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Aromatization of Cyclic Hydrocarbons via Thioether Elimination Reaction

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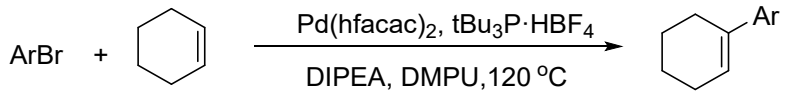
1. General information

Chemicals and solvents were purchased from commercial suppliers and used as received unless noted. All products were purified by flash chromatography on silica gel. The chemical yields referred are isolated products. ^{1}H NMR and ^{13}C NMR spectra were recorded on 400 MHz, 500MHz and 600 MHz Bruker spectrometers. Chemical shifts of ^{1}H were reported in part per million relative to the $CDCl_3$ residual peak (δ 7.260), the CD_3OD residual peak (δ 3.330), the $(CD_3)_2CO$ residual peak (δ 2.050). Chemical shifts of ^{13}C NMR were reported relative to $CDCl_3$ (δ 77.0), CD_3OD (δ 49.0), $(CD_3)_2CO$ (δ 206.0). The used abbreviations are as follows: s (singlet), d (doublet), t (triplet), quart. (quartet), quint (quintet), m (multiplet), br (broad). Structural assignments were made with additional information from NOE and HMBC experiments. Multiplets which arise from accidental equality of coupling constants of magnetically non-equivalent protons are marked as virtual (*virt.*). High resolution mass spectra (HRMS) data were measured on a ESI-microTOF II. Major elements, such as Zn, Cd, Cu, Ni, Cr et al. in reaction system were determined by using Microwave plasma-atomic emission spectrometry (Agilent/4210 MP-AES). Melting points were measured on a SGW® X-4B and are not corrected. Reactions were monitored by TLC analysis using silica gel 60 Å F-254 thin layer plates and compounds were visualized with a UV light at 254 nm or 365 nm.

2. Synthesis of phenylcyclohexene derivatives

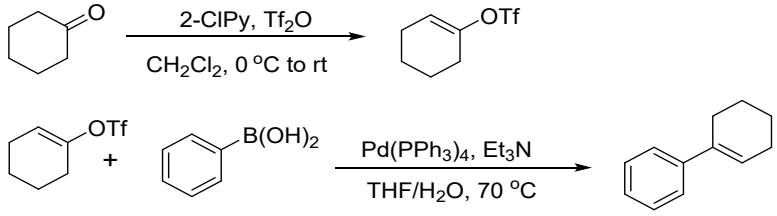
2.1 General procedure for the synthesis of phenyl-substituted cyclohexene



Phenyl-substituted cyclohexene were synthesized according to previously reported procedures:[1] Under a N_2 condition, a dry 15-mL reaction tube containing a magnetic stir bar was charged with $Pd(hfacac)_2$ (10 mg, 4 mol%), P-$^{t}Bu_3$·HBF_4 (12 mg, 8 mol%) and 2.5 mL of dry DMPU. After stirring at room temperature for 10 minutes, *p-tert*-butylphenyl bromide (105 mg, 0.50 mmol), DIPEA (95 mg, 1.5 equiv, 0.75 mmol), cyclohexene (205 mg, 5 equiv, 0.50 mmol) was added in sequence. The tube was capped tightly and the mixture was vigorous stirred in a 120 °C oil bath for 30 hours. After cooling down to room temperature, the solution was filtered through a small amount of silica gel. The residue was purified by flash chromatography (hexane) on silica gel to afford the corresponding 4'-(tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl as a white solid (96 mg, 90%). Other

chemical reagent were used as received from commercial sources unless noted.

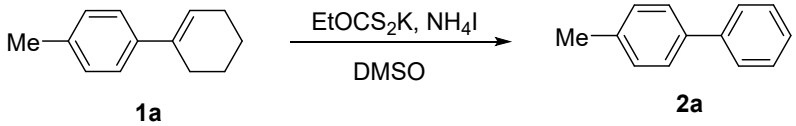
2.2 General procedure for the synthesis of substituted cyclohexenyl benzene



Cyclohexenyl benzene were also synthesized according to previously reported procedures:[2,3] To a solution of 4-*tert*-butylcyclohexanone (162 mg, 1.1 mmol) in anhydrous CH_2Cl_2 (5 mL) was added 2-chloropyiride (0.11 mL, 1.2 mmol, 1.1 equiv) at 0 °C. After stirring at 0 °C for 10 min, trifluoromethanesulfonic anhydride (0.21 mL, 1.3 mmol, 1.2 equiv) was added dropwise. The resulting solution was warmed to 30 °C and stirred for 2h under a nitrogen atmosphere. After the completion of the reaction, the solution was concentrated and the resulting cherry-color oil was purified by flash column chromatography on silica gel to afford 4-(tert-butyl)cyclohex-1-en-1-yl trifluoromethanesulfonate. Under a nitrogen atmosphere, a dry Schlenk tube was charged with THF (5 ml), deionized H_2O (1 mL) and Et_3N (5.0 mmol). Then phenylboronic acid (2.0 mmol) and the trifluoromethanesulfonate (1.0 mmol) were added. The reaction was stirred at 70 °C for 2 hours or until completion (TLC). Then H_2O (5 mL) was added and the resulting mixture was extracted with EtOAc (2*15 mL), then the organic phase was dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (hexane) on silica gel to afford the corresponding 4-(Tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl as a light yellow liquid (148 mg, 63%). Othe chemical reagent was used as received from commercial sources unless noted.

3. General procedures for dehydrogenation reaction

3.1. General methods for the synthesis of biphenyl derivatives

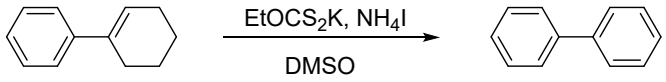


1a **2a**

A mixture of 4'-methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (0.5 mmol, 86 mg), $EtOCS_2K$ (80 mg, 1.0 equiv, 0.5 mmol), NH_4I (145 mg, 2 equiv, 1.0 mmol) were added in a 15 mL Schlenk tube. After stirring for 24 h at 150 °C, the solution was filtered through a small amount of silica gel, concentrated under vacuum. The residue was purified by flash chromatography (hexane, R_f = 0.8) on

silica gel which furnished product **2a** (76 mg, 90%) as a white solid. The following compounds 2c-2u and 2af-2ak were prepared by a similar method, unless otherwise note.

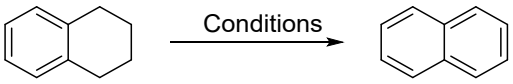
3.2. Synthesis of 1,1'-biphenyl 2b in 1 mmol-scale



2b

A mixture of 2,3,4,5-tetrahydro-1,1'-biphenyl (1.0 mmol) , $EtOCS_2K$ (160 mg, 1.0 mmol, 1 equiv.), NH_4I (190 mg, 2.0 mmol, 2 equiv.) and DMSO (3 mL) were added in a 15 mL Schlenk tube. After stirring for 12 h at 130 °C, the solution was filtered through a small amount of silica gel, concentrated under vacuum. The residue was purified by flash chromatography (Hexane, R_f=0.8) on silica gel which furnished product 1,1'-biphenyl **2b** (135mg, 88%) as a white solid.

3.3.Table S1. Optimization of reaction conditions for synthesis of naphthalene [a]

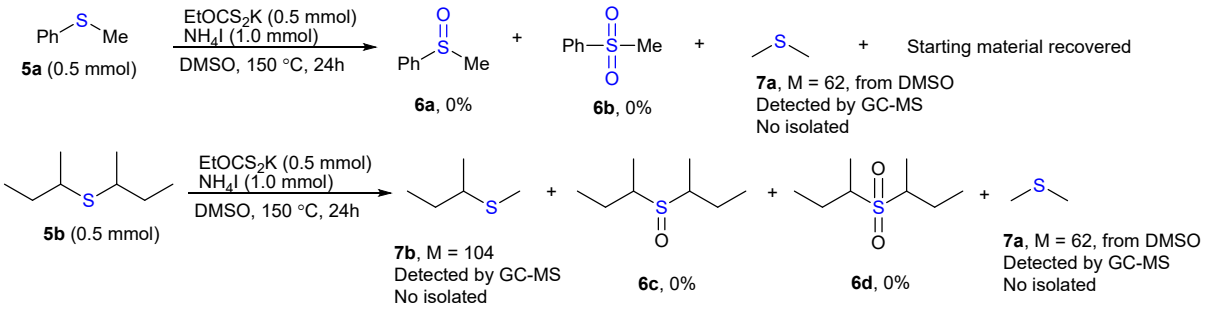


2v

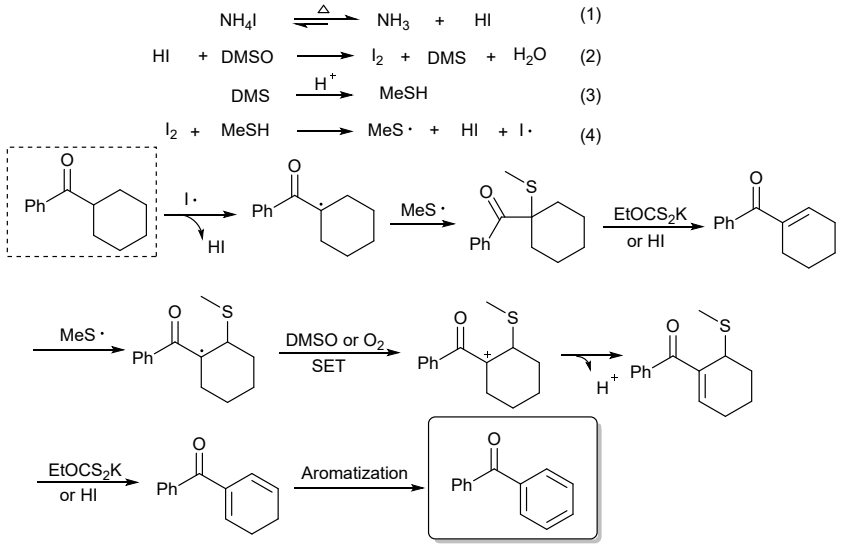
Entry	$EtOCS_2K$ (eq)	NH_4I (eq)	Addition	Time (h)	Yield [b](%)
1[c]	1	2	-	18	<5
2	1	2	-	18	17
3	1	2	LiO^tBu (1 eq)	18	22
4	1	2	KO^tBu (1 eq)	18	21
5	1	2	Na_2CO_3 (1 eq)	18	24
6	1	2	Cs_2CO_3 (1 eq)	18	23
7	1	2	Na_2CO_3 (1 eq)	36	44
8	1	2	Na_2CO_3 (2 eq)	36	<5
9	2	2	Na_2CO_3 (1 eq)	36	34
10	1	3	Na_2CO_3 (1 eq)	36	38
11	**1**	**2**	**Na_2CO_3 (1 eq)**	**72**	**95**

[a]Reaction conditions: 1,2,3,4-tetrahydronaphthalene (0.5 mmol), $EtOCS_2K$, NH_4I in DMSO (2 mL). [b]Isolated yields.

Scheme S1. Control experiments for thioether oxidation reaction.

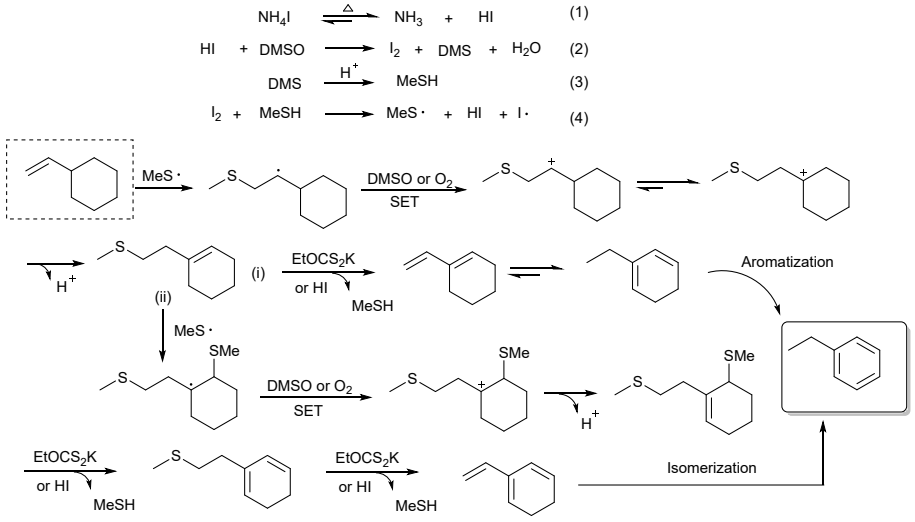


Scheme S2. Proposed mechanism for synthesis of 2v-2y, 2ad-2ae



For radical coupling reaction, see ref: B. Du, B. Jin, P. Sun, *Org. Lett*. 2014, **16**, 3032–3035.

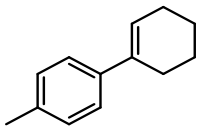
Scheme S3. Proposed mechanism for synthesis of 2af-2ah



For Isomerization of Alkene, see ref: (a) W. Chen, Y. Chen, X. Gu, Z. Chen, C. Y. Ho, *Nat Commun*., 2022, **13**, 5507; (b) B. A. Kustiana, S. A. Elsherbeni, T. G. Linford-Wood, R. L. Melen, M. N. Grayson, L. C. Morrill, *Chem*. Eur. *J.* 2022, **28**, e202202454; (c) S. De-Botton, D. S. O. A. Filippov, E. S. Shubina, N. V. Belkova, D. Gelman, *ChemCatChem* 2020, 5959.

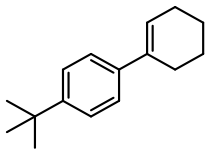
4. Analytical data of all products

4'-Methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (1a)[4]



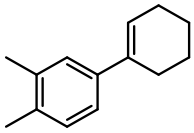
Yellow oil liquid, 76 mg, 88%. TLC (Hexane): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.13 (d, J = 8.1 Hz, 2H), 6.13 – 6.07 (m, 1H), 2.44 – 2.39 (m, 2H), 2.35 (s, 3H), 2.25 – 2.19 (m, 2H), 1.83 – 1.77 (m, 2H), 1.71 – 1.65 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.8, 136.3, 136.1, 128.8 (2C), 124.8 (2C), 123.9, 27.4, 25.8, 23.1, 22.2, 21.0.

4'-(Tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (1b)[1]



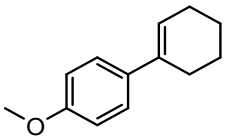
Light yellow liquid, 96 mg, 90%. TLC (Hexane): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (m, 4H), 6.21 – 6.07 (m, 1H), 2.46 – 2.40 (m, 2H), 2.25 – 2.19 (m, 2H), 1.84 – 1.76 (m, 2H), 1.71 – 1.64 (m, 2H), 1.34 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.4, 139.7, 136.2, 125.0 (2C), 124.5 (2C), 124.0, 34.4, 31.3 (3C), 27.3, 25.9, 23.1, 22.2.

3',4'-Dimethyl-2,3,4,5-tetrahydro-1,1'-biphenyl (1c)



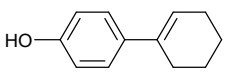
Yellow oil liquid, 81 mg, 87%. TLC (Hexane/ethyl acetate=100/1): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.16 (s, 1H), 7.14 – 7.10 (m, 1H), 7.07 (d, J = 7.8 Hz, 1H), 6.10 – 6.04 (m, 1H), 2.42 – 2.37 (m, 2H), 2.26 (s, 3H), 2.25 (s, 3H), 2.22 – 2.17 (m, 2H), 1.80 – 1.74 (m, 2H), 1.68 – 1.62 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 136.5, 136.1, 134.8, 129.4, 126.3, 123.8, 122.4, 27.5, 25.8, 23.1, 22.2, 19.9, 19.4. ESI-HRMS (*m/z*) $[M+Na]^+$ calcd for $C_{14}H_{18}Na$, 209.1301, found: 209.1296.

4'-Methoxy-2,3,4,5-tetrahydro-1,1'-biphenyl (1d)[4]



Brown liquid, 77 mg, 82%. TLC (Hexane): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 2H), 6.89 – 6.82 (m, 2H), 6.09 – 5.99 (m, 1H), 3.81 (s, 3H), 2.43 – 2.35 (m, 2H), 2.24 – 2.16 (m, 2H), 1.81 – 1.75 (m, 2H), 1.69 – 1.63 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 135.8, 135.3, 125.9 (2C), 123.1 (2C), 113.5, 55.2, 27.4, 25.8, 23.1, 22.2.

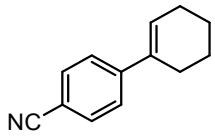
2',3',4',5'-Tetrahydro-[1,1'-biphenyl]-4-ol (1e)



White solid, 149 mg, 86%. m.p. 108-110 °C. TLC (Hexane/ethyl acetate=20/1): R_f=0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 2H), 6.82 – 6.74 (m, 2H), 6.07 – 5.99 (m, 1H), 5.33 (s, 1H), 2.40 – 2.35 (m, 2H), 2.23 – 2.17 (m, 2H), 1.81 – 1.74 (m, 2H), 1.69 – 1.62 (m, 2H). ^{13}C NMR (125 MHz, Chloroform-d) δ 154.2, 135.8, 135.5, 126.1 (2C), 123.2,

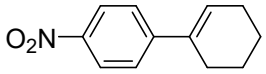
115.0 (2C), 27.4, 25.8, 23.0, 22.1. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{12}H_{15}O$, 175.1117, found: 175.1113.

2',3',4',5'-Tetrahydro-[1,1'-biphenyl]-4-carbonitrile (1f)



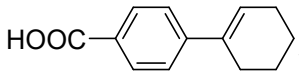
Brown solid, 164 mg, 90%. m.p. 64-66 °C. TLC (Hexane/ethyl acetate=1/1): R_f =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, J = 8.2 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 6.30 – 6.22 (m, 1H), 2.41 – 2.35 (m, 2H), 2.27 – 2.21 (m, 2H), 1.81 – 1.76 (m, 2H), 1.69 – 1.64 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.0, 135.3, 132.0, 128.4, 125.4, 119.2, 109.7, 27.0, 26.0, 22.7, 21.8. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{13}H_{14}N$, 184.1121, found: 184.1117.

4'-Nitro-2,3,4,5-tetrahydro-1,1'-biphenyl (1g)



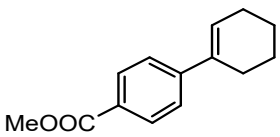
Brown liquid, 166 mg, 82%. TLC (Hexane/ethyl acetate=50/1): R_f =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 8.11 (m, 2H), 7.52 – 7.45 (m, 2H), 6.34 – 6.30 (m, 1H), 2.43 – 2.38 (m, 2H), 2.28 – 2.22 (m, 2H), 1.83 – 1.76 (m, 2H), 1.70 – 1.64 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 146.2, 135.1, 129.3, 125.3 (2C), 123.5 (2C), 27.0, 26.0, 22.7, 21.7. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{12}H_{14}NO^2$, 204.1019, found: 204.1014.

2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylic acid (1h)



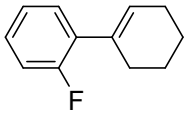
White solid, 161 mg, 80%. m.p. 200-202 °C. TLC(Hexane/ethyl cetate=5/1): R_f =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.51 – 7.44 (m, 2H), 6.32 – 6.25 (m, 1H), 2.46 – 2.41 (m, 2H), 2.28 – 2.21 (m, 2H), 1.84 – 1.76 (m, 2H), 1.72 – 1.64 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 172.2, 148.0, 135.8, 130.2, 127.6, 127.1, 124.8, 27.1, 26.0, 22.9, 21.9. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{13}H_{15}O_2$, 203.1067, found: 203.1067.

Methyl- 2',3',4',5'-tetrahydro-[1,1'-biphenyl]-4-carboxylate (1i)[1]



White solid, 97 mg, 90%. m.p. 85-87 °C. TLC(Hexane/ethyl cetate=50/1): R_f =0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.47 – 7.40 (m, 2H), 6.28 – 6.22 (m, 1H), 3.90 (s, 3H), 2.44 – 2.39 (m, 2H), 2.26 – 2.21 (m, 2H), 1.82 – 1.76 (m, 2H), 1.69 – 1.64 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 147.1, 135.9, 129.6 (2C), 128.0, 127.2, 124.7 (2C), 52.0, 27.1, 26.0, 22.9, 22.0.

2'-Fluoro-2,3,4,5-tetrahydro-1,1'-biphenyl (1j)

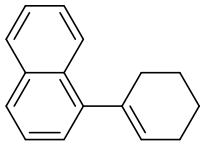


Brown liquid, 155 mg, 88%. TLC (Hexane/ethyl acetate=100/1): R_f=0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.15 (m, 2H), 7.07 (t, J = 7.5 Hz, 1H), 7.01 (dd, J = 11.2, 8.1 Hz, 1H), 5.97 – 5.90 (m, 1H), 2.40 – 2.34 (m, 2H), 2.24 – 2.17 (m, 2H), 1.80 – 1.74 (m, 2H), 1.71 – 1.67 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9 (d, J = 246.9 Hz), 133.7, 131.5 (d, J = 14.0 Hz), 129.3 (d, J = 4.7 Hz), 128.1 (d, J = 3.0 Hz), 127.8 (d, J = 8.3 Hz), 123.8 (d, J = 3.6 Hz), 115.6 (d, J = 23.0 Hz), 28.7 (d, J = 3.4 Hz), 25.7, 22.9, 22.0. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{12}H_{14}F$, 177.1074, found:177.1070.

2,2'',3,3'',4,4'',5,5''-Octahydro-1,1':4',1''-terphenyl (1k)

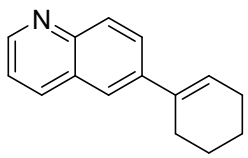
White solid, 126 mg, 81%. m.p. 107-109 °C. TLC (Hexane/ethyl acetate=100/1): R_f=0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 4H), 6.17 – 6.11 (m, 2H), 2.44 – 2.39 (m, 4H), 2.24 – 2.19 (m, 4H), 1.81 – 1.76 (m, 4H), 1.70 – 1.64 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7 (2C), 136.2 (4C), 124.6 (2C), 124.2 (2C), 27.3 (2C), 25.9 (2C), 23.1 (2C), 22.2 (2C). ESI-HRMS (*m/z*) $[M+Na]^+$ calcd for $C_{18}H_{22}Na$, 261.1614, found: 261.1609.

1-(Cyclohex-1-en-1-yl)naphthalene (1l)



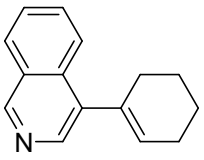
White solid, 185 mg, 89%. m.p. 50-51 °C. TLC (Hexane): R_f=0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 1H), 7.88 – 7.83 (m, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.51 – 7.46 (m, 2H), 7.44 (dd, J = 8.3, 7.0 Hz, 1H), 7.28 (dd, J = 7.0, 1.3 Hz, 1H), 5.83 – 5.76 (m, 1H), 2.42 – 2.38 (m, 2H), 2.32 – 2.26 (m, 2H), 1.90 – 1.85 (m, 2H), 1.84 – 1.78 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1, 137.6, 133.7, 131.4, 128.2, 127.2, 126.7, 125.8, 125.5, 125.5, 125.4, 124.8, 31.0, 25.5, 23.2, 22.3. ESI-HRMS (*m/z*) $[M+Na]^+$ calcd for $C_{16}H_{16}Na$, 231.1144, found: 231.1142.

6-(Cyclohex-1-en-1-yl)quinoline (1m)



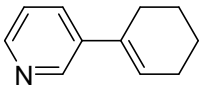
Yellow liquid, 177 mg, 85%. TLC (Hexane/ethyl acetate=5/1): R_f =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80 (dd, J = 4.2, 1.8 Hz, 1H), 8.08 – 7.96 (m, 2H), 7.79 (dd, J = 8.9, 2.1 Hz, 1H), 7.65 (d, J = 2.1 Hz, 1H), 7.29 (dd, J = 8.3, 4.2 Hz, 1H), 6.32 – 6.25 (m, 1H), 2.50 – 2.44 (m, 2H), 2.26 – 2.20 (m, 2H), 1.83 – 1.74 (m, 2H), 1.69 – 1.62 (m, 2H). ^{13}C NMR (125 MHz,$CDCl_3$) δ 149.5, 147.4, 140.3, 135.9, 135.5, 128.8, 128.1, 127.3, 126.4, 122.5, 121.0, 27.1, 25.9, 22.8, 21.9. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{15}H_{16}N$, 210.1277, found: 210.1272.

4-(Cyclohex-1-en-1-yl)isoquinoline (1n)



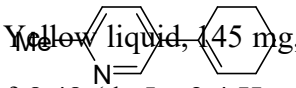
Yellow liquid, 171 mg, 82%. TLC (Hexane/ethyl acetate=5/1): R_f =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.12 (s, 1H), 8.32 (s, 1H), 7.94 (t, J = 7.5 Hz, 2H), 7.67 – 7.62 (m, 1H), 7.58 – 7.53 (m, 1H), 5.85 – 5.79 (m, 1H), 2.38 – 2.33 (m, 2H), 2.29 – 2.23 (m, 2H), 1.87 – 1.81 (m, 2H), 1.79 – 1.73 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.1, 141.3, 135.7, 134.2, 134.1, 129.9, 128.9, 128.3, 127.7, 126.8, 124.6, 30.7, 25.5, 23.0, 22.0. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{15}H_{16}N$, 210.1277, found: 210.1272.

3-(Cyclohex-1-en-1-yl)pyridine (1o)



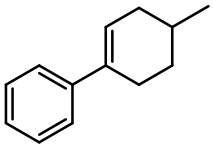
Yellow liquid, 135 mg, 85%. TLC (Hexane/ethyl acetate=5/1): R_f =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, J = 2.3 Hz, 1H), 8.44 (dd, J = 4.8, 1.6 Hz, 1H), 7.64 (dt, J = 8.0, 2.0 Hz, 1H), 7.22 (dd, J = 8.0, 4.8 Hz, 1H), 6.19 – 6.13 (m, 1H), 2.41 – 2.37 (m, 2H), 2.25 – 2.19 (m, 2H), 1.82 – 1.76 (m, 2H), 1.70 – 1.64 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.5, 146.5, 137.9, 133.8, 132.2, 126.7, 123.1, 27.0, 25.8, 22.8, 21.9. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{11}H_{14}N$, 160.1121, found: 160.1111.

5-(cyclohex-1-en-1-yl)-2-methylpyridine (1p)



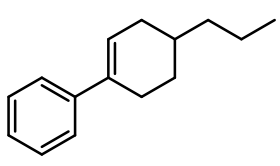
Yellow liquid, 145 mg, 84%. TLC (Hexane/ethyl acetate=3/1): R_f =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 2.4 Hz, 1H), 7.51 (dd, J = 8.1, 2.4 Hz, 1H), 7.04 (d, J = 8.1 Hz, 1H), 6.11 – 6.05 (m, 1H), 2.50 (s, 3H), 2.36 – 2.32 (m, 2H), 2.20 – 2.15 (m, 2H), 1.79 – 1.72 (m, 2H), 1.66 – 1.60 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 145.7, 134.9, 133.7, 132.5, 125.6, 122.5, 27.0, 25.7, 23.9, 22.7, 21.9. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{12}H_{16}N$, 174.1277, found: 174.1272.

4-Methyl-2,3,4,5-tetrahydro-1,1'-biphenyl (1q)



Light yellow liquid, 62 mg, 72%. TLC (Hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.3 Hz, 1H), 6.13 – 6.07 (m, 1H), 2.49 – 2.44 (m, 2H), 2.34 – 2.25 (m, 1H), 1.90 – 1.85 (m, 1H), 1.85 – 1.78 (m, 1H), 1.77 – 1.70 (m, 1H), 1.43 – 1.33 (m, 1H), 1.02 (d, J = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 136.1, 128.2 (2C), 126.5, 124.9 (2C), 124.3, 34.4, 31.3, 28.1, 27.4, 21.7. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{13}H_{17}$, 173.1325, found: 173.1322.

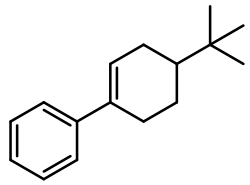
4-Propyl-2,3,4,5-tetrahydro-1,1'-biphenyl (1r)



Light yellow liquid, 68 mg, 68%. TLC (Hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.39 – 7.32 (m, 2H), 7.28 – 7.24 (m, 1H), 6.19 – 6.13 (m, 1H), 2.56 – 2.46 (m, 2H), 2.42 – 2.34 (m, 1H), 2.00 –

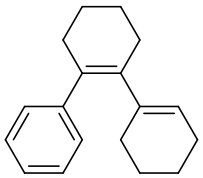
1.94 (m, 1H), 1.92 – 1.84 (m, 1H), 1.72 – 1.62 (m, 1H), 1.49 – 1.32 (m, 5H), 0.99 (t, J = 7.2 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 136.4, 128.1 (2C), 126.5, 124.9 (2C), 124.3, 38.7, 32.8, 32.6, 29.4, 27.4, 20.1, 14.4. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{15}H_{21}$, 201.1638, found: 201.1635.

4-(Tert-butyl)-2,3,4,5-tetrahydro-1,1'-biphenyl (1s)



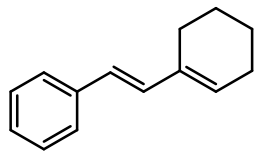
Light yellow liquid, 75 mg, 70%. TLC (Hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.41 (m, 2H), 7.36 – 7.31 (m, 2H), 7.26 – 7.22 (m, 1H), 6.19 – 6.15 (m, 1H), 2.59 – 2.53 (m, 1H), 2.53 – 2.41 (m, 1H), 2.34 – 2.24 (m, 1H), 2.07 – 1.96 (m, 2H), 1.45 – 1.29 (m, 2H), 0.96 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.2, 136.3, 128.2 (2C), 126.4 (2C), 124.9 (2C), 43.8, 32.2, 28.8, 27.5, 27.2 (3C), 24.4. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{16}H_{22}Na$, 237.1614, found: 237.1605.

6-(Cyclohex-1-en-1-yl)-2,3,4,5-tetrahydro-1,1'-biphenyl (1t)



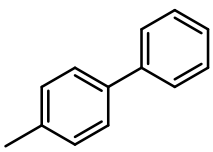
Light yellow liquid, 152 mg, 64%. TLC (Hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.12 (m, 5H), 5.27 (tt, J = 3.7, 1.8 Hz, 5H), 2.36 – 2.32 (m, 2H), 2.21 – 2.17 (m, 2H), 1.88 – 1.83 (m, 2H), 1.82 – 1.78 (m, 2H), 1.76 – 1.69 (m, 4H), 1.47 – 1.38 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.78, 139.87, 137.77, 131.88, 128.14 (2C), 127.42 (2C), 125.56, 125.11, 31.42, 30.27, 28.30, 25.31, 23.30, 23.10, 22.89, 22.08. ESI-HRMS (*m/z*) $[M+Na]^+$ calcd for $C_{18}H_{22}Na$, 261.1614, found: 261.1609.

2-(Cyclohex-1-en-1-yl)vinyl)benzene (1u) [5]



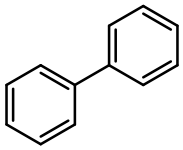
Light yellow liquid, 56 mg, 61%. TLC (Hexane/ethyl acetate=100/1): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H), 7.34 – 7.28 (m, 2H), 7.23 – 7.16 (m, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.45 (d, J = 16.2 Hz, 1H), 5.91 (t, J = 4.2 Hz, 1H), 2.31 – 2.27 (m, 2H), 2.23 – 2.17 (m, 2H), 1.77 – 1.62 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.0, 135.8, 132.6, 130.8, 128.5 (2C), 126.8, 126.1 (2C), 124.6, 26.1, 24.5, 22.5, 22.5.

4-Methyl-1,1'-biphenyl (2a)[6]



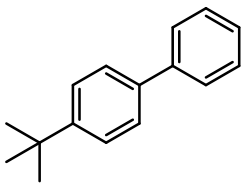
White solid, 76 mg, 90%. m.p. 44-47 °C. TLC (hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.2, 1.1 Hz, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.29 (d, J = 7.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 138.3, 137.0, 129.5 (2C), 128.7 (2C), 127.0, 126.9 (4C), 21.1.

Biphenyl (2b)[6]



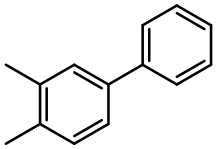
White solid, 71 mg, 93%. m.p. 68-70 °C. TLC (hexane): R_f=0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 4H), 7.46 (t, J = 7.7 Hz, 4H), 7.36 (t, J = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2 (2C), 128.7 (4C), 127.2 (2C), 127.2 (4C).

4-(Tert-butyl)-1,1'-biphenyl (2c)[6]



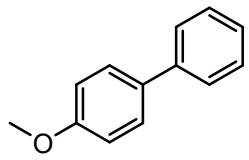
White solid, 89 mg, 85%. m.p. 50-52 °C. TLC (hexane): R_f=0.8. ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 141.0, 138.3, 128.7 (2C), 127.0 (2C), 127.0, 126.8 (2C), 125.7 (2C), 34.5, 31.4 (3C).

3,4-Dimethyl-1,1'-biphenyl (2d)[7]



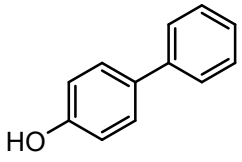
Yellow oil liquid, 75 mg, 82%. TLC (Hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 7.4 Hz, 2H), 7.48 (dd, J = 16.1, 8.3 Hz, 3H), 7.39 (q, J = 8.4, 7.4 Hz, 2H), 7.27 (d, J = 7.7 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 138.8, 136.8, 135.6, 130.0, 128.6 (2C), 128.4, 127.0 (2C), 126.9, 124.5, 19.9, 19.4.

4-Methoxy-1,1'-biphenyl (2e)[6]



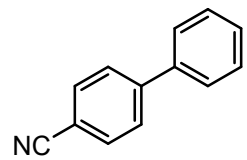
White solid, 78 mg, 85%. m.p. 88-90 °C. TLC (hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (t, J = 9.3 Hz, 4H), 7.45 (t, J = 7.1 Hz, 2H), 7.34 (t, J = 6.8 Hz, 1H), 7.04 – 6.98 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 140.8, 133.7, 128.7 (2C), 128.1 (2C), 126.7 (2C), 126.6, 114.1 (2C), 55.3.

Biphenyl-4-ol (2f)[8]



White solid, 56 mg, 66%. m.p. 164-166 °C. TLC (Hexane/ethyl acetate=20/1): R_f=0.4. ^{1}H NMR (500 MHz, CD_3OD) δ 7.55 – 7.51 (m, 2H), 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.29 – 7.22 (m, 1H), 6.91 – 6.84 (m, 2H), 4.94 (s, 1H). ^{13}C NMR (125 MHz, CD_3OD) δ 158.1, 142.4, 133.8, 129.7 (2C), 129.0 (2C), 127.4 (2C), 127.4, 116.6 (2C).

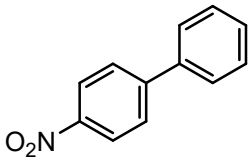
[1,1'-Biphenyl]-4-carbonitrile (2g)[8]



Yellow solid, 73 mg, 82%. m.p. 85-87 °C. TLC (Hexane/ethyl acetate=1/1): R_f =0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 4H), 7.59 (d, J = 7.2 Hz,

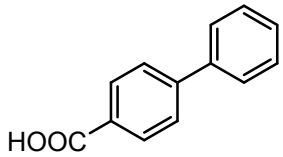
2H), 7.49 (t, J = 7.4 Hz, 2H), 7.43 (t, J = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.6, 139.1, 132.6 (2C), 129.1 (2C), 128.6, 127.7 (2C), 127.2 (2C), 118.9, 110.9.

4-Nitro-1,1'-Biphenyl (2h)[8]



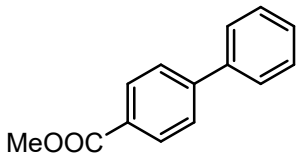
Yellow solid, 82 mg, 82%. m.p. 112-114 °C. TLC (Hexane/ethyl acetate=50/1): R_f=0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.63 (d, J = 8.5 Hz, 2H), 7.50 (t, J = 7.3 Hz, 2H), 7.45 (t, J = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 147.0, 138.7, 129.1 (2C), 128.9, 127.8 (2C), 127.4 (2C), 124.1 (2C).

[1,1'Biphenyl]-4-carboxylic acid (2i)[8]



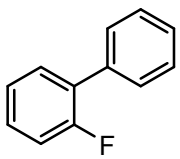
White solid, 69 mg, 70%. m.p. 220-222 °C. TLC (Hexane/ethyl acetate=5/1): R_f=0.4. ^{1}H NMR (500 MHz, CD_3COCD_3) δ 8.16 – 8.10 (m, 2H), 7.83 – 7.79 (m, 2H), 7.76 – 7.72 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.39 (m, 1H). ^{13}C NMR (125 MHz, CD_3COCD_3) δ 167.3, 146.1, 140.5, 131.0 (2C), 130.1 (2C), 129.8, 129.0, 127.9 (2C), 127.7 (2C).

4-(Methoxycarbonyl)biphenyl (2j)[8]



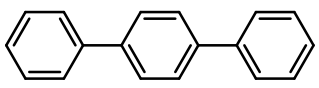
White solid, 28 mg, 26%. m.p. 116-118 °C. TLC (Hexane/ethyl acetate=5/1): R_f=0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 8.08 (m, 2H), 7.69 – 7.65 (m, 2H), 7.64 – 7.61 (m, 2H), 7.49 – 7.45 (m, 2H), 7.43 – 7.37 (m, 1H), 3.94 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 145.6, 140.0, 130.1 (2C), 128.9 (2C), 128.9, 128.1, 127.3 (2C), 127.0 (2C), 52.1.

2-Fluoro-1,1'-Biphenyl (2k)[9]



White solid, 73 mg, 85%. m.p. 71-73 °C. TLC (Hexane/ethyl acetate=100/1): R_f=0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dt, J = 8.1, 1.5 Hz, 2H), 7.48 (m, J = 7.7, 6.1 Hz, 3H), 7.44 – 7.39 (m, 1H), 7.35 (ddd, J = 9.7, 4.8, 2.1 Hz, 1H), 7.25 (td, J = 7.5, 1.4 Hz, 1H), 7.20 (ddd, J = 10.9, 8.2, 1.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7 (d, J = 247.7 Hz), 135.8, 130.8 (d, J = 3.6 Hz), 129.1, 129.0 (d, J = 3.0 Hz), 128.9 (d, J = 8.2 Hz), 128.4 (2C), 127.6 (2C), 124.3 (d, J = 3.7 Hz), 116.1 (d, J = 22.6 Hz).

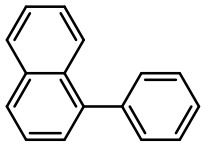
1,4-Diphenylbenzene (2l)[6]



White solid, 90 mg. 78%, m.p. 210-212 °C. TLC (Hexane/ethyl acetate=100/1): R_f =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (s, 4H), 7.66

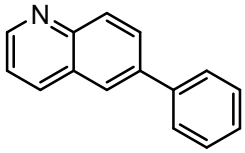
(d, J = 7.8 Hz, 4H), 7.47 (t, J = 7.7 Hz, 4H), 7.38 (d, J = 7.4 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7 (2C), 140.1 (2C), 128.8 (4C), 127.5 (4C), 127.3 (2C), 127.0 (4C).

1-Phenylnaphthalene (2m)[6]



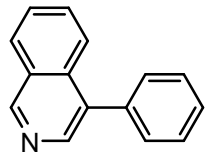
Yellow oil liquid, 84 mg, 82%. TLC (Hexane): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (t, J = 9.1 Hz, 2H), 7.93 (d, J = 8.2 Hz, 1H), 7.62 – 7.54 (m, 6H), 7.50 (dd, J = 7.6, 5.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 140.2, 133.7, 131.6, 130.0 (2C), 128.2 (2C), 127.6 (2C), 127.2, 126.9, 126.0 (2C), 125.7, 125.4.

6-Phenylquinoline (2n)[10]



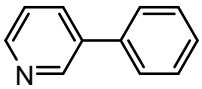
Brown solid, 87 mg, 85%. m.p. 114-116 °C. TLC (Hexane/ethyl acetate=5/1): R_f =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.33 (t, J = 7.6 Hz, 2H), 8.05 (d, J = 4.2 Hz, 2H), 7.72 (d, J = 7.5 Hz, 2H), 7.52 (t, J = 7.4 Hz, 3H), 7.43 (t, J = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 147.1, 140.2, 139.6, 136.8, 129.5, 129.5, 129.0 (2C), 128.5, 127.8, 127.5 (2C), 125.5, 121.5.

4-Phenylisoquinoline (2o)[11]



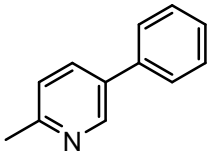
Yellow oil liquid, 82 mg, 80%. TLC (Hexane/ethyl acetate=5/1): R_f =0.4. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.49 (s, 1H), 8.05 – 7.98 (m, 1H), 7.90 (dd, J = 8.3, 1.1 Hz, 1H), 7.67 – 7.58 (m, 2H), 7.54 – 7.43 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 142.6, 136.8, 134.0, 133.2, 130.5, 129.9 (2C), 128.4 (2C), 128.2, 127.8, 127.7, 127.0, 124.6.

2-Phenylpyridine (2p)[6]



Yellow oil liquid, 64 mg, 82%. TLC (Hexane/ethyl acetate=3/1): R_f=0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 – 8.83 (m, 1H), 8.59 (dd, J = 4.9, 1.7 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.60 – 7.56 (m, 2H), 7.50 – 7.45 (m, 2H), 7.43 – 7.38 (m, 1H), 7.36 (m, J = 7.8, 4.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 148.2, 137.7, 136.6, 134.4, 129.0 (2C), 128.1, 127.1 (2C), 123.5.

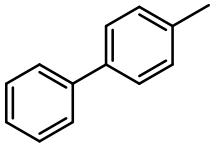
3-Methyl-5-phenylpyridine (2q)[12]



Yellow oil liquid, 66 mg, 78%. TLC (Hexane/ethyl acetate=3/1): R_f=0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.71 (dd, J = 8.0, 2.4 Hz, 1H), 7.51 (d, J = 7.5 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.34 (d, J = 7.4 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H),

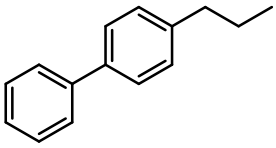
2.57 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 147.2, 137.6, 134.5, 133.5, 128.8, 127.6 (2C), 126.7, 123.0 (2C), 23.8.

Methyl-1,1'-biphenyl (2r)[6]



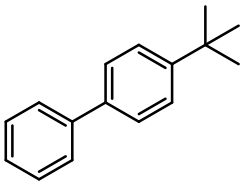
White solid, 59 mg, 70%. m.p. 44-47 °C. TLC (hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.54 – 7.50 (m, 2H), 7.45 (t, J = 8.4 Hz, 2H), 7.34 (t, J = 7.4 Hz, 1H), 7.29 – 7.26 (d, 2H), 2.42 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.1, 138.3, 137.0, 129.5 (2C), 128.7 (2C), 127.0, 127.0 (4C), 21.1.

4-Propyl-1,1'-biphenyl (2s)[13]



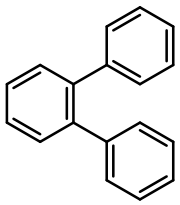
Yellow viscous liquid, 83 mg, 85%. TLC (hexane): R_f =0.8. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.51 (t, J = 7.7 Hz, 2H), 7.41 (t, J = 7.4 Hz, 1H), 7.34 (d, J = 8.1 Hz, 2H), 2.75 – 2.69 (m, 2H), 1.78 (h, J = 7.4 Hz, 2H), 1.08 (t, J = 7.3 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.8, 141.1, 138.5, 128.9 (2C), 128.7 (2C), 127.0 (2C), 126.9 (2C), 126.9, 37.7, 24.5, 13.9.

4-(Tert-butyl)-1,1'-biphenyl (2t)[6]



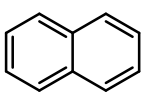
White solid, 87 mg, 83%. m.p. 50-52 °C. TLC (hexane): R_f =0.8. ^{1}H NMR (500 MHz,$CDCl_3$) δ 7.60 (d, J = 7.2 Hz, 2H), 7.55 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.44 (t, J = 7.7 Hz, 2H), 7.34 (s, 1H), 1.38 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 141.0, 138.3, 128.7 (2C), 127.0 (2C), 126.9, 126.8 (2C), 125.7 (2C), 34.5, 31.4 (3C).

1,2-Diphenylbenzene (2u)[14]



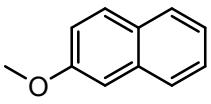
White solid, 90 mg, 78%. m.p. 55-57 °C.TLC (hexane): R_f =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 4H), 7.26 – 7.19 (m, 6H), 7.19 – 7.13 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.5 (2C), 140.5 (2C), 130.6 (2C), 129.9 (4C), 127.8 (4C), 127.5 (2C), 126.4 (2C).

Naphthalene (2v)[15]



White solid, 54 mg, 85%. m.p. 78-80 °C. TLC (hexane): R_f =0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, J = 6.2, 3.3 Hz, 4H), 7.49 (dd, J = 6.3, 3.2 Hz, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.4 (2C), 127.9 (4C), 125.8 (4C).

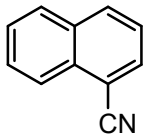
2-Methoxynaphthalene(2w)[15]



White solid, 44 mg, 56%. m.p. 70-72 °C. TLC (hexane): R_f =0.6. ^{1}H NMR (500

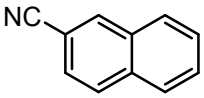
MHz, $CDCl_3$) δ 7.80 – 7.72 (m, 3H), 7.48 – 7.41 (m, 1H), 7.37 – 7.31 (m, 1H), 7.18 – 7.13 (m, 2H), 3.93 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.6, 134.5, 129.4, 128.9, 127.6, 126.7, 126.4, 123.6, 118.7, 105.7, 55.3.

1-Naphthonitrile (2x)[15]



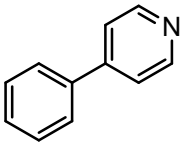
White solid, 50 mg, 65%. m.p. 36-38 °C. TLC (Hexane/ethyl acetate=3/1): R_f =0.7. ^1H NMR (500 MHz, $CDCl_3$) δ 8.24 (dd, J = 8.4, 1.2 Hz, 1H), 8.08 (d, J = 8.3 Hz, 1H), 7.95 – 7.89 (m, 2H), 7.73 – 7.66 (m, 1H), 7.66 – 7.59 (m, 1H), 7.56 – 7.49 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.3, 132.9, 132.6, 132.3, 128.6, 128.6, 127.5, 125.1, 124.9, 117.8, 110.2.

2-Naphthonitrile (2y)[16]



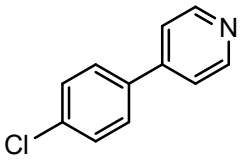
White solid, 47 mg, 61%. m.p. 63-35 °C. TLC (Hexane/ethyl acetate=3/1): R_f =0.7. ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.93 – 7.86 (m, 3H), 7.68 – 7.57 (m, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.6, 134.1, 132.2, 129.1, 129.0, 128.4, 128.0, 127.6, 126.3, 119.2, 109.3.

4-Phenylpyridine (2z)[12]



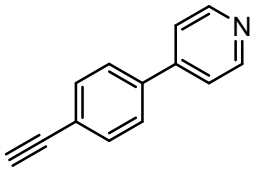
White solid, 72 mg, 93%. m.p. 69-71 °C. TLC (Hexane/ethyl acetate=20/1): R_f =0.7. ^1H NMR (500 MHz, $CDCl_3$) δ 8.73 – 8.65 (m, 2H), 7.70 – 7.64 (m, 2H), 7.57 – 7.43 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 148.2, 137.7, 136.6, 134.4, 129.0 (2C), 128.1, 127.1 (2C), 123.5.

4-(4-Chlorophenyl)pyridine (2aa)[17]



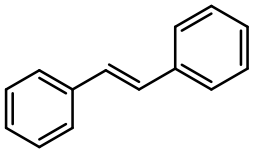
Viscous liquid, 71 mg, 75%. TLC (Hexane/ethyl acetate=1/1): R_f =0.5. ^1H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 5.9 Hz, 2H), 7.58 – 7.54 (m, 2H), 7.49 – 7.42 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8 (2C), 147.7, 136.3, 135.5, 129.4 (2C), 128.3 (2C) , 121.6 (2C).

4-(4-ethynylphenyl)pyridine (2ab)[18]



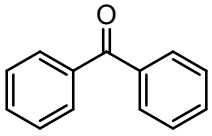
Light yellow solid, 45 mg, 51%. m.p.183-185 °C. TLC (Hexane/ethyl acetate=2/1): R_f =0.5. ^1H NMR (500 MHz, $CDCl_3$) δ 8.68 (d, J = 5.3 Hz, 2H), 7.61 (s, 4H), 7.54 – 7.51 (m, 2H), 3.19 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9 (2C), 147.8, 138.2, 132.9 (2C), 126.9 (2C), 123.1, 121.6 (2C), 83.0, 78.9.

1,2-Diphenylethene (2ac)[12]



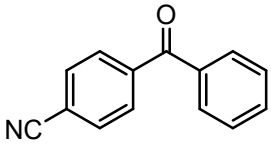
White solid, 74 mg, 82%. m.p. 122-125 °C. TLC (Hexane/ethylcetate=100/1): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 4H), 7.37 (dd, J = 8.4, 7.0 Hz, 4H), 7.30 – 7.27 (m, 2H), 7.13 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3 (2C), 128.7 (6C), 127.6 (2C) , 126.5 (4C).

Benzophenone (2ad)[19]



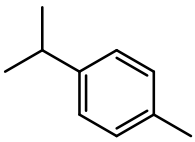
White solid, 53 mg, 58%. m.p. 52-54 °C. TLC (Hexane/ethyl acetate=20/1): R_f =0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 4H), 7.62 – 7.56 (m, 2H), 7.53 – 7.44 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 137.6 (2C), 132.4 (2C), 130.1 (4C), 128.3 (4C).

4-benzoylbenzonitrile (2ae)[19]



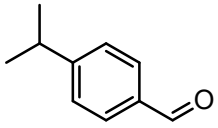
White solid, 57 mg, 55%. m.p. 110-112 °C. TLC (Hexane/ethyl acetate=10/1): R_f =0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.3 Hz, 2H), 7.84 – 7.76 (m, 4H), 7.67 – 7.62 (m, 1H), 7.52 (t, J = 7.7 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.0, 141.2, 136.3, 133.3, 132.2 (2C), 130.2 (2C), 130.1 (2C), 128.6 (2C), 118.0, 115.6.

***p*-Cymene (2af)**[20]



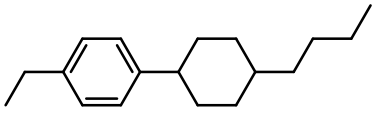
Colorless liquid, 45mg, 73%. TLC (hexane): R_f =0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 – 7.08 (m, 4H), 2.89 (s, 1H), 2.34 (s, 3H), 1.26 (d, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.9, 135.2, 129.0 (2C), 126.3 (2C), 33.7, 24.1 (2C), 21.0.

4-isopropylbenzaldehyde (2ag)[20]



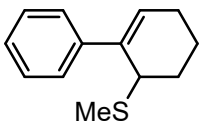
Colorless liquid, 27 mg, 38%. TLC (Hexane/ethyl acetate=20/1): R_f =0.7. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.85 – 7.78 (m, 2H), 7.41 – 7.36 (m, 2H), 3.03 – 2.93 (m, 1H), 1.28 (d, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 192.0, 156.2, 134.5, 130.0 (2C), 127.1 (2C), 34.5, 23.6 (2C).

(4-Butylcyclohexyl)-4-ethylbenzene (2ah)



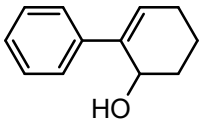
Yellow oil liquid, 90 mg, 78%. TLC (hexane): R_f =0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (s, 4H), 2.63 (q, J = 7.6 Hz, 2H), 2.44 (tt, J = 12.3, 3.2 Hz, 1H), 1.88 (t, J = 11.8 Hz, 4H), 1.45 (qd, J = 13.8, 13.2, 3.5 Hz, 2H), 1.31 (dt, J = 6.6, 3.6 Hz, 5H), 1.24 (t, J = 7.6 Hz, 5H), 1.11 – 1.00 (m, 2H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 141.5, 127.7 (2C), 126.7 (2C), 44.2, 37.3, 37.1, 34.4 (2C), 33.7 (2C), 29.2, 28.4, 23.0, 15.6, 14.2. ESI-HRMS (*m/z*) $[M+H]^+$ calcd for $C_{18}H_{29}$, 245.2264, found: 245.2258.

Methyl(2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-yl)sulfane (4a)



Yellow oil liquid, 23 mg, 22%. TLC (hexane): R_f=0.6. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 2H), 7.36 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 6.13 – 6.07 (m, 1H), 3.81 (s, 1H), 2.30 – 2.21 (m, 2H), 2.15 – 2.11 (m, 1H), 2.05 (s, 3H), 2.04 – 1.94 (m, 2H), 1.76 – 1.68 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.4, 137.3, 128.7, 128.2 (2C), 126.9, 125.9 (2C), 44.0, 28.7, 25.8, 17.6, 15.4. ESI-HRMS (*m/z*) $[M+Na]^+$ calcd for $C_{13}H_{16}NaS$, 227.0870, found: 227.0875.

2,3,4,5-Tetrahydro-[1,1'-biphenyl]-2-ol (4b)



Yellow oil liquid. TLC (Hexane/ethyl acetate=20/1): R_f=0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 2H), 7.37 – 7.32 (m, 2H), 7.28 – 7.23 (m, 1H), 6.20 – 6.14 (m, 1H), 4.79 – 4.67 (m, 1H), 2.32 – 2.23 (m, 1H), 2.22 – 2.13 (m, 1H), 2.00 – 1.94 (m, 1H), 1.90 – 1.84 (m, 1H), 1.83 – 1.75 (m, 1H), 1.72 – 1.66 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 139.1, 128.8, 128.6 (2C), 127.1, 126.0 (2C), 65.5, 31.6, 26.1, 17.4. ESI-HRMS (*m/z*) $[M+K]^+$ calcd for $C_{12}H_{14}OK$, 213.0676, found: 213.0671.

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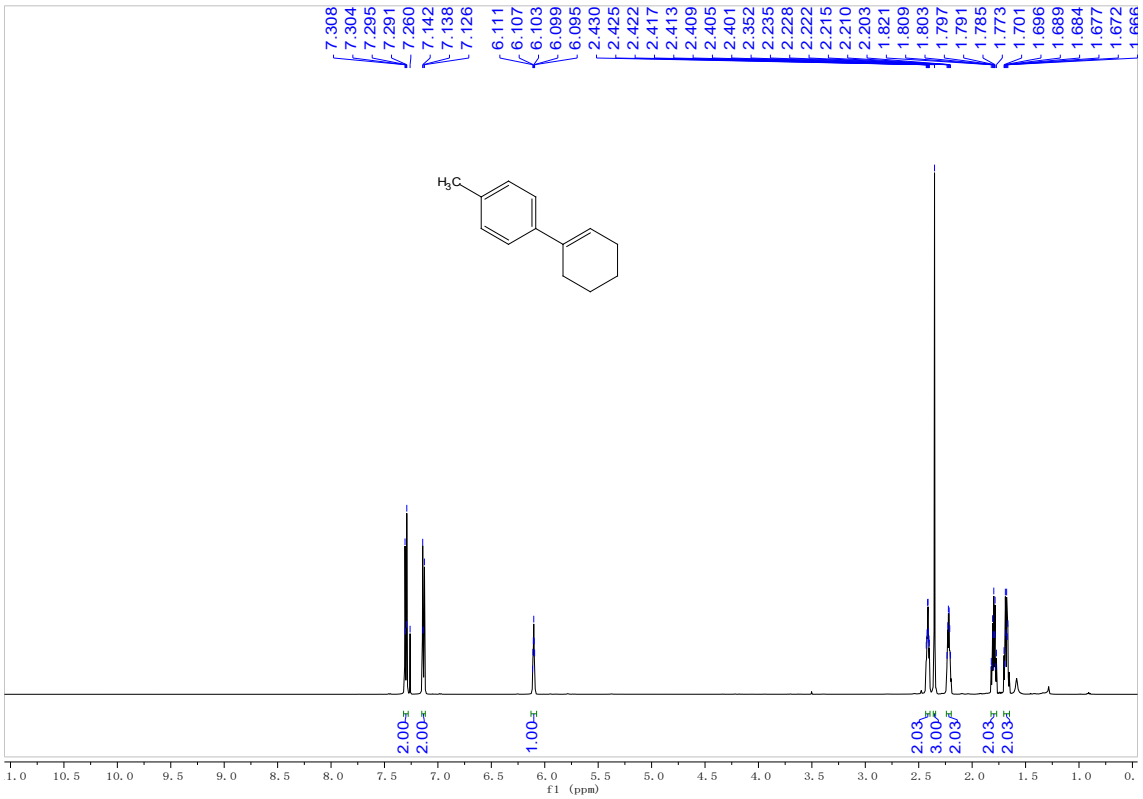
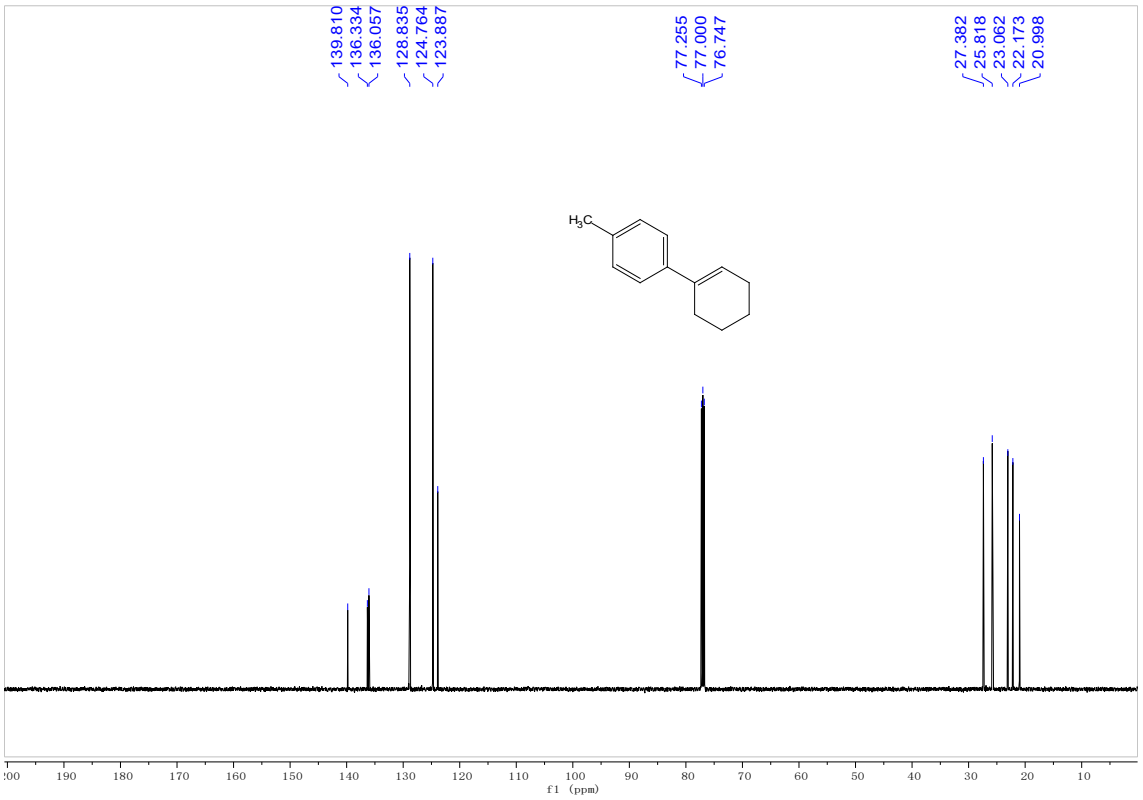
5. ^{1}H NMR and ^{13}C NMR spectra for products

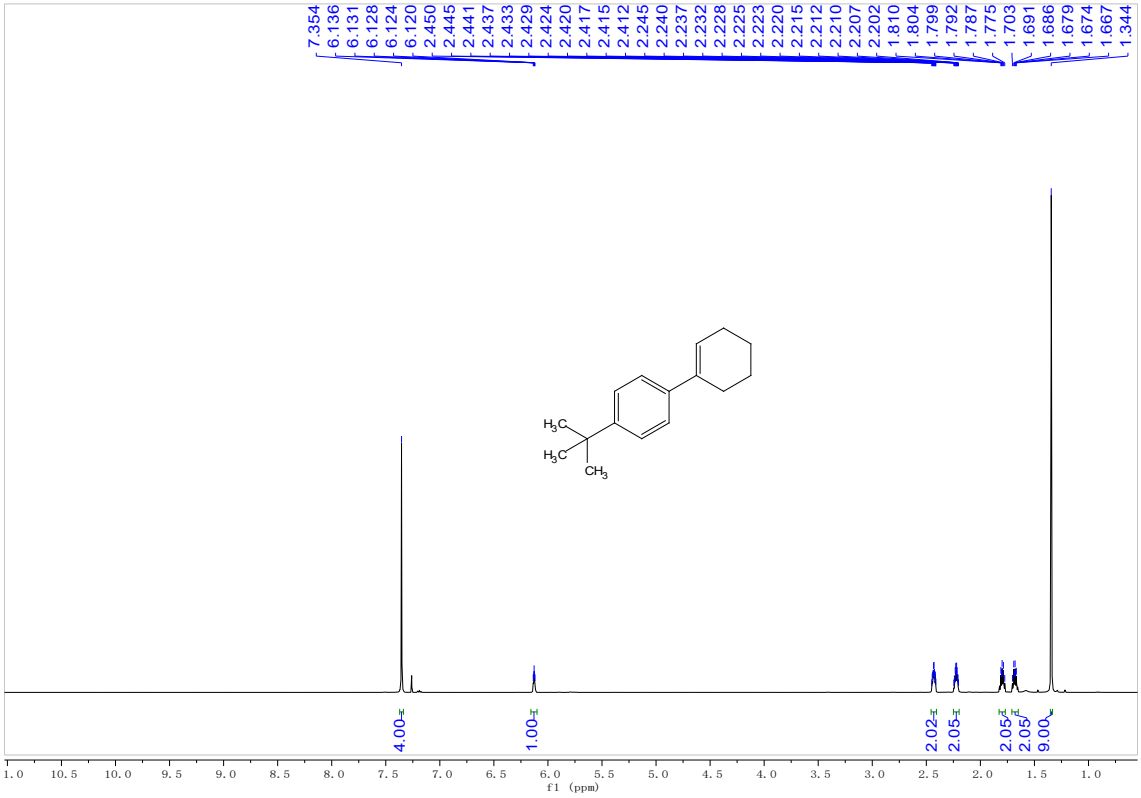
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1a**



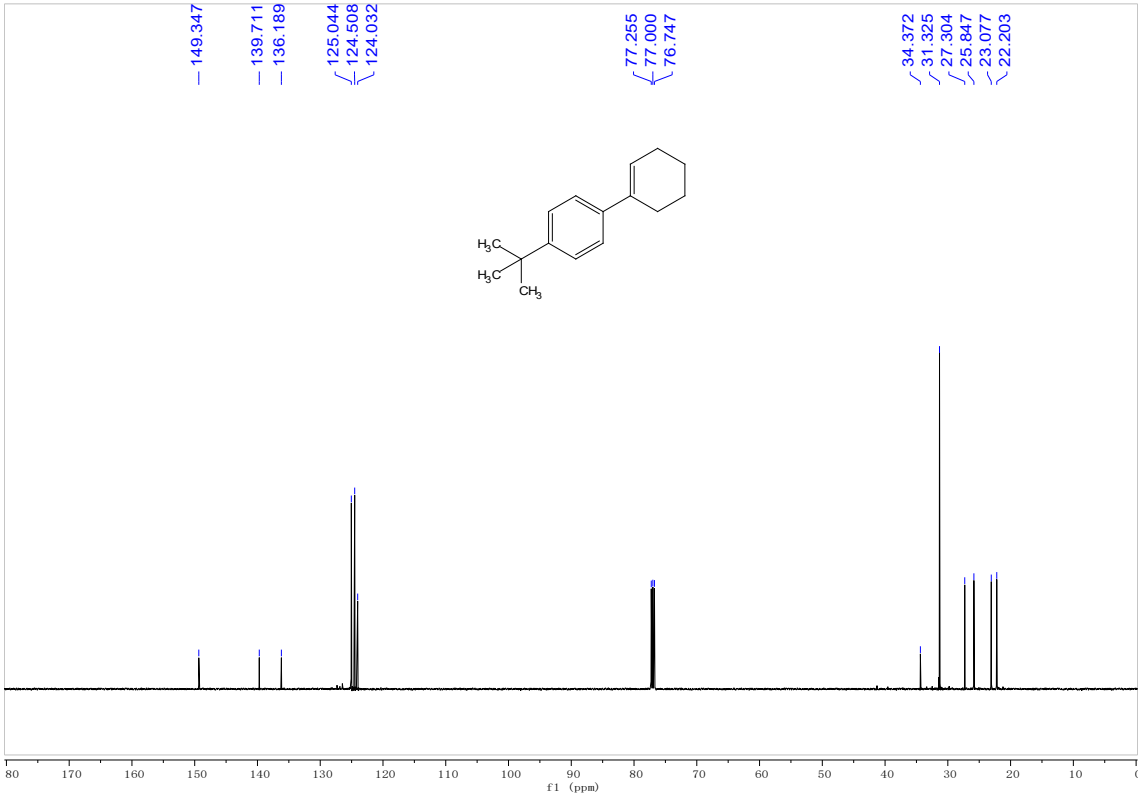
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1a**



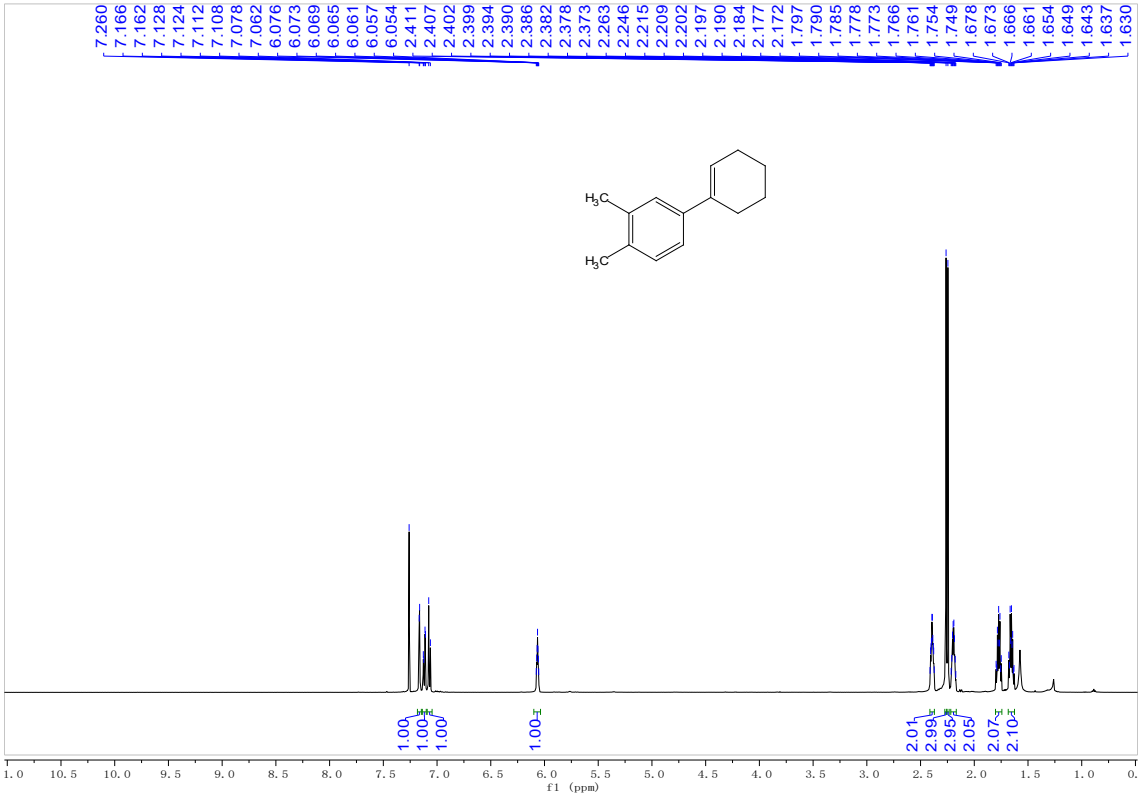
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1b**



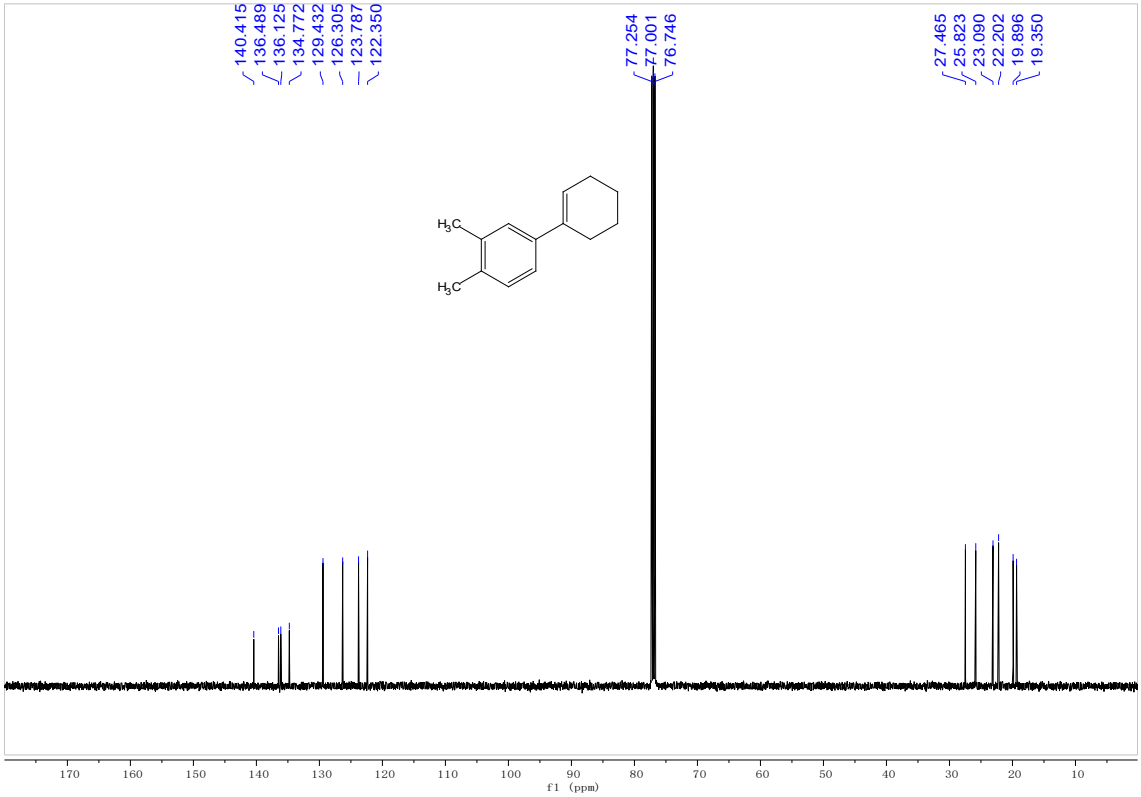
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1b**



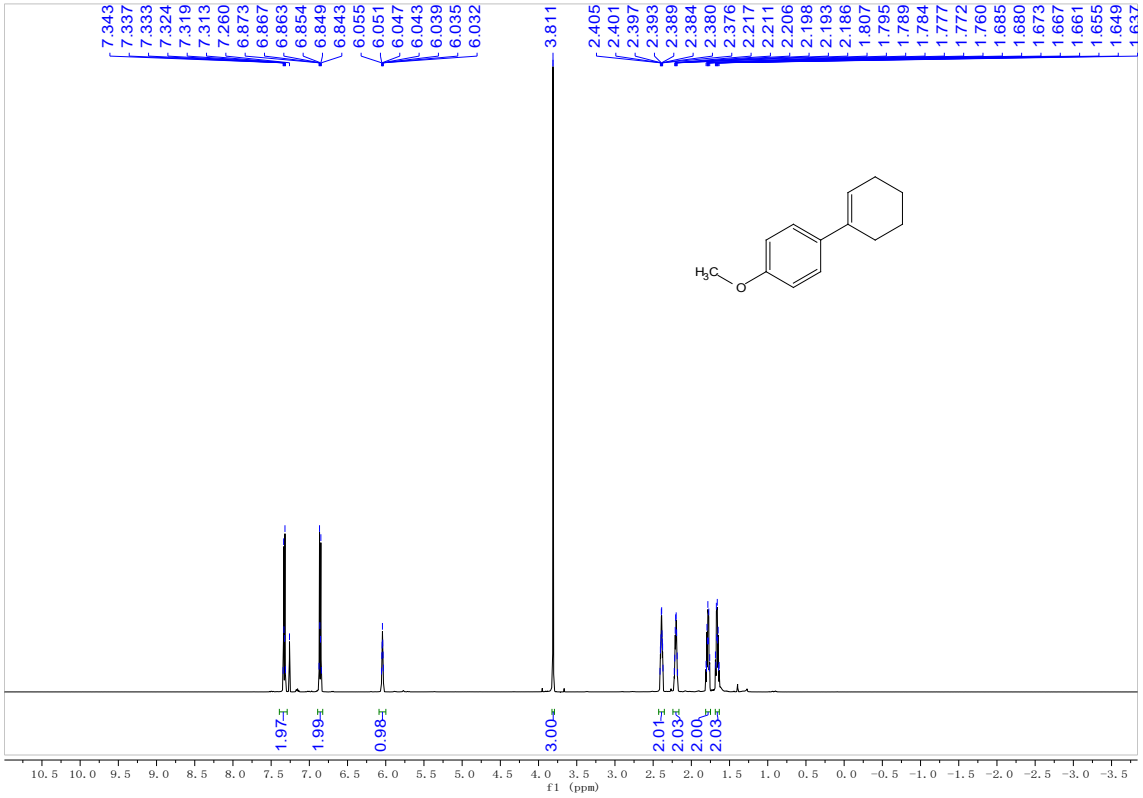
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1c**



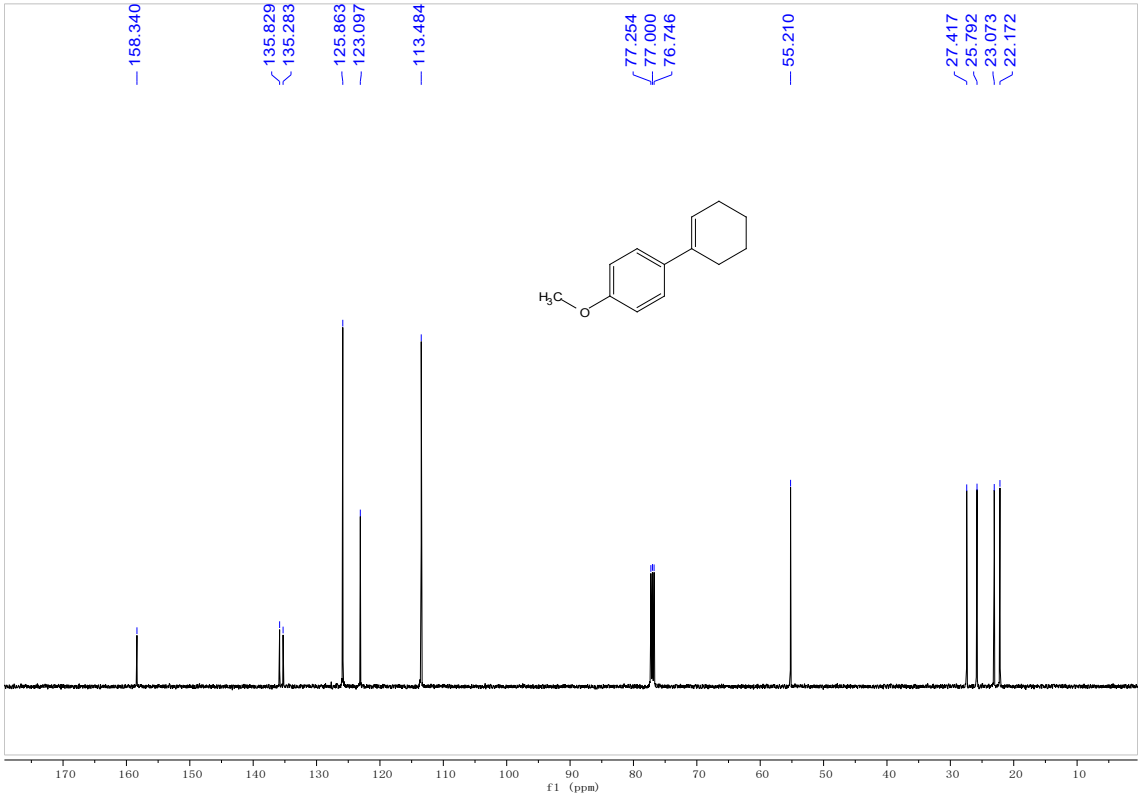
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1c**



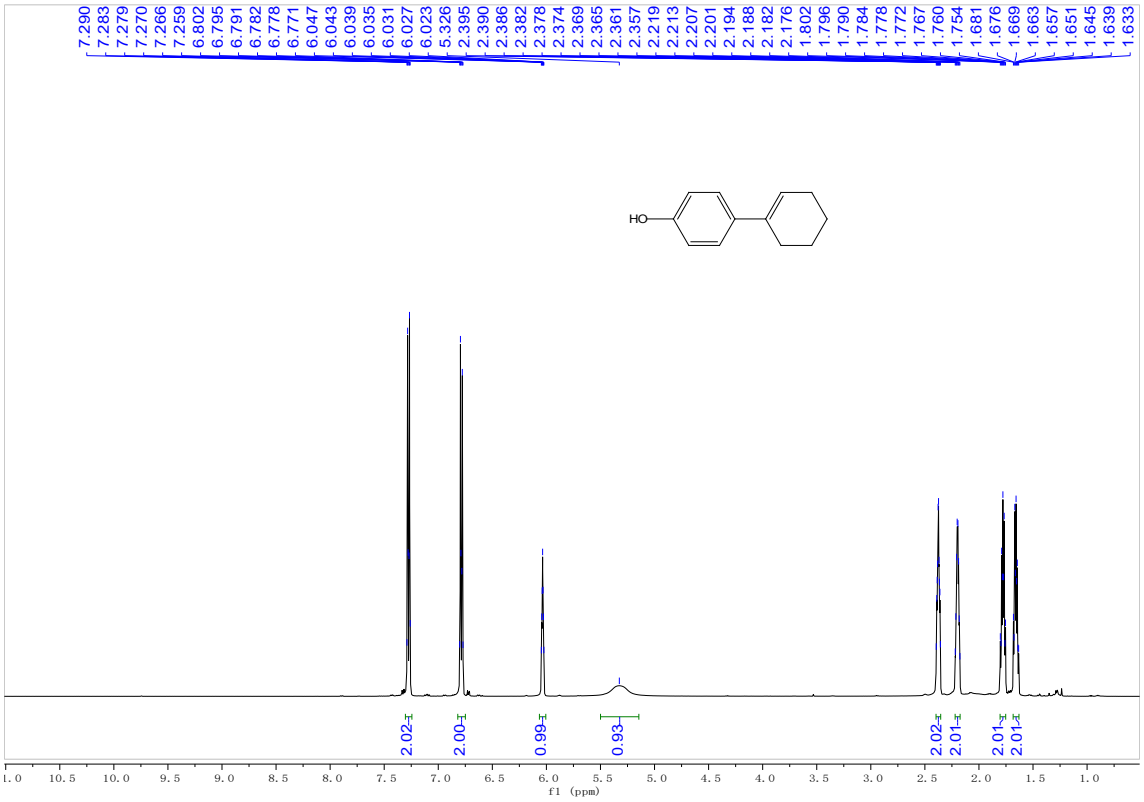
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1d**



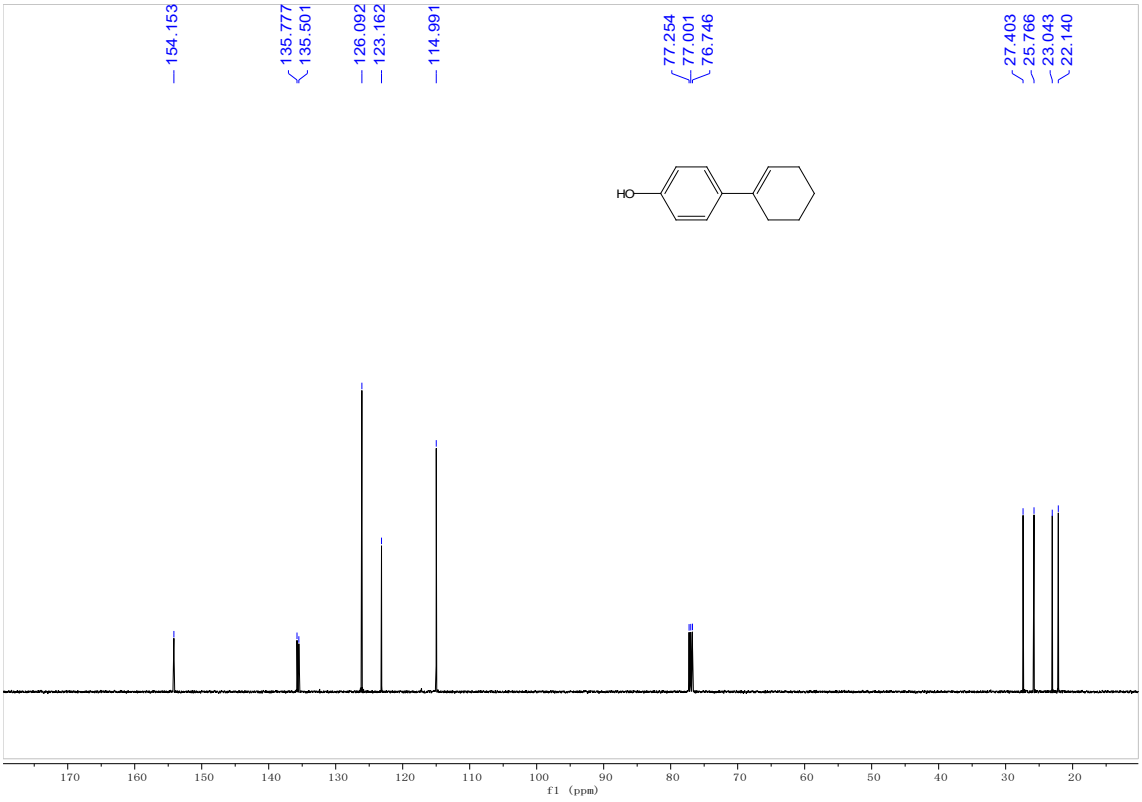
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1d**



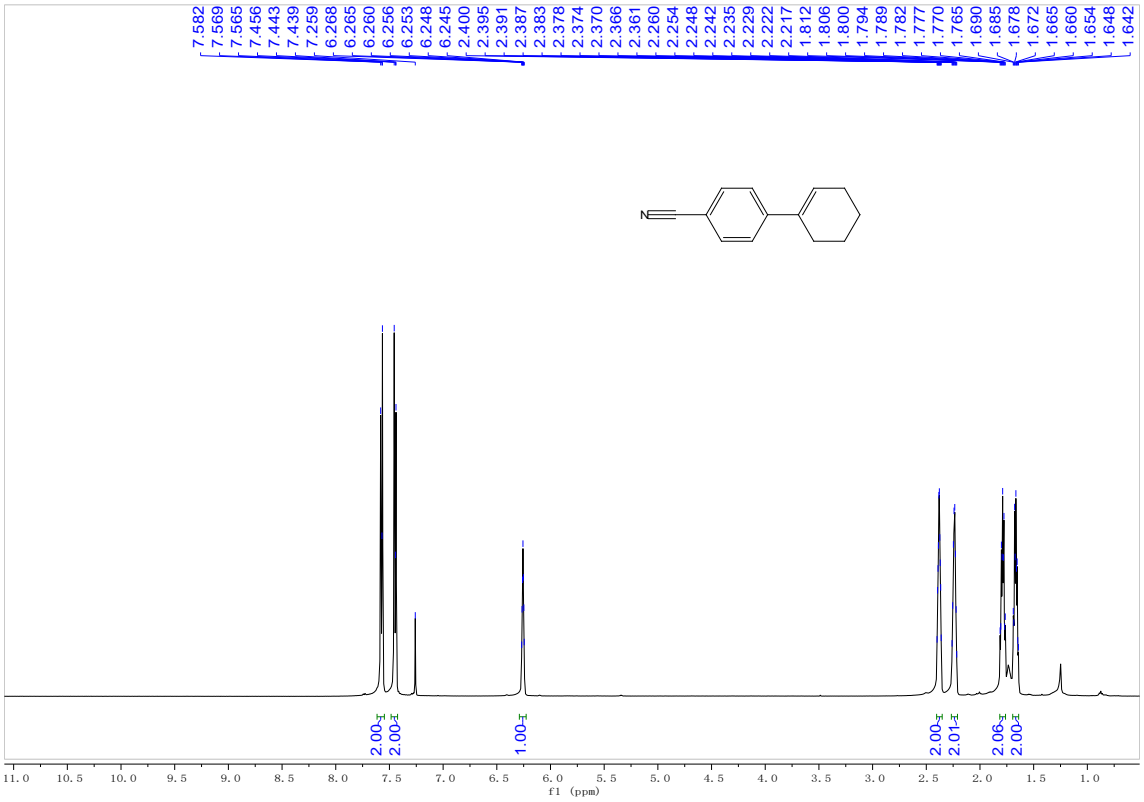
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1e**



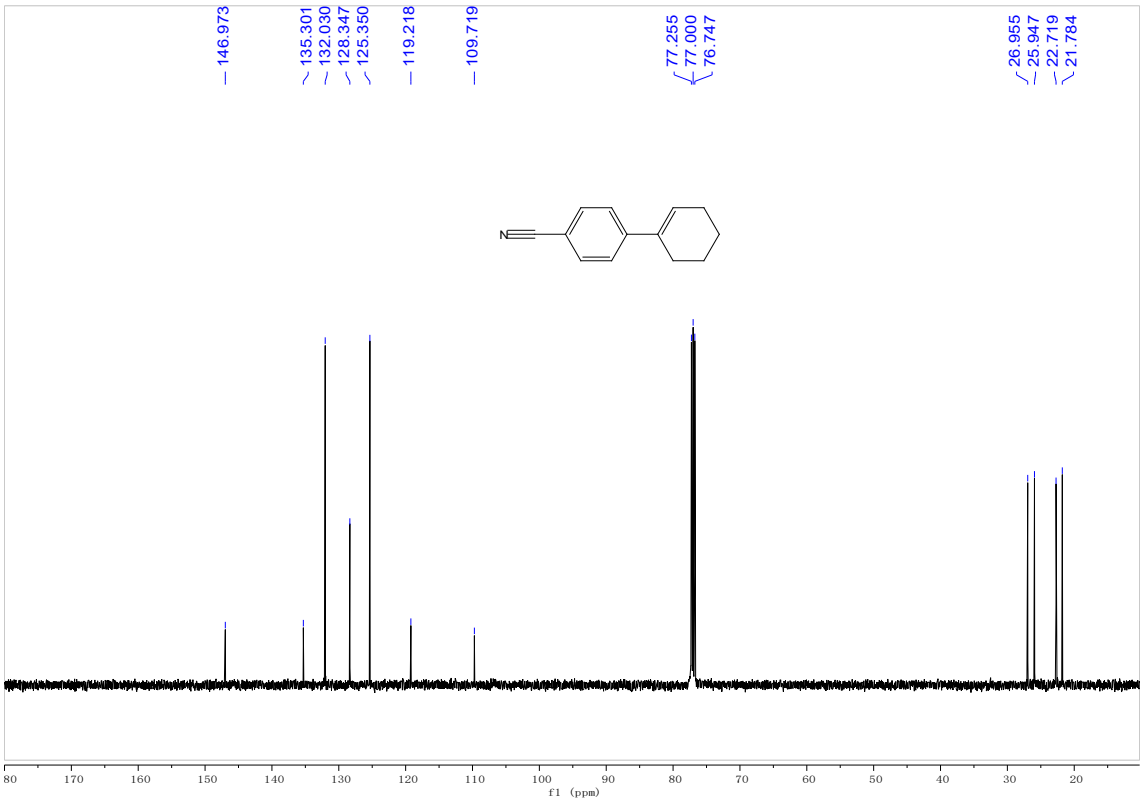
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1e**



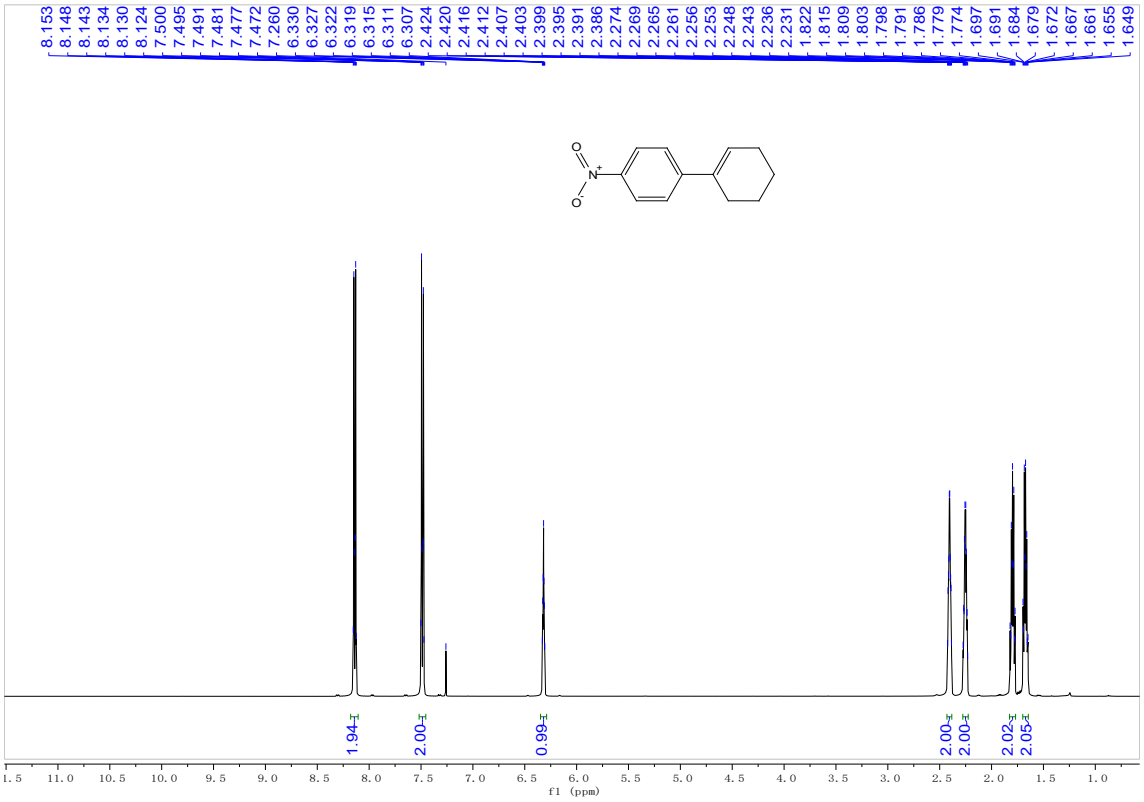
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1f**



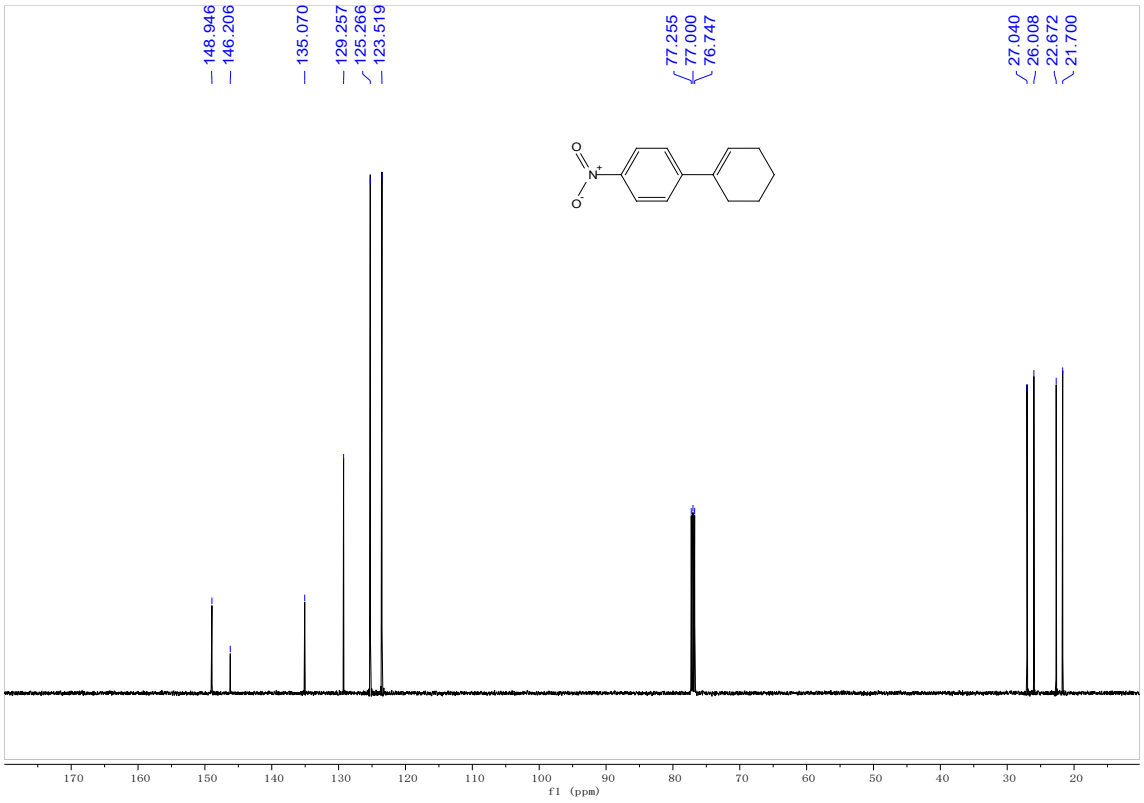
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1f**



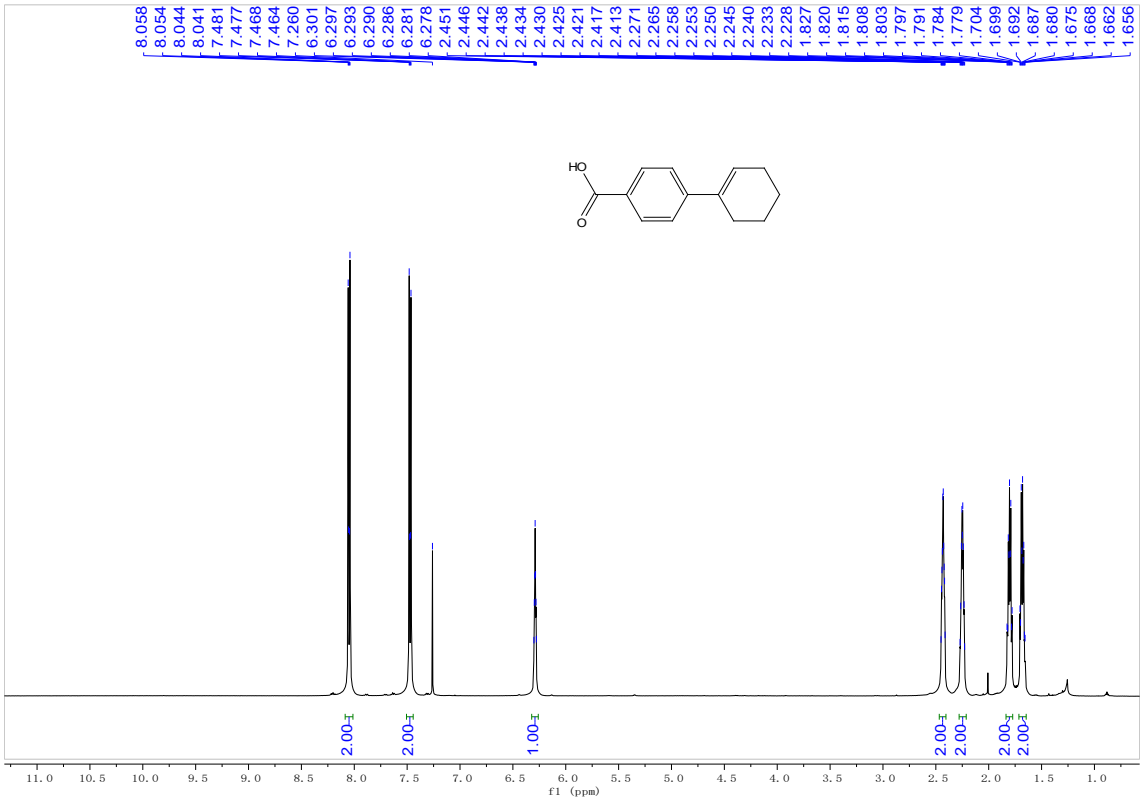
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1g**



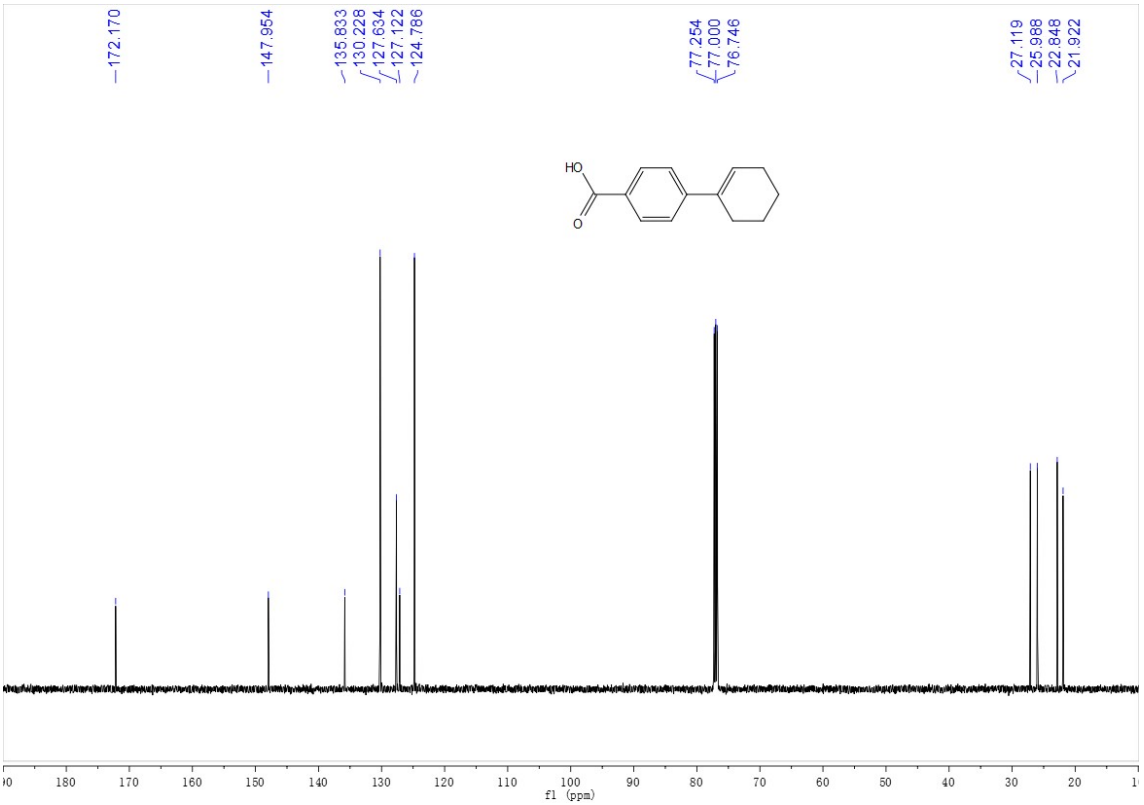
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1g**



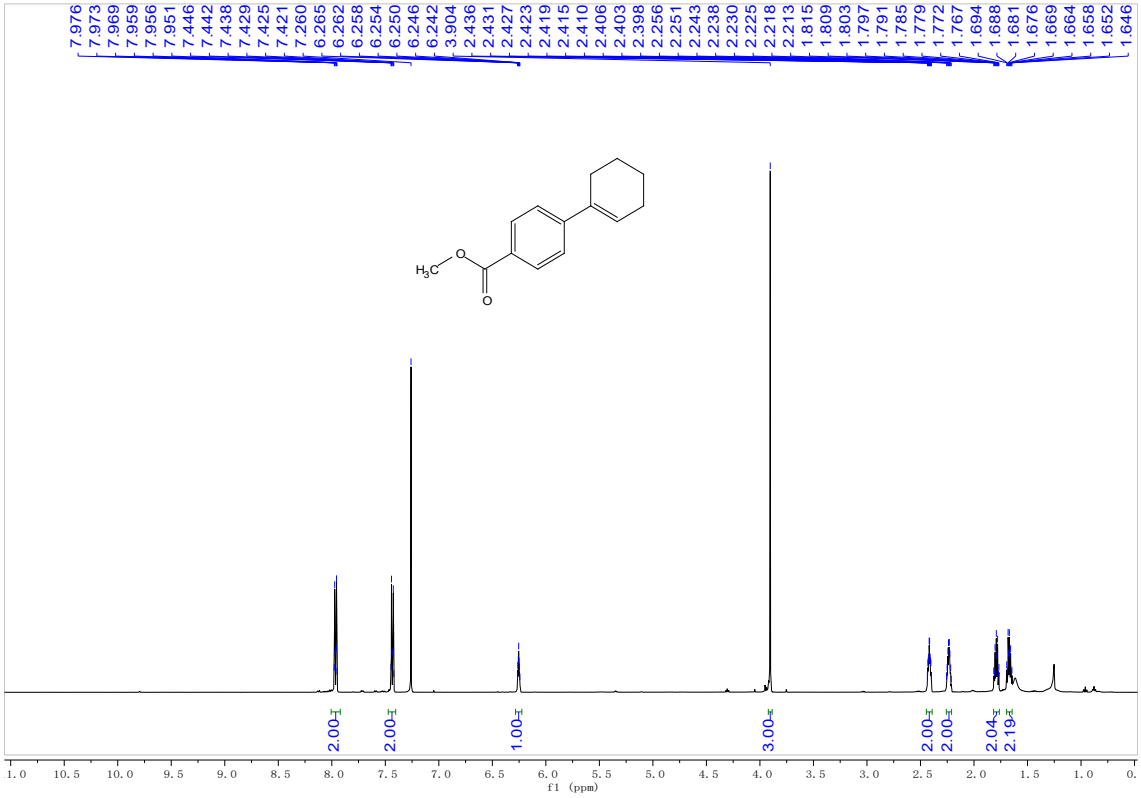
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1h**



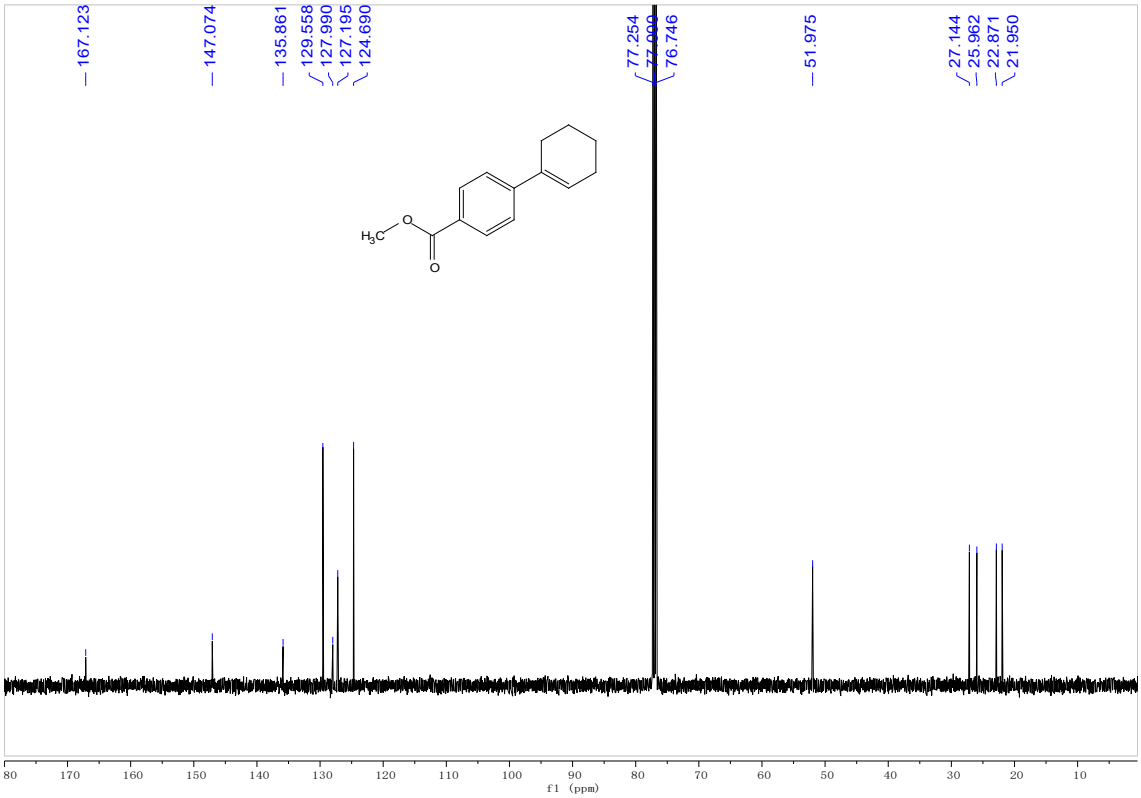
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1h**



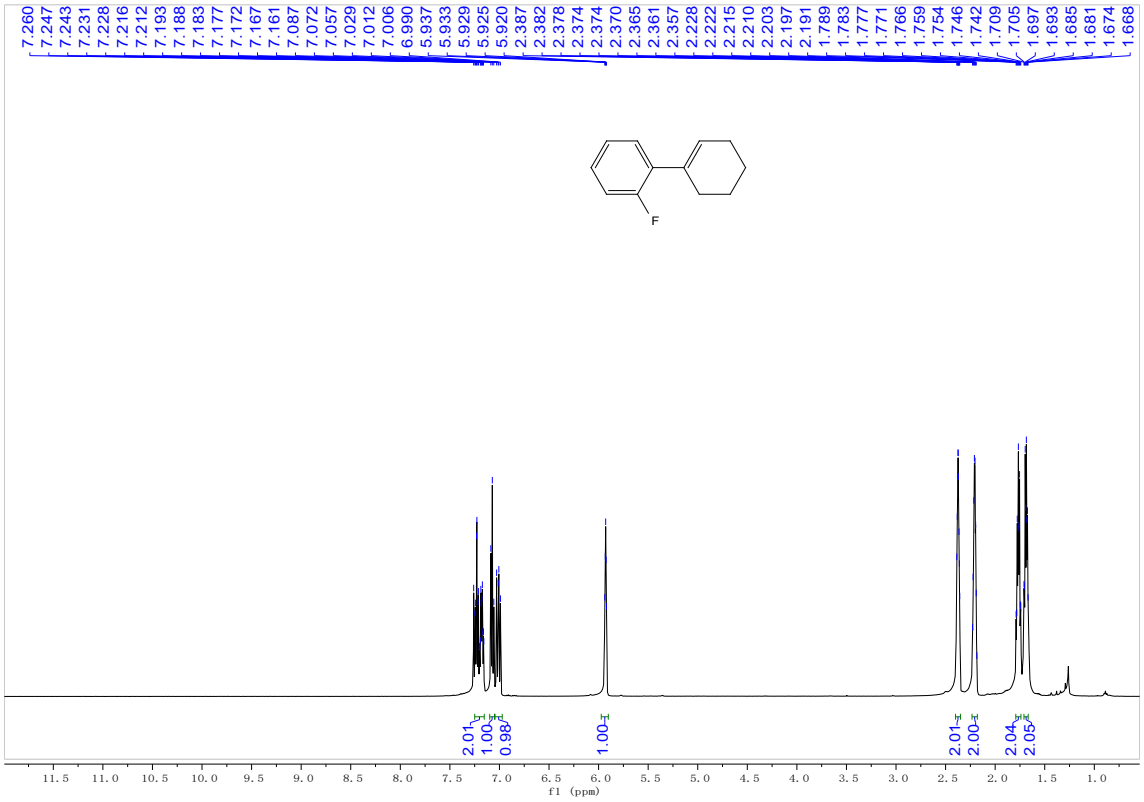
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1i**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1i**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1j**



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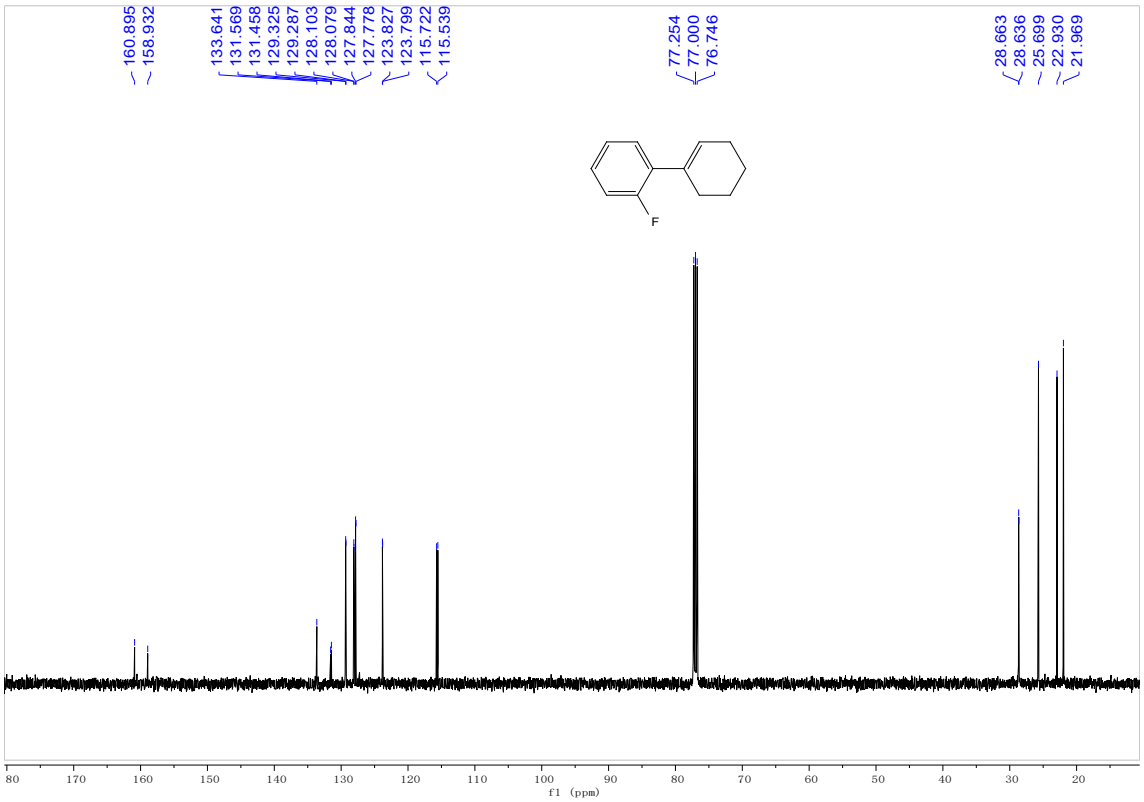
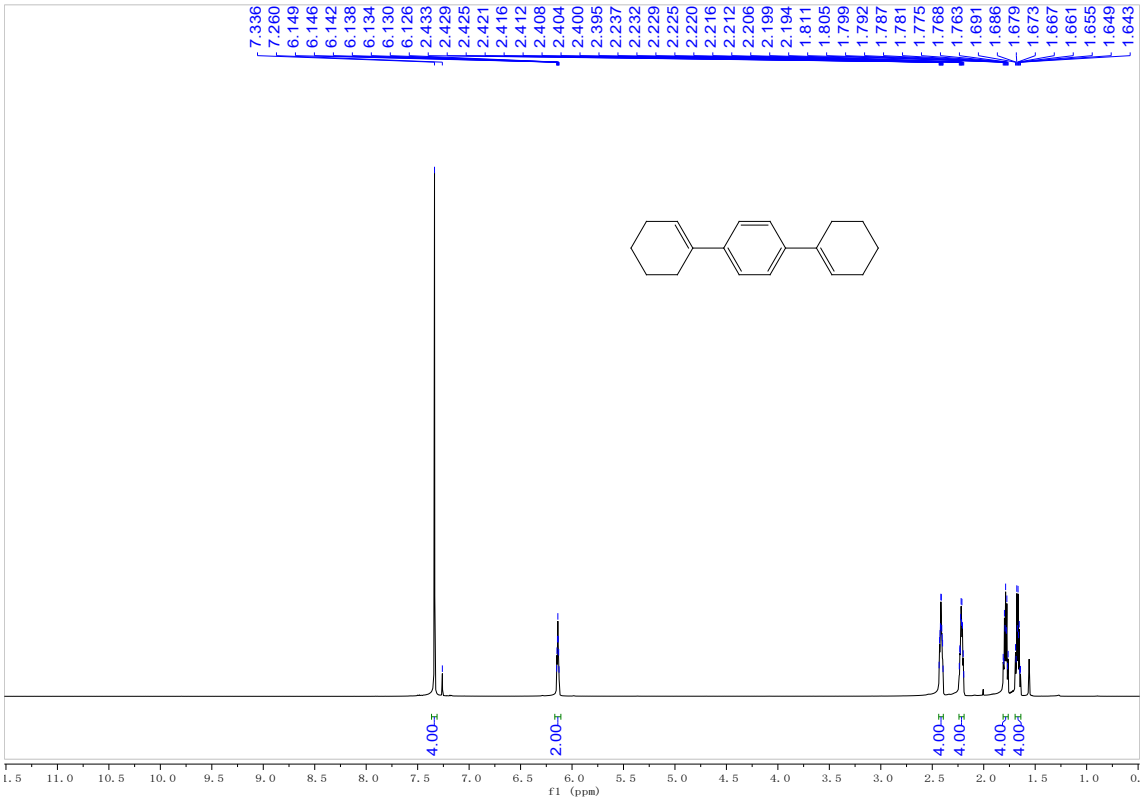
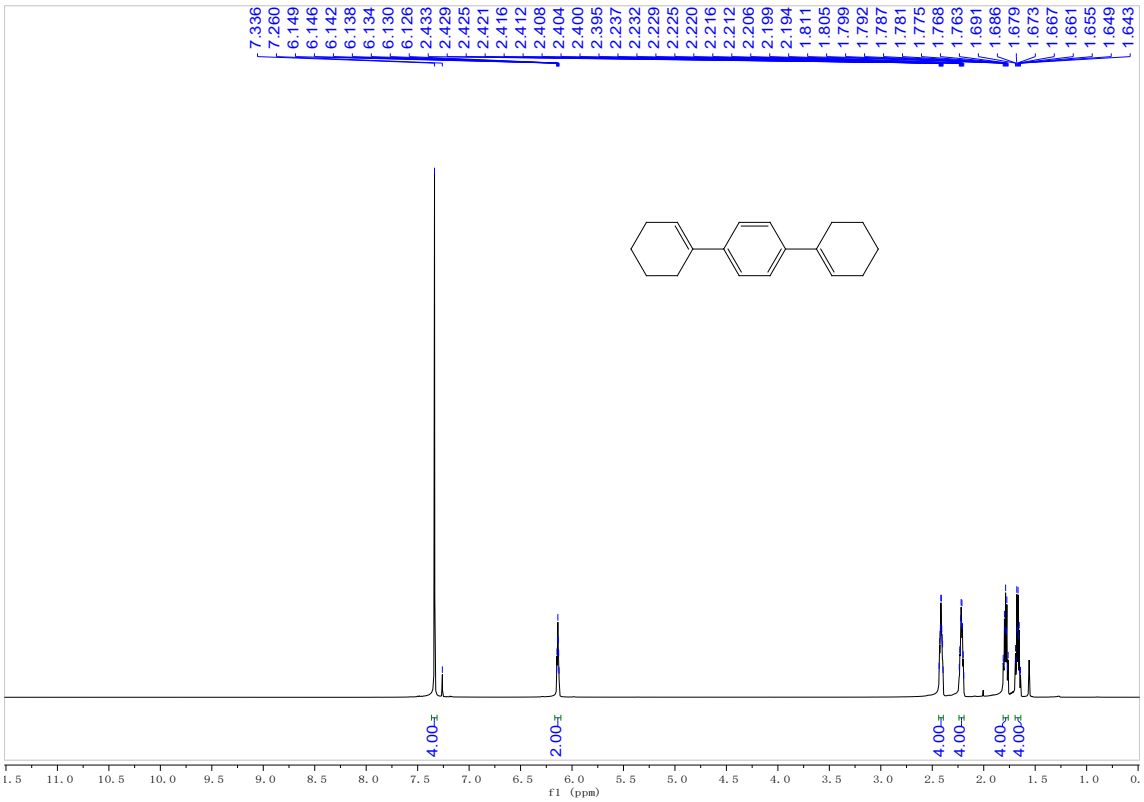


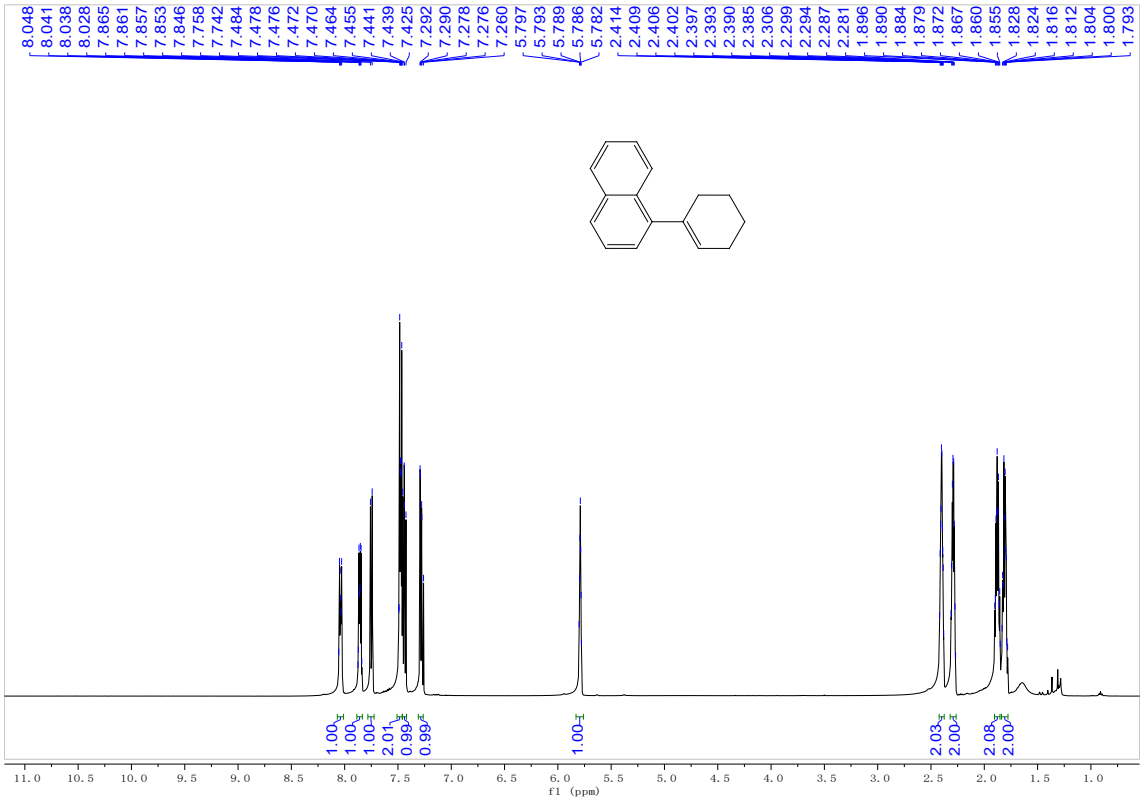
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1k**



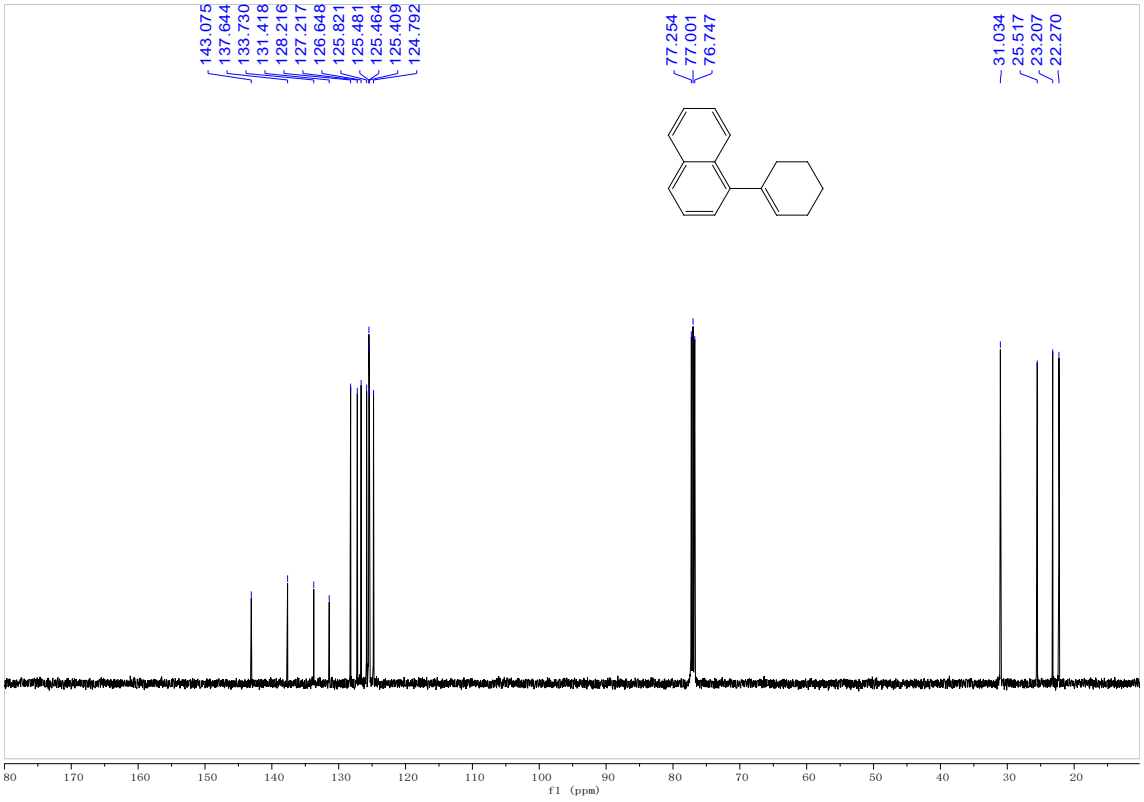
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1k**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1l**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1l**



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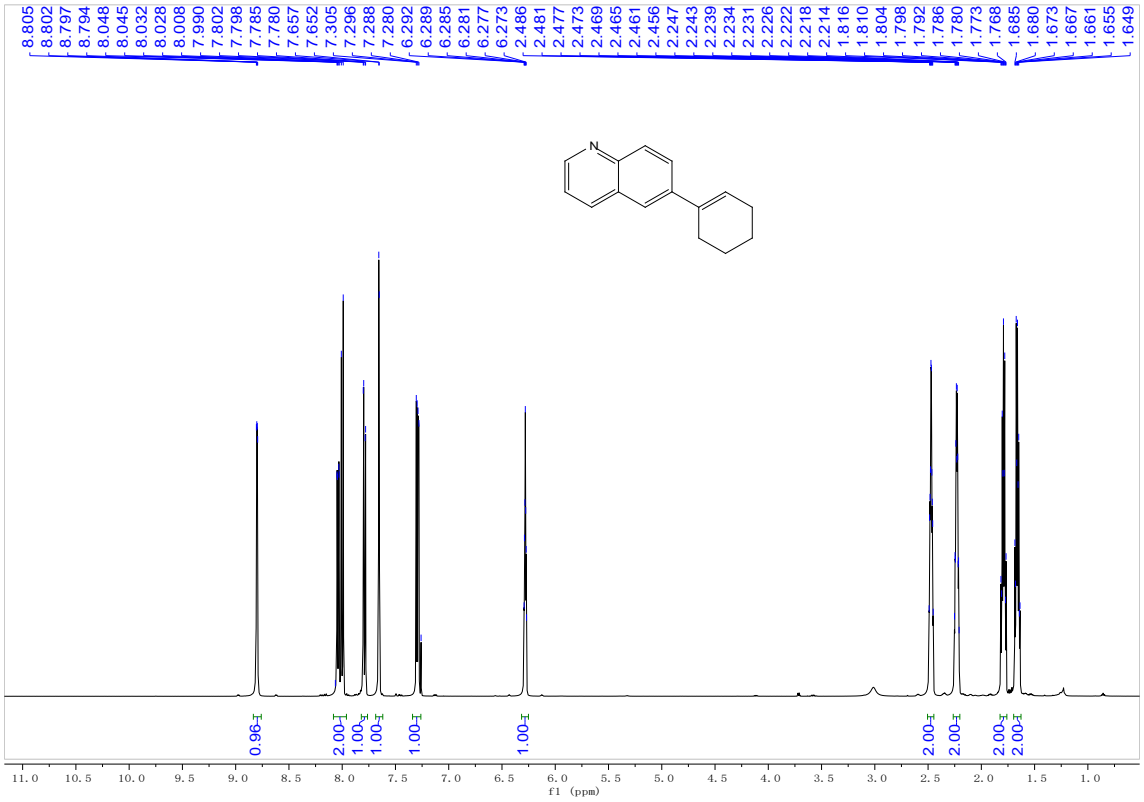
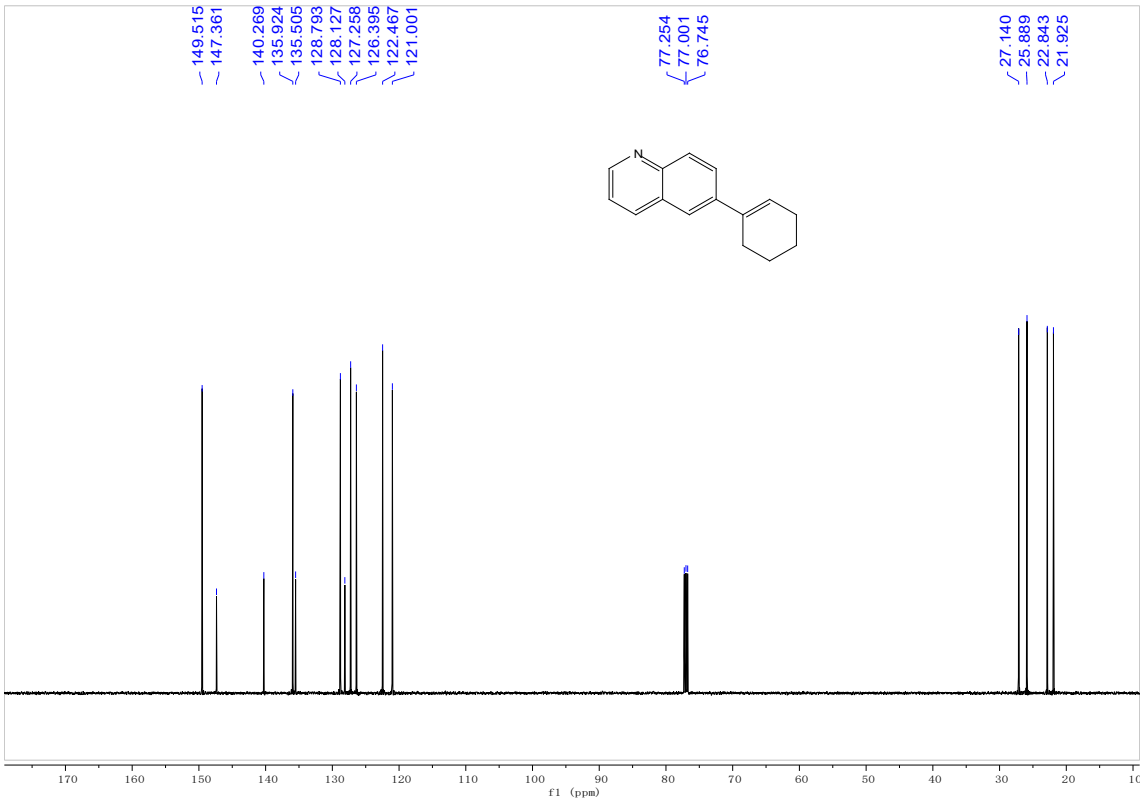
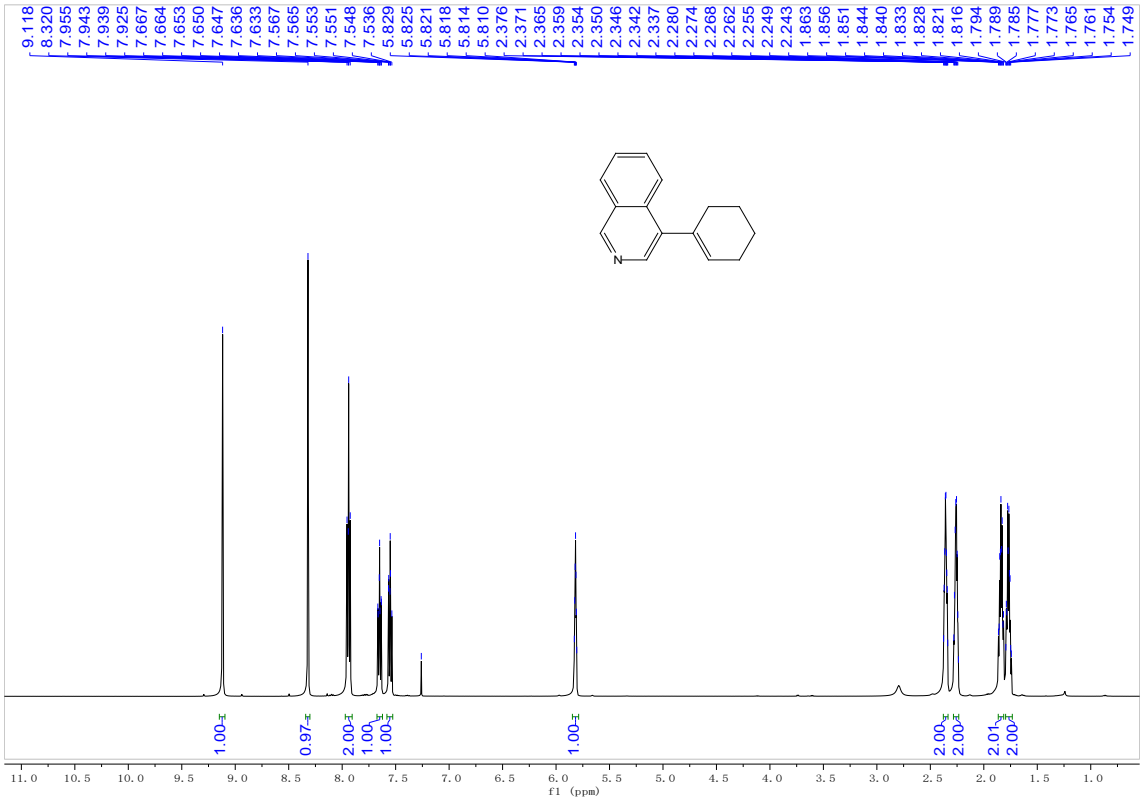


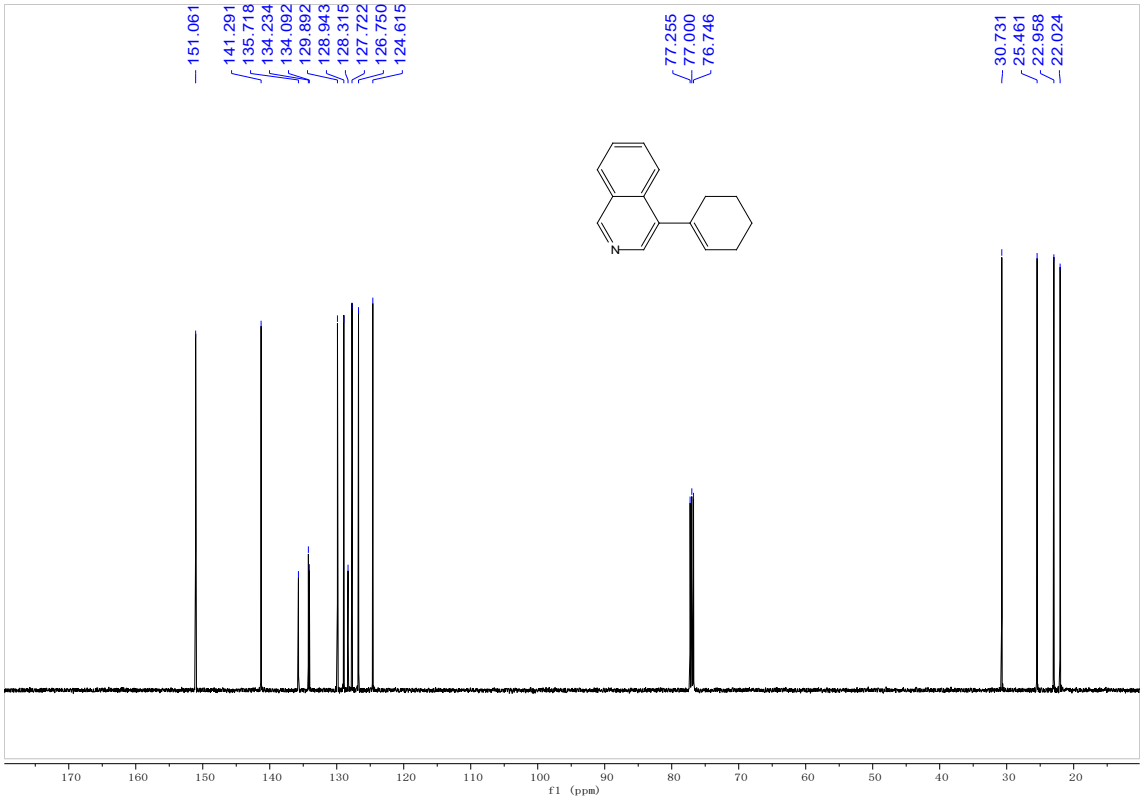
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1m**



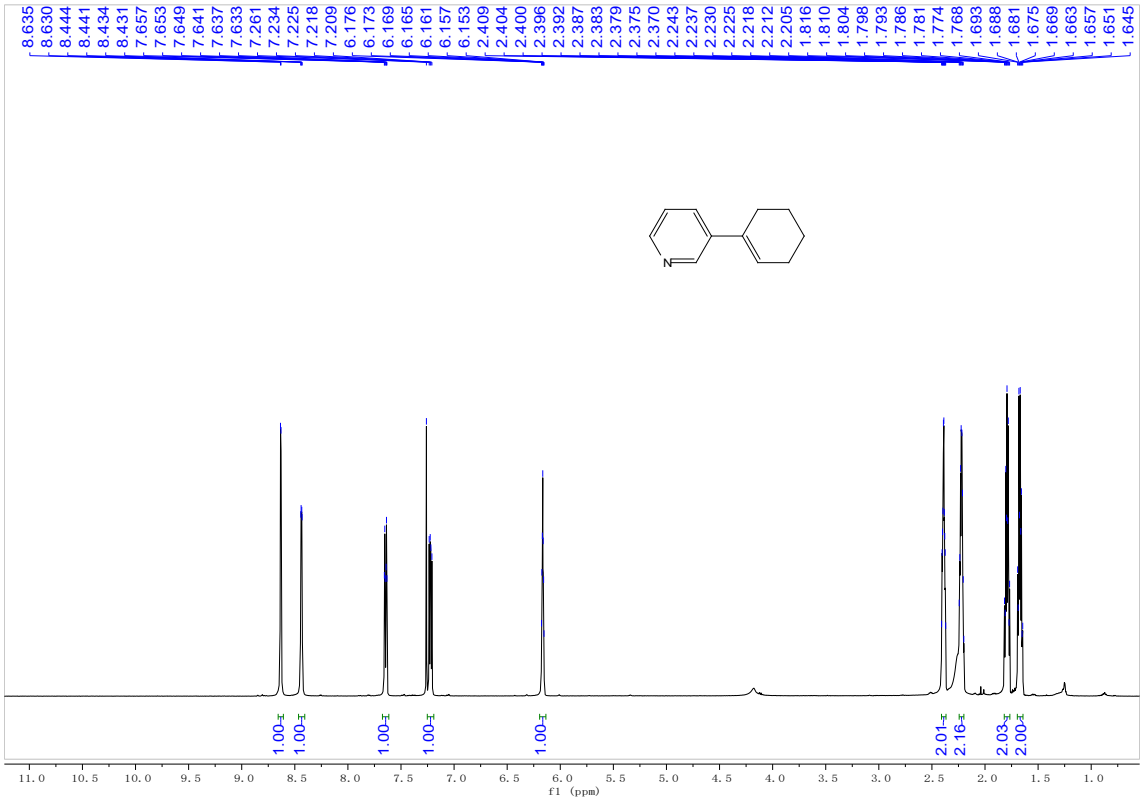
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1n**



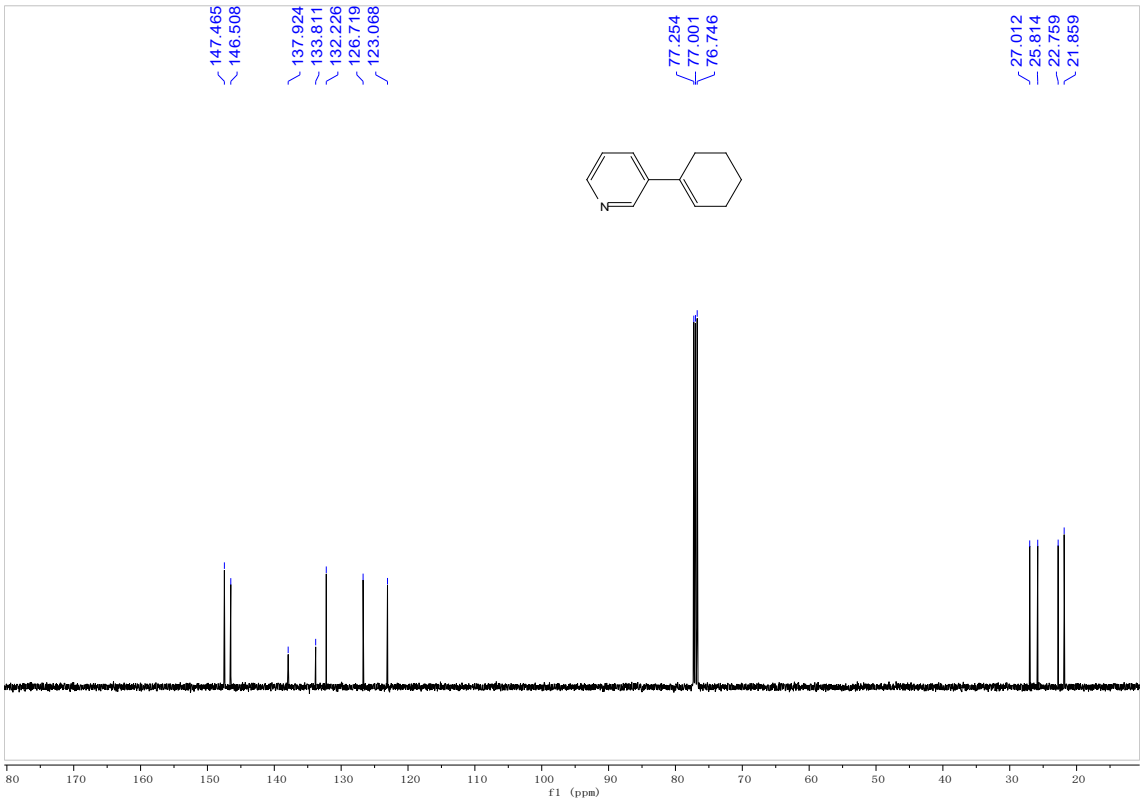
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1n**



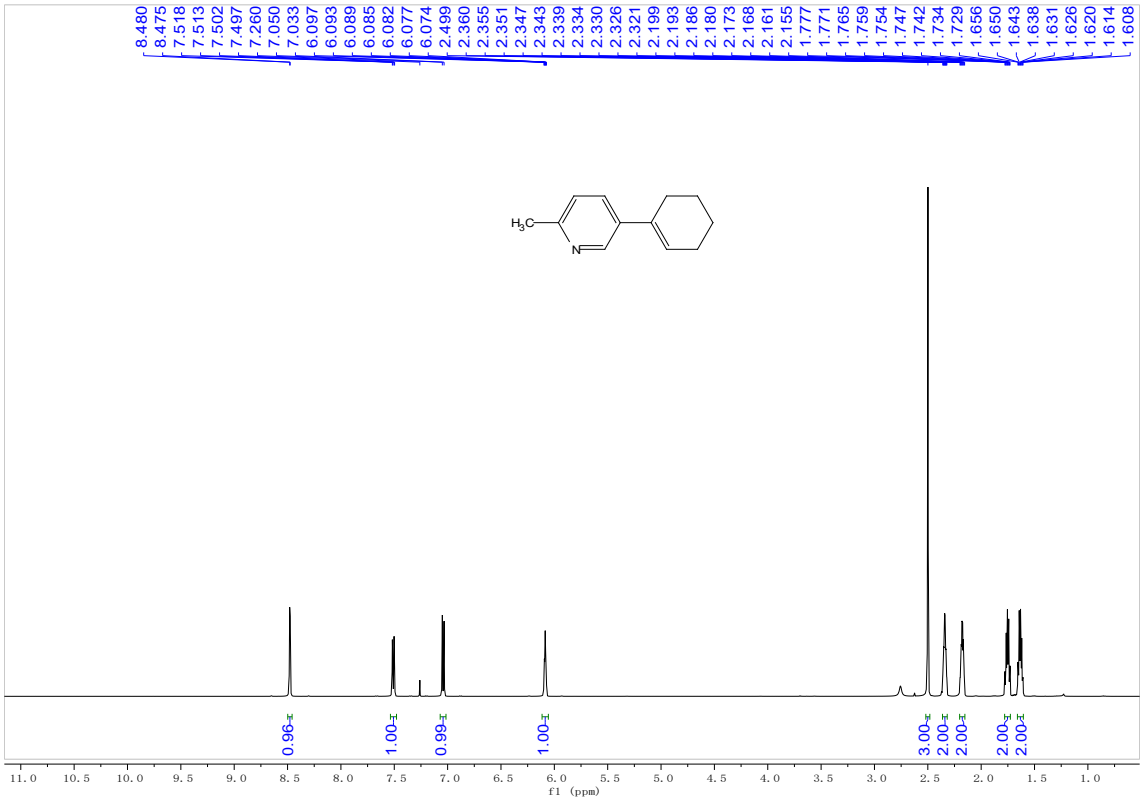
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1o**



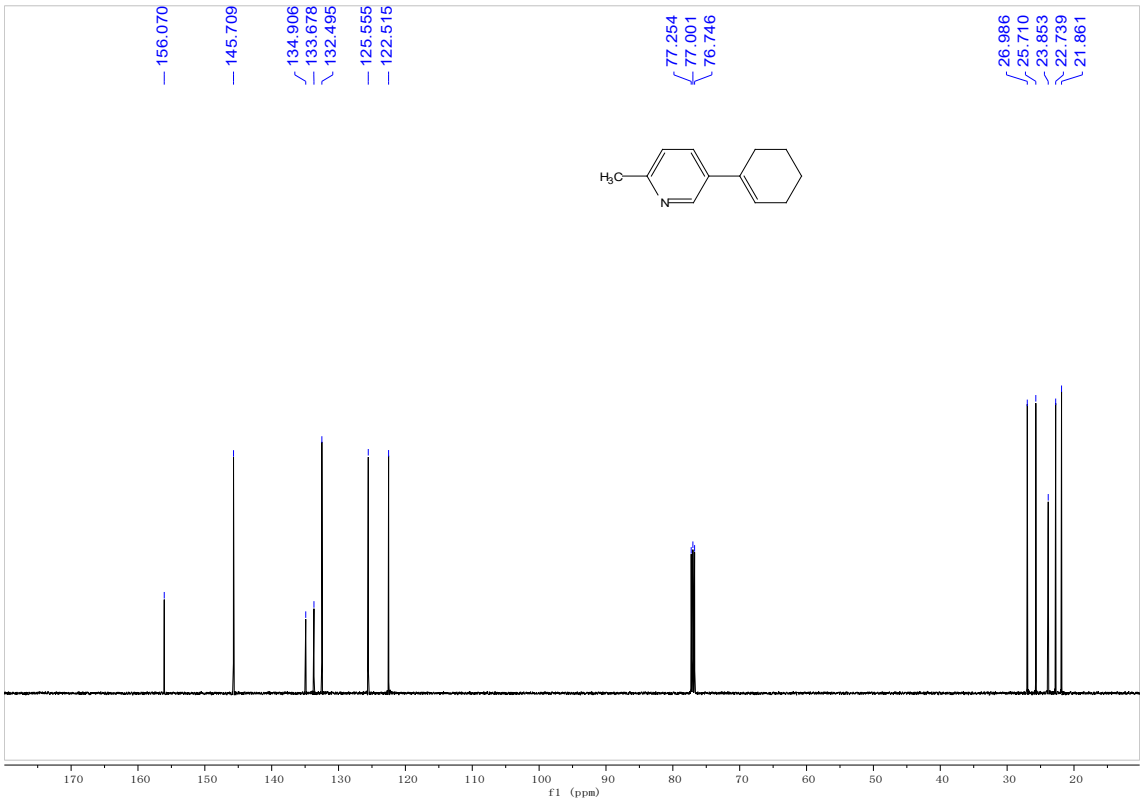
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1o**



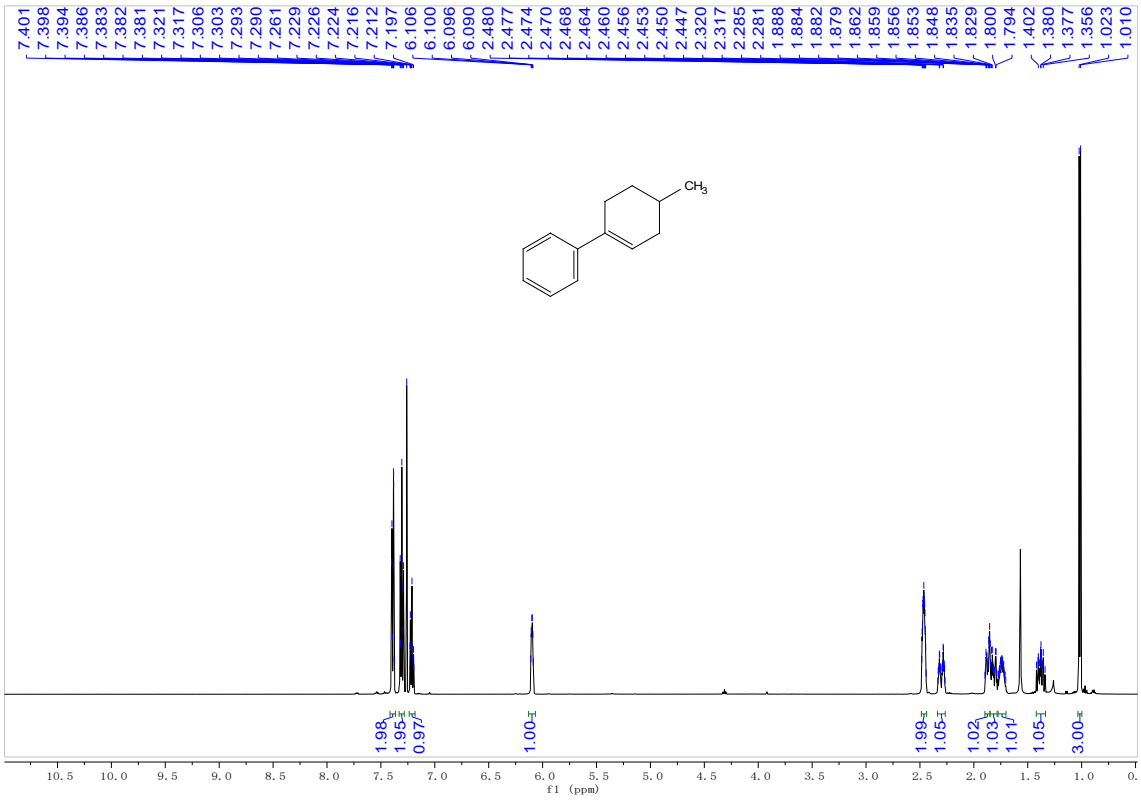
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1p**



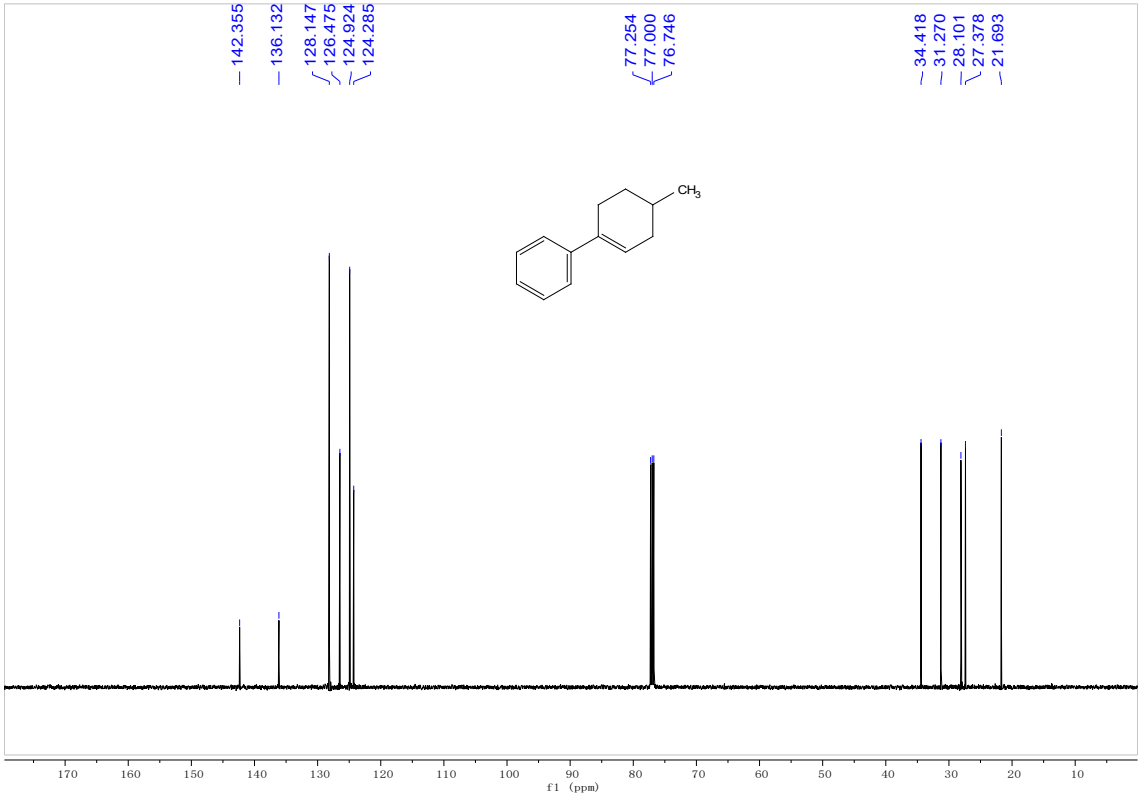
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1p**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1q**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1q**



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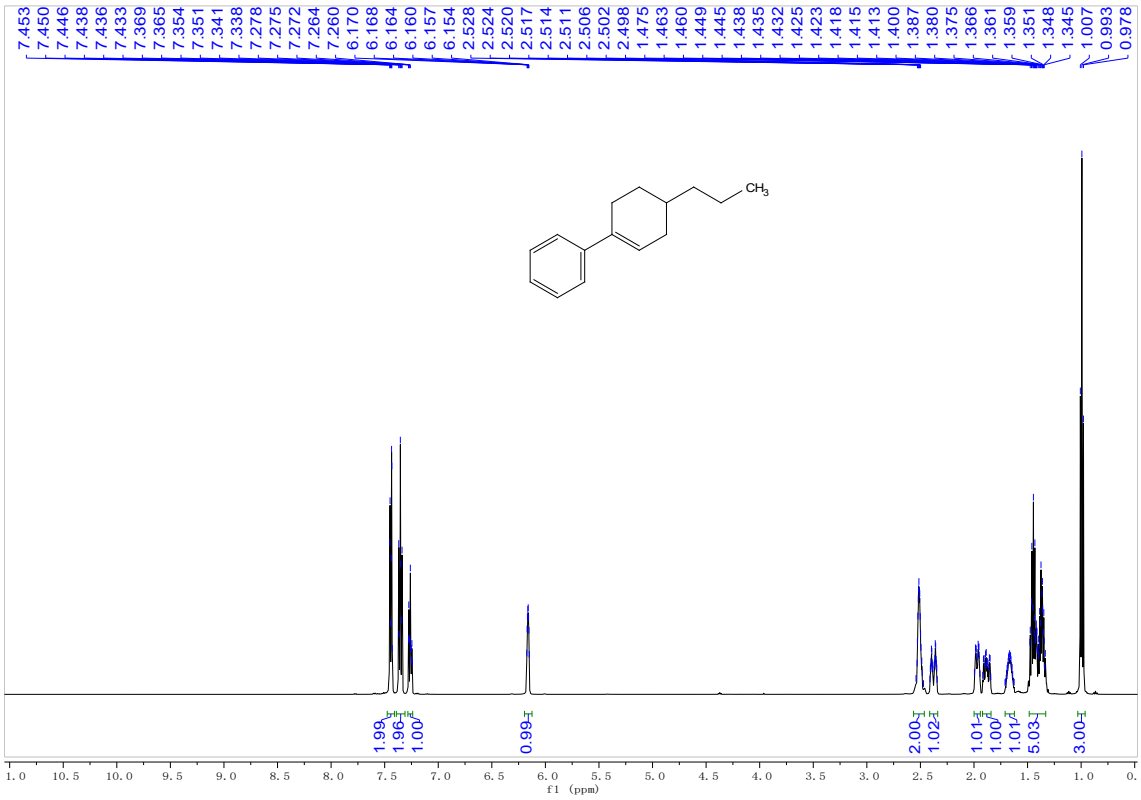
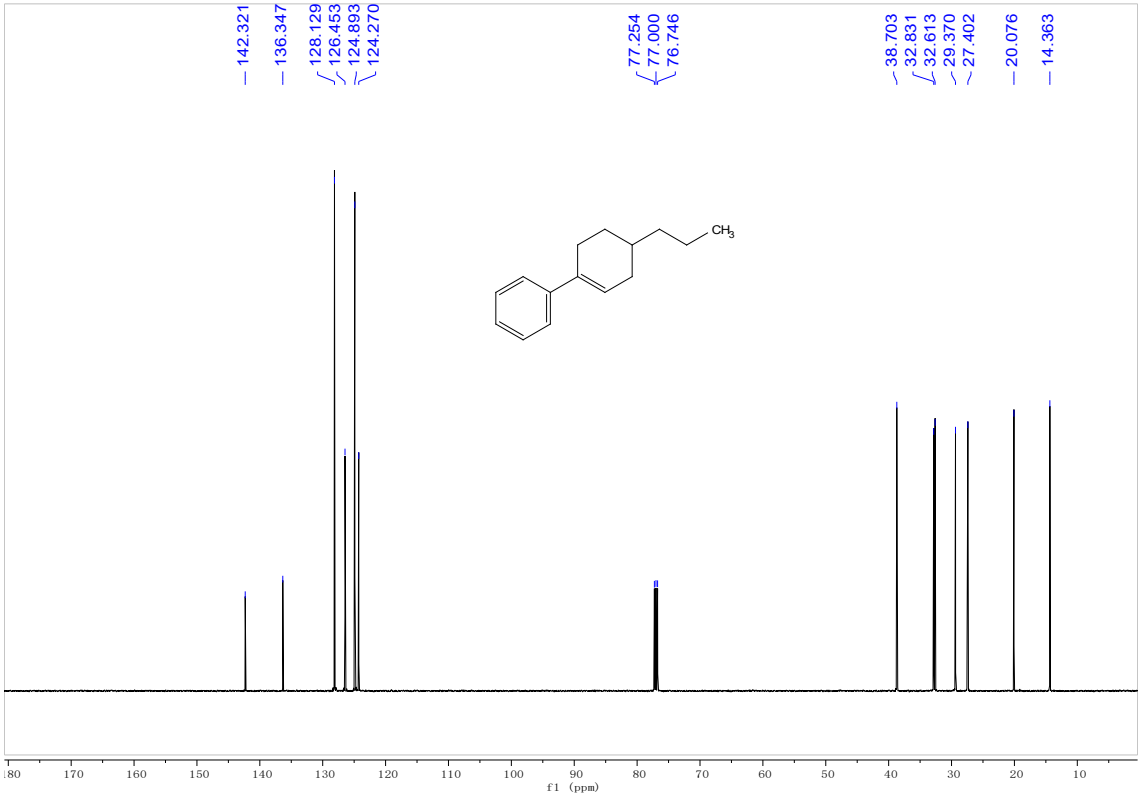
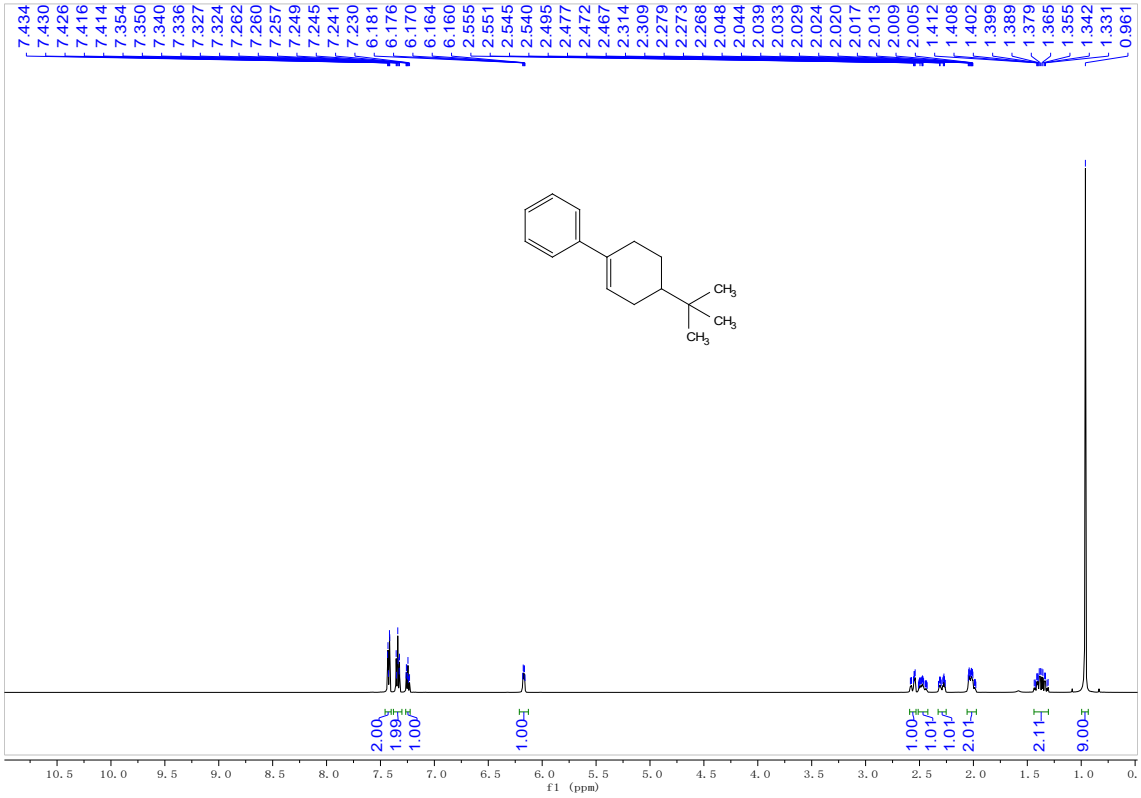


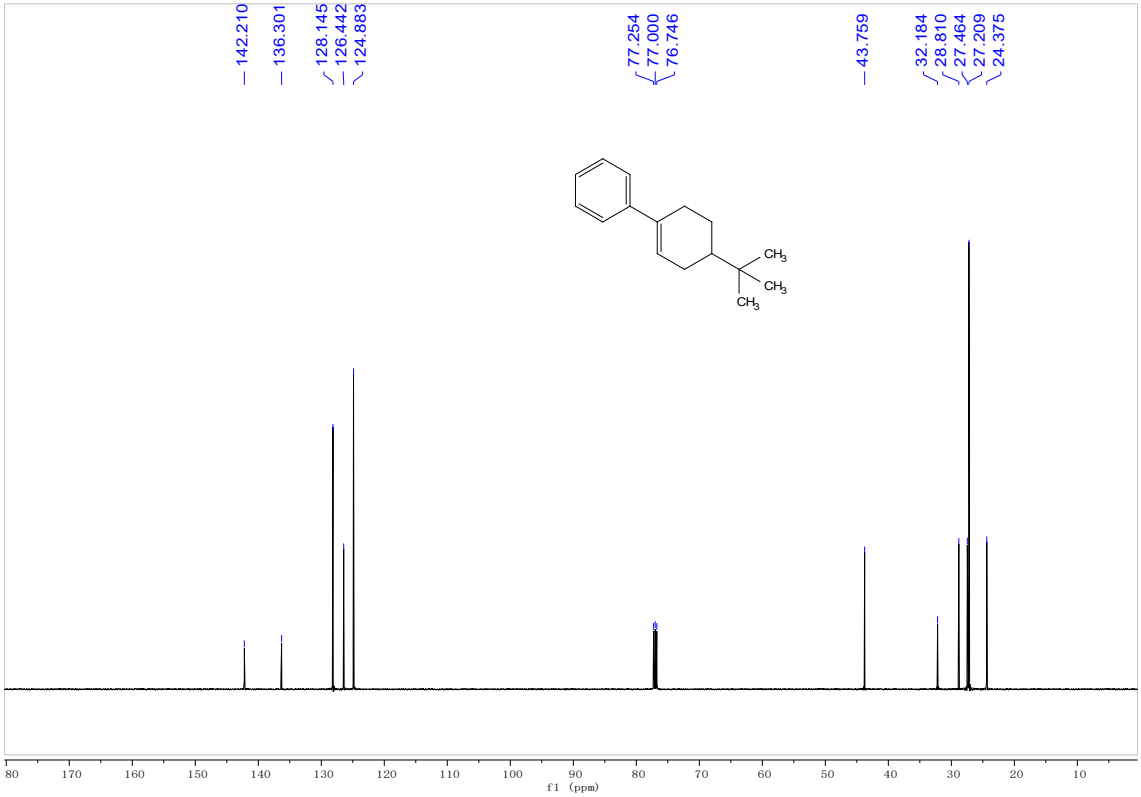
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1r**



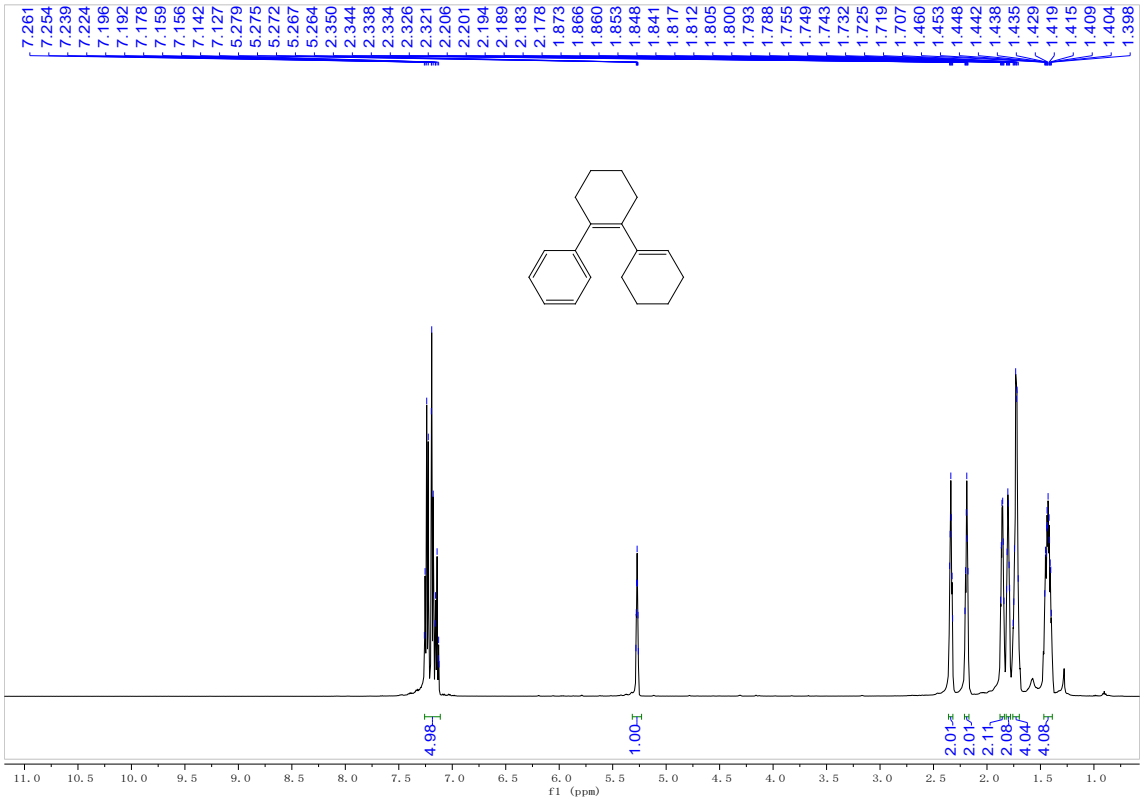
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1s**



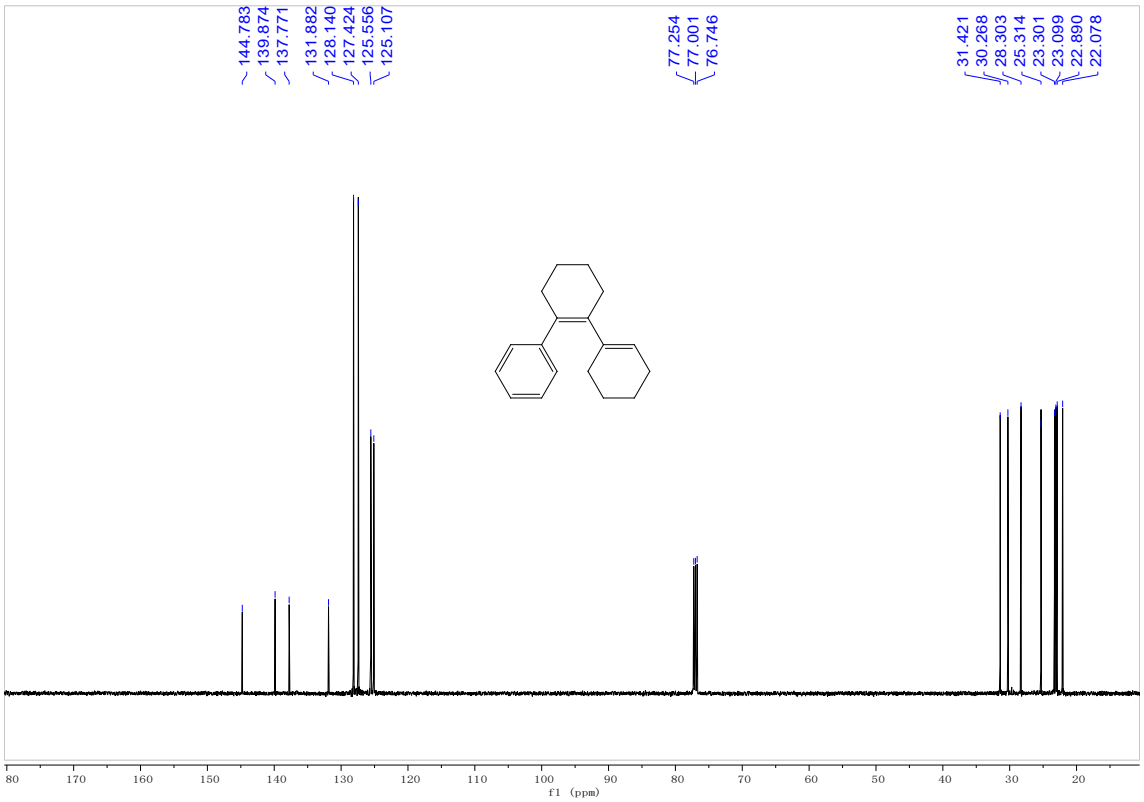
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1s**



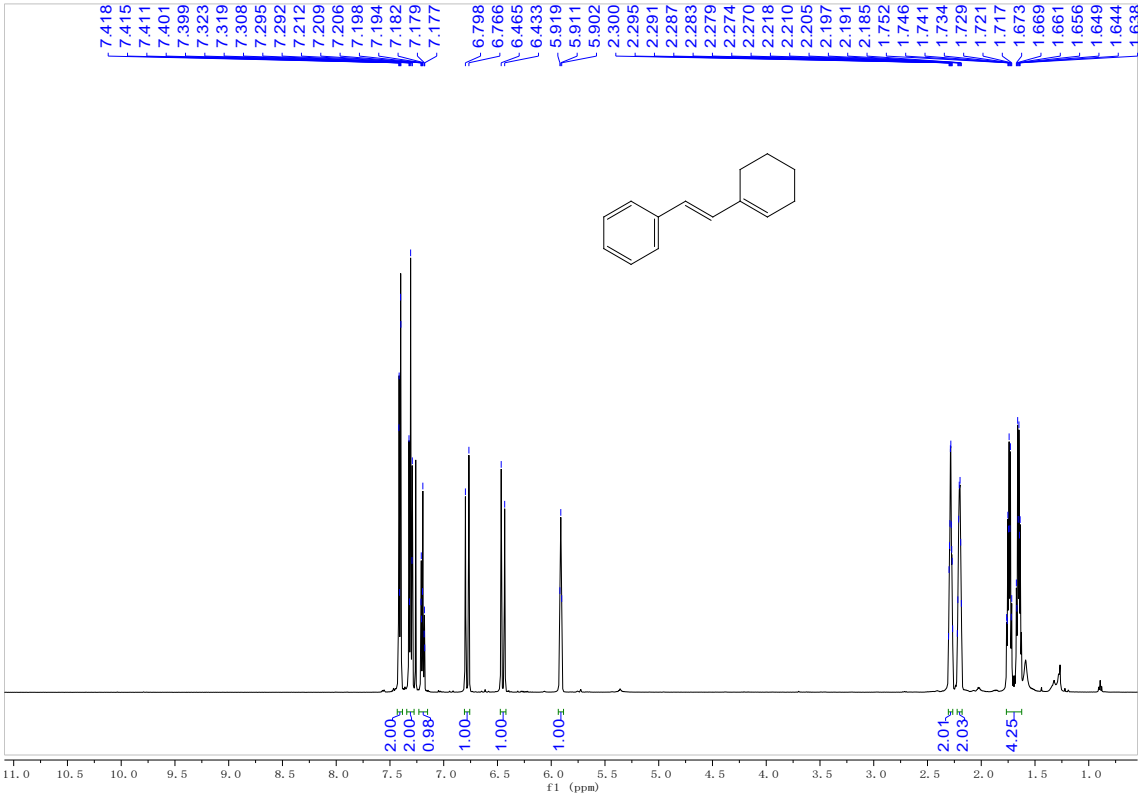
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1t**



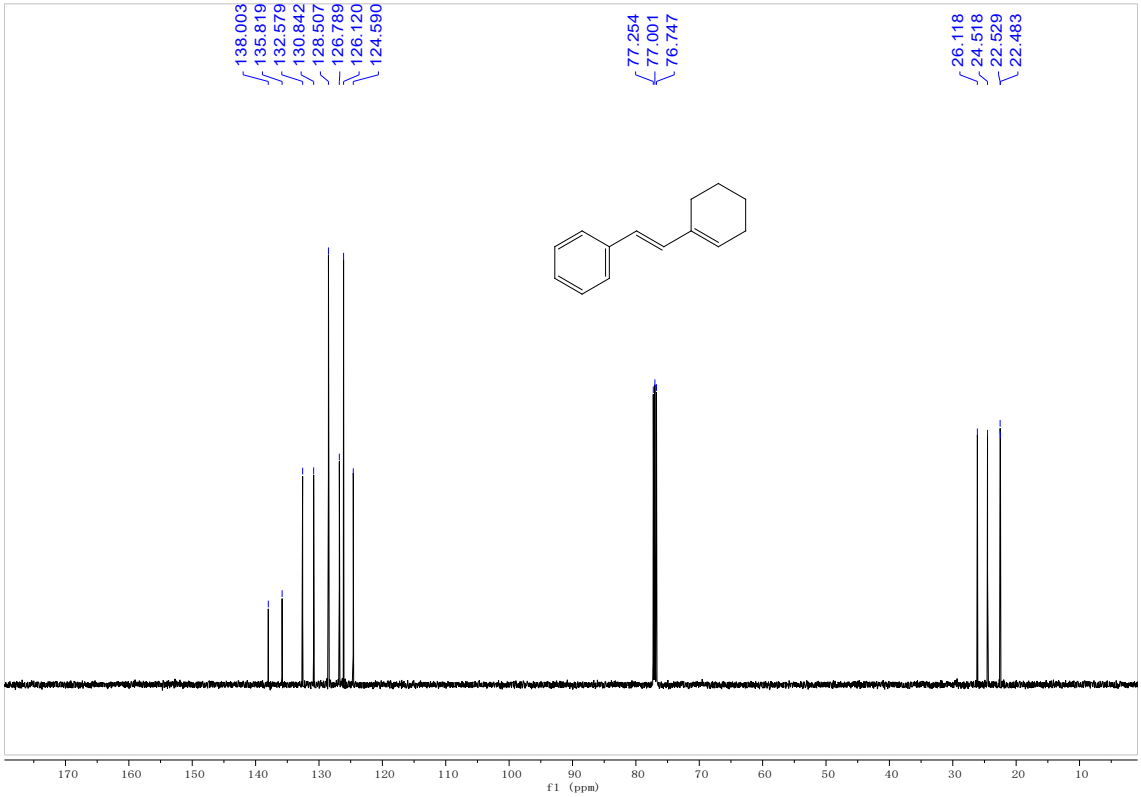
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1t**



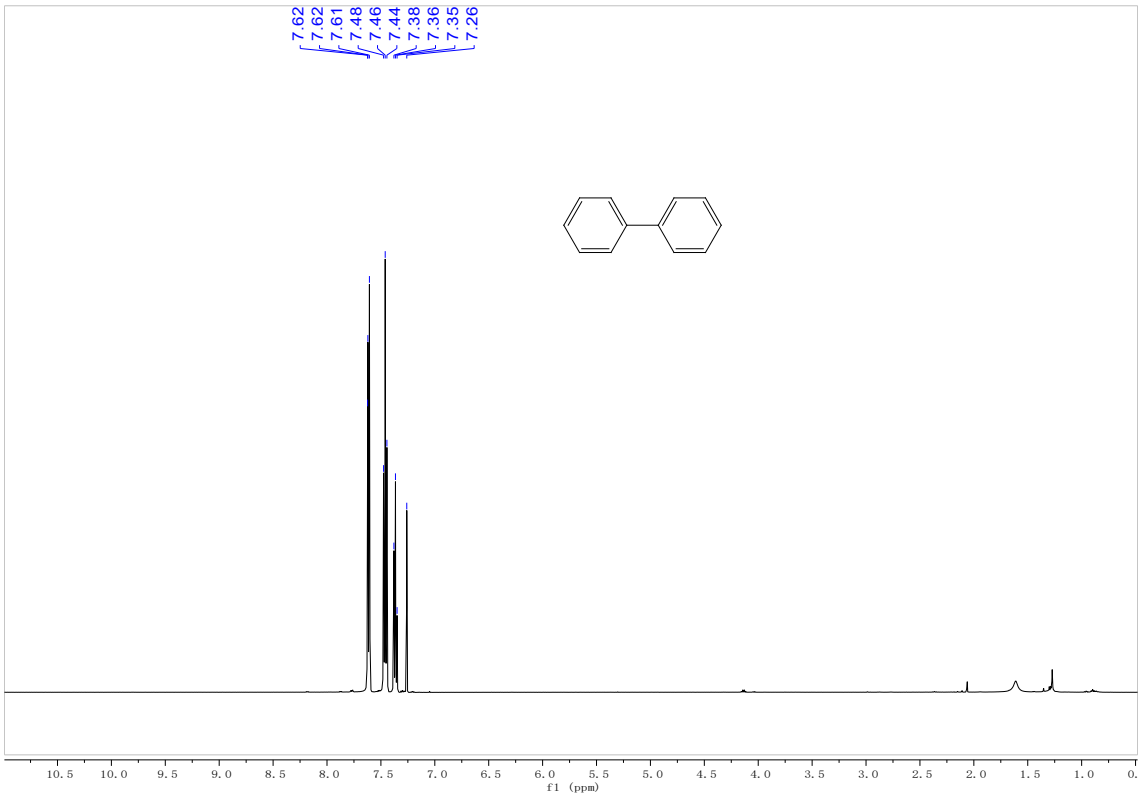
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **1u**



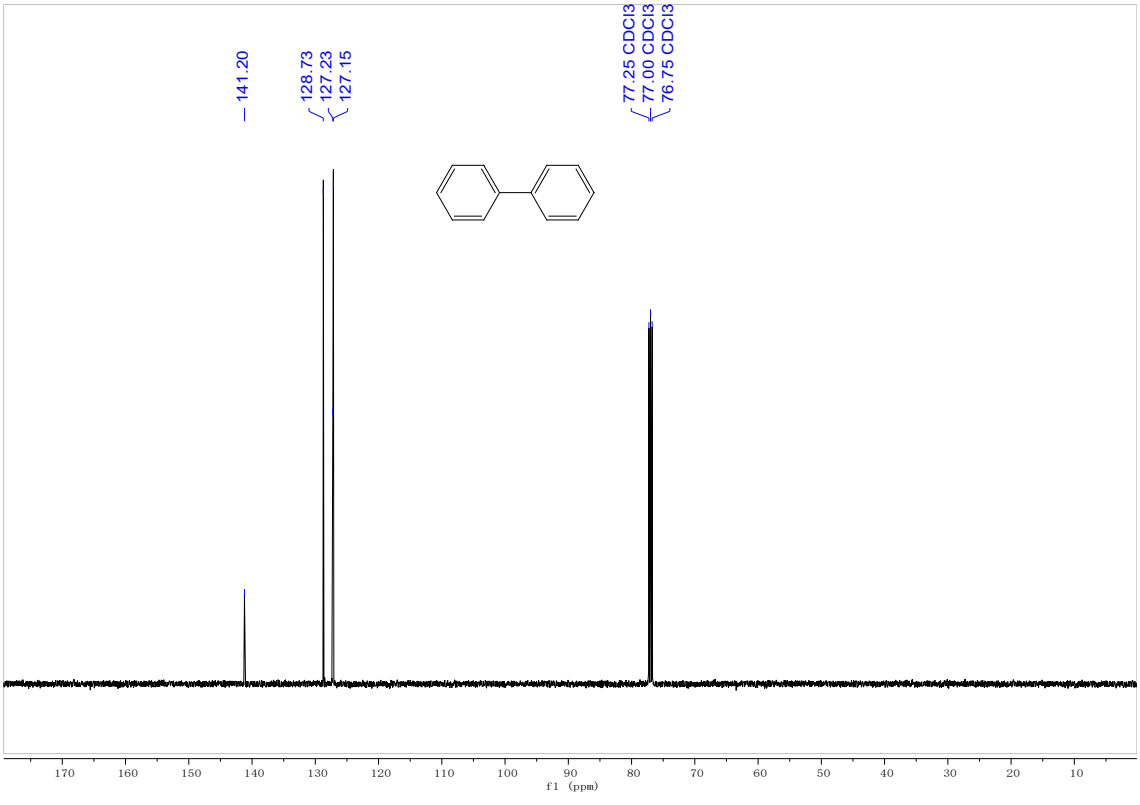
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **1u**



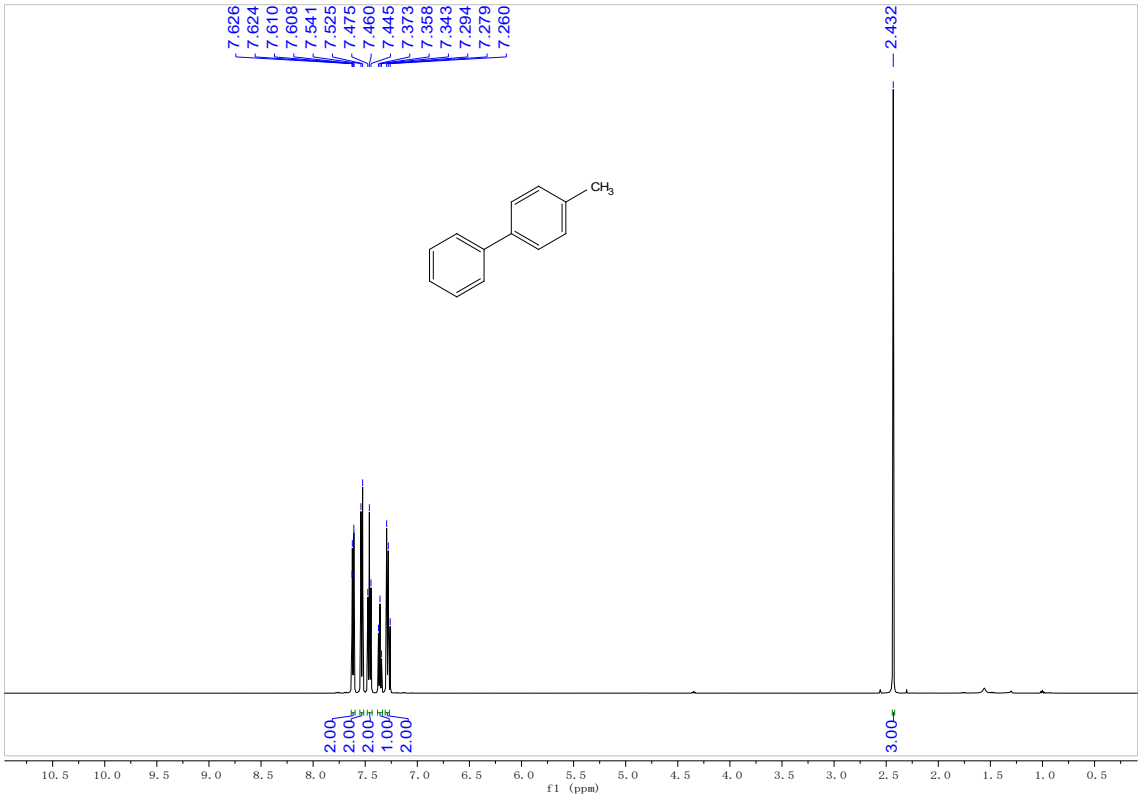
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2a**



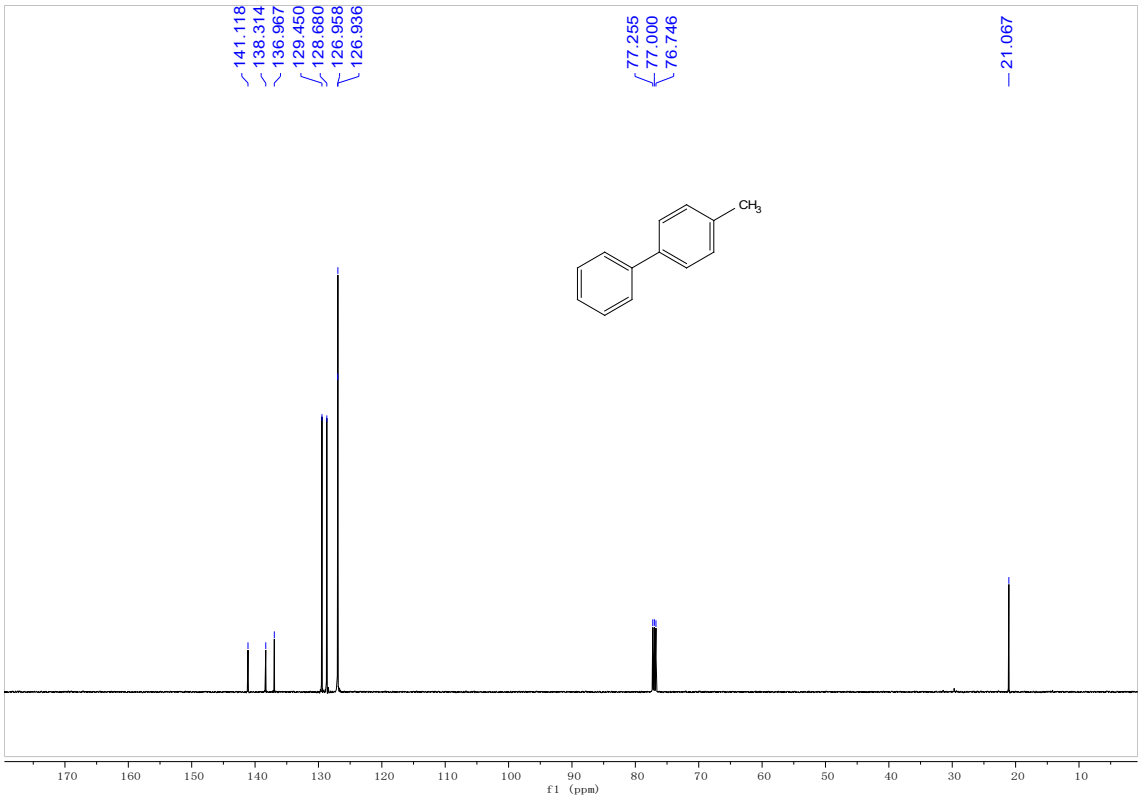
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2a**



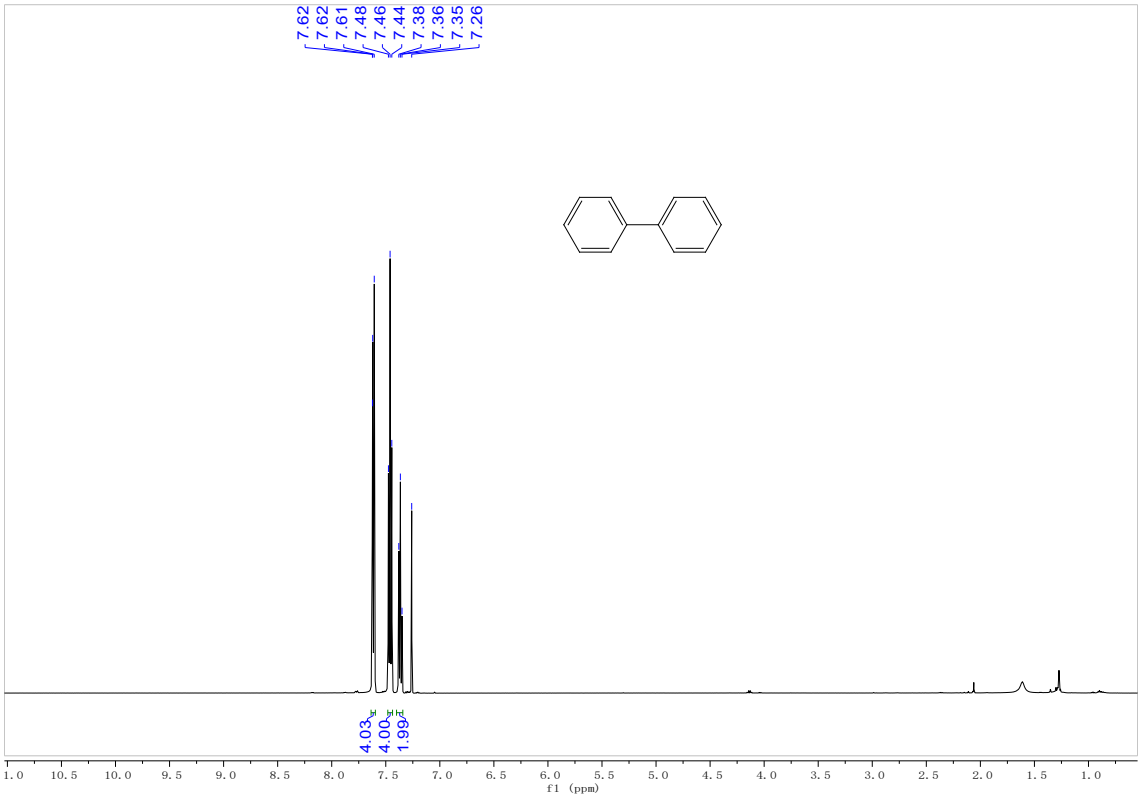
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2a**



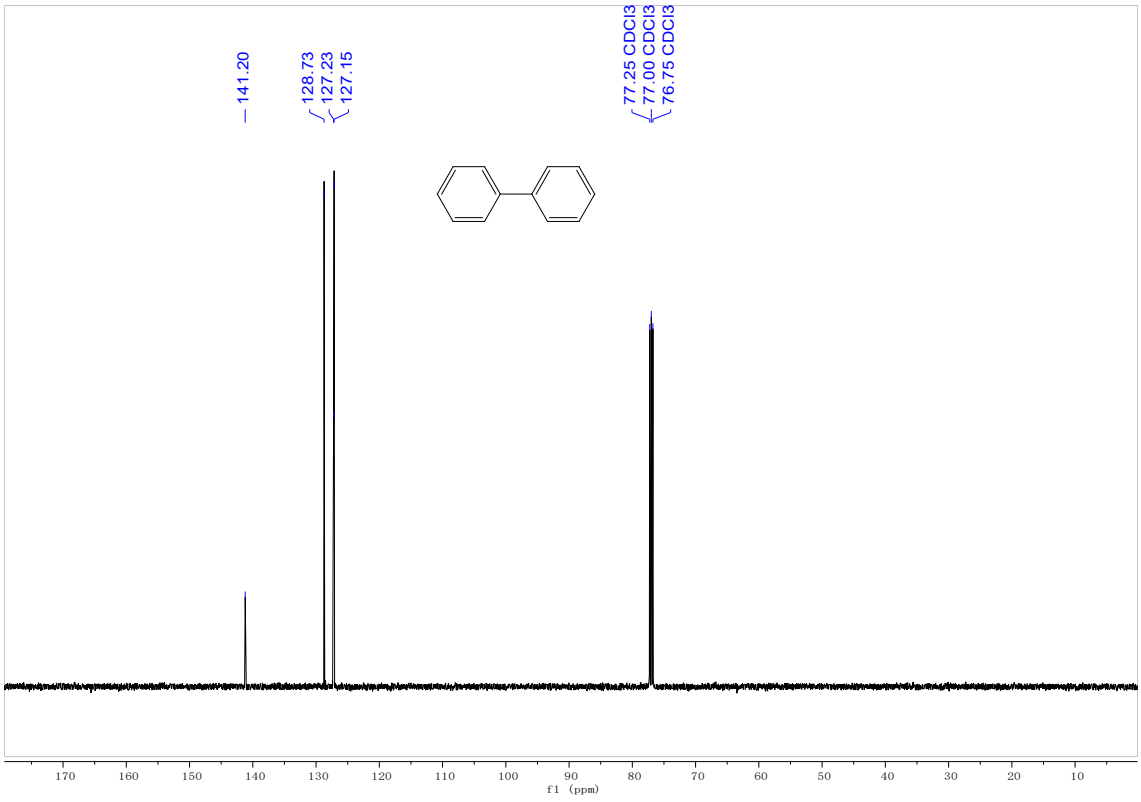
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2a**



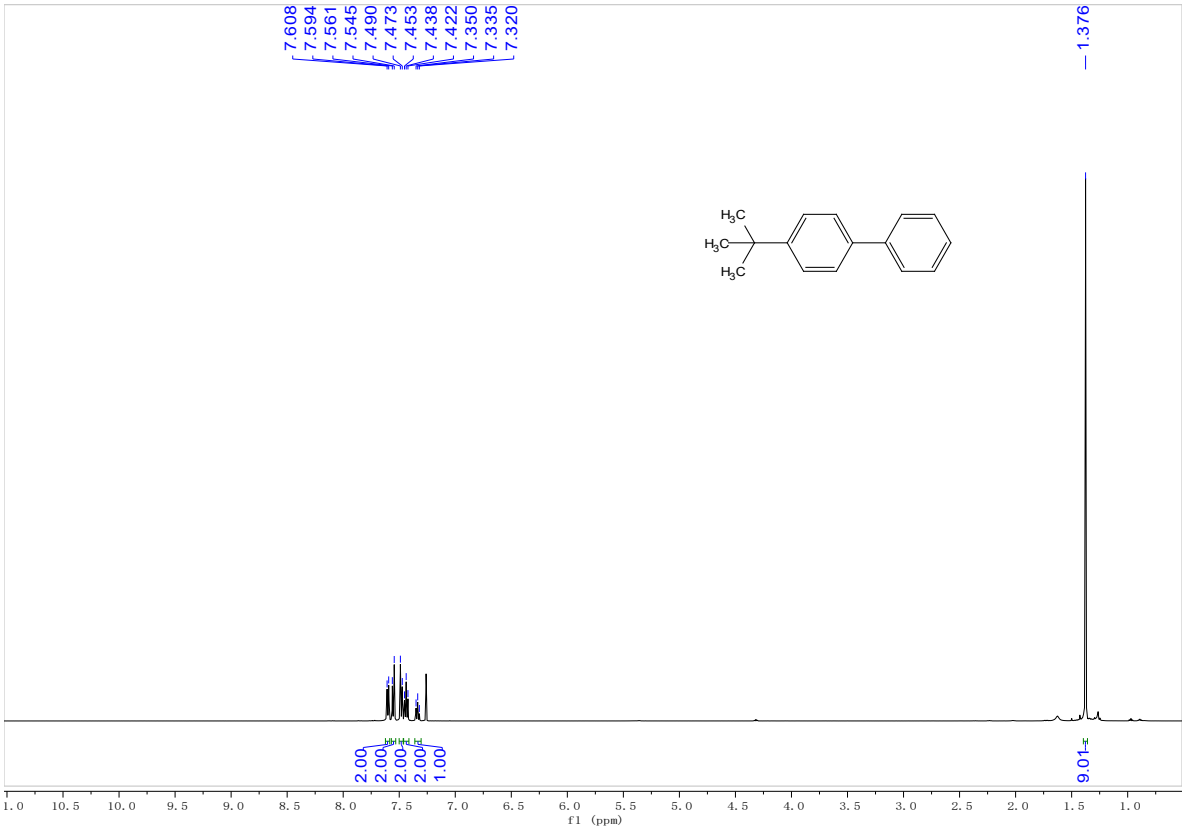
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2b**



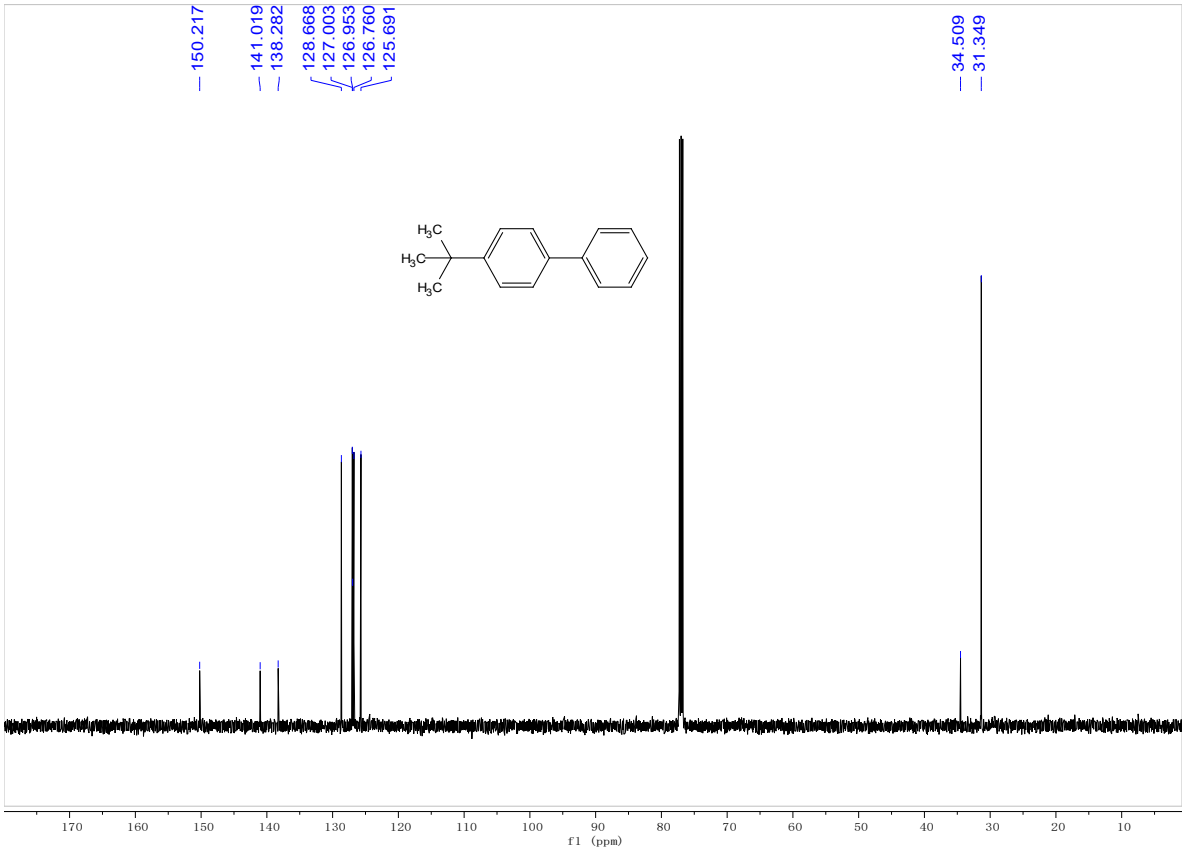
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2b**



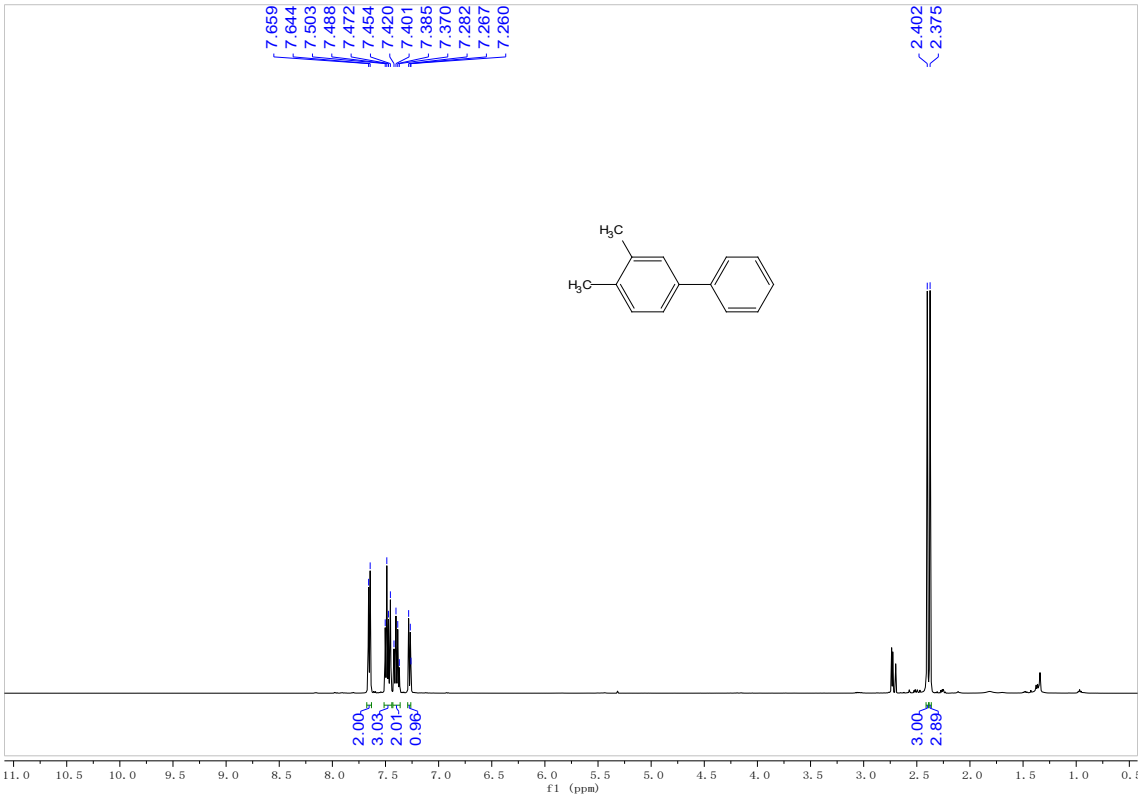
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2c**



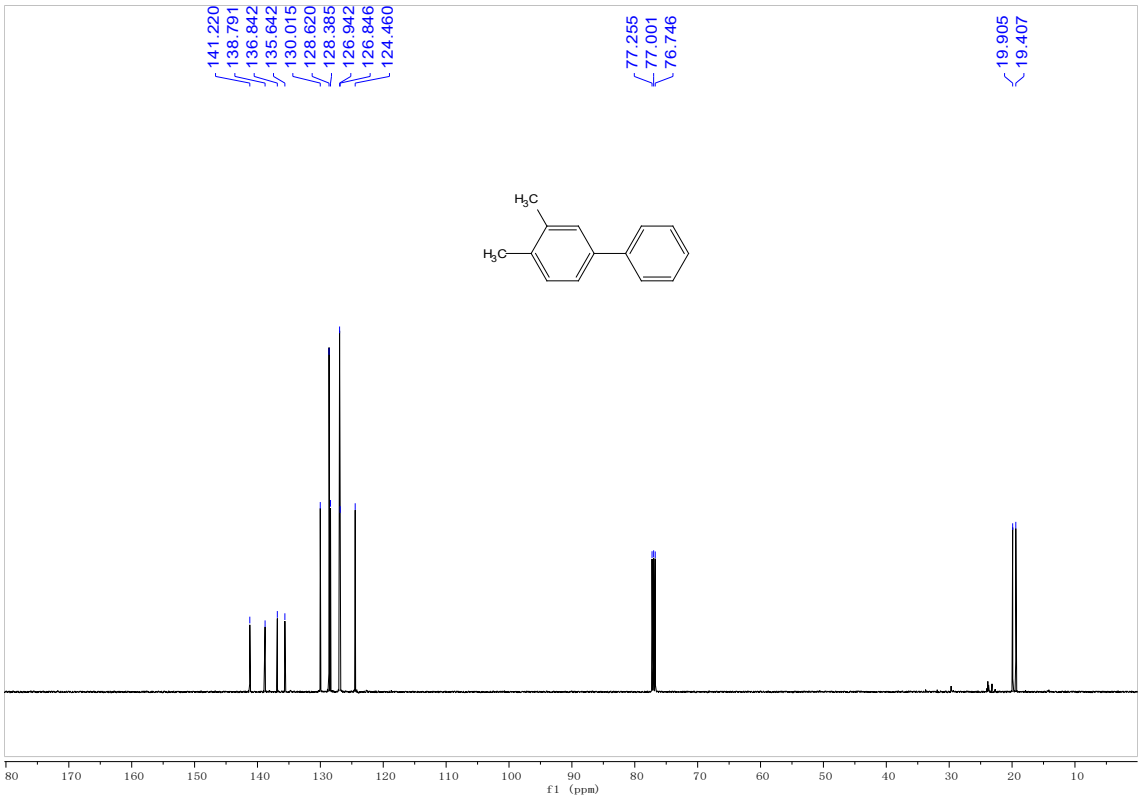
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2c**



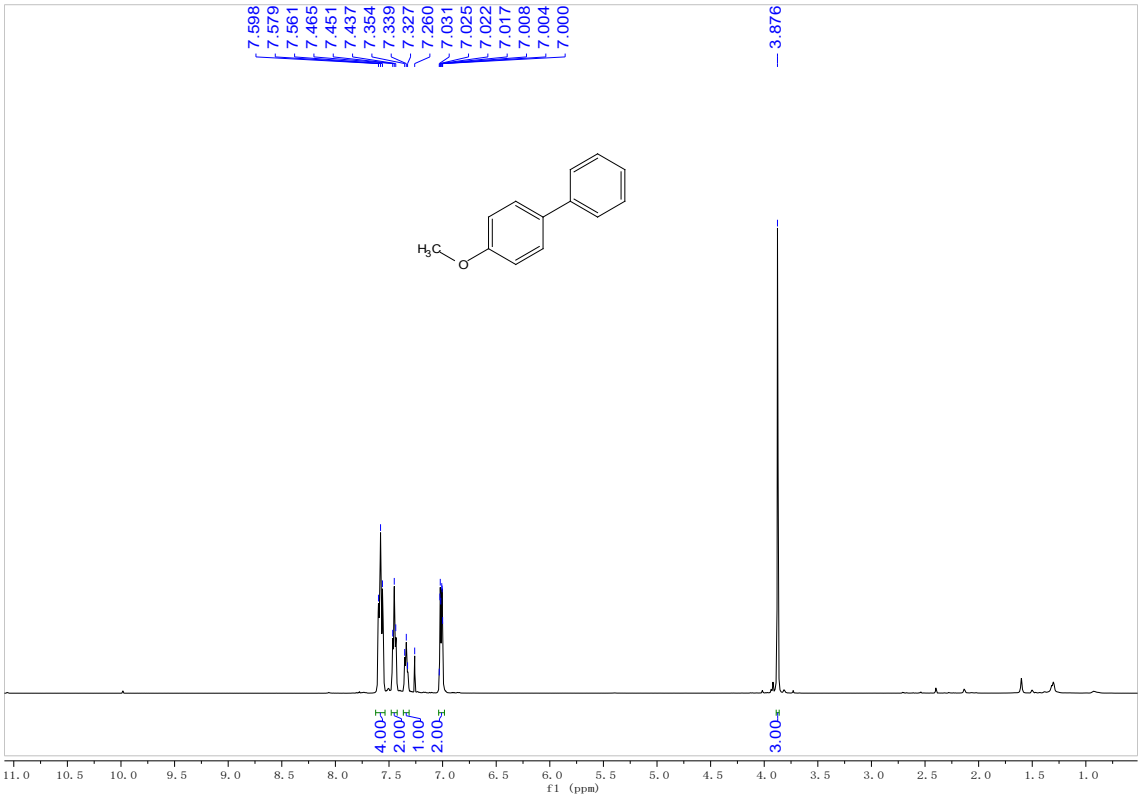
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2d**



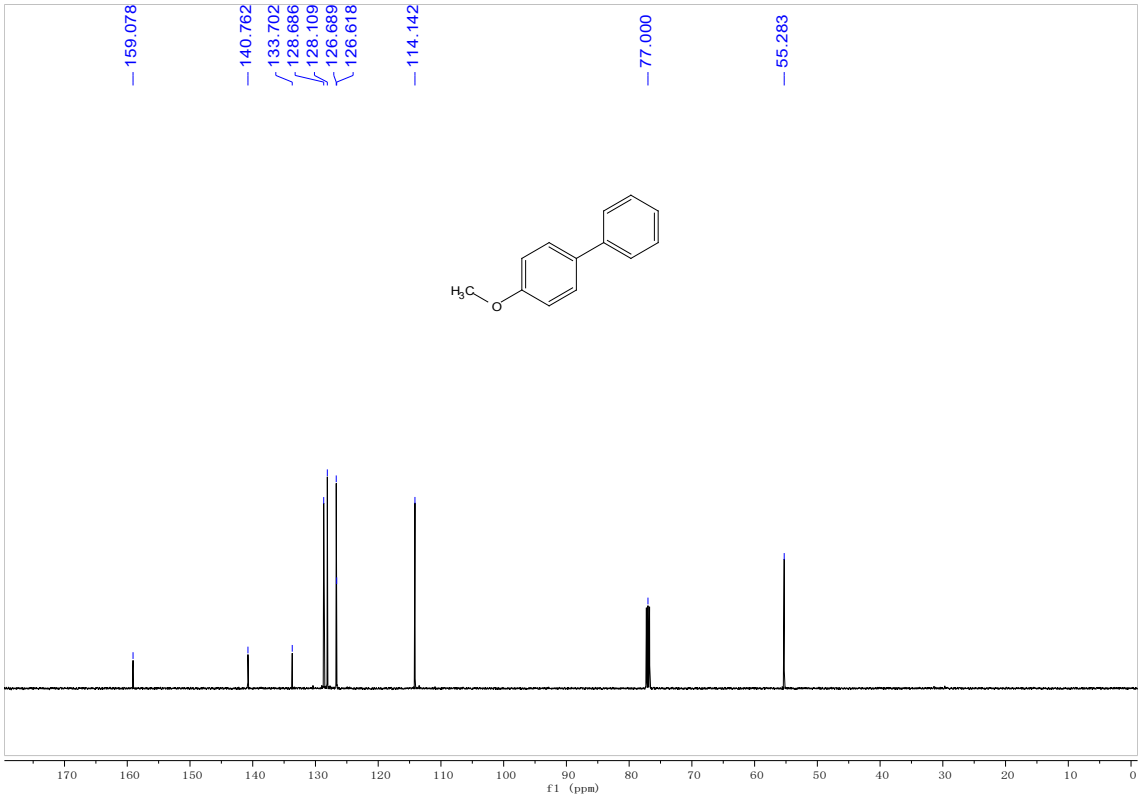
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2d**



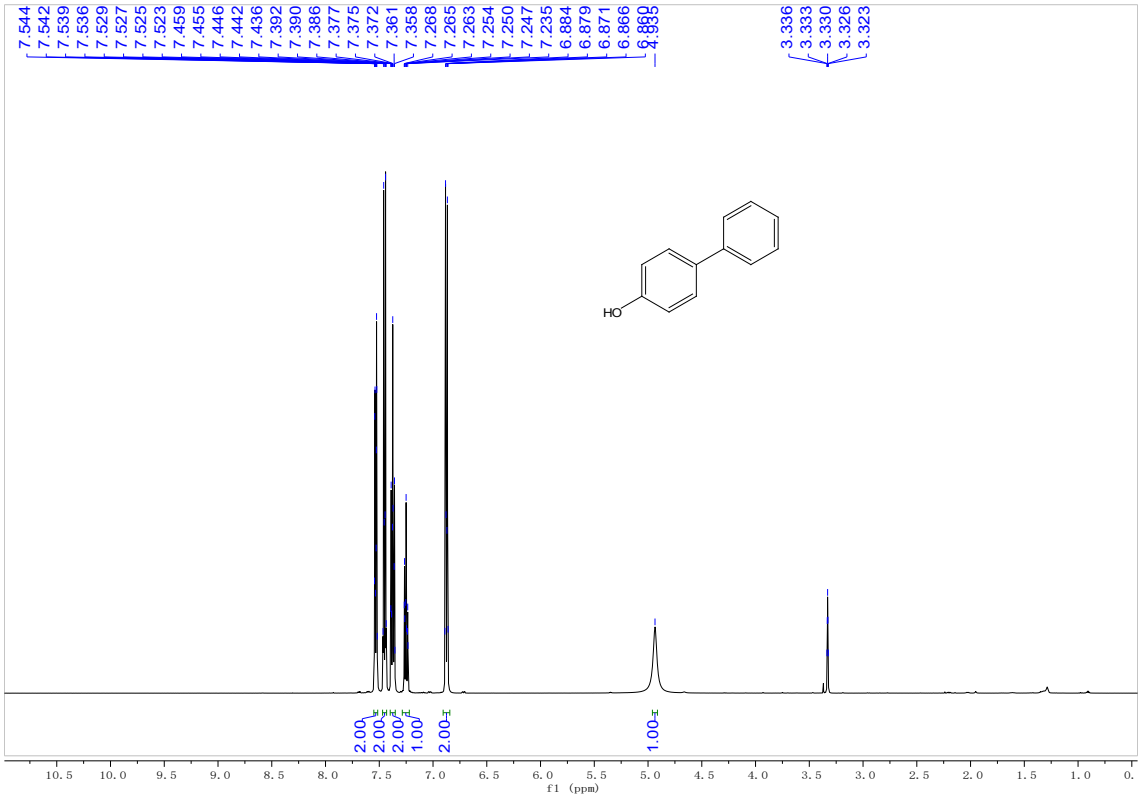
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2e**



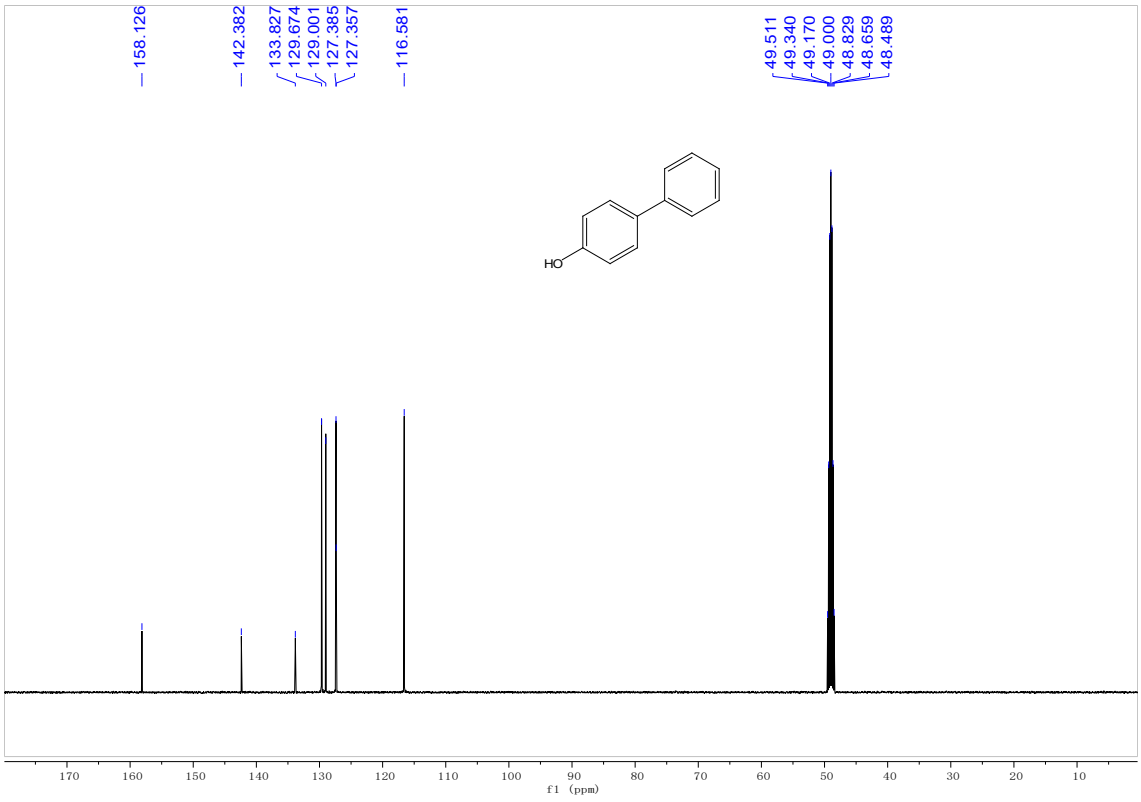
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2e**



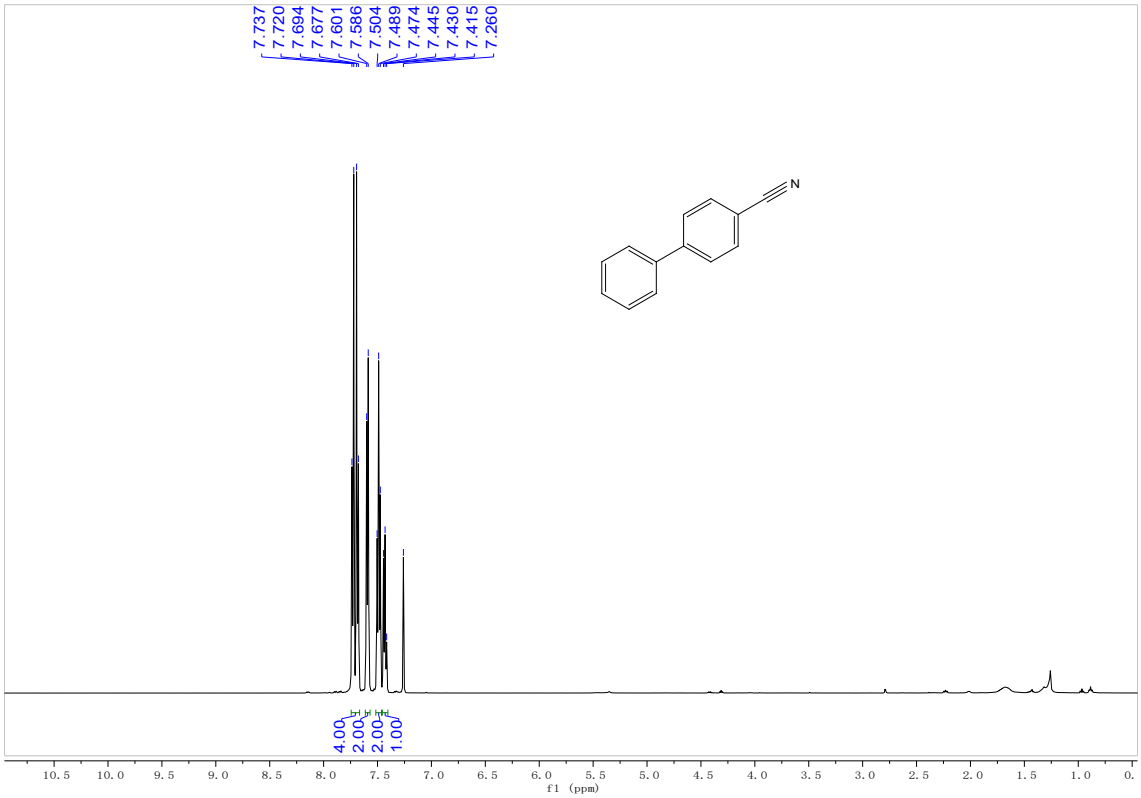
^{1}H NMR (500 MHz, CD_3OD) spectrum of compound **2f**



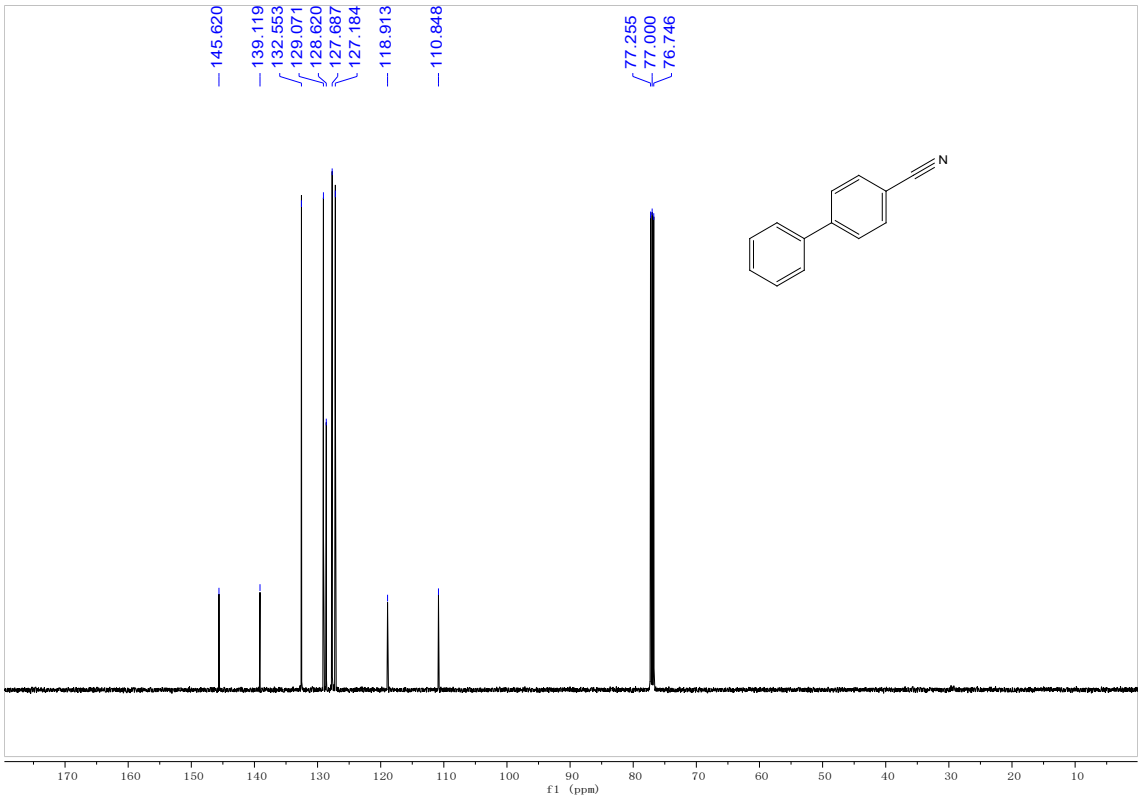
^{13}C NMR (125 MHz, CD_3OD) spectrum of compound **2f**



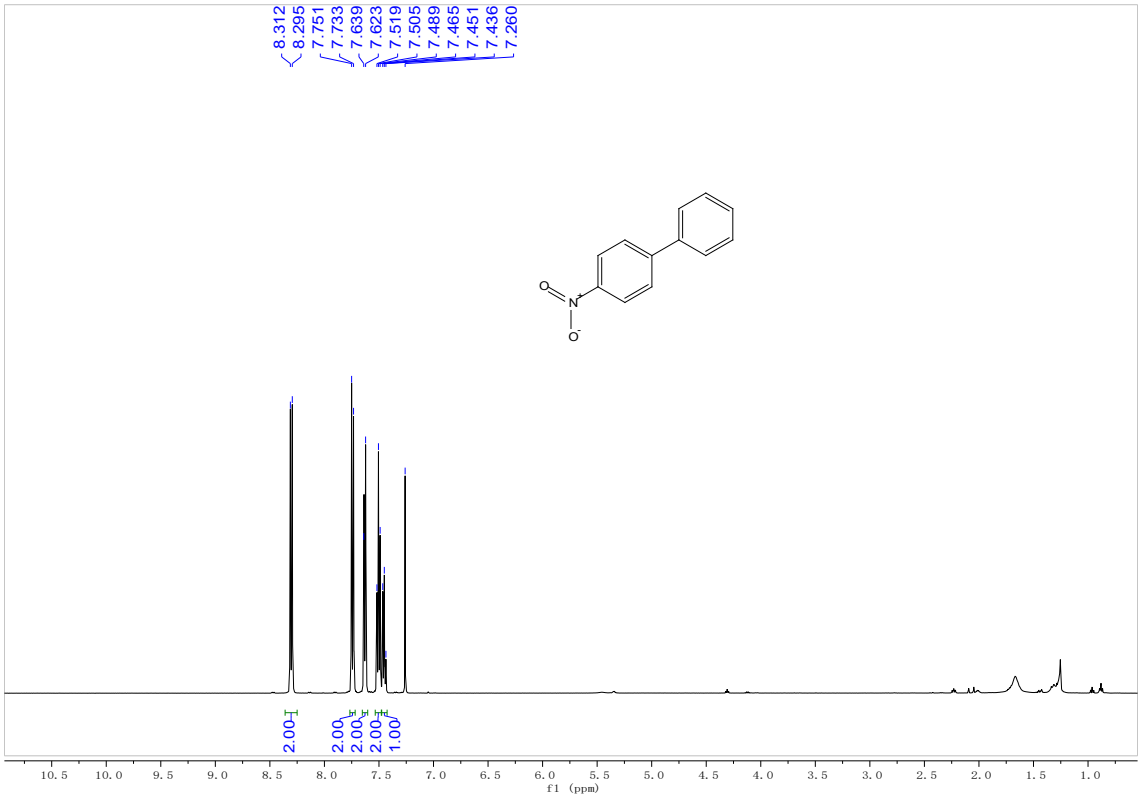
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2g**



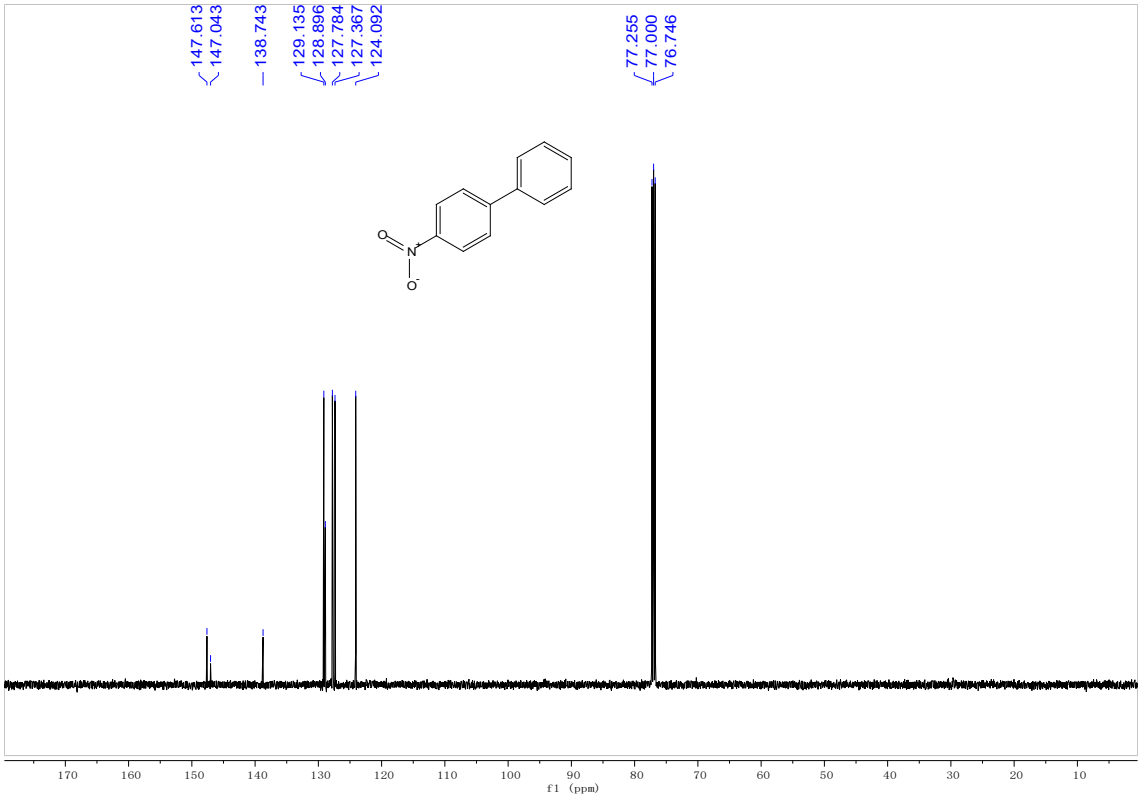
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2g**



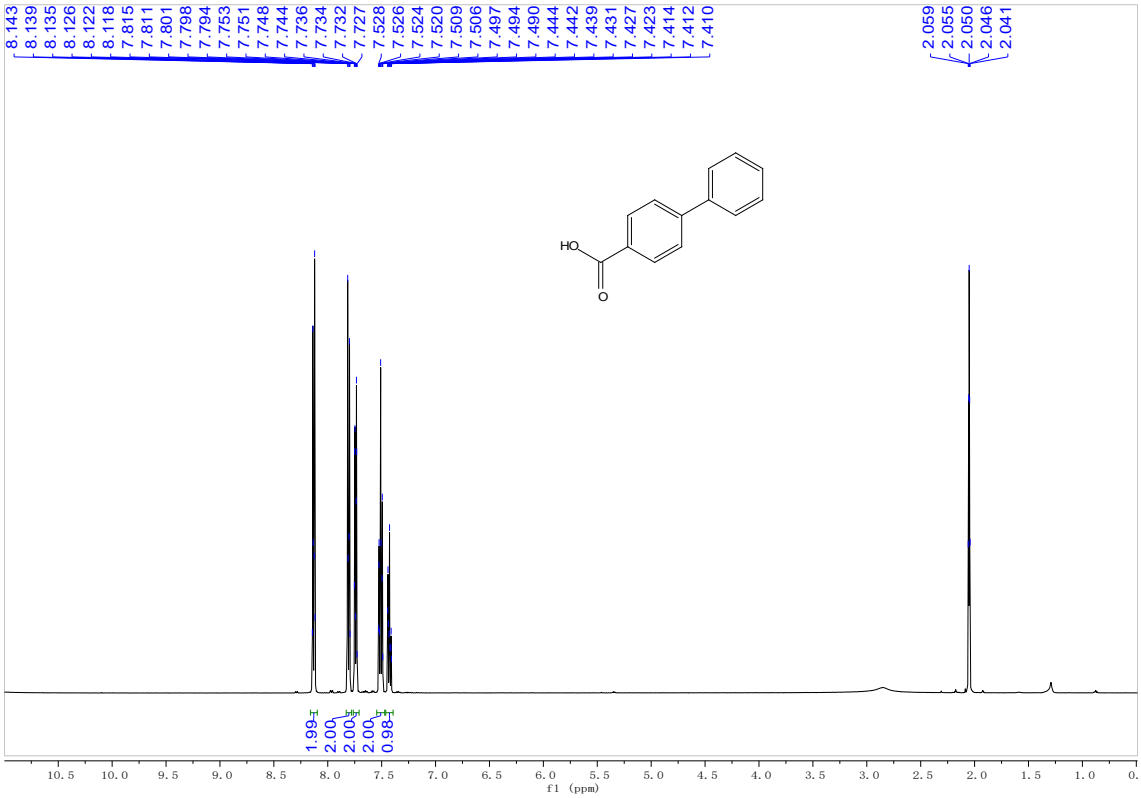
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2h**



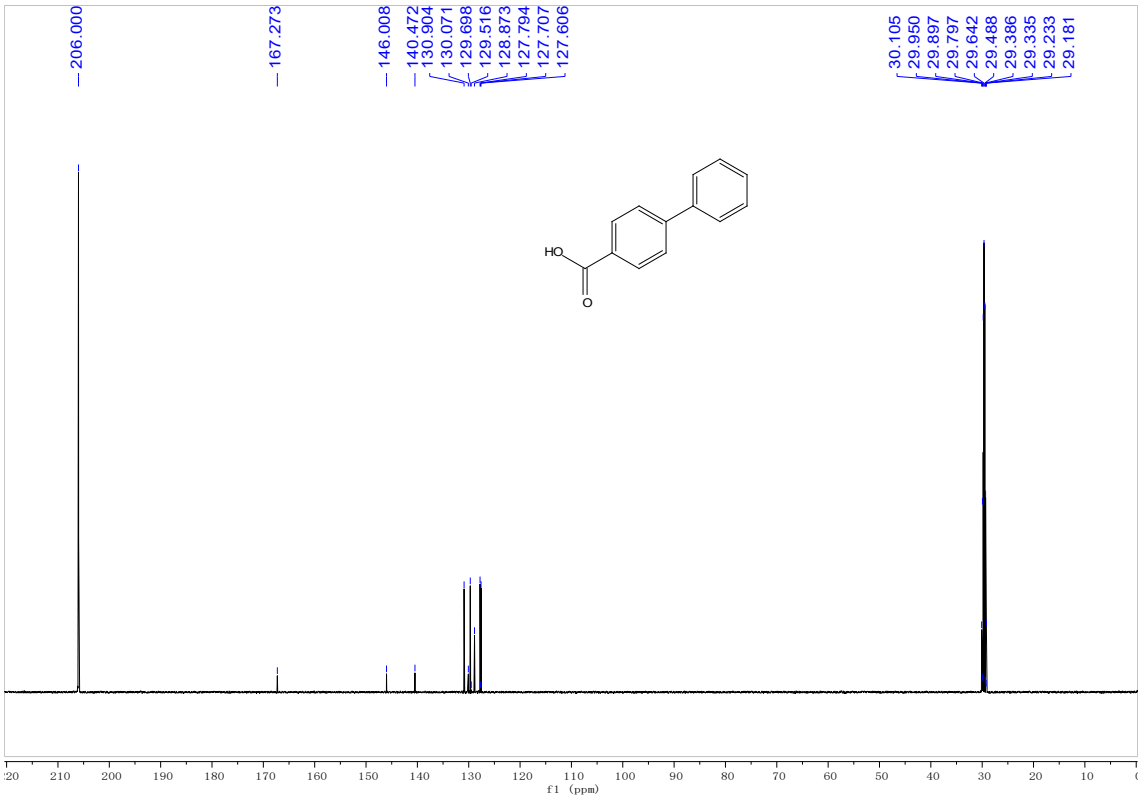
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2h**



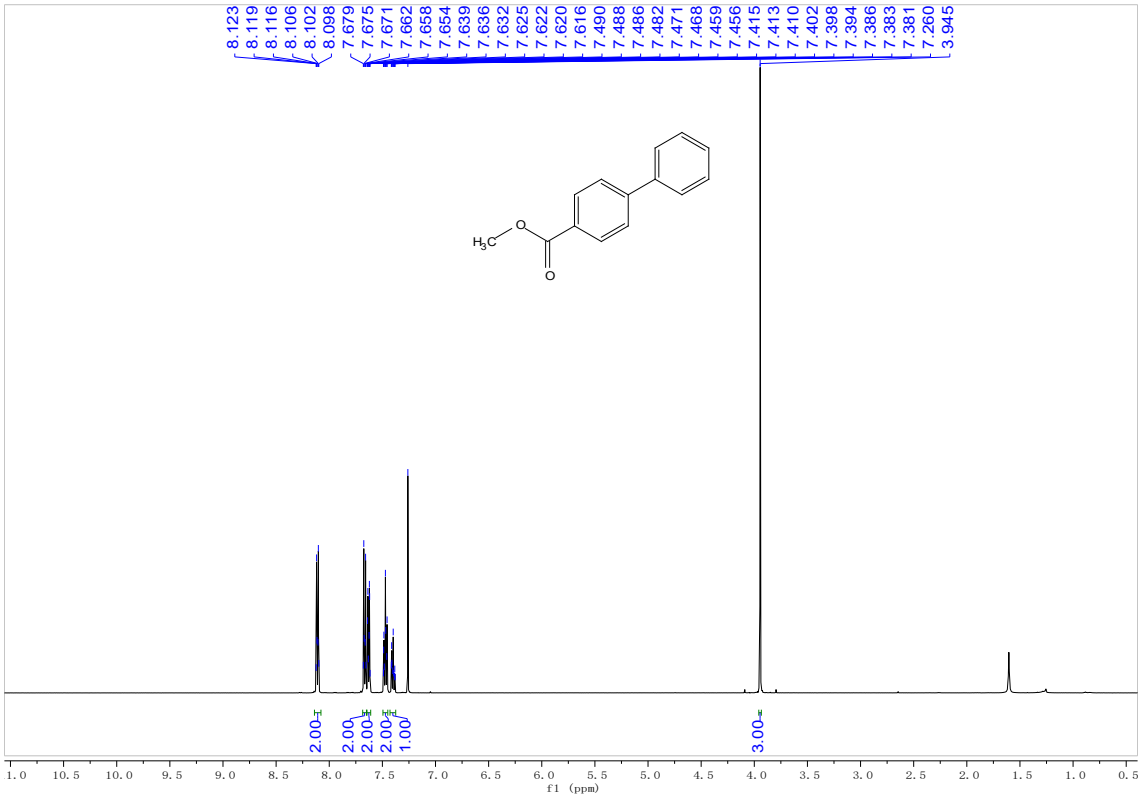
^{1}H NMR (500 MHz, $(CD_3)_2CO$) spectrum of compound **2i**



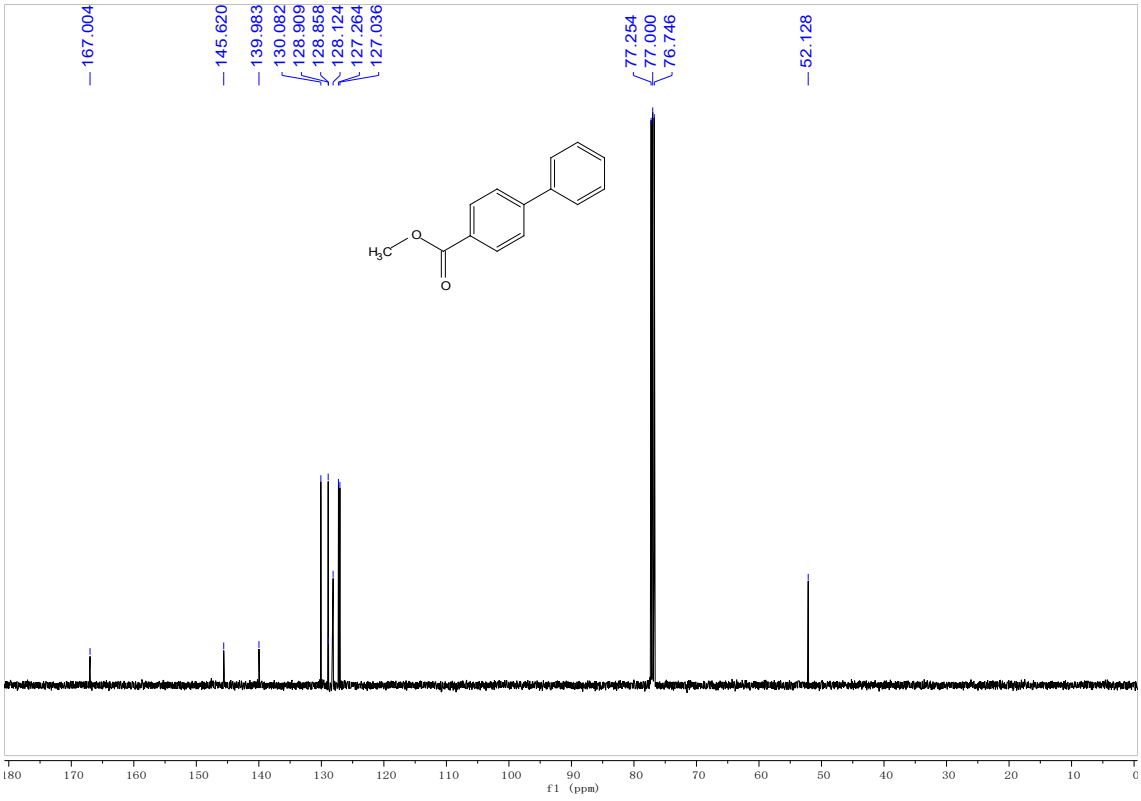
^{13}C NMR (125 MHz, $(CD_3)_2CO$) spectrum of compound **2i**



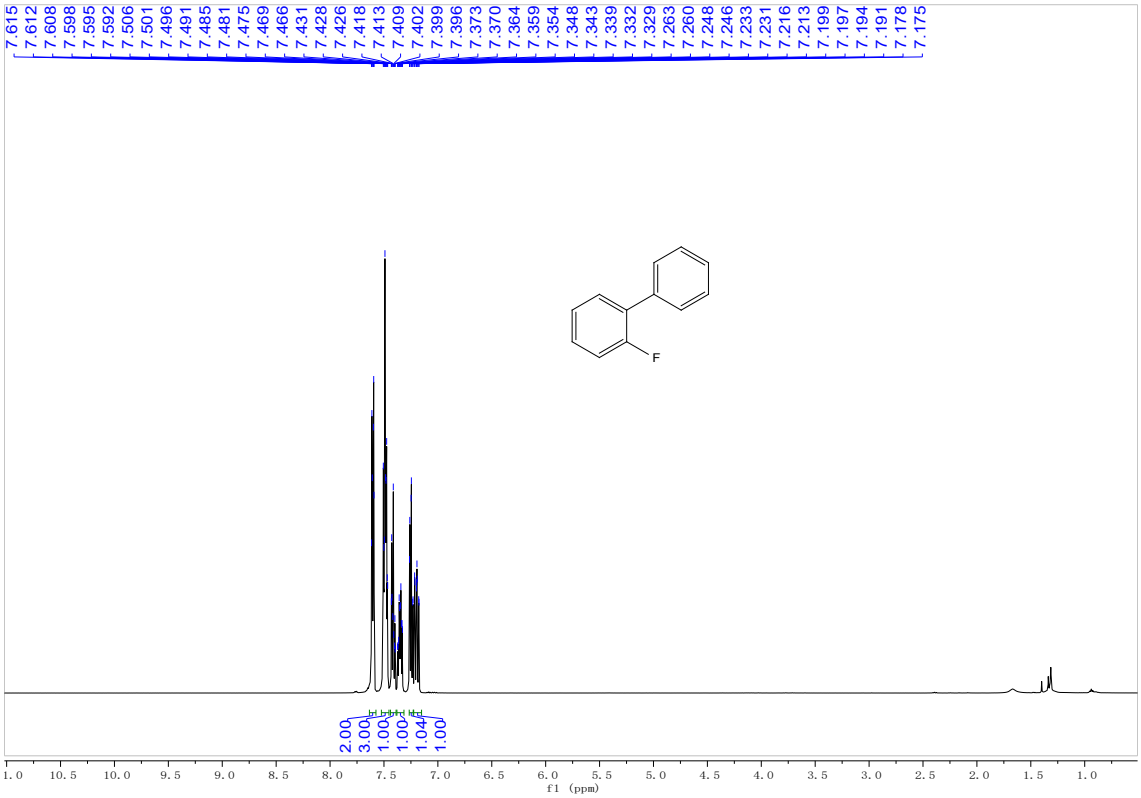
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2j**



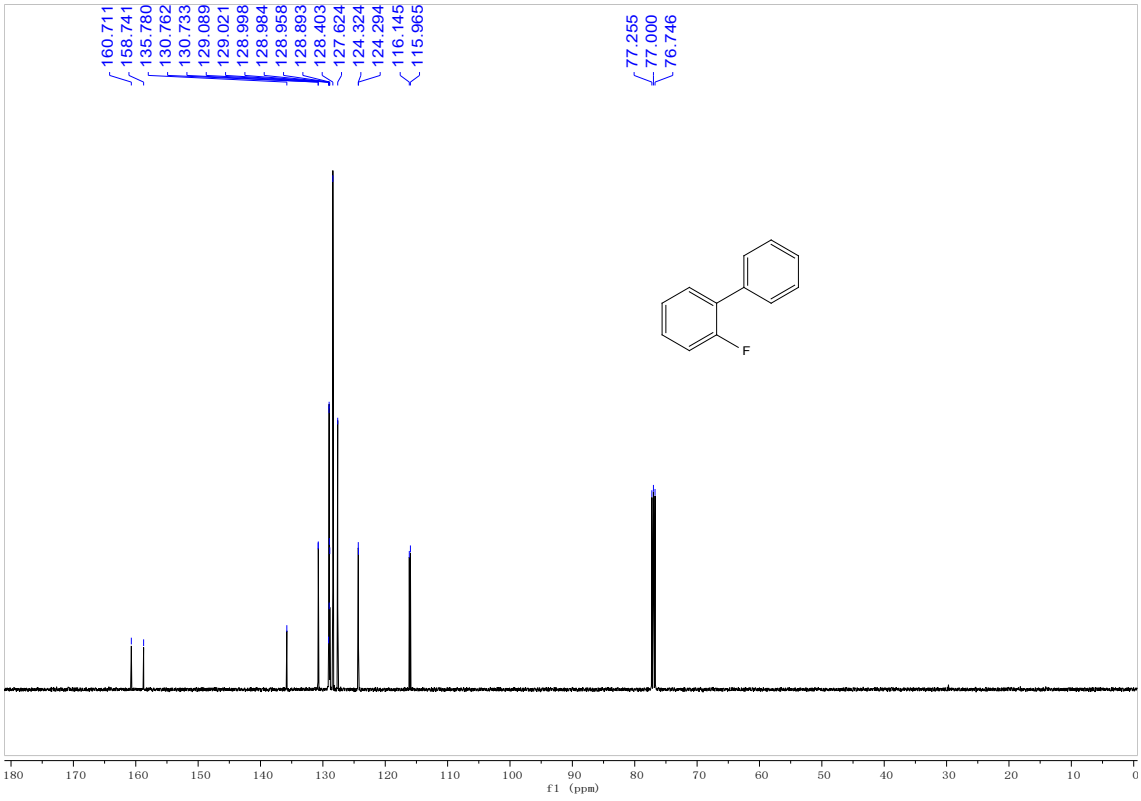
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2j**



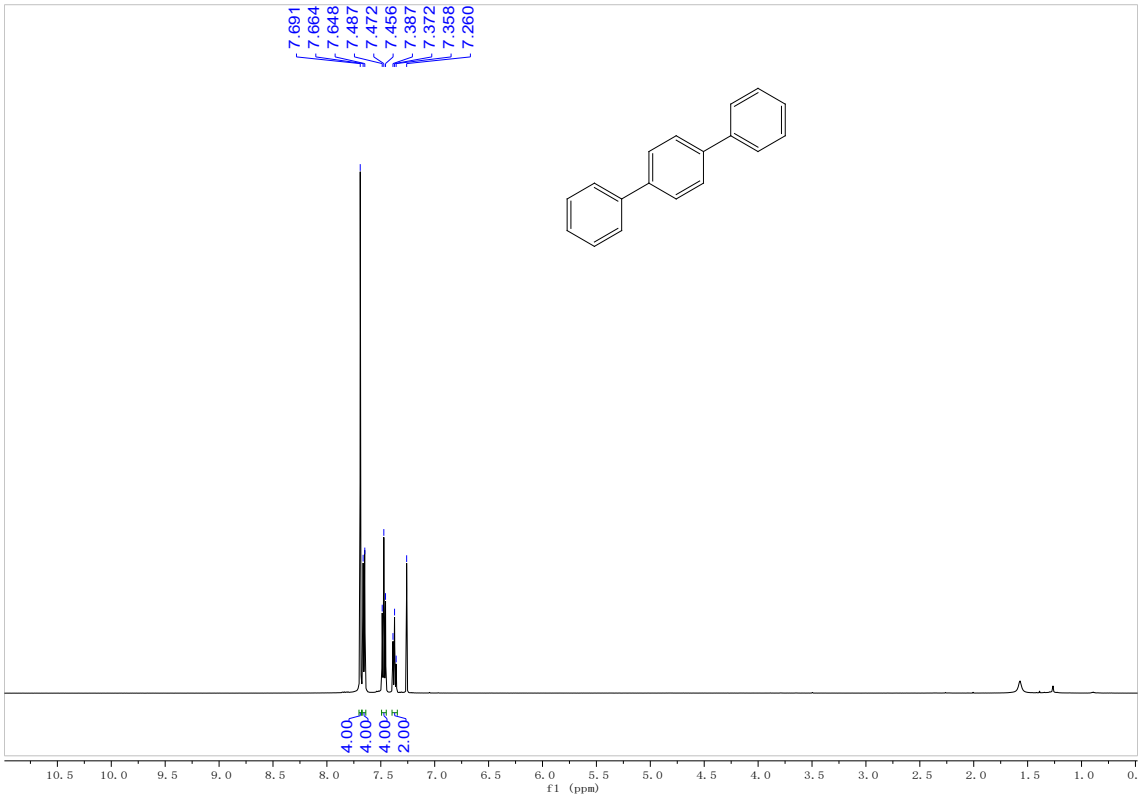
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2k**



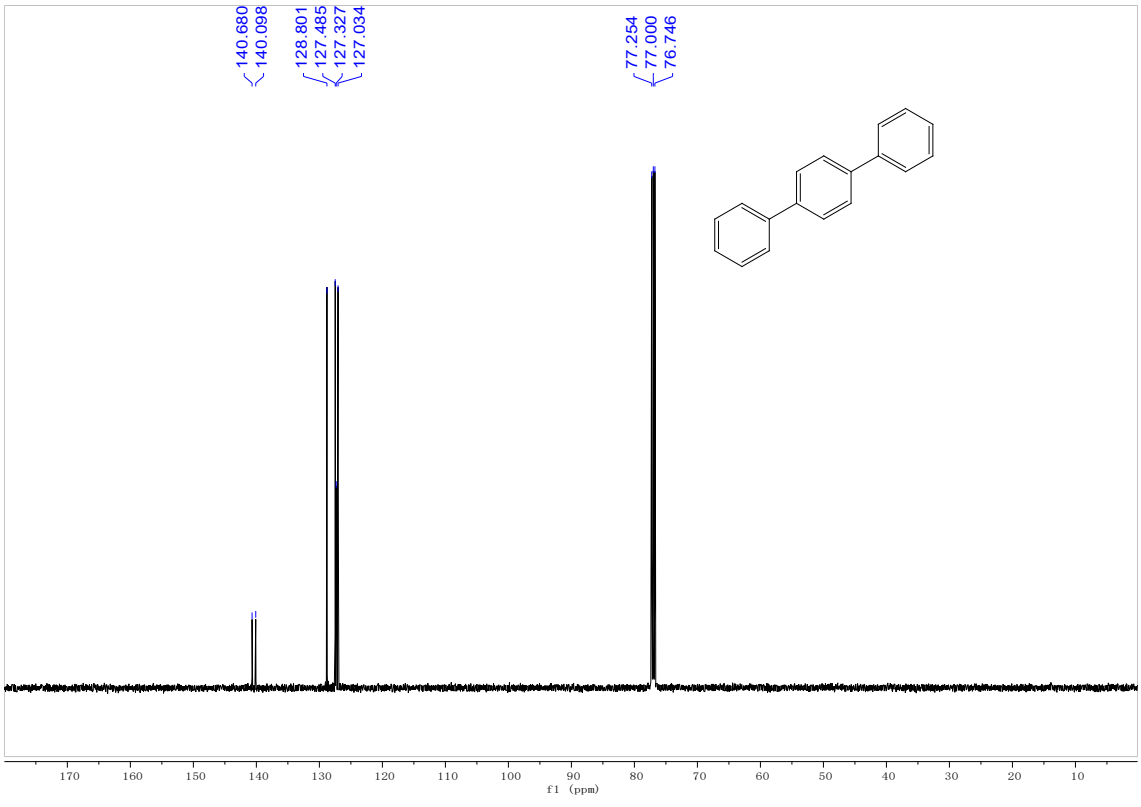
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2k**



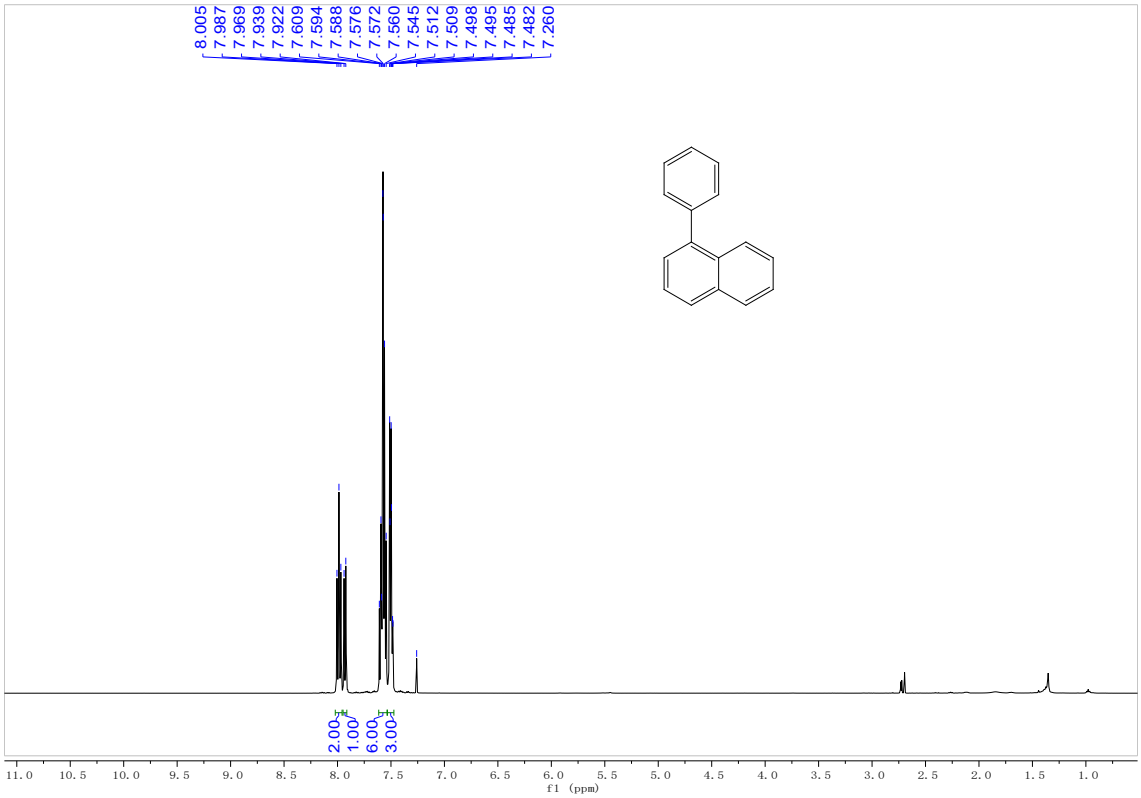
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2l**



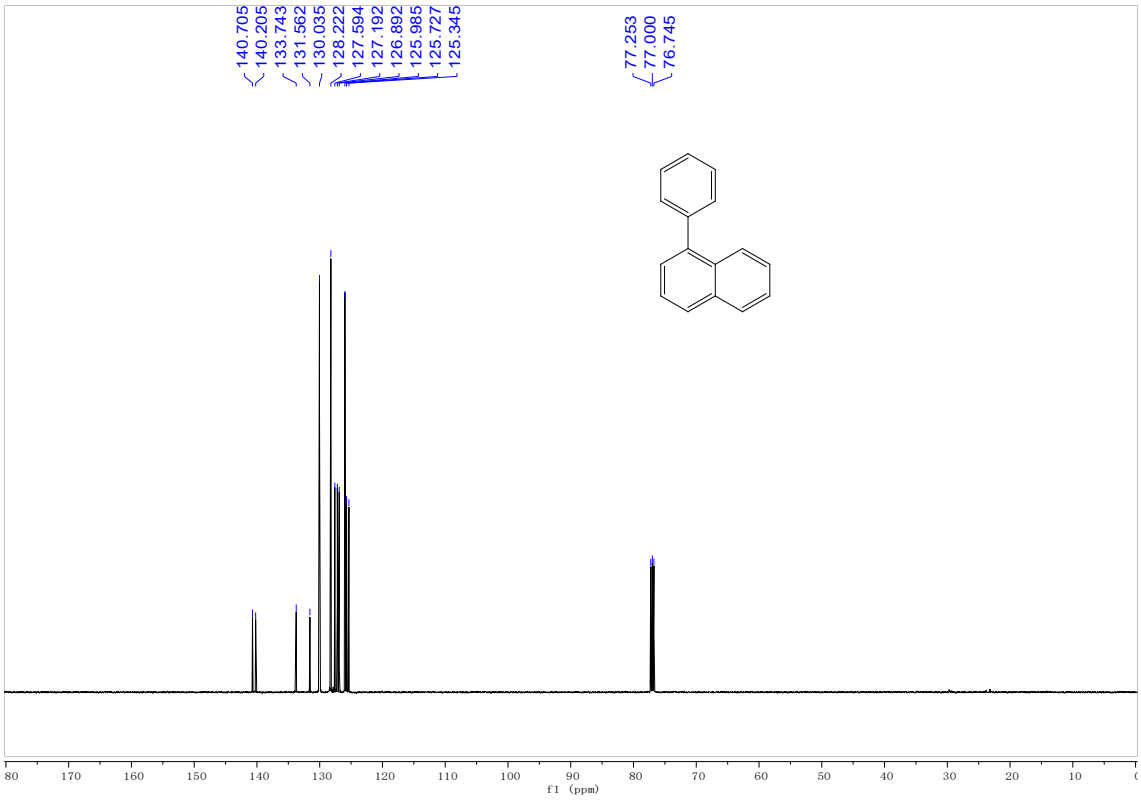
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2l**



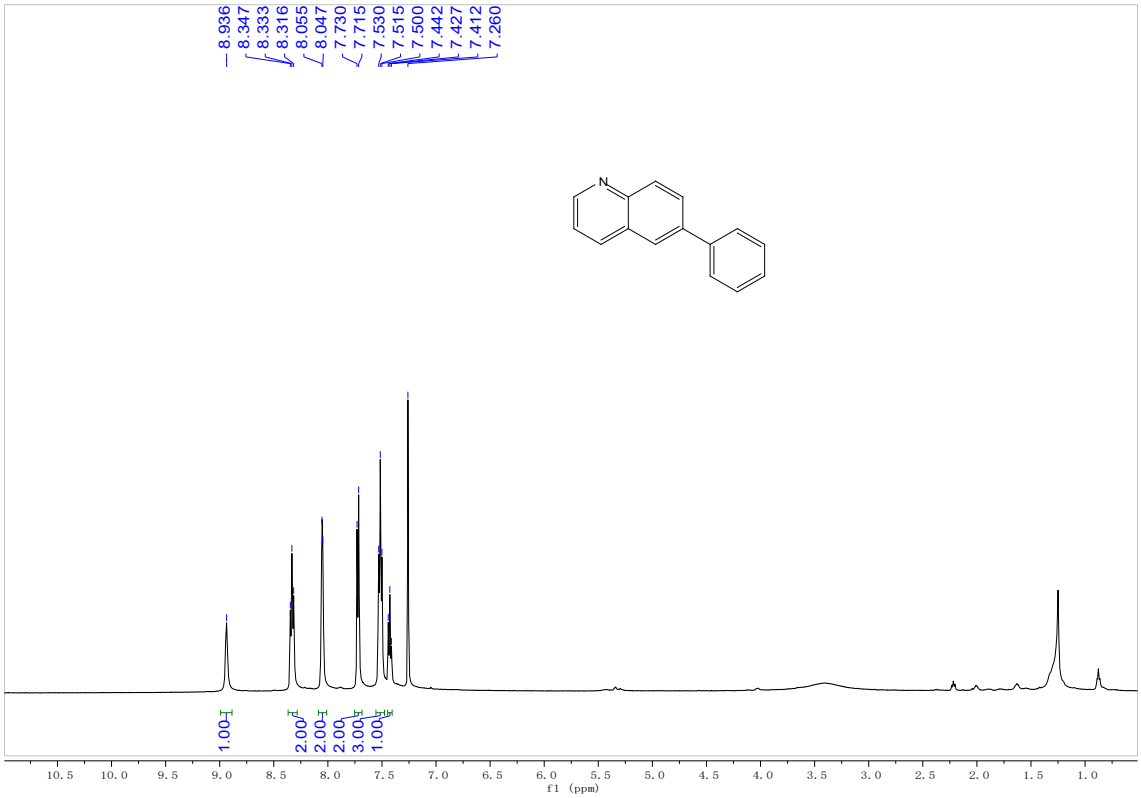
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2m**



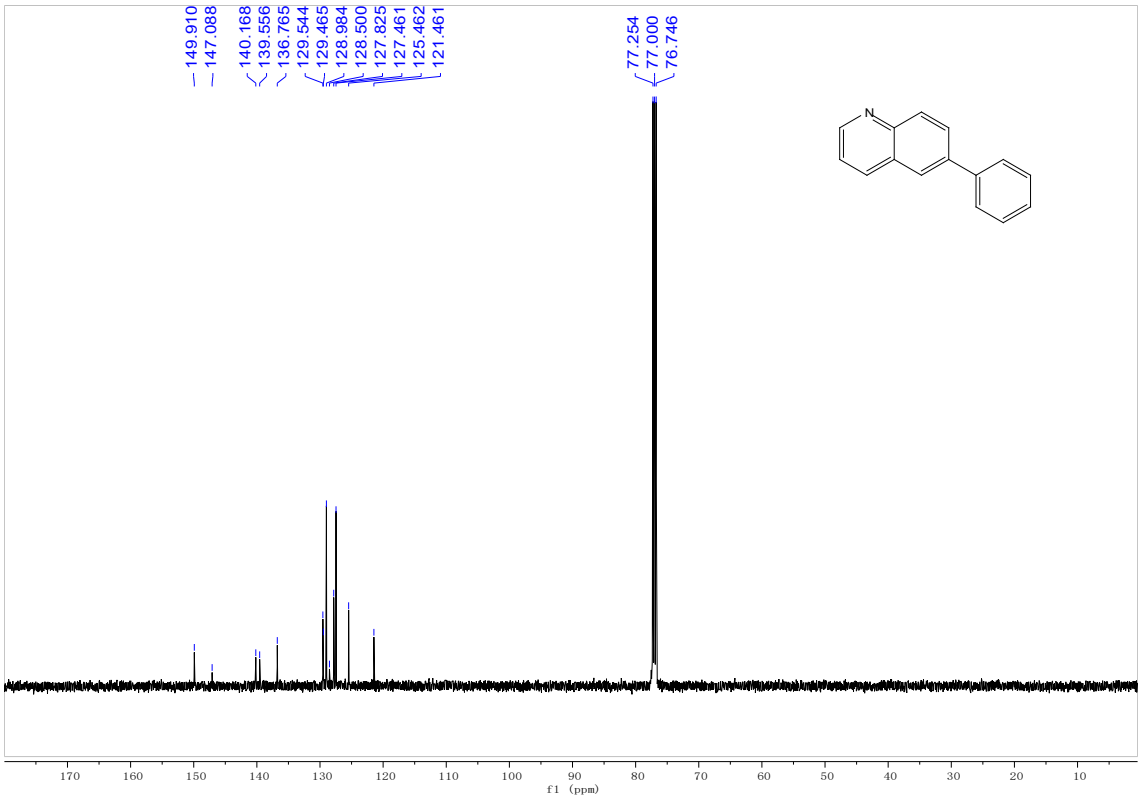
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2m**



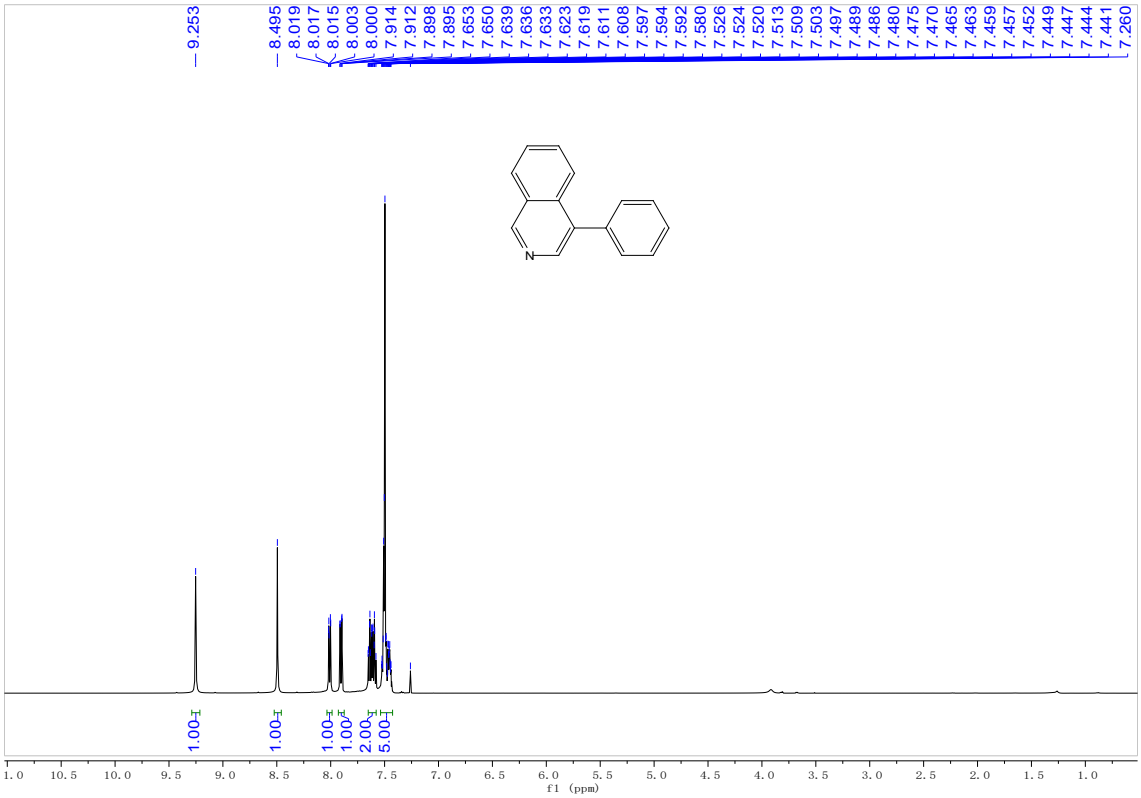
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2n**



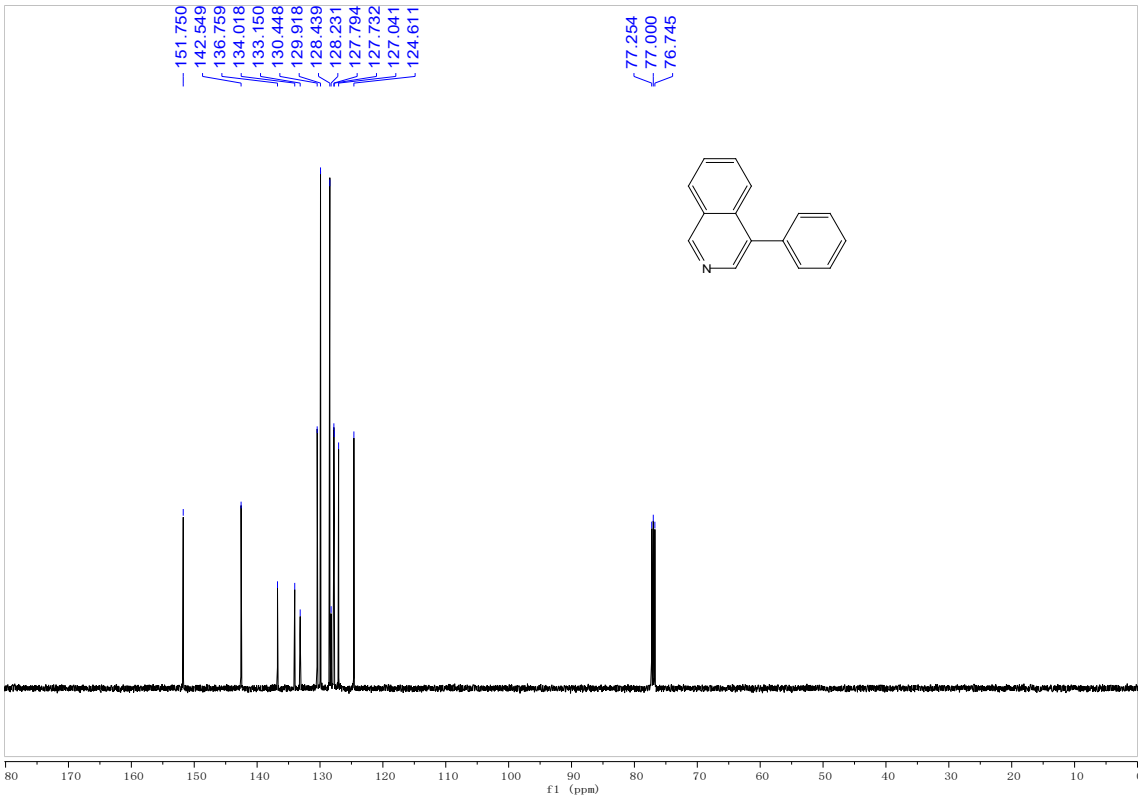
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2n**



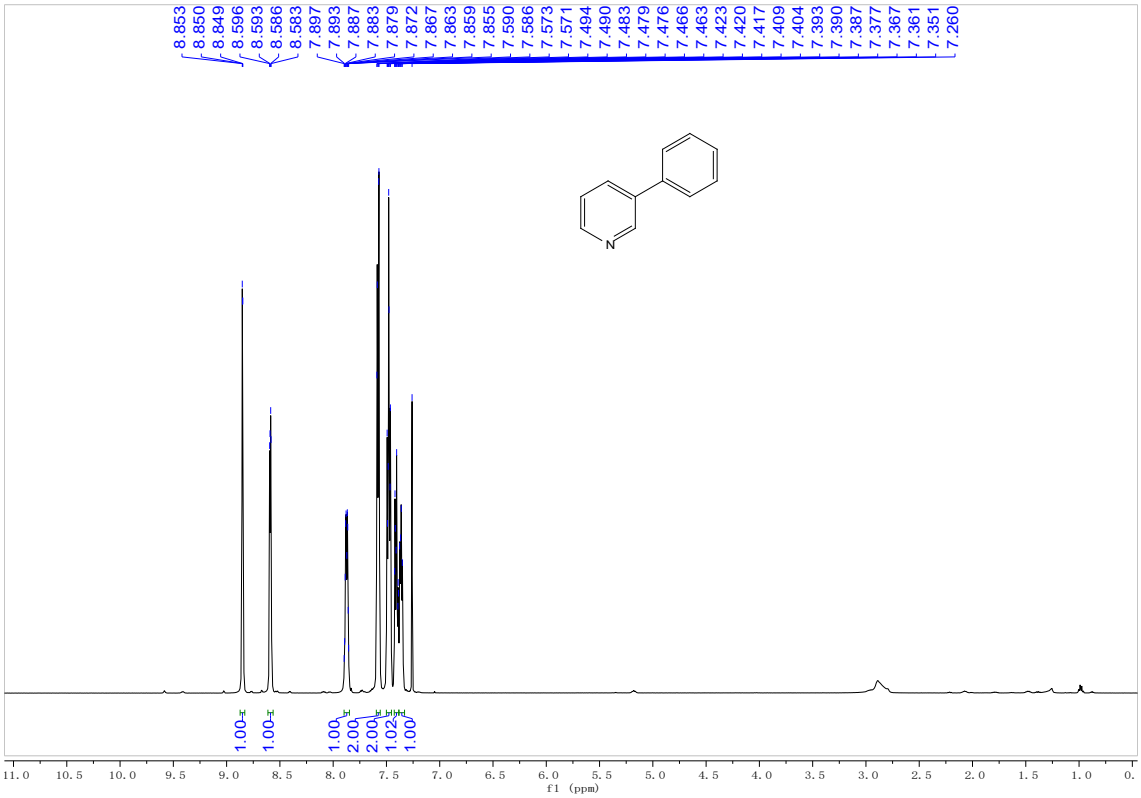
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2o**



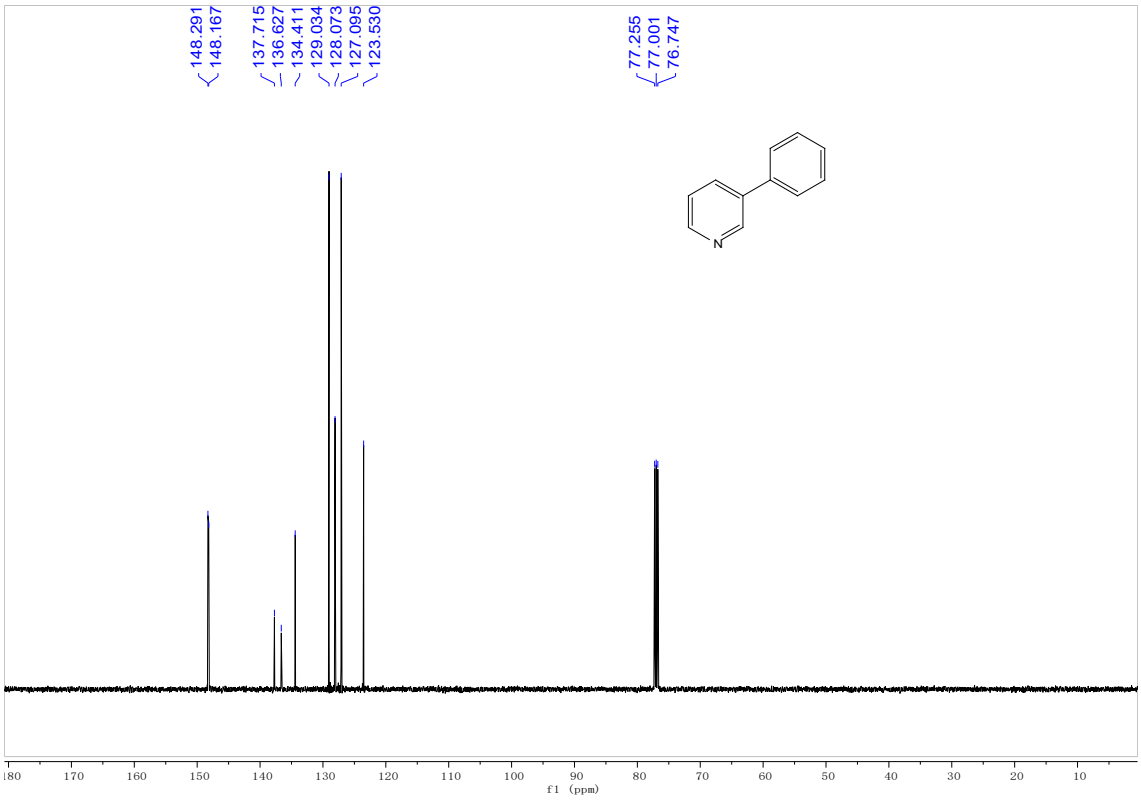
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2o**



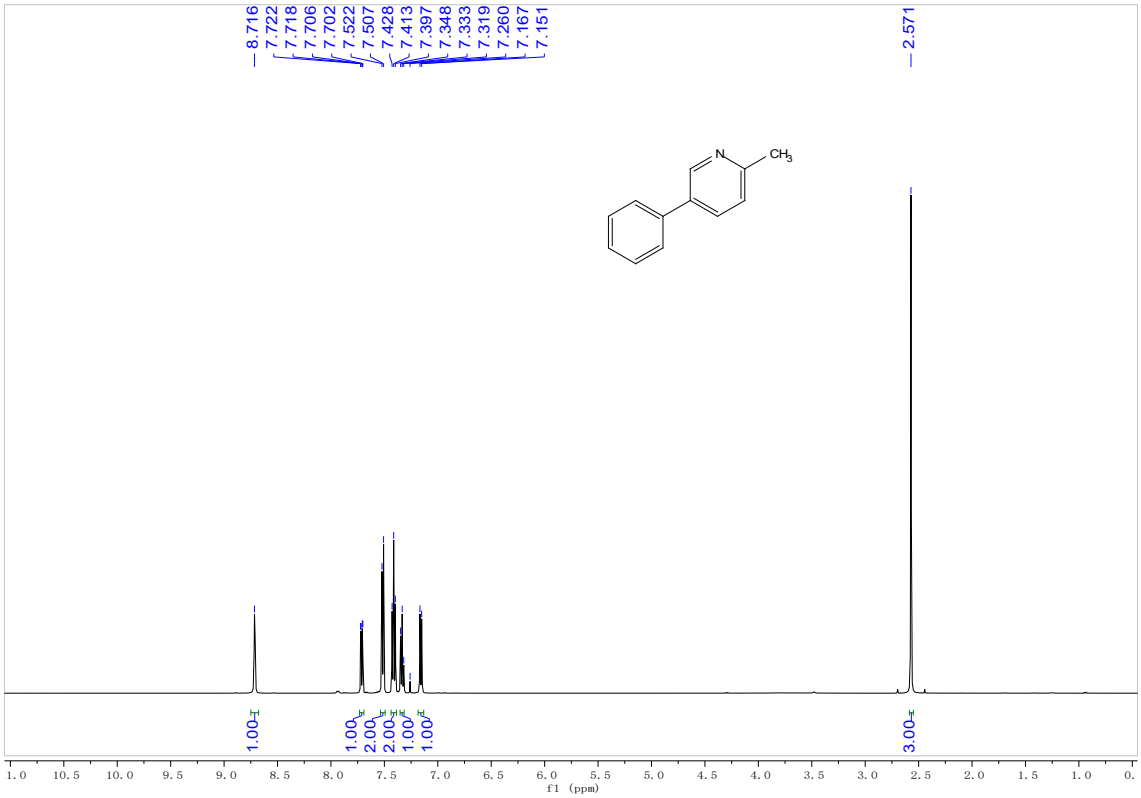
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2p**



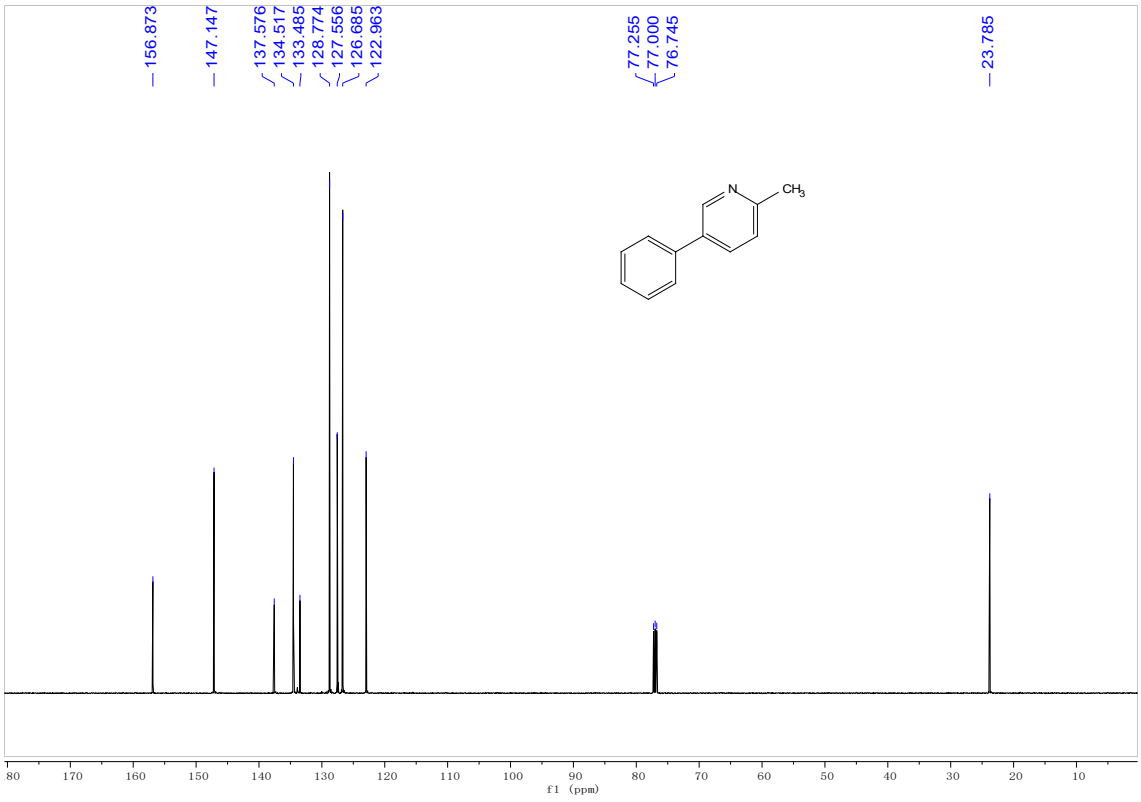
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2p**



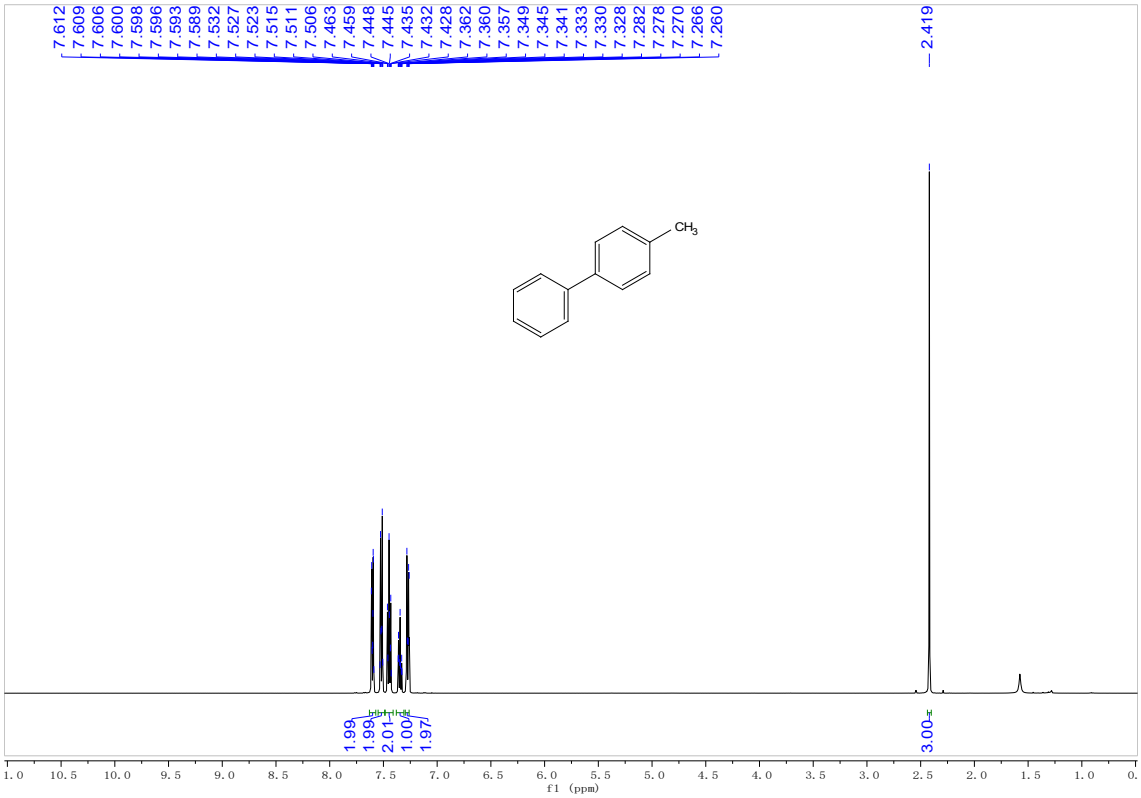
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2q**



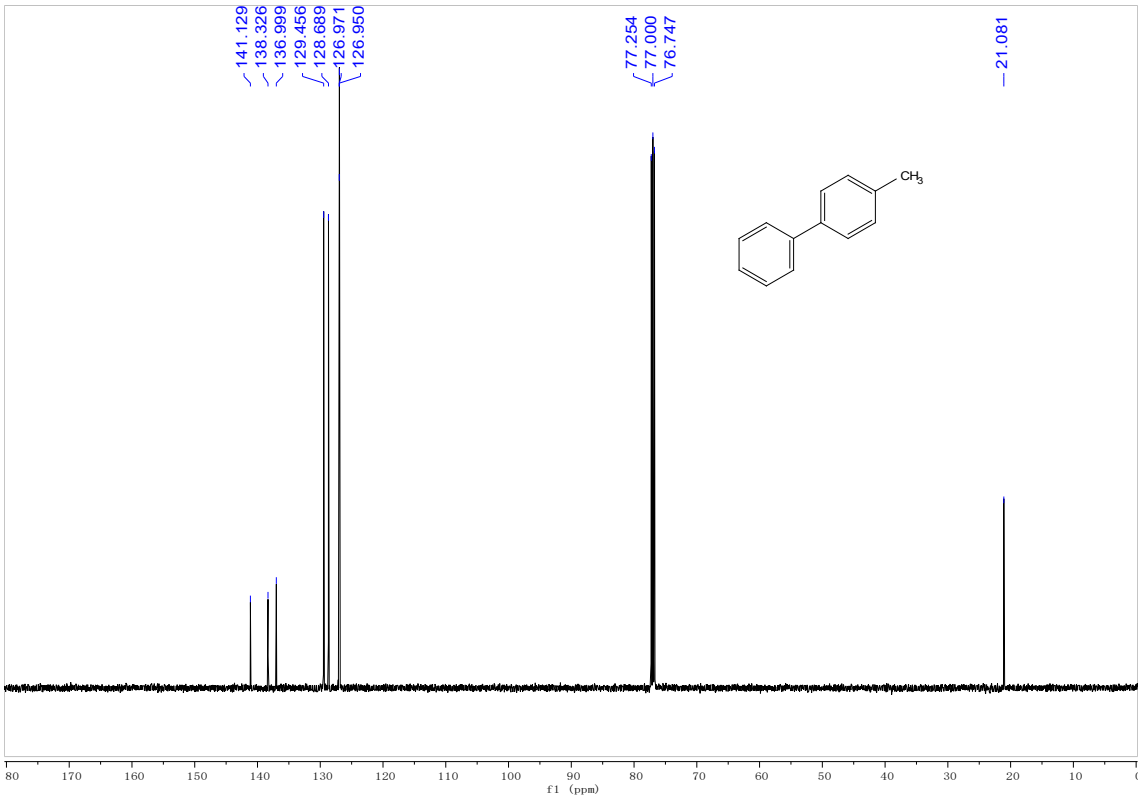
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2q**



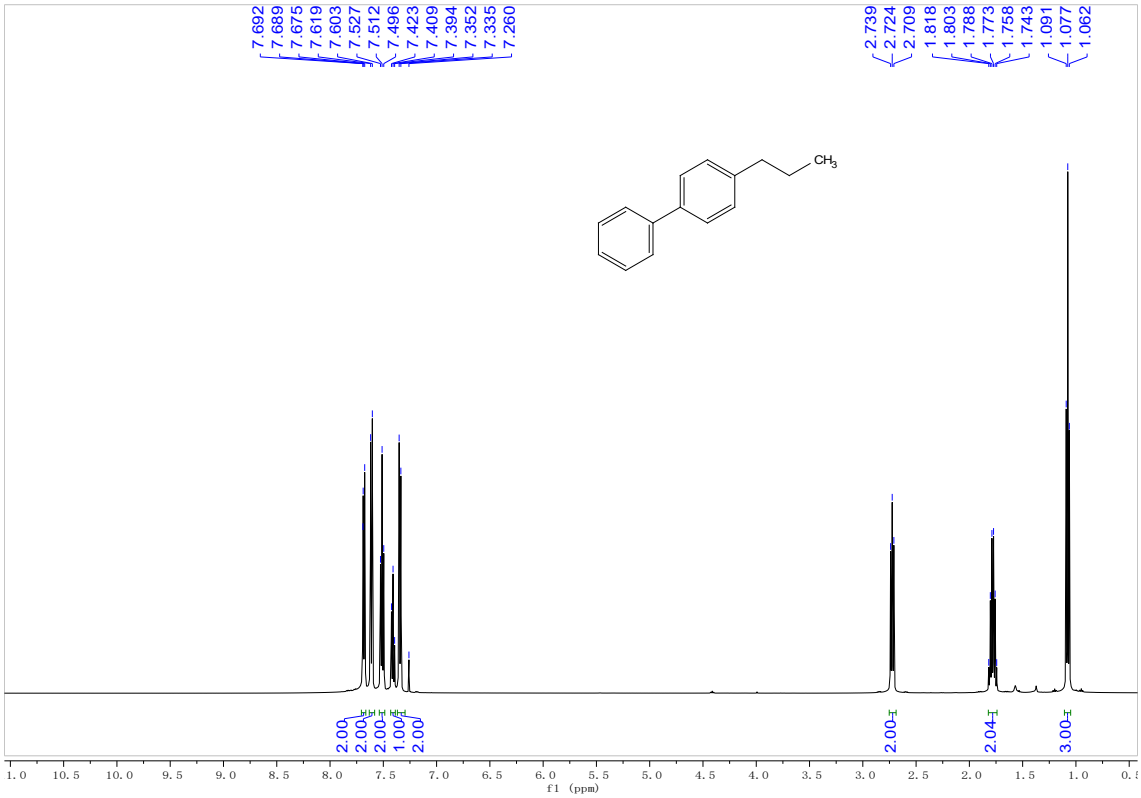
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2r**



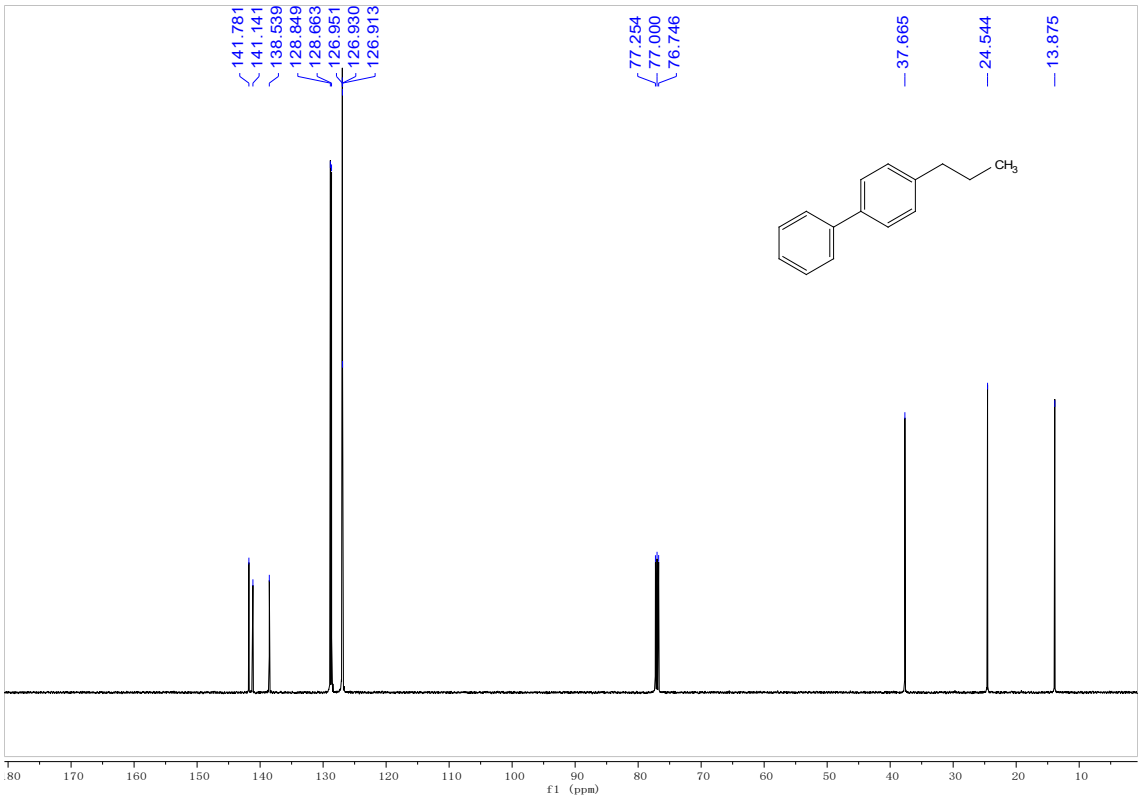
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2r**



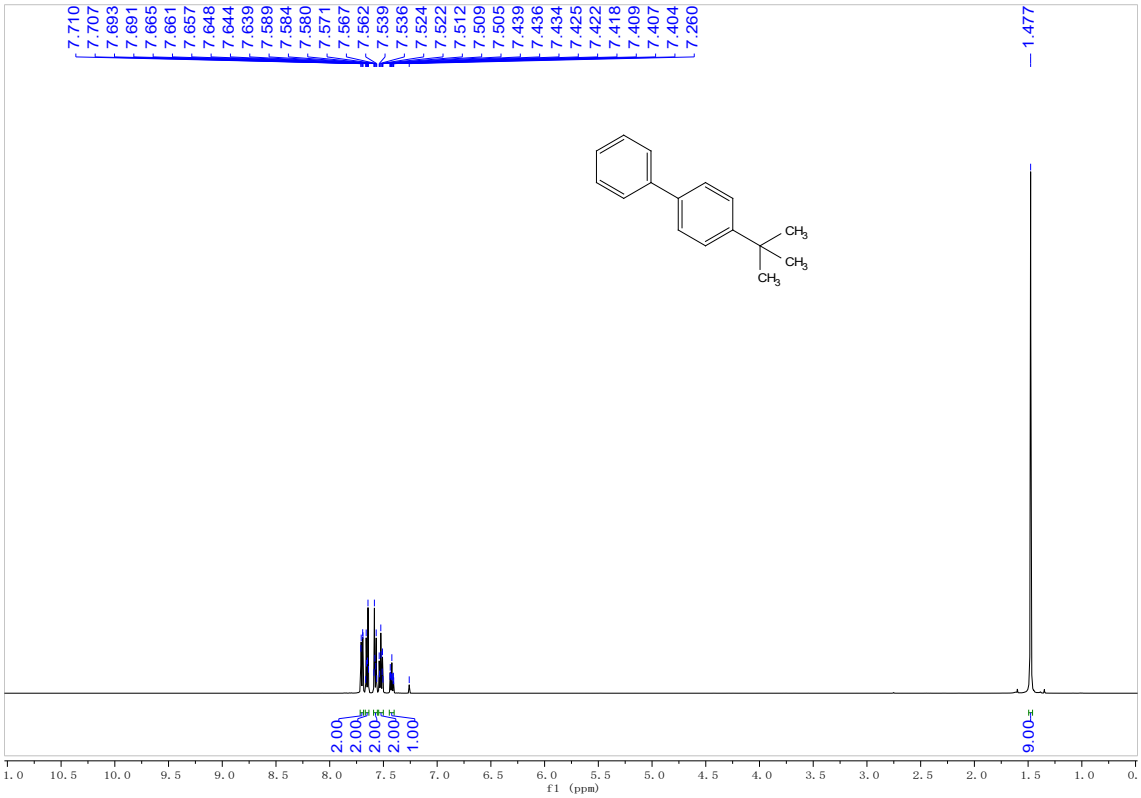
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2s**



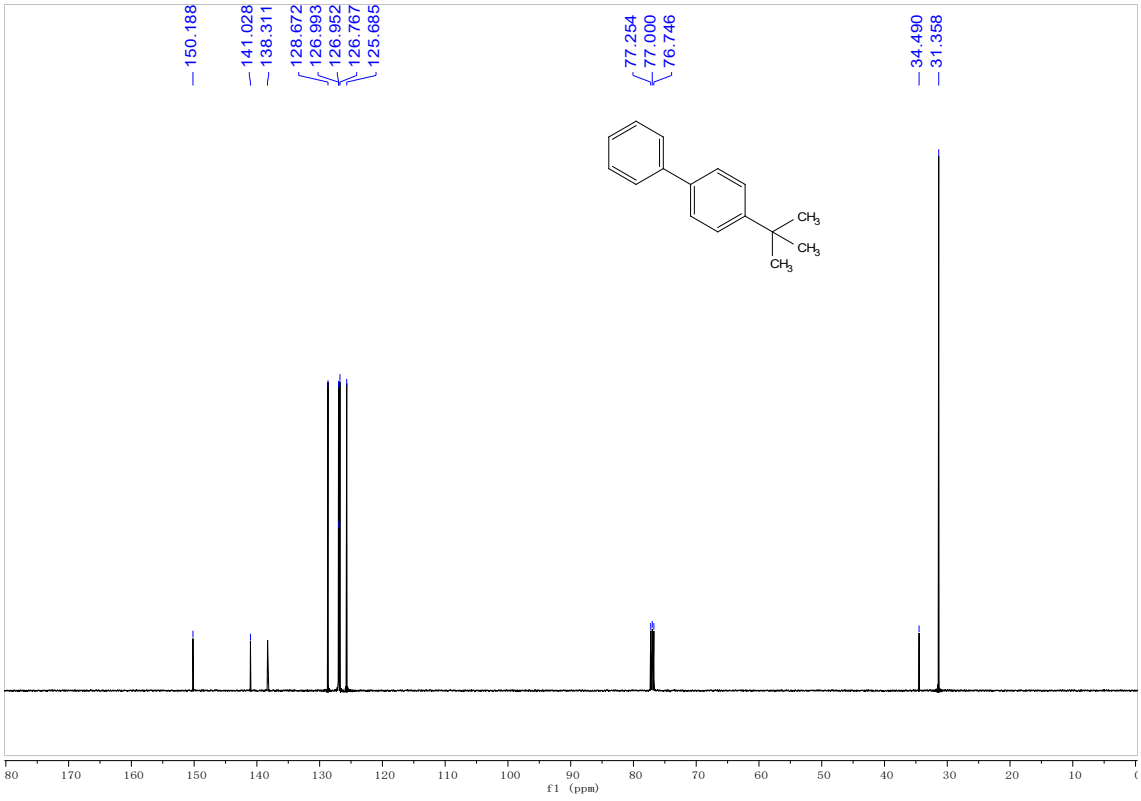
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2s**



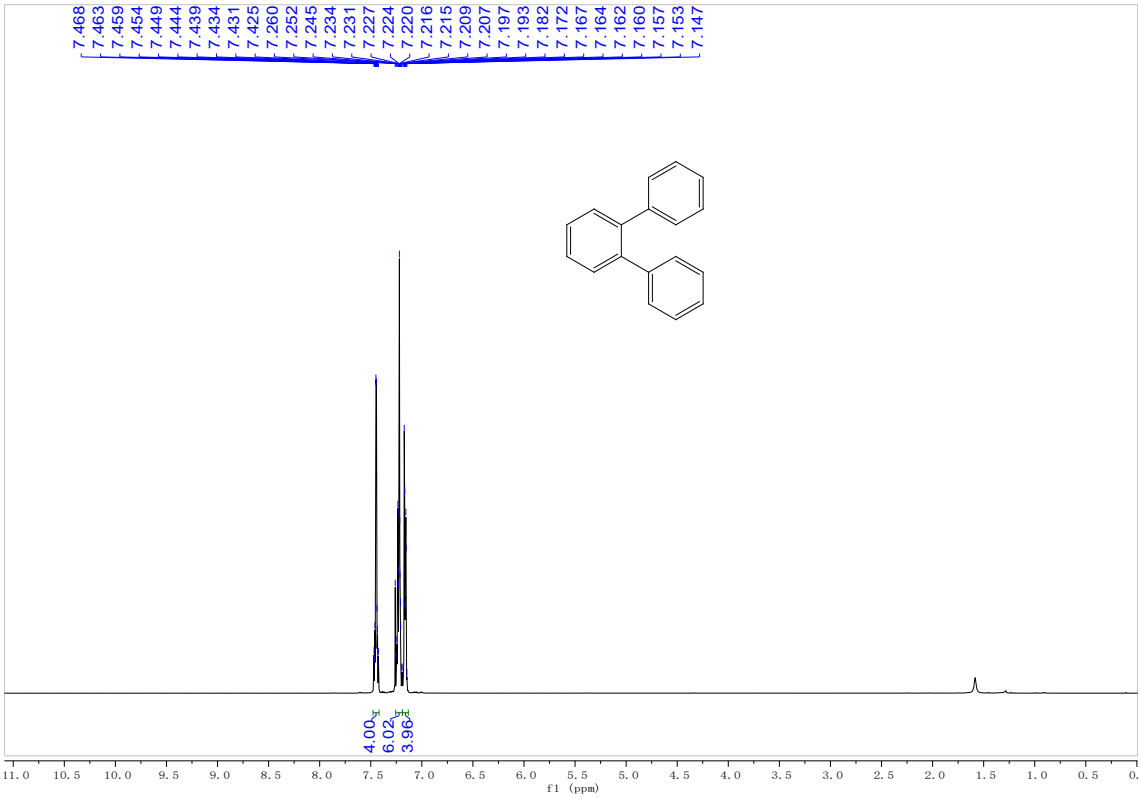
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2t**



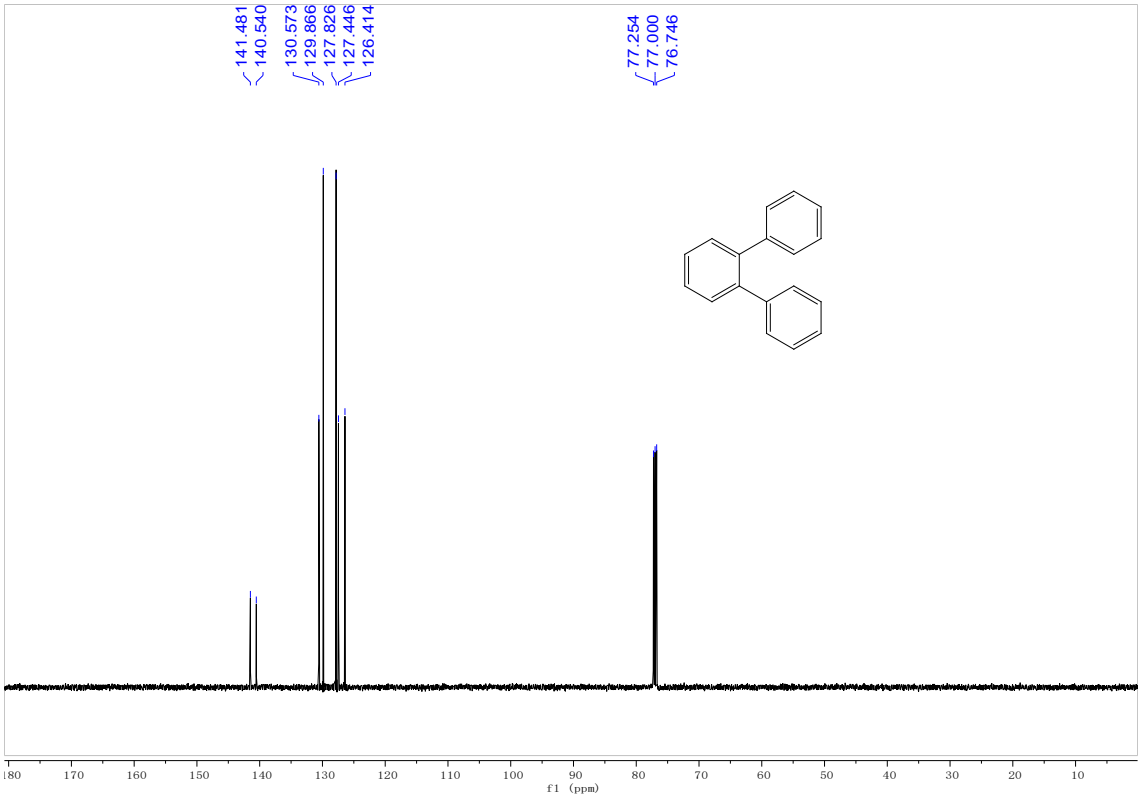
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2t**



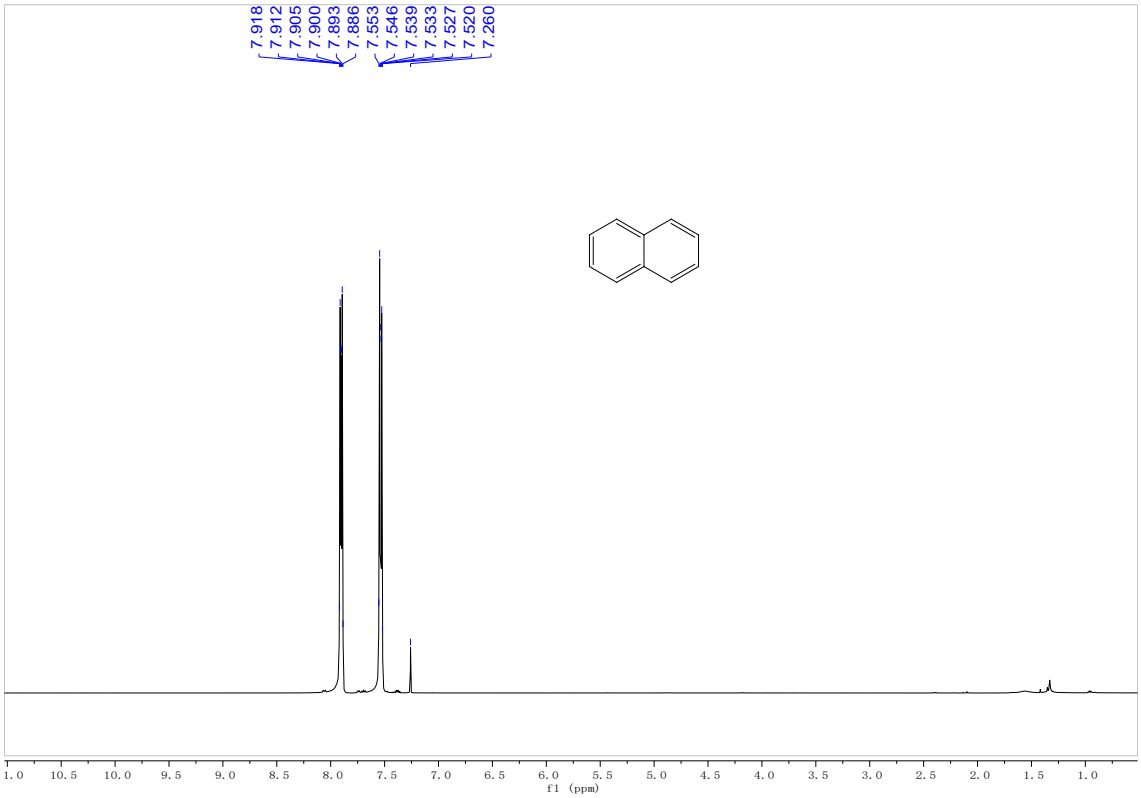
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2u**



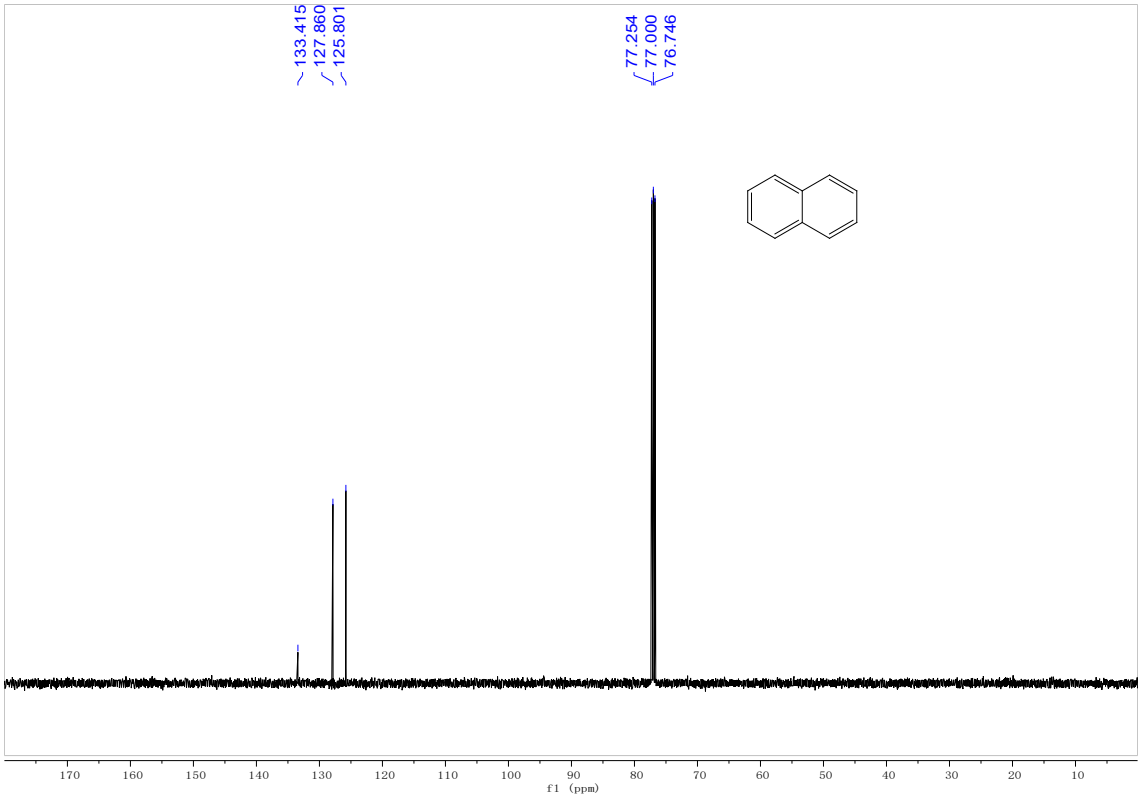
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2u**



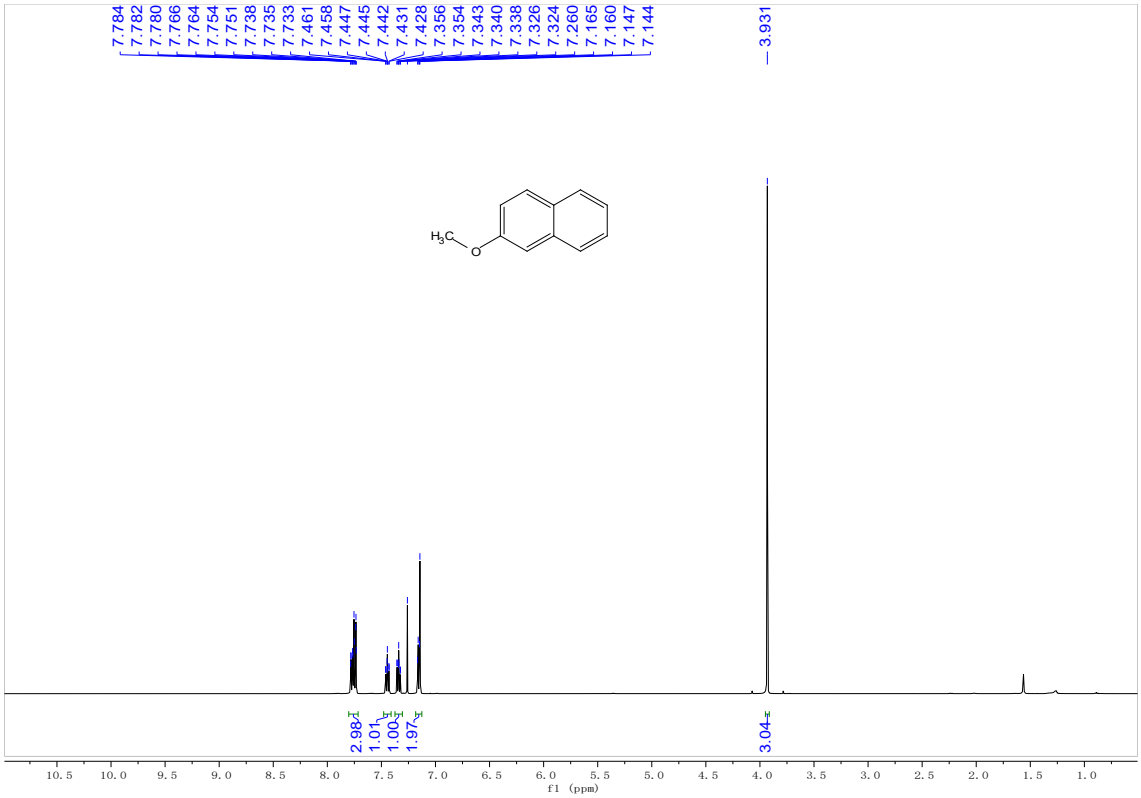
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2v**



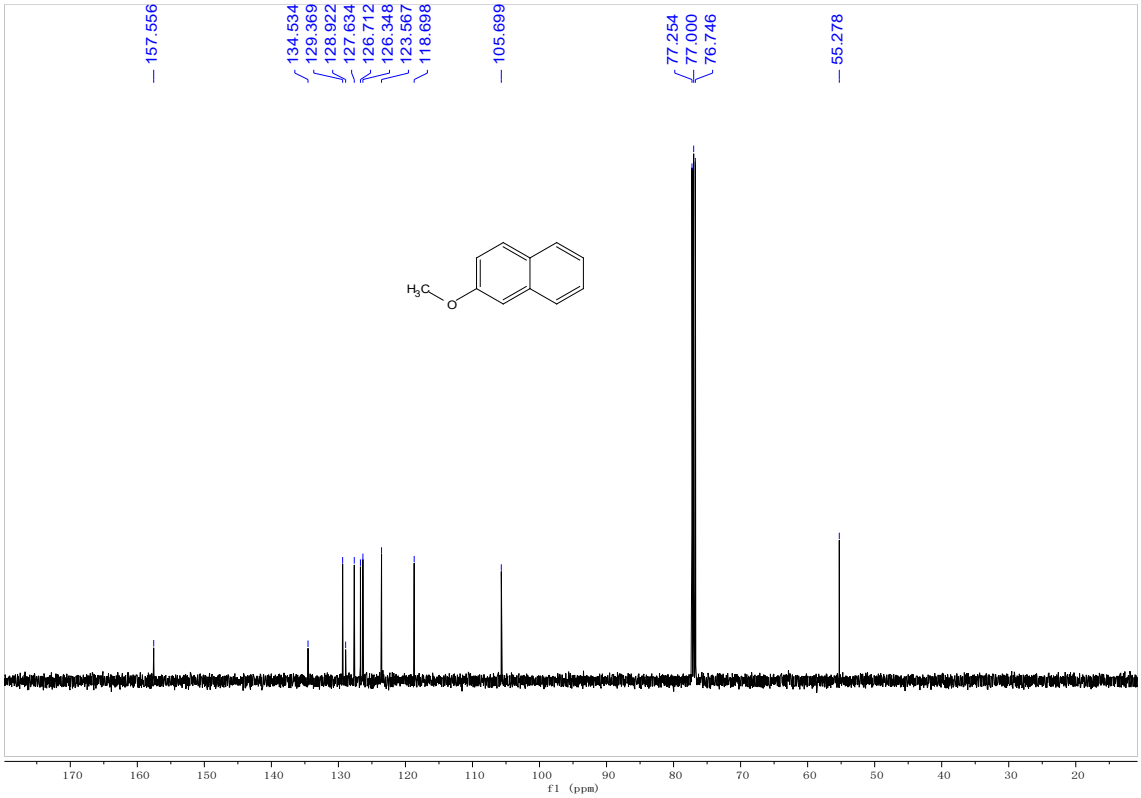
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2v**



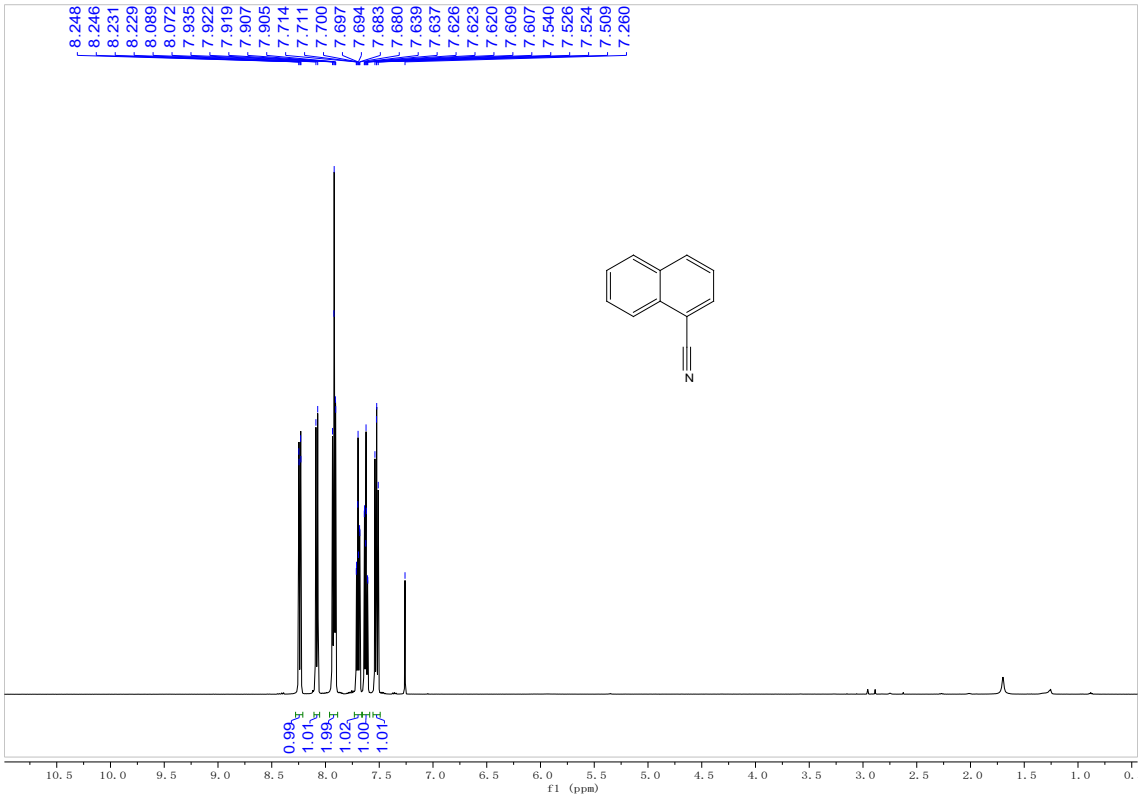
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2w**



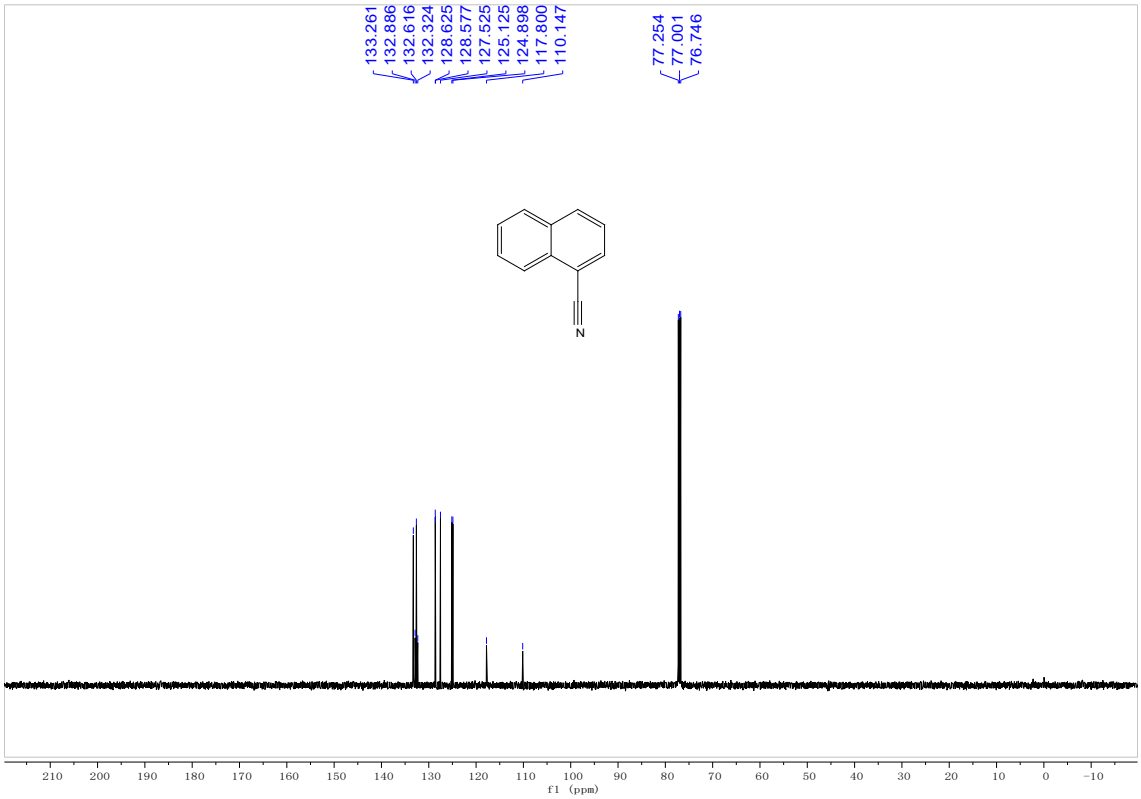
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2w**



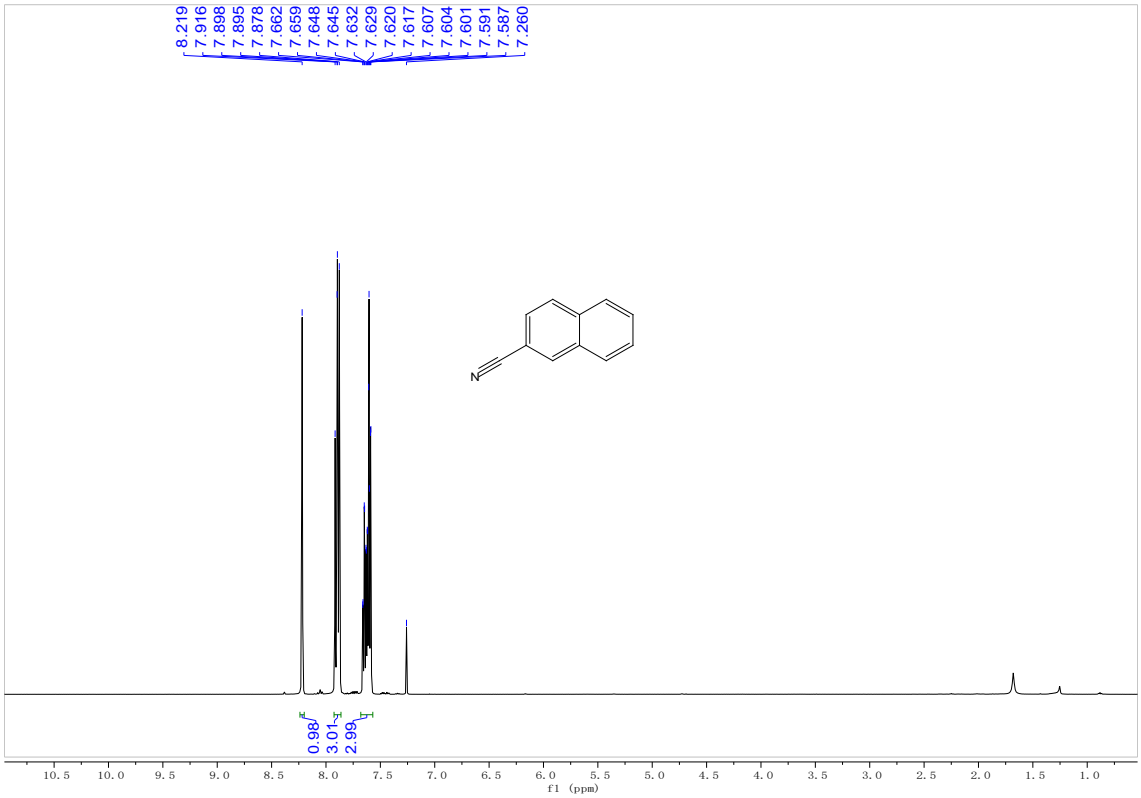
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2x**



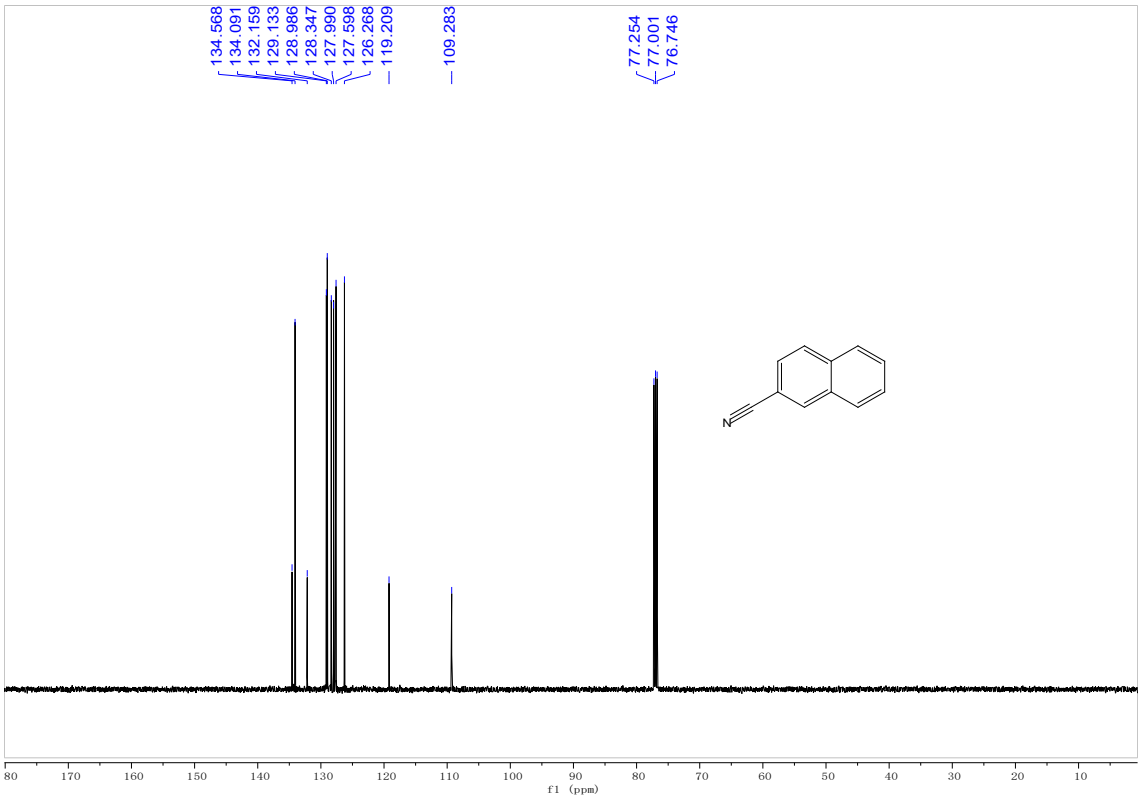
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2x**



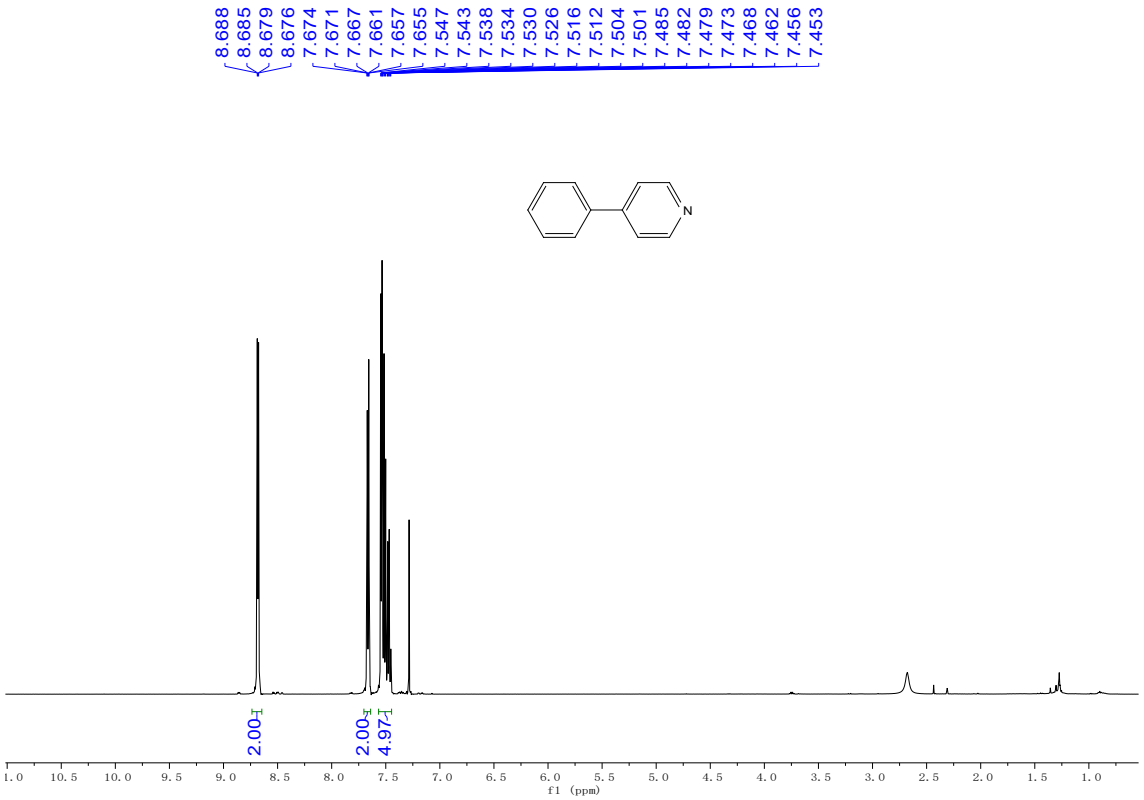
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2y**



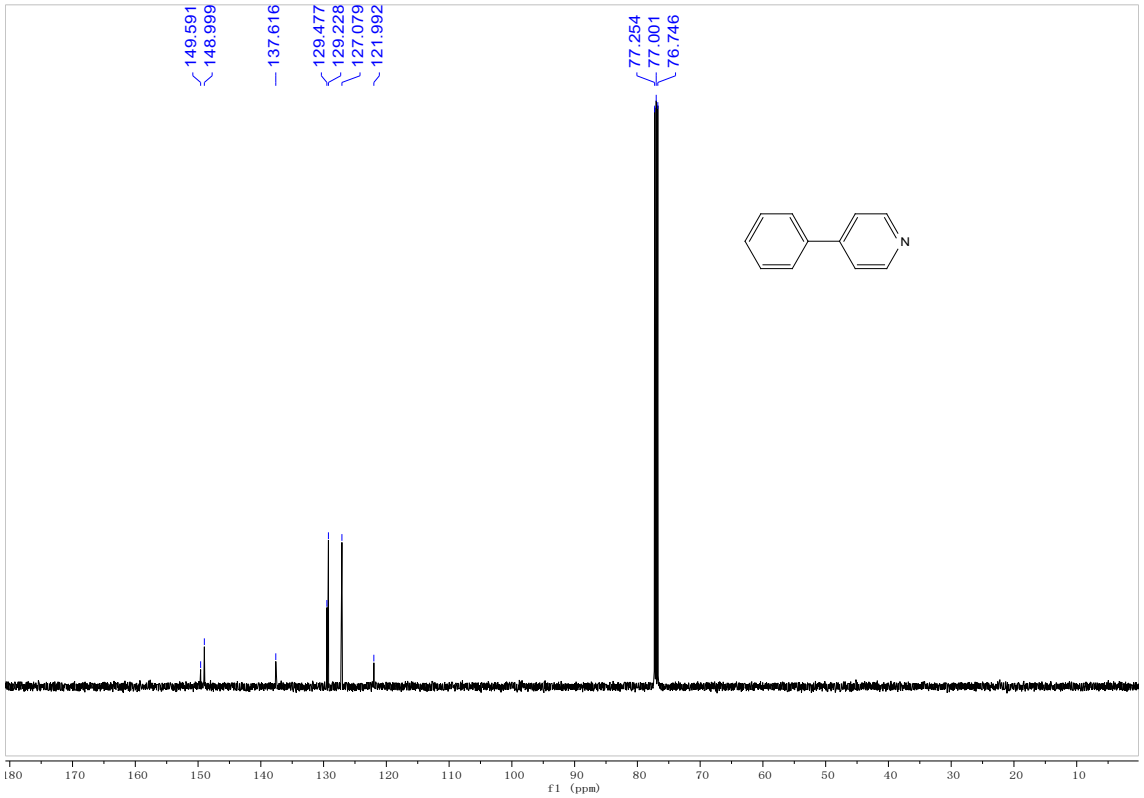
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2y**



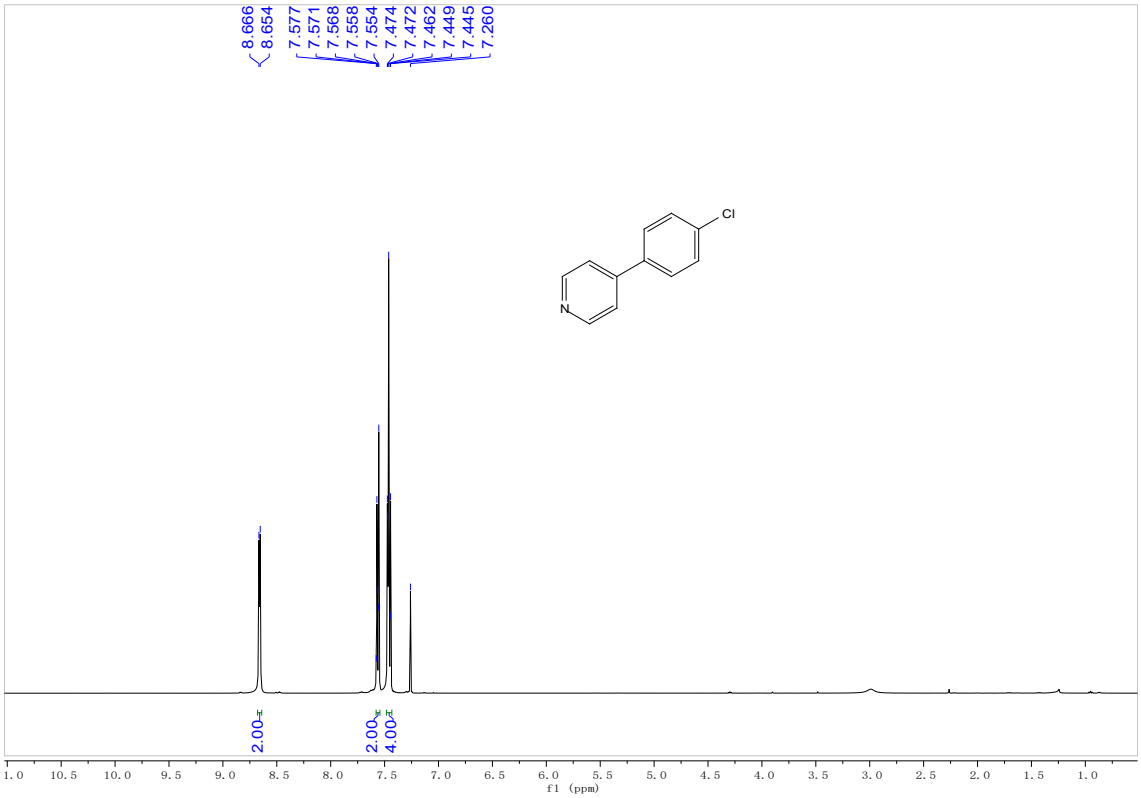
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2z**



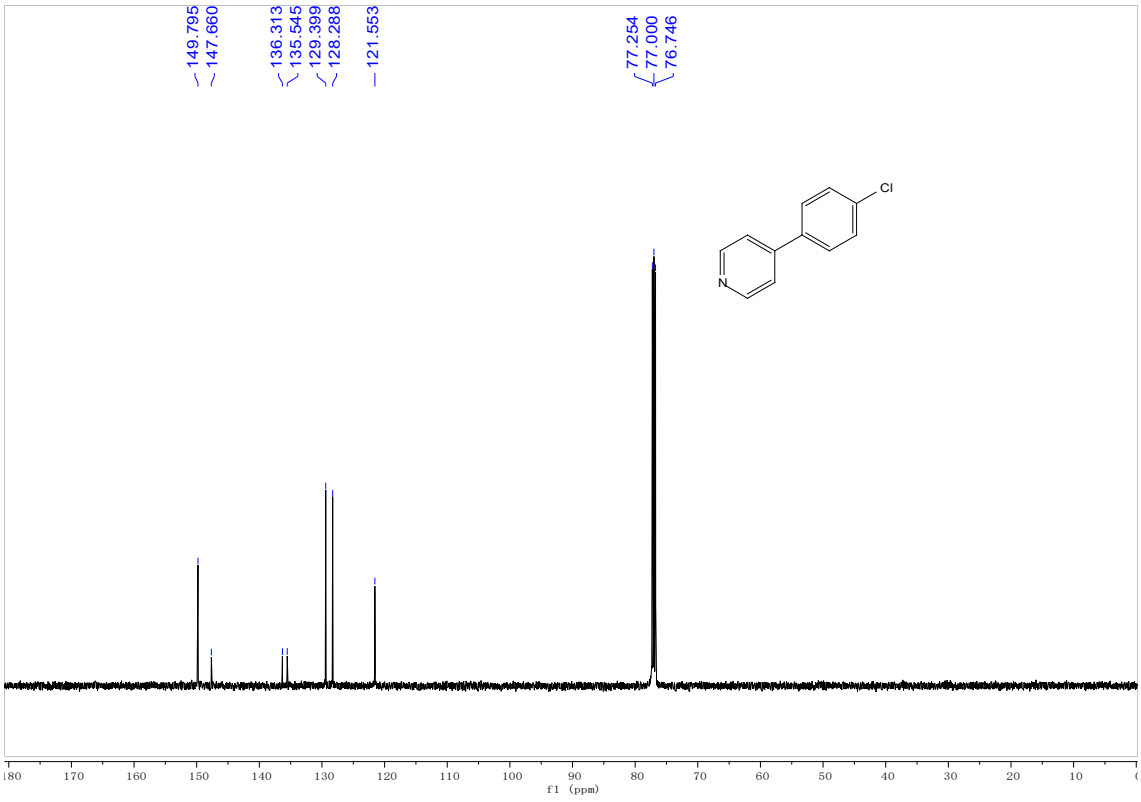
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2z**



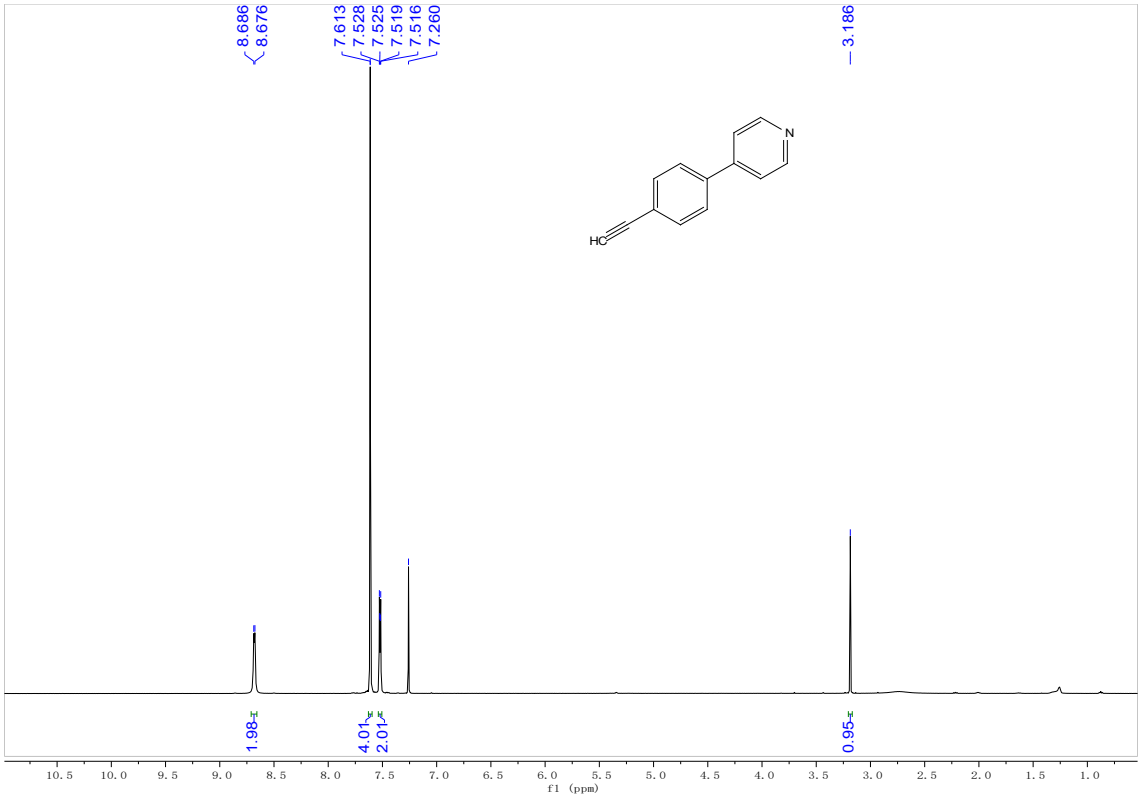
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2aa**



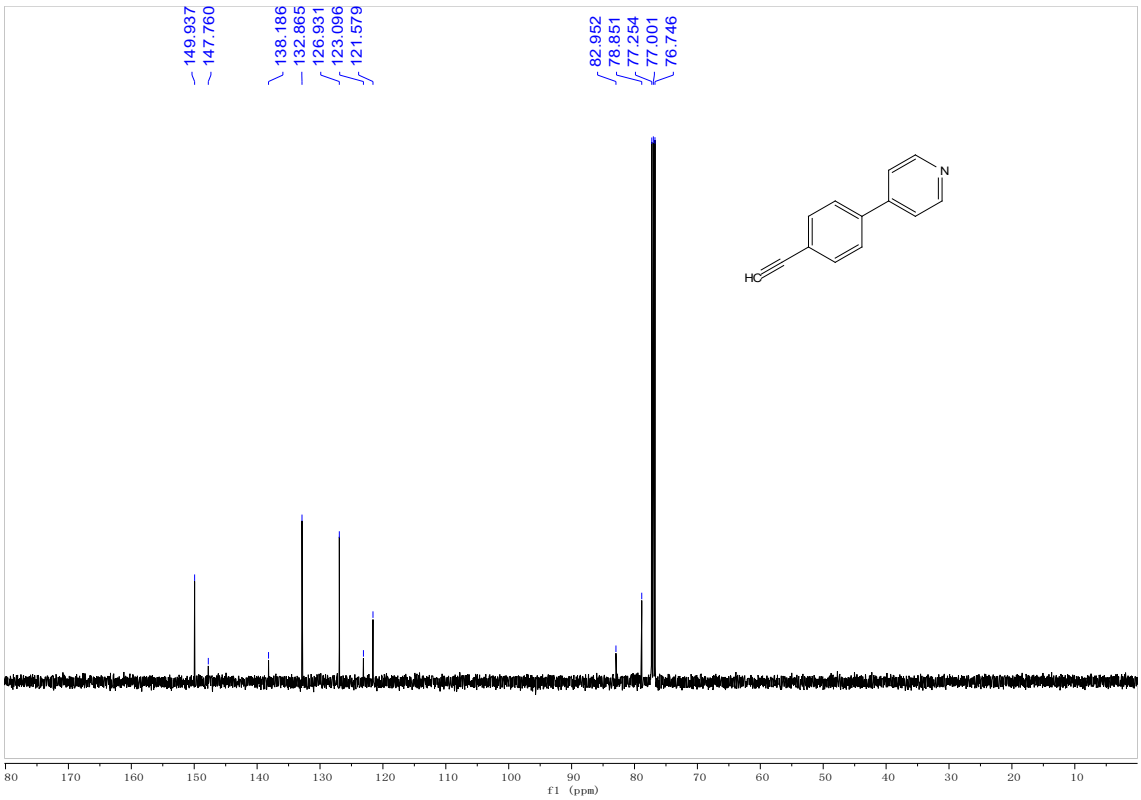
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2aa**



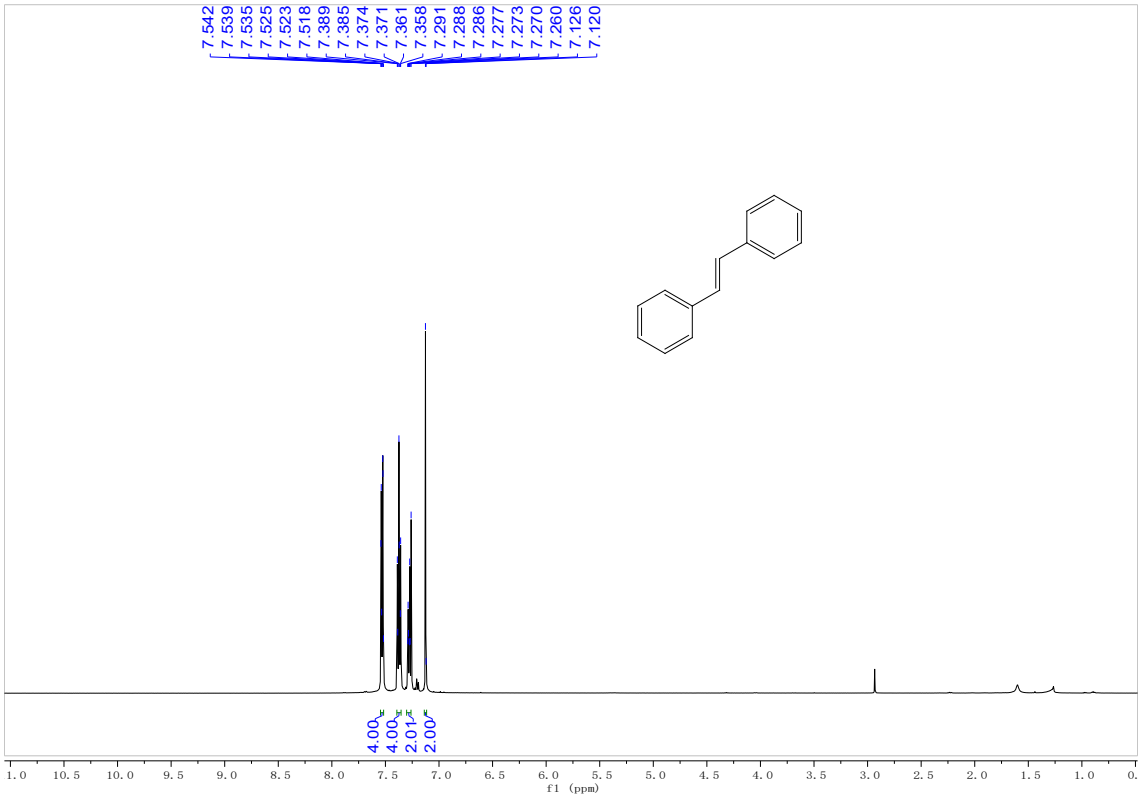
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2ab**



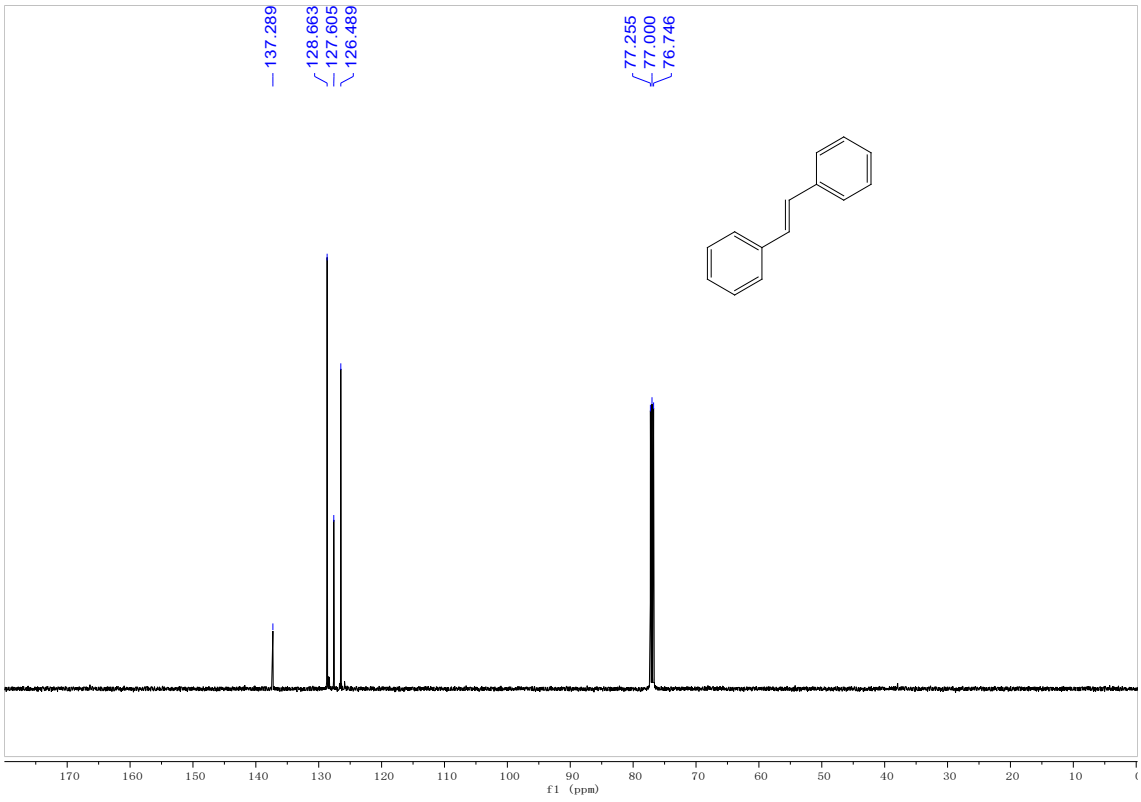
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2ab**



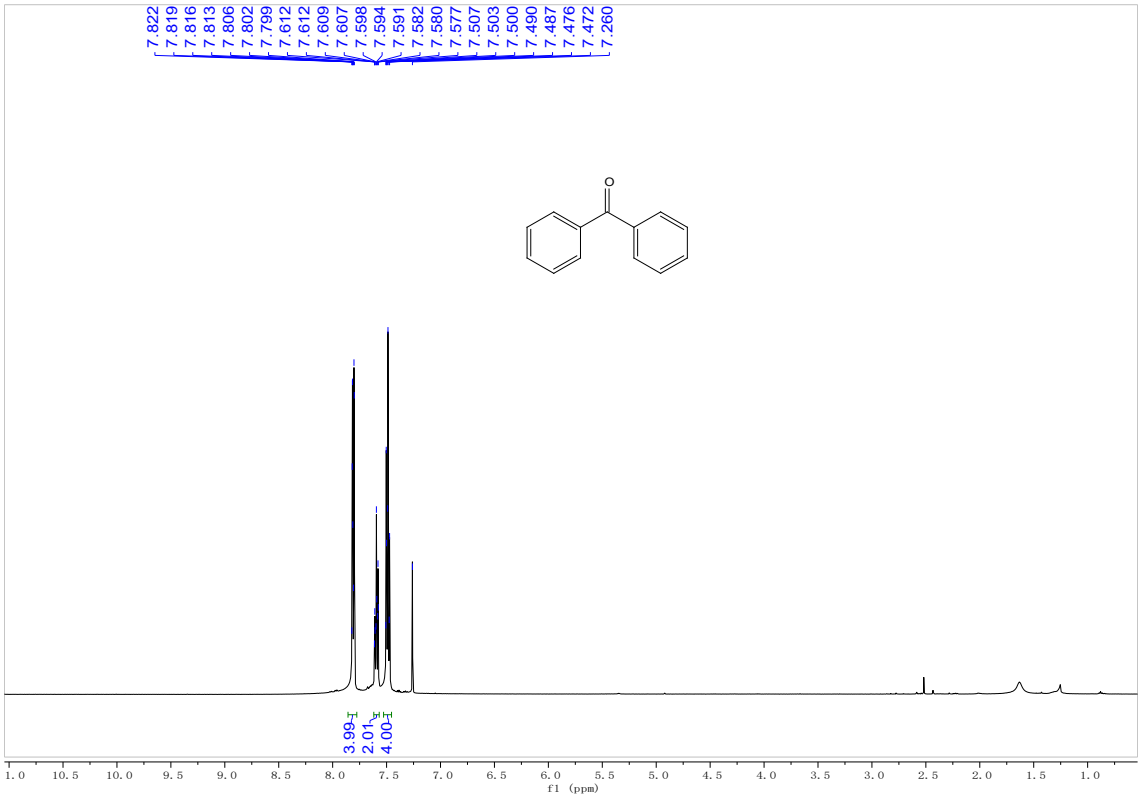
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2ac**



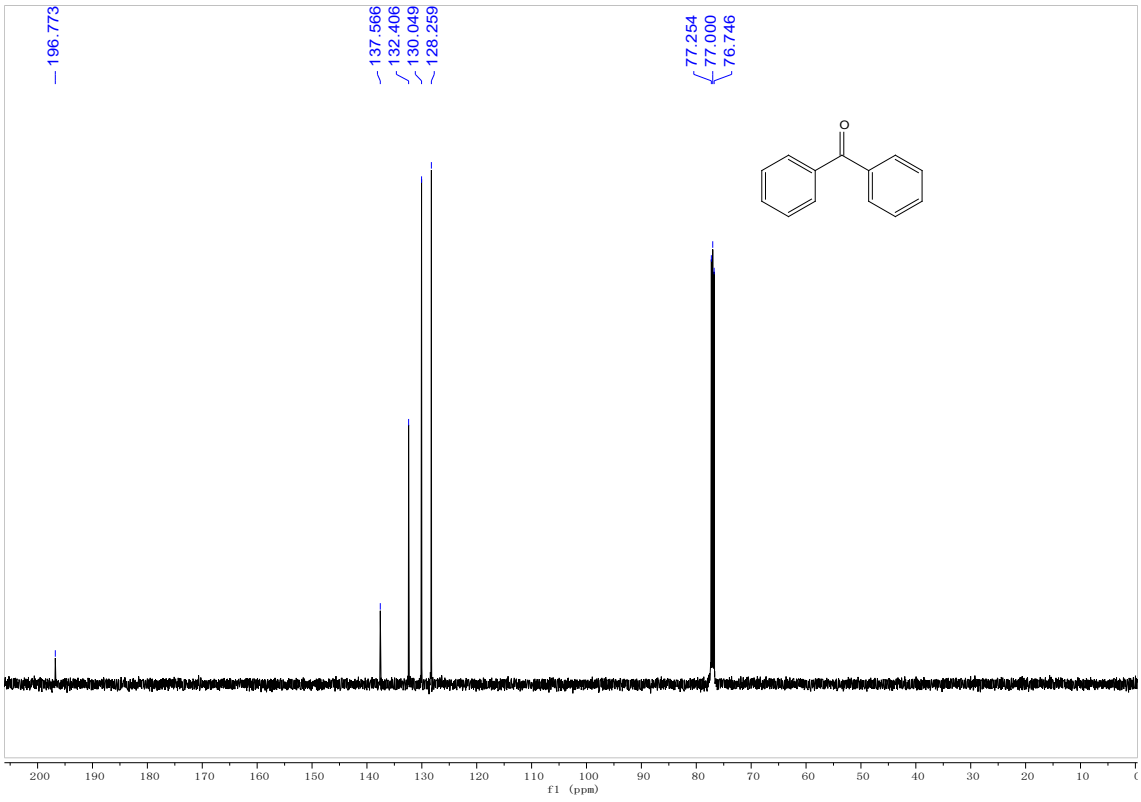
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2ac**



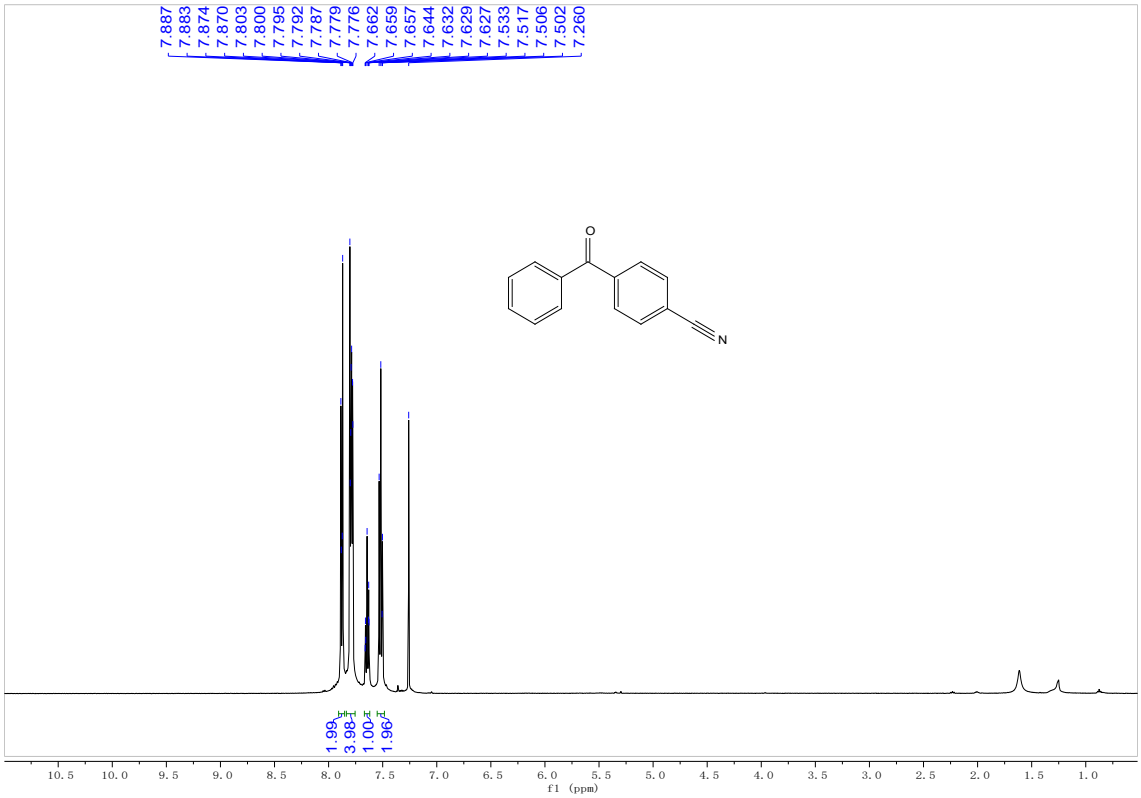
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2ad**



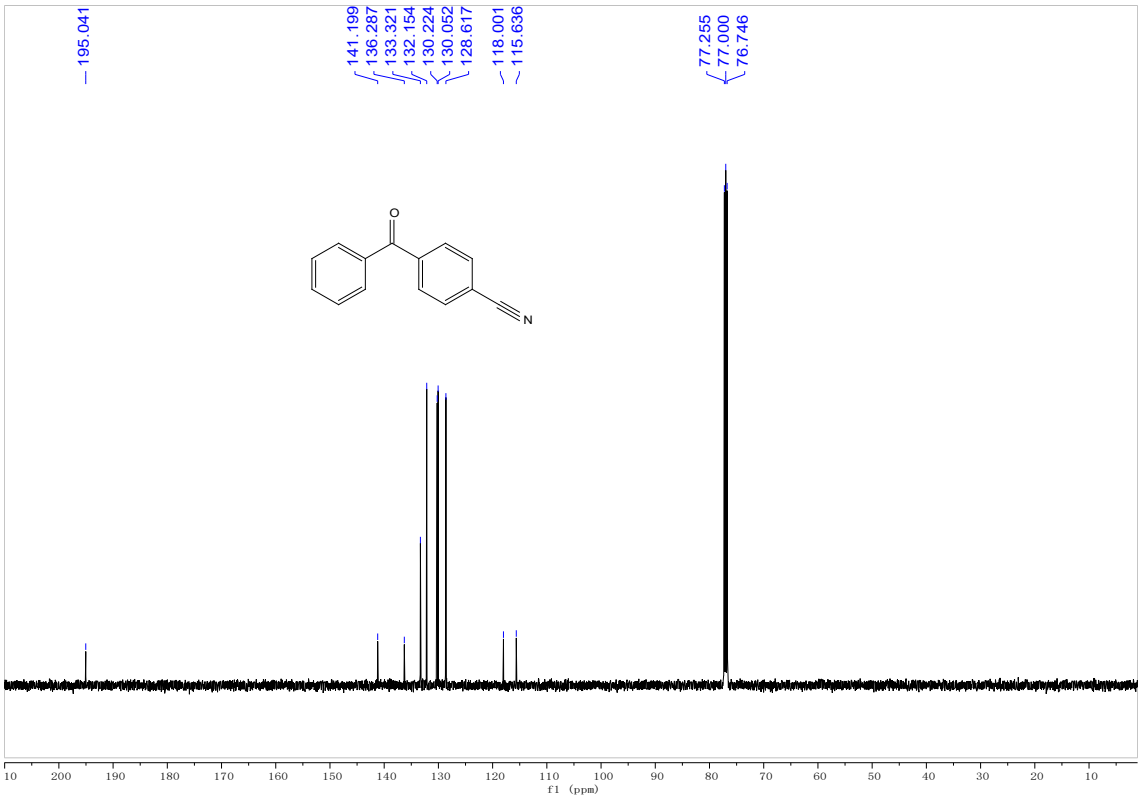
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2ad**



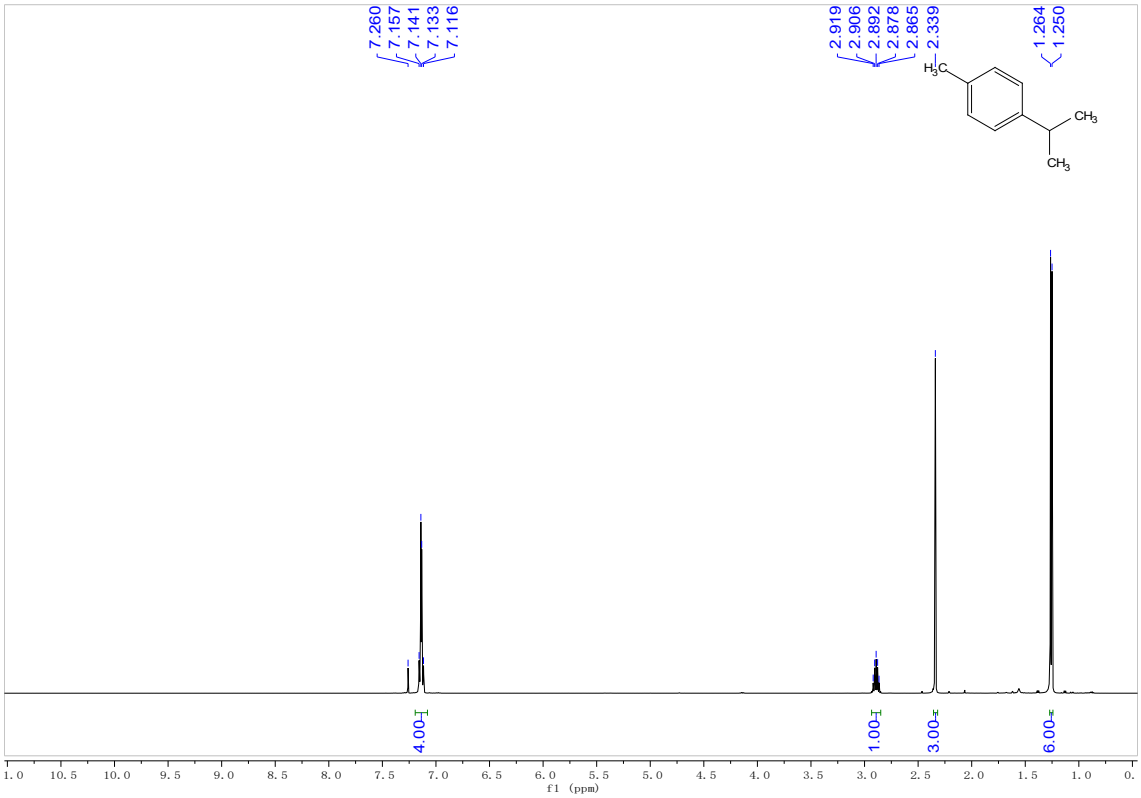
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2ae**



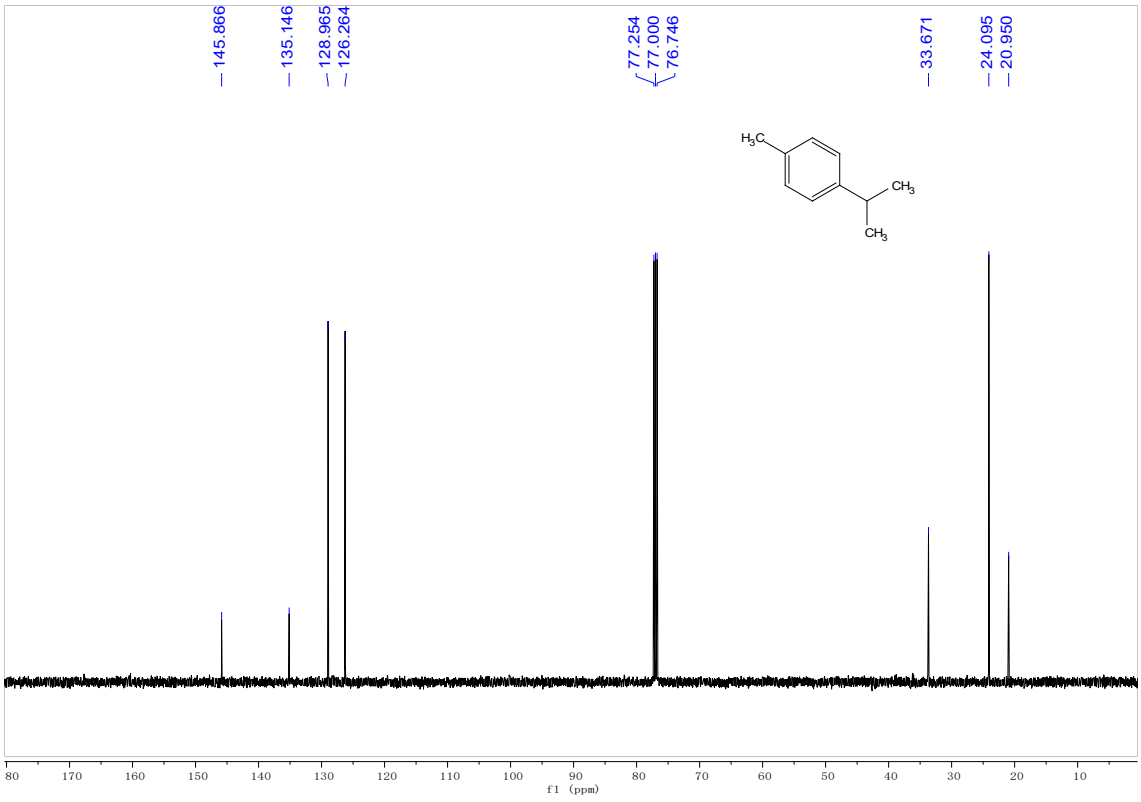
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2ae**



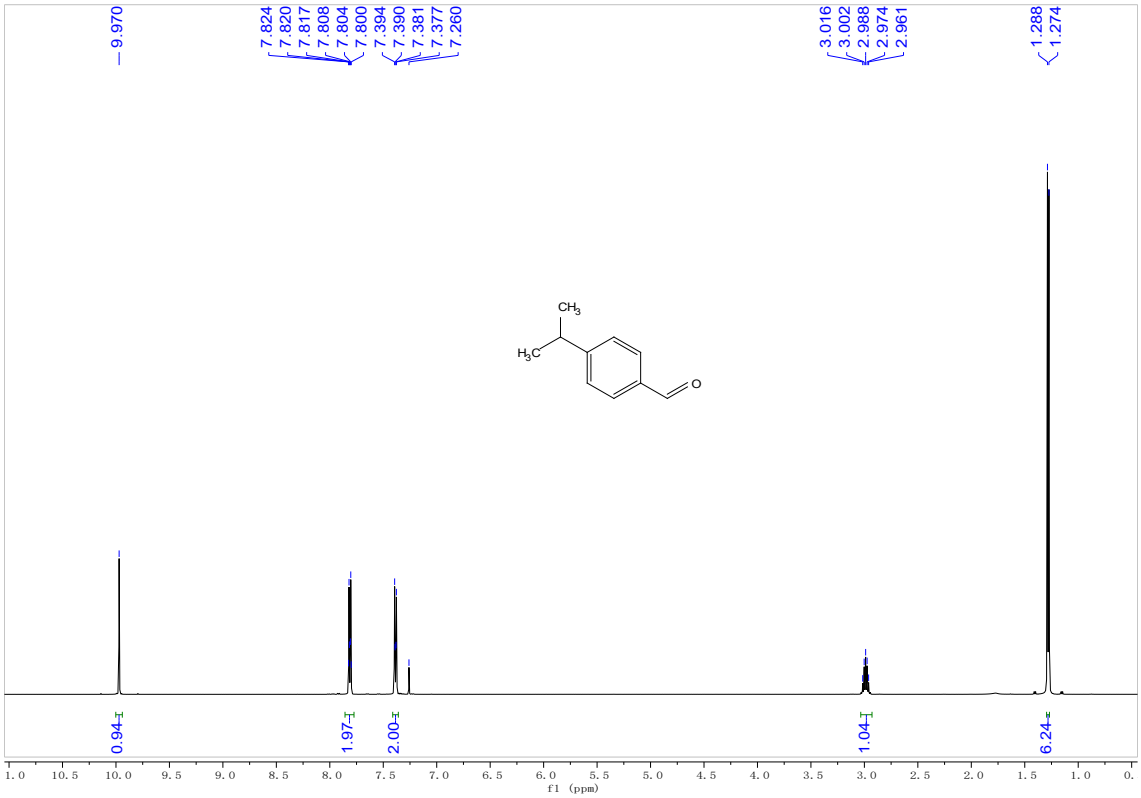
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2af**



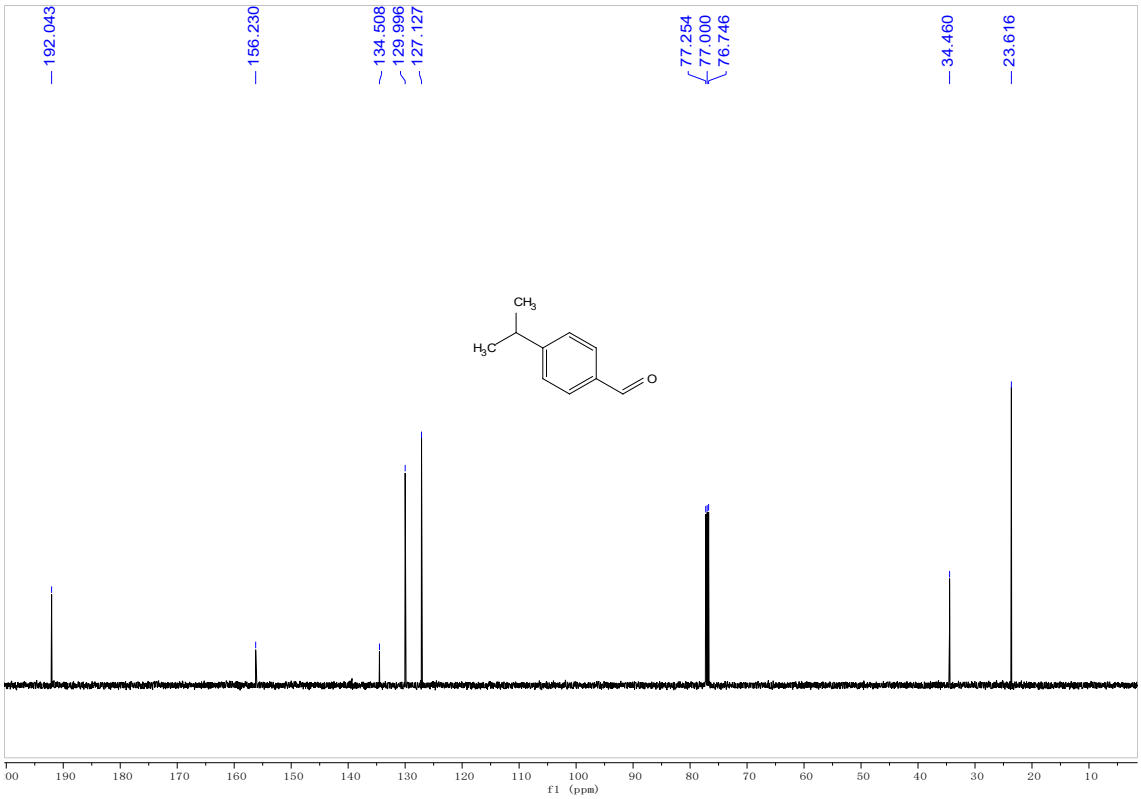
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2af**



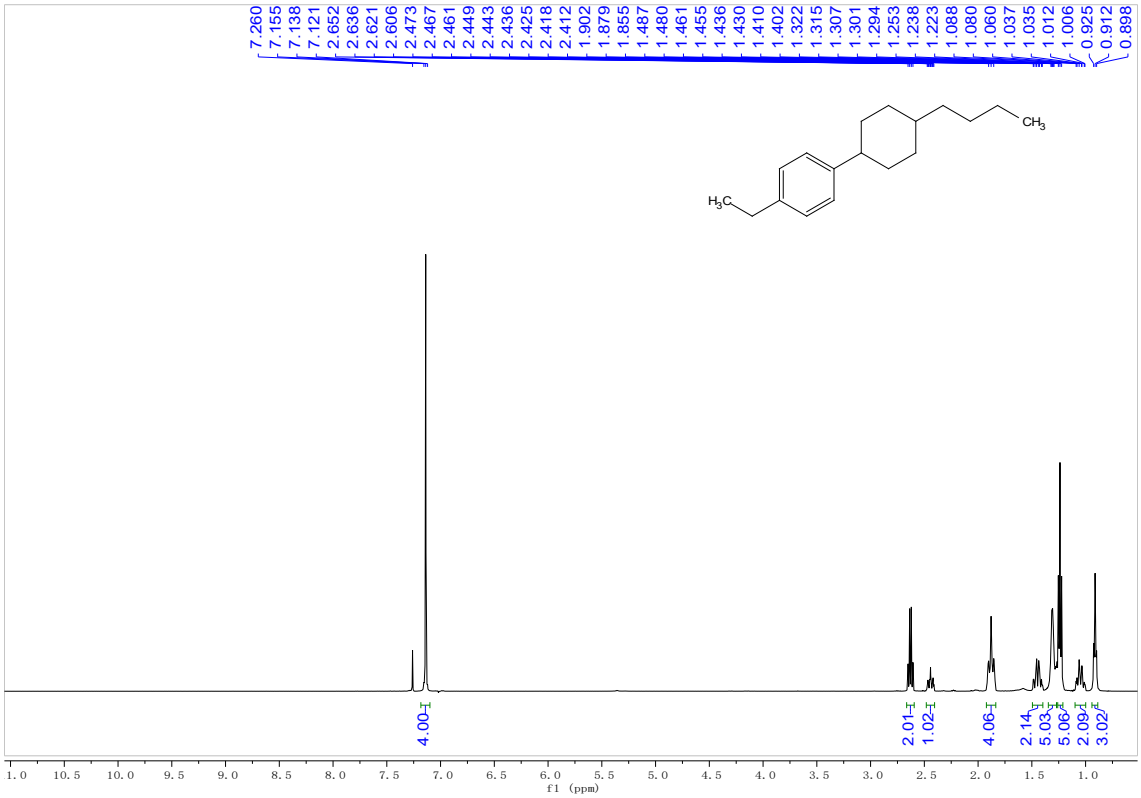
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2ag**



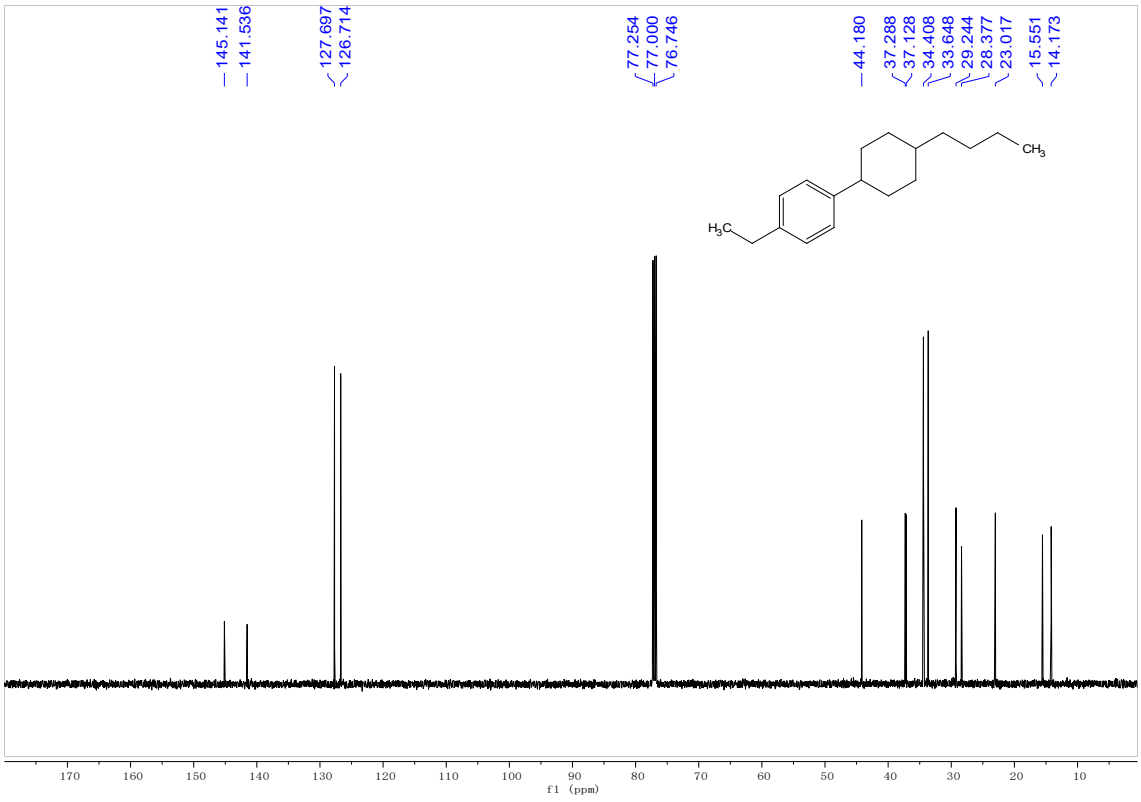
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2ag**



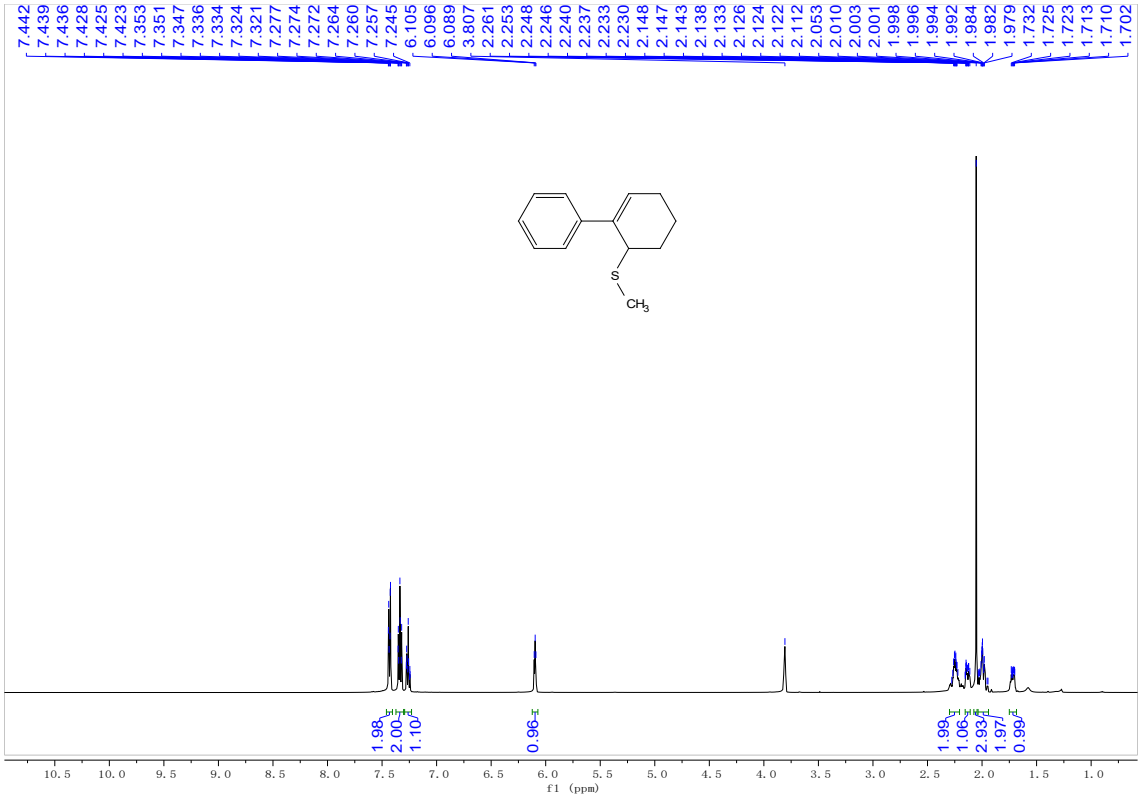
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **2ah**



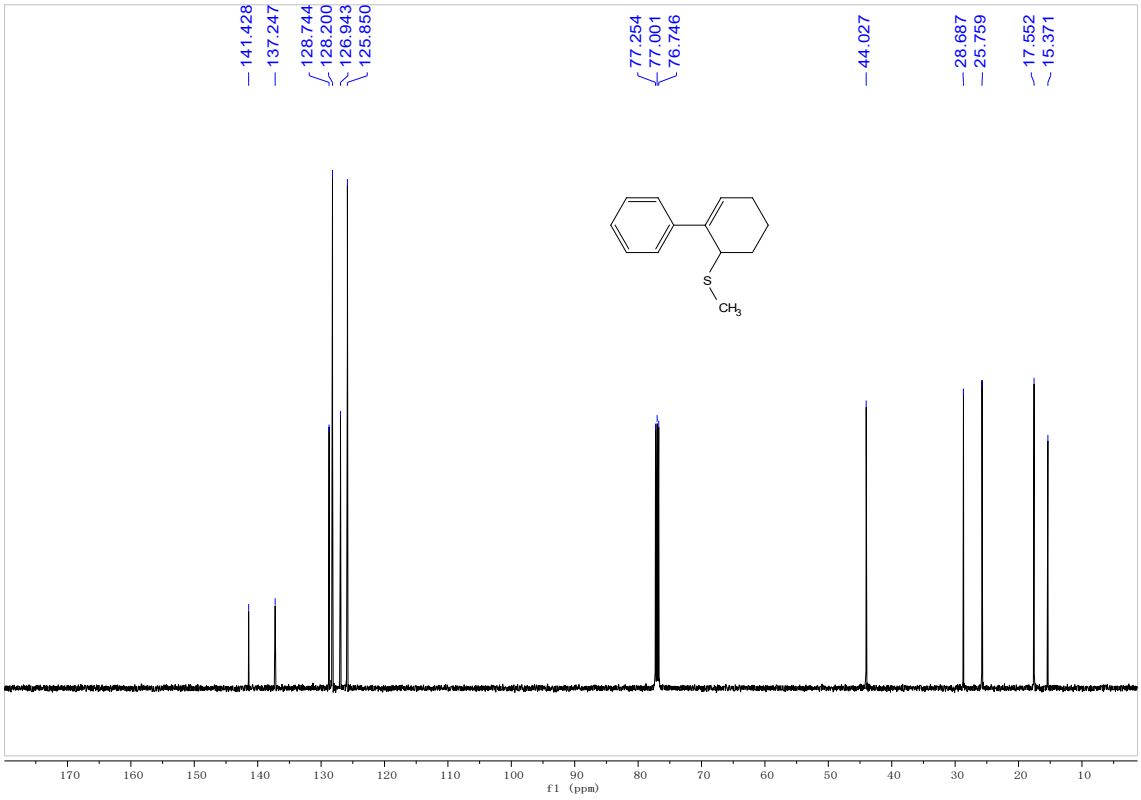
^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **2ah**



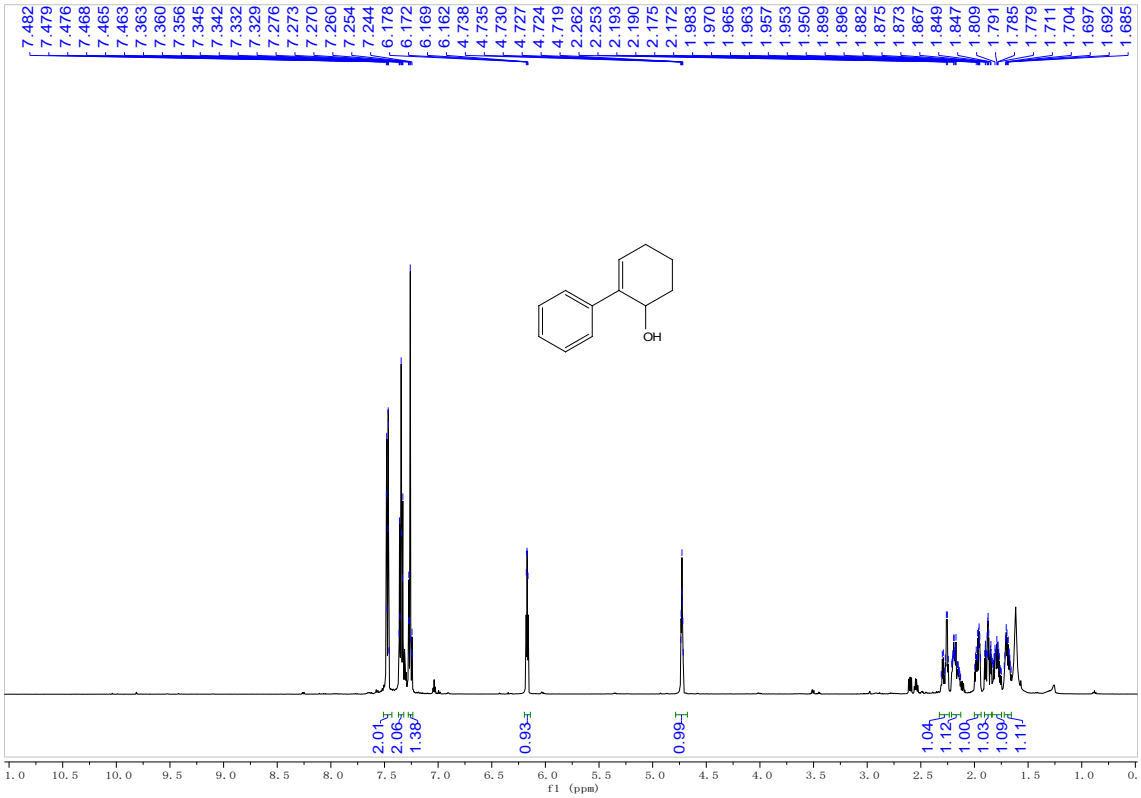
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4a**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4a**



^{1}H NMR (500 MHz, $CDCl_3$) spectrum of compound **4b**



^{13}C NMR (125 MHz, $CDCl_3$) spectrum of compound **4b**