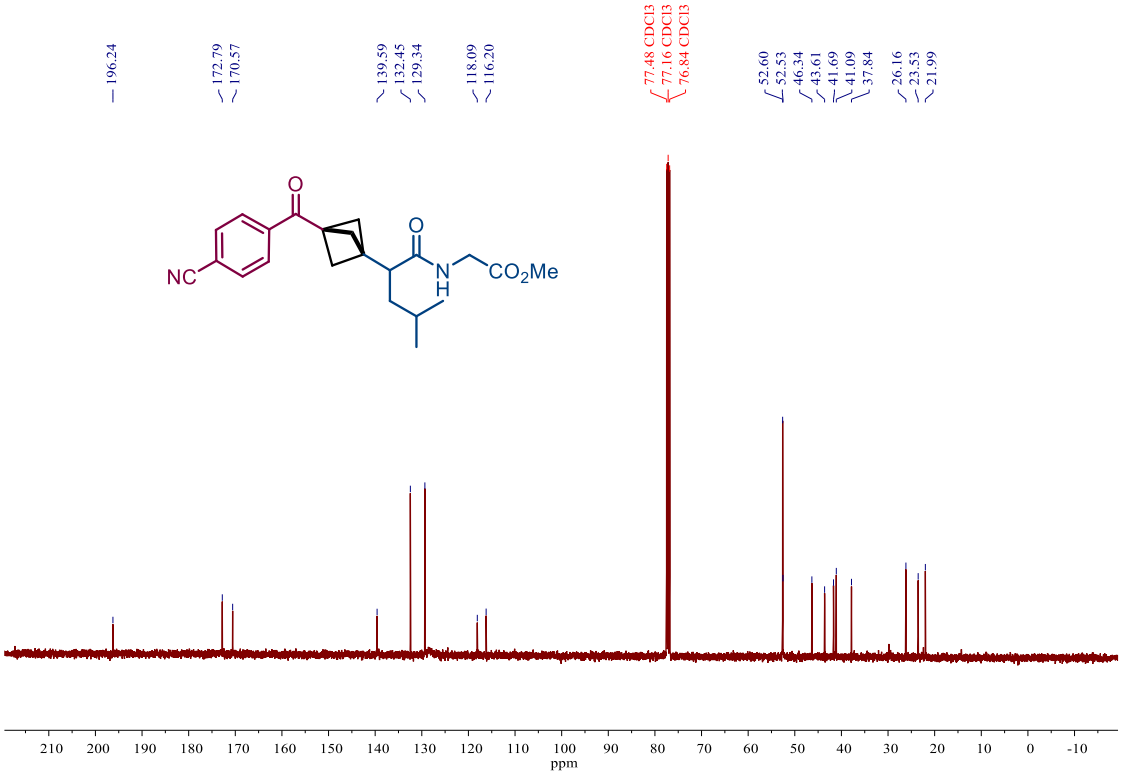
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 78



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 78



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound 79



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of compound 79