Supplementary Information

Co-catalyzed Cross-Coupling of Umpolung Carbonyls with Alkyl Halides under Mild Conditions

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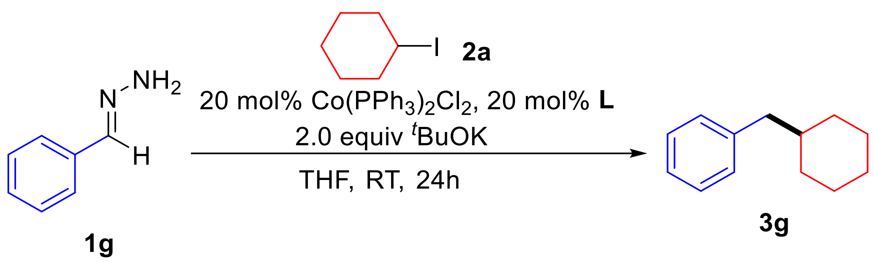
General Procedures.

All reactions were carried out in flame-dried glassware under an atmosphere of dry N_2 with the rigid exclusion of air and moisture using standard Schlenk techniques or in a glovebox. All solvents were purified and dried by standard techniques prior to use. Compounds **1**, **1'** and **2g**[1] were prepared according to literature procedures. All other chemicals were purchased from commercial sources and used as received unless otherwise specified. ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR spectra were recorded on a Varian Inova 400 spectrometer at 400 MHz, 101 MHz and 377 MHz, respectively or on either a Varian Inova or a Bruker 500 spectrometer at 500 MHz, 126 MHz and 477 MHz, respectively. All signals were reported in ppm unit with references to the residual solvent resonances of the deuterated solvents for proton and carbon chemical shifts, and to external $CFCl_3$ (0.00) for fluorine chemical shifts. EI-MS was obtained from the Agilent GC-MS system.

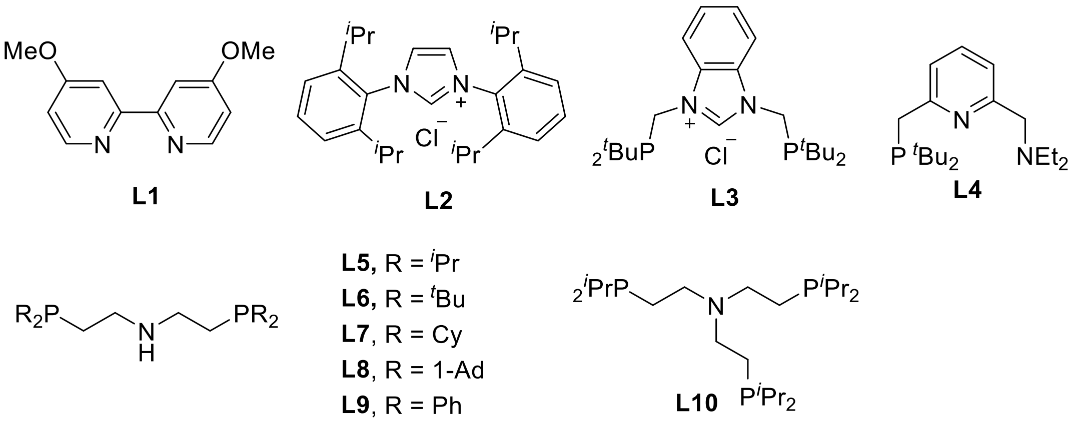
Optimization of reaction conditions

Table S1 Ligands screening for Co-catalyzed cross-coupling of aldehyde hydrazone with alkyl halide[a]



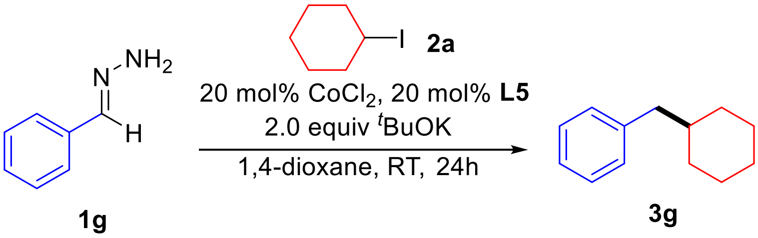
Entry	L	**3g** (%)[b]
1	-	n.p.
2	L1	8
3	1,10-phen	14
4	PMe_3	trace
5	PCy_3	7
6	$P^{n}Bu_3$	14
7	dppe	11
8	dppb	7

9	dppf	15
10	L2	9
11	L3	21
12	L4	12
13	L5	36
14	L6	21
15	L7	35
16	L8	28
17	L9	30



[a]General reaction conditions: **1g** (0.4 mmol, 2 equiv), **2a** (0.2 mmol), 20 mol% $Co(PPh_3)_2Cl_2$, ligand (40 mol% for monodentate ligand, 20 mol% for bidentate and multidentate ligand), and ^{t}BuOK (2.0 equiv) in 1.0 mL 1,4-dioxane for 24 h. [b]Yields were determined by crude ^{1}H NMR using CH_2Br_2 as an internal standard.

Table S2 Evaluation of the reaction temperature, concentration as well as the amounts of ligand and hydrazone[a]

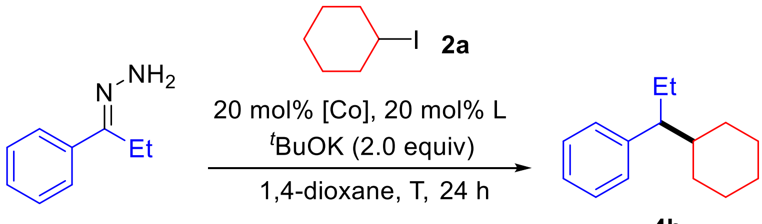


Entry	Variants	**3g** (%)[b]
1	none	66
2	2.0 mL 1,4-dioxane	55

3	5 equiv **1g**	28
4	30 mol% **L5**	64
5	80 °C	25
6	45 °C	41
7	0 °C, THF as solvent	23

[a]General reaction conditions: **1g** (0.4 mmol, 2 equiv), **2a** (0.2 mmol), 20 mol% $CoCl_2$, 20 mol% **L5**, and ^{t}BuOK (2.0 equiv) in 1.0 mL 1,4-dioxane for 24 h, $CoCl_2$ and **L5** being dissolved in 0.5 mL of 1,4-dioxane and stirred at r.t. for 1 h in advance. [b]Yields were determined by crude ^{1}H NMR using CH_2Br_2 as an internal standard.

Table S3. Optimization of Co-catalyzed cross-coupling of ketone hydrazone with alkyl halide[a]

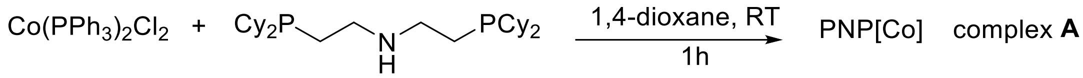


Entry	Pre-atalyst	L	T/ °C	Yield of **4** (%)[b]
1	$CoCl_2$	L5	RT	60
2	$Co(PPh_3)_3Cl$	L5	RT	66
3	$Co(acac)_3$	L5	RT	50
4	$Co(PPh_3)_3Cl$	L5	RT	52
5	$Co(PPh_3)_2Cl_2$	L6	RT	trace
6	$Co(PPh_3)_2Cl_2$	L7	RT	75
7	$Co(PPh_3)_2Cl_2$	L8	RT	50
8	$Co(PPh_3)_2Cl_2$	L9	RT	trace
9	$Co(PPh_3)_2Cl_2$	L7	80	35
10[c]	$Co(PPh_3)_3Cl$	L7	RT	68
11[d]	-	-	RT	70

[a]General reaction conditions: **1b’** (0.4 mmol, 2 equiv), **2a** (0.2 mmol), 20 mol% [Co]

pre-catalyst, 20 mol% **L**, and ^{t}BuOK (2.0 equiv) in 1.0 mL 1,4-dioxane for 24 h, [Co] pre-catalyst and **L** being dissolved in 0.5 mL of 1,4-dioxane and stirred at r.t. for 1 h in advance. [b]Yields were determined by crude ^{1}H NMR using CH_2Br_2 as an internal standard. [c]30 mol% **L**.[d]20 mol% Complex **A** was used as catalyst.

Preparation of Complex A.

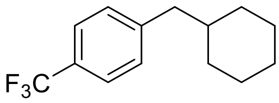


A flame-dried 25 mL flask equipped with a stir bar was charged with $Co(PPh_3)_2Cl_2$ (52 mg, 0. 08 mmol) and **L7** (38 mg, 0.08 mmol), followed by dry 1,4-dioxane (1.0 mL). The mixture was stirred at room temperature for 1h under an atmosphere of nitrogen. After the completion of the reaction, the solution was filtered and washed with 1,4-dioxane (1 mL x 3), the resultant residue was collected and dried to give complex **A** (50 mg) as a pink solid.

(Note: the exact structure of complex **A** is unclear, we failed to recrystallize the complex **A** from different solvents)

Synthesis of 3.

A flame-dried V-shape reaction vial (10 cm^3) equipped with a stir bar was charged with $CoCl_2$ (5.2 mg, 0. 04 mmol) and **L5** (120 mg, 10%wt in THF, 0.04 mmol), followed by dry 1,4-dioxane (0.5 mL). The mixture was stirred at room temperature for 1 h, to which were successively added **2** (0.20 mmol), **1** (0.4 mmol), potassium tert-butoxide (44.8 mg, 0.4 mmol) and dry 1,4-dioxane (0.5 mL). The vial was sealed with a rubber septum under an atmosphere of nitrogen, and then stirred at room temperature for 24 h. After the completion of the reaction, the solution was filtered in a short celite pad and washed with ethyl acetate (10 mL × 3). The solvent was removed under vacuum and the residue was purified by flash column chromatography to give the desired product **3**.



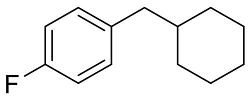
1-(cyclohexylmethyl)-4-(trifluoromethyl)benzene (CAS: 2281948-47-6).[2]

3a: colorless oil. Yield: 40%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H) (aromatic C*H*), 2.54 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.74 – 1.62 (m, 5H), 1.57 – 1.49 (m, 1H), 1.26 – 1.10 (m, 3H), 1.02 – 0.88 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 145.5 (q, $^4J_{CF}$ = 1.4 Hz), 129.4, 128.0 (q, $^2J_{CF}$ = 32.5 Hz), 125.0 (q, $^3J_{CF}$ = 4.3 Hz) (aromatic *C*), 124.4 (q, $^1J_{CF}$= 271.9 Hz) (*C*F_3), 43.9 (Ar*C*H_2), 39.6, 33.1, 26.5, 26.2 (cyclohexyl *C*).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -62.2.



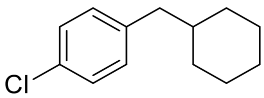
1-(cyclohexylmethyl)-4-fluorobenzene (CAS: 2227354-29-0).[2]

3b: colorless oil. Yield: 44%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.12 – 7.02 (m, 2H), 7.00 – 6.90 (m, 2H) (aromatic C*H*), 2.45 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.74 – 1.60 (m, 5H), 1.51 – 1.43 (m, 1H), 1.27 – 1.09 (m, 3H), 0.96 – 0.87 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 161.3 (d, *J* = 242.7 Hz), 137.0 (d, *J* = 3.2 Hz), 130.5 (d, *J* = 7.5 Hz), 114.9 (d, *J* = 20.9 Hz) (aromatic *C*), 43.4 (Ar*C*H_2), 40.0, 33.2, 26.7, 26.4 (cyclohexyl *C*).

^{19}F NMR (471 MHz, $CDCl_3$) δ -118.3.



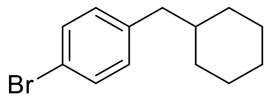
1-chloro-4-(cyclohexylmethyl)benzene (CAS: 98446-77-6).[2]

3c: colorless oil. Yield: 56%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.25 – 7.20 (m, 2H), 7.08 – 7.03 (m, 2H) (aromatic

C*H*), 2.45 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.75 – 1.59 (m, 5H), 1.54 – 1.40 (m, 1H), 1.27 – 1.10 (m, 3H), 0.99 – 0.86 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 139.9, 131.4, 130.6, 128.3 (aromatic *C*), 43.5 (ArCH_2), 39.9, 33.2, 26.7, 26.4 (cyclohexyl *C*).

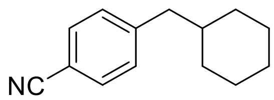


1-bromo-4-(cyclohexylmethyl)benzene (CAS: 1785619-14-8).[2]

3d: colorless oil. Yield: 51%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41 – 7.34 (m, 2H), 7.04 – 6.98 (m, 2H) (aromatic C*H*), 2.43 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.78 – 1.59 (m, 5H), 1.52 – 1.43 (m, 1H), 1.27 – 1.09 (m, 3H), 0.99 – 0.86 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 140.3, 131.1, 131.0, 119.3 (aromatic *C*), 43.5 (ArCH_2), 39.7, 33.1, 26.5, 26.3 (cyclohexyl *C*).

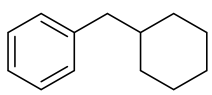


4-(cyclohexylmethyl)benzonitrile (CAS: 98446-82-3).[3]

3f: colorless oil. Yield: 58%. TLC: R_f = 0.7 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.55 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.2 Hz, 2H) (aromatic C*H*), 2.53 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.74 – 1.57 (m, 5H), 1.57 – 1.47 (m, 1H), 1.25 – 1.09 (m, 3H), 1.00 – 0.89 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 147.3, 132.0, 130.0, 119.3, 109.6 (*C*N & aromatic *C*), 44.3 (ArCH_2), 39.7, 33.1, 26.5, 26.3 (cyclohexyl *C*).

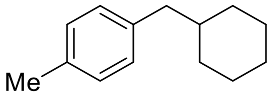


(cyclohexylmethyl)benzene (CAS: 3178-23-2).[2]

3g: colorless oil. Yield: 56%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 – 7.25 (m, 2H), 7.20 – 7.12 (m, 3H) (aromatic C*H*), 2.48 (d, *J* = 7.0 Hz, 2H) (PhCH_2), 1.72 – 1.61 (m, 5H), 1.53 – 1.46 (m, 1H), 1.23 – 1.12 (m, 3H), 1.00 – 0.89 (m, 2H) (cyclohexyl C*H*).

These data are identical to those reported in the literature.

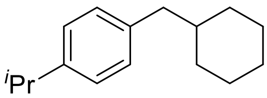


1-(cyclohexylmethyl)-4-methylbenzene (CAS: 92298-94-7).[2]

3h: colorless oil. Yield: 50%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 7.7 Hz, 2H), 7.03 (d, *J* = 8.2 Hz, 2H) (aromatic C*H*), 2.45 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 2.32 (s, 3H) (CH_3), 1.73 – 1.61 (m, 5H), 1.52 – 1.42 (m, 1H), 1.25 – 1.12 (m, 3H), 1.00 – 0.87 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 138.4, 135.1, 129.2, 128.9 (aromatic *C*), 43.8 (Ar*C*H_2), 40.0, 33.3, 26.7, 26.5, 21.2 (cyclohexyl *C* & *C*H_3).

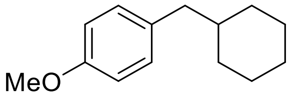


3i: colorless oil. Yield: 38%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (d, *J* = 8.1 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H) (aromatic C*H*), 2.94 – 2.83 (m, 1H) (C*H*($CH_3)_2$), 2.45 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.24 (d, *J* = 6.9 Hz, 6H) (CH(C$H_3)_2$), 1.73 – 1.66 (m, 4H), 1.66 – 1.60 (m, 1H), 1.53 – 1.45 (m, 1H), , 1.22 – 1.10 (m, 3H), 1.00 – 0.89 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 146.1, 138.8, 129.2, 126.2 (aromatic *C*), 43.9 (Ar*C*H_2), 39.9, 33.8, 33.4, 26.8, 26.5, 24.2. (cyclohexyl *C* & *iso*-propyl *C*).

HRMS (APCI) m/z: calcd for $C_{16}H_{23}^+$ $[M-H]^+$: 215.1794, found: 215.1803.

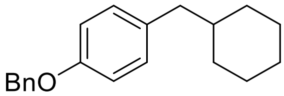


1-(cyclohexylmethyl)-4-methoxybenzene (13724-70-4).[4]

3j: colorless oil. Yield: 53%. TLC: R_f = 0.60 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.09 – 7.02 (m, 2H), 6.86 – 6.79 (m, 2H) (aromatic C*H*), 3.79 (s, 3H) (CH_3), 2.42 (d, *J* = 7.2 Hz, 2H) ($ArCH_2$), 1.74 – 1.62 (m, 5H), 1.52 – 1.41 (m, 1H), 1.26 – 1.13 (m, 3H), 0.99 – 0.85 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 157.7, 133.6, 130.2, 113.6 (aromatic *C*), 55.4 ($ArCH_2$), 43.3, 40.1, 33.2, 26.7, 26.5 (cyclohexyl *C* & OCH_3).

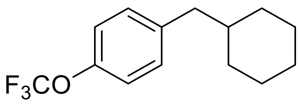


1-(benzyloxy)-4-(cyclohexylmethyl)benzene (CAS: 2281948-49-8).[2]

3k: white solid. Yield: 50%. TLC: R_f = 0.55 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49 – 7.43 (m, 2H), 7.40 (t, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.13 – 7.03 (m, 2H), 6.95 – 6.87 (m, 2H) (aromatic C*H*), 5.06 (s, 2H) (OCH_2), 2.45 (d, *J* = 7.2 Hz, 2H) ($ArCH_2Cy$), 1.77 – 1.59 (m, 5H), 1.53 – 1.39 (m, 1H), 1.32 – 1.09 (m, 3H), 1.04 – 0.86 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 157.0, 137.4, 133.9, 130.2, 128.7, 128.0, 127.6, 114.5 (aromatic *C*), 70.2 (OCH_2), 43.4 ($ArCH_2Cy$), 40.1, 33.3, 26.7, 26.5 (cyclohexyl *C*).

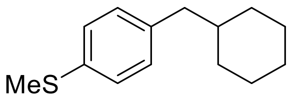


3l: colorless oil. Yield: 57%. TLC: R_f = 0.60 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.21 – 7.00 (m, 4H) (aromatic C*H*), 2.48 (d, *J* = 7.2 Hz, 2H) ($ArCH_2$), 1.73 – 1.62 (m, 5H), 1.54 – 1.46 (m, 1H), 1.26 – 1.10 (m, 3H), 1.00 – 0.88 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 147.4, 140.2, 130.4, 120.8 (aromatic *C*), 120.7 (q, *J* = 256.3 Hz) (CF_3), 43.5 ($ArCH_2$), 39.9, 33.2, 26.6, 26.4 (cyclohexyl *C*). ^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -57.9.

HRMS (APCI) m/z: calcd for $C_{14}H_{16}F_3O^+$ [M-H]$^+$: 257.1148, found: 257.1153.



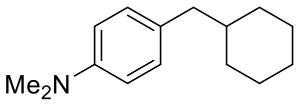
(4-(cyclohexylmethyl)phenyl)(methyl)sulfane (CAS: 716341-30-9).[5]

3m: colorless oil. Yield: 55%. TLC: R_f = 0.70 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.18 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.18 (dt, *J* = 8.4, 2.2 Hz, 2H) (aromatic C*H*), 2.47 (s, 3H) (CH_3), 2.44 (d, *J* = 7.2 Hz, 2H) ($ArCH_2$), 1.71 – 1.60 (m, 5H), 1.53 – 1.45 (m, 1H), 1.23 – 1.10 (m, 3H), 0.98 – 0.86 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 138.7, 135.0, 130.0, 127.1 (aromatic *C*), 43.7 ($ArCH_2$), 39.9, 33.2, 26.7, 26.4, 16.5 (cyclohexyl *C* & SCH_3).

HRMS (APCI) m/z: calcd for $C_{14}H_{21}S^+$ [M+H$^+$]: 221.1358, found: 221.1349.

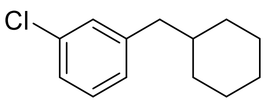


4-(cyclohexylmethyl)-*N*,*N*-dimethylaniline (CAS: 2243586-50-5).[2]

3n: colorless oil. Yield: 59%. TLC: R_f = 0.60 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.03 (dt, J = 8.7, 2.9 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H) (aromatic C*H*), 2.92 (s, 6H) (CH_3), 2.39 (d, *J* = 7.2 Hz, 2H) ($ArCH_2$), 1.76 – 1.61 (m, 5H), 1.53 – 1.41 (m, 1H), 1.26 – 1.10 (m, 3H), 0.99 – 0.85 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 149.0, 130.0, 113.4, 113.0 (aromatic *C*), 43.2, 41.1, 40.1, 33.3, 26.8, 26.5 (NCH_3, $ArCH_2$ & cyclohexyl *C*).



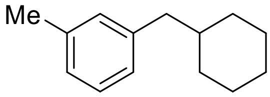
1-chloro-3-(cyclohexylmethyl)benzene (CAS: 220866-37-5).[2]

3o: colorless oil. Yield: 45%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 1H NMR (400 MHz, CDCl3) δ 7.24 – 7.07 (m, 3H), 7.01 (dt, *J* = 7.2, 1.7 Hz, 1H) (aromatic C*H*), 2.45 (d, *J* = 7.2 Hz, 2H) ($ArCH_2$), 1.76 –

1.57 (m, 5H), 1.53 – 1.43 (m, 1H), 1.28 – 1.07 (m, 3H), 1.02 – 0.83 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 143.6, 134.0, 129.4, 129.3, 127.5, 125.9 (aromatic *C*), 43.9 (Ar*C*H_2), 39.8, 33.2, 26.6, 26.4 (cyclohexyl *C*).

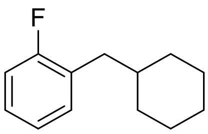


1-(cyclohexylmethyl)-3-methylbenzene (CAS: 93536-67-5).[2]

3p: colorless oil. Yield: 65%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (t, *J* = 7.5 Hz, 1H), 7.04 – 6.89 (m, 3H) (aromatic C*H*), 2.44 (d, *J* = 7.1 Hz, 2H) (ArCH_2), 2.33 (s, 3H) (CH_3), 1.75 – 1.60 (m, 5H), 1.53 – 1.43 (m, 1H), 1.28 – 1.12 (m, 3H), 1.01 – 0.87 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 141.5, 137.7, 130.1, 128.0, 126.4 (aromatic *C*), 44.2 (Ar*C*H_2), 39.9, 33.4, 26.7, 26.5, 21.6 (cyclohexyl *C* & *C*H_3).



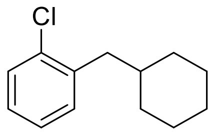
1-(cyclohexylmethyl)-2-fluorobenzene (CAS: 2281948-52-3).[2]

3q: colorless oil. Yield: 39%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 – 7.08 (m, 2H), 7.08 – 6.94 (m, 2H) (aromatic C*H*), 2.52 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.72 – 1.62 (m, 5H), 1.27 – 1.14 (m, 4H), 1.02 – 0.93 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 161.5 (d, *J* = 244.1 Hz), 131.7 (d, *J* = 5.2 Hz), 128.3 (d, *J* = 16.2 Hz), 127.4 (d, *J* = 7.9 Hz), 123.7 (d, *J* = 3.6 Hz), 115.2 (d, *J* = 22.5 Hz) (aromatic *C*), 124.4 (q, $^1J_{CF}$= 271.9 Hz) (*C*F_3), 38.3 (Ar*C*H_2), 38.9, 37.0, 33.2, 26.6, 26.4 (cyclohexyl *C*).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$): δ -114.7.

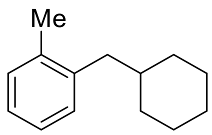


1-chloro-2-(cyclohexylmethyl)benzene (CAS: 2252403-02-2).[2]

3r: colorless oil. Yield: 43%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.34 – 7.32 (m, 1H), 7.18 – 7.14 (m, 2H), 7.14 – 7.09 (m, 1H) (aromatic C*H*), 2.61 (d, *J* = 7.0 Hz, 2H) (ArCH_2), 1.72 – 1.60 (m, 6H), 1.26 – 1.13 (m, 3H), 1.06 – 0.95 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 139.1, 134.4, 131.6, 129.6, 127.2, 126.4 (aromatic *C*), 41.5 (Ar*C*H_2), 38.3, 33.3, 26.7, 26.4 (cyclohexyl *C*).

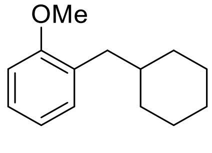


1-(cyclohexylmethyl)-2-methylbenzene (CAS: 92298-93-6).[2]

3s: colorless oil. Yield: 49%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.17 – 6.94 (m, 4H) (aromatic C*H*), 2.48 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 2.30 (s, 3H) (CH_3), 1.77 – 1.61 (m, 5H), 1.49 (m, 1H), 1.22 – 1.13 (m, 3H), 0.99 (m 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 139.8, 136.4, 130.3, 130.2 125.8, 125.6 (aromatic *C*), 41.4 (Ar*C*H_2), 38.9, 33.6, 26.8, 26.6, 19.7 (cyclohexyl *C* & *C*H_3).



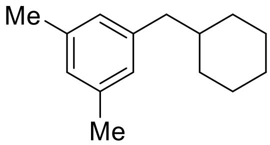
1-(cyclohexylmethyl)-2-methoxybenzene (CAS: 92300-32-8).[6]

3t: colorless oil. Yield:57%. TLC: R_f = 0.75 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.16 (td, *J* = 7.8, 1.8 Hz, 1H), 7.07 (dd, *J* = 7.4, 1.8 Hz, 1H), 6.89 – 6.82 (m, 2H) (aromatic C*H*), 3.81 (s, 3H) (CH_3), 2.49 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.71 – 1.59 (m, 5H), 1.59 – 1.54 (m, 1H), 1.26 – 1.11 (m, 3H), 1.02 –

0.88 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.8, 131.0, 130.0, 126.9, 120.2, 110.4 (aromatic *C*), 55.4 (Ar*C*H_2), 38.3, 38.1, 33.5, 26.8, 26.5 (cyclohexyl *C* & *C*H_3).

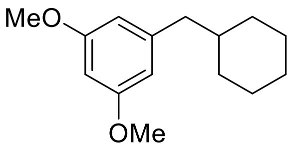


3u: colorless oil. Yield: 60%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.82 (s, 1H), 6.77 (s, 2H) (aromatic C*H*), 2.41 (d, *J* = 7.2 Hz, 2H) (ArC*H*$_2$), 2.30 (s, 6H) (C*H*$_3$), 1.76 – 1.59 (m, 5H), 1.53 – 1.44 (m, 1H), 1.28 – 1.09 (m, 3H), 0.98 – 0.88 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 141.5, 137.5, 127.3, 127.2 (aromatic *C*), 44.2 (Ar*C*H_2), 39.9, 33.4, 26.8, 26.5, 21.4 (cyclohexyl *C*).

HRMS (APCI) m/z: calcd for $C_{15}H_{21}^+$ [M-H]$^+$: 201.1638, found: 201.1646.



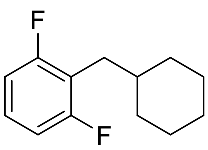
1-(cyclohexylmethyl)-3,5-dimethoxybenzene (CAS: 52692-16-7).[7]

3v: colorless oil. Yield: 65%. TLC: R_f = 0.6 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (m, 3H) (aromatic C*H*), 3.79 (s, 6H) (OC*H*$_3$), 2.43 (d, *J* = 7.2 Hz, 2H) (ArC*H*$_2$), 1.77 – 1.61 (m, 5H), 1.60 – 1.45 (m, 1H), 1.28 – 1.12 (m, 3H), 0.95 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 160.6, 144.0, 107.4, 97.6 (aromatic *C*), 55.3 (Ar*C*H_2), 44.6, 39.7, 33.4, 26.7, 26.5 (cyclohexyl *C* & *C*H_3).

HRMS (ESI) m/z: calcd for $C_{15}H_{22}O_2Na^+$ [M+Na$^+$]: 257.1512, found: 257.1507.



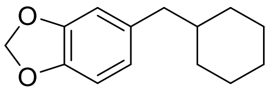
3w: colorless oil. Yield: 40%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.17 – 7.06 (m, 1H), 6.89 – 6.75 (m, 2H) (aromatic C*H*), 2.55 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.79 – 1.60 (m, 5H), 1.59 – 1.51 (m, 1H), 1.29 – 1.11 (m, 3H), 1.08 – 0.94 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): *δ* 161.9 (dd, *J* = 246.0, 9.2 Hz), 127.2 (t, *J* = 10.3 Hz), 117.0 (t, *J* = 20.7 Hz), 110.9 (dd, *J* = 19.5, 7.4 Hz) (aromatic *C*), 124.4 (q, $^1J_{CF}$= 271.9 Hz) (*C*F_3), 38.3 (Ar*C*H_2), 33.1, 29.9, 26.6, 26.4. (cyclohexyl *C*).

^{19}F{^{1}H} NMR (377 MHz, $CDCl_3$) δ -114.7.

HRMS (APCI) Calcd for $C_{13}H_{17}F_2^+$ [M+H$^+$]: 211.1292. Found: 211.1289.

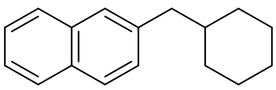


3x: colorless oil. Yield:55%. TLC: R_f = 0.6 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 6.71 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 1.7 Hz, 1H), 6.57 (dd, *J* = 7.9, 1.8 Hz, 1H) (aromatic C*H*), 5.91 (s, 2H) (OCH_2O), 2.40 (d, *J* = 7.1 Hz, 2H) (ArCH_2), 1.72 – 1.60 (m, 5H), 1.50 – 1.38 (m, 1H), 1.25 – 1.10 (m, 3H), 0.98 – 0.85 (m, 2H) (cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 147.5, 145.5, 135.4, 122.0, 109.6, 108.0, 100.8 (aromatic *C* & O*C*H_2O), 44.0 (Ar*C*H), 40.1, 33.2, 31.1, 26.7, 26.5 (cyclohexyl *C*).

HRMS (APCI) m/z: calcd for $C_{14}H_{19}O_2^+$ [M+H$^+$]: 219.1380, found: 219.1376.

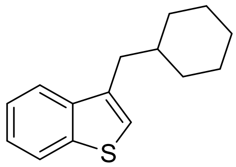


2-(cyclohexylmethyl)naphthalene (CAS: 38287-05-7).[2]

3y: colorless oil. Yield: 35%. TLC: R_f = 0.65 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.87 – 7.73 (m, 3H), 7.58 (s, 1H), 7.51 – 7.39 (m, 2H), 7.31 (dd, *J* = 8.4, 1.8 Hz, 1H) (aromatic C*H*), 2.65 (d, *J* = 7.2 Hz, 2H) (ArCH_2), 1.76 – 1.67 (m, 4H), 1.67 – 1.58 (m, 2H), 1.27 – 1.10 (m, 3H), 1.06 – 0.94 (m, 2H) (cyclohexyl C*H*).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 139.1, 133.6, 132.1, 128.2, 127.7, 127.6, 127.5, 127.4, 125.9, 125.1 (aromatic *C*), 44.4 (Ar*C*H_2), 39.9, 33.4, 26.7, 26.5 (cyclohexyl *C*).

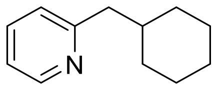


3-(cyclohexylmethyl)benzo[*b*]thiophene (CAS: 2281948-55-6).[2]

3z: colorless oil. Yield: 25%. TLC: R_f = 0.7 (*n*-hexane : ethyl acetate = 10 : 1).

^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.79 – 7.71 (m, 1H), 7.42 – 7.30 (m, 2H), 7.05 (s, 1H) (aromatic C*H*), 2.73 (d, *J* = 6.1 Hz, 2H) (ArC*H*$_2$), 1.80 – 1.63 (m, 6H), 1.22 – 1.17 (m, 2H), 1.07 – 0.96 (m, 2H), 0.90 – 0.78 (m, 1H) (cyclohexyl C*H*).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 140.6, 139.6, 135.8, 124.1, 123.8, 123.0, 122.1, 121.9 (aromatic *C*), 38.1 (Ar*C*H_2), 36.7, 33.7, 26.7, 26.4 (cyclohexyl *C*).

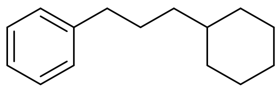


2-(cyclohexylmethyl)pyridine (CAS: 57756-06-6).[8]

3aa: colorless oil. Yield: 23%. TLC: R_f = 0.7 (*n*-hexane : ethyl acetate = 10 : 1).

^1H NMR (400 MHz, $CDCl_3$): δ 8.57 – 8.51 (m, 1H), 7.57 (td, *J* = 7.6, 1.9 Hz, 1H), 7.20 – 6.99 (m, 2H) (aromatic C*H*), 2.66 (d, *J* = 7.1 Hz, 2H) (ArC*H*$_2$), 1.82 – 1.72 (m, 1H), 1.70 – 1.63 (m, 5H), 1.27 – 1.16 (m, 3H), 1.09 – 0.93 (m, 2H) (cyclohexyl C*H*).

$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ 161.4, 149.2, 135.9, 123.6, 120.8 (aromatic *C*), 46.4 (Ar*C*H_2), 38.7, 33.2, 26.5, 26.2 (cyclohexyl *C*).

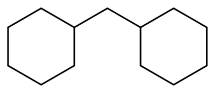


(3-cyclohexylpropyl)benzene (CAS: 170661-44-6).[2]

3ab: colorless oil. Yield: 59%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.26 (m, 2H), 7.22 – 7.11 (m, 3H), (aromatic C*H*), 2.58 (t, *J* = 7.8 Hz, 2H) (PhCH_2), 1.76 – 1.60 (m, 7H), 1.26 – 1.11 (m, 6H), 0.92 – 0.81 (m, 2H) (PhCH_2CH_2, CyCH_2 & cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 143.1, 128.5, 128.4, 125.7 (aromatic *C*), 37.7, 37.3, 36.4, 33.5, 29.0, 26.9, 26.6. (*C*H_2 & cyclohexyl *C*).



Dicyclohexylmethane (CAS: 3178-23-2).[9]

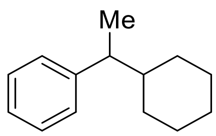
3ac: colorless oil. Yield: 30%. TLC: R_f = 0.80 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 – 1.59 (m, 10H), 1.38 – 1.08 (m, 9H), 1.00 (t, *J* = 8.8 Hz, 2H), 0.82 (qd, J = 12.8, 3.7 Hz, 3H).

These data are identical to those reported in the literature.

Synthesis of 4.

An flame-dried V-shape reaction vial (10 cm^3) equipped with a stir bar was charged with $Co(PPh_3)_2Cl_2$ (26 mg, 0. 04 mmol) and **L7** (19 mg, 0.04 mmol), followed by dry 1,4-dioxane (0.5 mL). The mixture was stirred at room temperature for 1 h, to which were successively added **2** (0.20 mmol), **1’** (0.4 mmol), potassium tert-butoxide (44.8 mg, 0.4 mmol) and dry 1,4-dioxane (0.5 mL). The vial was sealed with a rubber septum under an atmosphere of nitrogen, and then stirred at room temperature for 24 h. After the completion of the reaction, the solution was filtered in a short celite pad and washed with ethyl acetate (10 mL × 3). The solvent was removed under vacuum and the residue was purified by flash column chromatography to give the desired product **4**.

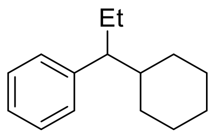


(1-cyclohexylethyl)benzene (CAS: 4413-16-5)[10].

4a: colorless oil. Yield: 66%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.30 – 7.25 (m, 2H), 7.24 – 7.12 (m, 3H) (aromatic C*H*), 2.48 – 2.40 (m, 1H) (PhC*H*), 1.92 – 1.84 (m, 1H), 1.77 – 1.71 (m, 1H), 1.68 – 1.56 (m, 2H), 1.48 – 1.33 (m, 2H), 1.26 – 1.20 (m, 4H), 1.15 – 1.01 (m, 2H), 0.99 – 0.88 (m, 1H), 0.87 – 0.75 (m, 1H) (CH_3 & cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 147.3, 128.2, 127.9, 125.8 (aromatic *C*), 46.1 (Ph*C*H), 44.4, 31.6, 30.8, 26.7, 19.0 (cyclohexyl *C* & *C*H_3).

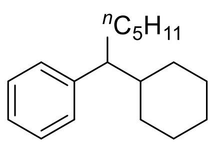


4b: colorless oil. Yield: 69% for iodide, 50% for bromide. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.28 – 7.23 (m, 2H), 7.19 – 7.14 (m, 1H), 7.11 – 7.06 (m, 2H) (aromatic C*H*), 2.20 – 2.15 (m, 1H) (PhC*H*), 1.91 – 1.86 (m, 1H), 1.86 – 1.78 (m, 1H), 1.75 – 1.68 (m, 1H), 1.64 – 1.55 (m, 2H), 1.56 – 1.49 (m, 1H), 1.49 – 1.37 (m, 2H), 1.28 – 1.16 (m, 1H), 1.16 – 1.01 (m, 2H), 0.94 – 0.86 (m, 1H), 0.80 – 0.71 (m, 1H) (CH_2CH_3 & cyclohexyl C*H*), 0.68 (t, *J* = 7.3 Hz, 3H) (CH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 144.6, 128.7, 127.9, 125.6 (aromatic *C*), 54.2 (Ph*C*H), 43.0, 31.4, 31.1, 26.7, 26.6, 25.3, 12.4 (cyclohexyl *C* & ethyl *C*).

HRMS (APCI) m/z: calcd for $C_{15}H_{21}^+$ [M-H]$^+$: 201.1638, found: 201.1643.



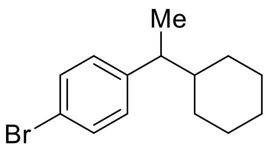
4c: colorless oil. Yield: 55%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.29 – 7.24 (m, 2H), 7.21 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H) (aromatic C*H*), 2.33 – 2.22 (m, 1H) (PhC*H*), 1.95 – 1.84 (m, 1H), 1.84 – 1.68 (m, 2H), 1.69 – 1.50 (m, 3H), 1.50 – 1.36 (m, 2H), 1.33 – 1.12 (m, 6H), 1.11 – 1.01 (m, 3H), 0.96 – 0.86 (m, 1H), 0.86 – 0.71 (m, 4H) (CH_2, CH_3 & cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 145.1, 128.7, 128.0, 125.7 (aromatic *C*), 52.4

(Ph*C*H), 43.5, 32.7, 32.2, 31.6, 31.2, 27.7, 26.7, 22.7, 14.2 (cyclohexyl *C* & n-pentyl *C*).

HRMS (APCI) m/z: calcd for $C_{18}H_{28}^+$ [M^+]: 244.2186, found: 244.2186.

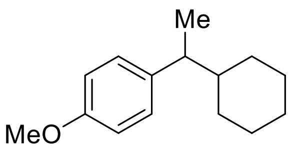


4d: colorless oil. Yield: 52%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.33 (m, 2H), 7.08 – 6.95 (m, 2H) (aromatic C*H*), 2.41 (p, *J* = 7.2 Hz, 1H) (ArC*H*), 1.89 – 1.81 (m, 1H), 1.77 – 1.69 (m, 1H), 1.67 – 1.57 (m, 2H), 1.45 – 1.38 (m, 1H), 1.38 – 1.30 (m, 1H), 1.29 – 1.21 (m, 1H), 1.20 (d, *J* = 7.0 Hz, 3H), 1.17 – 0.98 (m, 3H), 0.95 – 0.86 (m, 1H), 0.83 – 0.73 (m, 1H) ($CHCH_3$ & cyclohexyl C*H*).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.2, 131.2, 129.6, 119.4 (aromatic *C*), 45.6, 44.3, 31.5, 30.7, 26.6, 18.9 (Ar*C*H, cyclohexyl *C* & *C*H_3).

HRMS (APCI) m/z: calcd for $C_{14}H_{19}Br^+$ [M^+]: 266.0665, found: 266.0665.

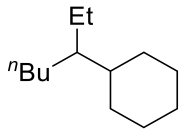


4e: colorless oil. Yield: 59%. TLC: R_f = 0.7 (*n*-hexane : ethyl acetate = 10 : 1).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 – 6.99 (m, 2H), 6.87 – 6.78 (m, 2H) (aromatic C*H*), 3.79 (s, 3H) (OC*H*$_3$), 2.40 (p, *J* = 7.2 Hz, 1H) (ArC*H*), 1.87 – 1.81 (m, 1H), 1.77 – 1.68 (m, 1H), 1.67 – 1.56 (m, 2H), 1.49 – 1.41 (m, 1H), 1.39 – 1.28 (m, 1H), 1.23 – 1.16 (m, 4H), 1.18 – 1.02 (m, 2H), 0.98 – 0.86 (m, 1H), 0.84 – 0.73 (m, 1H) ($CHCH_3$ & cyclohexyl C*H*).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 157.7, 139.3, 128.6, 113.5 (aromatic *C*), 55.4, 45.2, 44.5, 31.5, 30.8, 26.7, 19.1 (Ar*C*H, cyclohexyl *C* & *C*H_3).

HRMS (APCI) m/z: calcd for $C_{15}H_{23}O^+$ [$M+H^+$]: 219.1743, found: 219.1742.



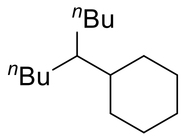
heptan-3-ylcyclohexane (CAS: 13456-14-9).[11]

4f: colorless oil. Yield: 35%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 1.76 – 1.68 (m, 2H), 1.67 – 1.61 (m, 1H), 1.59 – 1.55 (m, 2H), 1.36 – 1.23 (m, 6H), 1.23 – 1.07 (m, 6H), 1.05 – 0.93 (m, 3H) (C*H* & C*H*$_2$), 0.89 (t, *J* = 7.1 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 3H) (CH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 45.1, 40.0 (*C*H), 30.3, 30.1, 30.0, 27.2, 27.1, 23.4, 23.3 (*C*H$_2$), 14.3, 12.3 (*C*H$_3$).

HRMS (APCI) m/z: calcd for $C_{13}H_{25}^+$ $[M-H]^+$: 181.1951, found: 181.1951.



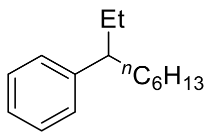
nonan-5-ylcyclohexane (CAS: 131284-82-7).[12]

4g: colorless oil. Yield: 37%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 1.72 (dt, *J* = 12.2, 3.1 Hz, 2H), 1.68 – 1.61 (m, 1H), 1.58 – 1.53 (m, 2H), 1.35 – 1.17 (m, 13H), 1.17 – 1.09 (m, 3H), 1.05 – 0.95 (m, 3H) (C*H* & C*H*$_2$), 0.89 (t, *J* = 7.0 Hz, 6H) (CH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 43.4, 40.4 (*C*H), 30.7, 30.3, 30.0, 27.2, 23.4 (*C*H$_2$), 14.3 (*C*H$_3$).

HRMS (APCI) m/z: calcd for $C_{15}H_{29}^+$ $[M-H]^+$: 209.2264, found: 209.2266.



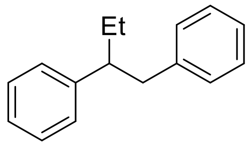
nonan-3-ylbenzene (CAS: 20216-87-9).[13]

4h: colorless oil. Yield: 30% for iodide, 15% for bromide. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.19 – 7.11 (m, 3H) (aromatic

C*H*), 2.42 – 2.34 (m, 1H) (C*H*), 1.67 – 1.52 (m, 4H), 1.29 – 1.11 (m, 8H) (CH_2), 0.84 (t, J = 7.0 Hz, 3H), 0.76 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.3, 128.3, 127.9, 125.8 (aromatic *C*), 48.0 (Ph*C*H), 36.7, 31.9, 29.9, 29.6, 27.8, 22.8, 14.2, 12.4 (CH_2 & CH_3).

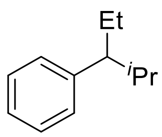


butane-1,2-diyldibenzene (CAS: 5223-59-6).[14]

4i: colorless oil. Yield: 47% for bromide, 40% for chloride. TLC: R_f = 0.65 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 – 7.26 (m, 2H), 7.26 – 7.11 (m, 6H), 7.10 – 7.00 (m, 2H) (aromatic C*H*), 2.97 – 2.88 (m, 2H), 2.78 – 2.70 (m, 1H) (PhC*H* & PhCH_2), 1.83 – 1.70 (m, 1H), 1.70 – 1.59 (m, 1H) (CH_2CH_3), 0.79 (t, J = 7.4 Hz, 3H) (CH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 145.2, 141.0, 129.3, 128.3, 128.2, 128.0, 126.1, 125.9 (aromatic *C*), 49.94, 43.63 (Ph*C*H & PhCH_2), 28.4 (CH_2), 12.3 (CH_3).

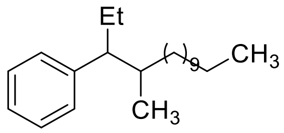


(2-methylpentan-3-yl)benzene (CAS: 19219-86-4).[15]

4j: colorless oil. Yield: 57% for iodide, 45% for bromide. TLC: R_f = 0.70 (*n*-hexane).

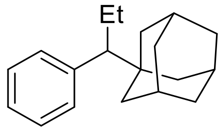
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 – 7.25 (m, 2H), 7.18 (tt, J = 7.2 Hz, 1.2 Hz, 1H), 7.12 – 7.09 (m, 2H) (aromatic C*H*), 2.18 – 2.12 (m, 1H) (PhC*H*), 1.89 – 1.75 (m, 2H) (CH_2), 1.61 – 1.50 (m, 1H) (C*H*(CH_3)$_2$), 0.95 (d, J = 6.6 Hz, 3H) (CH(CH_3)$_2$), 0.71 (t, J = 6.8 Hz, 6H) (CH_2CH_3).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 144.7, 128.8, 128.0, 125.8 (aromatic *C*), 55.2 (Ph*C*H) 33.3, 25.9, 21.2, 20.9, 12.6 (*C*H(CH_3)$_2$, CH_2 & CH_3).



4k: 70% nmr yield. **4k** was mixed with by-products tridecane and tridec-2-ene, which cannot be purified by column chromatography. The NMR spectra were not pure.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 2H), 7.24 – 7.13 (m, 1H), 7.14 – 7.07 (m, 2H) (aromatic C*H*), 2.36 – 2.24 (m, 1H) (PhC*H*), 1.83 – 1.74 (m, 1H) (PhCHC*H*), 1.69 – 1.56 (m, 2H), 1.29 – 1.22 (m, 20H) (CH_2), 0.92 – 0.85 (m, 6H), 0.70 (t, *J* = 10.8 Hz, 3H) (CH_3). ^{13}C NMR spectrum is not pure.

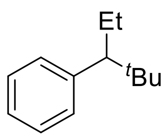


1-(1-phenylpropyl)adamantane (CAS: 116137-28-1).[16]

4l: colorless oil. Yield: 60%. TLC: R_f = 0.70 (*n*-hexane).

^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.26 – 7.23 (m, 2H), 7.21 – 7.16 (m, 1H), 7.09 (d, *J* = 6.8 Hz, 2H) (aromatic C*H*), 2.03 (dd, *J* = 12.1, 3.2 Hz, 1H) (PhC*H*), 1.93 – 1.88 (m, 3H), 1.88 – 1.80 (m, 1H), 1.69 – 1.58 (m, 8H), 1.54 – 1.58 (m, 2H), 1.36 (m, 3H) (CH_2 & C*H*), 0.64 (t, *J* = 7.3 Hz, 3H) (CH_3).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): *δ* 142.3, 127.5, 125.8 (aromatic *C*), 60.2 (Ph*C*H), 40.7, 37.3, 35.7, 29.0, 20.5, 13.4 (ethyl & adamantyl *C*).



(2,2-dimethylpentan-3-yl)benzene (CAS: 89675-53-6).[17]

4m: colorless oil. Yield: 35% for iodide, 51% for bromide. TLC: R_f = 0.70 (*n*-hexane).

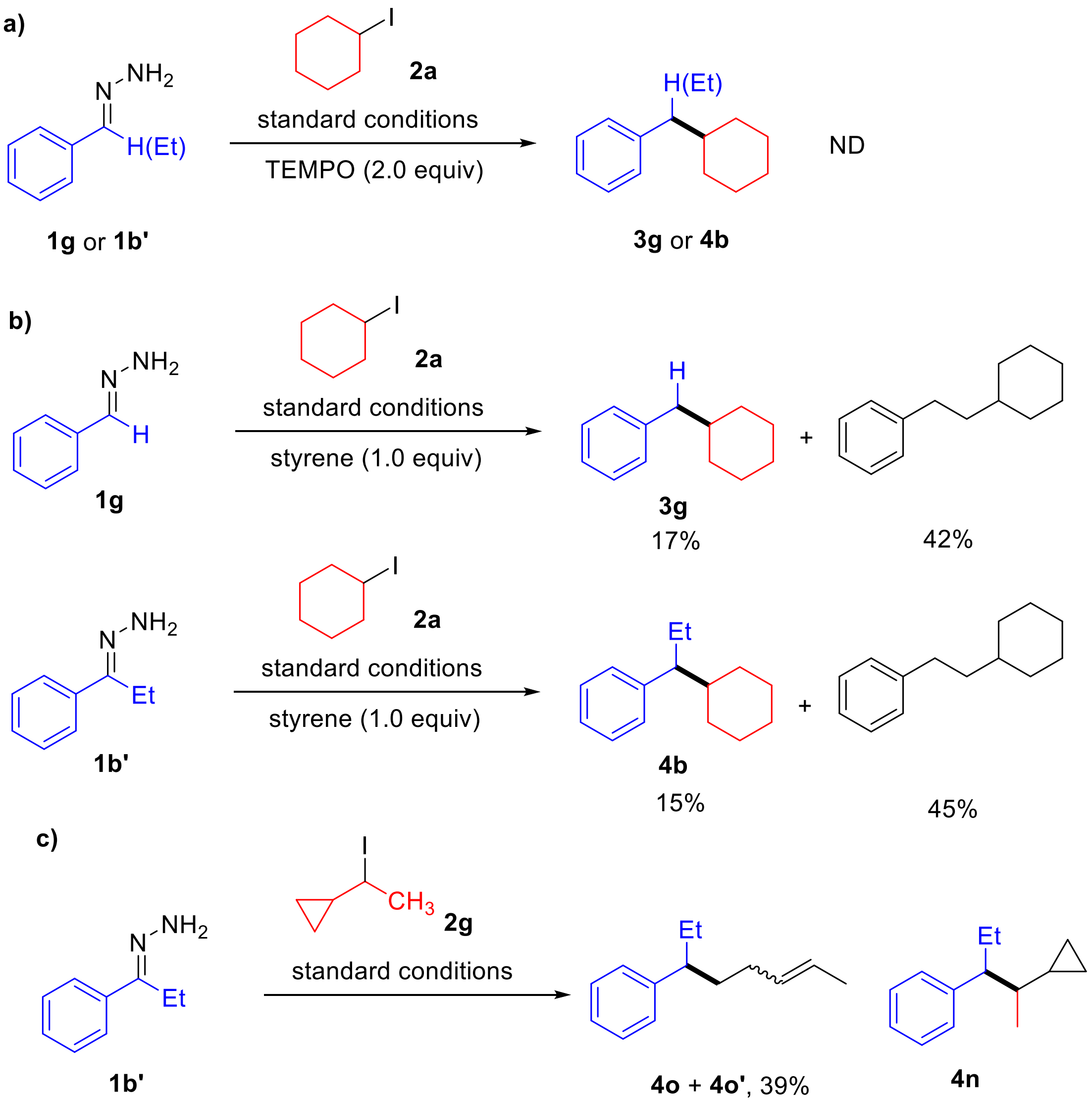
^{1}H NMR (500 MHz, $CDCl_3$): *δ* 7.27 – 7.24 (s, 1H), 7.21 – 7.15 (m, 1H), 7.13 (d, *J* = 6.7 Hz, 2H) (aromatic C*H*), 2.21 (dd, *J* = 12.1, 3.1 Hz, 1H) (PhC*H*), 1.87 – 1.79 (m, 1H), 1.70 – 1.62 (m, 1H) (CH_2), 0.86 (s, 9H) ($C(CH_3)_3$), 0.67 (t, *J* = 7.2 Hz, 3H)

($CH_2C\mathit{H}_3$).

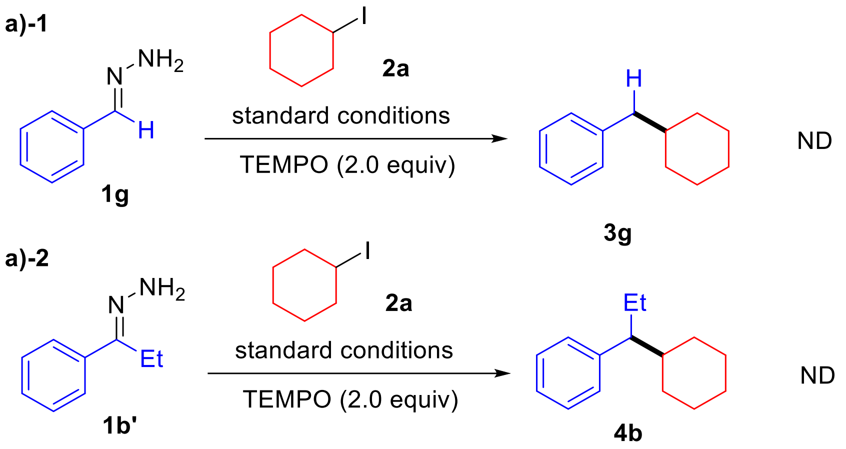
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 143.1, 127.6, 125.9 (aromatic *C*), 59.1 (Ph*C*H), 34.0, 28.5, 22.7, 13.4 (*C*(CH_3)$_3$, *C*H_2 & *C*H_3).

Mechanistic studies.

Control experiments.



Scheme S1 Control Experiments



A flame-dried V-shape reaction vial (10 cm^3) equipped with a stir bar was charged with $CoCl_2$ (5.2 mg, 0. 04 mmol) and **L5** (120 mg, 10%wt in THF, 0.04 mmol) or $Co(PPh_3)_2Cl_2$ (26 mg, 0. 04 mmol) and **L7** (19 mg, 0.04 mmol), followed by dry 1,4-dioxane (0.5 mL). The mixture was stirred at room temperature for 1 h, to which were successively added **2a** (42 mg, 0.20 mmol), **1g** (48 mg, 0.4 mmol) or **1b'** (60 mg, 0.4 mmol), potassium tert-butoxide (44.8 mg, 0.4 mmol), TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, 62 mg, 0.4 mmol) and dry 1,4-dioxane (0.5 mL). The vial was sealed with a rubber septum under an atmosphere of nitrogen, and then stirred at room temperature for 24 h. No desired cross-coupling product was detected either for **1g** or **1b'** after reaction.

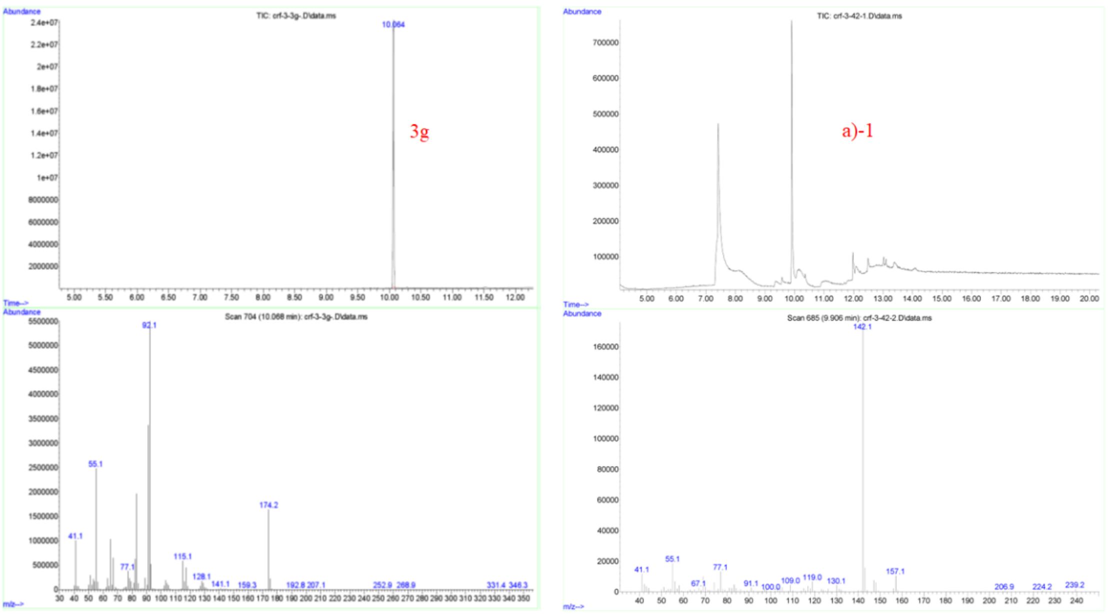


Figure S1 GC-MS results of pure **3g** (left) and experiment Scheme S1 a)-1 (right).

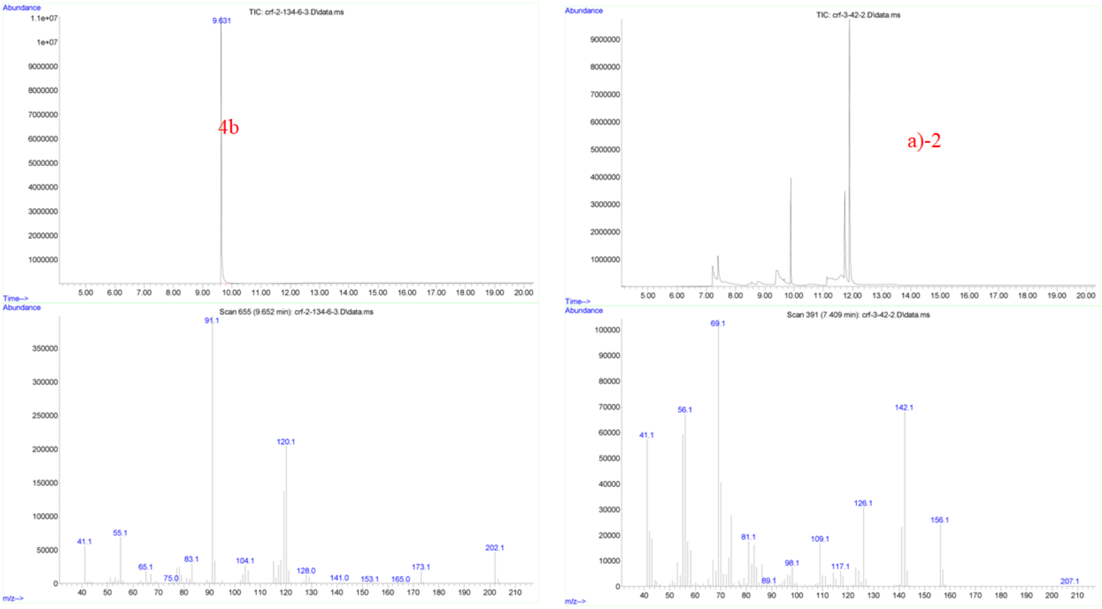
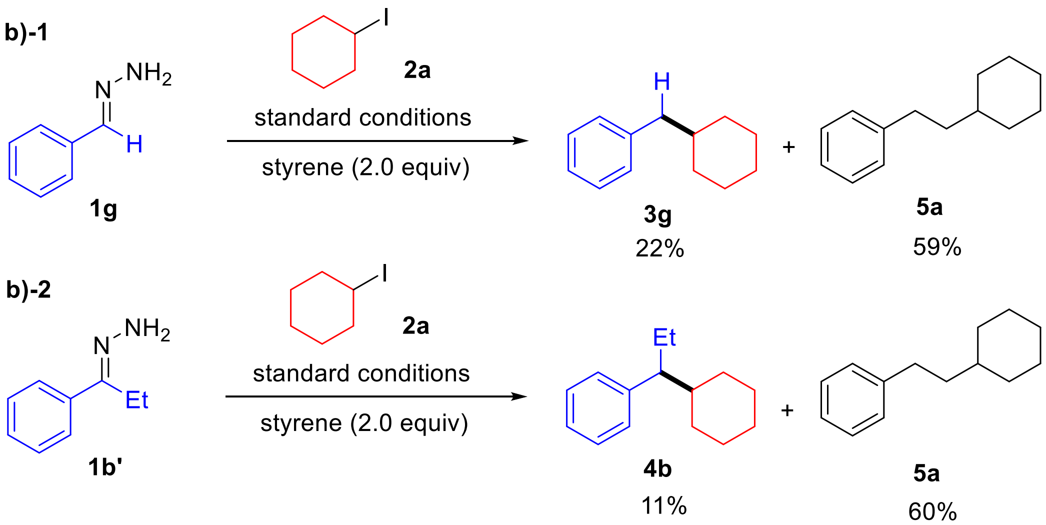


Figure S2 GC-MS results of pure **4b** (left) and experiment Scheme S1 a)-2 (right).



A flame-dried V-shape reaction vial (10 cm^3) equipped with a stir bar was charged with $CoCl_2$ (5.2 mg, 0. 04 mmol) and **L5** (120 mg, 10%wt in THF, 0.04 mmol) or $Co(PPh_3)_2Cl_2$ (26 mg, 0. 04 mmol) and **L7** (19 mg, 0.04 mmol), followed by dry 1,4-dioxane (0.5 mL). The mixture was stirred at room temperature for 1 h, to which were successively added **2a** (42 mg, 0.20 mmol), **1g** (48 mg, 0.4 mmol) or **1b'** (60 mg, 0.4 mmol), potassium tert-butoxide (44.8 mg, 0.4 mmol), styrene (40 mg, 0.4 mmol) and dry 1,4-dioxane (0.5 mL). The vial was sealed with a rubber septum under an atmosphere of nitrogen, and then stirred at room temperature for 24 h. After completion of the reaction, the solution was filtered in a short celite pad and washed with ethyl acetate (10 mL × 3). The reaction was monitored by GC-MS using 1,3,5-trimethoxybenzene (0.1 mmol) as internal standard.

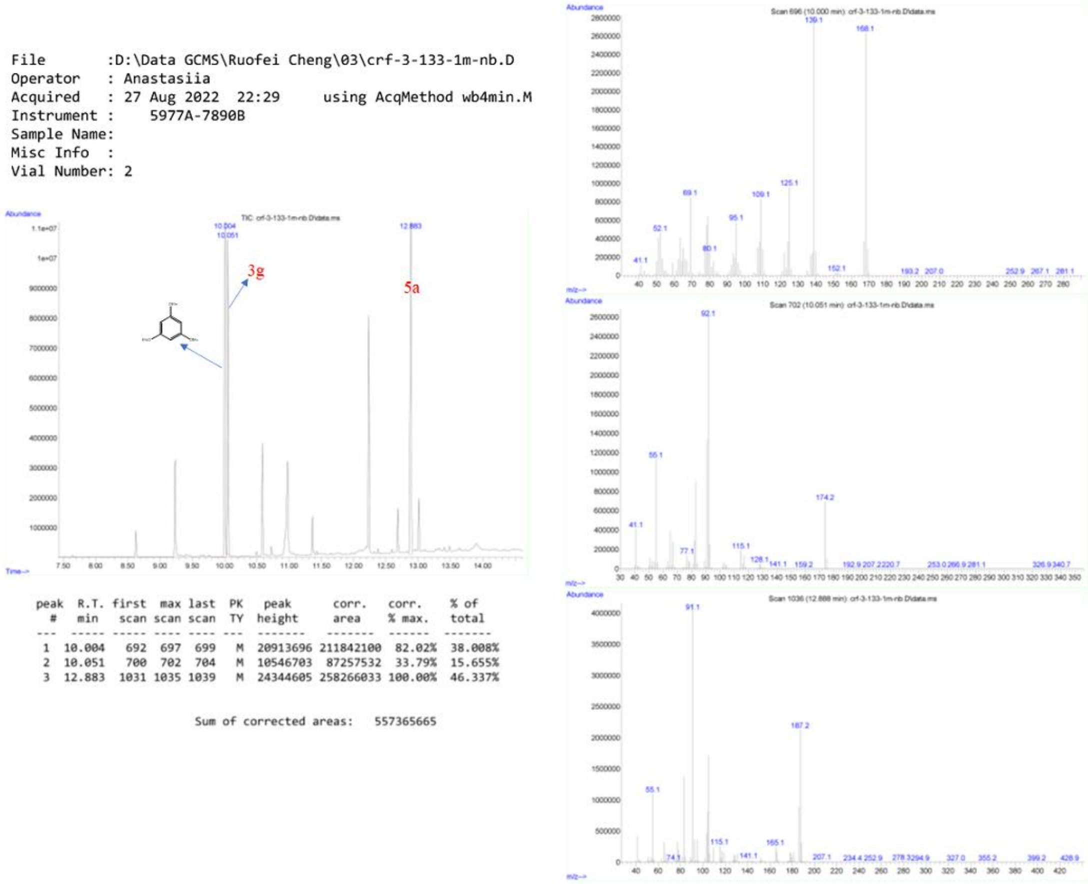
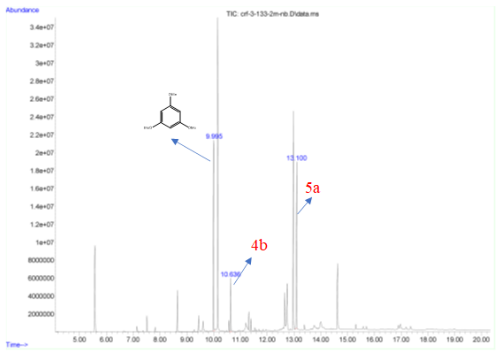
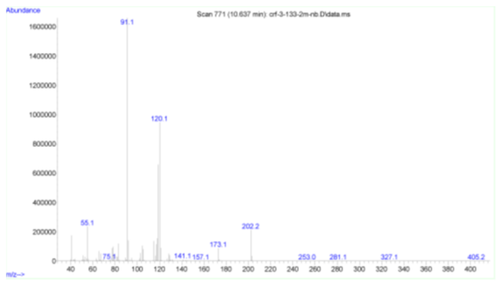


Figure S3 GC-MS result of experiment Scheme S1 b)-1.

```
File       :D:\Data GCMS\Ruofei Cheng\03\crf-3-133-2m-nb.D
Operator   : Anastasiia
Acquired   : 27 Aug 2022  22:53      using AcqMethod wb4min.M
Instrument :     5977A-7890B
Sample Name:
Misc Info  :
Vial Number: 3
```



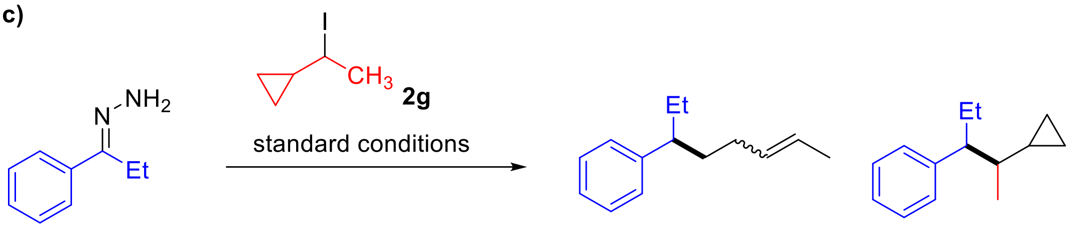


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	9.995	692	695	700	M	23209851	238586259	82.83%	41.192%
2	10.636	765	771	776	M	6062301	52572725	18.25%	9.077%
3	13.100	1056	1061	1064	M	18819539	288052721	100.00%	49.732%

Sum of corrected areas: 579211705

Figure S4 GC-MS result of experiment Scheme S1 b)-2.

c)

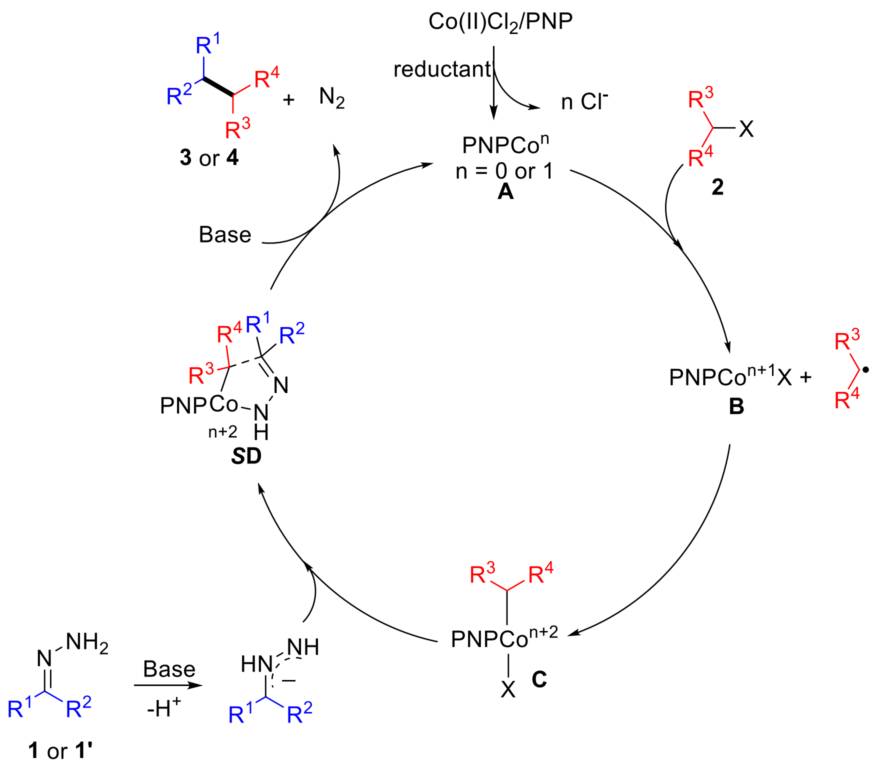


1b' **4n + 4n'**, 39% **4m'**

A flame-dried V-shape reaction vial (10 cm^3) equipped with a stir bar was charged with $Co(PPh_3)_2Cl_2$ (26 mg, 0. 04 mmol) and **L7** (19 mg, 0.04 mmol), followed by dry 1,4-dioxane (0.5 mL). The mixture was stirred at room temperature for 1 h, to which were successively added **2g** (40 mg, 0.20 mmol), **1b'** (60 mg, 0.4 mmol), potassium tert-butoxide (44.8 mg, 0.4 mmol), and dry 1,4-dioxane (0.5 mL). The vial was sealed with a rubber septum under an atmosphere of nitrogen, and then stirred at room temperature for 24 h. The solvent was removed under vacuum and the residue was purified by flash column chromatography to give a mixture of **4n** and **4n'** as coreless oil (15 mg, 39%)

4n and **4n'**: TLC: R_f = 0.70 (*n*-hexane) (^{1}H NMR spectrum is not pure).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30 – 7.27 (m, 1H), 7.20 – 7.15 (m, 1H), 7.15 – 7.09 (m, 2H) (aromatic C*H*), 5.50 – 5.23 (m, 2H) (alkenyl C*H*), 2.46 – 2.35 (m, 1H) (PhC*H*), 1.89 – 1.77 (m, 2H), 1.71 – 1.64 (m, 2H) (PhCHCH_2), 1.62 (d, J = 4.8 Hz, 3H) (CH=CHCH_3), 0.91 – 0.86 (m, 2H) (CH_2CH=CH), 0.76 (t, J = 7.4 Hz, 3H) (CH$_2$CH_3).



Scheme S2 Proposed reaction mechanism

NMR spectra of products

Figure S5 ^{1}H NMR of **3a**

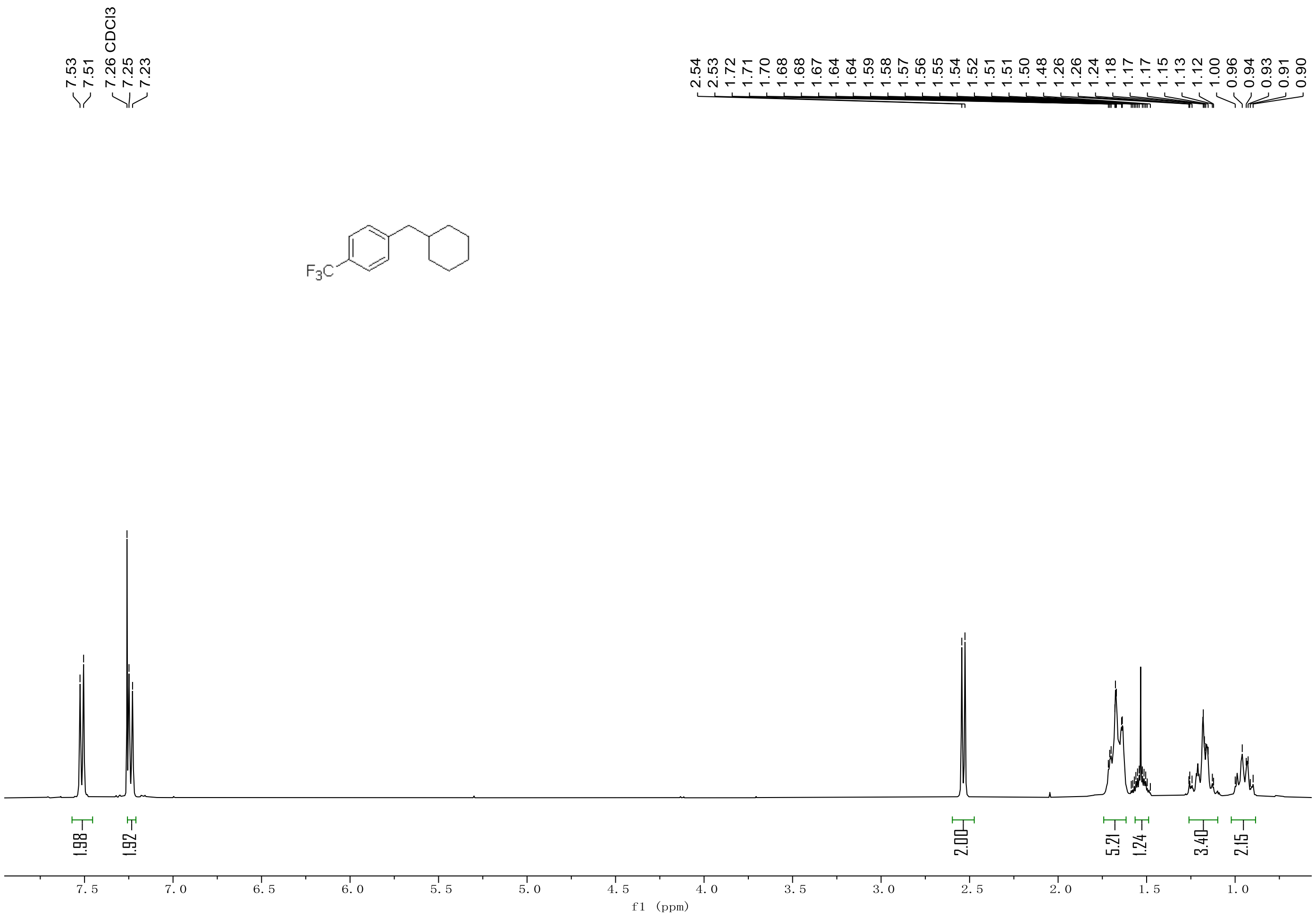


Figure S6 ^{13}C NMR of **3a**

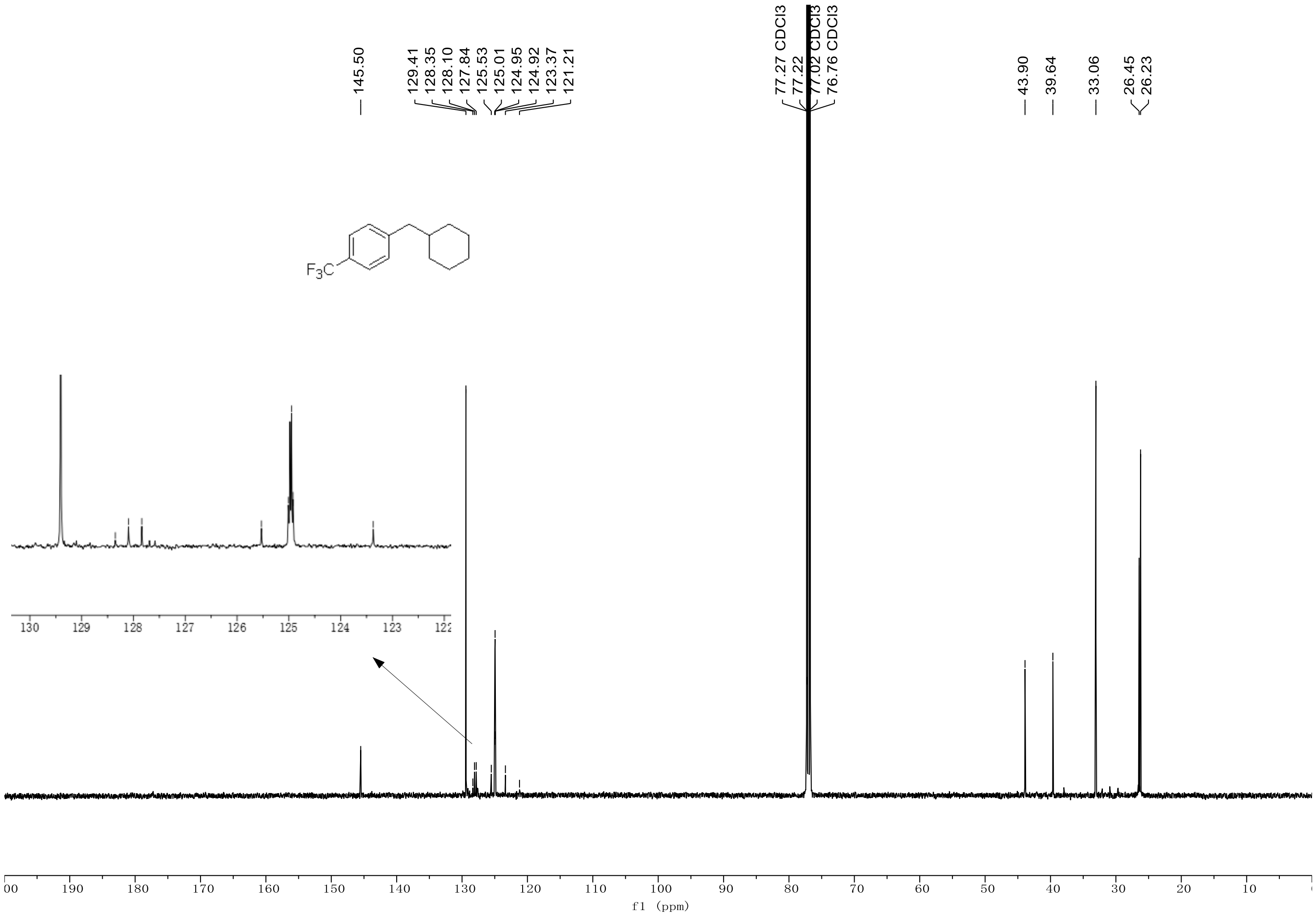


Figure S7 ^{19}F NMR of **3a**

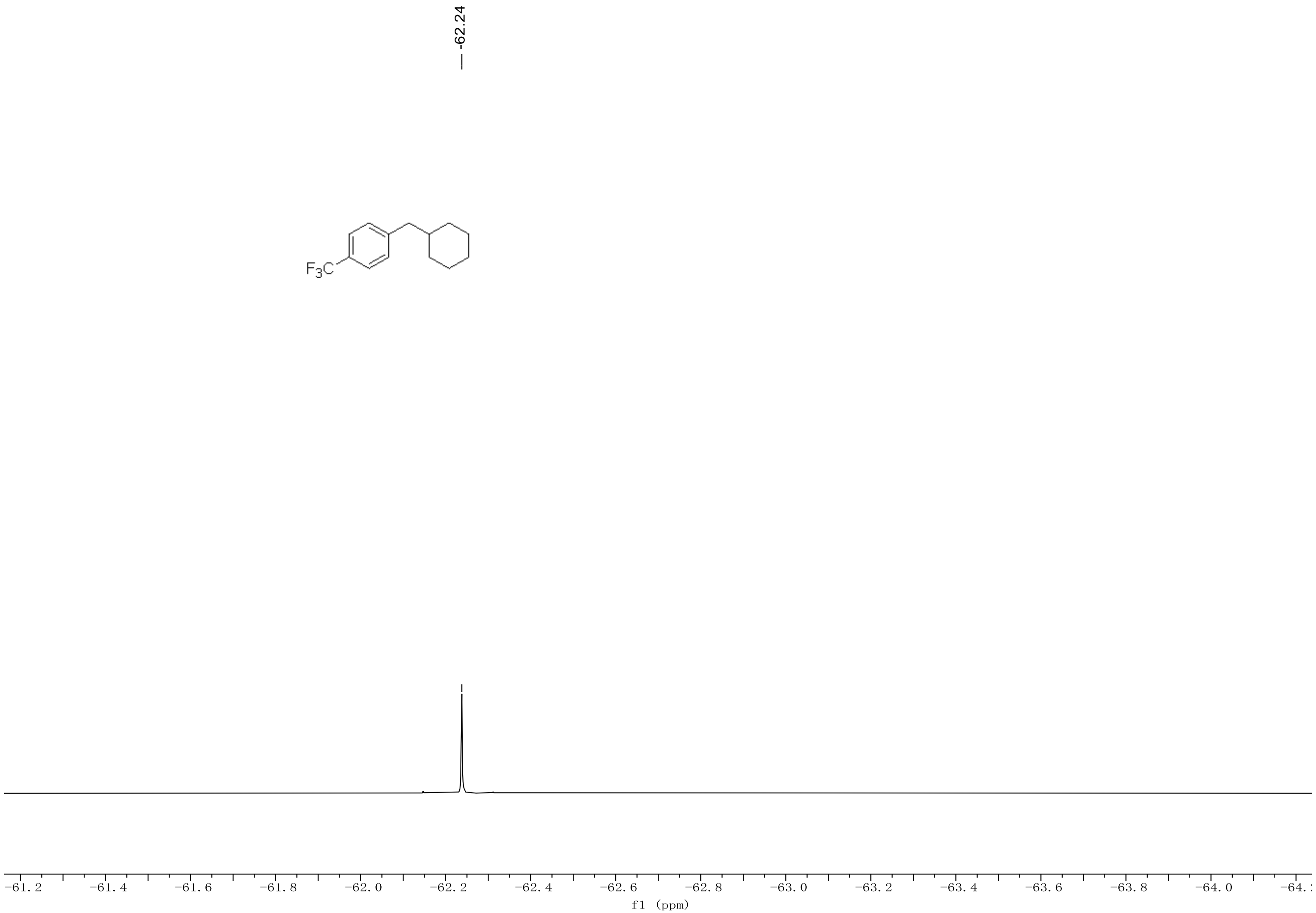


Figure S8 ^{1}H NMR of **3b**

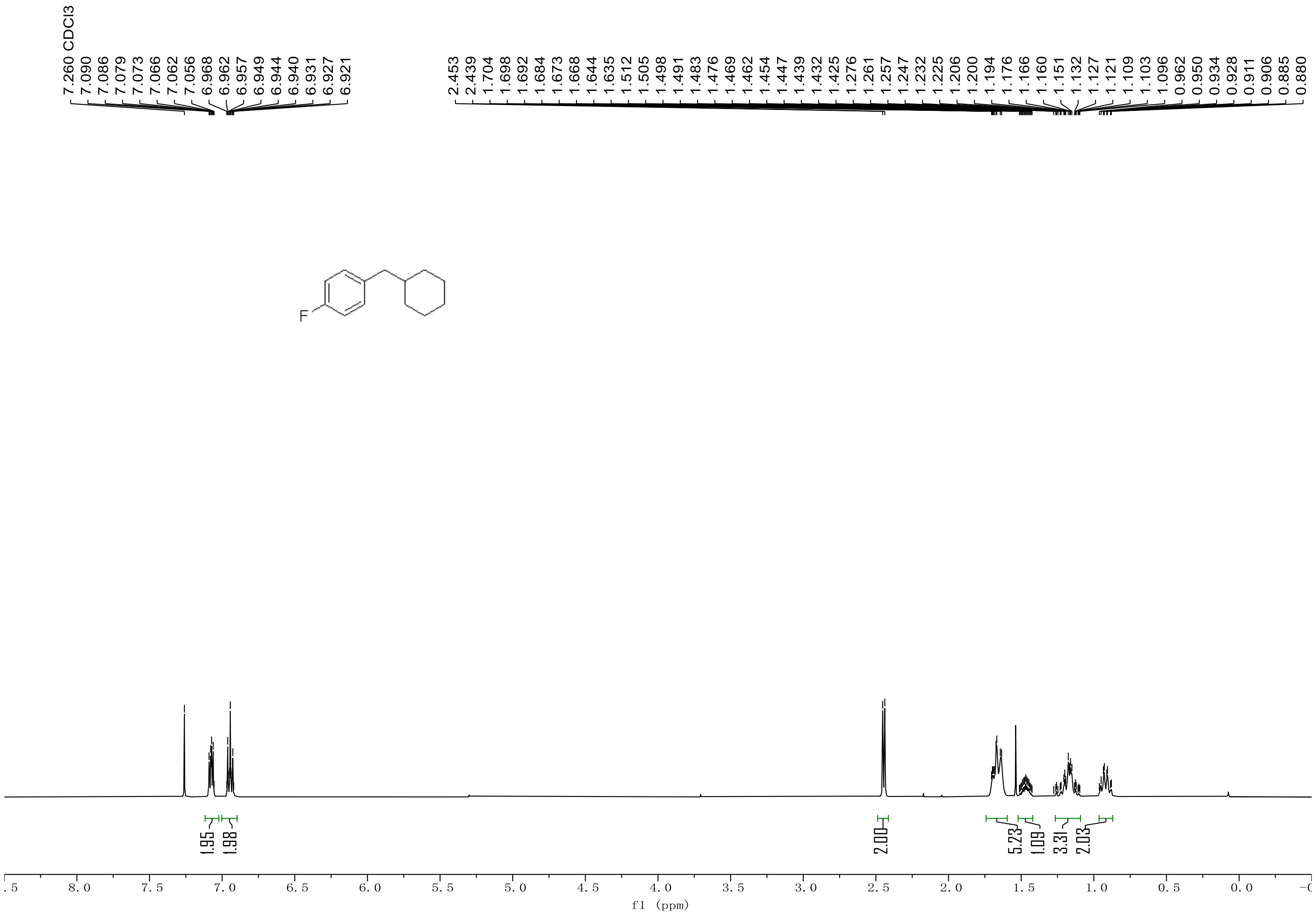


Figure S9 ^{13}C NMR of **3b**

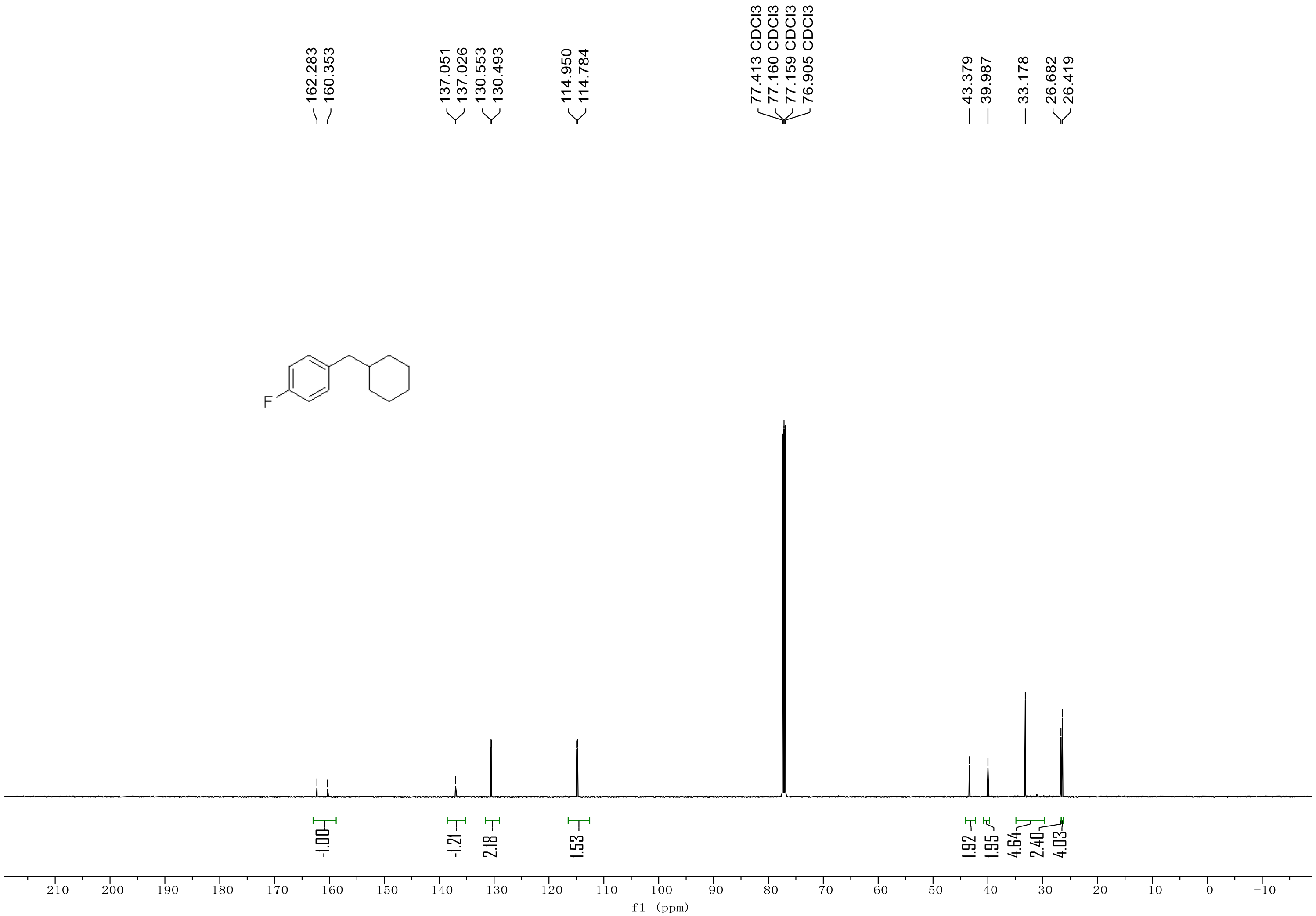


Figure S10 ^{19}F NMR of **3b**

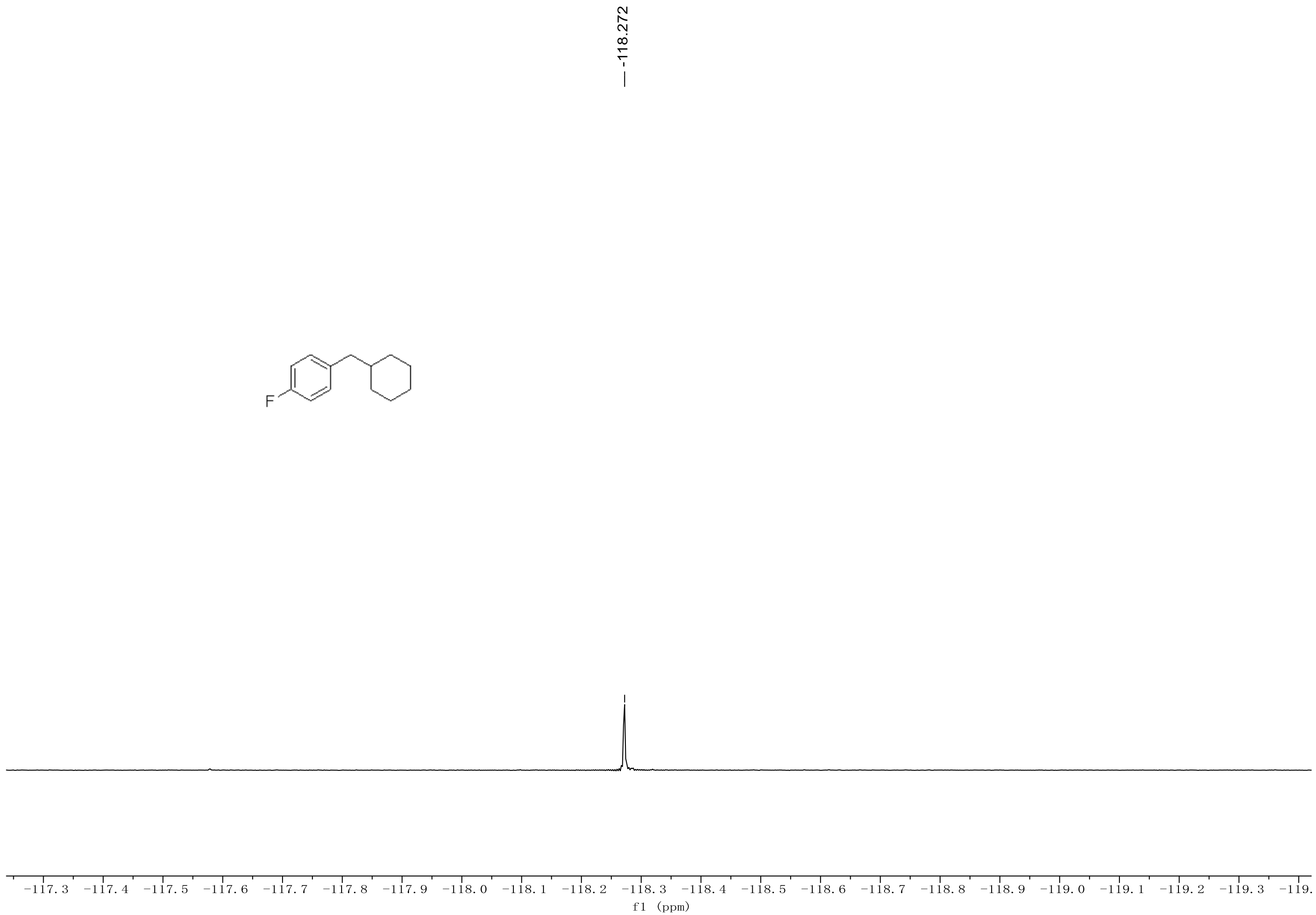


Figure S11 ^{1}H NMR of **3c**

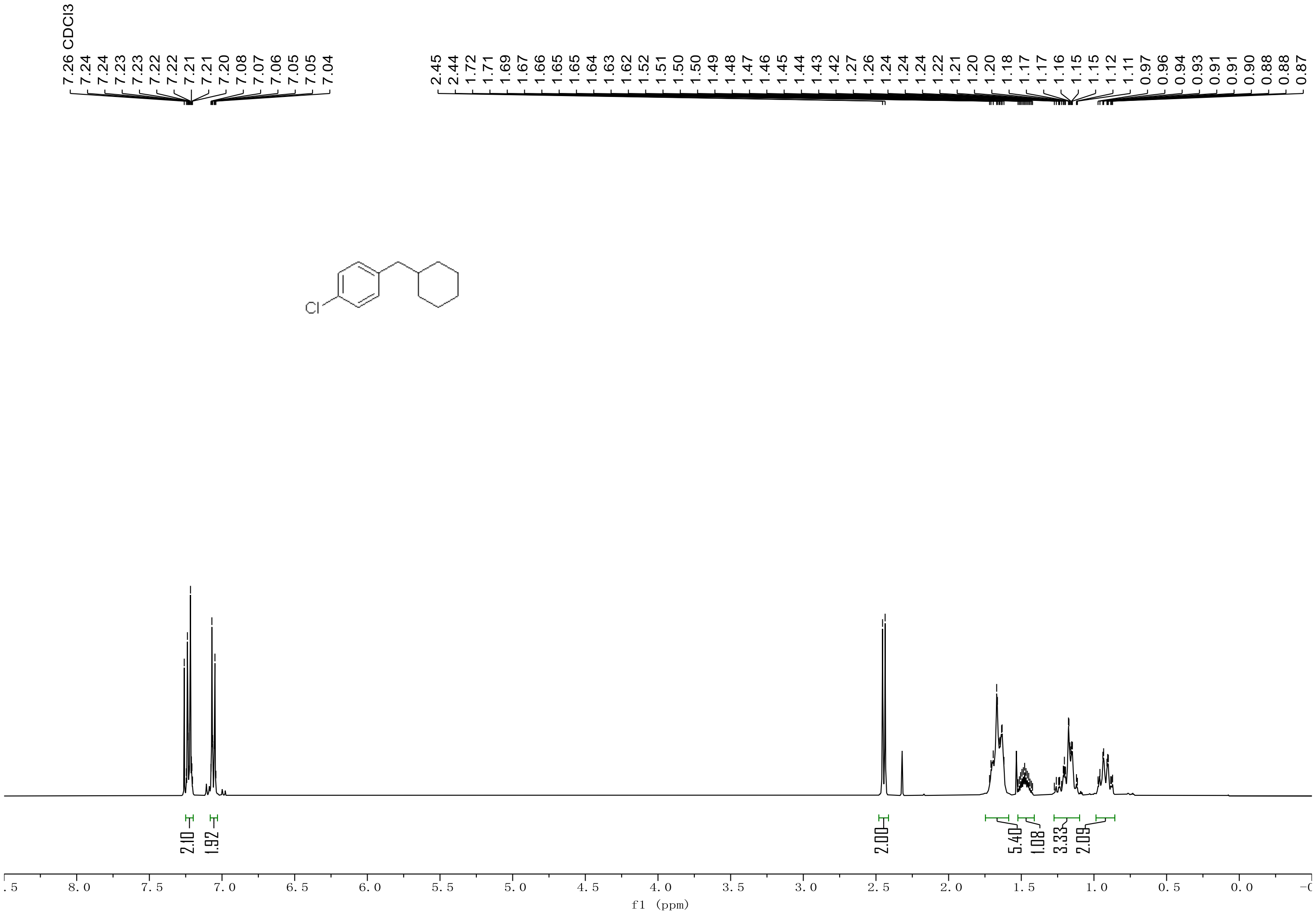


Figure S12 ^{13}C NMR of **3c**

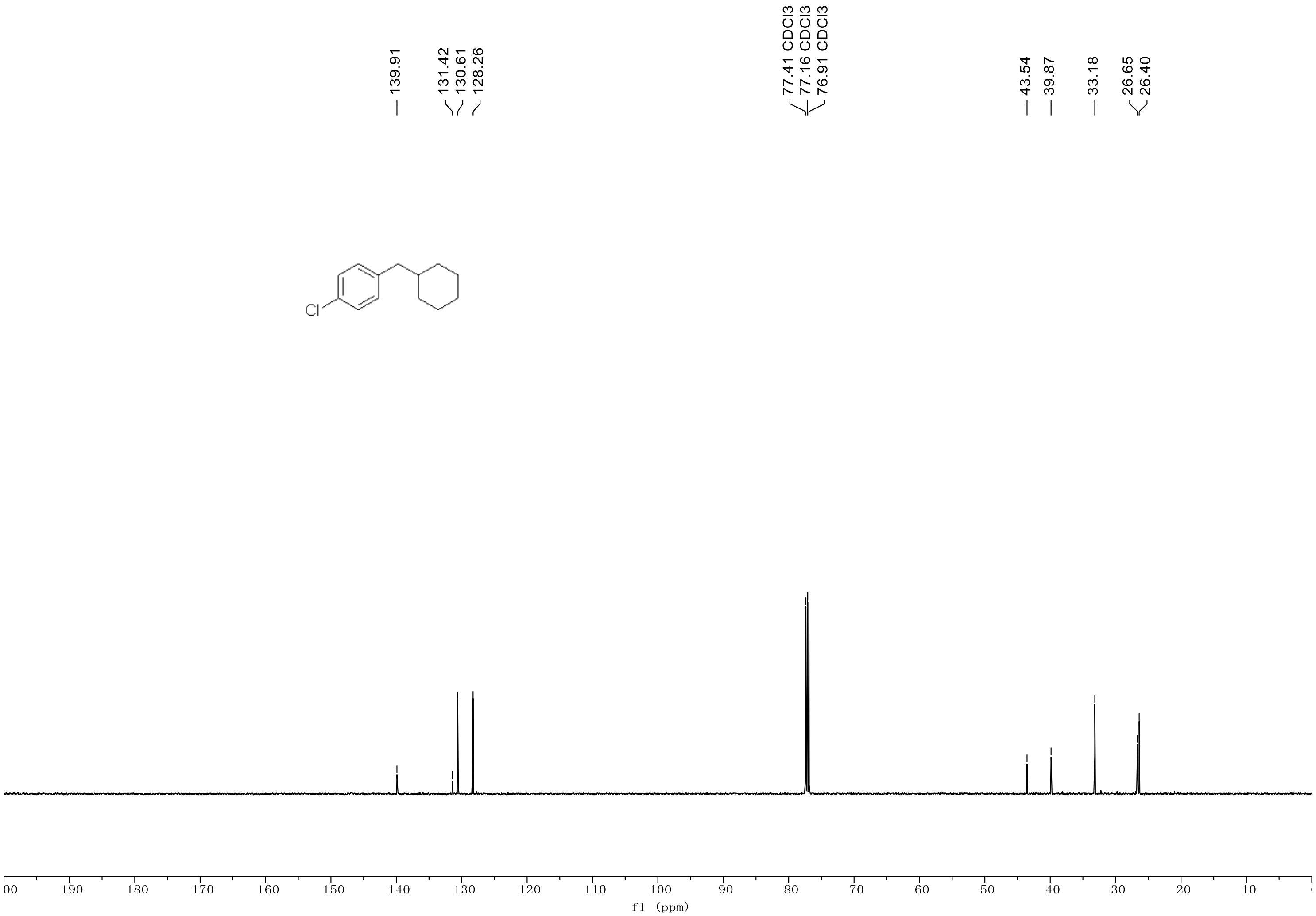


Figure S13 [1]H NMR of **3d**

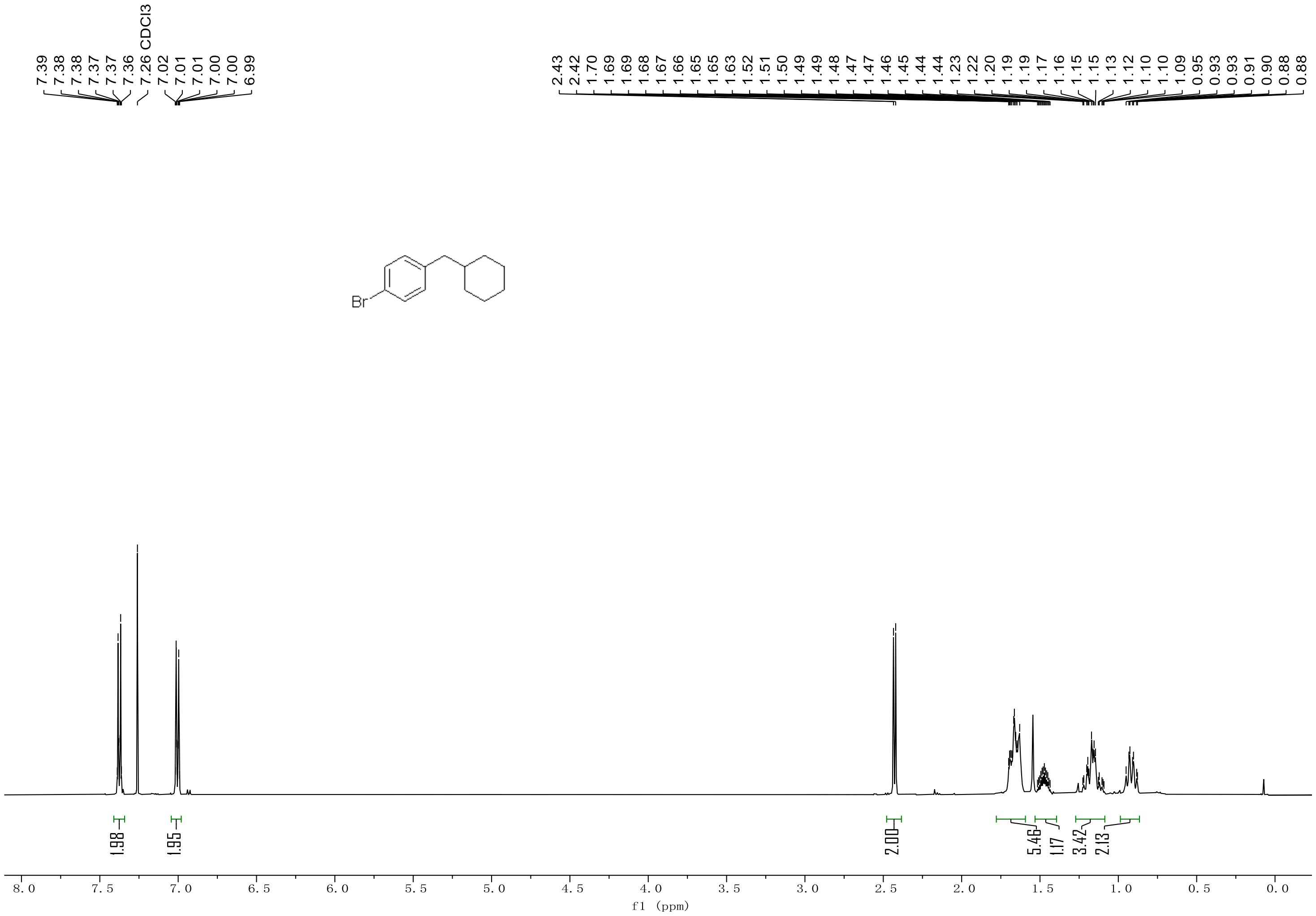


Figure S14 ^{13}C NMR of **3d**

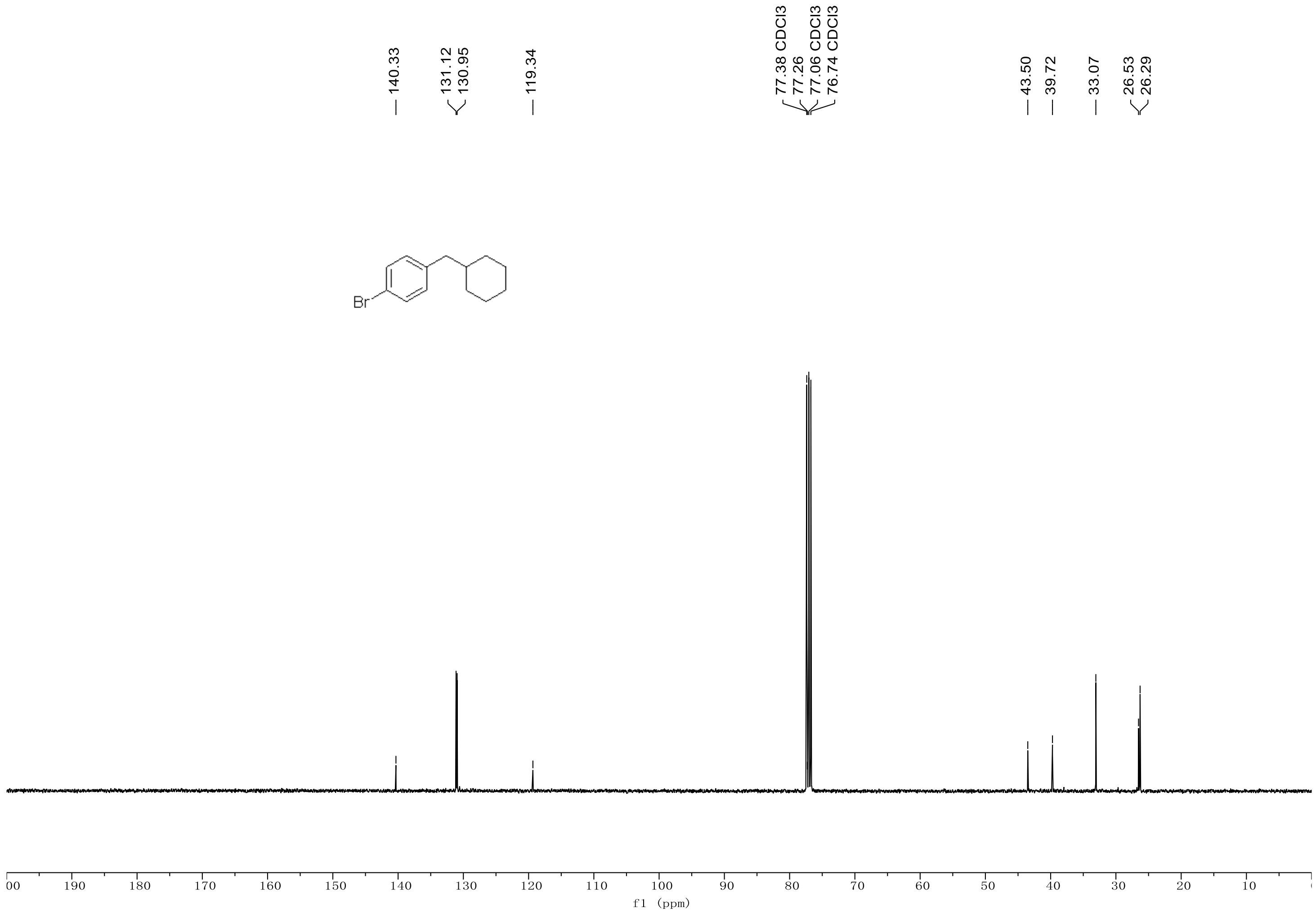


Figure S15 [1]H NMR of **3f**

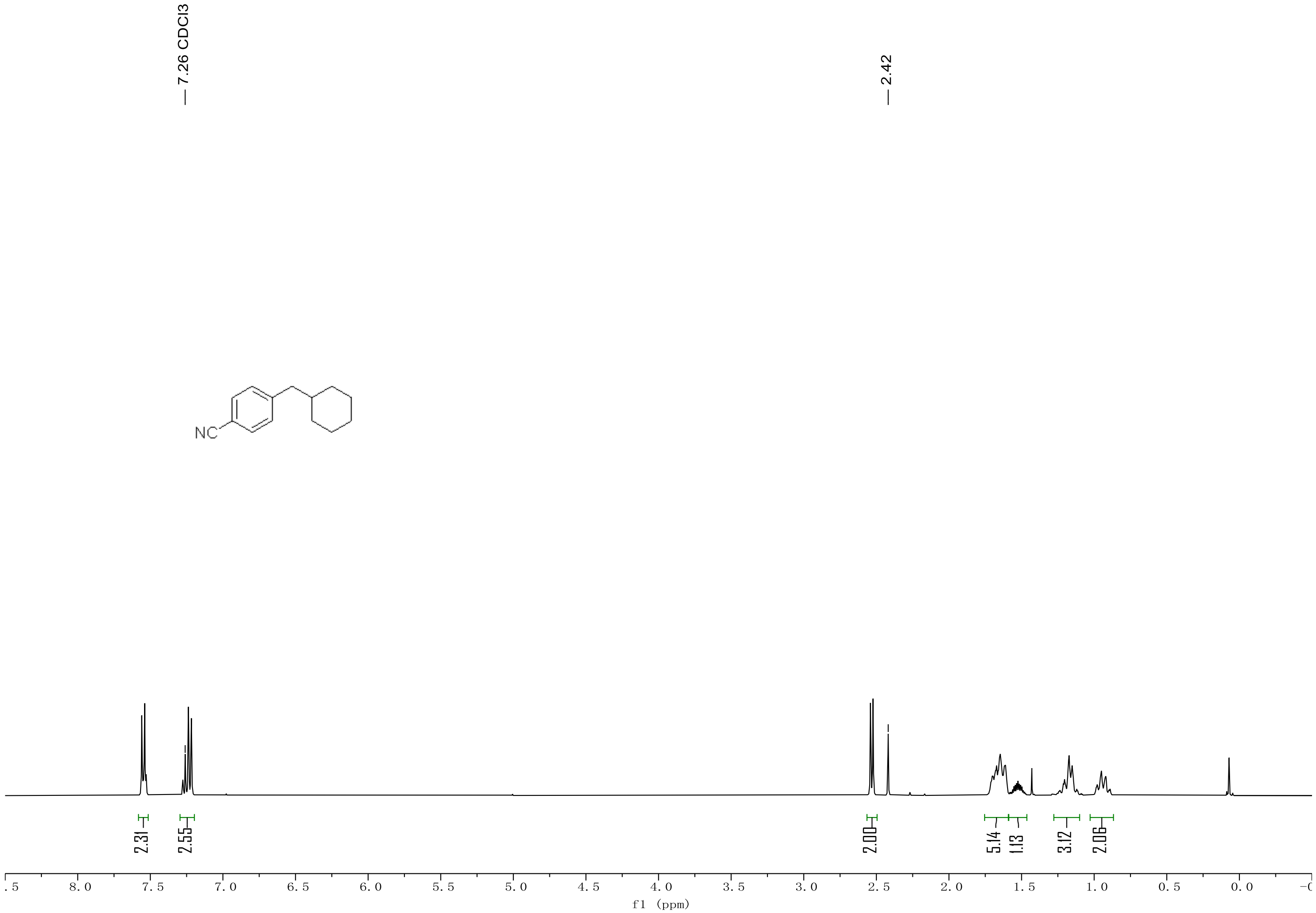


Figure S16 ^{13}C NMR of **3f**

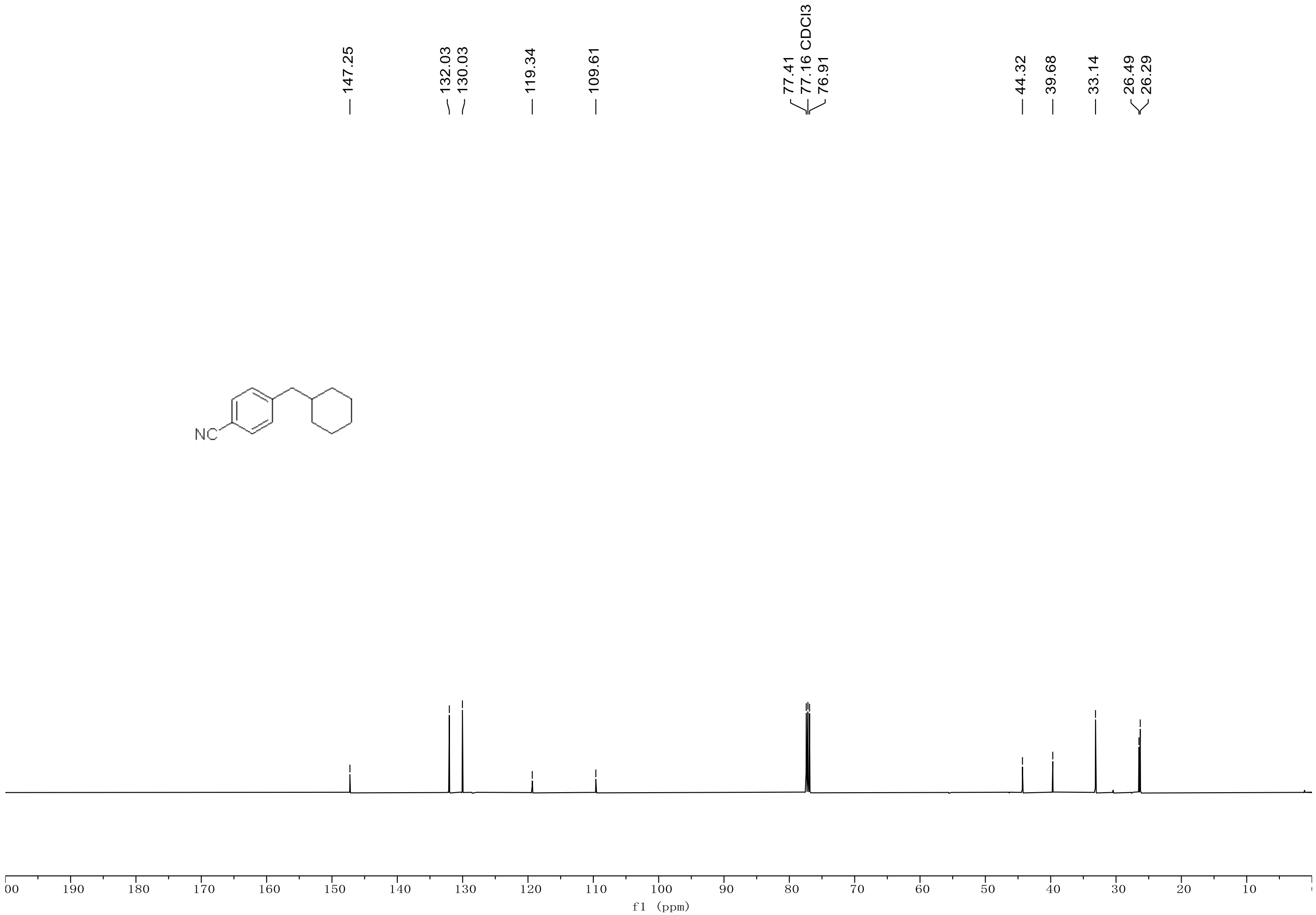


Figure S17 ^{1}H NMR of **3g**

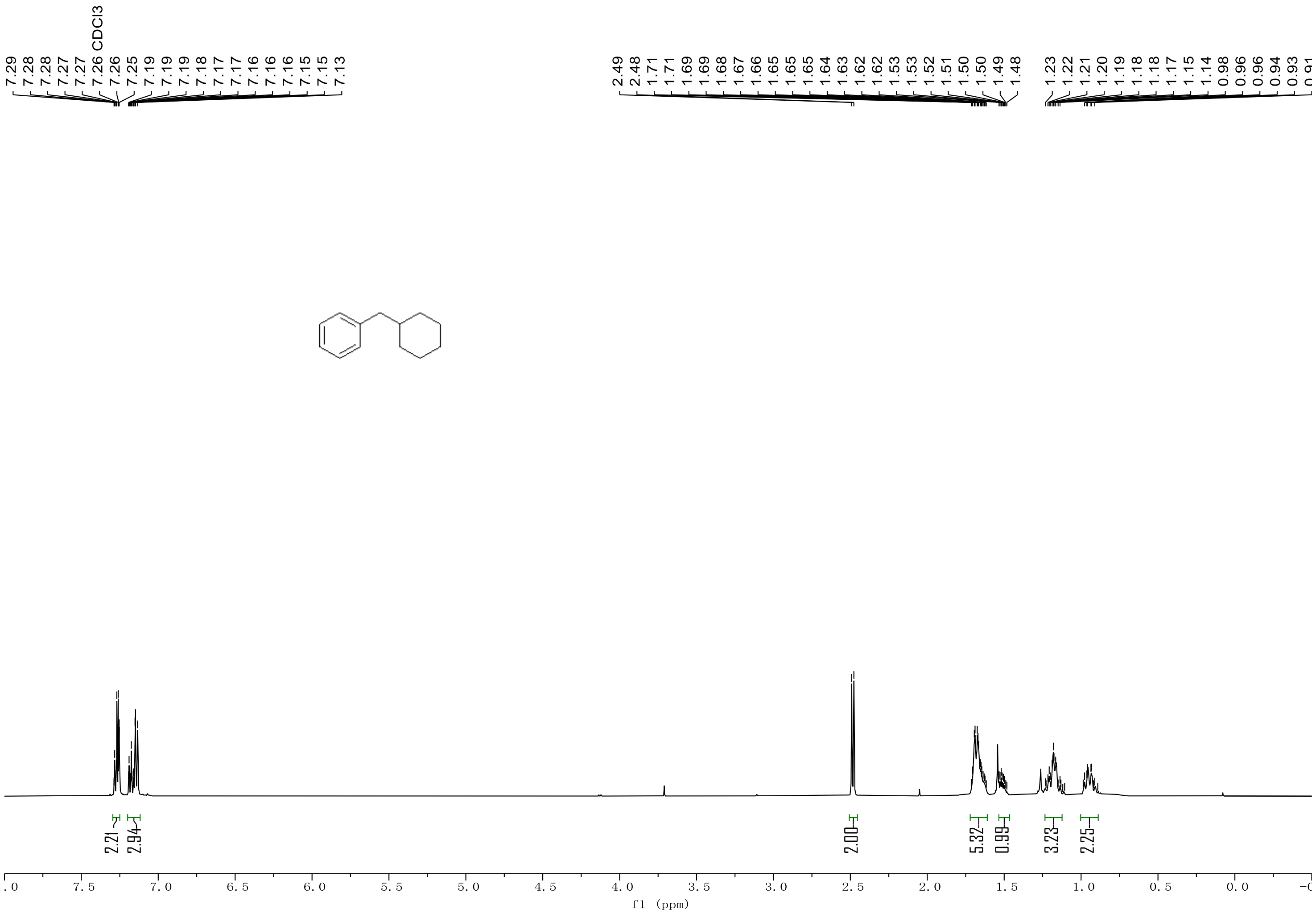


Figure S18 ^{1}H NMR of **3h**

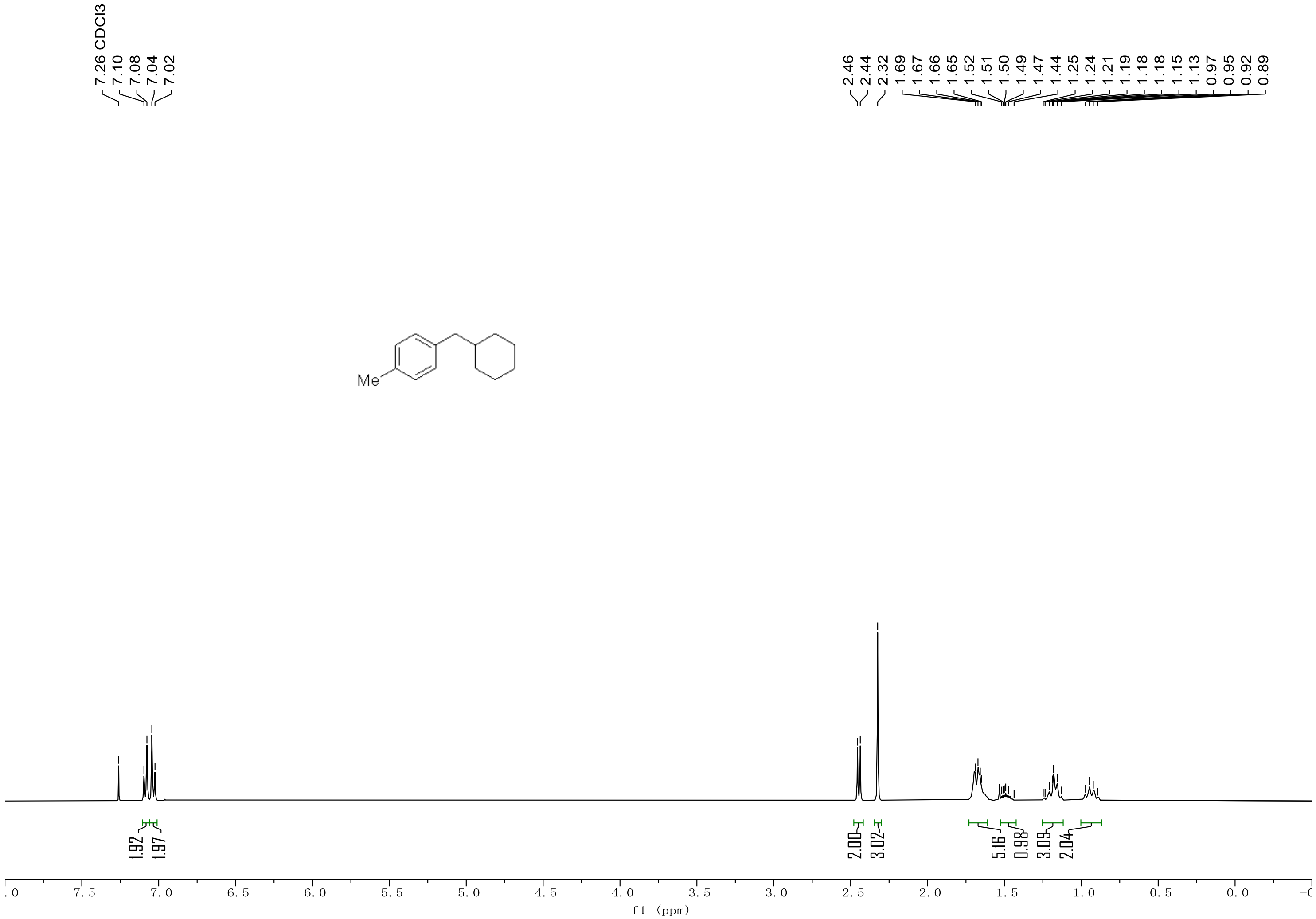


Figure S19 ^{13}C NMR of **3h**

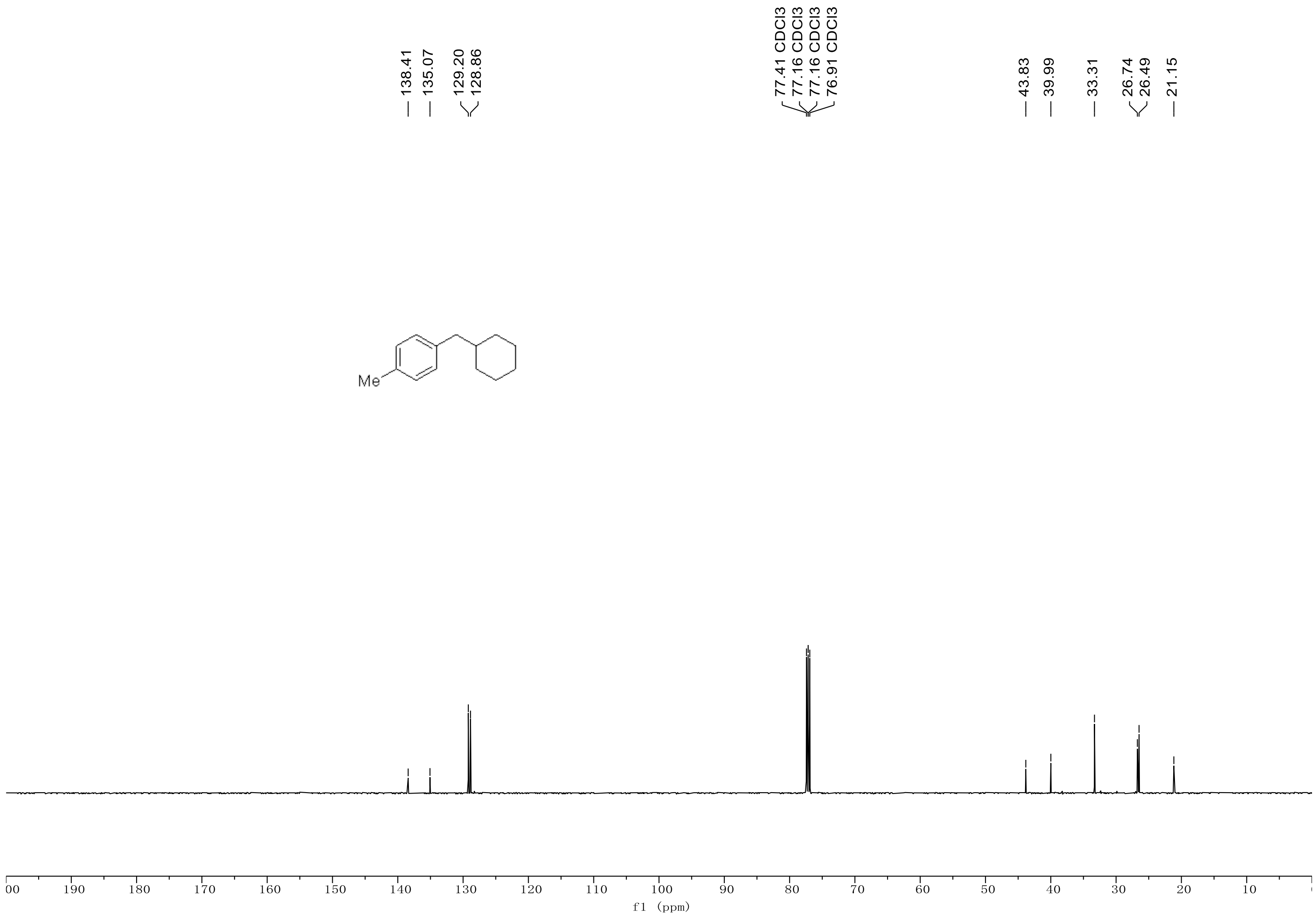


Figure S20 ^{1}H NMR of **3i**

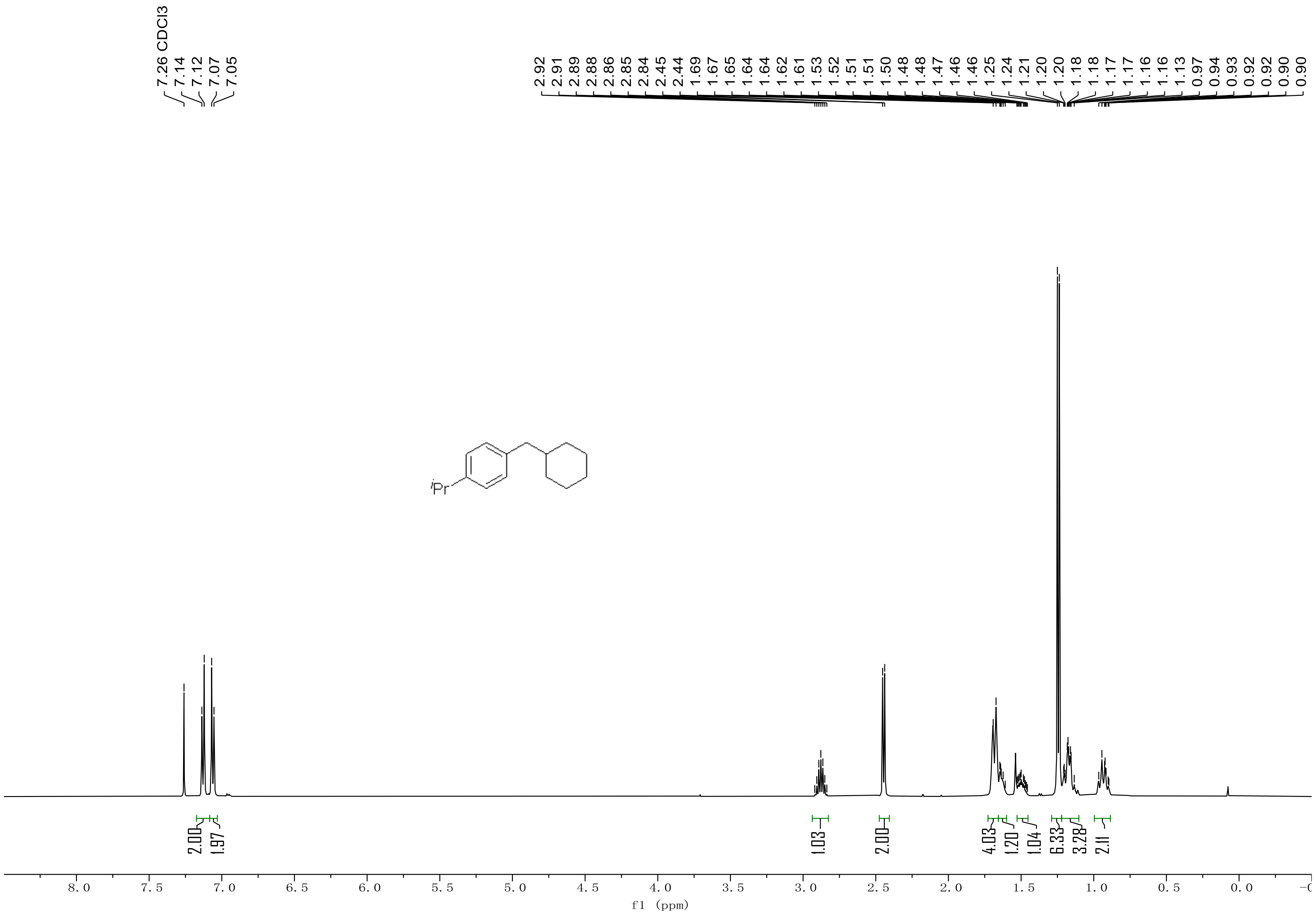


Figure S21 ^{13}C NMR of **3i**

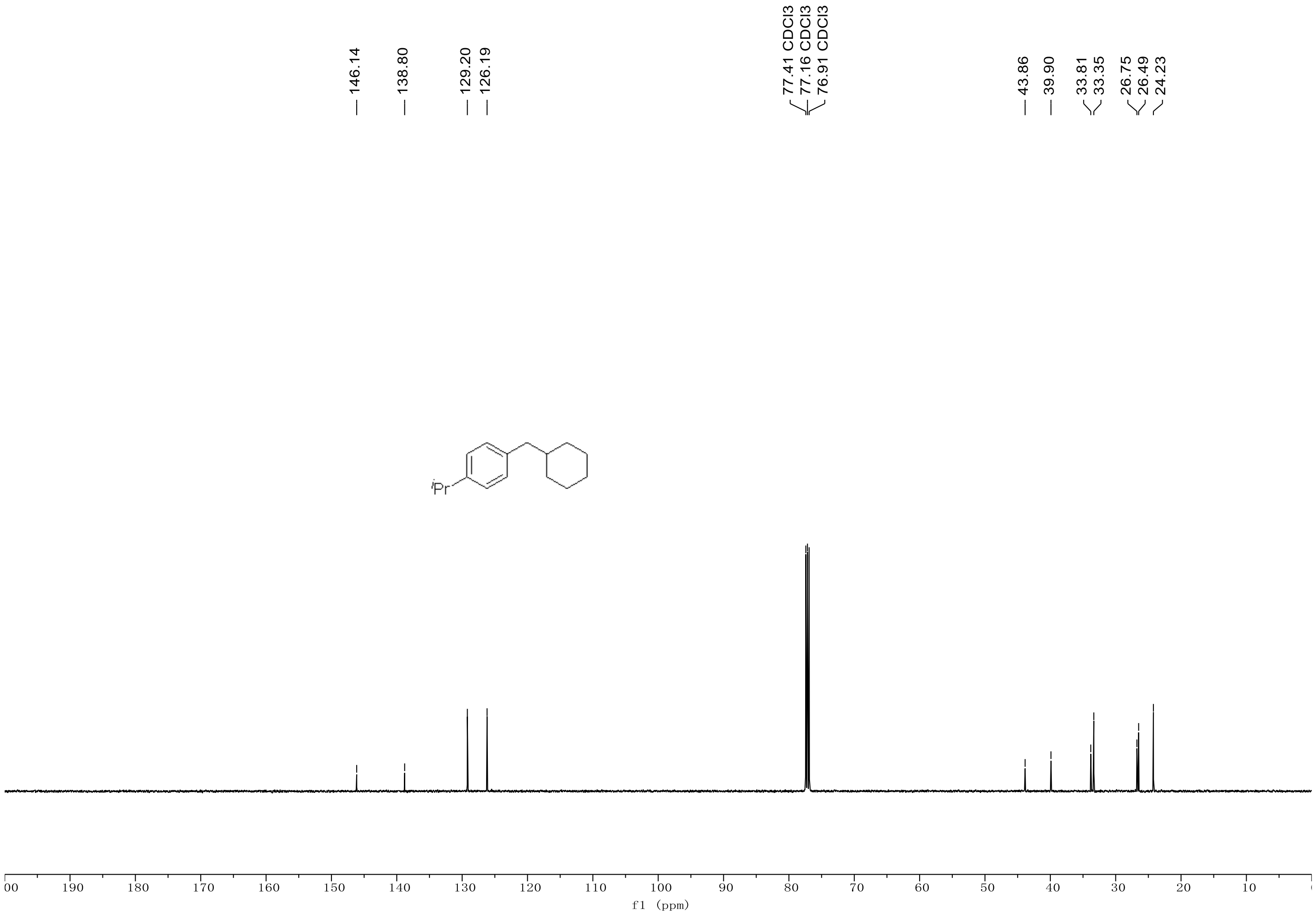


Figure S22 ^{1}H NMR of **3j**

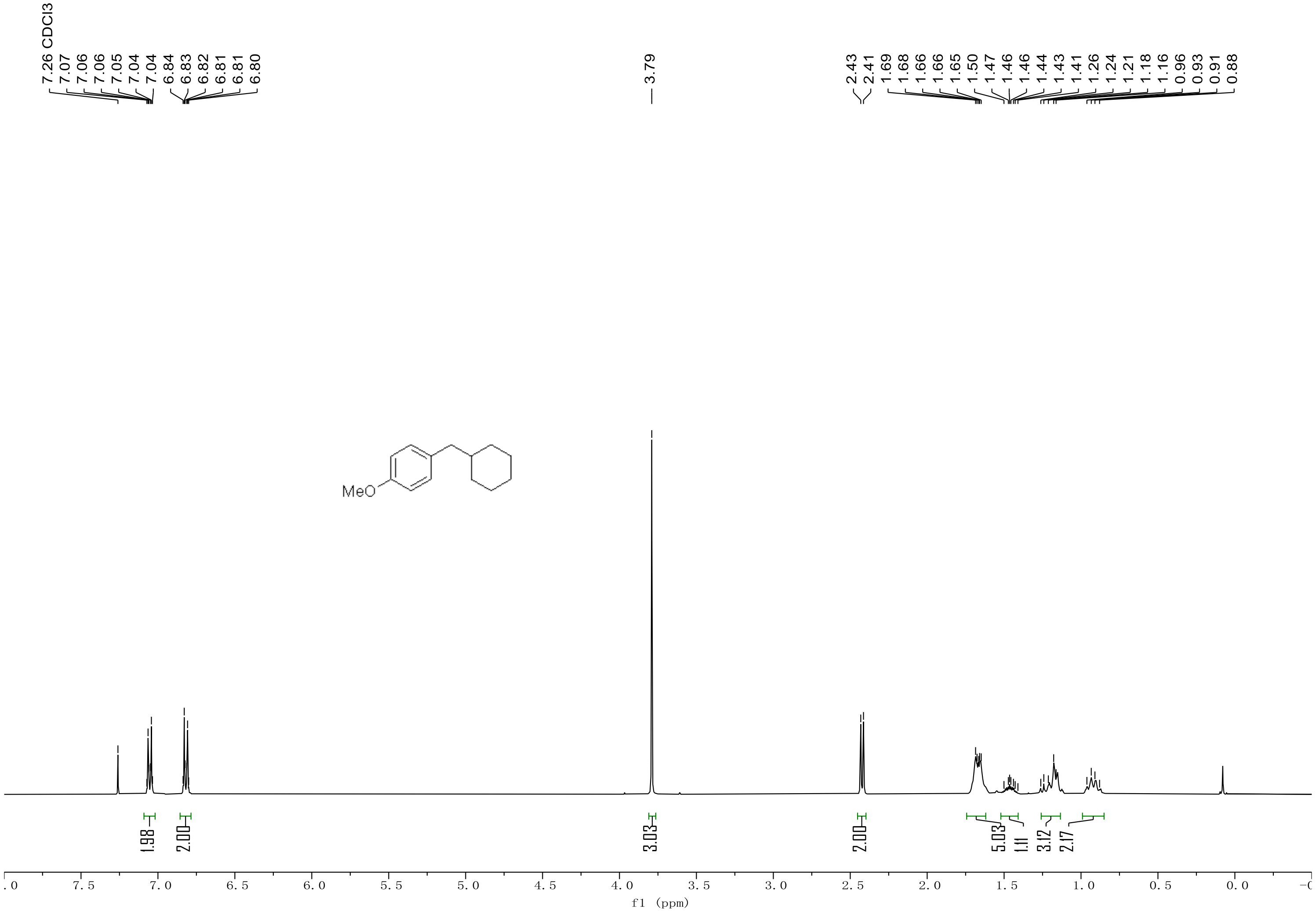


Figure S23 ^{13}C NMR of **3j**

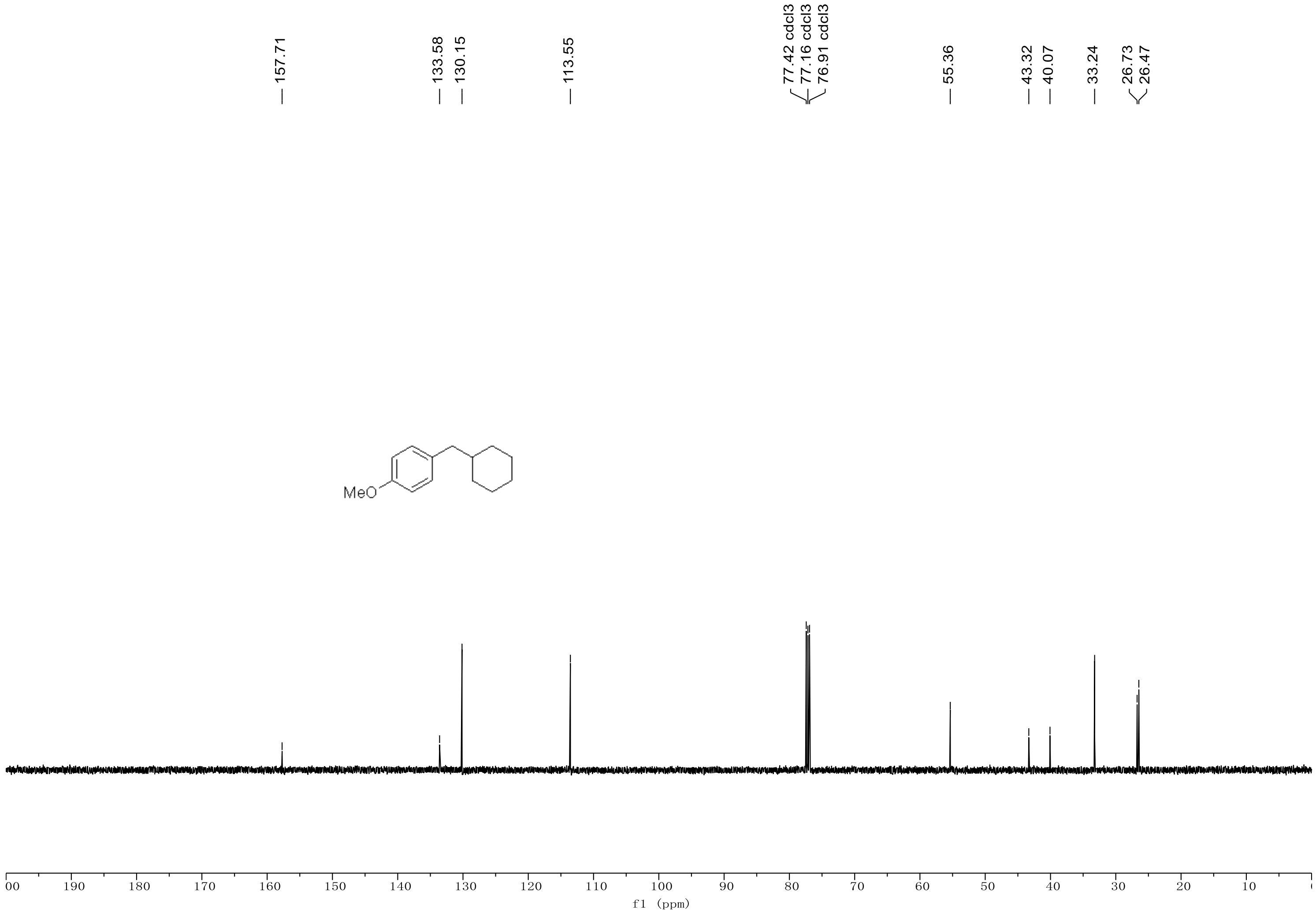


Figure S24 ^{1}H NMR of **3k**

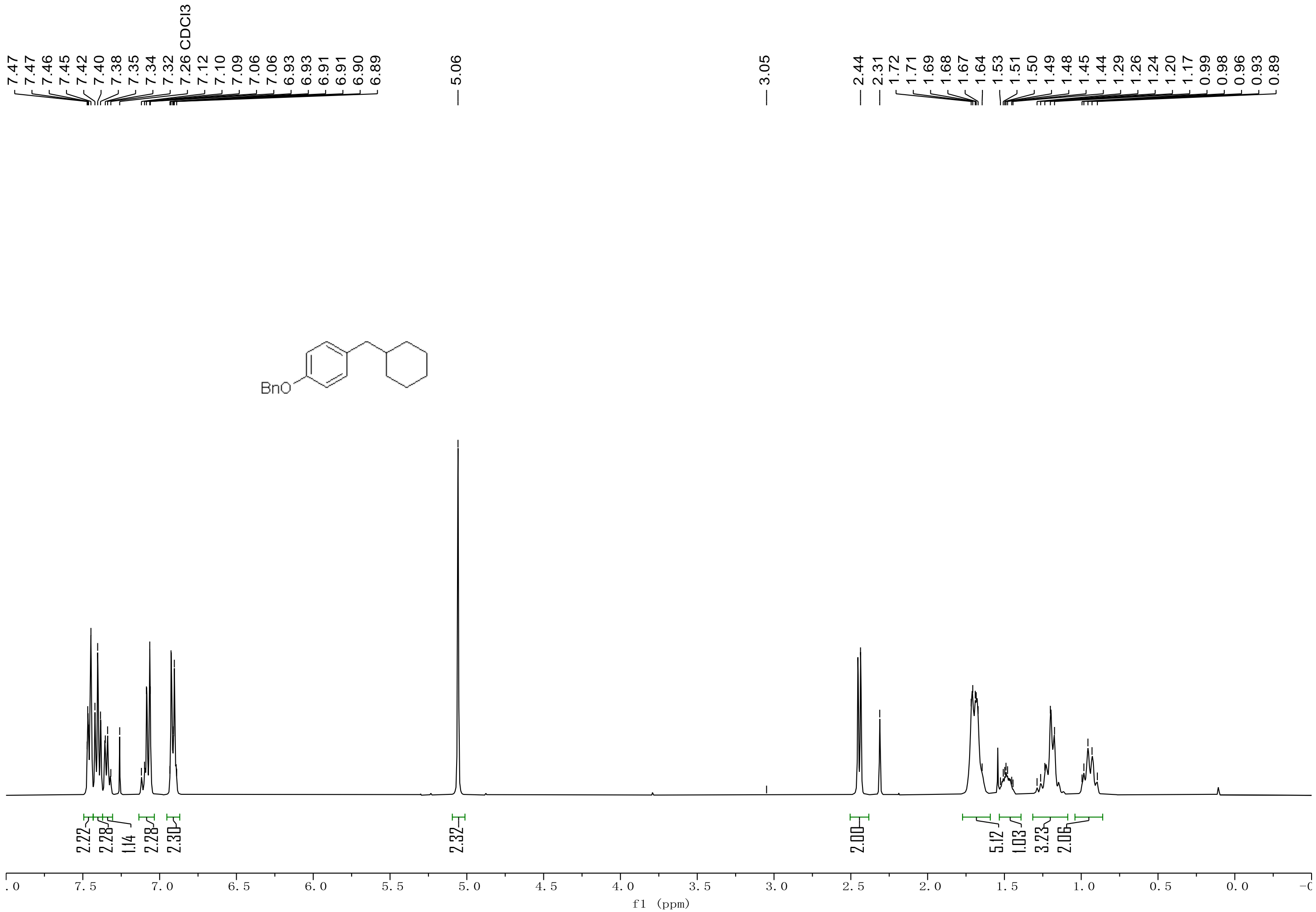


Figure S25 ^{13}C NMR of **3k**

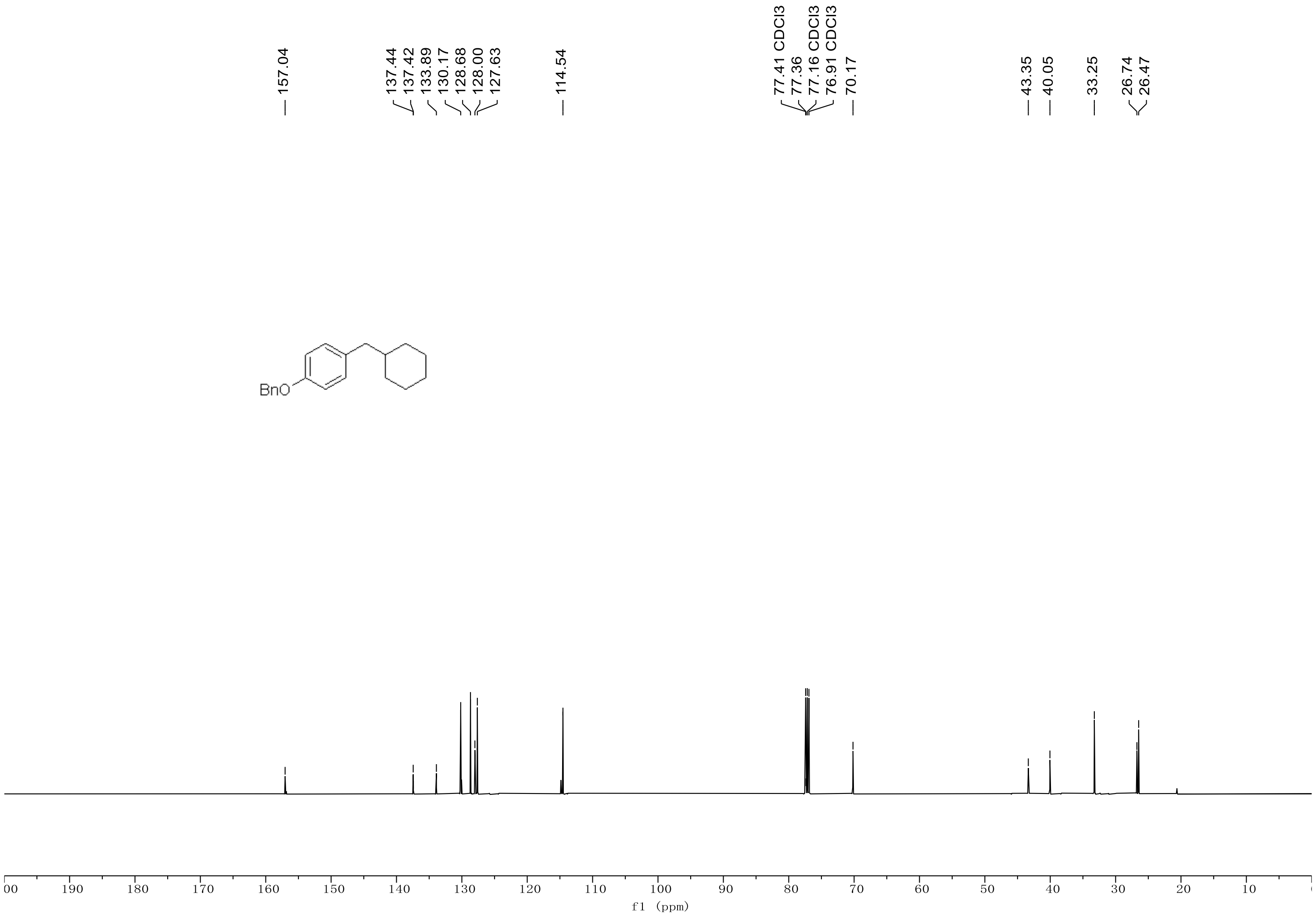


Figure S26 ^{1}H NMR of **3l**

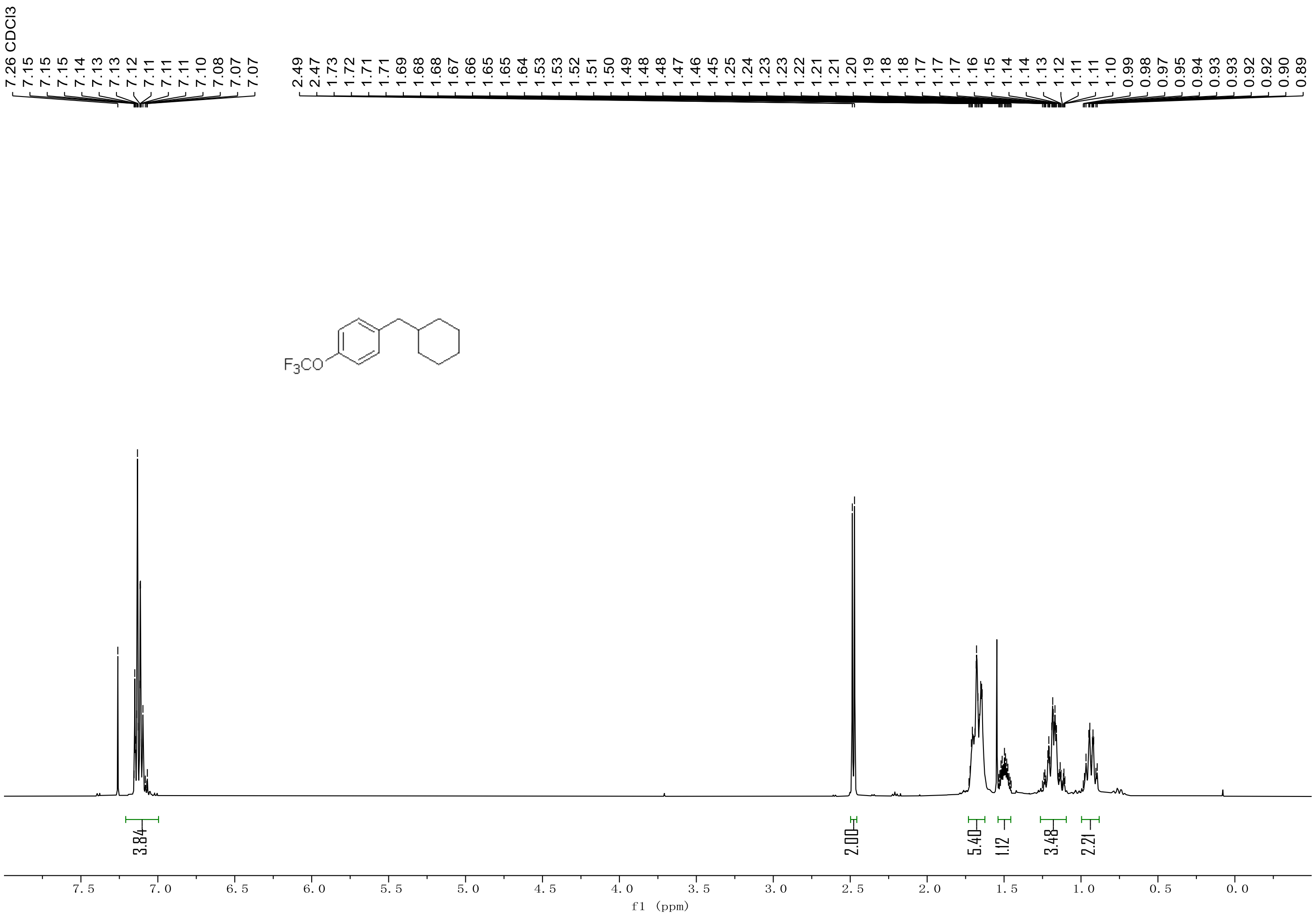


Figure S27 ^{13}C NMR of **3l**

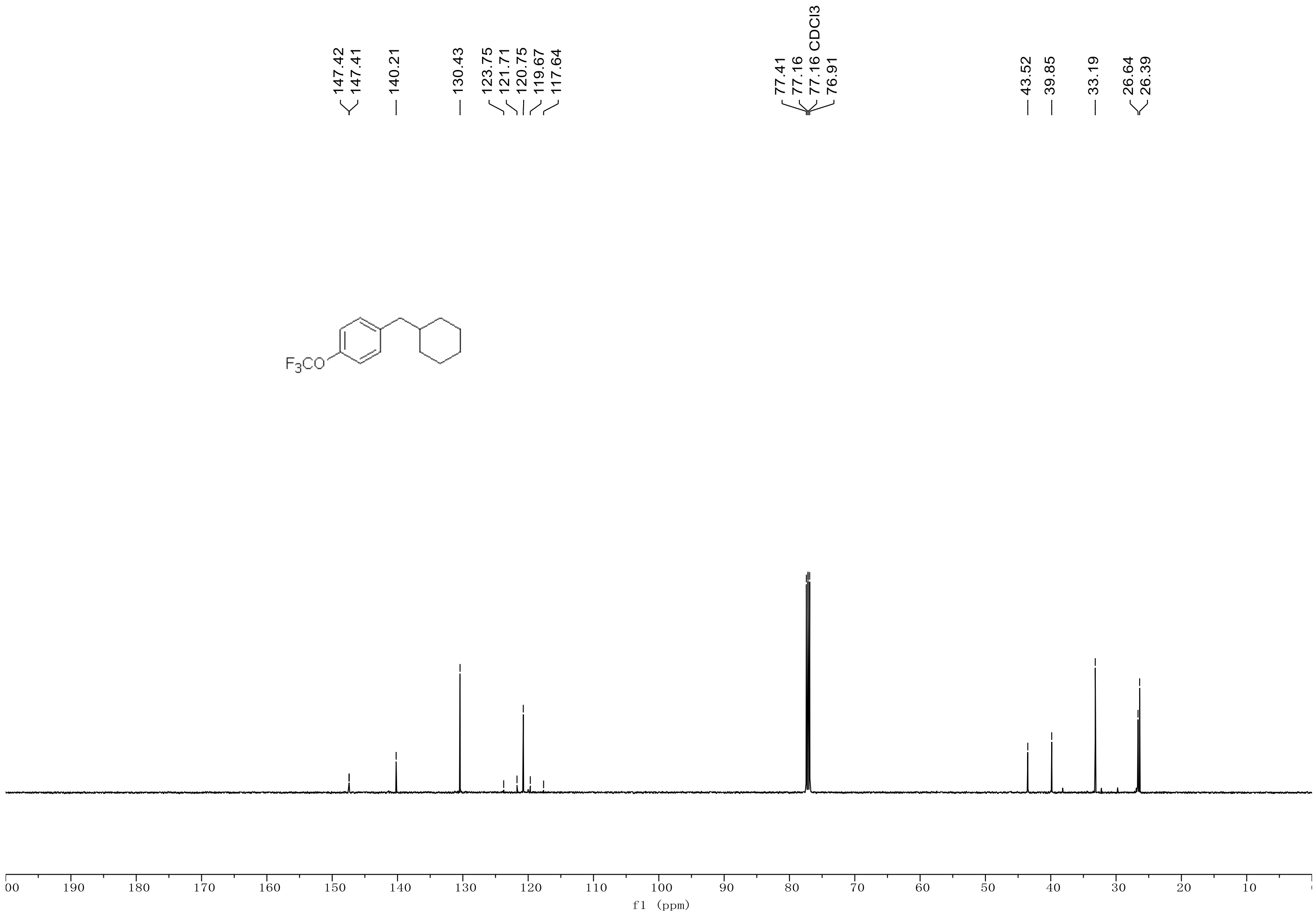


Figure S28 ^{19}F NMR of **3l**

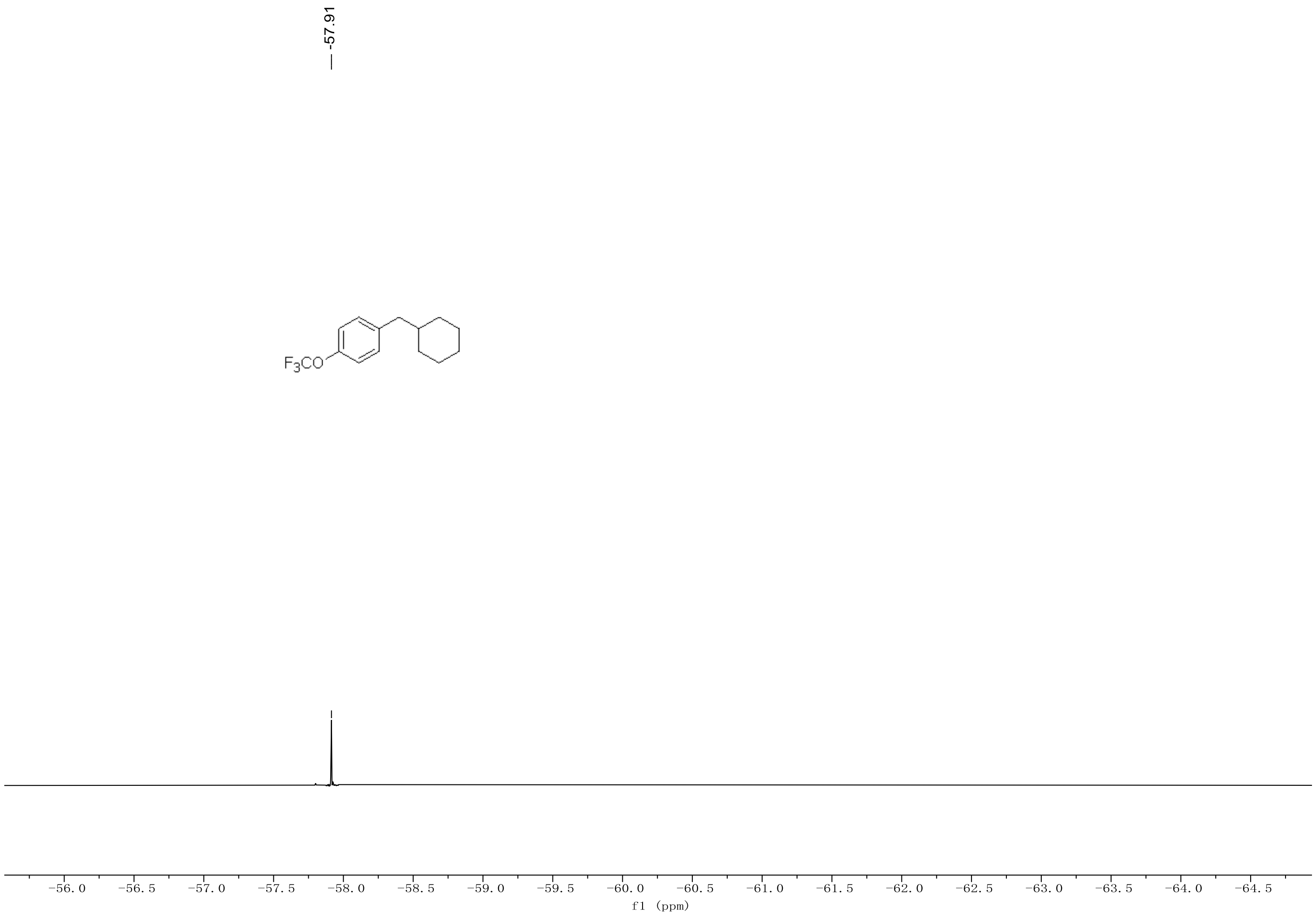


Figure S29 ^{1}H NMR of **3m**

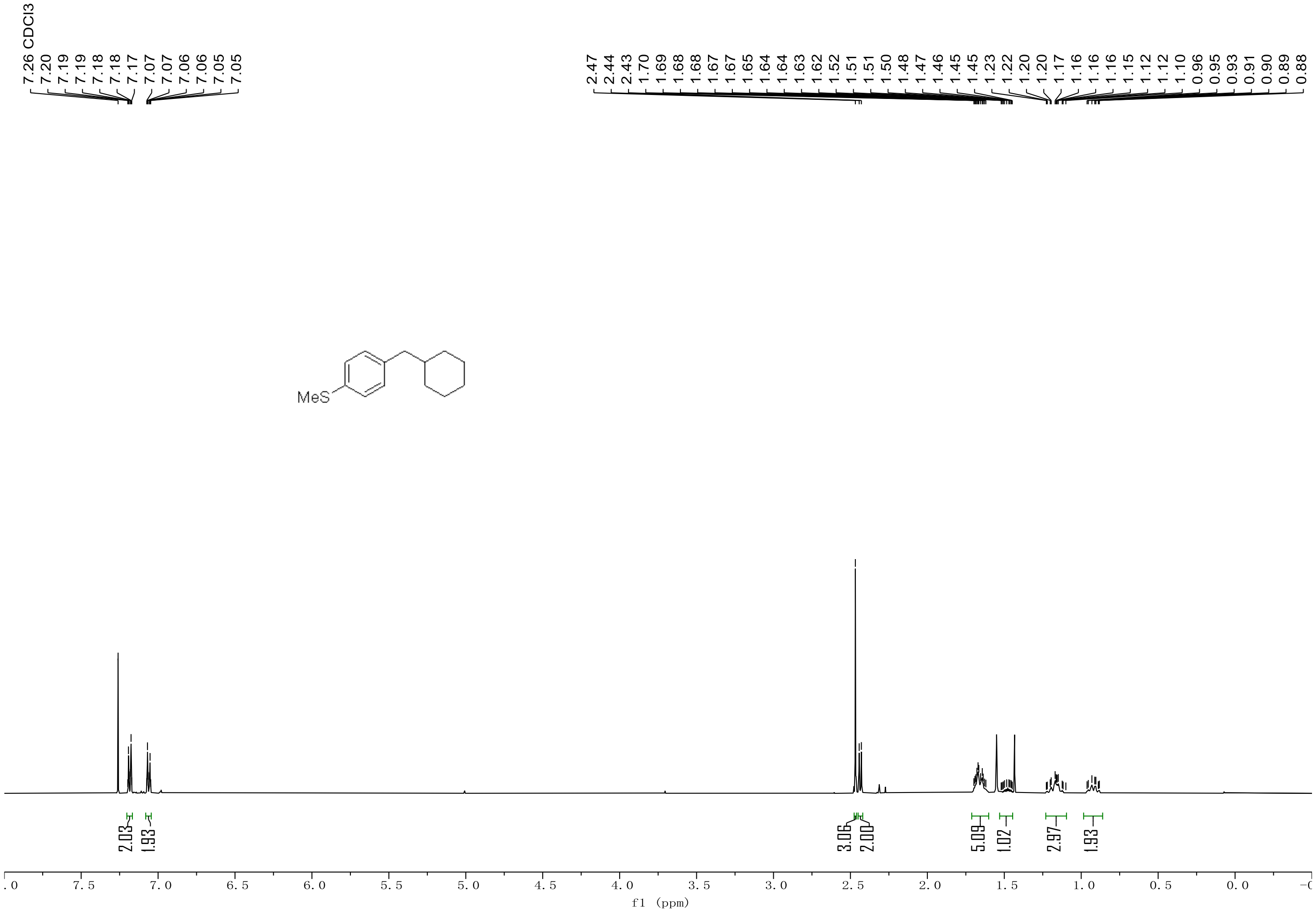


Figure S30 ^{13}C NMR of **3m**

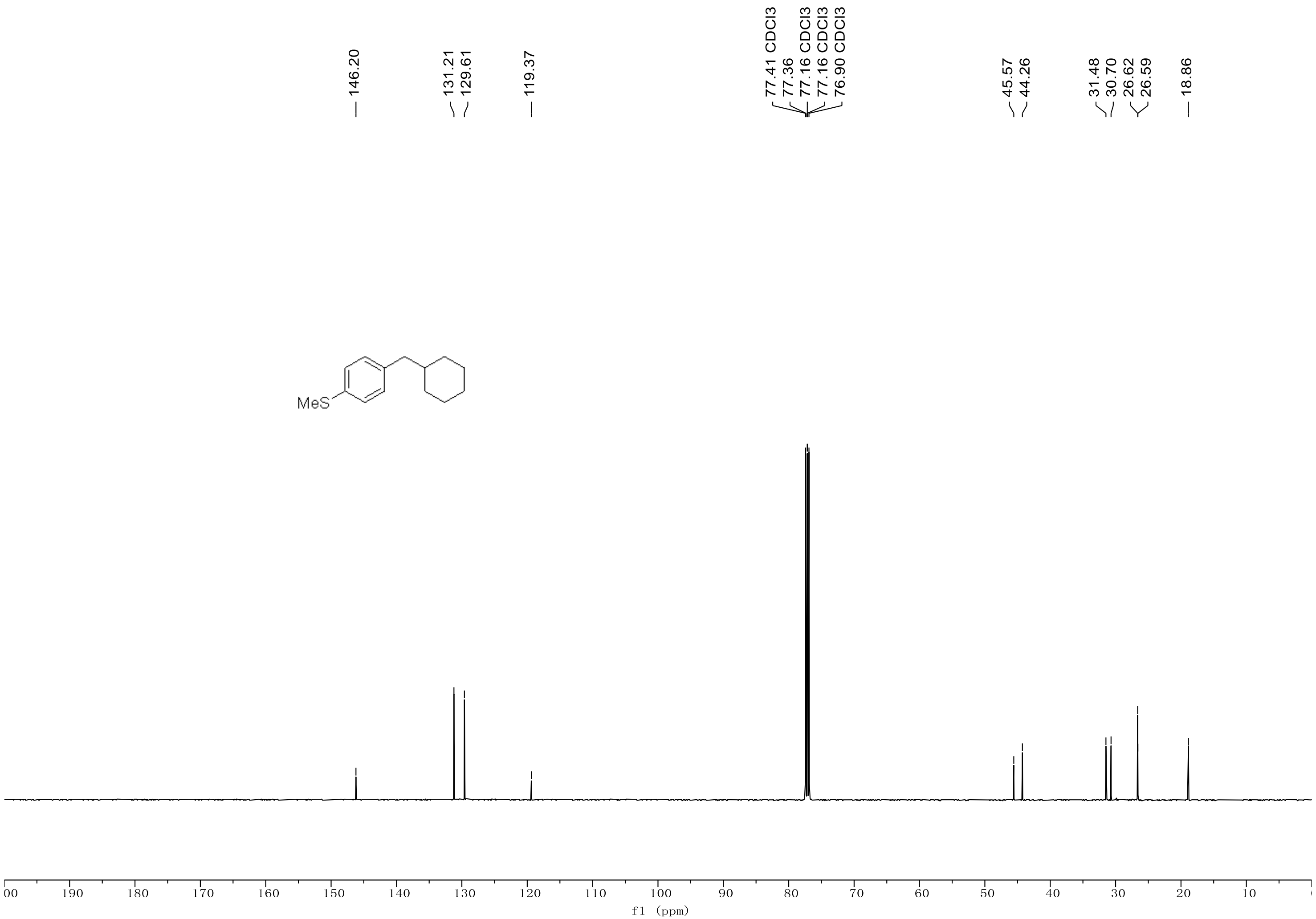


Figure S31 ^{1}H NMR of **3n**

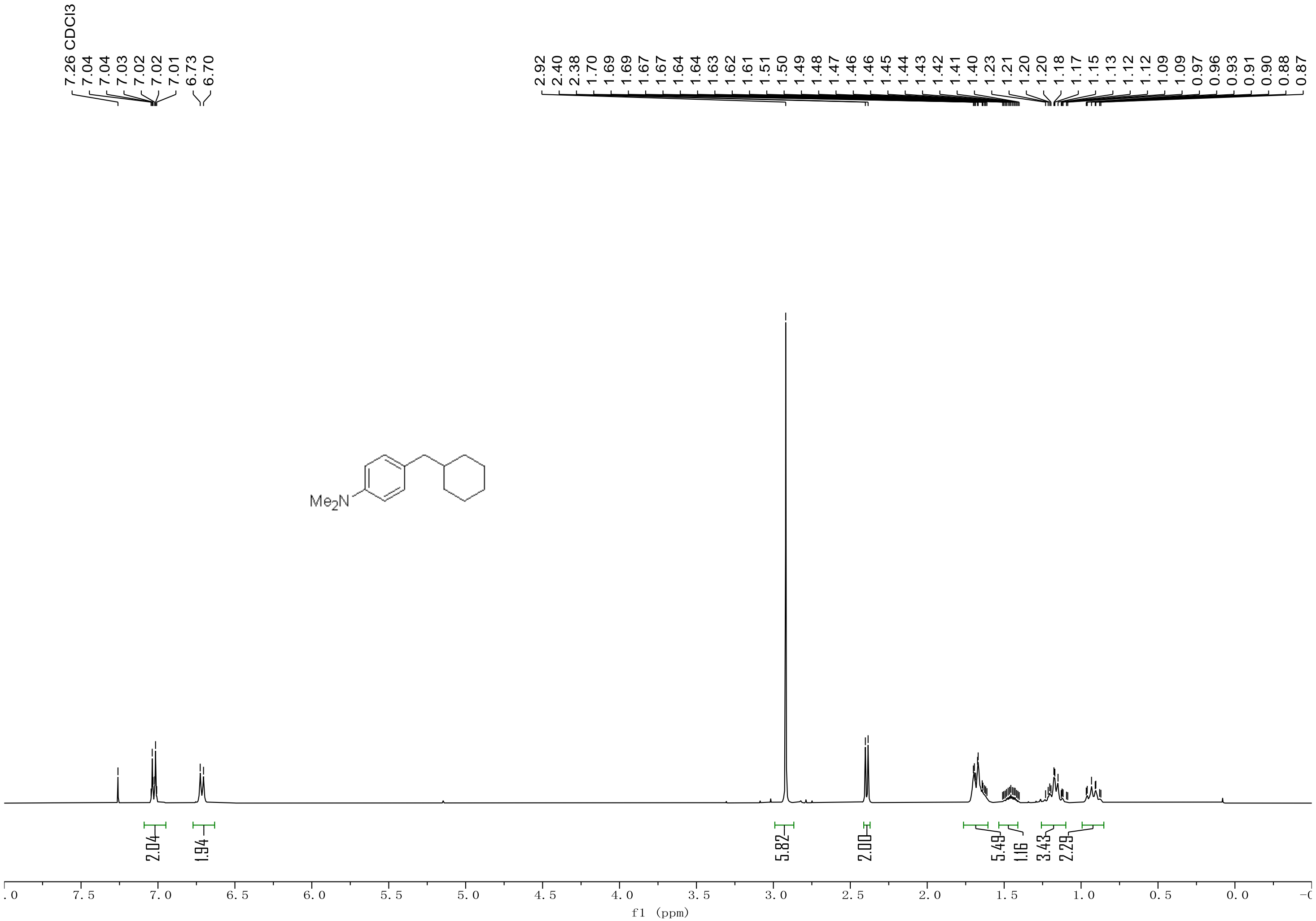


Figure S32 ^{13}C NMR of **3n**

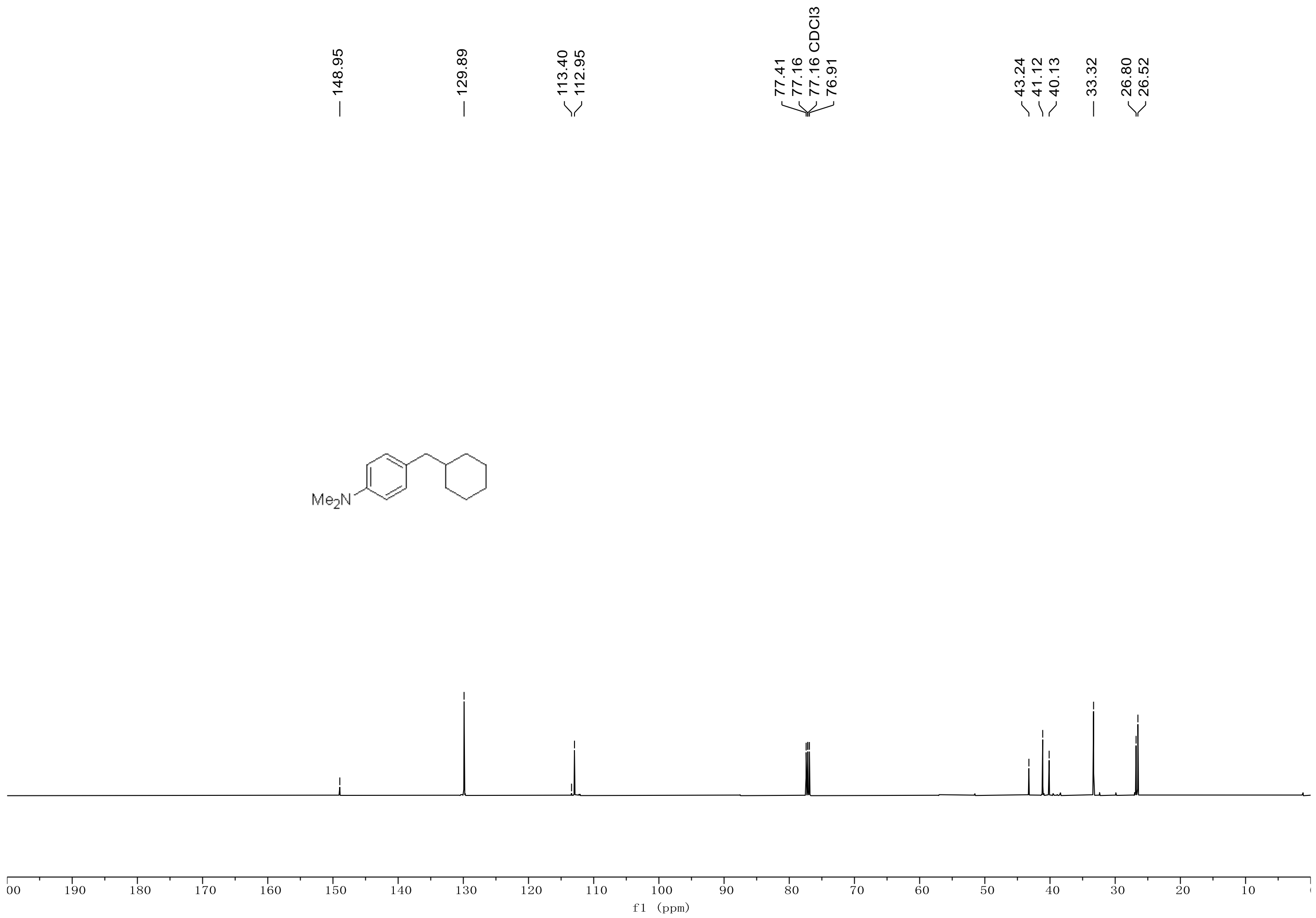


Figure S33 ^{1}H NMR of **3o**

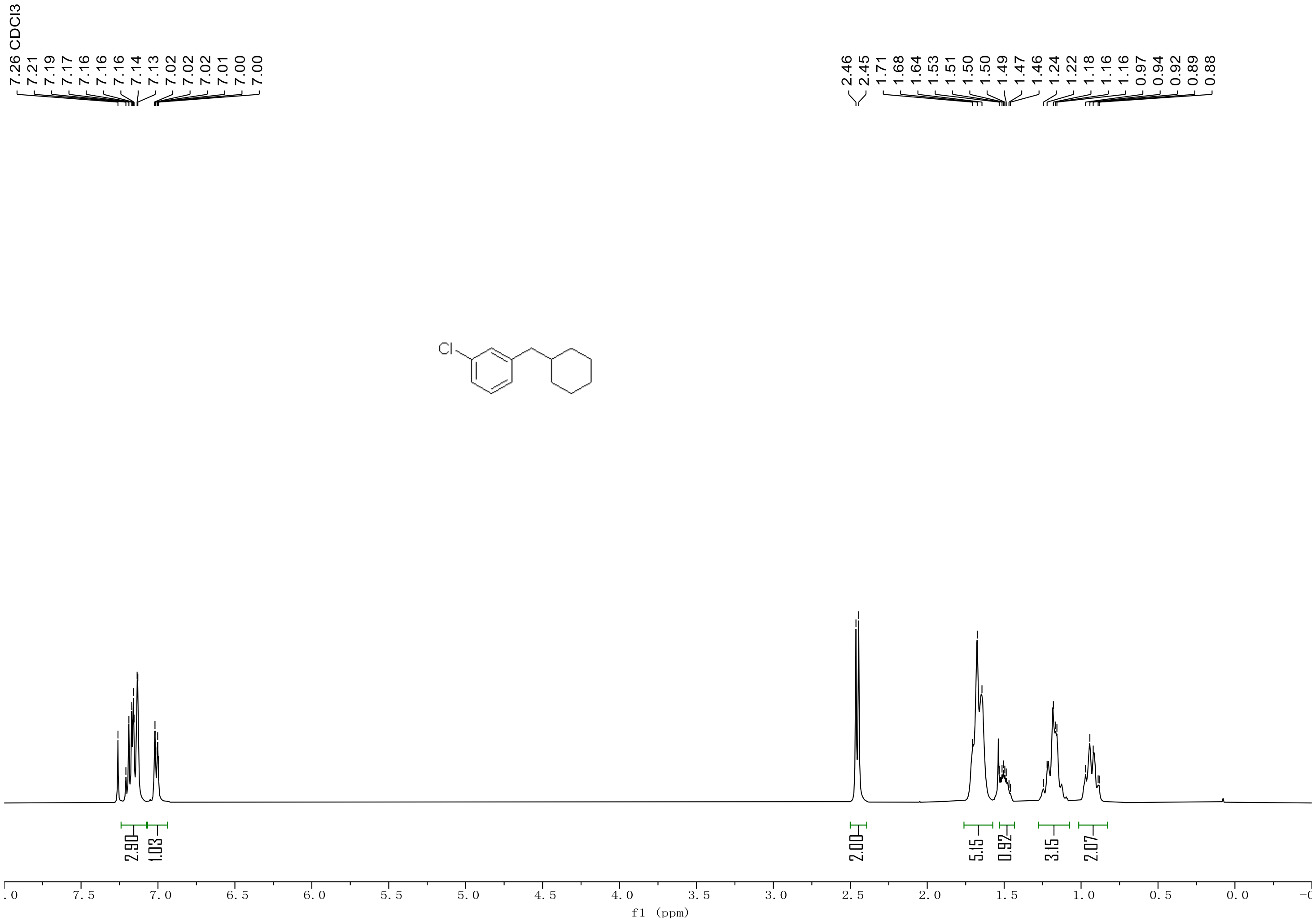


Figure S34 ^{13}C NMR of **3o**

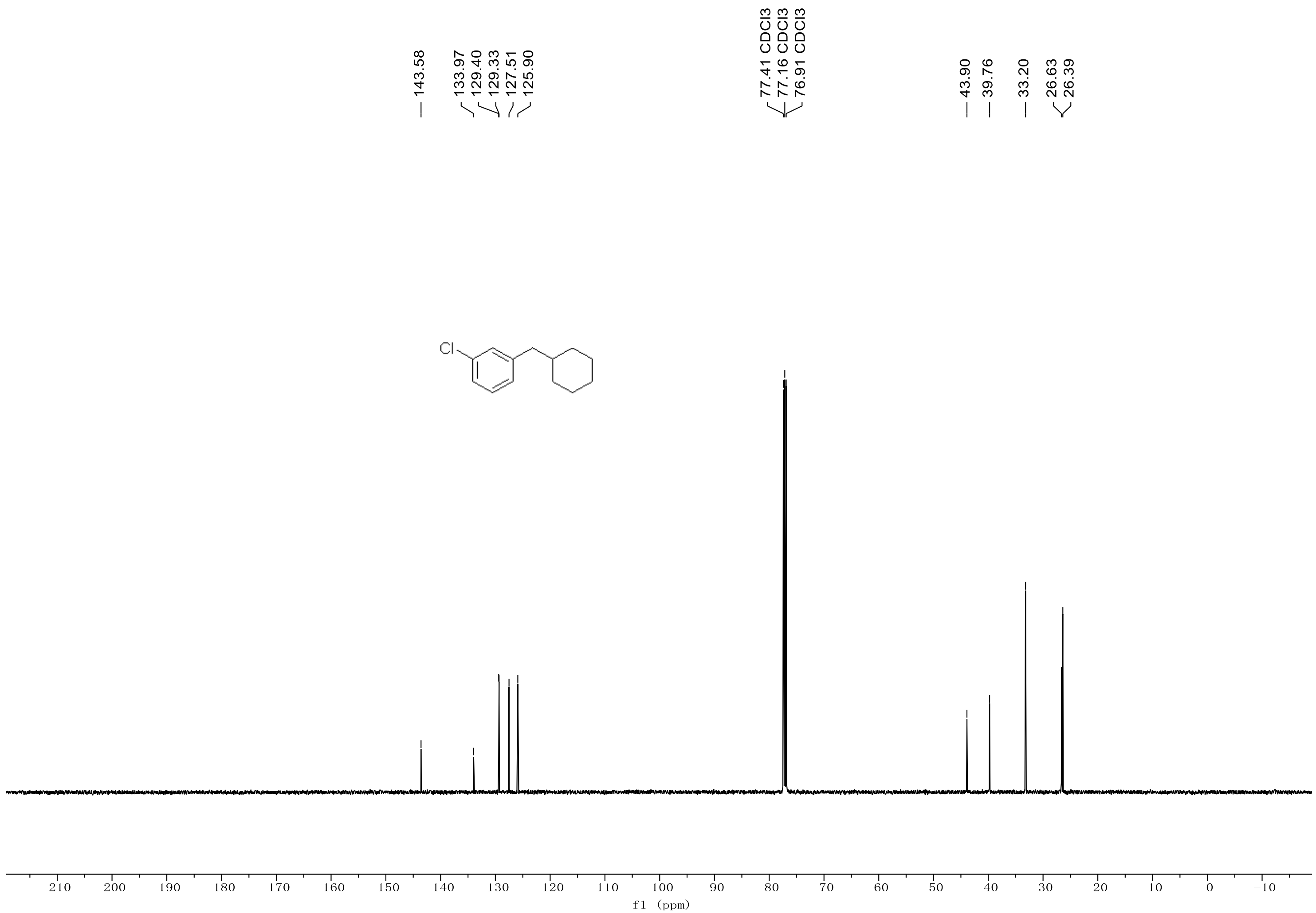


Figure S35 ^{1}H NMR of **3p**

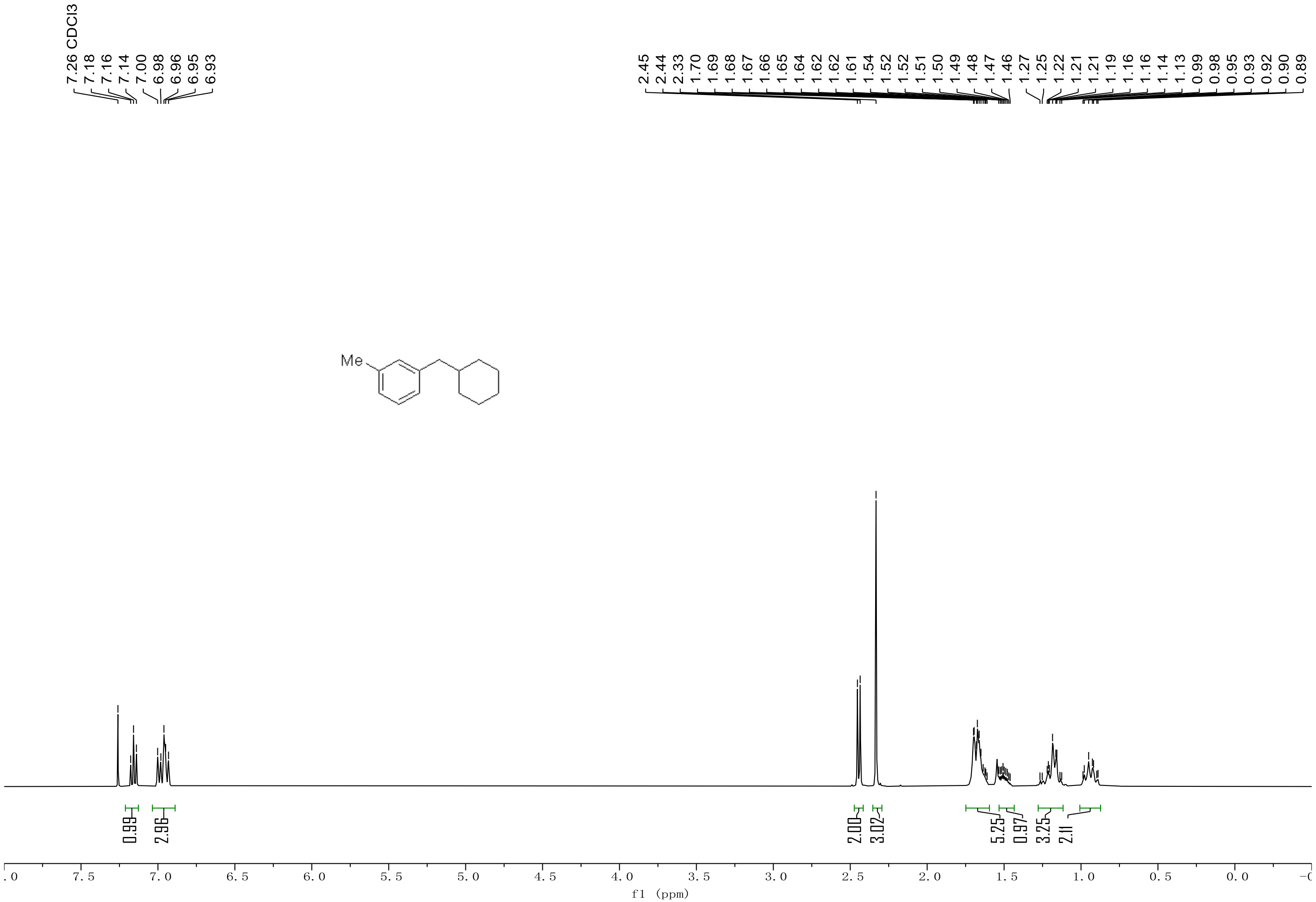


Figure S36 ^{13}C NMR of **3p**

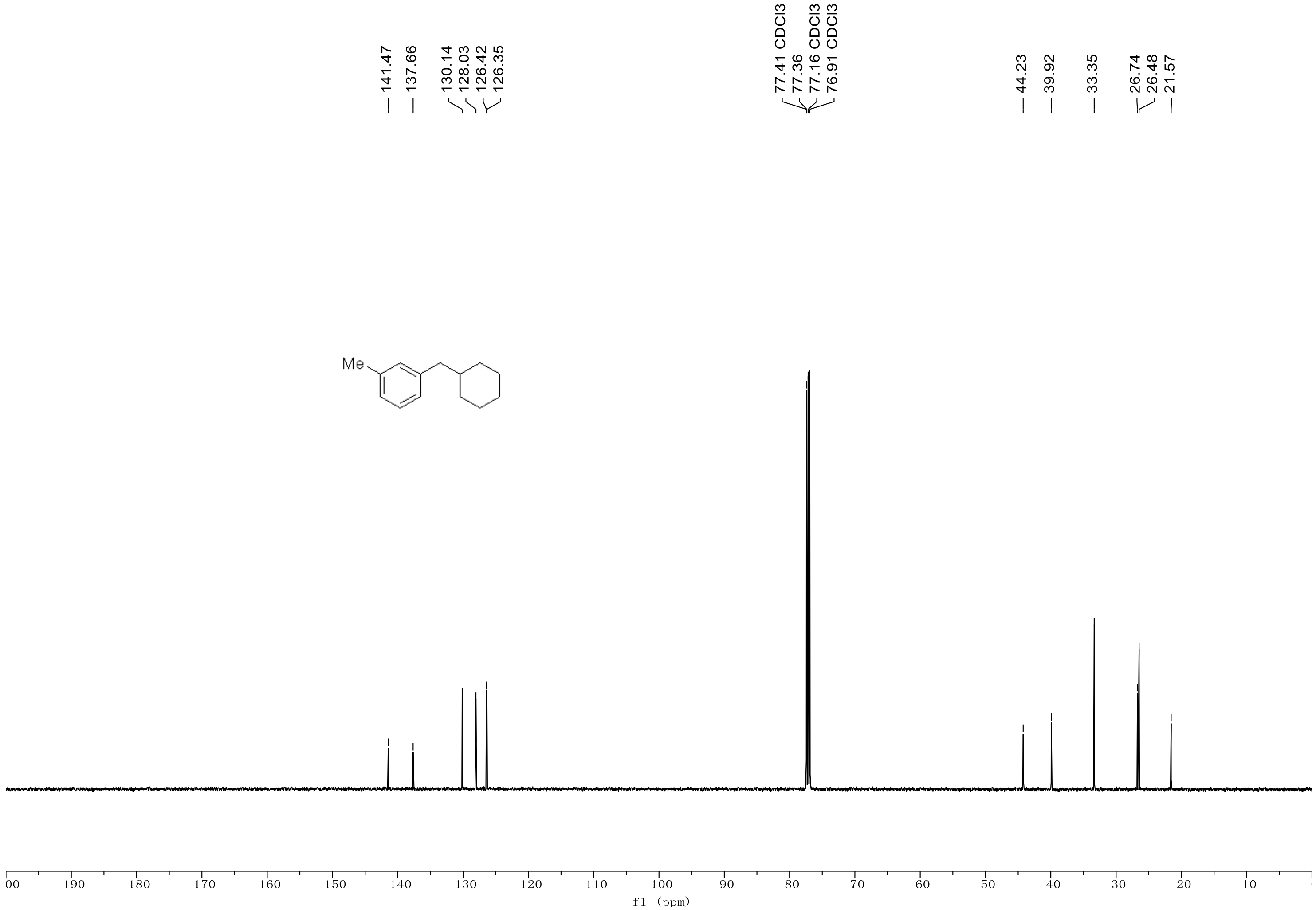


Figure S37 ^{1}H NMR of **3q**

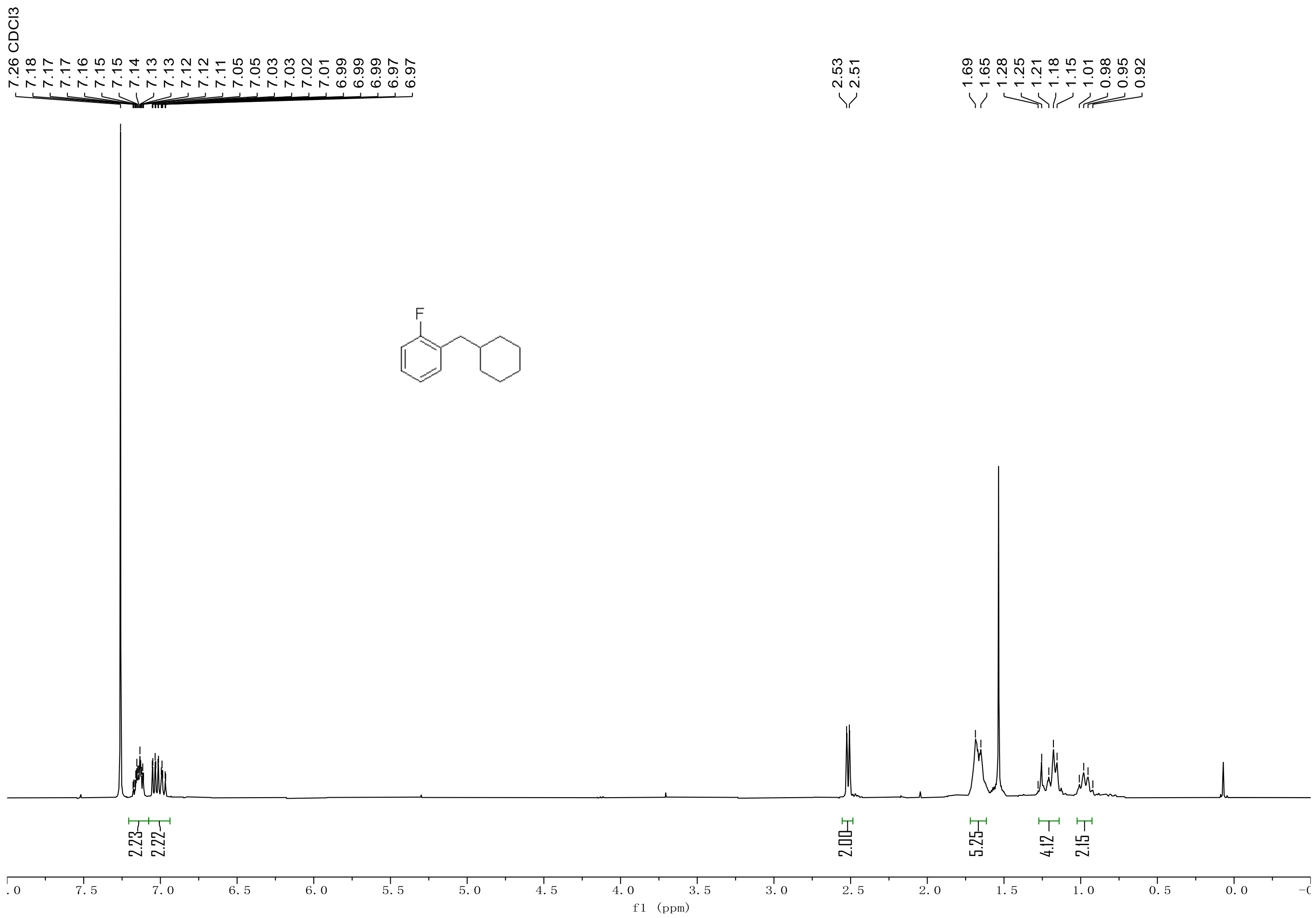


Figure S38 ^{13}C NMR of **3p**

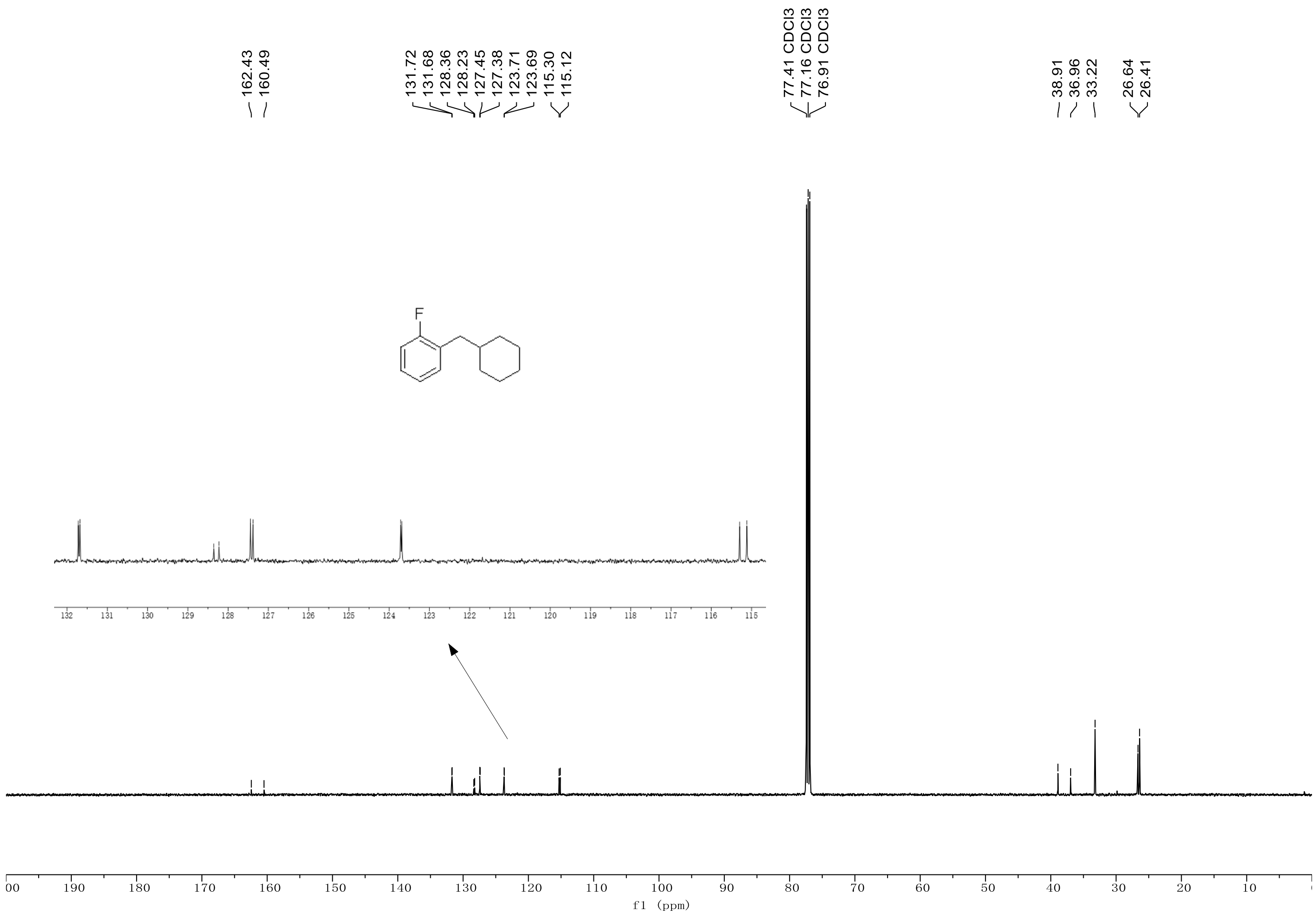


Figure S39 ^{19}F NMR of **3p**

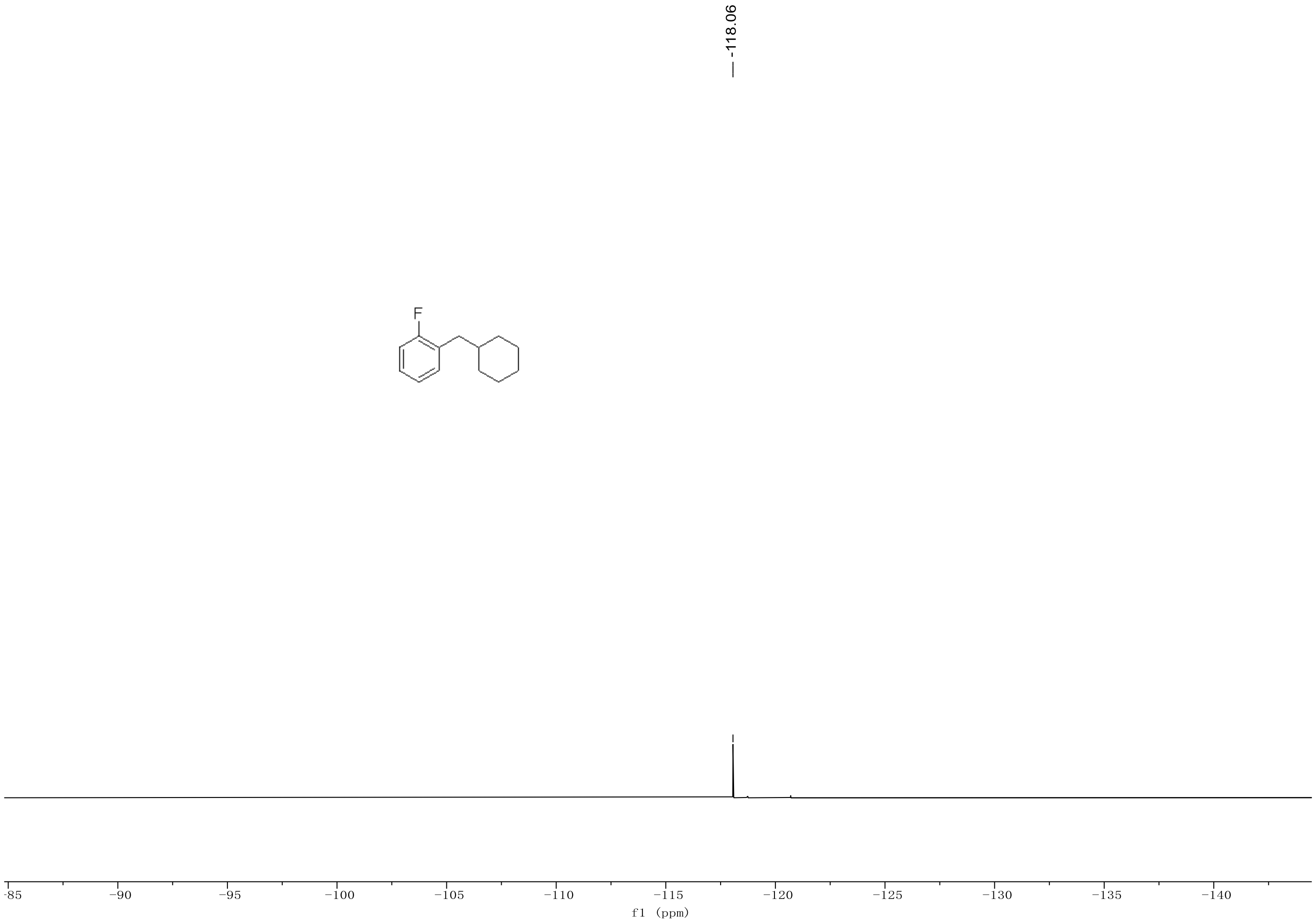


Figure 40 ^{1}H NMR of **3r**

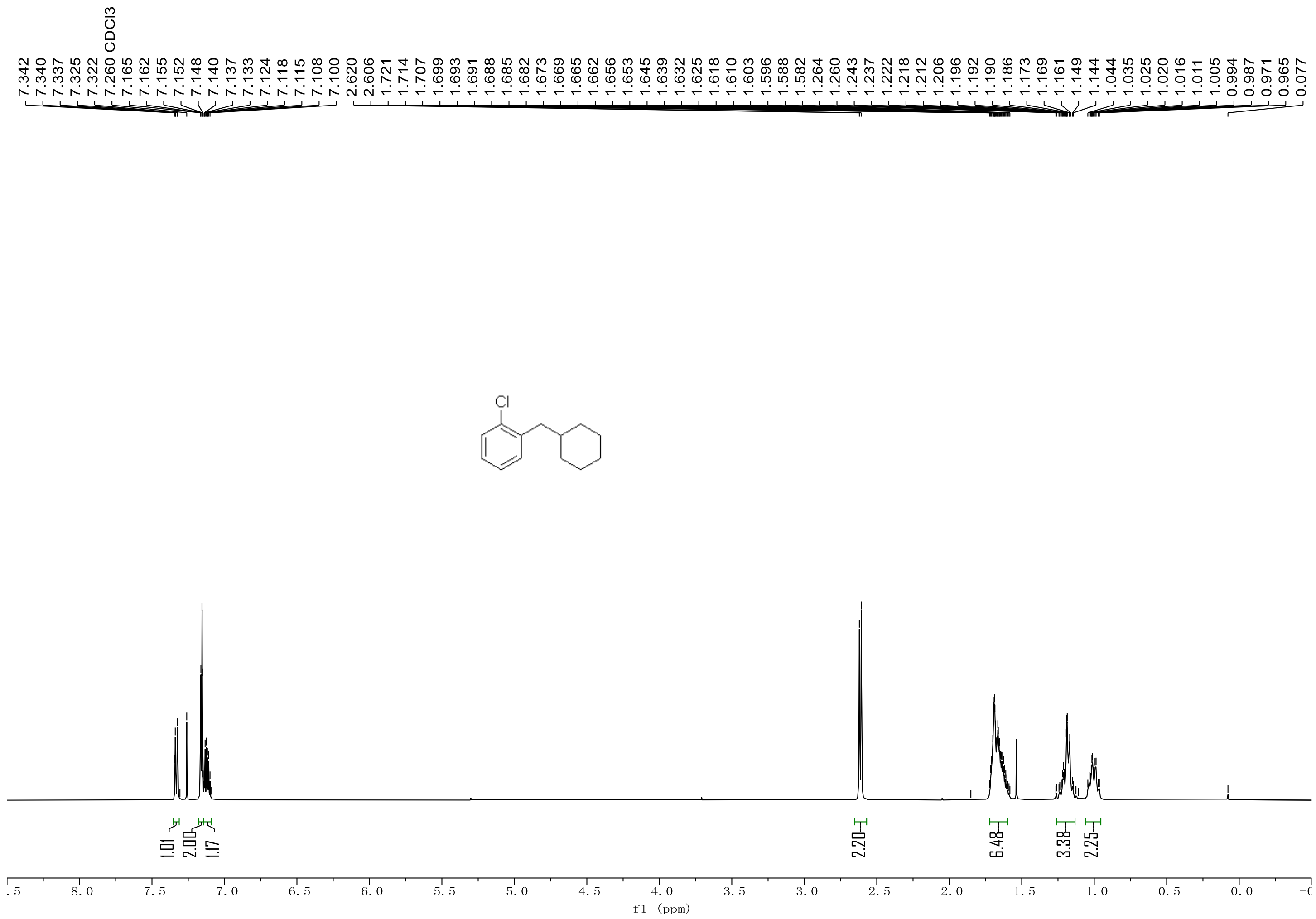


Figure S41 ^{13}C NMR of **3r**

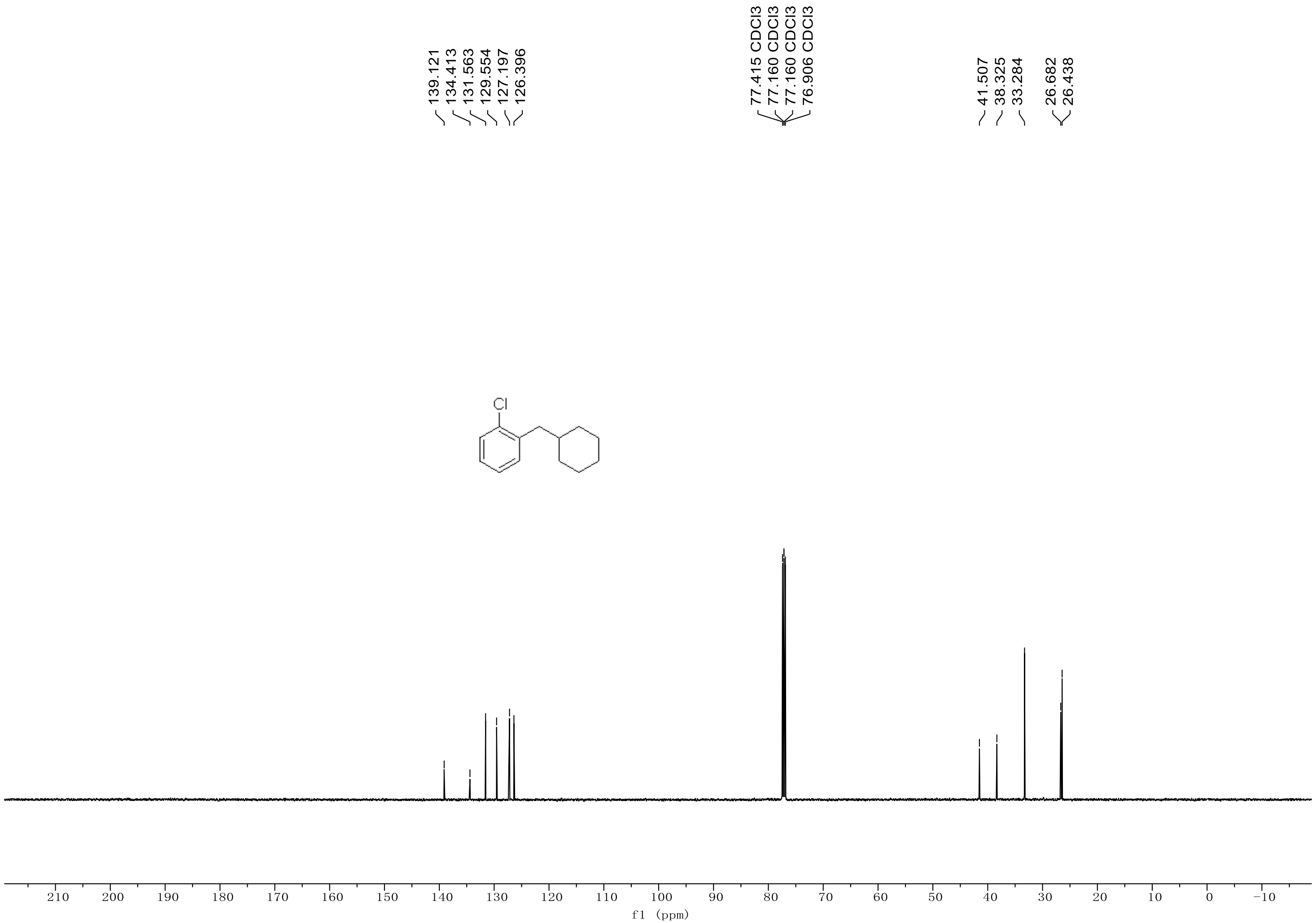


Figure S42 ^{1}H NMR of **3s**

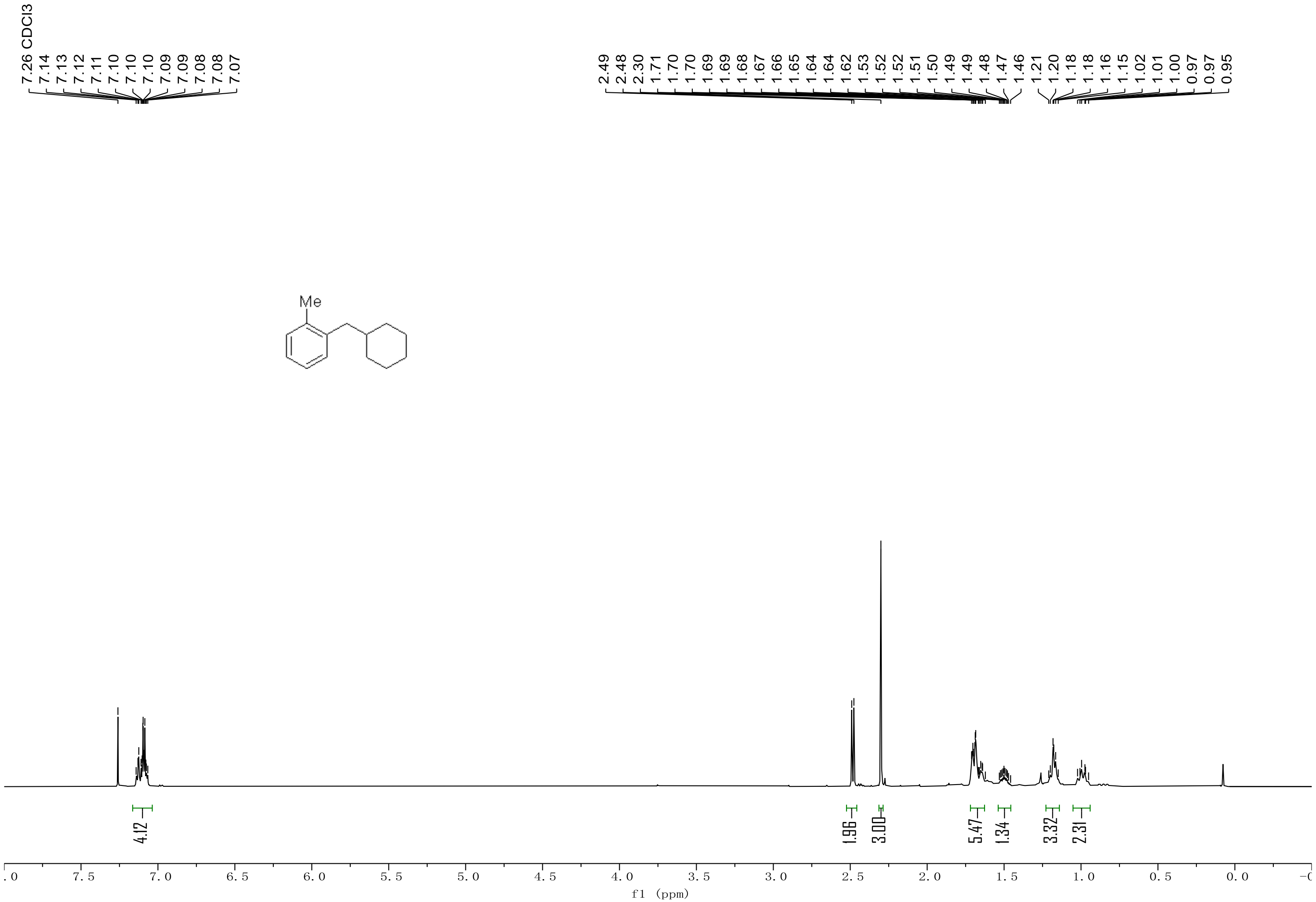


Figure S43 ^{13}C NMR of **3s**

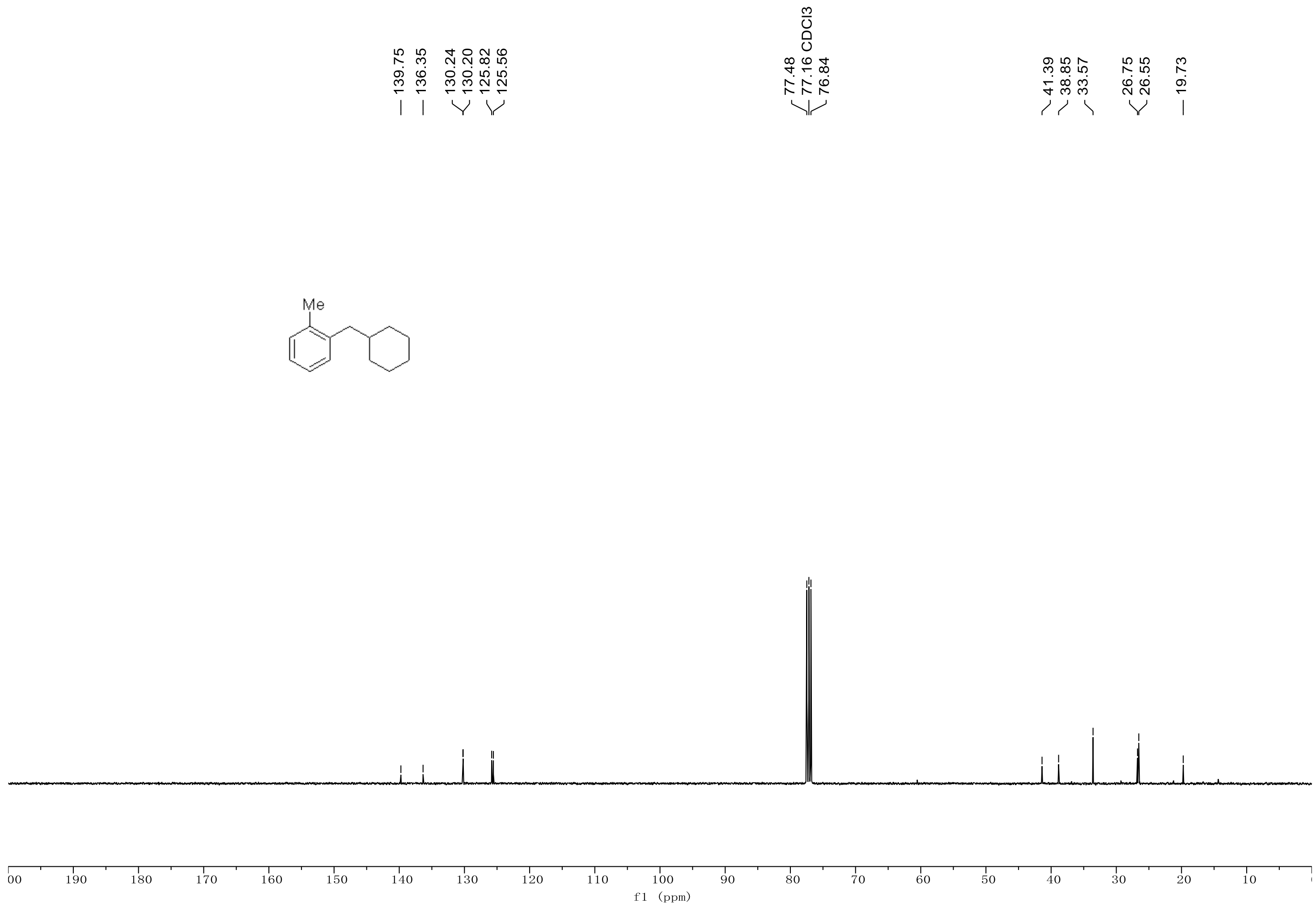


Figure S44 ^{1}H NMR of **3t**

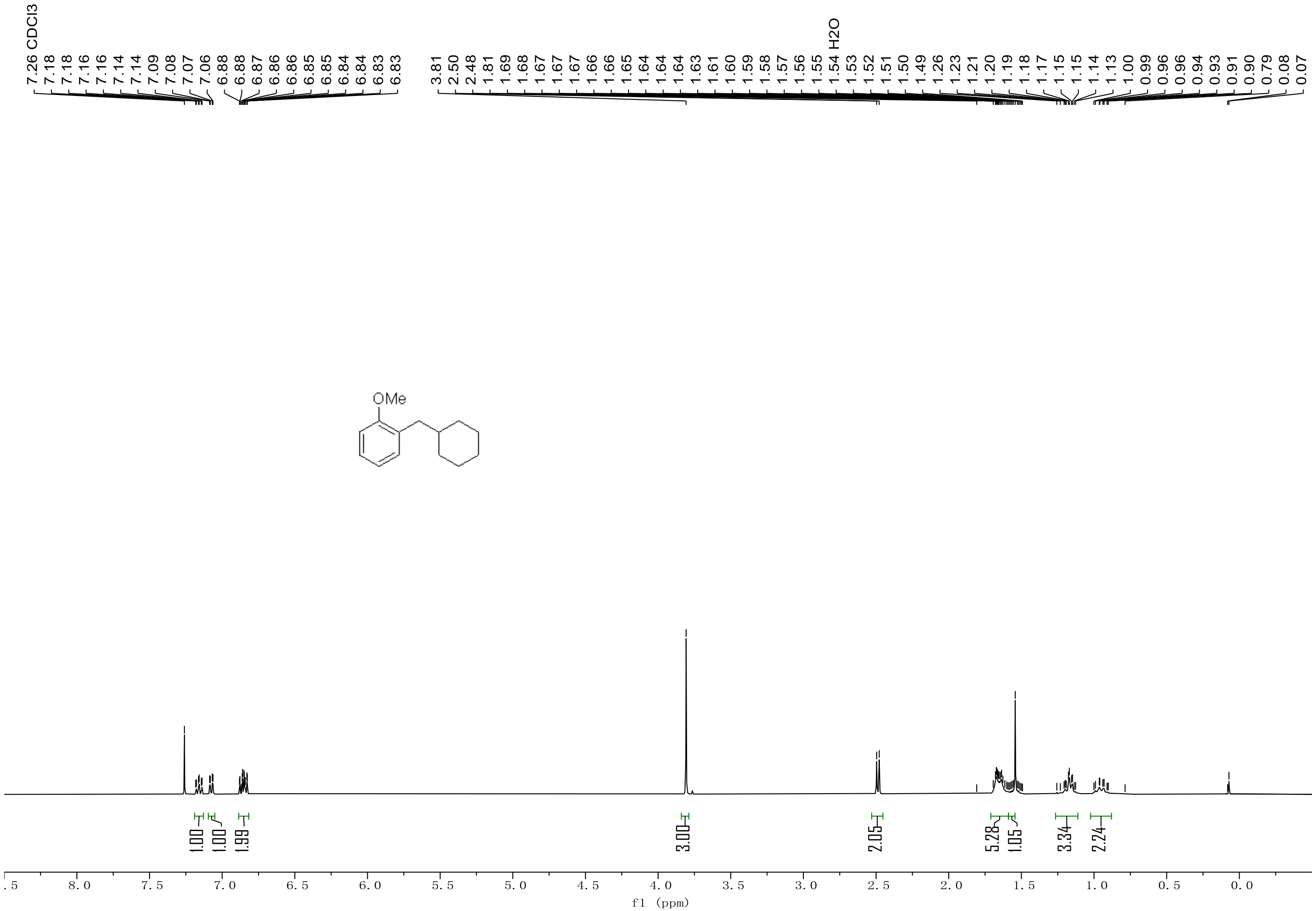


Figure S45 ^{13}C NMR of **3t**

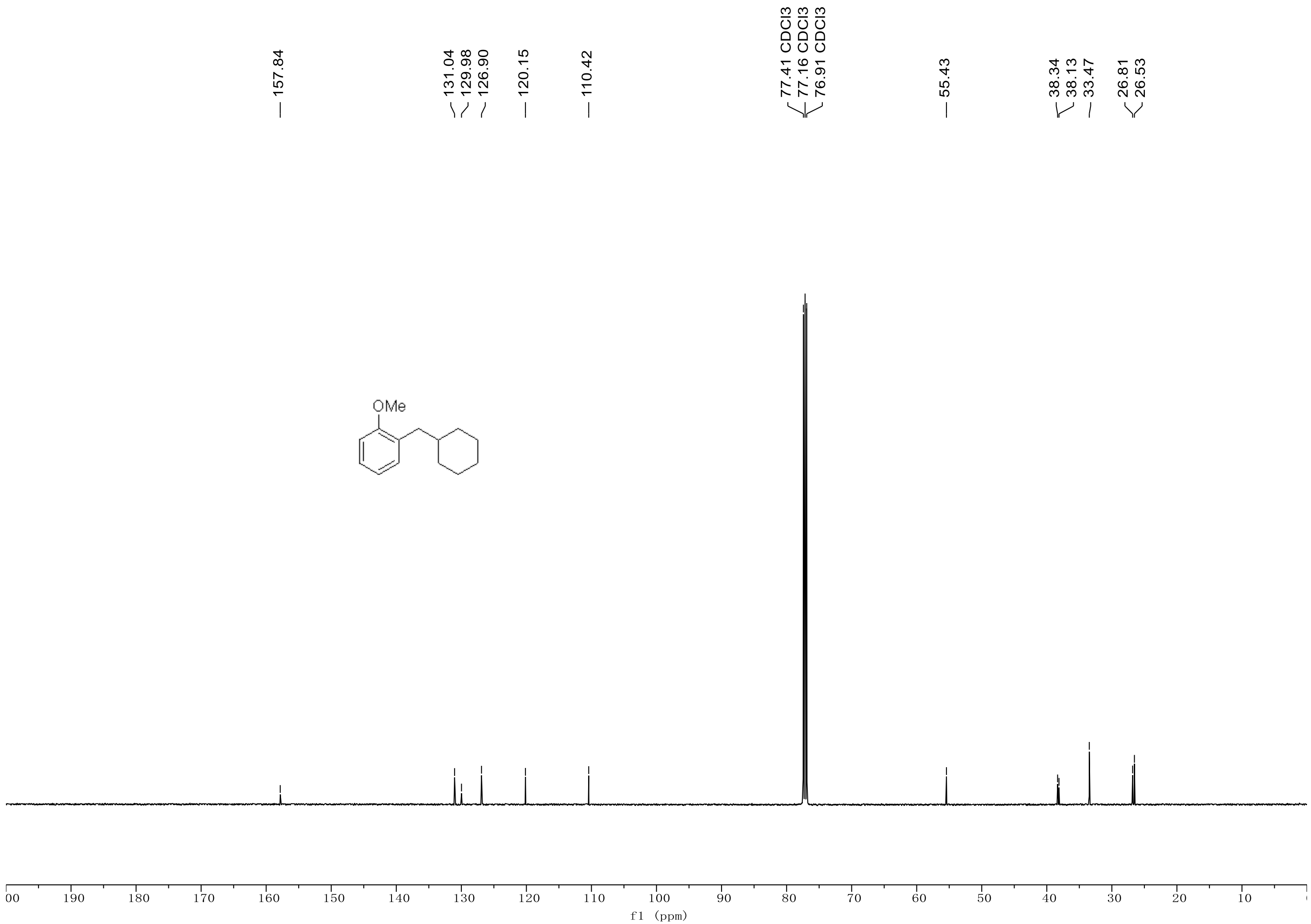

157.84
131.04
129.98
126.90
120.15
110.42
77.41 CDCl3
77.16 CDCl3
76.91 CDCl3
55.43
38.34
38.13
33.47
26.81
26.53
OMe
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Figure S46 ^{1}H NMR of **3u**

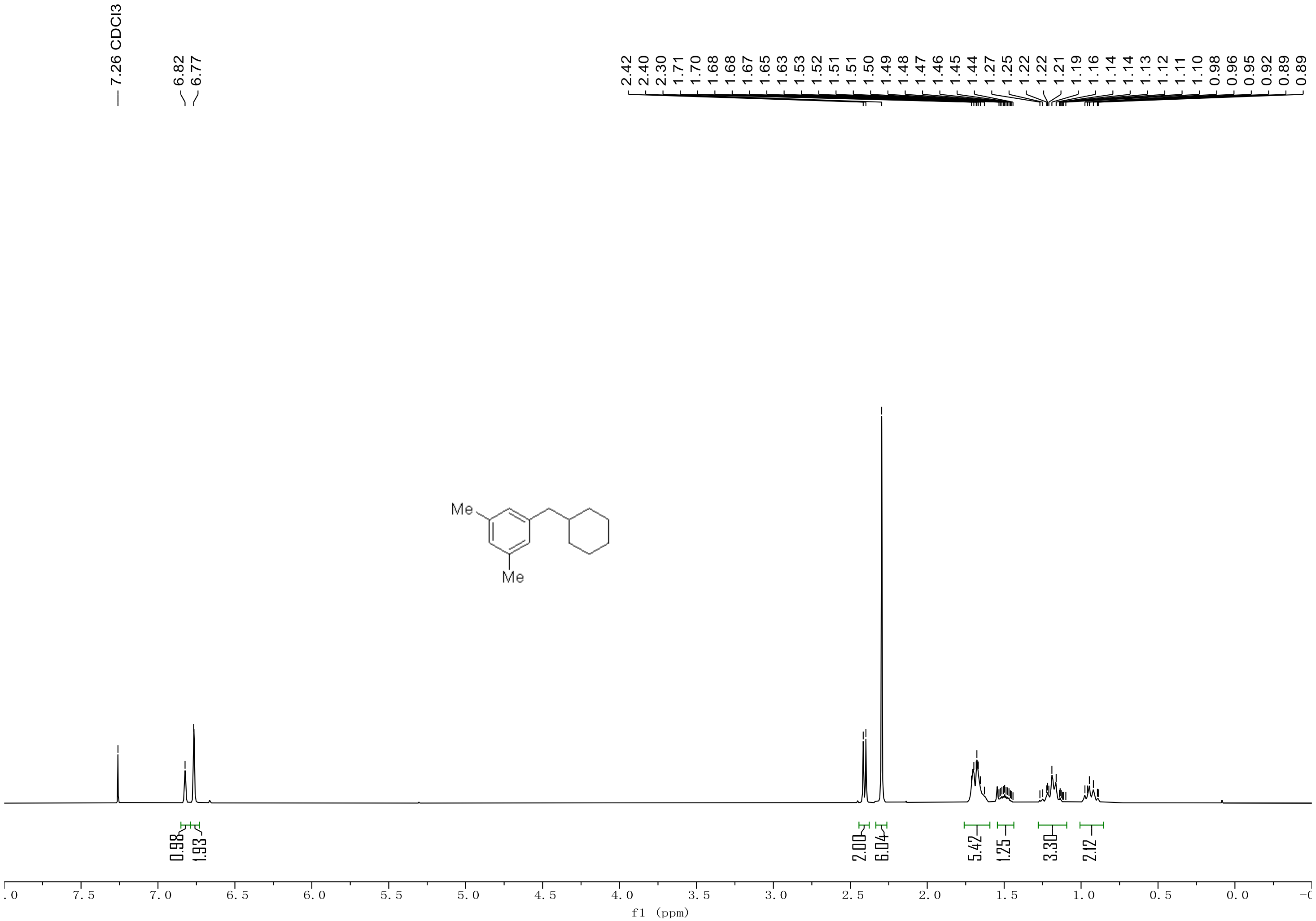


Figure S47 ^{13}C NMR of **3u**

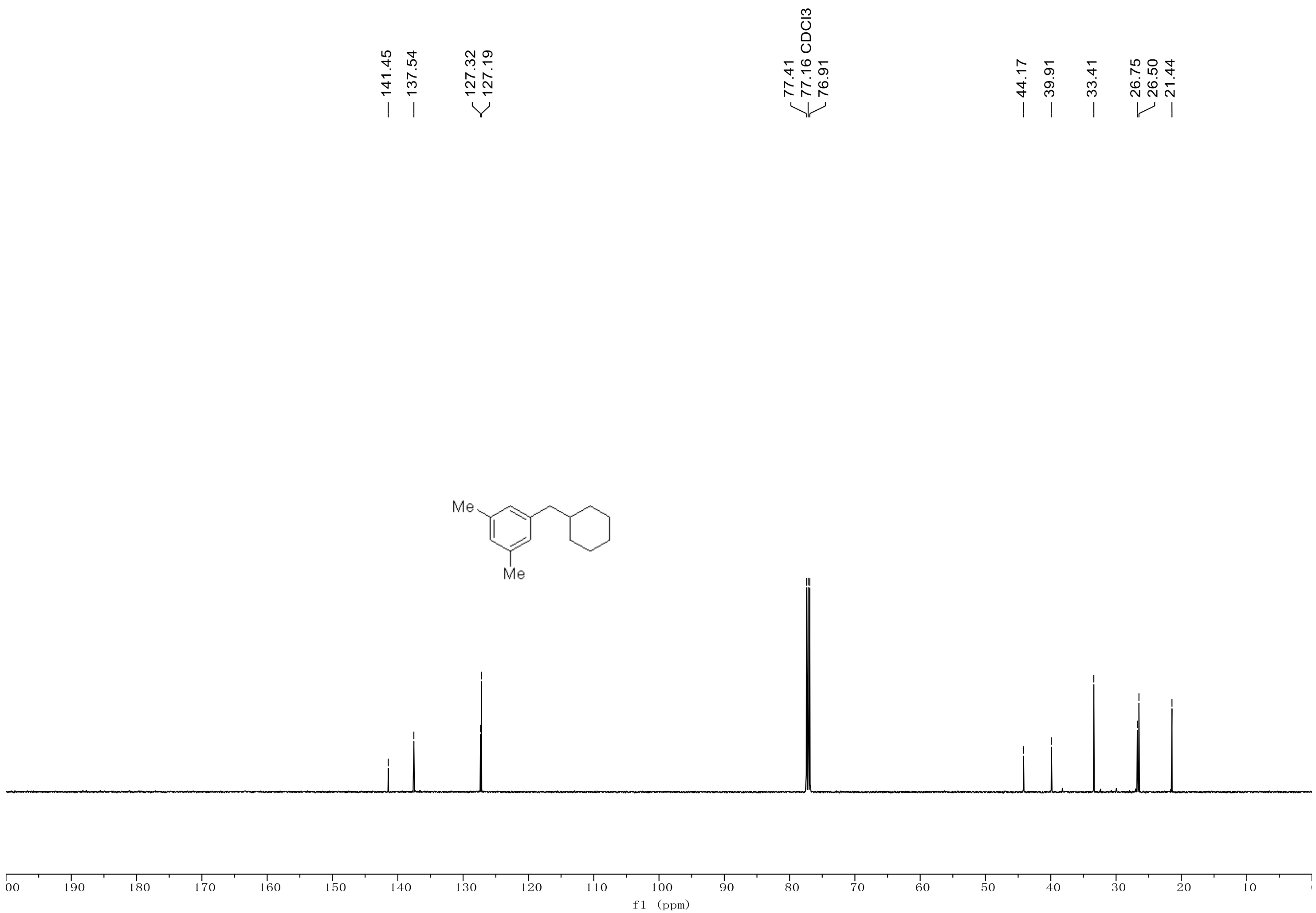


Figure S48 ^{1}H NMR of **3v**

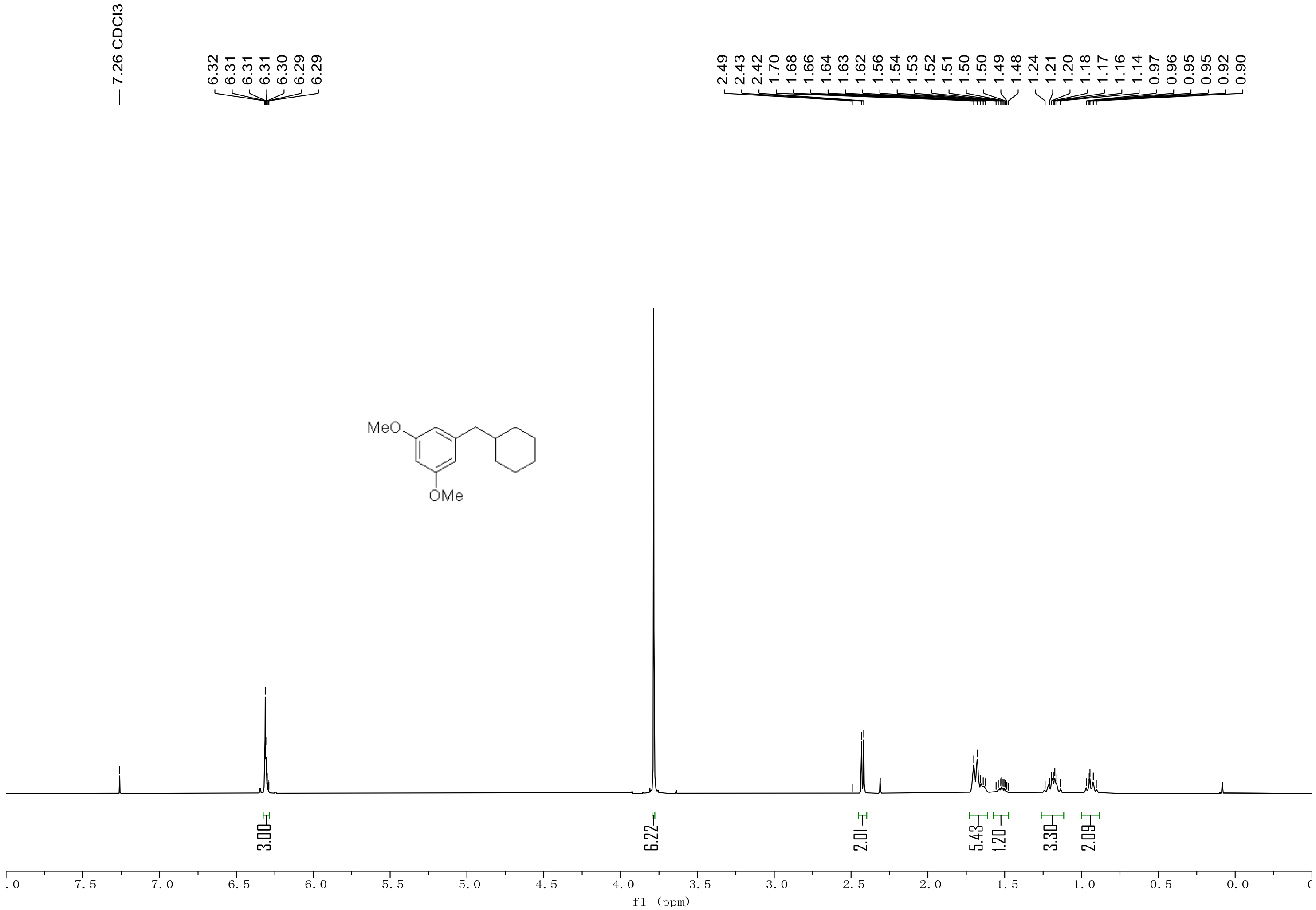


Figure S49 ^{13}C NMR of **3v**

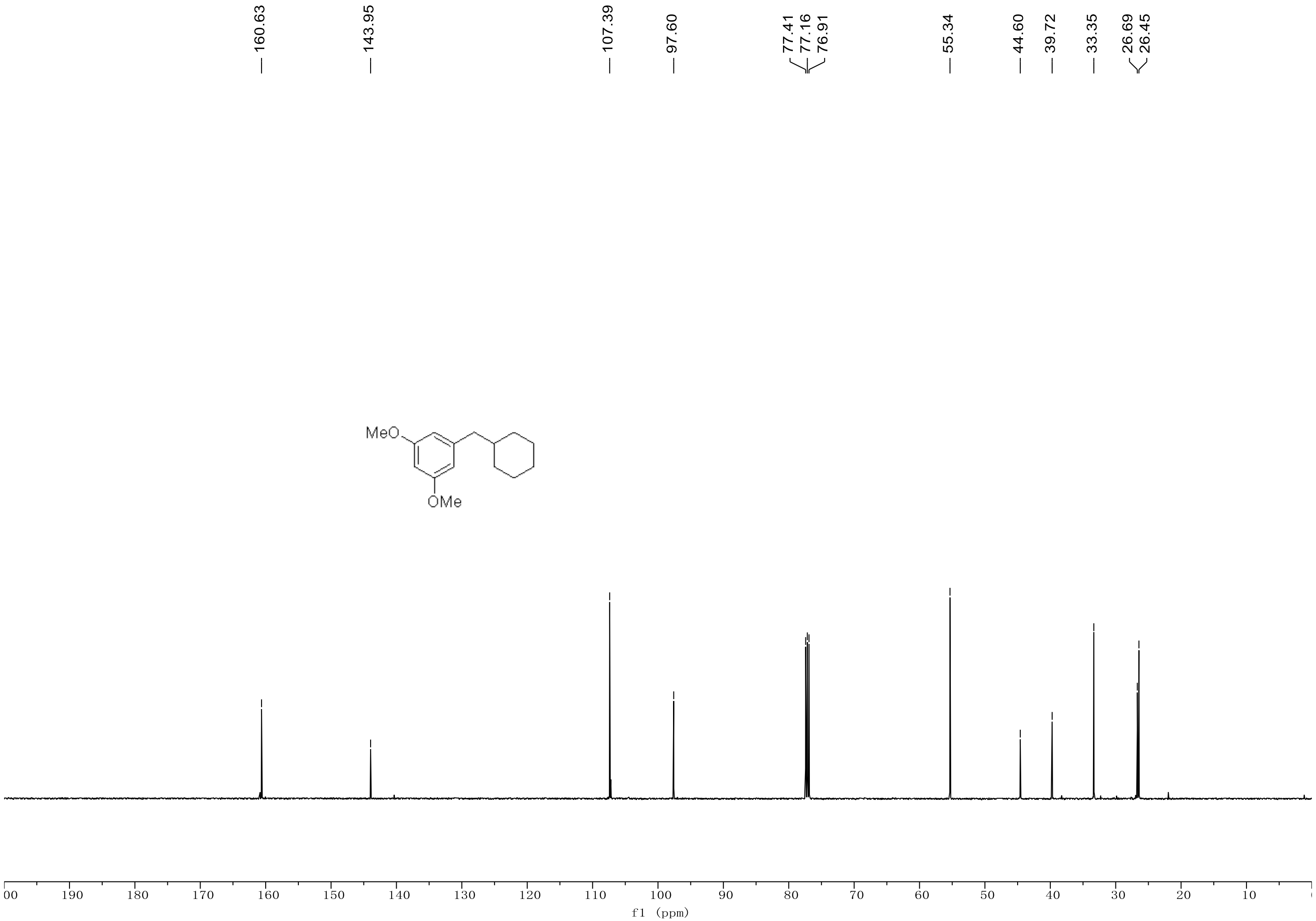


Figure S50 ^{1}H NMR of **3w**

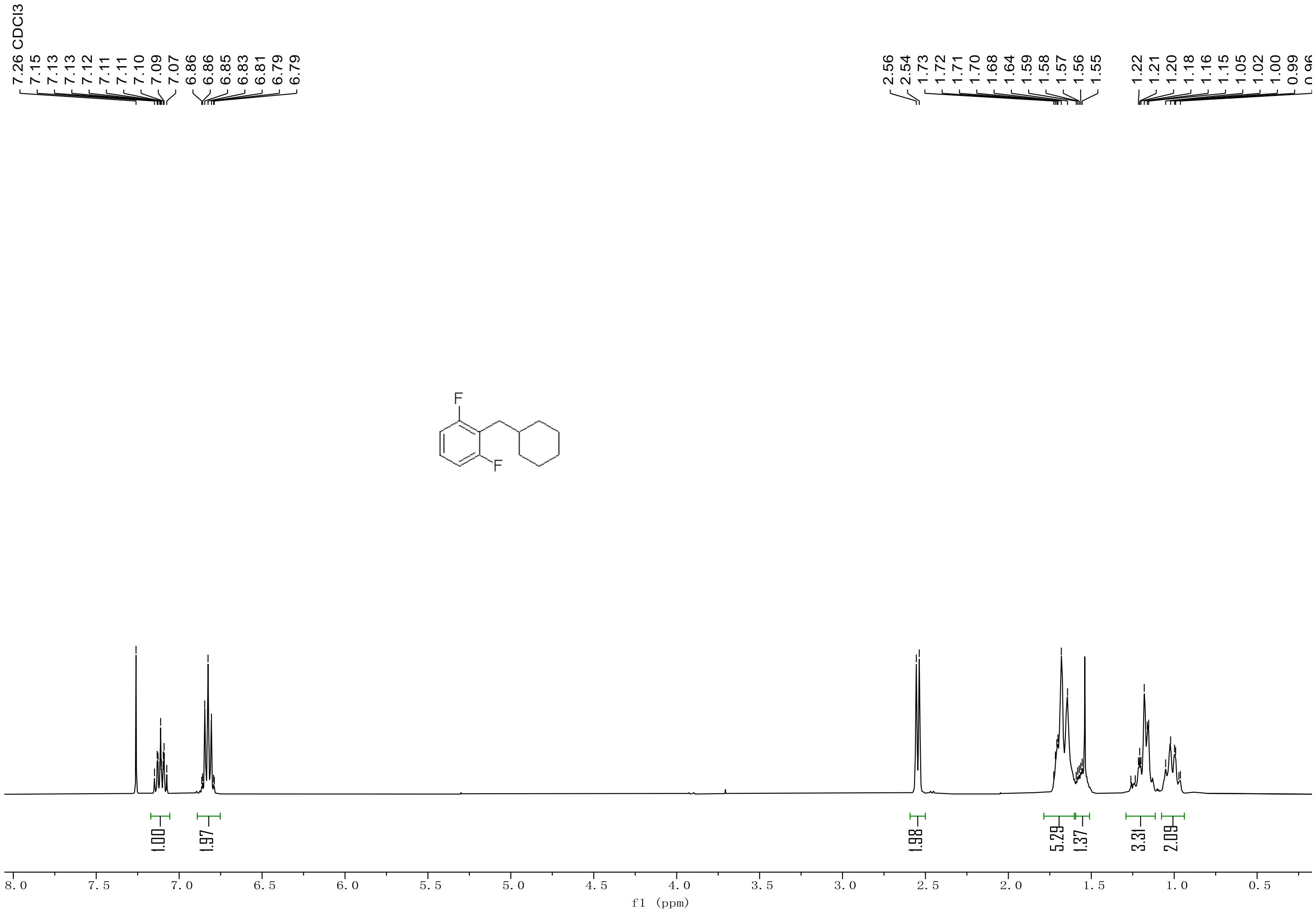


Figure S51 ^{13}C NMR of **3w**

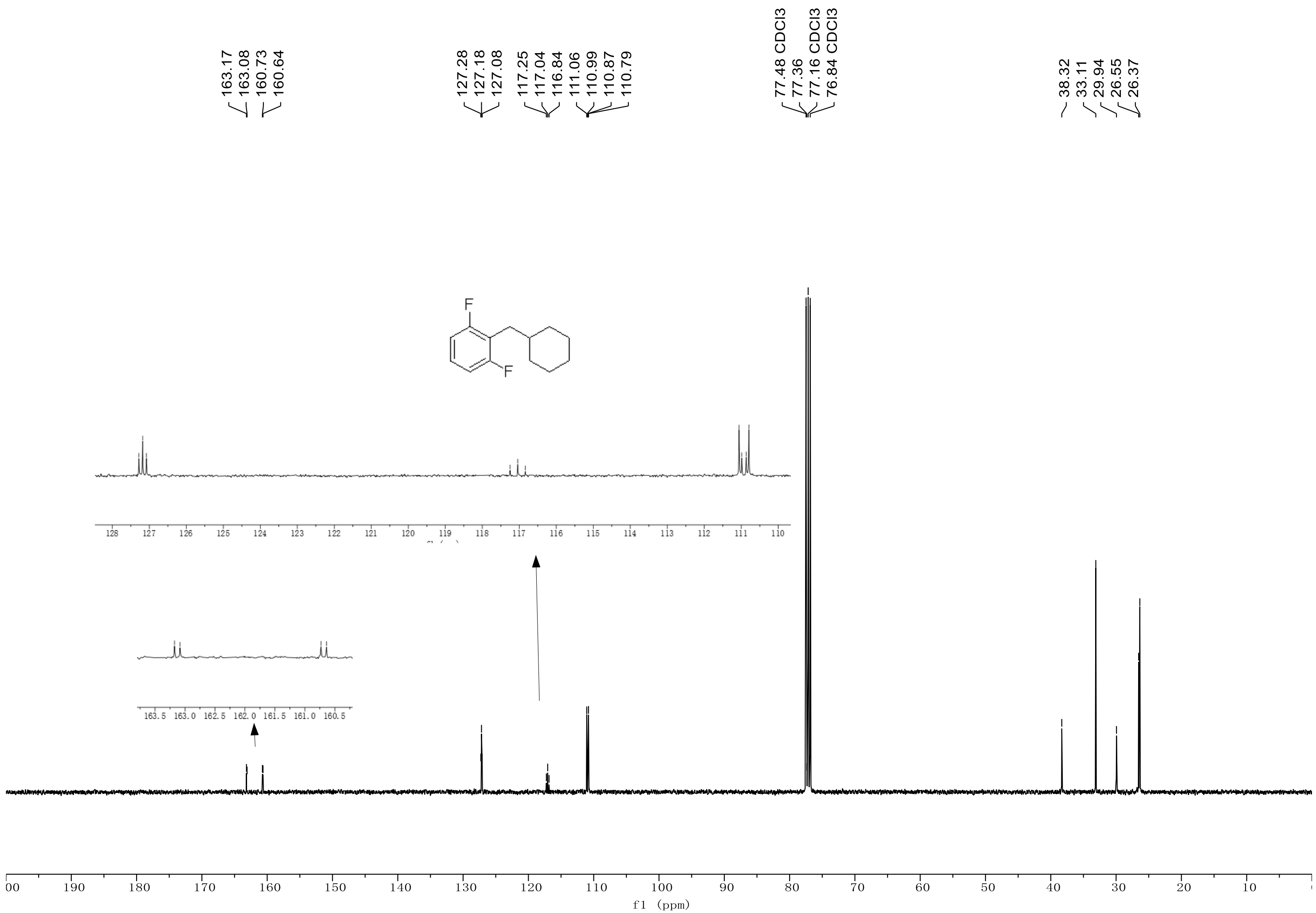


Figure S52 ^{19}F NMR of **3w**

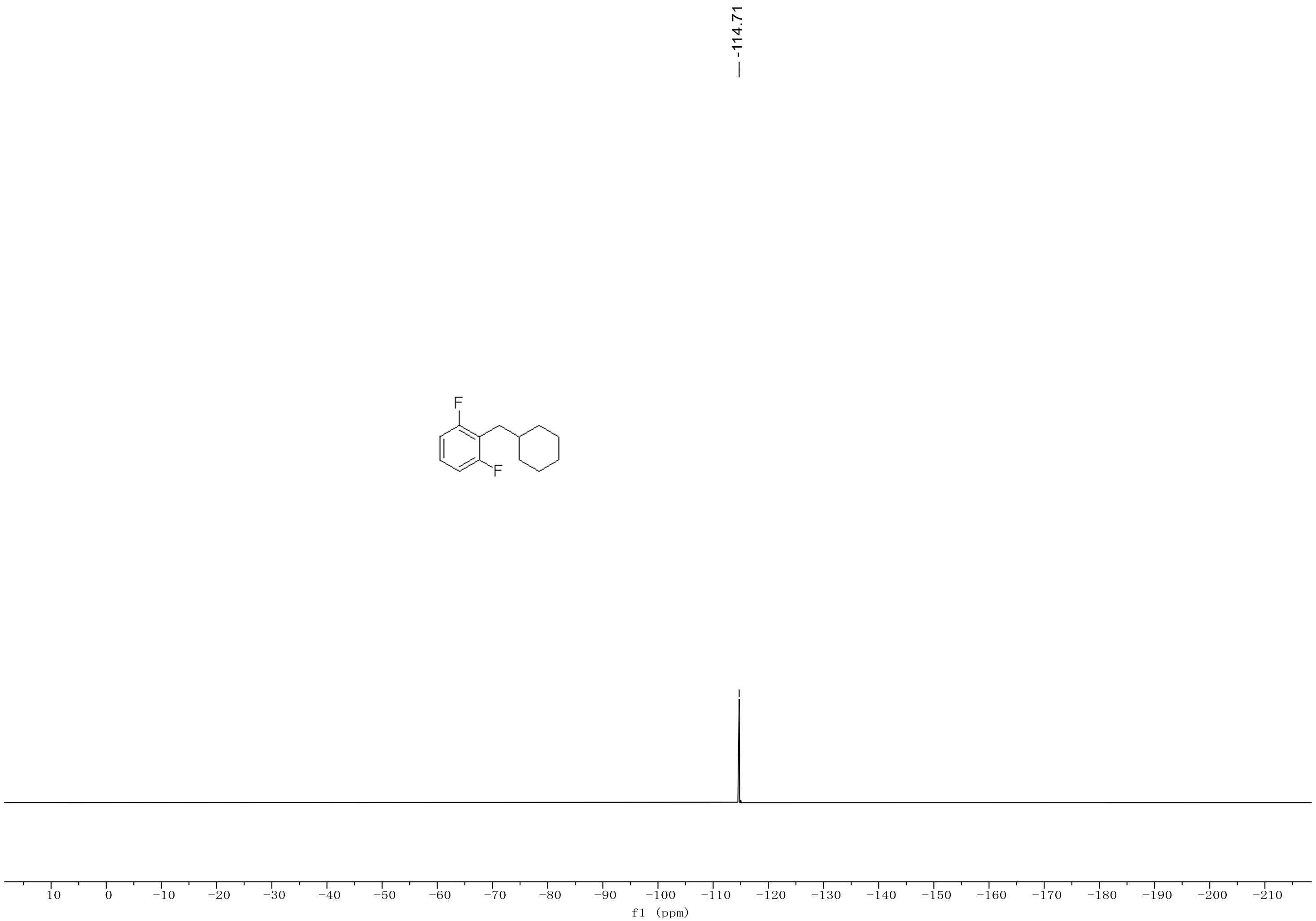


Figure S53 ^{1}H NMR of **3x**

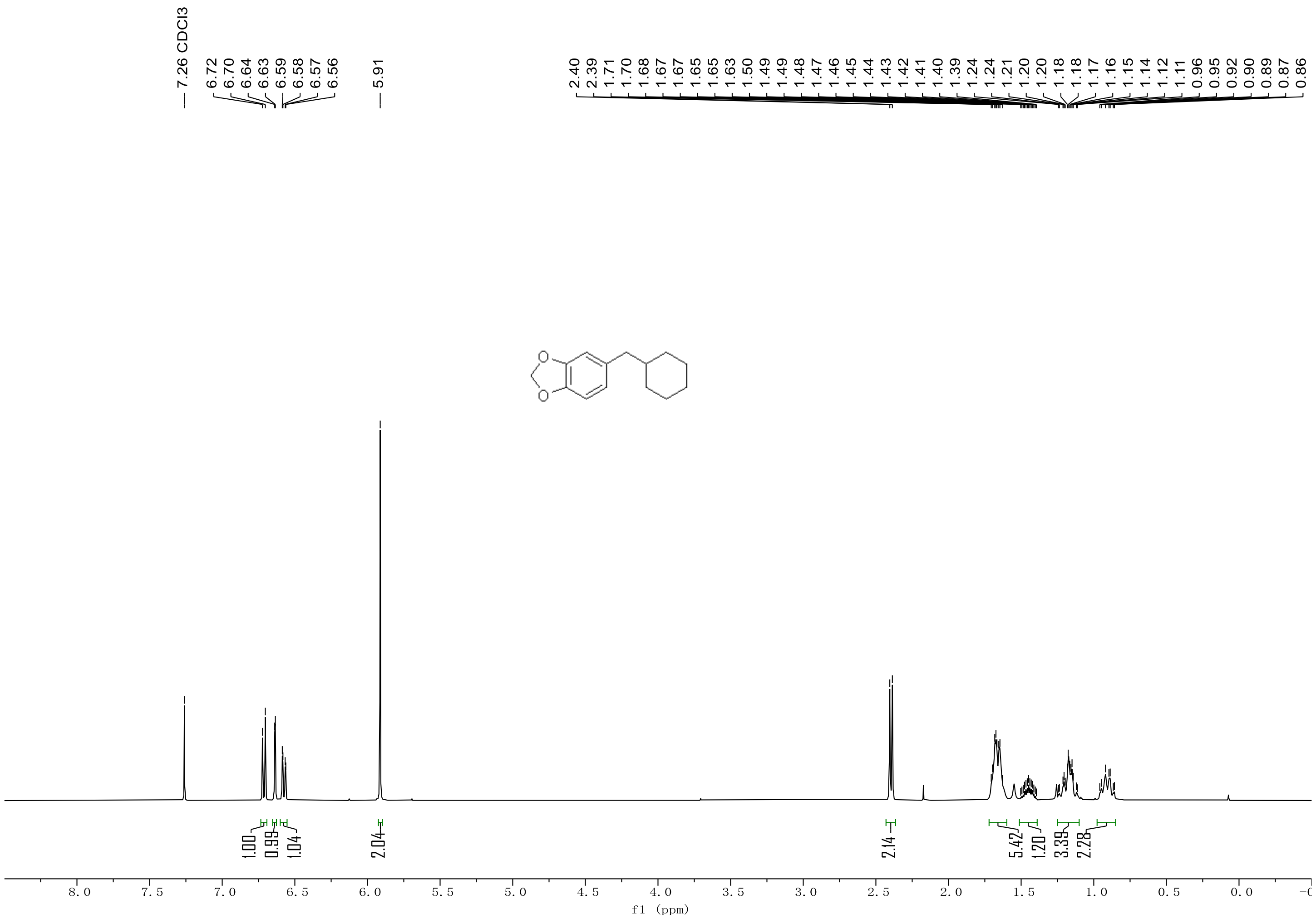


Figure S54 ^{13}C NMR of **3x**

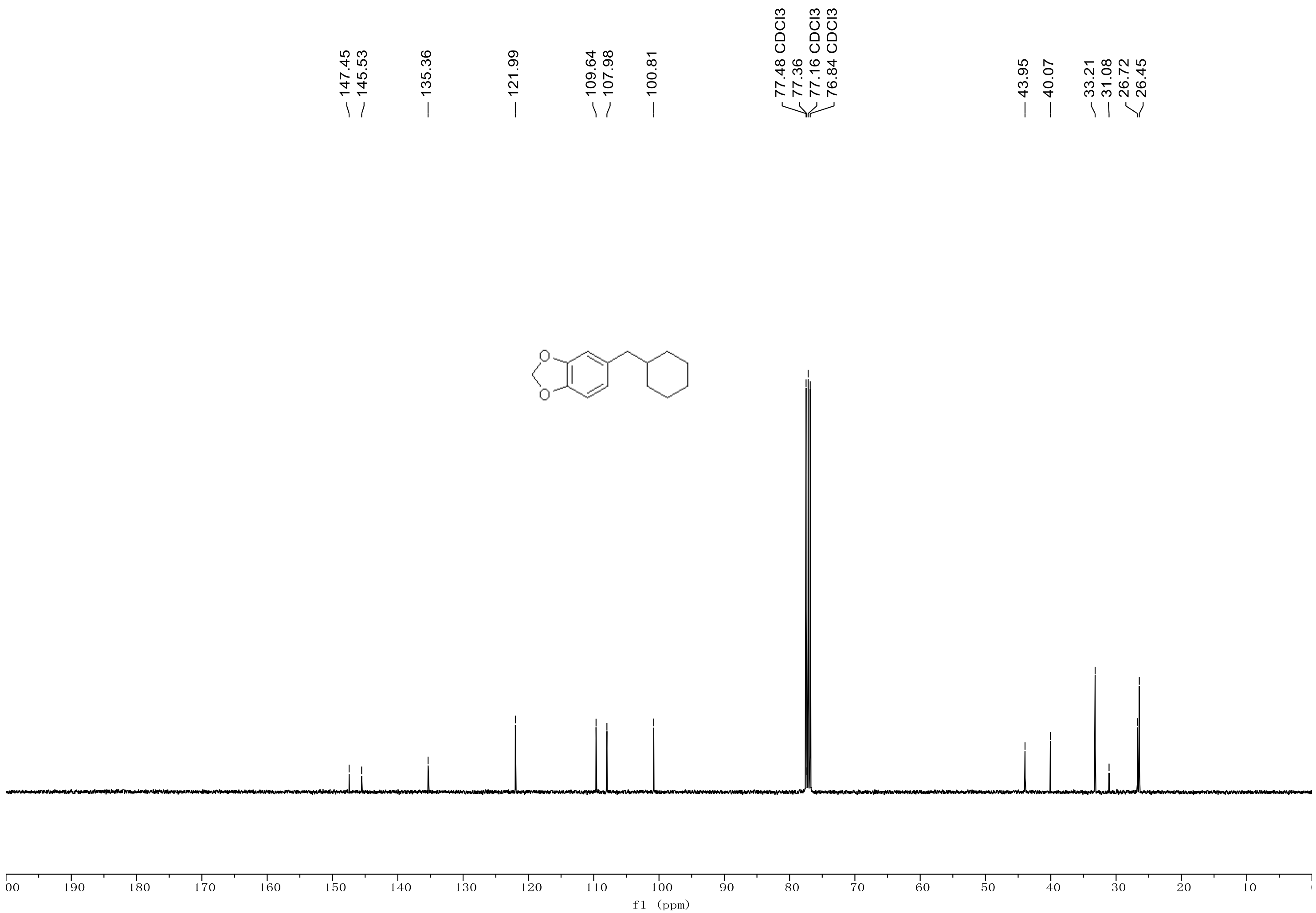


Figure S55 ^{1}H NMR of **3y**

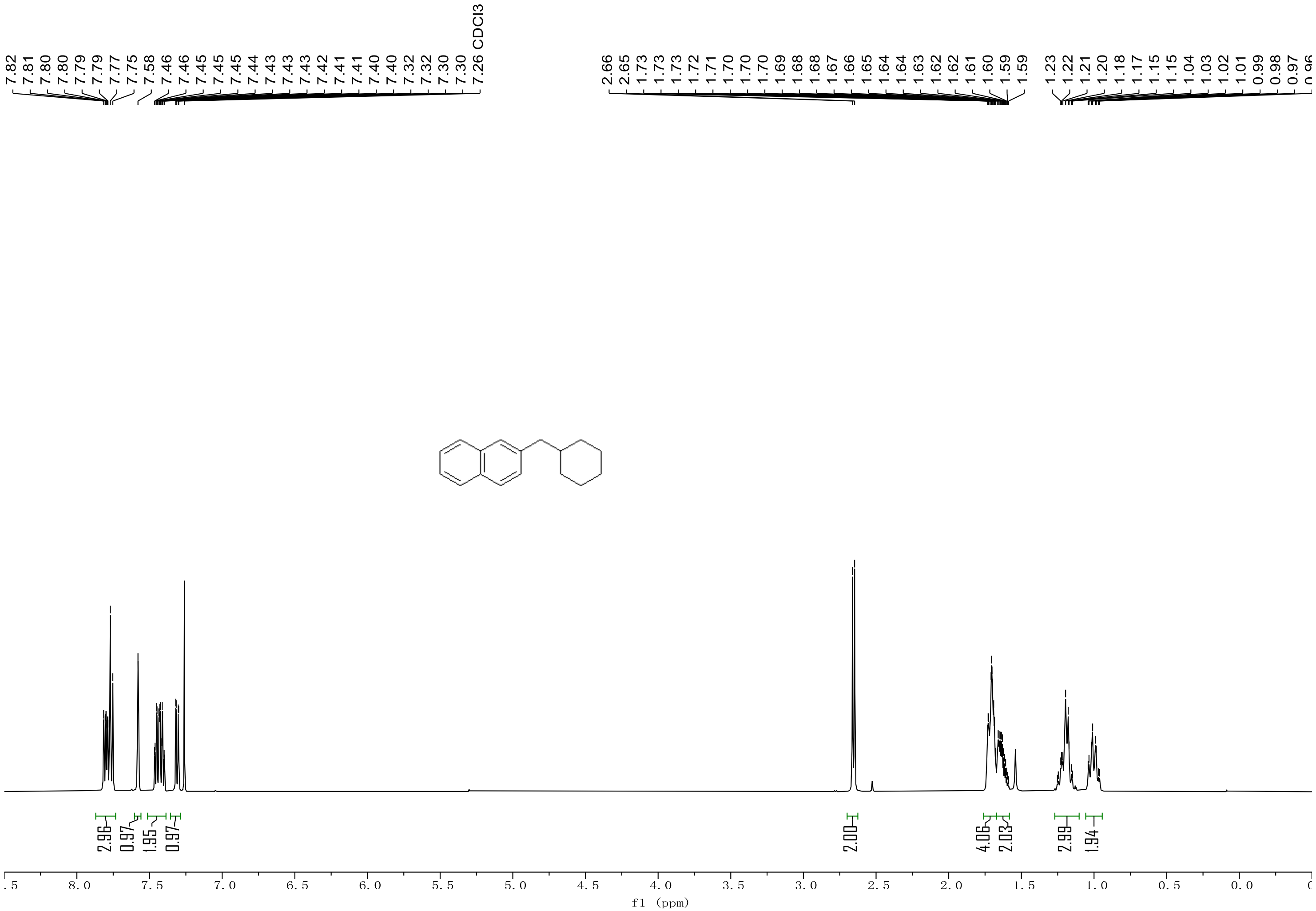


Figure S56 ^{13}C NMR of **3y**

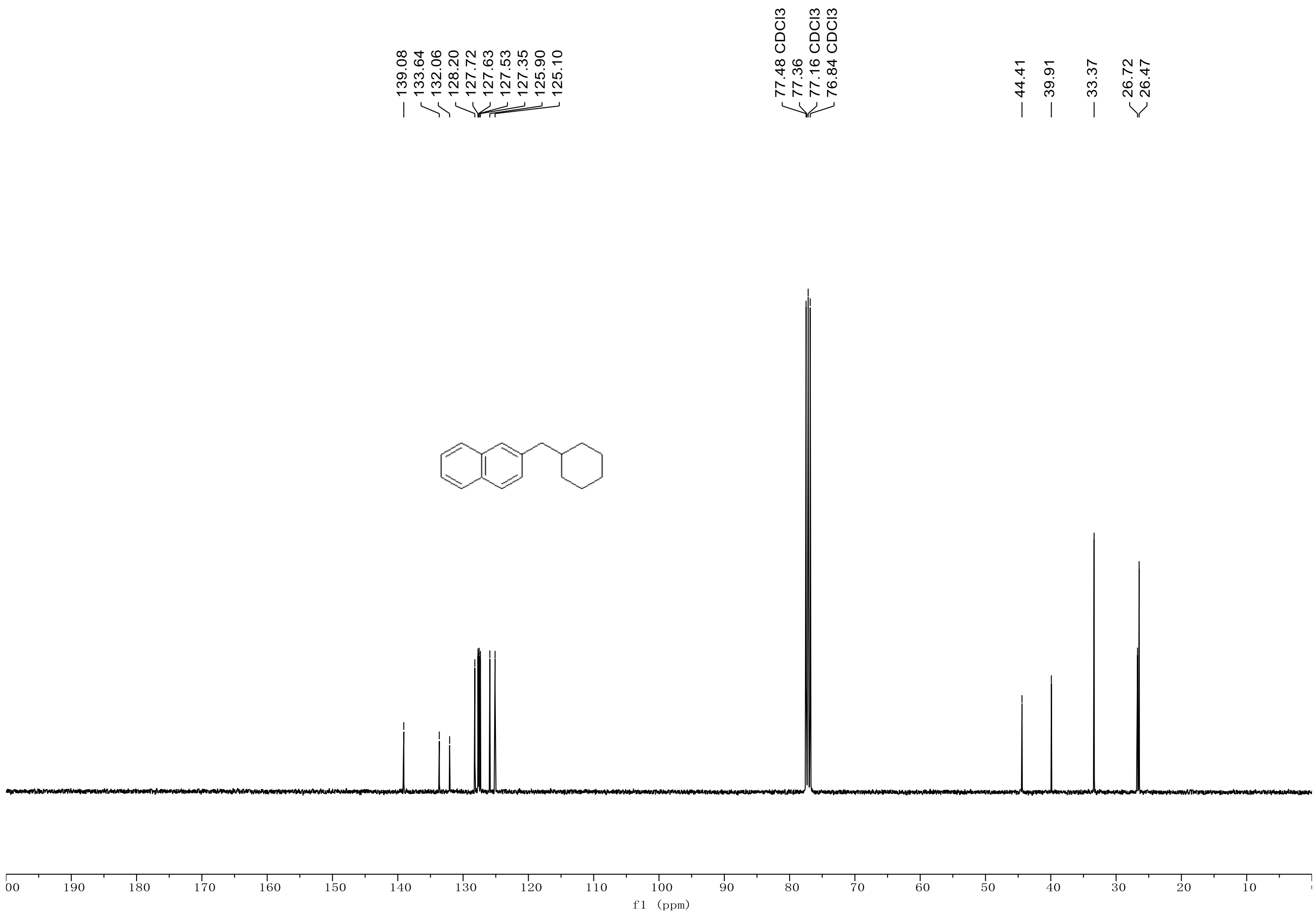


Figure S57 [1]H NMR of **3z**

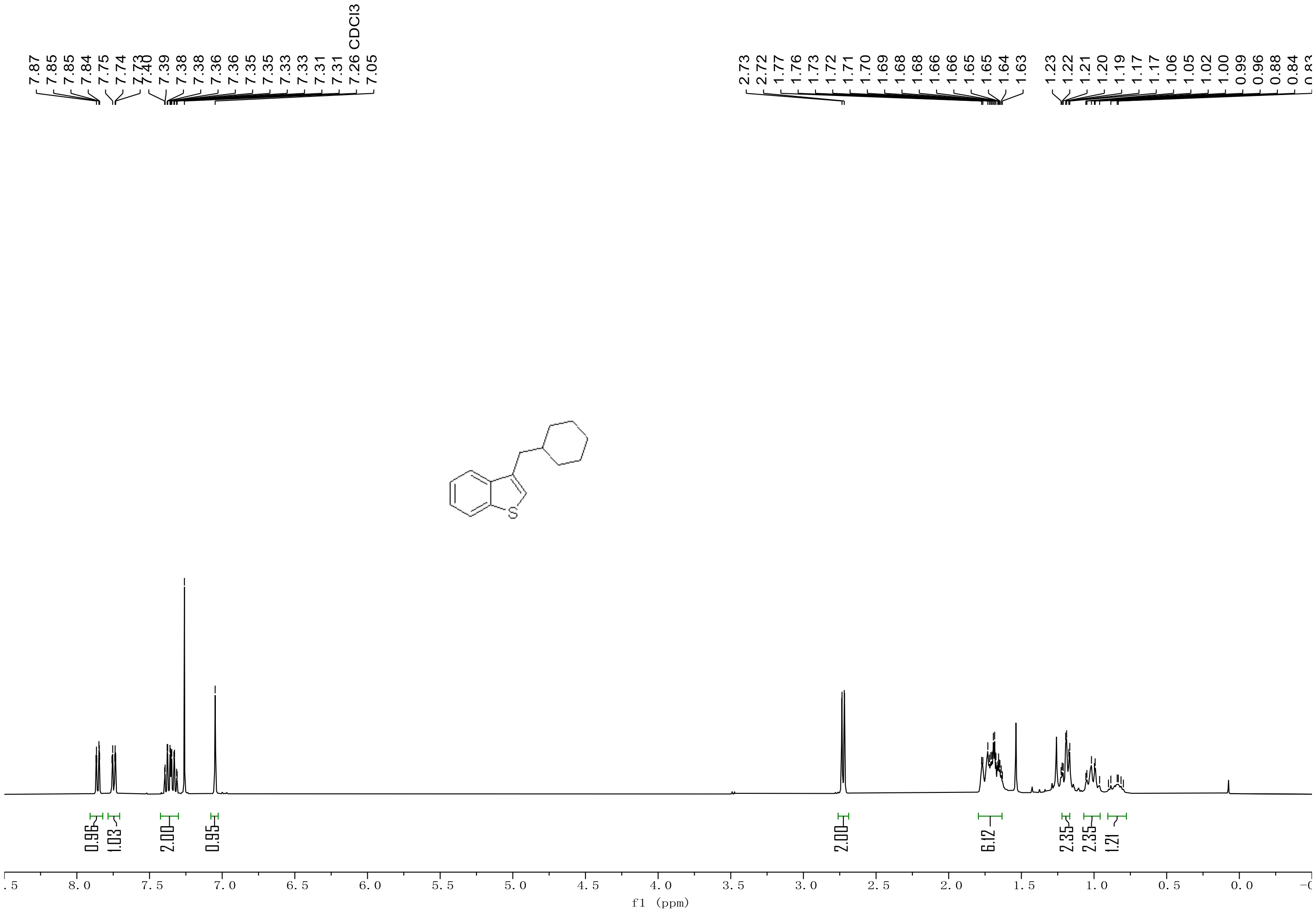


Figure S58 ^{13}C NMR of **3z**

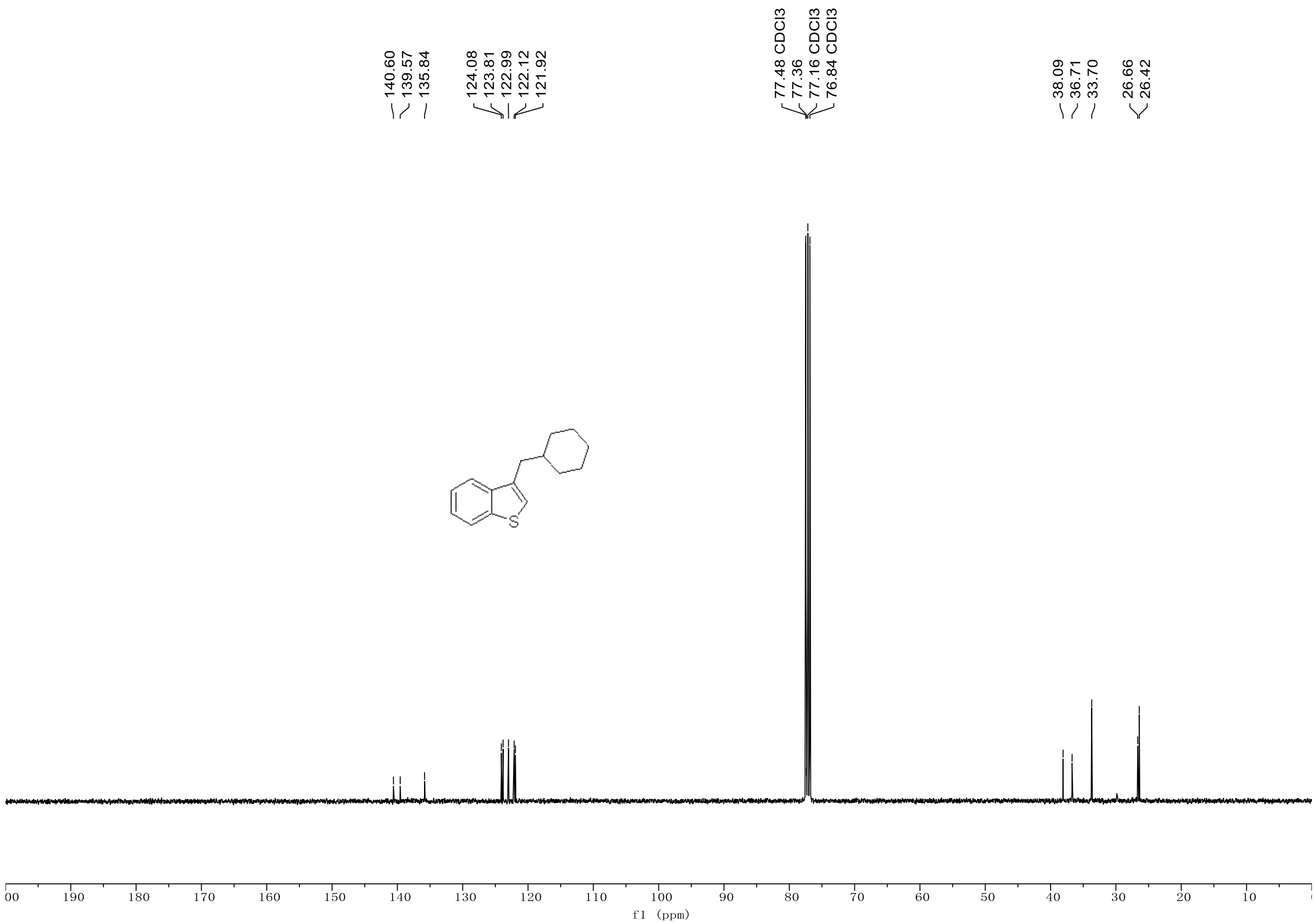


Figure S59 ^{1}H NMR of **3aa**

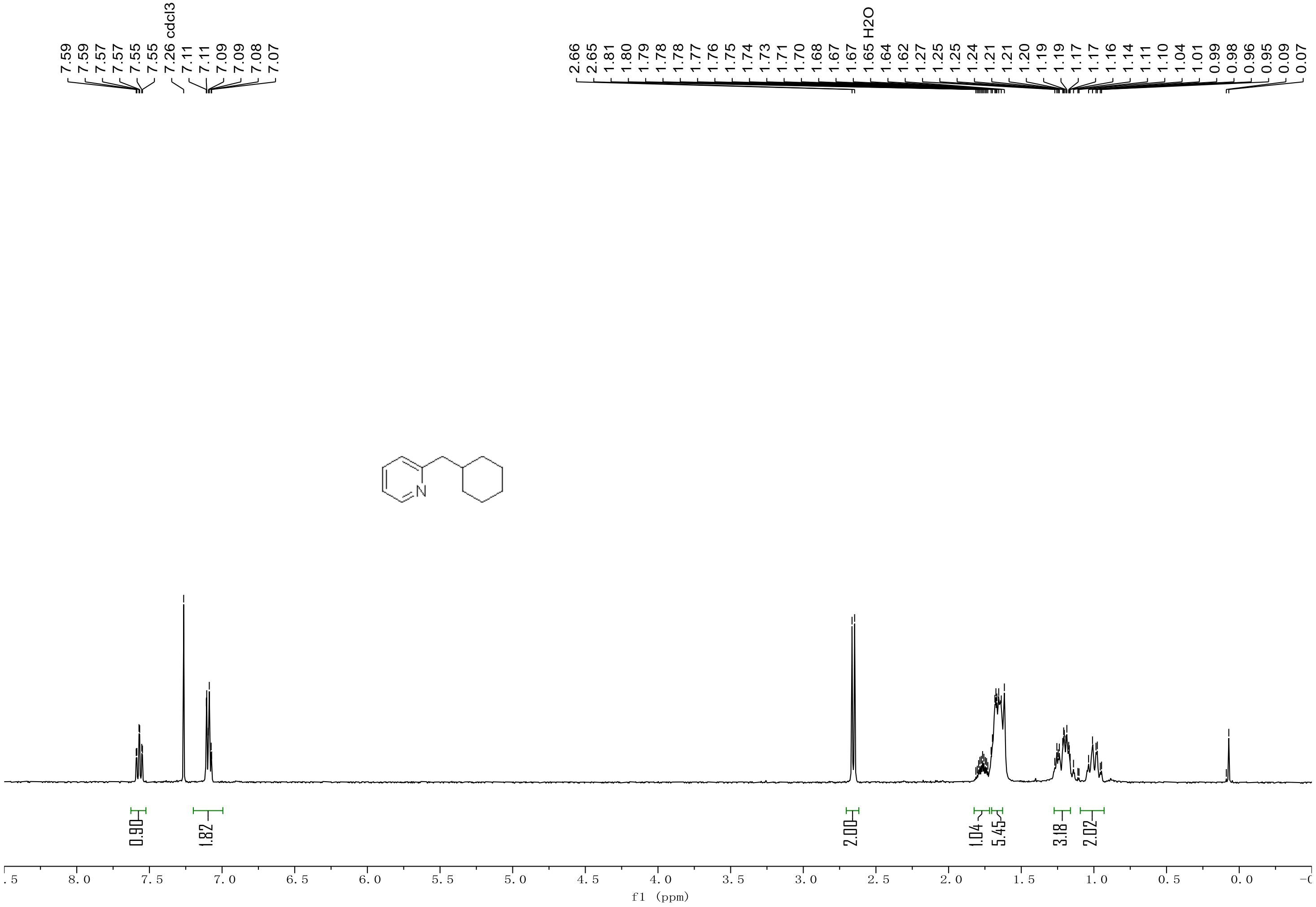


Figure S60 ^{13}C NMR of **3aa**

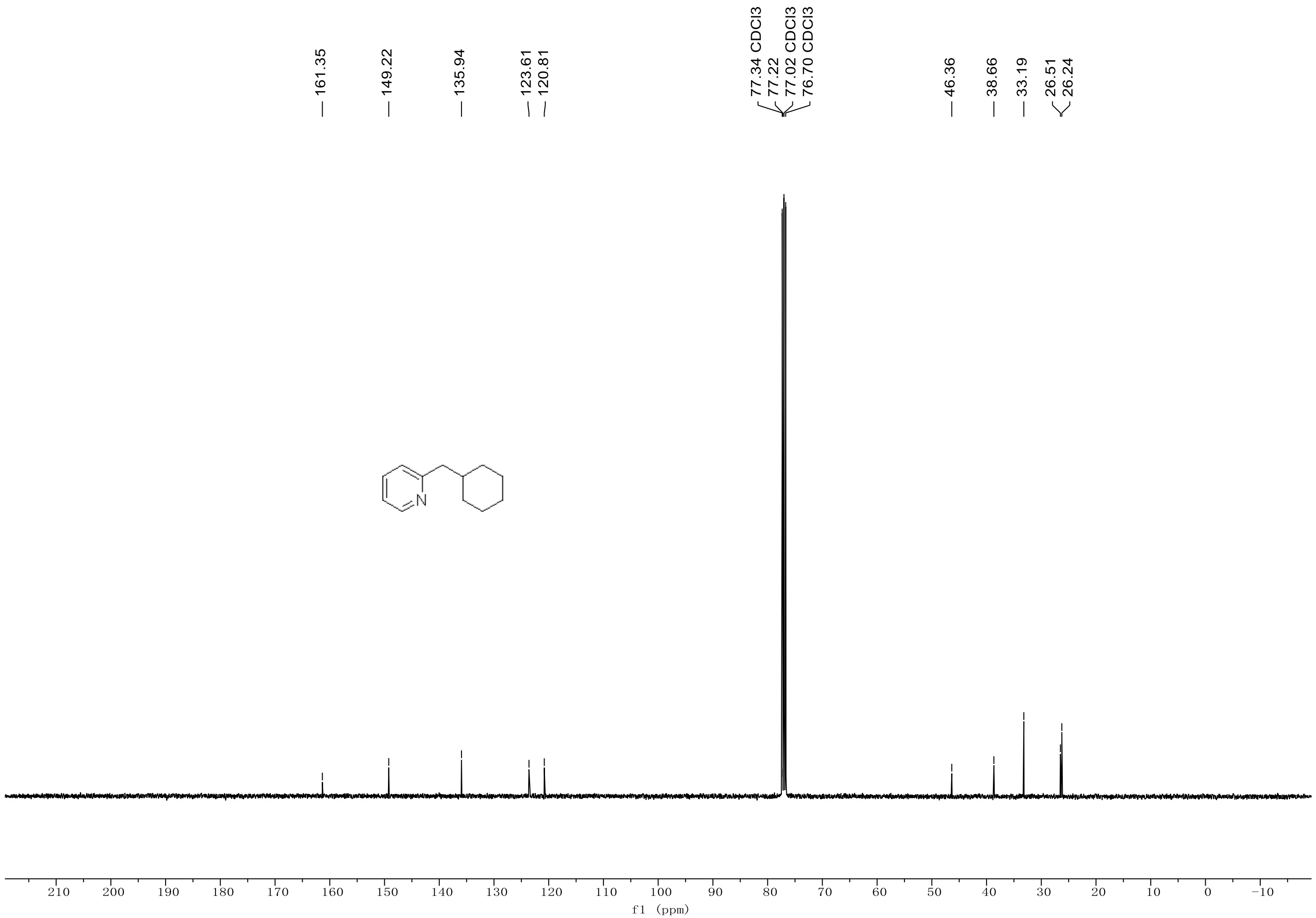


Figure S61 ^{1}H NMR of **3ab**

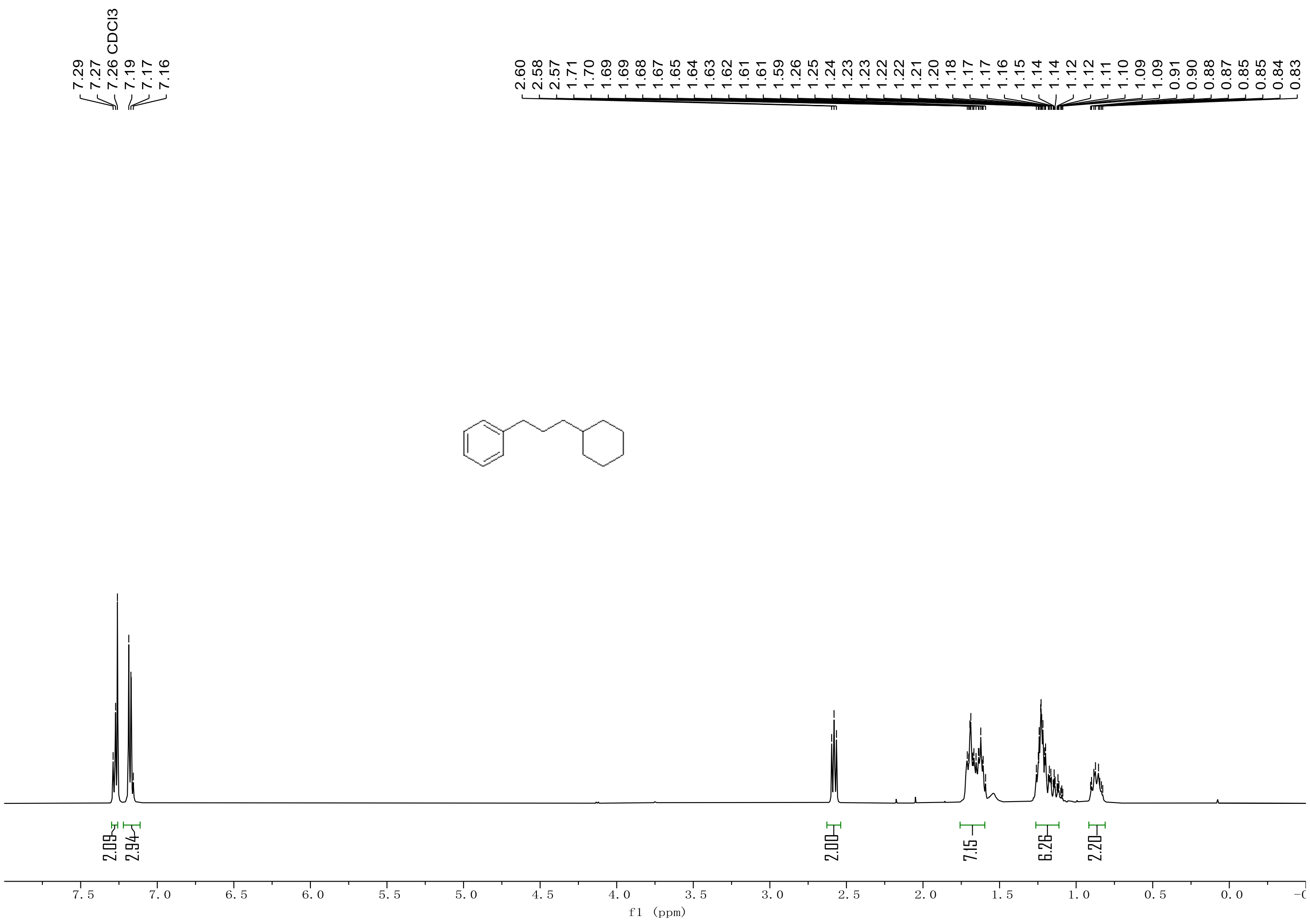


Figure S62 ^{13}C NMR of **3ab**

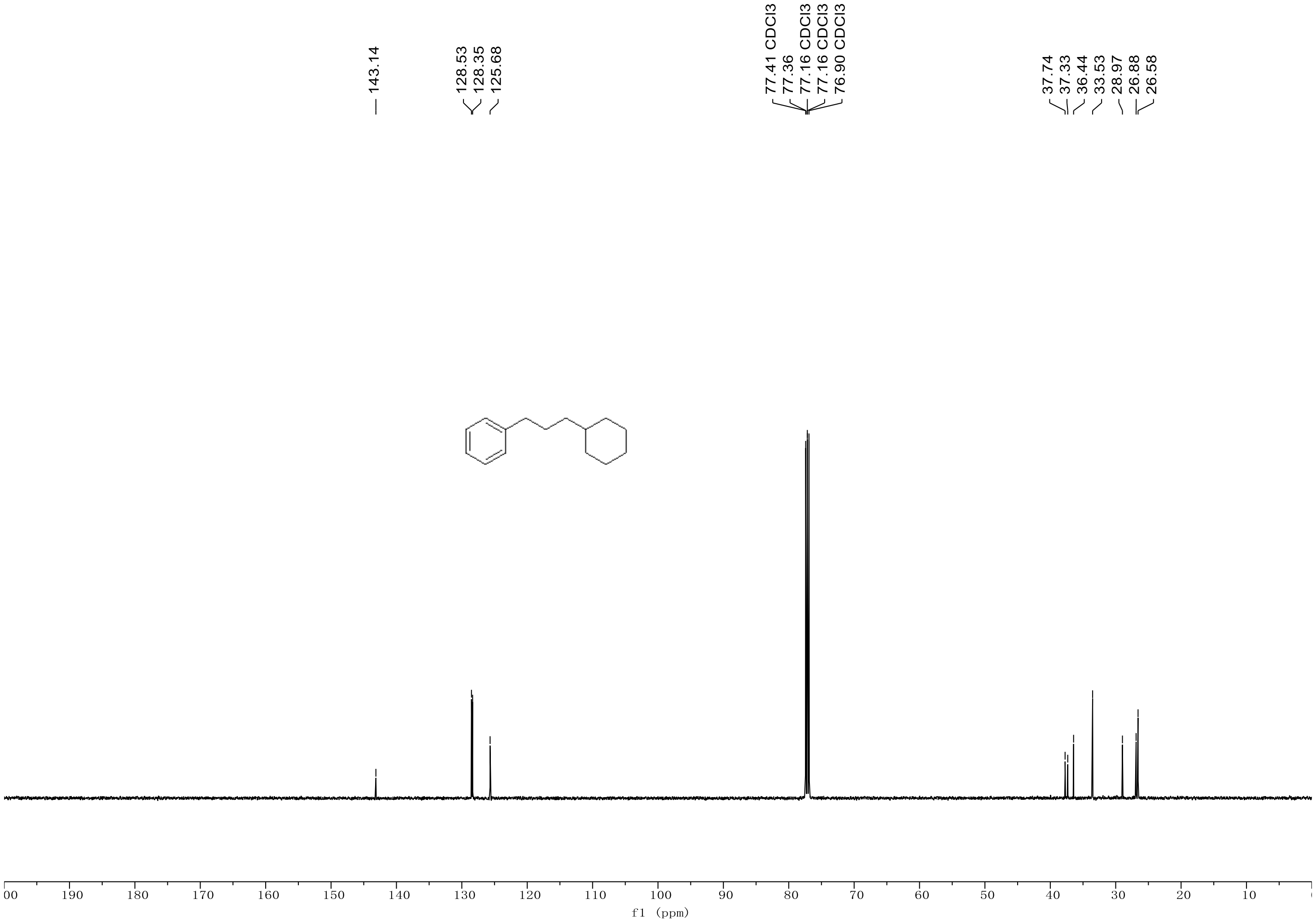


Figure S63 ^{1}H NMR of **3ac**

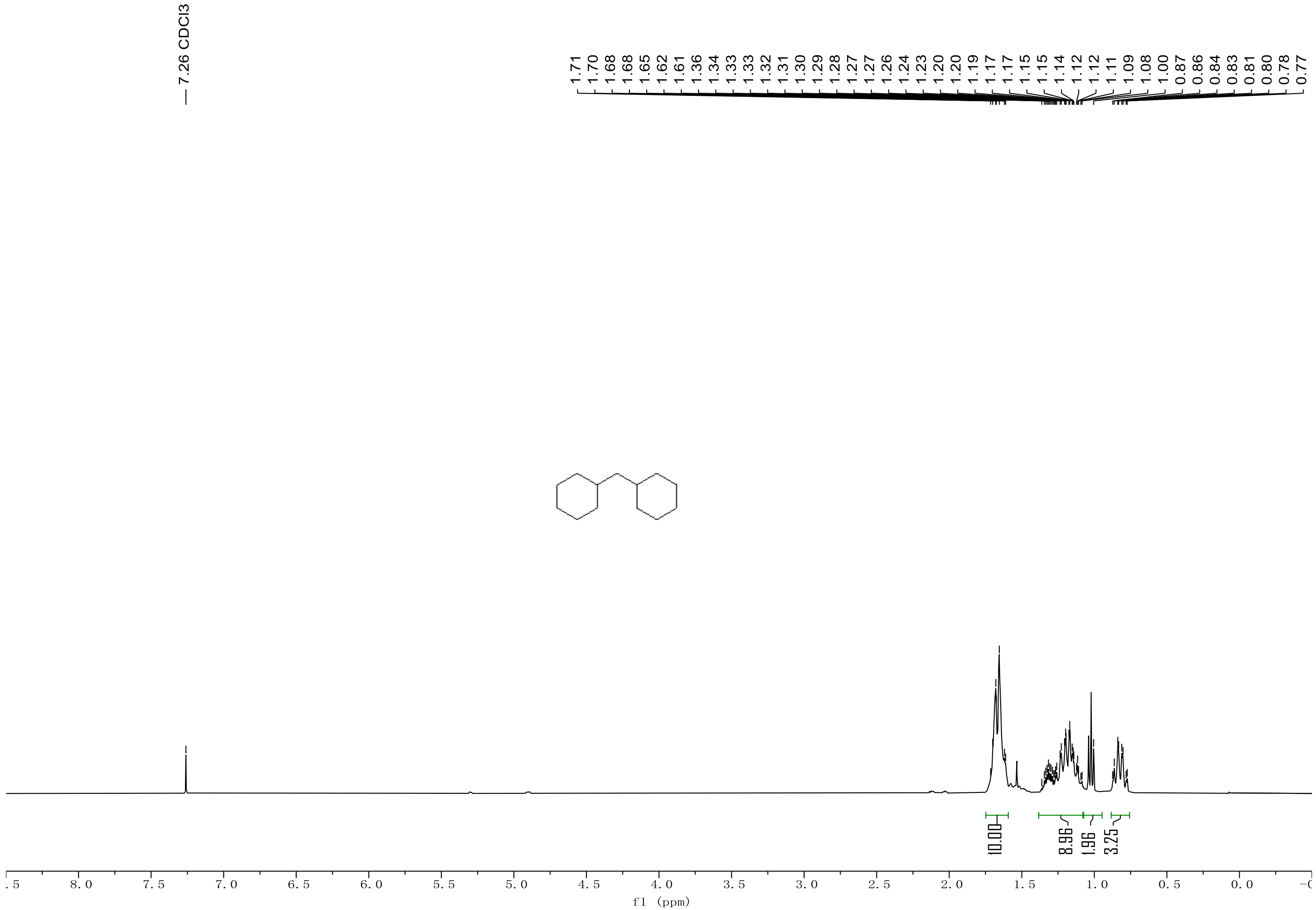


Figure S64 ^{1}H NMR of **4a**

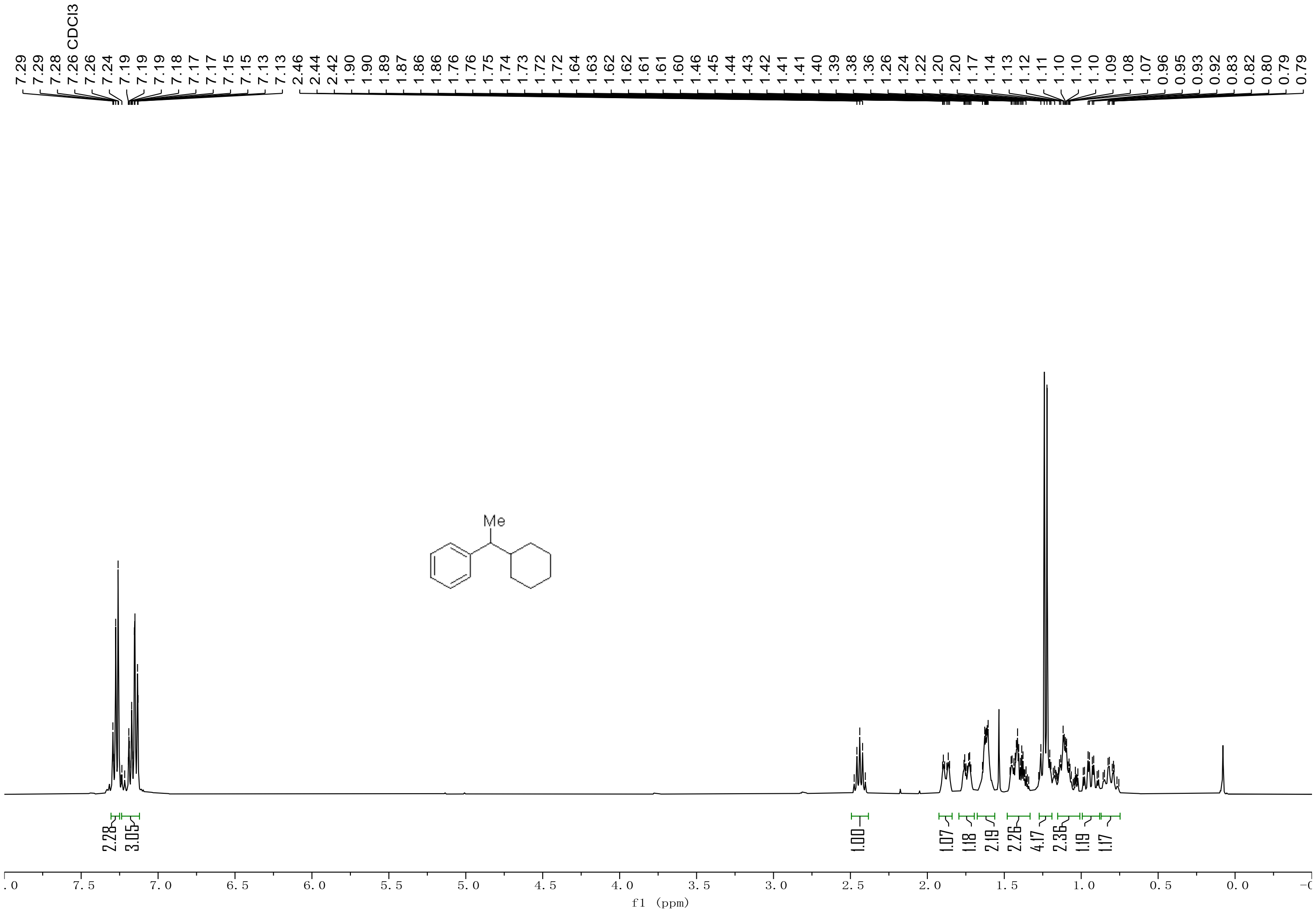


Figure S65 ^{13}C NMR of **4a**

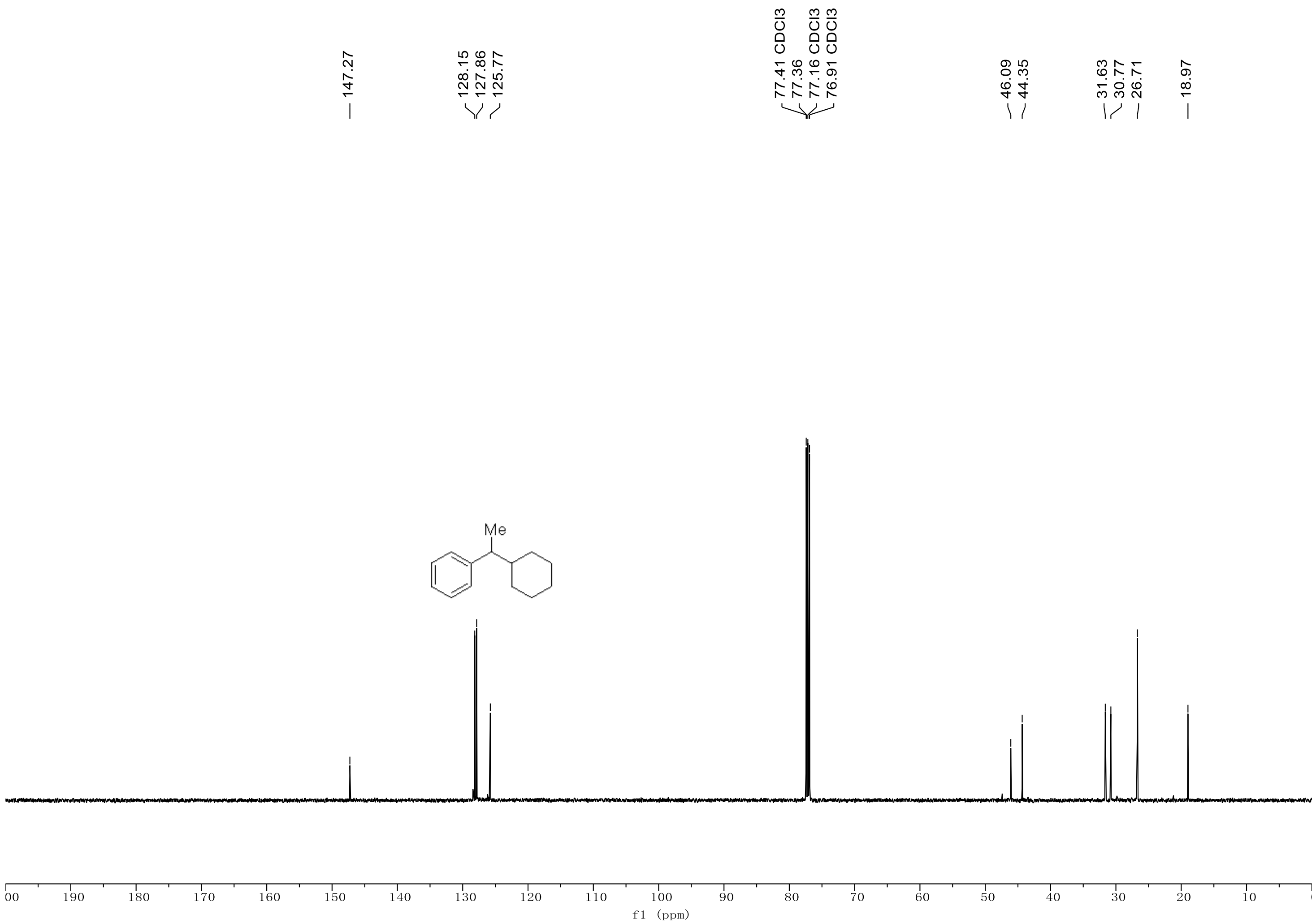


Figure S66 ^{1}H NMR of **4b**

Figure S67 ^{13}C NMR of **4b**

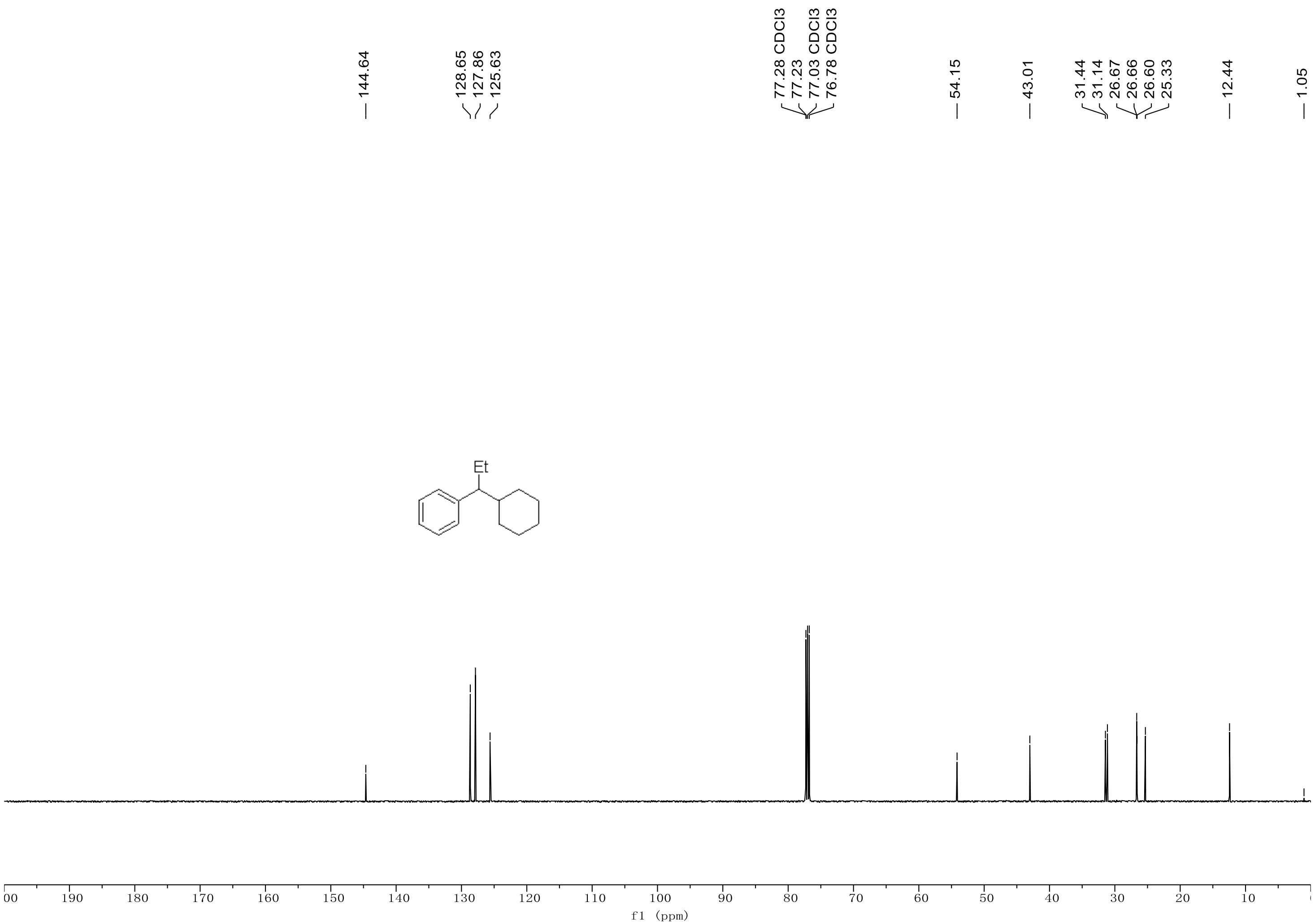


Figure S68 [1]H NMR of **4c**

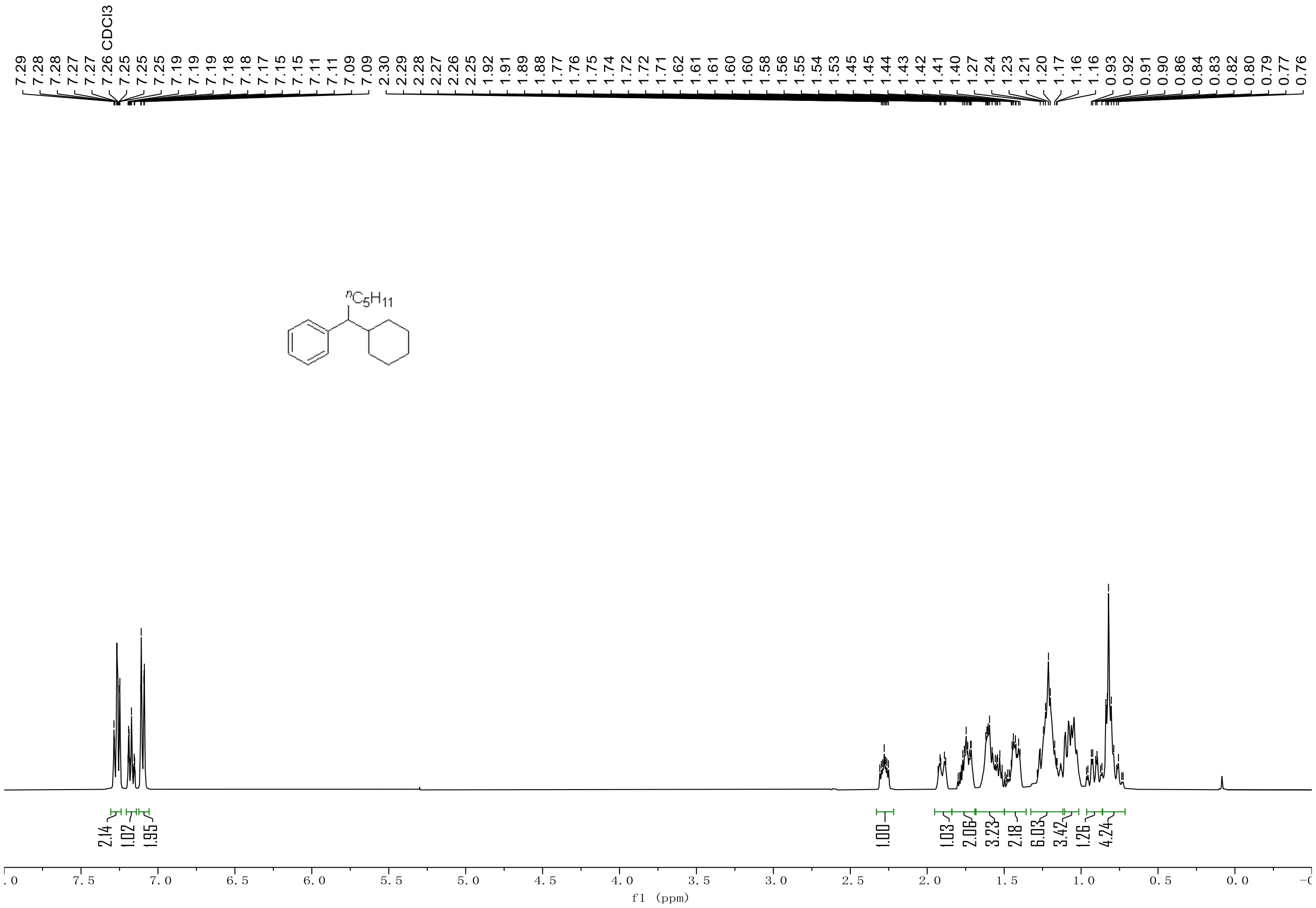


Figure S69 ^{13}C NMR of **4c**

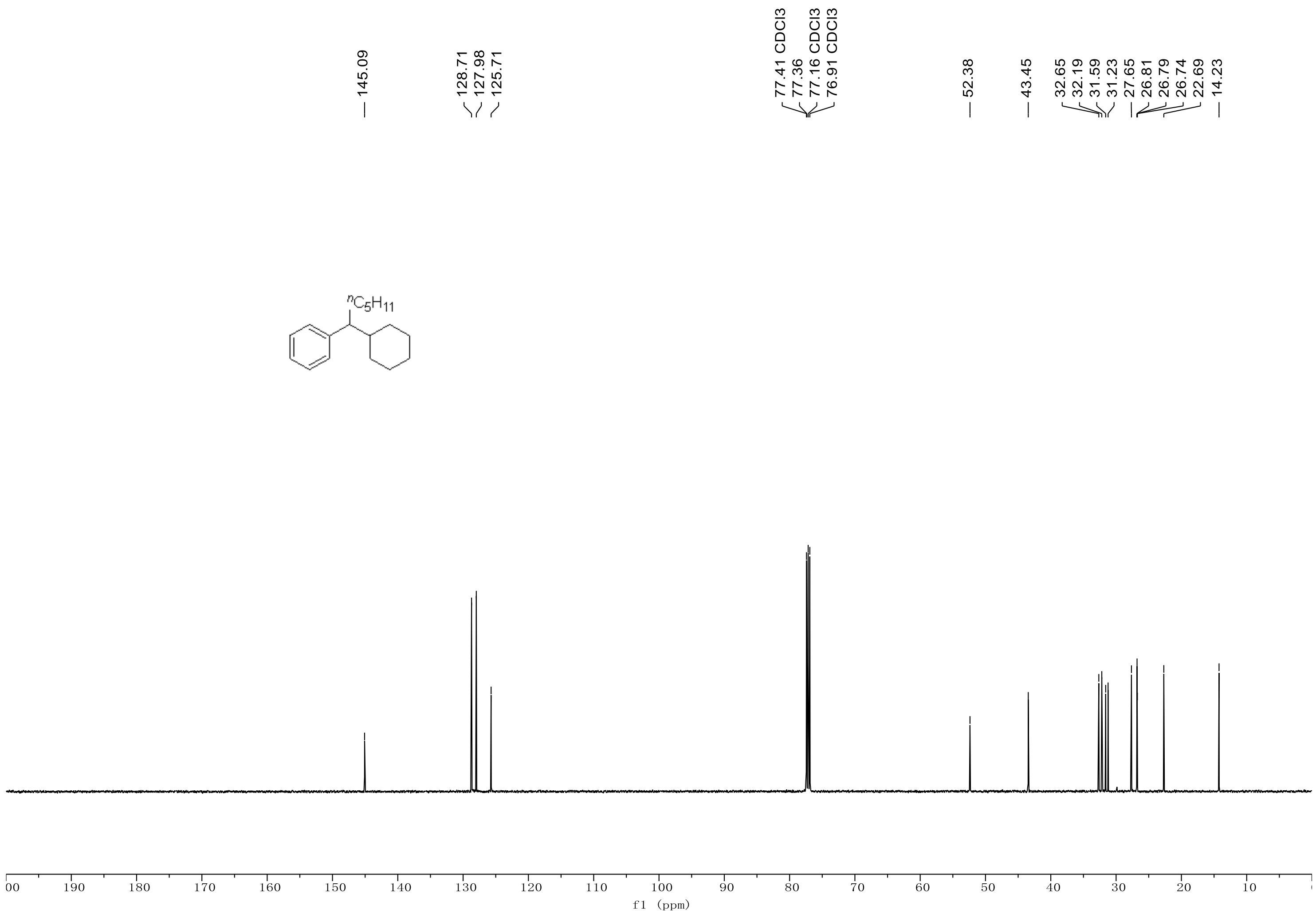


Figure S70 ^{1}H NMR of **4d**

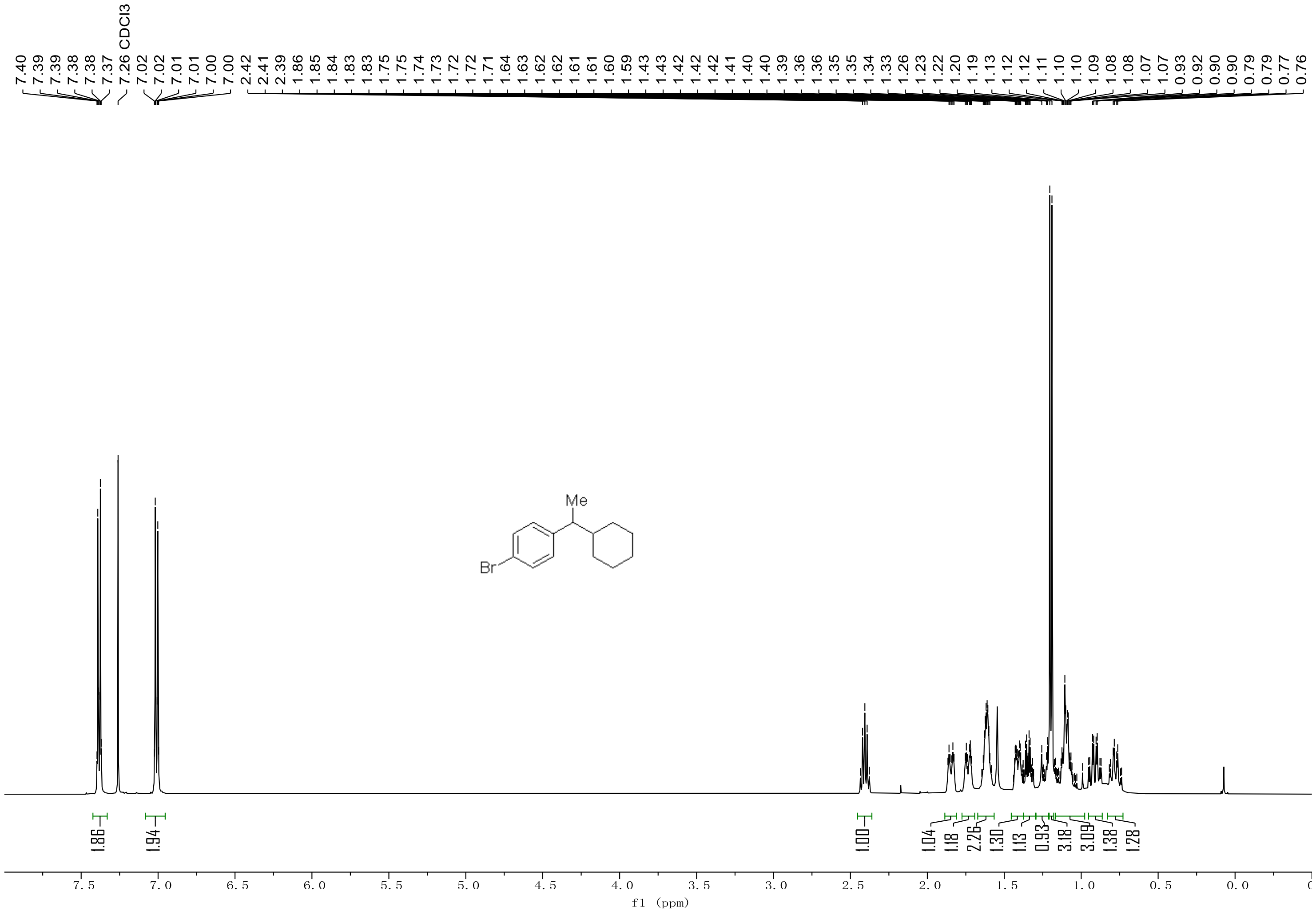


Figure S71 ^{13}C NMR of **4d**

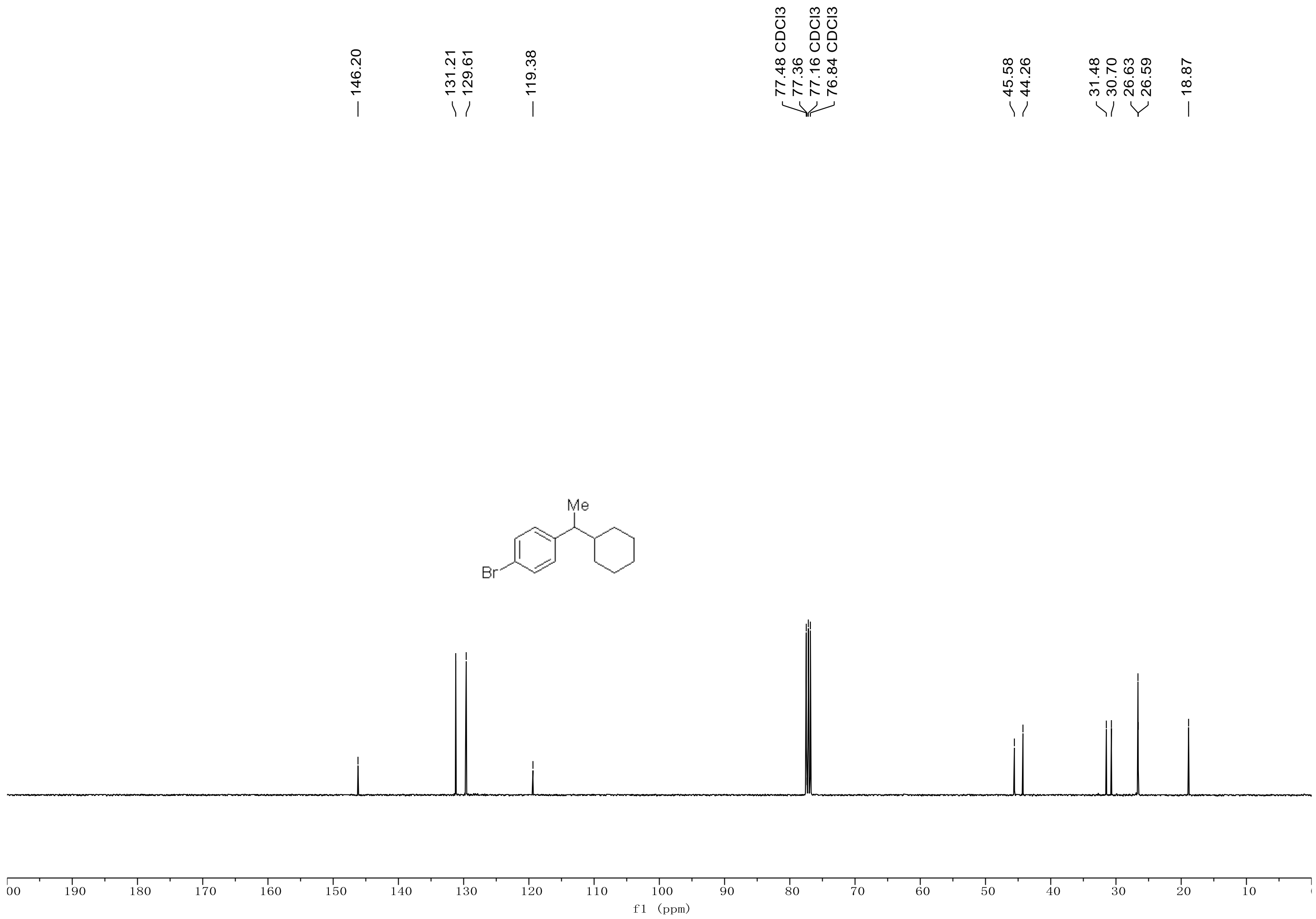


Figure S72 ^{1}H NMR of **4e**

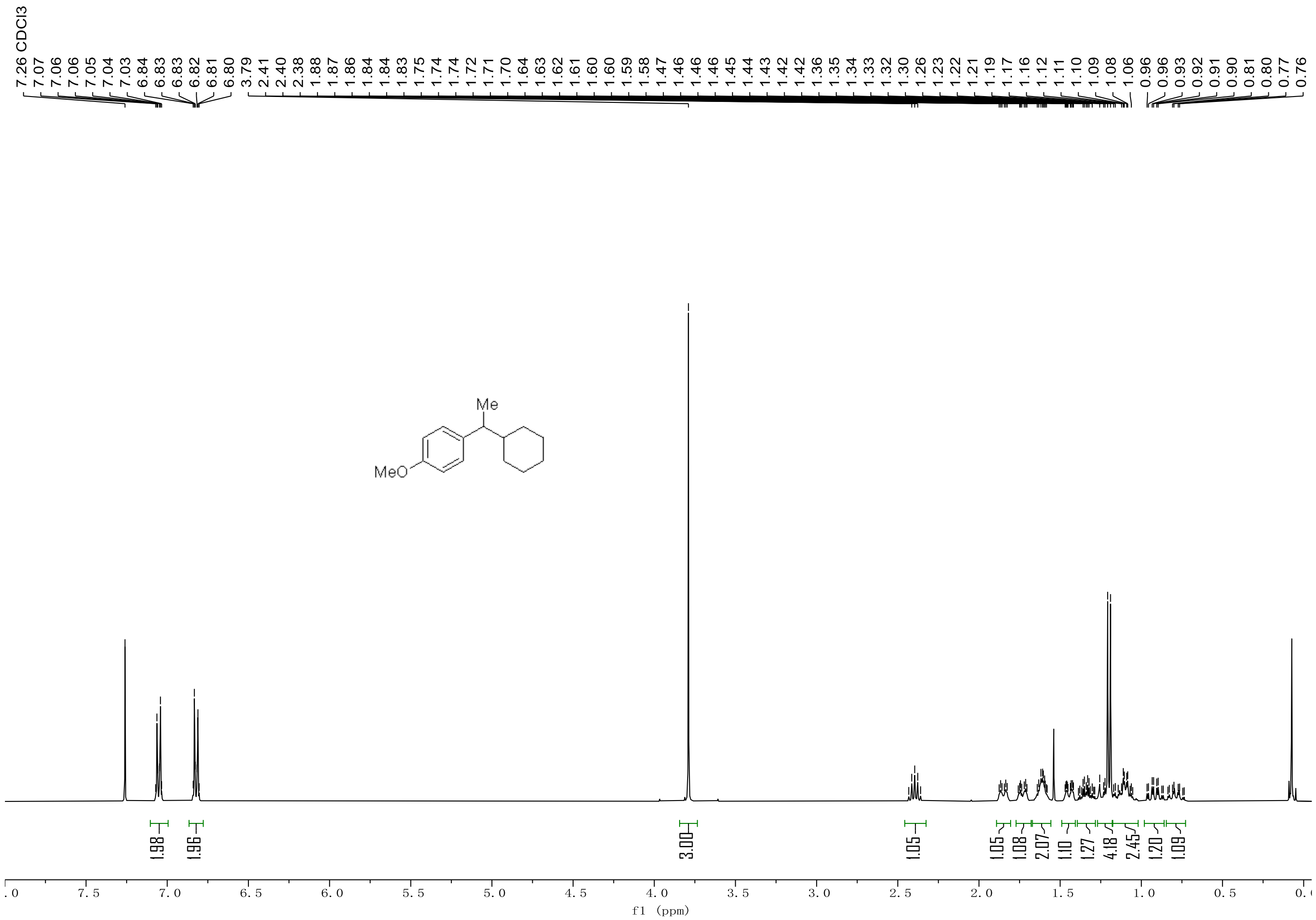


Figure S73 ^{13}C NMR of **4e**

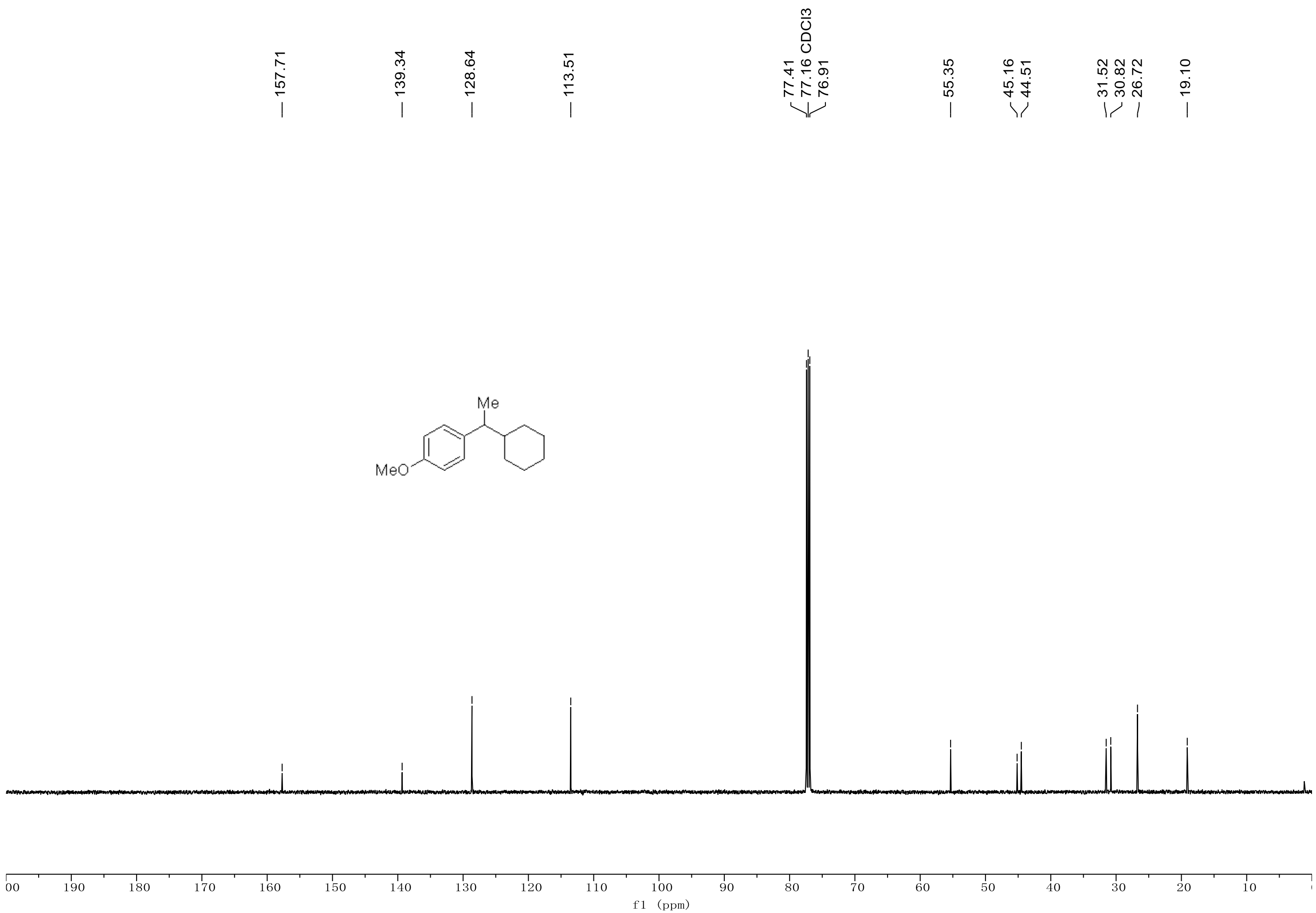


Figure S74 ^{1}H NMR of **4f**

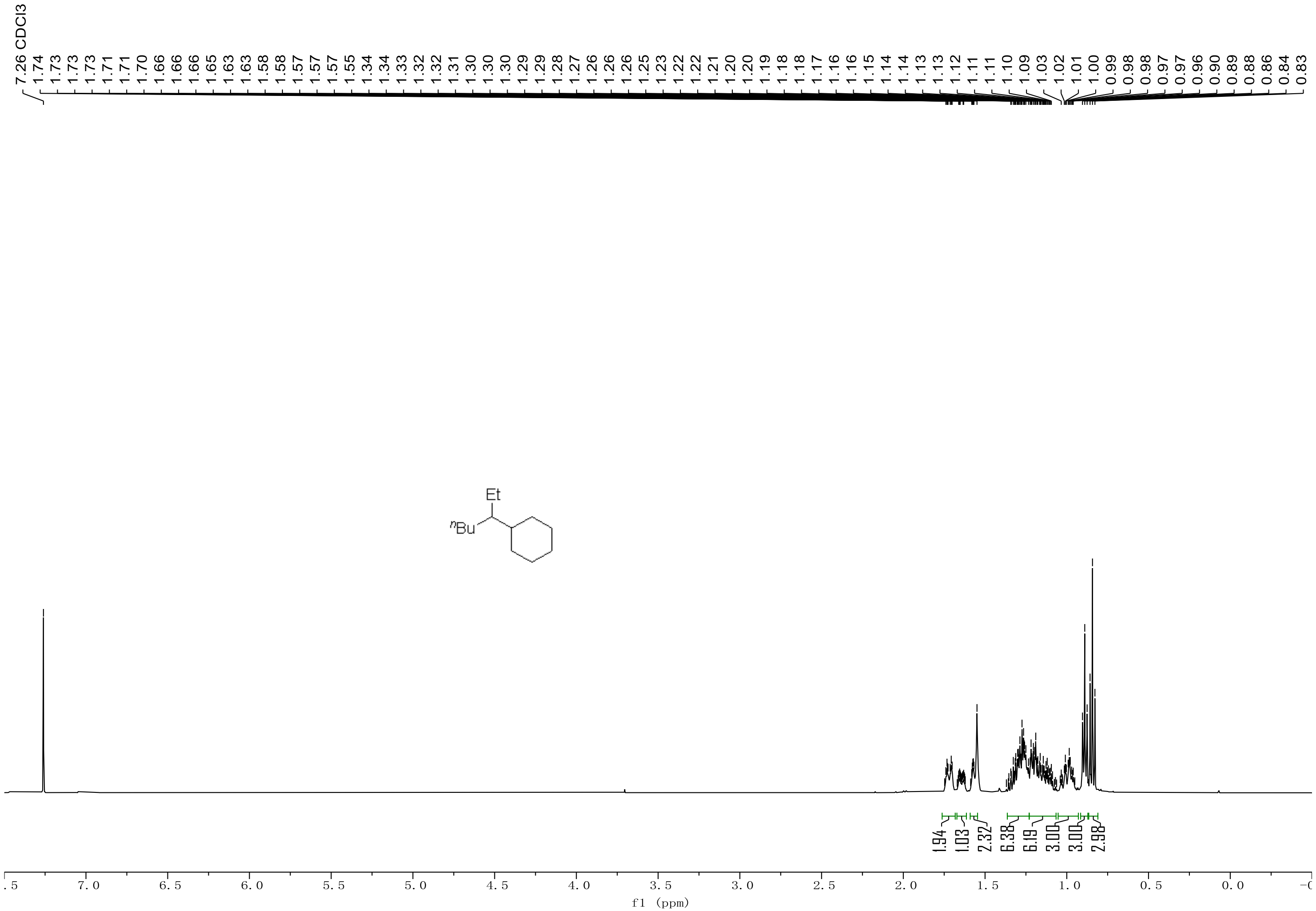


Figure S75 ^{1}H NMR of **4f**

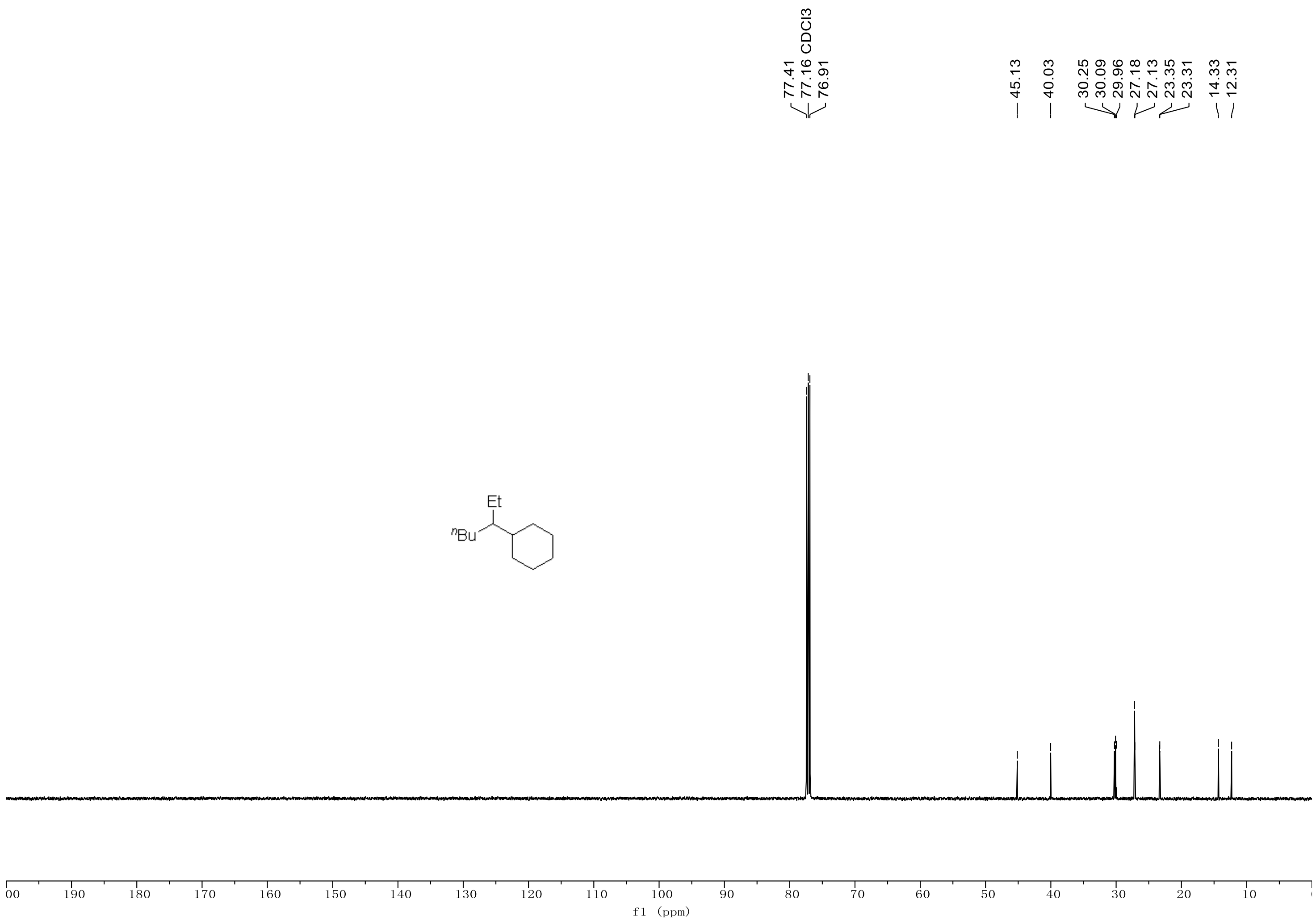


Figure S76 ^{1}H NMR of **4g**

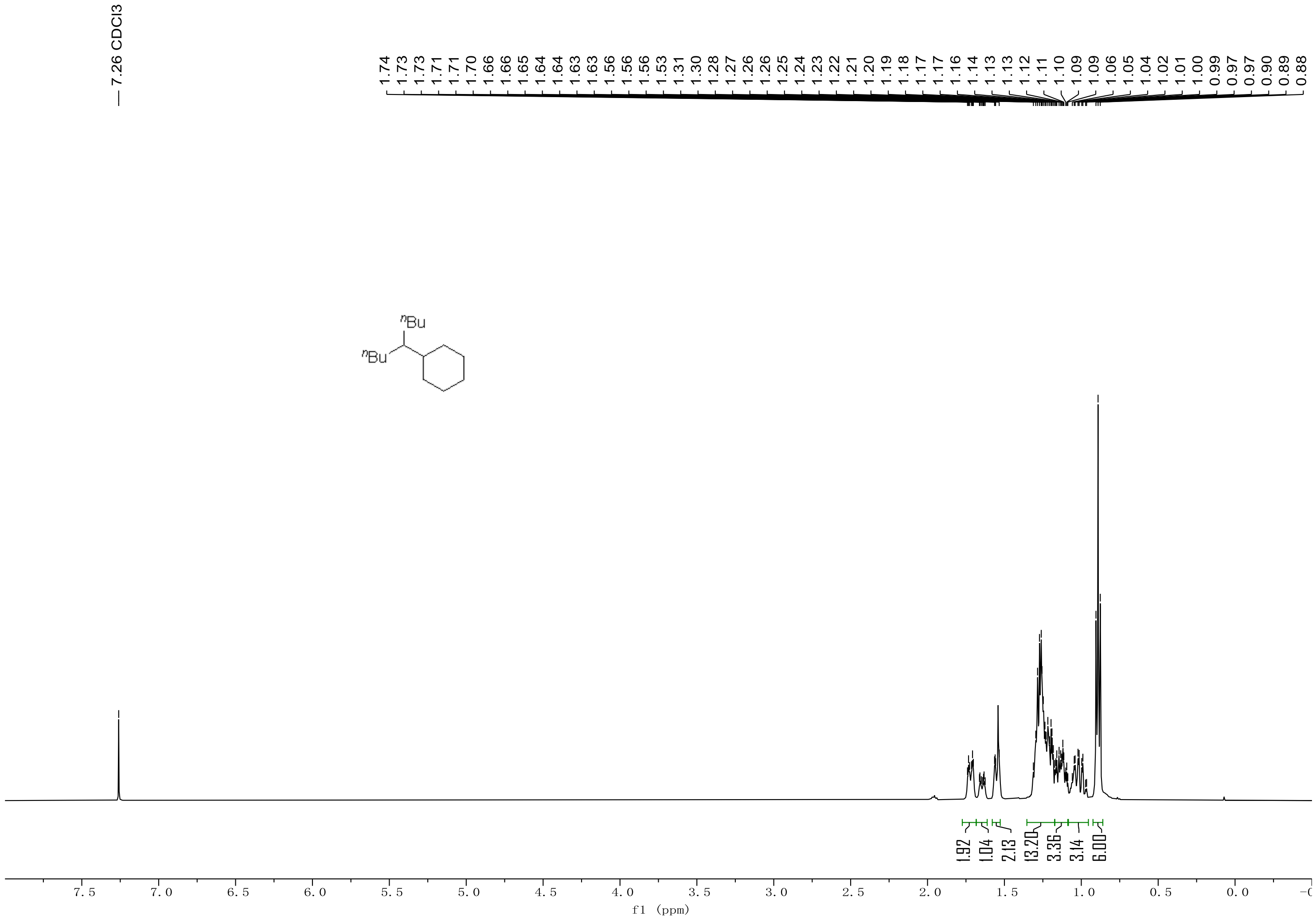


Figure S77 ^{1}H NMR of **4g**

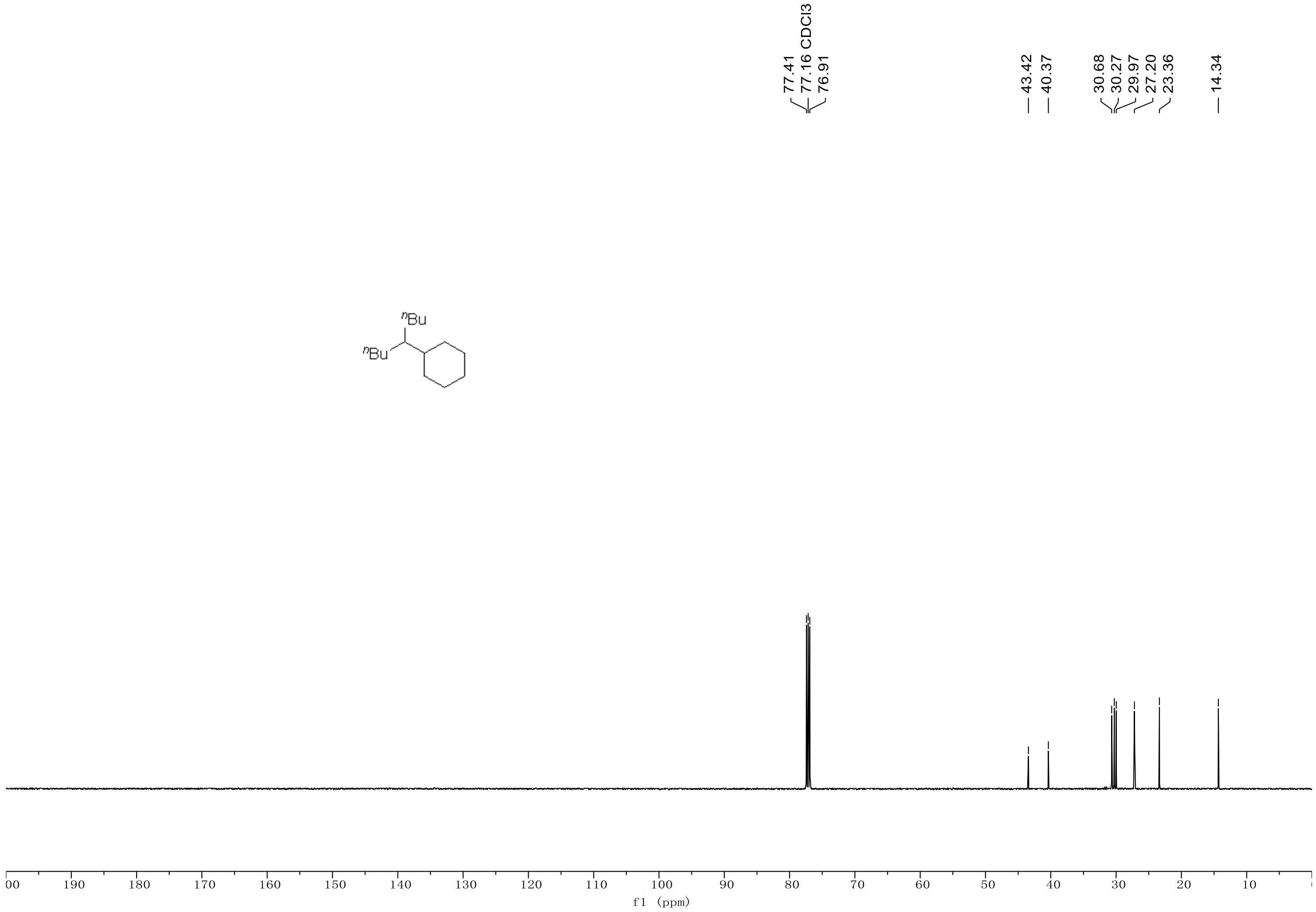


Figure S78 ^{1}H NMR of **4h**

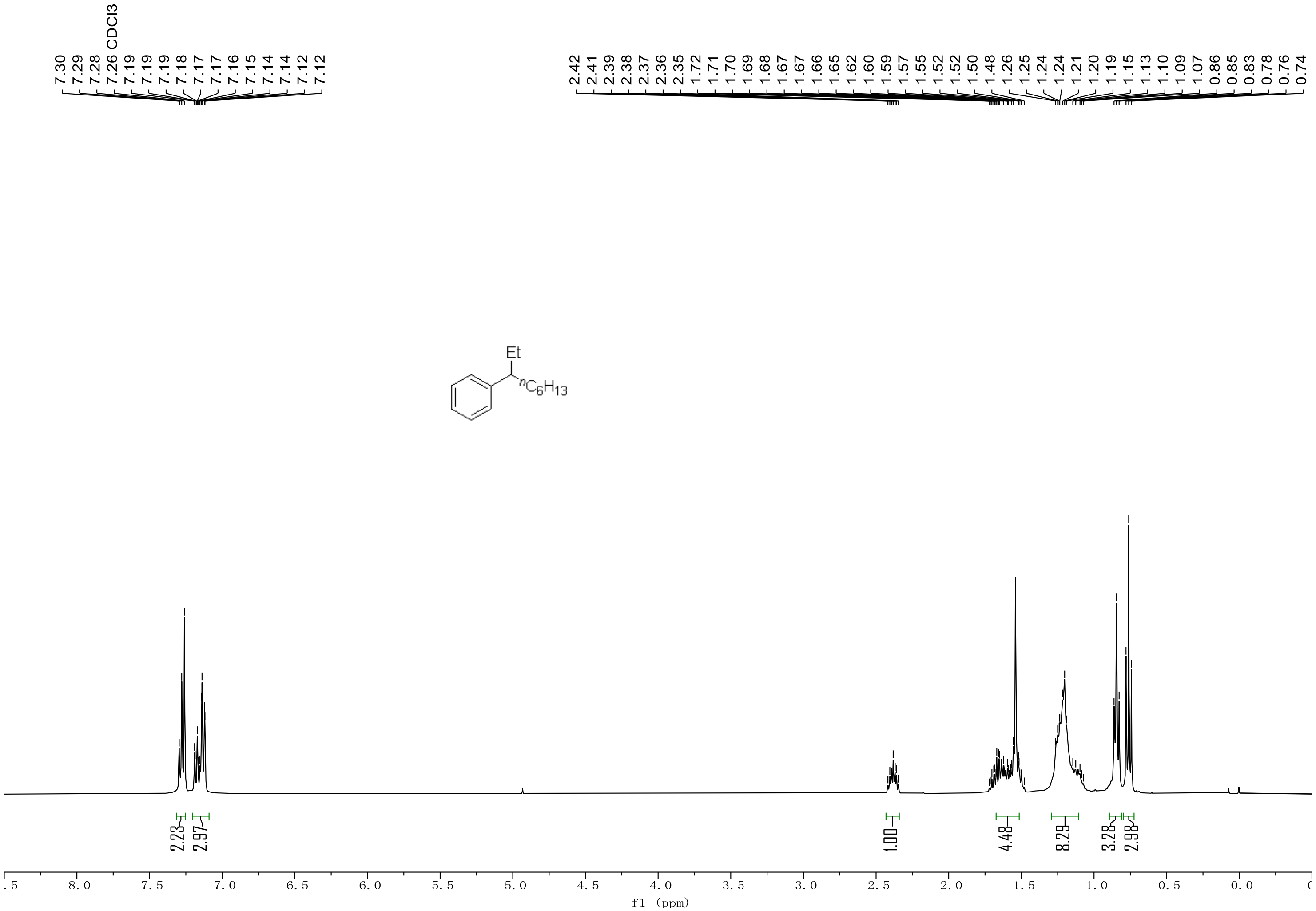


Figure S79 ^{13}C NMR of **4h**

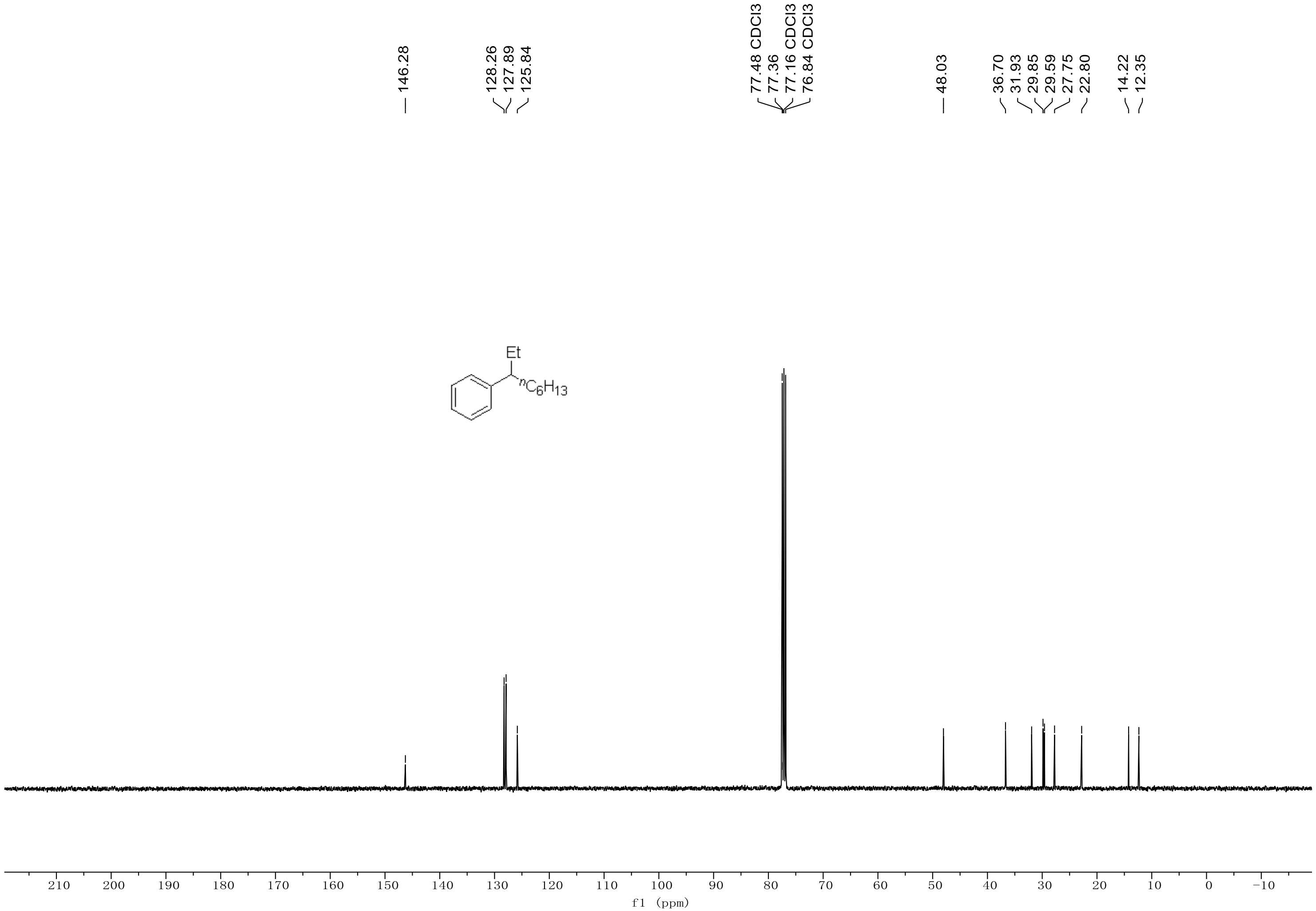


Figure S80 ^{1}H NMR of **4i**

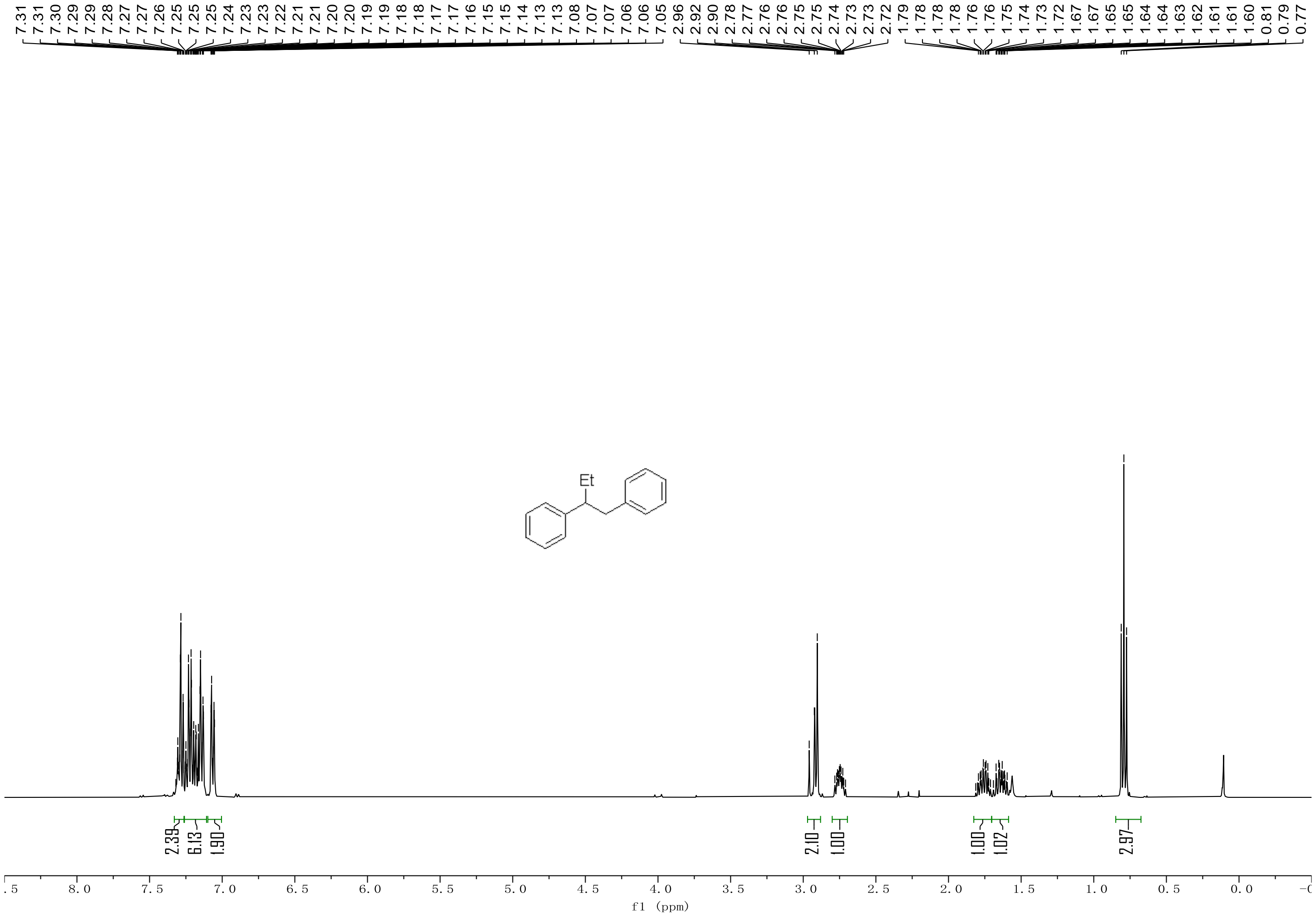


Figure S81^{3}C NMR of **4i**

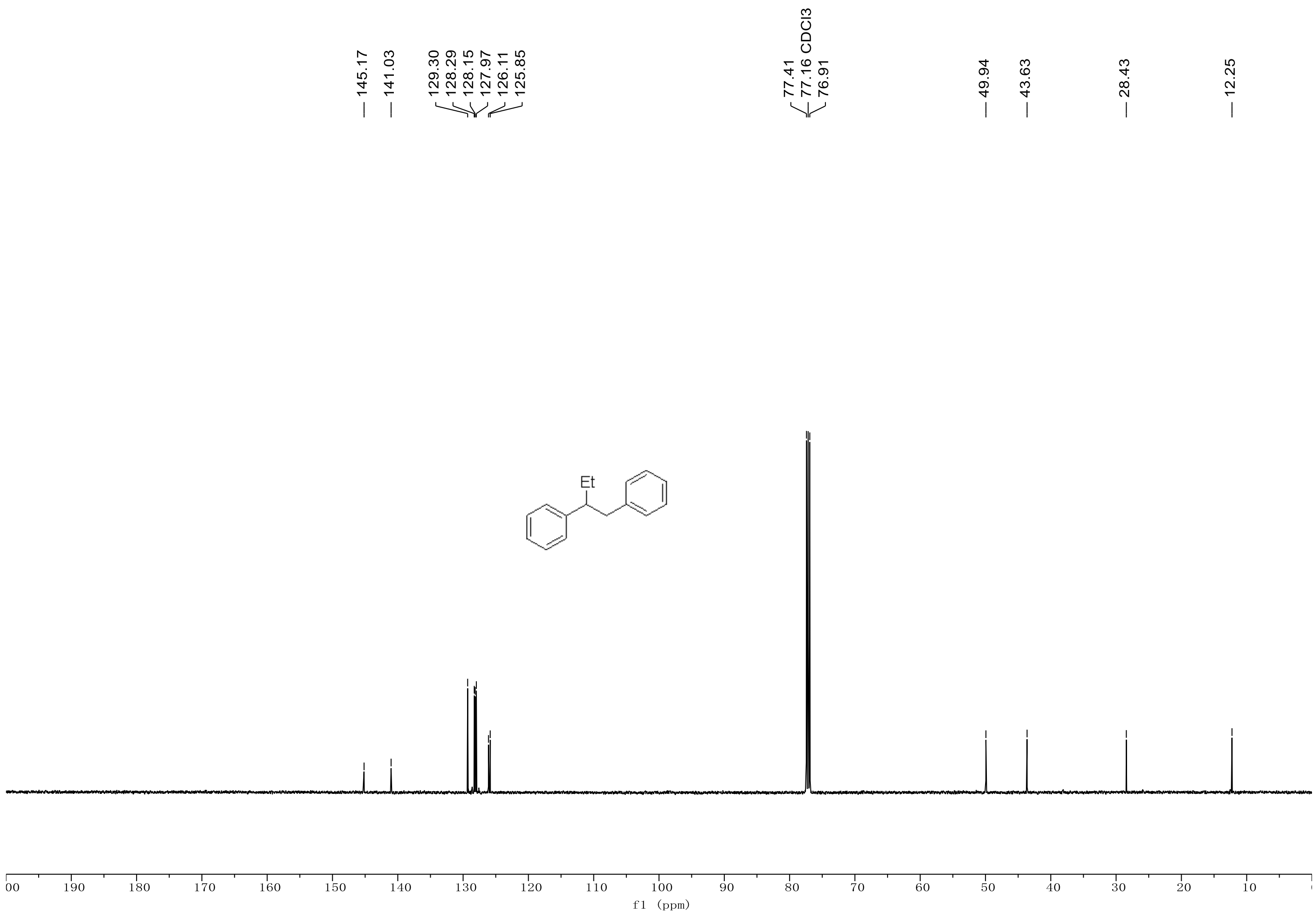


Figure S82 [1]H NMR of **4j**

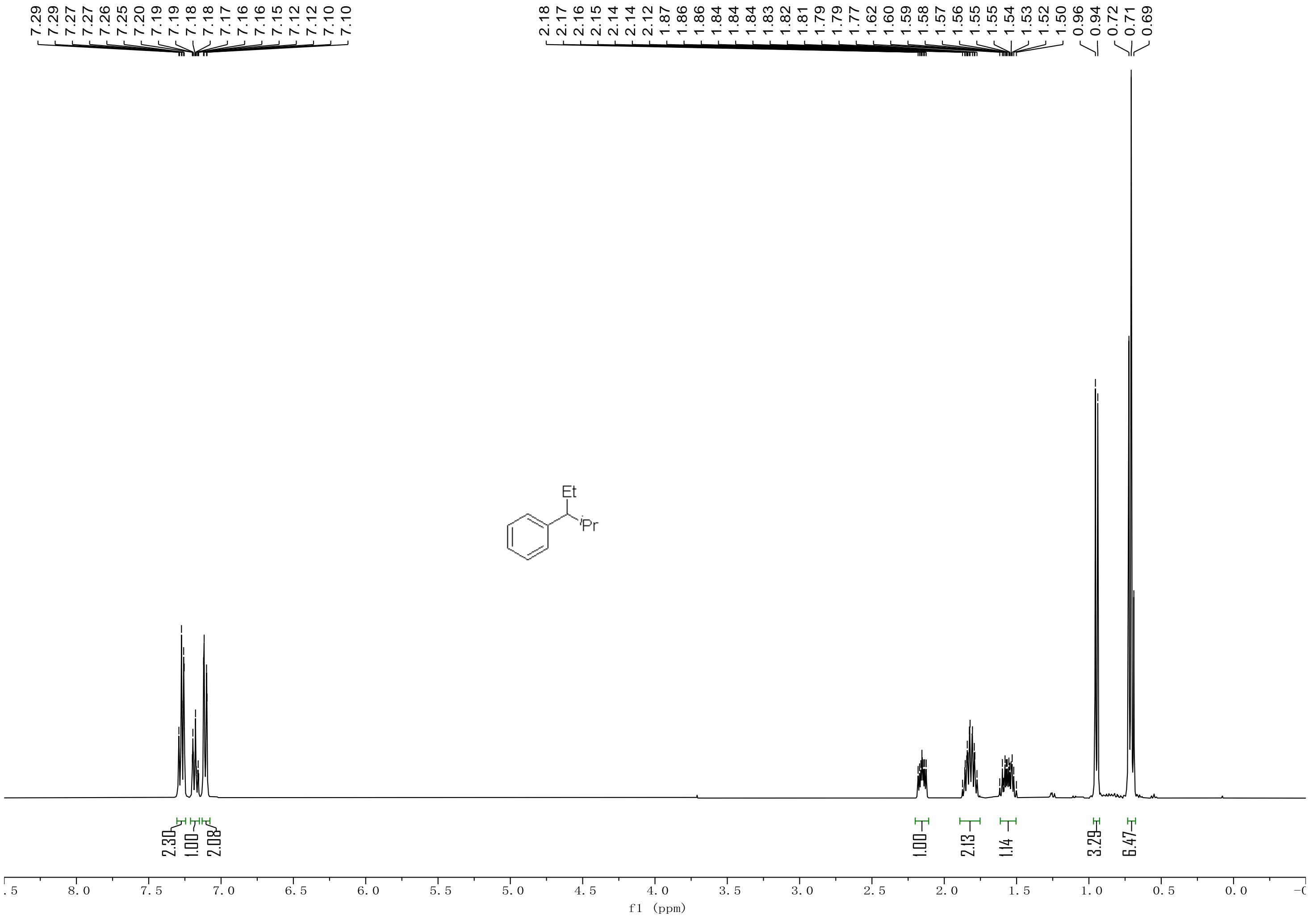


Figure S83 ^{13}C NMR of **4j**

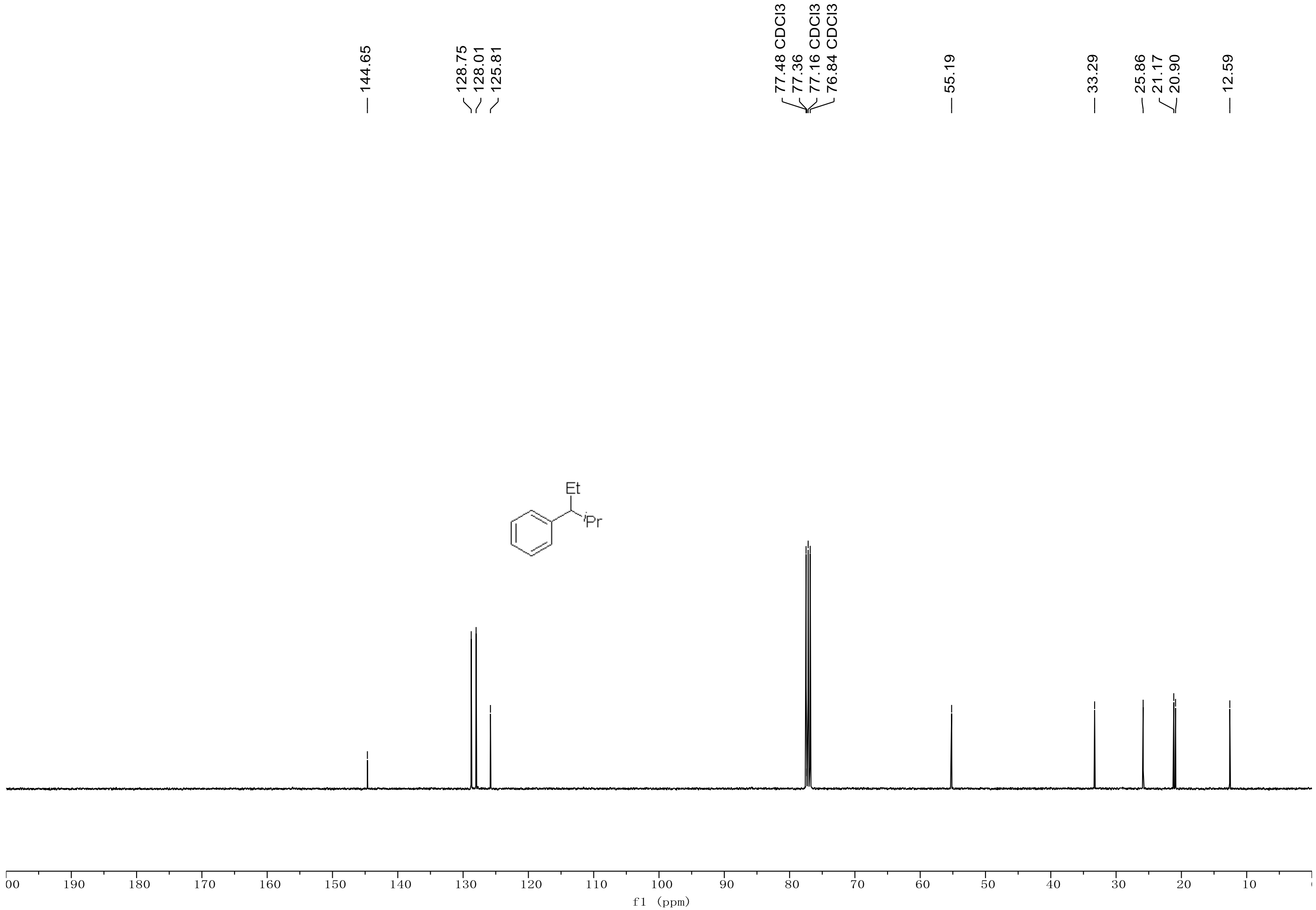


Figure S84 [1]H NMR of **4k**

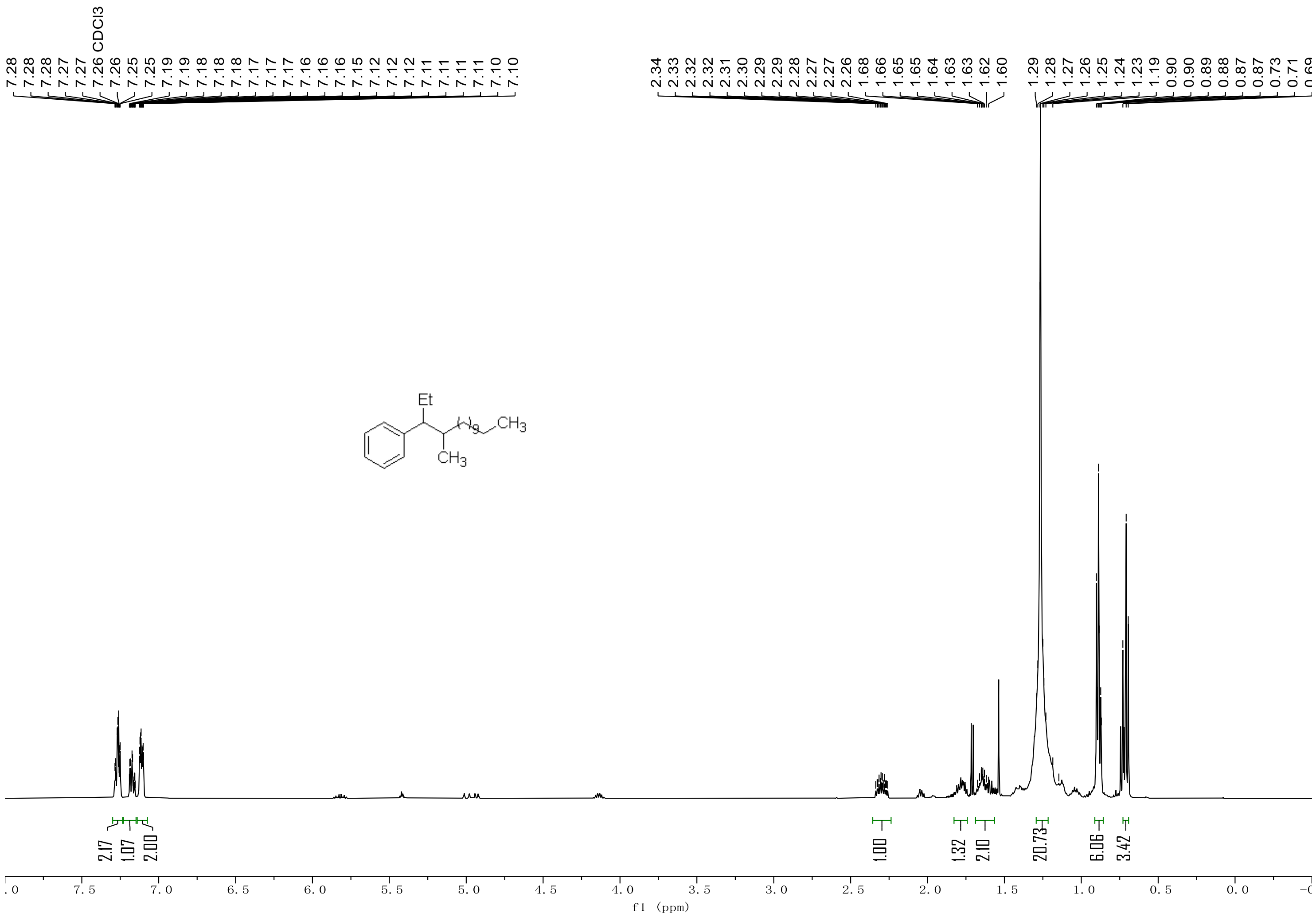


Figure S85 ^{1}H NMR of **4l**

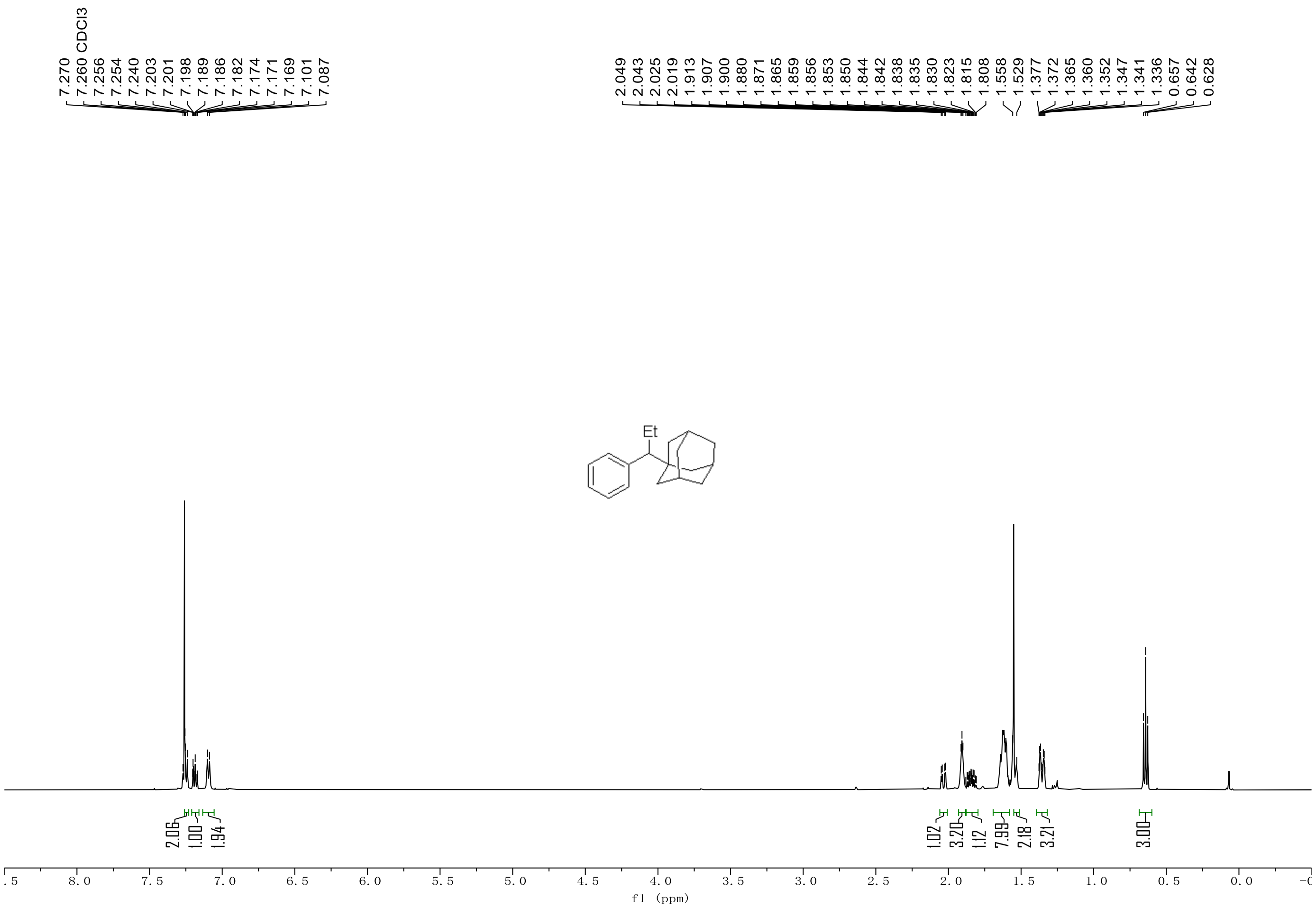


Figure S86 ^{13}C NMR of **4l**

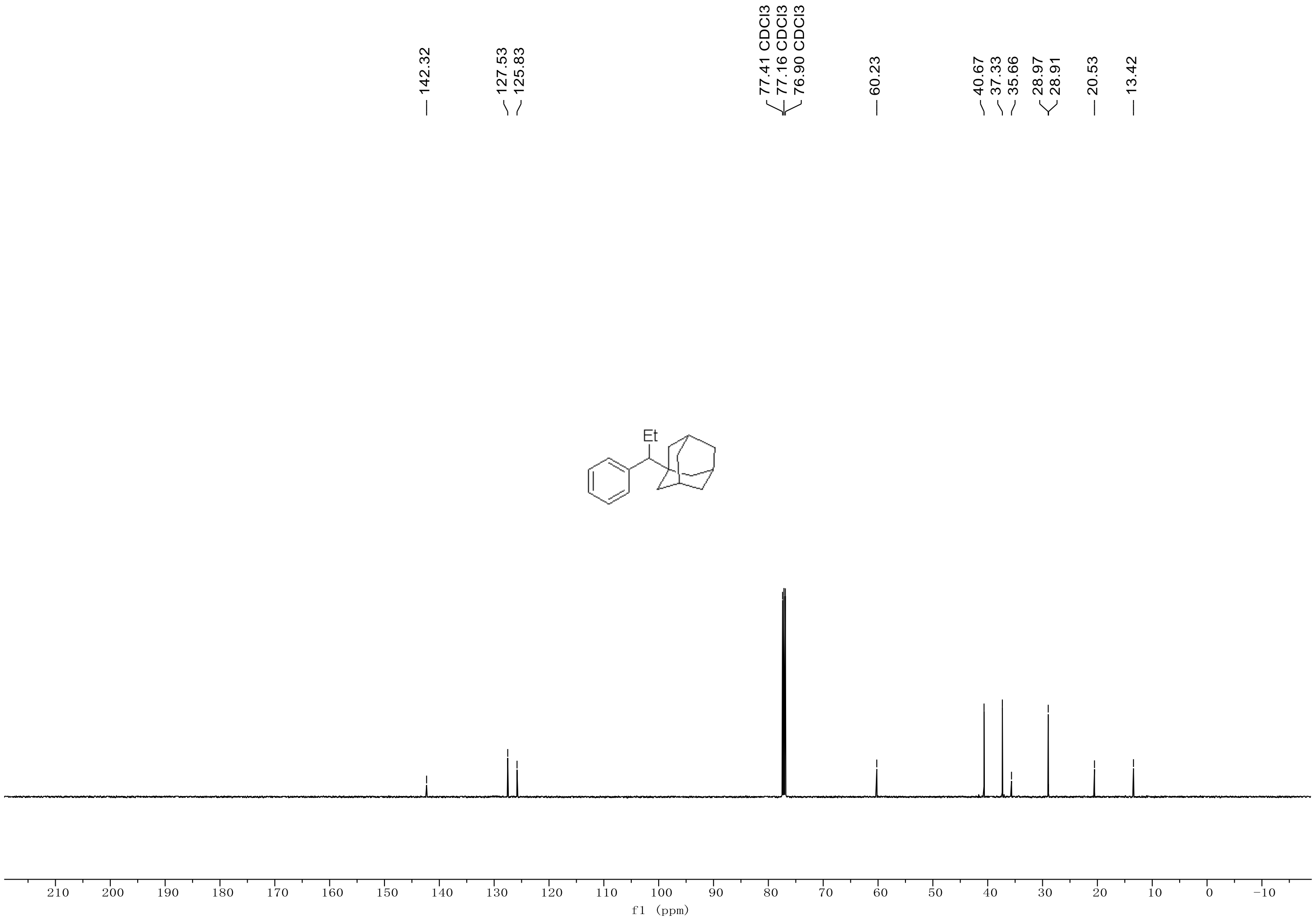


Figure S87 ^{1}H NMR of **4m**

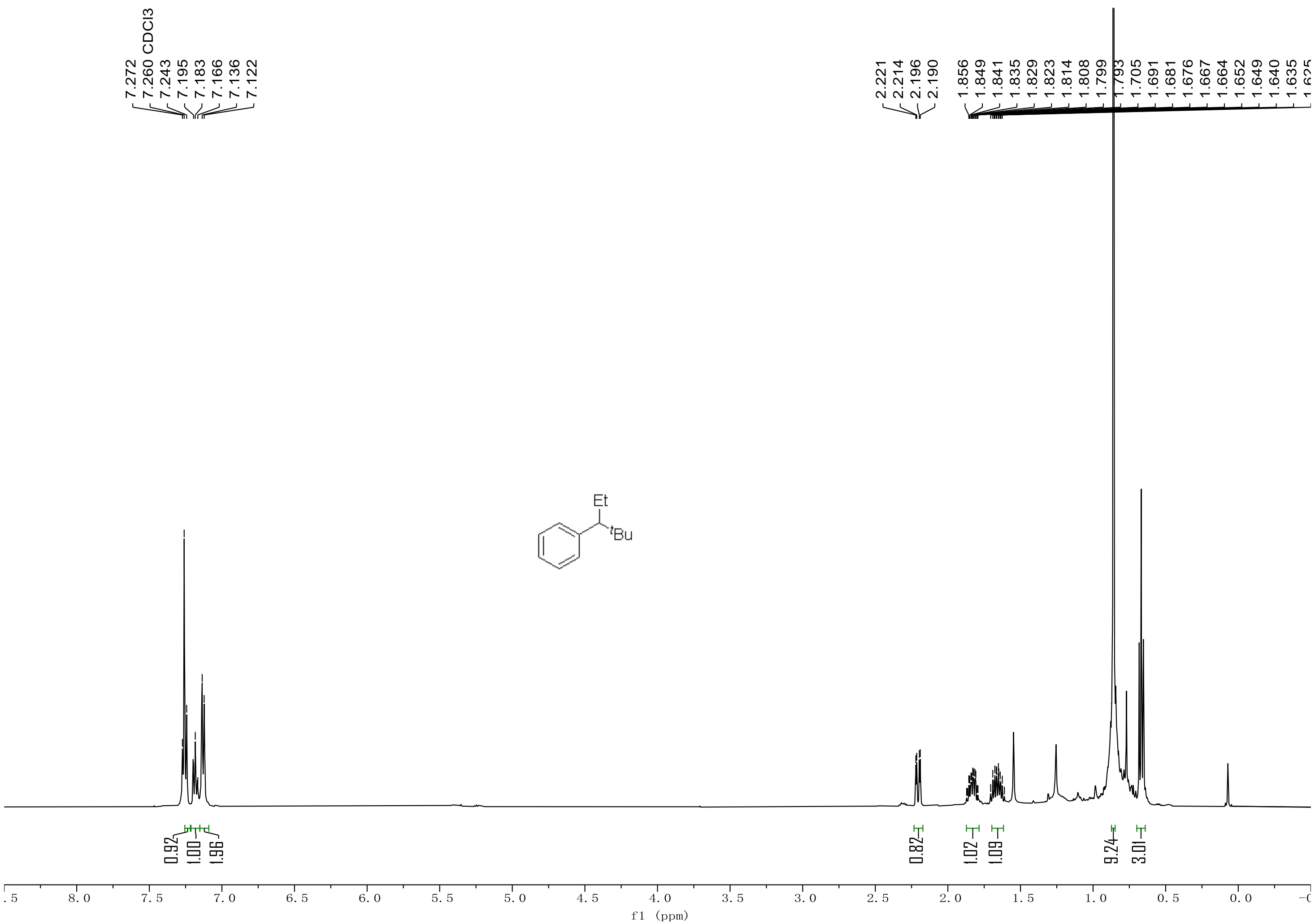


Figure S88 ^{13}C NMR of **4m**

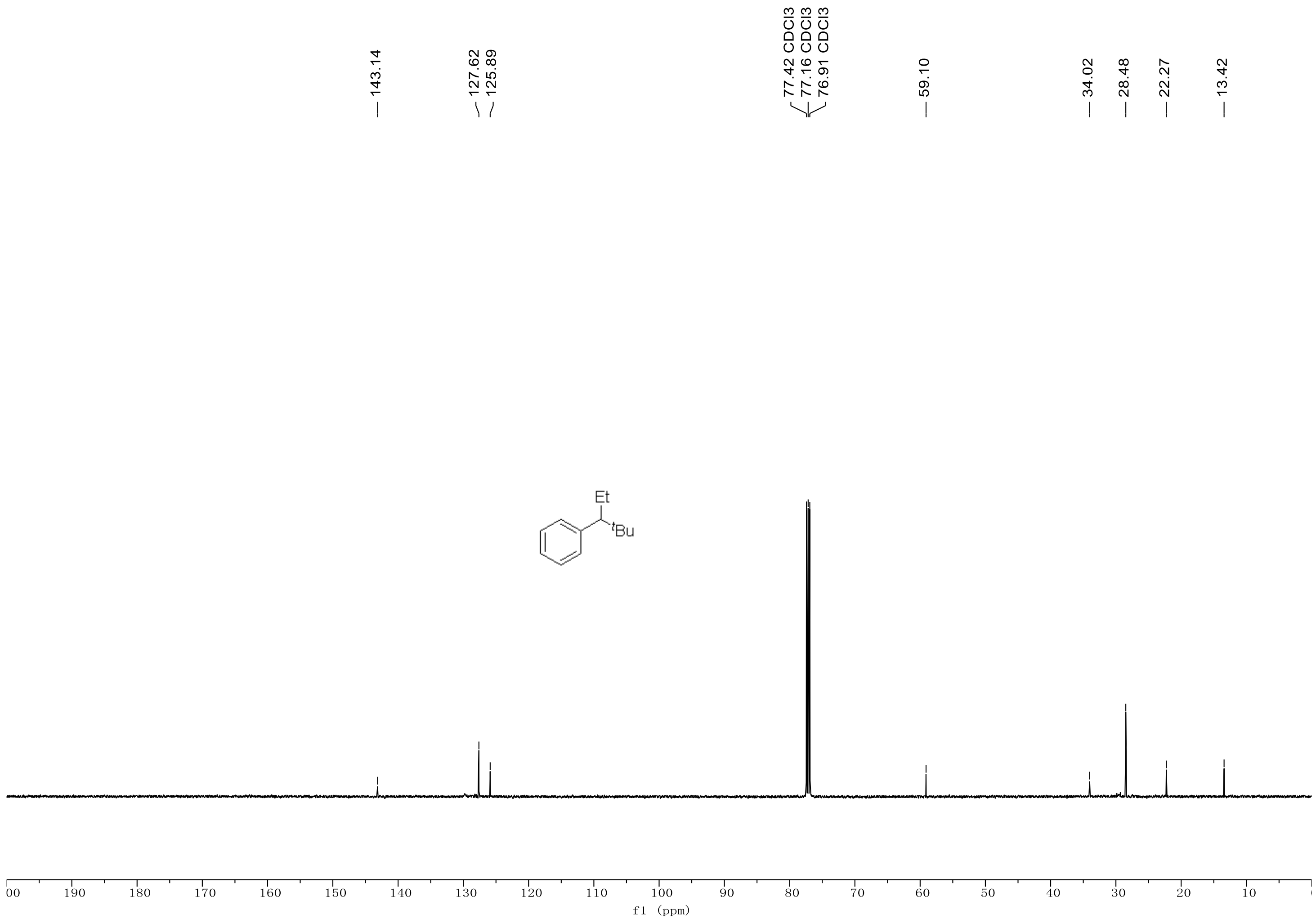
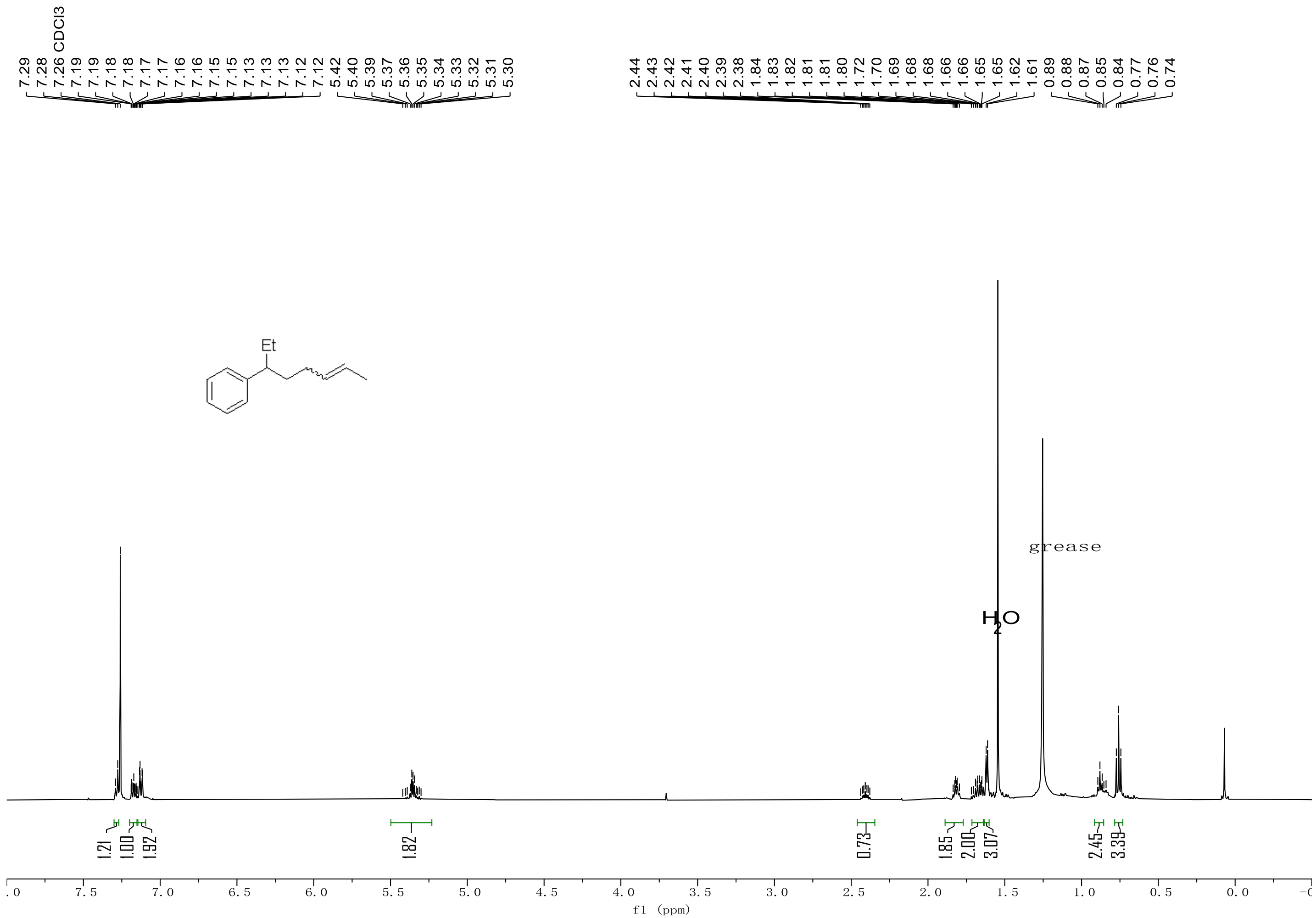


Figure S89 ^{1}H NMR of **4o** and **4o’**



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