Supplementary Information (SI) for Organic Chemistry Frontiers.

A Unified Strategy to access *N*-Heterocycles Enabled by Hypervalent Iodine(III) Reagent Mediated Imidate Radical Cyclization

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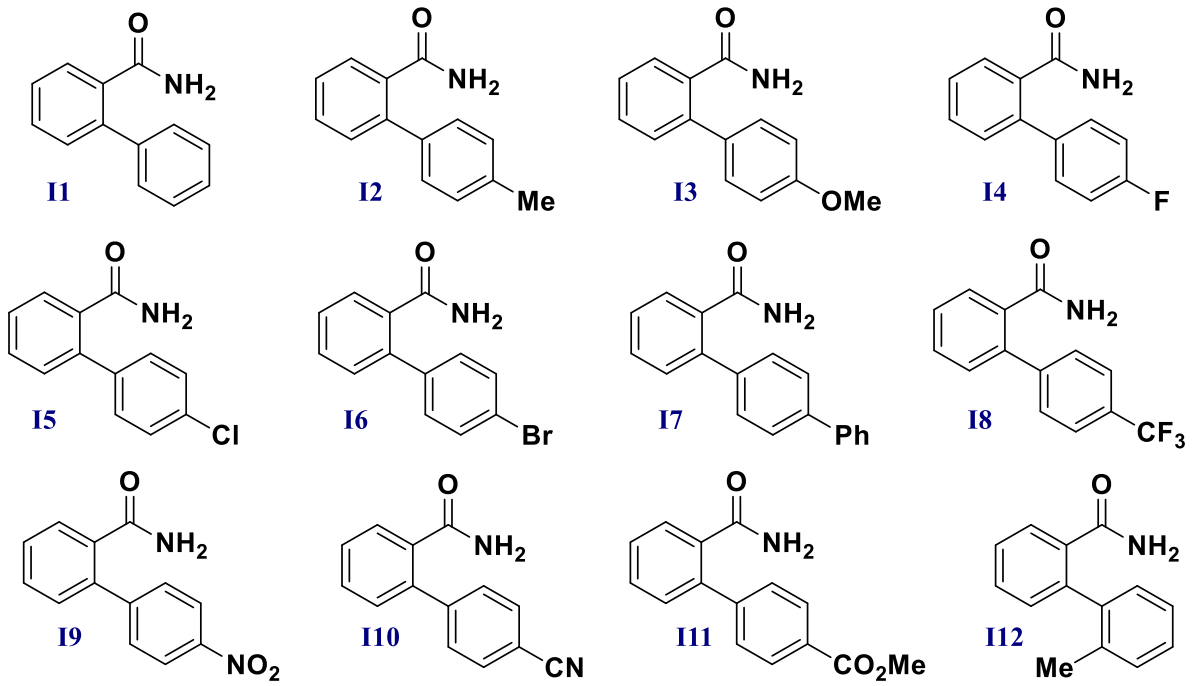
Table of Contents

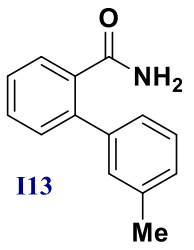
1. General Information

All commercial reagents were obtained from Spectrochem, Sigma-Aldrich, TCI, and BLD-Pharm, and used as received without further purification. PIFA was prepared according to a reported method.[1] Organic extracts were concentrated under reduced pressure using a Heidolph rotary evaporator. Thin-layer chromatography (TLC) was performed on Merck silica gel 60F254 precoated aluminium plates and visualized under UV light at 254 nm. Column chromatography was carried out using silica gel (100–200 mesh) for product purification. ^{1}H, $^{13}C\{^{1}H\}$, and ^{19}F NMR spectra were recorded on Bruker Avance NEO Ascend 400 and 500 MHz spectrometers. Chemical shifts are reported in ppm (δ scale), with residual solvent signals at 7.26 ppm ($CDCl_3$) and 2.50 ppm (DMSO-d_6) used as references. High-resolution mass spectra (HRMS) were recorded on Electrospray Ionization mode on WATERS-XEVO G3-TOF mass spectrometer coupled with Acquity H-class plus UPLC in positive (ESI) ion mode. FT-IR spectra were measured on a Bruker Tensor-27 spectrometer. Melting point were measured using Analab Thermocal melting point apparatus. HPLC graph was recorded on Agilent 1260 infinity II HPLC instrument. The enantioselectivity was determined by chiral HPLC analysis using Diacel chiralpak IC columns with a 254 nm wavelenght by using *i*-propanol (HPLC grade) and n-hexane (HPLC grade) as eluents at 25 °C.

2. Synthesis of starting materials

List of 2-aryl benzamides





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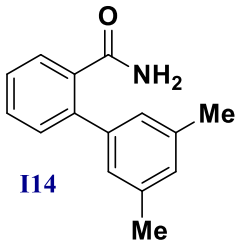

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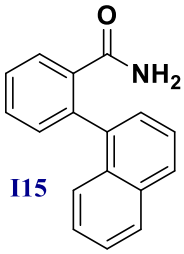

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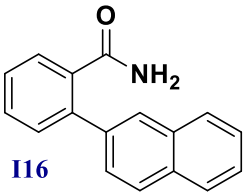

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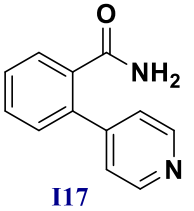

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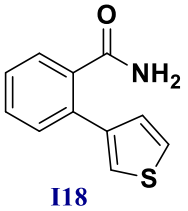

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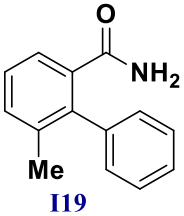

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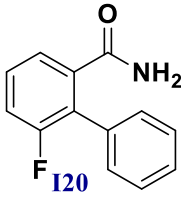

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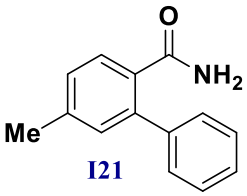

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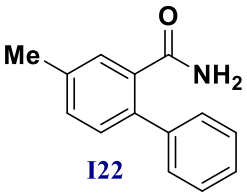

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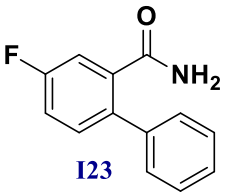

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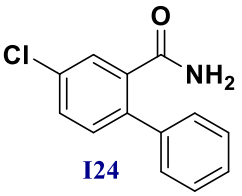

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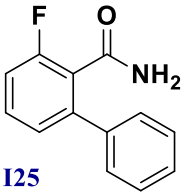

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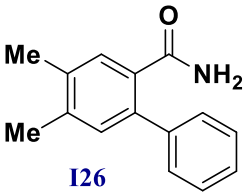

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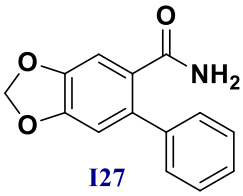

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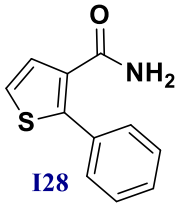

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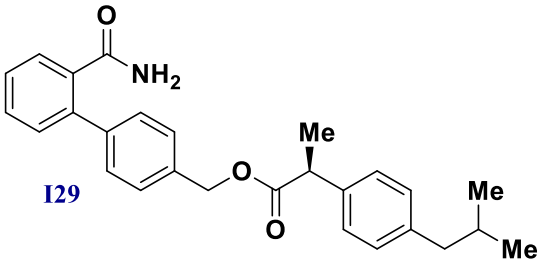

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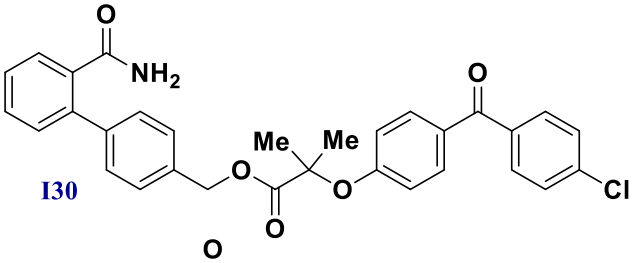

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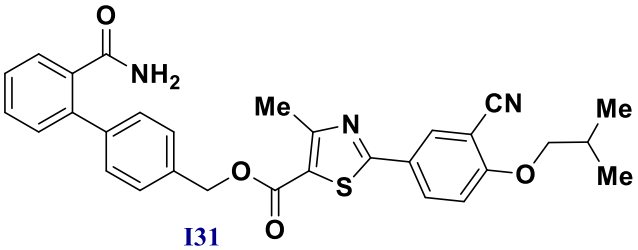

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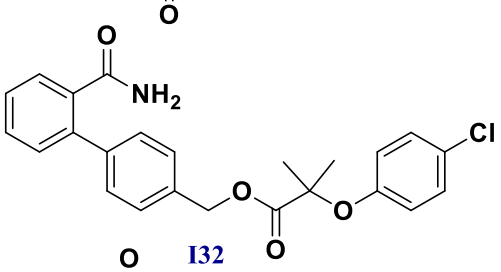

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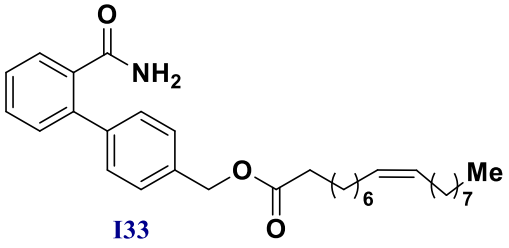

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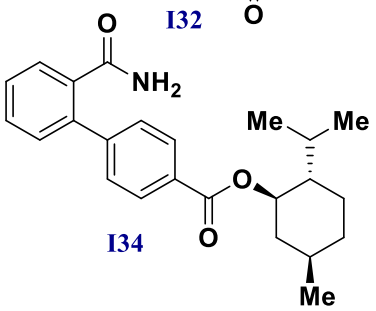
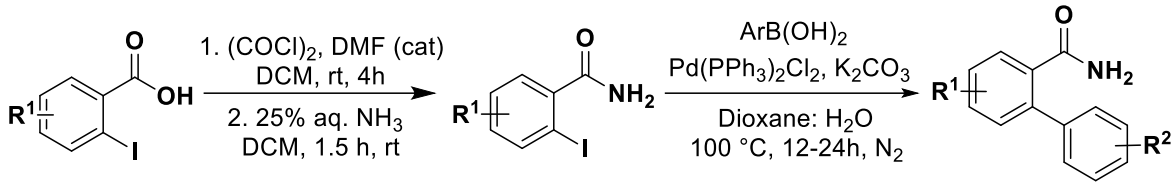


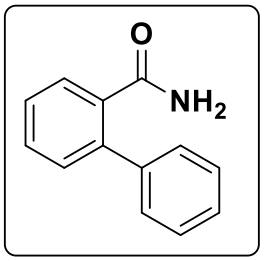
I34

2.1 General procedure for the synthesis of I1-I16 and I18-I28 (General Procedure A)



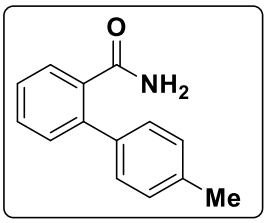
The 2-iodobenzoic acid derivatives (2 mmol, 1 equiv) and catalytic amount of DMF were dissolved in 6 mL dry dichloromethane in a 50 mL round-bottom flask equipped with a magnetic stir bar. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then oxalyl chloride (2.42 mmol, 1.2 equiv) was added drop wise to the reaction mixture at 0 °C and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride which was used directly for the next step. After dissolving the acid chloride in 4 mL of dry dichloromethane, 8 mL of aqueous ammonia was added dropwise at 0 °C and stirred continuously for 1.5 h at room temperature. the reaction was quenched with water, followed by extraction with DCM (3 × 20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure to afford 2-iodobenzamide derivatives which was used in the next step directly without further purification. In an oven-dried round-bottom flask equipped with a magnetic stir bar, the 2-iodobenzamide derivative was introduced under a nitrogen atmosphere. $Pd(PPh_3)_2Cl_2$ (5 mol%) was added, followed by arylboronic acid derivatives (1.2 equiv) and K_2CO_3 (3.0 equiv). A solvent mixture of 1,4-dioxane (8.5 mL) and deionized water (2.8 mL) was then added. The reaction mixture was stirred at 100 °C for 12 h or until completion as confirmed by TLC. After cooling to room temperature, water was added, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using a 20–30% ethyl acetate in hexane to yield the desired [1,1'-biphenyl]-2-carboxamide derivatives.

[1,1'-biphenyl]-2-carboxamide (I1)[2]



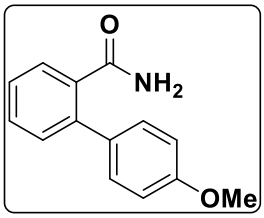
The title compound was prepared by following the general procedure A in 75% yield (296 mg, 1.5 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.76 (m, 1H), 7.53–7.48 (m, 1H), 7.47–7.34 (m, 4H), 7.42–7.35 (m, 3H), 5.62 (brs, 1H), 5.26 (brs, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.4, 140.2, 139.9, 134.4, 130.6, 130.4, 129.1, 128.8, 128.7, 128.0, 127.6. **IR** (neat) 3372, 3164, 1640, 1608, 1687, 1236, 1170 cm^{-1}.

4'-methyl-[1,1'-biphenyl]-2-carboxamide (I2)[3]



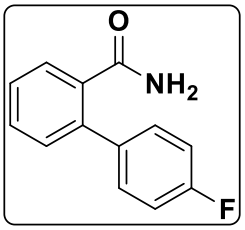
The title compound was prepared by following the general procedure A in 70% yield (296 mg, 1.4 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.52–7.45 (m, 1H), 7.44–7.38 (m, 1H), 7.37–7.30 (m, 3H), 7.26–7.21 (m, 2H), 5.63 (brs, 1H), 5.29 (brs, 1H), 2.40 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.5, 139.9, 137.8, 137.3, 134.3, 130.5, 130.4, 129.4, 129.1, 128.7, 127.4, 21.2. **IR** (neat) 3361, 3178, 1630, 1484, 1382, 1236, 1179, 1106 cm^{-1}.

4'-methoxy-[1,1'-biphenyl]-2-carboxamide (I3)[4]



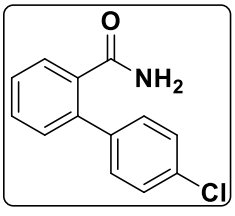
The title compound was prepared by following the general procedure A in 91% yield (413 mg, 1.82 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79–7.75 (m, 1H), 7.51–7.44 (m, 1H), 7.42–7.32 (m, 4H), 6.98–6.94 (m, 2H), 5.66 (brs, 1H), 5.31 (brs, 1H), 3.85 (s, 3H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$) δ 171.7, 159.4, 139.4, 134.3, 132.4, 130.3, 130.3, 129.9, 128.9, 127.1, 114.1, 55.2. **IR** (neat) 3317, 3165, 2947, 2837, 1640, 1603, 1515, 1371, 1232, 1170, 1101 cm^{-1}.

4'-fluoro-[1,1'-biphenyl]-2-carboxamide (I4)[5]



The title compound was prepared by following the general procedure A in 90% yield (387 mg, 1.80 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76–7.71 (m, 1H), 7.52–7.47 (m, 1H), 7.45–7.39 (m, 3H), 7.36–7.32 (m, 1H), 7.15–7.09 (m, 2H), 5.68 (brs, 1H), 5.31 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.4, 162.8 (d, *J* = 247.5 Hz), 138.9, 136.3, 134.7, 130.5 (d, *J* = 1.8 Hz), 130.7, 130.6, 129.0, 127.9, 115.8 (d, *J* = 21.5 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.22 to -114.28 (m, 1F); **IR** (neat) 3377, 3162, 1696, 1650, 1610, 1508, 1451, 1393, 1215 cm^{-1}.

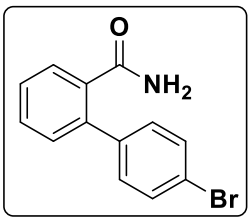
4'-chloro-[1,1'-biphenyl]-2-carboxamide (I5)[3]



The title compound was prepared by following the general procedure A in 41% yield (190 mg, 0.82 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73–7.69 (m, 1H), 7.52–7.48 (m, 1H), 7.45–7.42 (m, 1H), 7.42–7.36 (m, 4H), 7.35–7.32 (m, 1H), 5.87 (brs, 1H), 5.36 (brs, 1H).

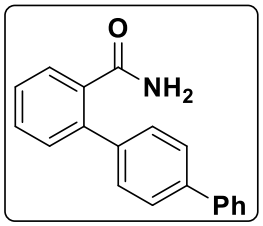
$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 171.4, 138.7, 138.7, 134.7, 134.3, 130.8, 130.4, 130.2, 129.0, 129.1, 128.0. **IR** (neat) 3363, 3173, 1650, 1628, 1387, 1692, 1218 cm^{-1}.

4'-bromo-[1,1'-biphenyl]-2-carboxamide (I6)



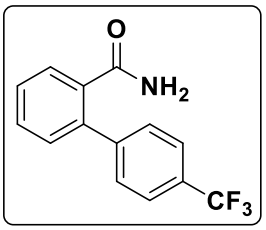
The title compound was prepared by following the general procedure A in 90% yield (497 mg, 1.8 mmol) as a white solid. **m.p.** 160-162 °C; **^1H NMR** (500 MHz, $CDCl_3$) δ 7.74-7.71 (m, 1H), 7.58-7.48 (m, 4H), 7.46-7.43 (m, 1H), 7.35-7.31 (m, 2H), 5.64 (brs, 1H), 5.31 (brs, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 171.2, 139.2, 138.7, 134.6, 132.0, 130.8, 130.4, 129.5, 128.8, 128.1, 122.5. **IR** (neat) 3368, 3180, 1650, 1477, 1389,1078, 1008 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{11}BrNO$ 276.0019, found 276.0038.

[1,1':4',1''-terphenyl]-2-carboxamide (I7)



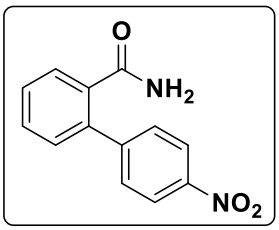
The title compound was prepared by following the general procedure A in 48% yield (0.96 mg, 166 mmol) as a white solid. **m.p.** 188-190 °C. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 1H), 7.69-7.61 (m, 4H), 7.55-7.50 (m, 3H), 7.49-7.36 (m, 5H), 5.82 (brs, 1H), 5.39 (brs, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 171.6, 140.9, 140.5, 139.6, 139.2, 134.6, 130.7, 130.5, 129.4, 129.2, 129.0, 127.8, 127.7, 127.5, 127.2. **IR** (neat) 3370, 3164, 1641, 1480, 1391, 1120, 1000 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{19}H_{15}NONa$ 296.1051, found 296.1039.

4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxamide (I8)



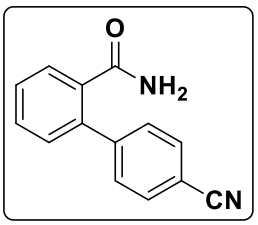
The title compound was prepared by following the general procedure A in 40% yield (212 mg, 0.80 mmol) as a white solid. **m.p.** 133-135 °C. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.73-7.70 (m, 1H), 7.68 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 7.54-7.51 (m, 1H), 7.49-7.45 (m, 1H), 7.39-7.35 (m, 1H), 5.80 (brs, 1H), 5.38 (brs, 1H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 171.2, 144.0, 138.6, 134.9, 130.8, 130.5, 130.1 (*q*, J = 32 Hz), 129.2, 128.8, 128.4, 126.4 (q, J = 272 Hz), 125.7 (q, J = 3.7 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.51. **IR** (neat) 3370, 3173, 1648, 1678, 1320, 1157, 1108, 1064, 1019 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}F_3NO$ 266.0793, found 266.0786.

4'-nitro-[1,1'-biphenyl]-2-carboxamide (I9)



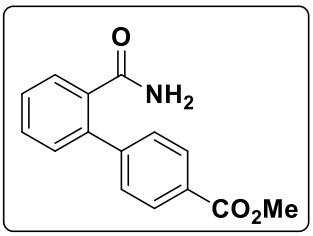
The title compound was prepared by following the general procedure A in 54% yield (262 mg, 1.08 mmol) as a white yellow solid. **m.p.** 168-170 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.30-8.27 (m, 2H), 7.71-7.69 (m, 1H), 7.64-7.60 (m, 2H), 7.58-7.54 (m, 1H), 7.52-7.48 (m, 1H), 7.42-7.38 (m, 1H), 5.77 (brs, 1H), 5.51 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.0, 147.6, 147.1, 138.0, 135.0, 131.0, 130.5, 129.7, 128.9, 128.6, 123.9. **IR** (neat) 3386, 3317, 3182, 1656, 1597, 1506, 1350, 1110 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{11}N_2O_3$ 243.0770, found 243.0757.

4'-cyano-[1,1'-biphenyl]-2-carboxamide (I10)



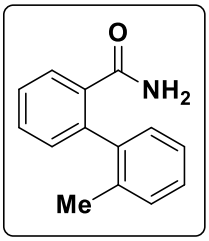
The title compound was prepared by following the general procedure A in 65% yield (289 mg, 1.3 mmol) as a white solid. **m.p.** 165-168 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73–7.67 (m, 3H), 7.58–7.52 (m, 3H), 7.51–7.45 (m, 1H), 7.39–7.34 (m, 1H), 5.70 (brs, 1H), 5.46 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.0, 145.1, 138.3, 135.0, 132.4, 130.9, 130.4, 129.6, 128.8, 128.6, 118.8, 111.8. **IR** (neat) 3377, 3175, 2225, 1645, 1610, 1484, 1484, 1380, 1236, 1121, 1048 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}N_2O$ 223.0871, found 223.0866.

methyl 2'-carbamoyl-[1,1'-biphenyl]-4-carboxylate (I11)



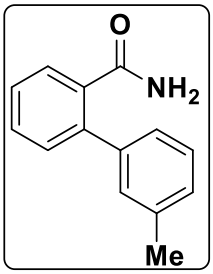
The title compound was prepared by following the general procedure A in 40% yield (204 mg, 0.8 mmol) as a white solid. **m.p.** 155- 157 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.67–7.62 (m, 1H), 7.54–7.49 (m, 2H), 7.47–7.44 (m, 1H), 7.37 (d, J = 7.6 Hz, 1H), 5.78 (brs, 1H), 5.40 (brs, 1H), 3.93 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 171.3, 166.9, 144.9, 140.0, 134.8, 130.8, 130.4, 130.0, 129.7, 128.9, 128.7, 128.3, 52.4. **IR** (neat) 3370, 3182, 1709, 1634, 1435, 1391, 1669, 1183,1108 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO_3$ 256.0968, found 256.0972.

2'-methyl-[1,1'-biphenyl]-2-carboxamide (I12)



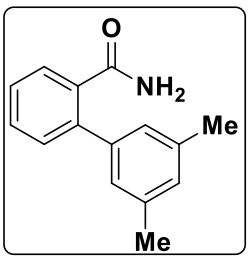
The title compound was prepared by following the general procedure A in 47% yield (199 mg, 0.94 mmol) as a yellow solid. **m.p.** 98-100 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04–8.00 (m, 1H), 7.54–7.49 (m, 1H), 7.48–7.43 (m, 1H), 7.35–7.27 (m, 3H), 7.24–7.19 (m, 2H), 5.71 (brs, 1H), 5.29 (brs, 1H), 2.12 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.1, 140.3, 139.8, 136.3, 133.3, 131.2, 130.7, 130.6, 129.9, 129.1, 128.6, 127.9, 126.4, 20.1. **IR** (neat) 3436, 3198, 2917, 1640, 1601, 1475, 1375, 1375, 1126, 1040 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075, found 212.1065.

3'-methyl-[1,1'-biphenyl]-2-carboxamide (I13)[6]



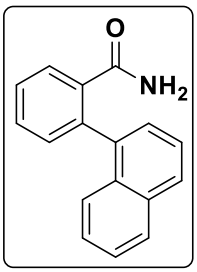
The title compound was prepared by following the general procedure A in 46% yield (194 mg, 0.92 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.78 (m, 1H), 7.51–7.47 (m, 1H), 7.44–7.40 (m, 1H), 7.36–7.29 (m, 2H), 7.26–7.19 (m, 3H), 5.74 (brs, 1H), 5.31 (brs, 1H), 2.39 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.5, 140.3, 140.2, 138.6, 134.2, 130.7, 130.6, 129.6, 129.3, 128.9, 128.8, 127.7, 126.0, 21.6. **IR** (neat) 3366, 3182, 2921, 1640, 1619, 1387, 1126 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075, found 212.1066.

3',5'-dimethyl-[1,1'-biphenyl]-2-carboxamide (I14)



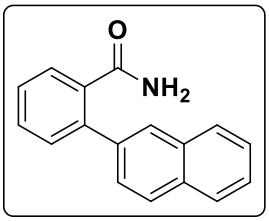
The title compound was prepared by following the general procedure A in 44% yield (198 mg, 0.88 mmol) as a yellow solid. **m.p.** 184-186 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84–7.78 (m, 1H), 7.50–7.44 (m, 1H), 7.43–7.38 (m, 1H), 7.34–7.30 (m, 1H), 7.06–7.01 (m, 3H), 5.63 (brs, 1H), 5.30 (brs, 1H), 2.35 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.31, 140.4, 140.3, 138.4, 134.1, 130.6, 130.5, 129.8, 129.4, 127.6, 126.7, 21.4. **IR** (neat) 3371, 3182, 2908, 1647, 1597, 1515, 1426, 1345, 1251, 1137, 1035 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{15}H_{15}NONa$ 248.1051, found 248.1043.

2-(naphthalen-1-yl)benzamide (I15)



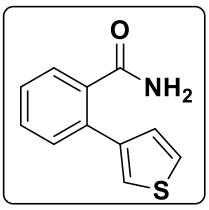
The title compound was prepared by following the general procedure A in 65% yield (321 mg, 1.3 mmol) as a yellow solid. **m.p.** 201-203 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04–8.01 (m, 1H), 7.91 (d, *J* = 8.3 Hz, 2H), 7.61–7.49 (m, 5H), 7.46–7.41 (m, 2H), 7.37–7.34 (m, 1H), 5.26 (brs, 1H), 5.14 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.2, 138.4, 138.2, 135.0, 133.8, 132.0, 131.6, 130.8, 129.8, 128.7, 128.5, 128.3, 127.0, 127.0, 126.5, 125.6. **IR** (neat) 3447, 3319, 3167, 2915, 1667, 1592, 1378, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}NONa$ 270.0895, found 270.088.

2-(naphthalen-2-yl)benzamide (I16)



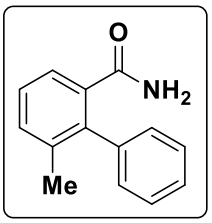
The title compound was prepared by following the general procedure A in 53% yield (262 mg, 1.06 mmol) as a yellow solid. **m.p.** 128-130 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94–7.83 (m, 5H), 7.59–7.51 (m, 4H), 7.49–7.45 (m, 2H), 5.48 (brs, 1H), 5.25 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.3, 139.9, 137.9, 134.6, 133.5, 132.9, 130.9, 130.8, 129.4, 128.5, 128.3, 127.9, 127.9, 127.7, 127.2, 126.8, 126.6. **IR** (neat) 3428, 3178, 1641, 1378, 1101, 1024 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{17}H_{13}NONa$ 270.0895, found 270.0885.

2-(thiophen-3-yl)benzamide (I18)



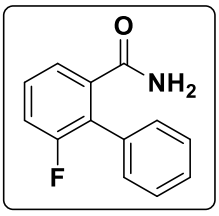
The title compound was prepared by following the general procedure A in 68% yield (276 mg, 1.36 mmol) as a white solid. **m.p.** 182-184 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76–7.70 (m, 1H), 7.50–7.45 (m, 1H), 7.43–7.37 (m, 4H), 7.23–7.19 (m, 1H), 5.62 (brs, 1H), 5.43 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.5, 140.6, 134.5, 134.4, 130.6, 130.3, 129.0, 128.6, 127.8, 126.3, 123.4; **IR** (neat) 3360, 3164, 1643, 1614, 1400, 1119 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{11}H_9NOSNa$ 226.0303, found 226.0283.

6-methyl-[1,1'-biphenyl]-2-carboxamide (I19)



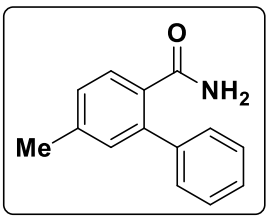
The title compound was prepared by following the general procedure A in 78% yield (330 mg, 1.5 mmol) as a white solid. **m.p.** 192-194 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66–7.62 (m, 1H), 7.45–7.41 (m, 2H), 7.40–7.34 (m, 2H), 7.34–7.30 (m, 1H), 7.26–7.23 (m, 2H), 5.59 (brs, 1H), 5.18 (brs, 1H), 2.10 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.3, 139.6, 139.2, 136.9, 135.2, 132.4, 129.1, 129.0, 127.9, 127.7, 126.6, 20.9. **IR** (neat) 3390, 3167, 1689, 1634, 1610, 1402, 1101 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1075, found 212.1091.

6-fluoro-[1,1'-biphenyl]-2-carboxamide (I20)



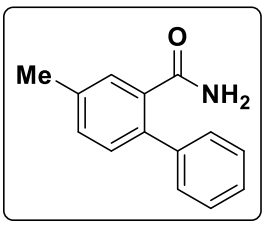
The title compound was prepared by following the general procedure A in 87% yield (373 mg, 1.74 mmol) as a yellow solid. **m.p.** 180-182 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (d, J = 7.7 Hz, 1H), 7.49–7.39 (m, 6H), 7.28–7.23 (m, 1H), 5.58 (brs, 1H), 5.20 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 159.6 (d, J = 247.2 Hz), 136.8, 136.8, 133.2, 129.8, 129.4 (d, J = 8.6 Hz), 128.9, 128.8, 124.9 (d, J = 3.6 Hz), 118.1 (d, J = 23.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.52. **IR** (neat) 3388, 3162, 1692, 1641, 1617, 1444, 1393, 1234, 1103 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{11}FNO$ 216.0825, found 216.0814.

5-methyl-[1,1'-biphenyl]-2-carboxamide (I21)[3]



The title compound was prepared by following the general procedure A [$Pd(PPh_3)_4$ was used instead of $Pd(PPh_3)_2Cl_2$] in 61% yield (258 mg, 1.22 mmol) as a yellow solid. **m.p.** 131-133 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, J = 7.9 Hz, 1H), 7.44–7.36 (m, 5H), 7.25–7.22 (m, 1H), 7.17–7.14 (m, 1H), 5.73 (brs, 1H), 5.24 (brs, 1H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.4, 141.0, 140.5, 140.1, 131.3, 131.3, 129.5, 128.9, 128.8, 128.5, 128.0, 21.5. **IR** (neat) 3372, 3171, 1641, 1621, 1488, 1390, 1137 cm^{-1}.

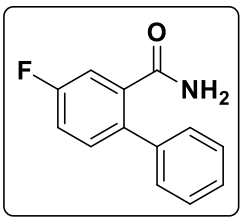
4-methyl-[1,1'-biphenyl]-2-carboxamide (I22)[3]



The title compound was prepared by following the general procedure A in 35% yield (148 mg, 0.7 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.44–7.35 (m, 5H), 7.33–7.30 (m, 1H), 7.2–7.24 (m, 1H), 5.75 (brs, 2H), 5.27 (brs, 2H), 2.42 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.7, 140.3, 137.7, 137.2, 134.1, 131.5, 130.5,

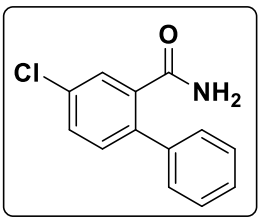
129.8, 129.0, 128.8, 127.9, 21.1. **IR** (neat) 3386, 3184, 1643, 1605, 1484, 1382, 1263, 1103 cm^{-1}.

4-fluoro-[1,1'-biphenyl]-2-carboxamide (I23)



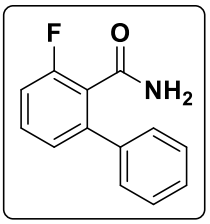
The title compound was prepared by following the general procedure A in 43% yield (185 mg, 0.86 mmol) as a white solid. **m.p.** 192-194 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54–7.49 (m, 1H), 7.46–7.38 (m, 5H), 7.35–7.31 (m, 1H), 7.23–7.18 (m, 1H), 5.64 (brs, 1H), 5.25 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.8, 163.1, 161.2, 139.4, 136.1 (d, J = 3.3 Hz), 136.0, 132.4 (d, J = 7.7 Hz), 129.0 (d, J = 2.2 Hz), 128.3, 117.8 (d, J = 21.3 Hz), 116.3 (d, J = 23.4 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.03 to -114.08 (m, 1F). **IR** (neat) 3172, 3175, 1642, 1617, 1433, 1370, 1254, 1200, 1123 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{11}FNO$ 216.0825, found 216.0807.

4-chloro-[1,1'-biphenyl]-2-carboxamide (I24)



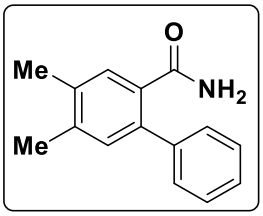
The title compound was prepared by following the general procedure A in 41% yield (190 mg, 0.82 mmol) as a white solid. **m.p.** 166-168 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80–7.78 (m, 1H), 7.49–7.40 (m, 6H), 7.32–7.29 (m, 1H), 5.46 (brs, 1H), 5.23 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 139.2, 138.4, 135.8, 134.0, 131.9, 130.8, 129.4, 129.0, 128.9, 128.5. **IR** (neat) 3372, 3172, 2928, 1738, 1643, 1601, 1426, 1370, 1361, 1252 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{11}ClNO$ 232.0529, found 232.0519.

3-fluoro-[1,1'-biphenyl]-2-carboxamide (I25)



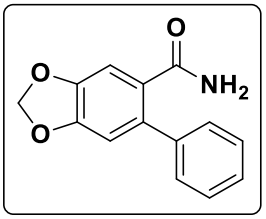
The title compound was prepared by following the general procedure A in 89% yield (383 mg, 1.78 mmol) as a yellow solid. **m.p.** 138-140 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48–7.45 (m, 2H), 7.44–7.37 (m, 4H), 7.20–7.18 (m, 1H), 7.14–7.09 (m, 1H), 5.90 (brs, 1H), 5.57 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.2, 160.5, 158.5, 142.0 (d, J = 3.2 Hz), 139.0 (d, J = 2.3 Hz), 131.0 (d, J = 8.9 Hz), 128.7 (d, J = 15.0 Hz), 128.2, 126.0 (d, J = 3.2 Hz), 123.8 (d, J = 17.4 Hz), 114.8 (d, J = 22.0 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.33 to -115.36 (m, 1F); **IR** (neat) 3434, 3116, 1654, 1619, 1460, 1384, 1238, 1095 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{11}FNO$ 216.0825, found 216.0815.

4,5-dimethyl-[1,1'-biphenyl]-2-carboxamide (I26)[3]



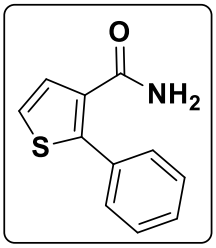
The title compound was prepared by following the general procedure A [$Pd(PPh_3)_4$ was used instead of $Pd(PPh_3)_2Cl_2$] in 64% yield (288 mg, 1.28 mmol) as a yellow solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.43–7.40 (m, 4H), 7.39–7.35 (m, 1H), 7.12 (s, 1H), 5.56 (brs, 1H), 5.22 (brs, 1H), 2.33 (s, 3H), 2.33 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.4, 140.4, 139.9, 137.7, 136.5, 131.9, 131.1, 130.7, 129.0, 128.8, 127.9, 19.8, 19.4. **IR** (neat) 3374, 3180, 1640, 1398, 1378, 1106, 1022 cm^{-1}.

6-phenylbenzo[d][1,3]dioxole-5-carboxamide (I27)



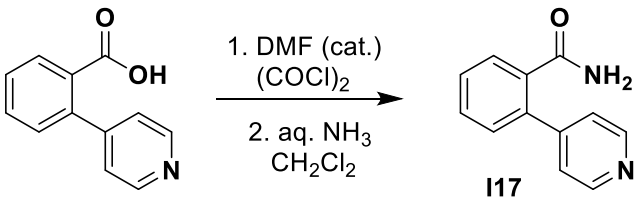
The title compound was prepared by following the general procedure A [$Pd(PPh_3)_4$ was used] in 67% yield (323 mg, 1.34 mmol) as a white solid. **m.p.** 200-202 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44–7.36 (m, 5H), 7.31 (s, 1H), 6.77 (s, 1H), 6.04 (s, 2H), 5.56 (brs, 1H), 5.13 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 149.6, 147.4, 140.3, 135.4, 129.0, 128.9, 128.1, 127.9, 110.4, 109.6, 102.0. **IR** (neat) 3370, 3178, 1634, 1600, 1480, 1431, 1400, 1232, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{12}NO_3$ 242.0817, found 242.0809.

2-phenylthiophene-3-carboxamide (I28)



The title compound was prepared by following the general procedure A in 93% yield (378 mg, 1.86 mmol) as a white solid. **m.p.** 126-128 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (d, J = 5.0 Hz, 1H), 7.48–7.43 (m, 5H), 7.01 (d, J = 5.0 Hz, 1H), 5.93 (brs, 1H), 5.55 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 164.2, 143.4, 135.6, 134.1, 131.3, 129.8, 129.3, 129.2, 128.9; **IR** (neat) 3408, 3171, 1612, 1435, 1387, 1558, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{11}H_{10}NOS$ 204.0483, found 204.0465.

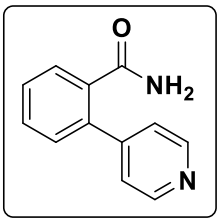
2.2 Procedure for the synthesis of I17



2-(pyridin-4-yl)benzoic acid synthesized according to the literature reported procedure[8].

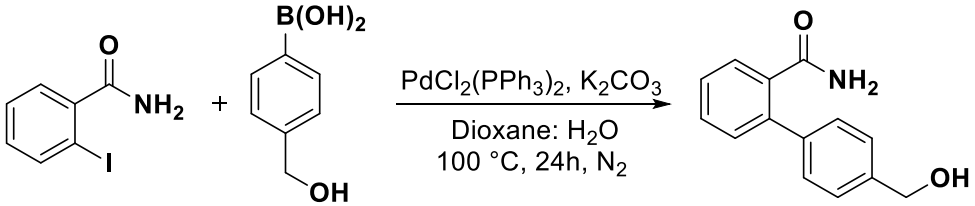
2-(Pyridin-4-yl)benzoic acid (2 mmol) and a catalytic amount of DMF were dissolved in 6 mL of dry CH_2Cl_2 in a round-bottom flask. The solution was cooled to 0 °C and stirred for 5 min. Oxalyl chloride (2.42 mmol, 1.2 equiv) was then added dropwise at 0 °C, and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was concentrated under reduced pressure. The crude acid chloride was dissolved in 4 mL of dry CH_2Cl_2, and 8 mL of aq. NH_3 was added dropwise at 0 °C. The reaction was then stirred at room temperature for 1.5 h. Then, the mixture was quenched with water and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to obtain 2-(pyridin-4-yl)benzamide **I17**.

2-(pyridin-4-yl)benzamide (I17)



47% yield (186 mg, 0.94 mmol) as a white solid. **m.p.** 182-184 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.76–8.60 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.57–7.52 (m, 1H), 7.51–7.46 (m, 1H), 7.44–7.36 (m, 3H), 5.85 (brs, 1H), 5.56 (brs, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.0, 149.7, 148.5, 137.3, 135.0, 130.9, 130.2, 129.0, 128.7, 127.7, 124.0. **IR** (neat) 3264, 3080, 1597, 1389, 1218, 1128, 1070, 1022 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{12}H_{11}N_2O$ 199.0866, found 199.0872.

2.3 Preparation of 4'-(hydroxymethyl)-[1,1'-biphenyl]-2-carboxamide (I55)

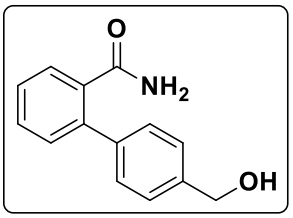


I55

Under nitrogen atmosphere, oven-dried round-bottom flask equipped with a magnetic stir bar, 2-iodobenzamide (2 mmol) was added. To this, $Pd(PPh_3)_2Cl_2$ (5 mol%) was introduced, followed by (4-(hydroxymethyl)phenyl)boronic acid (1.2 equiv) and K_2CO_2 (3.0 equiv.). Then, 1,4-dioxane (8.5 mL) and deionized H_2O (2.8 mL) was added to the mixture. The reaction mixture was stirred at 100 °C for 24 h. Then it was cooled to room temperature and diluted with water. The aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with aq. NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography using 30–

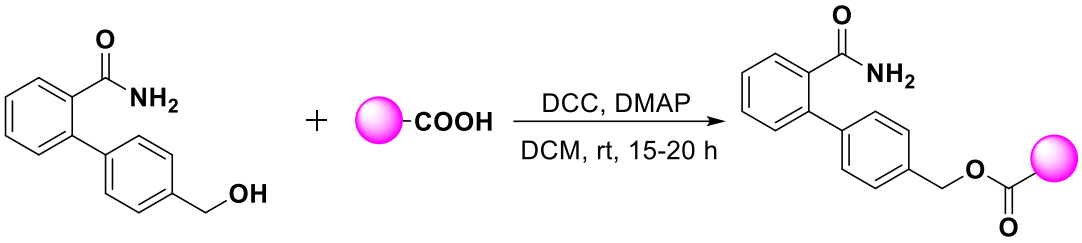
40% ethyl acetate in hexane, affording the 4'-(hydroxymethyl)-[1,1'-biphenyl]-2-carboxamide **I55**.

4'-(hydroxymethyl)-[1,1'-biphenyl]-2-carboxamide (I55)



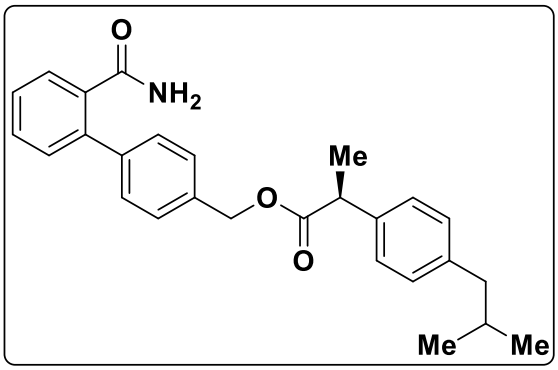
57% yield (275 mg, 1.14 mmol) as a yellow solid. **m.p.** 130-132 ºC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.79–7.74 (m, 1H), 7.54–7.47 (m, 1H), 7.47–7.39 (m, 5H), 7.38–7.33 (m, 1H), 5.84 (brs, 1H), 5.32 (brs, 1H), 4.75 (s, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.7, 140.8, 139.7, 139.6, 134.4, 130.8, 130.6, 129.2, 129.1, 127.8, 127.4, 65.0. **IR** (neat) 3326, 3156, 1643, 1608, 1389, 1048, 1006 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{14}NO_2$ 228.1019, found 228.1032.

2.4 General procedure for the Synthesis of I29 to I33 (General Procedure B)



A solution of 4'-(hydroxymethyl)-[1,1'-biphenyl]-2-carboxamide **I55** (1 mmol) in CH_2Cl_2 (3 mL) was cooled to 0 °C, and the corresponding acid (1.2 equiv) was added. Then, a solution of DCC (1.5 equiv) and DMAP (0.5 equiv) in CH_2Cl_2 (2 mL) was added dropwise. The reaction mixture was then stirred at room temperature for 20 hours. After completion of the reaction, the crude mixture was passed through a silica gel pad, washed with CH_2Cl_2, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography using a EtOAc/hexane (30–50%) to yield the desired coupled product **I29** to **I33**.

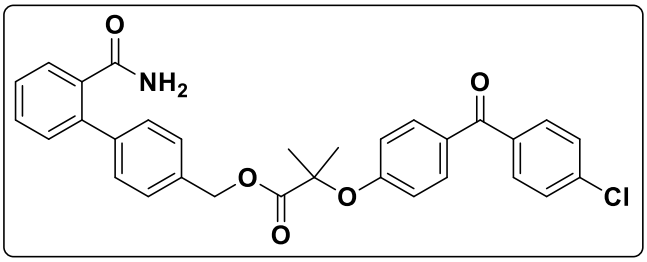
(2'-carbamoyl-[1,1'-biphenyl]-4-yl)methyl (*S*)-2-(4-isobutylphenyl)propanoate (I29)



The title compound was prepared by following the general procedure B in 87% yield (362 mg, 0.87 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.78–7.75 (m, 1H), 7.52–7.48 (m, 1H), 7.45–7.41 (m, 1H), 7.40–7.37 (m, 2H), 7.34–7.32 (m, 1H), 7.29–7.27 (m, 2H), 7.24–7.20 (m, 2H), 7.12–7.08 (m, 2H), 5.48 (brs, 1H), 5.22 (brs, 1H), 5.18–5.12 (m, 2H), 3.78 (q, J = 7.1 Hz, 1H), 2.45 (d, J = 7.2 Hz, 2H), 1.89–

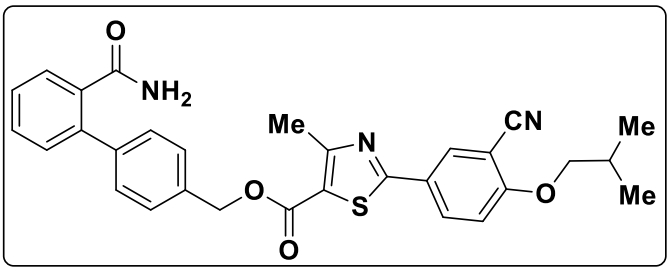
1.80 (m, 1H), 1.53 (d, J = 7.1 Hz, 3H), 0.89 (d, J = 6.6 Hz, 6H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 174.7, 171.2, 140.8, 140.0, 139.5, 137.7, 136.1, 134.5, 130.7, 130.5, 129.5, 129.2, 129.0, 128.1, 127.9, 127.4, 66.0, 45.3, 45.2, 30.3, 22.5, 18.6. **IR** (neat) 3390, 3184, 2957, 2928, 1731, 1640, 1453, 1382, 1660, 1073 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{27}H_{29}NO_3Na$ 438.2045, found 438.2045.

(2'-carbamoyl-[1,1'-biphenyl]-4-yl)methyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (I30)



The title compound was prepared by following the general procedure B in 79% yield (417 mg, 0.79 mmol) as a white solid. **m.p.** 140-142 °C. **^1H NMR** (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.6, 1.5 Hz, 1H), 7.67–7.64 (m, 4H), 7.49–7.45 (m, 1H), 7.44–7.37 (m, 5H), 7.32–7.28 (m, 3H), 6.81–6.78 (m, 2H), 5.96 (brs, 1H), 5.43 (brs, 1H), 5.24 (s, 2H), 1.70 (s, 6H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 194.5, 173.6, 171.7, 159.7, 140.5, 139.2, 138.6, 136.4, 134.8, 134.8, 132.2, 131.3, 130.7, 130.5, 130.4, 129.0, 128.8, 128.7, 128.7, 127.9, 117.4, 79.6, 67.0, 25.6. **IR** (neat) 3454, 3321, 3162, 2932, 2855, 1738, 1652, 1600, 1380, 1255, 1172, 1132 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{31}H_{26}ClNO_5Na$ 550.1397, found 550.1395.

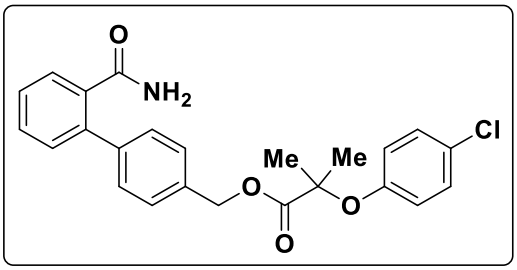
(2'-carbamoyl-[1,1'-biphenyl]-4-yl)methyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (I31)



The title compound was prepared by following the general procedure B in 36 % yield (189 mg, 0.36 mmol) as a white solid. **m.p.** 170-172 °C; **^1H NMR** (500 MHz, $CDCl_3$) δ 8.18 (d, J = 2.2 Hz, 1H), 8.10 (dd, J = 8.8, 2.3 Hz, 1H), 7.75 (dd, J = 7.6, 1.5 Hz, 1H), 7.53–7.48 (m, 5H), 7.47–7.40 (m, 1H), 7.37 (dd, J = 7.6, 1.3 Hz, 1H), 7.01 (d, J = 8.8 Hz, 1H), 5.59 (brs, 1H), 5.38 (s, 2H), 5.33 (brs, 1H), 3.90 (d, J = 6.4 Hz, 2H), 2.79 (s, 3H), 2.26–2.14 (m, 1H), 1.09 (d, J = 6.7 Hz, 6H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$) δ 171.4, 167.7, 162.7, 161.9, 161.9, 140.4, 139.4, 135.4, 134.6, 132.8, 132.3, 130.8, 130.6, 129.2, 129.0, 128.5, 128.0, 126.0, 121.4, 115.5, 112.8, 103.2, 75.9, 66.6, 28.3, 19.2, 17.7. **IR** (neat) 3370, 3181, 2963, 2228, 1716, 1644, 1507,

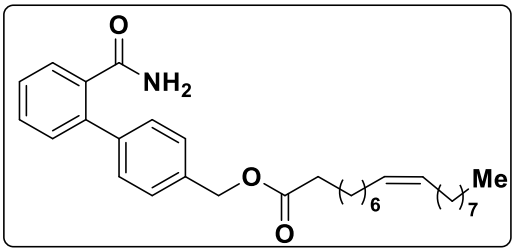
1369, 1252, 1080 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{30}H_{28}N_3O_4S$ 526.1795 found 526.1803.

(2'-carbamoyl-[1,1'-biphenyl]-4-yl)methyl 2-(4-chlorophenoxy)-2-methylpropanoate (I32)



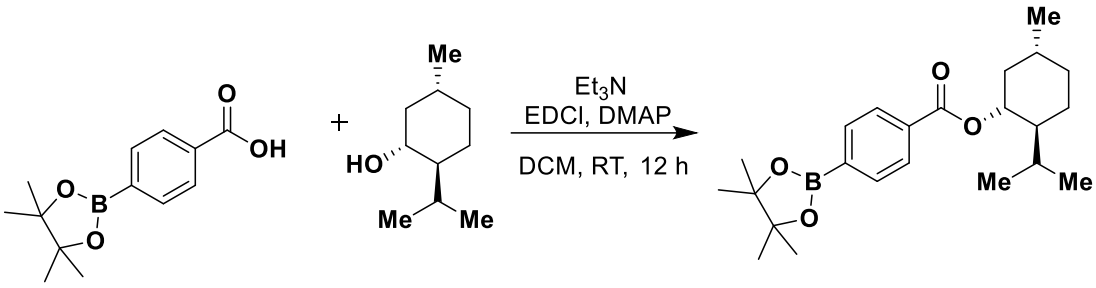
The title compound was prepared by following the general procedure B in 54% yield (229 mg, 0.54 mmol) as a white solid. **m.p.** 64-66 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.75–7.71 (m, 1H), 7.53–7.48 (m, 1H), 7.45–7.39 (m, 3H), 7.37–7.34 (m, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.15–7.11 (m, 2H), 6.75–6.71 (m, 2H), 5.84 (brs, 1H), 5.35 (brs, 1H), 5.23 (s, 2H), 1.61 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.9, 171.6, 154.1, 140.4, 139.4, 135.1, 134.5, 130.8, 130.6, 129.2, 129.1, 129.0, 128.6, 127.9, 127.34, 120.6, 79.7, 66.9, 25.5. **IR** (neat) 3456, 3293, 3178, 2921, 1720, 1650, 1605, 1484, 1387, 1278 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{22}ClNO_4Na$ 446.1135, found 446.1158.

(2'-carbamoyl-[1,1'-biphenyl]-4-yl)methyl oleate (I33)



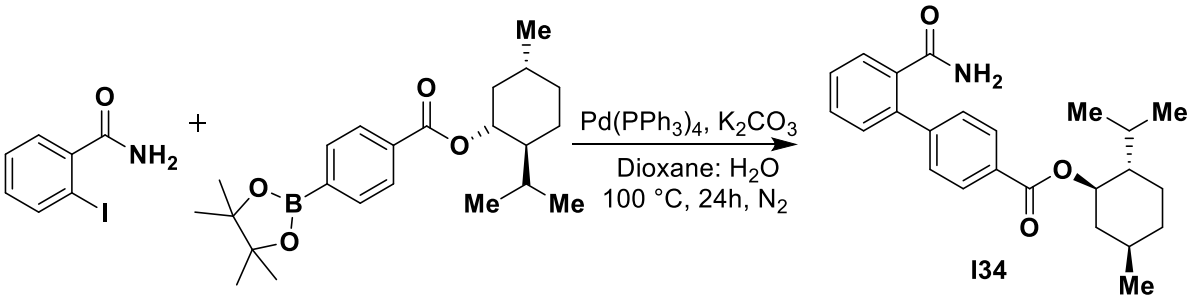
The title compound was prepared by following the general procedure B in 52% yield (256 mg, 0.52 mmol) as a white solid. **m.p.** 84-86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77–7.74 (m, 1H), 7.52–7.48 (m, 1H), 7.46–7.42 (m, 3H), 7.42–7.39 (m, 2H), 7.36–7.34 (m, 1H), 5.64 (brs, 1H), 5.35–5.29 (m, 3H), 5.15 (s, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.03–1.98 (m, 4H), 1.95–1.89 (m, 2H), 1.72–1.63 (m, 4H), 1.35–1.27 (m, 14H), 1.17–1.06 (m, 2H), 0.87 (t, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.8, 171.4, 140.1, 139.5, 136.1, 134.6, 130.7, 130.5, 130.2, 129.9, 129.1, 128.5, 127.9, 65.8, 49.4, 34.4, 34.0, 32.0, 29.9, 29.8, 29.6, 29.4, 29.3, 27.4, 27.3, 25.7, 25.1, 22.8, 14.2. **IR** (neat) 3377, 3189, 2823, 2853, 1731, 1625, 1389, 1155 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{32}H_{46}NO_3$ 492.3478, found 492.3487.

2.5 Procedure for the synthesis of (1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate



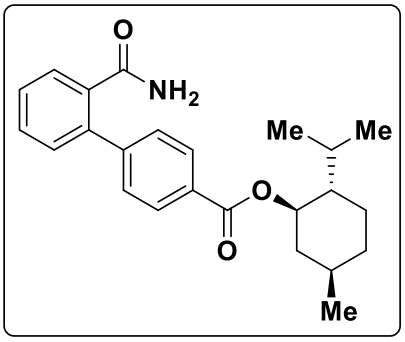
The Bpin derivative was synthesized by following a previously reported literature procedure[9]. In a 25 mL round-bottom flask, triethylamine (2.2 equiv.) was added to a dry DCM (0.2 M) solution containing the menthol (2.5 mmol, 1.0 equiv), DMAP (0.2 equiv), 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (2.5 mmol, 1.0 equiv), and EDCI (2.0 equiv). The reaction mixture was stirred at room temperature for 12 hours. Upon completion, the reaction mixture was quenched with water and extracted three times with DCM. The combined organic layers were washed with saturated brine (10 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (5% EA/Hexane) to afford the corresponding pinacol borate derivative.

2.6 Procedure for the synthesis of I34



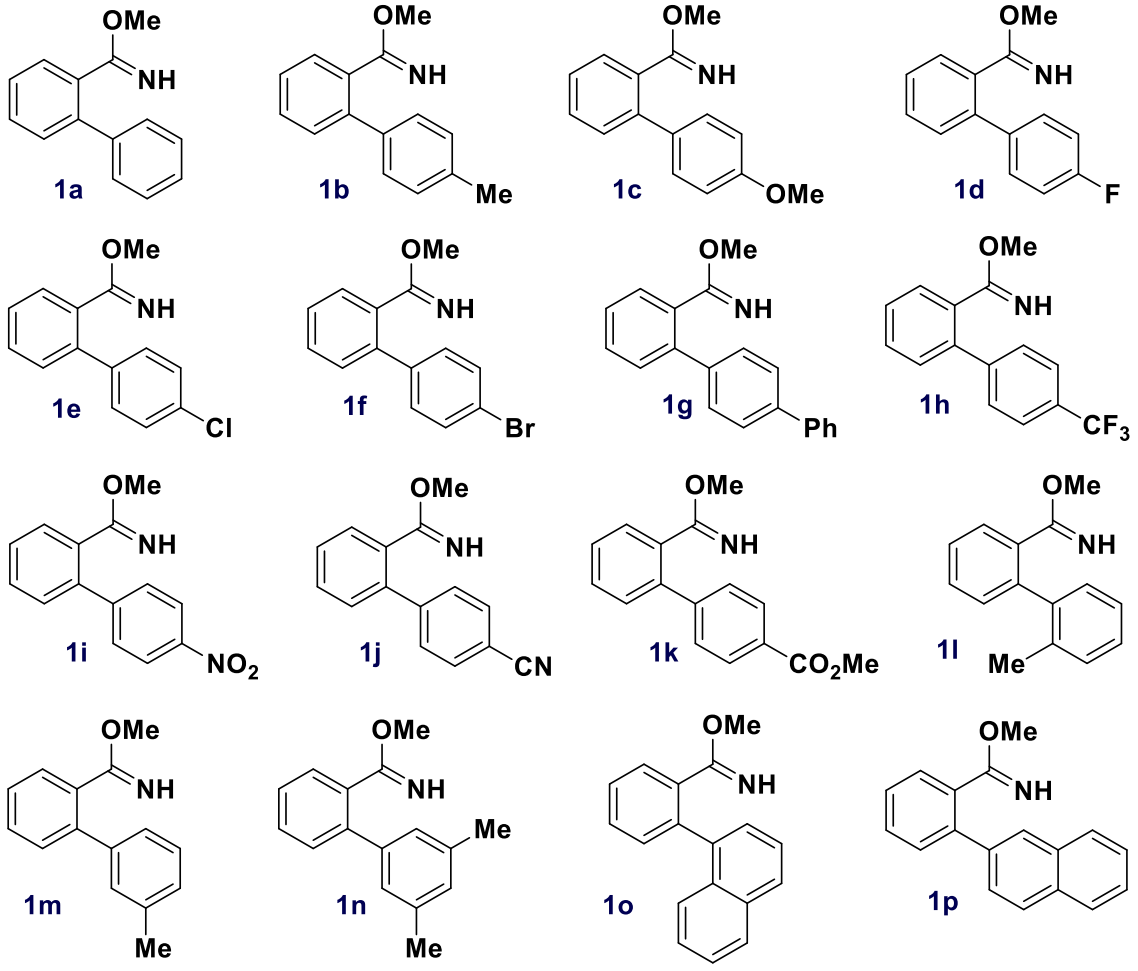
In a nitrogen atmosphere, oven-dried round-bottom flask equipped with a magnetic stir bar, 2-iodobenzamide (1 mmol) was added. To the above mixture, $Pd(PPh_3)_4$ (5 mol%) was added, followed by corresponding pinacol borate (1.2 equiv.) and K_2CO_2 (3.0 equiv.). Then, 1,4-dioxane (5 mL) and deionized H_2O (2 mL) was added to the mixture. The reaction mixture was stirred at 100 °C for 24 hours. Then it was cooled to room temperature and diluted with water. The aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with aq. NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography using 15–20% ethyl acetate in hexane, afford product **I34**.

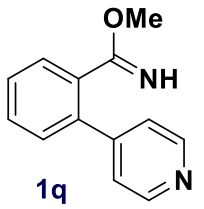
(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2'-carbamoyl-[1,1'-biphenyl]-4-carboxylate (I34)



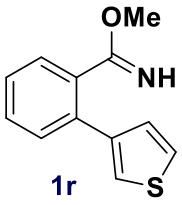
47% yield (178 mg, 0.47 mmol) as a colorless viscous liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10–8.08 (m, 2H), 7.76–7.71 (m, 1H), 7.55–7.49 (m, 3H), 7.49–7.42 (m, 1H), 7.40–7.34 (m, 1H), 5.77 (brs, 1H), 5.37 (brs, 1H), 4.99–4.91 (m, 1H), 2.17–2.09 (m, 1H), 2.03–1.93 (m, 1H), 1.78–1.70 (m, 2H), 1.62–1.52 (m, 2H), 1.18–1.08 (m, 2H), 0.95–0.91 (m, 6H), 0.92–0.86 (m, 1H), 0.80 (d, J = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.3, 165.9, 144.7, 139.1, 134.7, 130.8, 130.4, 130.0, 129.0, 128.9, 128.3, 75.2, 47.4, 41.1, 34.4, 31.6, 26.6, 25.0, 22.2, 20.9, 16.6. **IR** (neat) 3381, 3149, 2988, 2868, 1705, 1647, 1380, 1274, 1103 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{24}H_{29}NO_3Na$, 402.2045 found 402.2050.

List of 2-aryl benzimidates

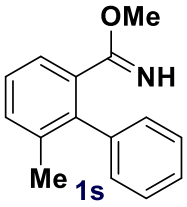




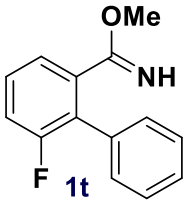
1q



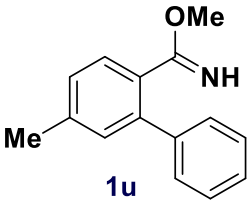
1r



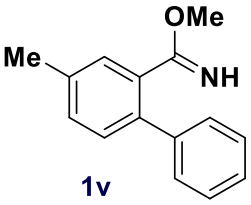
1s



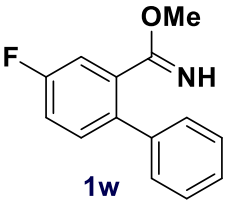
1t



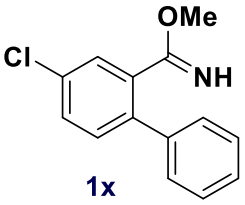
1u



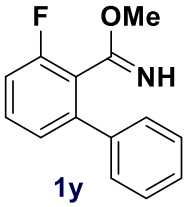
1v



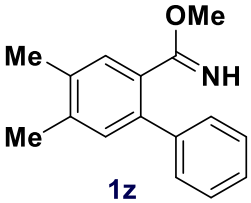
1w



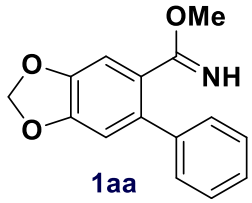
1x



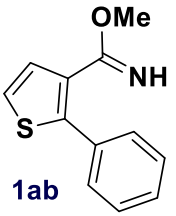
1y



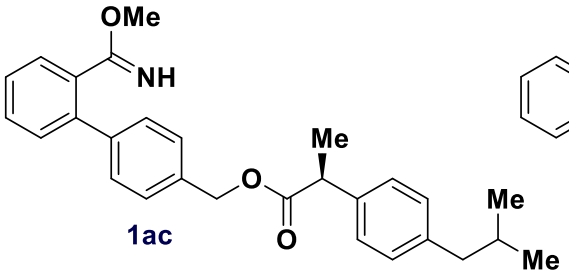
1z



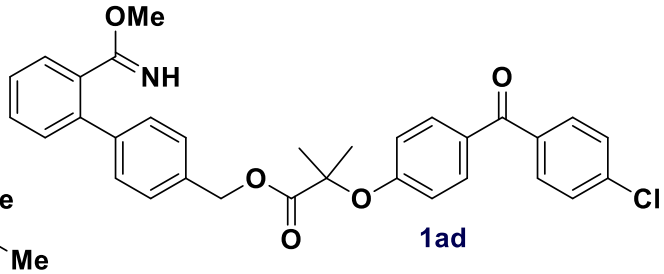
1aa



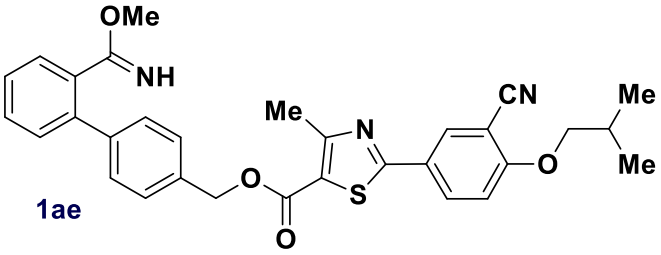
1ab



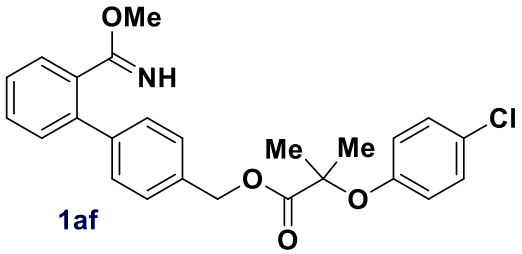
1ac



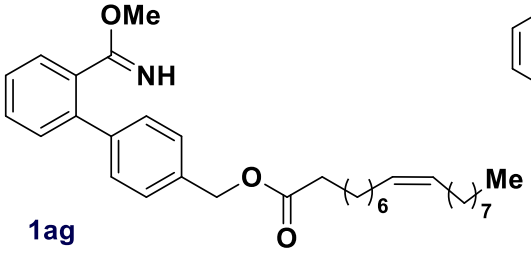
1ad



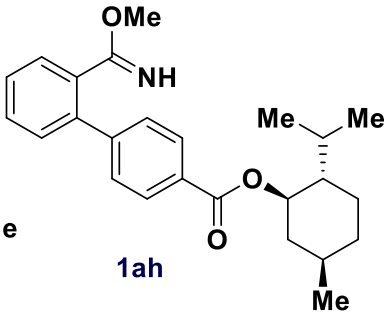
1ae



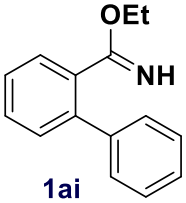
1af



1ag

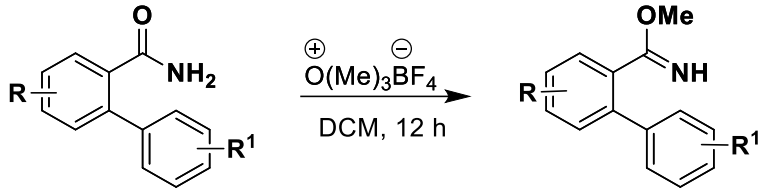


1ah



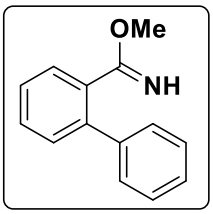
1ai

2.7 General procedure for the synthesis of 1a–1ah (General Procedure C)



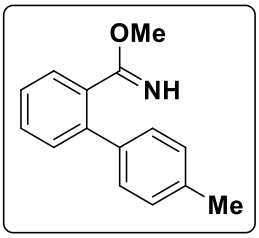
A solution of biphenyl carboxamide derivatives (0.5 mmol, 1.0 equiv.) in 6 mL of DCM was cooled to 0 °C, followed by the addition of trimethyloxonium tetrafluoroborate (1.5 equiv.). The reaction mixture was then allowed to warm to room temperature and stirred overnight. After completion, 1.5 mL of methanol was added to the reaction mixture, which was then concentrated under reduced pressure. The resulting crude product was purified by column chromatography using deactivated silica gel and using an ethyl acetate/hexane (5–20%) to afford the desired methyl biphenyl carbimidate derivatives **1**.

methyl [1,1'-biphenyl]-2-carbimidate (1a)



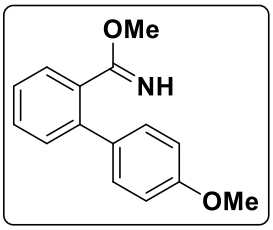
The title compound was prepared by following the general procedure C in 66% yield (70 mg, 0.33 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.48–7.44 (m, 1H), 7.42–7.34 (m, 7H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 140.6, 140.4, 134.2, 130.6, 130.0, 128.6, 128.5, 128.2, 127.6, 127.5, 53.4. **IR** (neat) 3324, 2926, 2857, 1727, 1566, 1460, 1367, 1238, 1092 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{14}NO$ 212.1070, found 212.1078.

methyl 4'-methyl-[1,1'-biphenyl]-2-carbimidate (1b)



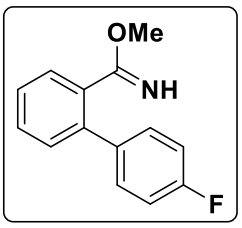
The title compound was prepared by following the general procedure C in 56% yield (63 mg, 0.28 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56–7.53 (m, 1H), 7.46–7.42 (m, 1H), 7.38–7.34 (m, 2H), 7.27–7.24 (m, 2H), 7.22–7.19 (m, 2H), 3.73 (s, 3H), 2.39 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 140.4, 137.6, 137.4, 134.0, 130.6, 130.0, 129.3, 128.4, 128.2, 127.2, 53.4, 21.3; **IR** (neat) 3321, 2926, 2857, 1727, 1655, 1460, 1367, 1238, 1092 cm^{-1}; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1226 , found 226.1245.

methyl 4'-methoxy-[1,1'-biphenyl]-2-carbimidate (1c)



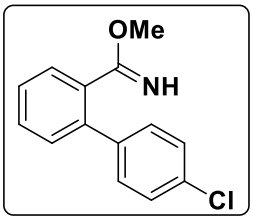
The title compound was prepared by following the general procedure C in 66% yield (80 mg, 0.33 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55–7.51 (m, 1H), 7.46–7.41 (m, 1H), 7.37–7.32 (m, 2H), 7.31–7.27 (m, 2H), 6.96–6.91 (m, 2H), 3.84 (s, 3H), 3.73 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.7, 159.3, 140.0, 134.0, 133.0, 130.6, 130.0, 129.7, 128.2, 127.1, 114.1, 55.4, 53.5. **IR** (neat) 3318, 2940, 1632, 1580, 1340, 1172, 1080 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO_2$ 242.1176, found 242.1200.

methyl 4'-fluoro-[1,1'-biphenyl]-2-carbimidate (1d)



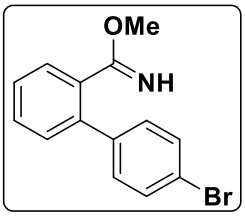
The title compound was prepared by following the general procedure C in 52% yield (60 mg, 0.26 mmol) as a yellow solid. **m.p.** 38-40 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56–7.51 (m, 1H), 7.49–7.42 (m, 1H), 7.42–7.34 (m, 1H), 7.36–7.28 (m, 3H), 7.13–7.05 (m, 2H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 162.6 (d, J = 246.8 Hz), 139.3, 136.7 (d, J = 3.4 Hz),134.3, 130.5, 130.2, 130.1, 128.3, 127.6, 115.5 (d, J = 21.5 Hz), 53.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.03 to -115.09 (m, 1F). **IR** (neat) 3310, 2940, 1632, 1598, 1515, 1437, 1353, 1221, 1660, 1070 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}FNO$ 230.0976, found 230.0980.

methyl 4'-chloro-[1,1'-biphenyl]-2-carbimidate (1e)



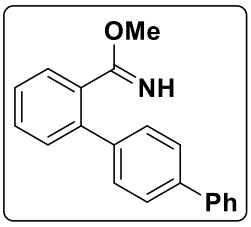
The title compound was prepared by following the general procedure C in 96% yield (114 mg, 0.46 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57–7.52 (m, 1H), 7.50–7.43 (m, 1H), 7.43–7.34 (m, 3H), 7.36–7.31 (m, 1H), 7.32–7.26 (m, 2H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 139.1, 139.0, 134.2, 133.8, 130.4, 130.2, 129.8, 128.7, 128.4, 127.8, 53.6. **IR** (neat) 3328, 2948, 1641, 1442, 1340, 1168, 1080 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}ClNO$ 246.0680, found 246.0660.

methyl 4'-bromo-[1,1'-biphenyl]-2-carbimidate (1f)



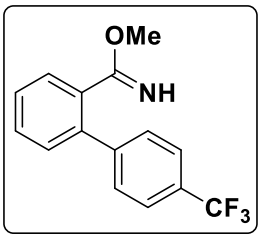
The title compound was prepared by following the general procedure C in 62% yield (90 mg, 0.31 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55–7.51 (m, 3H), 7.48–7.43 (m, 1H), 7.41–7.37 (m, 1H), 7.34–7.31 (m, 1H), 7.25–7.21 (m, 2H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.7, 140.4, 134.2, 130.6, 130.1, 129.0, 128.3, 127.5, 127.3, 127.2, 53.5. **IR** (neat) 3321, 2948, 1641, 1442, 1340, 1168, 1075, 1005 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}BrNO$ 290.0181, found 290.0177.

methyl [1,1':4',1''-terphenyl]-2-carbimidate (1g)



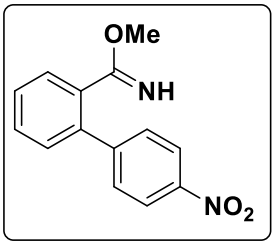
The title compound was prepared by following the general procedure C in 77% yield (111 mg, 0.38 mmol) as a white solid. **m.p.** 86-88 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66–7.62 (m, 4H), 7.50–7.35 (m, 9H), 7.31 (s, 1H), 3.74 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.8, 140.4, 139.9, 139.6, 134.2, 130.6, 130.1, 129.0, 128.3, 127.5, 127.3, 127.2, 53.5. **IR** (neat) 3308, 2941, 1632, 1435, 1345, 1168, 1070 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{18}NO$ 288.1383, found 288.1403.

methyl 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbimidate (1h)



The title compound was prepared by following the general procedure C in 51% yield (71 mg, 0.25 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67–7.64 (m, 2H), 7.58–7.55 (m, 1H), 7.51–7.46 (m, 3H), 7.45–7.41 (m, 1H), 7.37–7.35 (m, 1H), 3.67 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.4, 144.4, 138.8, 134.4, 130.4, 130.3, 129.8 (q, J = 32 Hz), 128.8, 128.5, 128.3, 125.5 (q, J = 3.8 Hz), 124.3 (q, J = 272 Hz), 53.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.48. **IR** (neat) 3326, 2948, 1639, 1437, 1318, 1168, 1119, 1068 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{13}F_3NO$ 280.0949, found 280.0957.

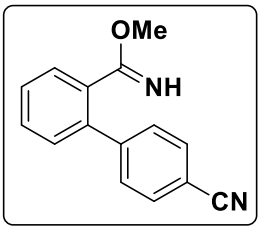
methyl 4'-nitro-[1,1'-biphenyl]-2-carbimidate (1i)



The title compound was prepared by following the general procedure C in 77% yield (99 mg, 0.38 mmol) as a yellow solid. **m.p.** 80-82 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28–8.24 (m, 2H), 7.55–7.50 (m, 3H), 7.49–7.44 (m, 1H), 7.39–7.35 (m, 2H), 3.66 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.4, 147.6, 147.4, 137.8, 134.6, 130.4, 130.2,

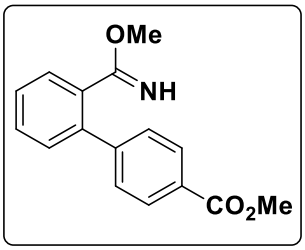
129.4, 128.8, 128.6, 123.8, 53.7. **IR** (neat) 3335, 2939, 1645, 1592, 1515, 149, 1340, 1168, 1070 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}N_2O_3$ 257.0921, found 257.0930.

methyl 4'-cyano-[1,1'-biphenyl]-2-carbimidate (1j)



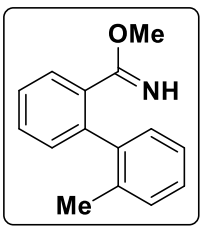
The title compound was prepared by following the general procedure C in 64% yield (76 mg, 0.32 mmol) as a white solid. **m.p.** 84-86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71–7.67 (m, 2H), 7.57–7.54 (m, 1H), 7.52–7.42 (m, 4H), 7.35–7.32 (m, 1H), 3.64 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.2, 145.6, 138.2, 134.4, 132.3, 130.4, 130.2, 129.2, 128.6, 128.6, 118.9, 111.4, 53.5. **IR** (neat) 3313, 2943, 2231, 1632, 1605, 1451, 1356, 1172, 1070, 1044 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{13}N_2O$ 237.1022, found 237.1034.

methyl 2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-carboxylate (1k)



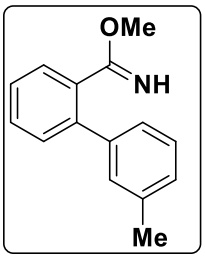
The title compound was prepared by following the general procedure C in 50% yield (67 mg, 0.25 mmol) as a white solid. **m.p.** 53-55 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09–8.05 (m, 2H), 7.57–7.53 (m, 1H), 7.50–7.46 (m, 1H), 7.44–7.40 (m, 3H), 7.39–7.36 (m, 1H), 3.94 (s, 3H), 3.65 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.4, 167.0, 145.5, 139.2, 134.4, 130.3, 130.2, 129.8, 129.3, 128.5, 128.4, 128.13, 53.5, 52.3. **IR** (neat) 3326, 2939, 1714, 1647, 1597, 1429, 1340, 1272, 1174, 1075 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO_3$ 270.1175, found 270.1157.

methyl 2'-methyl-[1,1'-biphenyl]-2-carbimidate (1l)



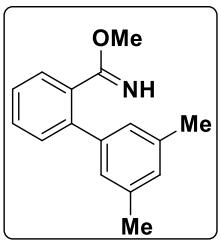
The title compound was prepared by following the general procedure C in 70% yield (79 mg, 0.35 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72–7.69 (m, 1H), 7.49–7.45 (m, 1H), 7.43–7.38 (m, 1H), 7.30–7.21 (m, 4H), 7.15–7.12 (m, 1H), 3.70 (s, 3H), 2.08 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.2, 140.5, 140.3, 135.7, 133.4, 130.8, 130.4, 130.0, 129.2, 128.0, 127.9, 127.5, 126.1, 53.5, 20.0. **IR** (neat) 3326, 2942, 1636, 1439, 1338, 1075, 1042 cm-1. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232, found 226.1235.

methyl 3'-methyl-[1,1'-biphenyl]-2-carbimidate (1m)



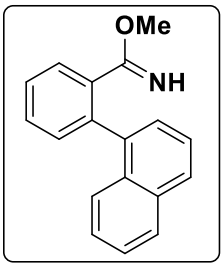
The title compound was prepared by following the general procedure C in 62% yield (70 mg, 0.31 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 1H), 7.47–7.43 (m, 1H), 7.39–7.35 (m, 2H), 7.30–7.27 (m, 1H), 7.19–7.13 (m, 3H), 3.72 (s, 3H), 2.39 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.6, 138.2, 133.9, 130.6, 130.0, 129.2, 128.4, 128.4, 128.2, 127.4, 125.6, 53.6, 21.6. **IR** (neat) 3324, 2945, 1639, 1433, 1347, 1165, 1073 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232, found 226.1237.

methyl 3',5'-dimethyl-[1,1'-biphenyl]-2-carbimidate (1n)



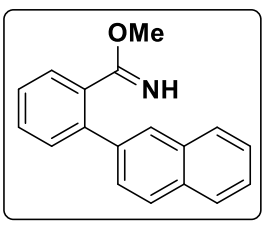
The title compound was prepared by following the general procedure C in 54% yield (65 mg, 0.27 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57–7.51 (m, 1H), 7.47–7.39 (m, 1H), 7.39–7.32 (m, 2H), 7.00–6.95 (m, 3H), 3.72 (s, 3H), 2.34 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 140.6, 140.5, 138.0, 134.0, 130.6, 129.9, 129.3, 128.1, 127.3, 126.3, 53.4, 21.4. **IR** (neat) 3332, 2945, 1639, 1601, 1445, 1340, 1168, 1070 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{17}NONa$ 262.1208, found 262.1221.

methyl 2-(naphthalen-1-yl)benzimidate (1o)



The title compound was prepared by following the general procedure C in 93% yield (121 mg, 0.46 mmol) as a white solid. **m.p.** 65-67 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92–7.85 (m, 2H), 7.75–7.72 (m, 1H), 7.57–7.46 (m, 5H), 7.42–7.36 (m, 3H), 7.07 (brs, 1H), 3.50 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.2, 139.0, 138.4, 134.8, 133.7, 131.9, 131.8, 129.9, 128.4, 128.3, 128.0, 127.9, 126.7, 126.4, 126.1, 125.6, 125.4, 53.3. **IR** (neat) 3330, 3060, 3010, 2937, 1632, 1431, 1340, 1340, 1170, 1080 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{16}NO$ 262.1226, found 262.1232.

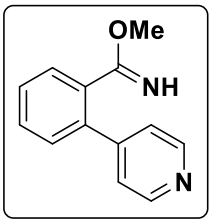
methyl 2-(naphthalen-2-yl)benzimidate (1p)



The title compound was prepared by following the general procedure C in 74% yield (97 mg, 0.37 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91–7.83 (m, 4H), 7.60 (d, J = 7.6 Hz, 1H), 7.53–7.46 (m, 5H), 7.44–7.40 (m, 1H), 7.31 (s, 1H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.2, 138.2, 134.4, 133.5, 132.7, 130.9, 130.10, 128.3, 128.2,

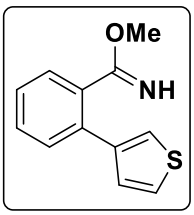
128.1, 127.8, 127.6, 127.3, 126.8, 126.4, 126.3, 53.6. **IR** (neat) 3321, 2939, 1636, 1435, 1336, 1165, 1073 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{16}NO$ 262.1226, found 262.1231.

methyl 2-(pyridin-4-yl)benzimidate (1q)



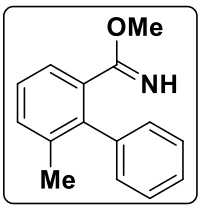
The title compound was prepared by following the general procedure C in 30% yield (32 mg, 0.15 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65–8.62 (m, 2H), 7.58–7.55 (m, 1H), 7.53–7.49 (m, 1H), 7.47–7.44 (m, 1H), 7.38–7.35 (m, 1H), 7.30–7.28 (m, 2H), 3.65 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.3, 150.0, 149.8, 137.3, 134.4, 130.4, 130.1, 128.8, 128.6, 123.3, 53.6. **IR** (neat) 3344, 2828, 1641, 1597, 1435, 1349, 1179, 1086 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{13}N_2O$ 213.1022, found 213.1028.

methyl 2-(thiophen-3-yl)benzimidate (1r)



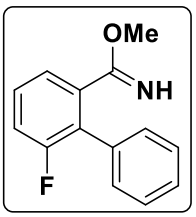
The title compound was prepared by following the general procedure C in 73% yield (79 mg, 0.36 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51–7.49 (m, 1H), 7.43–7.40 (m, 2H), 7.36–7.32 (m, 2H), 7.30–7.28 (m, 1H), 7.12 (dd, J = 5.0, 1.4 Hz, 1H), 3.77 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.7, 140.8, 134.7, 134.0, 130.2, 130.0, 128.1, 128.0, 127.5, 125.8, 122.6, 53.5. **IR** (neat) 3321, 2943, 1636, 1437, 1342, 1168, 1075 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{12}H_{11}NOSNa$ 240.0459, found 240.0467.

methyl 6-methyl-[1,1'-biphenyl]-2-carbimidate (1s)



The title compound was prepared by following the general procedure C in 69% yield (78 mg, 0.34 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51–7.46 (m, 3H), 7.45–7.39 (m, 2H), 7.39–7.33 (m, 1H), 7.29–7.25 (m, 2H), 7.13 (brs, 1H), 3.65 (s, 3H), 2.20 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.3, 139.8, 139.6, 137.0, 135.0, 131.6, 128.9, 128.5, 127.4, 127.4, 125.2, 53.2, 20.8. **IR** (neat) 3328, 2943, 1636, 1435, 1336, 1079, 1011 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232, found 226.1235.

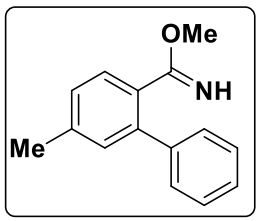
methyl 6-fluoro-[1,1'-biphenyl]-2-carbimidate (1t)



The title compound was prepared by following the general procedure C in 82% yield (94 mg, 0.41 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.45–7.41 (m, 2H), 7.40–7.35 (m, 3H), 7.34–7.31 (m, 2H), 7.24–7.19 (m, 1H), 3.64 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.0 (d, J =

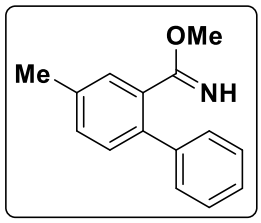
3.2 Hz), 160.8, 158.8, 136.5 (d, J = 2.9 Hz), 133.4, 129.5 (d, J = 1.6 Hz), 129.1 (d, J = 8.7 Hz), 128.5, 128.3, 123.8 (d, J = 3.6 Hz), 117.4 (d, J = 23.4 Hz), 53.5. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.59 to -114.62 (m, 1F). **IR** (neat) 3328, 2948, 1640, 1433, 1336, 1241, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}FNO$ 230.0981, found 230.0988.

methyl 5-methyl-[1,1'-biphenyl]-2-carbimidate (1u)



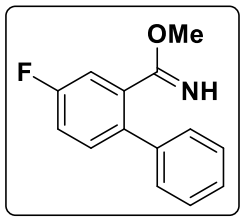
The title compound was prepared by following the general procedure C in 58% yield (65 mg, 0.29 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47 (d, J = 7.7 Hz, 1H), 7.41–7.37 (m, 2H), 7.36–7.32 (m, 3H), 7.20–7.16 (m, 2H), 3.69 (s, 3H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.8, 140.4, 140.2, 131.4, 131.1, 128.5, 128.5, 128.3, 128.1, 127.6, 53.5, 21.4. **IR** (neat) 3328, 2945, 1634, 1435, 1336, 1192, 1161, 1075 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232, found 226.1234.

methyl 4-methyl-[1,1'-biphenyl]-2-carbimidate (1v)



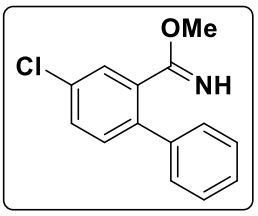
The title compound was prepared by following the general procedure C in 90% yield (101 mg, 0.45 mmol) as a white solid. **m.p.** 48-50 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.36 (m, 3H), 7.35–7.31 (m, 3H), 7.28–7.25 (m, 2H), 3.70 (s, 3H), 2.41 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.7, 140.6, 137.6, 137.3, 133.9, 130.8, 130.5, 128.8, 128.5, 128.5, 127.4, 53.5, 21.1. **IR** (neat) 3308, 2945, 1636, 1435, 1336, 1196, 1119, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1226, found 226.1235.

methyl 4-fluoro-[1,1'-biphenyl]-2-carbimidate (1w)



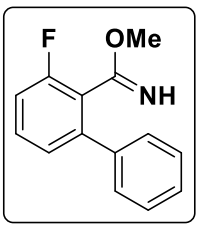
The title compound was prepared by following the general procedure C in 83% yield (95 mg, 0.41 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42–7.25 (m, 7H), 7.18–7.14 (m, 1H), 3.71 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.8, 162.8, 160.8, 139.7, 136.6 (d, J = 3.4 Hz), 135.4 (d, J = 7.3 Hz), 132.3 (d, J = 7.9 Hz), 128.6 (d, J = 10.6 Hz), 127.8,116.9 (d, J = 21.0 Hz), 115.3 (d, J = 23.1 Hz), 53.6. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -114.63 to -114.68 (m, 1F). **IR** (neat) 3332, 2943, 1643, 1608, 1580, 1477, 1446, 1336, 1258, 1073 cm^{-1}; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}FNO$ 230.0976, found 230.0995.

methyl 4-chloro-[1,1'-biphenyl]-2-carbimidate (1x)



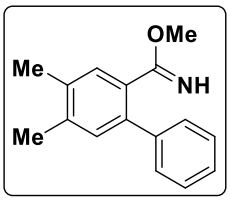
The title compound was prepared by following the general procedure C in 69% yield (85 mg, 0.34 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.3 Hz, 1H), 7.44–7.35 (m, 4H), 7.33–7.28 (m, 3H), 3.71 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.9, 139.5, 138.9, 135.3, 133.5, 131.9, 130.0, 128.7, 128.4, 128.3, 128.0, 53.6. **IR** (neat) 3332, 2943, 1647, 1473, 1168, 1326, 1026 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}ClNO$ 246.0680, found 246.0694.

methyl 3-fluoro-[1,1'-biphenyl]-2-carbimidate (1y)



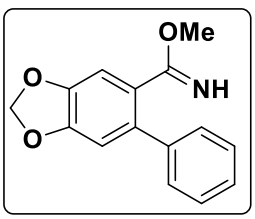
The title compound was prepared by following the general procedure C in 92% yield (105 mg, 0.46 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.43–7.33 (m, 6H), 7.20–7.17 (m, 1H), 7.13–7.08 (m, 1H), 3.70 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 165.7, 160.4, 158.4,142.2 (d, *J* = 2.8 Hz), 139.4 (d, *J* = 2.3 Hz), 130.7 (d, *J* = 9.0 Hz), 128.4 (d, *J* = 23.7 Hz), 128.0, 125.8, 123.3 (d, *J* = 16.6 Hz), 114.7 (d, *J* = 22.0 Hz), 53.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.47 to -115.50 (m, 1F). **IR** (neat) 3332, 2948, 1647, 1608, 1460, 1338, 1235, 1080 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{13}FNO$ 230.0976, found 230.0981.

methyl 4,5-dimethyl-[1,1'-biphenyl]-2-carbimidate (1z)



The title compound was prepared by following the general procedure C in 78% yield (93 mg, 0.39 mmol) as a white solid. **m.p.** 66-68 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.31 (m, 6H), 7.14 (s, 1H), 3.71 (s, 3H), 2.32 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.7, 138.8, 138.0, 135.9, 131.9, 131.3, 129.4, 128.5, 128.5, 127.4, 53.4, 19.8, 19.4. **IR** (neat) 3337, 2940, 1625, 1425, 1333, 1183, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{16}H_{17}NONa$ 262.1208, found 262.1221.

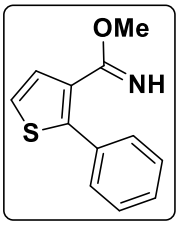
methyl 6-phenylbenzo[d][1,3]dioxole-5-carbimidate (1aa)



The title compound was prepared by following the general procedure C in 88% yield (112 mg, 0.44 mmol) as a white solid. **m.p.** 71-73 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.35 (m, 2H), 7.34–7.32 (m, 1H), 7.32–7.28 (m, 2H), 7.05 (s, 1H), 6.80 (s, 1H), 6.03 (s, 2H), 3.68 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.8, 148.9, 147.0, 140.5, 135.7, 128.6, 128.6, 127.6,

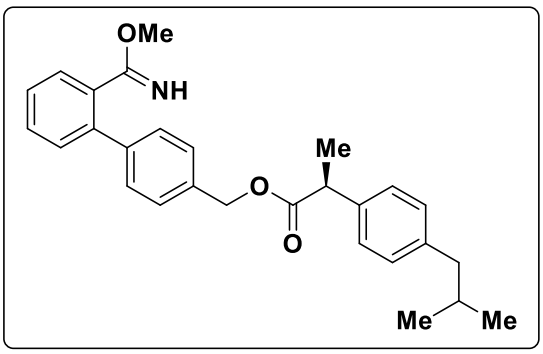
127.4, 110.7, 108.5, 101.8, 53.6. **IR** (neat) 3306, 2923, 1630, 1608, 1482, 1442, 1362, 1236, 1061, 1026 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO_3$ 256.0974, found 256.0977.

methyl 2-phenylthiophene-3-carbimidate (1ab)



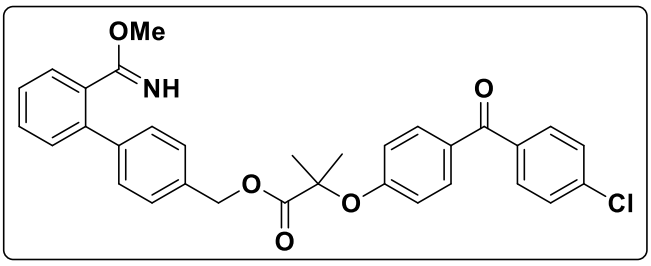
The title compound was prepared by following the general procedure C in 75% yield (81 mg, 0.37 mmol) as a white solid. **m.p.** 38-40 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.48–7.36 (m, 7H), 7.04–6.99 (m, 1H), 3.84 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.0, 144.0, 135.6, 130.9, 129.3, 129.1, 128.8, 128.4, 127.2, 53.3. **IR** (neat) 3332, 2938, 1623, 1440, 1316, 1132, 1101, 1057 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{12}H_{12}NOS$ 218.0634, found 218.0618.

(2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-yl)methyl (S)-2-(4-isobutylphenyl)propanoate (1ac)



The title compound was prepared by following the general procedure C in 90% yield (193 mg, 0.45 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60–7.55 (m, 1H), 7.50–7.44 (m, 1H), 7.42–7.36 (m, 1H), 7.37–7.31 (m, 1H), 7.32–7.26 (m, 2H), 7.28–7.23 (m, 2H), 7.25–7.19 (m, 2H), 7.13–7.07 (m, 2H), 5.19–5.09 (m, 2H), 3.77 (q, J = 7.1 Hz, 1H), 3.71 (s, 3H), 2.45 (d, J = 7.2 Hz, 2H), 1.88–1.80 (m, 1H), 1.53 (d, J = 7.1 Hz, 3H), 0.90 (d, J = 6.6 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 174.7, 170.8, 140.8, 140.3, 140.0, 137.7, 135.6, 130.6, 130.3, 129.5, 128.6, 128.5, 128.0, 127.6, 127.4, 66.1, 54.0, 45.3, 45.2, 30.3, 22.5, 18.6. **IR** (neat) 3326, 2952, 1734, 1639, 1453, 1336, 1161, 1075, 1006 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{32}NO_3$ 430.2382, found 430.2401.

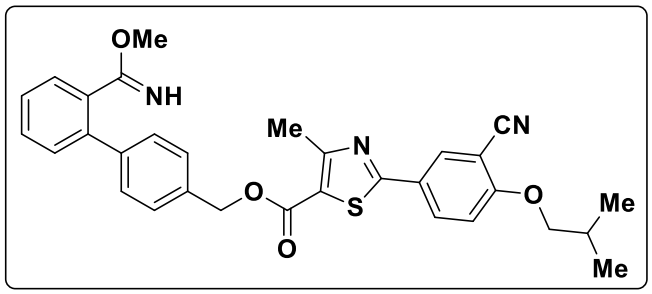
(2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-yl)methyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (1ad)



The title compound was prepared by following the general procedure C in 63% yield (170 mg, 0.31 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69–7.64 (m, 4H), 7.57–7.54 (m, 1H), 7.47–7.43 (m, 1H), 7.41–7.37 (m, 3H), 7.32–7.28 (m, 5H), 6.82–6.80 (m, 2H), 5.23 (s, 2H), 3.67 (s, 3H), 1.69 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 194.3, 173.6, 170.4,

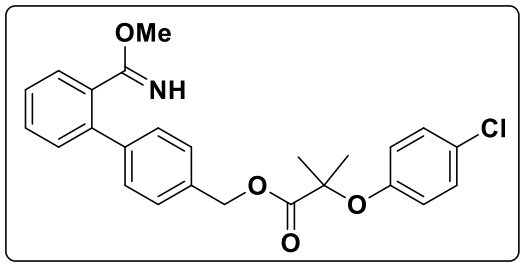
159.7, 140.9, 139.6, 138.5, 136.4, 134.4, 134.1, 132.1, 131.3, 130.5, 130.5, 130.2, 128.7, 128.6, 128.6, 128.3, 127.7, 117.5, 79.6, 67.2, 53.5, 25.6. **IR** (neat) 3326, 2941, 1738, 1643, 1594, 1345, 1280, 1247, 1172, 1128 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{32}H_{28}ClNO_5Na$ 564.1554, found 564.1558.

(2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-yl)methyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (1ae)



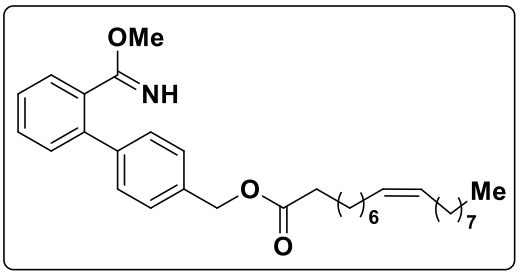
The title compound was prepared by following the general procedure C in 36% yield (97 mg, 0.18 mmol) as a white solid. **m.p.** 141-143 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 2.3 Hz, 1H), 8.09 (dd, *J* = 8.8, 2.3 Hz, 1H), 7.61–7.56 (m, 1H), 7.50–7.44 (m, 3H), 7.43–7.34 (m, 4H), 7.00 (d, *J* = 8.9 Hz, 1H), 5.37 (s, 2H), 3.89 (d, *J* = 6.5 Hz, 2H), 3.73 (s, 3H), 2.79 (s, 3H), 2.26–2.14 (m, 1H), 1.09 (d, *J* = 6.7 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 167.6, 162.7, 162.0, 161.8, 140.8, 139.8, 135.0, 132.7, 132.3, 130.6, 130.3, 128.8, 128.4, 128.4, 127.7, 126.1, 121.6, 115.5, 112.8, 103.2, 75.8, 66.7, 53.8, 28.3, 19.2, 17.7. **IR** (neat) 3328, 2917, 2850, 2222, 1714, 1634, 1453, 1350, 1256, 1103, 1011 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{31}H_{29}N_3O_4SNa$ 562.1777 found 562.1777.

(2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-yl)methyl 2-(4-chlorophenoxy)-2-methylpropanoate (1af)



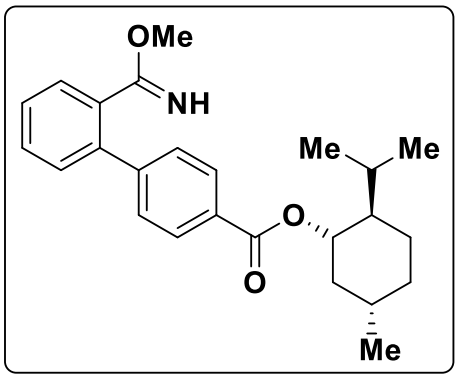
The title compound was prepared by following the general procedure C in 61% yield (134 mg, 0.30 mmol) as a pale yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.51–7.43 (m, 1H), 7.43–7.29 (m, 6H), 7.14 (d, *J* = 8.6 Hz, 2H), 6.77–6.70 (m, 2H), 5.23 (s, 2H), 3.69 (s, 3H), 1.61 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.9, 170.4, 154.1, 140.9, 139.7, 134.6, 134.2, 130.6, 130.1, 129.2, 128.7, 128.6, 128.3, 127.7, 127.4, 120.6, 79.7, 67.0, 53.5, 25.5. **IR** (neat) 3326, 2992, 2945, 1734, 1636, 1485, 1342, 1278, 1234, 1170, 1132, 1079 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{25}ClNO_4$ 438.1472, found 438.1491.

(2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-yl)methyl oleate (1ag)



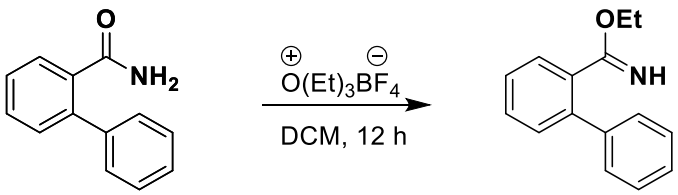
The title compound was prepared by following the general procedure C in 75% yield (190 mg, 0.37 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59–7.53 (m, 1H), 7.50–7.43 (m, 1H), 7.42–7.32 (m, 6H), 5.37–5.31 (m, 2H), 5.15 (s, 2H), 3.72 (s, 3H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.04–1.97 (m, 4H), 1.71–1.61 (m, 2H), 1.38–1.21 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.8, 170.5, 140.5, 139.9, 135.6, 134.0, 130.6, 130.2, 129.9, 128.7, 128.4, 128.3, 127.6, 127.3, 65.9, 53.6, 34.5, 32.0, 30.7, 29.9, 29.8, 29.7, 29.5, 29.3, 29.3, 29.2, 27.4, 27.3, 25.1, 22.8, 14.3. **IR** (neat) 3326, 2919, 2855, 1738, 1636, 1451, 1345, 1165, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{33}H_{48}NO_3$ 506.3629, found 506.3631.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 2'-(imino(methoxy)methyl)-[1,1'-biphenyl]-4-carboxylate (1ah)



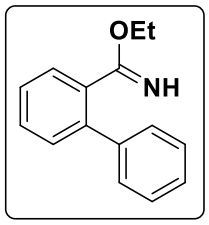
The title compound was prepared by following the general procedure C in 66% yield (130 mg, 0.33 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.9 Hz, 2H), 7.57–7.54 (m, 1H), 7.50–7.46 (m, 1H), 7.44–7.39 (m, 3H), 7.36 (d, *J* = 7.6 Hz, 1H), 4.99–4.91 (m, 1H), 3.69 (s, 3H), 2.17–2.13 (m, 1H), 2.01–1.96 (m, 1H), 1.77–1.71 (m, 2H), 1.60–1.53 (m, 2H), 1.16–1.07 (m, 2H), 0.97–0.87 (m, 7H), 0.81 (d, *J* = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.4 166.0, 145.2, 139.3, 134.3, 130.4, 130.2, 130.0, 129.8, 128.5, 128.4, 128.1, 75.1, 53.6, 47.4, 41.1, 34.5, 31.6, 26.6, 23.8, 22.2, 20.9, 16.6. **IR** (neat) 3330, 2950, 2868, 1712, 1636, 1455, 1340, 1260, 1172, 1103 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{32}NO_3$ 394.2382, found 394.2392.

2.7.1 Procedure for the synthesis of 1ai



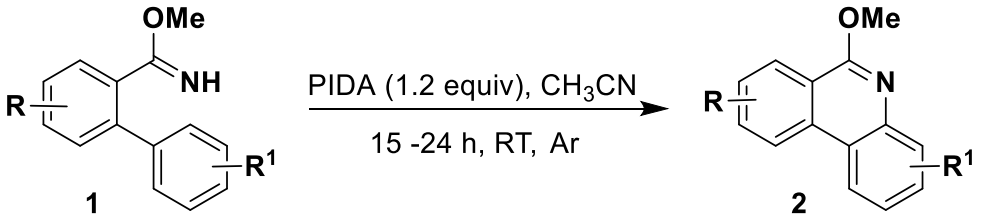
1ai

A solution of biphenyl carboxamide derivatives (0.5 mmol, 1.0 equiv.) in 6 mL of DCM was cooled to 0 °C, followed by the addition of triethylloxonium tetrafluoroborate (1.5 equiv.). The reaction mixture was then allowed to warm to room temperature and stirred overnight. After completion, 1.5 mL of methanol was added to the reaction mixture, which was then concentrated under reduced pressure. The resulting crude product was purified by column chromatography using deactivated silica gel and using an ethyl acetate/hexane (10%) to afford the desired ethyl biphenyl carbimidate derivatives **1ai**.



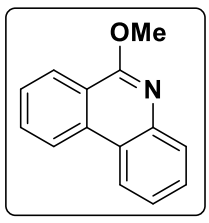
60% yield (67 mg, 0.3 mmol) as a light-yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 1H), 7.50 – 7.45 (m, 1H), 7.43 – 7.32 (m, 7H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.03 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.8, 140.8, 140.7, 133.7, 130.6, 130.4, 128.5, 128.5, 128.5, 127.5, 63.0, 13.8; **IR** (neat) 3058, 2978, 1716, 1634, 1450, 1371, 1281, 1072 cm^{-1}; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232, found 226.1246.

3. General procedure for the synthesis of phenanthridine 2 (General Procedure D)



Methyl biphenyl carbimidate **1** (0.1 mmol, 1.0 equiv.) and PIDA (0.12 mmol, 1.2 equiv.) were combined in a vial, and 0.5 mL of CH_3CN was added. The resulting mixture was stirred at room temperature under an argon atmosphere for 15–24 hours, with the progress of the reaction monitored by TLC. Afterwards, the solvent evaporated under reduced pressure, and the crude residue was purified by flash column chromatography on silica gel using a gradient of hexane/ethyl acetate (99:1 to 33:1) to obtain the target cyclized product **2**.

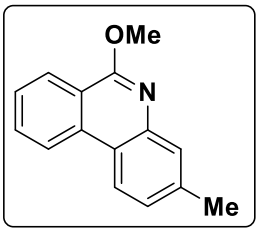
6-methoxyphenanthridine (2a)



The title compound was prepared by following the general procedure D in 98% yield (20.5 mg, 0.098 mmol) as a white solid. **m.p.** 44-46 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.3 Hz, 1H), 8.44–8.41 (m, 1H), 8.37–8.35 (m, 1H), 7.91 (dd, *J* = 8.2, 1.4 Hz, 1H), 7.82–7.78 (m, 1H), 7.65–7.61 (m, 2H), 7.51–7.47 (m, 1H), 4.25 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.3, 143.4, 134.9, 131.0, 128.9, 127.9, 127.3, 125.2, 124.5, 122.6, 122.2, 122.0, 120.2, 53.8. **IR** (neat) 2945, 2846,

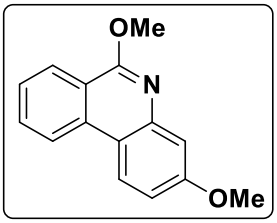
1725, 1720, 1577, 1429, 1356, 1311, 1223, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{12}NO$ 210.0913, found 210.0916.

6-methoxy-3-methylphenanthridine (2b)



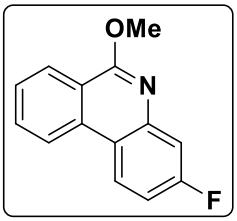
The title compound was prepared by following the general procedure D in 90% yield (20.1 mg, 0.09 mmol) as a white solid. **m.p.** 46-48 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.2 Hz, 1H), 8.34 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 7.79–7.75 (m, 1H), 7.72 (s, 1H), 7.62–7.58 (m, 1H), 7.31 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.23 (s, 3H), 2.55 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.5 143.6, 139.0, 135.1, 130.9, 127.8, 126.8, 126.1, 125.2, 122.0, 121.8, 120.3, 120.0, 53.6, 21.6. **IR** (neat) 2910, 2846, 1583, 1490, 1436, 1358, 1311, 1223, 1170, 1095 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1077.

3,6-dimethoxyphenanthridine (2c)



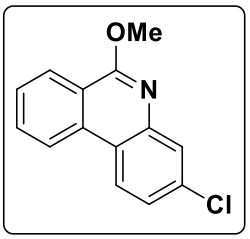
The title compound was prepared by following the general procedure D in 71% yield (17 mg, 0.071 mmol) as a white solid. **m.p.** 92-94 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42–8.36 (m, 1H), 8.35–8.27 (m, 2H), 7.80–7.73 (m, 1H), 7.59–7.52 (m, 1H), 7.35 (s, 1H), 7.15–7.08 (m, 1H), 4.23 (s, 1H), 3.97 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.5, 159.9, 145.0, 135.1, 131.0, 126.2, 125.2, 123.4, 121.5, 119.1, 116.4, 114.8, 108.7, 55.7, 53.8. **IR** (neat) 2926, 2846, 1617, 1581, 1484, 1433, 1358, 1212, 1163, 1028 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO_2$ 240.1019, found 240.1035.

3-fluoro-6-methoxyphenanthridine (2d)



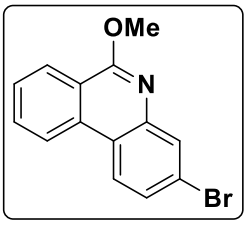
The title compound was prepared by following the general procedure D in 73% yield (16.6 mg, 0.073 mmol) as a white solid. **m.p.** 50-52 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.3 Hz, 1H), 8.38–8.32 (m, 2H), 7.82–7.78 (m, 1H), 7.64–7.60 (m, 1H), 7.55 (dd, *J* = 10.2, 2.7 Hz, 1H), 7.24–7.20 (m, 1H), 4.22 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 163.1 (d, *J* = 246.7 Hz), 160.2, 145.0 (d, *J* = 12.2 Hz), 134.6, 131.3, 127.2, 125.3, 123.9 (d, *J* = 9.9 Hz), 121.8, 119.7, 119.2 (d, *J* = 2.2 Hz), 113.0 (d, *J* = 4.0 Hz), 112.9 (d, *J* = 40.5 Hz), 53.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.79 to -112.84 (m, 1F). **IR** (neat) 2954, 2855, 1727, 1586, 1482, 1362, 1223, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}FNO$ 228.0825, found 228.0845.

3-chloro-6-methoxyphenanthridine (2e)



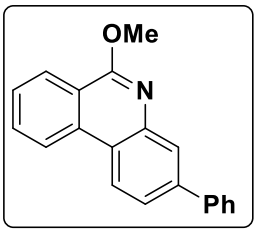
The title compound was prepared by following the general procedure D in 86% yield (21 mg, 0.086 mmol) as a white solid. **m.p.** 123-125 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.2 Hz, 1H), 8.35–8.32 (m, 1H), 8.29 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 2.2 Hz, 1H), 7.82–7.79 (m, 1H), 7.66–7.62 (m, 1H), 7.42 (dd, *J* = 8.7, 2.2 Hz, 1H), 4.22 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.1, 144.2, 134.4, 134.4, 131.3, 127.6, 127.3, 125.3, 124.9, 123.5, 121.9, 121.1, 120.1, 54.0. **IR** (neat) 2919, 2853, 1590, 1482, 1351, 1311, 1221, 1081 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}ClNO$ 244.0524, found 244.0519.

3-bromo-6-methoxyphenanthridine (2f)



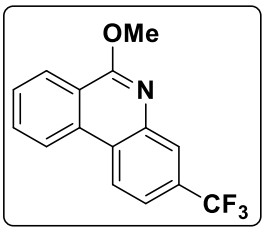
The title compound was prepared by following the general procedure D in 75% yield (21.6 mg, 0.075 mmol) as a white solid. **m.p.** 106-108 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.2 Hz, 1H), 8.33 (dd, *J* = 8.1, 1.4 Hz, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 8.06 (d, *J* = 2.1 Hz, 1H), 7.83–7.78 (m, 1H), 7.67–7.63 (m, 1H), 7.56 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.21 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.0, 144.0, 134.4, 131.3, 130.5, 127.7, 127.6, 125.3, 123.6, 122.5, 121.9, 121.5, 120.2, 53.9. **IR** (neat) 2923, 2848, 1725, 1586, 1477, 1433, 1356, 1318, 1218, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}BrNO$ 288.0019, found 288.0036.

6-methoxy-3-phenylphenanthridine (2g)



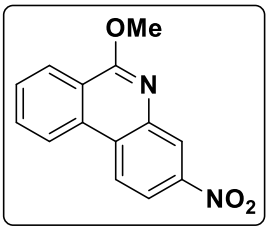
The title compound was prepared by following the general procedure D in 51% yield (14.6 mg, 0.051 mmol) as a white solid. **m.p.** 116-118 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.2 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.38–8.36 (m, 1H), 8.17–8.15 (m, 1H), 7.84–7.79 (m, 3H), 7.77–7.73 (m, 1H), 7.67–7.62 (m, 1H), 7.53–7.48 (m, 2H), 7.42–7.38 (m, 1H), 4.26 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.7, 143.8, 141.6, 140.8, 134.7, 131.1, 129.0, 127.7, 127.5, 127.3, 126.0, 125.2, 123.6, 122.8, 122.0, 121.7, 120.2, 53.8. **IR** (neat) 2941, 2853, 1588, 1473, 1353, 1318, 1314, 1218, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{16}NO$ 286.1226, found 286.1254.

6-methoxy-3-(trifluoromethyl)phenanthridine (2h)



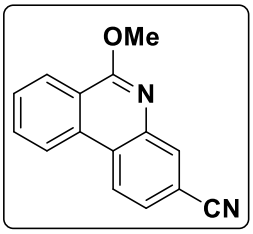
The title compound was prepared by following the general procedure D in 58% yield (16.1 mg, 0.058 mmol) as a white solid. **m.p.** 104-106 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50–8.46 (m, 2H), 8.39–8.35 (m, 1H), 8.17 (s, 1H), 7.86–7.82 (m, 1H), 7.72–7.65 (m, 2H), 4.23 (s, 3H). **^{13}C {^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.2, 143.1, 134.0, 131.4, 130.6 (q, J = 32.5 Hz), 128.5, 125.4, 125.3 (q, J = 37 Hz), 124.4 (q, J = 273 Hz), 123.1, 122.4, 120.8, 120.4 (q, J = 3.5 Hz), 54.02. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.19. **IR** (neat) 2923, 2853, 1586, 1537, 1364, 1325, 1287, 1227, 1159, 1112 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{11}F_3NO$ 278.0787, found 278.0805.

6-methoxy-3-nitrophenanthridine (2i)



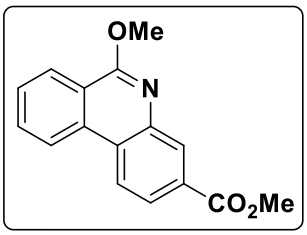
The title compound was prepared by following the general procedure D in 39% yield (9.9 mg, 0.039 mmol) as a light yellow solid. **m.p.** 170-172 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.72 (d, J = 2.4 Hz, 1H), 8.52–8.47 (m, 2H), 8.41–8.38 (m, 1H), 8.25 (dd, J = 8.9, 2.4 Hz, 1H), 7.91–7.87 (m, 1H), 7.78–7.75 (m, 1H), 4.25 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.8, 147.8, 143.4, 133.5, 131.8, 129.4, 127.5, 125.6, 123.5, 123.3, 122.8, 121.2, 118.4, 54.3. **IR** (neat) 2921, 2953, 1743, 1583, 1508, 1466, 1327, 1216, 1095 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}N_2O_3$ 255.0764, found 255.0779.

6-methoxyphenanthridine-3-carbonitrile (2j)



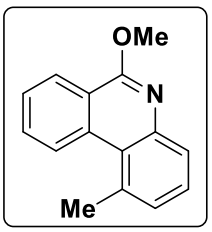
The title compound was prepared by following the general procedure D in 34% yield (8 mg, 0.034 mmol) as a light yellow solid. **m.p.** 166-168 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52–8.44 (m, 2H), 8.42–8.36 (m, 1H), 8.20 (s, 1H), 7.92–7.84 (m, 1H), 7.78–7.71 (m, 1H), 7.70–7.64 (m, 1H), 4.24 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.5, 143.2, 133.7, 132.7, 131.7, 129.1, 126.4, 126.1, 125.5, 123.4, 122.5, 121.1, 119.1, 112.0, 54.2. **IR** (neat) 2923, 2853, 2222, 1588, 1486, 1356, 1236, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{11}N_2O$ 235.0866, found 235.0881.

methyl 6-methoxyphenanthridine-3-carboxylate (2k)



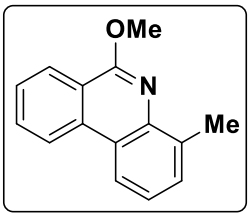
The title compound was prepared by following the general procedure D in 40% yield (10.7 mg, 0.04 mmol) as a white solid. **m.p.** 136-138 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.8 Hz, 1H), 8.51 (d, *J* = 8.2 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 8.39–8.34 (m, 1H), 8.09 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.86–7.80 (m, 1H), 7.73–7.66 (m, 1H), 4.24 (s, 3H), 3.99 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.2, 159.8, 143.0, 134.1, 131.3, 130.2, 129.9, 128.5, 126.2, 125.3, 124.7, 122.6, 122.4, 120.9, 54.0, 52.4. **IR** (neat) 2928, 2853, 1720, 1588, 1488, 1364, 1309, 1216, 1183, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{14}NO_3$ 268.0968, found 268.0981.

6-methoxy-1-methylphenanthridine (2l)



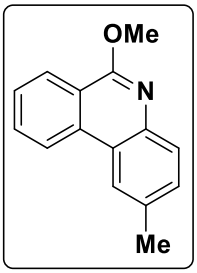
The title compound was prepared by following the general procedure D in 13% yield (2.9 mg, 0.013 mmol) as a white solid. **m.p.** 48-50 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.5 Hz, 1H), 8.48–8.41 (m, 1H), 7.86–7.76 (m, 2H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.55–7.47 (m, 1H), 7.33 (d, *J* = 7.3 Hz, 1H), 4.24 (s, 3H), 3.07 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.9, 144.7, 136.2, 135.3, 130.3, 129.1, 128.0, 126.8, 126.6, 126.5, 125.1, 122.3, 121.0, 53.9, 26.8. **IR** (neat) 2924, 2845, 1722, 1580, 1472, 1308, 1235, 1033 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1078.

6-methoxy-4-methylphenanthridine (2m)



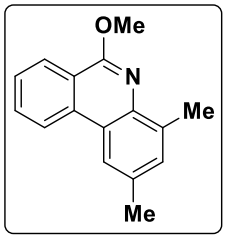
The title compound was prepared by following the general procedure D in 59% yield (13.3 mg, 0.059 mmol) as a white solid. **m.p.** 48-50 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52–8.50 (m, 1H), 8.37–8.35 (m, 1H), 8.30–8.28 (m, 1H), 7.81–7.77 (m, 1H), 7.64–7.61 (m, 1H), 7.52–7.50 (m, 1H), 7.40–7.37 (m, 1H), 4.24 (s, 3H), 2.77 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.1, 141.9, 135.9, 135.3, 130.7, 129.6, 127.1, 125.0, 124.0, 122.3, 122.3, 120.0, 119.9, 53.5, 18.4. **IR** (neat) 2923, 2850, 1583, 1460, 1345, 1316, 1225, 1101, 1033 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1081.

6-methoxy-2-methylphenanthridine (2m')



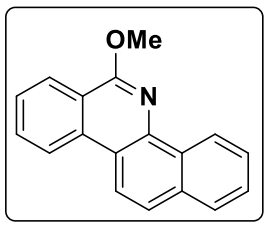
The title compound was prepared by following the general procedure D in 28% yield (6.3 mg, 0.028 mmol) as a white solid. **m.p.** 46-48 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.3 Hz, 1H), 8.37–8.32 (m, 1H), 8.21 (s, 1H), 7.83–7.78 (m, 2H), 7.64–7.60 (m, 1H), 7.47–7.44 (m, 1H), 4.24 (s, 3H), 2.57 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.9, 134.7, 134.1, 130.9, 130.5, 127.6, 127.2, 125.2, 122.4, 122.1, 122.0, 120.2, 53.9, 21.8. **IR** (neat) 2920. 2848, 1621, 1580, 1462, 1321, 1230, 1015 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1078.

6-methoxy-2,4-dimethylphenanthridine (2n)



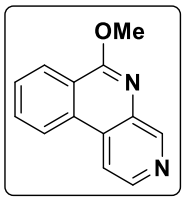
The title compound was prepared by following the general procedure D in 71% yield (16.8 mg, 0.071 mmol) as a white solid. **m.p.** 68-70 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50–8.47 (m, 1H), 8.35–8.33 (m, 1H), 8.07 (s, 1H), 7.79–7.75 (m, 1H), 7.63–7.59 (m, 1H), 7.35 (s, 1H), 4.22 (s, 3H), 2.73 (s, 3H), 2.54 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 157.6 140.0, 135.6, 135.0, 133.3, 131.2, 130.5, 126.9, 124.9, 122.2, 122.1, 119.9, 119.7, 53.4, 21.8, 18.2. **IR** (neat) 2915, 2846, 1590, 1466, 1431, 1356, 1316, 1223, 1101 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO$ 238.1232, found 238.1252.

6-methoxybenzo[c]phenanthridine (2p)



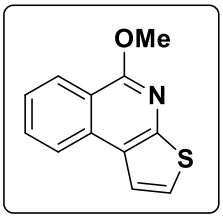
The title compound was prepared by following the general procedure D in 93% yield (24.1 mg, 0.093 mmol) as a white solid. **m.p.** 90-92 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.31–9.25 (m, 1H), 8.56 (d, *J* = 8.1 Hz, 1H), 8.47–8.39 (m, 2H), 7.98–7.92 (m, 1H), 7.89–7.80 (m, 2H), 7.74–7.67 (m, 1H), 7.69–7.61 (m, 2H), 4.39 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.0, 140.0, 135.3, 133.7, 131.5, 130.9, 127.7, 127.1, 126.9, 126.3, 125.1, 125.0, 124.8, 122.3, 120.2, 119.8, 118.5, 53.8. **IR** (neat) 2943, 2846, 1577, 1521, 1453, 1353, 1316, 1210, 1079 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{14}NO$ 260.1070, found 260.1094.

6-methoxybenzo[c][1,7]naphthyridine (2q)



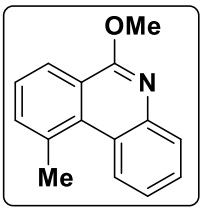
The title compound was prepared by following the general procedure D in 53% yield (11.1 mg, 0.053 mmol) as a yellow solid. **m.p.** 94-96 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.67–8.62 (m, 1H), 8.50 (d, *J* = 8.2 Hz, 1H), 8.41–8.39 (m, 1H), 8.19 (d, *J* = 5.2 Hz, 1H), 7.90–7.86 (m, 1H), 7.80–7.76 (m, 1H), 4.25 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.6, 150.4, 143.0, 138.9, 132.8, 131.6, 129.9, 128.2, 125.5, 122.7, 122.0, 115.8, 54.2. **IR** (neat) 2923, 2850, 1592, 1517, 1477, 1351, 1320, 1214, 1141, 1092 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{13}H_{10}N_2ONa$ 233.0691, found 233.0701.

5-methoxythieno[2,3-c]isoquinoline (2r)



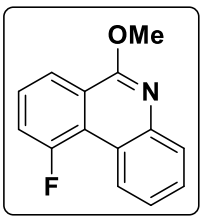
The title compound was prepared by following the general procedure D in 49% yield (10.5 mg, 0.049 mmol) as a white solid. **m.p.** 70-72 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.27–8.24 (m, 1H), 8.07–8.04 (m, 1H), 7.70–7.66 (m, 1H), 7.61 (d, *J* = 5.9 Hz, 1H), 7.49–7.45 (m, 1H), 7.24 (d, *J* = 5.8 Hz, 1H), 4.12 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.3, 153.3, 133.8, 131.0, 125.9, 125.4, 123.5, 122.7, 121.3, 119.9, 117.9, 54.3. **IR** (neat) 2923, 2850, 1730, 1556, 1473, 1410, 1218, 1104 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{12}H_{10}NOS$ 216.0483, found 216.0502.

6-methoxy-10-methylphenanthridine (2s)



The title compound was prepared by following the general procedure D in 49% yield (10.9 mg, 0.049 mmol) as a white solid. **m.p.** 60-62 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71–8.68 (m, 1H), 8.36–8.33 (m, 1H), 7.95 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.66–7.61 (m, 2H), 7.56–7.52 (m, 1H), 7.49–7.46 (m, 1H), 4.23 (s, 3H), 3.09 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.7, 144.4, 135.2, 135.2, 134.2, 128.3, 128.1, 126.8, 126.8, 124.2, 123.8, 123.5, 121.7, 53.8, 26.8; **IR** (neat) 2945, 2850, 1556, 1473, 1435, 1349, 1303, 1237, 1157, 1110 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1077.

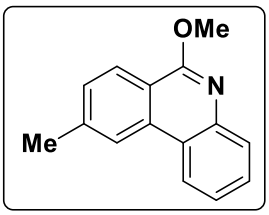
10-fluoro-6-methoxyphenanthridine (2t)



The title compound was prepared by following the general procedure D in 91% yield (20.7 mg, 0.091 mmol) as a white solid. **m.p.** 83-85 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.85–8.81 (m, 1H), 8.20–8.18 (m, 1H), 7.93–7.90 (m, 1H), 7.68–7.64 (m, 1H), 7.60–7.55 (m, 1H), 7.53–7.48 (m, 2H), 4.23 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.6 (d, *J* = 253.6 Hz), 158.5 (d, *J* =

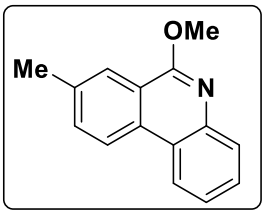
3.7 Hz), 143.6, 129.1 (d, J = 2.2 Hz), 127.8, 127.6 (d, J = 9.2 Hz), 127.1 (d, J = 22.2 Hz), 125.0 (d, J = 2.2 Hz), 124.0 (d, J = 10.7 Hz), 122.5 (d, J = 4.8 Hz), 121.1 (d, J = 4.1 Hz), 120.4 (d, J = 4.8 Hz), 117.7 (d, J = 23.4 Hz), 54.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.96 to -111.00 (m, 1F). **IR** (neat) 2919, 2853, 1588, 1477, 1437, 1356, 1305, 1245, 1214, 1152, 1017 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}FNO$ 228.0825, found 228.0818.

6-methoxy-9-methylphenanthridine (2u)



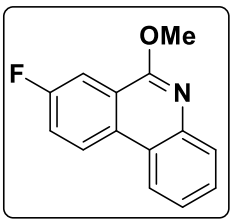
The title compound was prepared by following the general procedure D in 80% yield (17.9 mg, 0.080 mmol) as a white solid. **m.p.** 70-72 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.42–8.39 (m, 1H), 8.28 (s, 1H), 8.24 (d, J = 8.2 Hz, 1H), 7.90–7.87 (m, 1H), 7.63–7.59 (m, 1H), 7.49–7.44 (m, 2H), 4.23 (s, 3H), 2.61 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.4, 143.6, 141.3, 135.0, 129.0, 128.7, 127.9, 125.0, 124.3, 122.6, 122.2, 121.8, 118.2, 53.7, 22.4. **IR** (neat) 2921, 2850, 1595, 1500, 1431, 1353, 1314, 1227, 1230, 1097, 1033 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1088.

6-methoxy-8-methylphenanthridine (2v)



The title compound was prepared by following the general procedure D in 93% yield (20.8 mg, 0.093 mmol) as a white solid. **m.p.** 65-67 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40–8.36 (m, 2H), 8.15 (s, 1H), 7.92–7.89 (m, 1H), 7.65–7.58 (m, 2H), 7.50–7.45 (m, 1H), 4.24 (s, 3H), 2.57 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.2, 142.9, 137.4, 132.7, 132.6, 128.4, 127.8, 124.7, 124.5, 122.8, 122.0, 122.0, 120.2, 53.8, 21.8. **IR** (neat) 2921, 2855, 1579, 1428, 1437, 1358, 1316, 1227, 1092 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1084.

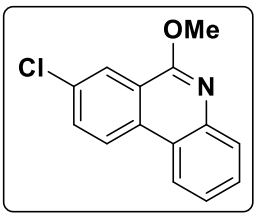
8-fluoro-6-methoxyphenanthridine (2w)



The title compound was prepared by following the general procedure D in 63% yield (14.3 mg, 0.063 mmol) as a white solid. **m.p.** 90-92 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50–8.45 (m, 1H), 8.37–8.34 (m, 1H), 7.97 (dd, J = 9.3, 2.8 Hz, 1H), 7.92–7.88 (m, 1H), 7.65–7.60 (m, 1H), 7.56–7.47 (m, 2H), 4.23 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.7 (d, J = 247.8 Hz), 158.6 (d, J = 3.6 Hz), 143.0, 131.5 (d, J = 2.2 Hz), 128.8, 128.1, 124.8, 124.5 (d, J = 8.4 Hz), 122.2, 122.0, 121.6 (d, J = 8.6 Hz), 119.9 (d, J = 23.6 Hz), 110.2 (d, J = 22.4 Hz), 53.9. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.59 to -112.64 (m, 1F). **IR** (neat) 2926, 2848,

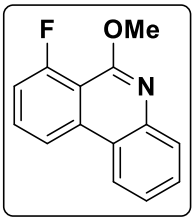
1563, 1423, 1348, 1228, 1121, 1162 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}FNO$ 228.0825, found 228.0820.

8-chloro-6-methoxyphenanthridine (2x)



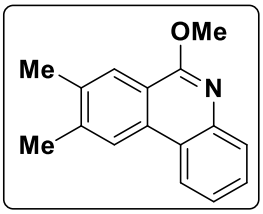
The title compound was prepared by following the general procedure D in 74% yield (18 mg, 0.074 mmol) as a white solid. **m.p.** 88-90 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41–8.37 (m, 1H), 8.35–8.32 (m, 1H), 8.32–8.30 (m, 1H), 7.91–7.88 (m, 1H), 7.74–7.70 (m, 1H), 7.66–7.61 (m, 1H), 7.50–7.46 (m, 1H), 4.22 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.3, 143.3, 133.3, 133.2, 131.5, 129.2, 128.0, 124.9, 124.7, 123.7, 122.1, 122.0, 121.2, 53.9. **IR** (neat) 2920, 2850, 1988, 1489, 1348, 1316, 1220, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}ClNO$ 244.0529, found 244.0526.

7-fluoro-6-methoxyphenanthridine (2y)



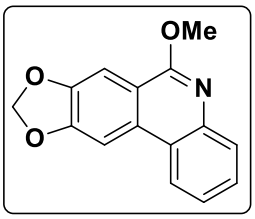
The title compound was prepared by following the general procedure D in 44% yield (10 mg, 0.044 mmol) as a white solid. **m.p.** 60-62 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.38–8.36 (m, 1H), 8.31–8.29 (m, 1H), 7.89–7.86 (m, 1H), 7.75–7.70 (m, 1H), 7.66–7.62 (m, 1H), 7.50–7.46 (m, 1H), 7.33–7.28 (m, 1H), 4.24 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.4, 159.3, 158.0 (d, J = 5.8 Hz), 143.4, 137.9 (d, J = 2.0 Hz), 131.6 (d, J = 9.5 Hz), 129.6, 127.8, 124.9, 122.7, 121.5 (d, J = 2.8 Hz), 118.0 (d, J = 4.2 Hz), 114.3 (d, J = 23.0 Hz), 54.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -107.32 to -107.35 (m, 1F). **IR** (neat) 2923, 2850, 1577, 1444, 1340, 1309, 1230, 1121, 1159 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{11}FNO$ 228.0825, found 228.0832.

6-methoxy-8,9-dimethylphenanthridine (2z)



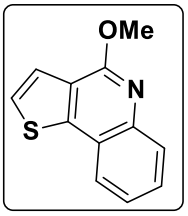
The title compound was prepared by following the general procedure D in 84% yield (19.9 mg, 0.084 mmol) as a white solid. **m.p.** 86-88 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.41–8.35 (m, 1H), 8.24 (s, 1H), 8.09 (s, 1H), 7.89 (d, J = 8.1 Hz, 1H), 7.62–7.55 (m, 1H), 7.49–7.42 (m, 1H), 4.24 (s, 3H), 2.52 (s, 3H), 2.47 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.3, 143.0, 140.8, 136.9, 133.2, 128.3, 127.7, 125.1, 124.3, 122.6, 122.4, 122.0, 118.5, 53.8, 20.9, 20.2. **IR** (neat) 2926, 2850, 1623, 1580, 1531, 1358, 1314, 1227, 1092 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO$ 238.1226, found 238.1241.

6-methoxy-[1,3]dioxolo[4,5-j]phenanthridine (2aa)



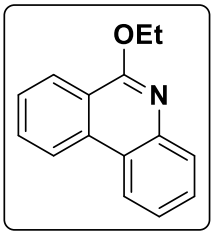
The title compound was prepared by following the general procedure D (PhCl was used instead of CH_3CN as a solvent) in 67% yield (17 mg, 0.067 mmol) as a white solid. **m.p.** 126- 128 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23–8.19 (m, 1H), 7.89–7.85 (m, 1H), 7.79 (s, 1H), 7.65 (s, 1H), 7.60–7.55 (m, 1H), 7.45–7.41 (m, 1H), 6.12 (s, 2H), 4.20 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.8, 151.3, 148.1, 143.0, 132.2, 128.2, 127.9, 124.2, 122.7, 121.9, 115.9, 102.9, 101.9, 100.4, 53.7. **IR** (neat) 2912, 1623, 1583, 1455, 1318, 1230, 1132, 1028 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{12}NO_3$ 254.0812, found 254.0835.

4-methoxythieno[3,2-c]quinoline (2ab)



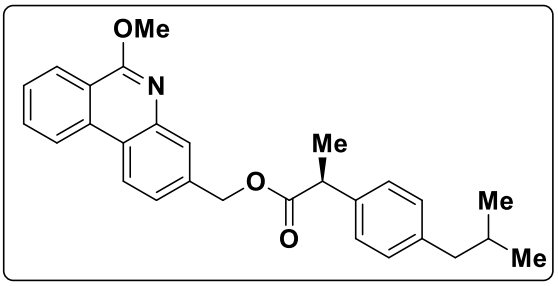
The title compound was prepared by following the general procedure D in 44% yield (9.5 mg, 0.044 mmol) as a white solid. **m.p.** 65-67 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19–8.13 (m, 1H), 7.98 (d, J = 8.0 Hz, 1H), 7.92–7.87 (m, 1H), 7.79–7.74 (m, 1H), 7.66–7.58 (m, 1H), 7.51–7.44 (m, 1H), 4.25 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 157.2, 144.6, 144.5, 131.1, 128.2, 127.8, 124.4, 123.6, 123.4, 122.6, 122.1, 53.8. **IR** (neat) 2921, 2853, 1734, 1566, 1480, 1356, 1230, 1112 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{12}H_{10}NOS$ 216.0483, found 216.0500.

6-ethoxyphenanthridine (2ac)



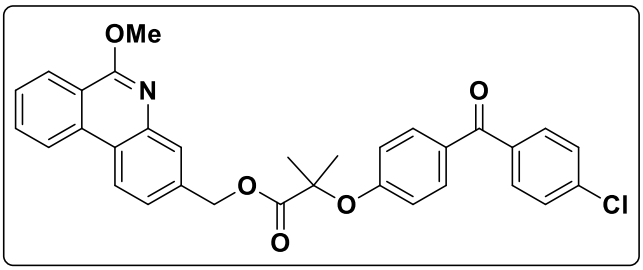
The title compound was prepared by following the general procedure D in 71% yield (15.8 mg, 0.07 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, J = 8.3 Hz, 1H), 8.44 – 8.38 (m, 2H), 7.91 – 7.88 (m, 1H), 7.82 – 7.78 (m, 1H), 7.66 – 7.60 (m, 2H), 7.50 – 7.46 (m, 1H), 4.72 (q, J = 7.1 Hz, 2H), 1.56 (t, J = 7.1 Hz, 3H); **^{13}C NMR (**126 MHz, $CDCl_3$) δ 159.0, 143.4, 134.9, 131.0, 128.7, 127.8, 127.3, 125.2, 124.4, 122.5, 122.2, 122.0, 120.3, 62.2, 14.8; **IR** (neat) 2970, 2924, 1589, 1462, 1398, 1373, 1338, 1316, 1225, 1084 cm^{-1}; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1084, found 224.1075.

(6-methoxyphenanthridin-3-yl)methyl (*S*)-2-(4-isobutylphenyl)propanoate (2ad)



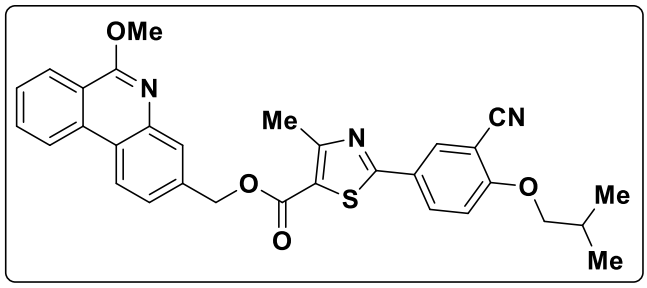
The title compound was prepared by following the general procedure D in 74% yield (31.6 mg, 0.074 mmol) and 95:5 er as a white solid. **m.p.** 52-54 °C. The enantiomeric excess of the product was determined by chiral stationary phase HPLC. **HPLC** (Chiralpak IC column, hexane: ^{i}PrOH = 95:05, 0.5 mL/min, 254 nm), t_R = 19.52 min (major), 20.55 min (minor). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.2 Hz, 1H), 8.38–8.31 (m, 2H), 7.85 (s, 1H), 7.82–7.78 (m, 1H), 7.66–7.62 (m, 1H), 7.34 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.12–7.10 (m, 2H), 5.36–5.24 (m, 2H), 4.24 (s, 1H), 3.82 (q, *J* = 7.2 Hz, 1H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.91–1.79 (m, 1H), 1.55 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 174.7, 159.6, 143.2, 140.7, 137.8, 136.9, 134.6, 131.1, 129.5, 127.5, 127.4, 127.0, 125.2, 124.0, 122.5, 122.2, 122.0, 120.2, 66.3, 53.9, 45.3, 45.2, 30.3, 22.5, 18.7. **IR** (neat) 2954, 2923, 2850, 1723, 1590, 1486, 1358, 1318, 1230, 1163 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{28}H_{30}NO_3$ 428.2220, found 428.2235.

(6-methoxyphenanthridin-3-yl)methyl 2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate (2ae)



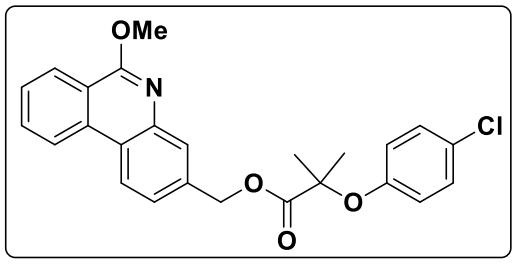
The title compound was prepared by following the general procedure D in 85% yield (45.9 mg, 0.085 mmol) as a sticky yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.3 Hz, 1H), 8.35–8.30 (m, 2H), 7.85–7.80 (m, 2H), 7.67–7.64 (m, 1H), 7.61–7.58 (m, 2H), 7.57–7.54 (m, 2H), 7.34–7.32 (m, 3H), 6.83–6.79 (m, 2H), 5.38 (s, 2H), 4.20 (s, 3H), 1.71 (s, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 194.2, 173.6, 159.8, 159.7, 142.9, 138.4, 136.4, 135.8, 134.5, 132.1, 131.4, 131.2, 130.4, 128.6, 127.8, 127.6, 125.4, 124.6, 122.6, 122.5, 122.1, 120.2, 117.4, 79.6, 67.3, 54.3, 25.6. **IR** (neat) 2941, 2853, 1736, 1660, 1592, 1360, 1278, 1240, 1134, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{32}H_{27}ClNO_5$ 540.1572, found 540.1550.

(6-methoxy-2,3,10,10a-tetrahydrophenanthridin-3-yl)methyl 2-(3-cyano-4-isobutoxyphenyl)-4-methylthiazole-5-carboxylate (2af)



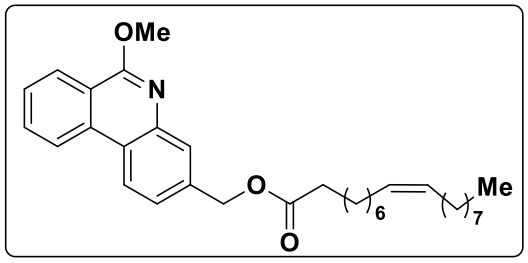
The title compound was prepared by following the general procedure D in 73% yield (39.2 mg, 0.073 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.2 Hz, 1H), 8.45 (d, *J* = 8.3 Hz, 1H), 8.37 (d, *J* = 8.0 Hz, 1H), 8.20–8.16 (m, 1H), 8.11–8.05 (m, 1H), 8.03 (s, 1H), 7.87–7.80 (m, 1H), 7.70–7.63 (m, 1H), 7.56 (d, *J* = 8.3 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 5.52 (s, 2H), 4.28 (s, 3H), 3.89 (d, *J* = 6.5 Hz, 2H), 2.79 (s, 3H), 2.26–2.14 (m, 1H), 1.08 (d, *J* = 6.7 Hz, 6H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.6, 162.7, 162.90, 161.8, 159.8, 143.0, 136.4, 134.6, 132.8, 132.3, 131.4, 127.8, 127.2, 126.1, 125.4, 124.4, 122.8, 122.5, 122.1, 121.6, 120.3, 115.5, 112.8, 103.1, 75.8, 66.9, 28.3, 19.2, 17.7. **IR** (neat) 2926, 2855, 2227, 1707, 1592, 1429, 1367, 1267, 1097, 1008 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{31}H_{28}N_3O_4S$ 538.1795, found 538.1813.

(6-methoxyphenanthridin-3-yl)methyl 2-(4-chlorophenoxy)-2-methylpropanoate (2ag)



The title compound was prepared by following the general procedure D in 96% yield (41.8 mg, 0.096 mmol) as a white solid. **m.p.** 74-76 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1H), 8.38–8.34 (m, 2H), 7.84–7.78 (m, 2H), 7.68–7.62 (m, 1H), 7.37–7.33 (m, 1H), 7.12–7.06 (m, 2H), 6.77–6.72 (m, 2H), 5.38 (s, 2H), 4.24 (s, 3H), 1.63 (s, 6H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 173.9, 159.7, 154.1, 143.4, 135.9, 134.5, 131.1, 129.2, 127.8, 127.6, 127.3, 125.2, 124.4, 122.6, 122.6, 122.1, 120.6, 120.4, 79.7, 67.2, 53.9, 25.5. **IR** (neat) 2923, 2950, 1727, 1581, 1579, 1486, 1350, 1320, 1227, 1146, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{23}ClNO_4$ 436.1310, found 436.1326.

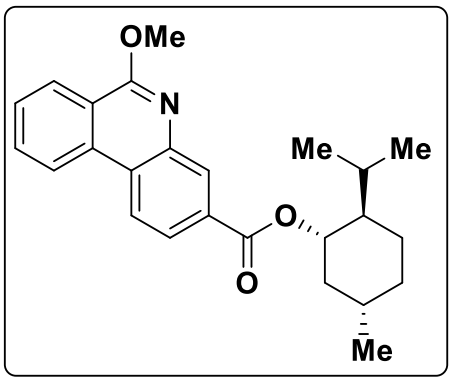
(6-methoxyphenanthridin-3-yl)methyl oleate (2ah)



The title compound was prepared by following the general procedure D in 69% yield (34.7 mg, 0.069 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.2 Hz, 1H), 8.40 (d, *J* = 8.3 Hz, 1H), 8.38–8.32 (m, 1H), 7.90 (s, 1H), 7.83–7.79 (m, 1H), 7.66–7.62 (m, 1H), 7.48–7.45 (m, 1H), 5.36–5.32 (m, 2H), 5.30 (s, 2H), 4.24 (s, 3H), 2.41 (t, *J* = 7.6 Hz, 2H), 2.03–1.97 (m, 4H), 1.71–1.65 (m, 2H), 1.36–1.24 (m, 20H), 0.88

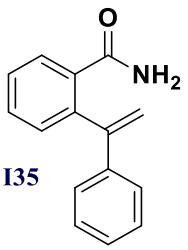
(t, J = 6.8 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.9, 159.7, 143.4, 136.9, 134.6, 131.1, 130.1, 129.9, 127.5, 127.2, 125.2, 124.2, 122.6, 122.3, 122.0, 120.3, 66.0, 53.9, 34.5, 32.0, 29.9, 29.8, 29.6, 29.5, 29.3, 29.3, 29.2, 27.4, 27.3, 25.1, 22.8, 14.2. **IR** (neat) 2923, 2853, 1736, 1586, 1353, 1325, 1227, 1161 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{33}H_{46}NO_3$ 504.3478, found 504.3482.

(1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl 6-methoxy-10,10a-dihydrophenanthridine-3-carboxylate (2ai)

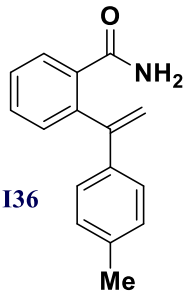


The title compound was prepared by following the general procedure D in 59% yield (23.1 mg, 0.059 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58–8.56 (m, 1H), 8.53 (d, J = 8.2 Hz, 1H), 8.46 (d, J = 8.5 Hz, 1H), 8.38 (d, J = 8.0 Hz, 1H), 8.14–8.11 (m, 1H), 7.86–7.82 (m, 1H), 7.72–7.68 (m, 1H), 5.07–4.98 (m, 1H), 4.26 (s, 3H), 2.21–2.15 (m, 1H), 2.09–2.03 (m, 1H), 1.79–1.72 (m, 2H), 1.70–1.56 (m, 3H), 1.21–1.12 (m, 2H), 0.95 (d, J = 6.7 Hz, 6H), 0.83 (d, J = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 166.3, 159.9, 143.0, 134.2, 131.3, 131.1, 129.6, 128.4, 126.0, 125.4, 124.9, 122.6, 122.4, 120.9, 75.1, 54.0, 47.4, 41.2, 34.5, 31.6, 26.6, 23.7, 22.2, 21.0, 16.6. **IR** (neat) 2950, 2866, 1712, 1590, 1462, 1358, 1305, 1263, 1218, 1097, 1030 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{25}H_{30}NO_3$ 392.2220, found 392.2228.

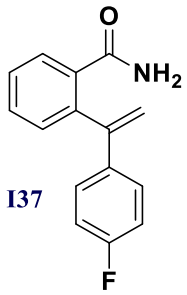
4. List of intermediates for the synthesis of other *N*-heterocycles



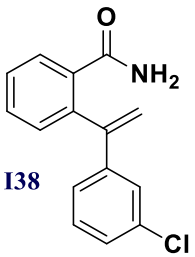
I35



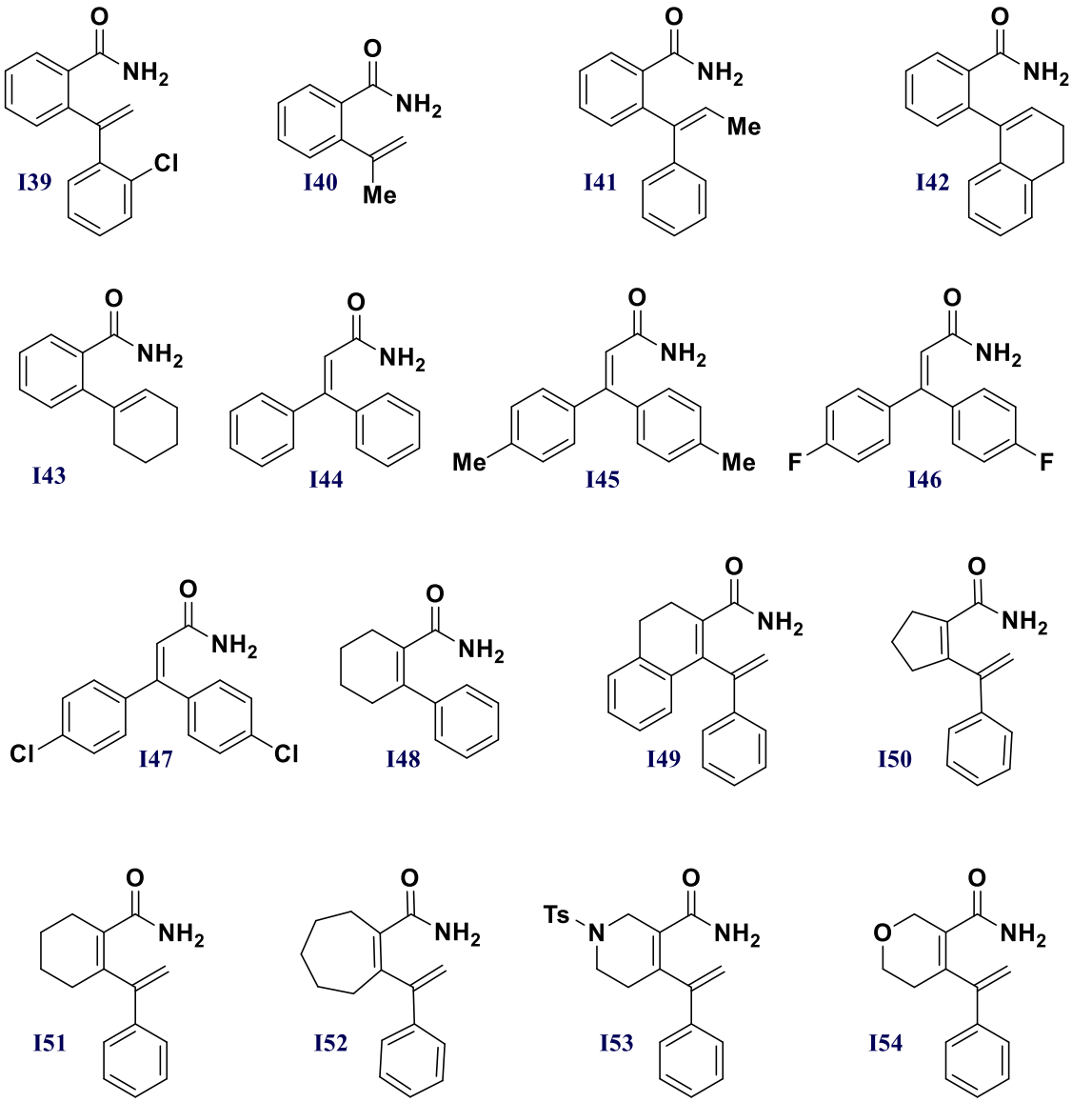
I36



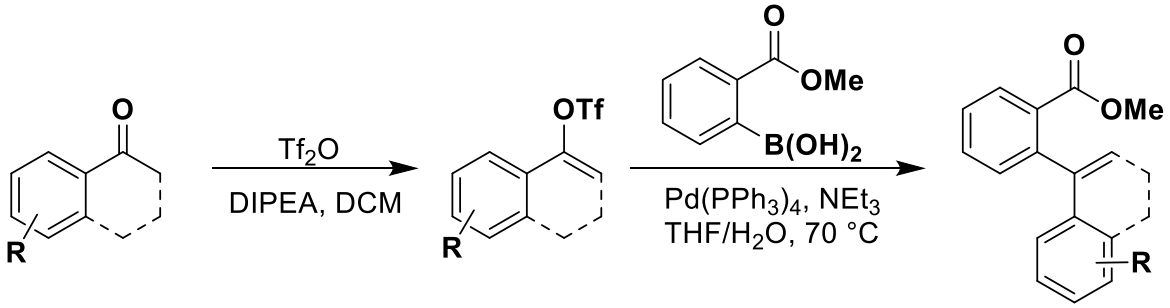
I37



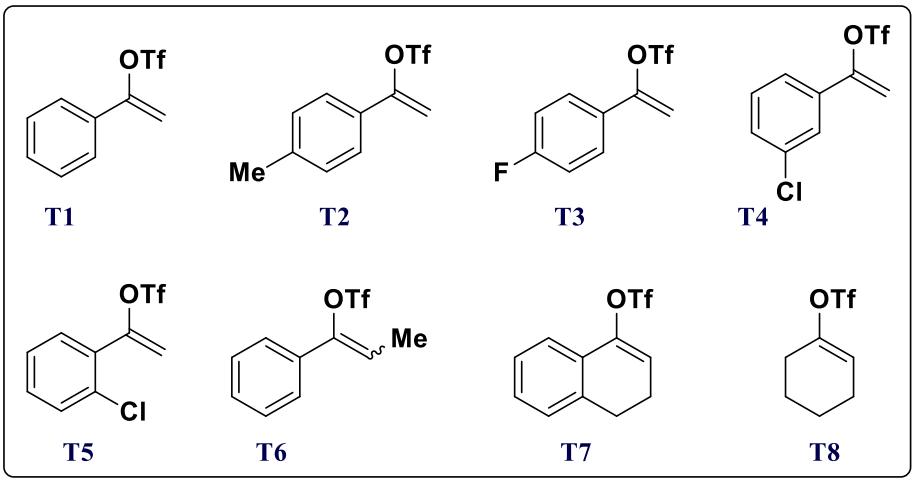
I38



4.1 General procedure for the synthesis of I35-I39 and I41-I43 (General Procedure E)

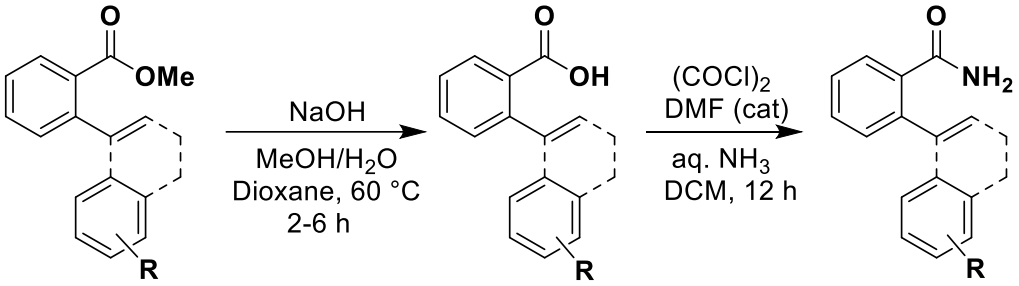


T1-T7[10a] and **T8**[10b] are previously known compounds and were prepared following the reported procedure.



A solution of the ketone (6 mmol, 1 equiv) in dichloromethane (12 mL) was prepared. Trifluoromethanesulfonic anhydride (7.2 mmol, 1.2 equiv) was added to this solution at room temperature. While cooling the reaction mixture in an ice-water bath, *N*,*N*-diisopropylethylamine (8.4 mmol, 1.4 equiv) was added dropwise. The mixture was then allowed to gradually warm to room temperature and stirred for 1.5 h. An additional portion of trifluoromethanesulfonic anhydride (1.8 mmol) was added, followed by *N*,*N*-diisopropylethylamine (3 mmol). The reaction mixture was stirred at room temperature for another 2 h. Toluene (18 mL) and silica gel (3 g) were added, and the mixture was concentrated under reduced pressure. The resulting suspension was filtered through a celite pad. The solid residue on the filter was washed with toluene (10 mL), and the combined filtrate was evaporated under vacuum to afford the crude product. The crude triflate was purified by column chromatography using 1–5% ethyl acetate in hexane as the eluent.

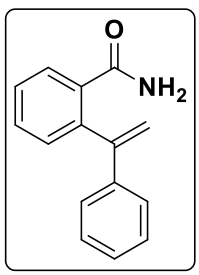
In a 50 mL oven-dried round-bottom flask equipped with a magnetic stir bar, the triflate substrate (3 mmol, 1 equiv) were charged under a nitrogen atmosphere. $Pd(PPh_3)_4$ (5 mol%), (2-(methoxycarbonyl)phenyl)boronic acid (2.0 equiv), and triethylamine (5.0 equiv) were then added, followed by THF (15 mL) and deionized water (3 mL). The reaction mixture was stirred at 70 °C for 2 h or until complete, as determined by TLC. Then water was added, and the mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated under reduced pressure. The corresponding crude ester product was purified by column chromatography using 1–5% ethyl acetate in hexane as the eluent.



Dissolve the methyl 2-(1-phenylvinyl)benzoate derivative (1.5 mmol, 1 equiv) in a mixture of 1,4-dioxane, methanol, and water (12.6 mL, 1:1:1, v/v/v). Add NaOH (5 equiv), and stir the reaction mixture at 60 °C for 2–4 hours or until ester completely consumed, as monitored by TLC. Upon completion, concentrate the reaction mixture under reduced pressure. Dilute the resulting residue with water (10 mL) and wash the aqueous layer with ethyl acetate (10 mL). Acidify the aqueous phase with 3 M hydrochloric acid to pH ~2, then extract with ethyl acetate (20 mL x 3). Wash the combined organic layers with brine, dry over Na_2SO_4, filter, and concentrate under reduced pressure to afford the 2-(1-phenylvinyl)benzoic acid derivative as a white solid which was used directly in the next step without further purification.

The 2-(1-phenylvinyl)benzoic acid derivative and a catalytic amount of DMF were dissolved in 3.7 mL of dry CH_2Cl_2 in a round-bottom flask. The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Oxalyl chloride (1.2 equiv) was then added dropwise at 0 °C, and the mixture was stirred at room temperature for 4 hours. Upon completion, the reaction mixture was concentrated under reduced pressure to afford the corresponding acid chloride. The crude acid chloride was dissolved in 3 mL of dry CH_2Cl_2, and 4.2 mL of aq. NH_3 was added dropwise at 0 °C. The reaction mixture was then stirred at room temperature for 10 hours. After completion, the reaction was quenched with water and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography using a 20-30% mixture of EtOAc in hexane.

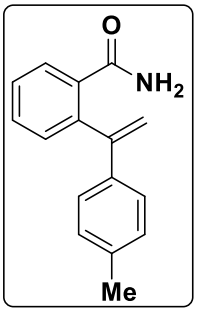
2-(1-phenylvinyl)benzamide (I35)



The title compound was prepared by following the general procedure E in 58% yield (194 mg, 0.87 mmol) as a white solid. **m.p.** 116-118 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.81–7.79 (m, 1H), 7.51–7.48 (m, 1H), 7.46–7.43 (m, 1H), 7.34–7.31 (m, 1H), 7.30–7.26 (m, 5H), 5.99 (brs, 1H), 5.85 (s, 1H), 5.47 (brs, 1H), 5.40 (s, 1H). **^{13}C{^{1}H} NMR** δ 170.6, 149.2, 139.9, 139.8, 134.5,

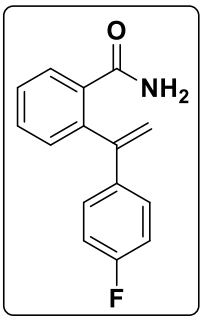
131.1, 130.9, 129.2, 128.6, 128.4, 128.3, 126.9, 115.9. **IR** (neat) 3359, 3173, 1760, 1650, 1617, 1411, 1013 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{14}NO$ 224.1070, found 224.1072.

2-(1-(*p*-tolyl)vinyl)benzamide (I36)



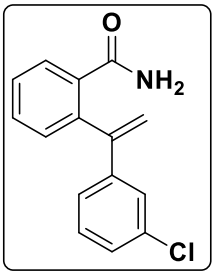
The title compound was prepared by following the general procedure E in 48% yield (171 mg, 0.72 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.82–7.79 (m, 1H), 7.50–7.46 (m, 1H), 7.45–7.41 (m, 1H), 7.32–7.29 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.03 (brs, 1H), 5.82 (s, 1H), 5.58 (brs, 1H), 5.33 (s, 1H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 149.1, 140.1, 138.4, 136.8, 134.4, 131.0, 130.9, 129.4, 129.3, 128.2, 126.7, 115.0, 21.3. **IR** (neat) 3463, 3335, 3187, 2929,1654, 1594, 1371, 1119, 1019 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO$ 238.1232, found 238.1219.

2-(1-(4-fluorophenyl)vinyl)benzamide (I37)



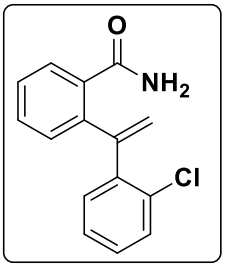
The title compound was prepared by following the general procedure E in 73% yield (264 mg, 1.1 mmol) as a white solid. **m.p.** 152-154 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77–7.72 (m, 1H), 7.52–7.46 (m, 1H), 7.47–7.40 (m, 1H), 7.32 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.26–7.20 (m, 2H), 7.00–6.92 (m, 2H), 5.94 (brs, 1H), 5.75 (s, 1H), 5.73 (brs, 1H), 5.36 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 162.8 (d, *J* = 248.2 Hz), 148.4, 136.1 (d, *J* = 3.3 Hz), 139.8, 134.6, 131.0 (d, *J* = 1.7 Hz), 129.0, 128.72 (d, *J* = 8.0 Hz), 128.4, 115.6, 115.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.68, to -113.74 (m, 1F). **IR** (neat) 3456, 3133, 1656, 1588, 1502, 1375, 1223, 1154, 1099 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{13}FNO$ 242.0981, found 242.0968.

2-(1-(3-chlorophenyl)vinyl)benzamide (I38)



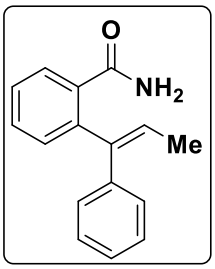
The title compound was prepared by following the general procedure E in 44% yield (170 mg, 0.66 mmol) as a white solid. **m.p.** 82-84 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58–7.54 (m, 1H), 7.36–7.31 (m, 1H), 7.30–7.25 (m, 1H), 7.17–7.14 (m, 1H), 7.13–7.10 (m, 1H), 7.09–7.01 (m, 2H), 6.95–6.92 (m, 1H), 5.73 (brs, 2H), 5.64 (s, 1H), 5.26 (s, 1H); **^{13}C{^{1}H} NMR R** (126 MHz, $CDCl_3$) δ 170.6, 148.1, 141.9, 139.3, 134.7, 134.5, 131.1, 131.0, 129.8, 128.9, 128.5, 128.3, 126.9, 125.4, 117. **IR** (neat) 3377, 3191, 2928, 1647, 1597, 1389, 1160, 1080 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{13}ClNO$ 258.0686, found 258.0672.

2-(1-(2-chlorophenyl)vinyl)benzamide (I39)



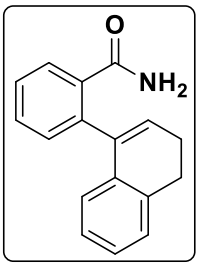
The title compound was prepared by following the general procedure E in 40% yield (155 mg, 0.6 mmol) as a white solid. **m.p.** 136-138 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64–7.58 (m, 1H), 7.41–7.28 (m, 4H), 7.30–7.22 (m, 2H), 7.21–7.15 (m, 1H), 6.10 (brs, 1H), 5.75 (brs, 2H), 5.74 (s, 1H), 5.66 (s, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.9, 146.0, 139.8, 139.3, 134.6, 132.5, 132.5, 130.4, 130.2, 129.8, 129.4, 128.9, 128.1, 127.1, 122.2. **IR** (neat) 3474, 3191, 2930, 1640,1612, 1367, 1044 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{13}ClNO$ 258.0686, found 258.0673.

(*E*)-2-(1-phenylprop-1-en-1-yl)benzamide (I41)



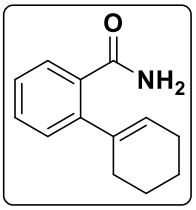
The title compound was prepared by following the general procedure E in 57% yield (203 mg, 0.85 mmol) as a yellow solid. **m.p.** 112-114 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.05–7.99 (m, 1H), 7.58–7.51 (m, 1H), 7.49–7.42 (m, 1H), 7.30–7.24 (m, 2H), 7.26–7.16 (m, 4H), 6.55 (brs, 1H), 6.46 (q, J = 7.0 Hz, 1H), 6.41 (brs, 1H), 1.68 (d, J = 6.9 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.0, 141.2, 140.2, 137.9, 133.4, 131.7, 131.4, 130.3, 128.8, 128.0, 127.7, 126.3, 126.0, 15.8. **IR** (neat) 3390, 3178, 2930, 1660, 1590, 1444, 1382, 1163, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO$ 238.1232, found 238.1218.

2-(3,4-dihydronaphthalen-1-yl)benzamide (I42)



The title compound was prepared by following the general procedure E in 78% yield (292 mg, 1.17 mmol) as a white solid. **m.p.** 125-127 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.6, 1.6 Hz, 1H), 7.52–7.45 (m, 1H), 7.47–7.41 (m, 1H), 7.29–7.26 (m, 1H), 7.20–7.13 (m, 2H), 7.09–7.05 (m, 1H), 6.71–6.68 (m, 1H), 6.10 (t, J = 4.6 Hz, 1H), 6.05 (brs, 1H), 5.63 (brs, 1H), 2.89 (t, J = 8.1 Hz, 2H), 2.48–2.43 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.7, 139.2, 138.4, 135.9, 134.8, 134.6, 131.1, 131.0, 129.5, 129.1, 128.0, 127.9, 127.8, 127.0, 124.9, 28.0, 23.7. **IR** (neat) 3380, 3164, 2930, 1641, 1384, 1101, 1026 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO$ 250.1232, found 250.1221.

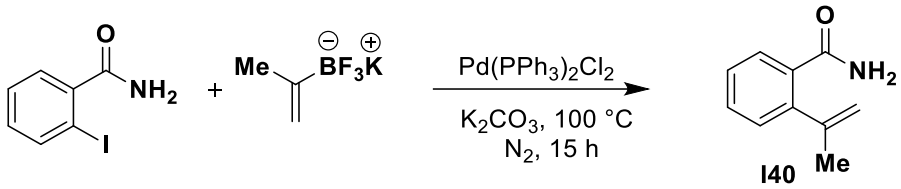
2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carboxamide (I43)



The title compound was prepared by following the general procedure E in 59% yield (178 mg, 0.88 mmol) as a yellow solid. **m.p.** 143-145 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (dd, J = 7.7, 1.5 Hz, 1H), 7.42–7.37 (m, 1H), 7.34–7.30 (m, 1H), 7.16 (dd, J = 7.6, 1.4 Hz, 1H), 6.37 (brs, 1H), 5.85 (brs, 1H),

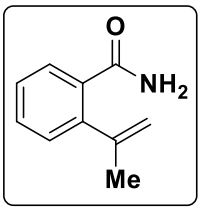
5.84–5.79 (m, 1H), 2.31–2.25 (m, 2H), 2.22–2.17 (m, 2H), 1.78–1.72 (m, 2H), 1.70–1.65 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.2, 143.0, 140.2, 132.8, 131.0, 129.5, 129.3, 127.6, 127.3, 30.6, 25.7, 23.4, 21.9. **IR** (neat) 3394, 3175, 2928, 1634, 1617, 1448, 1383, 1101 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{16}NO$ 202.1232, found 202.1217.

4.2 Procedure for the synthesis of I40



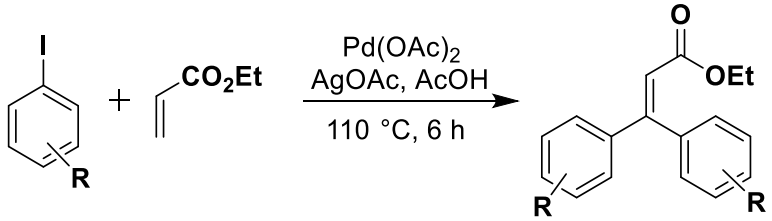
In a N_2 atmosphere, oven-dried round-bottom flask equipped with a magnetic stir bar, 2-iodobenzamide (2 mmol) was added. To this, $Pd(PPh_3)_2Cl_2$ (5 mol%) was added, followed by potassium trifluoro(prop-1-en-2-yl)borate (1.2 equivalents) and K_2CO_2 (3.0 equiv.). Then, 1,4-dioxane (8.5 mL) and deionized H_2O (2.8 mL) was added to the mixture. The reaction mixture was stirred at 100 °C for 15 h. The mixture was cooled to room temperature and diluted with water. The aqueous layer was extracted with EtOAc, and the combined organic extracts were washed with aq. NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography using 30–40% ethyl acetate in hexane, affording the 2-(prop-1-en-2-yl)benzamide **I40**.

2-(prop-1-en-2-yl)benzamide (I40)

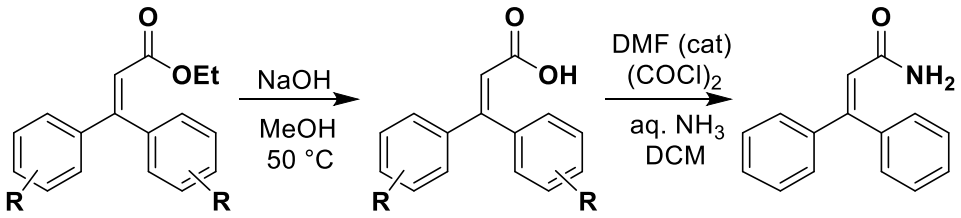


40% yield (130 mg, 0.80 mmol) as a white solid. **m.p.** 101-103 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (dd, J = 7.7, 1.5 Hz, 1H), 7.42–7.39 (m, 1H), 7.35–7.31 (m, 1H), 7.22 (dd, J = 7.5, 1.4 Hz, 1H), 6.33 (brs, 2H), 5.26–5.21 (m, 1H), 5.12–5.08 (m, 1H), 2.12 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.30, 146.9, 142.4, 132.9, 130.9, 129.1, 128.9, 127.6, 116.1, 24.5. **IR** (neat) 3377, 3173, 2917, 1640, 1391, 1177 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{10}H_{12}NO$ 162.0919, found 162.0902.

4.3 General procedure for the synthesis of I44 to I47 (General Procedure F)



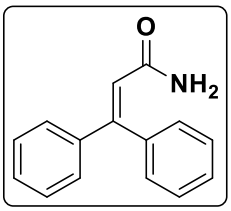
A suspension of AgOAc (10 mmol, 2 equiv) and $Pd(OAc)_2$ (5 mol%) in AcOH (4.1 mL) was prepared, followed by the addition of iodobenzene (5 mmol, 1 equiv) and ethyl acrylate (1.65 mmol, 0.35 equiv). The reaction mixture was stirred under an argon atmosphere at 110 °C for 12 hours. After completion, the mixture was allowed to cool to room temperature and diluted with ethyl acetate (5 mL). It was then filtered through a pad of Celite and washed with ethyl acetate (60 mL). The combined filtrate was concentrated under reduced pressure, and the crude product was purified by column chromatography (hexane/ethyl acetate = 15:1) to afford the ethyl 3,3-diphenylacrylate derivatives as a yellow oil.



The corresponding ester (1.3 mmol, 1 equiv) was dissolved in a mixture of NaOH (5.0 equiv) in 0.8 mL of water and 3.5 mL of methanol, and the reaction mixture was stirred at 50 °C for 6 hours. Upon completion, methanol was removed under reduced pressure, and the residue was diluted with water. The aqueous phase was acidified with 3 N HCl and extracted with diethyl ether. The combined organic extracts were washed sequentially with water and brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to afford the desired 3,3-diphenylacrylic acid derivatives. Which was used directly used in the next step without further purification.

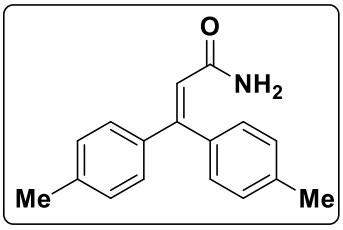
The 3,3-diphenylacrylic acid derivative and a catalytic amount of DMF were dissolved in 3.6 mL of anhydrous dichloromethane in a round-bottom flask. The solution was cooled to 0 °C and stirred for 5 minutes before oxalyl chloride (1.2 equiv) was added dropwise at the same temperature. The reaction mixture was then allowed to warm to room temperature and stirred for 4 hours. Afterwards, the solvent was removed under reduced pressure to yield the crude acid chloride. This intermediate was dissolved in 3 mL of dry dichloromethane, followed by dropwise addition of 4.2 mL of aqueous ammonia at 0 °C. The mixture was stirred at room temperature for 10 hours. The reaction was quenched with water and extracted with DCM (3 × 15 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography using 20–30% ethyl acetate in hexane to afford the 3,3-diphenylacrylamide derivatives.

3,3-diphenylacrylamide (I44)[11]



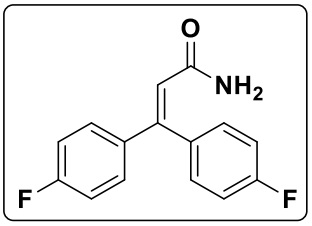
The title compound was prepared by following the general procedure F in 83% yield (241 mg, 1.1 mmol) as a white solid. **m.p.** 150-152 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.41 (m, 3H), 7.38–7.27 (m, 7H), 6.39 (s, 1H), 5.48 (brs, 1H), 5.11 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.8, 151.1, 140.7, 138.2, 129.3, 129.1, 128.9, 128.8, 128.5, 128.0, 121.8. **IR** (neat) 3386, 3182, 2926, 1608, 1380, 1182, 1118 cm^{-1}.

3,3-di-*p*-tolylacrylamide (I45)[11]



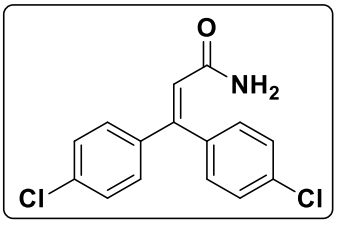
The title compound was prepared by following the general procedure F in 88% yield (287 mg, 1.14 mmol) as a white solid. **m.p.** 155-157 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25 (d, J = 8.1 Hz, 2H), 7.18–7.15 (m, 4H), 7.12 (d, J = 8.3 Hz, 2H), 6.35 (s, 1H), 5.44 (brs, 1H), 5.15 (brs, 1H), 2.41 (s, 3H), 2.35 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.0, 151.9, 139.6, 139.1, 137.9, 135.3, 129.8, 129.4, 129.3, 128.1, 120.4, 21.5, 21.4. **IR** (neat) 3388, 3184, 2921, 1645, 1601, 1391, 1333, 1183, 1115 cm^{-1}.

3,3-bis(4-fluorophenyl)acrylamide (I46)[12]



The title compound was prepared by following the general procedure F in 50% yield (168 mg, 0.65 mmol) as a white solid. **m.p.** 118-120 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28–7.18 (m, 4H), 7.14–7.07 (m, 2H), 7.05–6.98 (m, 2H), 6.29 (s, 1H), 5.78 (brs, 1H), 5.27 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.4, 164.3 (d, J = 50.6 Hz), 162.3 (d, J = 49.8 Hz), 149.7, 136.9 (d, J = 3.3 Hz), 134.0 (d, J = 3.6 Hz), 131.4 (d, J = 8.2 Hz), 130.1 (d, J = 8.3 Hz), 121.4.116.0 (d, J = 21.7 Hz), 115.7 (d, J = 21.6 Hz). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -111.66 to -111.71 (m, 1F), 111.85 to 111.90 (m, 1F). **IR** (neat) 3487, 3347, 2921, 1661, 1597, 1502, 1426, 1320, 1227 cm^{-1}.

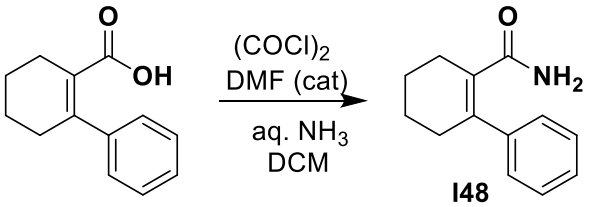
3,3-bis(4-chlorophenyl)acrylamide (I47)



The title compound was prepared by following the general procedure F in 40% yield (151 mg, 0.52 mmol) as a white solid. **m.p.** 130-132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.36 (m, 2H), 7.32–7.27 (m, 2H), 7.23–7.17 (m, 2H), 7.19–7.14 (m, 2H),

6.32 (s, 1H), 5.79 (brs, 1H), 5.31 (s, 1H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 168.1, 149.5, 138.9, 136.3, 135.6, 135.2, 130.9, 129.5, 129.2, 128.9, 121.9. **IR** (neat) 3470, 3308, 3162, 2923, 1661, 1601, 1381, 1325, 1088, 1015 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{12}Cl_2NO$ 292.0296, found 292.0284.

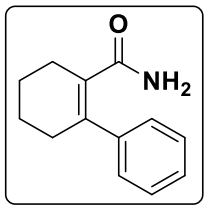
4.4 Procedure for the synthesis of I48



3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylic acid was prepared according to the previous reported procedures[13]. The compound **I48** was prepared as described in the following procedure.

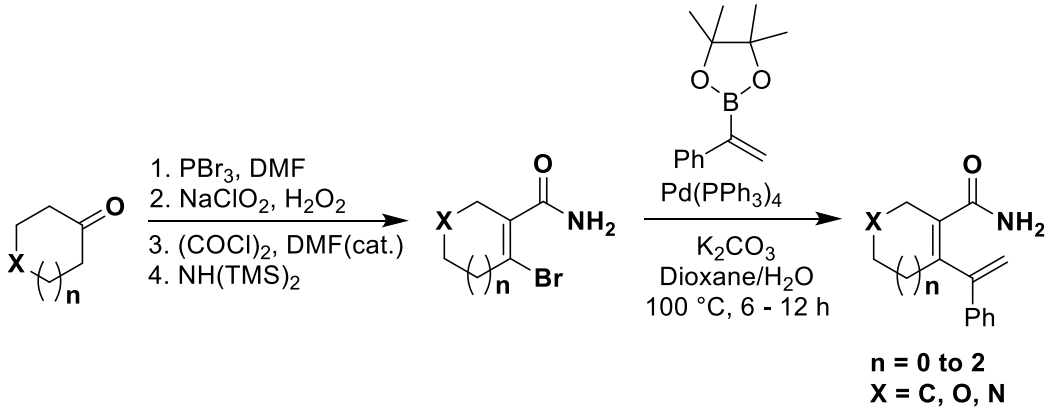
3,4,5,6-Tetrahydro-[1,1'-biphenyl]-2-carboxylic acid (1.9 mmol, 1 equiv) and a catalytic amount of DMF were dissolved in 4.7 mL of dry dichloromethane in a round-bottom flask. The reaction mixture was cooled to 0 °C and stirred for 5 minutes before adding oxalyl chloride (1.2 equiv) dropwise at the same temperature. The reaction was then allowed to warm to room temperature and stirred for an additional 4 h. Then, the solvent was removed under reduced pressure to obtain the crude acid chloride. The crude intermediate was dissolved in 3.9 mL of dry DCM, and 5.4 mL of aq. ammonia was added dropwise at 0 °C. The mixture was stirred at room temperature for 10 h. The reaction was then quenched with water and extracted with DCM (3 × 15 mL). The combined organic phases were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography using 30-40% ethyl acetate in hexane to afford the 3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide **I48**.

3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide (I48)



50% yield (191 mg, 0.95 mmol) as a yellow solid. **m.p.** 120-122 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36–7.32 (m, 2H), 7.31–7.28 (m, 1H), 7.26–7.22 (m, 2H), 5.27 (brs, 1H), 4.92 (brs, 1H), 2.47–2.42 (m, 2H), 2.40–2.34 (m, 2H), 1.77–1.70 (m, 4H). **$^{13}C\{^{1}H\}$ NMR** (126 MHz, $CDCl_3$) δ 173.1, 142.4, 140.9, 131.5, 128.9, 127.8, 127.4, 32.3, 27.0, 22.8, 22.1. **IR** (neat) 3416, 3198, 2926, 2861, 1634, 1601, 1446, 1390, 1160 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_{16}NO$ 202.1232, found 202.1217.

4.5 General procedure for the synthesis of I49 to I54 (General Procedure G)[14]



A solution of DMF (30 mmol) in CH_2Cl_2 (20 mL) was cooled to 0 °C and slowly treated with PBr_3 (37.5 mmol), followed by stirring for 1 hour. To this mixture, a solution of cyclic ketone (10 mmol, 1 equiv) in CH_2Cl_2 (4.5 mL) was added dropwise, and the reaction was stirred at 25 °C for 24 hours. The reaction was quenched by pouring the mixture onto ice and adjusting the pH to 7 with $NaHCO_3$. The resulting mixture was allowed to warm to room temperature and extracted three times with ethyl acetate. The combined organic extracts were washed with sat. $NaHCO_3$ solution, brine, and water. The organic layer was dried over Na_2SO_3, filtered, and concentrated under reduced pressure. The crude product was used as such in the next step.

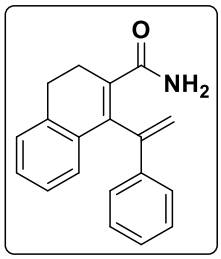
To a stirred mixture of crude carbaldehyde derivative in acetonitrile (10 mL) was added a solution of sodium chlorite (1.4 equiv) in water (15 mL) at 0 °C. Then, NaH_2PO_4 (0.32 g) in water (5 mL), and 30% aqueous hydrogen peroxide (1.2 mL) was added dropwise over 2 h at 0 °C. After the addition was complete, the mixture was stirred for an additional 2 h at 108 °C. The reaction was then quenched by pouring it into sat. aq. Na_2CO_3, 25 mL) and washed with diethyl ether (15 mL); the ether layer was discarded. The aqueous layer was then acidified with 1 N HCl (100 mL) and extracted with diethyl ether (3 × 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to yield cyclic carboxylic acid derivative. Which was used directly without further purification for the next step.

To a solution of the crude cyclic carboxylic acid derivatives in CH_2Cl_2 (40 mL) at 0 °C, 3–4 drops of dry DMF followed by oxalyl chloride (3 equiv) was added, the reaction mixture was stirred at room temperature for 4 h. Then, hexamethyldisilazane (7.5 equiv) was added

dropwise at 0 °C, and the mixture was stirred overnight at room temperature. After cooling the reaction mixture at 0 °C, MeOH (15 mL) was added, and the stirring was continued for an additional 3 h at room temperature. H_2O was added, and the mixture was extracted with CH_2Cl_2. The organic layer was then washed with brine. The combined organic layers were dried over Na_2SO_4 and concentrated to afford cyclohexene carboxamide derivative. The crude product was used directly in the next step.

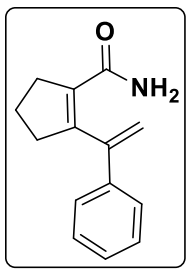
In an oven-dried round-bottom flask equipped with a magnetic stir bar, the crude cyclohexene carboxamide derivative was added under a nitrogen atmosphere. $Pd(PPh_3)_4$ (5 mol%), 4,4,5,5-tetramethyl-2-(1-phenylvinyl)-1,3,2-dioxaborolane (1.2 equiv), and K_2CO_3, (3.0 equiv) were added, followed by a mixture of 1,4-dioxane (0.25 M) and H_2O (0.5 M). The reaction was stirred at 100 °C for 12 h. The reaction was monitored by TLC to establish the consumption of starting material. After cooling, water was added, and the mixture was extracted with ethyl acetate. The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude residue was purified by column chromatography using a gradient of 30–40% ethyl acetate in hexane to afford the desired product.

1-(1-phenylvinyl)-3,4-dihydronaphthalene-2-carboxamide (I49)



The title compound was prepared by following the general procedure G in 15% overall yield (413 mg, 1.5 mmol) as a yellow solid. **m.p.** 86-88 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.50–7.44 (m, 2H), 7.35–7.25 (m, 3H), 7.21–7.16 (m, 2H), 7.18–7.12 (m, 1H), 7.10–7.03 (m, 1H), 6.05 (s, 1H), 5.92 (brs, 1H), 5.63 (brs, 1H), 5.38 (s, 1H), 2.93 (t, J = 8.0 Hz, 1H), 2.73 (t, J = 8.0 Hz, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.9, 145.3, 139.4, 138.0, 136.9, 133.9, 132.3, 129.2, 128.7, 128.6, 127.6, 127.1, 126.8, 126.0, 116.7, 28.2, 25.6. **IR** (neat) 3461, 3390, 3156, 1652, 1493, 1448, 1404 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{18}NO$ 276.1388, found 276.1382.

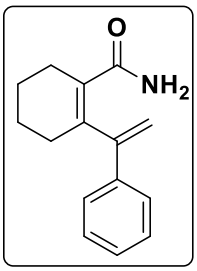
2-(1-phenylvinyl)cyclopent-1-ene-1-carboxamide (I50)



The title compound was prepared by following the general procedure G in 32% overall yield (682 g 3.2 mmol) as a white solid. **m.p.** 72-74 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.35 (m, 2H), 7.36–7.28 (m, 3H), 6.10 (brs, 1H), 5.74 (brs, 1H), 5.69 (s, 1H), 5.28 (s, 1H), 2.86–2.81 (m, 2H), 2.65–2.60 (m, 2H), 1.96–1.90 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.1, 148.8,

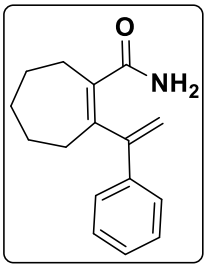
146.0, 137.2, 134.6, 128.9, 128.7, 126.2, 114.4, 40.4, 34.6, 21.8. **IR** (neat) 3430, 3147, 2940, 1661, 1597, 1404, 1154 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO$ 214.1232, found 214.1215.

2-(1-phenylvinyl)cyclohex-1-ene-1-carboxamide (I51)



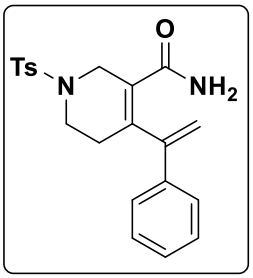
The title compound was prepared by following the general procedure G in 28% overall yield (636 mg, 2.8 mmol) as a yellow solid. **m.p.** 80-82 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44–7.39 (m, 2H), 7.39–7.32 (m, 2H), 7.34–7.27 (m, 1H), 5.74 (brs, 1H), 5.61 (s, 1H), 5.28 (brs, 1H), 5.21 (s, 1H), 2.49–2.44 (m, 2H), 2.19–2.14 (m, 2H), 1.77–1.71 (m, 2H), 1.70–1.64 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 172.5, 149.6, 141.0, 137.9, 132.0, 129.0, 128.4, 126.2, 113.6, 31.2, 26.6, 22.5, 22.3. **IR** (neat) 3463, 3114, 2932, 1661, 1605, 1390, 1338, 1157 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{18}NO$ 228.1388, found 228.1376.

2-(1-phenylvinyl)cyclohept-1-ene-1-carboxamide (I52)



The title compound was prepared by following the general procedure G in 29% overall yield (700 g, 2.9 mmol) as a white solid. **m.p.** 90-92 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44–7.39 (m, 2H), 7.40–7.33 (m, 2H), 7.34–7.29 (m, 1H), 5.55 (brs, 2H), 5.51 (s, 1H), 5.34 (brs, 1H), 5.20 (s, 1H), 2.59–2.54 (m, 2H), 2.30–2.25 (m, 2H), 1.84–1.78 (m, 2H), 1.70–1.65 (m, 2H), 1.56–1.52 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.8, 150.2, 146.5, 138.2, 137.8, 129.0, 128.5, 126.6, 113.2, 34.8, 32.5, 31.0, 27.1, 26.0. **IR** (neat) 3460, 3146, 2928, 1630, 1408, 1365, 1165 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{20}NO$ 242.1545, found 242.1539.

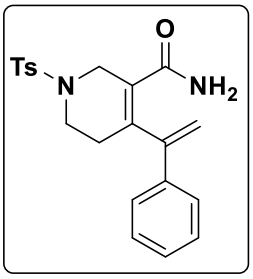
4-(1-phenylvinyl)-1-tosyl-1,2,5,6-tetrahydropyridine-3-carboxamide (I53)



The title compound was prepared by following the general procedure G in 23% overall yield (880 g, 2.3 mmol) as a yellow liquid. (NMR data for rotamers) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.74–7.71 (m, 1.60H), 7.69–7.64 (m, 1.22H), 7.56–7.53 (m, 0.64H), 7.48–7.44 (m, 1.12H), 7.36–7.31 (m, 6.12H), 6.36 (brs, 0.18H), 5.98 (brs, 0.64H), 5.91 (brs, 0.22H), 5.67 (s, 0.79H), 5.42 (brs, 0.64H), 5.18 (s, 0.80H), 3.99–3.95 (m, 1.56H), 3.90–3.89 (m, 0.35H), 3.27 (t, J = 5.8 Hz, 0.34H), 3.23 (t, J = 5.8 Hz, 1.46H), 2.64–2.61 (m, 0.31H), 2.44 (s, 2.33H), 2.43 (s, 0.52H), 2.40–2.37 (m, 1.80H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.5, 166.1, 147.9, 144.3, 144.0, 140.6, 136.3, 134.5, 133.2, 133.0, 132.3, 132.2, 132.1, 132.1, 131.4, 130.0, 129.9, 129.2, 129.0, 128.7, 128.6, 129.00, 127.8, 127.7,

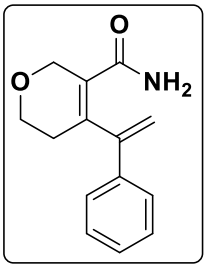
126.1, 114.6, 46.8, 45.6, 43.2, 42.7, 34.4, 31.4, 25.0, 21.7. **IR** (neat) 3310, 3181, 2923, 1650, 1336, 1165, 1117 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{21}H_{23}N_2O_3$ 405.1249, found 405.1243.

4-(1-phenylvinyl)-1-tosyl-1,2,5,6-tetrahydropyridine-3-carboxamide (I53)



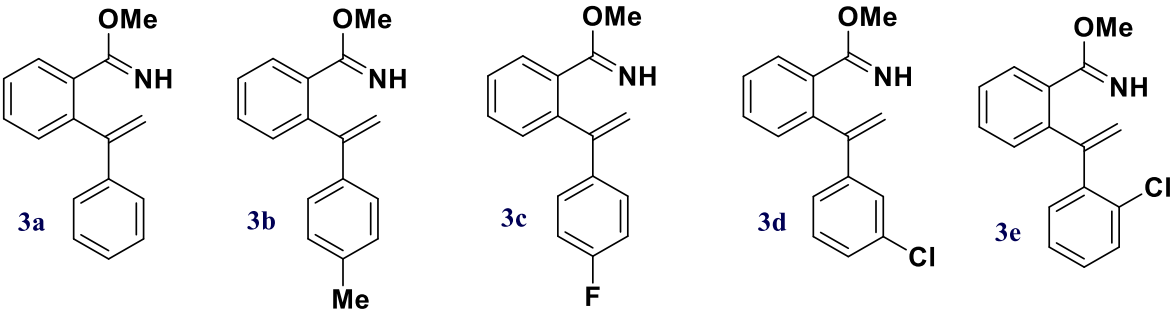
The title compound was prepared by following the general procedure G in 23% overall yield (880 g, 2.3 mmol) as a yellow liquid. (Rotamers was observed). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.2 Hz, 1.43H), 7.71–7.61 (m, 1.47H), 7.38–7.28 (m, 6.11H), 6.37 (brs, 0.23H), 5.99 (brs, 0.80H), 5.67 (s, 0.82H), 5.51 (brs, 0.63H), 5.18 (s, 0.83H), 3.99–3.95 (m, 1.44H), 3.92–3.87 (m, 0.45H), 3.27 (t, *J* = 5.8 Hz, 0.50H), 3.22 (t, *J* = 5.8 Hz, 1.50H), 2.66–2.59 (m, 0.46H), 2.44 (s, 2.29H), 2.43 (s, 0.69H), 2.43–2.36 (m, 2.56H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.5, 166.1, 147.9, 144.3, 144.0, 140.6, 136.3, 134.5, 133.2, 133.0, 132.3, 132.2, 132.1, 132.1, 131.4, 130.0, 129.9, 129.2, 129.0, 128.7, 128.6, 129.00, 127.8, 127.7, 126.1, 114.6, 46.8, 45.6, 43.2, 42.7, 34.4, 31.4, 25.0, 21.7. **IR** (neat) 3310, 3181, 2923, 1650, 1336, 1165, 1117 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{21}H_{23}N_2O_3SNa$ 405.1249, found 405.1243.

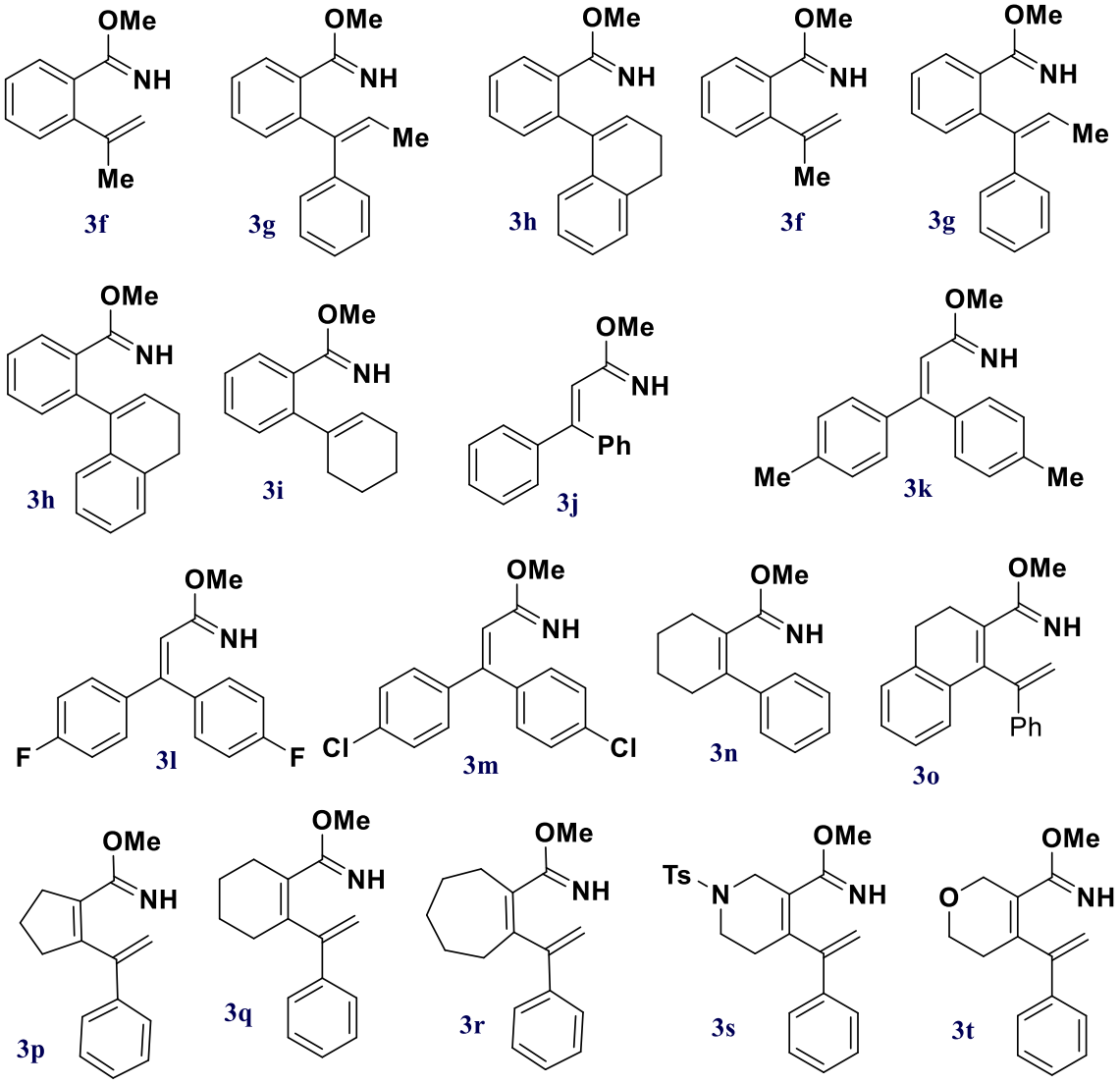
4-(1-phenylvinyl)-5,6-dihydro-2H-pyran-3-carboxamide (I54)



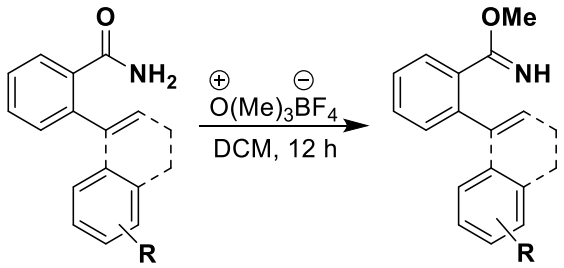
The title compound was prepared by following the general procedure G in 23% overall yield (527 mg, 2.3 mmol) as a yellow solid. **m.p.** 128-130 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.41–7.31 (m, 3H), 6.06 (brs, 1H), 5.72 (s, 1H), 5.48 (brs, 1H), 5.30 (s, 1H), 4.50 (t, *J* = 2.6 Hz, 2H), 3.83 (t, *J* = 5.5 Hz, 2H), 2.33–2.26 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 168.7, 148.3, 140.5, 136.7, 130.1, 129.2, 128.9, 126.2, 114.5, 65.9, 64.2, 30.8. **IR** (neat) 3483, 3158, 1656, 1402, 1174, 1110, 1024 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO_2$ 230.1176, found 230.1182.

List of imidate for the synthesis of other *N*-heterocycles





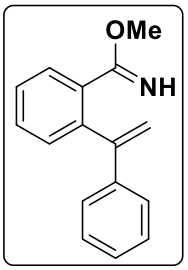
4.6 General procedure for the synthesis of 3a-3i (General Procedure H)



Trimethyloxonium tetrafluoroborate (1.5 equiv) was added to a solution of 2-(1-phenylvinyl)benzamide (0.5 mmol, 1.0 equiv) in CH_2Cl_2(6 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred overnight. Then, the reaction was quenched with methanol (1.5 mL) and concentrated under reduced pressure. The resulting crude residue was purified by column chromatography on deactivated silica gel using a gradient

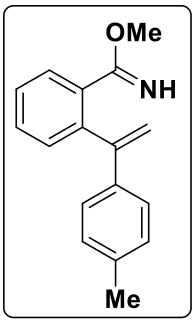
of hexane/ethyl acetate (5–10%) to yield the desired methyl 2-(1-phenylvinyl)benzimidate derivatives.

methyl 2-(1-phenylvinyl)benzimidate (3a)



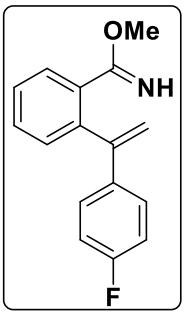
The title compound was prepared by following the general procedure H in 66% yield (78 mg, 0.33 mmol) as a pale yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 1H), 7.49–7.44 (m, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.28–7.23 (m, 5H), 5.71 (s, 1H), 5.32 (s, 1H), 3.59 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.0, 149.0, 140.4, 140.2, 131.0, 130.2, 128.2, 128.0, 127.9, 127.9, 127.0, 125.1, 115.5, 53.8. **IR** (neat) 3324, 2945, 1639, 1437, 1338, 1170, 1075 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO$238.1232, found 238.1239.

methyl 2-(1-(p-tolyl)vinyl)benzimidate (3b)



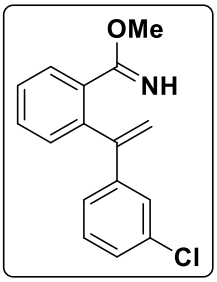
The title compound was prepared by following the general procedure H in 70% yield (88 mg, 0.35 mmol) as pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.56–7.50 (m, 1H), 7.47–7.39 (m, 1H), 7.41–7.34 (m, 1H), 7.37–7.31 (m, 1H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 1H), 5.25 (s, 1H), 3.57 (s, 3H), 2.32 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.0, 150.0, 140.7, 137.8, 137.5, 131.1, 130.2, 129.0, 128.0, 127.9, 127.0, 114.8, 53.7, 21.3. **IR** (neat) 3330, 2945, 1636, 1515, 1437, 1338, 1070 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{18}NO$ 252.1388 , found 252.1395.

methyl 2-(1-(4-fluorophenyl)vinyl)benzimidate (3c)



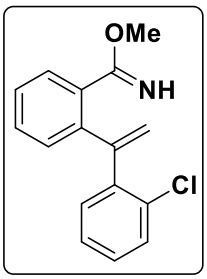
The title compound was prepared by following the general procedure H in 55% yield (70 mg, 0.27 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52–7.47 (m, 1H), 7.48–7.41 (m, 1H), 7.42–7.35 (m, 1H), 7.37–7.32 (m, 1H), 7.23–7.16 (m, 2H), 7.00–6.91 (m, 2H), 5.64 (s, 1H), 5.30 (s, 1H), 3.53 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 162.6 (d, *J* = 247.2 Hz), 148.3, 140.1, 136.5 (d, *J* = 3.5 Hz), 134.3, 131.0, 130.1, 128.8 (d, *J* = 8.1 Hz), 128.2, 128.0, 115.4, 115.1 (d, *J* = 21.6 Hz) 53.4. **^{19}F NMR** (471 MHz, $CDCl_3$) δ ^{19}F NMR (471 MHz, $CDCl_3$) δ -114.32 to -114.38 (m, 1F). **IR** (neat) 3330, 2948, 1639, 1600, 1506, 1368, 1227, 1160, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{15}FNO$ 256.1132, found 256.1118.

methyl 2-(1-(3-chlorophenyl)vinyl)benzimidate (3d)



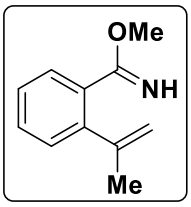
The title compound was prepared by following the general procedure H in 83% yield (113 mg, 0.41 mmol) as a yellow liquid **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54–7.51 (m, 1H), 7.50–7.46 (m, 1H), 7.45–7.41 (m, 1H), 7.39–7.35 (m, 1H), 7.30–7.22 (m, 3H), 7.15–7.11 (m, 1H), 5.73 (s, 1H), 5.39 (s, 1H), 3.57 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.7, 148.1, 142.2, 140.5, 134.5, 134.4, 131.0, 130.1, 129.5, 128.3, 128.0, 128.0, 127.2, 125.4, 116.6, 53.3. **IR** (neat) 3328, 2945, 1636, 1577, 1440, 1347, 1314, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{15}ClNO$ 272.0837, found 272.0819.

methyl 2-(1-(2-chlorophenyl)vinyl)benzimidate (3e)



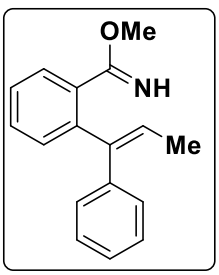
The title compound was prepared by following the general procedure H in 81% yield (110 mg, 0.40 mmol) as a pale yellow solid. **m.p.** 46-48 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.31 (m, 5H), 7.25–7.20 (m, 3H), 5.67 (s, 1H), 5.59 (s, 1H), 3.57 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.5, 146.6, 139.6, 139.6, 134.1, 133.0, 132.1, 130.4, 130.1, 129.8, 129.0, 128.0, 127.9, 126.5, 121.1, 53.4. **IR** (neat) 3324, 2943, 1636, 1430, 1330, 1168, 1066, 1040 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{15}ClNO$ 272.0837, found 272.0836.

methyl 2-(prop-1-en-2-yl)benzimidate (3f)



The title compound was prepared by following the general procedure H in 69% yield (60.4 mg, 0.34 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52–7.46 (m, 1H), 7.40–7.33 (m, 1H), 7.33–7.26 (m, 1H), 7.26–7.20 (m, 1H), 5.20–5.16 (m, 1H), 5.02–4.98 (m, 1H), 3.89 (s, 3H), 2.04 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.3, 145.7, 142.7, 132.5, 130.1, 129.2, 127.8, 127.3, 115.8, 53.8, 23.9. **IR** (neat) 3330, 2943, 1636, 1437, 1342, 1095, 1073 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{11}H_{14}NO$ 176.1075, found 176.1078.

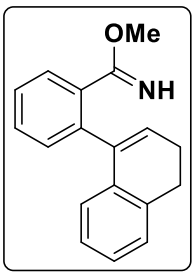
methyl (*E*)-2-(1-phenylprop-1-en-1-yl)benzimidate (3g)



The title compound was prepared by following the general procedure H in 43% yield (54 mg, 0.215 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67–7.63 (m, 1H), 7.48–7.44 (m, 1H), 7.41–7.36 (m, 1H), 7.24–7.16 (m, 6H), 6.31 (q, J = 6.9 Hz, 1H), 3.67 (s, 3H), 1.65 (d, J = 7.0 Hz, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.1, 141.2, 141.1, 138.4,

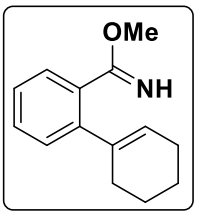
134.1, 131.6, 130.2, 128.4, 128.2, 127.6, 127.1, 126.6, 125.1, 53.4, 15.8. **IR** (neat) 3335, 2941, 1641, 1435, 1347, 1165, 1070 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for C17H18NO 252.1388, found 252.1392.

methyl 2-(3,4-dihydronaphthalen-1-yl)benzimidate (3h)



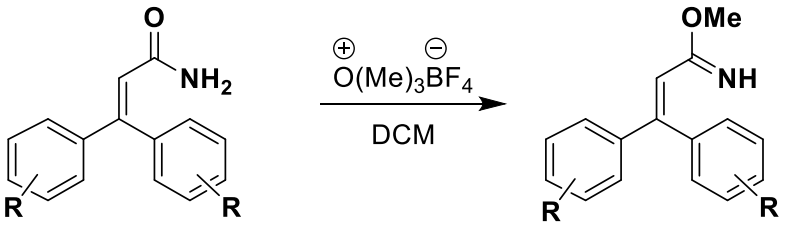
The title compound was prepared by following the general procedure H in 68% yield (90 mg, 0.34 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.47–7.43 (m, 1H), 7.40–7.37 (m, 1H), 7.30 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.18–7.16 (m, 1H), 7.14–7.11 (m, 1H), 7.06–7.02 (m, 1H), 6.66–6.64 (m, 1H), 6.05 (t, *J* = 4.6 Hz, 1H), 3.58 (s, 3H), 2.88-2.84 (m, 2H), 2.45-2.39 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 169.5, 139.2, 139.2, 136.1, 134.9, 133.9, 131.2, 130.3, 128.4, 127.8, 127.7, 127.6, 127.4, 126.5, 124.6, 53.3, 28.2, 23.7. **IR** (neat) 3328, 2940, 1634, 1435, 1336, 1160, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{18}NO$ 264.1388, found 264.1398.

methyl 2',3',4',5'-tetrahydro-[1,1'-biphenyl]-2-carbimidate (3i)



The title compound was prepared by following the general procedure H in 76% yield (82 mg, 0.38 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53–7.48 (m, 1H), 7.38–7.32 (m, 1H), 7.30–7.23 (m, 1H), 7.17 (dd, *J* = 7.6, 1.4 Hz, 1H), 5.72–5.70 (m, 1H), 3.89 (s, 3H), 2.20–2.15 (m, 4H), 1.76–1.70 (m, 2H), 1.69–1.63 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.3, 143.6, 138.9, 132.3, 130.1, 129.6, 127.8, 127.2, 126.9, 53.7, 29.8, 25.7, 23.3, 22.0. **IR** (neat) 3321, 2930, 1641, 1442, 1336, 1163, 1073 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{18}NO$ 216.1388, found 216.1391.

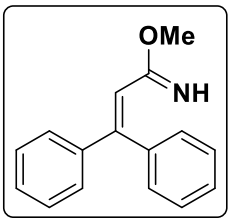
4.7 General procedure for the synthesis of 3j-3m (General Procedure I)



To a solution of 3,3-diphenylacrylamide derivatives (0.5 mmol, 1.0 equiv) in dichloromethane (6 mL), trimethyloxonium tetrafluoroborate (1.5 equiv) was added at 0 °C. The reaction mixture was gradually warmed to room temperature and stirred overnight. After completion, the reaction was quenched with methanol (1.5 mL) and concentrated under reduced pressure. The crude product was then purified by column chromatography on deactivated silica gel using

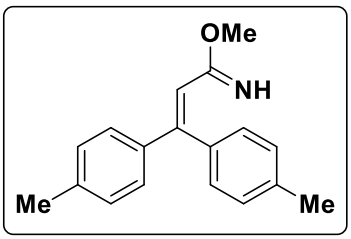
a hexane/ethyl acetate gradient (5–10%) to afford the desired methyl 3,3-diphenylacrylimidate derivatives.

methyl 3,3-diphenylacrylimidate (3j)



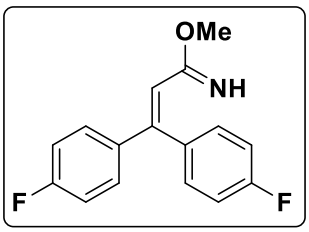
The title compound was prepared by following the general procedure I in 65% yield (76 mg, 0.32 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44–7.39 (m, 3H), 7.34–7.29 (m, 3H), 7.29–7.26 (m, 2H), 7.24–7.22 (m, 2H), 6.33 (s, 1H), 3.67 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.6, 150.7, 141.1, 138.5, 129.2, 129.1, 129.0, 128.6, 128.5, 128.0, 119.2, 52.8. **IR** (neat) 3340, 2943, 1625, 1442, 1367, 1307, 1177 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{16}NO$ 238.1232, found 238.1239.

methyl 3,3-di-*p*-tolylacrylimidate (3k)



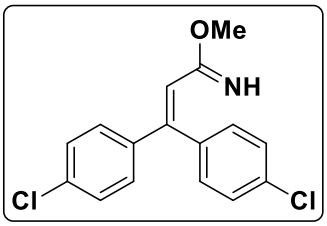
The title compound was prepared by following the general procedure I in 88% yield (117 mg, 0.44 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22 (d, J = 7.6 Hz, 2H), 7.19–7.13 (m, 2H), 7.14–7.07 (m, 4H), 6.27 (s, 1H), 3.68 (s, 1H), 2.39 (s, 3H), 2.34 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.8, 151.1, 139.2, 138.5, 138.4, 135.5, 129.7, 129.2, 129.1, 128.0, 117.9, 52.9, 21.5, 21.3. **IR** (neat) 3348, 2948, 1718, 1628, 1600, 1429, 1375, 1303, 1148, 1079 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{20}NO$ 266.1539, found 266.1515.

methyl 3,3-bis(4-fluorophenyl)acrylimidate (3l)



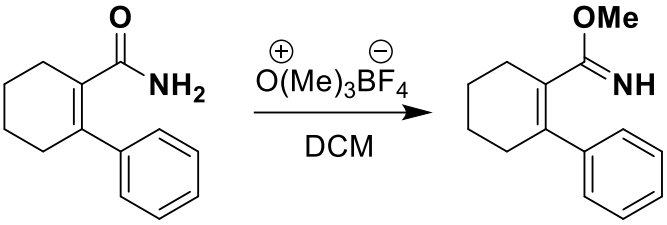
The title compound was prepared by following the general procedure I in 83% yield (113 mg, 0.41 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.24–7.17 (m, 4H), 7.13–7.08 (m, 2H), 7.03–6.98 (m, 2H), 6.26 (s, 1H), 3.66 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.5, 164.2 (d, J = 52.8 Hz), 162.2 (d, J = 51.6 Hz), 148.5, 137.1 (d, J = 3.4 Hz), 134.3 (d, J = 3.5 Hz), 131.2 (d, J = 8.3 Hz), 129.8 (d, J = 8.3 Hz), 119.6, 116.0 (d, J = 21.6 Hz), 115.6 (d, J = 21.7 Hz), 53.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.15 to -112.18 (m, 1F), 112.53 to -112.59 (m, 1F); **IR** (neat) 3344, 2945, 1632, 1599, 1504, 1308, 1227, 1154, 1086 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{14}F_2NO$ 274.1043, found 274.1056.

methyl 3,3-bis(4-chlorophenyl)acrylimidate (3m)



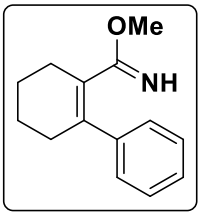
The title compound was prepared by following the general procedure I in 82% yield (125 mg, 0.41 mmol) as a pale yellow liquid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 2H), 7.30–7.25 (m, 2H), 7.18–7.12 (m, 4H), 6.30 (s, 1H), 3.66 (s, 3H); **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 167.3, 148.1, 139.2, 136.6, 135.4, 134.9, 130.7, 129.3, 129.2, 128.9, 120.2, 53.0; **IR** (neat) 3352, 2941, 1625, 1488, 1437, 1362, 1307, 1081 cm^{-1}; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{14}Cl_2NO$ 306.0453, found 306.0455.

4.8 Procedure for the synthesis of 3n



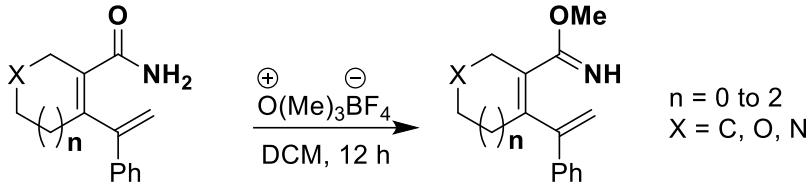
To a solution of 3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxamide (0.5 mmol, 1.0 equiv) in dichloromethane (6 mL), trimethyloxonium tetrafluoroborate (1.5 equiv) was added at 0 °C. The mixture was gradually warmed to room temperature and stirred overnight. After completion, the reaction was quenched with methanol (1.5 mL) and concentrated under reduced pressure. The crude product was then purified by column chromatography on deactivated silica gel using a hexane/ethyl acetate gradient (5%) to afford the methyl 3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carbimidate.

methyl 3,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carbimidate (3n)



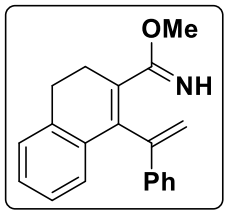
75% yield (81 mg, 0.37 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.25–7.21 (m, 1H), 7.17–7.14 (m, 2H), 3.57 (s, 3H), 2.39–2.33 (m, 4H), 1.76–1.72 (m, 4H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 172.1, 142.8, 130.1, 128.4, 127.3, 127.2, 125.4, 53.0, 31.9, 27.8, 22.7, 22.3. **IR** (neat) 3326, 2923, 1625, 1437, 1327, 1081 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{18}NO$ 216.1388, found 216.1387.

4.9 General procedure for the synthesis of 3o-3t (General Procedure J)



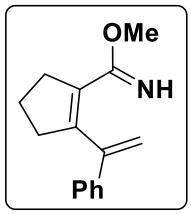
Trimethyloxonium tetrafluoroborate (1.5 equiv.) was added to a solution of phenylvinyl cyclic carboxamide derivatives (0.5 mmol, 1.0 equiv) in dichloromethane (6 mL) at 0 °C. The reaction mixture was then allowed to warm to room temperature and stirred for 12 h. The reaction was quenched with methanol (1.5 mL) and the solvent was removed under reduced pressure. The crude residue was purified by column chromatography on deactivated silica gel using a 5–10% ethyl acetate in hexane to yield the desired phenylvinyl cyclic carbimidate derivatives.

methyl 1-(1-phenylvinyl)-3,4-dihydronaphthalene-2-carbimidate (3o)



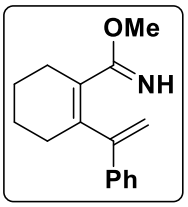
The title compound was prepared by following the general procedure J in 66% yield (95 mg, 0.33 mmol) as a pale yellow solid. **m.p.** 74-76 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46–7.40 (m, 2H), 7.32–7.21 (m, 3H), 7.20–7.13 (m, 3H), 7.11–7.04 (m, 1H), 5.92 (s, 1H), 5.24 (s, 1H), 3.64 (s, 3H), 2.92 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.7, 145.5, 139.4, 138.9, 136.3, 134.2, 131.1, 128.7, 128.2, 128.1, 127.5, 126.9, 126.8, 126.2, 116.0, 52.9, 28.2, 26.1. **IR** (neat) 3321, 2932, 1645, 1435, 1345, 1325, 1188, 1073 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{20}NO$ 290.1545, found 290.1549.

methyl 2-(1-phenylvinyl)cyclopent-1-ene-1-carbimidate (3p)



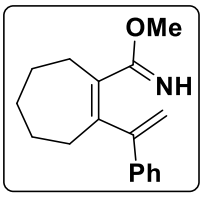
The title compound was prepared by following the general procedure J in 62% yield (70 mg, 0.31 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 5H), 5.54 (d, *J* = 1.2 Hz, 1H), 5.22 (d, *J* = 1.2 Hz, 1H), 3.47 (s, 3H), 2.75–2.72 (m, 2H), 2.68–2.63 (m, 2H), 1.99–1.92 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.5, 146.8, 145.7, 139.2, 132.6, 128.5, 127.9, 126.5, 114.8, 52.5, 39.5, 35.3, 22.4. **IR** (neat) 3339, 2948, 1623, 1437, 1320, 1066 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{18}NO$ 228.1388, found 228.1378.

methyl 2-(1-phenylvinyl)cyclohex-1-ene-1-carbimidate (3q)



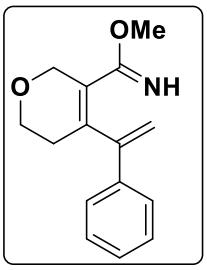
The title compound was prepared by following the general procedure J in 59% yield (76 mg, 0.29 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39–7.33 (m, 2H), 7.35–7.28 (m, 2H), 7.29–7.22 (m, 1H), 5.44 (s, 1H), 5.08 (s, 1H), 3.54 (s, 3H), 2.36–2.32 (m, 2H), 2.17–2.13 (m, 2H), 1.75–1.70 (m, 2H), 1.69–1.64 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.8, 150.0, 139.1, 130.7, 128.5, 127.8, 126.7, 113.0, 53.0, 30.7, 27.4, 22.5, 22.4. **IR** (neat) 3339, 2928, 2855, 1665, 1446, 1383, 1265, 1066 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{20}NO$ 242.1543, found 242.1545.

methyl 2-(1-phenylvinyl)cyclohept-1-ene-1-carbimidate (3r)



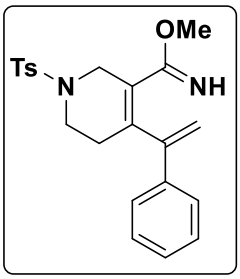
The title compound was prepared by following the general procedure J in 48% yield (61 mg, 0.24 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.34–7.30 (m, 2H), 7.29–7.26 (m, 1H), 5.34 (s, 1H), 5.04 (s, 1H), 3.56 (s, 3H), 2.47–2.44 (m, 2H), 2.26–2.23 (m, 2H), 1.82–1.77 (m, 2H), 1.67–1.62 (m, 2H), 1.54–1.49 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 173.0, 151.2, 146.1, 138.9, 136.9, 128.5, 127.9, 127.1, 112.3, 52.8, 34.4, 32.5, 31.8, 27.0, 26.1. **IR** (neat) 3280, 2923, 2848, 1654, 1446, 1383, 1265, 1066 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{22}NO$ 256.1701, found 256.1690.

methyl 4-(1-phenylvinyl)-5,6-dihydro-2H-pyran-3-carbimidate (3s)



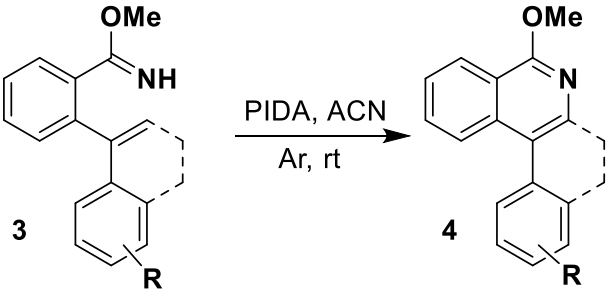
The title compound was prepared by following the general procedure J in 47% yield (57 mg, 0.23 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40–7.34 (m, 2H), 7.37–7.30 (m, 2H), 7.32–7.27 (m, 1H), 5.56 (s, 1H), 5.19 (s, 1H), 4.36 (t, J = 2.6 Hz, 2H), 3.83 (t, J = 5.5 Hz, 1H), 3.55 (s, 3H), 2.32–2.27 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.5, 148.3, 139.0, 138.1, 129.5, 128.7, 128.3, 126.6, 114.2, 66.1, 64.3, 52.9, 30.4. **IR** (neat) 3335, 2945, 2848, 1632, 1440, 1320, 1185, 1101, 1050 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{18}NO_2$ 244.1332, found 244.1342.

methyl 4-(1-phenylvinyl)-1-tosyl-1,2,5,6-tetrahydropyridine-3-carbimidate (3t)



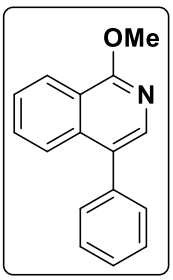
The title compound was prepared by following the general procedure J in 50% yield (99 mg, 0.25 mmol) as a yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73–7.70 (m, 2H), 7.37–7.34 (m, 3H), 7.29–7.27 (m, 2H), 7.25–7.23 (m, 2H), 5.51 (s, 1H), 5.05 (s, 1H), 3.86 (t, *J* = 2.6 Hz, 2H), 3.54 (s, 3H), 3.23 (t, *J* = 5.8 Hz, 2H), 2.46 (s, 3H), 2.36–2.33 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 167.2, 147.7, 143.9, 139.3, 137.6, 133.3, 129.8, 128.6, 128.2, 127.8, 127.6, 126.3, 114.2, 52.8, 45.7, 42.7, 30.5, 21.6. **IR** (neat) 3352, 2919, 2853, 1670, 1440, 1332, 1159, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_3S$ 397.1580, found 397.1588.

5. General procedure for the synthesis of isoquinoline derivatives 4a-4i (General Procedure K)



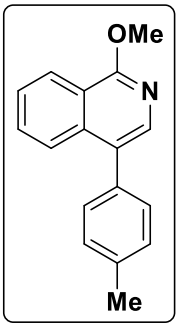
A solution of methyl 2-(1-phenylvinyl)benzimidate derivative **3** (0.1 mmol, 1.0 equiv.) in CH_3CN (0.5 mL) was treated with PIDA (0.12 mmol, 1.2 equiv.) and stirred at room temperature under an argon atmosphere for 15–24 hours. The reaction progress was monitored by TLC. Upon completion, the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 99:1 to 33:1) to yield the cyclized product **4**.

1-methoxy-4-phenylisoquinoline (4a)



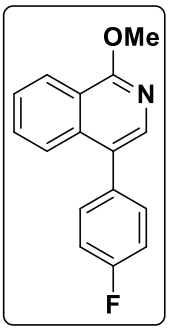
The title compound was prepared by following the general procedure K in 75% yield (17.6 mg, 0.075 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.37–8.31 (m, 1H), 7.98 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.66–7.62 (m, 1H), 7.58–7.55 (m, 1H), 7.52–7.47 (m, 4H), 7.46–7.42 (m, 1H), 4.20 (s, 3H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.6, 139.1, 137.6, 136.5, 130.7, 130.3, 128.6, 128.1, 127.6, 126.7, 124.8, 124.5, 119.4, 54.0. **IR** (neat) 2921, 2857, 1531, 1570, 1508, 1460, 1367, 1241, 1092 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{14}NO$ 236.1075, found 236.1077.

1-methoxy-4-(*p*-tolyl)isoquinoline (4b)



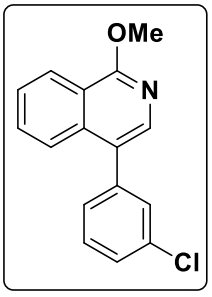
The title compound was prepared by following the general procedure K in 90% yield (22.4 mg, 0.09 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36–8.30 (m, 1H), 7.96 (s, 1H), 7.85–7.79 (m, 1H), 7.66–7.59 (m, 1H), 7.59–7.52 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.19 (s, 3H), 2.46 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.5, 139.1, 137.3, 136.6, 134.6, 130.6, 130.2, 129.4, 128.0, 126.6, 124.9, 124.5, 119.4, 54.0, 21.4. **IR** (neat) 2923, 2855, 1570, 1515, 1445, 1364, 1241, 1161, 1095 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO$ 250.1226, found 250.1248.

4-(4-fluorophenyl)-1-methoxyisoquinoline (4c)



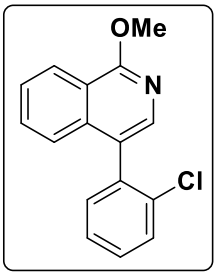
The title compound was prepared by following the general procedure K in 89% yield (22.5 mg, 0.089 mmol) as a white solid. **m.p.** 102-104 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.35–8.32 (m, 1H), 7.93 (s, 1H), 7.75–7.73 (m, 1H), 7.66–7.62 (m, 1H), 7.58–7.55 (m, 1H), 7.44–7.41 (m, 2H), 7.21–7.17 (m, 2H), 4.18 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.5 (d, *J* = 246.4 Hz), 160.7, 139.3, 136.5, 124.6 (d, *J* = 4.9 Hz), 133.5 (d, *J* = 3.5 Hz), 131.9 (d, *J* = 7.9 Hz), 130.8, 127.0, 126.8, 119.4, 115.6 (d, *J* = 21.2 Hz), 54.0. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -115.02, to -115.08 (m, 1F). **IR** (neat) 2945, 2859, 1566, 1506, 1451, 1371, 1212, 1159, 1092 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{13}FNO$ 254.0976, found 254.0965.

4-(3-chlorophenyl)-1-methoxyisoquinoline (4d)



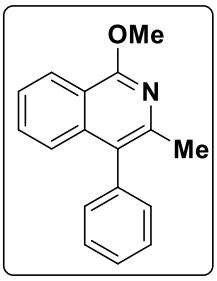
The title compound was prepared by following the general procedure K in 76% yield (20.5 mg, 0.76 mmol) as a white solid. **m.p.** 81-83 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36–8.33 (m, 1H), 7.94 (s, 1H), 7.76 (d, *J* = 8.3 Hz, 1H), 7.68–7.64 (m, 1H), 7.60–7.56 (m, 1H), 7.48–7.46 (m, 1H), 7.44–7.40 (m, 2H), 7.38–7.34 (m, 1H), 4.19 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.9, 139.4, 139.2, 136.2, 134.5, 131.0, 130.3, 129.9, 128.5, 127.8, 126.9, 126.7, 124.7, 124.4, 119.4, 54.2. **IR** (neat) 2923, 2855, 1623, 1563, 1500, 1453, 1362, 1232, 1095 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{13}ClNO$ 270.0680, found 270.0667.

4-(2-chlorophenyl)-1-methoxyisoquinoline (4e)



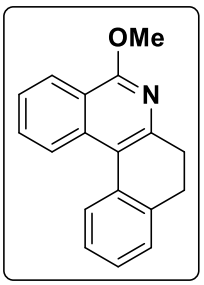
The title compound was prepared by following the general procedure K in 66% yield (17.8 mg, 0.066 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.36–8.31 (m, 1H), 7.93 (s, 1H), 7.63–7.59 (m, 1H), 7.58–7.53 (m, 2H), 7.42–7.36 (m, 4H), 4.20 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.0, 139.7, 136.6, 136.3, 135.0, 132.8, 130.8, 129.8, 129.4, 126.9, 126.8, 125.6, 124.9, 124.5, 119.3, 54.1. **IR** (neat) 2922, 2853, 1592, 1562, 1437, 1360, 1236, 1157, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{13}ClNO$ 270.0680, found 270.0696.

1-methoxy-3-methyl-4-phenylisoquinoline (4g)



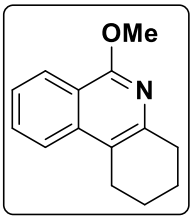
The title compound was prepared by following the general procedure K in 77% yield (19.2 mg, 0.077 mmol) as a white solid. **m.p.** 46-48 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.28–8.25 (m, 1H), 7.52–7.48 (m, 3H), 7.46–7.41 (m, 2H), 7.31–7.27 (m, 3H), 4.18 (s, 3H), 2.36 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.5, 145.9, 138.5, 138.3, 130.8, 130.3, 128.6, 127.3, 125.4, 124.9, 124.9, 124.0, 117.8, 53.7, 22.9. **IR** (neat) 2923, 2857, 1621, 1572, 1504, 1442, 1362, 1331, 1236, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{16}NO$ 250.1232, found 250.1234.

5-methoxy-7,8-dihydrobenzo[a]phenanthridine (4h)



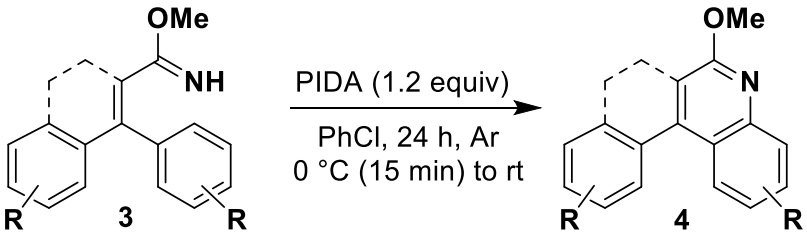
The title compound was prepared by following the general procedure K in 58% yield (15.2 mg, 0.058 mmol) as a white solid. **m.p.** 83-85 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.43 (d, J = 8.5 Hz, 1H), 8.34–8.28 (m, 1H), 7.87–7.81 (m, 1H), 7.71–7.64 (m, 1H), 7.54–7.47 (m, 1H), 7.39–7.30 (m, 2H), 7.28–7.21 (m, 1H), 4.18 (s, 3H), 3.01 (t, J = 8.0 Hz, 2H), 2.90 (t, J = 8.0 Hz, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.7, 150.6, 138.5, 135.1, 133.7, 130.6, 127.9, 127.5, 126.5, 126.2, 125.5, 124.8, 124.2, 119.4, 118.8, 54.0, 32.4, 29.4. **IR** (neat) 2926, 2848, 1619, 1568, 1502, 1448, 1373, 1254, 1188, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{16}NO$ 262.1226, found 262.1243.

6-methoxy-1,2,3,4-tetrahydrophenanthridine (4i)



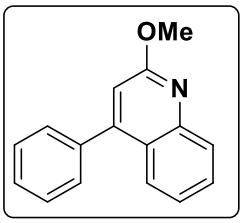
The title compound was prepared by following the general procedure K in 42% yield (9 mg, 0.042 mmol) as a pale yellow liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.24–8.21 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.67–7.63 (m, 1H), 7.48–7.44 (m, 1H), 4.11 (s, 3H), 2.95–2.89 (m, 4H), 1.94–1.89 (m, 4H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 158.7, 146.7, 137.8, 130.3, 125.3, 124.6, 121.8, 118.4, 118.1, 53.6, 32.8, 24.5, 23.3, 23.1. **IR** (neat) 2930, 2857, 1621, 1577, 1455, 1369, 1333, 1221, 1121, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO$ 214.1226, found 214.1235.

5.1 General procedure for the synthesis of quinoline derivatives 4j-4n (General Procedure L)



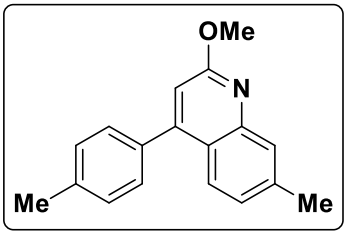
Methyl 3,3-diphenylacrylimidate derivative **3** (0.1 mmol, 1.0 equiv.) was dissolved in 0.5 mL of PhCl, and PIDA (0.12 mmol, 1.2 equiv.) was added at 0 °C. The resulting mixture was stirred at 0 °C for 15 min, then at room temperature under an argon atmosphere for 15–24 h, with the reaction progress monitored by TLC. The solvent was then evaporated under reduced pressure, and the crude residue was purified by flash column chromatography on silica gel using a hexane/ethyl acetate (99:1 to 33:1) to afford the desired cyclized product **4**.

2-methoxy-4-phenylquinoline (4j)



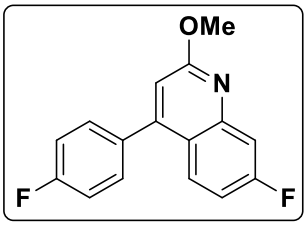
The title compound was prepared by following the general procedure L in 71% yield (16.7 mg, 0.071 mmol) as a white solid. **m.p.** 70-72 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.3 Hz, 1H), 7.79–7.76 (m, 1H), 7.65–7.61 (m, 1H), 7.53–7.46 (m, 5H), 7.35–7.31 (m, 1H), 6.87 (s, 1H), 4.12 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.2, 151.4, 147.3, 138.1, 129.6, 129.5, 128.6, 128.5, 127.7, 126.0, 124.2, 124.2, 113.0, 53.6. **IR** (neat) 2926, 2853, 1736, 1608, 1568, 1462, 1375, 1349, 1207, 1015 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{14}NO$ 236.1070, found 236.1084.

2-methoxy-7-methyl-4-(*p*-tolyl)quinoline (4k)



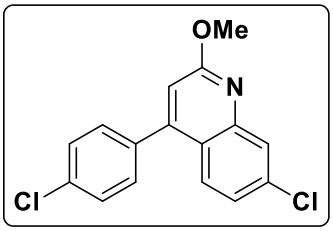
The title compound was prepared by following the general procedure L in 56% yield (14.7 mg, 0.056 mmol) as a white solid. **m.p.** 74-76 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.68 (d, *J* = 8.4 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.18–7.13 (m, 1H), 6.79 (s, 1H), 4.10 (s, 3H), 2.52 (s, 3H), 2.46 (s, 3H). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 162.4, 151.3, 147.4, 139.8, 138.3, 135.4, 129.4, 129.3, 127.1, 126.1, 125.7, 122.2, 111.8, 53.5, 21.7, 21.4. **IR** (neat) 2921, 2850, 1594, 1563, 1506, 1440, 1336, 1200, 1037 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{18}H_{18}NO$ 264.1383, found 264.1366.

7-fluoro-4-(4-fluorophenyl)-2-methoxyquinoline (4l)



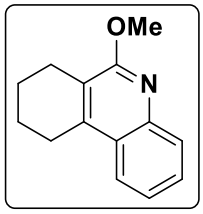
The title compound was prepared by following the general procedure L in 55% yield (14.9 mg, 0.055 mmol) as a white solid. **m.p.** 126-128 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.70–7.66 (m, 1H), 7.57 (dd, *J* = 10.4, 2.7 Hz, 1H), 7.45–7.41 (m, 2H), 7.23–7.19 (m, 2H), 7.12–7.07 (m, 1H), 6.78 (s, 1H), 4.10 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 164.3 (d, *J* = 58.9 Hz), 163.0, 162.4 (d, *J* = 58.4 Hz), 150.2, 148.8 (d, *J* = 13.2 Hz), 133.9 (d, *J* = 3.5 Hz), 131.1 (d, *J* = 8.2 Hz), 127.7 (d, *J* = 10.1 Hz), 121.1, 115.8 (d, *J* = 21.6 Hz), 113.8 (d, *J* = 24.2 Hz), 112.3 (d, *J* = 2.7 Hz), 112.1 (d, *J* = 20.8 Hz), 53.8. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.79 to -110.84 (m, 1F); -112.98 to -113.04 (m, 1F). **IR** (neat) 2921, 2835, 1577, 1504, 1462, 1351, 1210, 1106, 1040 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{12}F_2NO$ 272.0881, found 272.0872.

7-chloro-4-(4-chlorophenyl)-2-methoxyquinoline (4m)



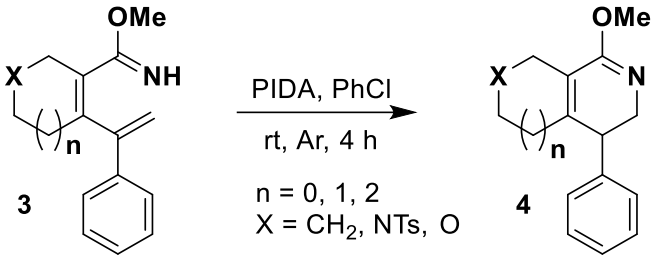
The title compound was prepared by following the general procedure L in 60% yield (18.2 mg, 0.060 mmol) as a white solid. **m.p.** 130-132 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.2 Hz, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.52–7.46 (m, 2H), 7.42–7.35 (m, 2H), 7.31–7.25 (m, 1H), 6.81 (s, 1H), 4.09 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 162.8, 149.9, 148.0, 136.0, 135.7, 135.0, 130.7, 129.1, 127.0, 126.8, 125.1, 122.4, 113.1, 53.8. **IR** (neat) 3063, 2921, 2855, 1597, 1453, 1367, 1322, 1212 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{12}Cl_2NO$ 304.0296, found 304.0288.

6-methoxy-7,8,9,10-tetrahydrophenanthridine (4n)



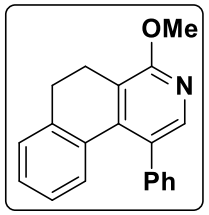
The title compound was prepared by following the general procedure L in 71% yield (15.1 mg, 0.071 mmol) as a pale yellow solid. **m.p.** 84-86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85–7.79 (m, 2H), 7.58–7.52 (m, 1H), 7.39–7.33 (m, 1H), 4.08 (s, 3H), 3.05–3.01 (m, 2H), 2.73–2.69 (m, 2H), 1.94–1.89 (m, 2H), 1.88–1.83 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.0, 143.2, 128.2, 127.5, 125.2, 123.8, 122.6, 121.6, 53.6, 25.5, 23.8, 22.3, 22.2. **IR** (neat) 2921, 2857, 1736, 1636, 1442, 1402, 1333, 1236, 1084 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{14}H_{16}NO$ 214.1226, found 214.1235.

5.2 General procedure for the synthesis of isoquinoline derivatives 4o-4t (General Procedure M)



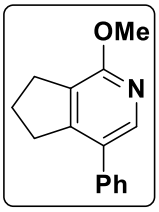
Methyl phenylvinyl cyclic carbimidate derivative **3** (0.1 mmol, 1.0 equiv.) was dissolved in PhCl (0.5 mL), Then PIDA (0.12 mmol, 1.2 equiv.) was added and stirred at room temperature under an argon atmosphere for 4 hours, with the progress monitored by TLC. After completion, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 99:1 to 33:1) to afford the cyclized product **4**.

4-methoxy-1-phenyl-5,6-dihydrobenzo[f]isoquinoline (4o)



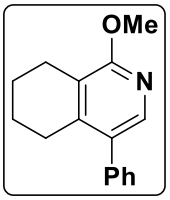
The title compound was prepared by following the general procedure M in 68% yield (19.5 mg, 0.068 mmol) as a yellow solid. **m.p.** 100-102 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.38–7.30 (m, 3H), 7.28–7.23 (m, 3H), 7.16–7.11 (m, 1H), 6.87–6.82 (m, 2H), 4.04 (s, 3H), 2.88–2.84 (m, 2H), 2.82–2.78 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.1, 146.3, 142.2, 140.0, 139.8, 132.0, 129.9, 129.5, 128.7, 128.5, 128.3, 127.9, 127.1, 125.6, 120.8, 53.8, 28.8, 21.6. **IR** (neat) 2928, 2850, 1732, 1577, 1457, 2380, 1267, 1196 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{20}H_{18}NO$ 288.1388, found 288.1400.

1-methoxy-4-phenyl-6,7-dihydro-5H-cyclopenta[c]pyridine (4p)



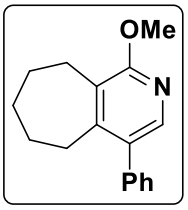
The title compound was prepared by following the general procedure M in 68% yield (15.3 mg, 0.068 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.47–7.38 (m, 4H), 7.37–7.30 (m, 1H), 4.02 (s, 3H), 2.98 (t, *J* = 7.4 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.15–2.05 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.1, 154.2, 144.0, 138.2, 128.6, 128.5, 127.2, 125.7, 53.5, 33.2, 29.2, 24.9. **IR** (neat) 2958, 2851, 1540, 1455, 1380, 1330, 1252, 1088 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO$ 226.1232, found 226.1239.

1-methoxy-4-phenyl-5,6,7,8-tetrahydroisoquinoline (4q)



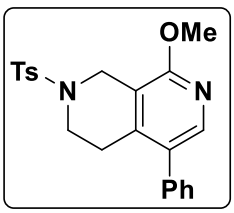
The title compound was prepared by following the general procedure M in 72% yield (18.4 mg, 0.072 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.42–7.39 (m, 2H), 7.36–7.33 (m, 1H), 7.29 7.26 (m, 2H), 3.99 (s, 3H), 2.65 (t, *J* = 6.5 Hz, 2H), 2.54 (t, *J* = 6.3 Hz, 2H), 1.83–1.77 (m, 2H), 1.70–1.65 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 161.4, 145.9, 142.6, 138.5, 131.4, 129.8, 128.3, 127.2, 119.8, 53.6, 28.3, 23.3, 22.4, 22.2. **IR** (neat) 2964, 2859, 1588, 1462, 1378, 1333, 1247, 1090 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{16}H_{18}NO$ 240.1388, found 240.1398.

1-methoxy-4-phenyl-6,7,8,9-tetrahydro-5H-cyclohepta[c]pyridine (4r)



The title compound was prepared by following the general procedure M in 41% yield (10.4 mg, 0.041 mmol) as a white solid. **m.p.** 48-50 °C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.43 – 7.39 (m, 2H), 7.37 – 7.34 (m, 1H), 7.26 – 7.23 (m, 2H), 3.98 (s, 3H), 2.94 – 2.91 (m, 2H), 2.72 – 2.70 (m, 2H), 1.89 – 1.83 (m, 2H), 1.66 – 1.56 (m, 4H); **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 160.7 152.6, 143.8, 139.1, 131.4, 130.0, 128.4, 127.1, 125.4, 53.9, 32.7, 31.1, 27.1, 26.9, 25.9; **IR** (neat) 2917, 2850, 1586, 1460, 1380, 1260, 1203, 1115, 1160, 1013 cm^{-1}; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{17}H_{20}NO$ 254.1545, found 254.1551.

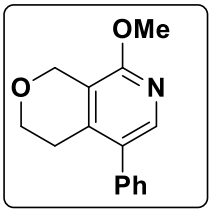
8-methoxy-5-phenyl-2-tosyl-1,2,3,4-tetrahydro-2,7-naphthyridine (4s)



The title compound was prepared by following the general procedure M in 27% yield (11.1 mg, 0.027 mmol) as a white solid. **m.p.** 208-210 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 2H), 7.44–7.38 (m, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 7.2 Hz, 2H), 4.17 (s, 2H), 3.99 (s, 3H), 3.25 (t, *J* = 5.7 Hz, 2H), 2.75 (t, *J* = 5.5 Hz, 2H), 2.43

(s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.6, 143.9, 142.6, 137.1, 133.3, 131.0, 129.9, 129.6, 128.6, 127.9, 127.7, 115.2, 53.9, 43.4, 42.9, 28.0, 21.7. **IR** (neat) 2923. 2850, 1738, 1460, 1364, 1161, 1055, 1033, 1011 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{22}H_{23}N_2O_3S$ 395.1429, found 395.1427.

8-methoxy-5-phenyl-3,4-dihydro-1H-pyrano[3,4-c]pyridine (4t)

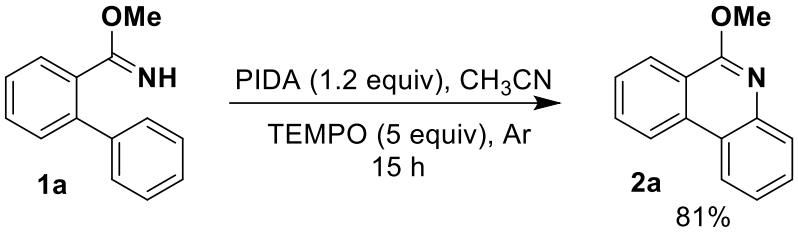


The title compound was prepared by following the general procedure M in 47% yield (12.1 mg, 0.047 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.46–7.39 (m, 2H), 7.40–7.33 (m, 1H), 7.32–7.26 (m, 2H), 4.73–4.71 (m, 2H), 3.98 (s, 3H), 3.85 (t, *J* = 5.5 Hz, 2H), 2.68–2.65 (m, 2H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 159.2, 143.8, 142.7, 137.3, 131.0, 129.6, 128.6, 127.5, 117.7, 64.3, 64.0, 53.5, 27.3. **IR** (neat) 2927, 2845, 1748, 1454, 1363, 1150, 1056, 1028 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{15}H_{16}NO_2$ 242.1181, found 242.1189.

6. Control experiment

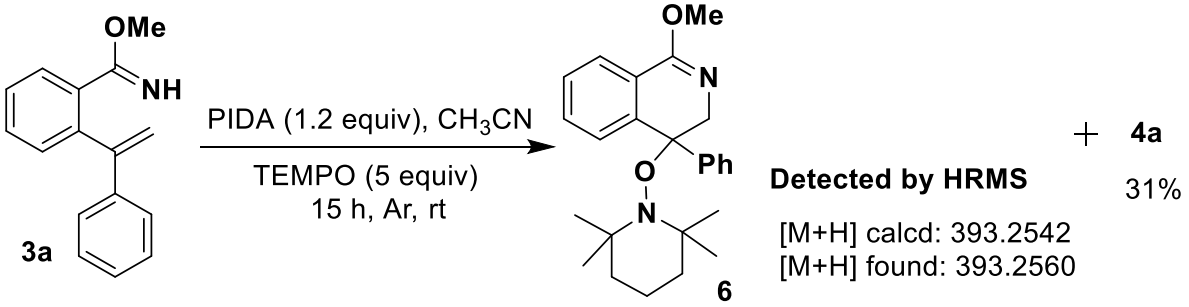
6.1 Radical inhibiting experiment:

(i) Reaction of **1a** and PIDA in the presence of TEMPO

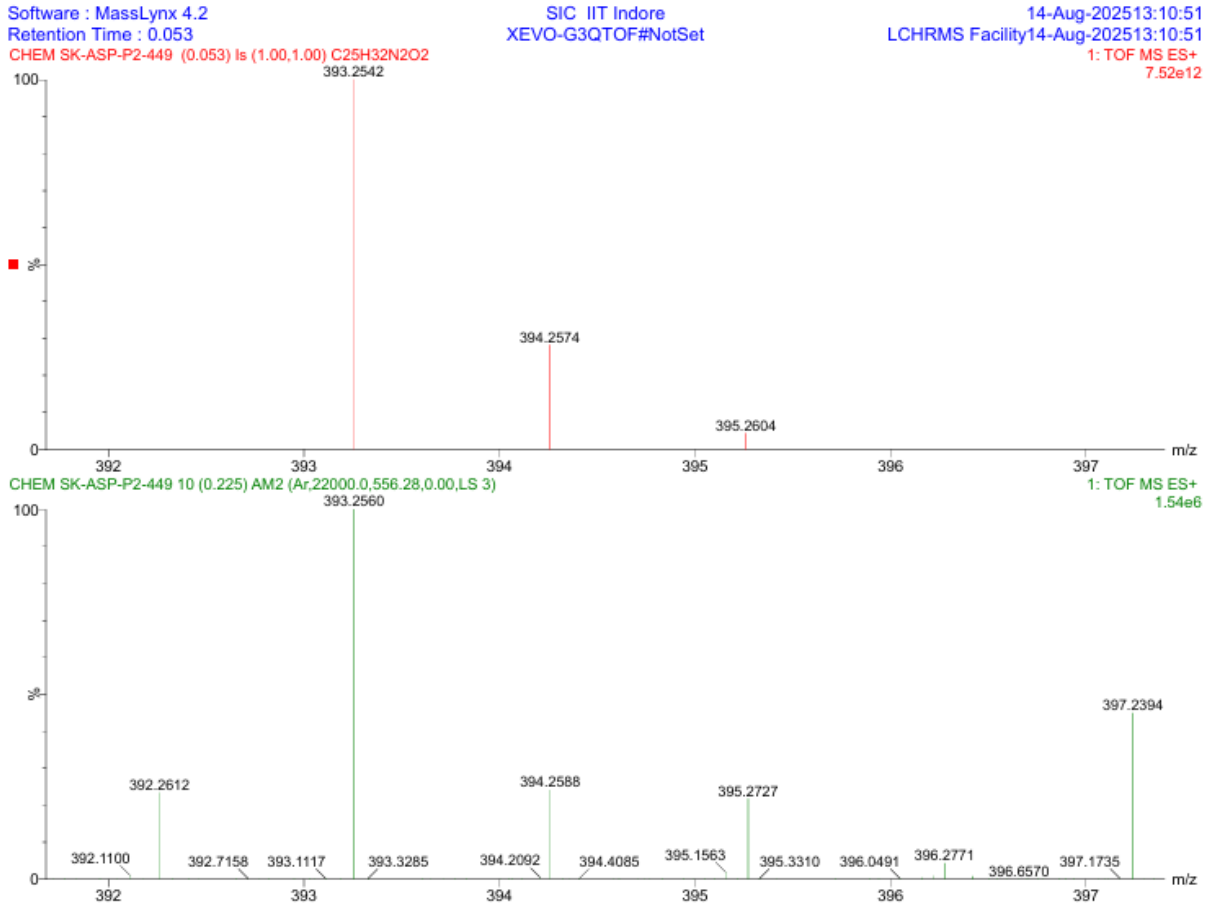


In an oven-dried glass vial equipped with a magnetic stir bar, methyl [1,1′-biphenyl]-2-carbimidate **1a** (0.1 mmol) was added, followed by PIDA (1.2 equiv) dissolved in CH_3CN (0.5 mL). TEMPO (5 equiv) was then added, and the reaction mixture was stirred at room temperature under an argon atmosphere for 15 h. Upon completion, the solvent was removed under reduced pressure, and the crude residue was purified by column chromatography on silica gel (hexane) to yield product **2a** as a white solid in 81% yield.

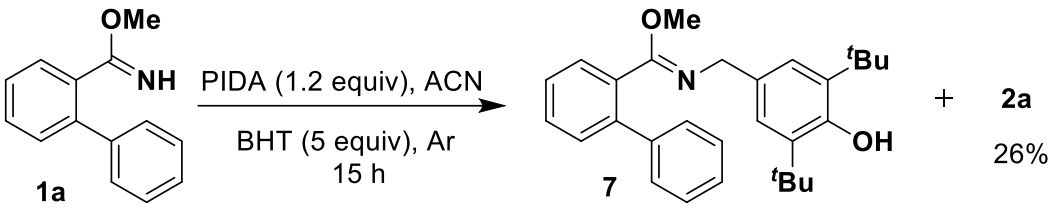
(ii) Reaction of **3a** and PIDA in the presence of TEMPO



In a reaction vial, methyl 2-(1-phenylvinyl)benzimidate **3a** (0.1 mmol) was combined with PIDA (1.2 equiv) and TEMPO (5 equiv) in CH_3CN (0.5 mL) and stirred at room temperature for 15 h under an argon atmosphere. Then, the solvent was removed under reduced pressure, and the crude residue was purified by silica gel column chromatography (hexane) to yield product **4a** in 31% yield. After the reaction, the crude mixture was further analyzed by HRMS.



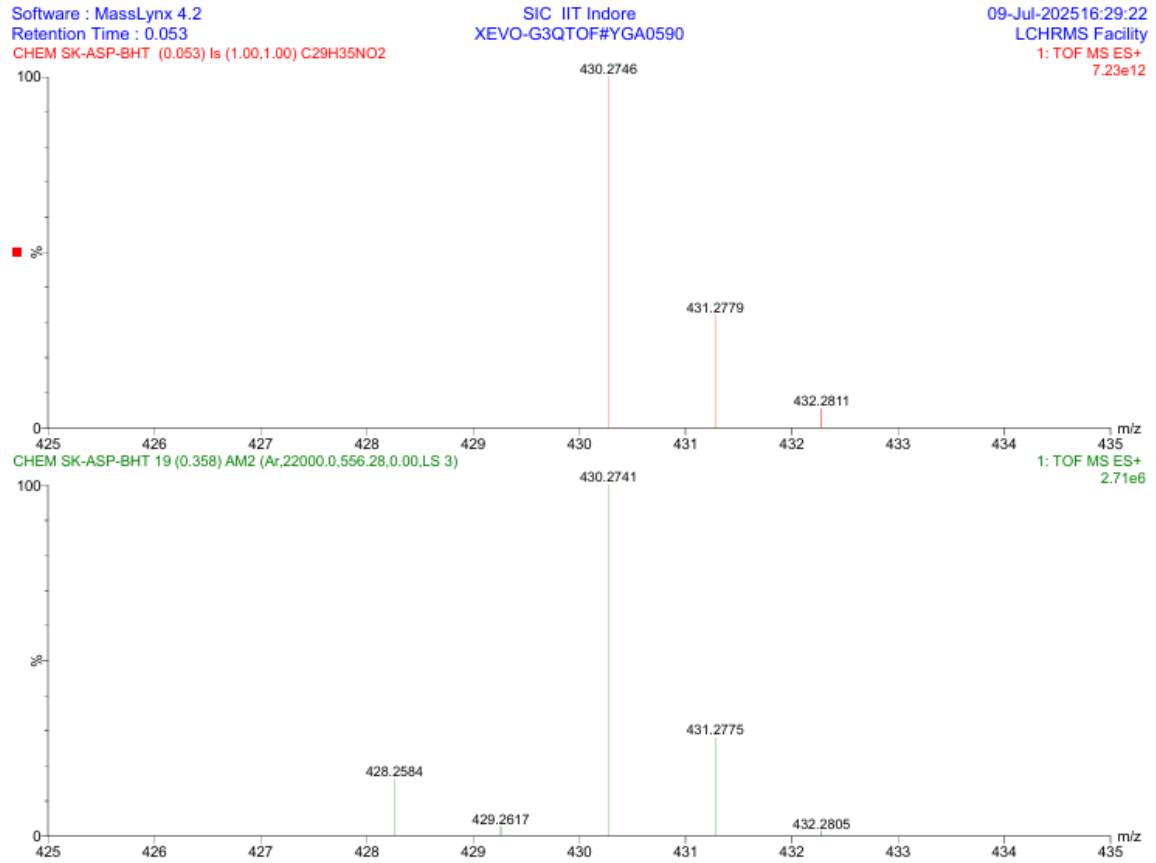
(iii) Reaction of **3a** and PIDA in the presence of BHT



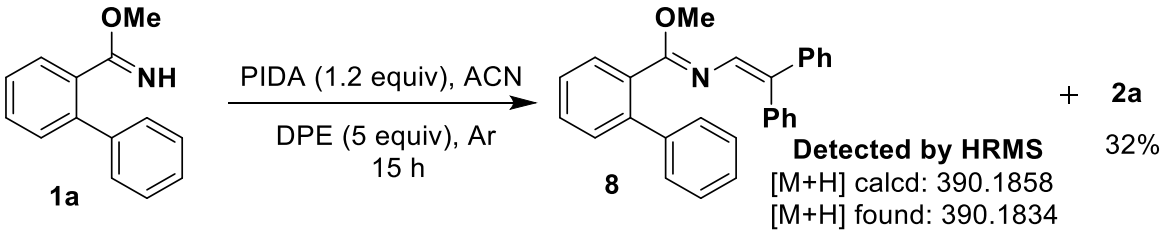
Detected by HRMS
[M+H] calcd:430.2746
[M+H] found: 430.2741

A reaction tube was charged with methyl [1,1'-biphenyl]-2-carbimidate **1a** (0.1 mmol), PIDA (1.2 equiv), and BHT (5 equiv) in CH_3CN (0.5 mL) and stirred at room temperature for 15 h

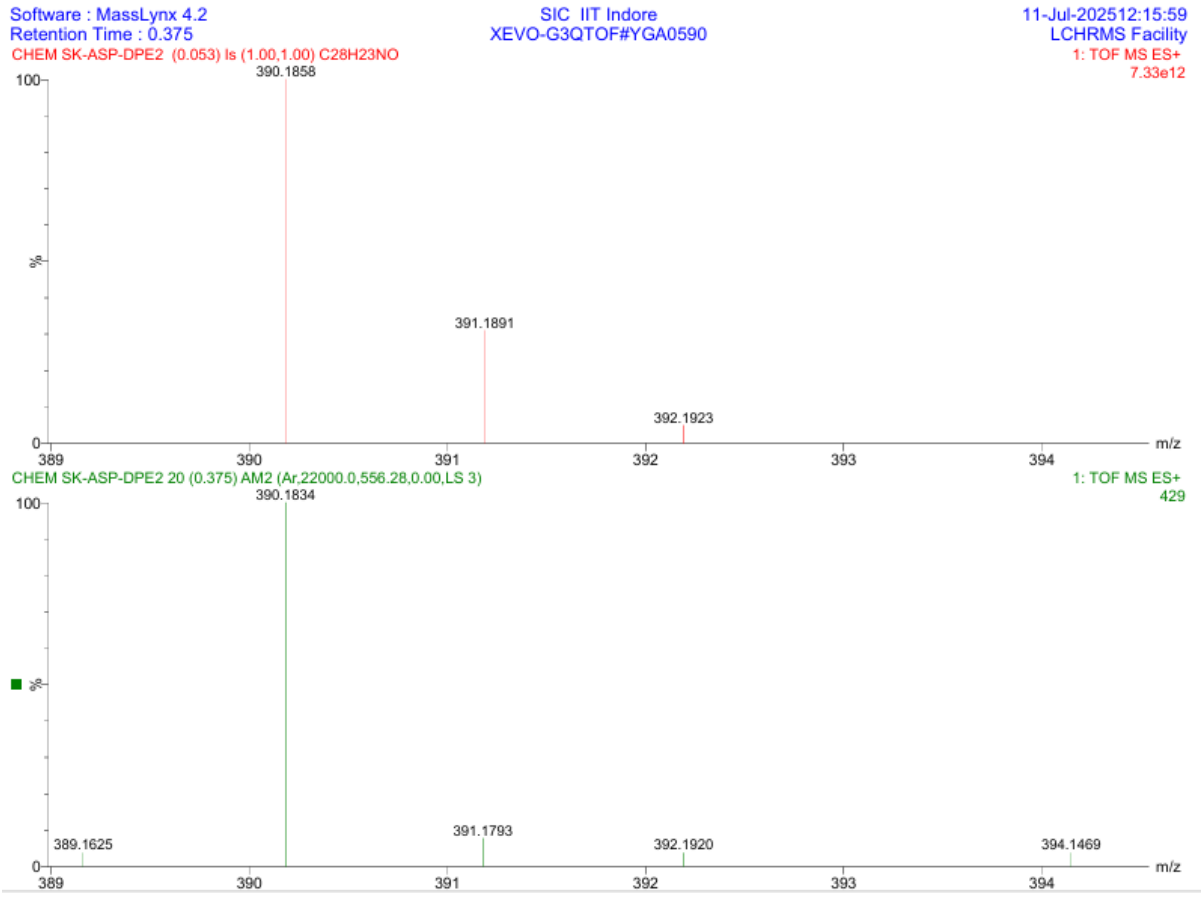
under an argon atmosphere. The solvent was concentrated in vacuo and residue was then purified by column chromatography on silica gel (hexane) to afford product **2a** as a white solid in 26% yield. After completion of reaction, the crude mixture was analyzed through HRMS.



(iv) <u>Reaction with DPE</u>

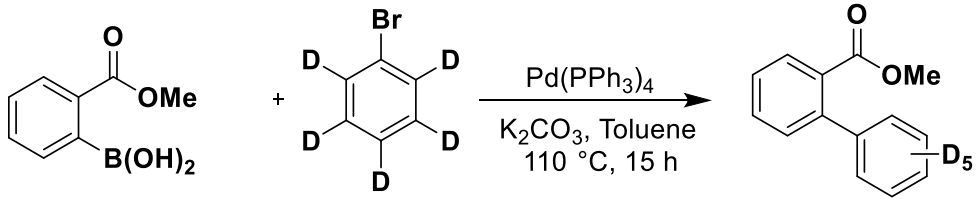


A reaction tube was charged with methyl [1,1'-biphenyl]-2-carbimidate **1a** (0.1 mmol), PIDA (1.2 equiv), and DPE (5 equiv) in CH_3CN (0.5 mL) and stirred at room temperature for 15 h under an argon atmosphere. The solvent was concentrated in vacuo and residue was then purified by column chromatography on silica gel (hexane) to afford product **2a** as a white solid in 32% yield. After completion of reaction, the crude mixture was analyzed through HRMS.

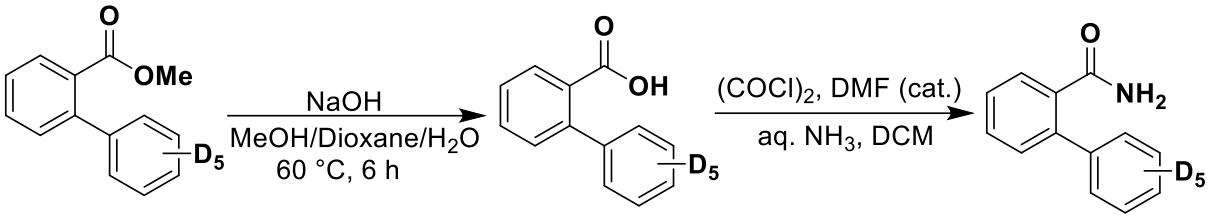


6.2 Procedure for the synthesis of [D5]-1a

methyl [1,1'-biphenyl]-2-carboxylate-2',3',4',5',6'-d_5 was synthesized as per previously reported method.[15]



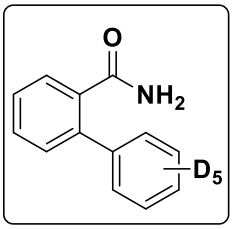
An oven-dried round-bottom flask equipped with a magnetic stir bar was charged with (2-(methoxycarbonyl)phenyl)boronic acid (2 mmol, 1 equiv.) under a nitrogen atmosphere. $Pd(PPh_3)_4$ (5 mol%), 1-bromobenzene-2,3,4,5,6-d_5 (1.1 equiv.), and K_2CO_3 (3.0 equiv.) were added, followed by toluene (20 mL) and aqueous ethanol (95% v/v, 10 mL). The reaction mixture was stirred at 110 °C for 15 h, with progress monitored by TLC until complete consumption of the starting material. After cooling, the mixture was quenched with water and extracted with ethyl acetate. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by column chromatography (2% ethyl acetate in hexane) to yield the desired compound (70% yield).



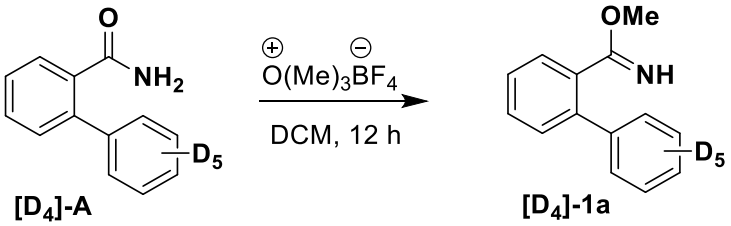
The corresponding ester (1.8 mmol, 1 equiv.) was dissolved in a 1:1:1 mixture of 1,4-dioxane, methanol, and water (22 mL). NaOH (5 equiv.) was added, and the reaction was stirred at 60 °C for 6 h. The mixture was concentrated under reduced pressure, diluted with water (15 mL), and washed with ethyl acetate (10 mL). The aqueous phase was acidified to pH ~2 with 3 M HCl and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the corresponding carboxylic acid as a white solid, which was used directly without further purification.

The obtained acid derivative and a catalytic amount of DMF were dissolved in dry CH_2Cl_2 (8 mL) in a round-bottom flask, cooled to 0 °C, and stirred for 5 min. Oxalyl chloride (1.2 equiv.) was added dropwise at 0 °C, and the reaction was stirred at room temperature for 4 h. The solvent was removed under reduced pressure to afford the crude acid chloride, which was dissolved in dry CH_2Cl_2 (4 mL). aq. NH_3 (8 mL) was added dropwise at 0 °C, and the mixture was stirred at room temperature for 10 h. After completion, the reaction was quenched with water and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude residue was purified by column chromatography (20% EtOAc in hexane) to give the desired [1,1'-biphenyl]-2',3',4',5',6'-*d*5-2-carboxamide **([D4]-A)**.

[1,1'-biphenyl]-2',3',4',5',6'-d5-2-carboxamide ([D4]-A)

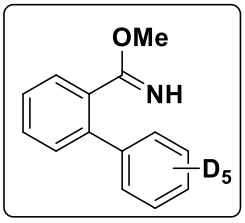


77% yield (280 mg, 1.4 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80–7.77 (m, 1H), 7.53–7.49 (m, 1H), 7.45–7.42 (m, 1H), 7.38–7.35 (m, 1H), 5.66 (brs, 1H), 5.27 (brs, 1H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 171.5, 140.1, 140.00, 134.4, 130.7, 130.6, 129.2, 128.9, 128.9, 128.1, 127.8; **IR** (neat) 3375, 3163, 1694, 1642, 1618, 1390, 1115 cm^{-1}. **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{13}H_7D_5NO$ 203.1227, found 203.1240.



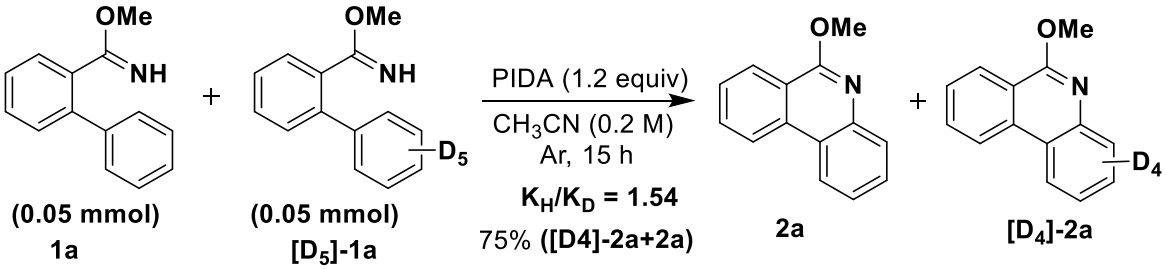
A solution of biphenyl carboxamide derivative **[D4]-A** (0.5 mmol, 1.0 equiv.) in 6 mL of DCM was cooled to 0 °C, followed by the addition of trimethyloxonium tetrafluoroborate (1.5 equiv.). The reaction mixture was then allowed to warm to room temperature and stirred overnight. After completion, 1.5 mL of methanol was added to the reaction mixture, which was then concentrated under reduced pressure. The resulting crude product was purified by column chromatography using deactivated silica gel and using an ethyl acetate/hexane (5%) to afford the desired methyl biphenyl carbimidate derivatives **[D4]-1a**.

methyl [1,1'-biphenyl]-2',3',4',5',6'-*d*5-2-carbimidate ([D4]-1a)

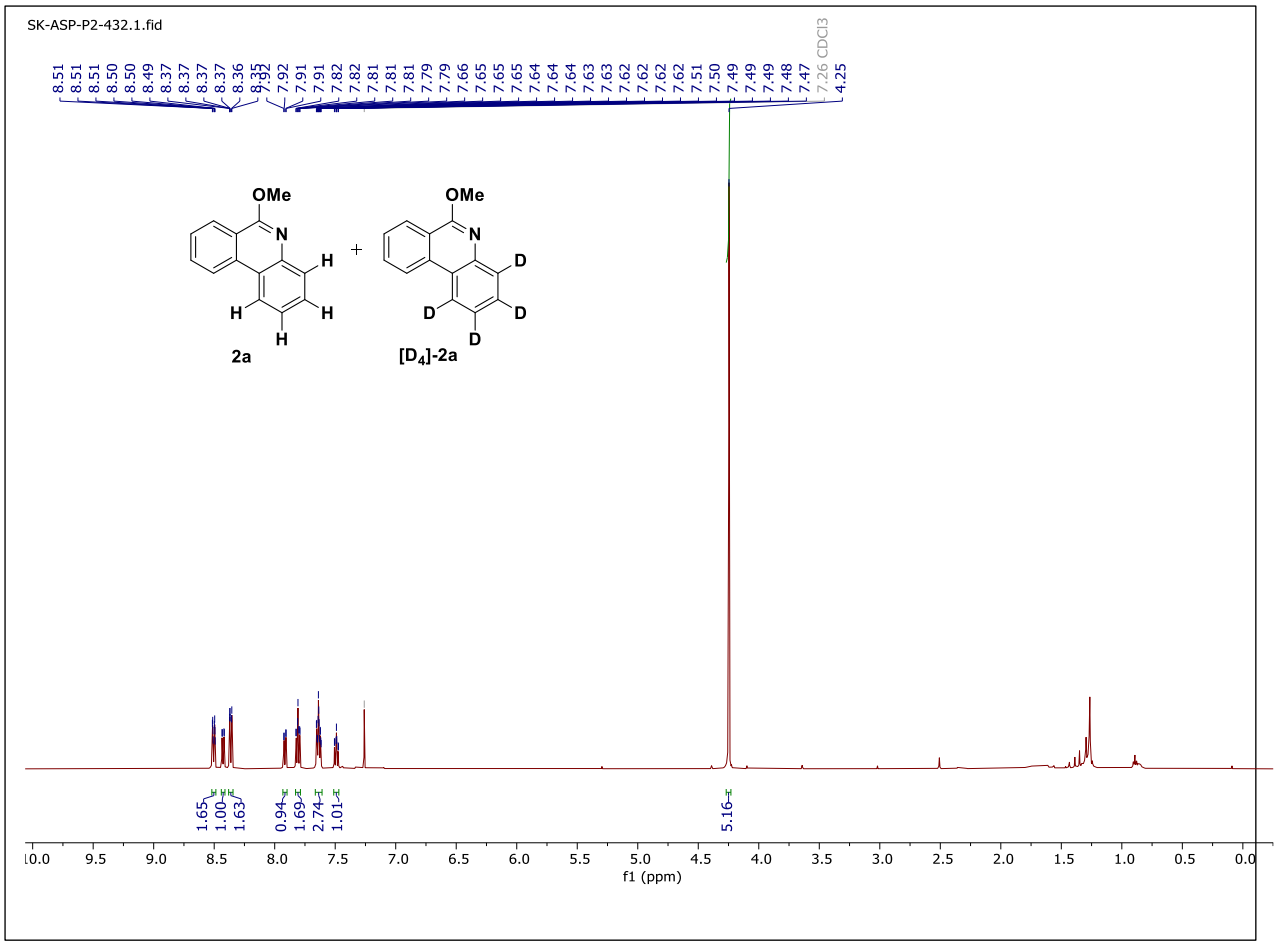


50% yield (108 mg, 0.5 mmol) as a colorless liquid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 1H), 7.48–7.45 (m, 1H), 7.39–7.35 (m, 2H), 3.69 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, $CDCl_3$) δ 170.6, 140.5, 140.3, 134.1, 130.6, 130.0, 128.6, 128.5, 128.2, 127.6, 127.5, 53.5. **IR** (neat) 3322, 2941, 1640, 1435, 1339, 1164, 1077 cm^{-1}. **HRMS** (ESI) m/z $[M+Na]^+$ calcd for $C_{14}H_9D_5NONa$ 239.1203, found 239.1225.

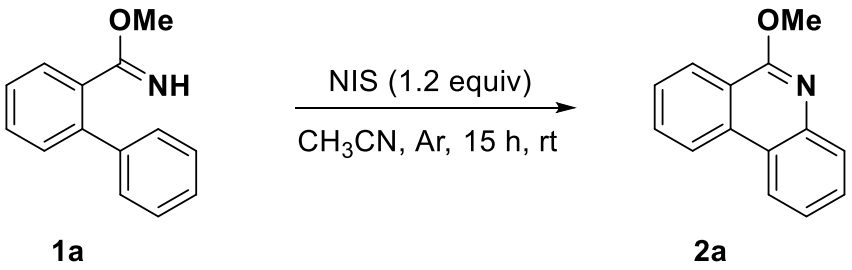
6.3 Competing Kinetic Isotope Effect (KIE) Experiment



General procedure: The compound **1a** (0.05 mmol) and **[D5]-1a** (0.05 mmol) and PIDA (0.12 mmol, 1.2 equiv.) were combined in a vial, and 0.5 mL of CH_3CN was added. The resulting mixture was stirred at room temperature under an argon atmosphere for 15 h. After that, the solvent was evaporated under reduced pressure, and the crude residue was purified by flash column chromatography on silica gel using a hexane to obtain the mixture of cyclized product **2a+[D4]-2a** (yield 75%).



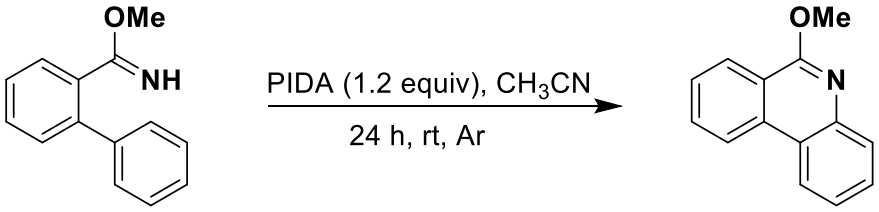
6.4 Reaction with NIS



1a **2a**

A reaction tube was charged with methyl [1,1'-biphenyl]-2-carbimidate **1a** (0.1 mmol) and *N*-Iodosuccinimide (1.2 equiv) in CH_3CN (0.5 mL) and stirred at room temperature for 15 h under an argon atmosphere. The solvent was concentrated in vacuo and residue was then purified by column chromatography on silica gel (hexane) to afford product **2a** as a white solid in 56% yield.

6.5 Procedure for the large-scale reaction

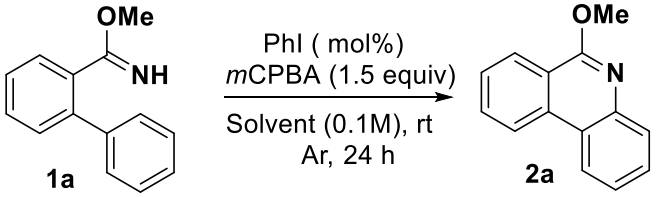


(1 g, 4.73 mmol) (0.96 g, 97%)

Methyl [1,1′-biphenyl]-2-carbimidate (4.73 mmol, 1.0 equiv.) and PIDA (5.67 mmol, 1.2 equiv.) were placed in a round-bottom flask, followed by the addition of CH_3CN (0.2 M). The mixture was stirred at room temperature under an argon atmosphere for 24 hours. After completion, the solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel using a hexane to afford the desired 6-methoxyphenanthridine product (960 mg, 4.58 mmol, 97% as a white solid).

7. Optimization table and procedure for the catalytic reaction

7.1 Optimization table



1a 0.1 mmol **2a**

Entry	PhI (mol%)	Solvent	Yield[a]
1	10	CH_3CN:AcOH (40:1)	29
2	10	CH_3CN:AcOH (20:1)	25
3	20	HFIP:AcOH (1:5)	05
4	20	CH_3CN:AcOH (40:1)	61
5	20	CH_3CN	46
6	20	CH_3CN:AcOH (40:1) (0.5 mL)	65
7	20	1,2-DCE:AcOH (40:1)	49
8	20	PhCl:AcOH (40:1)	68
9	**20**	**PhCl:AcOH (40:1) (0.5 mL)**	**77**
10	20	PhCl:AcOH (50:1) (0.5 mL)	60
11	20	PhCl:AcOH (40:1) (0.5 mL)	39[b]

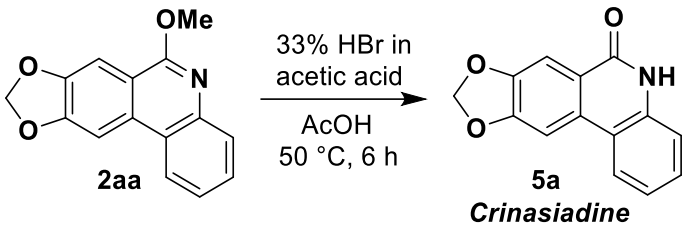
[a] Isolated yield. [b] Using 1.2 equiv. of *m*CPBA.

7.2 General procedure for the catalytic reaction

An oven-dried 5 mL glass vial equipped with a magnetic stir bar was charged with methyl [1,1'-biphenyl]-2-carbimidate **1a** (0.1 mmol), followed by iodobenzene and *m*CPBA in the mixture of PhCl:AcOH (40:1). The reaction mixture was stirred at room temperature for 24 h under an argon atmosphere. After completion, the solvent was removed under reduced pressure, and the crude residue was purified by silica gel column chromatography (hexane) to obtained the desired product as a white solid.

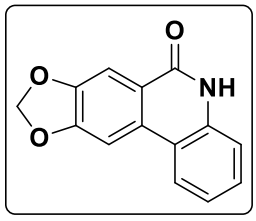
8. Synthetic application of phenanthridine and cyclization of imine

8.1 Procedure for the synthesis of Crinasiadine (5a)



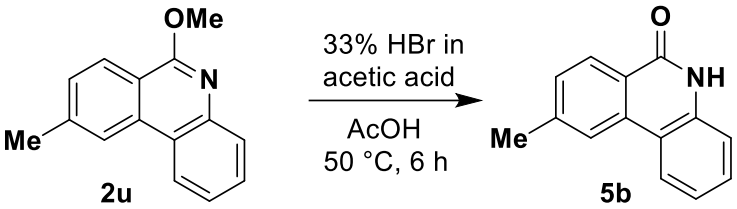
An oven-dried vial equipped with a magnetic stir bar was charged with compound **2aa** (0.1 mmol, 1 equiv), followed by the addition of 33% HBr in acetic acid (0.4 mmol, 4 equiv) and excess AcOH (0.15 mL). The reaction mixture was stirred at 50 °C for 6 h. After completion, the mixture was cooled to room temperature and poured onto ice. Saturated aqueous $NaHCO_3$ solution (5 mL) was added, and the product was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by column chromatography (30-40% EtOAc/hexane) to afford compound **5a**.

[1,3]dioxolo[4,5-j]phenanthridin-6(5*H*)-one (5a)[7]



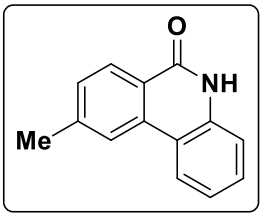
42% yield (10 mg, 0.042 mmol) as a yellow solid. **^{1}H NMR** (500 MHz, DMSO-D_6) δ 11.62 (s, 1H), 8.29 (d, *J* = 8.0 Hz, 1H), 8.04 (s, 1H), 7.64 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 6.23 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 157.9, 151.4, 148.0, 141.7, 131.7, 128.1, 126.8, 124.2, 122.5, 122.1, 114.6, 102.1, 101.5, 100.6. **IR** (neat) 2919, 2856, 1709, 1657, 1463, 1365, 1182, 1079 cm^{-1}.

8.2 Procedure for the synthesis of Phenaglydon (5b)



An oven-dried vial equipped with a magnetic stir bar was charged with compound **2u** (0.1 mmol, 1 equiv), followed by the addition of 33% HBr in acetic acid (0.4 mmol, 4 equiv) and excess AcOH (0.15 mL). The reaction mixture was stirred at 50 °C for 6 h. Upon completion, the mixture was cooled to room temperature and poured onto ice. Saturated aqueous $NaHCO_3$ solution (5 mL) was added, and the product was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude residue was purified by column chromatography (20% EtOAc/hexane) to afford compound **5b** as a white solid in 91% yield.

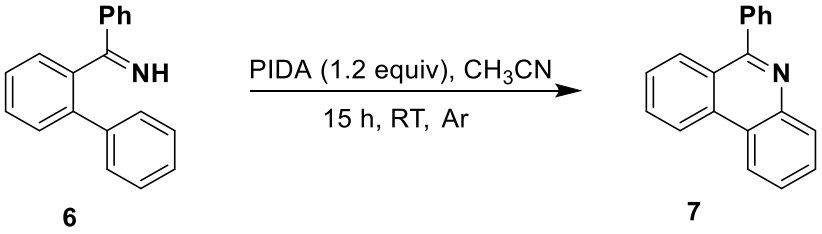
9-methylphenanthridin-6(5*H*)-one (5b)[7]



91% yield (19 mg, 0.091 mmol) as a white solid. **m.p.** 220-222 °C; **^{1}H NMR** (500 MHz, DMSO-D_6) δ 11.55 (s, 1H), 8.33 (d, J = 8.0 Hz, 1H), 8.28 (s, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.45–7.41 (m, 2H), 7.34–7.31 (m, 1H), 7.24–7.20 (m, 1H), 2.47 (s, 3H). **^{13}C{^{1}H} NMR** (126 MHz, DMSO-D_6) δ 160.9, 143.1, 136.7, 134.3, 129.5, 129.2, 127.5, 123.4, 123.2, 122.5, 122.2, 117.6, 116.1, 21.6. **IR** (neat) 2871, 1659, 1607, 1417, 1658, 1154, 1034 cm^{-1}.

8.3 Cyclization of imine

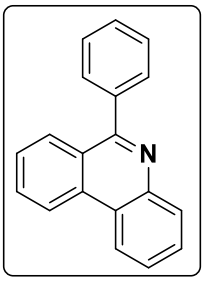
[1,1'-biphenyl]-2-yl(phenyl)methanimine **6** was prepared according to the previous reported procedures[16].



[1,1'-biphenyl]-2-yl(phenyl)methanimine **6** (0.1 mmol, 1.0 equiv.) and PIDA (0.12 mmol, 1.2 equiv.) were combined in a vial, and 0.5 mL of CH_3CN was added. The resulting mixture was stirred at room temperature under an argon atmosphere for 15 hours. After that, the solvent was

evaporated under reduced pressure, and the crude residue was purified by flash column chromatography on silica gel using a gradient of hexane/ethyl acetate (99:1) to obtain the target cyclized product **7**.

6-phenylphenanthridine (7)[17]



47% yield (12 mg, 0.047 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.65 – 8.61 (m, 1H), 8.31 (s, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.86 (m, 1H), 7.79 – 7.69 (m, 4H), 7.66 – 7.61 (m, 1H), 7.60 – 7.52 (m, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4, 139.4, 143.6, 133.8, 131.1, 130.4, 130.0, 129.3, 129.2, 128.6, 127.4, 127.3, 125.3, 123.9, 122.4, 122.1; **IR** (neat) 3062, 1583, 1473, 1458, 1442, 1401, 1328, 1138, 1072 cm^{-1}; ; **HRMS** (ESI) m/z $[M+H]^+$ calcd for $C_{19}H_{14}N$ 256.1126, found 256.1118.

9. References

1. F. C. Sousa e Silva, N. T. Van and S. E. Wengryniuk, Direct C–H α-arylation of enones with $ArI(O_2CR)_2$ reagents, *J. Am. Chem. Soc.*, 2020, **142**, 64.

2. M. A. Patel and A. R. Kapdi, Ambient-temperature, metal-free, CDI-mediated *ex-situ* conversion of acids to amides: A useful late-stage strategy, *Chem Asian J.*, 2023, **18**, e202300672.

3. D. -D. Li, T. -T. Yuan and G-W. Wang, Palladium-catalyzed *ortho*-arylation of benzamides *via* direct sp^2 C−H bond activation, *J. Org. Chem.*, 2012, **77**, 3341.

4. J. Wei, X. Shao, H. Zhao, H. Yang, S. Qiu and H. Zhai, Palladium-catalyzed arylation of C(sp^2)−H bonds with 2-(1- methylhydrazinyl)pyridine as the bidentate directing group. *ACS Omega,* 2021, **6**, 25151.

5. K. Shin, S-W. Park and S. Chang, Cp*Ir(III)-Catalyzed mild and broad C−H arylation of arenes and alkenes with aryldiazonium salts leading to the external oxidant free approach, *J. Am. Chem. Soc.*, 2015, **137**, 8584.

6. T. Parsharamulu, T.; D. Venkanna, M. L. Kantam, S. K. Bhargava and P. Srinivasu. The first example of *ortho*-arylation of benzamides over Pd/mesoporous silica: A novel approach for direct sp^2 C−H bond activation, *Ind. Eng. Chem. Res.*, 2014, **53**, 20075.

7. S. Zou, Z. Zhang, C. Chen and C. Xi, MeOTf-catalyzed intramolecular acyl-cyclization of aryl isocyanates: Efficient access to phenanthridin-6(5*H*)-one and 3,4-dihydroisoquinolin-1(2*H*)-one derivatives, *Asian J. Org. Chem.*, 2021, **10**, 355.

8. X-Z. Tao, J-J. Dai, J. Zhou, J. Xu and H-J. Xu, Electrochemical C-O bond formation: Facile access to aromatic lactones, *Chem. Eur., J.* 2018, **24**, 6932.

9. Y. Zheng, Z. Liu, Q. Huang and Y. Xie, *Ipso*-Nitration of Boronic Esters Enabled by Ferric Nitrate Nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) in HFIP, *Org. Lett.,* 2025, **27**, 2997.

10. (a) J. Tummatorn, K. Punjajom, W. Rodphon, S. Ruengsangtongkul, N. Chaisan, K. Lumyong, C. Thongsornkleeb, P. Nimnual and S. Ruchirawat, Chemoselective synthesis of 1,1-disubstituted vinyl triflates from terminal alkynes using TfOH in the presence of $TMSN_3$, *Org. Lett*., 2019, **21**, 4694; (b) T. S-B. Lou, S. W. Bagley and M. C. Willis, Cyclic alkenylsulfonyl fluorides: Palladium-catalyzed synthesis and functionalization of compact multifunctional reagents, *Angew. Chem.*, 2019, **131**, 19035.

11. P. B. Rathod, K. S. A. Kumar, M. Kumar, A. K. Debnath, A. K. Pandey and A. A. Athawale, Palladium acetate and Pd nanoparticles loaded hexamethylenetetramine anchored magnetically

retrievable assemblies for catalyzing Mizoroki-Heck type mono and *gem*-dicoupling reactions, *ChemistrySelect*, 2020, **5**, 1961.

12. K. Hiesinger, J. S. Kramer, S. Beyer, T. Eckes, S. Brunst, C. Flauaus, S. K. Wittmann, L. Weizel, A. Kaiser, S. B. M. Kretschmer, S. George, C. Angioni, J. Heering, G. Geisslinger, M, S. -Zsilavecz, A. Schmidtko, D. Pogoryelov, J. Pfeilschifter, B. Hofmann, D. Steinhilber, S. Schwalm and S. Proschak, Design, synthesis, and structure−activity relationship studies of dual inhibitors of soluble epoxide hydrolase and 5-lipoxygenase, *J. Med. Chem.*, 2020, **63**, 11498.

13. A. Jolit, P. M. Walleser, G, P. A. Yap and M. A. Tius, Catalytic enantioselective Nazarov cyclization: Construction of vicinal all-carbon-atom quaternary stereocenters, *Angew. Chem. Int. Ed.*, 2014, **53**, 6180.

14. H. Ren, Z. Li and P. Knochel, Chemoselective C(sp^3)-H bond activation for the preparation of condensed *N*-heterocycles, *Chem. Asian J.*, 2007, **2**, 416.

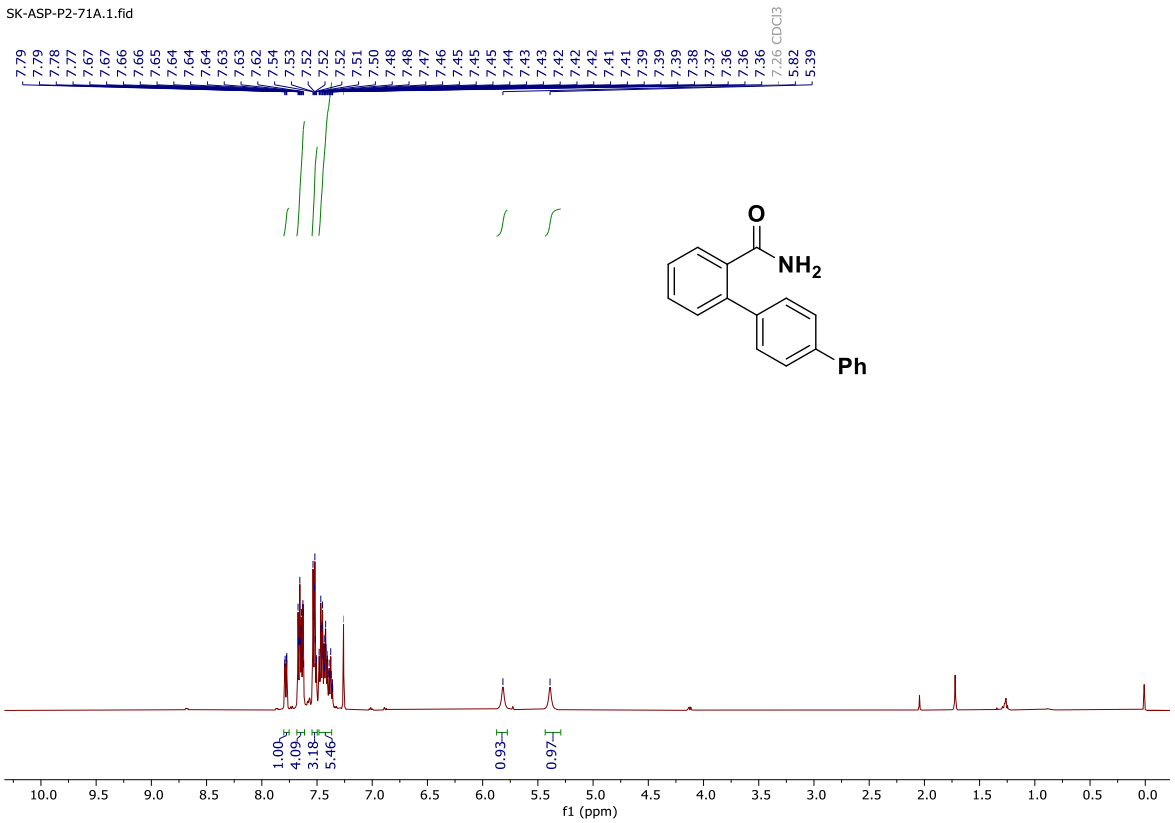
15. N. P. Ramirez, I. Bosque and J. C. G. -Gomez, Photocatalytic dehydrogenative lactonization of 2-arylbenzoic acids, *Org. Lett.*, 2015, **17**, 4550.

16. Y. Wu, F. -W. Wu, K. Zhou, Y. Li, L. Chen, S. Wang, Z. -Y. Xu, S. -J. Lou and D. -Q. Xu, Rapid access to 9-arylfluorene and spirobifluorene through Pd-catalyzed C-H arylation/deaminative annulation. *Chem. Commun*., 2022, **58**, 6280.

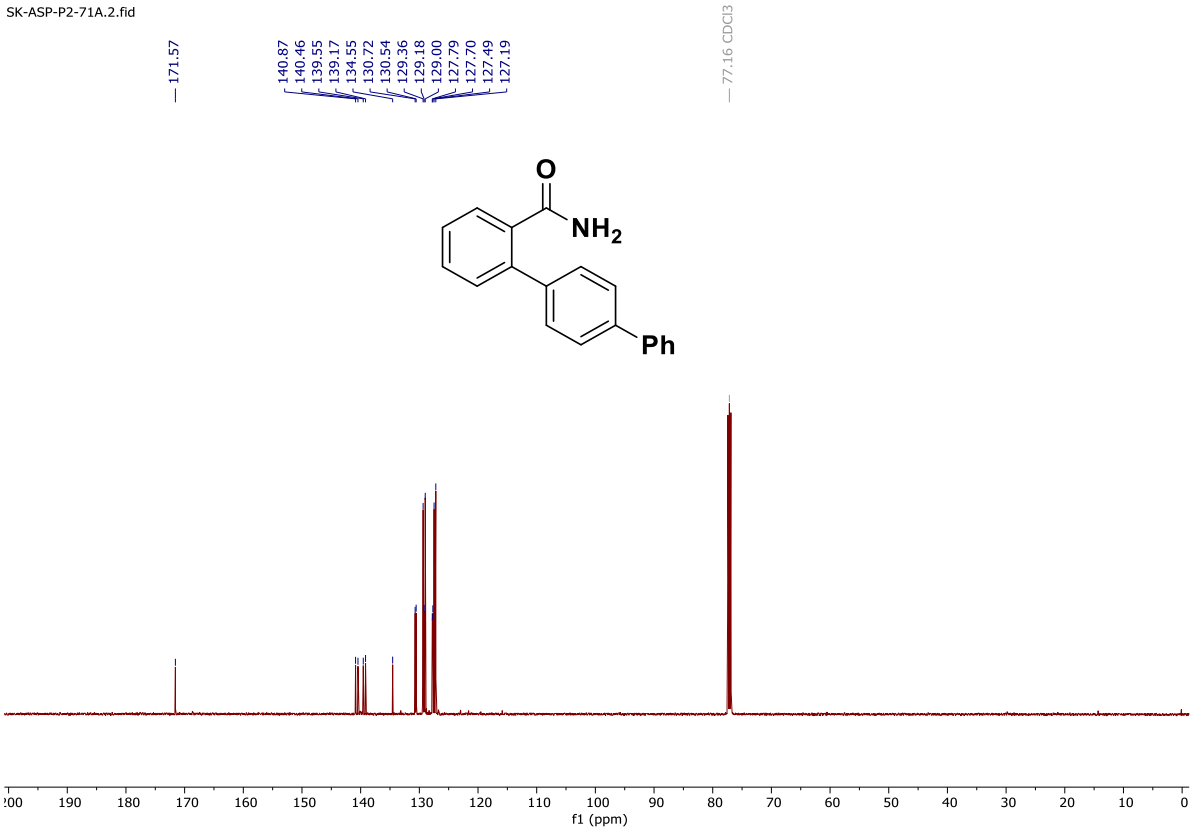
17. X. -Y. Su and P. -Q. Huang, Tf_2O-promoted Morgan-Walls reaction: from a flexible approach to functionalized phenanthridines and quinazolines to the short and divergent total syntheses of alkaloids. *Synthesis*, 2023, **55**, 877.

10. ^{1}H, ^{13}C and ^{19}F NMR Spectra

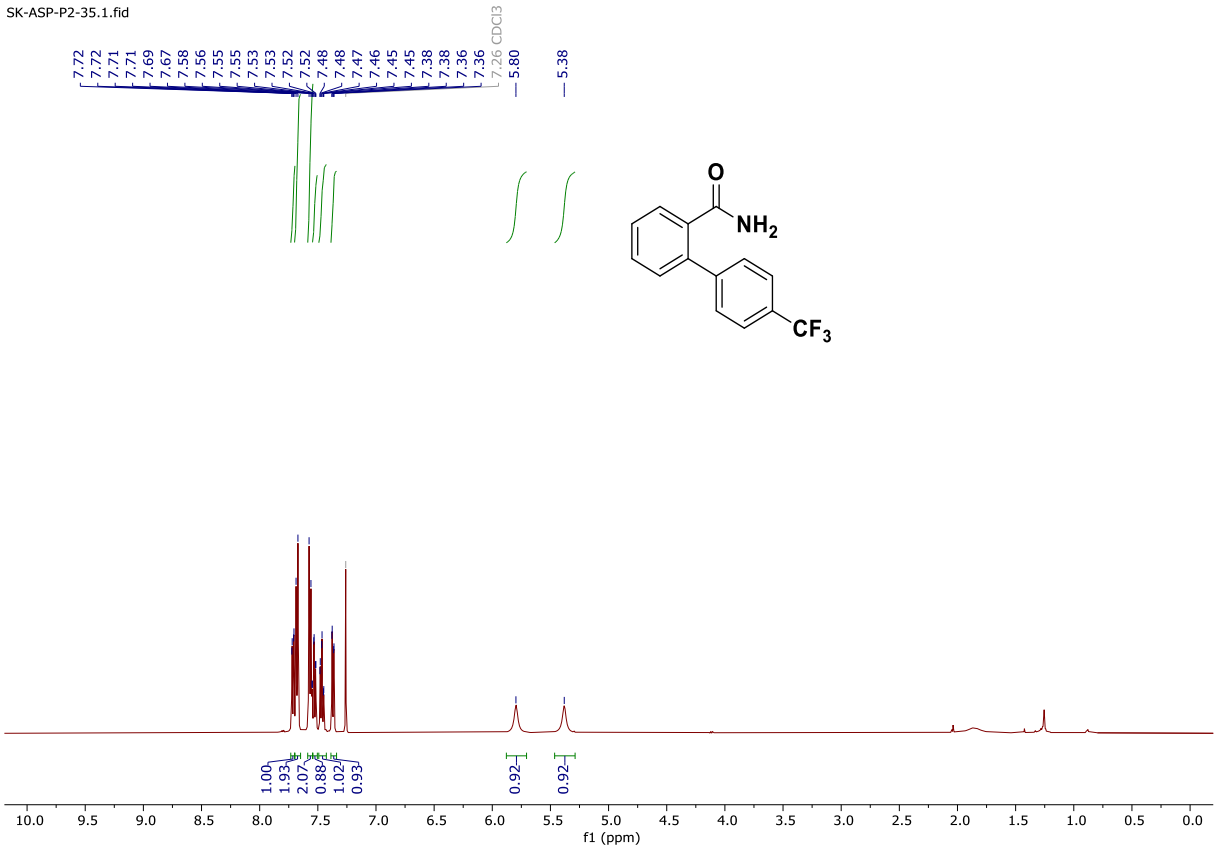
^{1}H NMR spectrum of I7 in $CDCl_3$ [500 MHz]



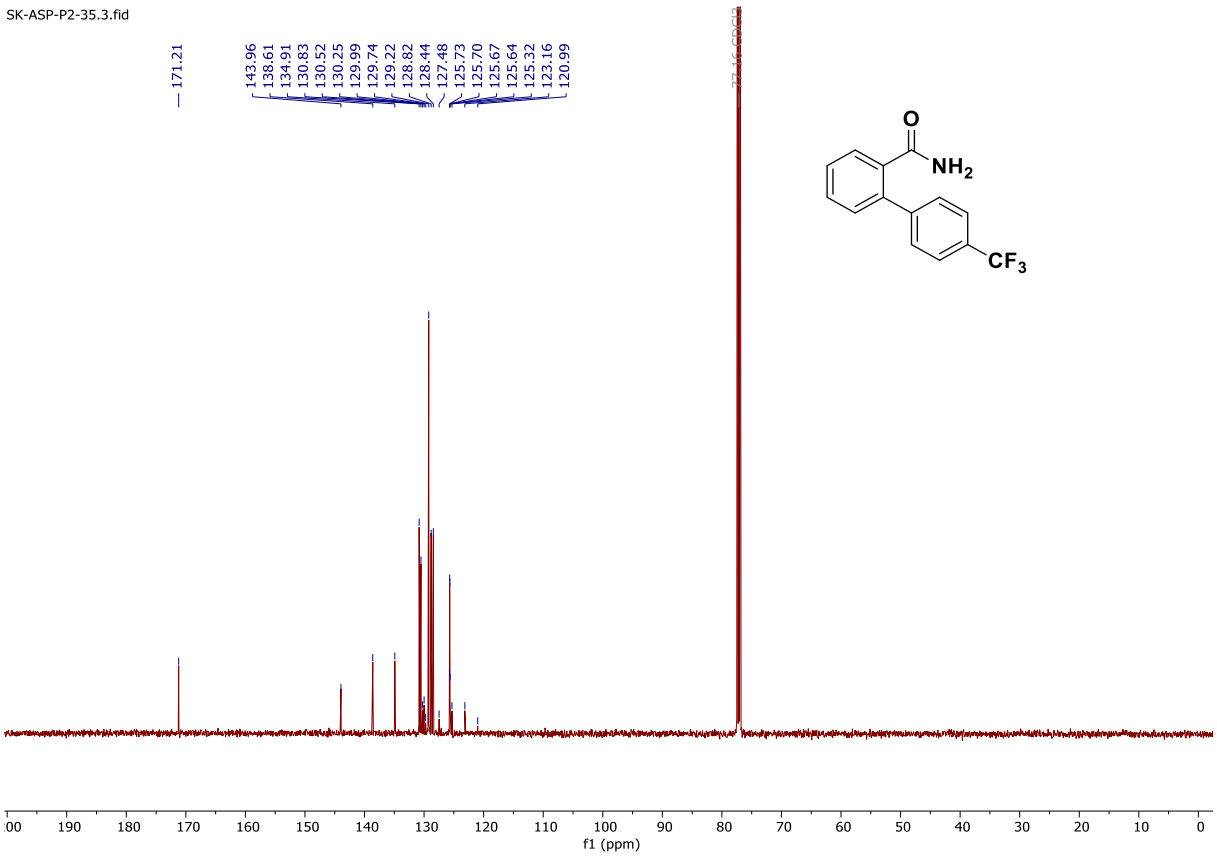
$^{13}C\{^{1}H\}$ NMR spectrum of I7 in $CDCl_3$ [126 MHz]



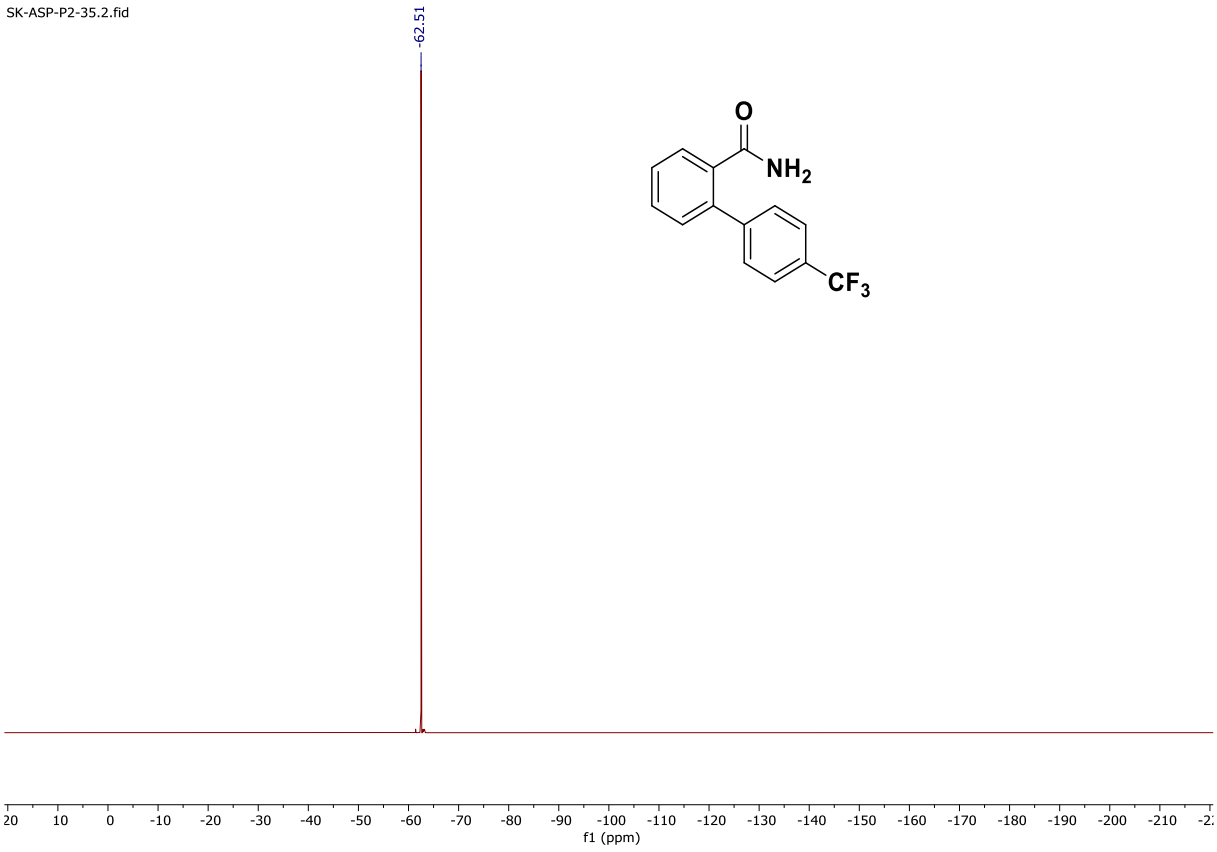
^{1}H NMR spectrum of I8 in $CDCl_3$ [500 MHz]



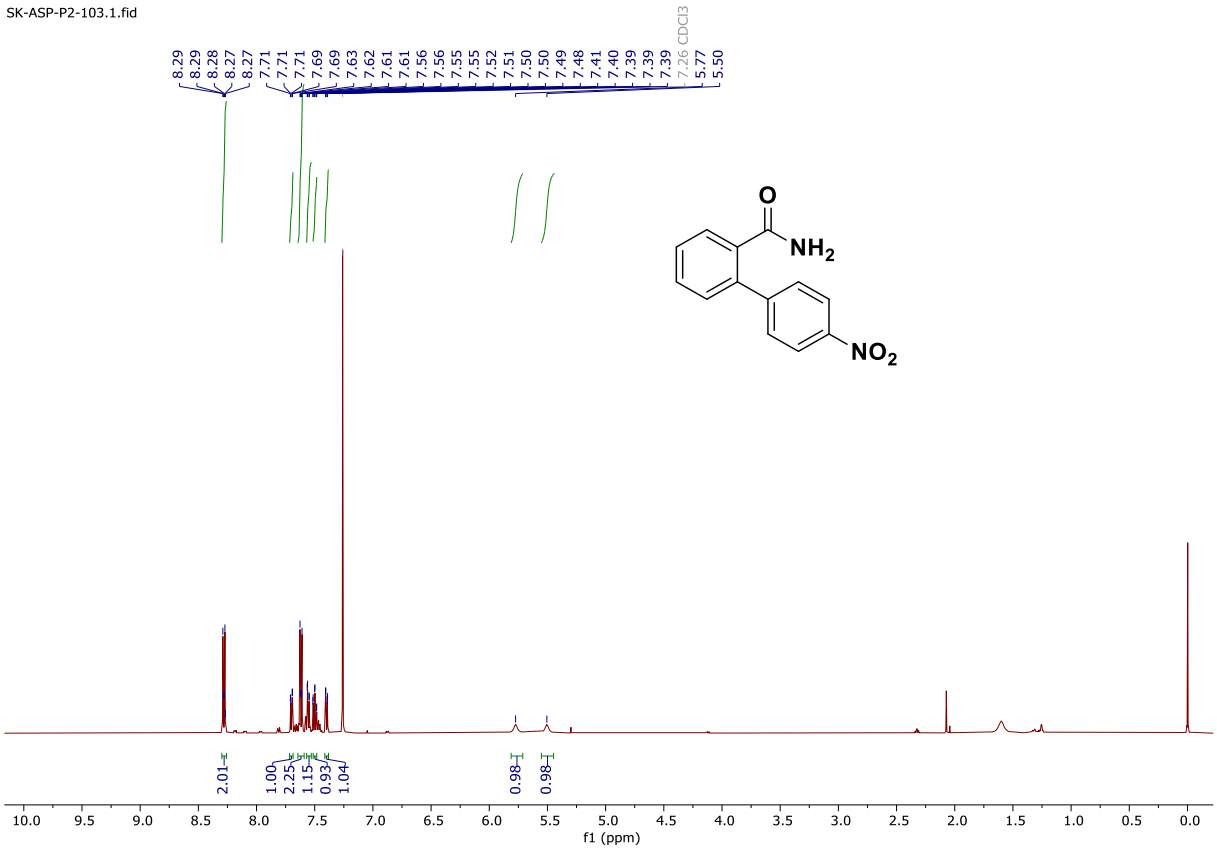
^{13}C{^{1}H} NMR spectrum of I8 in $CDCl_3$ [126 MHz]



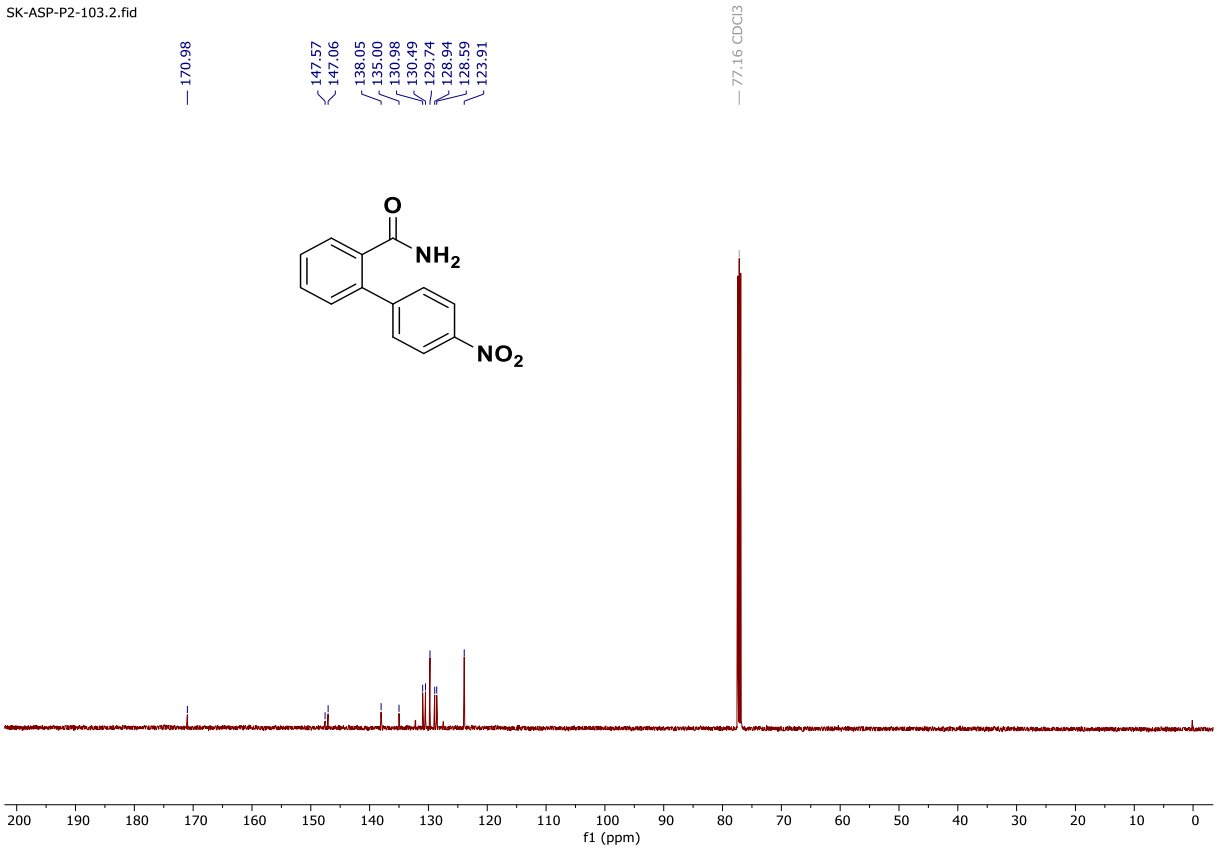
^{19}F NMR spectrum of I8 in $CDCl_3$ [471 MHz]



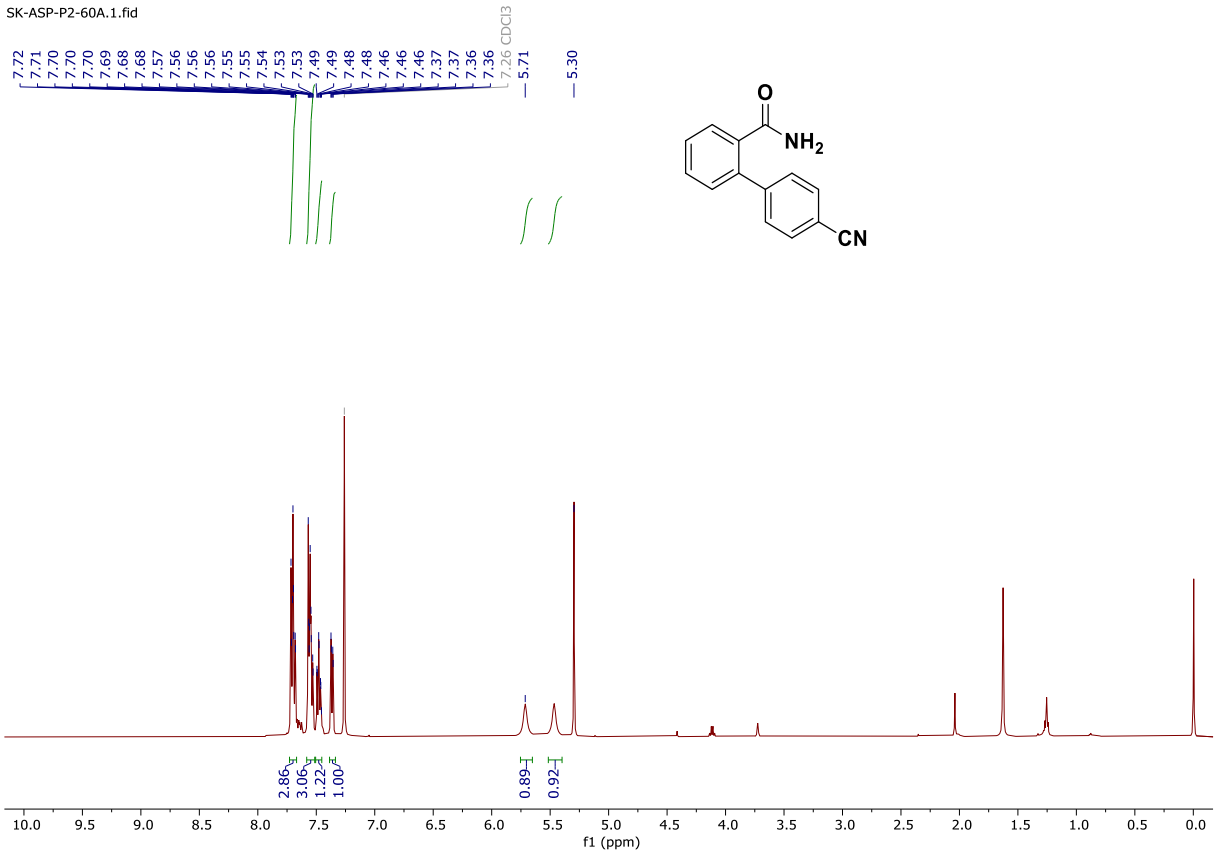
^{1}H NMR spectrum of I9 in $CDCl_3$ [500 MHz]



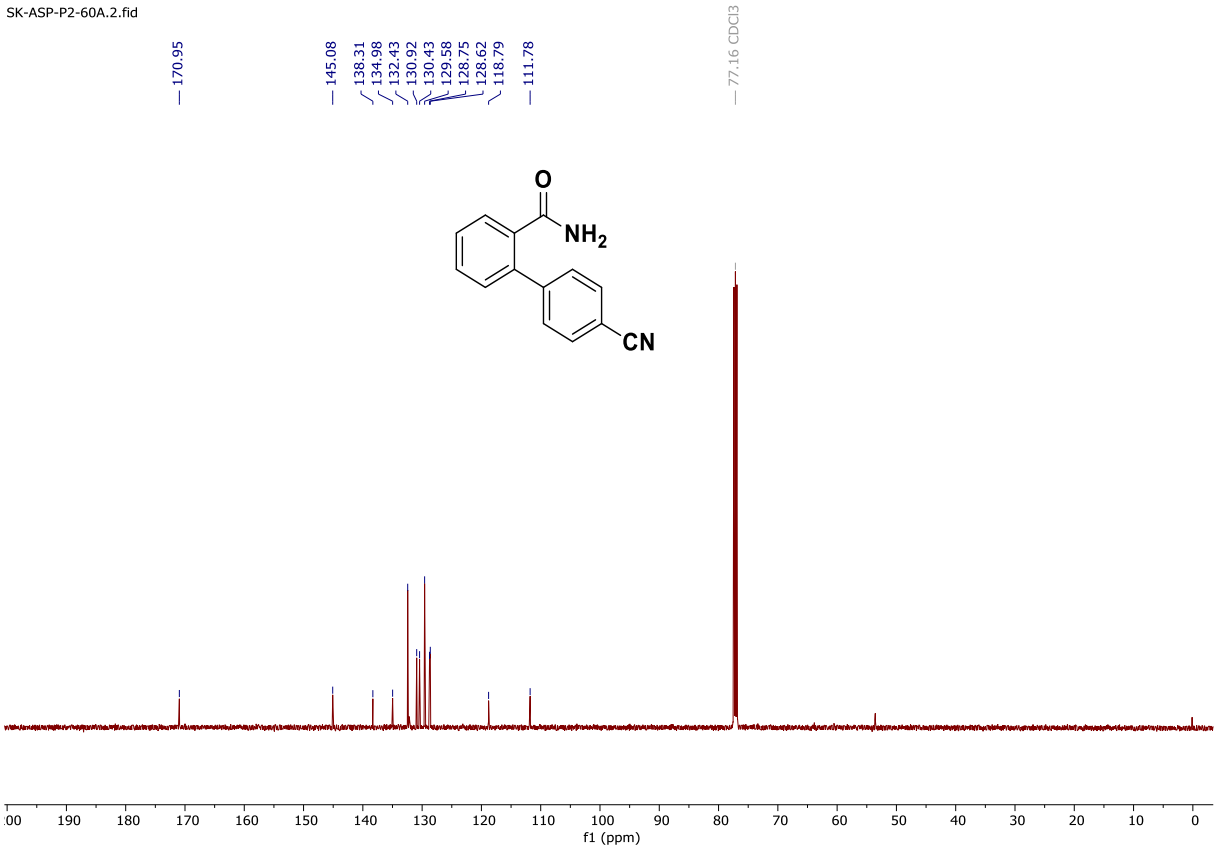
$^{13}C\{^{1}H\}$ NMR spectrum of I9 in $CDCl_3$ [126 MHz]



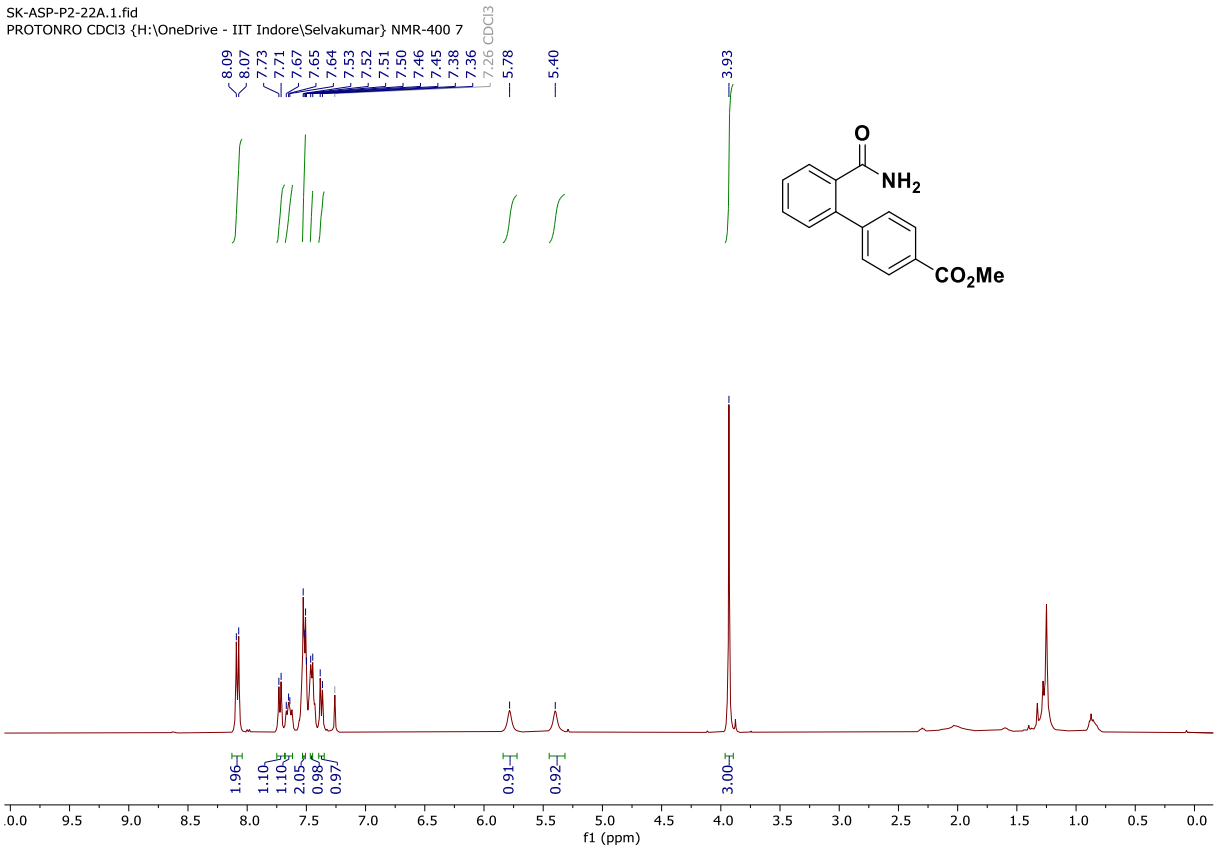
^{1}H NMR spectrum of I10 in $CDCl_3$ [500 MHz]



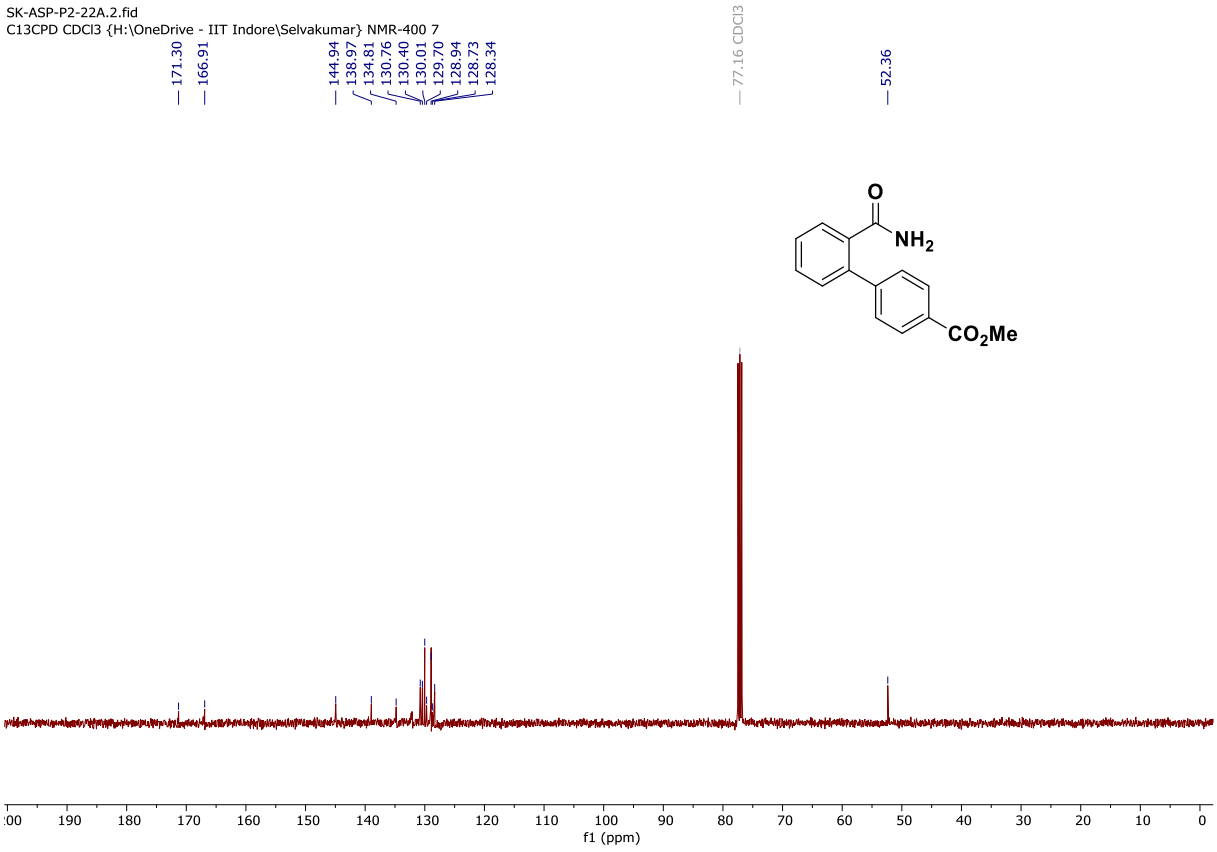
$^{13}C\{^{1}H\}$ NMR spectrum of I10 in $CDCl_3$ [126 MHz]



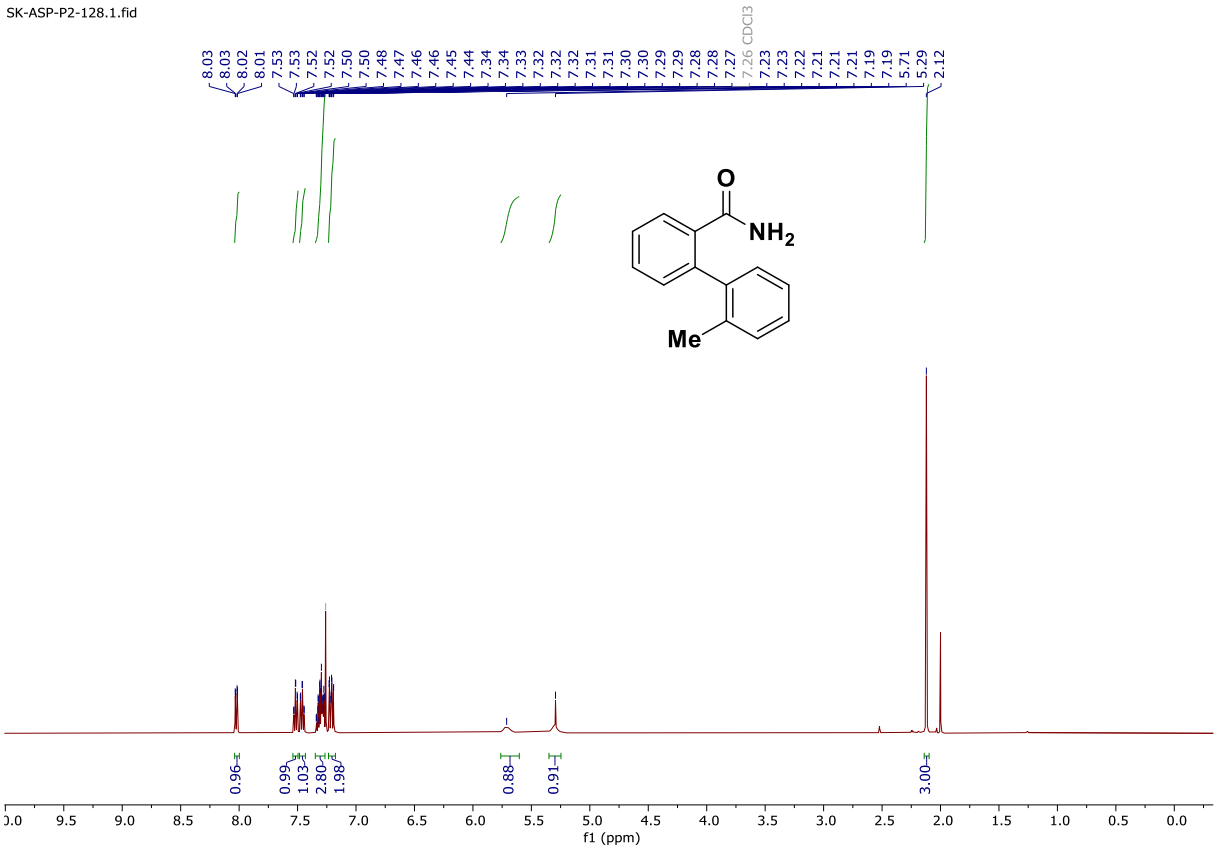
^{1}H NMR spectrum of I11 in $CDCl_3$ [400 MHz]



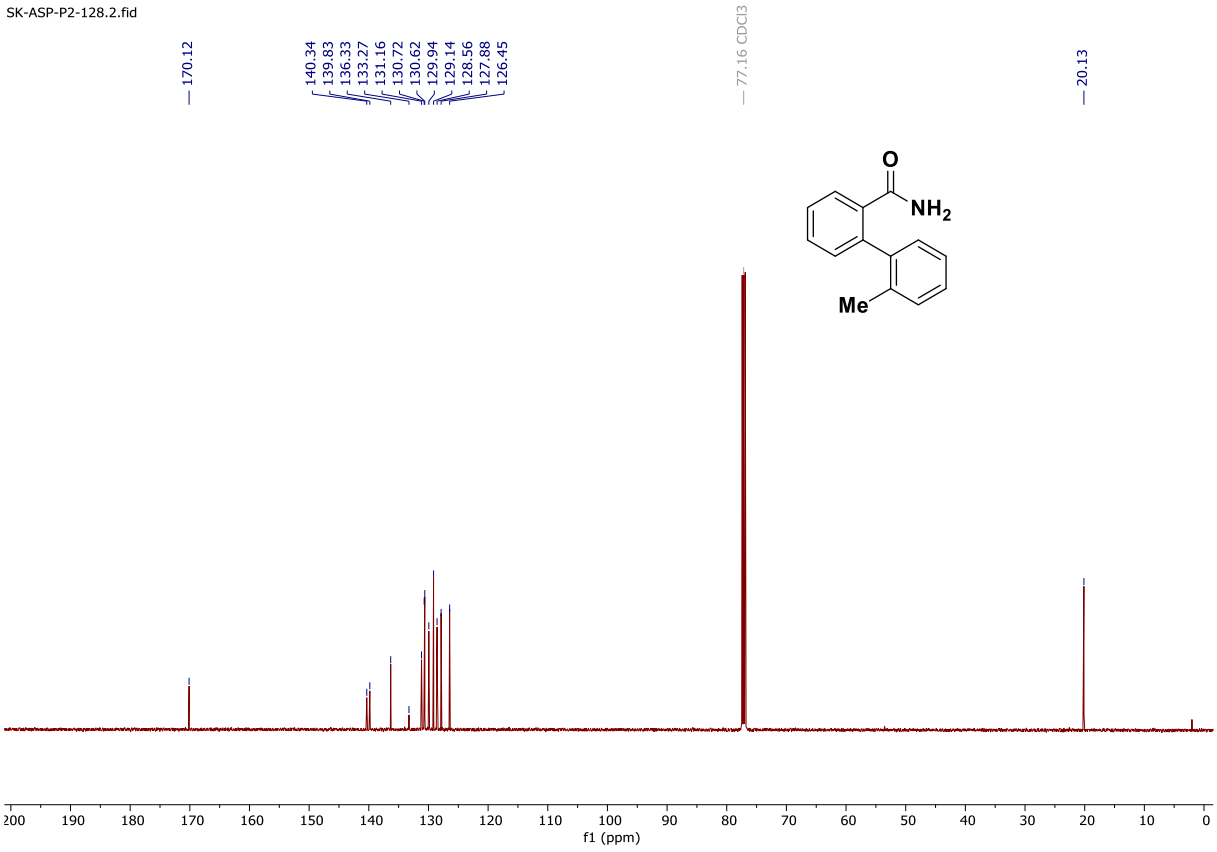
$^{13}C\{^{1}H\}$ NMR spectrum of I11 in $CDCl_3$ [101 MHz]



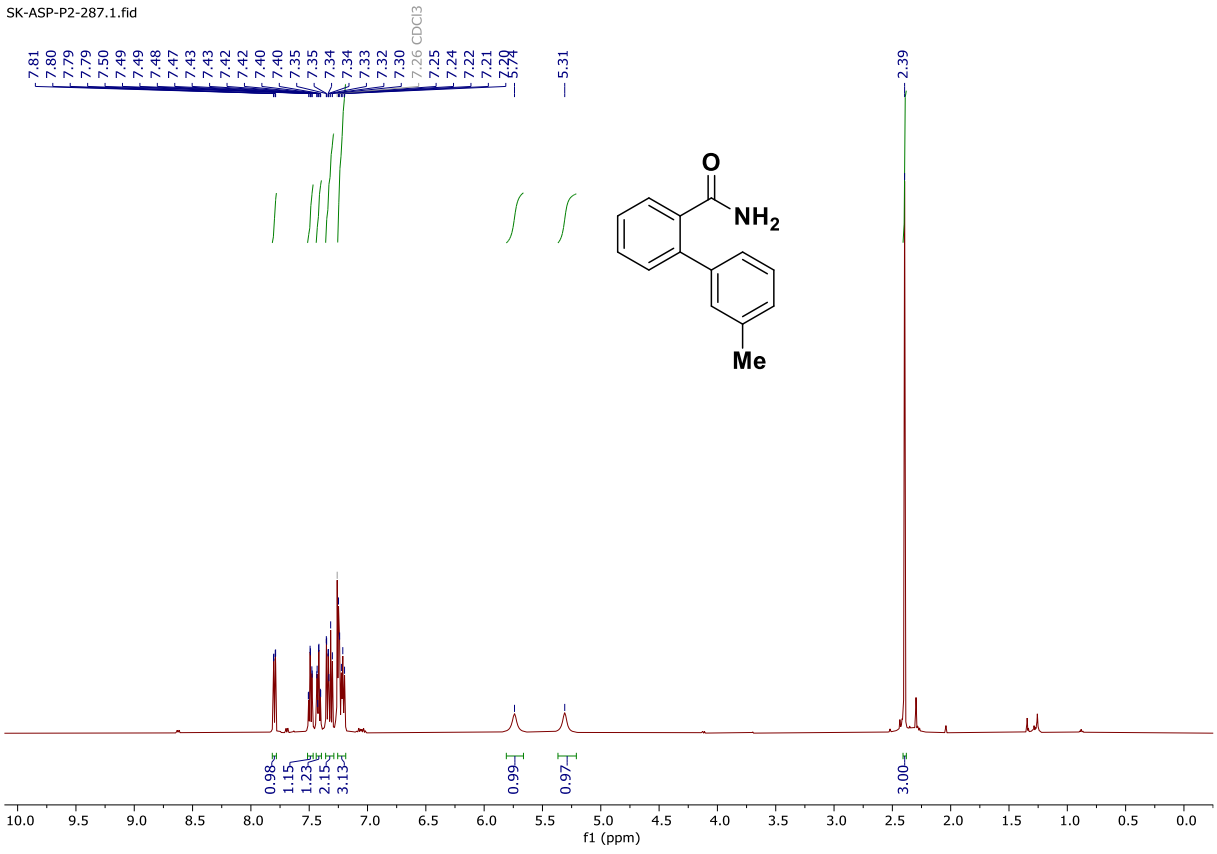
^{1}H NMR spectrum of I12 in $CDCl_3$ [500 MHz]



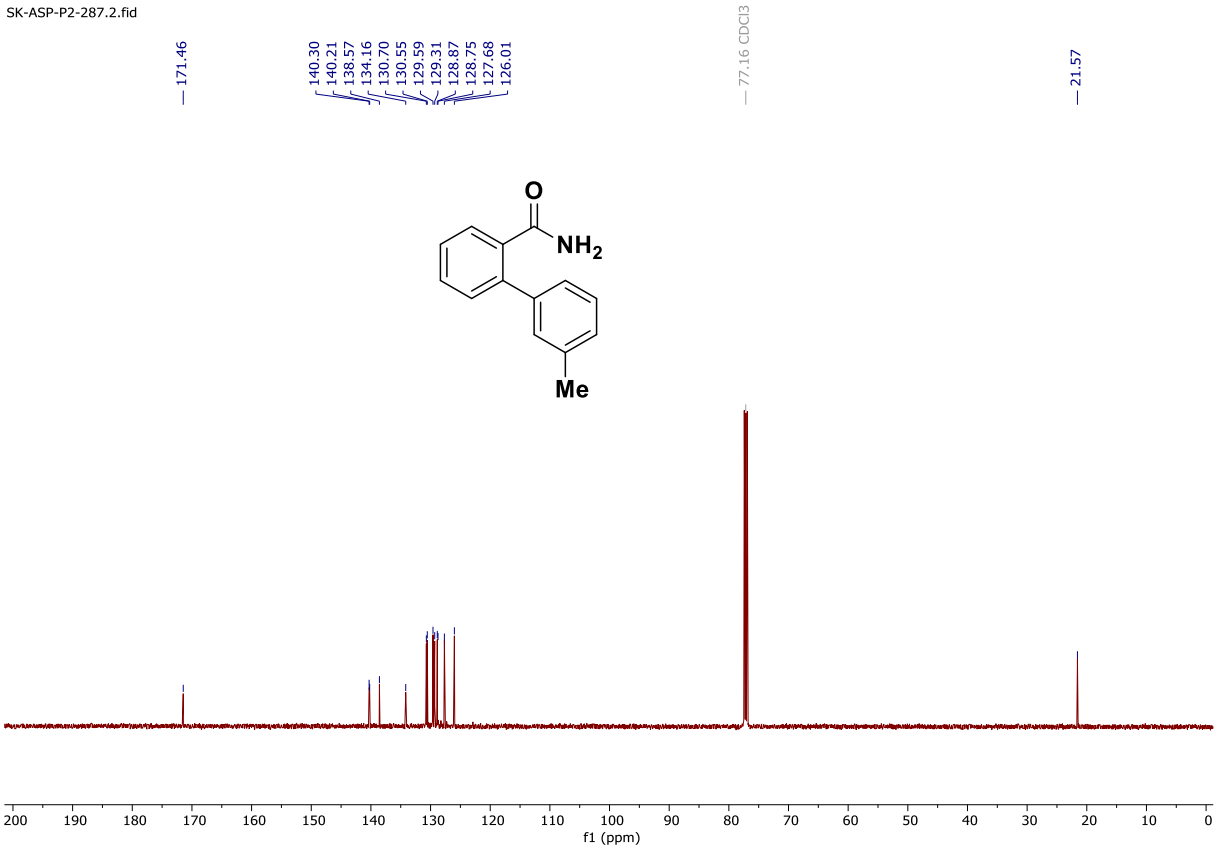
$^{13}C\{^{1}H\}$ NMR spectrum of I12 in $CDCl_3$ [126 MHz]



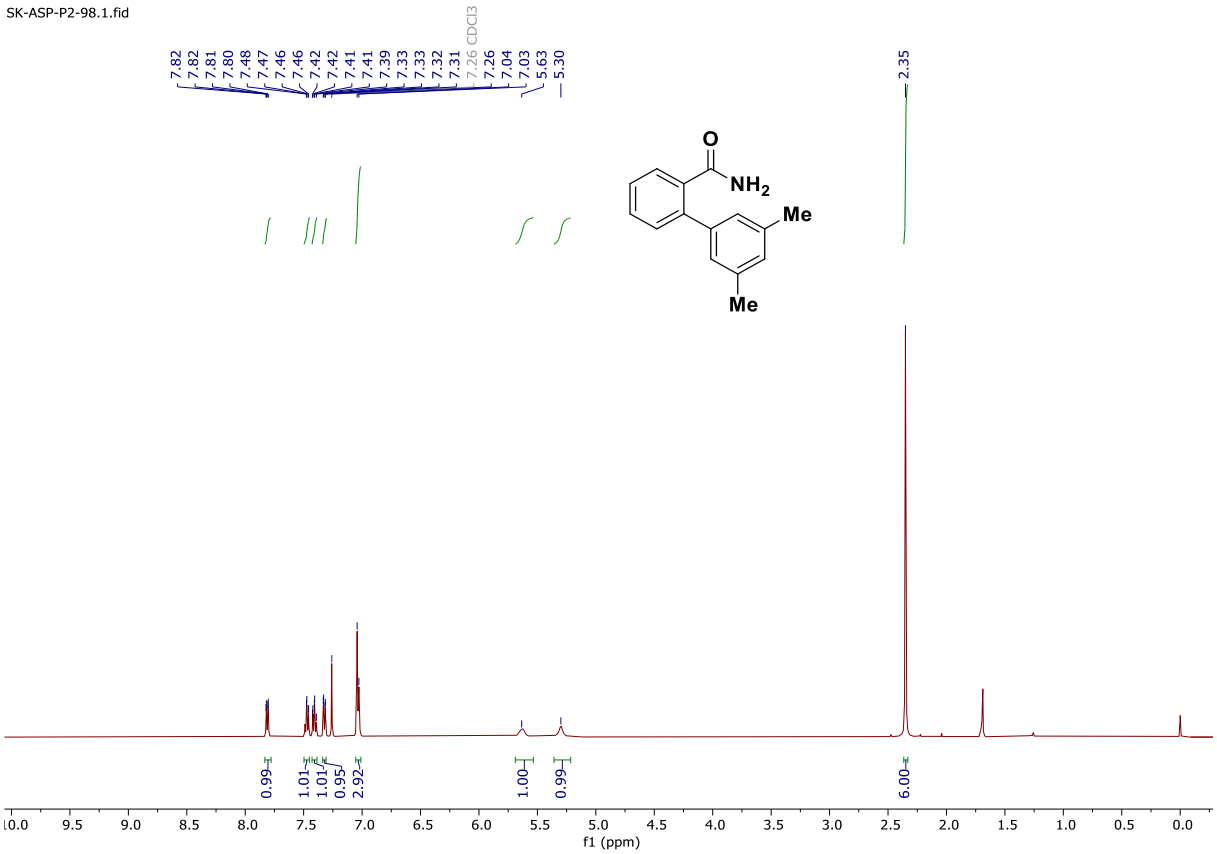
^{1}H NMR spectrum of I13 in $CDCl_3$ [500 MHz]



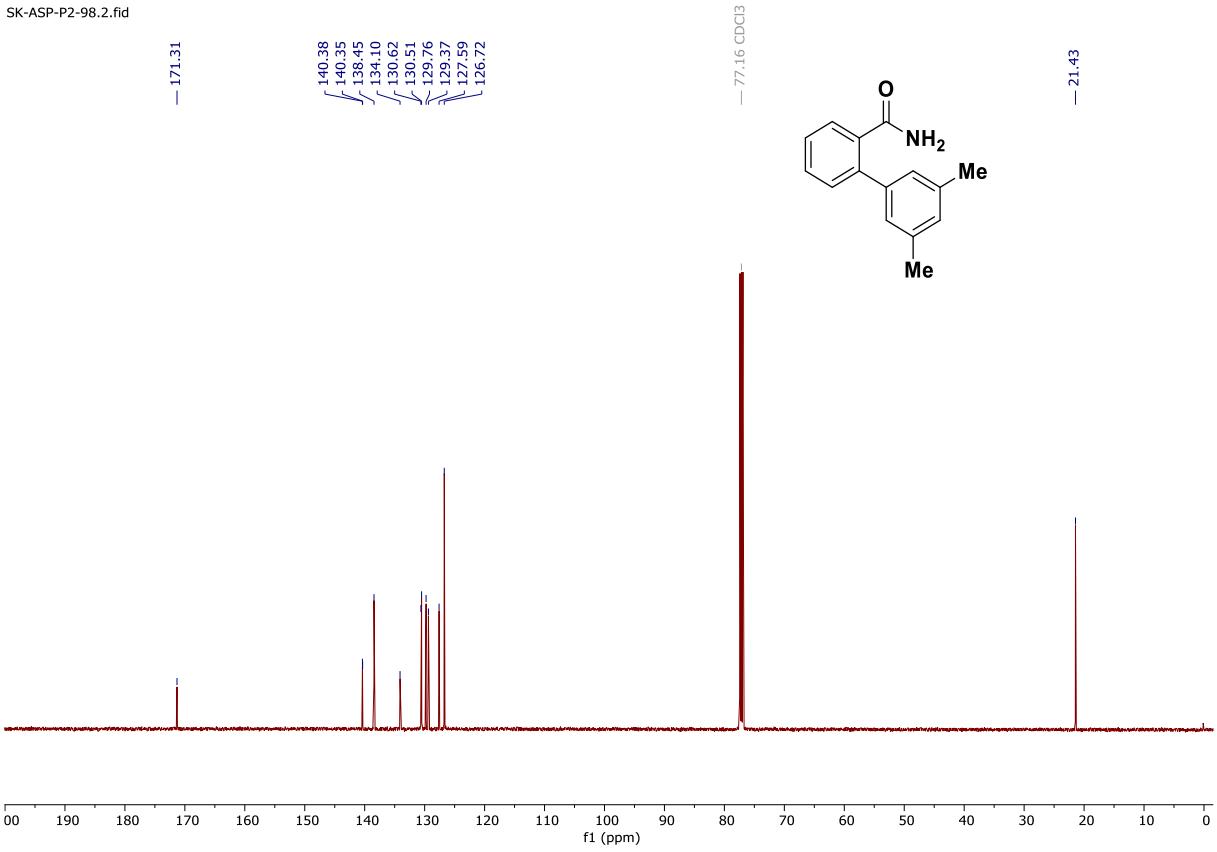
$^{13}C\{^{1}H\}$ NMR spectrum of I13 in $CDCl_3$ [126 MHz]



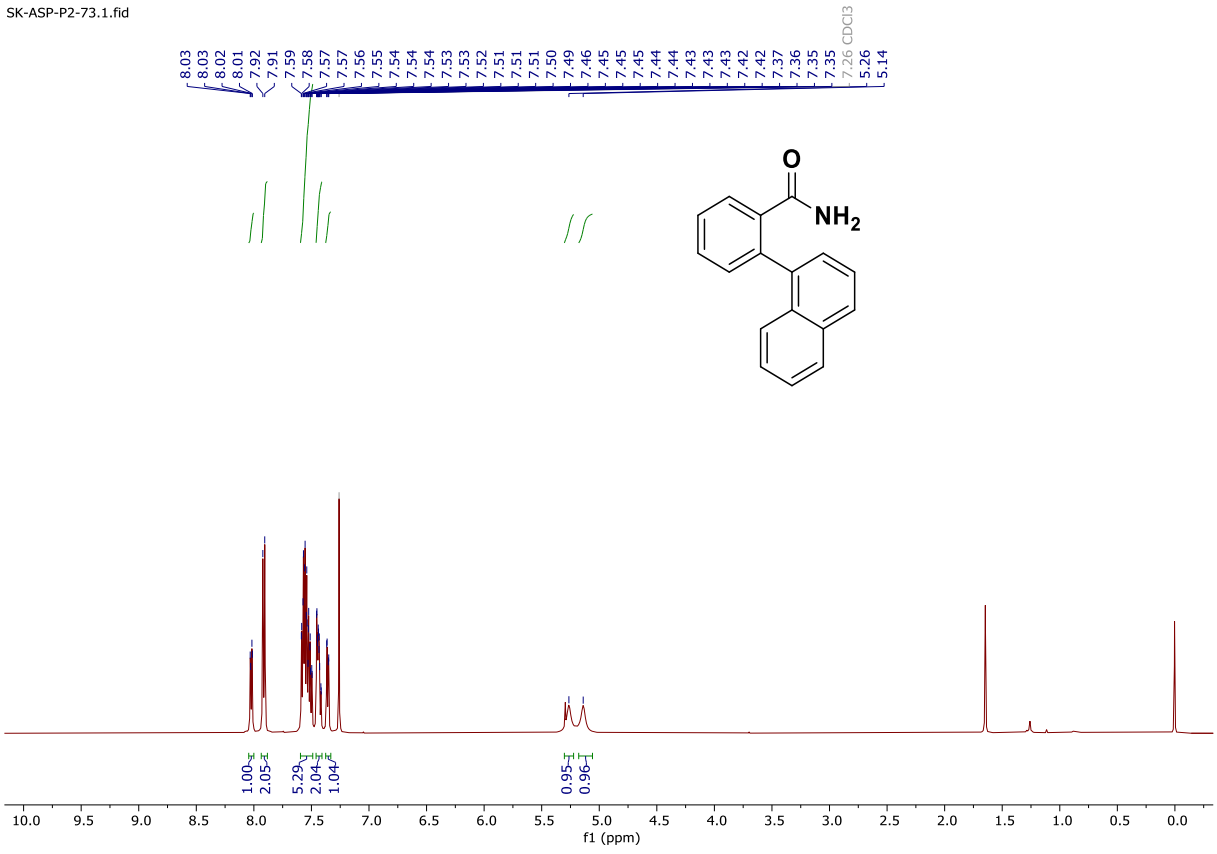
^{1}H NMR spectrum of I14 in $CDCl_3$ [500 MHz]



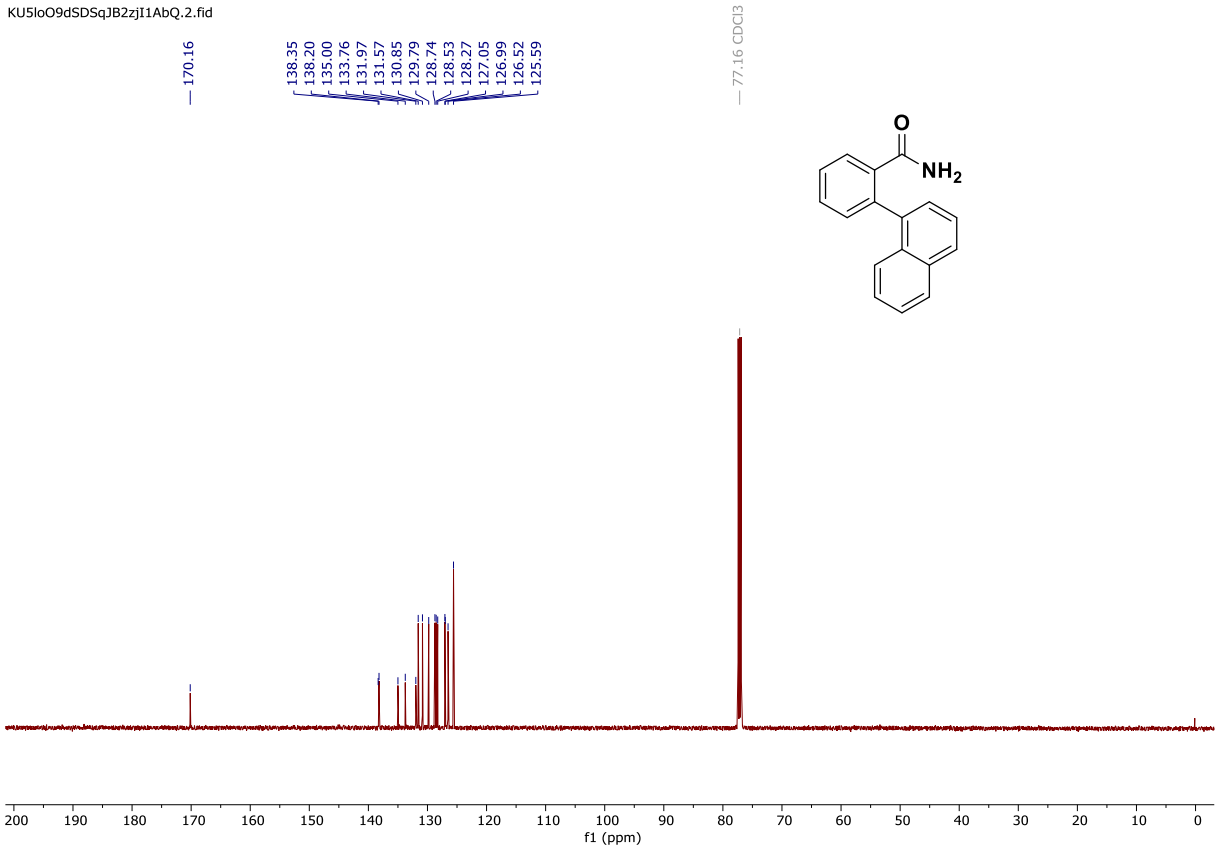
$^{13}C\{^{1}H\}$ NMR spectrum of I14 in $CDCl_3$ [126 MHz]



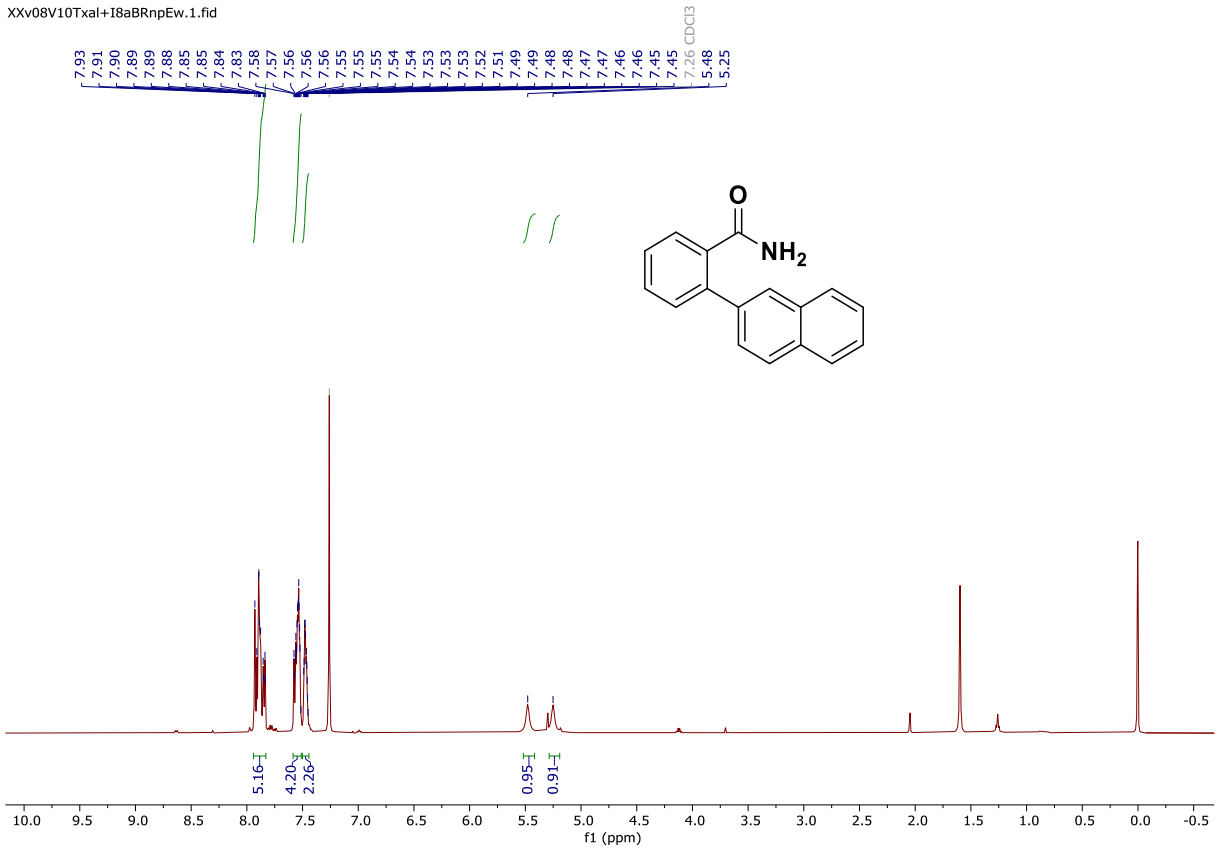
^{1}H NMR spectrum of I15 in $CDCl_3$ [500 MHz]



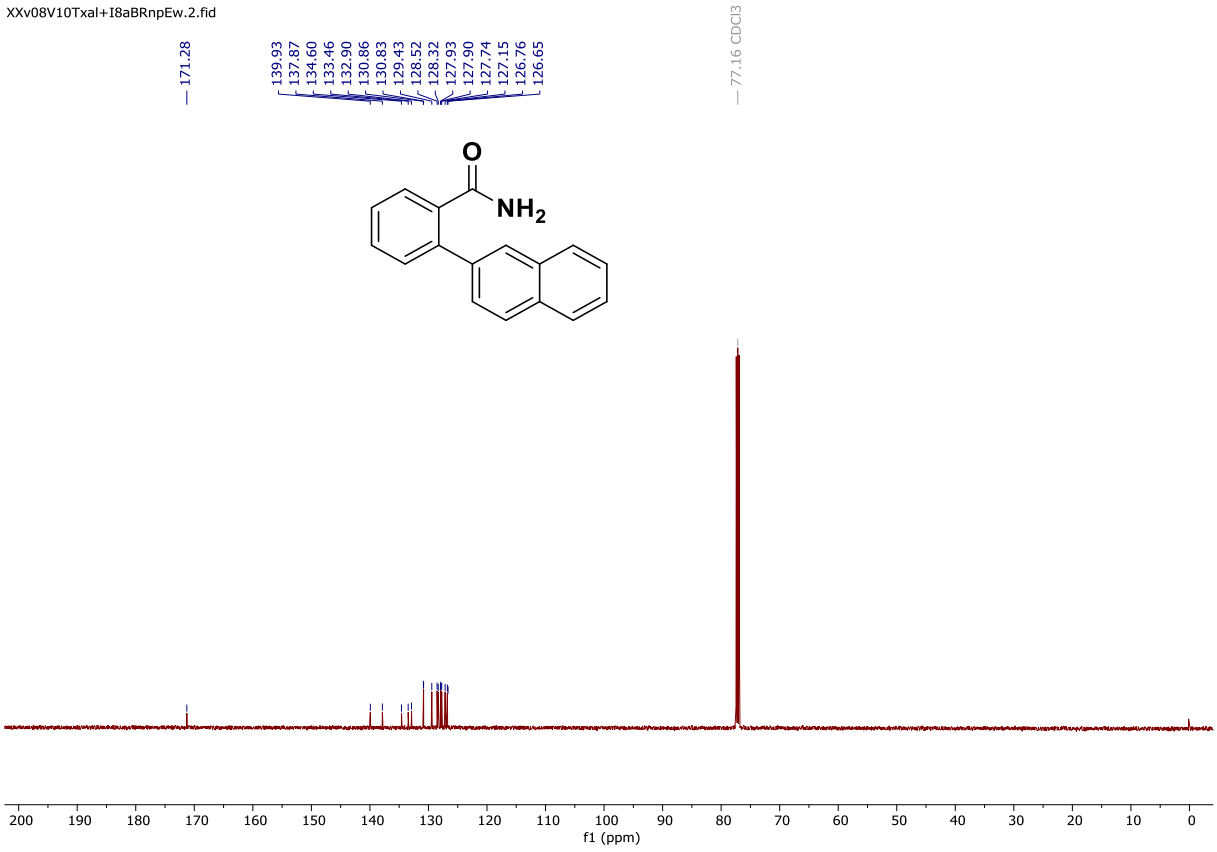
$^{13}C\{^{1}H\}$ NMR spectrum of I15 in $CDCl_3$ [126 MHz]



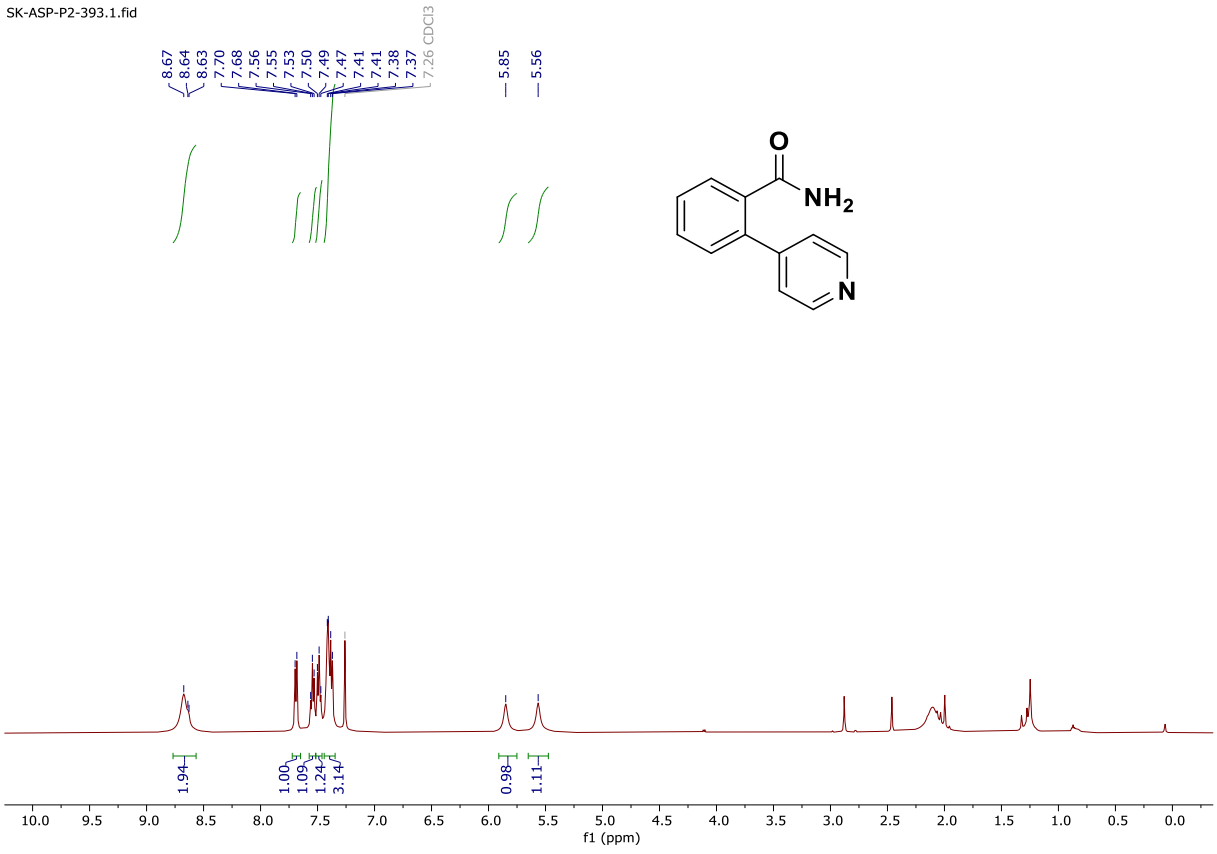
^{1}H NMR spectrum of I16 in $CDCl_3$ [500 MHz]



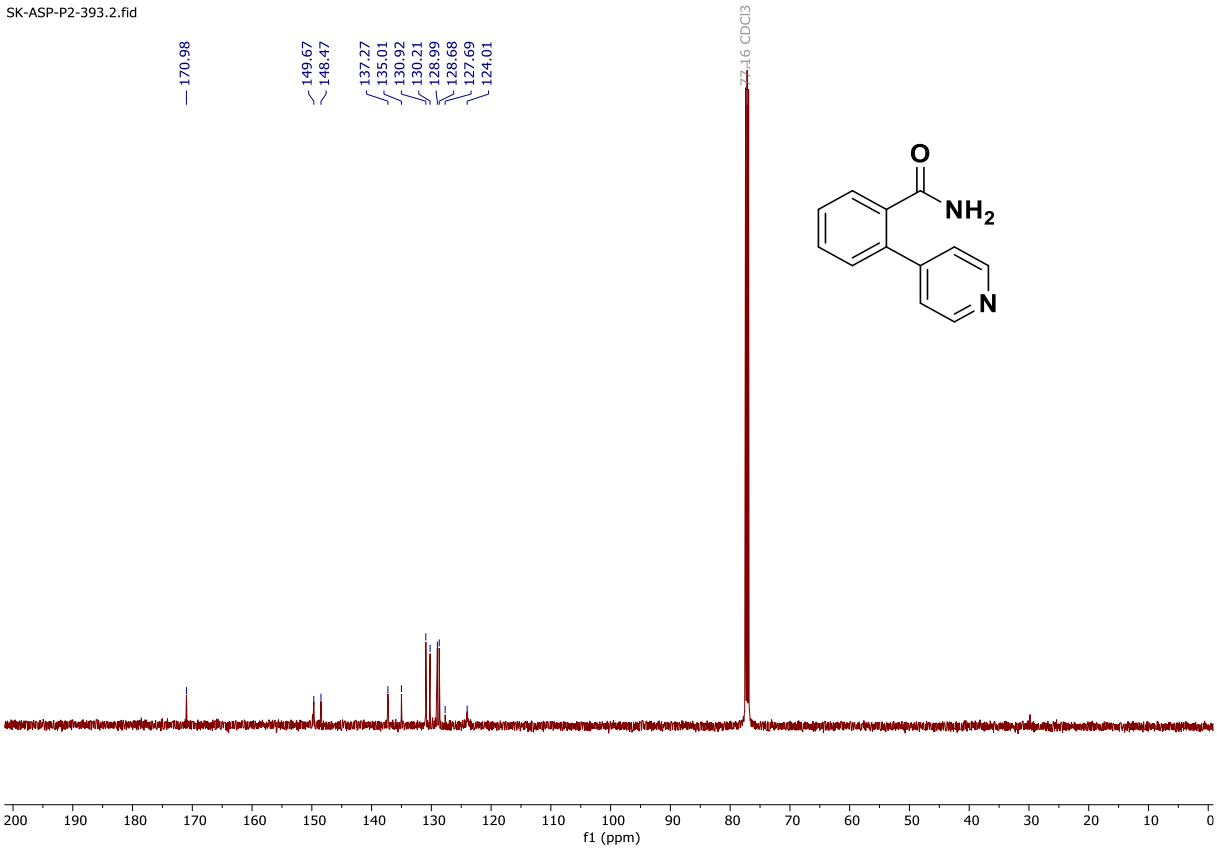
$^{13}C\{^{1}H\}$ NMR spectrum of I16 in $CDCl_3$ [126 MHz]



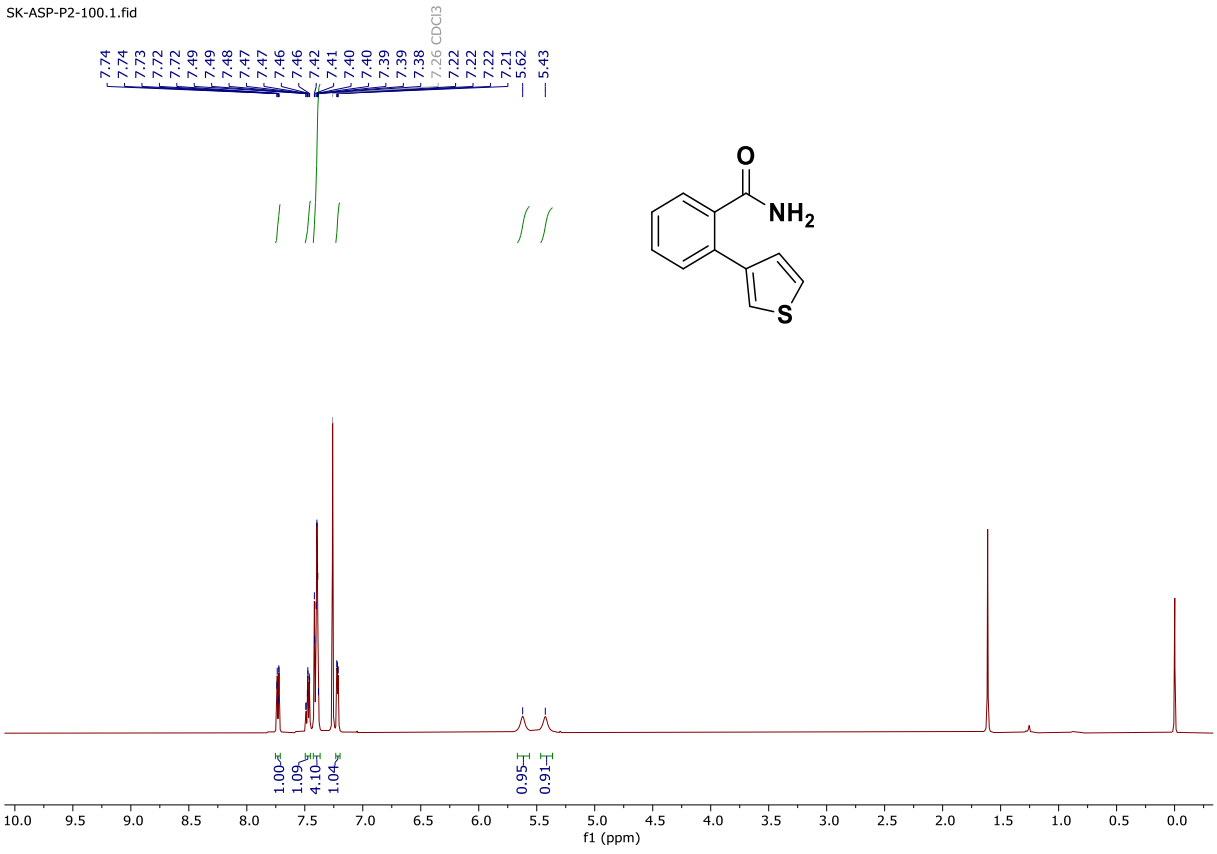
^{1}H NMR spectrum of I17 in $CDCl_3$ [500 MHz]



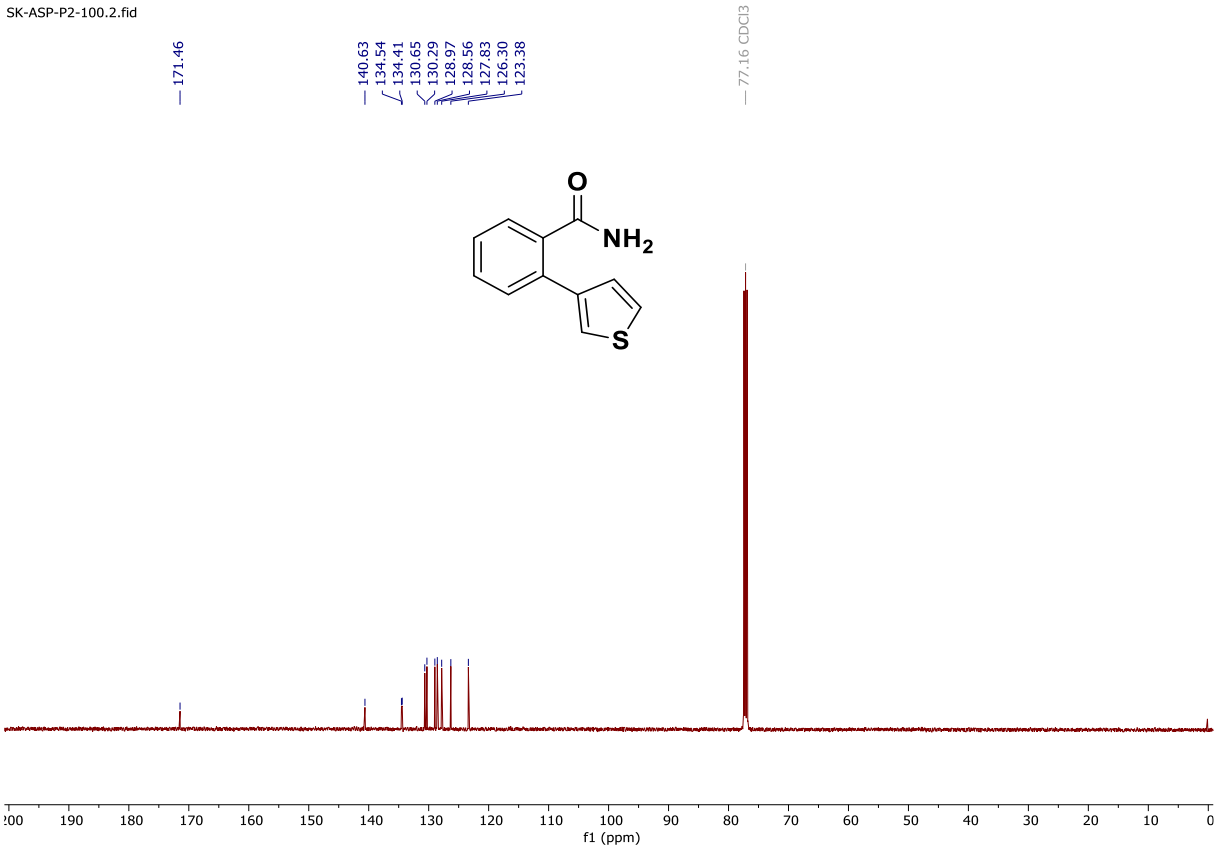
$^{13}C\{^{1}H\}$ NMR spectrum of I17 in $CDCl_3$ [126 MHz]



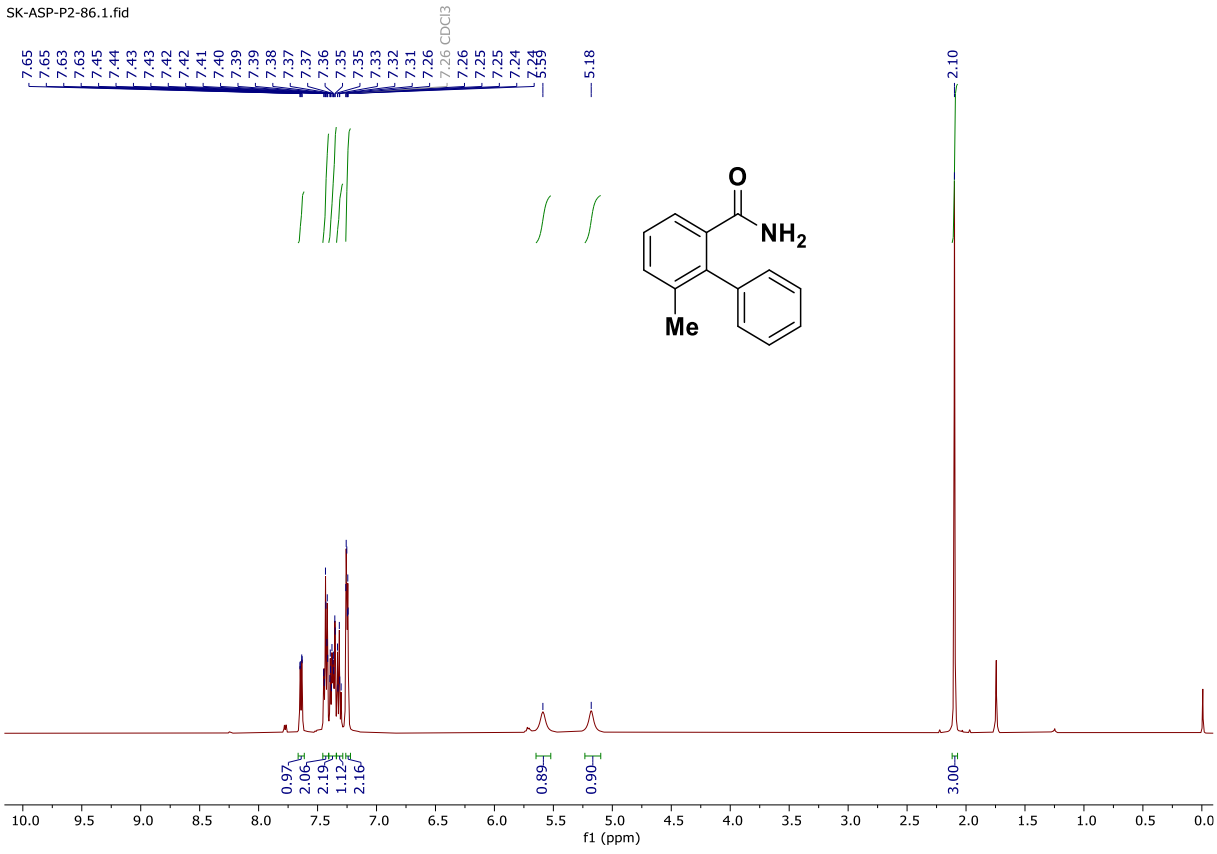
^{1}H NMR spectrum of I18 in $CDCl_3$ [500 MHz]



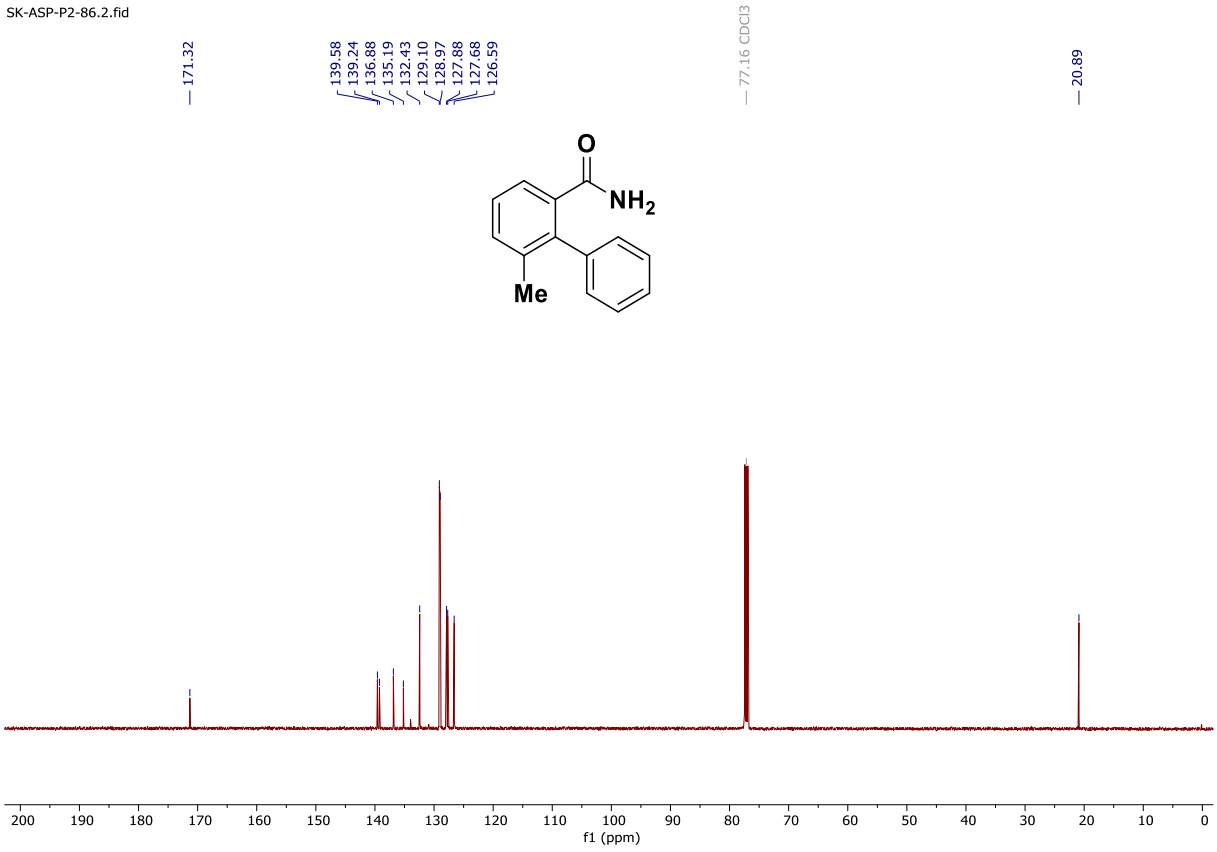
$^{13}C\{^{1}H\}$ NMR spectrum of I18 in $CDCl_3$ [126 MHz]



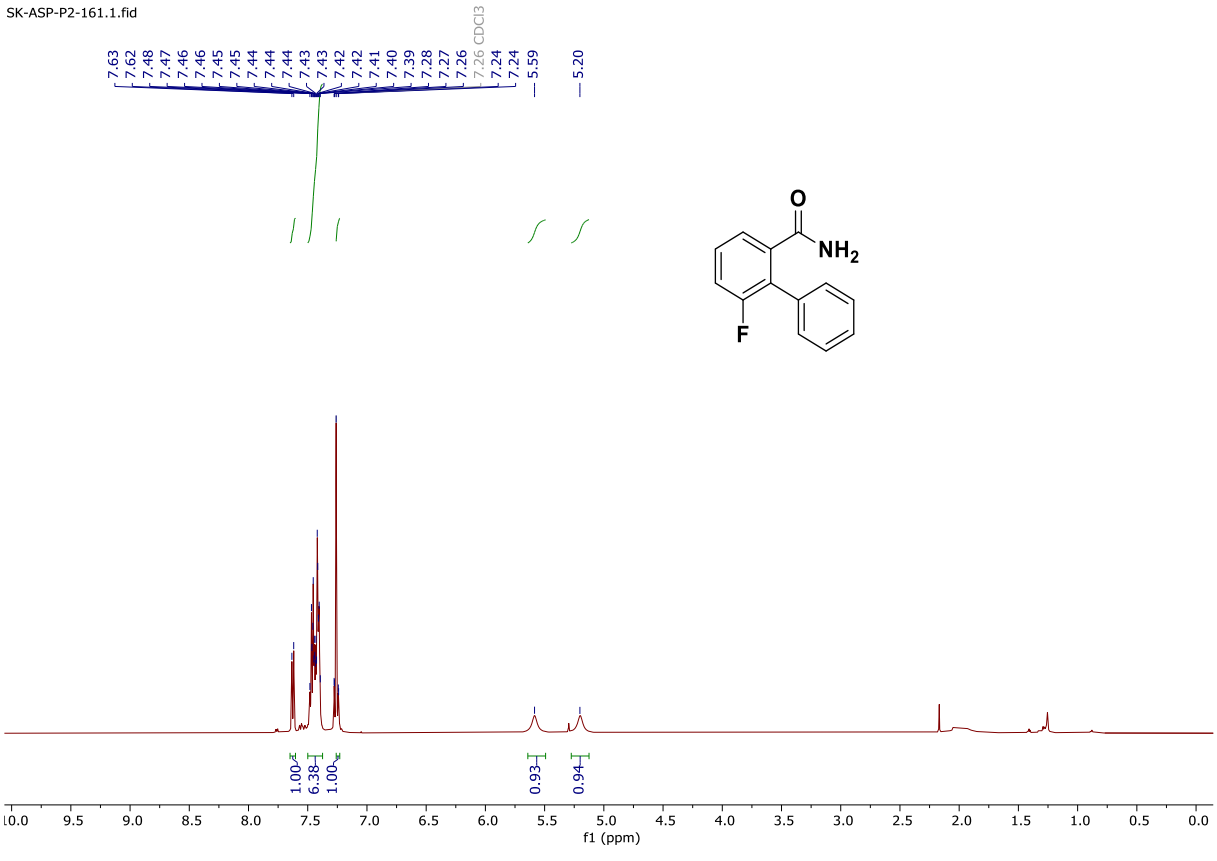
^{1}H NMR spectrum of I19 in $CDCl_3$ [500 MHz]



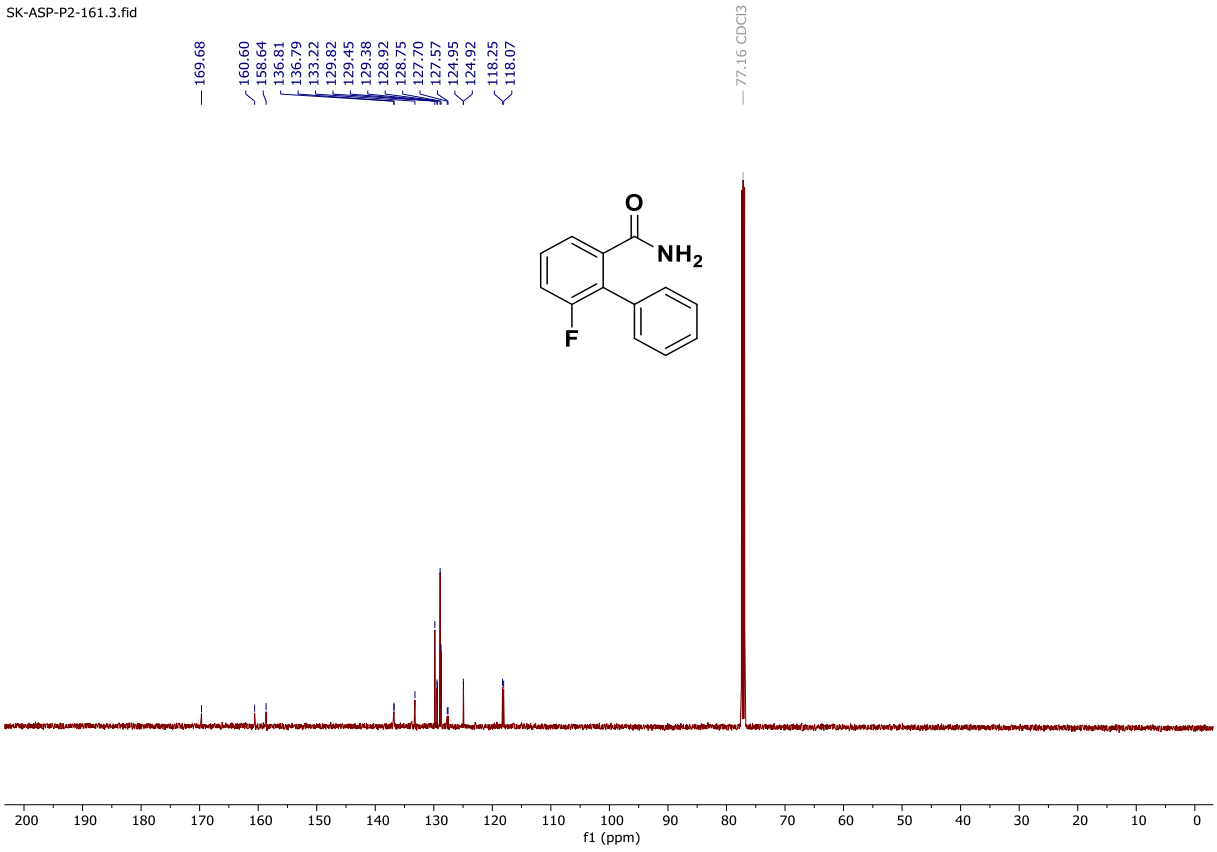
$^{13}C\{^{1}H\}$ NMR spectrum of I19 in $CDCl_3$ [126 MHz]



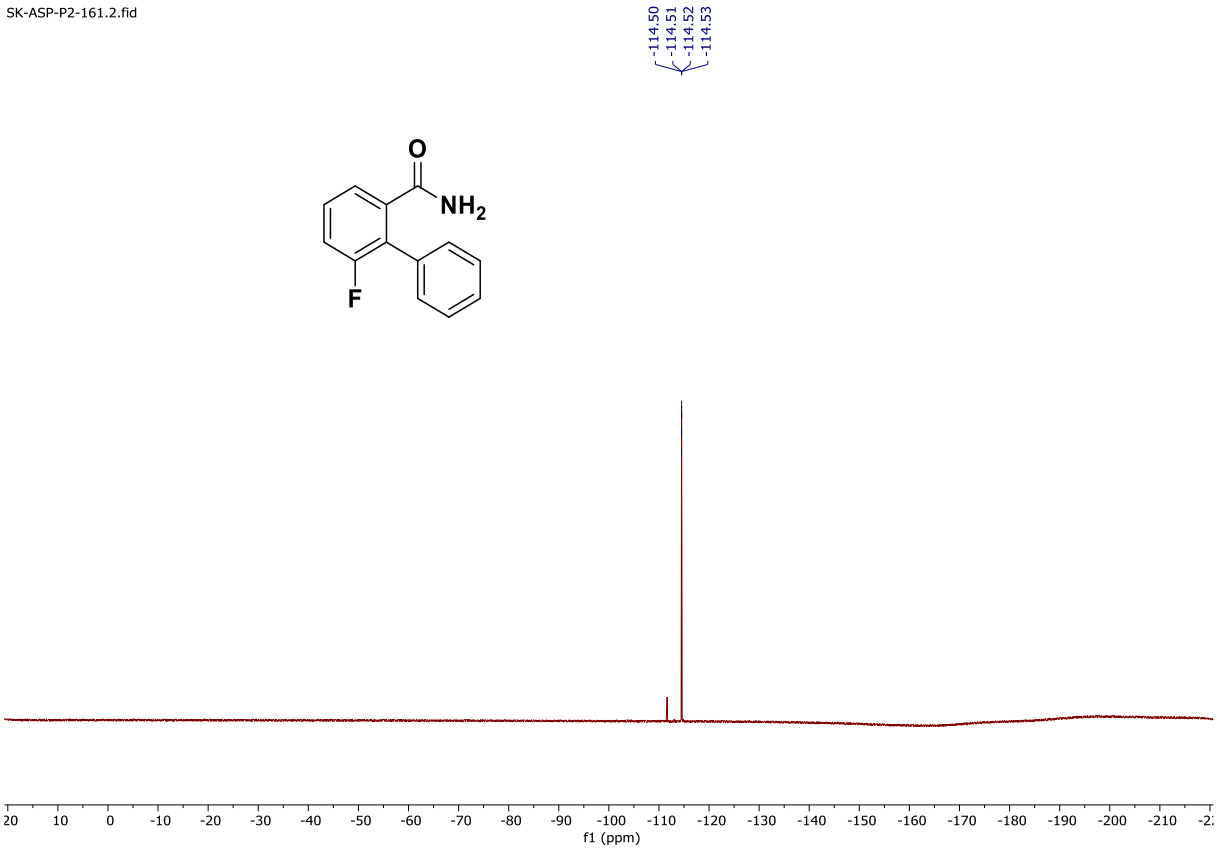
^{1}H NMR spectrum of I20 in $CDCl_3$ [500 MHz]



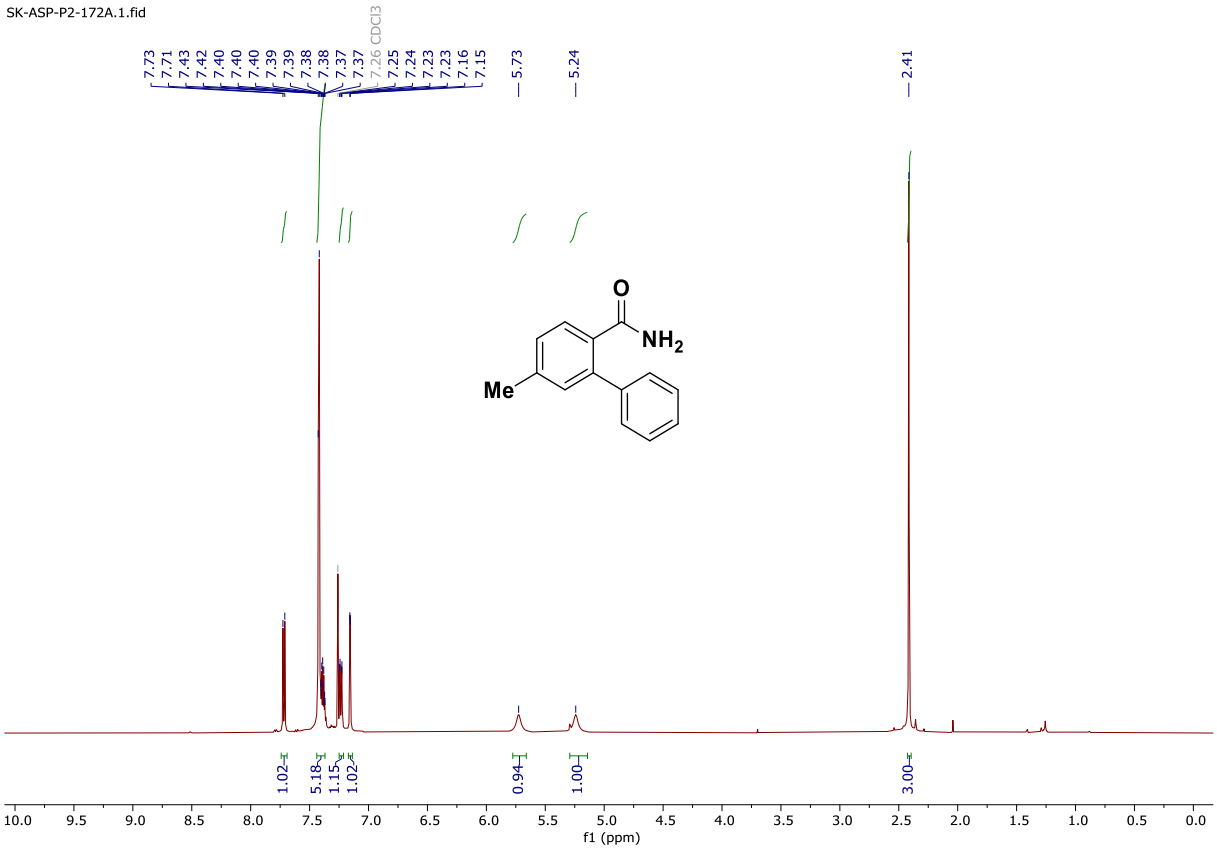
$^{13}C\{^{1}H\}$ NMR spectrum of I20 in $CDCl_3$ [126 MHz]



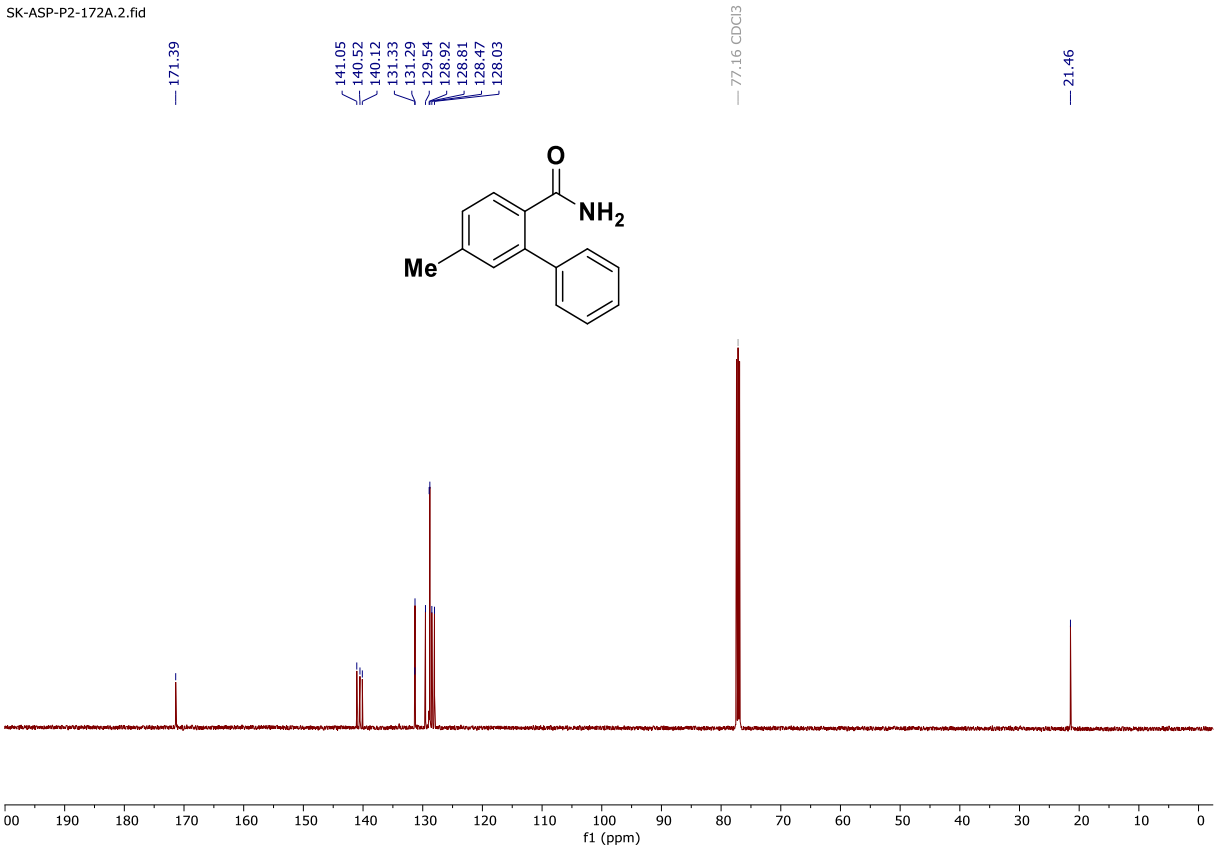
^{19}F NMR spectrum of I20 in $CDCl_3$ [471 MHz]



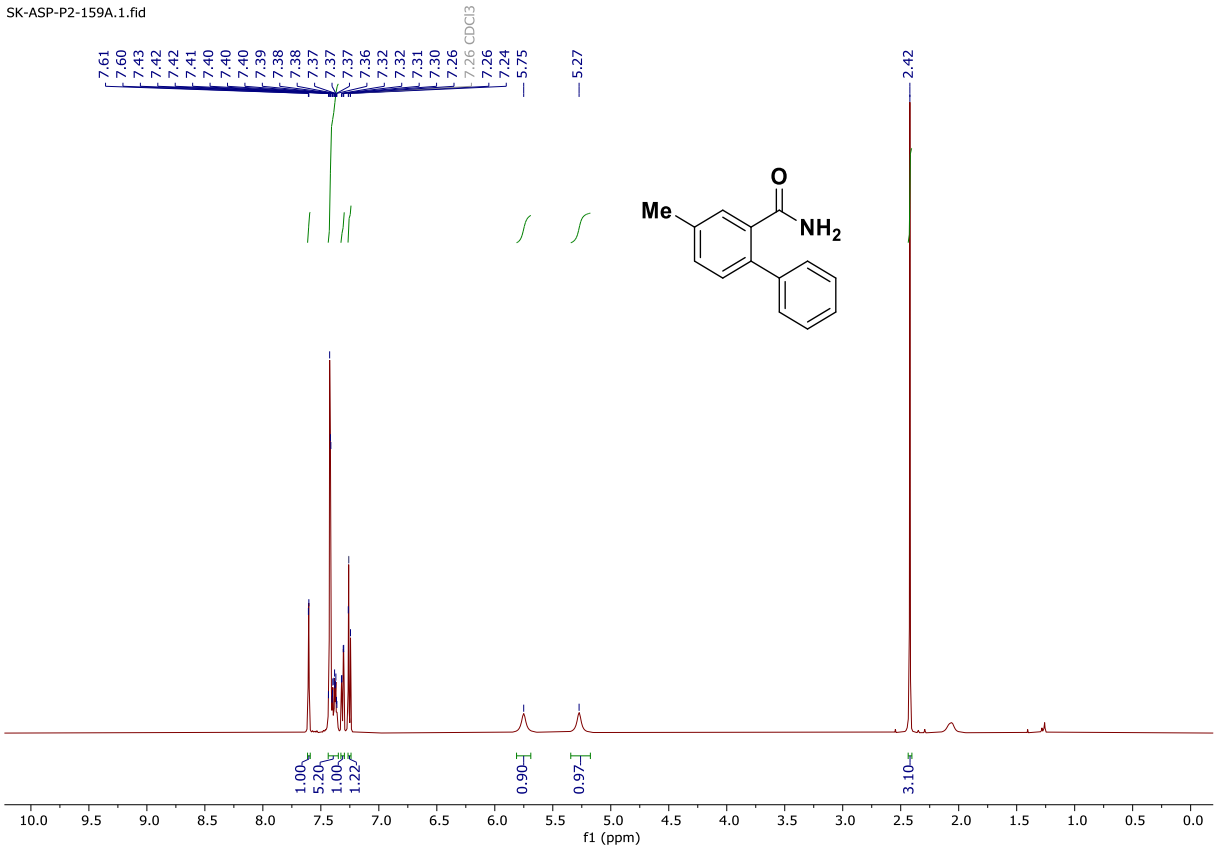
^{1}H NMR spectrum of I21 in $CDCl_3$ [500 MHz]



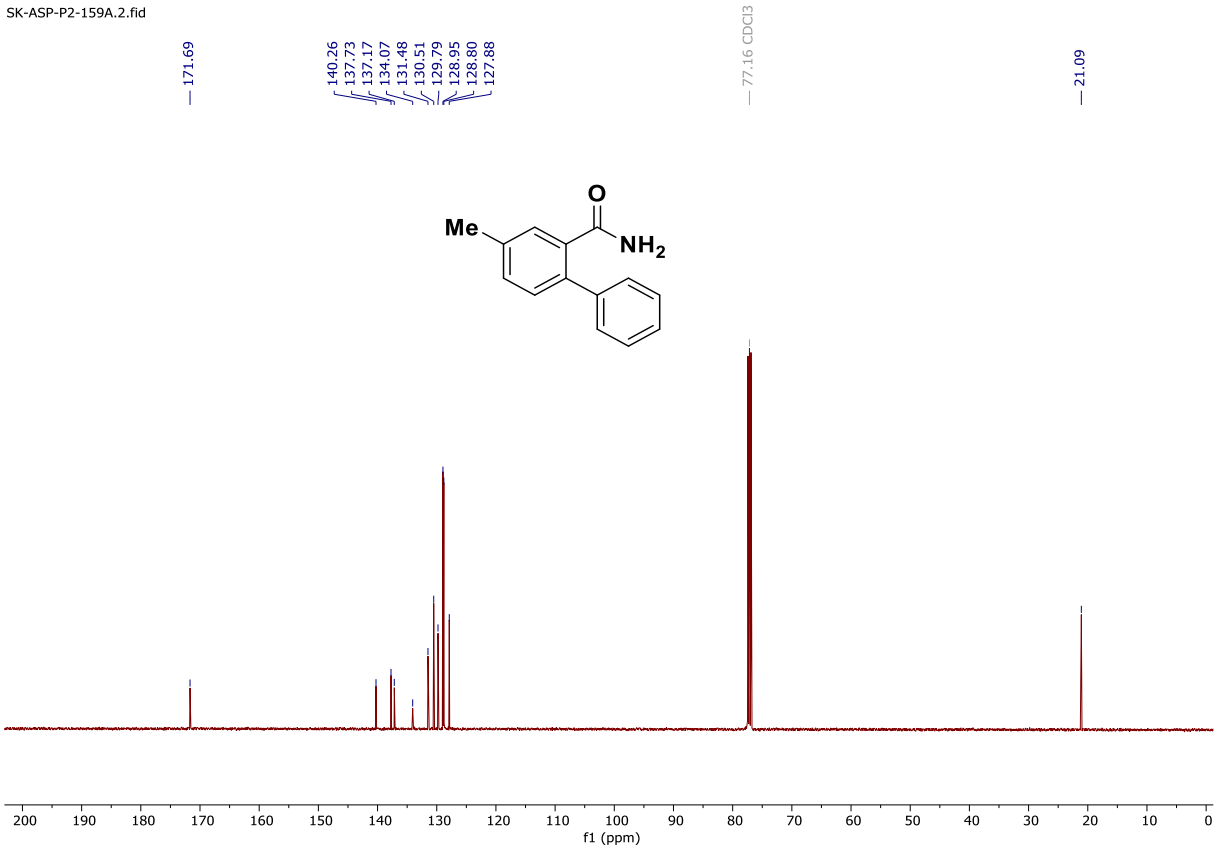
^{13}C{^{1}H} NMR spectrum of I21 in $CDCl_3$ [126 MHz]



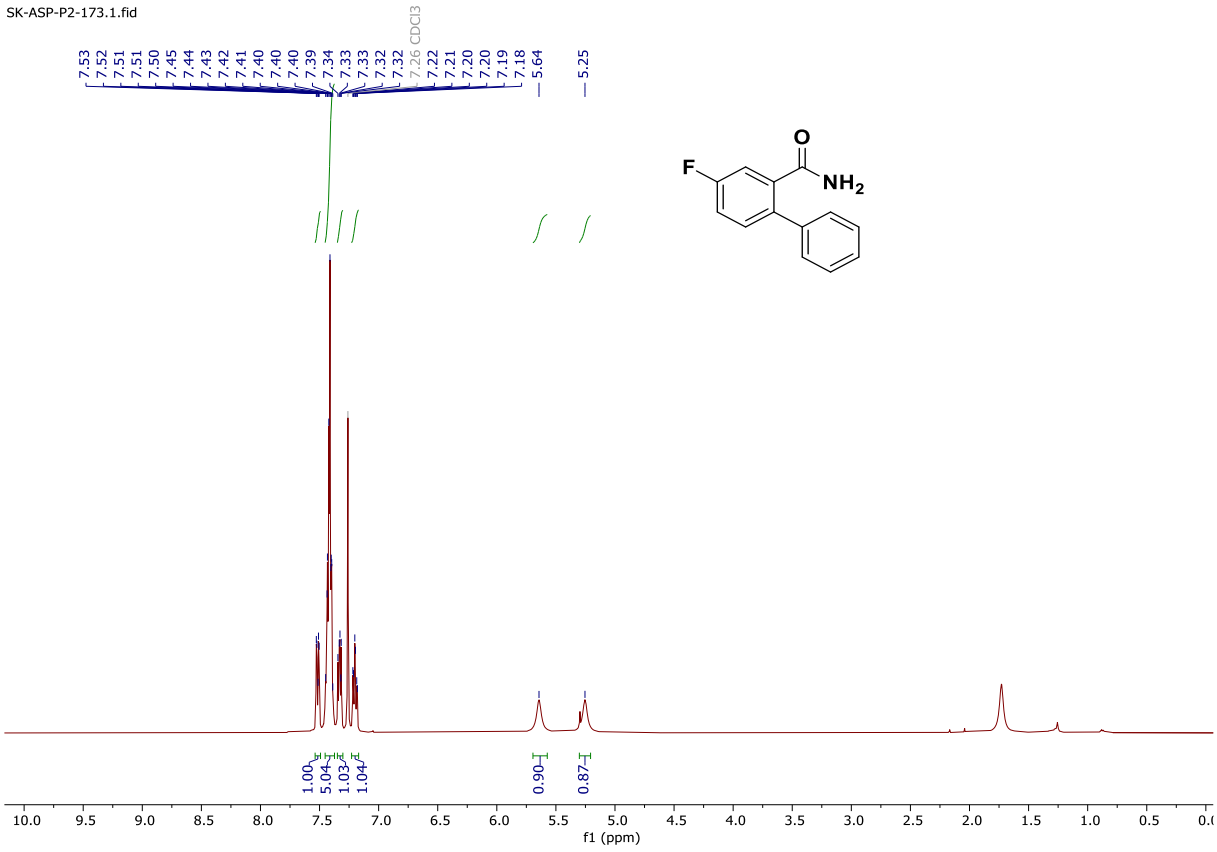
^{1}H NMR spectrum of I22 in $CDCl_3$ [500 MHz]



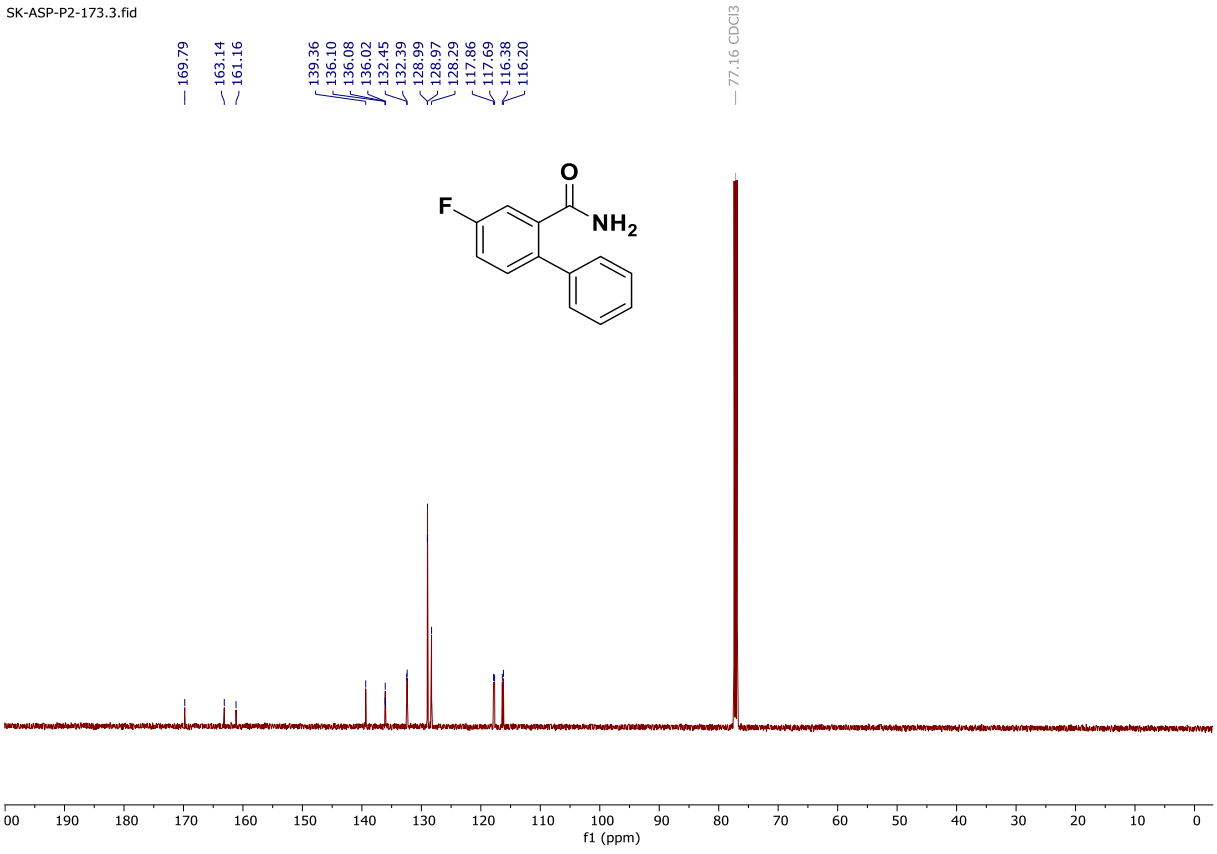
^{13}C{^{1}H} NMR spectrum of I22 in $CDCl_3$ [126 MHz]



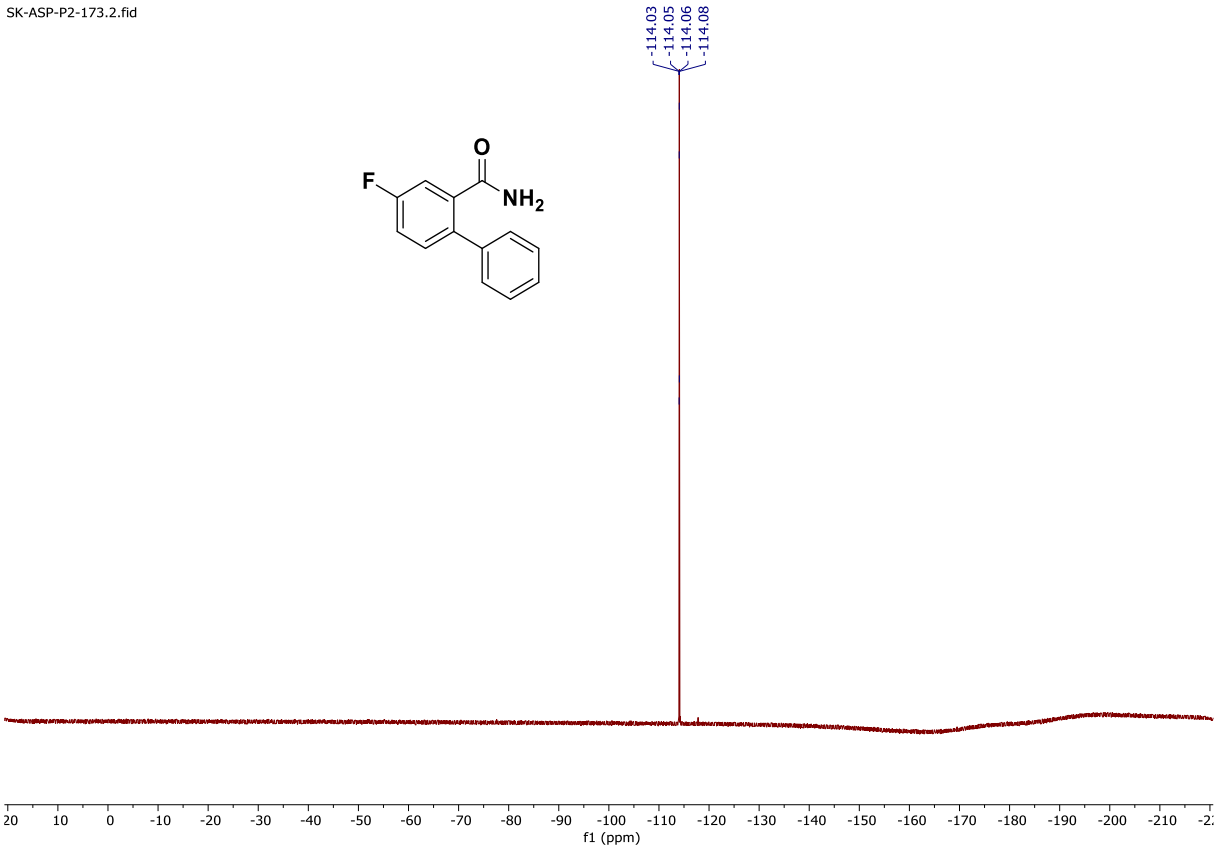
^{1}H NMR spectrum of I23 in $CDCl_3$ [500 MHz]



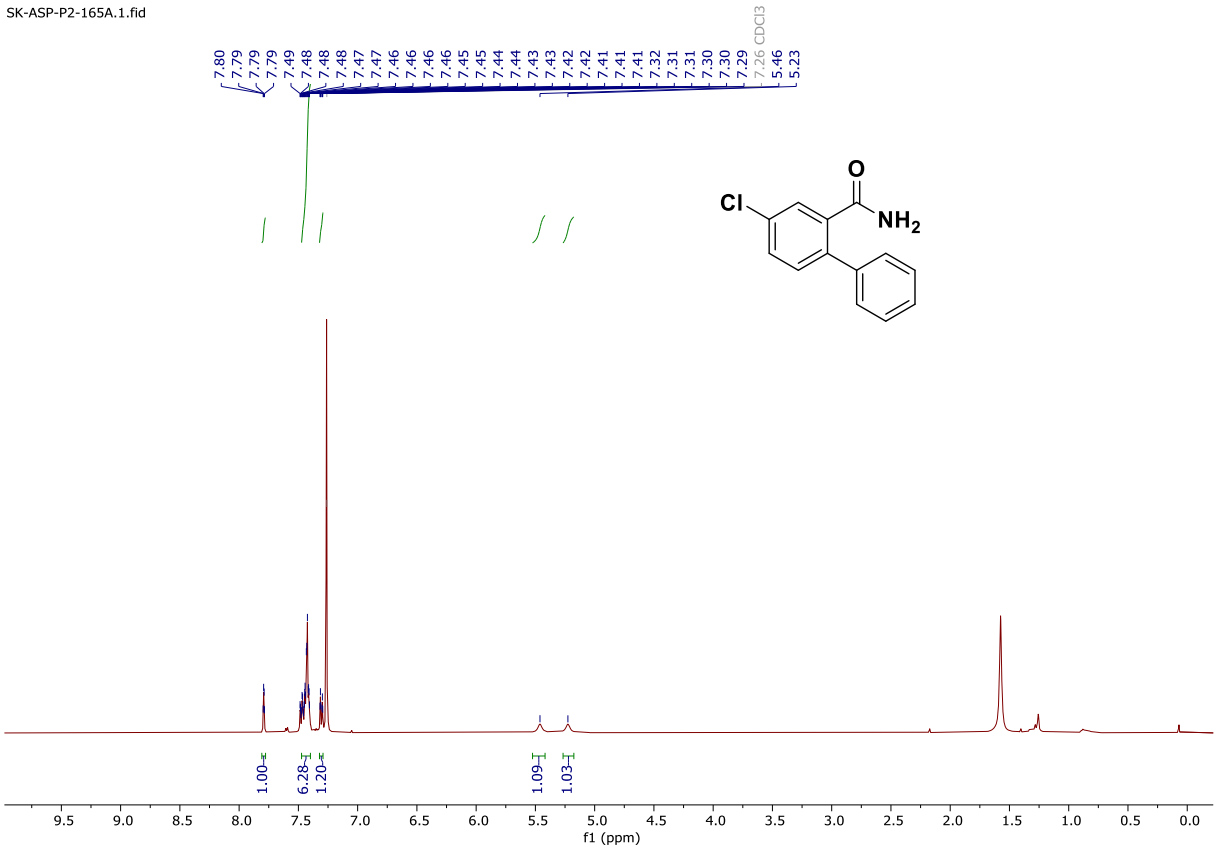
^{13}C{^{1}H} NMR spectrum of I23 in $CDCl_3$ [126 MHz]



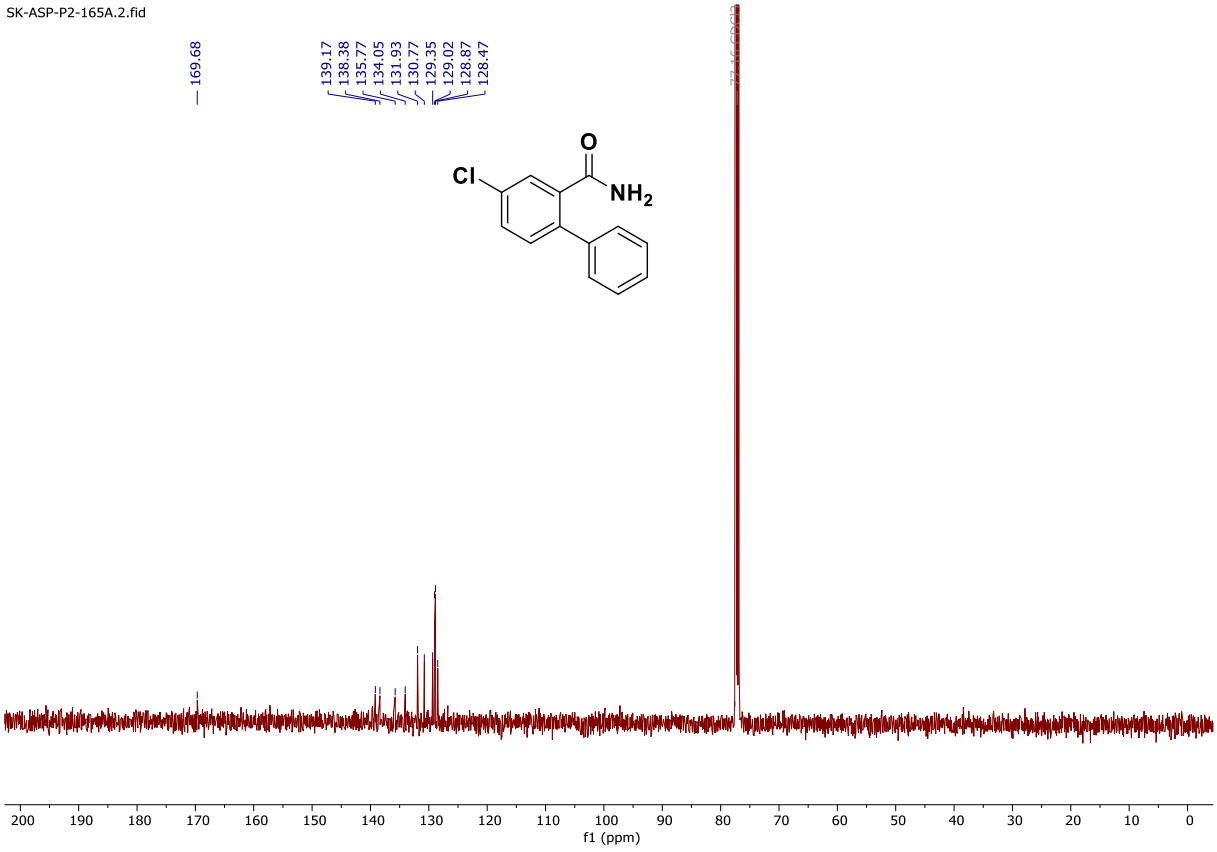
^{19}F NMR spectrum of I23 in $CDCl_3$ [471 MHz]



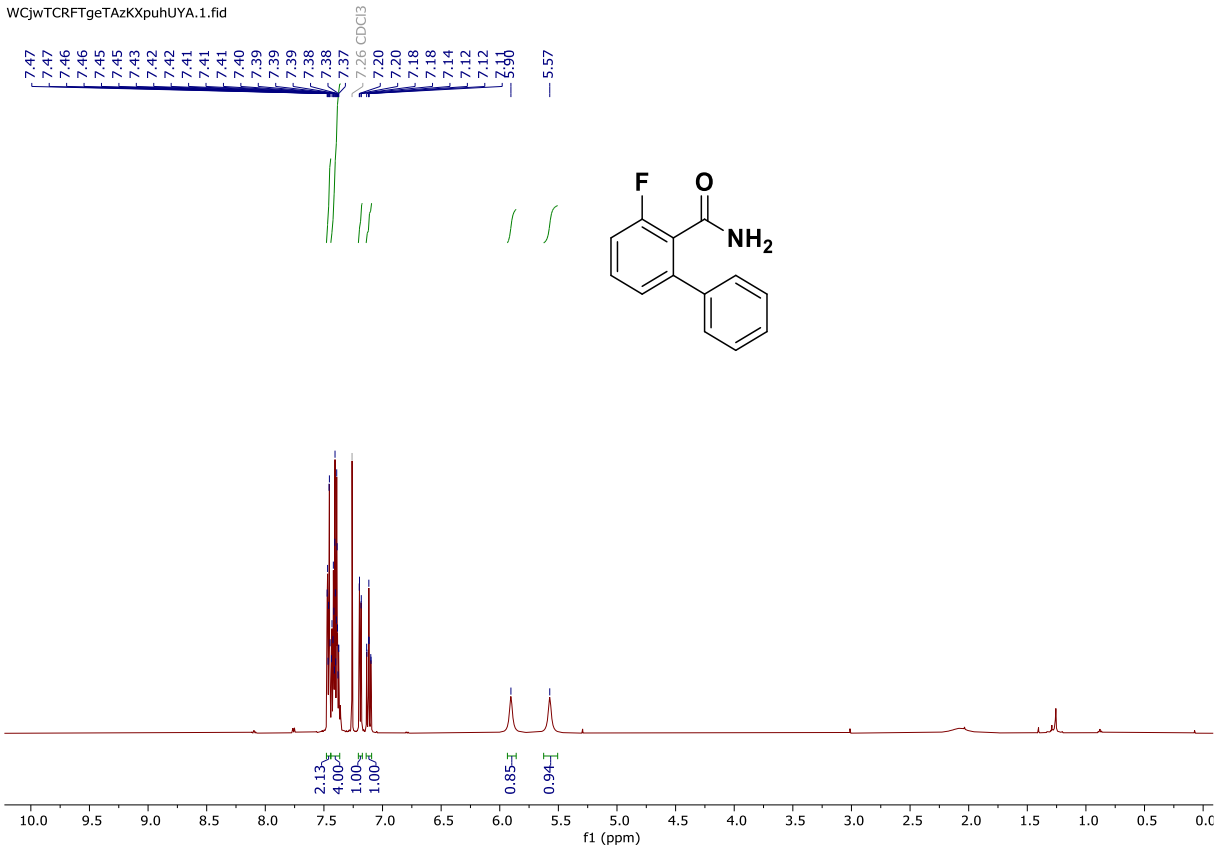
^{1}H NMR spectrum of I24 in $CDCl_3$ [500 MHz]



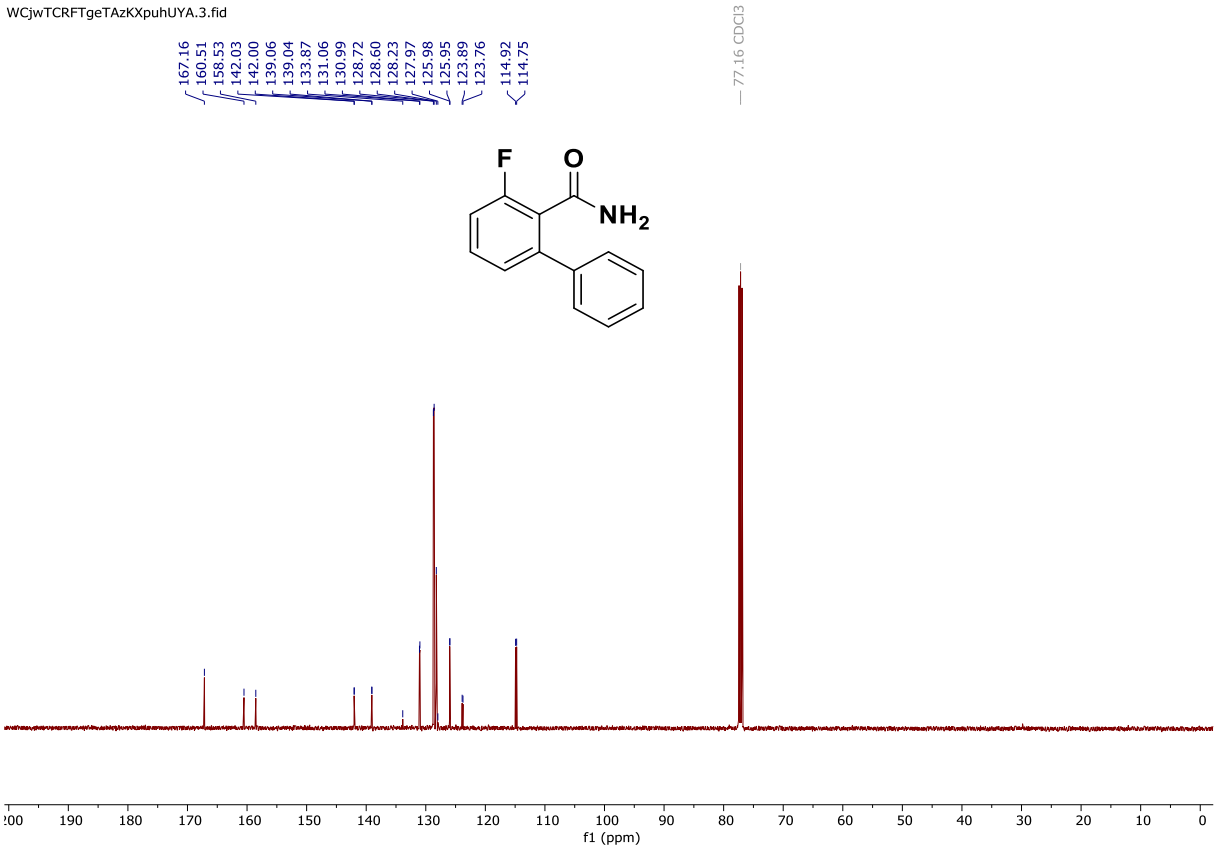
$^{13}C\{^{1}H\}$ NMR spectrum of I24 in $CDCl_3$ [126 MHz]



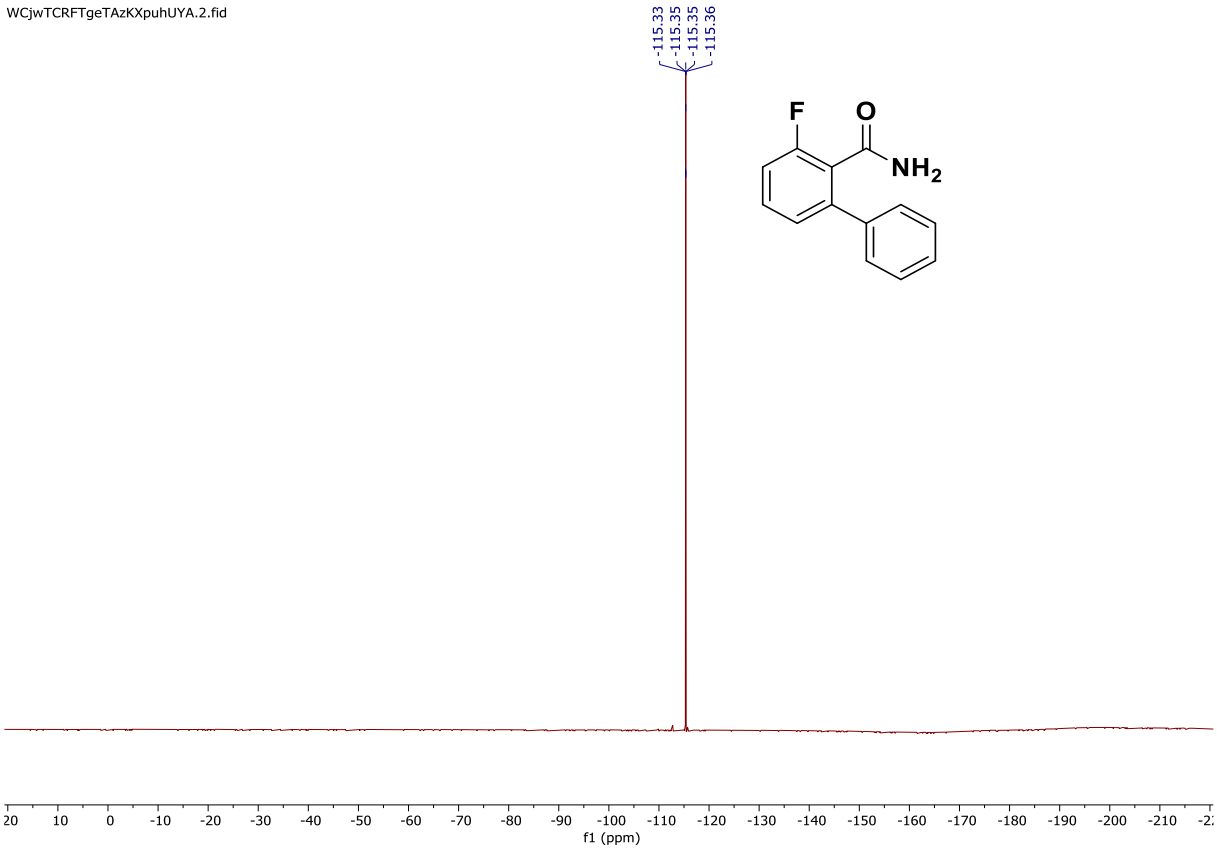
^{1}H NMR spectrum of I25 in $CDCl_3$ [500 MHz]



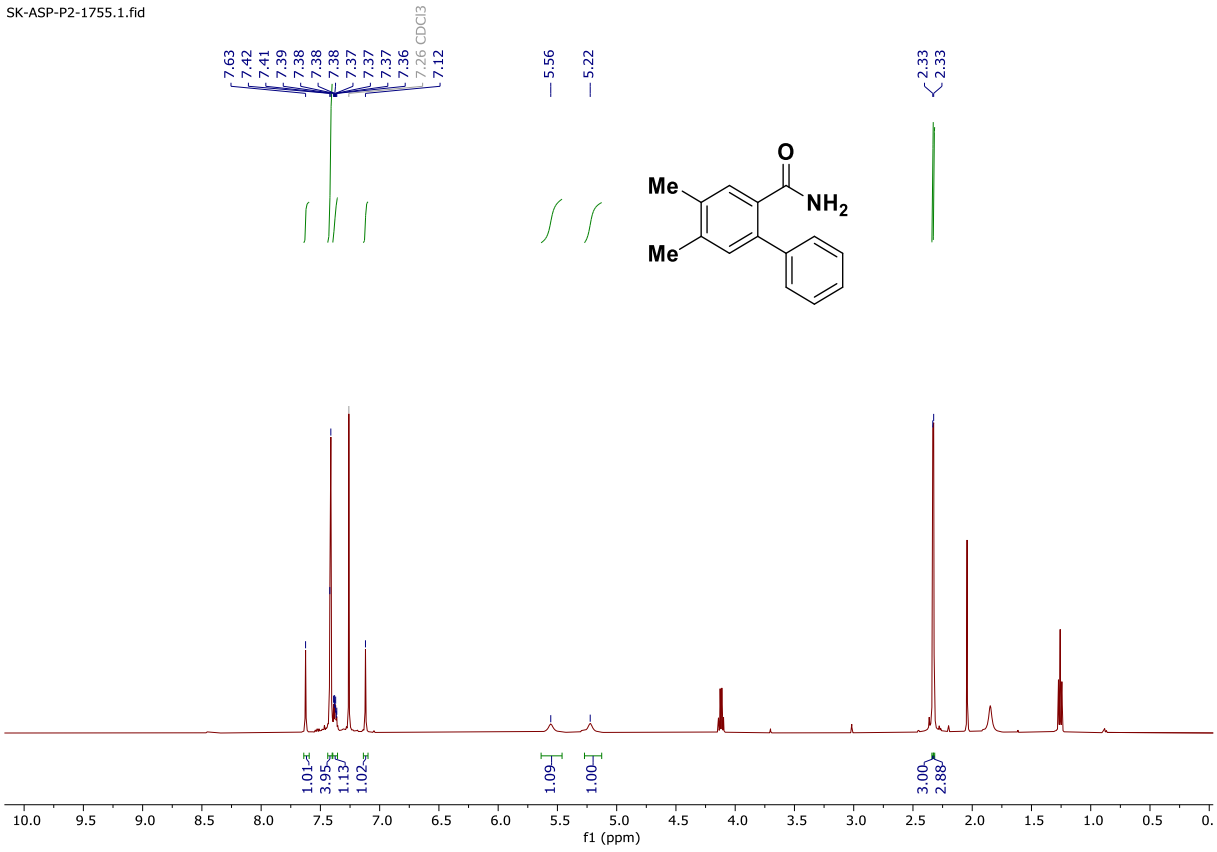
$^{13}C\{^{1}H\}$ NMR spectrum of I25 in $CDCl_3$ [126 MHz]



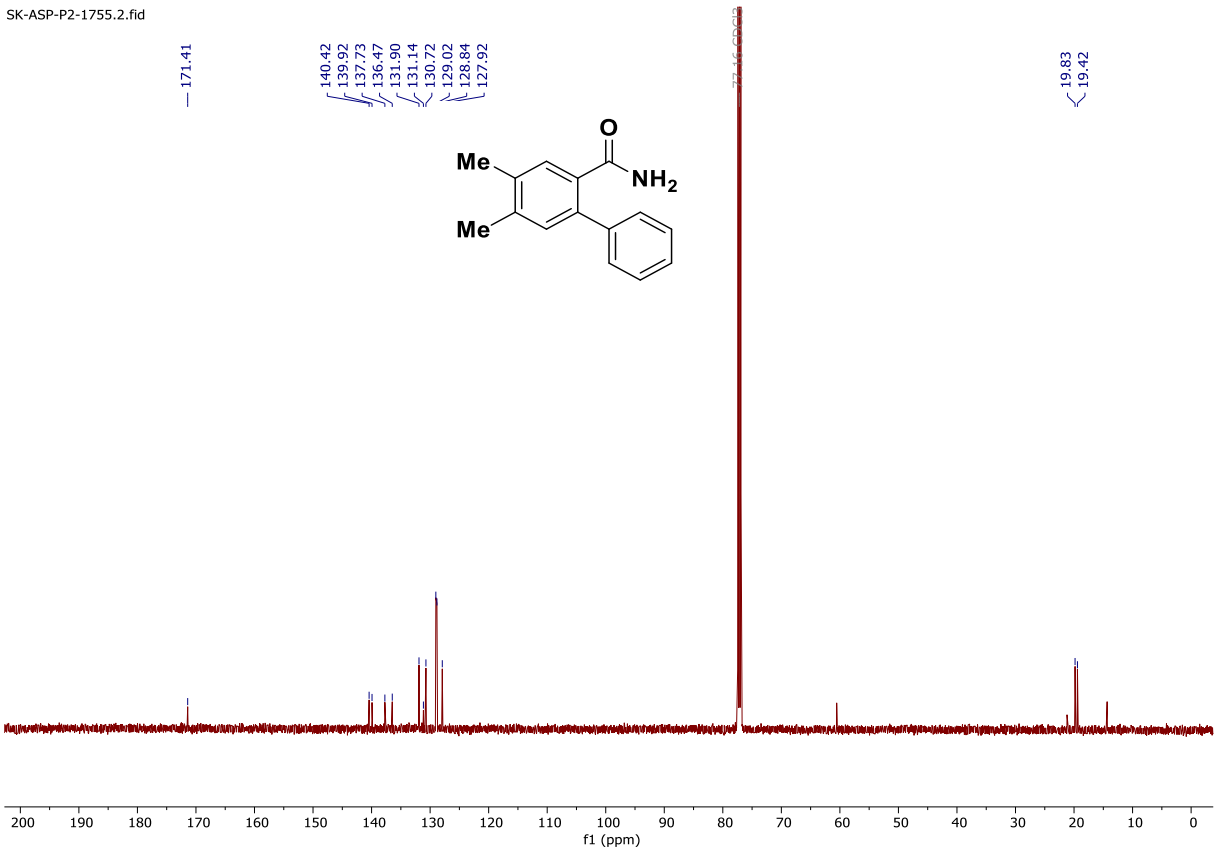
^{19}F NMR spectrum of I25 in $CDCl_3$ [471 MHz]



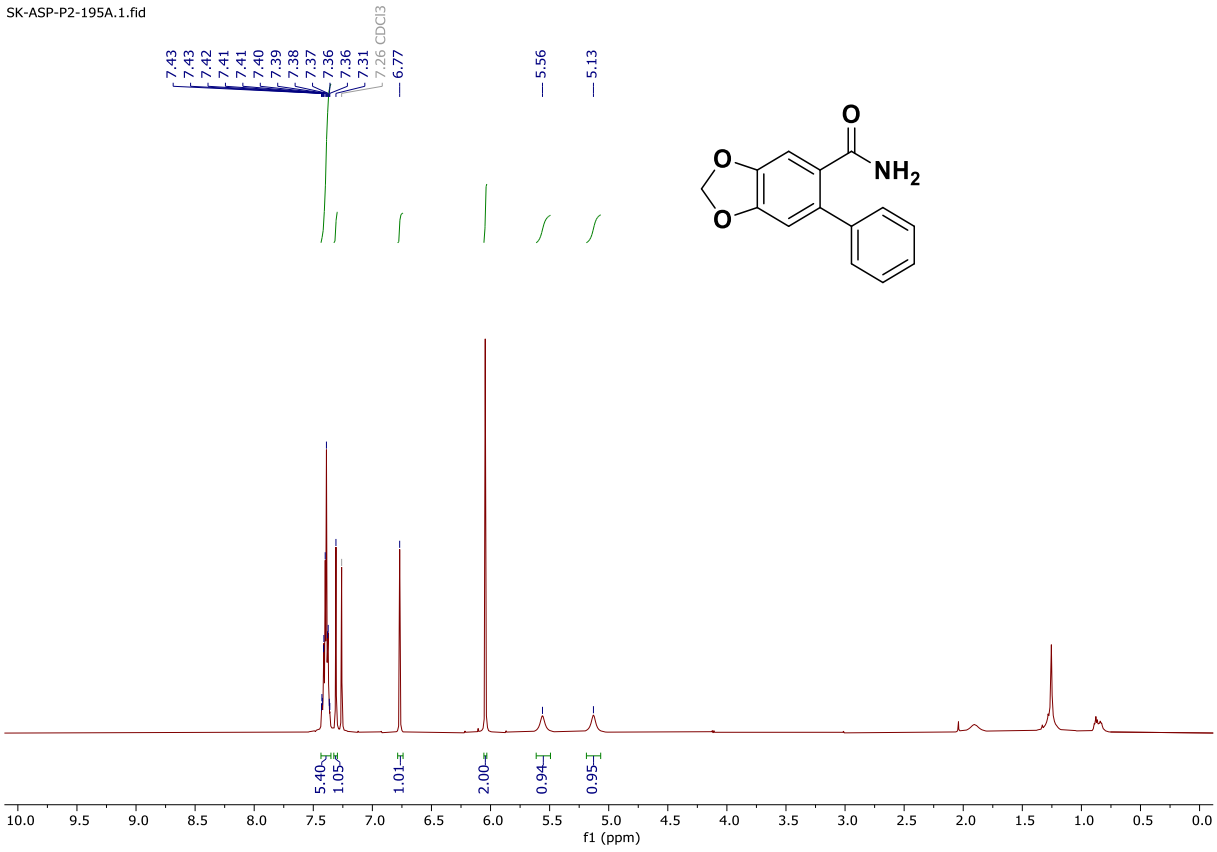
^{1}H NMR spectrum of I26 in $CDCl_3$ [500 MHz]



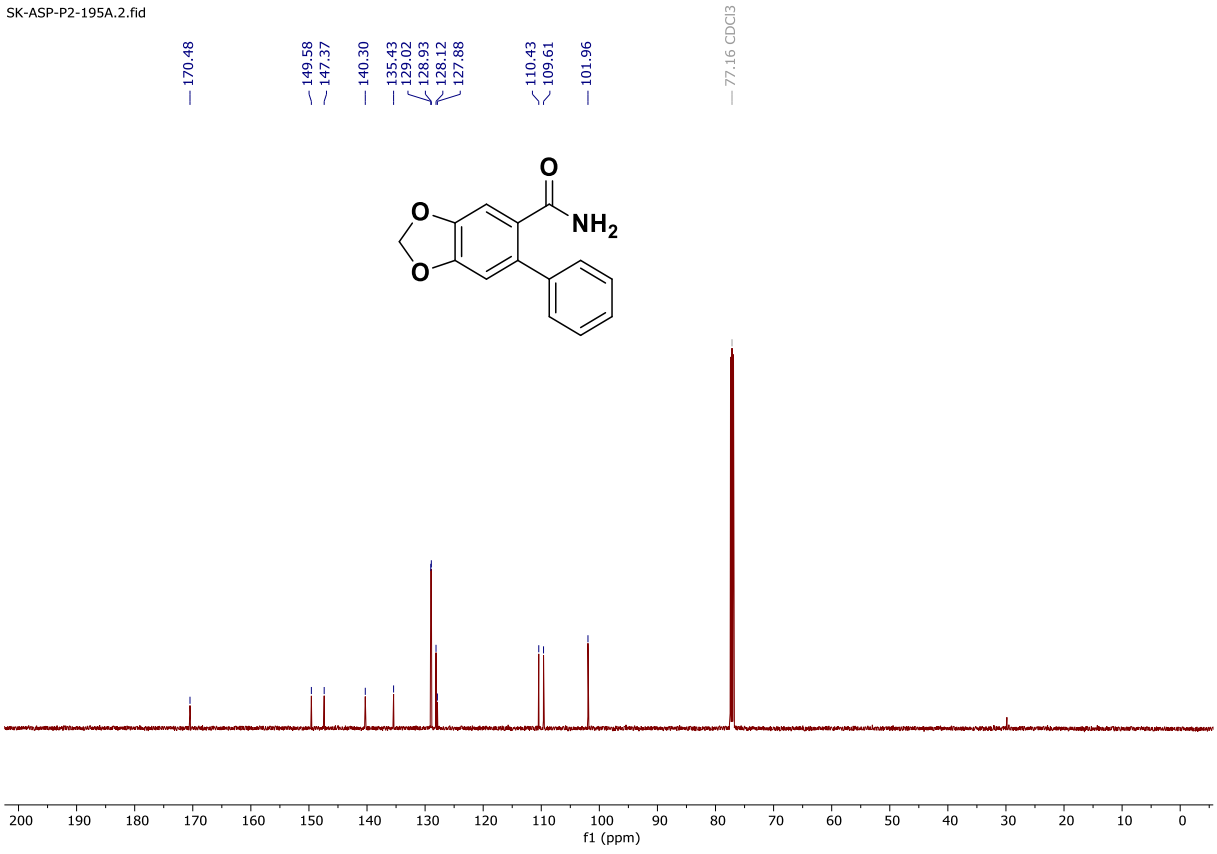
^{13}C{^{1}H} NMR spectrum of I26 in $CDCl_3$ [126 MHz]



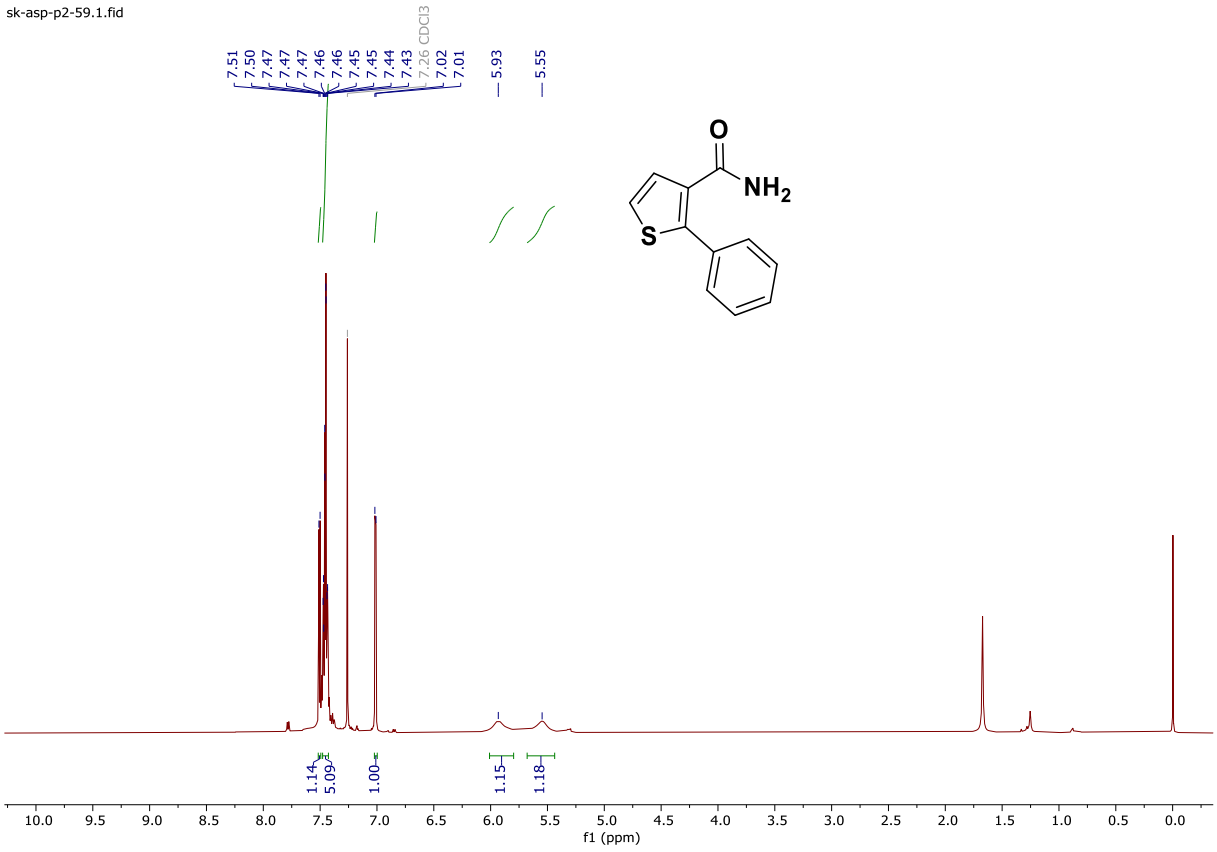
^{1}H NMR spectrum of I27 in $CDCl_3$ [500 MHz]



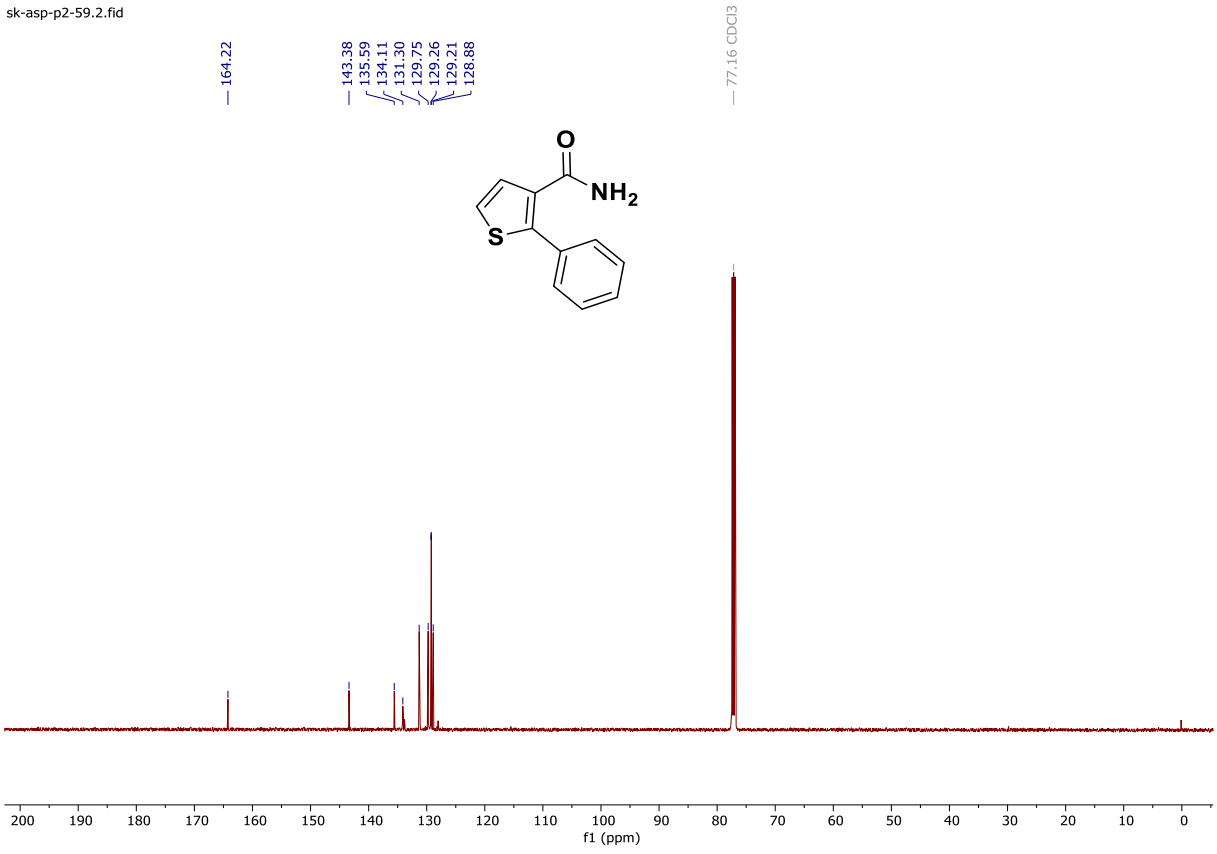
^{13}C{^{1}H} NMR spectrum of I27 in $CDCl_3$ [126 MHz]



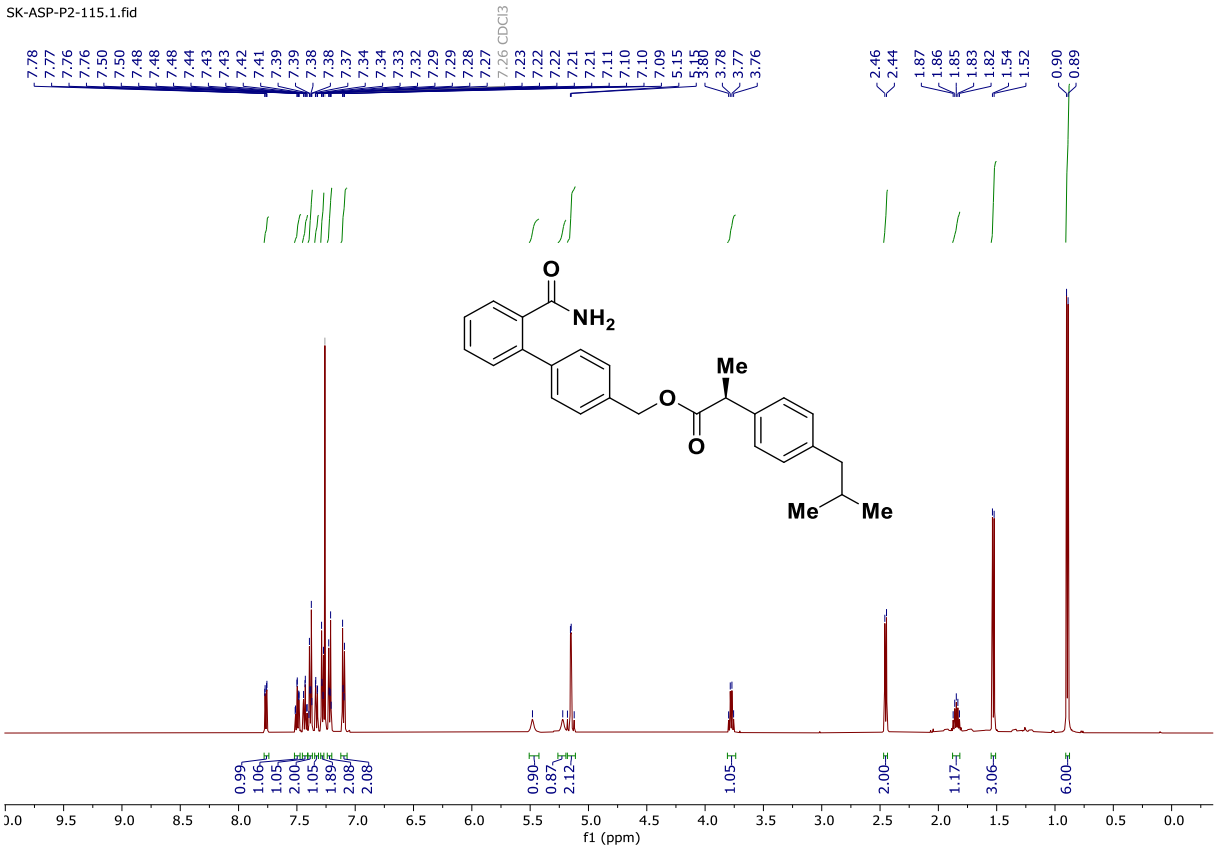
^{1}H NMR spectrum of I28 in $CDCl_3$ [500 MHz]



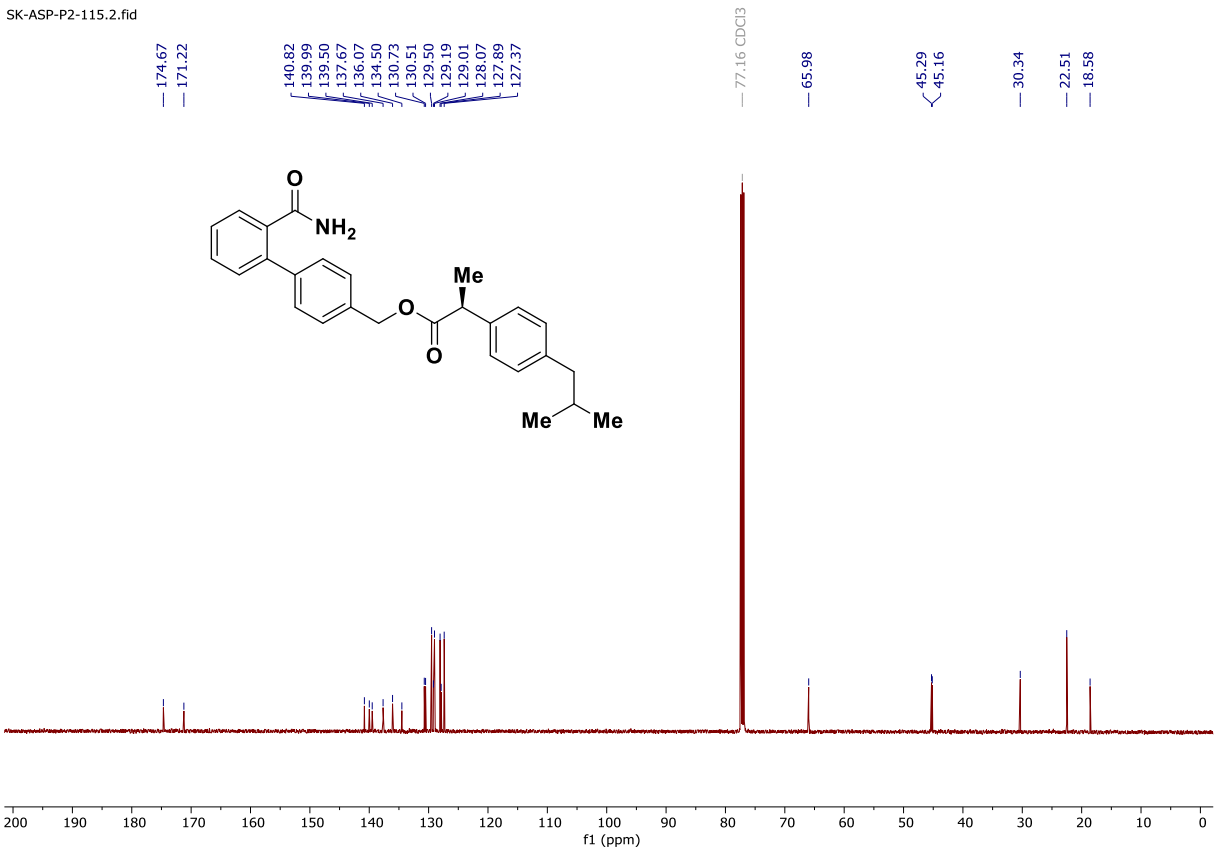
^{13}C{^{1}H} NMR spectrum of I28 in $CDCl_3$ [126 MHz]



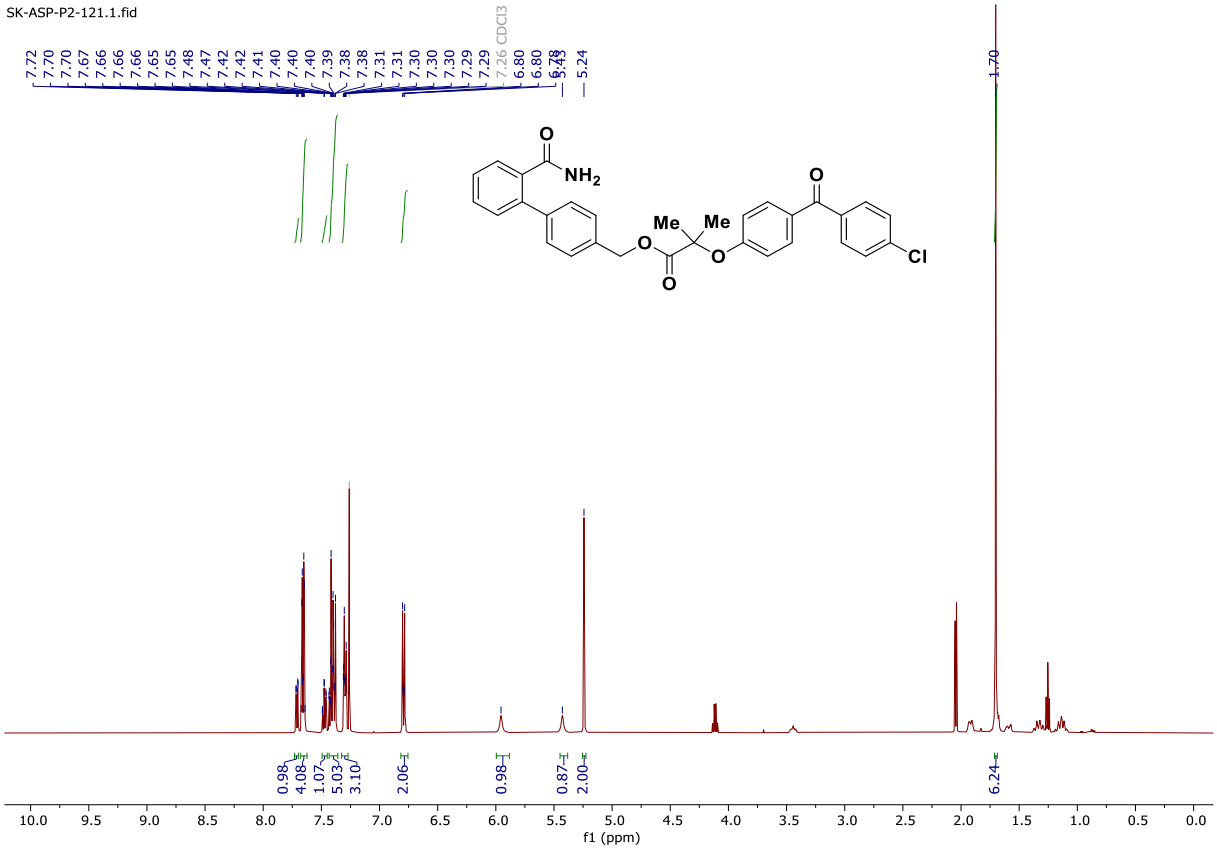
^{1}H NMR spectrum of I29 in $CDCl_3$ [500 MHz]



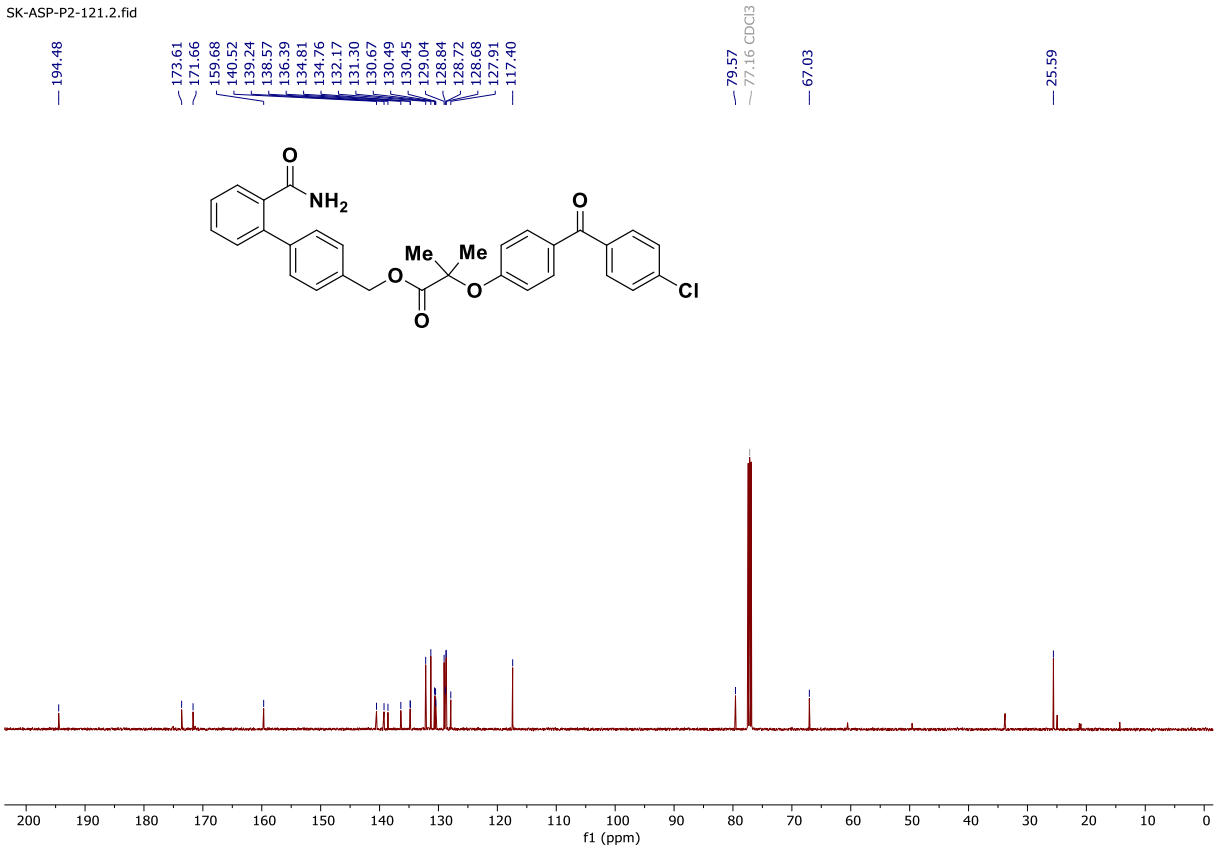
^{13}C{^{1}H} NMR spectrum of I29 in $CDCl_3$ [126 MHz]



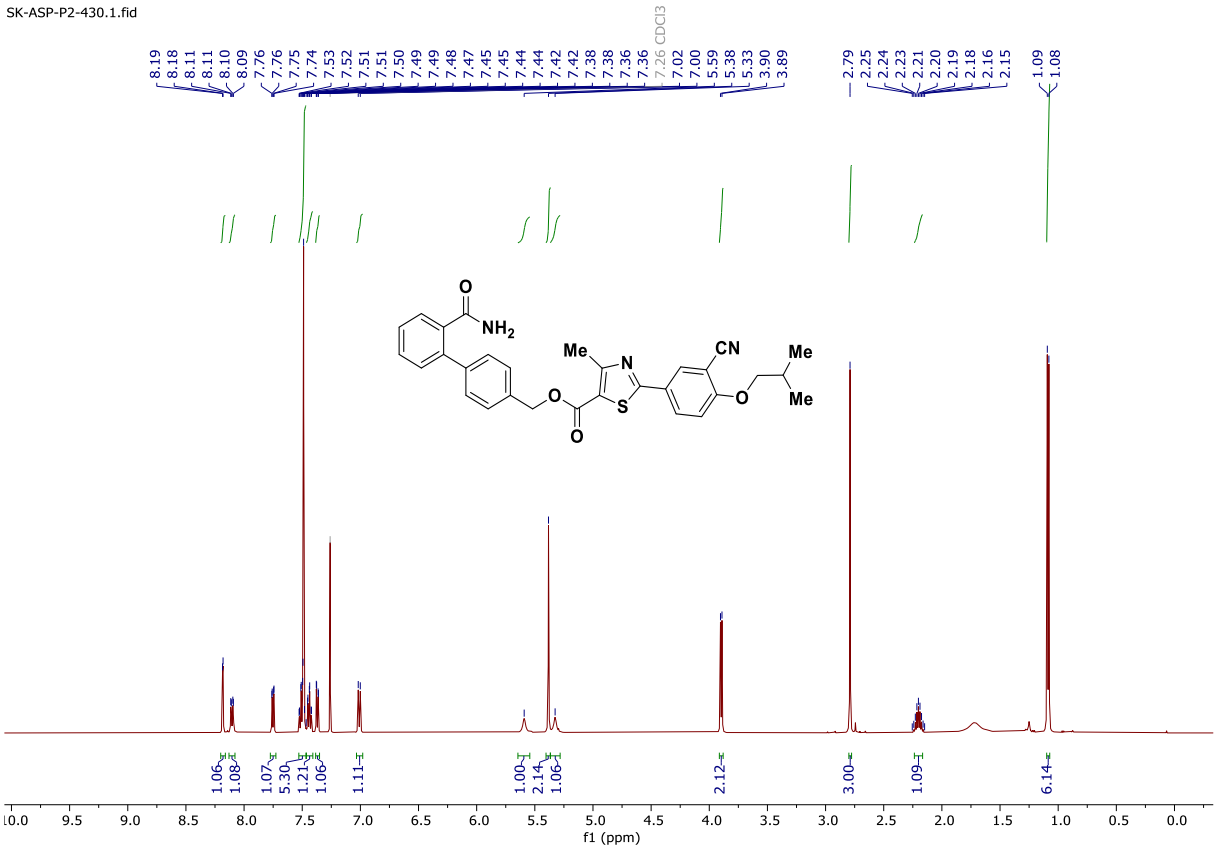
^{1}H NMR spectrum of I30 in $CDCl_3$ [500 MHz]



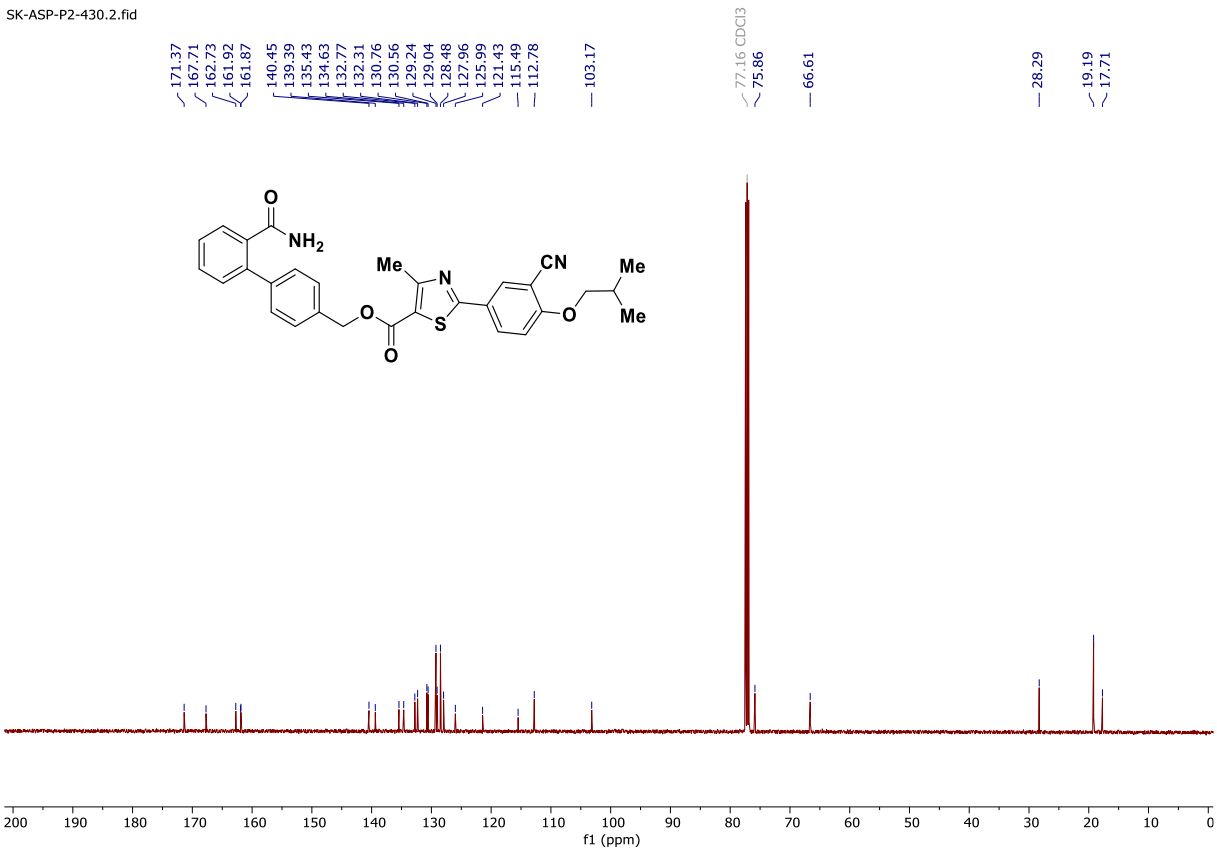
^{13}C{^{1}H} NMR spectrum of I30 in $CDCl_3$ [126 MHz]



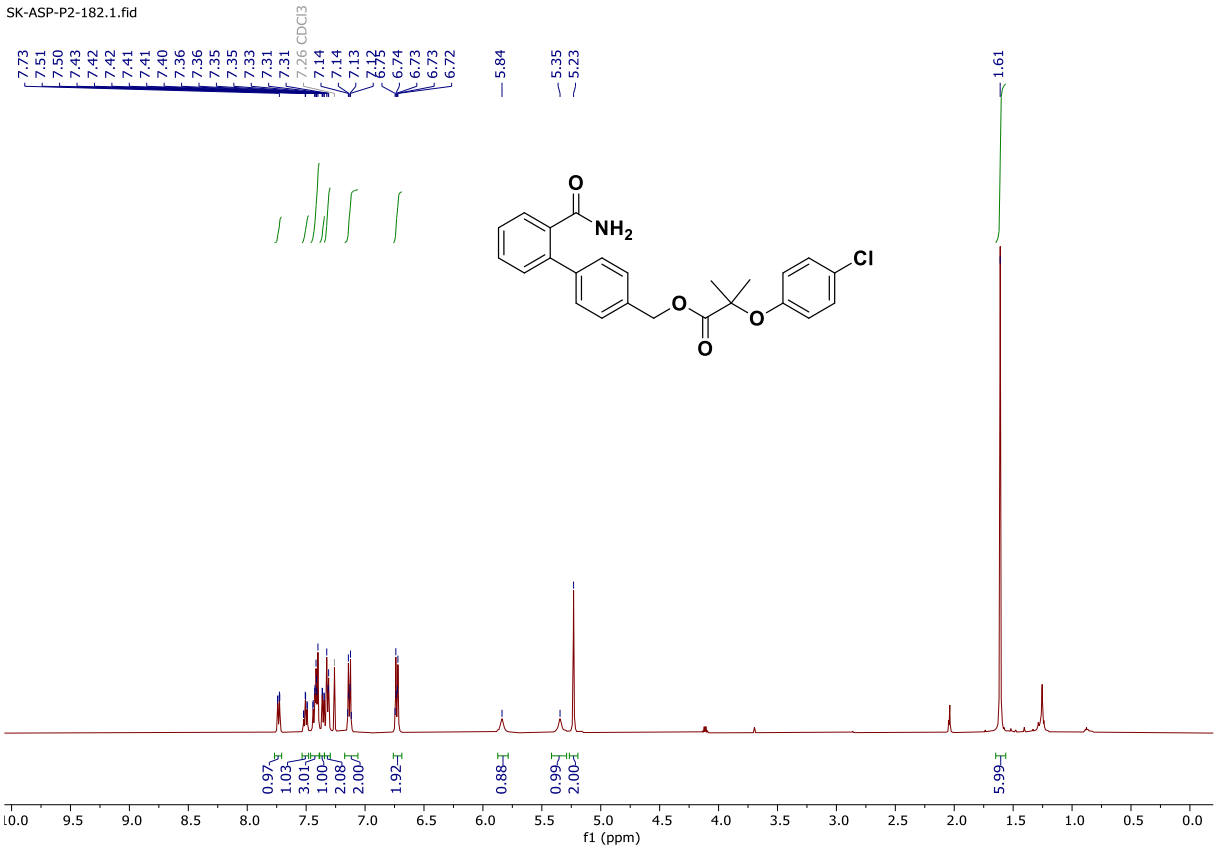
^{1}H NMR spectrum of I31 in $CDCl_3$ [500 MHz]



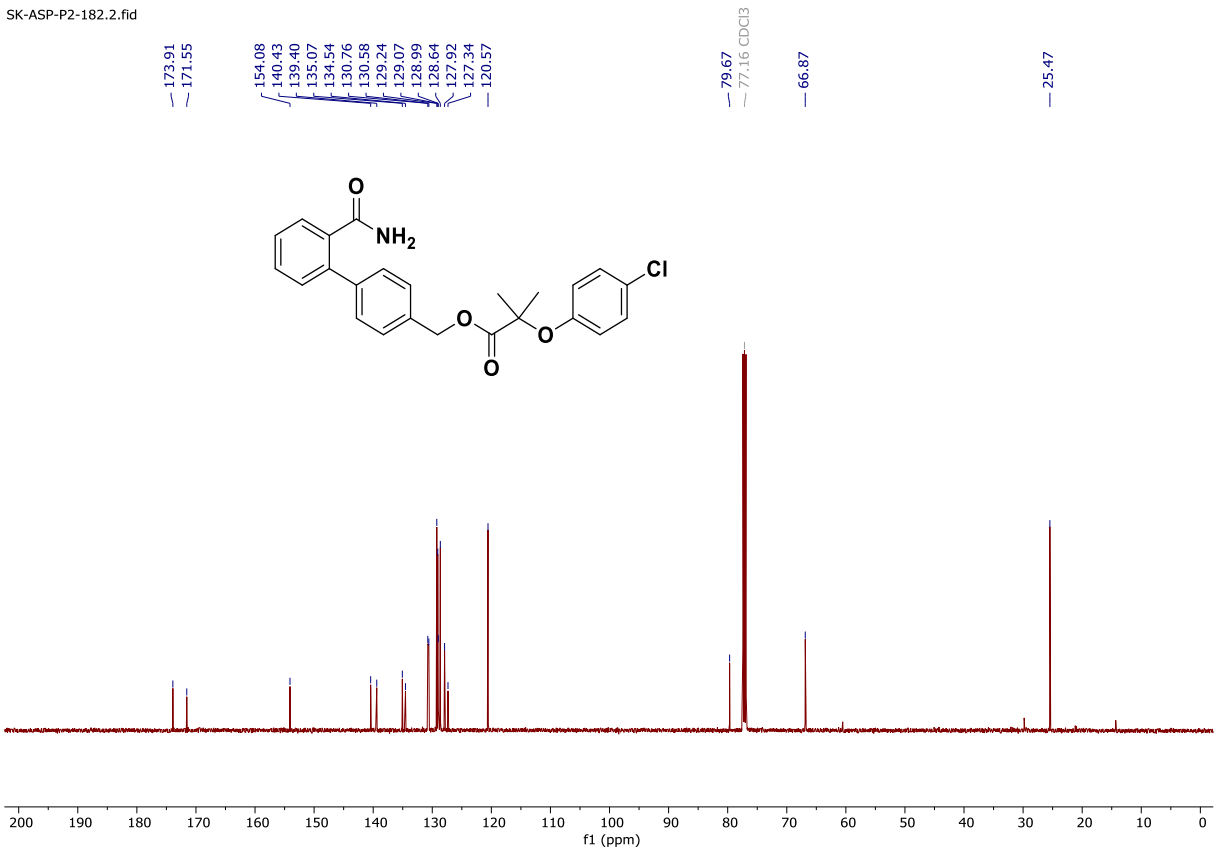
$^{13}C\{^{1}H\}$ NMR spectrum of I31 in $CDCl_3$ [126 MHz]



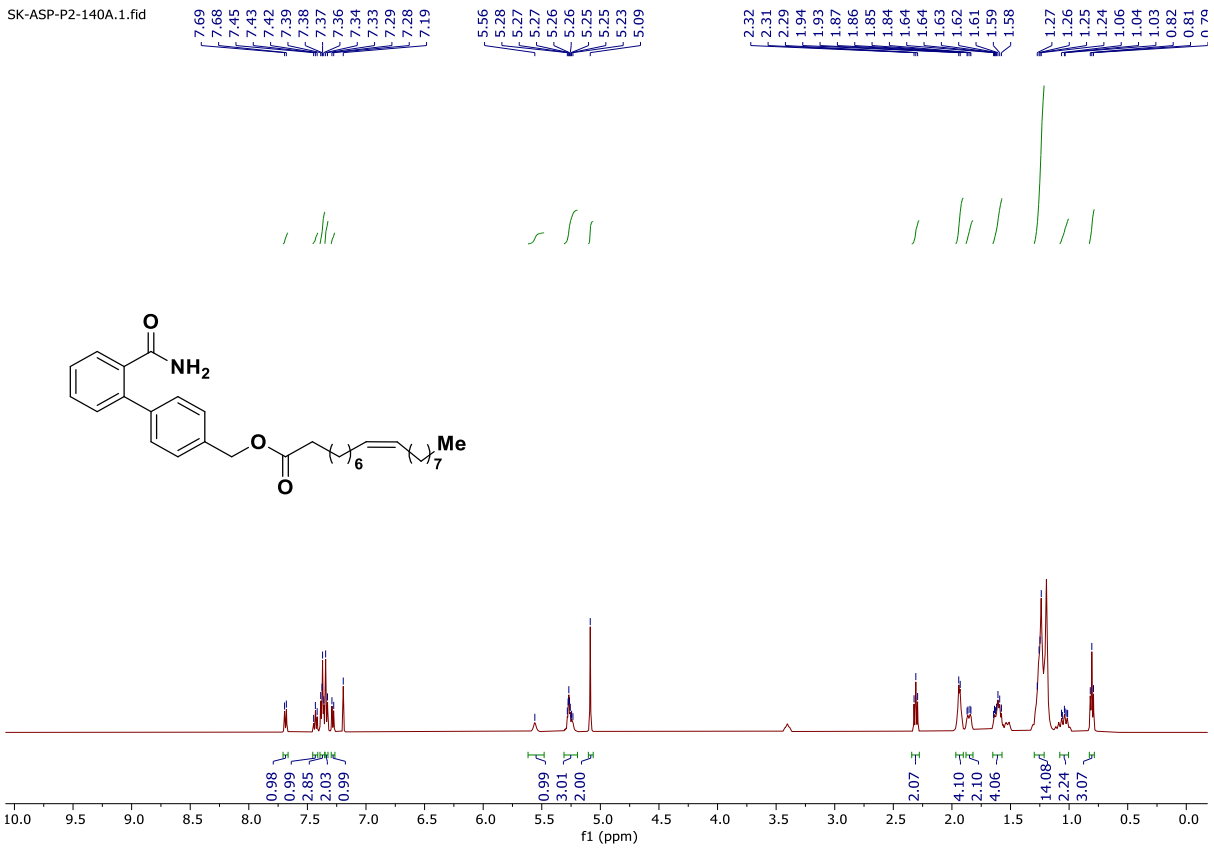
^{1}H NMR spectrum of I32 in $CDCl_3$ [500 MHz]



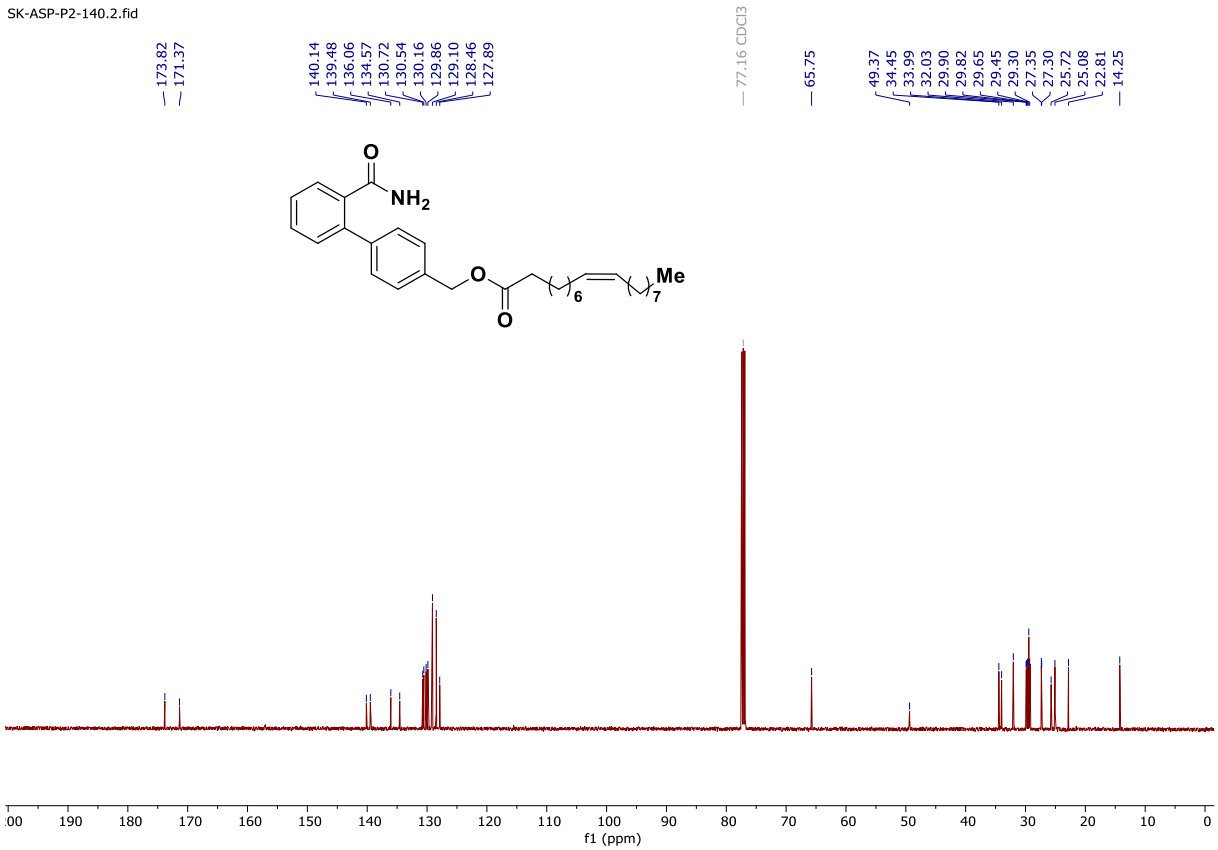
^{13}C{^{1}H} NMR spectrum of I32 in $CDCl_3$ [126 MHz]



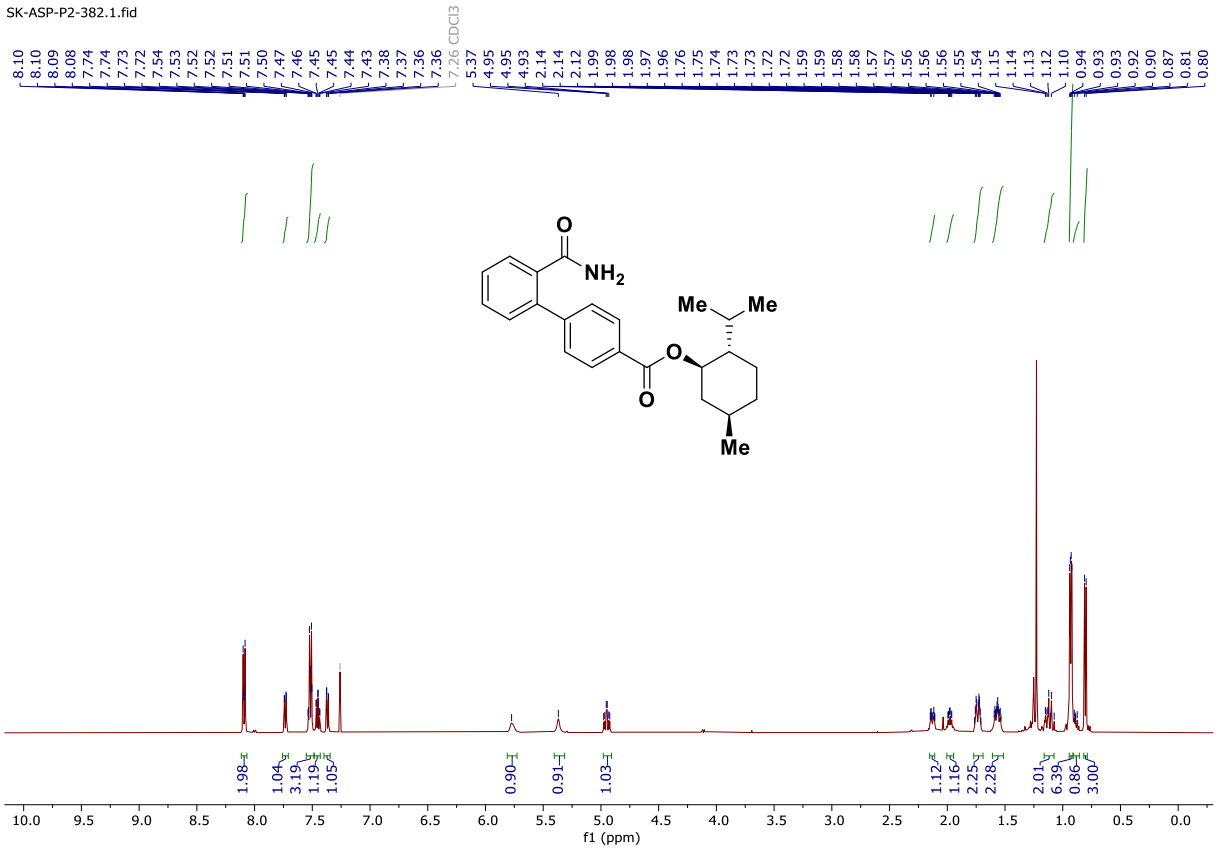
^{1}H NMR spectrum of I33 in $CDCl_3$ [500 MHz]



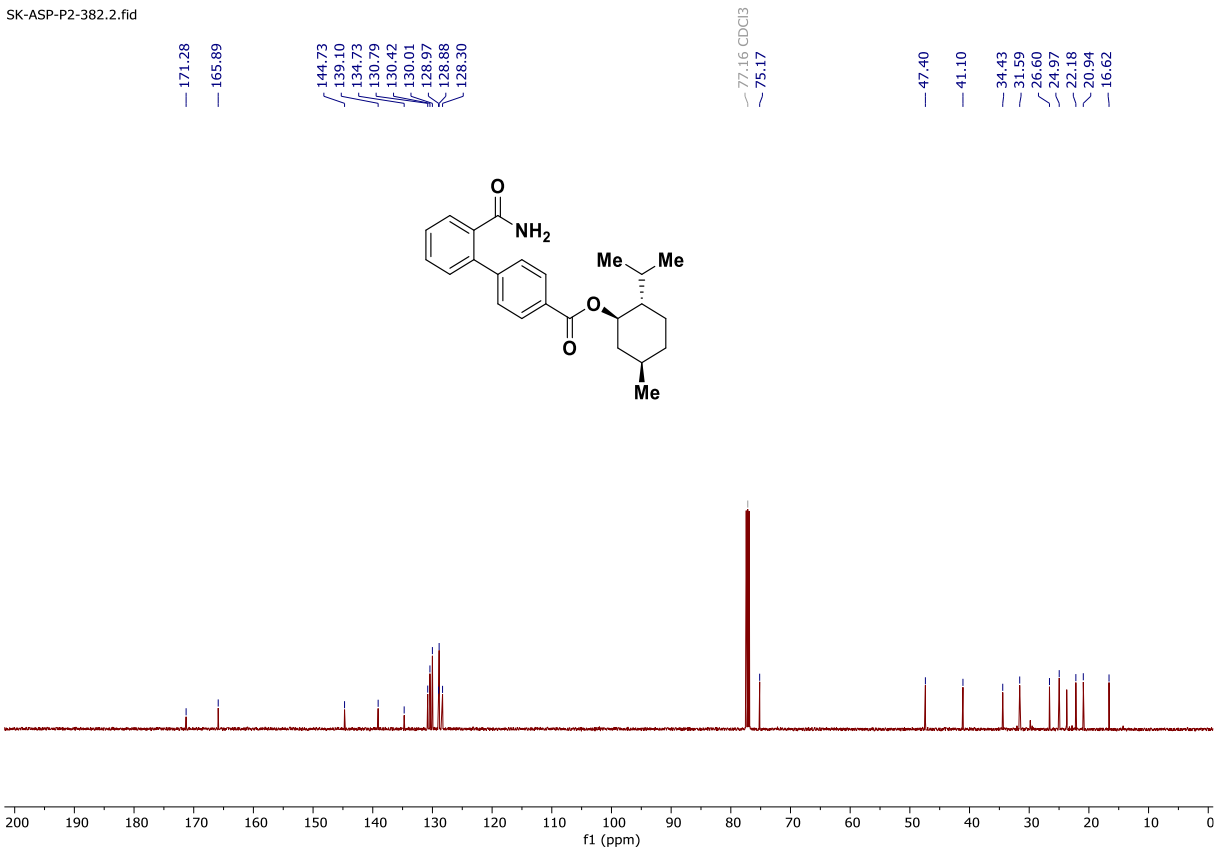
$^{13}C\{^{1}H\}$ NMR spectrum of I33 in $CDCl_3$ [126 MHz]



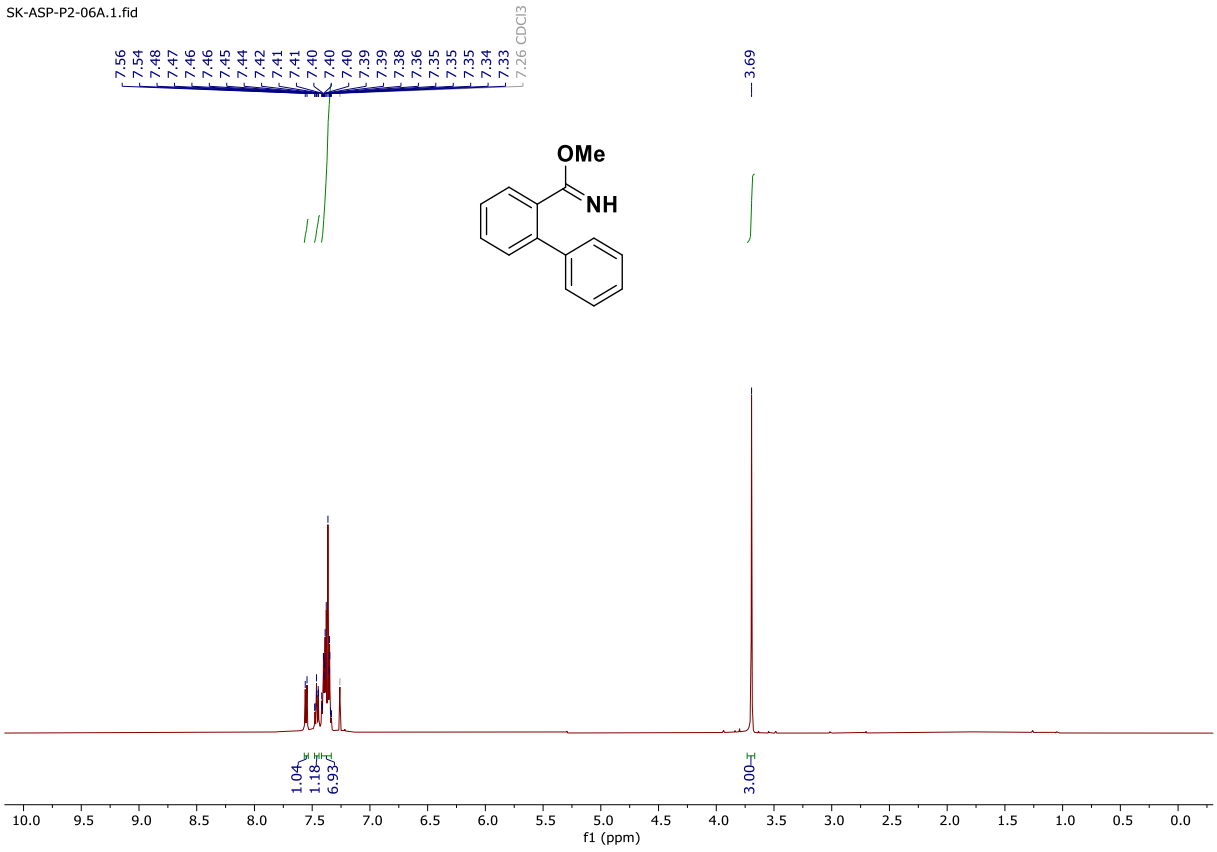
^{1}H NMR spectrum of I34 in $CDCl_3$ [500 MHz]



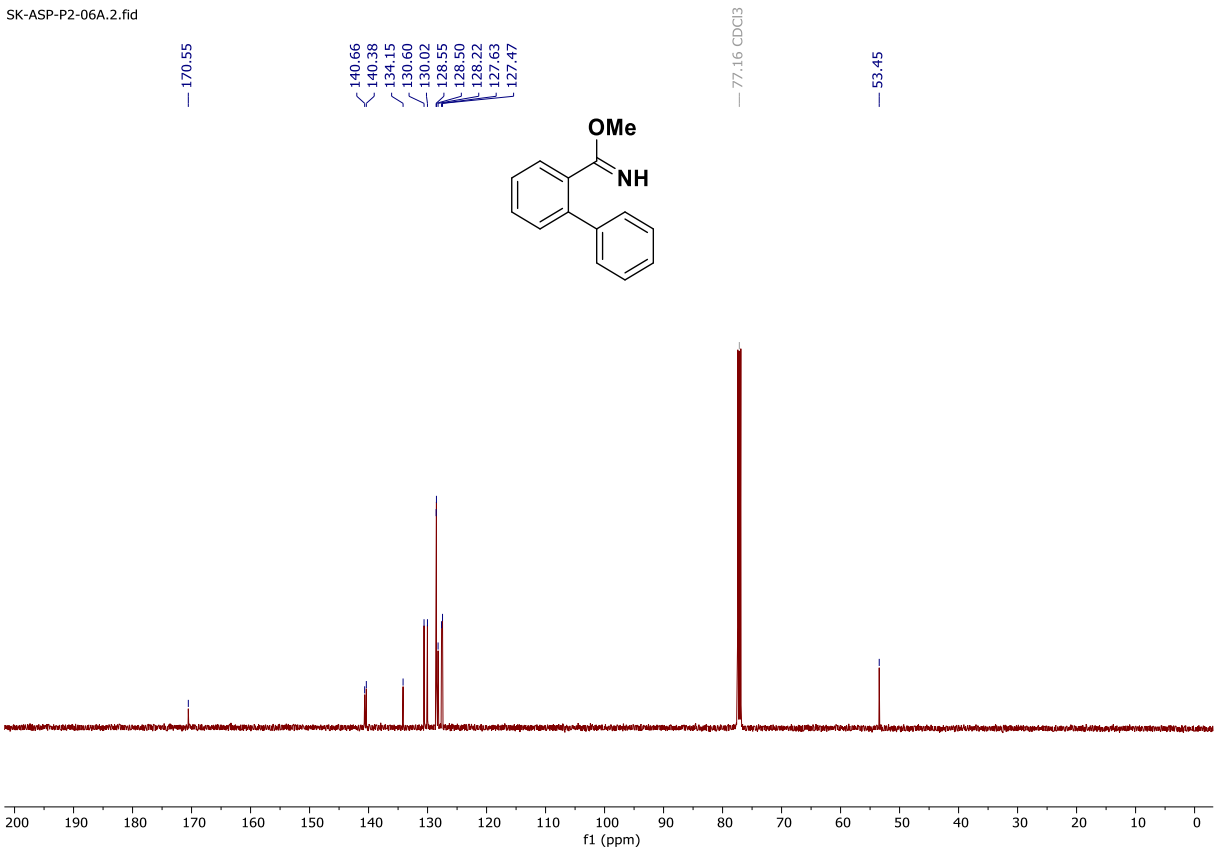
^{13}C{^{1}H} NMR spectrum of I34 in $CDCl_3$ [126 MHz]



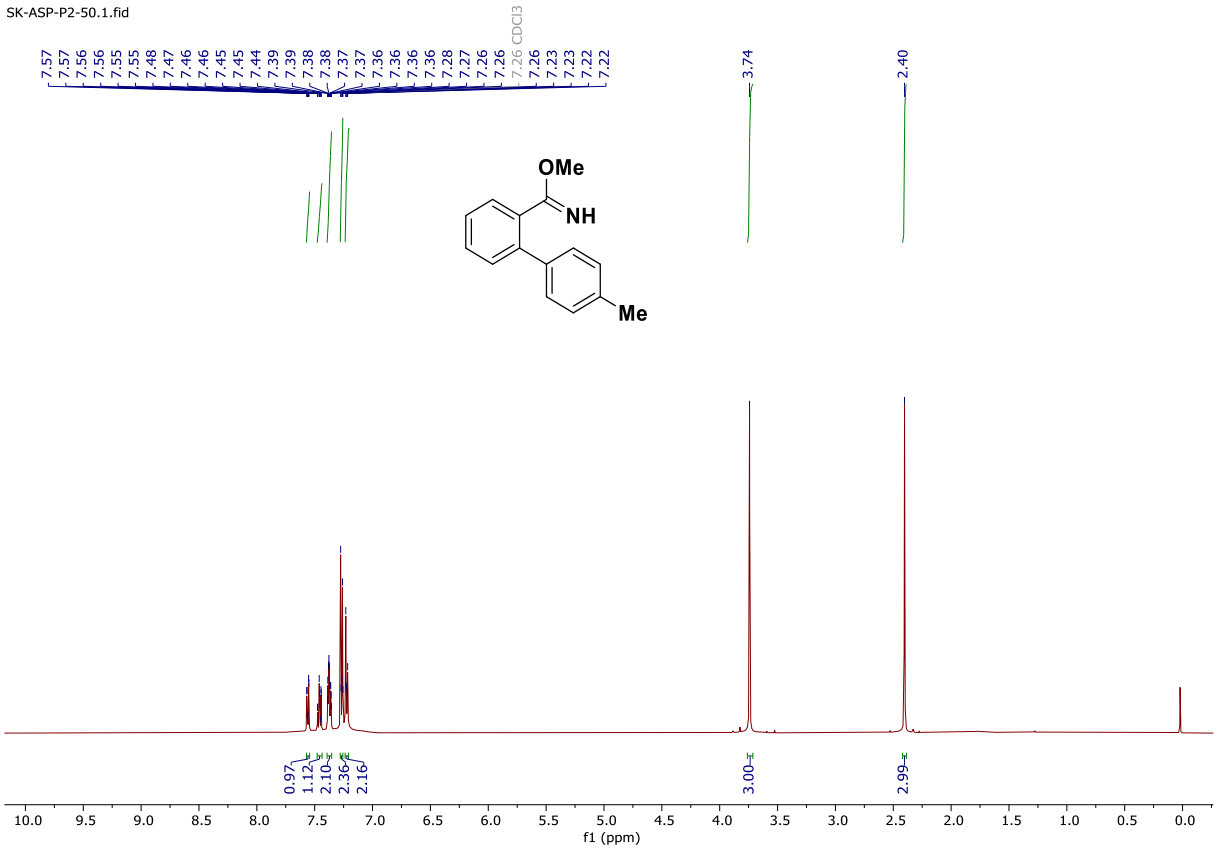
^{1}H NMR spectrum of 1a in $CDCl_3$ [500 MHz]



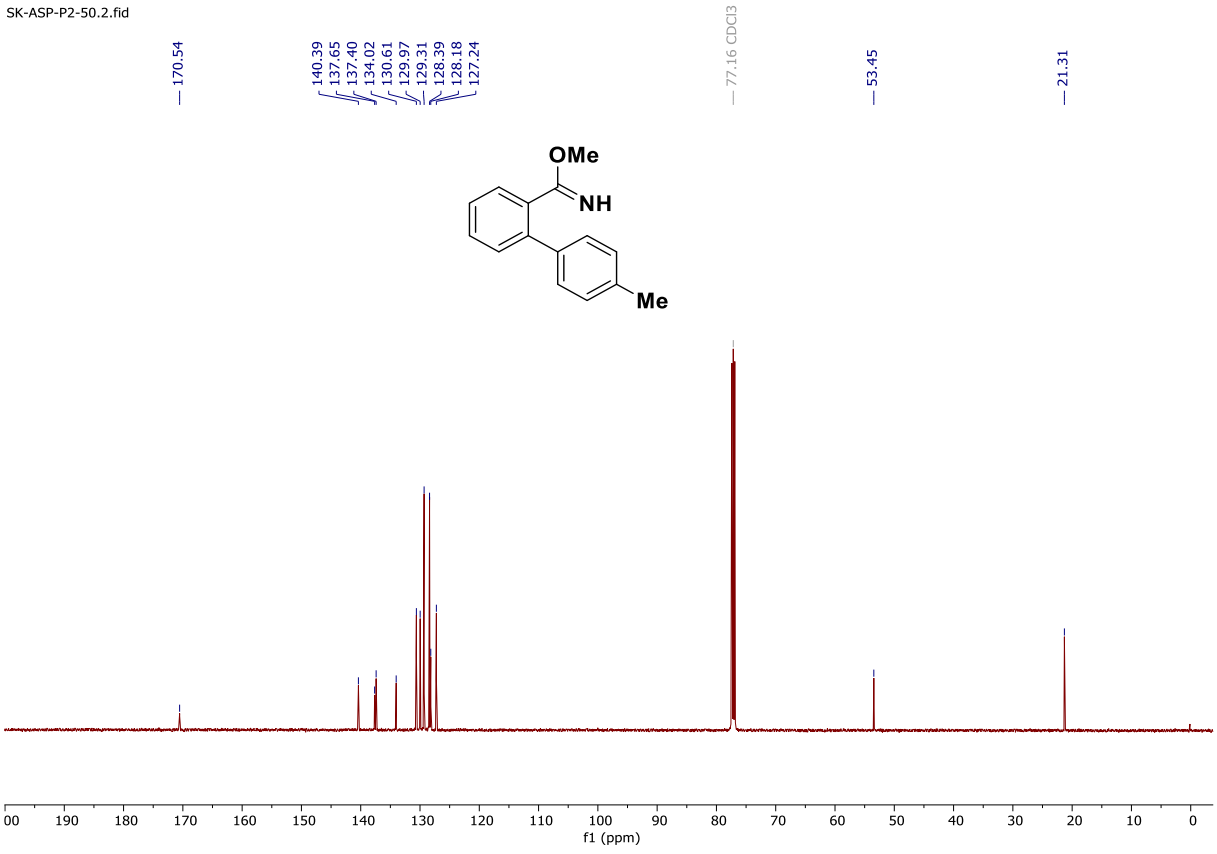
^{13}C{^{1}H} NMR spectrum of 1a in $CDCl_3$ [126 MHz]



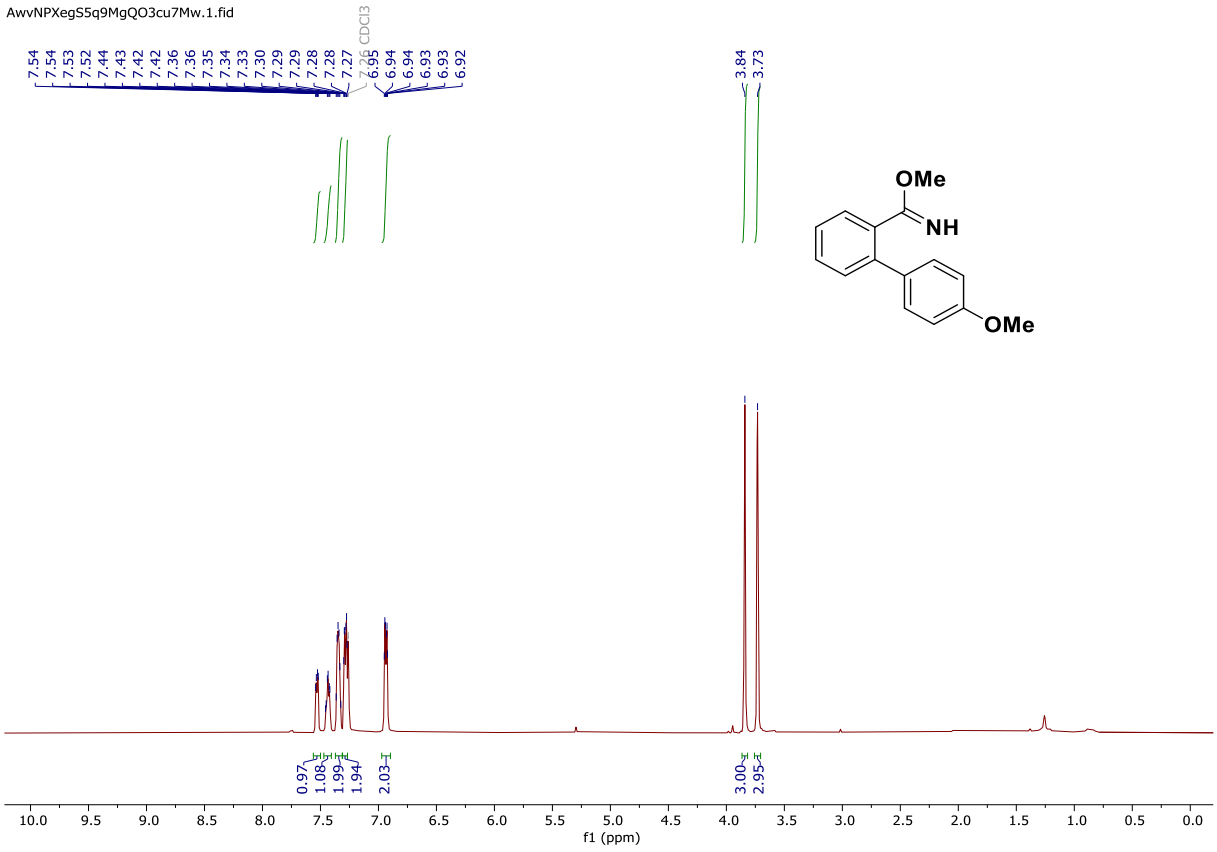
^{1}H NMR spectrum of 1b in $CDCl_3$ [500 MHz]



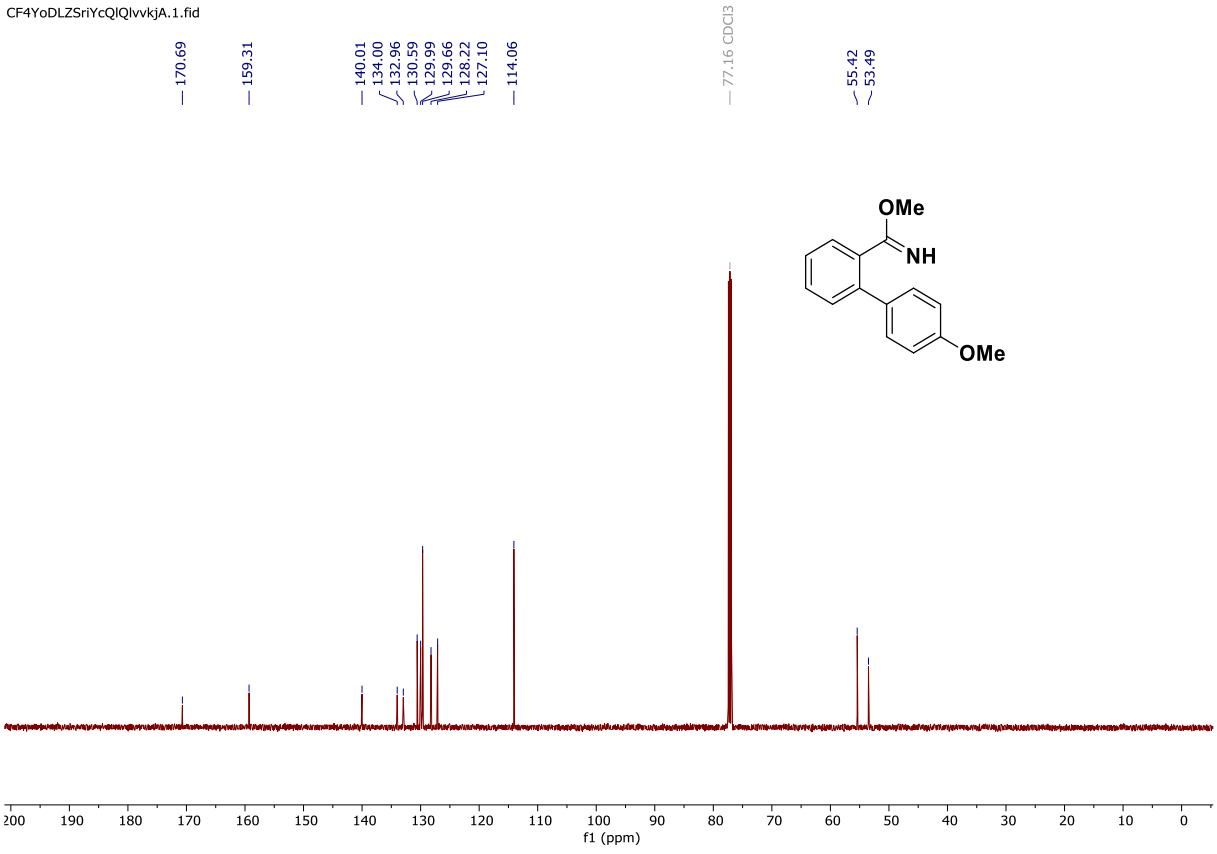
^{13}C{^{1}H} NMR spectrum of 1b in $CDCl_3$ [126 MHz]



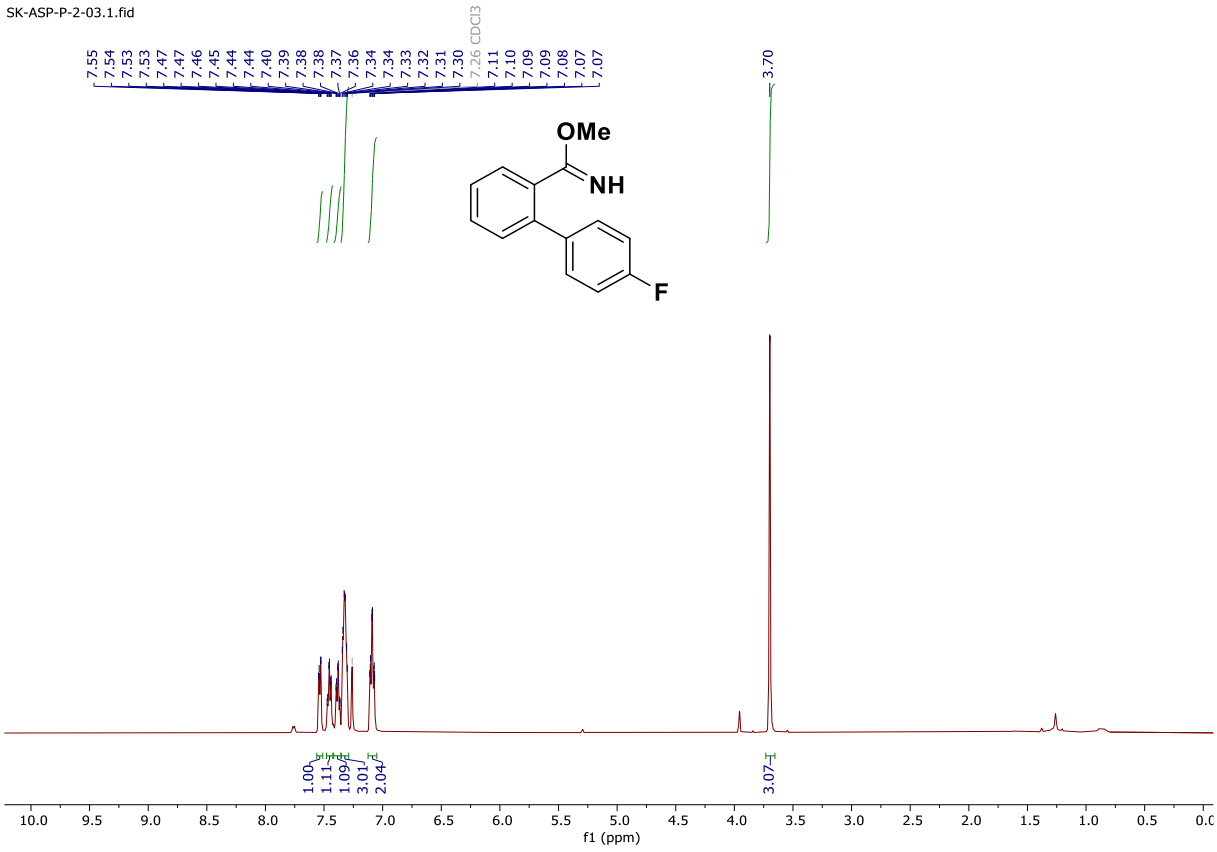
^{1}H NMR spectrum of 1c in $CDCl_3$ [500 MHz]



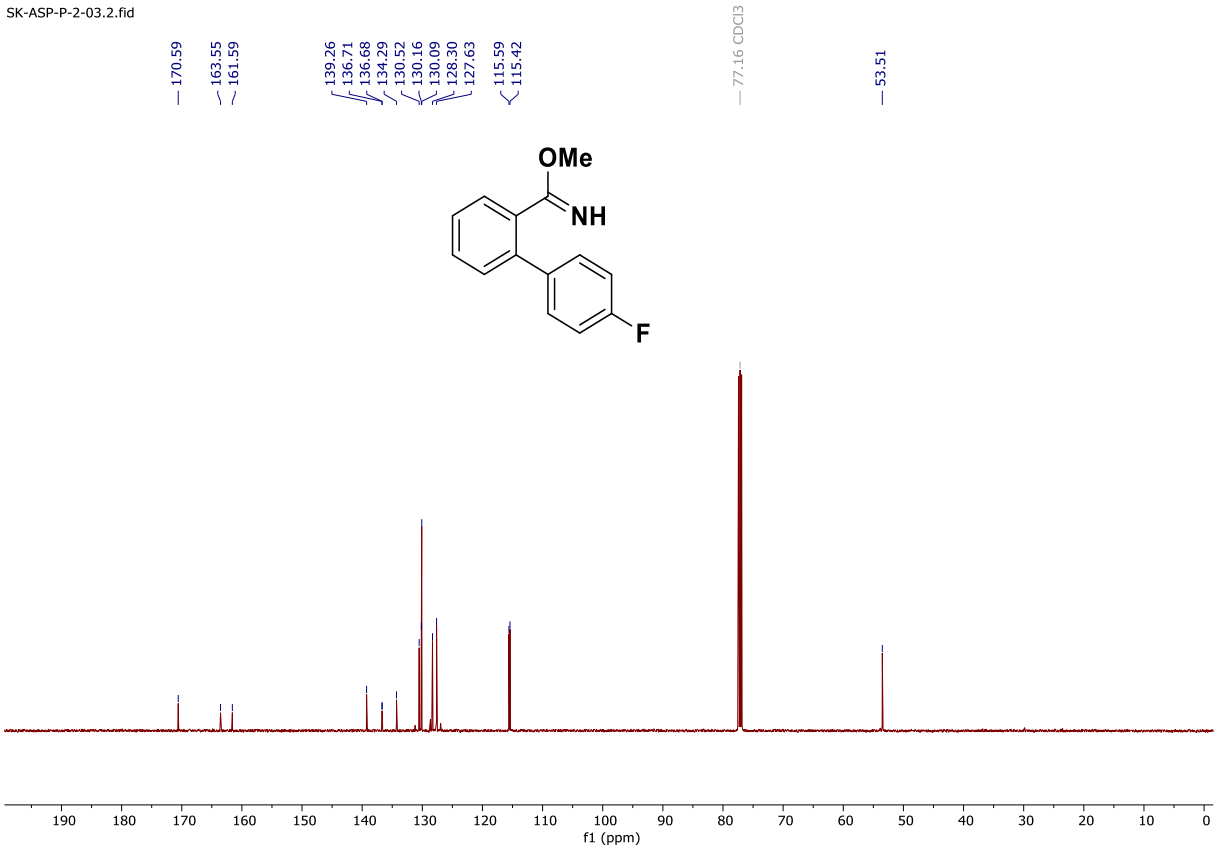
^{13}C{^{1}H} NMR spectrum of 1c in $CDCl_3$ [126 MHz]



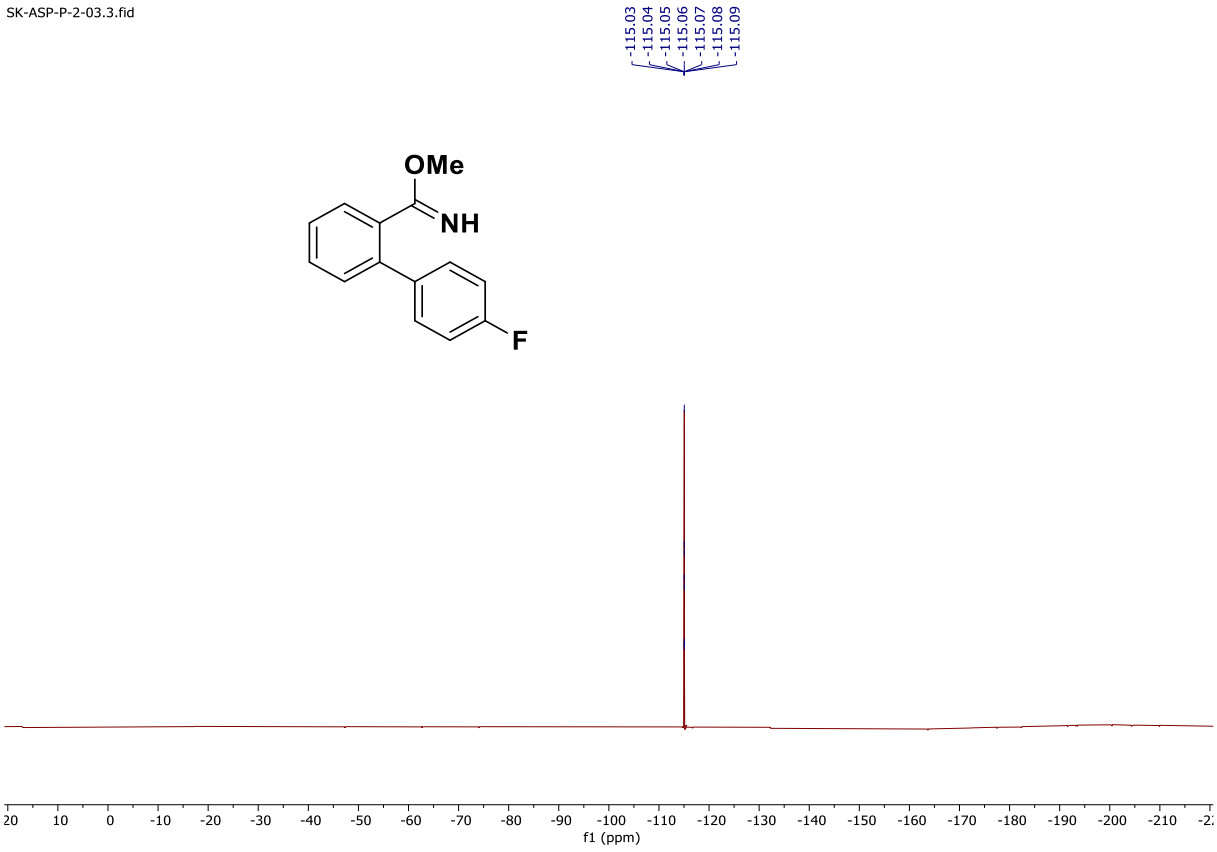
^{1}H NMR spectrum of 1d in $CDCl_3$ [500 MHz]



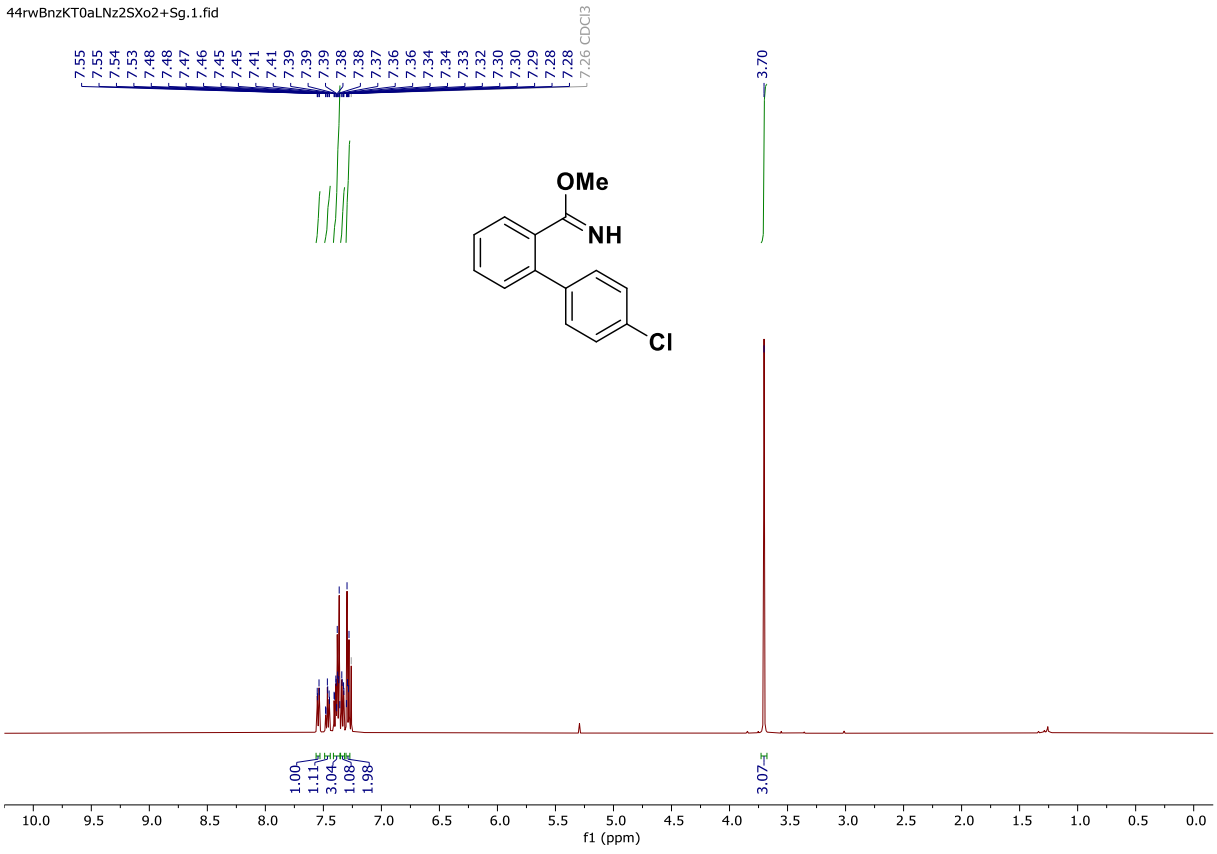
^{13}C{^{1}H} NMR spectrum of 1d in $CDCl_3$ [126 MHz]



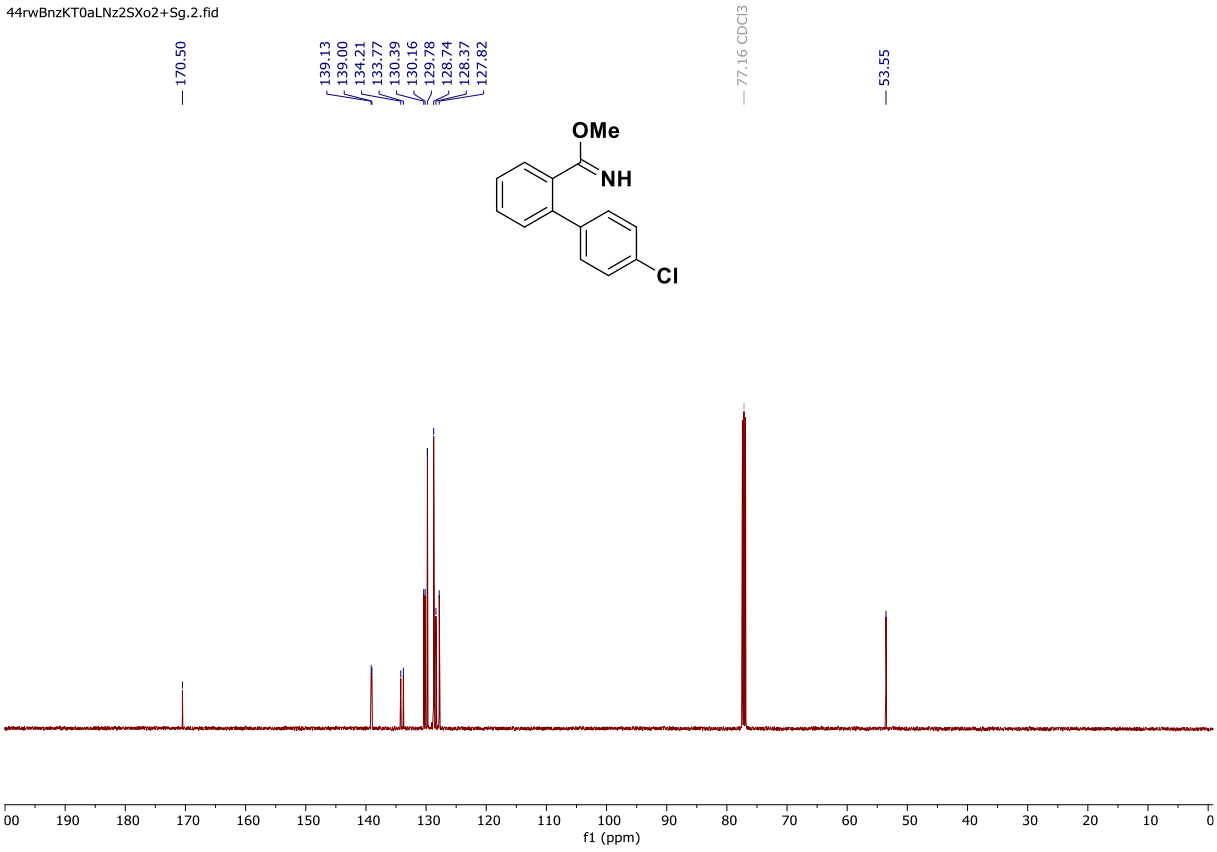
^{19}F NMR spectrum of 1d in $CDCl_3$ [471 MHz]



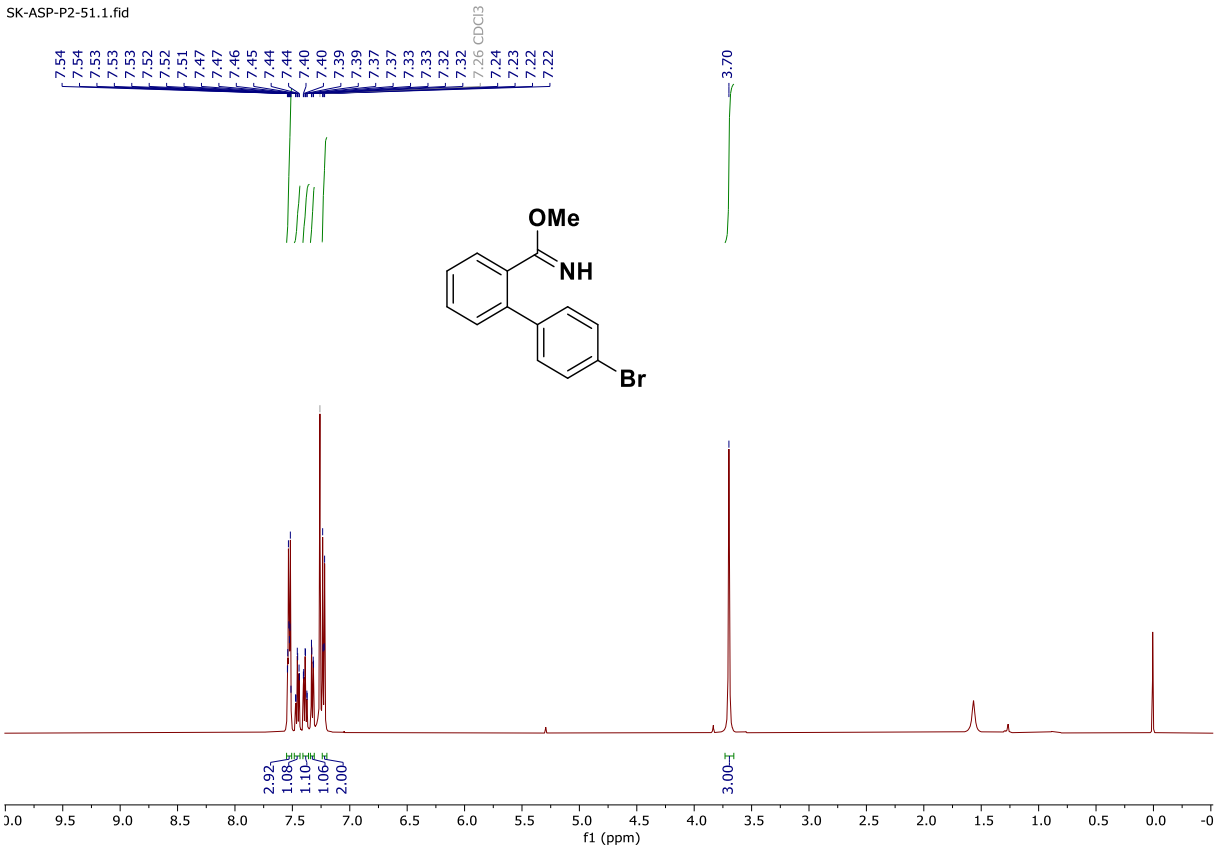
^{1}H NMR spectrum of 1e in $CDCl_3$ [500 MHz]



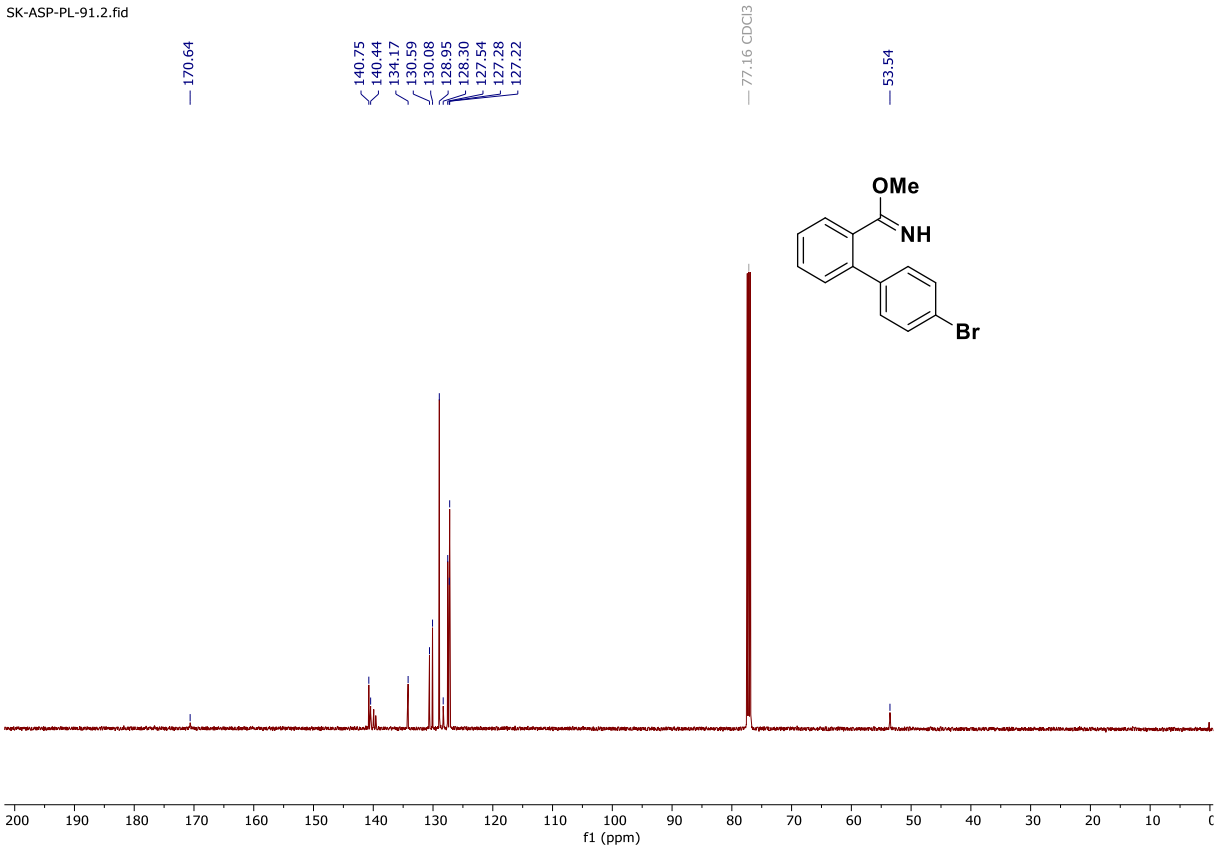
$^{13}C\{^{1}H\}$ NMR spectrum of 1e in $CDCl_3$ [126 MHz]



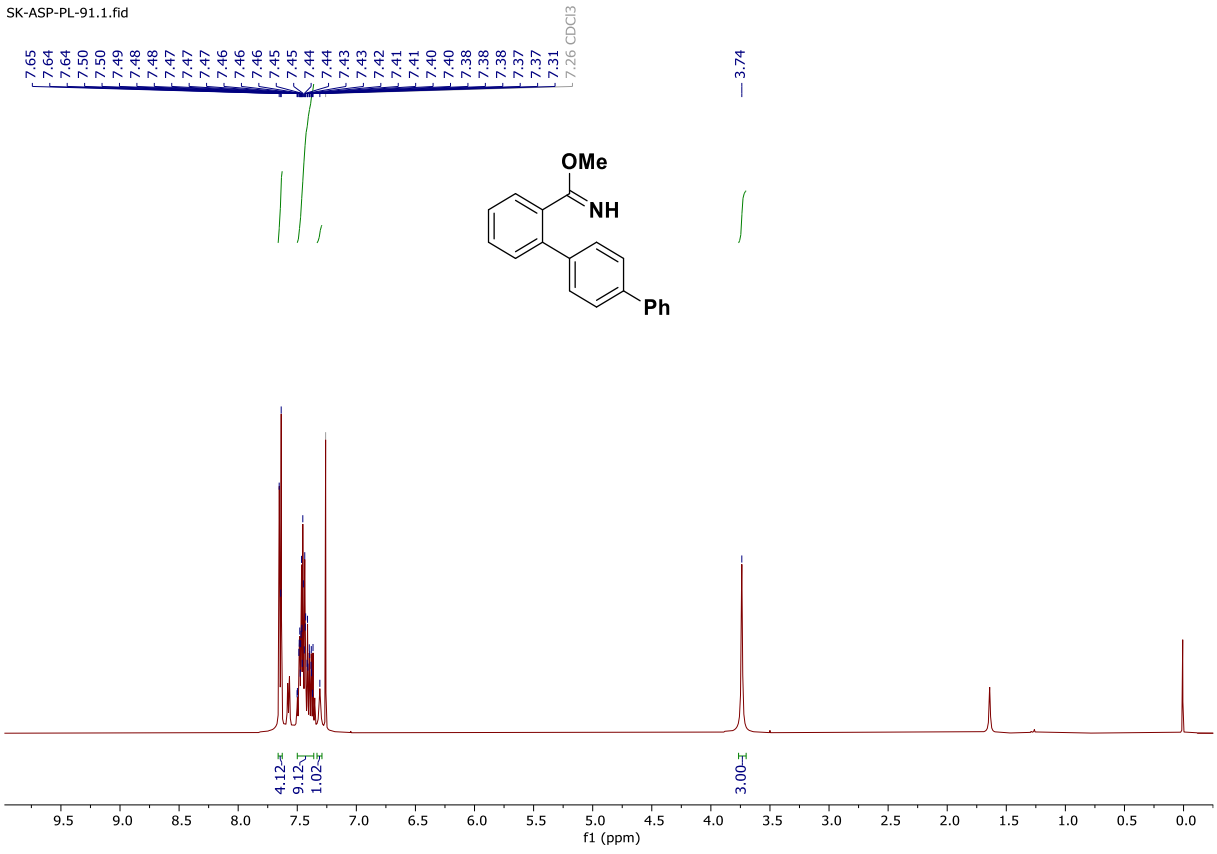
^{1}H NMR spectrum of 1f in $CDCl_3$ [500 MHz]



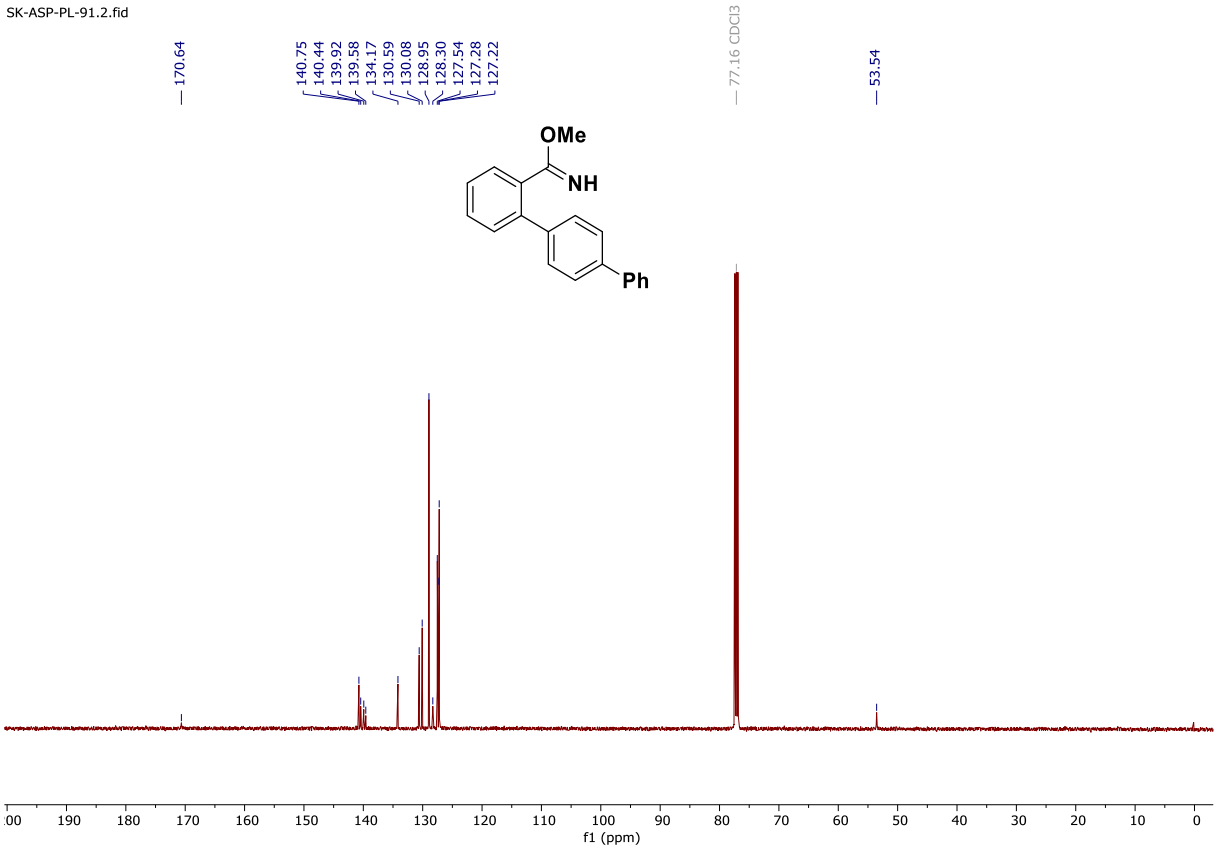
$^{13}C\{^{1}H\}$ NMR spectrum of 1f in $CDCl_3$ [126 MHz]



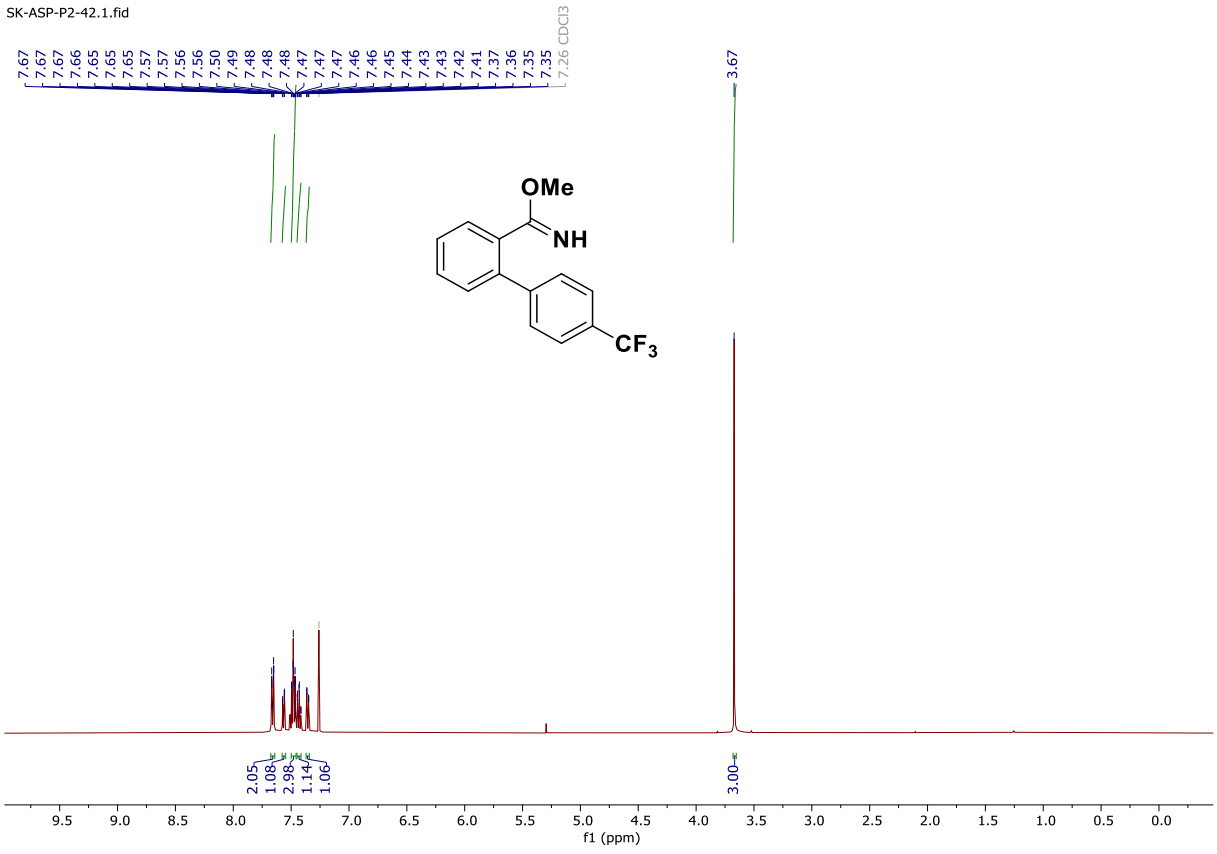
^{1}H NMR spectrum of 1g in $CDCl_3$ [500 MHz]



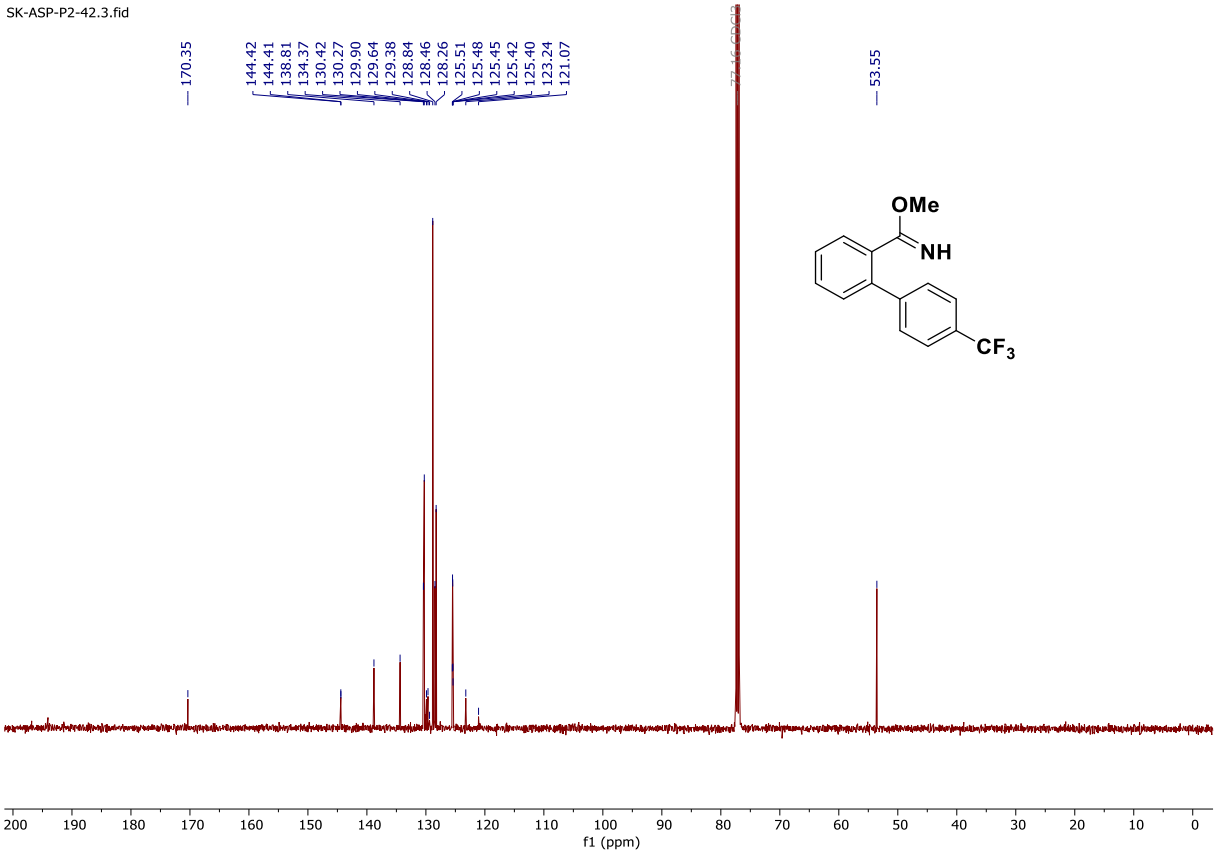
$^{13}C\{^{1}H\}$ NMR spectrum of 1g in $CDCl_3$ [126 MHz]



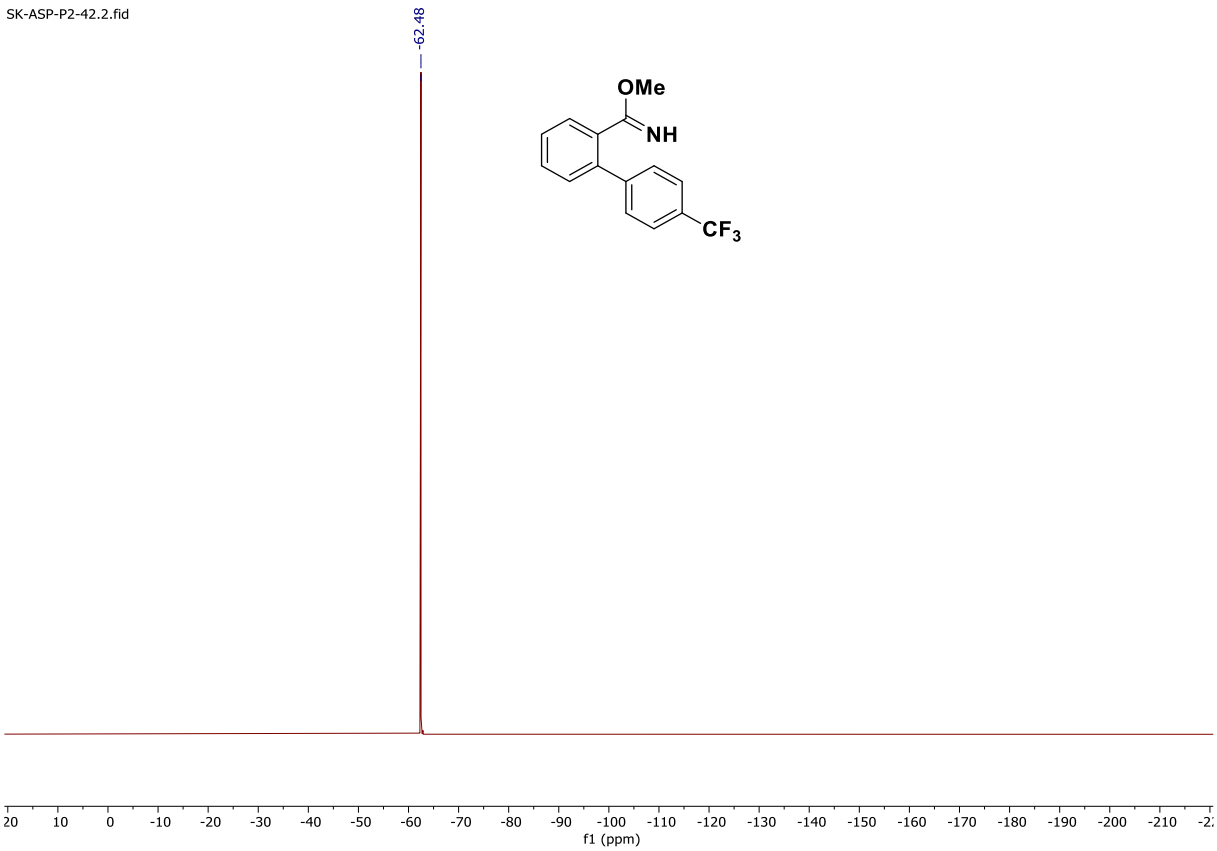
^{1}H NMR spectrum of 1h in $CDCl_3$ [500 MHz]



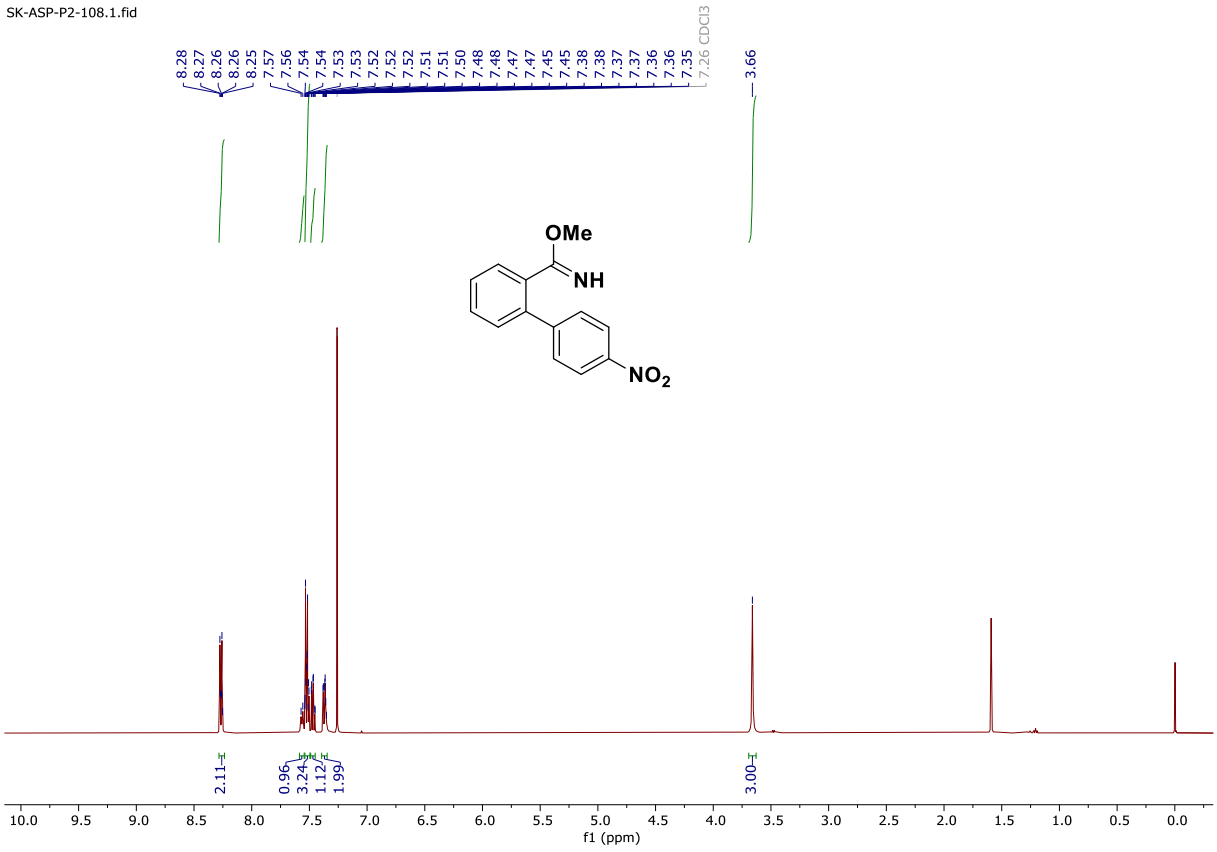
$^{13}C\{^{1}H\}$ NMR spectrum of 1h in $CDCl_3$ [126 MHz]



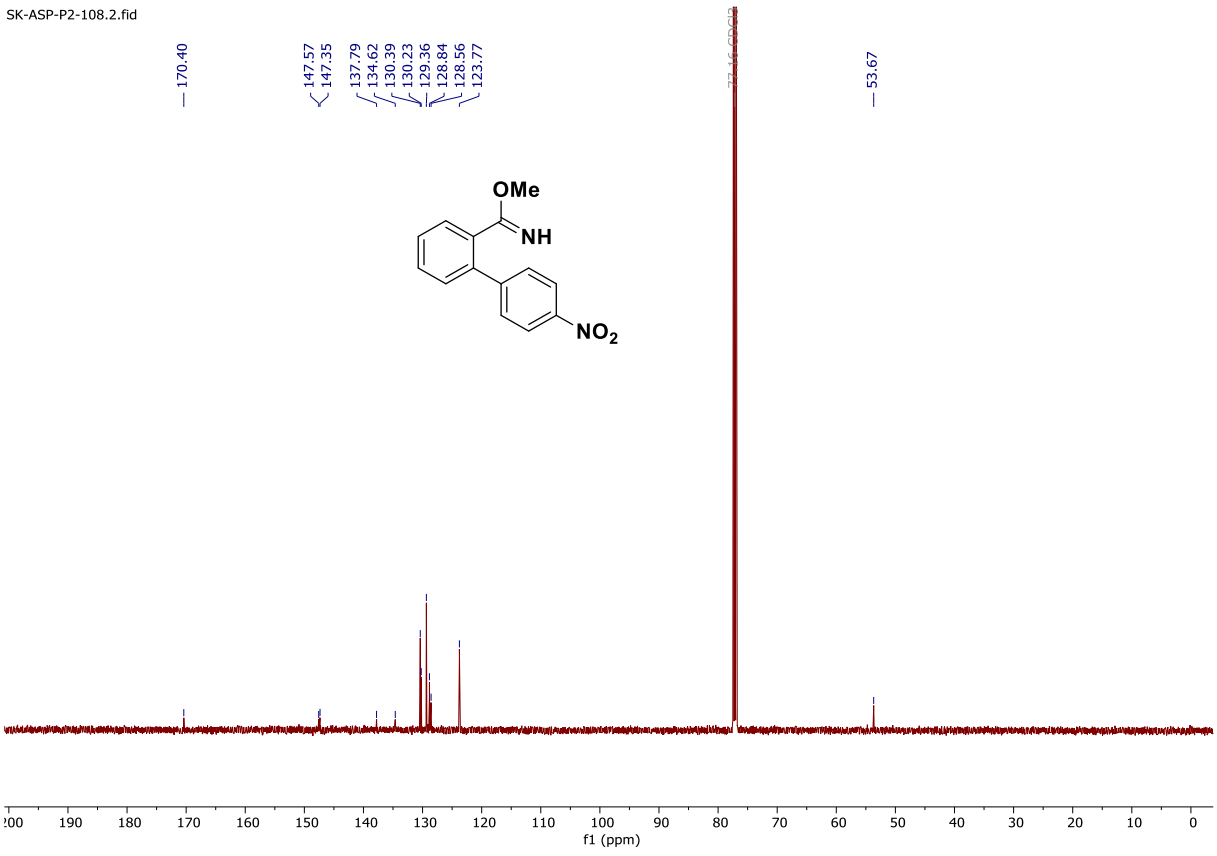
^{19}F NMR spectrum of 1h in $CDCl_3$ [471 MHz]



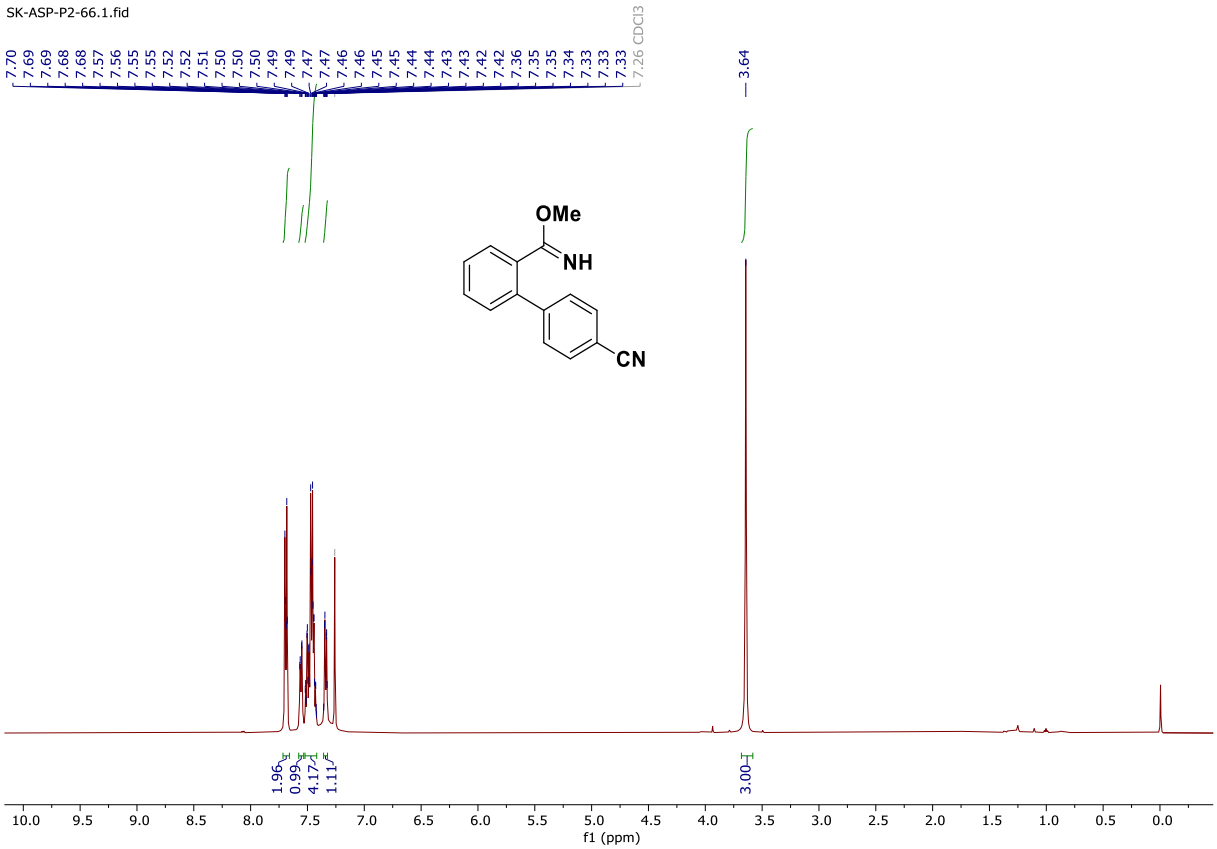
^{1}H NMR spectrum of 1i in $CDCl_3$ [500 MHz]



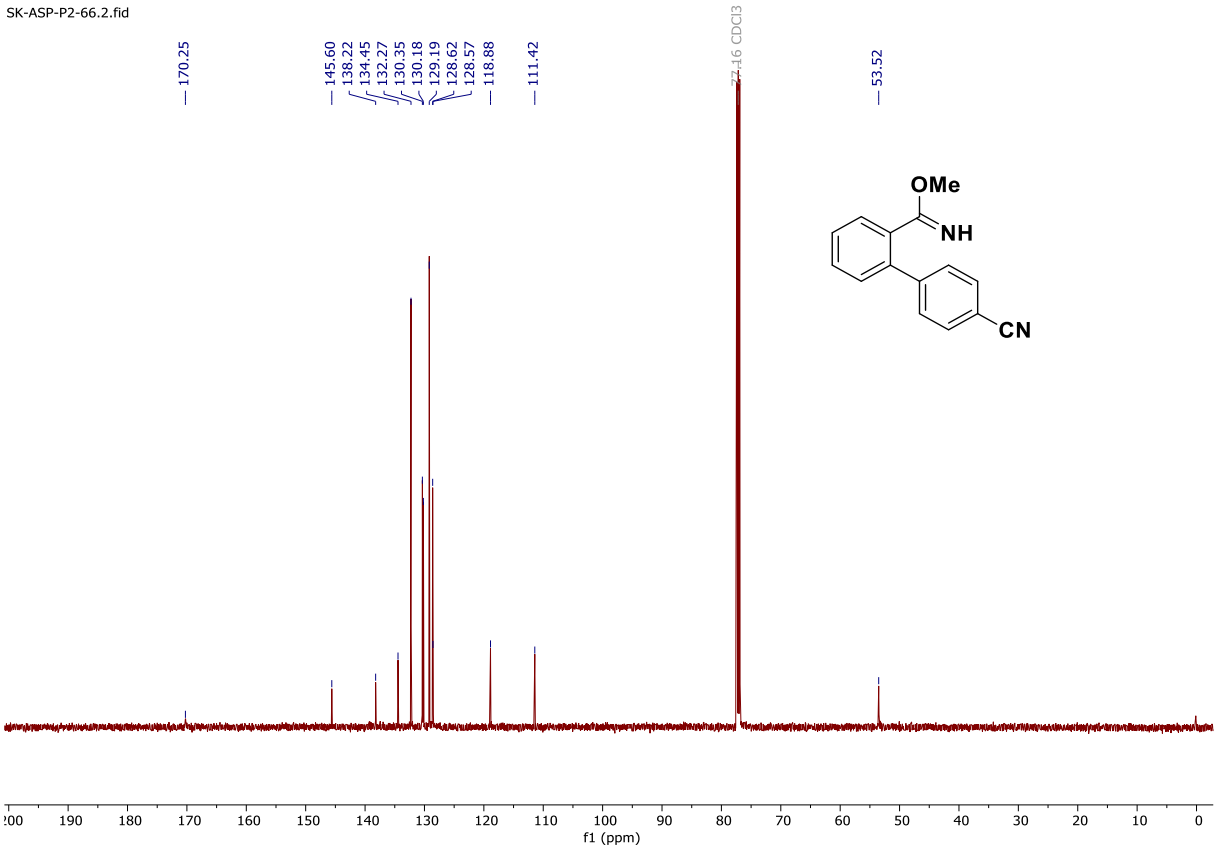
^{13}C{^{1}H} NMR spectrum of 1i in $CDCl_3$ [126 MHz]



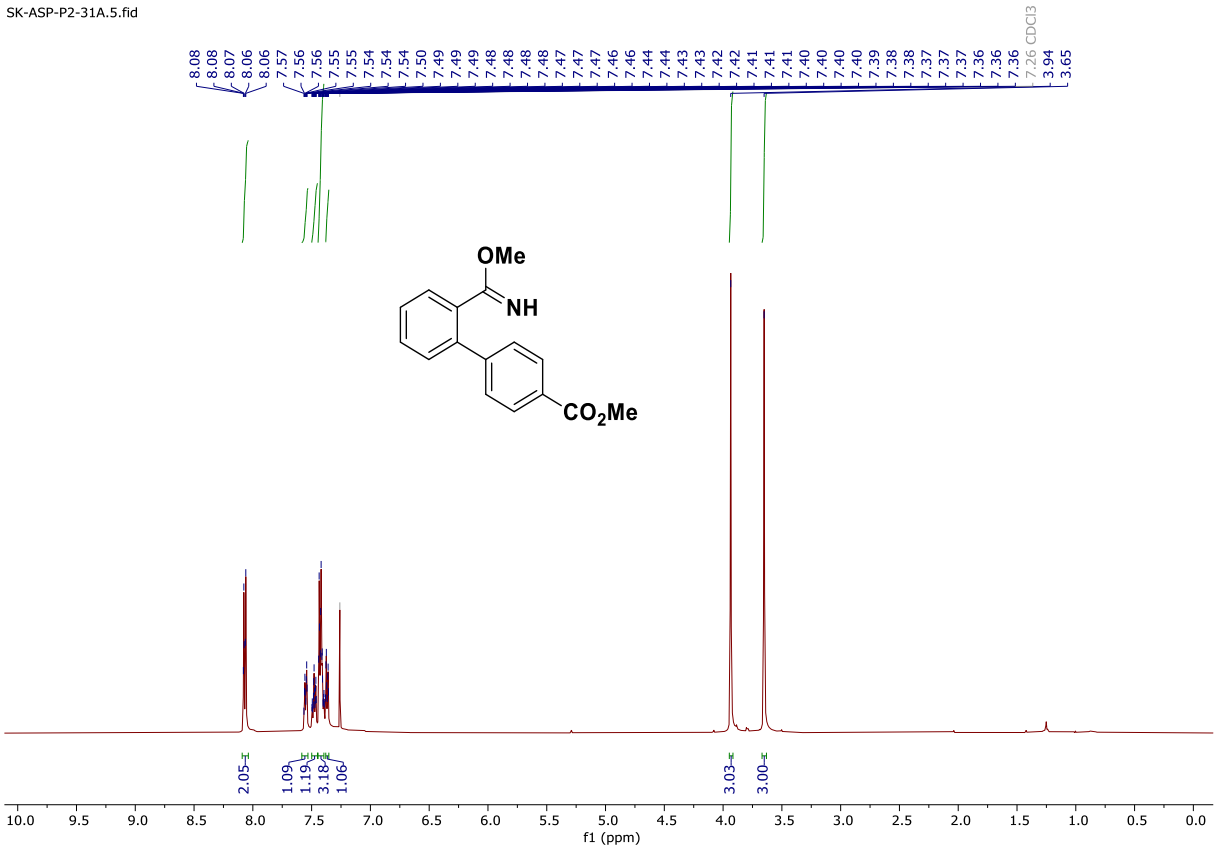
^{1}H NMR spectrum of 1j in $CDCl_3$ [500 MHz]



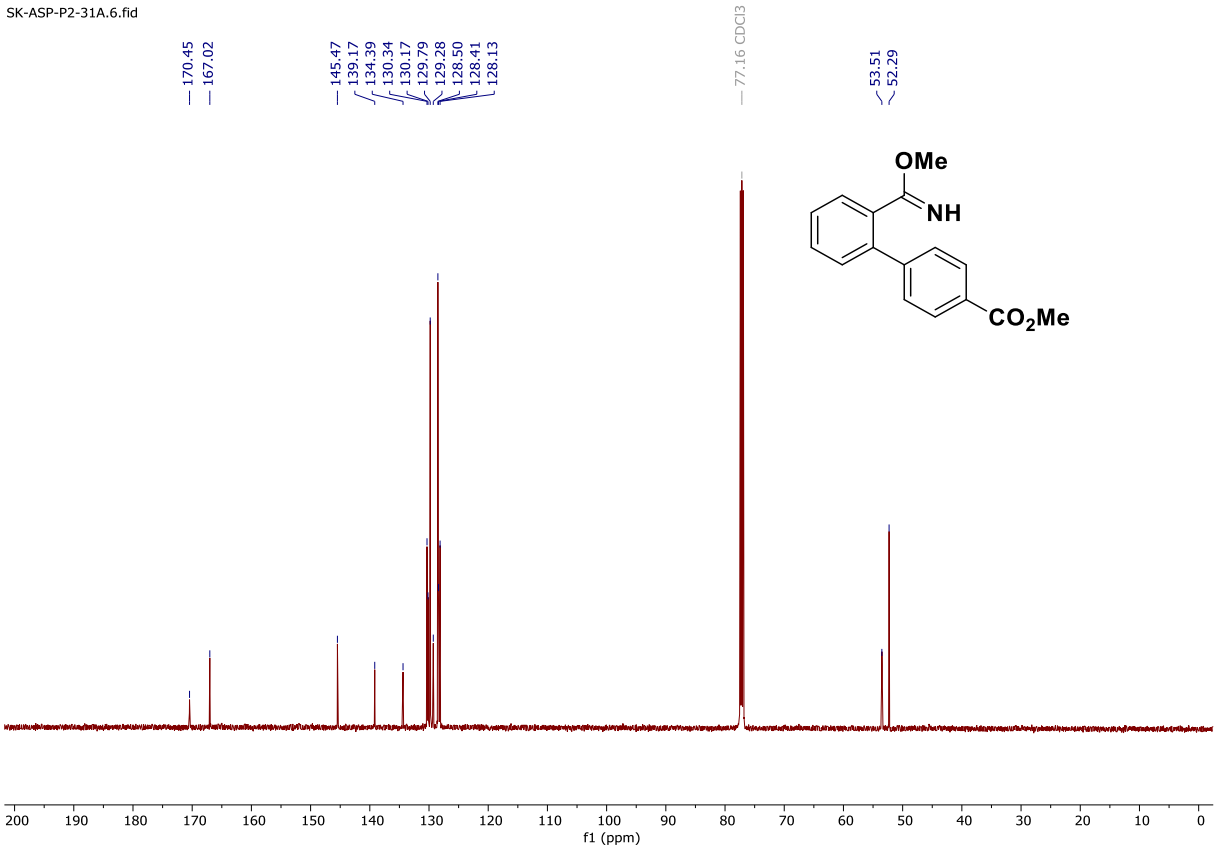
^{13}C{^{1}H} NMR spectrum of 1j in $CDCl_3$ [126 MHz]



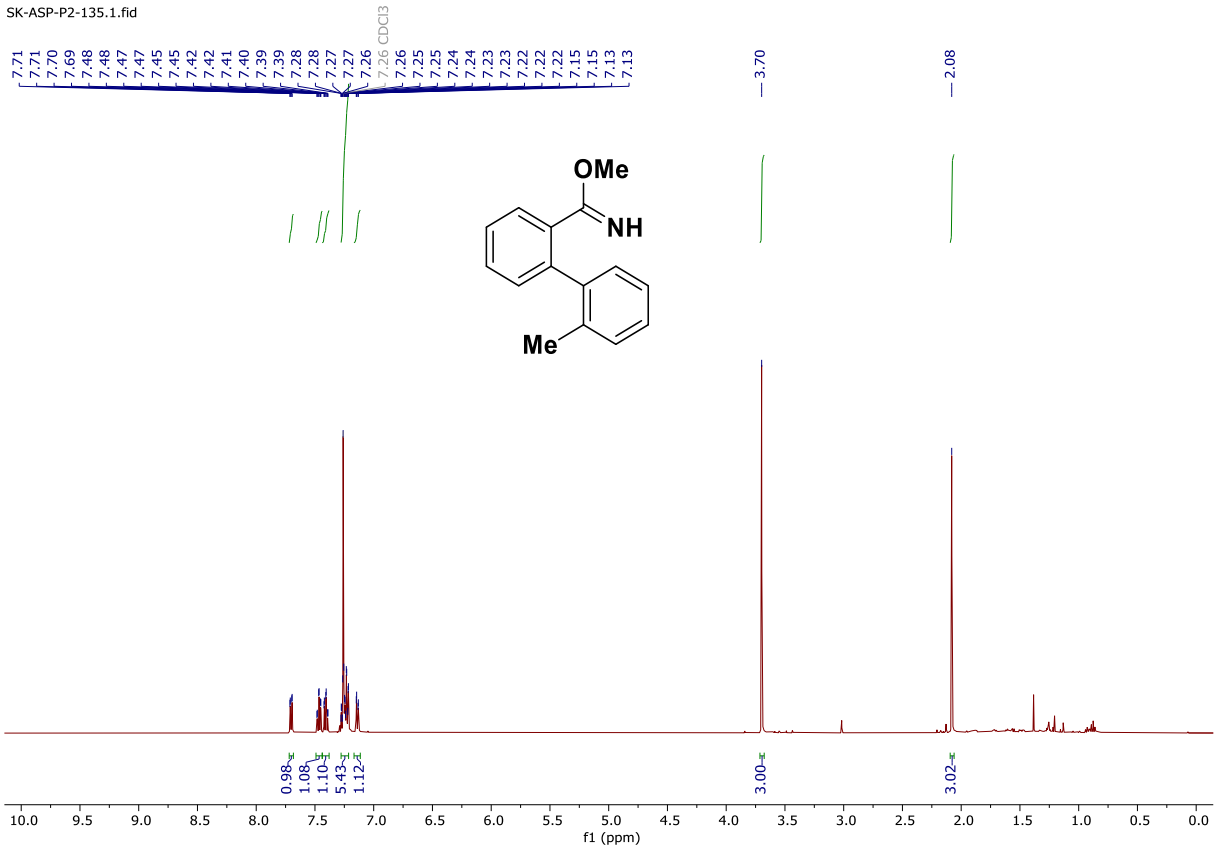
^{1}H NMR spectrum of 1k in $CDCl_3$ [500 MHz]



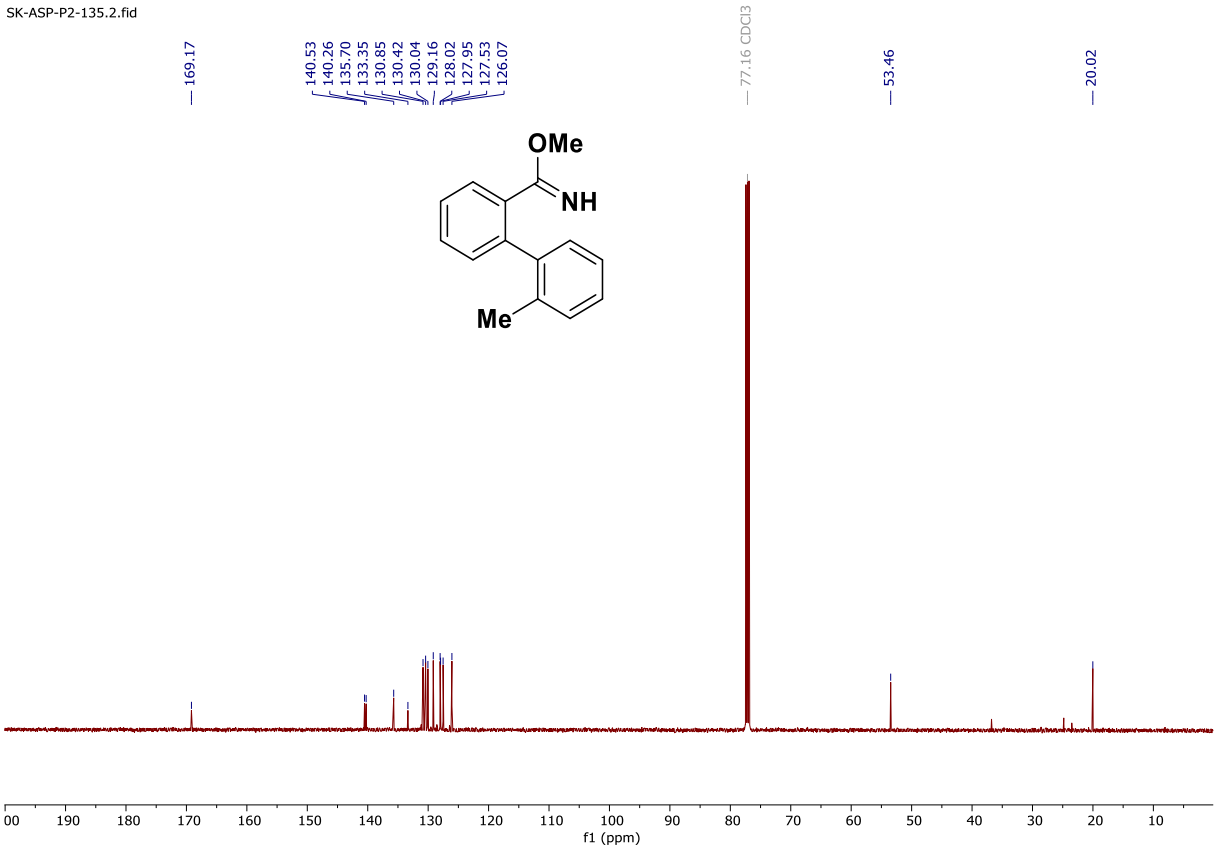
^{13}C{^{1}H} NMR spectrum of 1k in $CDCl_3$ [126 MHz]



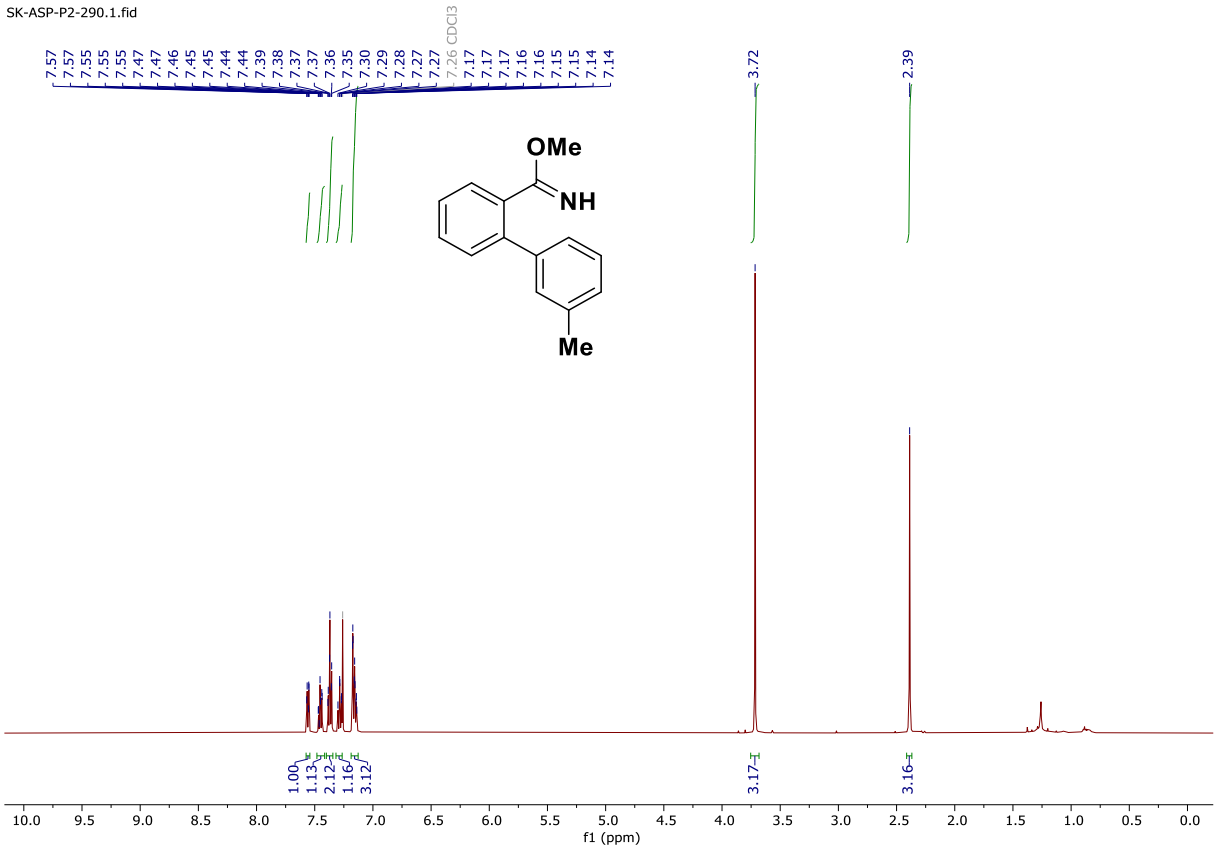
^{1}H NMR spectrum of 1l in $CDCl_3$ [500 MHz]



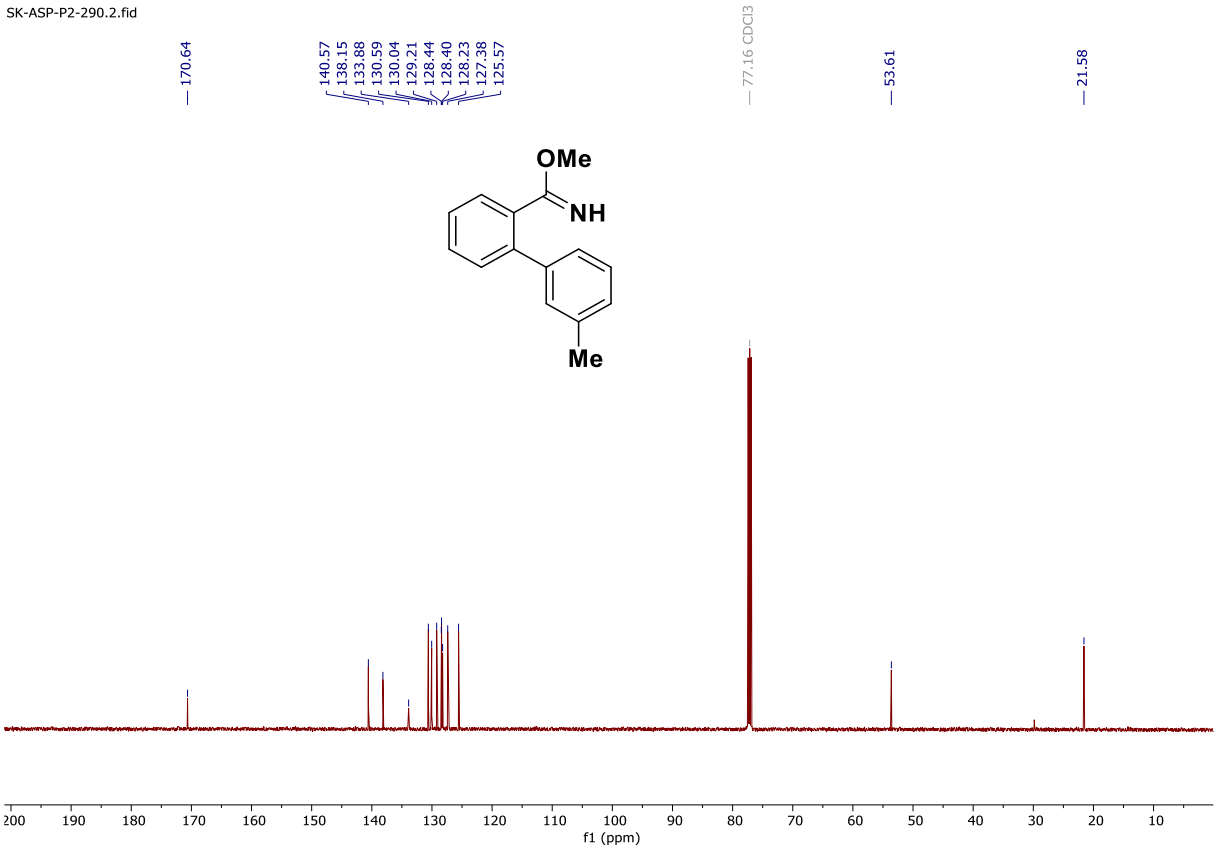
^{13}C{^{1}H} NMR spectrum of 1l in $CDCl_3$ [126 MHz]



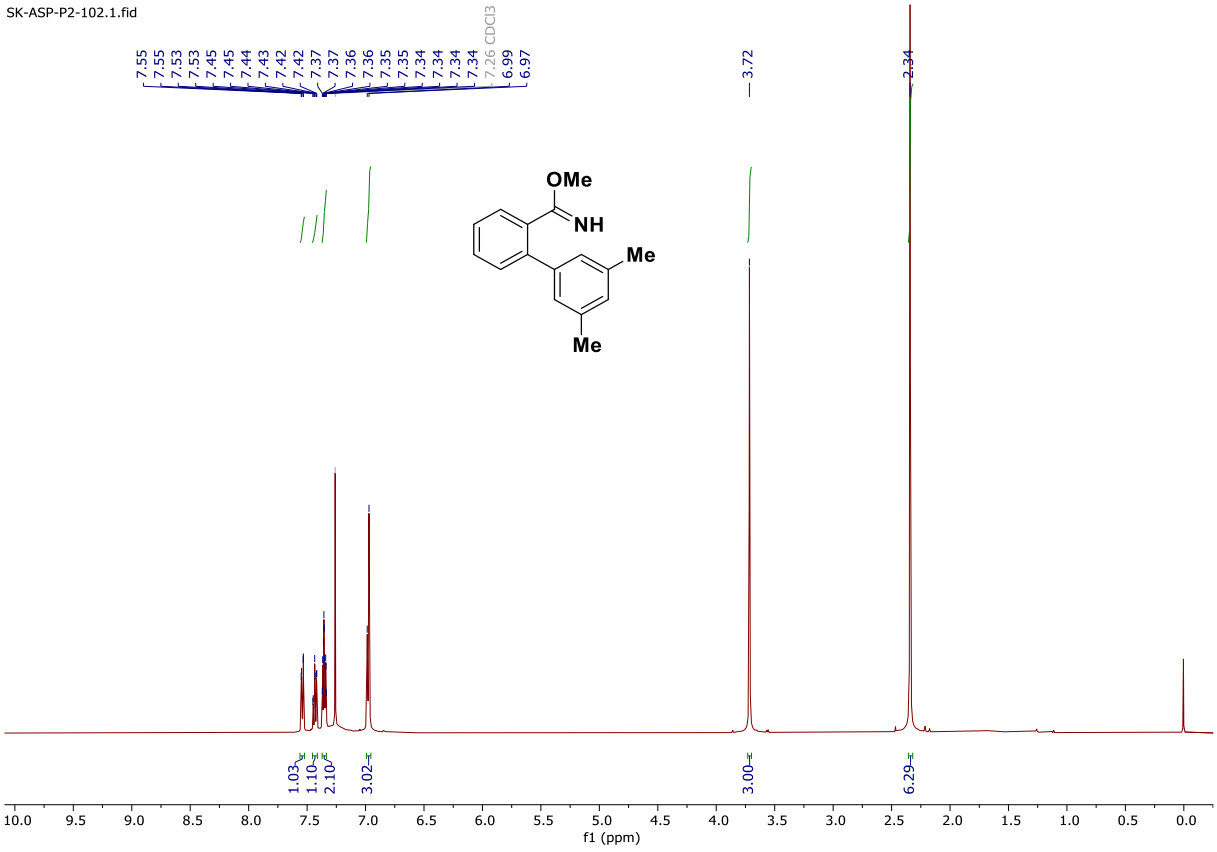
^{1}H NMR spectrum of 1m in $CDCl_3$ [500 MHz]



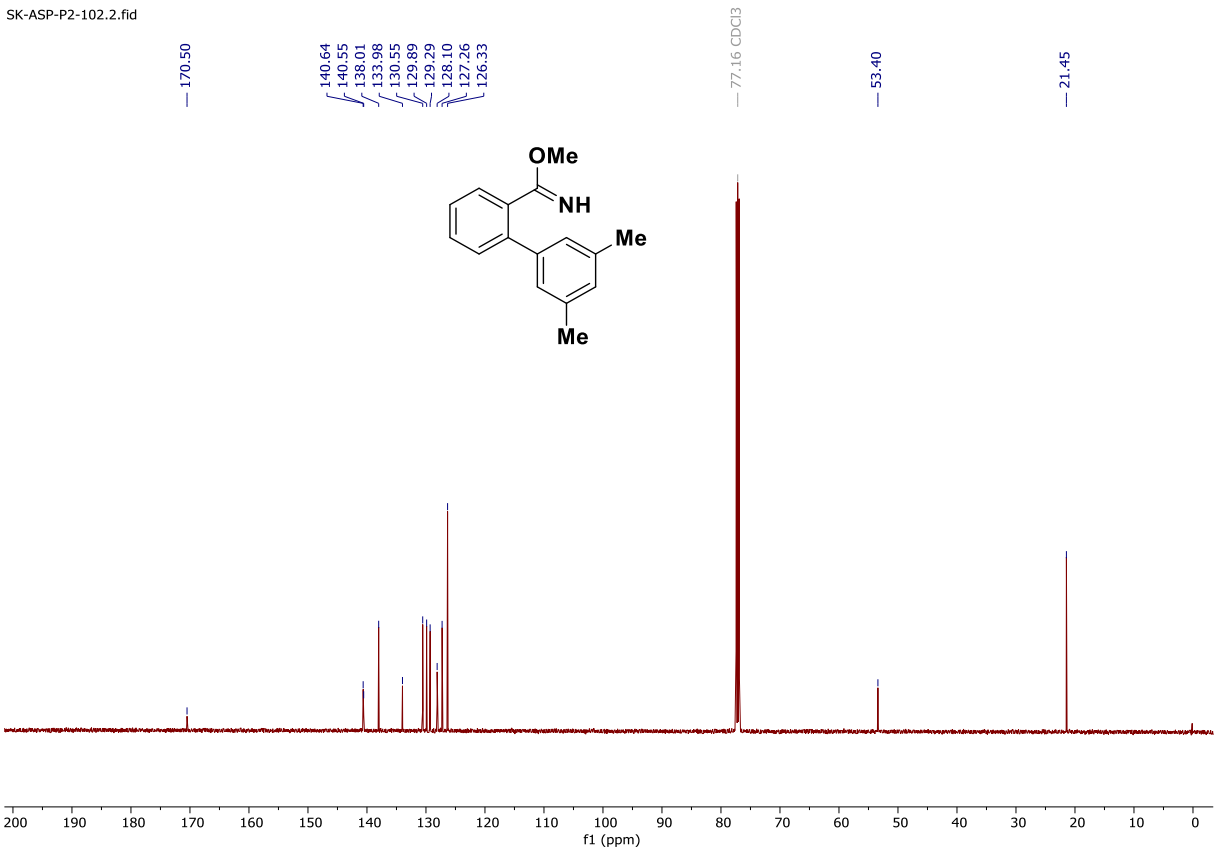
^{13}C{^{1}H} NMR spectrum of 1m in $CDCl_3$ [126 MHz]



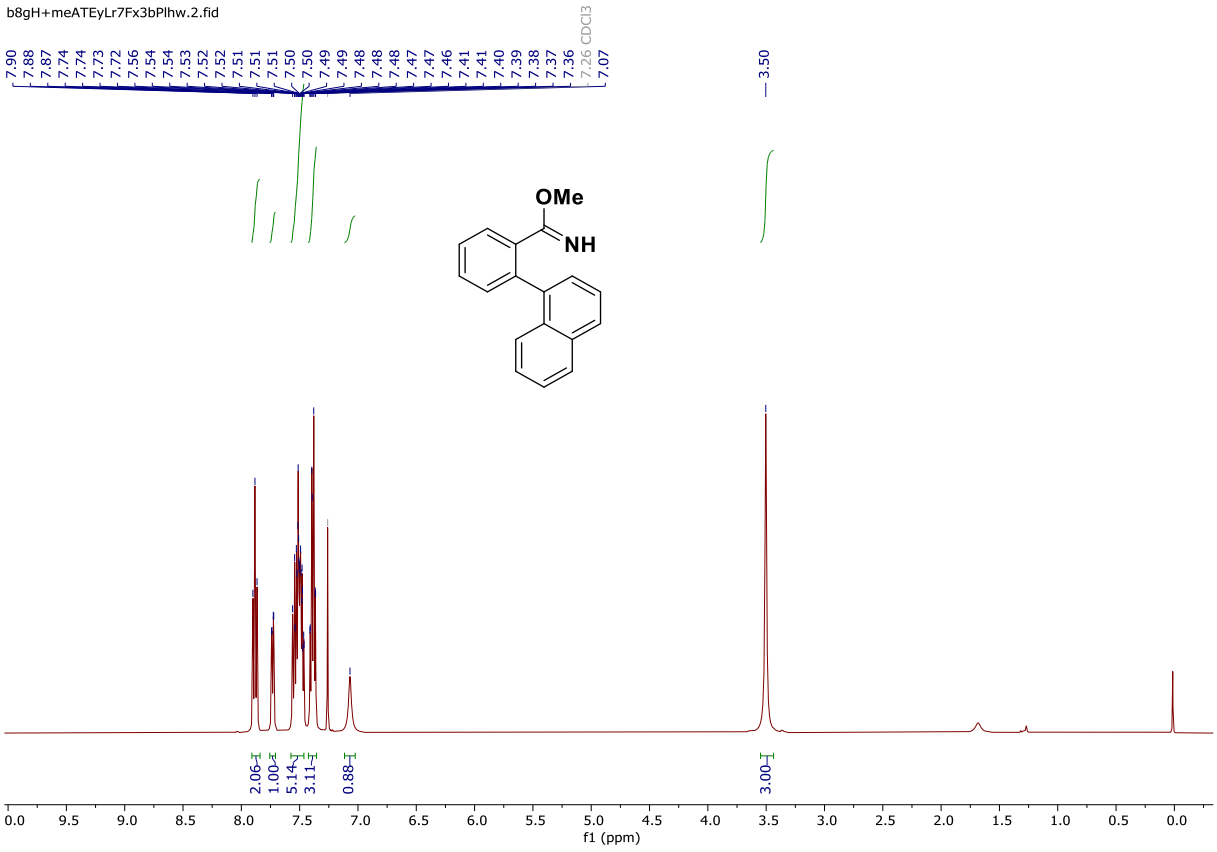
^{1}H NMR spectrum of 1n in $CDCl_3$ [500 MHz]



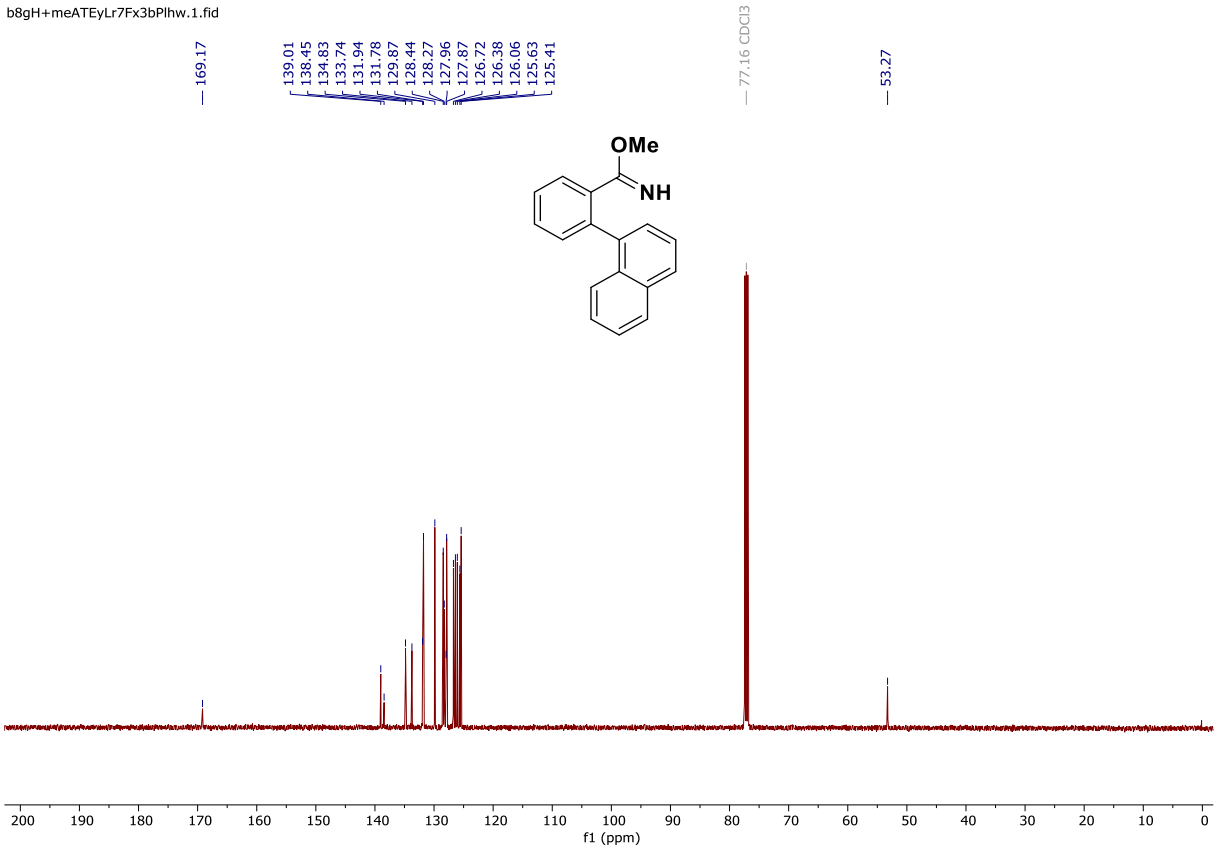
^{13}C{^{1}H} NMR spectrum of 1n in $CDCl_3$ [126 MHz]



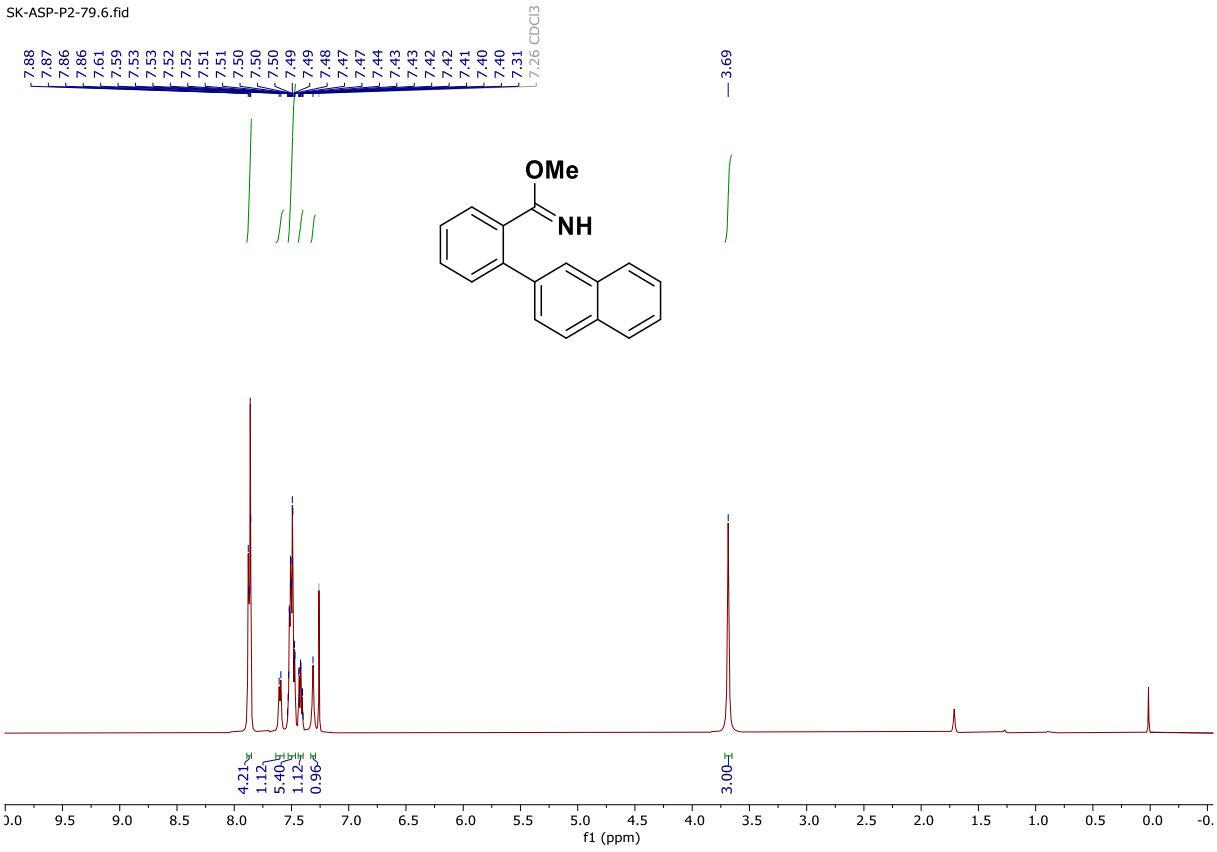
^{1}H NMR spectrum of 1o in $CDCl_3$ [500 MHz]



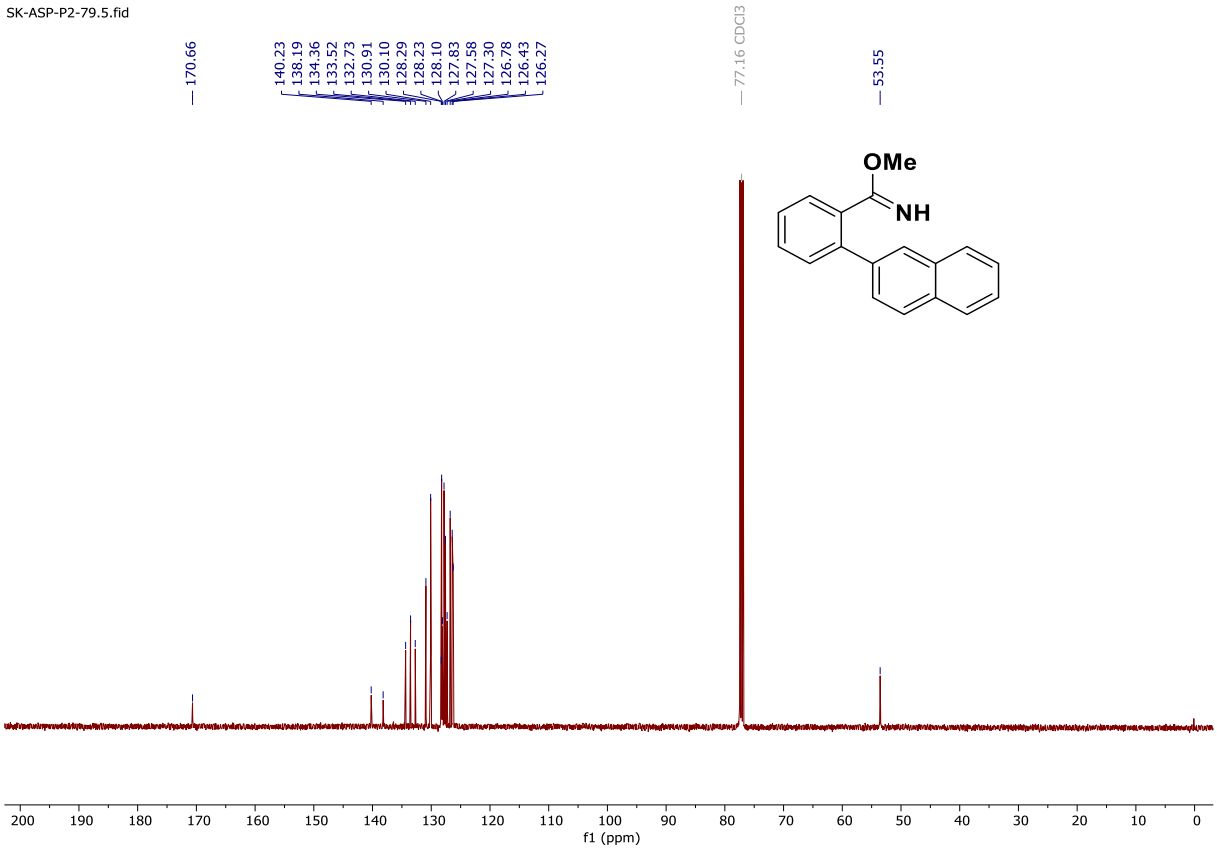
^{13}C{^{1}H} NMR spectrum of 1o in $CDCl_3$ [126 MHz]



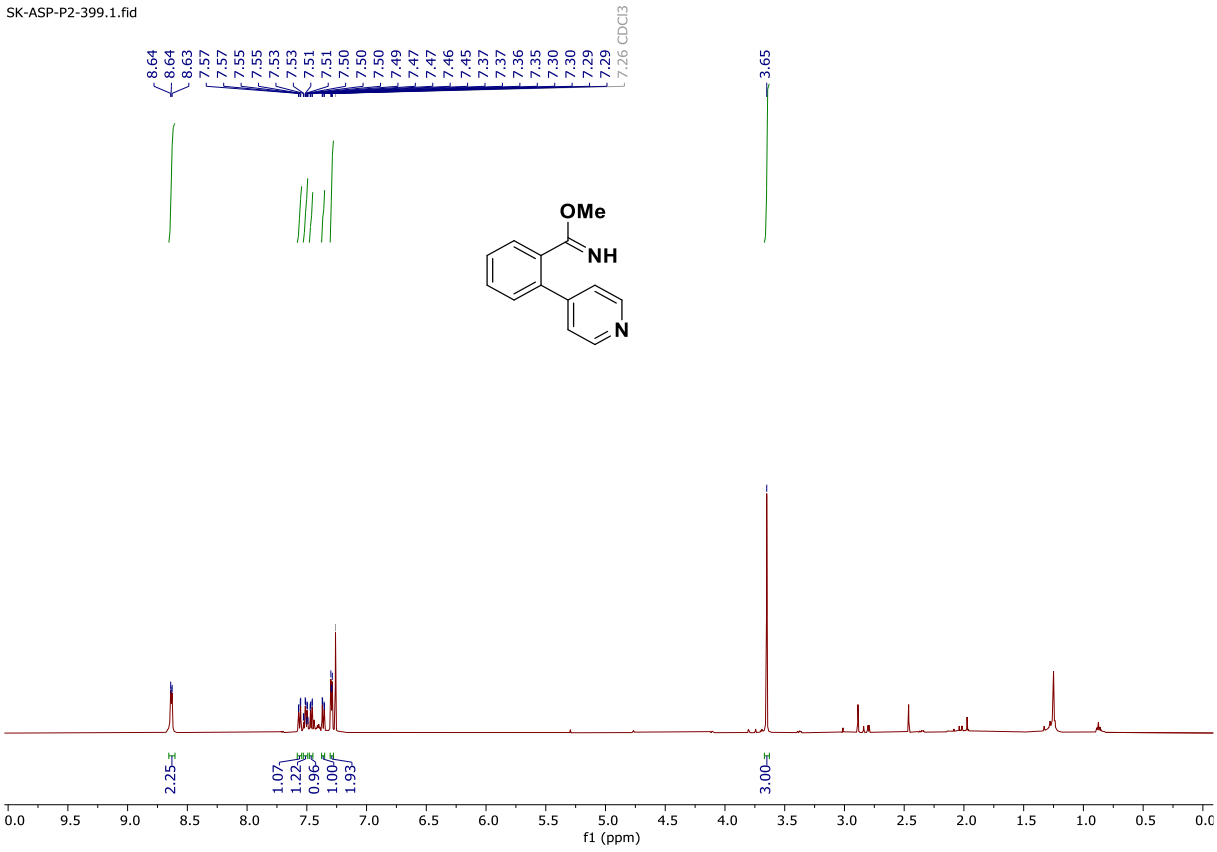
^{1}H NMR spectrum of 1p in $CDCl_3$ [500 MHz]



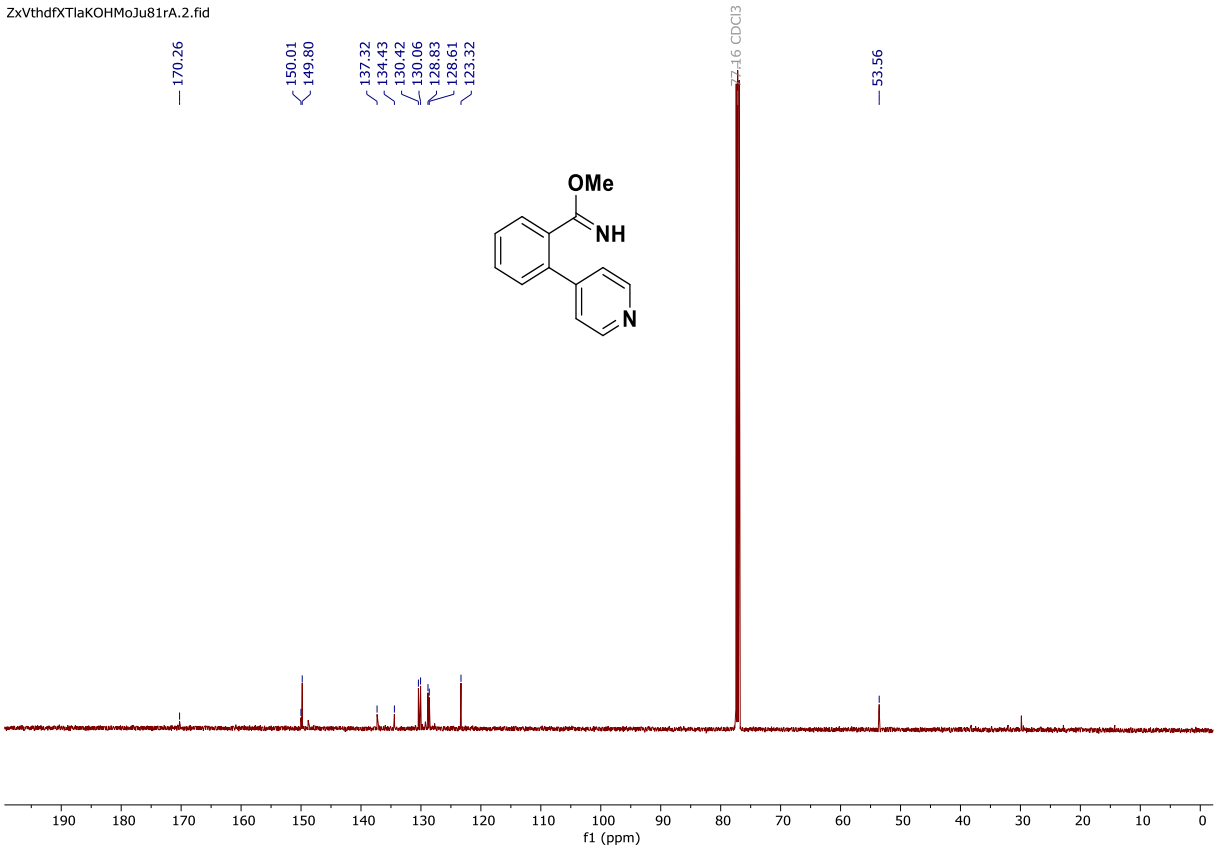
^{13}C{^{1}H} NMR spectrum of 1p in $CDCl_3$ [126 MHz]



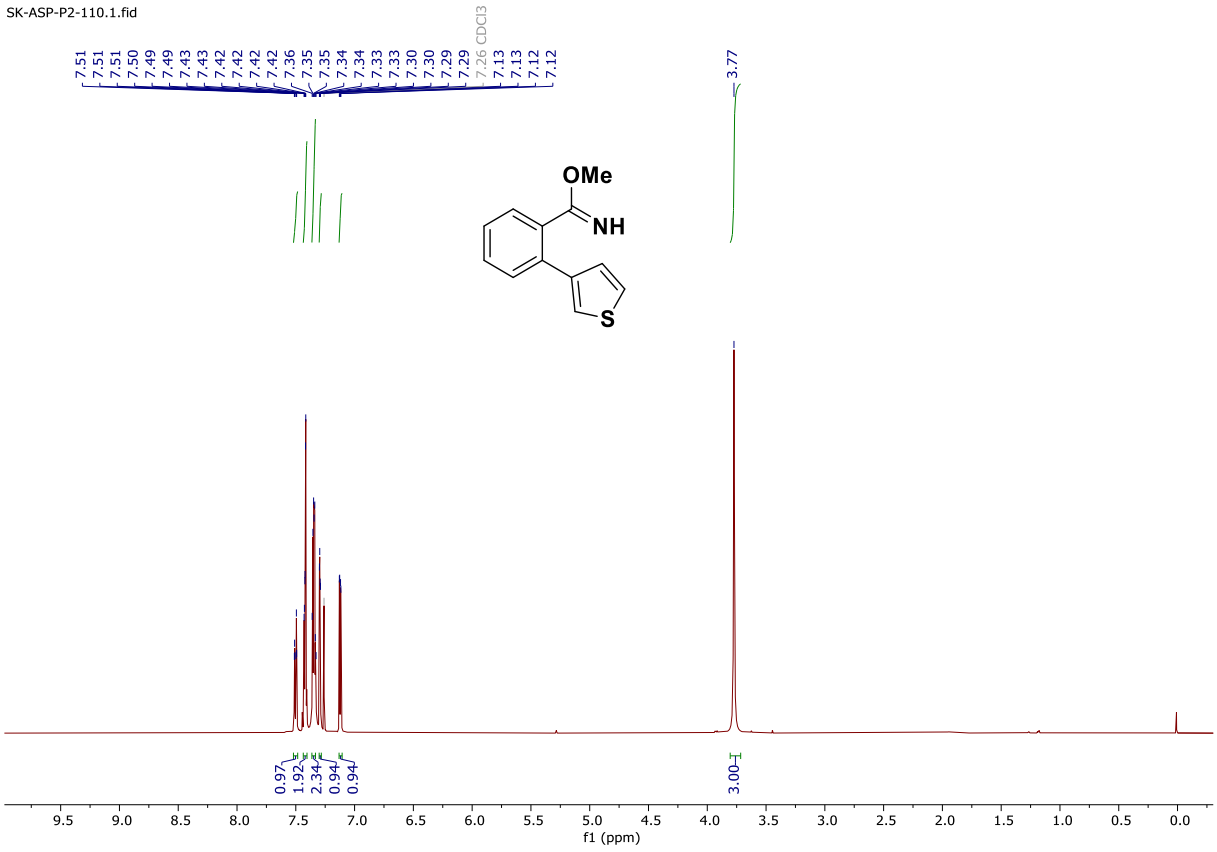
^{1}H NMR spectrum of 1q in $CDCl_3$ [500 MHz]



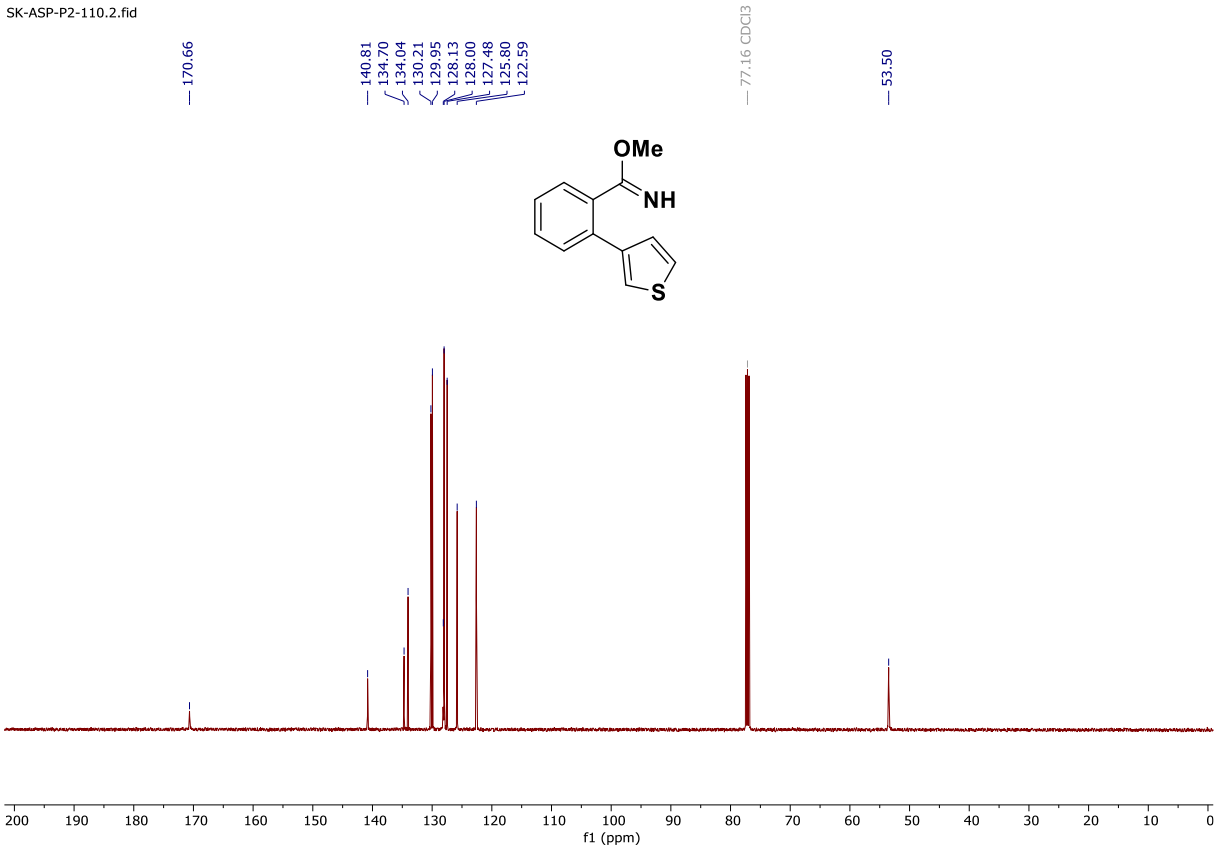
^{13}C{^{1}H} NMR spectrum of 1q in $CDCl_3$ [126 MHz]



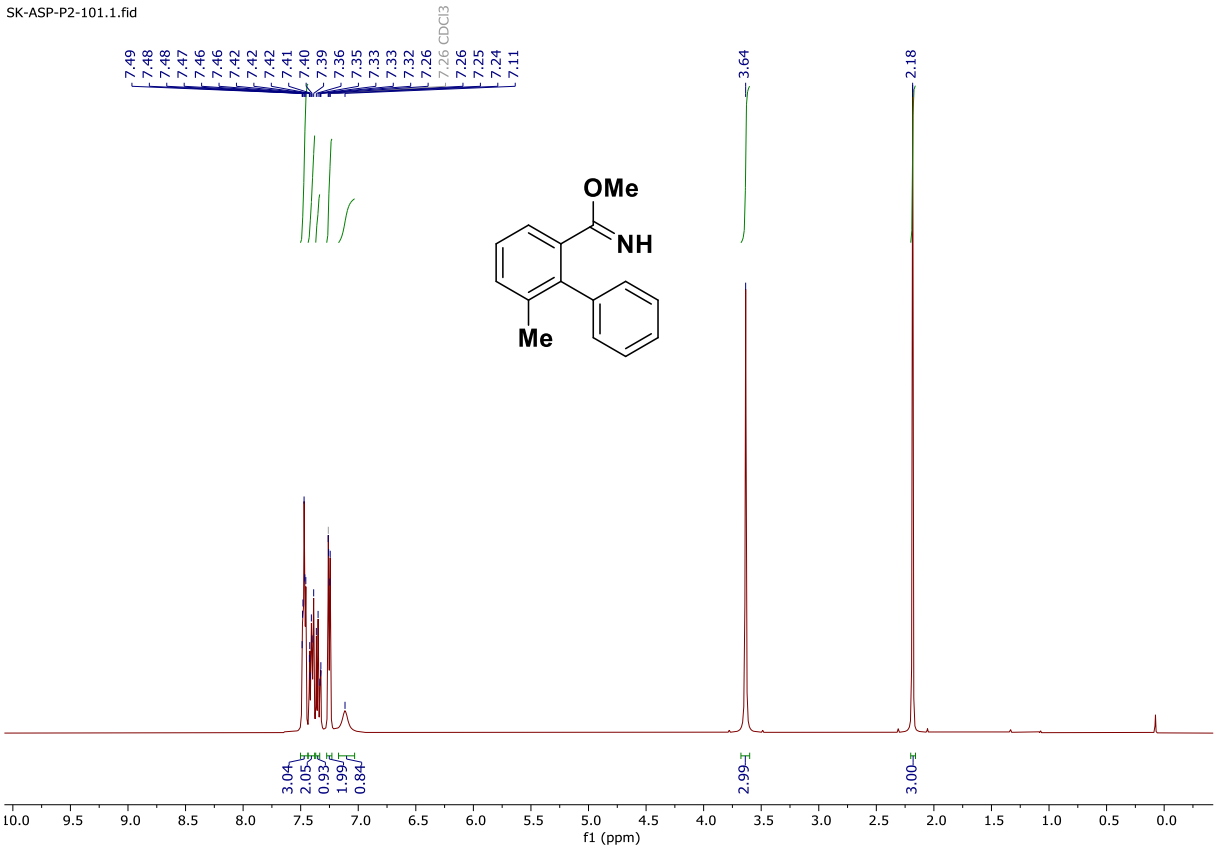
^{1}H NMR spectrum of 1r in $CDCl_3$ [500 MHz]



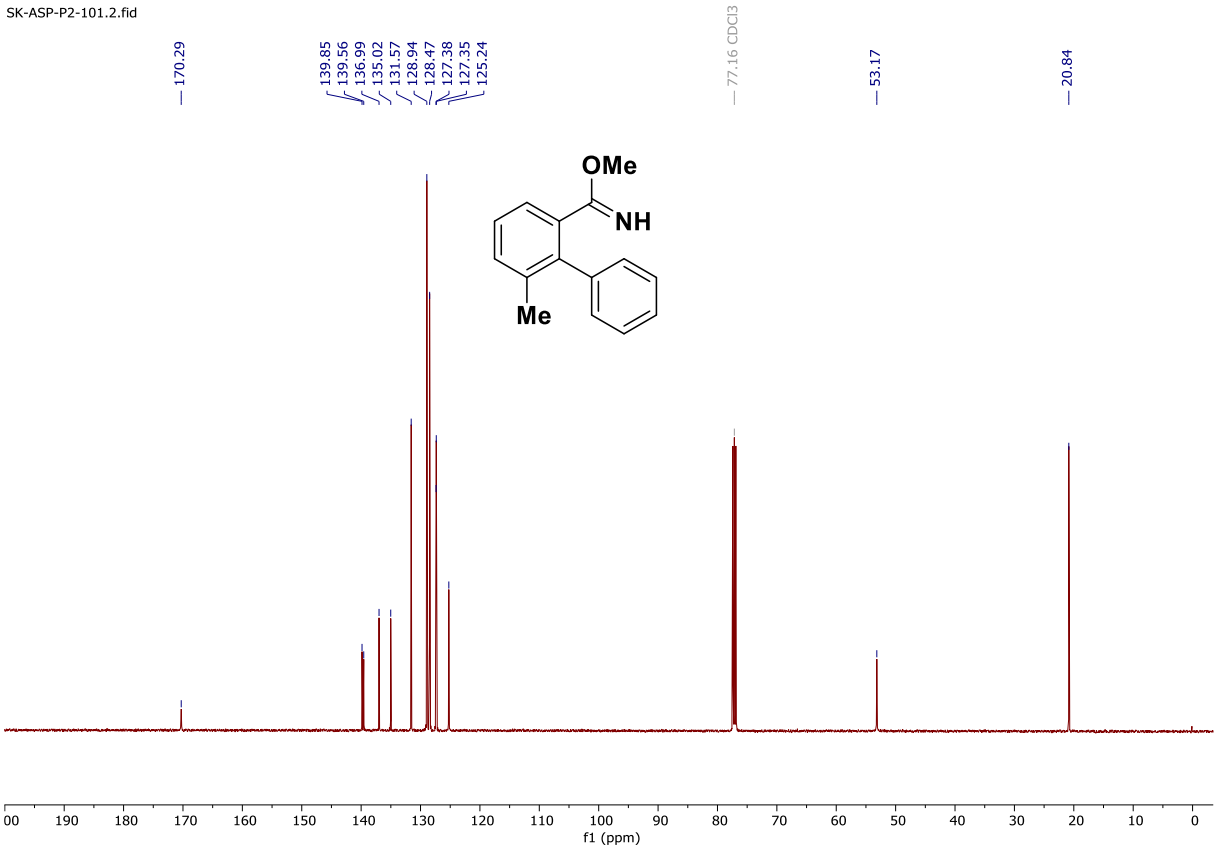
^{13}C{^{1}H} NMR spectrum of 1r in $CDCl_3$ [126 MHz]



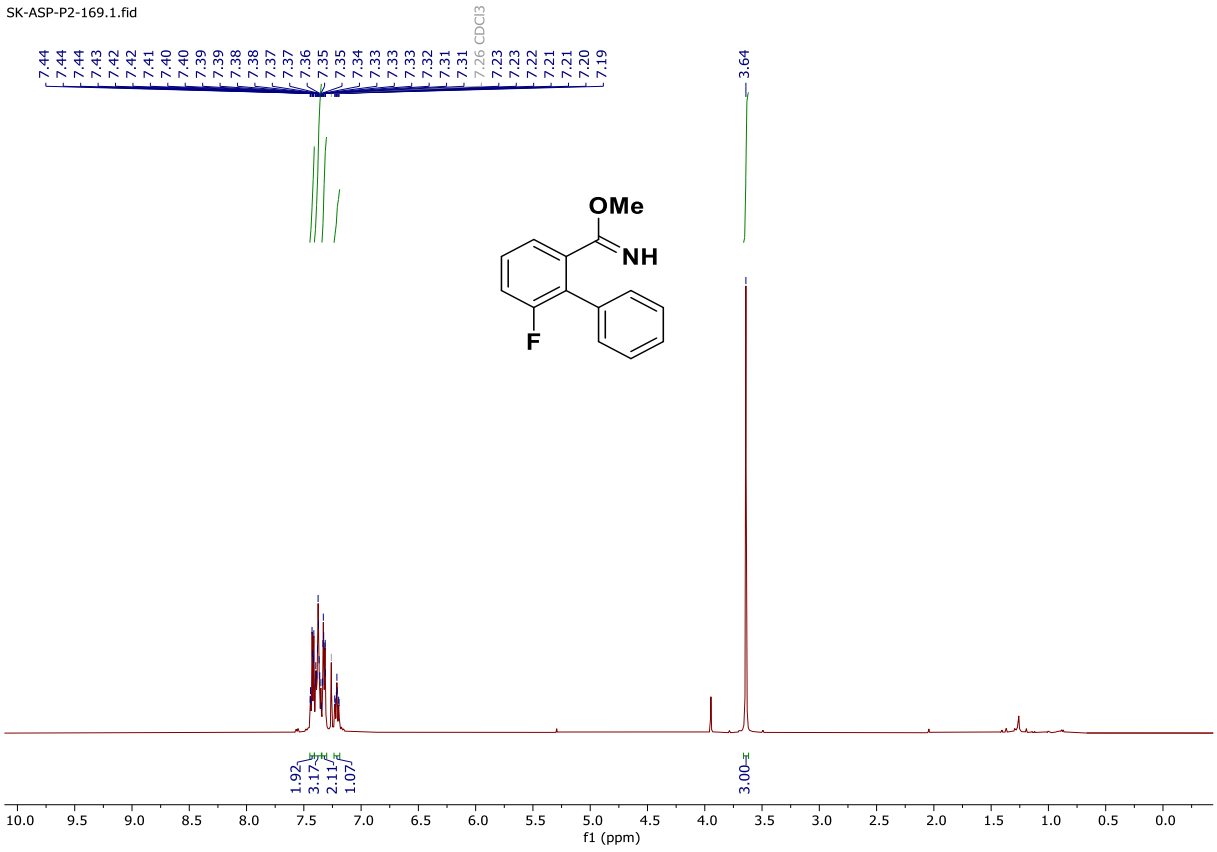
^{1}H NMR spectrum of 1s in $CDCl_3$ [500 MHz]



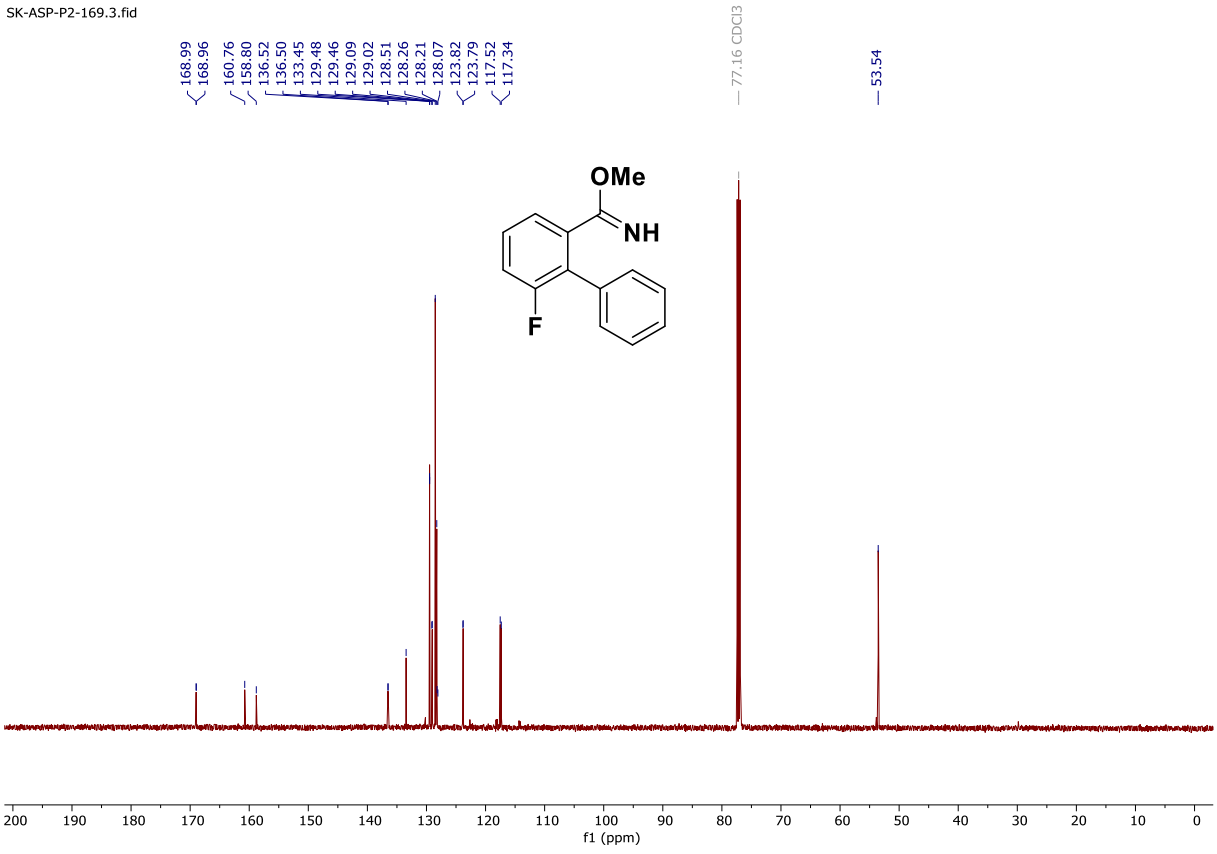
^{13}C{^{1}H} NMR spectrum of 1s in $CDCl_3$ [126 MHz]



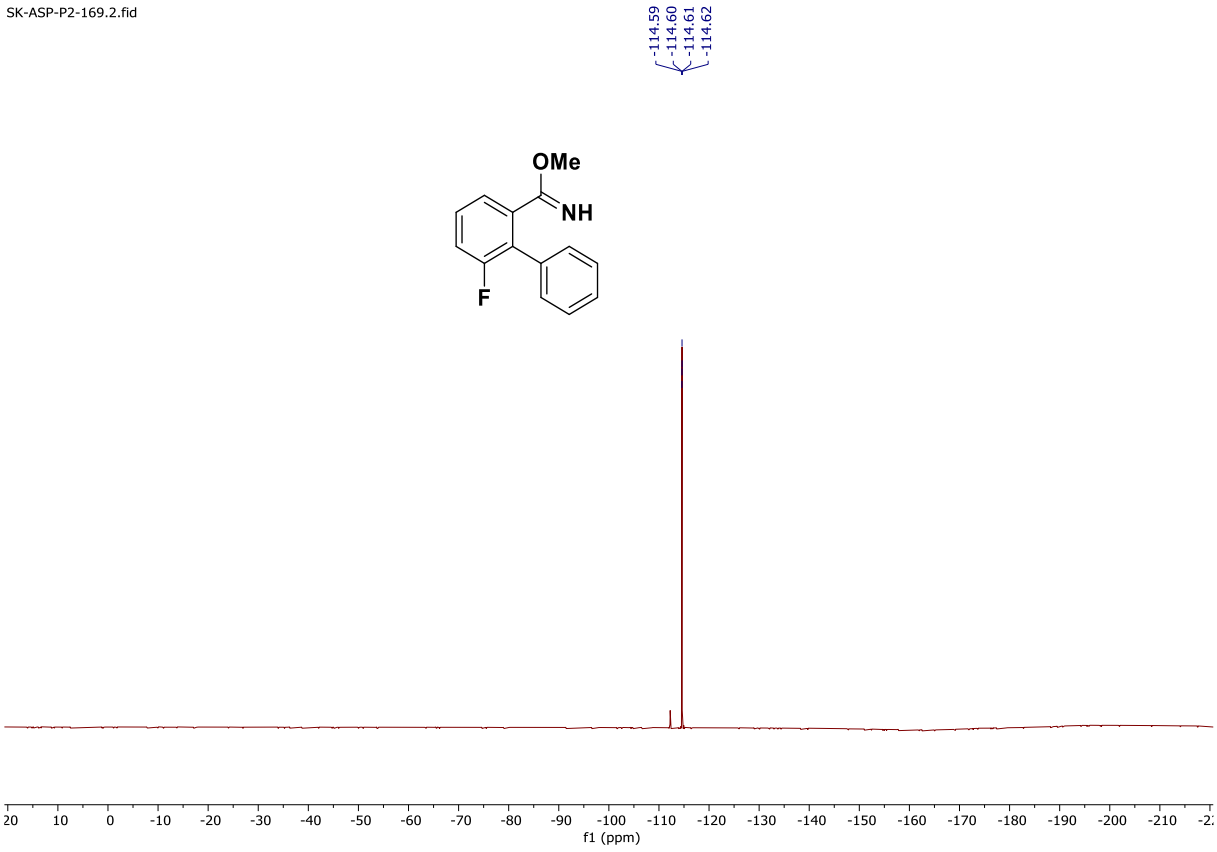
^{1}H NMR spectrum of 1t in $CDCl_3$ [500 MHz]



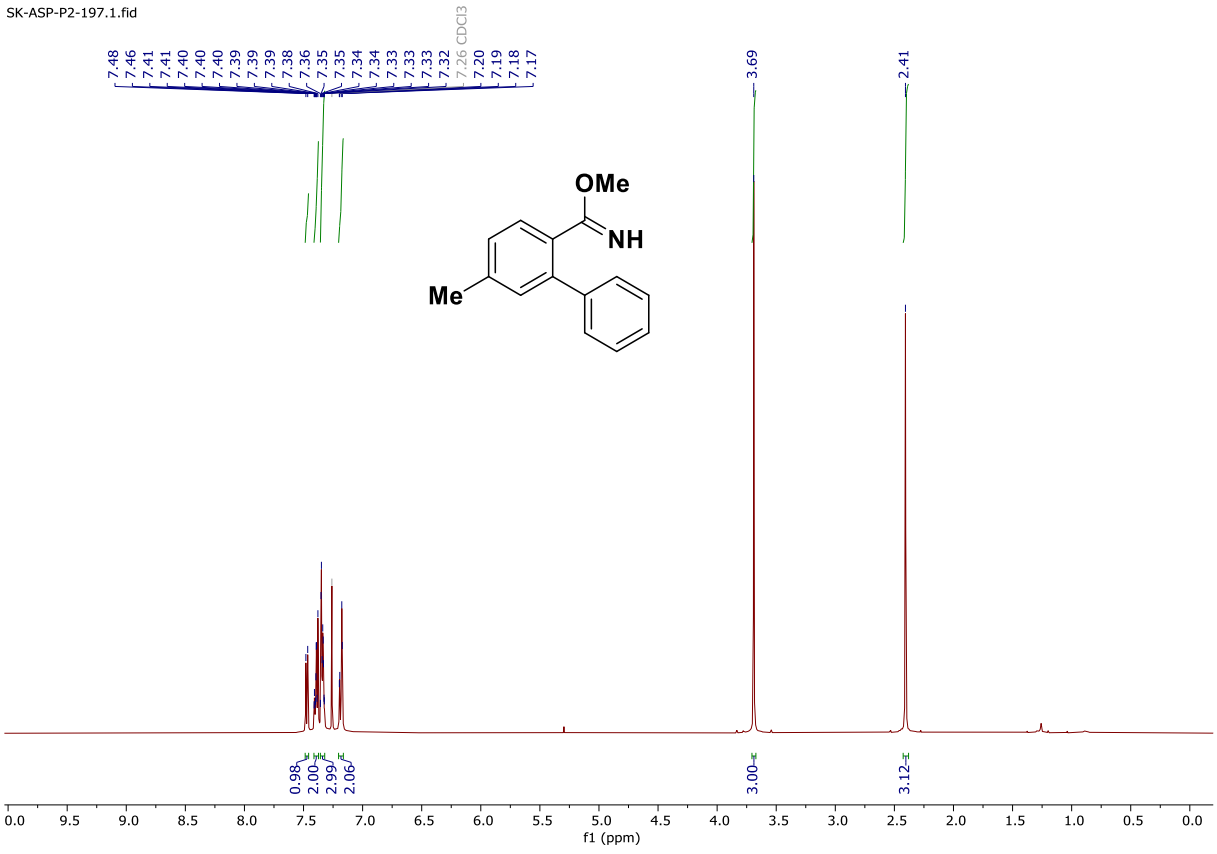
^{13}C{^{1}H} NMR spectrum of 1t in $CDCl_3$ [126 MHz]



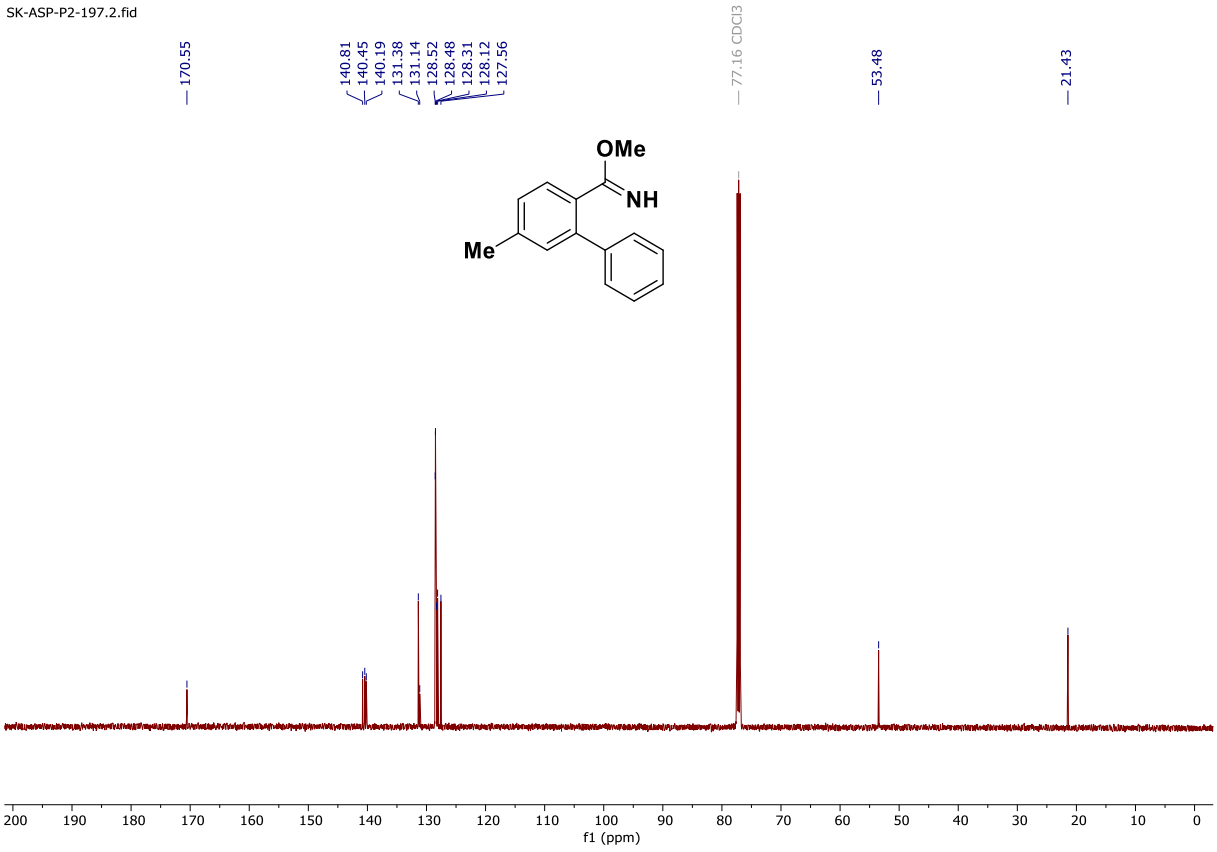
^{19}F NMR spectrum of 1t in $CDCl_3$ [471 MHz]



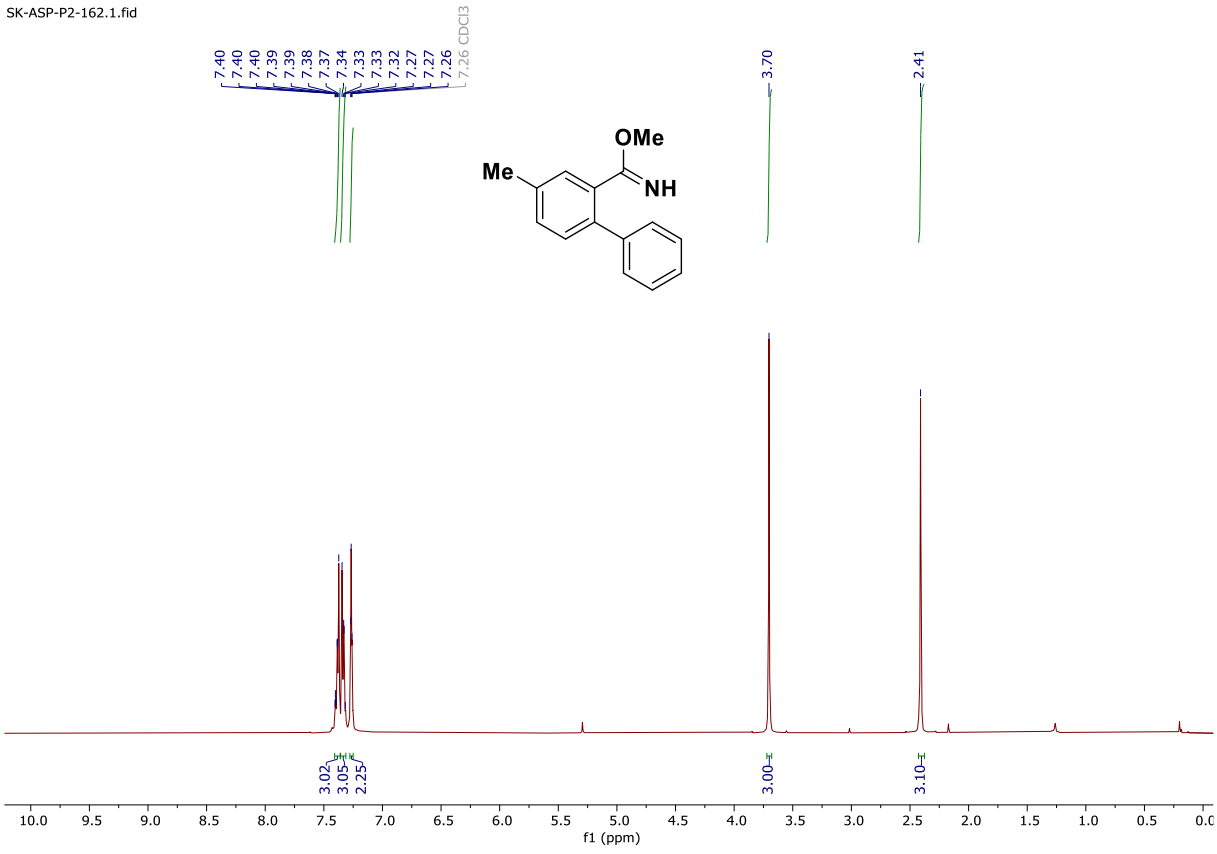
^{1}H NMR spectrum of 1u in $CDCl_3$ [500 MHz]



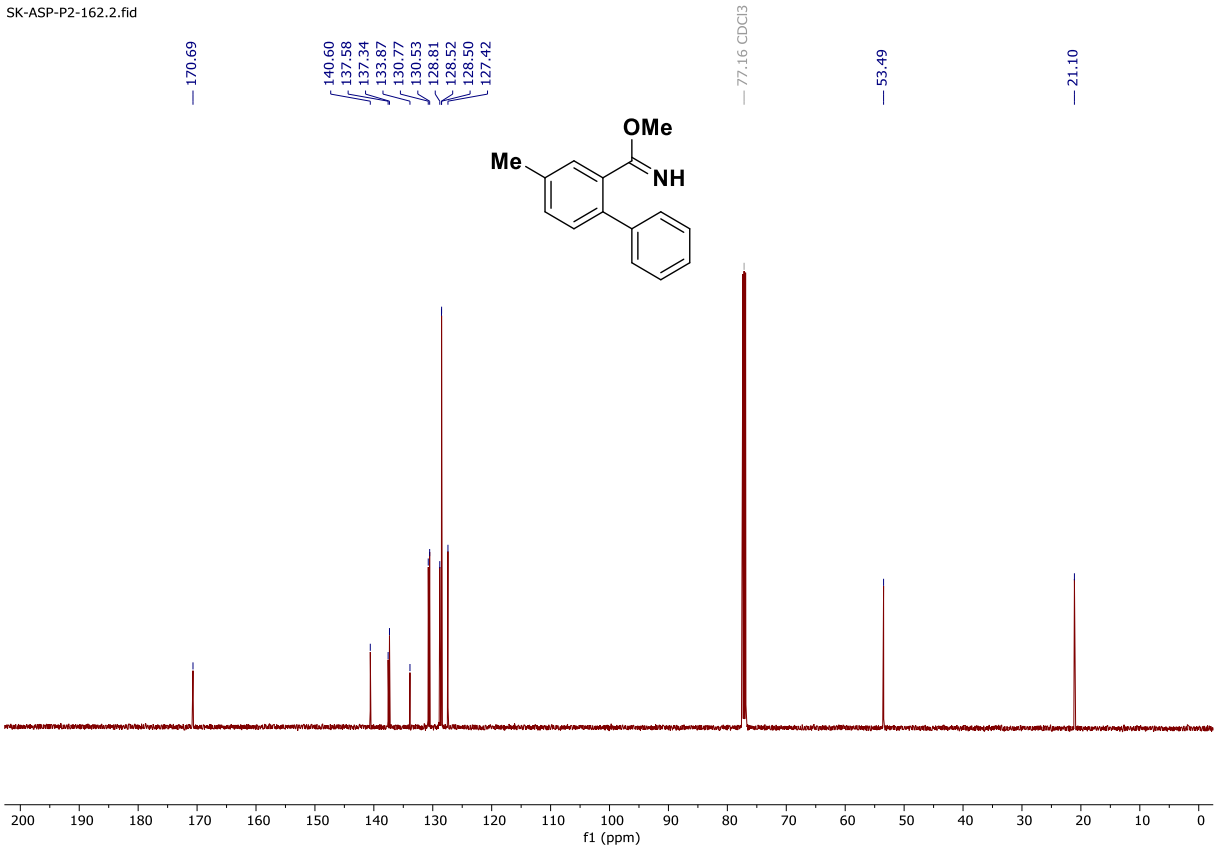
$^{13}C\{^{1}H\}$ NMR spectrum of 1u in $CDCl_3$ [126 MHz]



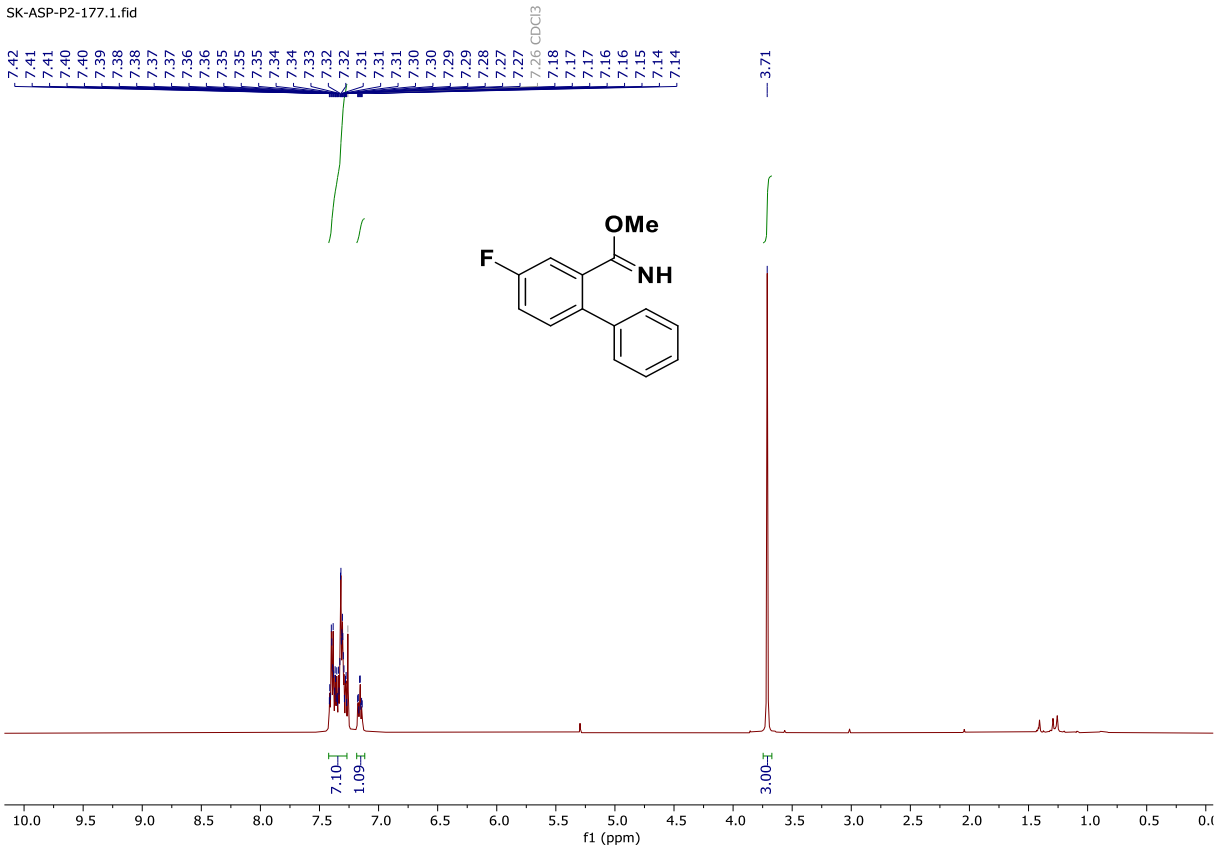
^{1}H NMR spectrum of 1v in $CDCl_3$ [500 MHz]



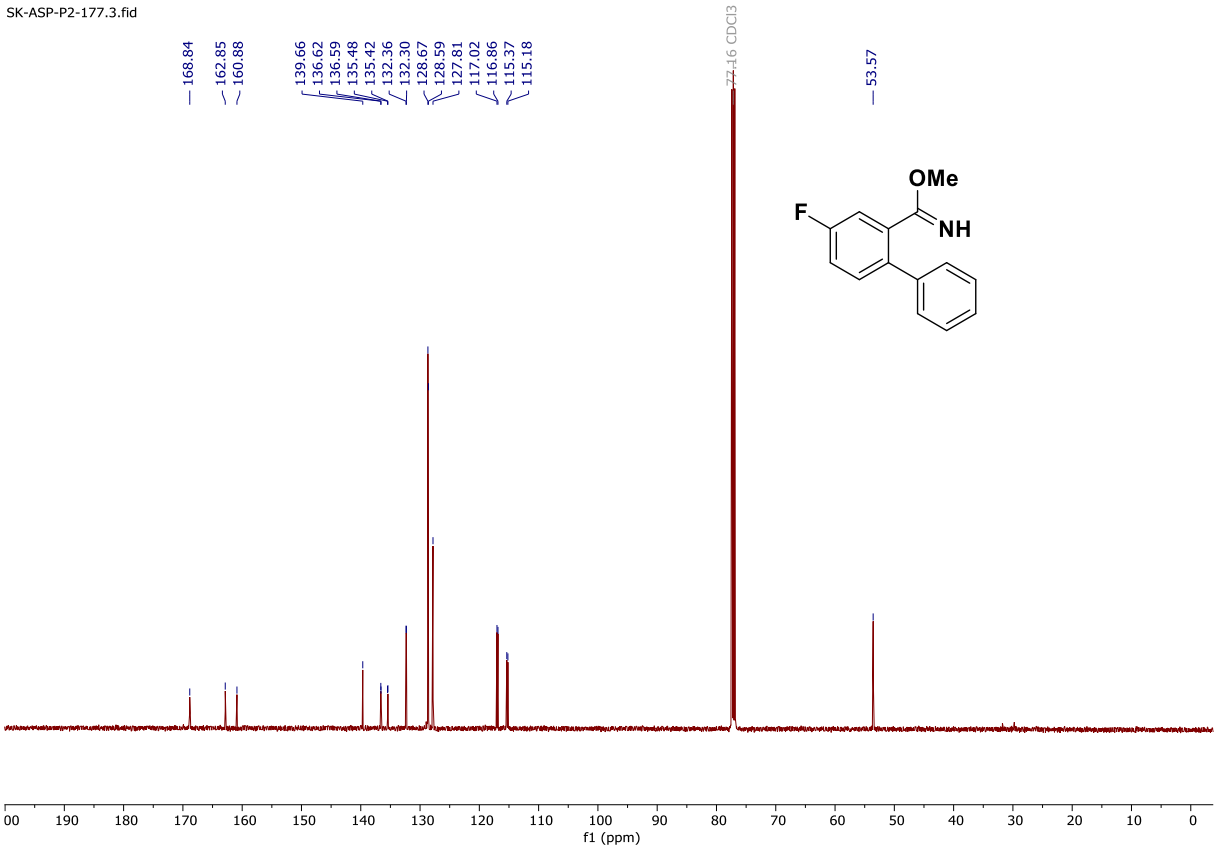
$^{13}C\{^{1}H\}$ NMR spectrum of 1v in $CDCl_3$ [126 MHz]



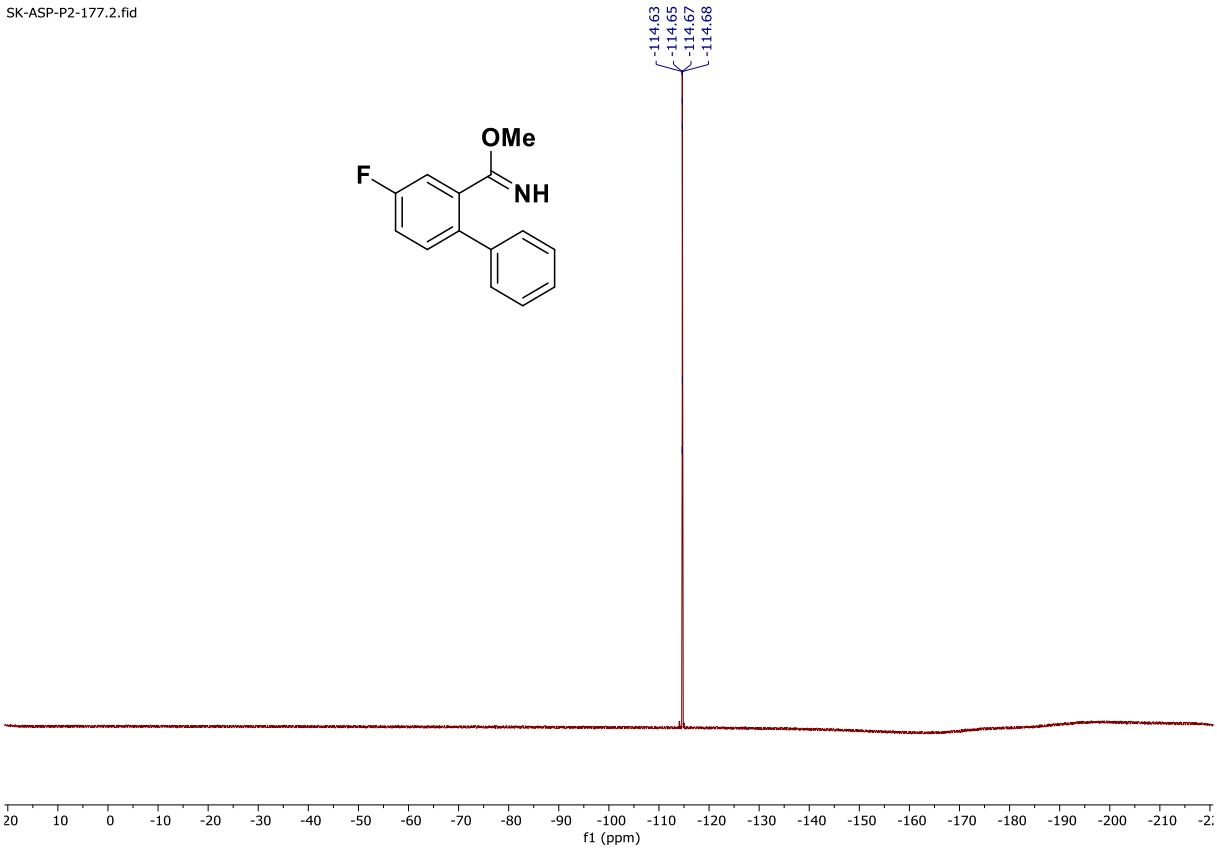
^{1}H NMR spectrum of 1w in $CDCl_3$ [500 MHz]



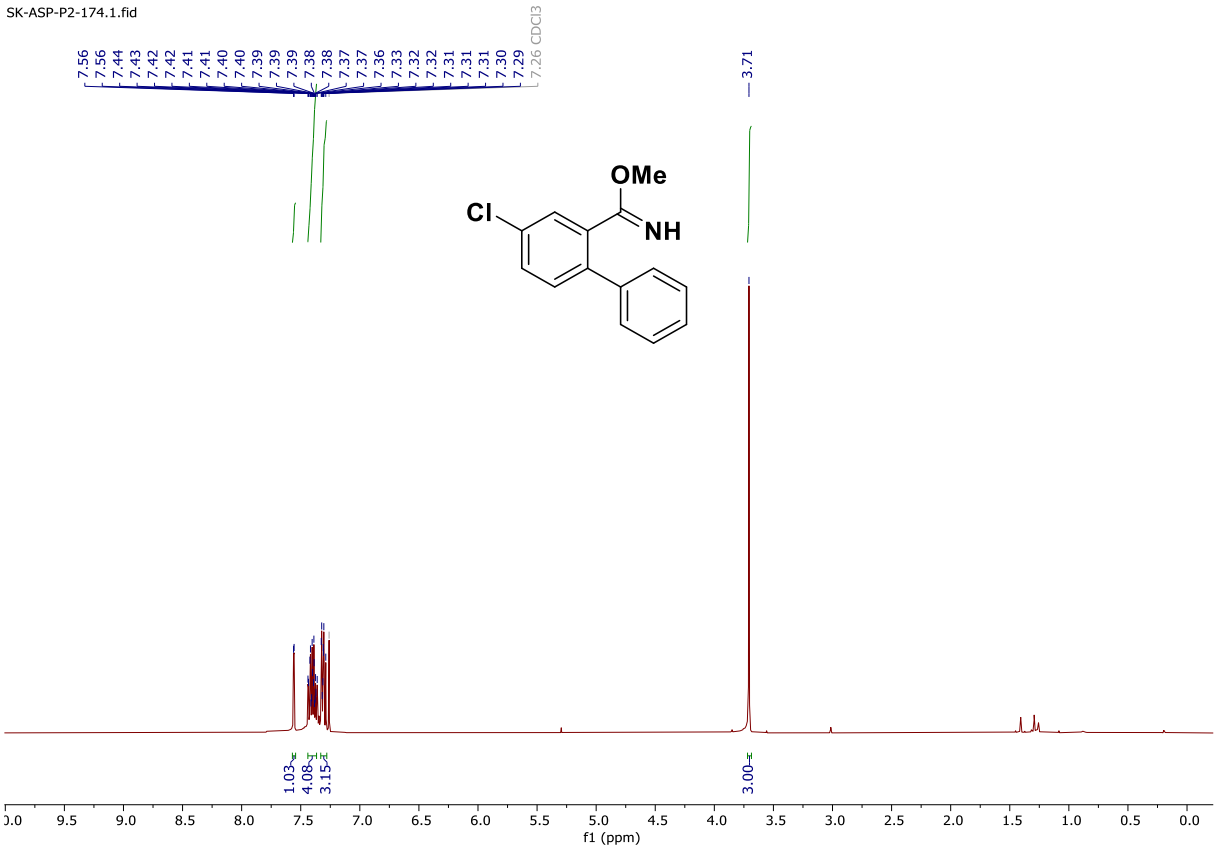
$^{13}C\{^{1}H\}$ NMR spectrum of 1w in $CDCl_3$ [126 MHz]



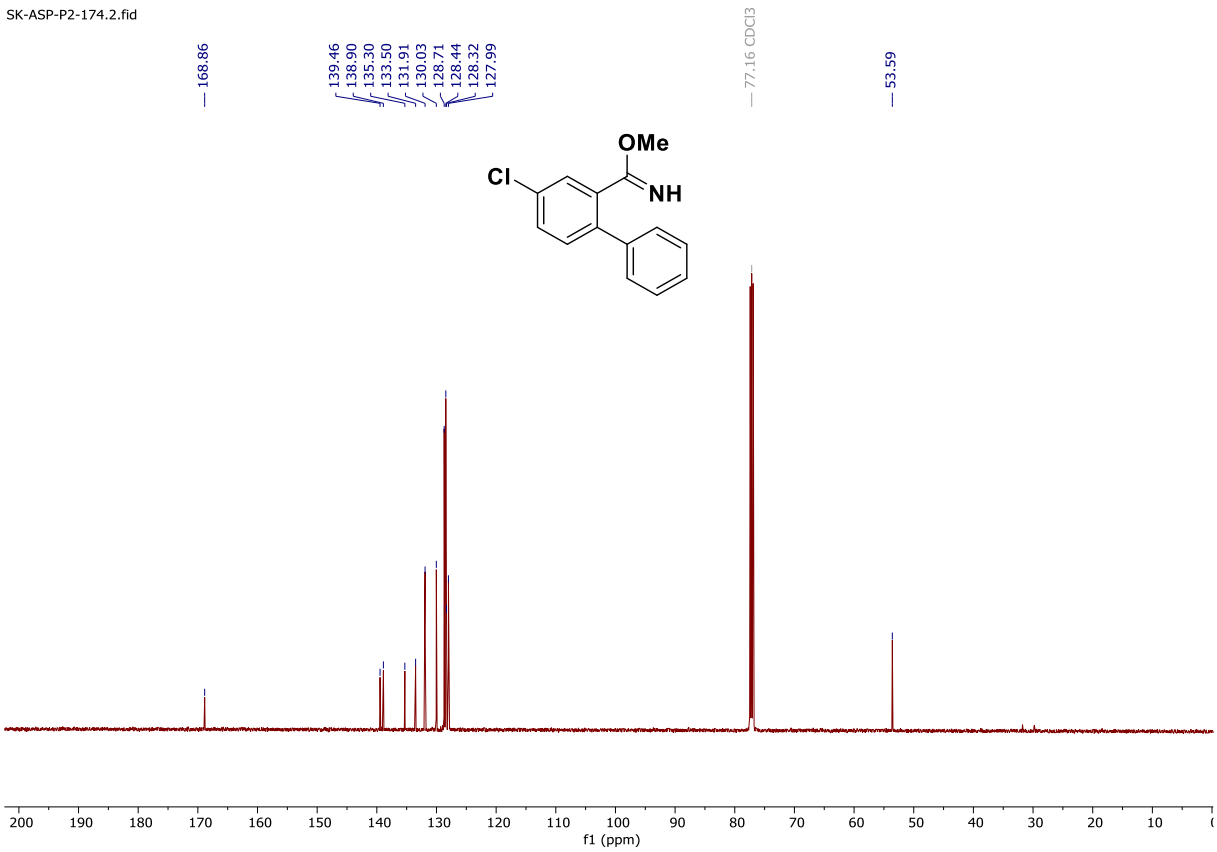
^{19}F NMR spectrum of 1w in $CDCl_3$ [471 MHz]



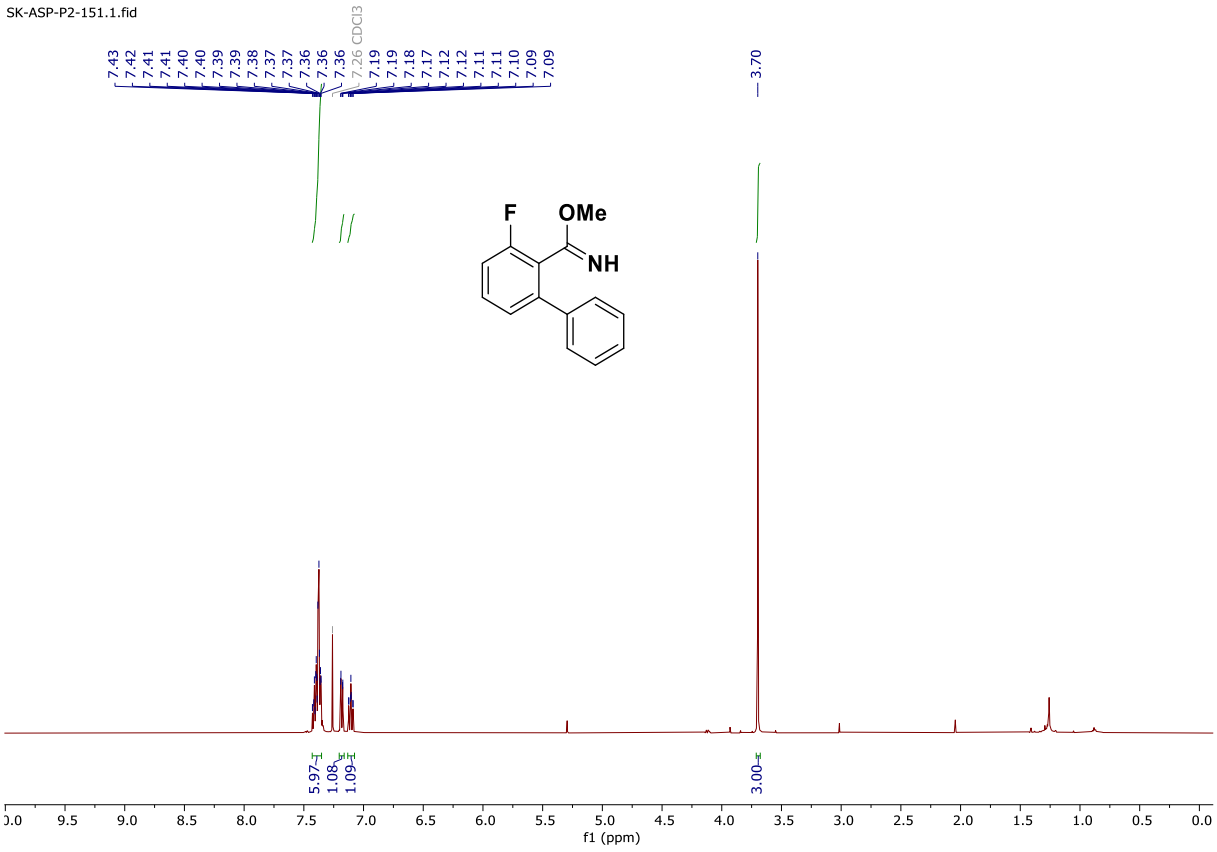
^{1}H NMR spectrum of 1x in $CDCl_3$ [500 MHz]



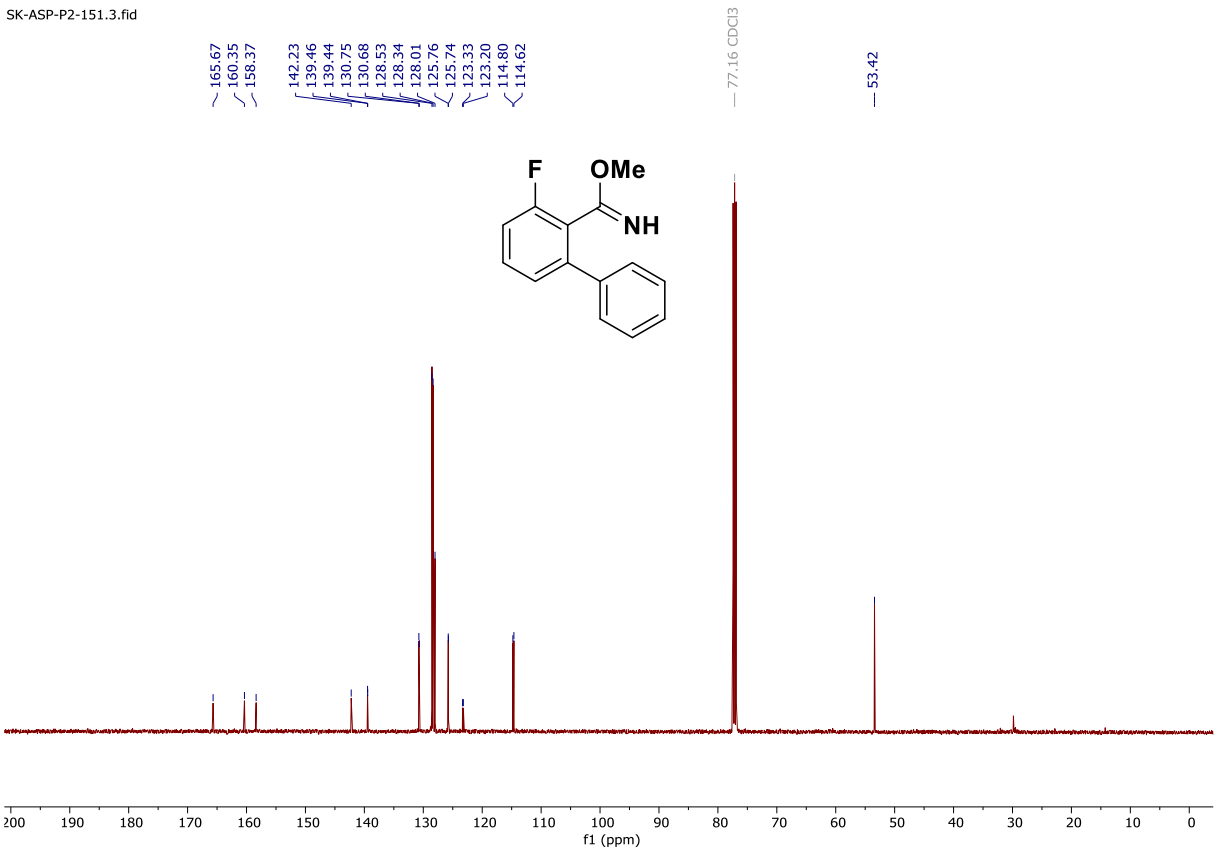
^{13}C{^{1}H} NMR spectrum of 1x in $CDCl_3$ [126 MHz]



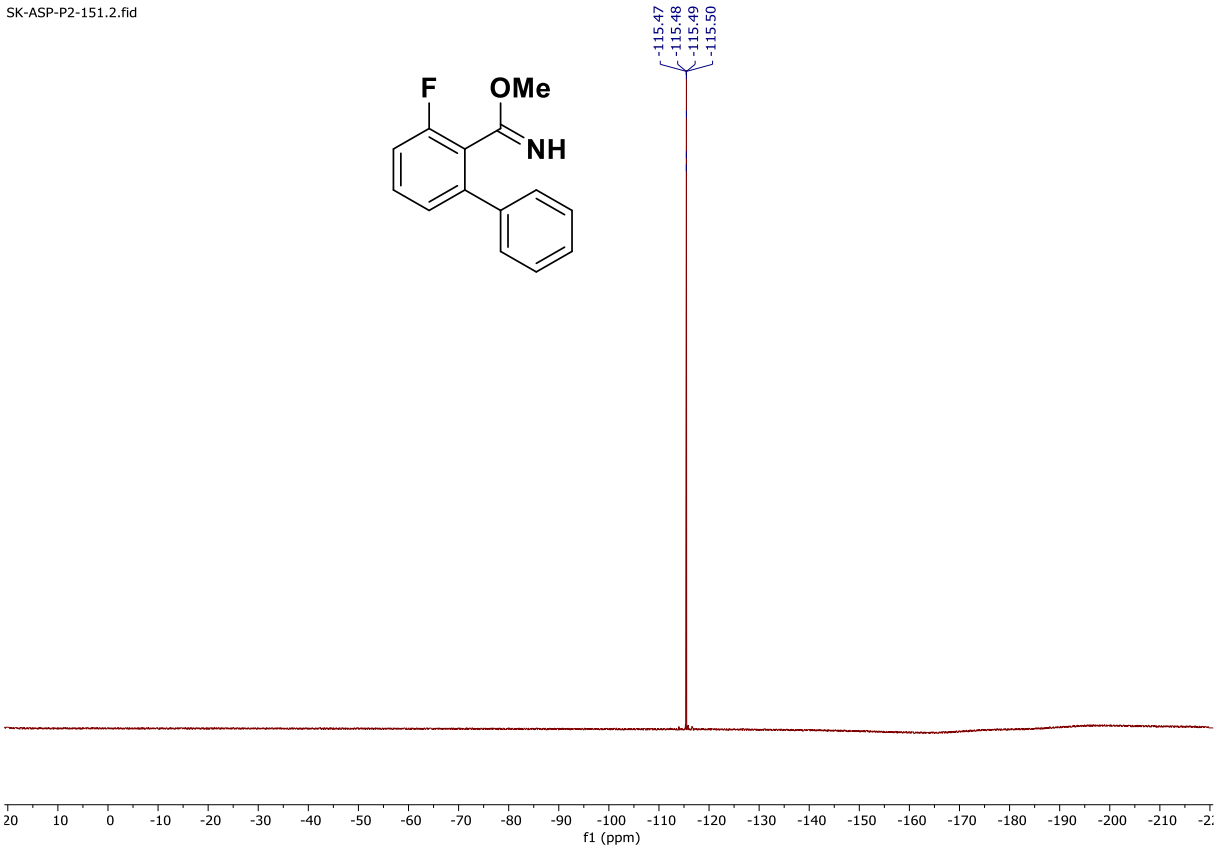
^{1}H NMR spectrum of 1y in $CDCl_3$ [500 MHz]



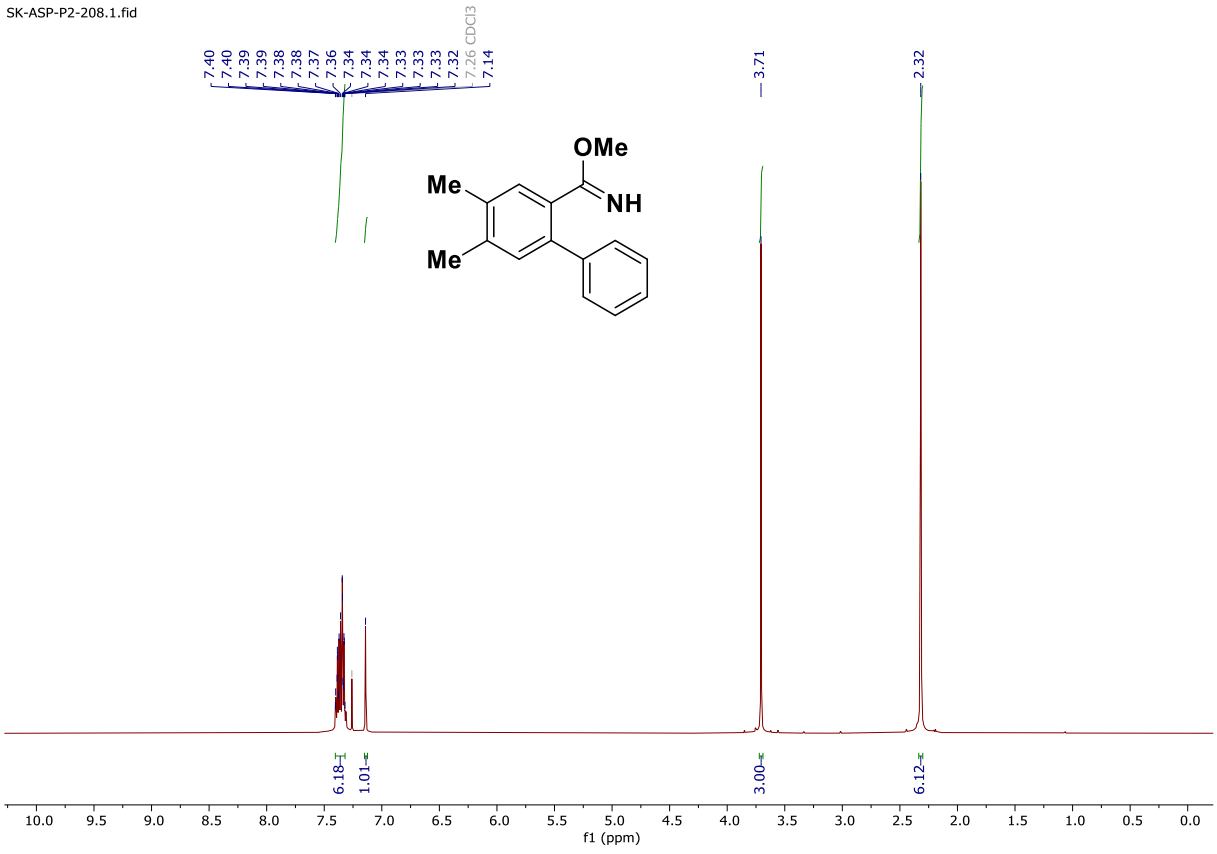
^{13}C{^{1}H} NMR spectrum of 1y in $CDCl_3$ [126 MHz]



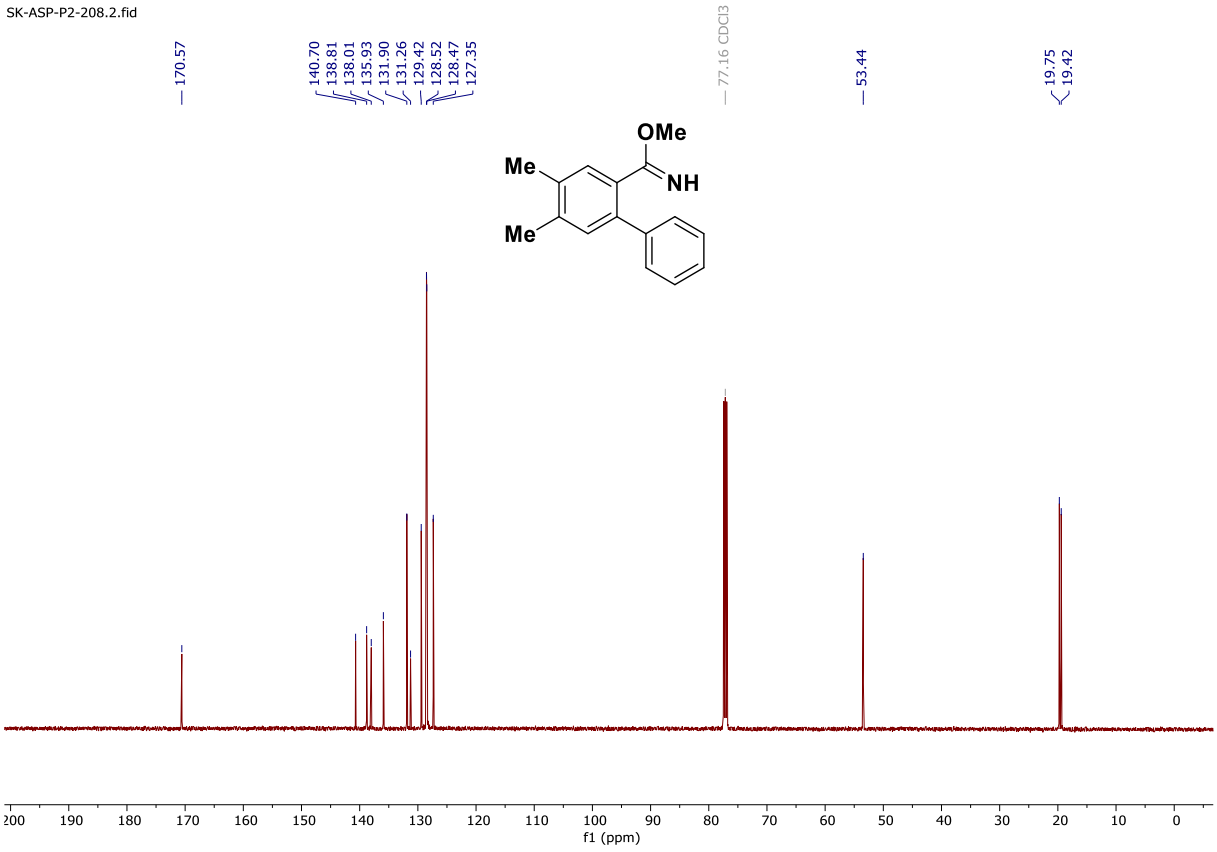
^{19}F NMR spectrum of 1y in $CDCl_3$ [471 MHz]



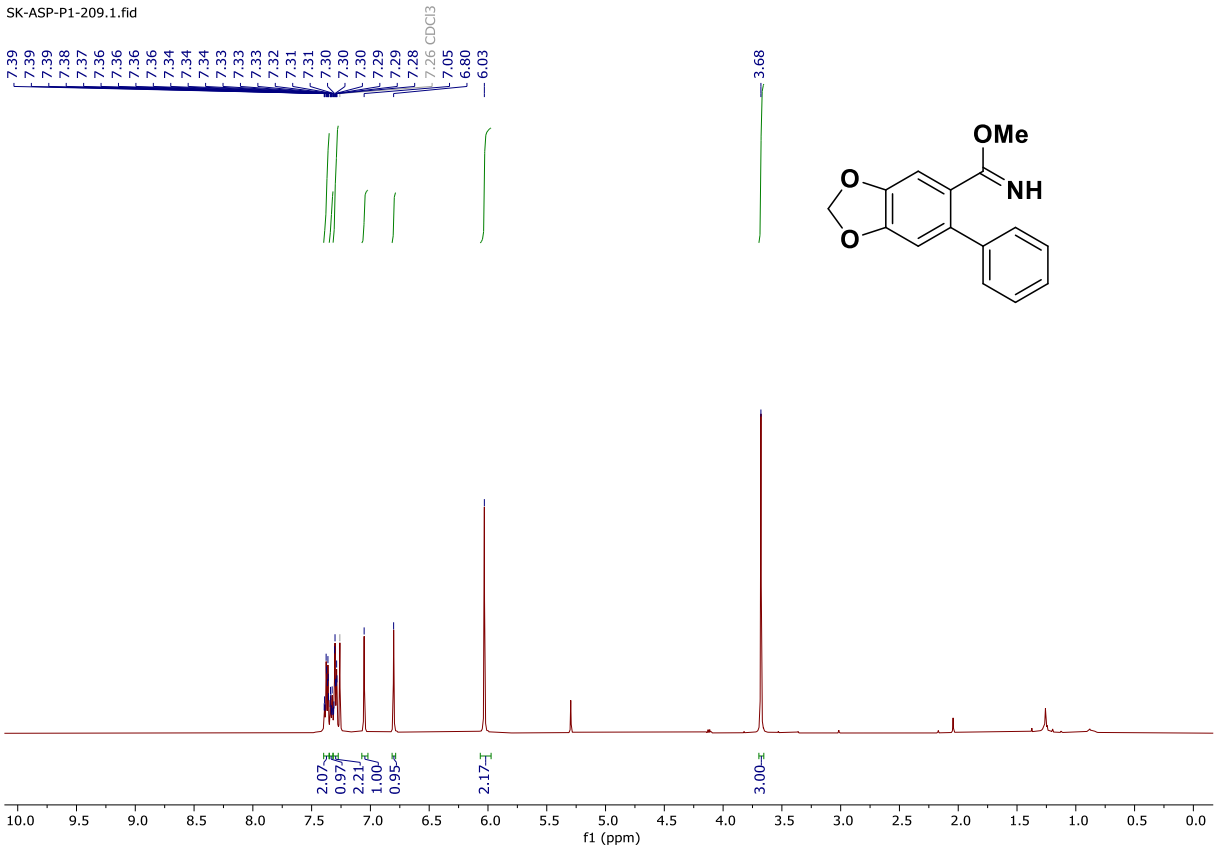
^{1}H NMR spectrum of 1z in $CDCl_3$ [500 MHz]



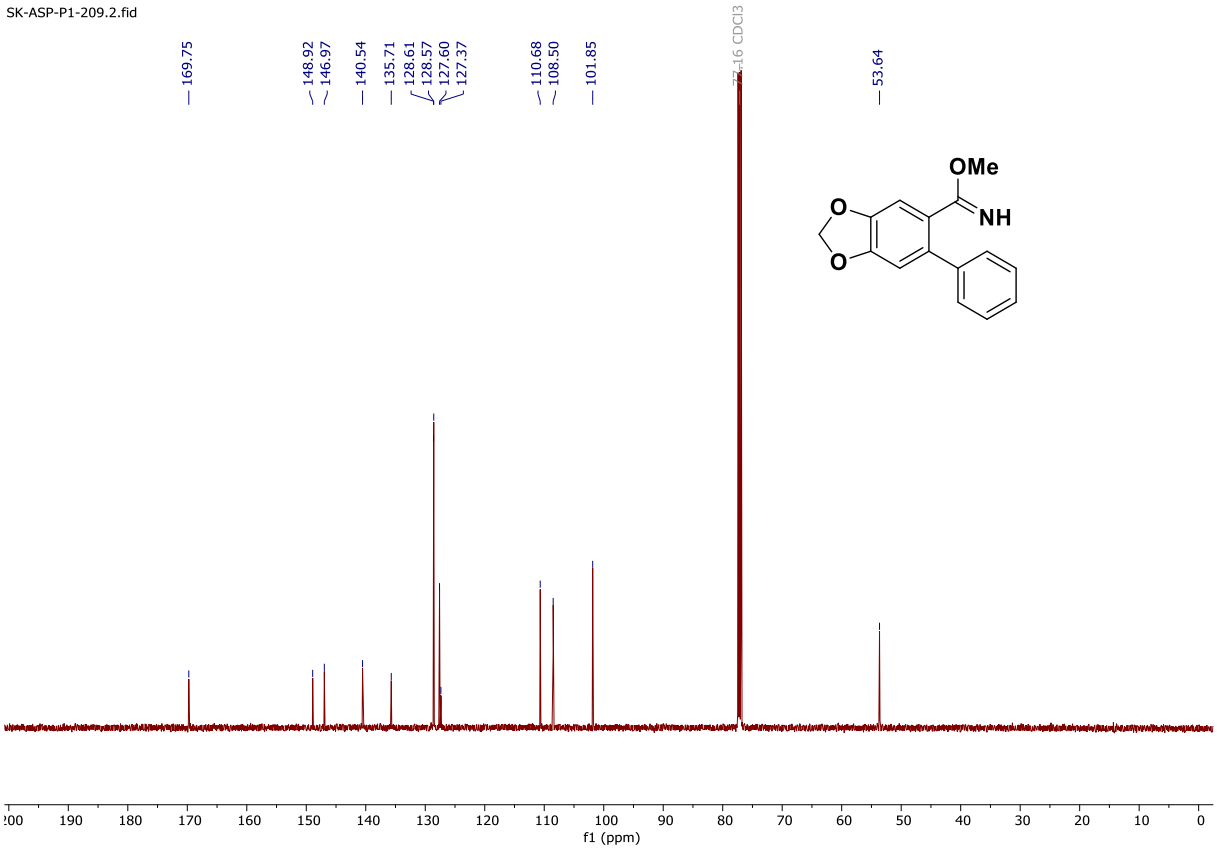
$^{13}C\{^{1}H\}$ NMR spectrum of 1z in $CDCl_3$ [126 MHz]



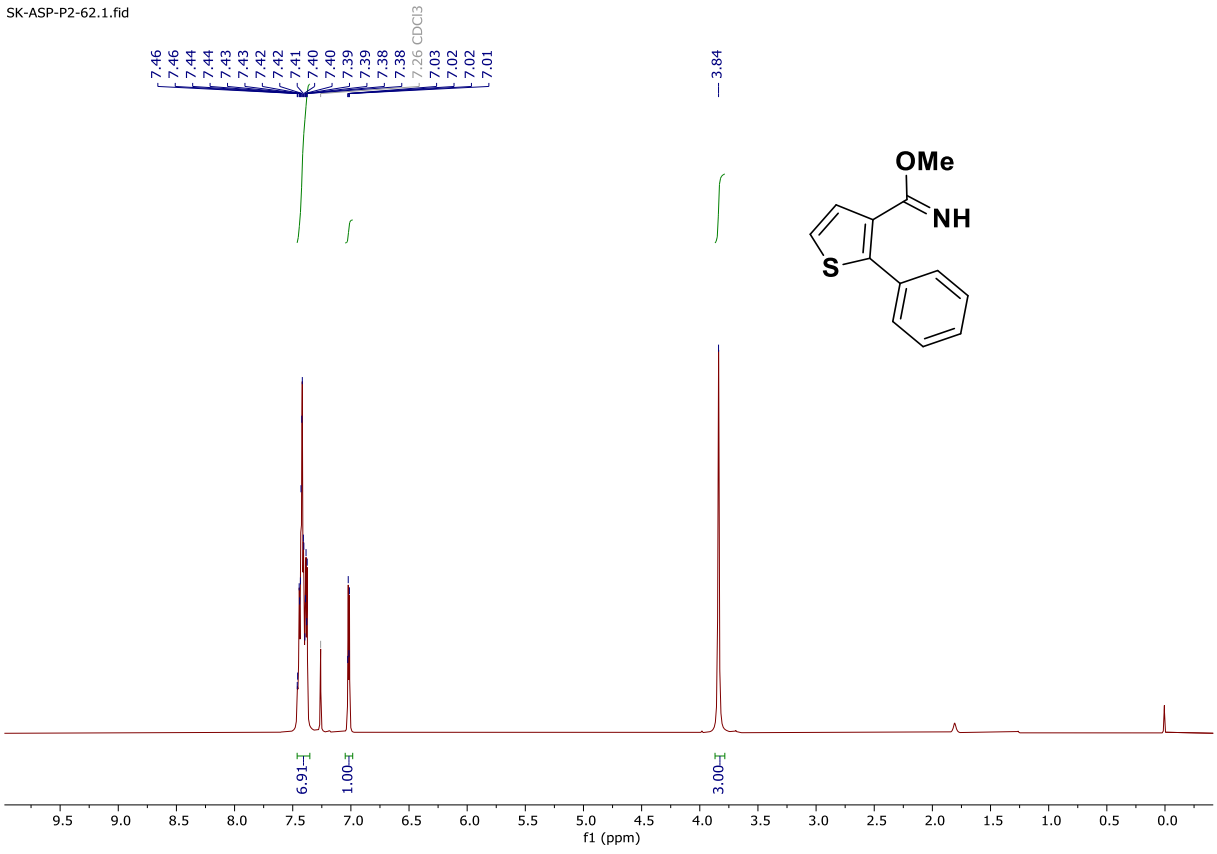
^{1}H NMR spectrum of 1aa in $CDCl_3$ [500 MHz]



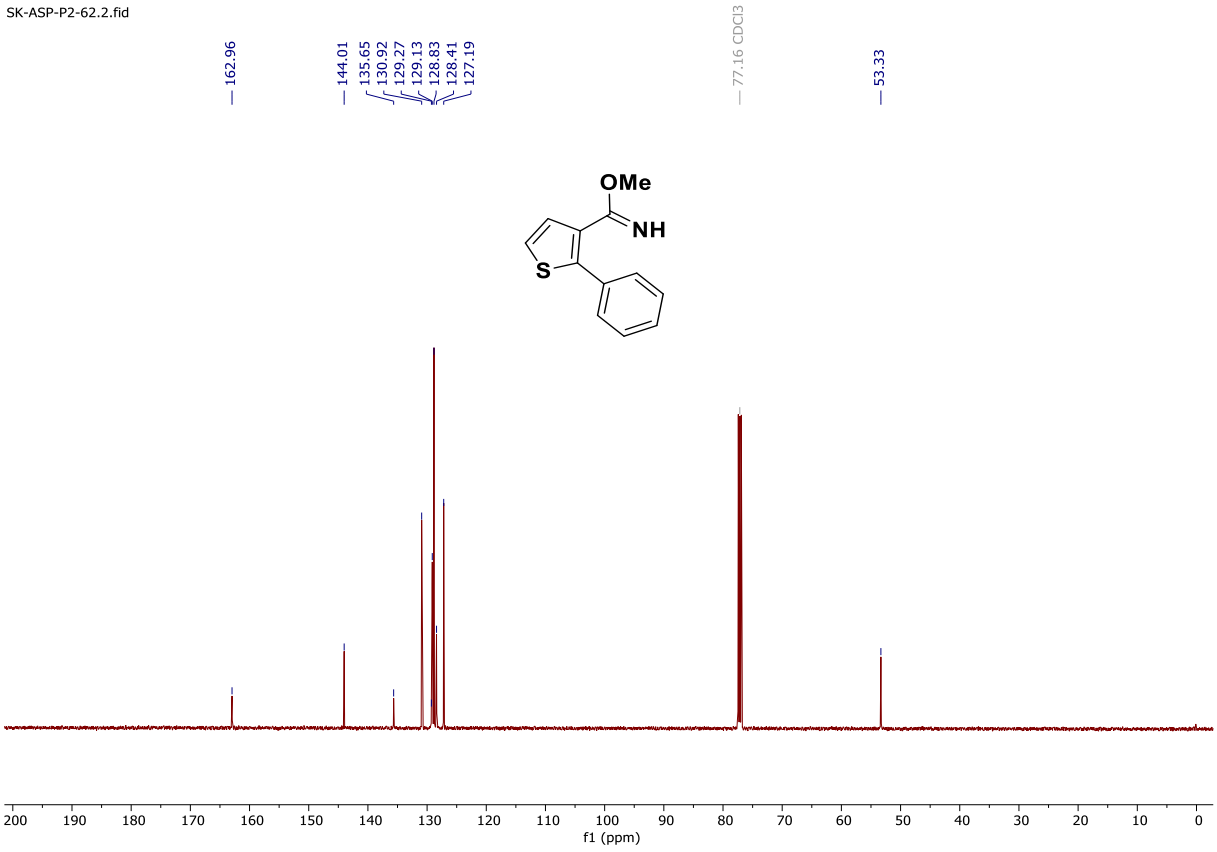
$^{13}C\{^{1}H\}$ NMR spectrum of 1aa in $CDCl_3$ [126 MHz]



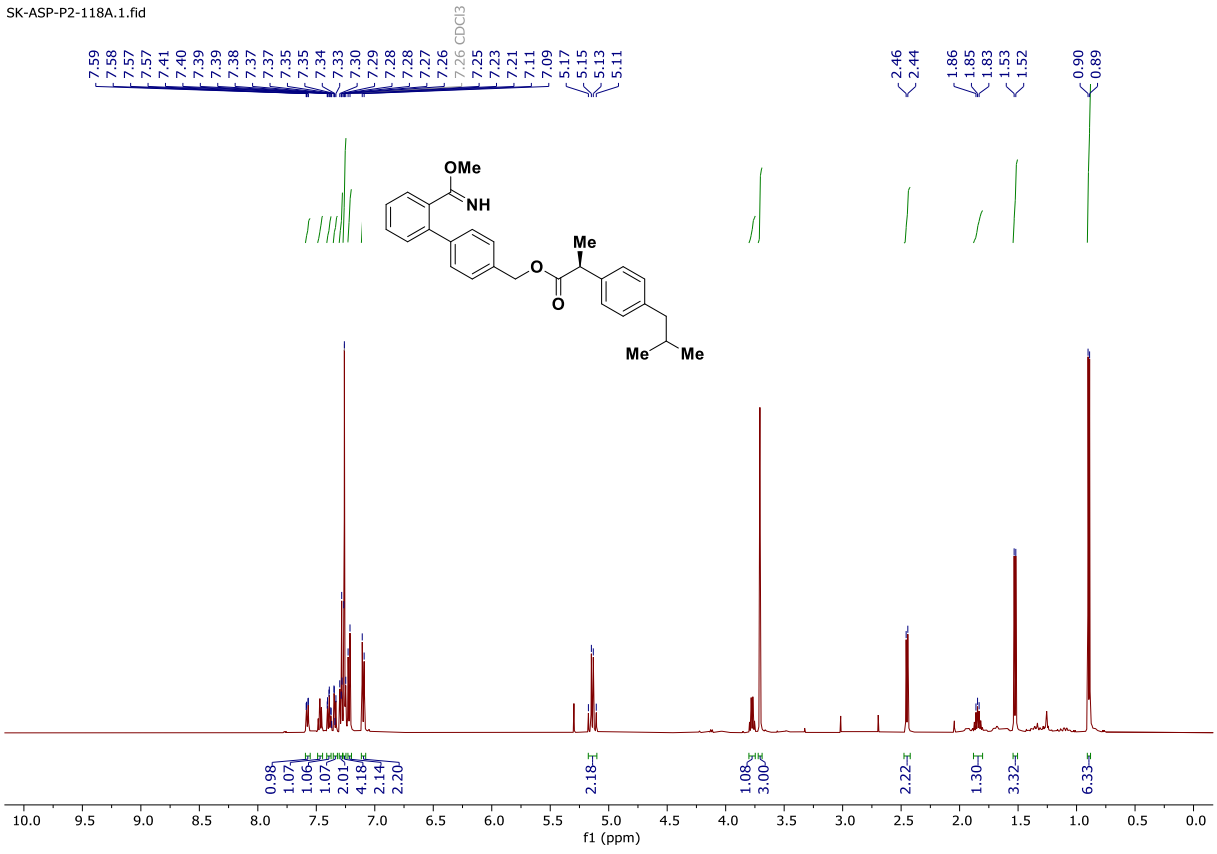
^{1}H NMR spectrum of 1ab in $CDCl_3$ [500 MHz]



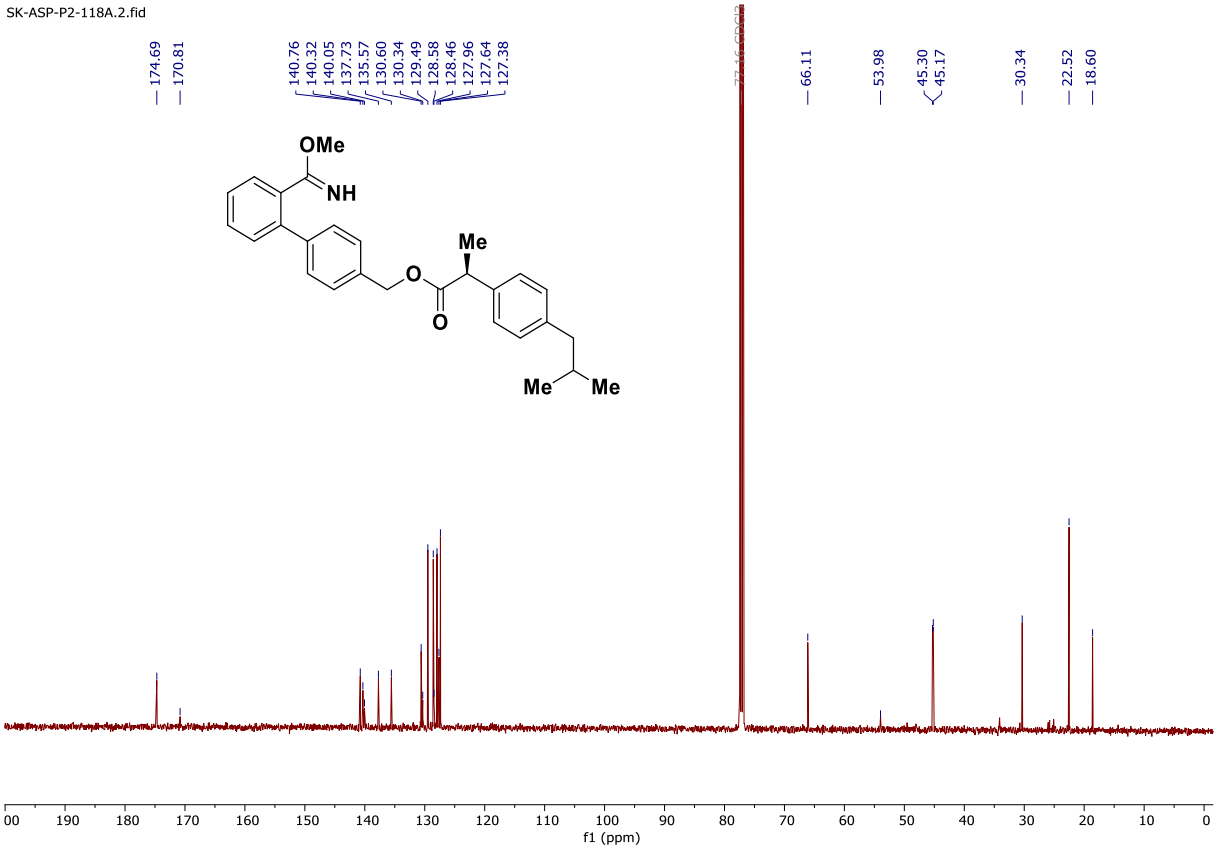
$^{13}C\{^{1}H\}$ NMR spectrum of 1ab in $CDCl_3$ [126 MHz]



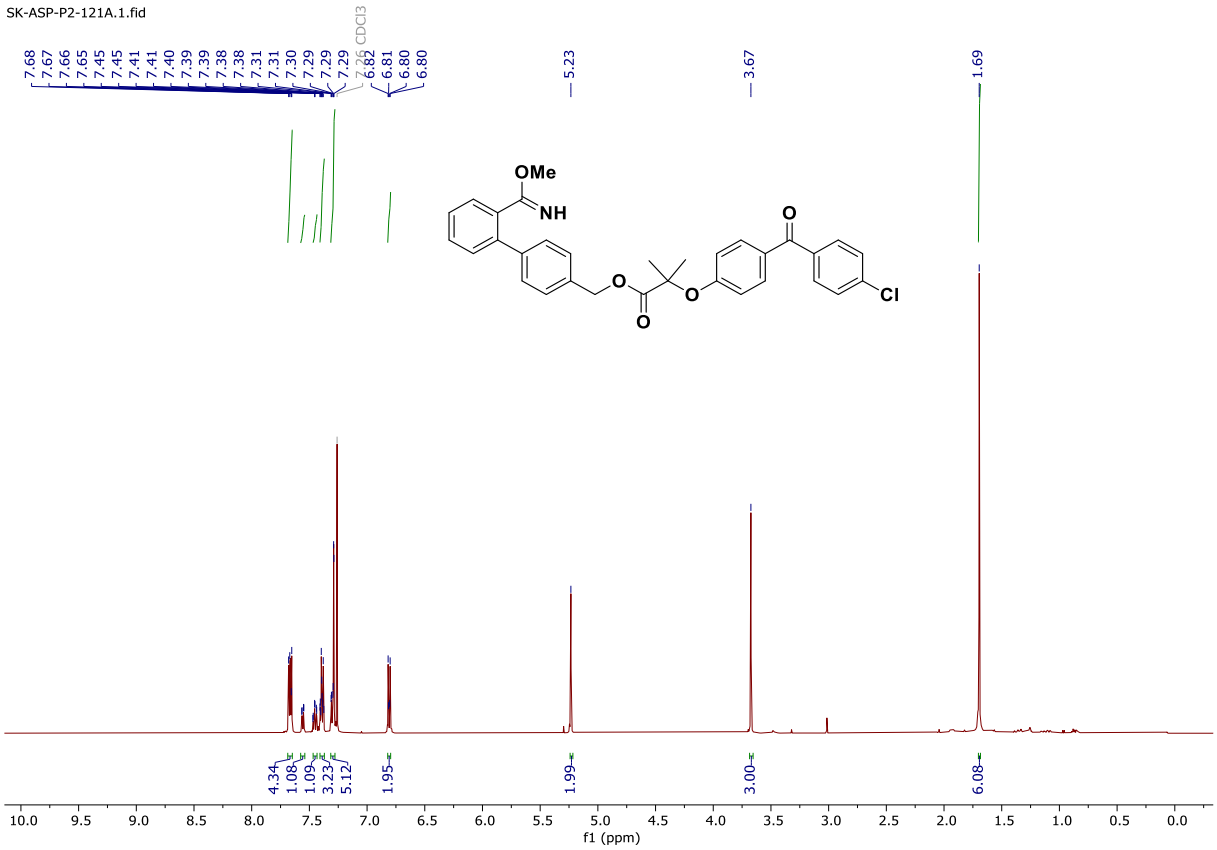
^{1}H NMR spectrum of 1ac in $CDCl_3$ [500 MHz]



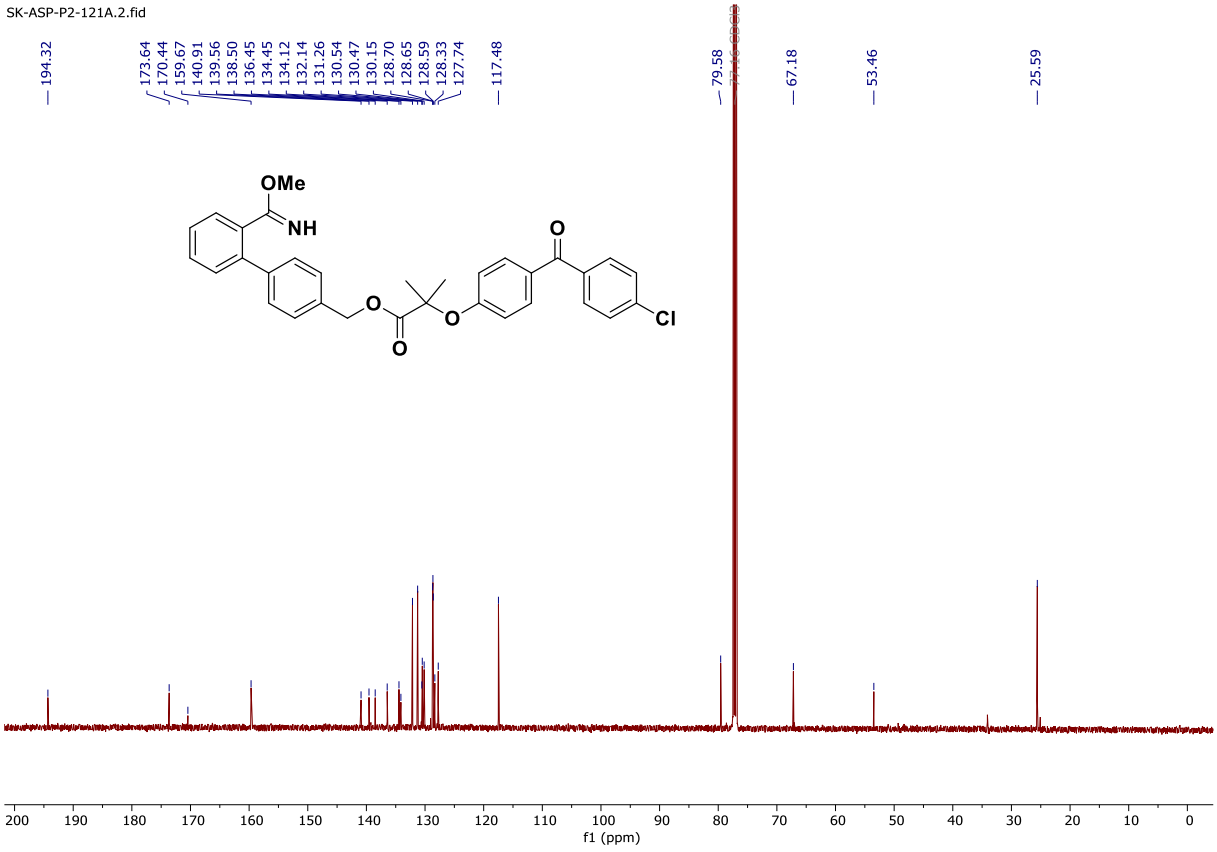
$^{13}C\{^{1}H\}$ NMR spectrum of 1ac in $CDCl_3$ [126 MHz]



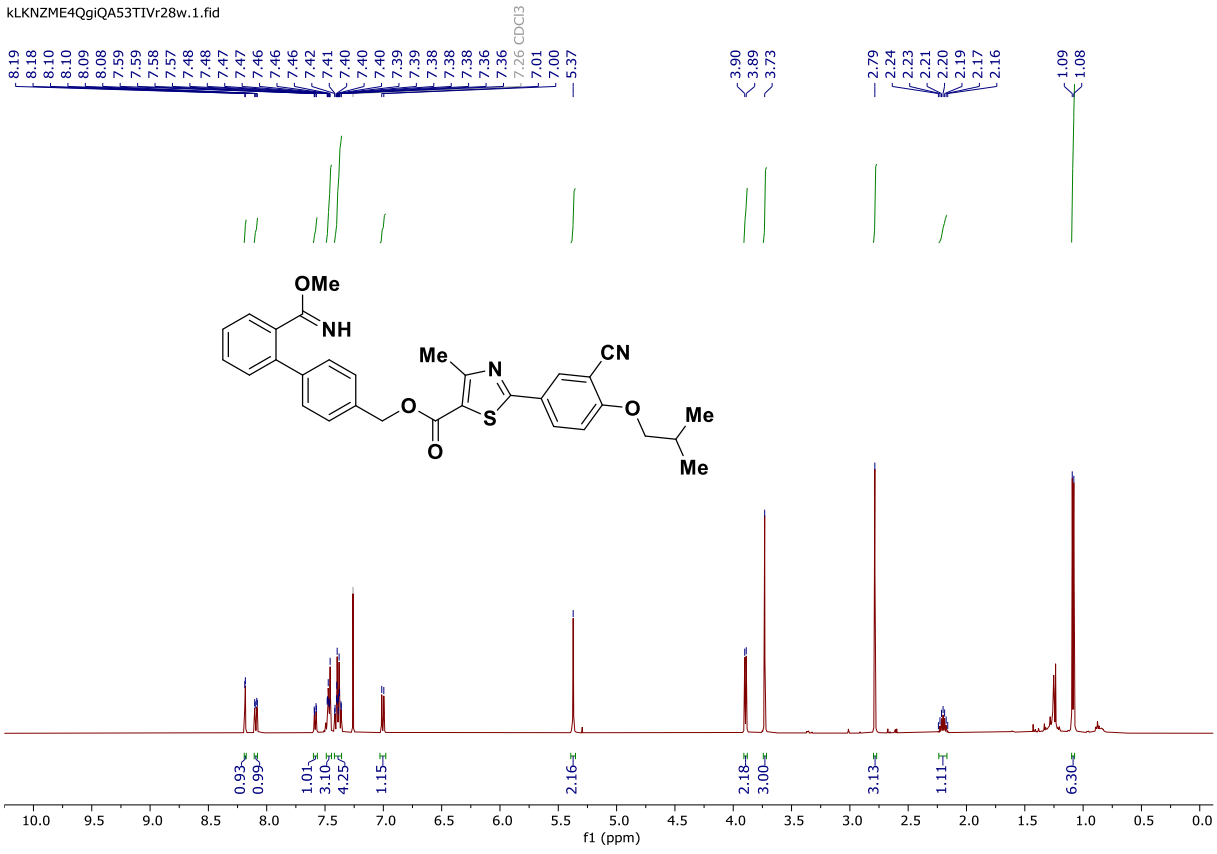
^{1}H NMR spectrum of 1ad in $CDCl_3$ [500 MHz]



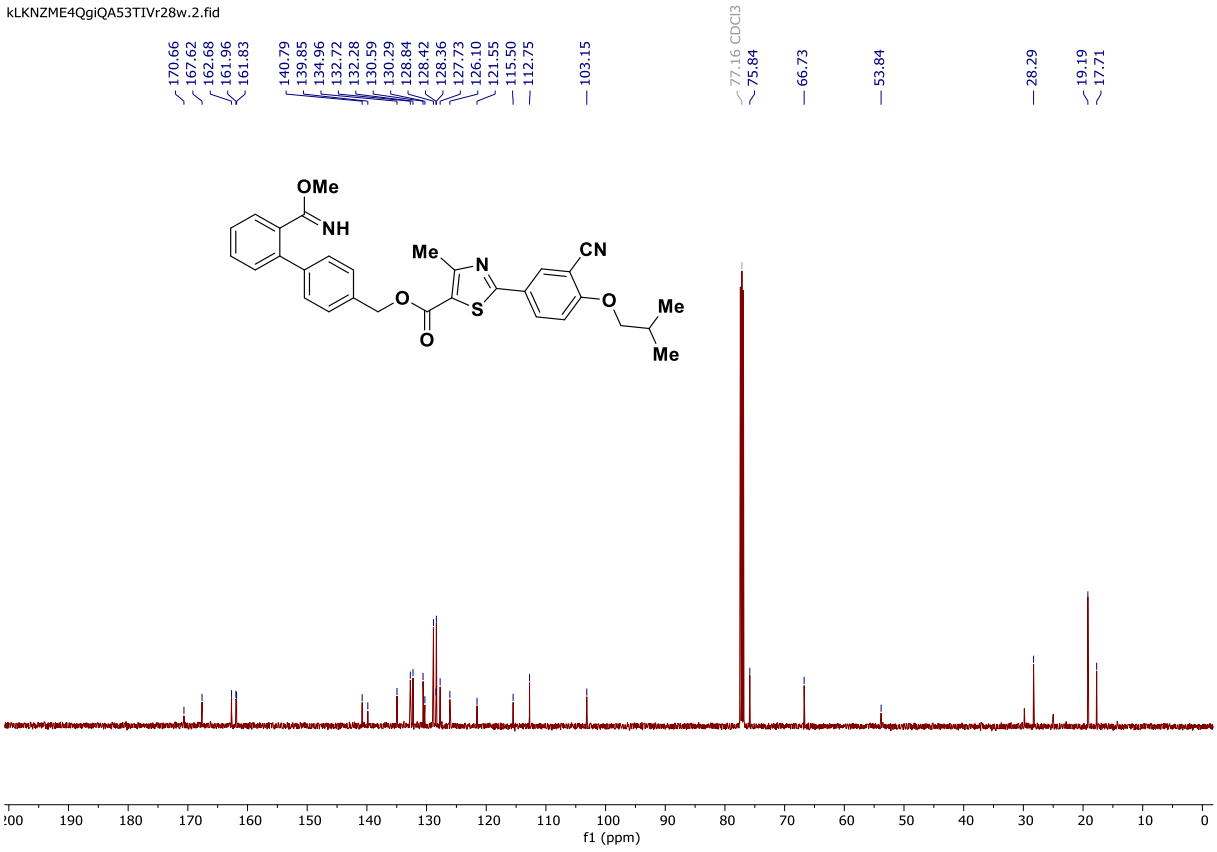
$^{13}C\{^{1}H\}$ NMR spectrum of 1ad in $CDCl_3$ [126 MHz]



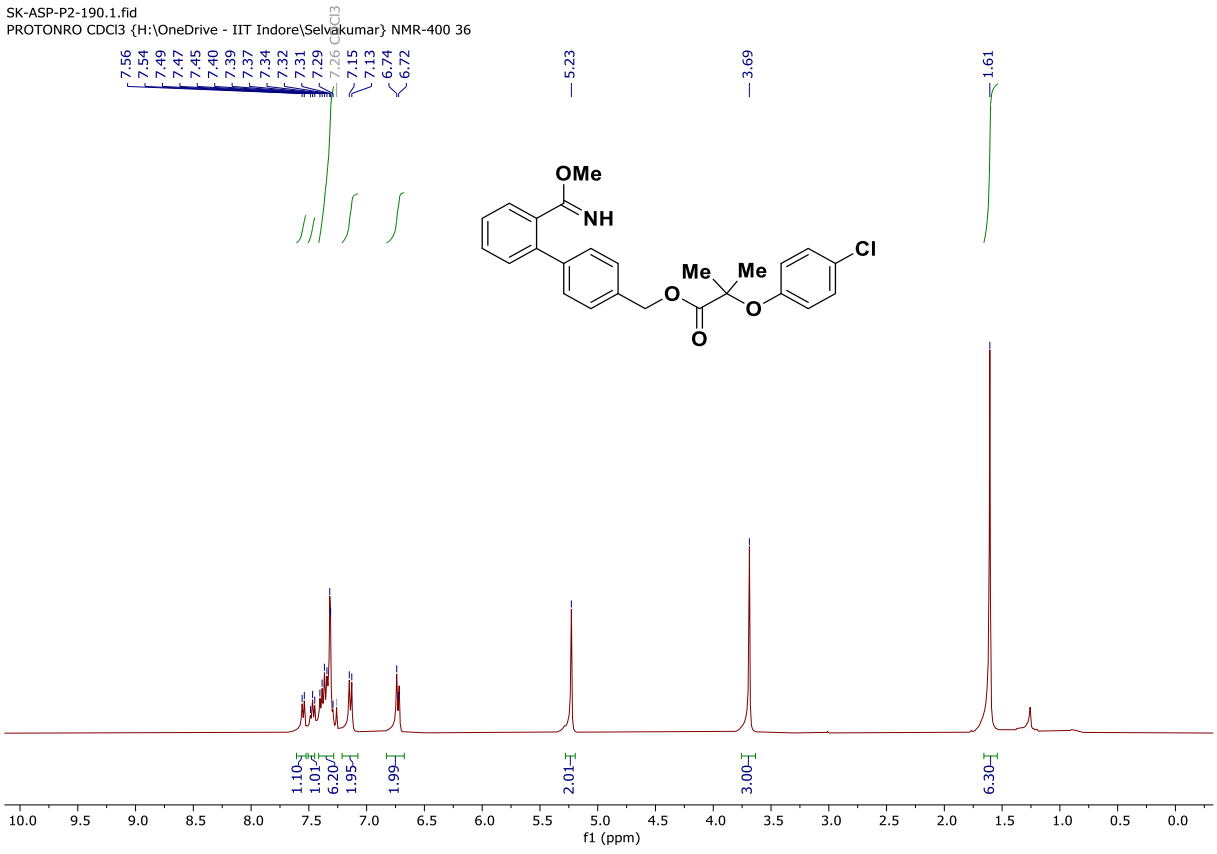
^{1}H NMR spectrum of 1ae in $CDCl_3$ [500 MHz]



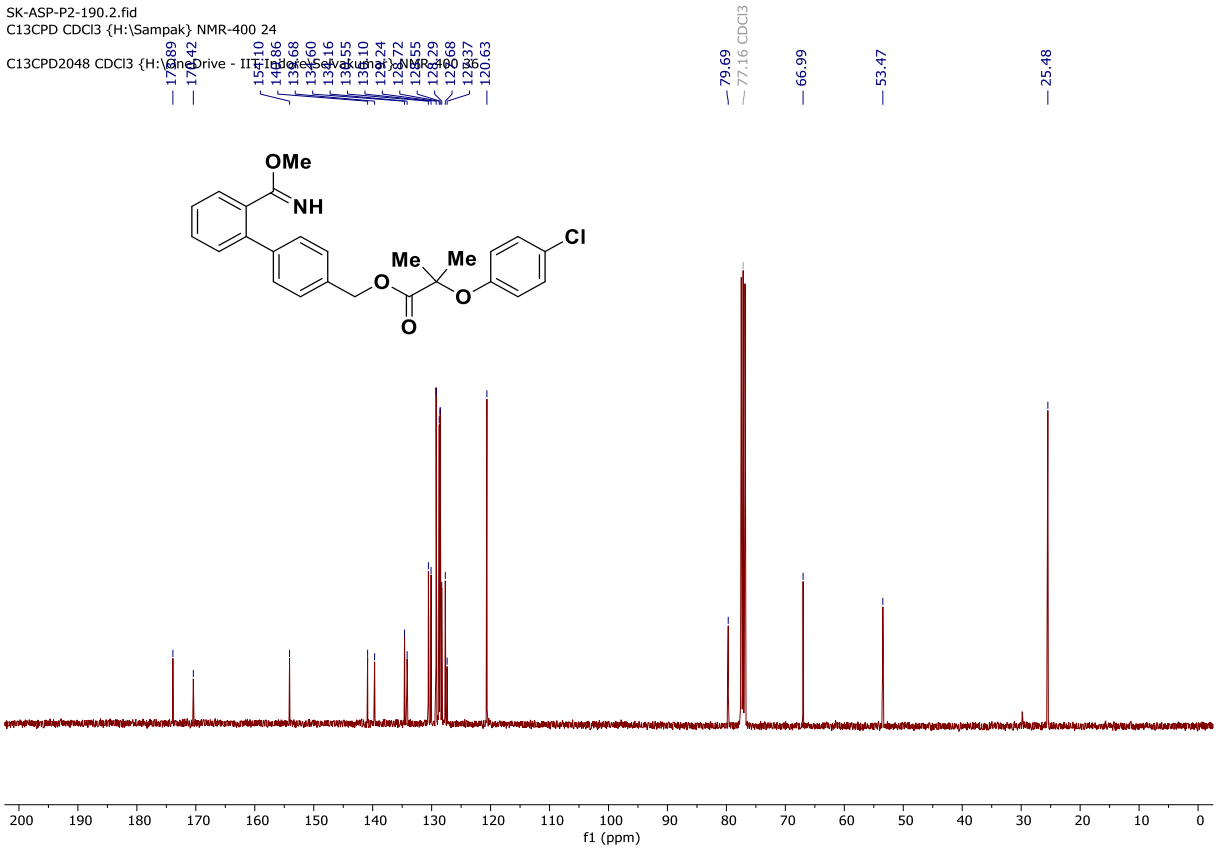
$^{13}C\{^{1}H\}$ NMR spectrum of 1ae in $CDCl_3$ [126 MHz]



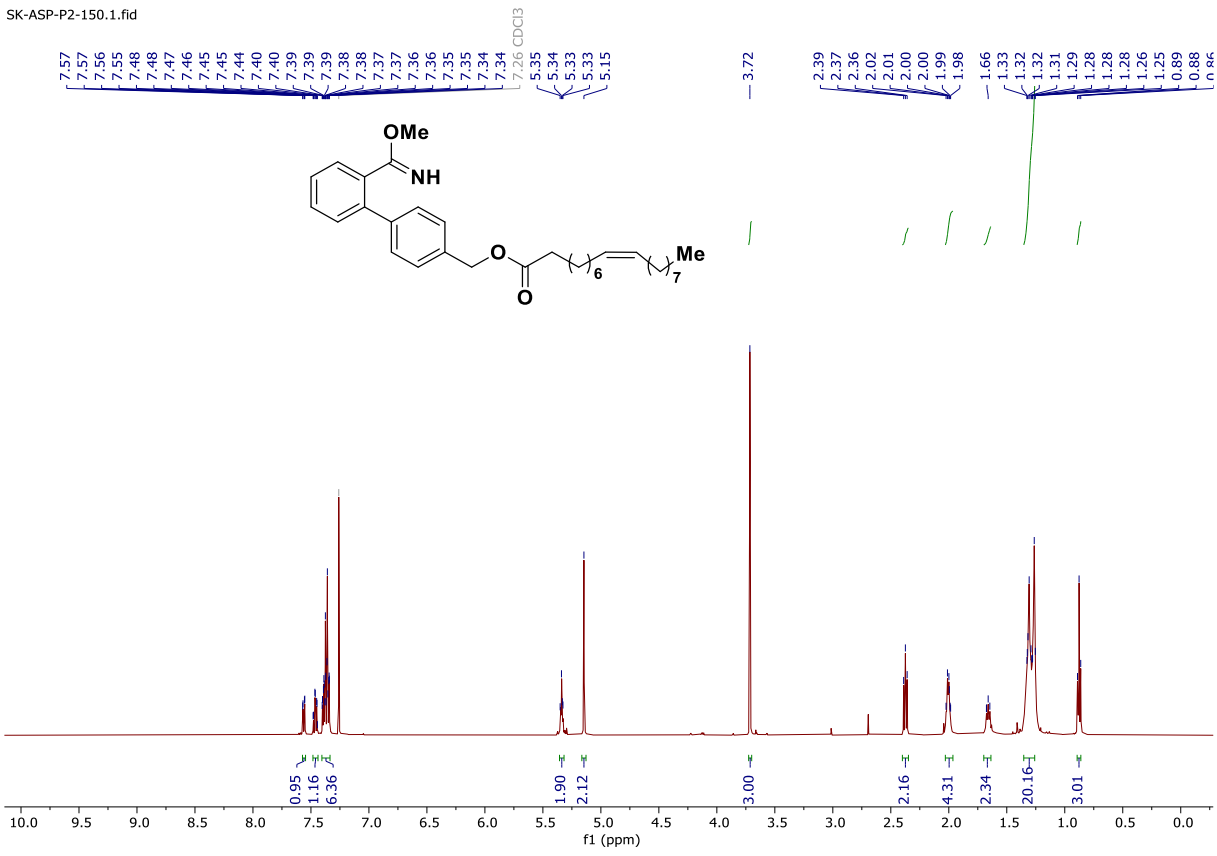
^{1}H NMR spectrum of 1af in $CDCl_3$ [400 MHz]



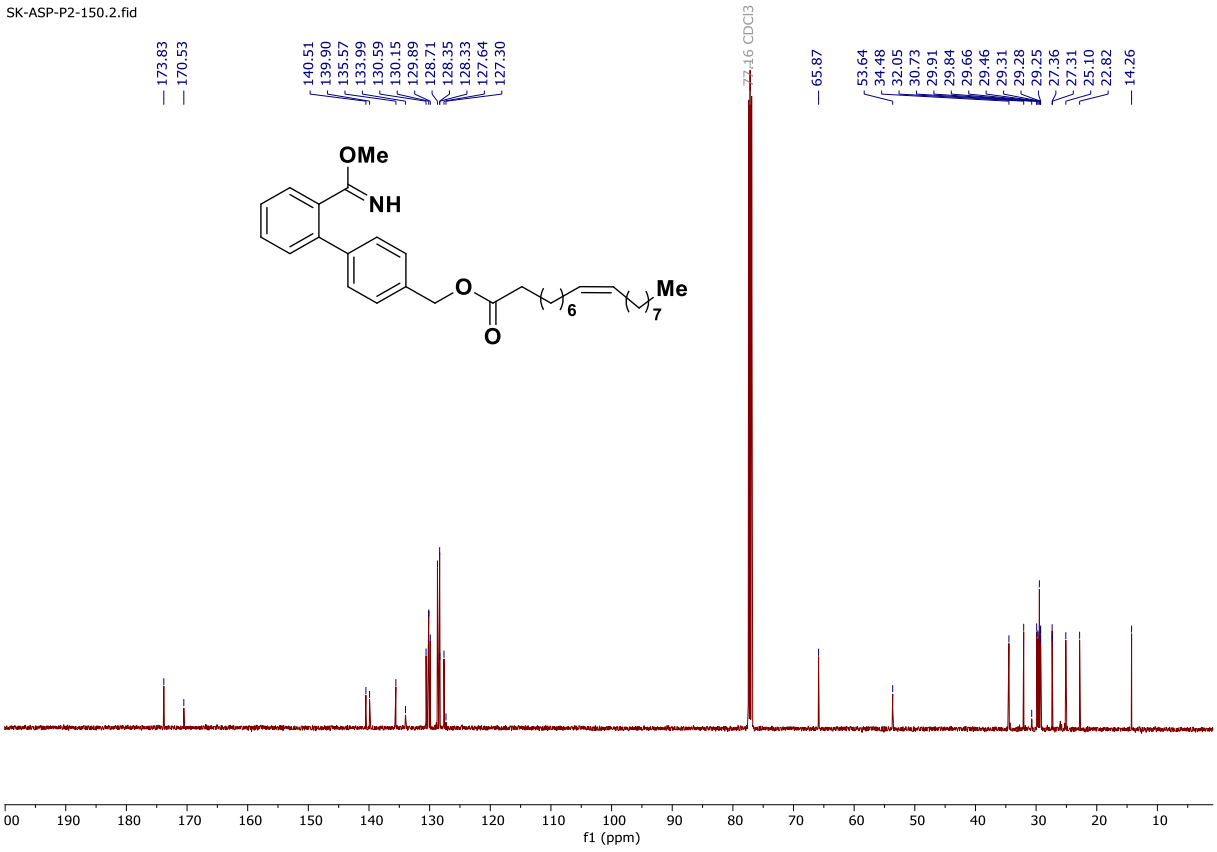
$^{13}C\{^{1}H\}$ NMR spectrum of 1af in $CDCl_3$ [101 MHz]



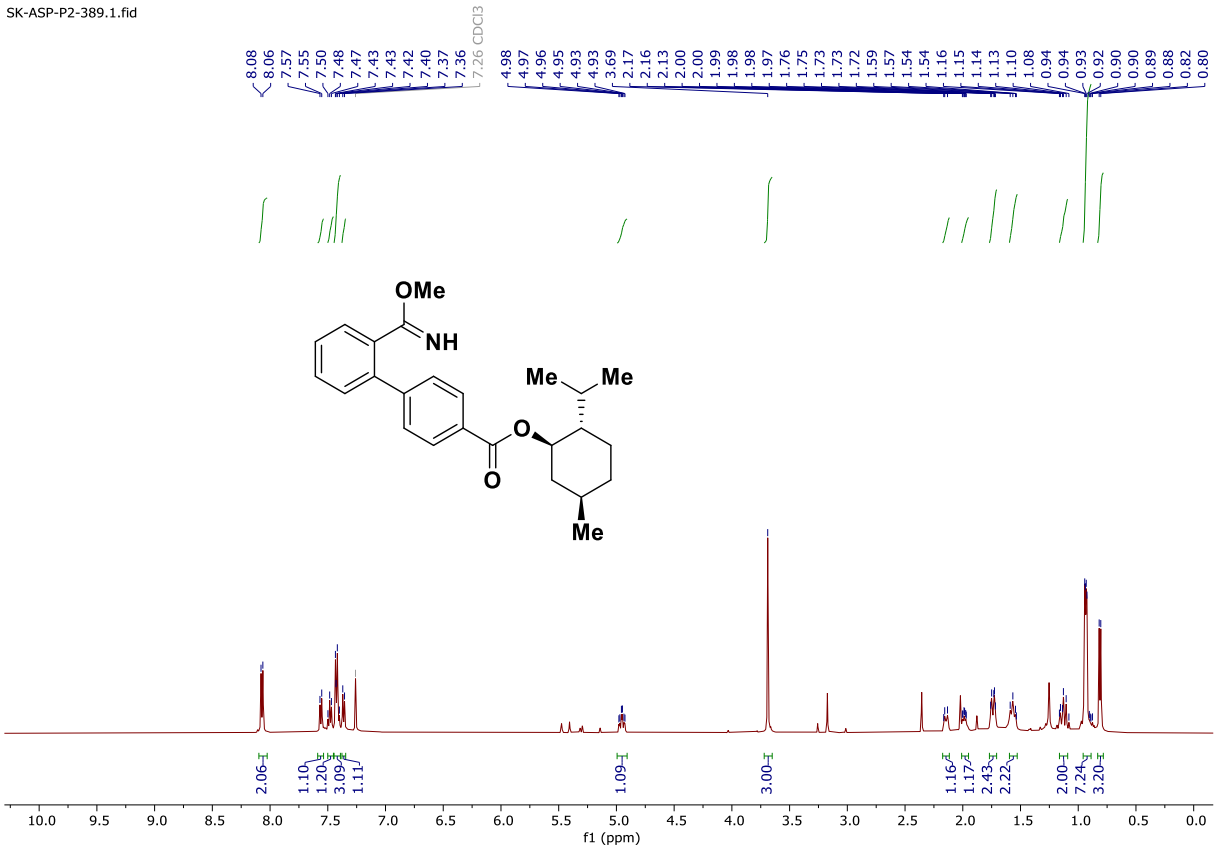
^{1}H NMR spectrum of 1ag in $CDCl_3$ [500 MHz]



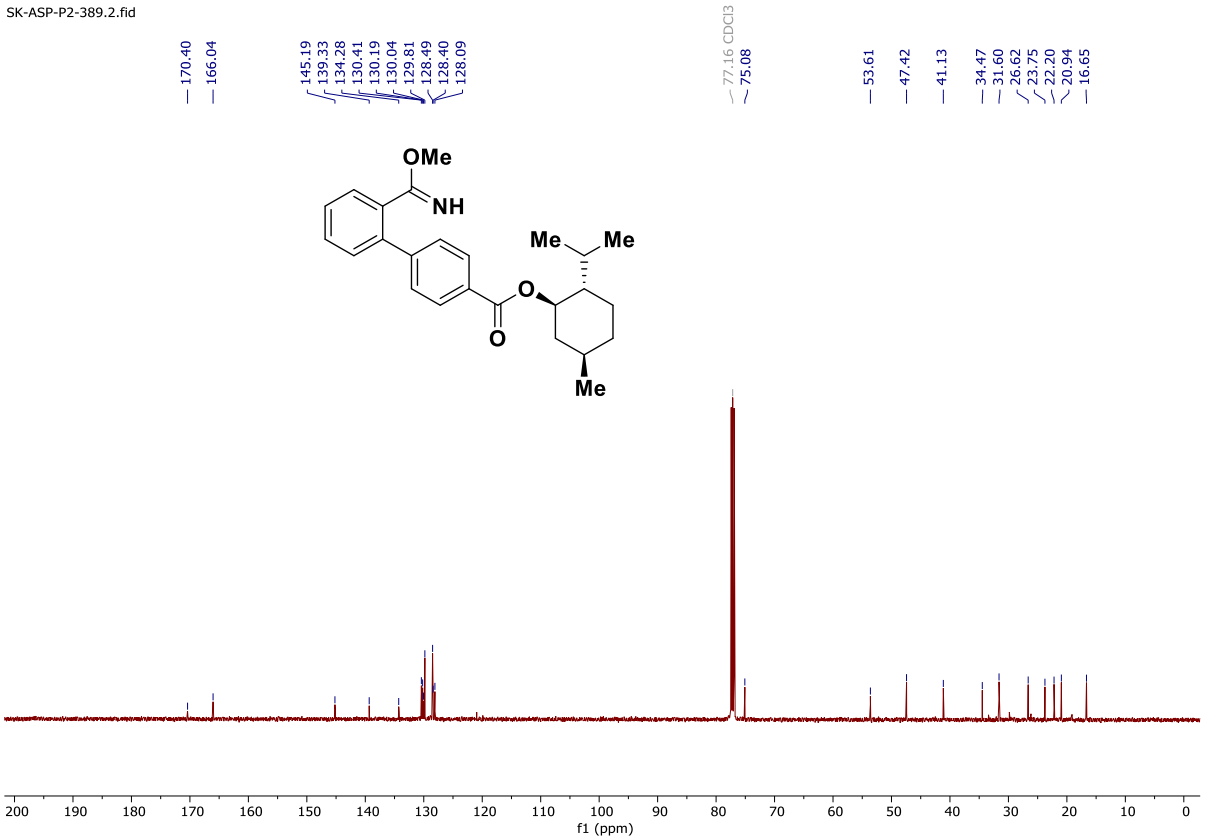
$^{13}C\{^{1}H\}$ NMR spectrum of 1ag in $CDCl_3$ [126 MHz]



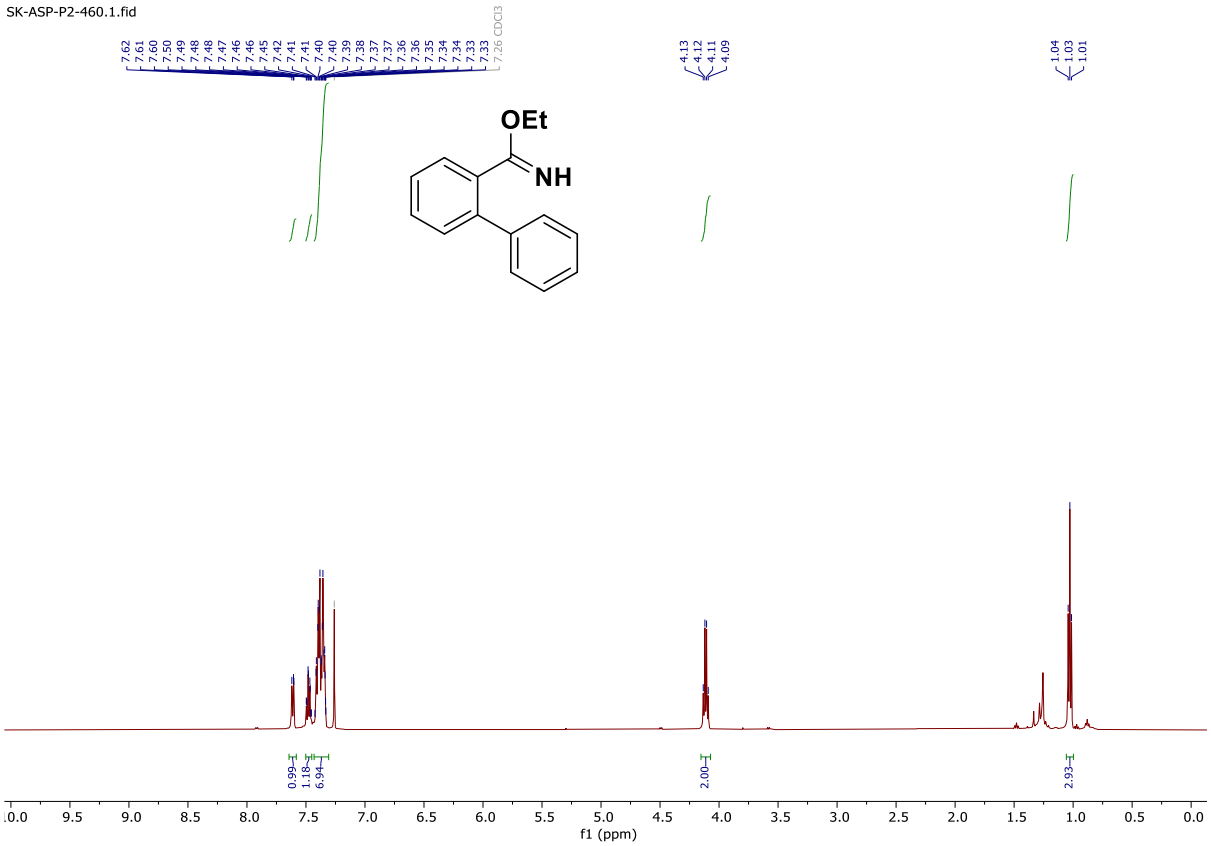
^{1}H NMR spectrum of 1ah in $CDCl_3$ [500 MHz]



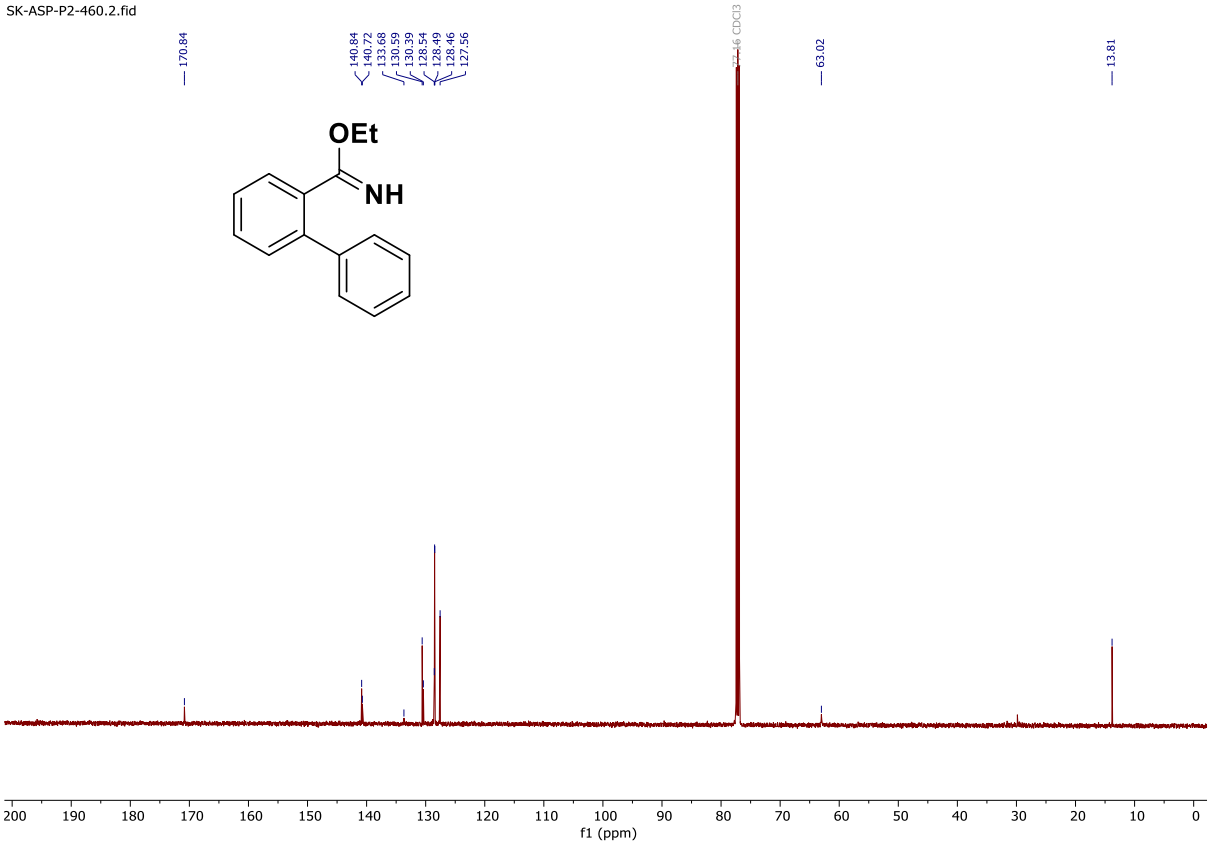
$^{13}C\{^{1}H\}$ NMR spectrum of 1ah in $CDCl_3$ [126 MHz]



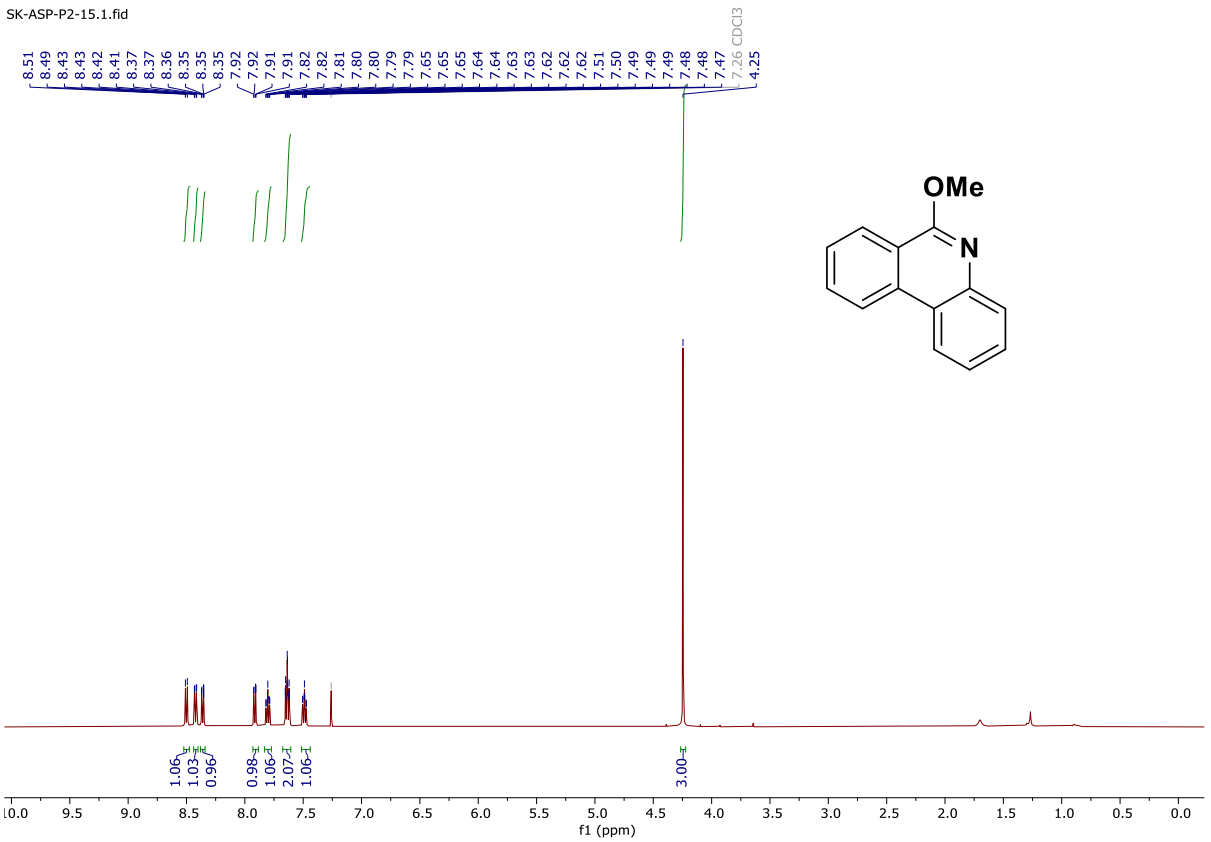
^{1}H NMR spectrum of 1ai in $CDCl_3$ [500 MHz]



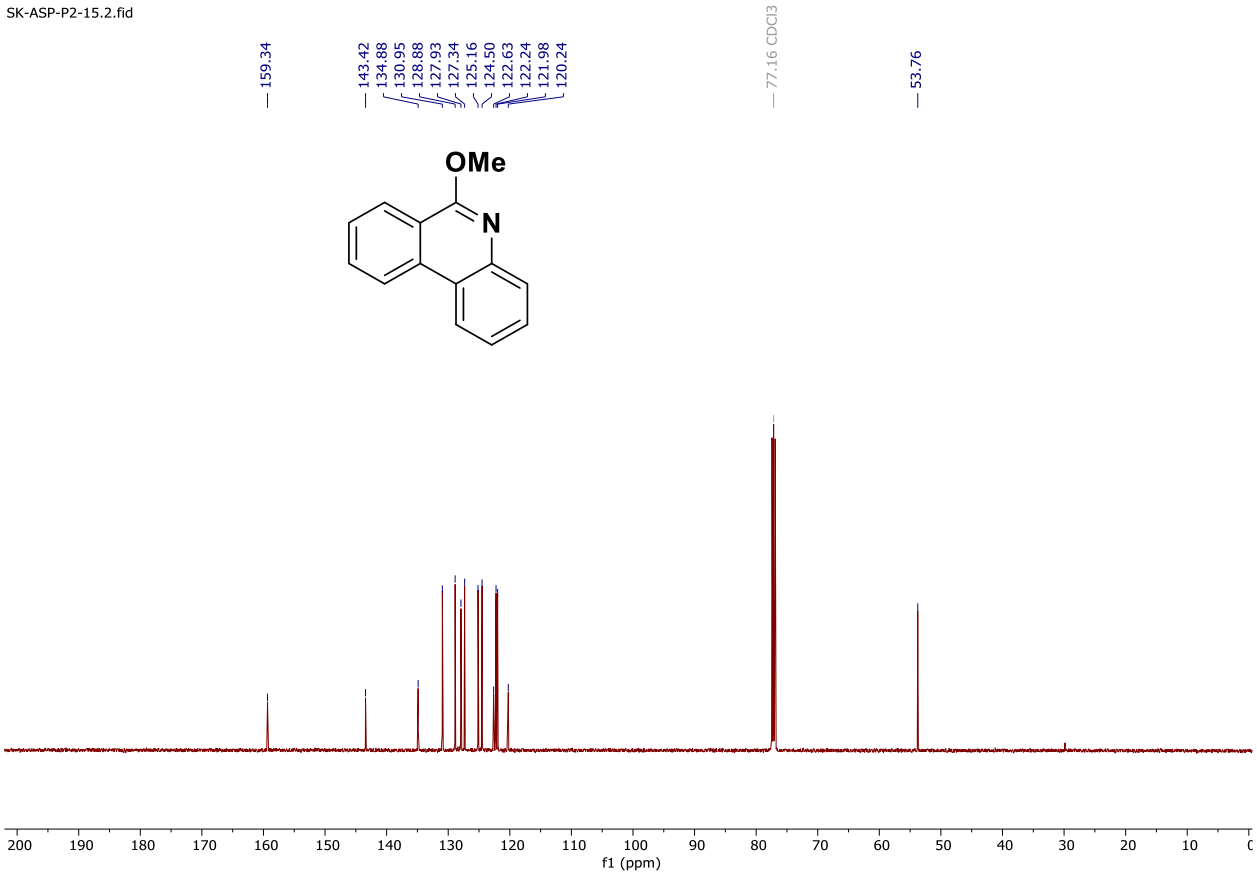
$^{13}C\{^{1}H\}$ NMR spectrum of 1ai in $CDCl_3$ [126 MHz]



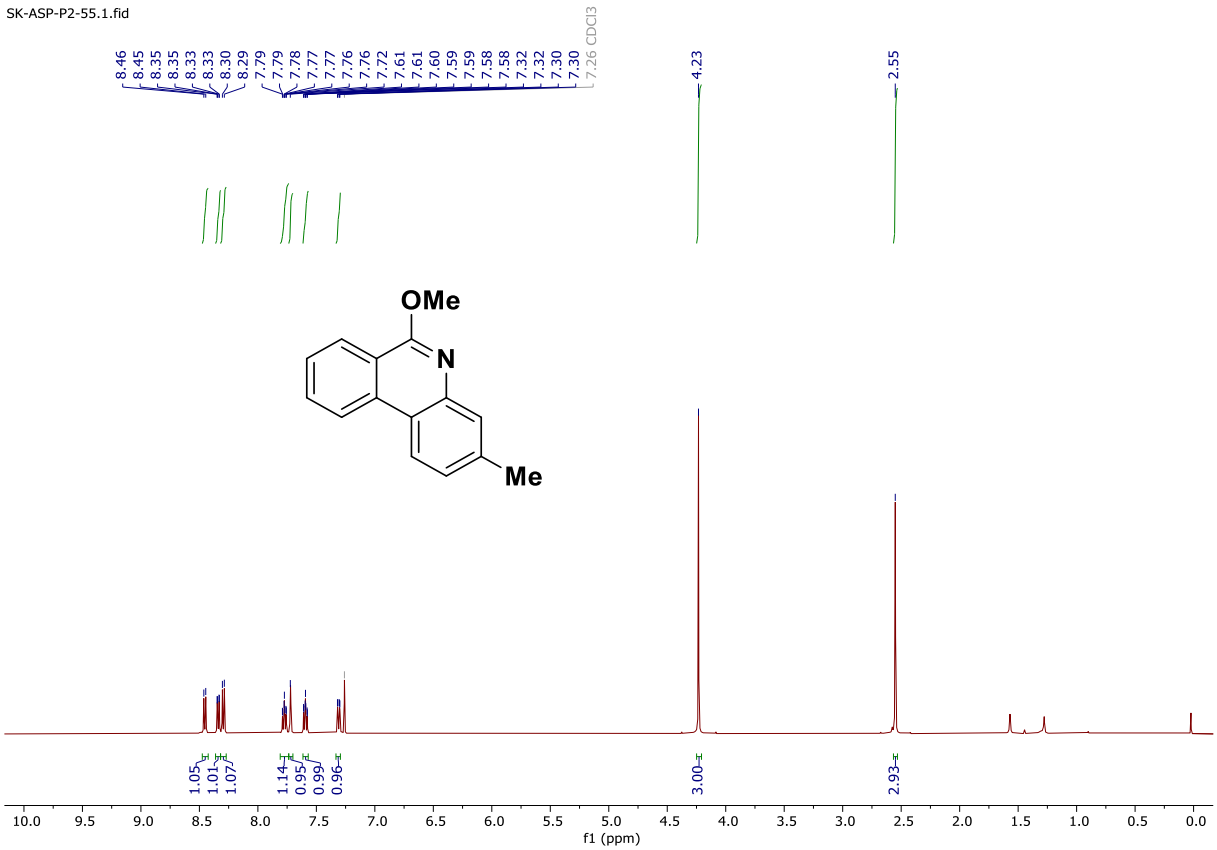
^{1}H NMR spectrum of 2a in $CDCl_3$ [500 MHz]



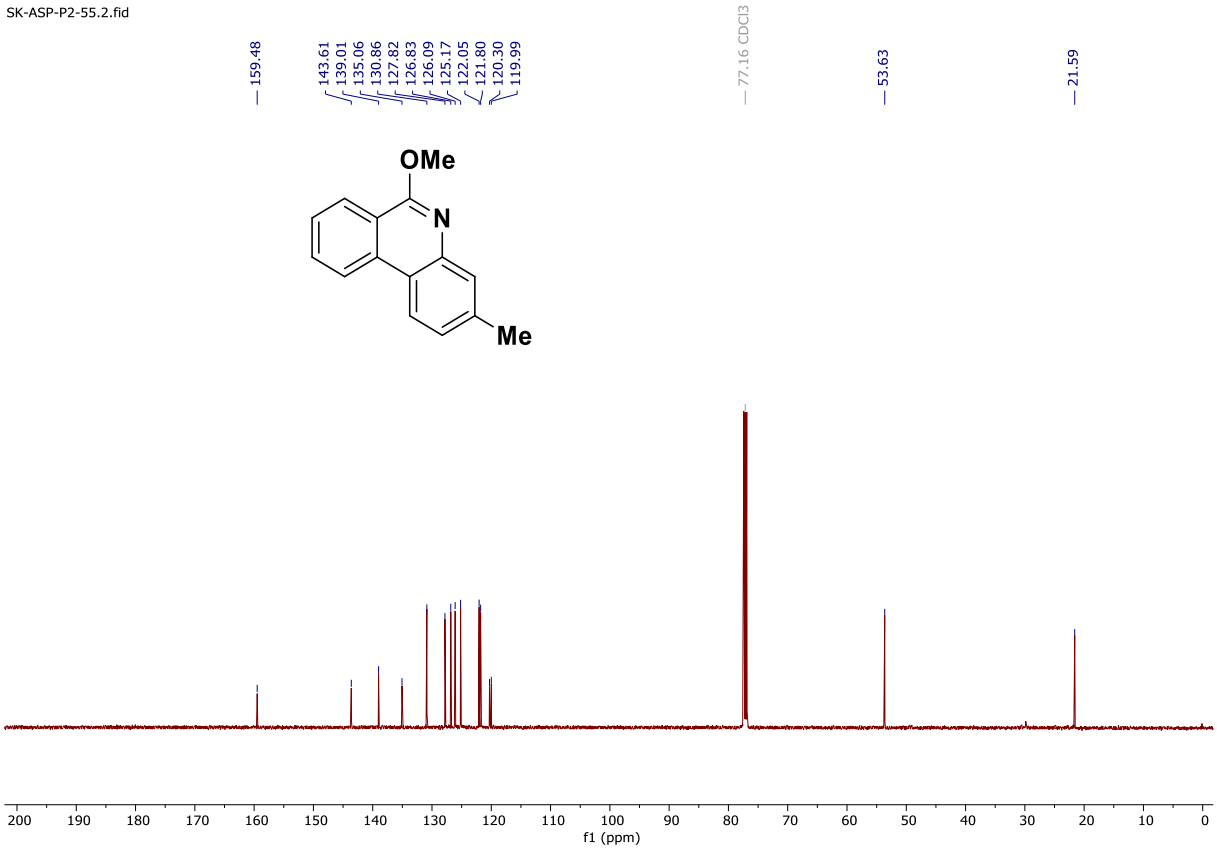
$^{13}C\{^{1}H\}$ NMR spectrum of 2a in $CDCl_3$ [126 MHz]



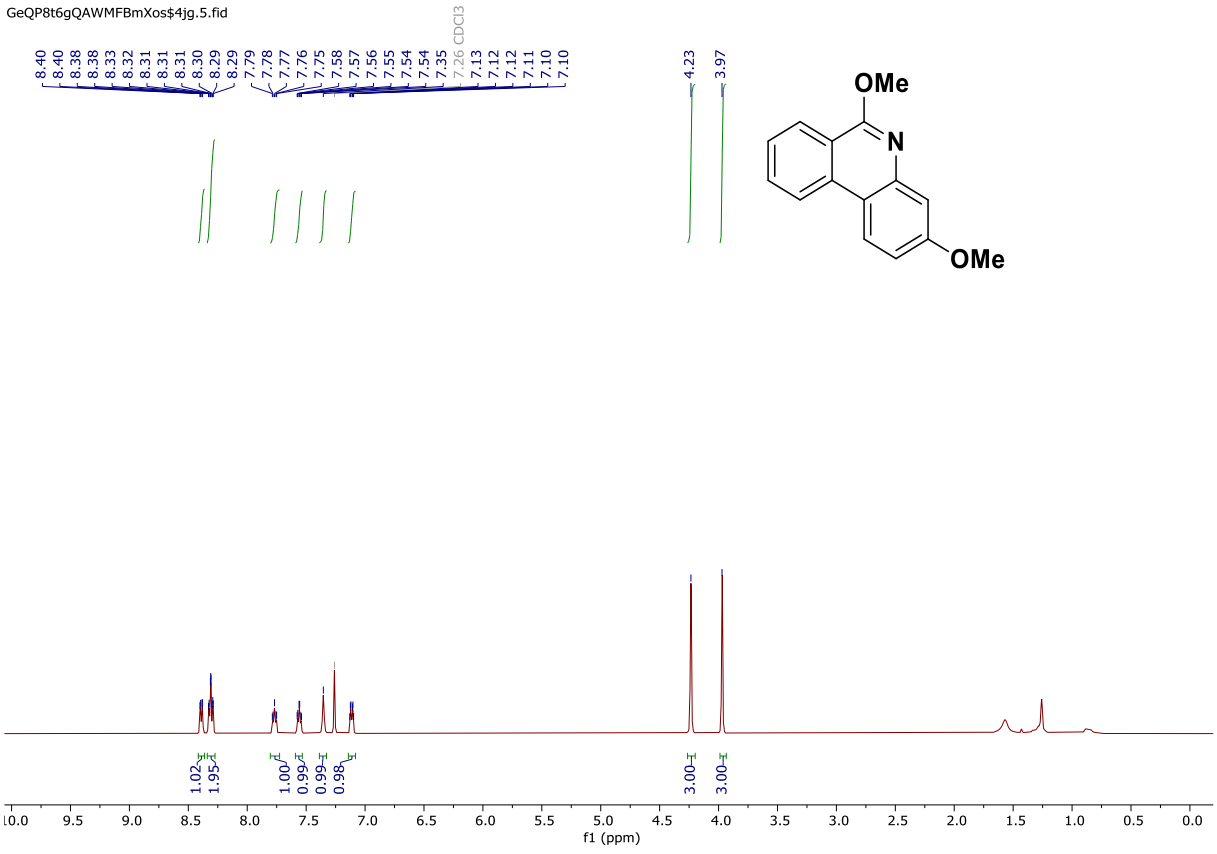
^{1}H NMR spectrum of 2b in $CDCl_3$ [500 MHz]



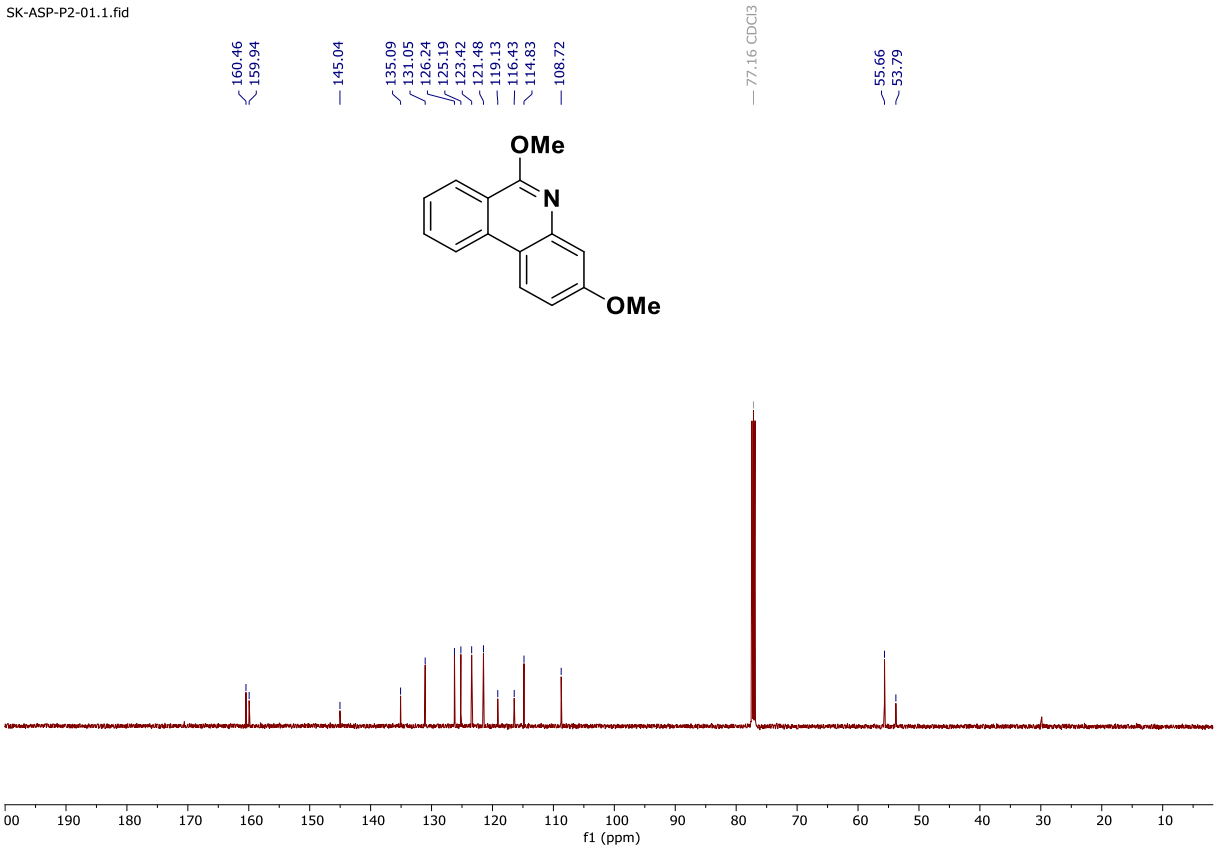
$^{13}C\{^{1}H\}$ NMR spectrum of 2b in $CDCl_3$ [126 MHz]



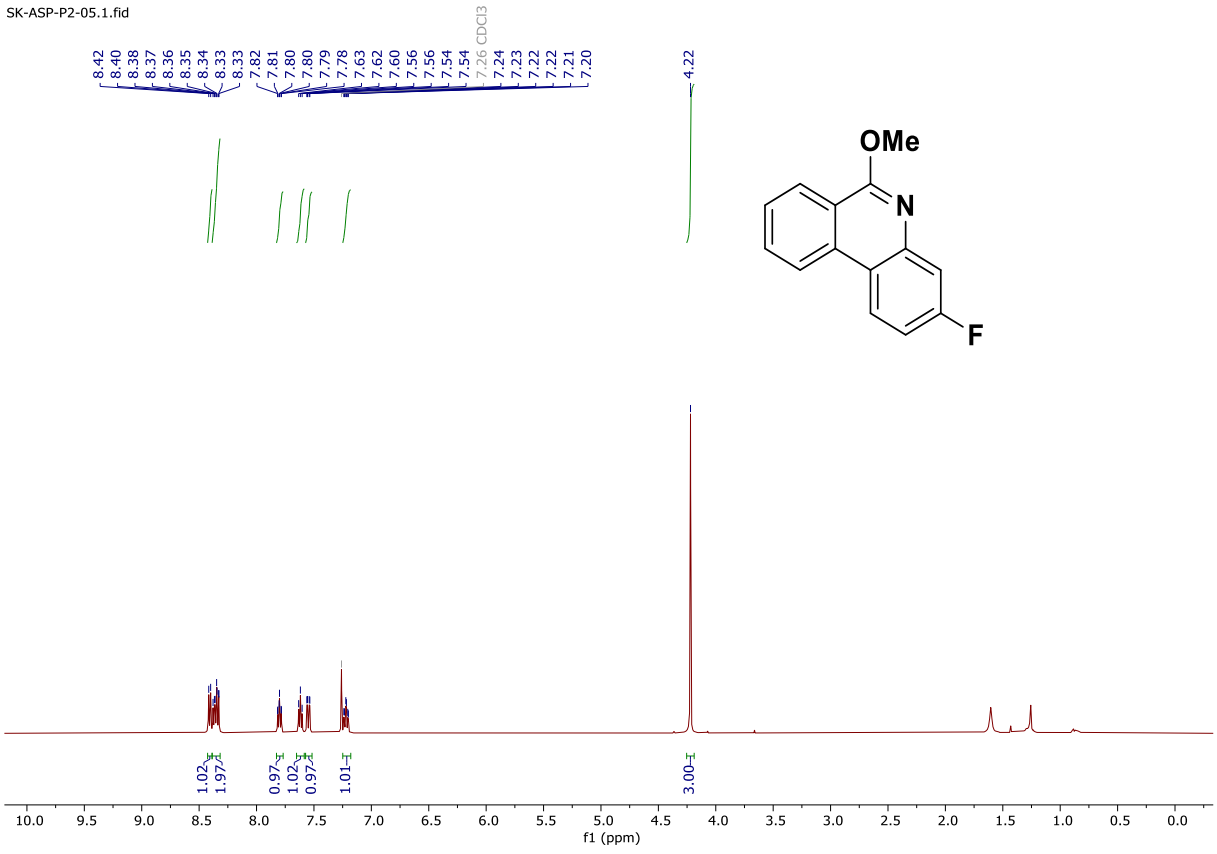
^{1}H NMR spectrum of 2c in $CDCl_3$ [500 MHz]



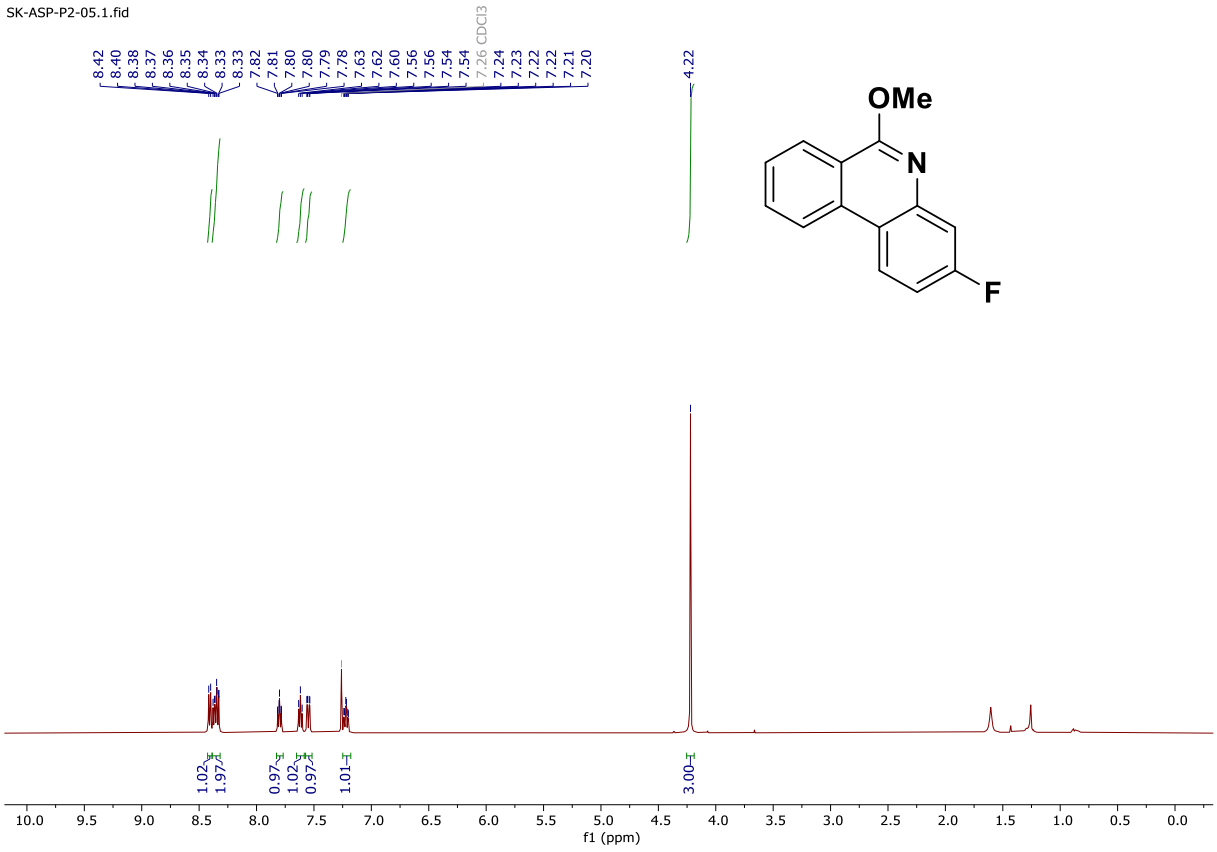
$^{13}C\{^{1}H\}$ NMR spectrum of 2c in $CDCl_3$ [126 MHz]



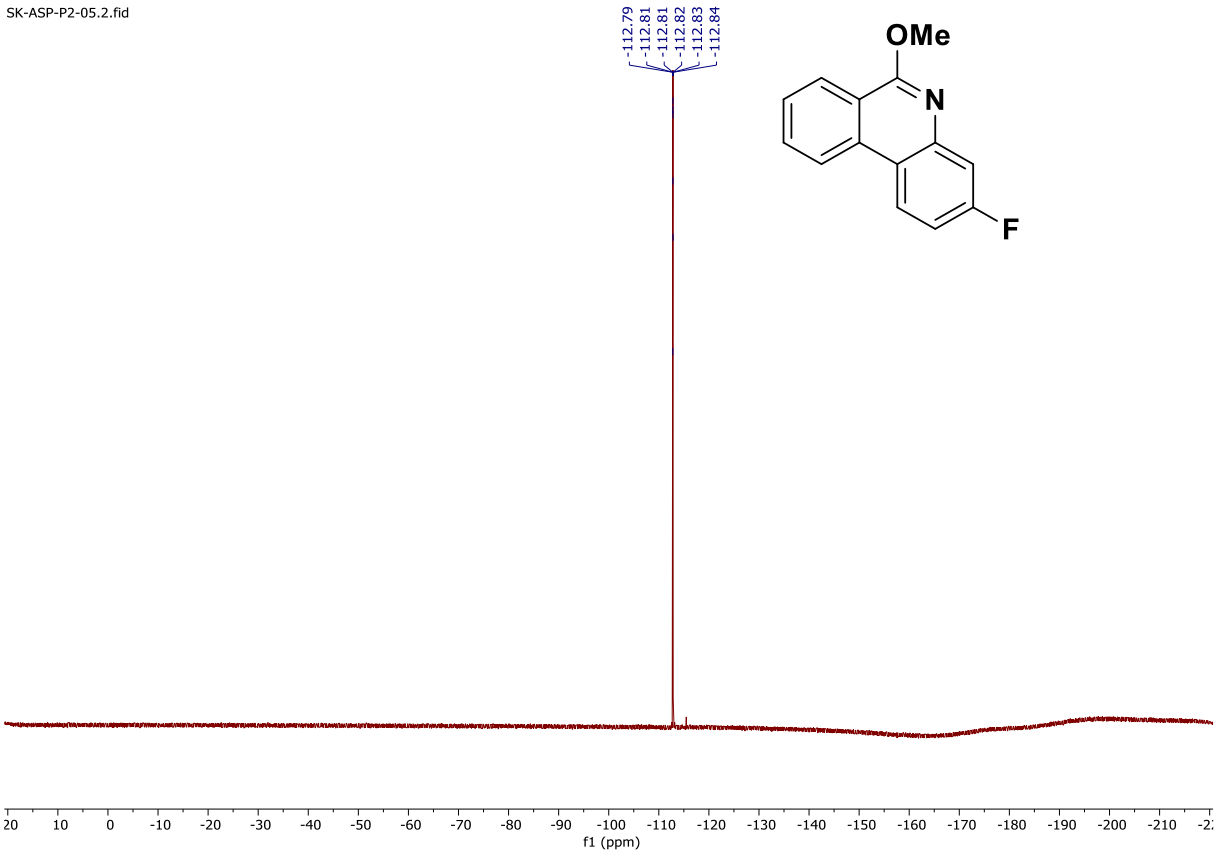
^{1}H NMR spectrum of 2d in $CDCl_3$ [500 MHz]



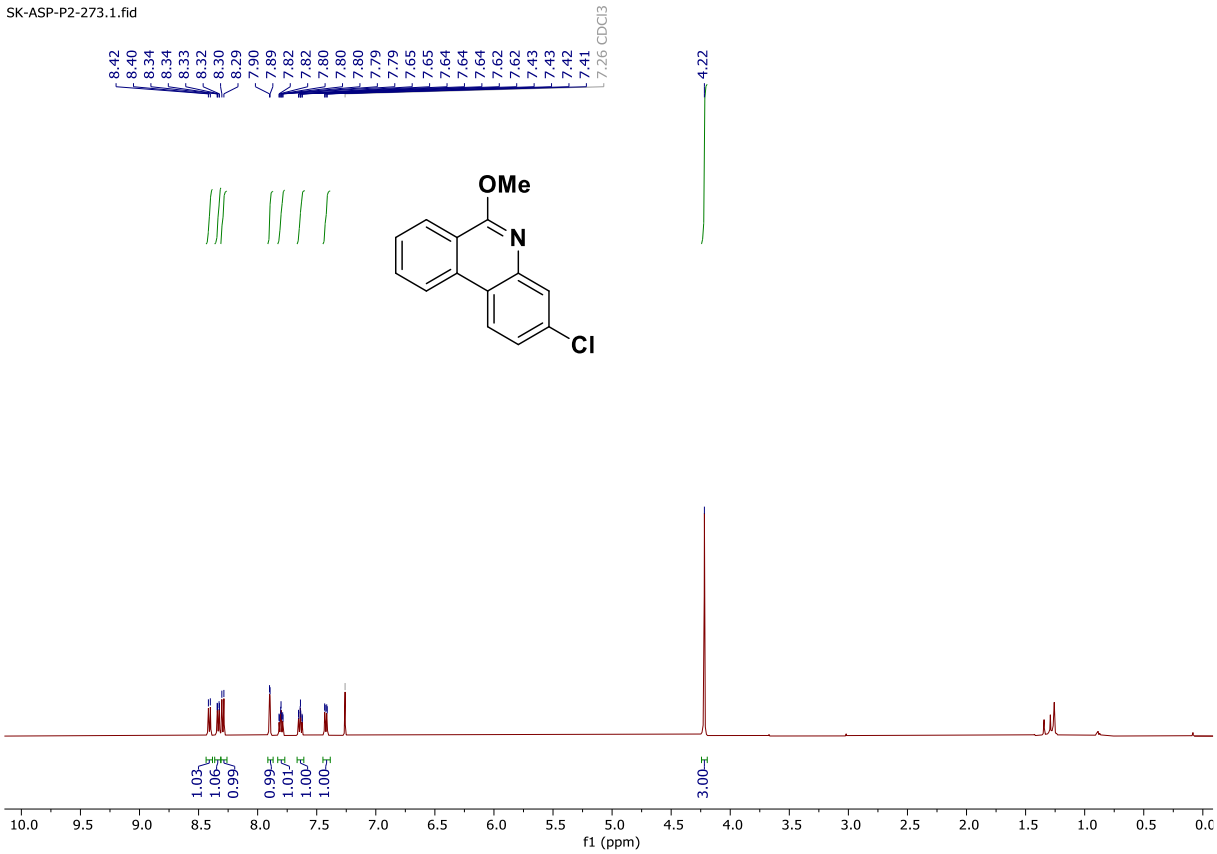
$^{13}C\{^{1}H\}$ NMR spectrum of 2d in $CDCl_3$ [126 MHz]



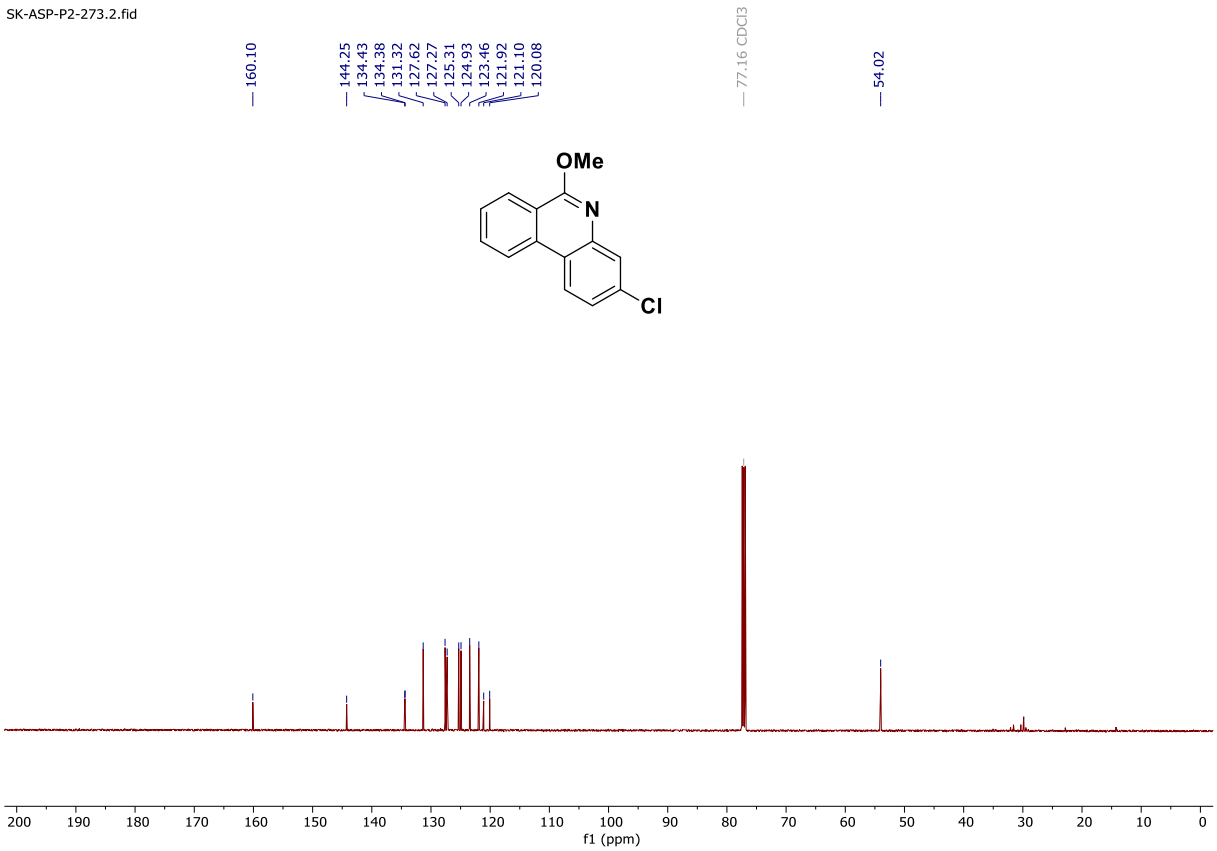
^{19}F NMR spectrum of 2d in $CDCl_3$ [471 MHz]



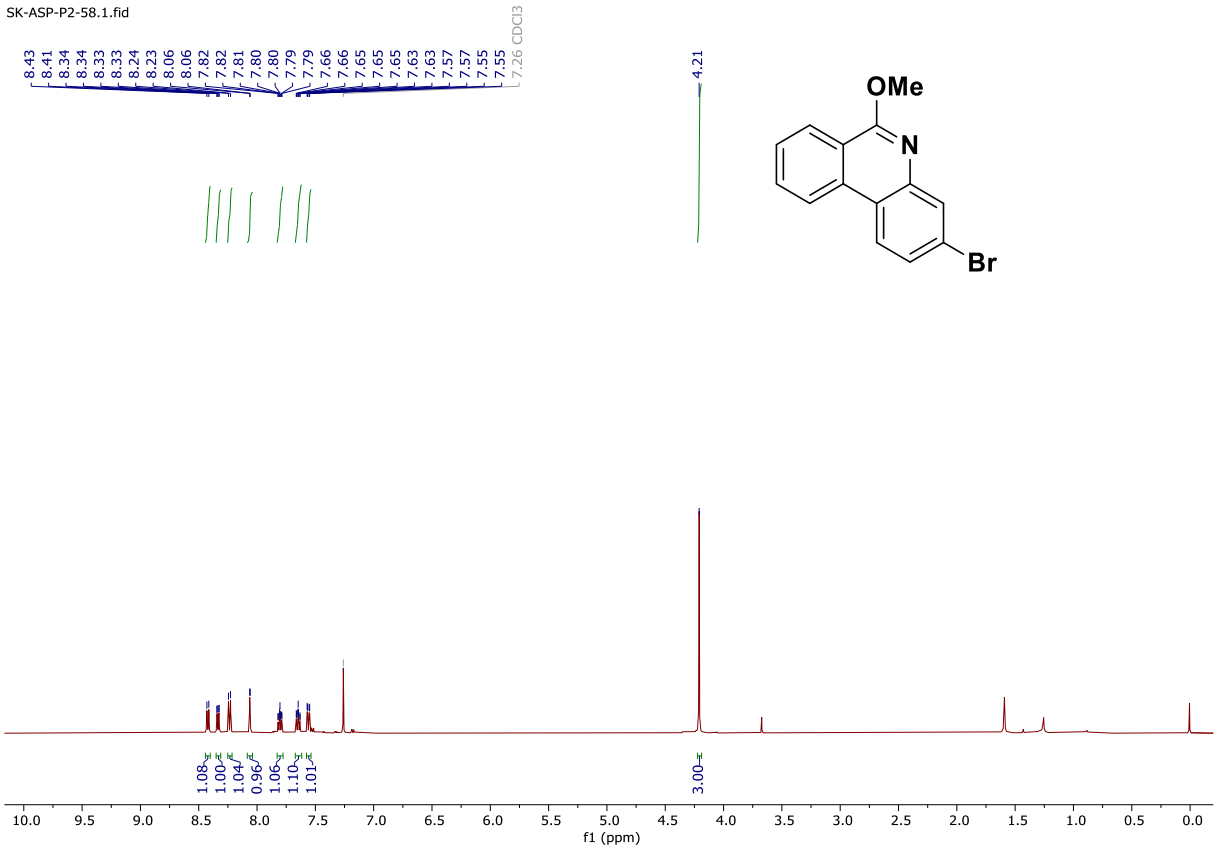
^{1}H NMR spectrum of 2e in $CDCl_3$ [500 MHz]



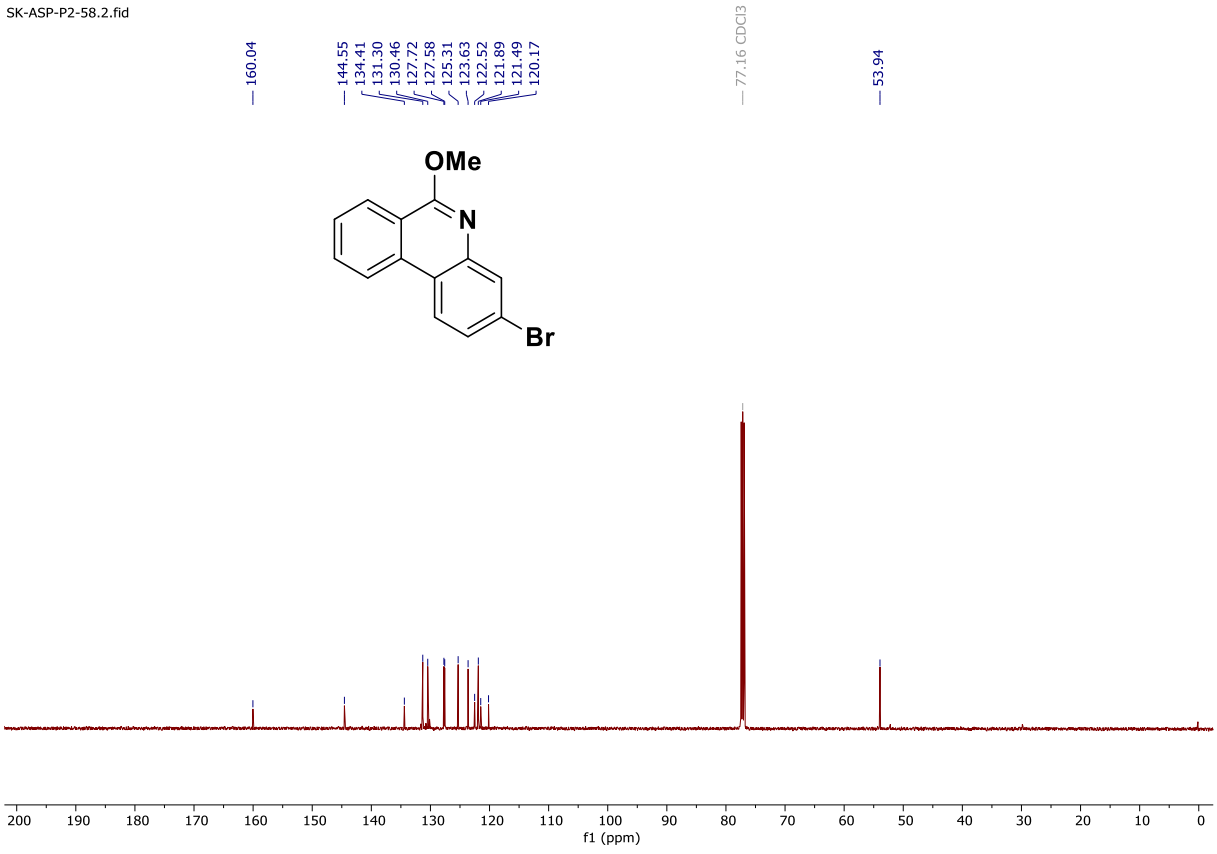
^{13}C{^{1}H} NMR spectrum of 2e in $CDCl_3$ [126 MHz]



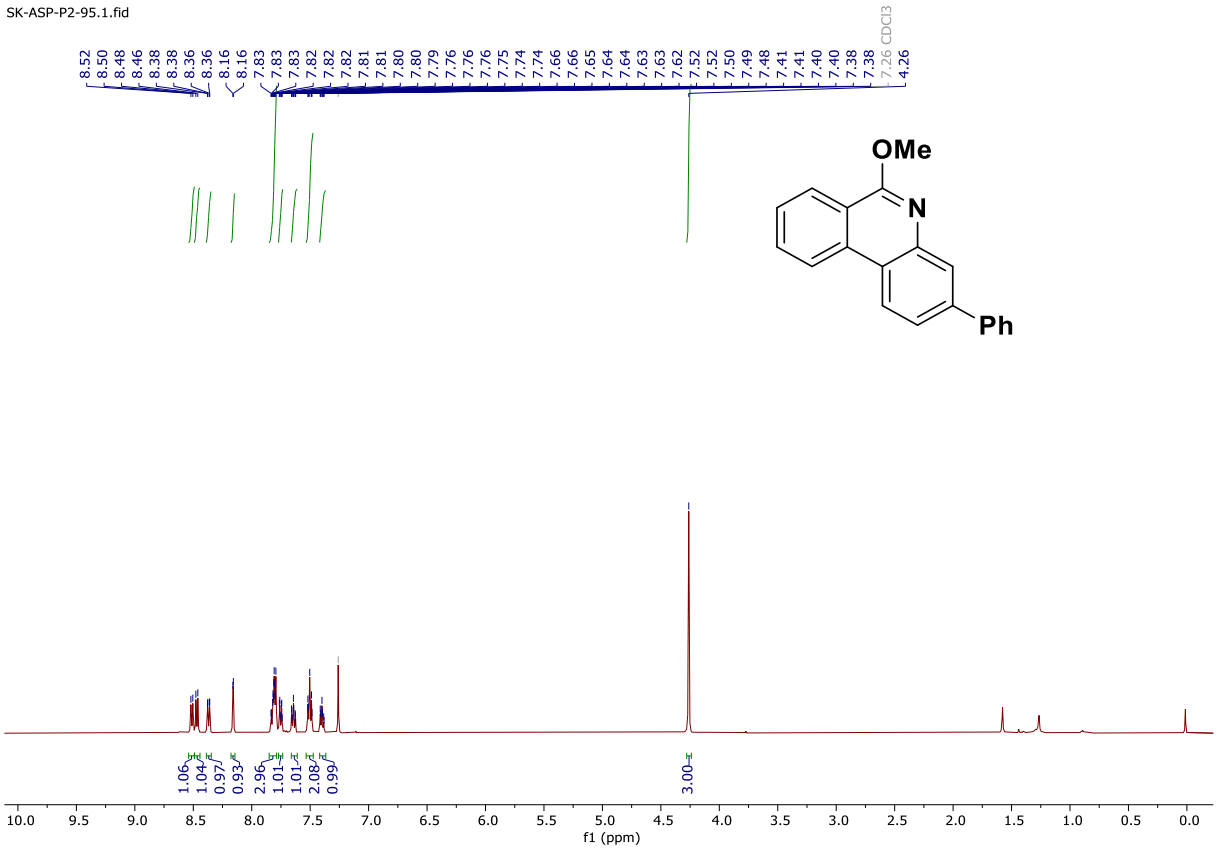
^{1}H NMR spectrum of 2f in $CDCl_3$ [500 MHz]



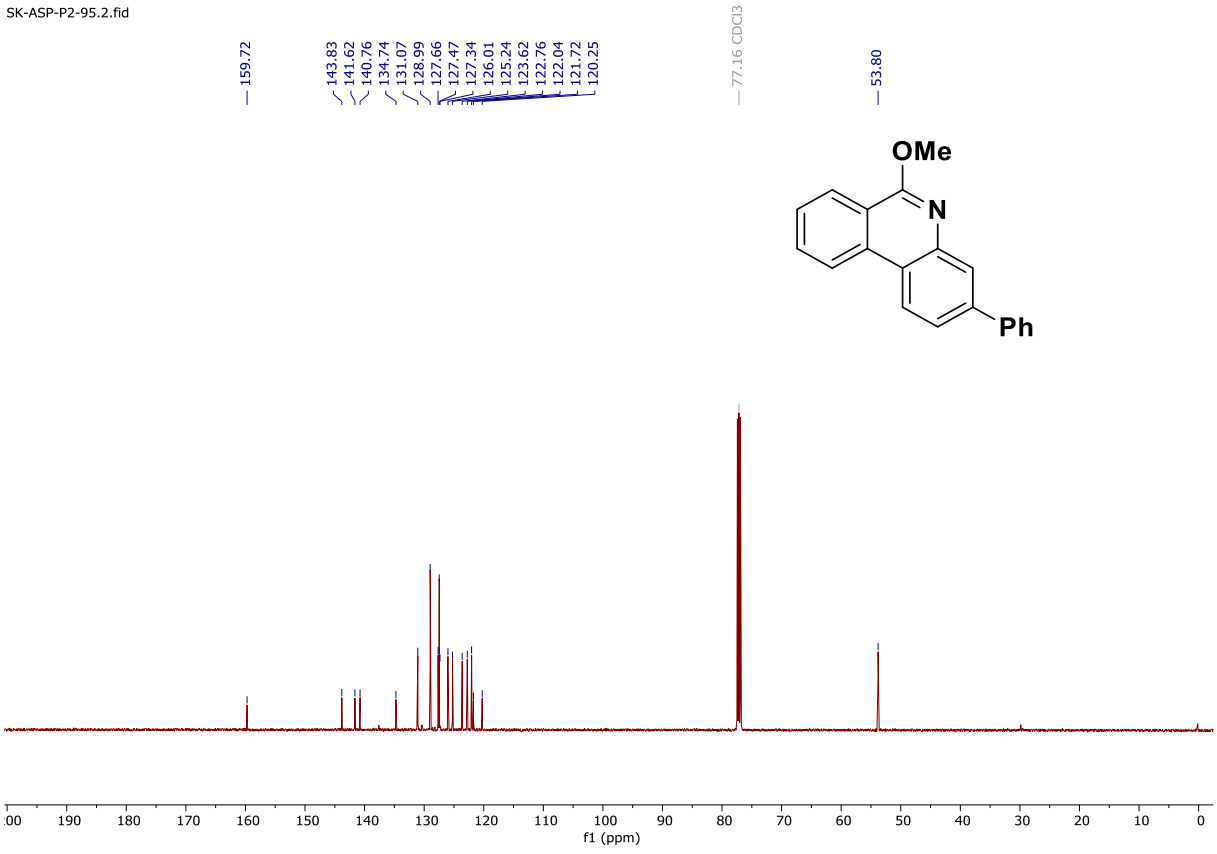
^{13}C{^{1}H} NMR spectrum of 2f in $CDCl_3$ [126 MHz]



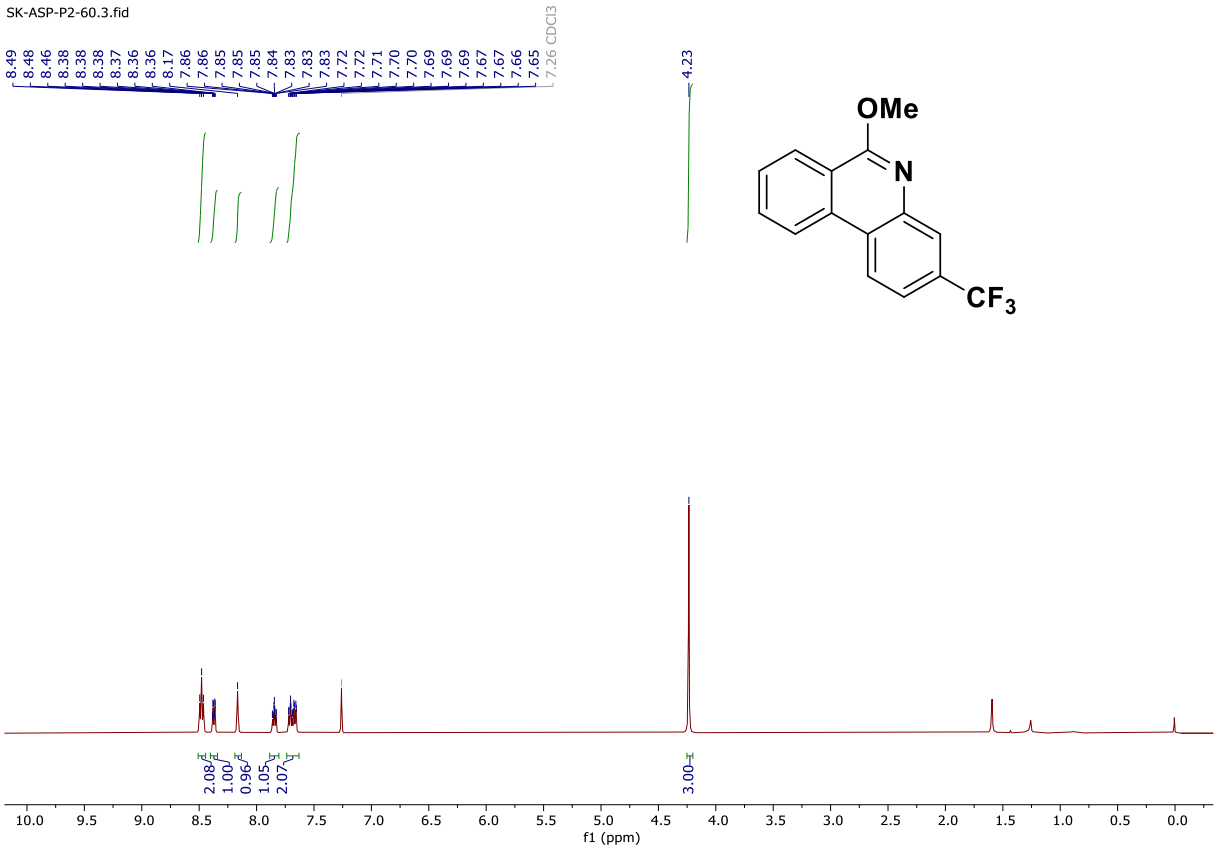
^{1}H NMR spectrum of 2g in $CDCl_3$ [500 MHz]



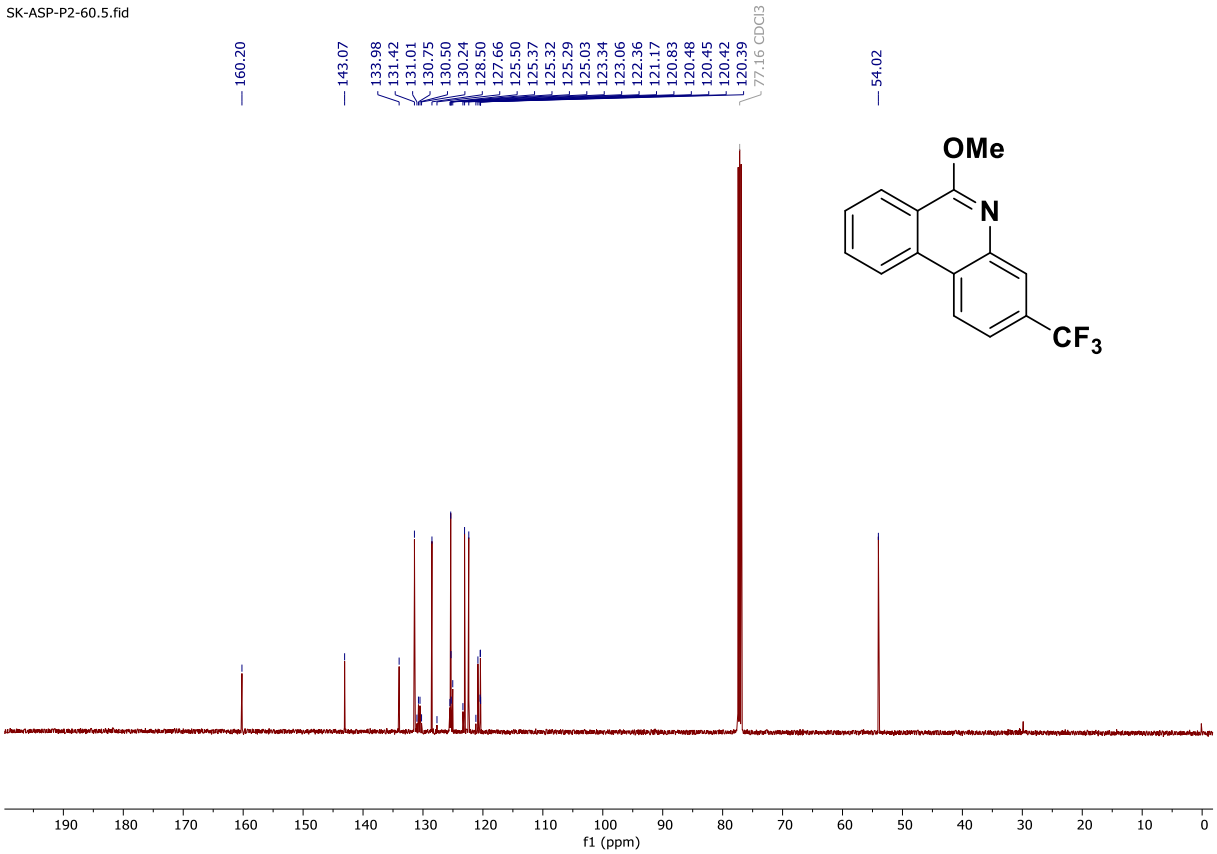
^{13}C{^{1}H} NMR spectrum of 2g in $CDCl_3$ [126 MHz]



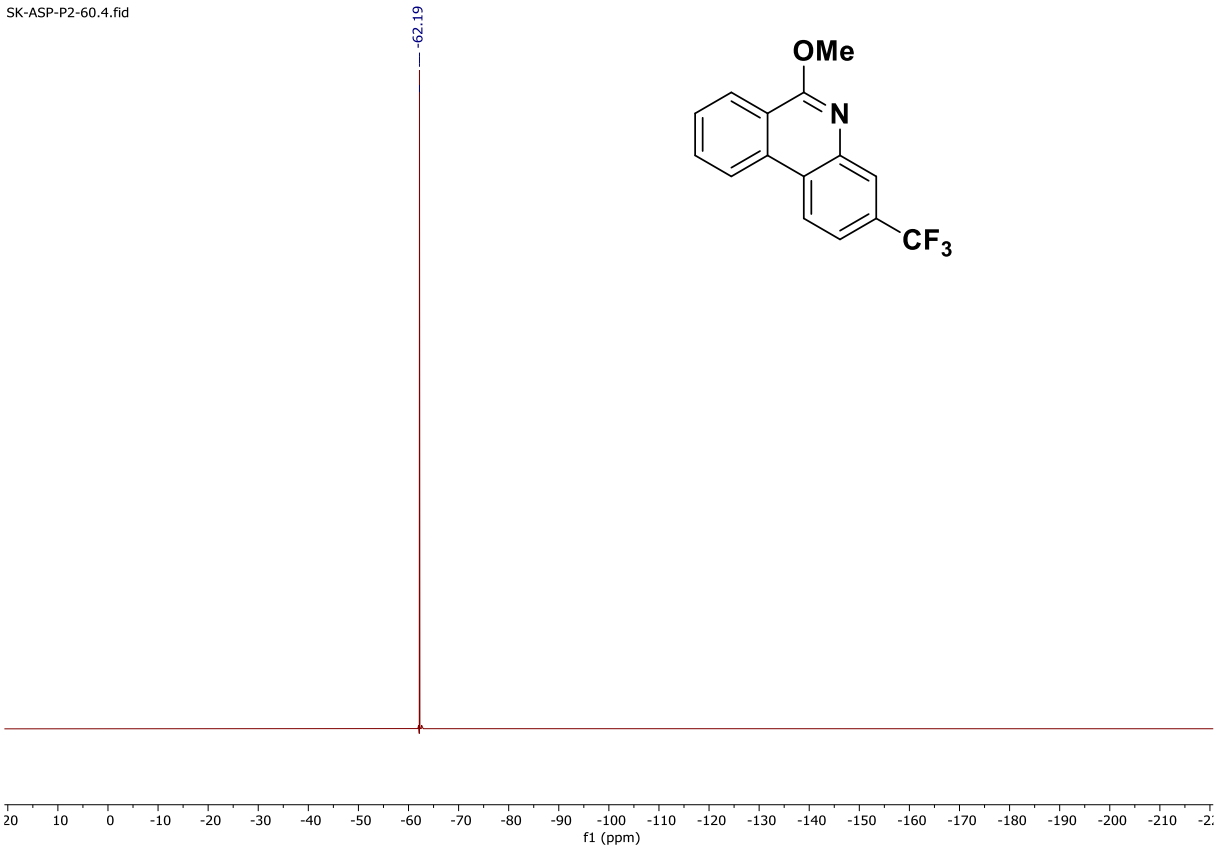
^{1}H NMR spectrum of 2h in $CDCl_3$ [500 MHz]



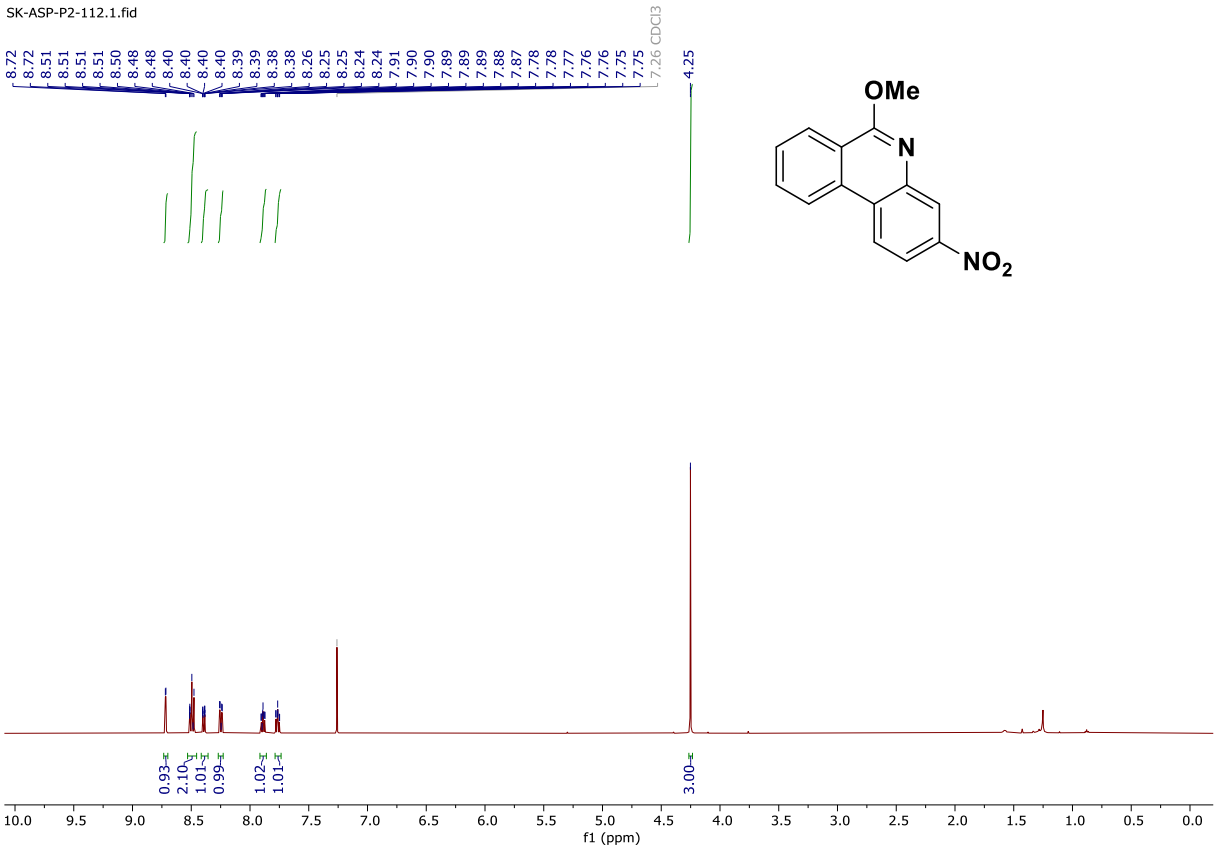
^{13}C{^{1}H} NMR spectrum of 2h in $CDCl_3$ [126 MHz]



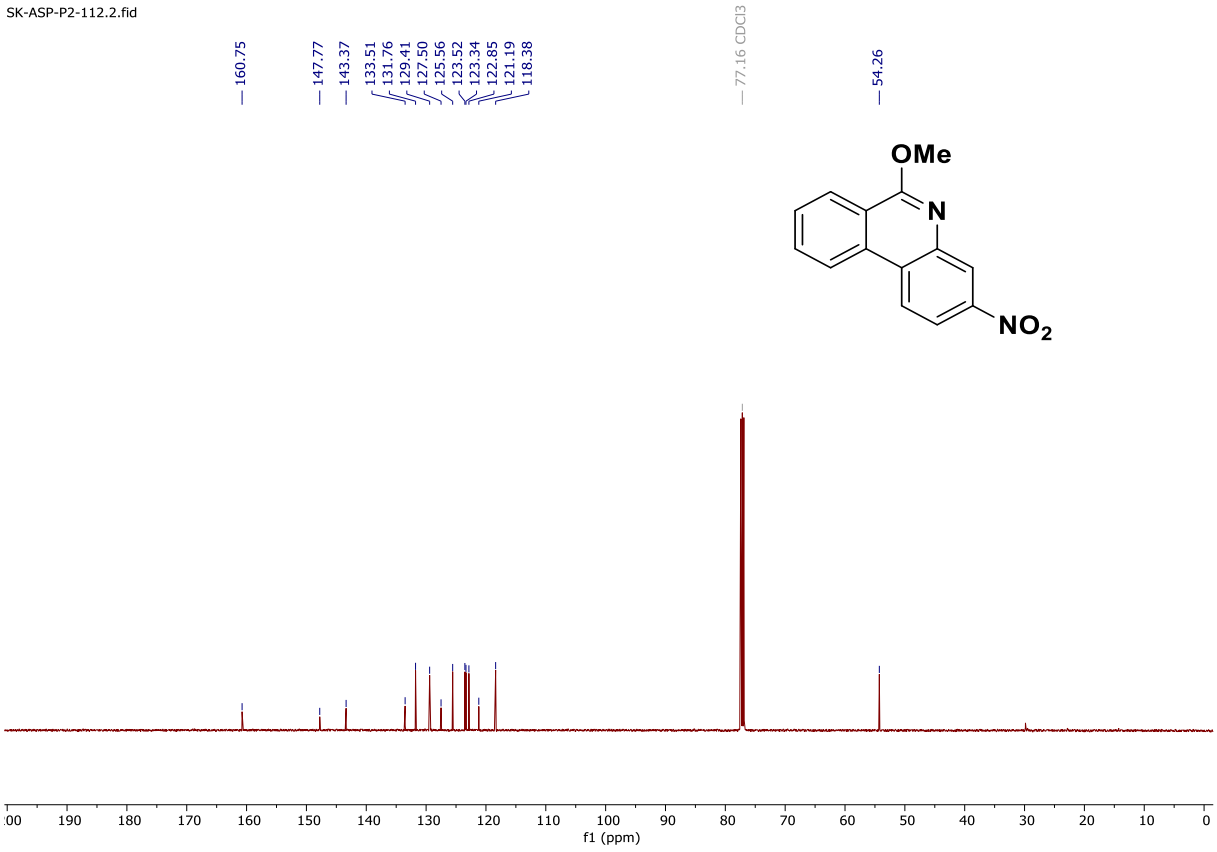
^{19}F NMR spectrum of 2h in $CDCl_3$ [471 MHz]



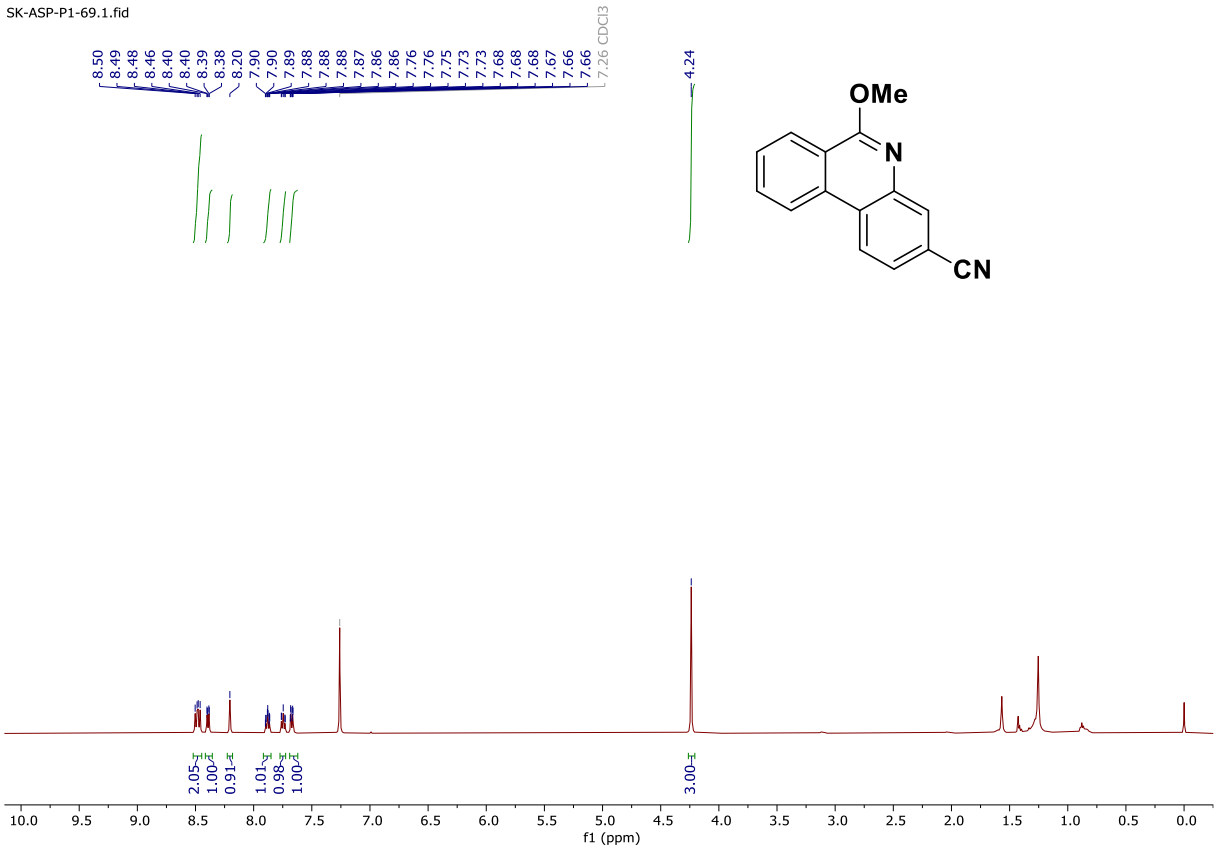
^{1}H NMR spectrum of 2i in $CDCl_3$ [500 MHz]



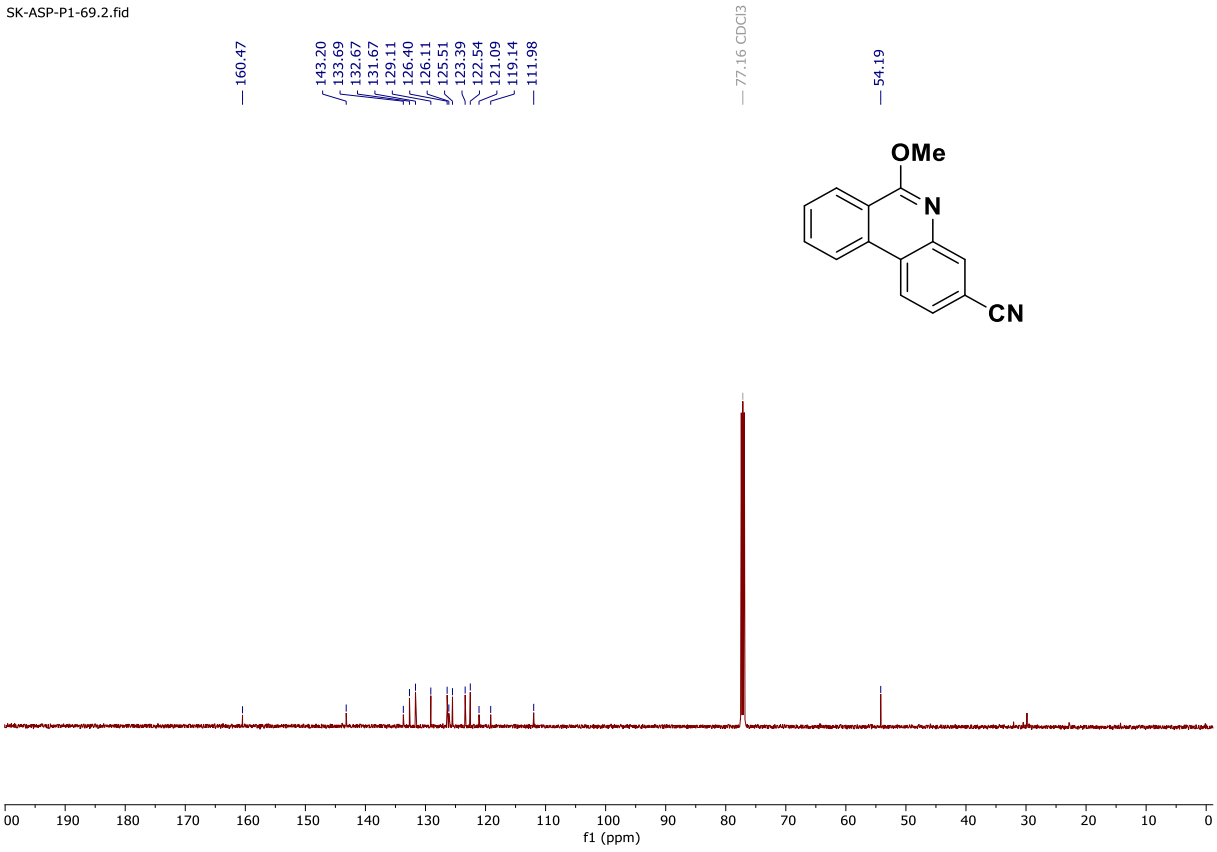
$^{13}C\{^{1}H\}$ NMR spectrum of 2i in $CDCl_3$ [126 MHz]



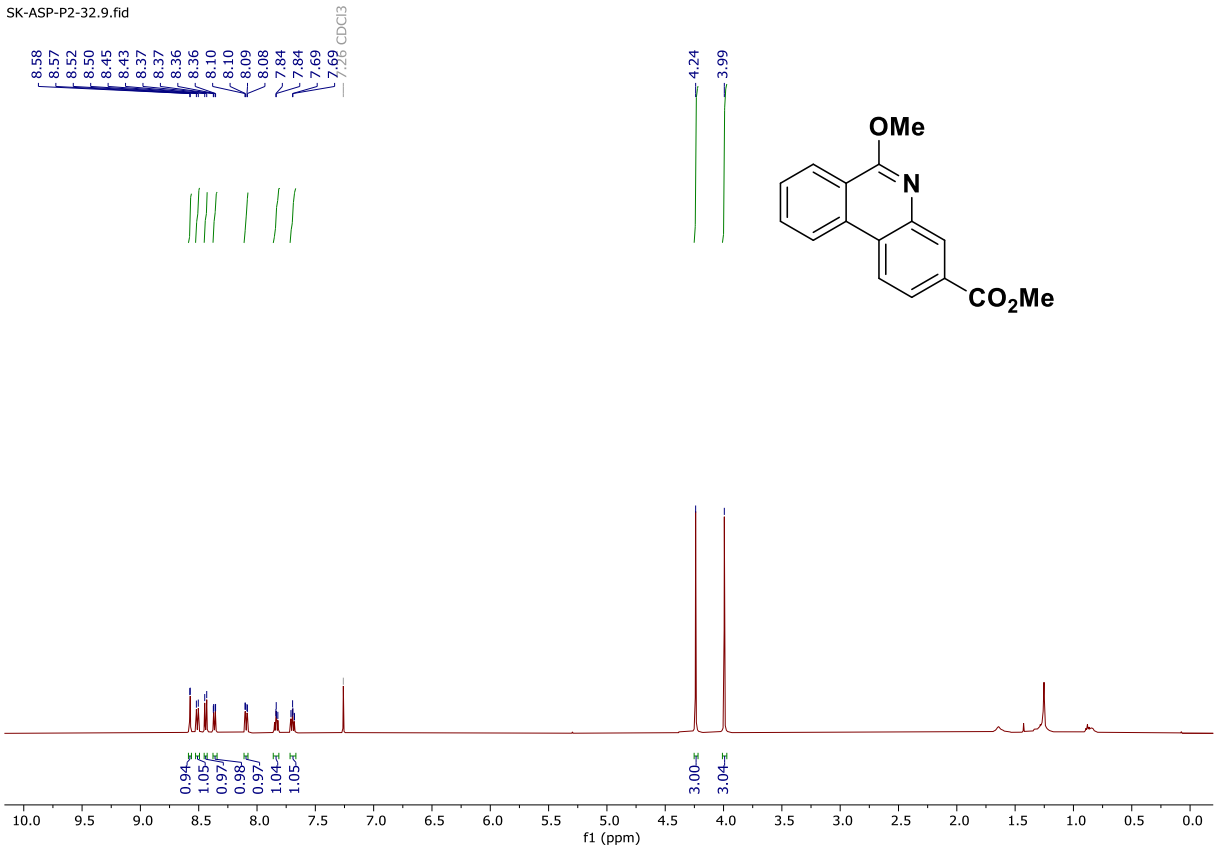
^{1}H NMR spectrum of 2j in $CDCl_3$ [500 MHz]



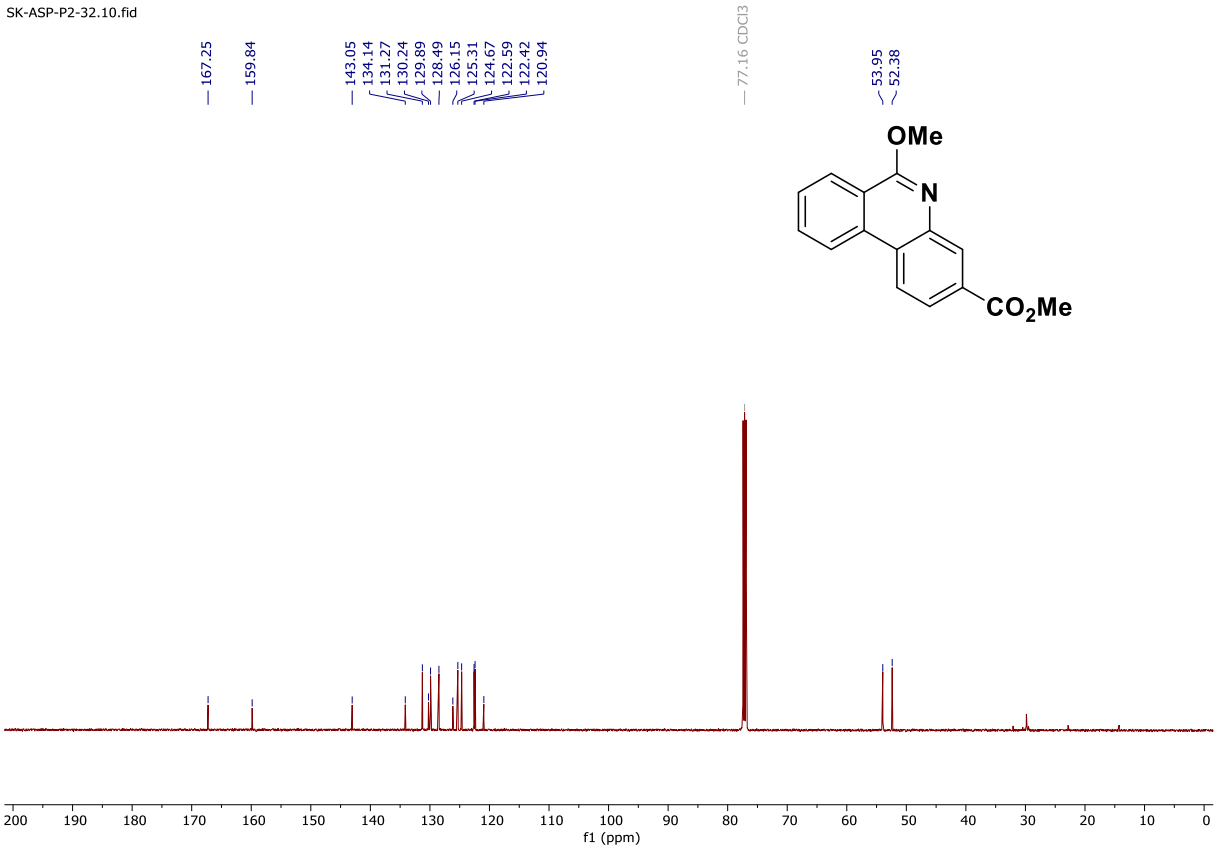
$^{13}C\{^{1}H\}$ NMR spectrum of 2j in $CDCl_3$ [126 MHz]



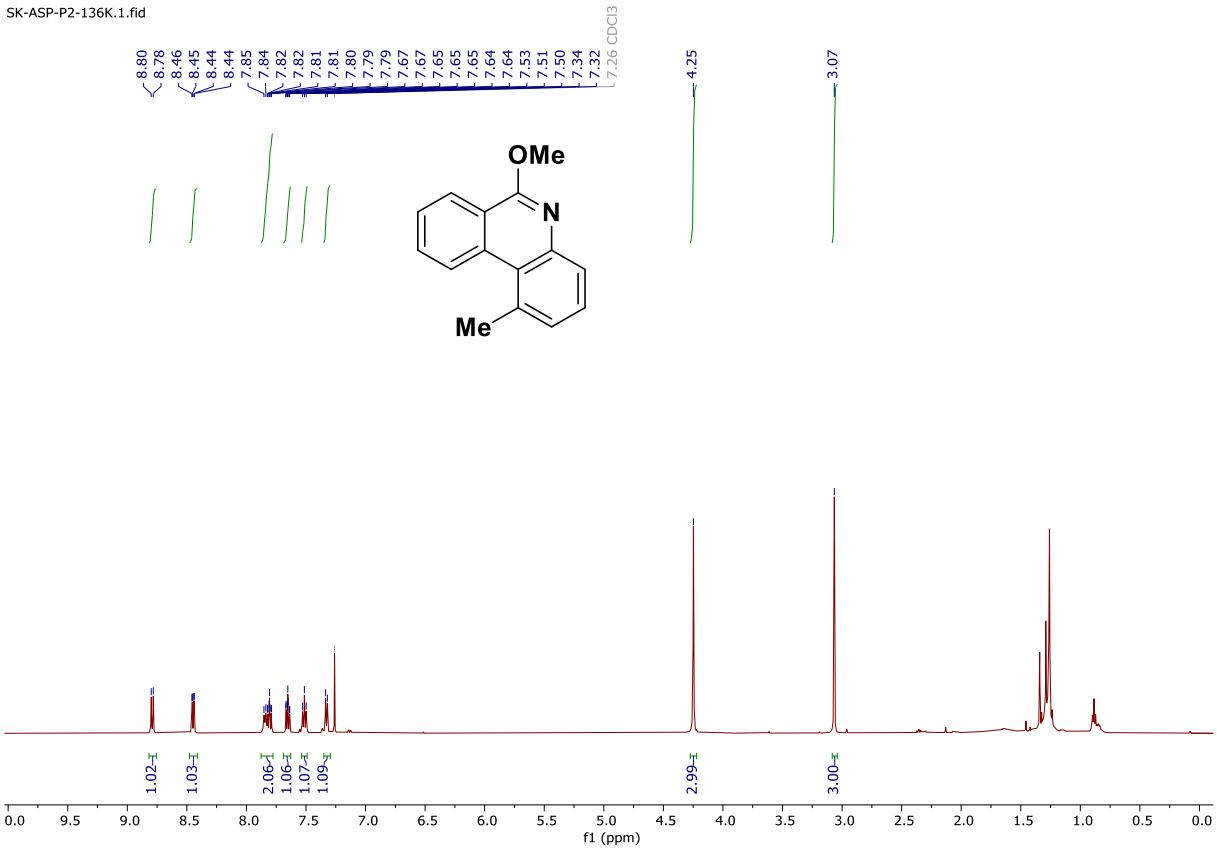
^{1}H NMR spectrum of 2k in $CDCl_3$ [500 MHz]



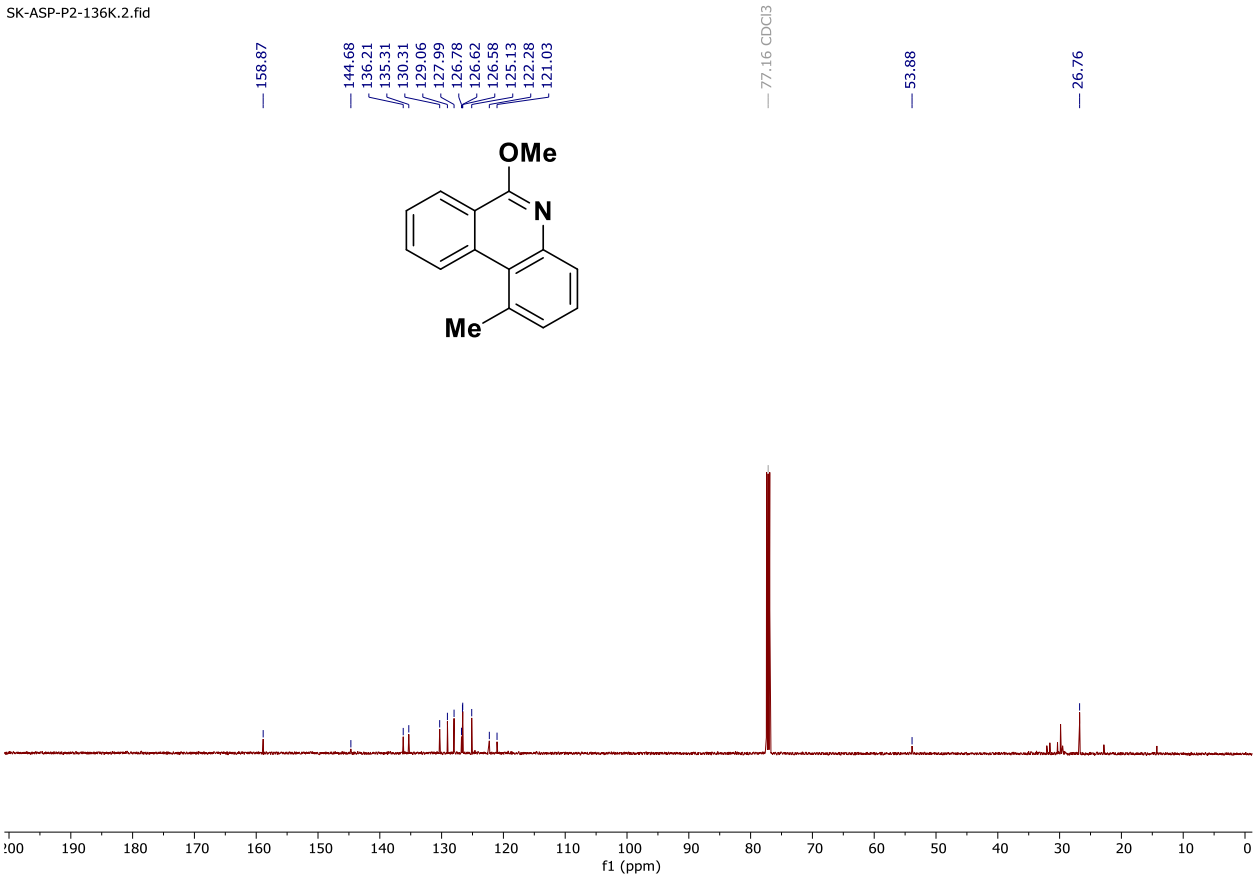
$^{13}C\{^{1}H\}$ NMR spectrum of 2k in $CDCl_3$ [126 MHz]



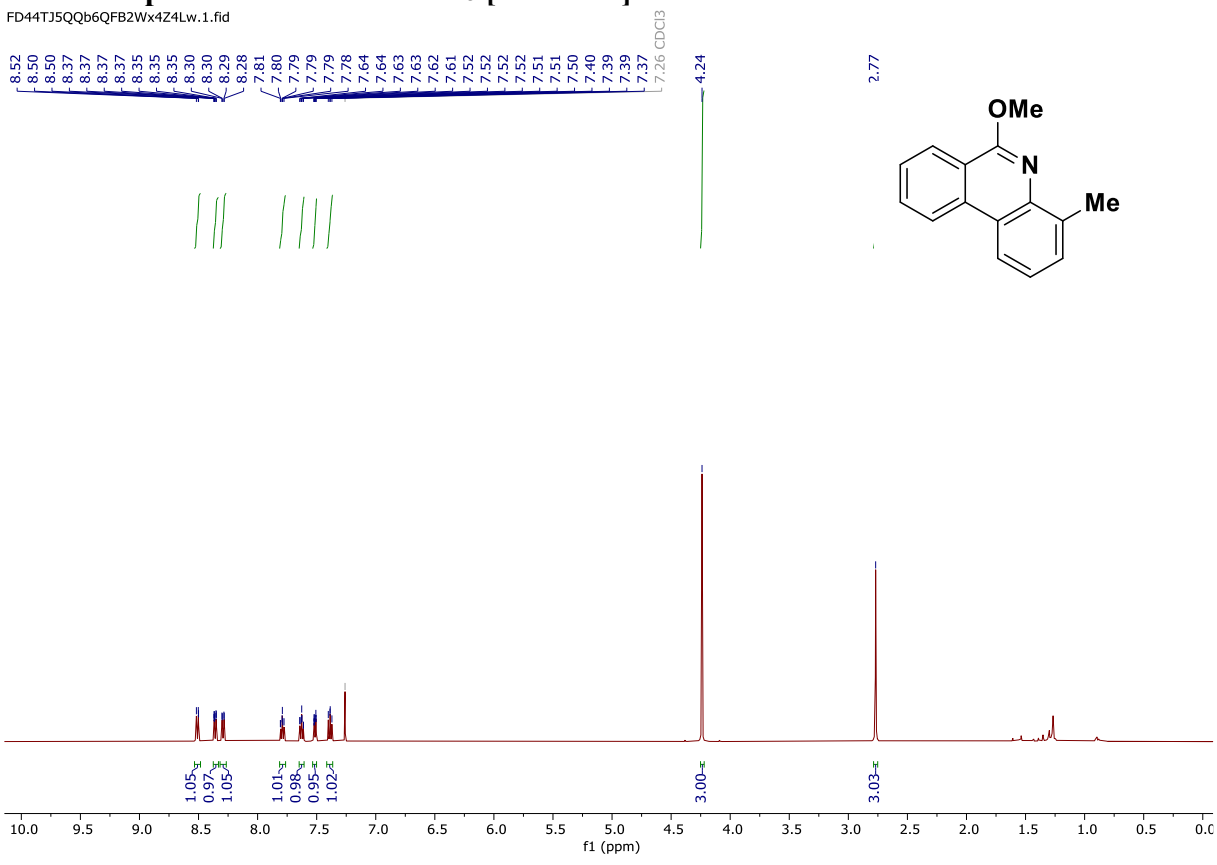
^{1}H NMR spectrum of 2l in $CDCl_3$ [500 MHz]



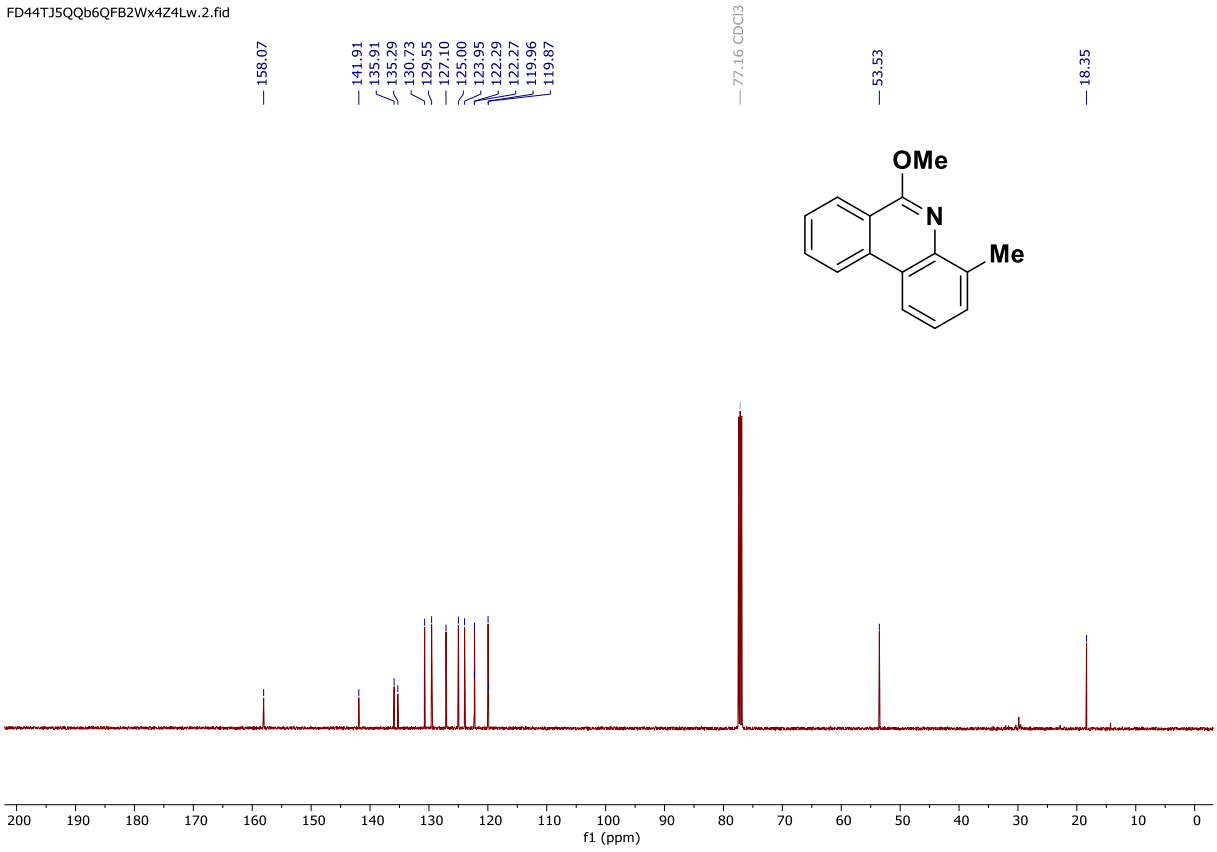
$^{13}C\{^{1}H\}$ NMR spectrum of 2l in $CDCl_3$ [126 MHz]



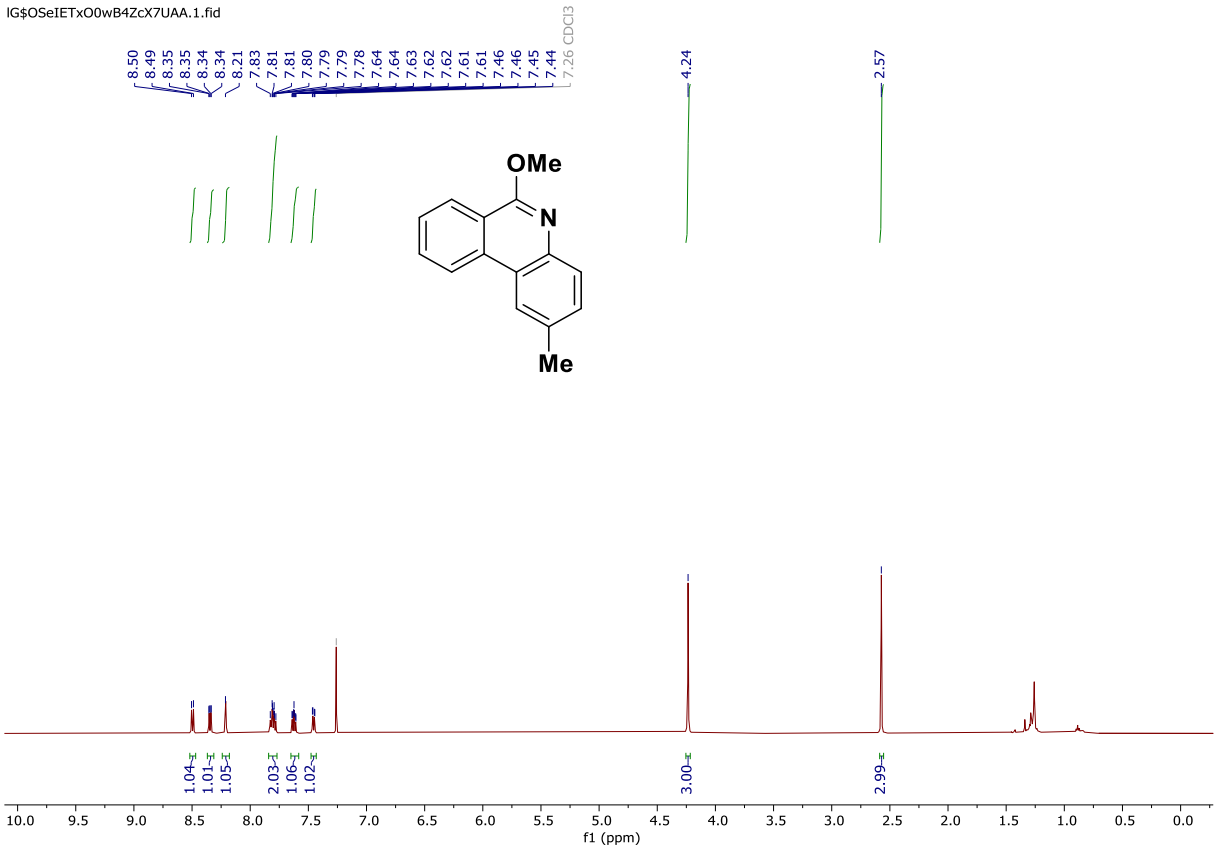
^{1}H NMR spectrum of 2m in $CDCl_3$ [500 MHz]



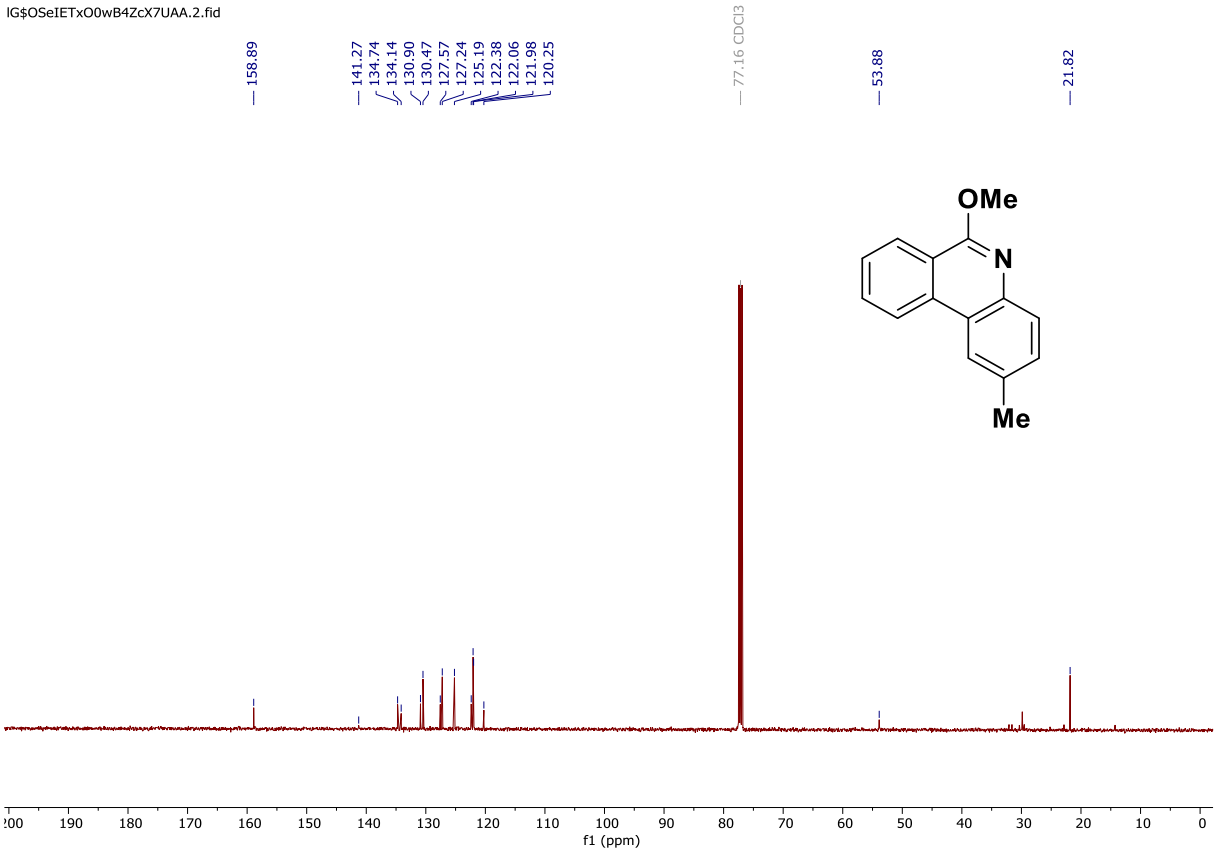
$^{13}C\{^{1}H\}$ NMR spectrum of 2m in $CDCl_3$ [126 MHz]



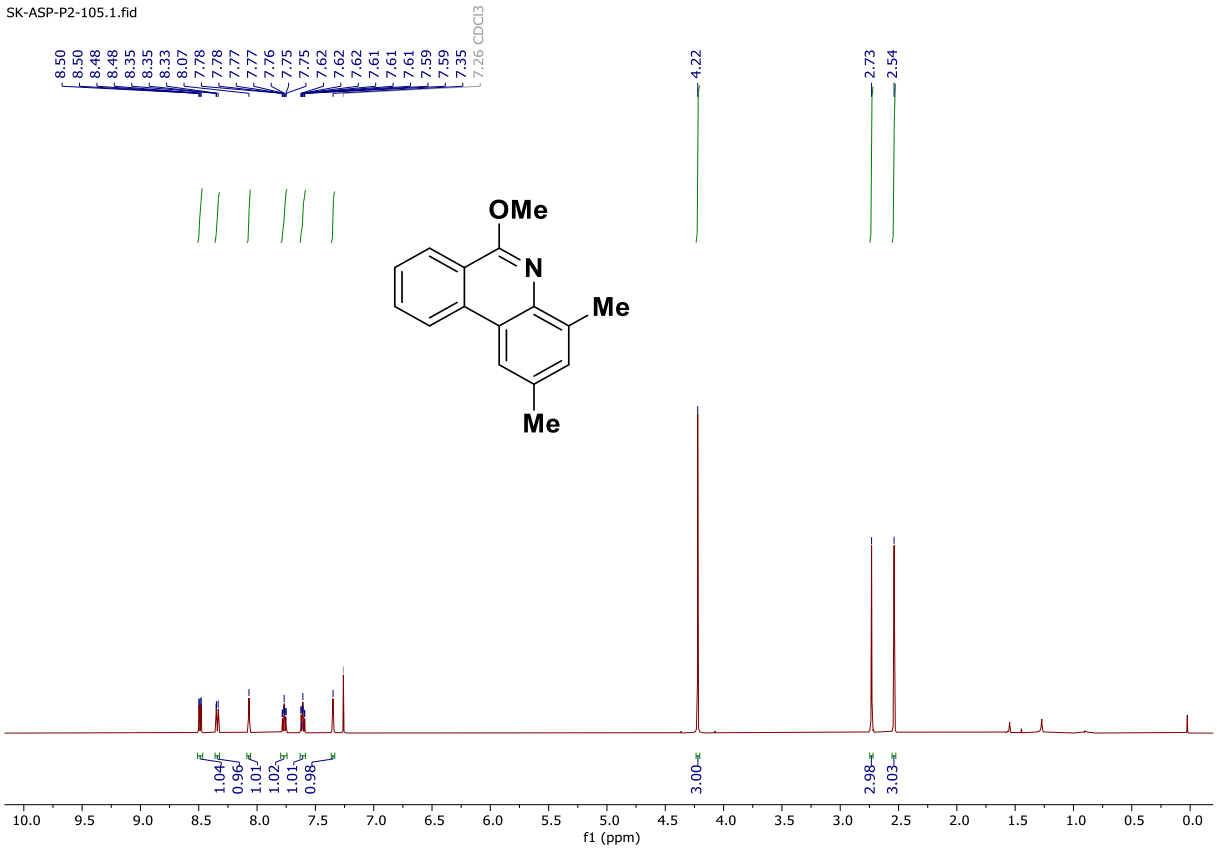
^{1}H NMR spectrum of 2m` in $CDCl_3$ [500 MHz]



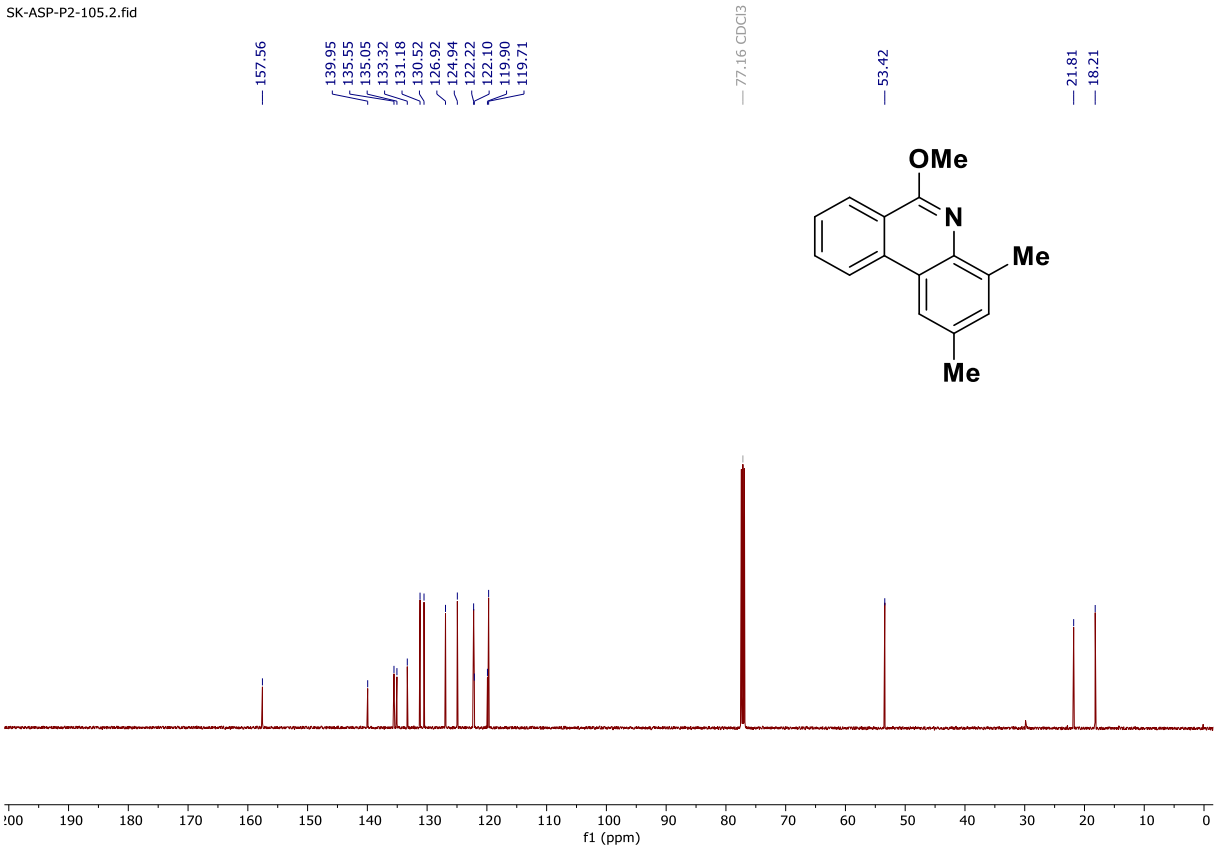
$^{13}C\{^{1}H\}$ NMR spectrum of 2m` in $CDCl_3$ [126 MHz]



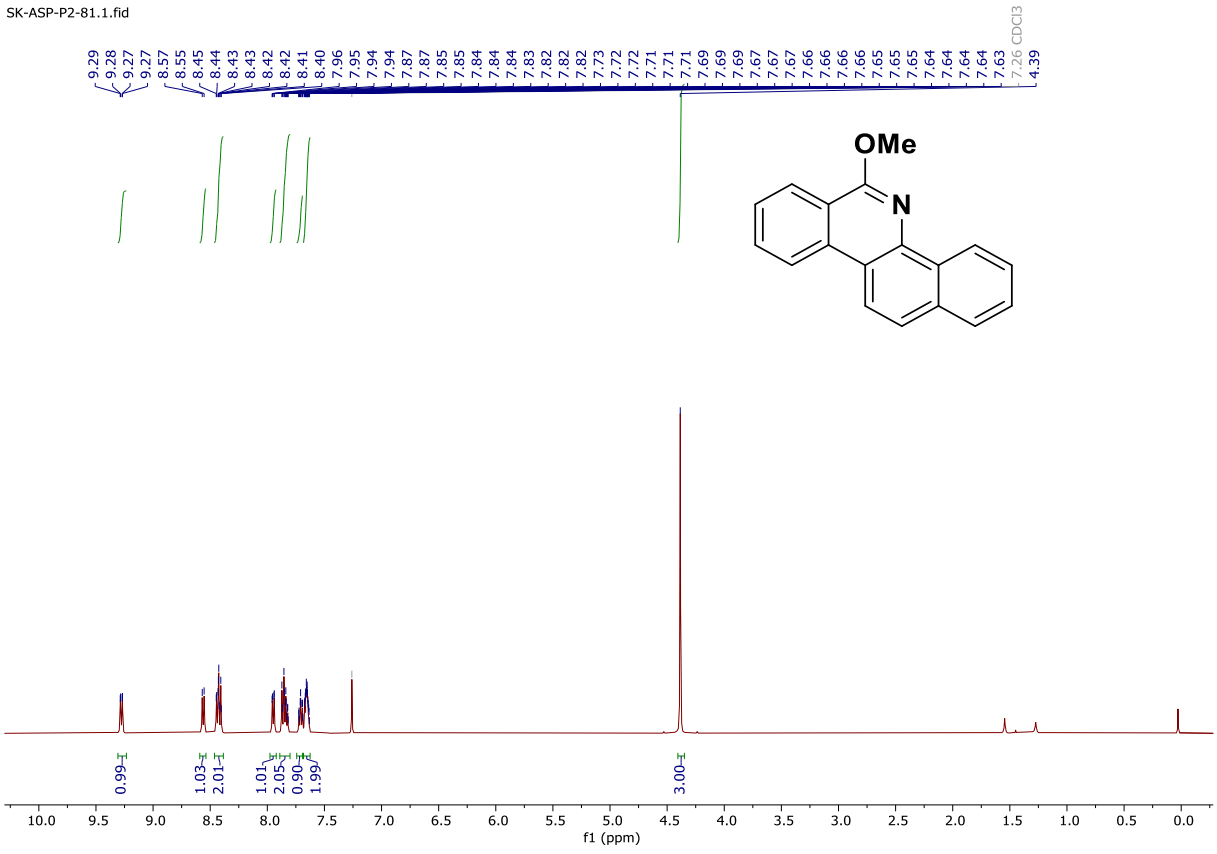
^{1}H NMR spectrum of 2n in $CDCl_3$ [500 MHz]



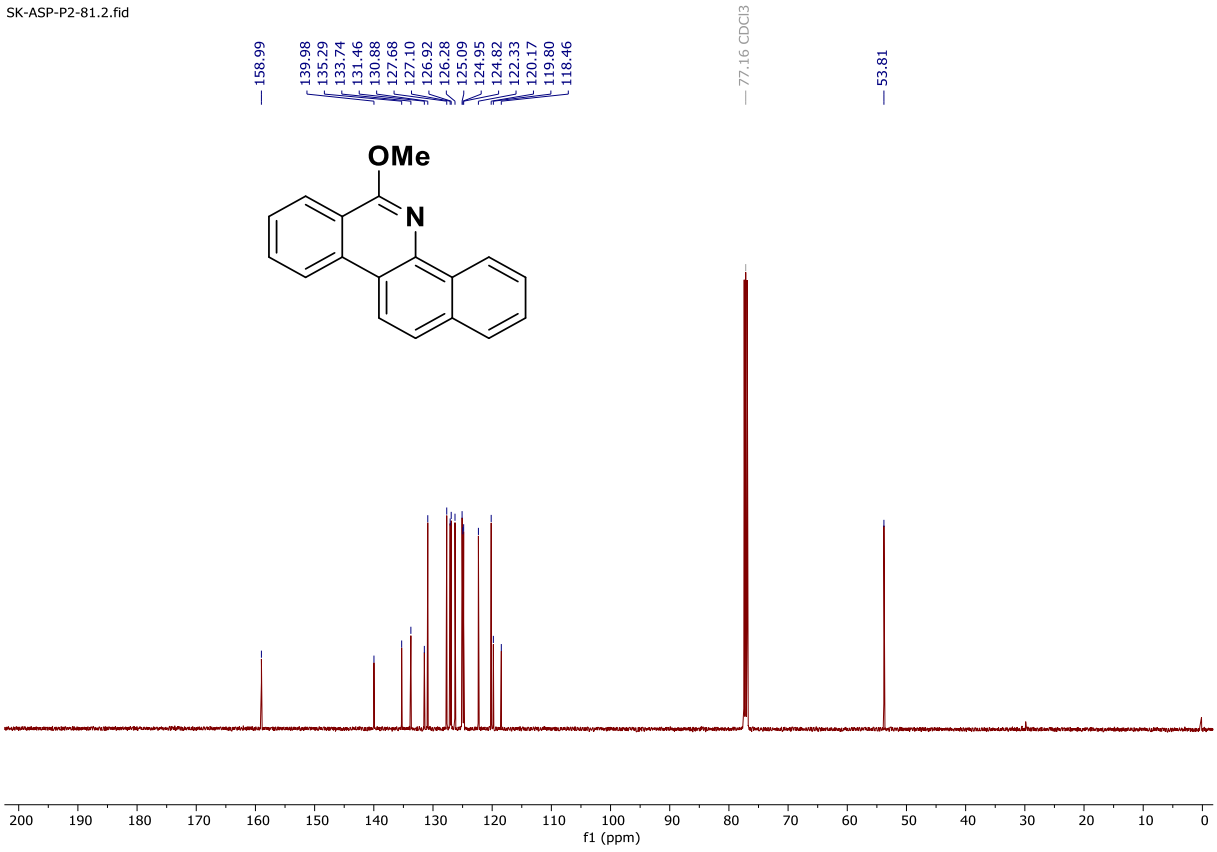
$^{13}C\{^{1}H\}$ NMR spectrum of 2n in $CDCl_3$ [126 MHz]



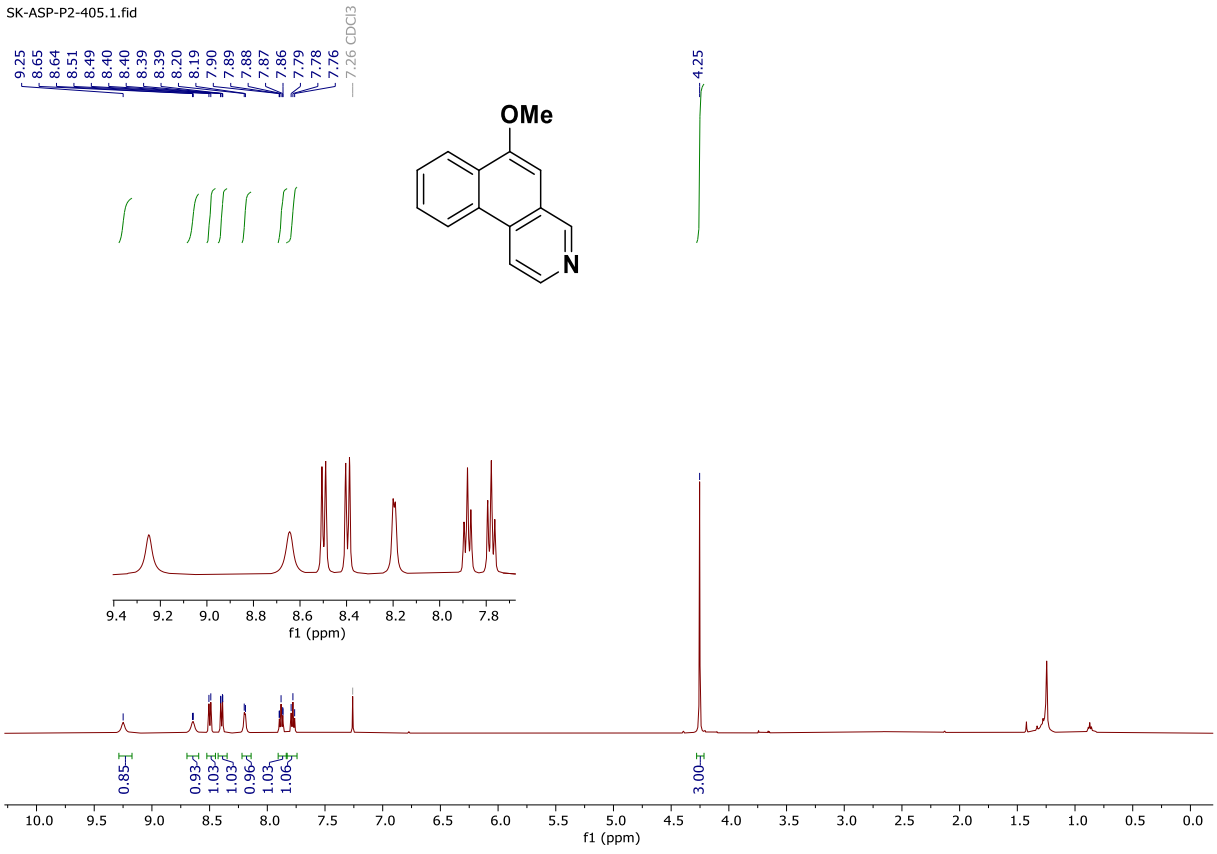
^{1}H NMR spectrum of 2p in $CDCl_3$ [500 MHz]



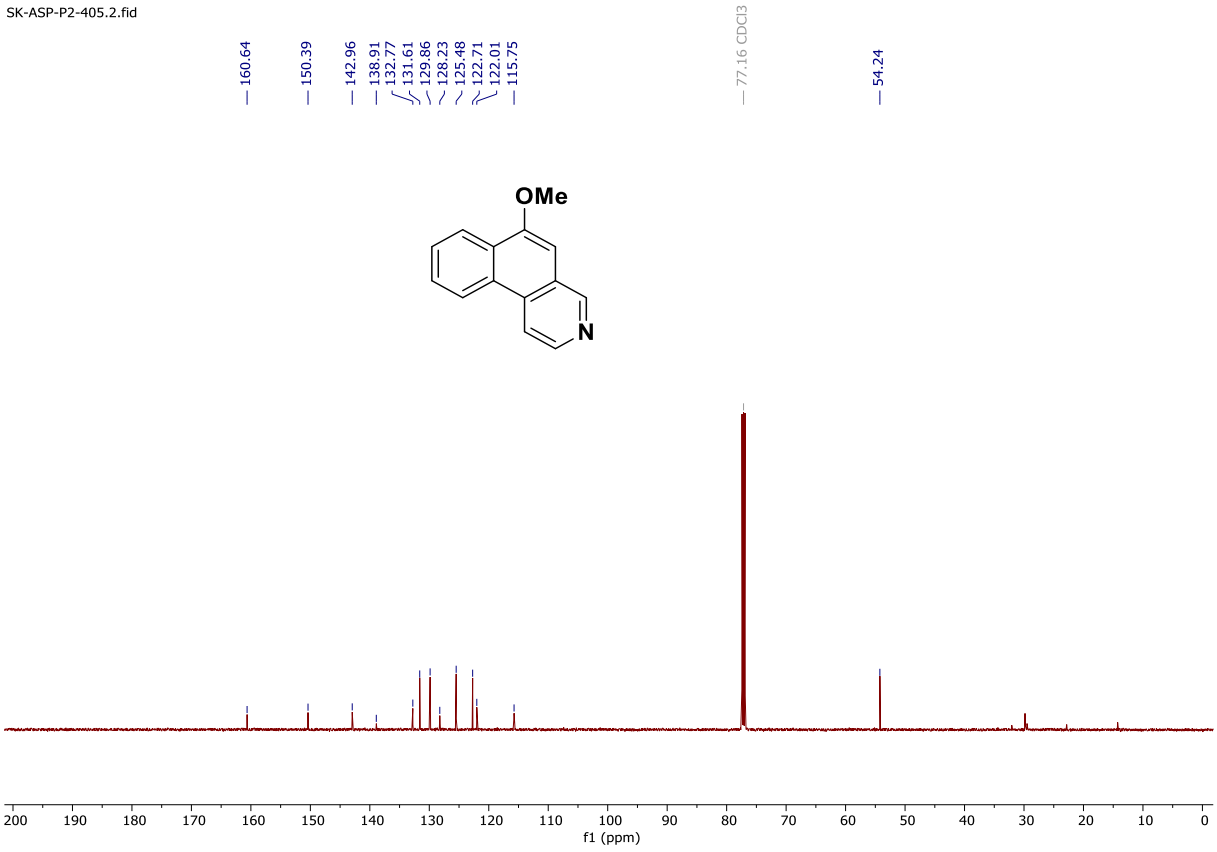
$^{13}C\{^{1}H\}$ NMR spectrum of 2p in $CDCl_3$ [126 MHz]



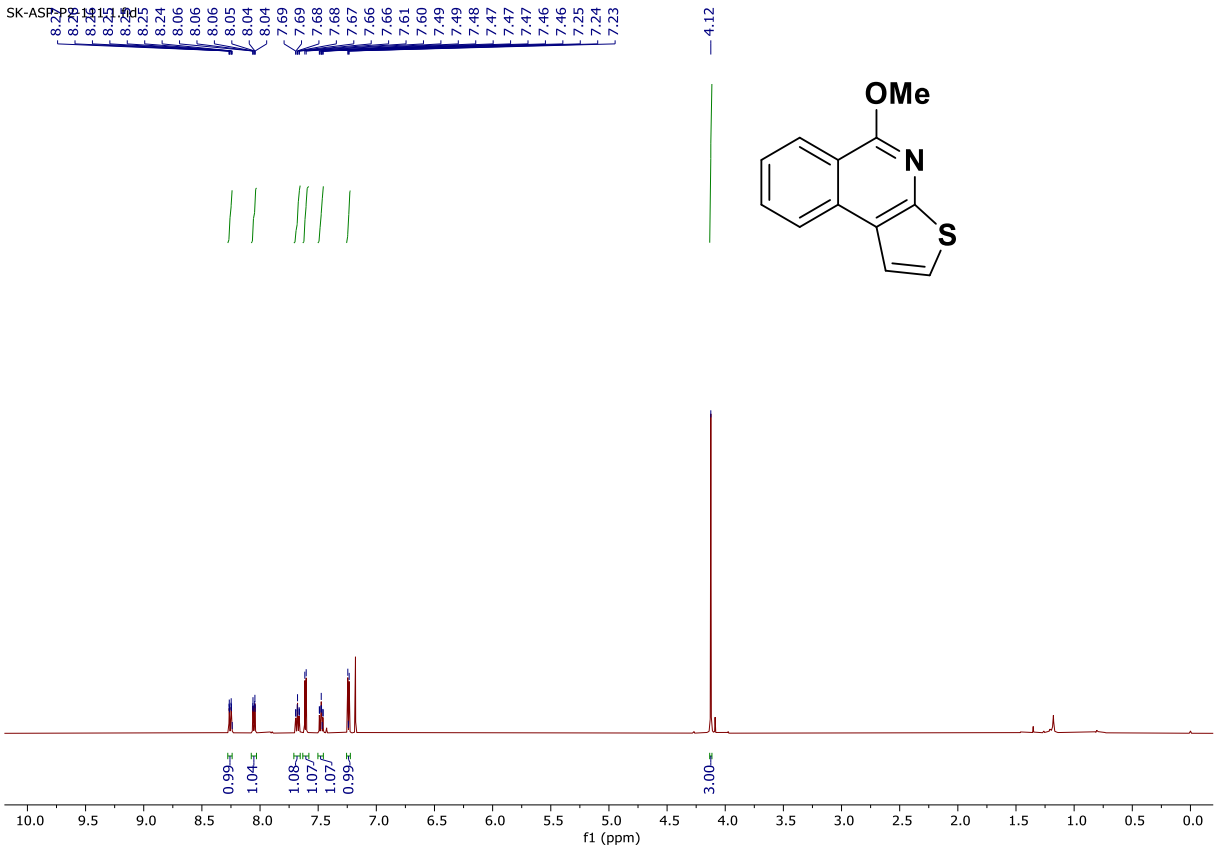
^{1}H NMR spectrum of 2q in $CDCl_3$ [500 MHz]



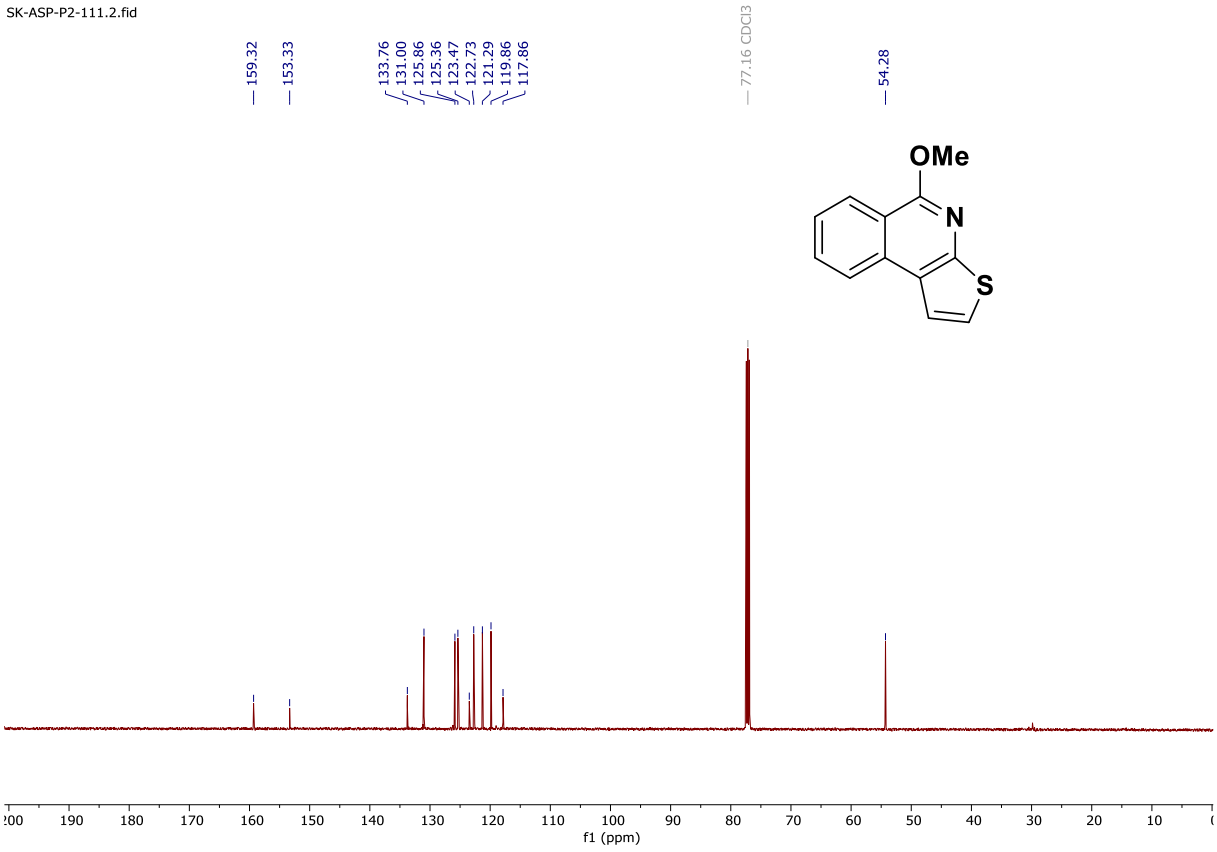
$^{13}C\{^{1}H\}$ NMR spectrum of 2q in $CDCl_3$ [126 MHz]



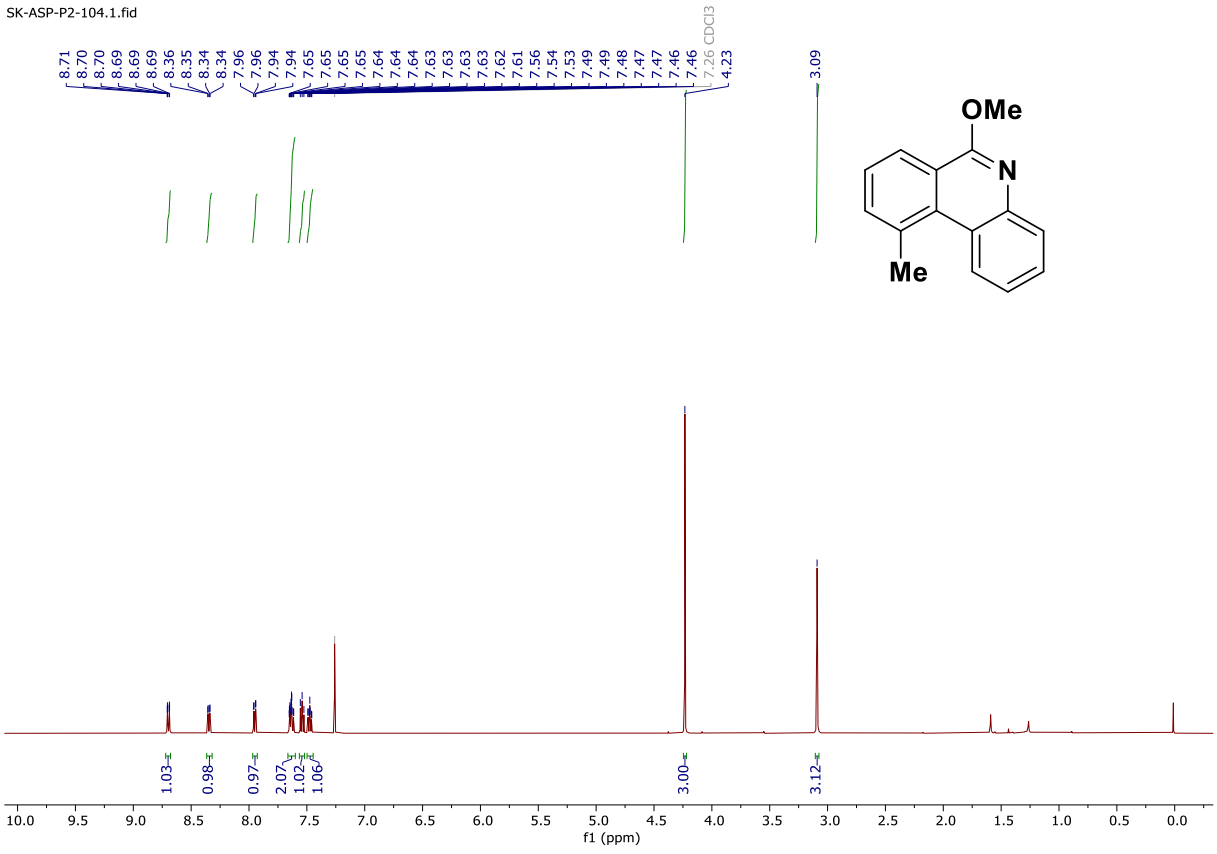
^{1}H NMR spectrum of 2r in $CDCl_3$ [500 MHz]



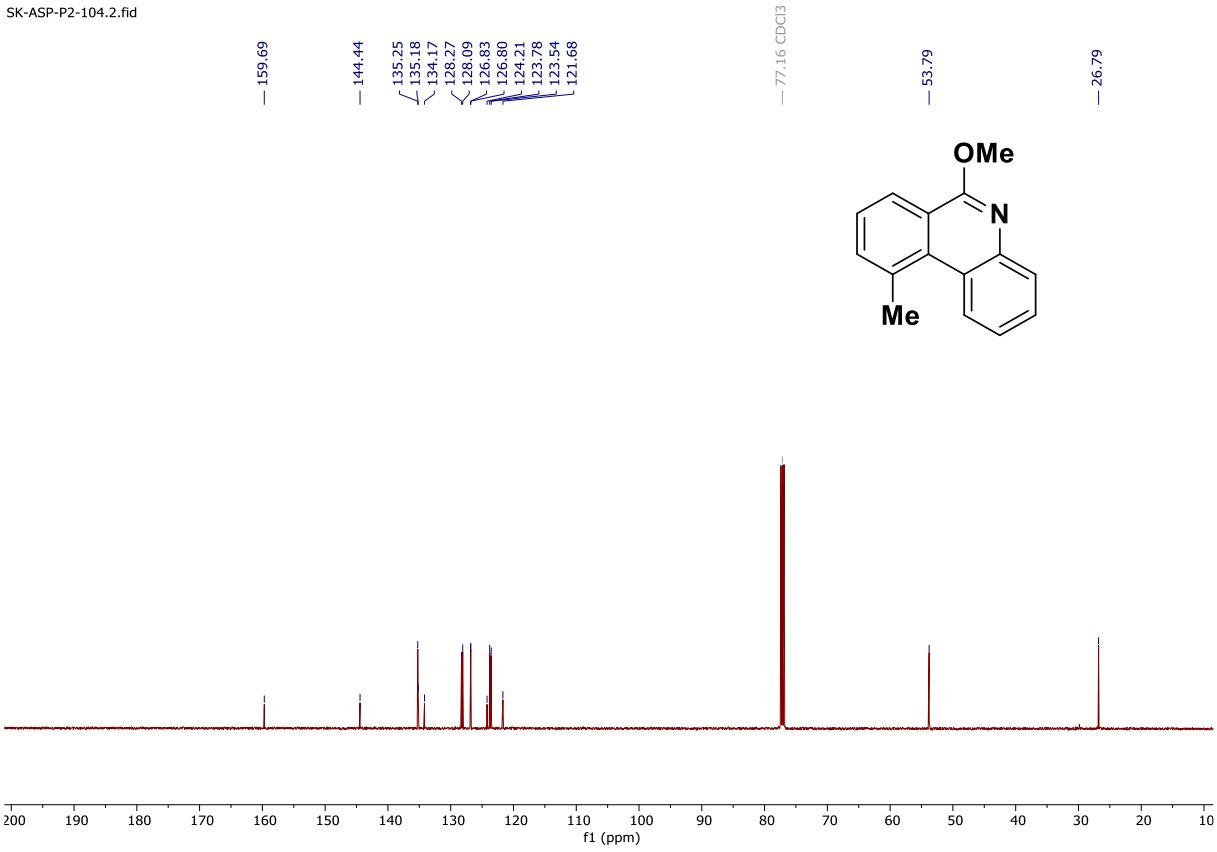
$^{13}C\{^{1}H\}$ NMR spectrum of 2r in $CDCl_3$ [126 MHz]



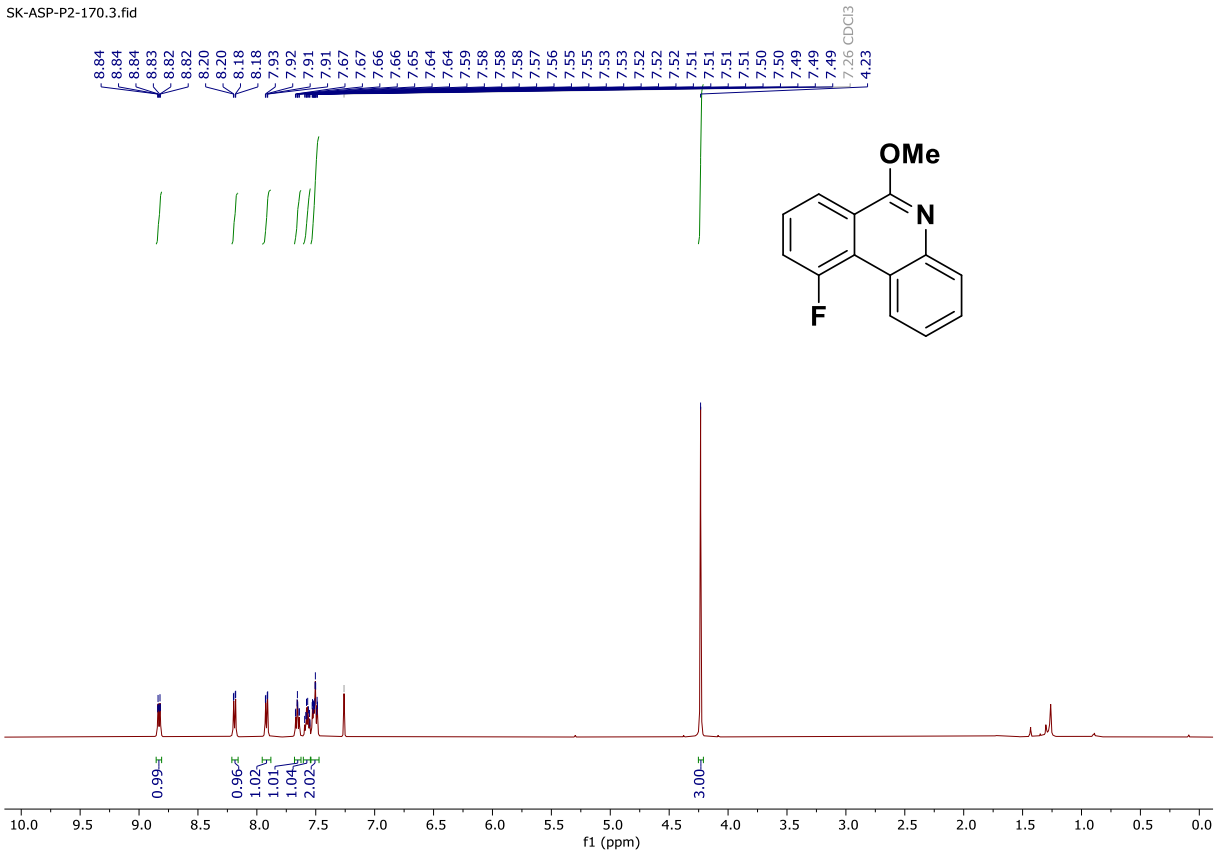
^{1}H NMR spectrum of 2s in $CDCl_3$ [500 MHz]



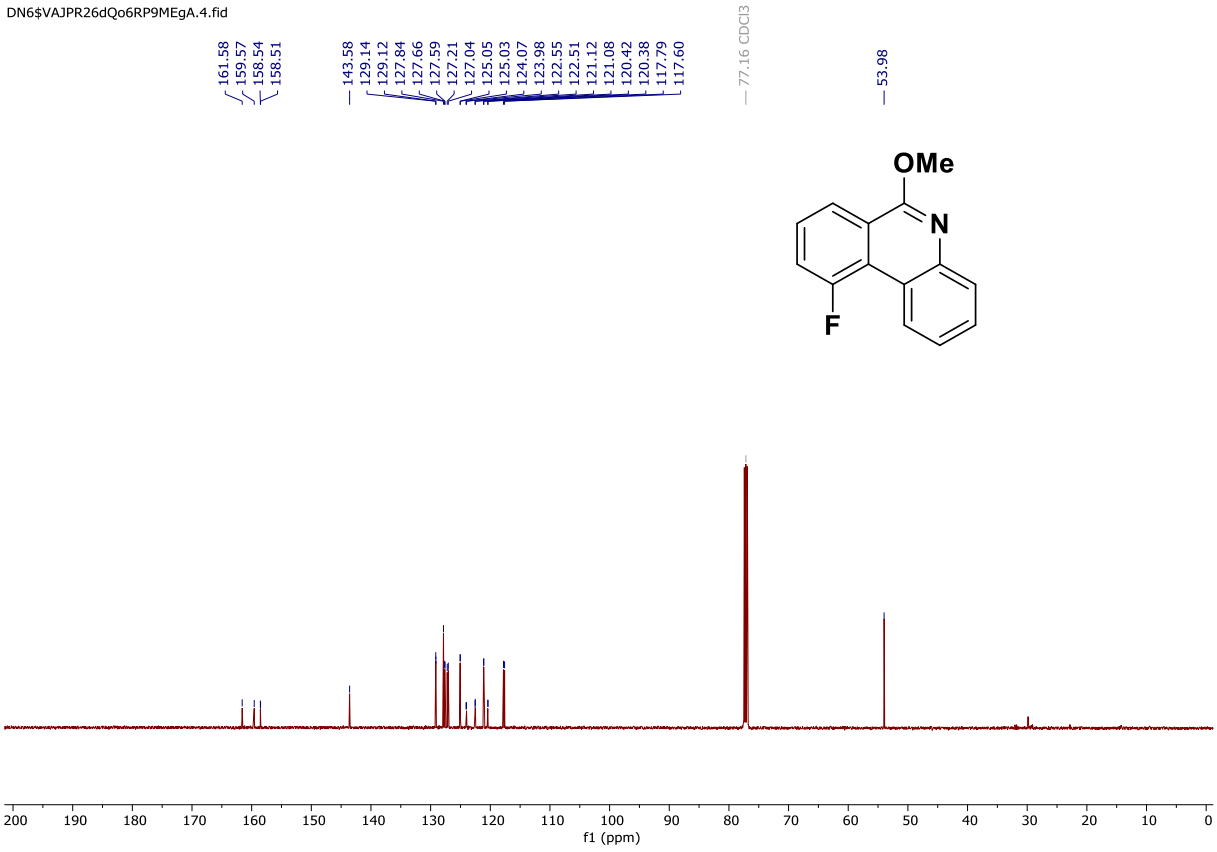
$^{13}C\{^{1}H\}$ NMR spectrum of 2s in $CDCl_3$ [126 MHz]



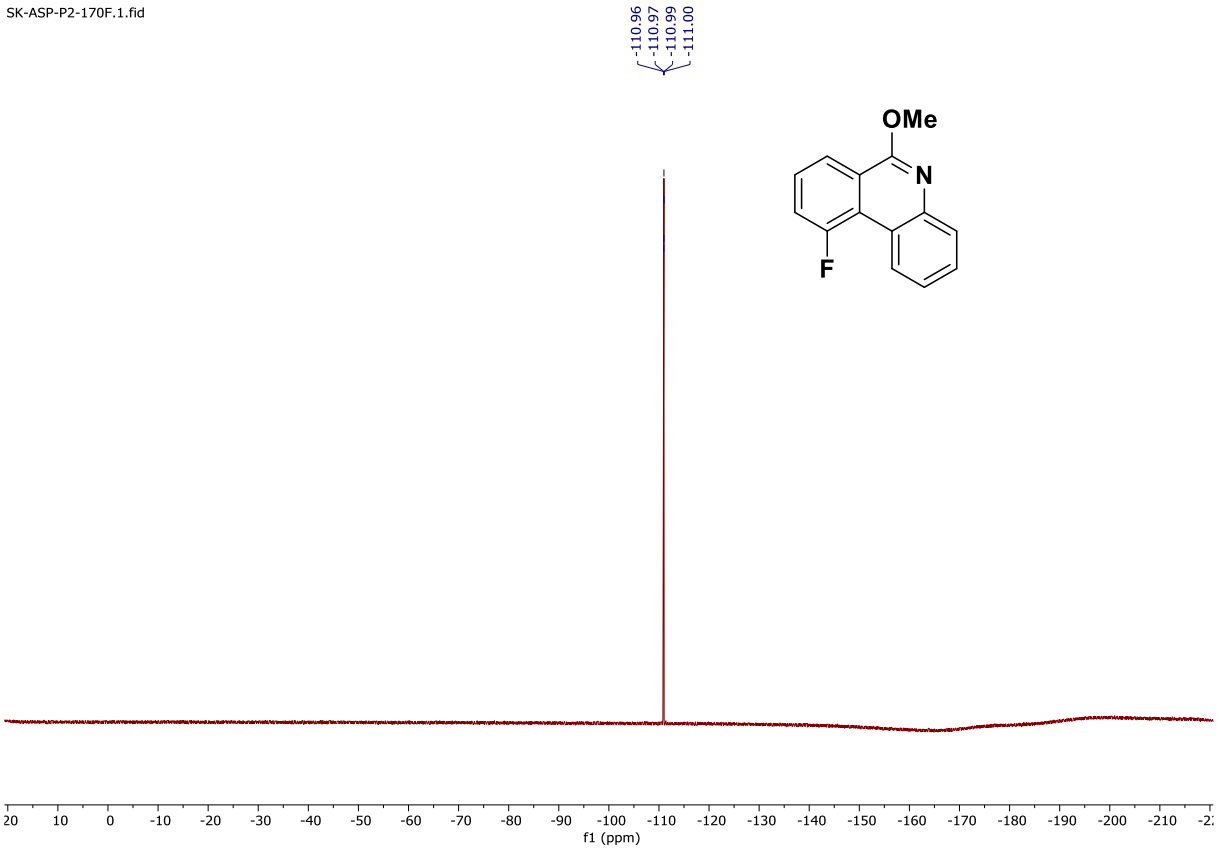
^{1}H NMR spectrum of 2t in $CDCl_3$ [500 MHz]



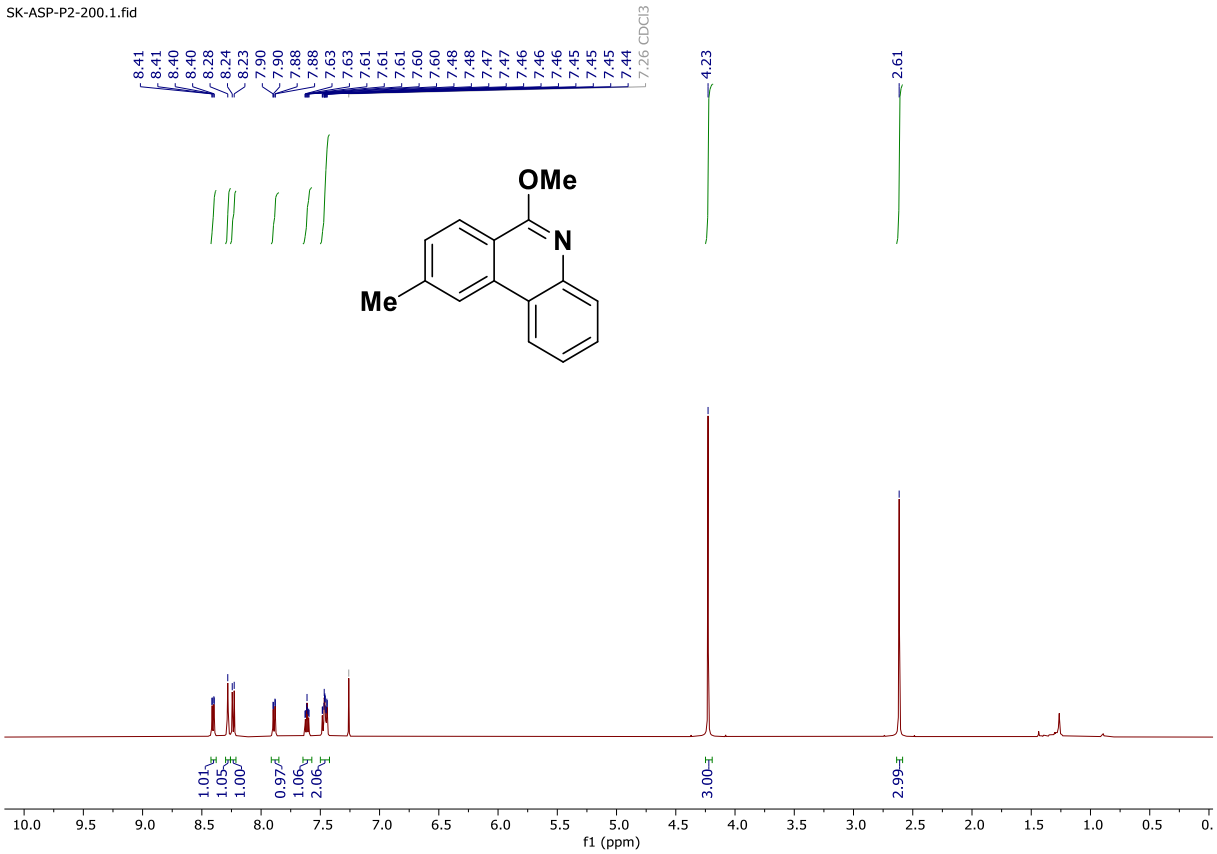
$^{13}C\{^{1}H\}$ NMR spectrum of 2t in $CDCl_3$ [126 MHz]



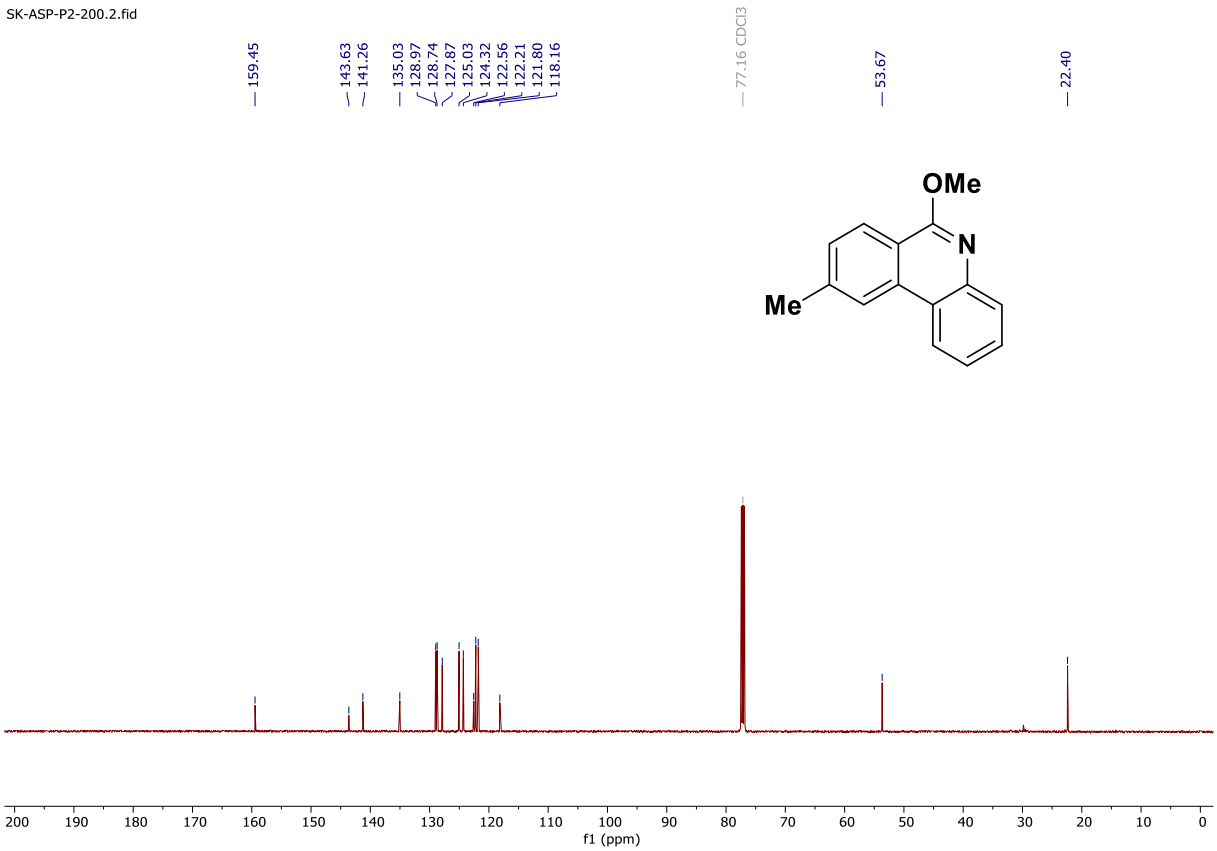
^{19}F NMR spectrum of 2t in $CDCl_3$ [471 MHz]



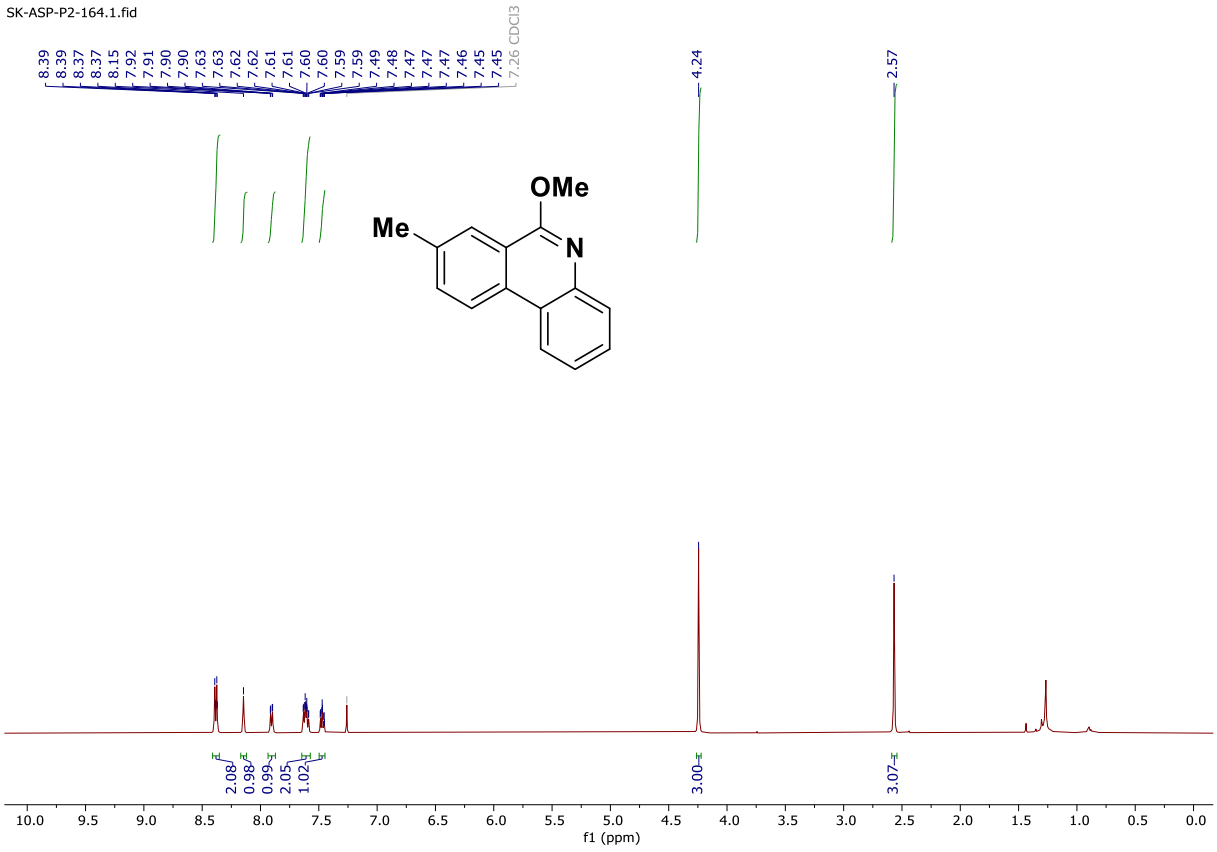
^{1}H NMR spectrum of 2u in $CDCl_3$ [500 MHz]



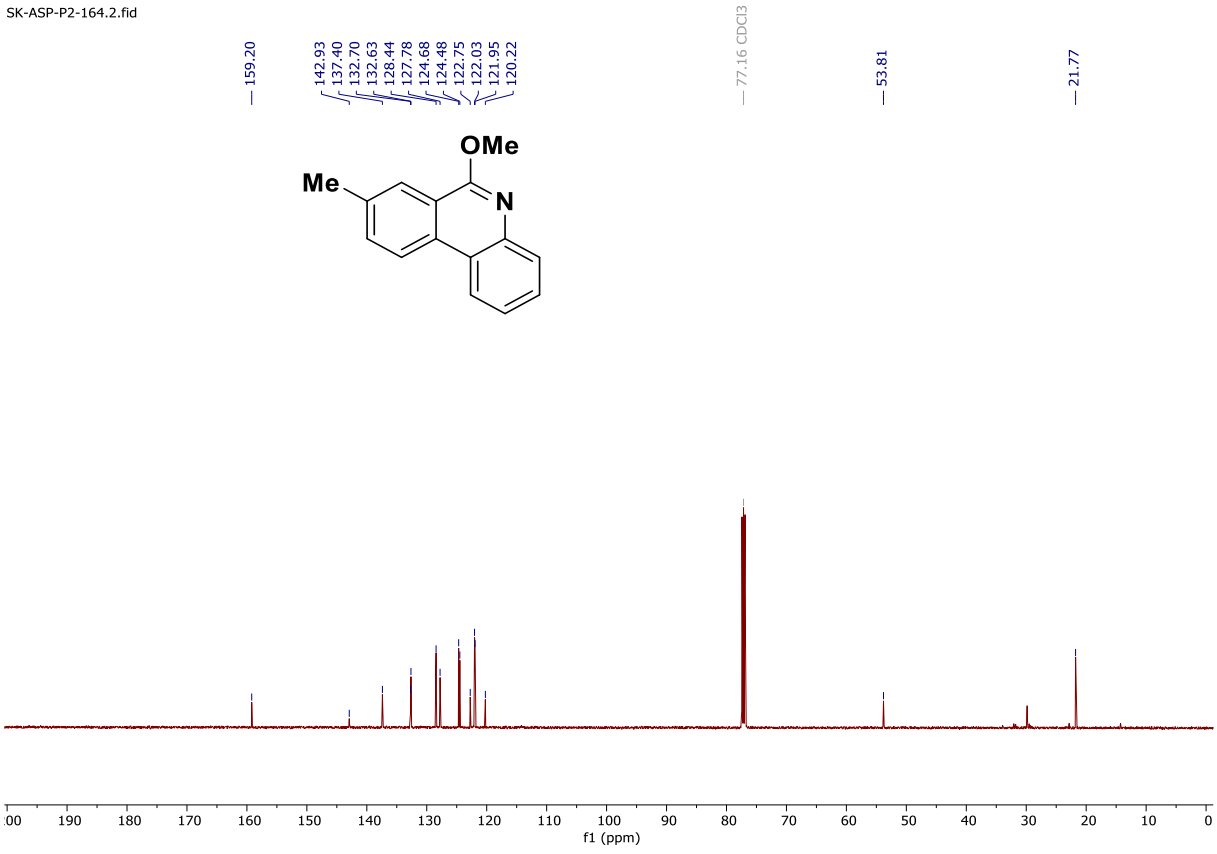
^{13}C{^{1}H} NMR spectrum of 2u in $CDCl_3$ [126 MHz]



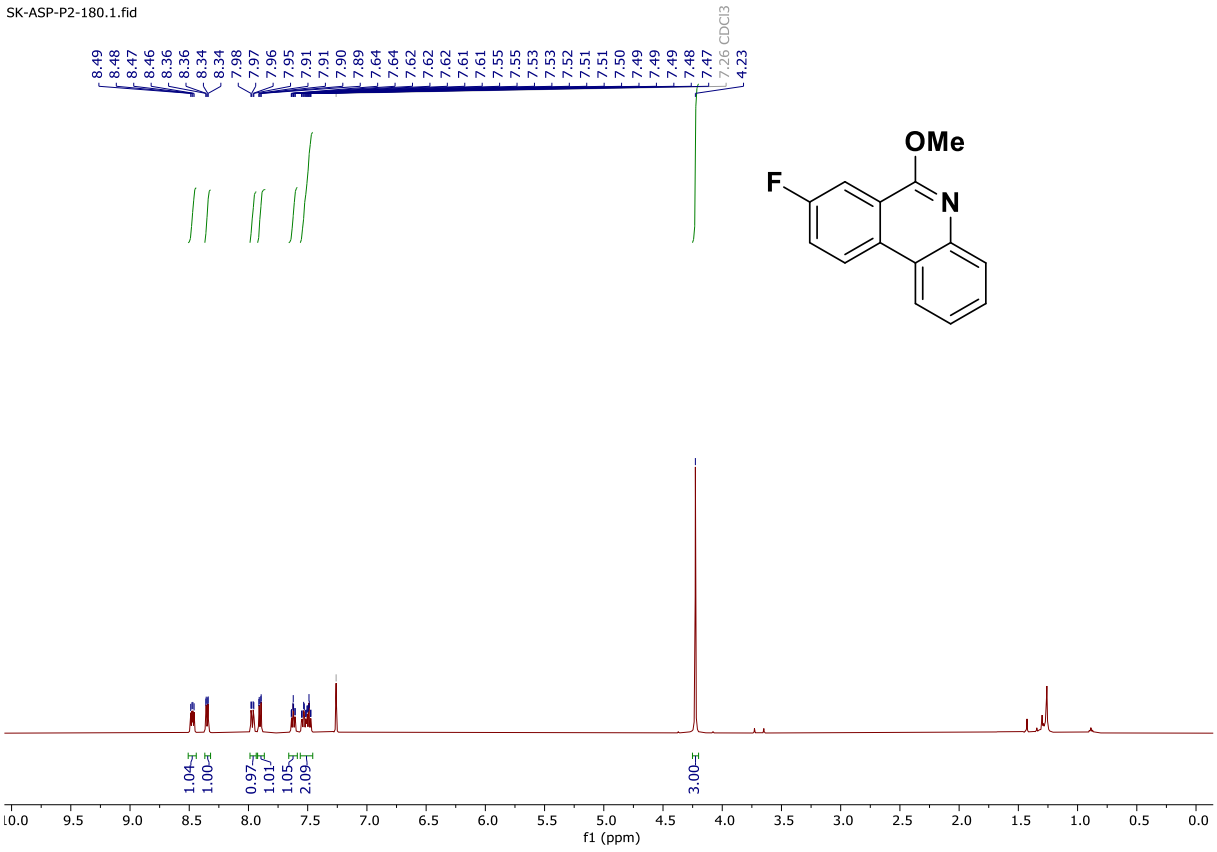
^{1}H NMR spectrum of 2v in $CDCl_3$ [500 MHz]



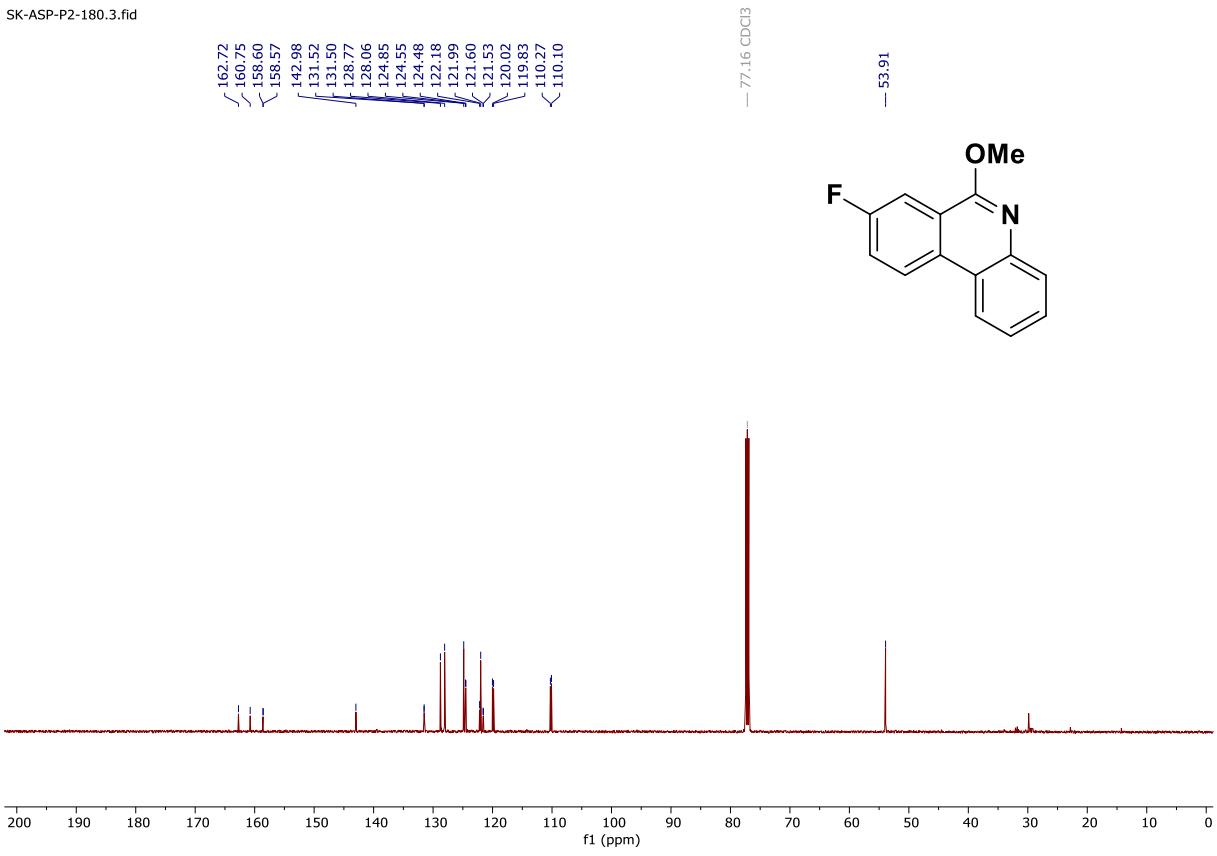
^{13}C{^{1}H} NMR spectrum of 2v in $CDCl_3$ [126 MHz]



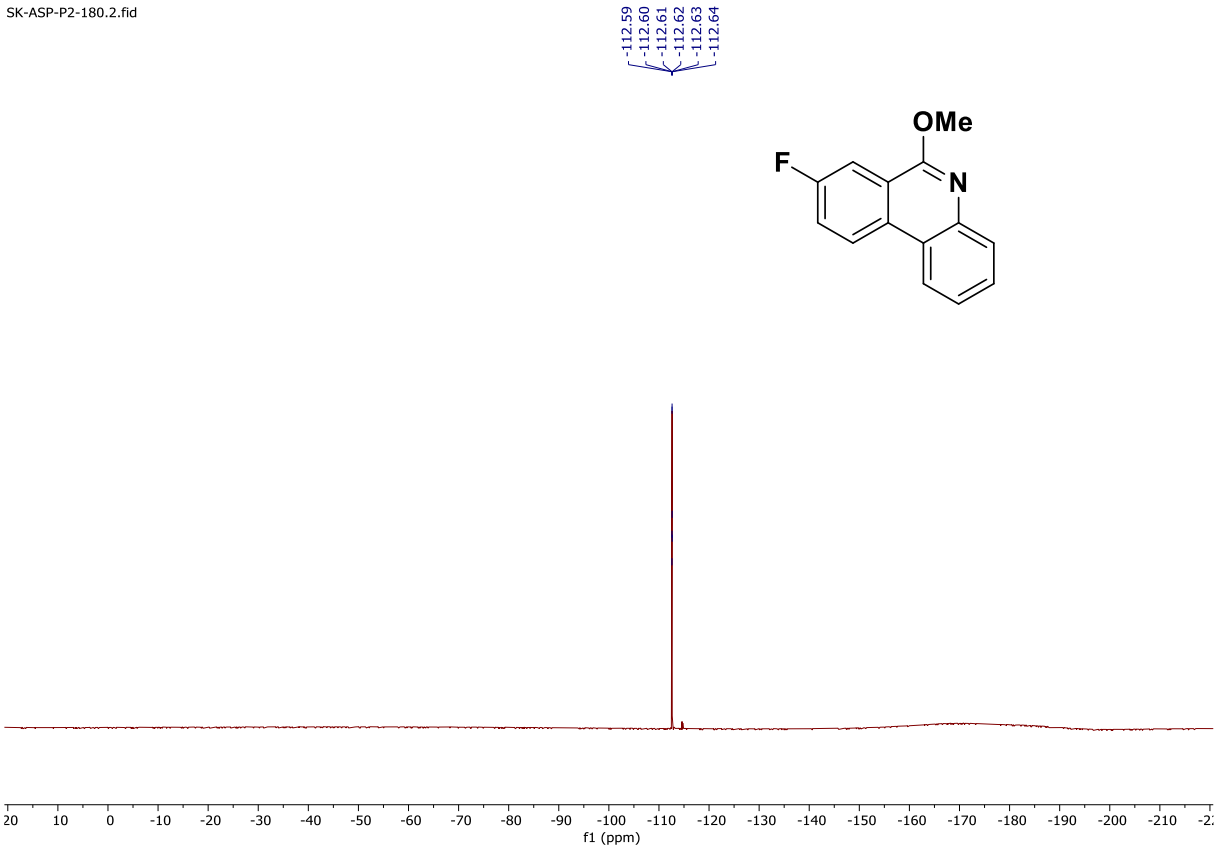
^{1}H NMR spectrum of 2w in $CDCl_3$ [500 MHz]



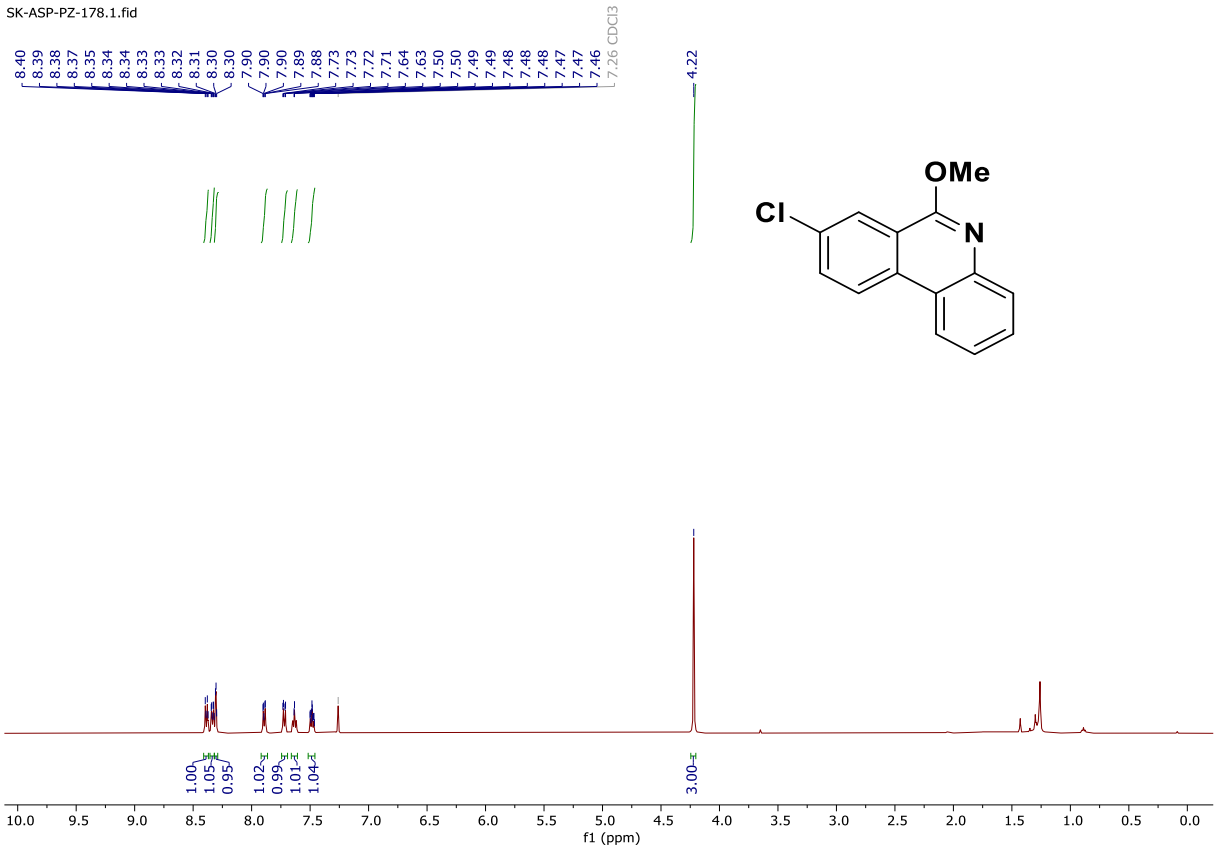
^{13}C{^{1}H} NMR spectrum of 2w in $CDCl_3$ [126 MHz]



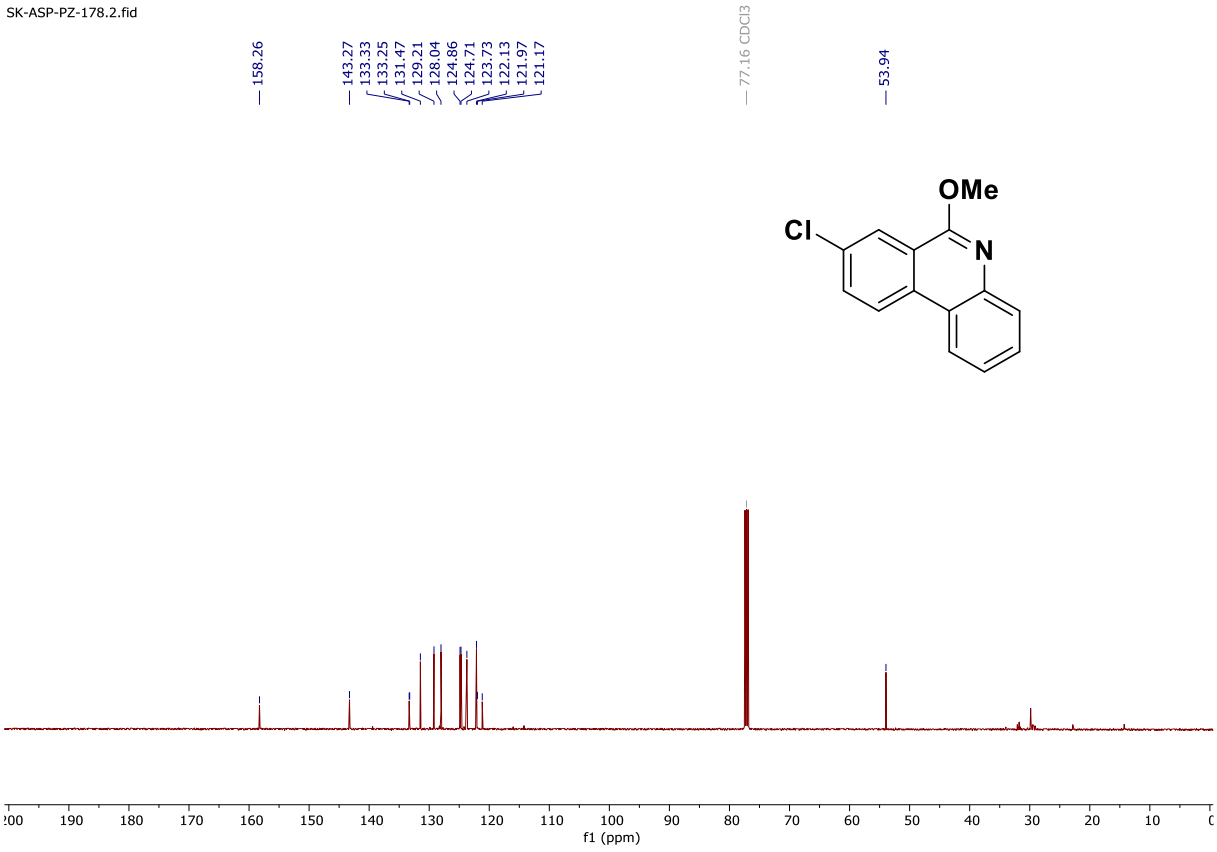
^{19}F NMR spectrum of 2w in $CDCl_3$ [471 MHz]



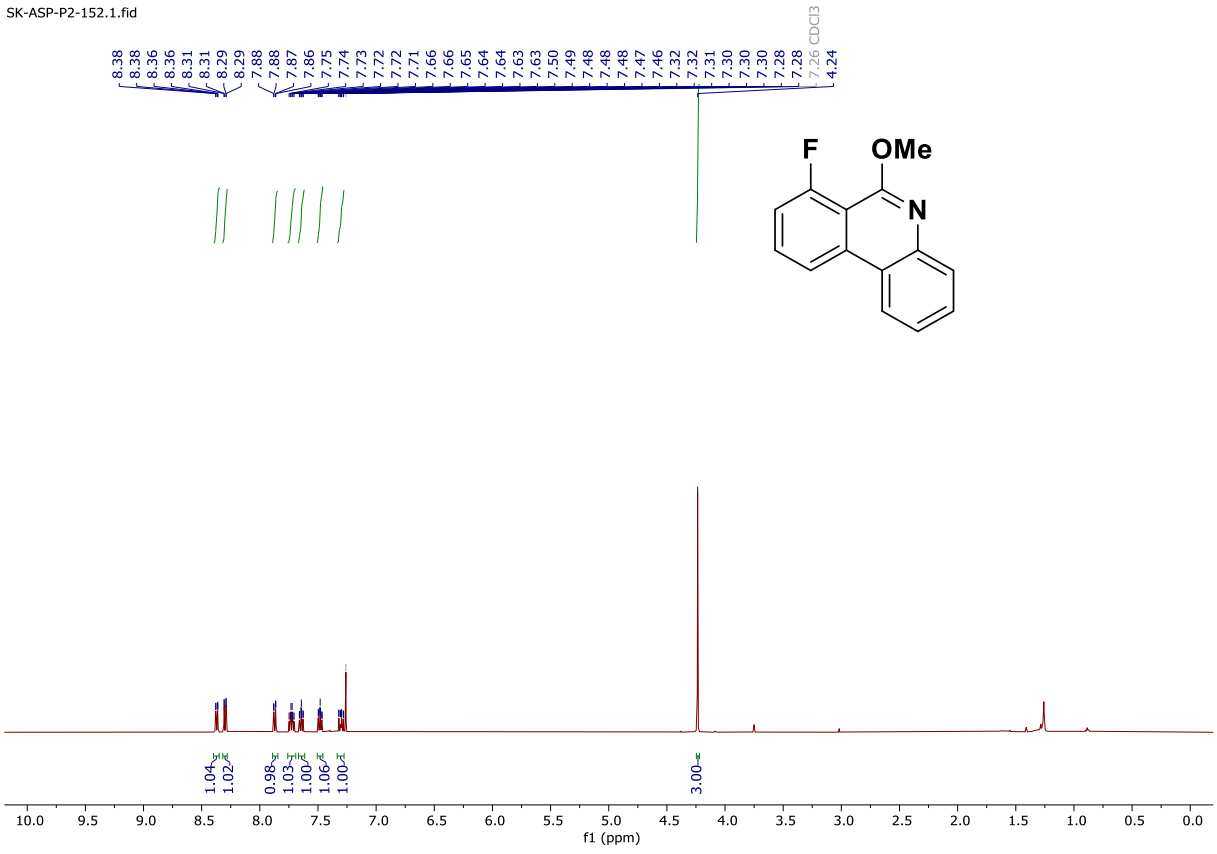
^{1}H NMR spectrum of 2x in $CDCl_3$ [500 MHz]



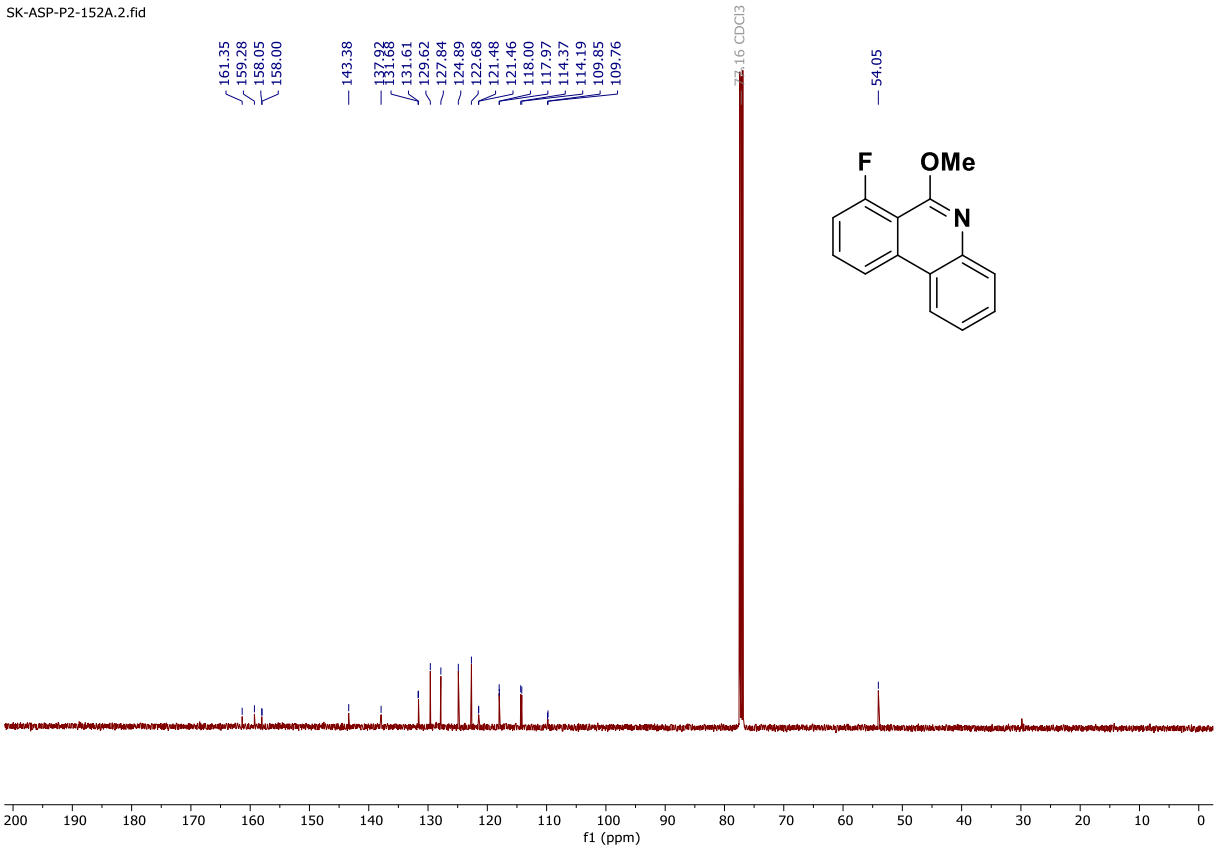
$^{13}C\{^{1}H\}$ NMR spectrum of 2x in $CDCl_3$ [126 MHz]



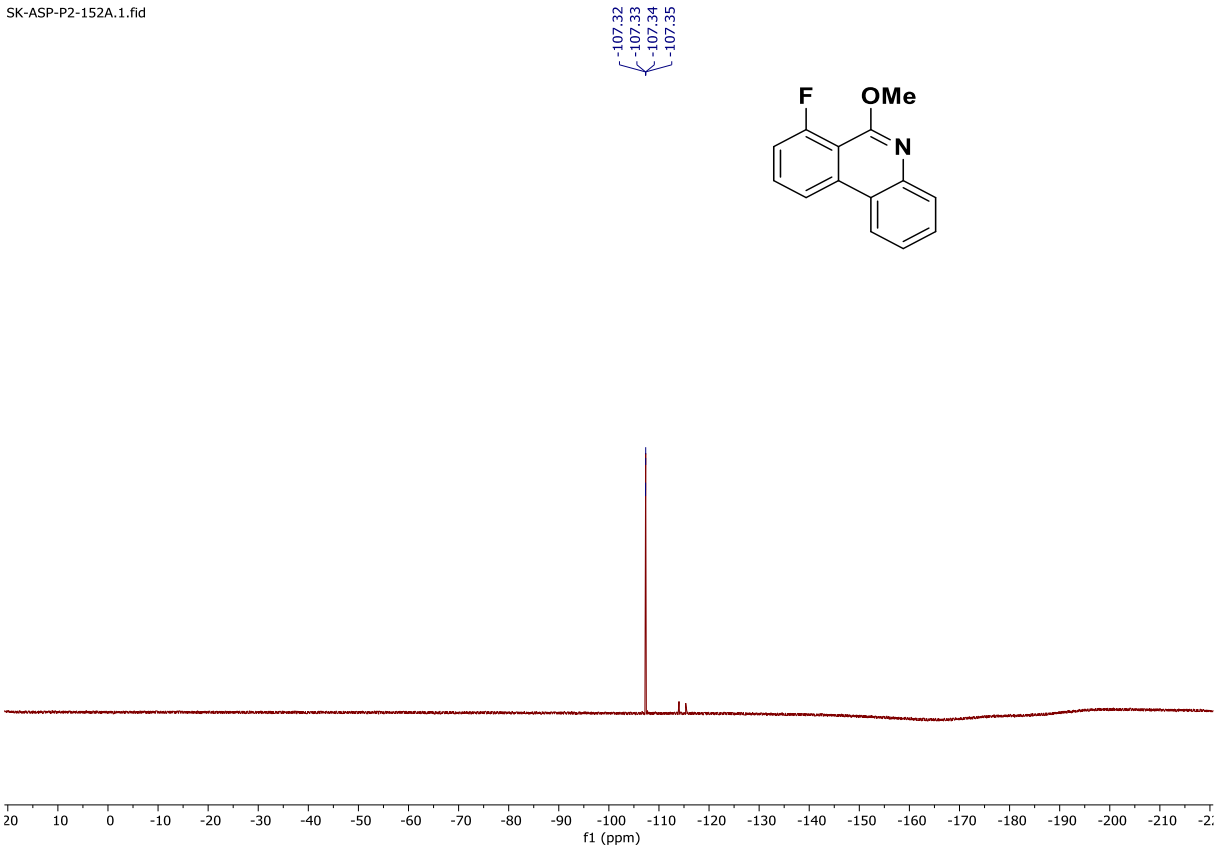
^{1}H NMR spectrum of 2y in $CDCl_3$ [500 MHz]



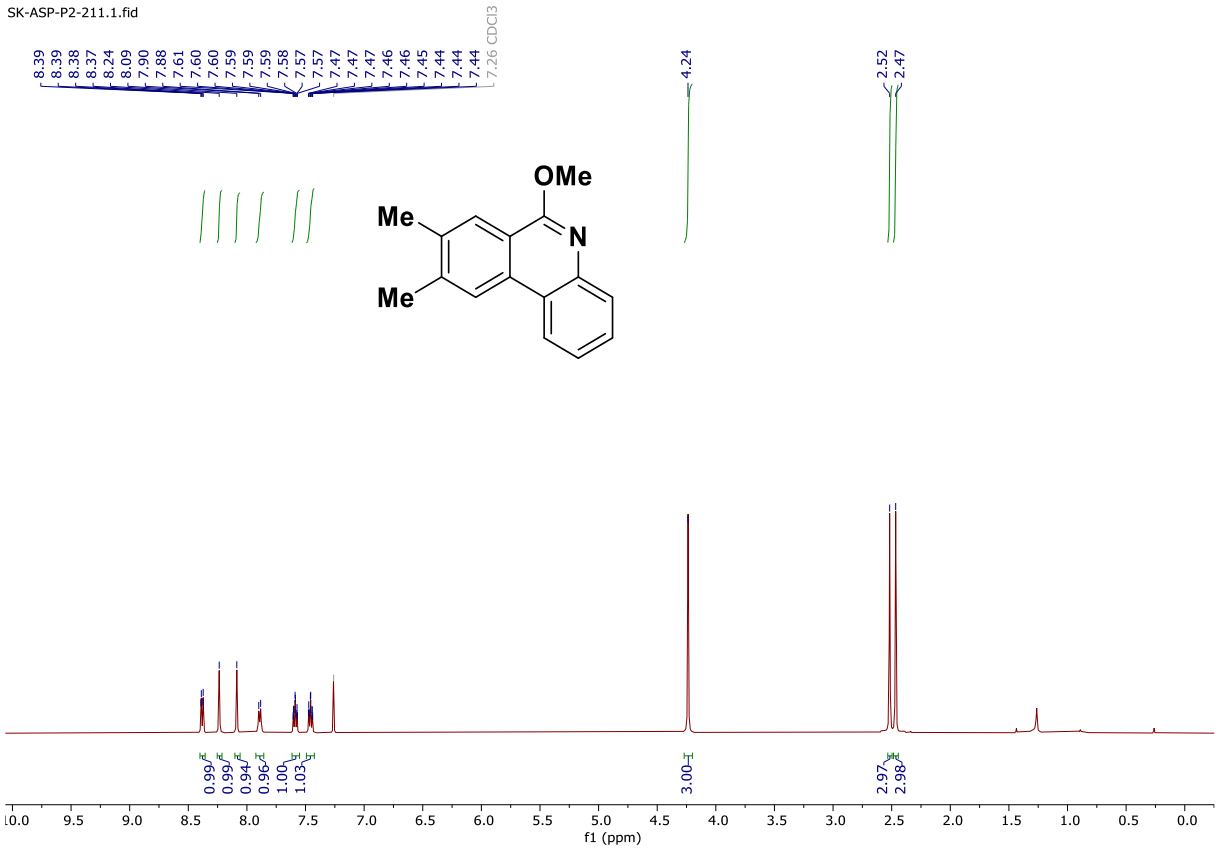
$^{13}C\{^{1}H\}$ NMR spectrum of 2y in $CDCl_3$ [126 MHz]



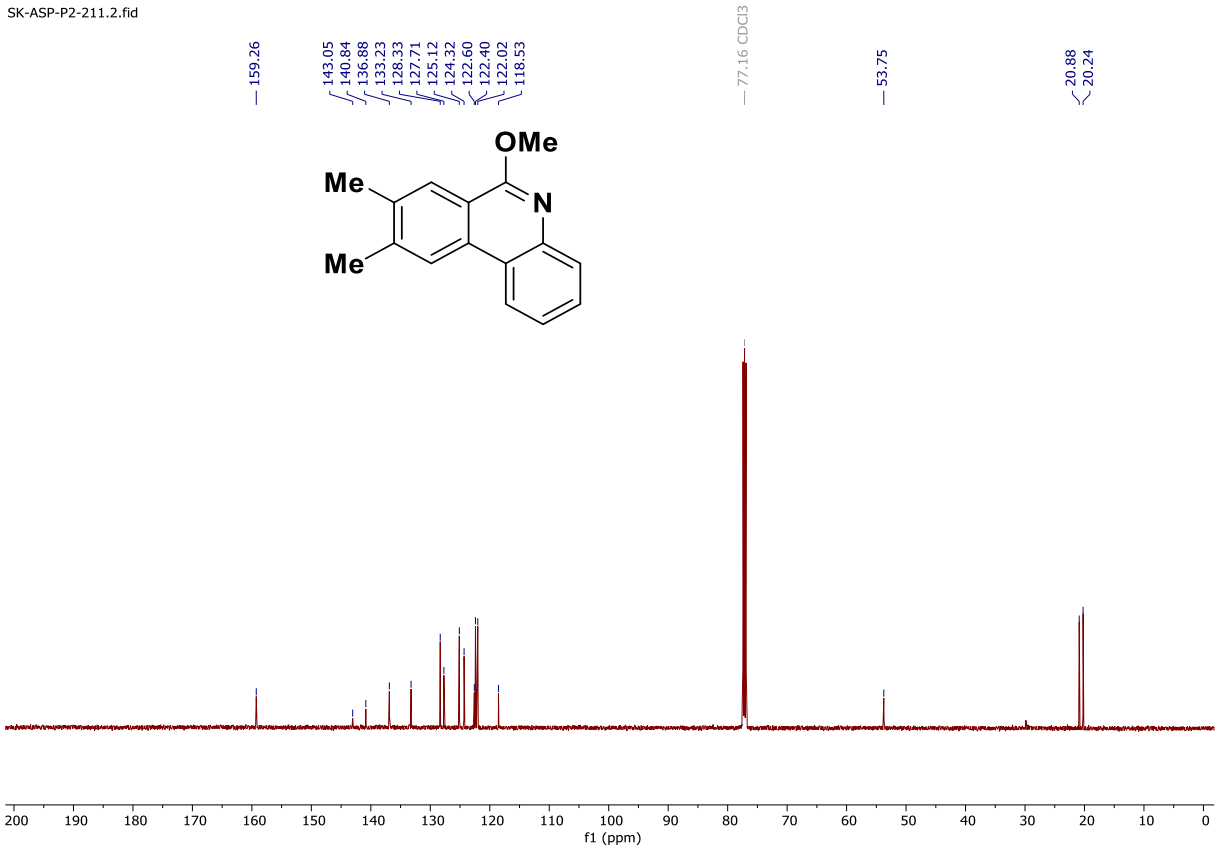
^{19}F NMR spectrum of 2y in $CDCl_3$ [471 MHz]



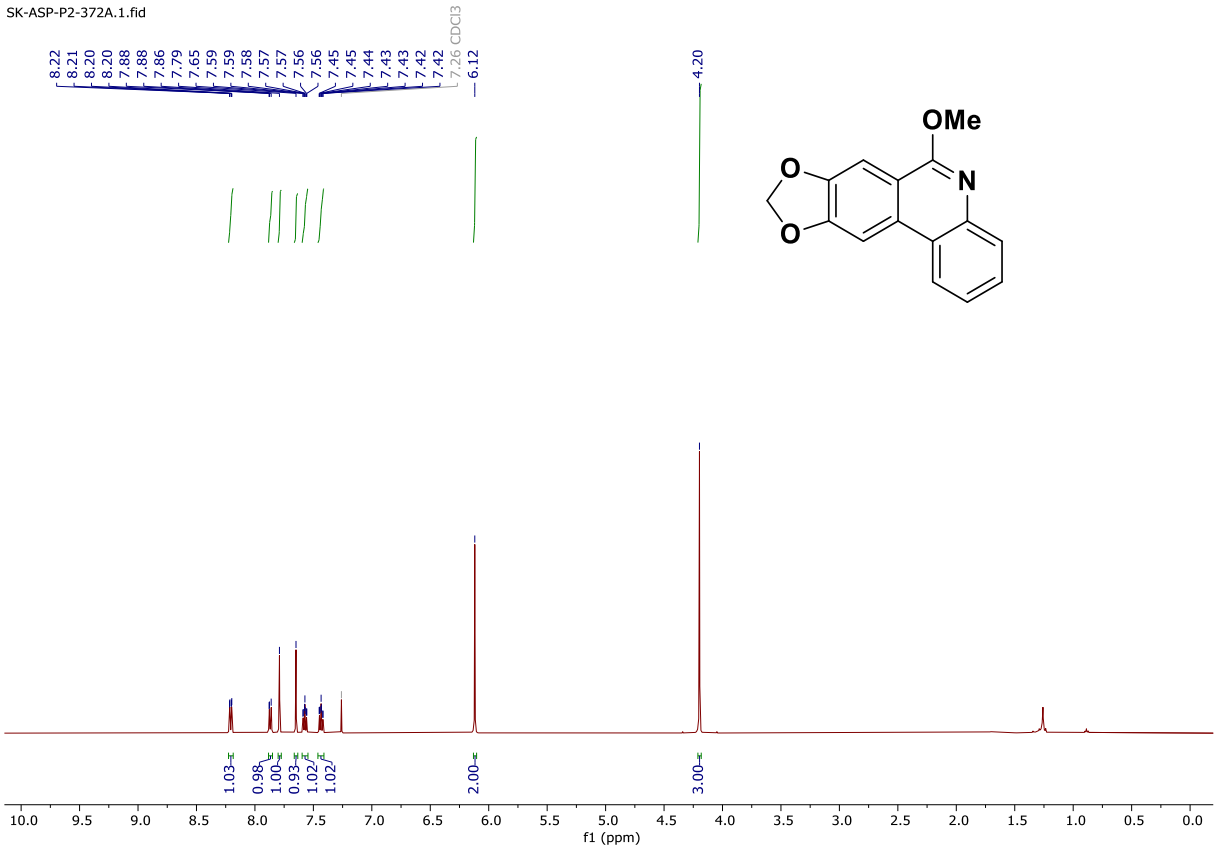
^{1}H NMR spectrum of 2z in $CDCl_3$ [500 MHz]



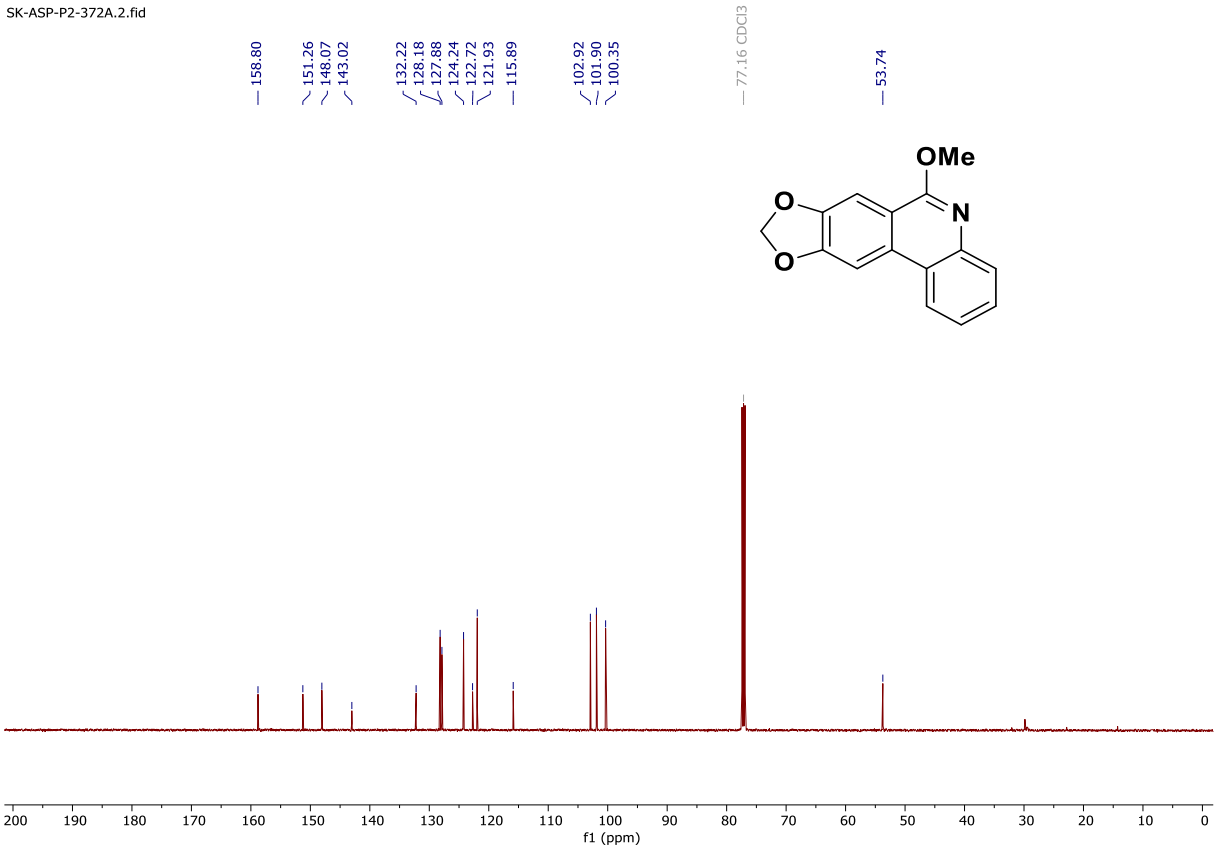
^{13}C{^{1}H} NMR spectrum of 2z in $CDCl_3$ [126 MHz]



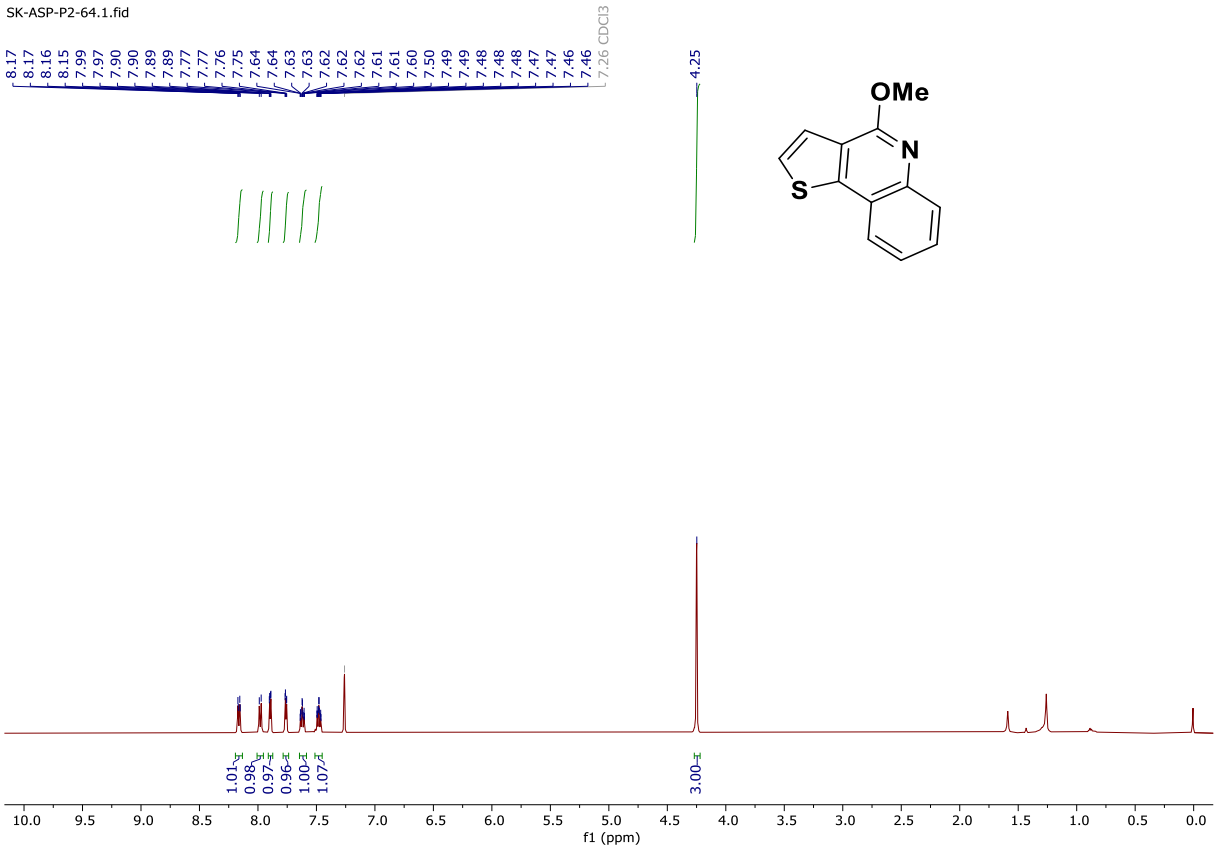
^{1}H NMR spectrum of 2aa in $CDCl_3$ [500 MHz]



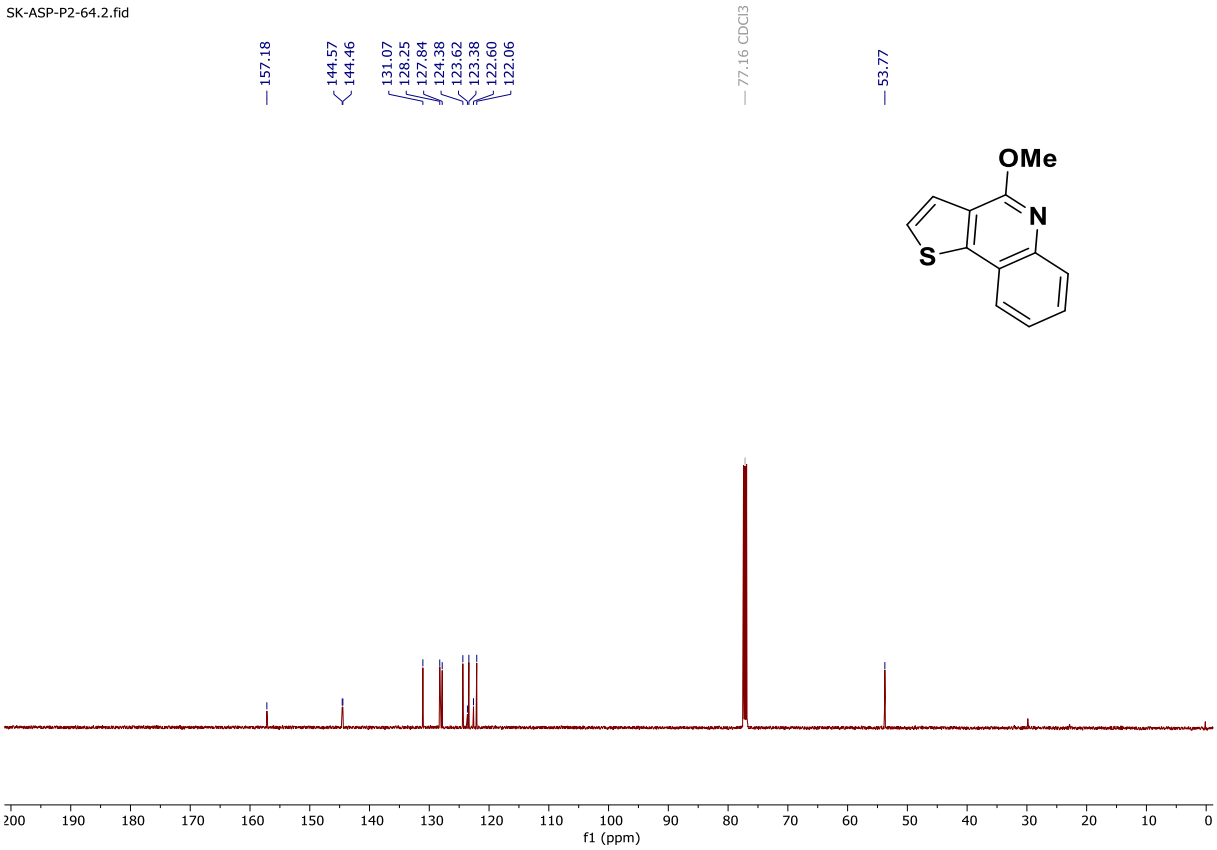
^{13}C{^{1}H} NMR spectrum of 2aa in $CDCl_3$ [126 MHz]



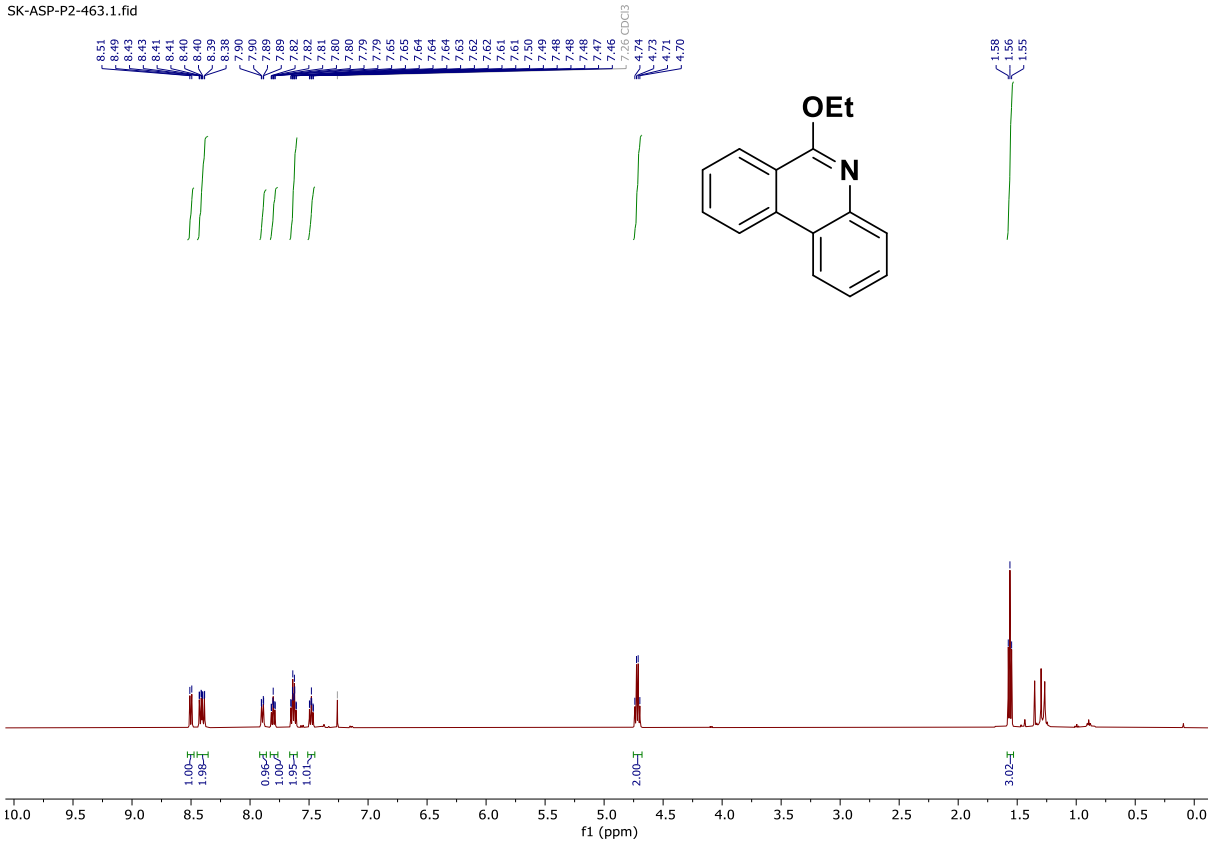
^{1}H NMR spectrum of 2ab in $CDCl_3$ [500 MHz]



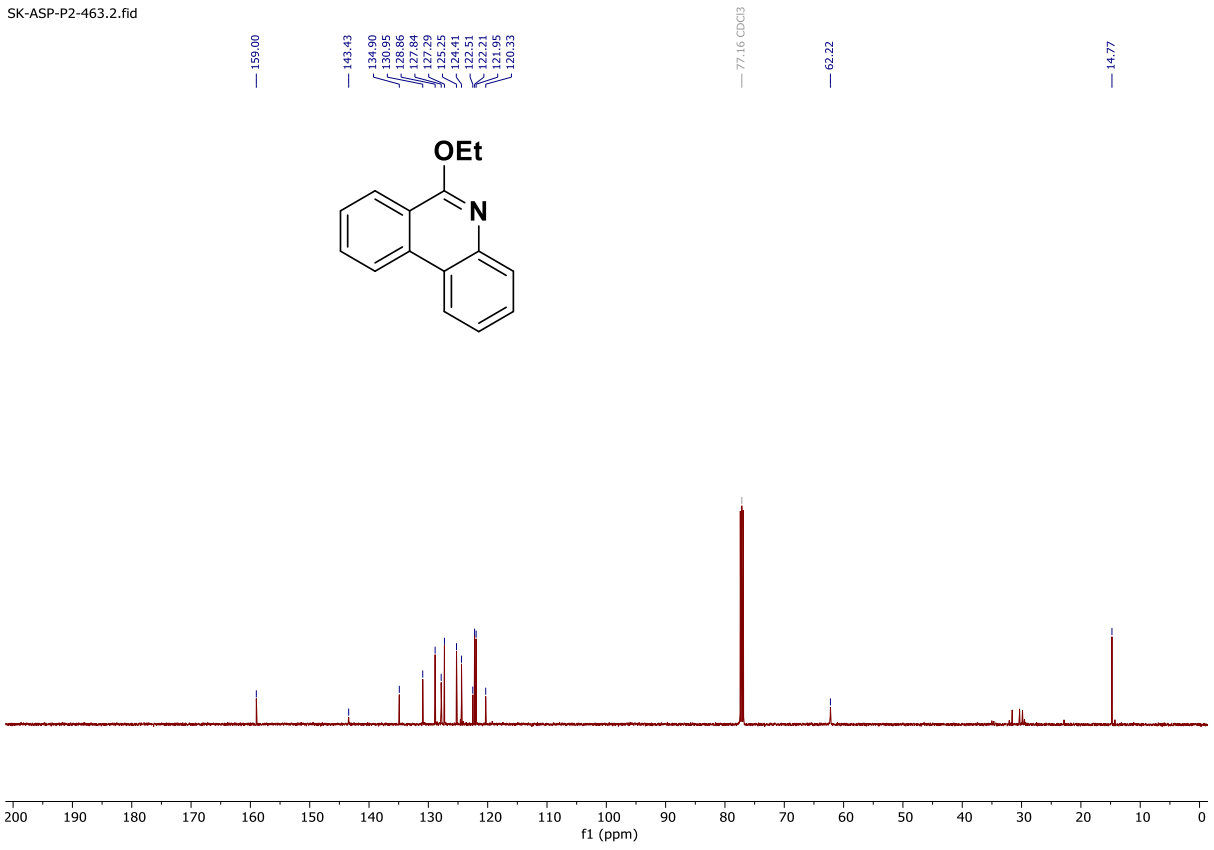
^{13}C{^{1}H} NMR spectrum of 2ab in $CDCl_3$ [126 MHz]



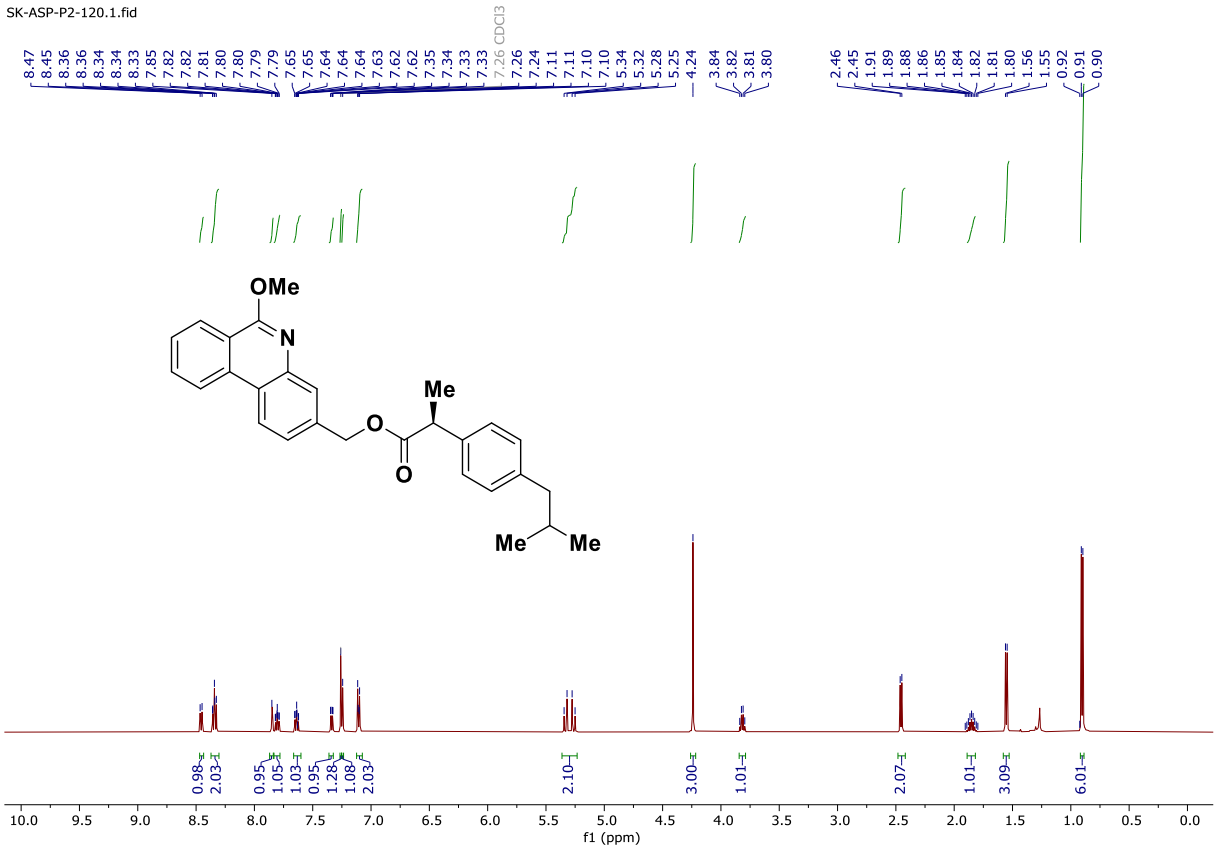
^{1}H NMR spectrum of 2ac in $CDCl_3$ [500 MHz]



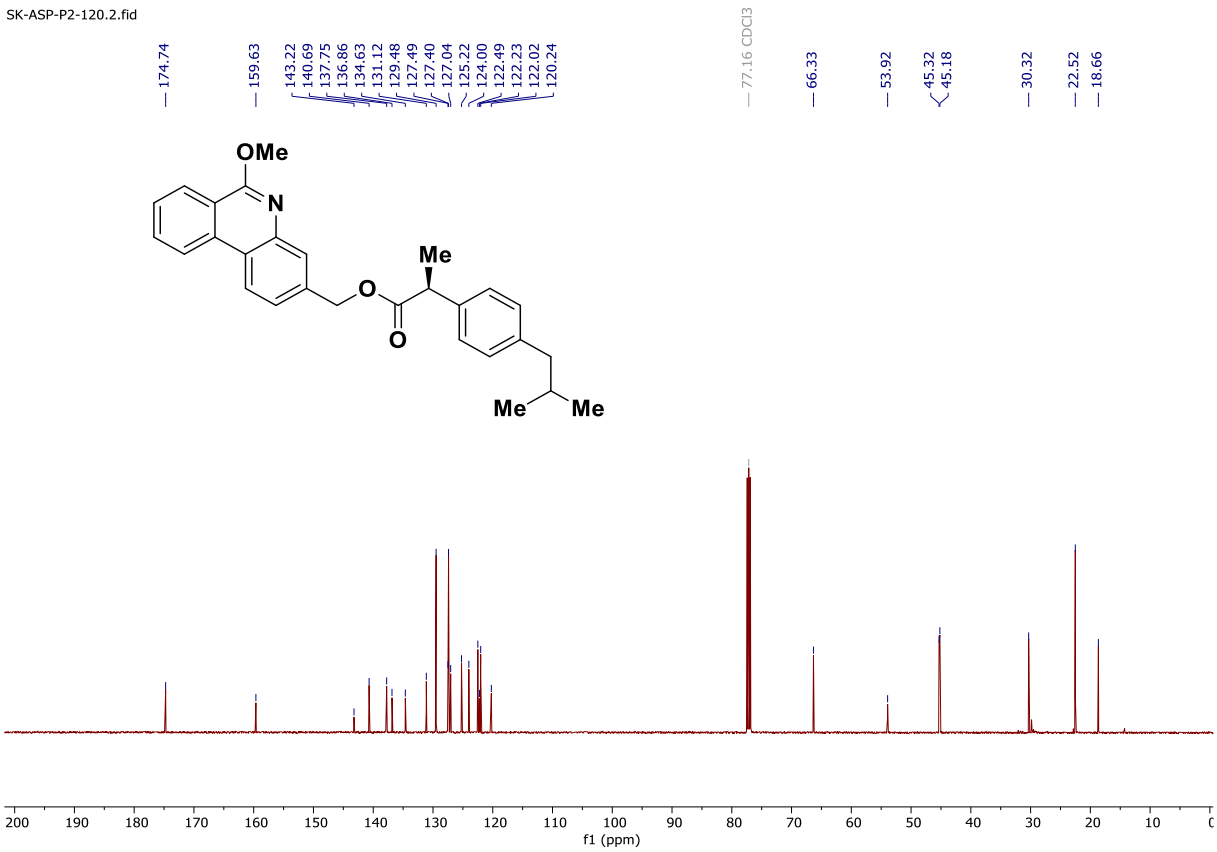
^{13}C{^{1}H} NMR spectrum of 2ac in $CDCl_3$ [126 MHz]



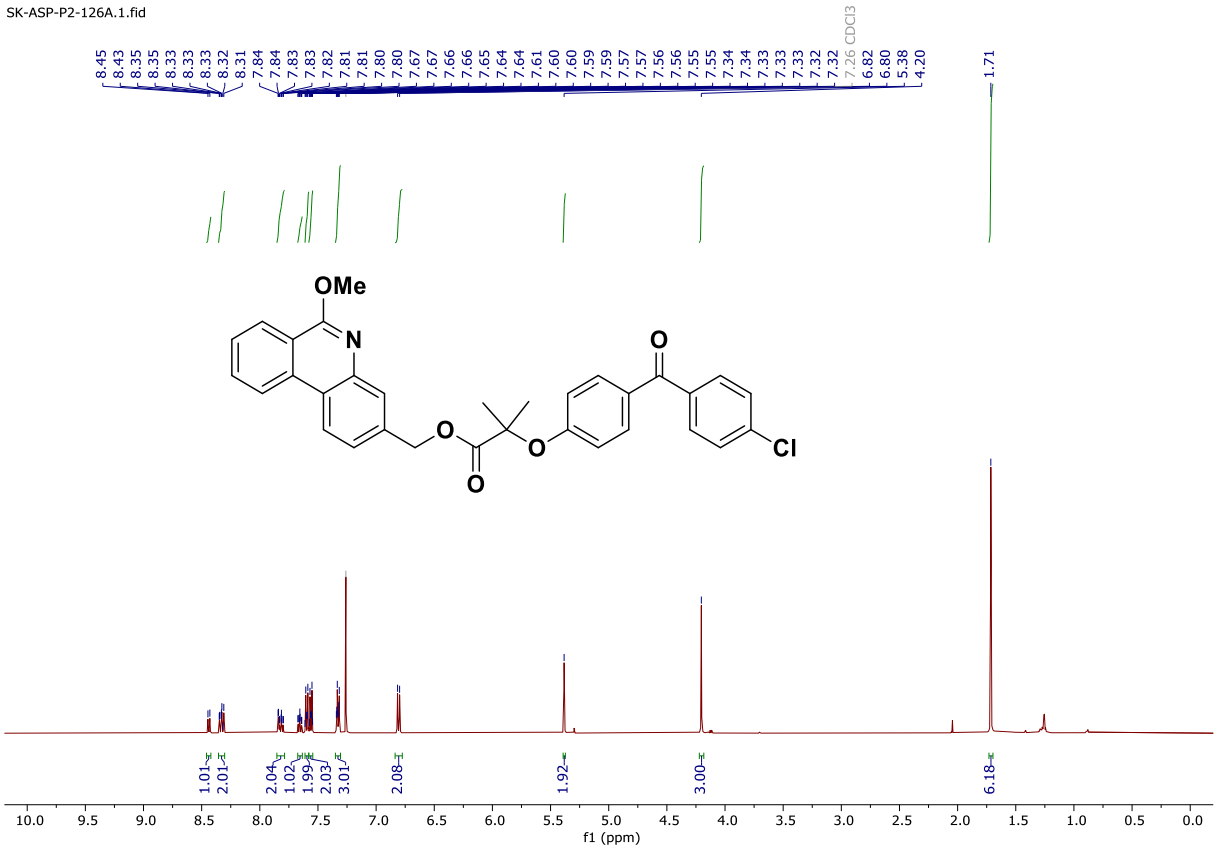
^{1}H NMR spectrum of 2ad in $CDCl_3$ [500 MHz]



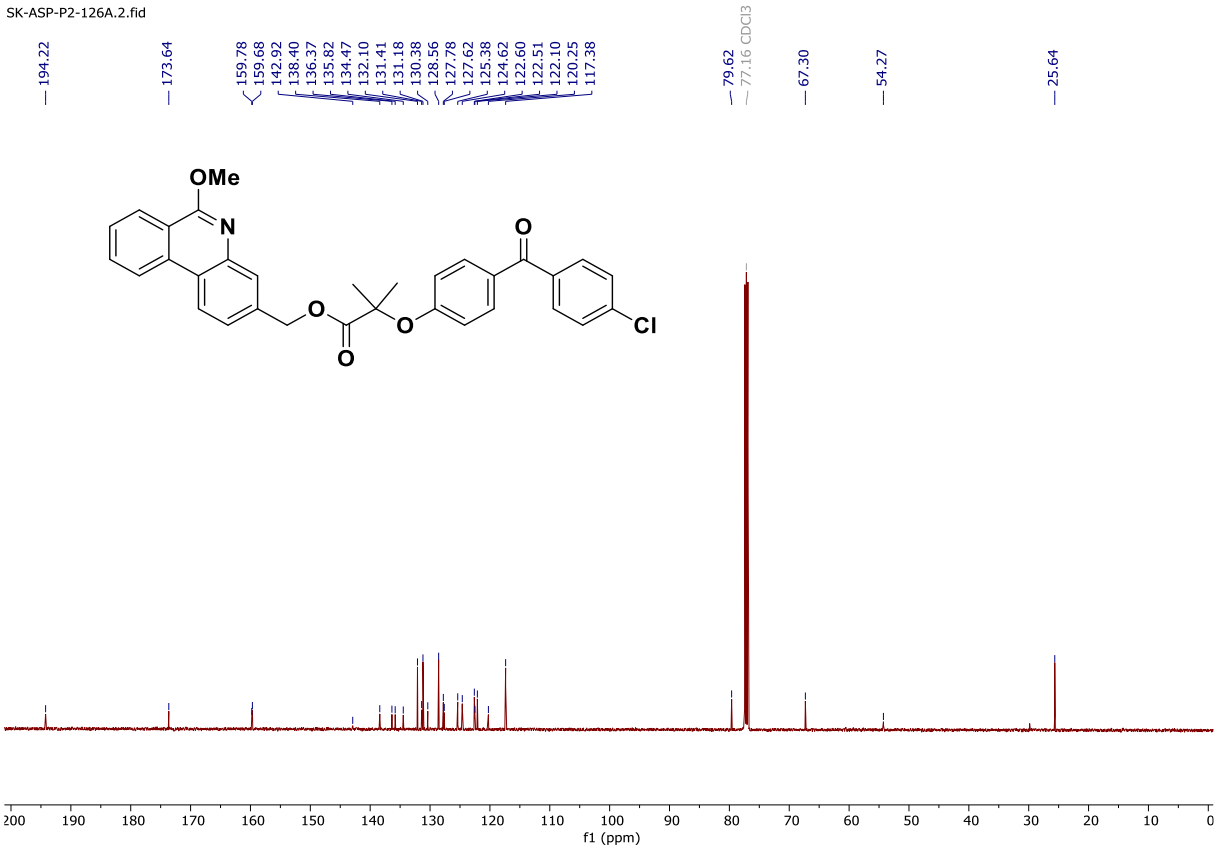
^{13}C{^{1}H} NMR spectrum of 2ad in $CDCl_3$ [126 MHz]



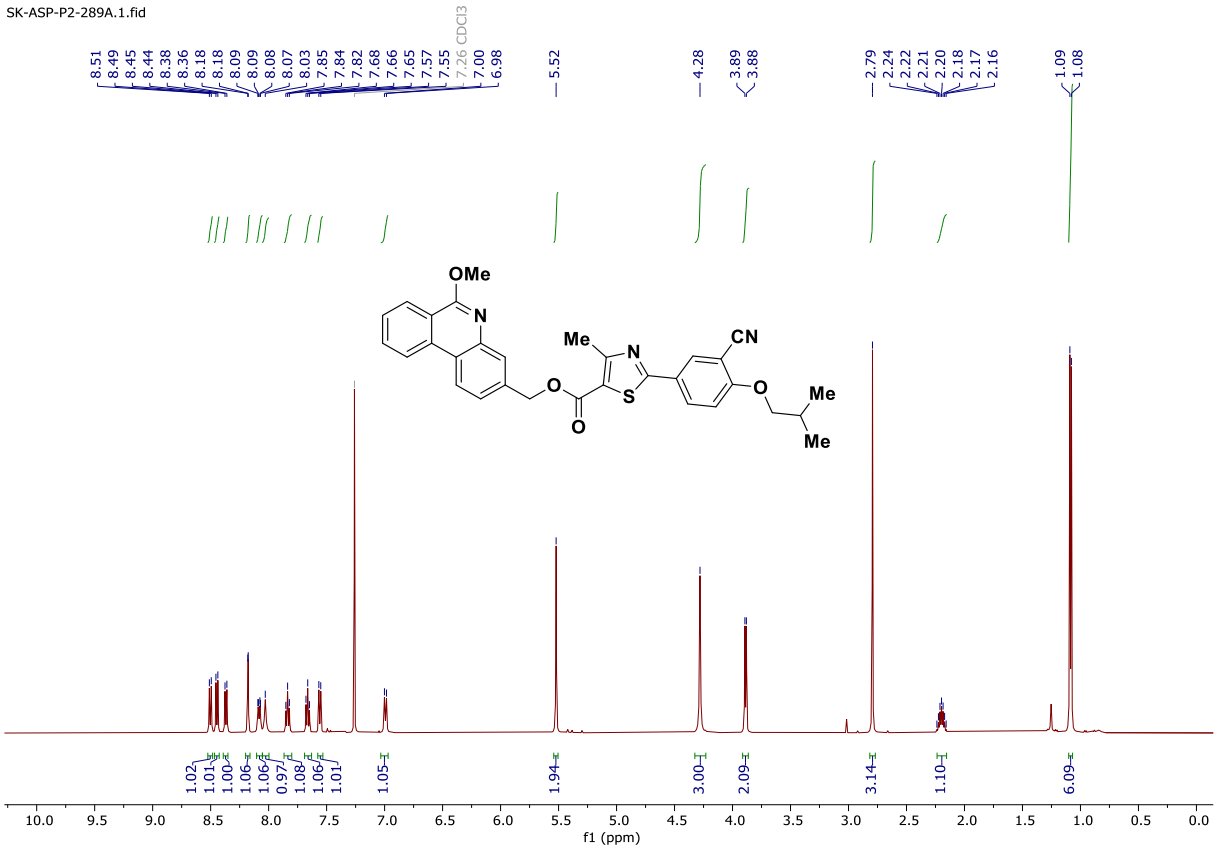
^{1}H NMR spectrum of 2ae in $CDCl_3$ [500 MHz]



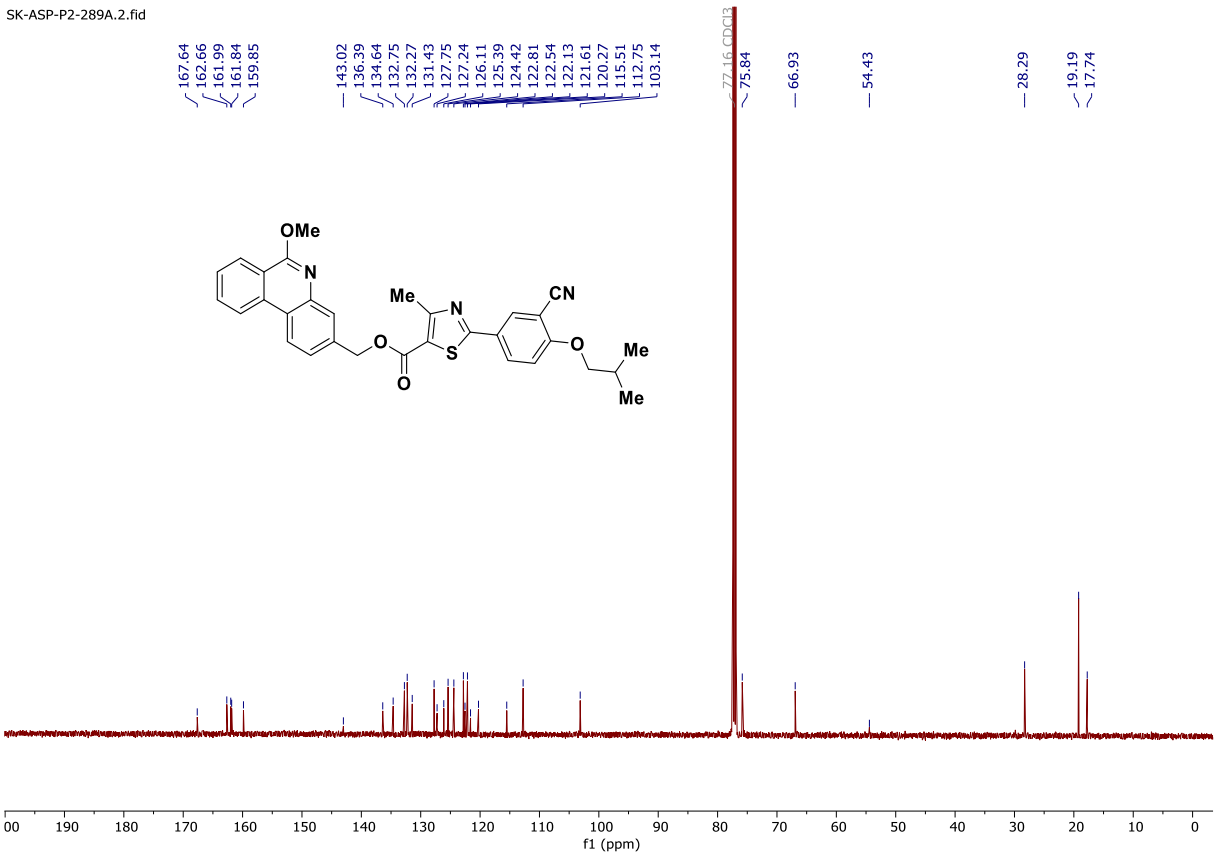
^{13}C{^{1}H} NMR spectrum of 2ae in $CDCl_3$ [126 MHz]



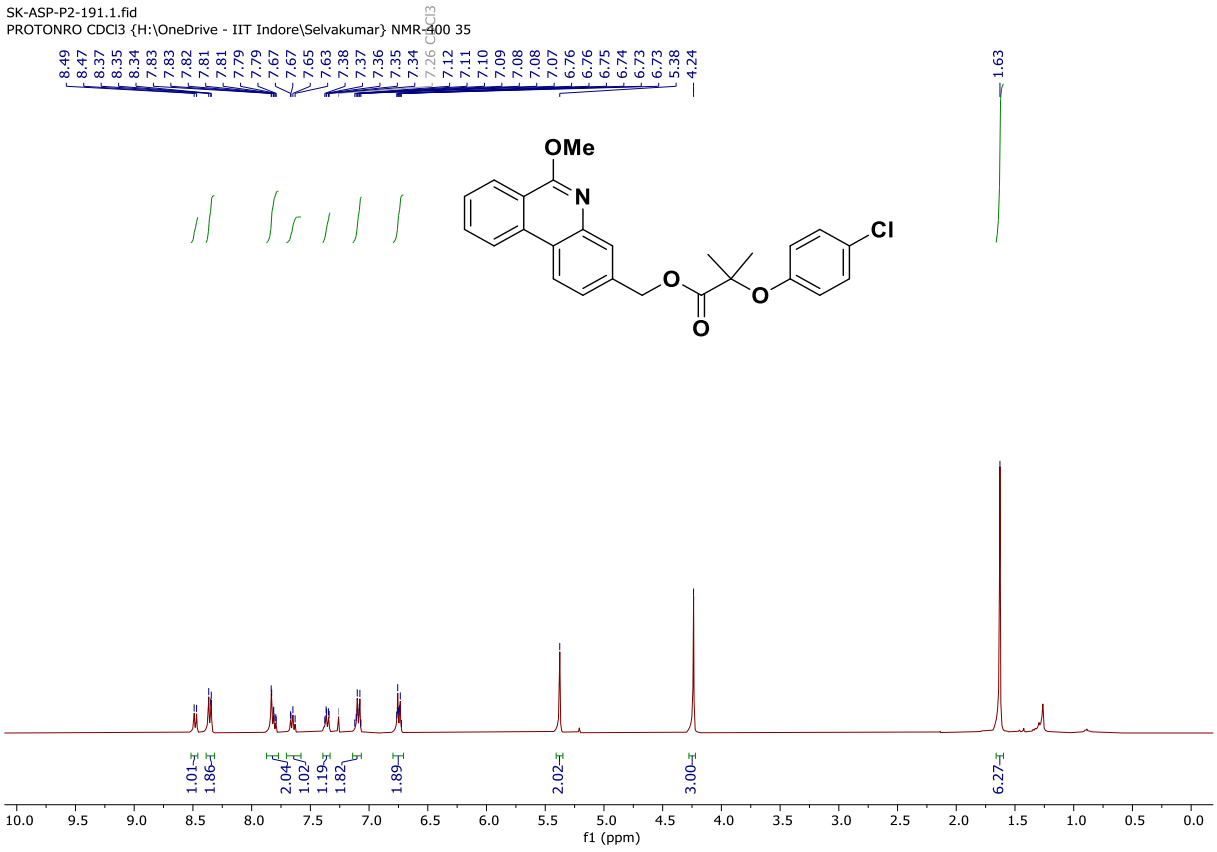
^{1}H NMR spectrum of 2af in $CDCl_3$ [500 MHz]



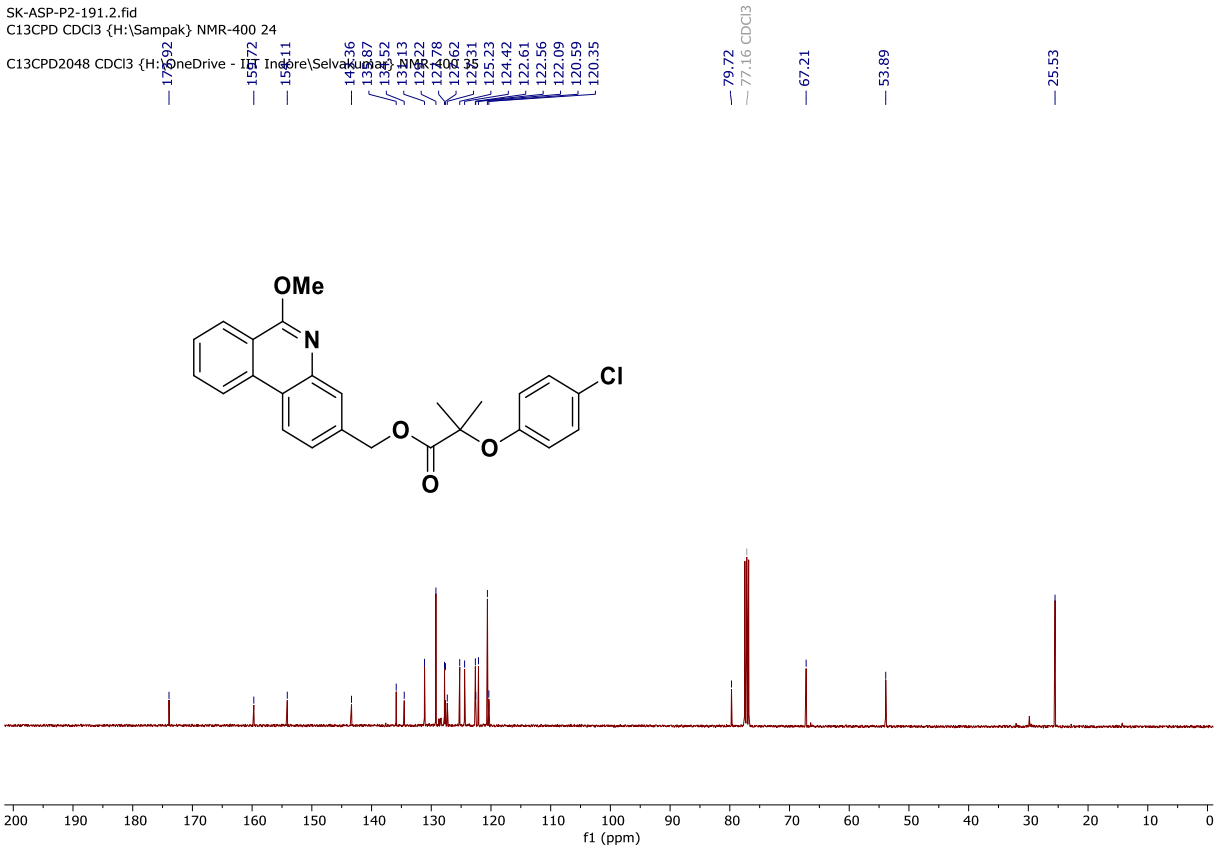
^{13}C{^{1}H} NMR spectrum of 2ae in $CDCl_3$ [126 MHz]



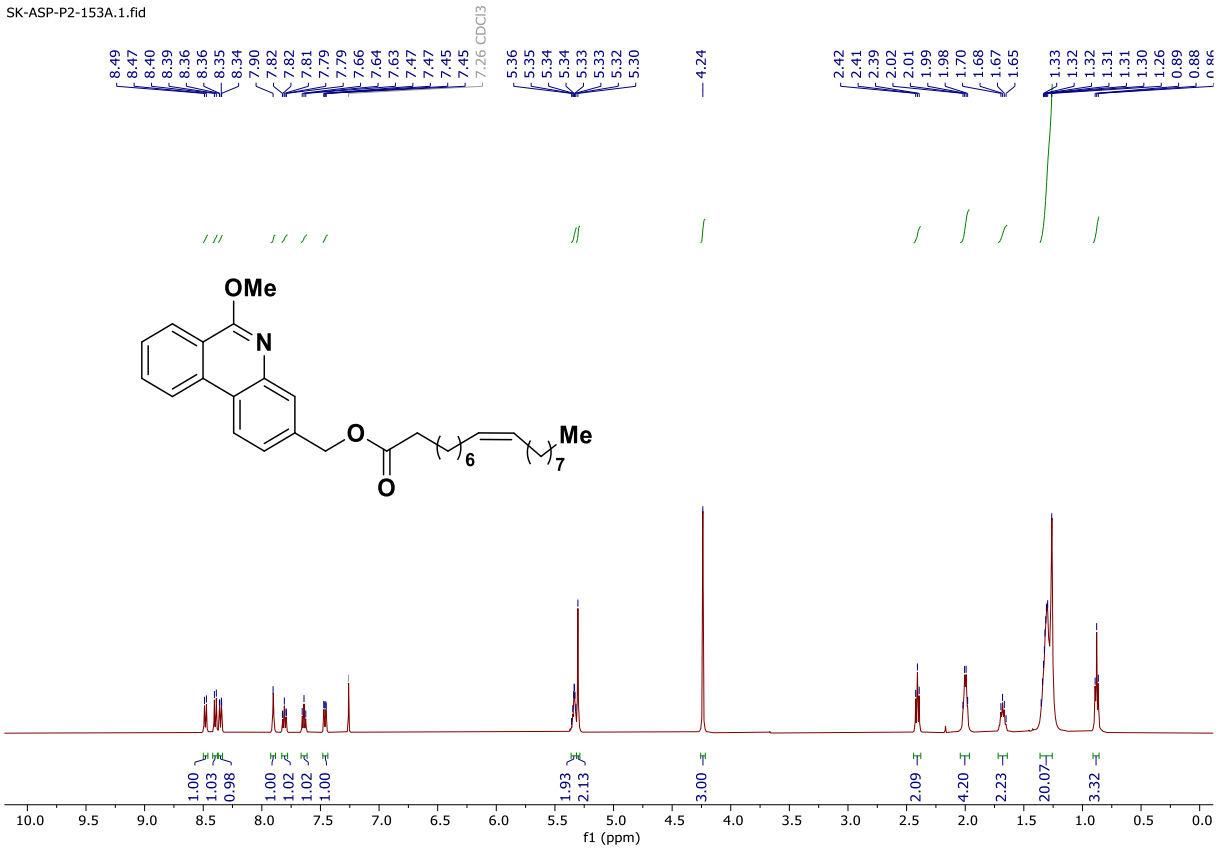
^{1}H NMR spectrum of 2ag in $CDCl_3$ [400 MHz]



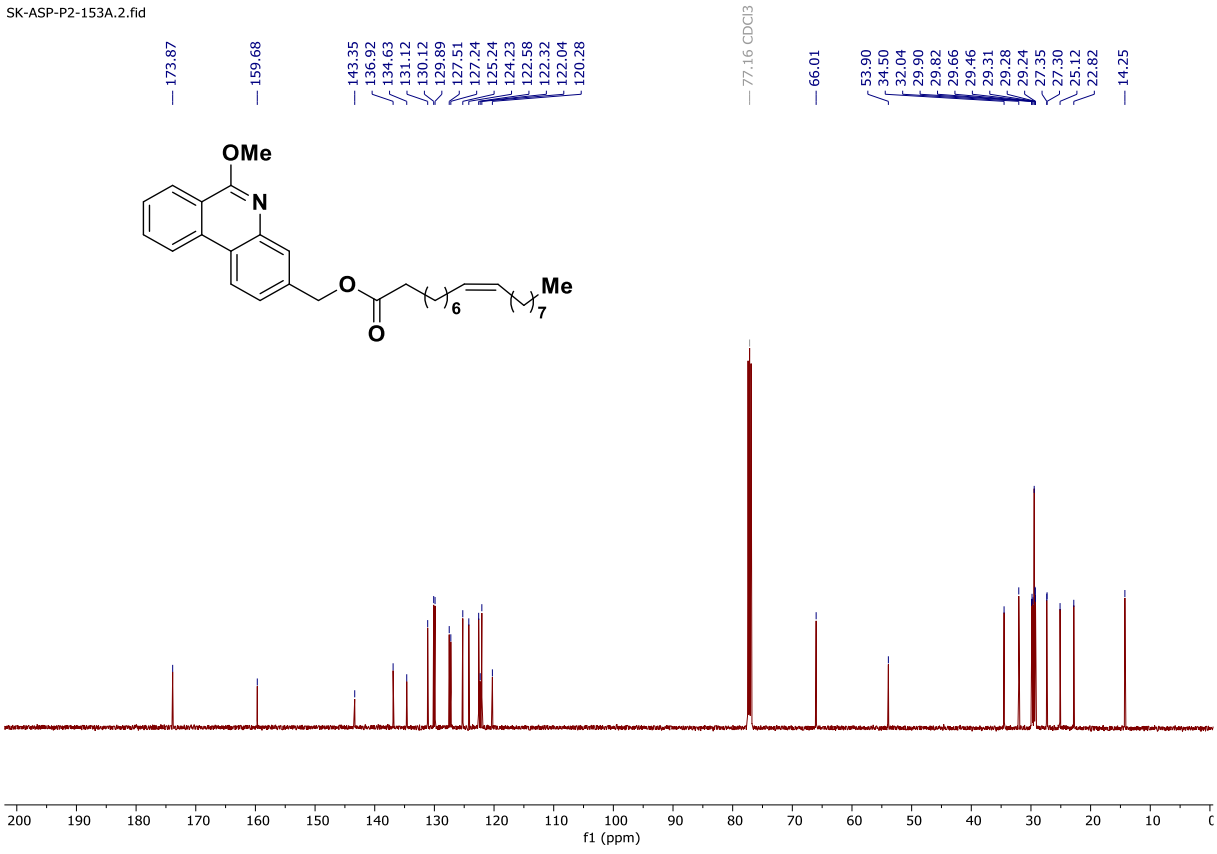
^{13}C{^{1}H} NMR spectrum of 2ag in $CDCl_3$ [101 MHz]



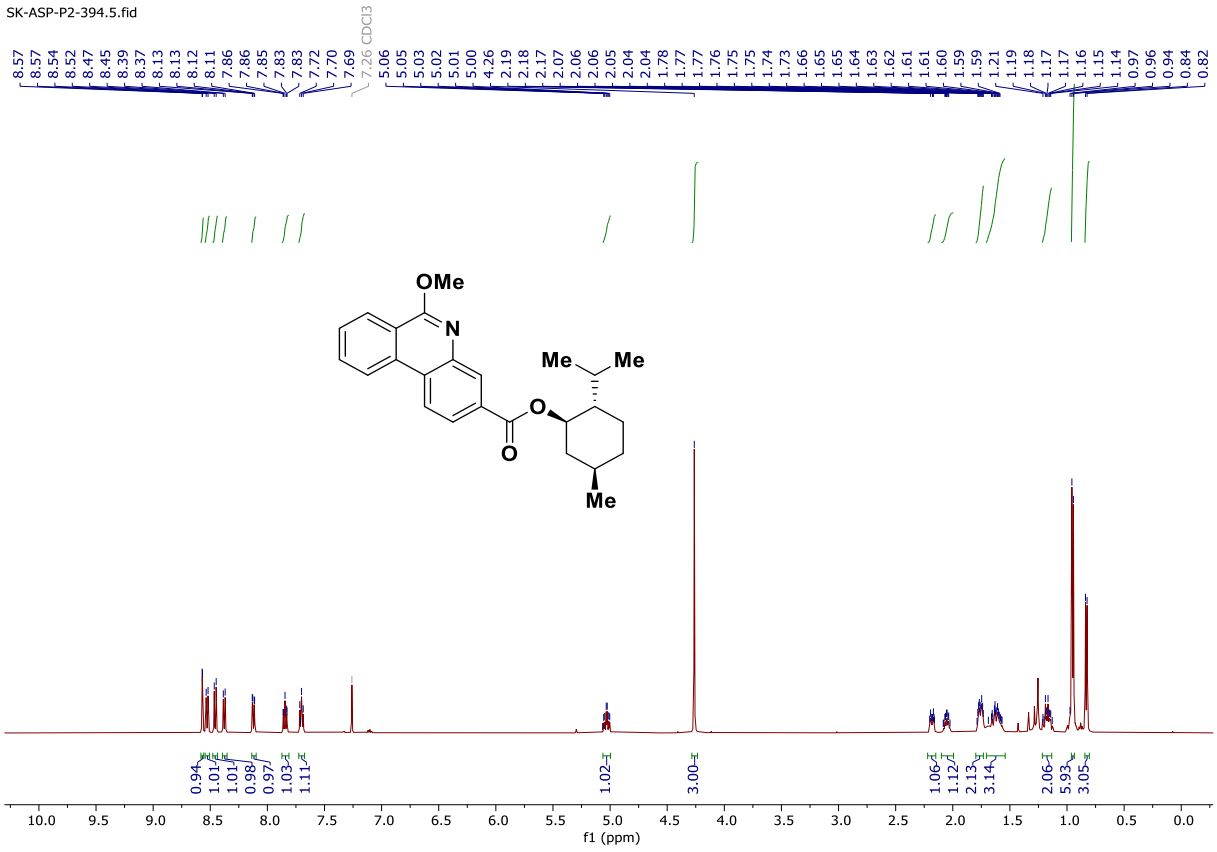
^{1}H NMR spectrum of 2ah in $CDCl_3$ [500 MHz]



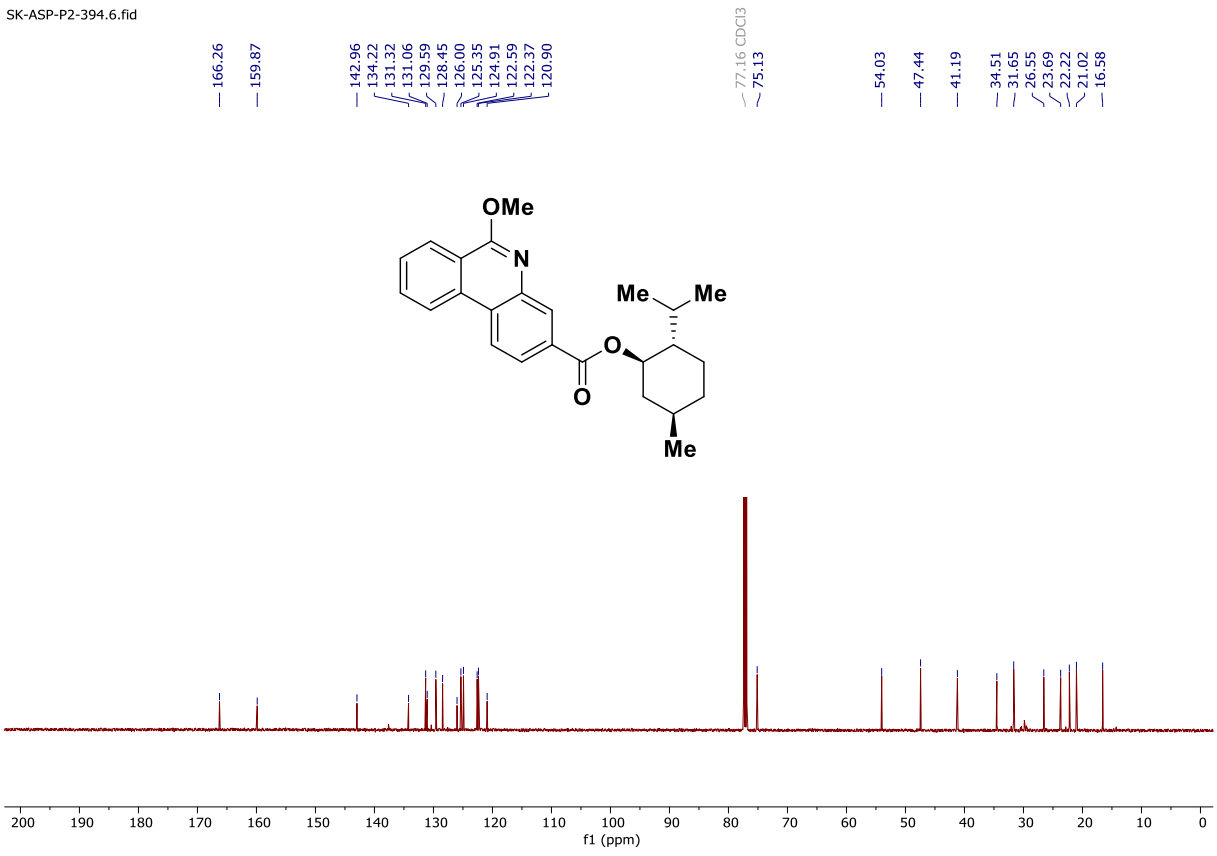
^{13}C{^{1}H} NMR spectrum of 2ah in $CDCl_3$ [126 MHz]



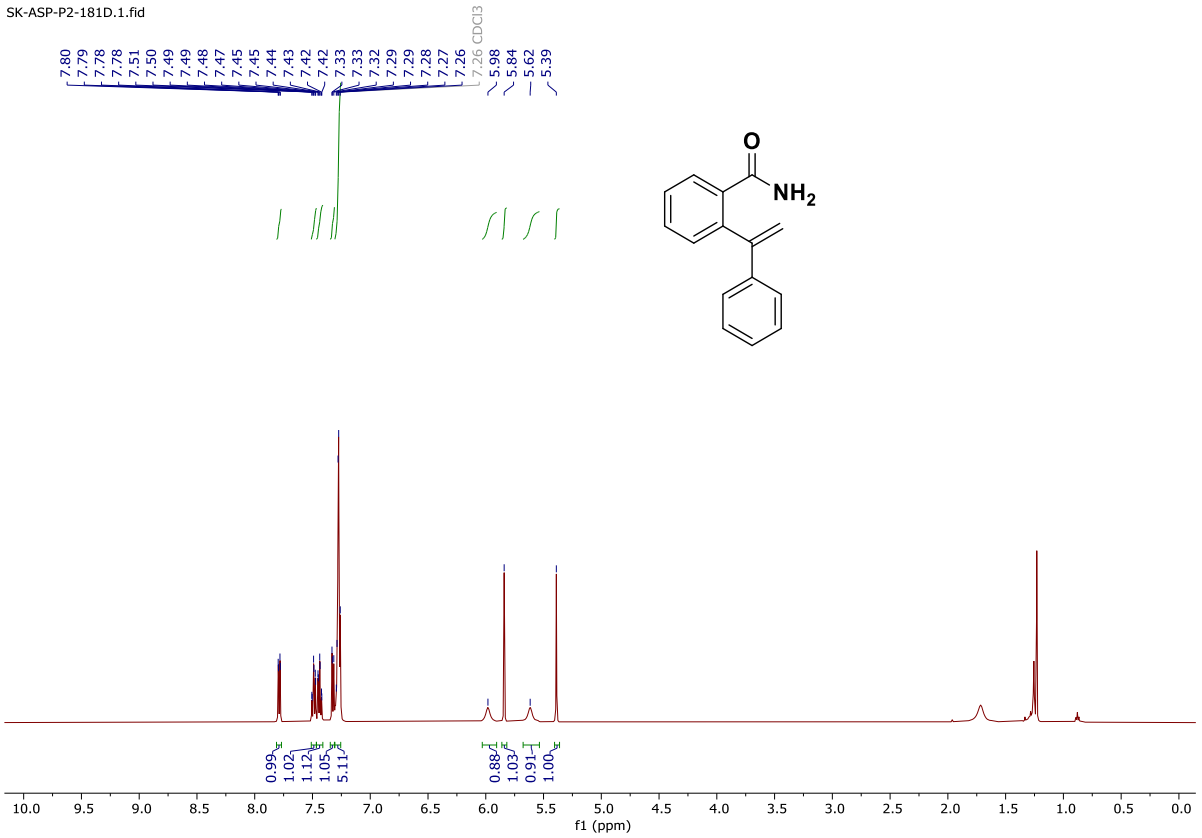
^{1}H NMR spectrum of 2ai in $CDCl_3$ [500 MHz]



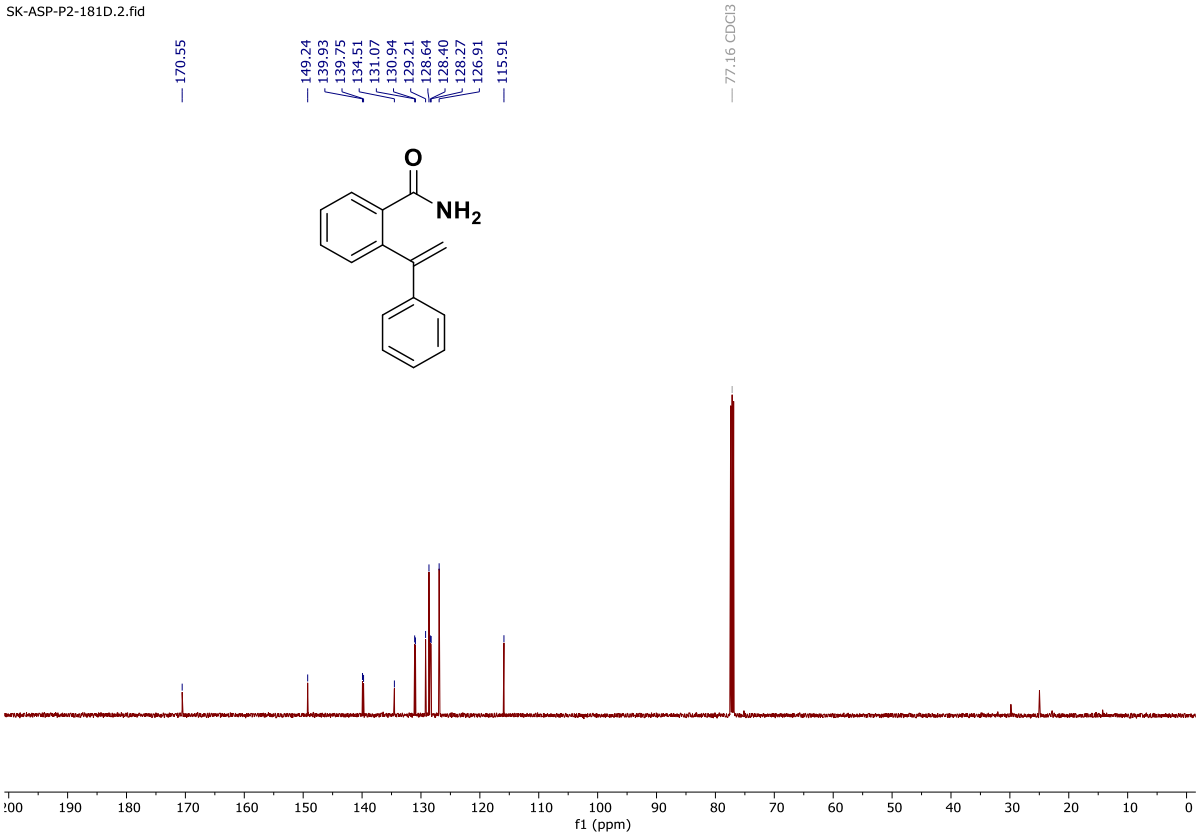
^{13}C{^{1}H} NMR spectrum of 2ai in $CDCl_3$ [126 MHz]



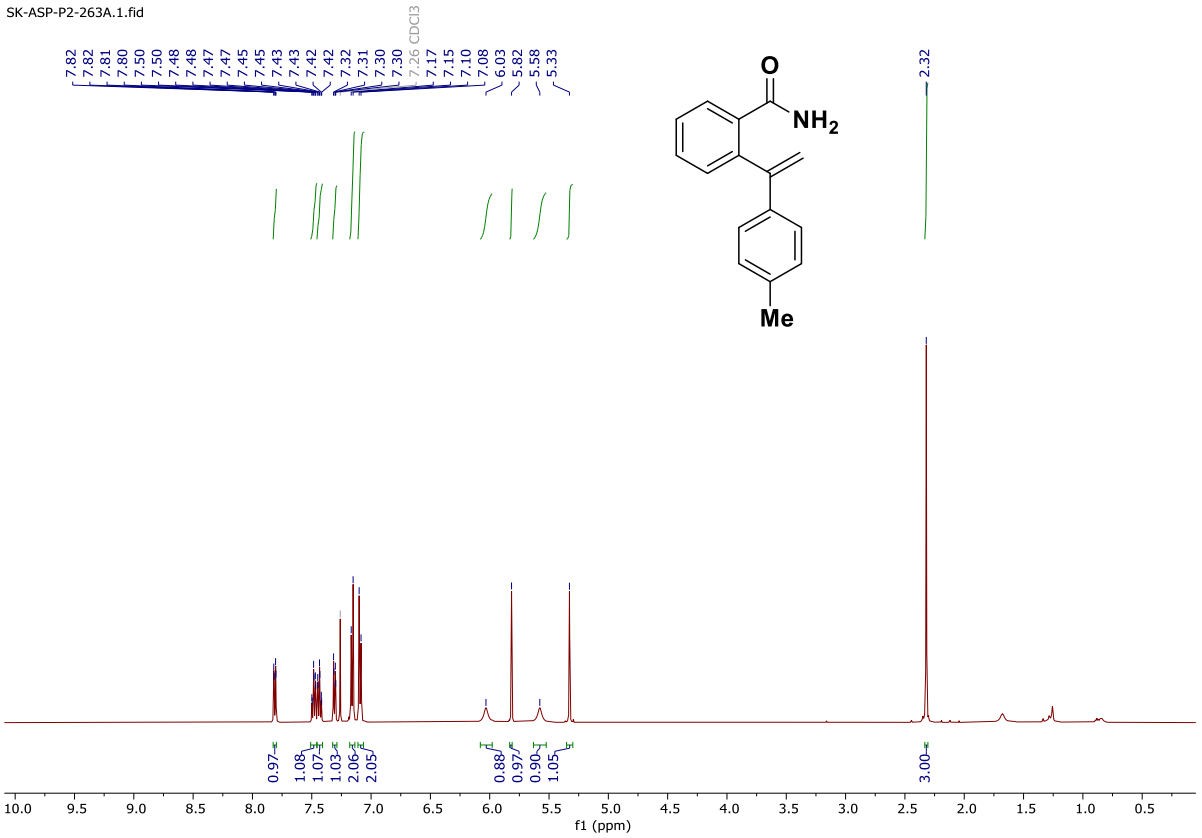
^{1}H NMR spectrum of I35 in $CDCl_3$ [500 MHz]



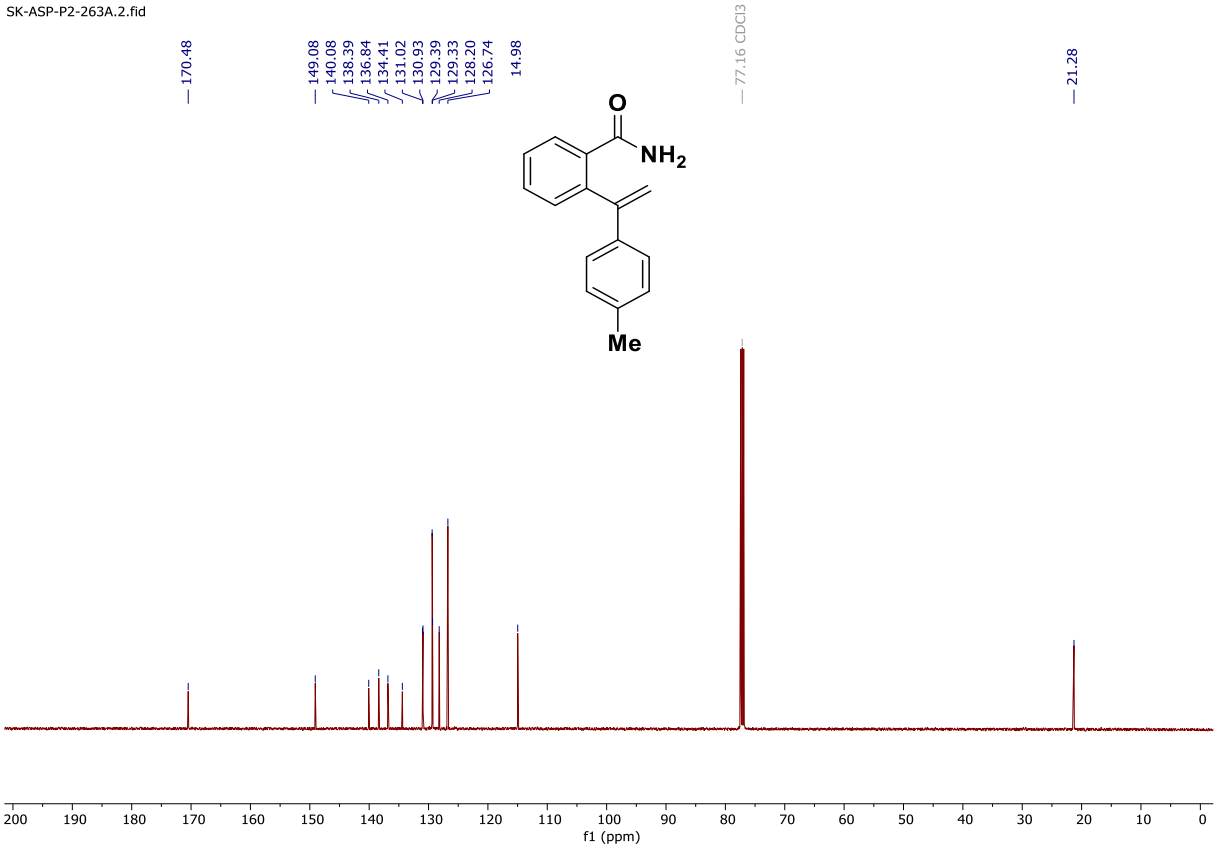
^{13}C{^{1}H} NMR spectrum of I35 in $CDCl_3$ [126 MHz]



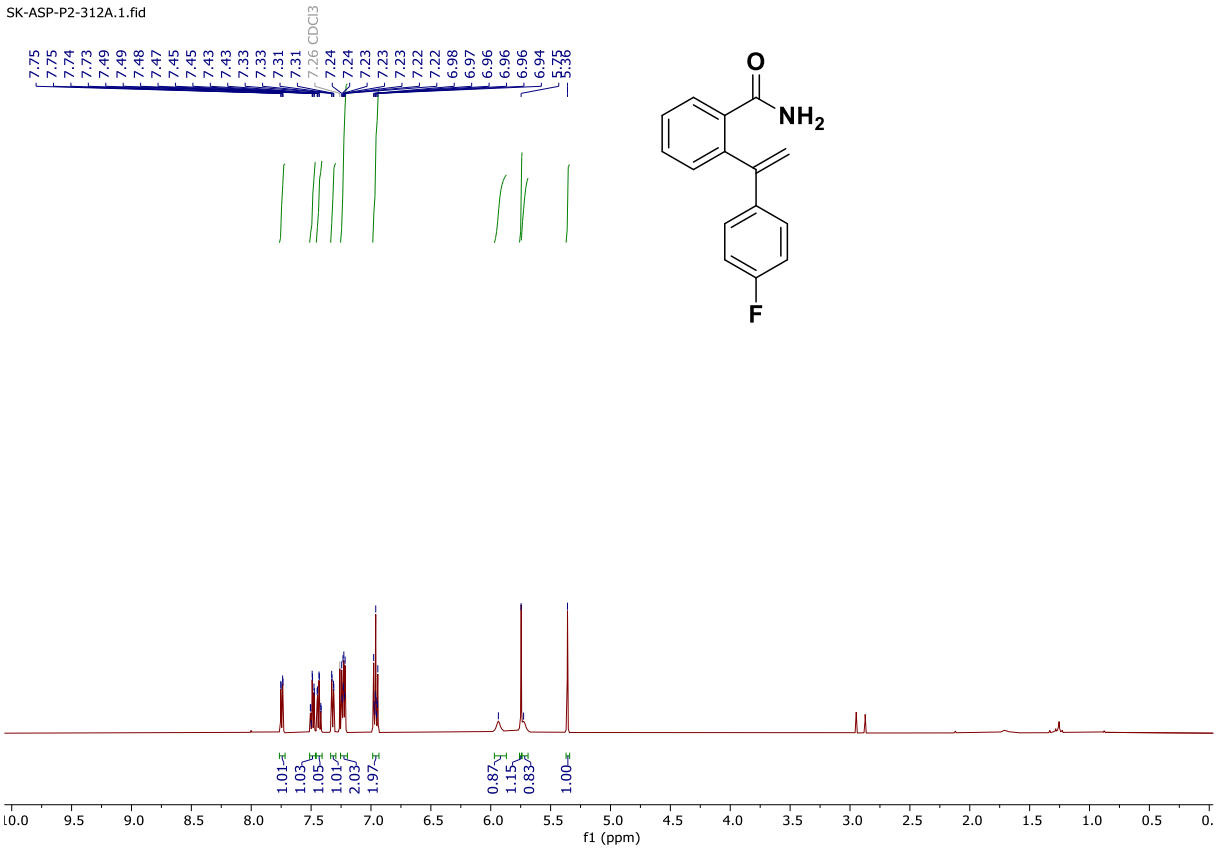
^{1}H NMR spectrum of I36 in $CDCl_3$ [500 MHz]



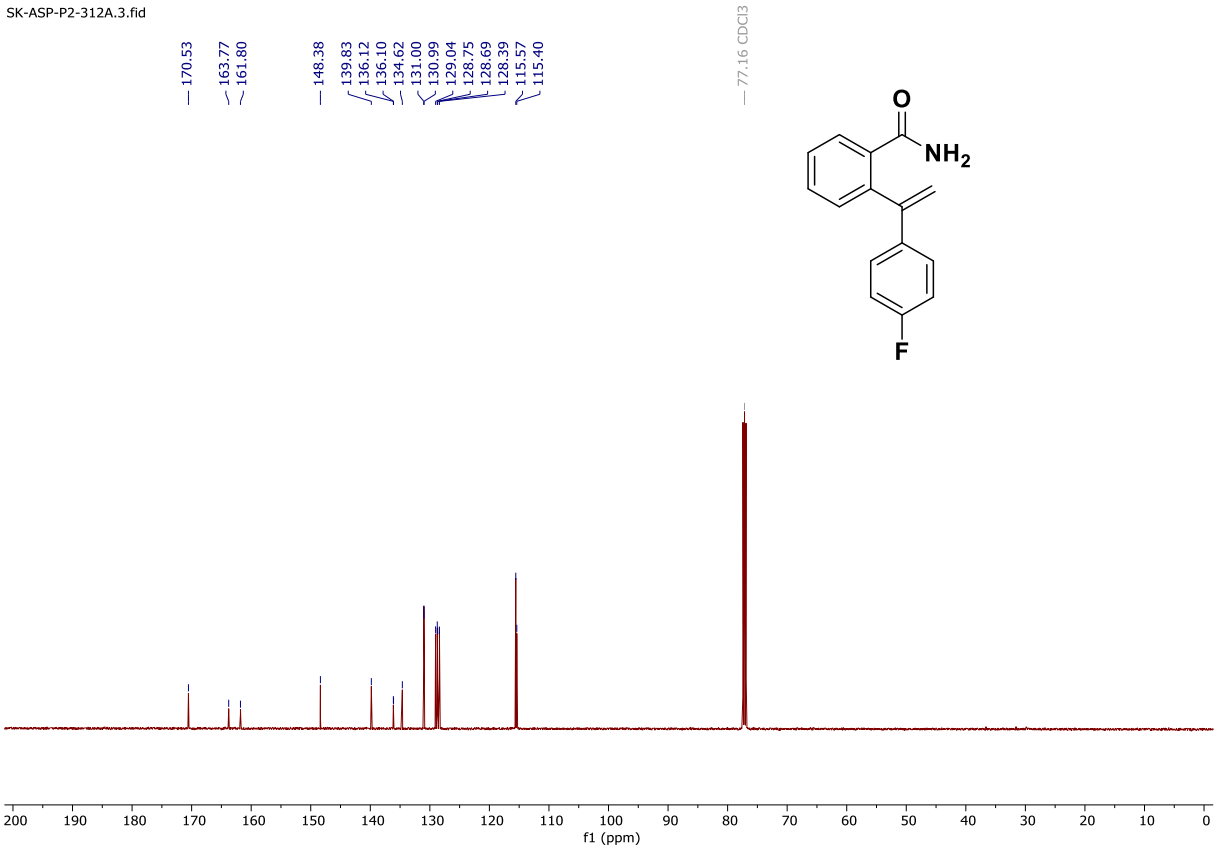
^{13}C{^{1}H} NMR spectrum of I36 in $CDCl_3$ [126 MHz]



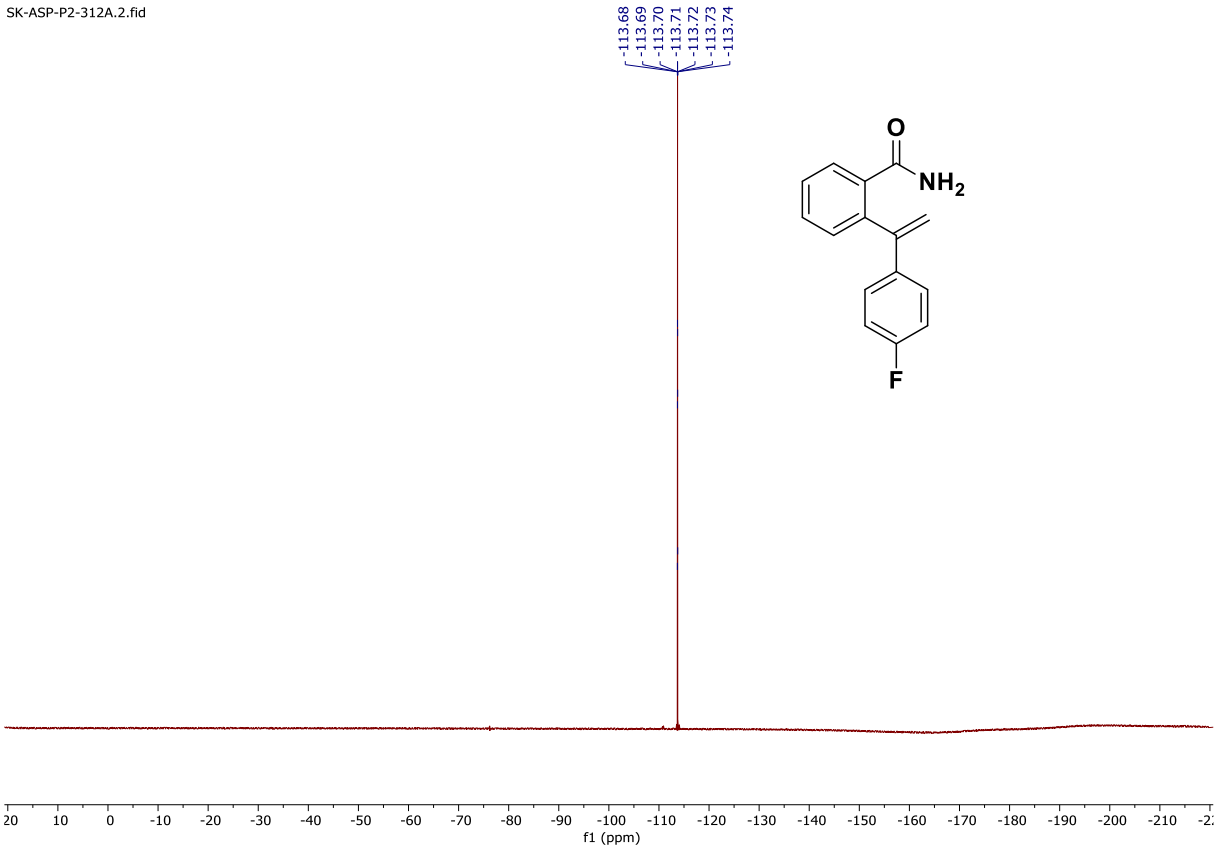
^{1}H NMR spectrum of I37 in $CDCl_3$ [500 MHz]



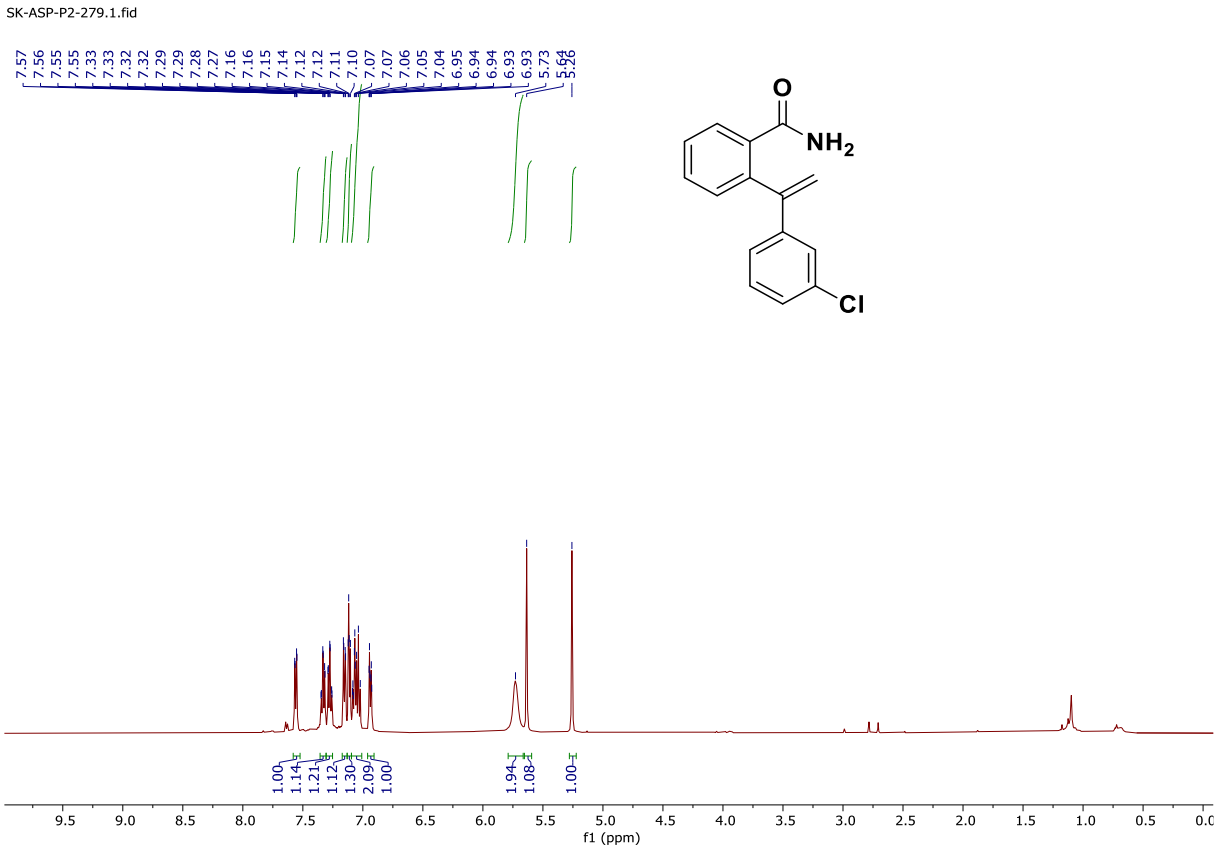
^{13}C{^{1}H} NMR spectrum of I37 in $CDCl_3$ [126 MHz]



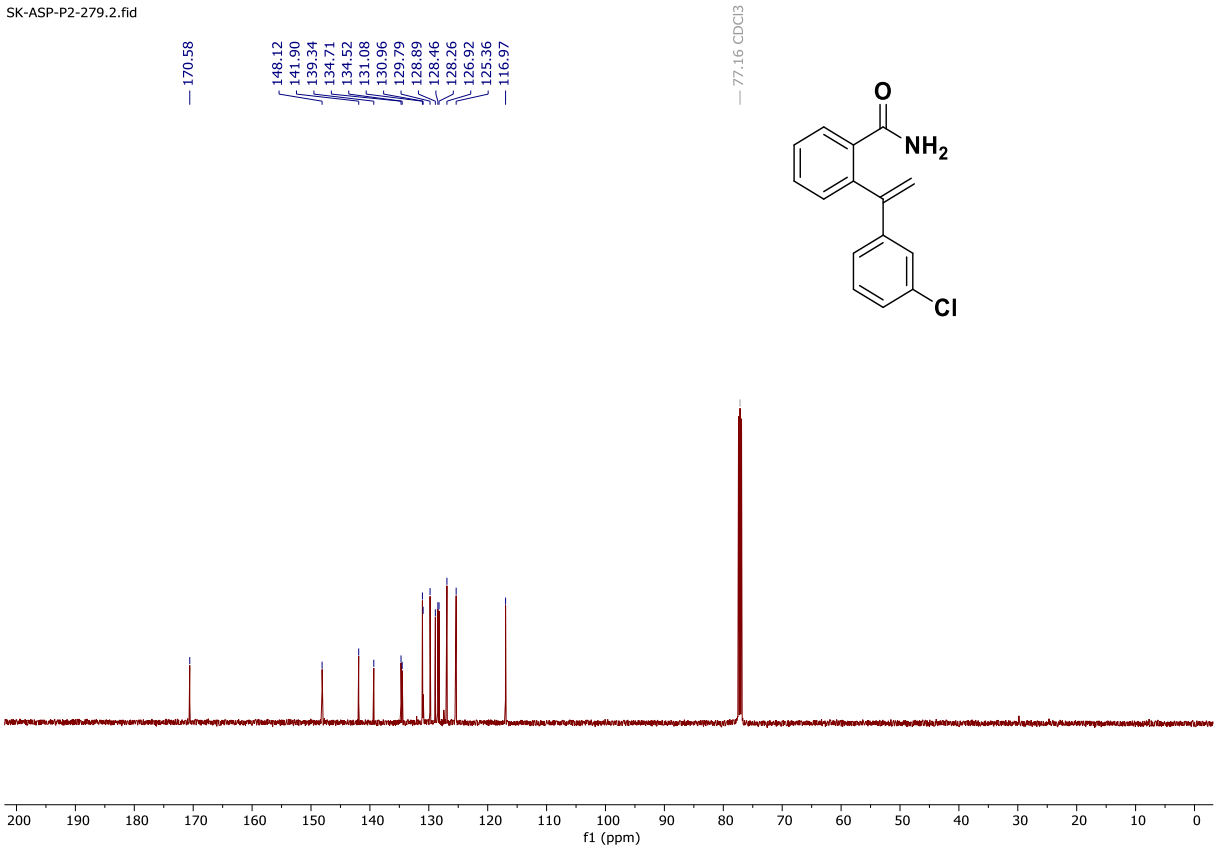
^{19}F NMR spectrum of I37 in $CDCl_3$ [471 MHz]



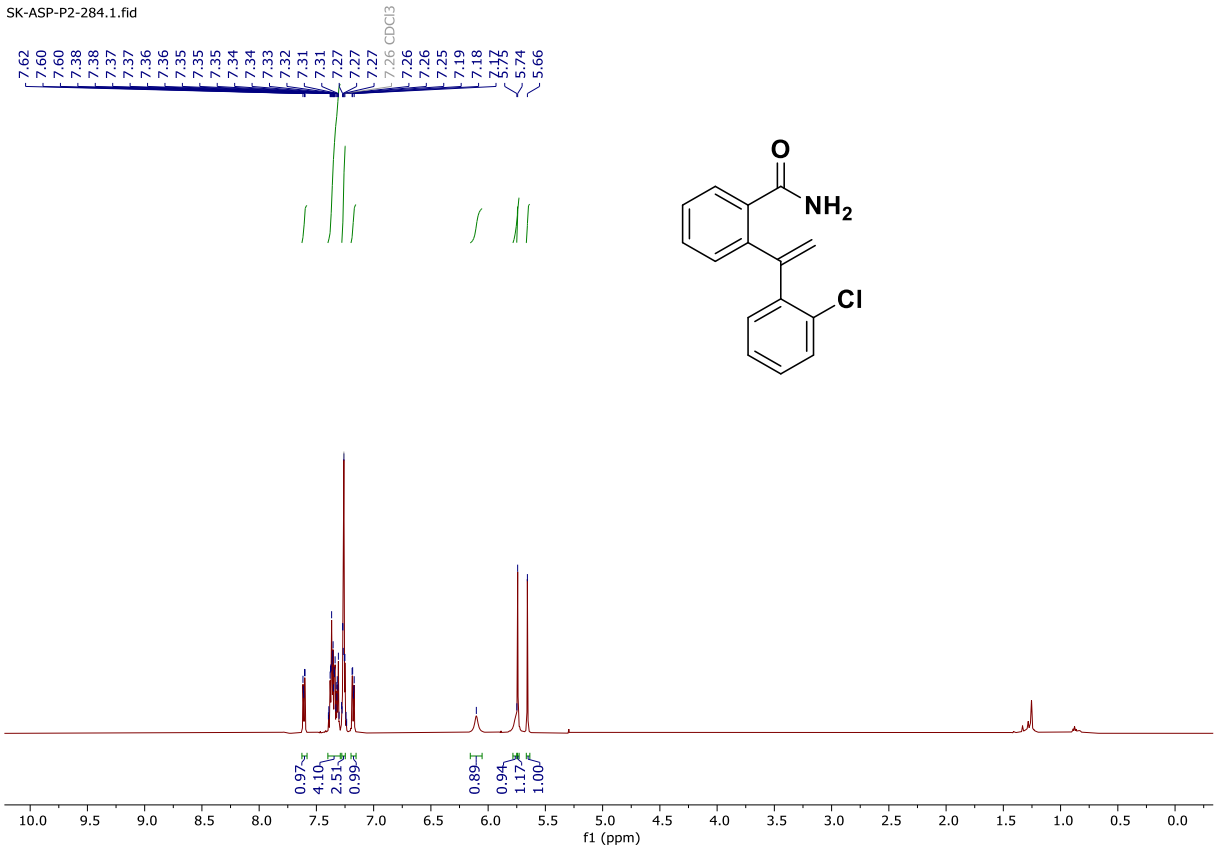
^{1}H NMR spectrum of I38 in $CDCl_3$ [500 MHz]



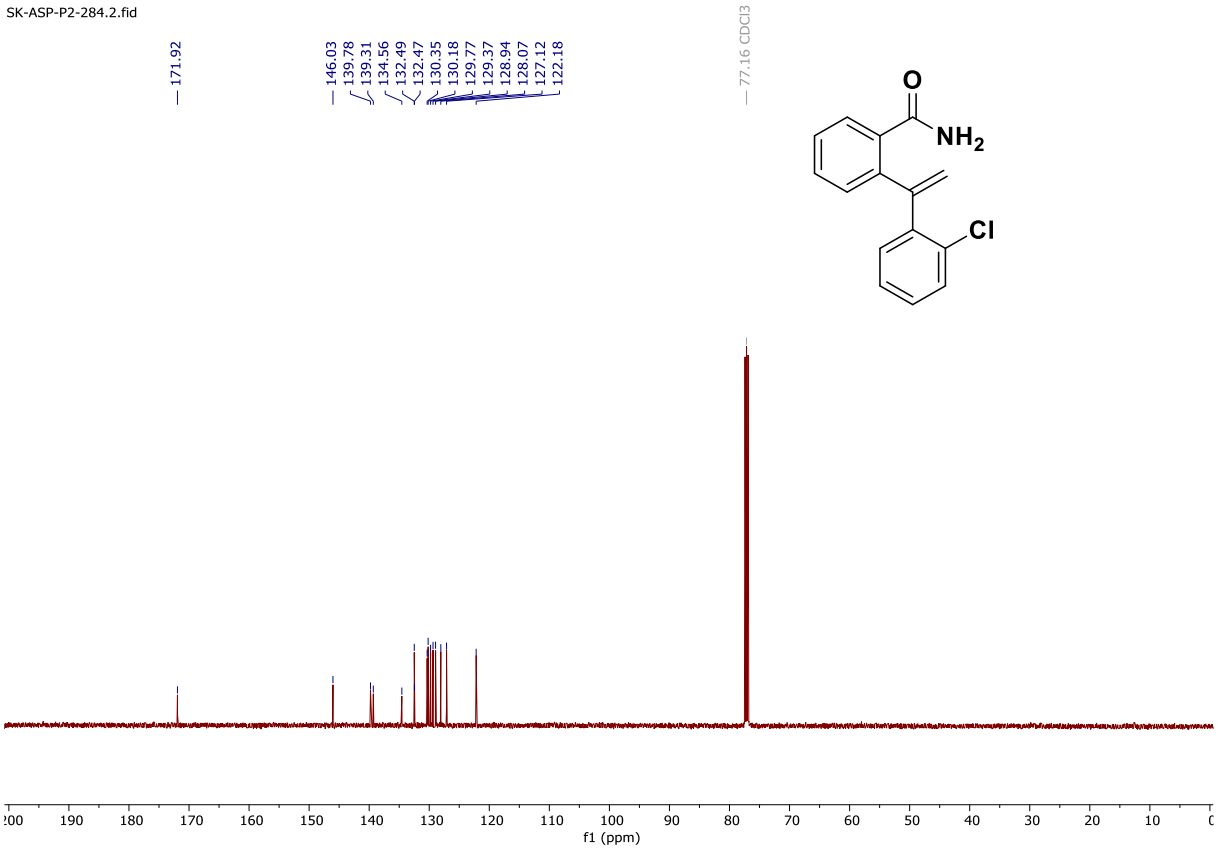
$^{13}C\{^{1}H\}$ NMR spectrum of I38 in $CDCl_3$ [126 MHz]



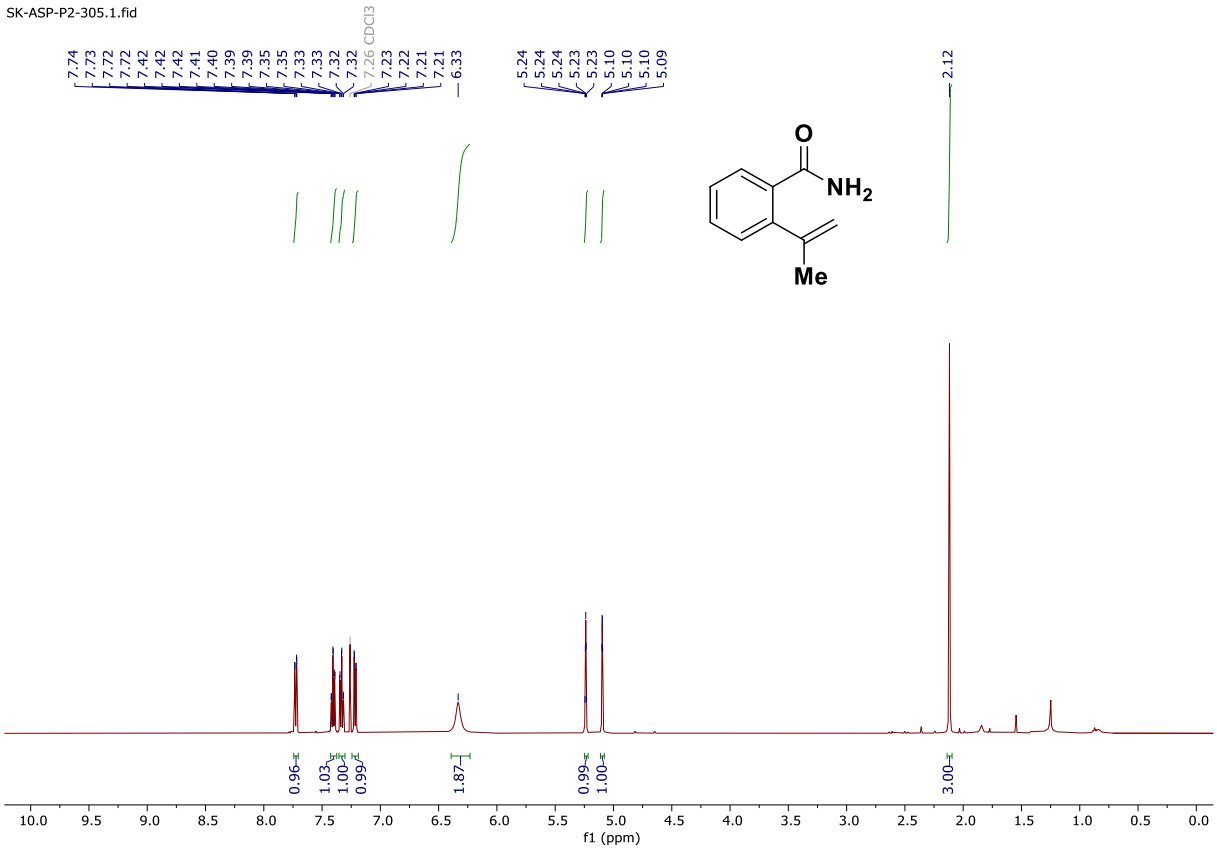
^{1}H NMR spectrum of I39 in $CDCl_3$ [500 MHz]



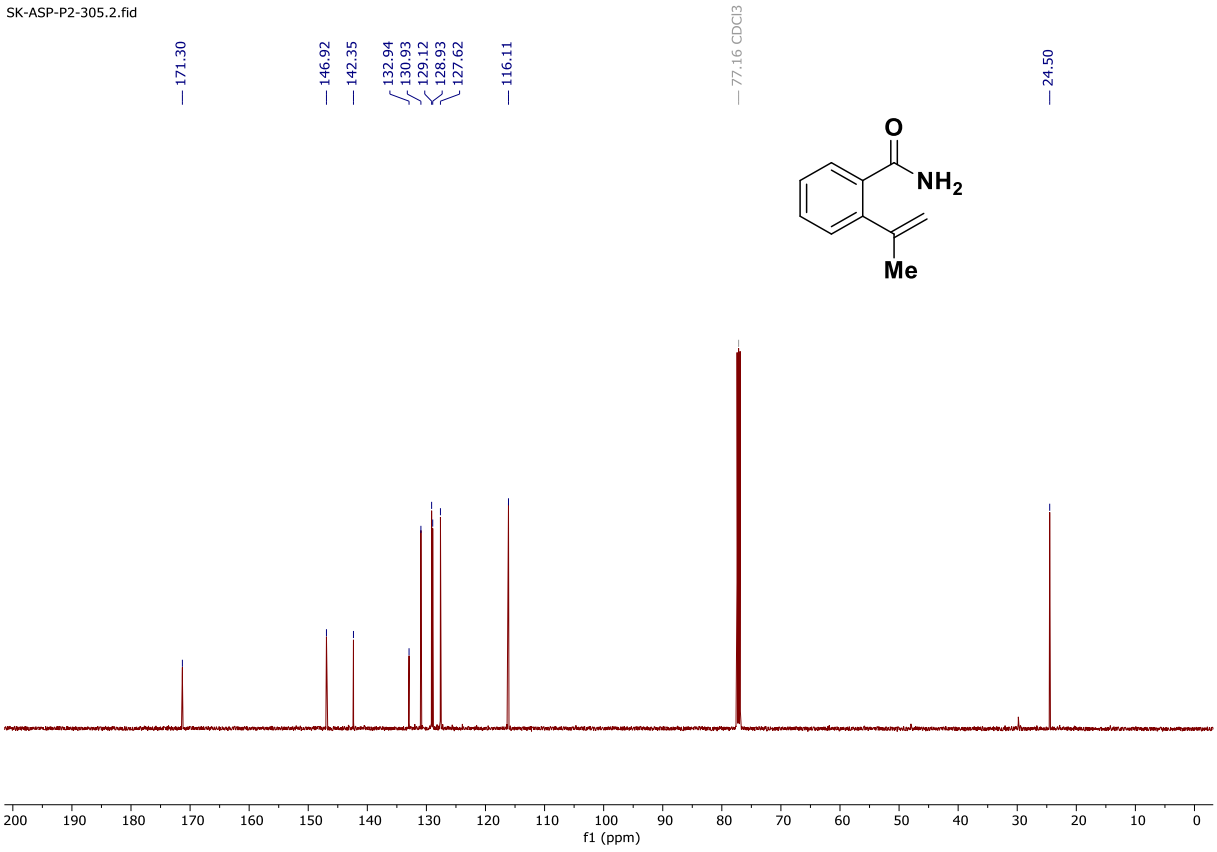
$^{13}C\{^{1}H\}$ NMR spectrum of I39 in $CDCl_3$ [126 MHz]



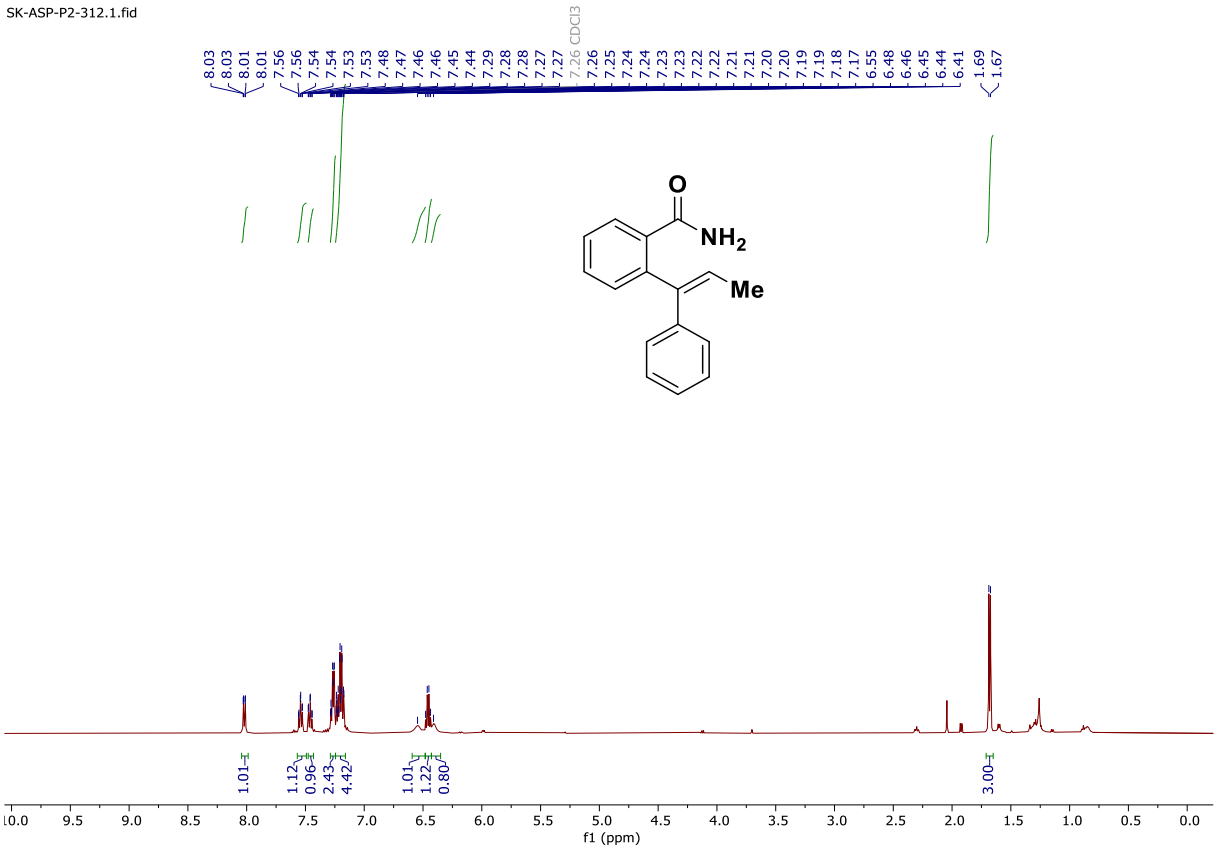
^{1}H NMR spectrum of I40 in $CDCl_3$ [500 MHz]



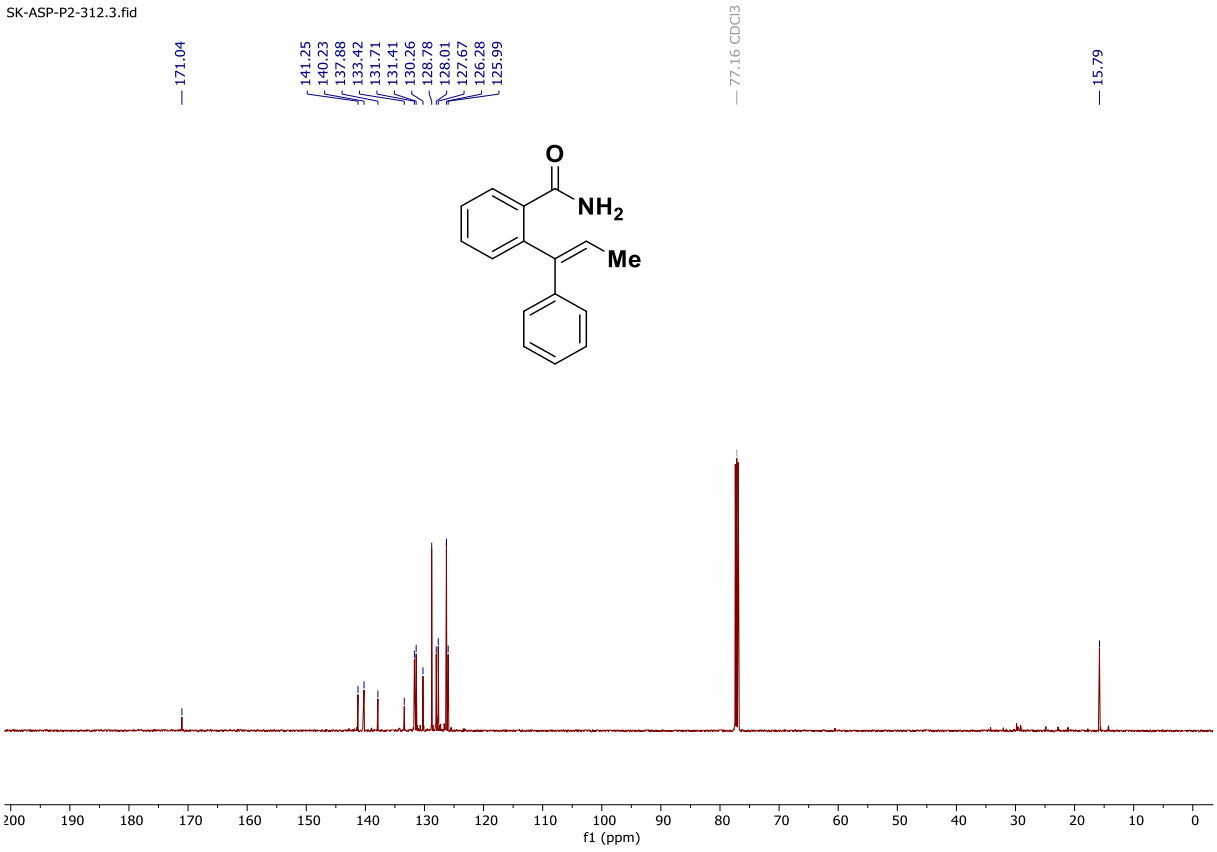
$^{13}C\{^{1}H\}$ NMR spectrum of I40 in $CDCl_3$ [126 MHz]



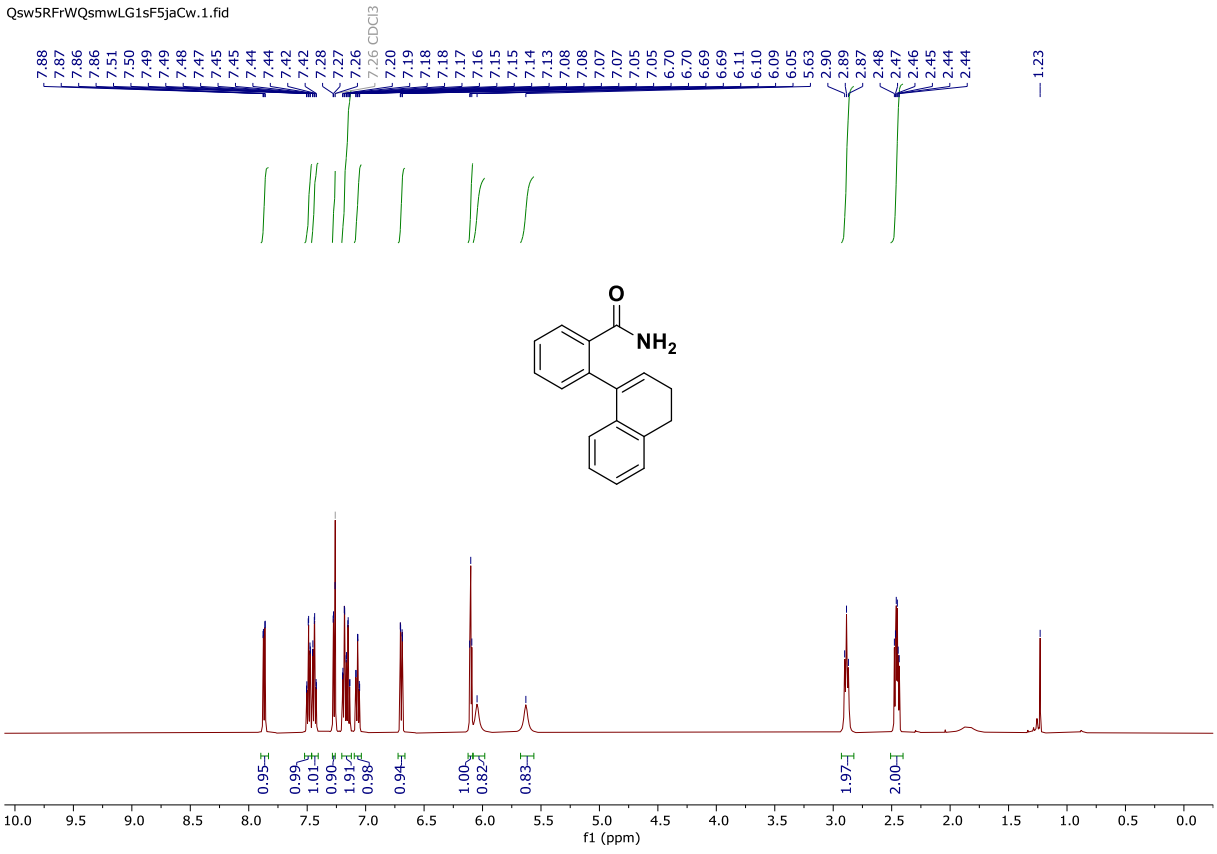
^{1}H NMR spectrum of I41 in $CDCl_3$ [500 MHz]



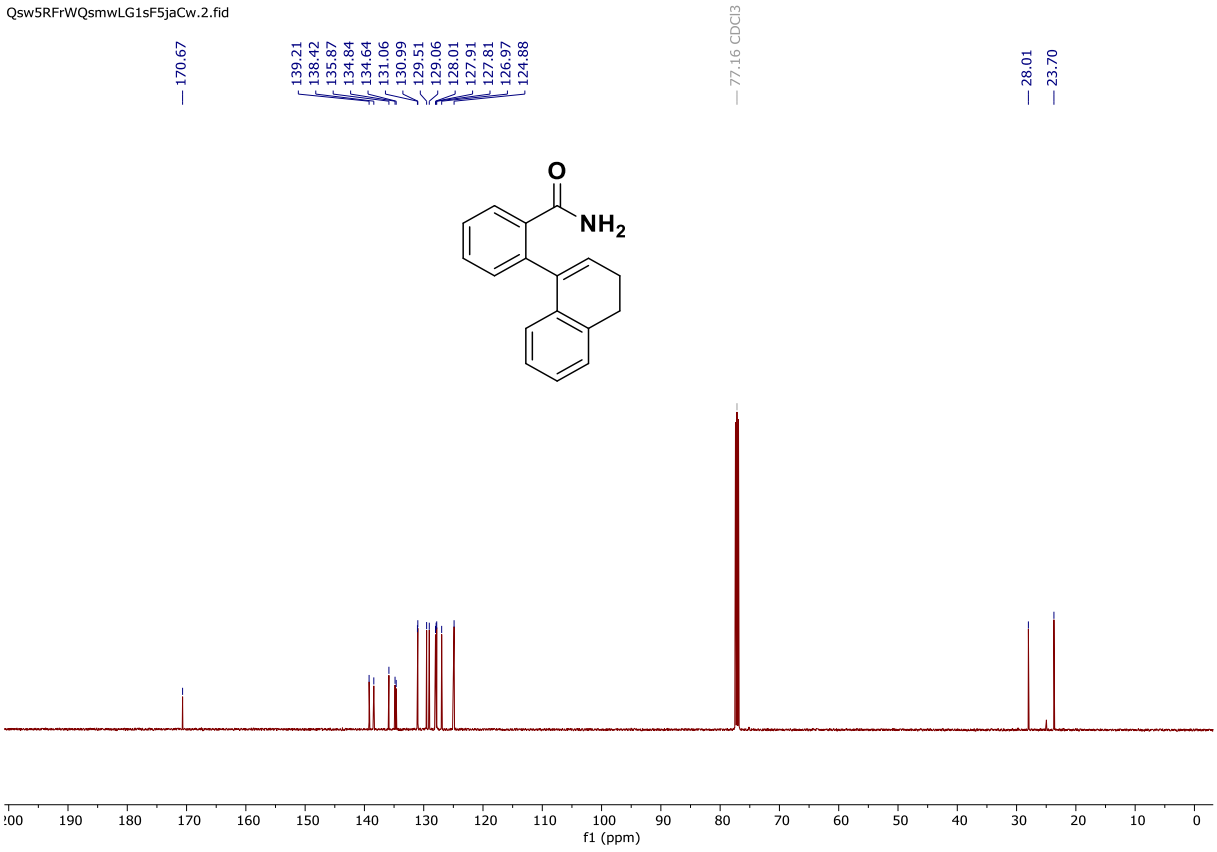
$^{13}C\{^{1}H\}$ NMR spectrum of I41 in $CDCl_3$ [126 MHz]



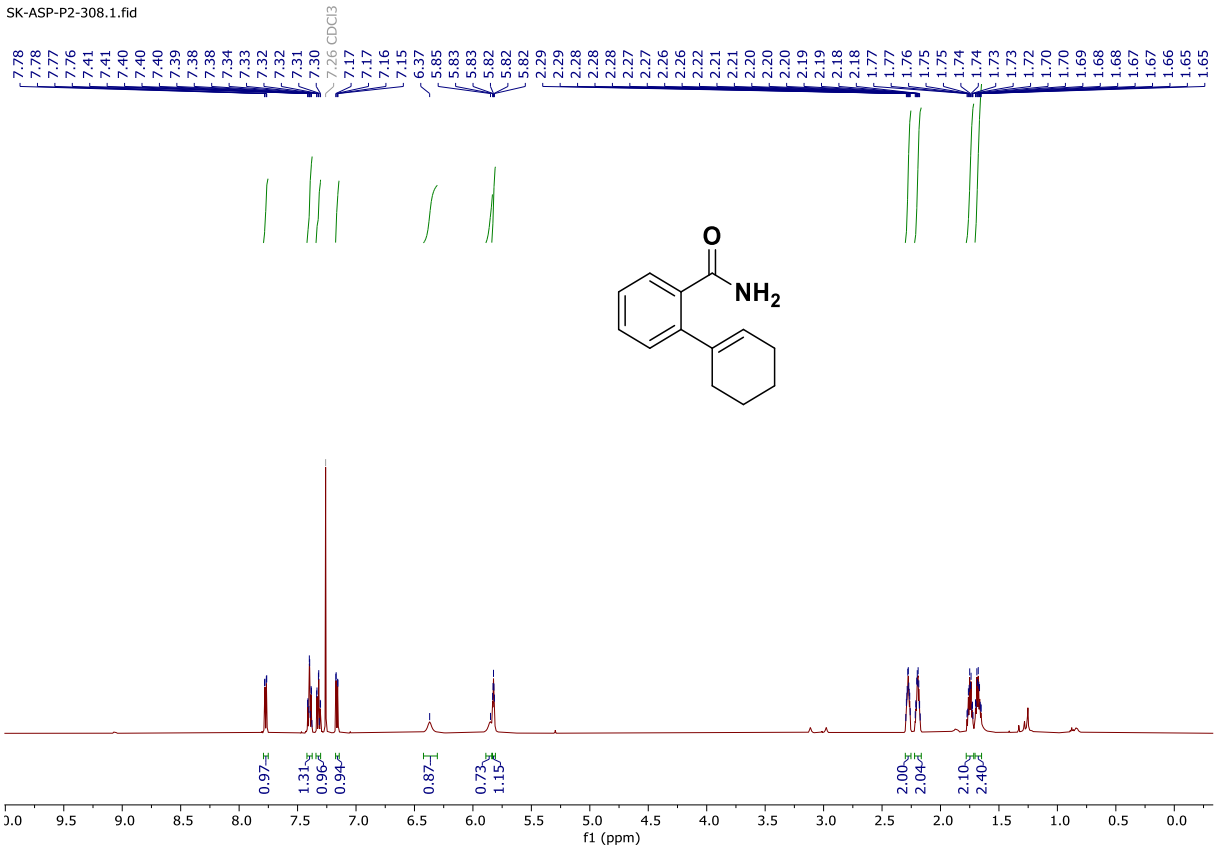
^{1}H NMR spectrum of I42 in $CDCl_3$ [500 MHz]



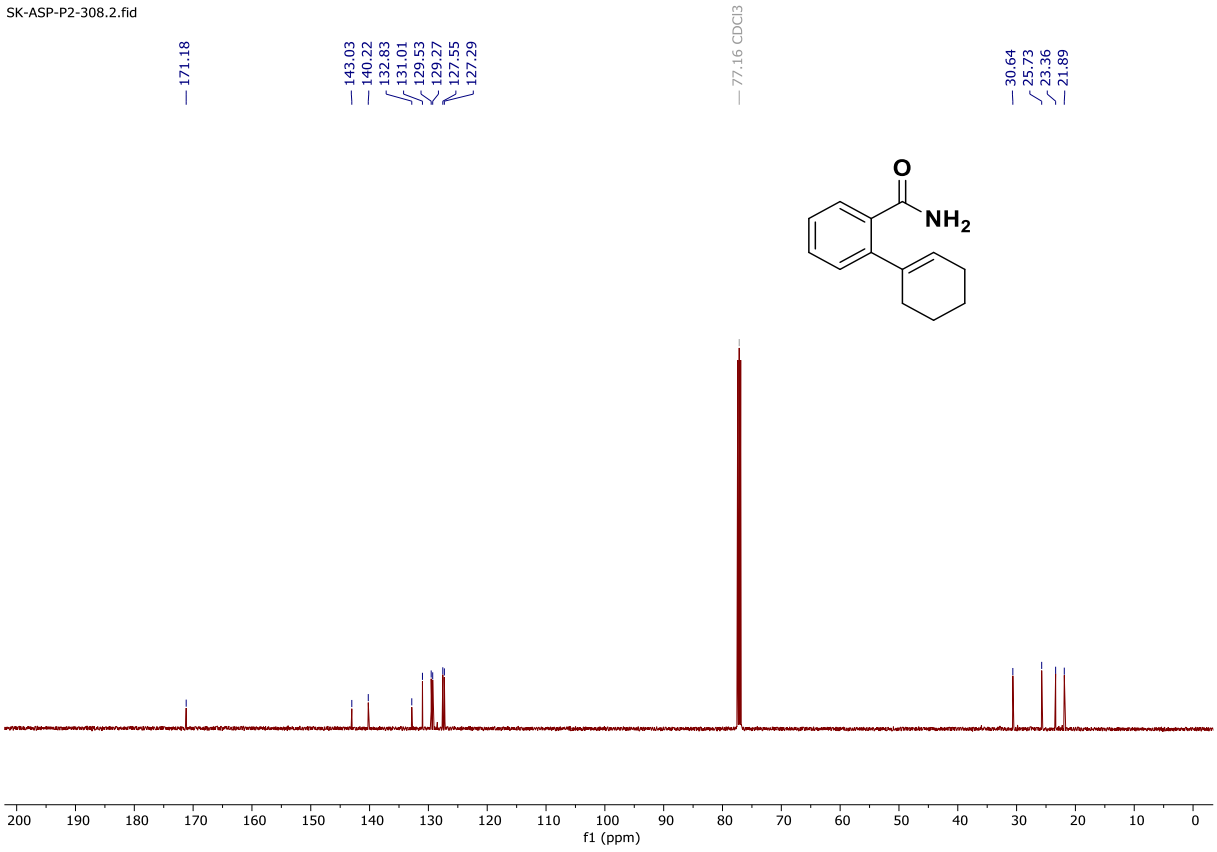
$^{13}C\{^{1}H\}$ NMR spectrum of I42 in $CDCl_3$ [126 MHz]



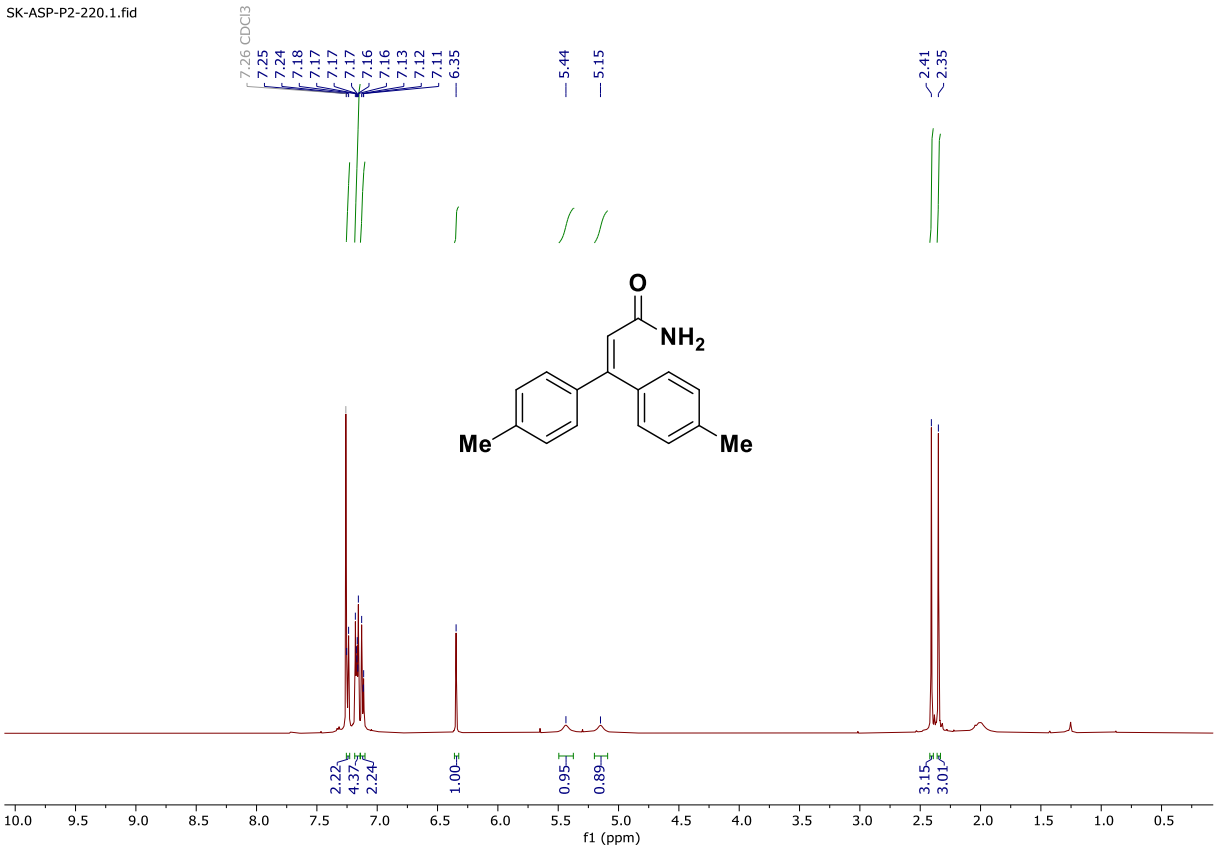
^{1}H NMR spectrum of I43 in $CDCl_3$ [500 MHz]



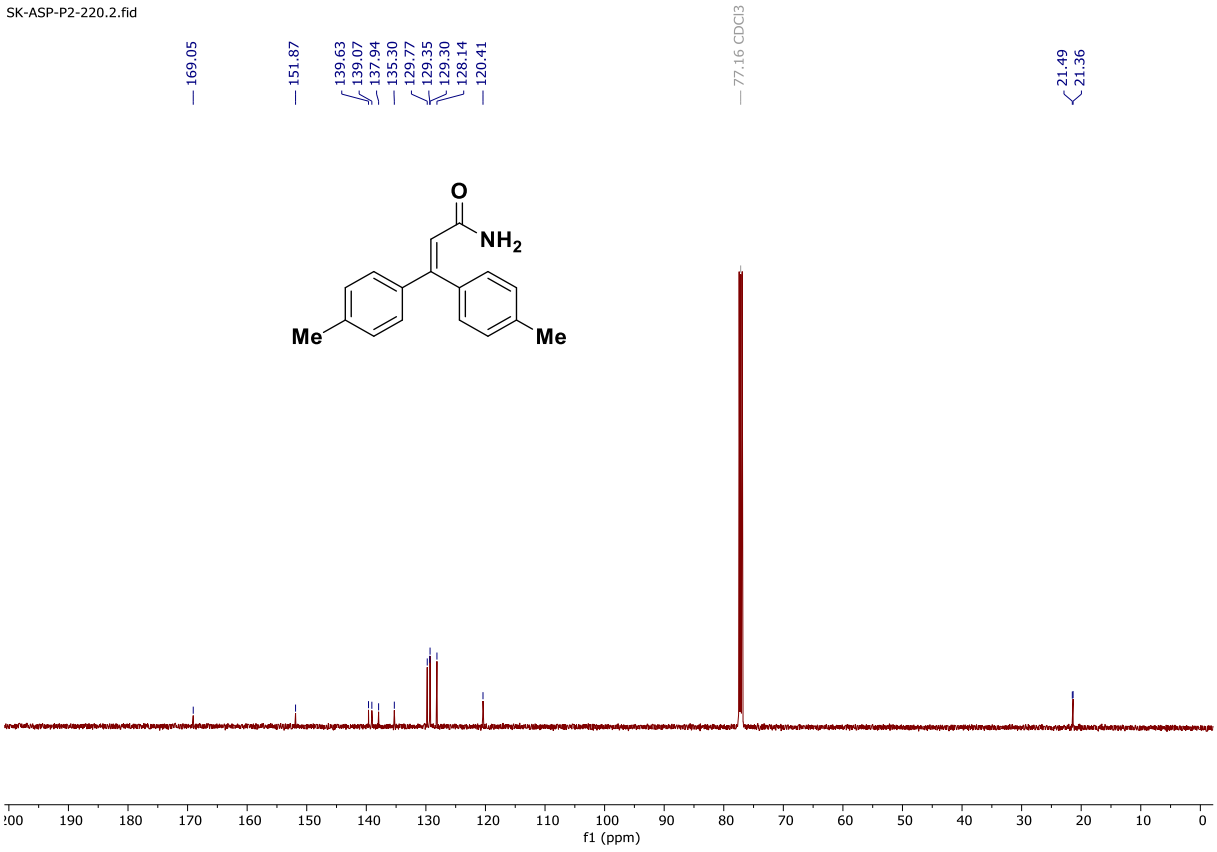
$^{13}C\{^{1}H\}$ NMR spectrum of I43 in $CDCl_3$ [126 MHz]



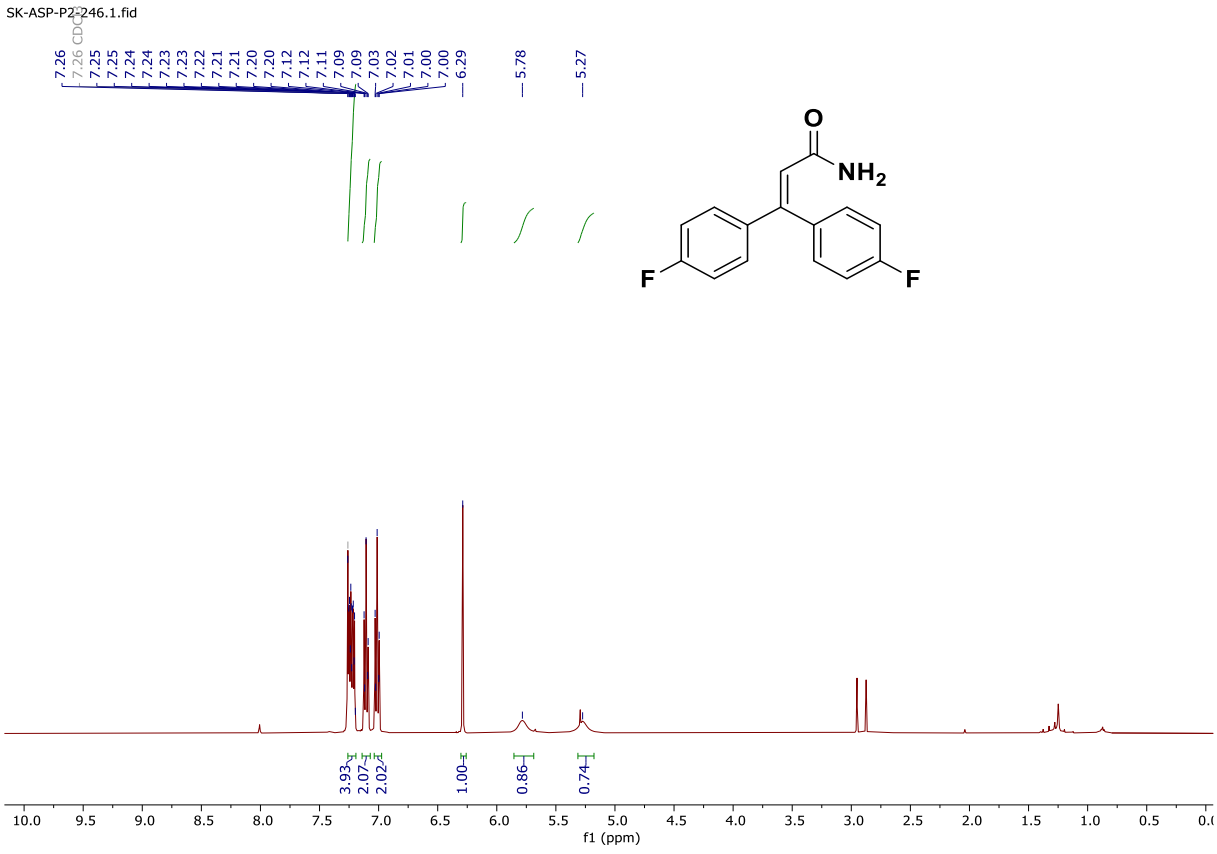
^{1}H NMR spectrum of I45 in $CDCl_3$ [500 MHz]



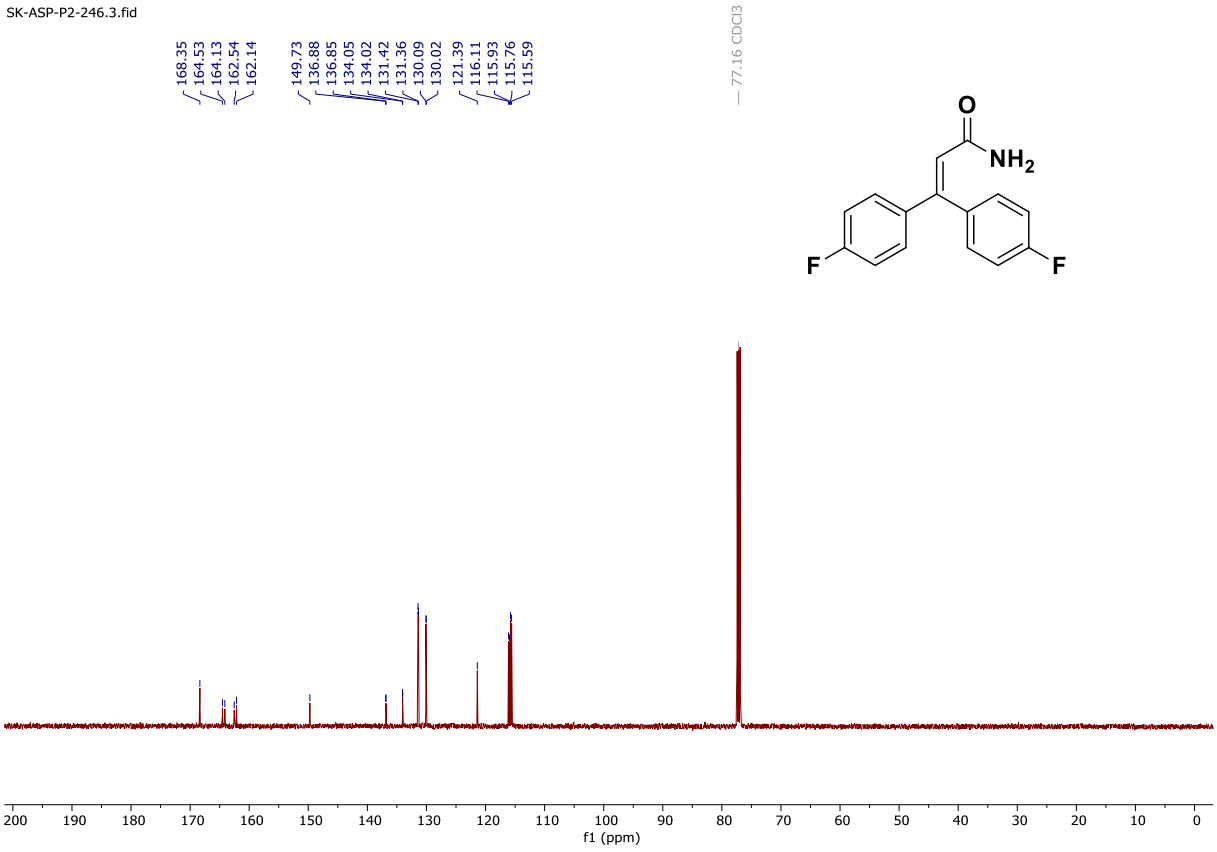
$^{13}C\{^{1}H\}$ NMR spectrum of I45 in $CDCl_3$ [126 MHz]



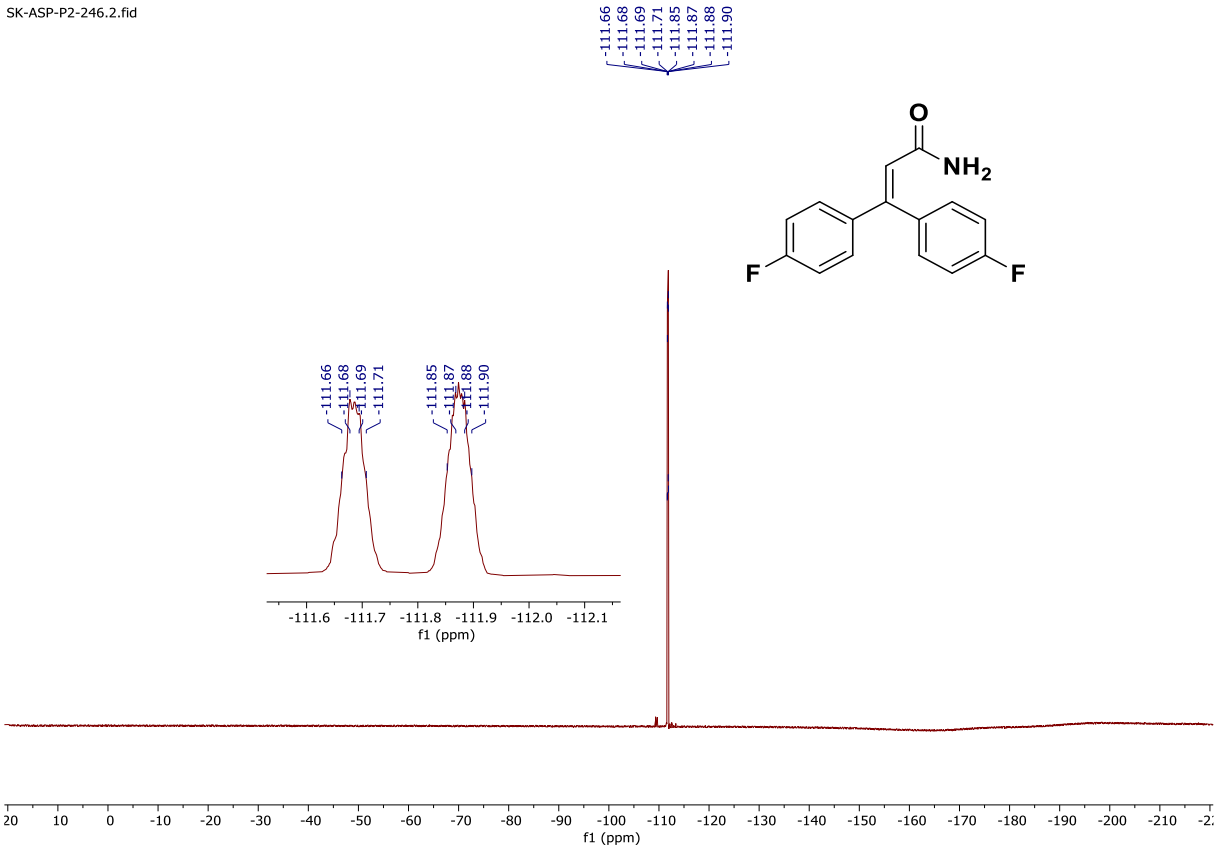
^{1}H NMR spectrum of I46 in $CDCl_3$ [500 MHz]



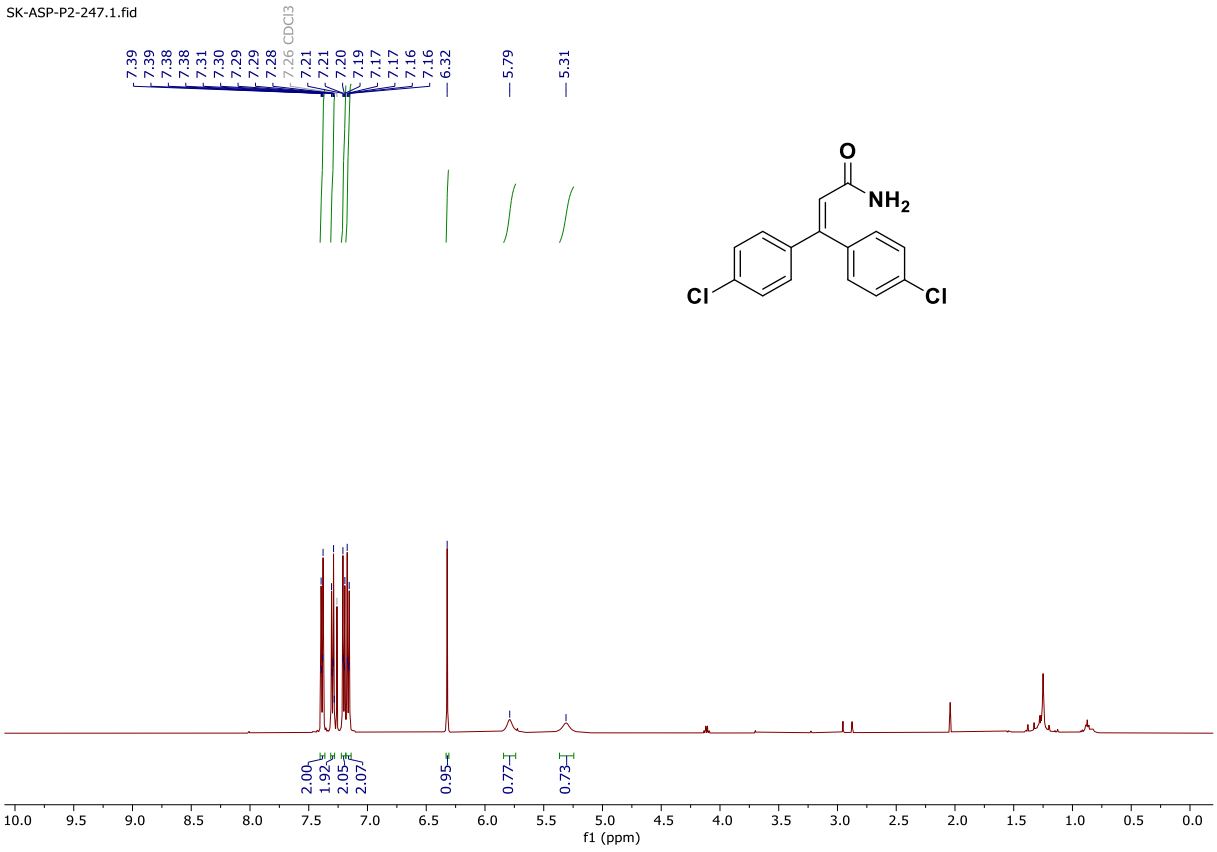
$^{13}C\{^{1}H\}$ NMR spectrum of I46 in $CDCl_3$ [126 MHz]



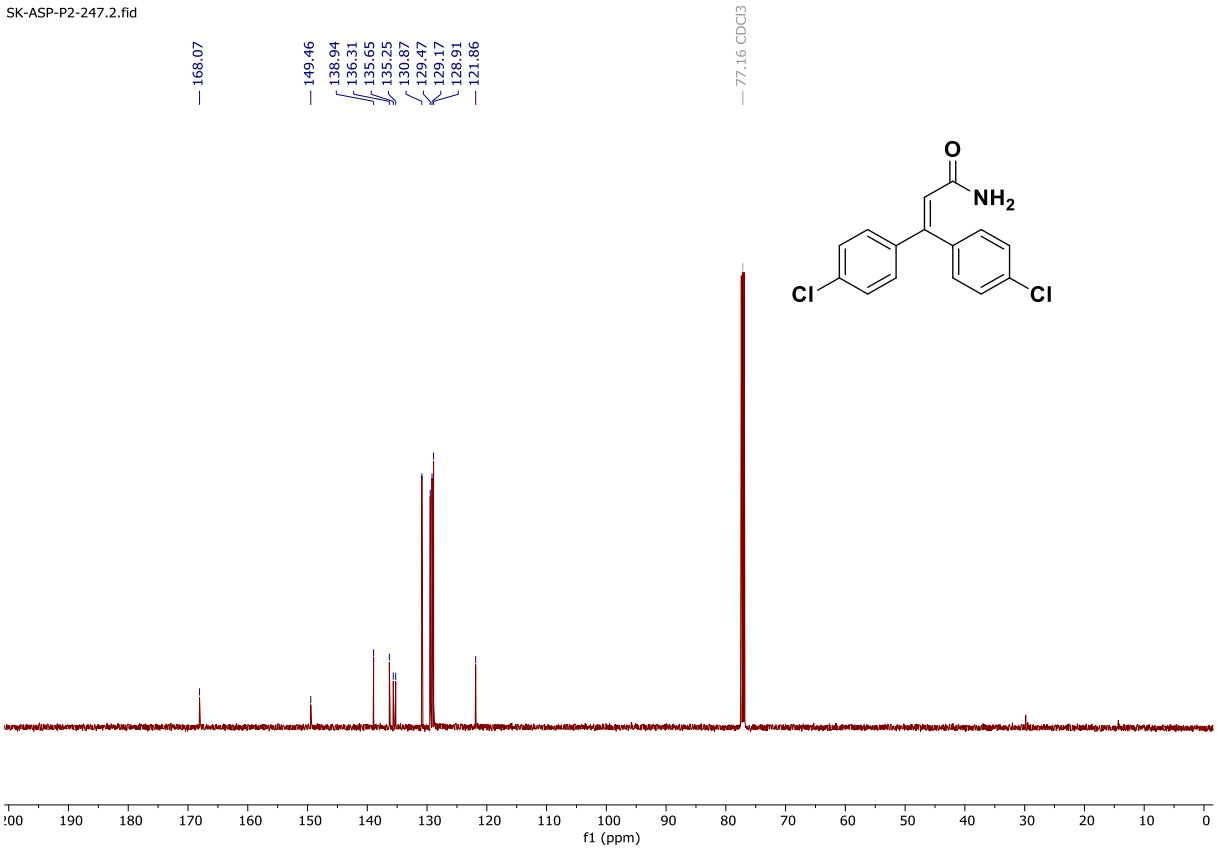
^{19}F NMR spectrum of I46 in $CDCl_3$ [471 MHz]



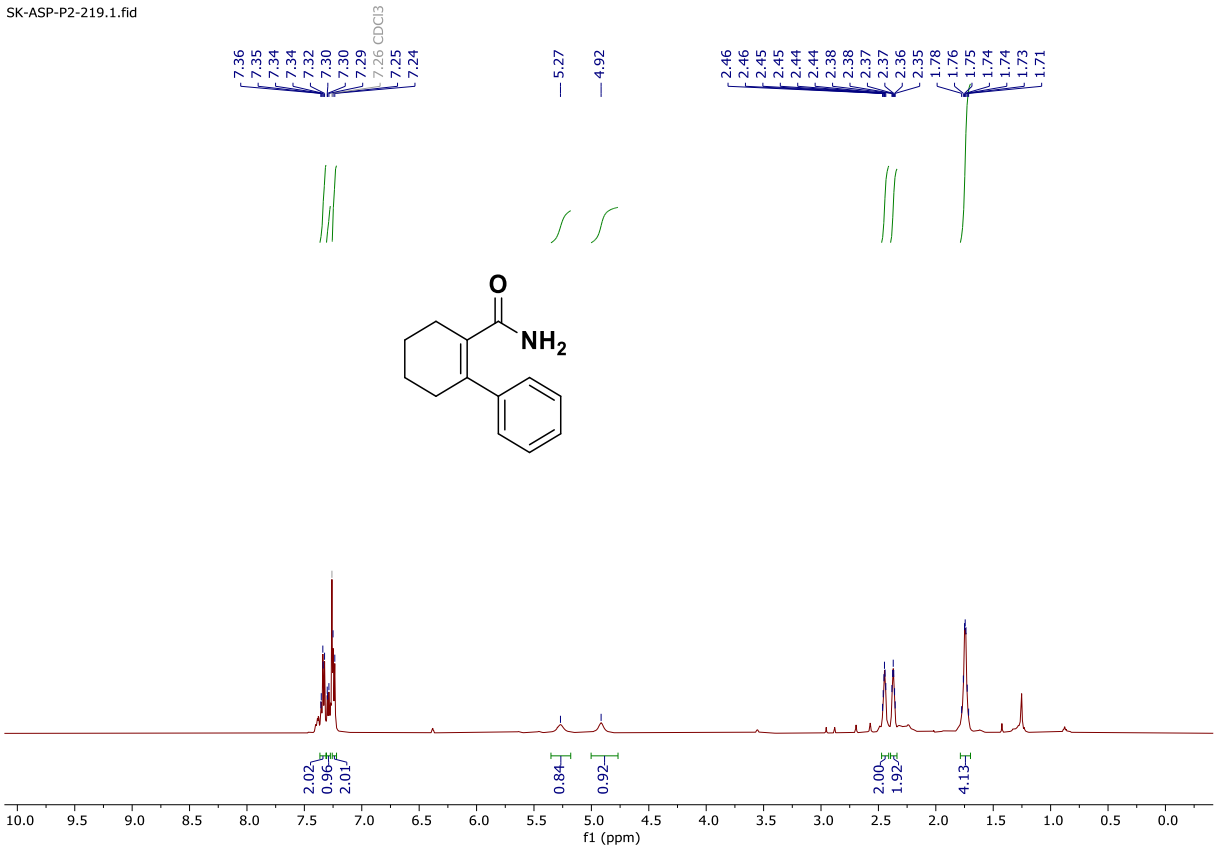
^{1}H NMR spectrum of I47 in $CDCl_3$ [500 MHz]



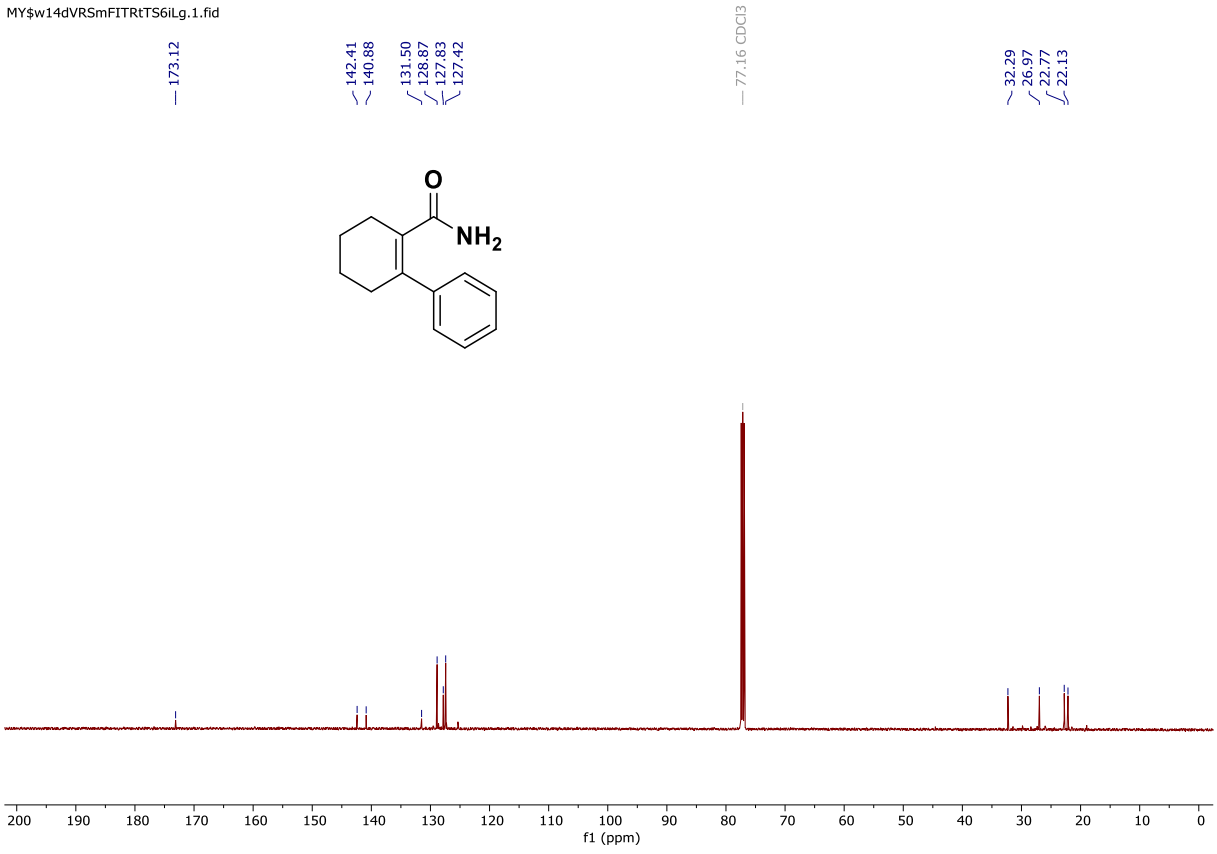
^{13}C{^{1}H} NMR spectrum of I47 in $CDCl_3$ [126 MHz]



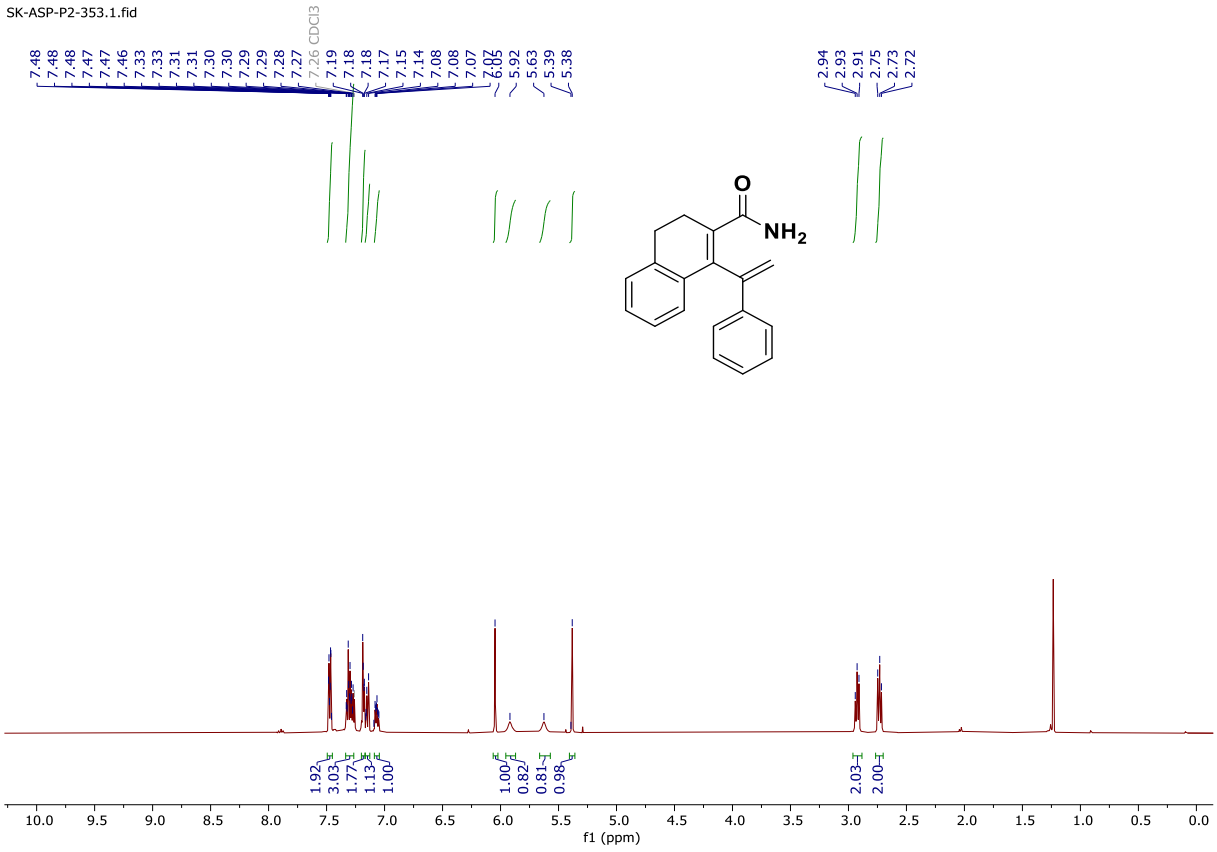
^{1}H NMR spectrum of I48 in $CDCl_3$ [500 MHz]



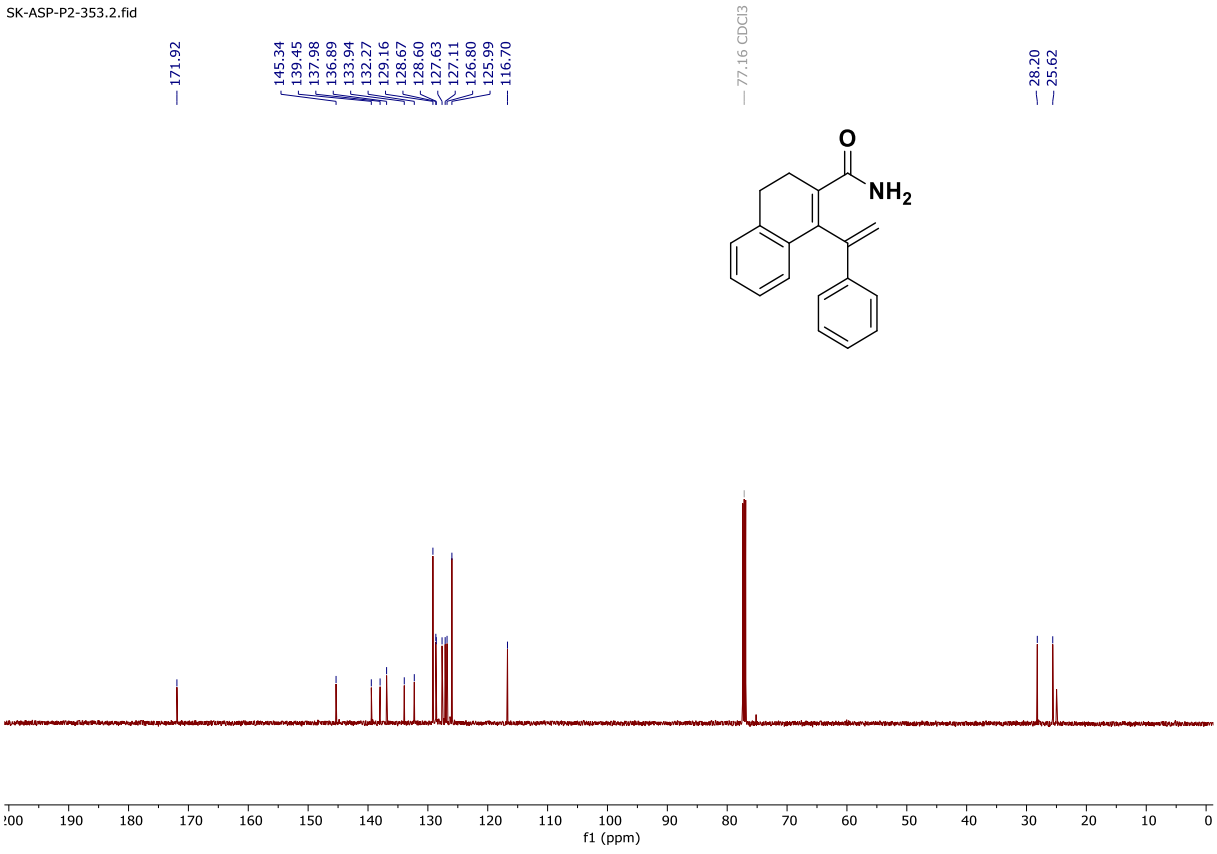
^{13}C{^{1}H} NMR spectrum of I48 in $CDCl_3$ [126 MHz]



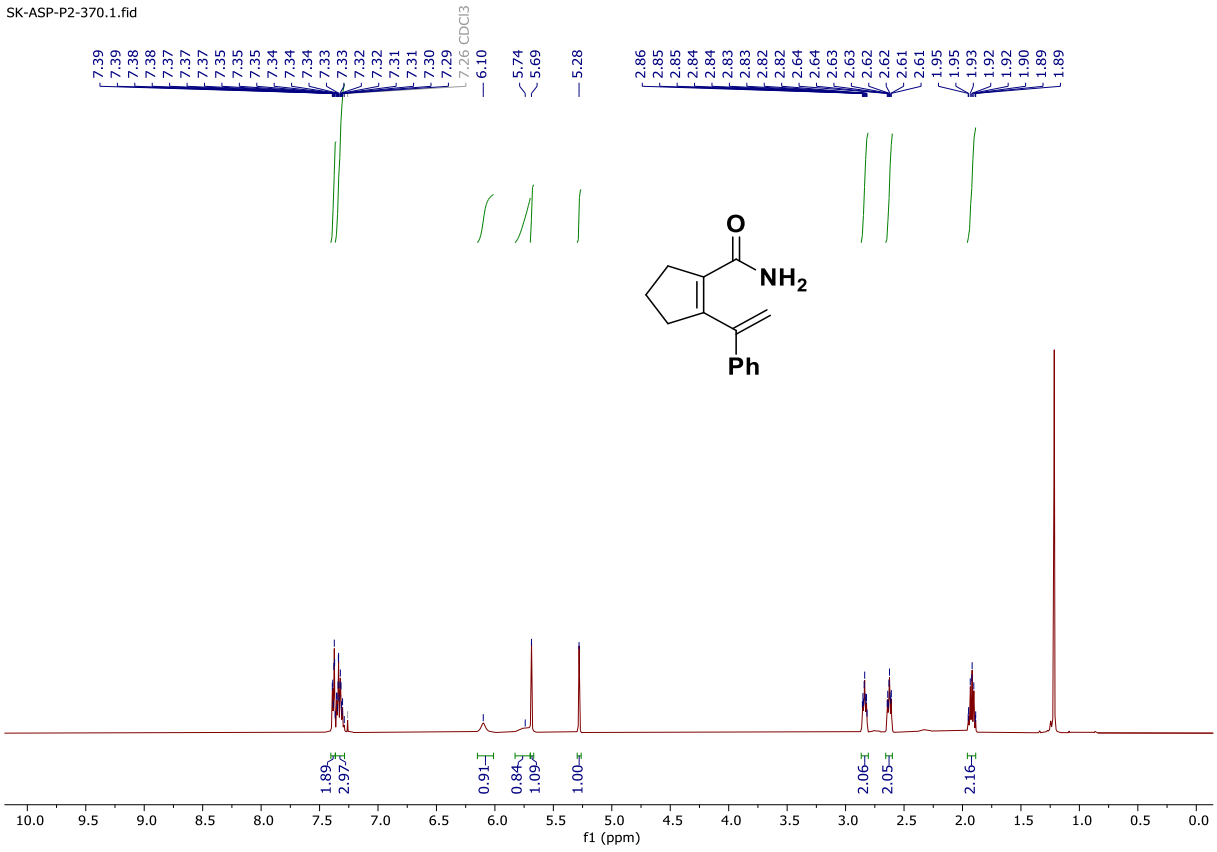
^{1}H NMR spectrum of I49 in $CDCl_3$ [500 MHz]



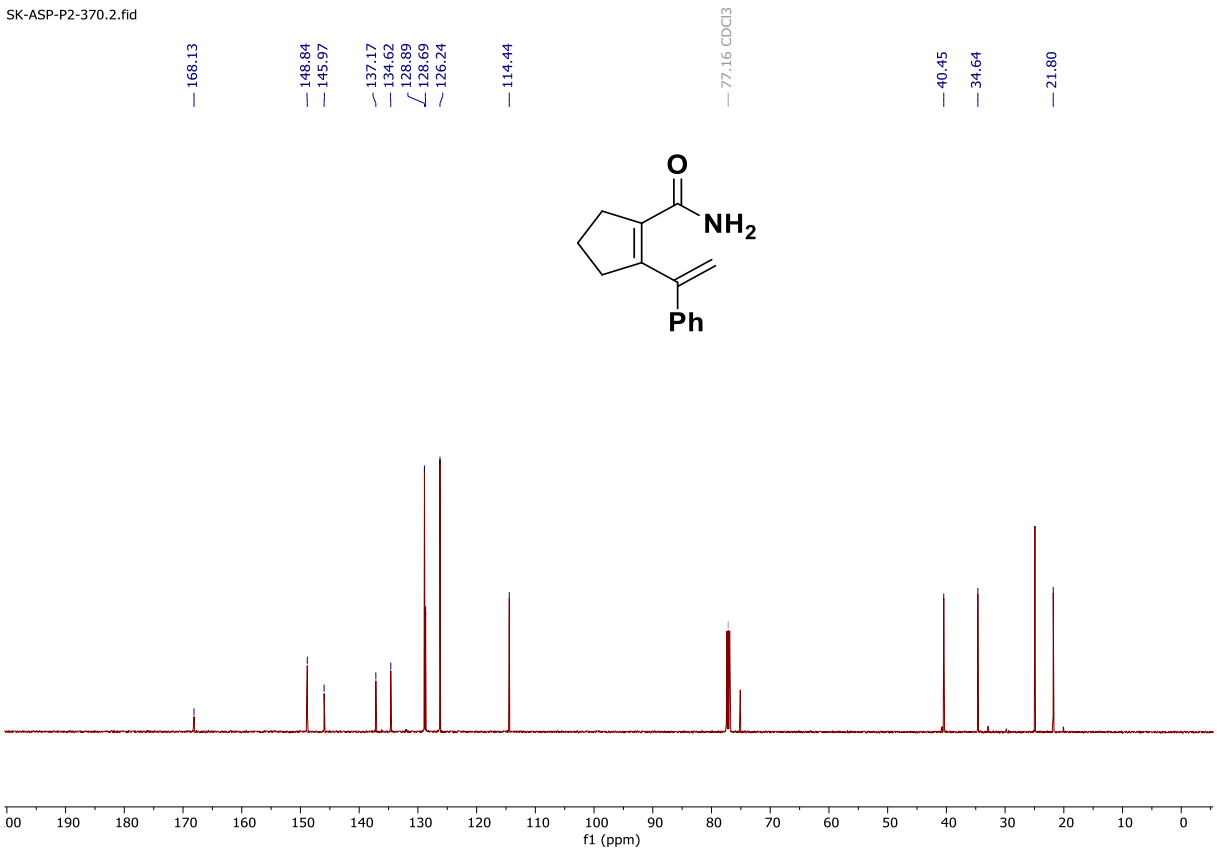
^{13}C{^{1}H} NMR spectrum of I49 in $CDCl_3$ [126 MHz]



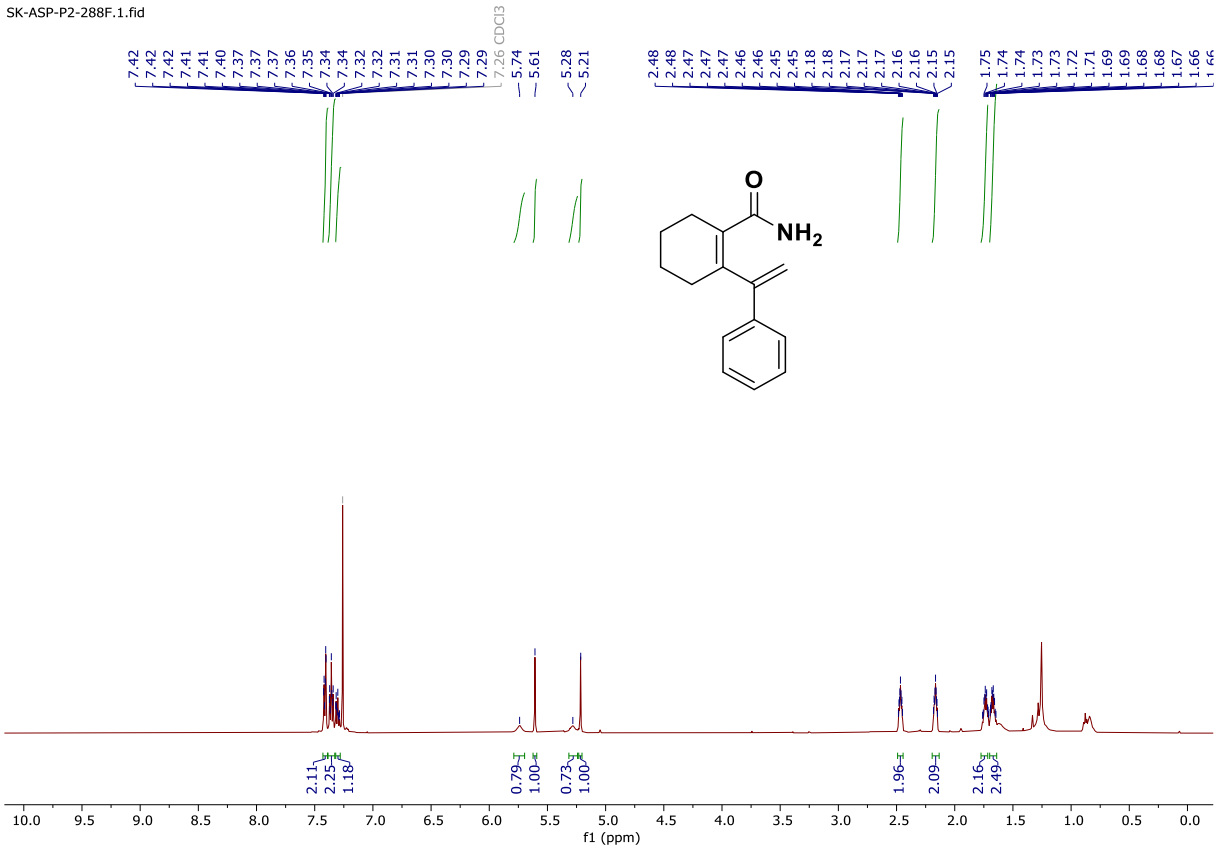
^{1}H NMR spectrum of I50 in $CDCl_3$ [500 MHz]



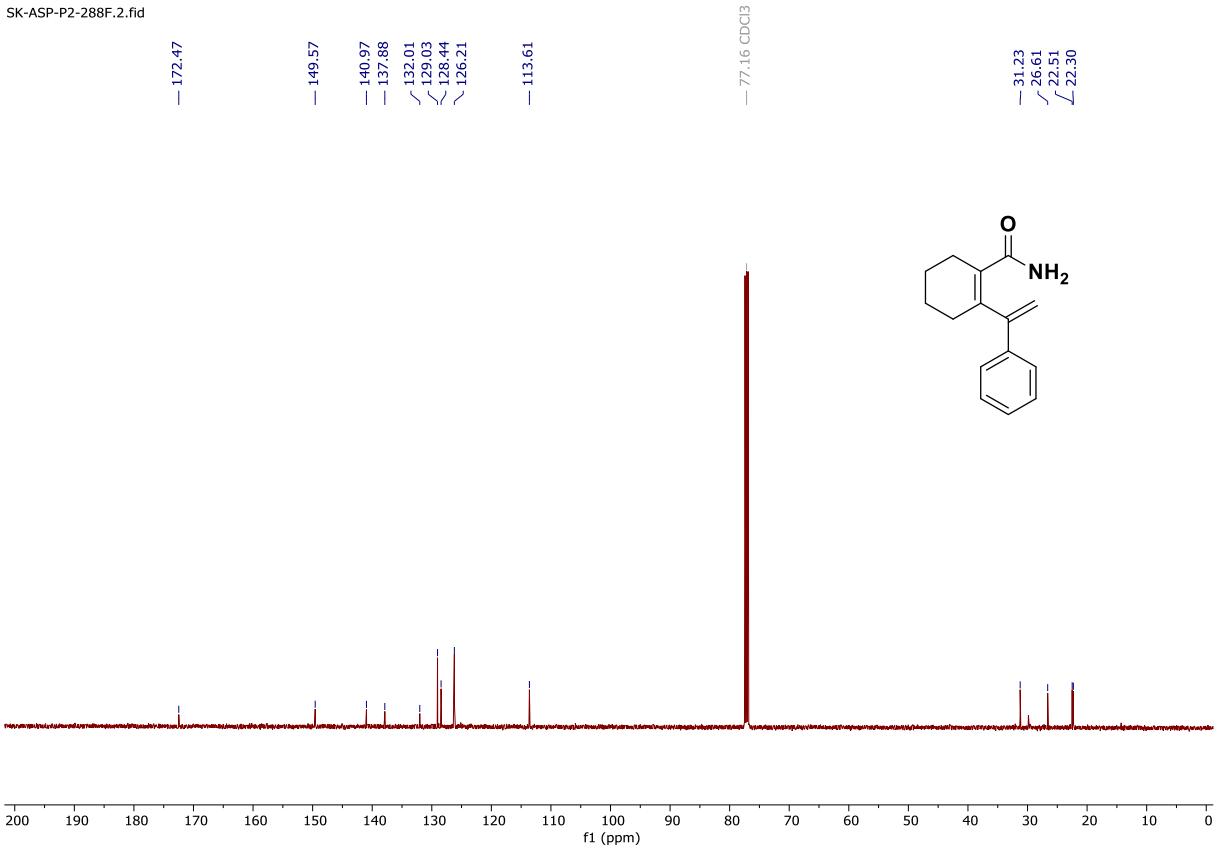
^{13}C{^{1}H} NMR spectrum of I50 in $CDCl_3$ [126 MHz]



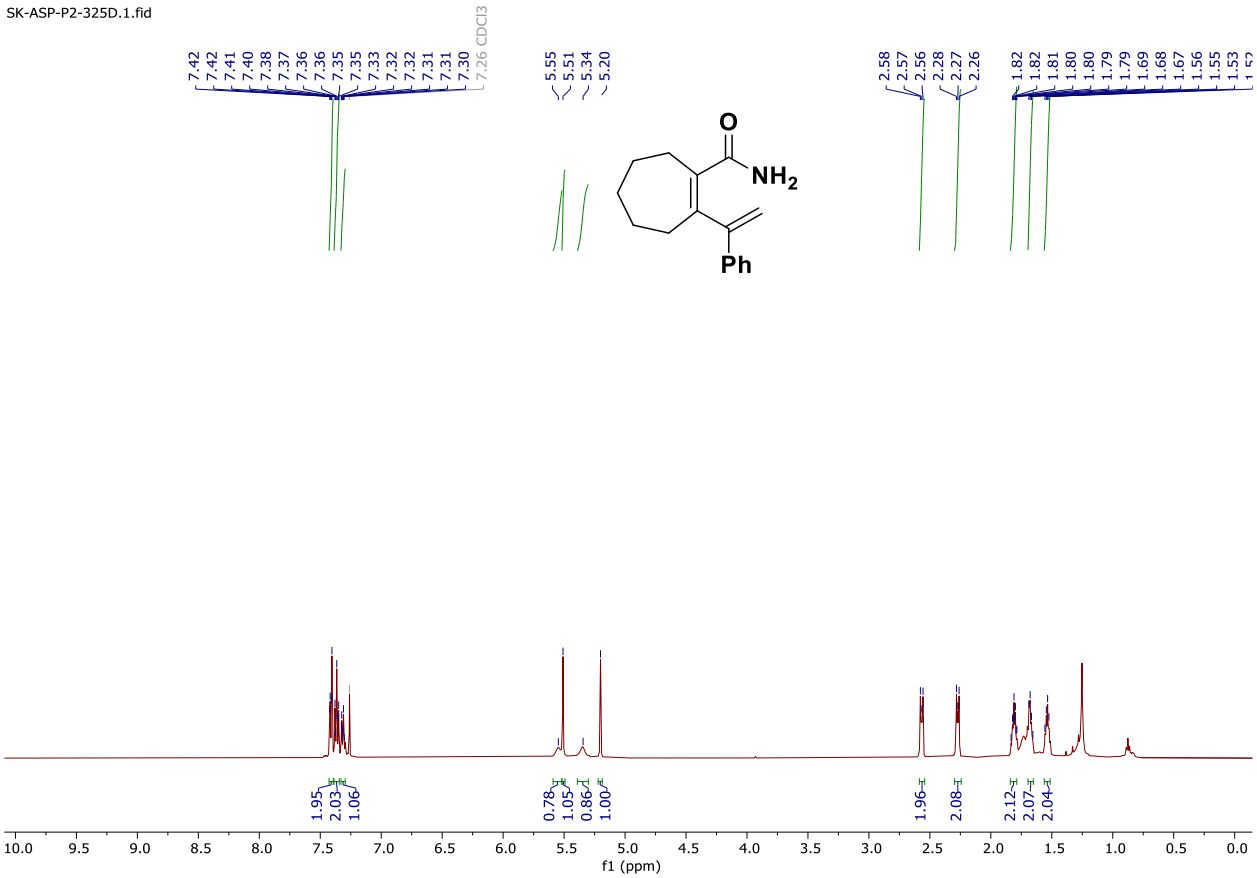
^{1}H NMR spectrum of I51 in $CDCl_3$ [500 MHz]



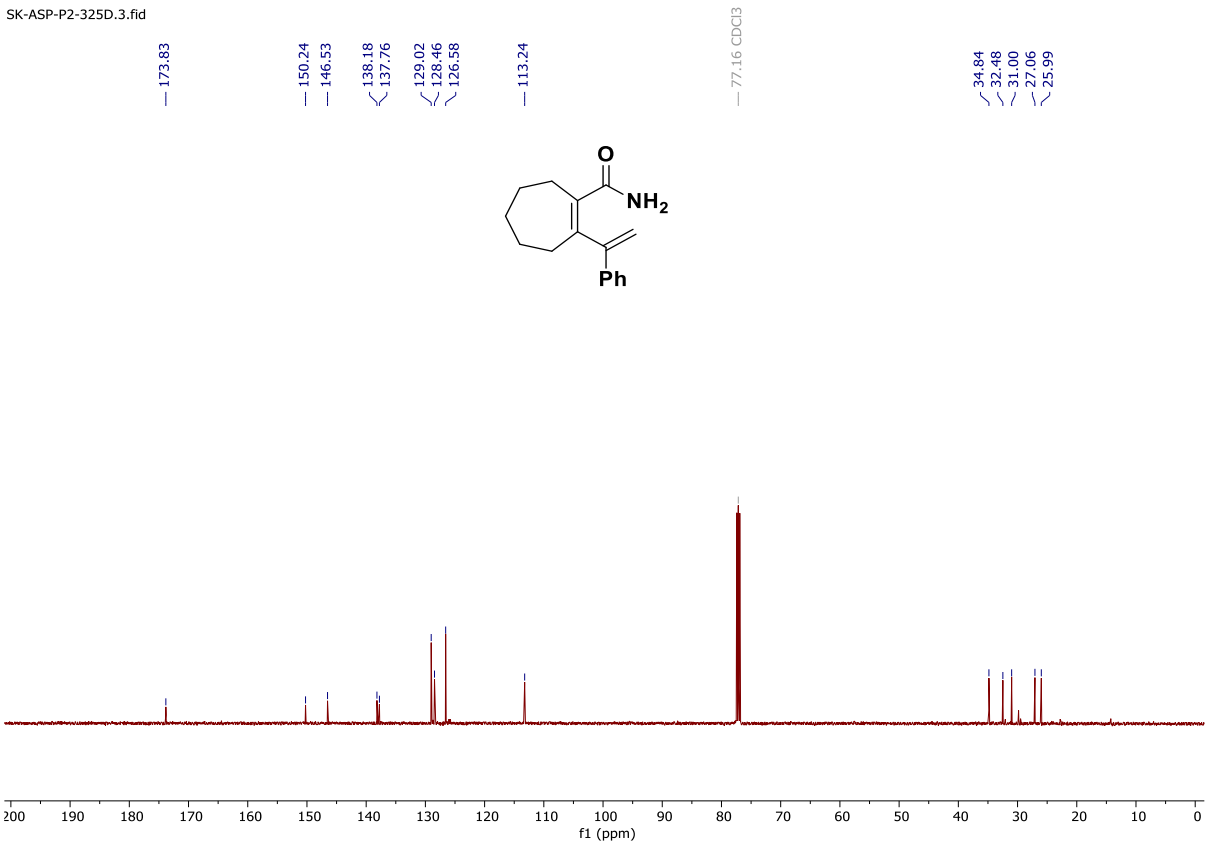
^{13}C{^{1}H} NMR spectrum of I51 in $CDCl_3$ [126 MHz]



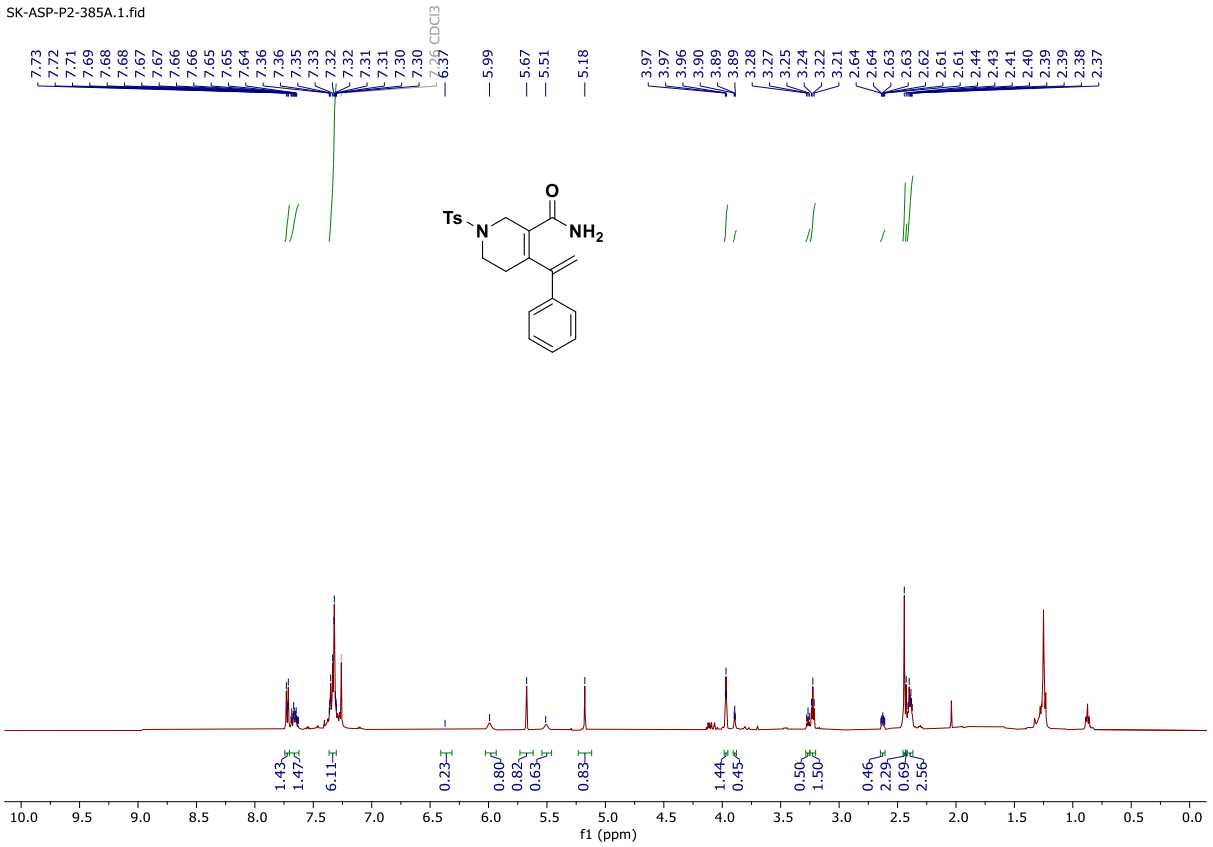
^{1}H NMR spectrum of I52 in $CDCl_3$ [500 MHz]



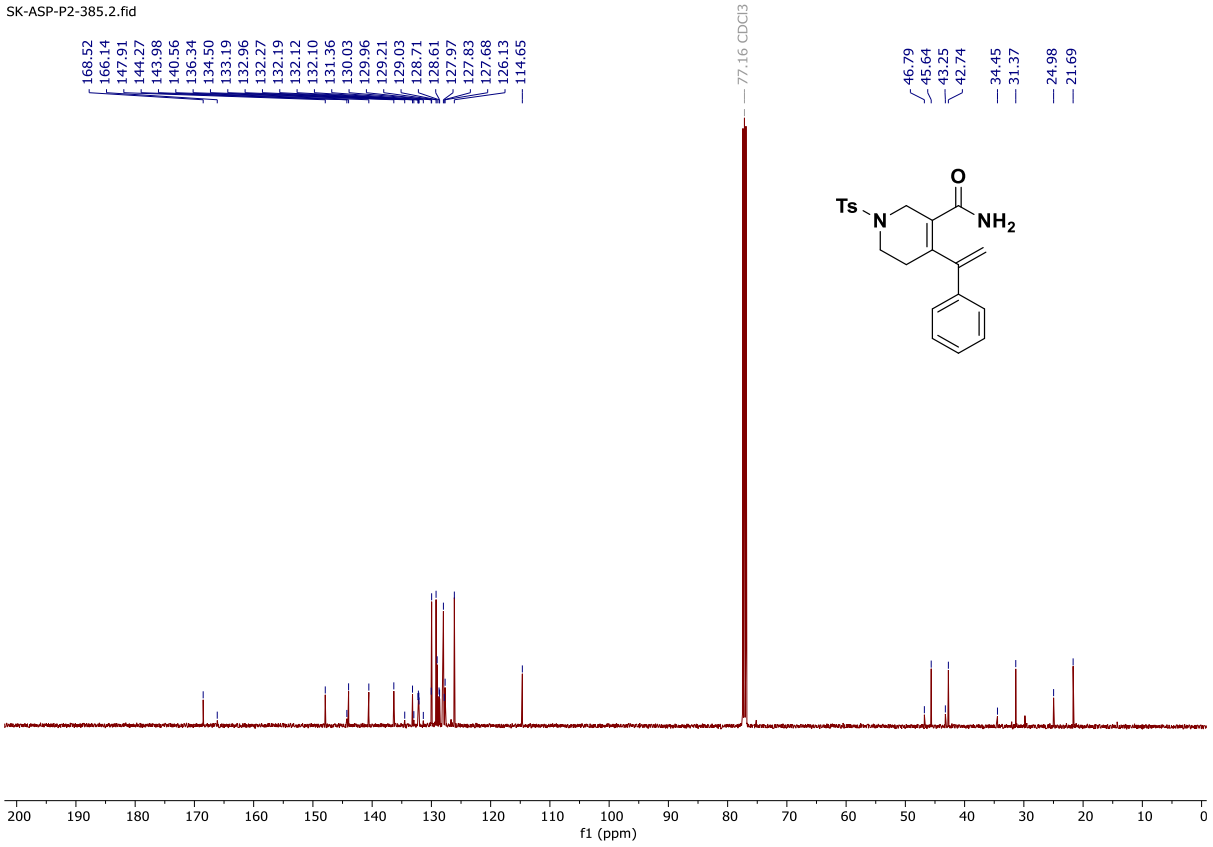
^{13}C{^{1}H} NMR spectrum of I52 in $CDCl_3$ [126 MHz]



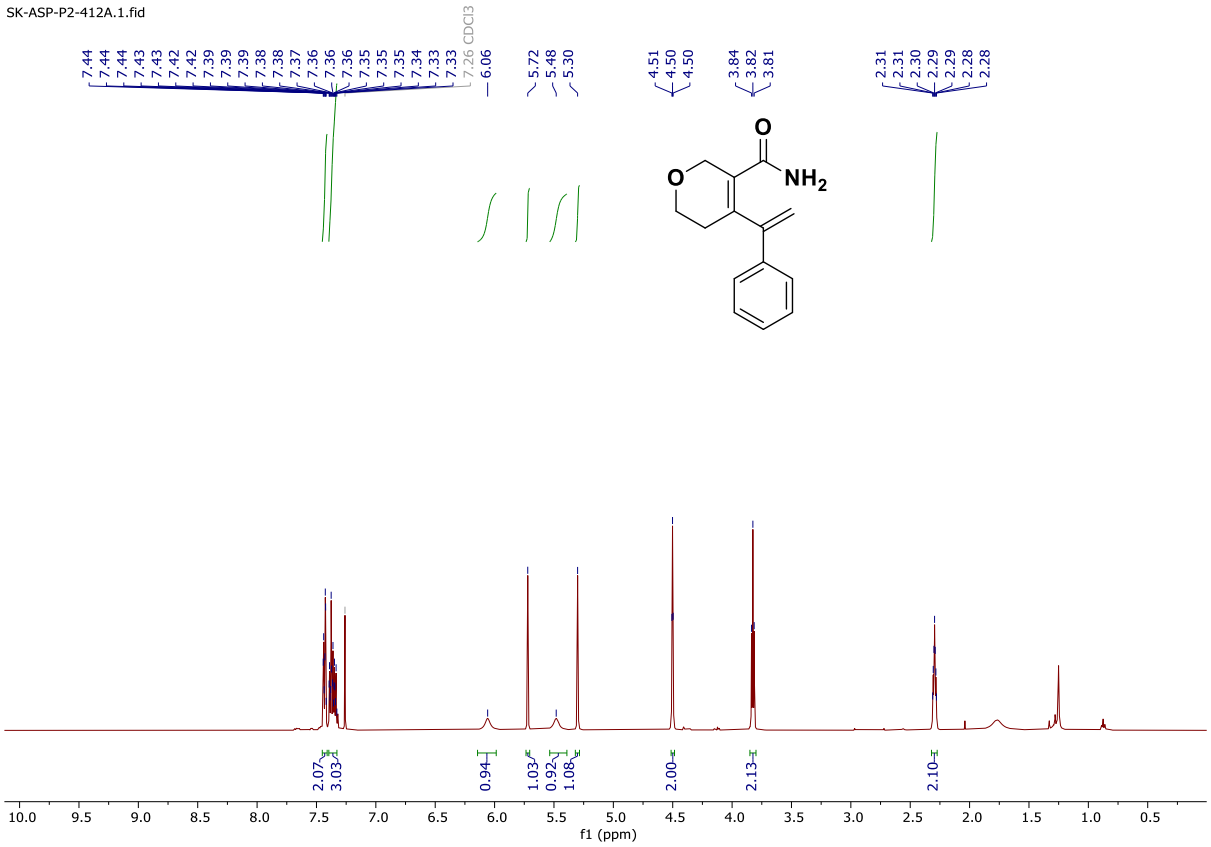
^{1}H NMR spectrum of I53 in $CDCl_3$ [500 MHz]



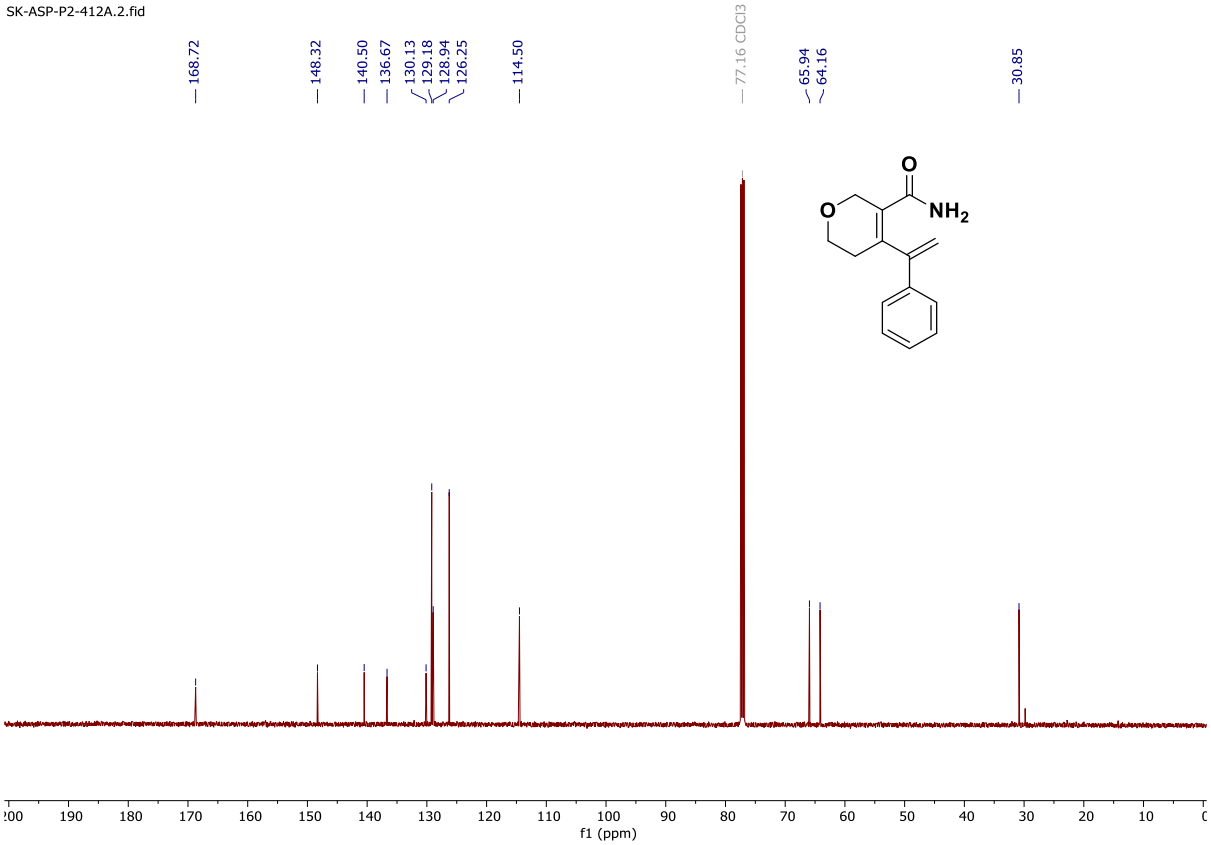
^{13}C{^{1}H} NMR spectrum of I53 in $CDCl_3$ [126 MHz]



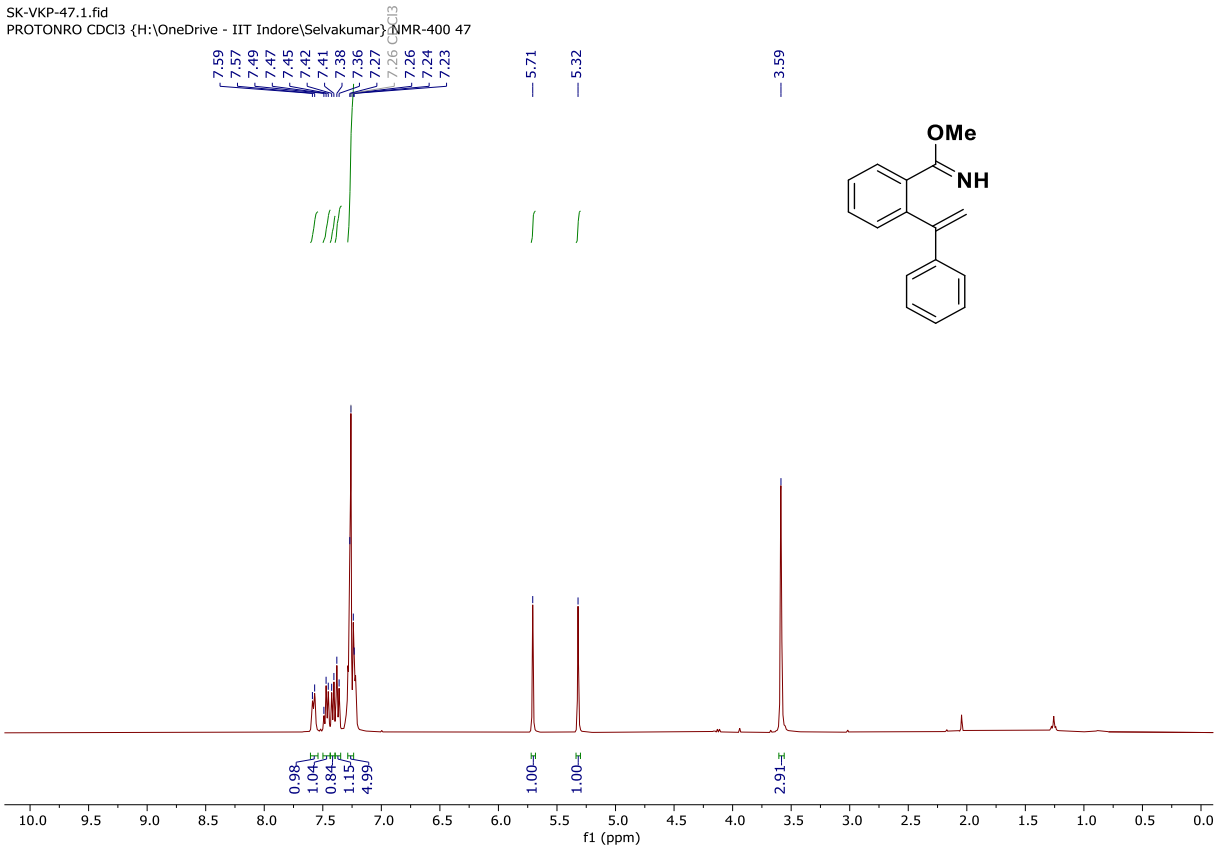
^{1}H NMR spectrum of I54 in $CDCl_3$ [500 MHz]



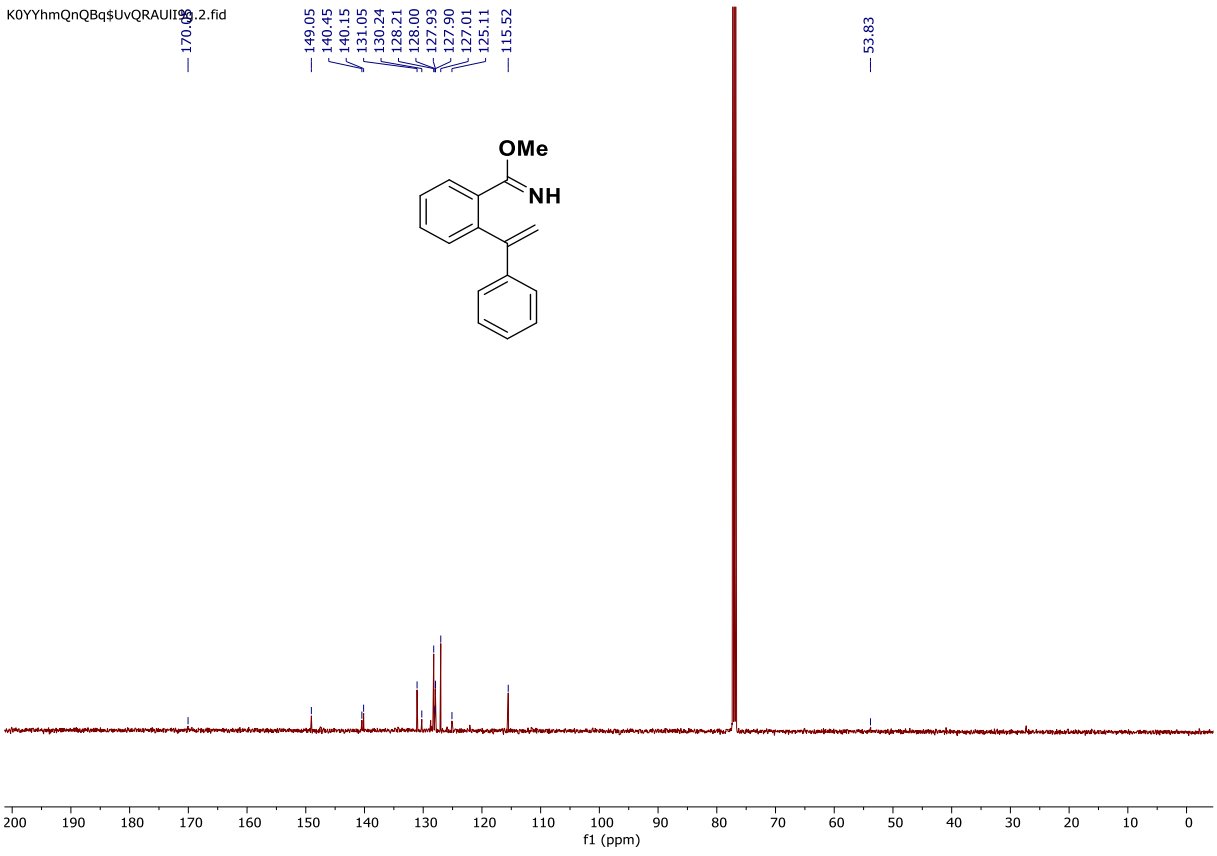
^{13}C{^{1}H} NMR spectrum of I54 in $CDCl_3$ [126 MHz]



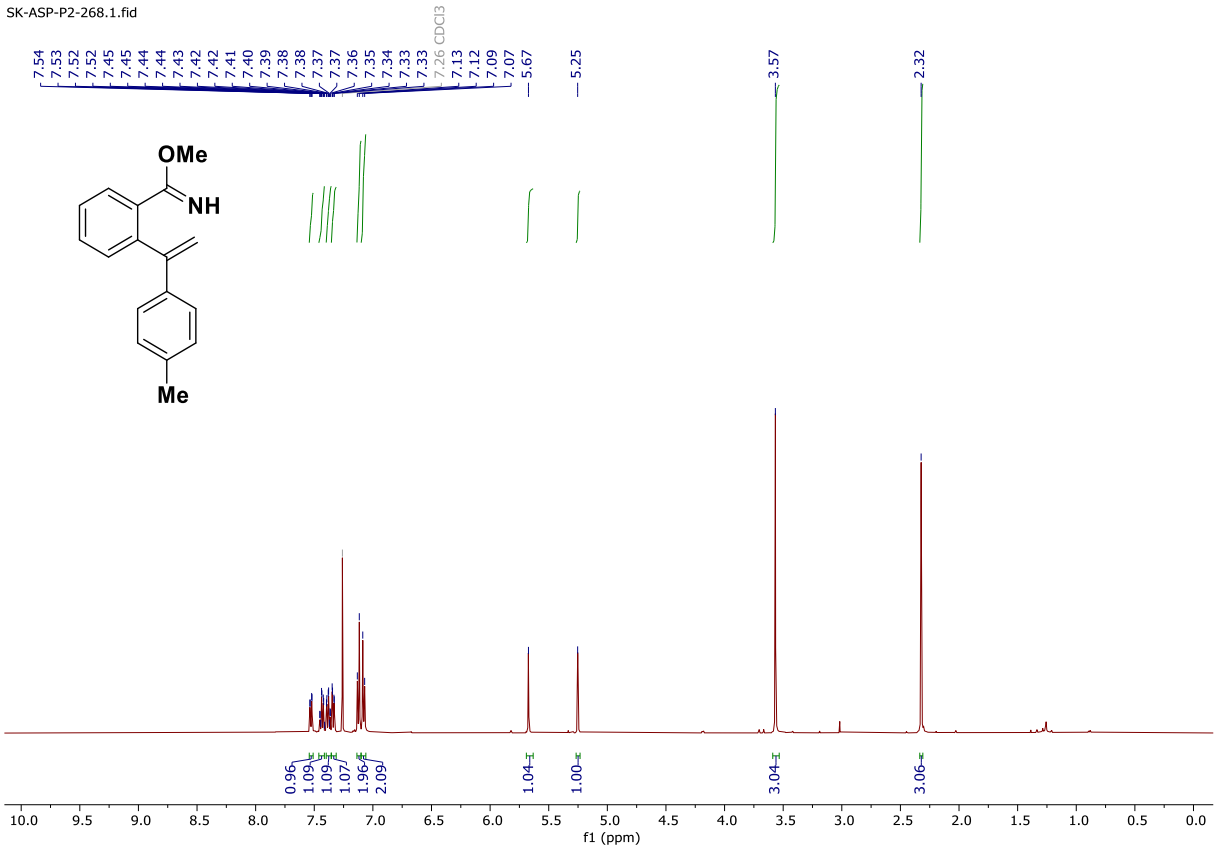
^{1}H NMR spectrum of 3a in $CDCl_3$ [400 MHz]



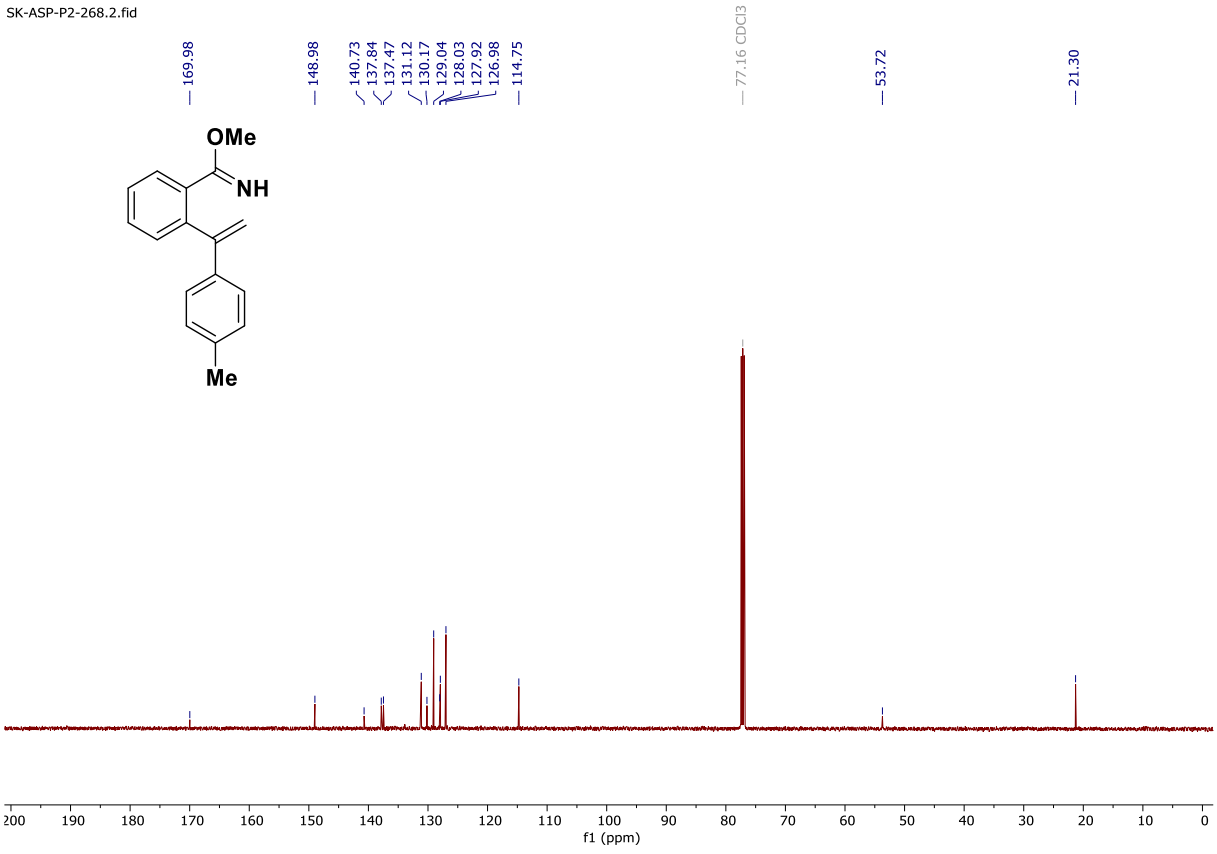
^{13}C{^{1}H} NMR spectrum of 3a in $CDCl_3$ [126 MHz]



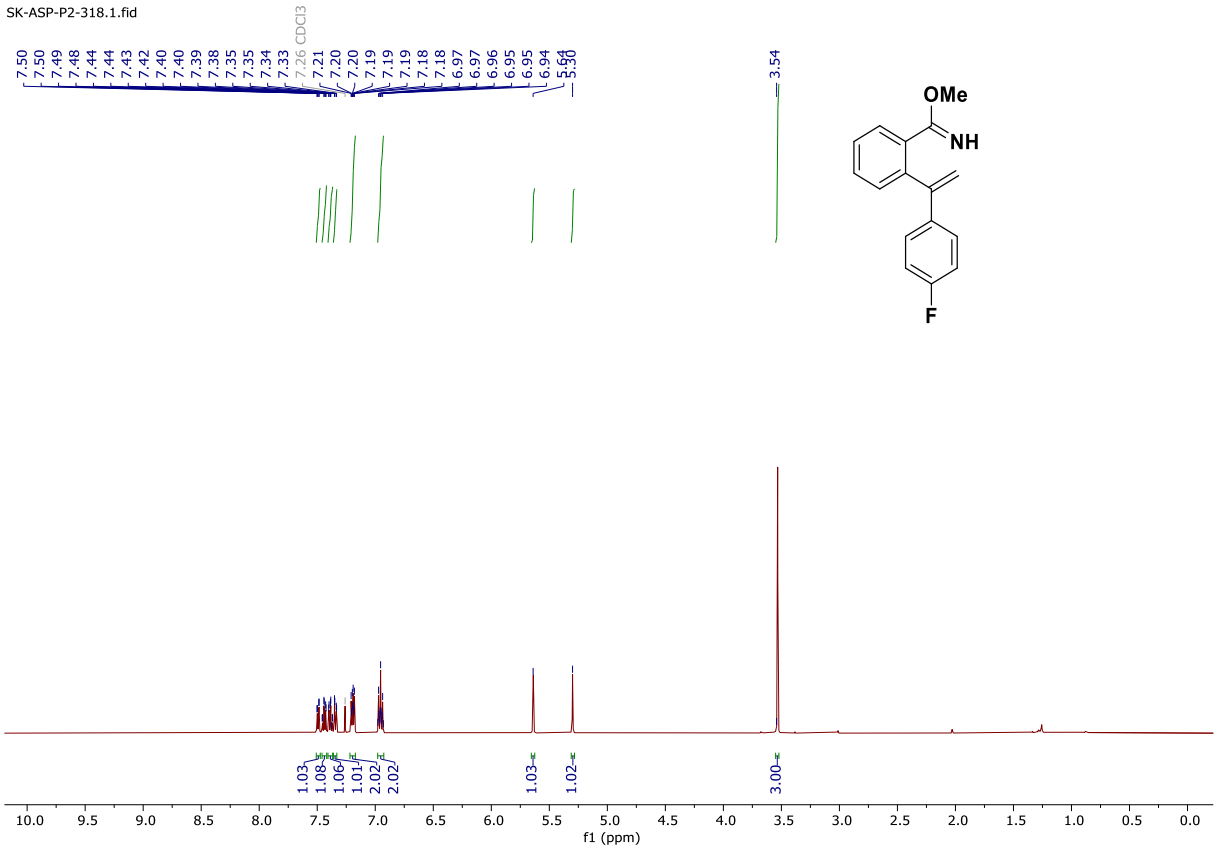
^{1}H NMR spectrum of 3b in $CDCl_3$ [500 MHz]



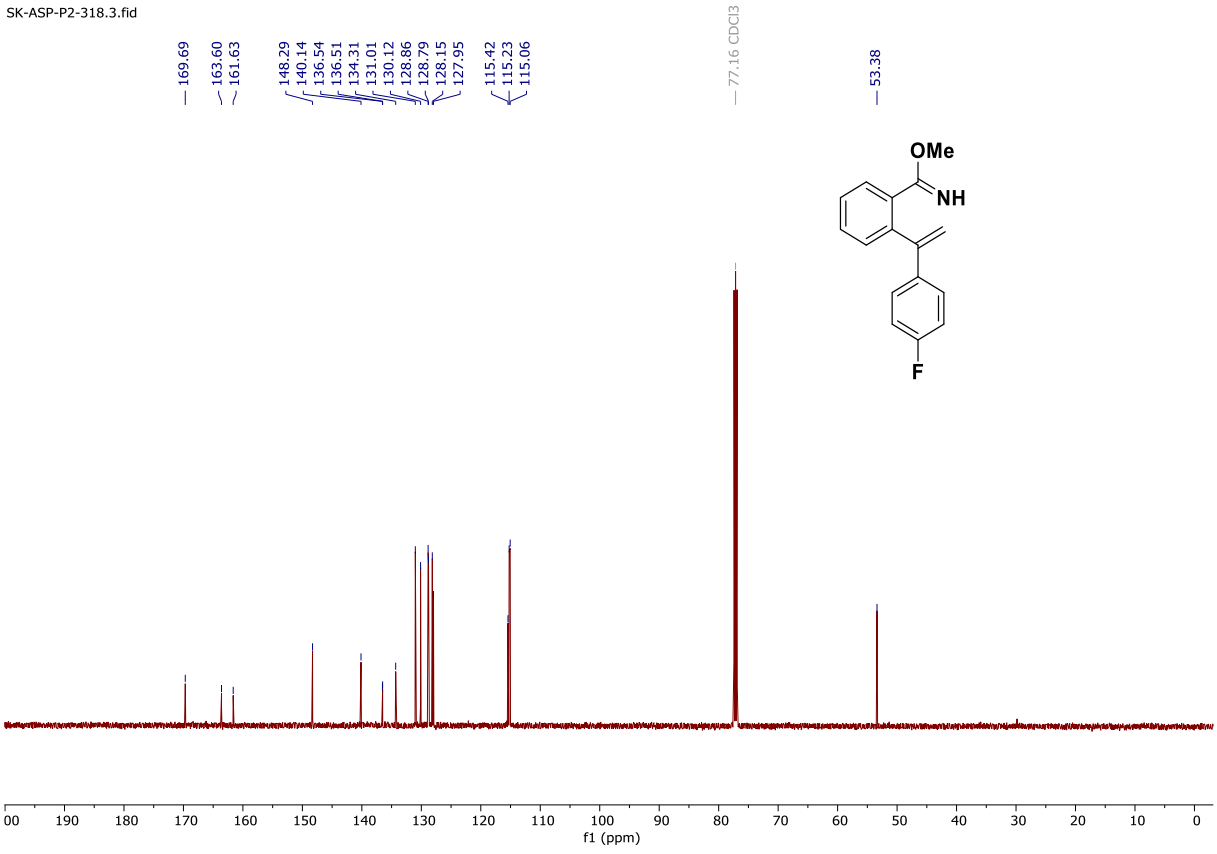
^{13}C{^{1}H} NMR spectrum of 3b in $CDCl_3$ [126 MHz]



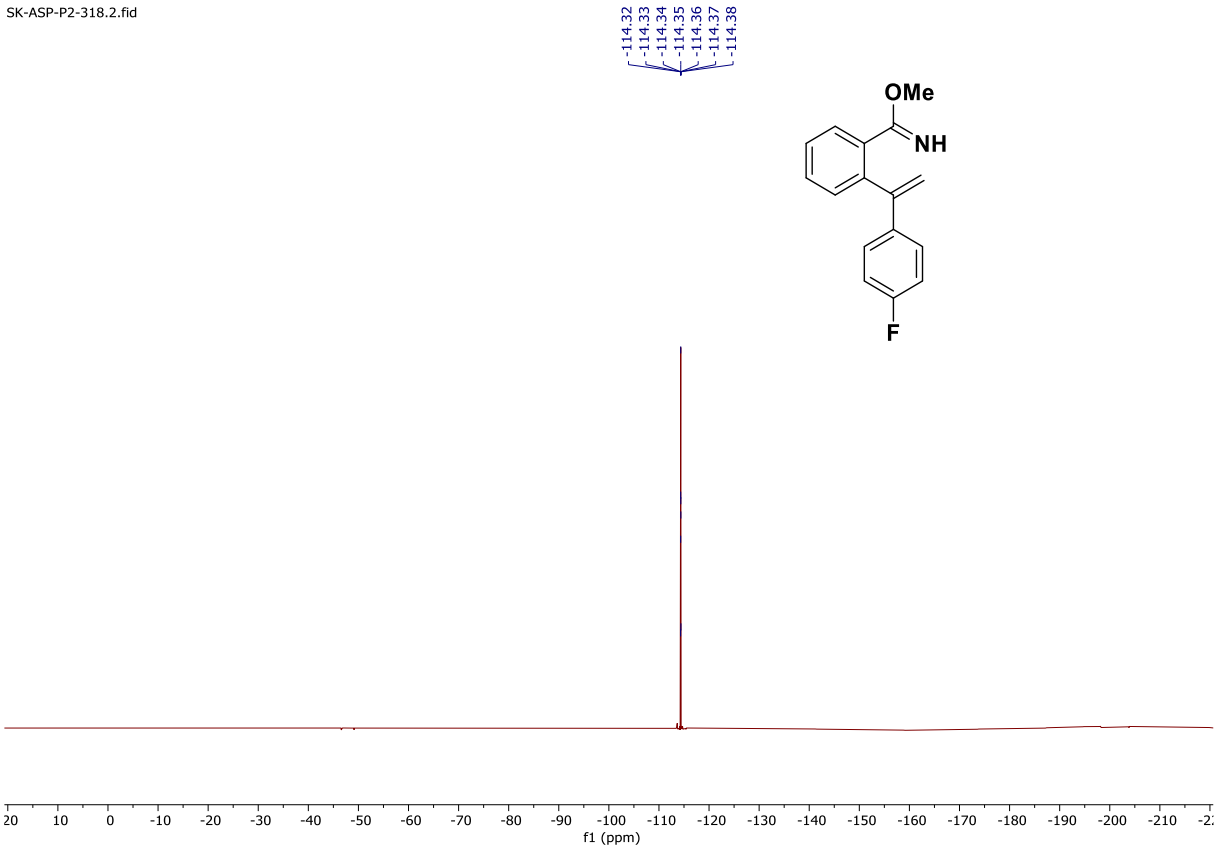
^{1}H NMR spectrum of 3c in $CDCl_3$ [500 MHz]



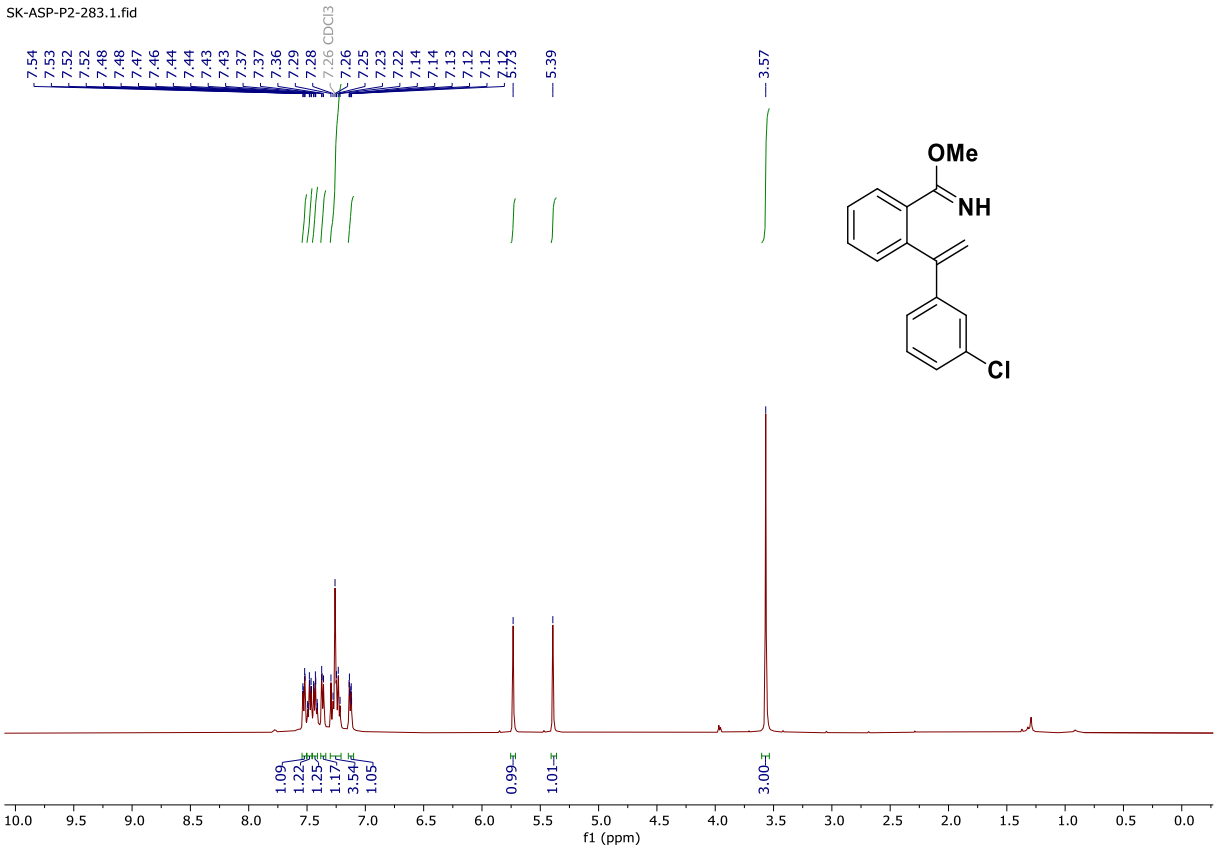
^{13}C{^{1}H} NMR spectrum of 3c in $CDCl_3$ [126 MHz]



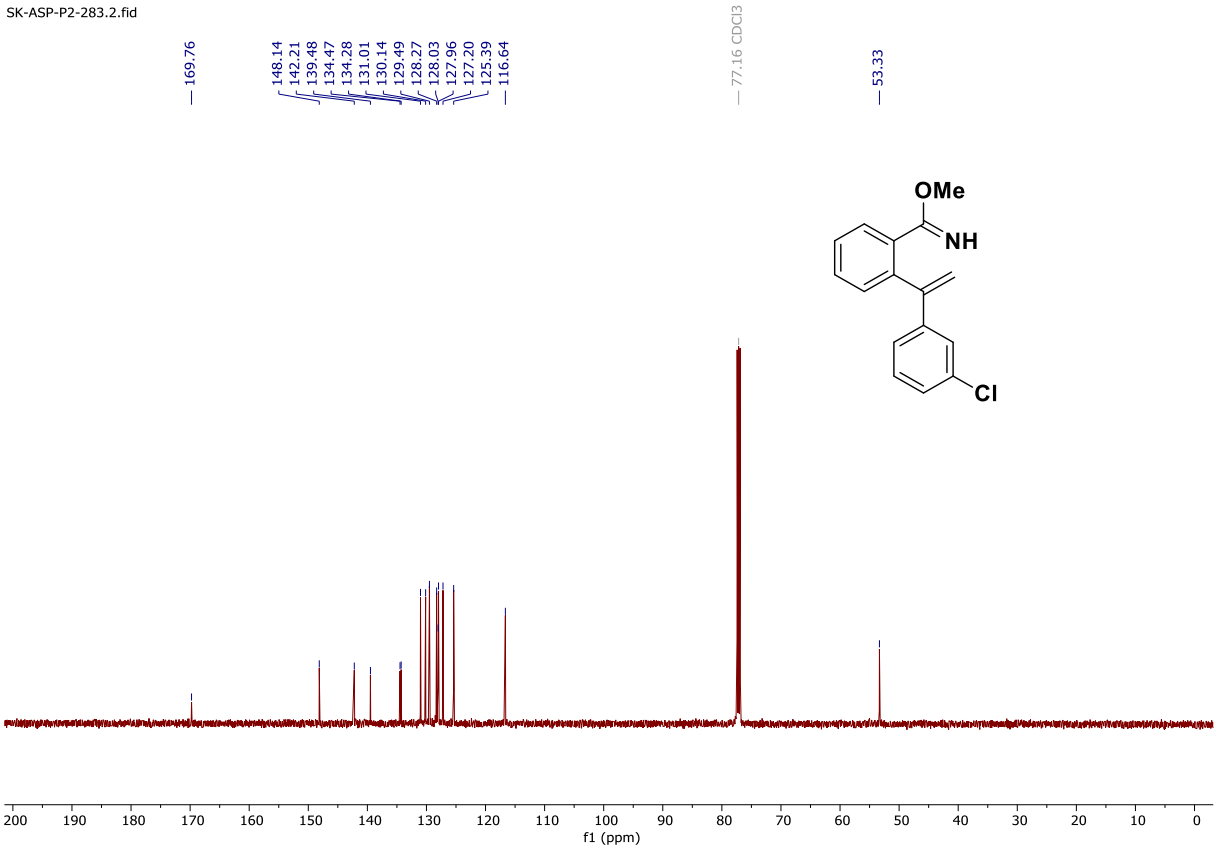
^{19}F NMR spectrum of 3c in $CDCl_3$ [471 MHz]



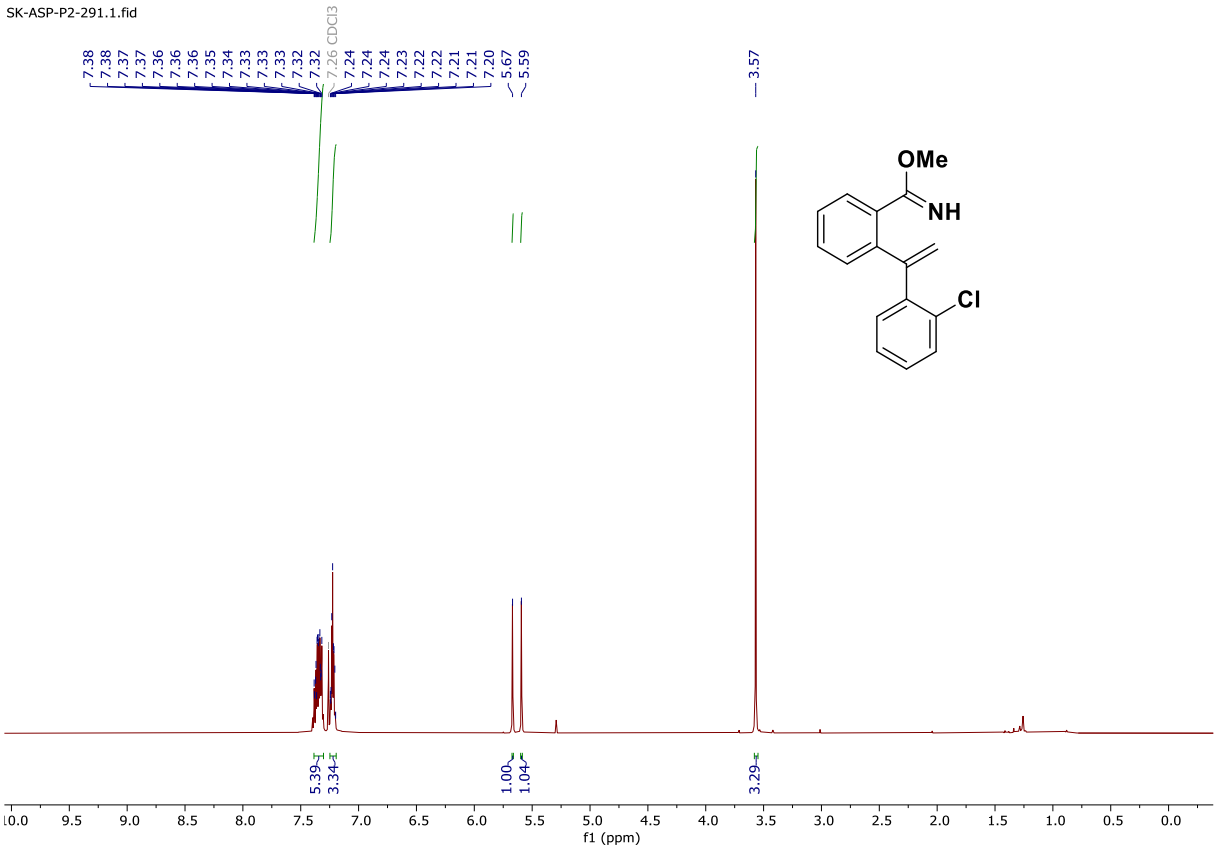
^{1}H NMR spectrum of 3d in $CDCl_3$ [500 MHz]



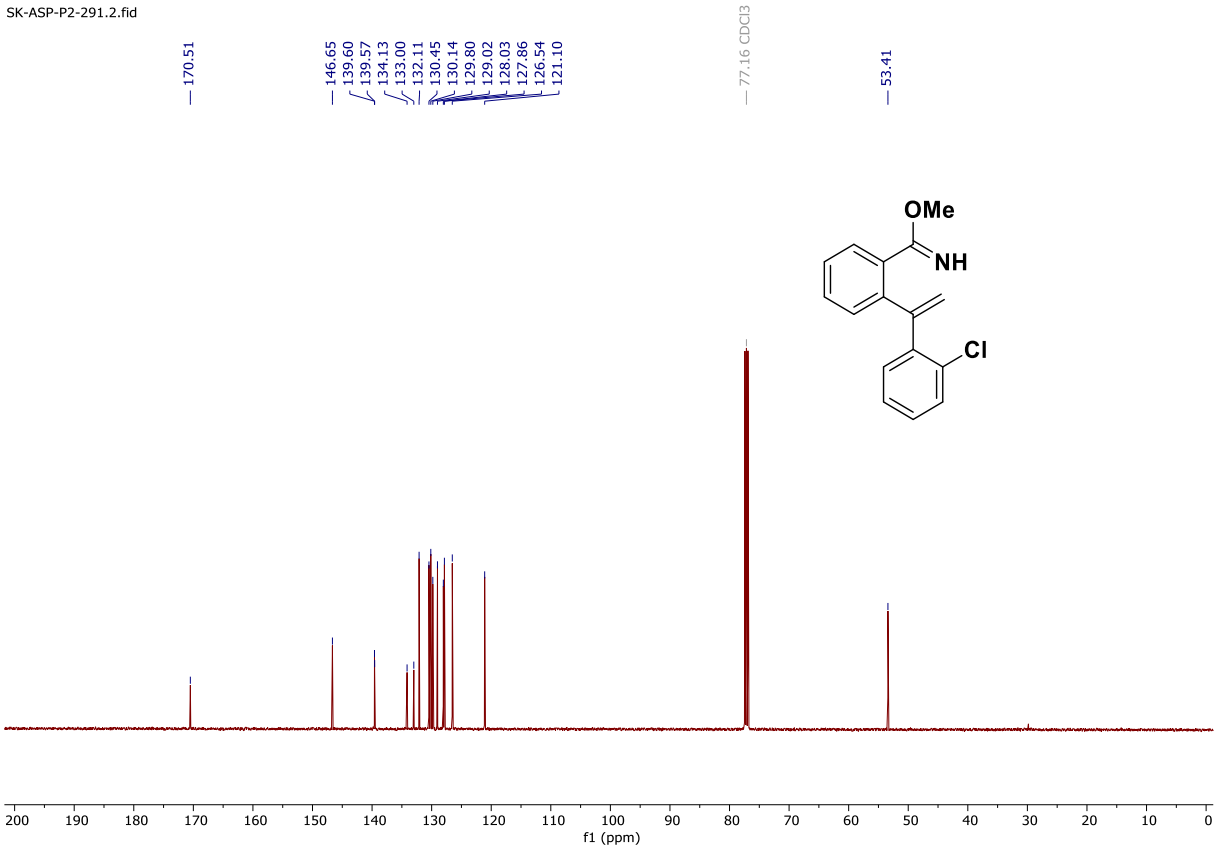
$^{13}C\{^{1}H\}$ NMR spectrum of 3d in $CDCl_3$ [126 MHz]



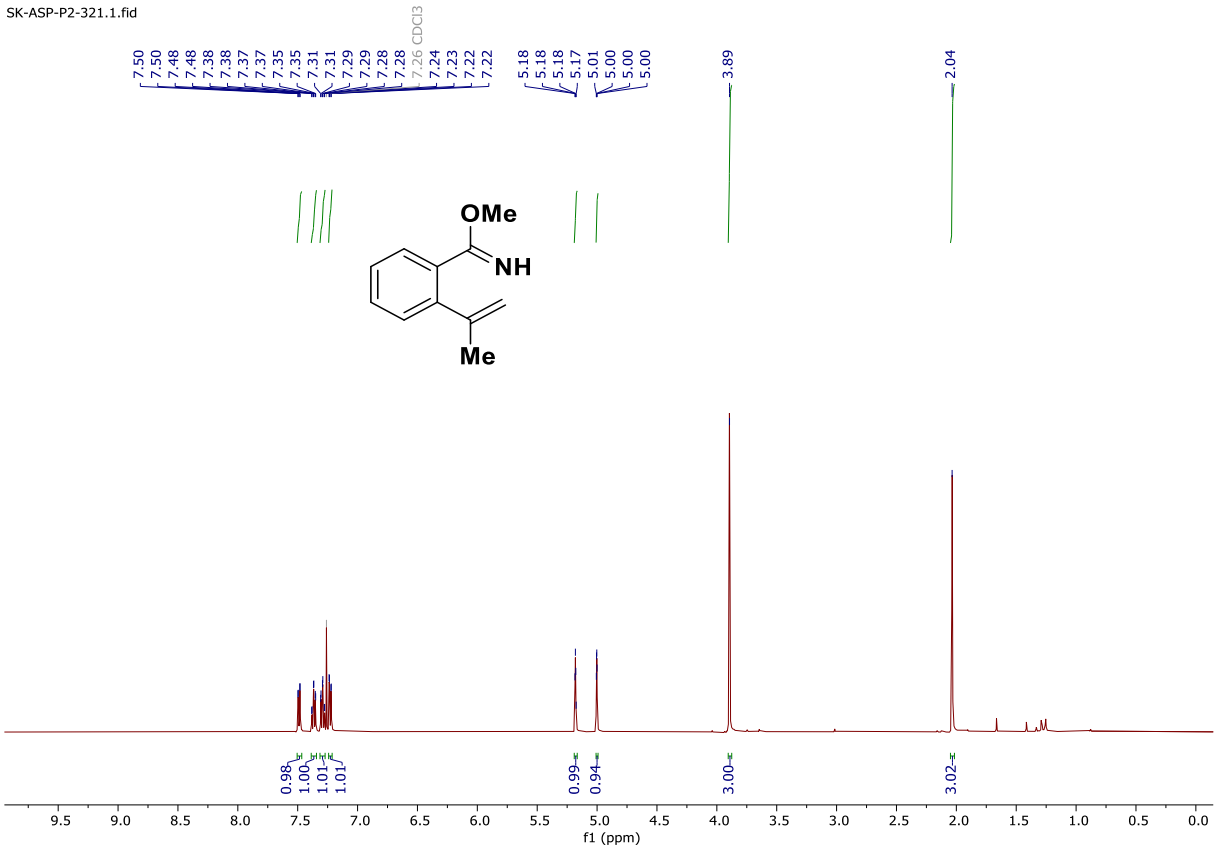
^{1}H NMR spectrum of 3e in $CDCl_3$ [500 MHz]



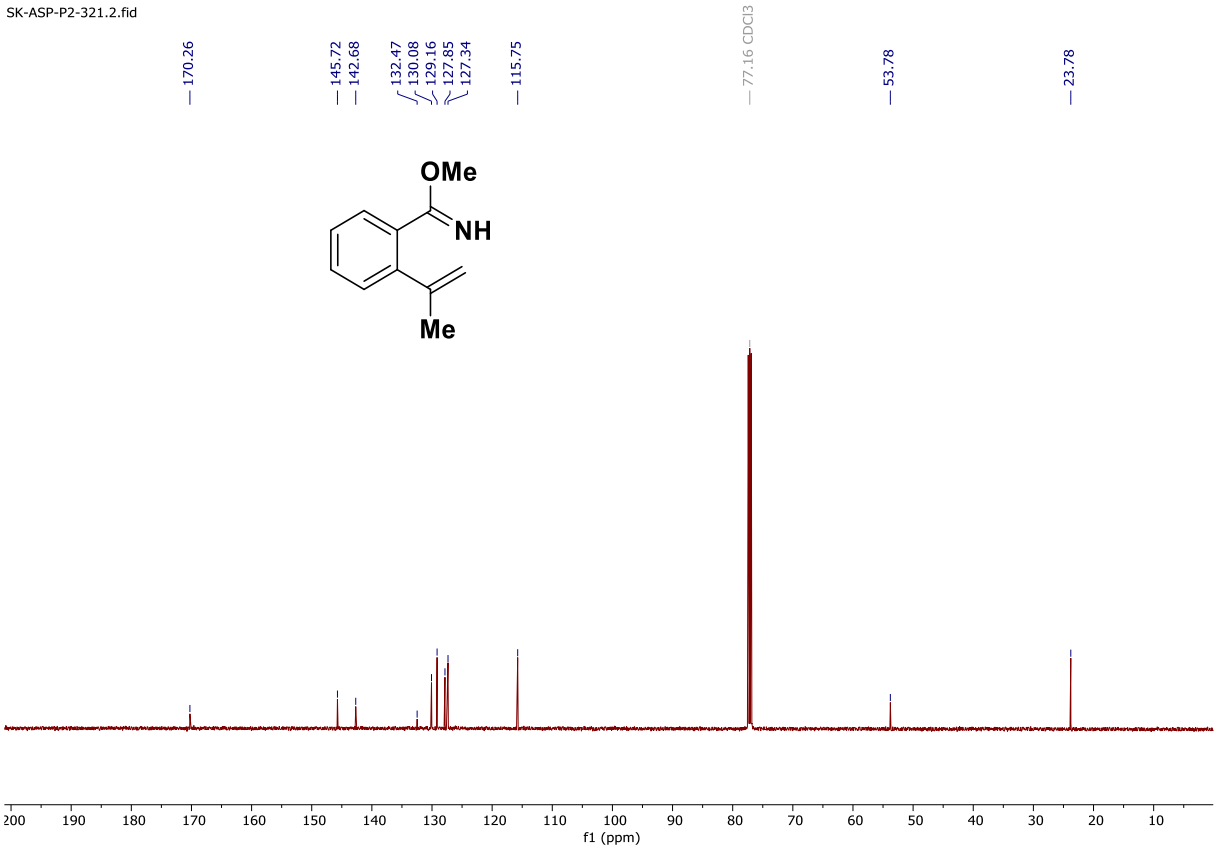
$^{13}C\{^{1}H\}$ NMR spectrum of 3e in $CDCl_3$ [126 MHz]



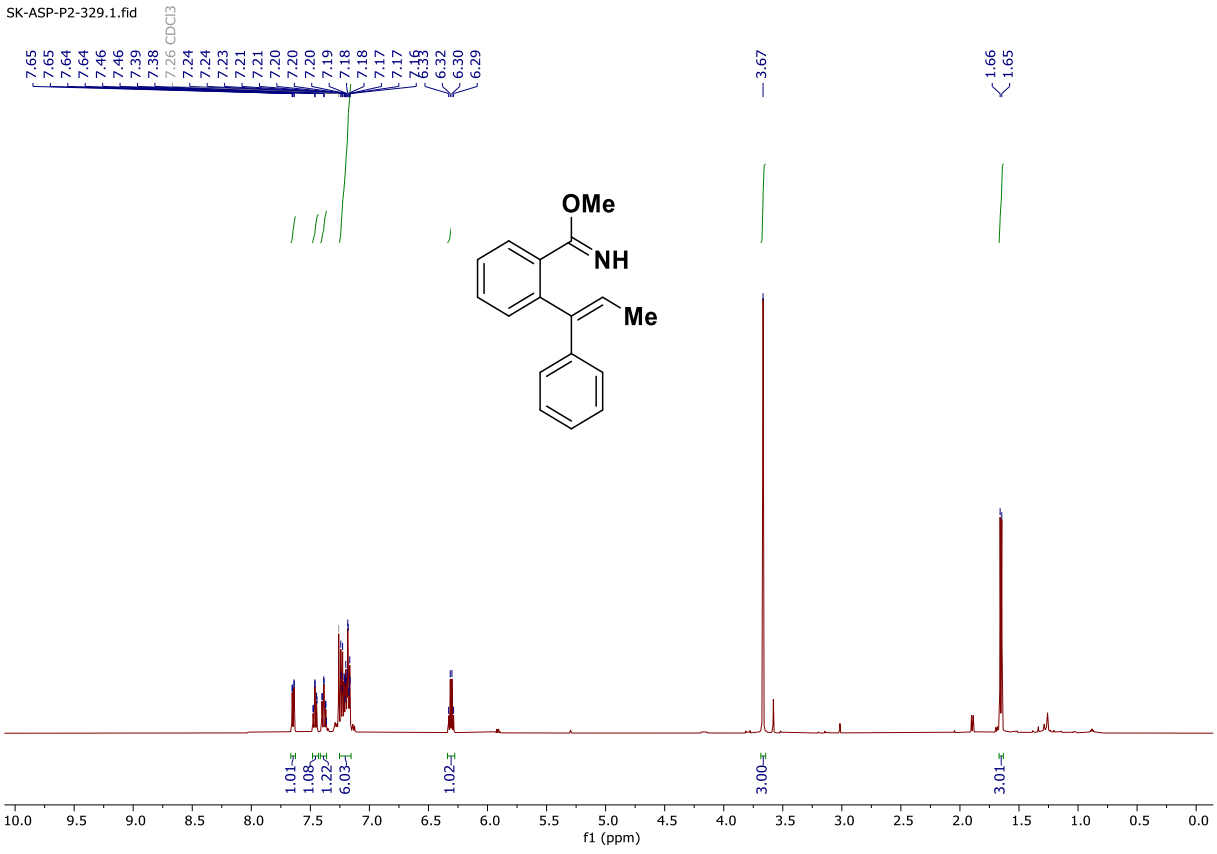
^{1}H NMR spectrum of 3f in $CDCl_3$ [500 MHz]



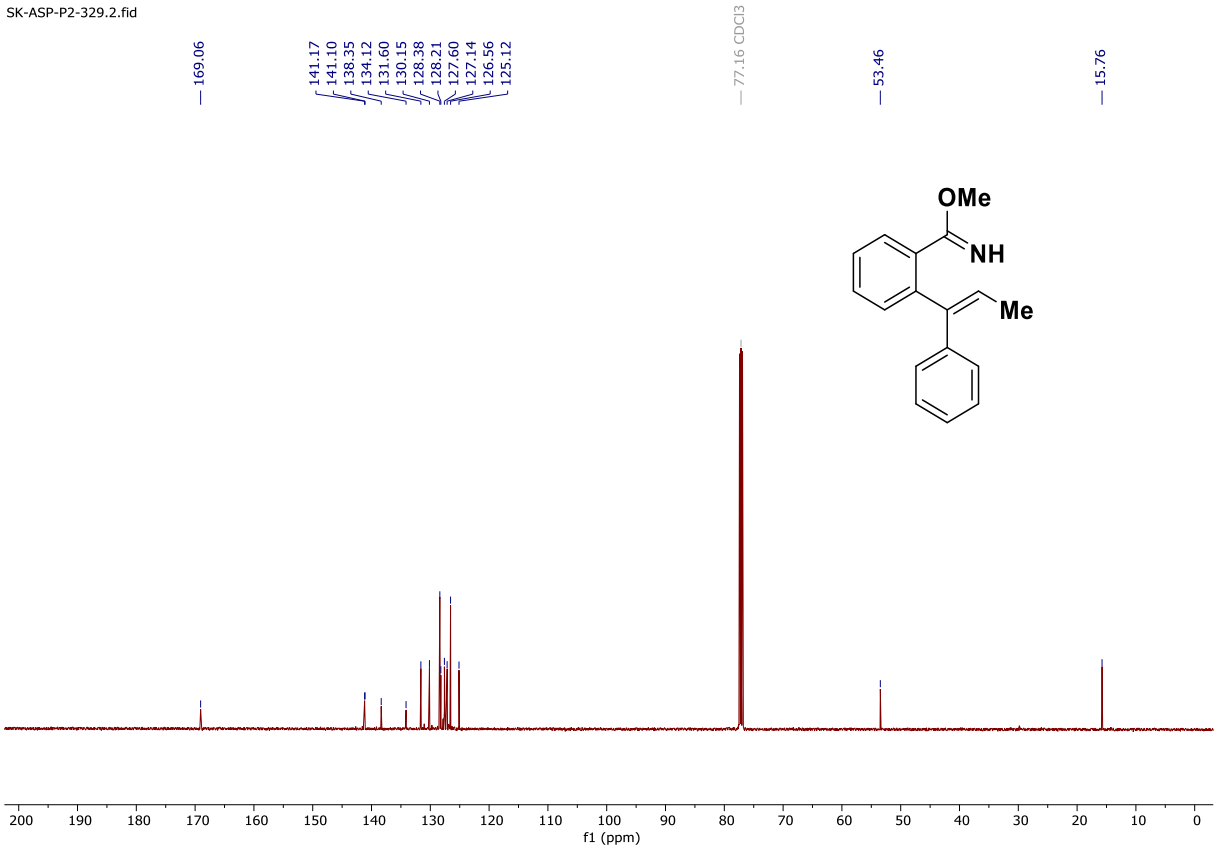
$^{13}C\{^{1}H\}$ NMR spectrum of 3f in $CDCl_3$ [126 MHz]



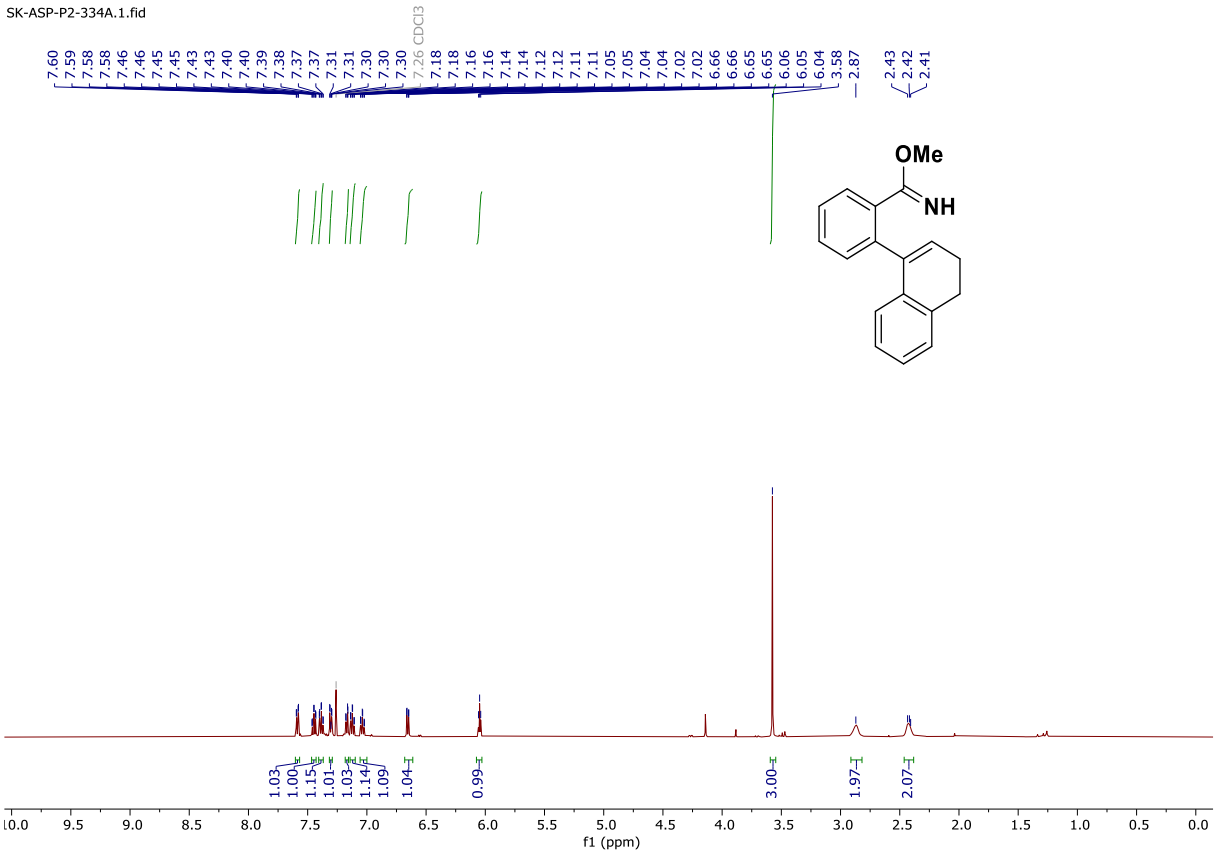
^{1}H NMR spectrum of 3g in $CDCl_3$ [500 MHz]



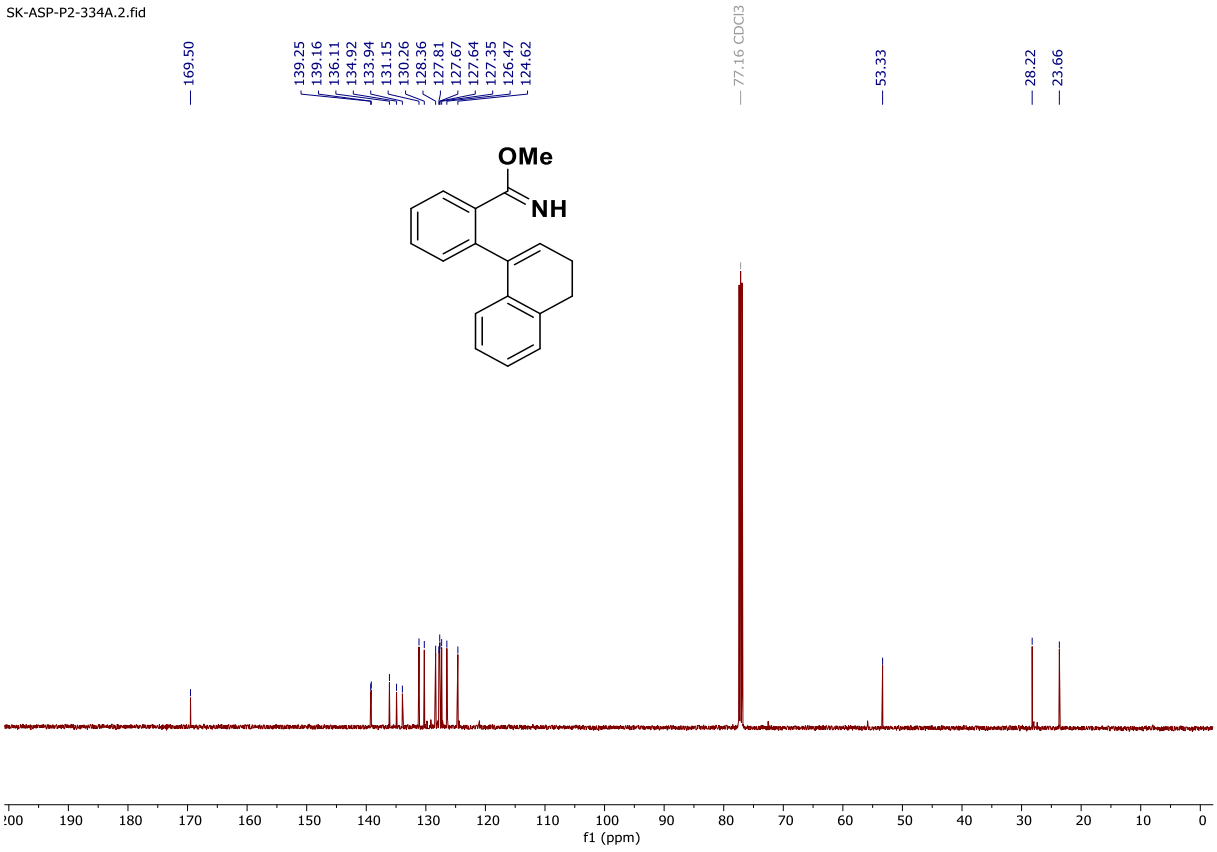
$^{13}C\{^{1}H\}$ NMR spectrum of 3g in $CDCl_3$ [126 MHz]



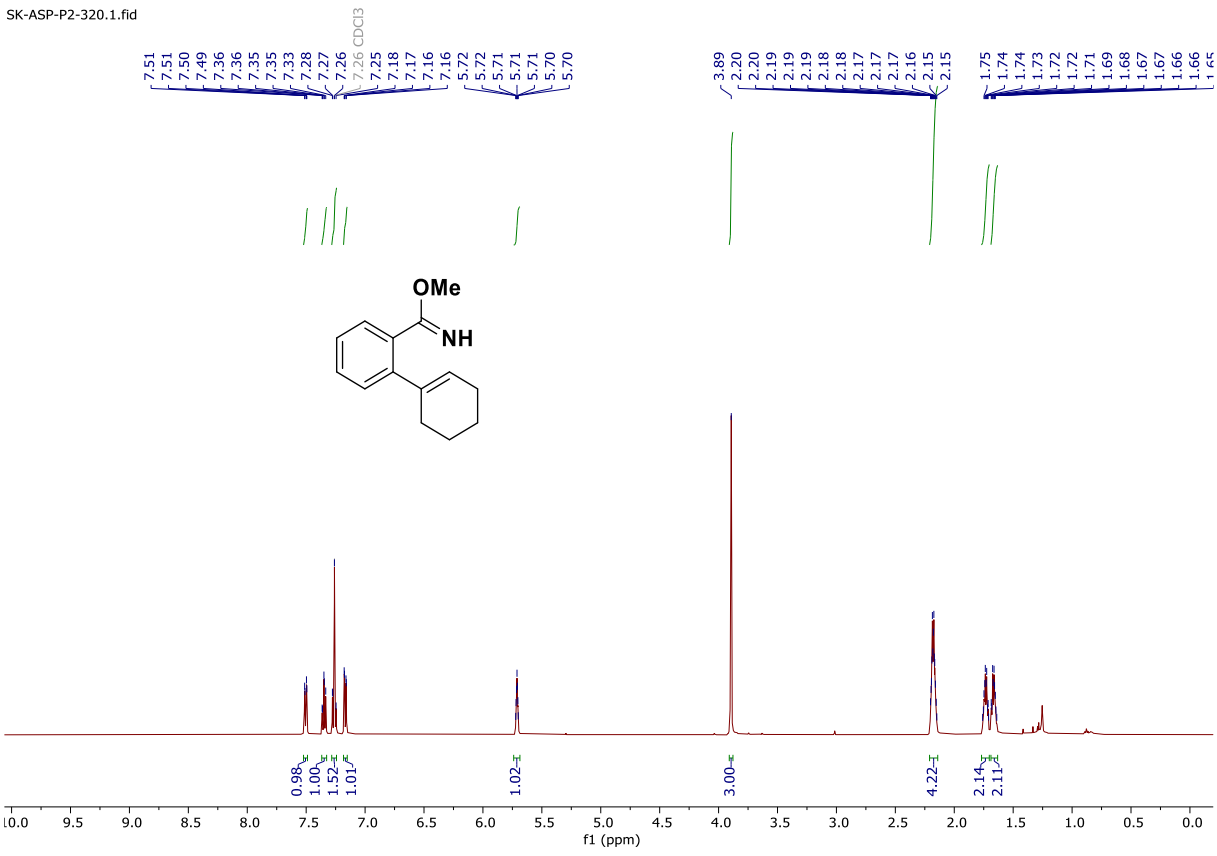
^{1}H NMR spectrum of 3h in $CDCl_3$ [500 MHz]



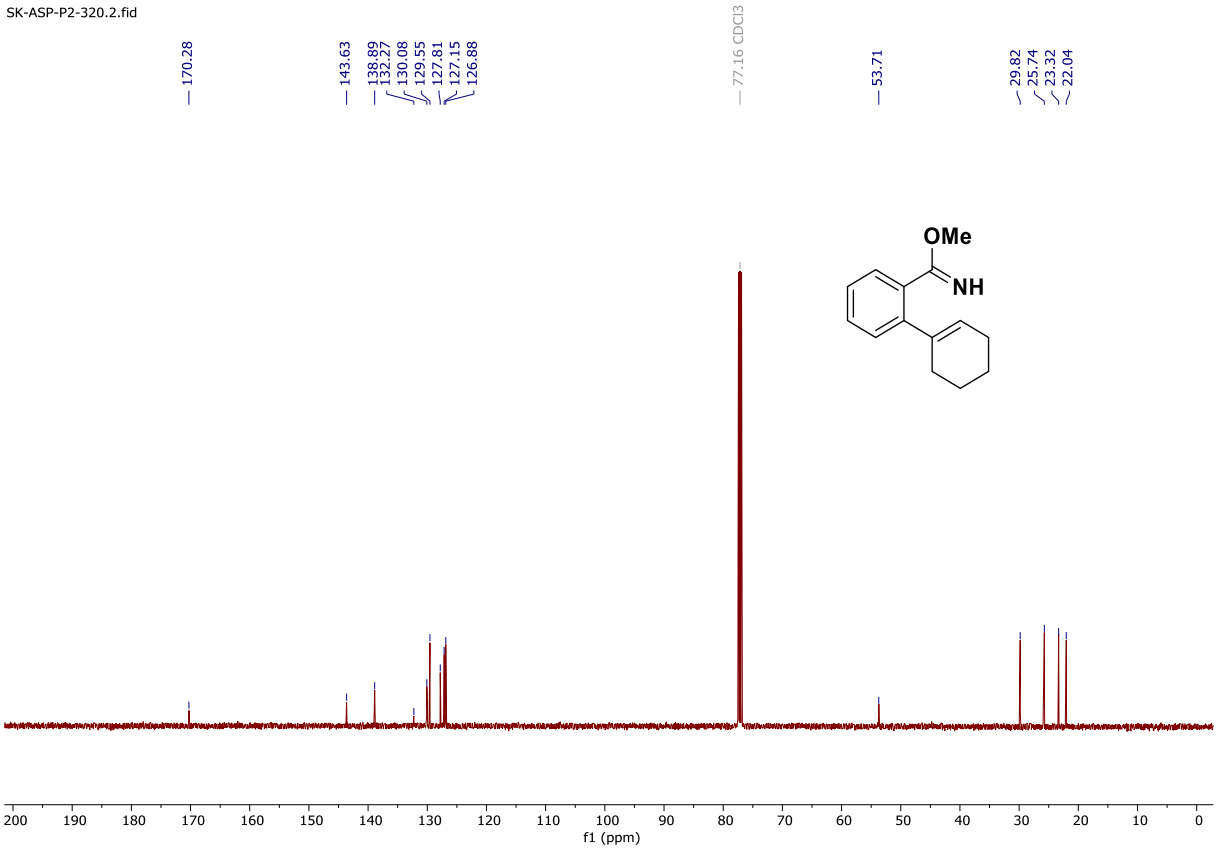
$^{13}C\{^{1}H\}$ NMR spectrum of 3h in $CDCl_3$ [126 MHz]



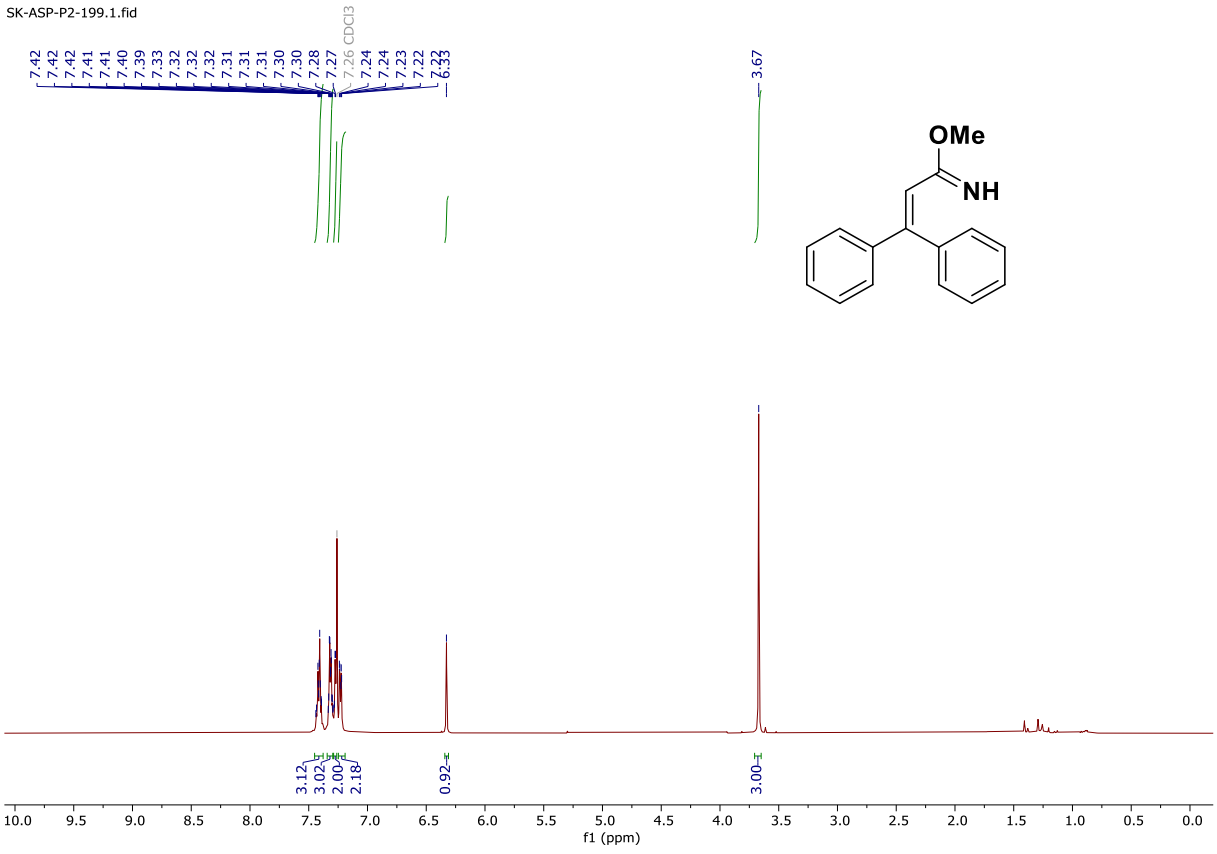
^{1}H NMR spectrum of 3i in $CDCl_3$ [500 MHz]



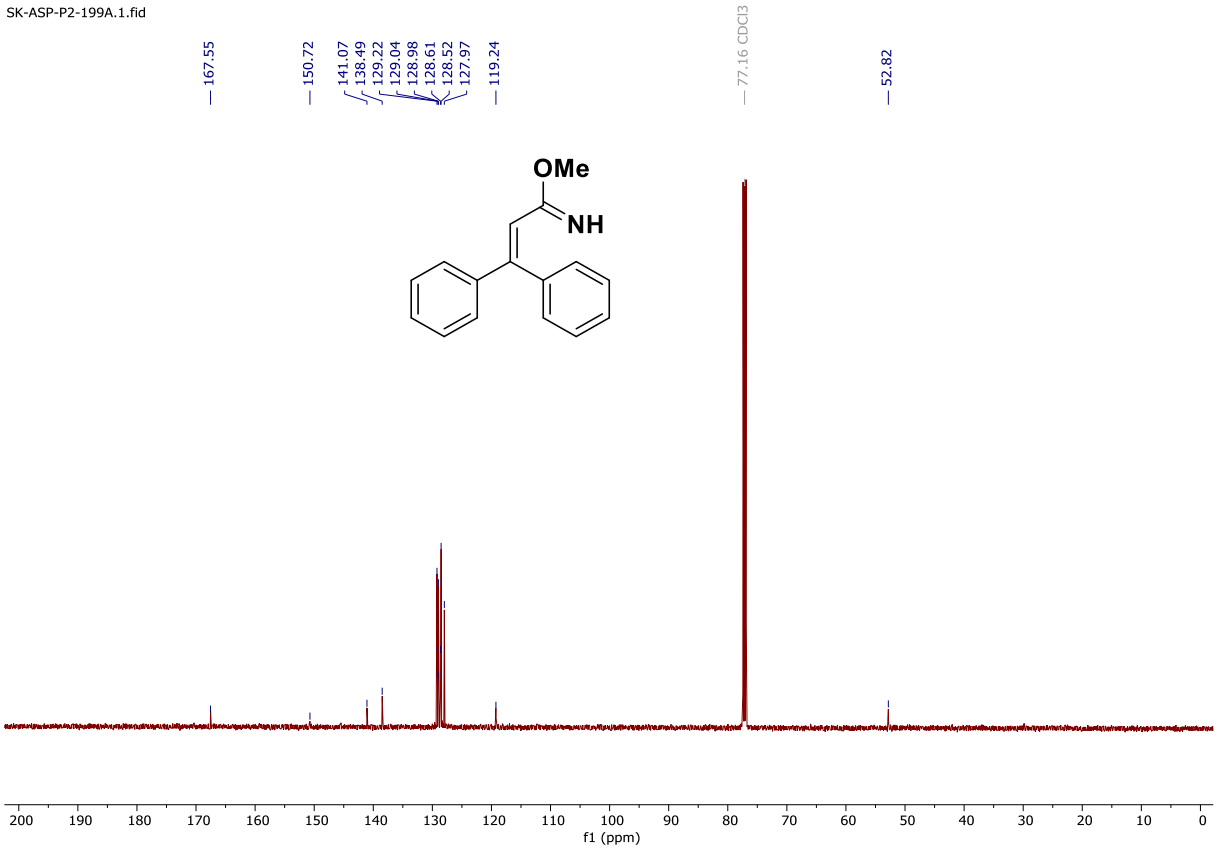
$^{13}C\{^{1}H\}$ NMR spectrum of 3i in $CDCl_3$ [126 MHz]



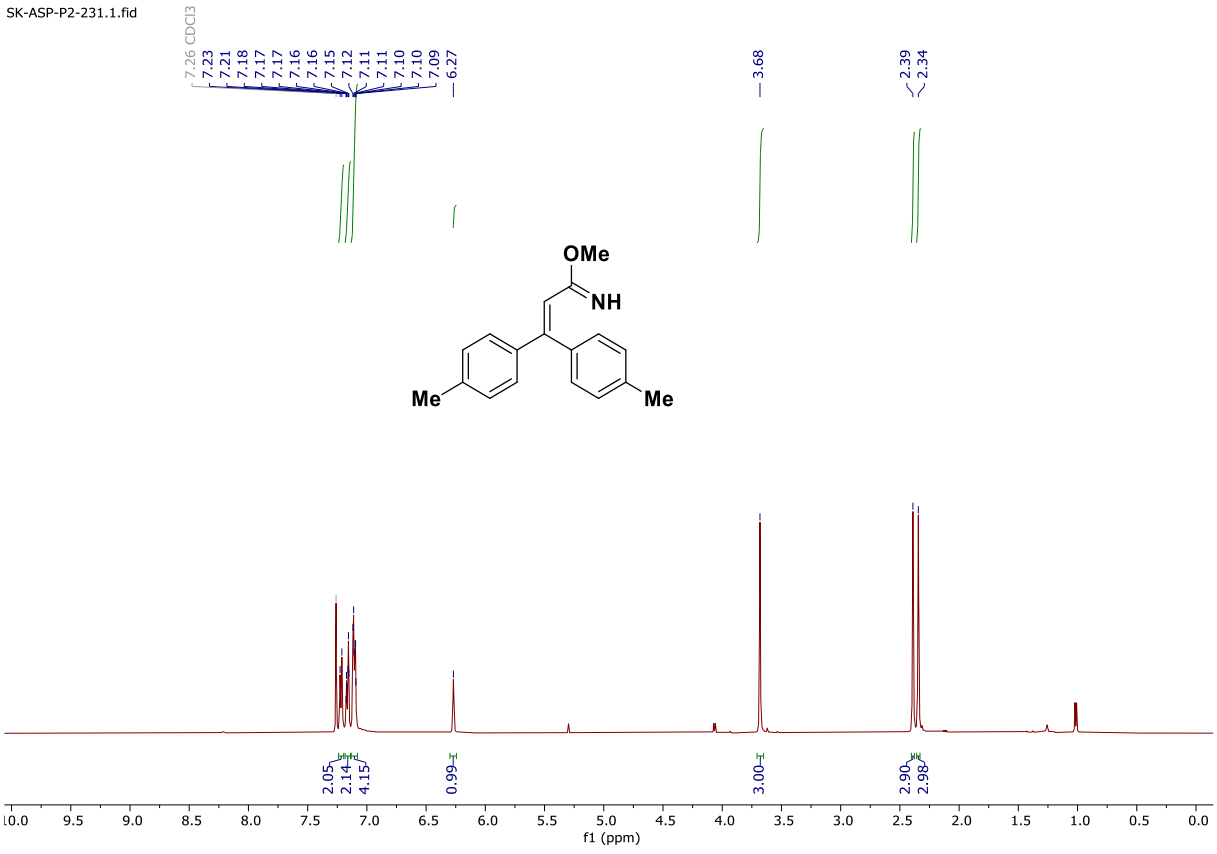
^{1}H NMR spectrum of 3j in $CDCl_3$ [500 MHz]



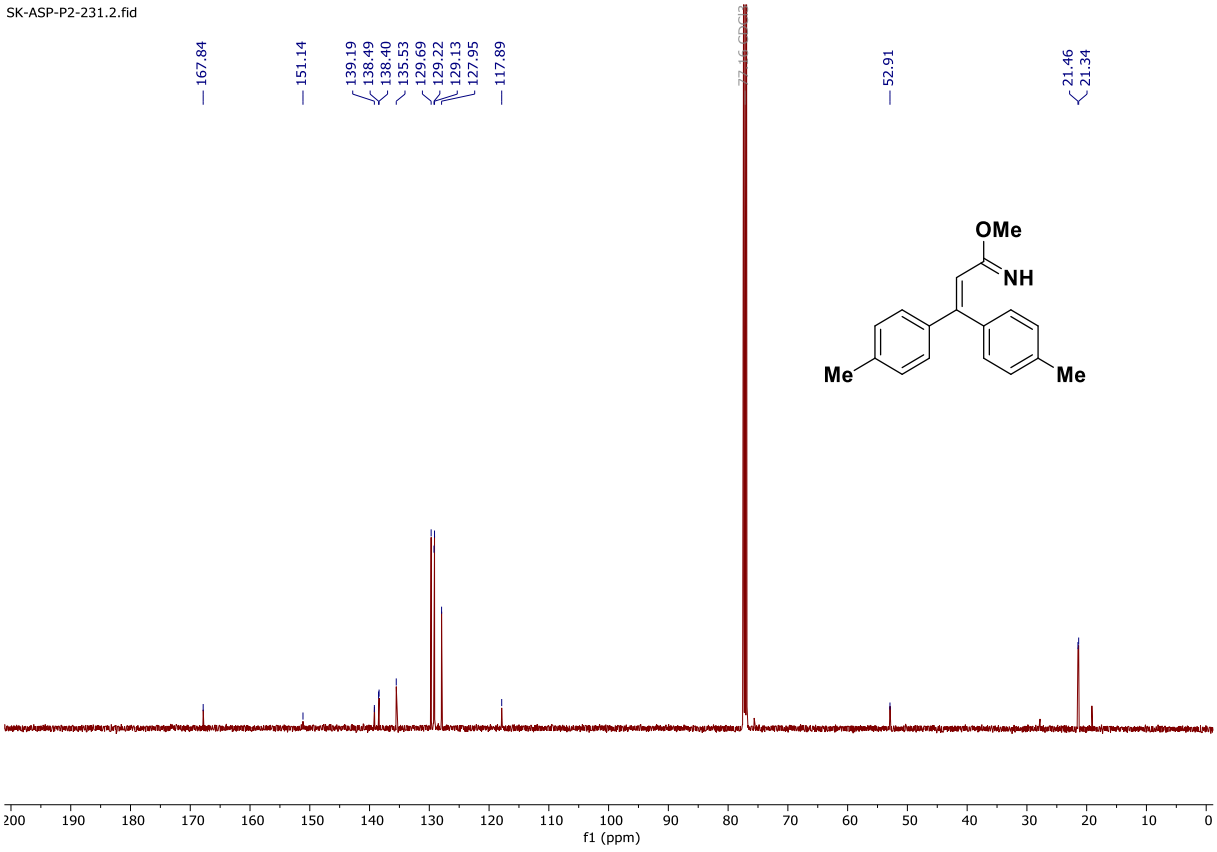
$^{13}C\{^{1}H\}$ NMR spectrum of 3j in $CDCl_3$ [126 MHz]



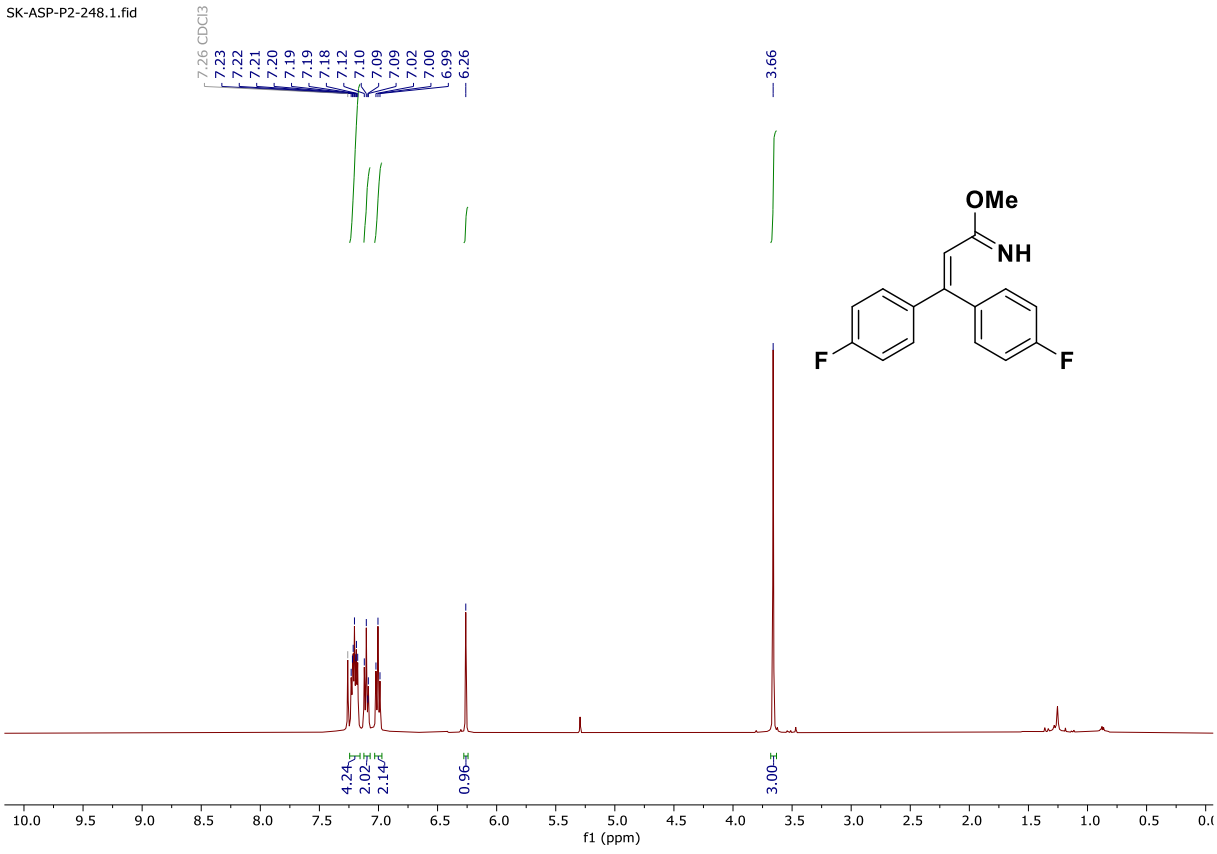
^{1}H NMR spectrum of 3k in $CDCl_3$ [500 MHz]



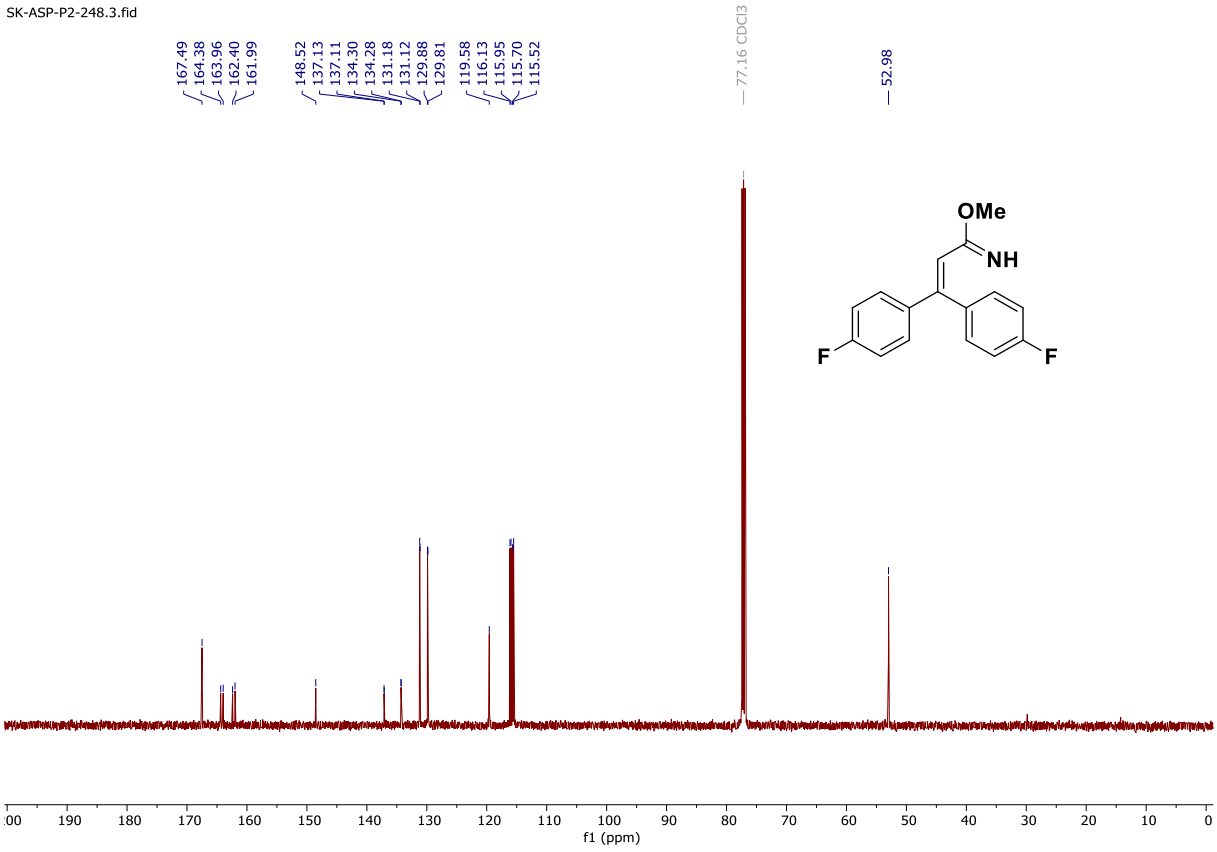
$^{13}C\{^{1}H\}$ NMR spectrum of 3k in $CDCl_3$ [126 MHz]



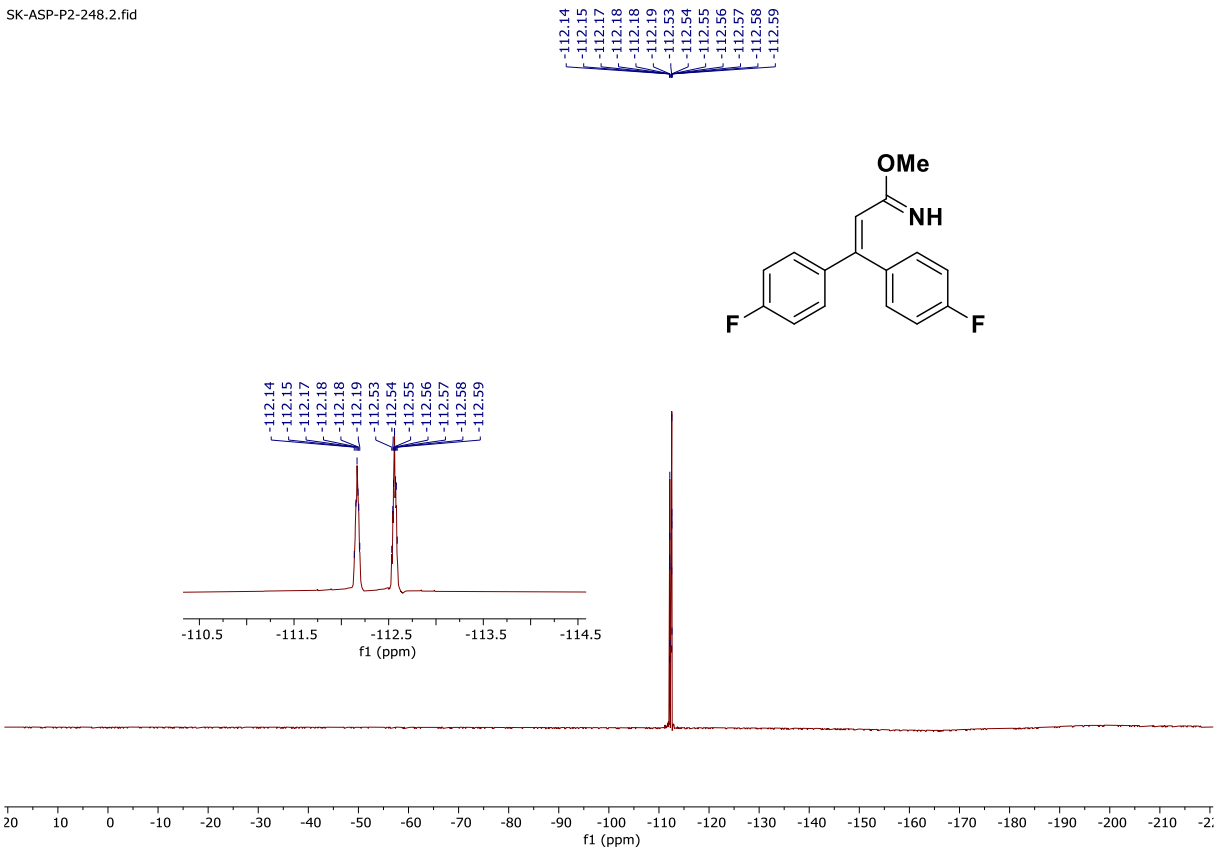
^{1}H NMR spectrum of 3l in $CDCl_3$ [500 MHz]



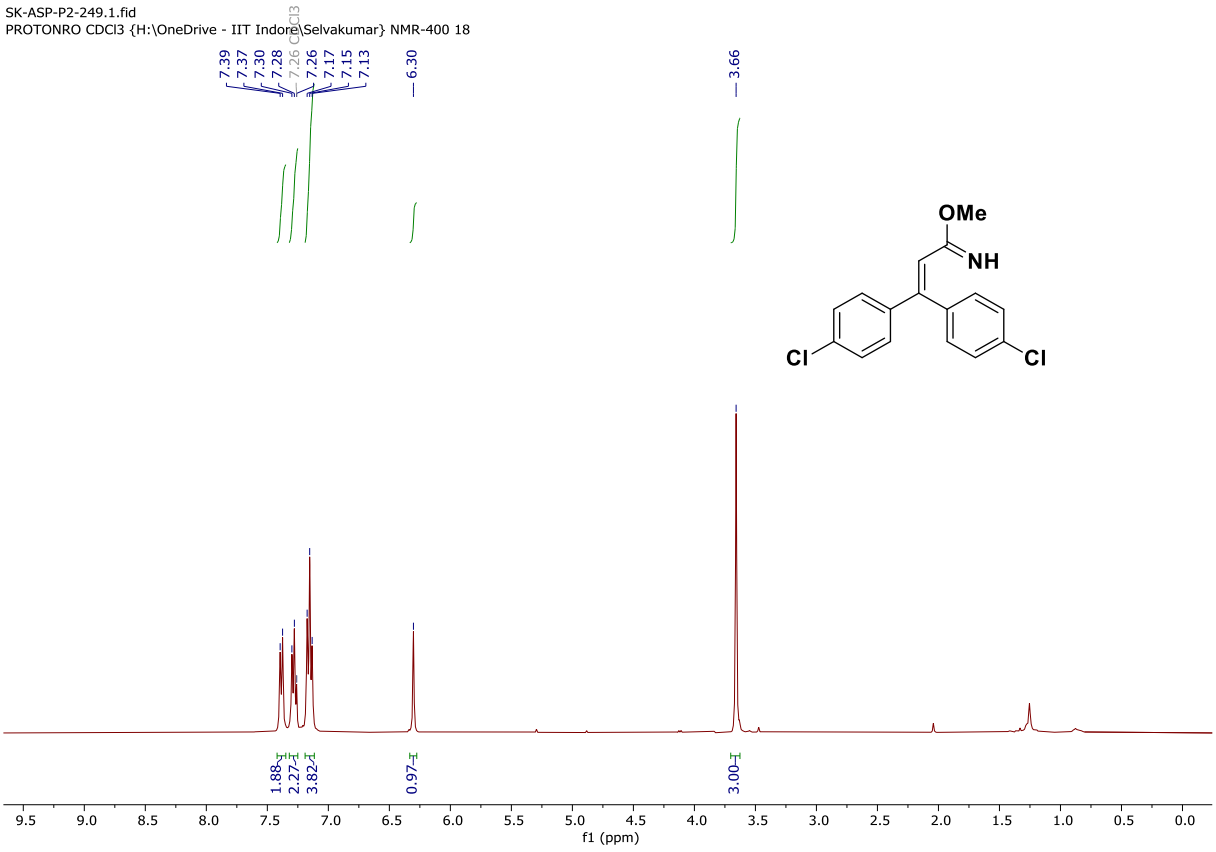
$^{13}C\{^{1}H\}$ NMR spectrum of 3l in $CDCl_3$ [126 MHz]



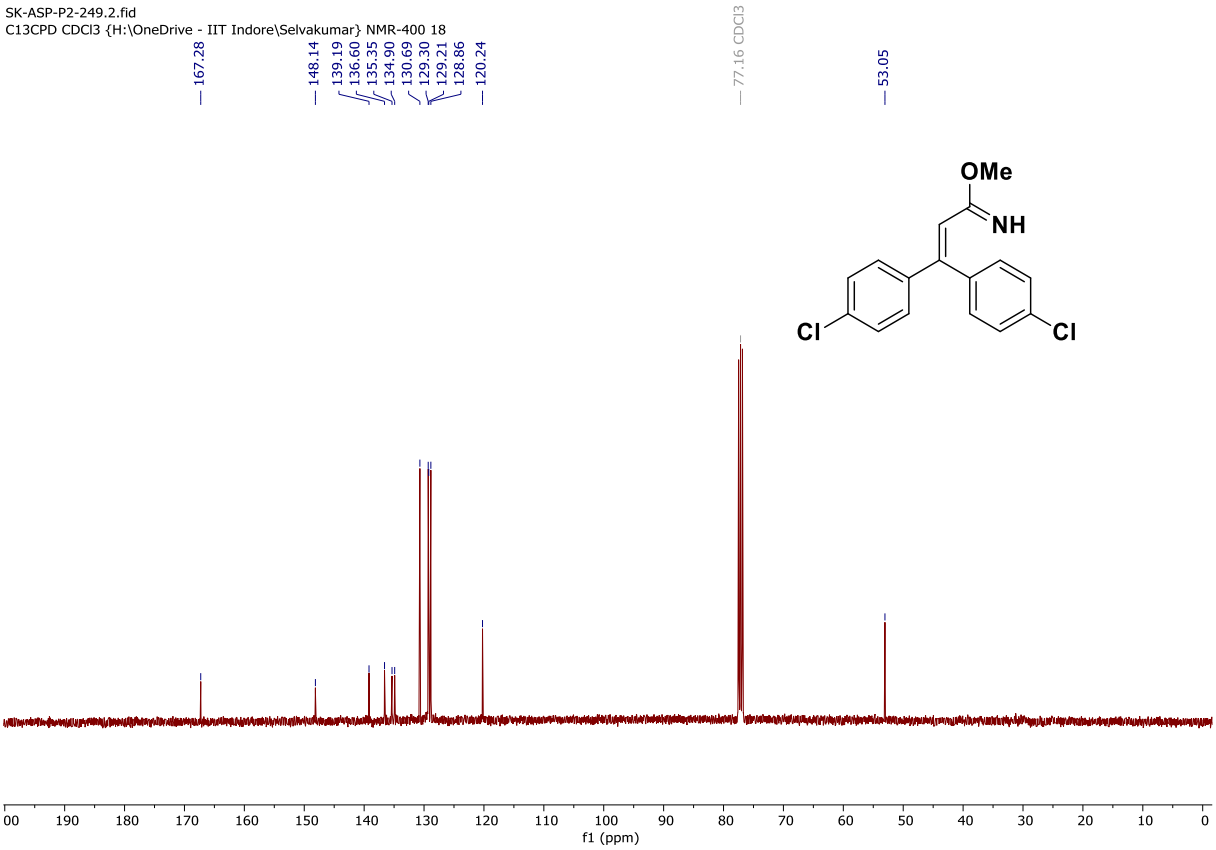
^{19}F NMR spectrum of 3l in $CDCl_3$ [471 MHz]



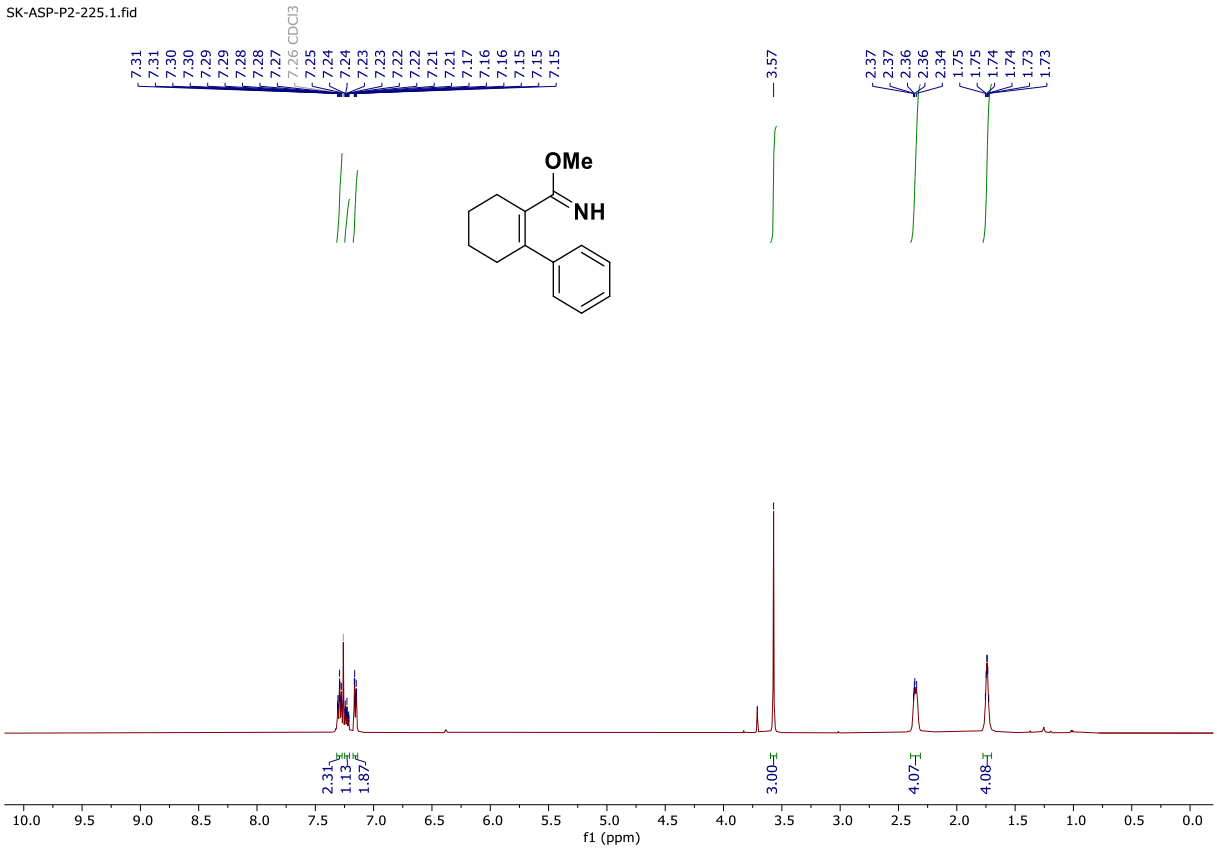
^{1}H NMR spectrum of 3m in $CDCl_3$ [400 MHz]



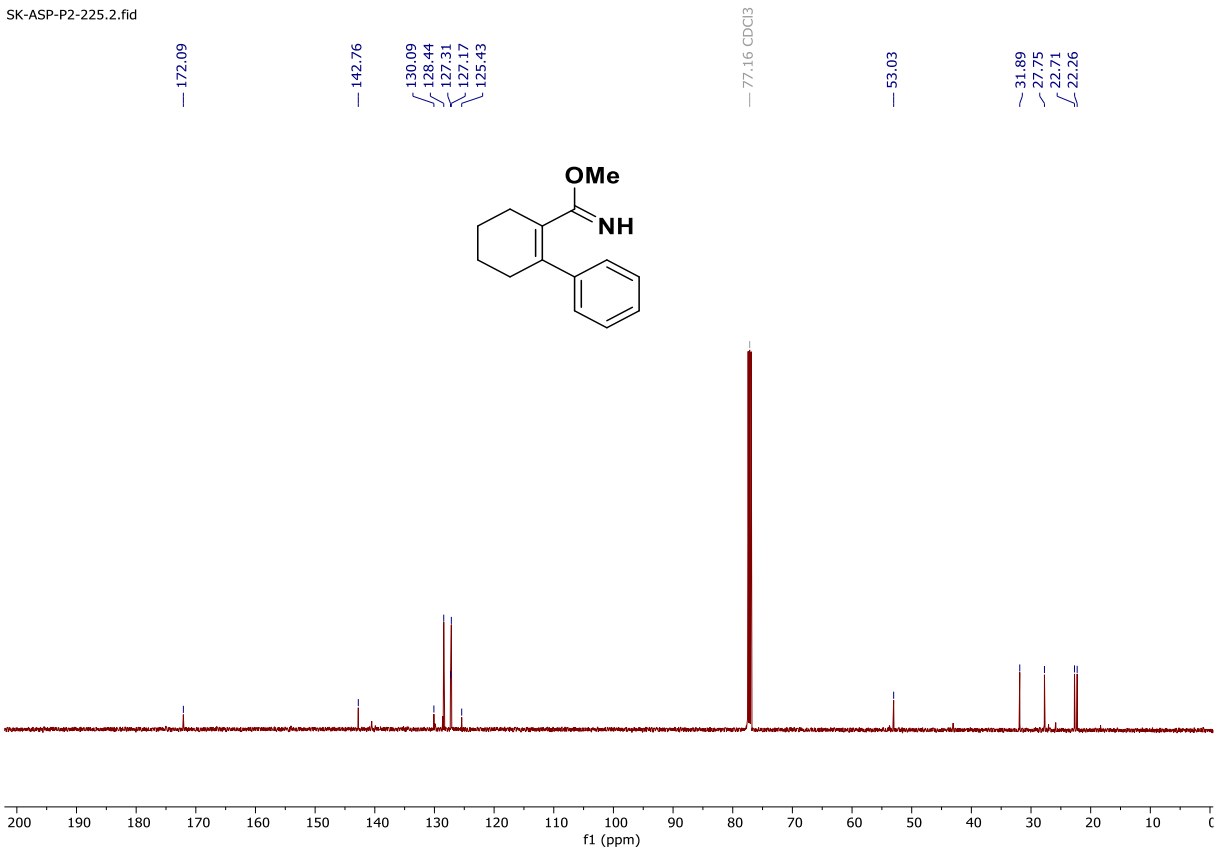
^{13}C{^{1}H} NMR spectrum of 3m in $CDCl_3$ [101 MHz]



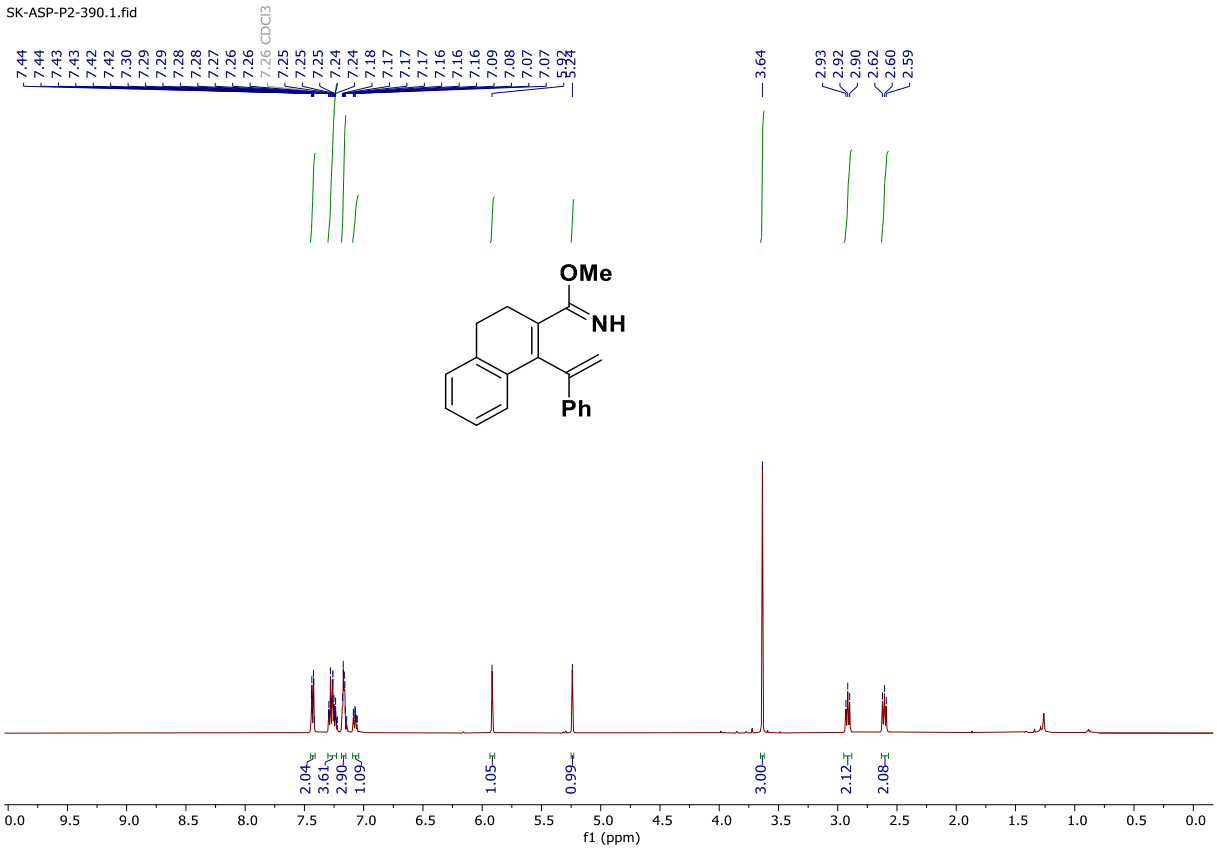
^{1}H NMR spectrum of 3n in $CDCl_3$ [500 MHz]



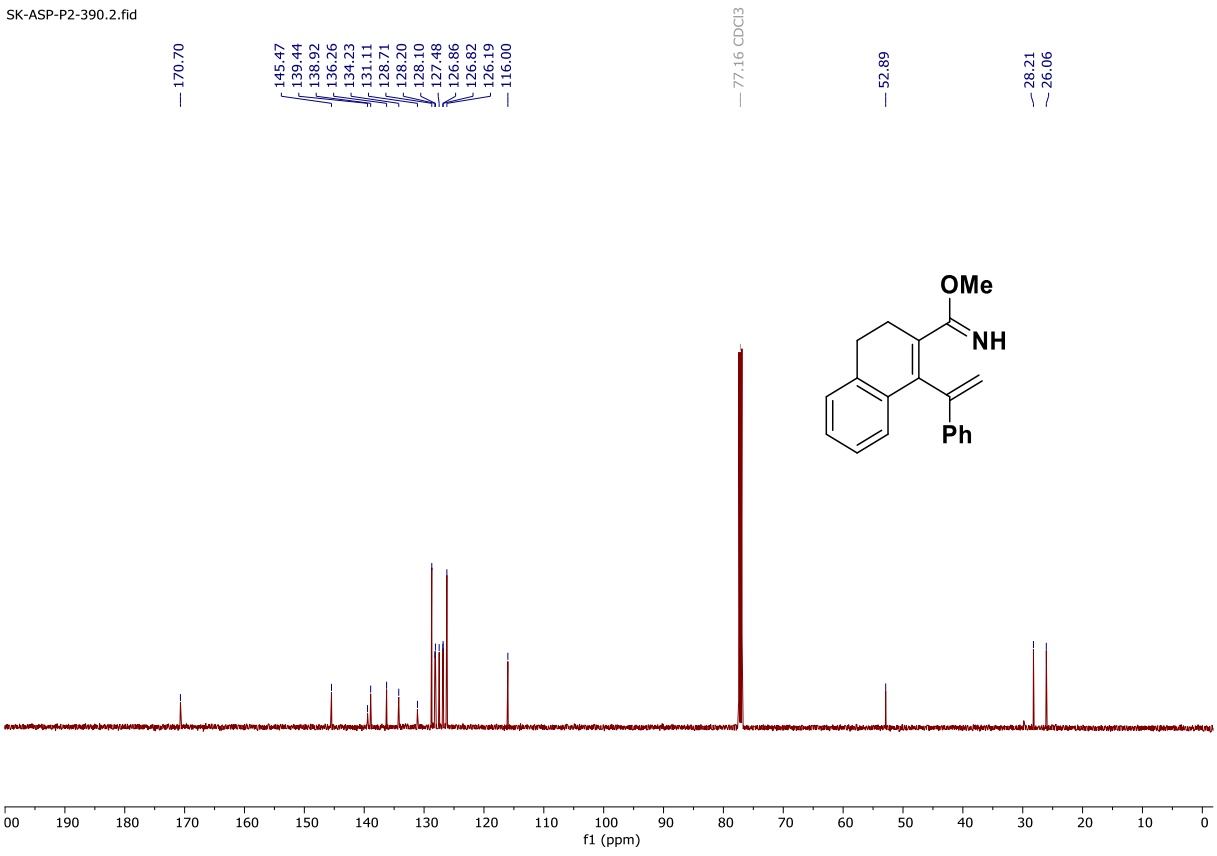
^{13}C{^{1}H} NMR spectrum of 3n in $CDCl_3$ [126 MHz]



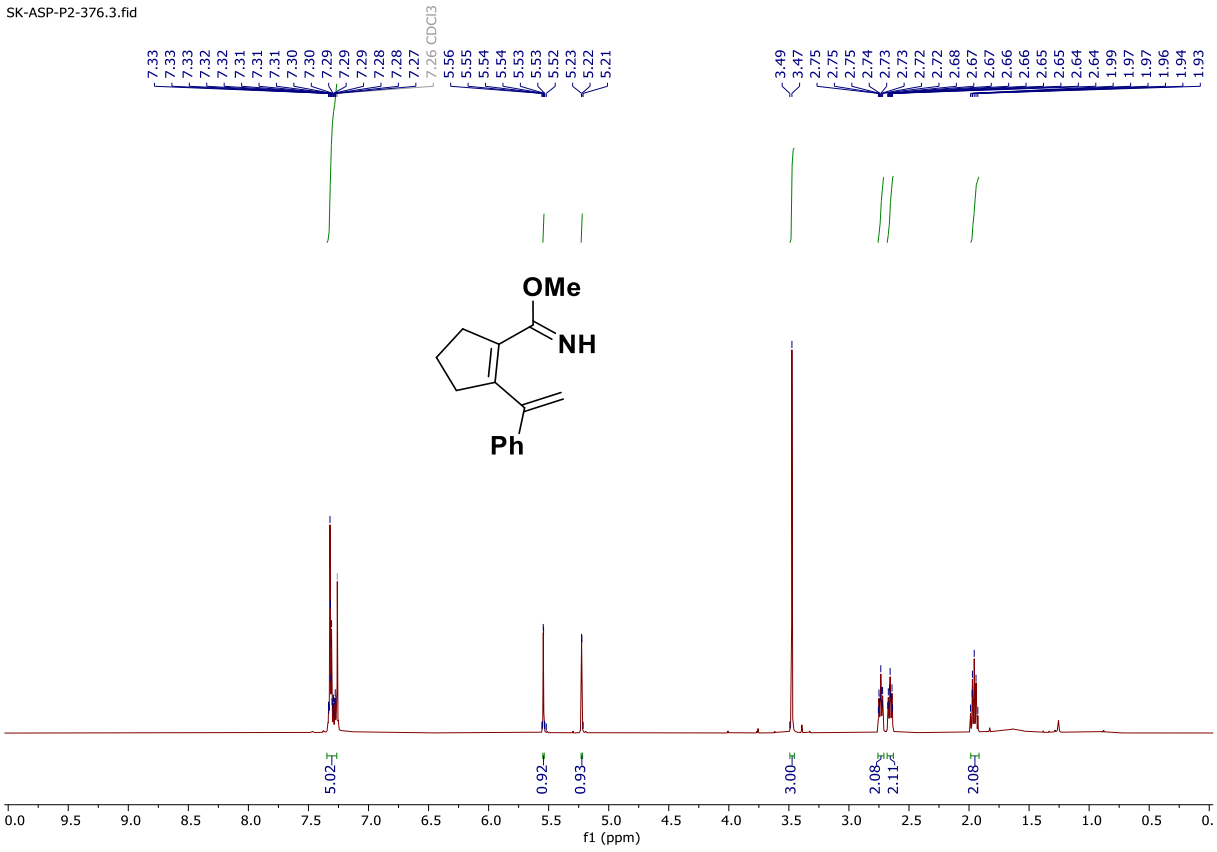
^{1}H NMR spectrum of 3o in $CDCl_3$ [500 MHz]



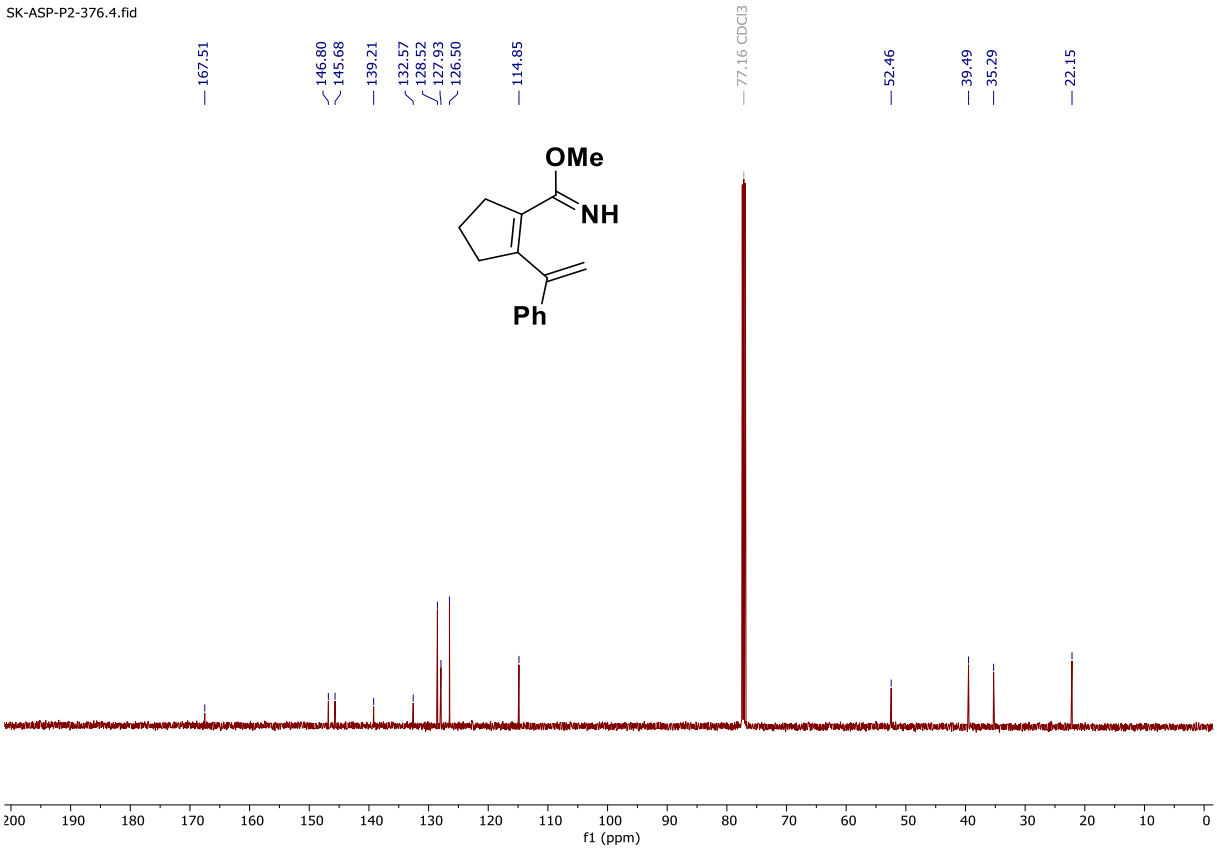
^{13}C{^{1}H} NMR spectrum of 3o in $CDCl_3$ [126 MHz]



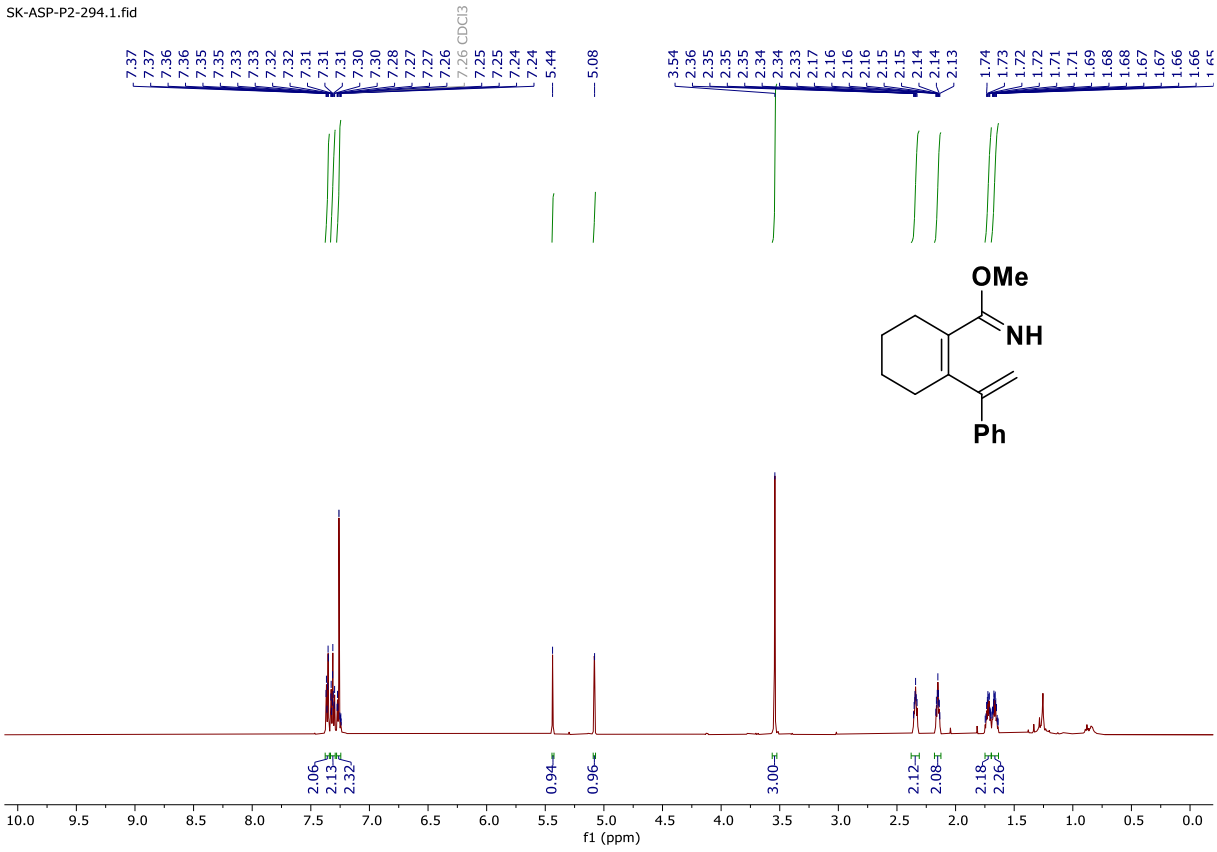
^{1}H NMR spectrum of 3p in $CDCl_3$ [500 MHz]



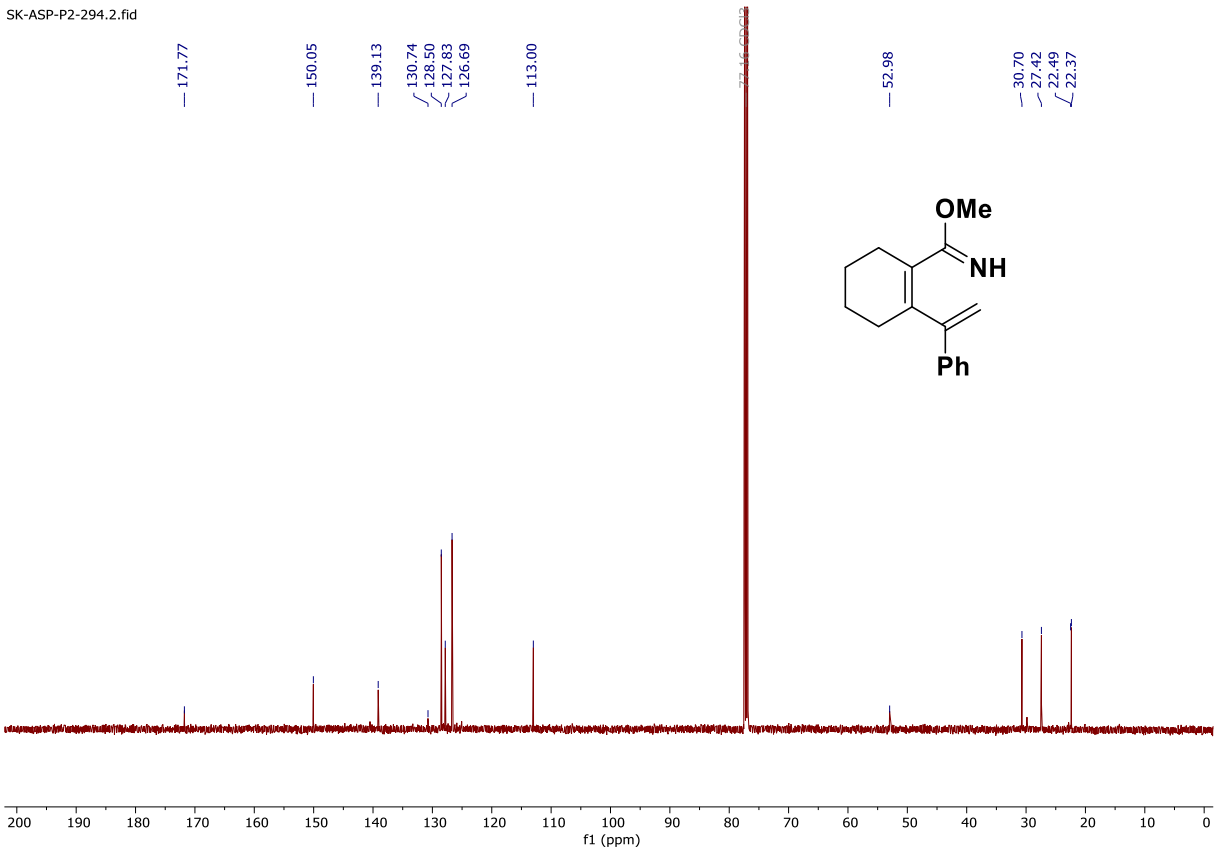
^{13}C{^{1}H} NMR spectrum of 3p in $CDCl_3$ [126 MHz]



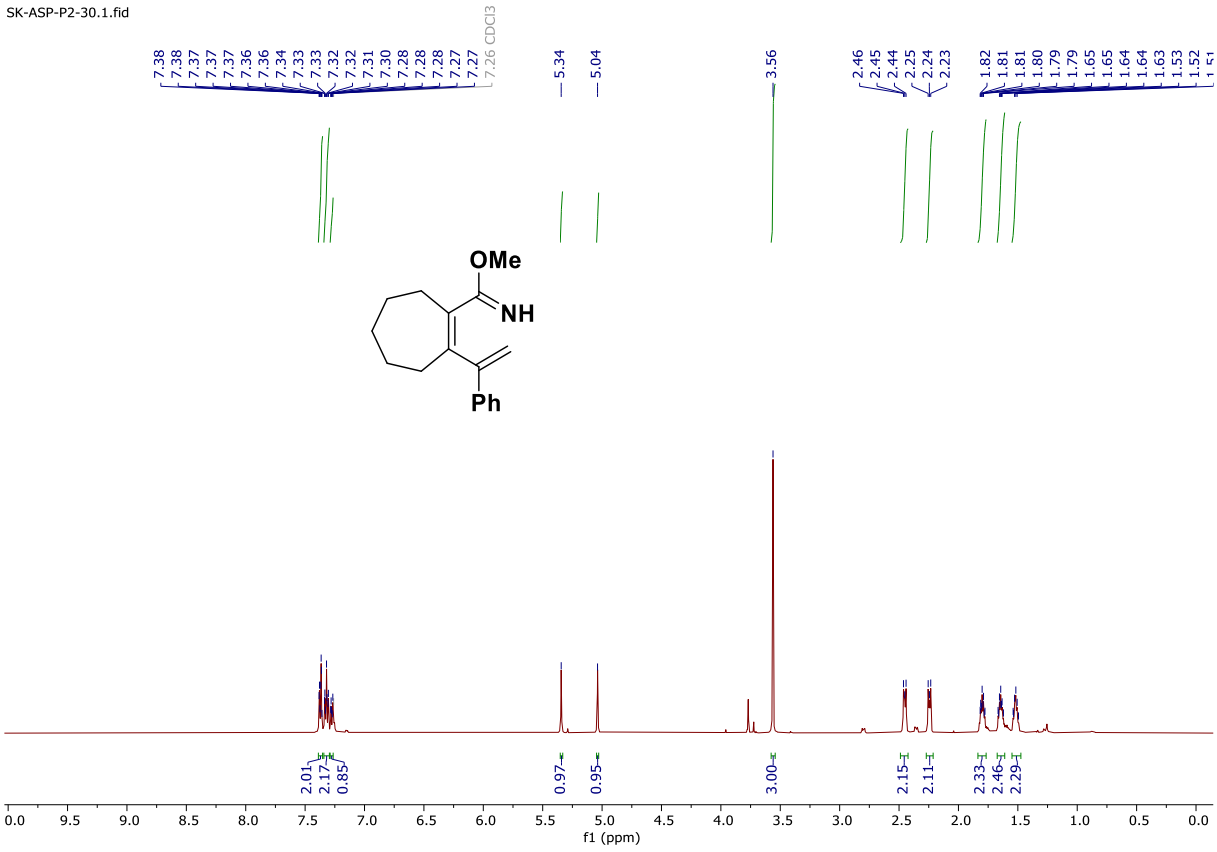
^{1}H NMR spectrum of 3q in $CDCl_3$ [500 MHz]



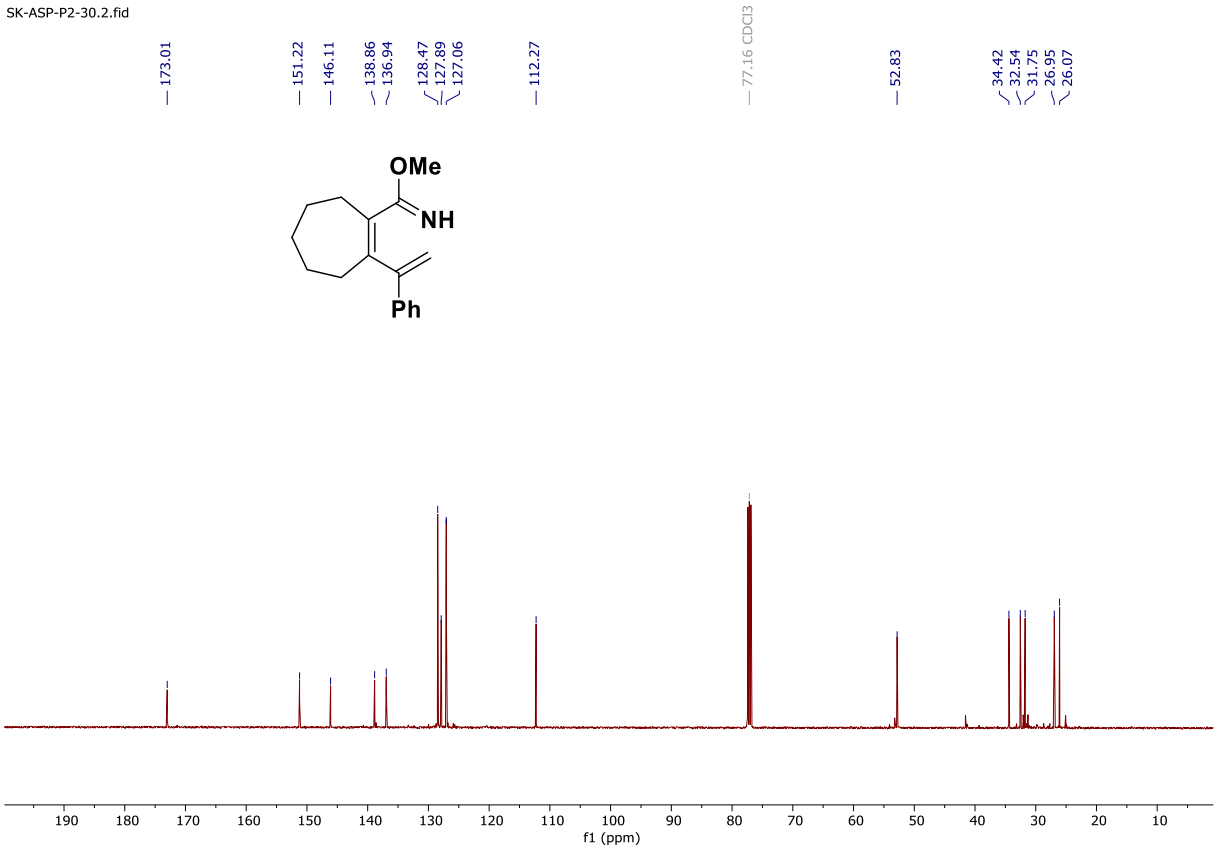
^{13}C{^{1}H} NMR spectrum of 3q in $CDCl_3$ [126 MHz]



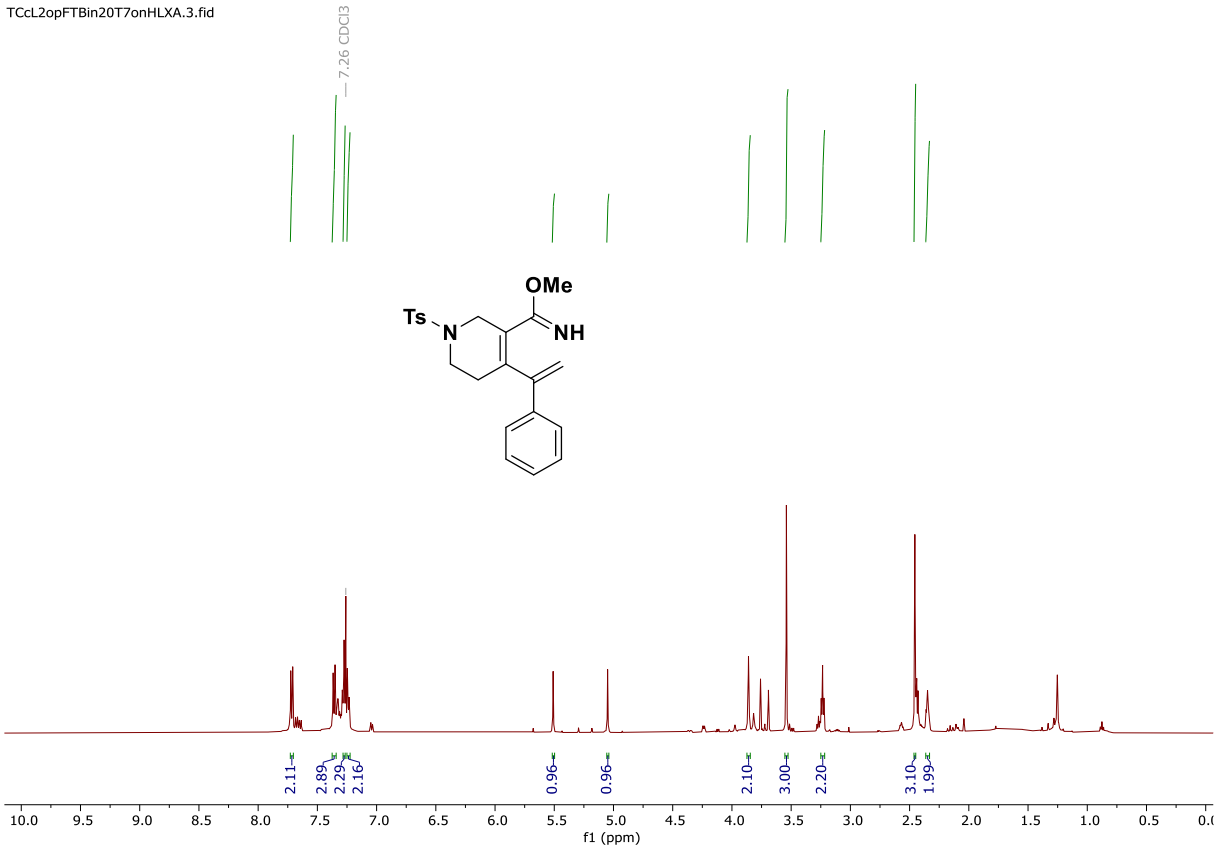
^{1}H NMR spectrum of 3r in $CDCl_3$ [500 MHz]



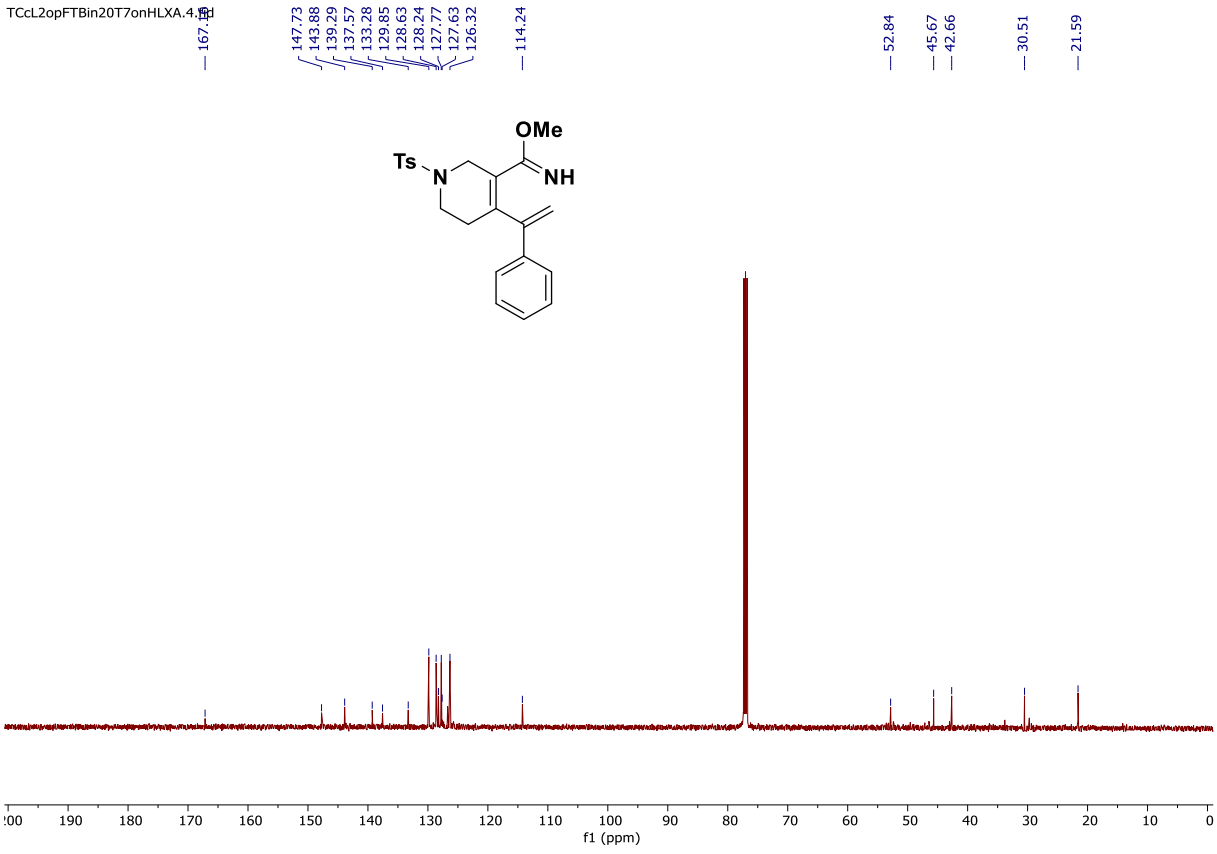
^{13}C{^{1}H} NMR spectrum of 3r in $CDCl_3$ [126 MHz]



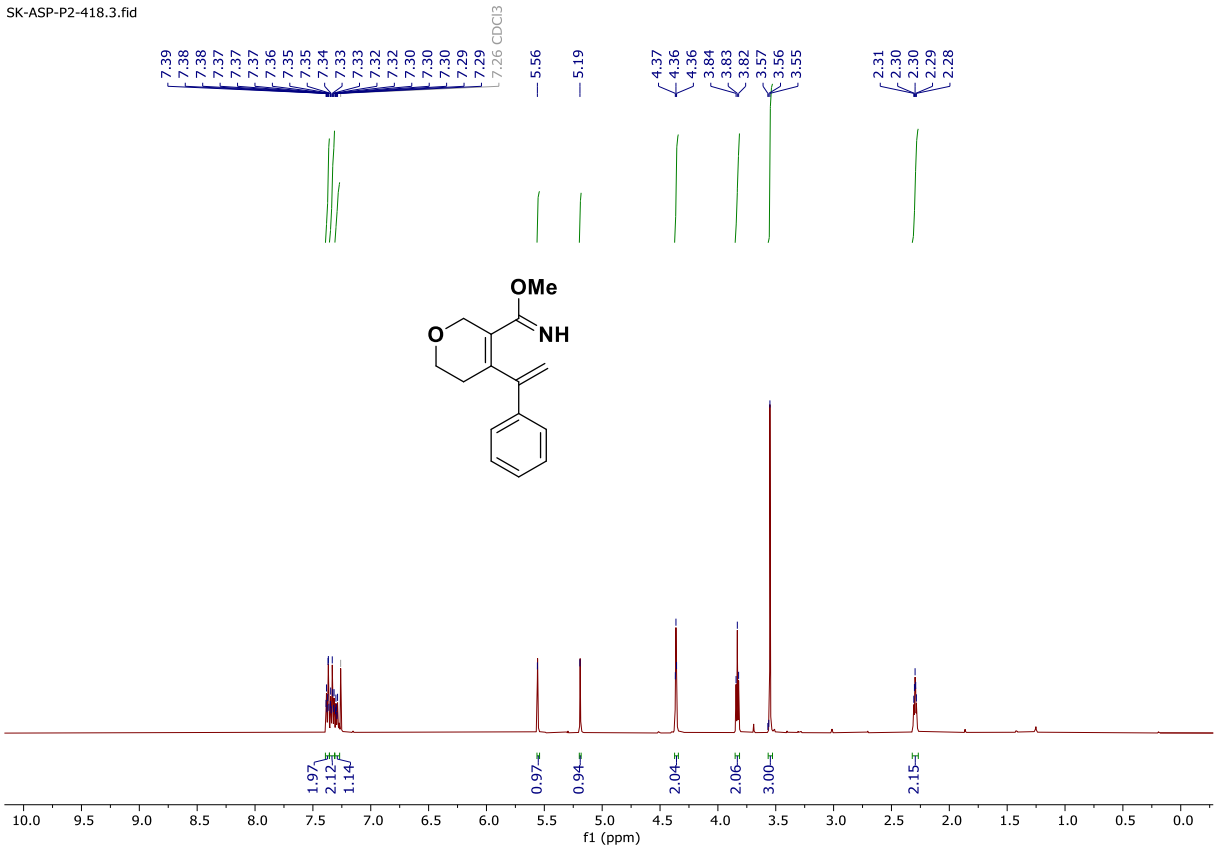
^{1}H NMR spectrum of 3s in $CDCl_3$ [500 MHz]



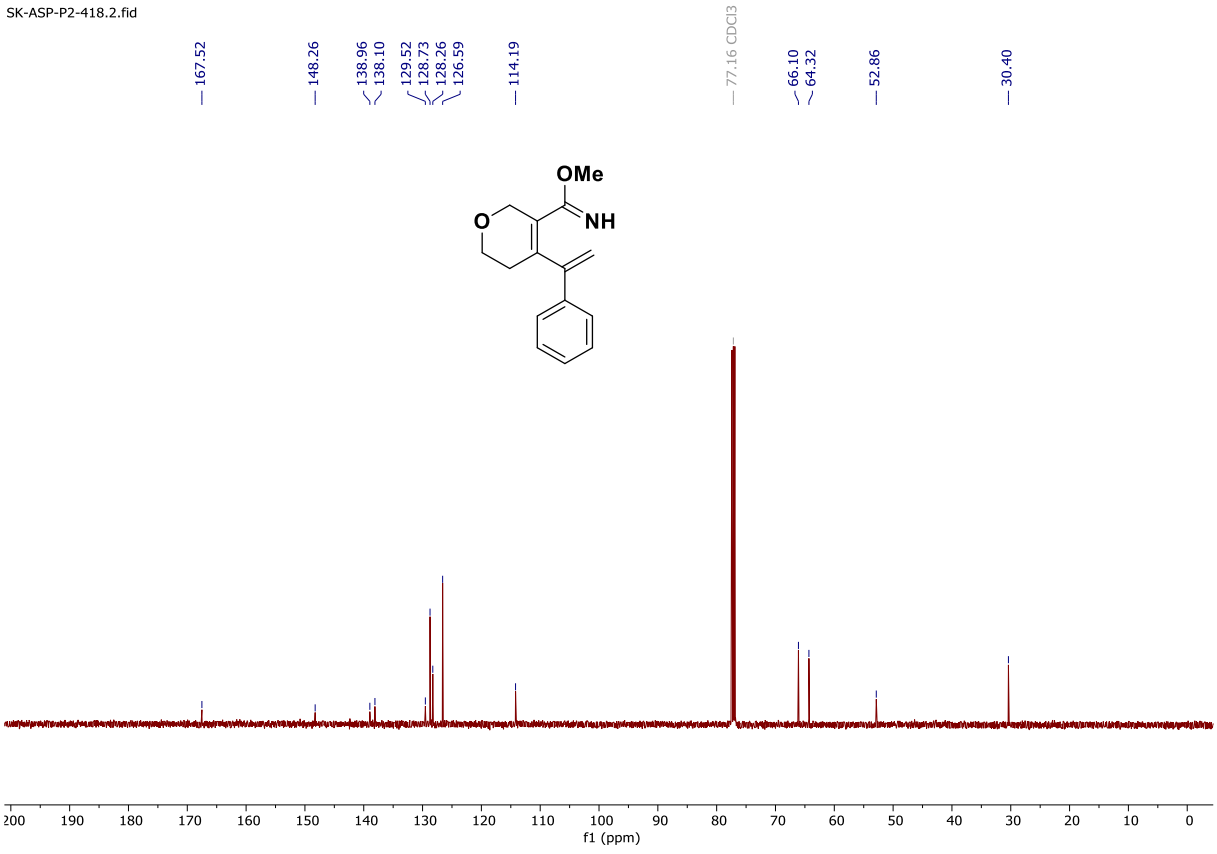
^{13}C{^{1}H} NMR spectrum of 3s in $CDCl_3$ [126 MHz]



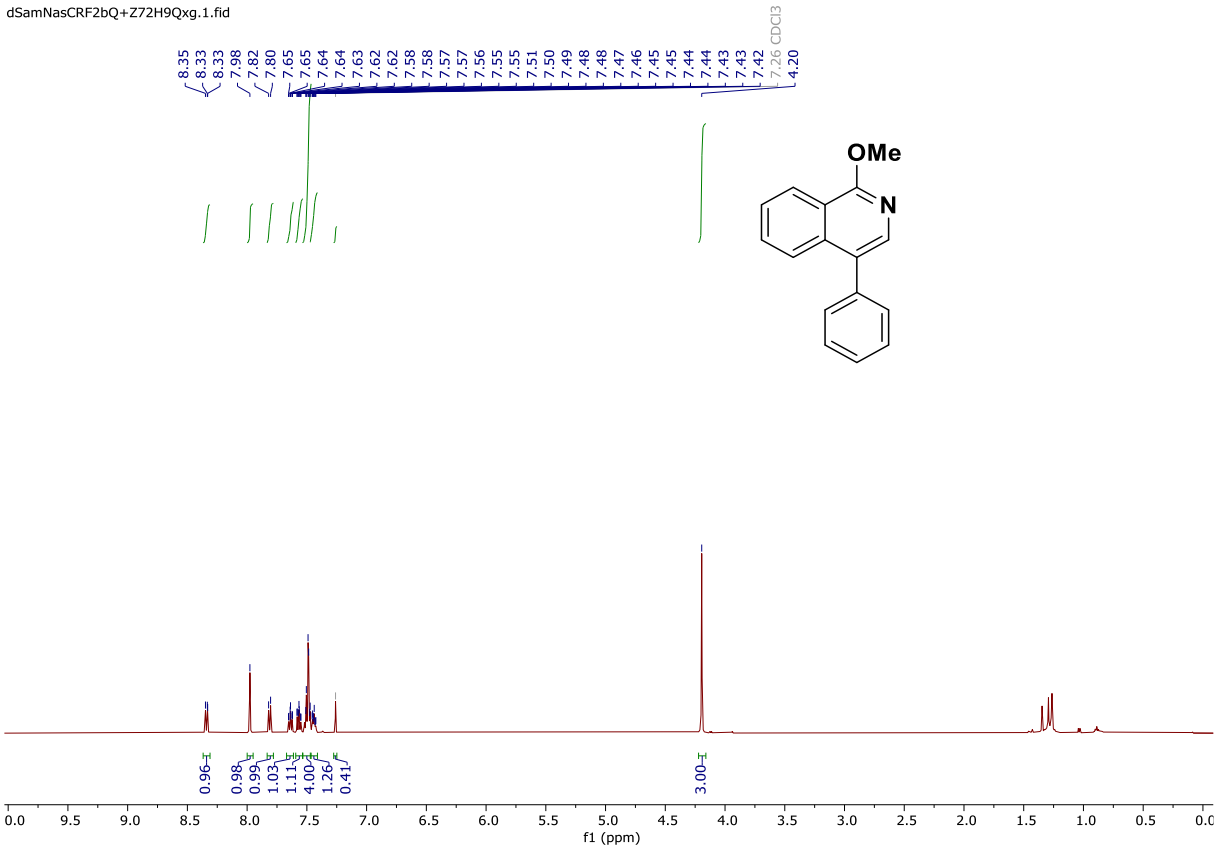
^{1}H NMR spectrum of 3t in $CDCl_3$ [500 MHz]



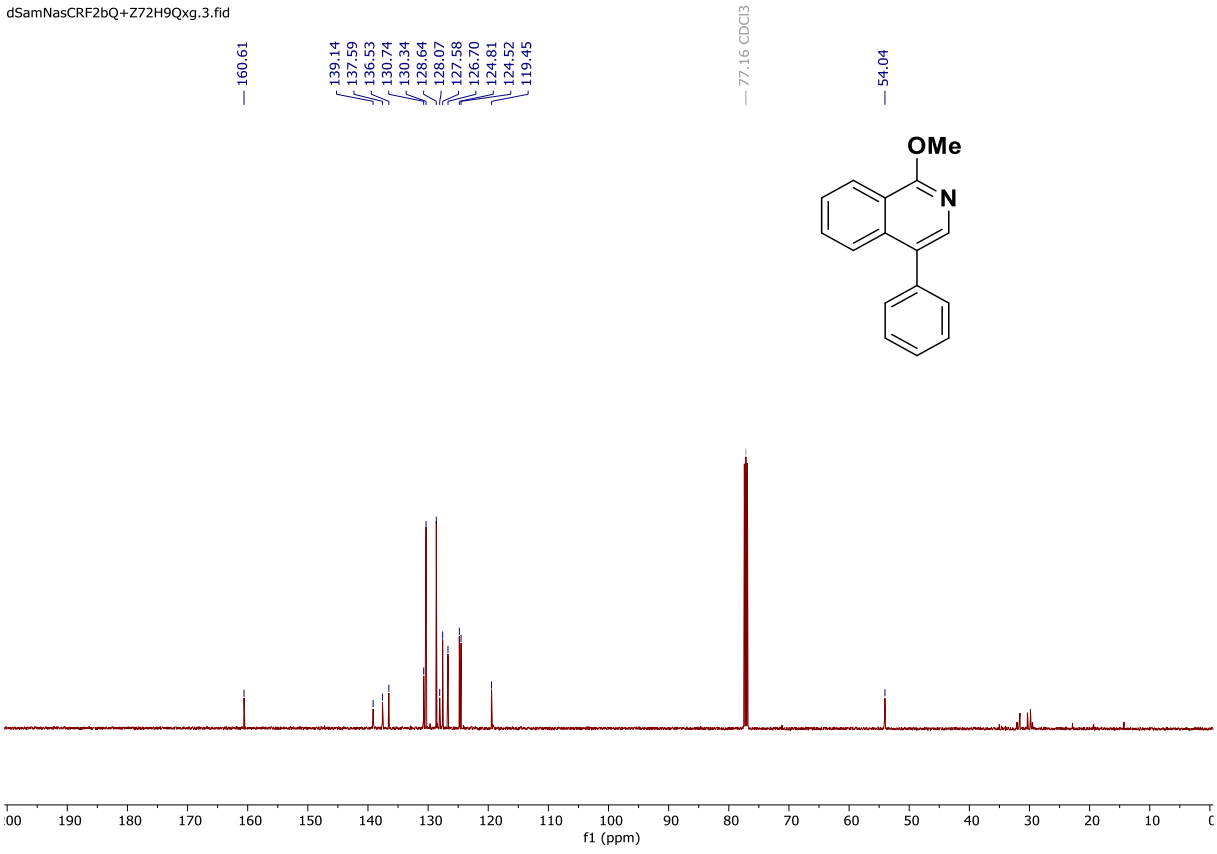
^{13}C{^{1}H} NMR spectrum of 3t in $CDCl_3$ [126 MHz]



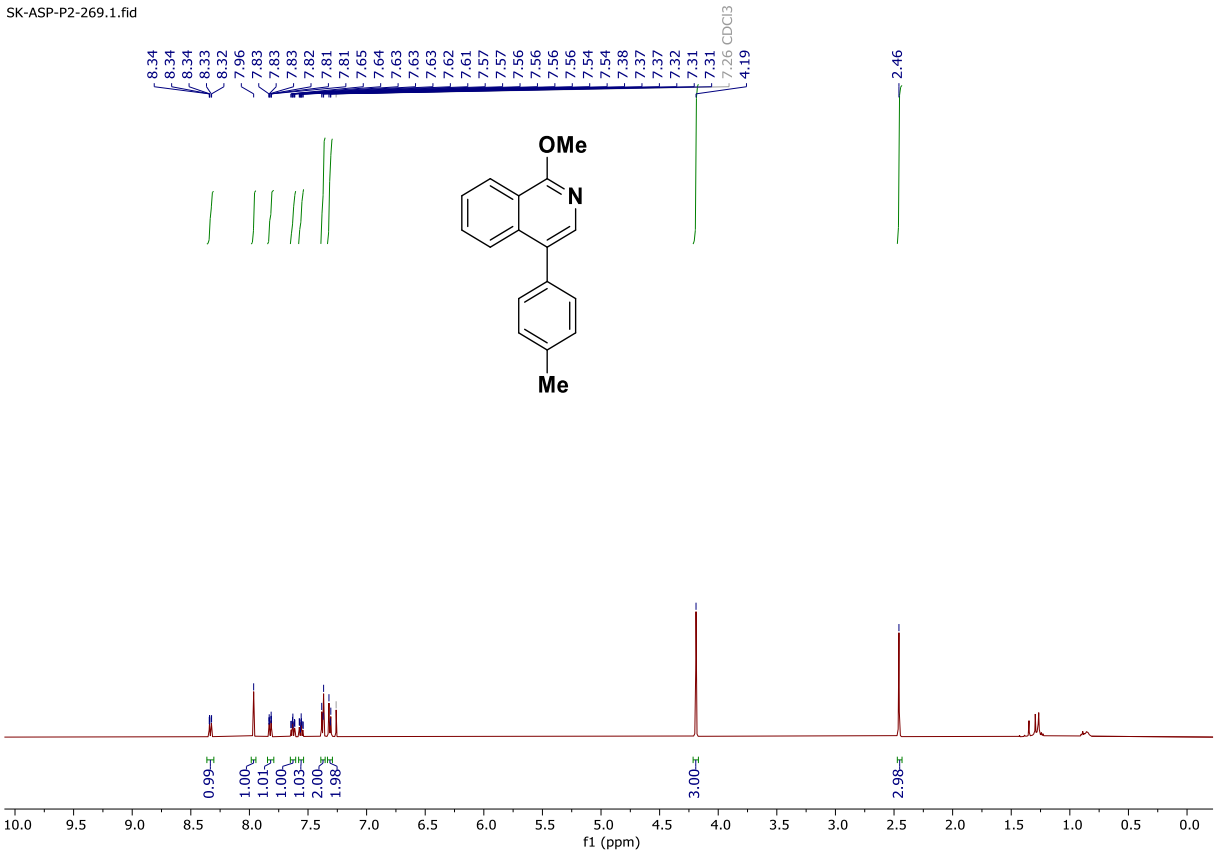
^{1}H NMR spectrum of 4a in $CDCl_3$ [500 MHz]



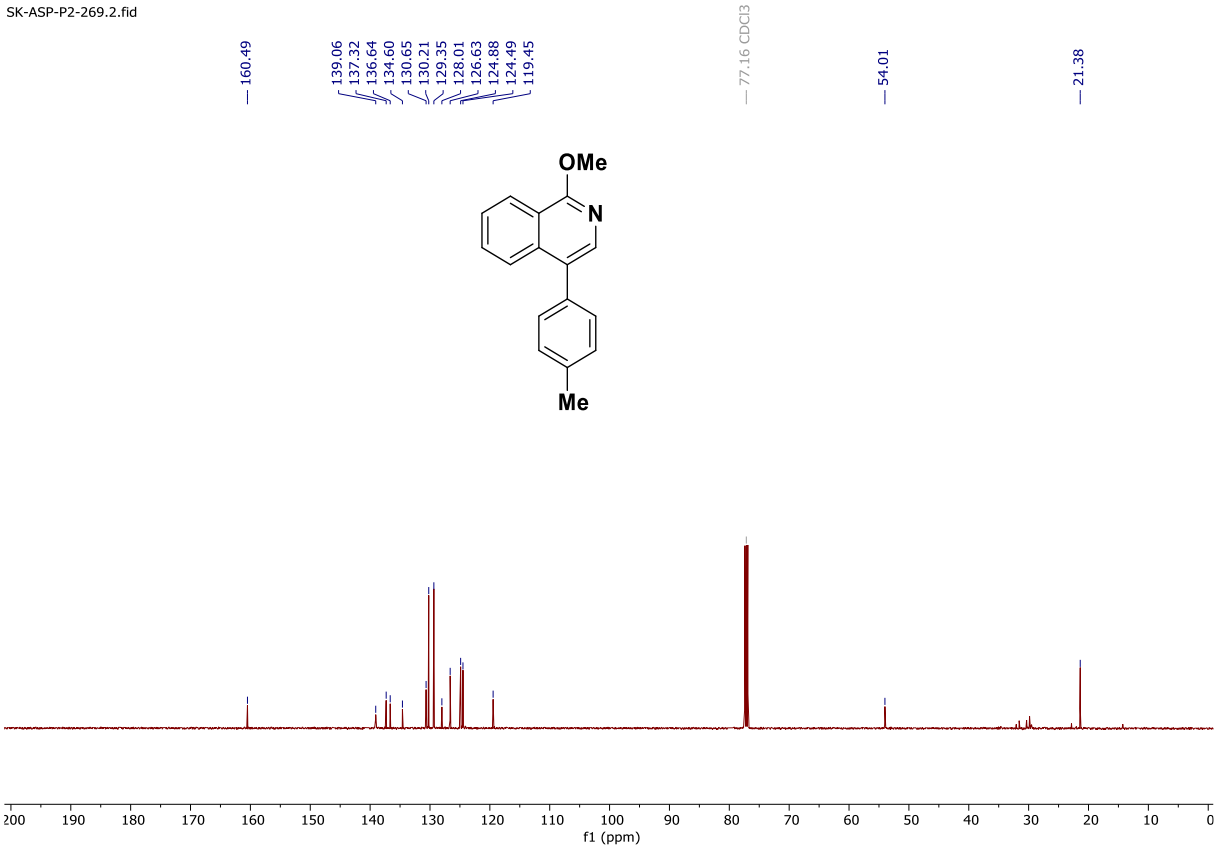
^{13}C{^{1}H} NMR spectrum of 4a in $CDCl_3$ [126 MHz]



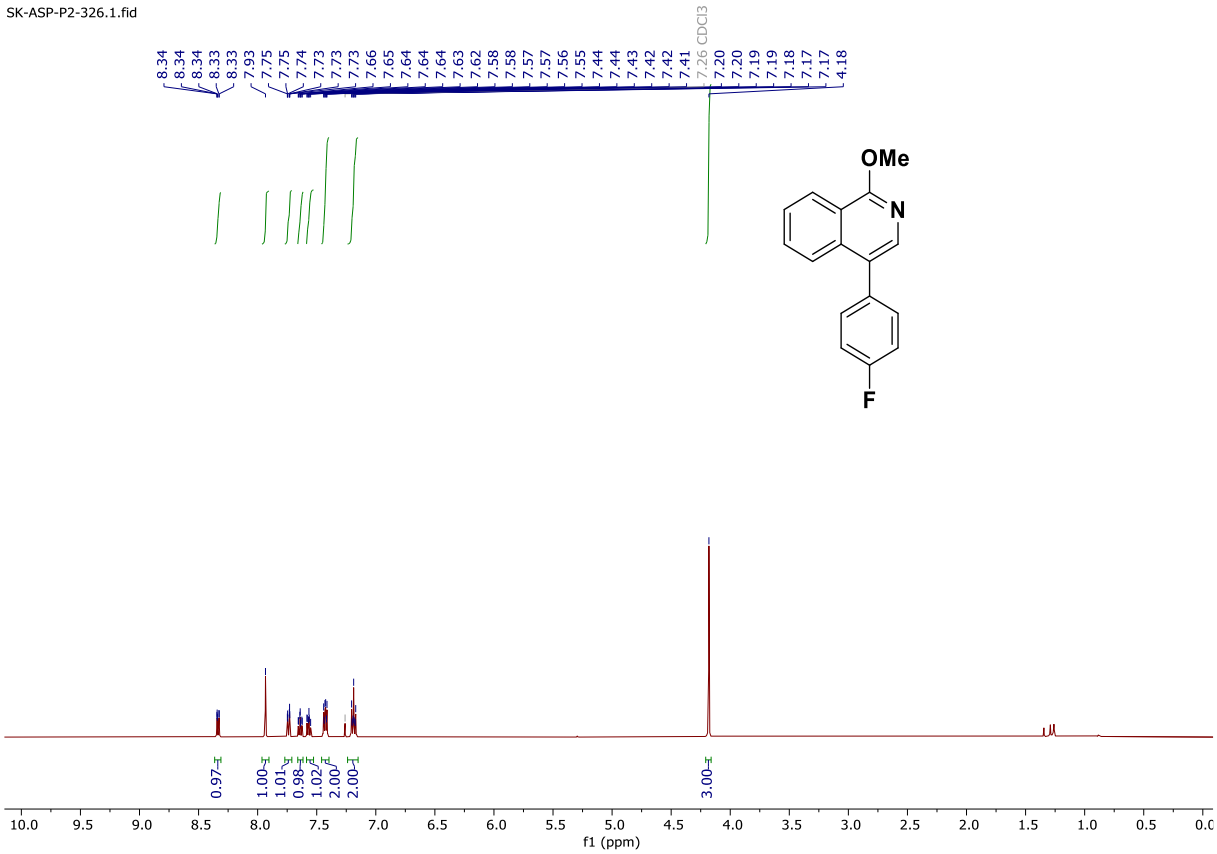
^{1}H NMR spectrum of 4b in $CDCl_3$ [500 MHz]



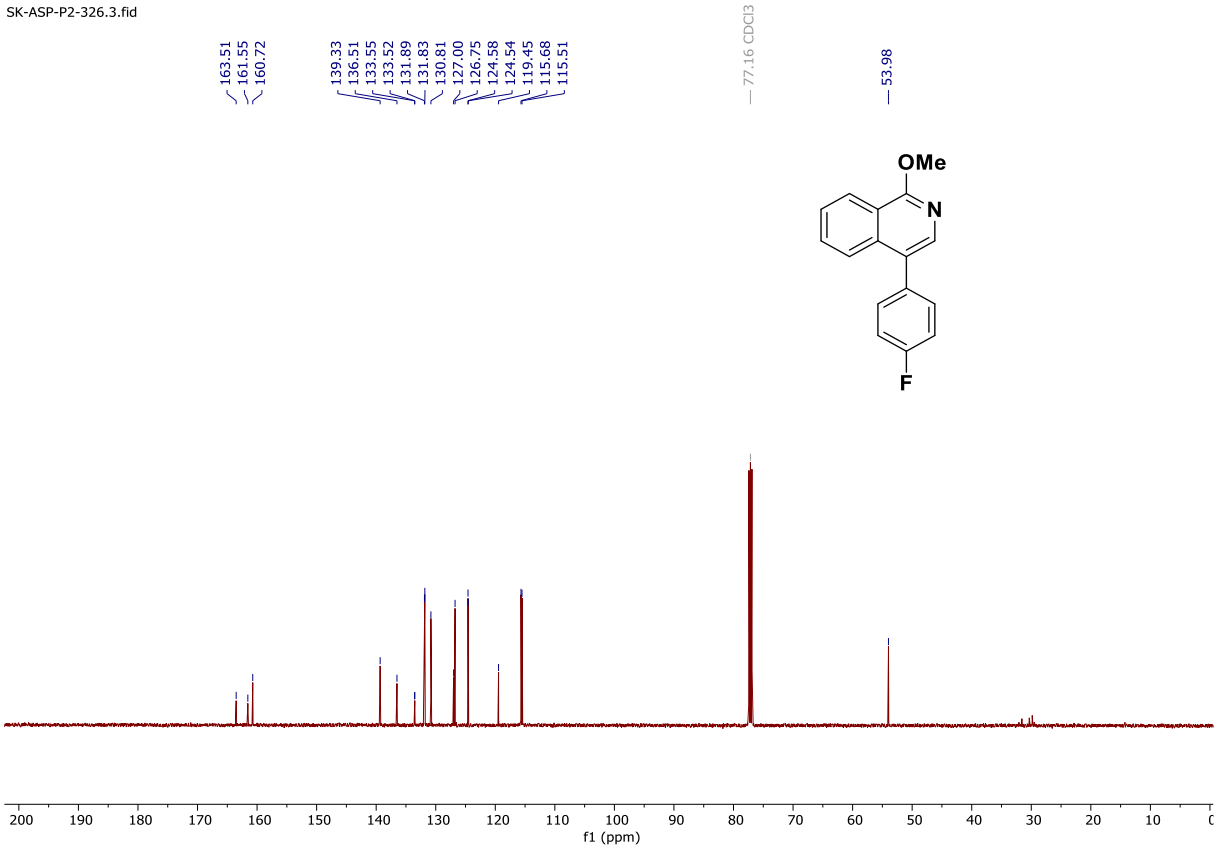
^{13}C{^{1}H} NMR spectrum of 4b in $CDCl_3$ [126 MHz]



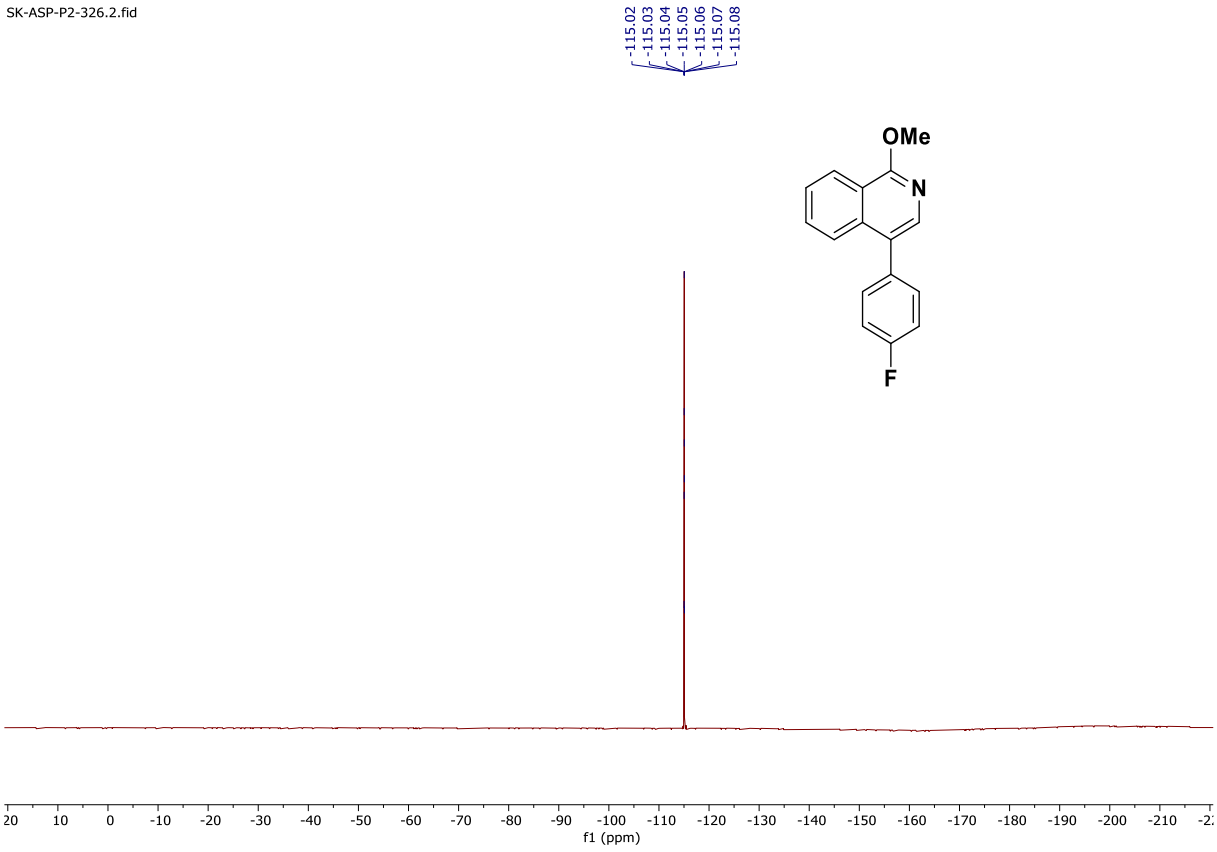
^{1}H NMR spectrum of 4c in $CDCl_3$ [500 MHz]



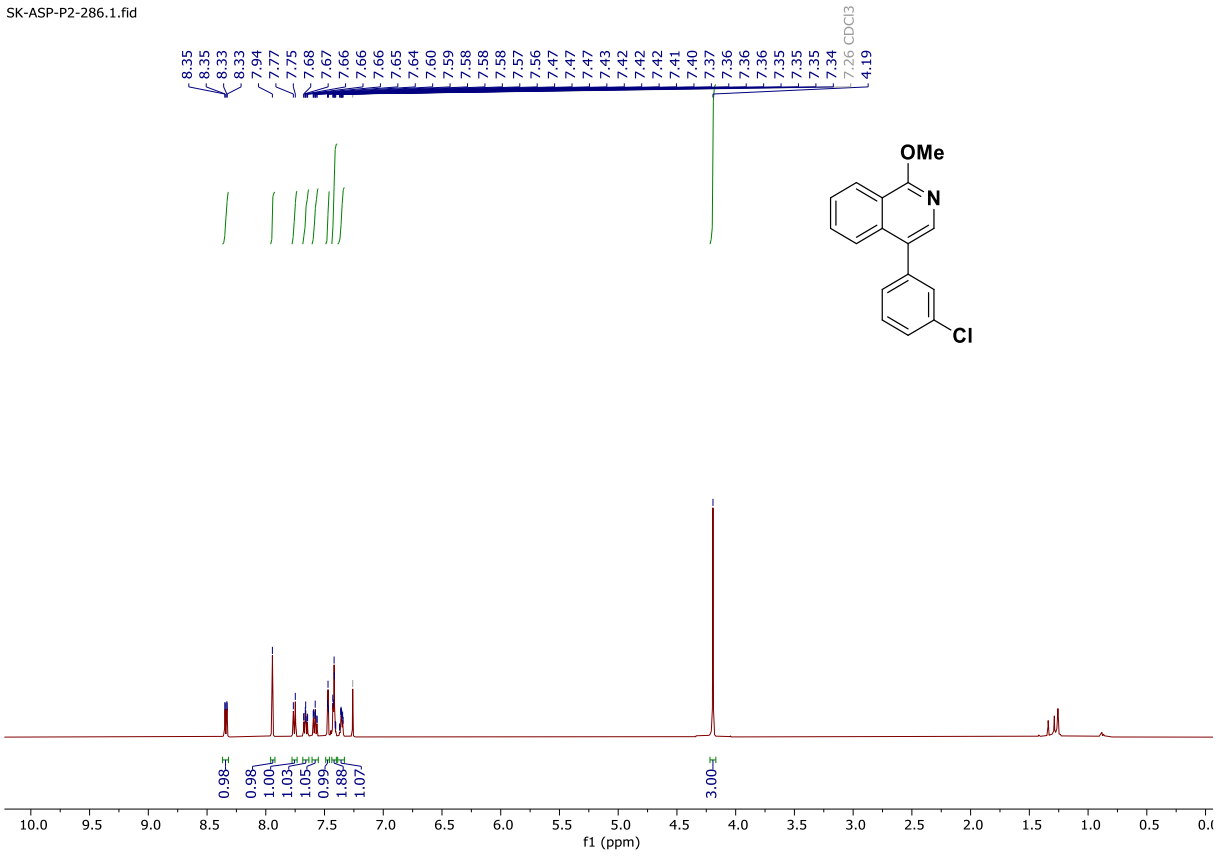
^{13}C{^{1}H} NMR spectrum of 4c in $CDCl_3$ [126 MHz]



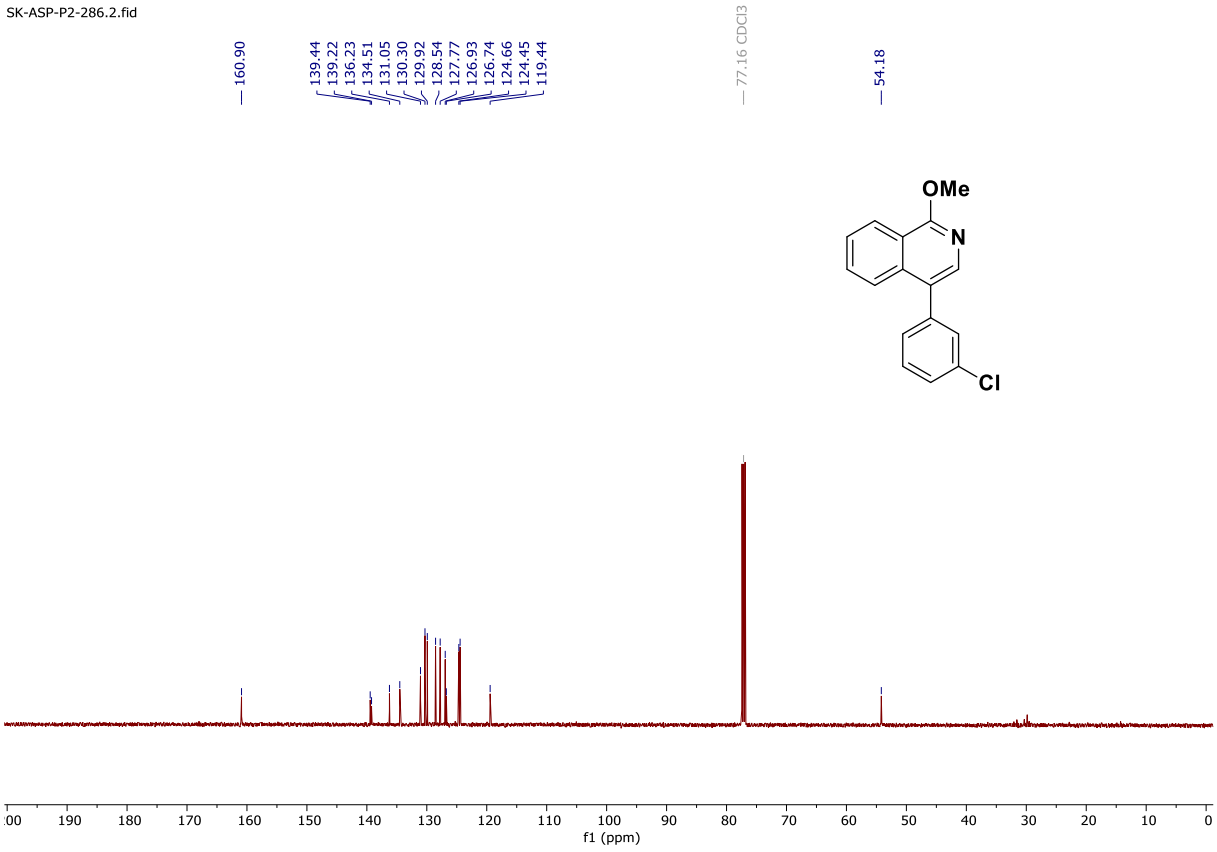
^{19}F NMR spectrum of 4c in $CDCl_3$ [471 MHz]



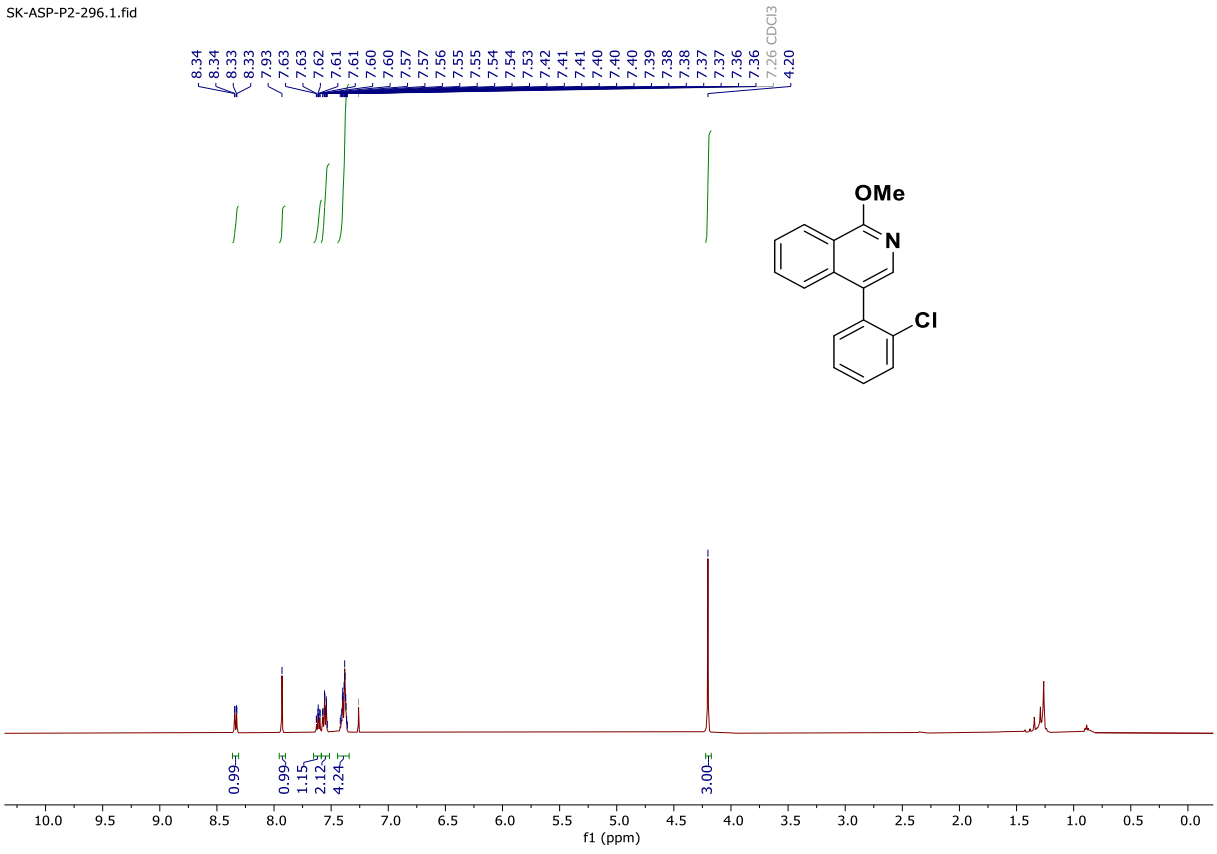
^{1}H NMR spectrum of 4d in $CDCl_3$ [500 MHz]



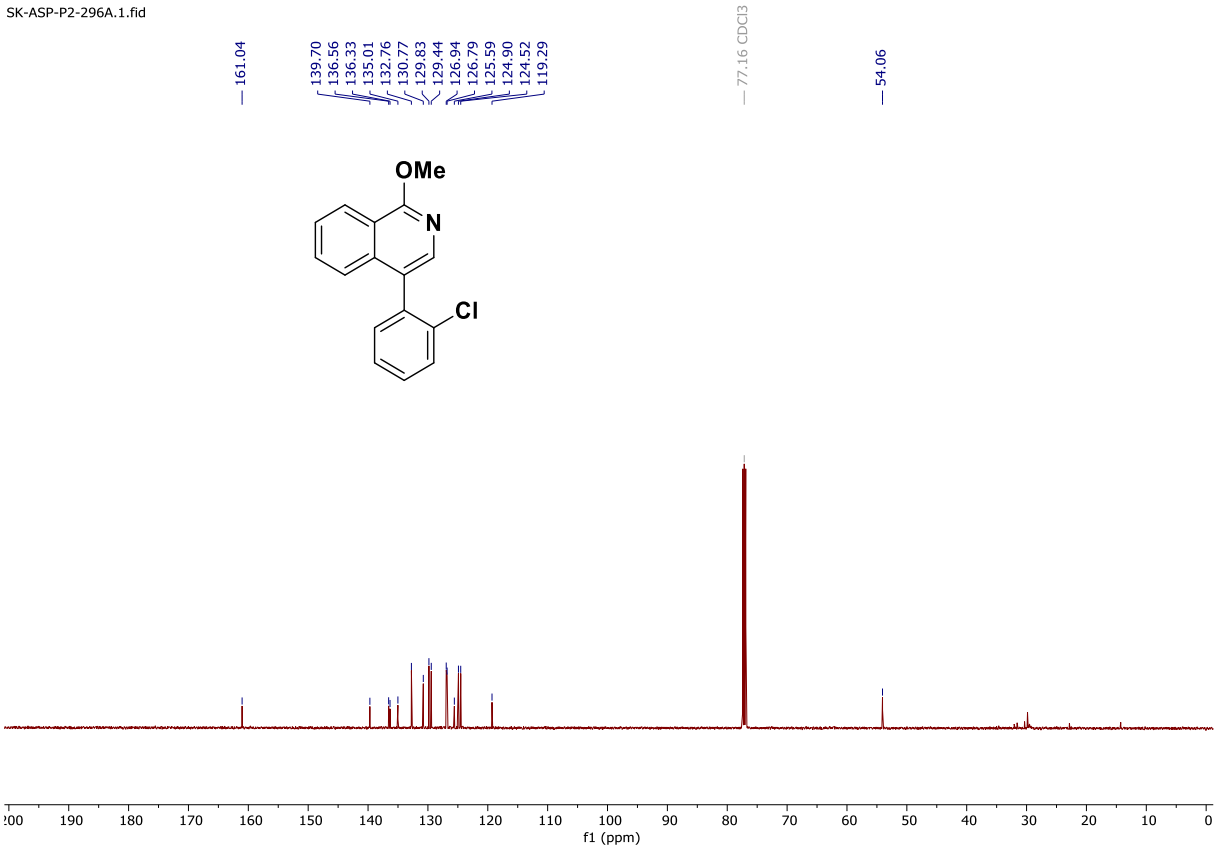
$^{13}C\{^{1}H\}$ NMR spectrum of 4d in $CDCl_3$ [126 MHz]



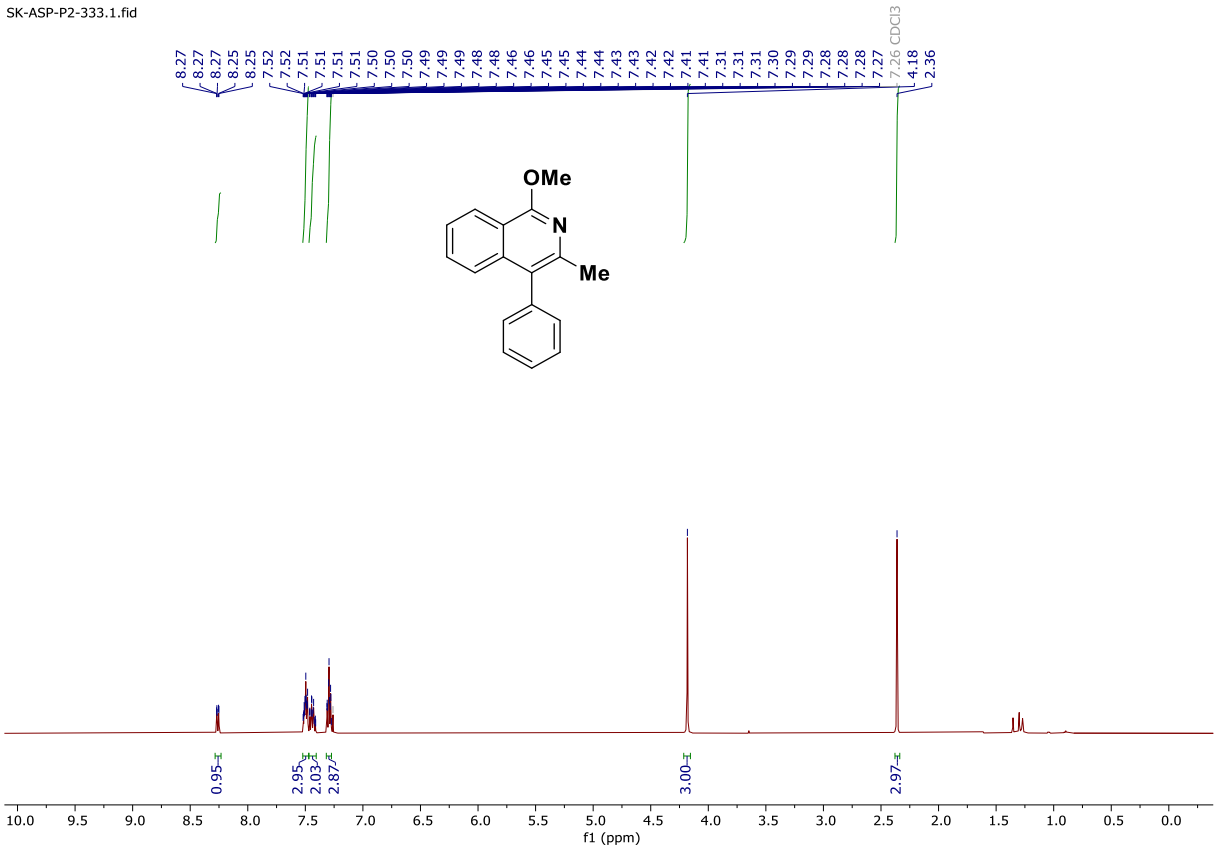
^{1}H NMR spectrum of 4e in $CDCl_3$ [500 MHz]



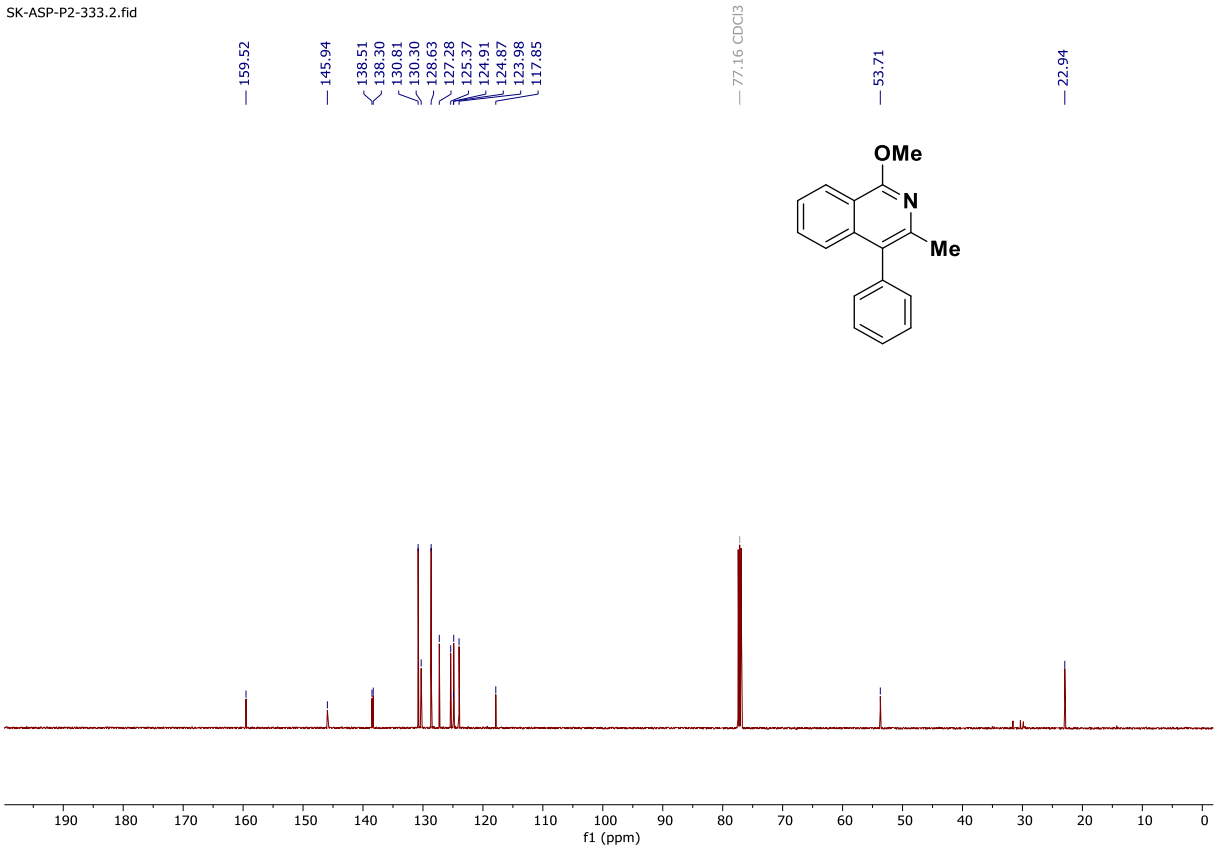
$^{13}C\{^{1}H\}$ NMR spectrum of 4e in $CDCl_3$ [126 MHz]



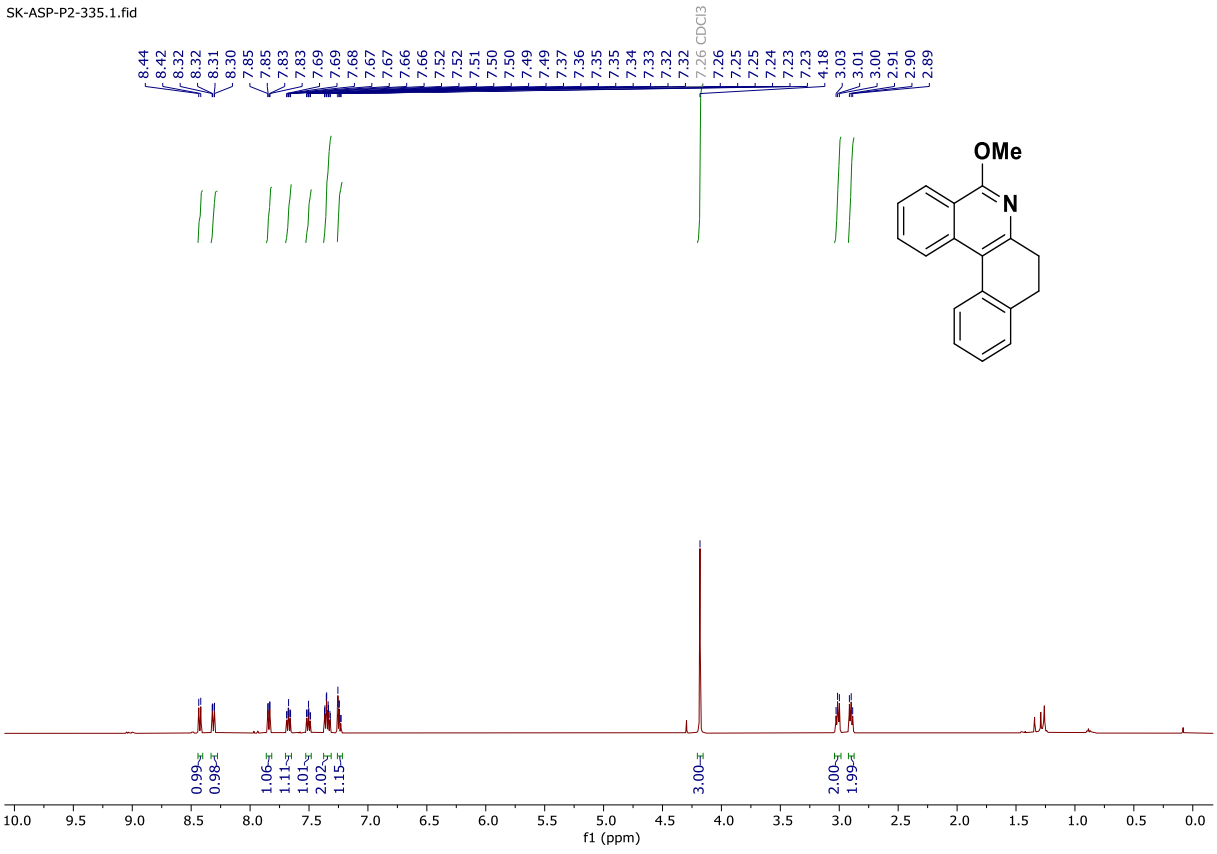
^{1}H NMR spectrum of 4g in $CDCl_3$ [500 MHz]



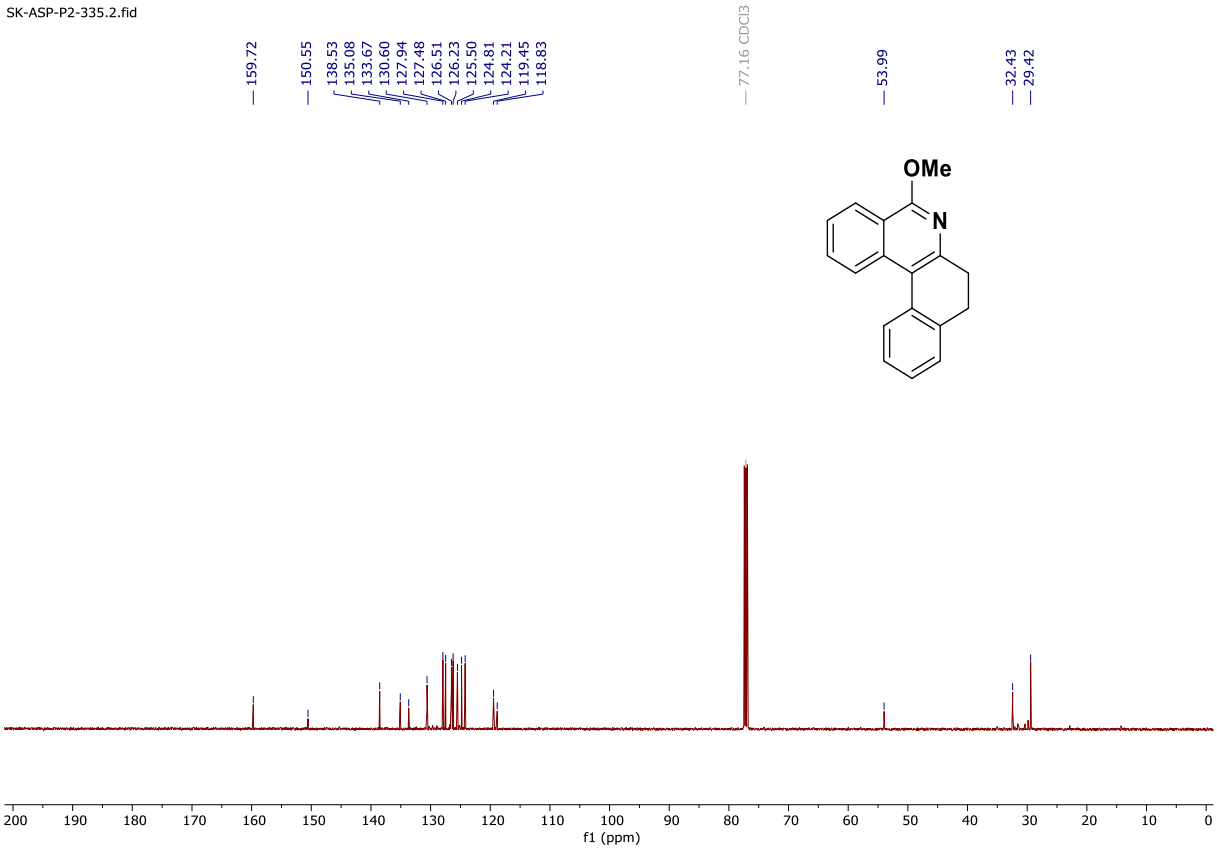
$^{13}C\{^{1}H\}$ NMR spectrum of 4g in $CDCl_3$ [126 MHz]



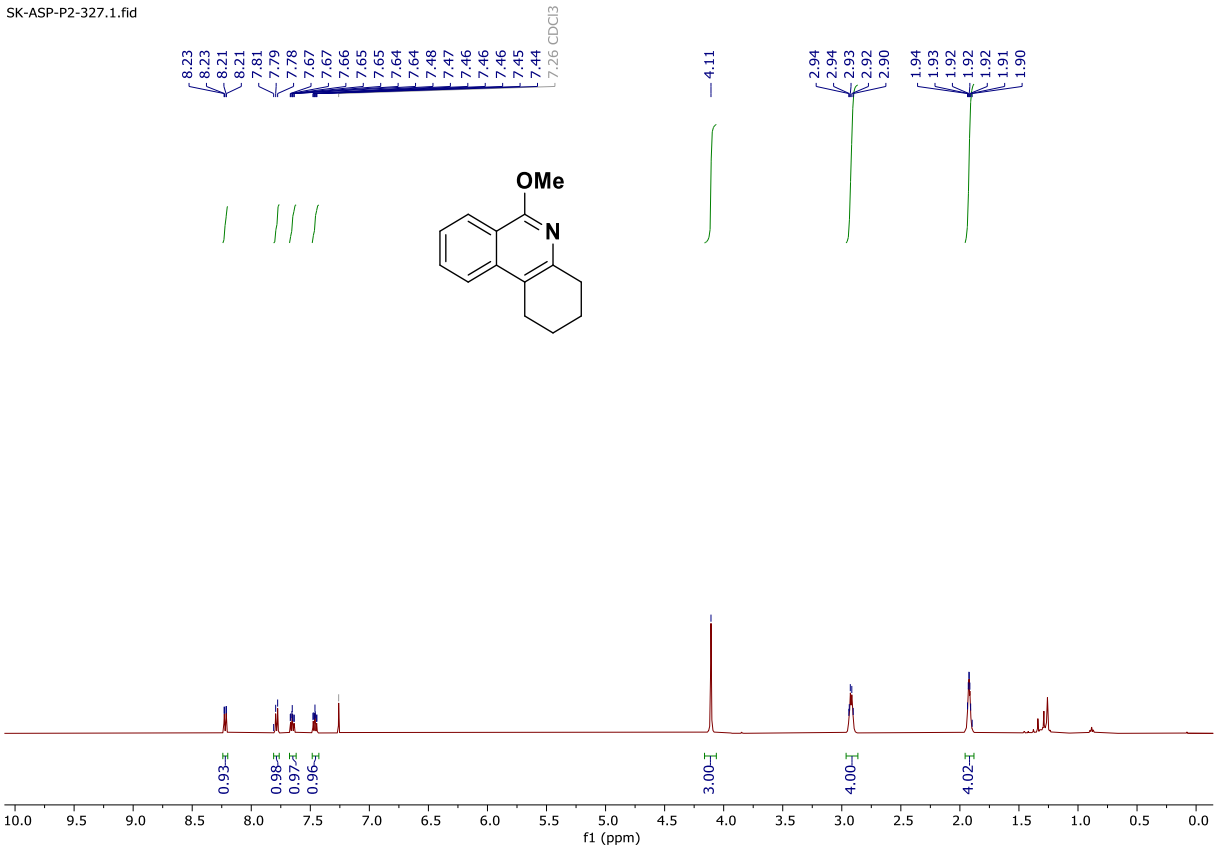
^{1}H NMR spectrum of 4h in $CDCl_3$ [500 MHz]



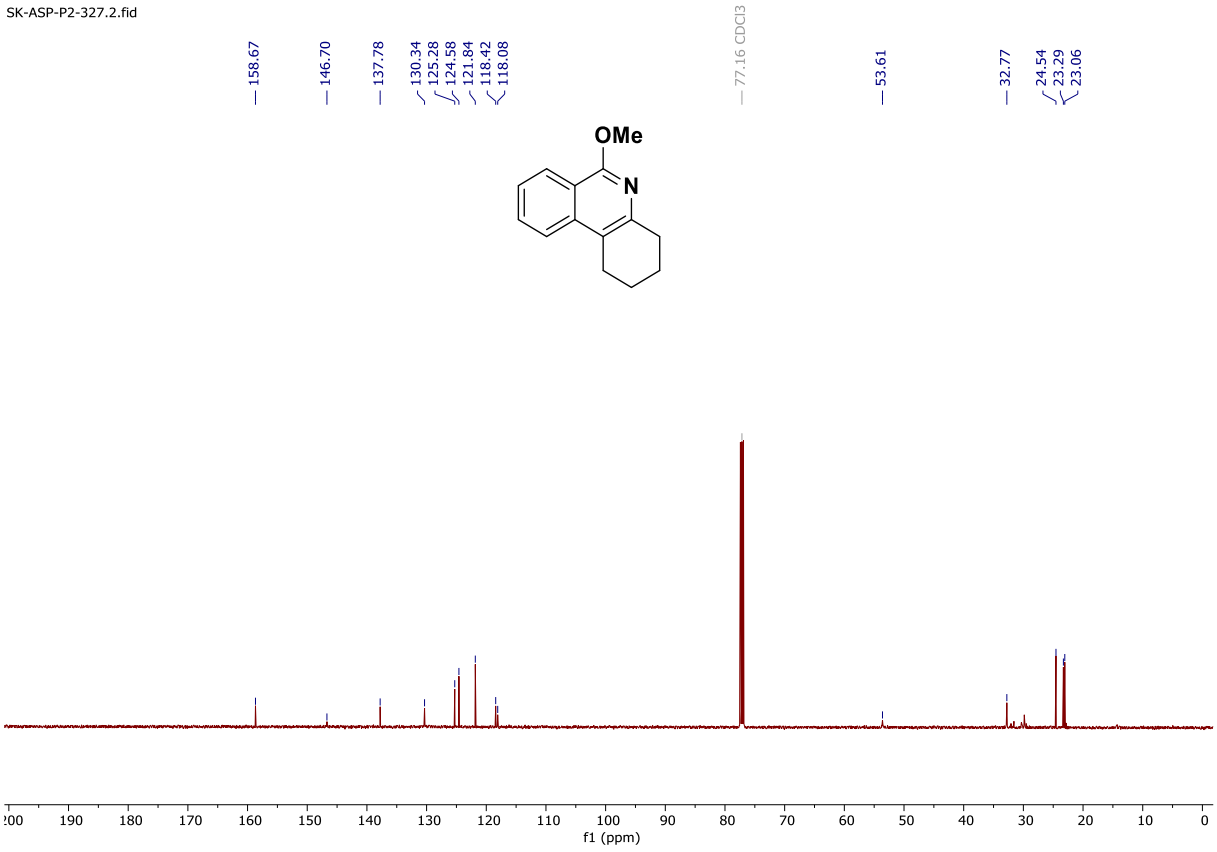
$^{13}C\{^{1}H\}$ NMR spectrum of 4h in $CDCl_3$ [126 MHz]



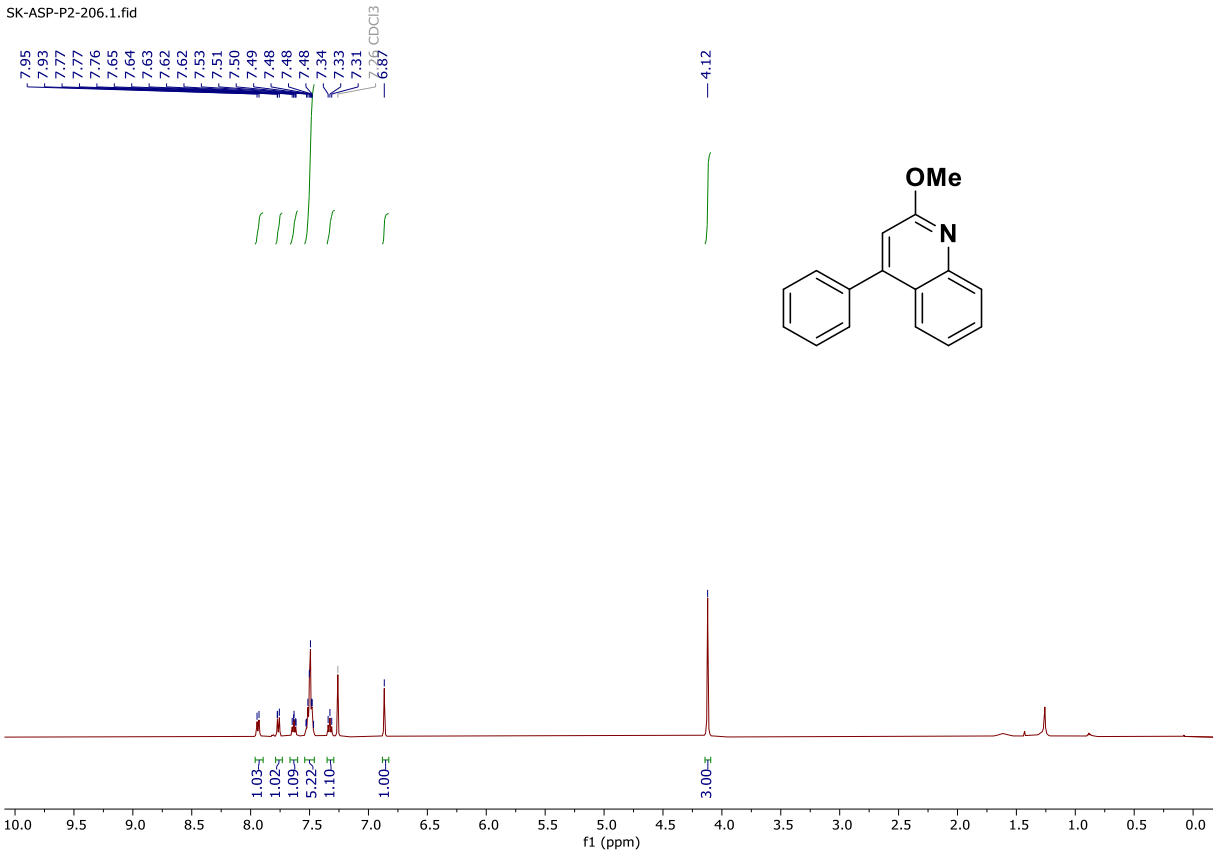
^{1}H NMR spectrum of 4i in $CDCl_3$ [500 MHz]



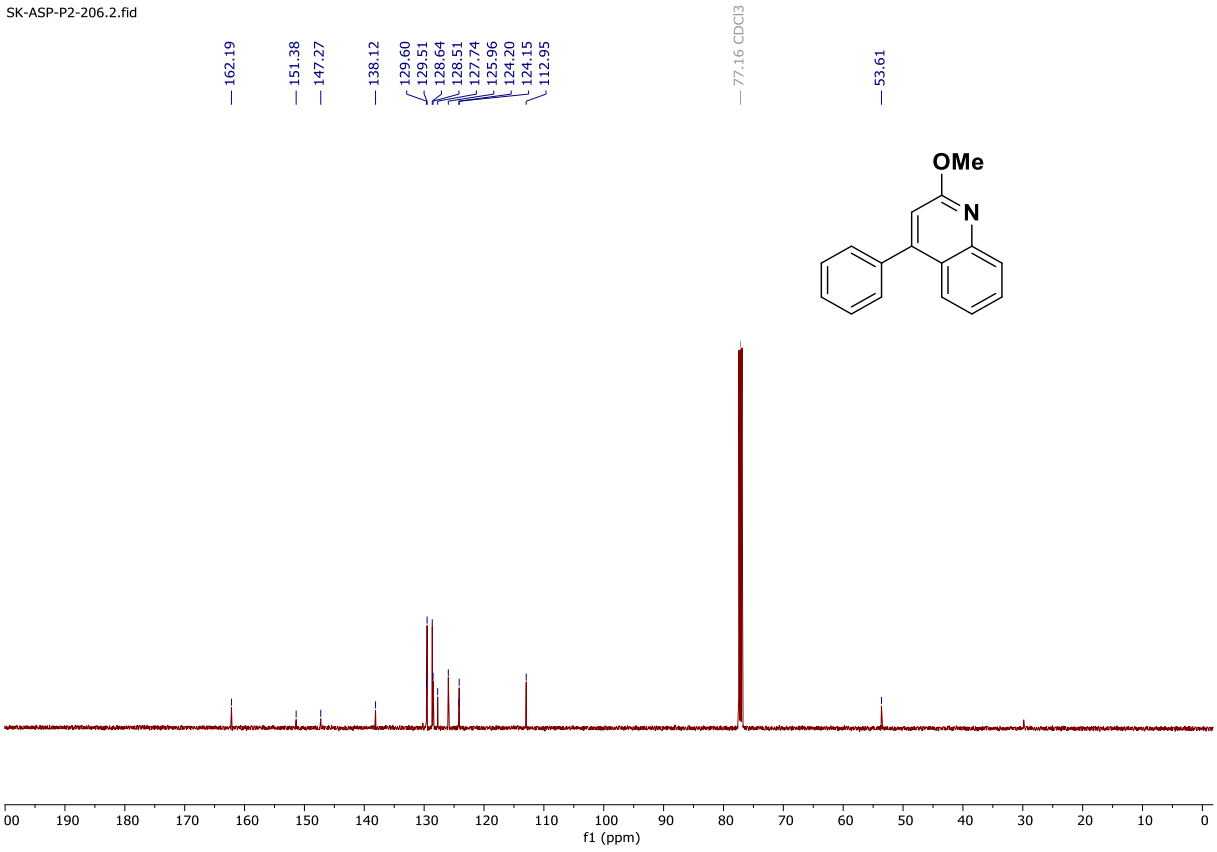
$^{13}C\{^{1}H\}$ NMR spectrum of 4i in $CDCl_3$ [126 MHz]



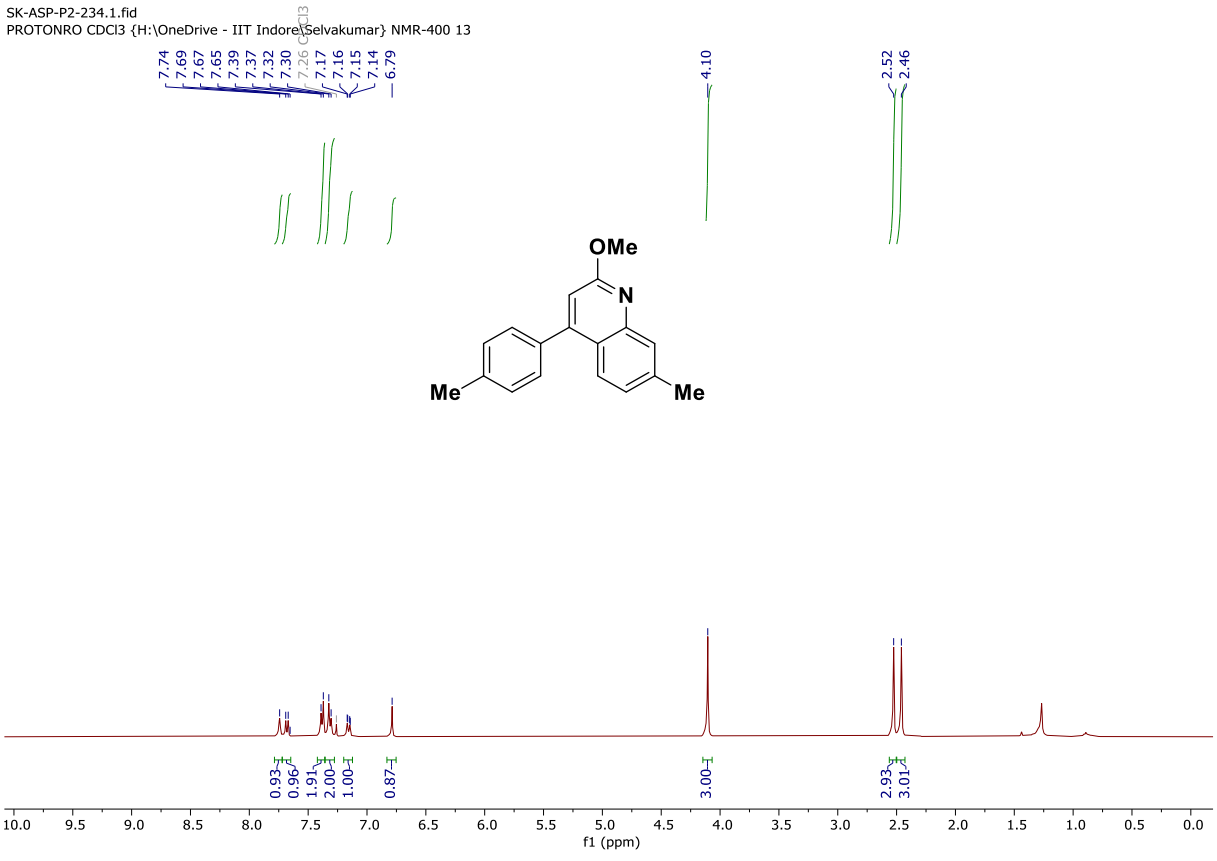
^{1}H NMR spectrum of 4j in $CDCl_3$ [500 MHz]



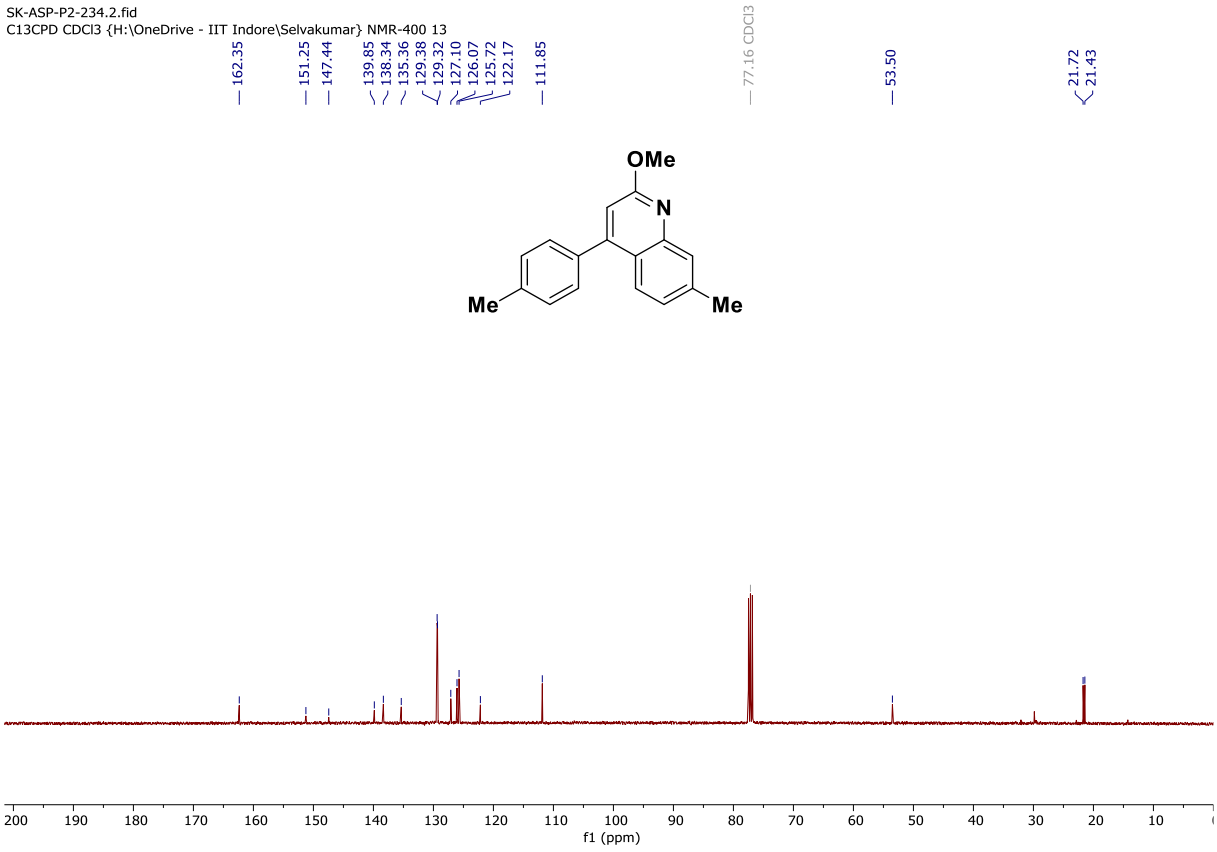
$^{13}C\{^{1}H\}$ NMR spectrum of 4j in $CDCl_3$ [126 MHz]



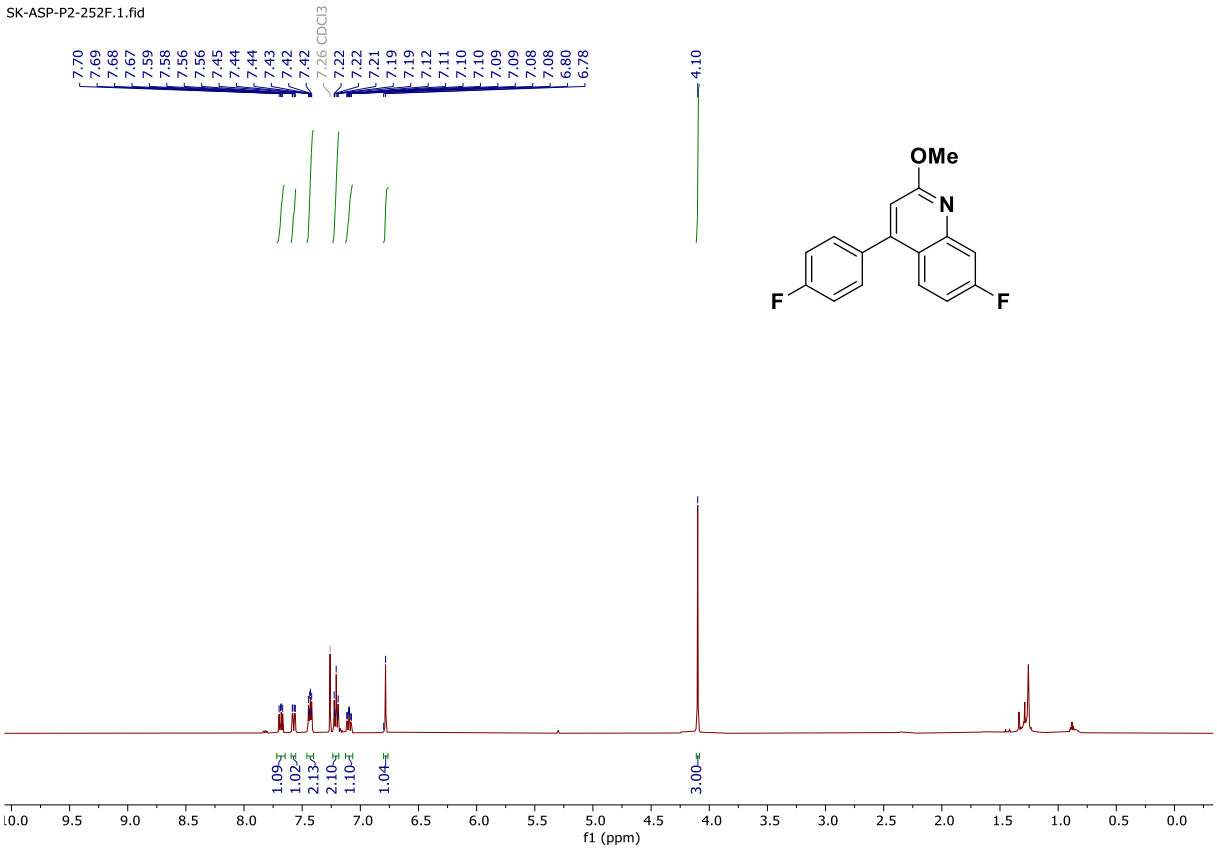
^{1}H NMR spectrum of 4k in $CDCl_3$ [400 MHz]



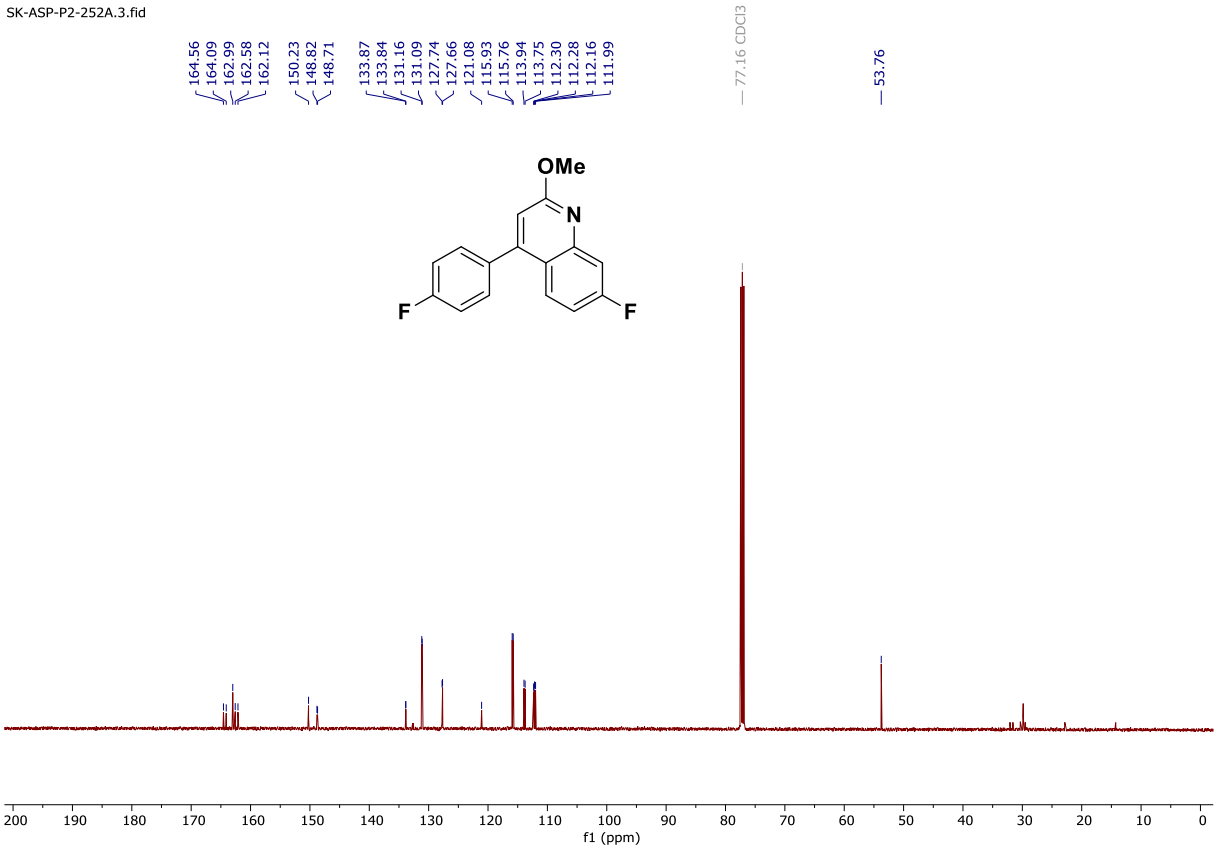
$^{13}C\{^{1}H\}$ NMR spectrum of 4k in $CDCl_3$ [101 MHz]



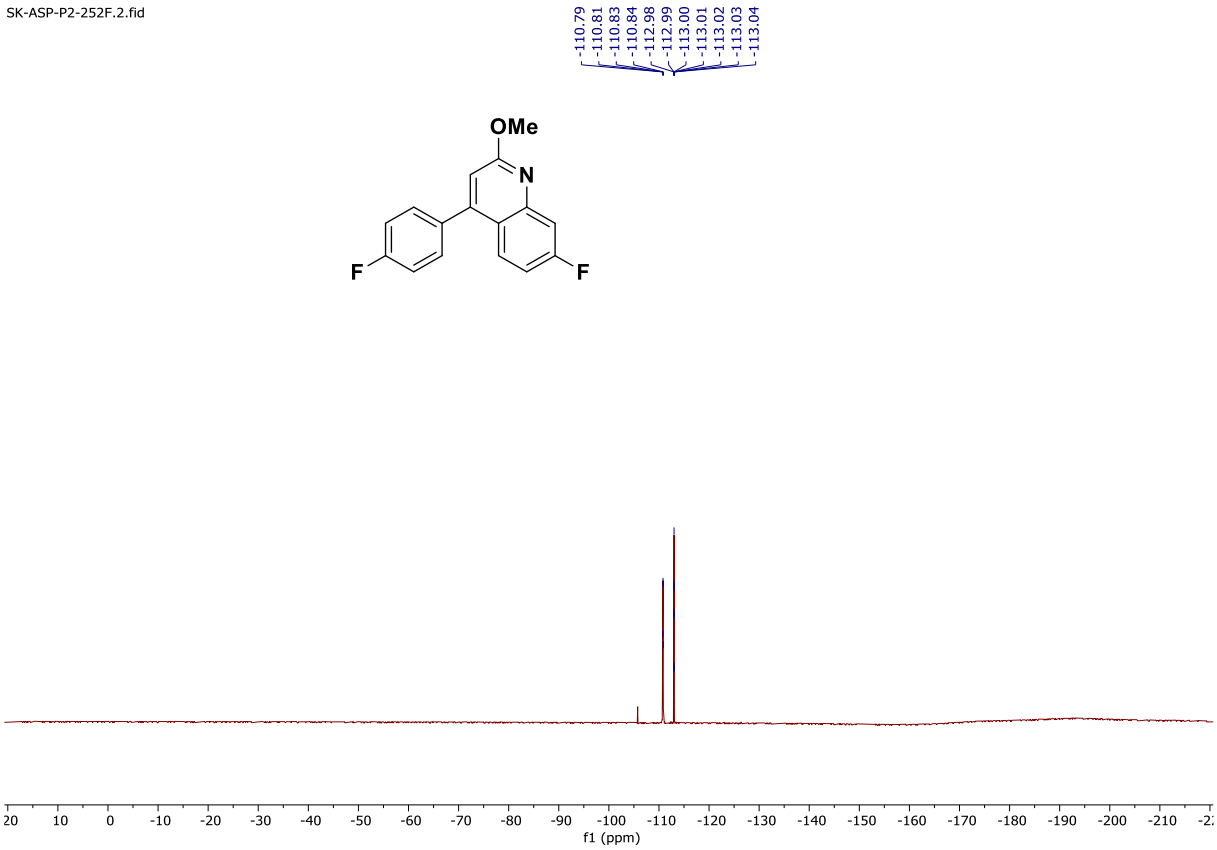
^{1}H NMR spectrum of 4l in $CDCl_3$ [500 MHz]



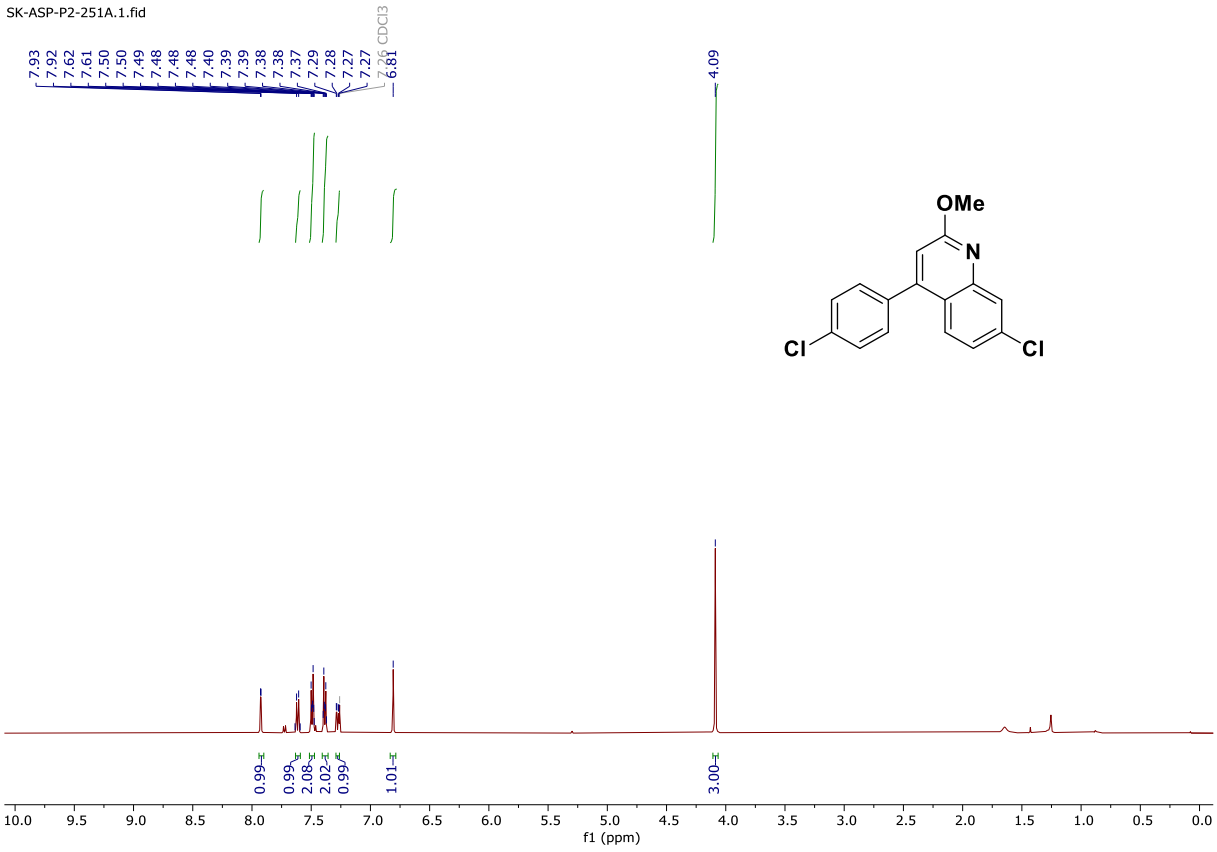
$^{13}C\{^{1}H\}$ NMR spectrum of 4l in $CDCl_3$ [126 MHz]



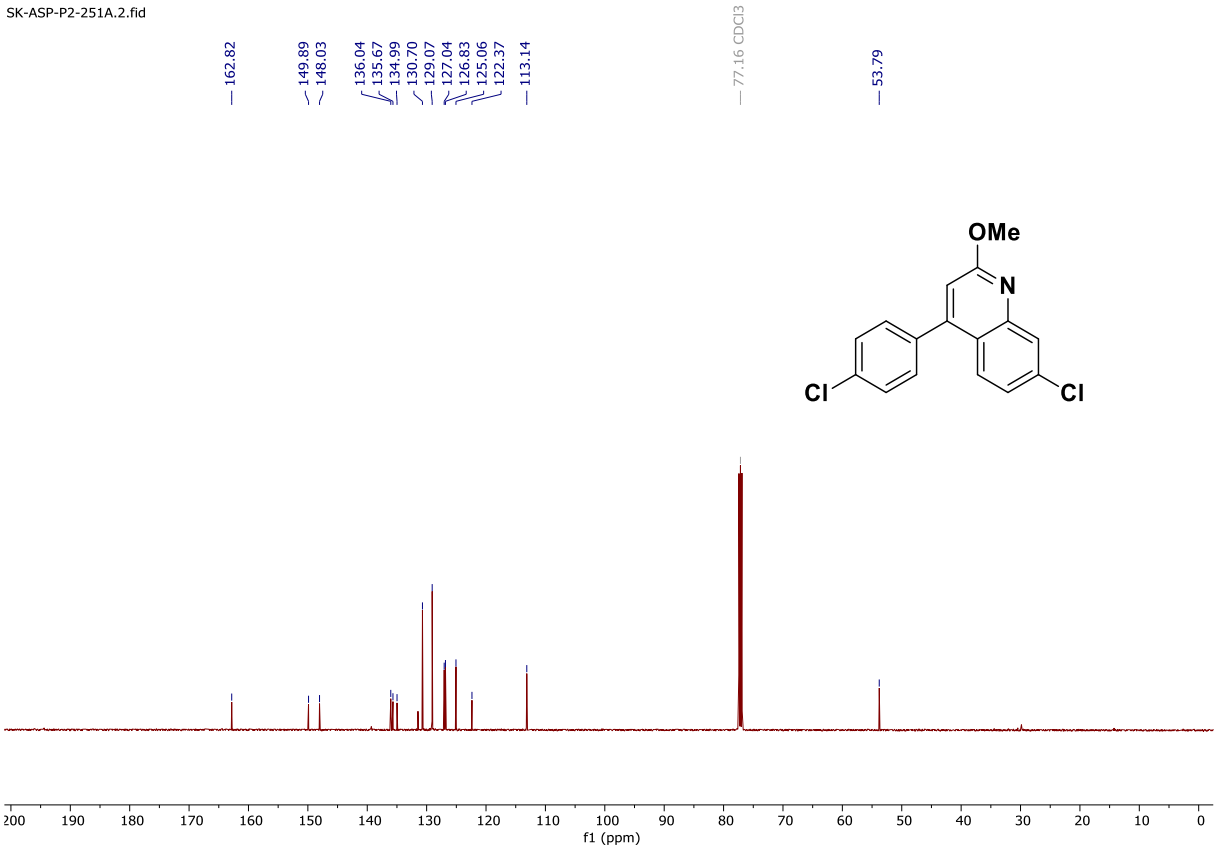
^{19}F NMR spectrum of 4l in $CDCl_3$ [471 MHz]



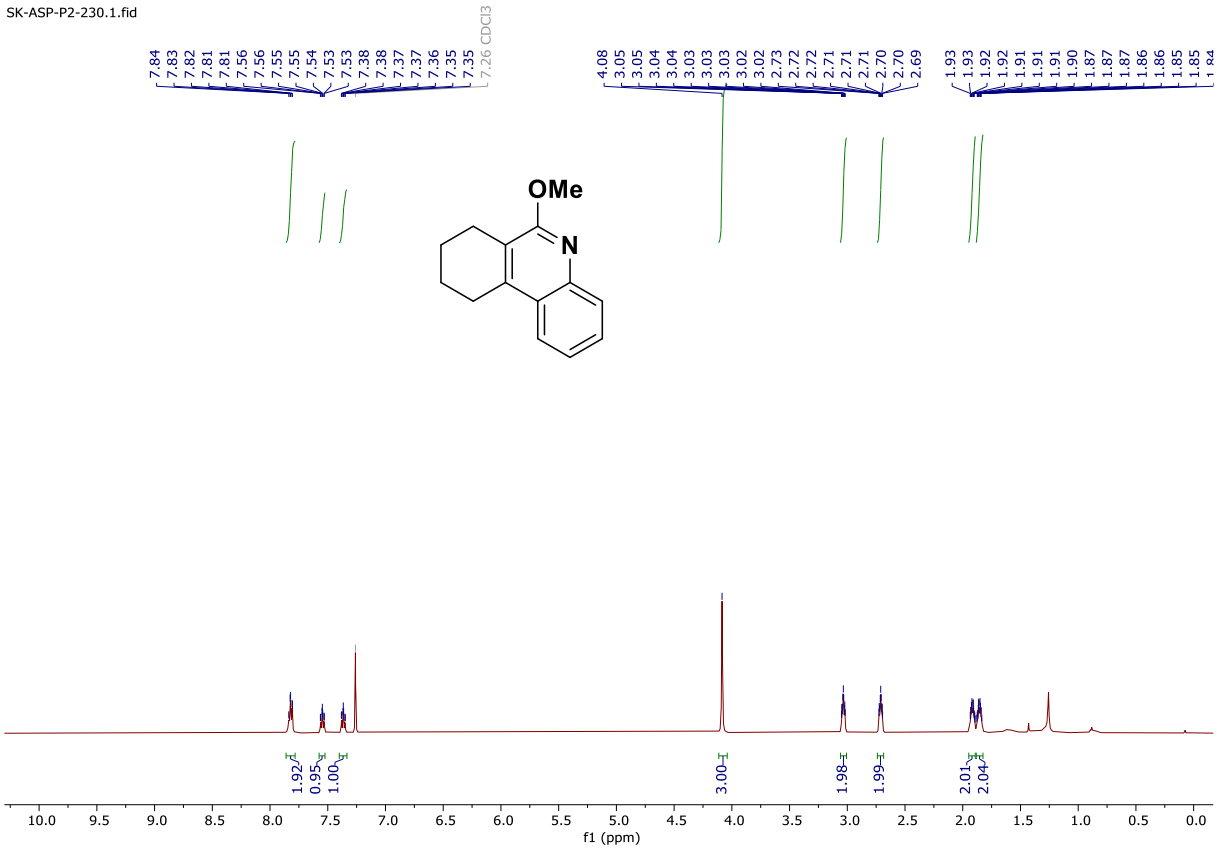
^{1}H NMR spectrum of 4m in $CDCl_3$ [500 MHz]



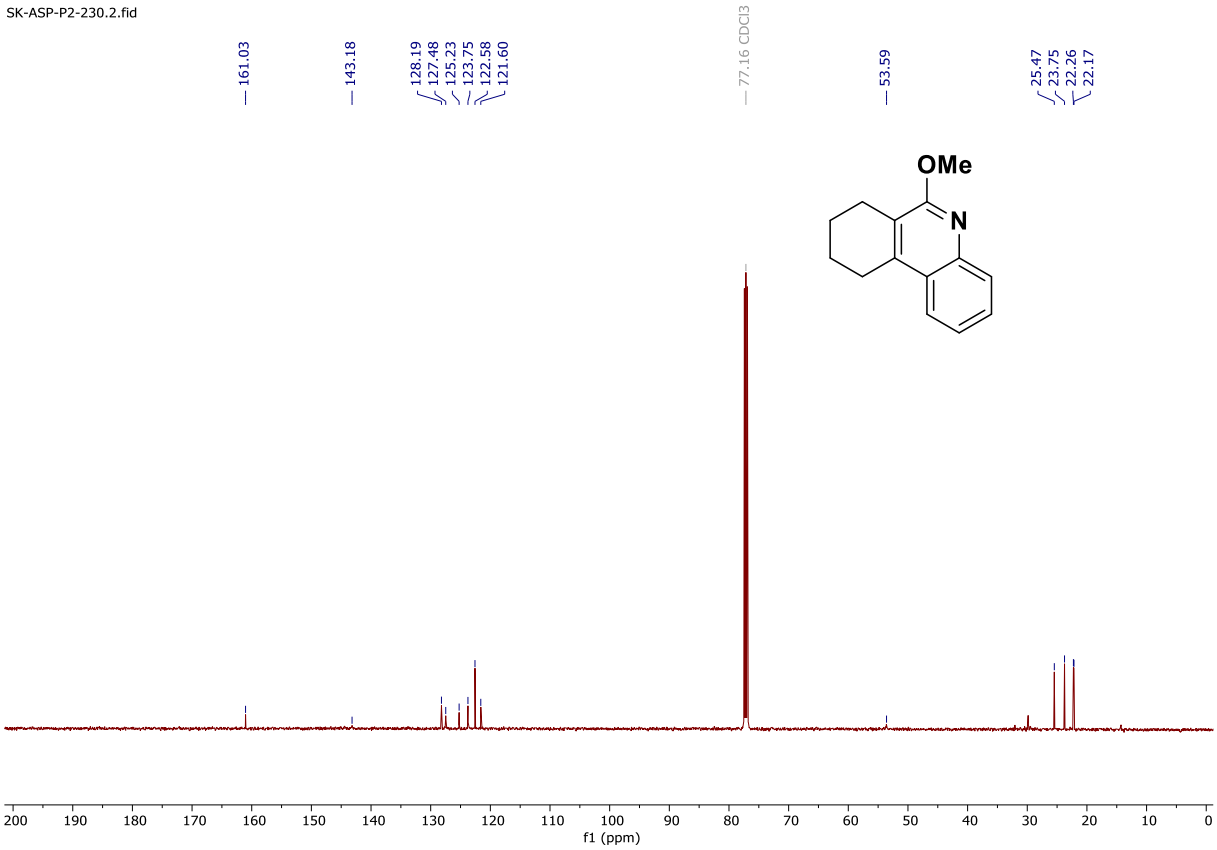
^{13}C{^{1}H} NMR spectrum of 4m in $CDCl_3$ [126 MHz]



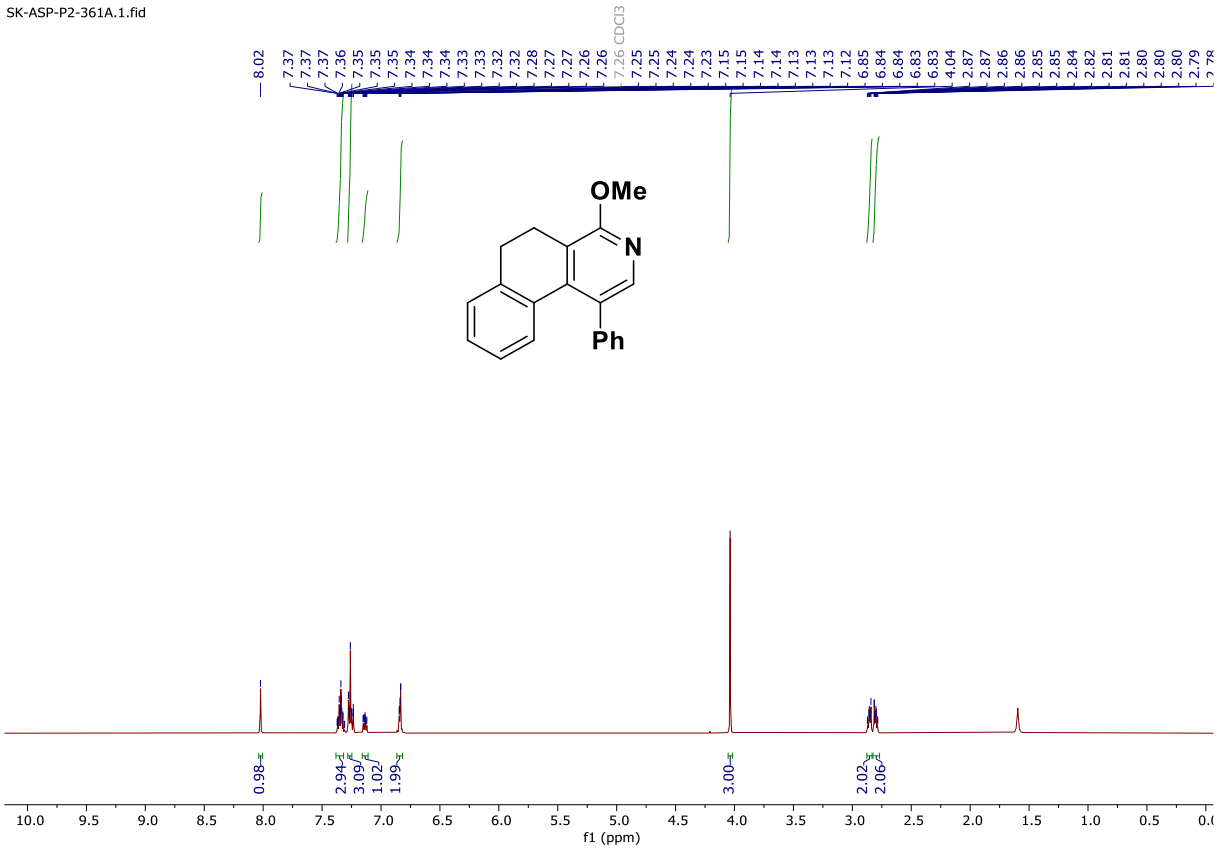
^{1}H NMR spectrum of 4n in $CDCl_3$ [500 MHz]



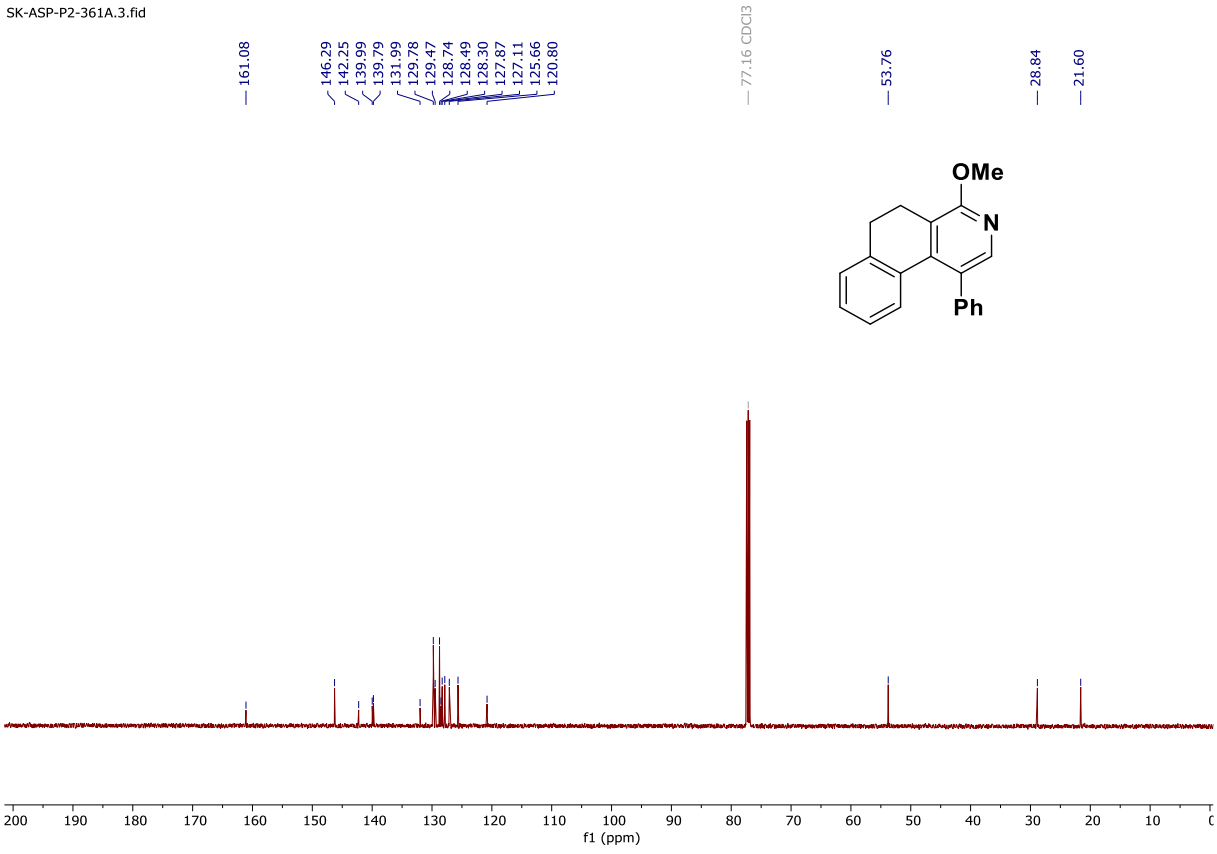
^{13}C{^{1}H} NMR spectrum of 4n in $CDCl_3$ [126 MHz]



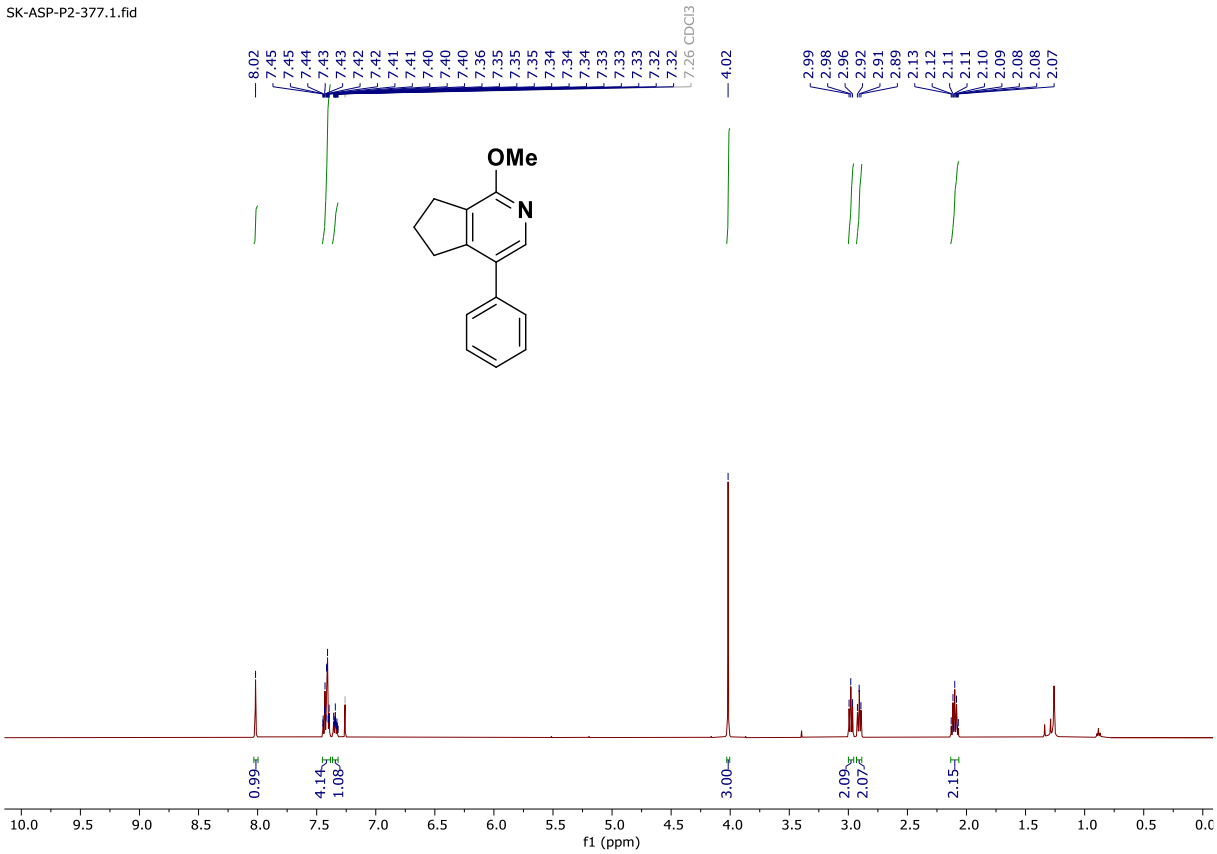
^{1}H NMR spectrum of 4o in $CDCl_3$ [500 MHz]



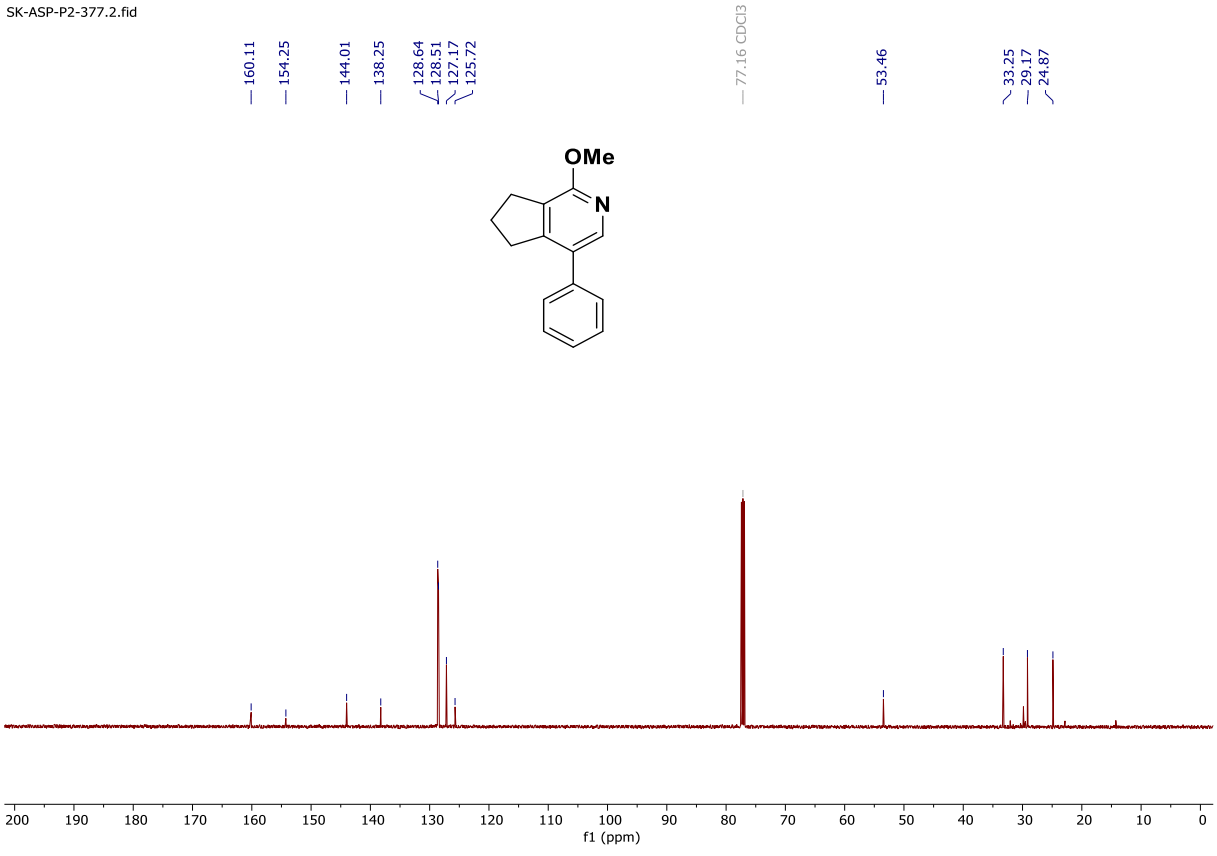
^{13}C{^{1}H} NMR spectrum of 4o in $CDCl_3$ [126 MHz]



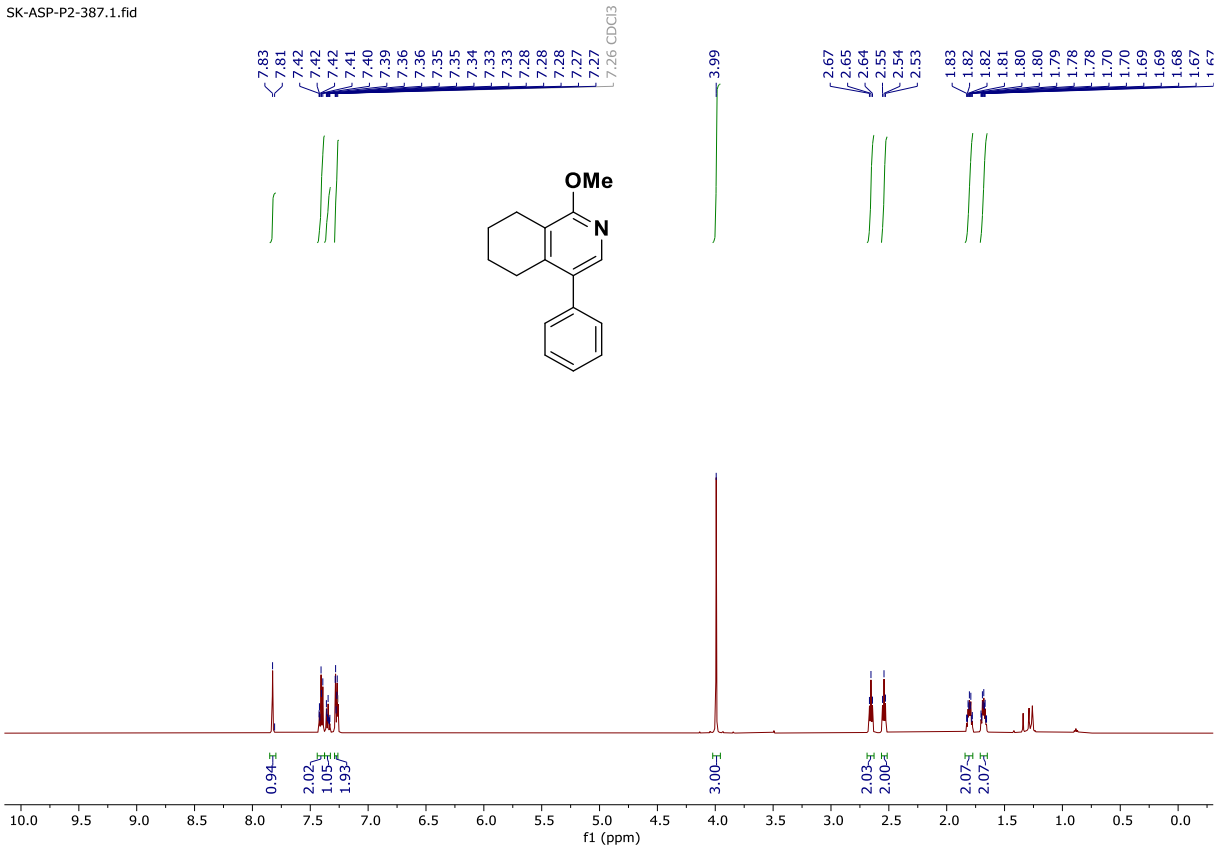
^{1}H NMR spectrum of 4p in $CDCl_3$ [500 MHz]



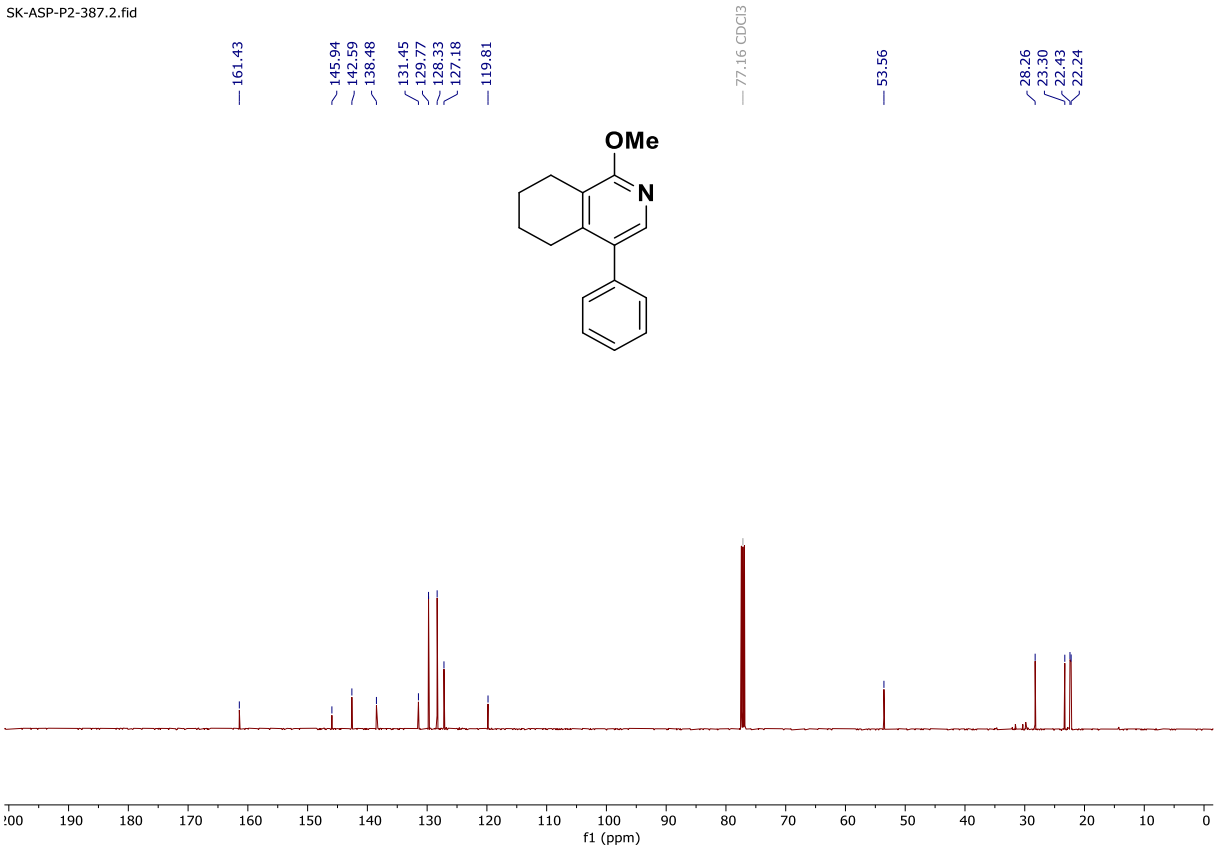
^{13}C{^{1}H} NMR spectrum of 4p in $CDCl_3$ [126 MHz]



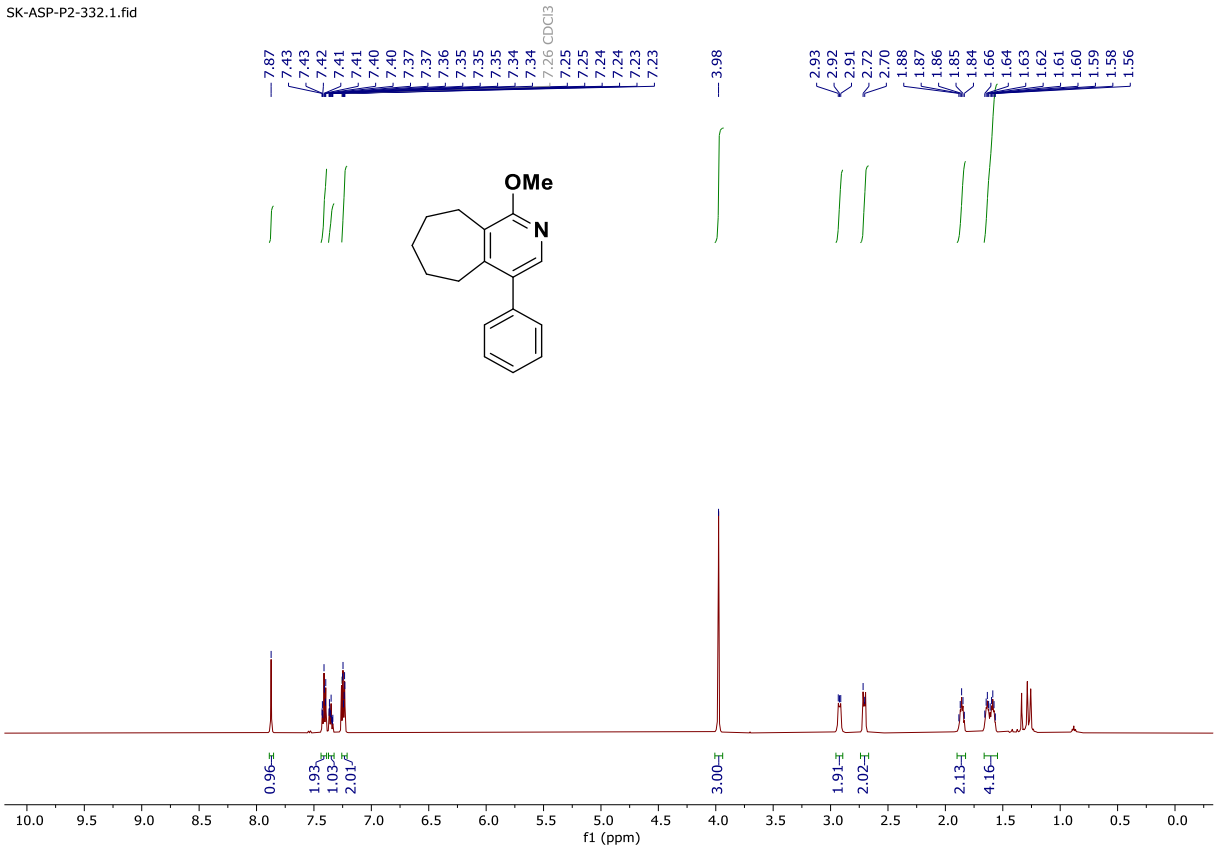
^{1}H NMR spectrum of 4q in $CDCl_3$ [500 MHz]



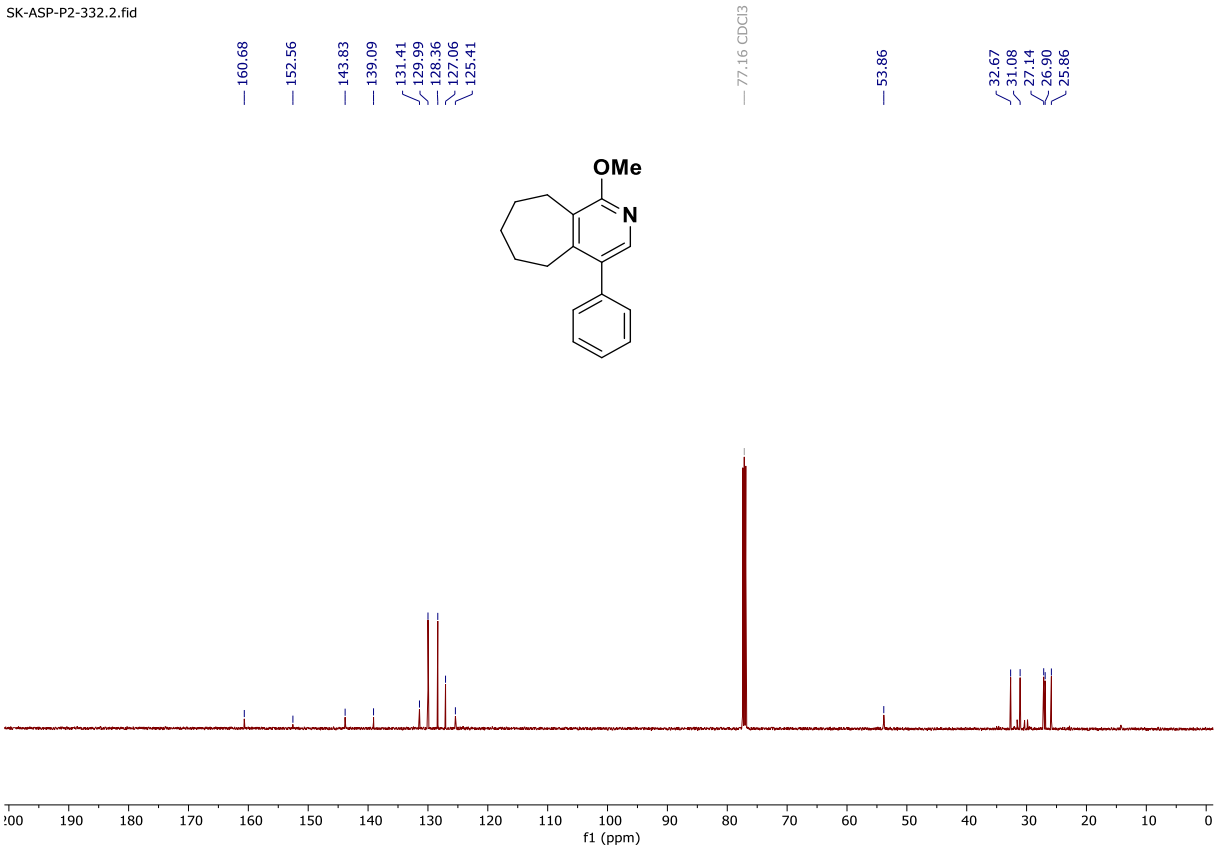
^{13}C{^{1}H} NMR spectrum of 4q in $CDCl_3$ [126 MHz]



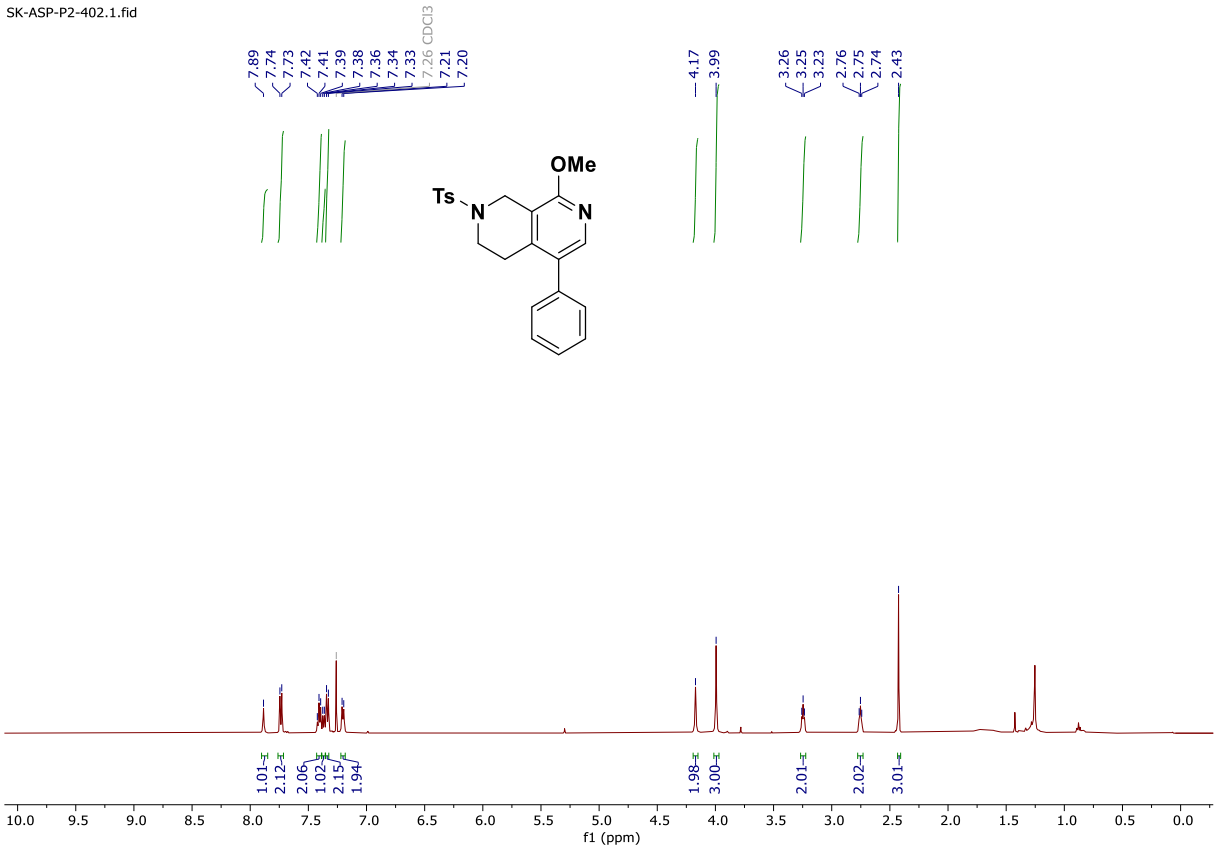
^{1}H NMR spectrum of 4r in $CDCl_3$ [500 MHz]



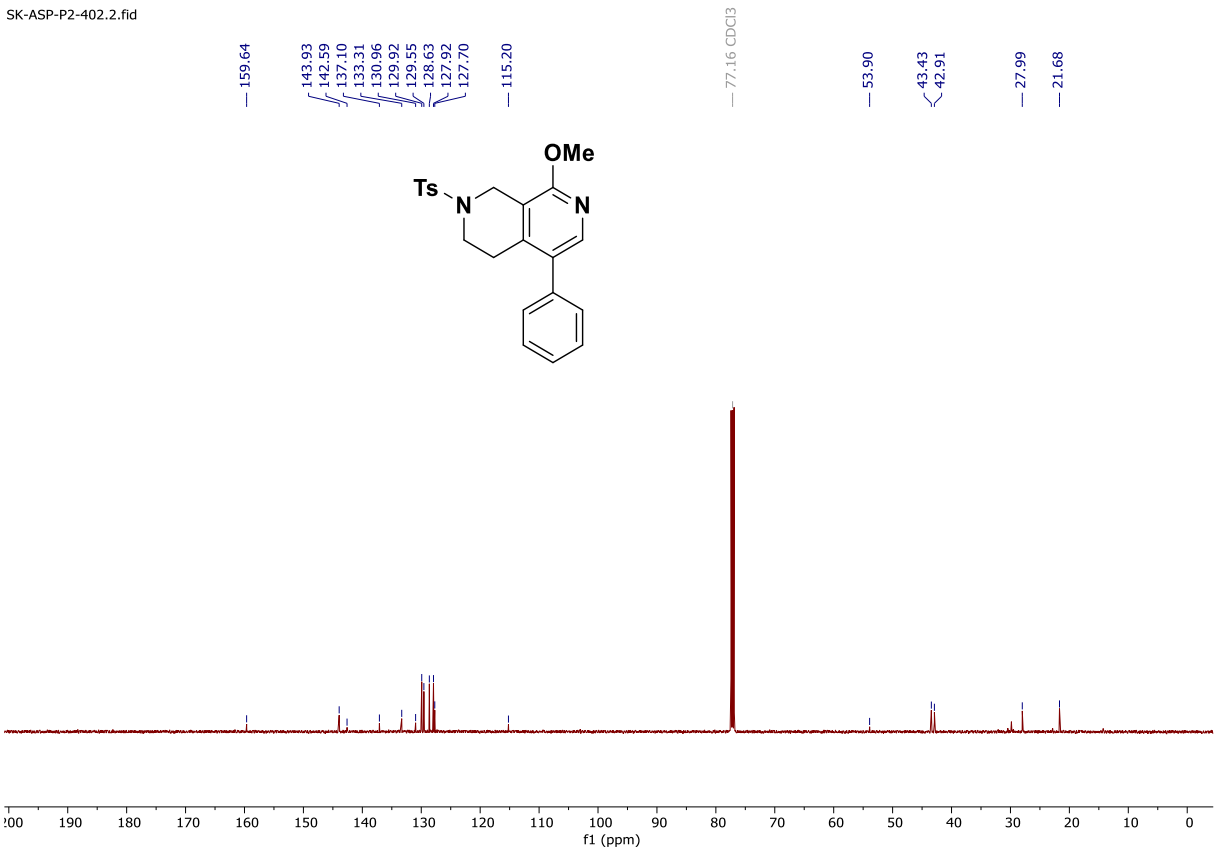
^{13}C{^{1}H} NMR spectrum of 4r in $CDCl_3$ [126 MHz]



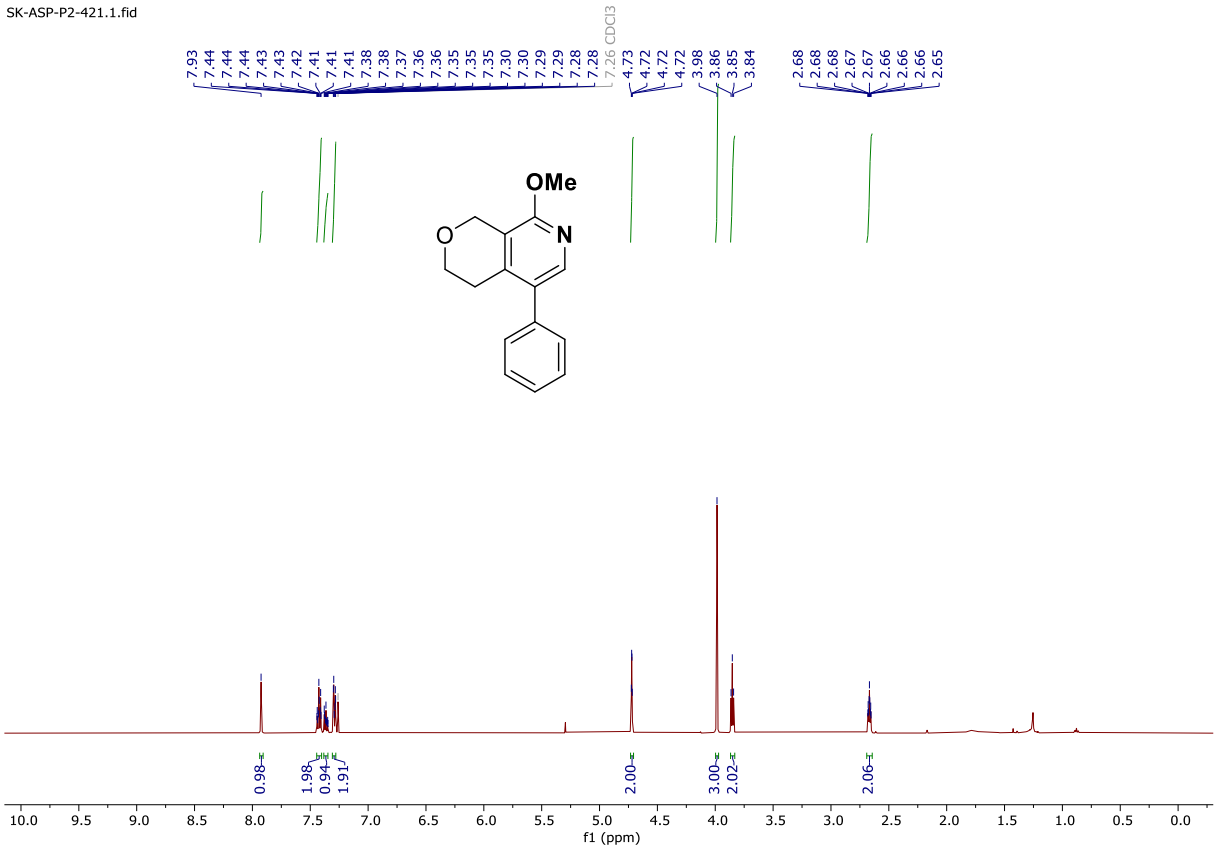
^{1}H NMR spectrum of 4s in $CDCl_3$ [500 MHz]



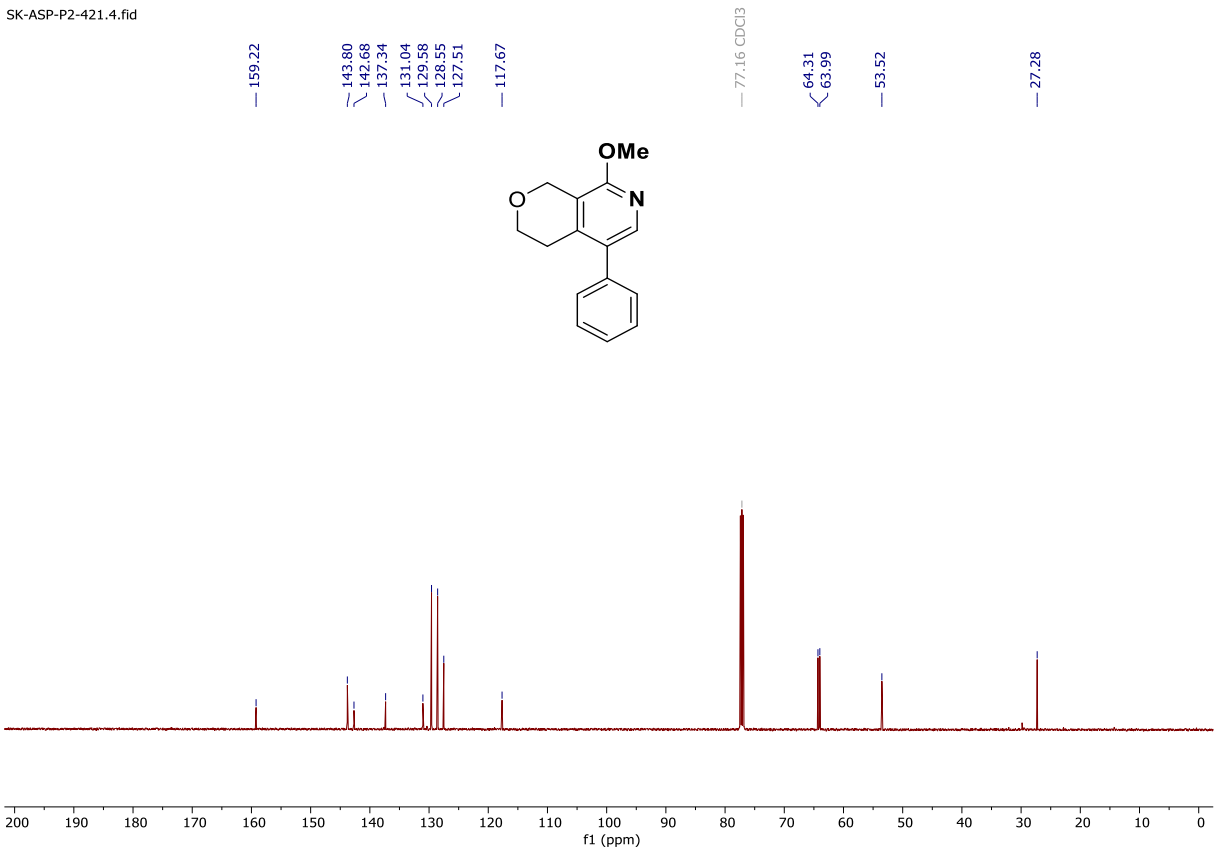
^{13}C{^{1}H} NMR spectrum of 4s in $CDCl_3$ [126 MHz]



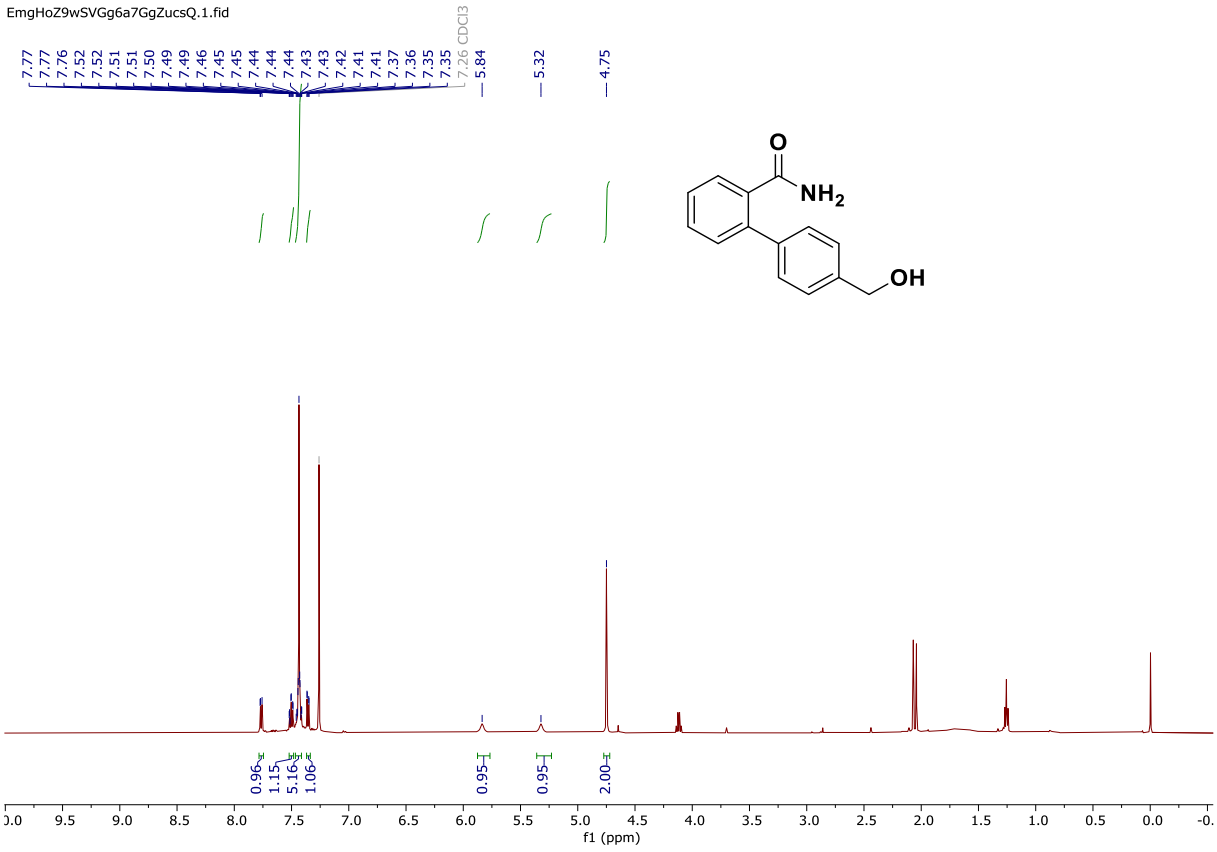
^{1}H NMR spectrum of 4t in $CDCl_3$ [500 MHz]



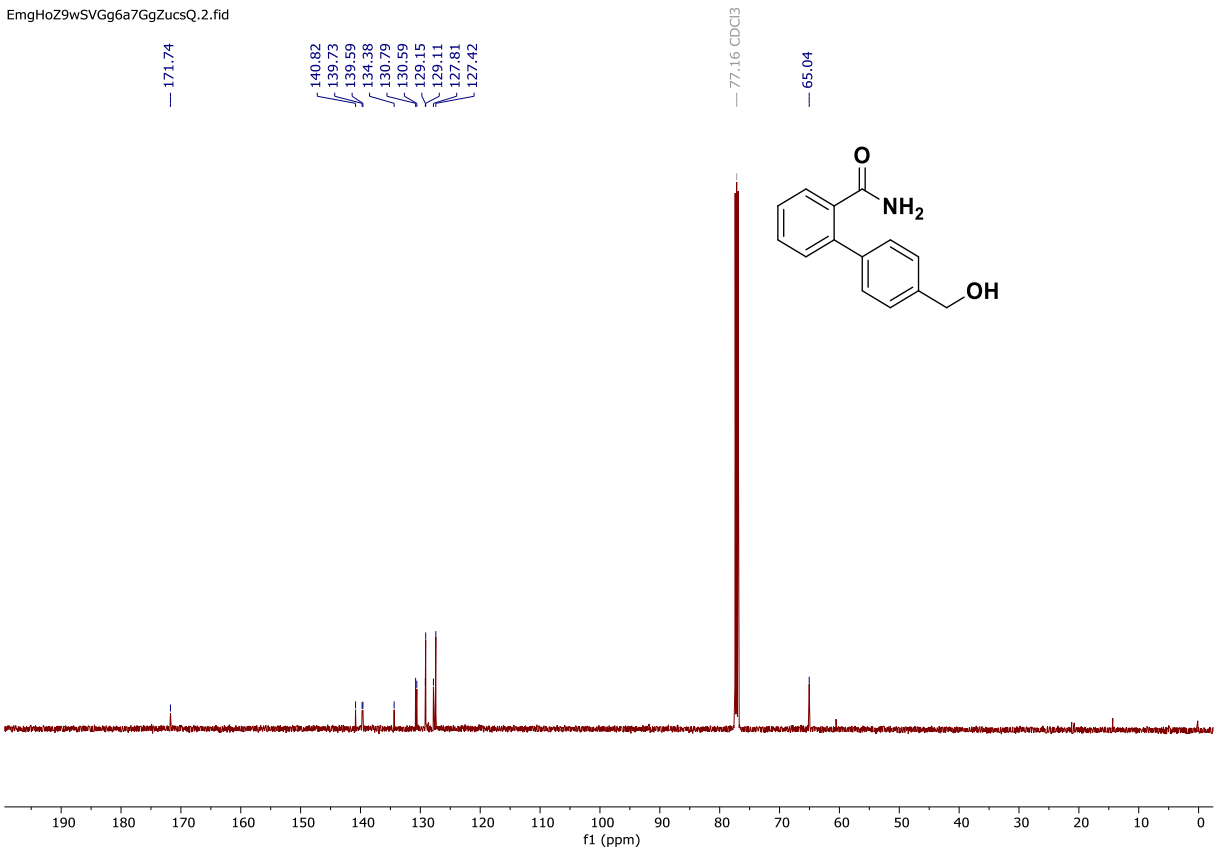
^{13}C{^{1}H} NMR spectrum of 4t in $CDCl_3$ [126 MHz]



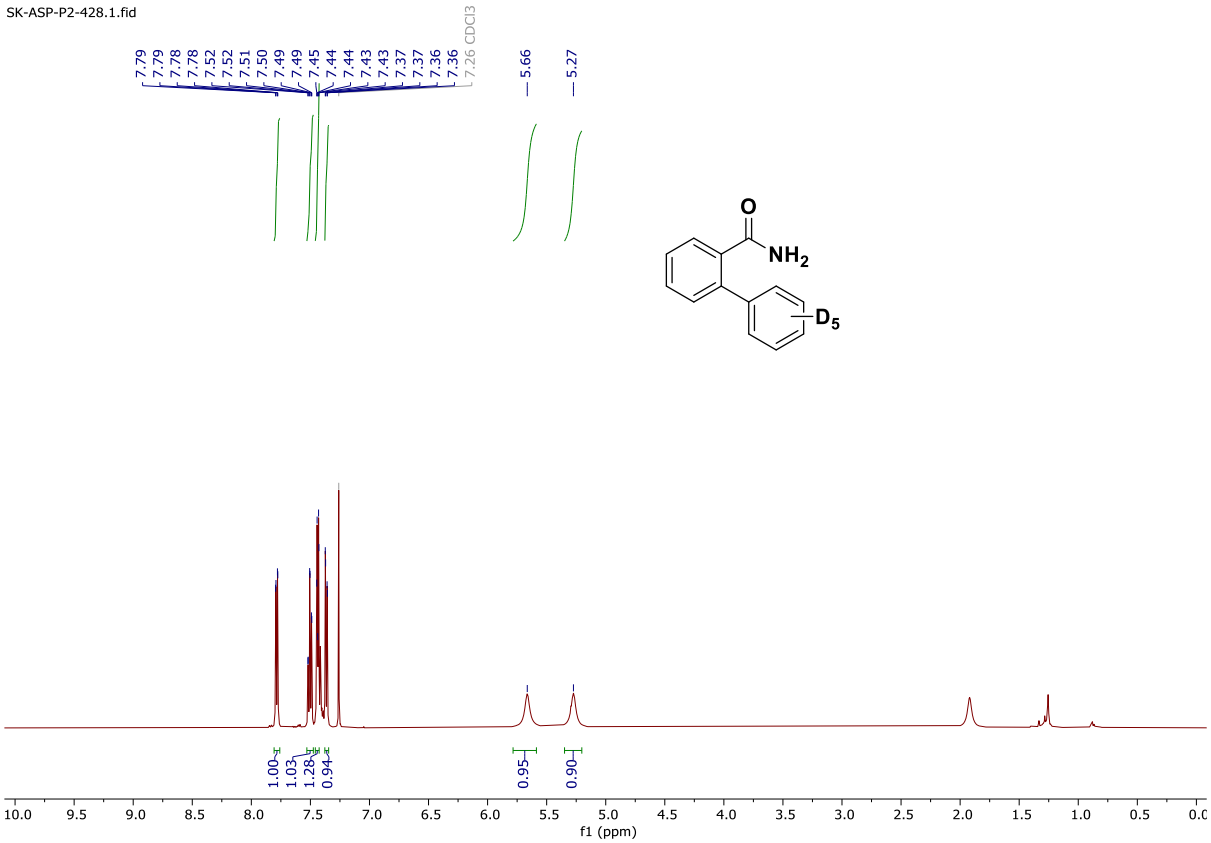
^{1}H NMR spectrum of I55 in $CDCl_3$ [500 MHz]



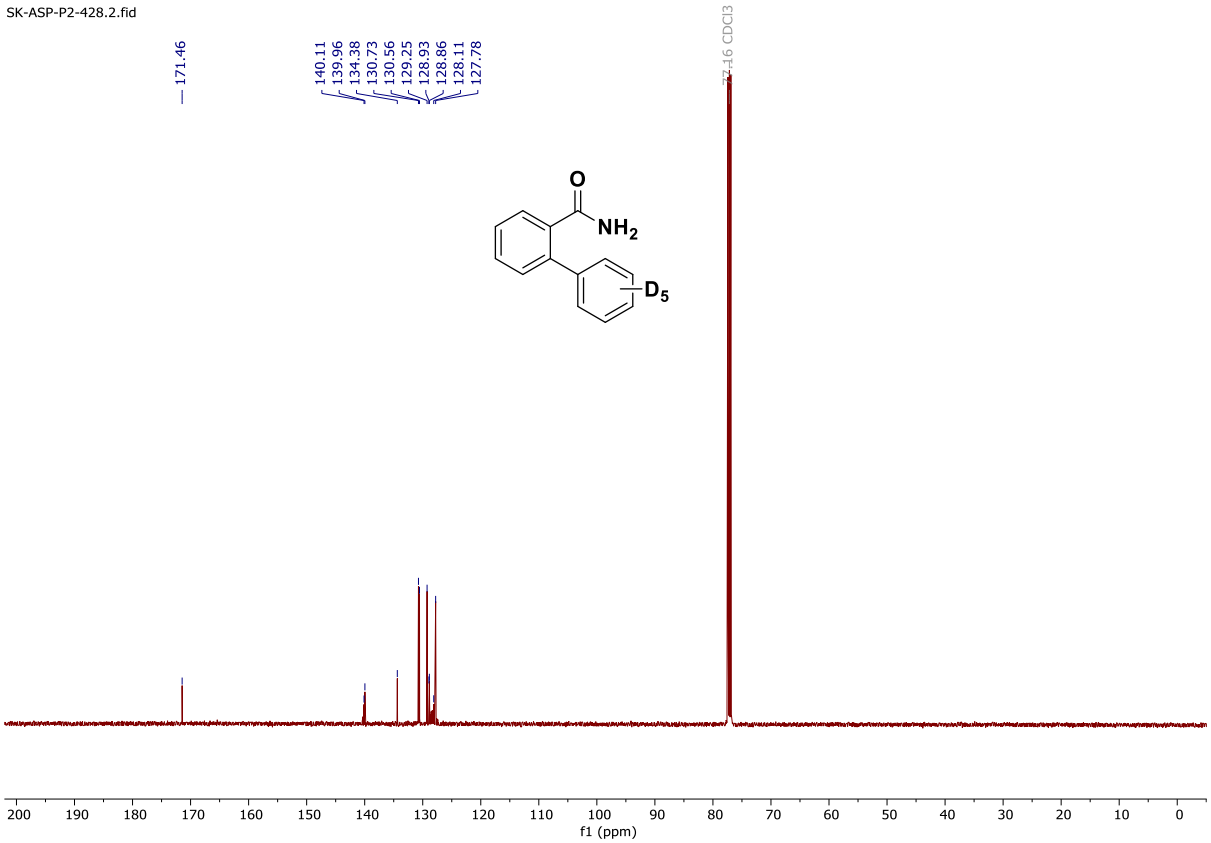
^{13}C{^{1}H} NMR spectrum of I55 in $CDCl_3$ [126 MHz]



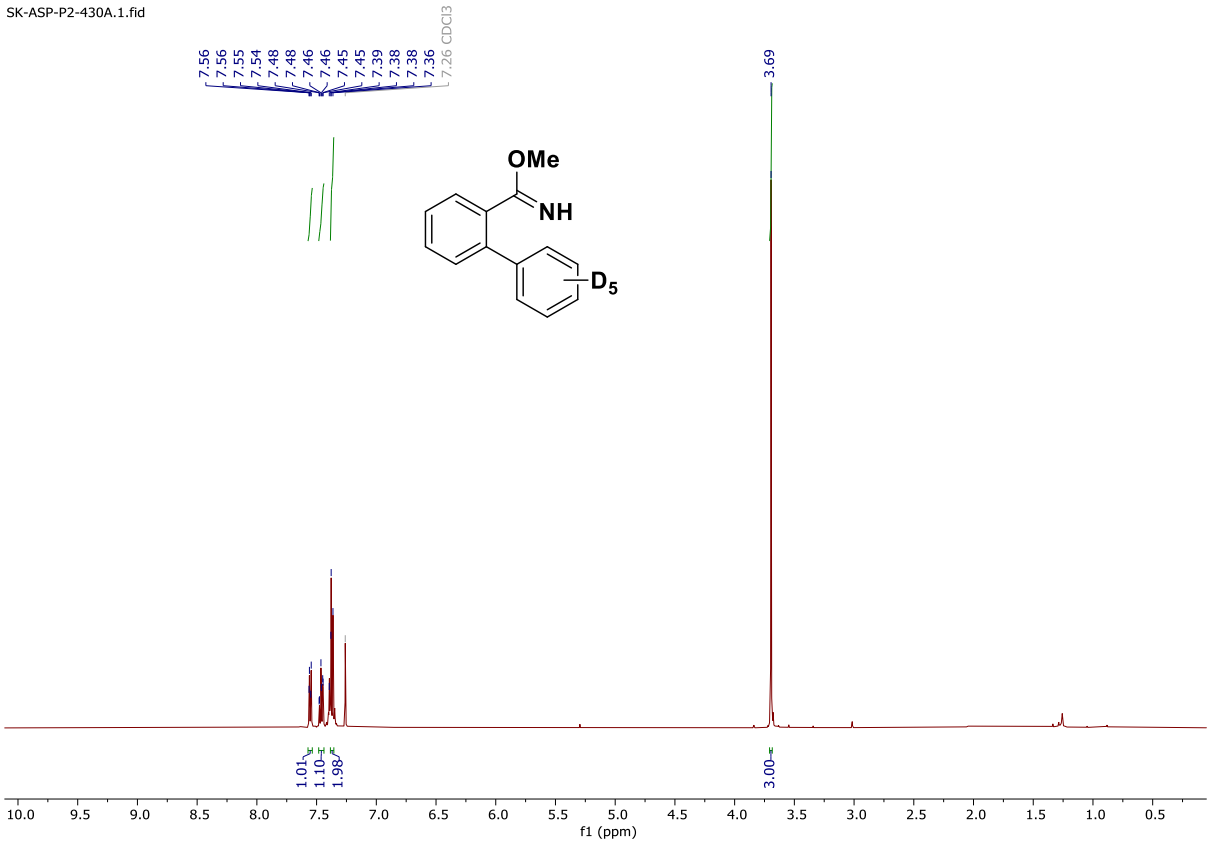
^{1}H NMR spectrum of [D_5]-A in $CDCl_3$ [500 MHz]



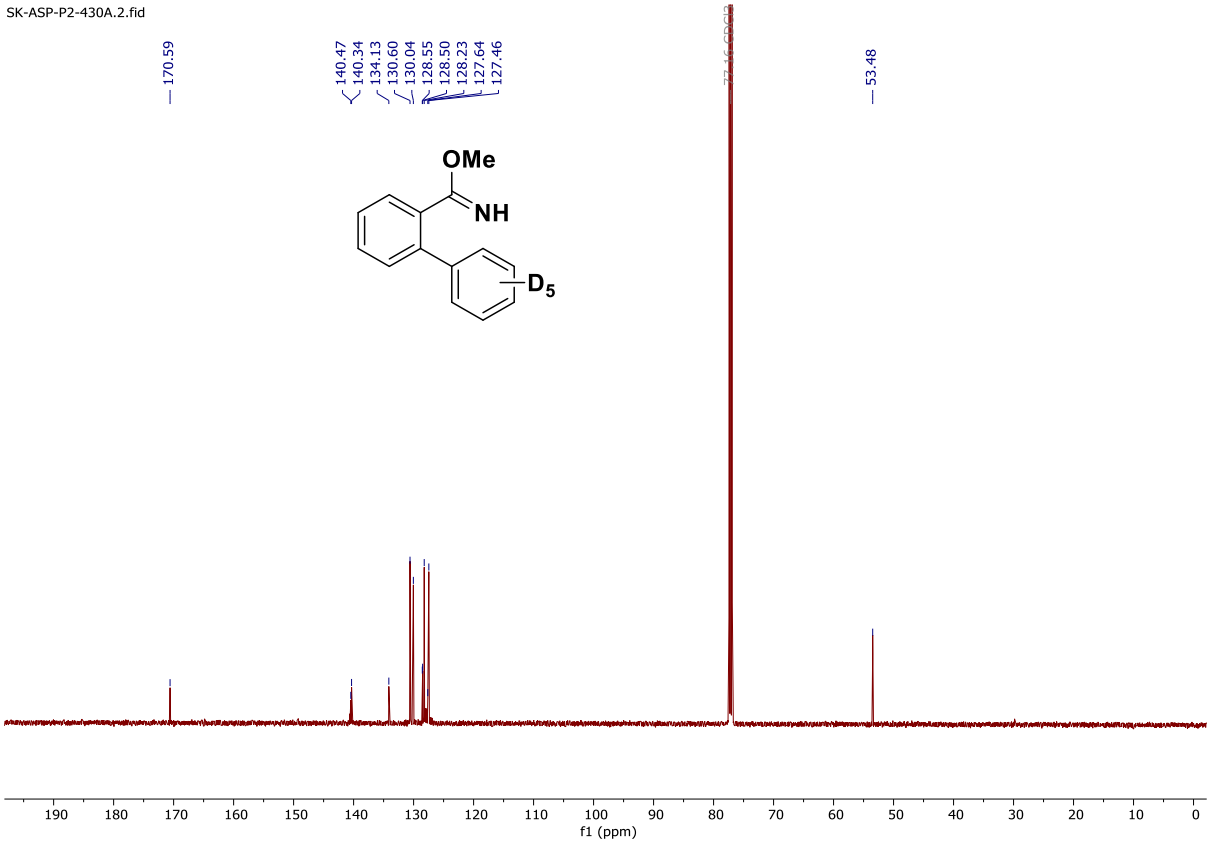
^{13}C{^{1}H} NMR spectrum of [D_5]-A in $CDCl_3$ [126 MHz]



^{1}H NMR spectrum of [D_5]-1a in $CDCl_3$ [500 MHz]

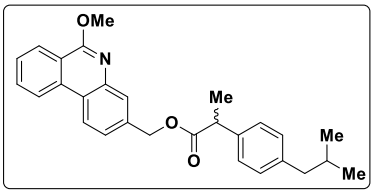


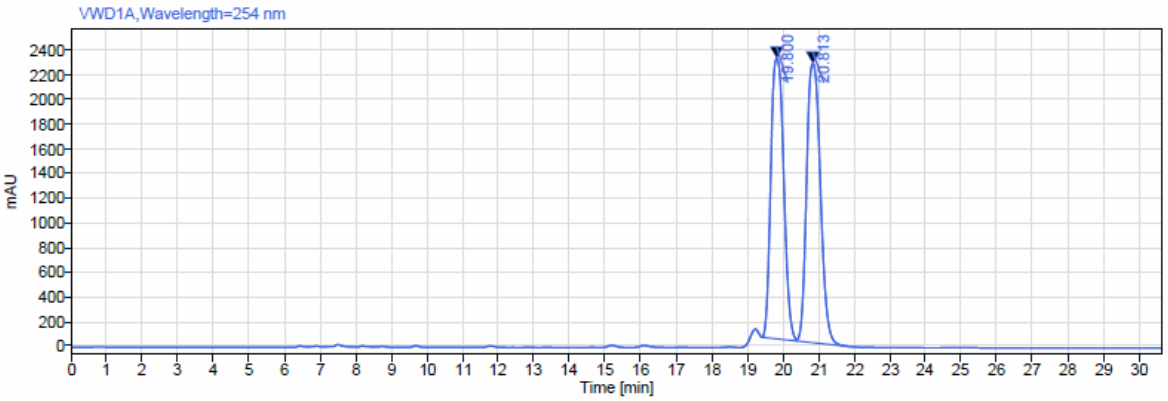
^{13}C{^{1}H} NMR spectrum of [D_5]-1a in $CDCl_3$ [126 MHz]



11. HPLC for compound 2ad

Racemic

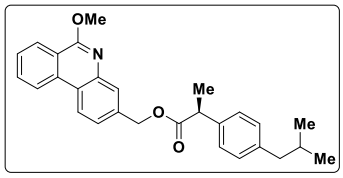


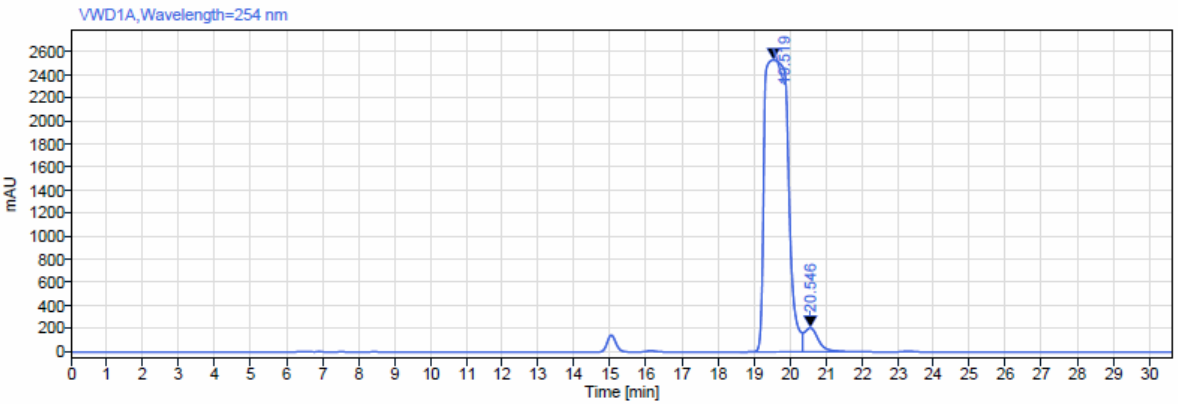


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
19.800	BV	0.98	56928.30	2265.33	48.45	
20.813	VI	1.47	60567.81	2254.69	51.55	
		Sum	**117496.11**			

Chiral





Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
19.519	BV	1.75	114963.00	2529.97	95.38	
20.546	VI	1.17	5568.17	206.33	4.62	
		Sum	**120531.16**			