

Supporting Information

Beyond Directed *ortho* Metalation: Ru-Catalyzed C_{Ar}-OMe Activation/Cross Coupling Reaction by Amide Chelation

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General information

Melting points were obtained on a Fisher Scientific Melting Point Apparatus and are uncorrected. IR spectra were recorded on a BOMEM FT-IR or Varian 1000 FT-IR spectrometers. ^1H and ^{13}C spectra were recorded on Bruker Avance-400 or 500 MHz spectrometers. The chemical shifts of ^1H and ^{13}C NMR signals are quoted relative to internal CHCl_3 ($\delta = 7.26$) and CDCl_3 ($\delta = 77.0$) or tetramethylsilane ($\delta = 0.0$). ^1H NMR data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, etc.), coupling constant (Hz) and relative intensity. ^{13}C NMR data are reported as follows: chemical shift in ppm (δ). The GC-MS analyses were performed on an Agilent 6890 GC coupled with an Agilent 5973 inert MS under EI conditions. High resolution mass spectra were obtained on a GCT Mass Spectrometer (Waters, Micromass) and a QSTAR XL hybrid mass Spectrometer (Applied Biosystems/MDS Sciex).

All Ru-catalyzed experiments were carried out under nitrogen in dried and sealed vials. All Pd-catalyzed Suzuki cross coupling reactions were carried out under a nitrogen atmosphere in sealed vials (not dried). Caution: manipulation of reactants, catalyst and degassed solvent should be performed in a glovebag. The temperatures shown in catalytic reaction conditions are recorded from oil bath. The substrates, *ortho*-methoxy benzamides and boroneopentylates were prepared from commercially available starting materials. All reactions involving alkyllithiums were carried out under an argon atmosphere in oven-dried glassware, using syringe-septum cap techniques. Alkyllithiums were purchased from Sigma-Aldrich Chemicals Co. and titrated biweekly against N-benzylbenzamide.¹ Anhydrous toluene and THF were obtained by treatment under the Pure-Solv SPS-4-4 solvent purification system (Innovative Technology, Inc.) and toluene was degassed before use. The catalysts, $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ and $\text{Pd}(\text{PPh}_3)_4$ were obtained from Strem Chemicals, Inc., USA. All purchased chemicals were used without further purification. Flash column chromatography was carried out using Silica gel 60 (230-400 mesh).

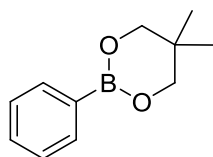
Preparation of starting materials

1. General Procedure A for preparation of boroneopentylates

A THF solution of an organoboronic acid and 2,2-dimethylpropane-1,3-diol (neopentyl glycol) (1.03-1.20 equiv) was refluxed for 40 min under a Dean Stark apparatus, the reaction mixture was cooled and concentrated *in vacuo*. The residue was subjected to flash SiO_2 column chromatography (eluent: EtOAc/hexanes or CH_2Cl_2 /hexanes) to yield the product.

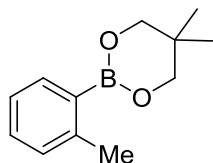
Following the General Procedure A, boroneopentylates were prepared as described below except 5,5-dimethyl-2-(pyridin-3-yl)-1,3,2-dioxaborinane which was purchased from Sigma-Aldrich Chemicals Co.

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane



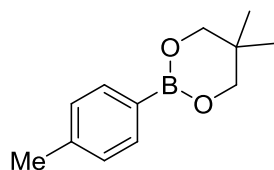
According to General Procedure A and using the following materials: phenylboronic acid (6.22 g, 50 mmol), neopentyl glycol (6.31 g, 60 mmol) and THF (60 mL), the title compound (9.51 g, 99% yield) was obtained as a colorless solid. mp: 62-63 °C (hexanes) (lit² 61-63 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.82 (d, *J* = 6.7 Hz, 2H), 7.44 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 2H), 3.78 (s, 4H), 1.04 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 133.79 (2C), 130.63, 127.54 (2C), 72.29 (2C), 31.86, 21.89 (2C). The physical and spectral data were consistent with those previously reported.²

5,5-Dimethyl-2-(2-methylphenyl)-1,3,2-dioxaborinane



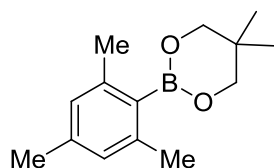
To a solution of 2-methylphenyl bromide (864 mg, 5.0 mmol) in THF (8 mL) at -78 °C was added *n*-BuLi (2.7 mL, 5.3 mmol, 1.94 M in hexanes) slowly. After 5 min, B(O*i*-Pr)₃ (1.3 mL, 5.5 mmol) was added at -78 °C and the cooling bath was removed to allow the mixture to warm to 0 °C. Neopentyl glycol (632 mg, 6.0 mmol) in THF (8 mL) was added at 0 °C. The mixture was allowed to warm to rt and stirred at rt for 30 min before treatment with saturated aq. NH₄Cl (5 mL) and water (10 mL). The resultant mixture was extracted with EtOAc (3 x 20 mL) and the combined organic extract was washed with brine, dried (MgSO₄) and concentrated *in vacuo*. After purification of the residue via flash SiO₂ column chromatography (eluent: EtOAc/hexanes), the title compound (884 mg, 87% yield) was obtained as a colorless oil. ¹H NMR (400 MHz, CDCl₃): δ 7.75 (d, *J* = 7.1 Hz, 1H), 7.30 (t, *J* = 6.8 Hz, 1H), 7.22-7.11 (m, 2H), 3.79 (s, 4H), 2.54 (s, 3H), 1.05 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 143.90, 134.78, 129.99, 129.91, 124.63, 72.23 (2C), 31.61, 22.36, 21.86 (2C). The physical and spectral data were consistent with those previously reported.³

5,5-Dimethyl-2-(4-methylphenyl)-1,3,2-dioxaborinane



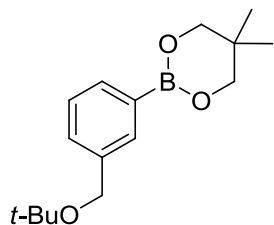
According to General Procedure A and using the following materials: 4-methylphenylboronic acid (0.69 g, 5 mmol), neopentyl glycol (0.63 g, 6 mmol) and THF (25 mL), the title compound (0.90 g, 89% yield) was obtained as a colorless solid. mp: 91-93 °C (hexanes) (lit⁴ 92-95 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, *J* = 7.7 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 3.77 (s, 4H), 2.37 (s, 3H), 1.03 (s, 6H);⁵ ¹³C NMR (101 MHz, CDCl₃): δ 140.64, 133.86 (2C), 128.37 (2C), 72.24 (2C), 31.86, 21.89 (2C), 21.63. The physical and spectral data were consistent with those reported.^{4,5}

2-Mesityl-5,5-dimethyl-1,3,2-dioxaborinane



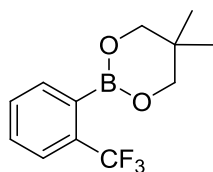
According to General Procedure A and using the following materials: mesitylboronic acid (502 mg, 3.0 mmol), neopentyl glycol (379 mg, 3.6 mmol) and THF (20 mL), the title compound (522 mg, 75% yield) was obtained as a colorless solid. mp: 46-47 °C (hexanes) (lit⁶ 47 °C); ¹H NMR (400 MHz, CDCl₃) δ 6.79 (s, 2H), 3.79 (s, 4H), 2.38 (s, 6H), 2.26 (s, 3H), 1.11 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 140.65 (2C), 137.99, 127.27 (2C), 72.19 (2C), 31.58, 22.21 (2C), 22.12 (2C), 21.14. The physical and spectral data were consistent with those previously reported.⁶

2-(3-(*t*-Butoxymethyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane



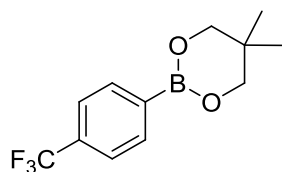
According to General Procedure A and using the following materials: 3-(*t*-butoxymethyl)phenylboronic acid (425 mg, 2.0 mmol), neopentyl glycol (253 mg, 2.4 mmol) and THF (15 mL), the title compound (536 mg, 97% yield) was obtained as a colorless solid. mp: 74-75 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2970, 1478, 1431, 1415, 1377, 1362, 1342, 1320, 1250, 1221, 1195, 1129, 1065, 707 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.76 (s, 1H), 7.70 (d, *J* = 7.3 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 4.45 (s, 2H), 3.77 (s, 4H), 1.30 (s, 9H), 1.03 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 138.79, 132.95, 132.70, 130.06, 127.60, 73.29, 72.25 (2C), 64.27, 31.84, 27.70 (3C), 21.88 (2C); MS EI *m/z* (rel. int.): 276 (*M*⁺, 6), 220 (18), 219 (48), 203 (100), 202 (19), 117 (18), 91 (14), 57 (17), 56 (19); HRMS *m/z* (EI, *M*⁺): calcd. for C₁₆H₂₅BO₃, 276.1897; found 276.1906.

5,5-Dimethyl-2-(2-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane



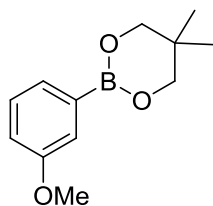
According to General Procedure A and using the following materials: 2-(trifluoromethyl)phenylboronic acid (0.58 g, 3.0 mmol), neopentyl glycol (0.38 g, 3.6 mmol) and THF (25 mL), the title compound (0.71 g, 92% yield) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 6.9 Hz, 1H), 7.65 (d, J = 7.1 Hz, 1H), 7.55-7.37 (m, 2H), 3.80 (s, 4H), 1.07 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 133.87, 133.10 (q, $^2J_{\text{C-F}}$ = 31.0 Hz), 130.67, 129.23, 125.26 (q, $^3J_{\text{C-F}}$ = 4.9 Hz), 124.61 (q, $^1J_{\text{C-F}}$ = 273.2 Hz), 72.62 (2C), 31.76, 21.84 (2C). The physical and spectral data were consistent with those previously reported.⁷

5,5-Dimethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborinane



According to General Procedure A and using the following materials: 4-(trifluoromethyl)phenylboronic acid (0.98 g, 5 mmol), neopentyl glycol (0.63 g, 6 mmol) and THF (25 mL), the title compound (1.21 g, 94% yield) was obtained as a colorless solid. mp: 108-110 °C (EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.91 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 7.8 Hz, 2H), 3.79 (s, 4H), 1.03 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 134.09 (2C), 132.25 (q, $^2J_{\text{C-F}}$ = 31.7 Hz), 124.30 (q, $^1J_{\text{C-F}}$ = 272.2 Hz), 124.14 (q, $^3J_{\text{C-F}}$ = 3.6 Hz, 2C), 72.37 (2C), 31.88, 21.82 (2C). The physical and spectral data were consistent with those previously reported.³

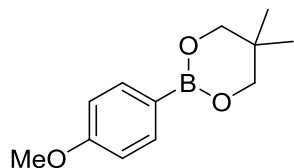
2-(3-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane



According to General Procedure A and using the following materials: 3-methoxyphenylboronic acid (0.78 g, 5 mmol), neopentyl glycol (0.63 g, 6 mmol) and THF (25 mL), the title compound (1.08 g, 98% yield) was obtained as a colorless solid. mp: 68-69 °C (EtOAc/hexanes) (lit⁸ 68-71 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.41 (d, J = 7.1 Hz, 1H), 7.35 (d, J = 2.1 Hz, 1H), 7.29 (t, J

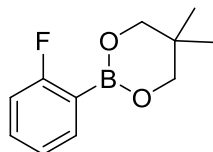
= 7.7 Hz, 1H), 6.99 (dd, J = 7.8, 2.1 Hz, 1H), 3.84 (s, 3H), 3.78 (s, 4H), 1.03 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 159.01, 128.72, 126.23, 117.91, 117.21, 72.29 (2C), 55.13, 31.85, 21.88 (2C). The physical and spectral data were consistent with those previously reported.⁸

2-(4-Methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane



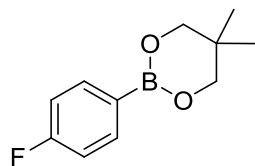
According to General Procedure A and using the following materials: 4-methoxyphenylboronic acid (1.57 g, 10 mmol), neopentyl glycol (1.26 g, 12 mmol) and THF (50 mL), the title compound (2.20 g, 99% yield) was obtained as colorless solid. mp: 55-56 °C (EtOAc/hexanes) (lit⁹ 59-60 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.76 (d, J = 8.5 Hz, 2H), 6.90 (d, J = 8.5 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 4H), 1.02 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 161.69, 135.46, 113.09, 72.19, 54.98, 31.83, 21.87. The physical and spectral data were consistent with those previously reported.⁹

2-(2-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane



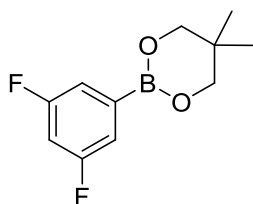
According to General Procedure A and using the following materials: 2-fluorophenylboronic acid (428 mg, 3.0 mmol), neopentyl glycol (379 mg, 3.6 mmol) and THF (20 mL), the title compound (590 mg, 95% yield) was obtained as a colorless solid. mp: 39-40 °C (hexanes) (lit¹⁰ 40 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.75-7.70 (m, 1H), 7.43-7.34 (m, 1H), 7.12 (t, J = 7.3 Hz, 1H), 7.01 (t, J = 9.0 Hz, 1H), 3.80 (s, 4H), 1.04 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 167.09 (d, $^1J_{\text{C-F}}$ = 249.7 Hz), 136.12 (d, $^3J_{\text{C-F}}$ = 8.0 Hz), 132.46 (d, $^3J_{\text{C-F}}$ = 8.8 Hz), 123.42 (d, $^4J_{\text{C-F}}$ = 3.1 Hz), 115.28 (d, $^2J_{\text{C-F}}$ = 24.6 Hz), 72.41 (2C), 31.78, 21.82 (2C). The physical and spectral data were consistent with those previously reported.¹⁰

2-(4-Fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane



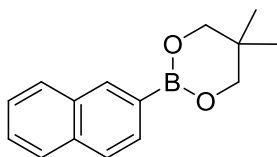
According to General Procedure A and using the following materials: 4-fluorophenylboronic acid (0.98 g, 7.0 mmol), neopentyl glycol (0.76 g, 7.2 mmol) and THF (50 mL), the title compound (1.43 g, 99% yield) was obtained as a colorless solid. mp: 65-66 °C (EtOAc/hexanes) (lit¹¹ 64-67 °C); ¹H NMR (400 MHz, CDCl₃): δ 7.79 (dd, *J* = 8.2, 6.4 Hz, 2H), 7.03 (t, *J* = 8.9 Hz, 2H), 3.76 (s, 4H), 1.02 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 164.81 (d, ¹*J*_{C-F} = 249.0 Hz), 135.96 (d, ³*J*_{C-F} = 8.0 Hz, 2C), 114.56 (d, ²*J*_{C-F} = 20.0 Hz, 2C), 72.28 (2C), 31.86, 21.86 (2C). The physical and spectral data were consistent with those previously reported.¹¹

2-(3,5-Difluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane



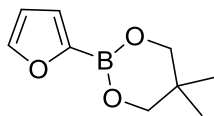
According to General Procedure A and using the following materials: 3,5-difluorophenylboronic acid (484 mg, 3.0 mmol), neopentyl glycol (379 mg, 3.6 mmol) and THF (15 mL), the title compound (678 mg, 99% yield) was obtained as a colorless oil. IR (KBr): ν_{max} 2965, 2939, 2894, 2876, 1588, 1481, 1433, 1379, 1352, 1333, 1256, 1118, 1002, 976, 873, 701, 691 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.34-7.19 (m, 2H), 6.83 (tt, *J* = 9.0, 2.4 Hz, 1H), 3.76 (s, 4H), 1.02 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 162.75 (dd, ^{1,3}*J*_{C-F} = 248.7, 11.0 Hz, 2C), 115.86 (dd, ^{2,4}*J*_{C-F} = 16.9, 5.5 Hz, 2C), 105.82 (t, ²*J*_{C-F} = 25.2 Hz), 72.37 (2C), 31.87, 21.80 (2C); MS EI *m/z* (rel. int.): 226 (*M*⁺, 51), 183 (14), 56 (100); HRMS *m/z* (EI, *M*⁺): calcd. for C₁₁H₁₃BF₂O₂, 226.0977; found 226.0977.

2-(Naphthalen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane



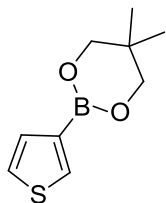
According to General Procedure A and using the following materials: naphthalene-2-ylboronic acid (0.86 g, 5 mmol), neopentyl glycol (0.63 g, 6 mmol) and THF (30 mL), the title compound (1.11 g, 93% yield) was obtained as a colorless solid. mp: 103-104 °C (EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃): δ 8.38 (s, 1H), 7.96-7.76 (m, 4H), 7.57-7.40 (m, 2H), 3.85 (s, 4H), 1.07 (s, 6H); ¹³C NMR (101 MHz, CDCl₃): δ 135.01, 134.83, 132.87, 129.90, 128.63, 127.62, 126.75, 126.58, 125.55, 72.38 (2C), 31.92, 21.91 (2C). The physical and spectral data were consistent with those previously reported.³

2-(Furan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane



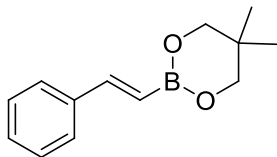
According to General Procedure A and using the following materials: furan-2-ylboronic acid (0.58 g, 5 mmol), neopentyl glycol (0.63 g, 6 mmol) and THF (25 mL), the title compound (0.84 g, 93% yield) was obtained as a colorless solid. mp: 87-88 °C (EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.61 (d, J = 2.0 Hz, 1H), 6.97 (d, J = 3.3 Hz, 1H), 6.41 (dd, J = 3.2, 1.6 Hz, 1H), 3.75 (s, 4H), 1.01 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 146.56, 121.41, 110.13, 72.23 (2C), 32.05, 21.82 (2C). The physical and spectral data were consistent with those previously reported.¹²

2-(Thiophen-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane



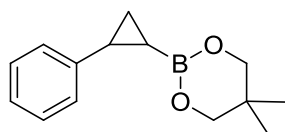
According to General Procedure A and using the following materials: thiophen-3-ylboronic acid (0.94 g, 7.0 mmol), neopentyl glycol (0.88 g, 8.4 mmol) and THF (35 mL), the title compound (1.26 g, 92% yield) was obtained as a pale solid. mp: 96-98 °C (EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3): δ 7.84 (dd, J = 2.6, 0.8 Hz, 1H), 7.38 (dd, J = 4.8, 0.9 Hz, 1H), 7.31 (dd, J = 4.8, 2.7 Hz, 1H), 3.75 (s, 4H), 1.02 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 134.83, 131.62, 124.95, 72.19 (2C), 31.90, 21.89 (2C). The physical and spectral data were consistent with those previously reported.³

(*E*)-5,5-Dimethyl-2-styryl-1,3,2-dioxaborinane



According to General Procedure A and using the following materials: (*E*)-styrylboronic acid (0.91 g, 6.0 mmol), neopentyl glycol (0.70 g, 6.6 mmol) and THF (15 mL), the title compound (1.27 g, 98% yield) was obtained as a colorless solid. mp: 46-47 °C (hexanes) (lit² 41-44°C); ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 7.2 Hz, 2H), 7.40-7.16 (m, 4H), 6.11 (d, J = 18.3 Hz, 1H), 3.69 (s, 4H), 1.00 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 147.09, 137.77, 128.47 (3C), 126.96 (2C), 72.16 (2C), 31.83, 21.84 (2C). The physical and spectral data were consistent with those previously reported.²

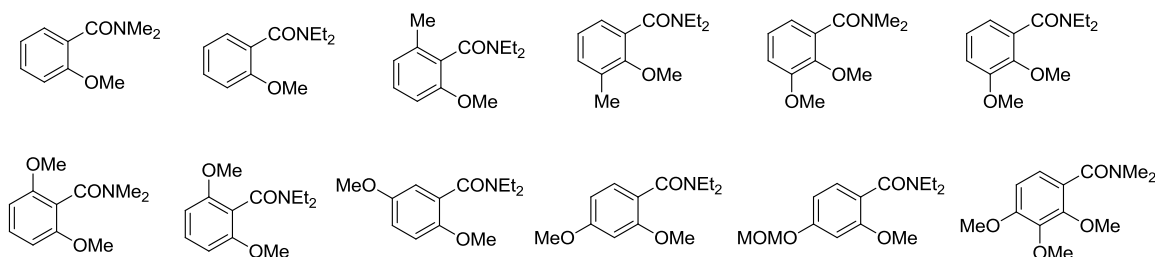
2-(2-Phenylcyclopropyl)-5,5-dimethyl-1,3,2-dioxaborinane



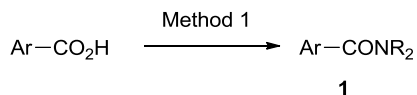
According to General Procedure A and using the following materials: *trans*-2-phenylcyclopropylboronic acid (512 mg, 3.0 mmol), neopentyl glycol (379 mg, 3.6 mmol) and THF (15 mL), the title compound (488 mg, 71% yield) was obtained as a colorless oil. IR (KBr): ν_{max} 2962, 2932, 2886, 1477, 1418, 1397, 1341, 1286, 1256, 1232, 1197, 1089, 765, 697 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.22 (t, J = 7.4 Hz, 2H), 7.16-6.99 (m, 3H), 3.58 (s, 4H), 2.03 (dt, J = 8.0, 5.3 Hz, 1H), 1.10 (ddd, J = 8.0, 6.9, 3.5 Hz, 1H), 1.02-0.87 (m, 7H), 0.18 (ddd, J = 9.7, 6.8, 5.5 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 143.95, 128.15 (2C), 125.57 (2C), 125.27, 72.07 (2C), 31.77, 21.78 (2C), 21.56, 14.74; MS EI m/z (rel. int.): 230 (M^+ , 100), 229 (17), 157 (18), 144 (17), 143 (12), 130 (13), 129 (14), 117 (23), 116 (72), 115 (23); HRMS m/z (EI, M^+): calcd. for $\text{C}_{14}\text{H}_{19}\text{BO}_2$, 230.1478; found 230.1479.

2. Procedures for preparation of *ortho*-methoxy benzamides 1

1) From 2-MeO benzoic acids:

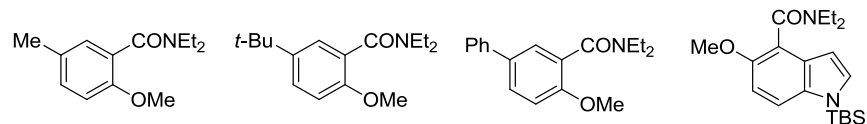


The above starting materials **1** were prepared by using Method 1 below.

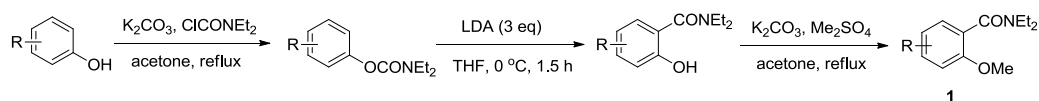


Method 1: To a suspension of a carboxylic acid substrate (1 equiv) in toluene at rt was added SOCl_2 (2 equiv) slowly. Then, DMF (0.05 equiv) was added. The mixture was stirred at rt for 0.5-1 h. After concentration *in vacuo*, the residue was dissolved in CH_2Cl_2 and cooled to 0 $^\circ\text{C}$. After addition of Et_3N (1.2 equiv)/ HNMe_2 (1.3 equiv) or Et_3N (2.5 equiv)/ $\text{HNMe}_2\cdot\text{HCl}$ (1.3 equiv) at 0 $^\circ\text{C}$, the resulting mixture was warmed to rt and stirred at rt for additional 0.5 h. Then, the reaction mixture was quenched by H_2O and the whole was extracted with EtOAc or ether. The combined organic extract was washed with brine, dried (MgSO_4) and concentrated *in vacuo*. The residue was subjected to flash SiO_2 column chromatography (eluent: EtOAc/hexanes) to yield the target compound.

2) via anionic *ortho* Fries rearrangement:



The above starting materials **1** were prepared via anionic *ortho* Fries rearrangement (Method 2) as shown below.



Method 2: A mixture of a phenol (1 equiv), K_2CO_3 (1.5 equiv) and $ClCONEt_2$ (1.2 equiv) in acetone was refluxed overnight. Cooled to rt, the reaction mixture was filtered. After concentration of the filtrate *in vacuo*, the residue was dissolved in THF. Then, LDA (3 equiv) was added at 0 °C slowly. After stirred at 0 °C for 1.5 h, the reaction mixture was quenched by saturated NH_4Cl solution, acidified by 1 N HCl and extracted by EtOAc. After concentration *in vacuo*, the residue was dissolved in acetone. Then, K_2CO_3 (1.5 equiv) and Me_2SO_4 (1.2 equiv) was added at rt respectively. The resulting mixture was refluxed overnight. Cooled to rt, the reaction mixture was filtered. After concentration of the filtrate *in vacuo*, the residue was subjected to flash SiO_2 column chromatography (eluent: EtOAc/hexanes) to yield the target compound.

Control experiments

Following the General Procedure B shown in the next section, the results were obtained as listed in the table below.

Entry	Amide	Time (h)	Product	Yield (%) ^a
1		20		96
2		85	no reaction	— ^b
3		85		7 ^c

^a Yields of isolated and purified products, ^b Starting amide recovered (98%), ^c Starting amide recovered (88%).

General Procedure B for products

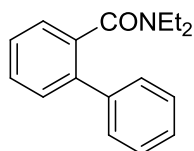
General Procedure B for synthesis of *ortho*-substituted benzamides on 0.2 to 0.5 mmol scale.

A solution of *ortho*-anisamide (1 equiv), substituted boroneopentylate (1.5 equiv), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (4 mol%) in toluene (0.3-1 M) was heated at 125-135 °C (oil bath temperature) in a sealed vial for 20 h. The reaction mixture was cooled to rt and concentrated *in vacuo*. The residue was purified by flash SiO_2 column chromatography (eluent: EtOAc/hexanes). Caution: manipulation of reactants, catalyst and degassed solvent should be performed in a glovebox.

Experimental data of products

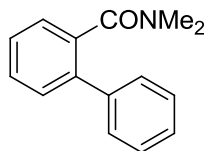
Amide-directed C-OMe activation of benzamides/C-C bond formation. Synthesis of compounds 2a-r in Table 3 and 2v-2aj in Table 4.

N,N-Diethyl-2-phenylbenzamide (2a)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (87 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2a** (73 mg, 96% yield) was obtained as a yellow oil. ^1H NMR (500 MHz, CDCl_3): δ 7.50-7.45 (m, 2H), 7.45-7.28 (m, 7H), 3.80-3.68 (m, 1H), 3.05-2.82 (m, 2H), 2.69-2.57 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 3H), 0.72 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.49, 139.78, 138.33, 136.34, 129.36, 128.87, 128.83 (2C), 128.24 (2C), 127.50, 127.48, 126.94, 42.18, 38.26, 13.32, 11.89. The physical and spectral data were consistent with those previously reported.¹³

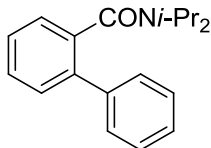
N,N-Dimethyl-2-phenylbenzamide (2b)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-dimethyl-2-methoxybenzamide (54 mg, 0.30 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (87 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and

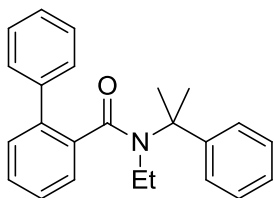
toluene (0.4 mL), the title compound **2b** (62 mg, 92% yield) was obtained as a light yellow oil. ^1H NMR (400 MHz, CDCl_3) δ ppm 7.53-7.29 (m, 9H), 2.84 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ ppm 171.27, 139.90, 138.63, 135.73, 129.27, 129.26, 128.44 (2C), 128.33 (2C), 127.65, 127.55, 127.37, 37.91, 34.49. The physical and spectral data were consistent with those previously reported.¹⁴

N,N-Diisopropyl-2-phenylbenzamide (2c)

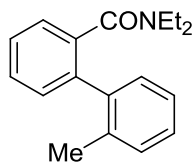


According to General Procedure B and using the following materials refluxed in 20 h: N,N-diisopropyl-2-methoxybenzamide (118 mg, 0.5 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (114 mg, 0.6 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 4 mol%) and toluene (1 mL), the title compound **2c** (46 mg, 33% yield) was obtained as a light yellow solid. mp 107-109 °C (EtOAc/hexanes) (lit¹⁵ 107-108 °C); ^1H NMR (400 MHz, CDCl_3) δ ppm 7.60-7.52 (m, 2H), 7.45-7.27 (m, 7H), 3.43 (sept., $J = 6.7$ Hz, 1H), 3.22 (sept., $J = 6.8$ Hz, 1H), 1.52 (d, $J = 6.8$ Hz, 3H), 1.28 (d, $J = 6.8$ Hz, 3H), 0.89 (d, $J = 6.6$ Hz, 3H), 0.33 (d, $J = 6.6$ Hz, 3H);¹⁵ ^{13}C NMR (101 MHz, CDCl_3) δ ppm 170.24, 139.80, 137.93, 137.67, 129.30 (2C), 129.20, 128.42, 128.23 (2C), 127.53, 127.47, 126.54, 50.47, 45.53, 20.79, 20.70, 19.44, 19.39. The physical and spectral data were consistent with those reported.¹⁵

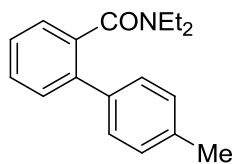
N-Ethyl-N-cumyl-2-phenylbenzamide (2d)



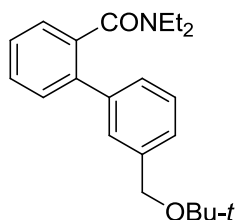
According to General Procedure B and using the following materials refluxed in 20 h: N-ethyl-N-cumyl-2-methoxybenzamide (45 mg, 0.15 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (43 mg, 0.23 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (6 mg, 4 mol%) and toluene (0.3 mL), the title compound **2d** (26 mg, 50% yield) was obtained as a pale solid. mp 121-122 °C (EtOAc/hexanes); IR (KBr) ν_{max} 2980, 1638, 1395, 1287, 748, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.56-7.28 (m, 9H), 7.27-7.18 (m, 2H), 7.15 (t, $J = 6.7$ Hz, 1H), 7.01 (d, $J = 6.5$ Hz, 2H), 3.05 (m, 2H), 1.65 (s, 3H), 1.61 (s, 3H), 0.86 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ ppm 170.99, 148.43, 140.16, 138.02, 137.94, 129.63, 129.36, 128.38, 128.36, 128.05, 127.41, 127.15, 127.09, 125.69, 124.32, 61.74, 41.30, 29.55, 26.91, 16.61. MS EI m/z (rel. int.) 343 (M^+ , 7), 238 (25), 224 (75), 181 (100), 153 (17), 152 (25), 119 (20); HRMS m/z (EI, M^+) calcd for $\text{C}_{24}\text{H}_{25}\text{NO}$, 343.1936, found 343.1935.

N,N-Diethyl-2-(*o*-tolyl)benzamide (2e)

According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (42 mg, 0.2 mmol), 2-(2-methylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (61 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2e** (44 mg, 82% yield) was obtained as a yellow solid. mp: 64-65 °C (EtOAc/hexanes) (lit¹⁶ 67-68 °C); ^1H NMR (400 MHz, CDCl_3): δ 7.62-6.86 (m, 8H), 4.02-3.42 (m, 1H), 3.40-2.44 (m, 3H), 2.22 (s, 3H), 1.14-0.51 (m, 6H) (atropisomers involved¹⁷); ^{13}C NMR (101 MHz, CDCl_3): δ 170.03, 137.14 (brs), 130.69 (brs), 130.22 (brs), 130.02, 128.13 (brs), 127.61, 127.32, 126.38 (brs), 125.07 (brs), 42.26 (brs), 37.80, 20.22, 13.65, 11.73 (atropisomers involved¹⁷). The physical and spectral data were consistent with those reported.¹⁶

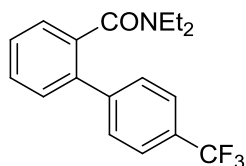
N,N-Diethyl-2-(4-methylphenyl)benzamide (2f)

According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(4-methylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (92 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2f** (77 mg, 96% yield) was obtained as a yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.31 (m, 6H), 7.17 (d, J = 7.7 Hz, 2H), 3.80-3.64 (m, 1H), 3.14-2.84 (m, 2H), 2.76-2.55 (m, 1H), 2.36 (s, 3H), 0.92 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.63, 138.31, 137.21, 136.89, 136.27, 129.33, 128.92 (2C), 128.82, 128.66 (2C), 127.21, 126.95, 42.21, 38.31, 21.08, 13.34, 11.96. The physical and spectral data were consistent with those previously reported.¹⁸

N,N-Diethyl-2-(3-*t*-butoxymethylphenyl)benzamide (2g)

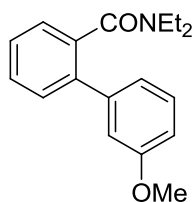
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(3-*t*-butoxymethylphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (124 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2g** (95 mg, 93% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2973, 2933, 1630, 1470, 1459, 1431, 1363, 1290, 1195, 1090, 1071, 757 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.39 (m, 3H), 7.38-7.31 (m, 5H), 4.46 (s, 2H), 3.81-3.65 (m, 1H), 3.07-2.90 (m, 2H), 2.74-2.58 (m, 1H), 1.28 (s, 9H), 0.90 (t, $J = 7.1$ Hz, 3H), 0.74 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.50, 140.00, 139.64, 138.43, 136.29, 129.46, 128.82, 128.24, 127.69, 127.58, 127.39, 126.93, 126.47, 73.41, 63.94, 42.33, 38.38, 27.64 (3C), 13.39, 11.99; MS EI m/z (rel. int.): 339 (M^+ , 15), 209 (24), 194 (45), 193 (100), 181 (48), 152 (30), 72 (39); HRMS m/z (EI, M^+): calcd. for $\text{C}_{22}\text{H}_{29}\text{NO}_2$, 339.2198; found 339.2205.

N,N-Diethyl-2-((4-trifluoromethyl)phenyl)benzamide (2h)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-((4-trifluoromethyl)phenyl)-5,5-dimethyl-1,3,2-dioxaborinane (116 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2h** (86 mg, 90% yield) was obtained as a light yellow solid. mp: 81-82 $^{\circ}\text{C}$ (EtOAc/hexanes); IR (KBr): ν_{max} 2977, 1628, 1430, 1326, 1290, 1165, 1125, 1109, 1069, 767 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.68-7.57 (m, 4H), 7.51-7.33 (m, 4H), 3.83-3.62 (m, 1H), 3.13-2.83 (m, 2H) 2.77-2.58 (m, 1H), 0.88 (t, $J = 7.1$ Hz, 3H), 0.78 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 169.99, 143.39, 136.88, 136.41, 129.70 (q, $^2J_{\text{C-F}} = 32.7$ Hz), 129.36, 129.20 (2C), 129.08, 128.32, 126.96, 125.17 (q, $^3J_{\text{C-F}} = 3.7$ Hz, 2C), 124.13 (q, $^1J_{\text{C-F}} = 271.9$ Hz), 42.29, 38.37, 13.42, 11.85; MS EI m/z (rel. int.): 321 (M^+ , 31), 320 (52), 249 (100), 201 (33), 152 (18); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{18}\text{F}_3\text{NO}$, 321.1340; found 321.1334.

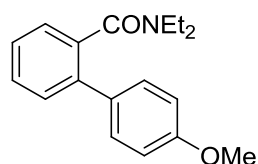
N,N-Diethyl-2-(3-methoxyphenyl)benzamide (2i)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(3-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (91 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%)

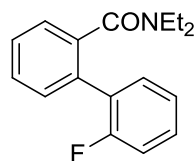
and toluene (0.4 mL), the title compound **2i** (79 mg, 93% yield) was obtained as a light yellow oil. IR (KBr): $\nu_{\max}$ 2972, 2935, 1627, 1602, 1581, 1464, 1429, 1318, 1291, 1221, 1094, 1053, 783, 761, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.32 (m, 4H), 7.27 (t, J = 8.1 Hz, 1H), 7.10-6.99 (m, 2H), 6.87 (dd, J = 8.2, 2.4 Hz, 1H), 3.81 (s, 3H), 3.78-3.68 (m, 1H), 3.09-2.89 (m, 2H), 2.74-2.59 (m, 1H), 0.90 (t, J = 7.1 Hz, 3H), 0.75 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.45, 159.35, 141.16, 138.23, 136.35, 129.26, 129.24, 128.82, 127.56, 126.91, 121.21, 114.11, 113.44, 55.22, 42.24, 38.26, 13.38, 11.92; MS EI m/z (rel. int.): 283 (M^+ , 46), 282 (45), 211 (100), 168 (18), 72 (17); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572; found 283.1574.

N,N-Diethyl-2-(4-methoxyphenyl)benzamide (**2j**)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (99 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2j** (83 mg, 98% yield) was obtained as light yellow solid. mp: 46-47 $^{\circ}\text{C}$ (EtOAc/hexanes); IR (KBr): $\nu_{\max}$ 2973, 2935, 1626, 1518, 1485, 1458, 1428, 1289, 1244, 1180, 1035, 836, 764 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.46-7.29 (m, 6H), 6.90 (d, J = 8.8 Hz, 2H), 3.81 (s, 3H), 3.78-3.66 (m, 1H), 3.10-2.86 (m, 2H), 2.71-2.59 (m, 1H), 0.93 (t, J = 7.1 Hz, 3H), 0.73 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.68, 159.16, 137.90, 136.20, 132.31, 129.94 (2C), 129.23, 128.82, 127.05, 126.94, 113.66 (2C), 55.25, 42.19, 38.33, 13.36, 12.08; MS EI m/z (rel. int.): 283 (M^+ , 36), 282 (30), 211 (100), 168 (19); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572; found 283.1572.

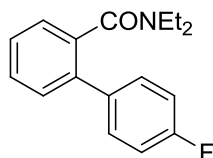
N,N-Diethyl-2-(2-fluorophenyl)benzamide (**2k**)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(2-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (94 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2k** (70 mg, 87% yield) was obtained as a light yellow oil. IR (KBr): $\nu_{\max}$ 2974, 2935, 1632, 1482, 1456, 1426, 1290, 1221, 1090, 757 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.49-7.35 (m, 5H), 7.34-7.27 (m, 1H), 7.18-7.04 (m, 2H), 4.01-3.53 (m, 1H), 3.30-2.56 (m, 3H), 0.86 (t, J = 7.1 Hz, 3H), 0.80 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ

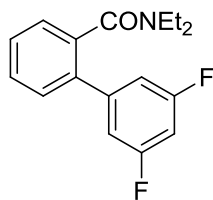
169.85, 159.44 (d, $^1J_{C-F} = 246.0$ Hz), 137.19, 132.31, 132.09 (d, $^4J_{C-F} = 3.0$ Hz), 130.63 (d, $^4J_{C-F} = 2.1$ Hz), 129.43 (d, $^3J_{C-F} = 8.1$ Hz), 128.34, 128.02, 127.09 (d, $^2J_{C-F} = 15.0$ Hz), 126.58, 123.85 (d, $^3J_{C-F} = 3.6$ Hz), 115.34 (d, $^2J_{C-F} = 22.3$ Hz), 42.14, 38.04, 13.50, 11.80; MS EI m/z (rel. int.): 271 (M^+ , 42), 270 (58), 199 (100), 170 (25); HRMS m/z (EI, M^+): calcd. for $C_{17}H_{18}FNO$, 271.1372; found 271.1368.

N,N-Diethyl-2-(4-fluorophenyl)benzamide (2l)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(4-fluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (94 mg, 0.45 mmol), $RuH_2(CO)(PPh_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2l** (77 mg, 95% yield) was obtained as a light yellow solid. mp: 57-59 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2975, 2935, 1627, 1515, 1485, 1470, 1458, 1428, 1290, 1223, 1161, 1097, 840, 763 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.50-7.30 (m, 6H), 7.05 (t, $J = 8.6$ Hz, 2H), 3.83-3.63 (m, 1H), 3.12-2.84 (m, 2H), 2.75-2.57 (m, 1H), 0.91 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.31, 162.43 (d, $^1J_{C-F} = 247.0$ Hz), 137.19, 136.32, 135.83 (d, $^4J_{C-F} = 3.3$ Hz), 130.49 (d, $^3J_{C-F} = 8.0$ Hz, 2C), 129.33, 128.91, 127.61, 126.87, 115.14 (d, $^2J_{C-F} = 21.4$ Hz, 2C), 42.22, 38.32, 13.39, 12.00. MS EI m/z (rel. int.): 271 (M^+ , 24), 270 (50), 199 (100), 171 (18), 170 (28); HRMS m/z (EI, M^+): calcd. for $C_{17}H_{18}FNO$, 271.1372; found 271.1382.

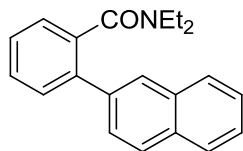
N,N-Diethyl-2-(3,5-difluorophenyl)benzamide (2m)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(3,5-difluorophenyl)-5,5-dimethyl-1,3,2-dioxaborinane (102 mg, 0.45 mmol), $RuH_2(CO)(PPh_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2m** (79 mg, 91% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2976, 2935, 1625, 1592, 1433, 1414, 1338, 1292, 1120, 1093, 988, 864, 763 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.49-7.32 (m, 4H), 7.07-6.96 (m, 2H), 6.78 (tt, $J = 8.9, 2.3$ Hz, 1H), 3.98-3.66 (m, 1H), 3.16-2.86 (m, 2H), 2.84-2.65 (m, 1H), 0.97 (t, $J = 7.1$ Hz, 3H), 0.83 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.78, 162.70 (dd, $^{1,3}J_{C-F} = 248.7, 12.9$ Hz, 2C), 142.93 (t, $^3J_{C-F} = 9.6$

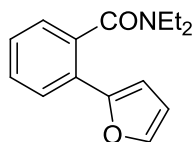
Hz), 136.29, 135.99 (t, $^4J_{C-F} = 2.3$ Hz), 129.14, 129.11, 128.50, 127.00, 111.82 (dd, $^2J_{C-F} = 25.8$ Hz, 7.17 Hz, 2C), 102.85 (t, $^2J_{C-F} = 25.2$ Hz), 42.39, 38.44, 13.49, 11.82; MS EI m/z (rel. int.): 289 (M^+ , 27), 288 (50), 217 (100), 189 (18), 188 (28); HRMS m/z (EI, M^+): calcd. for $C_{17}H_{17}F_2NO$, 289.1278; found 289.1278.

N,N-Diethyl-2-(naphthalen-2-yl)benzamide (2n)



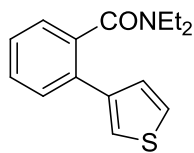
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (62 mg, 0.30 mmol), 2-(naphthalen-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (108 mg, 0.45 mmol), $RuH_2(CO)(PPh_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2n** (73 mg, 81% yield) was obtained as a light yellow solid. mp: 52-53 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2974, 2933, 1625, 1474, 1458, 1424, 1290, 1089, 774, 761 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.96 (s, 1H), 7.90-7.79 (m, 3H), 7.63 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.55-7.45 (m, 4H), 7.44-7.39 (m, 2H), 3.82-3.58 (m, 1H), 3.09-2.84 (m, 2H), 2.71-2.52 (m, 1H), 0.80 (t, $J = 7.1$ Hz, 3H), 0.71 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.57, 138.19, 137.21, 136.52, 133.15, 132.54, 129.70, 128.98, 128.21, 127.92, 127.74, 127.60, 127.54, 127.16, 126.96, 126.19, 126.07, 42.36, 38.47, 13.41, 12.00; MS EI m/z (rel. int.): 303 (M^+ , 30), 232 (48), 231 (100), 203 (21), 202 (54), 72 (21); HRMS m/z (EI, M^+): calcd. for $C_{21}H_{21}NO$, 303.1623; found 303.1624.

N,N-Diethyl-2-(furan-2-yl)benzamide (2o)



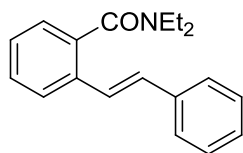
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (42 mg, 0.2 mmol), 2-(furan-2-yl)-5,5-dimethyl-1,3,2-dioxaborinane (54 mg, 0.3 mmol), $RuH_2(CO)(PPh_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2o** (41 mg, 84% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2974, 2935, 1631, 1460, 1428, 1381, 1292, 1272, 1222, 1094, 1011, 761 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 7.71 (dd, $J = 7.9, 0.6$ Hz, 1H), 7.44 (dd, $J = 1.7, 0.6$ Hz, 1H), 7.38 (td, $J = 7.9, 1.6$ Hz, 1H), 7.29 (td, $J = 7.4, 1.2$ Hz, 1H), 7.24 (dd, $J = 7.5, 1.1$ Hz, 1H), 6.64 (dd, $J = 3.4, 0.6$ Hz, 1H), 6.42 (dd, $J = 3.4, 1.8$ Hz, 1H), 3.75 (q, $J = 7.0$ Hz, 1H), 3.38 (q, $J = 7.0$ Hz, 1H), 3.12-2.91 (m, 2H), 1.24 (t, $J = 7.1$ Hz, 3H), 0.86 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.61, 151.61, 142.25, 133.85, 128.62, 127.47, 127.09, 126.81, 126.09, 111.64, 108.16, 42.59, 38.72, 13.34, 12.28; MS EI m/z (rel. int.): 243 (M^+ , 78), 171 (100), 143 (28), 115 (45); HRMS m/z (EI, M^+): calcd. for $C_{15}H_{17}NO_2$, 243.1259; found 243.1253.

N,N-Diethyl-2-(thiophen-3-yl)benzamide (2p)



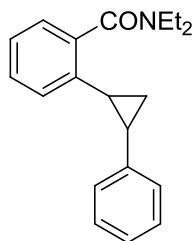
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (42 mg, 0.2 mmol), 2-(thiophen-3-yl)-5,5-dimethyl-1,3,2-dioxaborinane (59 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2p** (35 mg, 67% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2973, 2933, 1625, 1459, 1428, 1291, 1089, 860, 801, 774, 754 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.51-7.29 (m, 6H), 7.27 (dd, $J = 5.0, 1.3$ Hz, 1H), 3.81-3.66 (m, 1H), 3.22-3.08 (m, 1H), 3.02-2.87 (m, 1H), 2.82-2.68 (m, 1H), 1.04 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J = 7.1$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.68, 140.11, 136.08, 132.84, 128.86, 128.75, 128.19, 127.39, 126.80, 125.44, 123.17, 42.34, 38.48, 13.29, 12.18; MS EI m/z (rel. int.): 259 (M^+ , 29), 258 (15), 188 (36), 187 (100), 160 (19), 115 (48); HRMS m/z (EI, M^+): calcd. for $\text{C}_{15}\text{H}_{17}\text{NOS}$, 259.1031; found 259.1035.

(E)-N,N-Diethyl-2-styrylbenzamide (2q)



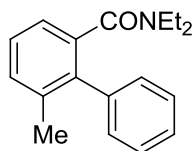
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (42 mg, 0.2 mmol), (E)-2-styryl-5,5-dimethyl-1,3,2-dioxaborinane (65 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2q** (32 mg, 58% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2973, 1628, 1598, 1495, 1485, 1469, 1458, 1449, 1428, 1381, 1285, 1075, 963, 762, 692 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 7.8$ Hz, 1H), 7.46 (d, $J = 7.3$ Hz, 2H), 7.40-7.18 (m, 6H), 7.13 (d, $J = 16.7$ Hz, 1H), 7.09 (d, $J = 17.7$ Hz, 1H), 4.05-3.68 (m, 1H), 3.56-3.22 (m, 1H), 3.10 (q, $J = 7.0$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.35, 137.01, 136.35, 133.63, 130.82, 128.75, 128.65 (2C), 127.84, 127.53, 126.56 (2C), 126.18, 125.25, 125.02, 42.82, 38.89, 13.87, 12.96; MS EI m/z (rel. int.): 279 (M^+ , 22), 208 (27), 207 (49), 179 (40), 178 (100), 177 (21), 176 (25), 152 (21), 77 (20), 57 (31), 56 (40); HRMS m/z (EI, M^+): calcd. for $\text{C}_{19}\text{H}_{21}\text{NO}$, 279.1623; found 279.1639.

N,N-Diethyl-2-(2-phenylcyclopropyl)benzamide (2r)



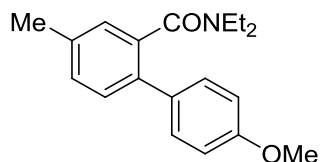
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxybenzamide (42 mg, 0.2 mmol), 2-(2-phenylcyclopropyl)-5,5-dimethyl-1,3,2-dioxaborinane (69 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.4 mL), the title compound **2r** (49 mg, 83% yield) was obtained as a yellow solid. mp: 52-53 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2973, 2933, 1631, 1602, 1494, 1472, 1459, 1428, 1291, 1072, 755, 698 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.39-6.87 (m, 9H), 3.90-3.64 (m, 1H), 3.40-2.68 (m, 3H), 2.37-1.29 (m, 4H), 1.14-0.78 (m, 6H) (atropisomers involved¹⁷); ^{13}C NMR (101 MHz, CDCl_3): δ 170.62, 142.11, 141.94, 137.89, 137.71, 128.75, 128.31, 128.24, 128.11, 126.16, 126.00, 125.75, 125.73, 125.54, 125.43, 125.18, 124.94, 123.04, 42.53, 42.45, 38.43, 28.83, 26.08, 25.15, 24.31, 17.25, 17.12, 13.90, 13.64, 12.45, 12.28 (atropisomers involved¹⁷); MS EI m/z (rel. int.): 293 (M^+ , 2), 189 (100), 160 (29), 132 (13), 91 (14); HRMS m/z (EI, M^+): calcd. for $\text{C}_{20}\text{H}_{23}\text{NO}$, 293.1780; found 293.1780.

3-Methyl-2-phenyl-N,N-diethylbenzamide (2v)



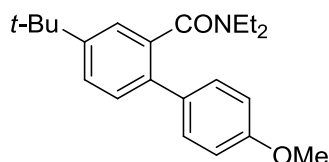
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxy-3-methylbenzamide (44 mg, 0.2 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (57 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2v** (45 mg, 85% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2973, 2932, 1633, 1478, 1456, 1441, 1426, 1330, 1315, 1291, 1122, 796, 773, 749, 703 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.23 (m, 6H), 7.22-7.13 (m, 2H), 3.86-3.67 (m, 1H), 3.20-3.02 (m, 1H), 2.82-2.61 (m, 2H), 2.15 (s, 3H), 0.91 (t, J = 7.1 Hz, 3H), 0.59 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.22, 138.39, 137.78, 137.43, 136.37, 130.25, 128.60 (br), 128.37 (br), 127.46, 127.33 (br, 2C), 127.14, 123.17, 42.17, 37.57, 20.50, 13.57, 11.52; MS EI m/z (rel. int.): 267 (M^+ , 25), 266 (51), 195 (95), 166 (32), 165 (100), 152 (61), 56 (34); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{18}\text{H}_{22}\text{NO}$, 268.1701; found 268.1692.

N,N-Diethyl-5-methyl-2-(4-methoxyphenyl)benzamide (2w)



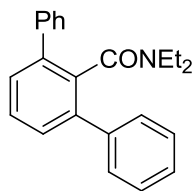
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxy-5-methylbenzamide (44 mg, 0.2 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (66 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2w** (55 mg, 92% yield) was obtained as a light yellow solid. mp: 113-114 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2972, 2934, 1627, 1520, 1474, 1461, 1437, 1293, 1247, 1180, 1091, 1038, 821 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.40 (d, J = 8.8 Hz, 2H), 7.29-7.19 (m, 2H), 7.15 (s, 1H), 6.89 (d, J = 8.8 Hz, 2H), 3.82 (s, 3H), 3.78-3.65 (m, 1H), 3.12-2.88 (m, 2H), 2.75-2.58 (m, 1H), 2.38 (s, 3H), 0.95 (t, J = 7.1 Hz, 3H), 0.73 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.88, 158.99, 136.88, 136.04, 135.03, 132.32, 129.88 (2C), 129.61, 129.13, 127.51, 113.63 (2C), 55.25, 42.20, 38.28, 20.94, 13.37, 12.12; MS EI m/z (rel. int.): 297 (M^+ , 32), 296 (29), 225 (100), 182 (20), 165 (16), 153 (24), 152 (17); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{19}\text{H}_{24}\text{NO}_2$, 298.1807; found 298.1823.

N,N-Diethyl-5-*tert*-butyl-2-(4-methoxyphenyl)benzamide (2x)



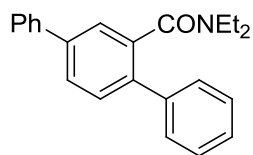
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxy-5-*tert*-butylbenzamide (53 mg, 0.2 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (66 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2x** (64 mg, 94% yield) was obtained as a light yellow solid. mp: 89-92 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2965, 1629, 1610, 1522, 1489, 1474, 1461, 1434, 1294, 1261, 1248, 1180, 1138, 828 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.36 (m, 3H), 7.34 (d, J = 2.0 Hz, 1H), 7.29 (d, J = 8.1 Hz, 1H), 6.89 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.80-3.69 (m, 1H), 3.08-2.87 (m, 2H), 2.75-2.57 (m, 1H), 1.34 (s, 9H), 0.95 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 171.22, 159.01, 150.00, 135.74, 135.01, 132.29, 129.89 (2C), 128.91, 125.90, 123.86, 113.64 (2C), 55.24, 42.22, 38.40, 34.53, 31.22, 13.38, 12.14; MS EI m/z (rel. int.): 339 (M^+ , 32), 267 (67), 211 (39), 165 (26), 72 (43), 57 (100); HRMS m/z (EI, M^+): calcd. for $\text{C}_{22}\text{H}_{29}\text{NO}_2$, 339.2198; found 339.2179.

N,N-Diethyl-2,6-diphenylbenzamide (2y)



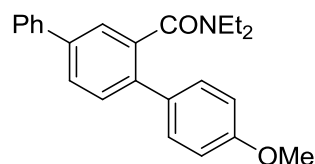
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-6-phenyl-2-methoxybenzamide (28 mg, 0.10 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (29 mg, 0.15 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (4 mg, 4 mol%) and toluene (0.3 mL), the title compound **2y** (9 mg, 27% yield) was obtained as a light yellow solid. mp: 82-83 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2361, 2341, 1628, 1458, 1440, 1285, 768, 755, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.42 (m, 5H), 7.41-7.28 (m, 8H), 3.10 (q, $J = 7.1$ Hz, 2H), 2.79 (q, $J = 7.1$ Hz, 2H), 0.64 (t, $J = 7.1$ Hz, 3H), 0.47 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.62, 140.20 (2C), 139.27 (2C), 135.33, 129.32 (4C), 129.02 (2C), 128.34, 127.94 (4C), 127.34 (2C), 42.22, 37.52, 12.84, 11.41; MS EI m/z (rel. int.): 329 (M^+ , 15), 258 (15), 257 (100), 252 (49), 228 (18); HRMS m/z (EI, M^+): calcd. for $\text{C}_{23}\text{H}_{23}\text{NO}$, 329.1780; found 329.1790.

N,N-Diethyl-2,5-diphenylbenzamide (2z)



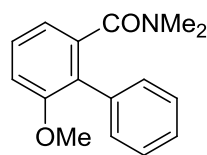
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-5-phenyl-2-methoxybenzamide (57 mg, 0.2 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (57 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (19 mg, 10 mol%) and toluene (0.6 mL), the title compound **2z** (65 mg, 98% yield) was obtained as a light yellow solid. mp: 128-130 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2974, 2933, 1627, 1473, 1458, 1433, 1272, 1093, 758, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.74-7.63 (m, 3H), 7.62 (d, $J = 1.5$ Hz, 1H), 7.54 (d, $J = 6.8$ Hz, 2H), 7.51-7.43 (m, 3H), 7.43-7.30 (m, 4H), 3.87-3.70 (m, 1H), 3.13-2.90 (m, 2H), 2.79-2.61 (m, 1H), 0.93 (t, $J = 7.1$ Hz, 3H), 0.74 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.42, 140.37, 139.94, 139.38, 137.22, 136.77, 129.88, 128.83 (2C), 128.81 (2C), 128.32 (2C), 127.61, 127.57, 127.52, 127.01 (2C), 125.60, 42.27, 38.34, 13.42, 11.96; MS EI m/z (rel. int.): 329 (M^+ , 37), 328 (40), 257 (100), 228 (25); HRMS m/z (EI, M^+): calcd. for $\text{C}_{23}\text{H}_{23}\text{NO}$, 329.1780; found 329.1783.

N,N-Diethyl-2-(4-methoxyphenyl)-5-phenylbenzamide (2aa)

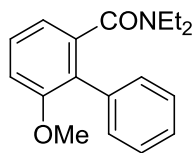


According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-5-phenyl-2-methoxybenzamide (57 mg, 0.2 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (66 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (7 mg, 4 mol%) and toluene (0.6 mL), the title compound **2aa** (70 mg, 97% yield) was obtained as a pale solid. mp: 139-141 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2972, 2934, 1626, 1522, 1473, 1459, 1433, 1295, 1272, 1256, 1244, 1180, 1036, 829, 767, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.70-7.61 (m, 3H), 7.59 (d, $J = 1.3$ Hz, 1H), 7.51-7.40 (m, 5H), 7.36 (t, $J = 7.2$ Hz, 1H), 6.93 (d, $J = 8.5$ Hz, 2H), 3.83 (s, 3H), 3.79-3.67 (m, 1H), 3.17-2.91 (m, 2H), 2.78-2.62 (m, 1H), 0.98 (t, $J = 7.1$ Hz, 3H), 0.75 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.66, 159.26, 139.99, 139.90, 136.85, 136.60, 131.92, 129.95 (2C), 129.74, 128.81 (2C), 127.52, 127.48, 126.96 (2C), 125.61, 113.76 (2C), 55.28, 42.32, 38.45, 13.46, 12.14; MS EI m/z (rel. int.): 359 (M^+ , 50), 358 (36), 288 (30), 287 (100), 216 (28), 215 (79), 77 (32), 72 (39), 57 (30), 56 (51); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{24}\text{H}_{26}\text{NO}_2$, 360.1963; found 360.1979.

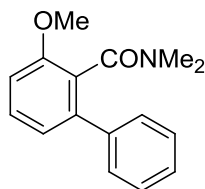
N,N-Dimethyl-2-phenyl-3-methoxybenzamide (2ab)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-dimethyl-2,3-dimethoxybenzamide (63 mg, 0.30 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (87 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2ab** (70 mg, 91% yield) was obtained as a light yellow solid. mp: 83-84 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2936, 1635, 1579, 1502, 1466, 1455, 1433, 1395, 1257, 1053, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.45-7.28 (m, 6H), 6.99 (dd, $J = 8.4, 2.3$ Hz, 2H), 3.76 (s, 3H), 2.73 (s, 3H), 2.47 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.63, 156.32, 138.19, 135.29, 129.98 (2C), 129.02, 127.64 (2C), 127.45, 127.34, 119.02, 111.55, 55.81, 38.05, 34.23; MS EI m/z (rel. int.): 255 (M^+ , 48), 211 (100), 196 (24); HRMS m/z (EI, M^+): calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_2$, 255.1259; found 255.1267.

N,N-Diethyl-2-phenyl-3-methoxybenzamide (2ac)

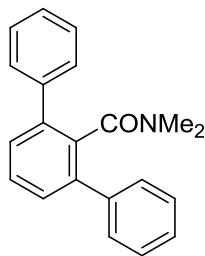
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2,3-dimethoxybenzamide (71 mg, 0.30 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (87 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2ac** (74 mg, 87% yield) was obtained as a light yellow solid. mp: 79-80 °C (EtOAc/hexanes); IR (KBr) ν_{max} 2972, 2934, 1629, 1459, 1426, 1297, 1255, 1059, 801, 744, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.44-7.27 (m, 6H), 6.97 (t, $J = 7.9$ Hz, 2H), 3.80-3.67 (m, 4H), 3.13-2.99 (m, 1H), 2.86-2.72 (m, 1H), 2.71-2.56 (m, 1H), 0.84 (t, $J = 7.1$ Hz, 3H), 0.66 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 169.70, 156.36, 138.62, 135.22, 130.16 (2C), 128.92, 127.64 (2C), 127.24, 127.20, 118.51, 111.22, 55.78, 42.04, 37.74, 13.50, 11.64; MS EI m/z (rel. int.): 283 (M^+ , 64), 282 (69), 212 (13), 211 (100), 196 (35), 168 (15); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572; found 283.1563.

N,N-Dimethyl-2-methoxy-6-phenylbenzamide (2ad)

According to General Procedure B and using the following materials refluxed in 20 h: N,N-dimethyl-2,6-dimethoxybenzamide (42 mg, 0.2 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (57 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (7 mg, 4 mol%) and toluene (0.6 mL), the title compound **2ad** (35 mg, 68% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2935, 1639, 1593, 1583, 1570, 1500, 1466, 1429, 1394, 1309, 1270, 1256, 1123, 1098, 1059, 1019, 761, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.50-7.42 (m, 2H), 7.41-7.28 (m, 4H), 6.99 (dd, $J = 7.7, 0.6$ Hz, 1H), 6.93 (d, $J = 8.3$ Hz, 1H), 3.87 (s, 3H), 2.86 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.59, 155.79, 140.21, 139.74, 129.62, 128.52 (2C), 128.17 (2C), 127.48, 125.06, 122.01, 109.84, 55.89, 37.63, 34.26; MS EI m/z (rel. int.): 255 (M^+ , 8), 211 (100), 168 (29), 152 (29), 139 (44), 72 (16); HRMS m/z (EI, M^+): calcd. for $\text{C}_{16}\text{H}_{17}\text{NO}_2$, 255.1259; found 255.1257.

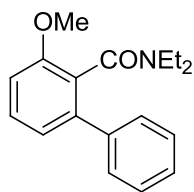
Plus di-C-OMe activation/phenylation product:

N,N-dimethyl-2,6-diphenylbenzamide



The title compound (13 mg, 22% yield) was obtained as a light yellow solid. mp: 95-97 °C; IR (KBr): ν_{max} 2925, 1636, 1497, 1390, 1056, 756, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.51-7.42 (m, 5H), 7.42-7.30 (m, 8H), 2.62 (s, 3H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 169.69, 140.33 (2C), 139.55 (2C), 134.78, 129.08 (2C), 128.70 (5C), 128.14 (4C), 127.45 (2C), 37.68, 34.00; MS EI m/z (rel. int.): 301 (M^+ , 8), 258 (29), 257 (100), 229 (17), 228 (40), 227 (21), 226 (29), 202 (17), 77 (19); HRMS m/z (EI, M^+): calcd for $\text{C}_{21}\text{H}_{19}\text{NO}$, 301.1467; found 301.1470.

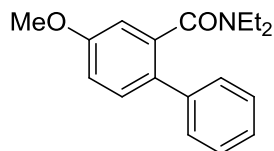
N,N-Diethyl-2-methoxy-6-phenylbenzamide (2ae)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2,6-dimethoxybenzamide (71 mg, 0.30 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (86 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.4 mL), the title compound **2ae** (51 mg, 60% yield) was obtained as a pale solid. mp: 79-80 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2975, 2935, 1632, 1583, 1569, 1465, 1423, 1283, 1265, 761, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.48 (d, J = 6.7 Hz, 2H), 7.41-7.27 (m, 4H), 6.97 (d, J = 7.7 Hz, 1H), 6.92 (d, J = 8.3 Hz, 1H), 3.85 (s, 3H), 3.84-3.73 (m, 1H), 3.05-2.87 (m, 2H), 2.77-2.63 (m, 1H), 0.84-0.72 (m, 6H); ^{13}C NMR (101 MHz, CDCl_3): δ 167.59, 155.75, 140.03, 139.61, 129.31, 128.92 (2C), 128.01 (2C), 127.38, 125.56, 121.96, 109.78, 55.69, 42.14, 37.88, 13.26, 11.85; MS EI m/z (rel. int.): 283 (M^+ , 8), 211 (100), 206 (18); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572; found 283.1570.

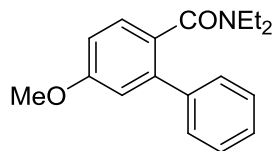
Plus, di-C-OMe activation/phenylation product **2y** (22 mg, 23% yield) was obtained.

N,N-Diethyl-2-phenyl-5-methoxybenzamide (2af)



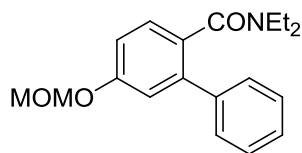
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2,5-dimethoxybenzamide (71 mg, 0.30 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (87 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (28 mg, 10 mol%) and toluene (0.4 mL), the title compound **2af** (64 mg, 75% yield) was obtained as a light yellow solid. mp: 55-56 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2972, 2935, 1628, 1608, 1478, 1433, 1315, 1291, 1269, 1230, 1086, 1047, 830, 773, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.47-7.40 (m, 2H), 7.37-7.27 (m, 4H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 6.89 (d, J = 2.6 Hz, 1H), 3.84 (s, 3H), 3.80-3.69 (m, 1H), 3.06-2.89 (m, 2H), 2.71-2.56 (m, 1H), 0.89 (t, J = 7.1 Hz, 3H), 0.73 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.21, 158.96, 139.47, 137.27, 130.88, 130.65, 128.77 (2C), 128.20 (2C), 127.05, 115.04, 111.93, 55.42, 42.17, 38.25, 13.35, 11.88; MS EI m/z (rel. int.): 283 (M^+ , 41), 282 (38), 211 (100), 168 (17); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572; found 283.1564.

N,N-Diethyl-2-phenyl-4-methoxybenzamide (2ag)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2,4-dimethoxybenzamide (71 mg, 0.3 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (87 mg, 0.45 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (11 mg, 4 mol%) and toluene (0.6 mL), the title compound **2ag** (76 mg, 89% yield) was obtained as a light yellow solid. mp 64-65 °C (EtOAc/hexanes); IR (KBr) ν_{max} 2972, 2935, 1625, 1468, 1428, 1290, 1271, 1036, 772, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ ppm 7.47 (d, J = 6.6 Hz, 2H), 7.40-7.27 (m, 4H), 6.96-6.85 (m, 2H), 3.84 (s, 3H), 3.79-3.63 (m, 1H), 3.16-2.78 (m, 2H), 2.73-2.48 (m, 1H), 0.86 (t, J = 7.1 Hz, 3H), 0.72 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ ppm 170.52, 159.70, 139.97, 139.76, 129.02, 128.70 (2C), 128.44, 128.24 (2C), 127.59, 114.62, 112.97, 55.33, 42.23, 38.29, 13.35, 11.90. MS EI m/z (rel. int.) 283 (M^+ , 11), 282 (16), 211 (100); HRMS m/z (EI, M^+) calcd for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572, found 283.1574.

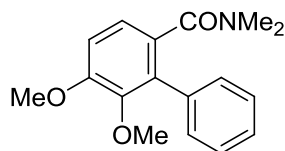
N,N-Diethyl-4-methoxymethoxy-2-phenylbenzamide (2ah)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-4-methoxymethoxy-2-methoxy-benzamide (54 mg, 0.2 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (57 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (7 mg, 4 mol%) and toluene (0.6 mL), the title compound **2ah** (61 mg, 98% yield) was obtained as a light yellow solid. mp: 63-64

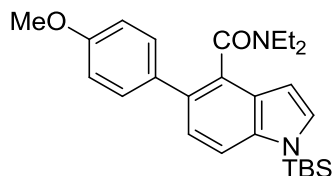
$^{\circ}\text{C}$ (EtOAc/hexanes); IR (KBr): ν_{max} 2972, 2934, 1626, 1468, 1430, 1314, 1289, 1220, 1184, 1154, 1095, 1079, 996, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.47 (dd, J = 8.0, 1.4 Hz, 2H), 7.39-7.27 (m, 4H), 7.08-7.02 (m, 2H), 5.21 (s, 2H), 3.85-3.63 (m, 1H), 3.49 (s, 3H), 3.15-2.84 (m, 2H), 2.74-2.49 (m, 1H), 0.88 (t, J = 7.1 Hz, 3H), 0.72 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.45, 157.44, 139.98, 139.60, 130.10, 128.72 (2C), 128.41, 128.25 (2C), 127.61, 116.96, 115.18, 94.40, 56.07, 42.25, 38.32, 13.36, 11.90; MS EI m/z (rel. int.): 313 (M^+ , 24), 312 (50), 241 (100), 211 (65), 168 (28), 139 (33); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{19}\text{H}_{24}\text{NO}_3$, 314.1756; found 314.1760.

N,N-Dimethyl-2-phenyl-3,4-dimethoxybenzamide (2ai)



According to General Procedure B and using the following materials refluxed in 20 h: N,N-dimethyl-2,3,4-trimethoxybenzamide (48 mg, 0.2 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (57 mg, 0.3 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (7 mg, 4 mol%) and toluene (0.6 mL), the title compound **2ai** (51 mg, 90% yield) was obtained as a colorless solid. mp: 101-102 $^{\circ}\text{C}$ (EtOAc/hexanes); IR (KBr): ν_{max} 2936, 1633, 1596, 1479, 1450, 1394, 1296, 1273, 1258, 1122, 1021, 767, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.43 (d, J = 6.8 Hz, 2H), 7.39-7.28 (m, 3H), 7.11 (d, J = 8.4 Hz, 1H), 6.95 (d, J = 8.4 Hz, 1H), 3.90 (s, 3H), 3.45 (s, 3H), 2.71 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.65, 153.43, 146.17, 135.14, 133.25, 130.16, 129.77 (2C), 127.69 (2C), 127.46, 122.79, 111.72, 60.47, 55.91, 38.11, 34.34; MS EI m/z (rel. int.): 285 (M^+ , 39), 241 (100), 226 (47); HRMS m/z (EI, M^+): calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_3$, 285.1365; found 285.1360.

1-(tert-Butyldimethylsilyl)-N,N-diethyl-5-(4-methoxyphenyl)-1H-indole-4-carboxamide (2aj)



According to General Procedure B and using the following materials refluxed in 20 h: 1-(*t*-butyldimethylsilyl)-N,N-diethyl-5-methoxy-1H-indole-4-carboxamide (36 mg, 0.10 mmol), 2-(4-methoxyphenyl)-5,5-dimethyl-1,3,2-dioxaborinane (33 mg, 0.15 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (9 mg, 10 mol%) and toluene (0.6 mL), the title compound **2aj** (26 mg, 60% yield) was obtained as a light yellow oil. IR (KBr): ν_{max} 2957, 2932, 1626, 1521, 1464, 1424, 1288, 1247, 1150, 839, 809, 789, 753 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.43 (m, 3H), 7.20 (d, J = 3.2 Hz, 1H), 7.15 (d, J = 8.6 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 6.57 (d, J = 2.7 Hz, 1H), 3.83 (s, 3H), 3.78-3.66 (m, 1H), 3.33-3.17 (m, 1H), 3.05-2.93 (m, 1H), 2.78-2.66 (m, 1H), 1.03 (t, J = 7.1 Hz, 3H), 0.94

(s, 9H), 0.65 (t, $J = 7.1$ Hz, 3H), 0.64 (s, 3H), 0.58 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.17, 158.56, 140.26, 133.58, 131.94, 130.29 (2C), 129.36, 129.30, 127.41, 122.98, 114.10, 113.53 (2C), 104.05, 55.27, 42.35, 38.19, 26.23 (3C), 19.43, 13.65, 12.37, -3.96, -4.02; MS EI m/z (rel. int.): 436 (M^+ , 38), 364 (100), 321 (16), 258 (17), 73 (31), 57 (16); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{26}\text{H}_{37}\text{N}_2\text{O}_2\text{Si}$, 437.2624; found 437.2626.

Synthesis of teraryls in Scheme 2

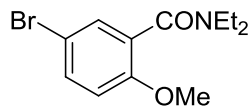
1. General Procedure C for bromination of *ortho*-methoxy benzamides

To a mixture of an *ortho*-MeO benzamide and NH_4OAc (0.1 equiv) in MeCN at rt was added NBS (1.05 equiv) quickly. The reaction was stirred at rt for 2 min to 4 h and monitored by TLC analysis until the completion. After removal of the solvent, water and EtOAc were added to the residue, the layers were separated and the water layer was extracted with EtOAc. The combined organic extract was washed with brine, dried (MgSO_4) and concentrated *in vacuo*. The residue was subjected to flash SiO_2 column chromatography (eluent: EtOAc/hexanes) to yield the product.

2. General Procedure D for Suzuki cross coupling

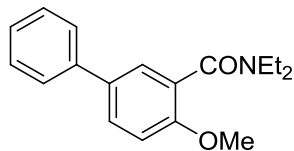
A mixture of a bromide substrate, a boronic acid (1.5 equiv), a degassed 2 M aqueous solution of Na_2CO_3 (3 equiv) and $\text{Pd}(\text{PPh}_3)_4$ (2 mol%) in toluene was heated at 120-130 $^\circ\text{C}$ (oil bath temperature) in a sealed vial for 15 h. The reaction progress was monitored by GC-MS analysis. The reaction mixture was cooled to rt and extracted with EtOAc. Then, the combined organic extract was washed with brine, dried (MgSO_4) and concentrated *in vacuo*. Finally, the residue was subjected to flash SiO_2 column chromatography (eluent: EtOAc/hexanes) to yield the product.

5-Bromo-N,N-diethyl-2-methoxybenzamide (2, Scheme 2)



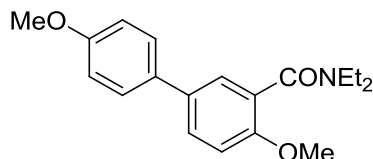
According to General Procedure C and using the following materials stirred in 10 min: N,N-diethyl-2-methoxybenzamide (622 mg, 3.0 mmol), NH_4OAc (23 mg, 0.3 mmol), NBS (567 mg, 3.2 mmol) and MeCN (15 mL), the title compound (781 mg, 91% yield) was obtained as a light yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.37 (dd, $J = 8.8, 2.5$ Hz, 1H), 7.26 (d, $J = 2.4$ Hz, 1H), 6.75 (d, $J = 8.8$ Hz, 1H), 3.76 (s, 3H), 3.56-3.45 (m, 2H), 3.15-3.05 (m, 2H), 1.19 (t, $J = 7.1$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 166.84, 154.22, 132.41, 130.02, 128.71, 112.77, 112.68, 55.69, 42.72, 38.81, 13.84, 12.71. The physical and spectral data were consistent with those previously reported.

N,N-Diethyl-2-methoxy-5-phenylbenzamide (3, Scheme 2)



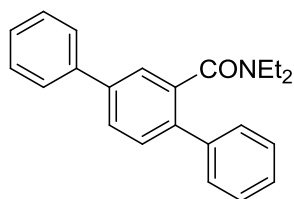
According to General Procedure D and using the following materials: 5-bromo-2-methoxy-N,N-diethylbenzamide (229 mg, 0.8 mmol), phenylboronic acid (146 mg, 1.2 mmol), a degassed 2 M aqueous solution of Na_2CO_3 (1.2 mL, 2.4 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (19 mg, 2 mol%) and toluene (1.2 mL), the title compound (208 mg, 92% yield) was obtained as a light yellow solid. mp: 85-87 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2973, 2935, 1633, 1485, 1475, 1461, 1436, 1275, 1251, 1087, 1020, 763, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.60-7.49 (m, 3H), 7.48-7.36 (m, 3H), 7.31 (t, $J = 7.3$ Hz, 1H), 6.97 (d, $J = 8.6$ Hz, 1H), 3.85 (s, 3H), 3.66-3.52 (m, 2H), 3.25-3.11 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.53, 154.67, 140.11, 133.82, 128.70 (2C), 128.34, 127.25, 126.87, 126.66 (2C), 126.07, 111.27, 55.65, 42.79, 38.81, 13.98, 12.88; MS EI m/z (rel. int.): 283 (M^+ , 24), 282 (23), 211 (100); HRMS m/z (EI, M^+): calcd. for $\text{C}_{18}\text{H}_{21}\text{NO}_2$, 283.1572; found 283.1575.

N,N-Diethyl-2-methoxy-5-(4-methoxyphenyl)benzamide (4, Scheme 2)



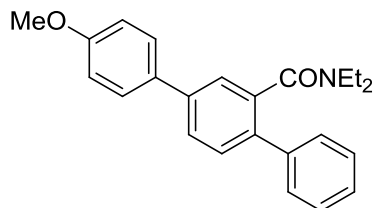
According to General Procedure D and using the following materials: 5-bromo-2-methoxy-N,N-diethylbenzamide (100 mg, 0.35 mmol), 4-methoxyphenylboronic acid (80 mg, 0.53 mmol), a degassed 2 M aqueous solution of Na_2CO_3 (0.55 mL, 1.05 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (8 mg, 2 mol%) and toluene (0.55 mL), the title compound (104 mg, 95% yield) was obtained as a colorless solid. mp: 58-60 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2971, 2936, 1633, 1609, 1494, 1474, 1462, 1438, 1276, 1244, 1181, 1087, 1051, 1021, 822 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.54-7.41 (m, 3H), 7.38 (d, $J = 2.2$ Hz, 1H), 7.01-6.85 (m, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.64-3.50 (m, 2H), 3.24-3.11 (m, 2H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 168.62, 158.82, 154.21, 133.54, 132.74, 127.88, 127.69 (2C), 127.19, 125.66, 114.15 (2C), 111.27, 55.65, 55.29, 42.79, 38.79, 13.98, 12.88; MS EI m/z (rel. int.): 313 (M^+ , 32), 312 (25), 241 (100), 183 (15), 139 (26); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{19}\text{H}_{24}\text{NO}_3$, 314.1756; found 314.1746.

N,N-Diethyl-2,5-diphenylbenzamide (5, Scheme 2)



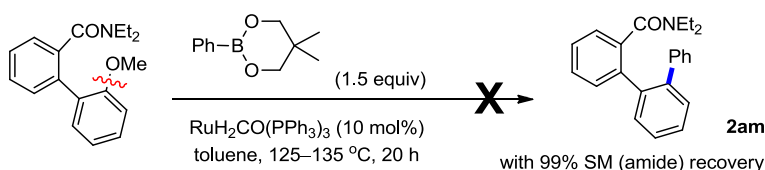
Procedure and data in details, see Compound **2z** at page S21.

N,N-Diethyl-2-phenyl-5-(4-methoxyphenyl)benzamide (6, Scheme 2)



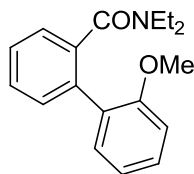
According to General Procedure B and using the following materials refluxed in 20 h: N,N-diethyl-2-methoxy-5-(4-methoxyphenyl)benzamide (31 mg, 0.10 mmol), 2-phenyl-5,5-dimethyl-1,3,2-dioxaborinane (29 mg, 0.15 mmol), $\text{RuH}_2(\text{CO})(\text{PPh}_3)_3$ (9 mg, 10 mol%) and toluene (0.5 mL), the title compound (33 mg, 93% yield) was obtained as a light yellow solid. mp: 117-118 °C (EtOAc/hexanes); IR (KBr): ν_{max} 2972, 2933, 1627, 1521, 1473, 1460, 1439, 1317, 1290, 1272, 1245, 1181, 1093, 826, 773, 702 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 7.63 (dd, J = 8.0, 1.9 Hz, 1H), 7.61-7.48 (m, 5H), 7.45 (d, J = 8.0 Hz, 1H), 7.42-7.29 (m, 3H), 6.99 (d, J = 8.7 Hz, 2H), 3.85 (s, 3H), 3.81-3.69 (m, 1H), 3.11-2.89 (m, 2H), 2.76-2.58 (m, 1H), 0.92 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 170.54, 159.38, 139.97, 139.45, 136.67, 136.56, 132.40, 129.82, 128.78 (2C), 128.29 (2C), 128.02 (2C), 127.47, 127.05, 125.08, 114.27 (2C), 55.31, 42.26, 38.32, 13.39, 11.94; MS EI m/z (rel. int.): 359 (M^+ , 54), 358 (47), 287 (100), 216 (29), 215 (71), 72 (28), 56 (37); HRMS m/z (ESI, $[\text{M}+1]^+$): calcd. for $\text{C}_{24}\text{H}_{26}\text{NO}_2$, 360.1963; found 360.1955.

Failure for expansion to a *remote* amide-directed C-OMe activation/coupling reaction for 2am



The amide starting material (prepared as shown below) failed to undergo a *remote* amide-directed C-OMe activation/coupling reaction and was recovered quantitatively indicative of inability of achieving a preferred conformation and large-ring coordination to attain C-OMe bond activation.

N,N-diethyl-2-(2-methoxyphenyl)benzamide

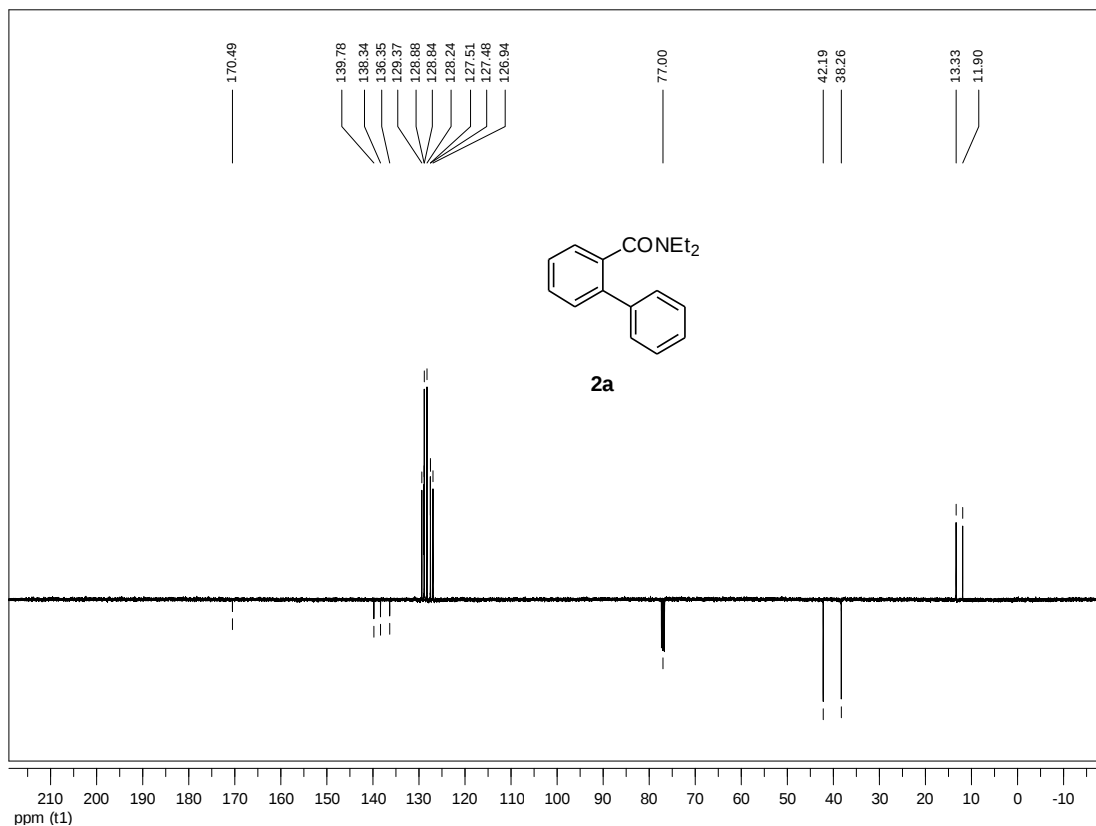
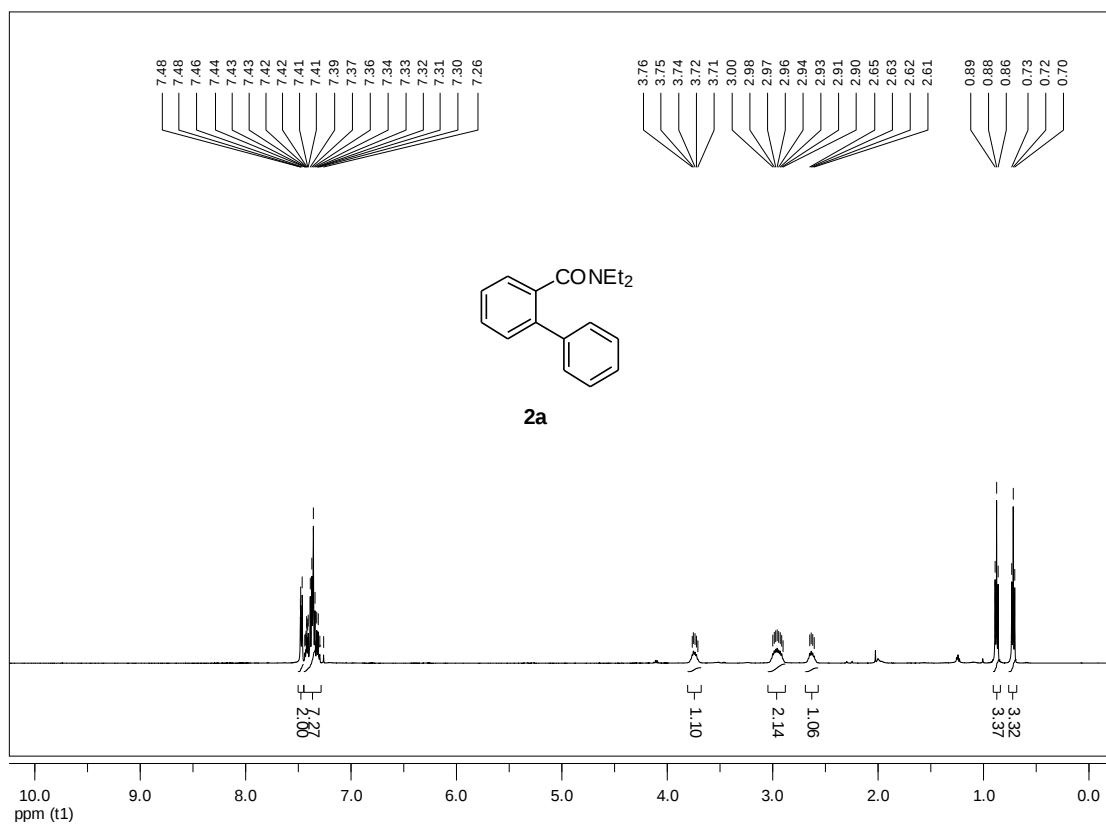


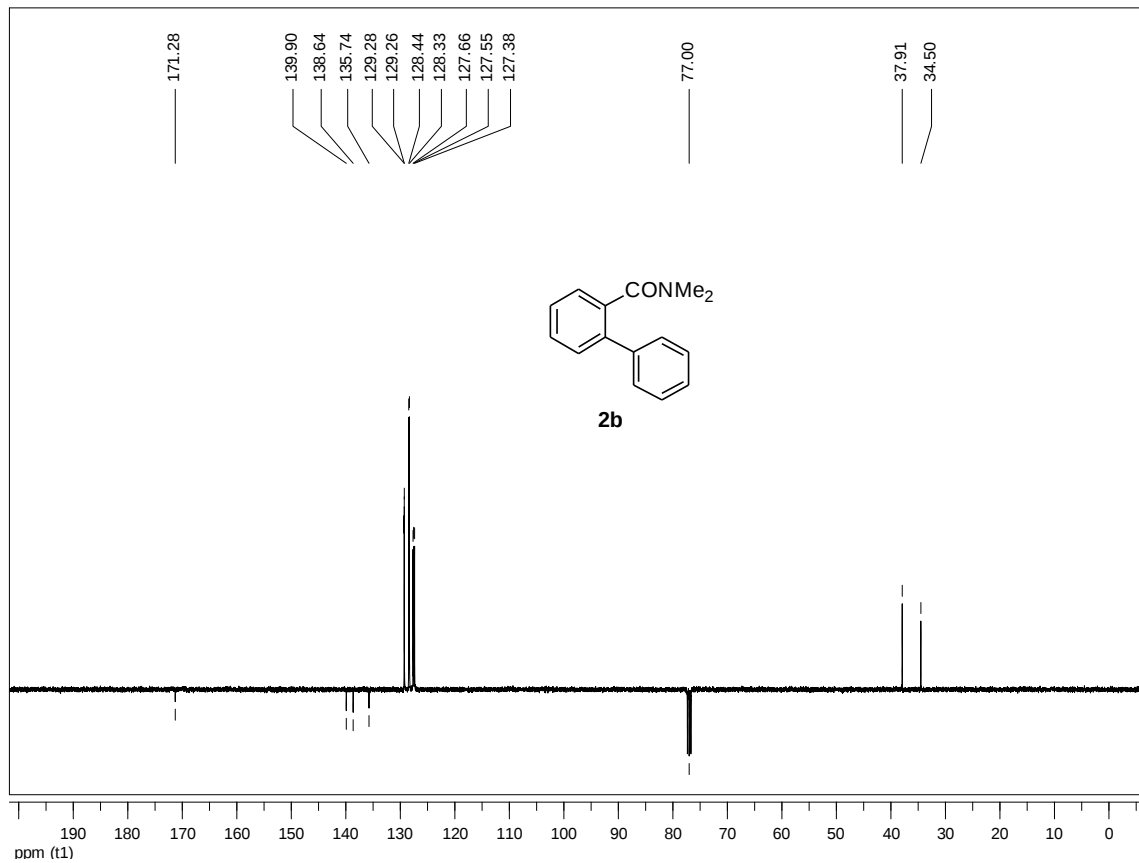
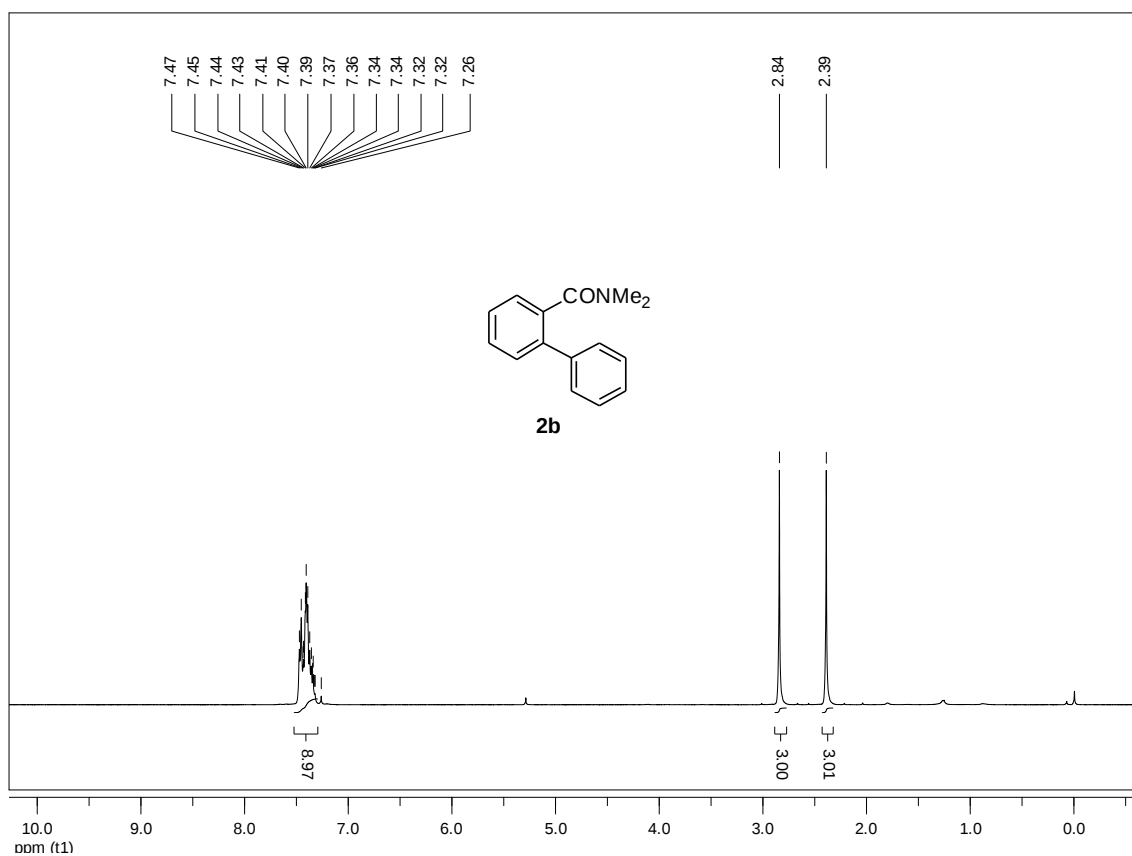
According to General Procedure D and using the following materials: N,N-diethyl-2-iodobenzamide (243 mg, 0.8 mmol), 2-methoxyphenylboronic acid (188 mg, 1.2 mmol), a degassed 2 M aqueous solution of Na₂CO₃ (1.2 mL, 2.4 mmol) and Pd(PPh₃)₄ (18 mg, 2 mol%) and toluene (1.2 mL), the title compound (221 mg, 98% yield) was obtained as a light yellow oil. IR (KBr): $\nu_{\max}$ 2971, 2934, 1630, 1502, 1482, 1462, 1428, 1290, 1255, 1233, 1090, 1026, 755 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 7.46-7.33 (m, 4H), 7.33-7.27 (m, 2H), 7.00-6.84 (m, 2H), 3.75 (s, 3H), 3.75-3.58 (m, 1H), 3.30-3.04 (m, 1H), 3.02-2.56 (m, 2H), 0.84 (t, J = 7.1 Hz, 3H), 0.77 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ 170.31, 156.29, 137.16, 135.19, 131.60, 130.95, 128.94, 128.43, 127.90, 127.24, 126.48, 120.32, 110.43, 55.24, 41.98, 37.93, 13.60, 11.87; MS EI m/z (rel. int.): 283 (M⁺, 20), 282 (26), 252 (47), 211 (100), 196 (71), 168 (61), 152 (20), 139 (44); HRMS m/z (EI, M⁺): calcd. for C₁₈H₂₁NO₂, 283.1572; found 283.1565.

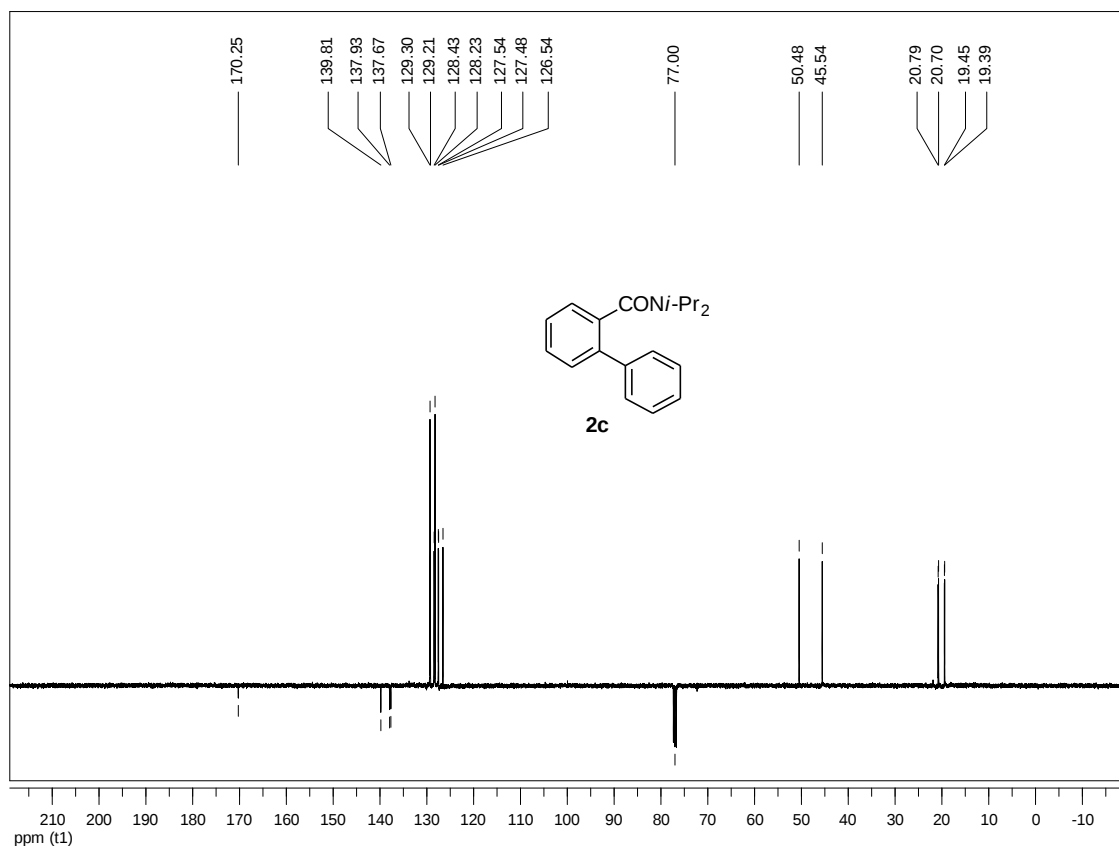
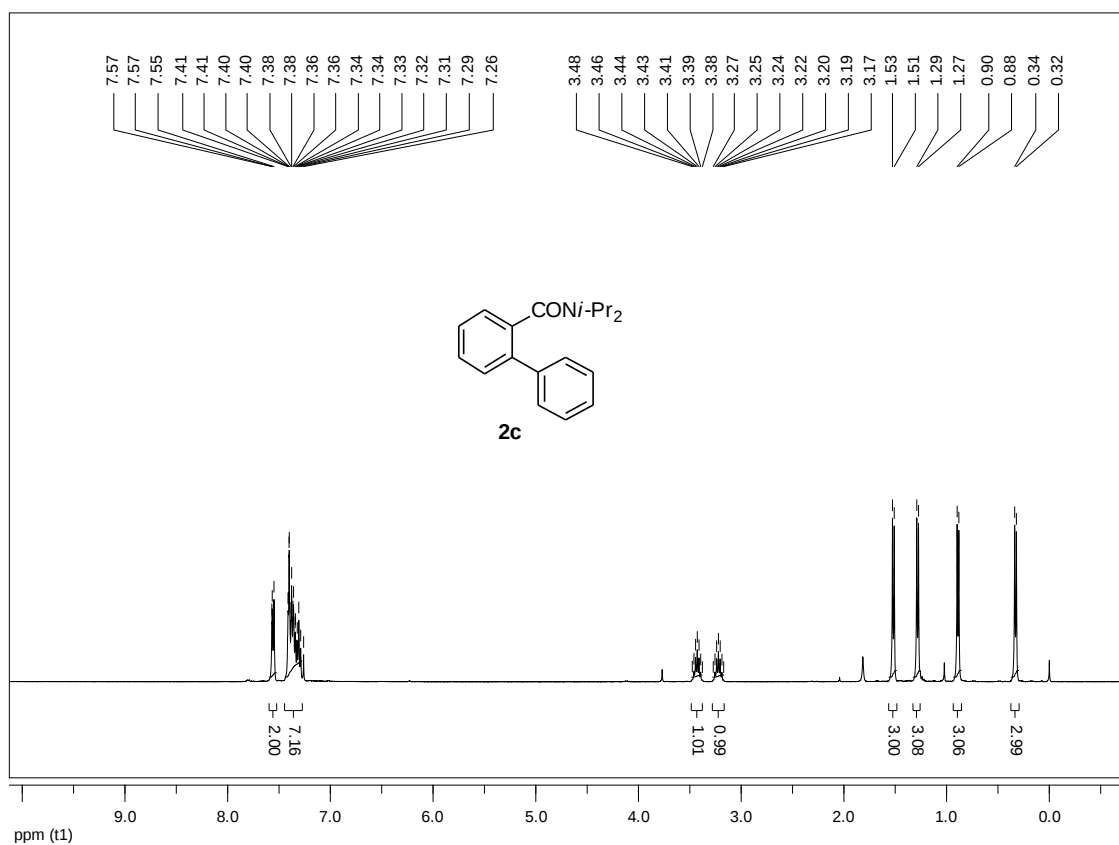
References

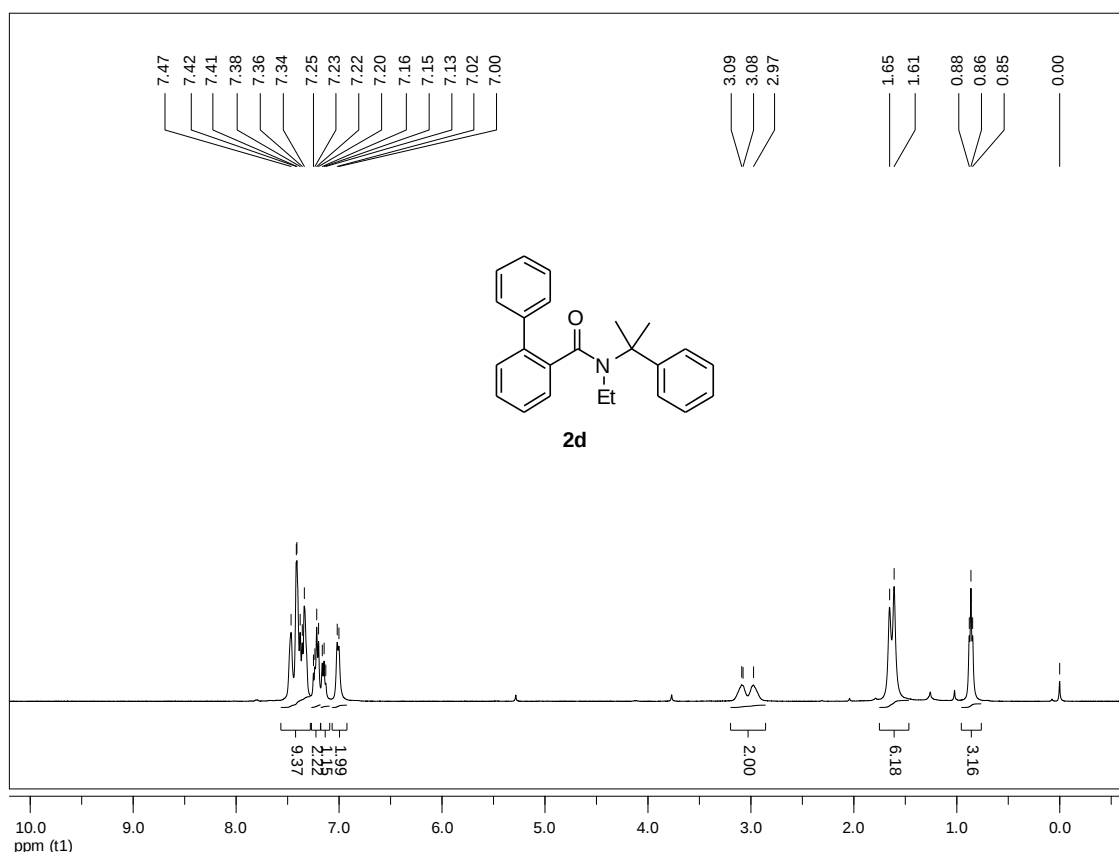
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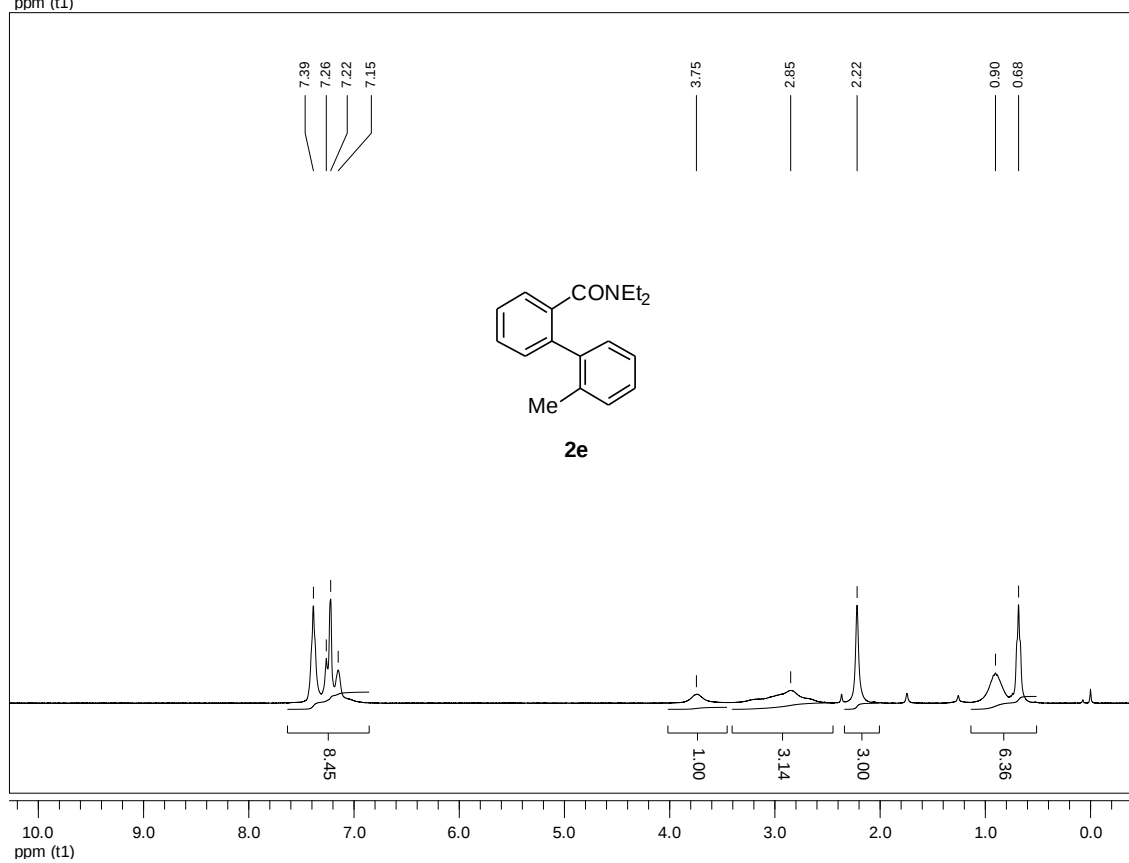
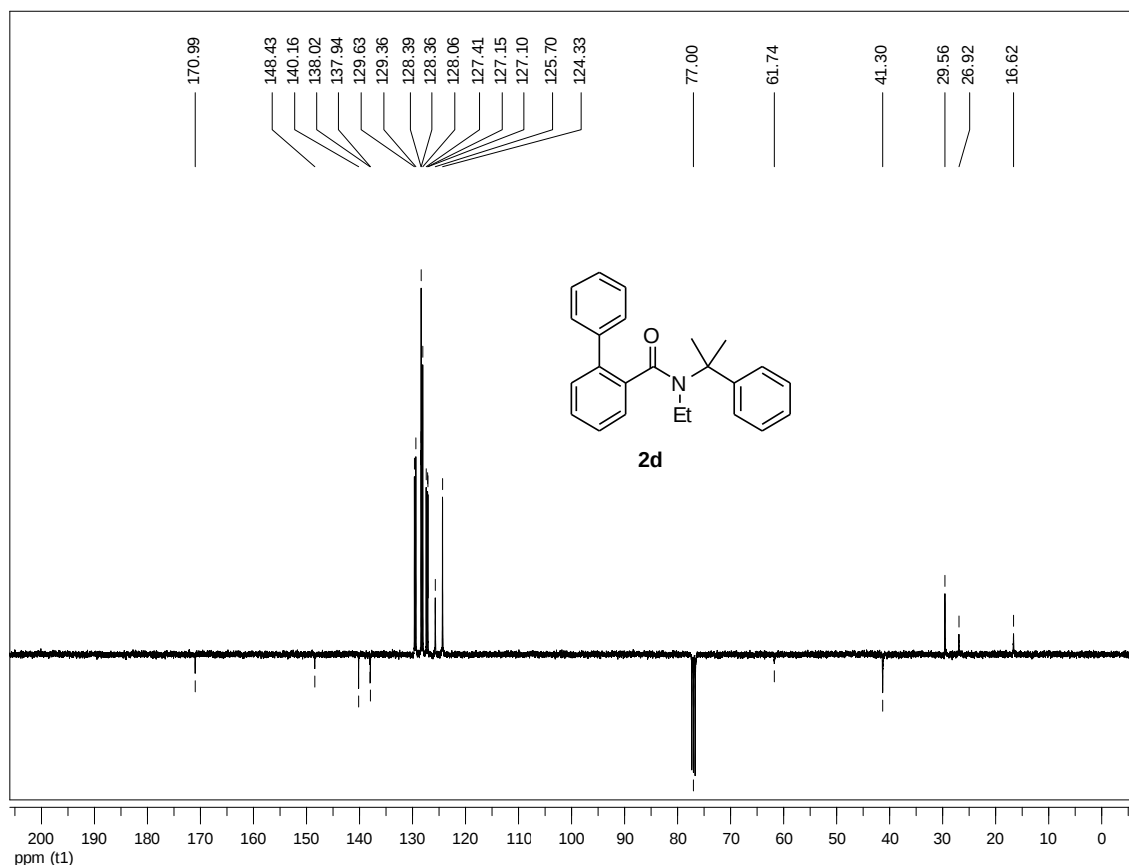
NMR spectra of products

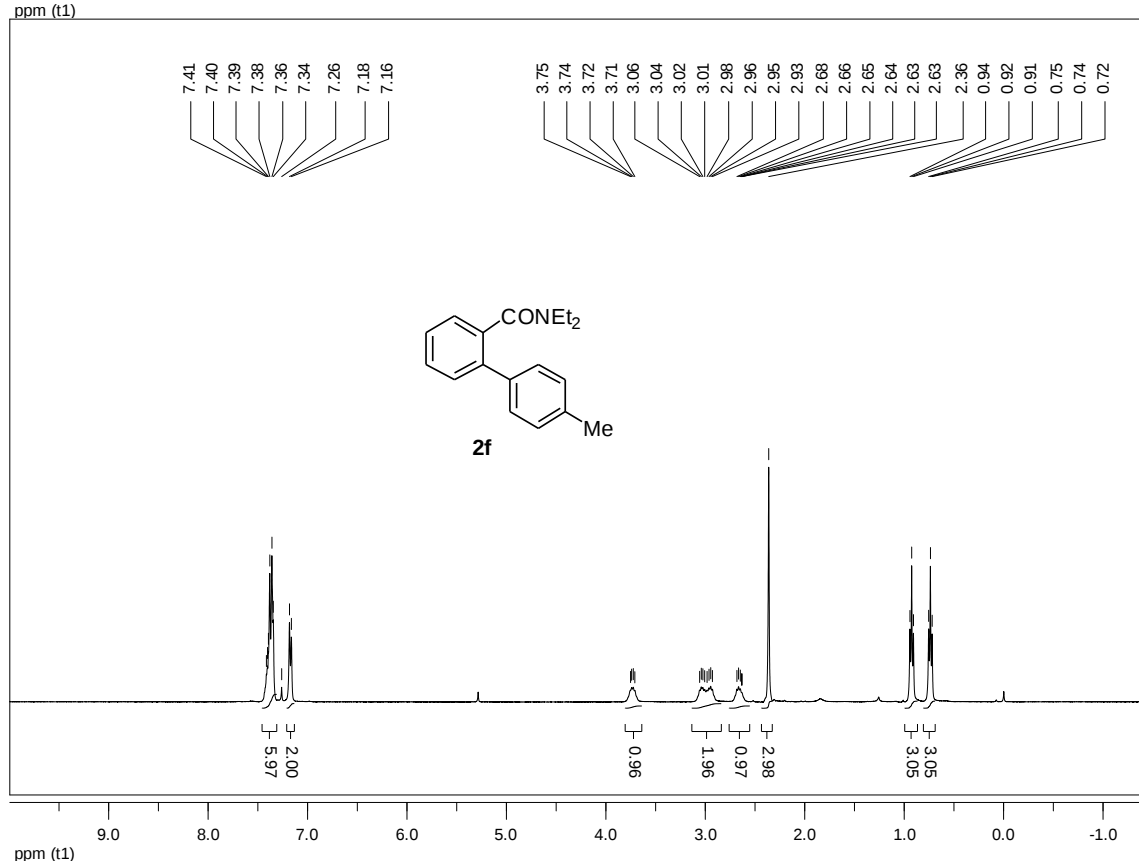
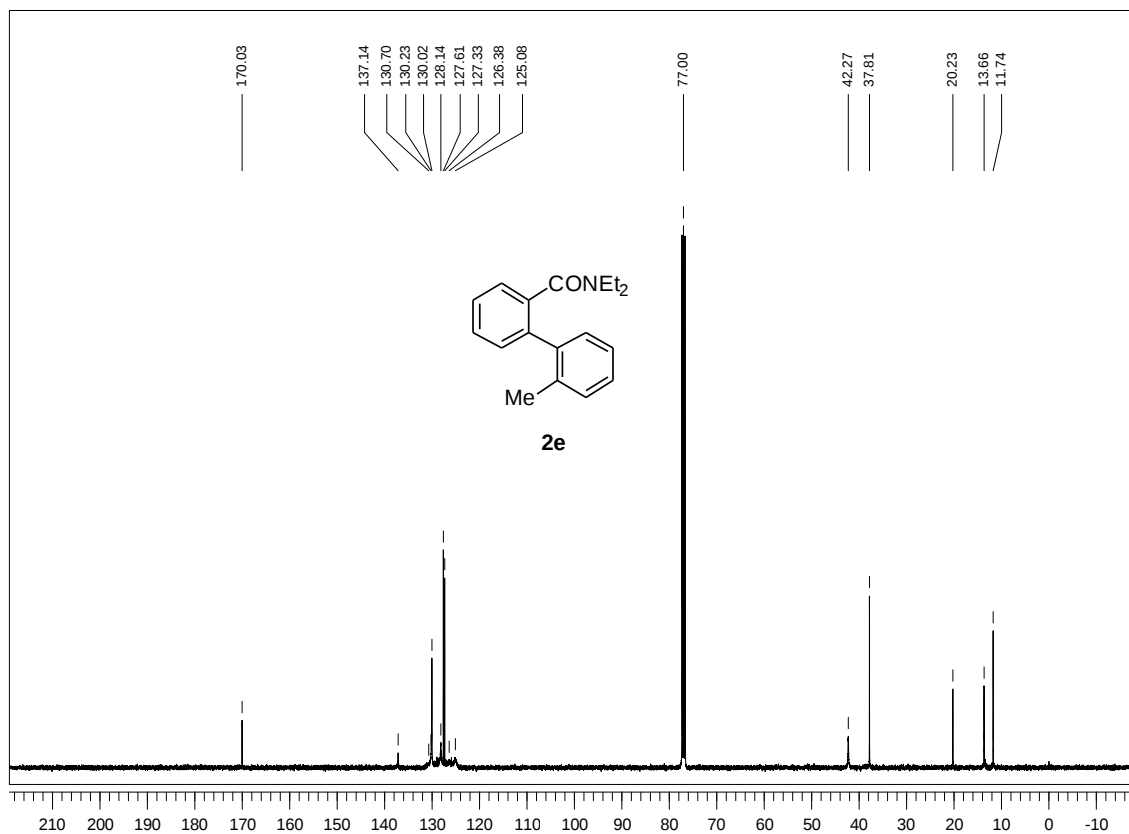


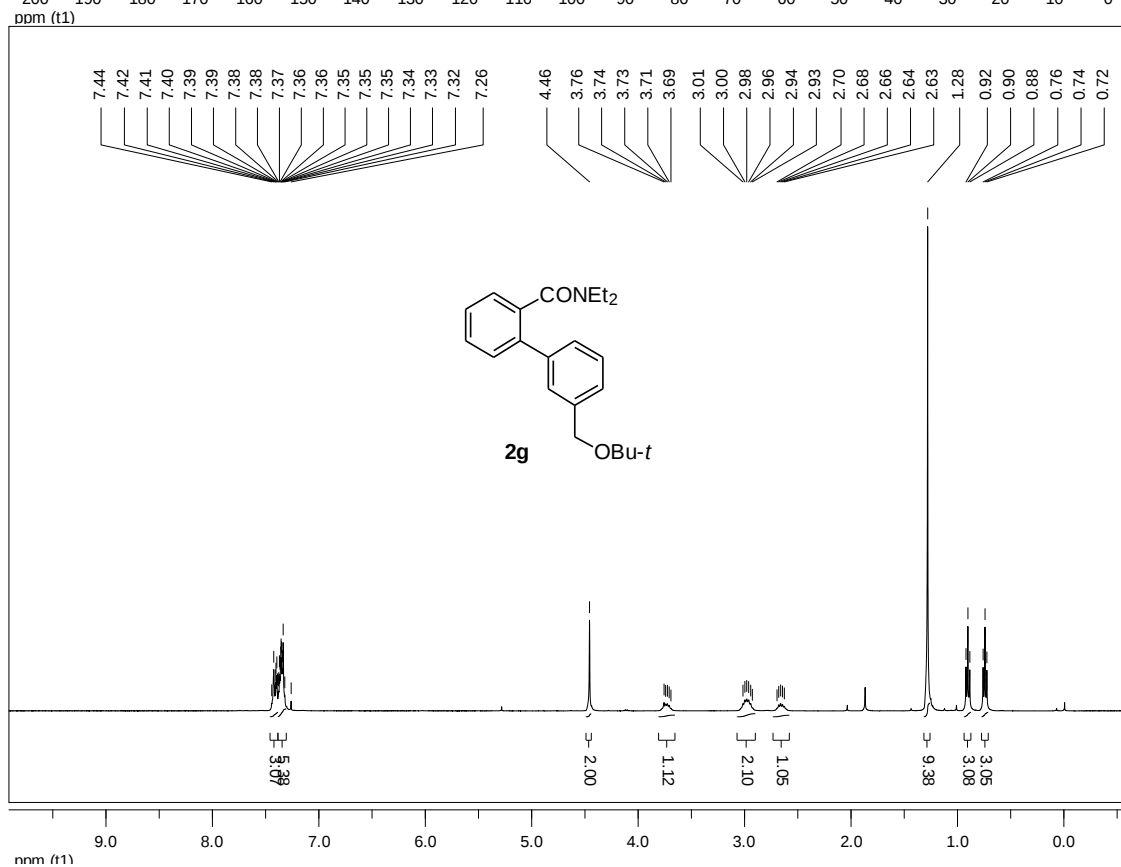
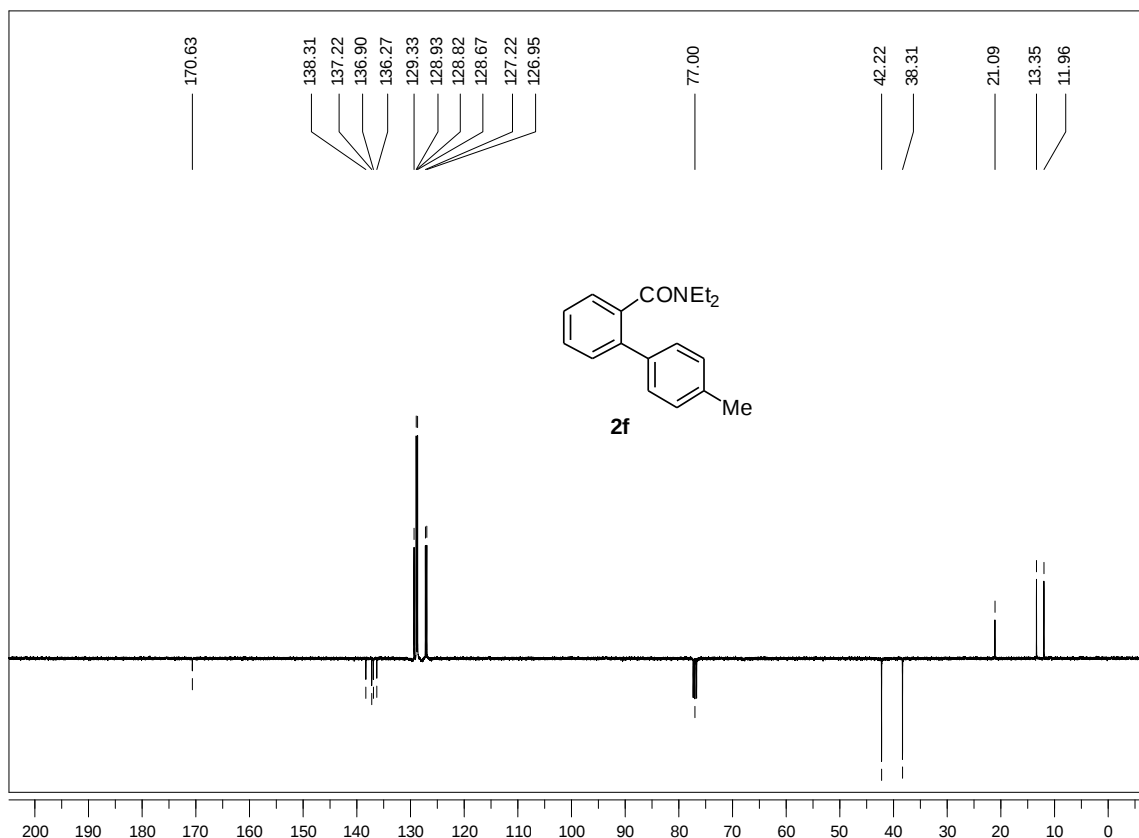


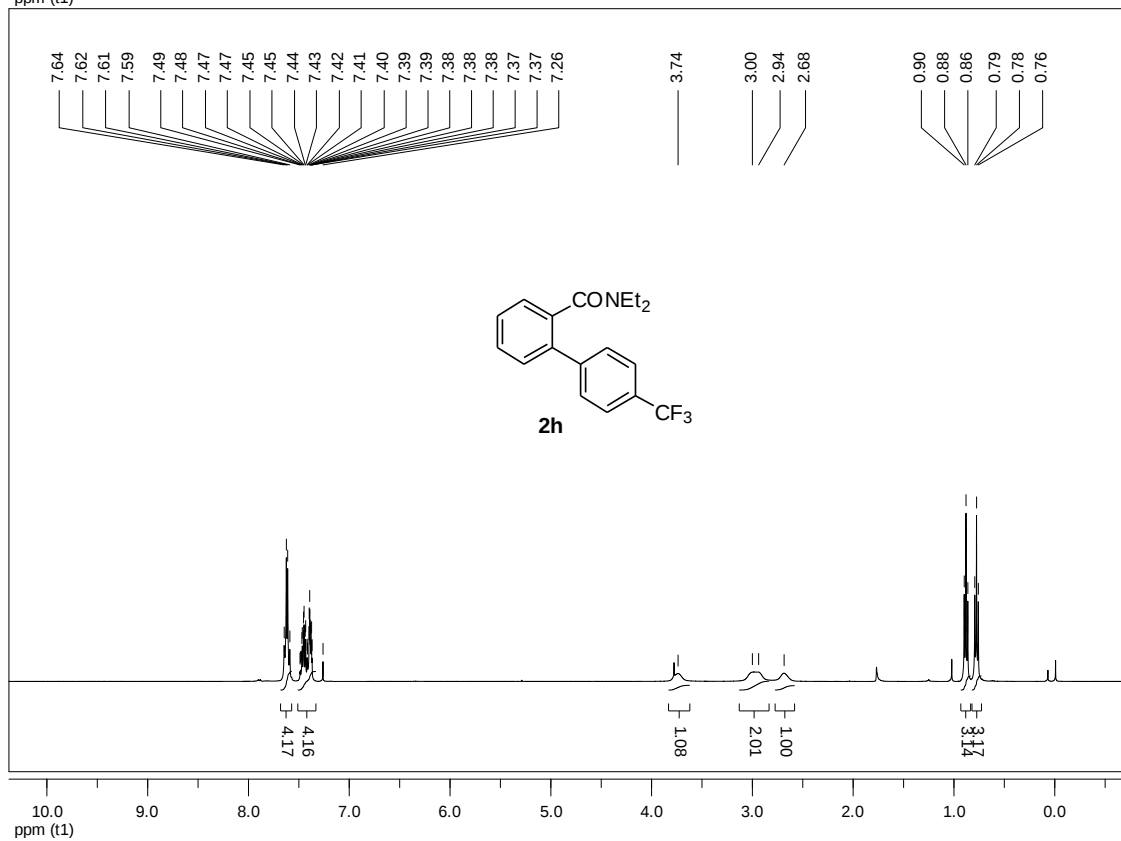
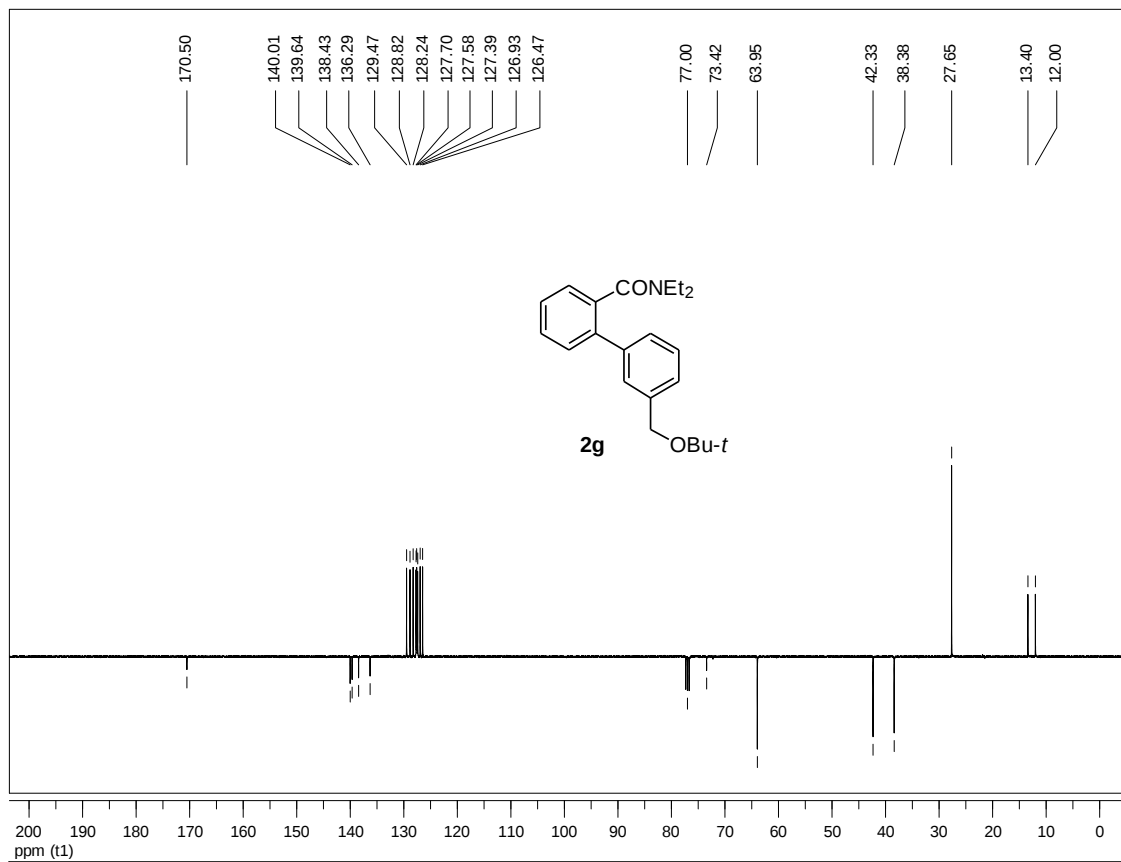


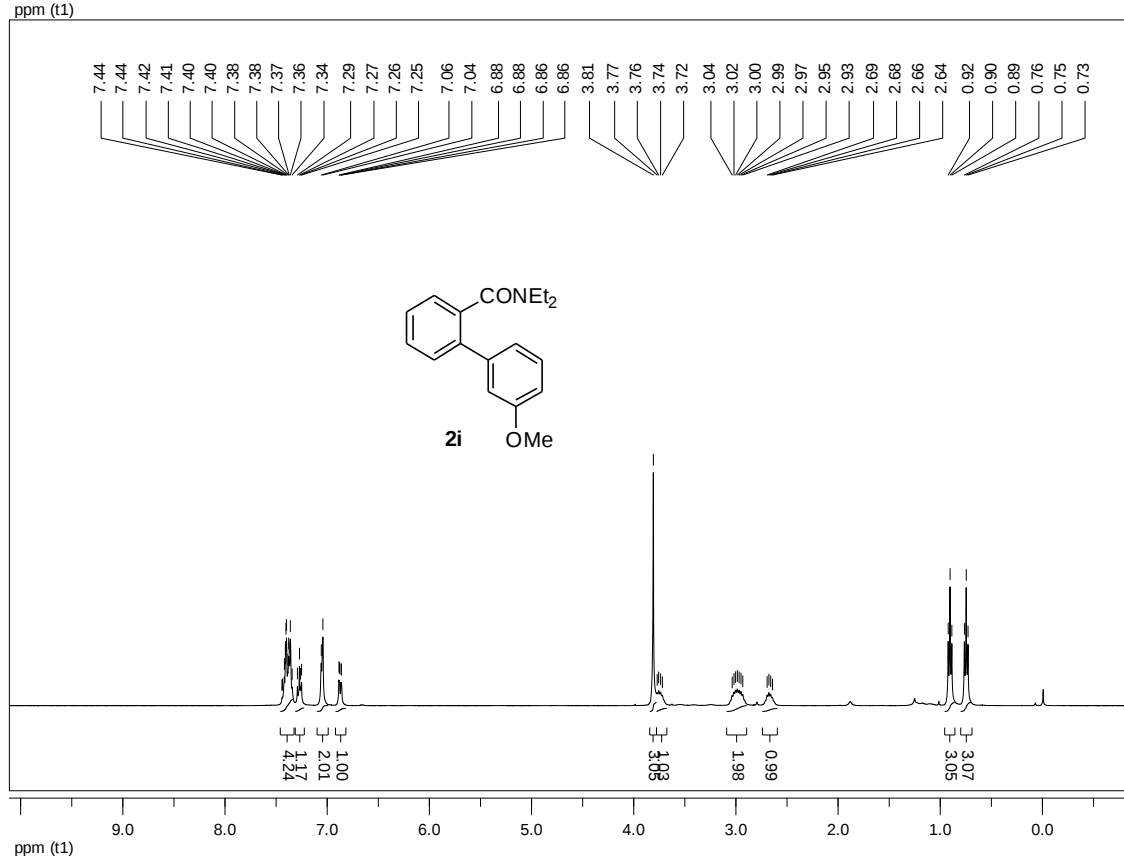
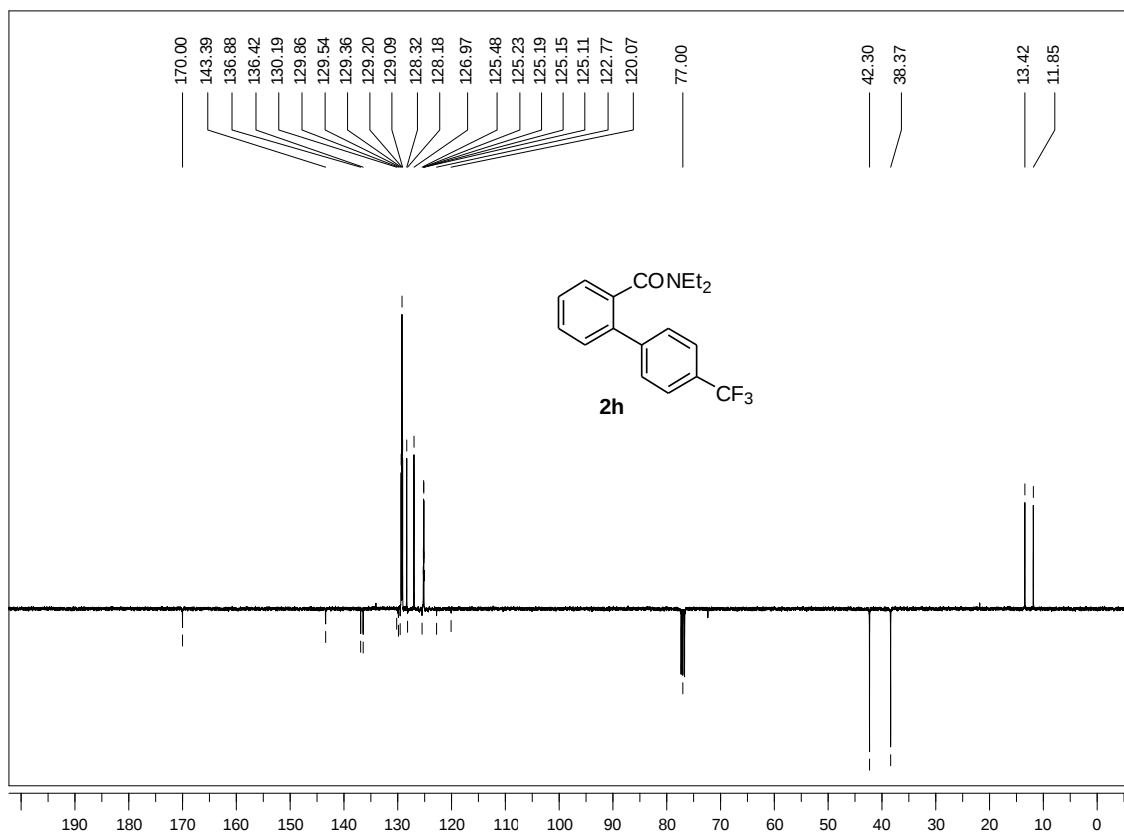


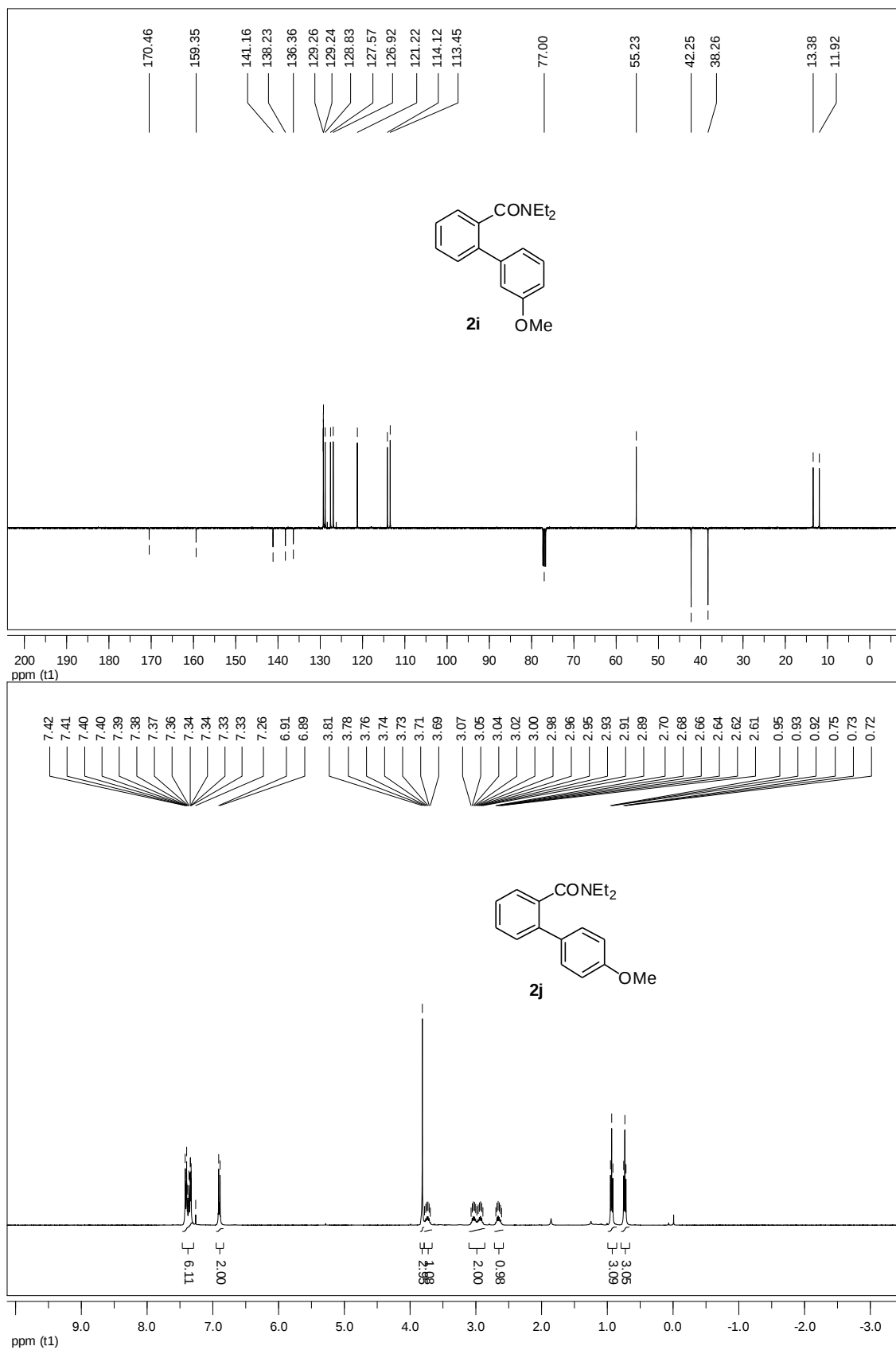


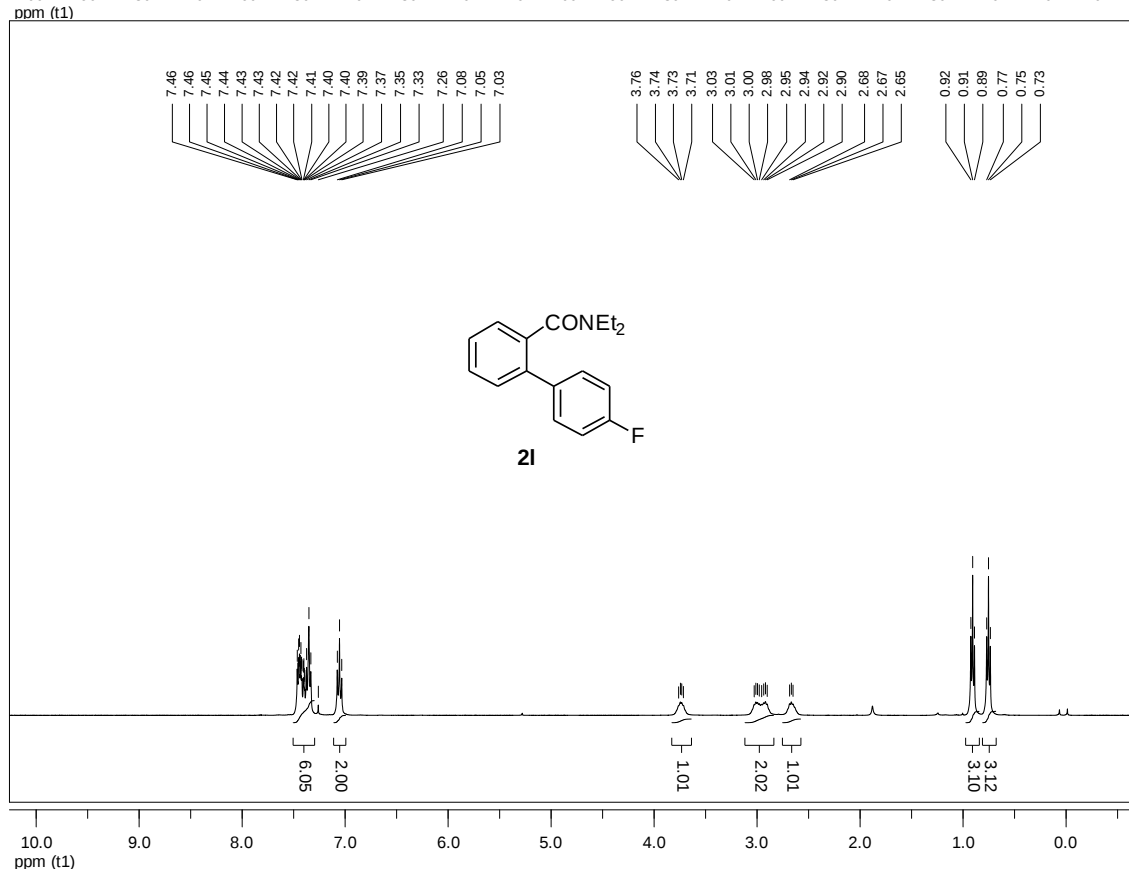
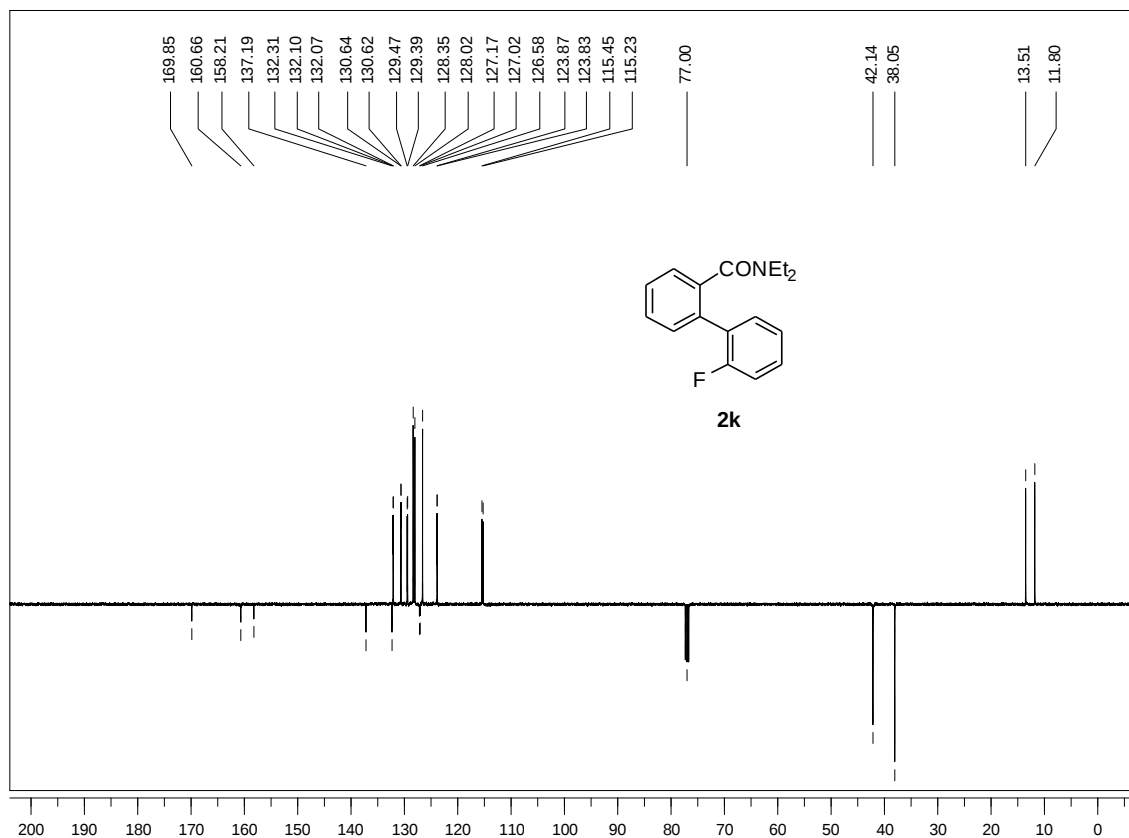


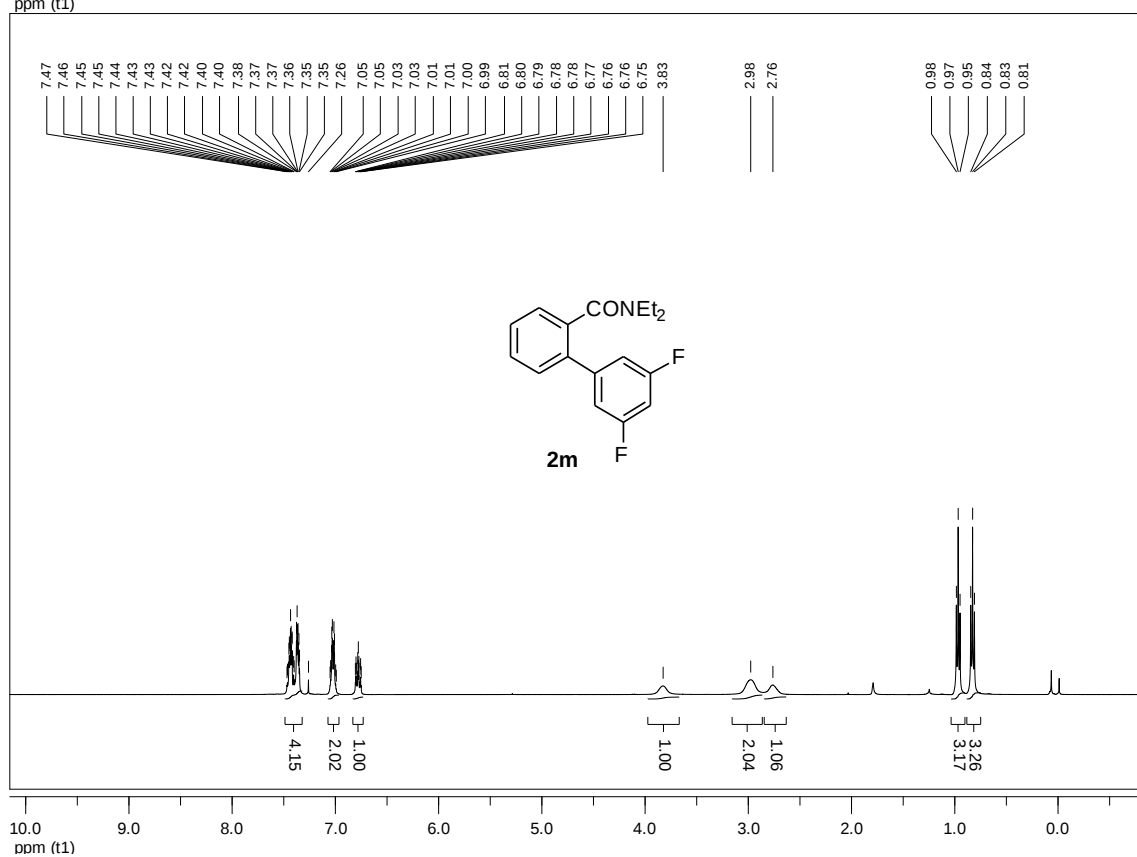
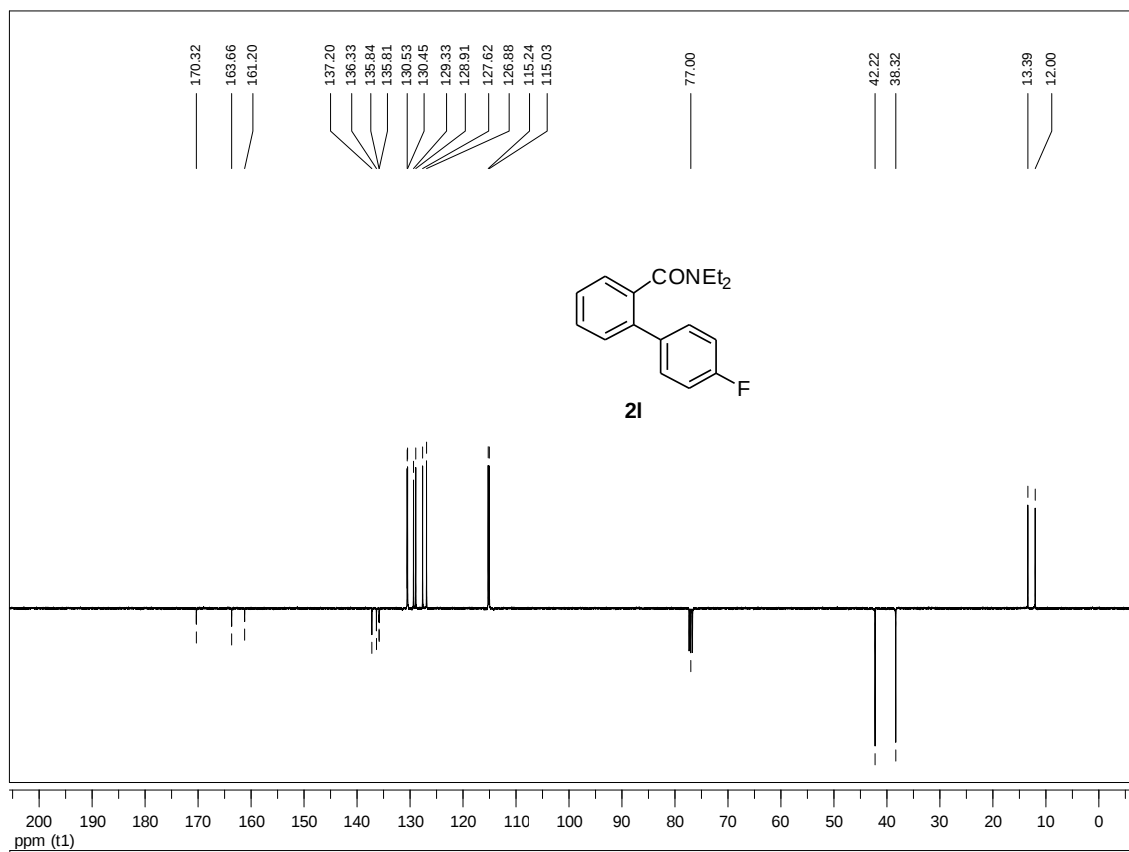


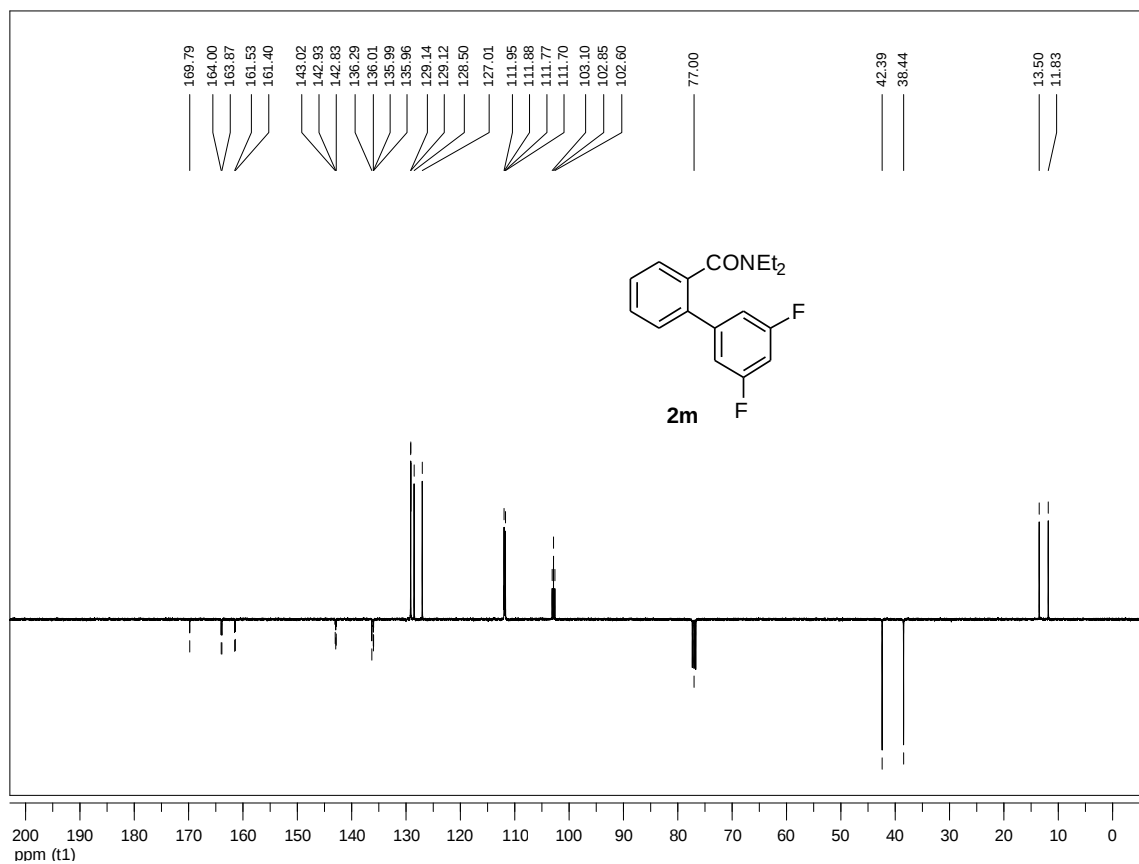


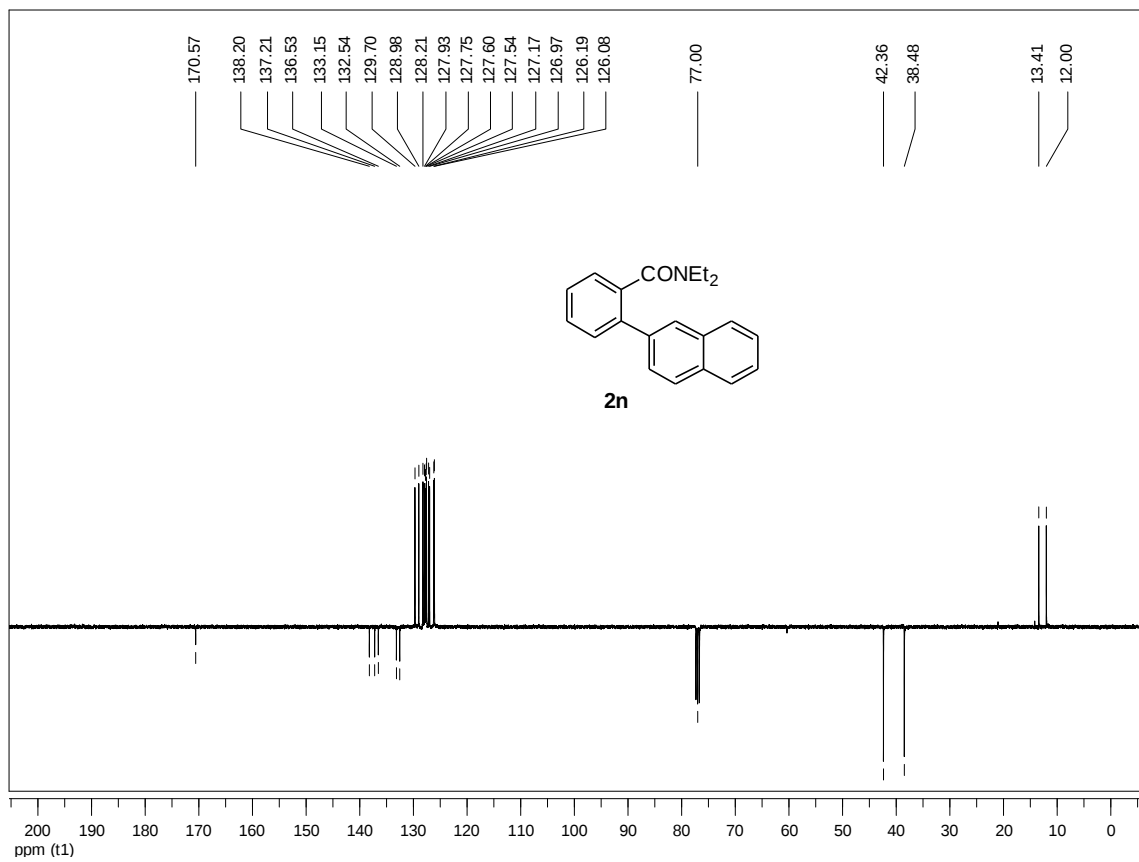
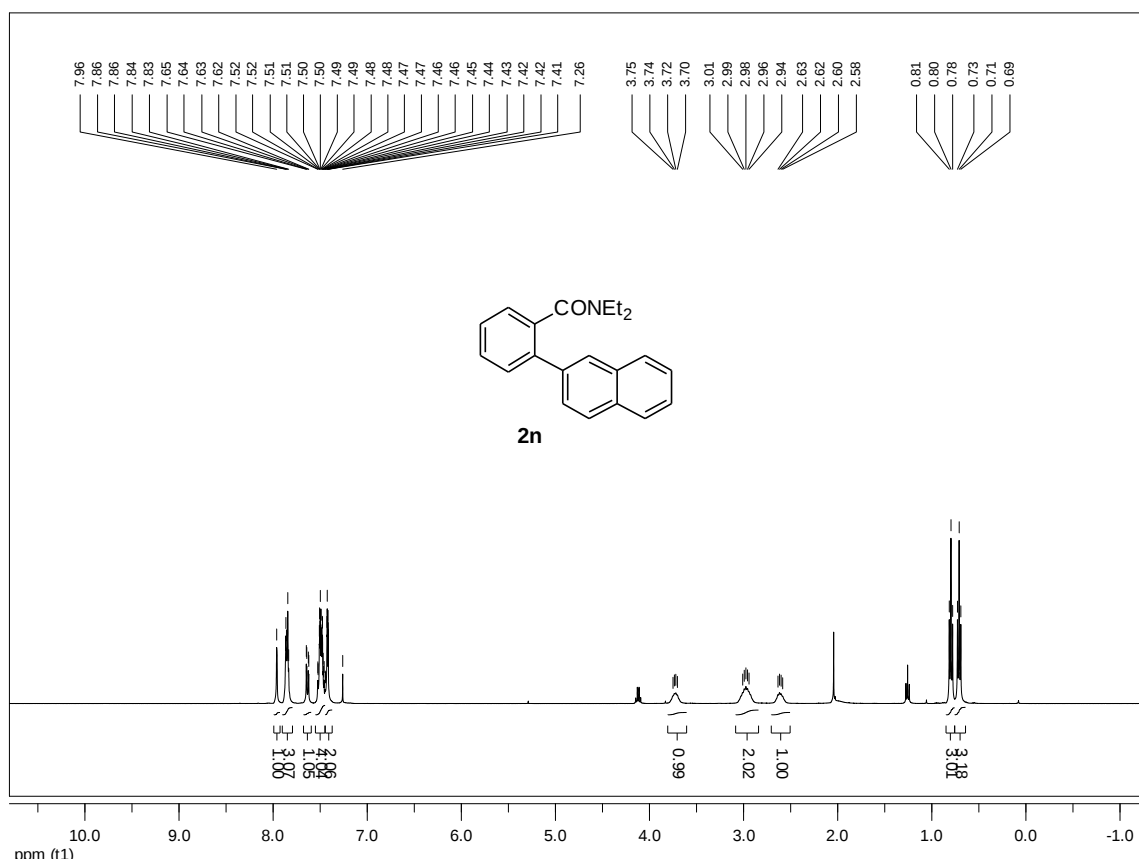


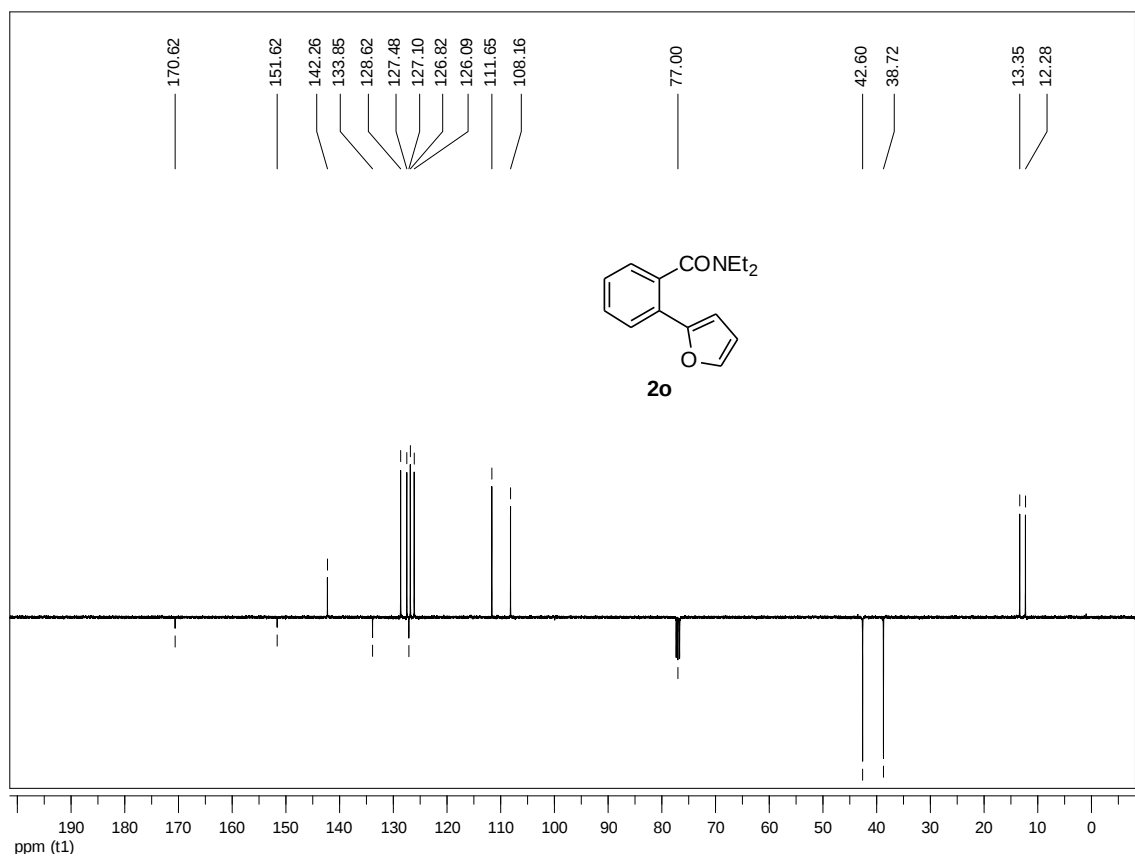
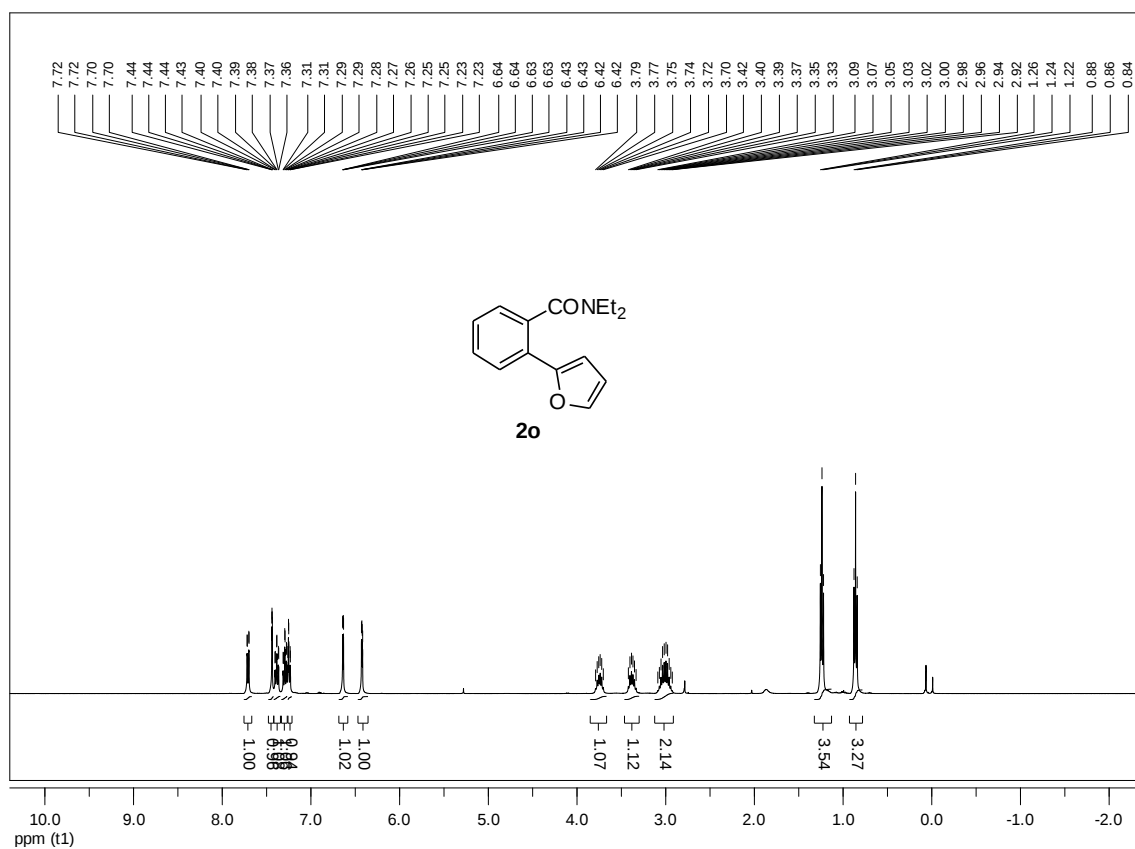


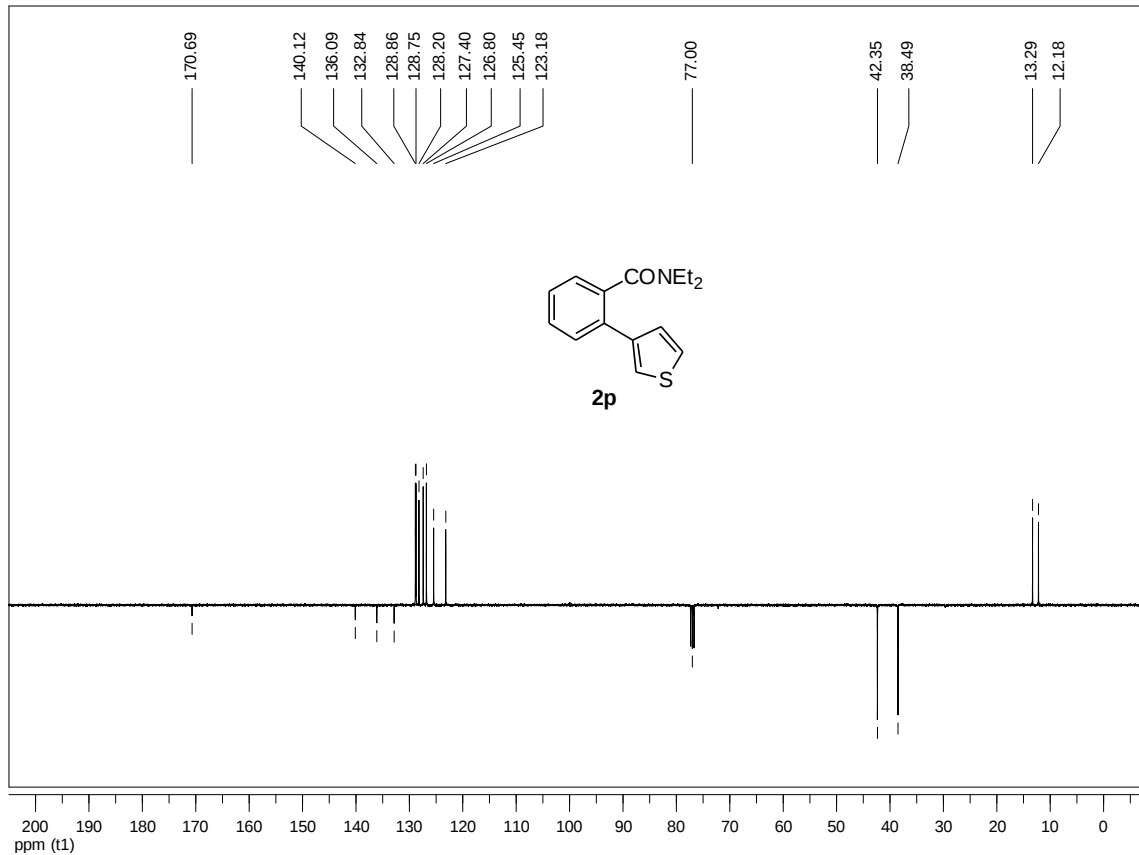
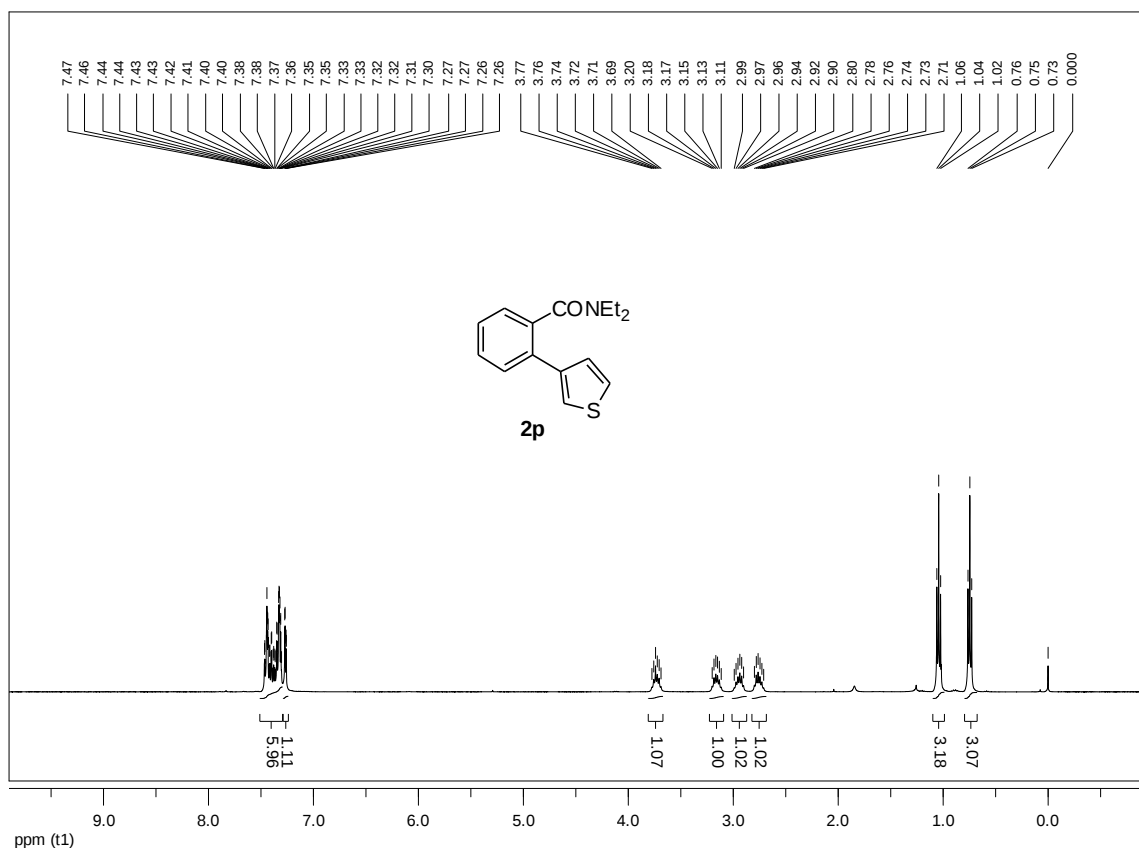


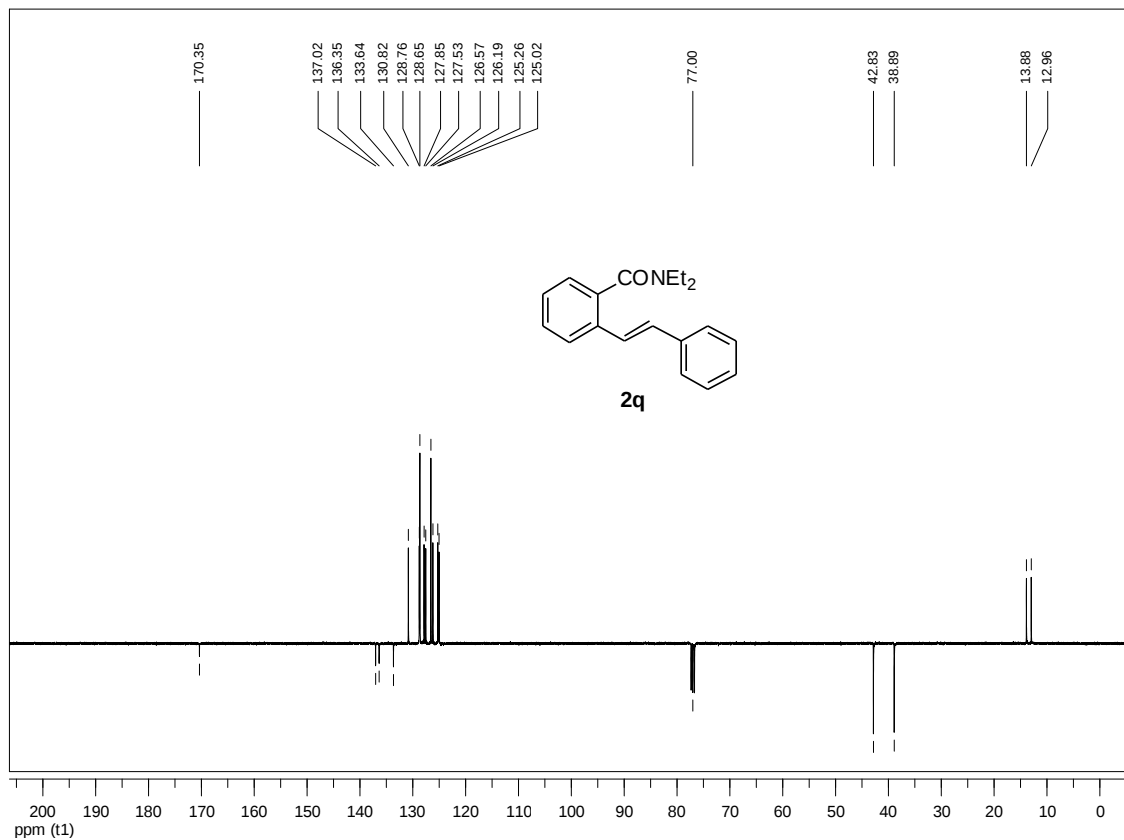
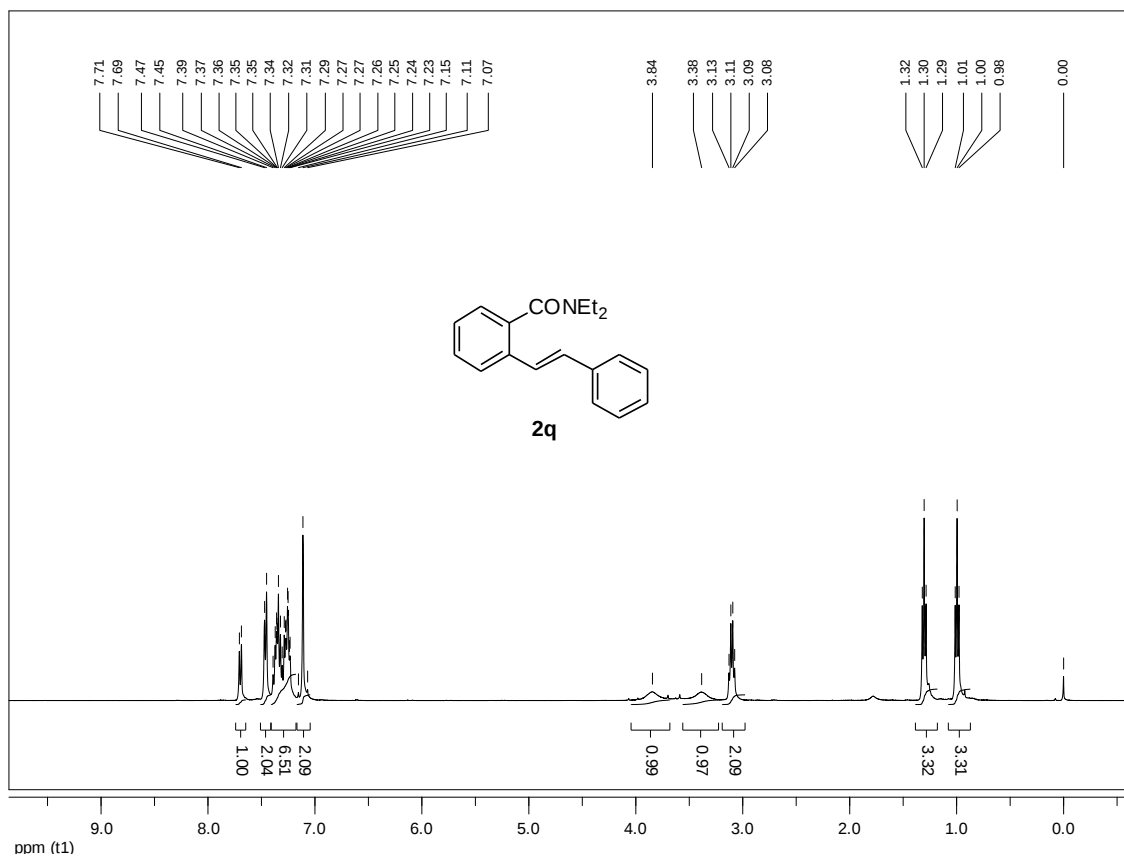


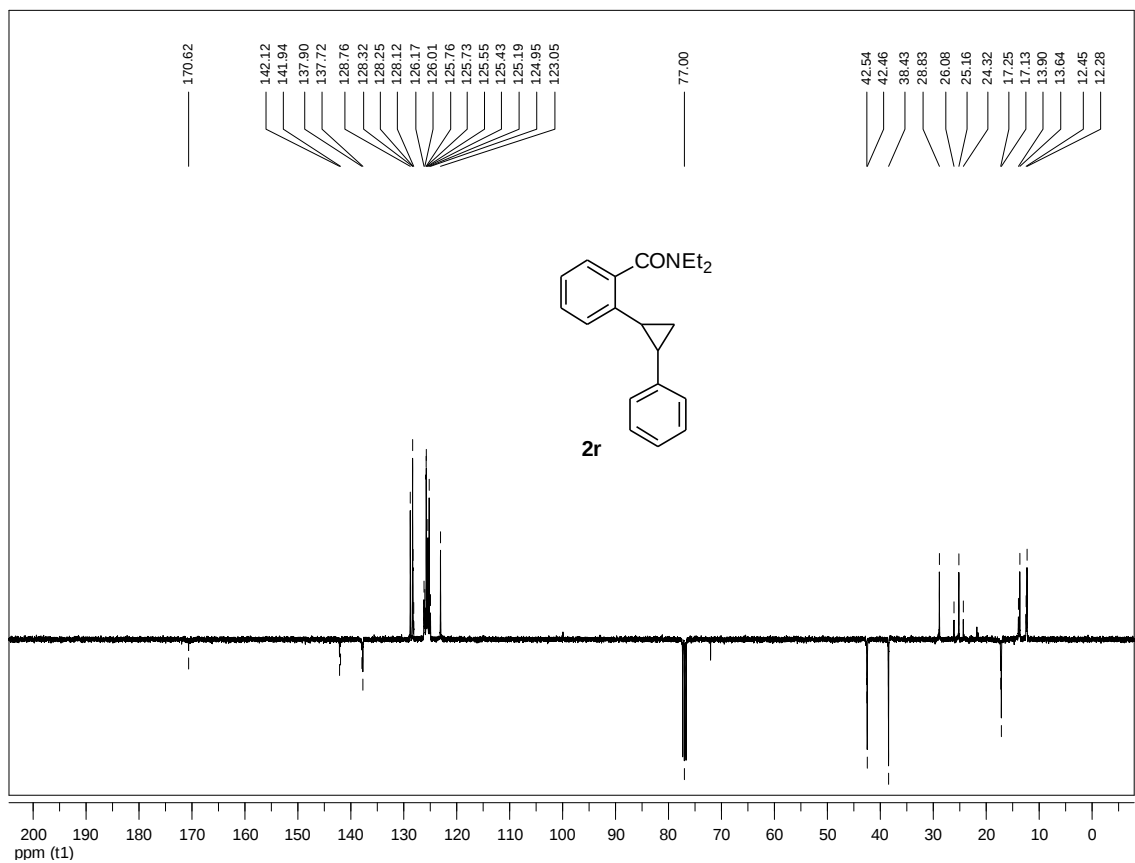
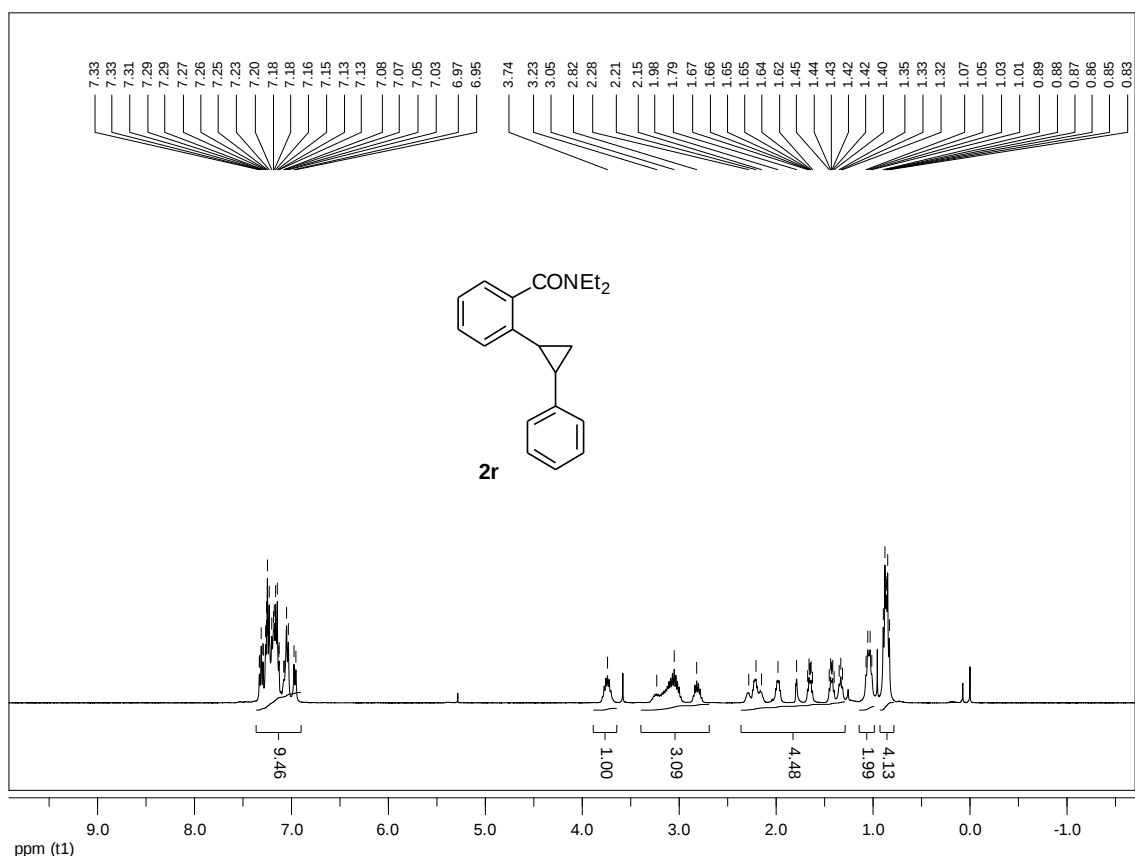


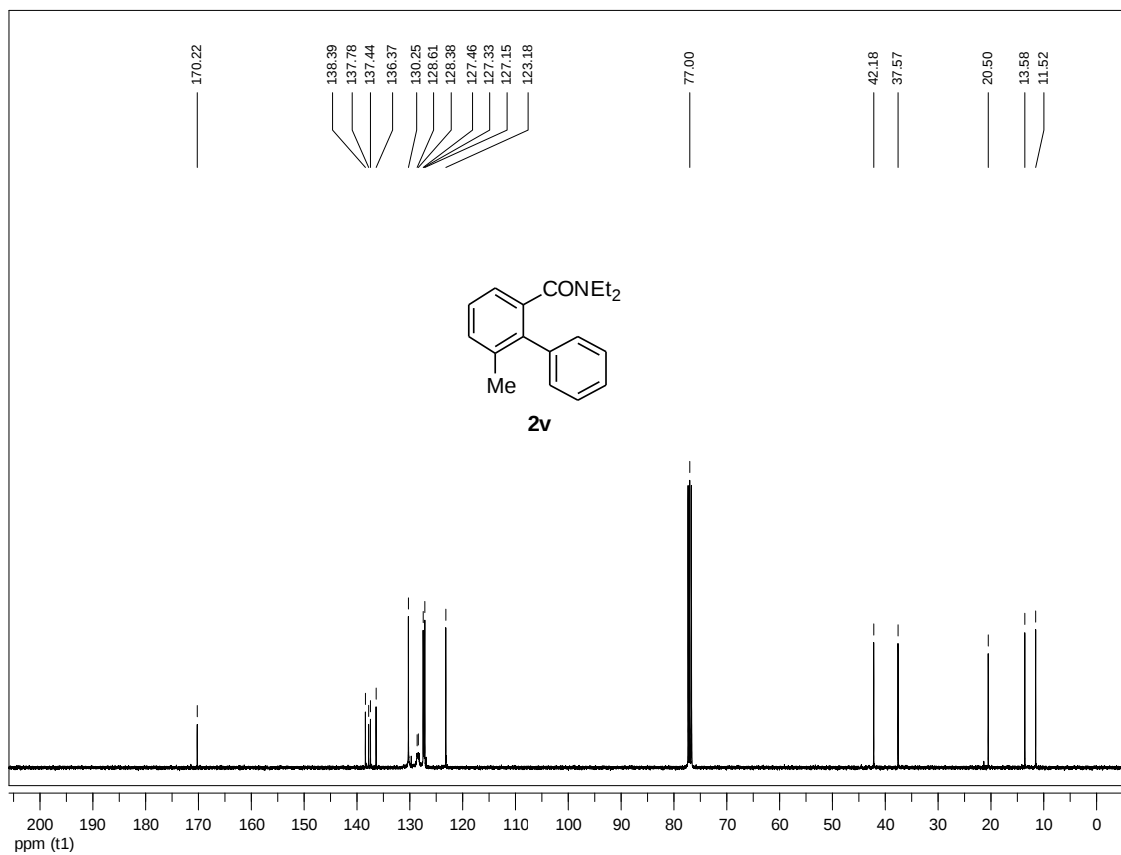
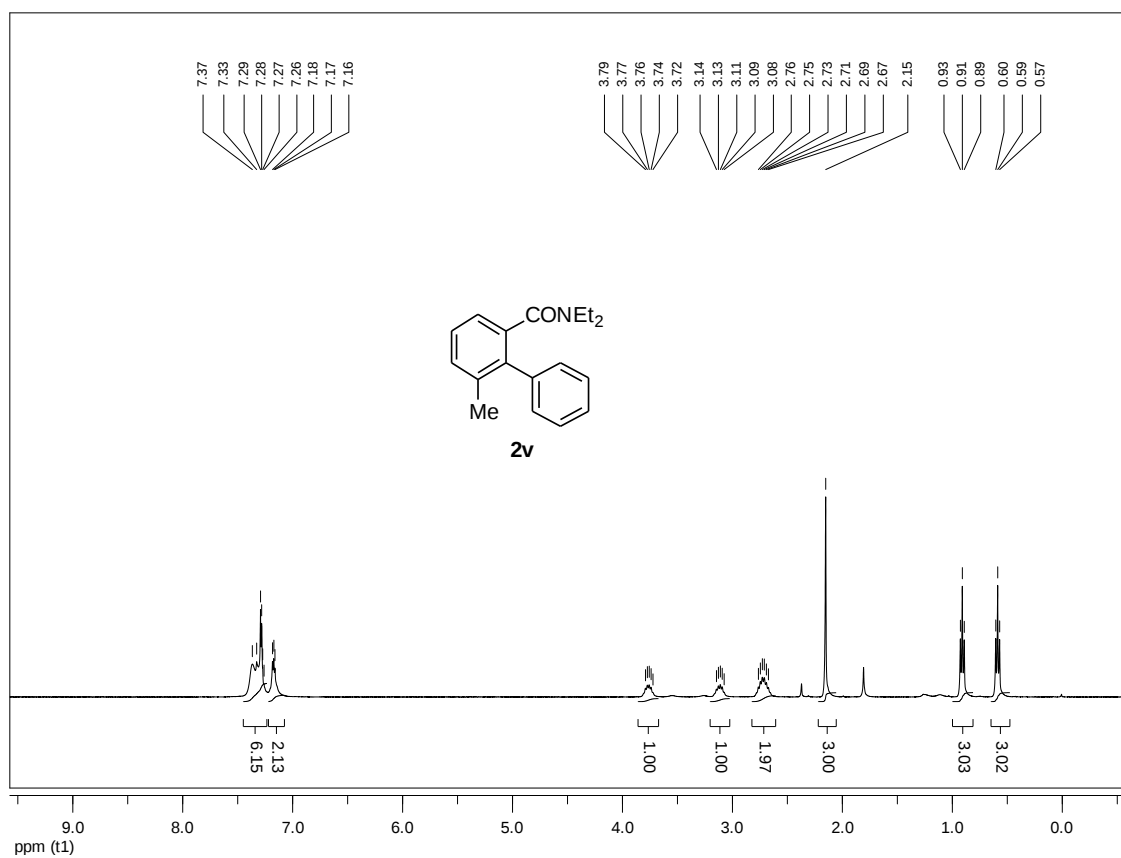


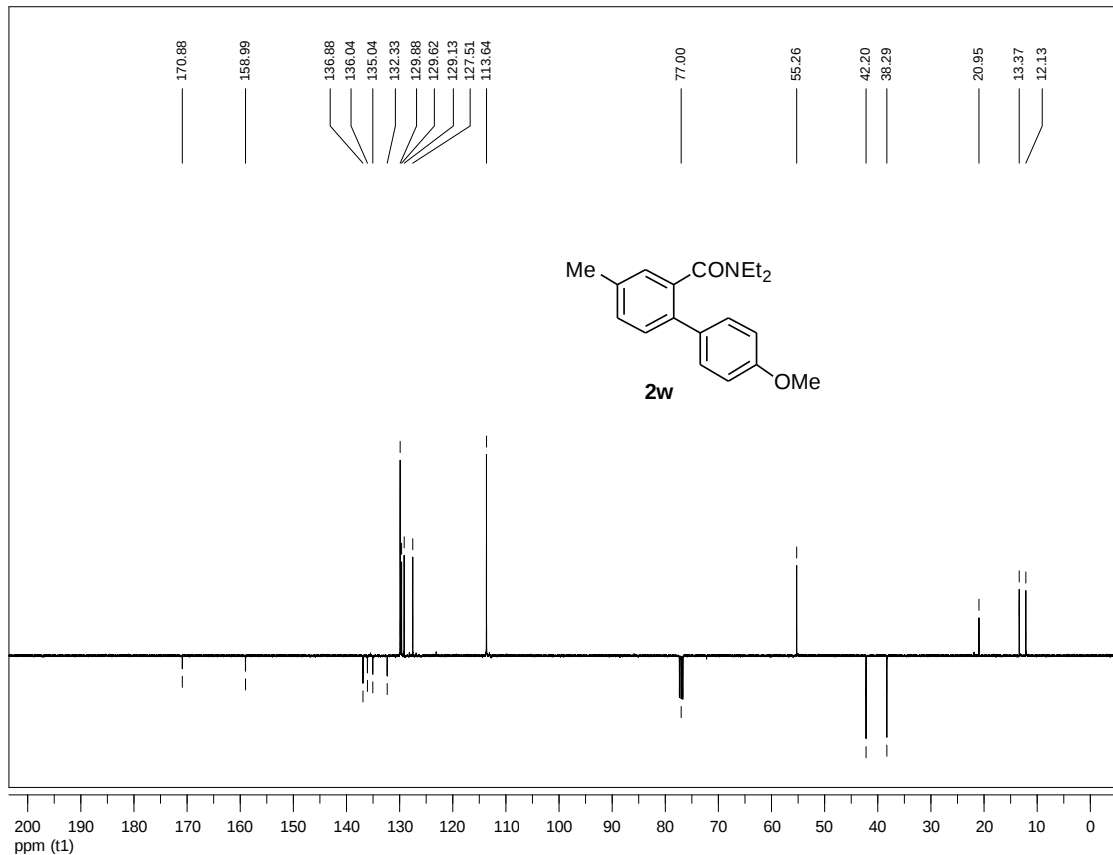
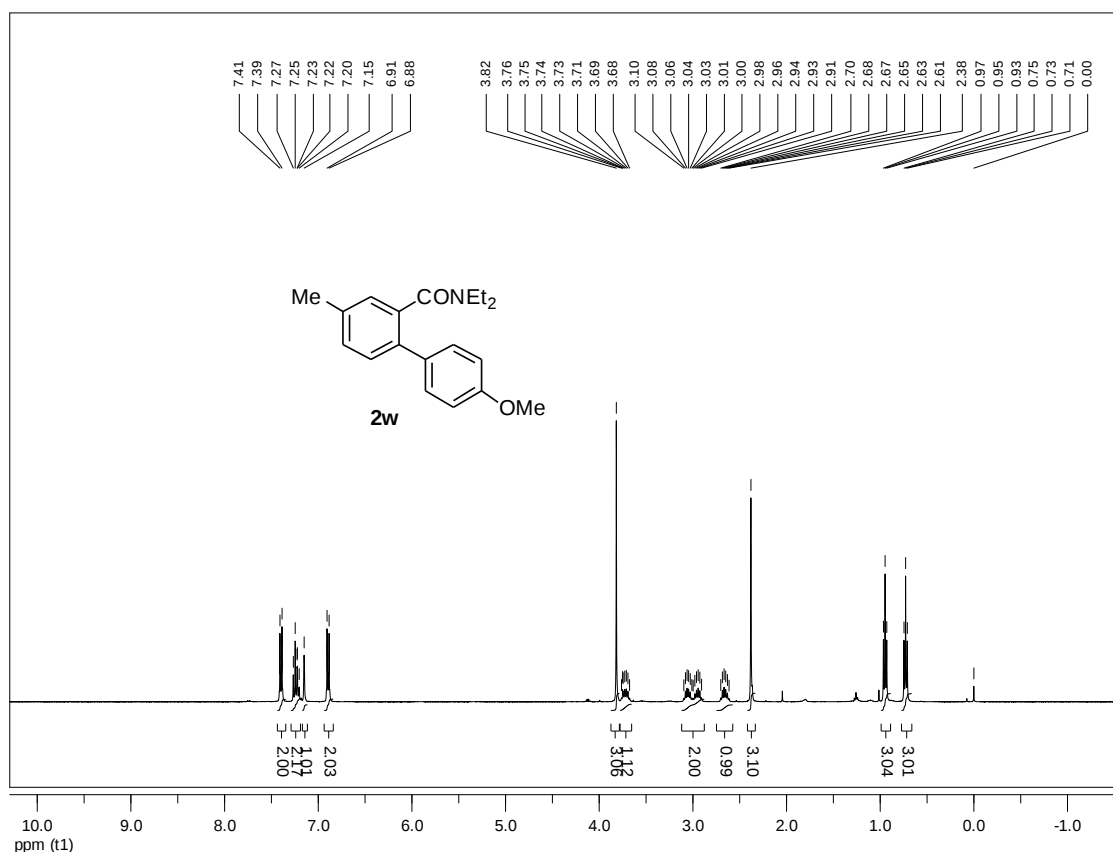


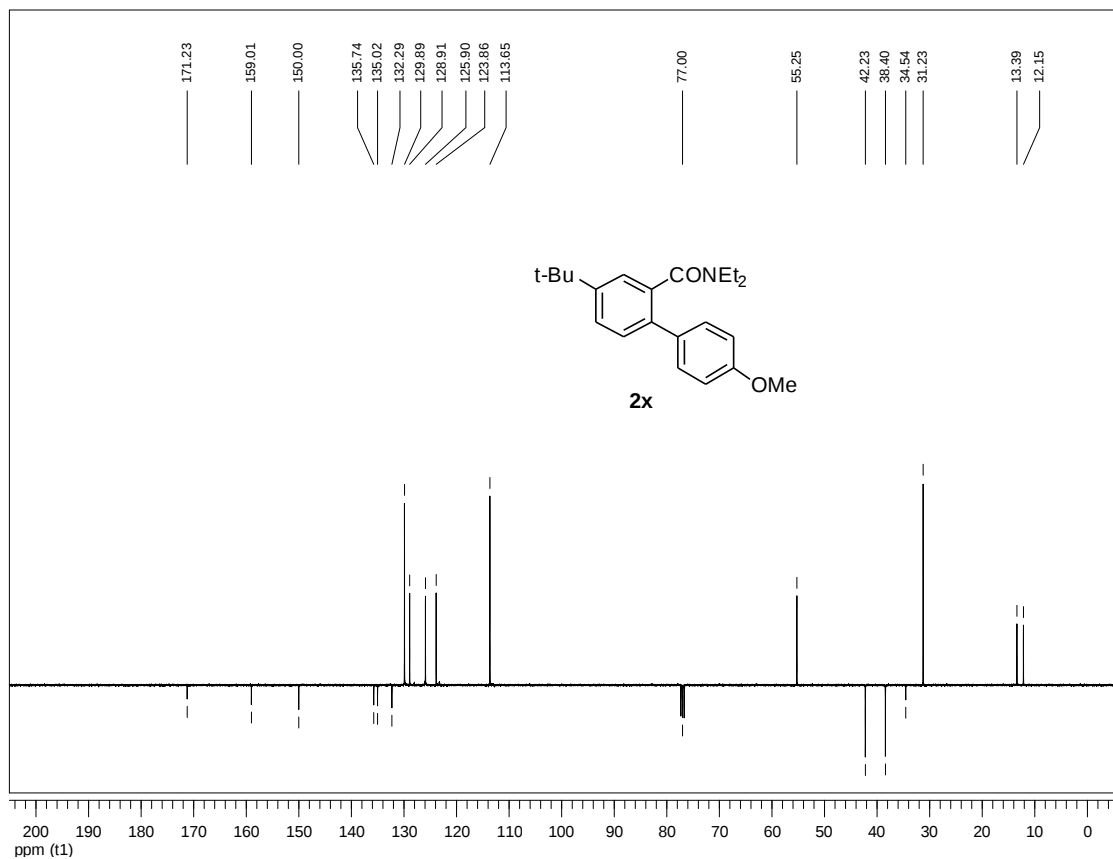
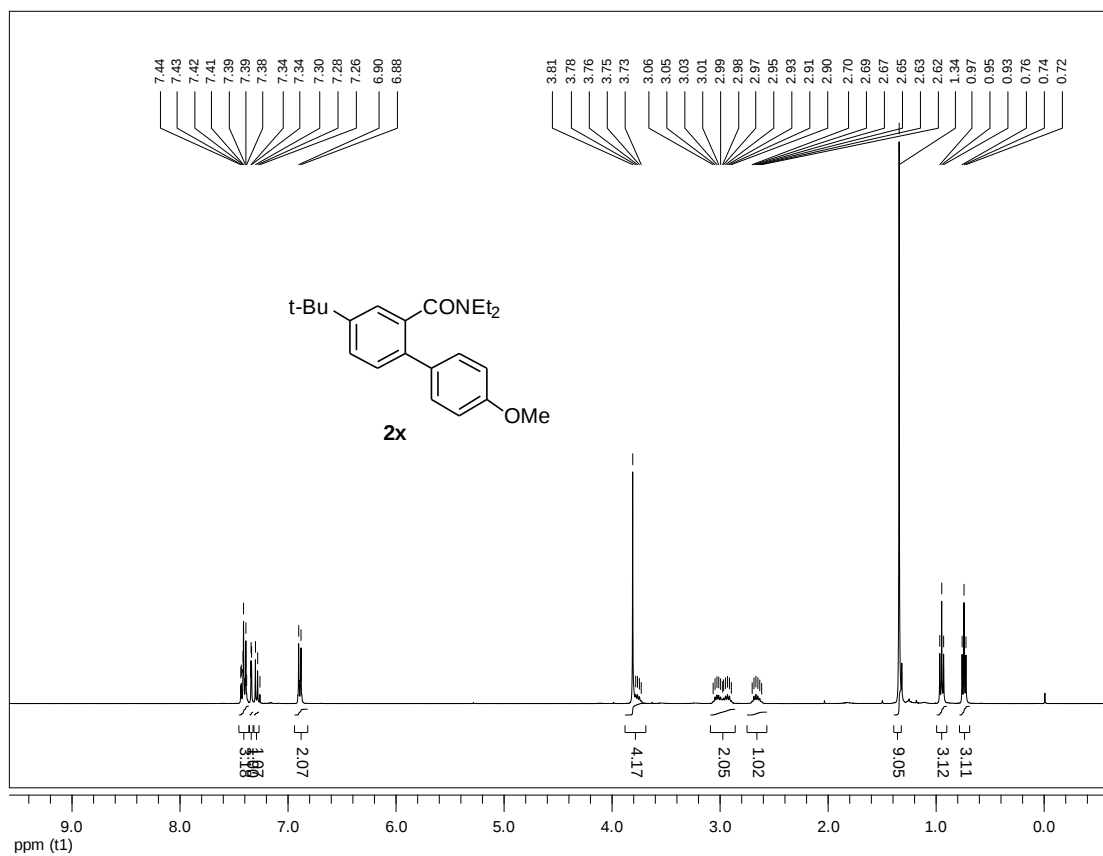


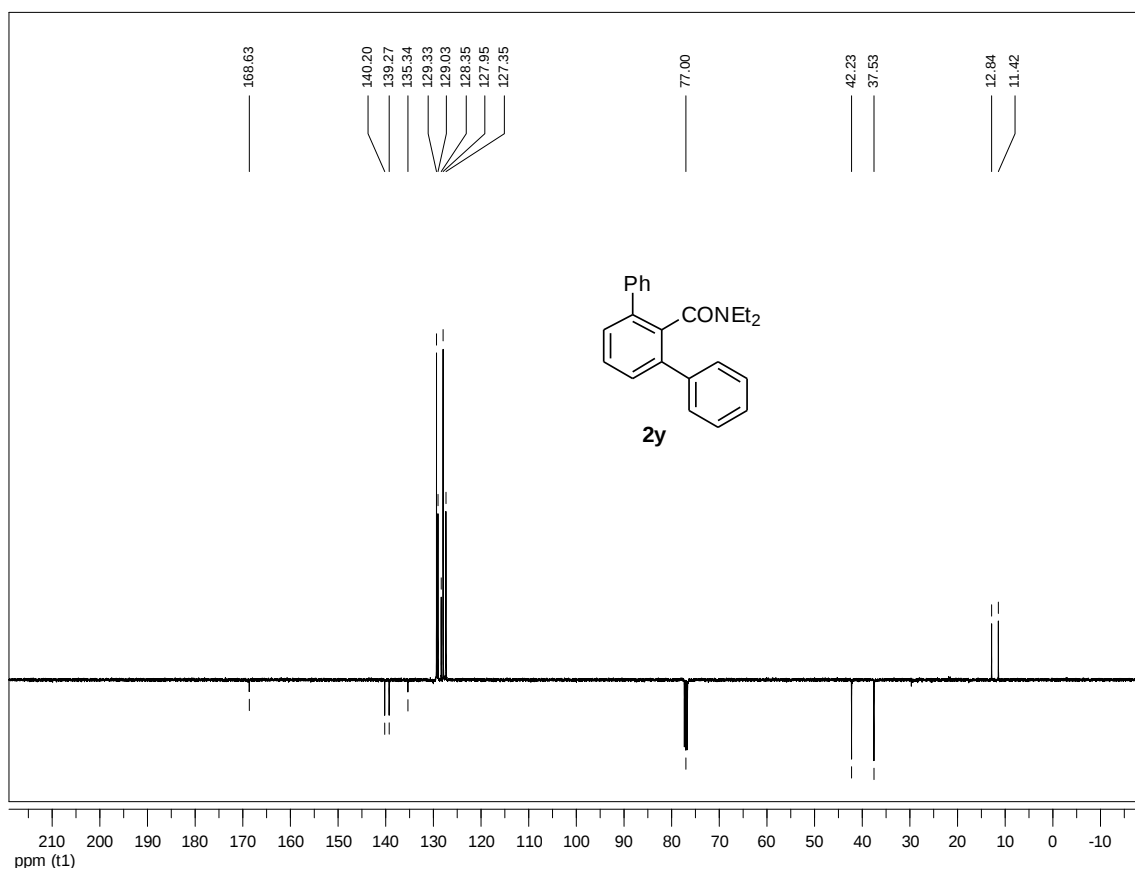
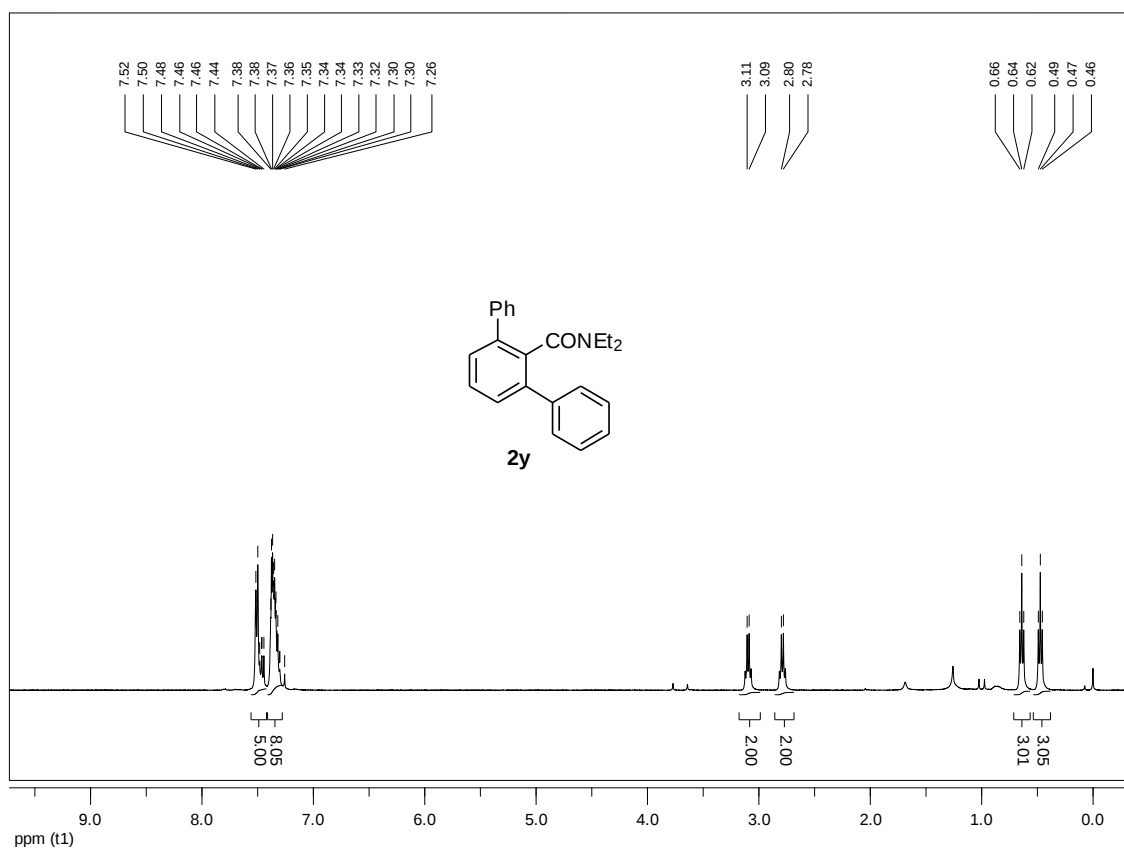


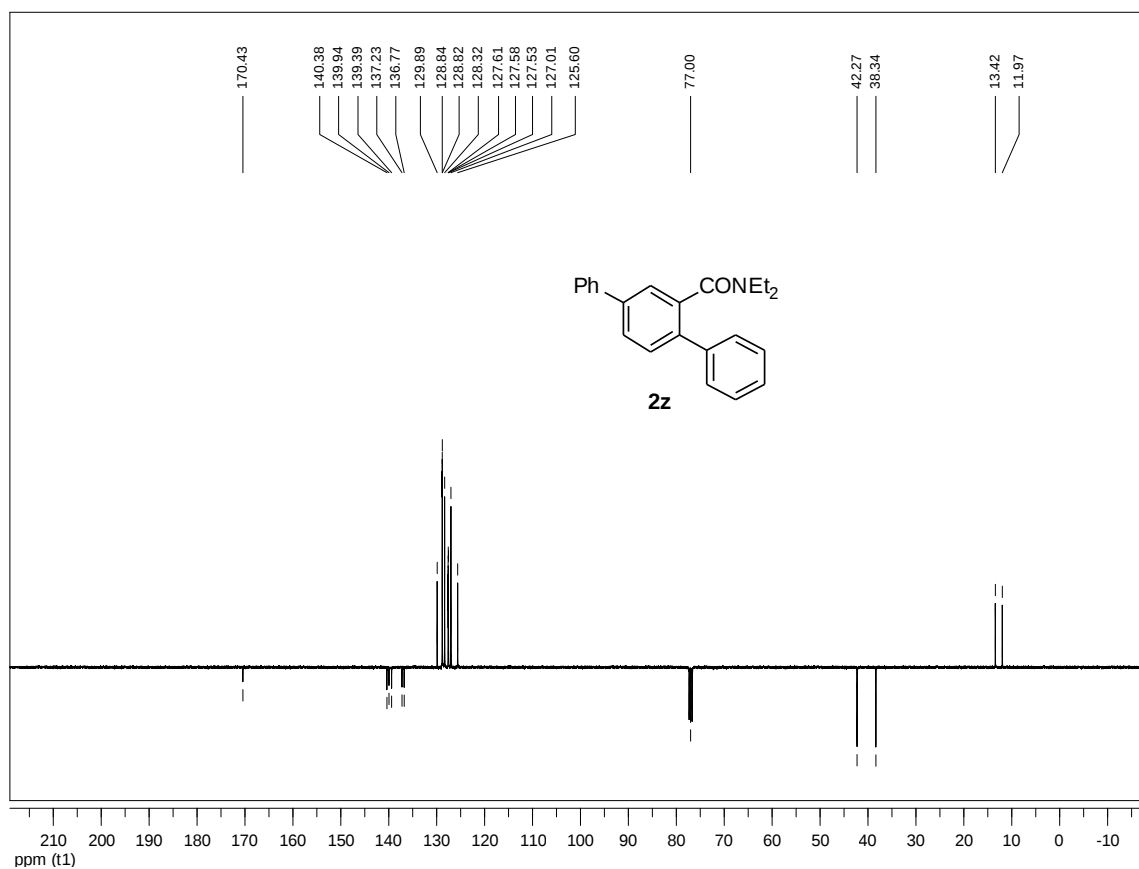
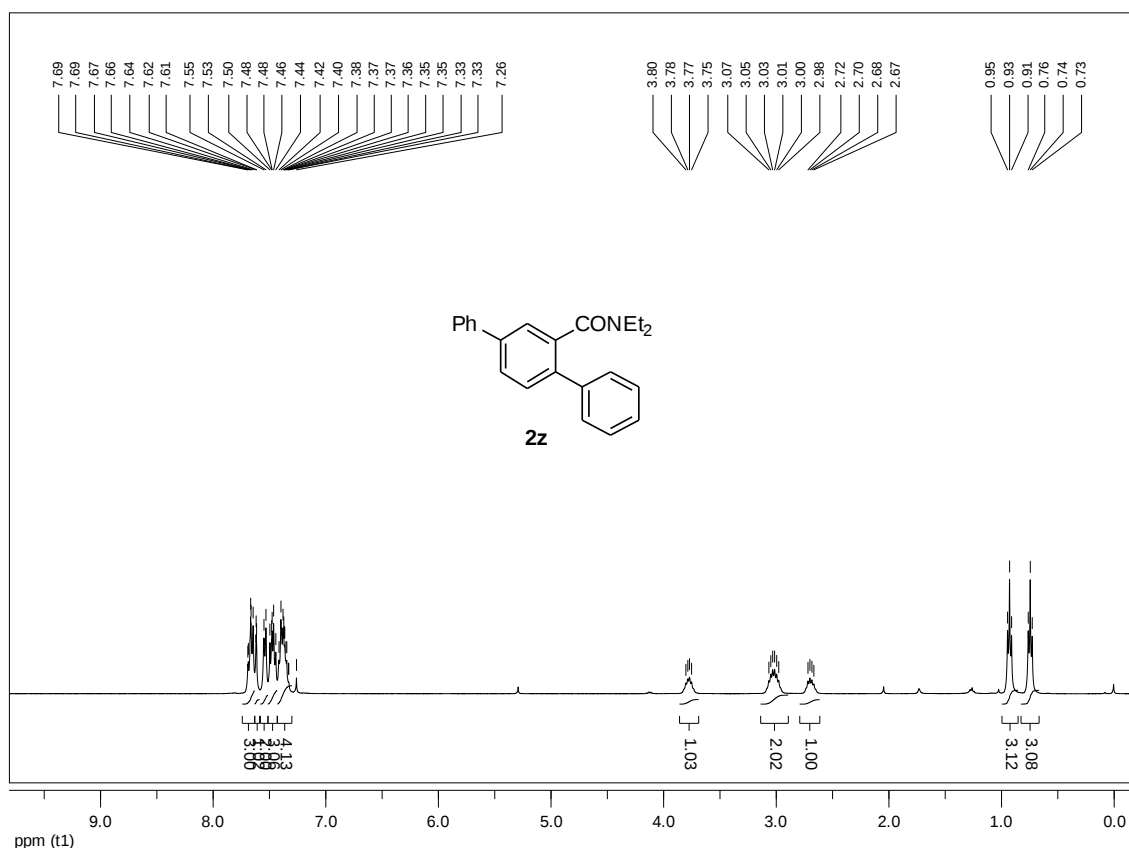


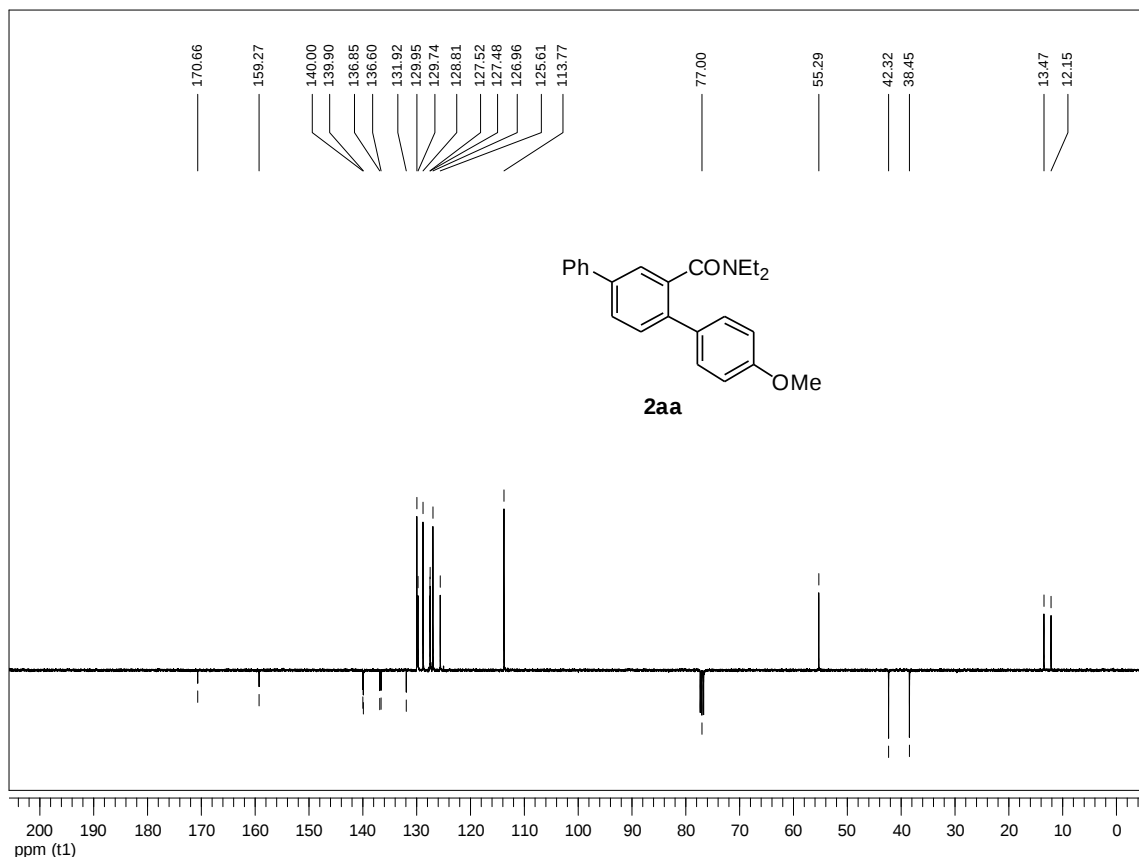
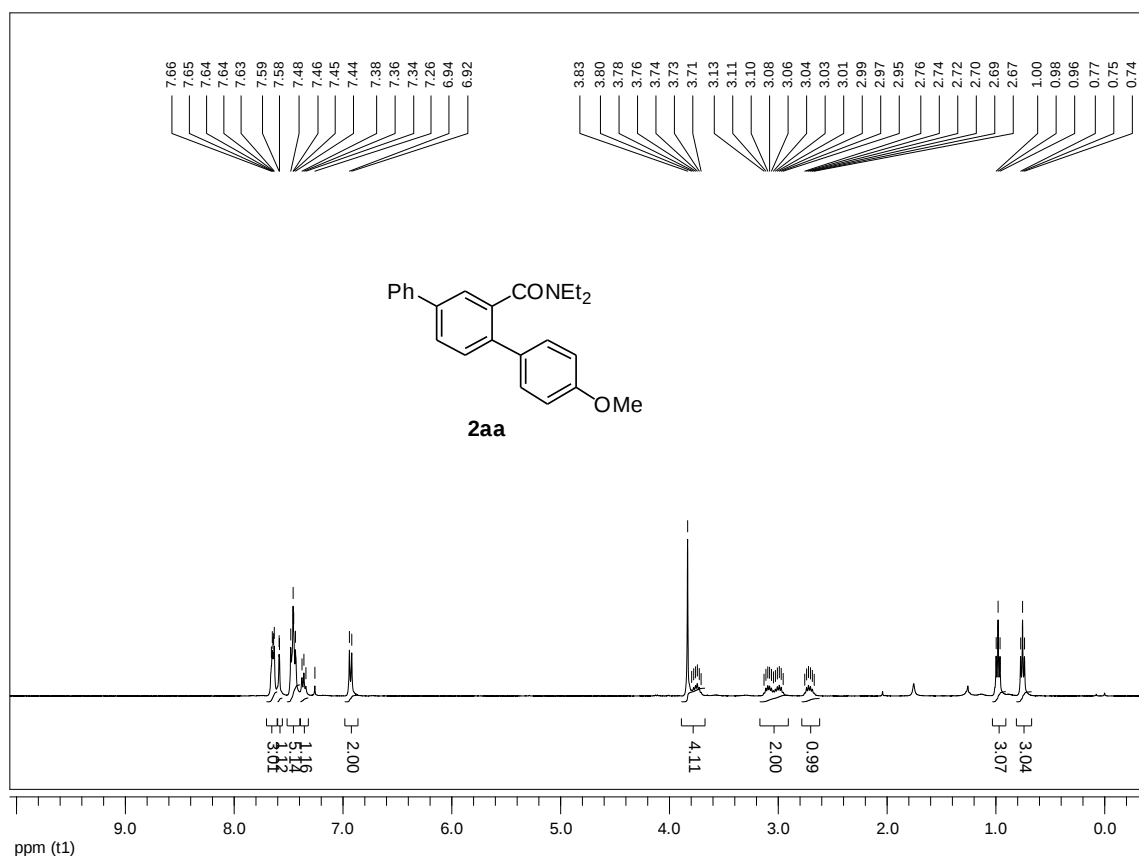


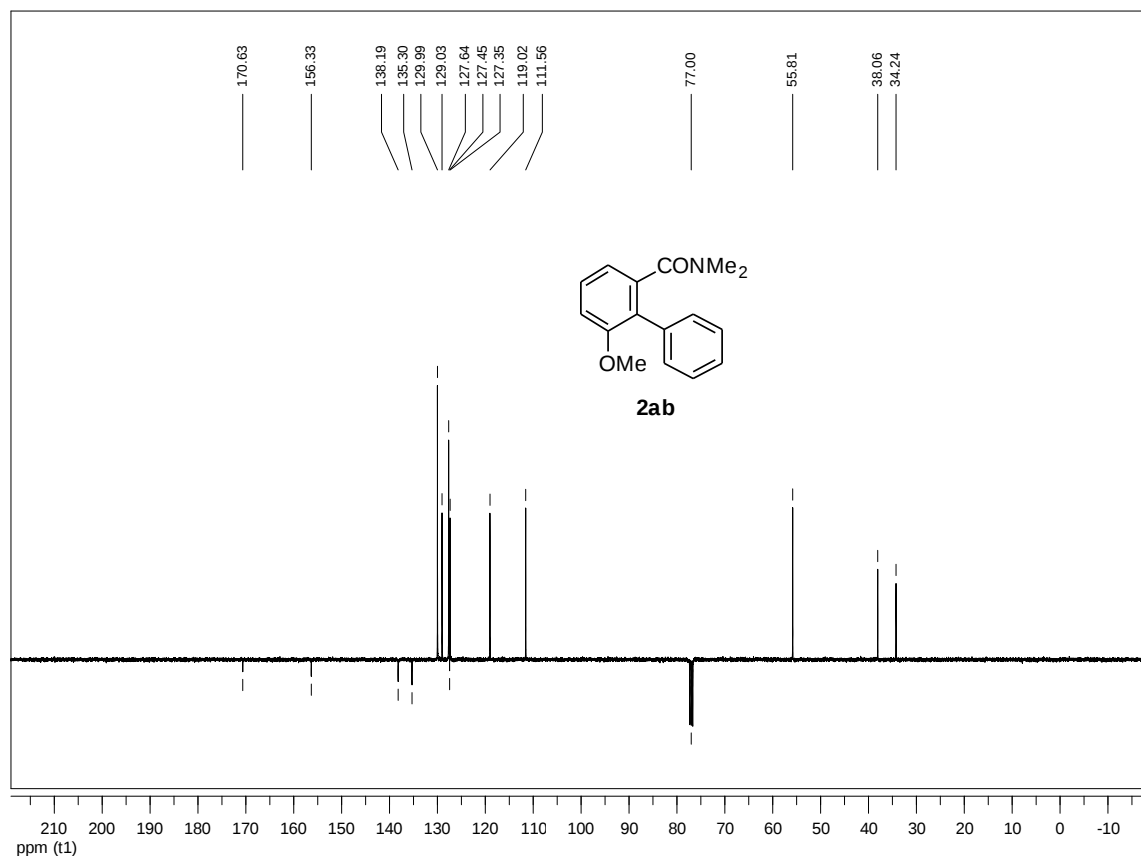
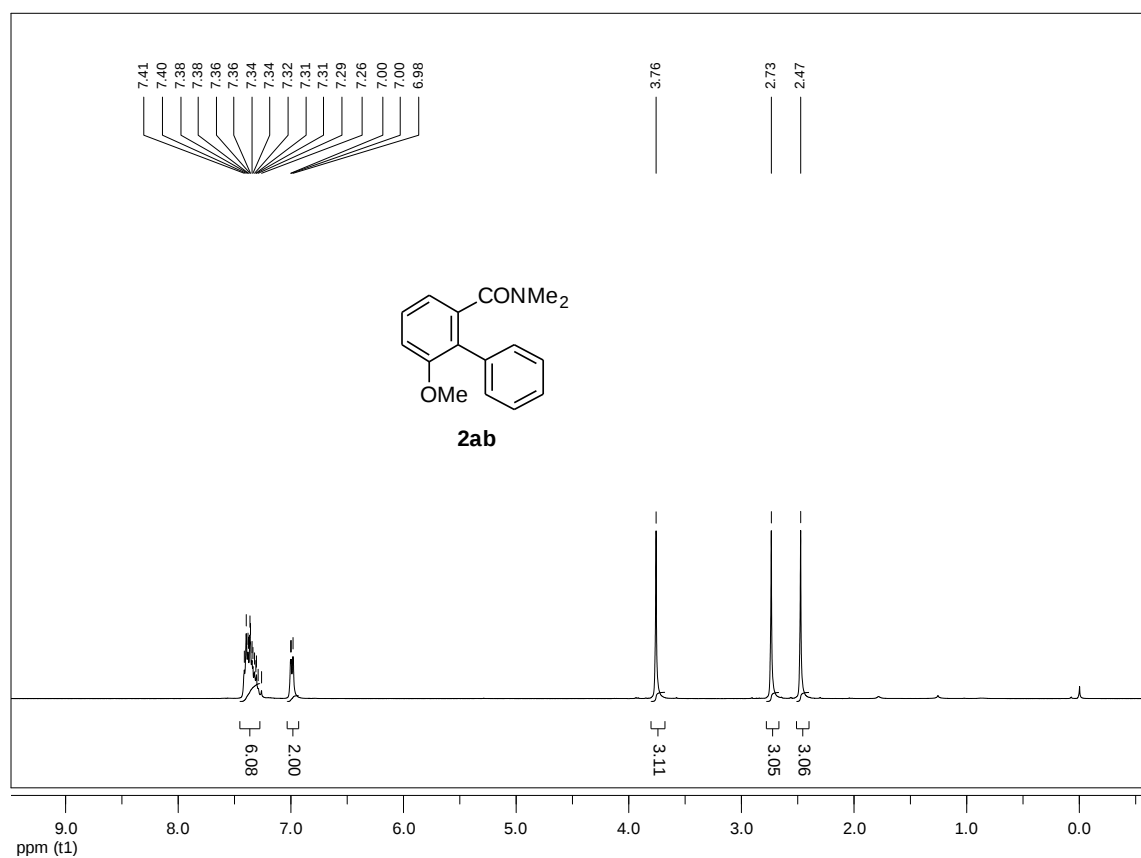


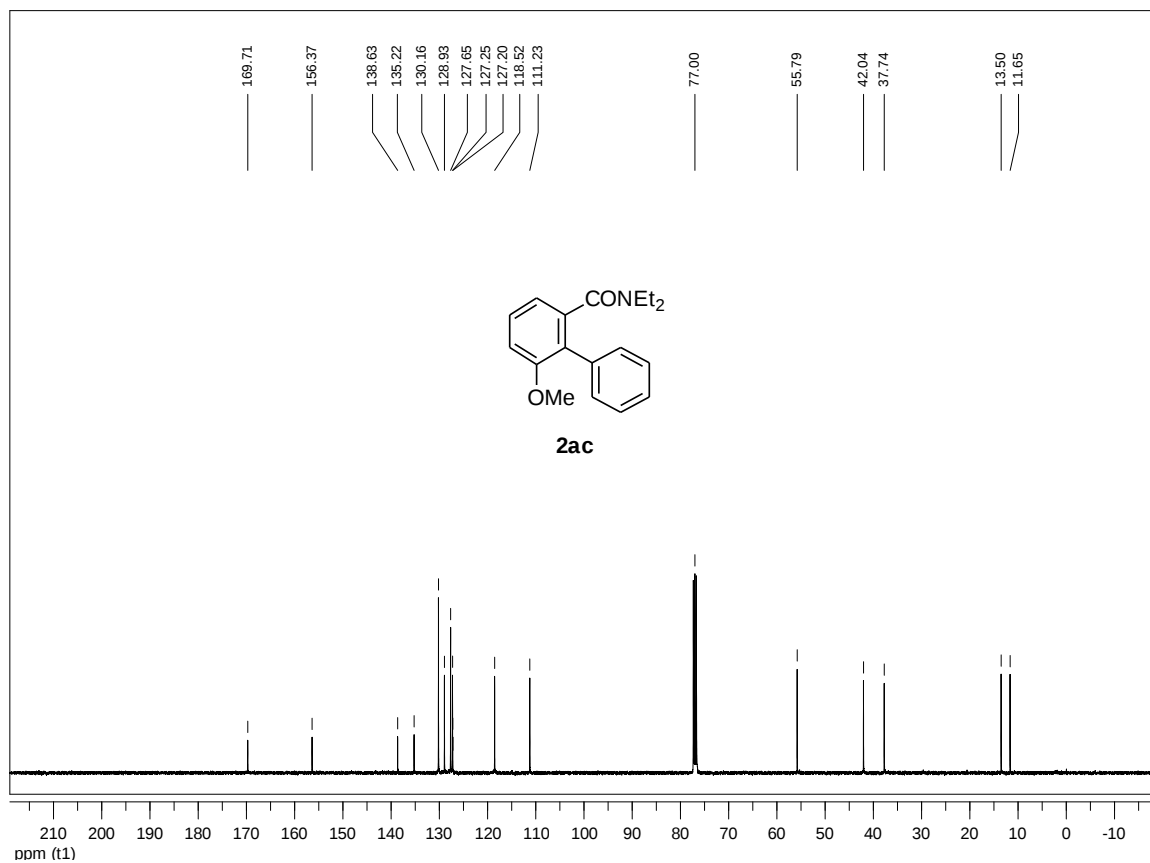
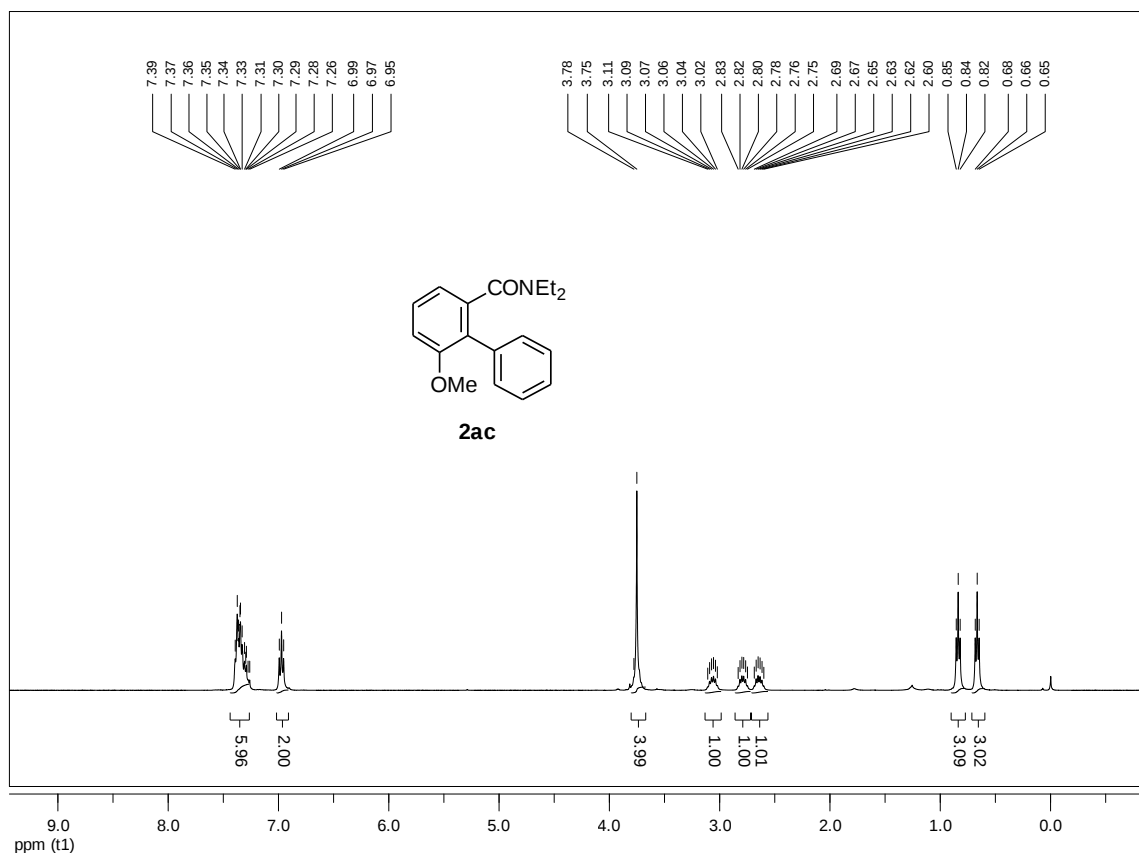


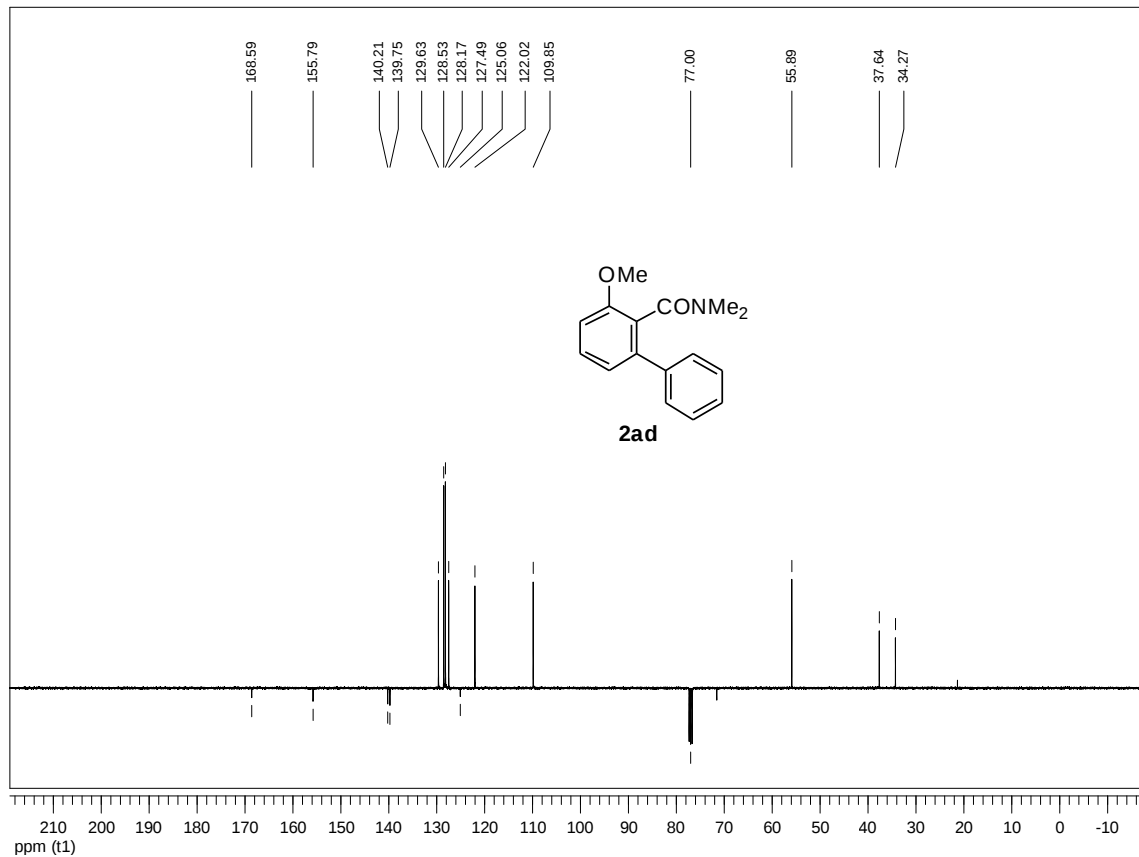
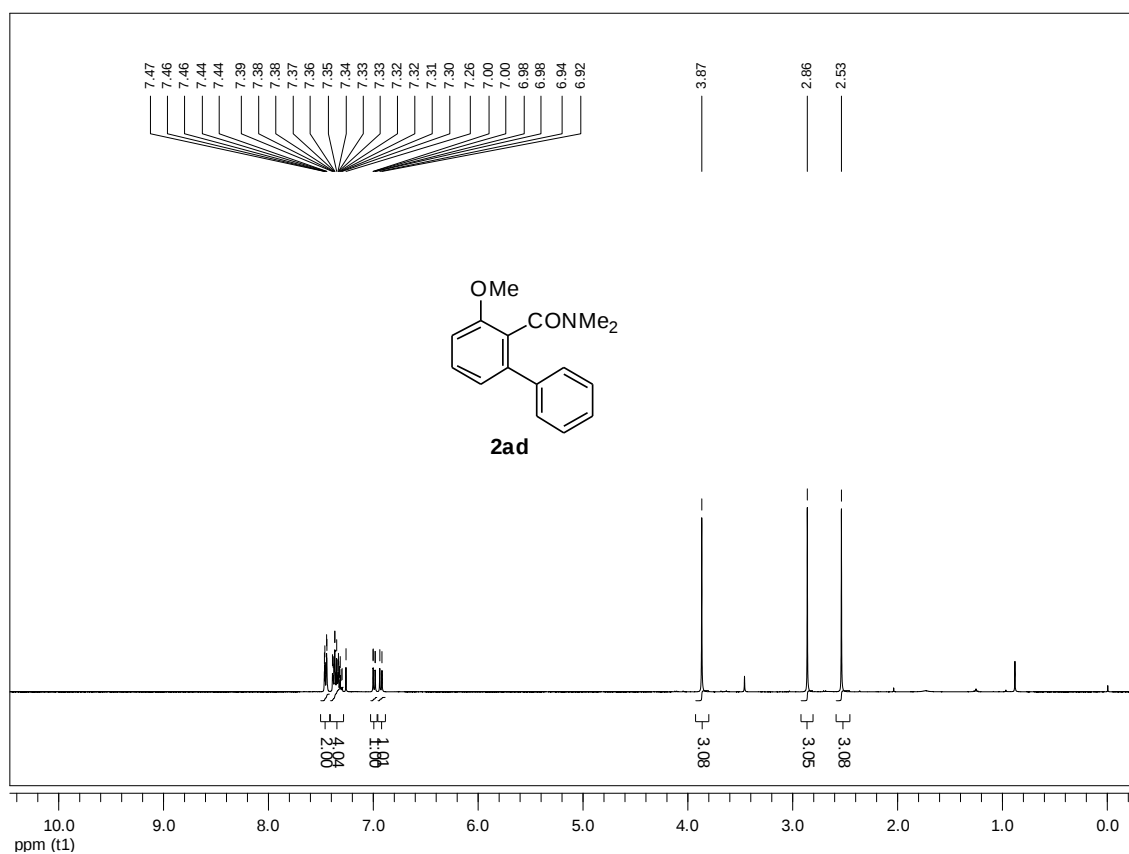


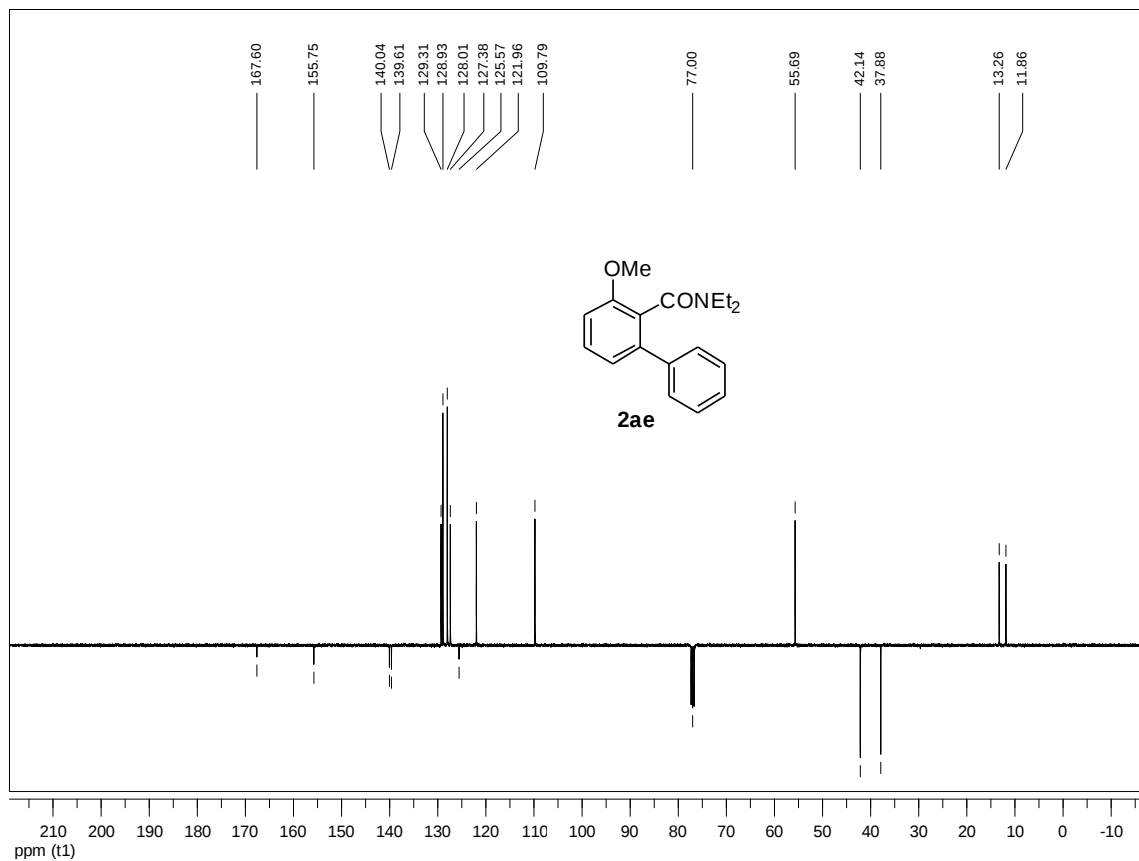
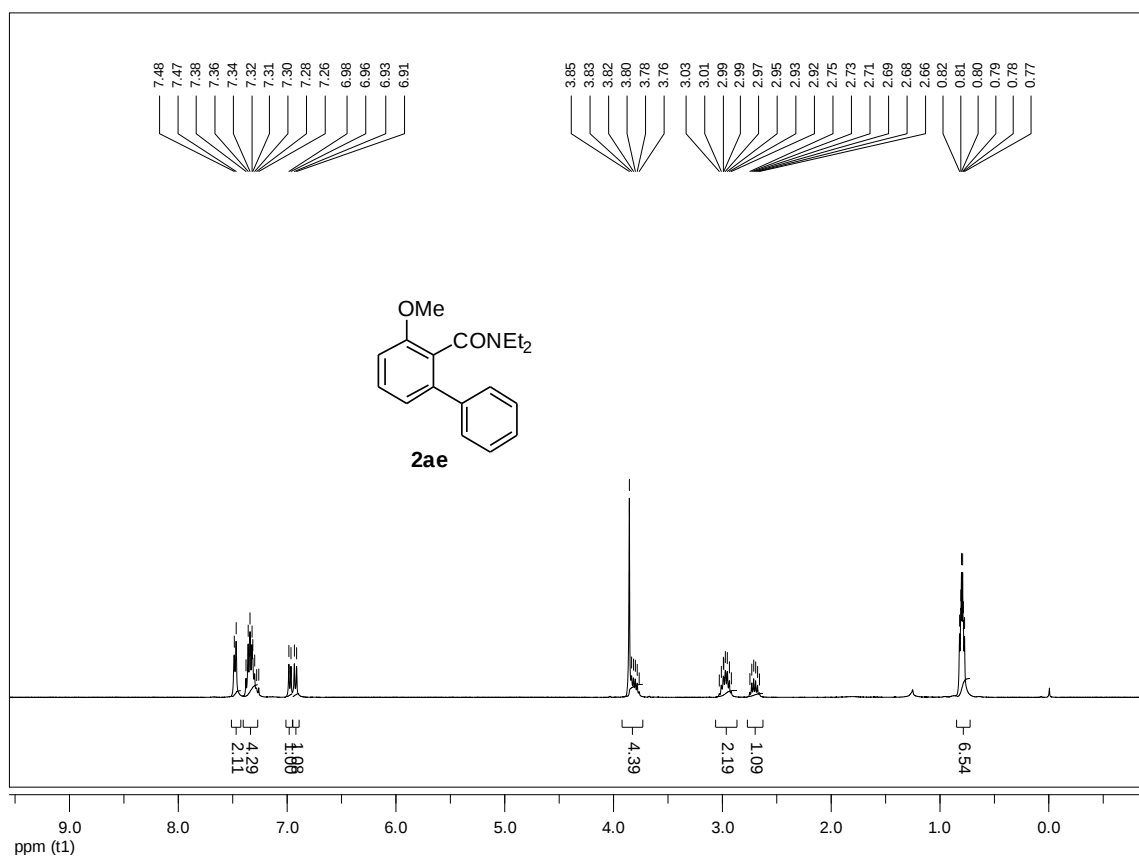


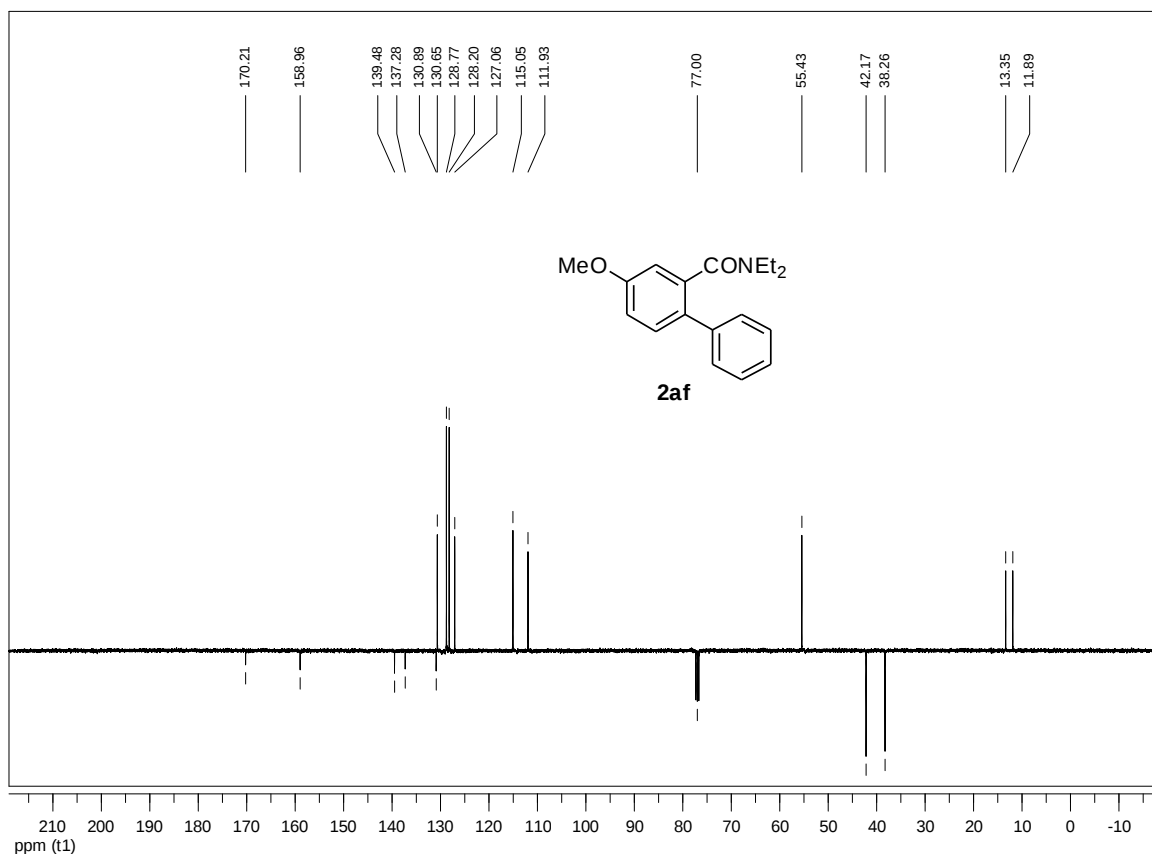
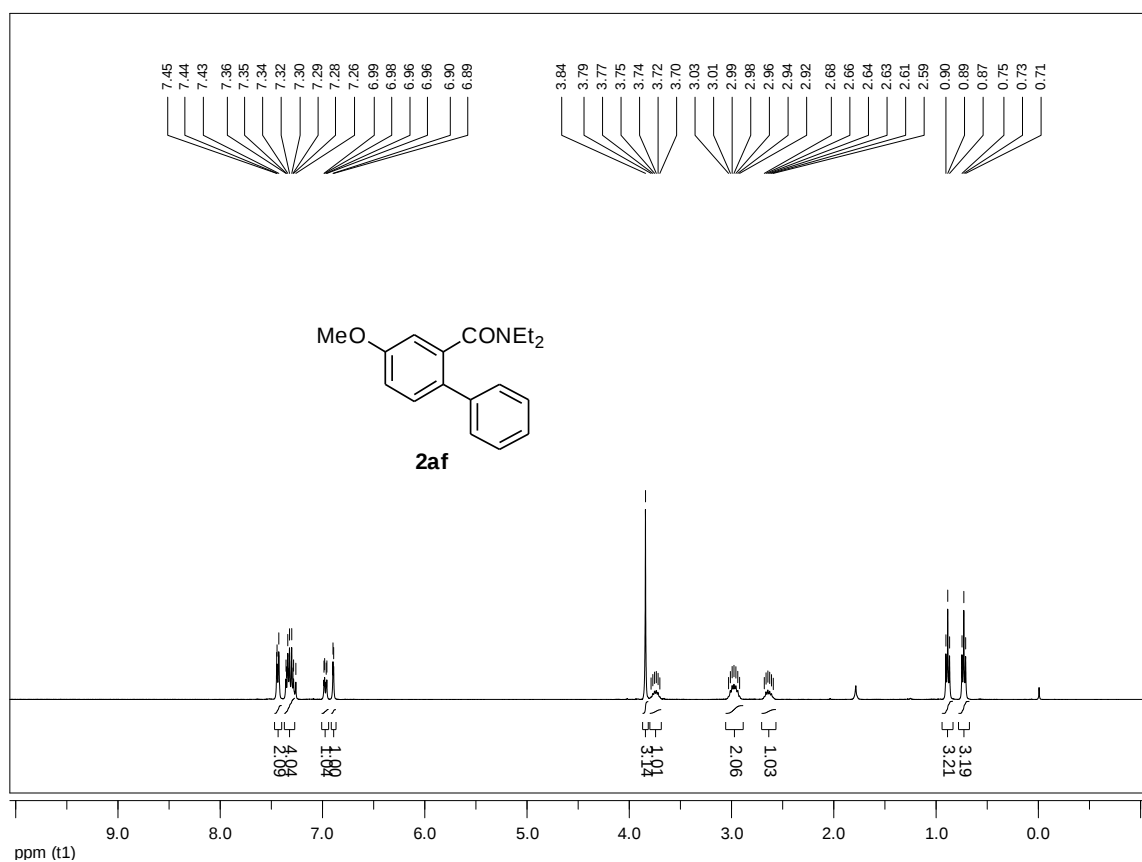


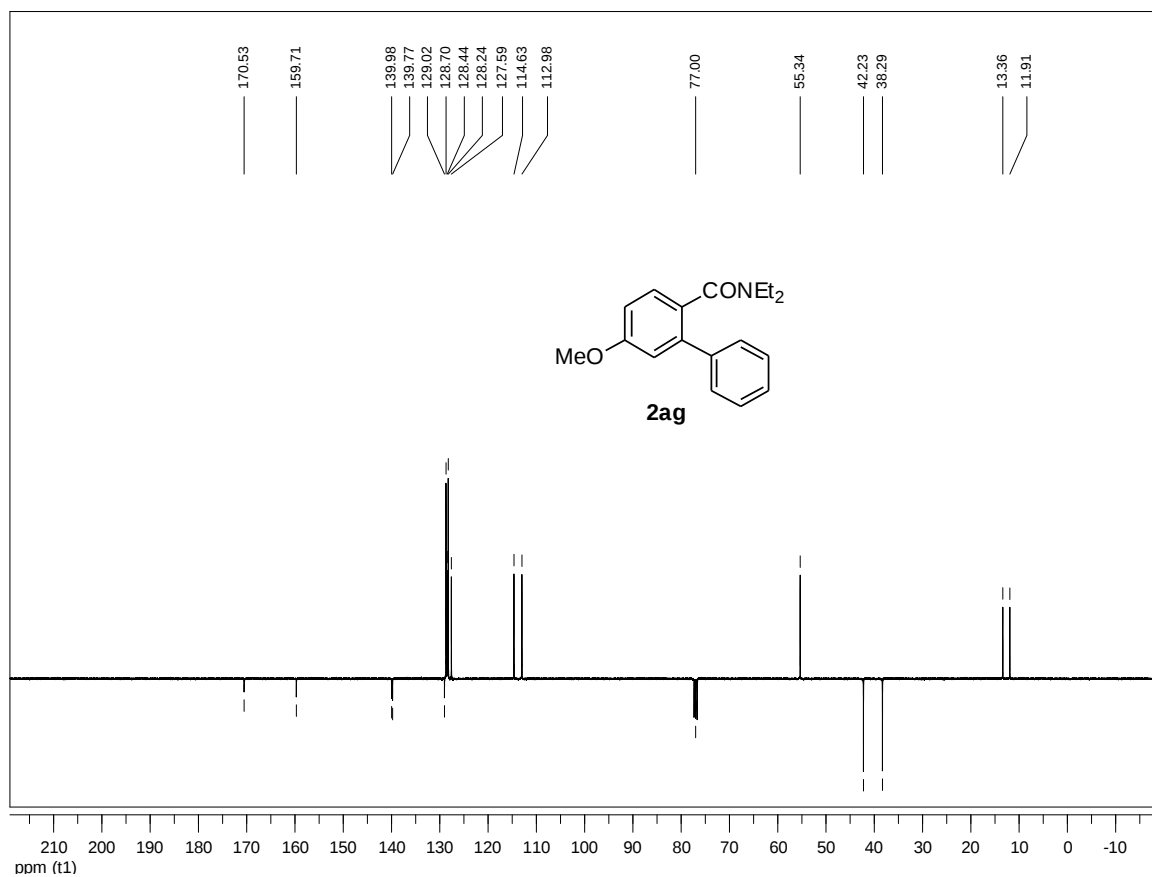
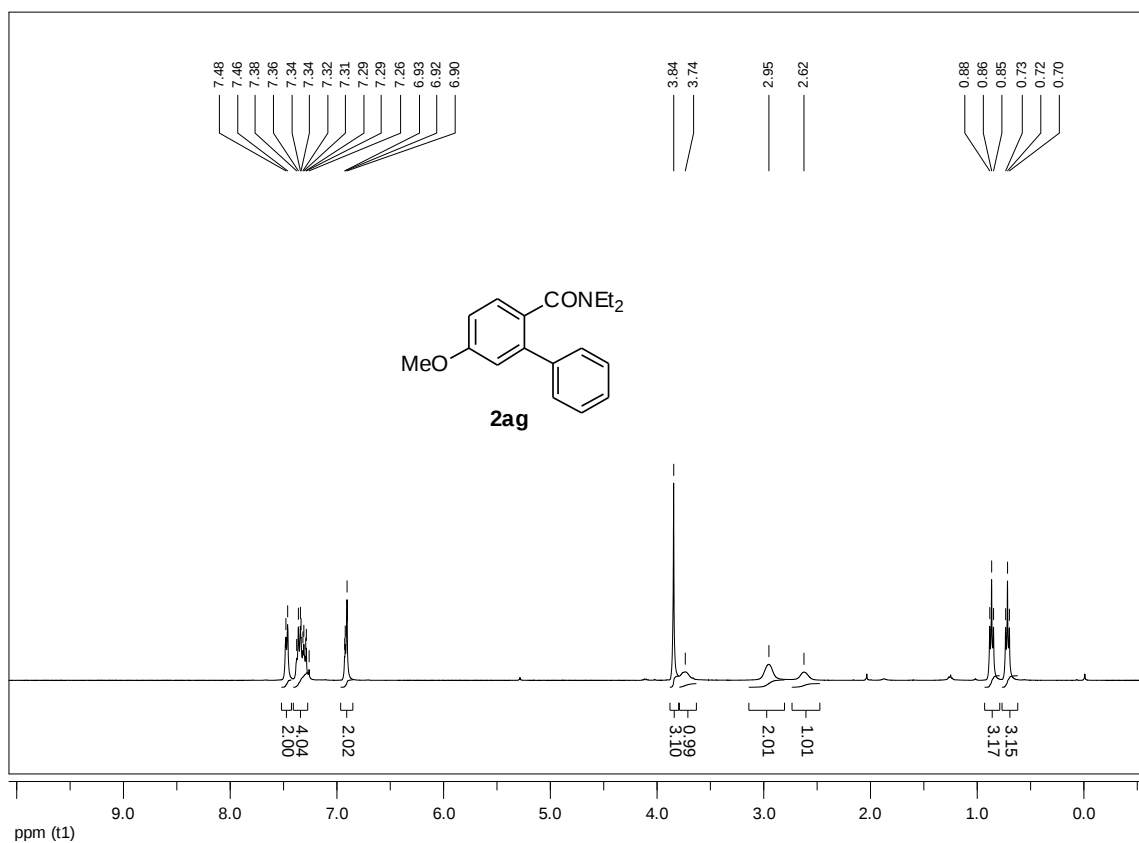


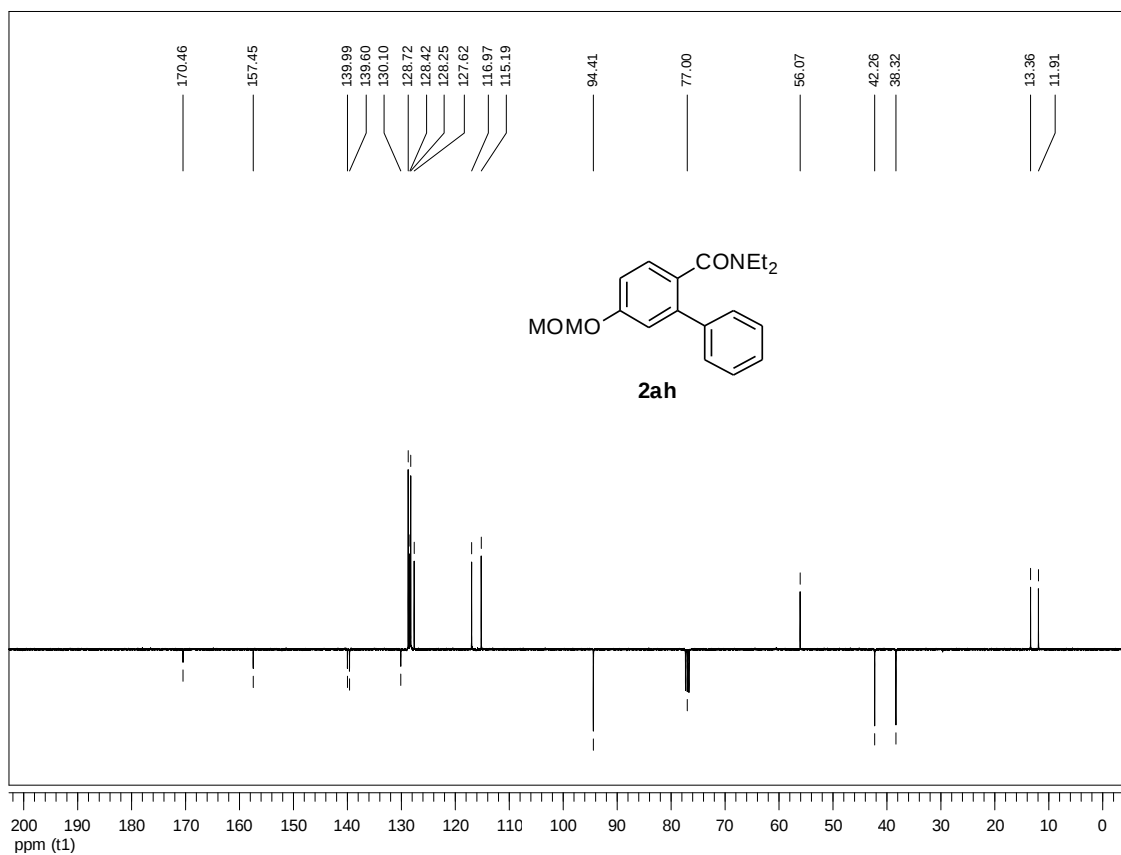
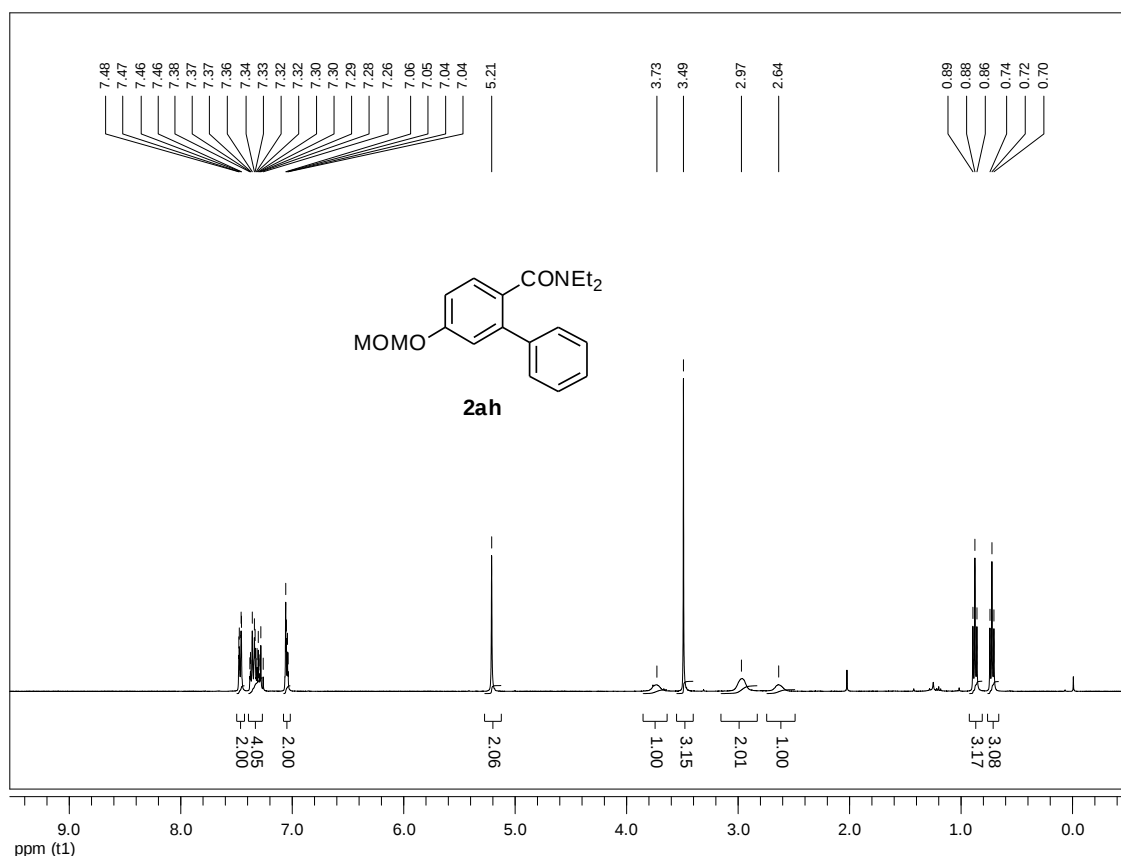


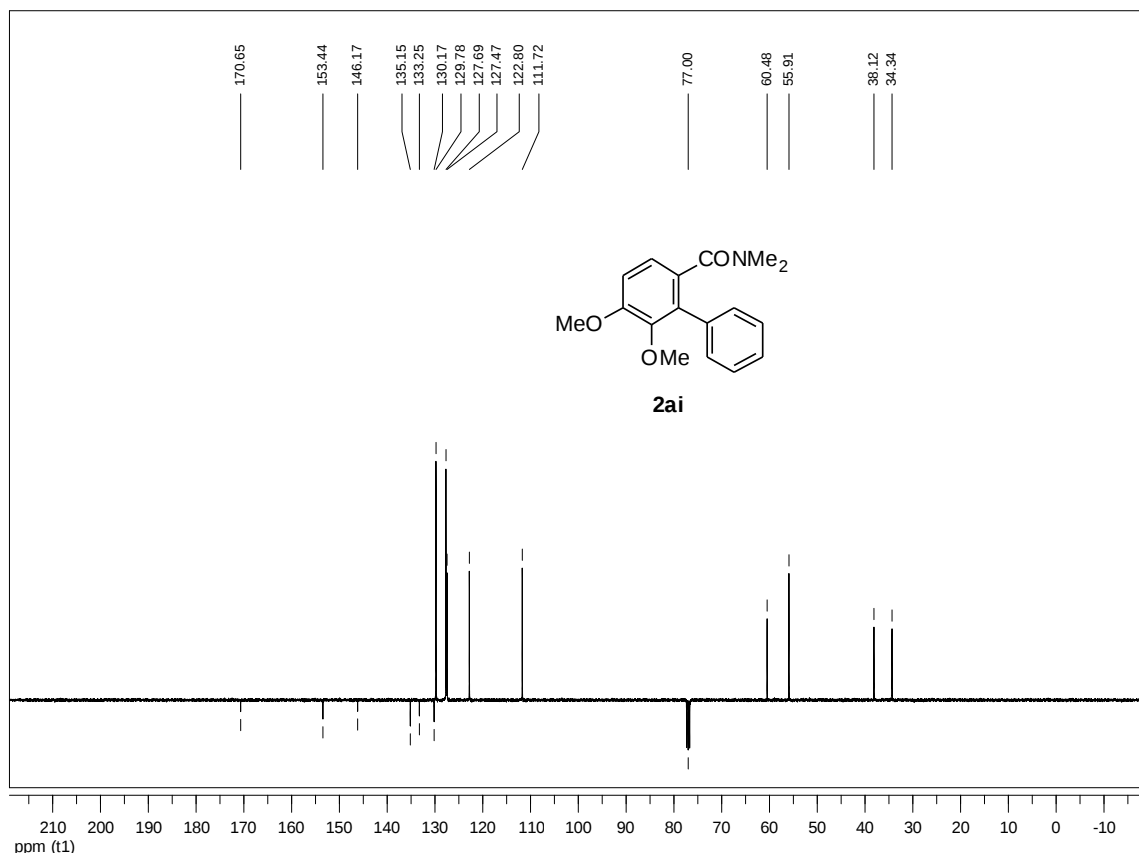
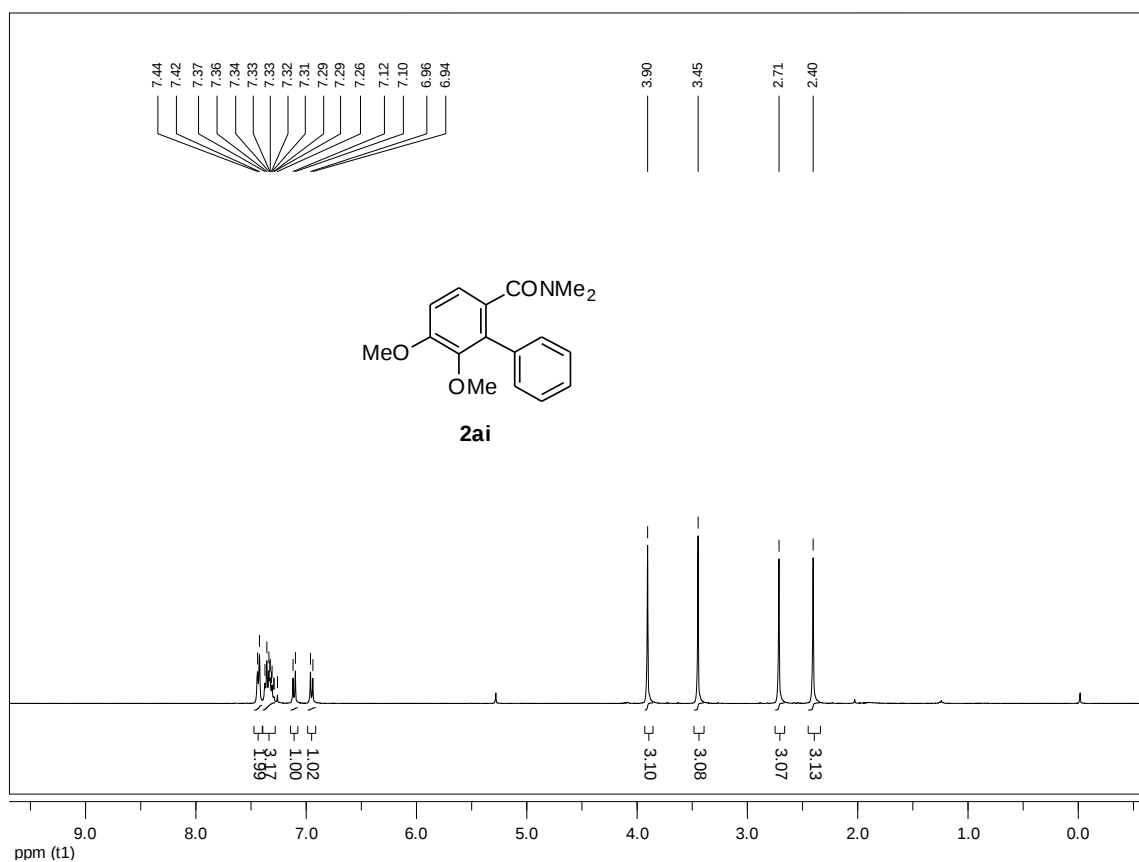


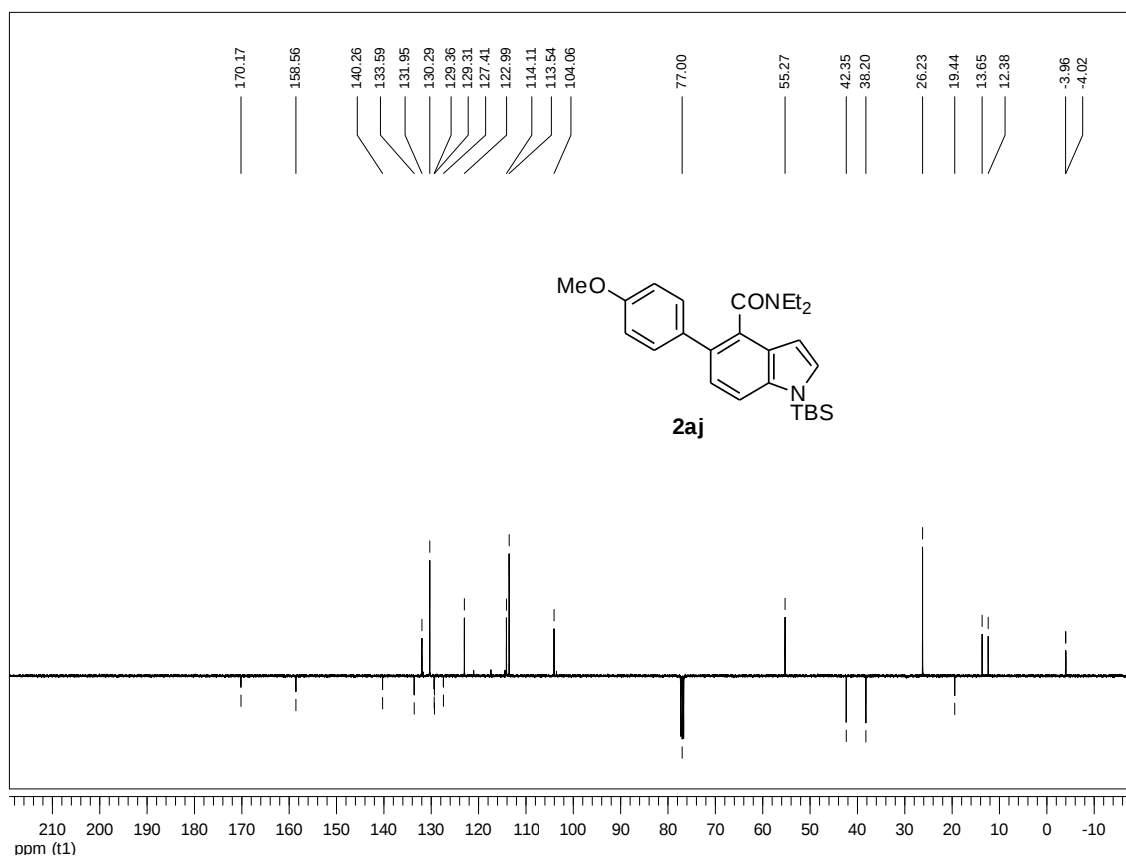
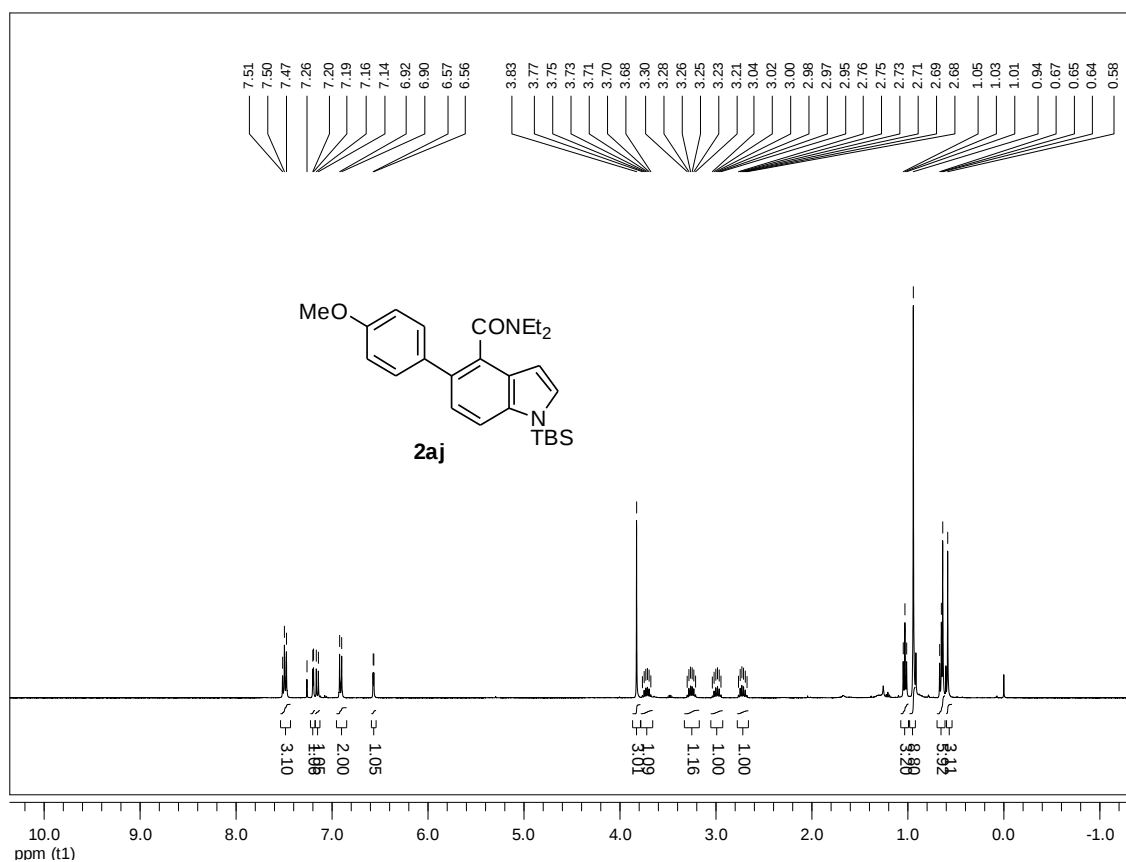


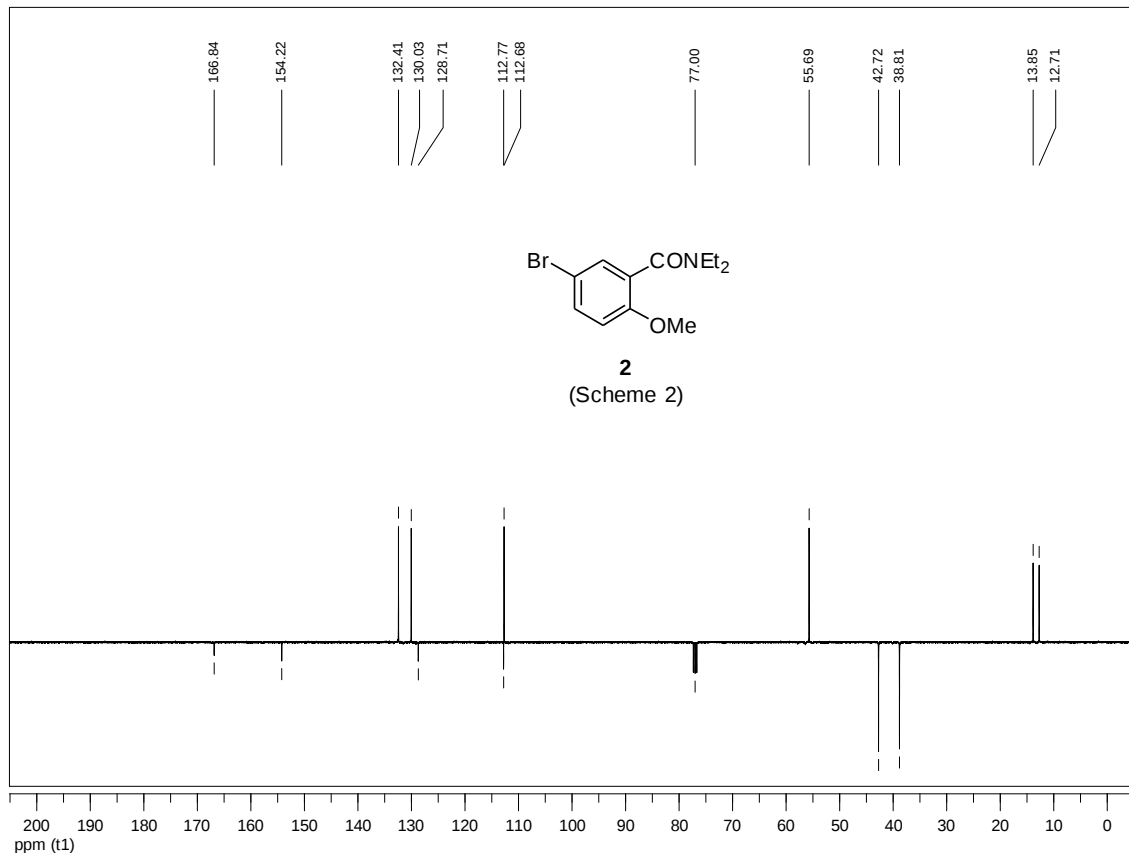
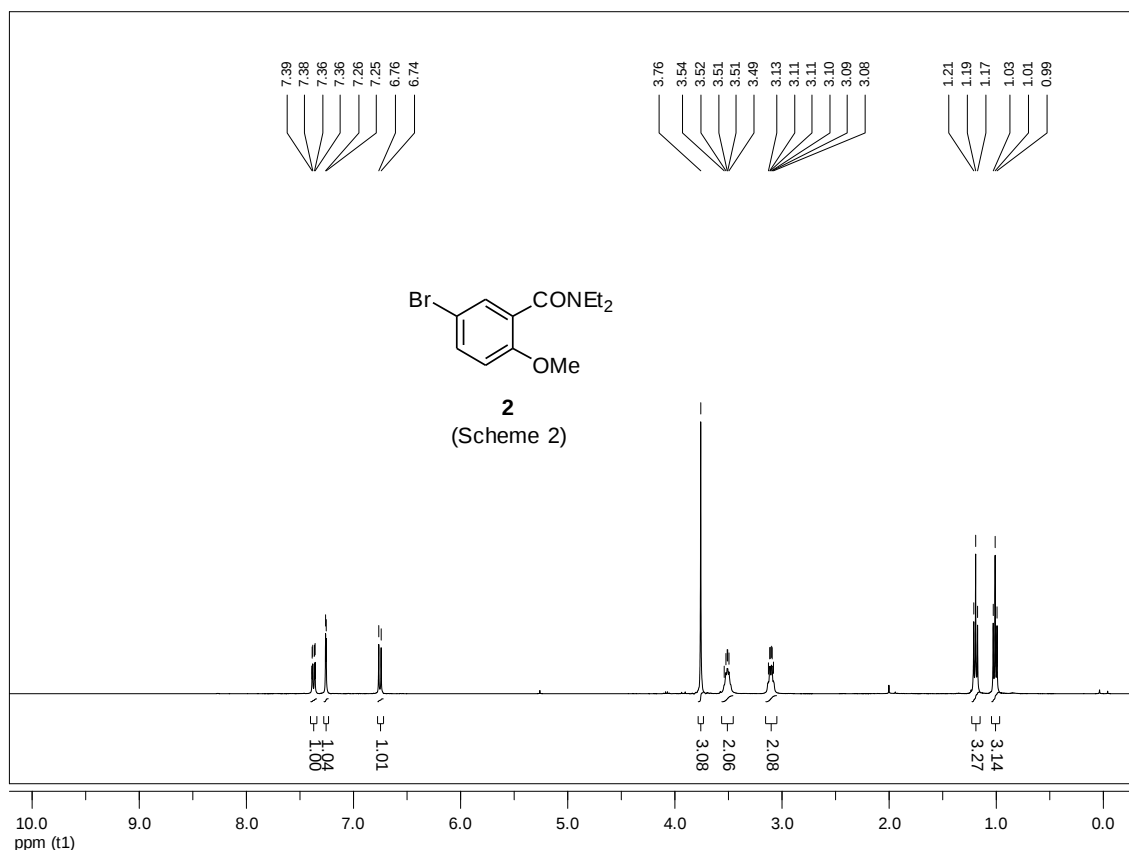


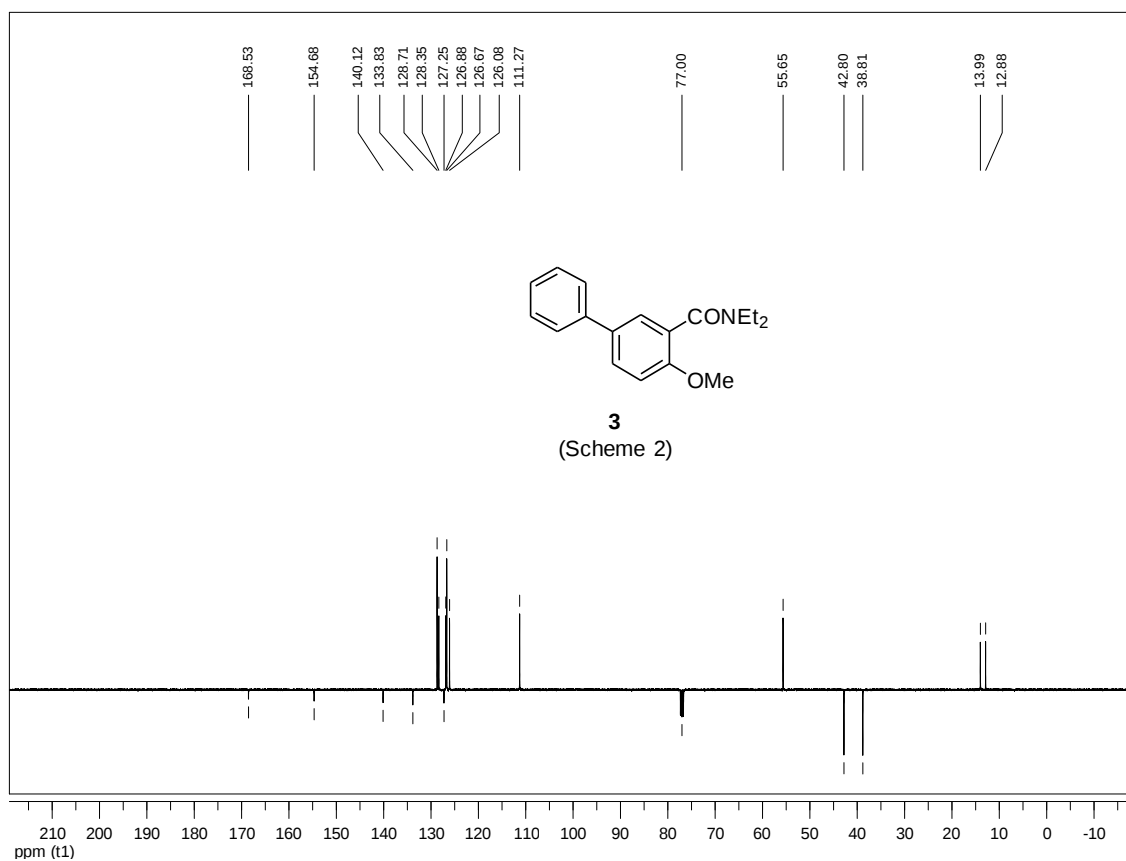
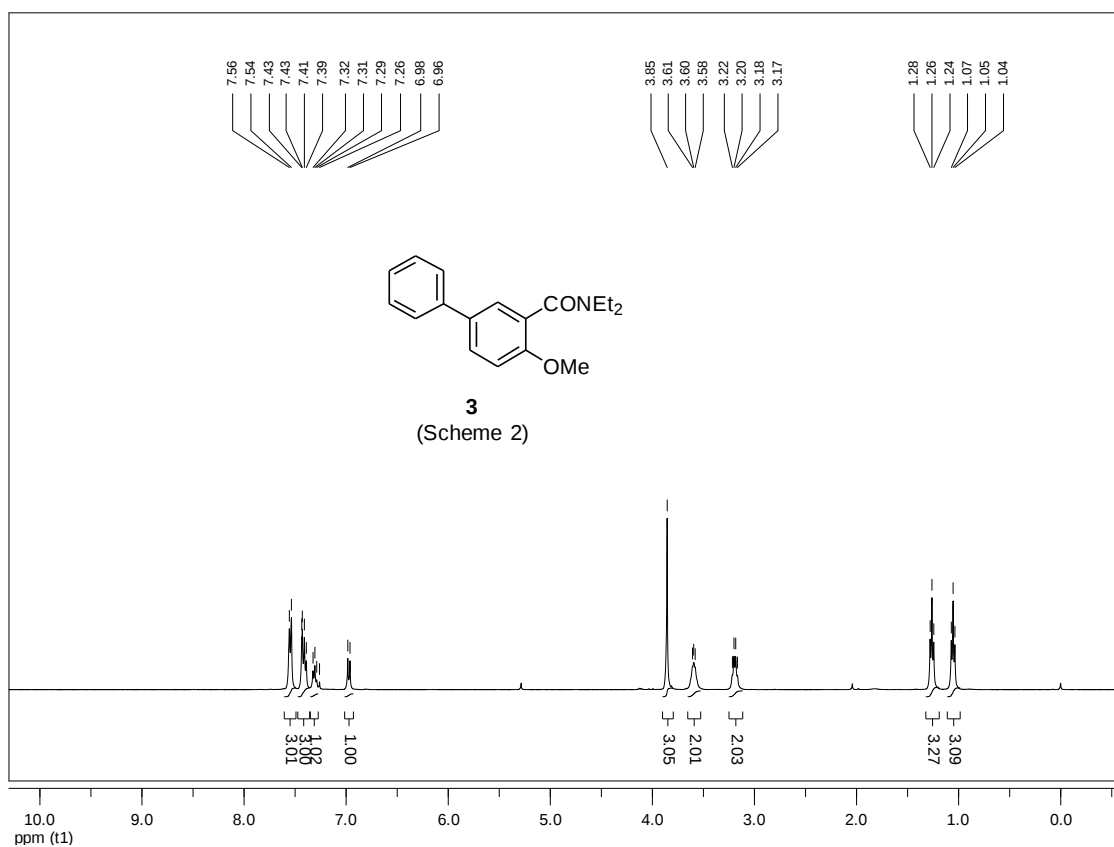


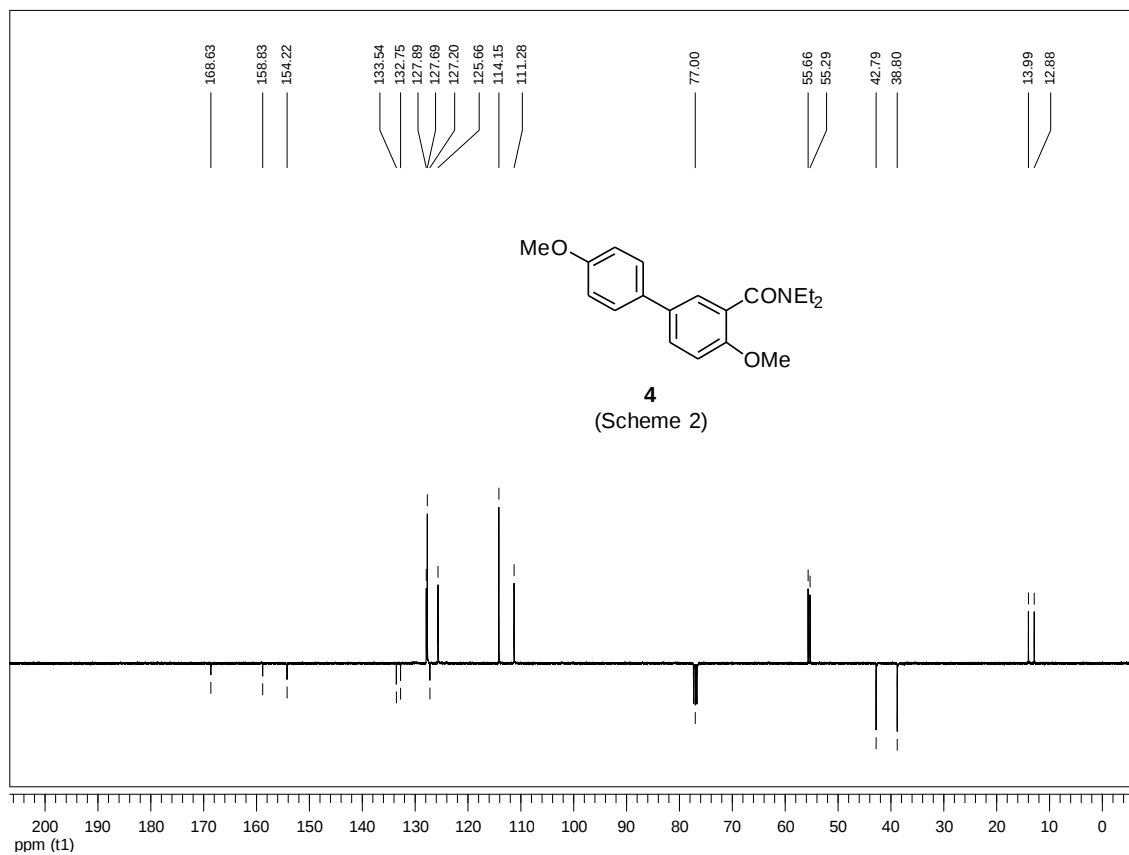
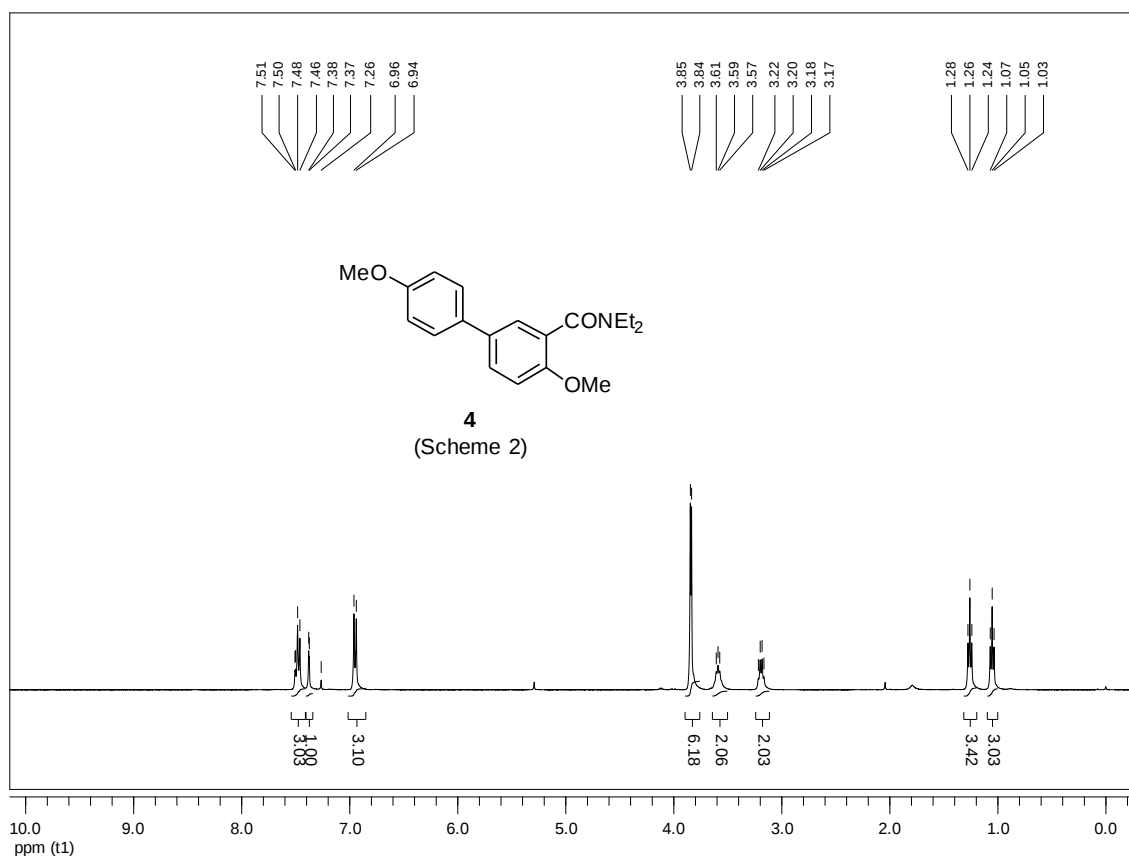


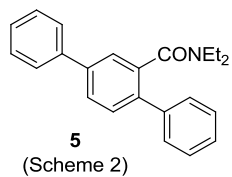












Note: Spectra of **5** in Scheme 2, see spectra of Compound **2z** at page S53.

