Supporting Information

Organocatalytic Decarboxylative Alkylation of N-Hydroxy-phthalimide Esters Enabled by Pyridine-Boryl Radicals

Liuzhou Gao,[a,‡] Guoqiang Wang,[a,‡] Jia Cao,[a] Dandan Yuan,[a] Xu Cheng,[b] Xuewen Guo,[c] and Shuhua Li[a,*]

[a]*Key Laboratory of Mesoscopic Chemistry of Ministry of Education, Institute of Theoretical and Computational Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China.*

[b]*Institute of Chemistry and Biomedical Sciences, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, P. R. China.*

[c]*Center of Modern Analysis, Nanjing University, Nanjing, 210093, P. R. China.*

[‡]*These authors contributed equally to this work.*

[*]Email: shuhua@nju.edu.cn

Table of Contents

Computational Investigations

Computational Methods: All DFT calculations were carried out with Gaussian 09 package.[1]. Geometry optimizations and vibrational frequencies of all the stationary points were calculated by using the M06-2X[2]/6-31G(d,p) method. A "broken-symmetry" guess was used for calculations on open-shell systems. Each of the species was identified to be a minimum (number of imaginary frequencies, NIMAG=0) or a transition state (NIMAG=1). To confirm that each transition state connects the desired reactants and products along the reaction path, we performed intrinsic reaction coordinate (IRC)[3] calculations at the M06-2X/6-31G (d, p) level of theory. In order to obtain reliable energies, single point energies (Esol) are computed at the M06-2X/cc-PVTZ level. The solvent effect was treated with the polarizable continuum model (PCM)[4] with benzene as the solvent. The calculated gas-phase Gibbs free energies refer to 298.15 K and 1 atm. The 3D structures were generated with CLY view.[5]

Formation of the pyridine-boryl radical using 4-carboethoxypyridine and B_2pin_2

As shown in Figure S1, the formation of the 4-carboethoxypyridine-boryl radical (**A**) proceed through a [3,3]-sigmatropic rearrangement/homolytic C-C cleavage pathway. The rate-determining step of this reaction is [3,3]-sigmatropic rearrangement (the cleavage of B-B bond and the formation of C-C bond). DFT calculations suggest that 4-carboethoxypyridine has a comparable barrier for [3,3]-sigmatropic rearrangement (24.6 kcal/mol) as 4-cyanopyridine (24.4 kcal/mol) previously used for the generation of pyridine-boryl radical.[6]

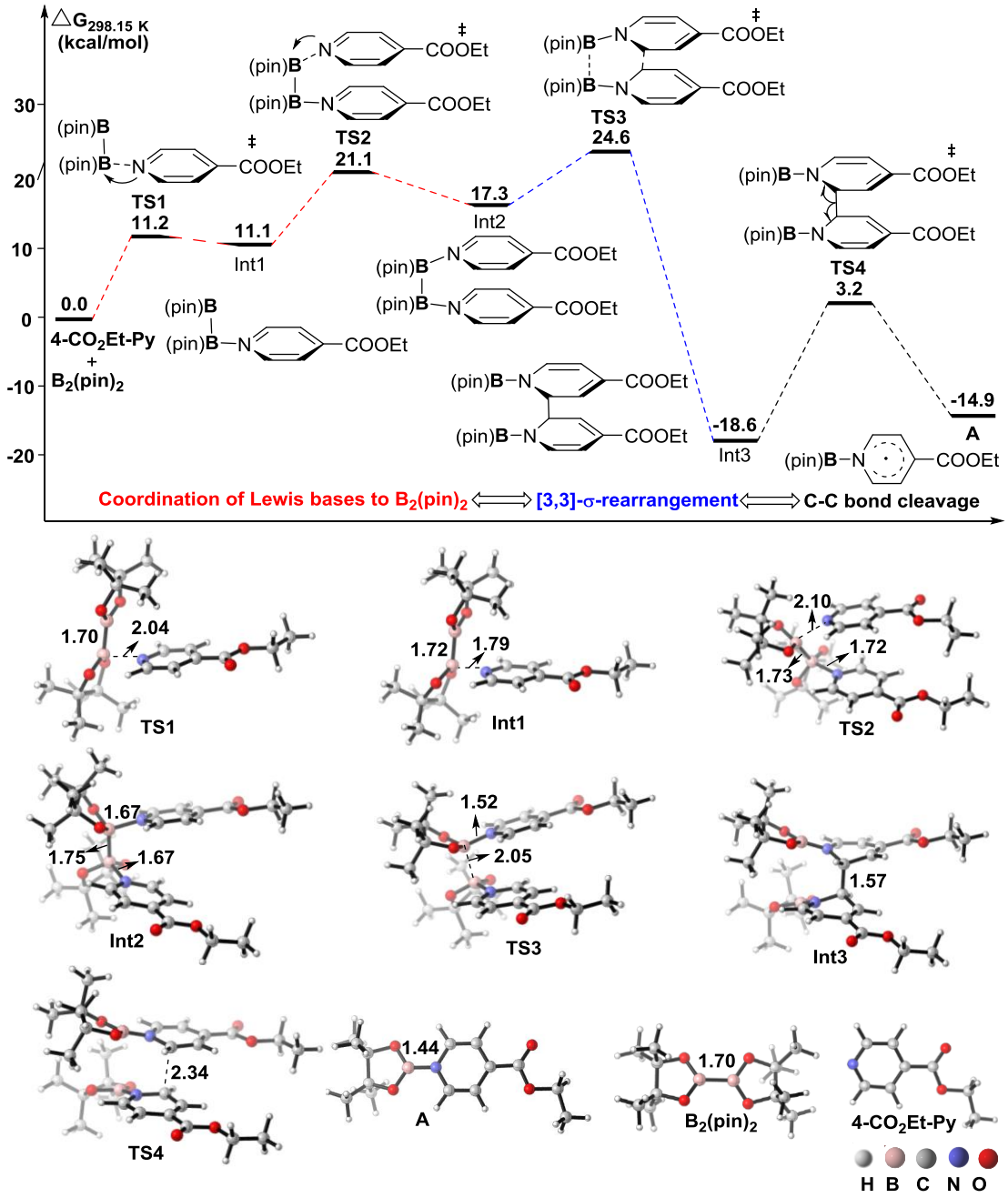


Figure S1. Gibbs energy profile for the generation of pyridine-boryl radical using 4-carbethoxypyridine and $B_2(pin)_2$ in the solvent (benzene). Interatomic distances are in Å.

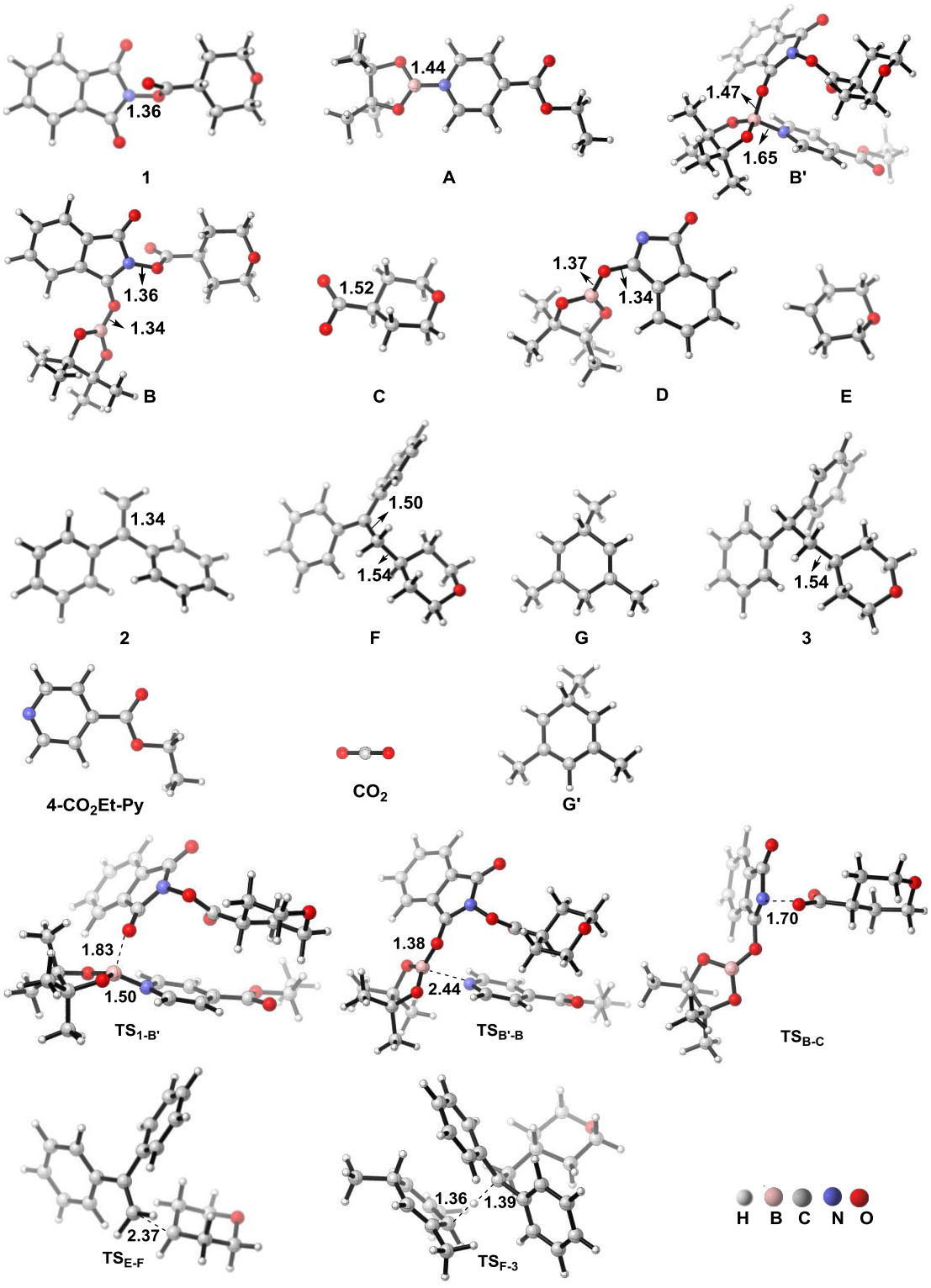


Figure S2. Optimized structures involved in 4-carboethoxypyridine-boryl radical (**A**) promoted the decarboxylative Alkylation of N-hydroxyphthalimide Esters (**1**) using 1,1-diphenylethylene (**2**). Interatomic distances are in Å.

The results of single electron transfer (SET) process

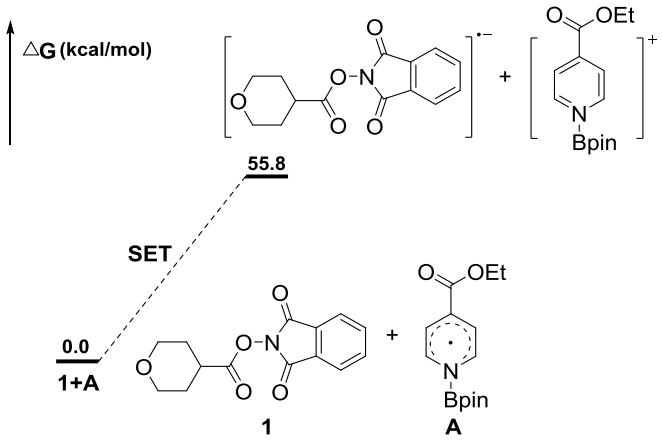


Figure S3 A possible SET process between pyridine-boryl radical (**A**) and NHPI ester **1**

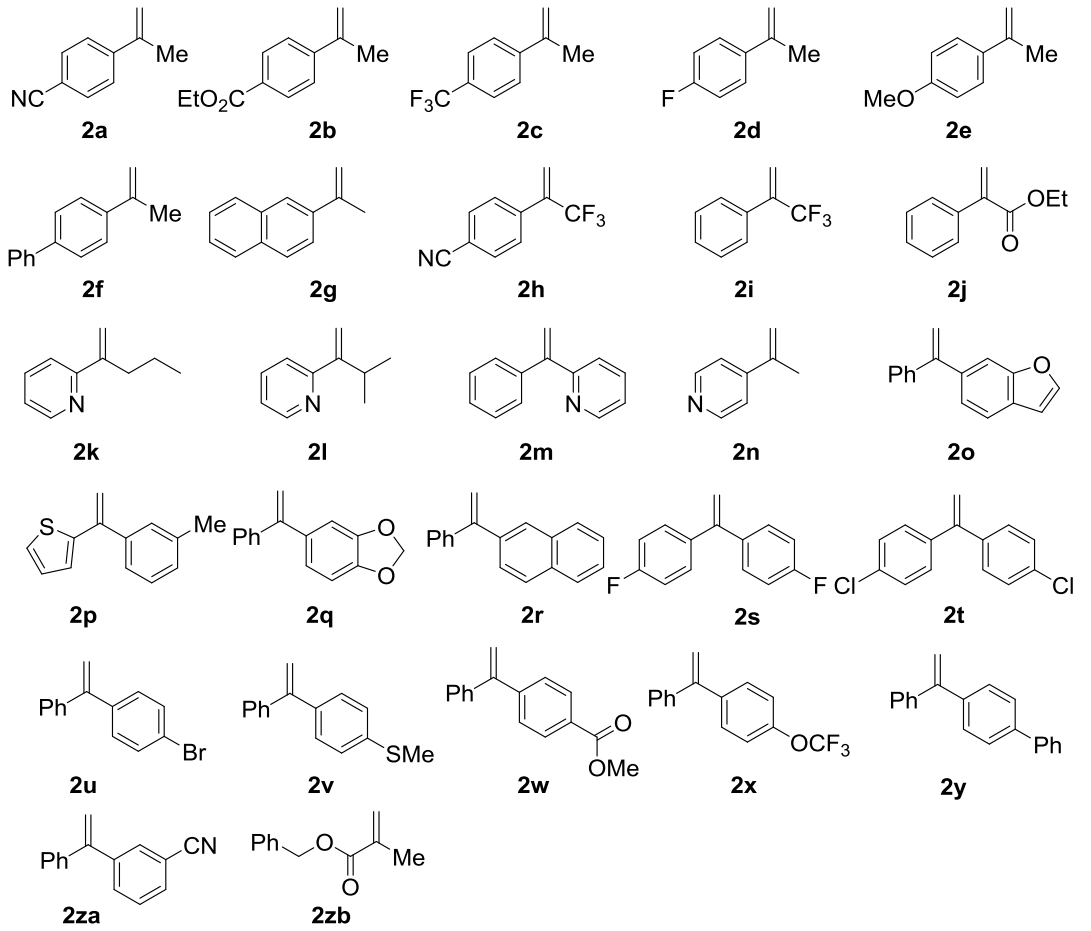
Our calculations show that a single electron transfer (SET) process from the pyridine-boryl radical (**A**) to NHPI ester **1** is not thermodynamically favorable, as shown in Figure S3.

Experimental Studies on Substrate Scope

General information

Unless otherwise noted, all reactions were performed under argon atmosphere. Dry acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2), methyl tert-butyl ether (MTBE), ethyl acetate (EA) and benzotrifluoride (CF_3-Ph) were purchased from Acros and used as received. All NMR spectra were recorded on a Bruker AVANCE Ⅲ–400 spectrometer at room temperature with $CDCl_3$ as the solvent and TMS as the internal standard. Chemical shifts (δ) were reported in ppm with respect to the residue solvent peak. Coupling constant (*J*) were reported in Hert (Hz), abbreviations for signal couplings are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using neat thin film technique. The electron paramagnetic resonance (EPR) spectra were obtained using a Bruker EMX-10/2 EPR spectrometer at 298.15 K. High-resolution mass spectra (HRMS) were recorded on Thermo Quest Finnigan LCQDECA system equipped with electrospray ionization (ESI), or Atmospheric Pressure Chemical Ionization (APCI).

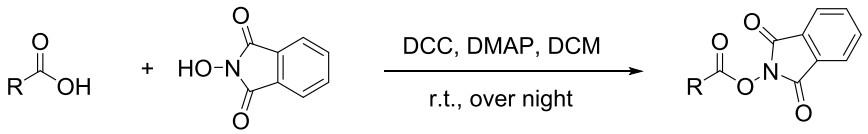
Preparation of Olefins Substrates:



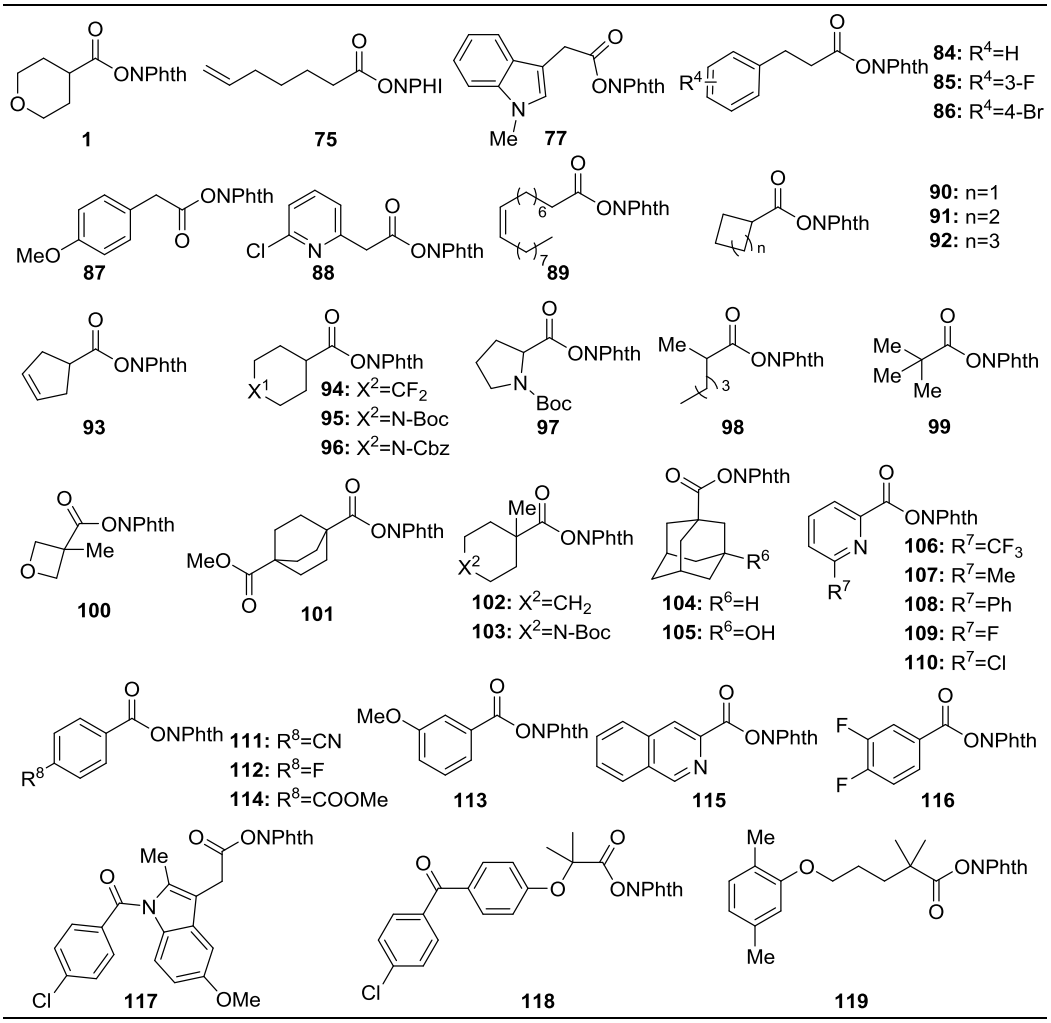
Above alkenes **2a**[7], **2b** and **2w**[8]**, 2f** and **2g**[9]**, 2h**[10], **2k, 2l and 2n**[11], **2s-2u**[12], **2m**[13], **2o**[14] **2p-2r and 2v**[15], **2x**, **2za**[16], **2y**[17] were synthesized according to the reported procedure. All synthesized alkenes matched known ^{1}H and ^{13}C NMR spectra. Unless otherwise noted, all other materials obtained from commercial suppliers were used without further purification.

Preparation of starting materials

General procedures for synthesis of N-hydroxyphthalimide (NHPI) esters

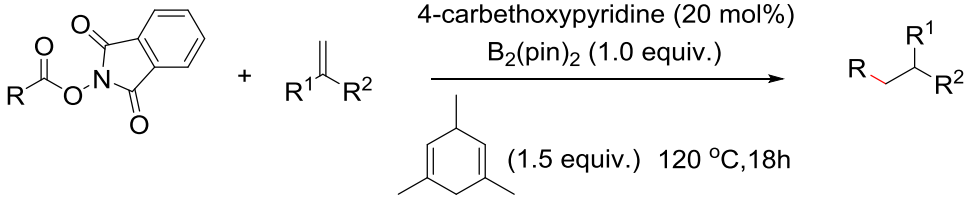


General Procedure A: In a 100 mL round-bottomed flask, the carboxylic acid (1.0 eq.), *N*-Hydroxyphthalimide (1.0 eq.), *N,N´*-dicyclohexylcarbodiimide (1.0 eq.) and DMAP (0.1 eq.) were combined in dry dichloromethane (0.2 M) and the reaction mixture was allowed to stir at room temperature overnight. Then, the white precipitate was filtered off, the solution was concentrated by evaporation of the solvent, followed by flash column chromatography on silica gel to afford the desired N-hydroxyphthalimide (NHPI) esters.



NHPI ester **1**, **80**, **86**, **89**, **94**, **95** and **117**[18], **79**, **84**, **87**, **97-100** and **105-110**[19], **90-92**, **96** and **101-104**[20], **93**[21], **111-114**[22], **119**[23] were prepared according to the reported procedure. All synthesized substrates matched known ^{1}H and ^{13}C NMR spectra. All other starting materials were synthesized according to Method A.

General procedure for the Organocatalytic Decarboxylative Alkylation of N-Hydroxyphthalimide Esters using alkenes



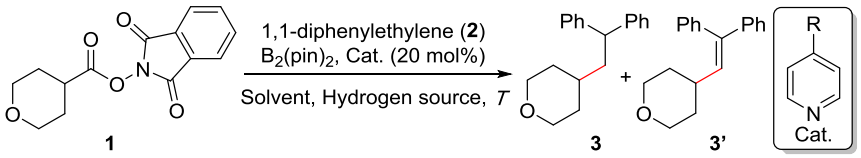
General Procedure B: In an oven-dried 10 ml Schlenk flask equipped with a magnetic stir bar, N-(acyloxy)phthalimide (0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (0.2 mmol, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (0.3 mmol, 1.5 equiv.), olefin (0.4 mmol, 2.0 equiv.), 4-carbethoxypyridine (0.04 mmol, 20 mol%) and CF_3-Ph (1 mL) was added in turn. Then, the reaction mixture was heated at 120 ℃ for 18 h. After cooling to room temperature, the mixture was concentrated under vacuum and the residue was purified by preparative TLC on silca gel to afford the corresponding product.

Optimization studies of the reaction conditions

To explore the possibility of the proposed reaction, we began our study by evaluating the reaction of N-(acyloxy)phthalimides **1** and 1,1-diphenylethylene **2** as the substrates (see Table S1). When 1 was treated with 20 mol% 4-cyanopyrdine (0.02 equiv.), 1,1-diphenylethylene (2.0 equiv.), B_2pin_2 (1.0 equiv.) and 1,3,5-trimethyl-1,4-cyclohexadiene (1.0 equiv.) in $PhCF_3$, the desired reductive decarboxylative adduct **3** was formed in 63% yield (entry 1), together with a small amount of byproduct (**3'**, 14%) generated from the disproportionation of the diaryl radical intermediate (**F**). 4-Carboethoxypyridine was found to be the most suitable catalyst to afford the decarboxylative adduct (entry 5). Pyridine or other substituted pyridines exhibit less reactivity toward this trans-formation (entry 2-4). $PhCF_3$ was found to be the optimal solvent for this reaction (entry 5-8). With 4-carboethoxypyridine as the catalyst and $PhCF_3$ as the solvent, elevating the temperature to 120 °C could improve the selectivity and 3 was isolated in 76% yield (entry 9, 10). In the absence of a hydrogen source, the ratio of **3**/**3'** was 50%:31% (entry 11). When Et_3SiH or Hantzsch ester was adopted as the hydrogen source, the yield of **3** also diminished (entry 12, 13). Thus, the use of

1,3,5-trimethyl-1,4-cyclohexadiene is crucial to suppress the disproportionation of the diaryl radical intermediate (**F**).

Table S1 Optimization of the reaction conditions[a]



entry	R	H-donor	Solvent	Ratio (**3**/**3'**)[b]
1	-CN	TMe-1,4-CHD	$PhCF_3$	63%:14%
2	-H	TMe-1,4-CHD	$PhCF_3$	N. R.
3	$-CF_3$	TMe-1,4-CHD	$PhCF_3$	trace
4	-Ph	TMe-1,4-CHD	$PhCF_3$	trace
5	$-CO_2Et$	TMe-1,4-CHD	$PhCF_3$	70%:20%
6	$-CO_2Et$	TMe-1,4-CHD	MTBE	61%:23%
7	$-CO_2Et$	TMe-1,4-CHD	CH_3CN	40%:13%
8	$-CO_2Et$	TMe-1,4-CHD	EA	67%:22%
9	$-CO_2Et$	TMe-1,4-CHD	$PhCF_3$	57%:16%[c]
10	**$-CO_2Et$**	**TMe-1,4-CHD**	**$PhCF_3$**	**81%:9% (76%)[d]**
11	$-CO_2Et$	-	$PhCF_3$	50%:31%
12	$-CO_2Et$	Et_3SiH	$PhCF_3$	52%:32%
13	$-CO_2Et$	Hantzsch Ester	$PhCF_3$	58%:16%

[a] Reaction conditions: 1 (0.2 mmol), 2 (0.4 mmol), $B_2(pin)_2$ (0.2 mmol), catalyst (0.04 mmol), H-donor (0.2 mmol) in solvent (1.0 ml), 18 h, 100 ℃, under Ar. TMe-1,4-CHD = 1,3,5-trimethyl-1,4-cyclo-hexadiene. [b] Yields were deter-mined by ^{1}H-NMR analysis of the crude mixture using CH_2Br_2 as the internal standard. [c] Performed at 80 ℃, 0.3 mmol H-donor was used. [d] Isolated yield of **3** (at 120 ℃, 0.3 mmol H-donor was used).

Experimental Studies on the Reaction Mechanism

Electron Paramagnetic Resonance (EPR) Experiments

The EPR spectrum (for the Microwave frequency = 9.7754 GHz, g=2.0031) of the pyridine-boryl radical (**A**) were obtained (as shown in Figure S4) through the addition of 4-carbethoxypyridine (0.2 equiv.) to a 0.2 M solution of $B_2(pin)_2$ in MTBE (1 mL) (blue line). This result gives supportive evidence for the formation of 4-carbethoxypyridine-boryl radical, which is consistent with our DFT calculations.

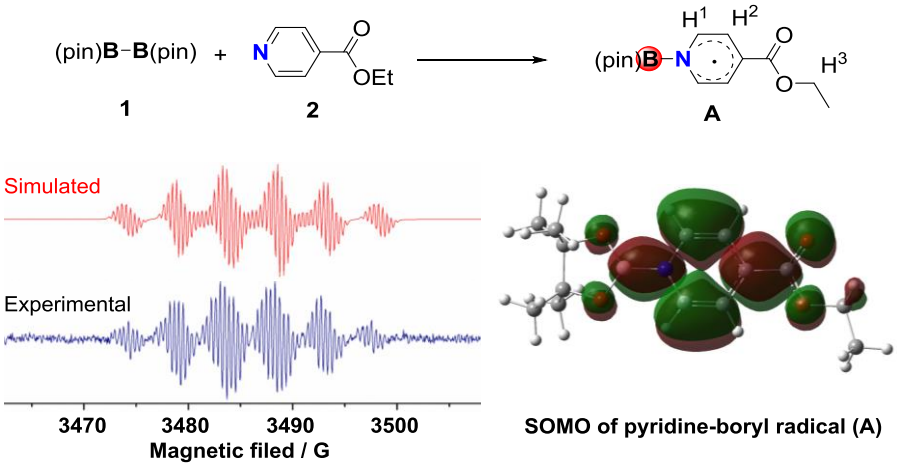


Figure S4. Left：Experimental (blue) and computer-simulated (red) EPR spectra of pyridine-boryl radical (**A**). Simulations were performed with the SimFonia package. Right: Optimized structure and SOMO (cutoff: 0.015, spin alpha) of pyridine-boryl radical (**A**) at the M06-2X/6-31G** level.

Table S2. The EPR parameters obtained from computer simulations of the experimental spectra.

simulations	Gauss
B^{11}	4.87
B^{10}	0.39
H^1	0.79
H^2	0.39
N	4.83
H^3	0.45

Temperature	298 K
G value	2.0031
Solvent	MTBE
MWFQ	9.7754GHz

The control experiments

NHPI ester **75** was adopted as a radical clock. In the presence of 4-carbethoxypyridine and $B_2(pin)_2$ at 120 °C, the product **76** is generated from the 5-exo radical cyclization in 65% yield (as shown in Figure S5). This result supports the involvement of the carbon radical intermediate in the proposed pathway.

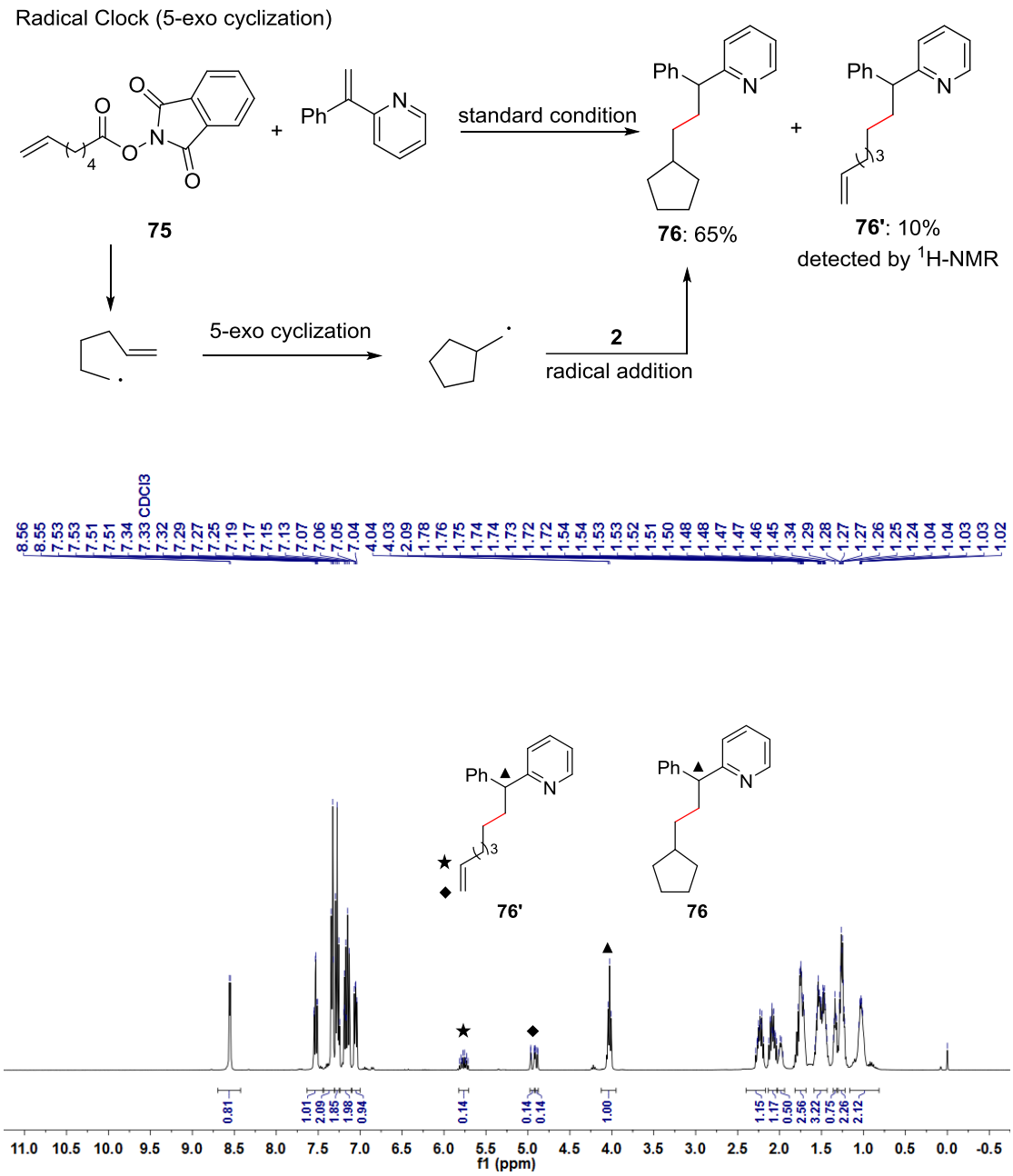
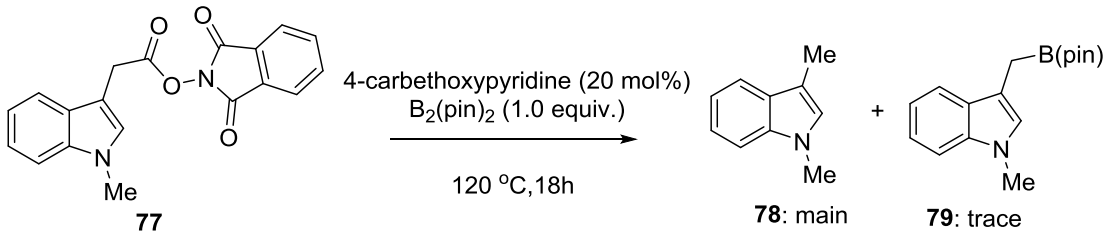


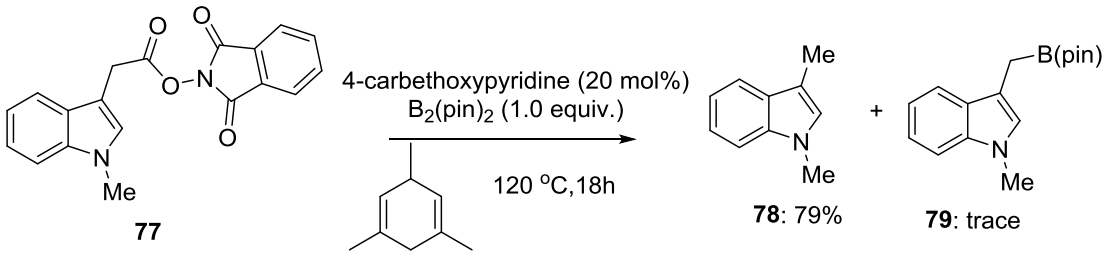
Figure S5. ^{1}H NMR analysis of a crude mixture of two products.

When the substrate **77** was subjected to the standard condition in the absence of alkenes and H-donor, a trace amount of C-B coupling product **79** was detected by GC-MS analysis (Figure S6). When the 1,3,5-trimethyl-1,4-cyclohexadiene (H-donor) was added, the decaboxylative reduction product **78** was isolated in 79% yield. In contrast, when the 1,1-diphenylethylene and H-donor was added, the decarboxylative radical could be trapped and the desired adduct (**83**) was obtained in 76% yield. The formation of phthalimide-B(pin) **D** could be detected by crude HRMS analysis (Figure S7) of the reaction mixture of **77** and 1,1-diphenylethylene.

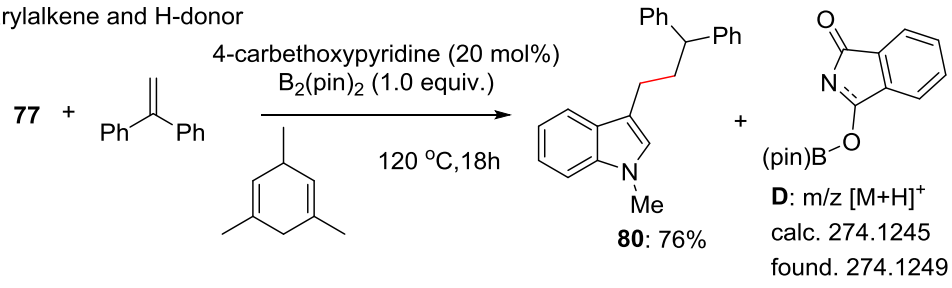
a. In the absence of diarylalkene and H-donor

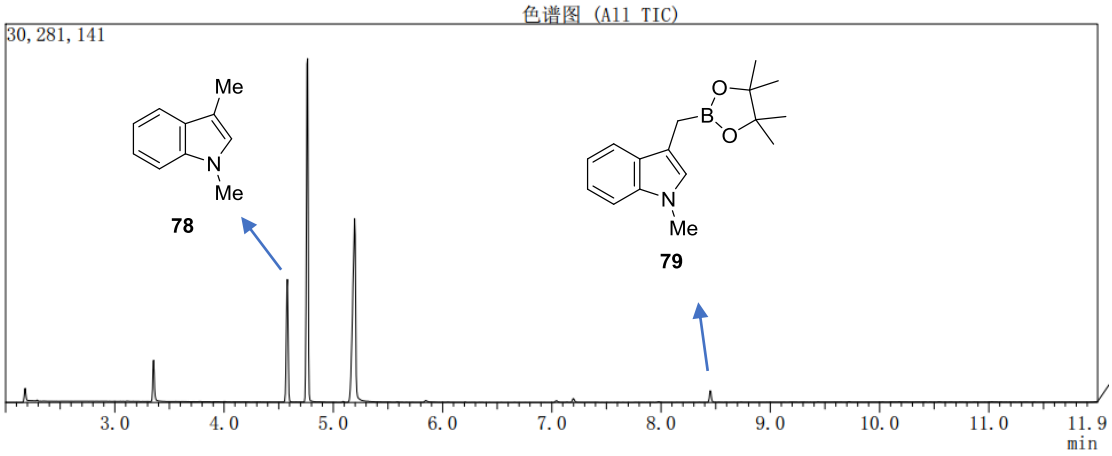


b. In the absence of diarylalkene

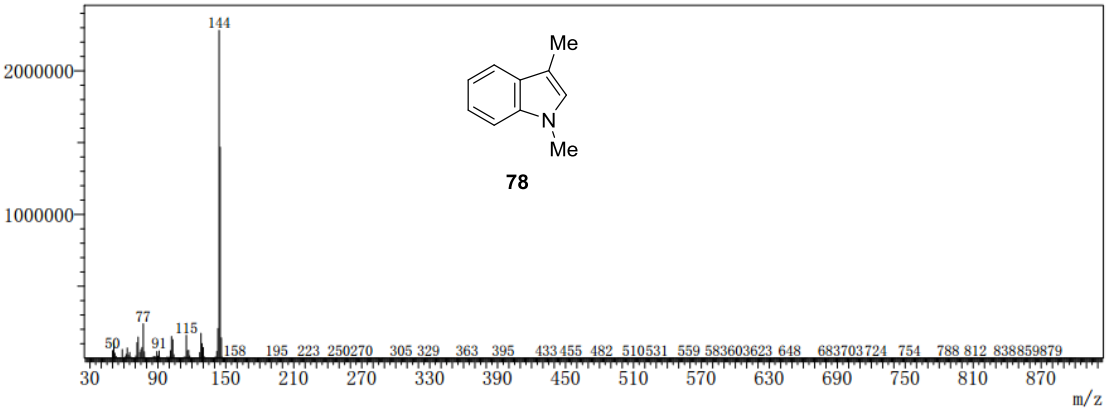


c. With diarylalkene and H-donor

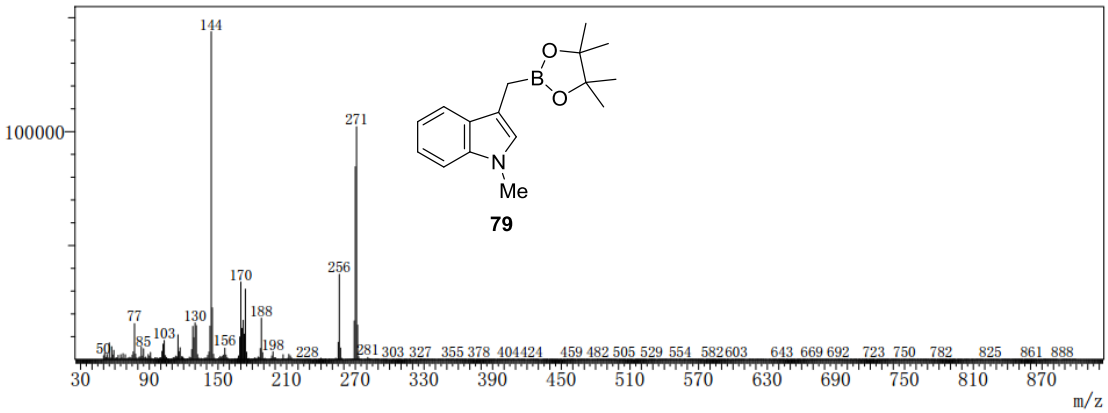




流路号:1　保留时间:4.585(扫描数:518)
质量峰:648
原始模式:平均 4.585-4.585(518-518)　基峰:144.10(2282118)
背景模式:无　组 1 - 事件 1　Scan



流路号:1　保留时间:8.455(扫描数:1292)
质量峰:722
原始模式:平均 8.455-8.455(1292-1292)　基峰:144.10(143873)
背景模式:无　组 1 - 事件 1　Scan



峰表 TIC

峰号	保留时间	I.Time	F.Time	峰面积	峰面积%	峰高	峰高%	积/高度	标记	名称
1	4.578	4.520	4.630	11354358	90.75	9807156	91.31	1.16	MI	
2	8.451	8.395	8.510	1156667	9.25	933143	8.69	1.24	MI	
				12511025	100.00	10740299	100.00			

Figure S6. GC-MS analysis of the crude reaction mixture of **77**, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

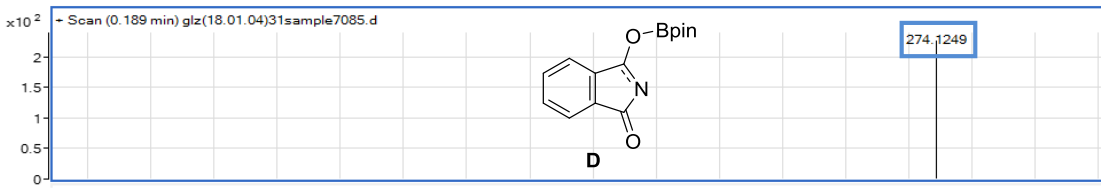
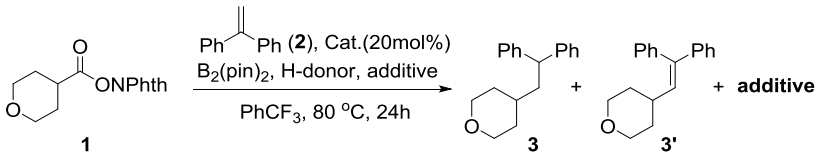


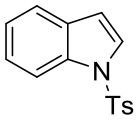
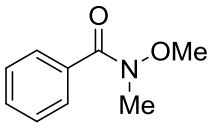
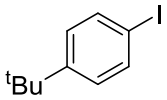
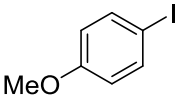
Figure S7. HRMS analysis of the crude reaction mixture of **77**, $B_2(pin)_2$, 1,1-diphenylethylene, 1,3,5-trimethyl-1,4-cyclohexadiene and 4-carbethoxypyridine in $PhCF_3$.

As we know, the reductive cleavage of sulfonamide,[24] N-oxy-substituted amide,[25] and aryl iodides[26] are classical organic redox reactions employing electron reductants. We conducted the decarboxylative alkylation of NHPI esters **1** and 1,1-diphenylethylene using these electron acceptors as additives (Table S3, substrates **81-83**). It was found that the present reaction system was compatible with these additives, the decarboxylative radical addition related product (3 and 3') could be formed as expected, leaving these electron acceptors untouched. These control experiments also revealed that this decarboxylative alkylation is likely to proceed *via* a pyridine-boryl radical association-triggered NHPI ester fragmentation pathway rather than a SET process.

Table S3. The influence of different additives in the reaction of **1** with 1,1-diphenylethylene[a]

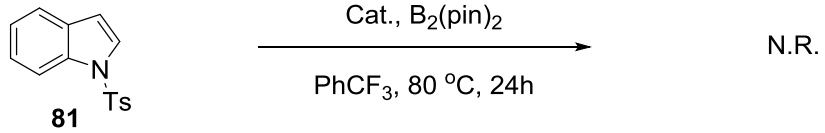


1 3 3'

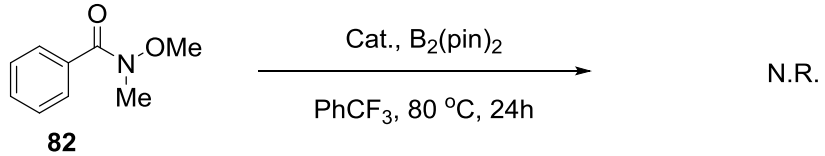
Entry	Additives	Yield of 3 & 3'	Additive remaining
1[b]	—	57%:16%	—
2		65%:10%	93%
3		61%:14%	91%
4		60%:12%	95%
5		56%:11%	92%

[a] Reaction conditions: **1** (0.2 mmol), 2 (0.4 mmol), addtives (0.2 mmol), $B_2(pin)_2$ (0.2 mmol), catalyst (0.04 mmol), H-donor (0.3 mmol) in $PhCF_3$ (1.0 ml), 24 h, 80 ℃, under Ar. Yields were deter-mined by ^{1}H-NMR analysis of the crude mixture using CH_2Br_2 as the internal standard. [b] Performed at 80 ℃, 18h.

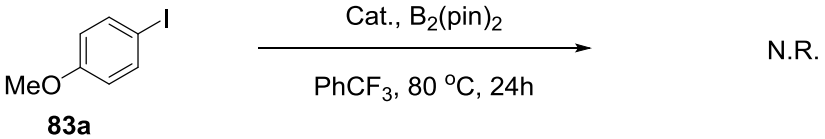
Control experiments



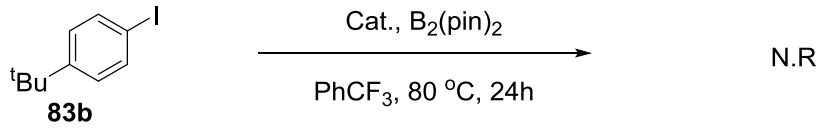
81



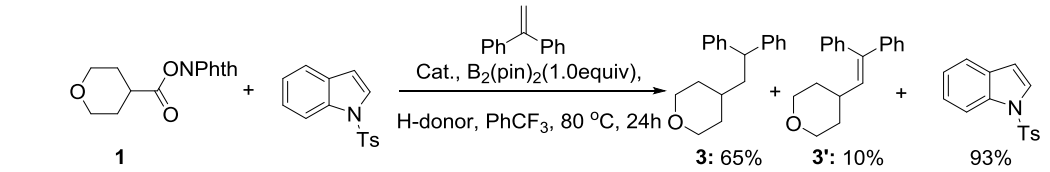
82



83a



83b



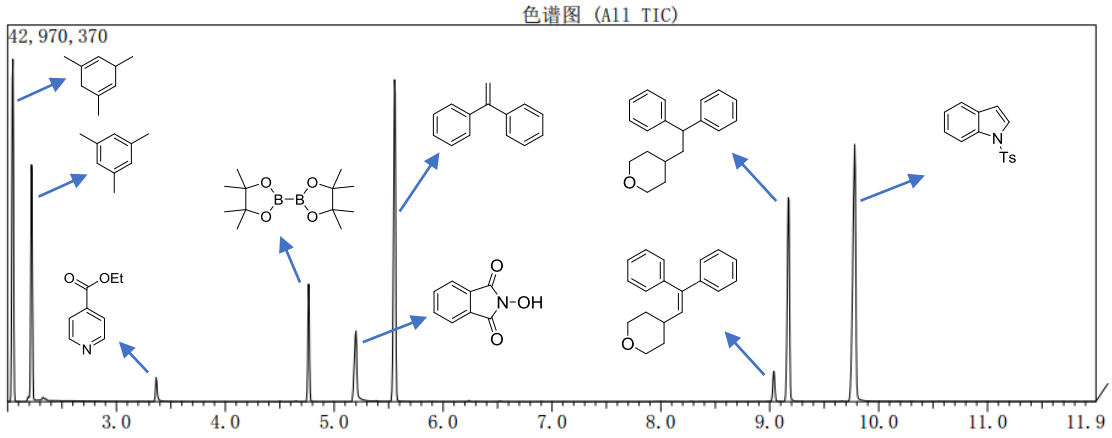
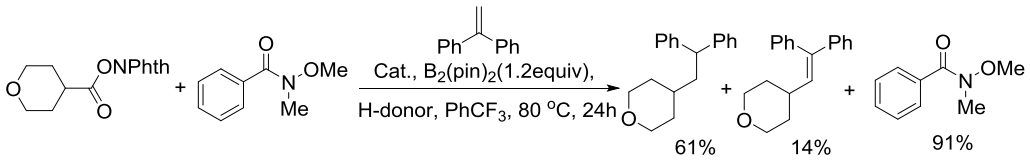


Figure S8. GC-MS analysis of the crude reaction mixture of NHPI ester **1**, **81**, 1,1-diphenylethylene, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.



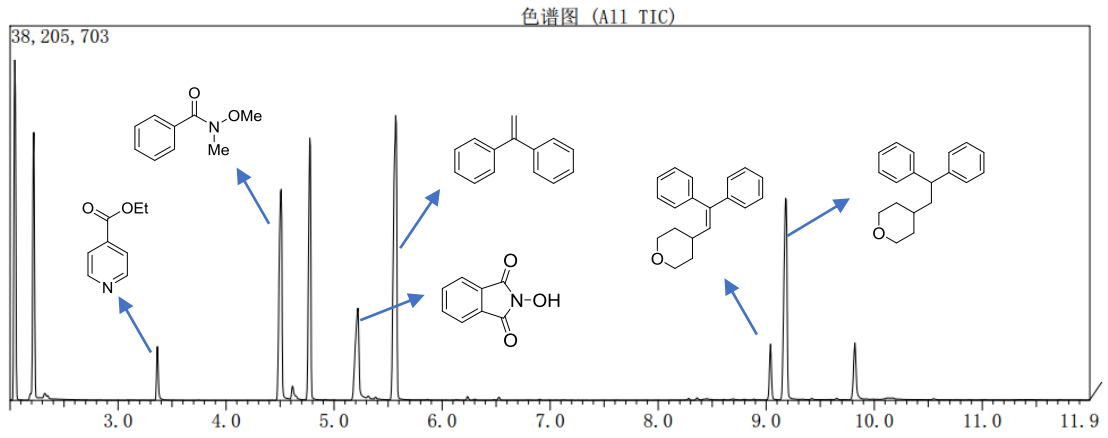


Figure S9. GC-MS analysis of the crude reaction mixture of NHPI ester **1**, **82**, 1,1-diphenylethylene, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

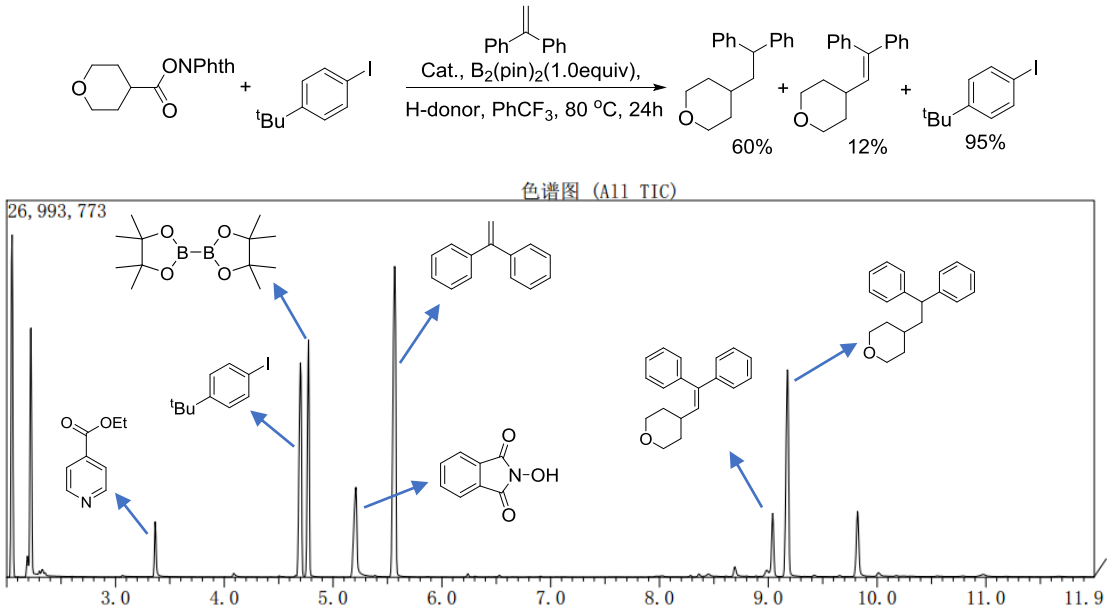


Figure S10. GC-MS analysis of the crude reaction mixture of NHPI ester **1**, **83a**, 1,1-diphenylethylene, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

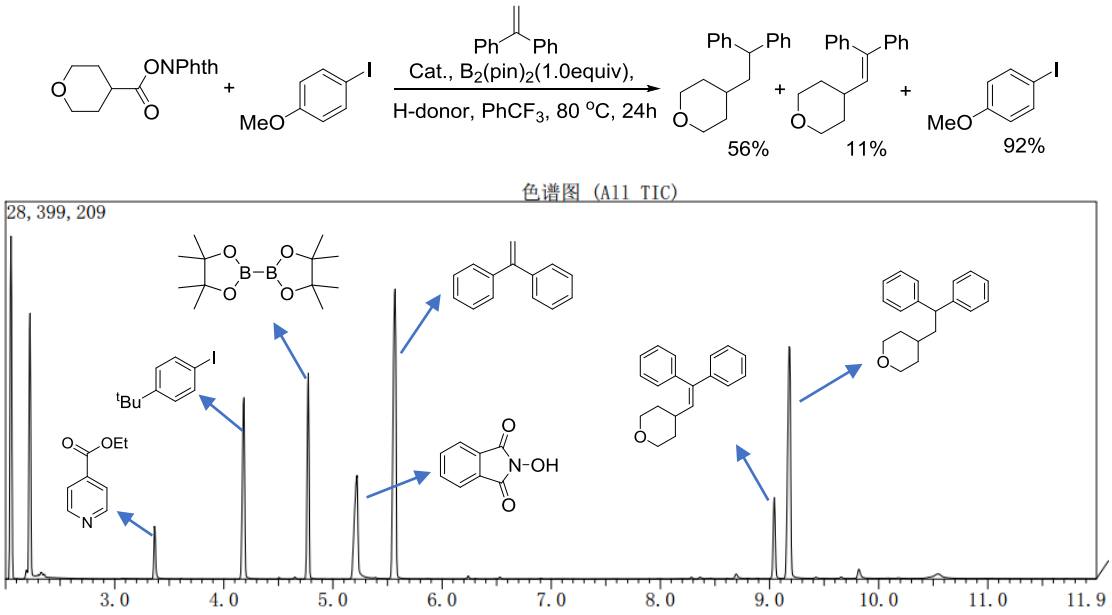


Figure S11. GC-MS analysis of the crude reaction mixture of NHPI ester **1**, **83b**, 1,1-diphenylethylene, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

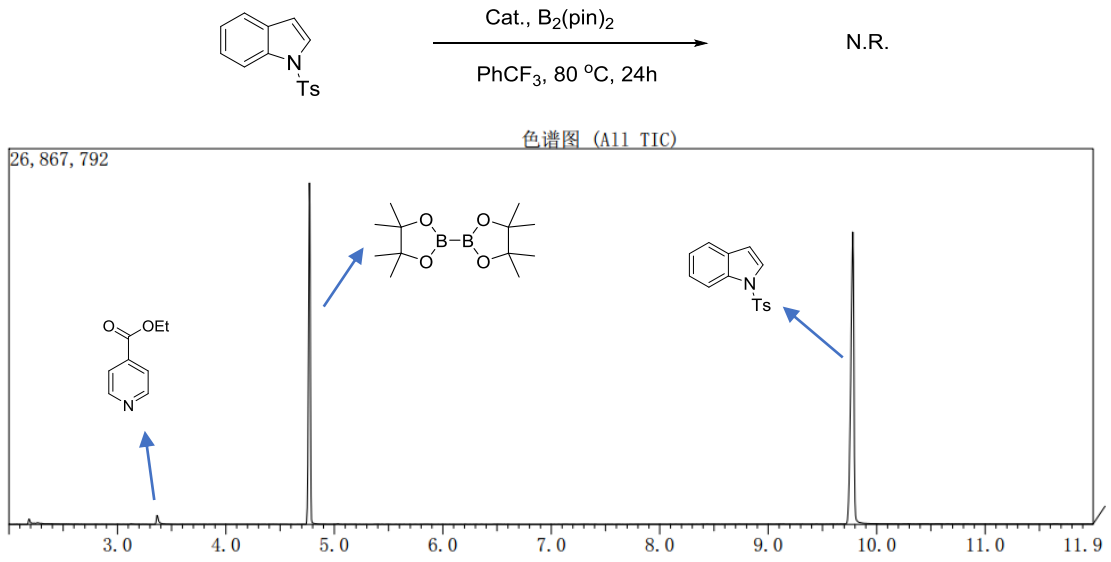


Figure S12. GC-MS analysis of the crude reaction mixture of **81**, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

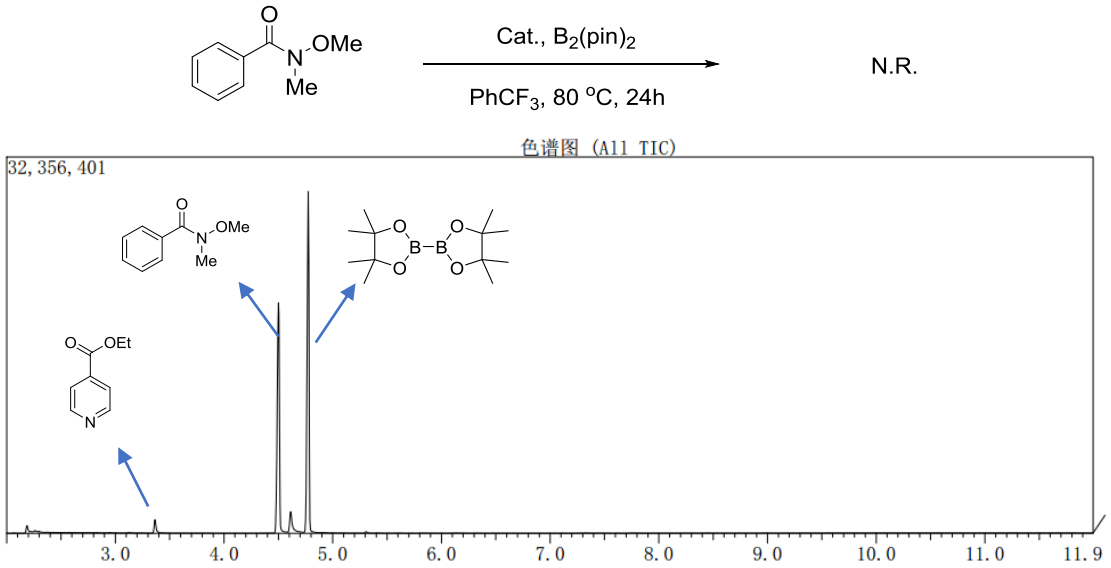


Figure S13. GC-MS analysis of the crude reaction mixture of **82**, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

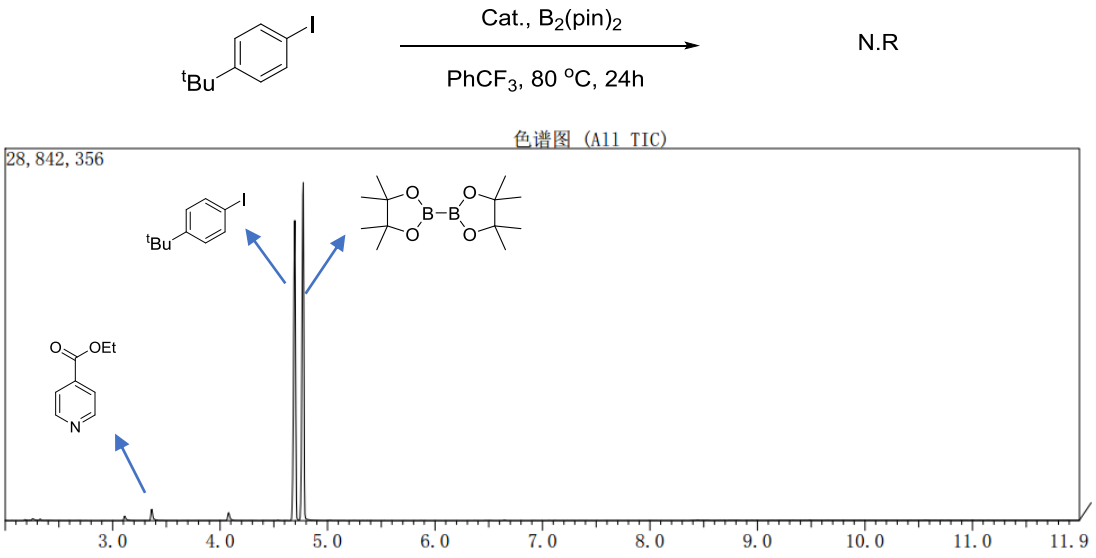


Figure S14. GC-MS analysis of the crude reaction mixture of **83a**, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

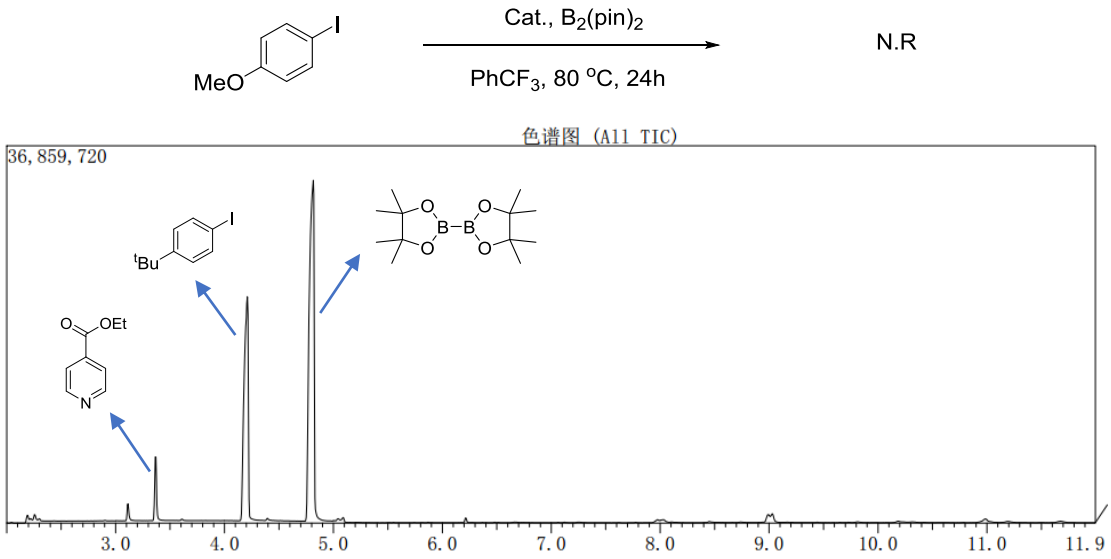
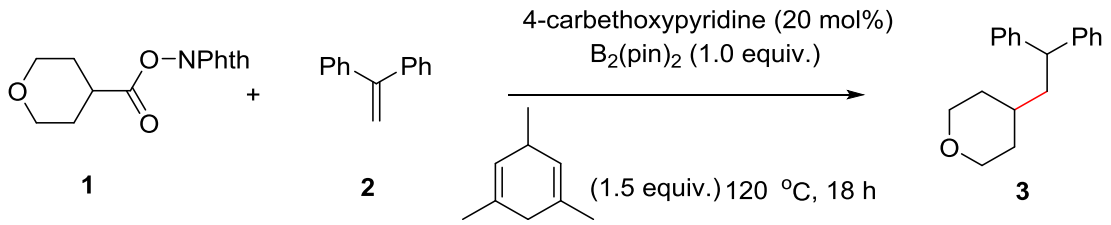


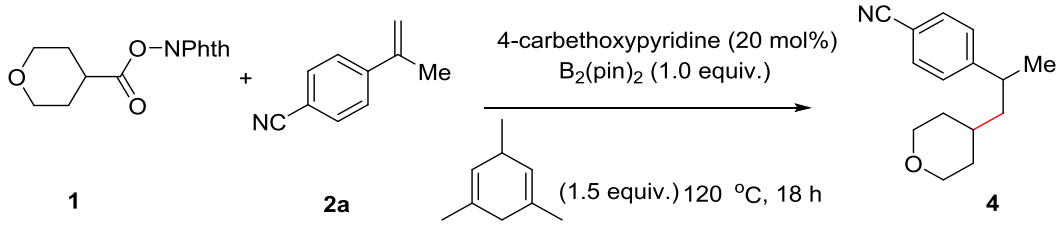
Figure S15. GC-MS analysis of the crude reaction mixture of **83b**, $B_2(pin)_2$ and 4-carbethoxypyridine in $PhCF_3$.

Spectroscopic Characterization of the Radical Addition Products



3: Prepared following *general procedure B* using **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **3** (40.5 mg, 76% yield).

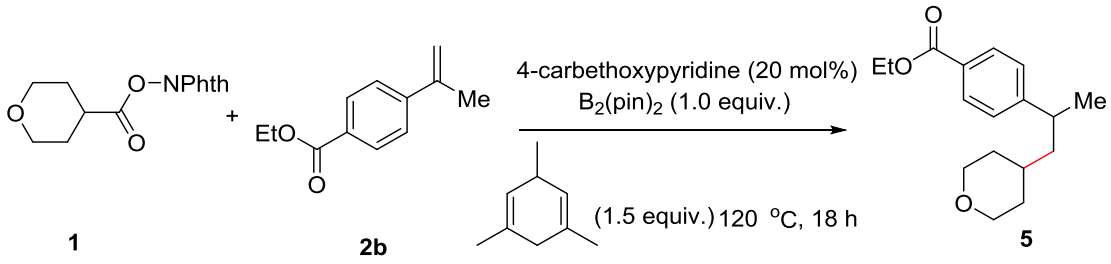
3: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.25 (m, 8H), 7.24-7.17 (m, 2H), 4.09 (t, *J* = 8.0 Hz, 1H), 3.97-3.91 (m, 2H), 3.32-3.26 (m, 2H), 2.04-2.01 (m, 2H), 1.67 (d, *J* = 11.9 Hz, 2H), 1.41-1.31 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 128.6, 127.9, 126.3, 68.0, 47.7, 43.1, 33.2, 32.5. **IR** (film): 2923, 2839, 2758, 1598, 1493, 1465, 1135, 1092 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{23}O$ $[M+H]^+$ 267.1743, found 267.1739.



4: Prepared following *general procedure B* using **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (57.3 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **4** (40.2 mg, 87% yield).

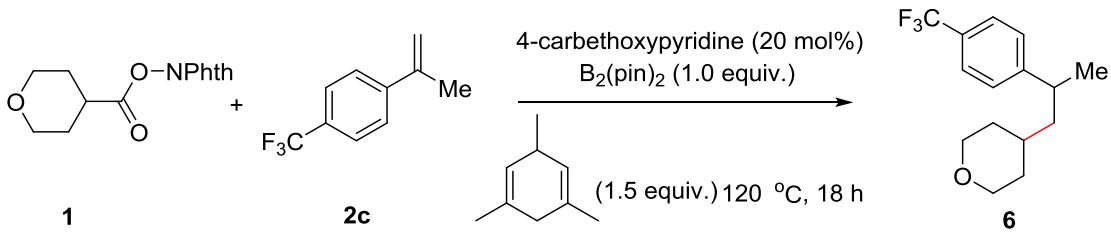
4: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 3.96-3.84 (m, 2H), 3.31-3.23 (m, 2H), 2.94-2.85 (m, 1H), 1.62-1.54 (m,

2H), 1.52-1.47 (m, 2H), 1.30-1.26 (m, 3H), 1.22 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 132.4, 127.8, 119.1, 109.9, 67.9, 45.2, 36.7, 33.3 and 33.0, 32.6, 22.6. **IR** (film): 2926, 2840, 2226, 1607, 1504, 1455, 1095, 1016 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_{19}NNaO$ $[M+Na]^+$ 252.1359, found 252.1352.



5: Prepared following *general procedure B* using **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2b** (76.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **5** (40.0 mg, 73% yield).

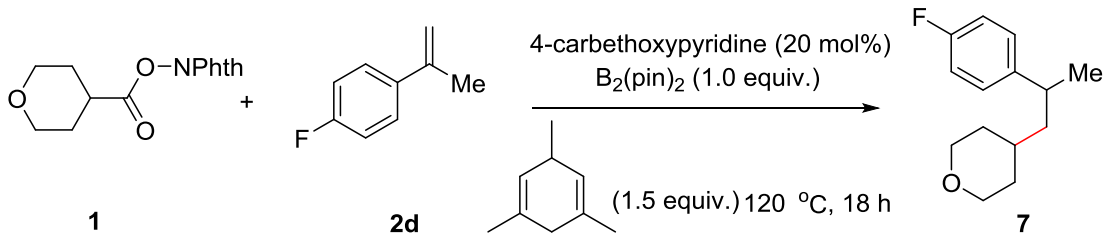
5: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H), 4.35 (q, *J* = 7.2 Hz, 2H), 4.02-3.79 (m, 2H), 3.28-3.21 (m, 2H), 3.00-2.75 (m, 1H), 1.64-1.55 (m, 2H), 1.50-1.42 (m, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.33-1.23 (m, 3H), 1.22 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 152.9, 129.9, 128.5, 127.0, 68.0, 60.9, 45.4, 36.6, 33.5 and 33.0, 32.6, 22.85, 14.47. **IR** (film): 2957, 2926, 2840, 1715, 1609, 1275, 1103, 1017 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{17}H_{25}O_3$ $[M+H]^+$ 277.1798, found 277.1792.



6: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2c** (74.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the

reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **6** (28.4 mg, 52% yield).

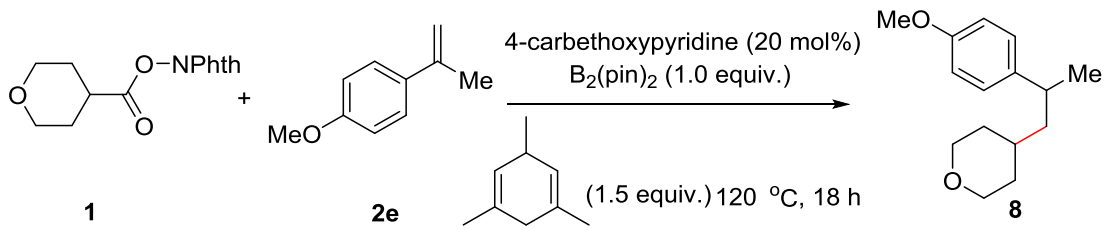
6: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.95-3.86 (m, 2H), 3.32-3.24 (m, 2H), 2.94-2.85 (m, 1H), 1.64-1.56 (m, 2H), 1.52-1.45 (m, 2H), 1.39-1.25 (m, 3H), 1.24 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.7, 128.4 (q, $J_{C\text{-}F}$ = 32.2 Hz), 127.4, 124.5 (q, $J_{C\text{-}F}$ = 270.0 Hz), 125.5 (q, $J_{C\text{-}F}$ = 3.9 Hz), 68.0, 45.5, 36.5, 33.5 and 33.1, 32.6, 22.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.27. **IR** (film): 2958, 2927, 2842, 1618, 1327, 1124, 1068, 1016 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{15}H_{20}F_3O$ $[M+H]^+$ 273.1461, found 273.1462.



1 **2d** **7**

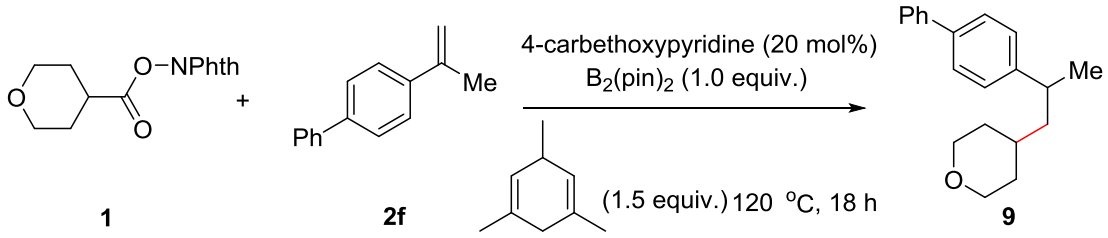
7: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2d** (54.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **7** (18.6 mg, 42% yield).

7: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.19-7.07 (m, 2H), 7.05-6.87 (m, 2H), 3.93-3.86 (m, 2H), 3.31-3.25 (m, 2H), 2.85-2.76 (m, 1H), 1.65-1.53 (m, 2H), 1.50-1.43 (m, 2H), 1.30-1.24 (m, 3H), 1.20 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.3 (d, $J_{C\text{-}F}$ = 243.4 Hz), 143.2, 128.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.2 (d, $J_{C\text{-}F}$ = 20.9 Hz), 68.1, 45.9, 35.8, 33.6 and 33.1, 32.6, 23.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.60. **IR** (film): 2956, 2840, 2758, 1603, 1509, 1222, 1098, 1015 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{14}H_{20}FO$ $[M+H]^+$ 223.1493, found 223.1496.



8: Prepared following *general procedure B* using **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2e** (59.3 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **8** (18.8 mg, 40% yield).

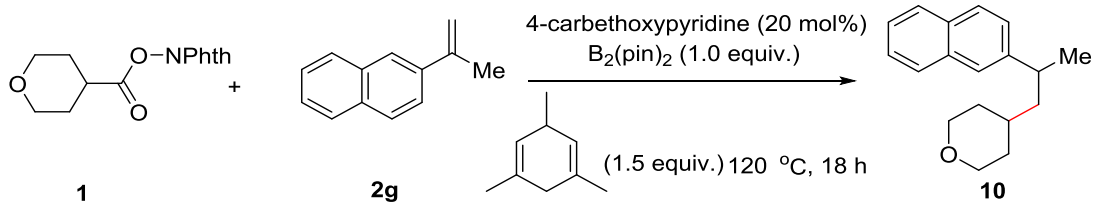
8: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.6 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 3.96-3.87 (m, 2H), 3.80 (s, 3H), 3.32-3.25 (m, 2H), 2.85-2.72 (m, 1H), 1.67-1.53 (m, 2H), 1.51-1.40 (m, 2H), 1.38-1.24 (m, 3H), 1.20 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 139.6, 127.8, 113.9, 68.1, 55.3, 45.9, 35.6, 33.6 and 33.1, 32.6, 23.3. **IR** (film): 2953, 2924, 2836, 1610, 1512, 1177, 1096, 1037 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_{23}F_3O$ $[M+H]^+$ 235.1693, found 235.1689.



9: Prepared following *general procedure B* using **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2f** (77.8 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **9** (24.6 mg, 44% yield).

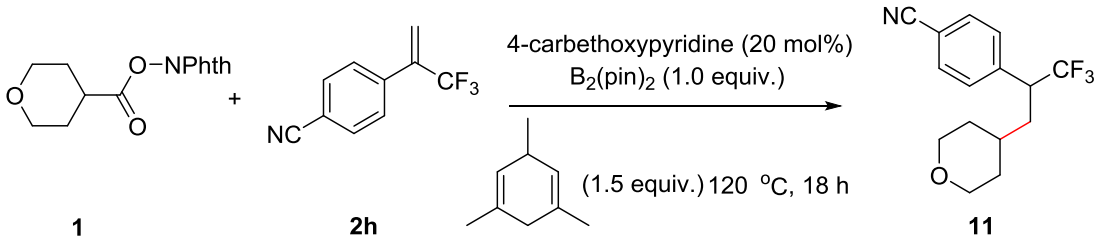
9: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.1, 1.1 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.37-7.27 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 3.94-3.88 (m, 2H), 3.32-3.26 (m, 2H), 2.95-2.79 (m, 1H), 1.68-1.58 (m, 2H), 1.55-1.45

(m, 2H), 1.43-1.36 (m, 1H), 1.35-1.27 (m, 2H), 1.25 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.7, 141.1, 139.0, 128.9, 127.4, 127.3, 127.1, 127.0, 68.1, 45.8, 36.1, 33.6 and 33.2, 32.6, 23.1. **IR** (film): 2954, 2923, 2839, 1600, 1486, 1450, 1095, 1015 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{24}NaO$ $[M+Na]^+$ 303.1719, found 303.1712.



10: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2g** (67.2 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **10** (31.1 mg, 61% yield).

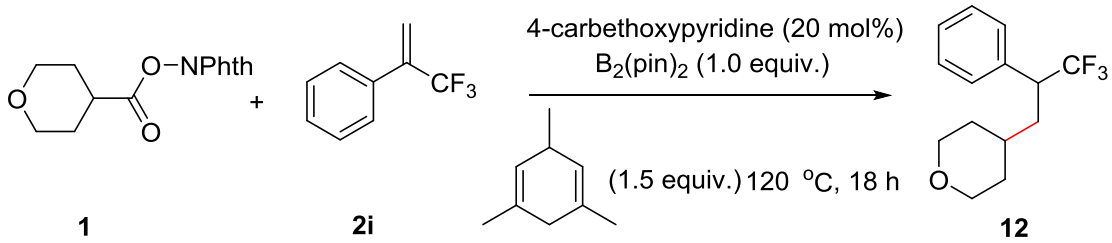
10: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.87 (m, 3H), 7.62 (s, 1H), 7.50-7.42 (m, 2H), 7.37 (dd, *J* = 8.5, 1.8 Hz, 1H), 4.00-3.87 (m, 2H), 3.30-3.24 (m, 2H), 3.08-2.95 (m, 1H), 1.77-1.70 (m, 2H), 1.61-1.49 (m, 2H), 1.42-1.27 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.0, 133.8, 132.3, 128.2, 127.7, 127.6, 126.0, 125.7, 125.3, 114.8, 68.1, 45.6, 36.7, 33.6 and 33.1, 32.7, 23.2. **IR** (film): 2954, 2923, 2839, 1599, 1506, 1236, 1095, 1015 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{18}H_{23}O$ $[M+H]^+$ 255.1743, found 255.1741.



11: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2h** (78.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the

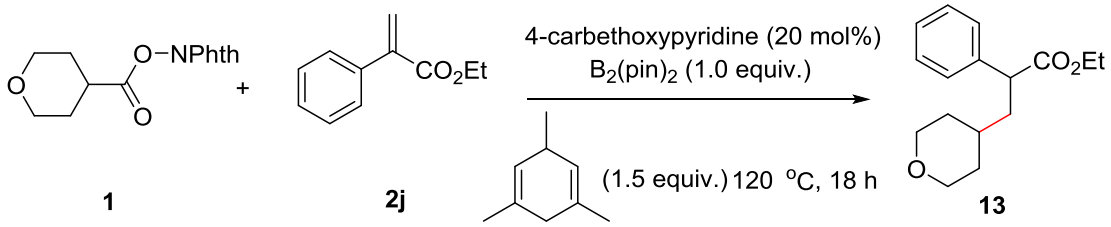
reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **11** (47.2 mg, 83% yield).

11: White solid, m.p.: 73-75 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 3.94-3.84 (m, 2H), 3.49-3.38 (m, 1H), 3.26-3.13 (m, 2H), 1.94-1.82 (m, 2H), 1.56-1.42 (m, 2H), 1.32-1.22 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.0, 132.7, 128.5 (q, $J_{C\text{-}F}$ = 280.1 Hz), 125.0, 118.4, 112.6, 67.6 (d, $J_{C\text{-}F}$ = 15.4 Hz), 47.1 (q, $J_{C\text{-}F}$ = 26.9 Hz), 35.5, 33.5, 31.7 (d, $J_{C\text{-}F}$ = 11.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.55. **IR** (film): 2935, 2843, 1600, 2230, 1611, 1453, 1109, 1014 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{15}H_{17}F_3NO$ $[M+H]^+$ 284.1257, found 284.1259.



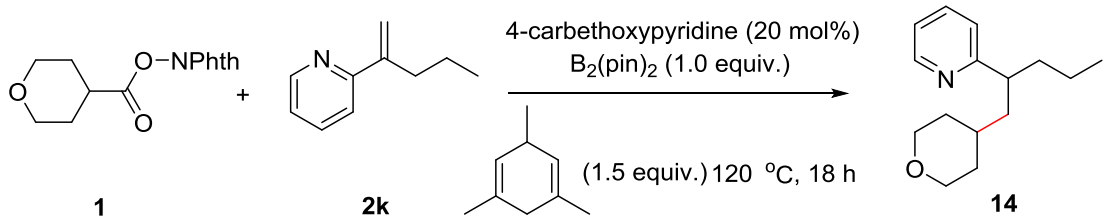
12: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2i** (68.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **12** (34.9 mg, 68% yield).

12: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 3H), 7.30-7.28 (m, 2H), 3.93-3.85 (m, 2H), 3.41-3.33 (m, 1H), 3.27-3.17 (m, 2H), 1.97-1.81 (m, 2H), 1.63-1.57 (m, 1H), 1.48-1.43 (m, 1H), 1.35-1.24 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.7, 129.1, 128.9, 128.4 (q, $J_{C\text{-}F}$ = 279.7 Hz), 125.8, 67.6 (d, $J_{C\text{-}F}$ = 15.4 Hz), 47.0 (q, $J_{C\text{-}F}$ = 26.5 Hz), 35.7, 33.7, 31.8 (d, $J_{C\text{-}F}$ = 23.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -69.88. **IR** (film): 2933, 2842, 2761, 1455, 1258, 1136, 1107, 1013 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{14}H_{18}F_3O$ $[M+H]^+$ 259.1304, found 259.1299.



13: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2j** (64.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **13** (32.0 mg, 61% yield).

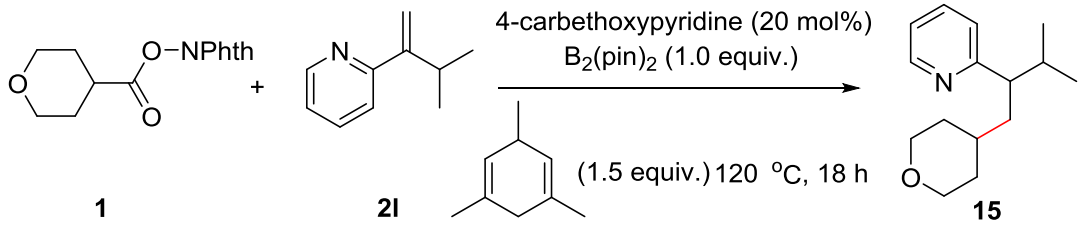
13: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.33 (m, 4H), 7.22-7.18 (m, 1H), 4.14-3.98 (m, 2H), 3.90-3.83 (m, 2H), 3.61 (t, *J* = 7.8 Hz, 1H), 3.24 (t, *J* = 11.3 Hz, 2H), 2.01-1.94 (m, 1H), 1.71-1.64 (m, 1H), 1.58-1.52 (m, 2H), 1.39-1.31 (m, 1H), 1.29-1.20 (m, 2H), 1.14 (t, *J* = 11.3, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.0, 139.2, 128.8, 128.0, 127.3, 67.9, 60.9, 48.6, 40.6, 33.1, 33.0 and 32.9, 14.2. **IR** (film): 2930, 2840, 2759, 1731, 1454, 1162, 1093, 1018 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{16}H_{22}O_3$ $[M+H]^+$ 263.1642, found 263.1648.



14: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2k** (58.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **14** (24.3 mg, 52% yield).

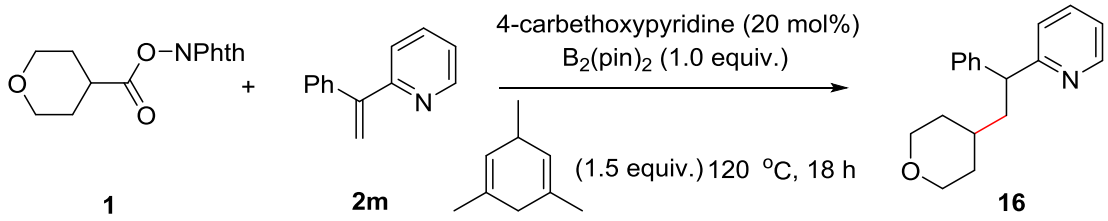
14: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56-8.54 (m, 1H), 7.61-7.56 (m, 1H), 7.20-6.95 (m, 2H), 3.91-3.83 (m, 2H), 3.27-3.19 (m, 2H), 2.89-2.83 (m, 1H), 1.76-1.64 (m, 3H), 1.59-1.49 (m, 2H), 1.44-1.40 (m, 1H), 1.28-1.18 (m, 4H), 1.15-1.07 (m, 1H),

0.84 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.4, 149.5, 136.3, 122.7, 121.2, 68.1, 44.4, 43.1, 38.7, 33.8, 32.9 and 32.8, 20.8, 14.3. **IR** (film): 2954, 2927, 2842, 1735, 1590, 1472, 1101, 1013 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1852, found 234.1854.



15: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2l** (58.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **3l** (32.1 mg, 69% yield).

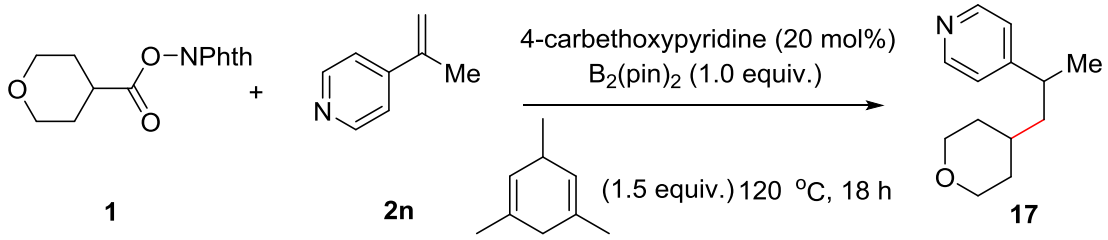
15: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 1H), 7.60-7.52 (m, 1H), 7.14-7.00 (m, 2H), 3.88-3.78 (m, 2H), 3.23-3.10 (m, 2H), 2.62-2.52 (m, 1H), 1.91-1.77 (m, 2H), 1.69-1.54 (m, 2H), 1.40-1.32 (m, 1H), 1.28-1.08 (m, 3H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 149.2, 136.0, 123.4, 121.2, 68.1, 51.4, 39.4, 34.2, 33.5, 32.8 and 32.5, 21.0, 20.9. **IR** (film): 2955, 2927, 2839, 1588, 1471, 1433, 1103, 1013 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_{24}NO$ $[M+H]^+$ 234.1852, found 234.1855.



16: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the

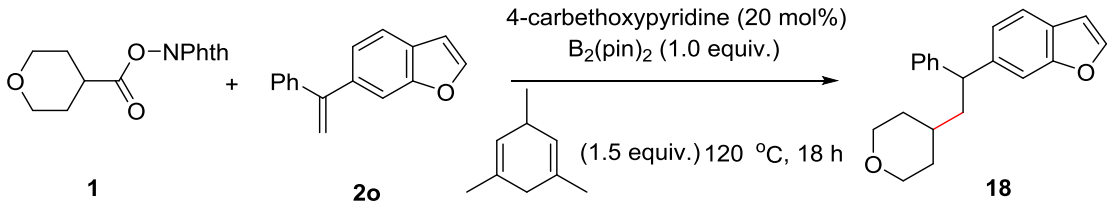
reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **16** (45.0 mg, 84% yield).

16: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 4.2 Hz, 1H), 7.62-7.58 (m, 1H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.13 (dd, *J* = 7.5, 4.9 Hz, 1H), 4.28 (t, *J* = 7.9 Hz, 1H), 3.95 (d, *J* = 11.4 Hz, 2H), 3.34-3.27 (m, 2H), 2.29-2.22 (m, 1H), 2.14-2.07 (m, 1H), 1.73-1.65 (m, 2H), 1.45-1.36 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 149.3, 143.7, 136.6, 128.6, 128.1, 126.5, 122.7, 121.4, 68.0, 50.2, 42.2, 33.3 and 33.1, 32.6. **IR** (film): 2927, 2839, 2758, 1734, 1588, 1431, 1094, 1013 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{18}H_{22}NO$ $[M+H]^+$ 268.1696, found 268.1696.



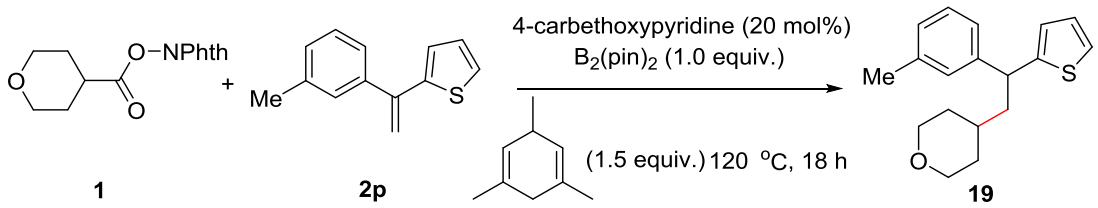
17: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2n** (47.7 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 3:1) to afford the product **17** (29.8 mg, 72% yield).

17: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 6.1 Hz, 2H), 7.14 (d, *J* = 6.1 Hz, 2H), 3.94-3.88 (m, 2H), 3.33-3.24 (m, 2H), 2.88-2.79 (m, 1H), 1.64-1.55 (m, 2H), 1.53-1.45 (m, 2H), 1.33-1.25 (m, 3H), 1.23 (d, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 149.7, 122.8, 67.9, 44.9, 36.1, 33.4 and 33.1, 32.6, 22.2. **IR** (film): 2957, 2925, 2841, 1597, 1413, 1137, 1096, 1015 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{13}H_{20}NO$ $[M+H]^+$ 206.1539, found 206.1539.



18: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2o** (88.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **18** (43.1 mg, 71% yield).

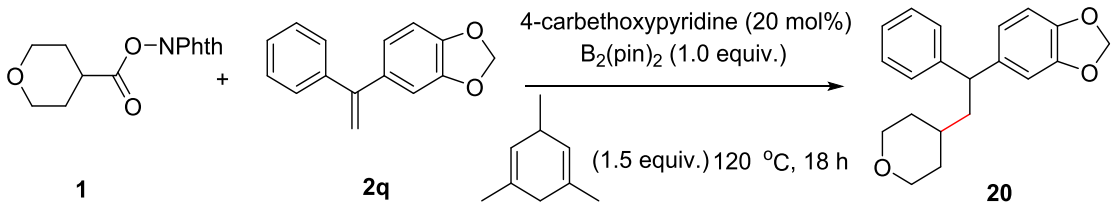
18: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 2.2 Hz, 1H), 7.48 (d, *J* = 1.8 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 1H), 7.32-7.27 (m, 4H), 7.21-7.17 (m, 2H), 6.73-6.72 (m, 1H), 4.18 (t, *J* = 8.0 Hz, 1H), 3.95-3.90 (m, 2H), 3.31-3.24 (m, 2H), 2.08-2.04 (m, 2H), 1.70-1.64 (m, 2H), 1.42-1.32 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.7, 145.5, 145.3, 139.6, 128.6, 127.8, 127.7, 126.2, 124.5, 119.9, 111.4, 106.7, 68.0, 47.5, 43.5, 33.3 and 33.2, 32.5. **IR** (film): 2922, 2841, 2758, 1600, 1466, 1261, 1091, 1013 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{21}H_{23}O_2$ $[M+H]^+$ 307.1693, found 307.1695.



19: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2p** (80.0 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **19** (27.3 mg, 48% yield).

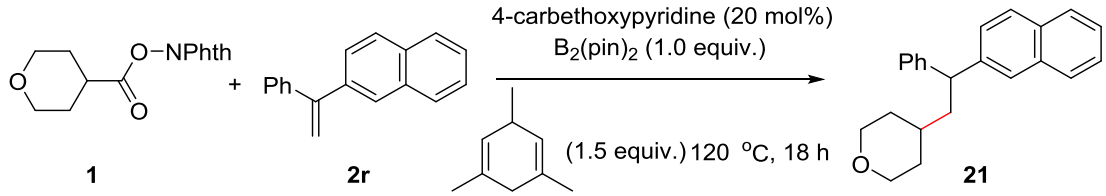
19: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.8 Hz, 1H), 7.14 (dd, *J* = 5.1-1.2 Hz, 1H), 7.11-7.06 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.92 (dd, *J* = 5.1-3.5 Hz, 1H), 6.83-6.82 (m, 1H), 4.26 (t, *J* = 7.9 Hz, 1H), 3.95-3.90 (m, 2H), 3.32-3.26 (m, 2H), 2.34 (s, 3H), 2.06-2.00 (m, 2H), 1.70-1.61 (m, 2H), 1.49-1.41 (m, 1H), 1.39-1.30 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 144.5, 138.3, 128.6, 128.4, 127.5, 126.7, 124.7, 123.7, 123.5, 68.0, 44.8, 43.3, 33.3 and 33.0, 32.6, 21.7. **IR** (film): 2922, 2840,

2758, 1605, 1444, 1236, 1094, 1013 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{18}H_{23}OS$ $[M+H]^+$ 287.1464, found 287.1464.



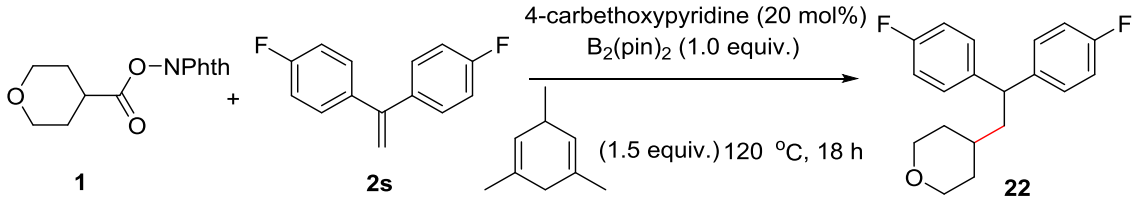
20: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2q** (89.6 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **20** (39.1 mg, 63% yield).

20: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.24 (m, 2H), 7.24-7.11 (m, 3H), 6.73-6.68 (m, 3H), 5.92-5.85 (m, 2H), 3.97 (t, *J* = 8.0 Hz, 1H), 3.90 (dd, *J* = 11.4, 3.2 Hz, 2H), 3.29-3.23 (m, 2H), 1.96-1.89 (m, 2H), 1.65-1.58 (m, 2H), 1.39-1.26 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 145.9, 145.1, 139.0, 128.6, 127.7, 126.3, 120.8, 108.3, 101.0, 68.0, 47.3, 43.2, 33.3 and 33.2, 32.5. **IR** (film): 2927, 2835, 2757, 1514, 1261, 1143, 1091, 1028 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{23}O_3$ $[M+H]^+$ 311.1642, found 311.1642.



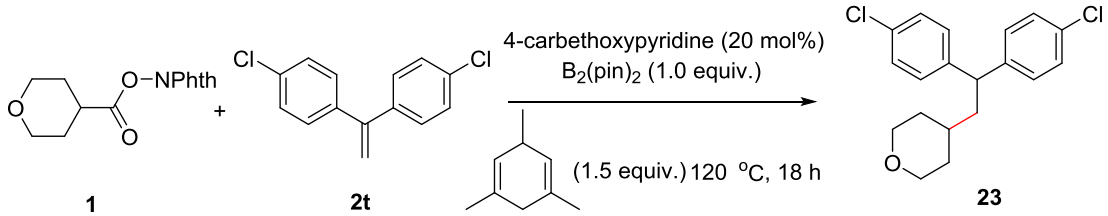
21: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2r** (92.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **21** (57.1 mg, 90% yield).

21: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.67 (m, 4H), 7.46-7.38 (m, 2H), 7.33 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.27-7.24 (m, 4H), 7.20-7.14 (m, 1H), 4.21 (t, *J* = 8.0 Hz, 1H), 3.93-3.87 (m, 2H), 3.23 (t, *J* = 11.0 Hz, 2H), 2.14-2.03 (m, 2H), 1.65 (t, *J* = 11.1 Hz, 2H), 1.44-1.29 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 142.4, 133.7, 132.3, 128.6, 128.3, 128.0, 127.8, 127.7, 126.8, 126.4, 126.1, 125.9, 125.6, 68.0, 47.7, 42.9, 33.4 and 33.2, 32.6. **IR** (film): 2923, 2839, 2757, 1598, 1493, 1134, 1091, 1013 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{23}H_{25}O$ $[M+H]^+$ 317.1900, found 317.1903.



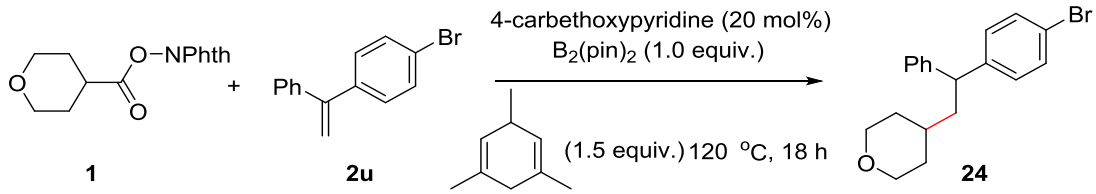
22: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2s** (86.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **22** (43.7 mg, 72% yield).

22: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23-7.10 (m, 4H), 7.05-6.89 (m, 4H), 4.03 (t, *J* = 8.0 Hz, 1H), 3.94-3.89 (m, 2H), 3.29-3.23 (m, 2H), 1.96-1.92 (m, 2H), 1.64-1.58 (m, 2H), 1.37-1.34 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.5 (d, $J_{C\text{-}F}$ = 244.8 Hz), 140.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 115.5 (d, $J_{C\text{-}F}$ = 21.0 Hz), 67.9, 46.2, 43.3, 33.2, 32.5. **IR** (film): 2925, 2841, 2759, 1602, 1506, 1223, 1157, 1097 cm^{-1}. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -116.79. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{20}F_2NaO$ $[M+Na]^+$ 325.1374, found 325.1371.



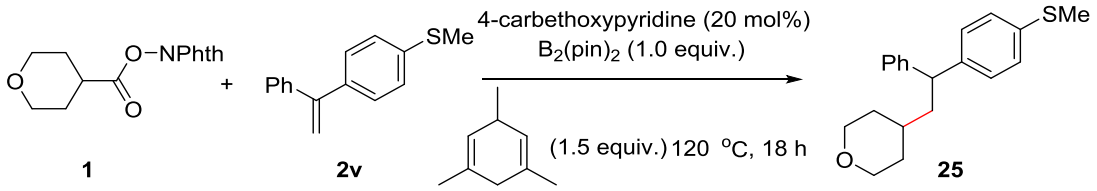
23: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2t** (99.7 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **23** (53.2 mg, 79% yield).

23: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.21 (m, 4H), 7.16-7.11 (m, 4H), 4.01 (t, *J* = 8.0 Hz, 1H), 3.93-3.89 (m, 2H), 3.26 (t, *J* = 11.4 Hz, 2H), 1.93 (dd, *J* = 7.7, 5.9 Hz, 2H), 1.60 (d, *J* = 9.5 Hz, 2H), 1.35-1.29 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.0, 132.2, 129.1, 128.9, 67.9, 46.5, 42.9, 33.2, 32.5. **IR** (film): 2925, 2841, 2758, 1488, 1447, 1231, 1091, 1013 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{19}H_{21}Cl_2O$ $[M+H]^+$ 335.0964, found 335.0966.



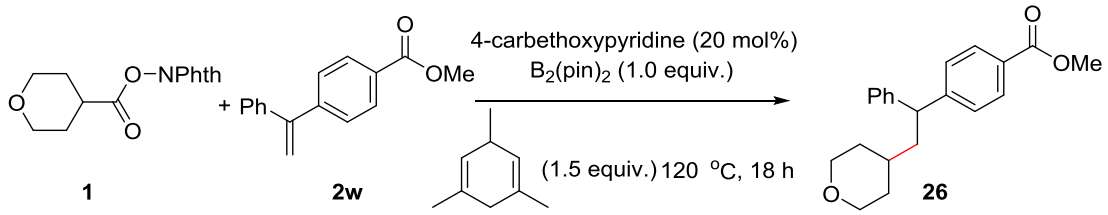
24: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2u** (103.7 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **24** (57.8 mg, 84% yield).

24: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.36 (m, 2H), 7.34-7.26 (m, 2H), 7.26-7.16 (m, 3H), 7.15-7.10 (m, 2H), 4.03 (t, *J* = 8.0 Hz, 1H), 3.96-3.90 (m, 2H), 3.27 (t, *J* = 11.3 Hz, 2H), 2.00-1.94 (m, 2H), 1.63 (d, *J* =11.1 Hz, 2H), 1.35-1.29 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.3, 144.0, 131.7, 129.6, 128.7, 127.8, 126.6, 120.1, 67.9, 47.1, 42.9, 33.2, 32.5. **IR** (film): 2924, 2840, 2758, 1486, 1450, 1231, 1099, 1010 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{19}H_{22}BrO$ $[M+H]^+$ 345.0849, found 345.0852.



25: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2v** (90.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **25** (51.7 mg, 83% yield).

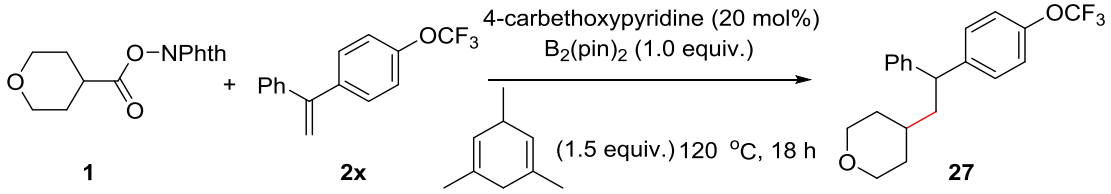
25: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (d, *J* =7.3 Hz, 2H), 7.18 (d, *J* =6.7 Hz, 2H), 7.16-7.11 (m, 5H), 3.98 (t, *J* = 8.0 Hz, 1H), 3.87 (dd, *J* = 10.7, 3.5 Hz, 2H), 3.22 (t, *J* = 11.0 Hz, 2H), 2.41 (s, 3H), 1.97-1.90 (m, 2H), 1.59 (d, *J* = 11.2 Hz, 2H), 1.37-1.25 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 142.0, 135.9, 128.6, 128.4, 127.8, 127.1, 126.3, 68.0, 47.1, 43.0, 33.3 and 33.2, 32.5, 16.1. **IR** (film): 2920, 2839, 2758, 1492, 1450, 1231, 1092, 1014 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{24}NaOS$ $[M+Na]^+$ 335.1440, found 335.1439.



26: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2w** (90.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **26** (56.5 mg, 87% yield).

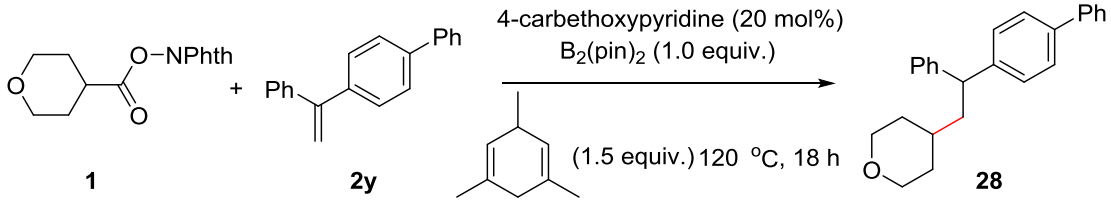
26: Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.30-7.22 (m, 4H), 7.22-7.12 (m, 3H), 4.07 (t, *J* = 8.0 Hz, 1H), 3.88 (d, *J* = 4.5 Hz, 2H), 3.84 (s, 3H), 3.21 (t, *J* = 11.4 Hz, 2H), 2.00-1.92 (m, 2H), 1.58 (d, *J* = 9.7 Hz, 2H), 1.33-1.26

(m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 150.4, 144.0, 130.0, 128.8, 128.3, 127.9, 127.8, 126.6, 67.9, 52.1, 47.7, 42.8, 33.2, 32.5. **IR** (film): 2925, 2840, 2758, 1722, 1609, 1435, 1280, 1101 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{21}H_{25}O_3$ $[M+H]^+$ 325.1798, found 325.1795.



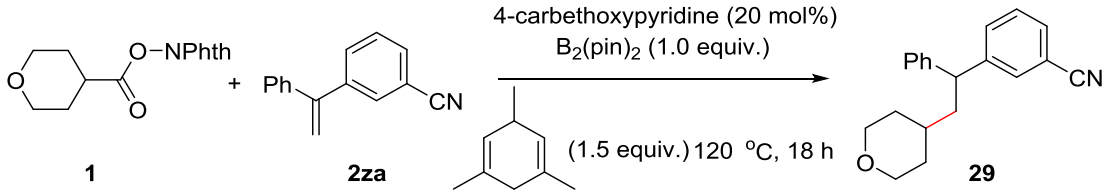
27: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2x** (105.7 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **27** (54.5 mg, 78% yield).

27: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.23 (m, 2H), 7.23-7.13 (m, 5H), 7.08 (d, *J* = 8.2 Hz, 2H), 4.07 (t, *J* = 8.0 Hz, 1H), 3.90-3.83 (m, 2H), 3.26-3.20 (m, 2H), 1.99-1.88 (m, 2H), 1.59 (t, *J* = 12.3 Hz, 2H), 1.33-1.22 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 144.3, 143.8, 129.1, 128.8, 127.9, 126.6, 121.1, 120.6 (d, J_{C-F} = 256.8 Hz), 67.9, 47.1, 43.1, 33.3 and 33.2, 32.5. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.85. **IR** (film): 2924, 2842, 2760, 1507, 1259, 1223, 1165, 1102 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{20}H_{22}F_3O_2$ $[M+H]^+$ 351.1566, found 351.1561.



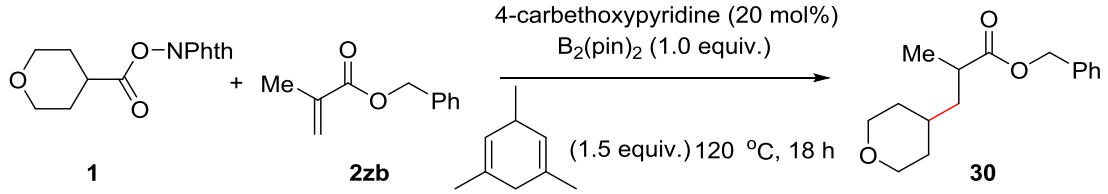
28: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2y** (102.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **28** (58.9 mg, 86% yield).

28: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.47 (m, 2H), 7.47-7.41 (m, 2H), 7.36-7.31 (m, 2H), 7.25-7.20 (m, 7H), 7.18-7.09 (m, 1H), 4.03 (t, *J* = 8.0 Hz, 1H), 3.85 (dd, *J* = 8.4, 6.9 Hz, 2H), 3.20 (t, *J* = 11.0 Hz, 2H), 1.99-1.94 (m, 2H), 1.59 (d, *J* = 12.3 Hz, 2H), 1.37-1.19 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.9, 144.1, 141.0, 139.1, 128.8, 128.7, 128.3, 127.9, 127.3, 127.2, 127.1, 126.4, 68.0, 47.4, 43.1, 33.3, 32.5. **IR** (film): 2923, 2839, 2758, 1599, 1487, 1135, 1091, 1008 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{25}H_{27}O$ $[M+H]^+$ 343.2056, found 343.2054.



29: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2za** (107.3 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **29** (47.6 mg, 82% yield).

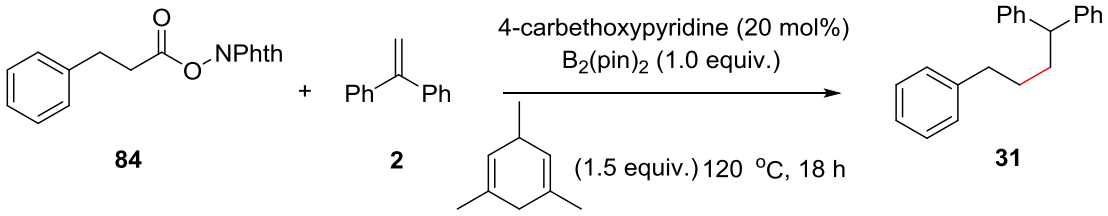
29: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 1.8 Hz, 1H), 7.45-7.42 (m, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.30-7.25 (m, 2H), 7.22-7.16 (m, 3H), 4.05 (t, *J* = 7.9 Hz, 1H), 3.90-3.85 (m, 2H), 3.25-3.19 (m, 2H), 2.01-1.88 (m, 2H), 1.63-1.54 (m, 2H), 1.32-1.26 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 143.3, 132.5, 131.4, 130.1, 129.4, 128.9, 127.8, 126.9, 119.0, 112.6, 67.8, 47.3, 42.7, 33.2 and 33.0, 32.4. **IR** (film): 2925, 2841, 2227, 1494, 1466, 1134, 1095, 1013 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{20}H_{22}O$ $[M+H]^+$ 292.1696, found 292.1697.



30: Prepared following *general procedure B using* **1** (55.0 mg, 0.2 mmol, 1.0 equiv.), **2zb** (70.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20

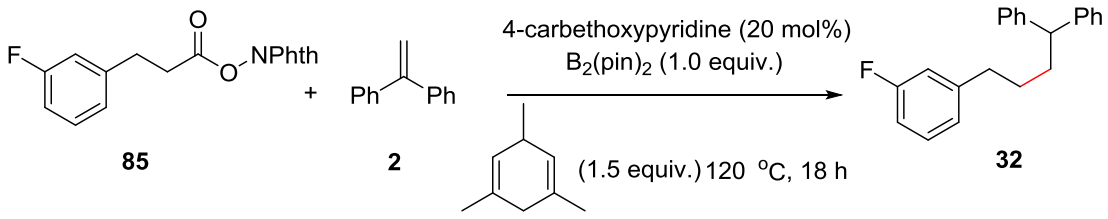
mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **30** (20.1 mg, 38% yield).

30: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.25 (m, 5H), 5.12 (q, *J* = 12.3 Hz, 2H), 3.92-3.87 (m, 2H), 3.30-3.22 (m, 2H), 2.65-2.56 (m, 1H), 1.70-1.59 (m, 2H), 1.50-1.39 (m, 2H), 1.33-1.21 (m, 3H), 1.17 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.7, 136.3, 128.7, 128.5, 128.3, 68.0, 66.2, 41.2, 36.6, 33.2, 32.9, 17.8. **IR** (film): 2931, 2841, 2758, 1732, 1455, 1167, 1150, 1097 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{16}H_{22}NaO_3$ $[M+Na]^+$ 285.1461, found 285.1465.



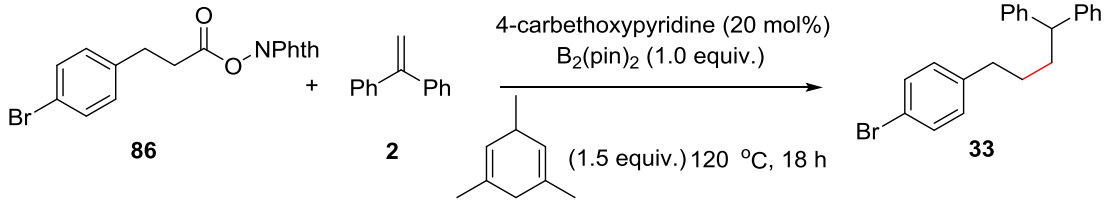
31: Prepared following *general procedure B using* **84** (56.3 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **31** (38.4 mg, 67% yield).

31: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32-7.24 (m, 10H), 7.24-7.11 (m, 5H), 3.96 (t, *J* = 7.8 Hz, 1H), 2.68 (t, *J* = 7.7 Hz, 2H), 2.16-2.10 (m, 2H), 1.69-1.60 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 142.4, 128.5, 128.4, 128.1, 128.0, 126.2, 125.8, 51.4, 36.0, 35.4, 29.9. **IR** (film): 3024, 2935, 2858, 1599, 1493, 1451, 1072, 1030 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{22}H_{23}$ $[M+H]^+$ 287.1794, found 287.1791.



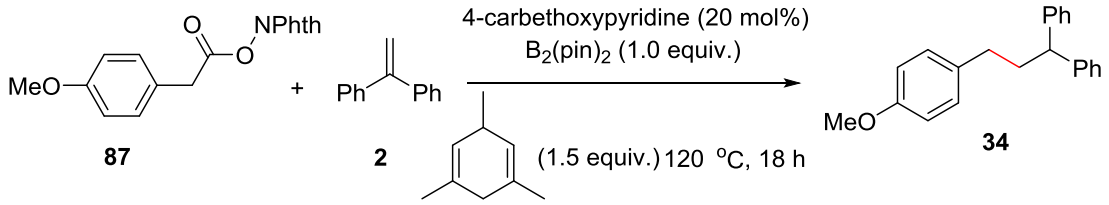
32: Prepared following *general procedure B using* **85** (59.9 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **32** (44.0 mg, 72% yield).

32: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.18 (m, 11H), 6.93-6.84 (m, 3H), 3.94 (t, *J* = 7.9 Hz, 1H), 2.66 (t, *J* = 7.7 Hz, 2H), 2.11 (q, *J* = 7.8 Hz, 2H), 1.67-1.59 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0 (d, $J_{C\text{-}F}$ = 245.1 Hz), 145.1, 144.9, 129.7 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.6, 127.9, 126.3, 124.2, 115.3 (d, $J_{C\text{-}F}$ = 20.8 Hz), 112.7 (d, $J_{C\text{-}F}$ = 21.0 Hz), 51.3, 35.7, 35.2, 29.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.85. IR (film): 3025, 2937, 2860, 1587, 1490, 1251, 1139, 1074 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{22}H_{22}FNa$ $[M+Na]^+$ 327.1519, found 327.1518.



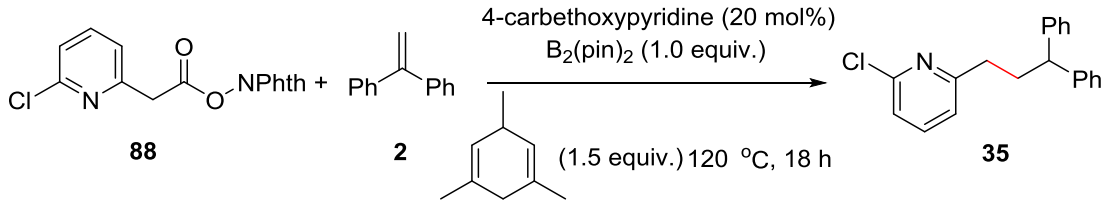
33: Prepared following *general procedure B using* **86** (74.8 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **33** (54.9 mg, 75% yield).

33: White crystal, mp. 85-87 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.3 Hz, 2H), 7.31-7.25 (m, 4H), 7.22 (d, *J* = 7.0 Hz, 4H), 7.20-7.14 (m, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 3.91 (t, *J* = 7.8 Hz, 1H), 2.59 (t, *J* = 7.6 Hz, 2H), 2.10-2.03 (m, 2H), 1.63-1.55 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 141.3, 131.4, 130.3, 128.6, 127.9, 126.3, 119.5, 51.4, 35.3, 35.2, 29.7. **IR** (film): 3024, 2936, 2858, 1598, 1487, 1450, 1071, 1010 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{22}H_{25}BrN$ $[M+NH_4]^+$ 382.1165, found 382.1164.



34: Prepared following *general procedure B using* **87** (62.3 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **34** (39.8 mg, 66% yield).

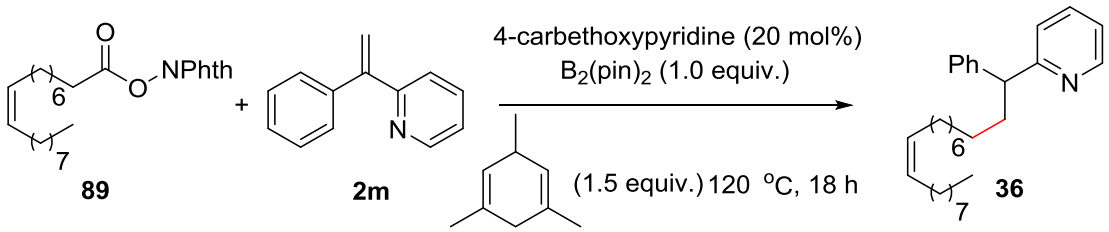
34: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.29 (m, 8H), 7.27-7.22 (m, 2H), 7.18-7.06 (m, 2H), 6.93-6.88 (m, 2H), 3.99 (t, *J* = 7.7 Hz, 1H), 3.84 (s, 3H), 2.62-2.58 (m, 2H), 2.46-2.40 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.9, 145.0, 134.2, 129.4, 128.6, 128.0, 126.3, 113.9, 55.3, 50.7, 37.7, 33.3. **IR** (film): 3025, 2933, 2833, 1610, 1511, 1244, 1176, 1034 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{22}H_{23}O$ $[M+H]^+$ 303.1743, found 303.1737.



38: Prepared following *general procedure B* using **88** (63.3 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **35** (38.4 mg, 62% yield).

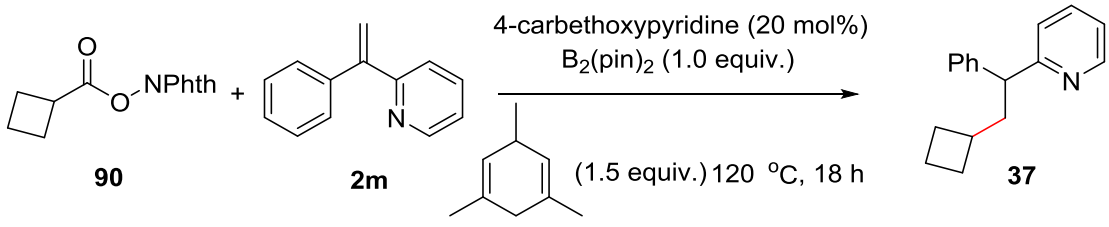
35: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.4 Hz, 1H), 7.39 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.30-7.26 (m, 4H), 7.25-7.14 (m, 7H), 3.86 (t, *J* = 7.8 Hz, 1H), 2.54 (dd, *J* = 9.0, 6.5 Hz, 2H), 2.35 (q, *J* = 7.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.7, 149.2, 144.2, 138.9, 136.3, 128.8, 127.9, 126.6, 124.0, 50.6, 36.8, 30.6. **IR** (film):

3025, 2930, 2862, 1493, 1458, 1383, 1105, 1024 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{19}ClN$ $[M+H]^+$ 308.1201, found 308.1196.



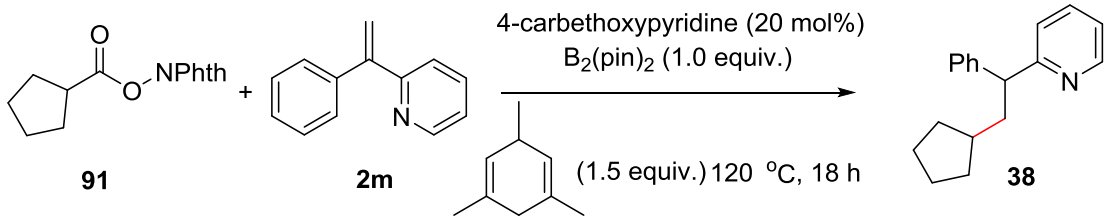
36: Prepared following *general procedure B using* **89** (85.5 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **36** (60.5 mg, 72% yield).

36: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60-8.54 (m, 1H), 7.58-7.50 (m, 1H), 7.34 (d, *J* = 7.2, 2H), 7.31-7.25 (m, 2H), 7.22-7.13 (m, 2H), 7.10-7.02 (m, 1H), 5.43-5.31 (m, 2H), 4.05 (t, *J* = 7.8 Hz, 1H), 2.28-2.18 (m, 1H), 2.12-2.05 (m, 1H), 2.04-1.96 (m, 4H), 1.34-1.20 (m, 24H), 0.93-0.85 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 149.3, 144.1, 136.4, 130.0, 129.9, 128.5, 128.1, 126.4, 122.7, 121.3, 53.9, 35.2, 32.0, 29.9, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 29.1, 28.0, 27.3, 22.8, 14.2. **IR** (film): 3004, 2924, 1588, 1466, 1431, 1147, 1071, 1031 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{30}H_{46}N$ $[M+H]^+$ 420.3625, found 420.3624.



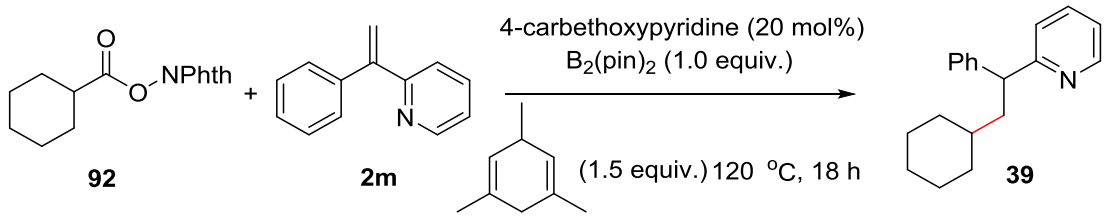
37: Prepared following *general procedure B using* **90** (49.0 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **37** (31.8 mg, 67% yield).

37: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55-8.53 (m, 1H), 7.54-7.50 (m, 1H), 7.33-7.23 (m, 4H), 7.19-7.10 (m, 2H), 7.07-7.02 (m, 1H), 3.93 (t, *J* = 7.5 Hz, 1H), 2.35-2.28 (m, 1H), 2.19-2.12 (m, 2H), 1.97-1.90 (m, 2H), 1.78-1.71 (m, 2H), 1.66-1.58 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2, 149.3, 144.1, 136.4, 128.5, 128.1, 126.4, 122.8, 121.3, 51.7, 42.4, 34.4, 28.4, 18.6. **IR** (film): 2968, 2854, 1588, 1452, 1431, 1147, 1049, 1031 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{17}H_{20}N$ $[M+H]^+$ 238.1590, found 238.1592.



38: Prepared following *general procedure B using* **91** (51.9 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **38** (41.3 mg, 82% yield).

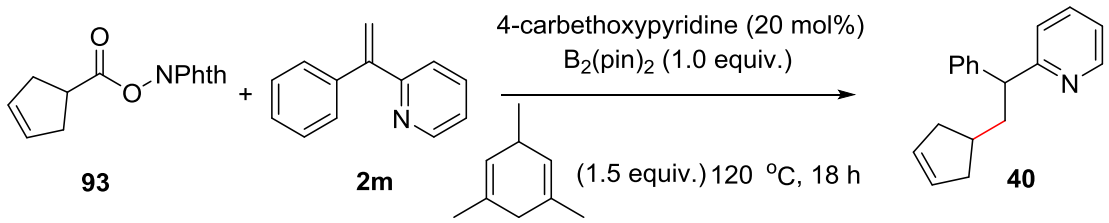
38: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.7 Hz, 1H), 7.47-7.43 (m, 1H), 7.29-7.25 (m, 2H), 7.21-7.17 (m, 2H), 7.13-7.04 (m, 2H), 6.99-6.96 (m, 1H), 4.04 (t, *J* = 7.9 Hz, 1H), 2.17-2.03 (m, 2H), 1.72-1.63 (m, 2H), 1.55-1.47 (m, 3H), 1.39-1.33 (m, 2H), 1.12-1.01 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 149.3, 144.2, 136.4, 128.5, 128.2, 126.4, 122.7, 121.3, 52.9, 41.7, 38.0, 32.9, 32.6, 25.3, 25.2. **IR** (film): 2928, 2856, 1581, 1467, 1429, 1150, 1069, 1027 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{18}H_{22}N$ $[M+H]^+$ 252.1747, found 252.1740.



39: Prepared following *general procedure B using* **92** (54.6 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-

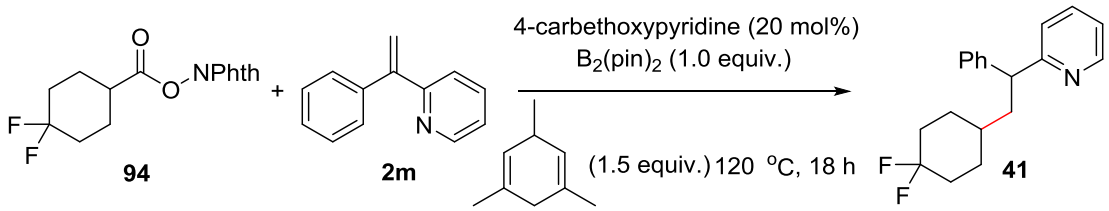
1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **39** (48.2 mg, 91% yield).

39: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 4.6 Hz, 1H), 7.67-7.63 (m, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33-7.24 (m, 2H), 7.19-7.16 (m, 1H), 4.35 (t, *J* = 7.9 Hz, 1H), 2.27-2.20 (m, 1H), 2.14-2.06 (m, 1H), 1.90 (t, *J* = 12.3 Hz, 2H), 1.79-1.69 (m, 3H), 1.29-1.20 (m, 4H), 1.14-1.04 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 149.3, 144.2, 136.4, 128.5, 128.2, 126.4, 122.7, 121.3, 50.7, 42.9, 35.1, 33.6, 33.3, 26.7, 26.3, 26.2. **IR** (film): 2921, 2850, 1587, 1448, 1431, 1147, 1071, 1032 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{24}N$ $[M+H]^+$ 266.1903, found 266.1905.



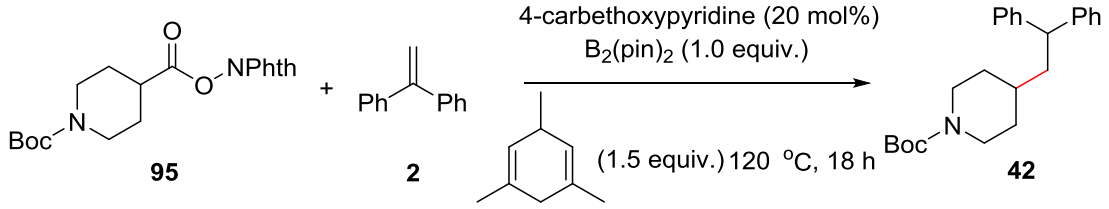
40: Prepared following *general procedure B using* **93** (74.8 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **40** (32.8 mg, 66% yield).

40: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48-8.47 (m, 1H), 7.48-7.44 (m, 1H), 7.30-7.25 (m, 2H), 7.22-7.17 (m, 2H), 7.14-7.05 (m, 2H), 7.00-6.96 (m, 1H), 5.56-5.52 (m, 2H), 4.03 (t, *J* = 7.8 Hz, 1H), 2.39-2.26 (m, 3H), 2.17-2.11 (m, 1H), 2.01-1.93 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.1, 149.4, 144.0, 136.5, 130.0, 129.9, 128.6, 128.2, 126.5, 122.8, 121.4, 52.7, 41.8, 39.1, 38.9, 35.9. **IR** (film): 2923, 2839, 1588, 1493, 1431, 1147, 1050, 1032 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{18}H_{20}N$ $[M+H]^+$ 250.1590, found 250.1591.



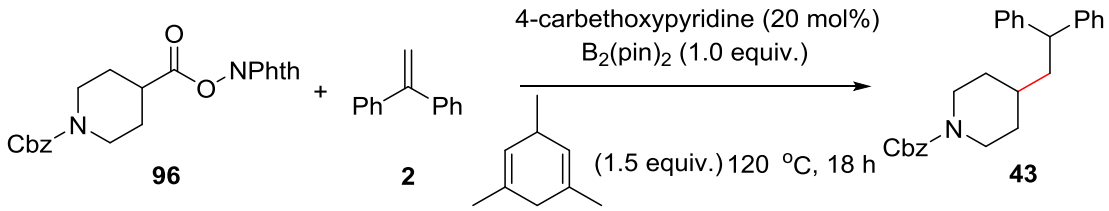
41: Prepared following *general procedure B using* **94** (61.8 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **41** (45.9 mg, 76% yield).

41: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68-8.56 (m, 1H), 7.58-7.53 (m, 1H), 7.37-7.27 (m, 4H), 7.24-7.17 (m, 1H), 7.16-7.16 (m, 1H), 7.11-7.07 (m, 1H), 4.19 (t, *J* = 8.0 Hz, 1H), 2.24-2.17 (m, 1H), 2.10-1.99 (m, 3H), 1.86-1.78 (m, 2H), 1.64-1.51 (m, 2H), 1.36-1.22 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8, 149.3, 143.6, 136.6, 128.7, 128.0, 126.6, 125.0 (d, $J_{C\text{-}F}$ = 240.3 Hz), 122.8, 121.5, 51.0, 40.9, 33.4 (m, 2×CH_2CF_2), 29.0 (dd, $J_{C\text{-}F}$ = 34.4, 9.2 Hz), 28.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -91.6 (d, *J* = 234.3 Hz, 1F), -101.8 (d, *J* = 234.5 Hz, 1F). **IR** (film): 2936, 2862, 1588, 1450, 1432, 1379, 1115, 1081 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{22}F_2N$ $[M+H]^+$ 302.1715, found 302.1715.



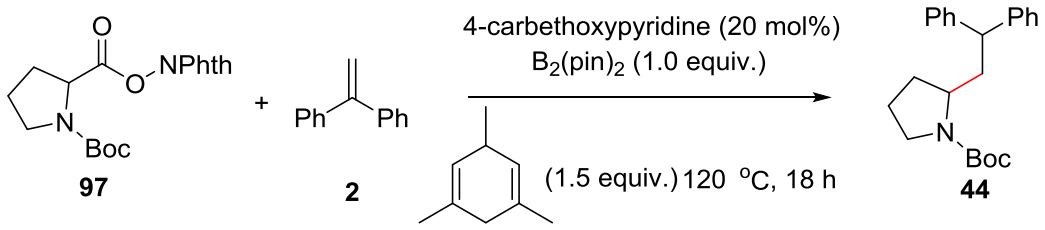
42: Prepared following *general procedure B using* **95** (74.8 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **42** (44.5 mg, 61% yield).

42: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 8H), 7.25-7.16 (m, 2H), 4.15-4.07 (m, 3H), 2.62 (d, *J* = 13.3 Hz, 2H), 2.03-2.00 (m, 2H), 1.73 (d, *J* = 12.0 Hz, 2H), 1.48 (s, 9H), 1.36-1.30 (m, 1H), 1.23-1.13 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 144.9, 128.6, 127.9, 126.3, 79.3, 47.9, 43.7, 42.7, 33.5, 32.3, 28.6. **IR** (film): 2974, 2849, 1693, 1474, 1422, 1244, 1167, 1072 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{24}H_{32}NO_2$ $[M+H]^+$ 366.2428, found 366.2427.



43: Prepared following *general procedure B using* **96** (81.8 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **43** (62.2 mg, 78% yield).

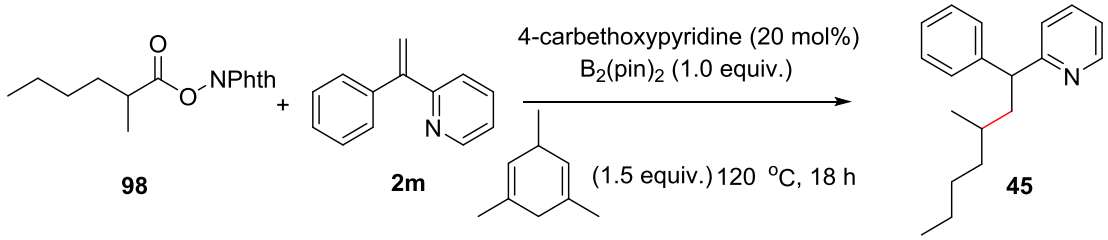
43: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47-7.03 (m, 15H), 5.08 (s, 2H), 4.09 (t, *J* = 11.9 Hz, 2H), 4.01 (t, *J* = 7.8 Hz, 1H), 2.61 (t, *J* = 12.7 Hz, 2H), 1.95 (t, *J* = 6.9 Hz, 2H), 1.74-1.62 (m, 2H), 1.32-1.26 (m, 1H), 1.18-1.12 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 144.9, 137.0, 128.6, 128.5, 128.0, 127.9, 127.8, 126.3, 67.0, 47.9, 44.1, 42.6, 33.4, 32.2. **IR** (film): 2923, 2850, 1694, 1434, 1279, 1238, 1121, 1073 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{27}H_{29}NNaO_2$ $[M+Na]^+$ 422.2091, found 422.2089.



44: Prepared following *general procedure B using* **97** (72.0 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20

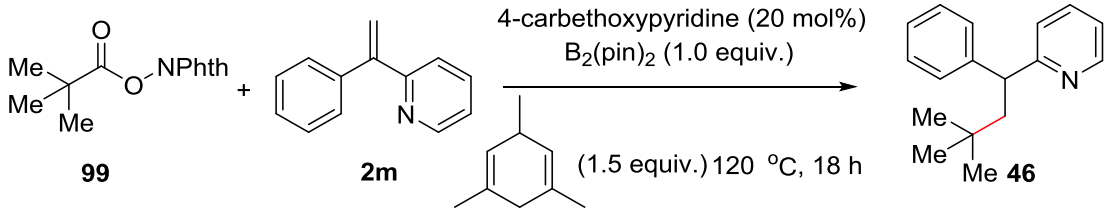
mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **44** (38.1 mg, 54% yield).

44: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65-6.95 (m, 10H), 3.94 (brs, 1H), 3.79-3.65 (m, 1H), 3.44-3.30 (m, 2H), 2.87-2.67 (m, 1H), 1.99-1.68 (m, 5H), 1.47 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.6, 145.5, 143.5, 128.6, 128.5, 128.3, 127.7, 126.4, 128.3, 79.4, 55.7, 48.8, 46.6 and 46.2, 39.8 and 39.4, 30.2 28.8, 23.9 and 23.16. **IR** (film): 2972, 2874, 1690, 1493, 1394, 1365, 1170, 1100 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{23}H_{30}NO_2$ $[M+H]^+$ 352.2271, found 352.2270.



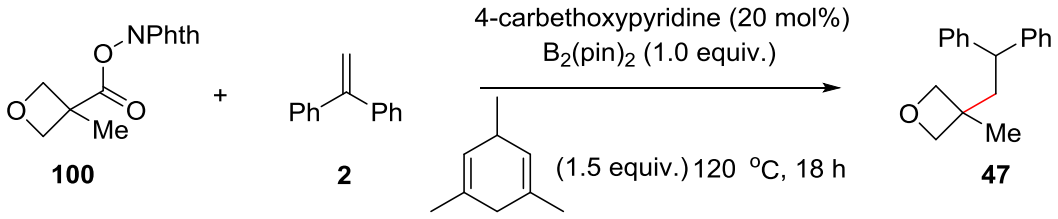
45: Prepared following *general procedure B using* **98** (55.1 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **45** (48.2 mg, 90% yield).

45: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 3.9 Hz, 1H), 7.53-7.49 (m, 1H), 7.33 (d, *J* = 7.4 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.18-7.11 (m, 2H), 7.05-7.02 (m, 1H), 4.18 (t, *J* = 9.5, 1H), 2.19-2.12 (m, 1H), 1.95-1.88 (m, 1H), 1.29-1.13 (m, 7H), 0.88 (d, *J* = 6.4, 3H), 0.84-0.81 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 149.3, 143.7, 136.5, 128.6, 128.3, 126.4, 122.6, 121.2, 51.4, 42.3, 37.1, 30.4, 29.1, 23.1, 19.7, 14.2. **IR** (film): 2955, 2926, 2857, 1587, 1469, 1431, 1147, 1031 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{26}N$ $[M+H]^+$ 268.2060, found 268.2061.



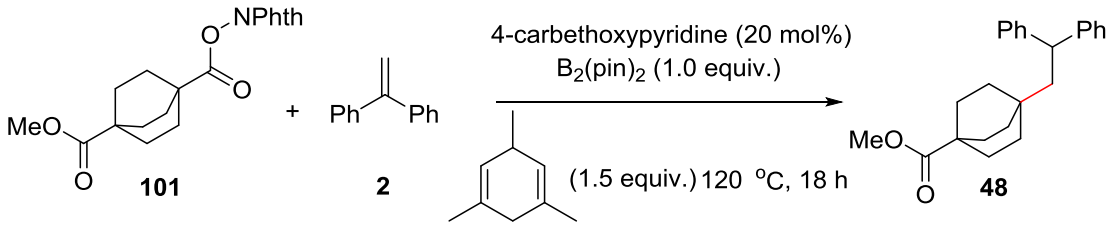
46: Prepared following *general procedure B using* **99** (55.1 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **46** (43.5 mg, 91% yield).

46: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.0 Hz, 1H), 7.41-7.36 (m, 1H), 7.27 (d, *J* = 7.7 Hz, 2H), 7.15-7.08 (m, 3H), 7.06-6.97 (m, 1H), 6.92-6.88 (m, 1H), 4.11-4.08 (m, 1H), 2.32 (dd, *J* = 14.0, 7.7 Hz, 1H), 1.89 (dd, *J* = 14.0, 5.6 Hz, 1H), 0.7 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.0, 149.2, 145.8, 136.5, 128.5, 128.0, 126.2, 122.9, 121.2, 50.8, 48.7, 31.5, 30.2. **IR** (film): 2955, 2926, 2870, 1587, 1469, 1431, 1377, 1051 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{17}H_{22}N$ $[M+H]^+$ 240.1747, found 240.1745.



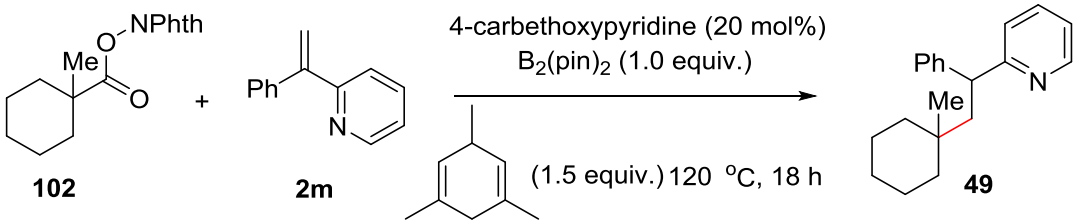
47: Prepared following *general procedure B using* **100** (52.2 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **47** (24.3 mg, 48% yield).

47: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 4.3 Hz, 8H), 7.22-7.14 (m, 2H), 4.18 (d, *J* = 5.7 Hz, 2H), 4.03-3.99 (m, 3H), 2.46 (d, *J* = 7.6 Hz, 2H), 1.43 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.8, 128.7, 127.9, 126.5, 83.2, 47.6, 44.4, 39.3, 23.8. **IR** (film): 3025, 2960, 2861, 1598, 1493, 1450, 1378, 1077 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{18}H_{20}O$ $[M+H]^+$ 253.1587, found 253.1587.



48: Prepared following *general procedure B using* **101** (71.4 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **48** (58.0 mg, 83% yield).

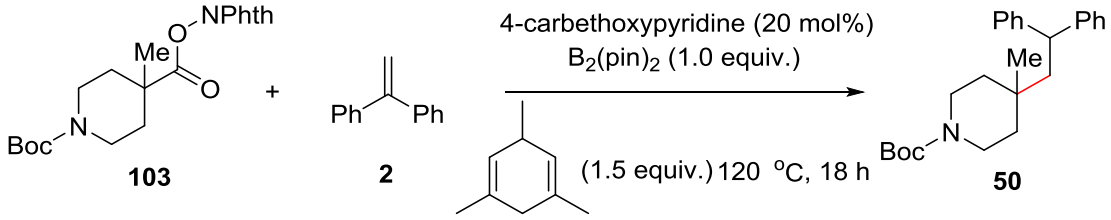
48: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 8H), 7.18-7.14 (m, 2H), 4.08 (t, *J* = 6.7 Hz, 1H), 3.63 (s, 3H), 2.05 (d, *J* = 6.7 Hz, 2H), 1.75-1.70 (m, 6H), 1.40-1.35 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.6, 146.6, 128.5, 127.8, 126.0, 51.7, 47.4, 47.3, 38.9, 31.7, 31.1, 28.7. **IR** (film): 3024, 2946, 2866, 1731, 1597, 1453, 1247, 1067 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{24}H_{28}NaO_2$ $[M+Na]^+$ 371.1982, found 371.1975.



49: Prepared following *general procedure B using* **102** (57.4 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **49** (48.0 mg, 86% yield).

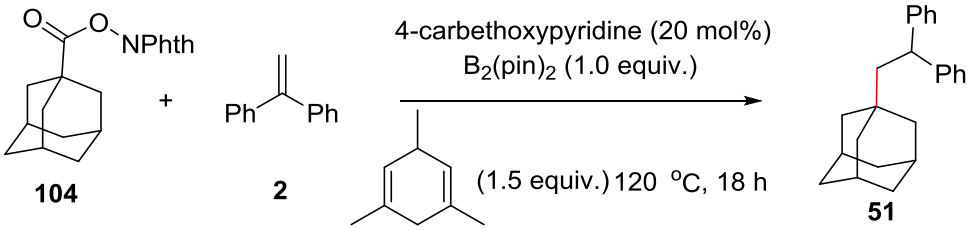
49: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64-8.62 (m, 1H), 7.64-7.58 (m, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.38-7.30 (m, 2H), 7.29-7.21 (m, 2H), 7.15-7.11 (m, 1H), 4.31-4.26 (m, 1H), 2.40-2.22 (m, 1H), 2.07-1.88 (m, 1H), 1.45-1.17 (m, 8H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.94-0.91 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6 and 164.1, 149.3

and 149.2, 144.5 and 143.7, 136.4 and 136.3, 128.5 and 128.5, 128.3 and 128.1, 126.4 and 126.3, 122.8 and 122.6, 121.3 and 121.2, 51.4 and 51.3, 42.7 and 42.3, 37.1, 36.8, 30.4 and 30.3, 29.1 and 29.0, 23.1, 19.9 and 19.6, 14.2. **IR** (film): 2955, 2926, 2857, 1587, 1469, 1431, 1147, 1031 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{26}N$ $[M+]^+$ 280.2060, found 280.2059.



50: Prepared following *general procedure B using* **103** (77.7 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **50** (37.9 mg, 50% yield).

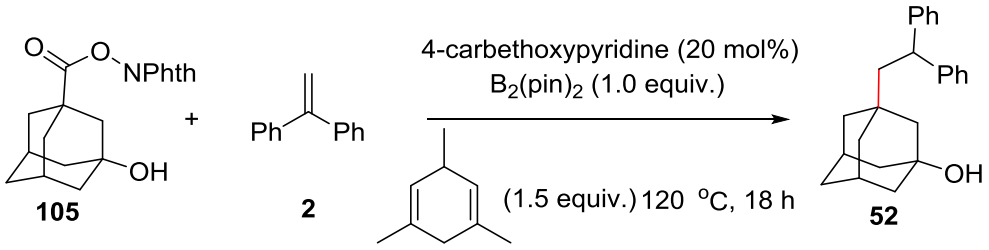
50: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26-7.18 (m, 8H), 7.16-7.05 (m, 2H), 4.05 (t, *J* = 6.6 Hz, 1H), 3.44 (brs, 2H), 3.08-3.01 (m, 2H), 2.11 (d, *J* = 6.7 Hz, 2H), 1.39 (s, 9H), 1.30-1.24 (m, 2H), 1.20-1.11 (m, 2H), 0.86 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 146.5, 128.7, 127.8, 126.2, 79.3, 48.0, 47.4, 40.1, 37.6, 32.7, 28.6, 23.7. **IR** (film): 2972, 2925, 2869, 1693, 1598, 1451, 1162, 1093 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{25}H_{33}NNaO_2$ $[M+Na]^+$ 402.2404, found 402.2400.



51: Prepared following *general procedure B using* **104** (65.1 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the

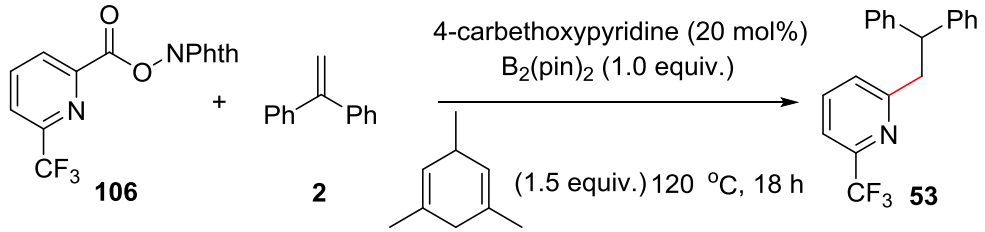
reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **51** (51.2 mg, 81% yield).

51: Colorless um. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 8H), 7.18-7.12 (m, 2H), 4.17 (t, *J* = 6.6 Hz, 1H), 2.01 (d, *J* = 6.6 Hz, 2H), 1.93-1.89 (m, 3H), 1.72-1.56 (m, 6H), 1.47 (d, *J* = 2.6 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 128.5, 127.9, 125.9, 50.7, 46.5, 43.2, 37.2, 33.7, 28.9. **IR** (film): 3024, 2900, 2844, 1598, 1492, 1450, 1080, 1031 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{24}H_{29}$ $[M+H]^+$ 317.2264, found 317.2269.



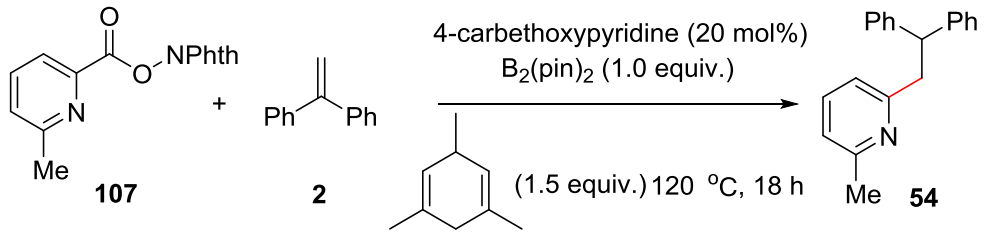
52: Prepared following *general procedure B using* **105** (65.1 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **52** (47.9 mg, 72% yield).

52: Colorless gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.20 (m, 8H), 7.20-7.07 (m, 2H), 4.13 (t, *J* = 6.7 Hz, 1H), 2.13-2.09 (m, 2H), 2.07 (d, *J* = 6.8 Hz, 2H), 1.79 (s, 1H), 1.66-1.54 (m, 4H), 1.50-1.45 (m, 2H), 1.43 (s, 2H), 1.38-1.29 (m, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 128.5, 127.8, 126.0, 69.1, 50.7, 49.4, 46.7, 44.7, 41.8, 37.3, 35.5, 30.8. **IR** (film): 3385, 3024, 2911, 2847, 1492, 1451, 1147, 1032 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{24}H_{28}NaO$ $[M+Na]^+$ 355.2032, found 355.2031.



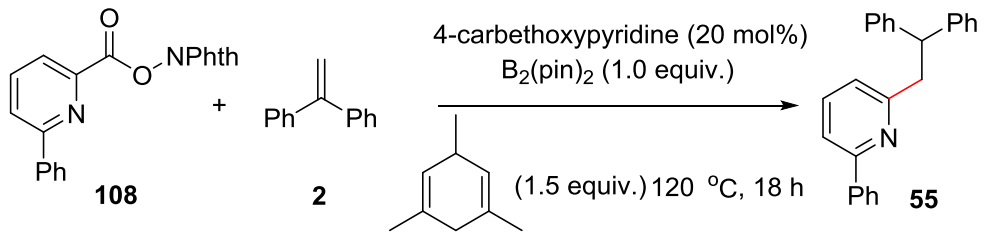
53: Prepared following *general procedure B using* **106** (67.2 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **53** (47.2 mg, 72% yield).

53: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.28-7.23 (m, 8H), 7.22-7.14 (m, 2H), 7.01 (d, *J* = 7.8 Hz, 1H), 4.65 (t, *J* = 8.0 Hz, 1H), 3.63 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 147.8 (q, $J_{C\text{-}F}$ = 34.3 Hz), 144.0, 137.2, 128.5, 128.1, 126.5, 126.4, 121.7 (q, $J_{C\text{-}F}$ = 274.2 Hz), 117.8 (q, $J_{C\text{-}F}$ = 3.0 Hz), 50.8, 44.0. **IR** (film): 3027, 2928, 1599, 1494, 1463, 1139, 1114, 1091 cm^{-1}. ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.04. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{17}F_3N$ $[M+H]^+$ 328.1308, found 328.1305.



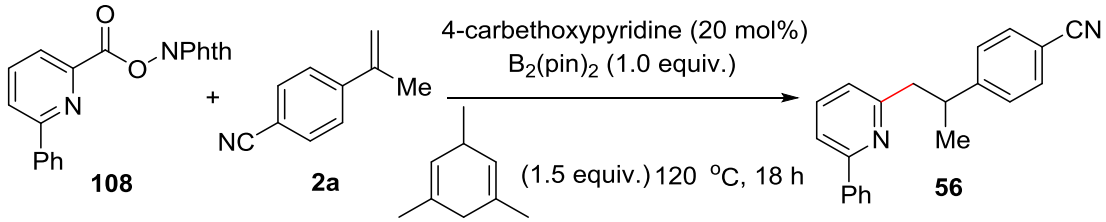
54: Prepared following *general procedure B using* **107** (56.5 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 2:1) to afford the product **54** (33.9 mg, 62% yield).

54: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 7.7 Hz, 1H), 7.22-7.16 (m, 8H), 7.14-7.08 (m, 2H), 6.84 (d, *J* = 7.6 Hz, 1H), 6.60 (d, *J* = 7.7 Hz, 1H), 4.56 (t, *J* = 7.9 Hz, 1H), 3.48 (d, *J* = 7.9 Hz, 2H), 2.49 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.3, 157.7, 144.5, 136.2, 128.3, 128.2, 128.1, 126.2, 120.2, 51.1, 44.3, 24.6. **IR** (film): 3026, 2924, 1715, 1591, 1454, 1395, 1153, 1078 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{20}N$ $[M+H]^+$ 274.1590, found 274.1590.



55: Prepared following *general procedure B using* **108** (68.8 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **55** (40.5 mg, 60% yield).

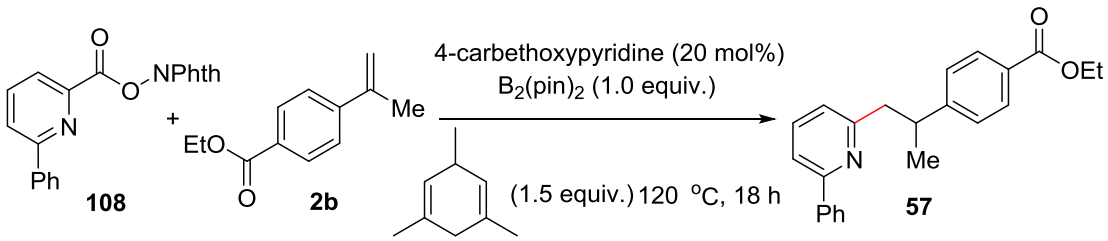
55: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04-7.87 (m, 2H), 7.46-7.36 (m, 5H), 7.31-7.20 (m, 8H), 7.15-7.07 (m, 2H), 6.84-6.77 (m, 1H), 4.74 (t, *J* = 7.9 Hz, 1H), 3.60 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.8, 156.7, 144.7, 139.8, 136.7, 128.8, 128.7, 128.4, 128.2, 127.1, 126.2, 122.1, 117.9, 51.0, 44.4. **IR** (film): 3026, 2925, 1570, 1493, 1447, 1154, 1081, 1029 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{25}H_{22}N$ $[M+H]^+$ 336.1747, found 336.1747.



56: Prepared following *general procedure B using* **108** (68.8 mg, 0.2 mmol, 1.0 equiv.), **2a** (57.3 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **56** (19.1 mg, 32% yield).

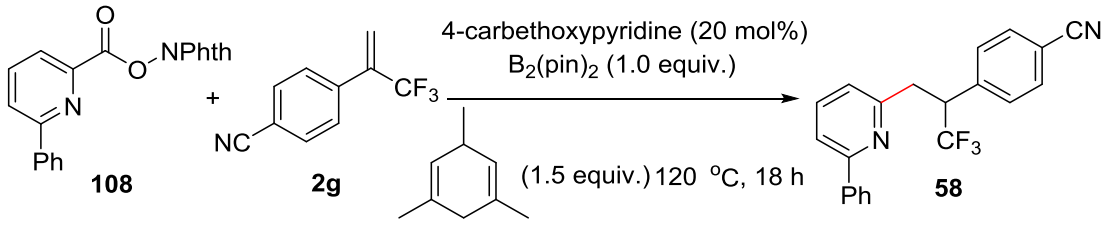
56: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.83 (m, 2H), 7.55-7.40 (m, 6H), 7.39-7.35 (m, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 1H), 3.63-3.44 (m, 1H), 3.06 (d, *J* = 7.5 Hz, 2H), 1.31 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.5, 157.0, 152.6, 139.6, 136.9, 132.3, 129.0, 128.8, 128.2, 127.0, 121.9, 119.2, 118.2, 109.9,

46.6, 40.4, 21.5. **IR** (film): 3060, 2962, 2926, 2226, 1606, 1569, 1446, 1156 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{21}H_{19}N_2$ $[M+H]^+$ 299.1543, found 299.1544.



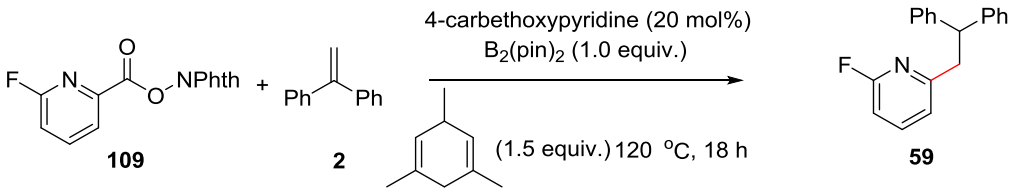
57: Prepared following *general procedure B using* **108** (68.8 mg, 0.2 mmol, 1.0 equiv.), **2b** (76.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **57** (24.2 mg, 35% yield).

57: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.93 (m, 4H), 7.58-7.44 (m, 4H), 7.44-7.36 (m, 1H), 7.32-7.27 (m, 2H), 6.86 (d, *J* = 7.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.56-3.47 (m, 1H), 3.17-3.08 (m, 2H), 1.40-1.34 (m, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 160.0, 156.9, 152.4, 139.8, 136.9, 129.8, 128.9, 128.8, 128.4, 127.3, 127.1, 122.0, 118.1, 60.9, 46.8, 40.4, 21.6, 14.5. **IR** (film): 3060, 2961, 1715, 1590, 1571, 1447, 1276, 1106 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{23}H_{24}NO_2$ $[M+H]^+$ 346.1802, found 346.1802.



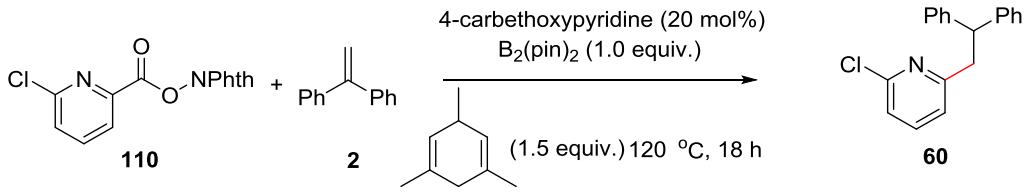
58: Prepared following *general procedure B using* **108** (68.8 mg, 0.2 mmol, 1.0 equiv.), **2g** (78.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **58** (32.0 mg, 45% yield).

58: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96-7.88 (m, 2H), 7.60-7.51 (m, 4H), 7.52-7.41 (m, 5H), 6.90 (dd, *J* = 7.9, 1.3 Hz, 1H), 4.47-4.34 (m, 1H), 3.64 (dd, *J* = 14.6, 4.2 Hz, 1H), 3.55 (dd, *J* = 14.6, 10.9 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 155.9, 140.2, 139.1, 137.4, 134.3, 132.3, 130.2, 129.3, 128.8, 126.8, 126.7 (q, $J_{C\text{-}F}$ = 280.1 Hz), 122.1, 118.5, 112.2, 49.2 (q, $J_{C\text{-}F}$ = 27.0 Hz), 37.1. **IR** (film): 3026, 2930, 2230, 1724, 1571, 1449, 1256, 1110 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{21}H_{16}F_3N_2$ $[M+H]^+$ 353.1260, found 353.1256.



59: Prepared following *general procedure B using* **109** (57.2 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **59** (32.3 mg, 60% yield).

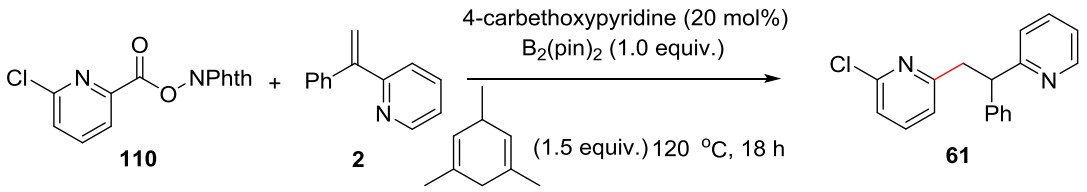
59: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.43 (m, 1H), 7.25-7.18 (m, 8H), 7.16-7.11 (m, 2H), 6.73 (dd, *J* = 7.4 Hz, 2.4 Hz, 1H), 6.64 (dd, *J* = 8.1 Hz, 2.8 Hz, 1H), 4.60 (t, *J* = 8.0 Hz, 1H), 3.45 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.4, 162.0, 159.2 (d, $J_{C\text{-}F}$ = 13.1 Hz), 144.0, 140.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.3 (d, $J_{C\text{-}F}$ = 44.2 Hz), 126.4, 121.1 (d, $J_{C\text{-}F}$ = 4.1 Hz), 106.8 (d, $J_{C\text{-}F}$ = 37.2 Hz), 50.7, 43.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.6. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{17}FN$ $[M+H]^+$ 278.1340, found 278.1340.



60: Prepared following *general procedure B using* **110** (60.4 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20

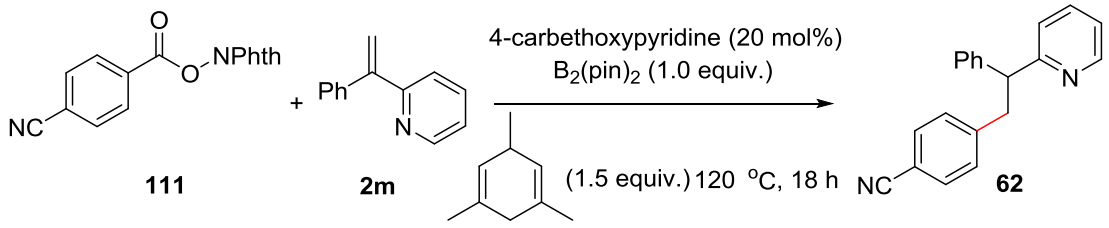
mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **60** (36.2 mg, 62% yield).

60: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.7 Hz, 1H), 7.25-7.20 (m, 8H), 7.20-7.09 (m, 2H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 4.57 (t, *J* = 8.0 Hz, 1H), 3.48 (d, *J* = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.1, 150.8, 143.9, 138.6, 128.5, 128.1, 126.4, 122.3, 121.7, 50.8, 43.9. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{17}ClN$ $[M+H]^+$ 294.1044, found 294.1044.



61: Prepared following *general procedure B using* **110** (60.4 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **61** (29.9 mg, 51% yield).

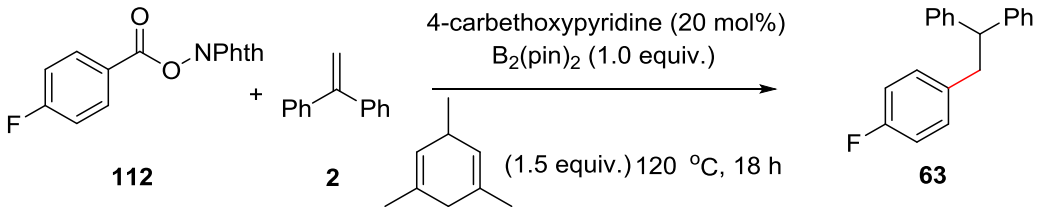
61: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.60-8.54 (m, 1H), 7.54-7.46 (m, 1H), 7.35-7.30 (m, 3H), 7.26-7.20 (m, 2H), 7.18-7.11 (m, 2H), 7.10-7.00 (m, 2H), 6.82 (dd, *J* = 7.5, 0.8 Hz, 1H), 4.70 (t, *J* = 7.9, 1H), 3.78 (dd, *J* = 13.7, 7.9, 1H), 3.50 (dd, *J* = 13.7, 7.9, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.5, 161.4, 150.7, 149.2, 143.0, 138.6, 136.5, 128.5, 128.2, 126.6, 123.7, 122.6, 121.6, 121.5, 52.9, 43.0. **HRMS** (ESI-TOF) exact mass calculated for $C_{18}H_{16}ClN_2$ $[M+H]^+$ 295.0997, found 295.0997.



62: Prepared following *general procedure B using* **111** (58.6 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-

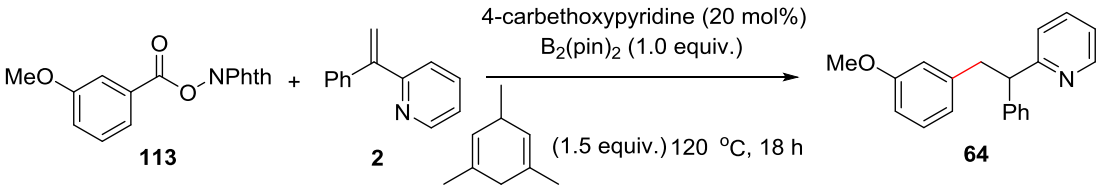
1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 2:1) to afford the product **62** (38.6 mg, 68% yield).

62: White solid, m.p.: 145-147 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70-8.48 (m, 1H), 7.78-7.73 (m, 2H), 7.67-7.62 (m, 2H), 7.58-7.50 (m, 1H), 7.40-7.33 (m, 2H), 7.26-7.16 (m, 4H), 7.12-7.08 (m, 1H), 4.80 (t, *J* = 8.1 Hz, 1H), 4.54 (dd, *J* = 13.6, 8.7 Hz, 1H), 4.43 (dd, *J* = 13.7, 7.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 160.8, 149.3, 140.4, 136.6, 134.4, 133.9, 132.0, 128.6, 127.2, 123.7, 123.6, 123.3, 121.9, 50.9, 42.4. **IR** (film): 3060, 2933, 2228, 1712, 1589, 1433, 1395, 1080 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{17}N_2$ $[M+H]^+$ 285.1386, found 285.1385.



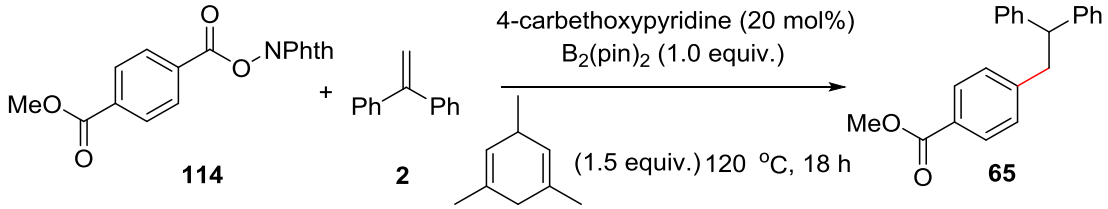
63: Prepared following *general procedure B using* **112** (57.0 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 30:1) to afford the product **63** (29.8 mg, 54% yield).

63: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.80 (m, 2H), 7.33-7.22 (m, 8H), 7.22-7.15 (m, 2H), 7.03-6.95 (m, 2H), 4.81 (d, *J* = 7.5 Hz, 2H), 4.46 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4 (d, $J_{C\text{-}F}$ = 153.7 Hz), 164.6, 141.2, 132.2 (d, $J_{C\text{-}F}$ = 9.3 Hz), 128.8, 128.4, 127.0, 115.6 (d, $J_{C\text{-}F}$ = 22.2 Hz), 67.4, 50.0. **IR** (film): 3062, 3028, 1720, 1603, 1507, 1451, 1271, 1117 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{20}H_{18}F$ $[M+H]^+$ 277.1387, found 277.1386.



64: Prepared following *general procedure B using* **113** (59.5 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **64** (23.9 mg, 41% yield).

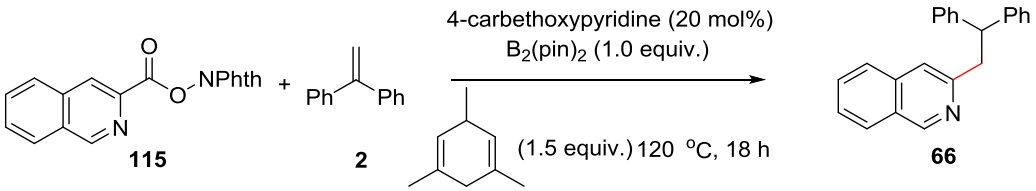
64: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62-8.58 (m, 1H), 7.54-7.48 (m, 1H), 7.36-7.32 (m, 2H), 7.30-7.24 (m, 2H), 7.21-7.15 (m, 1H), 7.14-7.04 (m, 3H), 6.68-6.62 (m, 2H), 6.58-6.54 (m, 1H), 4.36 (t, *J* = 7.8 Hz, 1H), 3.66 (s, 3H), 3.65-3.60 (m, 1H), 3.33 (dd, *J* = 13.6, 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.0, 159.4, 149.3, 143.4, 142.1, 136.5, 129.1, 128.5, 128.3, 126.6, 123.4, 121.6, 121.5, 114.7, 111.7, 55.4, 55.1, 41.4. **IR** (film): 3059, 2936, 1702, 1615, 1507, 1465, 1261, 1077 cm^{-1}. **HRMS** (APCI) exact mass calculated for $C_{20}H_{20}NO$ $[M+H]^+$ 290.1539, found 290.1539.



65: Prepared following *general procedure B using* **114** (58.6 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **65** (26.6 mg, 42% yield).

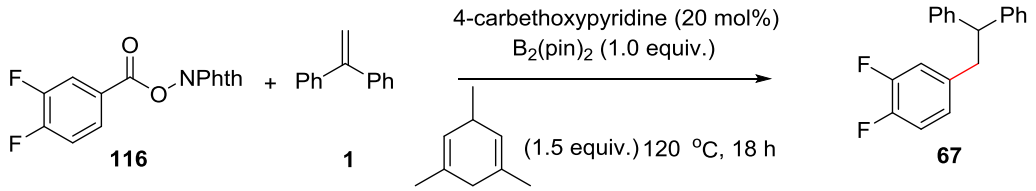
65: White solid, m.p.: 111-112 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.32-7.14 (m, 10H), 7.08 (d, *J* = 8.0 Hz, 2H), 4.25 (t, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 3.42 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 145.9, 144.0, 129.5,

129.2, 128.5, 128.1, 127.9, 126.5, 52.9, 52.0, 42.2. **IR** (film): 3060, 2928, 2758, 1721, 1608, 1435, 1280, 1102 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{22}H_{20}NaO_2$ $[M+Na]^+$ 339.1356, found 339.1353.



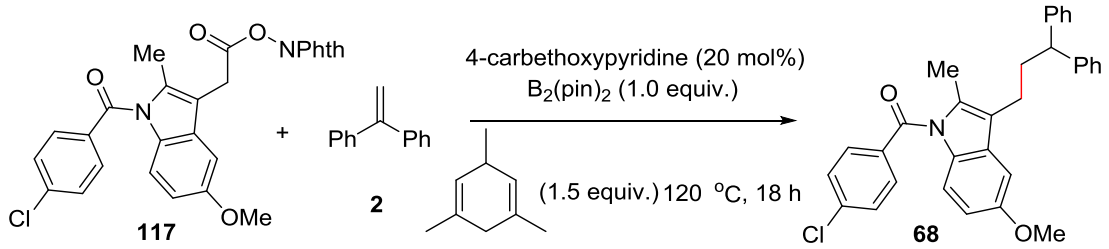
66: Prepared following *general procedure B using* **115** (63.6 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **66** (32.3 mg, 52% yield).

66: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 7.90-7.84 (m, 1H), 7.60-7.54 (m, 2H), 7.50-7.46 (m, 1H), 7.38-7.30 (m, 2H), 7.29-7.25 (m, 4H), 7.24-7.19 (m, 4H), 7.13-7.11 (m, 1H), 4.76 (t, *J* = 7.9 Hz, 1H), 3.66 (d, *J* = 7.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.2, 152.1, 144.5, 136.3, 130.3, 129.0, 128.5, 128.2, 127.6, 126.6, 126.3, 126.2, 119.6, 51.0, 44.2. **IR** (film): 3084, 2935, 2834, 1724, 1584, 1451, 1262, 1152 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{23}H_{20}N$ $[M+H]^+$ 310.1590, found 310.1595.



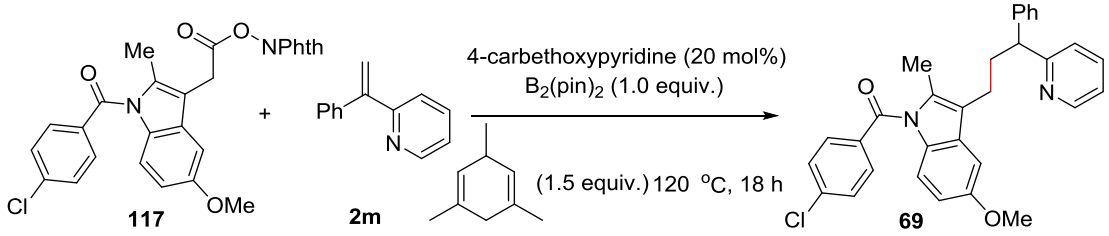
67: Prepared following *general procedure B using* **116** (60.6 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **67** (27.5 mg, 47% yield).

67: gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75-7.60 (m, 2H), 7.38-7.20 (m, 10H), 7.18-7.10 (m, 1H), 4.86 (d, *J* = 7.7 Hz, 2H), 4.50 (t, *J* = 7.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 153.7 (dd, J_{C-F} = 256.2, 12.7 Hz), 150.15 (dd, J_{C-F} = 250.0, 13.0 Hz), 141.0, 128.8, 128.3, 127.1, 126.6 (dd, J_{C-F} = 7.6, 3.8 Hz), 119.0 (d, J_{C-F} = 18.6 Hz), 117.5 (d, J_{C-F} = 18.0 Hz), 67.8, 50.00. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -130.1 (d, *J* = 21.0 Hz), -136.5 (d, *J* = 21.0 Hz). **HRMS** (APCI) exact mass calculated for $C_{20}H_{17}F_2$ $[M+H]^+$ 295.1293, found 295.1297.



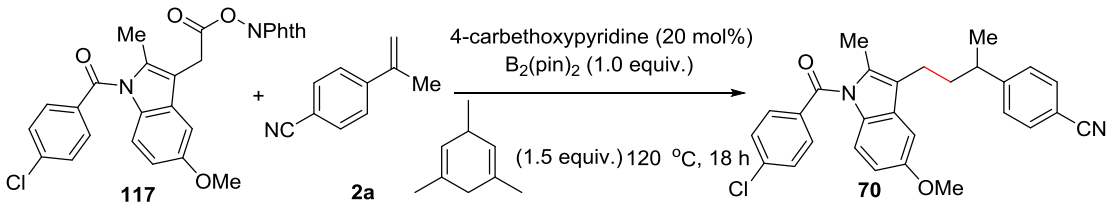
68: Prepared following *general procedure B using* **117** (104.0 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **68** (80.2 mg, 81% yield).

68: Yellow gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.35-7.30 (m, 8H), 7.25-7.18 (m, 2H), 6.94 (d, *J* = 8.9 Hz, 1H), 6.75 (s, 1H), 6.68 (d, *J* = 9.0 Hz, 1H), 4.02 (t, *J* = 7.6 Hz, 1H), 3.81 (s, 3H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.6 Hz, 2H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 155.9, 144.8, 139.0, 134.4, 134.0, 131.2, 131.1, 131.0, 129.1, 128.7, 127.9, 126.4, 119.7, 115.1, 111.3, 101.2, 55.8, 51.2, 35.6, 22.5, 13.4. **IR** (film): 2930, 2863, 1682, 1596, 1475, 1359, 1222, 1068 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{32}H_{29}ClNO_2$ $[M+H]^+$ 494.1881, found 494.1876.



69: Prepared following *general procedure B using* **117** (104.0 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **69** (82.0 mg, 84% yield).

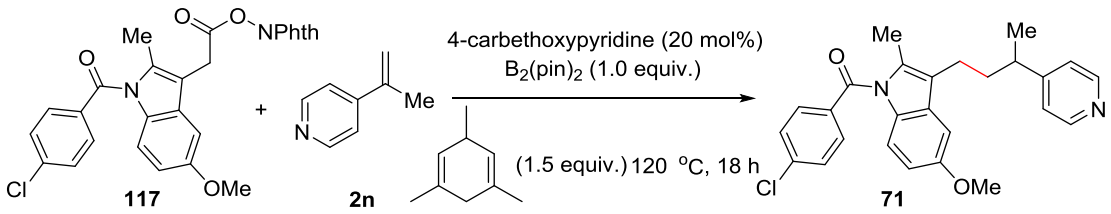
69: Yellow gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61-8.59 (m, 1H), 7.67-7.61 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.43 (m, 2H), 7.42-7.38 (m, 2H), 7.34-7.30 (m, 2H), 7.25-7.17 (m, 2H), 7.13-7.08 (m, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.83 (d, *J* = 2.5 Hz, 1H), 6.67-6.64 (m, 1H), 4.17 (t, *J* = 7.0 Hz, 1H), 3.81 (s, 3H), 2.70-2.60 (m, 3H), 2.45-2.34 (m, 1H), 2.20 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 163.6, 155.9, 149.3, 143.7, 138.9, 136.5, 134.4, 133.9, 131.3, 131.1, 131.0, 129.1, 128.7, 128.1, 126.7, 123.0, 121.5, 119.8, 115.0, 111.2, 101.4, 55.7, 53.4, 34.8, 22.4, 13.3. **IR** (film): 2929, 2832, 1679, 1589, 1475, 1324, 1223, 1088 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{31}H_{28}ClN_2O_2$ $[M+H]^+$ 495.1834, found 495.1834.



70: Prepared following *general procedure B using* **117** (104.0 mg, 0.2 mmol, 1.0 equiv.), **2a** (57.3 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **70** (67.2 mg, 74% yield).

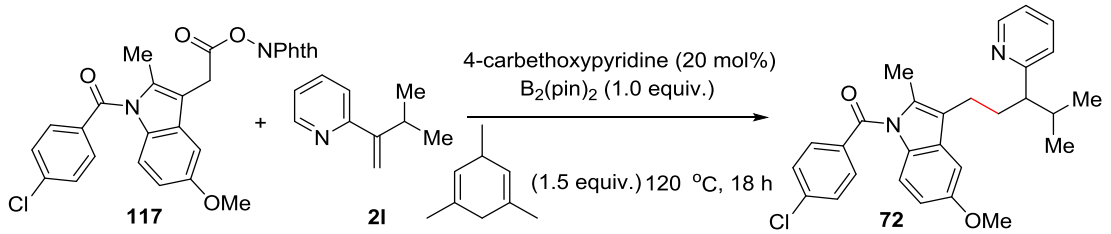
70: Yellow gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.51 (m, 4H), 7.49-7.42 (m, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 6.84 (d, *J* = 9.0 Hz, 1H), 6.72 (d, *J* = 2.5 Hz, 1H), 6.65-6.62 (m, 1H), 3.80 (s, 3H), 2.90-2.82 (m, 1H), 2.62-2.42 (m, 2H), 2.22 (s, 3H), 1.96-1.88 (m, 2H), 1.32 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 155.9, 152.8, 139.1, 134.3, 134.0, 132.4, 132.3, 131.1, 131.0, 129.2, 128.0, 119.3, 119.1, 115.1, 110.8,

110.1, 101.6, 55.8, 40.3, 37.5, 22.4, 22.1, 13.3. **IR** (film): 2928, 2858, 2226, 1681, 1606, 1476, 1223, 1088 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{28}H_{26}ClN_2O_2$ $[M+H]^+$ 457.1677, found 457.1670.



71: Prepared following *general procedure B using* **117** (104.0 mg, 0.2 mmol, 1.0 equiv.), **2n** (47.7 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **71** (68.4 mg, 79% yield).

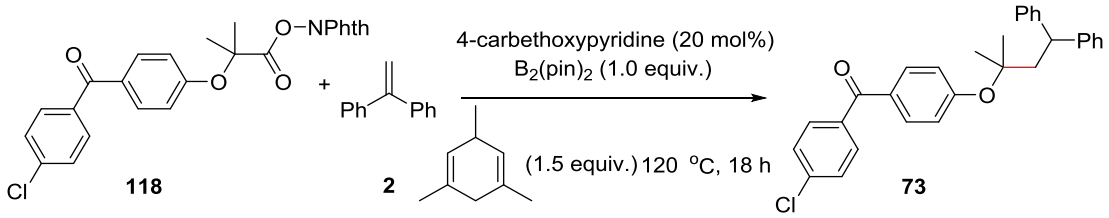
71: Yellow gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.67-8.43 (m, 2H), 7.65-7.58 (m, 2H), 7.50-7.39 (m, 2H), 7.20-7.16 (m, 2H), 6.84 (d, *J* = 8.9 Hz, 1H), 6.73 (d, *J* = 2.5 Hz, 1H), 6.65-6.62 (m, 1H), 3.79 (s, 3H), 2.84-2.74 (m, 1H), 2.62-2.42 (m, 2H), 2.22 (s, 3H), 1.95-1.87 (m, 2H), 1.31 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.3, 156.5, 155.9, 149.8, 139.1, 134.2, 134.0, 131.1, 131.0, 130.9, 129.1, 122.8, 119.3, 115.1, 111.0, 101.4, 55.8, 39.5, 37.1, 24.9, 22.0, 13.3. **IR** (film): 2929, 2833, 1682, 1597, 1475, 1317, 1222, 1088 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{26}H_{26}ClN_2O_2$ $[M+H]^+$ 433.1677, found 433.1677.



72: Prepared following *general procedure B using* **117** (104.0 mg, 0.2 mmol, 1.0 equiv.), **2l** (58.9 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the

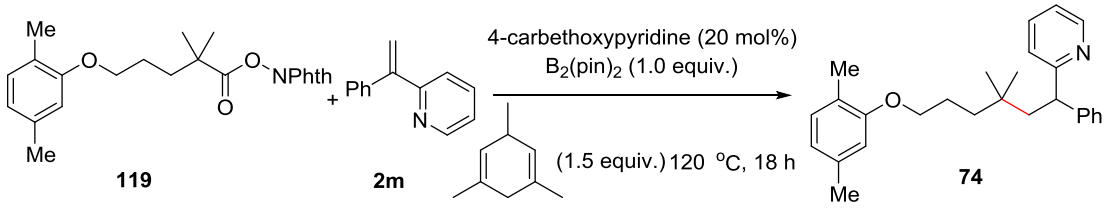
reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product 7**2** (50.2 mg, 54% yield).

72: Yellow gum. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66-8.60 (m, 1H), 7.68-7.58 (m, 3H), 7.50-7.40 (m, 2H), 7.19-7.11 (m, 2H), 6.88 (d, *J* = 8.9 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 6.65-6.62 (m, 1H), 3.82 (s, 3H), 2.62-2.54 (m, 1H), 2.50-2.40 (m, 1H), 2.35-2.27 (m, 1H), 2.15 (s, 3H), 2.13-1.93 (m, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.75 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.4, 164.2, 155.9, 149.3, 139.0, 136.0, 134.5, 133.7, 131.3, 131.1, 129.3, 129.1, 123.9, 121.4, 120.3, 115.1, 111.1, 101.6, 55.8, 54.9, 33.2, 31.8, 22.5, 21.0, 20.8, 13.3. **IR** (film): 2955, 2868, 1679, 1589, 1475, 1324, 1222, 1088 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{28}H_{30}ClN_2O_2$ $[M+H]^+$ 461.1990, found 461.1991.



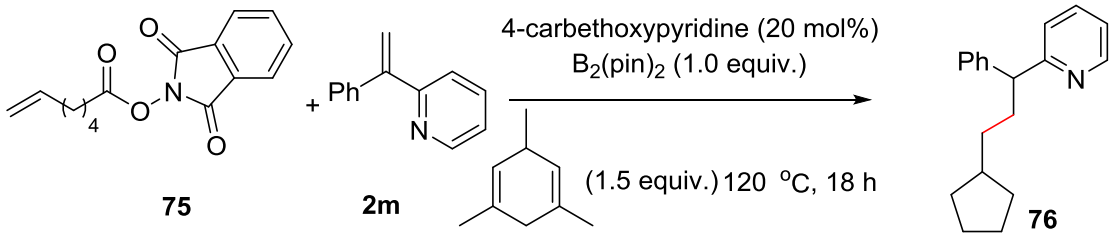
73: Prepared following *general procedure B using* **118** (92.8 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **73** (46.4 mg, 51% yield).

73: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (t, *J* = 7.4 Hz, 4H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.32 (d, *J* = 7.7 Hz, 4H), 7.26 (t, *J* = 7.9 Hz, 4H), 7.15 (t, *J* = 7.1 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 4.35 (t, *J* = 6.7 Hz, 1H), 2.63 (d, *J* = 6.4 Hz, 2H), 1.28 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.6, 160.2, 145.9, 138.5, 136.5, 131.8, 131.3, 131.2, 128.7, 128.6, 127.9, 126.3, 121.9, 82.0, 48.0, 47.5, 27.6. **IR** (film): 2975, 2934, 1656, 1596, 1494, 1253, 1124, 1089 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{30}H_{28}ClO_2$ $[M+H]^+$ 455.1772, found 455.1769.



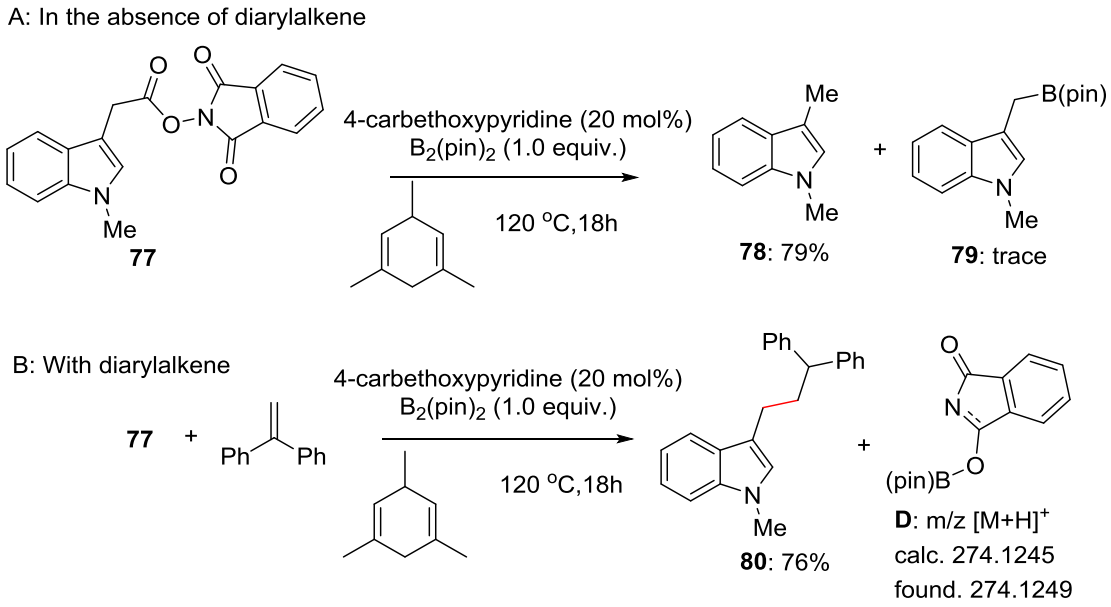
74: Prepared following *general procedure B using* **119** (79.1 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 5:1) to afford the product **74** (64.4 mg, 83% yield).

74: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 1H), 7.52-7.44 (m, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.24 (t, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 6.6 Hz, 2H), 6.64 (d, *J* = 7.4 Hz, 1H), 6.57 (s, 1H), 4.20 (t, *J* = 6.5 Hz, 1H), 3.78 (t, *J* = 6.5 Hz, 2H), 2.56-2.45 (m, 1H), 2.30 (s, 3H), 2.18 (s, 3H), 2.07-2.00 (m, 1H), 1.73-1.65 (m, 2H), 1.40-1.30 (m, 2H), 0.81 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.9, 157.2, 149.2, 145.8, 136.5, 130.3, 128.5, 128.1, 128.0, 126.2, 123.6, 123.0, 121.2, 120.7, 112.1, 68.6, 50.3, 46.4, 38.7, 33.8, 27.9, 24.4, 21.5, 16.0. **IR** (film): 2952, 2866, 1586, 1508, 1453, 1264, 1129, 1048 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{27}H_{34}NO$ $[M+H]^+$ 388.2635, found 388.2636.



Experimental procedure: Following *general procedure B*, a mixture of **75** (54.6 mg, 0.2 mmol, 1.0 equiv.), **2m** (72.5 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 eq.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxy-pyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) was stirred at 120 °C. After 18 h, with the described workup procedure, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **76** (34.3 mg, 65% yield).

76: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.7 Hz, 1H), 7.58-7.50 (m, 1H), 7.34 (d, *J* = 7.2 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.21-7.11 (m, 2H), 7.08-7.02 (m, 1H), 4.03 (t, *J* = 7.8 Hz, 1H), 2.28-2.18 (m, 1H), 2.12-2.03 (m, 1H), 1.82-1.71 (m, 3H), 1.58-1.44 (m, 4H), 1.28-1.22 (m, 2H), 1.08-0.96 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 149.3, 144.1, 136.5, 128.5, 128.1, 126.4, 122.7, 121.3, 54.3, 40.3, 34.6, 34.4, 32.8, 32.7, 25.3. **IR** (film): 2945, 2863, 1588, 1507, 1452, 1431, 1147, 1031 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{24}N$ $[M+H]^+$ 266.1903, found 266.1903.

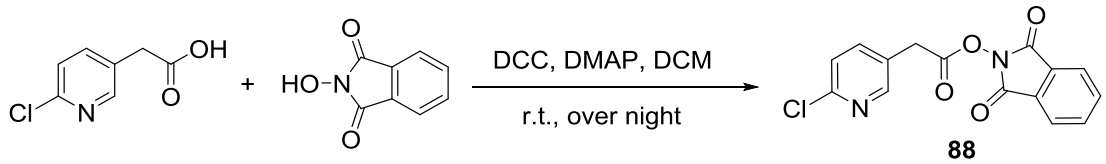


Experimental procedure: Condition A, a mixture of **77** (66.8 mg, 0.2 mmol, 1.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) was stirred at 120 °C. After 18 h, with the described workup procedure, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 20:1) to afford the product **78** (23.0 mg, 79% yield).

78: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.33-7.23 (m, 2H), 7.15 (t, *J* = 7.28 Hz, 1H), 6.84 (s, 1H), 3.74 (s, 3H), 2.37 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 137.1, 128.7, 128.1, 126.6, 121.5, 119.0, 118.6, 110.2, 109.1, 32.6, 9.7. **IR** (film): 2929, 2883, 1484, 1471, 1423, 1367, 1324, 1247 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{10}H_{12}N$ $[M+H]^+$ 146.0964, found 146.0960.

Condition B, a mixture of **77** (66.8 mg, 0.2 mmol, 1.0 equiv.), **2** (72.1 mg, 0.4 mmol, 2.0 equiv.), $B_2(pin)_2$ (50.8 mg, 1.0 equiv.), 1,3,5-trimethyl-1,4-cyclohexadiene (36.7 mg, 0.3 mmol, 1.5 equiv.), 4-carbethoxypyridine (6.0 mg, 20 mol%) and CF_3-Ph (1 mL) was stirred at 120 °C. After 18 h, following the described step, the reaction mixture was isolated with prepared TLC on silica (PE/EA = 10:1) to afford the product **80** (49.5 mg, 76% yield).

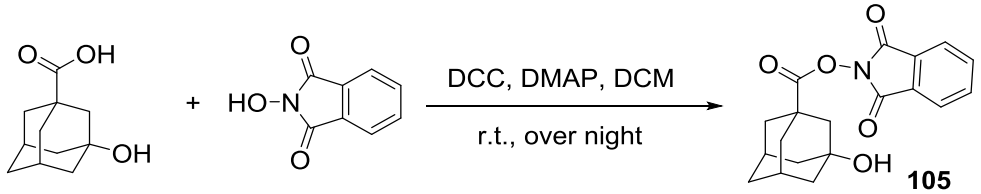
80: Colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.53 (m, 1H), 7.46-7.23 (m, 12H), 7.18-7.13 (m, 1H), 6.85 (t, *J* = 2.6 Hz, 1H), 4.13-4.07 (m, 1H), 3.78 (s, 3H), 2.82-2.77 (m, 2H), 2.60-2.52 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 137.2, 130.1, 128.6, 128.1, 127.6, 126.2, 121.6, 119.2, 118.6, 114.9, 109.2, 51.0, 36.4, 32.6, 23.5. **IR** (film): 3024, 2923, 1492, 1472, 1325, 1244, 1030, 1012 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{24}H_{24}N$ $[M+H]^+$ 326.1903, found 326.1903.



88

88: The carboxylic acid (1.0 g, 6.0 mmol) was coupled with N-hydroxyphthalimide according to g*eneral procedure A*. The crude residue was purified by flash column chromatography (petroleum ether/EtOAc = 5:1) to afford the corresponding NHPI ester **88** (0.9 g, 48%) as a white solid.

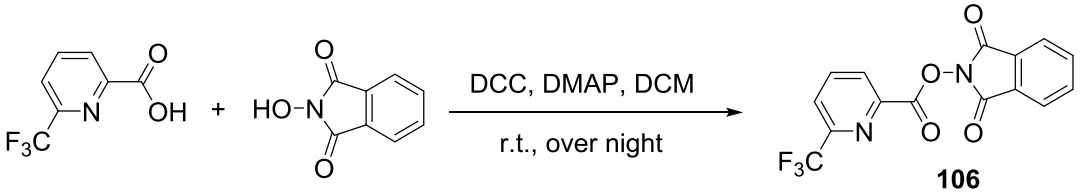
88: m.p.: 139-141 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 2.5 Hz, 1H), 7.91-7.85 (m, 2H), 7.80-7.76 (m, 2H), 7.74-7.71 (m, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 3.99 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 161.7, 151.2, 150.2, 139.7, 135.1, 128.8, 126.6, 124.6, 124.2, 34.3. **IR** (film): 2923, 1815, 1789, 1743, 1464, 1356, 1186, 1077 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_{10}ClN_2O_4$ $[M+H]^+$ 317.0324, found 317.0325.



105

105: The carboxylic acid (0.98 g, 5.0 mmol) was coupled with N-hydroxyphthalimide according to g*eneral procedure A*. The crude residue was purified by flash column chromatography (petroleum ether/EtOAc = 5:1) to afford the corresponding NHPI ester **105** (1.0 g, 59%) as a white solid.

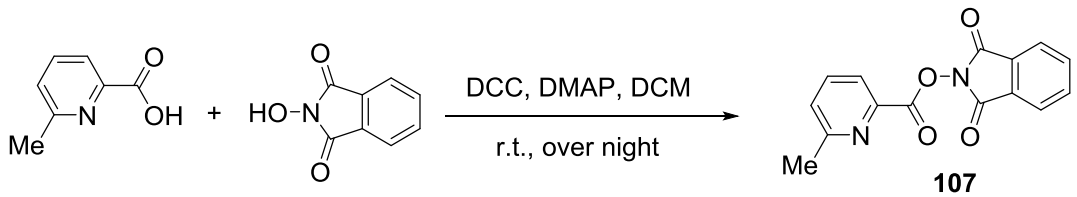
105: m.p.: 172-174 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89-7.84 (m, 2H), 7.80-7.74 (m, 2H), 2.35-2.31 (m, 2H), 2.07 (s, 2H), 2.04-2.01 (m, 4H), 1.76 (d, *J* = 2.6 Hz, 4H), 1.69 (s, 1H), 1.67-1.63 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 162.1, 134.8, 129.1, 124.0, 68.1, 45.9, 44.1, 43.7, 37.5, 34.8, 34.0, 30.2, 25.7, 25.0. **IR** (film): 3523, 2920, 2857, 1808, 1780, 1744, 1355, 1181 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{19}H_{20}NO_5$ $[M+H]^+$ 342.1336, found 342.1336.



106

106: The carboxylic acid (0.95 g, 5.0 mmol) was coupled with N-hydroxyphthalimide according to g*eneral procedure A*. The crude residue was purified by flash column chromatography (petroleum ether/EtOAc = 10:1) to afford the corresponding NHPI ester **106** (1.3g, 78%) as a white solid.

106: m.p.: 165-167 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 7.8 Hz, 1H), 8.17(t, *J* = 8.1 Hz, 1H), 8.02-7.98 (m, 1H), 7.94 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.83 (dd, *J* = 5.5, 3.1 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 160.7, 149.3 (q, $J_{C\text{-}F}$ = 35.9 Hz), 144.9, 139.4, 135.1, 134.8, 129.0, 125.1 (q, $J_{C\text{-}F}$ = 2.9 Hz), 124.3, 120.9 (q, $J_{C\text{-}F}$ = 275.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -67.78. **IR** (film): 3091, 2930, 1781, 1746, 1467, 1343, 1186, 1048 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_8F_3N_2O_4$ $[M+H]^+$ 337.0431, found 337.0431.

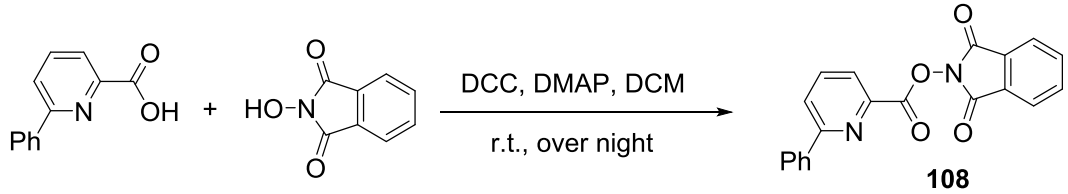


107

107: The carboxylic acid (0.69 g, 5.0 mmol) was coupled with N-hydroxyphthalimide according to g*eneral procedure A*. The crude residue was purified by flash column

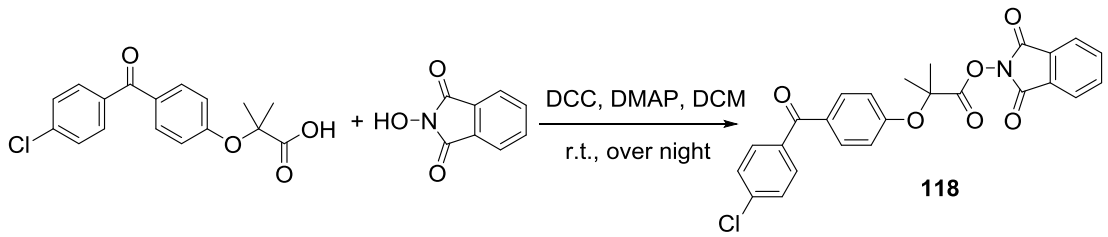
chromatography (SiO_2; 3:1 petroleum ether: EtOAc) to afford the corresponding NHPI ester **107** (0.87g, 62%) as a white solid.

107: m.p.: 190-192 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.9 Hz, 1H), 7.93-7.87(m, 2H), 7.84-7.78 (m, 3H), 7.45 (d, *J* = 7.8, 1H), 2.68 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.8, 160.0, 143.7, 137.4, 134.9, 131.3, 129.1, 128.5, 124.2, 116.7, 24.7. **IR** (film): 3514, 3068, 1771, 1742, 1594, 1465, 1374, 1050 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{15}H_{11}N_2O_4$ $[M+H]^+$ 283.0713, found 283.0713.



108: The carboxylic acid (1.0 g, 5.0 mmol) was coupled with N-hydroxyphthalimide according to g*eneral procedure A*. The crude residue was purified by flash column chromatography (petroleum ether/EtOAc = 10:1) to afford the corresponding NHPI ester **108** (1.5 g, 87%) as a white solid.

108: m.p.: 197-199 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.4 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 2H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 7.6 Hz, 1H), 7.97-7.90 (m, 2H), 7.85-7.80 (m, 2H), 7.54-7.45 (m, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 162.0, 161.8, 158.5, 144.4, 138.1, 137.9, 135.0, 130.0, 129.2, 129.1, 127.4, 125.1, 125.0, 124.2. **IR** (film): 3063, 1774, 1742, 1586, 1449, 1361, 1185, 1036 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{20}H_{13}N_2O_4$ $[M+H]^+$ 345.0870, found 345.0872.



118: The carboxylic acid (0.64 g, 2.0 mmol) was coupled with N-hydroxyphthalimide according to g*eneral procedure A*. The crude residue was purified by flash column chromatography (petroleum ether/EtOAc = 10:1) to afford the corresponding NHPI ester **118** (0.81 g, 86%) as a white solid.

118: m.p.: 123-125 ℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93-7.85 (m, 2H), 7.83-7.76 (m, 4H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 1.87 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.4, 170.5, 161.8, 158.7, 138.6, 136.4, 135.1, 132.2, 131.6, 131.4, 129.0, 128.7, 124.2, 118.6, 78.8, 25.9. **IR** (film): 3064, 2995, 1787, 1746, 1656, 1598, 1244, 1067 cm^{-1}. **HRMS** (ESI-TOF) exact mass calculated for $C_{25}H_{19}ClNO_6$ $[M+H]^+$ 464.0895, found 464.0895.

NMR Spectra

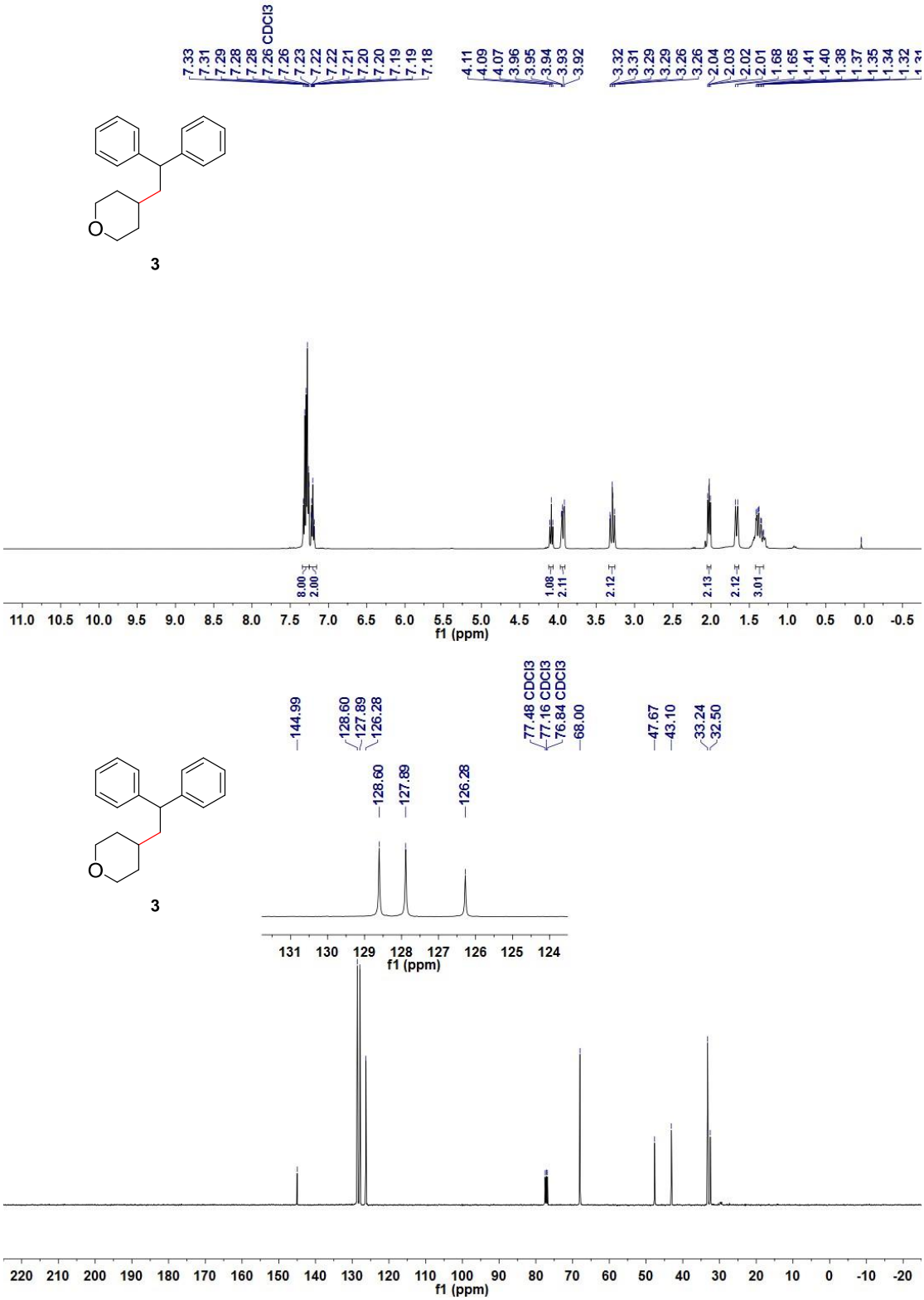


Figure S16. ^{1}H and ^{13}C NMR spectra for compound **3**

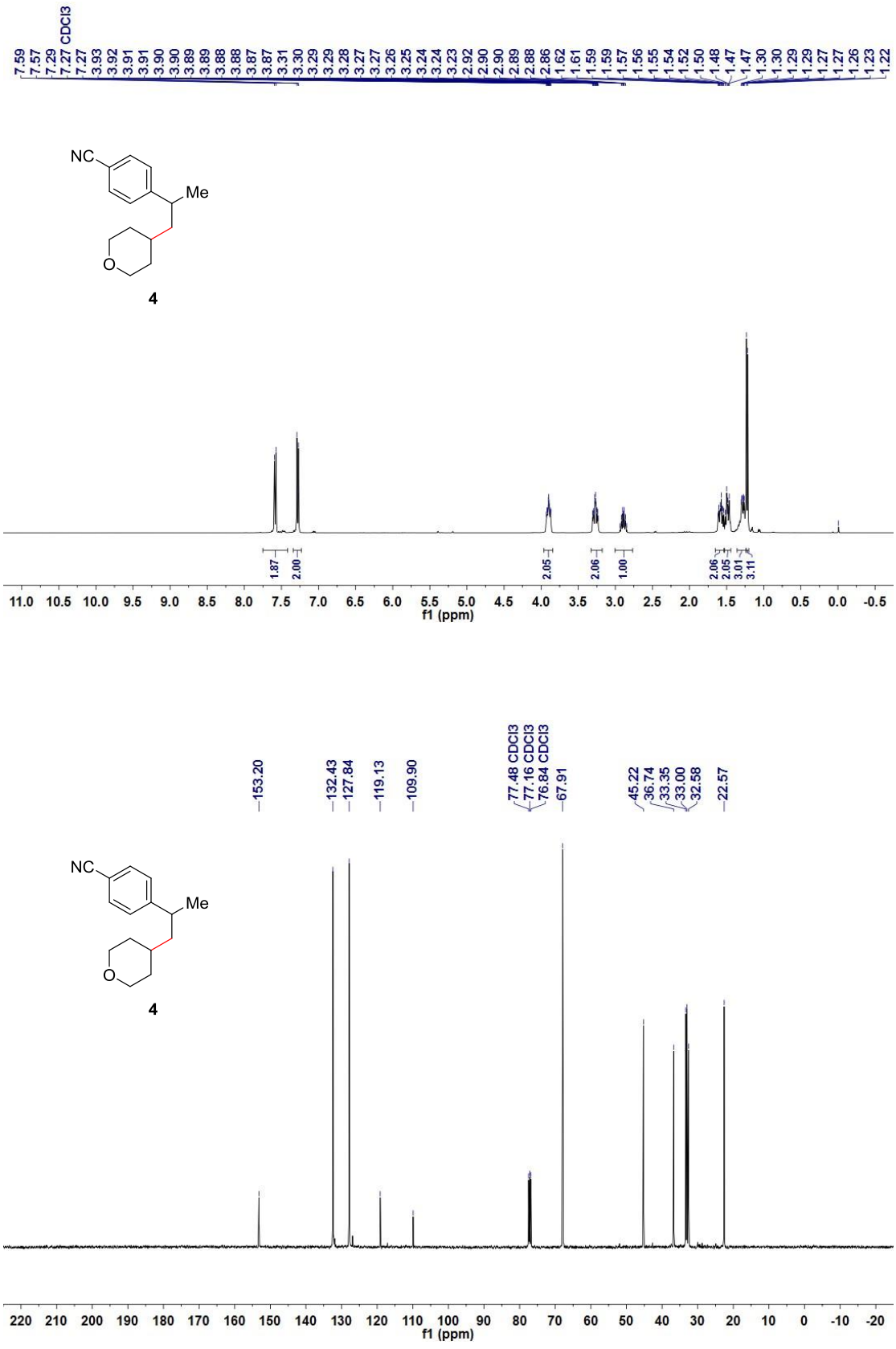


Figure S17. ^{1}H and ^{13}C NMR spectra for compound **4**

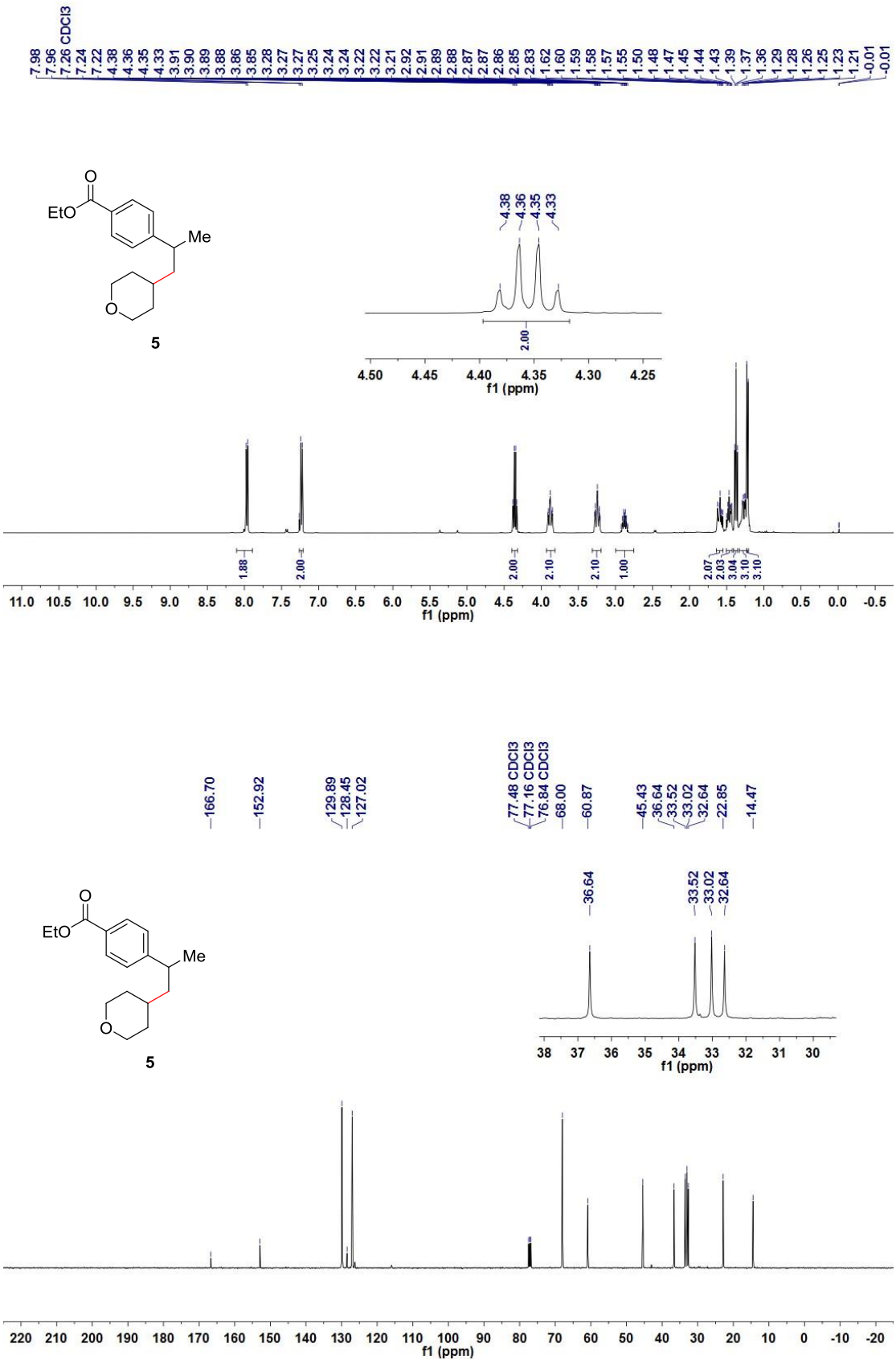


Figure S18. ^{1}H and ^{13}C NMR spectra for compound **5**

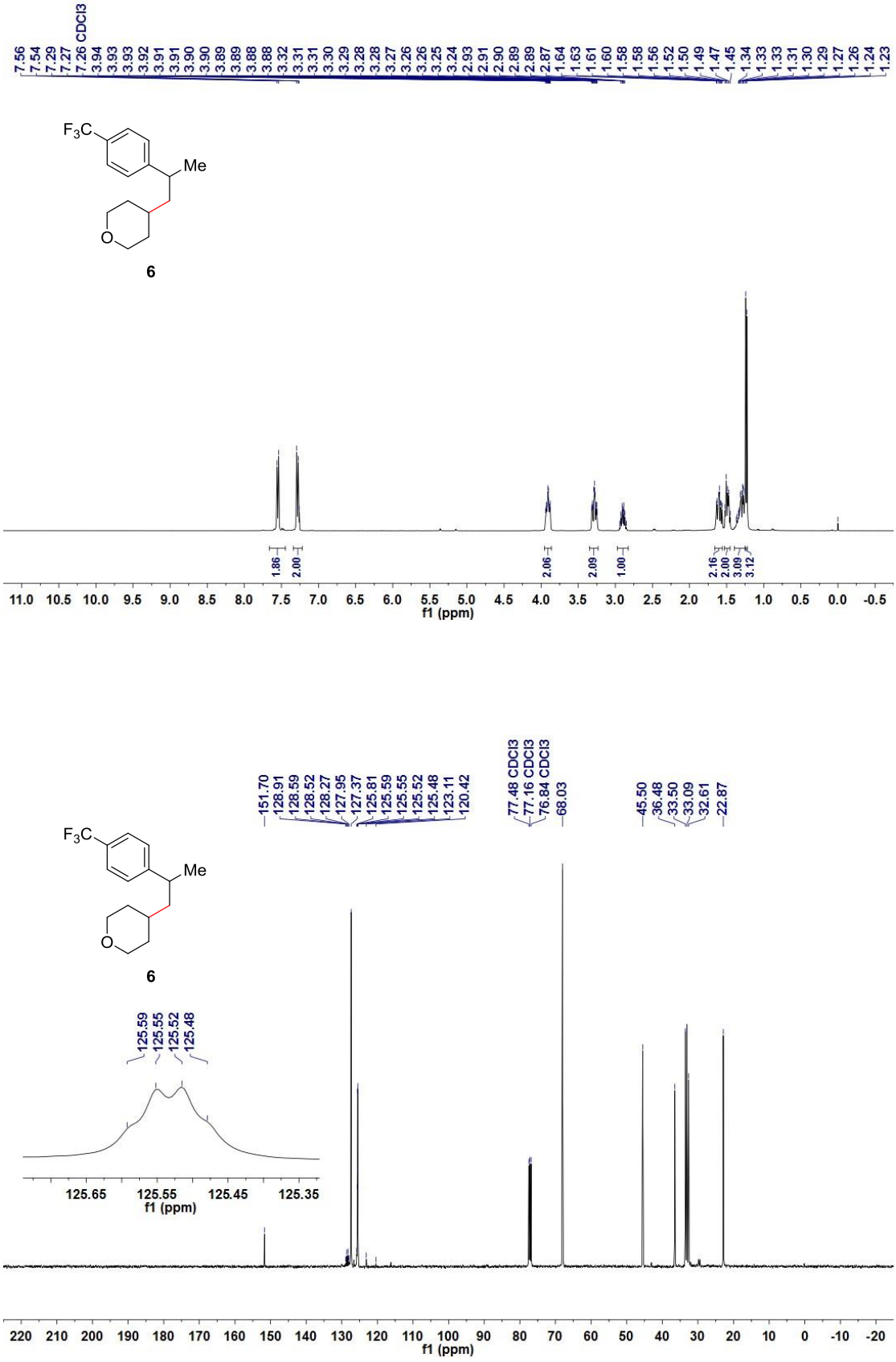


Figure S19 ^{1}H and ^{13}C NMR spectra for compound **6**

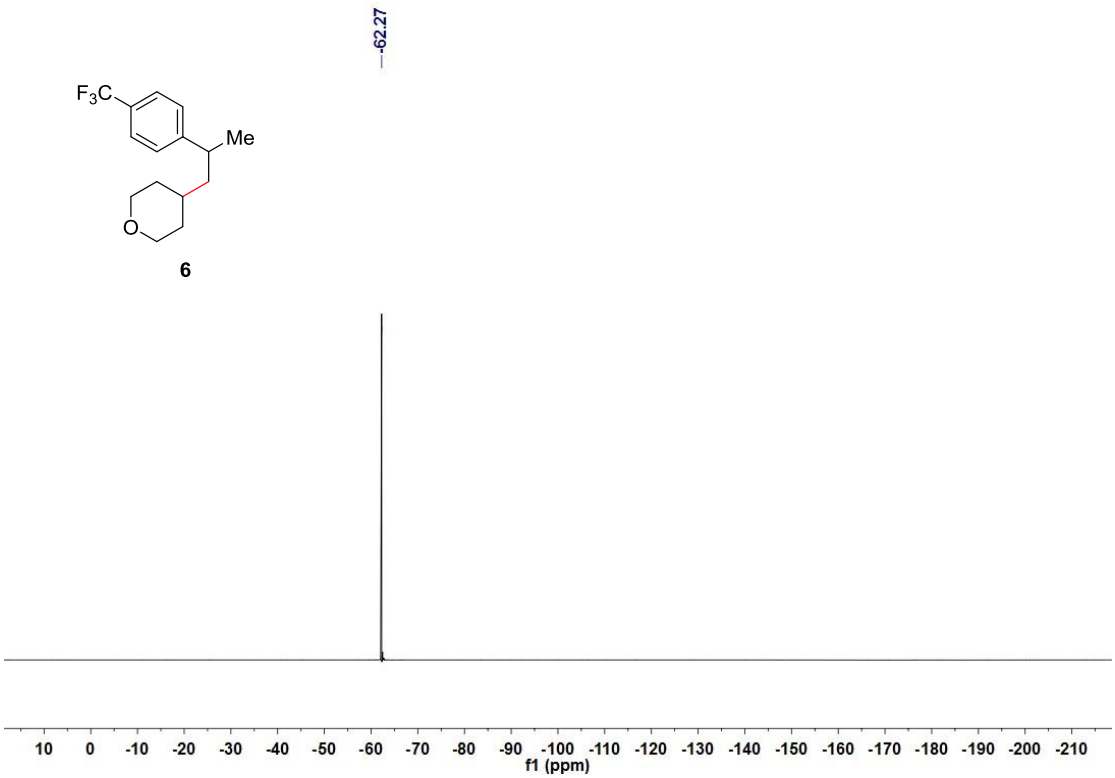


Figure 20. ^{19}F NMR spectra for compound **6**

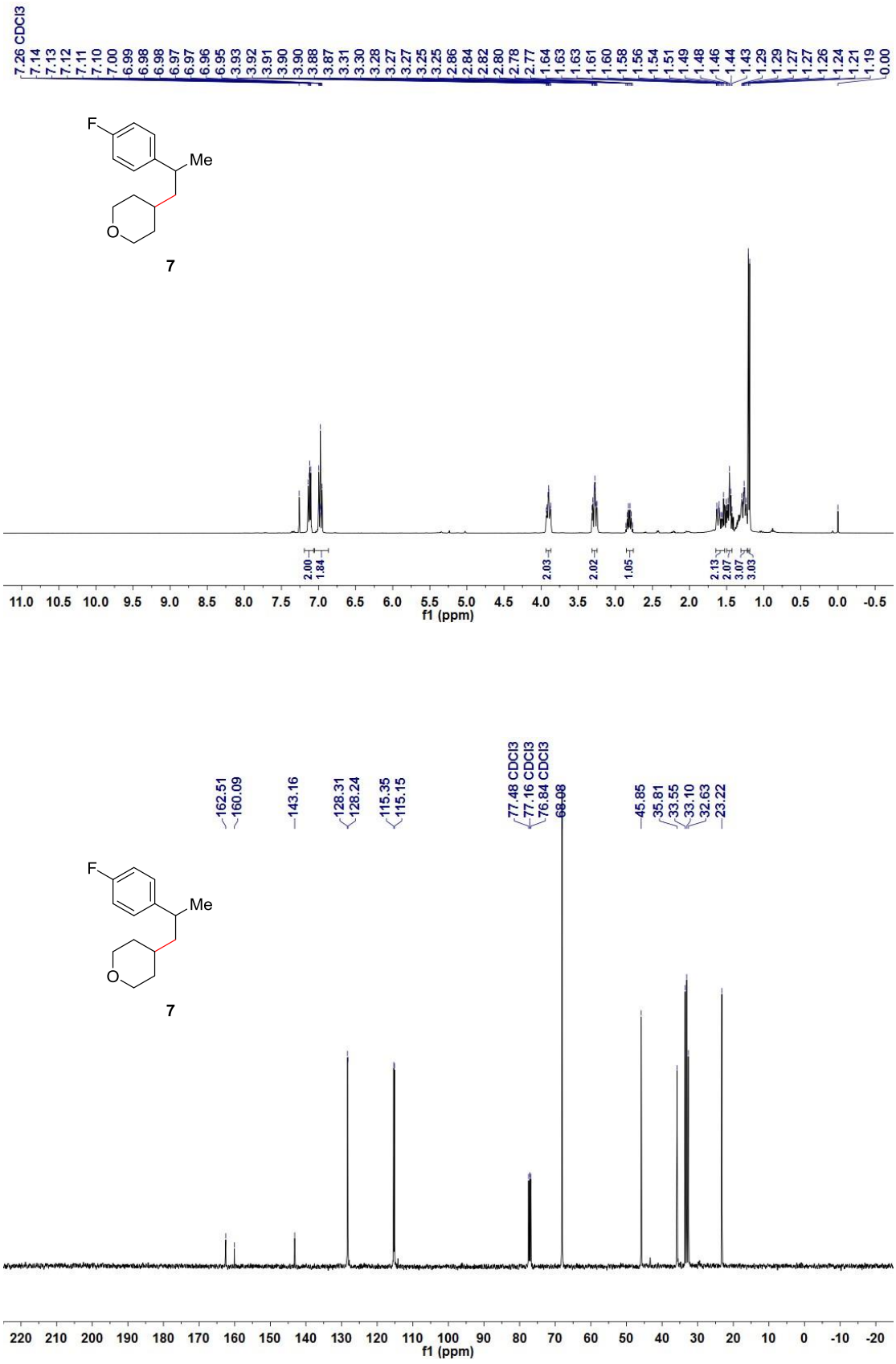


Figure S21. ^{1}H and ^{13}C NMR spectra for compound **7**

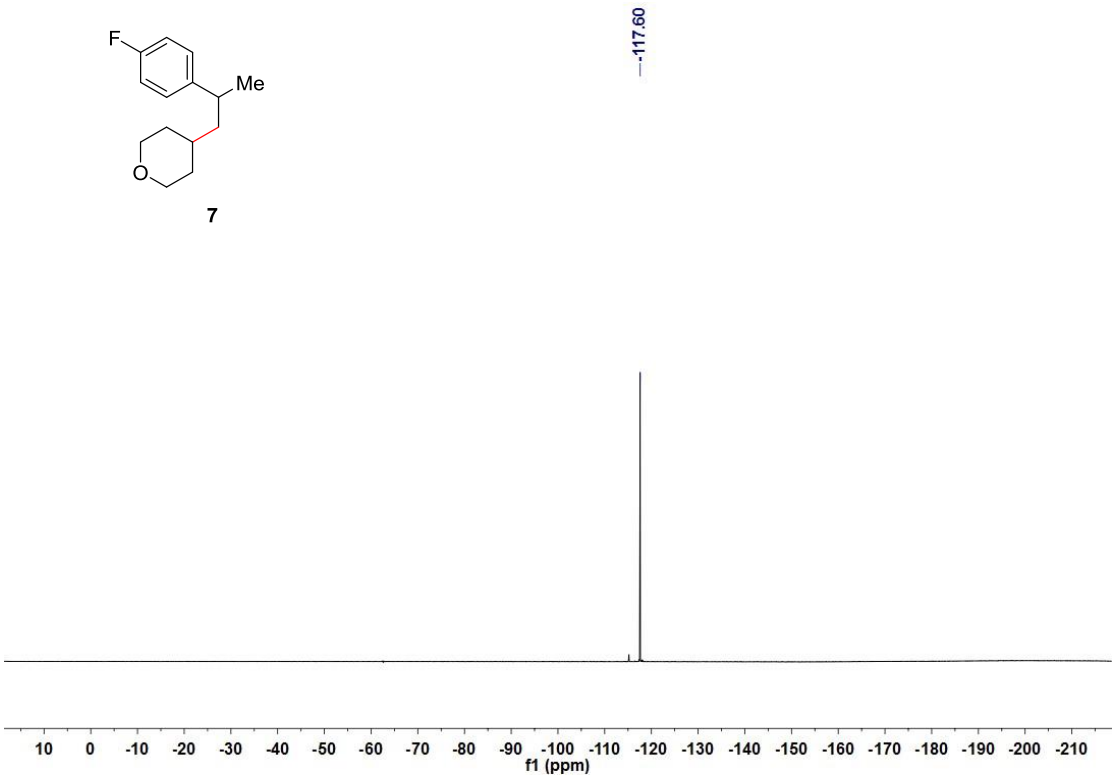


Figure S22. ^{19}F NMR spectra for compound **7**

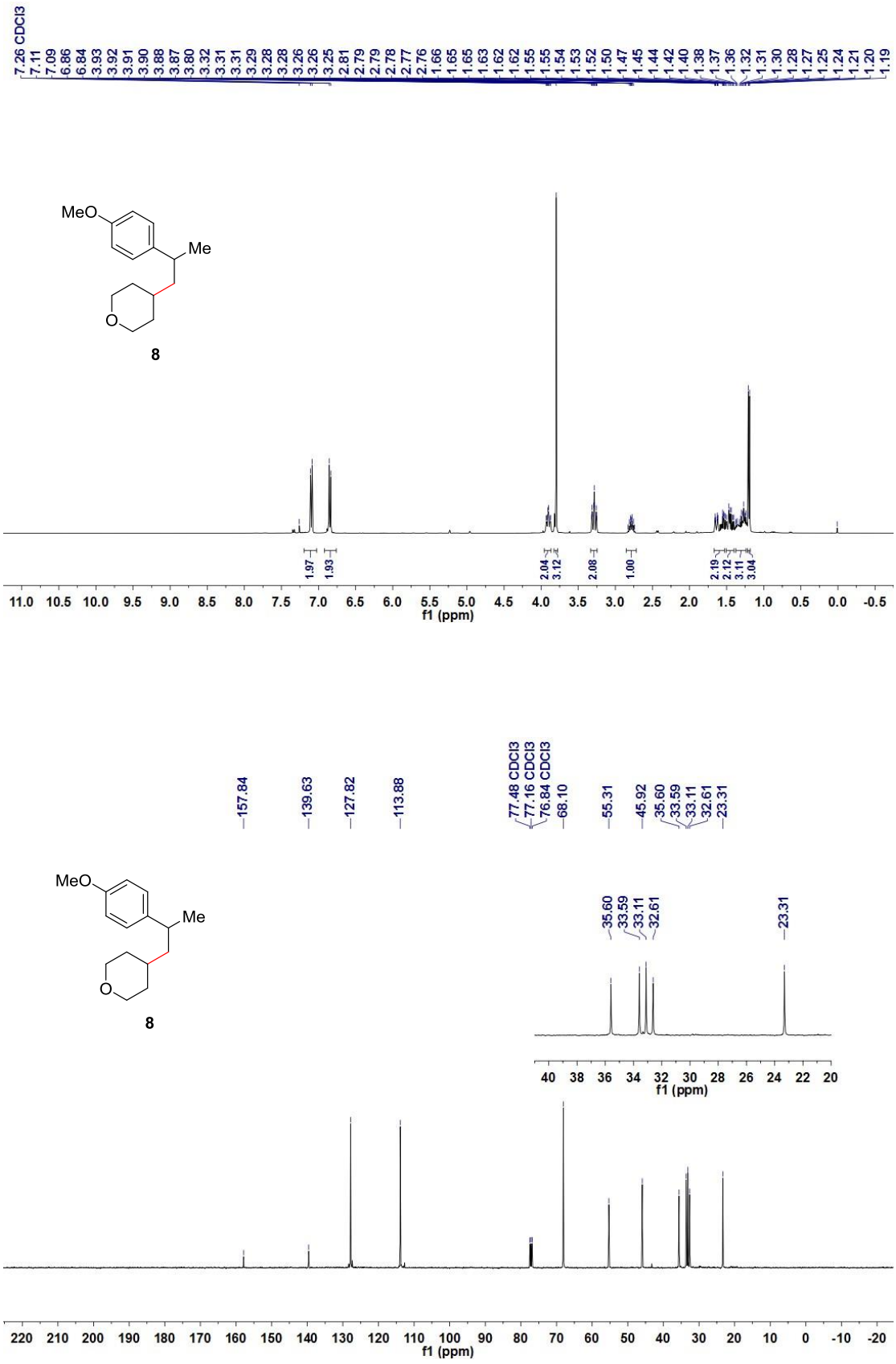


Figure S23. ^{1}H and ^{13}C NMR spectra for compound **8**

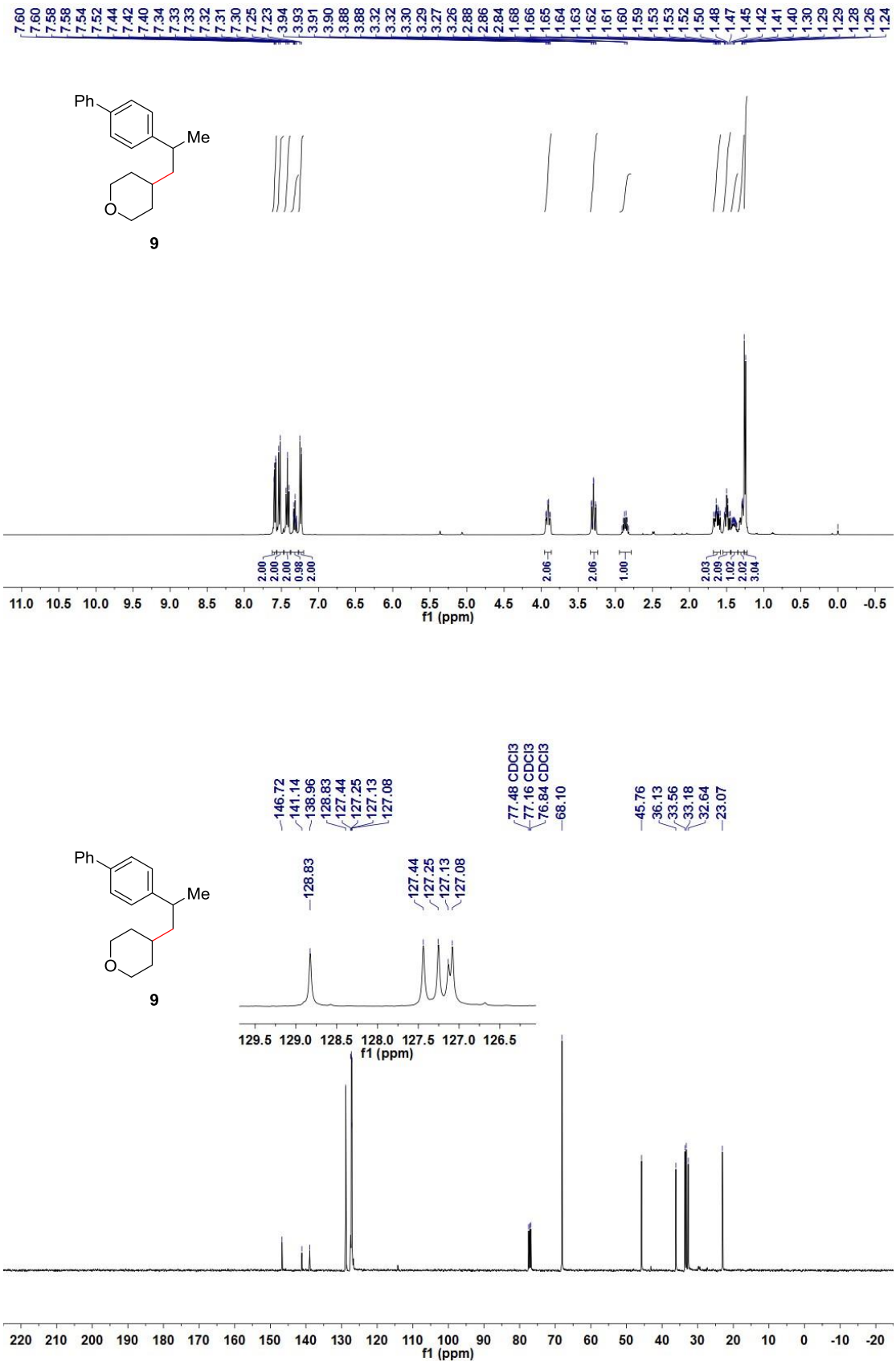


Figure S24. ^{1}H and ^{13}C NMR spectra for compound **9**

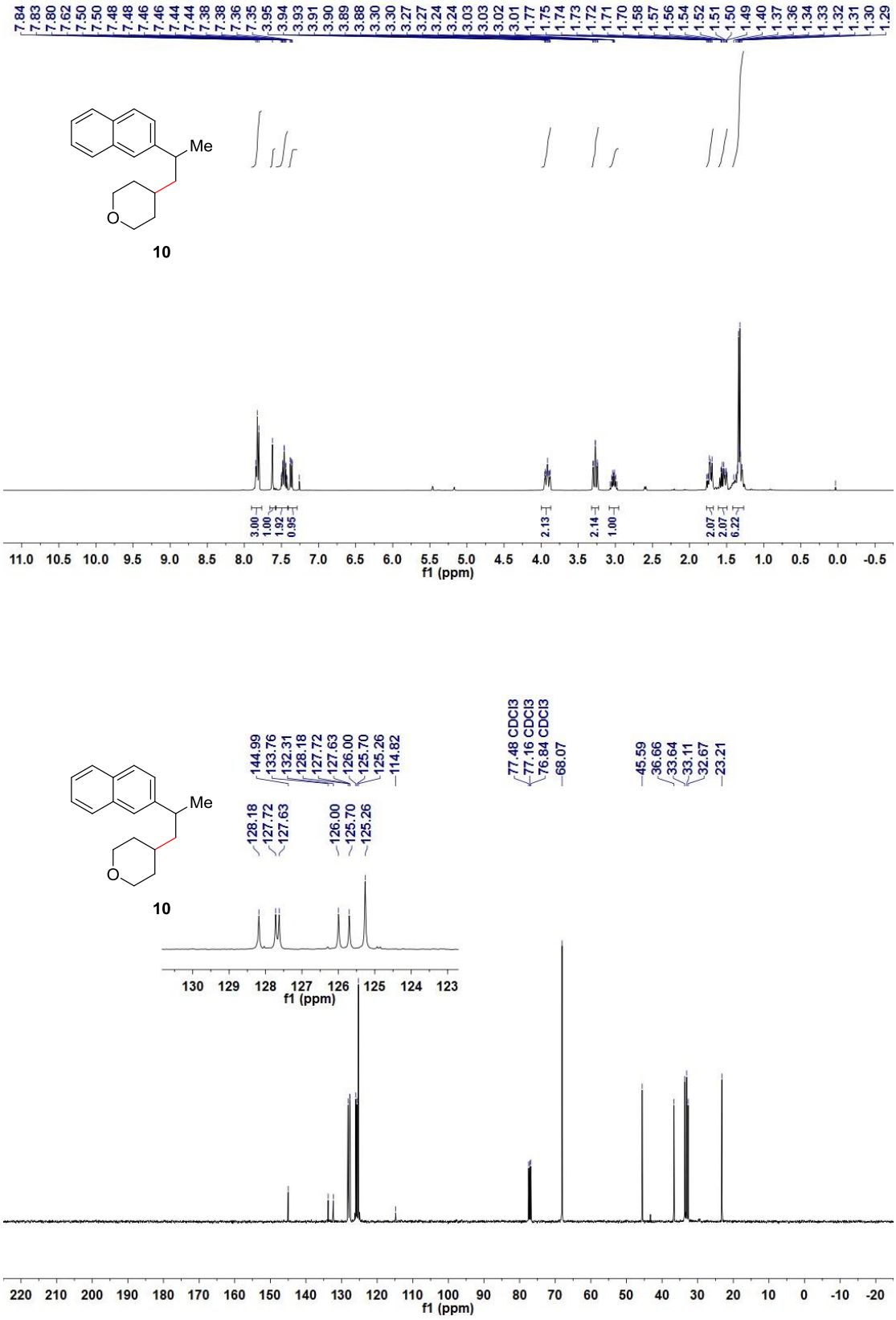


Figure S25. ^{1}H and ^{13}C NMR spectra for compound **10**

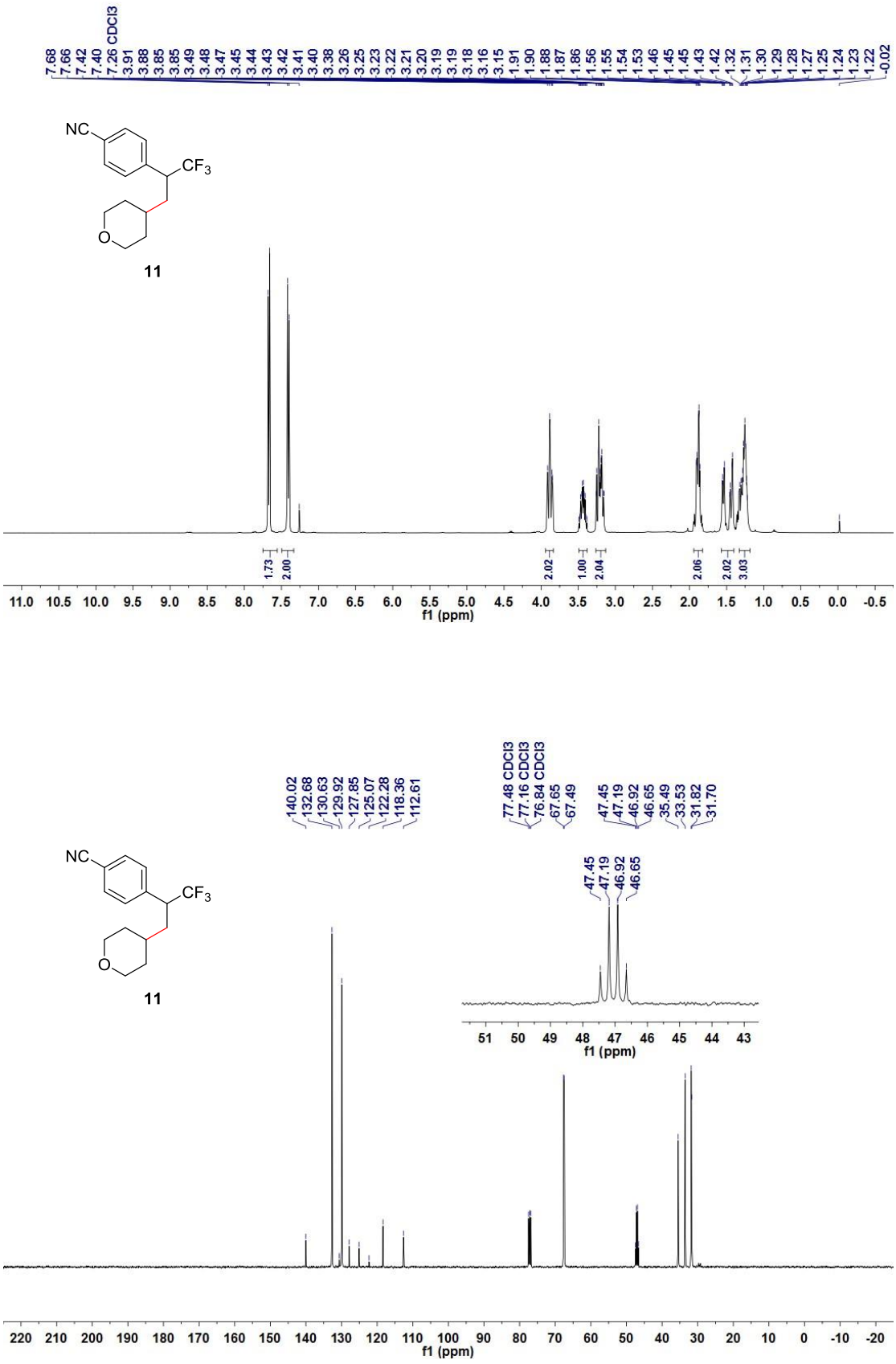


Figure S26. ^{1}H and ^{13}C NMR spectra for compound **11**

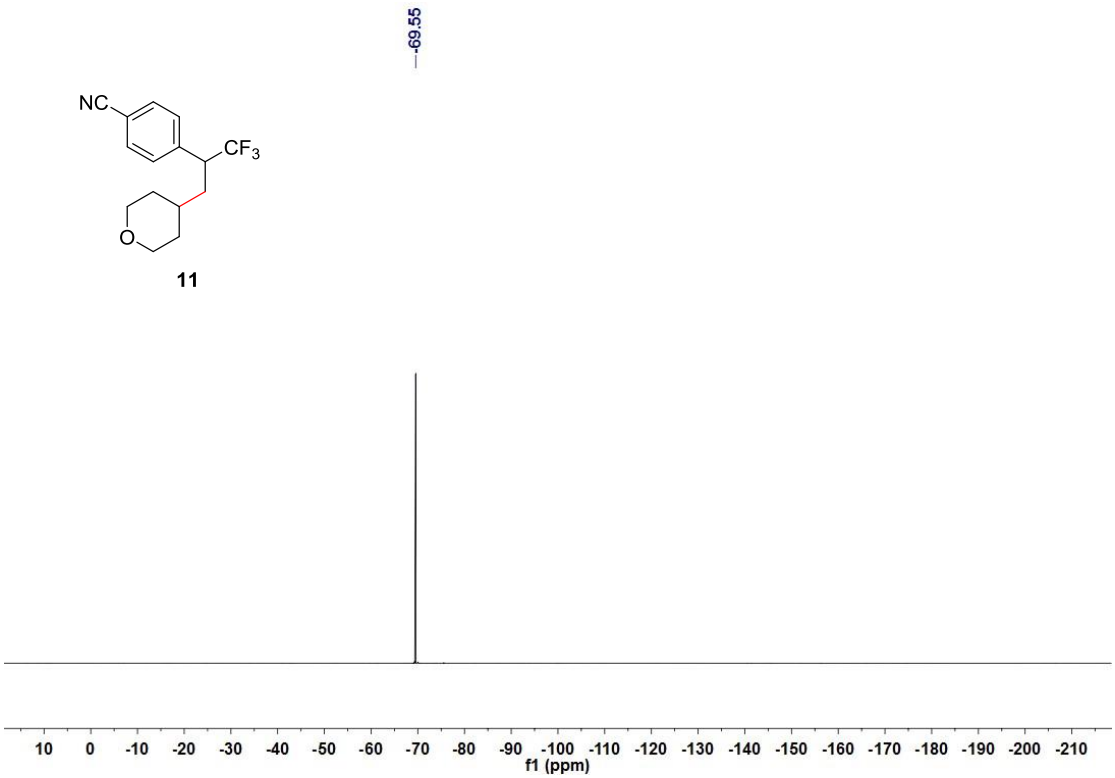


Figure S27. ^{19}F NMR spectra for compound **11**

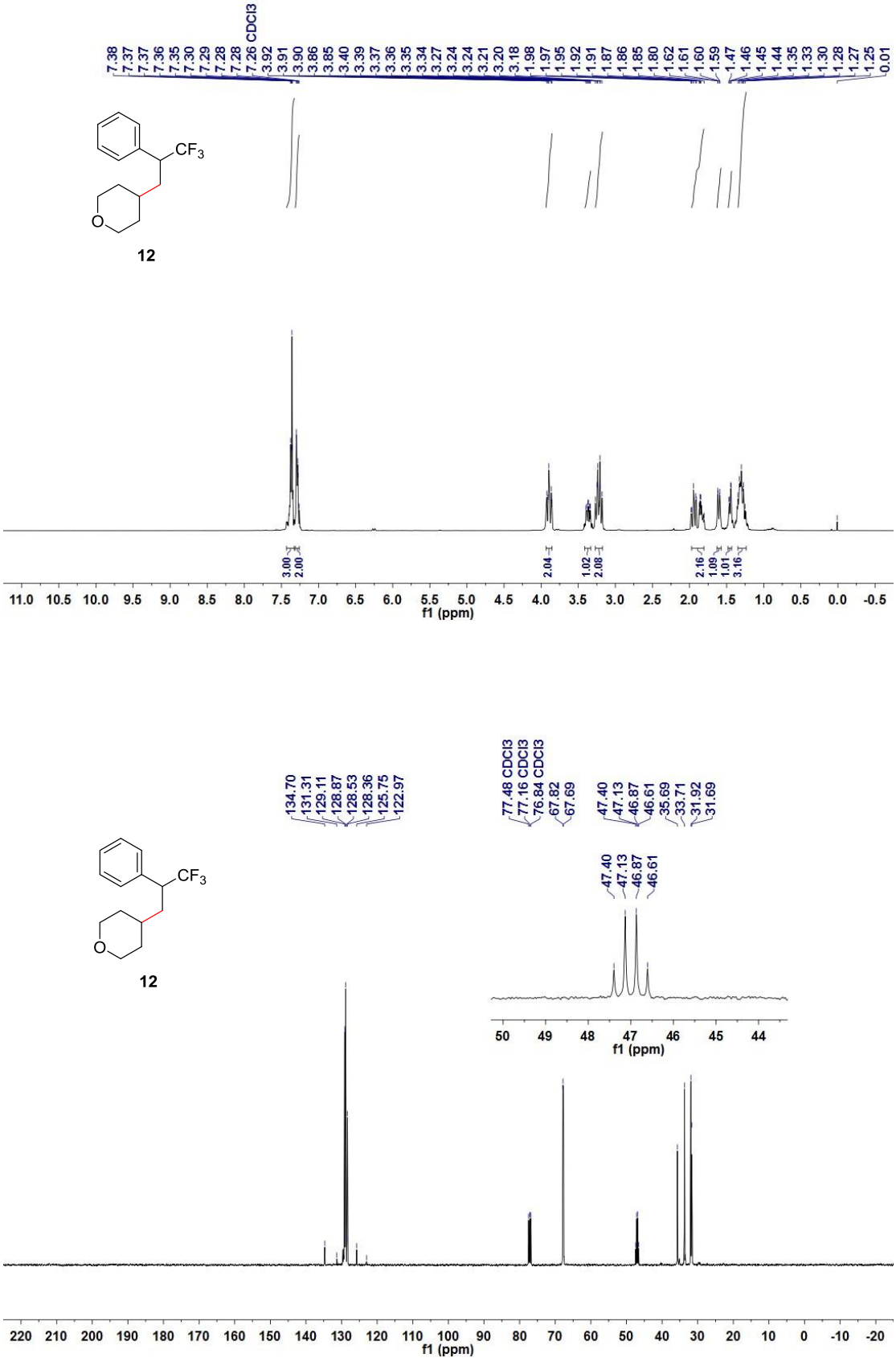


Figure S28. ^{1}H and ^{13}C NMR spectra for compound **12**

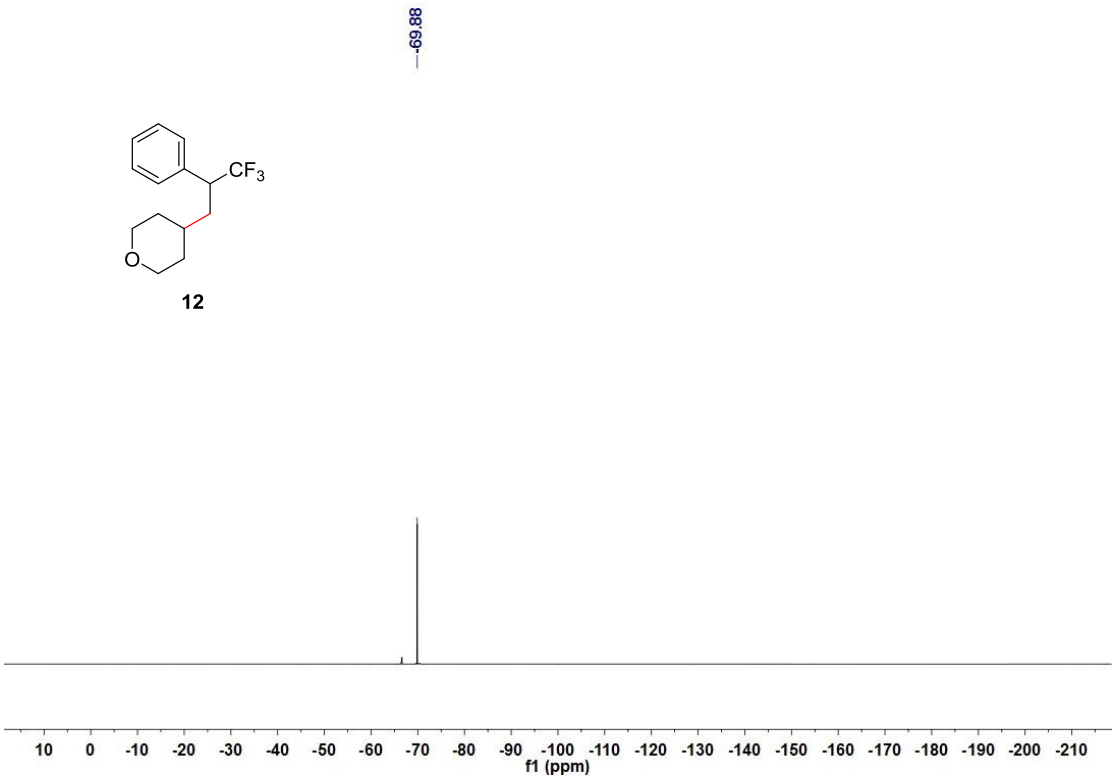


Figure S29. ^{19}F NMR spectra for compound **12**

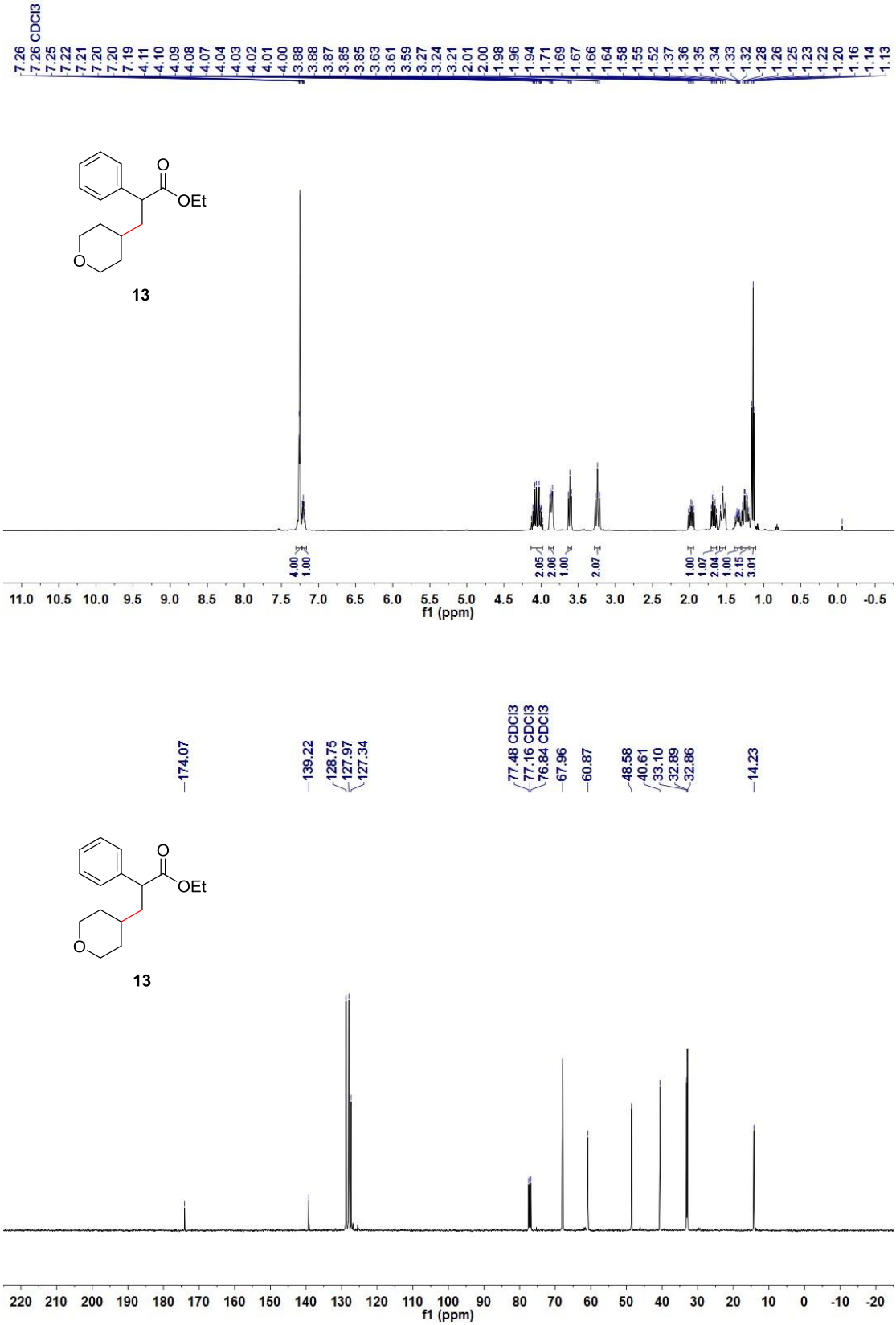


Figure S30. ^{1}H and ^{13}C NMR spectra for compound **13**

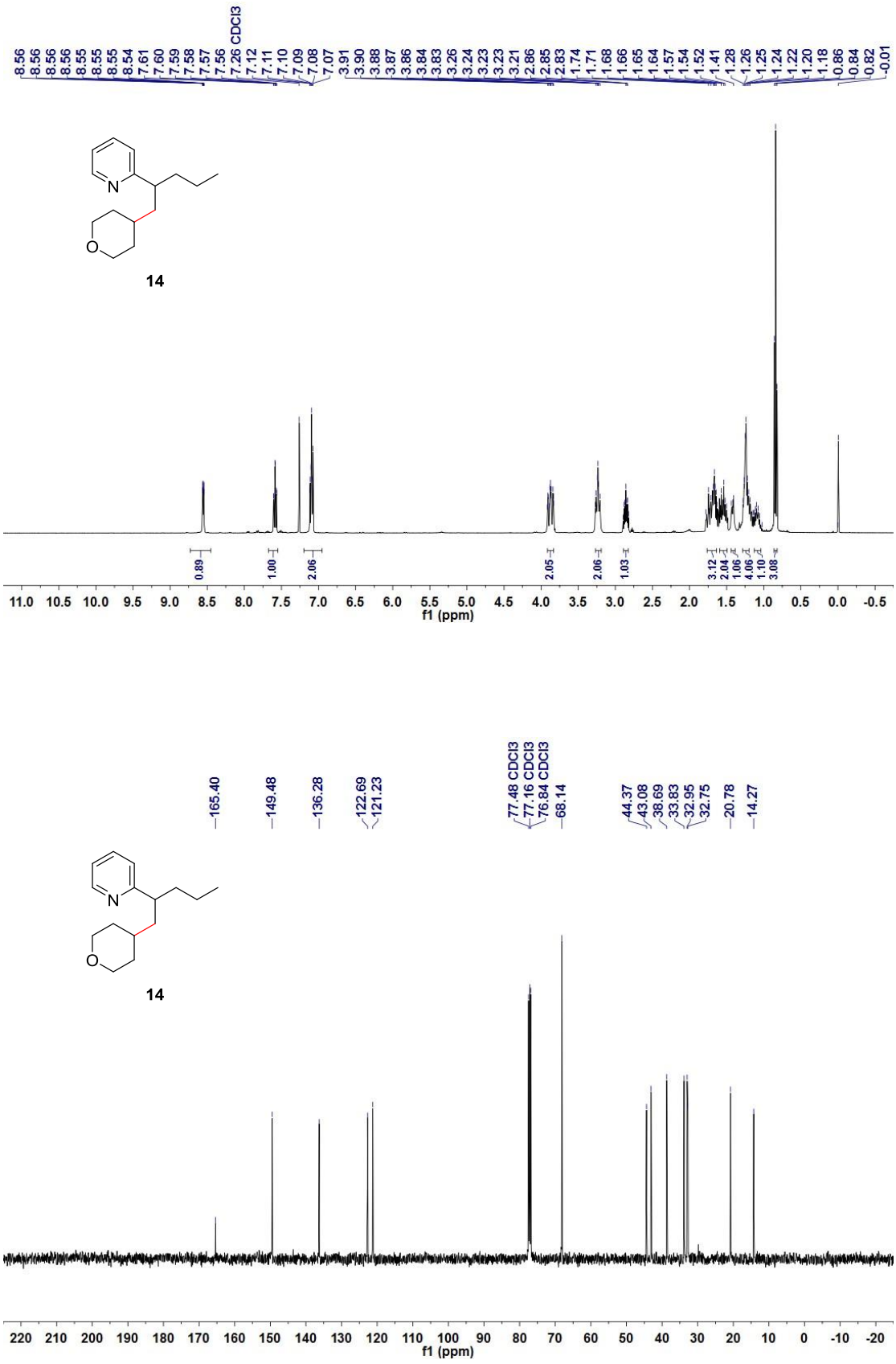


Figure S31. ^{1}H and ^{13}C NMR spectra for compound **14**

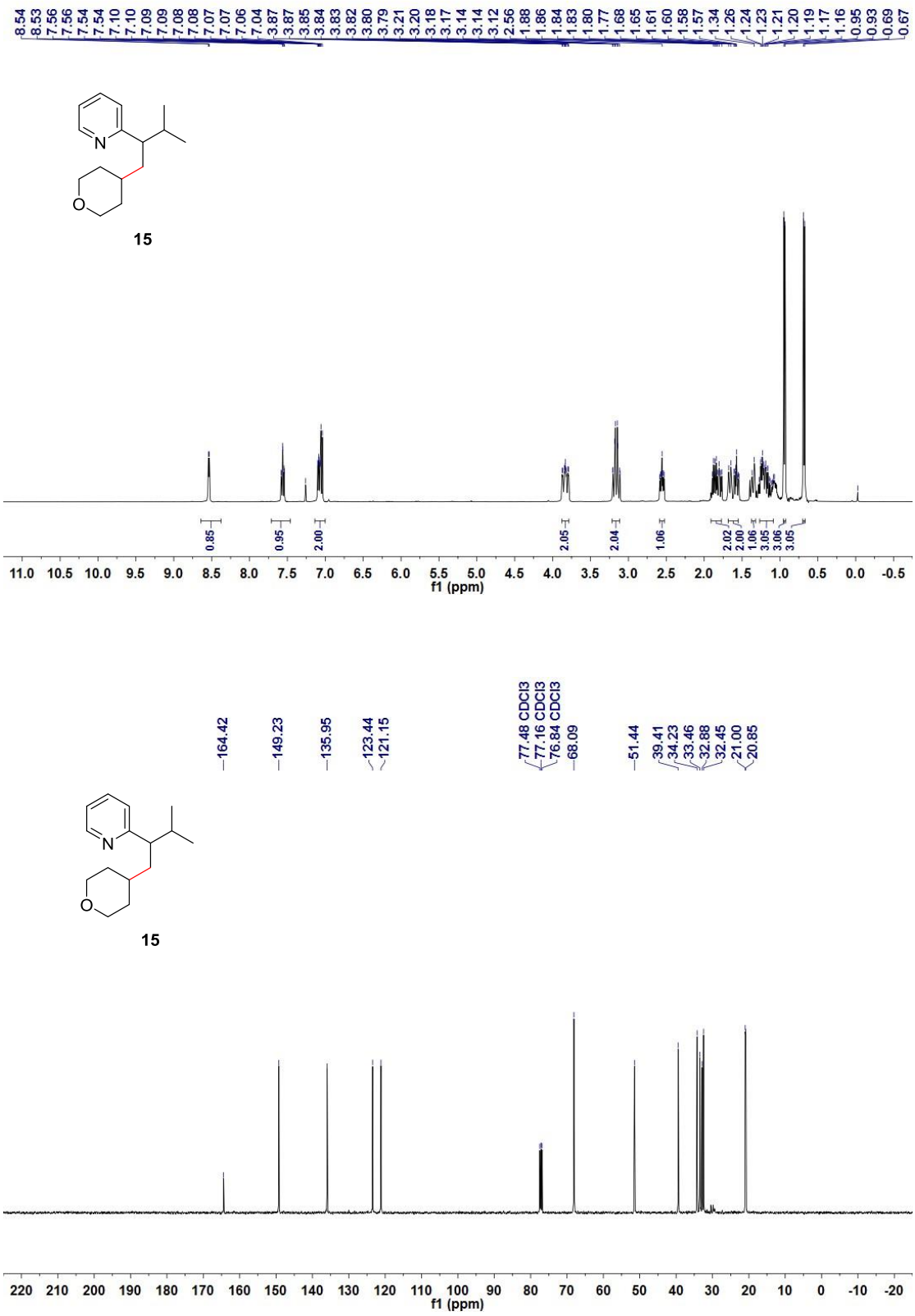


Figure S32. ^{1}H and ^{13}C NMR spectra for compound **15**

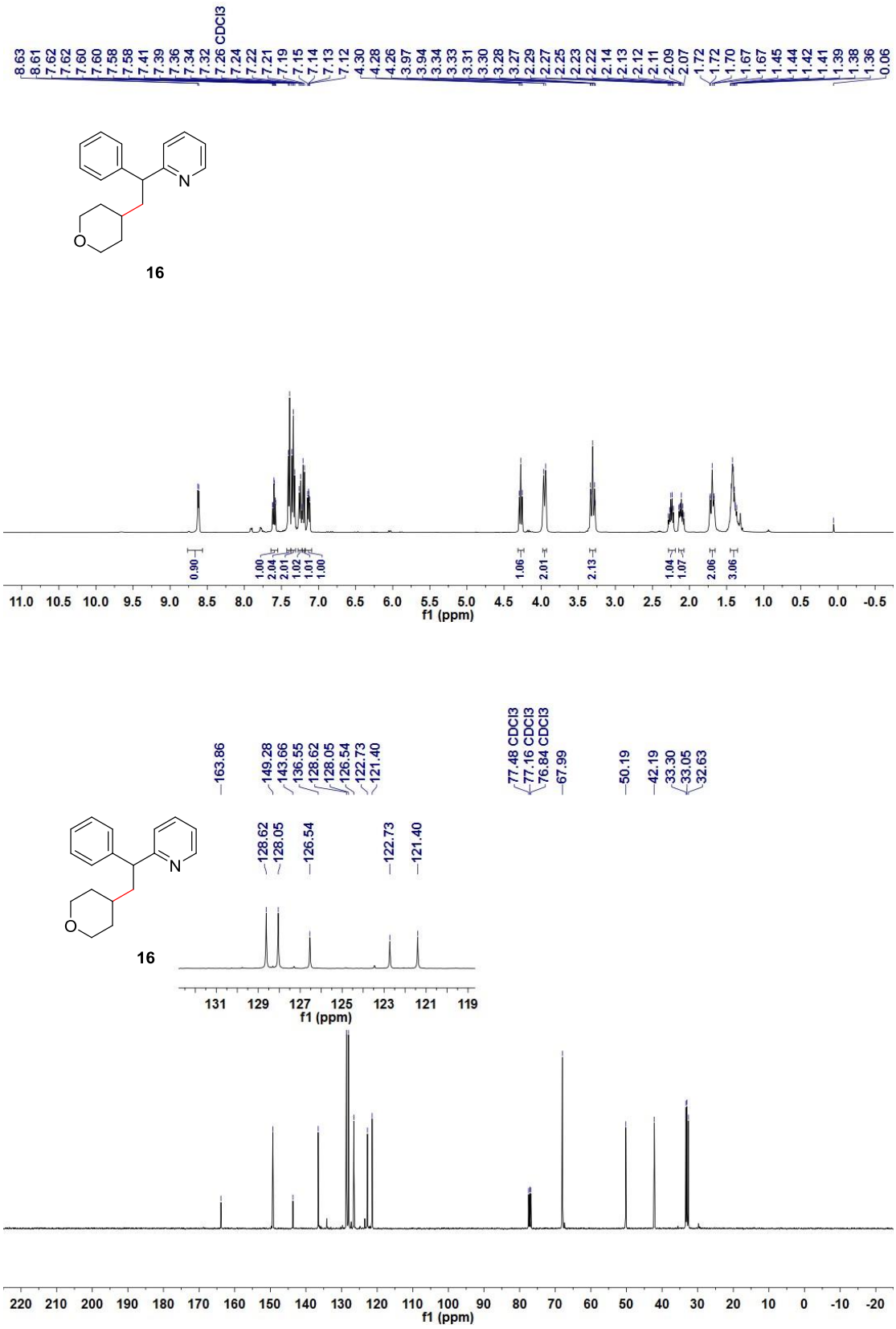


Figure S33. ^{1}H and ^{13}C NMR spectrum of compound **16**

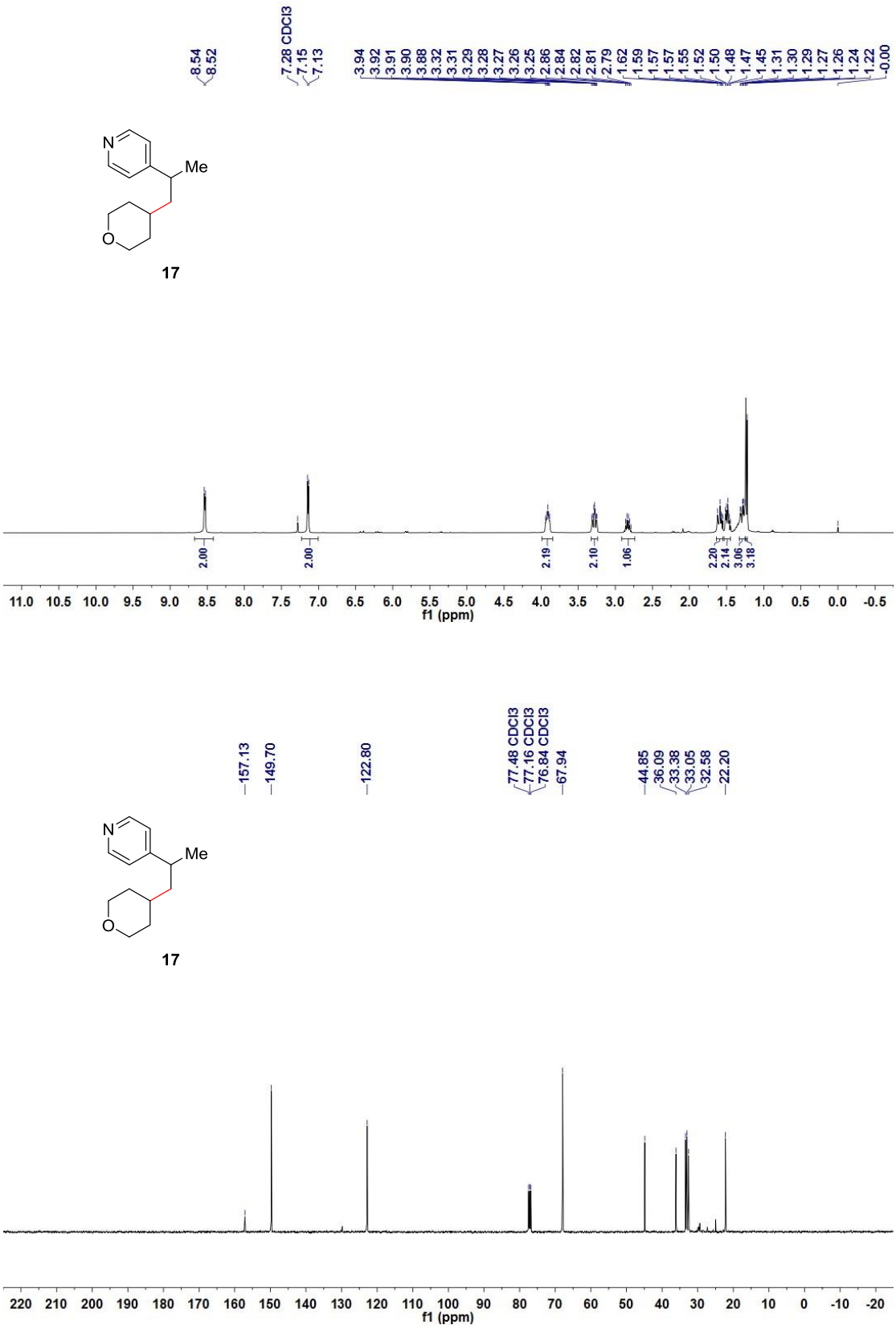


Figure S34. ^{1}H and ^{13}C NMR spectra for compound **17**

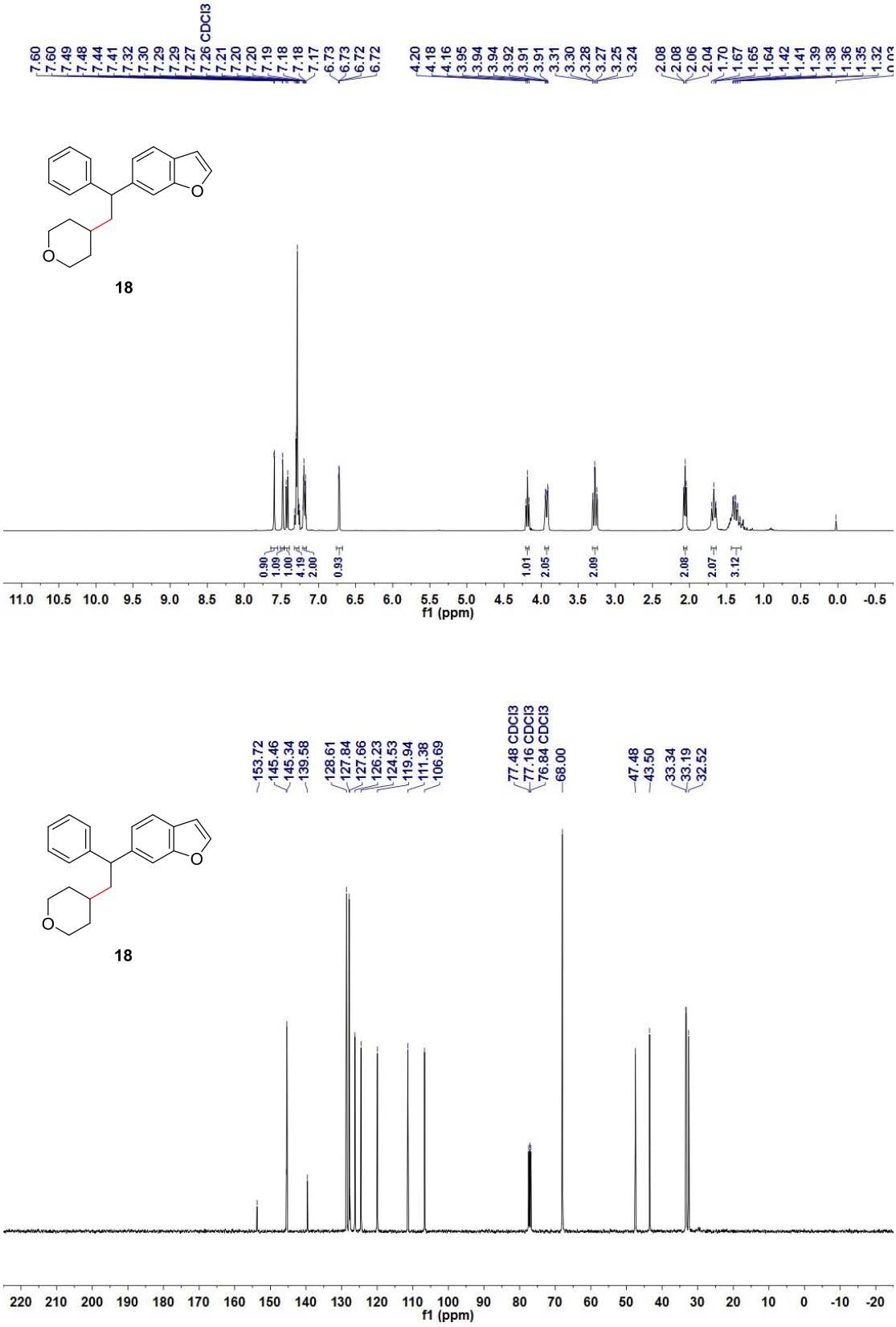


Figure S35. ^{1}H and ^{13}C NMR spectrum of compound **18**

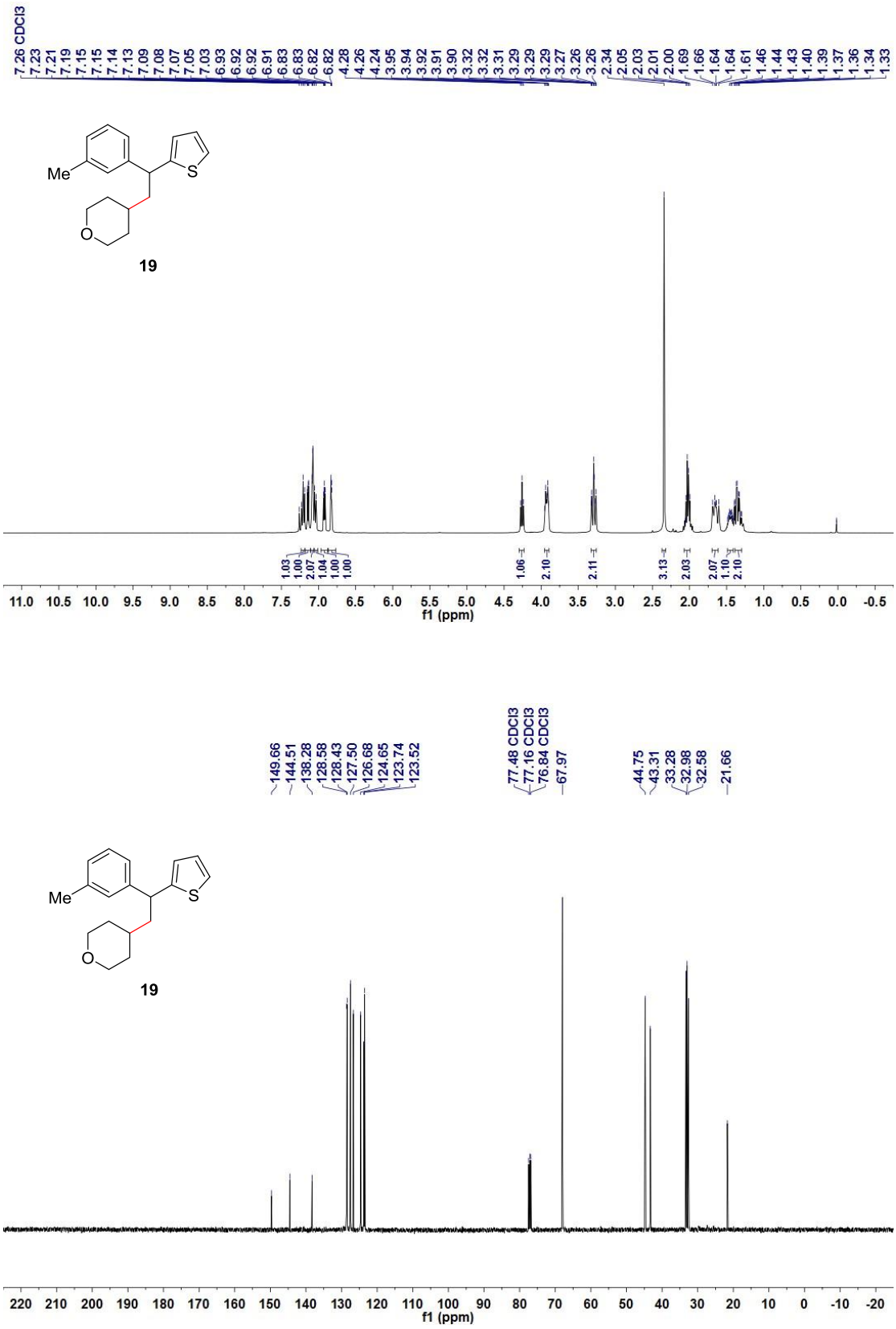


Figure S36. ^{1}H and ^{13}C NMR spectrum of compound **19**

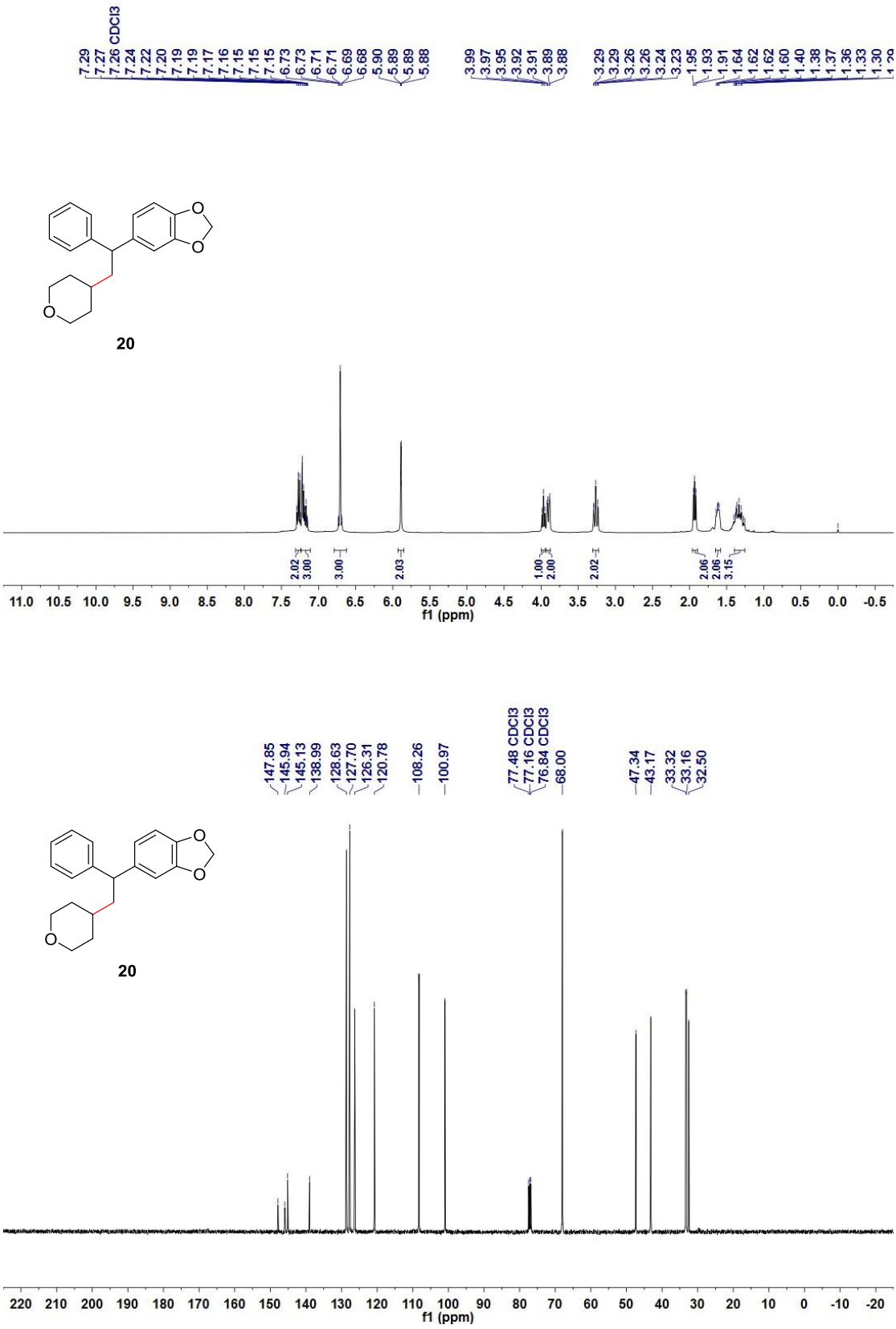


Figure S37. ^{1}H and ^{13}C NMR spectrum of compound **20**

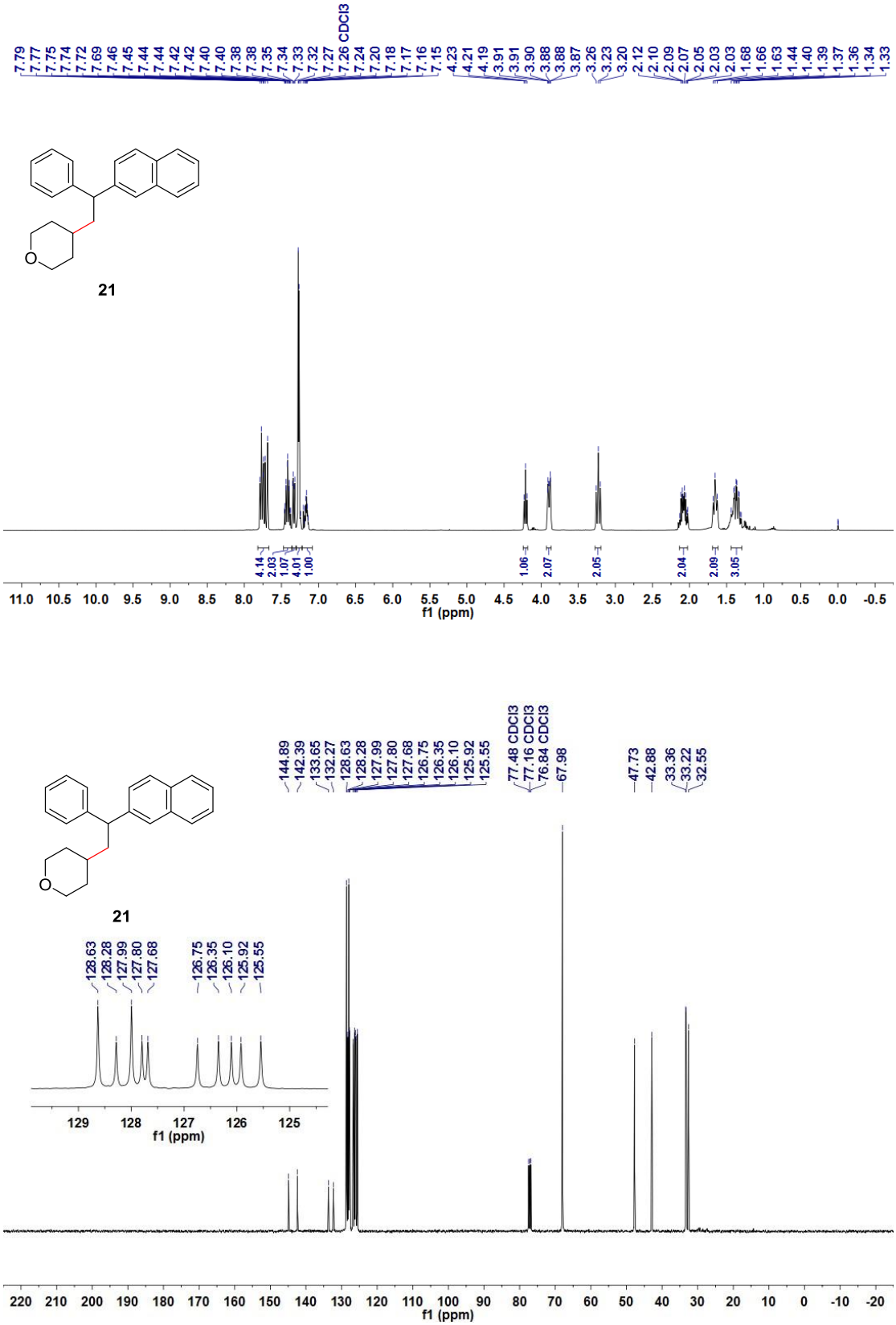


Figure S38. ^{1}H and ^{13}C NMR spectrum of compound **21**

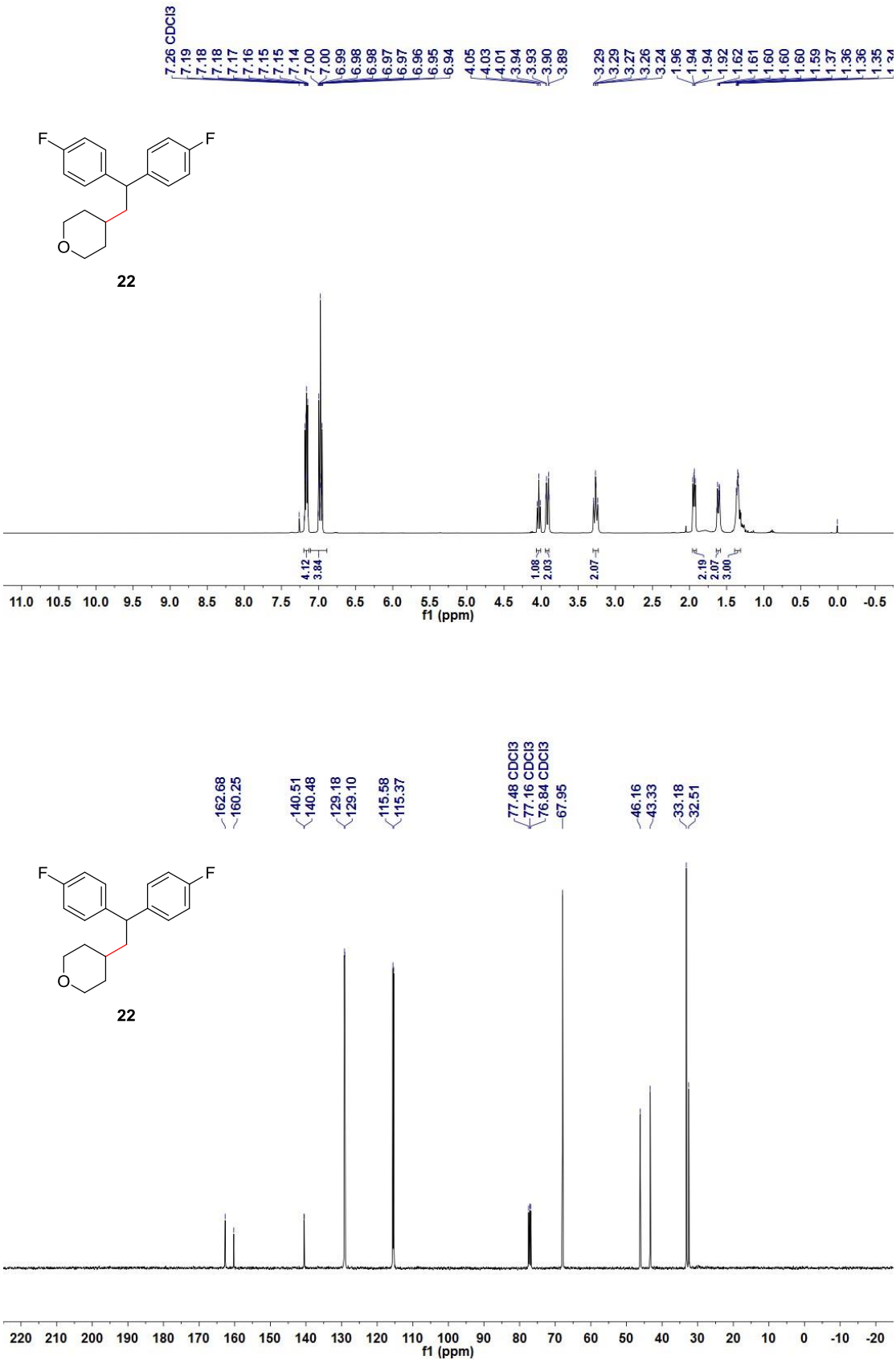


Figure S39. ^{1}H and ^{13}C NMR spectrum of compound **22**

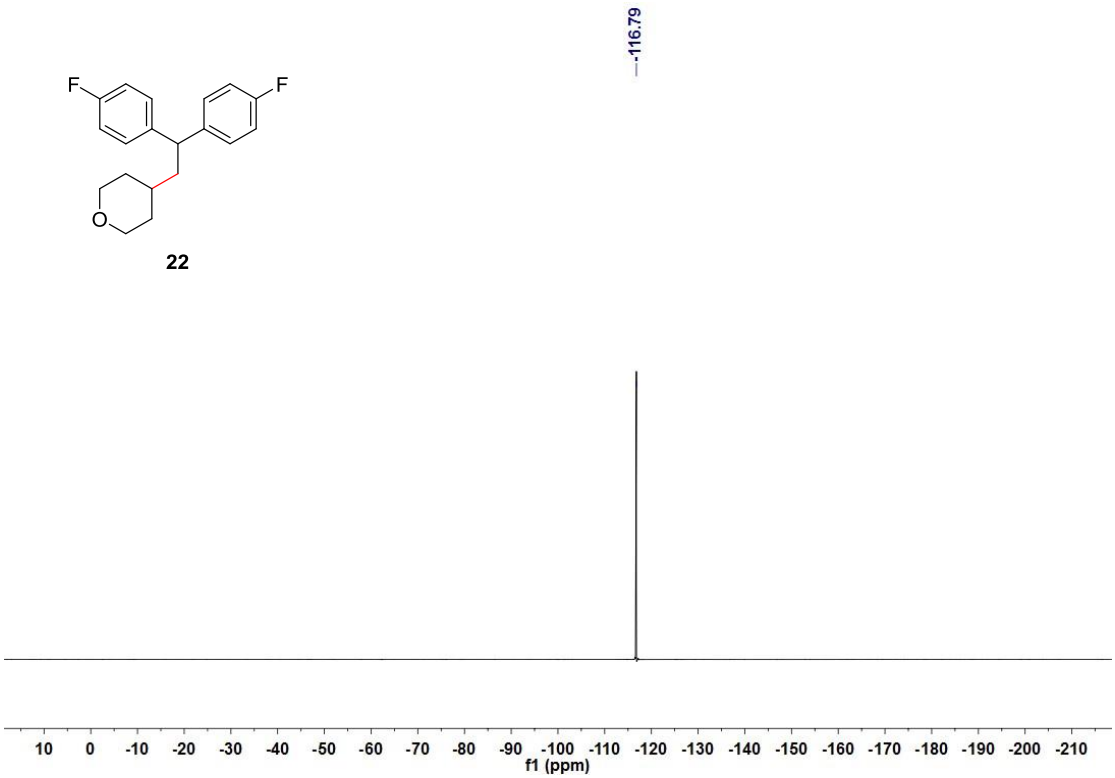


Figure S40. ^{19}F NMR spectrum of compound **22**

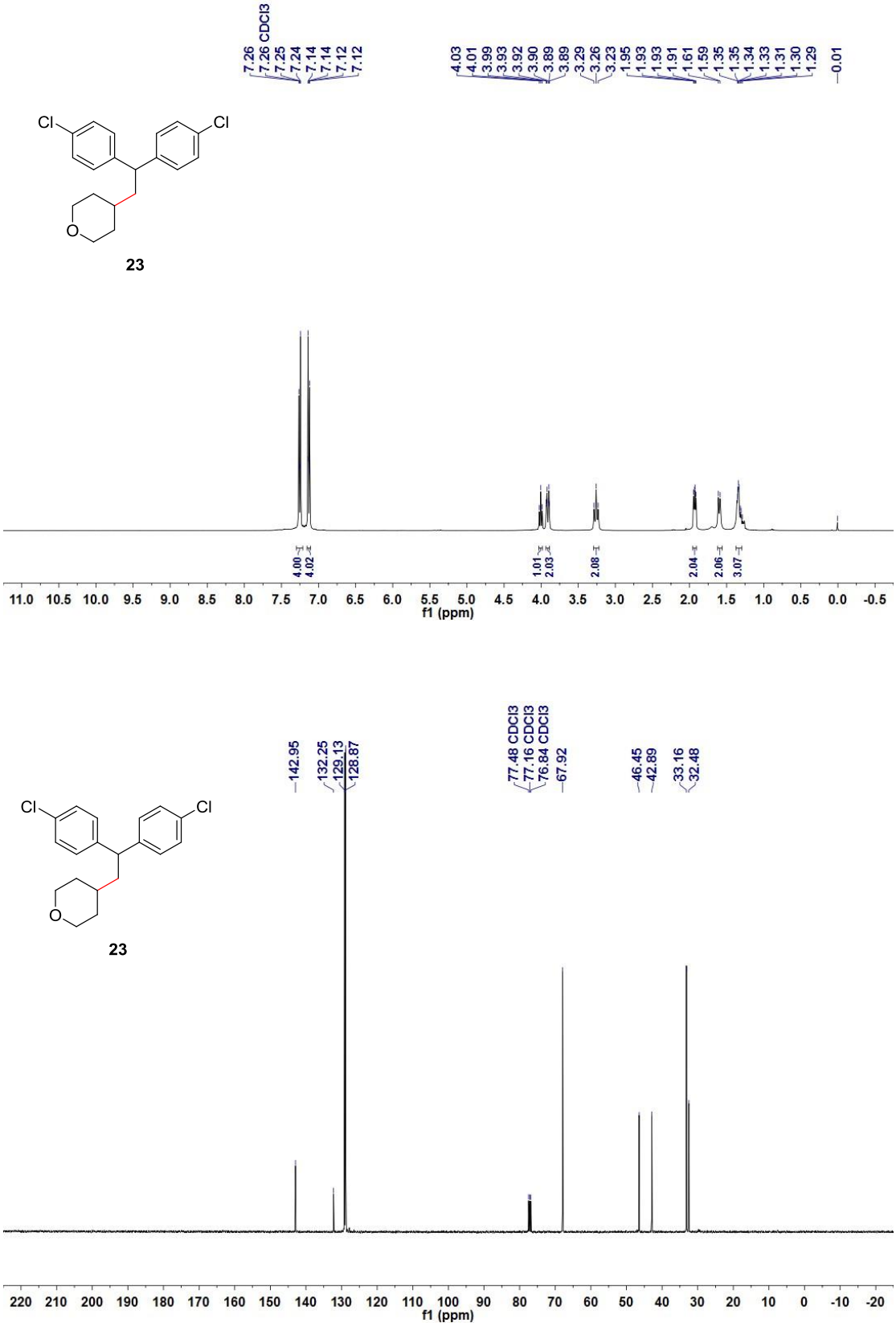


Figure S41. ^{1}H and ^{13}C NMR spectrum of compound **23**

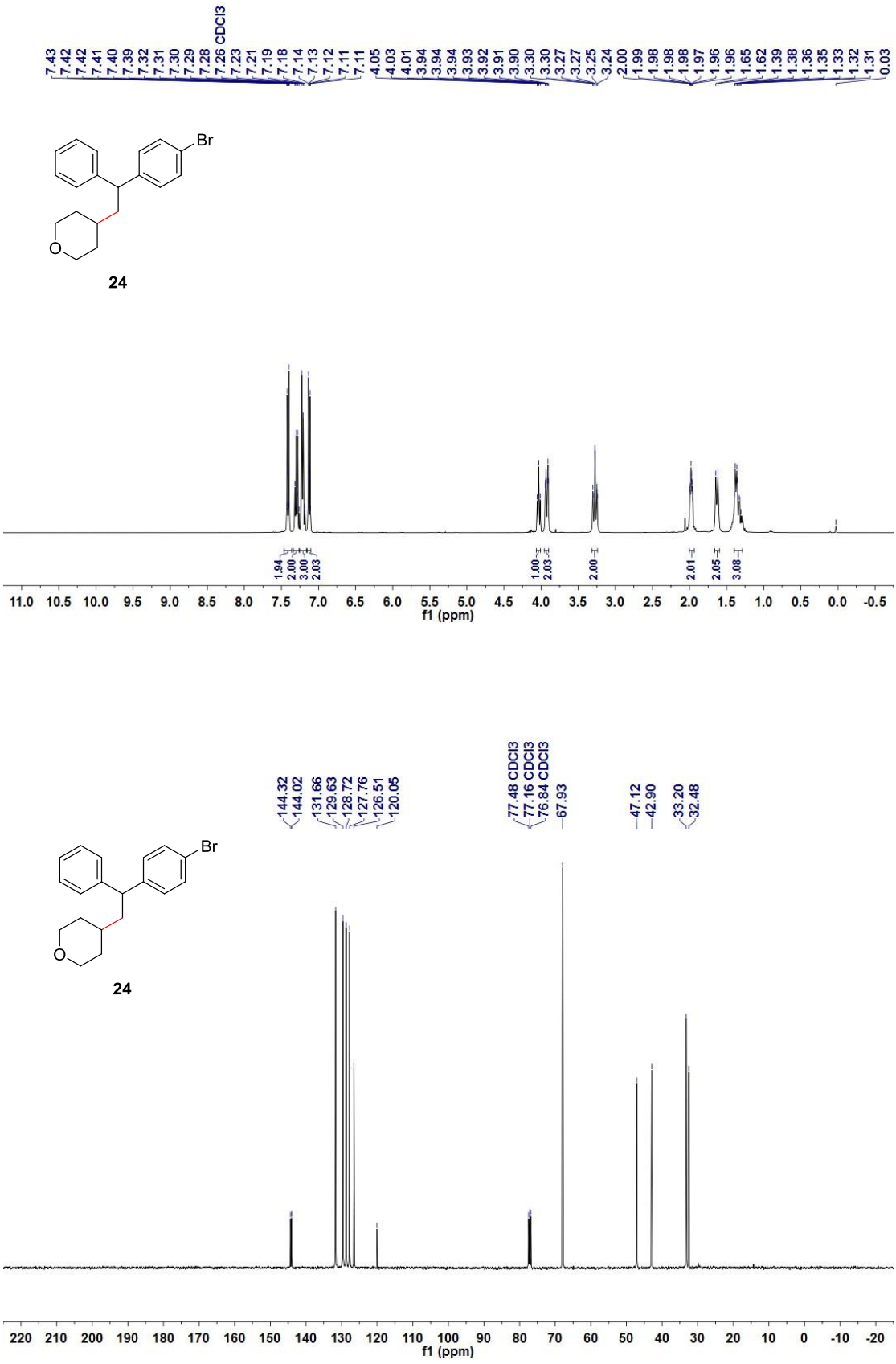


Figure S42. ^{1}H and ^{13}C NMR spectrum of compound **24**

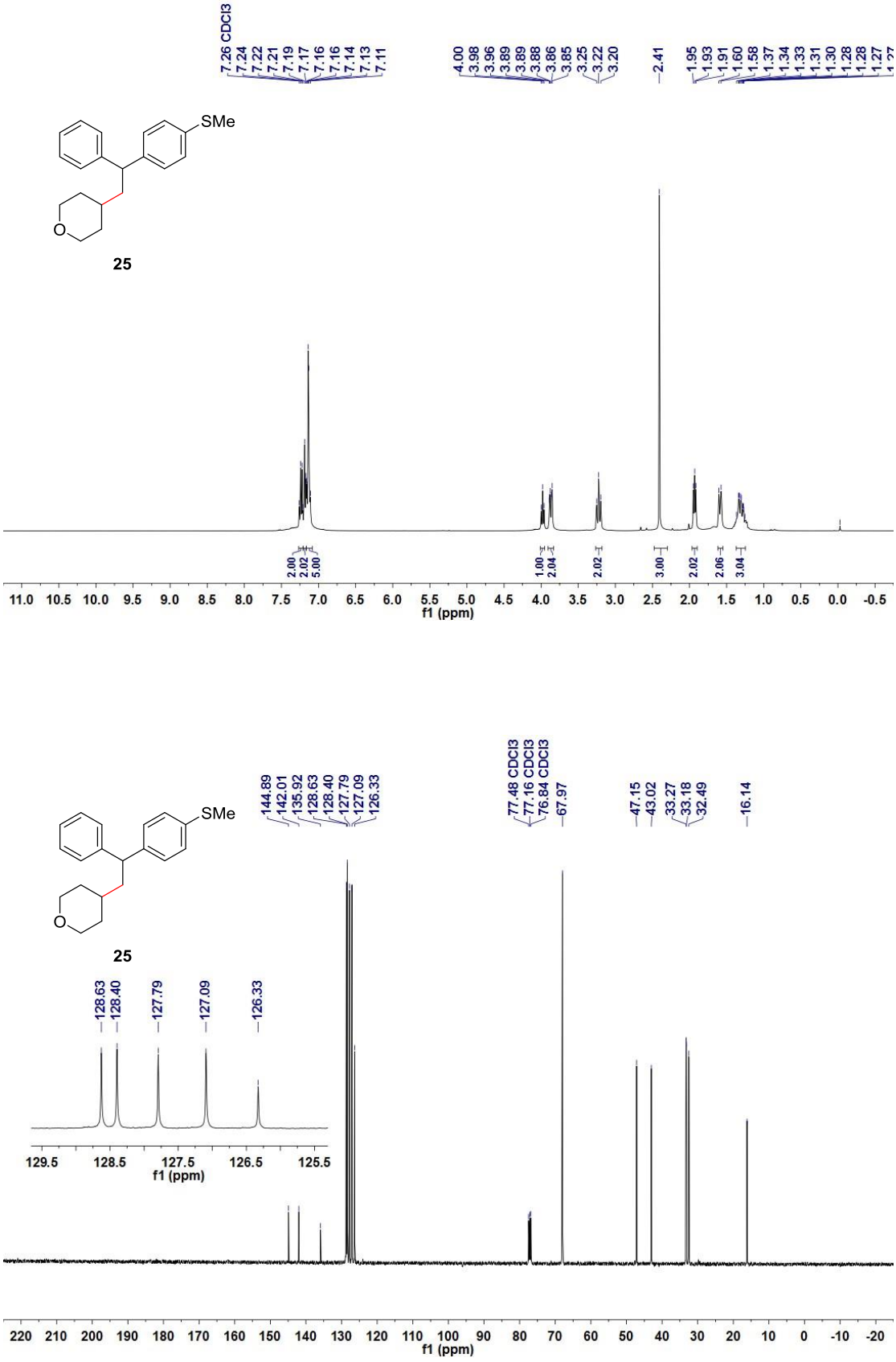


Figure S43. ^{1}H and ^{13}C NMR spectrum of compound **25**

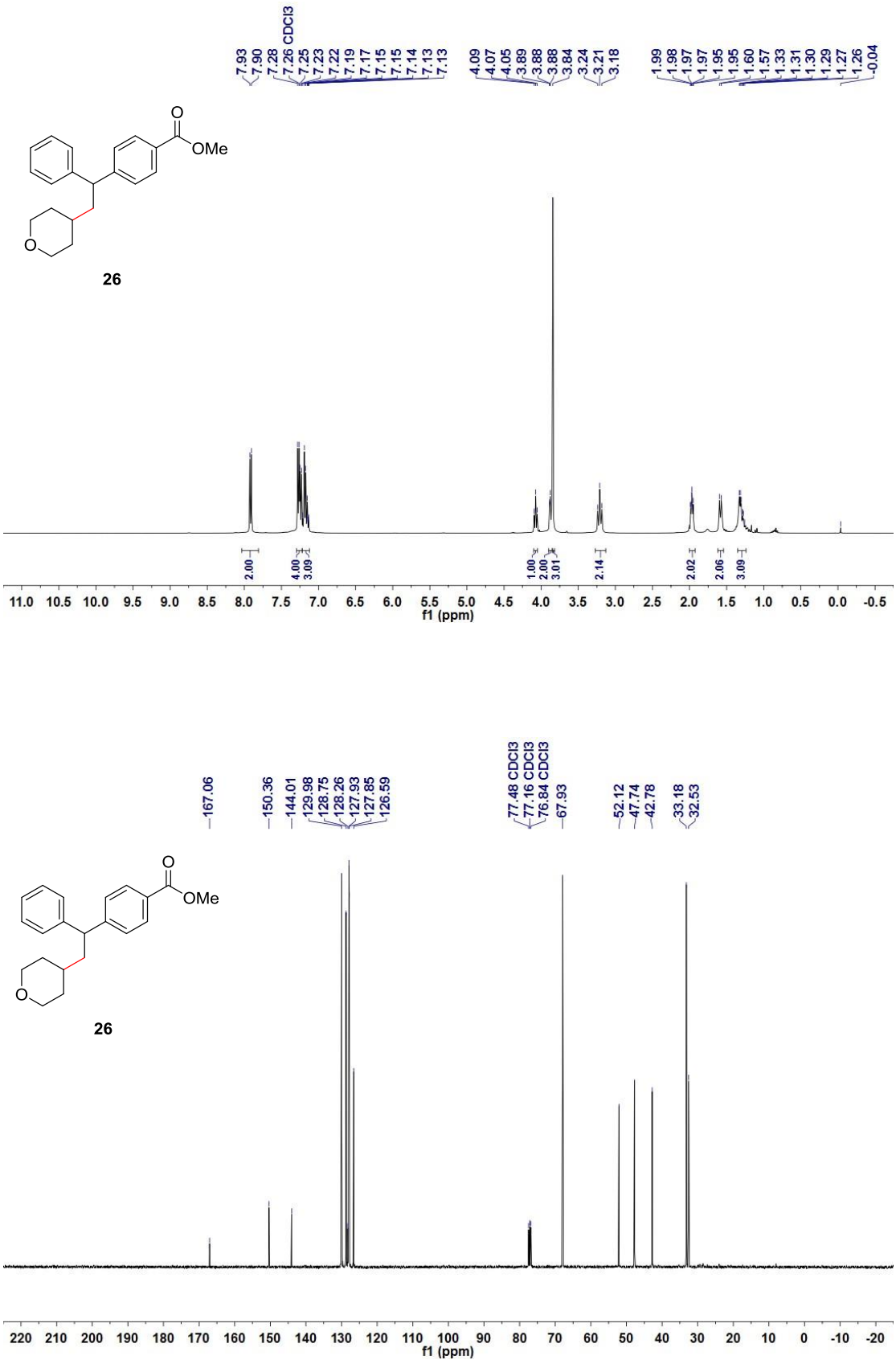


Figure S44. ^{1}H and ^{13}C NMR spectrum of compound **26**

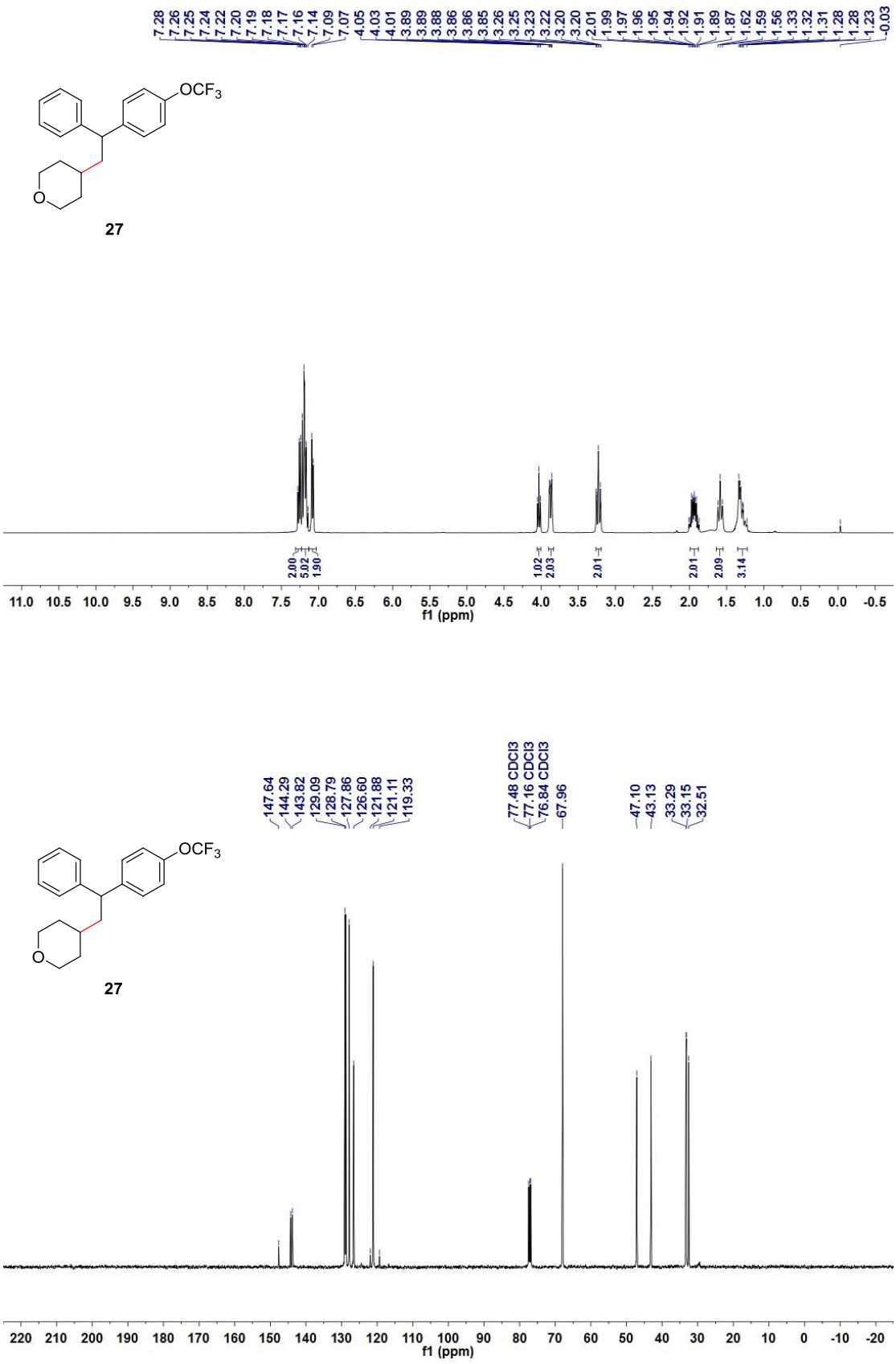


Figure S45. ^{1}H and ^{13}C NMR spectrum of compound **27**

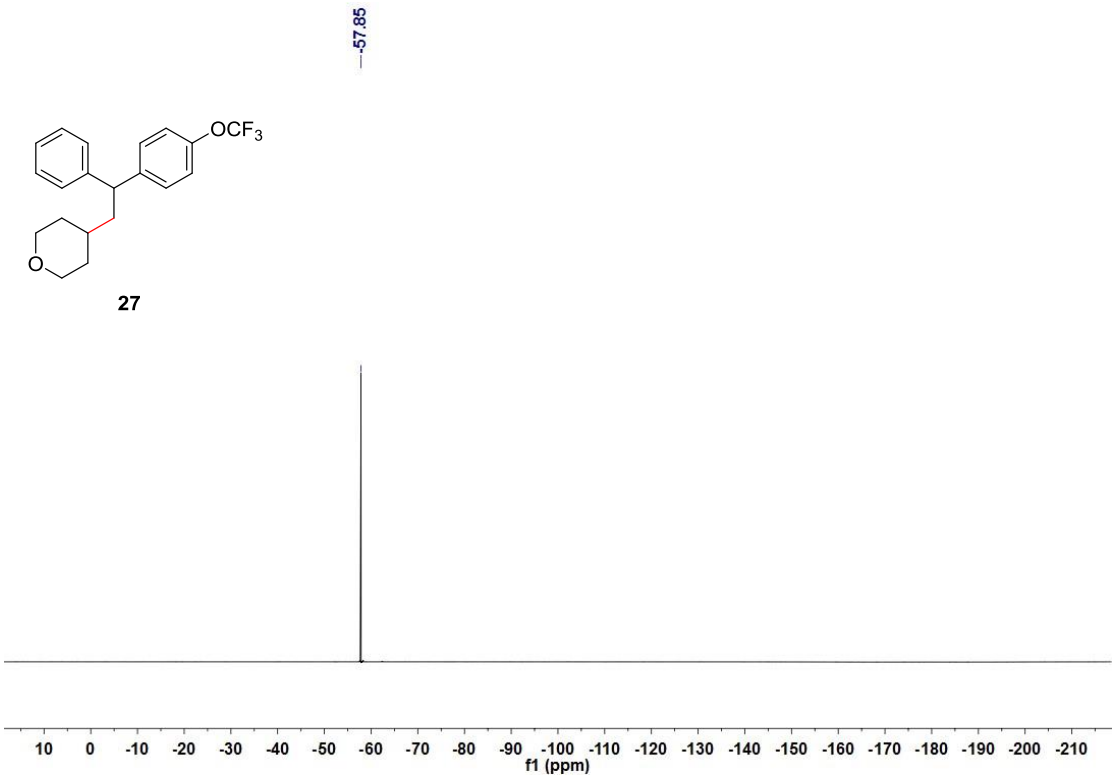


Figure S46. ^{19}F NMR spectrum of compound **27**

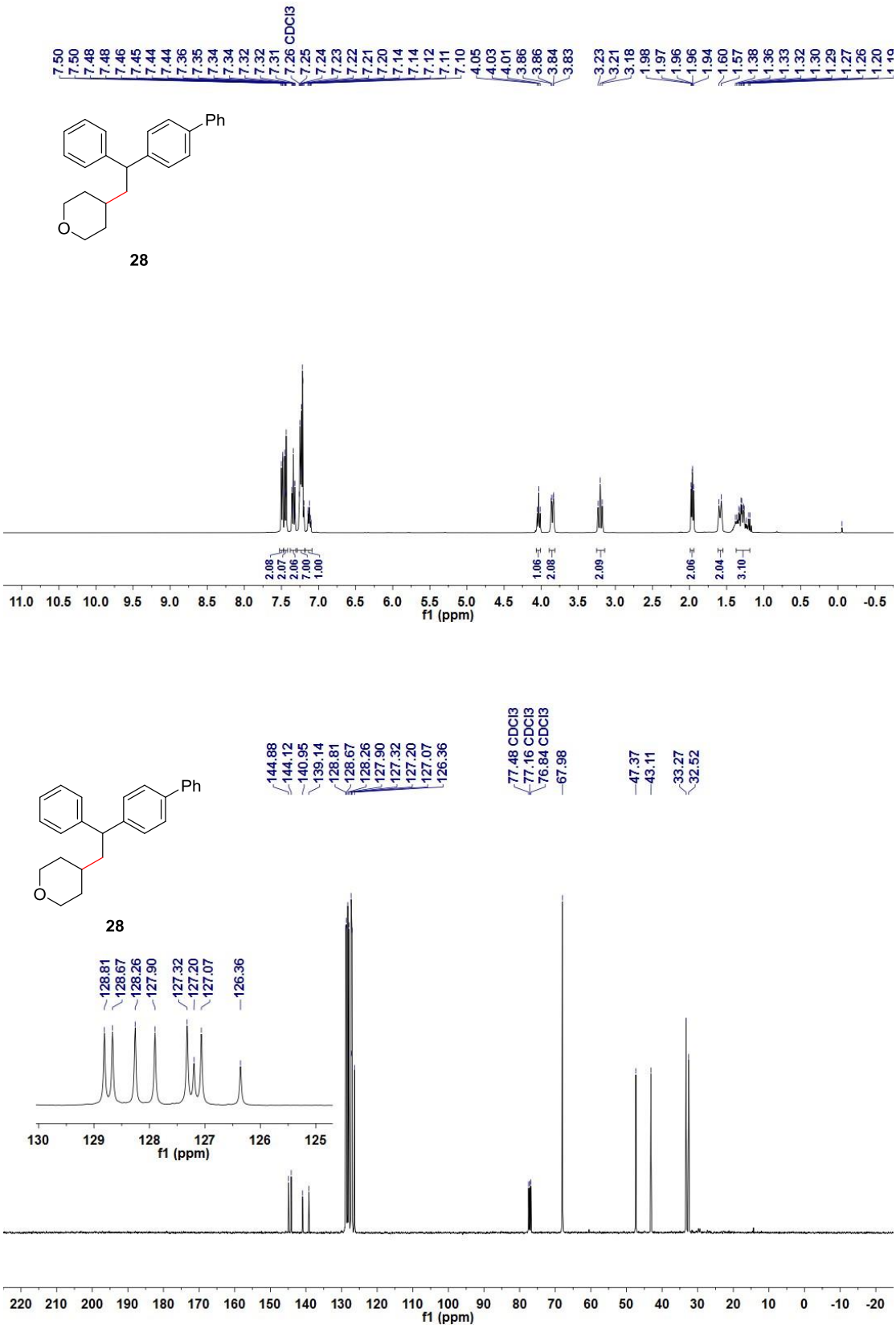


Figure S47. ^{1}H and ^{13}C NMR spectrum of compound **28**

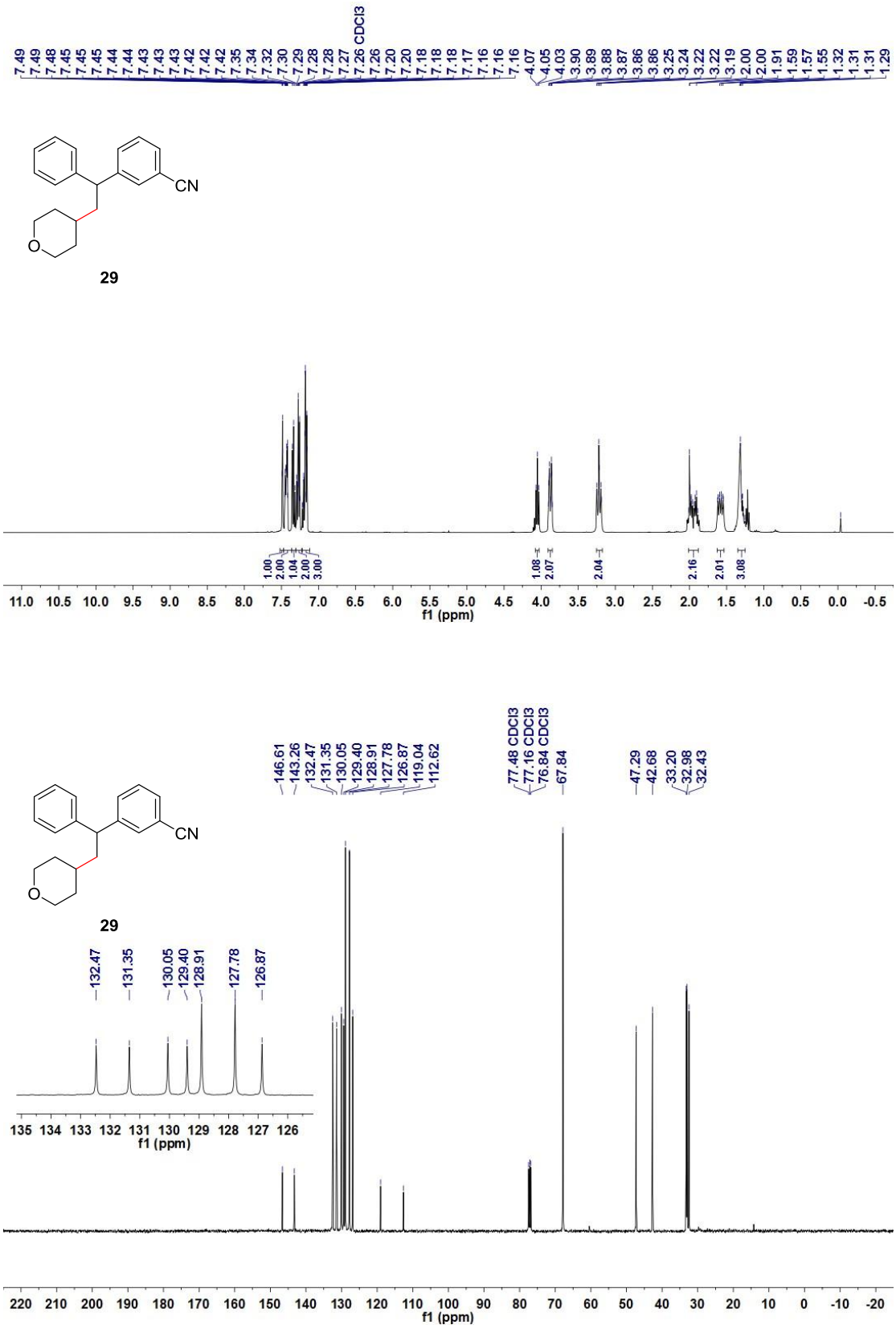


Figure S48. ^{1}H and ^{13}C NMR spectrum of compound **29**

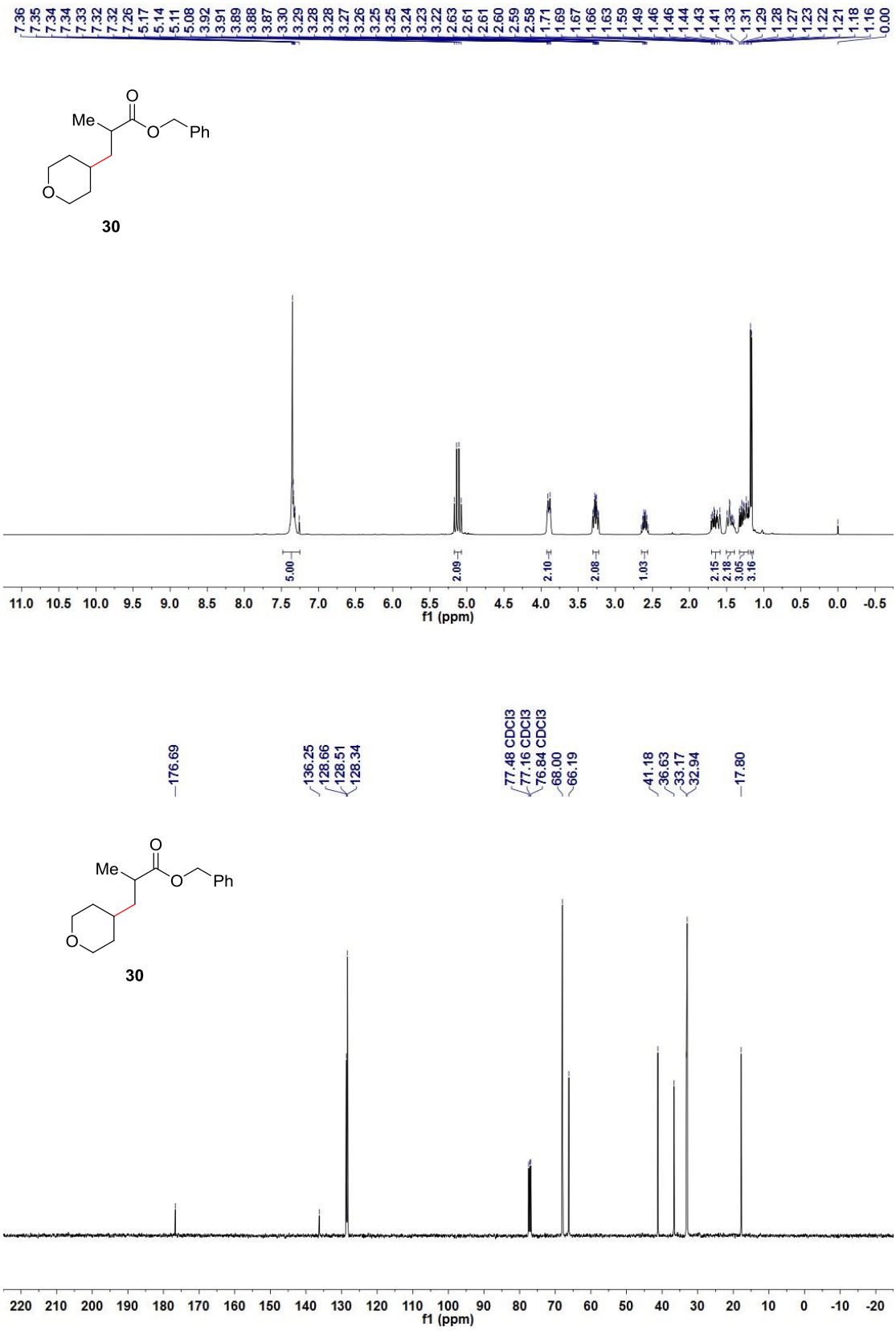


Figure S49. ^{1}H and ^{13}C NMR spectra for compound **30**

Figure S50. ^{1}H and ^{13}C NMR spectra for compound **31**

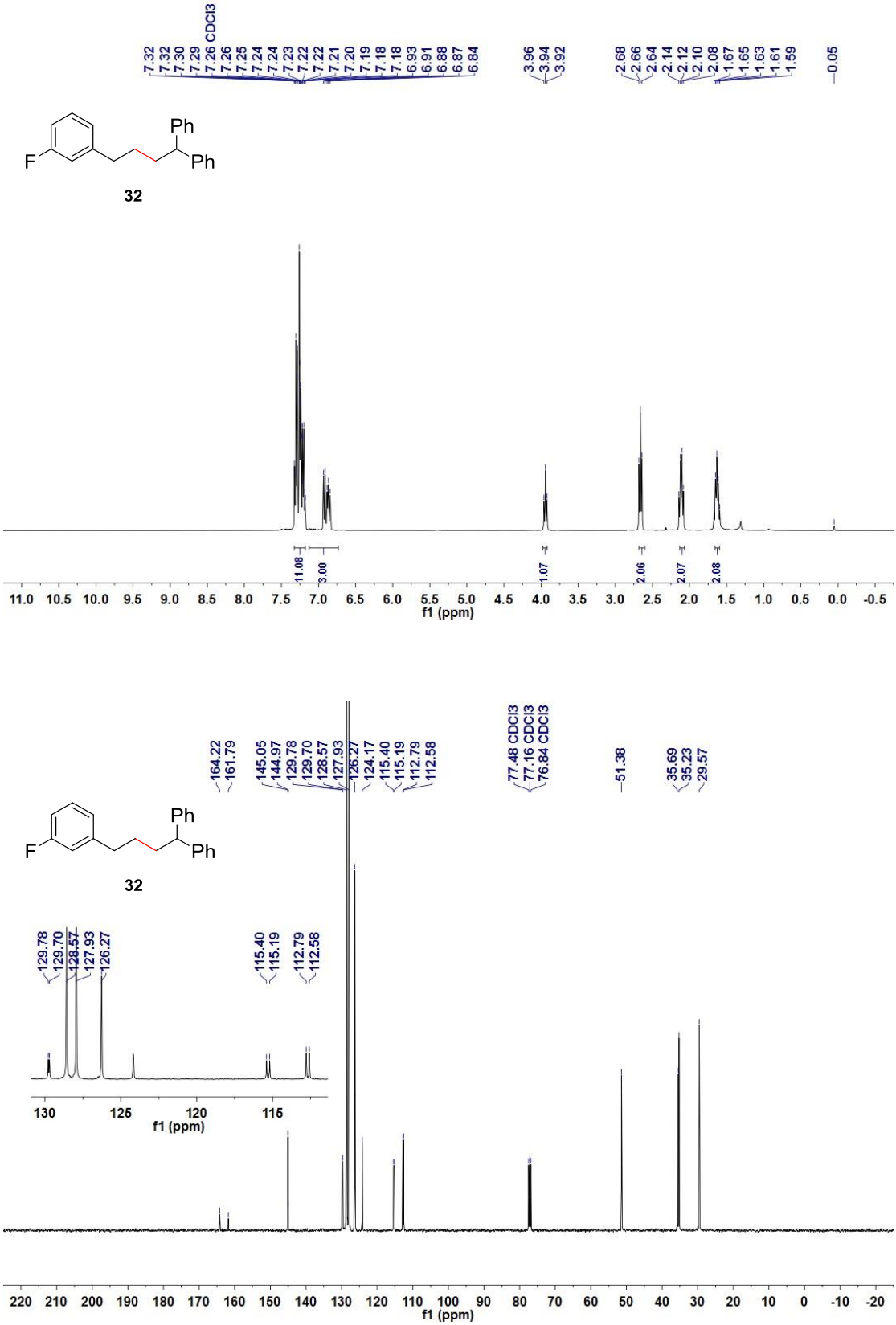


Figure S51. ^{1}H and ^{13}C NMR spectra for compound **32**

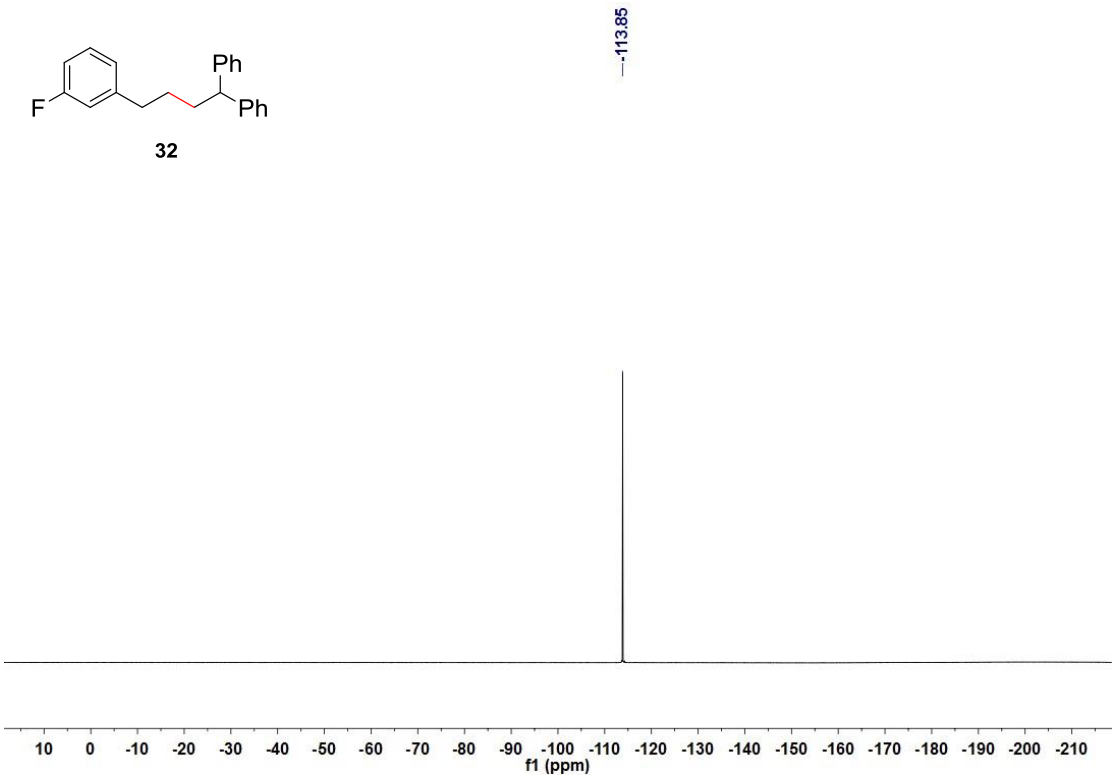


Figure S52. ^{19}F NMR spectra for compound **32**

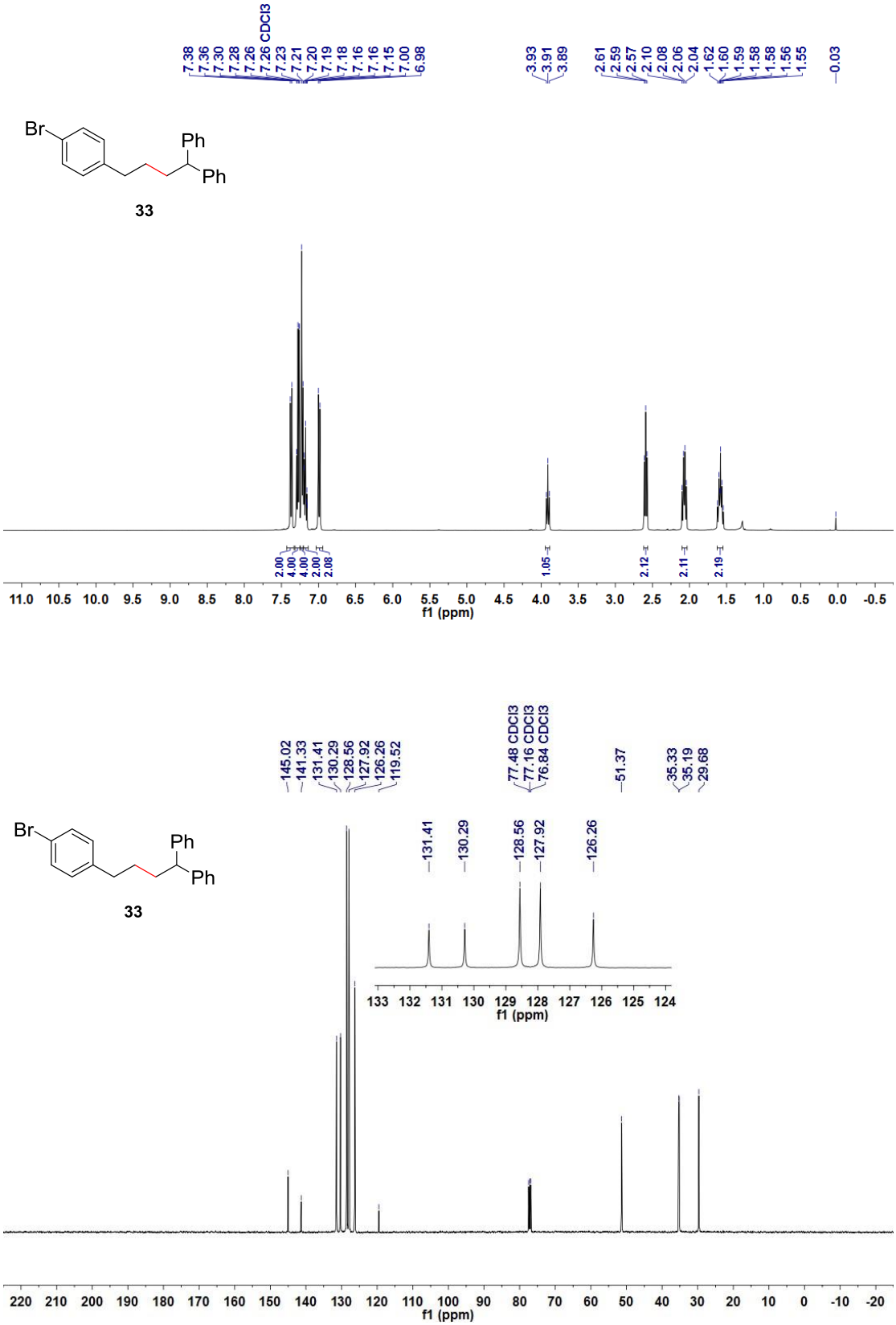


Figure S53. ^{1}H and ^{13}C NMR spectra for compound **33**

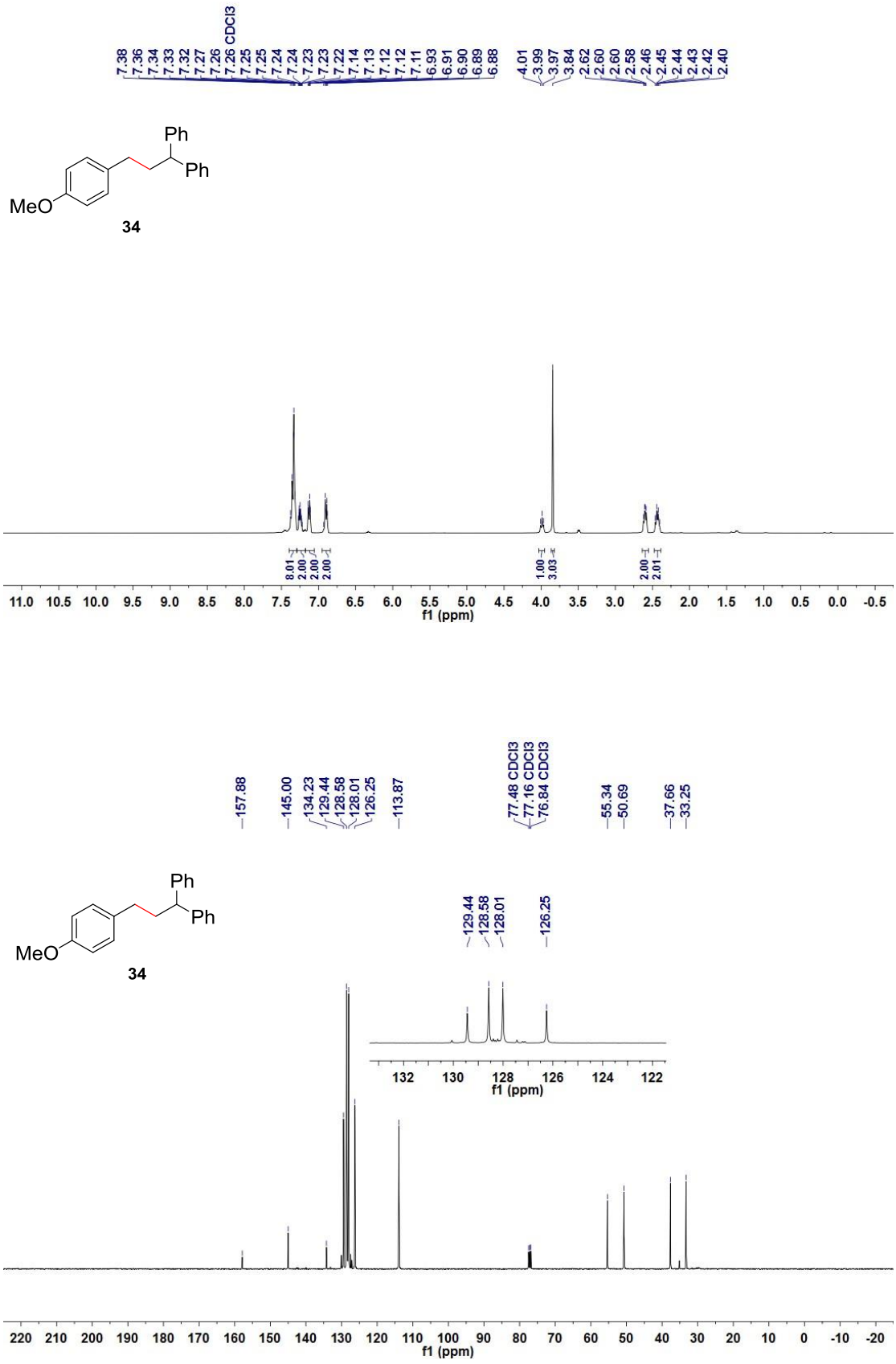


Figure S54. ^{1}H and ^{13}C NMR spectra for compound **34**

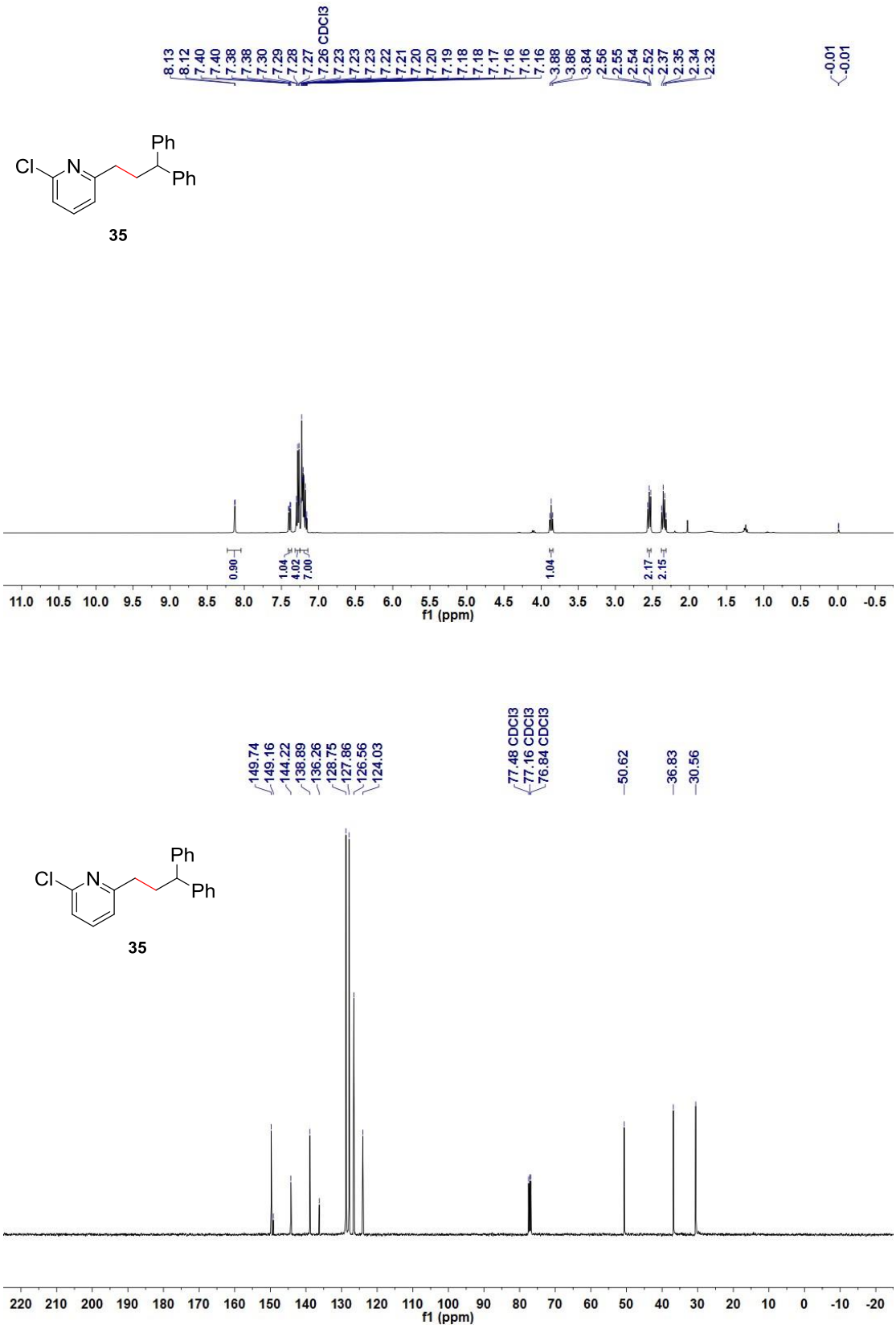


Figure S55. ^{1}H and ^{13}C NMR spectra for compound **35**

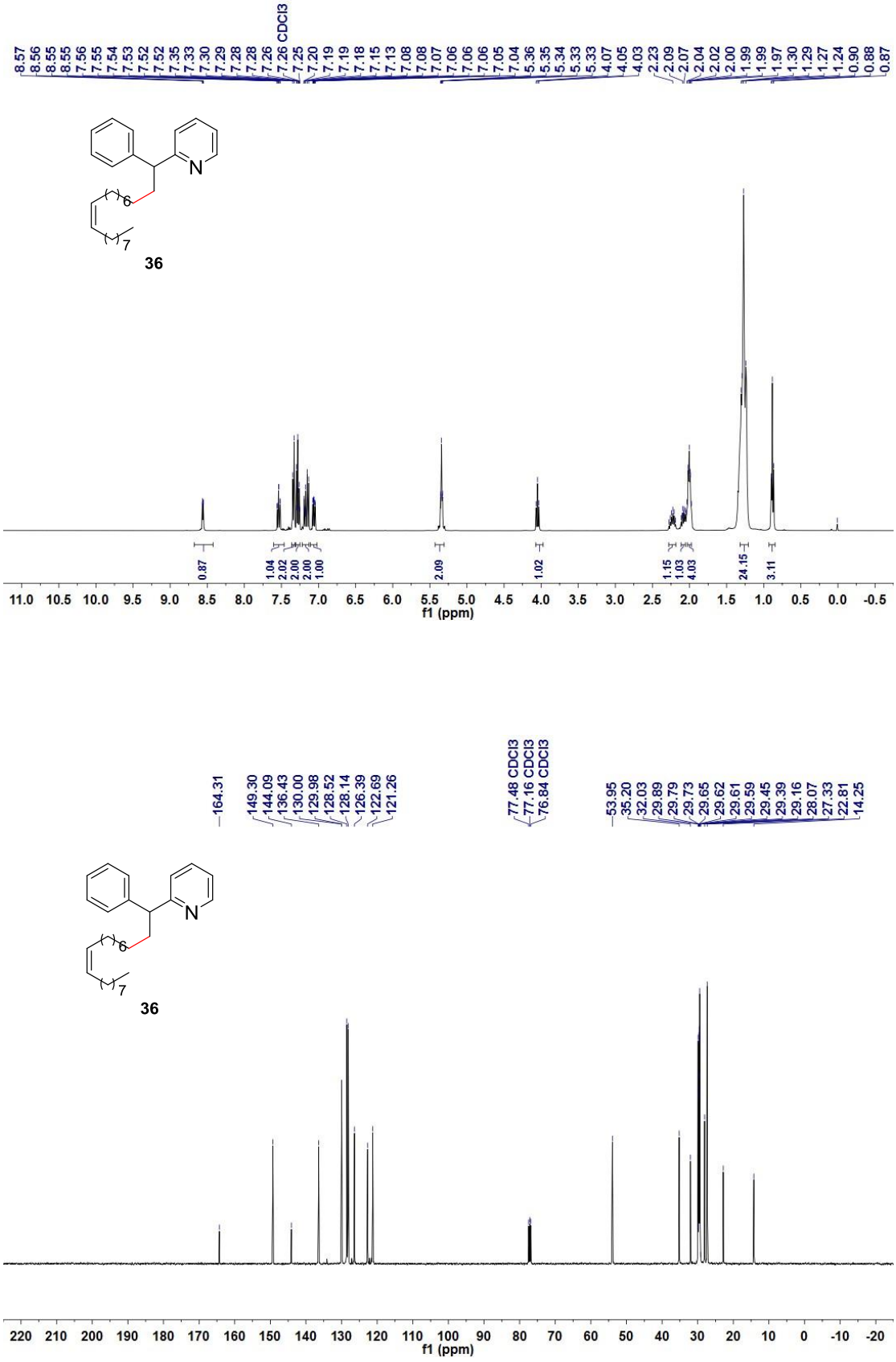


Figure S56. ^{1}H and ^{13}C NMR spectra for compound **36**

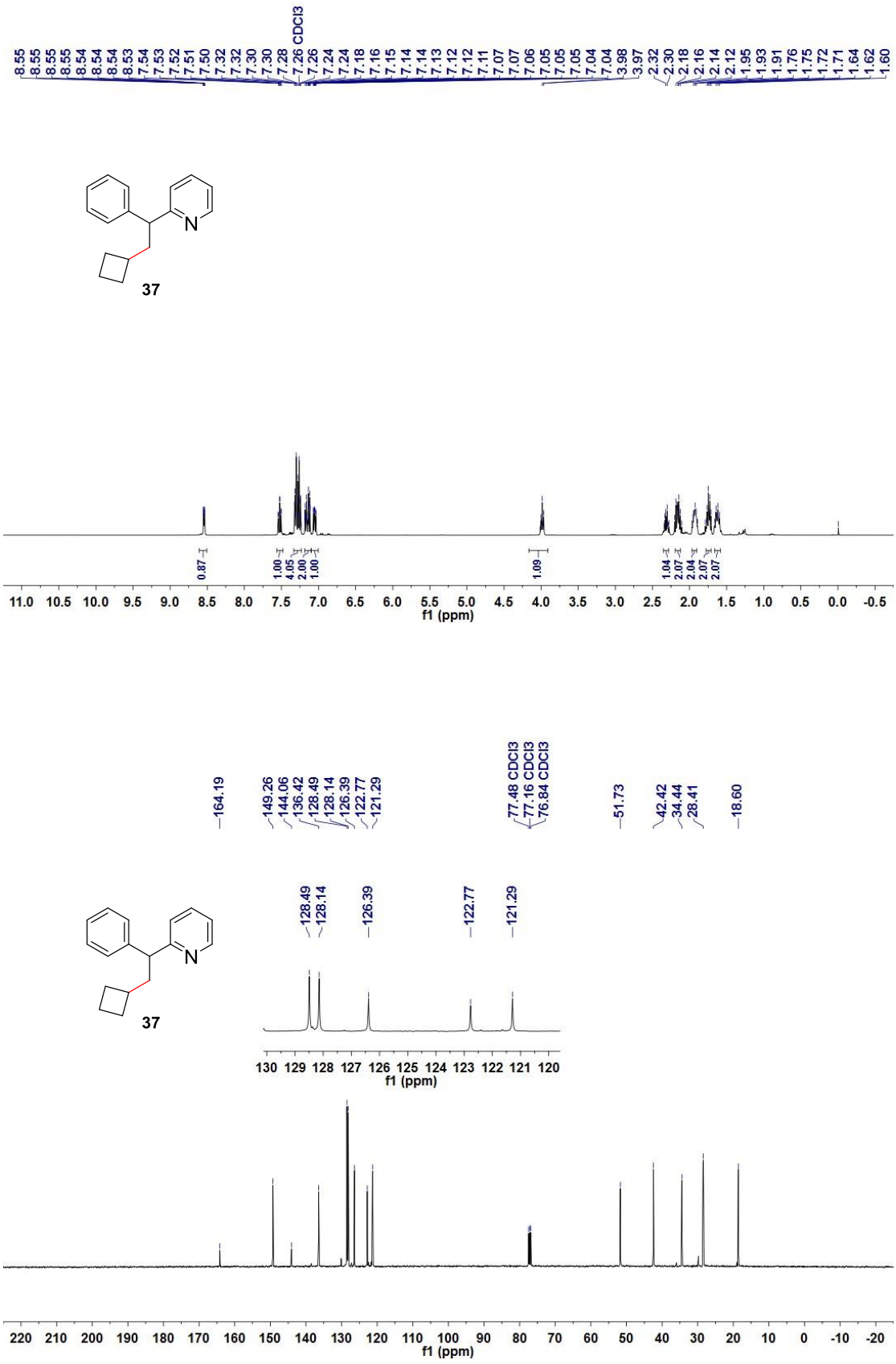


Figure S57. ^{1}H and ^{13}C NMR spectra for compound **37**

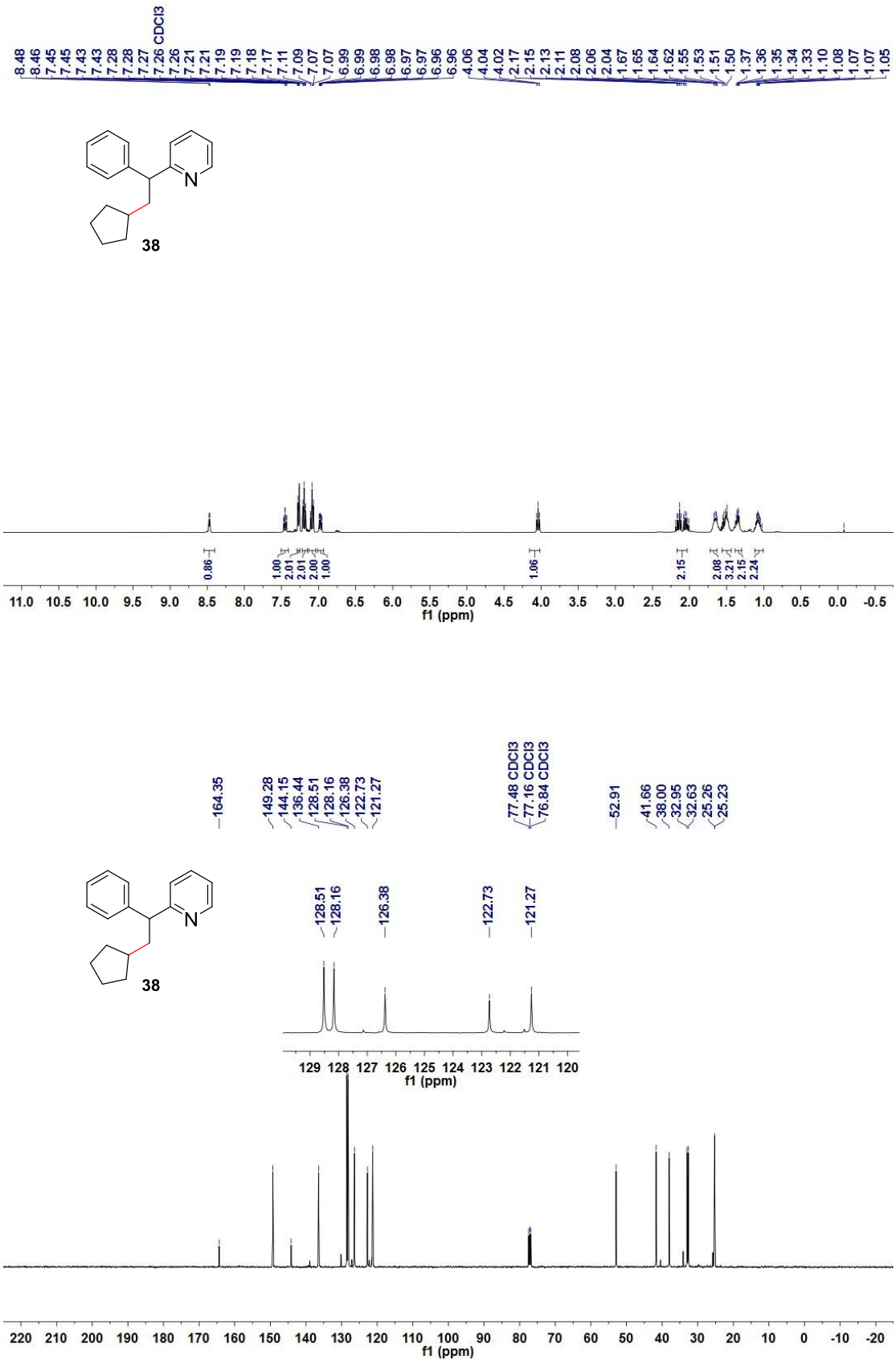


Figure S58. ^{1}H and ^{13}C NMR spectra for compound **38**

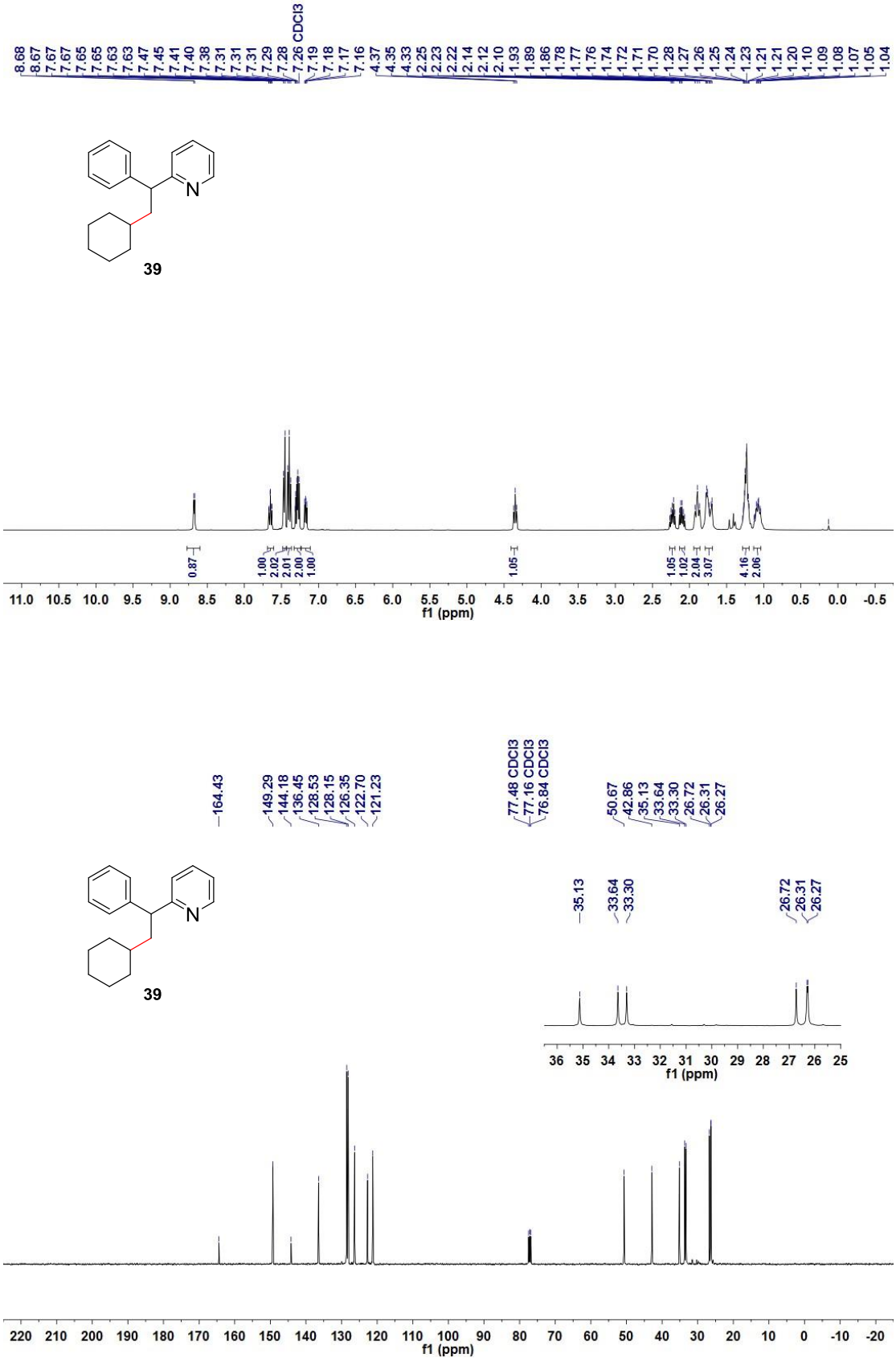


Figure S59. ^{1}H and ^{13}C NMR spectra for compound **39**

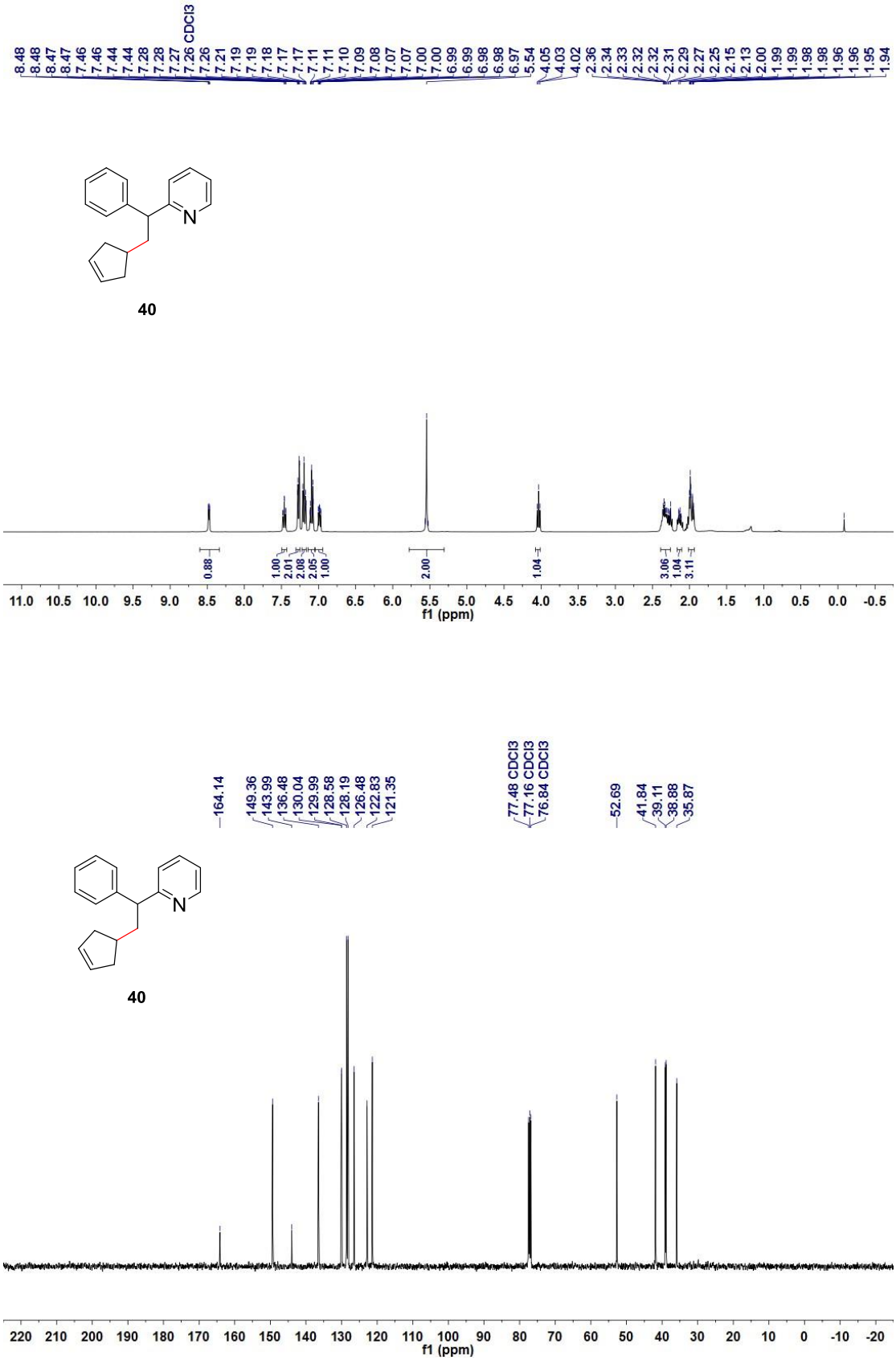


Figure S60. ^{1}H and ^{13}C NMR spectra for compound **40**

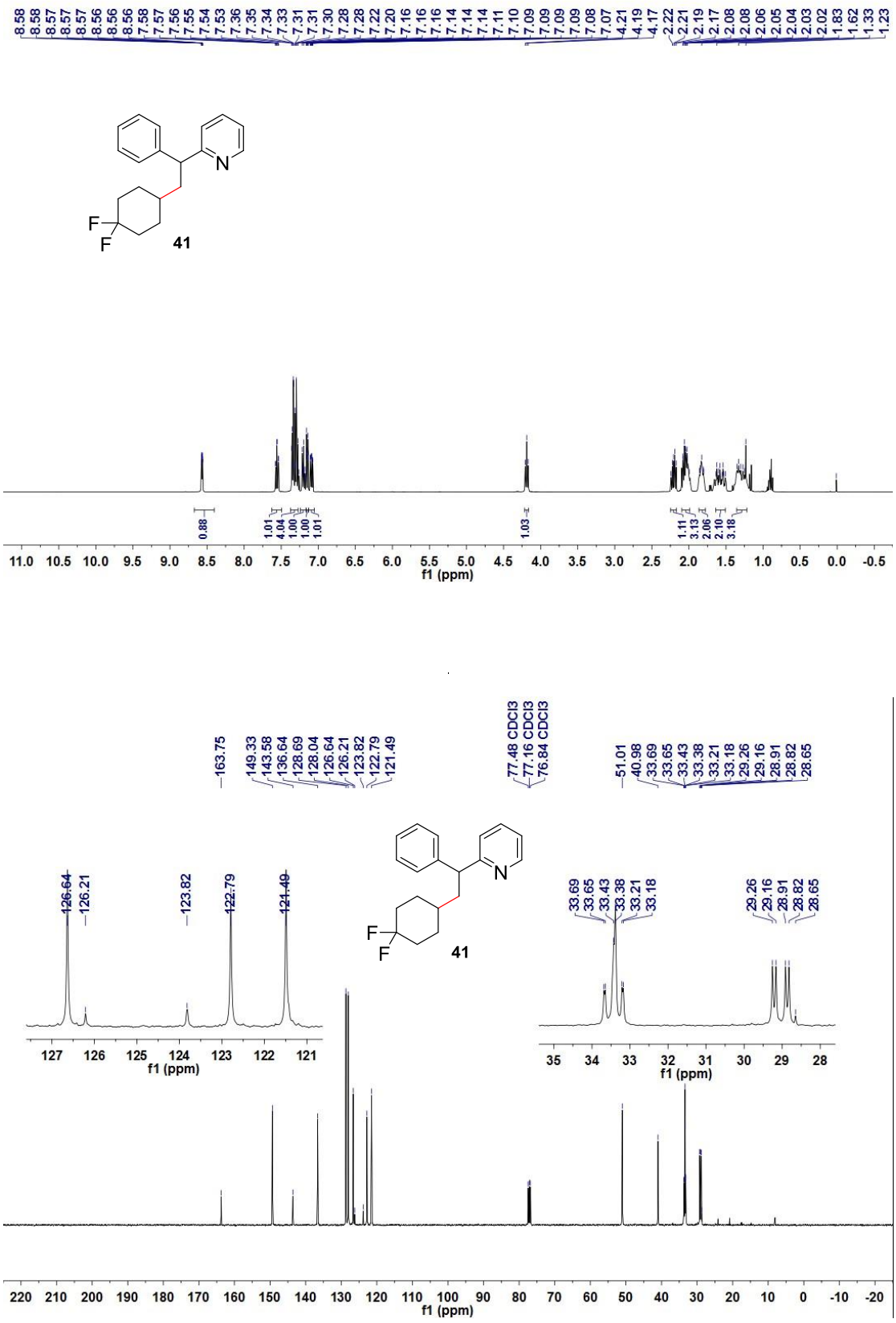


Figure S61. ^{1}H and ^{13}C NMR spectra for compound **41**

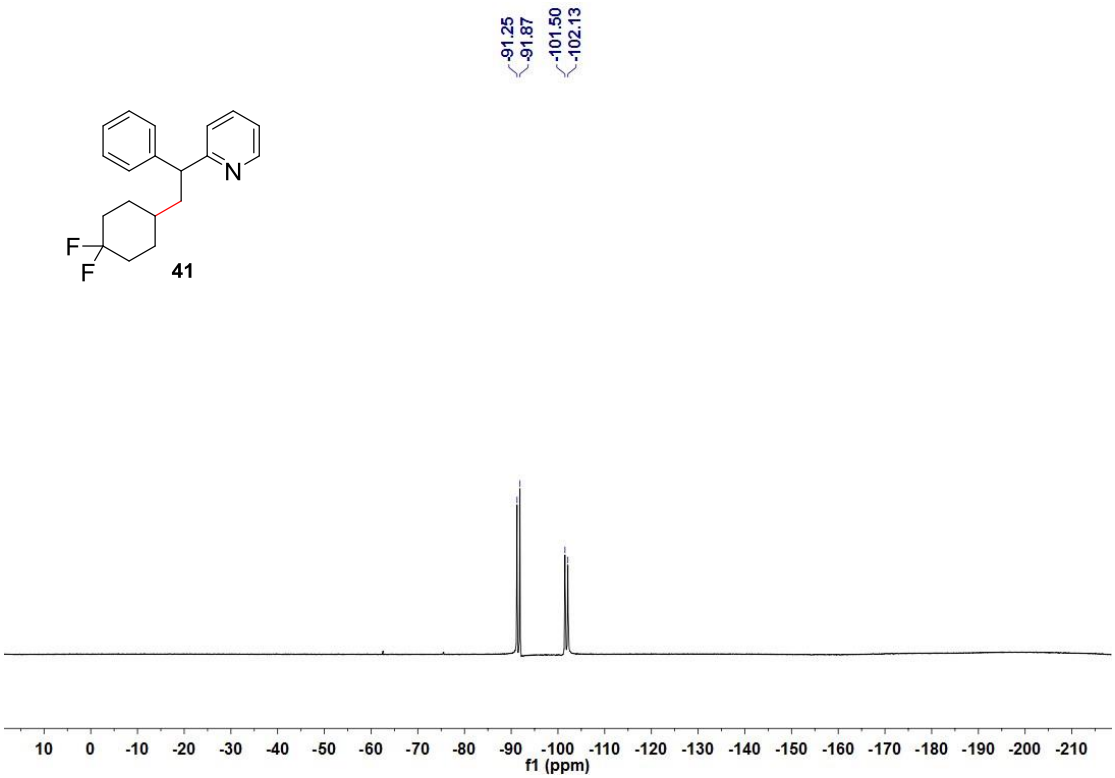


Figure S62. ^{19}F NMR spectra for compound **41**

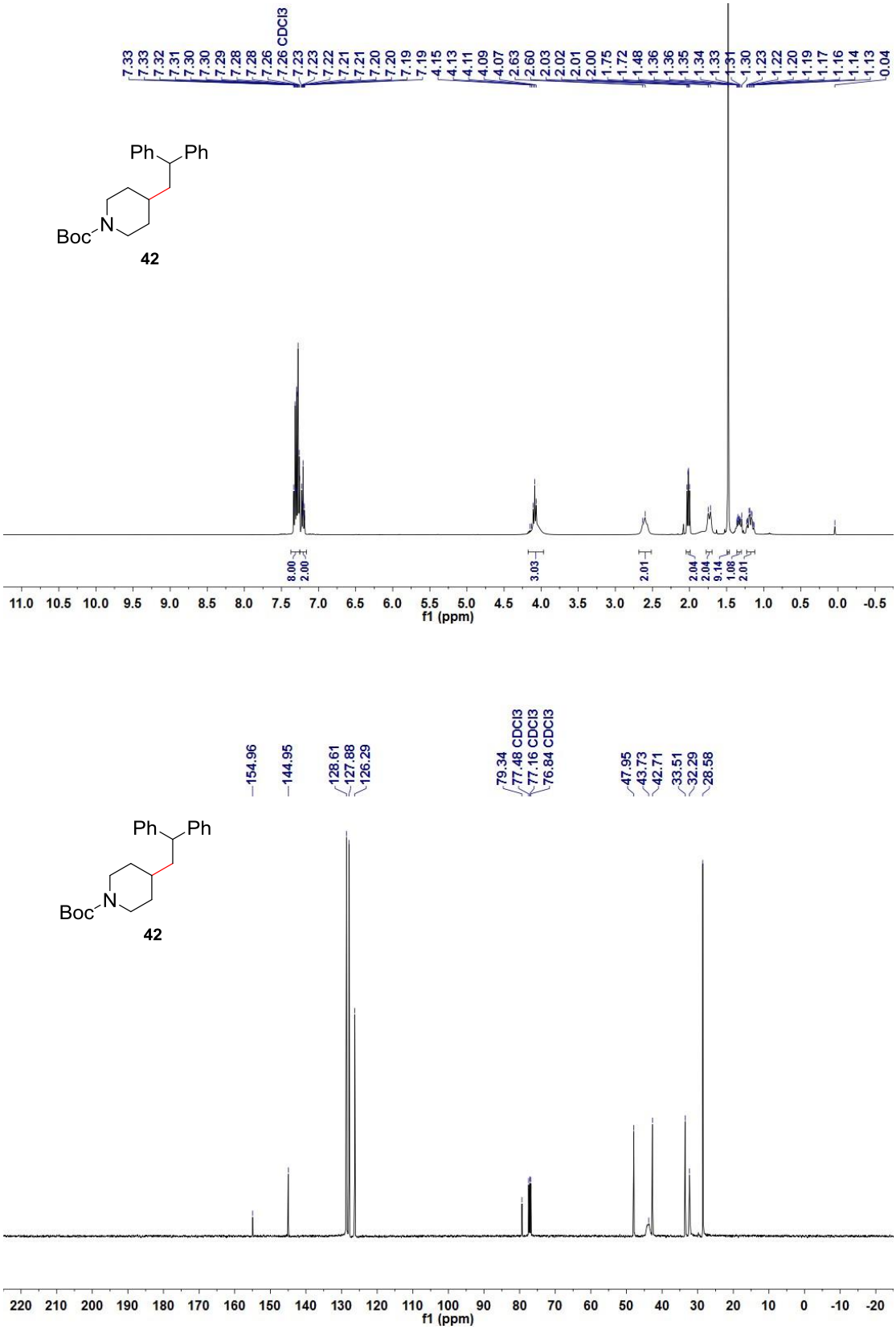


Figure S63. ^{1}H and ^{13}C NMR spectra for compound **42**

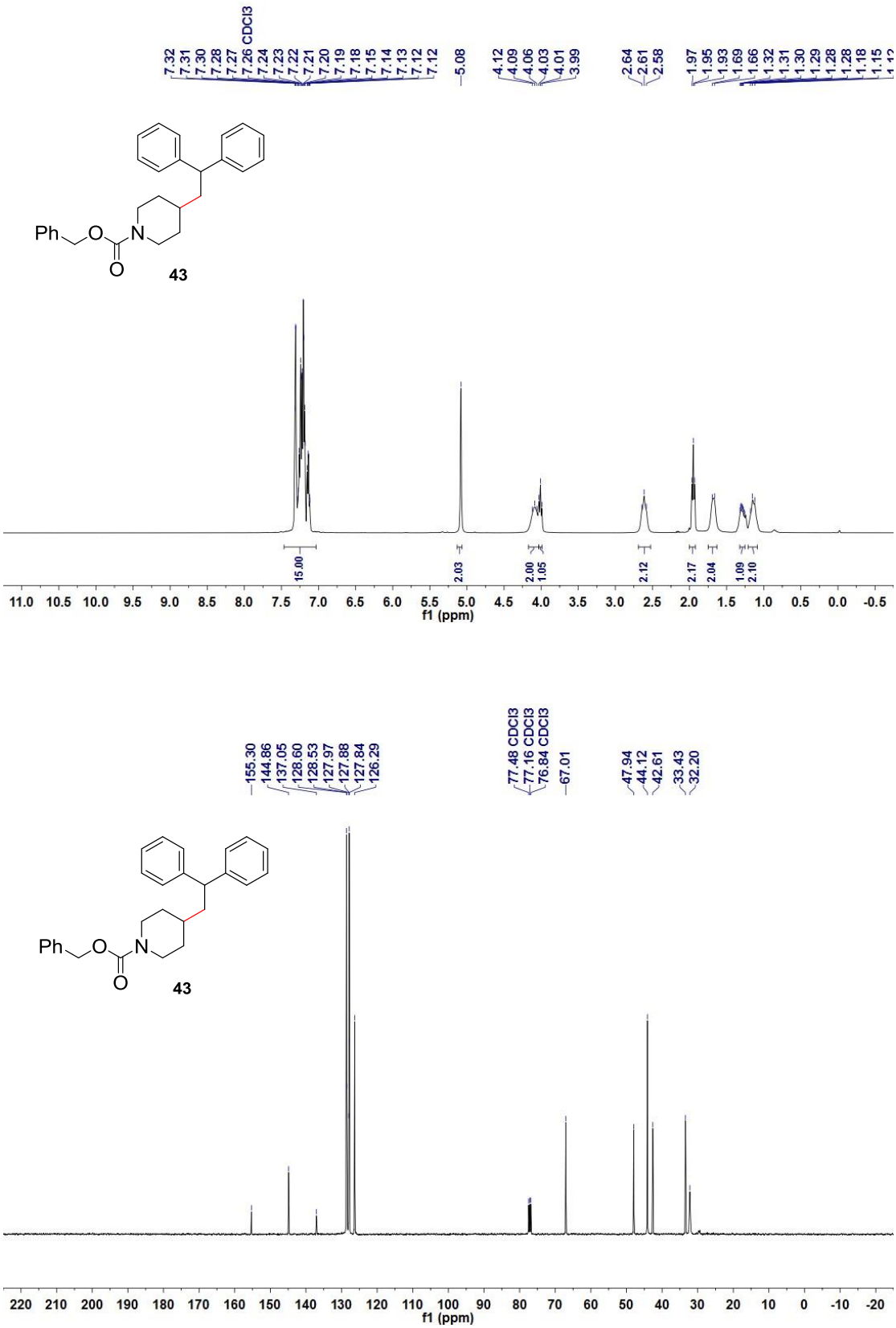


Figure S64. ^{1}H and ^{13}C NMR spectra for compound **43**

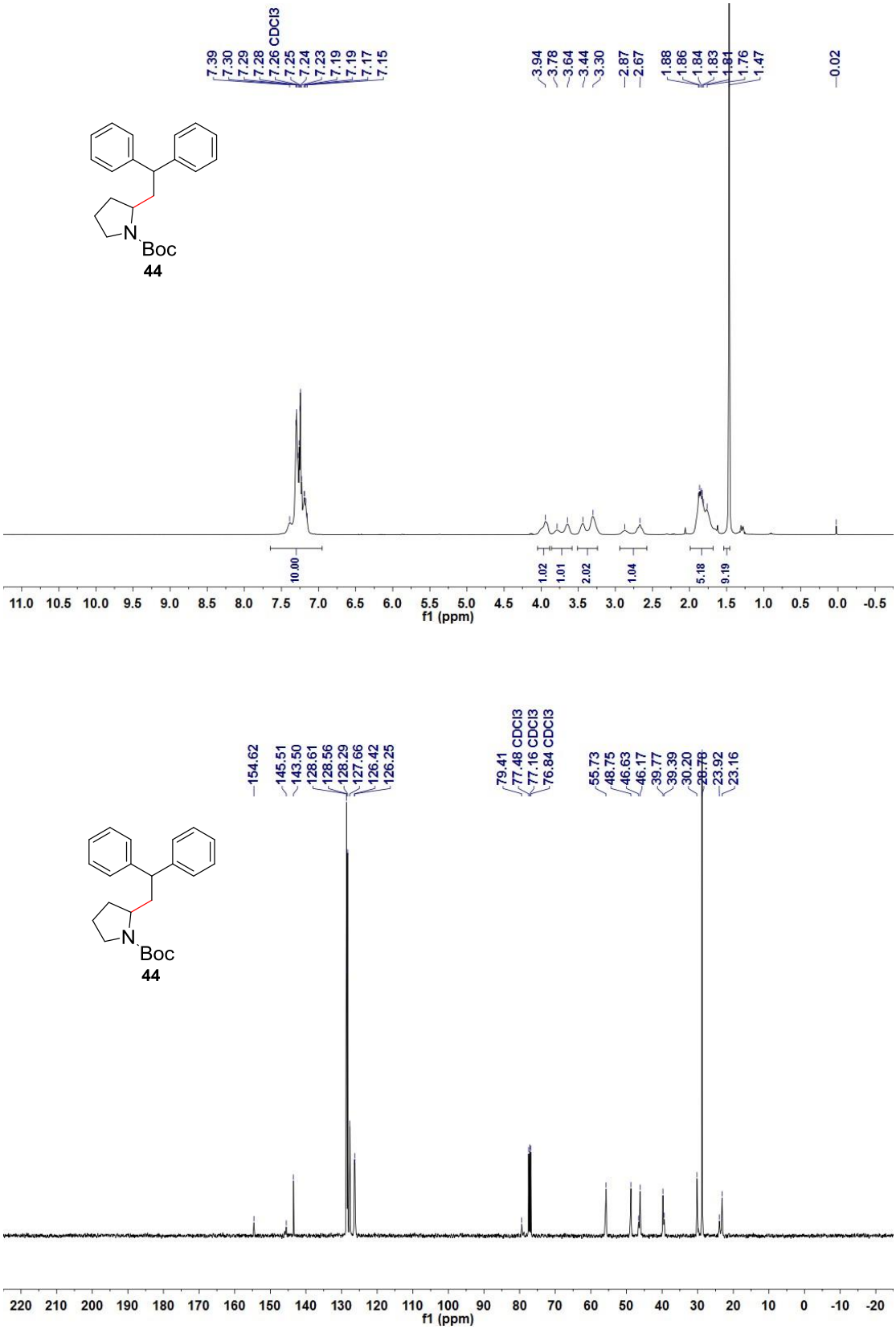


Figure S65. ^{1}H and ^{13}C NMR spectra for compound **44**

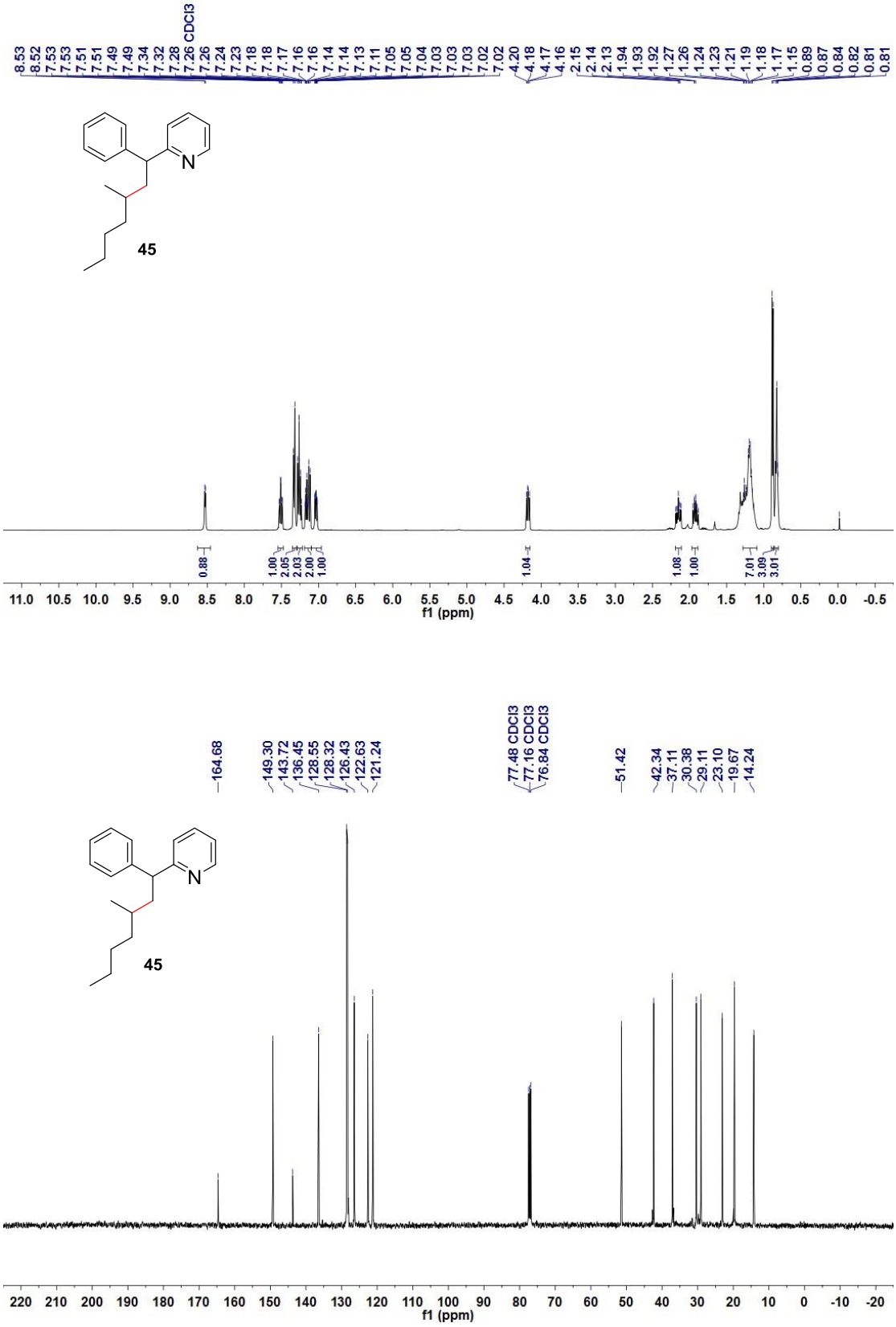


Figure S66. ^{1}H and ^{13}C NMR spectra for compound **45**

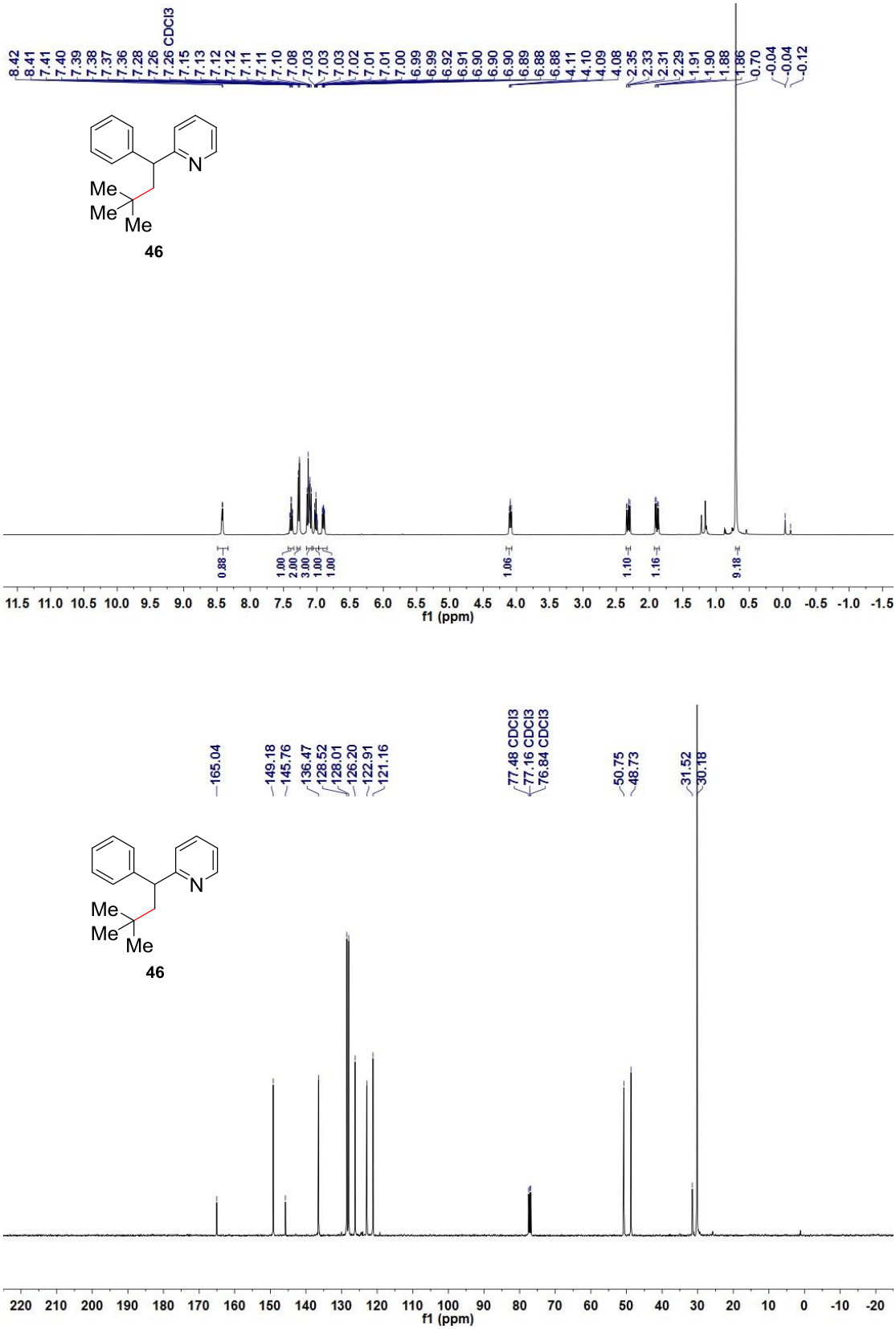


Figure S67. ^{1}H and ^{13}C NMR spectra for compound **46**

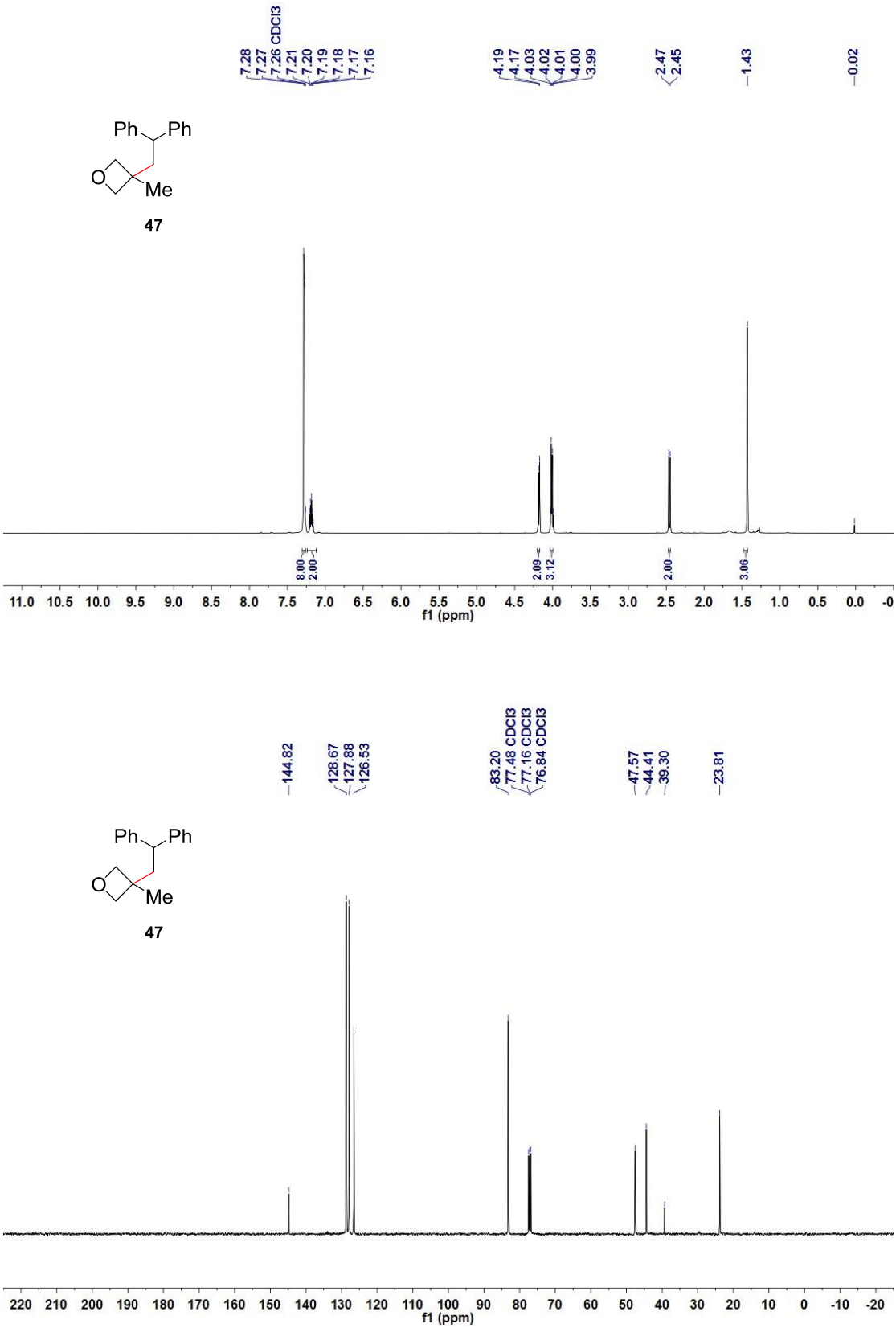


Figure S68. ^{1}H and ^{13}C NMR spectra for compound **47**

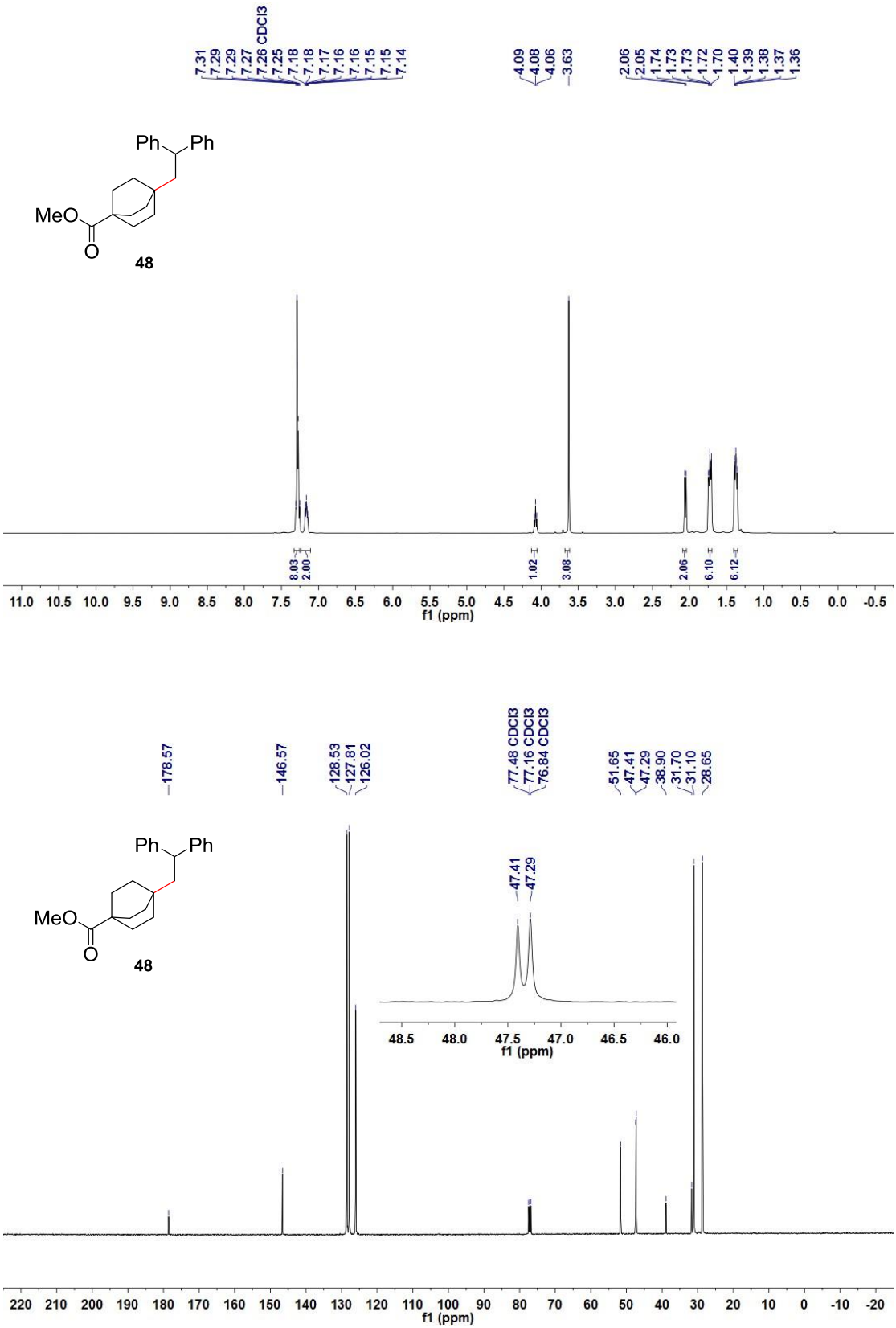


Figure S69. ^{1}H and ^{13}C NMR spectra for compound **48**

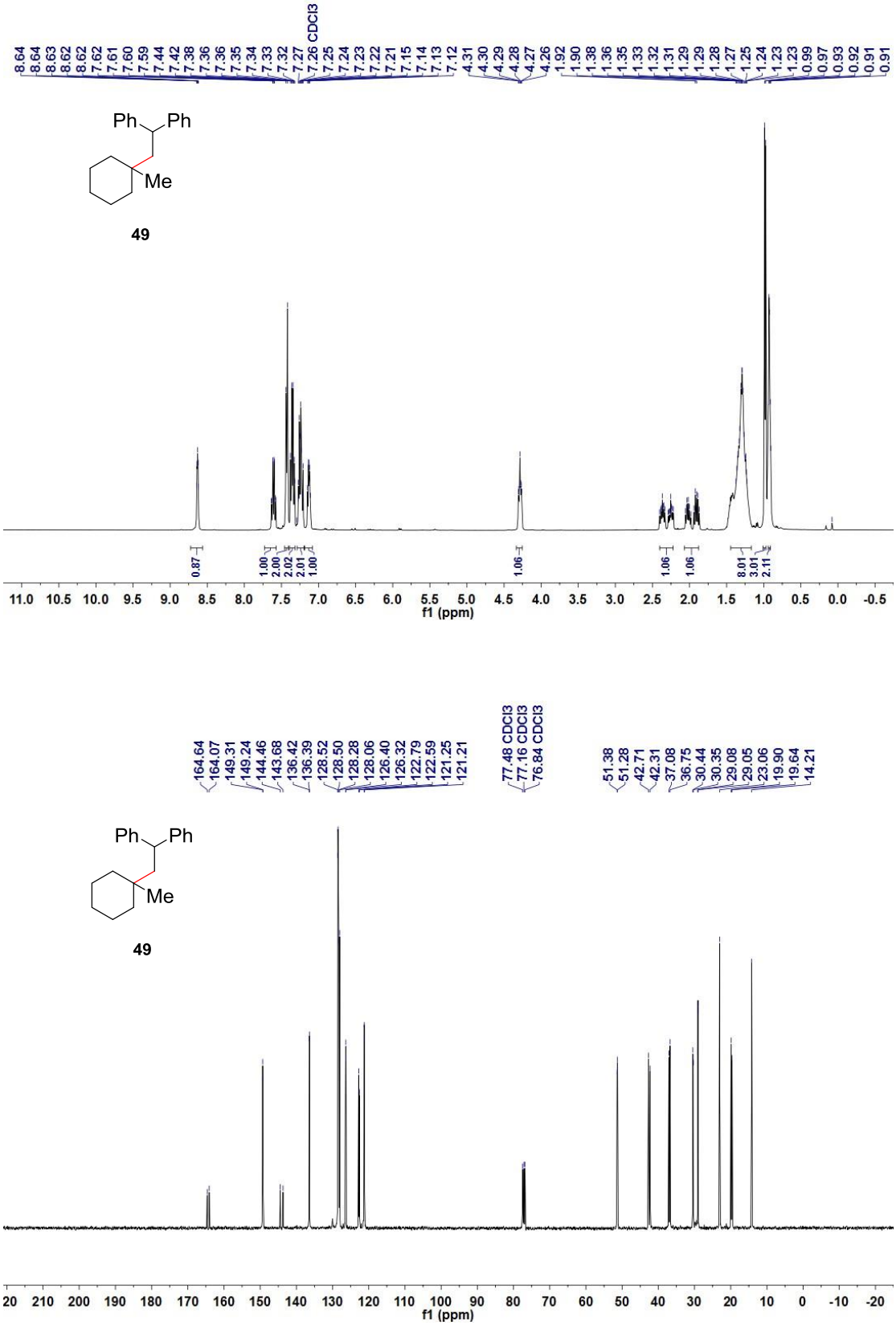


Figure S70. ^{1}H and ^{13}C NMR spectra for compound **49**

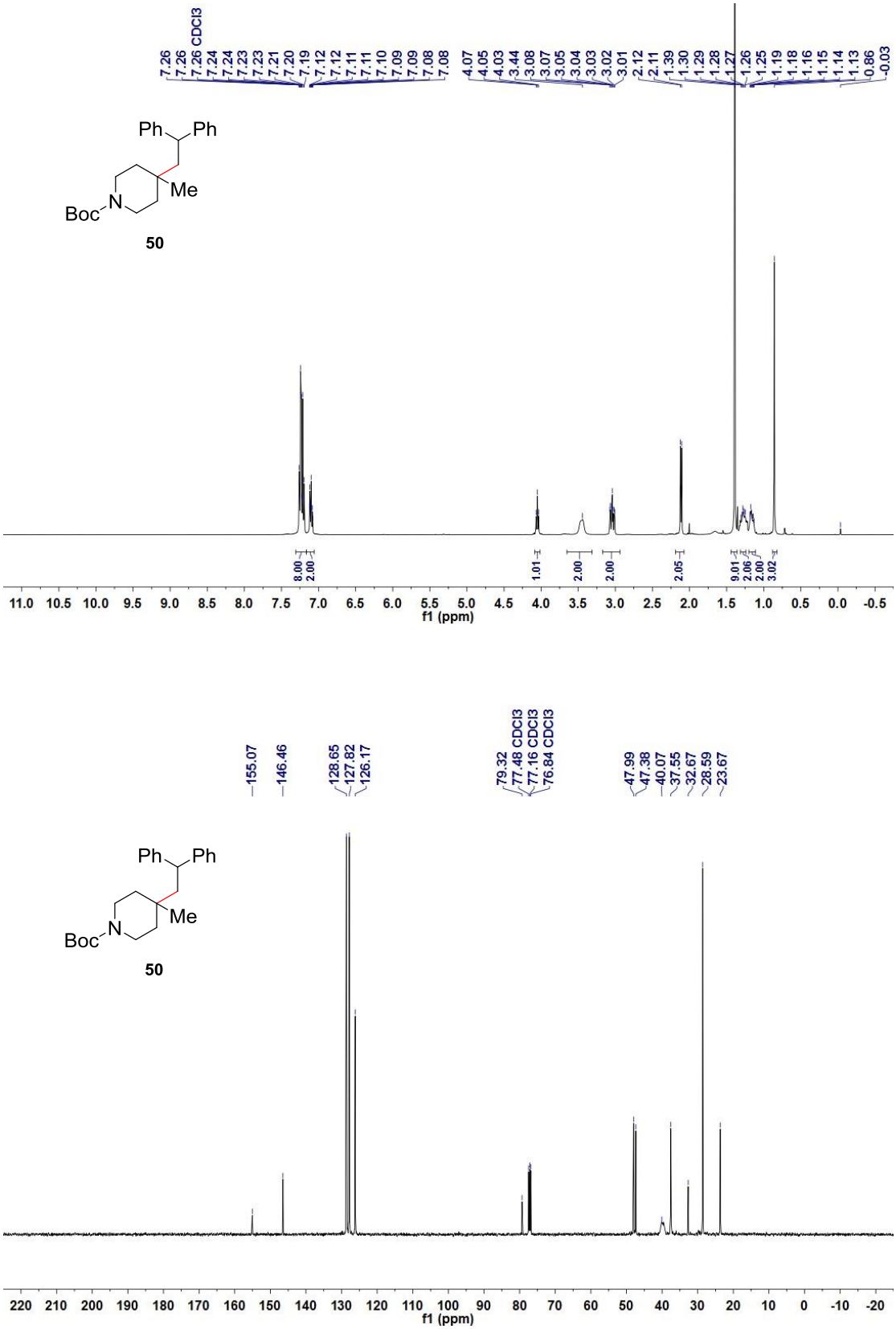


Figure S71. ^{1}H and ^{13}C NMR spectra for compound **50**

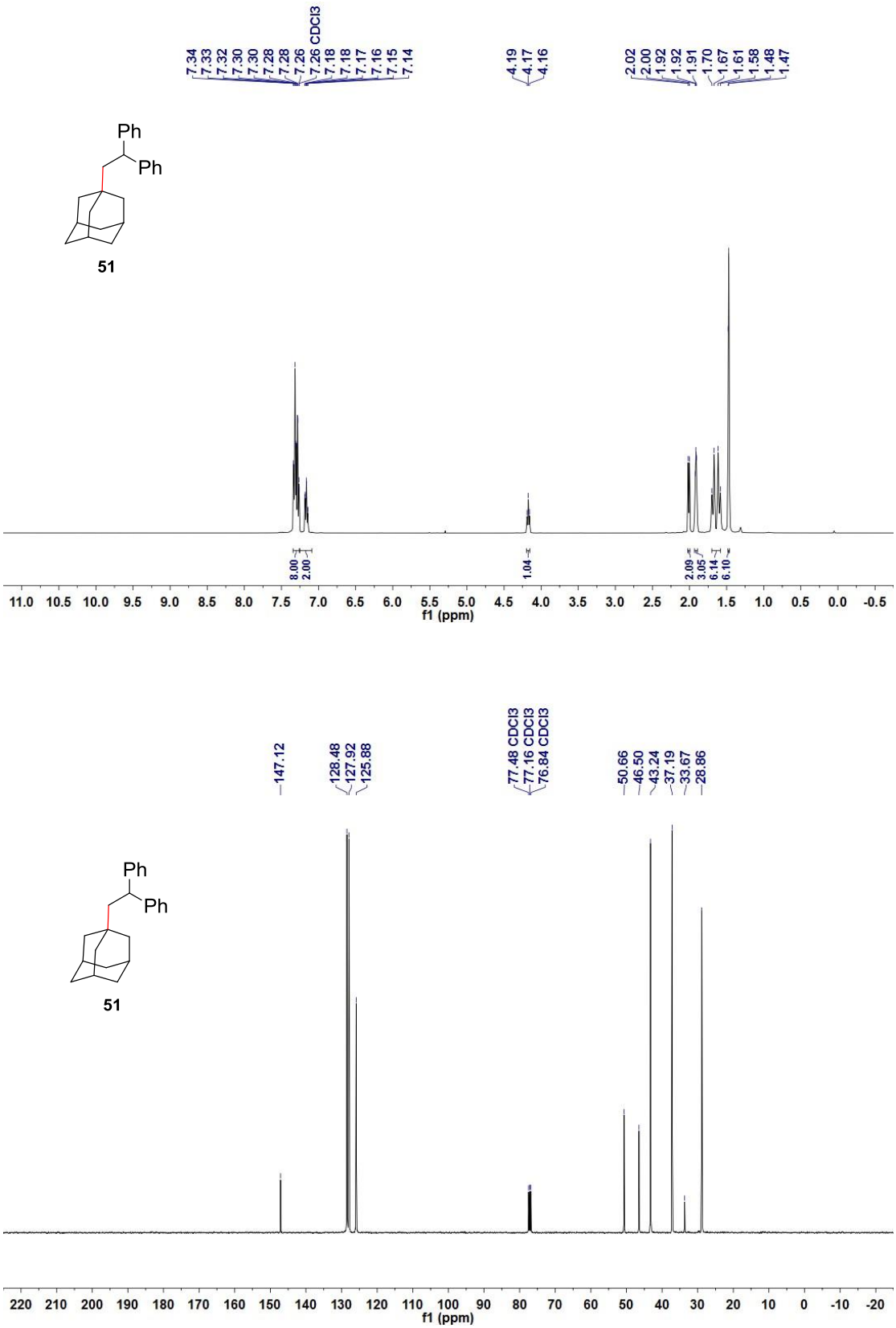


Figure S72. ^{1}H and ^{13}C NMR spectra for compound **51**

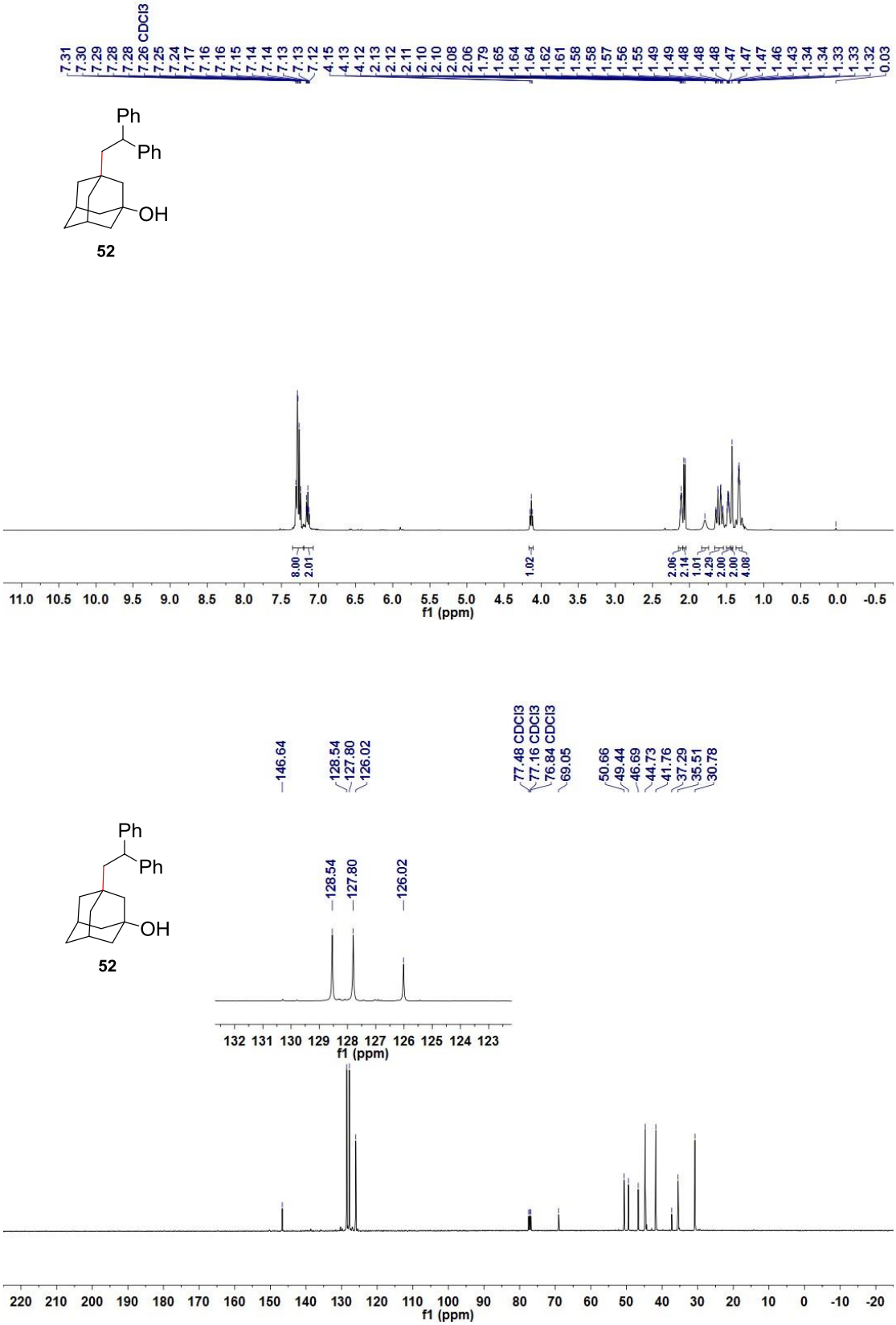


Figure S73. ^{1}H and ^{13}C NMR spectra for compound **52**

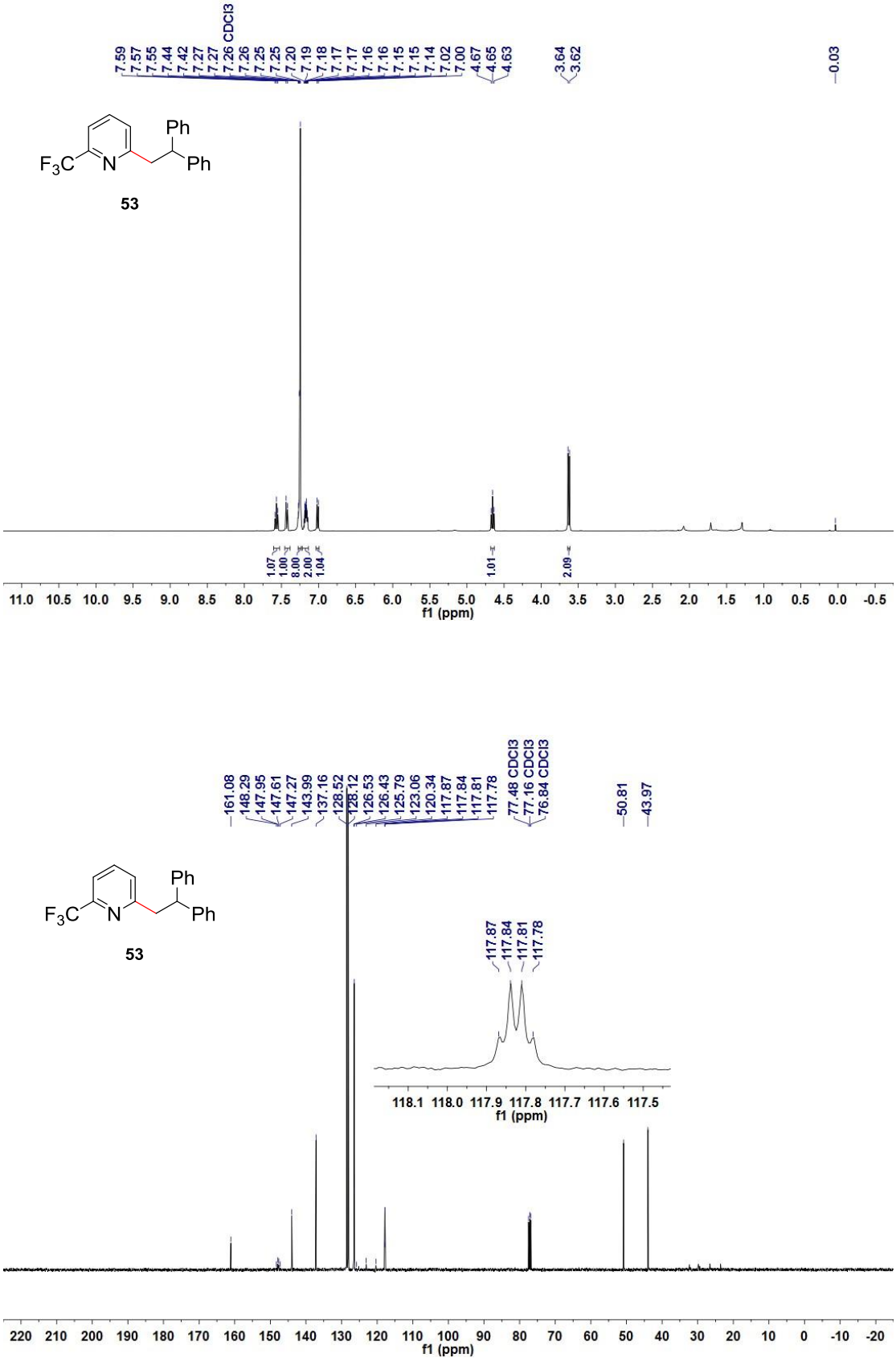


Figure S74. ^{1}H and ^{13}C NMR spectra for compound **53**

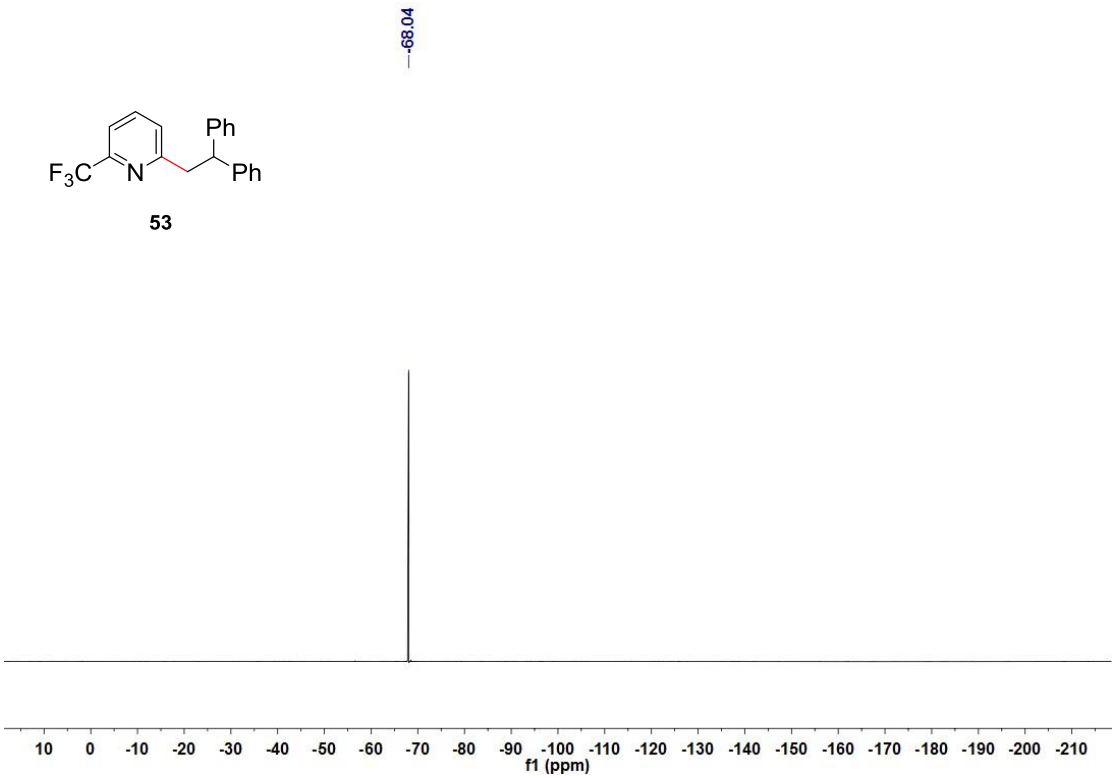


Figure S75. ^{19}F NMR spectra for compound **53**

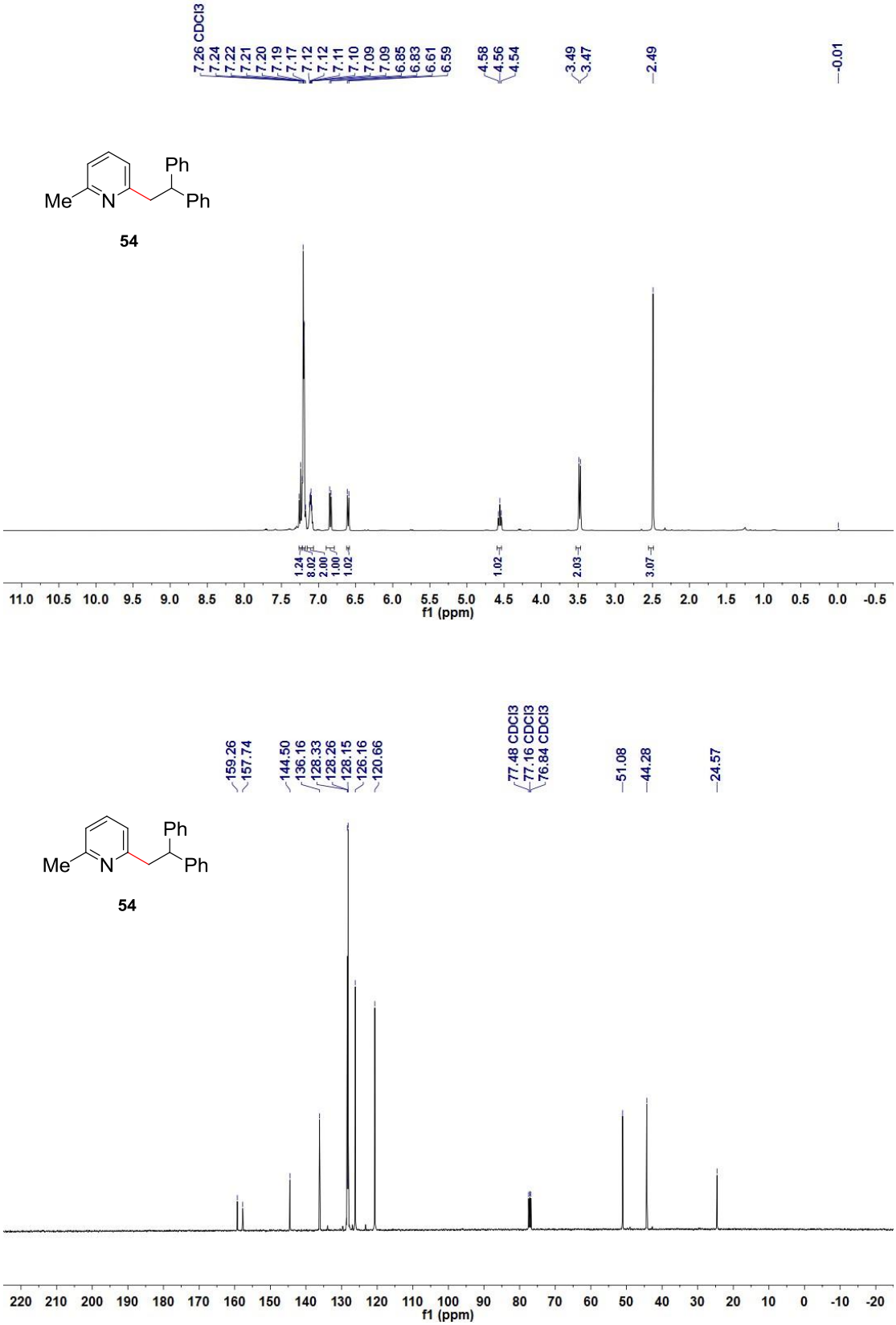


Figure S76. ^{1}H, ^{13}C and ^{19}F NMR spectra for compound **54**

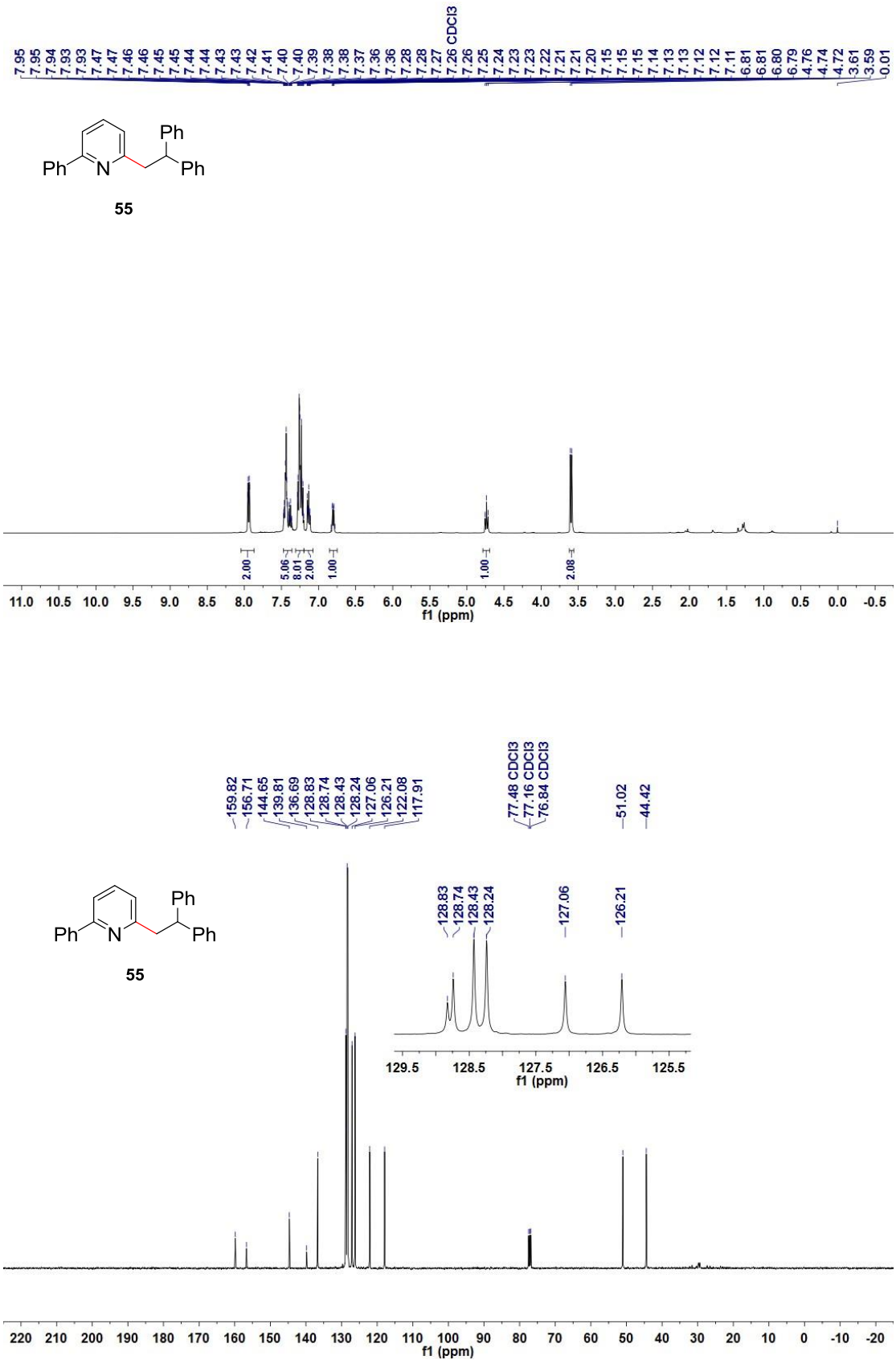


Figure S77. ^{1}H and ^{13}C NMR spectra for compound **55**

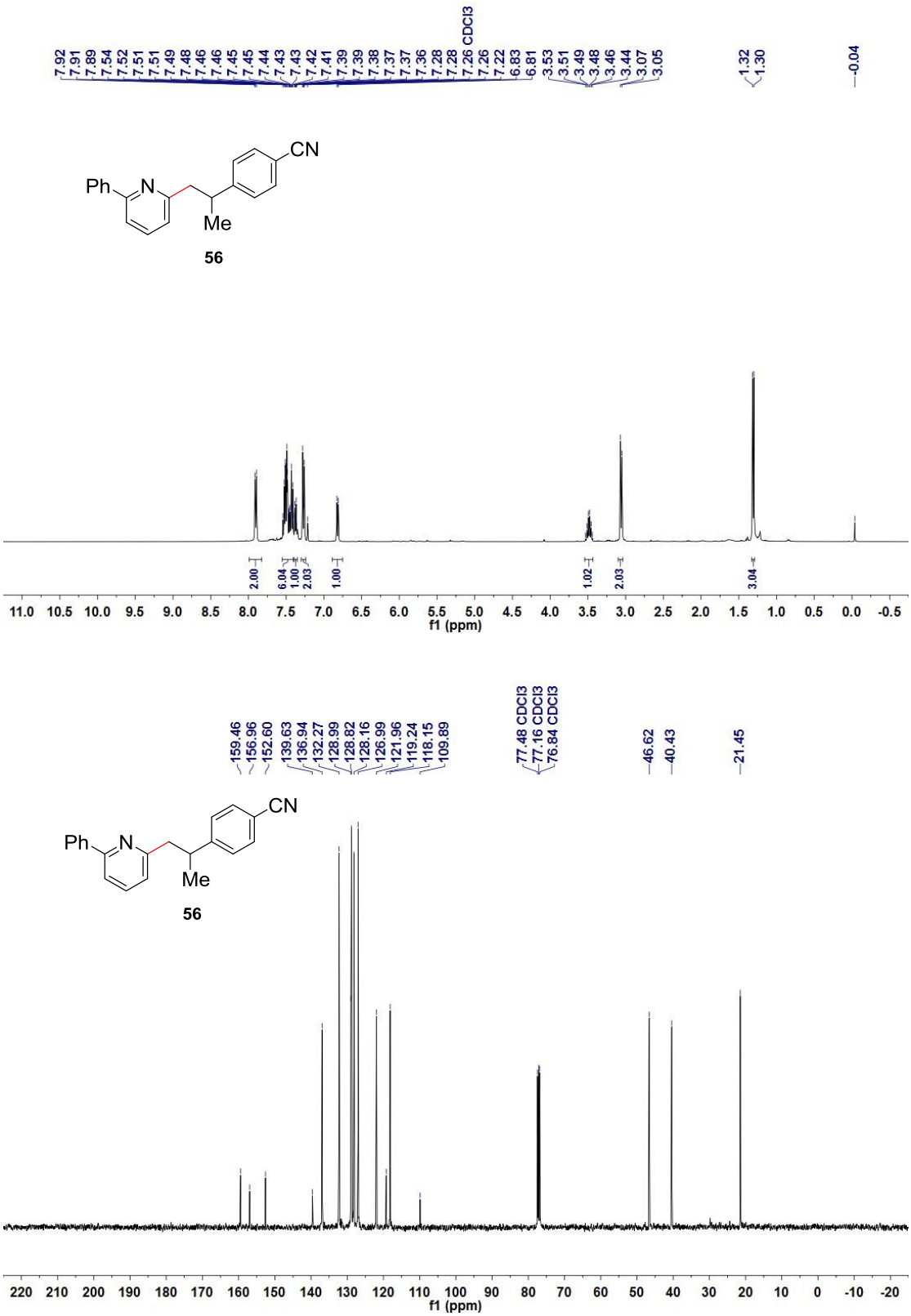


Figure S78. ^{1}H and ^{13}C NMR spectra for compound **56**

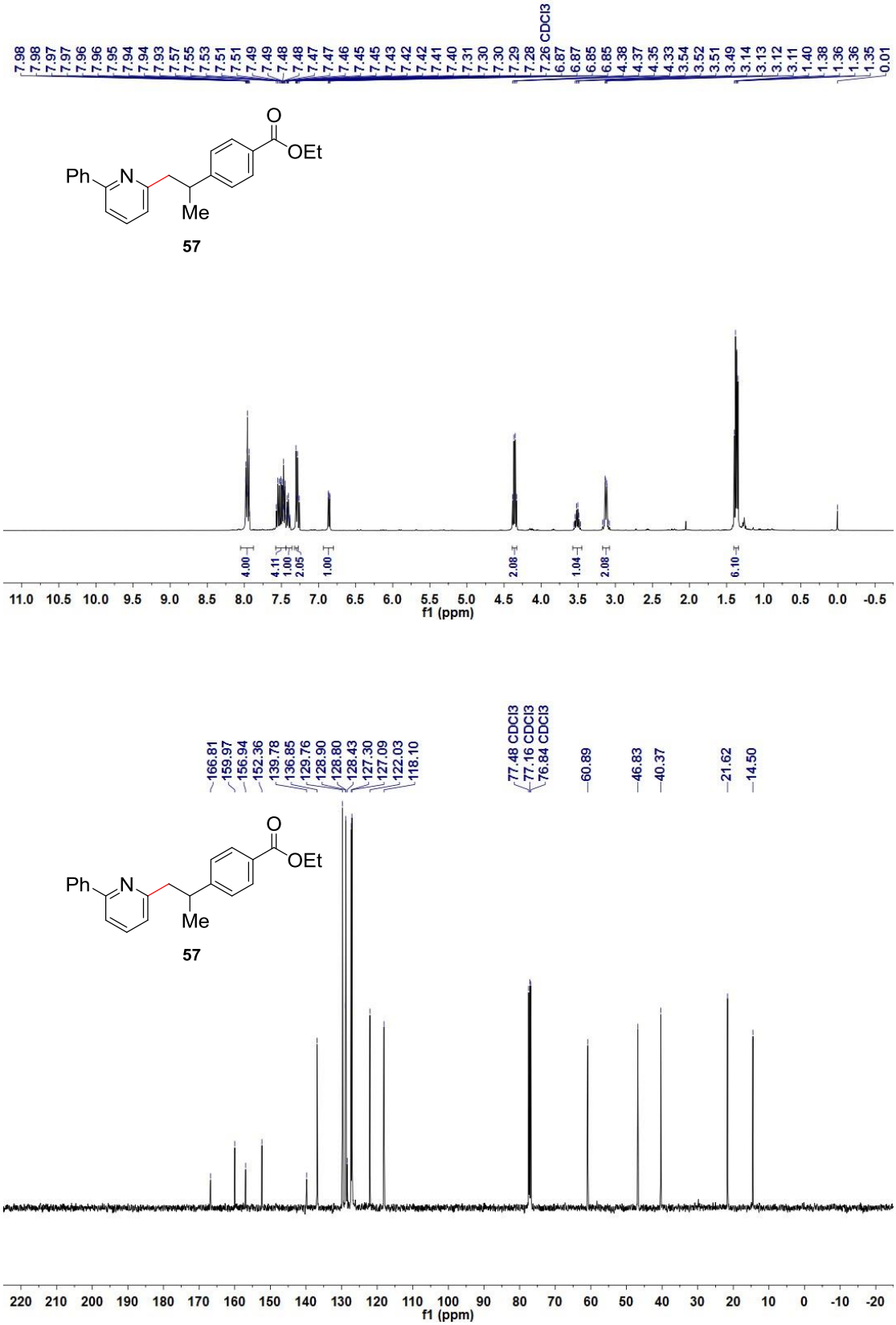


Figure S79. ^{1}H and ^{13}C spectra for compound **57**

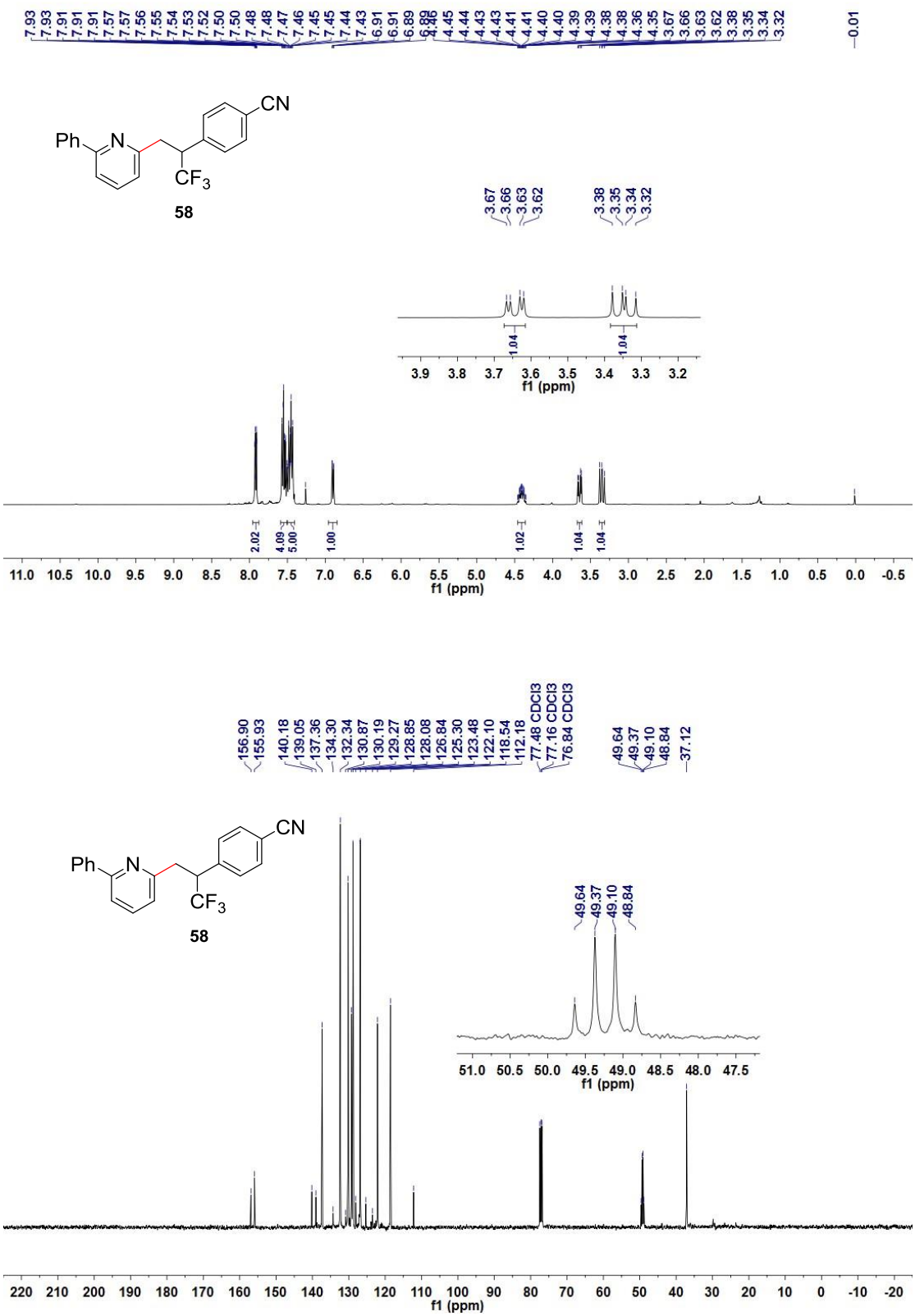


Figure S80. ^{1}H and ^{13}C NMR spectra for compound **58**

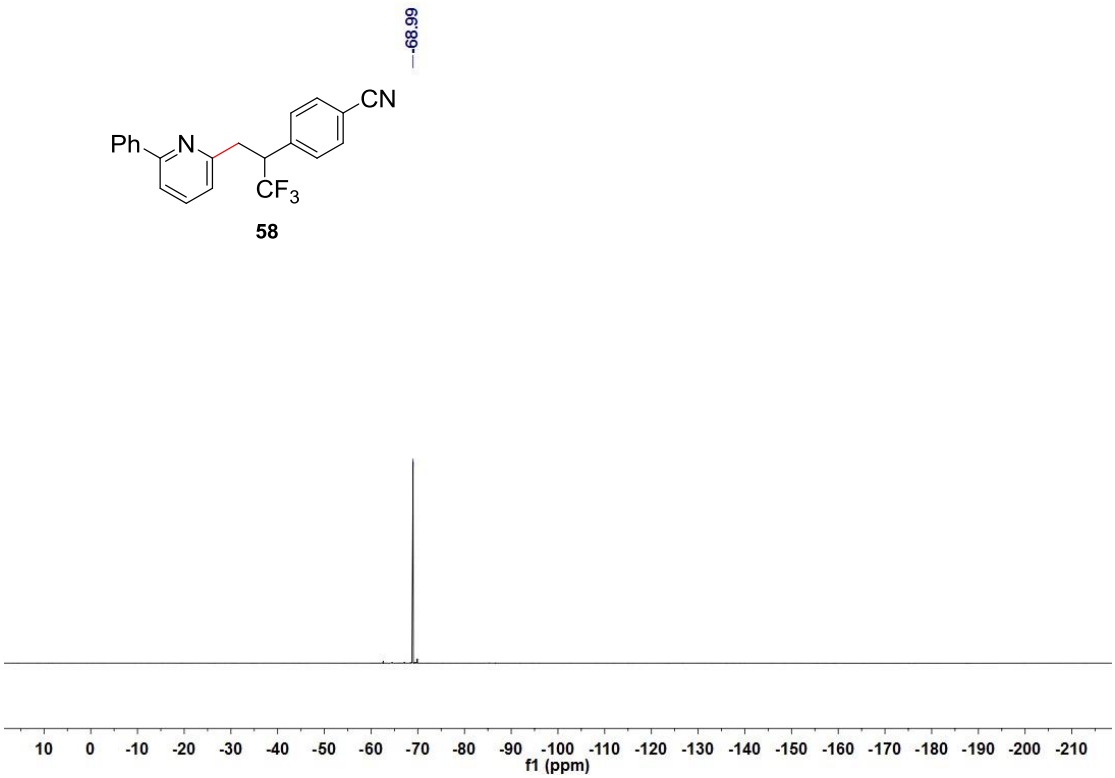


Figure S81. ^{19}F NMR spectra for compound **58**

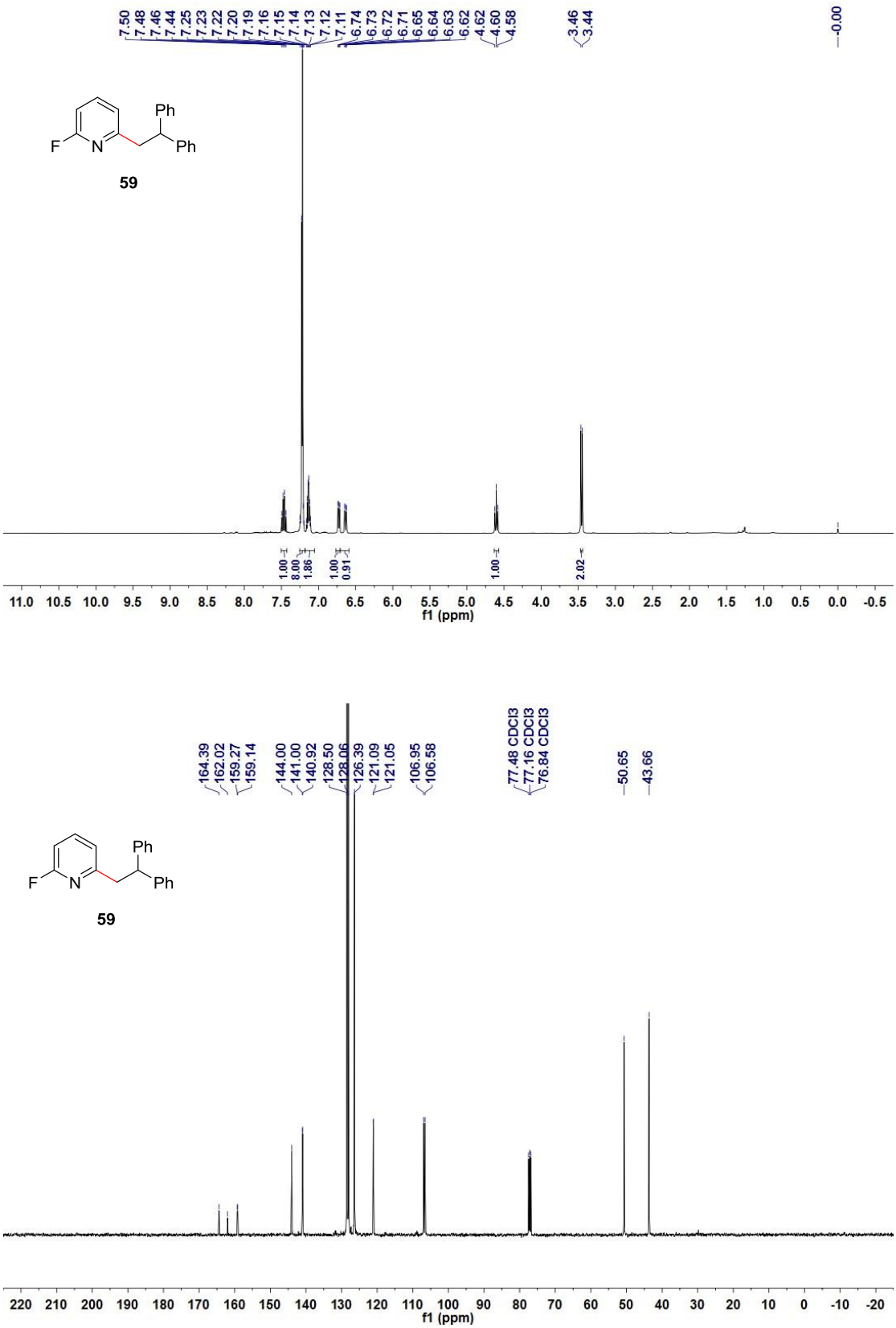


Figure S82. ^{1}H and ^{13}C NMR spectra for compound **59**

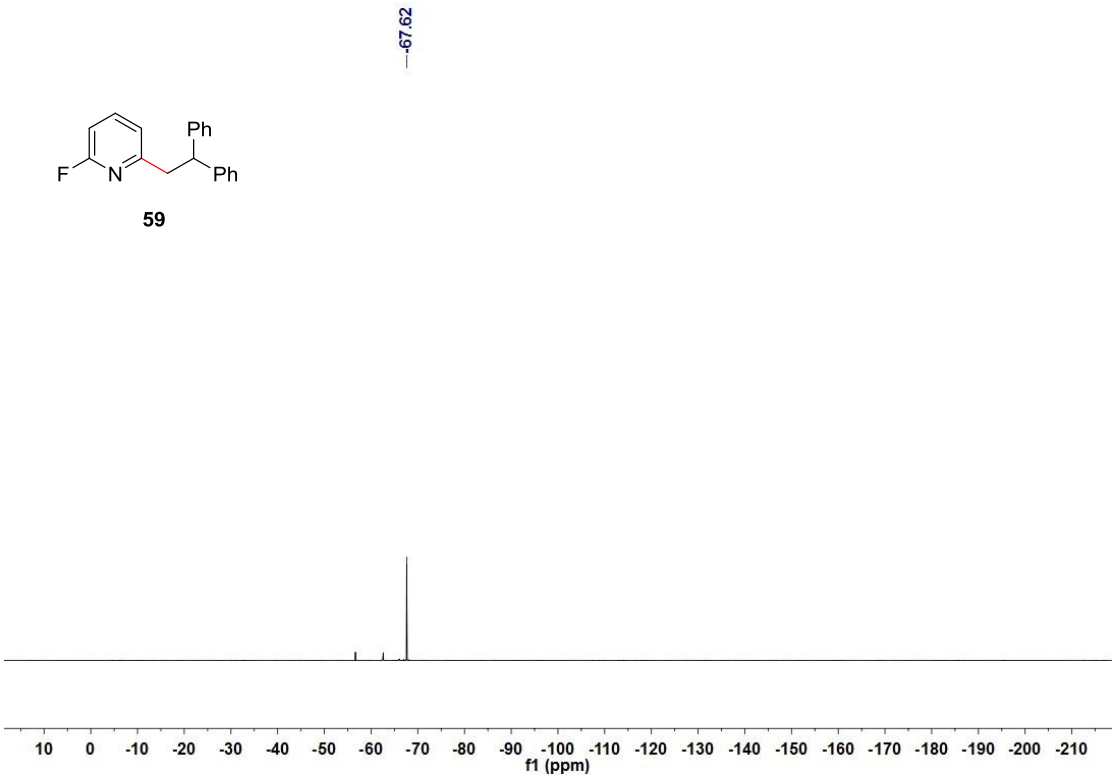


Figure S83. ^{19}F NMR spectra for compound **59**

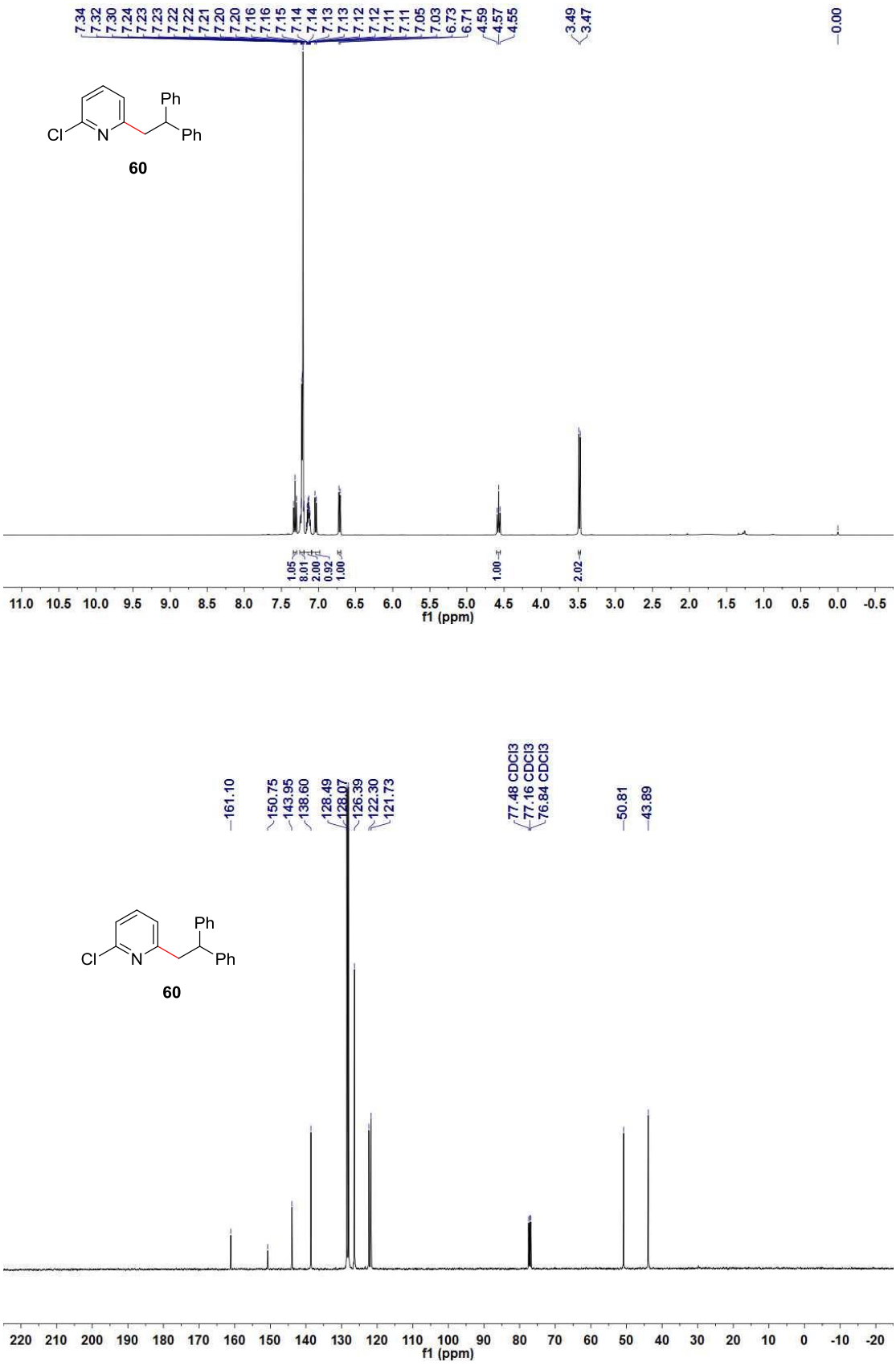


Figure S84. ^{1}H and ^{13}C NMR spectra for compound **60**

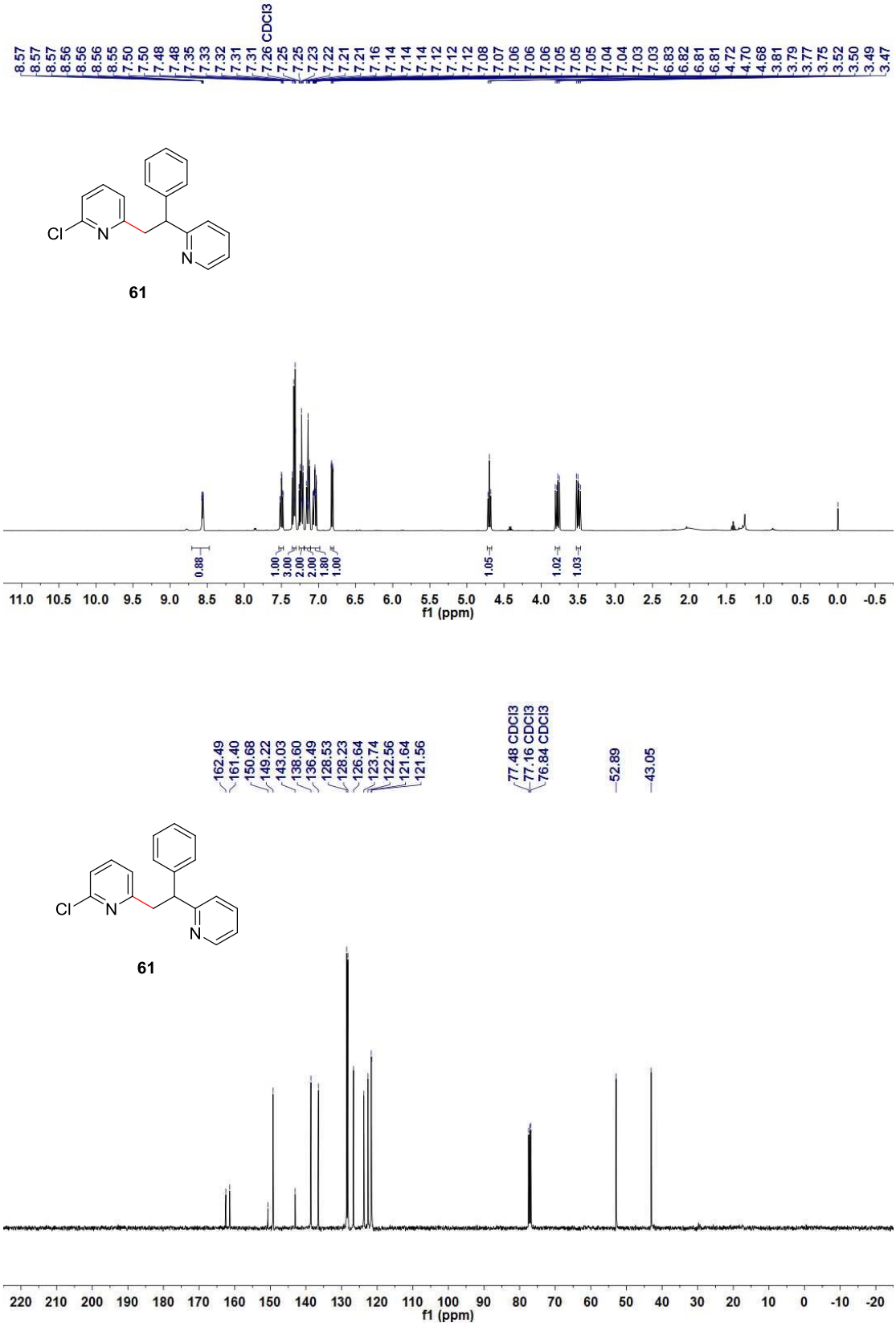


Figure S85. ^{1}H and ^{13}C NMR spectra for compound **61**

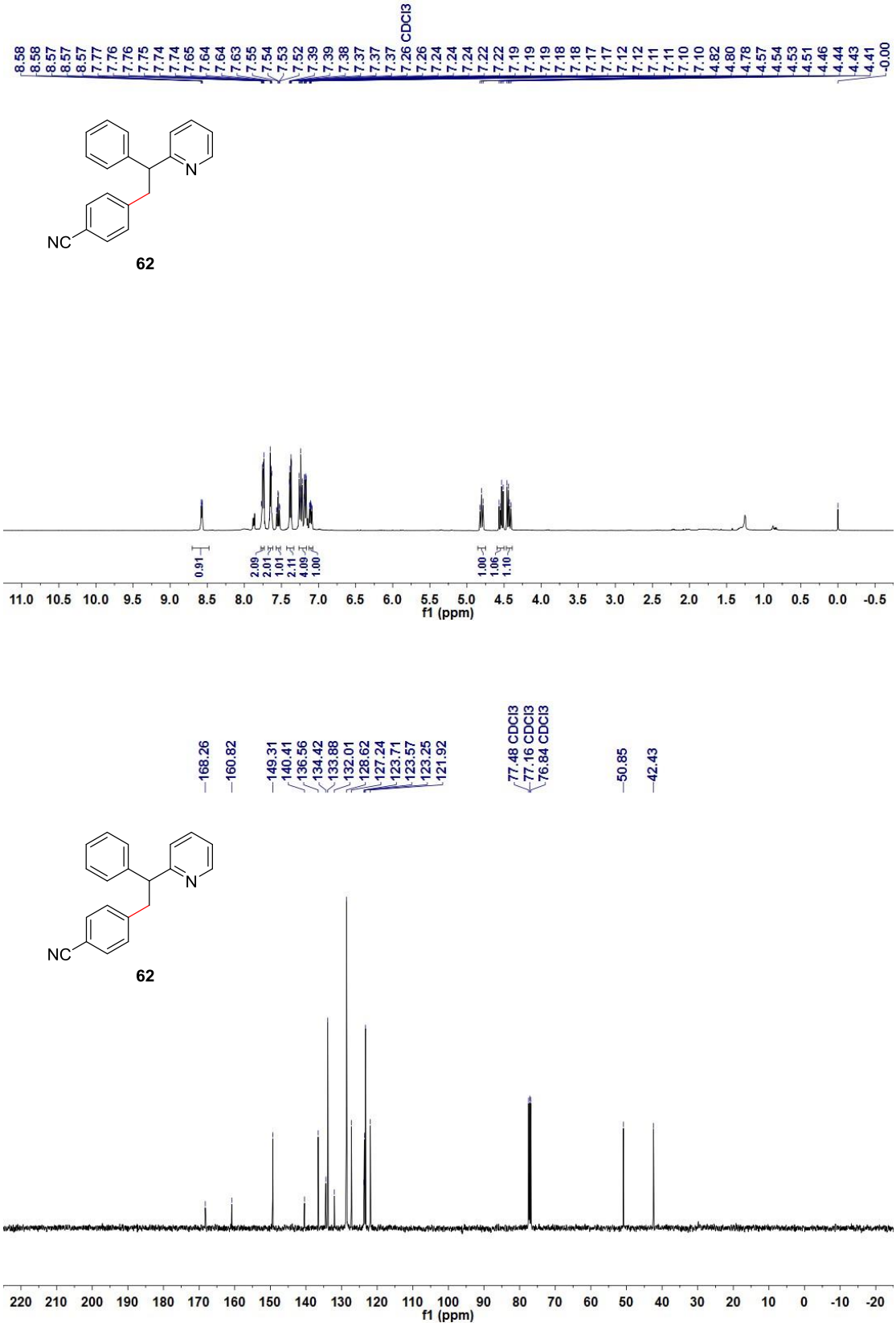


Figure S86. ^{1}H and ^{13}C NMR spectra for compound **62**

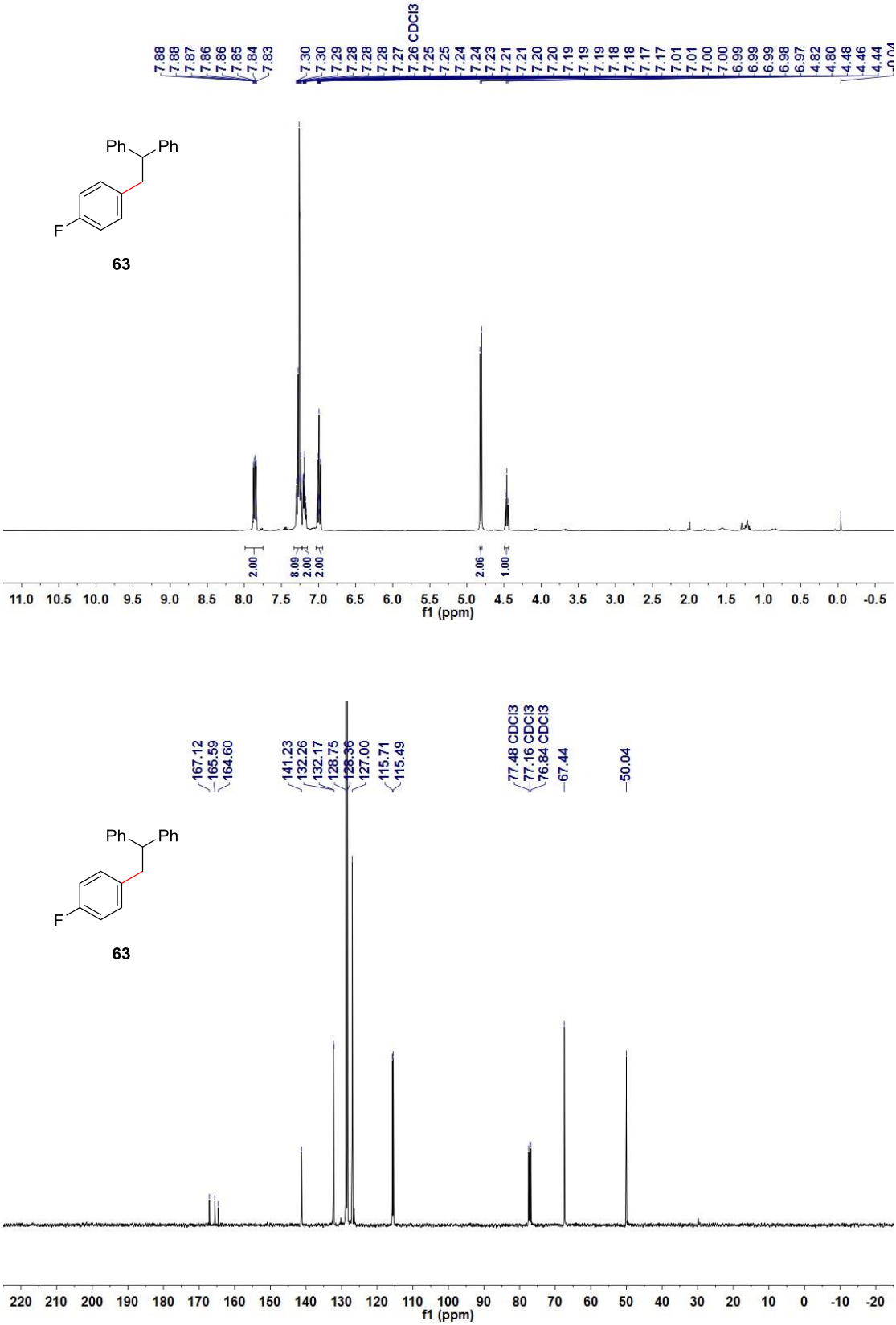


Figure S87. ^{1}H and ^{13}C NMR spectra for compound **63**

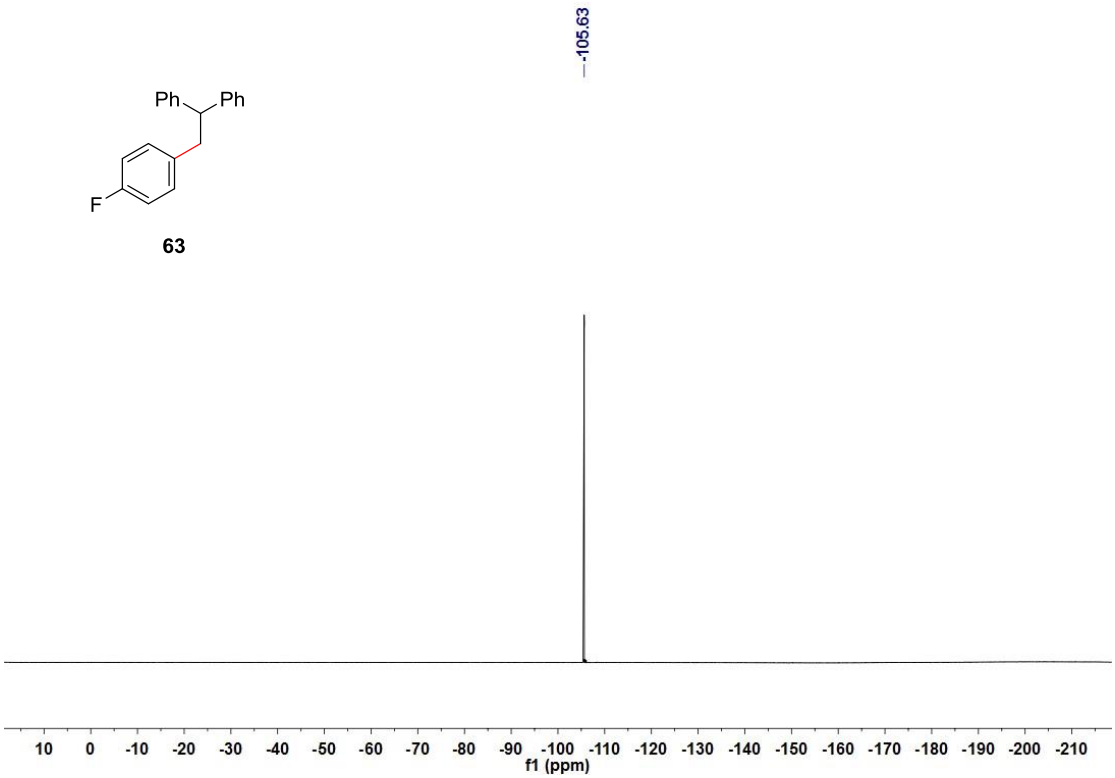


Figure S88. ^{19}F NMR spectra for compound **63**

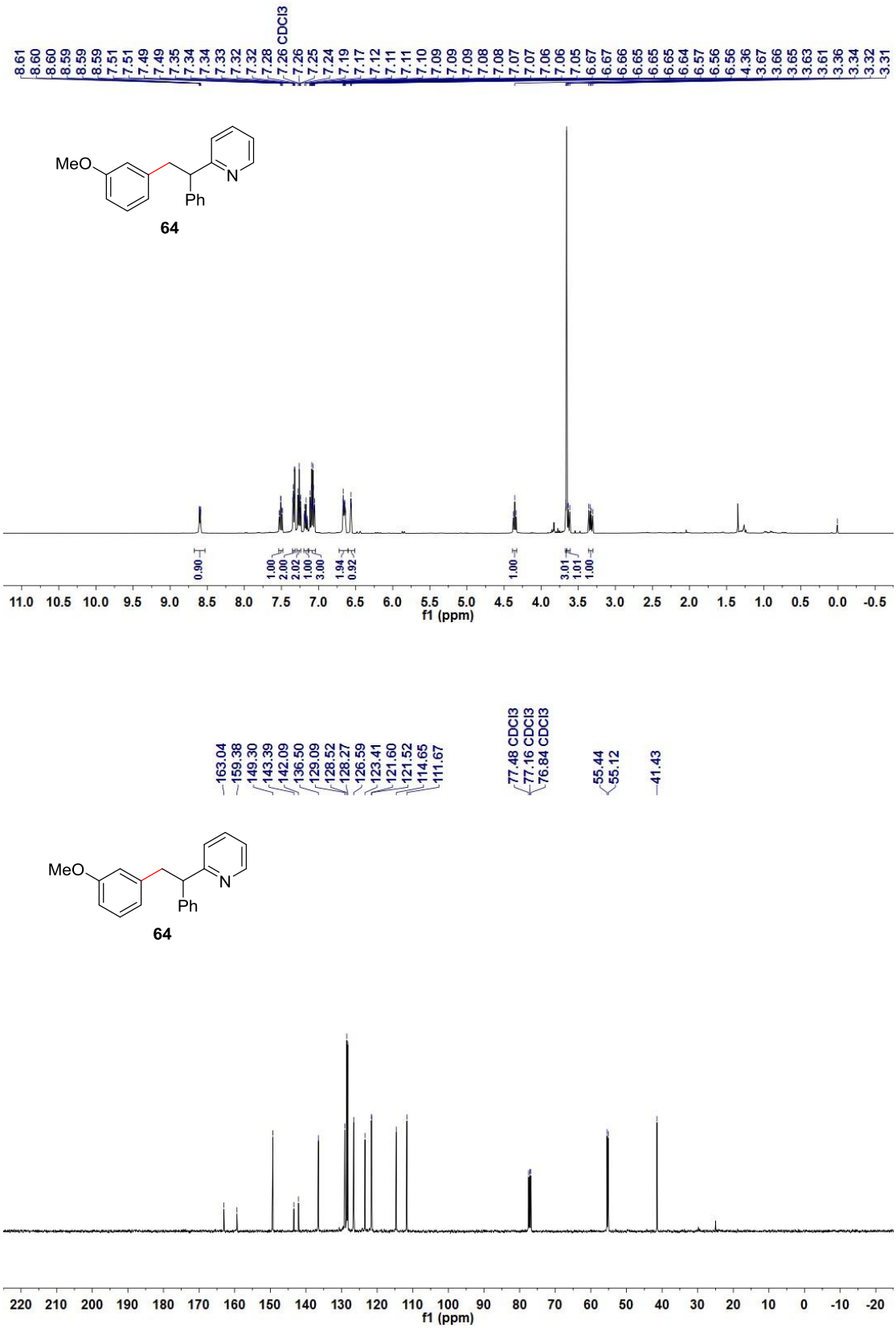


Figure S89. ^{1}H and ^{13}C NMR spectra for compound **64**

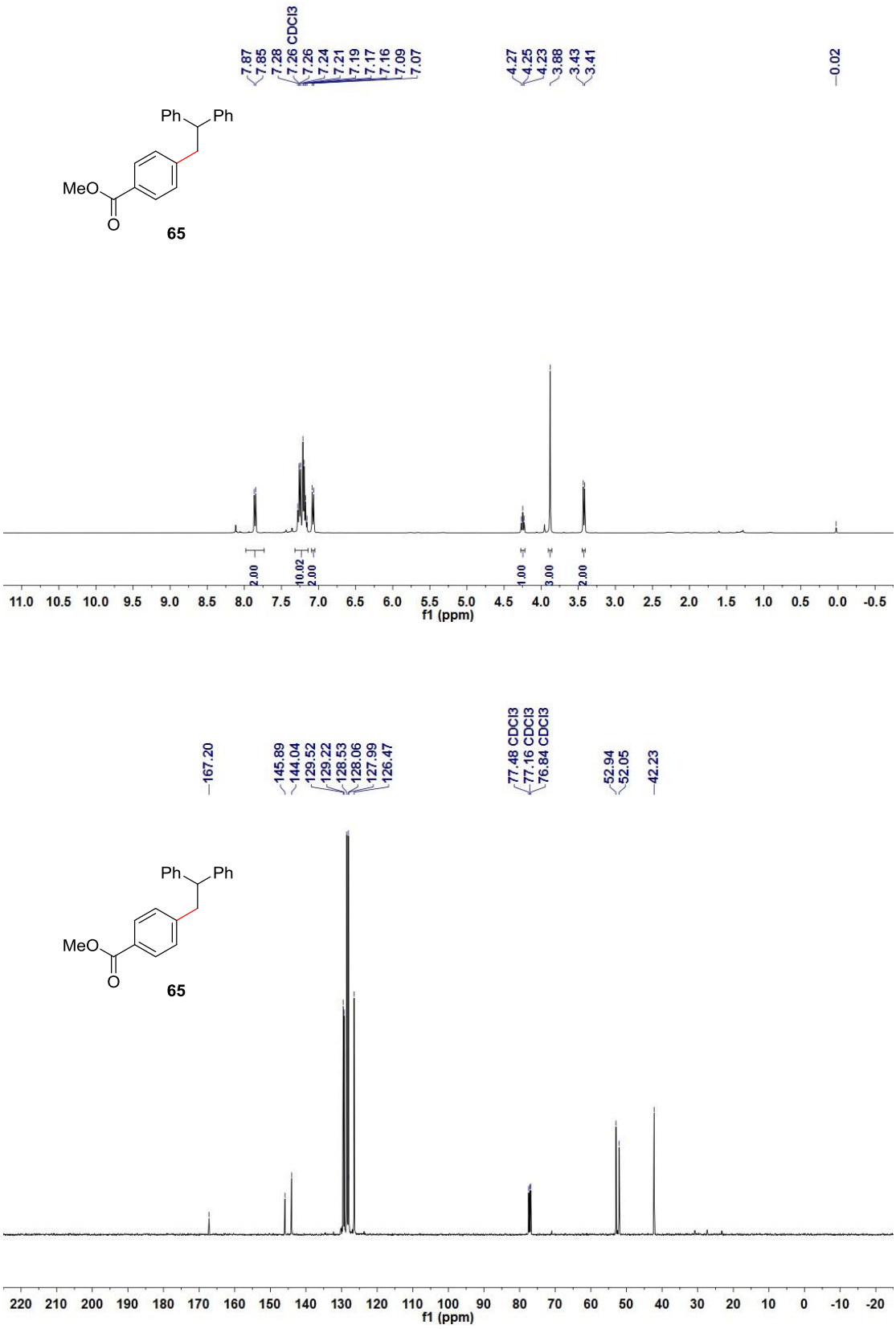


Figure S90. ^{1}H and ^{13}C NMR spectra for compound **65**

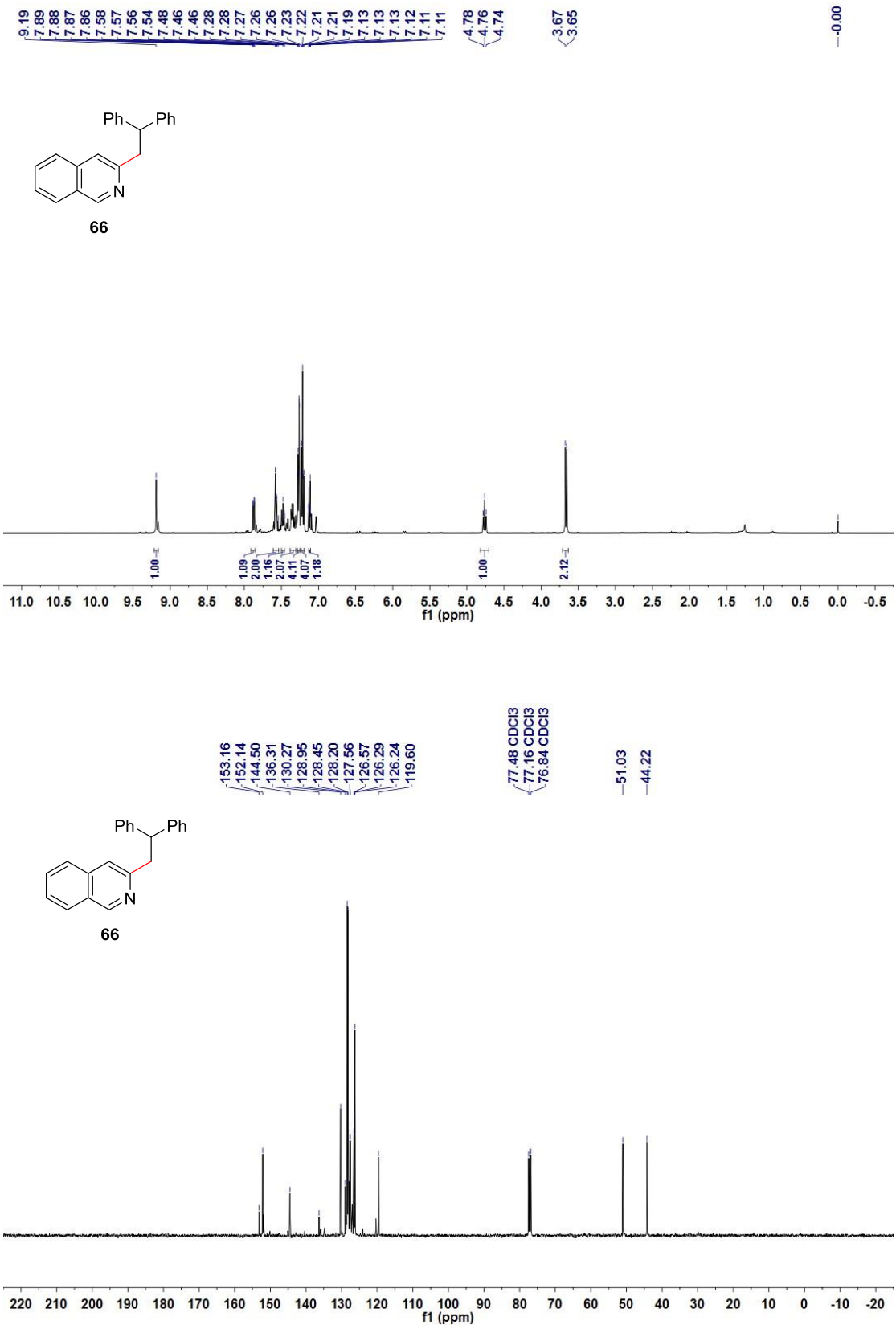


Figure S91. ^{1}H and ^{13}C NMR spectra for compound **66**

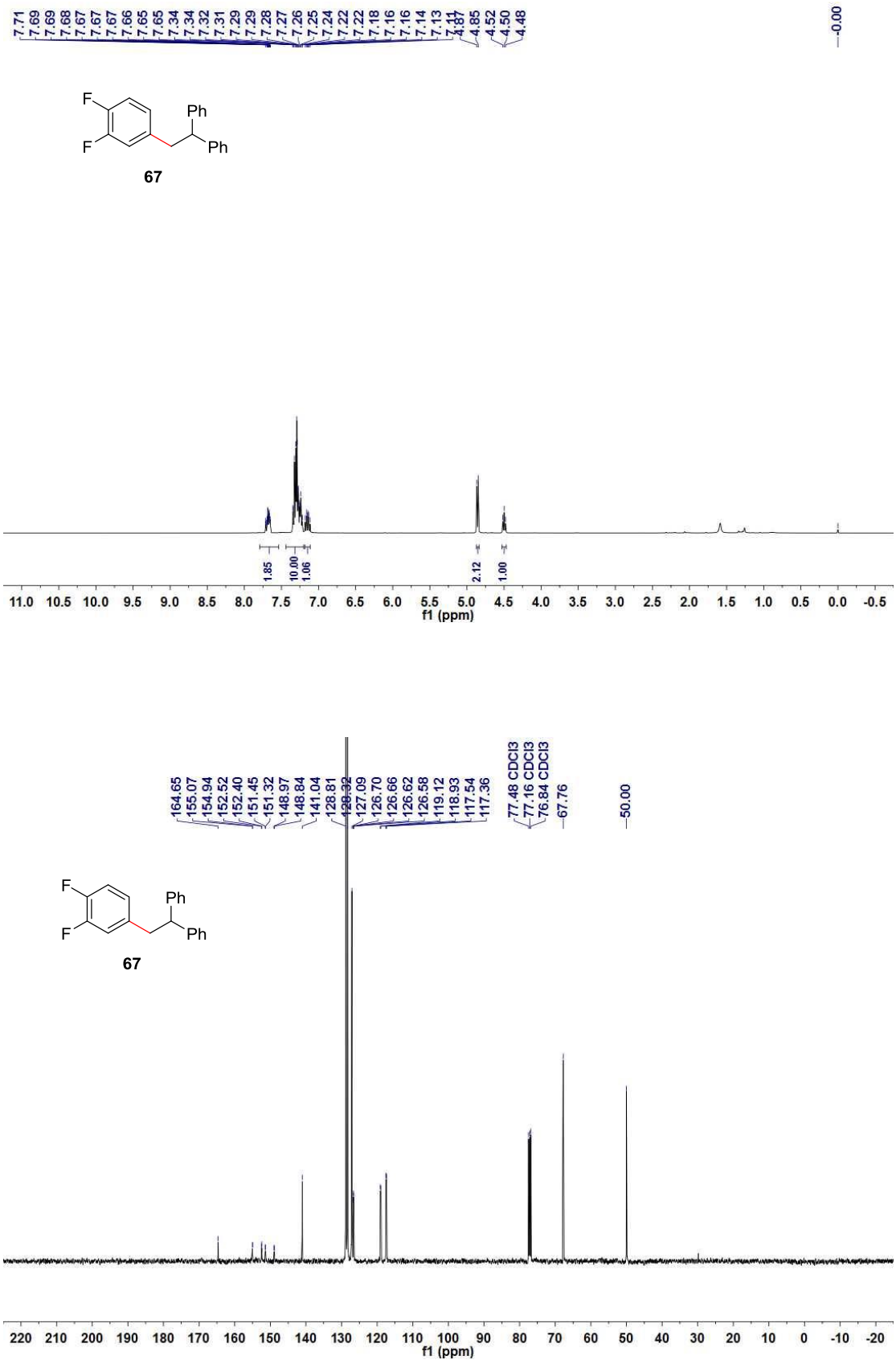


Figure S92. ^{1}H and ^{13}C NMR spectra for compound **67**

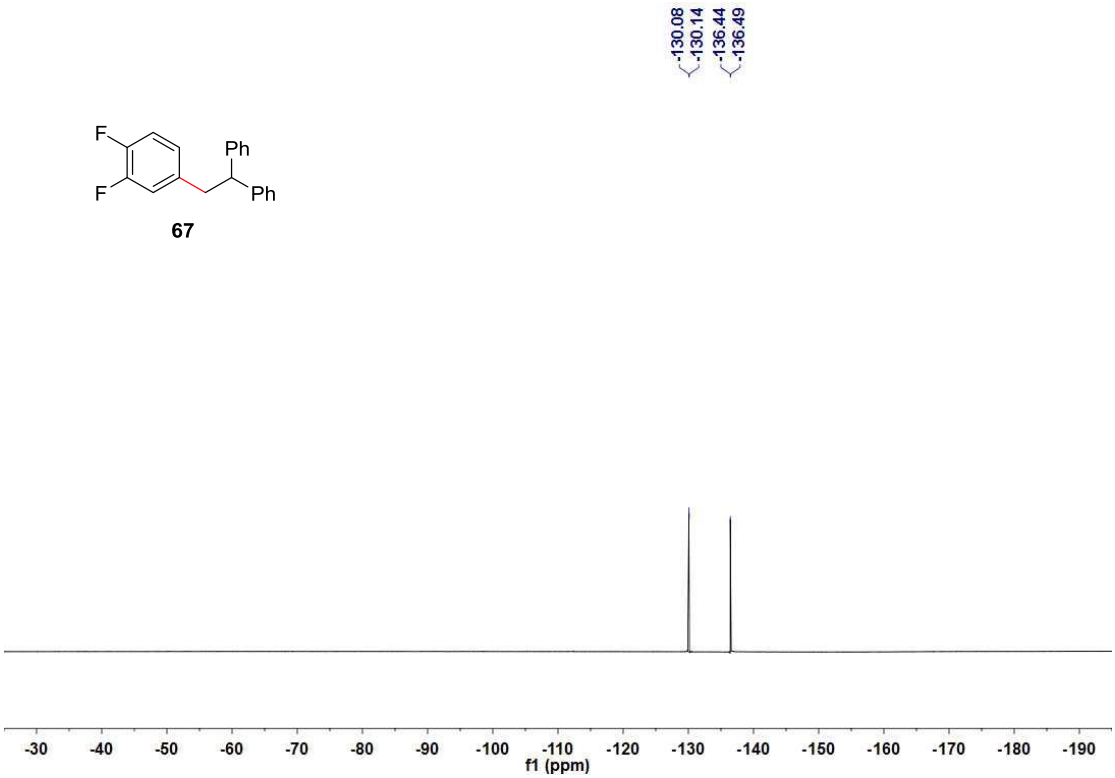


Figure S93. ^{19}F NMR spectra for compound **67**

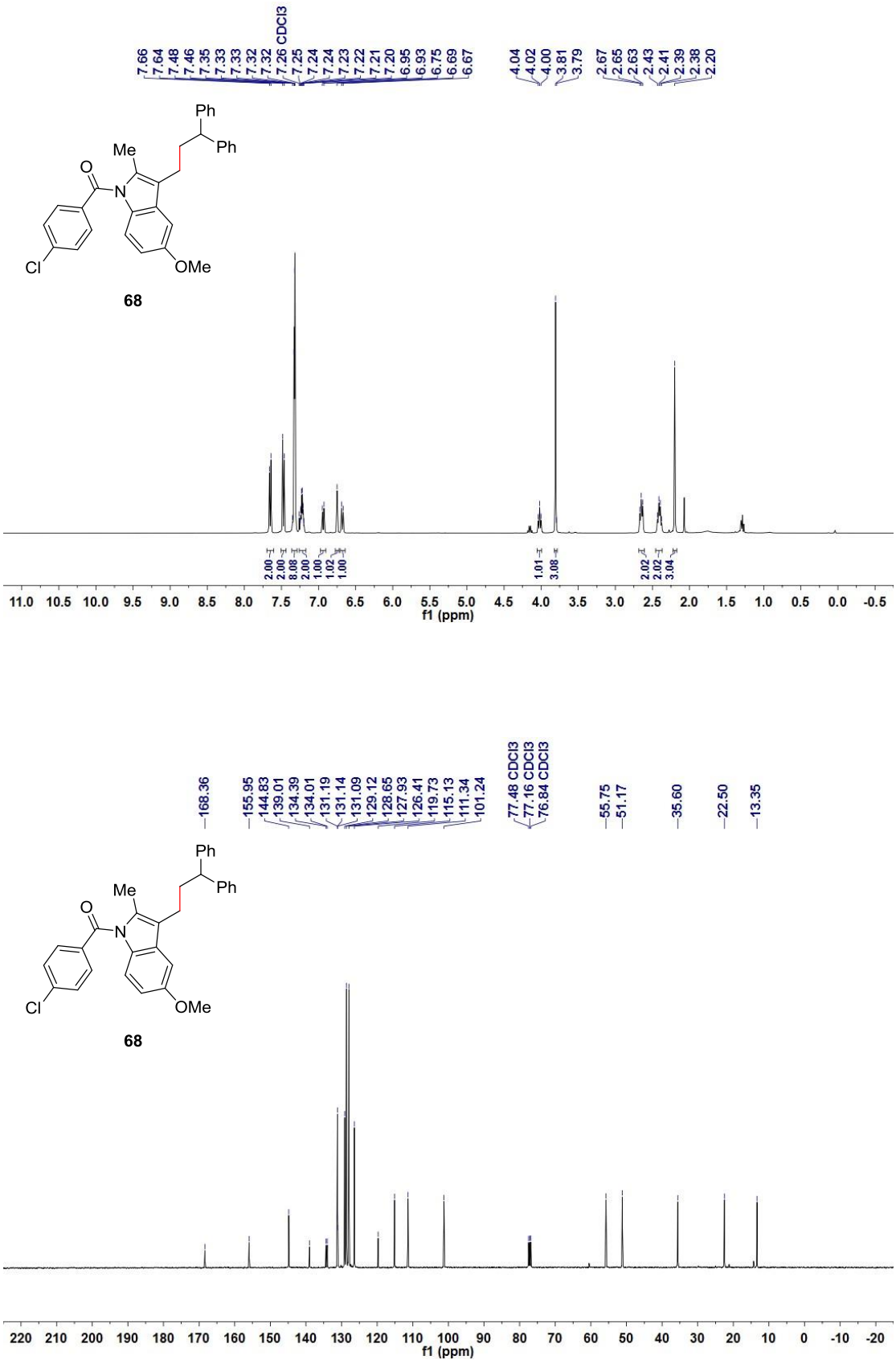


Figure S94. ^{1}H and ^{13}C NMR spectra for compound **68**

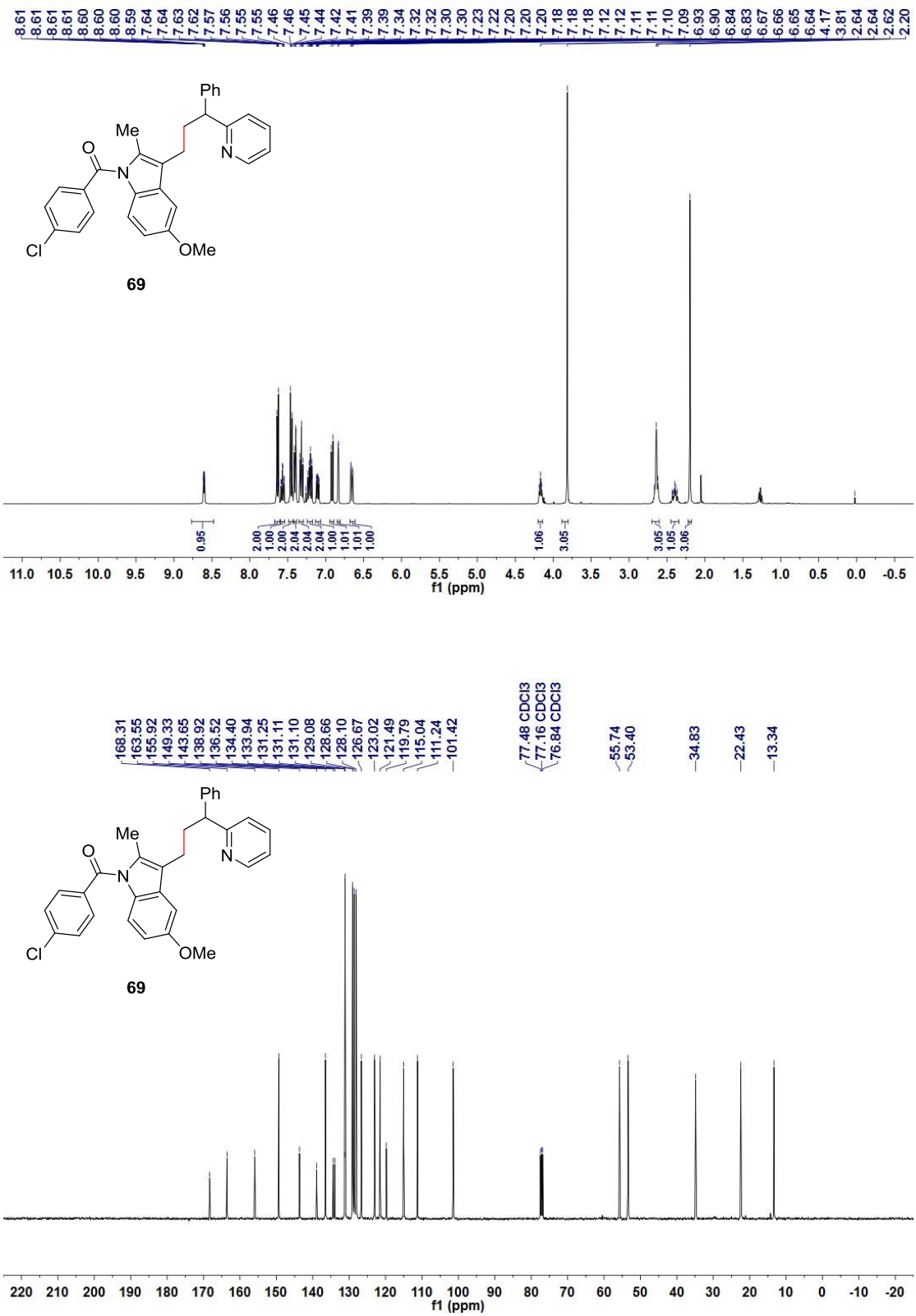


Figure S95. ^{1}H and ^{13}C NMR spectra for compound **69**

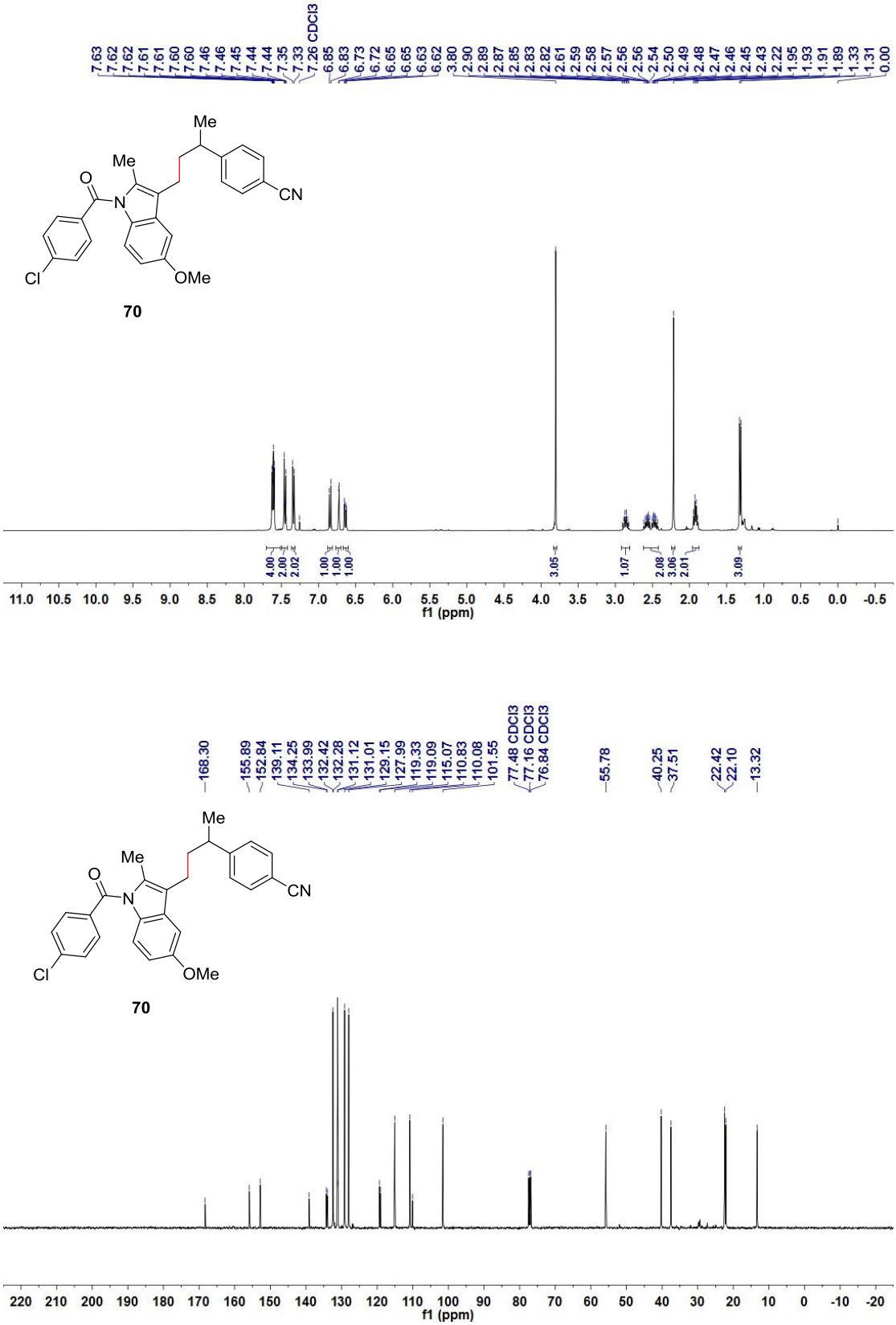


Figure S96. ^{1}H and ^{13}C NMR spectra for compound **70**

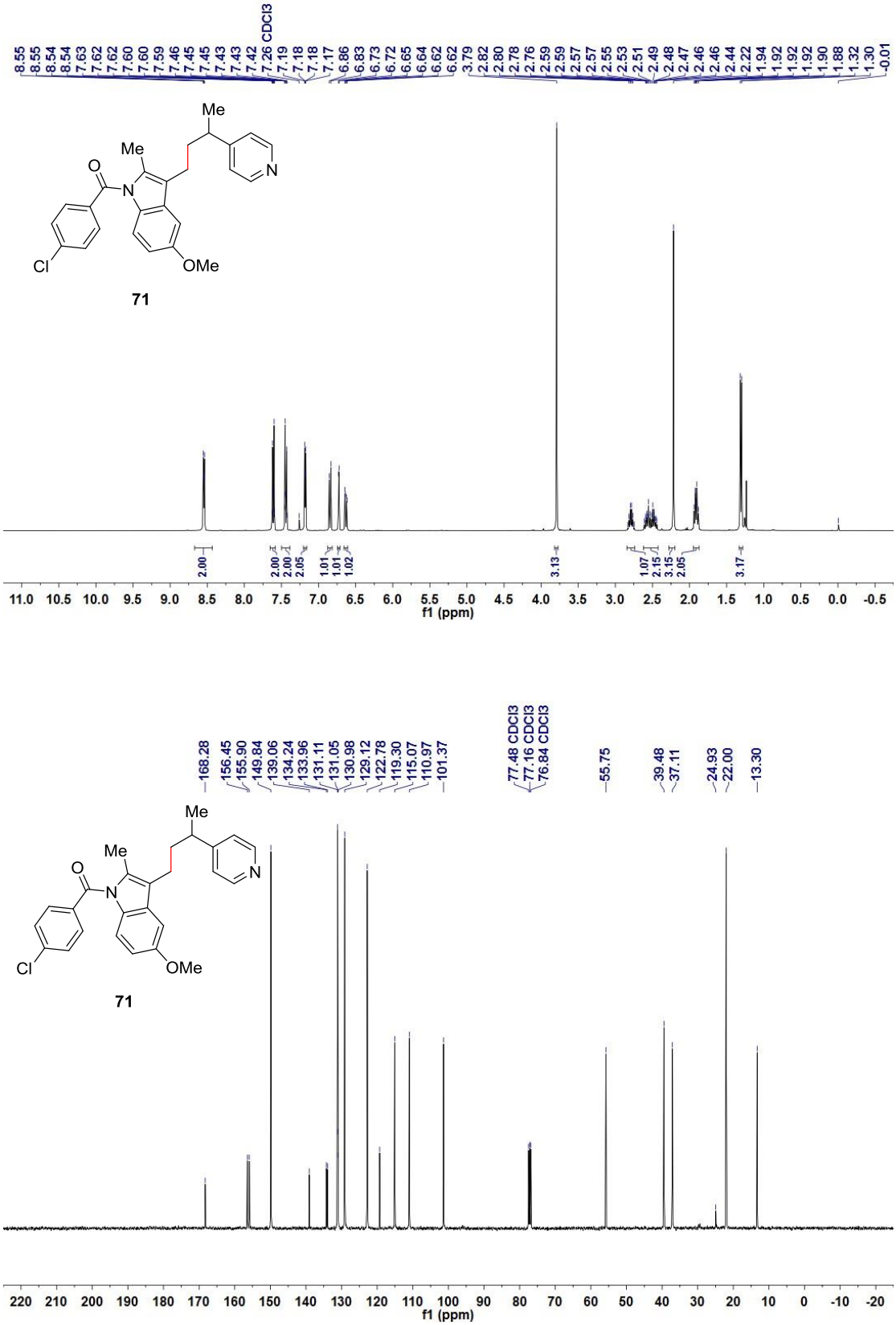


Figure S97. ^{1}H and ^{13}C NMR spectra for compound **71**

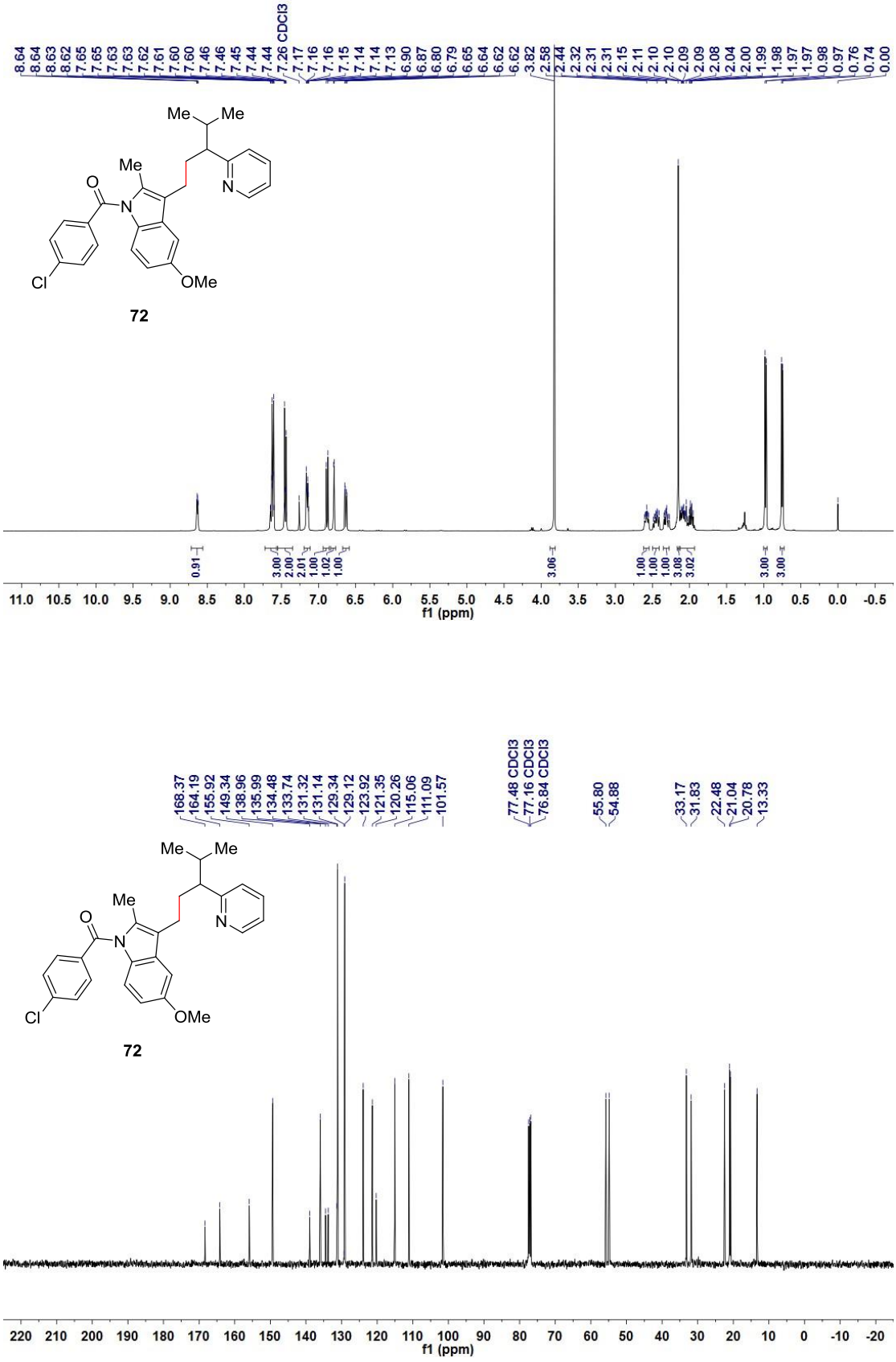


Figure S98. ^{1}H and ^{13}C NMR spectra for compound **72**

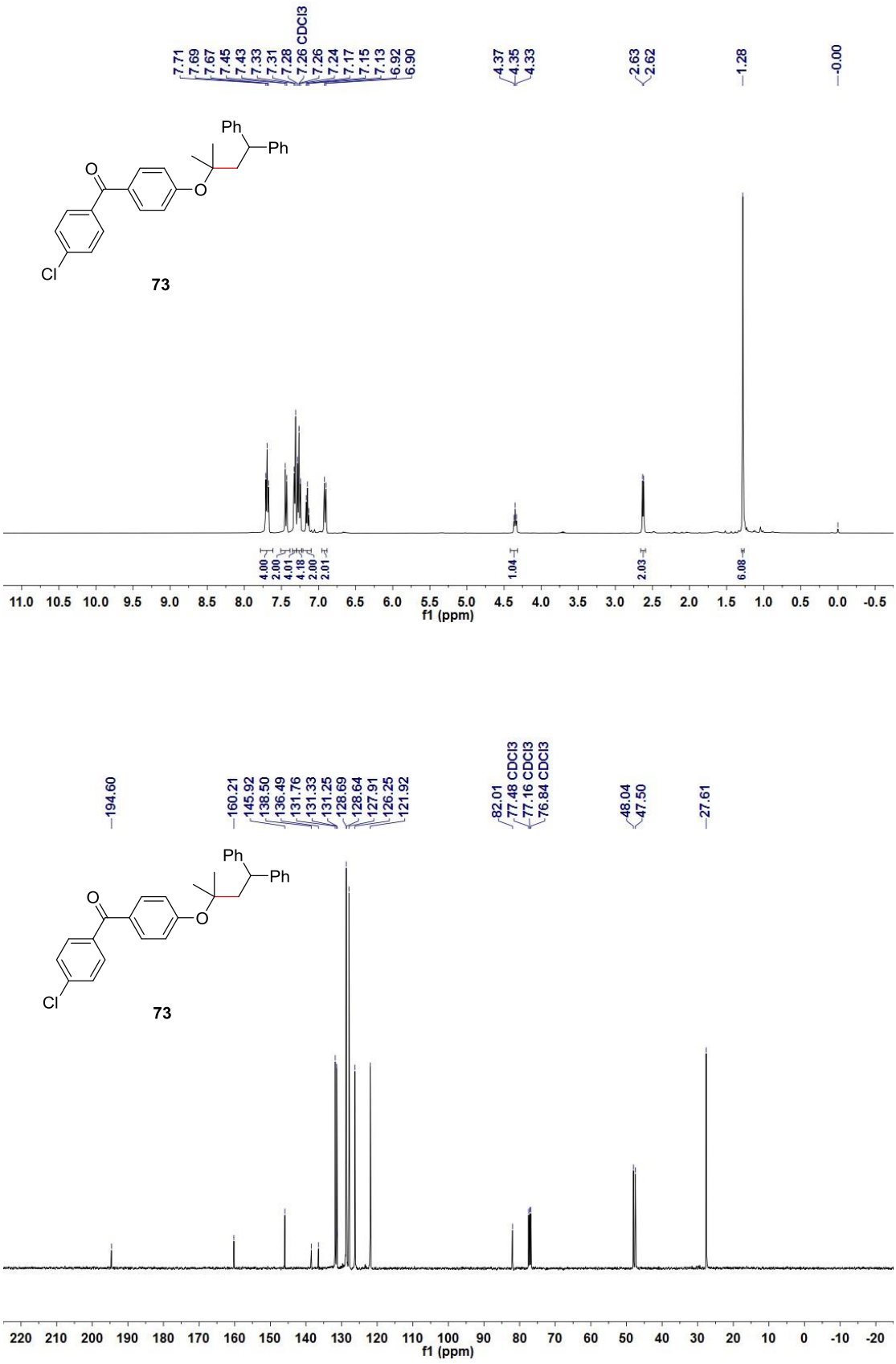


Figure S99. ^{1}H and ^{13}C NMR spectra for compound **73**

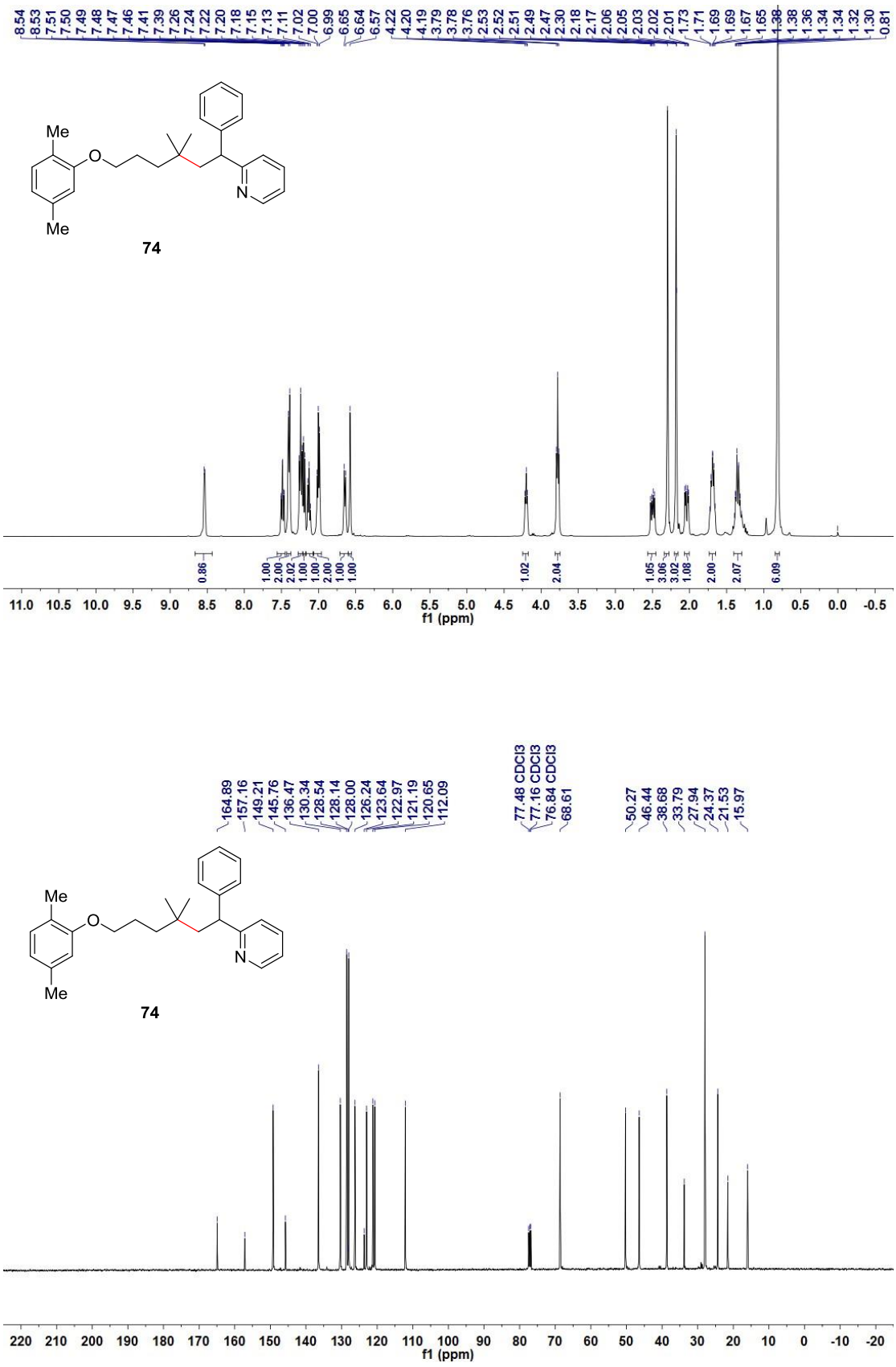


Figure S100. ^{1}H and ^{13}C NMR spectra for compound **74**

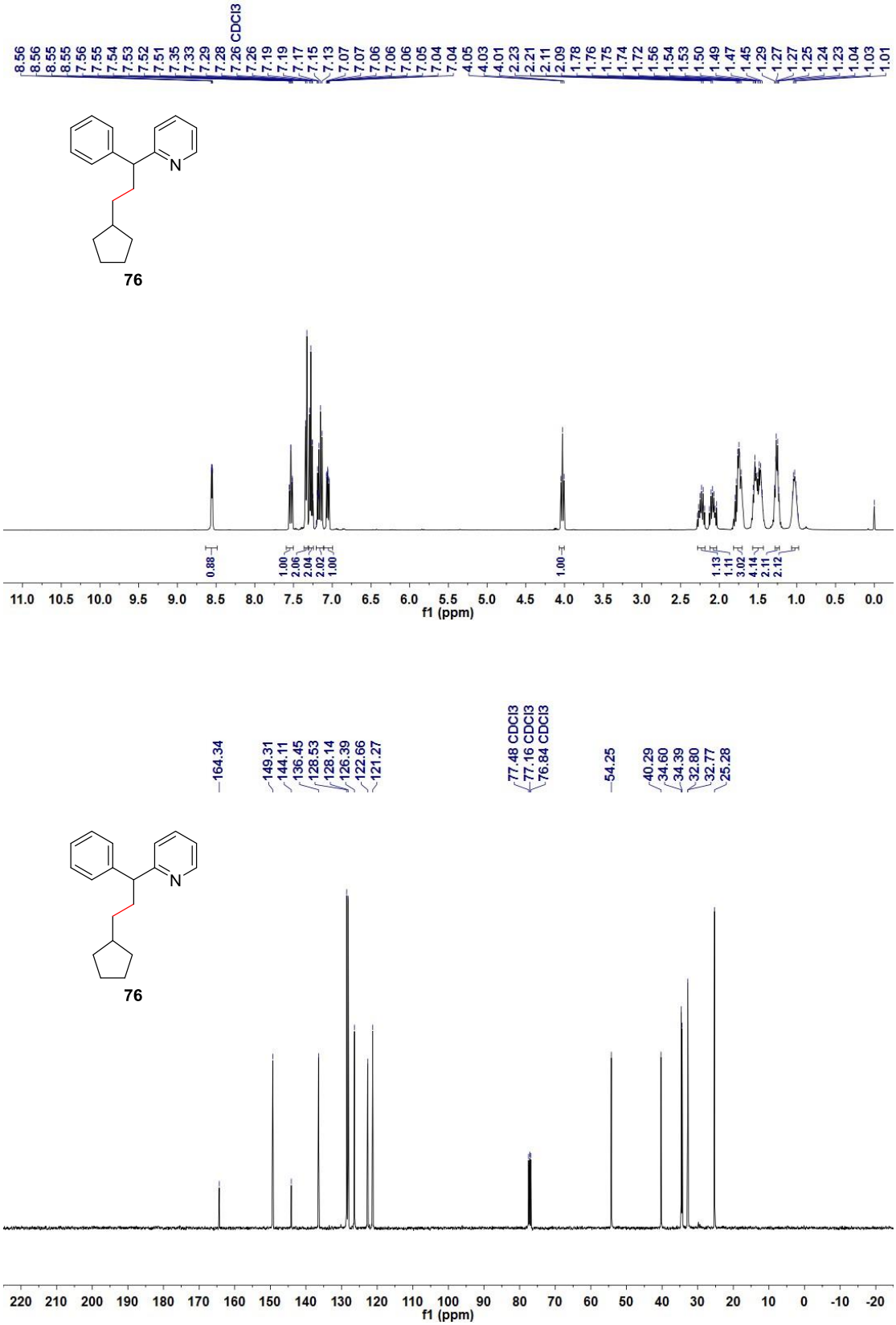


Figure S101. ^{1}H and ^{13}C NMR spectra for compound **76**

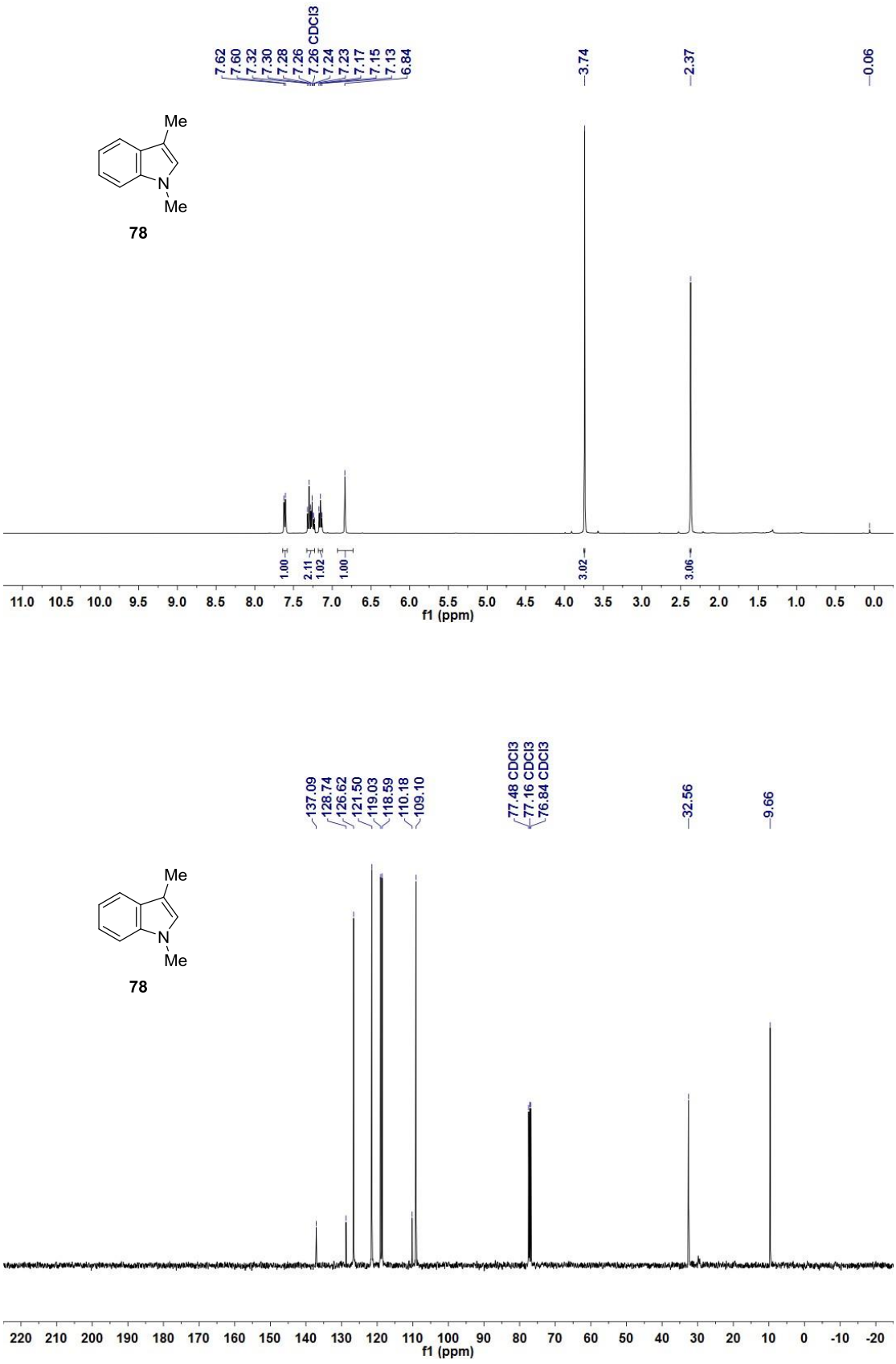


Figure S102. ^{1}H and ^{13}C NMR spectra for compound **78**

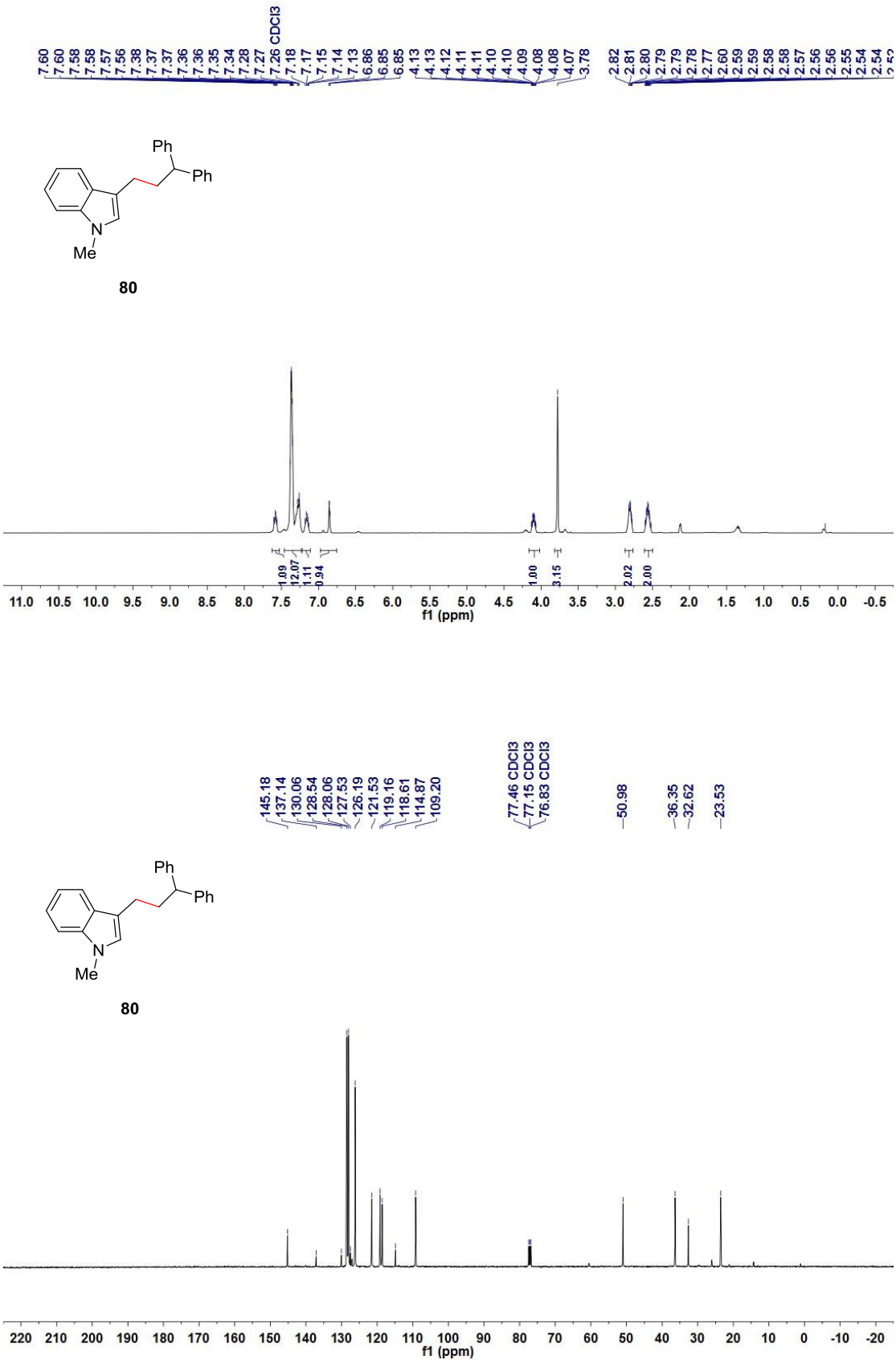


Figure S103. ^{1}H and ^{13}C NMR spectra for compound **80**

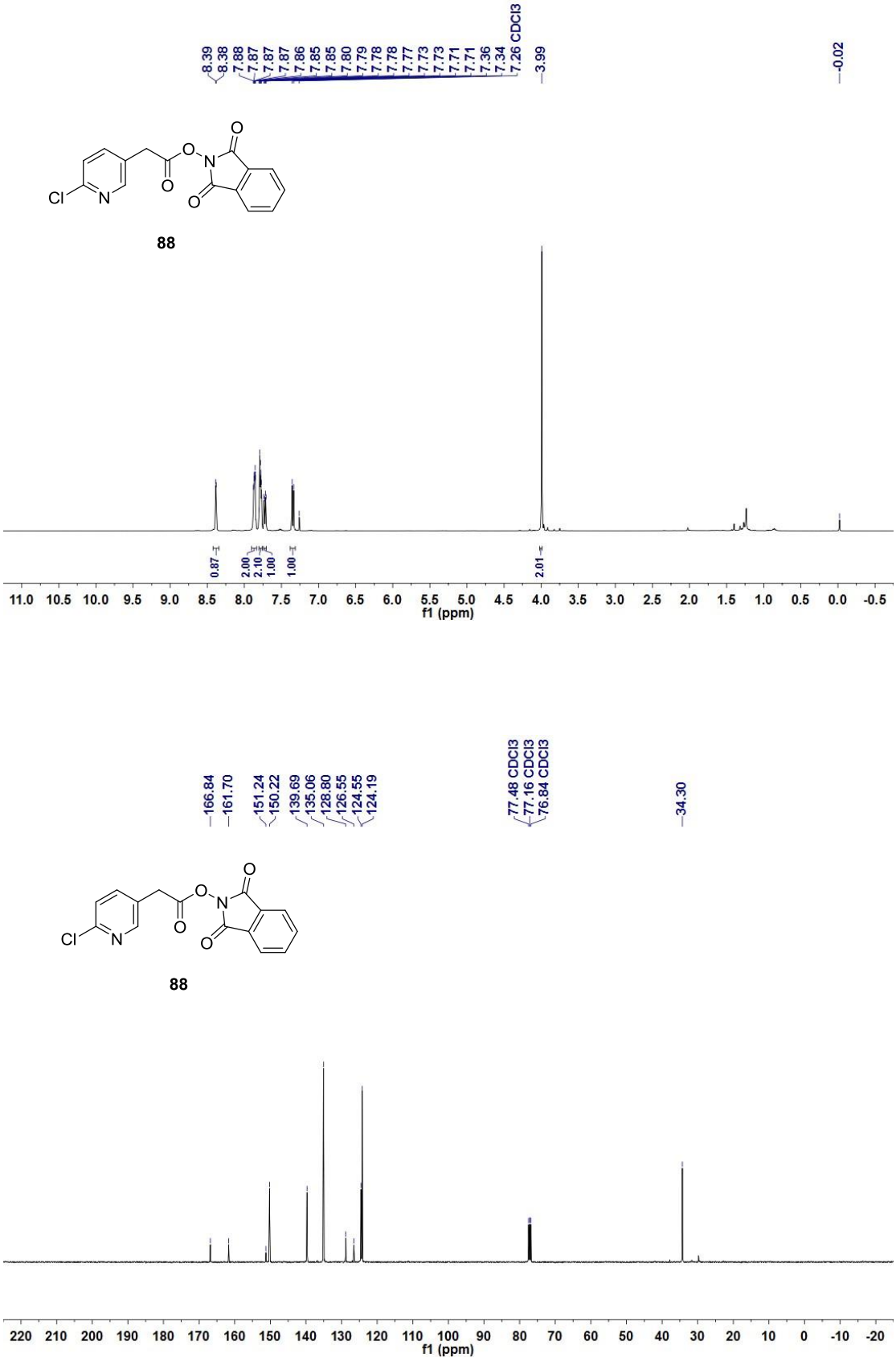


Figure S104. ^{1}H and ^{13}C NMR spectra for compound **88**

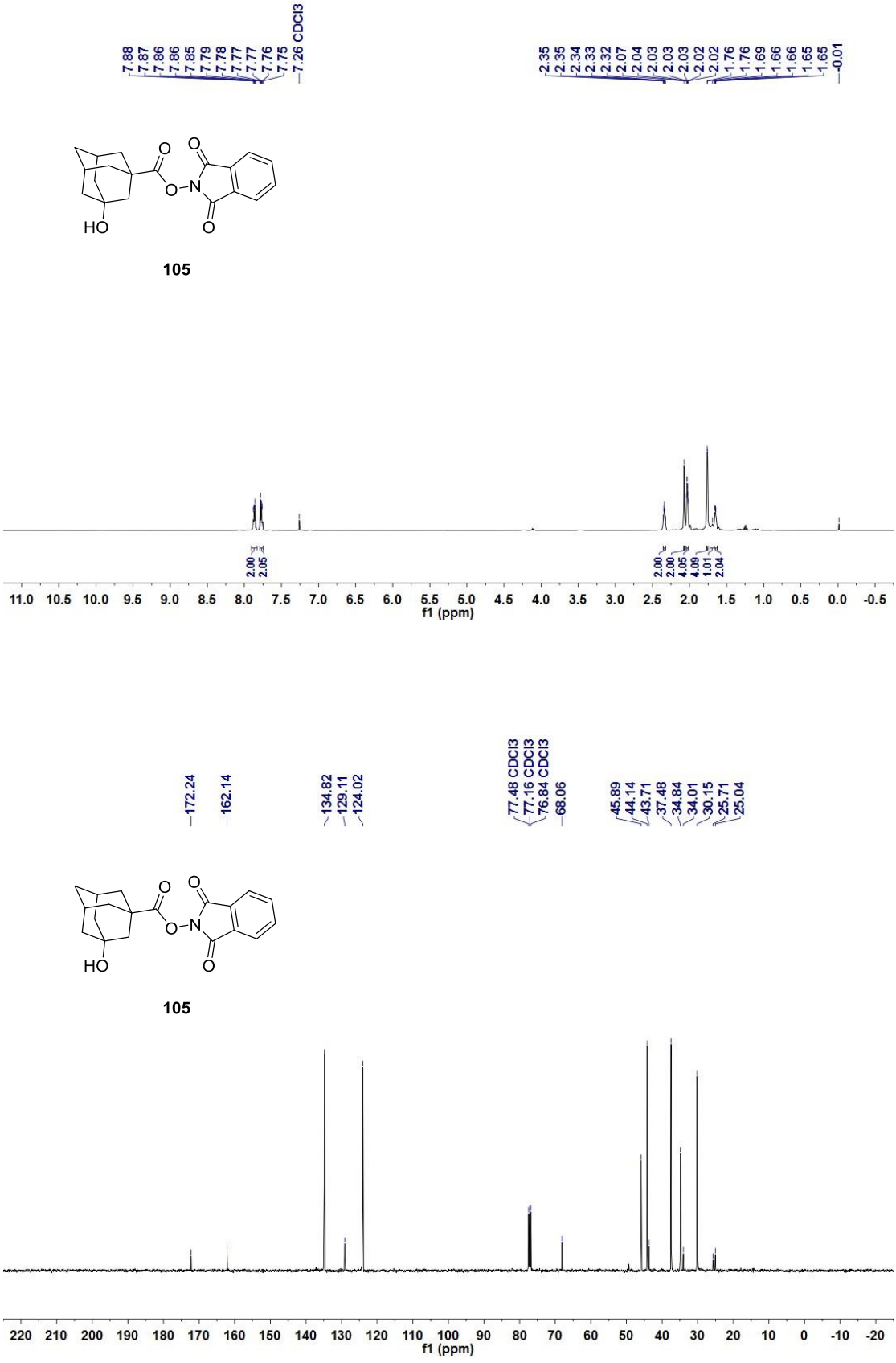


Figure S105. ^{1}H and ^{13}C NMR spectra for compound **105**

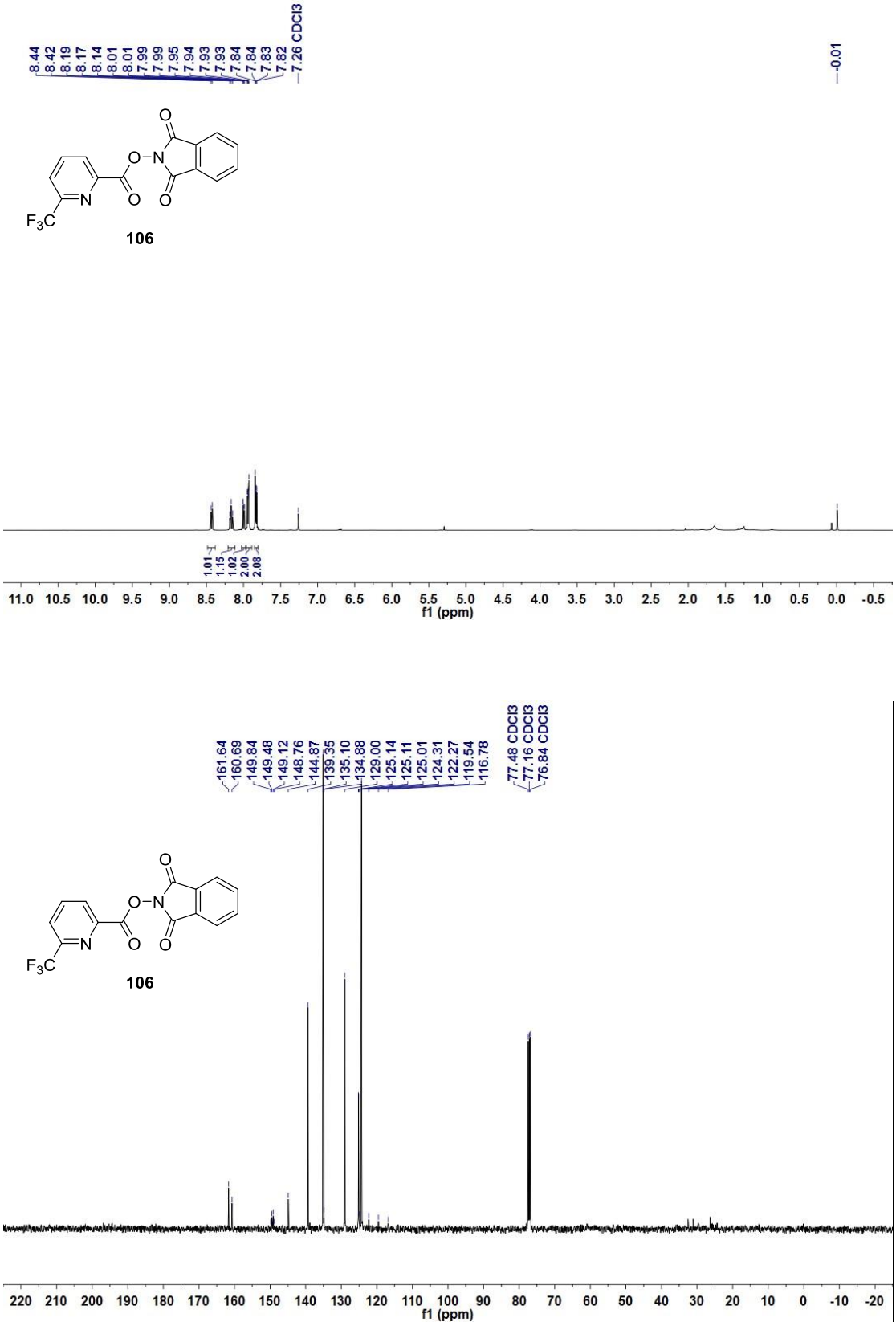


Figure S106. ^{11}H and ^{13}C NMR spectra for compound **106**

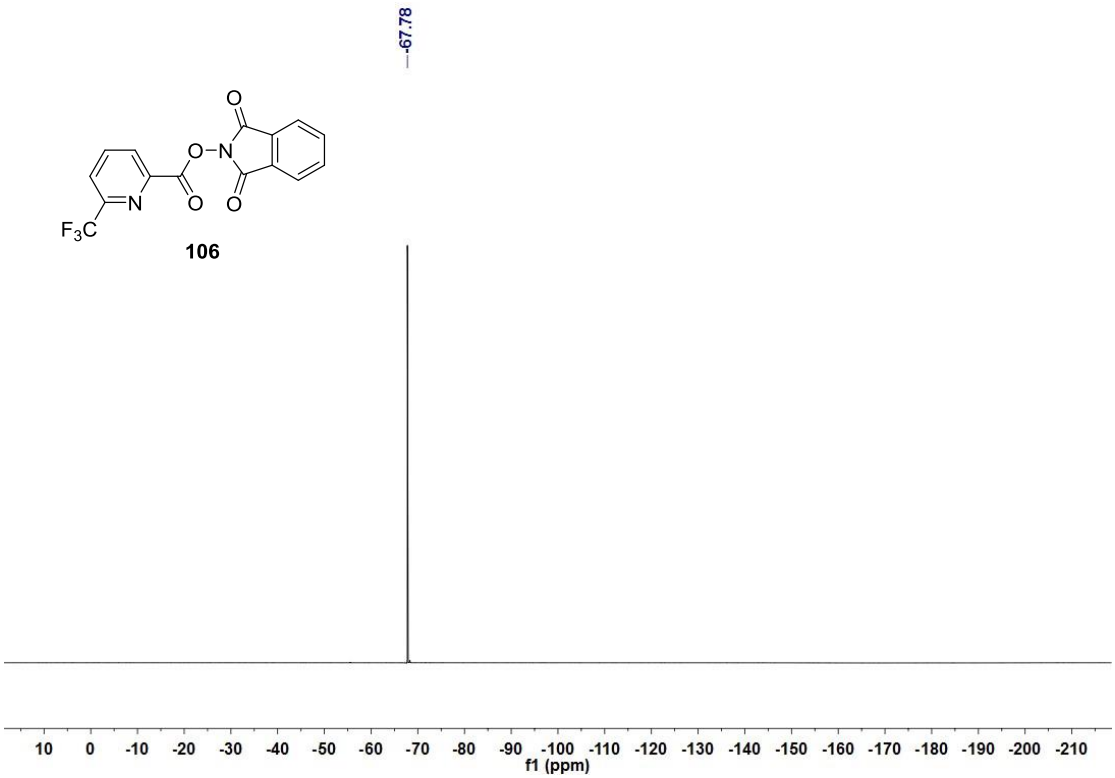


Figure S107. ^{19}F NMR spectra for compound **106**

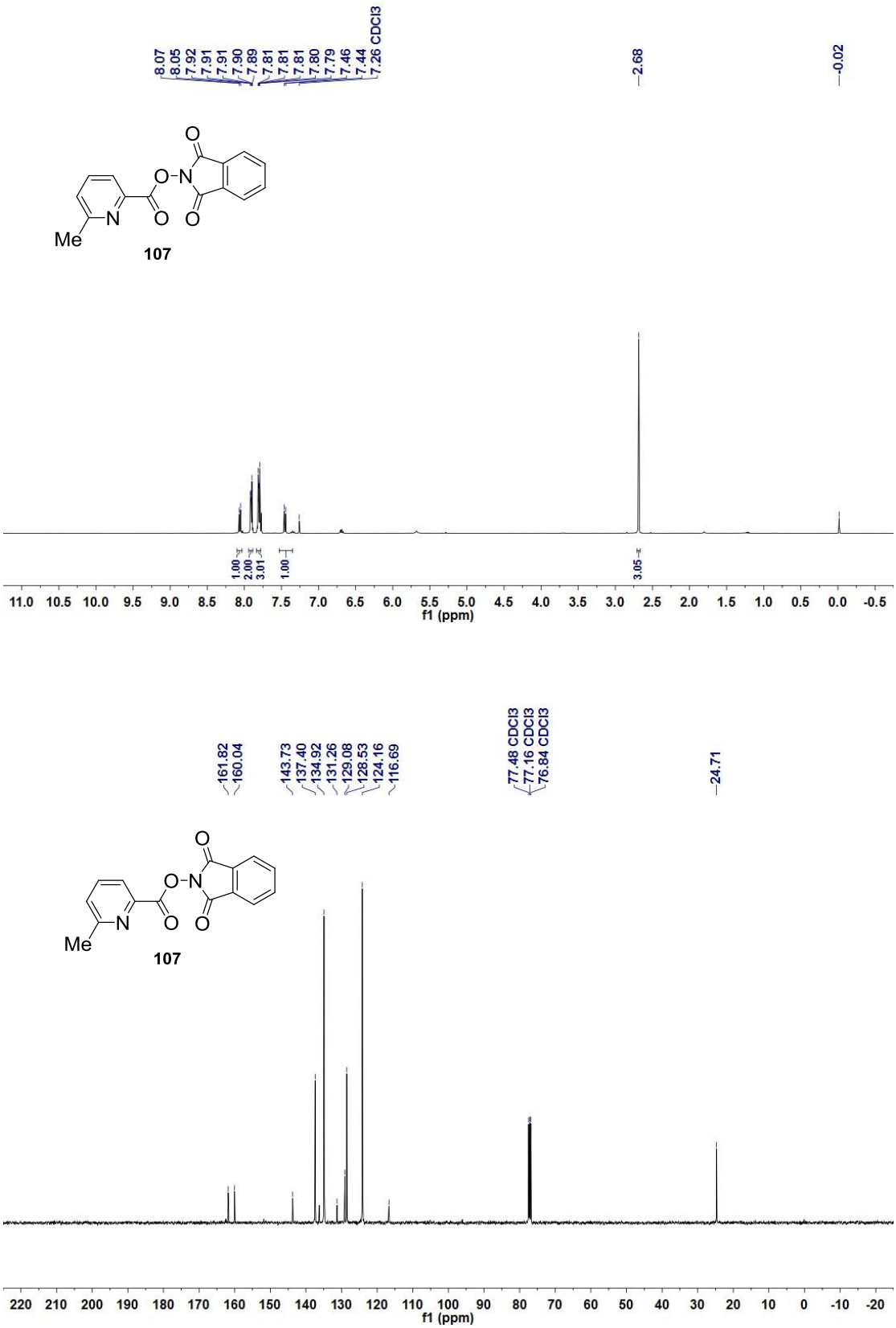


Figure S108. ^{1}H and ^{13}C NMR spectra for compound **107**

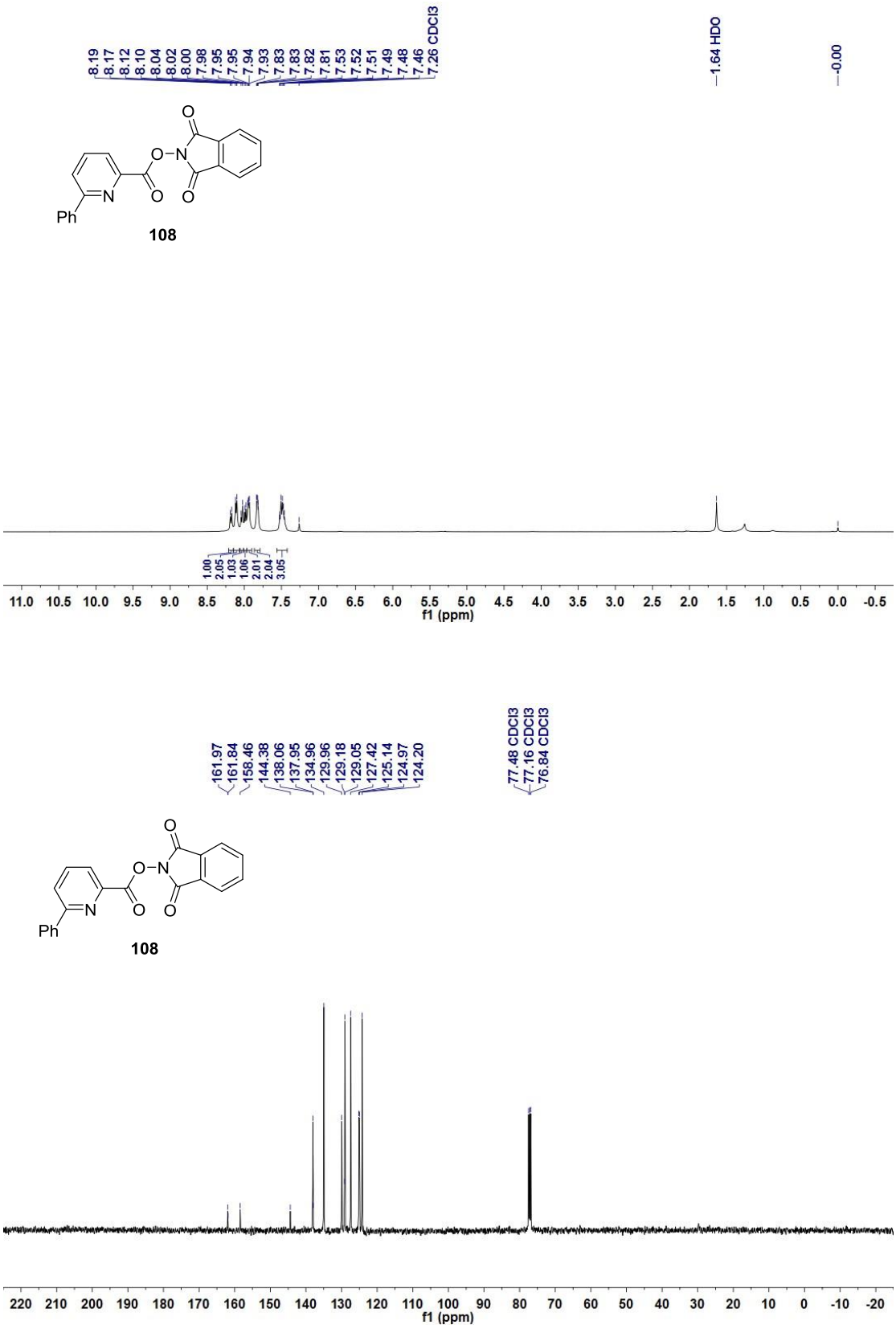


Figure S109. ^{1}H and ^{13}C NMR spectra for compound **108**

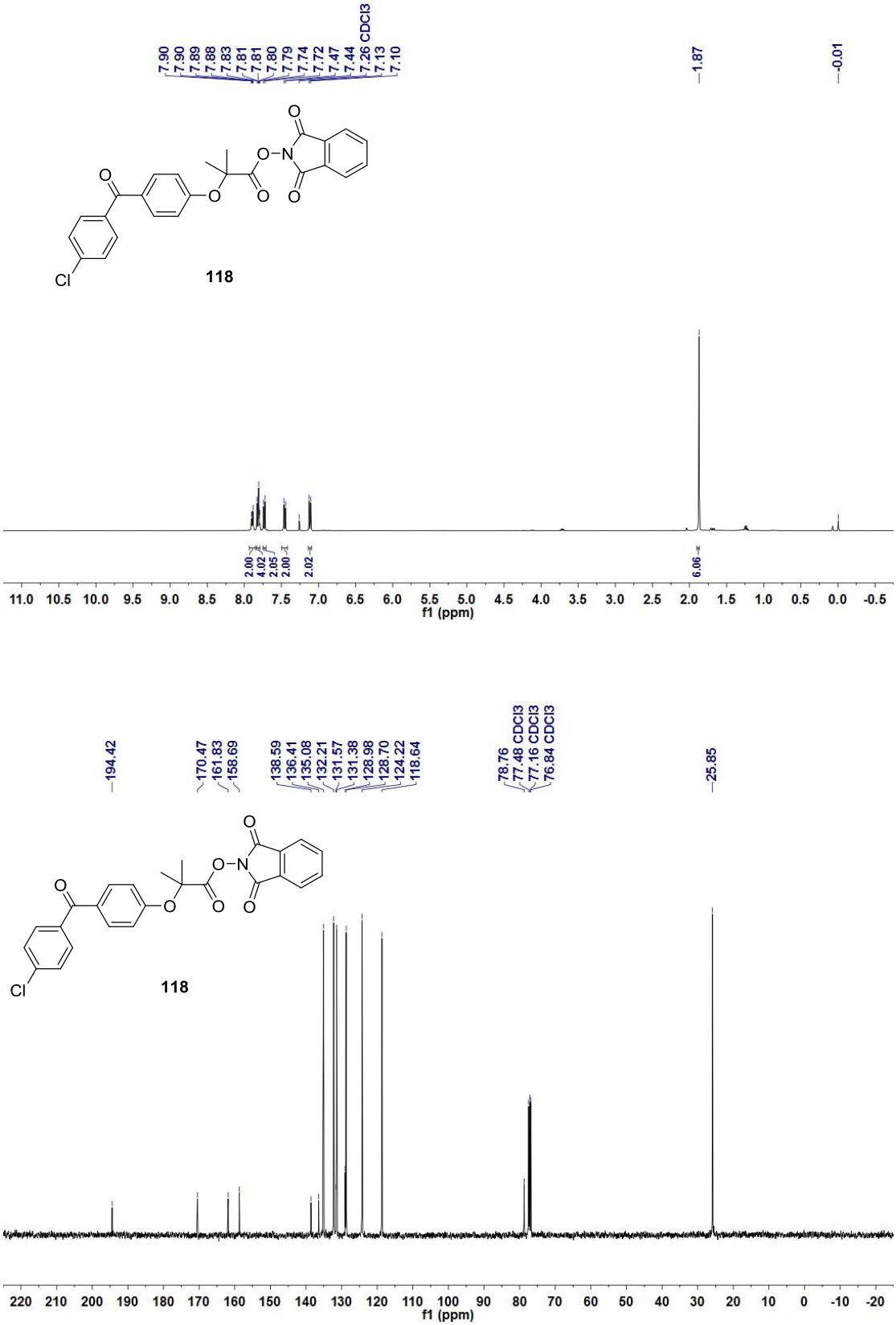


Figure S110. ^{1}H and ^{13}C NMR spectra for compound **118**

Cartesian Coordinates and Energies of the Optimized Structures

Geometry optimizations and characters of all the stationary points were calculated by using the M06-2X/6-31G(d,p) method. Single point energies (**Esol**, a.u.) are computed by using the M06-2X/cc-PVTZ method in solvent (benzene). The solvent effect was treated with the polarizable continuum model (PCM).

$B_2(pin)_2$

Thermal correction to Energy=	0.386465
Thermal correction to Enthalpy=	0.387410
Thermal correction to Gibbs Free Energy=	0.317567
Sum of electronic and zero-point Energies=	-821.850963
Sum of electronic and thermal Energies=	-821.830996
Sum of electronic and thermal Enthalpies=	-821.830052
Sum of electronic and thermal Free Energies=	-821.899895

Esol= -822.5113248

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.983316	0.771216	0.121323
2	6	0	−2.984318	−0.770954	−0.121017
3	5	0	−0.852521	−0.001044	−0.000791
4	8	0	−1.615850	1.126484	−0.175505
5	8	0	−1.616891	−1.127768	0.174390
6	6	0	−3.911930	−1.561628	0.787045
7	1	0	−4.950051	−1.244523	0.643069
8	1	0	−3.841079	−2.624930	0.545130
9	1	0	−3.646139	−1.432005	1.837128
10	6	0	−3.225811	1.141264	1.583506
11	1	0	−2.995912	2.200429	1.719796
12	1	0	−4.265493	0.967065	1.874794
13	1	0	−2.574000	0.561471	2.243265
14	6	0	−3.910920	1.563134	−0.785643
15	1	0	−4.949577	1.249158	−0.638732
16	1	0	−3.836450	2.626518	−0.545169
17	1	0	−3.648054	1.431548	−1.836211
18	6	0	−3.228725	−1.140847	−1.582902
19	1	0	−2.999765	−2.200191	−1.719377
20	1	0	−4.268620	−0.965913	−1.873020
21	1	0	−2.577226	−0.561569	−2.243422

22	6	0	2.983596	0.771162	−0.121128
23	6	0	2.984274	−0.771015	0.121420
24	5	0	0.852672	−0.001053	−0.000621
25	8	0	1.615871	1.126507	0.174454
26	8	0	1.617174	−1.127752	−0.175442
27	6	0	3.912748	−1.562024	−0.785450
28	1	0	4.950975	−1.246398	−0.639023
29	1	0	3.839975	−2.625408	−0.544457
30	1	0	3.649348	−1.431312	−1.835993
31	6	0	3.227254	1.141061	−1.583143
32	1	0	2.997399	2.200198	−1.719725
33	1	0	4.267192	0.966902	−1.873551
34	1	0	2.576016	0.561155	−2.243370
35	6	0	3.910465	1.563248	0.786479
36	1	0	4.949100	1.248337	0.641430
37	1	0	3.837203	2.626480	0.544961
38	1	0	3.645909	1.432812	1.836762
39	6	0	3.226956	−1.140878	1.583622
40	1	0	2.998071	−2.200271	1.719848
41	1	0	4.266444	−0.965708	1.875022
42	1	0	2.574514	−0.561762	2.243351

4-CO_2Et-Py

Thermal correction to Energy= 0.172053
Thermal correction to Enthalpy= 0.172997
Thermal correction to Gibbs Free Energy= 0.125685
Sum of electronic and zero-point Energies= -515.110293
Sum of electronic and thermal Energies= -515.100391
Sum of electronic and thermal Enthalpies= -515.099447
Sum of electronic and thermal Free Energies= -515.146759

Esol= -515.4597892
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.099182	1.270265	3.791147
2	6	0	−1.150541	2.923889	5.361103
3	6	0	0.131146	1.694752	3.296277
4	1	0	−1.596284	0.409065	3.351421
5	6	0	0.076027	3.433380	4.947785
6	1	0	−1.688875	3.390247	6.182383

7	1	0	0. 527990	4. 297100	5. 422078
8	7	0	−1. 737588	1. 863032	4. 801790
9	6	0	0. 727580	2. 802221	3. 892489
10	1	0	0. 612542	1. 181413	2. 472708
11	6	0	2. 047326	3. 347658	3. 445889
12	8	0	2. 581832	4. 307651	3. 946141
13	8	0	2. 568865	2. 650078	2. 429168
14	6	0	3. 838949	3. 121256	1. 950491
15	6	0	4. 256869	2. 210822	0. 817795
16	1	0	4. 552115	3. 106986	2. 779681
17	1	0	3. 727285	4. 160638	1. 628439
18	1	0	5. 222777	2. 530932	0. 420748
19	1	0	4. 349506	1. 180170	1. 166942
20	1	0	3. 522667	2. 239790	0. 009841

TS1

Thermal correction to Energy= 0.560722
Thermal correction to Enthalpy= 0.561666
Thermal correction to Gibbs Free Energy= 0.469270
Sum of electronic and zero-point Energies= -1336.973346
Sum of electronic and thermal Energies= -1336.943273
Sum of electronic and thermal Enthalpies= -1336.942329
Sum of electronic and thermal Free Energies= -1337.034724

Esol= -1337.9793036
Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.583552	2.107721	3.083275
2	6	0	-3.111374	4.268172	2.440394
3	6	0	-2.335182	2.503984	4.391761
4	1	0	-2.469668	1.080417	2.746556
5	6	0	-2.881172	4.754635	3.721456
6	1	0	-3.415869	4.898119	1.607925
7	1	0	-2.996049	5.804319	3.966022
8	7	0	-2.967573	2.975752	2.146352
9	6	0	-2.488417	3.853742	4.708275
10	1	0	-2.030016	1.788986	5.145954
11	6	0	-2.244243	4.386781	6.087404
12	8	0	-2.365710	5.550133	6.384520
13	8	0	-1.880609	3.428377	6.945386

14	6	0	-1.639633	3.870676	8.292595
15	6	0	-1.243262	2.655496	9.099741
16	1	0	-2.551078	4.342656	8.670901
17	1	0	-0.855182	4.632706	8.273863
18	1	0	-1.056699	2.944560	10.136483
19	1	0	-2.038963	1.907535	9.086177
20	1	0	-0.333943	2.204185	8.696882
21	6	0	-4.998416	2.702049	-0.847093
22	6	0	-4.986583	1.359797	-0.043081
23	8	0	-3.588013	1.157149	0.198521
24	5	0	-2.973398	2.416546	0.189004
25	8	0	-3.841280	3.386222	-0.349695
26	5	0	-1.280857	2.593340	0.232902
27	8	0	-0.616330	3.781670	0.004991
28	6	0	0.675391	3.683182	0.633593
29	6	0	0.913695	2.141750	0.665776
30	8	0	-0.430302	1.628758	0.738197
31	6	0	-6.229172	3.568100	-0.620060
32	6	0	-4.778797	2.486366	-2.345079
33	6	0	-5.523733	0.157010	-0.806392
34	6	0	-5.705723	1.471291	1.303290
35	6	0	1.688898	4.472609	-0.179346
36	6	0	0.529249	4.287185	2.030858
37	6	0	1.696320	1.641144	1.869890
38	6	0	1.527243	1.610427	-0.628169
39	1	0	-6.147236	4.480255	-1.217077
40	1	0	-7.138655	3.039593	-0.925078
41	1	0	-6.324631	3.854764	0.429166
42	1	0	-4.590042	3.456007	-2.812250
43	1	0	-3.905203	1.850522	-2.514467
44	1	0	-5.648616	2.027413	-2.824547
45	1	0	-5.483215	-0.727966	-0.165622
46	1	0	-6.565298	0.317549	-1.104507
47	1	0	-4.926824	-0.041466	-1.697725
48	1	0	-6.791600	1.503117	1.172357
49	1	0	-5.453667	0.594126	1.906161
50	1	0	-5.396093	2.365033	1.848932
51	1	0	1.440237	5.536119	-0.140455
52	1	0	2.697157	4.340030	0.226811
53	1	0	1.685691	4.160079	-1.224713
54	1	0	1.485786	4.320218	2.560476
55	1	0	0.147091	5.306592	1.932536
56	1	0	-0.183787	3.712860	2.632895
57	1	0	1.815590	0.556700	1.803430

58	1	0	2.692142	2.095512	1.900664
59	1	0	1.174232	1.871024	2.800810
60	1	0	2.577257	1.900926	-0.726246
61	1	0	1.462948	0.519767	-0.623933
62	1	0	0.975915	1.982321	-1.496301

Int1

Thermal correction to Energy= 0.560328
Thermal correction to Enthalpy= 0.561272
Thermal correction to Gibbs Free Energy= 0.469771
Sum of electronic and zero-point Energies= -1336.973900
Sum of electronic and thermal Energies= -1336.944057
Sum of electronic and thermal Enthalpies= -1336.943112
Sum of electronic and thermal Free Energies= -1337.034614

Esol= -1337.980038
Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.607238	2.130677	3.077429
2	6	0	-3.114393	4.309579	2.442307
3	6	0	-2.400067	2.514371	4.394353
4	1	0	-2.495392	1.110355	2.721808
5	6	0	-2.923093	4.773749	3.735860
6	1	0	-3.398815	4.939847	1.605109
7	1	0	-3.049111	5.819959	3.989078
8	7	0	-2.959930	3.017330	2.141974
9	6	0	-2.561469	3.860232	4.722601
10	1	0	-2.120240	1.789217	5.148469
11	6	0	-2.361475	4.376080	6.116157
12	8	0	-2.503389	5.533984	6.423269
13	8	0	-2.012793	3.408774	6.968749
14	6	0	-1.812061	3.830706	8.329960
15	6	0	-1.423668	2.605089	9.125384
16	1	0	-2.738357	4.285648	8.692415
17	1	0	-1.035374	4.600718	8.344269
18	1	0	-1.263952	2.877108	10.171099
19	1	0	-2.212144	1.850822	9.079425
20	1	0	-0.501036	2.169696	8.735706
21	6	0	-4.935639	2.695340	-0.761479
22	6	0	-4.966352	1.402661	0.114134

23	8	0	-3.582869	1.207820	0.415274
24	5	0	-2.972282	2.496089	0.428768
25	8	0	-3.851775	3.436826	-0.199932
26	5	0	-1.268115	2.624319	0.283800
27	8	0	-0.607361	3.815990	0.045121
28	6	0	0.724669	3.685128	0.574428
29	6	0	0.952128	2.143521	0.519121
30	8	0	-0.386357	1.636868	0.682840
31	6	0	-6.203282	3.536494	-0.700719
32	6	0	-4.579046	2.391684	-2.218741
33	6	0	-5.485550	0.162899	-0.601111
34	6	0	-5.743828	1.601389	1.419830
35	6	0	1.685495	4.507608	-0.268288
36	6	0	0.676524	4.221927	2.006508
37	6	0	1.830250	1.585778	1.628262
38	6	0	1.450910	1.668892	-0.844417
39	1	0	-6.091387	4.411604	-1.346636
40	1	0	-7.070141	2.963841	-1.047796
41	1	0	-6.396911	3.887185	0.315120
42	1	0	-4.354470	3.334030	-2.724447
43	1	0	-3.690058	1.756103	-2.266704
44	1	0	-5.398321	1.894907	-2.747407
45	1	0	-5.495687	-0.683588	0.091225
46	1	0	-6.506596	0.320316	-0.965280
47	1	0	-4.844330	-0.097122	-1.444690
48	1	0	-6.824108	1.615196	1.245415
49	1	0	-5.511771	0.770593	2.092761
50	1	0	-5.465034	2.535359	1.914849
51	1	0	1.437856	5.568113	-0.175473
52	1	0	2.716671	4.364368	0.071599
53	1	0	1.619627	4.233333	-1.322216
54	1	0	1.664750	4.223355	2.475627
55	1	0	0.298085	5.247054	1.982315
56	1	0	-0.001820	3.620704	2.623506
57	1	0	1.936089	0.505149	1.502656
58	1	0	2.828496	2.034664	1.593959
59	1	0	1.392133	1.773353	2.610384
60	1	0	2.493072	1.955004	-1.013919
61	1	0	1.374026	0.579829	-0.885910
62	1	0	0.835490	2.086125	-1.646410

TS2

Thermal correction to Energy= 0.734866

Thermal correction to Enthalpy= 0.735810
Thermal correction to Gibbs Free Energy= 0.621514
Sum of electronic and zero-point Energies= -1852.100586
Sum of electronic and thermal Energies= -1852.059827
Sum of electronic and thermal Enthalpies= -1852.058883
Sum of electronic and thermal Free Energies= -1852.173179

Esol= -1853.449854
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.733840	-2.502127	1.275897
2	6	0	1.440562	-1.794188	-0.914355
3	6	0	-0.579569	-2.284667	0.871487
4	1	0	0.973937	-2.840437	2.277609
5	6	0	0.099456	-1.624346	-1.232892
6	1	0	2.219787	-1.570817	-1.633131
7	1	0	-1.422771	-2.405541	1.545099
8	1	0	-0.230230	-1.255485	-2.201641
9	7	0	-0.879751	-1.845649	-0.352767
10	6	0	-3.095817	0.808850	2.708233
11	6	0	-3.291067	2.112767	1.870624
12	5	0	-2.189950	0.522355	0.597742
13	8	0	-2.065615	0.129144	1.990391
14	8	0	-3.087012	1.652080	0.538365
15	6	0	-4.683929	2.720842	1.964455
16	1	0	-4.936078	2.972451	3.000403
17	1	0	-4.725562	3.637381	1.369088
18	1	0	-5.431479	2.027576	1.575218
19	6	0	-4.343997	-0.076219	2.687015
20	1	0	-4.085150	-1.051130	3.109654
21	1	0	-5.159552	0.354362	3.276590
22	1	0	-4.679479	-0.235991	1.658360
23	6	0	-2.635188	1.037756	4.141114
24	1	0	-3.365590	1.636249	4.696161
25	1	0	-2.526756	0.075603	4.649824
26	1	0	-1.670066	1.548913	4.169424
27	6	0	-2.239498	3.177183	2.202381
28	1	0	-2.259918	3.942291	1.421355
29	1	0	-2.436192	3.656636	3.166592
30	1	0	-1.235410	2.744498	2.232953
31	6	0	-4.115726	-2.035214	-1.622229

32	6	0	-3.672631	-0.911864	-2.610369
33	5	0	-2.598633	-0.655769	-0.597893
34	8	0	-3.675913	-1.518141	-0.361194
35	8	0	-2.478070	-0.410501	-1.992678
36	6	0	-3.351882	-1.391817	-4.017453
37	1	0	-4.230723	-1.855932	-4.477752
38	1	0	-3.051436	-0.542156	-4.636852
39	1	0	-2.536262	-2.117927	-4.011071
40	6	0	-3.397571	-3.361052	-1.879059
41	1	0	-3.568507	-4.019541	-1.023235
42	1	0	-3.774328	-3.854584	-2.780406
43	1	0	-2.320385	-3.209746	-1.982108
44	6	0	-5.619142	-2.262544	-1.556006
45	1	0	-6.015727	-2.543781	-2.537627
46	1	0	-5.835610	-3.072199	-0.853837
47	1	0	-6.133537	-1.364542	-1.209413
48	6	0	-4.667021	0.249799	-2.653088
49	1	0	-4.211873	1.077026	-3.204668
50	1	0	-5.601718	-0.026914	-3.149993
51	1	0	-4.883447	0.599846	-1.638977
52	6	0	0.415771	0.893829	1.014727
53	6	0	1.710608	1.228241	0.640302
54	6	0	0.815831	2.024772	-1.447292
55	6	0	-0.444519	1.651067	-1.007799
56	1	0	0.158386	0.450540	1.971613
57	1	0	2.544049	1.046915	1.308488
58	1	0	0.963797	2.477554	-2.420676
59	7	0	-0.623296	1.098778	0.199565
60	1	0	-1.343116	1.747366	-1.608724
61	6	0	1.757000	-2.227533	0.372246
62	6	0	1.909201	1.804465	-0.610760
63	6	0	3.171357	-2.333544	0.846467
64	8	0	3.491385	-2.720634	1.943907
65	8	0	4.042181	-1.908744	-0.078188
66	6	0	5.418558	-1.899386	0.327078
67	6	0	6.217179	-1.379081	-0.846846
68	1	0	5.514730	-1.261377	1.212133
69	1	0	7.273429	-1.298229	-0.579133
70	1	0	6.124748	-2.048377	-1.704770
71	1	0	5.851653	-0.391209	-1.138993
72	6	0	3.265597	2.217295	-1.095559
73	8	0	3.462145	2.730389	-2.169524
74	8	0	4.225952	1.968937	-0.196912
75	6	0	5.540557	2.424614	-0.563660

76	6	0	6.463851	2.107109	0.590638
77	1	0	5.840316	1.924208	-1.489626
78	1	0	7.478111	2.437922	0.356449
79	1	0	6.132761	2.615431	1.498650
80	1	0	6.487005	1.031739	0.784567
81	1	0	5.490407	3.497430	-0.771379
82	1	0	5.710941	-2.912482	0.617698

Int2

Thermal correction to Energy= 0.736040
Thermal correction to Enthalpy= 0.736984
Thermal correction to Gibbs Free Energy= 0.618494
Sum of electronic and zero-point Energies= -1852.103663
Sum of electronic and thermal Energies= -1852.062194
Sum of electronic and thermal Enthalpies= -1852.061250
Sum of electronic and thermal Free Energies= -1852.179740

Esol= -1853.4529418
Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.394137	-2.979381	1.404116
2	6	0	1.612384	-2.021437	-0.439154
3	6	0	-0.748685	-2.363649	0.923825
4	1	0	0.372395	-3.591377	2.297913
5	6	0	0.426133	-1.441942	-0.864128
6	1	0	2.530131	-1.875422	-0.995237
7	1	0	-1.720290	-2.433795	1.399592
8	1	0	0.337326	-0.830664	-1.757518
9	7	0	-0.717916	-1.613213	-0.188283
10	6	0	-2.884740	0.630715	2.797232
11	6	0	-3.406747	1.855012	1.979863
12	5	0	-2.002574	0.585492	0.657185
13	8	0	-1.746216	0.214244	2.042052
14	8	0	-3.155776	1.452387	0.636246
15	6	0	-4.896264	2.128818	2.133312
16	1	0	-5.157684	2.315204	3.180788
17	1	0	-5.169753	3.012523	1.549670
18	1	0	-5.480155	1.283341	1.765190
19	6	0	-3.889323	-0.523883	2.797535
20	1	0	-3.403852	-1.404209	3.231201

21	1	0	-4.778164	-0.297175	3.394592
22	1	0	-4.185014	-0.763889	1.771317
23	6	0	-2.447988	0.957076	4.218398
24	1	0	-3.282902	1.361027	4.801076
25	1	0	-2.097139	0.046443	4.712324
26	1	0	-1.632496	1.683325	4.222949
27	6	0	-2.607471	3.127997	2.279662
28	1	0	-2.831948	3.870052	1.508101
29	1	0	-2.866632	3.550233	3.255747
30	1	0	-1.531501	2.929309	2.265519
31	6	0	-3.598175	-1.935973	-1.744216
32	6	0	-3.129040	-0.718152	-2.602002
33	5	0	-2.065132	-0.691038	-0.547548
34	8	0	-3.225806	-1.539755	-0.426828
35	8	0	-1.921198	-0.324603	-1.949677
36	6	0	-2.827030	-1.045698	-4.057471
37	1	0	-3.718763	-1.429682	-4.564667
38	1	0	-2.504019	-0.139381	-4.577650
39	1	0	-2.029628	-1.787226	-4.138648
40	6	0	-2.846625	-3.219863	-2.112259
41	1	0	-3.016327	-3.960932	-1.325955
42	1	0	-3.193939	-3.635724	-3.063405
43	1	0	-1.770666	-3.036287	-2.187921
44	6	0	-5.099399	-2.186673	-1.767434
45	1	0	-5.456944	-2.357571	-2.788802
46	1	0	-5.333953	-3.072640	-1.170356
47	1	0	-5.634490	-1.337059	-1.339482
48	6	0	-4.111026	0.452448	-2.509853
49	1	0	-3.650157	1.328180	-2.978326
50	1	0	-5.050588	0.244066	-3.031081
51	1	0	-4.315416	0.690265	-1.461077
52	6	0	0.509343	1.319368	0.788302
53	6	0	1.664340	1.900528	0.286207
54	6	0	0.327387	2.847743	-1.478741
55	6	0	-0.781218	2.232784	-0.922898
56	1	0	0.478458	0.712085	1.688099
57	1	0	2.616023	1.759132	0.783141
58	1	0	0.247909	3.455181	-2.372528
59	7	0	-0.676837	1.488422	0.188715
60	1	0	-1.781034	2.299016	-1.336665
61	6	0	1.593180	-2.801723	0.715117
62	6	0	1.568395	2.677693	-0.865928
63	6	0	2.819624	-3.471781	1.250398
64	8	0	2.825593	-4.166928	2.236882

65	8	0	3.903779	-3.211666	0.510717
66	6	0	5.118373	-3.835725	0.961399
67	6	0	6.217781	-3.414606	0.012894
68	1	0	5.312316	-3.518929	1.990264
69	1	0	7.163858	-3.867748	0.317438
70	1	0	5.991655	-3.735309	-1.006318
71	1	0	6.336294	-2.328828	0.018298
72	6	0	2.754846	3.352753	-1.479649
73	8	0	2.699938	4.019910	-2.483759
74	8	0	3.878087	3.134067	-0.786452
75	6	0	5.057127	3.765435	-1.315207
76	6	0	6.198512	3.438351	-0.379342
77	1	0	5.228770	3.389045	-2.327912
78	1	0	7.120973	3.894467	-0.745531
79	1	0	5.996393	3.821334	0.623266
80	1	0	6.347543	2.358157	-0.316102
81	1	0	4.873153	4.841007	-1.388244
82	1	0	4.969825	-4.919376	0.971077

TS3

Thermal correction to Energy= 0.735200
Thermal correction to Enthalpy= 0.736144
Thermal correction to Gibbs Free Energy= 0.622654
Sum of electronic and zero-point Energies= -1852.097189
Sum of electronic and thermal Energies= -1852.056789
Sum of electronic and thermal Enthalpies= -1852.055845
Sum of electronic and thermal Free Energies= -1852.169336

Esol= -1853.4453971
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.231228	-3.222449	-0.196661
2	6	0	-1.654860	-1.553045	0.789537
3	6	0	0.859194	-2.470350	0.145517
4	1	0	-0.110533	-4.175837	-0.697276
5	6	0	-0.522901	-0.822209	1.107663
6	1	0	-2.631598	-1.173873	1.066116
7	1	0	1.882181	-2.761274	-0.054232
8	1	0	-0.550001	0.109358	1.662003
9	7	0	0.722796	-1.269959	0.792108

10	6	0	3.005797	-0.757402	-2.642697
11	6	0	3.642392	0.655559	-2.420851
12	5	0	1.924605	0.362710	-0.960808
13	8	0	1.758914	-0.652566	-1.935612
14	8	0	3.178232	1.006958	-1.108866
15	6	0	5.162270	0.673700	-2.416721
16	1	0	5.560606	0.307496	-3.368727
17	1	0	5.515603	1.697850	-2.268940
18	1	0	5.550955	0.055320	-1.605500
19	6	0	3.827262	-1.873332	-1.999109
20	1	0	3.246845	-2.800112	-2.045786
21	1	0	4.768244	-2.037716	-2.532833
22	1	0	4.037045	-1.640681	-0.950896
23	6	0	2.708081	-1.092135	-4.097093
24	1	0	3.627463	-1.087426	-4.691974
25	1	0	2.267105	-2.090655	-4.157993
26	1	0	2.002942	-0.380892	-4.530501
27	6	0	3.093717	1.697893	-3.397419
28	1	0	3.406728	2.689708	-3.061167
29	1	0	3.464734	1.540132	-4.414298
30	1	0	1.999492	1.671178	-3.417242
31	6	0	3.642344	-0.655575	2.420866
32	6	0	3.005778	0.757401	2.642698
33	5	0	1.924584	-0.362692	0.960797
34	8	0	3.178195	-1.006968	1.108876
35	8	0	1.758902	0.652591	1.935594
36	6	0	2.708048	1.092146	4.097088
37	1	0	3.627421	1.087417	4.691982
38	1	0	2.267095	2.090676	4.157978
39	1	0	2.002885	0.380920	4.530488
40	6	0	3.093631	-1.697893	3.397430
41	1	0	3.406624	-2.689717	3.061186
42	1	0	3.464637	-1.540137	4.414314
43	1	0	1.999407	-1.671153	3.417237
44	6	0	5.162221	-0.673750	2.416758
45	1	0	5.560551	-0.307553	3.368770
46	1	0	5.515534	-1.697908	2.268985
47	1	0	5.550932	-0.055380	1.605542
48	6	0	3.827278	1.873310	1.999119
49	1	0	3.246882	2.800104	2.045782
50	1	0	4.768255	2.037675	2.532859
51	1	0	4.037074	1.640650	0.950911
52	6	0	-0.522867	0.822275	-1.107714
53	6	0	-1.654822	1.553115	-0.789582

54	6	0	-0.231184	3.222465	0.196699
55	6	0	0.859234	2.470370	-0.145498
56	1	0	-0.549971	-0.109276	-1.662081
57	1	0	-2.631560	1.173963	-1.066188
58	1	0	-0.110485	4.175833	0.697351
59	7	0	0.722831	1.269998	-0.792125
60	1	0	1.882221	2.761276	0.054274
61	6	0	-1.524902	-2.765678	0.119651
62	6	0	-1.524861	2.765719	-0.119644
63	6	0	-2.685165	-3.603581	-0.263654
64	8	0	-2.595514	-4.675264	-0.818035
65	8	0	-3.858761	-3.040075	0.072716
66	6	0	-5.022890	-3.808280	-0.262077
67	6	0	-6.229238	-3.006150	0.173187
68	1	0	-5.020536	-4.000768	-1.339000
69	1	0	-7.145672	-3.550356	-0.066243
70	1	0	-6.203792	-2.825702	1.250153
71	1	0	-6.254499	-2.042110	-0.339987
72	6	0	-2.685123	3.603602	0.263705
73	8	0	-2.595476	4.675239	0.818173
74	8	0	-3.858715	3.040125	-0.072730
75	6	0	-5.022863	3.808249	0.262175
76	6	0	-6.229187	3.006136	-0.173191
77	1	0	-5.020510	4.000589	1.339125
78	1	0	-7.145640	3.550273	0.066327
79	1	0	-6.203740	2.825851	-1.250185
80	1	0	-6.254403	2.042017	0.339836
81	1	0	-4.964938	-4.776172	0.244846
82	1	0	-4.964957	4.776211	-0.244617

Int3

Thermal correction to Energy= 0.739505
Thermal correction to Enthalpy= 0.740449
Thermal correction to Gibbs Free Energy= 0.624473
Sum of electronic and zero-point Energies= -1852.158406
Sum of electronic and thermal Energies= -1852.117616
Sum of electronic and thermal Enthalpies= -1852.116672
Sum of electronic and thermal Free Energies= -1852.232648

Esol= -1853.5162289
Input orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-0.689798	-3.056593	-0.150441
2	6	0	-2.037109	-1.253945	0.777254
3	6	0	0.435150	-2.407407	0.196337
4	1	0	-0.663210	-4.028325	-0.623546
5	6	0	-0.820815	-0.374185	0.689187
6	1	0	-2.964537	-0.853152	1.169849
7	1	0	1.425821	-2.827043	0.061288
8	1	0	-0.818847	0.389622	1.473269
9	7	0	0.399494	-1.167762	0.829913
10	6	0	2.843051	-0.716727	-2.754187
11	6	0	3.520514	0.687738	-2.590095
12	5	0	1.527885	0.658030	-1.534326
13	8	0	1.486499	-0.458813	-2.330624
14	8	0	2.761075	1.275124	-1.512027
15	6	0	4.984689	0.645183	-2.187687
16	1	0	5.578993	0.135581	-2.952659
17	1	0	5.364075	1.664544	-2.080518
18	1	0	5.115716	0.125524	-1.236796
19	6	0	3.422978	-1.766762	-1.811435
20	1	0	2.793055	-2.658838	-1.858856
21	1	0	4.438555	-2.046885	-2.105926
22	1	0	3.436622	-1.410204	-0.776271
23	6	0	2.814873	-1.242274	-4.180381
24	1	0	3.832913	-1.364853	-4.563643
25	1	0	2.322153	-2.217386	-4.197684
26	1	0	2.265731	-0.570851	-4.841975
27	6	0	3.324437	1.584937	-3.810119
28	1	0	3.634431	2.600522	-3.553112
29	1	0	3.918539	1.241276	-4.661236
30	1	0	2.271736	1.612696	-4.106533
31	6	0	3.520455	-0.687778	2.590120
32	6	0	2.843014	0.716699	2.754195
33	5	0	1.527851	-0.658040	1.534309
34	8	0	2.761032	-1.275152	1.512035
35	8	0	1.486468	0.458810	2.330598
36	6	0	2.814809	1.242253	4.180387
37	1	0	3.832841	1.364810	4.563676
38	1	0	2.322112	2.217377	4.197672
39	1	0	2.265632	0.570847	4.841969
40	6	0	3.324338	-1.584978	3.810138
41	1	0	3.634322	-2.600566	3.553135
42	1	0	3.918427	-1.241327	4.661268

43	1	0	2.271630	-1.612721	4.106530
44	6	0	4.984639	-0.645243	2.187743
45	1	0	5.578934	-0.135650	2.952728
46	1	0	5.364012	-1.664609	2.080580
47	1	0	5.115693	-0.125583	1.236855
48	6	0	3.422989	1.766716	1.811456
49	1	0	2.793081	2.658804	1.858848
50	1	0	4.438561	2.046824	2.105979
51	1	0	3.436663	1.410148	0.776296
52	6	0	-0.820799	0.374205	-0.689247
53	6	0	-2.037081	1.253980	-0.777333
54	6	0	-0.689763	3.056610	0.150387
55	6	0	0.435183	2.407410	-0.196372
56	1	0	-0.818828	-0.389602	-1.473329
57	1	0	-2.964508	0.853198	-1.169943
58	1	0	-0.663171	4.028340	0.623495
59	7	0	0.399521	1.167767	-0.829952
60	1	0	1.425857	2.827033	-0.061306
61	6	0	-1.966099	-2.502793	0.284584
62	6	0	-1.966063	2.502826	-0.284660
63	6	0	-3.150857	-3.404273	0.228350
64	8	0	-3.125251	-4.522418	-0.230709
65	8	0	-4.264041	-2.842259	0.729544
66	6	0	-5.435199	-3.667382	0.686916
67	6	0	-6.562889	-2.876664	1.312327
68	1	0	-5.644128	-3.931806	-0.354249
69	1	0	-7.483199	-3.465289	1.301675
70	1	0	-6.325098	-2.622161	2.347563
71	1	0	-6.736252	-1.950549	0.759446
72	6	0	-3.150813	3.404319	-0.228440
73	8	0	-3.125204	4.522455	0.230641
74	8	0	-4.264001	2.842311	-0.729632
75	6	0	-5.435155	3.667438	-0.686997
76	6	0	-6.562848	2.876731	-1.312416
77	1	0	-5.644085	3.931853	0.354171
78	1	0	-7.483156	3.465360	-1.301758
79	1	0	-6.325059	2.622237	-2.347655
80	1	0	-6.736216	1.950611	-0.759544
81	1	0	-5.233224	-4.597366	1.226950
82	1	0	-5.233177	4.597427	-1.227022

TS4

Thermal correction to Energy= 0.735866

Thermal correction to Enthalpy= 0.736811
Thermal correction to Gibbs Free Energy= 0.621117
Sum of electronic and zero-point Energies= -1852.121006
Sum of electronic and thermal Energies= -1852.080167
Sum of electronic and thermal Enthalpies= -1852.079223
Sum of electronic and thermal Free Energies= -1852.194917

Esol= -1853.4780759
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.564328	-3.335916	0.516271
2	6	0	-2.018077	-1.531125	1.206200
3	6	0	0.511239	-2.587320	0.828031
4	1	0	-0.444026	-4.342101	0.133862
5	6	0	-0.894853	-0.723182	1.391250
6	1	0	-2.998791	-1.096184	1.365844
7	1	0	1.528845	-2.944816	0.750102
8	1	0	-0.947979	0.240071	1.884692
9	7	0	0.385628	-1.286962	1.340001
10	6	0	2.756789	-1.304646	-2.313407
11	6	0	3.542472	0.044937	-2.156154
12	5	0	1.522473	0.213624	-1.181797
13	8	0	1.414276	-0.933980	-1.920109
14	8	0	2.800646	0.720516	-1.113450
15	6	0	4.985281	-0.109179	-1.709043
16	1	0	5.559329	-0.669719	-2.453456
17	1	0	5.440099	0.879062	-1.599207
18	1	0	5.047338	-0.629399	-0.752186
19	6	0	3.242157	-2.384214	-1.352452
20	1	0	2.526699	-3.210338	-1.372665
21	1	0	4.221477	-2.766379	-1.655225
22	1	0	3.311796	-2.000080	-0.330029
23	6	0	2.707143	-1.844632	-3.733600
24	1	0	3.718313	-2.047248	-4.100793
25	1	0	2.144025	-2.780867	-3.746215
26	1	0	2.218349	-1.142785	-4.410648
27	6	0	3.456079	0.931158	-3.396955
28	1	0	3.853145	1.919006	-3.151883
29	1	0	4.034621	0.517267	-4.226984
30	1	0	2.417490	1.049887	-3.719997
31	6	0	3.542532	-0.423224	2.852920

32	6	0	2.756876	0.926377	3.010093
33	5	0	1.522560	-0.591919	1.878528
34	8	0	2.800740	-1.098800	1.810191
35	8	0	1.414358	0.555703	2.616812
36	6	0	2.707236	1.466450	4.430252
37	1	0	3.718411	1.669066	4.797435
38	1	0	2.144138	2.402697	4.442809
39	1	0	2.218427	0.764654	5.107341
40	6	0	3.456042	-1.309407	4.093743
41	1	0	3.853077	-2.297279	3.848721
42	1	0	4.034563	-0.895514	4.923786
43	1	0	2.417433	-1.428079	4.416741
44	6	0	4.985372	-0.269160	2.405895
45	1	0	5.559387	0.291372	3.150341
46	1	0	5.440168	-1.257416	2.296103
47	1	0	5.047516	0.251047	1.449037
48	6	0	3.242261	2.005861	2.049053
49	1	0	2.526809	2.831991	2.069189
50	1	0	4.221582	2.388044	2.351798
51	1	0	3.311888	1.621620	1.026667
52	6	0	-0.894928	0.344840	-0.694437
53	6	0	-2.018162	1.152761	-0.509341
54	6	0	-0.564421	2.957568	0.180567
55	6	0	0.511149	2.208997	-0.131240
56	1	0	-0.948054	-0.618410	-1.187883
57	1	0	-2.998874	0.717806	-0.668957
58	1	0	-0.444126	3.963747	0.562996
59	7	0	0.385542	0.908647	-0.643238
60	1	0	1.528753	2.566507	-0.053326
61	6	0	-1.892751	-2.823146	0.734429
62	6	0	-1.892841	2.444780	-0.037562
63	6	0	-3.038854	-3.685688	0.436668
64	8	0	-2.956039	-4.819982	0.010692
65	8	0	-4.225098	-3.084422	0.684740
66	6	0	-5.379005	-3.881683	0.407204
67	6	0	-6.592544	-3.052445	0.767353
68	1	0	-5.373009	-4.163779	-0.650491
69	1	0	-7.506793	-3.616385	0.567368
70	1	0	-6.573722	-2.785296	1.826409
71	1	0	-6.616868	-2.131652	0.179600
72	6	0	-3.038949	3.307303	0.260239
73	8	0	-2.956138	4.441592	0.686229
74	8	0	-4.225190	2.706026	0.012185
75	6	0	-5.379102	3.503269	0.289755

76	6	0	-6.592638	2.674021	-0.070380
77	1	0	-5.373087	3.785350	1.347454
78	1	0	-7.506890	3.237947	0.129633
79	1	0	-6.573835	2.406888	-1.129441
80	1	0	-6.616938	1.753220	0.517361
81	1	0	-5.324632	-4.806063	0.990635
82	1	0	-5.324752	4.427659	-0.293664

A

Thermal correction to Energy=	0.367137
Thermal correction to Enthalpy=	0.368081
Thermal correction to Gibbs Free Energy=	0.297494
Sum of electronic and zero-point Energies=	-926.058697
Sum of electronic and thermal Energies=	-926.038573
Sum of electronic and thermal Enthalpies=	-926.037628
Sum of electronic and thermal Free Energies=	-926.108215

Esol= -926.7403969

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.190202	3.289635	2.128994
2	6	0	4.826573	4.403694	3.026399
3	5	0	2.739822	3.939334	3.716895
4	8	0	2.784992	3.394995	2.460960
5	8	0	3.939705	4.418194	4.170574
6	6	0	6.237991	4.107831	3.503558
7	1	0	6.913303	3.995263	2.649662
8	1	0	6.597534	4.937120	4.117320
9	1	0	6.271605	3.197722	4.103834
10	6	0	4.637824	1.885417	2.527298
11	1	0	4.004131	1.156472	2.017288
12	1	0	5.677975	1.703382	2.244484
13	1	0	4.536764	1.734365	3.605983
14	6	0	4.358496	3.502665	0.634459
15	1	0	5.420245	3.524763	0.369804
16	1	0	3.887795	2.678902	0.092640
17	1	0	3.893712	4.435128	0.311595
18	6	0	4.752216	5.788452	2.387880
19	1	0	5.008940	6.536962	3.140768
20	1	0	5.450185	5.879699	1.551498

21	1	0	3.741644	5.997662	2.025162
22	6	0	0.341891	3.449809	4.015356
23	6	0	-0.806631	3.501234	4.735630
24	6	0	-0.831276	4.125264	6.014334
25	6	0	0.386470	4.683907	6.492581
26	6	0	1.518486	4.618688	5.750118
27	1	0	0.416139	2.987166	3.039642
28	1	0	-1.710231	3.062031	4.331301
29	7	0	1.531255	4.002537	4.495264
30	1	0	2.469280	5.027727	6.066499
31	1	0	0.396211	5.165475	7.463350
32	6	0	-2.022913	4.218035	6.842462
33	8	0	-2.071226	4.745732	7.938852
34	8	0	-3.107627	3.644955	6.262253
35	6	0	-4.307148	3.708274	7.035523
36	6	0	-5.395079	3.028763	6.232072
37	1	0	-4.544977	4.756038	7.244346
38	1	0	-4.140157	3.215774	7.998659
39	1	0	-6.338759	3.049941	6.782328
40	1	0	-5.539091	3.536388	5.275536
41	1	0	-5.131753	1.987271	6.033746

1

Thermal correction to Energy= 0.276546
Thermal correction to Enthalpy= 0.277490
Thermal correction to Gibbs Free Energy= 0.213884
Sum of electronic and zero-point Energies= -971.533385
Sum of electronic and thermal Energies= -971.517081
Sum of electronic and thermal Enthalpies= -971.516136
Sum of electronic and thermal Free Energies= -971.579743

Esol= -972.1520234
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.033496	-1.726136	-3.104738
2	6	0	-2.736516	-2.198325	-3.320767
3	6	0	-1.653049	-1.694001	-2.597447
4	6	0	-1.920282	-0.710885	-1.662112
5	6	0	-3.213729	-0.239623	-1.447179
6	6	0	-4.292996	-0.732337	-2.157843

7	6	0	-0.988518	-0.002763	-0.734671
8	7	0	-1.794684	0.999567	-0.152682
9	6	0	-3.173070	0.792060	-0.370588
10	8	0	-1.388467	1.642416	0.980121
11	8	0	-4.058041	1.350472	0.218705
12	8	0	0.173336	-0.188718	-0.500673
13	6	0	-1.557037	0.858183	2.116605
14	8	0	-1.933383	-0.274349	2.054356
15	1	0	-4.852595	-2.143397	-3.681171
16	1	0	-2.571626	-2.973266	-4.061955
17	1	0	-0.642062	-2.056126	-2.750150
18	1	0	-5.295335	-0.359637	-1.976313
19	6	0	-2.145081	3.476137	4.839233
20	6	0	-2.449185	2.631374	3.605643
21	6	0	0.032829	2.480274	3.268091
22	6	0	0.169210	3.326870	4.530136
23	1	0	-3.377309	2.068566	3.746879
24	1	0	-2.094027	2.827376	5.730491
25	1	0	-2.928106	4.219928	5.003218
26	1	0	0.896535	1.816416	3.160523
27	1	0	0.002450	3.140044	2.396039
28	1	0	0.267610	2.670695	5.412182
29	1	0	1.055780	3.962834	4.479121
30	1	0	-2.579737	3.284968	2.736863
31	8	0	-0.935857	4.190626	4.695428
32	6	0	-1.270231	1.673117	3.346575
33	1	0	-1.210159	0.949381	4.167764

$TS_{1\text{-}B'}$

Thermal correction to Energy= 0.644031
Thermal correction to Enthalpy= 0.644975
Thermal correction to Gibbs Free Energy= 0.538417
Sum of electronic and zero-point Energies= -1897.600599
Sum of electronic and thermal Energies= -1897.564023
Sum of electronic and thermal Enthalpies= -1897.563079
Sum of electronic and thermal Free Energies= -1897.669637

Esol= -1898.8893511
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-7.060265	3.328320	-0.853613
2	6	0	-6.229016	2.328892	-0.339188
3	6	0	-5.588335	2.494845	0.889246
4	6	0	-5.806899	3.680554	1.566029
5	6	0	-6.623932	4.692663	1.047397
6	6	0	-7.270160	4.528436	-0.173420
7	6	0	-5.303787	4.091658	2.898971
8	7	0	-5.763613	5.429556	3.033820
9	6	0	-6.617955	5.817589	2.007116
10	8	0	-5.886879	5.980670	4.280146
11	8	0	-7.116276	6.945359	1.970747
12	8	0	-4.660569	3.499502	3.720359
13	6	0	-6.840888	5.287374	5.033417
14	8	0	-7.428151	4.352353	4.574212
15	1	0	-7.559741	3.164377	-1.802859
16	1	0	-6.091319	1.409475	-0.898288
17	1	0	-4.950715	1.728192	1.316376
18	1	0	-7.937073	5.295673	-0.549452
19	6	0	-6.132002	7.119699	8.367668
20	6	0	-5.821180	6.671827	6.939519
21	6	0	-7.346178	4.725273	7.390828
22	6	0	-7.563555	5.314256	8.778868
23	1	0	-5.626097	7.541398	6.305390
24	1	0	-6.985634	7.819074	8.353948
25	1	0	-5.275121	7.636563	8.806477
26	1	0	-8.230740	4.183387	7.045428
27	1	0	-6.509845	4.017087	7.422156
28	1	0	-8.447553	5.970684	8.763459
29	1	0	-7.731797	4.524975	9.516043
30	1	0	-4.920102	6.048558	6.942954
31	8	0	-6.418620	6.027046	9.212195
32	6	0	-7.007281	5.859296	6.414412
33	1	0	-7.887400	6.519143	6.344645
34	6	0	-8.583819	8.182834	-0.783806
35	6	0	-8.842115	9.451113	0.092241
36	5	0	-8.728227	7.607580	1.405607
37	8	0	-8.963484	7.119653	0.115980
38	8	0	-8.510724	8.982325	1.408963
39	6	0	-7.964209	10.646126	-0.241346
40	1	0	-8.123506	10.966289	-1.276214
41	1	0	-8.220334	11.479543	0.417562
42	1	0	-6.908516	10.411256	-0.099310
43	6	0	-7.104500	8.022016	-1.136515
44	1	0	-6.941489	7.041932	-1.592718

45	1	0	-6.786310	8.783231	-1.854251
46	1	0	-6.479024	8.096476	-0.242672
47	6	0	-9.441703	8.085335	-2.034300
48	1	0	-9.261923	8.942791	-2.690710
49	1	0	-9.186880	7.176182	-2.586528
50	1	0	-10.502786	8.046812	-1.783252
51	6	0	-10.315822	9.856265	0.106144
52	1	0	-10.465923	10.597884	0.894543
53	1	0	-10.624247	10.293820	-0.847601
54	1	0	-10.952235	8.992489	0.320795
55	6	0	-9.777718	5.667320	2.573918
56	6	0	-10.152515	5.037084	3.727181
57	6	0	-10.251488	5.769229	4.932038
58	6	0	-10.011422	7.169415	4.876318
59	6	0	-9.633075	7.751058	3.706755
60	1	0	-9.680502	5.154203	1.623828
61	1	0	-10.337039	3.969983	3.723438
62	7	0	-9.495939	7.017784	2.548401
63	1	0	-9.406560	8.804941	3.605097
64	1	0	-10.116956	7.760435	5.779019
65	6	0	-10.503599	5.164585	6.232598
66	8	0	-10.479202	5.773500	7.290969
67	8	0	-10.740521	3.835216	6.165839
68	6	0	-10.992995	3.196827	7.420813
69	6	0	-11.199937	1.724887	7.138614
70	1	0	-11.870344	3.657095	7.886135
71	1	0	-10.142491	3.369964	8.089615
72	1	0	-11.396680	1.187693	8.069379
73	1	0	-12.048747	1.579241	6.466676
74	1	0	-10.310407	1.297851	6.670043

B’

Thermal correction to Energy= 0.646314
Thermal correction to Enthalpy= 0.647259
Thermal correction to Gibbs Free Energy= 0.537141
Sum of electronic and zero-point Energies= -1897.617358
Sum of electronic and thermal Energies= -1897.580292
Sum of electronic and thermal Enthalpies= -1897.579347
Sum of electronic and thermal Free Energies= -1897.689465

Esol= -1898.9092708
Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-6.858398	3.054701	-0.585412
2	6	0	-6.208158	1.988416	0.076093
3	6	0	-5.650558	2.178325	1.329956
4	6	0	-5.753471	3.435574	1.918223
5	6	0	-6.419493	4.515289	1.264733
6	6	0	-6.968309	4.310835	-0.022154
7	6	0	-5.268399	3.879370	3.218973
8	7	0	-5.557884	5.266382	3.197961
9	6	0	-6.351717	5.641462	2.126446
10	8	0	-5.563335	5.964895	4.373237
11	8	0	-6.769180	6.882799	2.076262
12	8	0	-4.764110	3.308464	4.168567
13	6	0	-6.628813	5.624087	5.178139
14	8	0	-7.520798	4.915331	4.804163
15	1	0	-7.280525	2.882018	-1.570842
16	1	0	-6.143661	1.019312	-0.406945
17	1	0	-5.140944	1.378581	1.857999
18	1	0	-7.475725	5.121373	-0.530970
19	6	0	-6.103292	8.302305	7.899201
20	6	0	-6.321850	7.773758	6.483876
21	6	0	-5.250871	5.644693	7.263327
22	6	0	-5.102081	6.315192	8.624726
23	1	0	-7.212787	8.234939	6.043124
24	1	0	-6.999584	8.102989	8.512229
25	1	0	-5.929144	9.380776	7.890319
26	1	0	-5.365159	4.562036	7.375143
27	1	0	-4.352022	5.825453	6.666013
28	1	0	-5.974395	6.076159	9.257223
29	1	0	-4.203456	5.963219	9.136354
30	1	0	-5.462101	8.036715	5.860310
31	8	0	-4.969527	7.716723	8.501078
32	6	0	-6.468730	6.245431	6.537989
33	1	0	-7.382164	5.984576	7.086532
34	6	0	-8.581534	8.103250	-0.469169
35	6	0	-8.929678	9.190085	0.598395
36	5	0	-8.106790	7.312836	1.625557
37	8	0	-8.541405	6.911086	0.326823
38	8	0	-8.215290	8.722530	1.745481
39	6	0	-8.445160	10.590898	0.257974
40	1	0	-8.881700	10.935897	-0.685177
41	1	0	-8.744555	11.285596	1.047434

42	1	0	-7.357627	10.615504	0.176658
43	6	0	-7.193859	8.317228	-1.075781
44	1	0	-6.916208	7.425674	-1.644837
45	1	0	-7.175910	9.177133	-1.751767
46	1	0	-6.449200	8.467028	-0.288968
47	6	0	-9.621656	7.929200	-1.564431
48	1	0	-9.758799	8.862761	-2.119805
49	1	0	-9.289259	7.160759	-2.268062
50	1	0	-10.582529	7.619647	-1.149416
51	6	0	-10.423577	9.211796	0.930197
52	1	0	-10.573756	9.807846	1.835016
53	1	0	-11.011468	9.657025	0.122365
54	1	0	-10.797954	8.199861	1.113934
55	6	0	-9.551500	5.339960	2.503817
56	6	0	-10.319711	4.682033	3.453392
57	6	0	-10.636758	5.351608	4.629647
58	6	0	-10.189650	6.656454	4.826187
59	6	0	-9.424002	7.247641	3.838416
60	1	0	-9.268481	4.893523	1.555845
61	1	0	-10.653582	3.666425	3.284013
62	7	0	-9.120054	6.589532	2.710532
63	1	0	-9.036402	8.259510	3.893295
64	1	0	-10.441174	7.183146	5.739240
65	6	0	-11.442970	4.714482	5.722850
66	8	0	-11.722339	5.279431	6.751579
67	8	0	-11.803156	3.467436	5.420929
68	6	0	-12.560841	2.777632	6.432975
69	6	0	-12.809512	1.375327	5.926693
70	1	0	-13.489039	3.329668	6.607393
71	1	0	-11.985256	2.789089	7.362595
72	1	0	-13.380861	0.811202	6.667146
73	1	0	-13.376600	1.395955	4.993610
74	1	0	-11.864151	0.858148	5.749843

$TS_{B'-B}$

Thermal correction to Energy=	0.644966
Thermal correction to Enthalpy=	0.645910
Thermal correction to Gibbs Free Energy=	0.535409
Sum of electronic and zero-point Energies=	-1897.604954
Sum of electronic and thermal Energies=	-1897.567810
Sum of electronic and thermal Enthalpies=	-1897.566866
Sum of electronic and thermal Free Energies=	-1897.677366

Esol= -1898.8958324

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.132104	2.933727	2.275174
2	6	0	3.332328	4.009716	2.714830
3	6	0	2.076626	4.220270	2.167458
4	6	0	1.628071	3.342032	1.186656
5	6	0	2.419767	2.240527	0.751040
6	6	0	3.704462	2.050613	1.302629
7	6	0	0.369792	3.362916	0.446739
8	7	0	0.533791	2.298261	-0.468500
9	6	0	1.675014	1.561422	-0.247048
10	8	0	-0.533318	1.835249	-1.181442
11	8	0	1.944947	0.581939	-1.103145
12	8	0	-0.636670	4.043676	0.517785
13	6	0	-1.509913	1.287528	-0.358921
14	8	0	-1.322894	1.071983	0.802616
15	1	0	5.114964	2.795889	2.715200
16	1	0	3.709563	4.676997	3.482231
17	1	0	1.445469	5.046454	2.478569
18	1	0	4.322647	1.220962	0.984551
19	6	0	-4.076158	0.736872	-3.198729
20	6	0	-2.672867	0.852433	-2.610135
21	6	0	-3.662753	2.374218	-0.887513
22	6	0	-4.995842	2.184780	-1.605895
23	1	0	-2.100385	-0.060435	-2.806932
24	1	0	-4.595197	-0.126624	-2.746865
25	1	0	-4.038180	0.589380	-4.280625
26	1	0	-3.822644	2.539977	0.182200
27	1	0	-3.136167	3.247754	-1.286644
28	1	0	-5.550807	1.356328	-1.132722
29	1	0	-5.605956	3.088830	-1.541763
30	1	0	-2.146775	1.684144	-3.087965
31	8	0	-4.820066	1.917778	-2.981840
32	6	0	-2.801472	1.113979	-1.107575
33	1	0	-3.310512	0.266110	-0.632103
34	6	0	4.103482	-2.076359	0.018132
35	6	0	3.911960	-2.307543	-1.525311
36	5	0	2.630645	-0.591255	-0.832194
37	8	0	3.491775	-0.781471	0.216841
38	8	0	2.731445	-1.533838	-1.822338

39	6	0	5.045700	-1.711347	-2.357047
40	1	0	5.977524	-2.268554	-2.228049
41	1	0	4.760014	-1.742824	-3.410894
42	1	0	5.220605	-0.666383	-2.084298
43	6	0	5.553290	-1.993345	0.470294
44	1	0	5.588108	-1.818646	1.548657
45	1	0	6.074982	-2.932137	0.258424
46	1	0	6.080638	-1.177809	-0.027190
47	6	0	3.346366	-3.087652	0.874380
48	1	0	3.812252	-4.075483	0.819515
49	1	0	3.368583	-2.750564	1.914227
50	1	0	2.304897	-3.164847	0.557900
51	6	0	3.667314	-3.753708	-1.922218
52	1	0	3.545737	-3.817473	-3.006390
53	1	0	4.517989	-4.379991	-1.635412
54	1	0	2.763704	-4.146174	-1.453014
55	6	0	0.107746	-1.529227	1.363686
56	6	0	-1.222037	-1.804087	1.673570
57	6	0	-2.106761	-2.001886	0.620588
58	6	0	-1.633836	-1.954495	-0.689435
59	6	0	-0.286278	-1.688448	-0.893269
60	1	0	0.836911	-1.334562	2.146294
61	1	0	-1.566426	-1.823162	2.700247
62	7	0	0.564952	-1.472947	0.114187
63	1	0	0.143378	-1.633119	-1.891489
64	1	0	-2.320233	-2.107775	-1.515710
65	6	0	-3.576006	-2.184796	0.830417
66	8	0	-4.393656	-2.062505	-0.053115
67	8	0	-3.881478	-2.473017	2.096827
68	6	0	-5.285625	-2.610834	2.378960
69	6	0	-5.417515	-2.909809	3.854929
70	1	0	-5.688587	-3.412826	1.753695
71	1	0	-5.789787	-1.682560	2.094972
72	1	0	-6.471486	-3.026627	4.116845
73	1	0	-4.891967	-3.832862	4.108843
74	1	0	-4.999694	-2.095639	4.451016

B

Thermal correction to Energy=	0.471217
Thermal correction to Enthalpy=	0.472161
Thermal correction to Gibbs Free Energy=	0.384362
Sum of electronic and zero-point Energies=	-1382.472977
Sum of electronic and thermal Energies=	-1382.446411

Sum of electronic and thermal Enthalpies= -1382.445467
Sum of electronic and thermal Free Energies= -1382.533266

Esol= -1383.4208442
Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.686652	5.804596	-0.965413
2	6	0	-7.326616	6.351769	-0.540883
3	6	0	-8.562670	7.680564	1.194145
4	6	0	-9.838267	7.051338	0.645440
5	1	0	-6.544452	5.609207	-0.729707
6	1	0	-8.897356	4.866153	-0.423666
7	1	0	-8.702801	5.589165	-2.036327
8	1	0	-8.666723	7.891342	2.262935
9	1	0	-8.369323	8.630682	0.686343
10	1	0	-10.079798	6.138098	1.216048
11	1	0	-10.680710	7.741125	0.733682
12	1	0	-7.100082	7.243291	-1.133255
13	8	0	-9.717273	6.739073	-0.727624
14	6	0	-7.378836	6.724320	0.947188
15	6	0	-1.246323	11.243116	3.164378
16	6	0	-2.285150	11.937869	3.821769
17	6	0	-3.613081	11.652824	3.544659
18	6	0	-3.895108	10.667551	2.603206
19	6	0	-2.851157	9.967232	1.933877
20	6	0	-1.505723	10.265941	2.224383
21	6	0	-5.187748	10.153710	2.156765
22	7	0	-4.816987	9.218958	1.159927
23	6	0	-3.465107	9.036389	1.067357
24	8	0	-5.736368	8.393871	0.594772
25	8	0	-2.998565	8.058026	0.287530
26	8	0	-6.341173	10.369846	2.480062
27	6	0	-6.119703	7.365538	1.459686
28	8	0	-5.521576	7.123887	2.462381
29	1	0	-0.216204	11.485792	3.405574
30	1	0	-2.035954	12.699798	4.552414
31	1	0	-4.425799	12.169885	4.044308
32	1	0	-0.700461	9.746059	1.718423
33	6	0	-0.523619	7.750463	-2.239062
34	6	0	-0.151878	9.131412	-1.597219
35	8	0	-1.333686	9.432078	-0.813721

36	5	0	-1.929637	8.230045	-0.563733
37	8	0	-1.402560	7.174532	-1.243344
38	6	0	0.649940	6.811438	-2.457007
39	6	0	-1.341701	7.898491	-3.519010
40	6	0	0.077198	10.256388	-2.591087
41	6	0	1.014783	9.033337	-0.618353
42	1	0	0.291653	5.878991	-2.899544
43	1	0	1.376340	7.260244	-3.141759
44	1	0	1.148781	6.574051	-1.516401
45	1	0	-1.744035	6.920965	-3.794028
46	1	0	-2.179937	8.585306	-3.369036
47	1	0	-0.728598	8.270648	-4.344030
48	1	0	0.325682	11.174352	-2.053365
49	1	0	0.910854	10.010213	-3.256086
50	1	0	-0.813119	10.443054	-3.192976
51	1	0	1.959644	8.858610	-1.139478
52	1	0	1.091535	9.974584	-0.067918
53	1	0	0.858133	8.221823	0.099576
54	1	0	-7.514494	5.819188	1.550700

$TS_{B\text{-}C}$

Thermal correction to Energy= 0.468108
Thermal correction to Enthalpy= 0.469052
Thermal correction to Gibbs Free Energy= 0.381029
Sum of electronic and zero-point Energies= -1382.448537
Sum of electronic and thermal Energies= -1382.421987
Sum of electronic and thermal Enthalpies= -1382.421043
Sum of electronic and thermal Free Energies= -1382.509066

Esol= -1383.3931642
Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-10.036842	6.685852	0.138208
2	6	0	-8.904871	7.707996	0.156246
3	6	0	-7.681479	6.119914	1.661968
4	6	0	-8.895077	5.203856	1.543148
5	1	0	-8.866874	8.260448	-0.786870
6	1	0	-9.907148	6.007036	-0.722718
7	1	0	-11.007922	7.177457	0.040637
8	1	0	-6.771216	5.529779	1.807898

9	1	0	-7.793355	6.771261	2.533934
10	1	0	-8.746619	4.491459	0.712709
11	1	0	-9.043560	4.628607	2.460278
12	1	0	-9.082848	8.428265	0.963511
13	8	0	-10.084943	5.937029	1.334848
14	6	0	-7.569310	6.988791	0.410438
15	6	0	-2.056877	10.809588	2.983310
16	6	0	-3.072863	11.704917	3.324828
17	6	0	-4.247876	11.771680	2.568867
18	6	0	-4.351821	10.928523	1.482666
19	6	0	-3.341375	10.022790	1.139163
20	6	0	-2.170296	9.955770	1.884427
21	6	0	-5.466320	10.737681	0.515361
22	7	0	-4.986312	9.768498	-0.482533
23	6	0	-3.805914	9.324663	-0.051386
24	8	0	-6.178372	8.566941	-0.623147
25	8	0	-3.196176	8.328075	-0.697942
26	8	0	-6.550033	11.237320	0.479552
27	6	0	-6.457546	8.019830	0.553848
28	8	0	-5.941522	8.321037	1.608875
29	1	0	-1.157643	10.774327	3.590045
30	1	0	-2.947370	12.352223	4.186047
31	1	0	-5.053440	12.453839	2.819022
32	1	0	-1.373955	9.266839	1.628281
33	6	0	-0.026268	7.755202	-2.190042
34	6	0	0.248162	9.044612	-1.342965
35	8	0	-1.092888	9.483028	-1.012091
36	5	0	-1.879267	8.368226	-1.092810
37	8	0	-1.267276	7.273383	-1.622521
38	6	0	1.029016	6.670807	-2.058700
39	6	0	-0.301182	8.063625	-3.659382
40	6	0	0.959891	10.159418	-2.088653
41	6	0	0.954373	8.743077	-0.023813
42	1	0	0.757155	5.819410	-2.686952
43	1	0	2.002901	7.044982	-2.389728
44	1	0	1.114982	6.321100	-1.029021
45	1	0	-0.691407	7.163232	-4.138717
46	1	0	-1.047748	8.856762	-3.761165
47	1	0	0.609698	8.371413	-4.179646
48	1	0	1.106853	11.011471	-1.420645
49	1	0	1.941518	9.819354	-2.433488
50	1	0	0.379699	10.494981	-2.949100
51	1	0	1.999224	8.465345	-0.185186
52	1	0	0.924495	9.637246	0.604318

53	1	0	0.457000	7.924804	0.507401
54	1	0	-7.340071	6.366899	-0.464829

C

Thermal correction to Energy= 0.157540
Thermal correction to Enthalpy= 0.158485
Thermal correction to Gibbs Free Energy= 0.114768
Sum of electronic and zero-point Energies= -459.323111
Sum of electronic and thermal Energies= -459.314863
Sum of electronic and thermal Enthalpies= -459.313919
Sum of electronic and thermal Free Energies= -459.357636

Esol= -459.6457308
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-8.700068	5.901292	-1.020990
2	6	0	-7.355209	6.490416	-0.602421
3	6	0	-8.597762	7.605379	1.281879
4	6	0	-9.852981	6.936300	0.731108
5	1	0	-6.543386	5.806325	-0.869794
6	1	0	-8.832899	4.911790	-0.550203
7	1	0	-8.749071	5.771897	-2.104476
8	1	0	-8.663590	7.728671	2.366112
9	1	0	-8.495289	8.603374	0.843461
10	1	0	-10.008835	5.963740	1.228810
11	1	0	-10.735047	7.555111	0.910205
12	1	0	-7.194122	7.430920	-1.141300
13	8	0	-9.769685	6.750229	-0.667389
14	6	0	-7.374434	6.765718	0.909191
15	8	0	-5.002574	6.902833	0.905213
16	6	0	-6.109359	7.450087	1.393370
17	8	0	-6.037771	8.389202	2.148463
18	1	0	-7.421615	5.799923	1.435206

D (Bpin-Phth)

Thermal correction to Energy= 0.308615
Thermal correction to Enthalpy= 0.309559
Thermal correction to Gibbs Free Energy= 0.245632
Sum of electronic and zero-point Energies= -923.134368

Sum of electronic and thermal Energies= -923.116808
Sum of electronic and thermal Enthalpies= -923.115863
Sum of electronic and thermal Free Energies= -923.179790

Esol= -923.7604239
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.436450	0.778828	2.352964
2	6	0	1.210472	-0.325418	2.709713
3	6	0	1.595166	-1.274484	1.754927
4	6	0	1.171360	-1.069069	0.457944
5	6	0	0.392144	0.025031	0.102603
6	6	0	0.011855	0.974103	1.033325
7	6	0	1.405970	-1.843427	-0.814842
8	7	0	0.753709	-1.155596	-1.894203
9	6	0	0.189361	-0.133367	-1.369997
10	8	0	-0.465375	0.766287	-2.114194
11	8	0	2.027537	-2.863213	-0.931860
12	1	0	0.158663	1.500866	3.113853
13	1	0	1.520905	-0.444872	3.742482
14	1	0	2.204052	-2.134506	2.012998
15	1	0	-0.592995	1.832942	0.763701
16	6	0	-3.706988	2.212288	-2.158594
17	6	0	-3.668685	1.559452	-0.735021
18	8	0	-2.514034	0.689490	-0.830126
19	5	0	-1.730178	1.215997	-1.818600
20	8	0	-2.307285	2.225586	-2.527591
21	6	0	-4.238435	3.634779	-2.193568
22	6	0	-4.428051	1.342804	-3.185449
23	6	0	-4.885435	0.722001	-0.382128
24	6	0	-3.372886	2.571377	0.369068
25	1	0	-4.227266	4.002077	-3.222279
26	1	0	-5.269995	3.665262	-1.829234
27	1	0	-3.627969	4.303872	-1.585691
28	1	0	-4.233521	1.743749	-4.182437
29	1	0	-4.061587	0.312642	-3.153061
30	1	0	-5.507608	1.335948	-3.013865
31	1	0	-4.768231	0.311857	0.623686
32	1	0	-5.789501	1.338503	-0.399336
33	1	0	-5.009728	-0.108310	-1.078204
34	1	0	-4.233233	3.218673	0.557826

35	1	0	-3.134320	2.029900	1.288135
36	1	0	-2.518774	3.202354	0.102280

E

Thermal correction to Energy= 0.139080
Thermal correction to Enthalpy= 0.140024
Thermal correction to Gibbs Free Energy= 0.103914
Sum of electronic and zero-point Energies= -270.848318
Sum of electronic and thermal Energies= -270.842592
Sum of electronic and thermal Enthalpies= -270.841648
Sum of electronic and thermal Free Energies= -270.877758

Esol= -271.0791389
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.169814	-0.745885	0.211713
2	6	0	1.270793	0.737057	-0.163187
3	6	0	-1.271149	0.736562	-0.163187
4	6	0	-1.169442	-0.746393	0.211722
5	1	0	2.136878	1.192043	0.327936
6	1	0	1.167307	-0.848669	1.309220
7	1	0	2.012673	-1.315323	-0.188226
8	1	0	-2.137474	1.191342	0.327704
9	1	0	-1.447588	0.794738	-1.250260
10	1	0	-1.166943	-0.848965	1.309258
11	1	0	-2.012185	-1.316137	-0.188058
12	1	0	1.447409	0.795650	-1.250215
13	8	0	0.000286	-1.328367	-0.325791
14	6	0	-0.000325	1.434548	0.195485
15	1	0	-0.000508	2.486928	0.453691

CO_2

Thermal correction to Energy= 0.014581
Thermal correction to Enthalpy= 0.015525
Thermal correction to Gibbs Free Energy= -0.008735
Sum of electronic and zero-point Energies= -188.497064
Sum of electronic and thermal Energies= -188.494445
Sum of electronic and thermal Enthalpies= -188.493501
Sum of electronic and thermal Free Energies= -188.517761

Esol= -188.5924888

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	1.162797
2	6	0	0.000000	0.000000	0.000000
3	8	0	0.000000	0.000000	-1.162797

2

Thermal correction to Energy=	0.227700
Thermal correction to Enthalpy=	0.228644
Thermal correction to Gibbs Free Energy=	0.179092
Sum of electronic and zero-point Energies=	-540.260026
Sum of electronic and thermal Energies=	-540.249066
Sum of electronic and thermal Enthalpies=	-540.248122
Sum of electronic and thermal Free Energies=	-540.297674

Esol= -540.6553873

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000018	2.502191	0.000042
2	1	0	0.924136	3.064963	0.080658
3	1	0	-0.924082	3.064994	-0.080559
4	6	0	-0.000003	1.162805	0.000036
5	6	0	-1.276180	0.396979	-0.040610
6	6	0	-1.380472	-0.770973	-0.806121
7	6	0	-2.400964	0.836993	0.665549
8	6	0	-2.582881	-1.464806	-0.882095
9	1	0	-0.510816	-1.127143	-1.350623
10	6	0	-3.603340	0.141013	0.592566
11	1	0	-2.320323	1.720556	1.291705
12	6	0	-3.699094	-1.010463	-0.183841
13	1	0	-2.647814	-2.362871	-1.488291
14	1	0	-4.464127	0.492371	1.152879
15	1	0	-4.635844	-1.555900	-0.237472
16	6	0	1.276170	0.396981	0.040613
17	6	0	1.380535	-0.770879	0.806268

18	6	0	2.400877	0.836933	-0.665689
19	6	0	2.582951	-1.464690	0.882213
20	1	0	0.510921	-1.126977	1.350883
21	6	0	3.603269	0.140960	-0.592739
22	1	0	2.320183	1.720453	-1.291899
23	6	0	3.699100	-1.010414	0.183795
24	1	0	2.647968	-2.362675	1.488519
25	1	0	4.464004	0.492269	-1.153162
26	1	0	4.635862	-1.555831	0.237429

$TS_{E\text{-}F}$

Thermal correction to Energy=	0.369253
Thermal correction to Enthalpy=	0.370197
Thermal correction to Gibbs Free Energy=	0.303587
Sum of electronic and zero-point Energies=	-811.107850
Sum of electronic and thermal Energies=	-811.090526
Sum of electronic and thermal Enthalpies=	-811.089581
Sum of electronic and thermal Free Energies=	-811.156191

Esol= -811.7326581

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.205745	-1.228575	0.211444
2	6	0	3.055376	-0.785190	1.134004
3	6	0	1.507859	-1.262718	-0.769576
4	6	0	2.751477	-1.673013	-1.577112
5	1	0	3.301038	-1.004734	2.178111
6	1	0	4.400045	-2.304616	0.355208
7	1	0	5.124964	-0.678585	0.431074
8	1	0	0.630459	-1.826359	-1.102983
9	1	0	1.316625	-0.199286	-0.962259
10	1	0	2.918565	-2.758636	-1.479074
11	1	0	2.630580	-1.436419	-2.637659
12	1	0	2.947284	0.302751	1.026384
13	8	0	3.895332	-0.968301	-1.139852
14	6	0	0.075806	-0.343544	1.868370
15	1	0	-0.186561	-1.254285	2.395997
16	1	0	0.869132	0.256371	2.300523
17	6	0	-0.766229	0.190980	0.940112
18	6	0	-0.497521	1.540474	0.386548

19	6	0	-0.689664	1.815730	-0.976374
20	6	0	-0.003071	2.566990	1.203306
21	6	0	-0.380057	3.064044	-1.503666
22	1	0	-1.071063	1.031899	-1.624792
23	6	0	0.306073	3.815701	0.676016
24	1	0	0.117015	2.384958	2.267094
25	6	0	0.121375	4.069651	-0.680548
26	1	0	-0.526551	3.250796	-2.562912
27	1	0	0.682759	4.596502	1.329380
28	1	0	0.360557	5.044882	-1.092143
29	6	0	-1.904603	-0.598130	0.419575
30	6	0	-3.086265	0.027065	-0.007436
31	6	0	-1.847344	-1.999536	0.373207
32	6	0	-4.169560	-0.721080	-0.452706
33	1	0	-3.154099	1.110214	0.026294
34	6	0	-2.930534	-2.747259	-0.073648
35	1	0	-0.932926	-2.502100	0.676272
36	6	0	-4.098008	-2.111799	-0.488611
37	1	0	-5.076442	-0.215239	-0.769263
38	1	0	-2.859448	-3.830085	-0.105887
39	1	0	-4.943363	-2.694694	-0.839656
40	6	0	1.796689	-1.464863	0.685888
41	1	0	1.603508	-2.456494	1.096355

F

Thermal correction to Energy=	0.373134
Thermal correction to Enthalpy=	0.374078
Thermal correction to Gibbs Free Energy=	0.309917
Sum of electronic and zero-point Energies=	-811.165149
Sum of electronic and thermal Energies=	-811.148408
Sum of electronic and thermal Enthalpies=	-811.147464
Sum of electronic and thermal Free Energies=	-811.211624

Esol= -811.7916607

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.043898	-1.753709	-0.044255
2	6	0	2.895596	-1.531145	0.935207
3	6	0	2.217565	0.401812	-0.490179
4	6	0	3.409426	0.055437	-1.376968

5	1	0	2.585479	-2.487697	1.373544
6	1	0	3.730439	-2.467099	-0.826577
7	1	0	4.921333	-2.167783	0.459413
8	1	0	1.422280	0.850562	-1.094483
9	1	0	2.528017	1.152622	0.249040
10	1	0	3.086241	-0.627074	-2.182444
11	1	0	3.830213	0.951235	-1.840341
12	1	0	3.249278	-0.891029	1.754124
13	8	0	4.456527	-0.541826	-0.638848
14	6	0	0.592116	-0.537493	1.253428
15	1	0	0.377326	-1.442948	1.832401
16	1	0	0.995584	0.192243	1.964735
17	6	0	-0.671989	-0.017087	0.626528
18	6	0	-0.789645	1.414257	0.351471
19	6	0	-1.398564	1.881260	-0.832816
20	6	0	-0.241738	2.379878	1.218941
21	6	0	-1.460398	3.236434	-1.125938
22	1	0	-1.795141	1.159025	-1.539378
23	6	0	-0.313838	3.735550	0.927222
24	1	0	0.221562	2.066212	2.148574
25	6	0	-0.921484	4.174245	-0.246848
26	1	0	-1.922154	3.562672	-2.052772
27	1	0	0.105301	4.455013	1.623711
28	1	0	-0.970334	5.233486	-0.476621
29	6	0	-1.706592	-0.954369	0.242483
30	6	0	-3.046408	-0.546086	0.039579
31	6	0	-1.433155	-2.336537	0.114625
32	6	0	-4.036197	-1.457250	-0.293423
33	1	0	-3.307725	0.497041	0.181727
34	6	0	-2.427112	-3.241903	-0.225633
35	1	0	-0.423172	-2.702898	0.266253
36	6	0	-3.735539	-2.811760	-0.436985
37	1	0	-5.055637	-1.109715	-0.429584
38	1	0	-2.178622	-4.293775	-0.327627
39	1	0	-4.512206	-3.522301	-0.699649
40	6	0	1.714065	-0.848241	0.238783
41	1	0	1.317449	-1.539632	-0.520779

G

Thermal correction to Energy=	0.217604
Thermal correction to Enthalpy=	0.218548
Thermal correction to Gibbs Free Energy=	0.173520
Sum of electronic and zero-point Energies=	-351.001629

Sum of electronic and thermal Energies= -350.991867
Sum of electronic and thermal Enthalpies= -350.990923
Sum of electronic and thermal Free Energies= -351.035951

Esol= -351.3242603
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.246721	0.713810	-1.739730
2	6	0	2.000408	-0.481997	-2.017004
3	6	0	1.325091	0.860148	-1.914376
4	6	0	1.885191	1.766146	-0.849880
5	6	0	2.898062	1.389495	-0.069619
6	6	0	3.604616	0.065201	-0.159091
7	6	0	3.010870	-0.822773	-1.217317
8	1	0	1.377130	1.369526	-2.890317
9	1	0	3.271505	2.082607	0.684370
10	1	0	3.506271	-0.443606	0.813245
11	1	0	3.468673	-1.805356	-1.332974
12	6	0	1.227284	3.111723	-0.729227
13	1	0	0.158432	3.004658	-0.509894
14	1	0	1.682195	3.712120	0.061694
15	1	0	1.302105	3.668010	-1.670966
16	6	0	1.458368	-1.402166	-3.074139
17	1	0	1.992202	-2.354922	-3.090247
18	1	0	0.394357	-1.605797	-2.905668
19	1	0	1.539206	-0.945044	-4.067355
20	6	0	5.108893	0.270020	-0.406449
21	1	0	5.555058	0.885256	0.380833
22	1	0	5.635909	-0.688684	-0.429174
23	1	0	5.264732	0.771305	-1.365648

TS_{F-3}
Thermal correction to Energy= 0.587786
Thermal correction to Enthalpy= 0.588730
Thermal correction to Gibbs Free Energy= 0.501287
Sum of electronic and zero-point Energies= -1162.153976
Sum of electronic and thermal Energies= -1162.126392
Sum of electronic and thermal Enthalpies= -1162.125447
Sum of electronic and thermal Free Energies= -1162.212891

Esol= -1163.0943423

Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.295188	0.503903	-0.943996
2	6	0	2.093915	-0.055834	-2.125025
3	6	0	1.251158	1.075846	-1.700390
4	6	0	1.853756	2.032083	-0.756768
5	6	0	2.933840	1.675560	-0.044039
6	6	0	3.614343	0.340452	-0.164258
7	6	0	3.154531	-0.412262	-1.382442
8	1	0	0.650280	1.528787	-2.495261
9	1	0	3.342297	2.366880	0.692733
10	1	0	3.348479	-0.251011	0.731222
11	1	0	3.754207	-1.271229	-1.682033
12	6	0	1.147425	3.345113	-0.562607
13	1	0	0.112948	3.179012	-0.236145
14	1	0	1.650813	3.962281	0.185298
15	1	0	1.097659	3.909270	-1.500496
16	6	0	1.717230	-0.769980	-3.395632
17	1	0	2.311791	-1.675714	-3.535997
18	1	0	0.658329	-1.048303	-3.400669
19	1	0	1.879635	-0.117727	-4.261250
20	6	0	5.143291	0.496535	-0.165358
21	1	0	5.481471	1.013319	0.737645
22	1	0	5.635744	-0.479665	-0.201895
23	1	0	5.465803	1.077119	-1.034480
24	6	0	-2.902148	-4.676209	-0.700282
25	6	0	-1.845881	-3.692627	-1.193165
26	6	0	-3.432218	-1.869558	-0.600137
27	6	0	-4.389538	-2.964914	-0.142158
28	1	0	-0.844356	-4.114468	-1.040203
29	1	0	-2.724698	-4.902539	0.365862
30	1	0	-2.862809	-5.616131	-1.257169
31	1	0	-3.608988	-0.961095	-0.016562
32	1	0	-3.644696	-1.633071	-1.651441
33	1	0	-4.243778	-3.158201	0.935075
34	1	0	-5.430136	-2.667450	-0.294789
35	1	0	-1.977008	-3.542055	-2.273164
36	8	0	-4.206632	-4.163338	-0.869590
37	6	0	-0.959719	-1.331495	-1.042823
38	1	0	-0.038465	-1.857704	-1.324265

39	1	0	-1.367673	-0.919745	-1.975784
40	6	0	-0.591153	-0.183944	-0.111559
41	6	0	-1.687483	0.812567	0.102258
42	6	0	-2.286579	1.024230	1.352211
43	6	0	-2.199372	1.518525	-0.997135
44	6	0	-3.356327	1.903336	1.493183
45	1	0	-1.922665	0.476588	2.216147
46	6	0	-3.264230	2.400161	-0.856741
47	1	0	-1.749813	1.371664	-1.976200
48	6	0	-3.849995	2.596859	0.391734
49	1	0	-3.810643	2.040354	2.469743
50	1	0	-3.637955	2.935133	-1.724285
51	1	0	-4.683416	3.282535	0.504712
52	6	0	0.297660	-0.508499	1.030003
53	6	0	0.687661	0.495625	1.938829
54	6	0	0.860398	-1.785897	1.204336
55	6	0	1.566511	0.229564	2.979781
56	1	0	0.299714	1.502017	1.810551
57	6	0	1.741531	-2.052187	2.247102
58	1	0	0.598846	-2.590594	0.525273
59	6	0	2.097131	-1.049210	3.145018
60	1	0	1.846739	1.026921	3.661268
61	1	0	2.149434	-3.052045	2.358993
62	1	0	2.782528	-1.258753	3.959900
63	6	0	-1.976885	-2.342974	-0.478340
64	1	0	-1.761442	-2.501726	0.590185

G’

Thermal correction to Energy= 0.203779
Thermal correction to Enthalpy= 0.204723
Thermal correction to Gibbs Free Energy= 0.158577
Sum of electronic and zero-point Energies= -350.382069
Sum of electronic and thermal Energies= -350.372202
Sum of electronic and thermal Enthalpies= -350.371258
Sum of electronic and thermal Free Energies= -350.417404

Esol= -350.6914805
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.028304	-0.414238	-2.088569

2	6	0	1.464583	0.885266	-1.955171
3	6	0	1.913304	1.782973	-0.946686
4	6	0	2.901901	1.398754	-0.093475
5	6	0	3.583159	0.065740	-0.165053
6	6	0	3.017322	-0.810756	-1.241021
7	1	0	0.674152	1.196719	-2.633507
8	1	0	3.248343	2.087239	0.675204
9	1	0	3.451786	-0.445085	0.806713
10	1	0	3.450925	-1.803627	-1.346341
11	6	0	1.274033	3.145140	-0.852146
12	1	0	0.197726	3.058386	-0.672927
13	1	0	1.708861	3.733687	-0.041550
14	1	0	1.403677	3.700933	-1.786148
15	6	0	1.508989	-1.321848	-3.174728
16	1	0	2.013985	-2.290055	-3.159919
17	1	0	0.434622	-1.494756	-3.056750
18	1	0	1.658921	-0.873120	-4.161773
19	6	0	5.108014	0.240542	-0.347781
20	1	0	5.528140	0.844970	0.461623
21	1	0	5.611561	-0.730753	-0.349542
22	1	0	5.313894	0.740342	-1.297714

Supplementary References

[1]. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

[2]. a) Zhao, Y., Schultz, N. E., & Truhlar, D. G. Design of density functionals by combining the method of constraint satisfaction with parametrization for thermochemistry, thermochemical kinetics, and noncovalent interactions. *J. Chem. Theory. Comput.* **2**, 364-382 (2006). b) Zhao, Y., & Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **125**, 194101 (2006). c) Zhao, Y., & Truhlar, D. G. Density functional for spectroscopy: no long-range self-interaction error, good performance for Rydberg and charge-transfer states, and better performance on average than B3LYP for ground states. *J. Phys. Chem. A.* **110**, 13126-13130 (2006).

[3]. Gonzalez, C., & Schlegel, H. B. An improved algorithm for reaction path following. *J. Chem. Phys.* **90**, 2154-2161 (1989).

[4]. Tomasi, J., & Persico, M. Molecular interactions in solution: an overview of methods based on continuous distributions of the solvent. *Chem. Rev.* **94**, 2027-2094 (1994).

[5]. CYLview, 1.0b . C. Y. Legault, Universit éde Sherbrooke, **2009**. (http://www.cylview.org)

[6]. Wang, G., Zhang, H., Zhao, J., Li, W., Cao, J., Zhu, C. & Li, S. Homolytic cleavage of a B−B bond by the cooperative catalysis of two Lewis bases: Computational design and experimental verification. *Angew. Chem. Int. Ed.* **55**, 5985-5989 (2016).

[7]. Pratsch, G., & Overman, L. E. Synthesis of 2, 5-Diaryl-1, 5-dienes from Allylic Bromides Using Visible-Light Photoredox Catalysis. *J. Org. Chem.* **80**, 11388-11397 (2015).

[8]. Nakao, Y., Imanaka, H., Sahoo, A. K., Yada, A., & Hiyama, T. Alkenyl-and aryl [2-(hydroxymethyl) phenyl] dimethylsilanes: an entry to tetraorganosilicon reagents for the silicon-based cross-coupling reaction. *J. Am. Chem. Soc.* **127**, 6952-6953 (2005).

[9]. Huang, C. Y., & Doyle, A. G. Electron-Deficient Olefin Ligands Enable Generation of Quaternary Carbons by Ni-Catalyzed Cross-Coupling. *J. Am. Chem. Soc.* **137**, 5638-5641 (2015).

[10]. Ichitsuka T, Fujita T, Arita T, et al. Double C F Bond Activation through β−Fluorine Elimination: Nickel−Mediated [3+2] Cycloaddition of 2−Trifluoromethyl−1−alkenes with Alkynes[J]. *Angew. Chem.*, 2014, 126(29): 7694-7698.

[11]. Friedfeld, M. R., Margulieux, G. W., Schaefer, B. A., & Chirik, P. J. Bis (phosphine) cobalt Dialkyl Complexes for Directed Catalytic Alkene Hydrogenation. *J. Am. Chem. Soc.* **136**, 13178-13181 (2014).

[12]. Chatalova-Sazepin, C., Wang, Q., Sammis, G. M., & Zhu, J. Copper‐Catalyzed Intermolecular Carboetherification of Unactivated Alkenes by Alkyl Nitriles and Alcohols. *Angew. Chem. Int. Ed.* **54**, 5443-5446 (2015).

[13]. Beck, R., Camadanli, S., Flörke, U., & Klein, H. F. Reactivity Diversification–Synthesis and Exchange Reactions of Cobalt and Iron 2-Alkenylpyridine/-pyrazine Complexes Obtained by Vinylic C (sp^2)–H Activation. *Eur. J. Org. Chem*. **2015**, 2543-2559 (2015).

[14]. V. J. Cee, J. Lin, Z. Zhang, US 2012/0129828 A1, **2012**.

[15]. Tang, J., Hackenberger, D., & Goossen, L. J. Branched Arylalkenes from Cinnamates: Selectivity Inversion in Heck Reactions by Carboxylates as Deciduous Directing Groups. *Angew. Chem. Int. Ed.* **55**, 11296-11299 (2016).

[16]. Wang, T., Hu, Y., & Zhang, S. A novel and efficient method for the olefination of carbonyl compounds with Grignard reagents in the presence of diethyl phosphite. *Org. Biomol. Chem*. **8**, 2312-2315 (2010).

[17]. Brousmiche, D. W., Xu, M., Lukeman, M., & Wan, P. Photohydration and photosolvolysis of biphenyl alkenes and alcohols via biphenyl quinone methide-type intermediates and diarylmethyl carbocations. *J. Am. Chem. Soc.* **125**, 12961-12970 (2003).

[18]. Fawcett, A., Pradeilles, J., Wang, Y., Mutsuga, T., Myers, E. L., & Aggarwal, V. K. Photoinduced decarboxylative borylation of carboxylic acids. Science, **357**, 283-286 (2017).

[19]. Xue, W., & Oestreich, M. Copper‐Catalyzed Decarboxylative Radical Silylation of Redox−Active Aliphatic Carboxylic Acid Derivatives. *Angew. Chem. Int. Ed.* **56**, 11649 -11652 (2017).

[20]. Qin, T., Cornella, J., Li, C., Malins, L. R., Edwards, J. T., Kawamura, S., ... & Baran, P. S. A general alkyl-alkyl cross-coupling enabled by redox-active esters and alkylzinc reagents. *Science*, **352**, 801-805 (2016).

[21]. Cheng, W. M., Shang, R., Fu, M. C., & Fu, Y. Photoredox-Catalysed Decarboxylative Alkylation of N-Heteroarenes with N-(Acyloxy) phthalimides. *Chem. Eur. J.* **23**, 2537-2541 (2017).

[22]. Cheng, W. M., Shang, R., Zhao, B., Xing, W. L., & Fu, Y. Isonicotinate Ester Catalyzed Decarboxylative Borylation of (Hetero) Aryl and Alkenyl Carboxylic Acids through N-Hydroxyphthalimide Esters. *Org. lett.* **19**, 4291-4294 (2017).

[23]. Pratsch, G., Lackner, G. L., & Overman, L. E. Constructing quaternary carbons from N-(acyloxy) phthalimide precursors of tertiary radicals using visible-light photocatalysis. *J. Org. Chem.* **80**, 6025-6036 (2015).

[24]. Nájera, C. & Yus, M. Desulfonylation reactions: Recent developments. *Tetrahedron* **55**, 10547-10658 (1999).

[25]. Keck, G. E., Wager, T. T. & McHardy, S. F. Reductive cleavage of N O bonds in hydroxylamines and hydroxamic acid derivatives using samarium diiodide. *Tetrahedron* **55**, 11755-11772 (1999).

[26]. Zhang, L. & Jiao, L. Super electron donors derived from diboron. *Chem. Sci.* **9**, 2711-2722 (2018).