Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary Information

Cobalt-Catalyzed C(sp^2)–H/C(sp^3)–H Coupling via Directed C–H Activation and 1,5-Hydrogen Atom Transfer

Qiao Sun and Naohiko Yoshikai*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

Contents

Materials and Methods

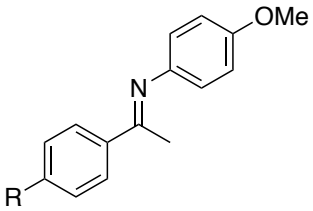
General. All reactions dealing with air- or moisture-sensitive compounds were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash column chromatography was performed using 40-63μm silica gel (Si 60, Merck). ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-300 (300 MHz), AV-500 (500 MHz) or BBFO-400 (400 MHz) NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0 ppm). ^{19}F NMR spectra are referenced to external CF_3CO_2H (–76.55 ppm). Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a glass capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 μm film thickness). High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points were determined using a capillary melting point apparatus and are uncorrected.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Anhydrous $CoBr_2$ (> 98%) and 1,3-bis(2,6-diisopropylphenyl)imidazolinium chloride (SIPr•HCl) were purchased from Alfa Aesar and used as received. THF and 1,2-dimethoxyethane (DME) were distilled over Na/benzophenone. Grignard reagents were prepared from the corresponding alkyl halides and magnesium turnings in anhydrous THF, and titrated before use.

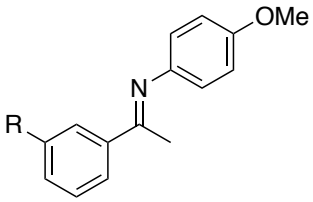
Preparation of Starting Materials

Preparation of Aryl Imines

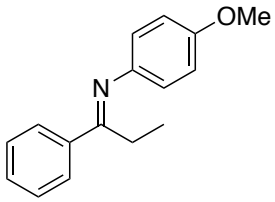
All imines (see below) were synthesized according to the literature procedures,[1] and purified by recrystallization or distillation. Spectral data for these compounds showed good agreement with the literature data.[2]



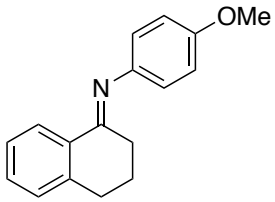
1a (R = H)
1b (R = Me)
1c (R = F)
1d (R = Cl)
1e (R = Ph)
1f (R = OMe)
1g (R = CF_3)



1h (R = CF_3)
1i (R = Cl)
1j (R = F)



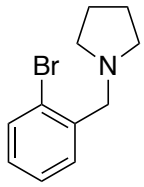
1k



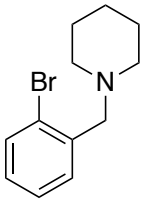
1l

Preparation of *N*-(2-Bromobenzyl)amines

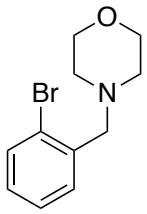
Cyclic amines were alkylated with 2-bromobenzyl bromide using the method reported by Li (2-bromobenzyl bromide/KOH/EtOH).[3] Acyclic amines were alkylated with 2-bromobenzyl bromide using the method reported by Mugesh (2-bromobenzyl bromide/TEA/toluene).[4] Spectral data for **2a**,[5] **2c**,[6] **2d**,[7] and **2f**[8] showed good agreement with the literature data.



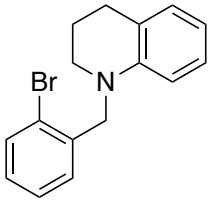
2a



2b



2c



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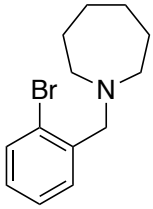
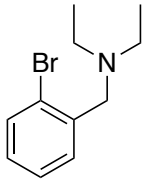
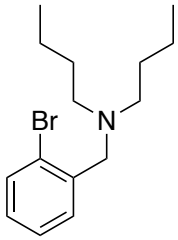


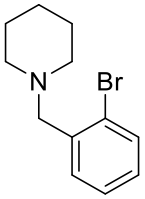
2e



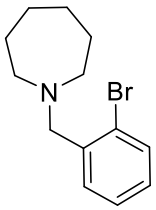
2f



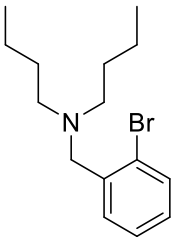
2g



1-(2-Bromobenzyl)piperidine (2b): Obtained in 74% yield as a light yellow oil. R_f 0.44 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53-7.49 (m, 2H), 7.29-7.25 (m, 1H), 7.09 (td, J = 7.6, 1.6 Hz, 1H), 3.55 (s, 2H), 2.47-2.44 (m, 4H), 1.62-1.56 (m, 4H), 1.48-1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 132.5, 130.6, 128.0, 127.1, 124.5, 62.5, 54.6, 26.0, 24.3; HRMS (ESI) Calcd for $C_{12}H_{17}NBr$ $[M + H]^+$ 254.0544, found 254.0536.



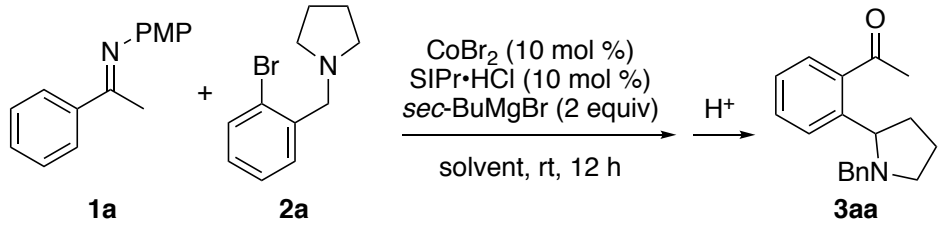
1-(2-Bromobenzyl)azepane (2e): Obtained in 71% yield as a light yellow oil. R_f 0.35 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 2H), 7.30-7.26 (m, 1H), 7.08 (td, J = 7.6, 1.6 Hz, 1H), 3.71 (s, 2H), 2.70-2.67 (m, 4H), 1.64-1.62 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.4, 132.5, 130.4, 127.9, 127.1, 124.2, 61.7, 55.8, 28.4, 27.1; HRMS (ESI) Calcd for $C_{13}H_{19}NBr$ $[M + H]^+$ 268.0701, found 268.0703.



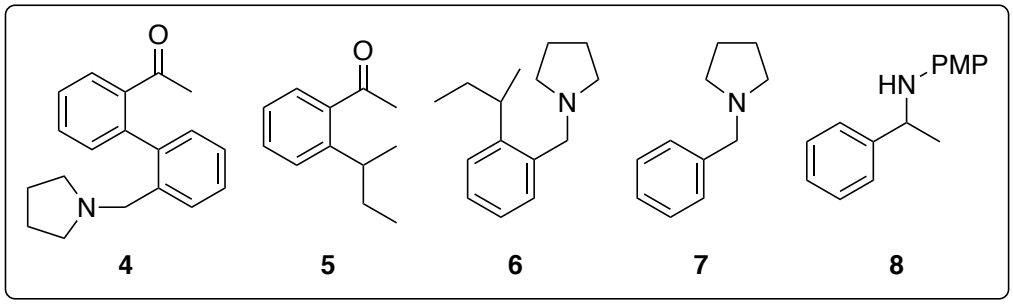
***N*-(2-Bromobenzyl)-*N*-butylbutan-1-amine (2g)**: obtained in 70% yield as a light yellow oil. R_f0.67 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59-7.50 (m, 2H), 7.30-7.26 (m, 1H), 7.08 (td, J = 7.6, 1.4 Hz, 1H), 3.63 (s, 2H), 2.46 (t, J = 7.3 Hz, 4H), 1.50-1.42 (m, 4H), 1.31 (sextet, J = 7.4 Hz, 4H), 0.89 (t, J = 7.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8, 132.4, 130.5, 127.8, 127.1, 124.0, 58.3, 54.0, 29.4, 20.6, 14.1; HRMS (ESI) Calcd for $C_{15}H_{25}NBr$ $[M + H]^+$ 298.1170, found 298.1170.

Cobalt-Catalyzed C(sp^2)–H/C(sp^3)–H Coupling between Aryl Imines and N-(2-Bromobenzyl)amines

Table S1. Formation of Byproducts[a]



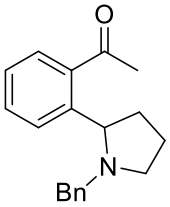
1a **2a** **3aa**



4 **5** **6** **7** **8**

entry	solvent	yield (%)[b]					
		3aa	**4**	**5**	**6**	**7**	**8**
1	THF	30	3	3	13	19	3
2[c]	THF/Et_2O (1:1)	34	4	1	2	14	5
3[c]	THF/DME (1:1)	47	5	1	16	20	2
4[d]	THF/DME (1:1)	55	0	5	0	19	6

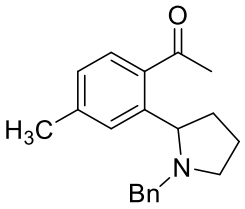
[a]The reaction was performed using 0.3 mmol of **1a** (c = 0.3 M) and 0.6 mmol of **2a**. [b]The yield of **3aa** was determined by ^{1}H NMR. The yields of **4**–**8** were estimated by GC using *n*-tridecane as an internal standard. [c]The amount of *sec*-BuMgBr was 2.2 equiv. [d]The reaction was performed using 0.4 mmol of **1a** and 0.2 mmol of **2a** (c = 0.2 M) at 0 °C.



Typical Procedure: 1-(2-(1-Benzylpyrrolidin-2-yl)phenyl)ethan-1-one (3aa). In a 10 ml Schlenk tube were placed 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol), (*E*)-*N*-(4-methoxyphenyl)-1-phenylethan-1-imine (**1a**, 90.1 mg, 0.40 mmol), 1,3-bis(2,6-

diisopropylphenyl)imidazolinium chloride (SIPr•HCl, 8.5 mg, 0.020 mmol), a freshly prepared THF solution of $CoBr_2$ (0.10 M, 0.20 mL, 0.020 mmol), and DME (0.50 ml). The resulting solution was cooled in an ice bath, followed by the addition of a THF solution of *sec*-BuMgBr (1.34 M, 0.30 ml, 0.40 mmol). The resulting mixture was stirred in the ice bath for 12 h, and then quenched by the addition of 3 N HCl (1.0 ml). The resulting mixture was stirred at room temperature for 1 h, and then neutralized with 3 N NaOH (2.0 ml) and extracted with EtOAc (3 x 10 ml). The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc = 10/1) to afford the title compound as a light yellow oil (27.4 mg, 49%).

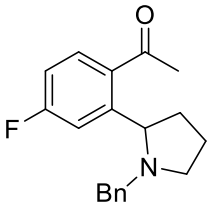
R_f 0.32 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.59 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.55-7.51 (m, 1H), 7.32-7.21 (m, 6H), 3.92 (t, *J* = 8.2 Hz, 1H), 3.81 (d, *J* = 13.1 Hz, 1H), 3.14-3.08 (m, 1H), 3.10 (d, *J* = 13.2 Hz, 1H), 2.61 (s, 3H), 2.51-2.42 (m, 1H), 2.24 (q, *J* = 8.9 Hz, 1H), 1.93-1.75 (m, 2H), 1.70-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4, 144.2, 139.7, 139.0, 131.7, 128.5, 128.0 (two signals overlapped), 127.9, 126.6, 126.1, 65.3, 58.5, 53.3, 35.0, 30.2, 22.7; HRMS (ESI) Calcd for $C_{19}H_{22}NO$ $[M + H]^+$ 280.1701, found 280.1699.



1-(2-(1-Benzylpyrrolidin-2-yl)-4-methylphenyl)ethan-1-one (3ba): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(*p*-tolyl)ethan-1-imine (**1b**, 95.7 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 20/1) of the crude product afforded the title compound as a brown oil (28.2 mg, 48%).

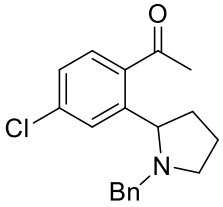
R_f 0.23 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.31-7.28 (m, 4H), 7.24-7.19 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 3.95 (t, *J* = 8.2 Hz, 1H), 3.77 (d, *J* = 13.0 Hz, 1H), 3.11-3.03 (m, 1H), 3.05 (d, *J* = 13.0 Hz, 1H), 2.58 (s, 3H), 2.49-2.40 (m, 1H), 2.42 (s, 3H), 2.22 (q, *J* = 8.9 Hz, 1H), 1.89-1.73 (m, 2H), 1.63-1.54 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.7, 144.7, 142.4, 139.9, 135.9, 128.8, 128.6, 128.5, 128.1, 126.8, 126.7, 65.3, 58.7, 53.4, 34.9, 30.0, 22.7, 21.7; HRMS (ESI) Calcd for $C_{20}H_{24}NO$

$[M + H]^+$ 294.1858, found 294.1863.



1-(2-(1-Benzylpyrrolidin-2-yl)-4-fluorophenyl)ethan-1-one (3ca): The typical procedure was applied to (*E*)-1-(4-fluorophenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (**1c**, 97.3 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 30/1) of the crude product afforded the title compound as a white solid (30.4 mg, 51%).

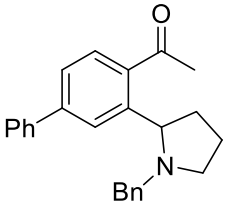
R_f 0.35 (hexane/EtOAc = 10/1); m.p. 92.9-95.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, *J* = 11.0, 2.7 Hz, 1H), 7.66 (dd, *J* = 8.6, 5.7 Hz, 1H), 7.31-7.27 (m, 4H), 7.25-7.19 (m, 1H), 6.96 (td, *J* = 8.1, 2.7 Hz, 1H), 4.03 (td, *J* = 8.0, 1.4 Hz, 1H), 3.76 (d, *J* = 13.1 Hz, 1H), 3.14-3.07 (m, 1H), 3.13 (d, *J* = 13.1 Hz, 1H), 2.58 (s, 3H), 2.52-2.42 (m, 1H), 2.25 (q, *J* = 8.9 Hz, 1H), 1.89-1.75 (m, 2H), 1.60-1.51 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 165.1 ($^1J_{C-F}$ = 250.5 Hz), 149.6 (d, $^3J_{C-F}$ = 7.6 Hz), 139.6, 134.3 (d, $^4J_{C-F}$ = 2.6 Hz), 131.2 (d, $^3J_{C-F}$ = 8.8 Hz), 128.6, 128.1, 126.8, 114.8 (d, $^2J_{C-F}$ = 22.8 Hz), 113.1 (d, $^2J_{C-F}$ = 22.1 Hz), 65.0, 58.8, 53.5, 35.0, 29.9, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –106.7; HRMS (ESI) Calcd for $C_{19}H_{21}NOF$ $[M + H]^+$ 298.1607, found 298.1616.



1-(2-(1-Benzylpyrrolidin-2-yl)-4-chlorophenyl)ethan-1-one (3da): The typical procedure was applied to (*E*)-1-(4-chlorophenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (**1d**, 103.9 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 40/1) of the crude product afforded the title compound as a light yellow oil (24.8 mg, 39%).

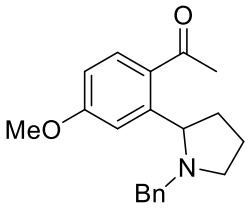
R_f 0.33 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, *J* = 2.1 Hz, 1H), 7.54 (d, *J* = 8.3 Hz, 1H), 7.31-7.19 (m, 6H), 3.93 (t, *J* = 8.1 Hz, 1H), 3.74 (d, *J* = 13.0 Hz, 1H), 3.14-3.07 (m, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 2.57 (s, 3H), 2.49-2.40 (m, 1H), 2.25 (q, *J* = 8.9

Hz, 1H), 1.89-1.72 (m, 2H), 1.62-1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.9, 147.4, 139.4, 138.2, 136.6, 129.8, 128.6, 128.3, 128.1, 126.8, 126.3, 64.9, 58.8, 53.5, 35.0, 30.0, 22.9; HRMS (ESI) Calcd for $C_{19}H_{21}NOCl$ $[M + H]^+$ 314.1312, found 314.1316.



1-(3-(1-Benzylpyrrolidin-2-yl)-[1,1'-biphenyl]-4-yl)ethan-1-one (3ea): The typical procedure was applied to (*E*)-1-([1,1'-biphenyl]-4-yl)-*N*-(4-methoxyphenyl)ethan-1-imine (**1e**, 120.6 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 20/1) of the crude product afforded the title compound as a white solid (23.5 mg, 33%).

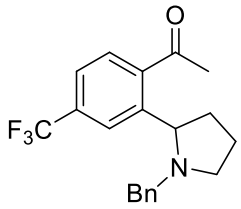
R_f 0.27 (hexane/EtOAc = 10/1); m.p. 98.5-101.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 1.7 Hz, 1H), 7.70-7.65 (m, 3H), 7.52 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.32-7.27 (m, 4H), 7.20 (t, *J* = 6.9 Hz, 1H), 4.03 (t, *J* = 8.1 Hz, 1H), 3.85 (d, *J* = 13.2 Hz, 1H), 3.17-3.11 (m, 1H), 3.15 (d, *J* = 13.3 Hz, 1H), 2.63 (s, 3H), 2.54-2.45 (m, 1H), 2.27 (q, *J* = 8.9 Hz, 1H), 1.92-1.75 (m, 2H), 1.70-1.61 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 145.4, 144.4, 140.3, 139.8, 137.3, 129.1, 128.9, 128.5, 128.1, 127.9, 127.3, 126.7 (two signals overlapped), 124.7, 65.4, 58.7, 53.6, 35.1, 30.1, 22.8; HRMS (ESI) Calcd for $C_{25}H_{26}NO$ $[M + H]^+$ 356.2014, found 356.2014.



1-(2-(1-Benzylpyrrolidin-2-yl)-4-methoxyphenyl)ethan-1-one (3fa): The typical procedure was applied to *(E)*-*N*,1-bis(4-methoxyphenyl)ethan-1-imine (**1f**, 102.1 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 8/1) of the crude product afforded the title compound as a light yellow oil (18.4 mg, 30%).

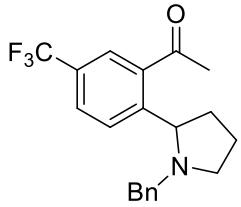
R_f 0.17 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, *J* = 2.7 Hz, 1H), 7.70 (d, *J* = 8.6 Hz, 1H), 7.32-7.27 (m, 4H), 7.23-7.19 (m, 1H), 6.79 (dd, *J* = 8.7, 2.7 Hz, 1H), 4.16

(t, J = 8.1 Hz, 1H), 3.88 (s, 3H), 3.80 (d, J = 13.2 Hz, 1H), 3.12-3.07 (m, 1H), 3.09 (d, J = 13.2 Hz, 1H), 2.57 (s, 3H), 2.54-2.47 (m, 1H), 2.24 (q, J = 8.9 Hz, 1H), 1.84-1.75 (m, 2H), 1.58-1.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.8, 162.8, 148.9, 140.1, 131.9, 130.5, 128.4, 128.1, 126.6, 112.3, 111.8, 65.4, 58.7, 55.4, 53.5, 34.7, 29.5, 22.9; HRMS (ESI) Calcd for $C_{20}H_{24}NO_2$ $[M + H]^+$ 310.1807, found 310.1805.



1-(2-(1-Benzylpyrrolidin-2-yl)-4-(trifluoromethyl)phenyl)ethan-1-one (3ga): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)ethan-1-imine (**1g**, 117.3 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 30/1) of the crude product afforded the title compound as a light yellow oil (14.5 mg, 21%).

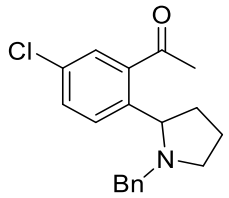
R_f 0.33 (hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.36 (s, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 7.9 Hz, 1H), 7.28-7.19 (m, 5H), 3.85 (t, J = 8.1 Hz, 1H), 3.69 (d, J = 12.9 Hz, 1H), 3.17-3.09 (m, 1H), 3.16 (d, J = 12.9 Hz, 1H), 2.60 (s, 3H), 2.46-2.39 (m, 1H), 2.29 (q, J = 8.9 Hz, 1H), 1.91-1.75 (m, 2H), 1.65-1.58 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 145.5, 141.9, 139.1, 133.1 (q, $^2J_{C\text{-}F}$ = 31.7 Hz), 128.7, 128.2, 127.8, 126.9, 125.4, 123.8 (q, $^1J_{C\text{-}F}$ = 272.0 Hz), 123.1, 65.1, 58.8, 53.6, 35.3, 30.4, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.0; HRMS (ESI) Calcd for $C_{20}H_{21}NOF_3$ $[M + H]^+$ 348.1575, found 348.1578.



1-(2-(1-Benzylpyrrolidin-2-yl)-5-(trifluoromethyl)phenyl)ethan-1-one (3ha): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 30/1) of the crude product afforded the title compound as a light yellow oil (42.1 mg, 61%).

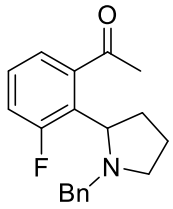
R_f 0.40 (hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.3 Hz, 1H), 7.77

(s, 1H), 7.74 (d, J = 8.3 Hz, 1H), 7.29-7.20 (m, 5H), 3.92 (t, J = 8.2 Hz, 1H), 3.71 (d, J = 13.1 Hz, 1H), 3.16-3.10 (m, 1H), 3.15 (d, J = 13.1 Hz, 1H), 2.62 (s, 3H), 2.49-2.41 (m, 1H), 2.27 (q, J = 8.9 Hz, 1H), 1.91-1.76 (m, 2H), 1.64-1.56 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 148.8, 139.2 (two signals overlapped), 128.9, 128.6 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 128.5, 128.1 (two signals overlapped), 126.8, 124.6 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 65.1, 58.6, 53.5, 35.2, 30.2, 22.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.5; HRMS (ESI) Calcd for $C_{20}H_{21}NOF_3$ $[M + H]^+$ 348.1575, found 348.1582.



1-(2-(1-Benzylpyrrolidin-2-yl)-5-chlorophenyl)ethan-1-one (3ia): The typical procedure was applied to (*E*)-1-(3-chlorophenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (**1i**, 103.9 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/Et_2O = 20/1) of the crude product afforded the compound **3ia** in a pure form (14.2 mg, 23%) as a light yellow oil and a mixture of **3ia** and *N*-(1-(3-chlorophenyl)ethyl)-4-methoxyaniline (reduced product of **1i**; 16.3 mg, 26%, ratio = 5:1 as determined by ^{1}H NMR) as a yellow oil. Characterization data of **3ia** are given below.

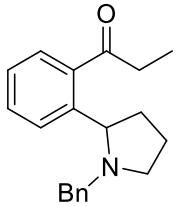
R_f 0.46 (hexane/EtOAc = 10/1); ^{1}H NMR (400MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 2.2 Hz, 1H), 7.46 (dd, J = 8.5, 2.2 Hz, 1H), 7.30-7.19 (m, 5H), 3.82 (t, J = 8.1 Hz, 1H), 3.73 (d, J = 13.1 Hz, 1H), 3.10-3.06 (m, 1H), 3.09 (d, J = 13.0 Hz, 1H), 2.57 (s, 3H), 2.44-2.35 (m, 1H), 2.22 (q, J = 8.9 Hz, 1H), 1.89-1.72 (m, 2H), 1.62-1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.1, 142.9, 140.3, 139.5, 131.9, 131.6, 129.8, 128.5, 128.1, 127.7, 126.8, 64.9, 58.5, 53.4, 35.1, 30.2, 22.8; HRMS (ESI) Calcd for $C_{19}H_{21}NOCl$ $[M + H]^+$ 314.1312, found 314.1310.



1-(2-(1-Benzylpyrrolidin-2-yl)-3-fluorophenyl)ethan-1-one (3ja): The typical procedure was applied to (*E*)-1-(3-fluorophenyl)-*N*-(4-methoxyphenyl)ethan-1-imine (**1j**, 97.3 mg, 0.40

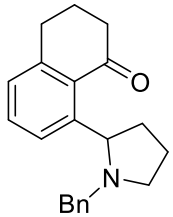
mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: Hex/EtOAc = 10/1) of the crude product afforded the title compound as a light yellow oil (31.6 mg, 53%).

R_f 0.17 (hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.18 (m, 6H), 7.07 (t, J = 9.3 Hz, 1H), 7.00 (d, J = 7.6 Hz, 1H), 3.97 (t, J = 8.5 Hz, 1H), 3.76 (d, J = 13.6 Hz, 1H), 3.23 (d, J = 13.6 Hz, 1H), 3.01-2.98 (m, 1H), 2.51 (s, 3H), 2.34 (q, J = 8.8 Hz, 1H), 2.28-2.21 (m, 1H), 2.04-1.86 (m, 2H), 1.75-1.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8 (d, $^4J_{C-F}$ = 2.0 Hz), 161.1 (d, $^1J_{C-F}$ = 247.0 Hz), 143.6 (d, $^3J_{C-F}$ = 3.0 Hz), 137.8, 129.3, 128.6 (d, $^2J_{C-F}$ = 13.0 Hz), 128.1, 128.0, 126.8, 121.8 (d, $^3J_{C-F}$ = 3.0 Hz), 116.4 (d, $^2J_{C-F}$ = 23.0 Hz), 60.5, 58.0, 52.8, 32.6, 31.7, 23.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ –114.4; HRMS (ESI) Calcd for $C_{19}H_{21}NOF$ $[M + H]^+$ 298.1607, found 298. 1612.



1-(2-(1-Benzylpyrrolidin-2-yl)phenyl)propan-1-one (3ka): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-phenylpropan-1-imine (**1k**, 95.7 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol) for 24 h. Silica gel chromatography (eluent: hexane/EtOAc = 30/1) of the crude product afforded the title compound as a light yellow oil (12.4 mg, 21%).

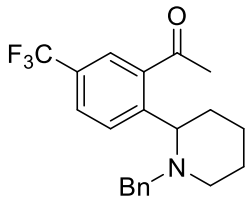
R_f 0.35 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (d, J = 7.5 Hz, 1H), 7.51-7.48 (m, 2H), 7.30-7.26 (m, 5H), 7.24-7.19 (m, 1H), 3.78 (d, J = 13.1 Hz, 1H), 3.72 (t, J = 8.2 Hz, 1H), 3.10-2.80 (m, 4H), 2.44-2.35 (m, 1H), 2.20 (q, J = 8.9 Hz, 1H), 1.91-1.72 (m, 2H), 1.69-1.60 (m, 1H), 1.21 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.1, 143.6, 139.7, 139.6, 131.2, 128.6, 128.1, 127.9, 126.9, 126.7, 126.2, 65.6, 58.4, 53.3, 35.7, 35.3, 22.7, 8.4; HRMS (ESI) Calcd for $C_{20}H_{24}NO$ $[M + H]^+$ 294.1858, found 294.1860.



8-(1-Benzylpyrrolidin-2-yl)-3,4-dihydronaphthalen-1(2H)-one (3la): The typical

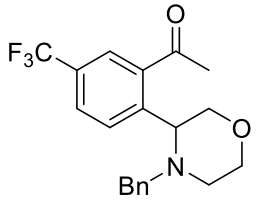
procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-3,4-dihydronaphthalen-1(2*H*)-imine (**1l**, 100.5 mg, 0.40 mmol) and 1-(2-bromobenzyl)pyrrolidine (**2a**, 48.0 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 10/1) of the crude product afforded the title compound as a light yellow oil (27.1 mg, 44%).

R_f 0.20 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.33-7.29 (m, 4H), 7.21 (t, *J* = 6.8 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 4.41 (t, *J* = 8.0 Hz, 1H), 3.78 (d, *J* = 13.1 Hz, 1H), 3.11-3.05 (m, 1H), 3.07 (d, *J* = 13.1 Hz, 1H), 2.98-2.94 (m, 2H), 2.76-2.55 (m, 3H), 2.24 (q, *J* = 8.8 Hz, 1H), 2.16-2.05 (m, 2H), 1.84-1.76 (m, 2H), 1.53-1.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 200.2, 148.2, 145.3, 140.2, 132.9, 131.5, 128.5, 128.1, 127.0, 126.6, 125.9, 65.5, 59.0, 53.5, 41.2, 34.2, 31.1, 22.94, 22.90; HRMS (ESI) Calcd for $C_{21}H_{24}NO$ $[M + H]^+$ 306.1858, found 306.1859.



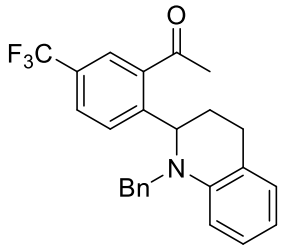
1-(2-(1-Benzylpiperidin-2-yl)-5-(trifluoromethyl)phenyl)ethan-1-one (3hb): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and 1-(2-bromobenzyl)piperidine (**2b**, 50.8 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 60/1) of the crude product afforded the title compound as a light yellow oil (15.9 mg, 22%).

R_f 0.38 (hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.7 Hz, 1H), 7.73-7.71 (m, 2H), 7.29-7.19 (m, 5H), 3.66 (dd, *J* = 10.4, 2.5 Hz, 1H), 3.59 (d, *J* = 13.5 Hz, 1H), 2.97 (d, *J* = 11.5 Hz, 1H), 2.84 (d, *J* = 13.6 Hz, 1H), 2.63 (s, 3H), 1.99-1.92 (m, 2H), 1.79 (d, *J* = 12.5 Hz, 1H), 1.64-1.36 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.8, 148.9, 139.6, 139.2, 129.2, 128.7 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 128.4, 128.1, 127.8 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 126.8, 124.1 (q, $^3J_{C\text{-}F}$ = 4.0 Hz), 123.7 (q, $^1J_{C\text{-}F}$ = 270.5 Hz), 63.8, 60.1, 53.2, 36.5, 30.7, 25.8, 24.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.5; HRMS (ESI) Calcd for $C_{21}H_{23}NOF_3$ $[M + H]^+$ 362.1732, found 362.1730.



1-(2-(4-Benzylmorpholin-3-yl)-5-(trifluoromethyl)phenyl)ethan-1-one (3hc): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and 4-(2-bromobenzyl)morpholine (**2c**, 51.2 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 10/1) of the crude product afforded the title compound as a light yellow oil (12.4 mg, 17%).

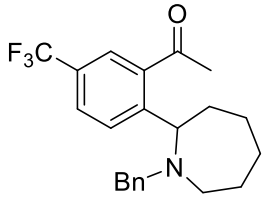
R_f 0.22 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (d, J = 8.2 Hz, 1H), 7.79-7.76 (m, 2H), 7.31-7.21 (m, 5H), 4.01-3.96 (m, 2H), 3.86 (d, J = 11.2 Hz, 1H), 3.71-3.62 (m, 2H), 3.35 (t, J = 11.2 Hz, 1H), 2.93 (d, J = 13.3 Hz, 1H), 2.79 (d, J = 11.8 Hz, 1H), 2.66 (s, 3H), 2.32 (td, J = 11.8, 3.3 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ 200.9, 143.1, 140.6, 137.9, 129.9, 129.6 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 128.6, 128.3, 127.9 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 127.1, 124.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.6 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 72.9, 67.4, 62.7, 59.6, 51.8, 30.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.7; HRMS (ESI) Calcd for $C_{20}H_{21}NO_2F_3$ $[M + H]^+$ 364.1524, found 364.1520.



1-(2-(1-Benzyl-1,2,3,4-tetrahydroquinolin-2-yl)-5-(trifluoromethyl)phenyl)ethan-1-one (3hd): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and 1-(2-bromobenzyl)-1,2,3,4-tetrahydroquinoline (**2d**, 60.4 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 60/1) of the crude product afforded the title compound as a light yellow solid (16.4 mg, 20%).

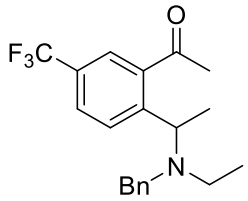
R_f 0.42 (hexane/EtOAc = 10/1); m.p. 126.7-129.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7,65 (d, J = 7.9 Hz, 1H), 7.53 (d, J = 8.1 Hz, 1H), 7.30-7.27 (m, 2H), 7.24-7.20 (m, 1H), 7.17 (d, J = 7.2 Hz, 2H), 7.07-7.02 (m, 2H), 6.65 (t, J = 7.2 Hz, 1H), 6.57 (d, J = 8.2 Hz, 1H), 5.43-5.41 (m, 1H), 4.63 (d, J = 17.2 Hz, 1H), 4.08 (d, J = 17.2 Hz, 1H), 2.69-2.49 (m, 5H),

2.45-2.36 (m, 1H), 2.13-2.07 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.2, 148.9, 145.1, 137.9, 137.2, 129.4, 129.3 (q, $^2J_{C\text{-}F}$ = 32.8 Hz), 128.9, 128.7, 128.0 (q, $^3J_{C\text{-}F}$ = 3.5 Hz), 127.6, 126.9, 126.4 (two signals overlapped), 123.6 (q, $^1J_{C\text{-}F}$ = 270.8 Hz), 122.1, 116.2, 110.8, 58.1, 53.3, 29.8, 28.4, 23.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.6; HRMS (ESI) Calcd for $C_{25}H_{23}NOF_3$ $[M + H]^+$ 410.1732, found 410.1732.



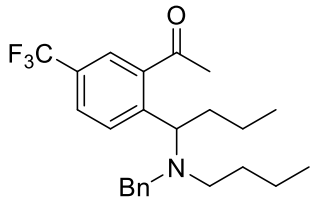
1-(2-(1-Benzylazepan-2-yl)-5-(trifluoromethyl)phenyl)ethan-1-one (3he): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and 1-(2-bromobenzyl)azepane (**2e**, 53.6 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 50/1) of the crude product afforded the title compound as a light yellow oil (48.4 mg, 64%).

R_f 0.52 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (d, *J* = 8.6 Hz, 1H), 7.70-7.68 (m, 2H), 7.25-7.15 (m, 5H), 4.23-4.21 (m, 1H), 3.51 (d, *J* = 13.8 Hz, 1H), 3.45 (d, *J* = 13.8 Hz, 1H), 2.99-2.79 (m, 2H), 2.53 (s, 3H), 1.97-1.82 (m, 3H), 1.73-1.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.6, 151.5, 139.7, 138.7, 129.1, 128.6, 128.3 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 128.1, 127.2 (q, $^3J_{C\text{-}F}$ = 3.3 Hz), 126.7, 124.3 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 64.7, 59.3, 50.3, 35.4, 30.3, 29.1, 27.2, 26.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.5; HRMS (ESI) Calcd for $C_{22}H_{25}NOF_3$ $[M + H]^+$ 376.1888, found 376.1885.



1-(2-(1-(Benzyl(ethyl)amino)ethyl)-5-(trifluoromethyl)phenyl)ethan-1-one (3hf): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and *N*-(2-bromobenzyl)-*N*-ethylethanamine (**2f**, 48.4 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 30/1) of the crude product afforded the title compound as a light yellow oil (40.5 mg, 58%).

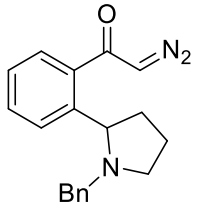
R_f 0.42 (hexane/EtOAc = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.62 (s, 1H), 7.28-7.19 (m, 5H), 4.50 (q, *J* = 6.6 Hz, 1H), 3.52 (d, *J* = 17.3 Hz, 1H), 3.45 (d, *J* = 17.2 Hz, 1H), 2.62-2.45 (m, 5H), 1.37 (d, *J* = 6.5 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.4, 148.7, 141.1, 139.9, 128.7 (two signals overlapped), 128.2, 128.1, 126.8, 126.7 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 270.7 Hz), 123.4 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 55.2, 54.3, 43.6, 30.5, 16.2, 11.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.5; HRMS (ESI) Calcd for $C_{20}H_{23}NOF_3$ $[M + H]^+$ 350.1732, found 350.1729.



1-(2-(1-(Benzyl(butyl)amino)butyl)-5-(trifluoromethyl)phenyl)ethan-1-one (3hg): The typical procedure was applied to (*E*)-*N*-(4-methoxyphenyl)-1-(3-(trifluoromethyl)phenyl)ethan-1-imine (**1h**, 117.3 mg, 0.40 mmol) and *N*-(2-bromobenzyl)-*N*-butylbutan-1-amine (**2g**, 59.7 mg, 0.20 mmol). Silica gel chromatography (eluent: hexane/EtOAc = 60/1) of the crude product afforded the title compound as a light yellow oil (35.7 mg, 44%).

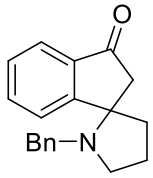
R_f 0.65 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, d_6-acetone): δ 7.94 (s, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.28-7.19 (m, 5H), 4.53 (dd, *J* = 8.8, 5.5 Hz, 1H), 3.69 (d, *J* = 13.9 Hz, 1H), 3.42 (d, *J* = 13.9 Hz, 1H), 2.62 (s, 3H), 2.57-2.50 (m, 1H), 2.36-2.29 (m, 1H), 2.03-1.94 (m, 1H), 1.89-1.80 (m, 1H), 1.39-1.04 (m, 6H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.3, 145.8, 142.1, 140.3, 128.8, 128.6 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 128.5, 128.1, 126.7, 126.4 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.8 (q, $^1J_{C\text{-}F}$ = 270.3 Hz), 123.6 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 59.1, 54.7, 50.0, 32.8, 30.6, 28.7, 20.5, 19.8, 14.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.6; HRMS (ESI) Calcd for $C_{24}H_{31}NOF_3$ $[M + H]^+$ 406.2358, found 406.2361.

Transformation of Product 3aa



1-(2-(1-Benzylpyrrolidin-2-yl)phenyl)-2-diazoethan-1-one (9): To a solution of LiHMDS (1.0 M, 2.49 mL) in 5.0 mL THF was added 1-(2-(1-benzylpyrrolidin-2-yl)phenyl)ethan-1-one (**3aa**, 642 mg, 2.30 mmol) in THF (4.6 mL) over 1 min at –78 ˚C. The resulting mixture was stirred at the same temperature for 30 min, followed by the addition of trifluoroethyl trifluoroacetate (541.1 mg, 2.76 mmol) over 2-3 min. After additional stirring for 3 h, the reaction mixture was allowed to warm to room temperature, stirred overnight and then poured into a separatory funnel together with Et_2O (20 mL) and sat. NH_4Cl (20 mL). The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure to afford a yellow oil. The oil was placed in a dry 50 mL 3-necked round-bottomed flask under a nitrogen atmosphere and dissolved in acetonitrile (9.3 mL). To this solution was added water (0.02 mL) and NEt_3 (0.23 mL), followed by the dropwise addition of *p*-acetamidobenzenesulfonyl azide (402.5 mg, 1.68 mmol) in acetonitrile (9.3 mL). The resulting solution was stirred at ambient temperature for 24 h, and then poured into a separatory funnel with Et_2O (20 mL). The organic layer was washed with 5% NaOH aqueous solution (3 x 10 mL), water (3 x 10 mL), and brine. The combined organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc = 8/1-1/1) to afford the desired product as a yellow oil (127.4 mg, 32 % based on recovered **3aa**) along with recovery of **3aa** (275.3 mg).

R_f 0.67 (hexane/EtOAc = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.35-7.19 (m, 7H), 5.59 (brs, 1H), 3.85 (brs, 1H), 3.79 (d, *J* = 13.1 Hz, 1H), 3.11-3.06 (m, 2H), 2.44-2.35 (m, 1H), 2.21 (q, *J* = 8.9 Hz, 1H), 1.89-1.61 (m, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 191.2, 143.9, 140.7, 139.8, 132.1, 129.5 (2C), 129.1 (2C), 128.6, 127.7, 127.5, 66.0, 58.9, 54.0, 36.3, 23.4; HRMS (ESI) Calcd for $C_{19}H_{20}N_3O$ $[M + H]^+$ 306.1606, found 306.1602.



1'-Benzylspiro[indene-1,2'-pyrrolidin]-3(2*H*)-one (10): A solution of 1-(2-(1-benzylpyrrolidin-2-yl)phenyl)-2-diazoethan-1-one (**9**, 127.4 mg, 0.42 mmol) in dichloromethane (20 mL) was added dropwise to a suspension of $Rh_2(OAc)_4$ in dichloromethane (9.3 mg, 0.02 mmol, 42 ml) at room temperature over a period of 6 h using a syringe pump. The resulting mixture was stirred for additional 20 h and then concentrated under reduced pressure. The crude product was purified by silica gel chromatography (eluent: hexane/EtOAc = 12/1) to afford the desired product as a light yellow oil (78.7 mg, 68 %).

R_f 0.24 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (t, *J* = 7.1 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.30-7.21 (m, 5H), 3.35 (d, *J* = 13.0 Hz, 1H), 3.17-3.09 (m, 2H), 2.93 (d, *J* = 18.7 Hz, 1H), 2.51-2.47 (m, 2H), 2.28-2.21 (m, 1H), 2.08-1.90 (m, 3H); ^{13}C NMR (100 MHz, CD_3CN): δ 204.7, 159.1, 140.9, 138.5, 136.1, 129.7, 129.2, 129.1, 127.7, 126.0, 123.2, 70.5, 53.7, 51.9, 43.1, 42.1, 22.4; HRMS (ESI) Calcd for $C_{19}H_{20}NO$ $[M + H]^+$ 278.1545, found 278.1545.

Reference

(1) (a) N. Mrsic, L. Panella, A. J. Minnaard, B. L. Feringa, J. G. de Vries, *J. Am. Chem. Soc.* **2009**, *131*, 8358. (b) F.-M. Gautier, S. Jones, S. J. Martin, *Org. Biomol. Chem.* **2009**, *7*, 229.

(2) **1a:** (a) J. S. M. Samec, A. H. Ell, J.-E. Bäckvall, *Chem. Eur. J.* **2005**, *11*, 2327. **1b:** (b) K. Kutlescha, G. T. Venkanna, R. Kempe, *Chem. Commun.* **2011**, *47*, 4183. **1c, 1f:** (c) T. Imamoto, N. Iwadate, K. Yoshida, *Org. Lett.* **2006**, *8*, 2289. **1d, 1g:** (d) C. Moessner, C. Bolm, *Angew. Chem., Int. Ed.* **2005**, *44*, 7564. **1e, 1h:** K. Gao, N. Yoshikai, *Angew. Chem., Int. Ed.* **2011**, 50, 6888. **1i, 1k, 1l:** N. Yoshikai, A. Matsumoto, J. Norinder, E. Nakamura, *Angew. Chem., Int. Ed.* **2009**, *48*, 2925. **1j:** P.-S. Lee, T. Fujita, N. Yoshikai, N. *J. Am. Chem. Soc*. **2011**, *133*, 17283.

(3) Z. Li, H.-J. Feiten, J. B. van Beilen, W. Duetz, B. Witholt, *Tetrahedron: Asymmetry* **1999**, *10*, 1323.

(4) K. P. Bhabak, G. Mugesh, *Chem. Eur. J*. **2008**, *14*, 8640.

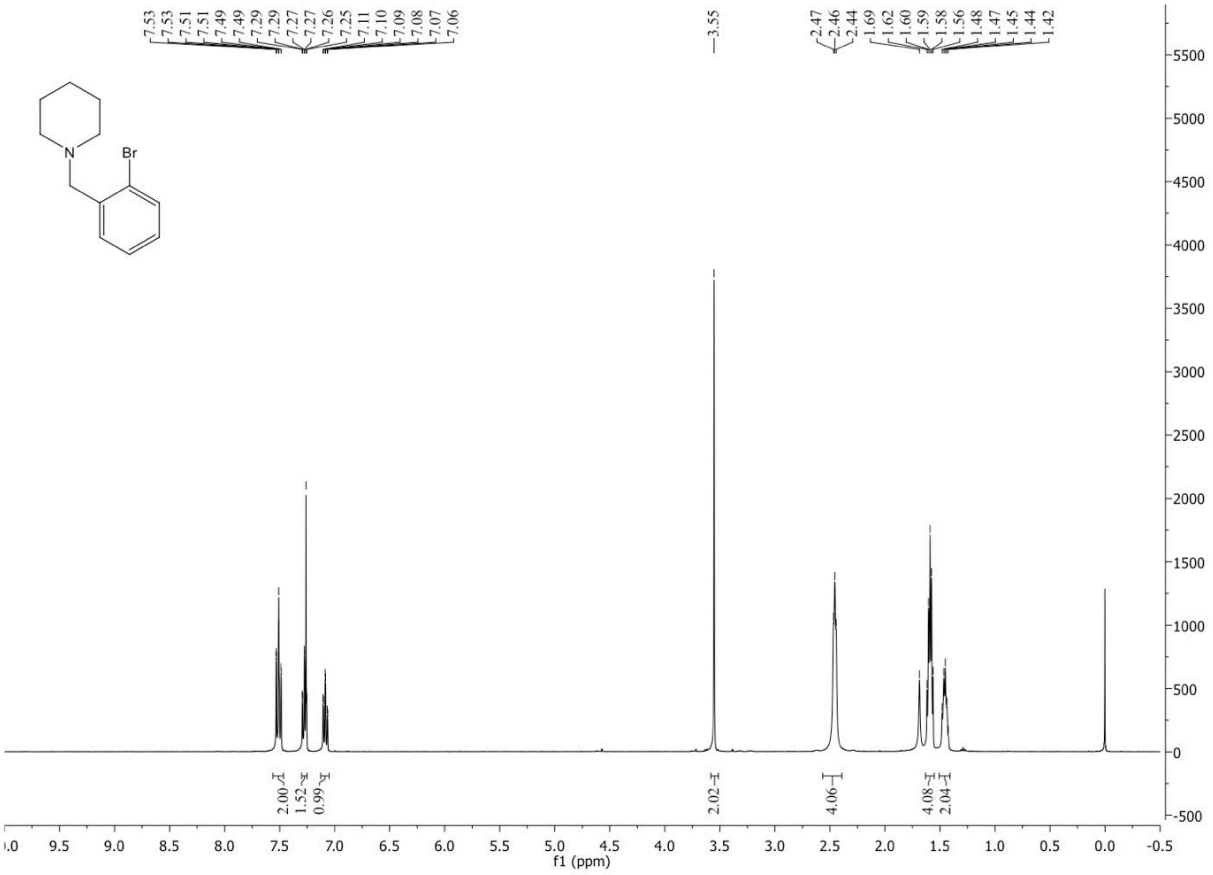
(5) S. R. Wilson, P. A. Zucker, R.-R. C. Huang, A. Spector, *J. Am. Chem. Soc.* **1989**, *111*, 5936.

(6) A. G. Avent, P. B. Hitchcock, G. J. Leigh, M. Togrou, *J. Organomet. Chem*. **2003**, *669*, 87.

(7) K. C. Majumdar, A. Taher, P. Debnath, *Synthesis* **2009**, *5*, 793.

(8) L. Soran, V. Coman, A. Soran, C. Silvestru, *Centr. Eur. J. Chem*. **2004**, *2*, 563.

NMR Spectra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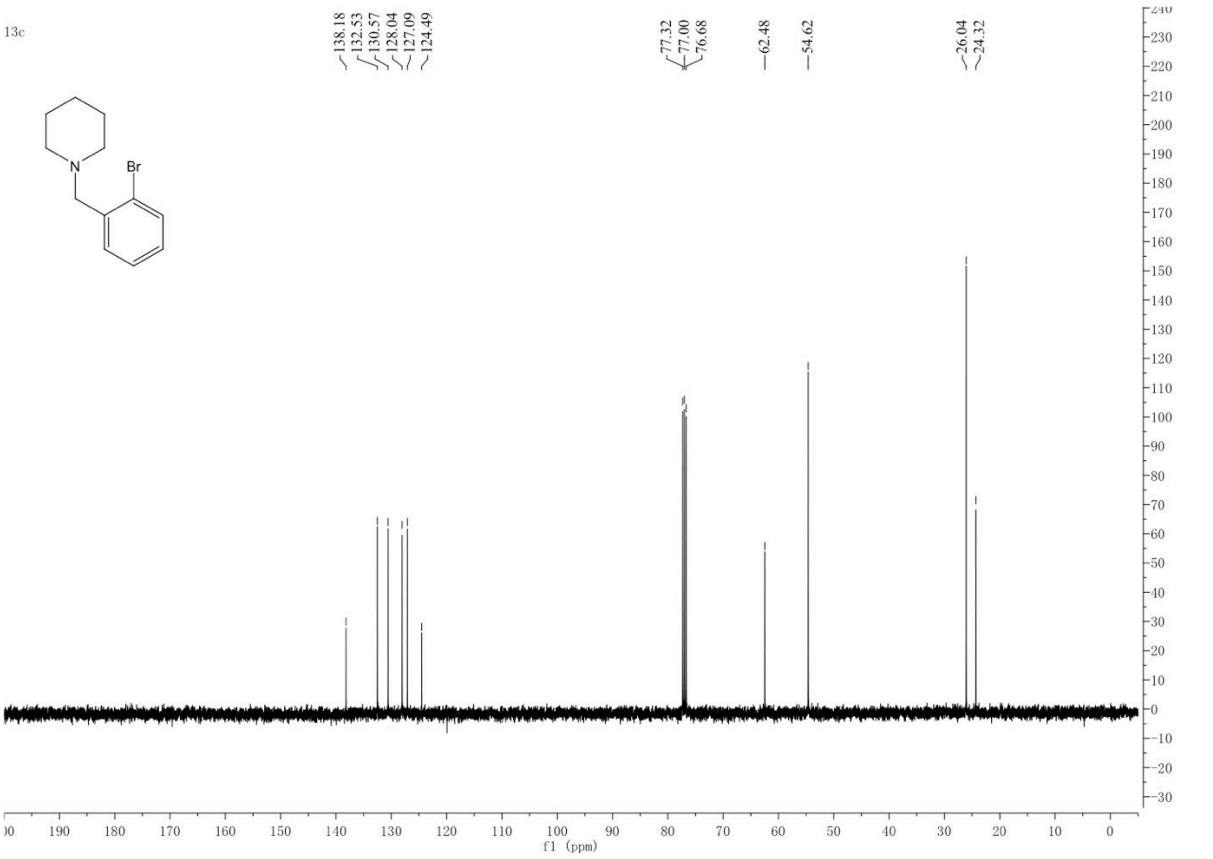
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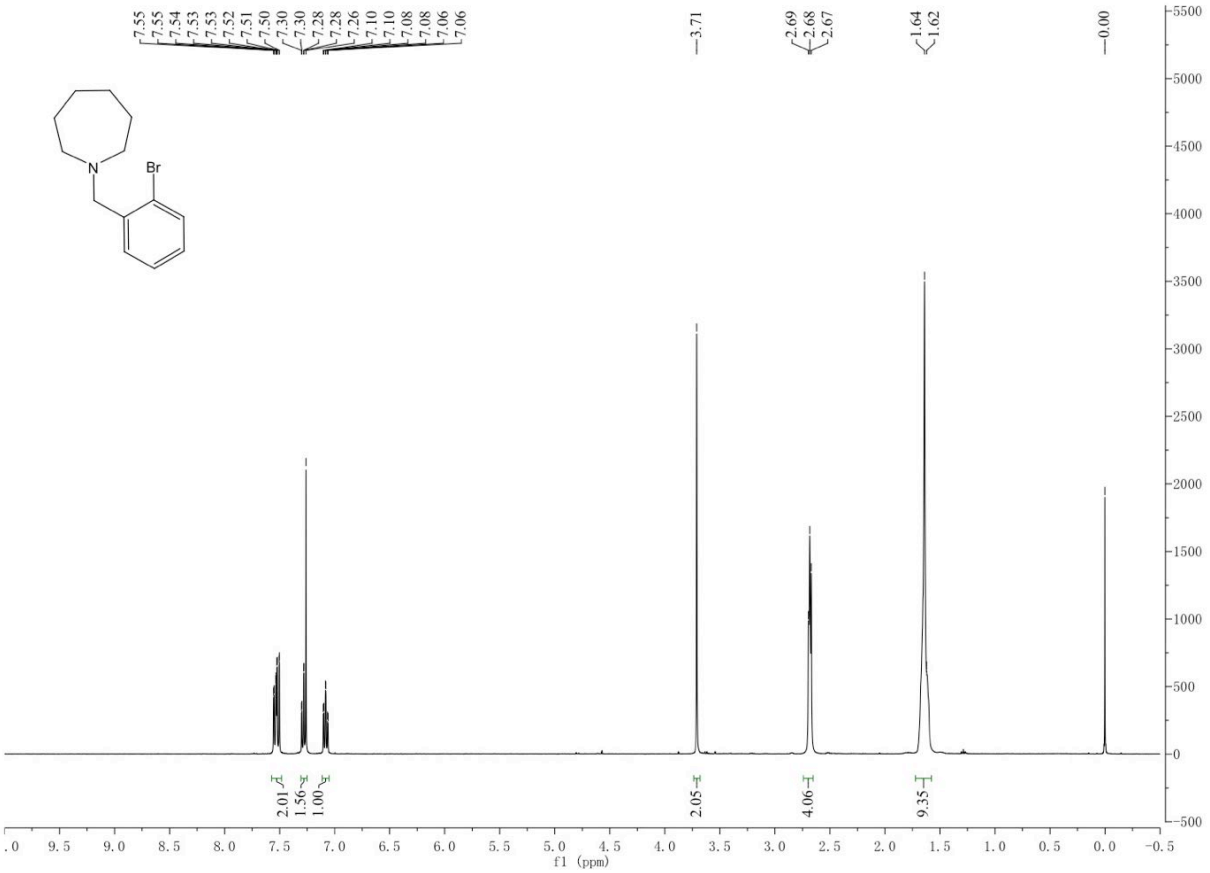
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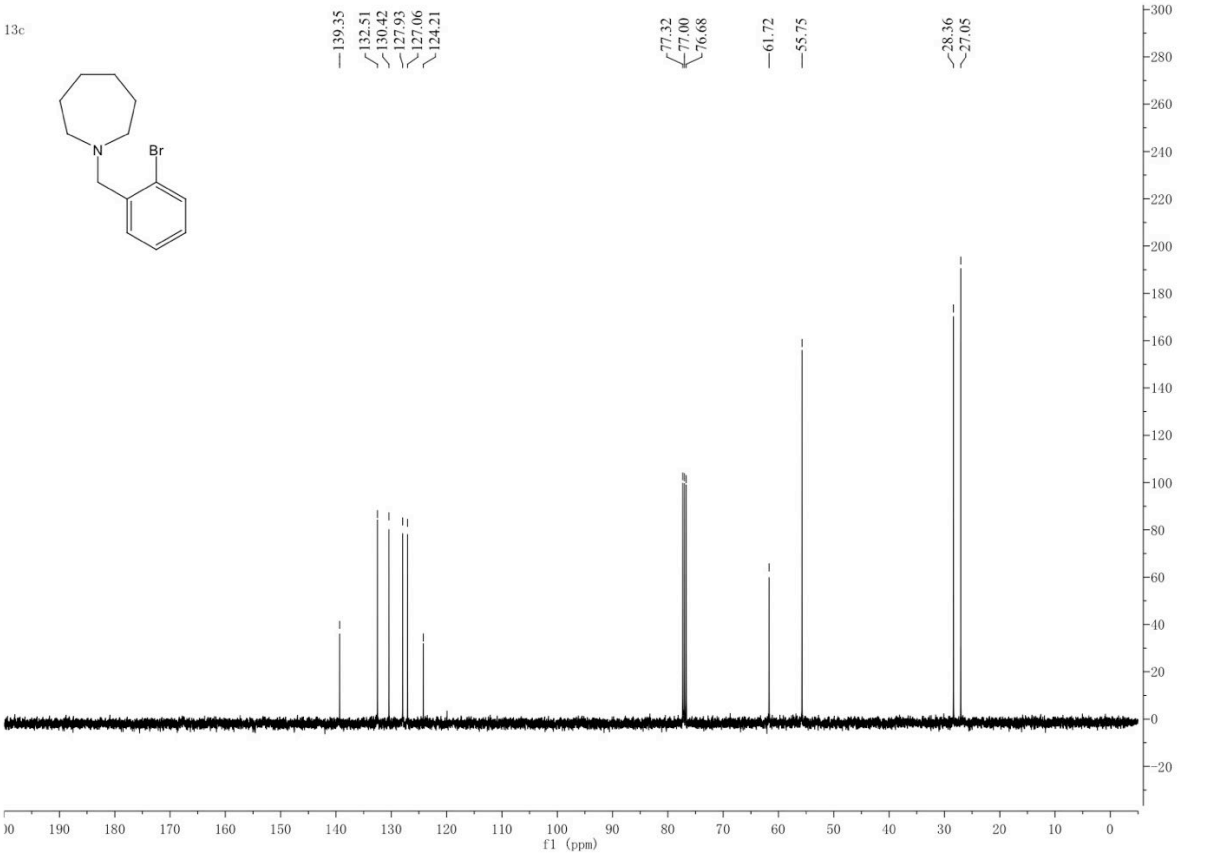
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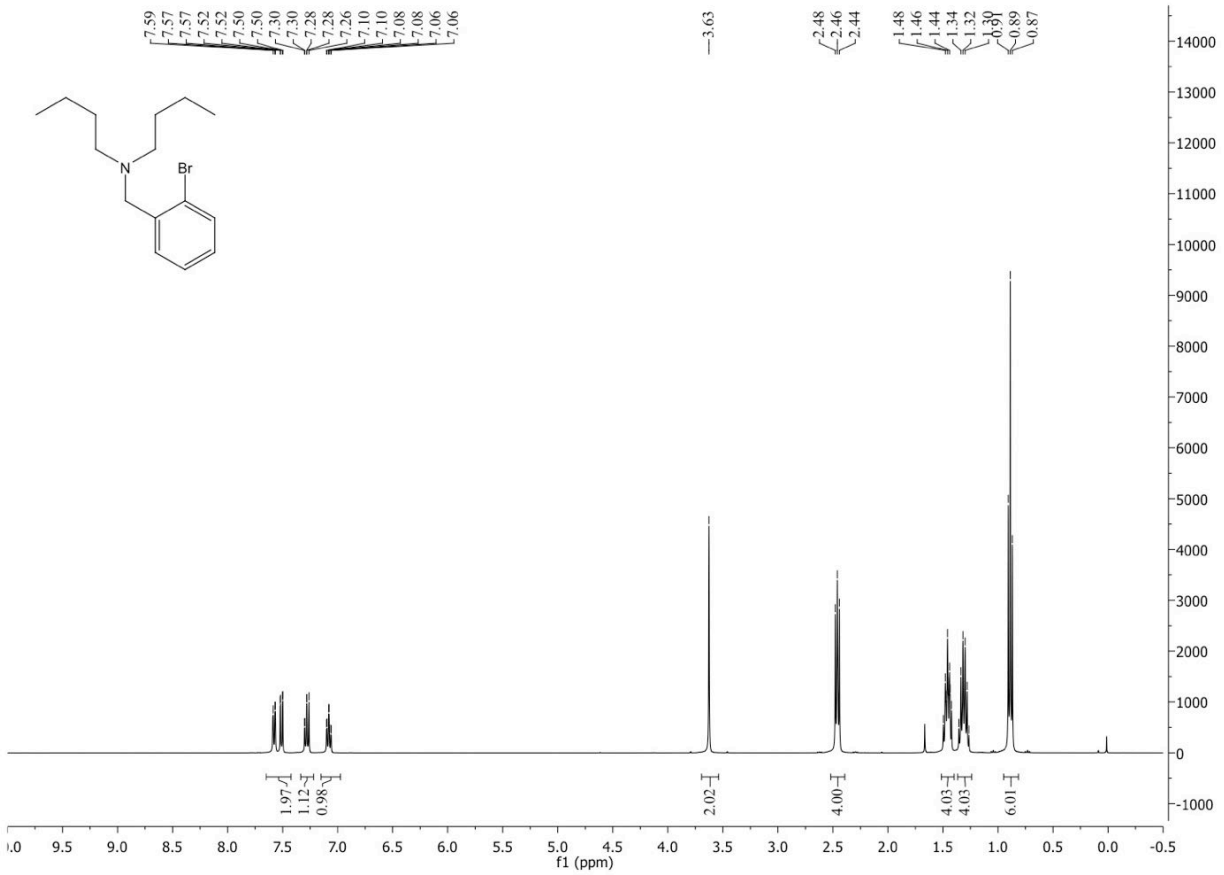
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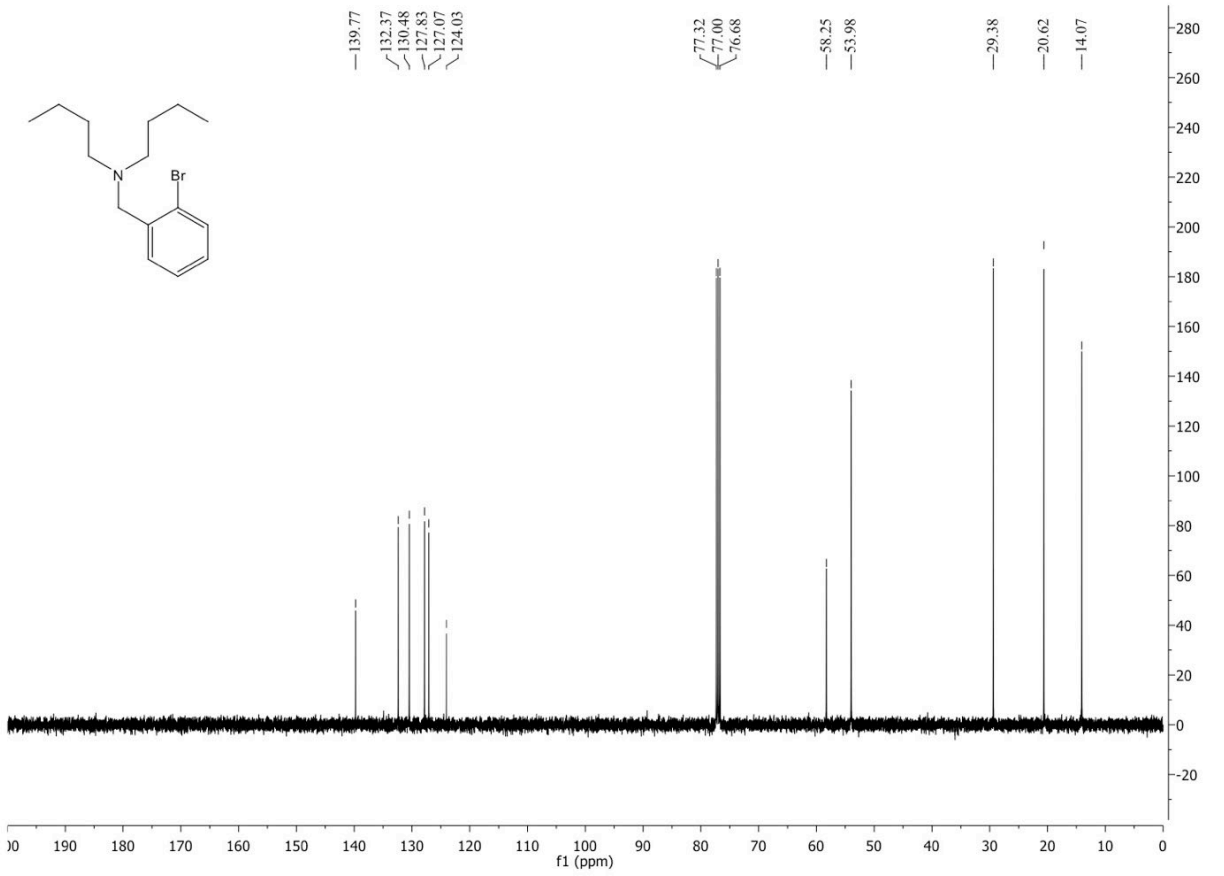
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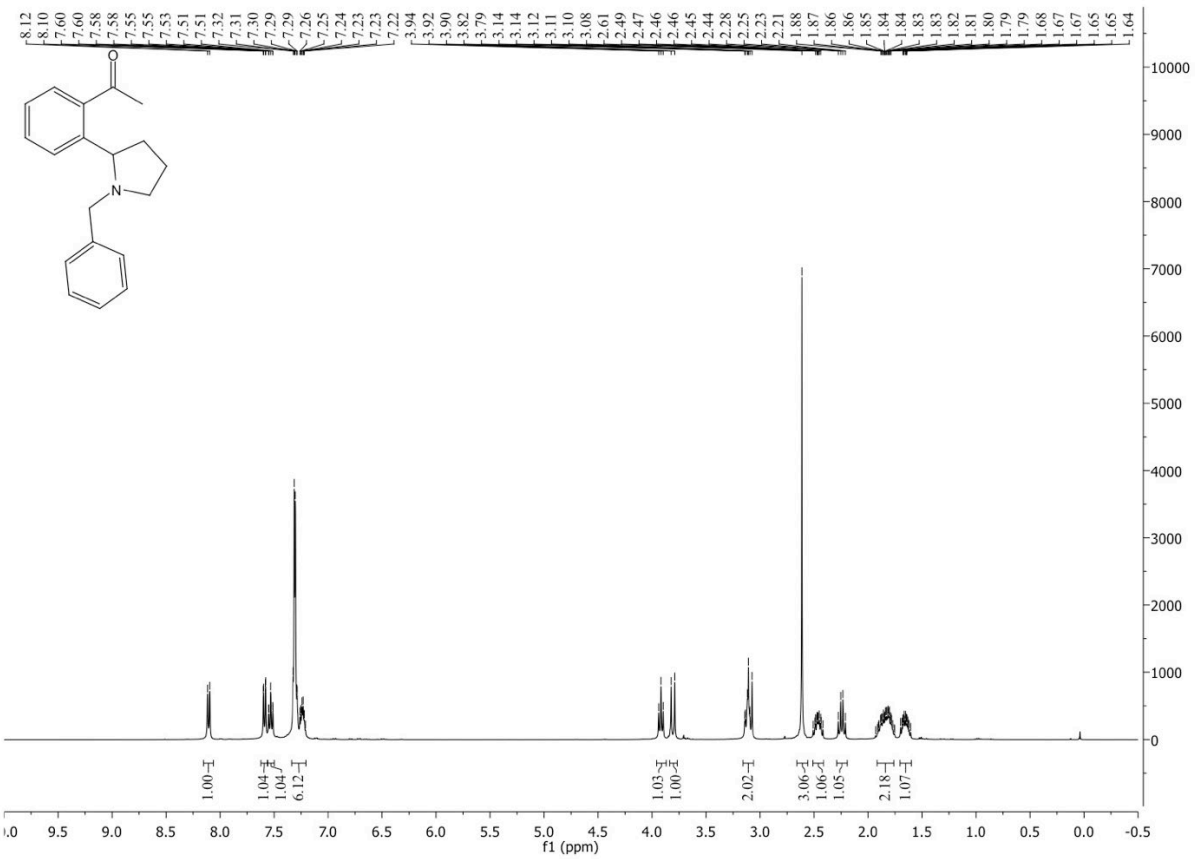
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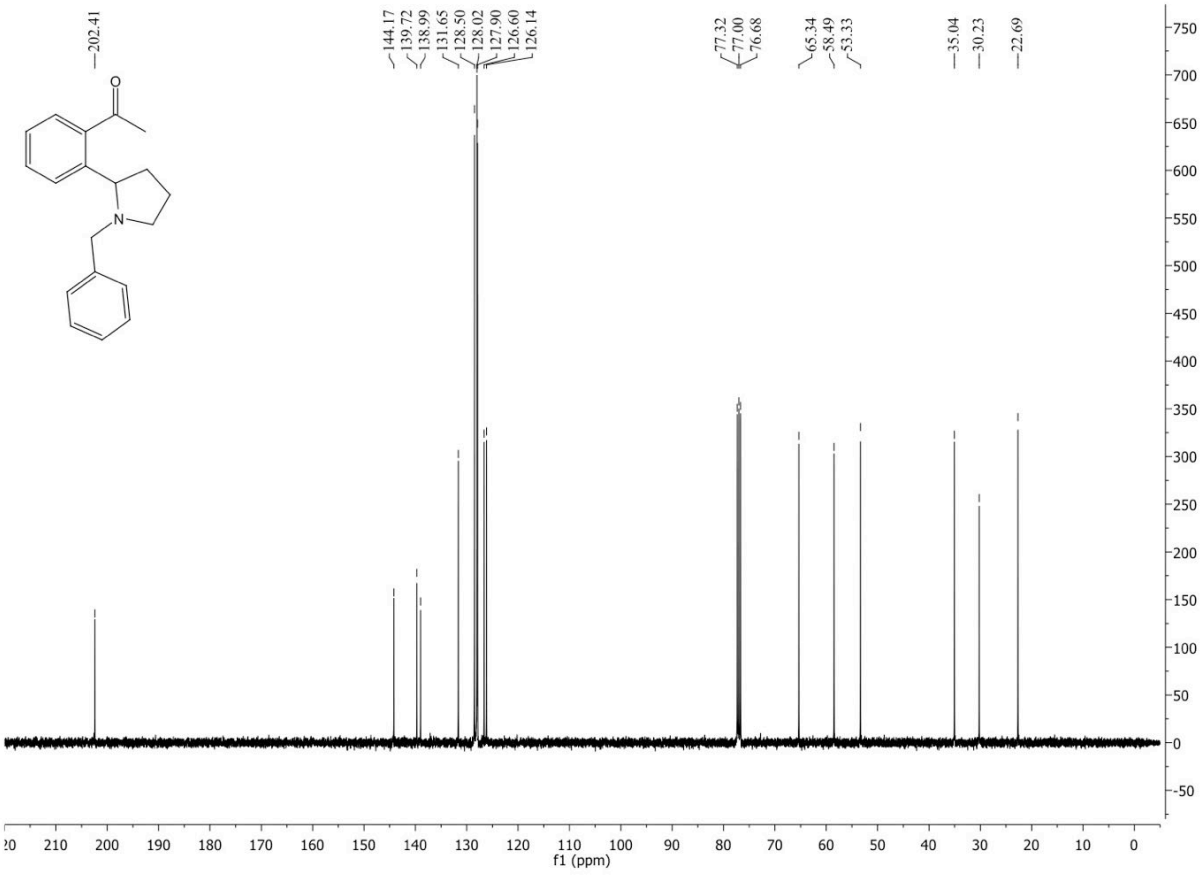
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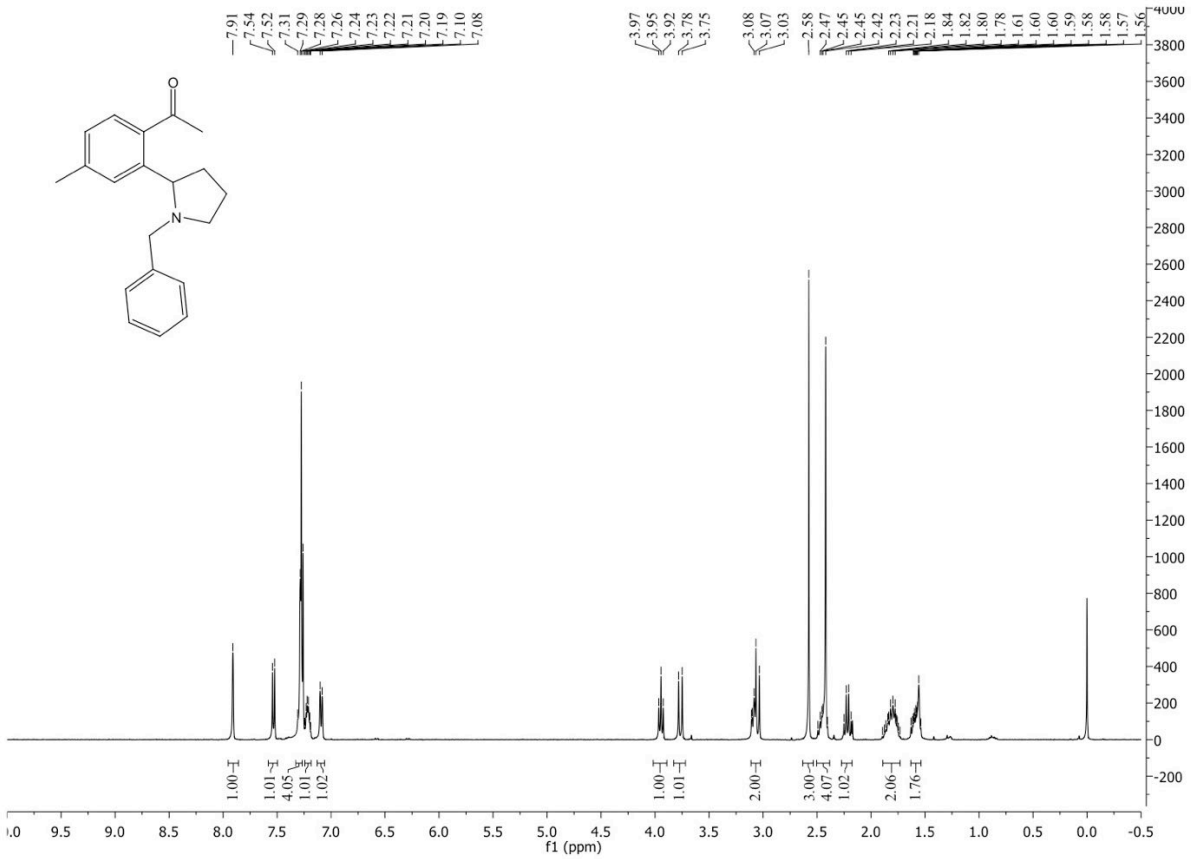
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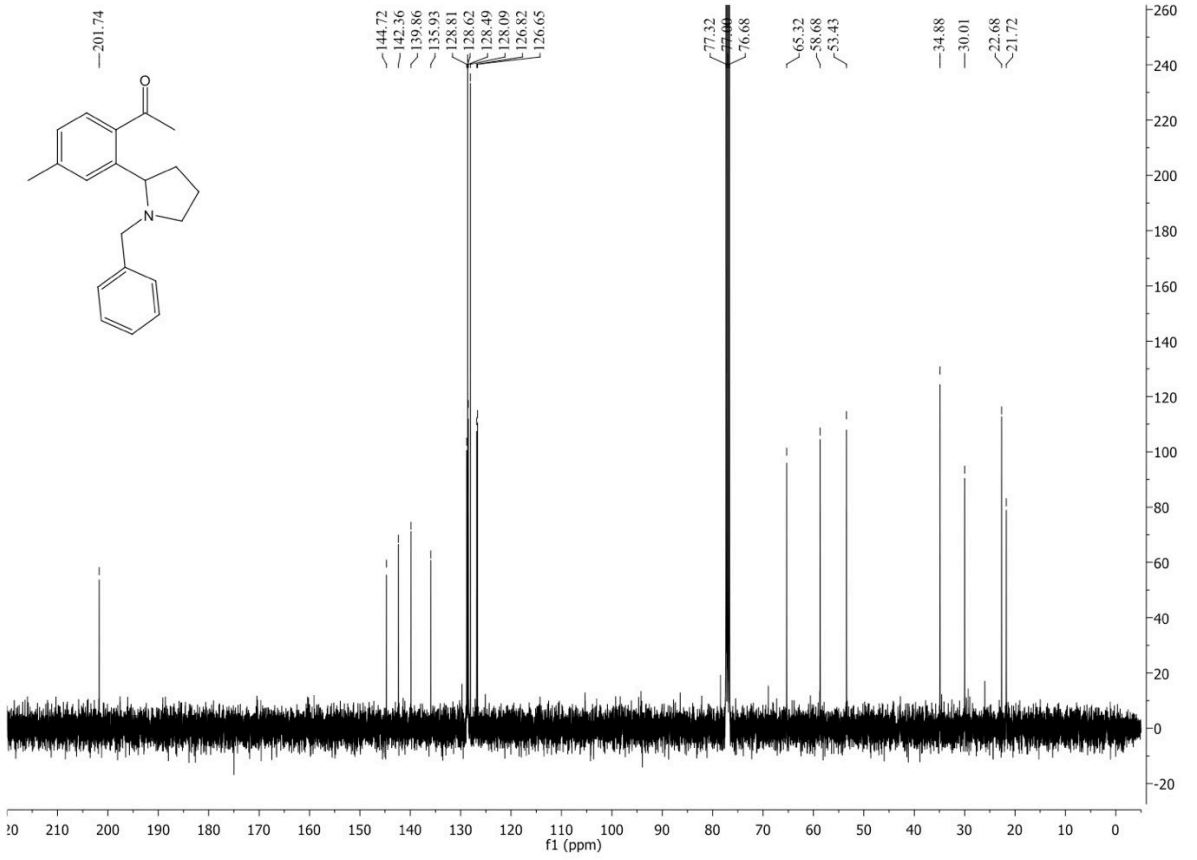
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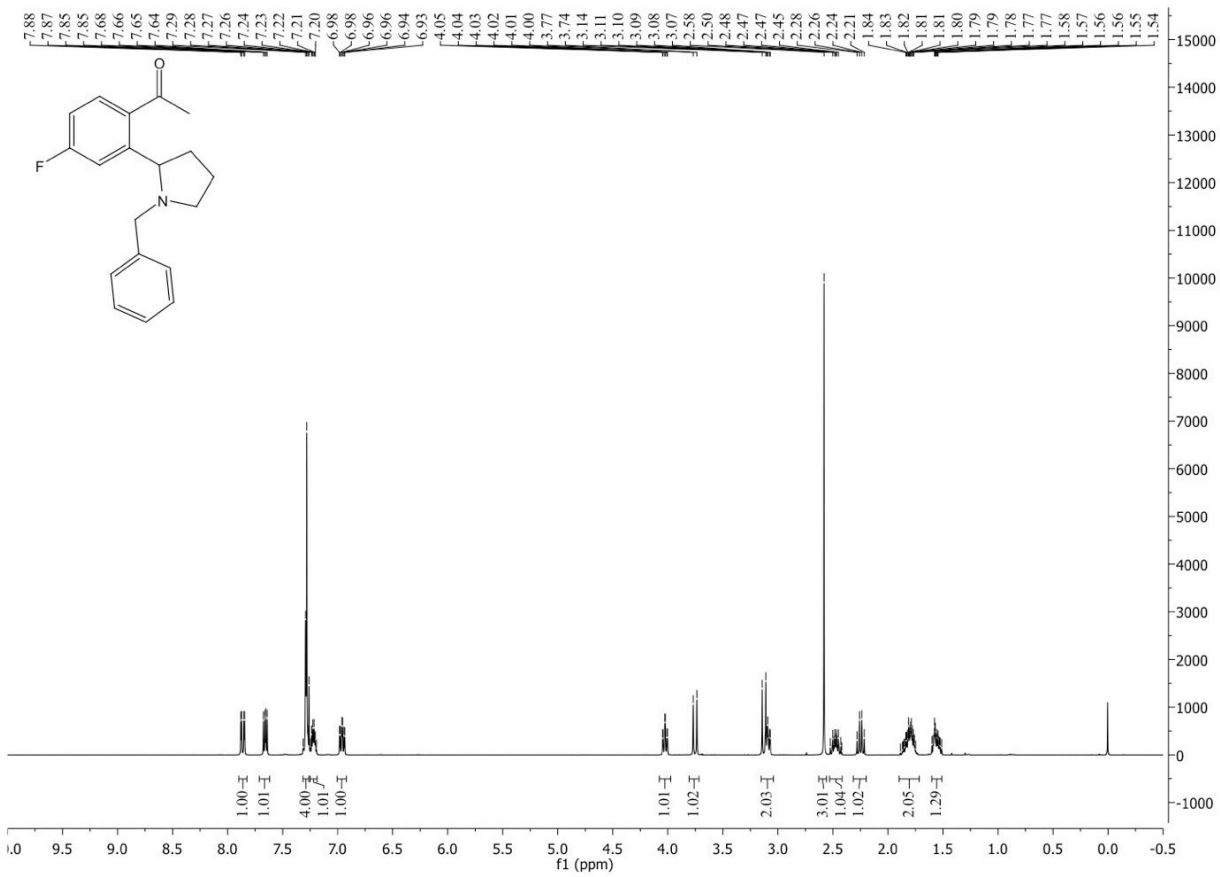
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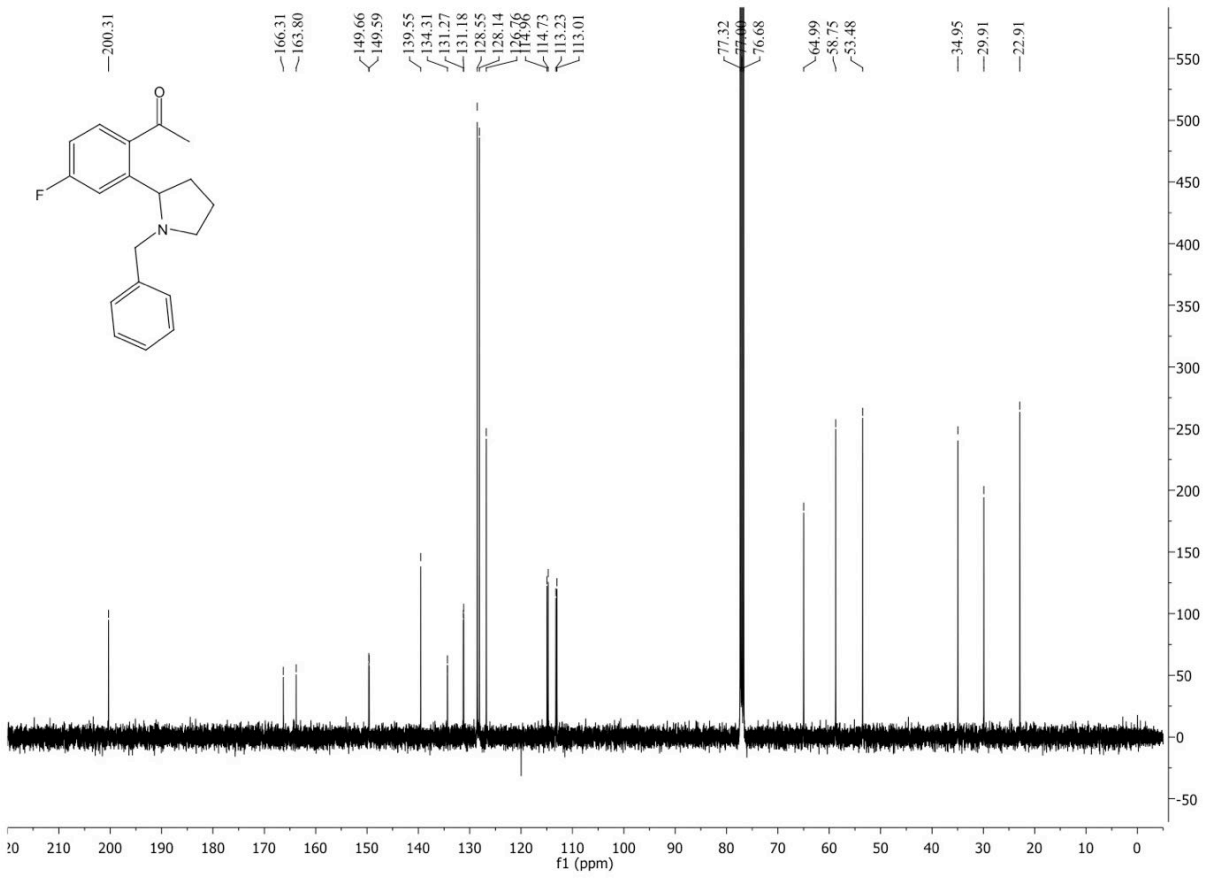
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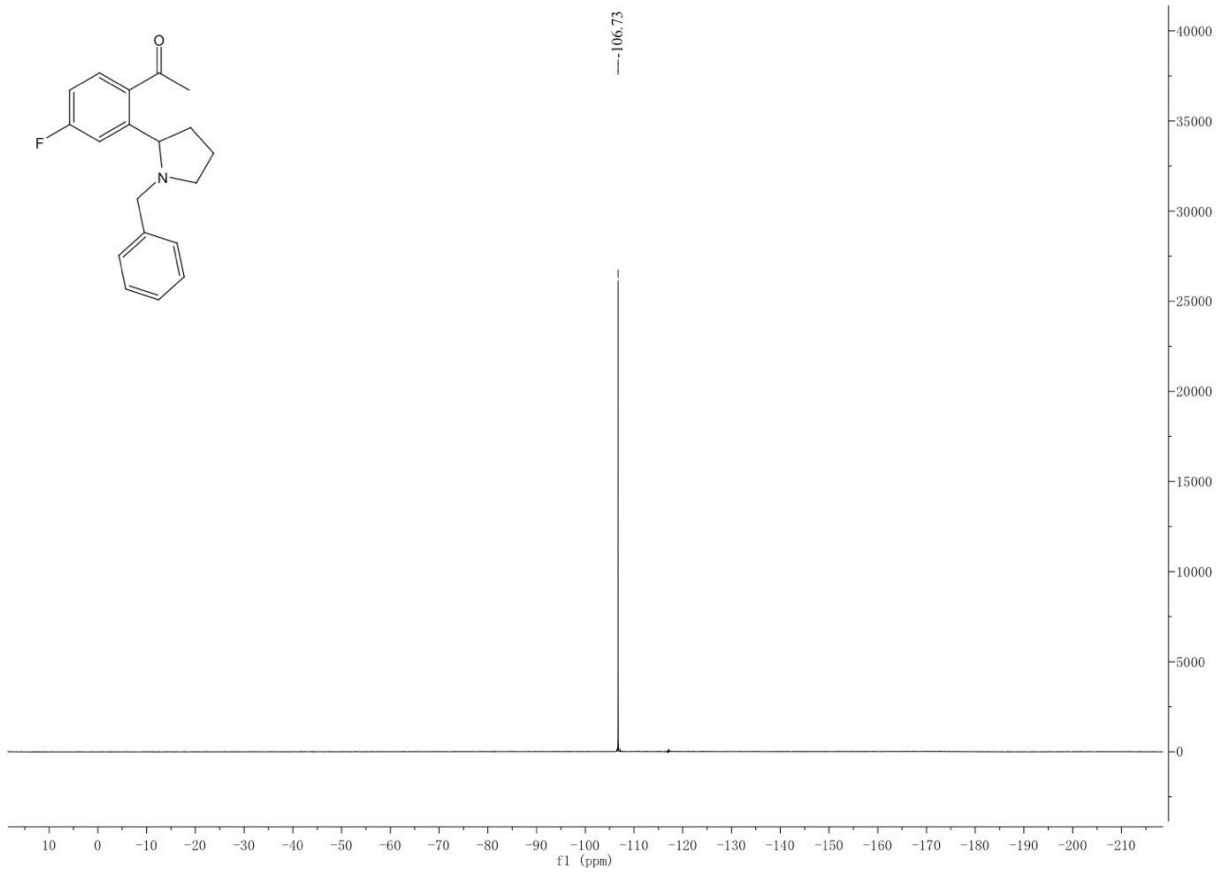
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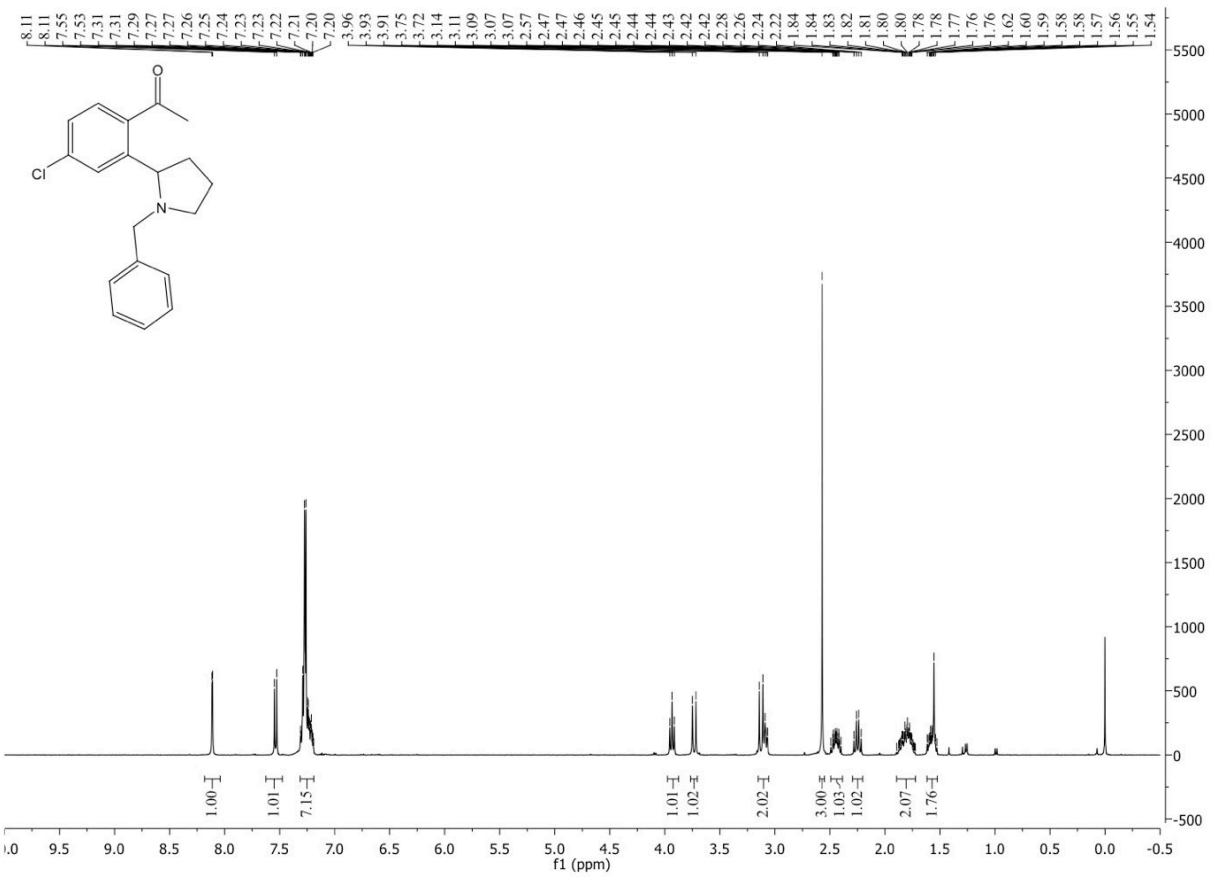
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2.24
2.22
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1.83
1.82
1.81
1.80
1.80
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1.78
1.77
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1.57
1.56
1.55
1.54
O
Cl
N
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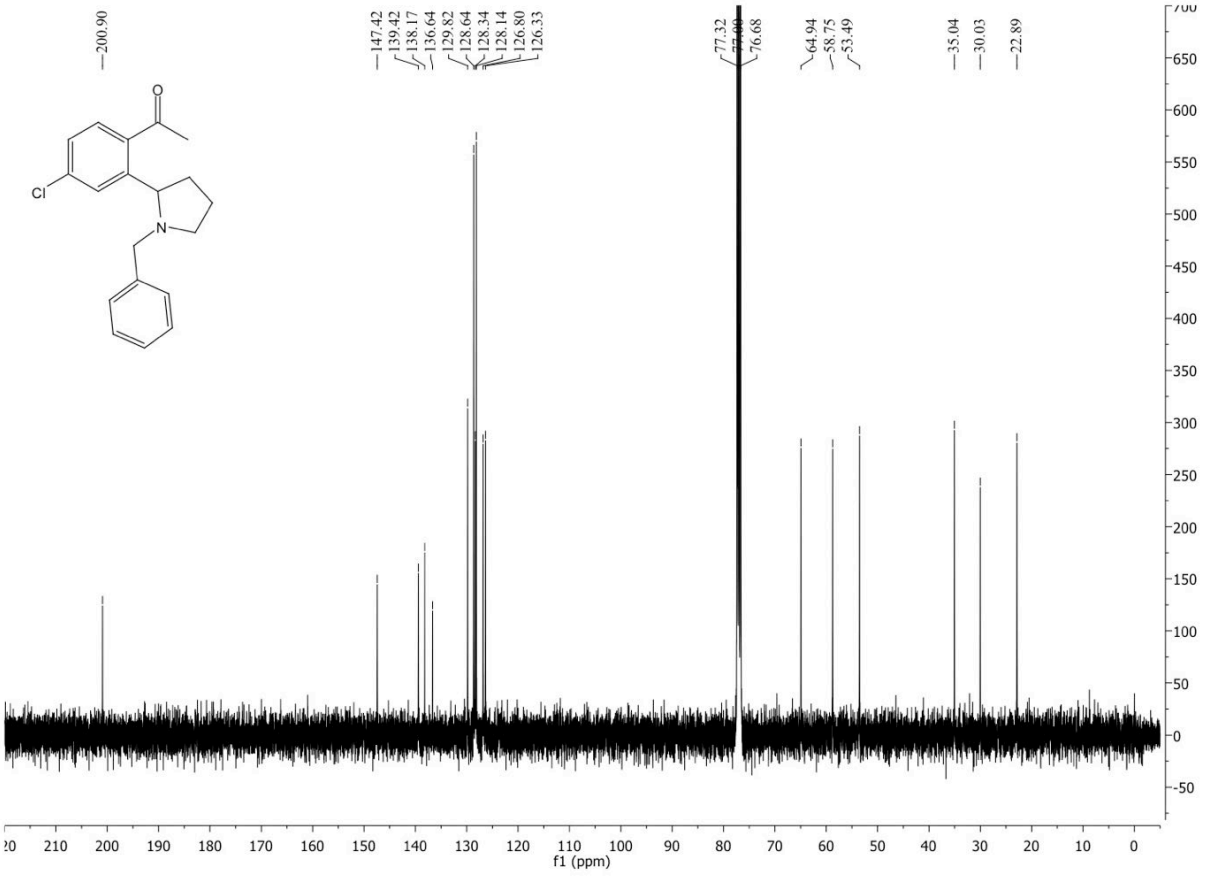
1.02
2.07
1.76
f1 (ppm)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53.49
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22.89
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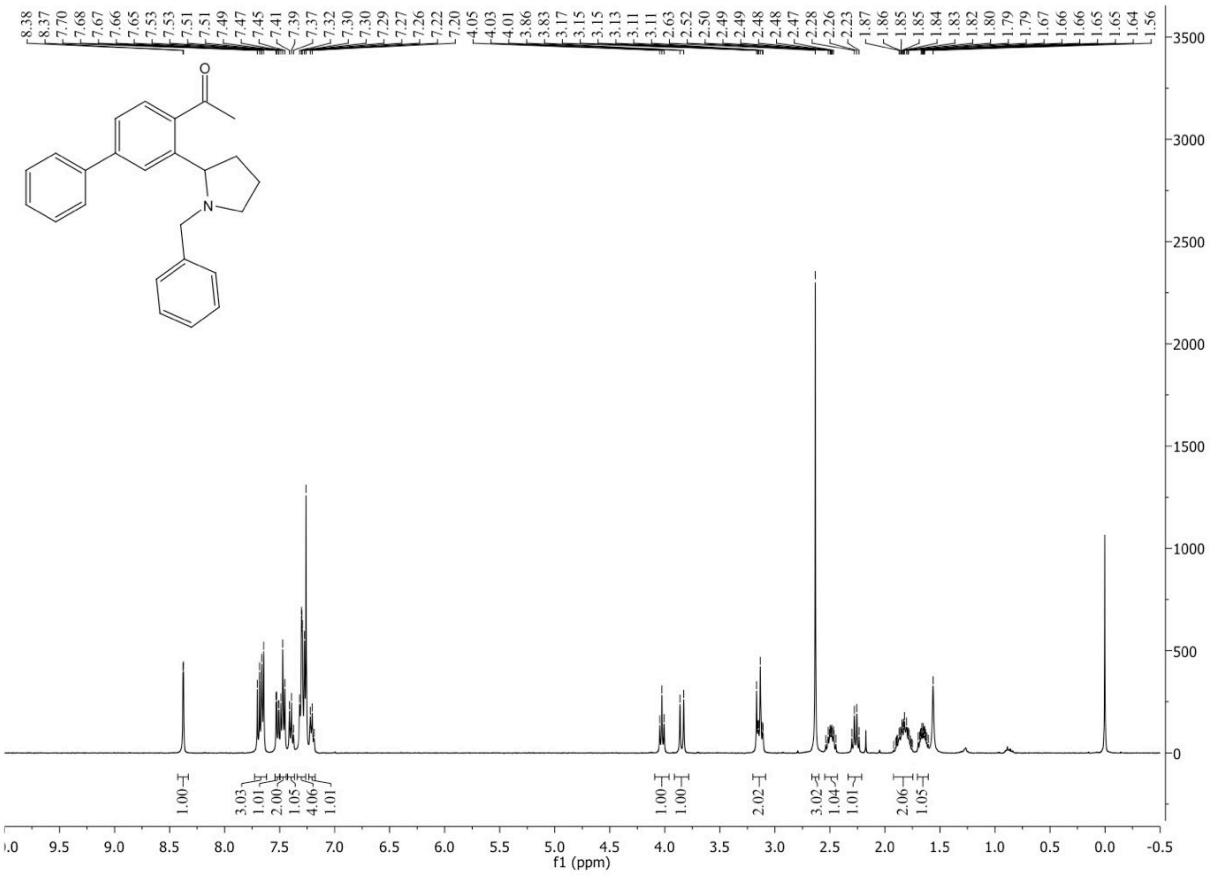
Cl
N
f1 (ppm)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7.22
7.20
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4.03
4.01
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3.83
3.17
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3.15
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3.11
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2.49
2.48
2.48
2.47
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2.26
2.23
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1.86
1.85
1.85
1.84
1.83
1.82
1.80
1.79
1.79
1.67
1.66
1.66
1.65
1.65
1.64
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1.01
2.00
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3.02
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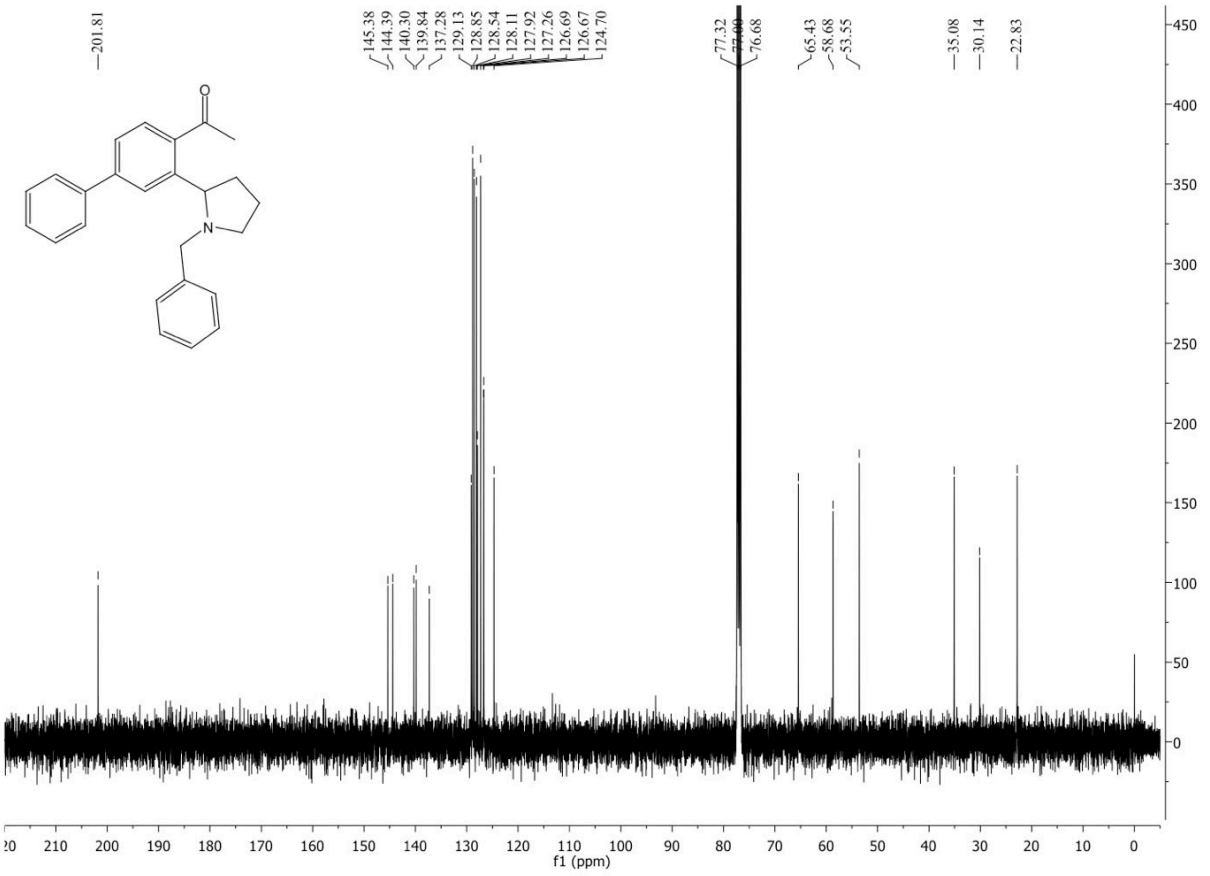
1.01
2.06
1.05
f1 (ppm)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126.67
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53.55
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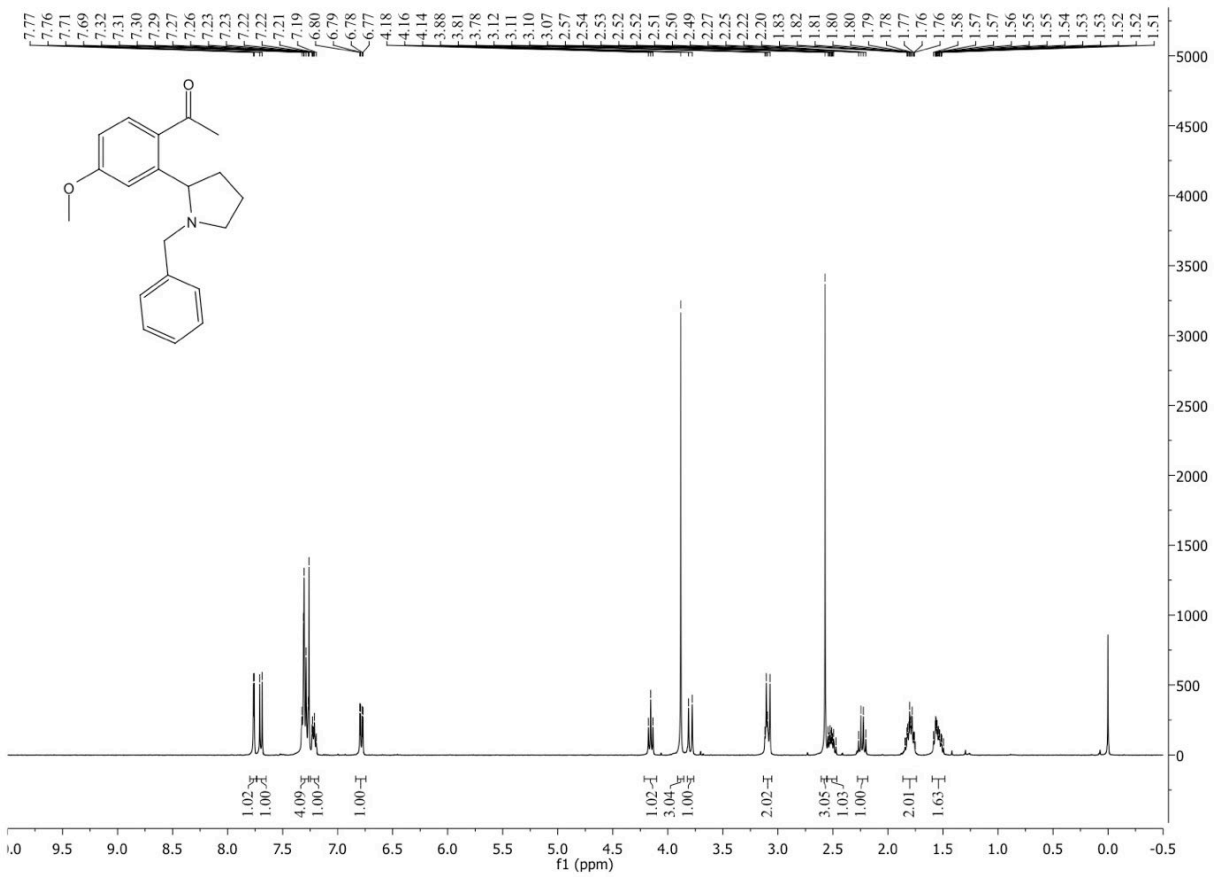
30.14
22.83
O
N
f1 (ppm)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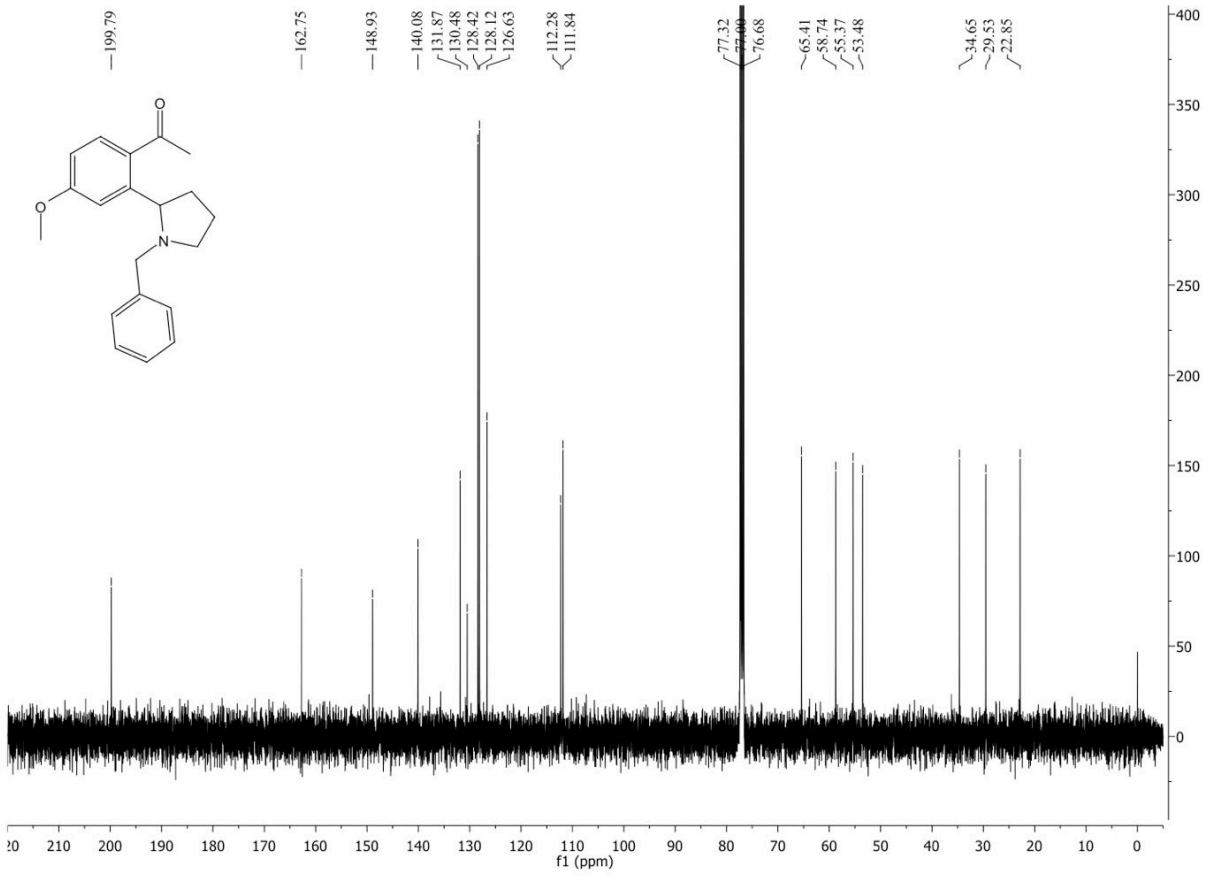
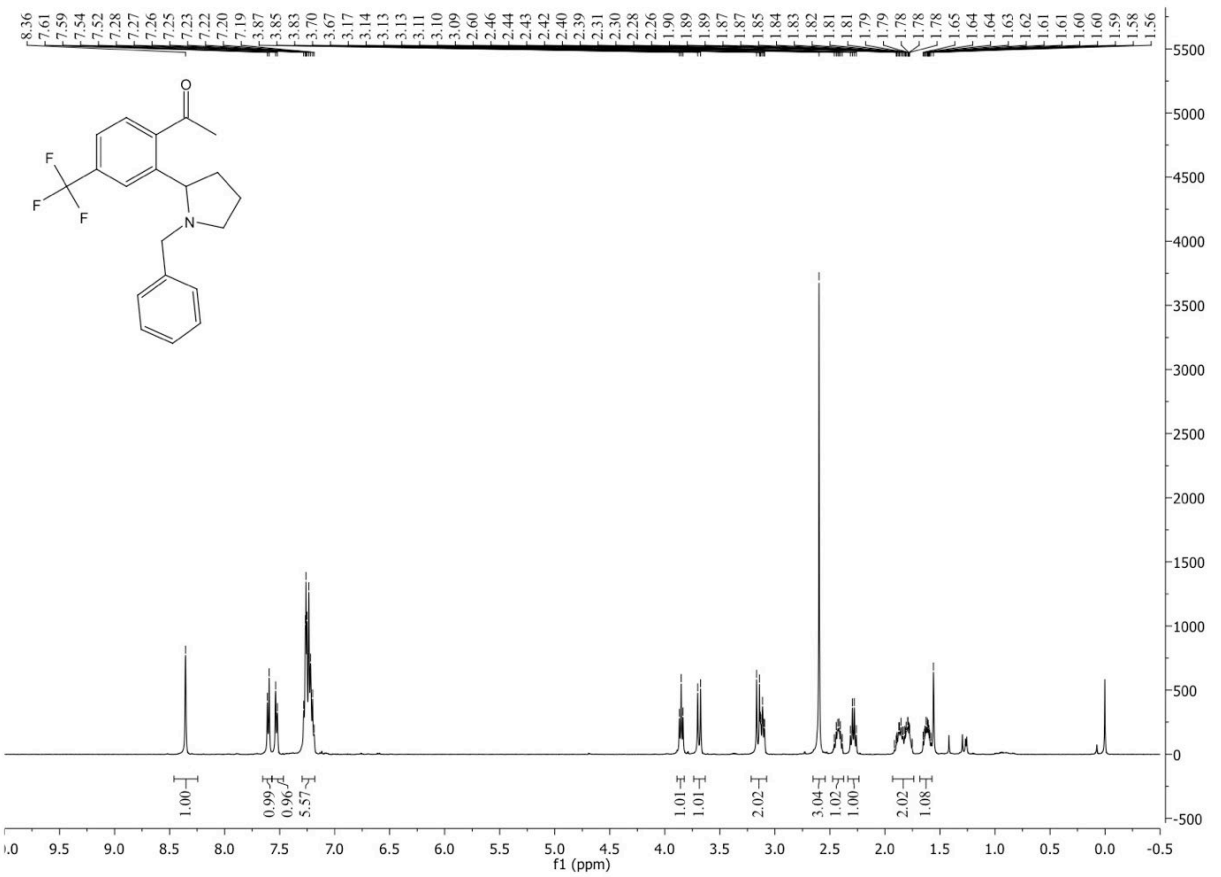
O
O
N
1.02 1.00 4.09 1.00 1.00 1.02 3.04 1.00 2.02 3.05 1.03 1.00 2.01 1.63
f1 (ppm)


199.79 162.75 148.93 140.08 131.87 130.48 128.42 128.12 126.63 112.28 111.84 77.32 77.00 76.68 65.41 58.74 55.37 53.48 34.65 29.53 22.85
O
O
N
f1 (ppm)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3.85
3.83
3.70
3.67
3.17
3.14
3.13
3.11
3.10
3.09
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1.62
1.61
1.61
1.60
1.60
1.59
1.58
1.56
O
F
F
F
N
1.00
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0.96
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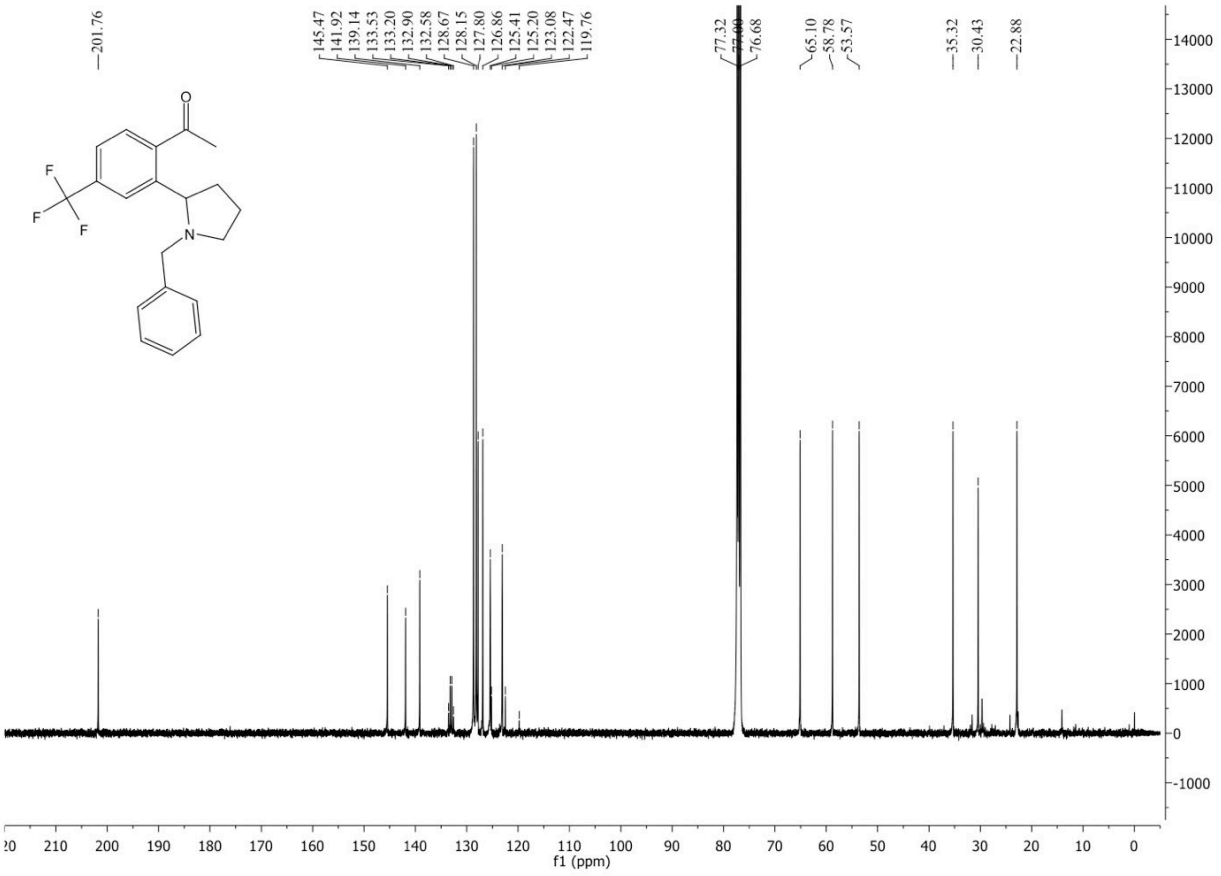
1.01
1.01
2.02
3.04
1.02
1.00
2.02
1.08
f1 (ppm)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132.90
132.58
128.67
128.15
127.80
126.86
125.41
125.20
123.08
122.47
119.76
77.32
77.00
76.68
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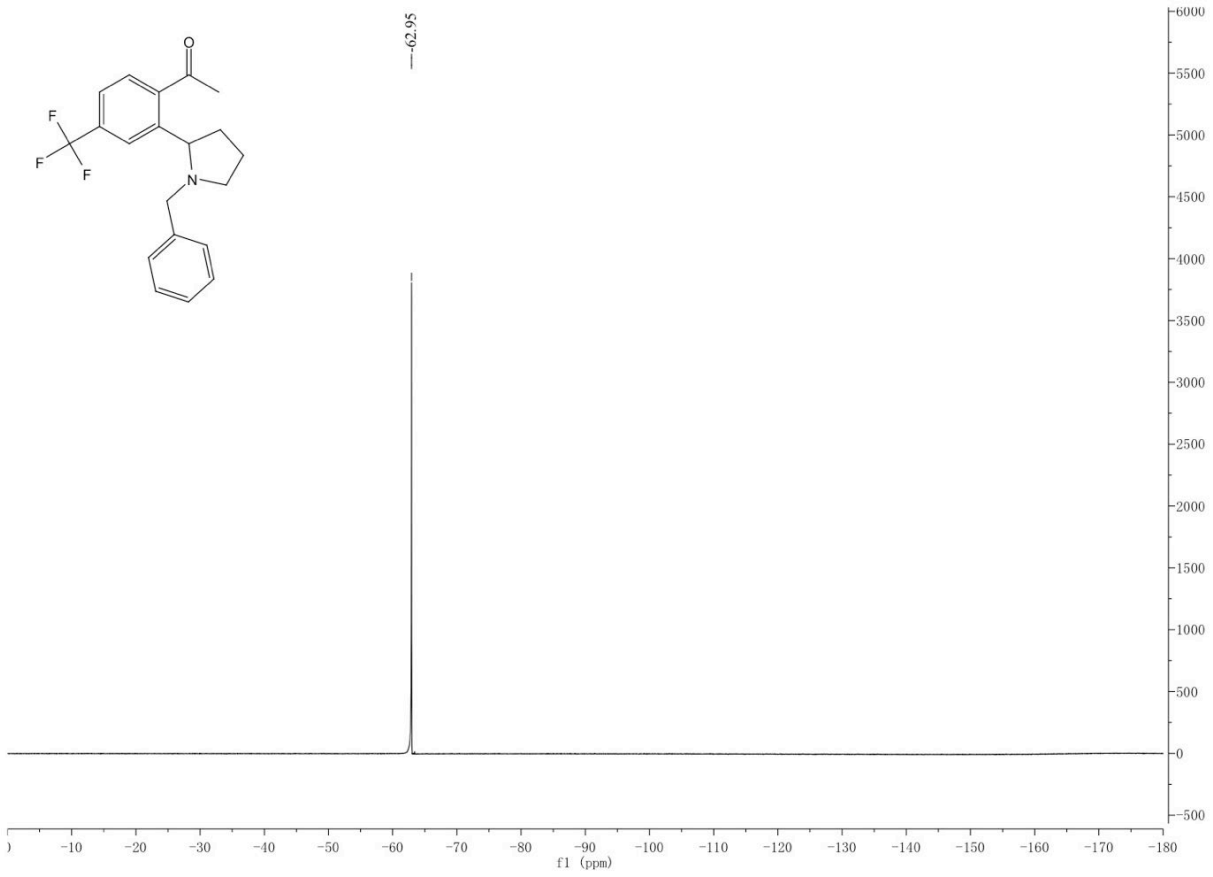
58.78
53.57
35.32
30.43
22.88
O
F
F
F
N
f1 (ppm)


-62.95
O
F
F
F
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5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-10
-20
-30
-40
-50
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-70
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-90
-100
-110
-120
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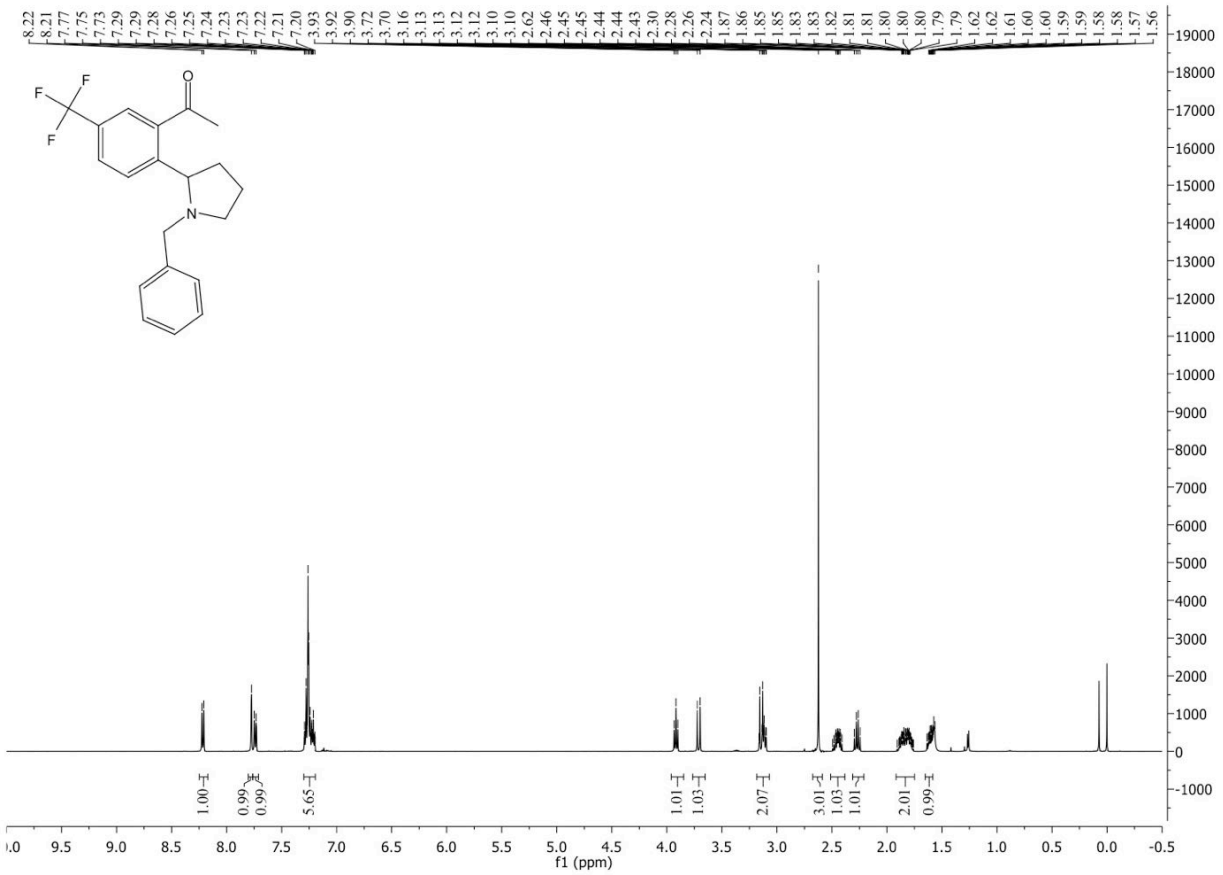
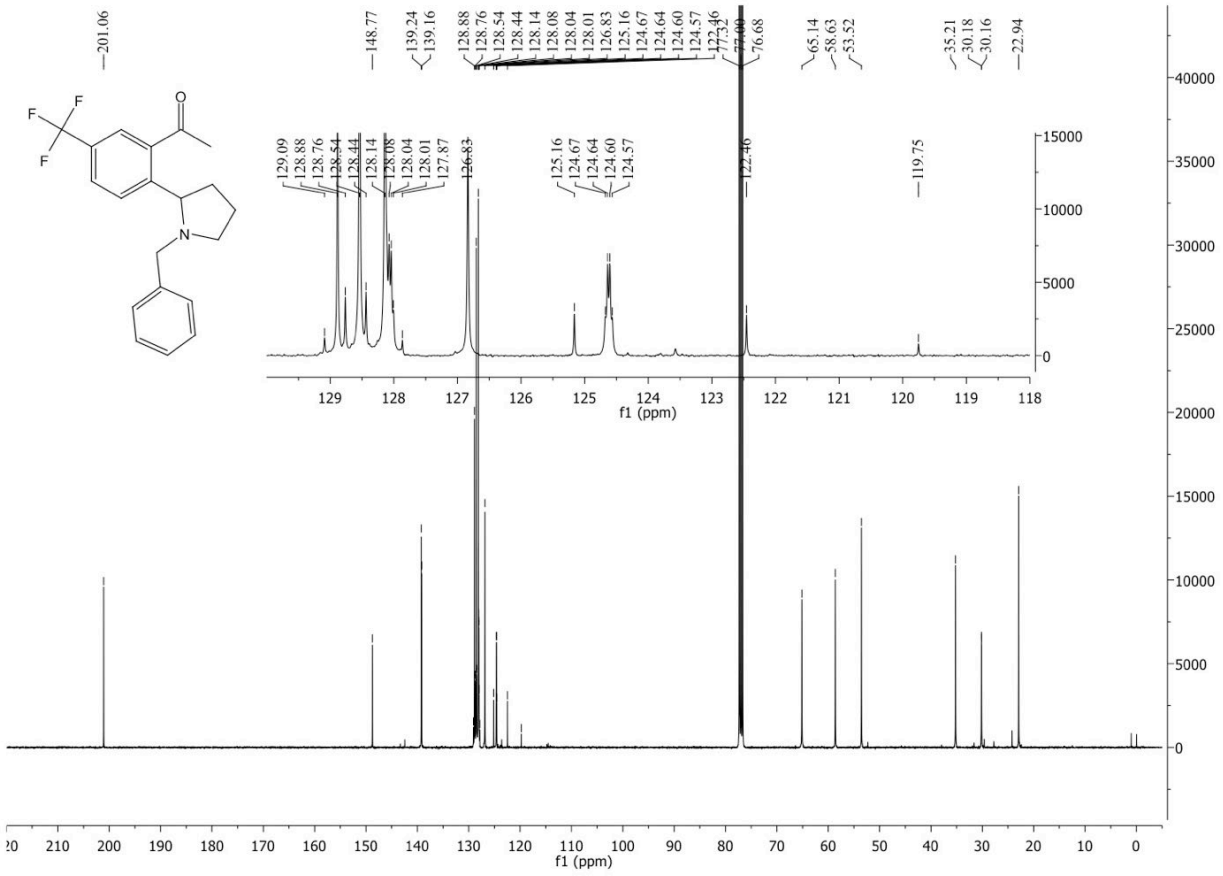
-140
-150
-160
-170
-180
f1 (ppm)


f1 (ppm)


f1 (ppm)


F
F
F
O
N
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9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-10
-20
-30
-40
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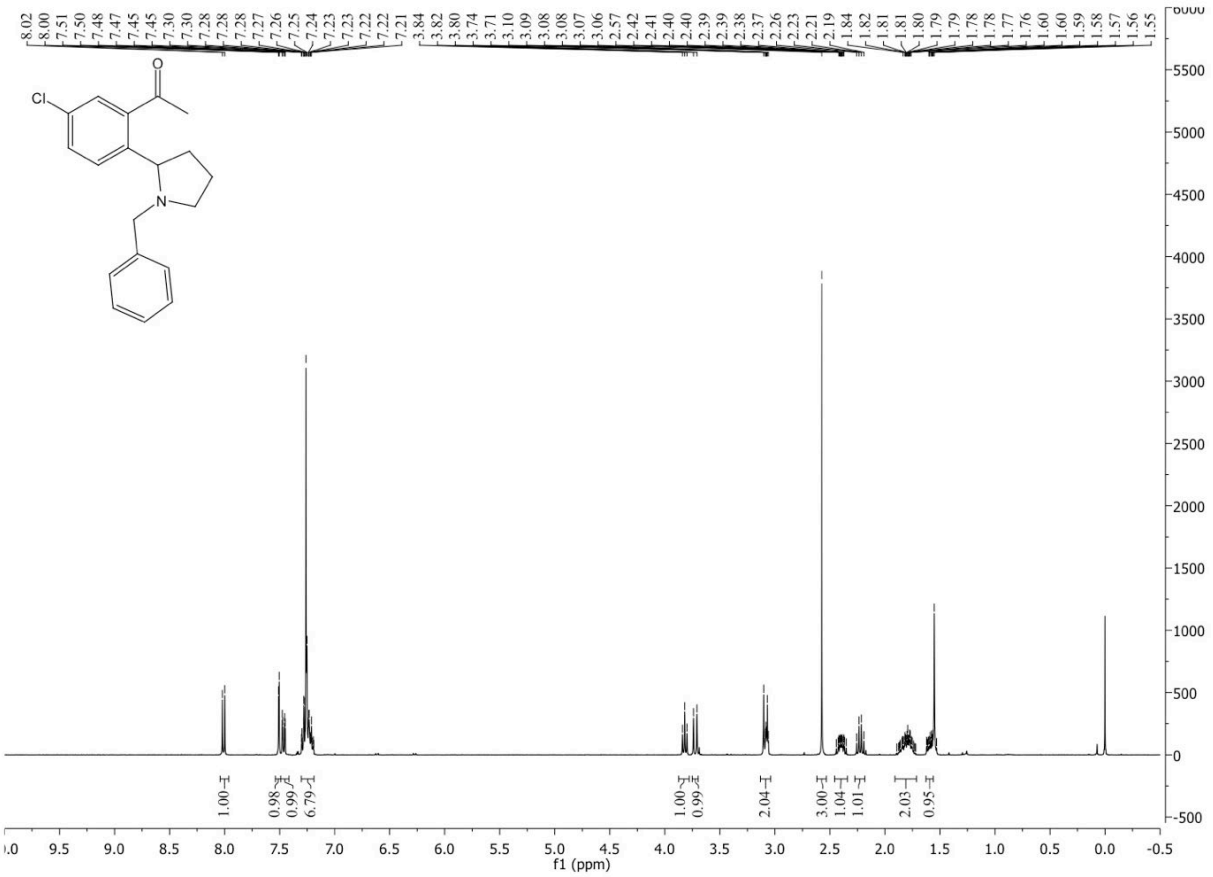
-140
-150
-160
-170
-180
f1 (ppm)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7.24
7.23
7.23
7.22
7.22
7.21
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3.82
3.80
3.74
3.71
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3.09
3.08
3.08
3.07
3.06
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1.80
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1.78
1.78
1.77
1.76
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1.60
1.59
1.58
1.57
1.56
1.55
Cl
O
N
1.00
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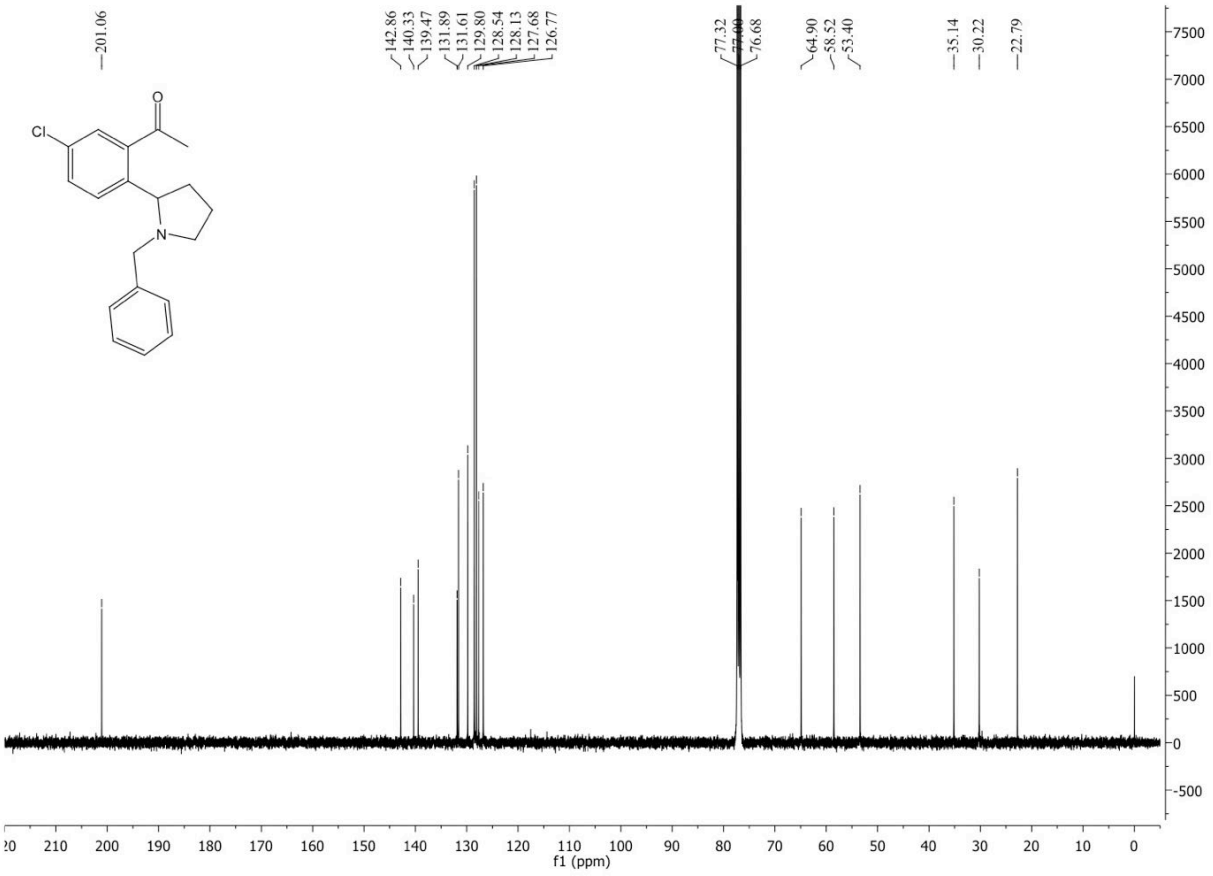
1.00
0.99
2.04
3.00
1.04
1.01
2.03
0.95
f1 (ppm)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127.68
126.77
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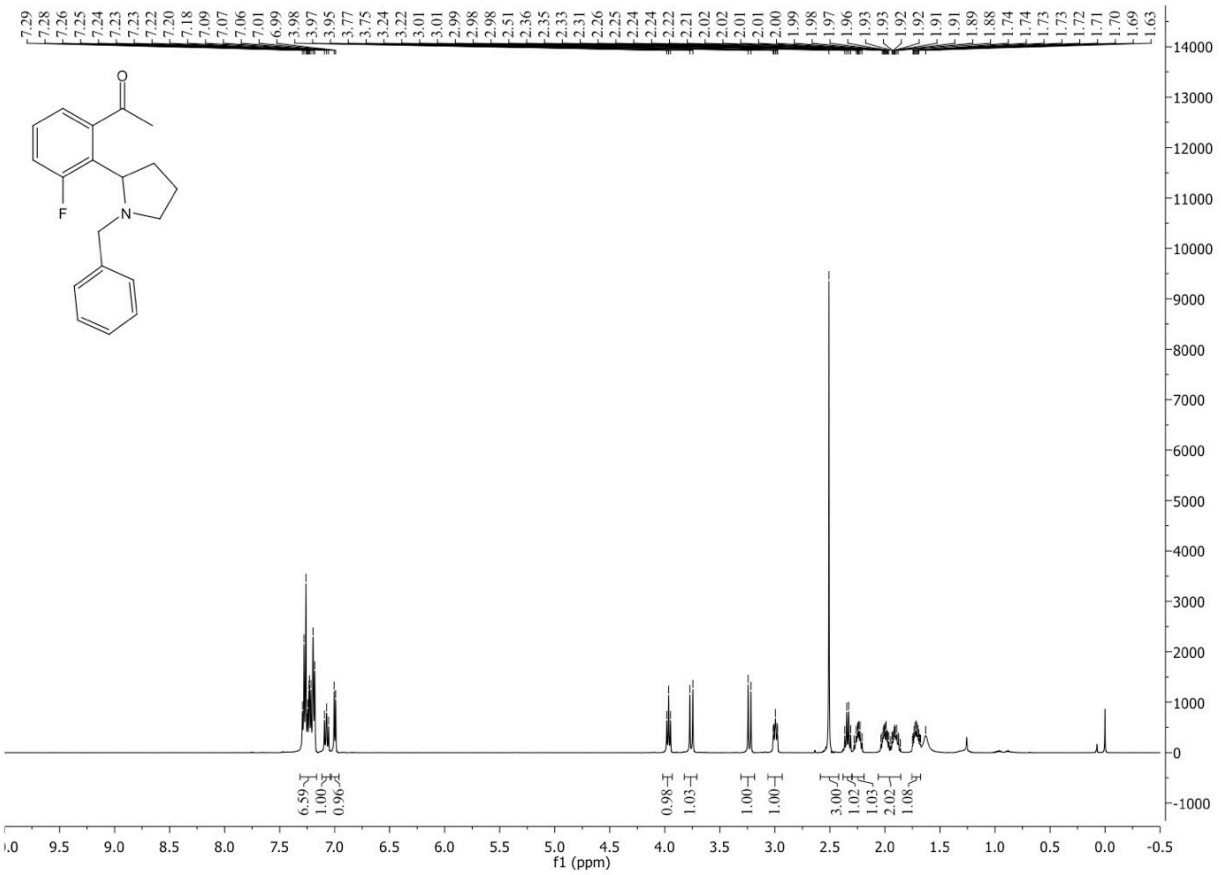
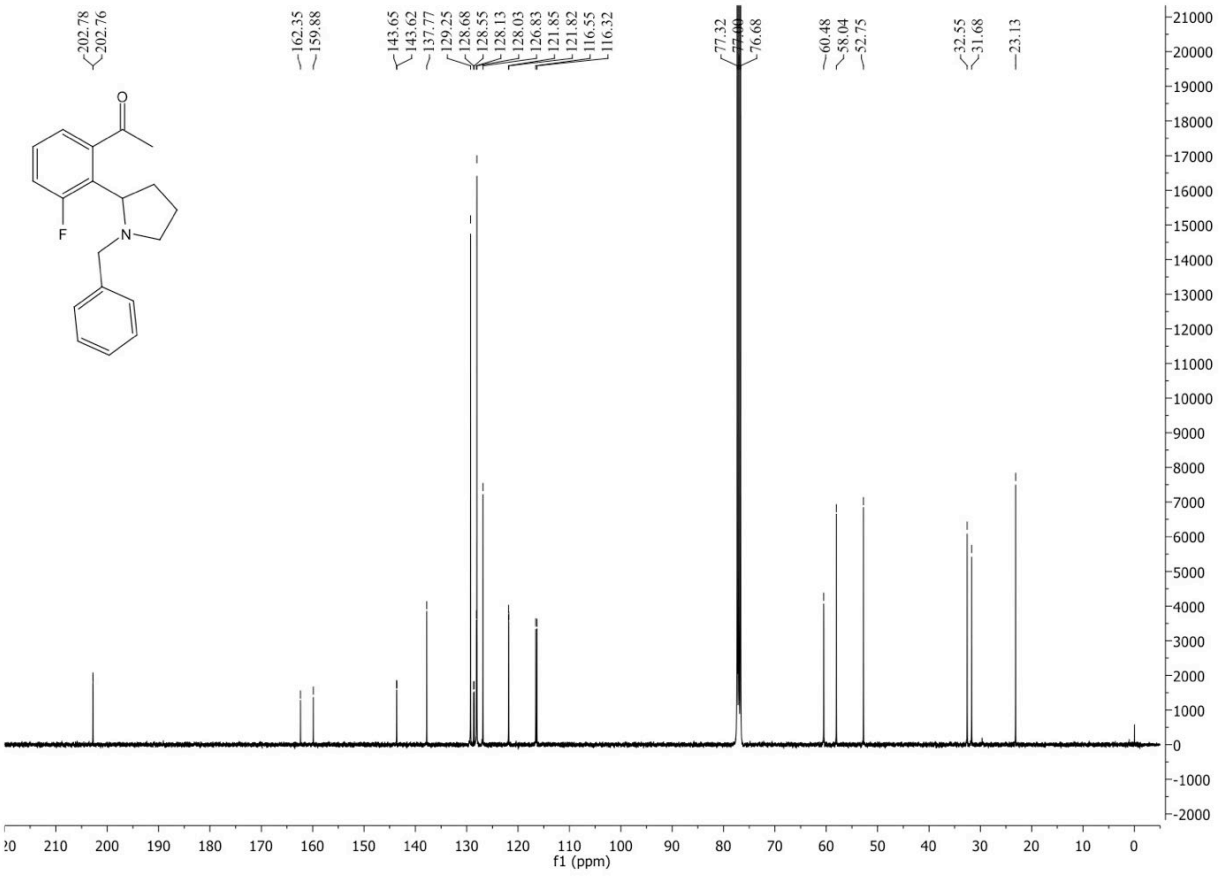
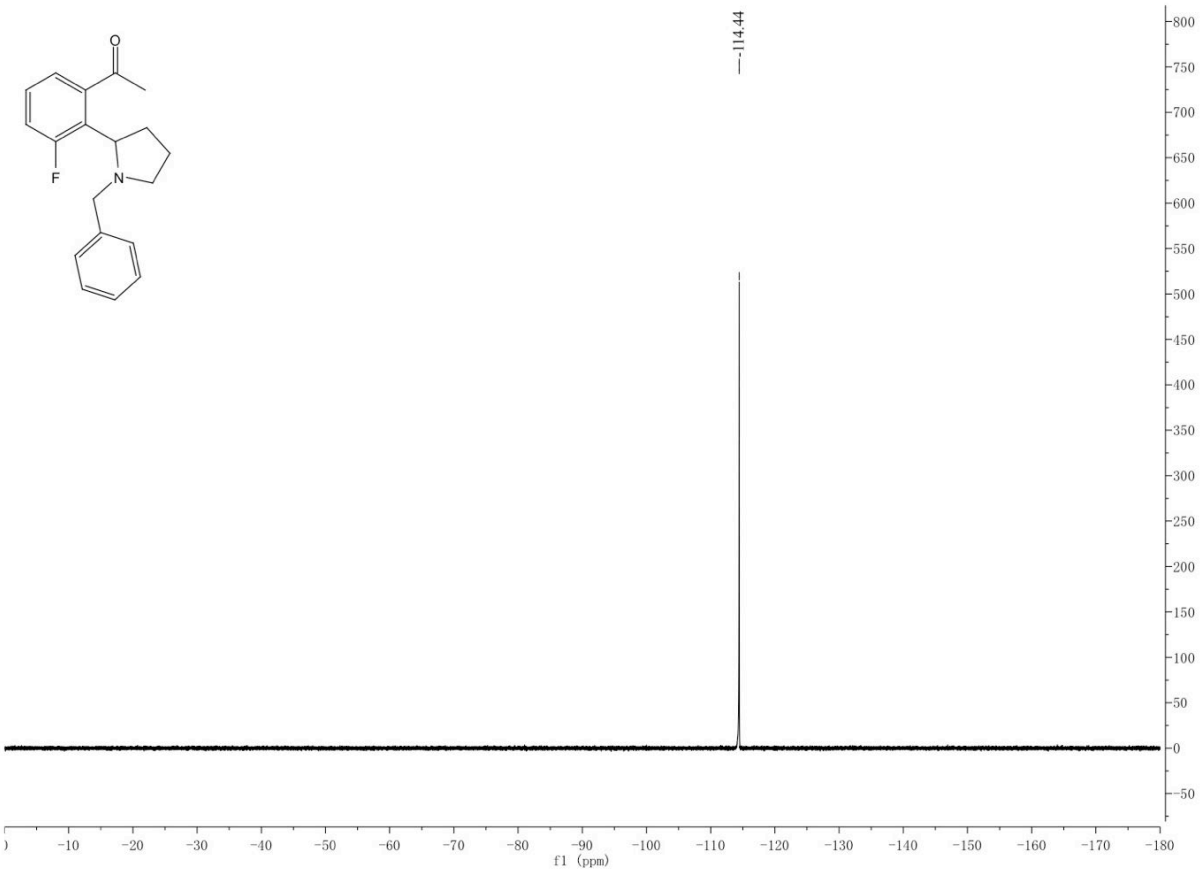
77.00
76.68
64.90
58.52
53.40
35.14
30.22
22.79
Cl
O
N
f1 (ppm)


7.29 7.28 7.26 7.25 7.24 7.23 7.23 7.22 7.20 7.18 7.09 7.07 7.06 7.01 6.99 3.98 3.97 3.95 3.77 3.75 3.24 3.22 3.01 3.01 2.99 2.98 2.98 2.51 2.36 2.35 2.33 2.31 2.26 2.25 2.24 2.24 2.22 2.21 2.02 2.02 2.01 2.01 2.00 1.99 1.98 1.97 1.96 1.93 1.93 1.92 1.92 1.91 1.91 1.89 1.88 1.74 1.74 1.73 1.73 1.72 1.71 1.70 1.69 1.63
O
F
N
6.59
1.00
0.96
0.98
1.03
1.00
1.00
3.00
1.02
1.03
2.02
1.08
f1 (ppm)


202.78 202.76 162.35 159.88 143.65 143.62 137.77 129.25 128.68 128.55 128.13 128.03 126.83 121.85 121.82 116.55 116.32 77.32 77.00 76.68 60.48 58.04 52.75 32.55 31.68 23.13
O
F
N
f1 (ppm)


O
F
N
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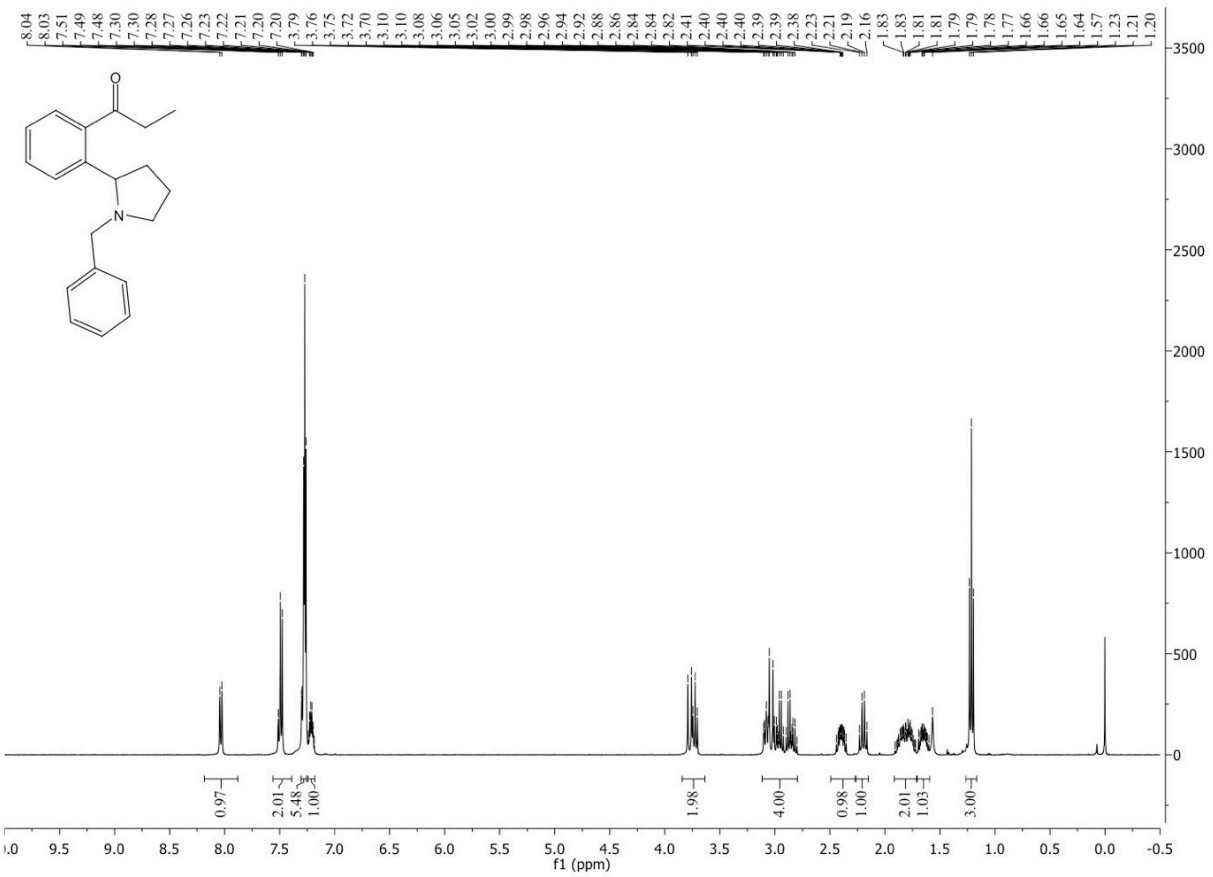
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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7.26
7.23
7.22
7.21
7.20
7.20
3.79
3.76
3.75
3.72
3.70
3.10
3.08
3.06
3.05
3.02
3.00
2.99
2.98
2.96
2.94
2.92
2.88
2.86
2.84
2.84
2.82
2.41
2.40
2.40
2.40
2.39
2.39
2.38
2.23
2.21
2.19
2.16
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1.83
1.81
1.81
1.79
1.79
1.78
1.77
1.66
1.66
1.65
1.64
1.57
1.23
1.21
1.20
O
N
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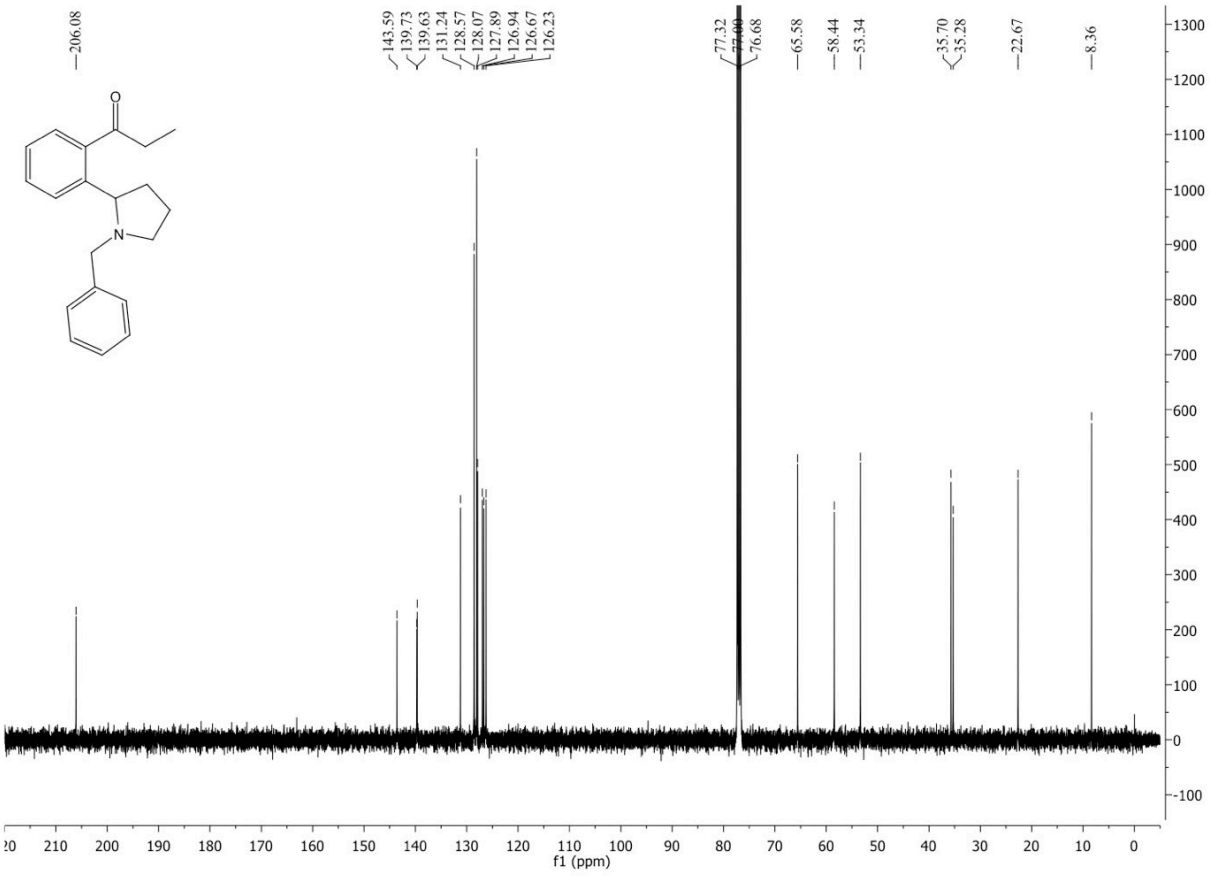
1.00
1.98
4.00
0.98
1.00
2.01
1.03
3.00
f1 (ppm)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126.67
126.23
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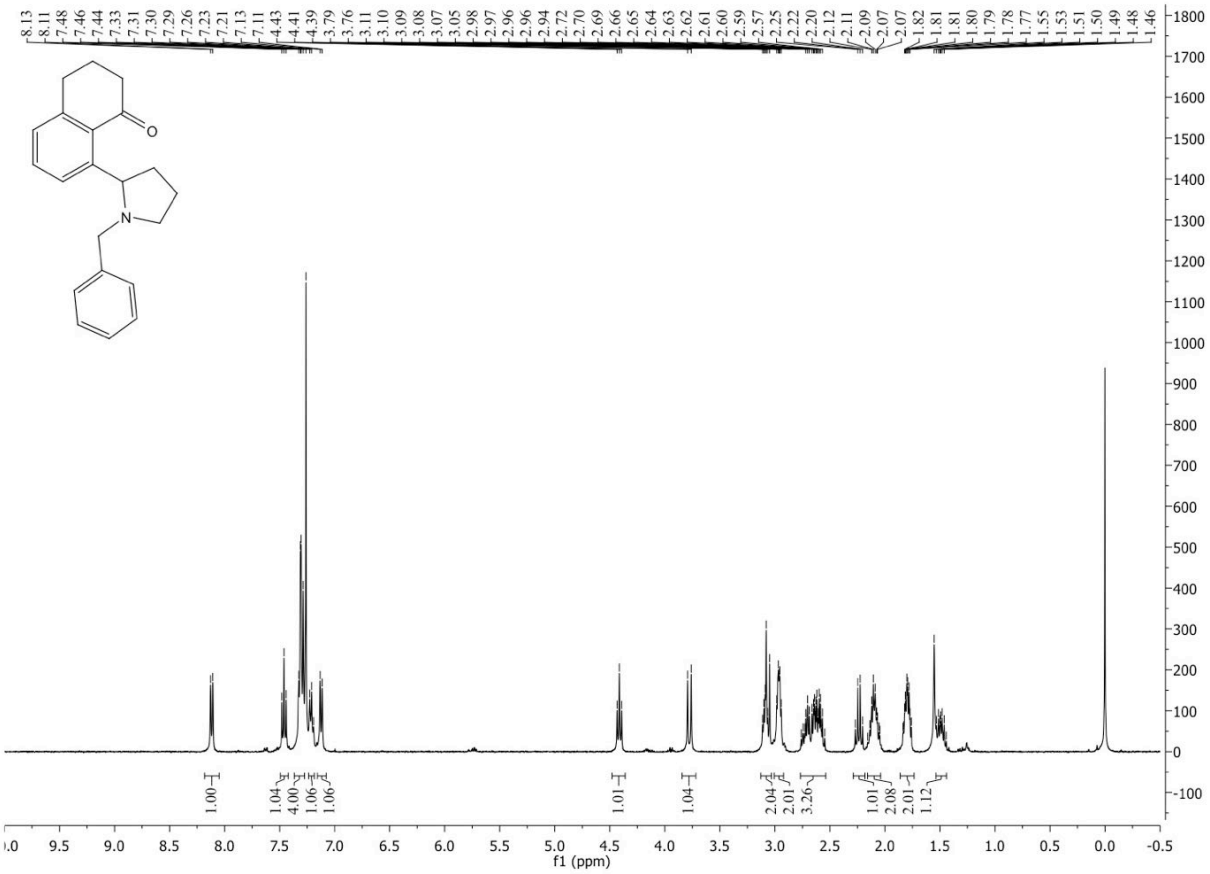
65.58
58.44
53.34
35.70
35.28
22.67
8.36
O
N
f1 (ppm)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7.13
7.11
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4.41
4.39
3.79
3.76
3.11
3.10
3.09
3.08
3.07
3.05
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2.97
2.96
2.96
2.94
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2.70
2.69
2.66
2.65
2.64
2.63
2.62
2.61
2.60
2.59
2.57
2.25
2.22
2.20
2.12
2.11
2.09
2.07
2.07
1.82
1.81
1.81
1.80
1.79
1.78
1.77
1.55
1.53
1.51
1.50
1.49
1.48
1.46
O
N
1.00
1.04
4.00
1.06
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1.04
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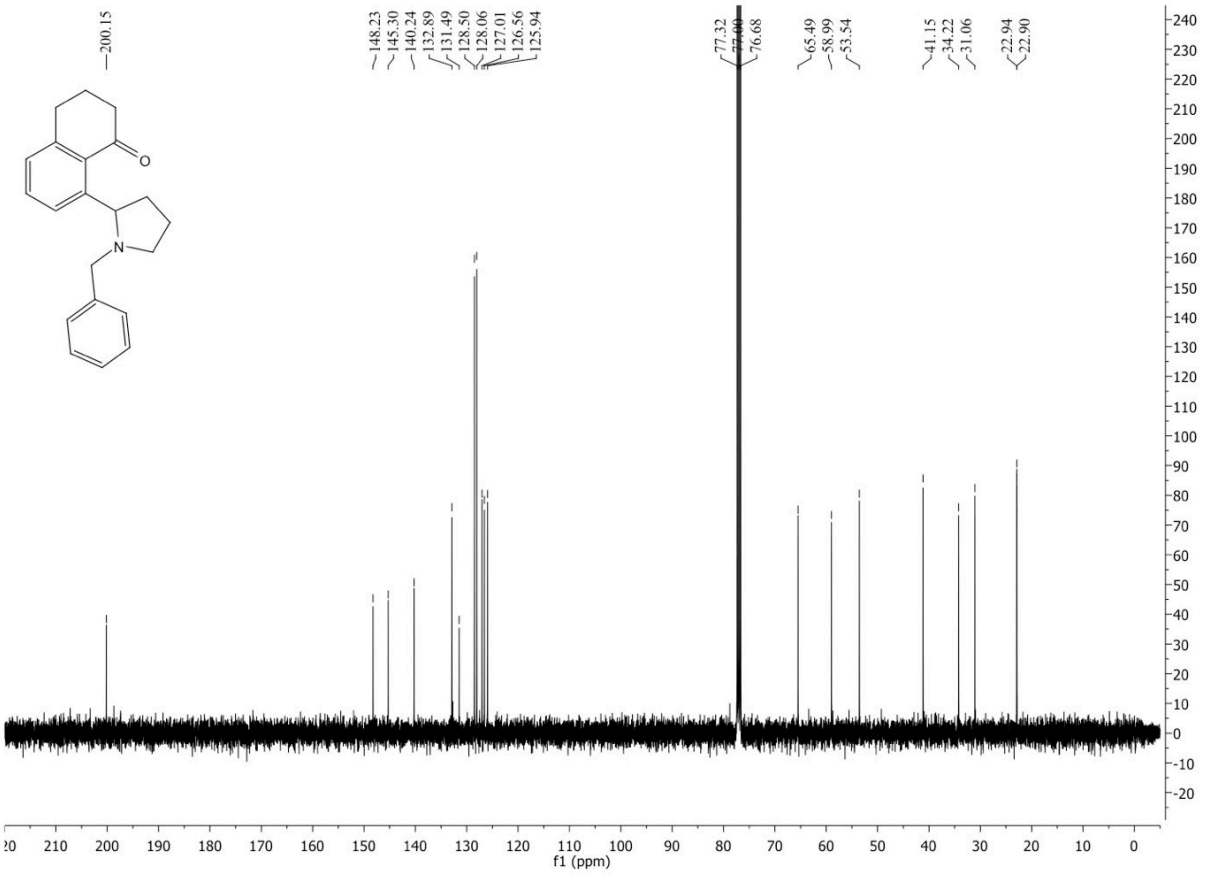
1.01
2.08
2.01
1.12
f1 (ppm)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128.06
127.01
126.56
125.94
77.32
77.00
76.68
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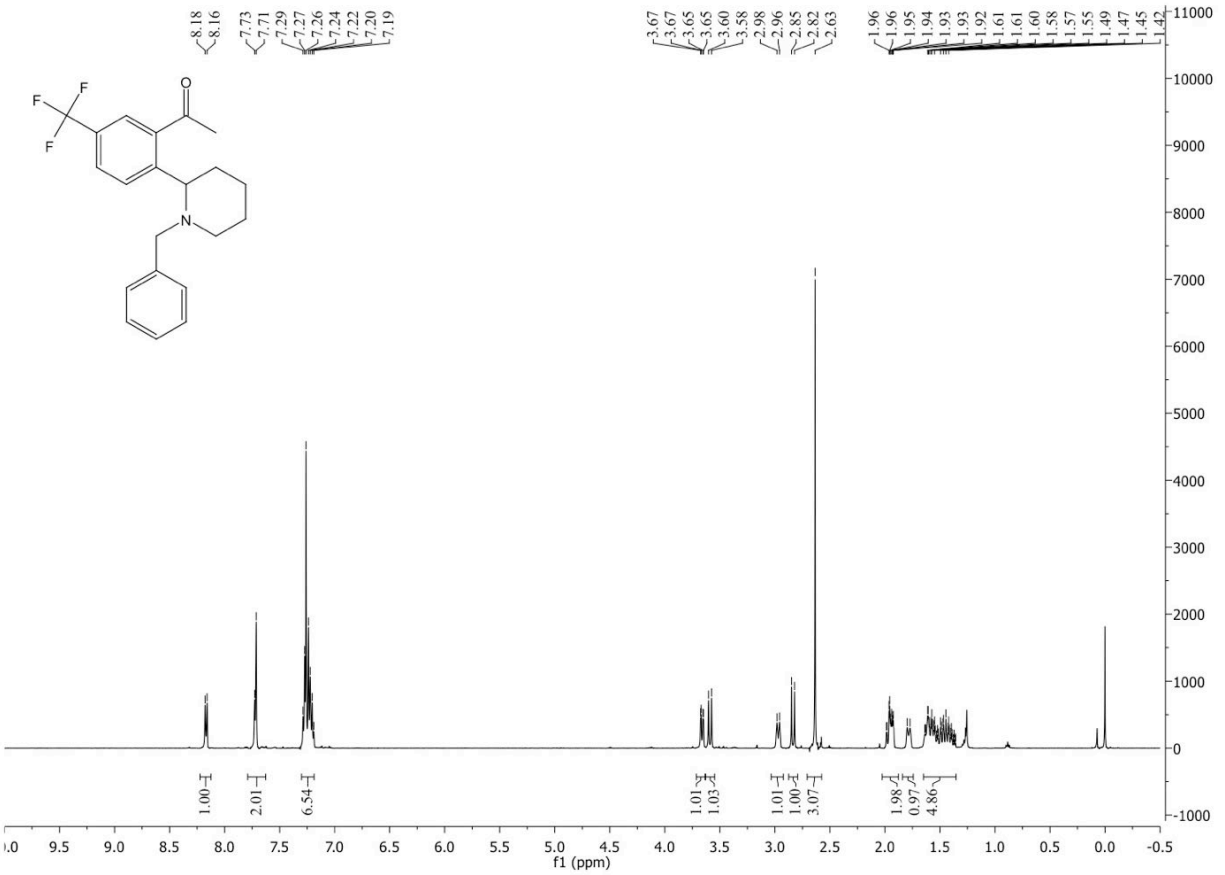
58.99
53.54
41.15
34.22
31.06
22.94
22.90
O
N
f1 (ppm)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3.65
3.65
3.60
3.58
2.98
2.96
2.85
2.82
2.63
1.96
1.96
1.95
1.94
1.93
1.93
1.92
1.61
1.61
1.60
1.58
1.57
1.55
1.49
1.47
1.45
1.42
F
F
F
O
N
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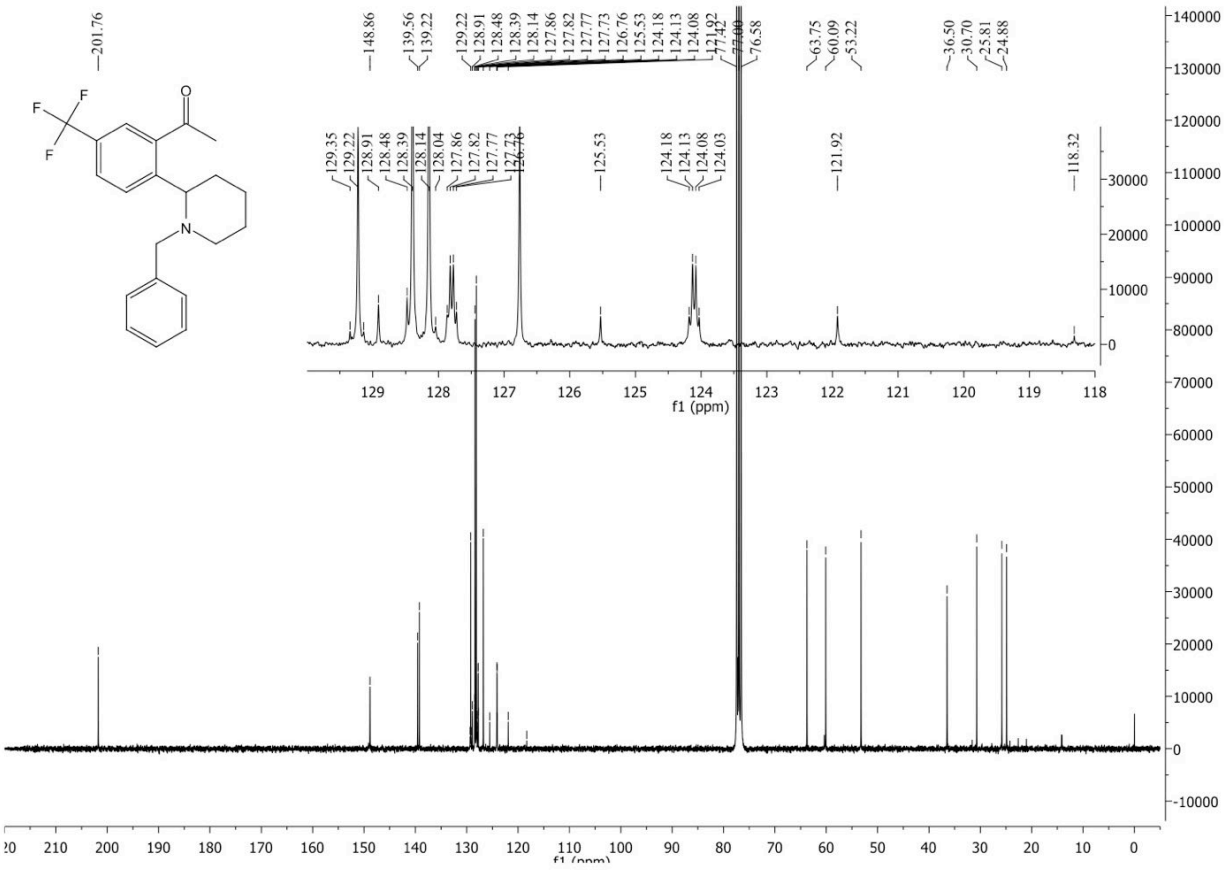
1.01
1.03
1.01
1.00
3.07
1.98
0.97
4.86
f1 (ppm)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128.04
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127.82
127.77
127.73
126.76
125.53
124.18
124.13
124.08
124.03
121.92
77.42
77.00
76.58
63.75
60.09
53.22
36.50
30.70
25.81
24.88
118.32
F
F
F
O
N
f1 (ppm)


F
F
F
O
N
-62.45
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-10
-20
-30
-40
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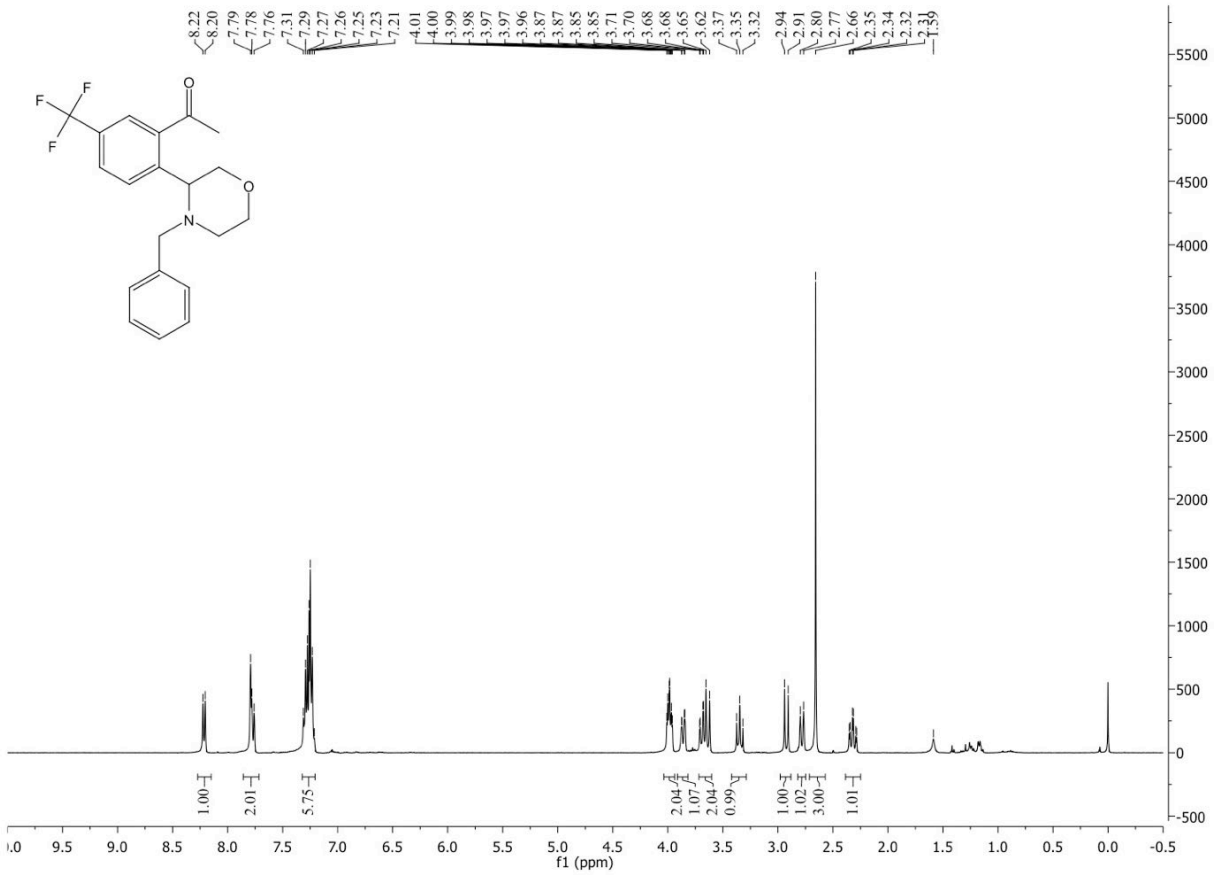
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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7.25
7.23
7.21
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4.00
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3.98
3.97
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3.96
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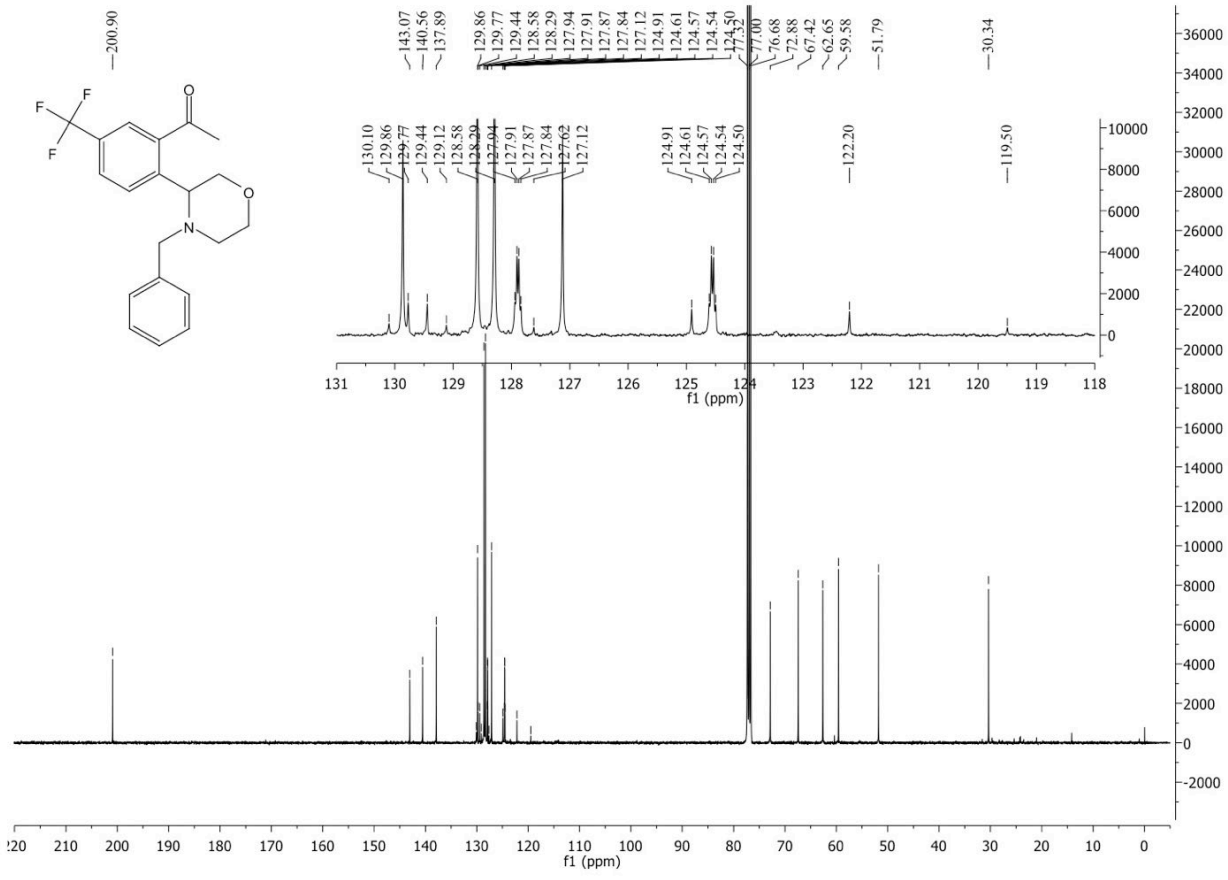
2.66
2.35
2.34
2.32
2.31
1.59
1.00
2.01
5.75
2.04
1.07
2.04
0.99
1.00
1.02
3.00
1.01
f1 (ppm)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128.58
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127.94
127.91
127.87
127.84
127.12
124.91
124.61
124.57
124.54
124.50
77.00
76.68
72.88
67.42
62.65
59.58
51.79
30.34
122.20
119.50
f1 (ppm)


F
F
F
O
O
N
-62.71
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-10
-20
-30
-40
-50
-60
-70
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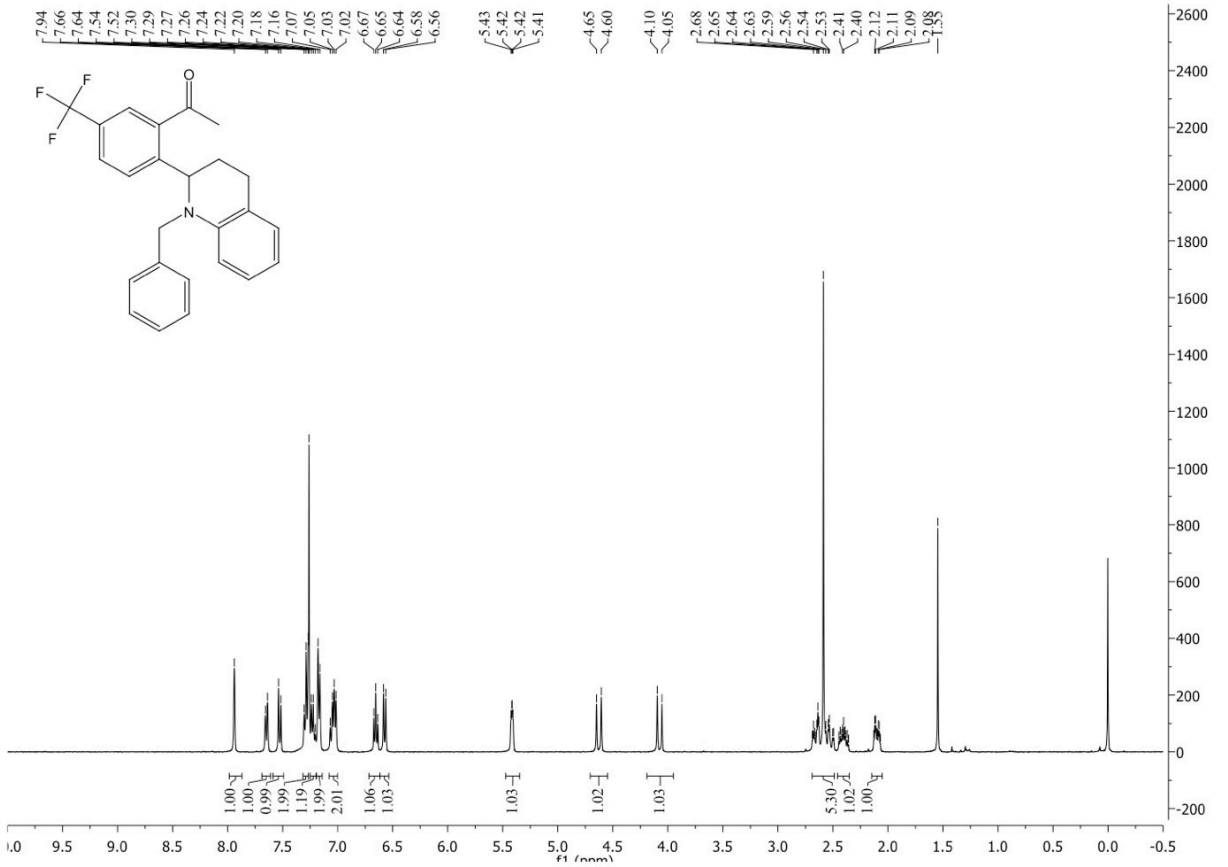
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)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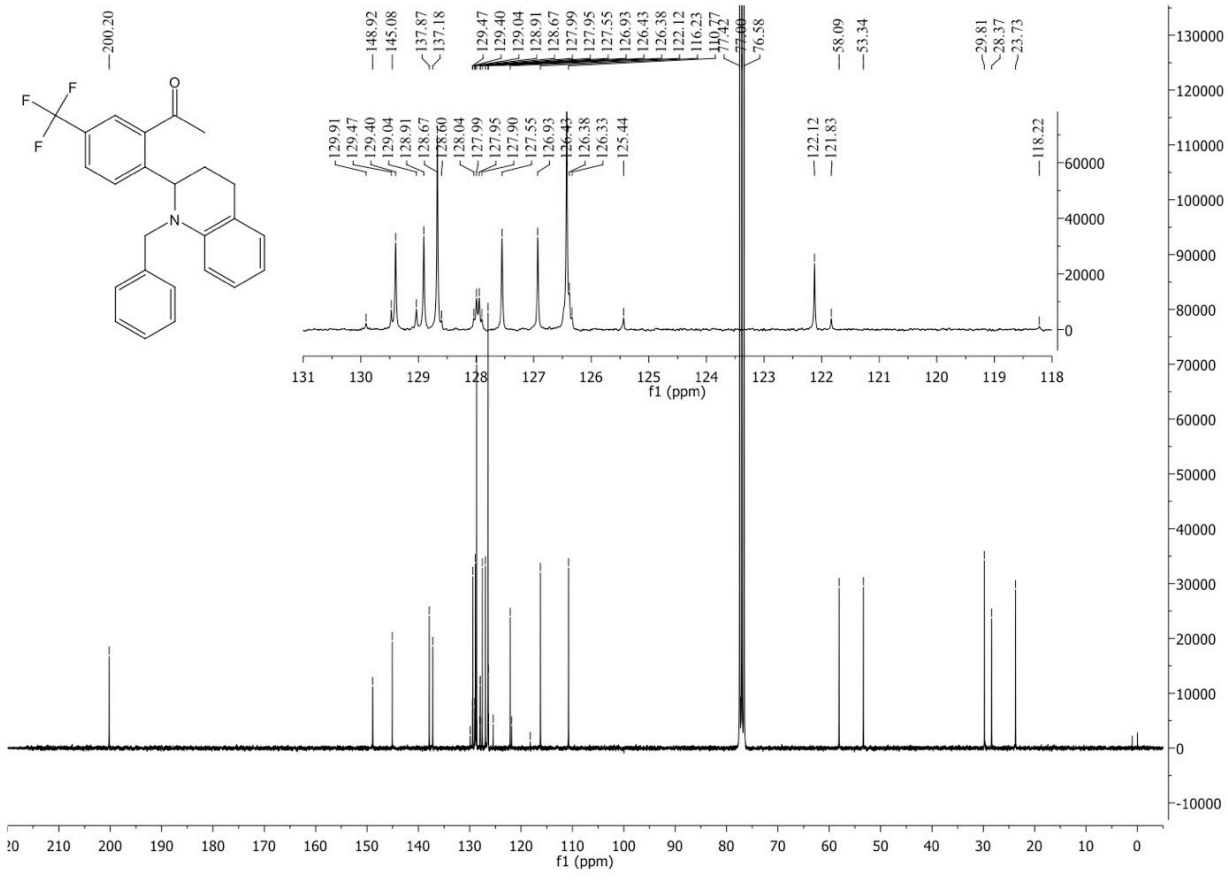
7.66
7.64
7.54
7.52
7.30
7.29
7.27
7.26
7.24
7.22
7.20
7.18
7.16
7.07
7.05
7.03
7.02
6.67
6.65
6.64
6.58
6.56
5.43
5.42
5.42
5.41
4.65
4.60
4.10
4.05
2.68
2.65
2.64
2.63
2.59
2.56
2.54
2.53
2.41
2.40
2.12
2.11
2.09
2.08
1.55
F
F
F
O
N
1.00
1.00
0.99
1.99
1.19
1.99
2.01
1.06
1.03
1.03
1.02
1.03
5.30
1.02
1.00
f1 (ppm)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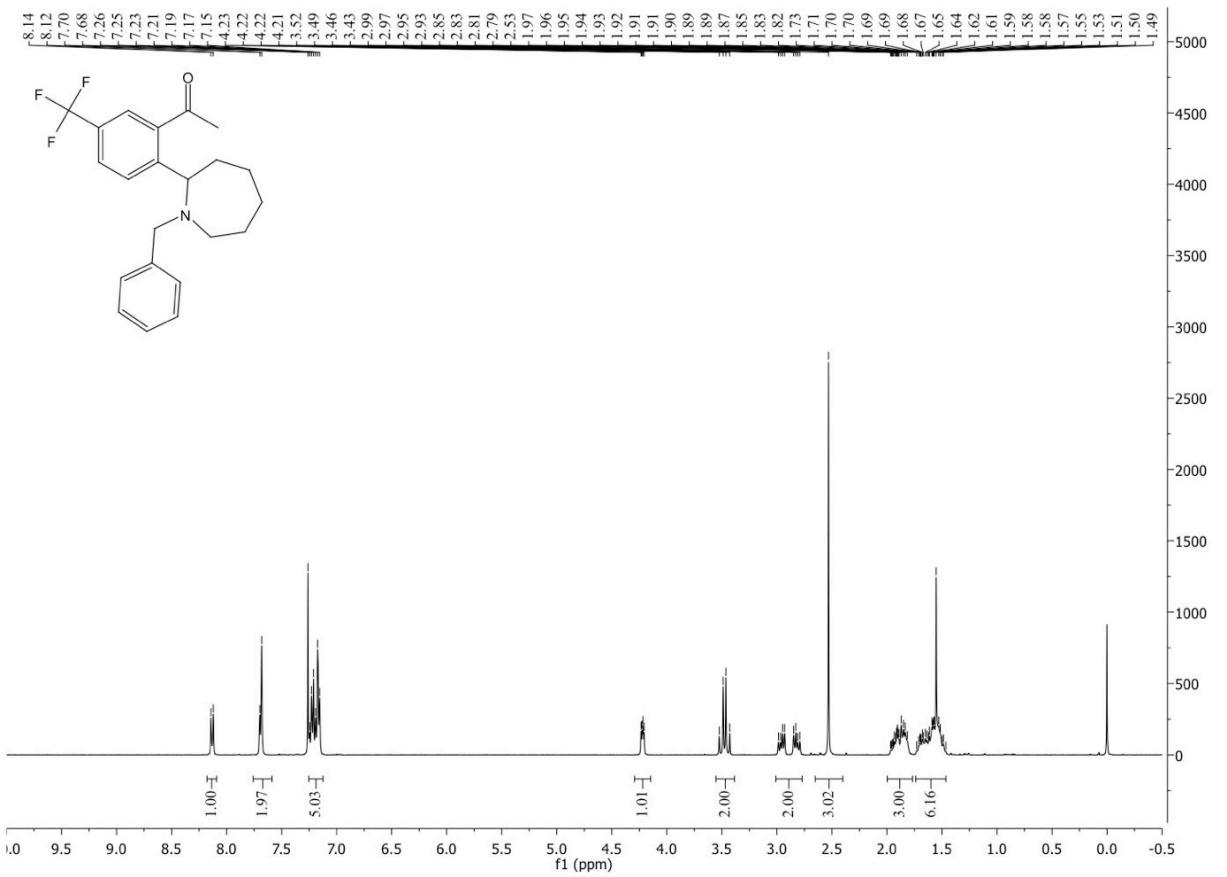
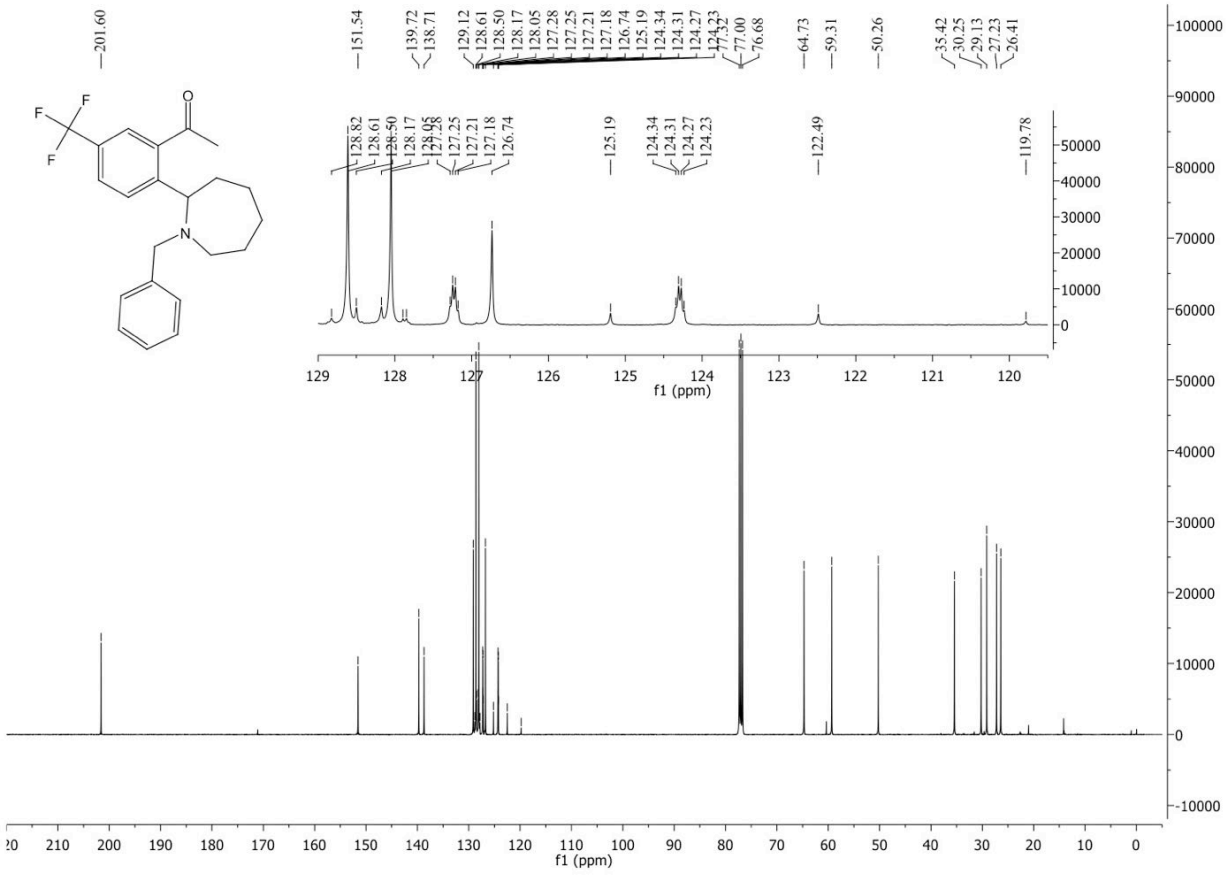
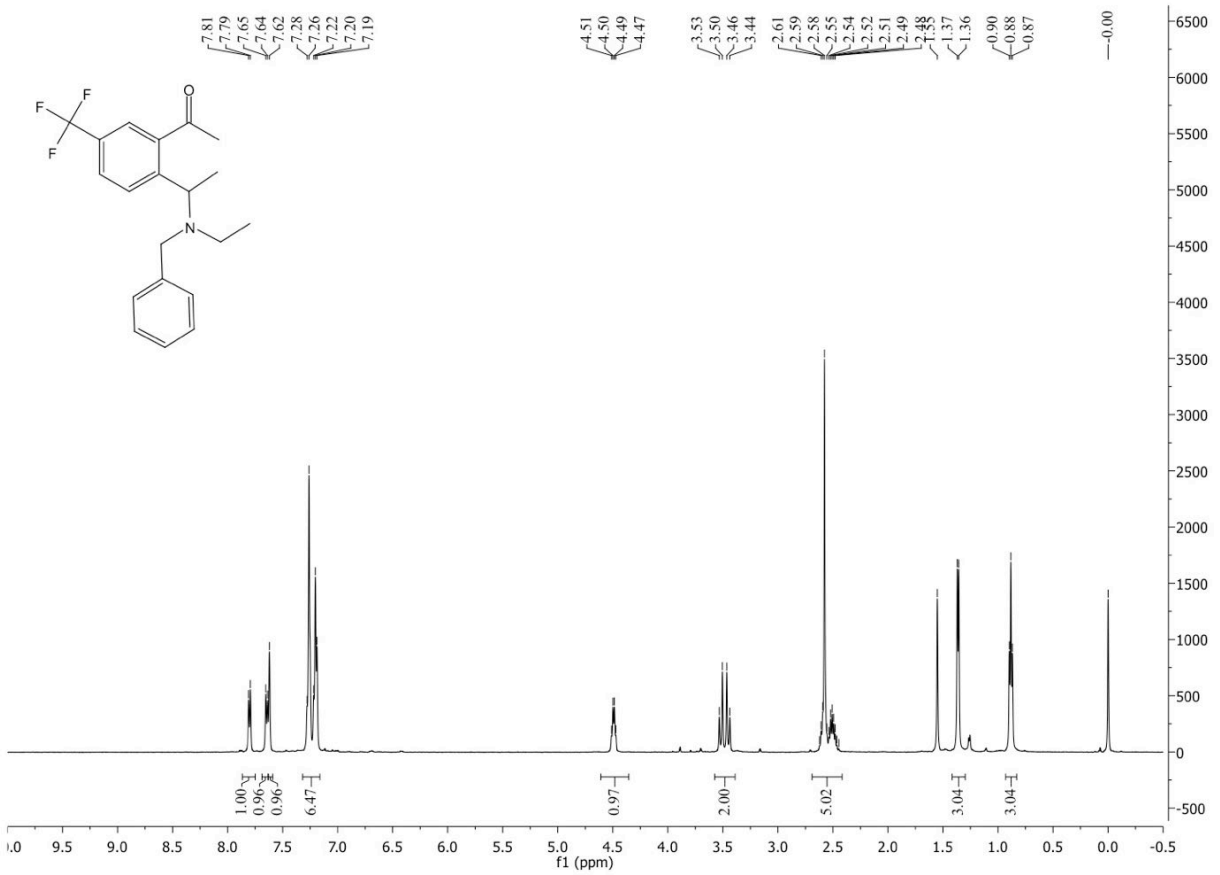
148.92
145.08
137.87
137.18
129.47
129.40
129.04
128.91
128.67
128.60
128.04
127.99
127.95
127.90
127.55
126.93
126.43
126.38
126.33
125.44
122.12
116.23
110.77
77.42
77.00
76.58
58.09
53.34
29.81
28.37
23.73
122.12
121.83
118.22
F
F
F
O
N
f1 (ppm)
f1 (ppm)


F
F
F
O
N
-62.60
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


F
F
F
O
N
f1 (ppm)


F
F
F
O
N
f1 (ppm)


F
F
F
O
N
-62.45
9000
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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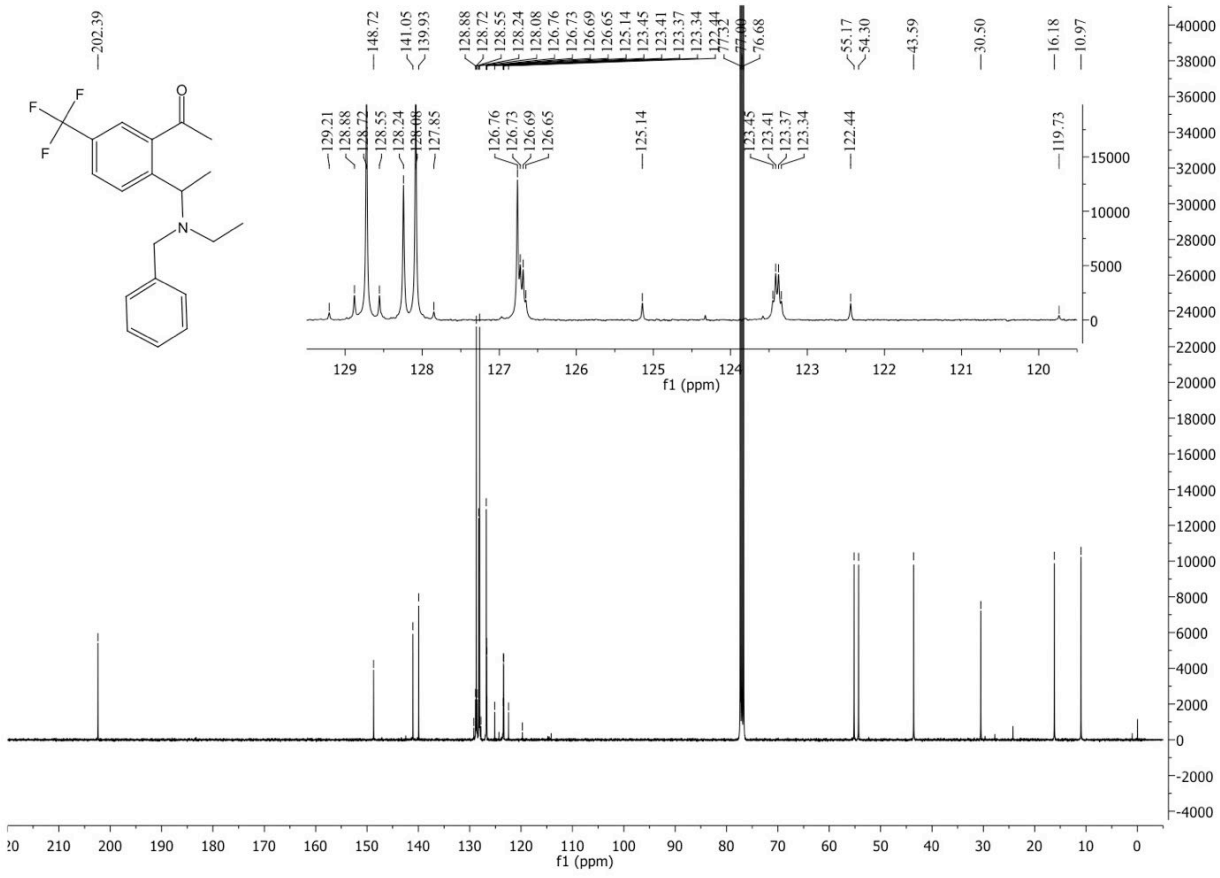
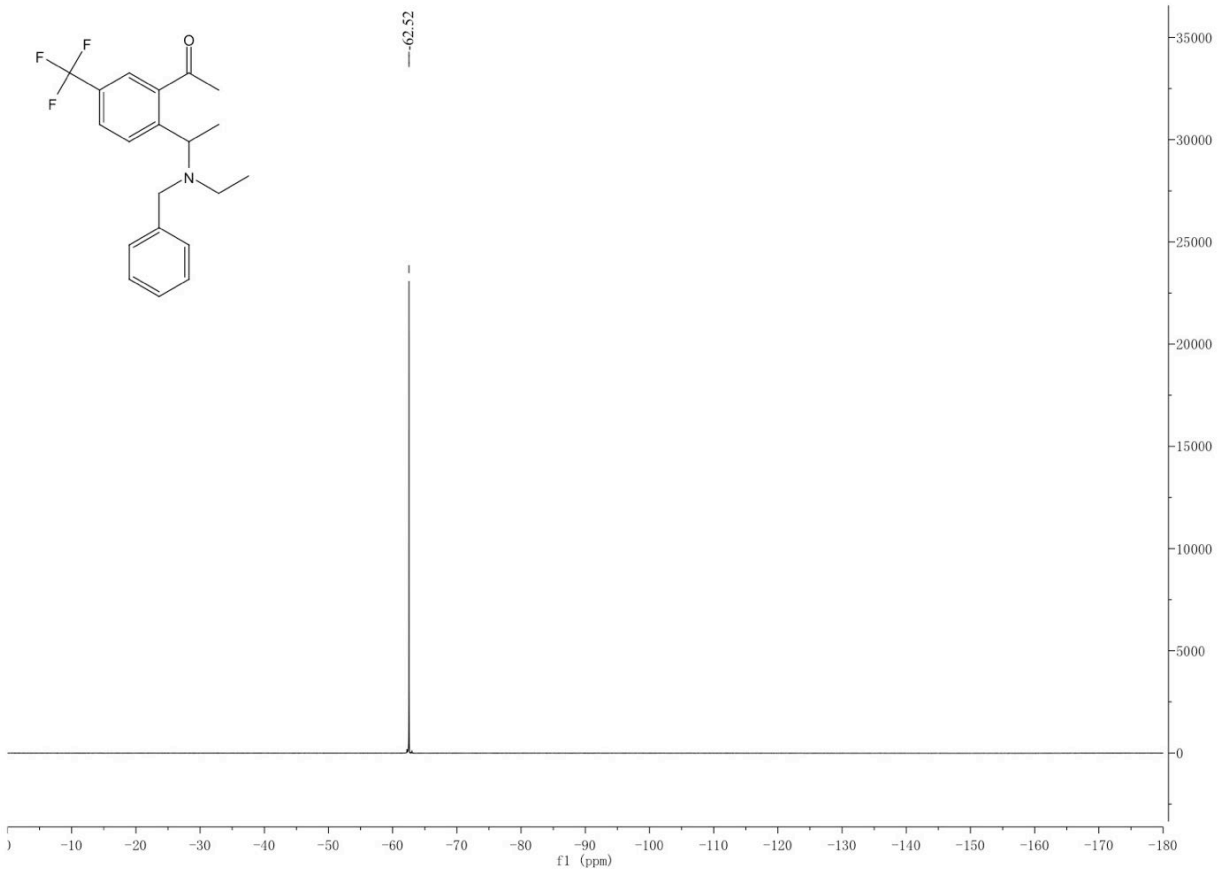
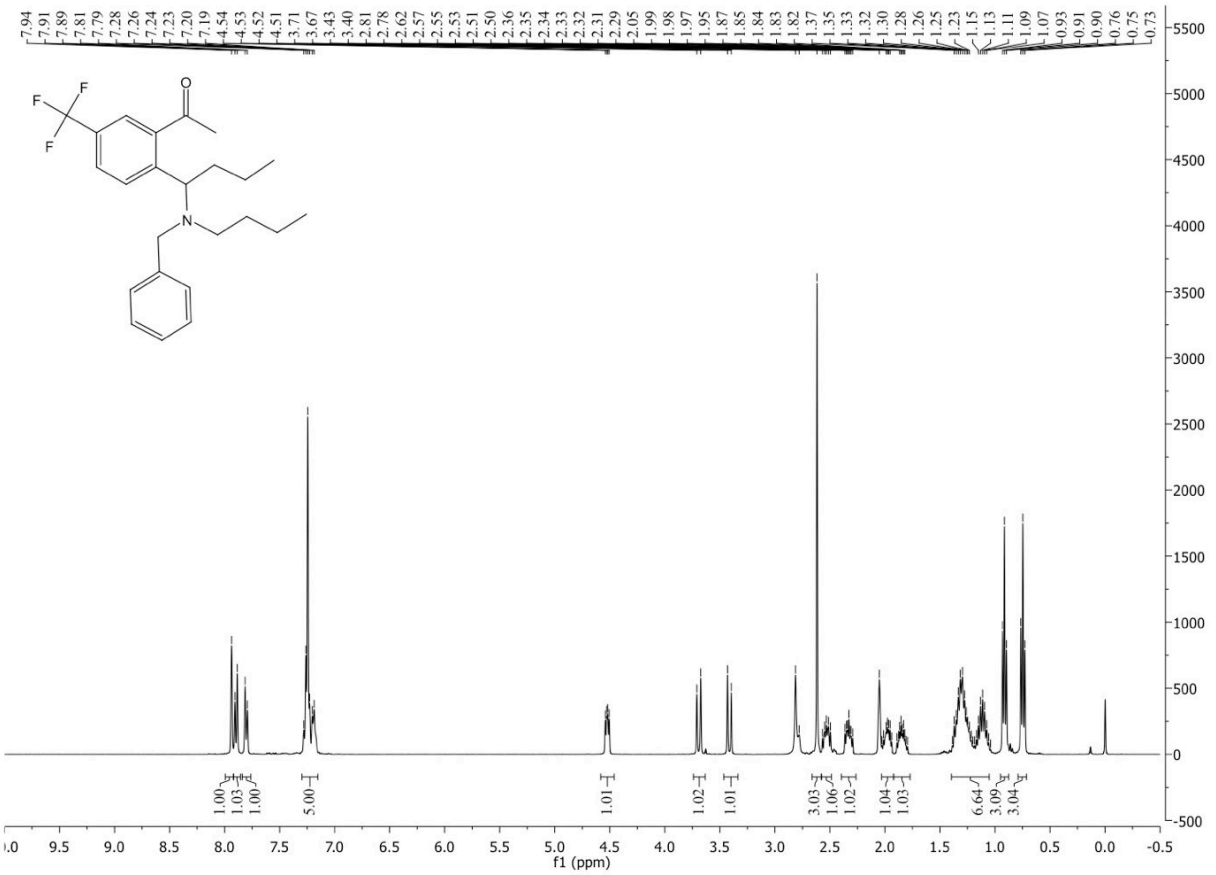
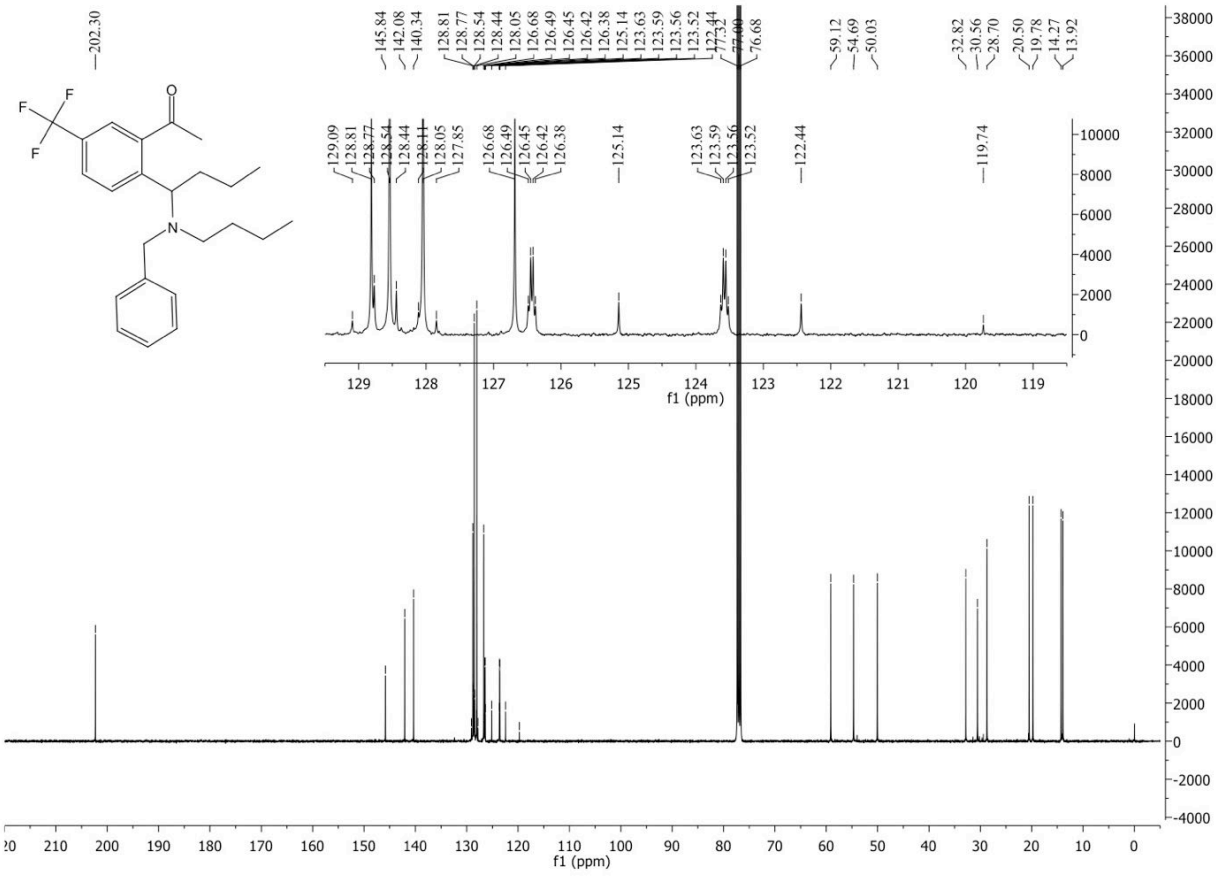
7.79
7.65
7.64
7.62
7.28
7.26
7.22
7.20
7.19
4.51
4.50
4.49
4.47
3.53
3.50
3.46
3.44
2.61
2.59
2.58
2.55
2.54
2.52
2.51
2.49
1.55
1.37
1.36
0.90
0.88
0.87
0.00
1.00
0.96
0.96
6.47
0.97
2.00
5.02
3.04
3.04
f1 (ppm)


202.39
148.72
141.05
139.93
128.88
128.72
128.55
128.24
128.08
126.76
126.73
126.69
126.65
125.14
123.45
123.41
123.37
123.34
122.44
77.32
77.00
76.68
55.17
54.30
43.59
30.50
16.18
10.97
129.21
128.88
128.72
128.55
128.24
128.08
127.85
126.76
126.73
126.69
126.65
125.14
123.45
123.41
123.37
123.34
122.44
119.73
f1 (ppm)
f1 (ppm)


F
F
F
O
N
-62.52
35000
30000
25000
20000
15000
10000
5000
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


7.94
7.91
7.89
7.81
7.79
7.28
7.26
7.24
7.23
7.20
7.19
4.54
4.53
4.52
4.51
3.71
3.67
3.43
3.40
3.81
2.78
2.62
2.57
2.55
2.53
2.51
2.50
2.36
2.35
2.34
2.33
2.32
2.31
2.29
2.05
1.99
1.98
1.97
1.95
1.87
1.85
1.84
1.83
1.82
1.37
1.35
1.33
1.32
1.30
1.28
1.26
1.25
1.23
1.15
1.13
1.11
1.09
1.07
0.93
0.91
0.90
0.76
0.75
0.73
F
F
F
O
N
1.00
1.03
1.00
5.00
1.01
1.02
1.01
3.03
1.06
1.02
1.04
1.03
6.64
3.09
3.04
f1 (ppm)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142.08
140.34
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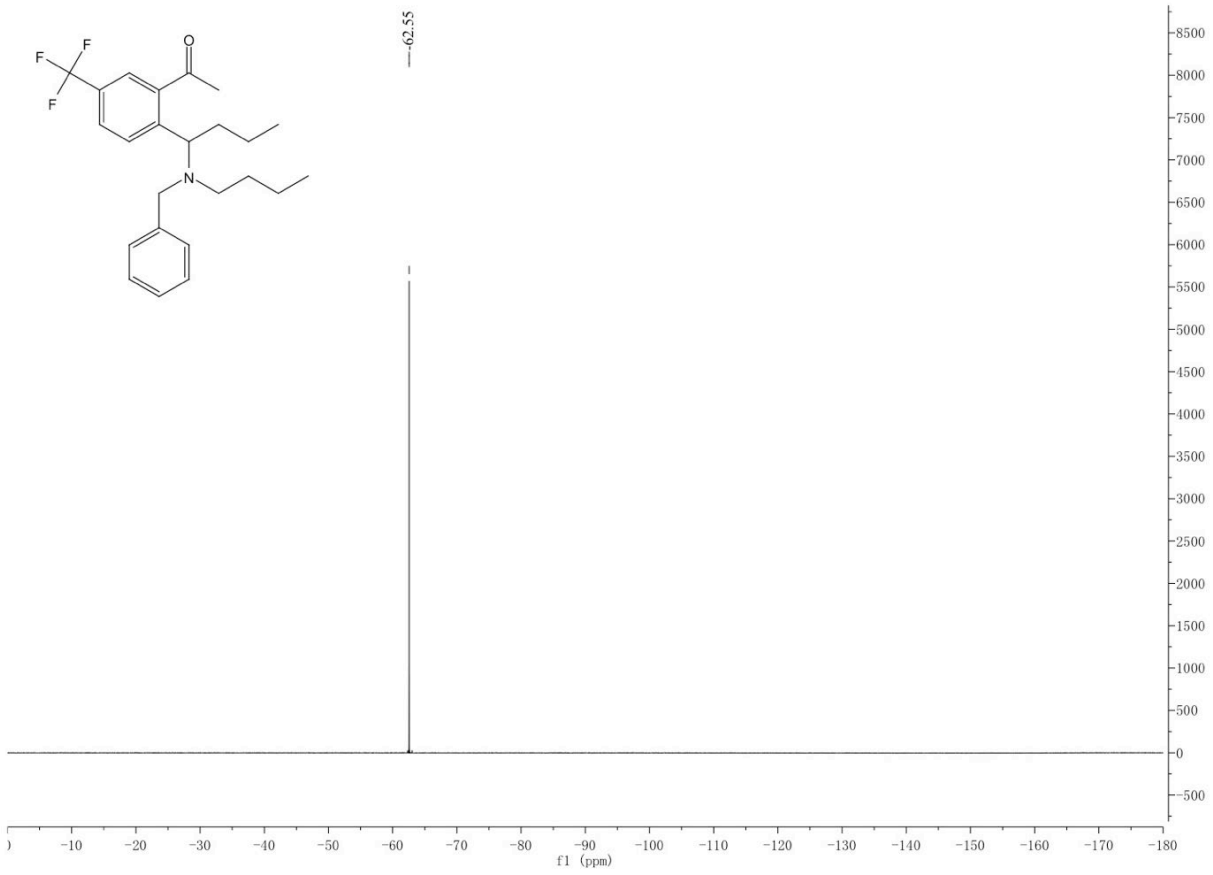
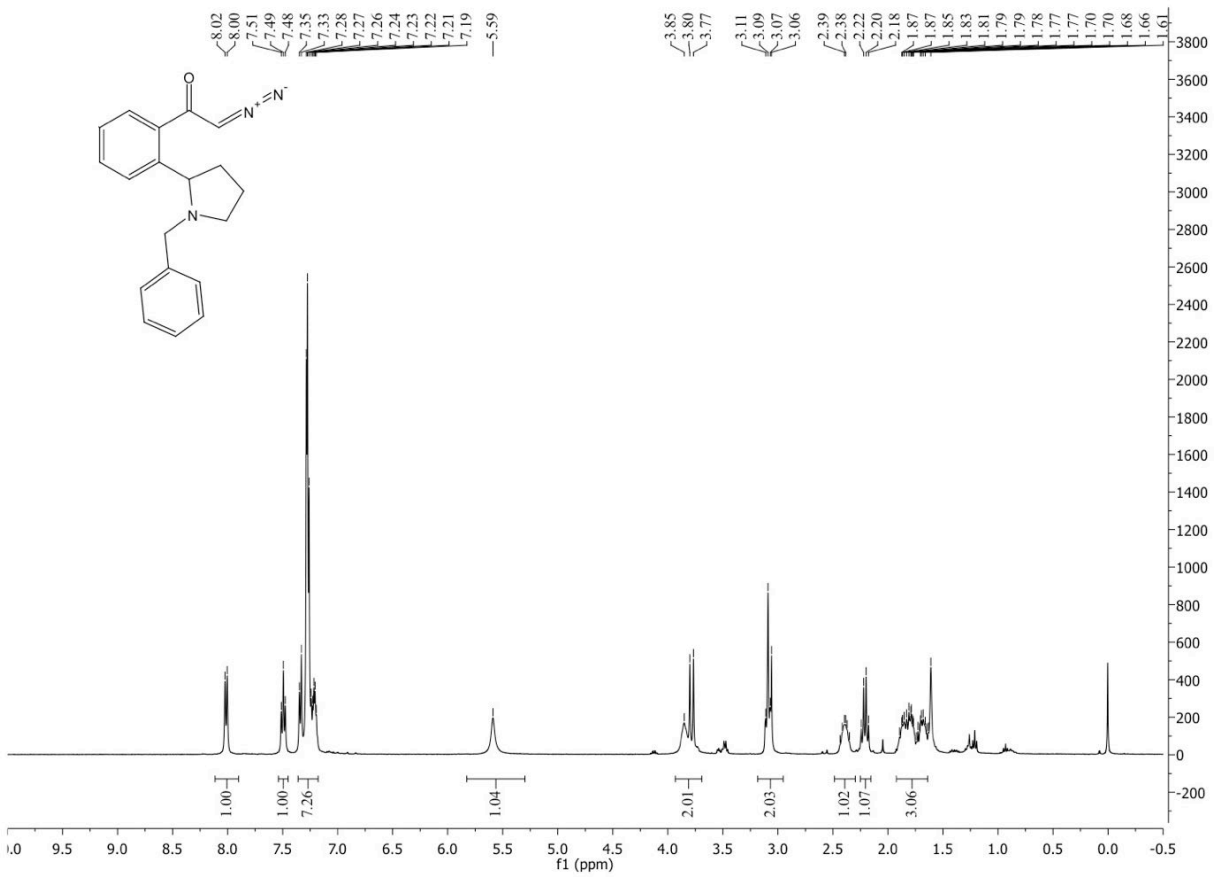
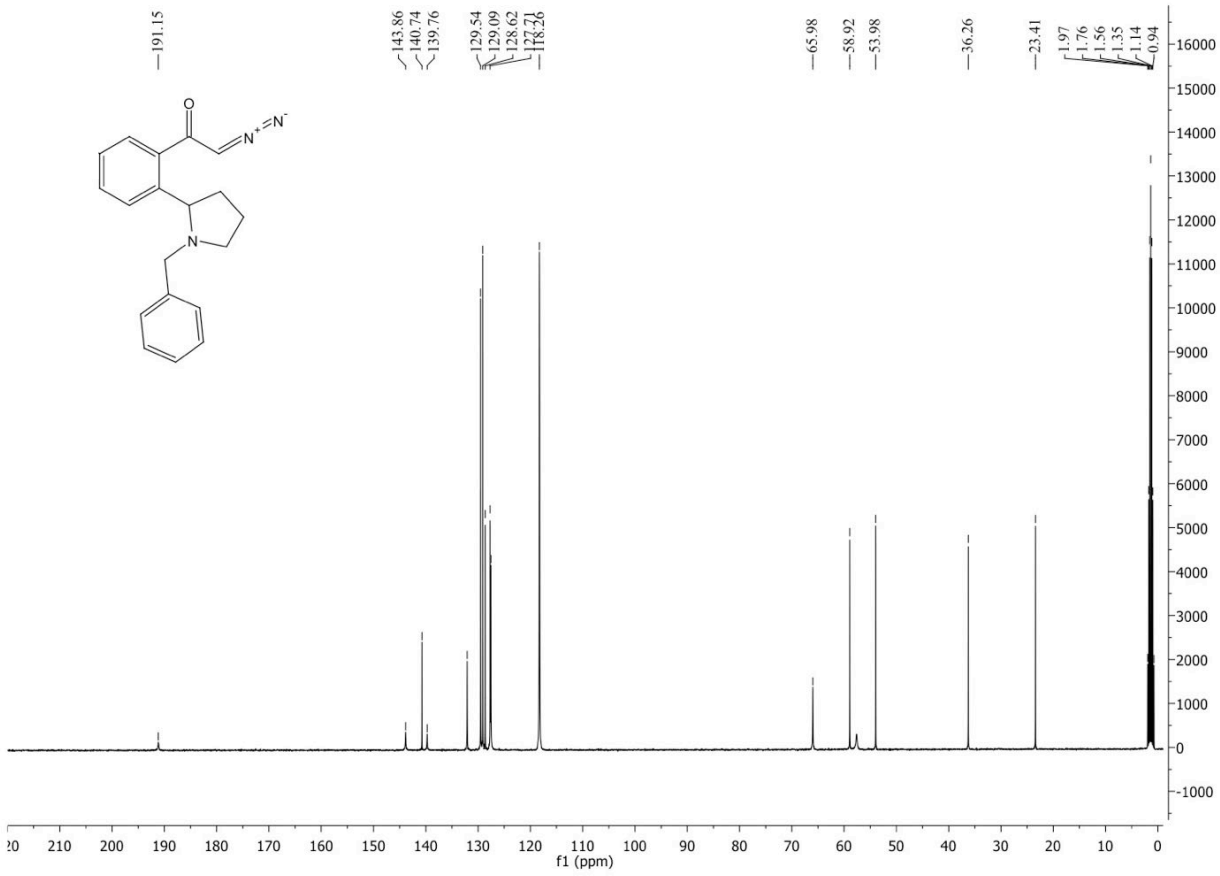
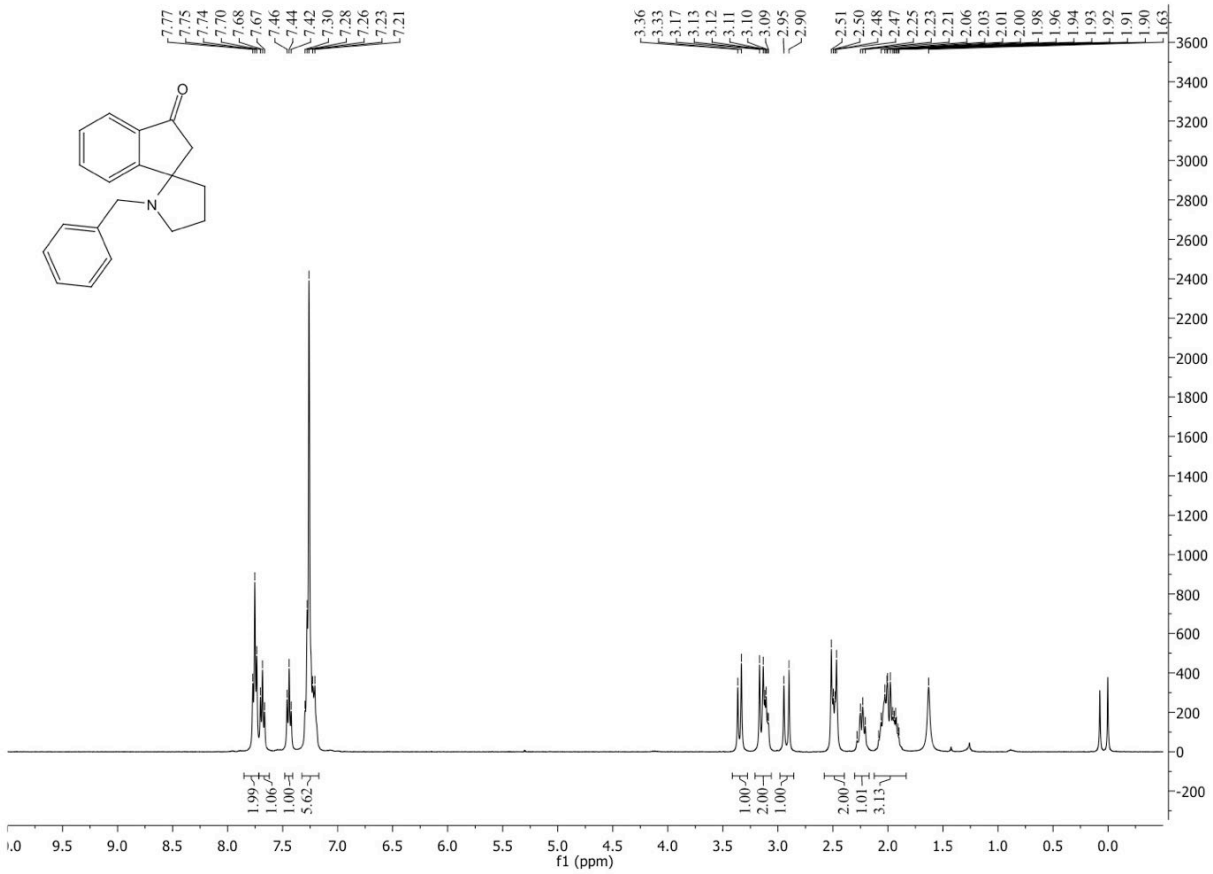
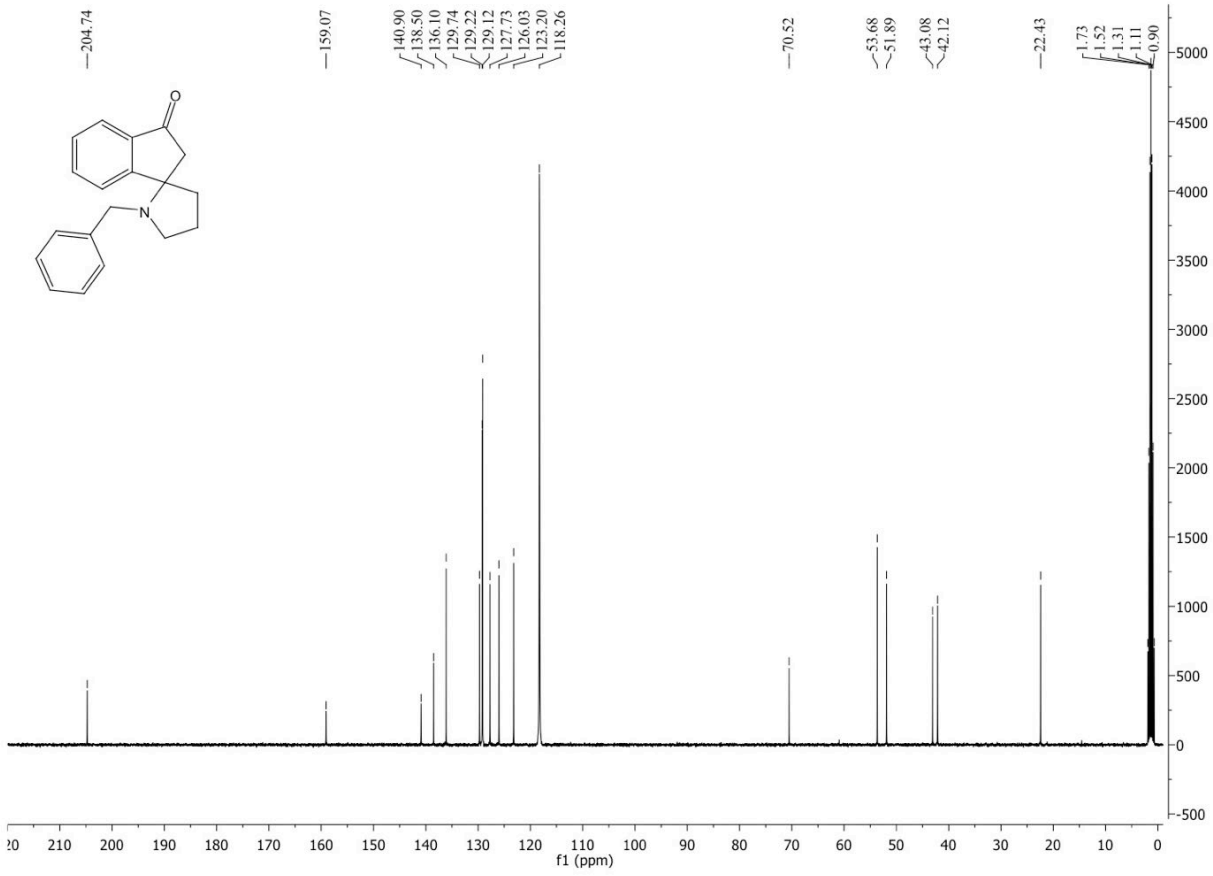
128.77
128.54
128.44
128.41
128.05
126.68
126.49
126.45
126.42
126.38
125.14
123.63
123.59
123.56
123.52
122.44
77.32
77.00
76.68
59.12
54.69
50.03
32.82
30.56
28.70
20.50
19.78
14.27
13.92
129.09
128.81
128.77
128.54
128.44
128.41
128.05
127.85
126.68
126.49
126.45
126.42
126.38
125.14
123.63
123.59
123.56
123.52
122.44
119.74
F
F
F
O
N
f1 (ppm)
f1 (ppm)


F
F
F
O
N
-62.55
8500
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1 (ppm)


8.02
8.00
7.51
7.49
7.48
7.35
7.33
7.28
7.27
7.26
7.24
7.23
7.22
7.21
7.19
5.59
3.85
3.80
3.77
3.11
3.09
3.07
3.06
2.39
2.38
2.22
2.20
2.18
1.87
1.87
1.85
1.83
1.81
1.79
1.79
1.78
1.77
1.77
1.70
1.70
1.68
1.66
1.61
1.00
1.00
7.26
1.04
2.01
2.03
1.02
1.07
3.06
f1 (ppm)


191.15
143.86
140.74
139.76
129.54
129.09
128.62
127.71
118.26
65.98
58.92
53.98
36.26
23.41
1.97
1.76
1.56
1.35
1.14
0.94
f1 (ppm)


7.77
7.75
7.74
7.70
7.68
7.67
7.46
7.44
7.42
7.30
7.28
7.26
7.23
7.21
3.36
3.33
3.17
3.13
3.12
3.11
3.10
3.09
2.95
2.90
2.51
2.50
2.48
2.47
2.25
2.23
2.21
2.06
2.03
2.01
2.00
1.98
1.96
1.94
1.93
1.92
1.91
1.90
1.63
O
N
1.99
1.06
1.00
5.62
1.00
2.00
1.00
2.00
1.01
3.13
f1 (ppm)


204.74
159.07
140.90
138.50
136.10
129.74
129.22
129.12
127.73
126.03
123.20
118.26
70.52
53.68
51.89
43.08
42.12
22.43
1.73
1.52
1.31
1.11
0.90
O
N
f1 (ppm)