Pd-Catalyzed *ortho*-Arylation of Phenylacetamides, Benzamides, and Anilides with Simple Arenes using Sodium Persulfate

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1. General considerations

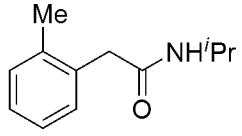
Commercial reagents were purchased from Sigma-Aldrich, Strem, or Alfa Aesar and used without further purification. Acid chlorides were synthesized by reactions of their corresponding carboxylic acids with thionyl chloride.[1] Dichloromethane (DCM) and dimethylformamide (DMF) were dried through two columns of activated alumina. Triethylamine was distilled over KOH prior to usage. All other solvents were purchased from Caledon or Fisher and used as received. All unactivated arene cross-coupling partners were

obtained from commercial sources. Syntheses of starting materials were conducted under N_2 or Ar unless otherwise stated. All catalytic reactions were conducted without any special precautions. Reactions were monitored by thin-layer chromatography (TLC) on EMD Silica Gel 60 F_{254} plates under UV light (254 μm) or gas chromatography (GC) on an Agilent 6890N Network GC instrument equipped with a flame-ionization detector (FID) and HP-5 column (30 m length, 0.32 mm inner diameter, 0.25 μm film thickness). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were recorded on a Varian Mercury 300, Varian Mercury 400, VRX-S (Unity) 400, or Bruker AV-III 400 spectrometer at ambient temperature. All NMR spectra are referenced to TMS or the residual solvent signal. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. Data for ^{13}C{^{1}H} NMR are reported as follows: chemical shift (δ ppm). Data for ^{19}F NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration.

Mass spectra (MS) were recorded on a Sciex Qstar Mass Spectrometer. High resolution mass spectra (HRMS) were recorded on a micromass 70S-250 spectrometer (EI) or an ABI/Sciex Qstar Mass Spectrometer (ESI). Melting point ranges were determined on a Gallenkamp melting point apparatus (uncorrected). Column chromatography was carried out on Silicycle Silica-P Flash Silica Gel (40-63 μm). Preparative layer chromatography was performed on EMD Silica Gel 60 F_{254} plates (254 μm).

Compound **1g** is commercially available from Sigma-Aldrich. All other starting materials were synthesized according to literature procedures. Compounds **1c**,[2] **1d**,[3-6] **1e**,[7] **1f**,[8] **1i**,[9, 10] **1j**,[10-12] **1l**,[9, 13] **1m**,[9, 13] **1p**,[14] **1q**[15] **1r**,[16-19] **1s**,[20] **1t**,[21-26] **1aa**[9, 11, 23-25, 27-36] and **1ab**[22, 37] are known compounds and were identified by NMR comparison to reported data. Products **2k**,[38] **2v**, **2w**[14], **2z**,[39] **2ab**,[40] **2ac**,[41, 42] and **2ad**,[43-47] have been reported in the literature.



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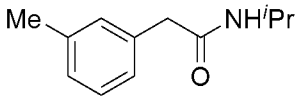

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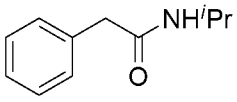

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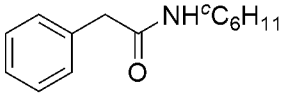

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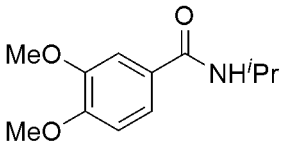

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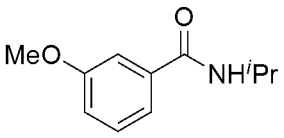

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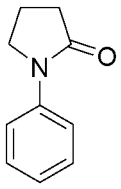

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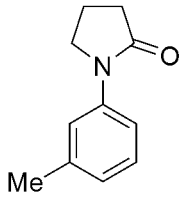

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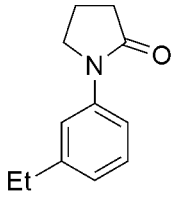

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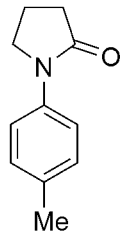

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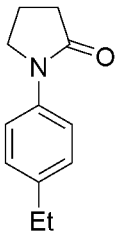

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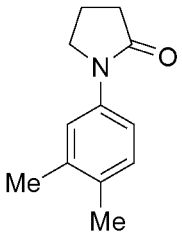

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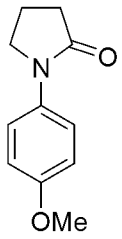

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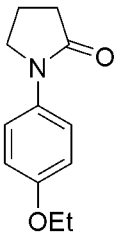

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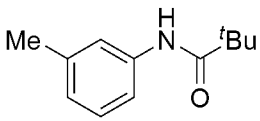

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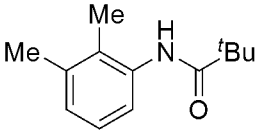

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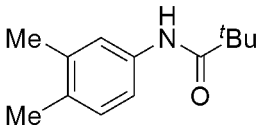

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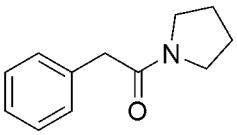

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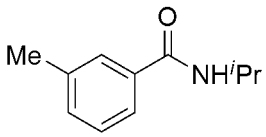

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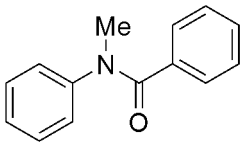

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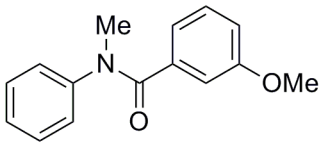

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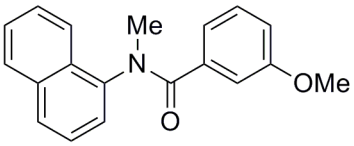

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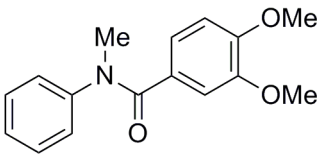

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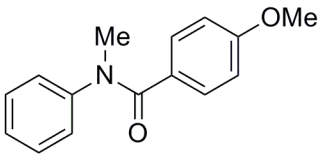

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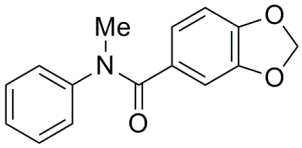

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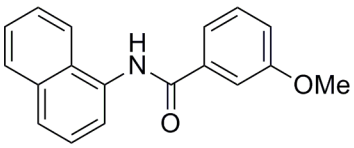

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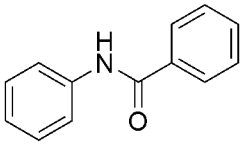

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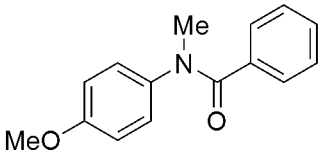


1ab

2. Experimental procedures

General procedure A: Arylation of N-isopropyl-2-o-tolylacetamide (1a) with benzene

In a one-dram vial equipped with a Teflon cap was added *N*-isopropyl-2-*o*-tolylacetamide (**1a**) (38.3 mg, 0.2 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), $Na_2S_2O_8$ (142.8 mg, 0.6 mmol), and benzene (1 mL). Subsequently, trifluoroacetic acid (76 μL, 1 mmol) was added. The vial was sealed with a Teflon cap and stirred on a heating block at 70 °C for 24 h. After cooling to ambient temperature, GC-FID analysis was conducted using dodecane (23 μL, 0.1 mmol) as internal standard. The target product **2a** was afforded in 99% GC yield. For isolation of the desired product, the experiment was conducted under the aforementioned conditions for 30 h, at which point 5 mol% $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%) was added and heating was maintained for an additional 18 h. After cooling to ambient temperature, the resulting mixture was diluted in 5 mL EtOAc and washed with 2 mL sat'd $NaHCO_3$. The aqueous phase was extracted with 3 x 5 mL EtOAc. The combined organic extracts were dried over Na_2SO_4, concentrated *in vacuo* and the resulting residue was purified by preparative thin-layer chromatography (eluent: EtOAc/CH_2Cl_2 = 2:98, v/v) to afford the target product **2a** as an off-white solid (41.8 mg, 81%).

General procedure B: Arylation of N-isopropyl-2-o-tolylacetamide (1a) with benzene under O_2

In a 25 mL Schlenk tube equipped with a Teflon stopcock was added *N*-isopropyl-2-*o*-tolylacetamide (**1a**) (38.3 mg, 0.2 mmol) and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%). The tube was evacuated and refilled with O_2 three times. Then benzene (1 mL) and trifluoroacetic acid (76 μL, 1 mmol) was added. The tube was sealed. The mixture was stirred on a heating block at 70 °C for 24 h. After cooling to ambient temperature, GC-FID analysis was conducted using dodecane (23 μL, 0.1 mmol) as internal standard. The target product **2a** was afforded in 73% GC yield.

General procedure C: Large-scale arylation of 1-phenyl-2-pyrrolidinone (1g) with benzene

In a 100 mL round-bottom flask was added 1-phenyl-2-pyrrolidinone (**1g**) (1.00 g, 6.2

mmol), $Pd(OAc)_2$ (139.4 mg, 0.62 mmol, 10 mol%), $Na_2S_2O_8$ (4.43 g, 18.6 mmol), and benzene (31 mL). Subsequently, trifluoroacetic acid (2.4 mL, 31 mmol) was added. The flask was sealed with a rubber septum and the mixture was stirred in an oil bath at 70 °C for 45 h. After cooling to ambient temperature, the resulting mixture was diluted in 50 mL EtOAc and washed with 50 mL sat'd $NaHCO_3$. The aqueous phase was extracted with 2 x 50 mL EtOAc. The combined organic extracts were dried over Na_2SO_4, filtered, concentrated *in vacuo* and the resulting residue was purified by silica gel column chromatography (eluent: hexanes/EtOAc = 9:1) to afford the target product **2k** as a brown viscous oil (1.30 g, 88%).

General procedure D: Intramolecular oxidative cross-coupling of N-methyl-N-phenylbenzamide (1t)

In a one-dram vial equipped with a Teflon cap was added *N*-methyl-*N*-phenylbenzamide (**1t**) (42.2 mg, 0.20 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), $Na_2S_2O_8$ (190.0 mg, 0.8 mmol), and 1,2-dichloroethane (1 mL). Subsequently, trifluoroacetic acid (76 μL, 1 mmol) was added. The vial was sealed with a Teflon cap and stirred on a heating block at 70 °C for 96 h. After cooling to ambient temperature, the resulting mixture was diluted in EtOAc and washed with 2 mL sat'd $NaHCO_3$. The aqueous phase was extracted with EtOAc. The combined organic extracts were concentrated *in vacuo* and the resulting residue was purified by preparative thin-layer chromatography (eluent: MeOH/CH_2Cl_2 = 2:98, v/v) to afford the target product **2y** as an off-white solid (25.1 mg, 60%).

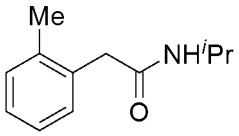
General procedure E: Arylation of bimetallic Pd complex (3a) with benzene

In a one-dram vial equipped with a Teflon cap was added palladacycle **3a** (23.0 mg, 0.028 mmol), $Na_2S_2O_8$ (26.7 mg, 0.112 mmol), and benzene (0.5 mL). Subsequently, trifluoroacetic acid (4.6 μL, 0.062 mmol) was added. The vial was sealed with a Teflon cap and stirred on a heating block at 70 °C for 16 h. After cooling to ambient temperature, the resulting mixture was diluted in 5 mL EtOAc and washed with 2 mL $NaHCO_3$ (aq.). The aqueous phase was extracted with 3 x 5 mL EtOAc. The combined organic extracts were dried over Na_2SO_4, concentrated *in vacuo* and the resulting residue was purified by preparative thin-layer chromatography (eluent: CH_2Cl_2/hexanes = 75:25, v/v) to afford the target product **2v** as an

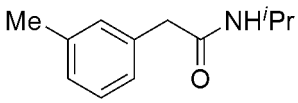
off-white solid (13.6 mg, 91%).

3. Analytical data

Starting materials

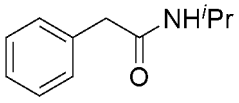


***N*-Isopropyl-2-*o*-tolylacetamide (1a):** Prepared by a known procedure.[48] To a 100 mL round-bottom flask was charged *m*-tolylacetic acid (1.5017 g, 10 mmol) and CH_2Cl_2 (40 mL). To the solution was added 1,1-carbonyldiimidazole (1.7837 g, 11 mmol) in portions. After stirring for 1 h, isopropylamine (1.72 mL, 11 mmol) was added via syringe and the reaction mixture was allowed to stir for an additional 15 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (87%). White solid; m.p. 130-131 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-71.8 (m, 4H), 5.11 (s, 1H), 4.14-4.06 (m, 1H), 3.57 (s, 2H), 2.31 (s, 3H), 1.06 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 137.2, 133.6, 130.8, 130.5, 127.8, 126.6, 42.1, 41.3, 22.6, 19.4. MS (EI) *m/z* 191 (M); HRMS (EI) *m/z* calc'd for $C_{12}H_{17}NO$ $[M]^+$: 191.1310; found: 191.1310.

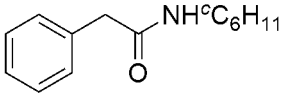


***N*-Isopropyl-2-*m*-tolylacetamide (1b):** Prepared by a known procedure.[48] To a 100 mL round-bottom flask was charged *m*-tolylacetic acid (1.5017 g, 10 mmol) and CH_2Cl_2 (40 mL). To the solution was added 1,1-carbonyldiimidazole (1.7837 g, 11 mmol) in portions. After stirring for 1 h, isopropylamine (1.72 mL, 11 mmol) was added via syringe and the reaction mixture was allowed to stir for an additional 19 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was

purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (92%). White solid; m.p. 71-72 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (t, J = 7.5 Hz, 1H), 7.14-7.06 (m, 3H), 5.23 (s, 1H), 4.12-4.06 (m, 1H), 3.52 (s, 2H), 2.38 (s, 3H), 1.10 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 138.7, 135.0, 130.2, 128.8, 128.0, 126.3, 44.0, 41.5, 22.6, 21.4. MS (EI) *m/z* 191 (M); HRMS (EI) *m/z* calc'd for $C_{12}H_{17}NO$ $[M]^+$: 191.1310; found: 191.1314.

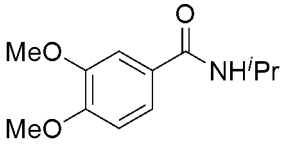


***N*-Isopropyl-2-phenylacetamide (1c):** Prepared by a known procedure.[49] To a 100 mL round-bottom flask was charged triethylamine (1.63 mL, 11.6 mmol), isopropylamine (1 mL, 11.6 mmol), and CH_2Cl_2 (40 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, phenylacetyl chloride (1.40 mL, 10.6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 12.5 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 90:10, v/v) to afford the title compound (69%). White solid. This compound has been reported in the literature.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, 2H, J = 7.2Hz), 7.29 (d, 1H, J = 7.2Hz), 7.24 (d, 2H, J = 6.7Hz), 5.19 (s, 1H, NH), 4.06 (dt, 1H, J = 6.6 Hz, J = 13.2 Hz), 3.53 (s, 2H), 1.06 (d, 6H, J = 6.6Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 135.3, 129.5, 129.1, 127.4, 44.1, 41.6, 22.7. MS (ESI) *m/z* 178.1 (M+H), 200 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{11}H_{16}NO$ $[M+H]^+$: 178.1226; found: 178.1226.

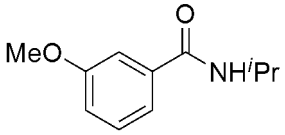


***N*-Cyclohexyl-2-phenylacetamide (1d)**: Prepared by a known procedure.[48] To a 100 mL round-bottom flask was charged phenylacetic acid (1.3615 g, 10 mmol) and CH_2Cl_2 (40 mL). To the solution was added 1,1-carbonyldiimidazole (1.7837 g, 11 mmol) in portions. After stirring for 1 h, cyclohexylamine (1.26 mL, 11 mmol) was added via syringe and the reaction mixture was allowed to stir for an additional 40.5 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine.

The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (77%). White solid. All spectral data are in agreement with reported literature data.[3-6] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (t, J = 7.1Hz, 2H), 7.29 (d, J = 7.2Hz, 1H), 7.25 (d, J = 1.6Hz, 1H), 7.24 (s, 1H), 5.23 (m, 1H), 3.79-3.72 (m, 1H), 3.54 (s, 1H), 1.82 (dd, J = 3.7Hz, J = 12.6Hz, 1H), 1.58 (t, J = 16.1Hz, 1H), 1.32 (dd, J = 11.7Hz, J = 25.1Hz, 1H), 1.11 (t, J = 11.4Hz, 1H), 1.01 (ddd, J = 2.7Hz, J = 12.4Hz, J = 23.3Hz, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 135.3, 129.5, 129.1, 127.4, 48.3, 44.2, 33.0, 25.6, 24.8.

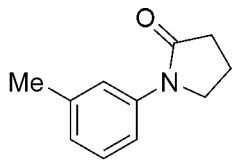


***N*-Isopropyl-3,4-dimethoxybenzamide (1d):** Prepared by a known procedure.[7] This compound has been reported in the literature.[7] White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.0 Hz, 1H), 7.24 (dd, J = 2.0, 8.3 Hz, 1H), 6.85 (d, J = 8.3 Hz, 1H), 5.90 (d, J = 6.2 Hz, 1H), 4.28 (m, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 1.26 (d, J = 6.6 Hz, 6H).

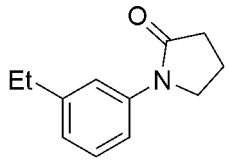


***N*-Isopropyl-3-methoxybenzamide (1e):** Prepared by a known procedure.[49] To a 100 mL round-bottom flask was charged triethylamine (1.80 mL, 12.9 mmol), isopropylamine (1.11 mL, 12.9 mmol), and CH_2Cl_2 (40 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, *m*-toluoyl chloride (1.60 mL, 11.7 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 16 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 90:10, v/v) to afford the title compound (70%). White solid. This compound has been reported in the literature.[8] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (m, 1H), 7.30 (t, J = 7.8 Hz, 1H), 7.25 (dt, J = 1.2, 7.6 Hz, 1H), 7.01 (ddd, J = 1.1, 2.6, 8.0 Hz, 1H), 5.97 (s, NH, 1H), 4.27 (m, 1H), 3.83 (s,

3H), 1.25 (d, J = 6.6 Hz, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 166.5, 159.8, 136.5, 129.4, 118.5, 117.4, 112.3, 55.4, 41.9, 22.8.

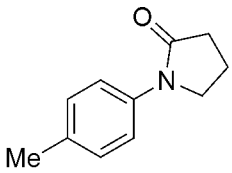


1-*m*-Tolylpyrrolidin-2-one (1h): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added *m*-toluidine (2.11 mL, 19.5 mmol), γ-butyrolactone (1 mL, 13.0 mmol), and 85% H_3PO_4 (87 μL, 1.3 mmol, 10 mol%). The mixture was heated to 180 °C in an oil bath for 14 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (95%). Pale orange solid. All spectral data are in agreement with reported literature data.[9, 10] ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.37 (d, J = 8.2 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 6.96 (d, J = 7.5 Hz, 1H), 3.85 (m, J = 7.2 Hz, 2H), 2.60 (t, J = 8.1 Hz, 2H), 2.36 (s, 3H), 2.15 (quintet, J = 7.5 Hz, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.3, 139.5, 138.8, 128.8, 125.5, 121.0, 117.3, 49.1, 32.9, 21.7, 18.2.

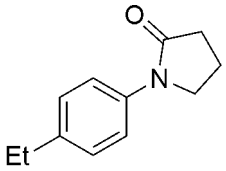


1-(3-Ethylphenyl)pyrrolidin-2-one (1i): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added *m*-ethylaniline (2.42 mL, 19.5 mmol), γ-butyrolactone (1 mL, 13.0 mmol), and 85% H_3PO_4 (87 μL, 1.3 mmol, 10 mol%). The mixture was heated to 180 °C in an oil bath for 24 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (77%). Deep red oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (s, 1H), 7.39 (dd, J = 1.2Hz, J = 8.2Hz, 1H), 7.27 (t, J = 7.8Hz,

1H), 6.99 (d, J = 7.6Hz, 1H), 3.85 (t, J = 7.0Hz, 2H), 2.66 (q, J = 7.6Hz, 2H), 2.60 (t, J = 8.1Hz, 2H), 2.14 (m, 2H), 1.24 (t, J = 7.6Hz, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.2, 145.1, 139.5, 128.8, 124.2, 119.8, 117.5, 49.0, 32.9, 29.1, 18.2, 15.7. MS (ESI) *m/z* 190 (M+H), 212 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{12}H_{16}NO$: 190.1226; found: 190.1230.

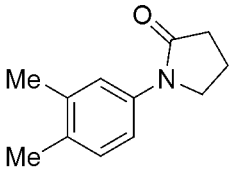


1-*p*-Tolylpyrrolidin-2-one (1j): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added *p*-toluidine (1.6073 g, 15 mmol), γ-butyrolactone (768.7 μL, 10 mmol), and conc. H_3PO_4 (67 μL, 1 mmol, 10 mol%). The mixture was heated to 180 °C in an oil bath for 19 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM to DCM/EtOAc = 9:1, v/v) to afford the title compound (67%). Light brown solid. All spectral data are in agreement with reported literature data.[10-12] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 8.5Hz, 2H), 7.17 (d, J = 8.3Hz, 2H), 3.84 (t, J = 7.0Hz, 2H), 2.60 (t, J = 8.1Hz, 2H), 2.33 (s, 3H), 2.15 (quintet, J = 7.5Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 174.2, 137.0, 134.3, 129.5, 120.2, 49.0, 32.8, 21.0, 18.2.

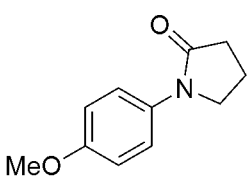


1-(4-Ethylphenyl)pyrrolidin-2-one (1k): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added *p*-ethylaniline (2.44 mL, 19.5 mmol), γ-butyrolactone (1 mL, 13 mmol), and conc. H_3PO_4 (87 μL, 1.3 mmol, 10 mol%). The mixture was heated to 180 °C in an oil bath for 16.5 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column

chromatography (eluent: DCM to DCM/EtOAc = 99:1, v/v) to afford the title compound (81%). Light pink solid; m.p. 73-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5Hz, 2H), 7.18 (d, J = 8.3Hz, 2H), 3.82 (t, J = 7.0Hz, 2H), 2.62 (dd, J = 7.6Hz, J = 15.2Hz, 2H), 2.58 (t, J = 8.0Hz, 2H), 2.12 (m, 2H), 1.21 (t, J = 7.6Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.1, 140.6, 137.2, 128.2, 120.2, 48.9, 32.7, 28.3, 18.1, 15.7. MS (ESI) *m/z* 190 (M+H), 212 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{12}H_{16}NO$ $[M+H]^+$: 190.1226; found: 190.1229.

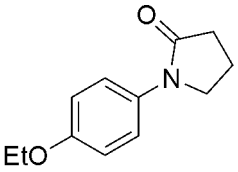


1-(3,4-Dimethylphenyl)pyrrolidin-2-one (1l): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added 3,4-dimethylaniline (2.3630g, 19.5 mmol), γ-butyrolactone (1 mL, 13.0 mmol), and 85% H_3PO_4 (87 μL, 1,3 mmol, 10 mol%). The mixture was heated to 180 °C in an oil bath for 17 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM to DCM/EtOAc = 19:5, v/v) to afford the title compound (69%). Pale pink solid; m.p. 70-71 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 2.1 Hz, 1H), 7.32-7.30 (m, 1H), 7.14 (d, J = 8.2 Hz, 1H), 3.86 (t, J = 7.0 Hz, 2H), 2.62 (t, J = 8.1 Hz, 2H), 2.30 (s, 3H), 2.26 (s, 3H), 2.21-2.13 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.0, 137.2, 137.0, 133.0, 129.8, 121.6, 117.7, 49.0, 32.6, 20.0, 19.2, 18.1. MS (EI) *m/z* 189 (M), 134 (M-55); HRMS (EI) *m/z* calc'd for $C_{12}H_{15}NO$ $[M]^+$: 189.1154; found: 189.1158.

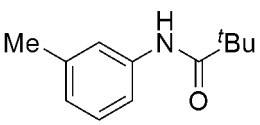


1-(4-Methoxyphenyl)pyrrolidin-2-one (1m): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added *p*-anisidine (2.4016g, 19.5 mmol), γ-butyrolactone (1 mL, 13.0 mmol), and 85% H_3PO_4 (87 μL, 1,3 mmol, 10

mol%). The mixture was heated to 180 °C in an oil bath for 14 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM to DCM/EtOAc = 9:1, v/v) to afford the title compound as a light brown solid (81%). All spectral data are in agreement with reported literature data.[9, 13] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, J = 9.1 Hz, 2H), 6.89 (d, J = 9.1 Hz, 2H), 3.82 (t, J = 7.6 Hz, 2H), 3.79 (s, 3H), 2.58 (t, J = 8.1 Hz, 2H), 2.14 (quintet, J = 7.7 Hz, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.0, 156.7, 132.8, 121.9, 114.1, 55.6, 49.3, 32.6, 18.1.

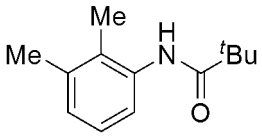


1-(4-Ethoxyphenyl)pyrrolidin-2-one (1n): Prepared by a modification to a known procedure.[50] In a 20 mL vial equipped with a Teflon cap was added *p*-phenetidine (2.52 mL, 19.5 mmol), γ-butyrolactone (1 mL, 13 mmol), and conc. H_3PO_4 (87 μL, 1. mmol, 10 mol%). The mixture was heated to 180 °C in an oil bath for 15.5 h. After cooling to ambient temperature, the resulting mixture was diluted with 50 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography to afford the title compound (70%). Dark pink solid; m.p. 112-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 9.0Hz, 2H), 6.87 (d, J = 9.0Hz, 2H), 4.00 (q, J = 7.0Hz, 2H), 3.80 (t, J = 7.0Hz, 2H), 2.57 (t, J = 8.1Hz, 2H), 2.13 (m, 2H), 1.39 (t, J = 7.0Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.9, 156.0, 132.7, 121.9, 114.8, 63.8, 49.3, 32.6, 18.1, 14.9. MS (ESI) *m/z* 206 (M+H), 228 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{12}H_{16}NO_2$ (M+H): 206.1175; found: 206.1174.

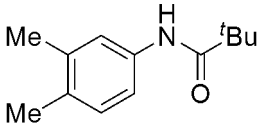


***N*-*m*-Tolylpivalamide (1o)**: Prepared by a known procedure.[49] All spectral data are in agreement with reported literature data.[14] Off-white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43

(s, 1H), 7.28 (d, J = 8.2Hz, 1H), 7.19 (t, J = 7.8Hz, 1H), 6.91 (d, J = 7.4Hz, 1H), 2.33 (s, 3H), 1.31 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7, 139.0, 138.1, 128.9, 125.1, 120.8, 117.1, 39.7, 27.8, 21.6.

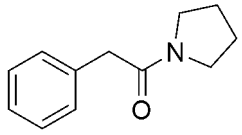


***N*-(2,3-Dimethylphenyl)pivalamide (1p):** Prepared by a known procedure.[49] To a 100 mL round-bottom flask was charged triethylamine (1.53 mL, 11 mmol), 2,3-dimethylaniline (1.22 mL, 10 mmol), and CH_2Cl_2 (40 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, pivaloyl chloride (1.35 mL, 11 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 17.5 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM) to afford the title compound (99%). Pale pink solid. All spectral data are in agreement with reported literature data.[14] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.0 Hz, 1H), 7.09 (t, J = 7.8 Hz, 1H), 7.00 (d, J = 7.5 Hz, 1H), 2.30 (s, 3H), 2.13 (s, 3H), 1.34 (s, 9H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 176.7, 137.4, 135.7, 129.2, 127.2, 126.0, 122.1, 39.7, 27.9, 20.7, 13.7.

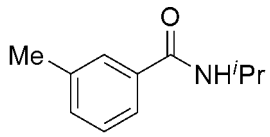


***N*-(3,4-Dimethylphenyl)pivalamide (1q):** Prepared by known procedures.[49] To a 100 mL round-bottom flask was charged triethylamine (1.53 mL, 11 mmol), 3,4-dimethylaniline (1.2118 g, 10 mmol), and 40 mL CH_2Cl_2. The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, pivaloyl chloride (1.35 mL, 11 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 16 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (94%). White solid. The spectral data are in agreement with

reported literature data.[15] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, J = 1.8 Hz, 1H), 7.22 (dd, J = 2.1, 8.1 Hz, 1H), 7.06 (d, J = 8.1 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H), 1.30 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.3, 138.4, 136.9, 132.8, 132.4, 130.9, 130.1, 129.5, 129.0, 127.9, 122.5, 39.8, 27.5, 19.9, 19.3. MS (EI) *m/z* 205 (M); HRMS (EI) *m*/*z* calc'd for $C_{13}H_{19}NO$ $[M]^+$: 205.1467; found: 205.1471.

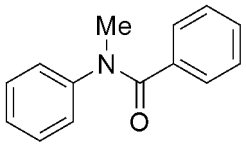


2-Phenyl-1-(pyrrolidin-1-yl)ethanone (1r): Prepared by a known procedure.[49] To a 100 mL round-bottom flask was charged triethylamine (1.63 mL, 11.6 mmol), pyrrolidine (0.97 mL, 11.6 mmol), and CH_2Cl_2 (40 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, phenylacetyl chloride (1.40 mL, 10.6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 12 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (75%). Yellow oil. All spectral data are in agreement with reported literature data.[16-19] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.21 (m, 5H), 3.65 (s, 1H), 3.49 (t, J = 6.7Hz, 2H), 3.42 (t, J = 6.6Hz, 2H), 1.94-1.81 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 169.6, 135.1, 129.1, 128.7, 126.8, 47.0, 46.1, 42.5, 26.3, 24.50.

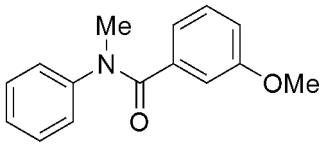


***N*-Isopropyl-3-methylbenzamide (1s):** Prepared by a known procedure.[49] To a 100 mL round-bottom flask was charged triethylamine (1.63 mL, 11.6 mmol), isopropylamine (1 mL, 11.6 mmol), and CH_2Cl_2 (40 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, *m*-toluoyl chloride (1.40 mL, 10.6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 17.5 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 25 mL 1M HCl, 25 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting

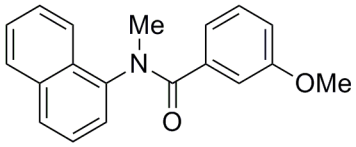
residue was purified by column chromatography (eluent: DCM/EtOAc = 95:5, v/v) to afford the title compound (99%). White solid. All spectral data are in agreement with reported literature data.[20] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (s, 1H), 7.52 (s, 1H), 7.30 (s, 1H), 7.28 (s, 1H), 5.94 (s, 1H), 4.28 (heptet, J = 6.6 Hz, 1H), 2.38 (s, 3H), 1.25 (d, J = 6.5 Hz, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.0, 138.5, 135.1, 133.1, 128.5, 127.7, 123.9, 42.0, 23.0, 21.5. MS (EI) *m/z* 177 (M); (ESI) *m/z* 178 (M+H), 200 (M+Na), 136(M-41); HRMS (EI) *m/z* calc'd for $C_{11}H_{15}NO$ $[M]^+$: 177.1154; found: 177.1155; (ESI) *m/z* calc'd for $C_{11}H_{16}NO$ $[M+H]^+$: 178.1226; found: 178.1224.



***N*-Methyl-*N*-phenylbenzamide (1t):** Prepared by a known procedure.[49] To a flame-dried round-bottom flask was charged triethylamine (1.05 mL, 7.5 mmol), *N*-methylaniline (0.54 mL, 5 mmol), and CH_2Cl_2 (20 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, benzoyl chloride (0.70 mL, 6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/hexanes = 1:3, v/v) to afford the title compound (100%). Orange oil. All spectral data are in agreement with reported literature data.[21-26] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30-7.28 (m, 2H), 7.23-7.19 (m, 3H), 7.17-7.11 (m, 3H), 7.04-7.02 (m, 2H), 3.50 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.7, 144.9, 135.9, 129.6, 129.1, 128.7, 127.7, 126.9, 126.5. MS (ESI) *m/z* 212 (M+H), 234 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{14}H_{13}NO$ $[M+H]^+$: 212.1069; found: 212.1080.

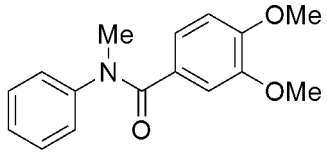


3-Methoxy-*N*-methyl-*N*-phenylbenzamide (1u): Prepared by a known procedure.[49] To a flame-dried round-bottom flask was charged triethylamine (1.05 mL, 7.5 mmol), *N*-methylaniline (0.54 mL, 5 mmol), and CH_2Cl_2 (20 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, 3-methoxybenzoyl chloride (0.82 mL, 6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/hexanes = 1:3, v/v) to afford the title compound (100%). This compound has been reported in the literature.[51] Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, J = 7.2 Hz, 2H), 7.14 (t, J = 7.3 Hz, 1H), 7.06-7.03 (m, 3H), 6.87-6.83 (m, 2H), 6.77 (dd, J = 2.2 Hz, J = 8.2 Hz, 1H), 3.65 (s, 3H), 3.49 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 158.9, 145.0, 137.1, 129.2, 129.2, 128.8, 126.8, 126.5, 121.2, 116.1, 113.7, 55.2, 38.4. MS (ESI) *m/z* 242 (M+H), 264 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{15}H_{15}NO_2$ $[M+H]^+$: 242.1175; found: 242.1180.



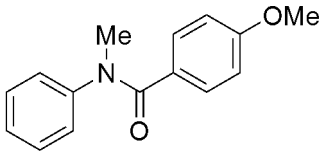
3-Methoxy-*N*-methyl-*N*-(naphthalen-1-yl)benzamide (1v): Prepared by a modification to a known procedure.[52] To a 100 mL round-bottom flask was charged 3-methoxy-*N*-(naphthalen-1-yl)benzamide (**1z**) (2.5594 g, 9.2 mmol) and 24 mL DMF. The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, NaH (60% oil dispersion, 480 mg, 12.0 mmol) was added and the reaction mixture was stirred for 1 h, upon which methyl iodide (747 μL, 12.0 mmol) was added. The resulting suspension was allowed to warm to room temperature over 16.5 h. The reaction mixture was diluted with 100 mL

EtOAc and washed with 4 x 25 mL water. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/CH_2Cl_2 = 2:98 to EtOAc/CH_2Cl_2 = 2.5:97.5, v/v) to afford the title compound (92%). White solid; m.p. 107-108 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, J = 8.4 Hz, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.67 (d, J = 8.2 Hz, 1H), 7.59 (t, J = 7.1 Hz, 1H), 7.49 (t, J = 7.0 Hz, 1H), 7.22 (t, J = 7.5 Hz, 1H), 7.07 (d, J = 7.2 Hz, 1H), 6.88-6.81 (m, 2H), 6.79 (s, 1H), 6.61 (dd, J = 1.4 Hz, J = 7.5 Hz, 1H), 3.52 (s, 3H), 3.32 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.5, 158.6, 141.2, 137.1, 134.5, 130.0, 128.7, 128.6, 128.1, 127.3, 126.5, 126.4, 125.6, 122.7, 120.2, 116.4, 112.3, 54.8, 38.4. MS (ESI) *m/z* 292 (M+H), 314 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{19}H_{18}NO_2$ $[M+H]^+$: 292.1332; found: 292.1333.

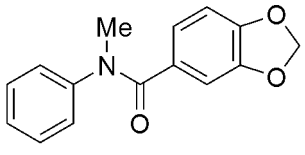


3,4-Dimethoxy-*N*-methyl-*N*-phenylbenzamide (1w): Prepared by a known procedure.[1,49] In a flame-dried flask, 3,4-dimethoxybenzoic acid (0.911 g, 5.00 mmol) was dissolved in thionyl chloride (15 mL). The reaction mixture was heated to 80 ºC for 20 min. After cooling to ambient temperature, the resulting solution was concentrated *in vacuo*. The crude product was carried on without further purification. To a flame-dried round-bottom flask was charged triethylamine (0.87 mL, 6.3 mmol), *N*-methylaniline (0.45 mL, 4.2 mmol), and CH_2Cl_2 (20 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, 3,4-dimethoxybenzoyl chloride (1.003 g, 5 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/hexanes = 1:3, v/v) to afford the title compound (100%). This compound has been reported in the literature.[53] Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (t, J = 1.3 Hz, 1H), 7.23 (t, J = 2.0 Hz, 1H), 7.17-7.13 (m, 1H), 7.07-7.04 (m, 2H), 6.93 (dd, J = 2.0 Hz,

J = 8.4 Hz, 1H), 6.85 (d, J = 2.0 Hz, 1H), 6.63 (d, J = 8.4 Hz, 1H), 3.81 (s, 3H), 3.64 (s, 3H), 3.49 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.0, 150.2, 147.9, 145.6, 129.2, 127.8, 126.8, 126.3, 122.8, 112.4, 109.9, 55.8, 55.7, 38.6. MS (ESI) m/z 272 (M+H), 294 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{16}H_{17}NO_3$ $[M+H]^+$: 272.1281; found: 272.1272.

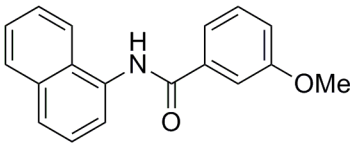


4-Methoxy-*N*-methyl-*N*-phenylbenzamide (1x): Prepared by a known procedure.[49] To a flame-dried round-bottom flask was charged triethylamine (1.05 mL, 7.5 mmol), *N*-methylaniline (0.54 mL, 5 mmol), and CH_2Cl_2 (20 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, 4-methoxybenzoyl chloride (1.024 g, 6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/hexanes = 1:3, v/v) to afford the title compound (100%). This compound has been reported in the literature.[54, 55] Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.22 (m, 4H), 7.16-7.12 (m, 1H), 7.05-7.03 (m, 2H), 6.67-6.65 (m, 2H), 3.73 (s, 3H), 3.48 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 160.6, 145.5, 130.9, 129.2, 128.0, 126.9, 126.3, 113.0, 55.2, 38.6. MS (ESI) *m/z* 242 (M+H), 264 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{15}H_{15}NO_2$ $[M+H]^+$: 242.1175; found: 242.1181.



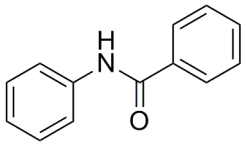
***N*-Methyl-*N*-phenylbenzo[d][1,3]dioxole-5-carboxamide (1y):** Prepared by a known procedure.[1,49] In a flame-dried flask, piperonylic acid (0.831 g, 5.00 mmol) was dissolved in thionyl chloride (15 mL). The reaction mixture was heated to 80 ºC for 20 min. After cooling

to ambient temperature, the resulting solution was concentrated *in vacuo*. The crude product was carried on without further purification. To a flame-dried round-bottom flask was charged triethylamine (0.87 mL, 6.3 mmol), *N*-methylaniline (0.45 mL, 4.2 mmol), and CH_2Cl_2 (20 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, piperonoyl chloride (5 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/hexanes = 1:3, v/v) to afford the title compound (100%). This compound has been reported in the literature.[26, 45, 56, 57] Light yellow oil. ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.27-7.23 (m, 2H), 7.16 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 7.7 Hz, 2H), 6.83-6.81 (m, 2H), 6.56 (d, J = 7.9 Hz, 1H), 5.90 (s, 2H), 3.47 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.0, 148.7, 147.0, 145.3, 129.7, 129.2, 126.7, 126.4, 124.0, 109.5, 107.5, 101.3, 38.6. MS (ESI) *m/z* 256 (M+H), 278 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{15}H_{13}NO_3$ $[M+H]^+$: 256.0968; found: 256.0956.

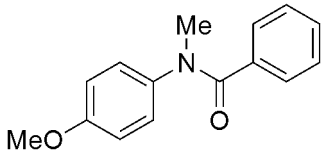


3-Methoxy-*N*-(naphthalen-1-yl)benzamide (1z): Prepared by a known procedure.[49] To a 100 mL round-bottom flask was charged triethylamine (3.06 mL, 22 mmol), 1-naphthylamine hydrochloride (1.7966 g, 10 mmol), and CH_2Cl_2 (40 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, 3-methoxybenzoyl chloride (1.50 mL, 11 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature over 14 h. The solution was diluted with 60 mL CH_2Cl_2 and washed sequentially with 50 mL 1M HCl, 50 mL 1M NaOH, and 25 mL brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by trituration in Et_2O to afford the title compound (92%). White solid; m.p. 164-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29

(s, 1H), 7.99 (d, J = 7.3Hz, 1H), 7.89 (dd, J = 2.9Hz, J = 9.2Hz, 2H), 7.74 (d, J = 8.2Hz. 1H), 7.56-7.46 (m, 5H), 7.41 (t, J = 7.9Hz, 1H), 7.11 (dd, J = 2.1Hz, J = 8.2Hz, 1H), 3.87 (s, 3H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 160.2, 136.5, 134.3, 132.5, 130.0, 128.9, 127.6, 126.5, 126.23, 126.18, 125.9, 121.4, 120.9, 119.0, 118.2, 112.8, 55.7. MS (ESI) *m/z* 278 (M+H), 300 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{18}H_{16}NO_2$ $[M+H]^+$: 278.1175; found: 278.1181.



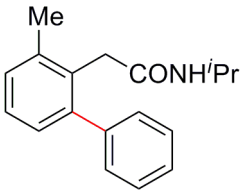
***N*-Phenylbenzamide (1aa):** Prepared by a known procedure.[49] To a flame-dried round-bottom flask was charged triethylamine (1.05 mL, 7.5 mmol), aniline (0.46 mL, 5 mmol), and CH_2Cl_2 (20 mL). The resulting solution was cooled to 0 ºC in an ice bath. Subsequently, benzoyl chloride (0.70 mL, 6 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by by trituration in Et_2O to afford the title compound (100%). All spectral data are in agreement with reported literature data.[9, 11, 23-25, 27-36] Light gray solid; m.p. 159-161 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.24 (s, 1H) 7.97-7.95 (m, 2H), 7.80-7.78 (m, 2H), 7.61-7.51 (m, 3H), 7.35 (t, J = 8.0 Hz, 2H), 7.10 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.5, 139.1, 135.0, 131.5, 128.6, 128.4, 127.6, 123.6, 120.3. MS (ESI) *m/z* 198 (M+H), 220 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{13}H_{11}NO$ $[M+H]^+$: 198.0913; found: 198.0914.



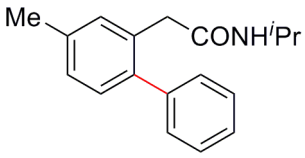
***N*-(4-Methoxyphenyl)-*N*-methylbenzamide (1ab):** Prepared by a known procedure.[1,49] In a flame-dried flask was charged triethylamine (1.05 mL, 7.5 mmol), 4-methoxy-*N*-methylaniline (0.686 g, 5.0 mmol), and dry CH_2Cl_2 (20 mL). The resulting

solution was cooled to 0 ºC in an ice bath. Subsequently, benzoyl chloride (0.70 mL, 5.0 mmol) was added dropwise and the reaction mixture was allowed to warm to room temperature overnight. The solution was diluted with CH_2Cl_2 and washed thrice with 1M HCl and the resulting aqueous layer was extracted thrice with CH_2Cl_2. The combined organic phases were then washed thrice with sat'd $NaHCO_3$ and the resulting aqueous layer was extracted thrice with CH_2Cl_2. Finally, the combined organic phases were washed twice with brine. The organic layer was dried over $MgSO_4$, concentrated *in vacuo* and the resulting residue was purified by column chromatography (eluent: EtOAc/hexanes = 1:3, v/v) to afford the title compound (100%). All spectral data are in agreement with reported literature data.[22, 37] Light orange solid; m.p. 77-79 ºC. ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.29 (d, J = 7.0 Hz, 2H), 7.24-7.14 (m, 3H), 6.95 (d, J = 8.7 Hz, 2H), 6.73 (d, J = 8.9 Hz, 2H), 3.73 (s, 3H), 3.45 (s, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.9, 170.9, 158.1, 138.0, 136.3, 129.6, 129.1, 129.0, 128.8, 128.4, 128.3, 127.9, 114.5, 55.6, 38.8.

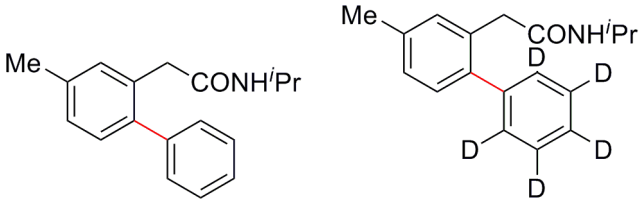
Arylation Products



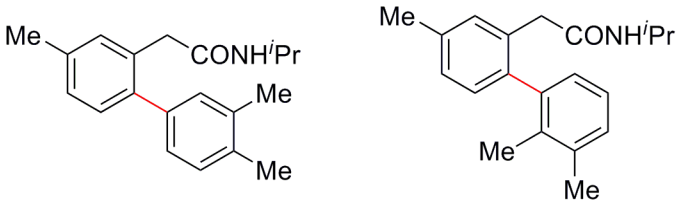
***N*-Isopropyl-2-(3-methylbiphenyl-2-yl)acetamide (2a):** Prepared from **1a** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC for 30 h, upon which 5 mol% $Pd(OAc)_2$ was added until a total of 48 h had elapsed (81%). Off-white solid; m.p. 154-155 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.24 (m, 3H), 7.19-7.14 (m, 4H), 7.07-7.05 (m, 1H), 5.00 (d, J = 7.1 Hz, 1H), 4.01-3.92 (m, 1H), 3.42 (s, 2H), 2.28 (s, 3H), 0.96 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.7, 143.4, 141.6, 138.0, 131.2, 129.9, 129.1, 128.3, 128.3, 127.2, 41.2, 38.7, 22.6, 20.2. MS (EI) *m/z* 267 (M); HRMS (EI) *m/z* calc'd for $C_{18}H_{21}NO$ $[M]^+$: 267.1623; found: 267.1627.



***N*-Isopropyl-2-(4-methylbiphenyl-2-yl)acetamide (2b):** Prepared from **1b** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 31 h (99%). Off-white solid; m.p. 95-96 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 3H), 7.20-7.18 (m, 2H), 7.11-7.06 (m, 3H), 4.94 (d, J = 5.6 Hz, 1H), 3.94-3.85 (m, 1H), 3.38 (s, 2H), 2.31 (s, 3H), 0.93 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 141.0, 139.6, 137.6, 132.4, 131.4, 130.4, 129.3, 128.4, 128.2, 127.2, 41.6, 41.3, 22.6, 21.1. MS (EI) *m/z* 267 (M); HRMS (EI) *m/z* calc'd for $C_{18}H_{21}NO$ $[M]^+$: 267.1623; found: 267.1629.



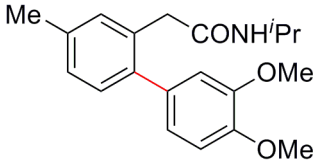
Using 0.5 mL benzene and 0.5 mL benzene-d_6, **2b** and its isotopomer **2b-d_5** was isolated in 87% with a ratio of 2.2:1 after 43.5 h. Off-white solid; m.p. 105-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 2.18H), 7.20-7.18 (m, 2H), 7.11-7.06 (m, 3H), 4.94 (d, J = 5.6 Hz, 1H), 3.94-3.85 (m, 1H), 3.38 (s, 2H), 2.31 (s, 3H), 0.93 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.1, 141.0, 139.6, 137.6, 132.4, 131.4, 130.4, 129.3, 128.4, 128.2, 127.2, 41.6, 41.3, 22.6, 21.1. HRMS (ESI) *m/z* calc'd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1695; found: 268.1699; calc'd for $C_{18}H_{17}D_5NO$ $[M+H]^+$: 273.2009; found: 273.2010.



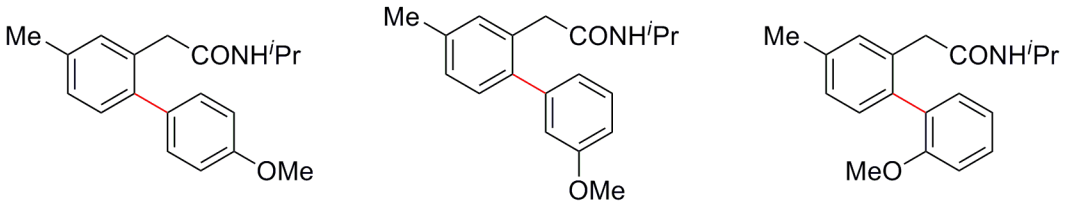
major:minor = 93:7

***N*-Isopropyl-2-(3',4,4'-trimethylbiphenyl-2-yl)acetamide/*N*-isopropyl-2-(2',3',4-trimethylbiphenyl-2-yl)acetamide (2c):** Prepared from **1b** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 1,2-dimethylbenzene in 61 h (95%). Beige solid; m.p. 94-96 ºC. This compound was isolated as an inseparable mixture of two isomers in a 93:7 ratio. The characterization of the major isomer is as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.04

(m, 4H), 6.95-6.91 (m, 2H), 4.95 (d, J = 6.7 Hz, 1H), 3.92-3.85 (m, 1H), 3.38 (s, 2H), 2.30 (s, 3H), 2.21 (s, 3H), 0.93 (d, J = 6.6 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 139.7, 138.5, 137.4, 136.5, 135.5, 132.5, 131.3, 130.5, 130.4, 129.6, 128.1, 126.6, 41.7, 41.3, 22.6, 21.1, 19.8, 19.4. MS (EI) *m/z* 295 (M); (ESI) *m/z* 296 (M+H), 318 (M+Na); HRMS (EI) *m/z* calc'd for $C_{20}H_{25}NO$ $[M]^+$: 295.1936; found: 295.1944; (ESI) *m/z* calc'd for $C_{20}H_{26}NO$ $[M+H]^+$: 296.2008; found: 296.2018.



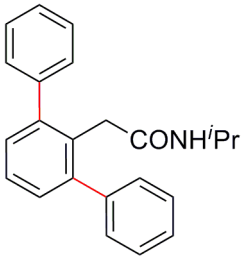
2-(3',4'-Dimethoxy-4-methylbiphenyl-2-yl)-*N*-isopropylacetamide (2d): Prepared from **1b** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 1,2-dimethoxybenzene in 44 h (99%). Orange solid; m.p. 150-152 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, J = 7.5Hz, 1H), 7.14-7.08 (m, 2H), 6.87 (d, J = 8.4Hz, 1H), 6.81 (s, 1H), 6.79 (d, J = 1.8Hz, 1H), 5.17 (d, J = 7.3Hz, 1H), 3.97 (td, J = 6.6Hz, J = 19.8Hz, 1H), 3.88 (d, J = 1.0Hz, 3H), 3.83 (d, J = 1.0Hz, 3H), 3.45 (s, 2H), 2.36 (s, 3H), 1.01 (dd, J = 1.0Hz, J = 6.5Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 148.6, 148.2, 139.4, 137.4, 133.7, 132.5, 131.3, 130.4, 128.1, 121.4, 112.7, 111.1, 55.93, 55.87, 41.6, 41.3, 29.7, 22.6, 21.1. MS (ESI) *m/z* 328 (M+H), 350 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{20}H_{26}NO_3$ $[M+H]^+$: 328.1907; found: 328.1908.



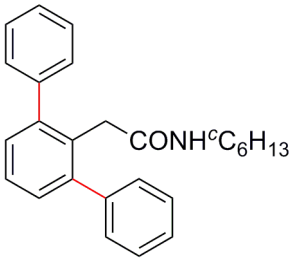
o:m:p = 9:13:78

***N*-Isopropyl-2-(4'-methoxy-4-methylbiphenyl-2-yl)acetamide/*N*-isopropyl-2-(3'-methoxy-4-methylbiphenyl-2-yl)acetamide/*N*-isopropyl-2-(2'-methoxy-4-methylbiphenyl-2-yl)acetamide (2e):** Prepared from **1b** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in anisole in 61 h (99%). Orange solid; m.p. 83-86 ºC. This compound was isolated as an inseparable mixture of three isomers in a 9:13:78 ratio (*ortho:meta:para*). The characterization of the *para* isomer is as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.04 (m, 5H), 6.85 (d, J = 8.7 Hz, 2H), 4.98 (d, J = 6.8 Hz, 1H), 3.95-3.87 (m, 1H), 3.75 (s, 3H),

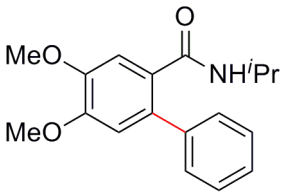
3.38 (s, 2H), 2.30 (s, 3H), 0.94 (d, J = 6.6 Hz, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 170.2, 158.8, 139.2, 137.3, 133.3, 132.6, 131.4, 130.5, 130.3, 128.2, 113.8, 55.3, 41.7, 41.3, 22.6, 21.1. MS (EI) *m/z* 297 (M); HRMS (EI) *m/z* calc'd for $C_{19}H_{23}NO_2$ $[M]^+$: 297.1729; found: 297.1727.



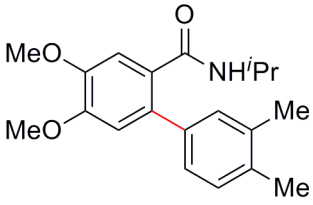
2-(2,6-Diphenylphenyl)-*N*-isopropylacetamide (2f): Prepared from **1c** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC for 30 h (67%). Off-white solid; m.p. 158-159 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.16 (m, 13H), 4.71 (d, J = 7.4 Hz, 1H), 3.85-3.74 (m, 1H), 3.35 (s, 2H), 0.87 (d, J = 6.6 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.7, 143.5, 141.5, 130.3, 129.7, 129.2, 128.2, 127.1, 126.9, 41.1, 38.7, 22.4. MS (EI) *m/z* 329 (M); HRMS (ESI) *m/z* calc'd for $C_{23}H_{23}NO$ $[M]^+$: 329.1780; found: 329.1780.



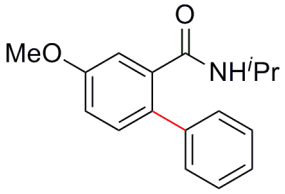
2-(2,6-Diphenylphenyl)-*N*-cyclohexylacetamide (2g): Prepared from **1d** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC for 38 h (68%). Off-white solid; m.p. 192-194 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (m, 11H), 7.20 (s, 1H), 7.18 (d, J = 8.3Hz, 1H), 4.79 (d, J = 8.1Hz, 1H), 3.51 (tdt, J = 3.9Hz, J = 8.1Hz, J = 12.1Hz, 1H), 3.36 (s, 2H), 1.64 (dd, J = 3.4Hz, J = 12.2Hz, 2H), 1.50 (t, J = 17.2Hz, 3H), 1.20 (q, J = 12.2Hz, 2H), 1.01 (m, 1H), 0.81 (ddd, J = 3.3Hz, J = 12.2Hz, J = 23.5Hz, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.8, 143.7, 141.6, 130.5, 129.8, 129.4, 128.4, 127.3, 127.1, 48.1, 38.9, 33.0, 25.6, 24.9. MS (ESI) *m/z* 370 (M+H), 392 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{26}H_{28}NO$ $[M+H]^+$: 370.2165; found: 370.2179.



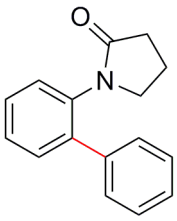
***N*-Isopropyl-4,5-dimethoxybiphenyl-2-carboxamide (2h):** Prepared from **1e** according to general procedure A with 5 mol% $Pd(OAc)_2$ at 60 ºC in 24 h (78%). White solid; m.p. 96 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.36 (m, 6H), 6.78 (s, 1H), 4.87 (d, J = 7.3 Hz, 1H), 4.01-3.93 (m, 4H), 3.91 (s, 3H), 0.81 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.6, 150.0, 148.4, 140.5, 132.7, 129.0, 128.7, 127.8, 127.7, 112.7, 112.0, 56.1, 56.0, 41.6, 22.1. HRMS (ESI) *m/z* calc'd for $C_{18}H_{22}NO_3$ $[M+H]^+$: 300.1594; found: 300.1592.



***N*-Isopropyl-4,5-dimethoxy-3',4'-dimethylbiphenyl-2-carboxamide (2i):** Prepared from **1e** according to general procedure A with 5 mol% $Pd(OAc)_2$ at 60 ºC in *o*-dimethylbenzene in 44 h (83%). Yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.20-7.10 (m, 3H), 6.77 (s, 1H), 4.99 (d, J = 7.8 Hz, 1H), 4.03-3.94 (m, 4H), 3.90 (s, 3H), 2.30 (d, J = 7.9 Hz, 6H), 0.82 (d, J = 6.6 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.5, 149.9, 148.0, 137.8, 136.8, 136.1, 132.9, 130.3, 129.8, 127.5, 126.2, 112.6, 112.0, 56.0, 55.9, 41.4, 22.0, 19.6, 19.4. HRMS (ESI) *m/z* calc'd for $C_{20}H_{26}NO_3$ $[M+H]^+$: 328.1907; found: 328.1914.

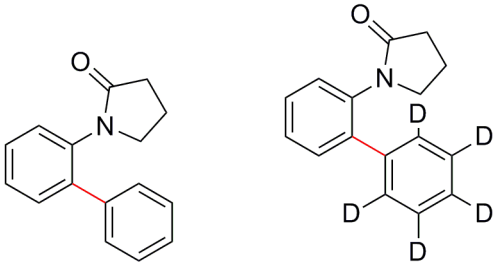


***N*-Isopropyl-4-methoxybiphenyl-2-carboxamide (2j):** Prepared from **1f** according to general procedure A with 5 mol% $Pd(OAc)_2$ at 60 ºC in 40 h (61%). Yellow solid; m.p. 100-101 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.33 (m, 5H), 7.28-7.26 (m, 2H), 7.01 (dd, J = 2.8, 8.5 Hz, 1H), 4.94 (d, J = 7.1 Hz, 1H), 4.05-3.95 (m, 1H), 3.87 (s, 3H), 0.83 (d, J = 6.4 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.0, 159.0, 140.0, 136.9, 131.8, 131.3, 128.9, 128.6, 127.4, 116.7, 113.2, 55.5, 41.6, 22.1. HRMS (ESI) *m/z* calc'd for $C_{17}H_{20}NO_2$ $[M+H]^+$: 270.1488; found: 270.1498.



1-(Biphenyl-2-yl)pyrrolidin-2-one (2k): Prepared from **1g** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 23 h (83%). All spectral data are in agreement with reported literature data.[38] Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 9H), 3.20 (t, J = 7.0 Hz, 2H), 2.42 (t, J = 8.1 Hz, 2H), 1.89-1.82 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.6, 139.6, 139.0, 136.2, 130.8, 128.5, 128.4, 128.3, 128.0, 127.5, 50.1, 31.1, 18.9.

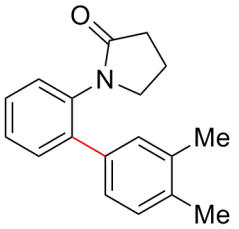
Competition experiment:



Using 0.5 mL benzene and 0.5 mL benzene-d_6, **2k** and its isotopomer **2k-*d*$_5$** was isolated in 99% with a ratio of 5.5:1 after 23 h. Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 7.70H), 3.20 (t, J = 7.0 Hz, 2H), 2.42 (t, J = 8.1 Hz, 2H), 1.89-1.82 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.6, 139.6, 139.0, 136.2, 130.8, 128.5, 128.4, 128.3, 128.0, 127.5, 50.1, 31.1, 18.9. MS (EI) 237 (M, **2k**), 242 (M, **2k-*d*$_5$**); HRMS (EI) *m/z* calc'd for $C_{16}H_{15}NO$ $[M]^+$: 237.1154; found 237.1145; calc'd for $C_{16}H_{10}D_5NO$ $[M]^+$: 242.1467; found 242.1460.

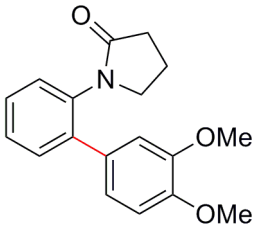
Stoichiometric experiment:

Prepared from **3b** according to general procedure E in 16 h (52%).

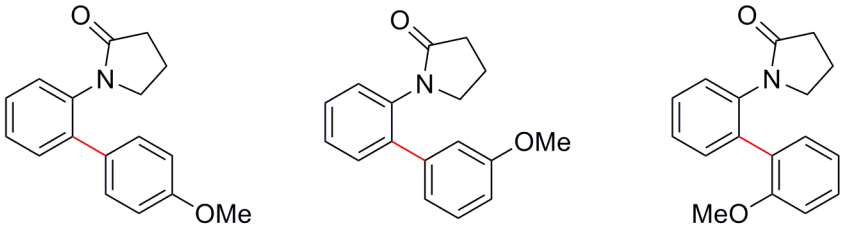


1-(3',4'-Dimethylbiphenyl-2-yl)pyrrolidin-2-one (2l): Prepared from **1g** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in *o*-dimethylbenzene in 24 h (89%).

Pale yellow viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 4H), 7.15-7.09 (m, 3H), 3.22 (t, J = 7.0 Hz, 2H), 2.43 (t, J = 8.1 Hz, 2H), 2.29 (s, 3H), 2.29 (s, 3H), 1.91-1.84 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.5, 139.4, 136.5, 136.1, 135.8, 130.8, 129.6, 129.4, 128.3, 128.1, 127.8, 125.6, 49.9, 31.2, 19.7, 19.4, 18.9. HRMS (ESI) *m/z* calc'd for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found: 266.1535.

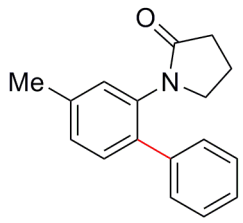


1-(3',4'-Dimethoxybiphenyl-2-yl)pyrrolidin-2-one (2m): Prepared from **1g** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 0.5 mL *o*-dimethoxybenzene (73%). Brown viscous oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 4H), 6.95-6.90 (m, 3H), 3.92 (s, 3H), 3.86 (s, 3H), 3.22 (t, J = 7.0 Hz, 2H), 2.44 (t, J = 8.1 Hz, 2H), 1.94-1.86 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.5, 148.6, 148.4, 139.4, 136.2, 131.7, 130.7, 128.4, 128.2, 128.0, 120.5, 111.5, 110.9, 55.8, 50.0, 31.2, 18.9. HRMS (ESI) *m/z* calc'd for $C_{18}H_{20}NO_3$ $[M+H]^+$: 298.1437; found: 298.1445.

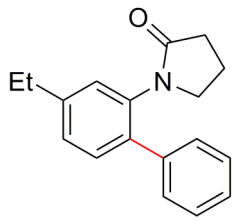


o:m:p = 4:11:85

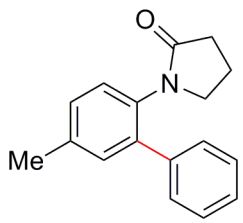
1-(4'-Methoxybiphenyl-2-yl)pyrrolidin-2-one/1-(3'-methoxybiphenyl-2-yl)pyrrolidin-2-one/1-(2'-methoxybiphenyl-2-yl)pyrrolidin-2-one (2n): Prepared from **1g** according to general procedure C with 10 mol% $Pd(OAc)_2$ at 70 ºC in anisole in 36 h (70%). Yellow viscous oil. This compound was isolated as an inseparable mixture of three isomers in a 4:11:85 ratio (*ortho:meta:para*). The characterization of the *para* isomer is as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 6.95-6.92 (m, 2H), 3.84 (s, 3H), 3.22 (t, J = 7.0 Hz, 2H), 2.43 (t, J = 8.1 Hz, 2H), 1.93-1.87 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.6, 159.1, 139.2, 136.2, 131.4, 130.8, 129.4, 128.3, 128.1, 127.9, 113.8, 55.2, 50.0, 31.2, 18.9. HRMS (ESI) *m/z* calc'd for $C_{17}H_{18}NO_2$ $[M+H]^+$: 268.1332; found: 268.1338.



1-(4-Methylbiphenyl-2-yl)pyrrolidin-2-one (2o): Prepared from **1h** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 31 h (99%). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.23 (m, 5H), 7.20 (d, J = 7.8 Hz, 1H), 7.11 (d, J = 8.8 Hz, 1H), 7.06 (s, 1H), 3.11 (t, J = 7.0 Hz, 2H), 2.36-2.32 (m, 2H), 1.81-1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.6, 139.1, 138.5, 136.7, 136.0, 130.6, 128.8, 128.8, 128.3, 128.3, 127.3, 50.2, 31.2, 20.9, 18.9. MS (EI) *m/z* 251 (M); HRMS (EI) *m/z* calc'd for $C_{17}H_{17}NO$ $[M]^+$: 251.1310; found: 251.1311.

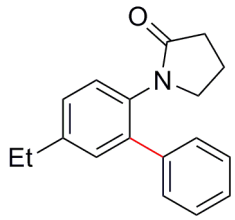


1-(4-Ethylbiphenyl-2-yl)pyrrolidin-2-one (2p): Prepared from **1i** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 47.5 h (97%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 5H), 7.23 (m, 3H), 3.19 (m, 2H), 2.69 (q, J = 7.6Hz, 2H), 2.41 (t, J = 8.1Hz, 2H), 1.85 (td, J = 7.5Hz, J = 15.2Hz, 2H), 1.26 (t, J = 7.6Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.8, 144.2, 139.5, 139.4, 133.9, 130.4, 128.5, 128.3, 128.2, 127.6, 76.8, 50.4, 31.3, 28.6, 19.0, 15.5. MS (ESI) *m/z* 266 (M+H), 288 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{18}H_{20}NO$: 266.1539; found: 266.1548.

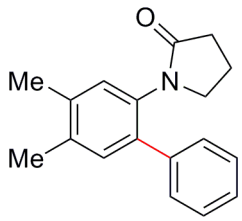


1-(5-Methylbiphenyl-2-yl)pyrrolidin-2-one (2q): Prepared from **1j** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 31 h (94%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.26 (m, 5H), 7.15-7.10 (m, 3H), 3.10 (t, J = 7.0 Hz, 2H), 2.33 (m, 5H), 1.77 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.7, 138.4, 138.2, 136.9, 132.7, 130.4,

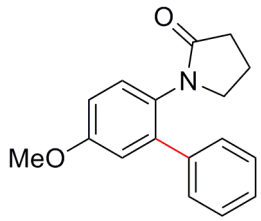
128.2, 127.3, 127.1, 126.5, 49.2, 30.2, 20.1, 17.9. MS (EI) *m/z* 251 (M); (ESI) *m/z* 252 (M+H), 274 (M+Na); HRMS (EI) *m/z* calc'd for $C_{17}H_{17}NO$ $[M]^+$: 251.1310; found: 251.1311; (ESI) *m/z* calc'd for $C_{17}H_{18}NO$ $[M+H]^+$: 252.1382; found: 252.1372.



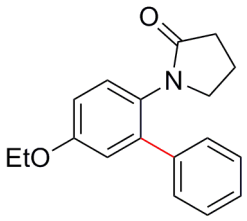
1-(5-Ethylbiphenyl-2-yl)pyrrolidin-2-one (2r): Prepared from **1d** according to general procedure C with 10 mol% $Pd(OAc)_2$ at 70 ºC in 56 h (80%). Yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, J = 8.5Hz, 2H), 7.18 (d, J = 8.3Hz, 2H), 3.82 (t, J = 7.0Hz, 2H), 2.62 (dd, J = 7.6Hz, J = 15.2Hz, 2H), 2.58 (t, J = 8.0Hz, 2H), 2.12 (m, 2H), 1.21 (t, J = 7.6Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 174.0, 140.6, 137.2, 128.2, 120.2, 48.9, 32.7, 28.3, 18.1, 15.7. MS (ESI) *m/z* 266 (M+H), 288 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found: 266.1540.



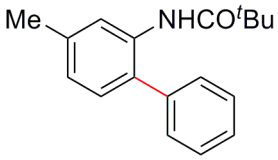
1-(4,5-Dimethylbiphenyl-2-yl)pyrrolidin-2-one (2s): Prepared from **1l** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 39 h (98%). Yellow solid; mp 95-96 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.22 (m, 5H), 7.09 (s, 1H), 7.01 (s, 1H), 3.10 (t, J = 7.0 Hz, 2H), 2.34 (t, J = 8.1 Hz, 2H), 2.22 (s, 3H), 2.21 (s, 3H), 1.81-1.83 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 175.7, 139.1, 137.1, 136.9, 136.6, 133.6, 131.8, 129.2, 128.3, 128.2, 127.2, 50.2, 31.1, 19.4, 19.3, 18.9. MS (EI) *m/z* 265 (M); (ESI) *m/z* 266 (M+H), 288 (M+Na); HRMS (EI) *m*/z calc'd for $C_{18}H_{19}NO$ $[M]^+$: 265.1467; found: 265.1472; (ESI) *m/z* calc'd for $C_{18}H_{20}NO$ $[M+H]^+$: 266.1539; found: 266.1550.



1-(5-Methoxybiphenyl-2-yl)pyrrolidin-2-one (2t): Prepared from **1m** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 47 h (99%). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 5H), 7.19 (s, 1H), 7.15 (d, J = 8.2 Hz, 1H), 6.87-6.84 (m, 2H), 3.75 (s, 3H), 3.09 (t, J = 7.0 Hz, 2H), 2.32 (t, J = 8.1 Hz, 2H), 1.80-1.73 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.8, 158.9, 140.8, 139.0, 129.4, 129.0, 128.3, 128.2, 127.6, 115.9, 113.9, 55.5, 50.3, 31.0, 18.8. MS (EI) *m/z* 267 (M); HRMS (EI) *m*/z calc'd for $C_{17}H_{17}NO_2$ $[M]^+$: 267.1259; found: 267.1253.

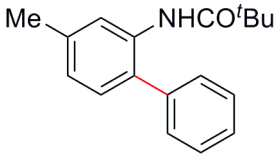


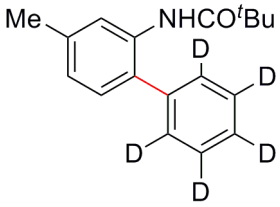
1-(5-Ethoxybiphenyl-2-yl)pyrrolidin-2-one (2u): Prepared from **1n** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 47.5 h (84%). Orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 5H), 7.19 (s, 1H), 7.12 (d, J = 9.3Hz, 1H), 6.84 (dd, J = 2.4Hz, J = 7.4Hz, 2H), 3.97 (q, J = 7.0Hz, 2H), 3.08 (t, J = 7.0Hz, 2H), 2.32 (t, J = 8.1Hz, 2H), 1.75 (m, 2H), 1.33 (t, J = 7.0Hz, 3H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.9, 158.4, 141.0, 139.2, 129.5, 129.0, 128.4, 128.4, 127.7, 116.7, 114.6, 63.9, 50.5, 31.2, 18.9, 14.9. MS (ESI) *m/z* 282 (M+H), 304 (M+Na); HRMS (EI) *m/z* calc'd for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1488; found 282.1488.



***N*-(4-Methylbiphenyl-2-yl)pivalamide (2v):** Prepared from **1o** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 30 h (99%). Yellow solid. All spectral data are in agreement with reported literature data.[14] ^{1}H NMR (400 MHz) δ 8.24 (s, 1H), 7.48 (t, 3H, J = 7.3Hz), 7.40 (t, J = 7.4Hz, 1H), 7.35 (d, J = 6.8Hz, 2H), 7.14 (d, J = 7.7Hz, 1H), 6.98 (dd, J = 0.9Hz, J = 7.7Hz, 1H), 2.40 (s, 3H), 1.10 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4, 138.6, 138.2, 135.0, 129.6, 129.5, 129.1, 128.0, 124.8, 121.5, 39.9, 27.5, 21.6.

Competition experiment:

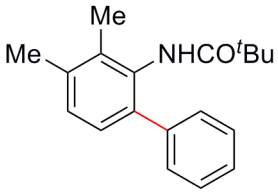




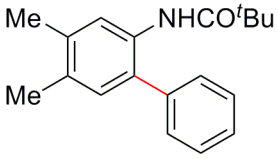
Using 0.5 mL benzene and 0.5 mL benzene-d_6, **2v** and its isotopomer **2v-*d*$_5$** was isolated in 78% with a ratio of 3.2:1 after 43.5 h. Yellow solid; m.p. 70-72 °C. ^{1}H NMR (400 MHz) δ 8.24 (s, 1H), 7.48 (t, J = 7.3Hz, 3H), 7.40 (t, J = 7.4Hz, 1.7H), 7.35 (d, J = 6.8Hz, 1H), 7.14 (d, J = 7.7Hz, 1H), 6.98 (dd, J = 0.9Hz, J = 7.7Hz, 1H), 2.40 (s, 3H), 1.10 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.4, 138.6, 138.2, 135.0, 129.6, 129.5, 129.1, 128.0, 124.8, 121.5, 39.9, 27.5, 21.6. HRMS (ESI) *m/z* calc'd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1695; found: 268.1698; calc'd for $C_{18}H_{17}D_5NO$ $[M+H]^+$: 273.2009; found: 273.2010.

Stoichiometric experiment:

Prepared from **3a** according to general procedure E in 16 h (91%).

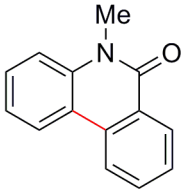


***N*-(3,4-dimethylbiphenyl-2-yl)pivalamide (2w):** Prepared from **1p** according to general procedure A with 10 mol% $Pd(OAc)_2$ at 70 ºC in 36 h (82%). White solid. All spectral data are in agreement with reported literature data.[14] ^{1}H NMR (400 MHz) δ 7.37 (dd, J = 7.3Hz, J = 14.6Hz, 2H), 7.27 (dd, J = 2.1Hz, J = 7.1Hz, 2H), 7.11 (AB quartet, J = 7.7Hz, J = 31.6Hz, 2H), 6.85 (s, NH, 1H), 2.34 (s, 3H), 2.14 (s, 3H), 1.11 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 176.9, 140.1, 137.4, 137.2, 135.1, 132.8, 129.1, 128.6, 128.3, 127.3, 127.0, 39.2, 27.6, 20.62, 14.9.

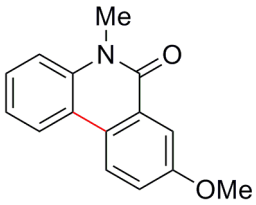


***N*-(4,5-Dimethylbiphenyl-2-yl)pivalamide (2x):** Prepared from **1q** according to general procedure C with 10 mol% $Pd(OAc)_2$ at 70 ºC in 62 h (94%). Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.21 (m, 3H), 7.19-7.17 (m, 2H), 7.06 (d, J = 7.7 Hz, 1H), 6.98 (d, J = 7.7 Hz, 1H), 6.76 (s, 1H), 2.25 (s, 3H), 2.05 (s, 3H), 1.02 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz,

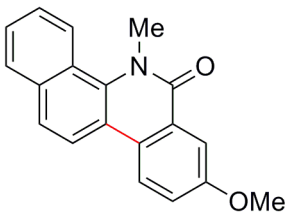
$CDCl_3$) δ 176.8, 140.1, 137.3, 137.1, 135.0, 132.7, 129.1, 128.5, 128.2, 127.2, 126.9, 39.1, 27.5, 20.5, 14.8. MS (EI) *m/z* 281 (M); (ESI) *m/z* 282 (M+H), 304 (M+Na); HRMS (EI) *m/z* calc'd for $C_{19}H_{23}NO$ $[M]^+$: 281.1780; found: 281.1784; (ESI) *m/z* calc'd for $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852; found: 282.1858.

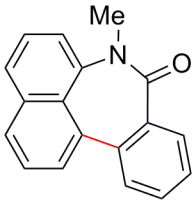


5-Methylphenanthridin-6(5H)-one (2y): Prepared from **1t** according to general procedure D in 96 h (60%). Off-white solid; m.p. 95-98 ºC. All spectral data are in agreement with reported literature data.[26, 52] ^1H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 7.8 Hz, 1H), 8.30-8.28 (m, 2H), 7.76, (t, J = 7.3 Hz, 1H), 7.61-7.54 (m, 2H), 7.43 (d, J = 8.2 Hz, 1H), 7.33 (t, J = 7.3 Hz, 1H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.1, 133.6, 132.4, 129.6, 128.9, 128.0, 125.6, 123.2, 122.5, 121.6, 119.3, 115.1, 30.00. MS (EI) *m/z* 209 (M); HRMS (EI) *m/z* calc'd for $C_{14}H_{11}NO$ $[M]^+$: 209.0841; found: 209.0844.

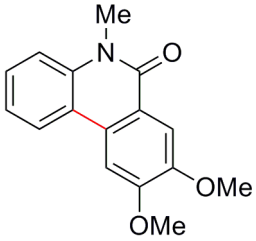


8-Methoxy-5-methylphenanthridin-6(5H)-one (2z): Prepared from **1u** according to general procedure D in 48 h (77%). Off-white solid; m.p. 135-137 ºC. All spectral data are in agreement with reported literature data.[42, 58] ^1H NMR (400 MHz, $CDCl_3$) δ 8.16-8.13 (m, 2H), 7.94 (d, 1H, J = 2.8 Hz), 7.47 (ddd, 1H, J = 1.4 Hz, J = 7.3 Hz, J = 8.4 Hz), 7.37 (d, 1H, J = 7.9 Hz), 7.33-7.26 (m, 2H), 3.95 (s, 3H), 3.80 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 159.5, 137.0, 128.4, 127.1, 126.8, 123.4, 122.6, 122.5, 122.2, 119.4, 114.9, 109.2, 55.7, 30.1. MS (EI) *m/z* 239 (M); HRMS (EI) *m/z* calc'd for $C_{15}H_{13}NO_2$ $[M]^+$: 239.0946; found: 239.0942.



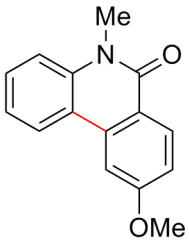


8-Methoxy-5-methylbenzo[c]phenanthridin-6(5H)-one/7-methylbenzo[e]naphtho[1,8-bc] azepin-8(7H)-one (2aa): Prepared from **1v** according to general procedure D in 15 h (63%). Orange solid; m.p. 111-115 ºC. This compound was isolated as an inseparable mixture of two isomers in a 2.4:1 ratio (*phenanthridin-6(5H)-one:azepin-8(7H)-one*). The characterization of the major isomer is as follows: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.30 (m, 1H), 8.20 (d, J = 9.0 Hz, 1H), 8.16 (d, J = 8.8 Hz, 1H), 7.97 (d, J = 2.8 Hz, 1H), 7.90-7.87 (m, 1H, overlap), 7.71 (d, J = 8.6 Hz, 1H), 7.52-7.49 (m, 2H, overlaps with minor isomer), 7.38-7.36 (m, 1H, overlaps with minor isomer), 4.06 (s, 3H), 3.98 (s, 3H). Minor isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.6 Hz, 1H), 8.59 (d, J = 9.0 Hz, 1H), 8.05 (d, J = 2.9 Hz, 1H), 7.90-7.87 (m, 1H, overlaps with major isomer), 7.62-7.59 (m, 2H), 7.52-7.49 (m, 2H, overlaps with major isomer), 7.38-7.36 (m, 1H, overlaps with major isomer), 4.00 (s, 3H), 3.92 (s, 3H). Assignment of the ^{13}C NMR could not be accomplished: ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 161.5, 159.6, 158.8, 135.2, 134.9, 134.3, 130.4, 129.6, 129.2, 128.8, 128.6, 128.5, 128.1, 127.5, 127.0, 126.7, 126.1, 125.3, 125.0, 124.7, 124.1, 123.9, 122.6, 121.2, 119.8, 117.3, 114.9, 114.2, 109.1, 108.7, 55.7, 55.7, 41.2, 30.8. MS (EI) *m/z* 289 (M); HRMS (EI) *m/z* calc'd for $C_{19}H_{15}NO_2$ $[M]^+$: 289.1103; found: 289.1110.

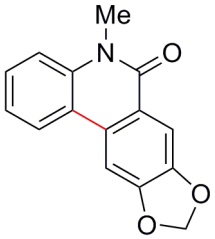


8,9-Dimethoxy-5-methylphenanthridin-6(5H)-one (2ab): Prepared from **1w** according to general procedure D in 42 h (60%). Off-white solid; m.p. 219-220 ºC. All spectral data are in agreement with reported literature data.[40] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 1.2 Hz, J = 8.1 Hz, 1H), 7.88 (s, 1H), 7.53 (s, 1H), 7.51-7.47 (m, 1H), 7.38-7.36 (m, 1H), 7.31-7.26

(m, 1H), 4.07 (m, 3H), 4.02 (m, 3H), 3.79 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 153.4, 150.0, 137.7, 128.8, 128.4, 122.8, 122.4, 119.8, 119.3, 115.2, 109.2, 102.7, 56.4, 56.3, 30.1. MS (EI) *m/z* 269 (M); HRMS (EI) *m/z* calc'd for $C_{16}H_{15}NO_3$ $[M]^+$: 269.1052; found: 269.1057.



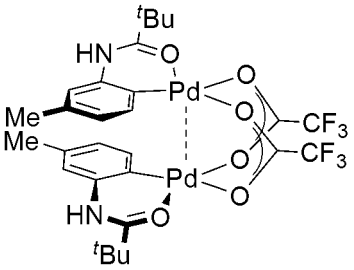
9-Methoxy-5-methylphenanthridin-6(5H)-one (2ac): Prepared from **1x** according to general procedure D in 96 h (33%). Starting material **1x** was isolated in 66% yield. Pale yellow solid; m.p. 135-137 ºC. All spectral data are in agreement with reported literature data.[39] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 8.9 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 2.2 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 7.42 (d, J = 8.4 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.16 (dd, J = 2.2 Hz, J = 8.9 Hz, 1H), 4.00 (s, 3H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 161.5, 138.6, 135.5, 131.1, 129.7, 123.3, 122.2, 119.4, 119.2, 115.9, 115.1, 104.5, 55.6, 29.7. MS (ESI) *m/z* 240 (M+H), 262 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{15}H_{14}NO_2$ $[M+H]^+$: 240.1019; found: 240.1019.



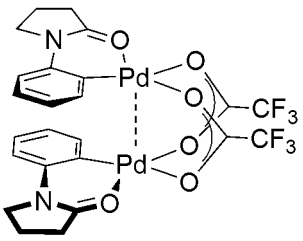
5-Methyl-[1,3]dioxolo[4,5-j]phenanthridin-6(5H)-one (2ad): Prepared from **1y** according to general procedure D in 96 h (30%). Pale yellow solid; m.p. 239-241 ºC. All spectral data are in agreement with reported literature data.[43-47] ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (dd, J = 1.3Hz, J = 8.1Hz, 1H), 7.91 (s, 1H), 7.61 (s, 1H), 7.51 (ddd, J = 1.4Hz, J = 7.2Hz, J = 8.5Hz, 1H), 7.40 (d, J = 7.8Hz, 1H), 7.32-7.28 (m, 1H), 6.12 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 152.2, 148.4, 137.5, 130.4, 128.9, 122.9, 122.4, 121.4, 119.3, 115.0,

107.1, 102.0, 100.4, 30.0. MS (ESI) *m/z* 254 (M+H), 276 (M+Na); HRMS (ESI) *m/z* calc'd for $C_{15}H_{11}NO_3$ $[M+H]^+$: 254.0811; found: 254.0799.

Palladium complexes



Bimetallic palladium complex (3a): In a one-dram vial was added *N*-(*m*-tolyl)pivalamide (**1o**) (19.1 mg, 0.1 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), and dichloromethane (1 mL). Trifluoroacetic acid (7.7 μL, 0.105 mmol) was subsequently added into the vial and the resulting solution was heated to 40 °C for 3 h. After cooling to ambient temperature, the reaction mixture was concentrated *in vacuo* and the resulting residue was suspended in a mixture of hexanes and $CHCl_3$ (hexanes:$CHCl_3$ = 9:1, v/v, 2 mL). The suspension was filtered through Celite and washed with 4 x 0.3 mL hexanes. The residue was washed with dichloromethane and the wash solution was subsequently collected and concentrated *in vacuo* to afford the bimetallic palladacycle **3a** as a yellow solid (36.6 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.03 (d, J = 8.1Hz, 1H), 6.72 (d, J = 8.0Hz, 1H), 6.33 (s, 1H), 2.24 (s, 3H), 0.89 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.1, 135.3, 134.0, 130.1, 125.1, 115.8, 112.0, 38.9, 27.2, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) –73.6. MS (ESI) *m/z* 296 ($C_{12}H_{16}NOPd$, i.e., monomer–TFA); HRMS (ESI) *m/z* calc'd for $C_{12}H_{16}NOPd$: 296.0261; found: 296.0255. Recrystallization from dichloromethane and hexanes gave a single crystal suitable for X-ray analysis.



Bimetallic palladium complex (3b): In a one-dram vial was added 1-phenylpyrrolidin-2-one (**1g**) (16.1 mg, 0.1 mmol), $Pd(OAc)_2$ (22.4 mg, 0.1 mmol), and dichloromethane (1 mL). Trifluoroacetic acid (7.7 μL, 0.105 mmol) was subsequently added into the vial and the resulting solution was heated to 40 °C for 3 h. After cooling to ambient temperature, the reaction mixture was concentrated *in vacuo* and the resulting residue was suspended in a mixture of hexanes and $CHCl_3$ (hexanes:$CHCl_3$ = 1:1, v/v, 2 mL). The suspension was filtered through Celite and washed with 4 x 0.3 mL hexanes followed by 1 x 0.3 mL $CHCl_3$. The residue was washed with dichloromethane and the wash solution was subsequently collected and concentrated *in vacuo* to afford the bimetallic palladacycle **3b** as a yellow solid (33.2 mg, 87%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.18 (t, J = 7.5Hz, 1H), 7.12 (d, J = 8.0Hz, 1H), 6.95 (t, J = 7.5Hz, 1H), 6.67 (d, J = 7.9Hz, 1H), 3.96 (br s, 1H), 3.59 (br s, 1H), 2.44 (br s, 1H), 1.98 (br s, 1H), 1.83 (br s, 1H), 1.62 (br s, 1H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ 172.2, 134.6, 132.3, 126.1, 124.2, 120.3, 114.2, 51.1, 31.9, 18.2. ^{19}F NMR (376 MHz, CD_2Cl_2) δ –74.0. MS (ESI) *m/z* 266 ($C_{10}H_{10}NOPd$, i.e., monomer–TFA); HRMS (ESI) *m/z* calc'd for $C_{10}H_{10}NOPd$: 296.9791; found: 265.9783. Recrystallization from dichloromethane and hexanes gave a single crystal suitable for X-ray analysis.

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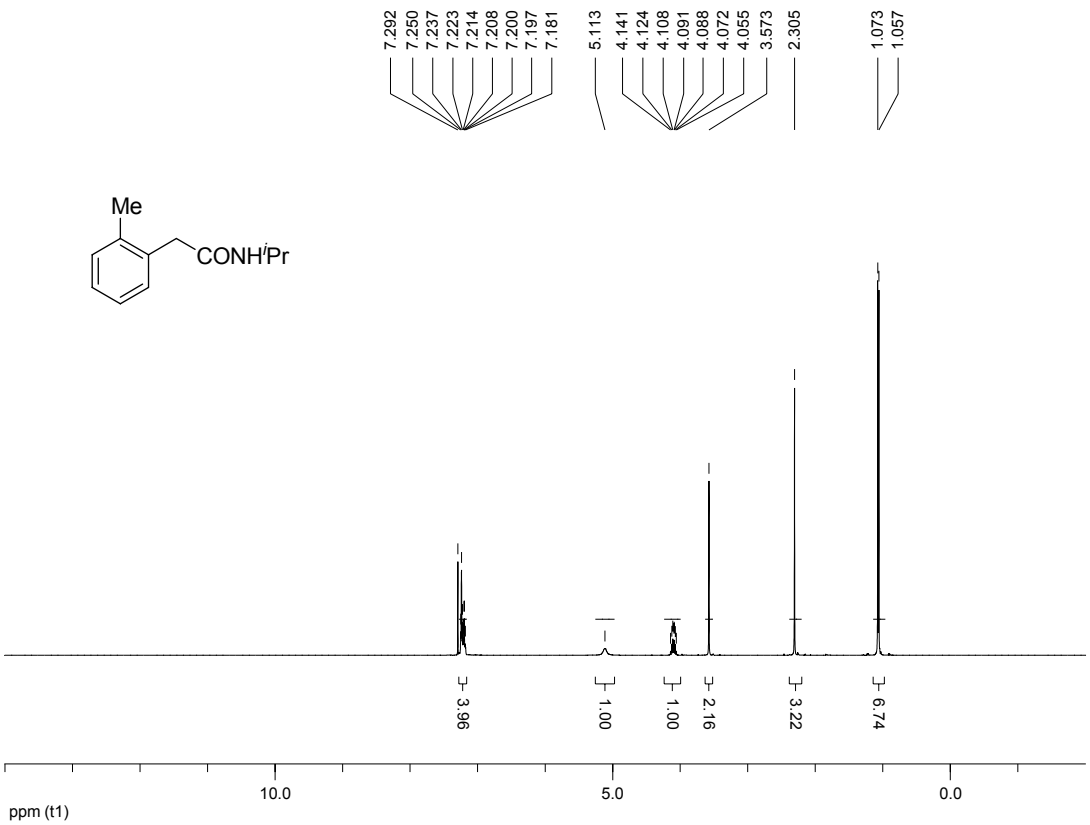
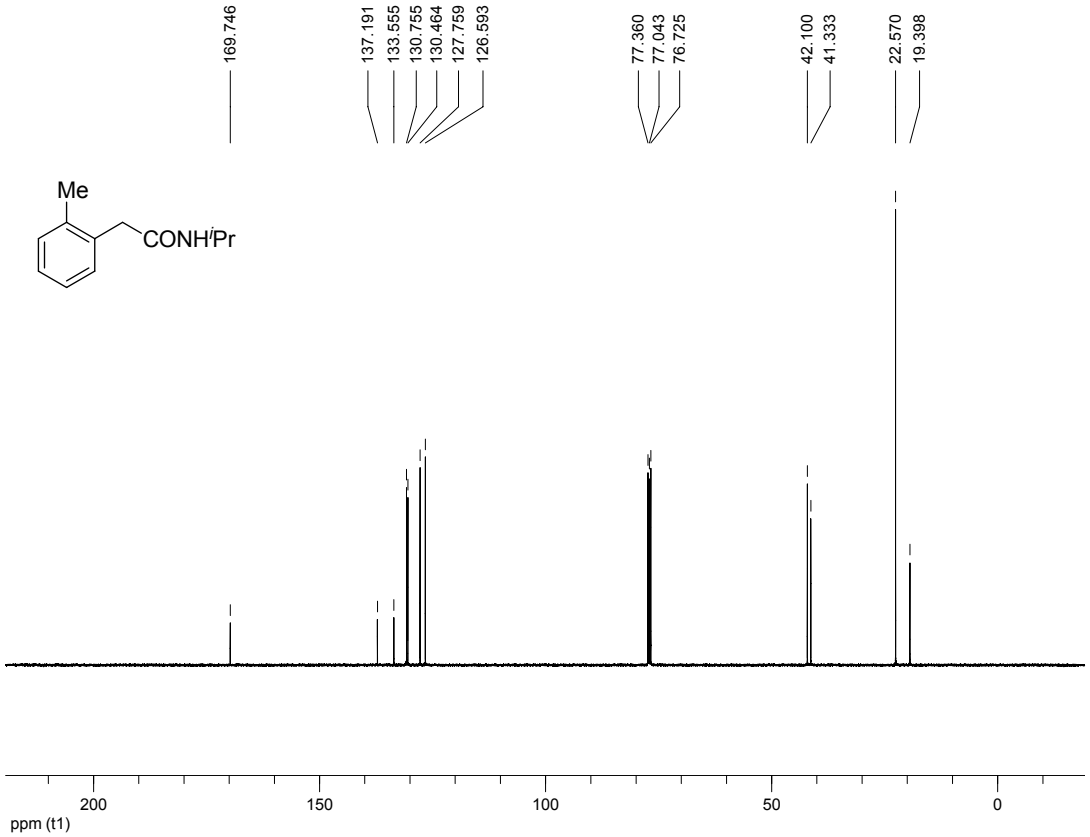
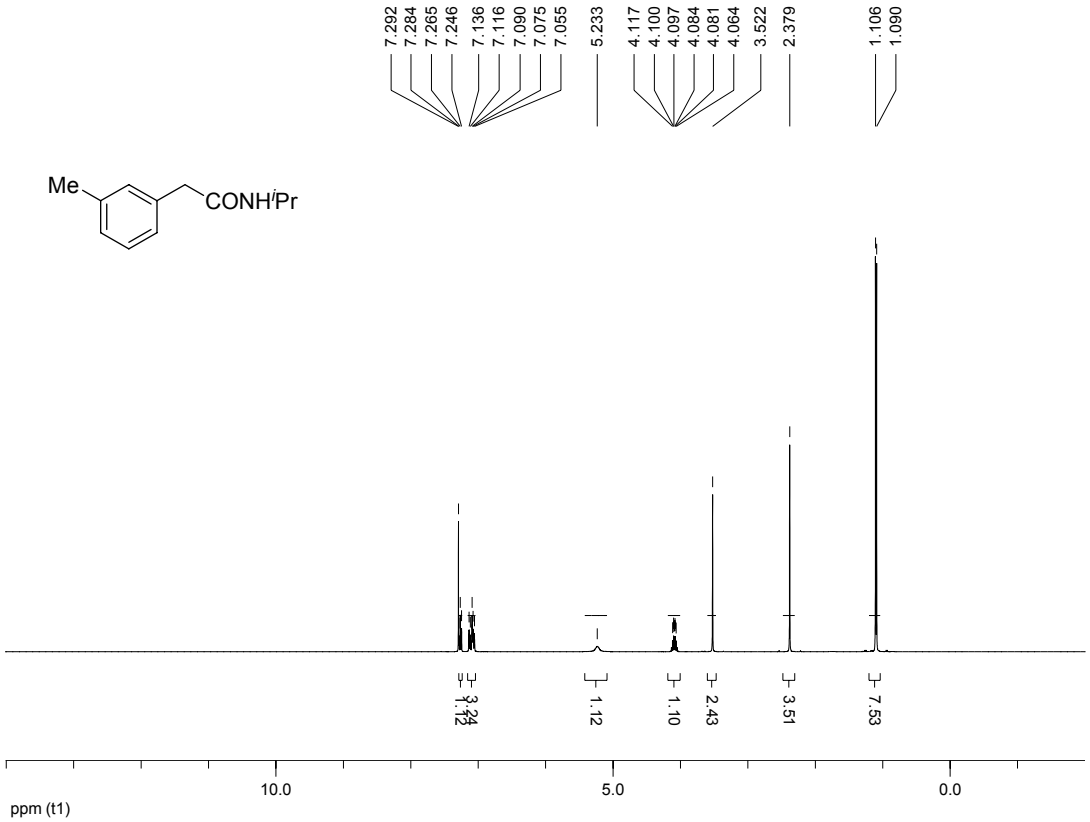
5. NMR Spectra for New Compounds

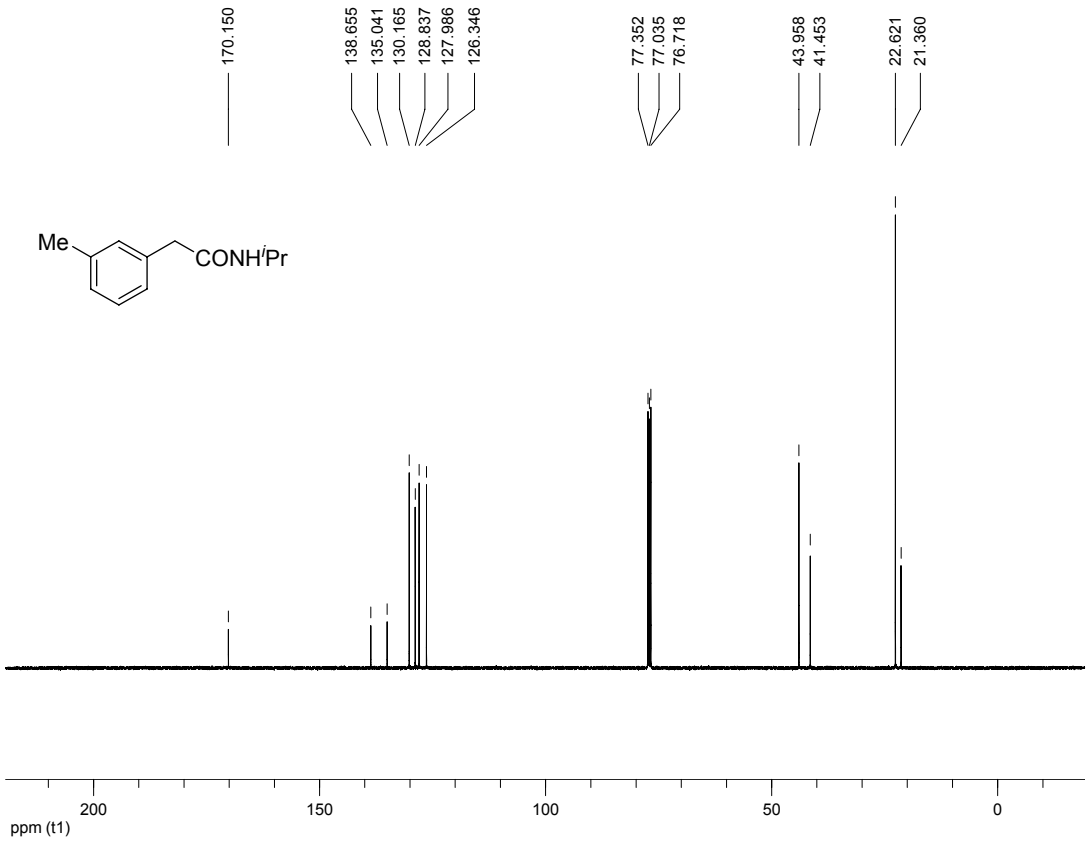
NMR spectra of compound **1a**



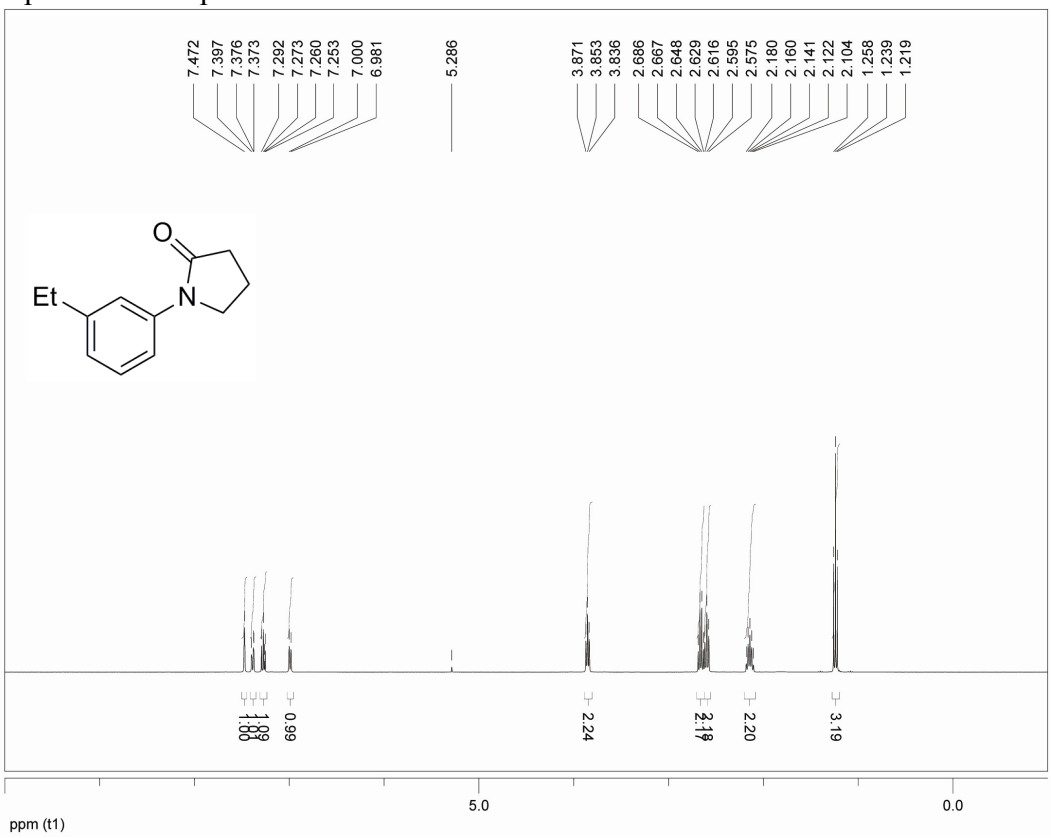


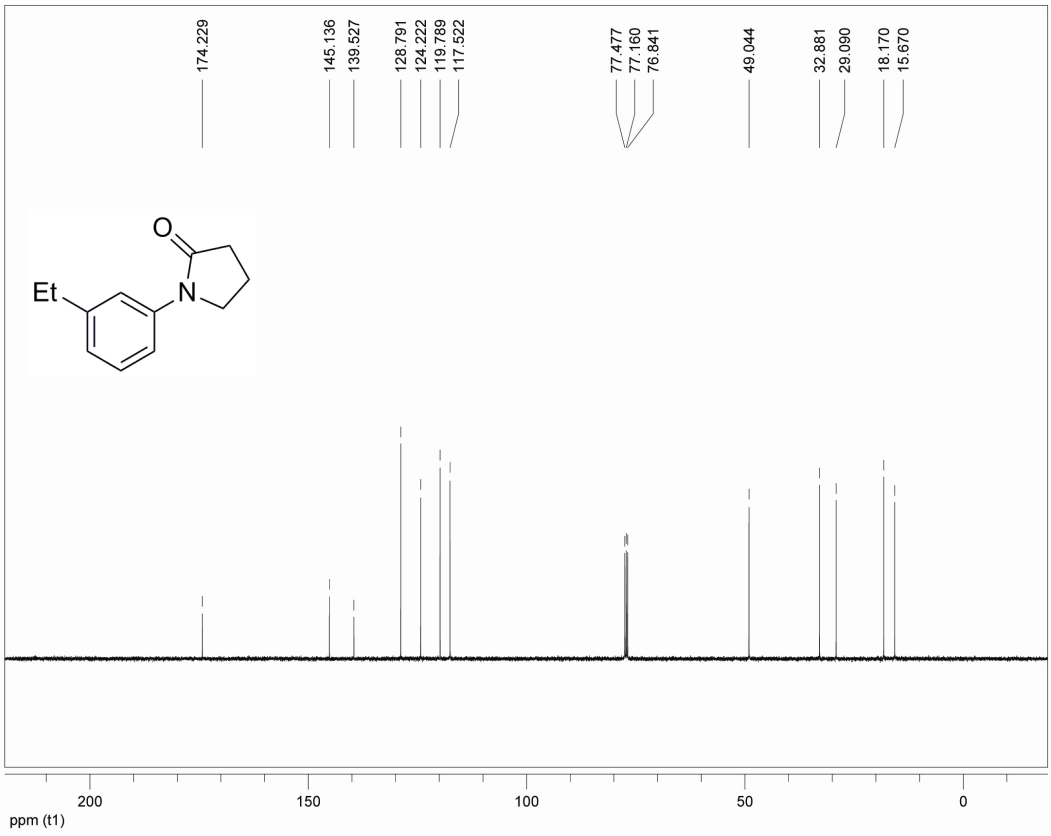
NMR spectra of compound **1b**



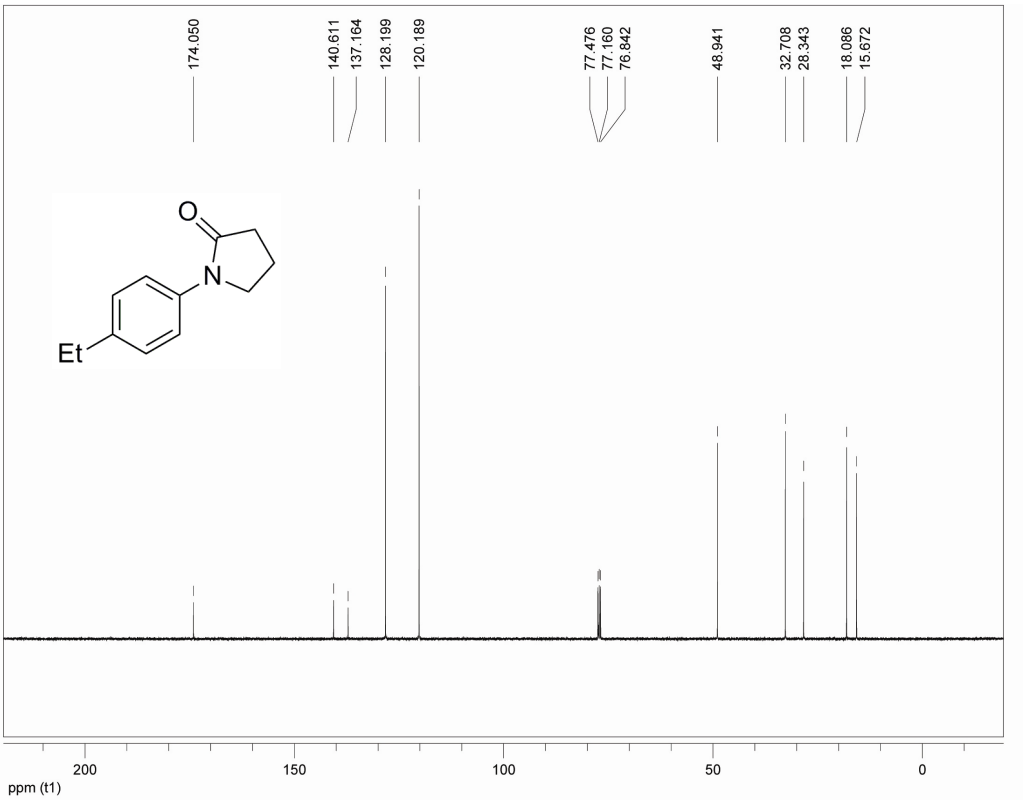


NMR spectra of compound **1i**

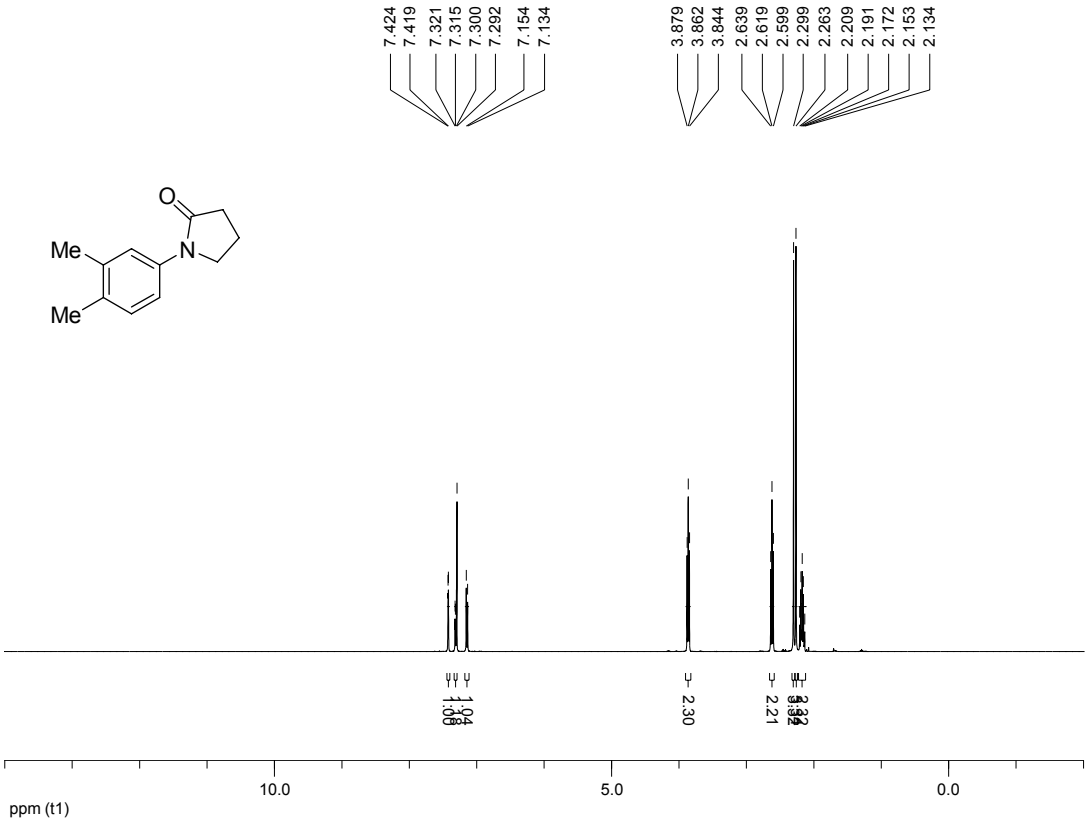


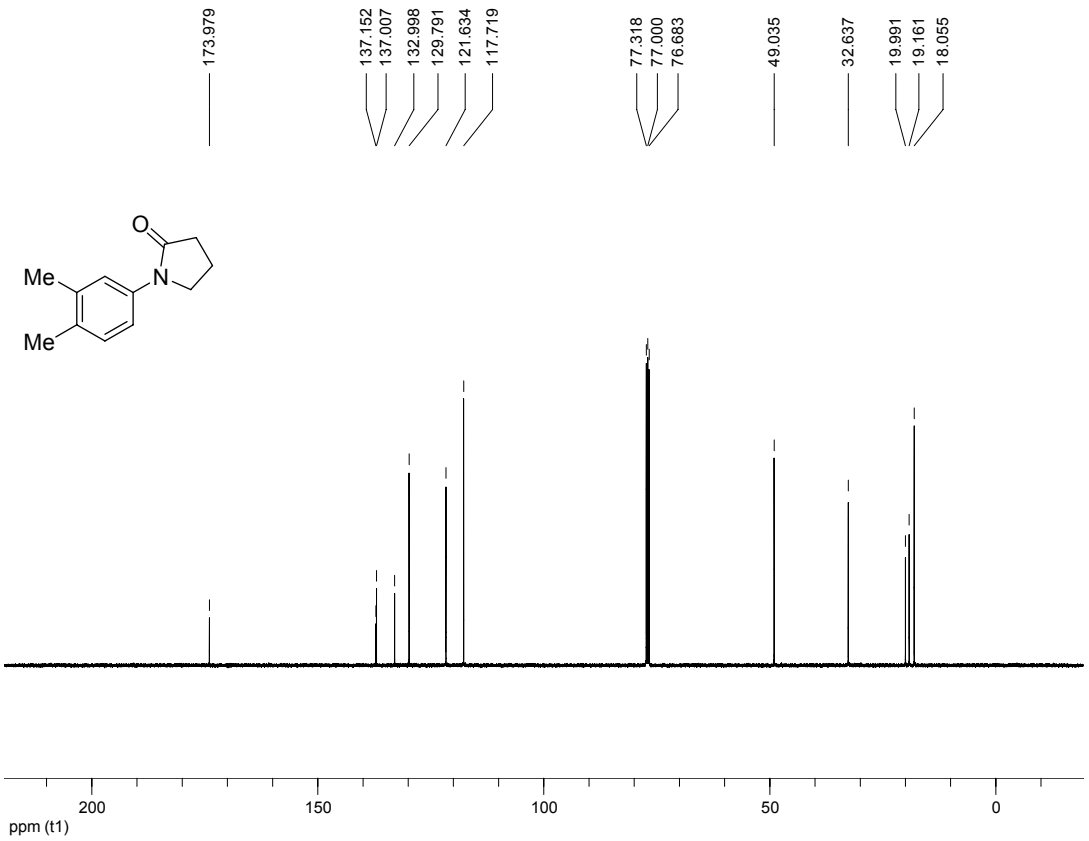


NMR spectra of compound **1k**

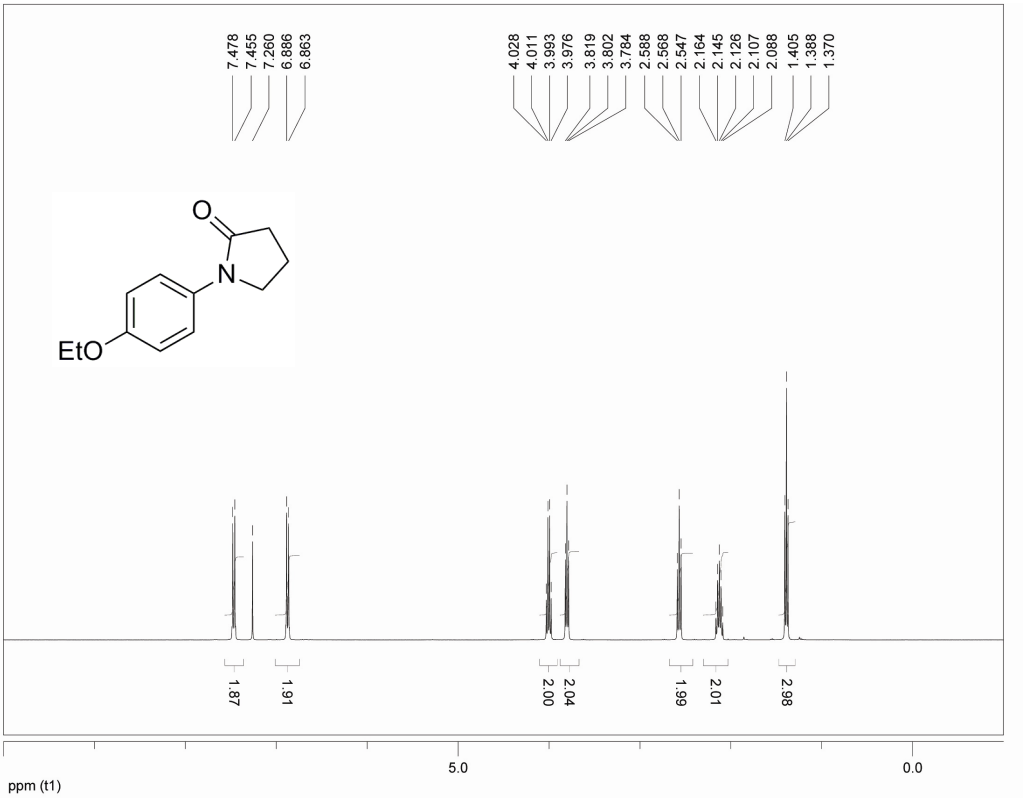


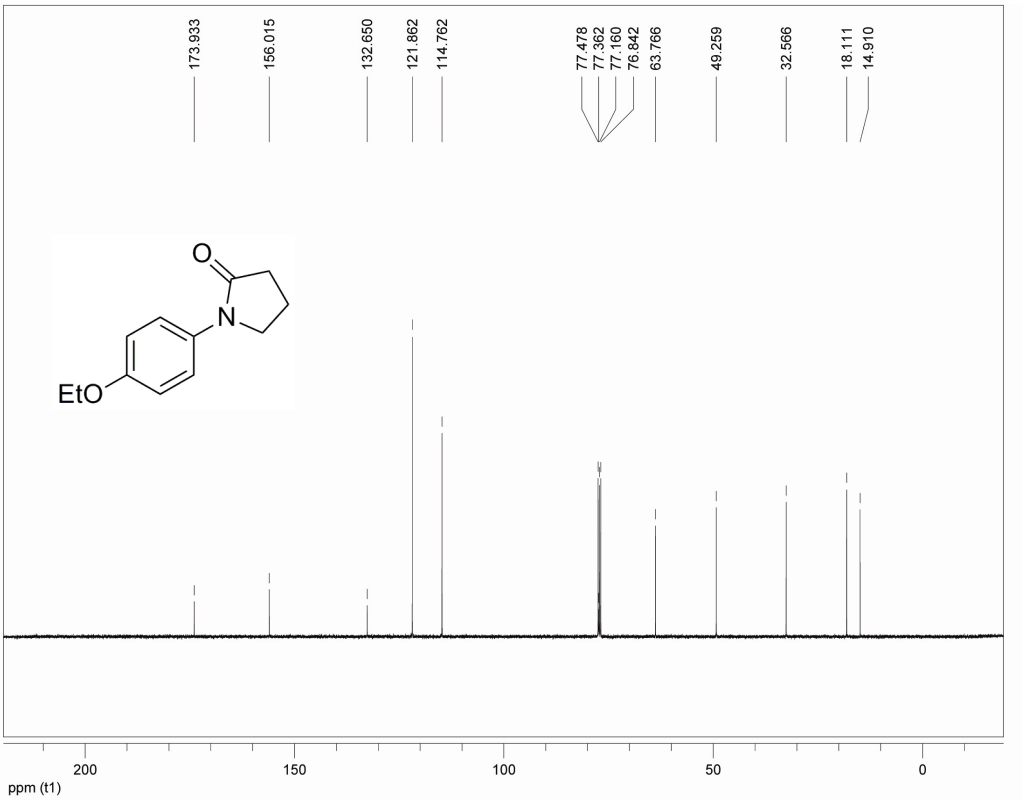
NMR spectra of compound **1l**



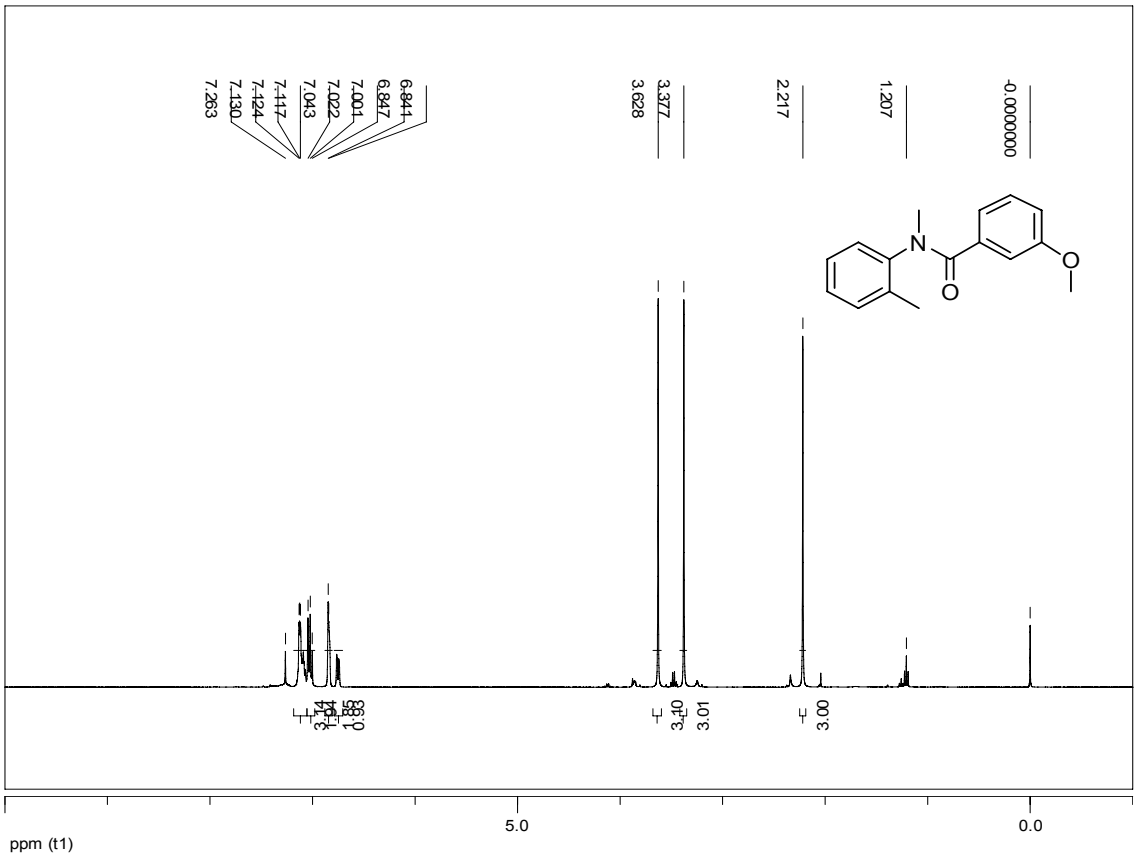


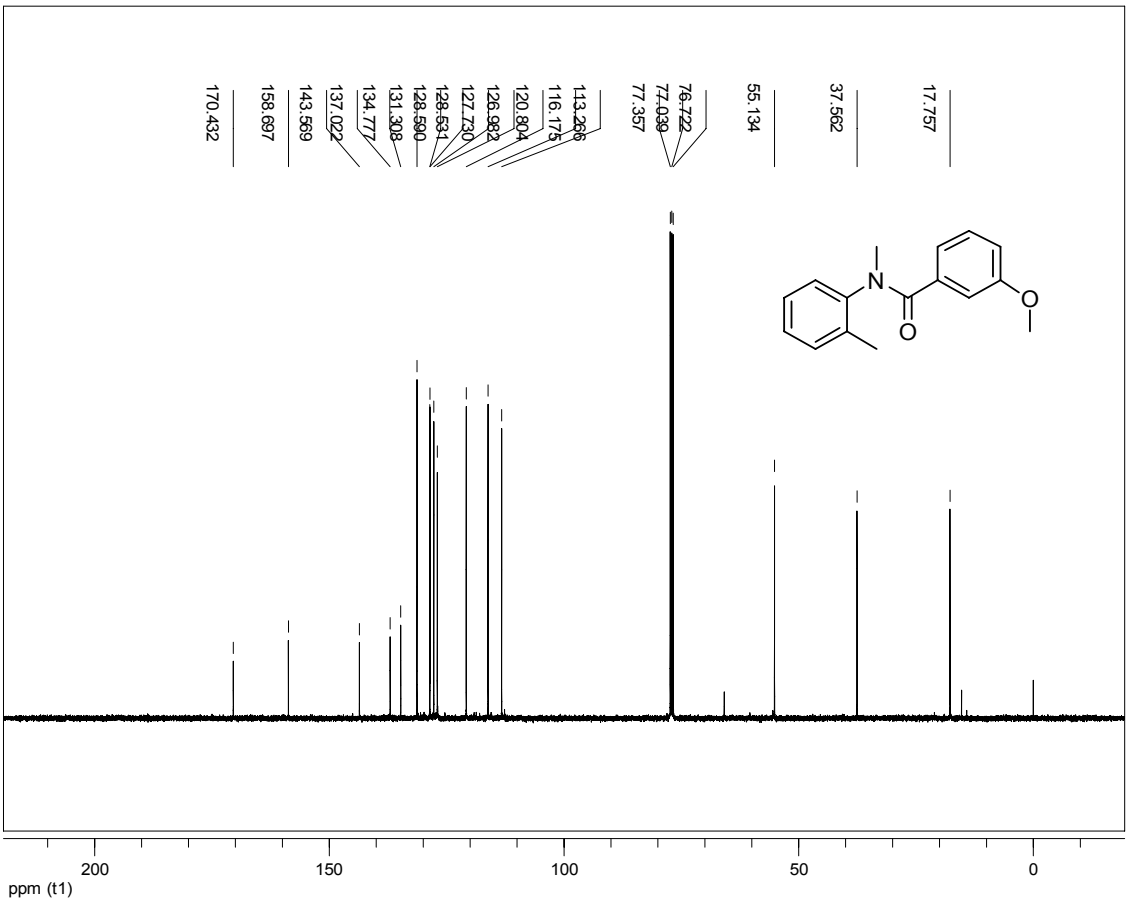
NMR spectra of compound **1n**



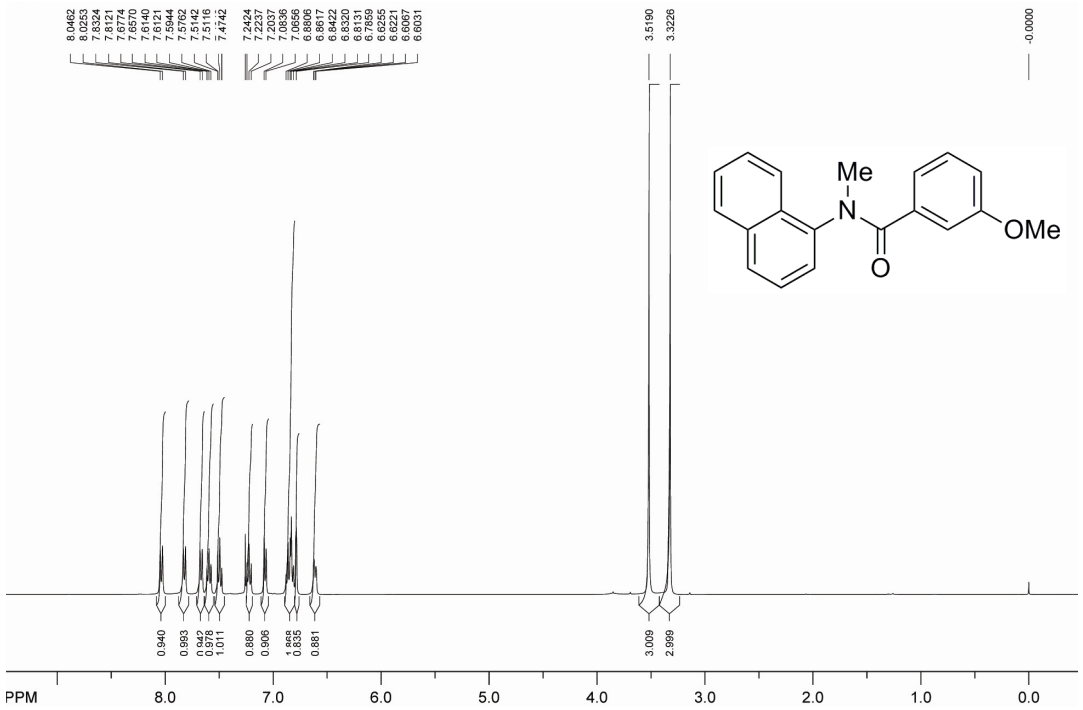


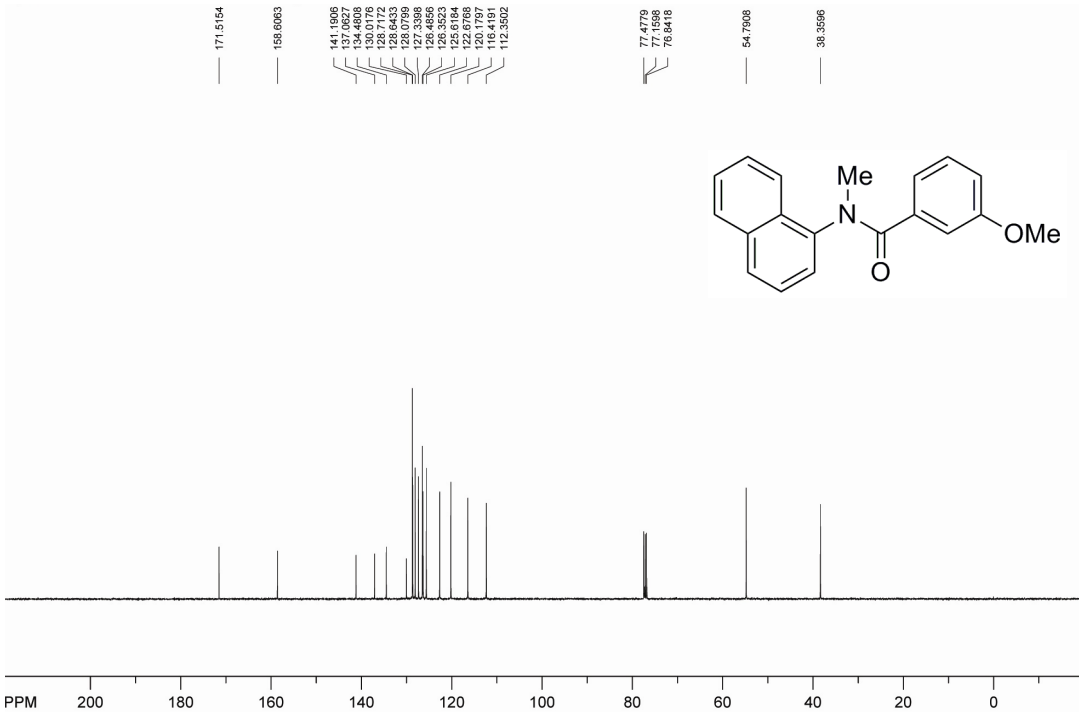
NMR spectra of compound **1y**



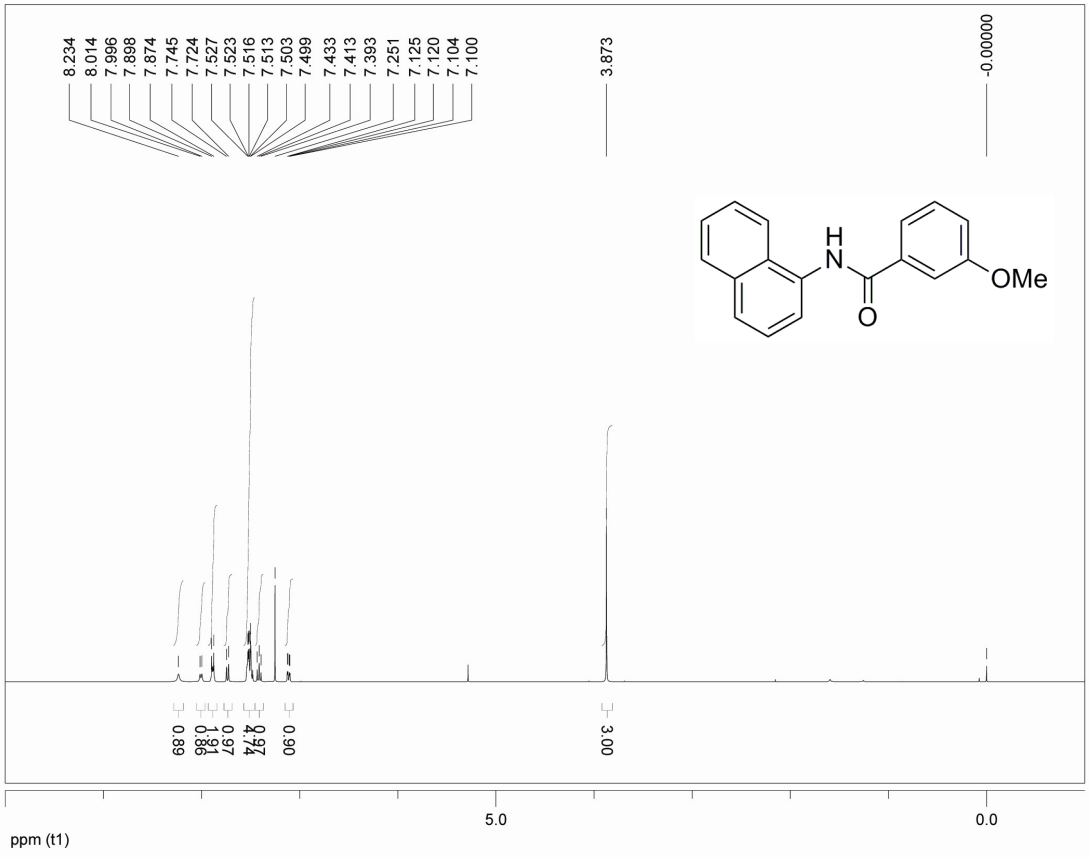


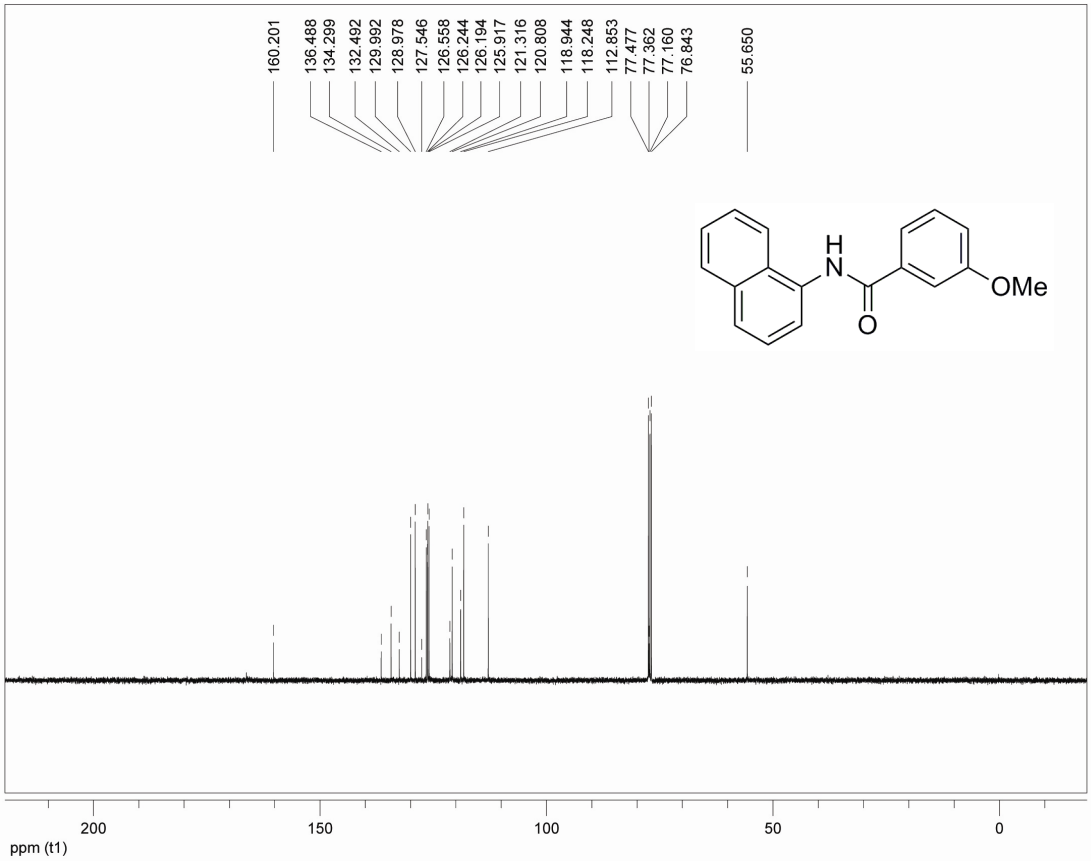
NMR spectra of compound **1z**



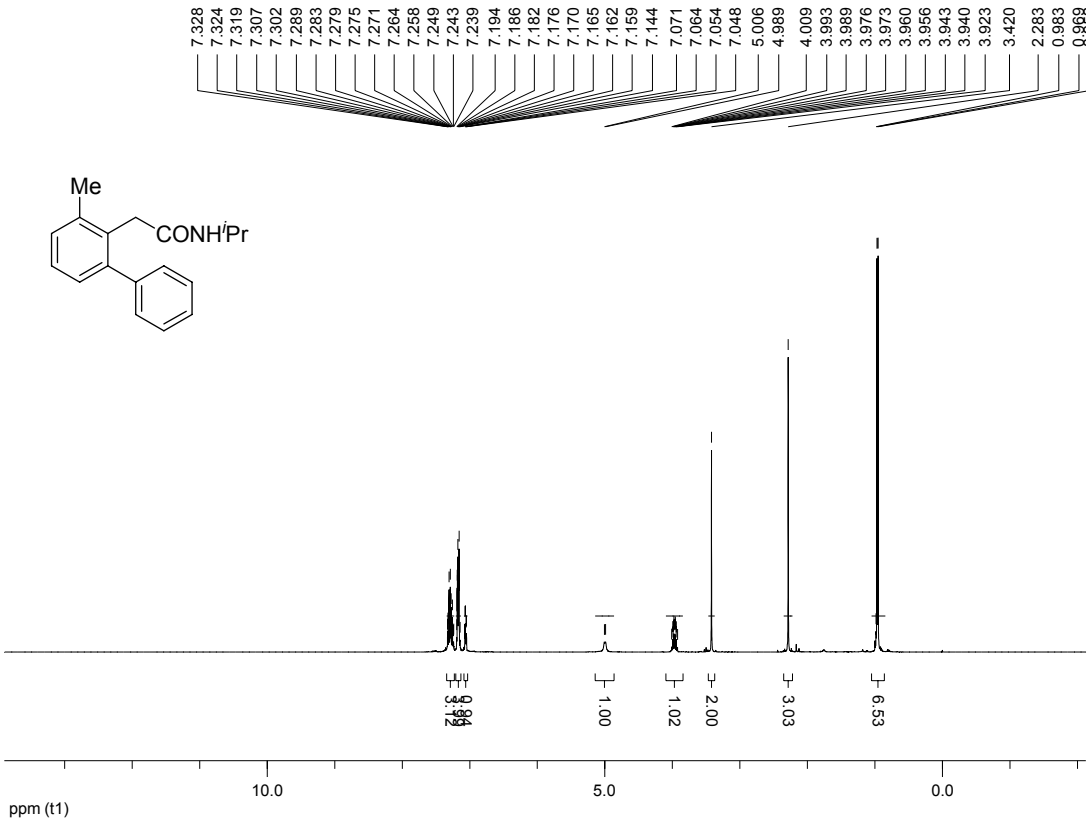


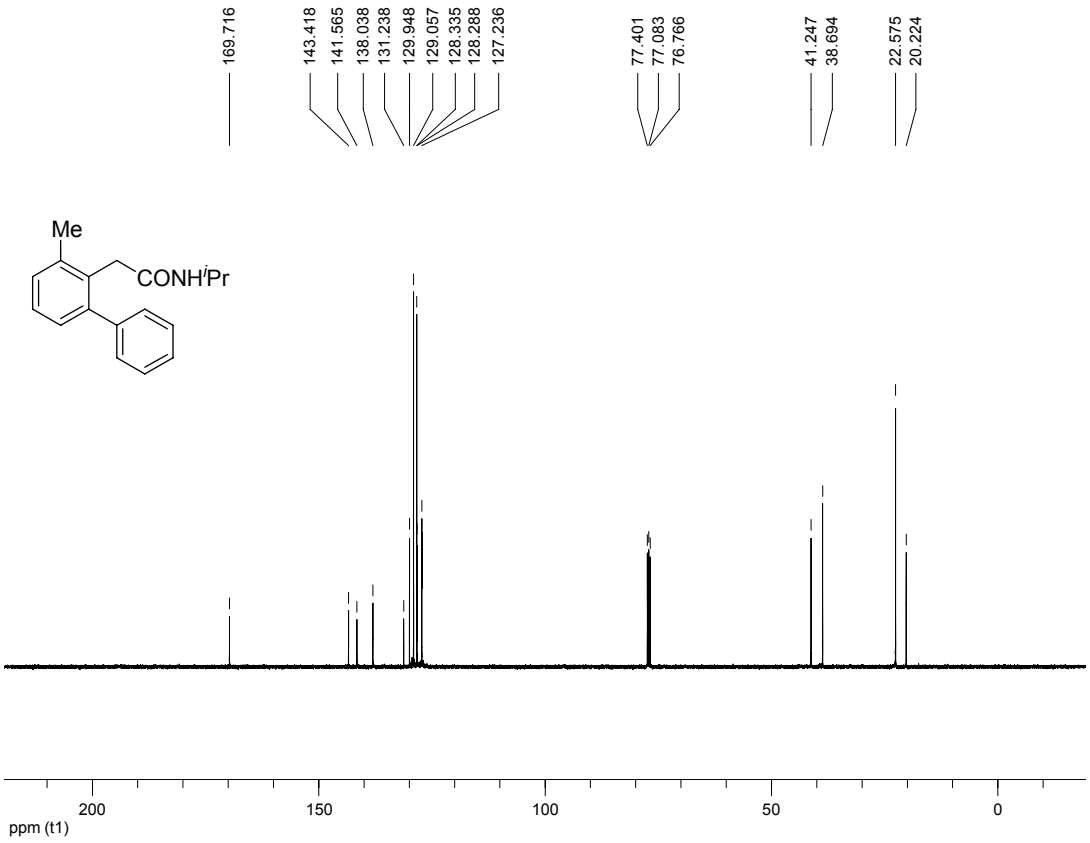
NMR spectra of compound **1aa**



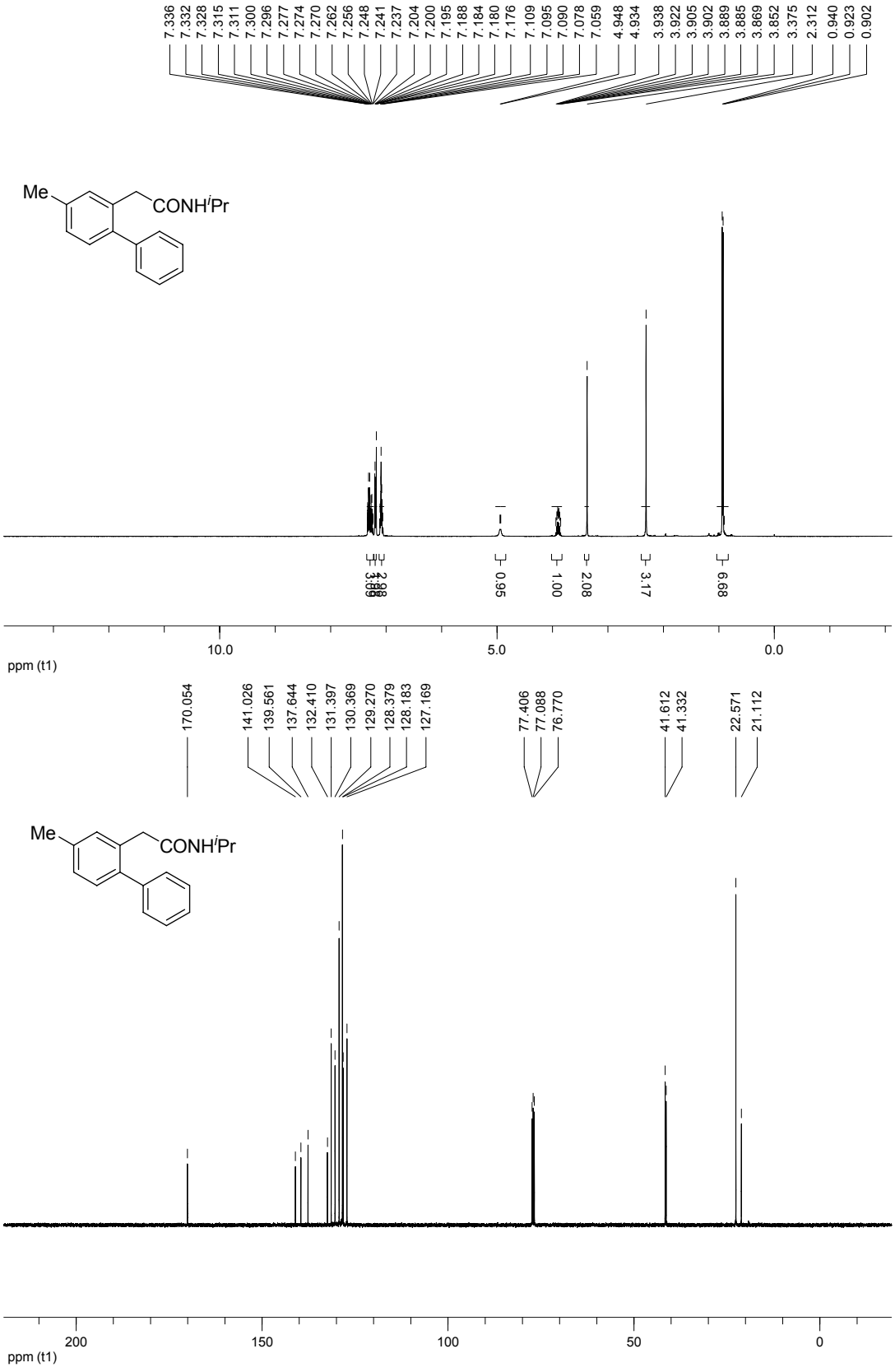


NMR spectra of compound **2a**

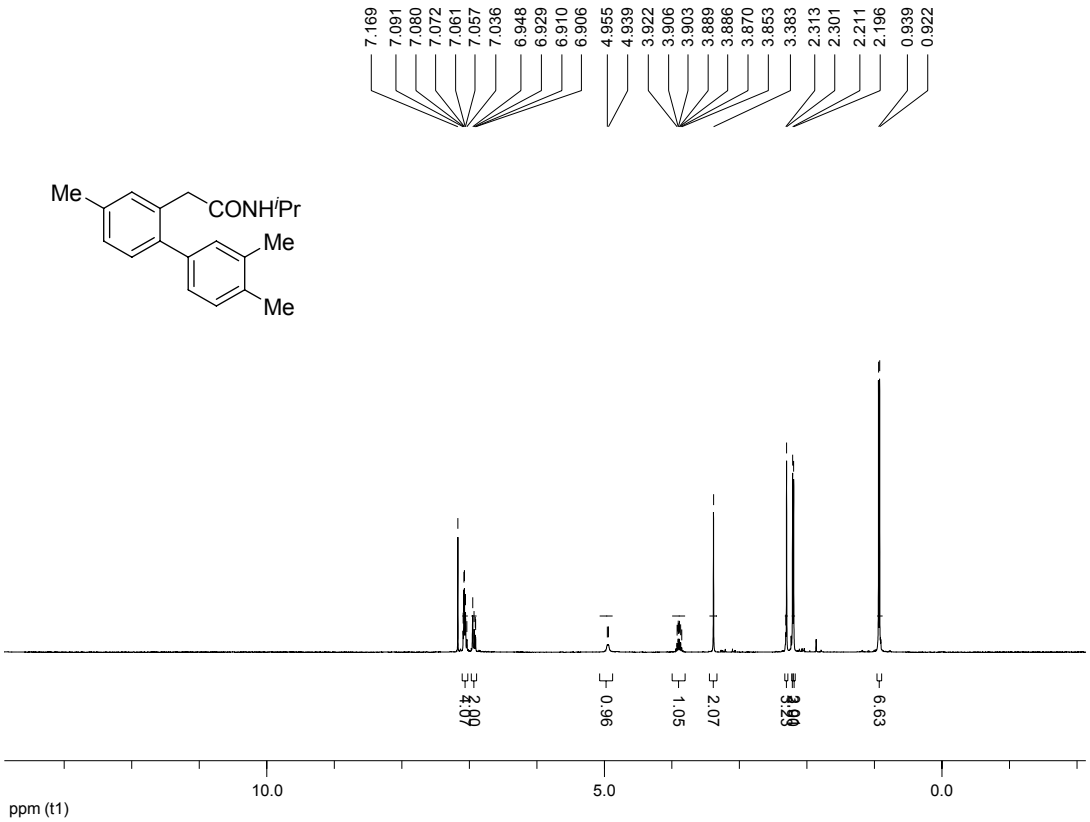


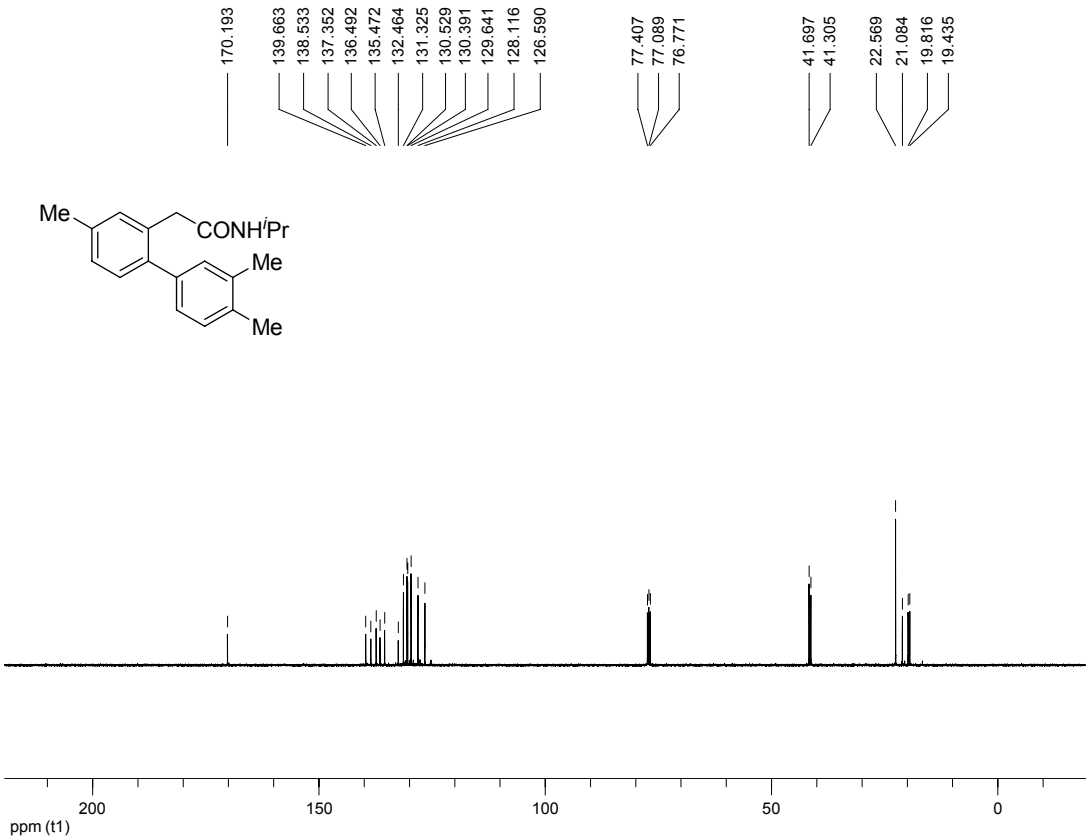


NMR spectra of compound **2b**

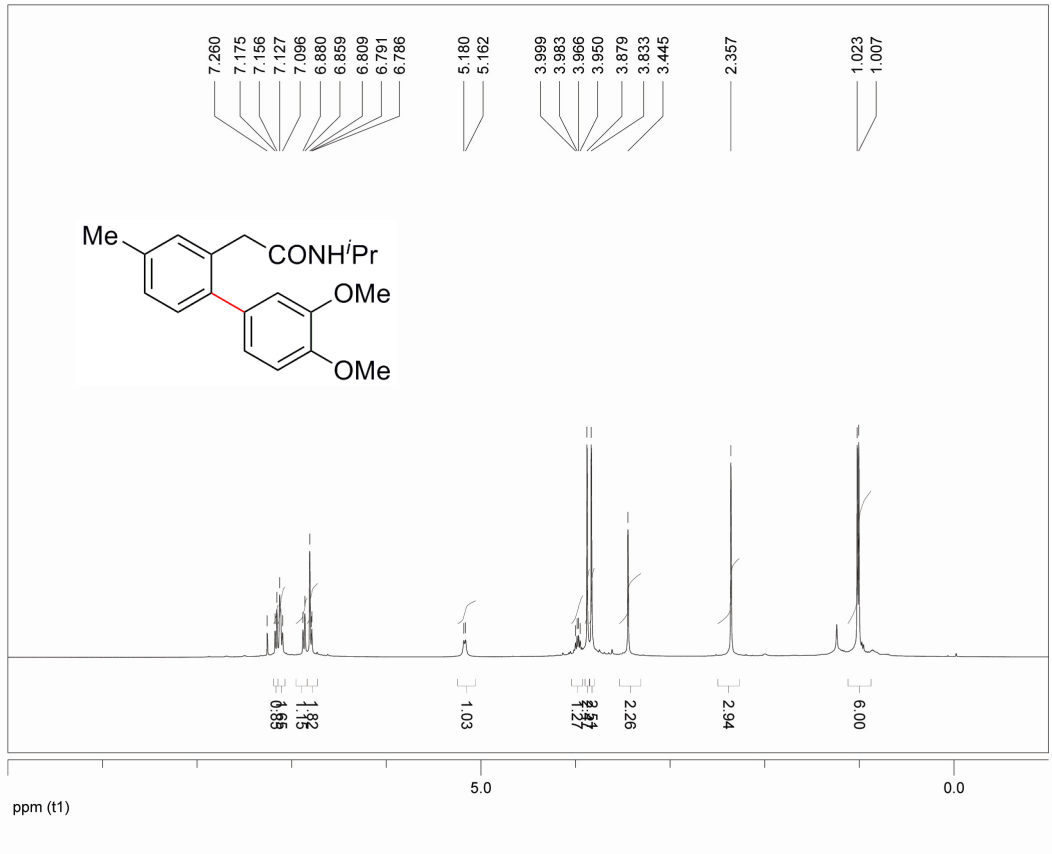


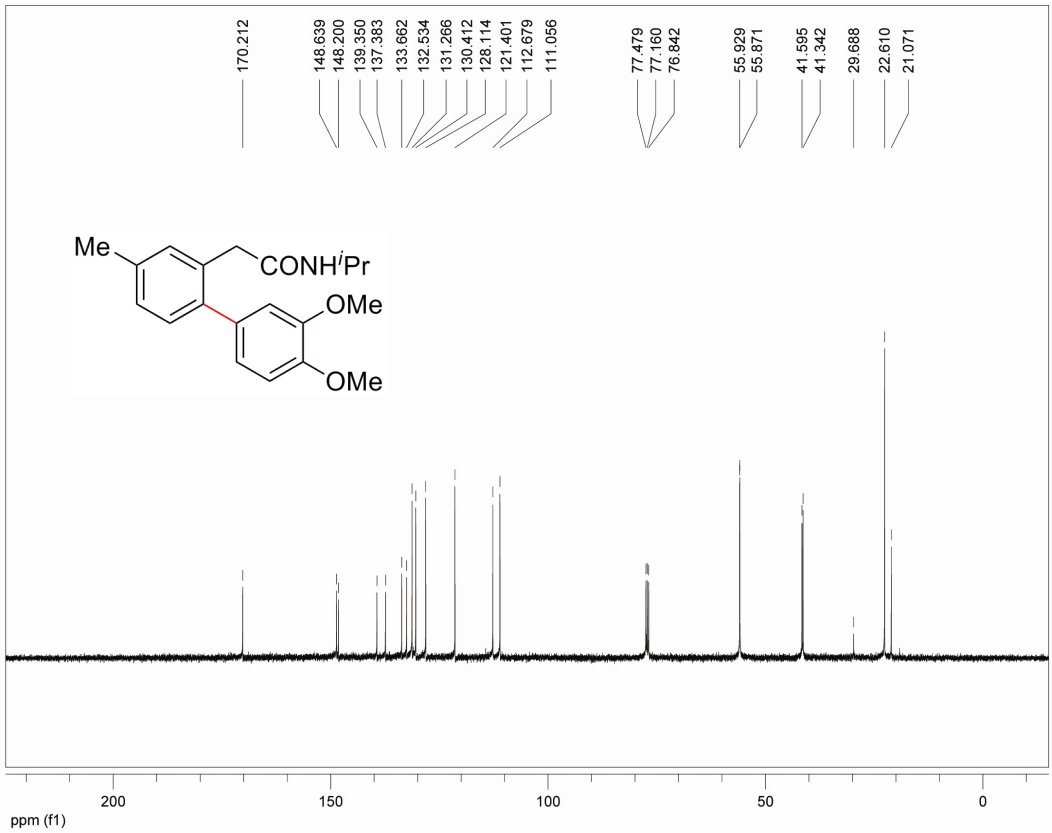
NMR spectra of compound **2c**



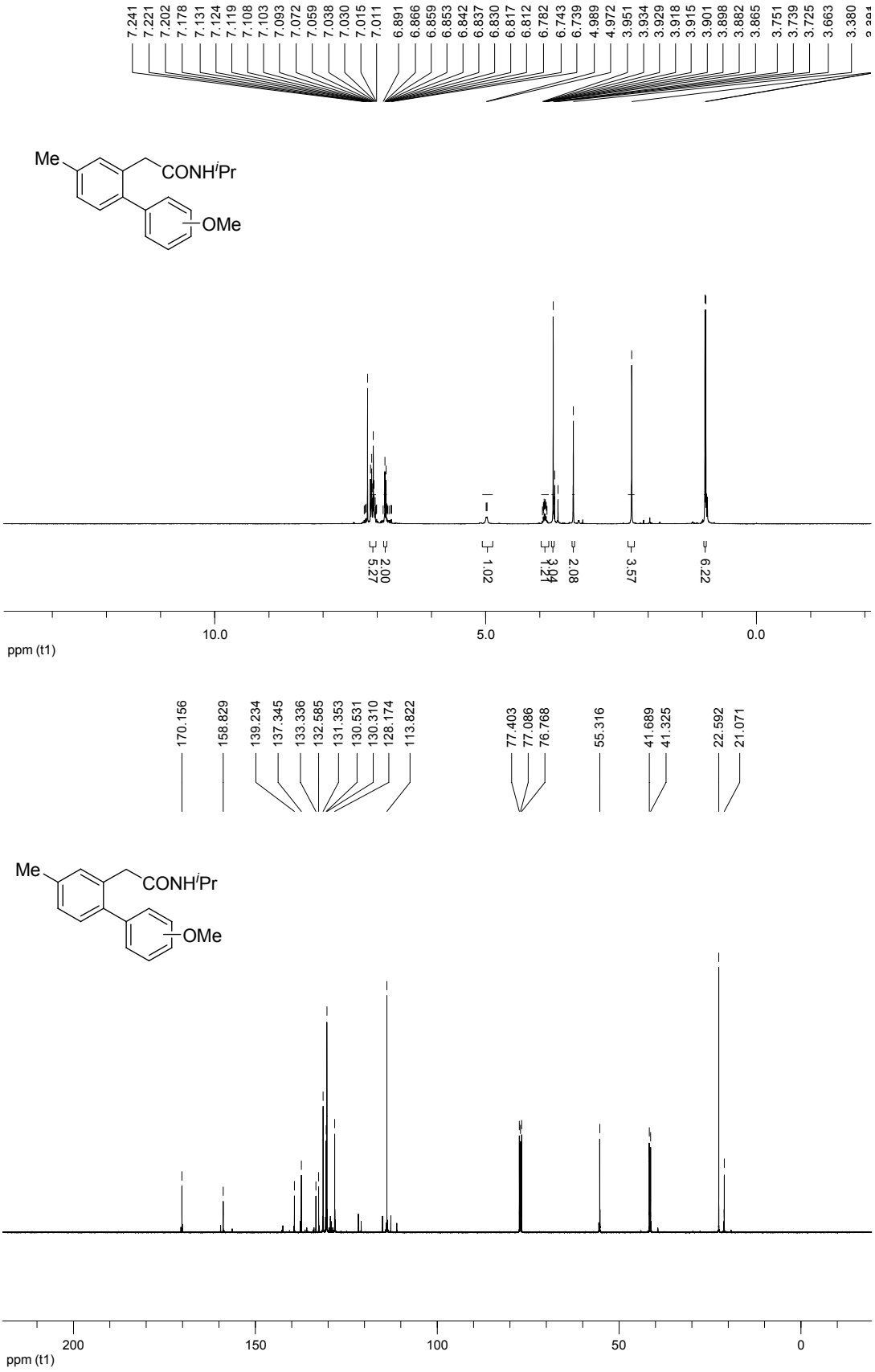


NMR spectra of compound **2d**

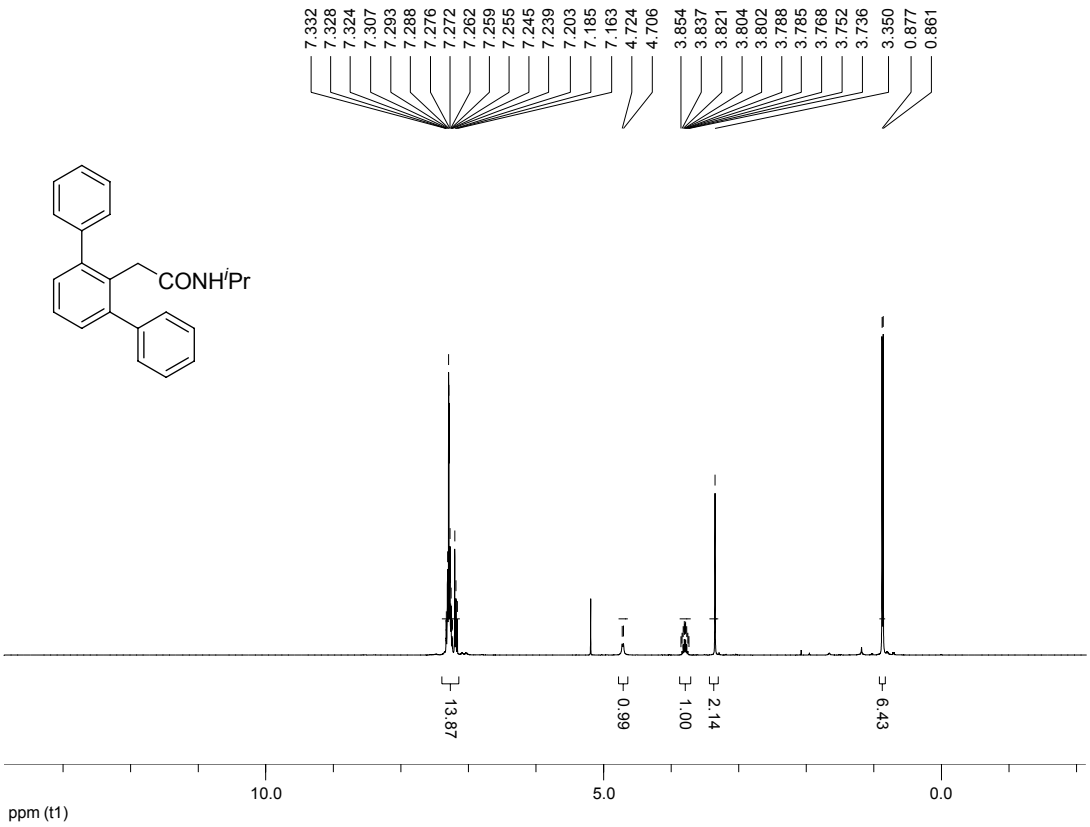


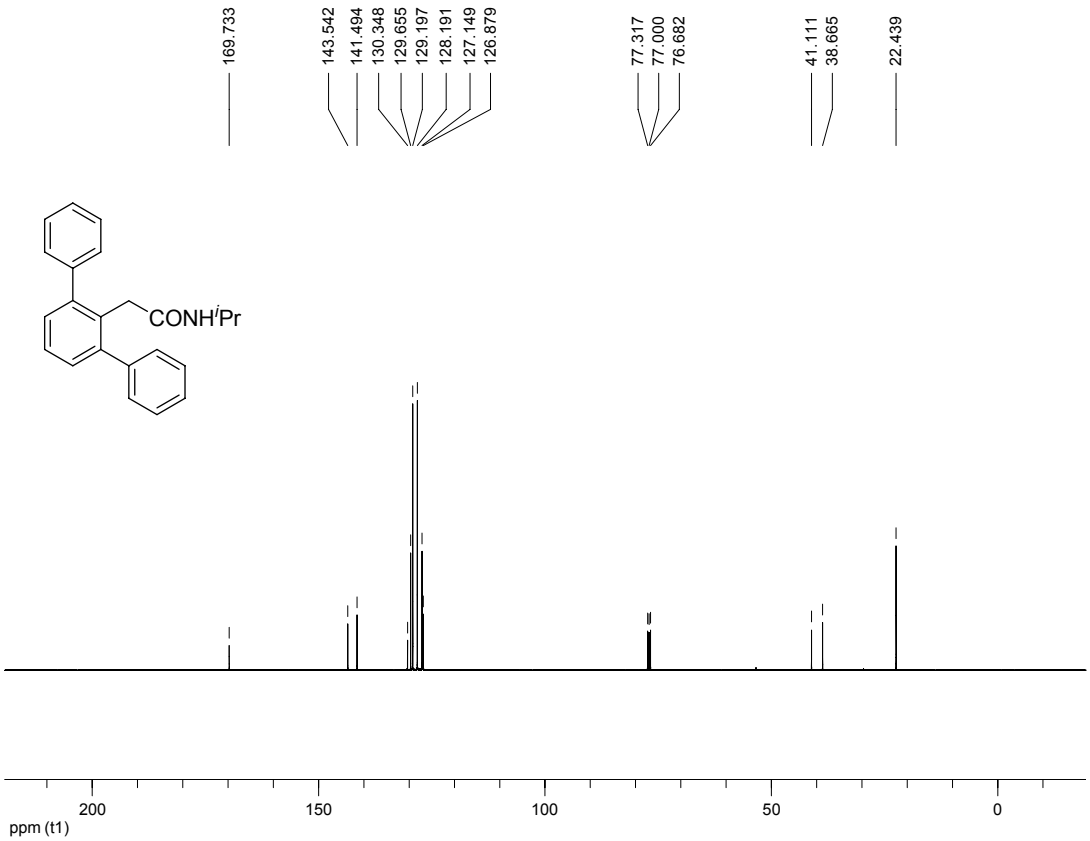


NMR spectra of compound **2e**

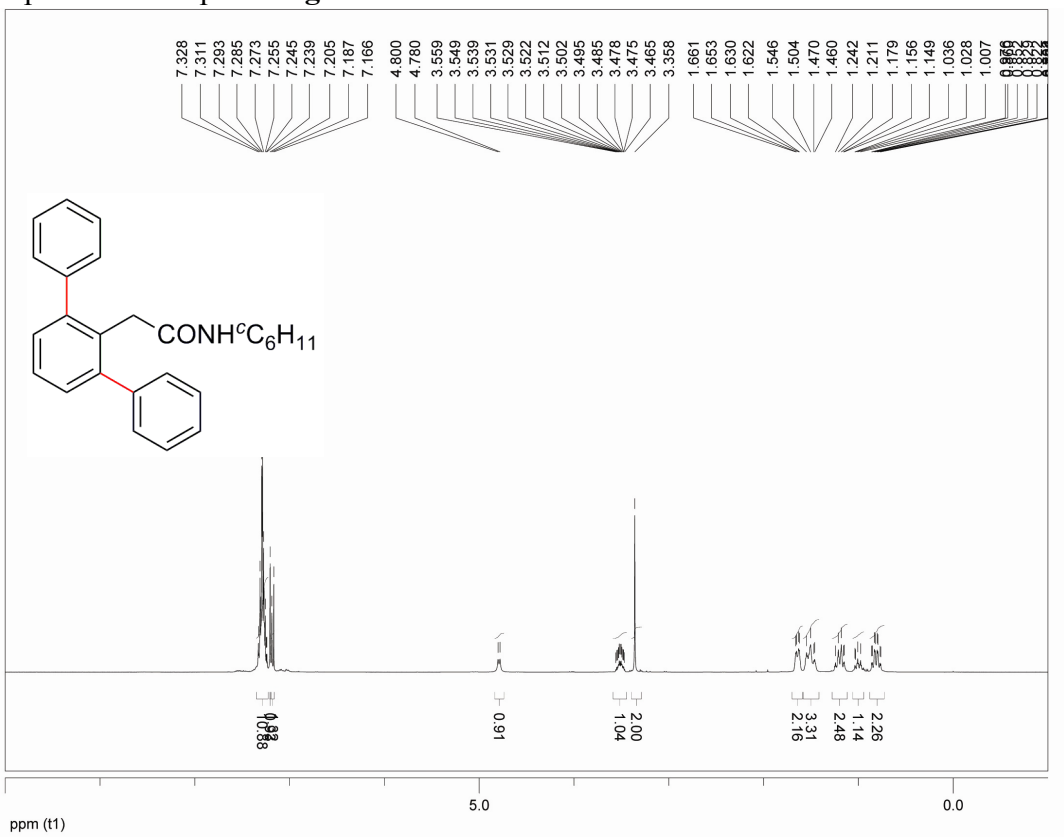


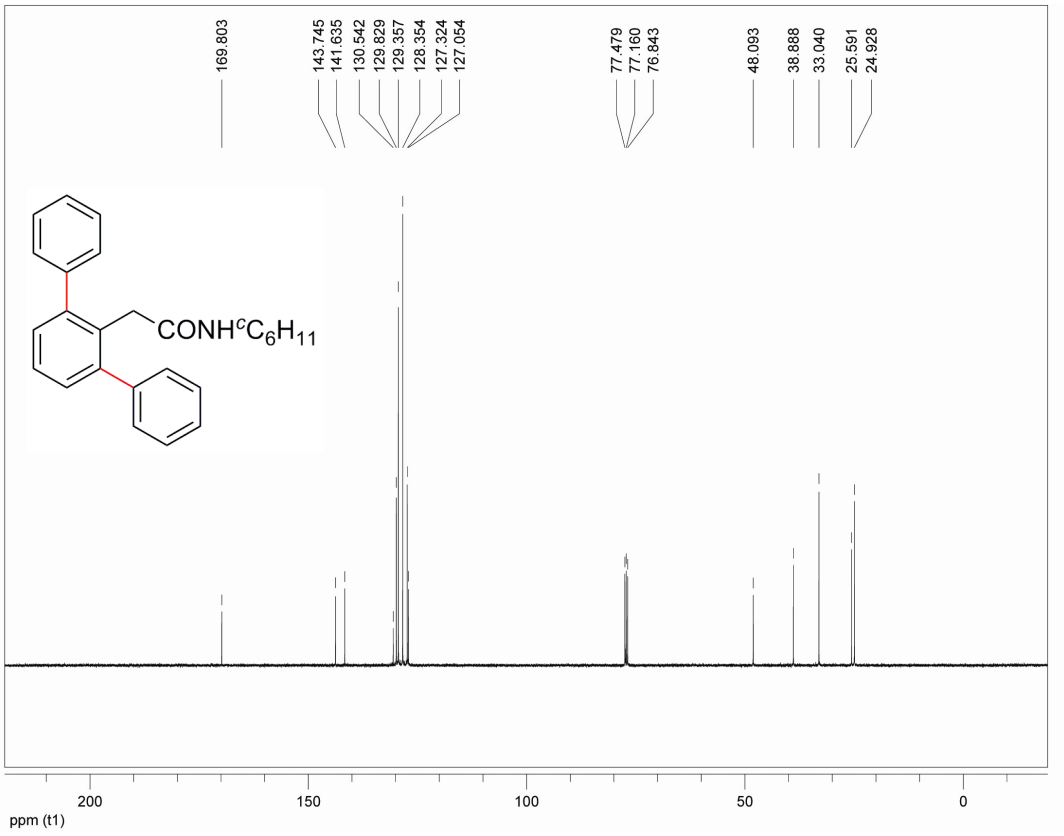
NMR spectra of compound **2f**



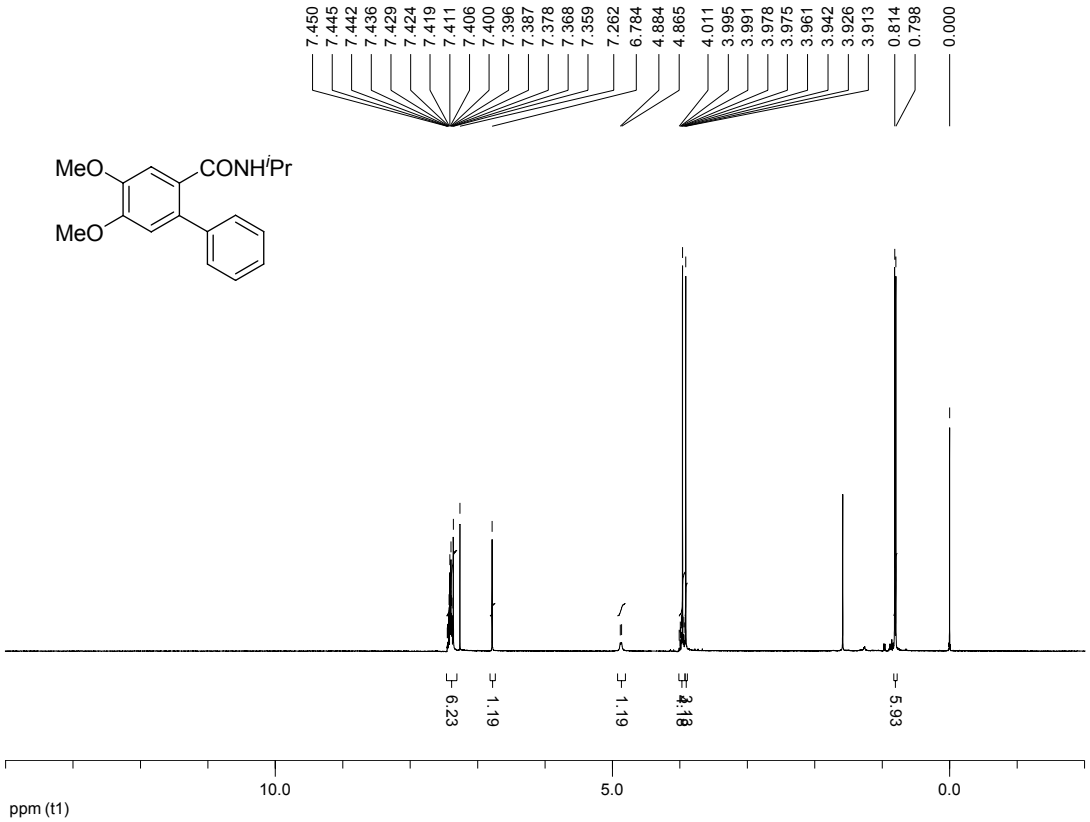


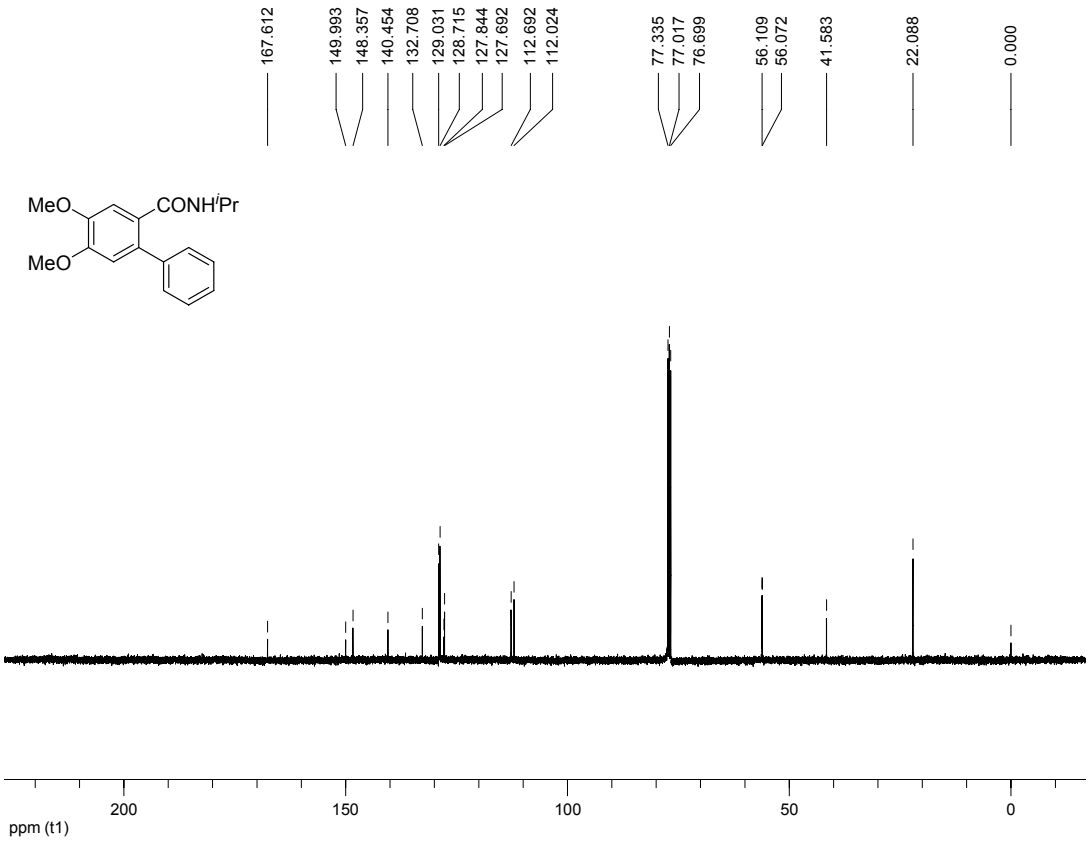
NMR spectra of compound **2g**



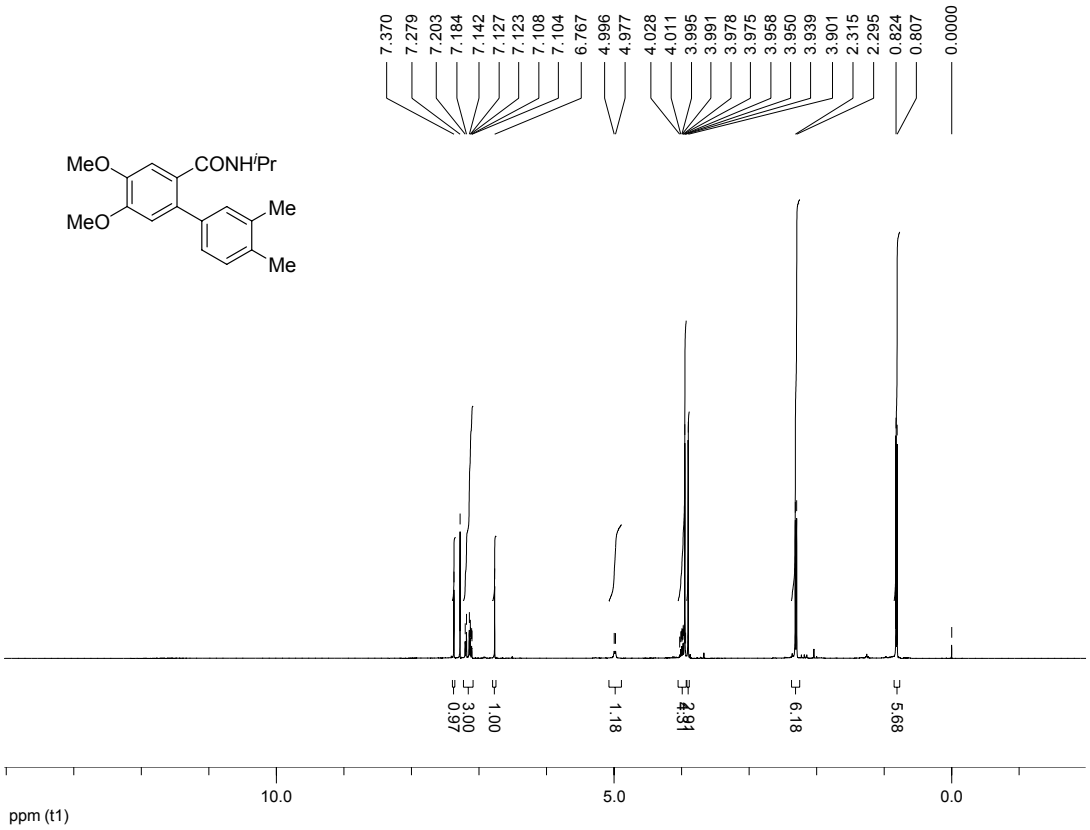


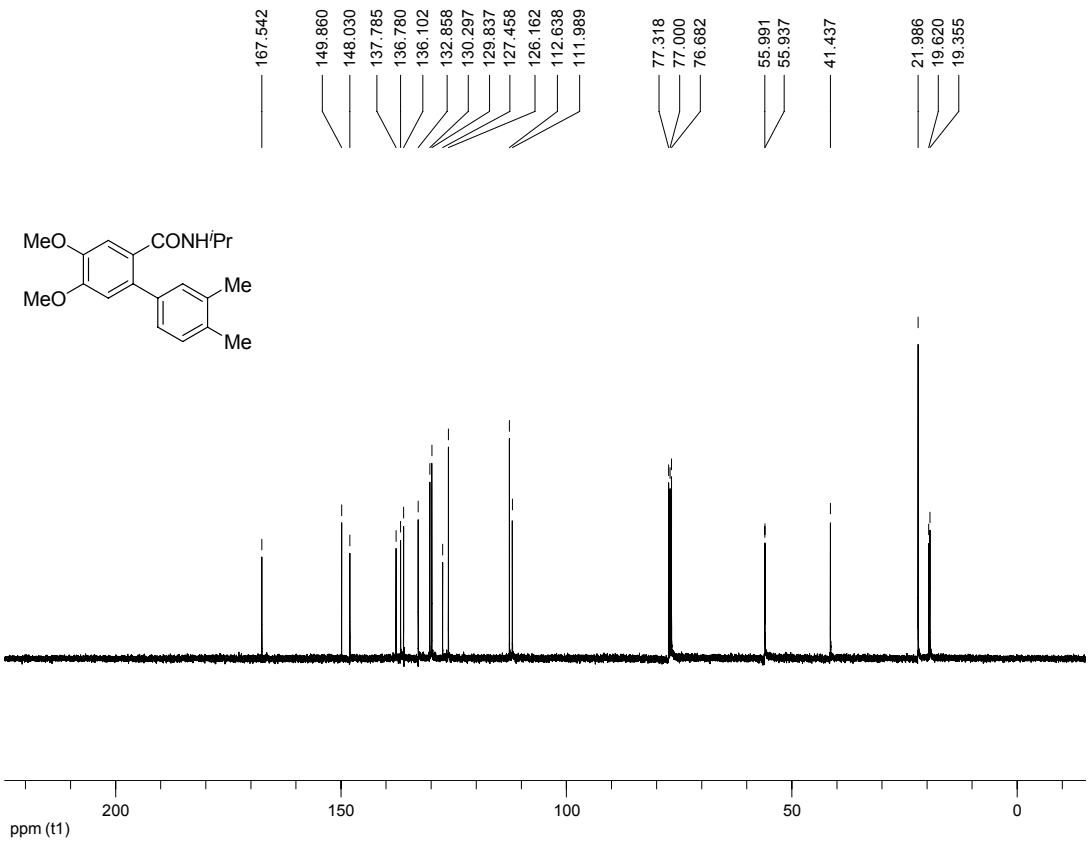
NMR spectra of compound **2h**



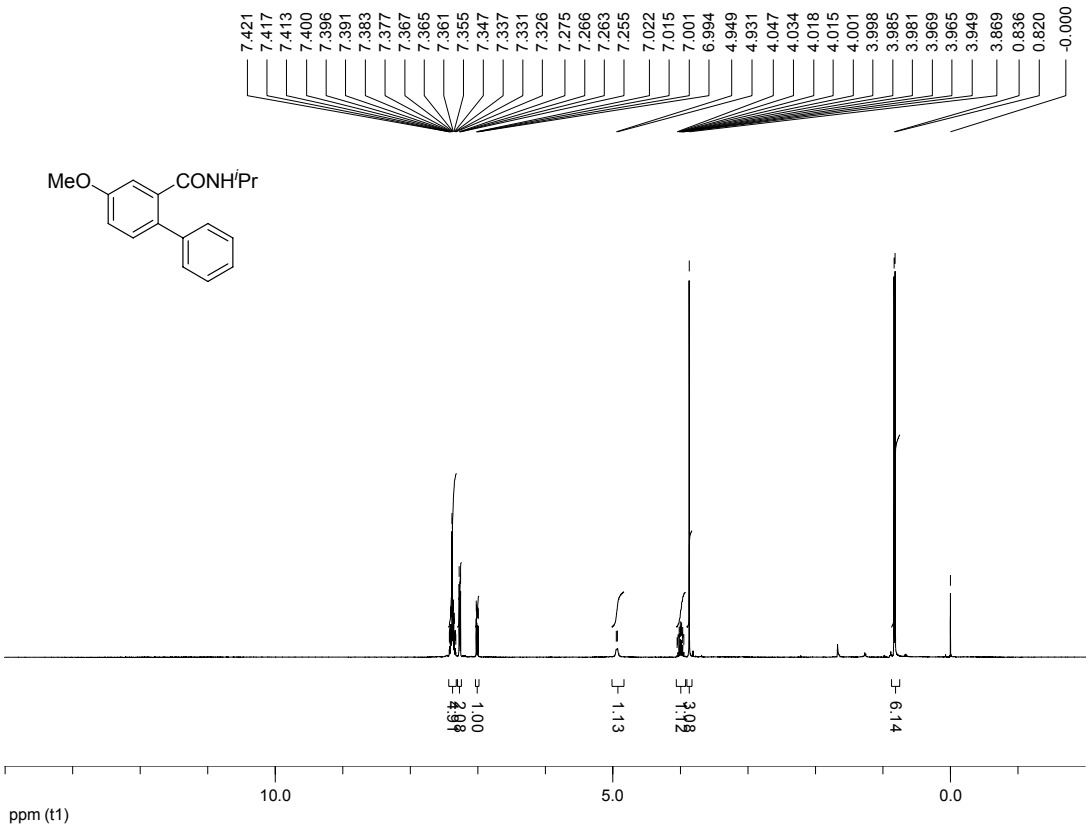


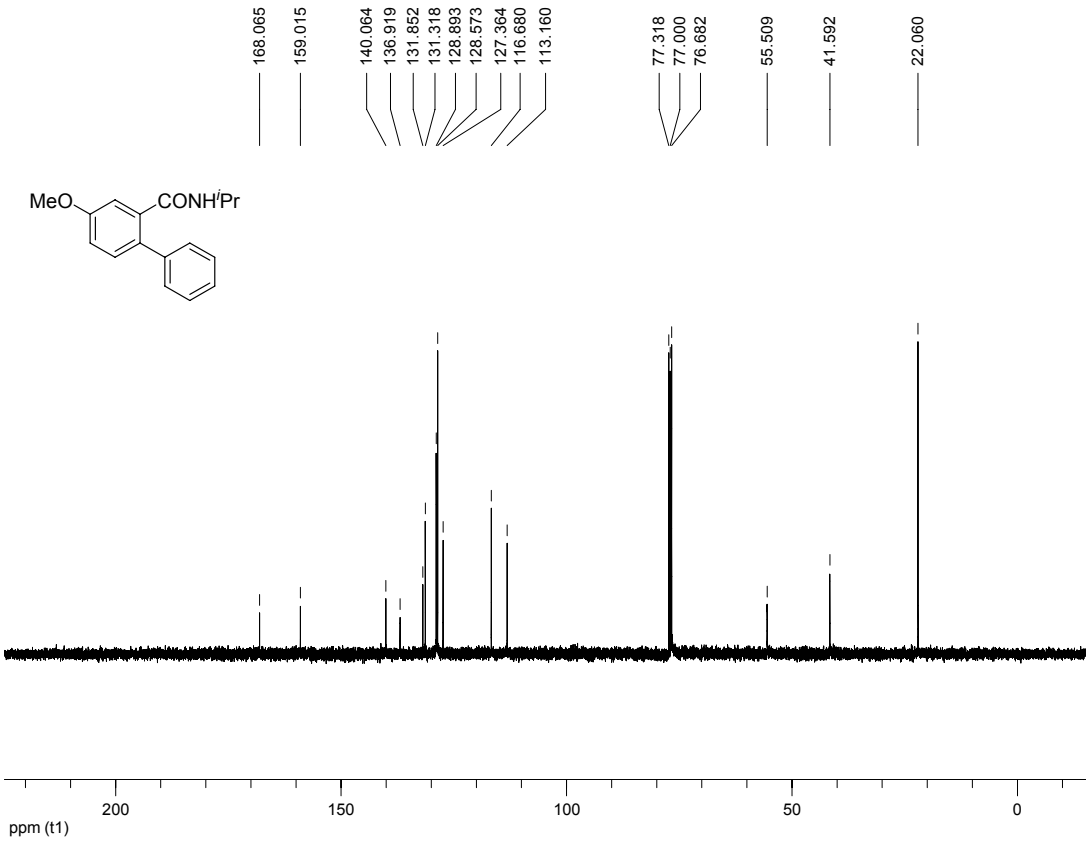
NMR spectra of compound **2i**



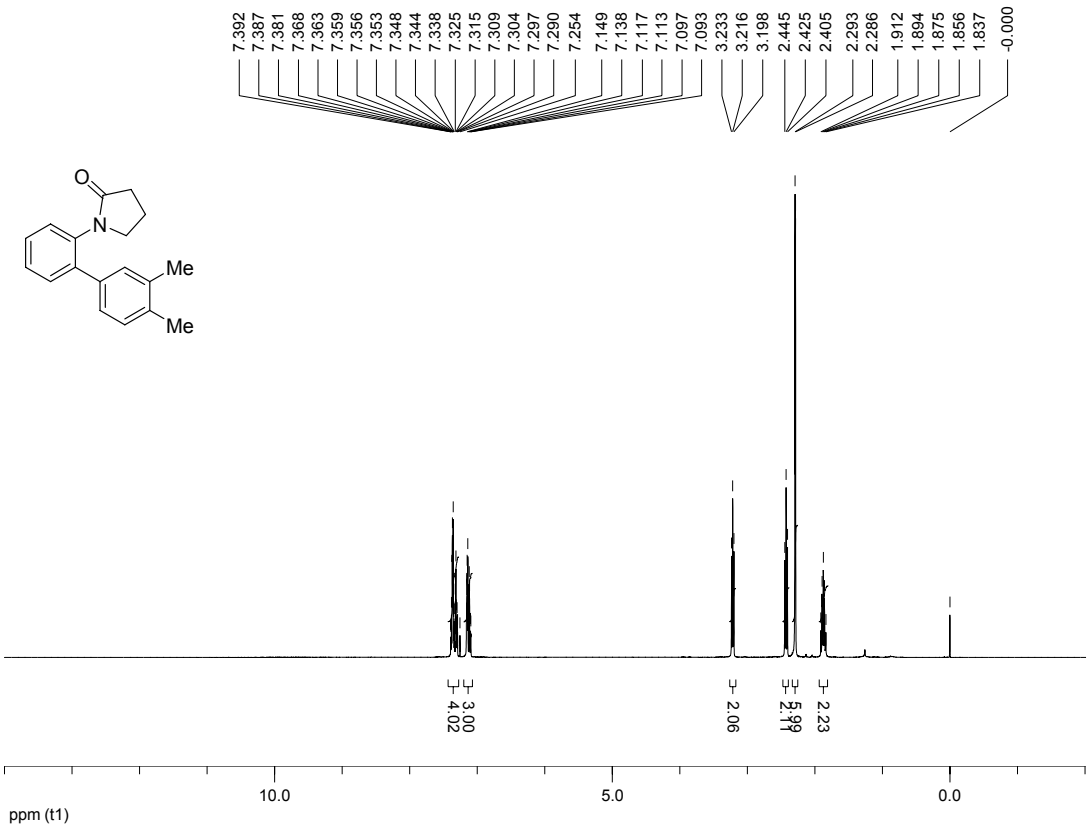


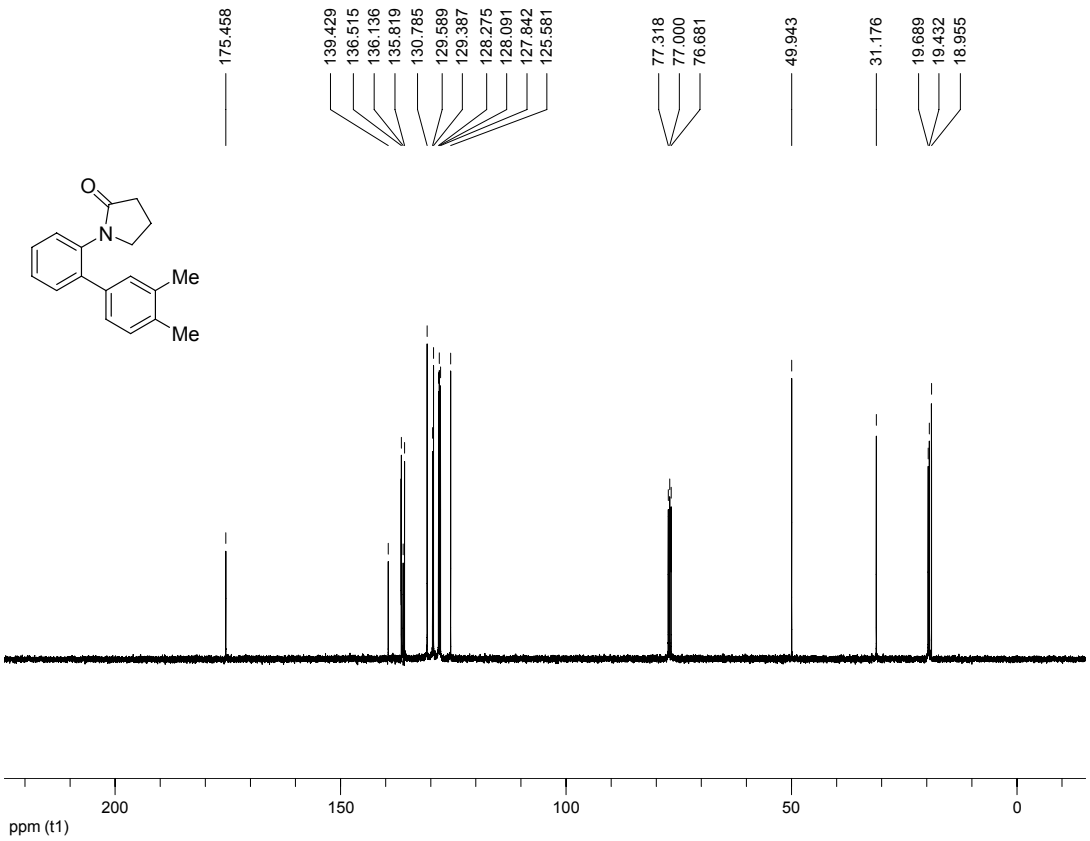
NMR spectra of compound **2j**



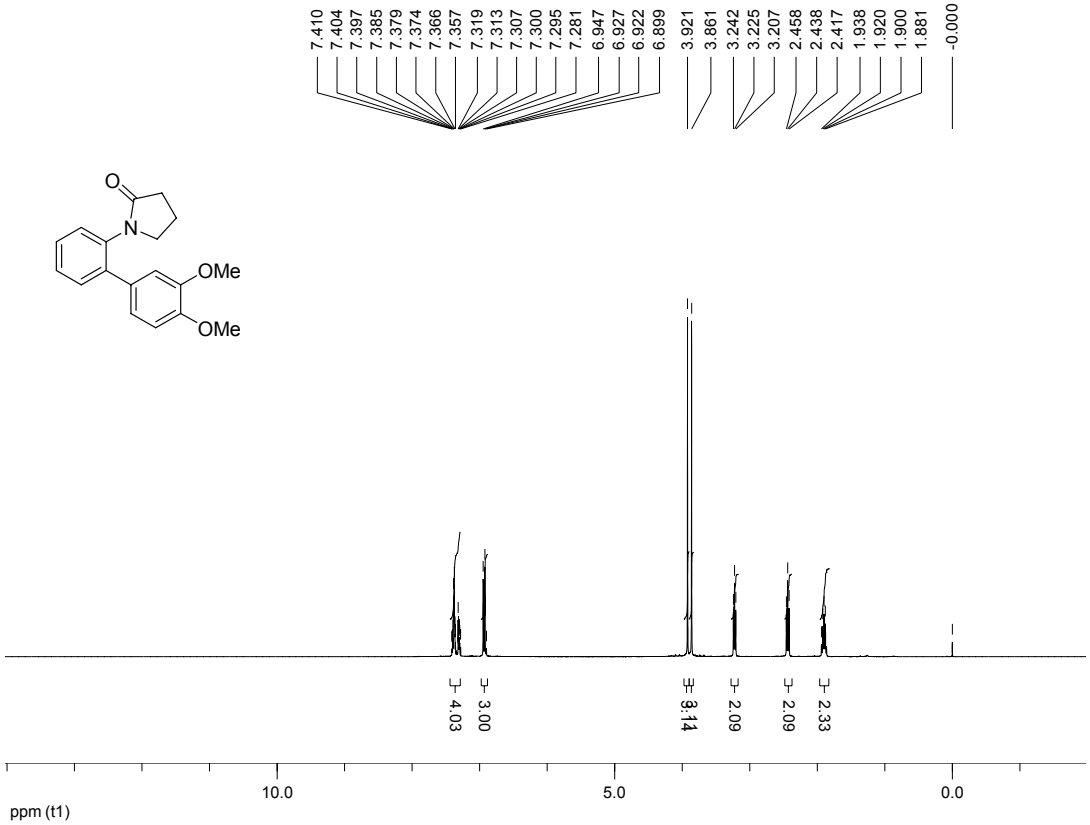


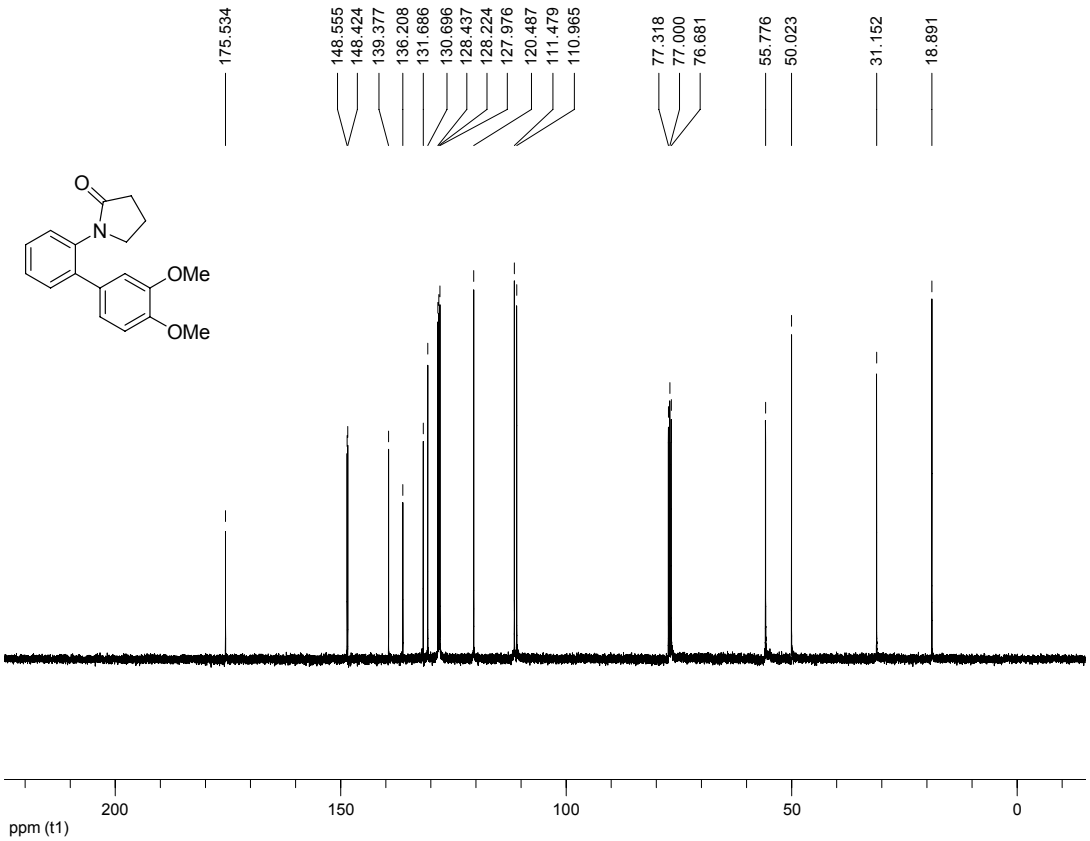
NMR spectra of compound **2l**



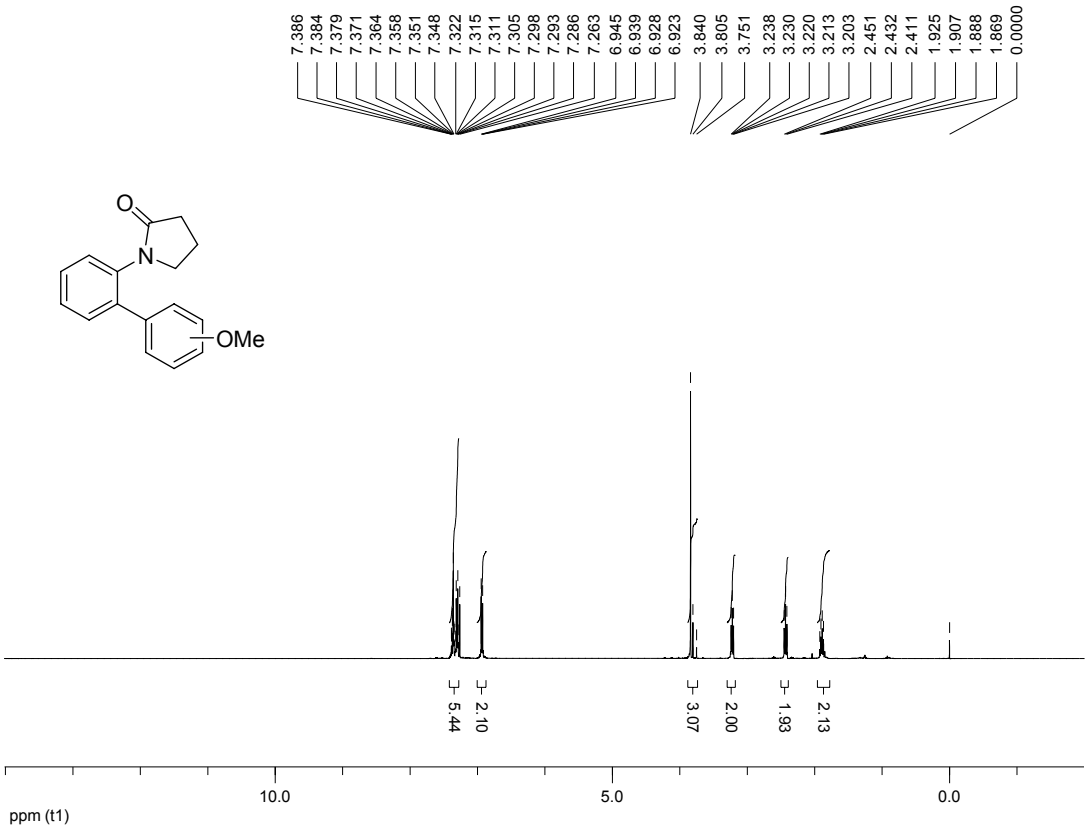


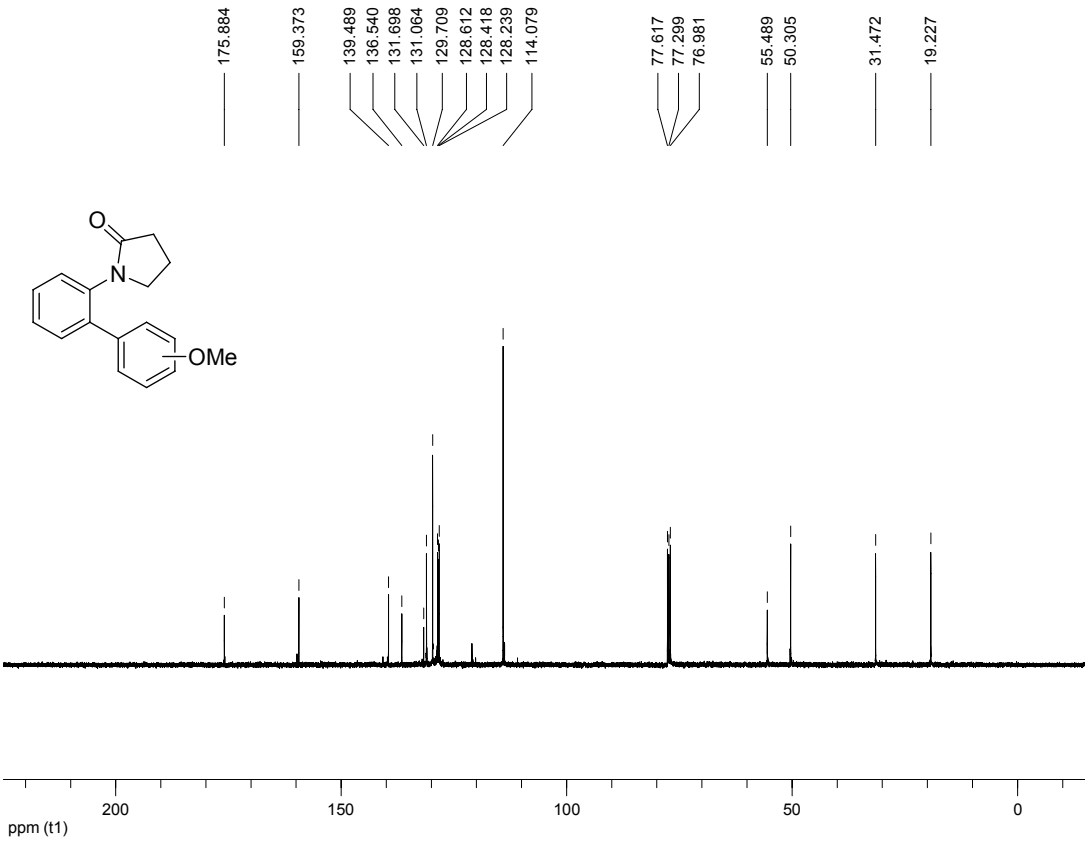
NMR spectra of compound **2m**



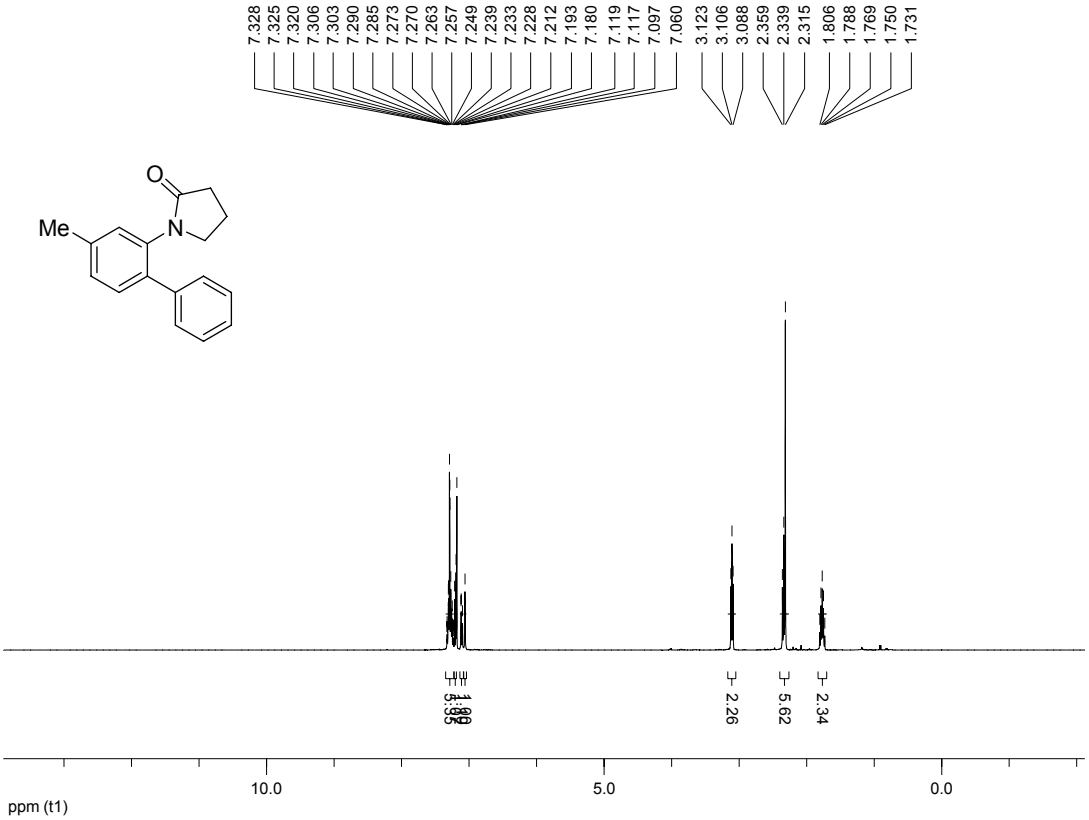


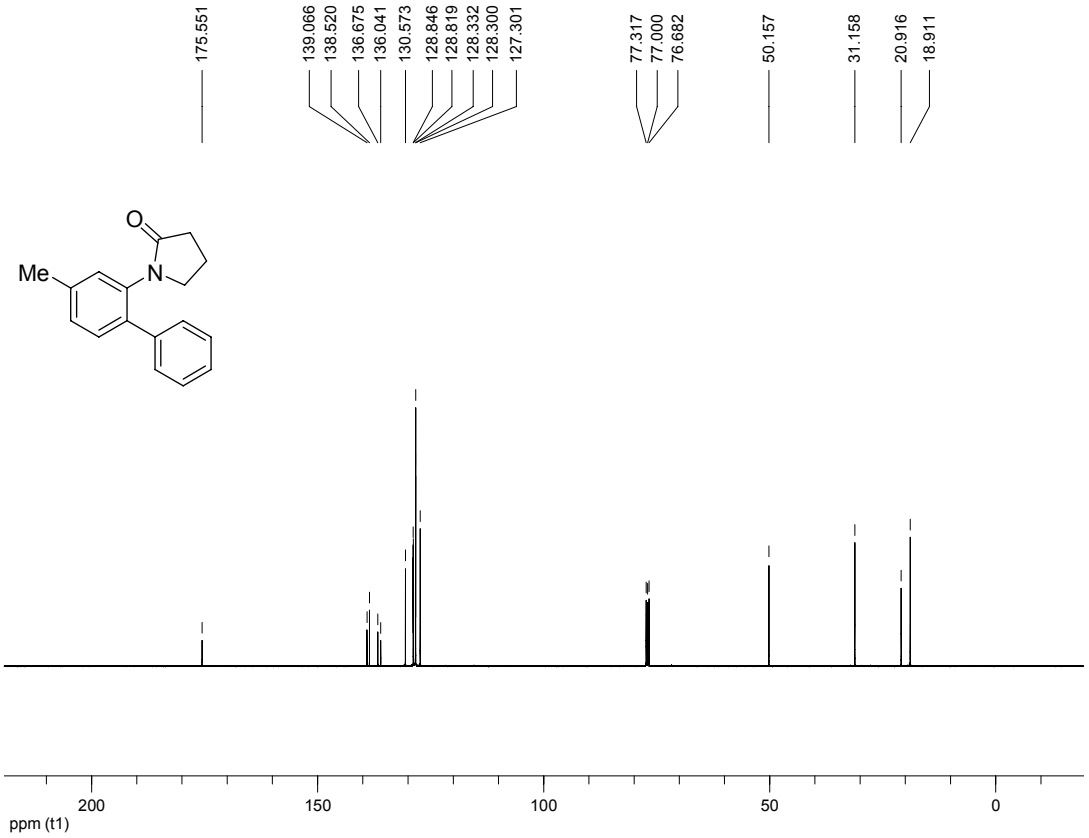
NMR spectra of compound **2n**



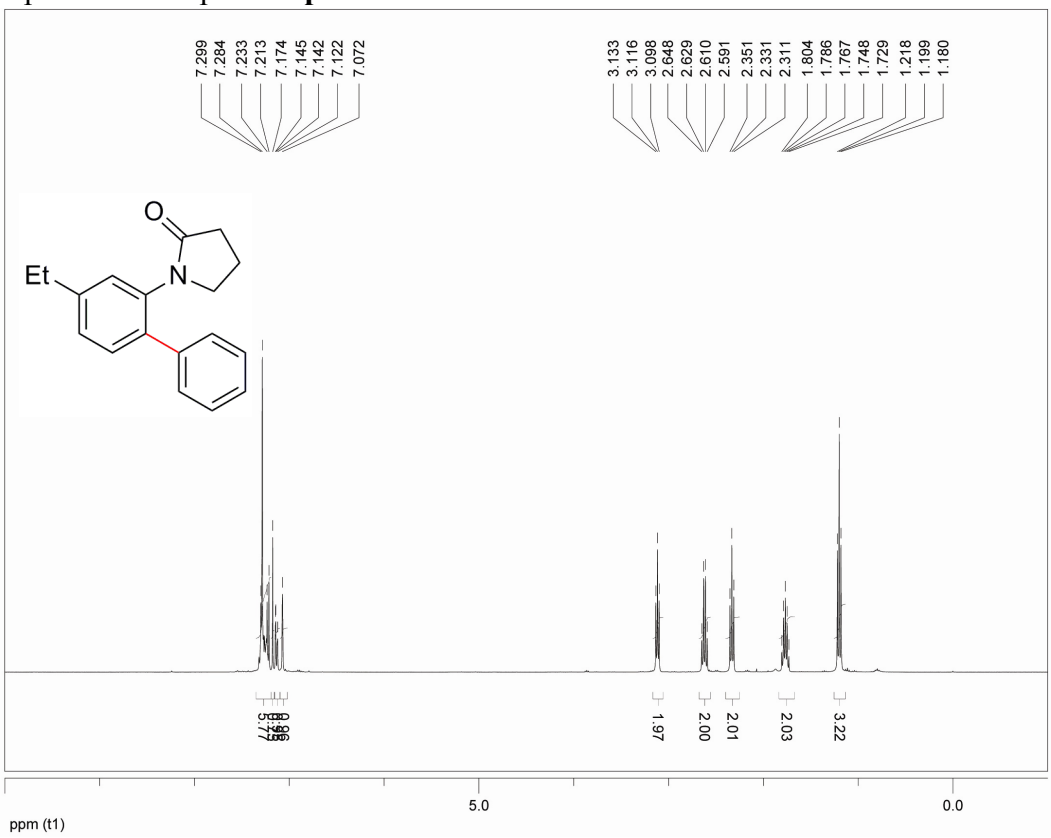


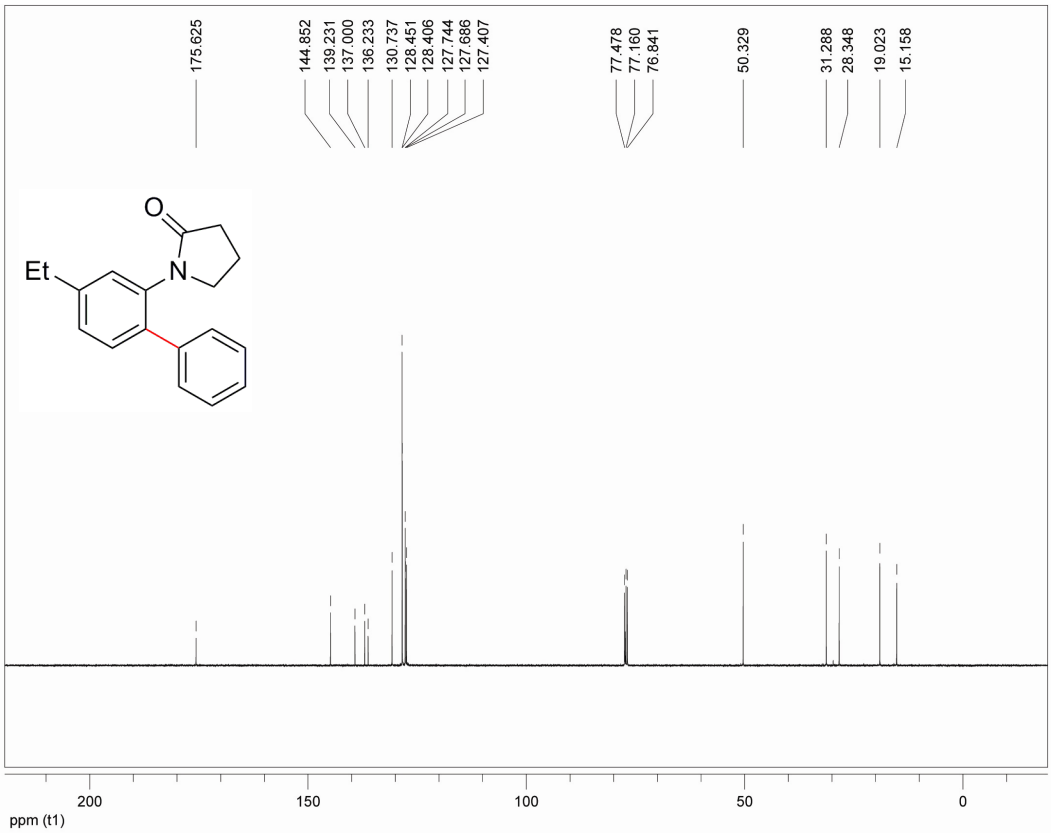
NMR spectra of compound **2o**



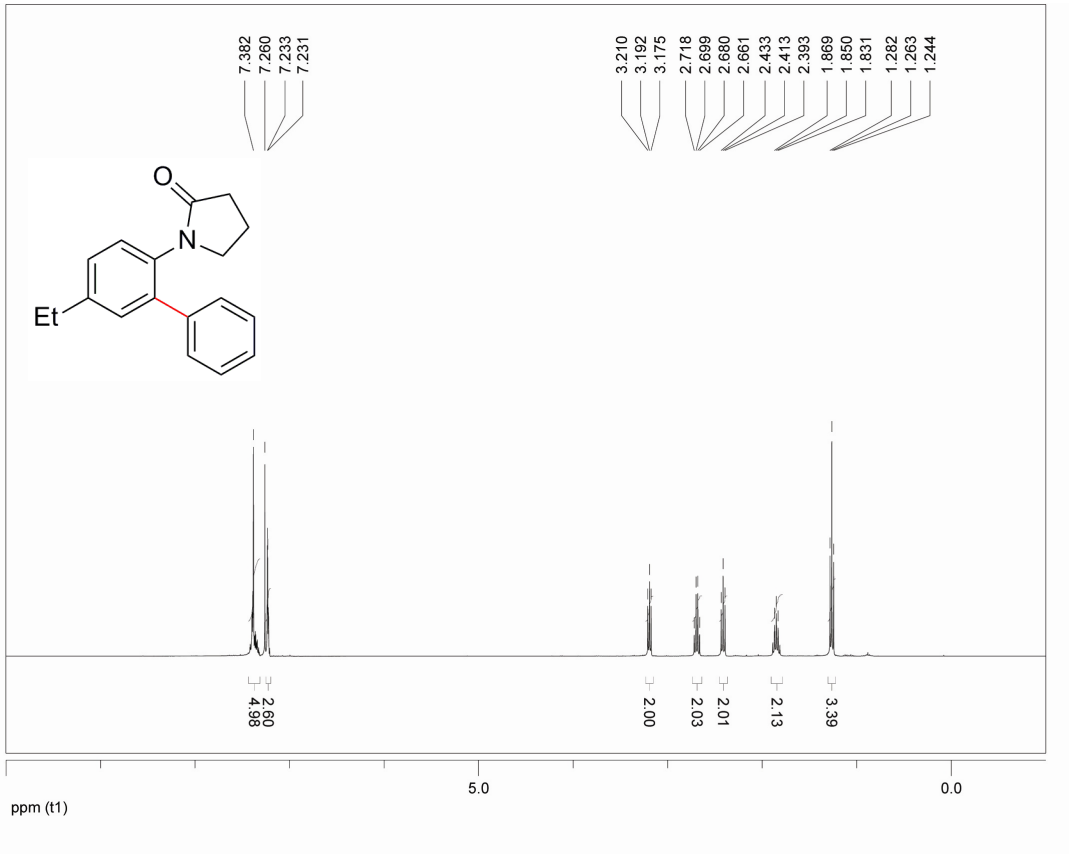


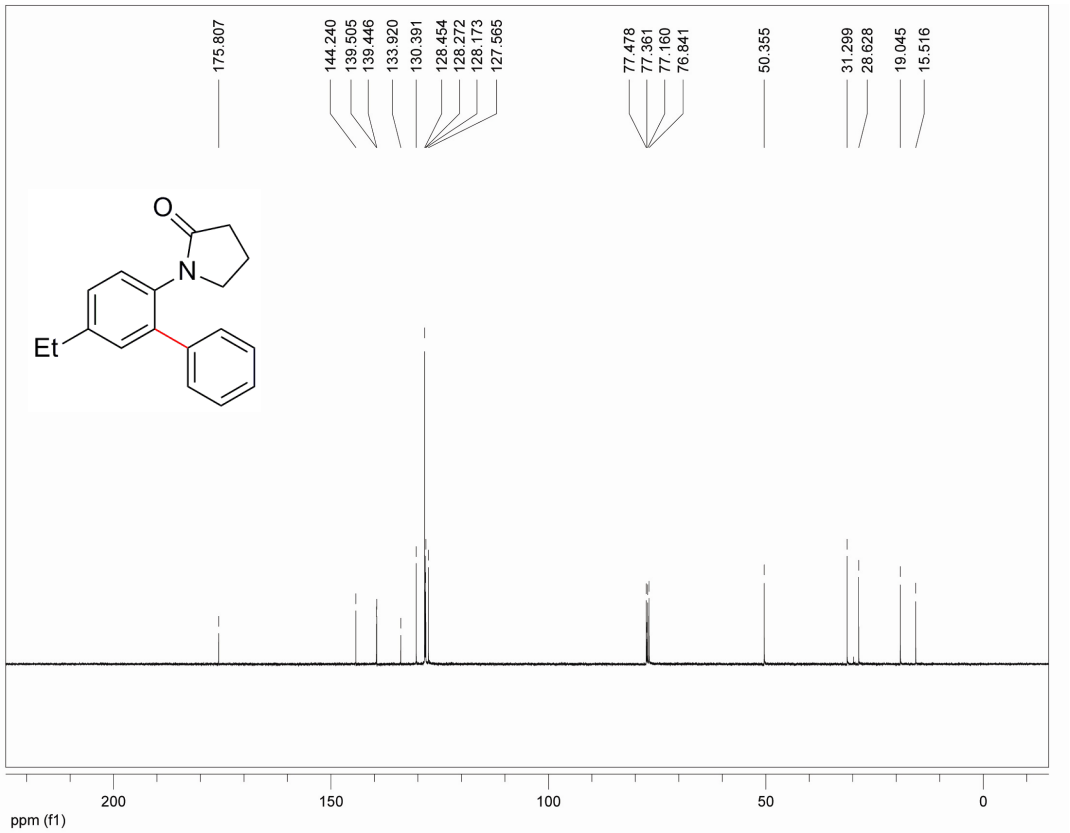
NMR spectra of compound **2p**



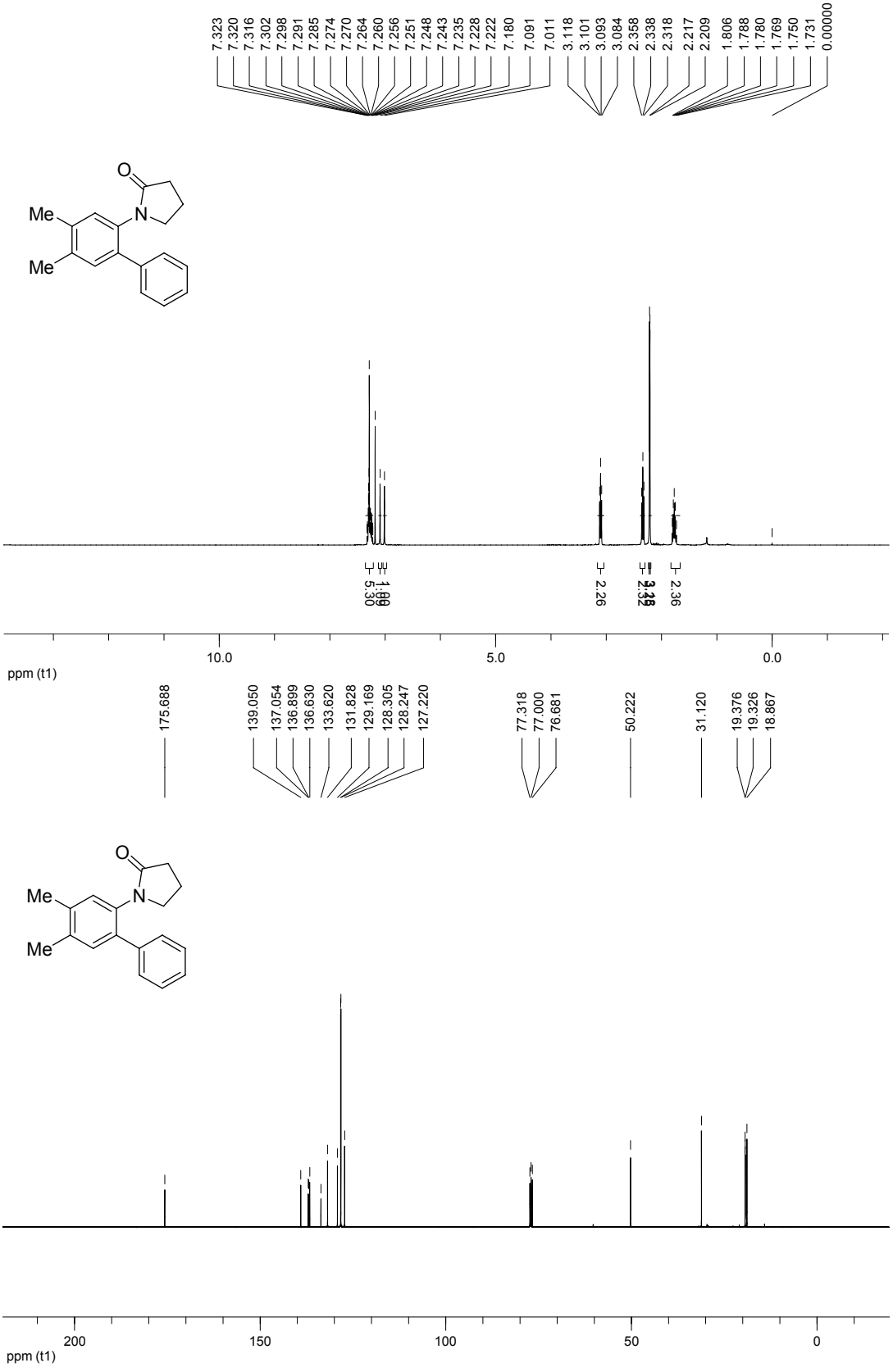


NMR spectra of compound **2r**

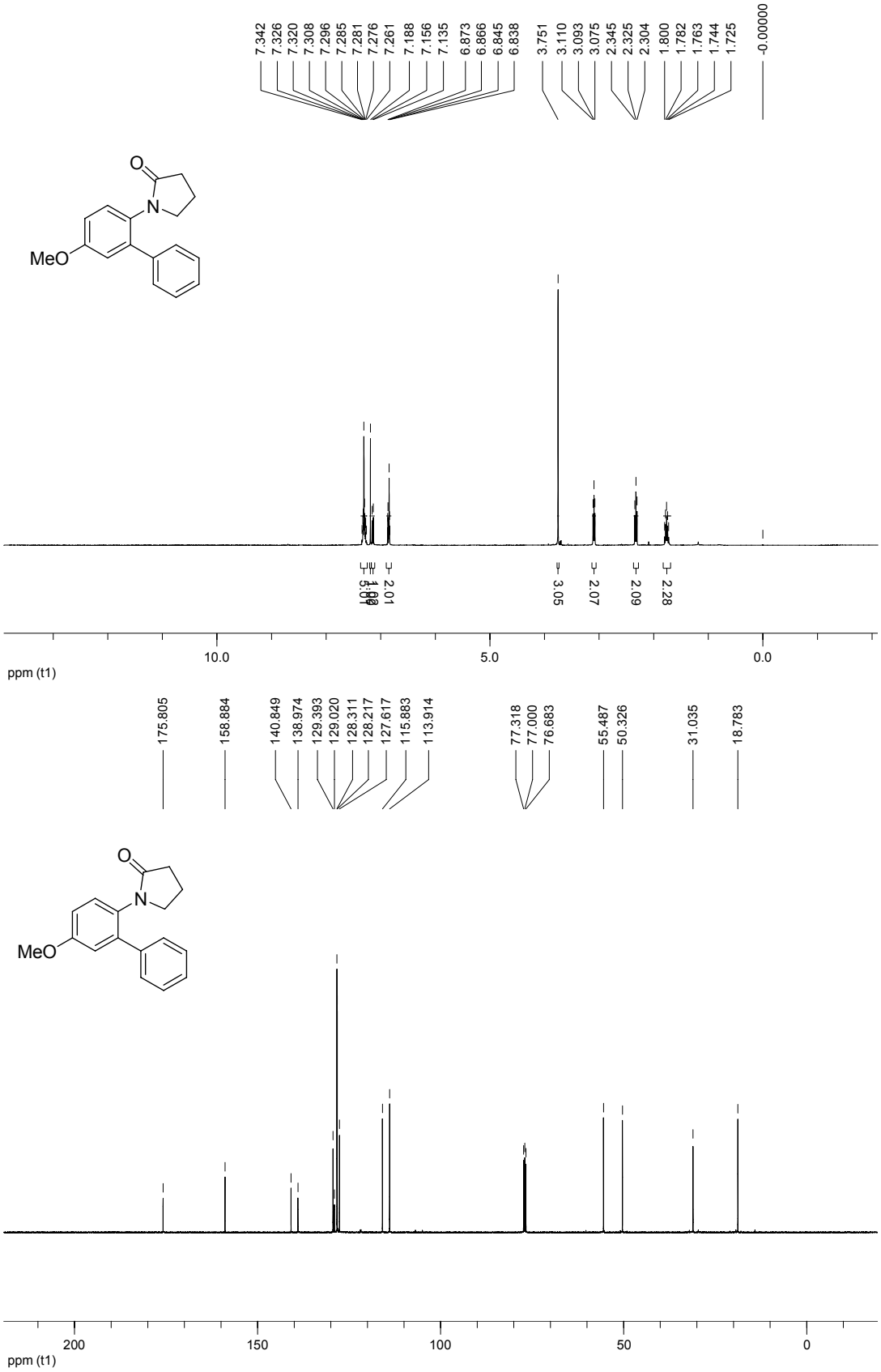




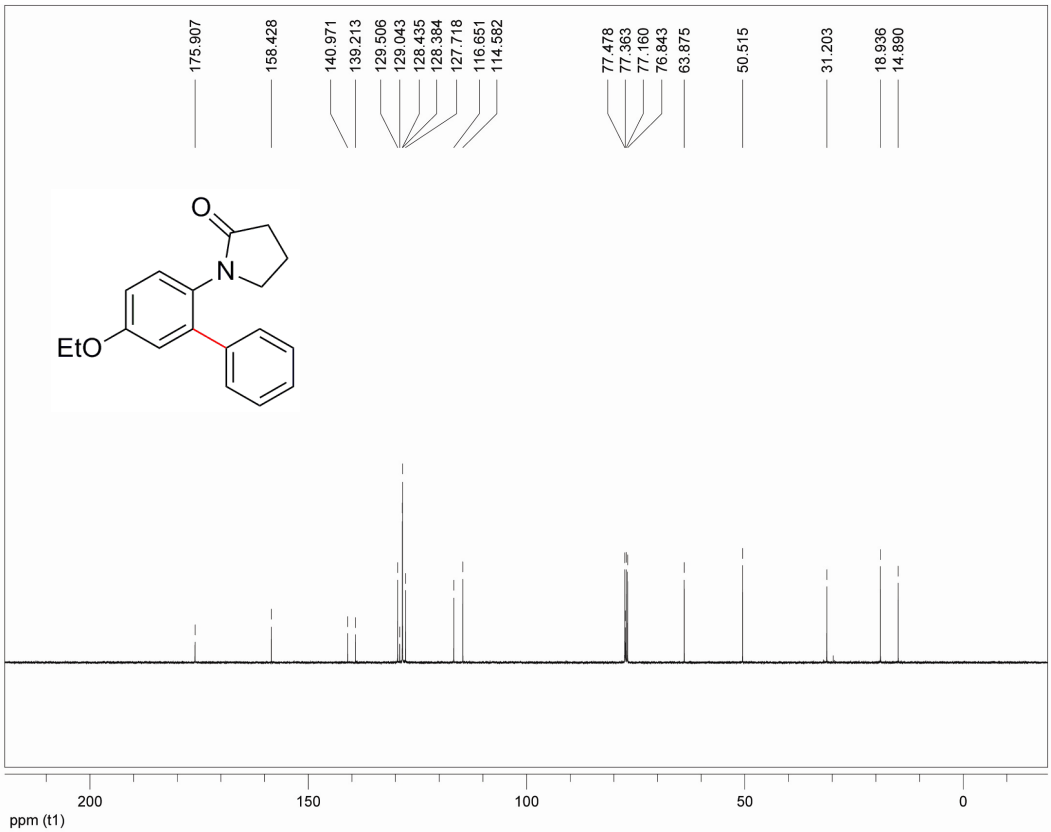
NMR spectra of compound **2s**



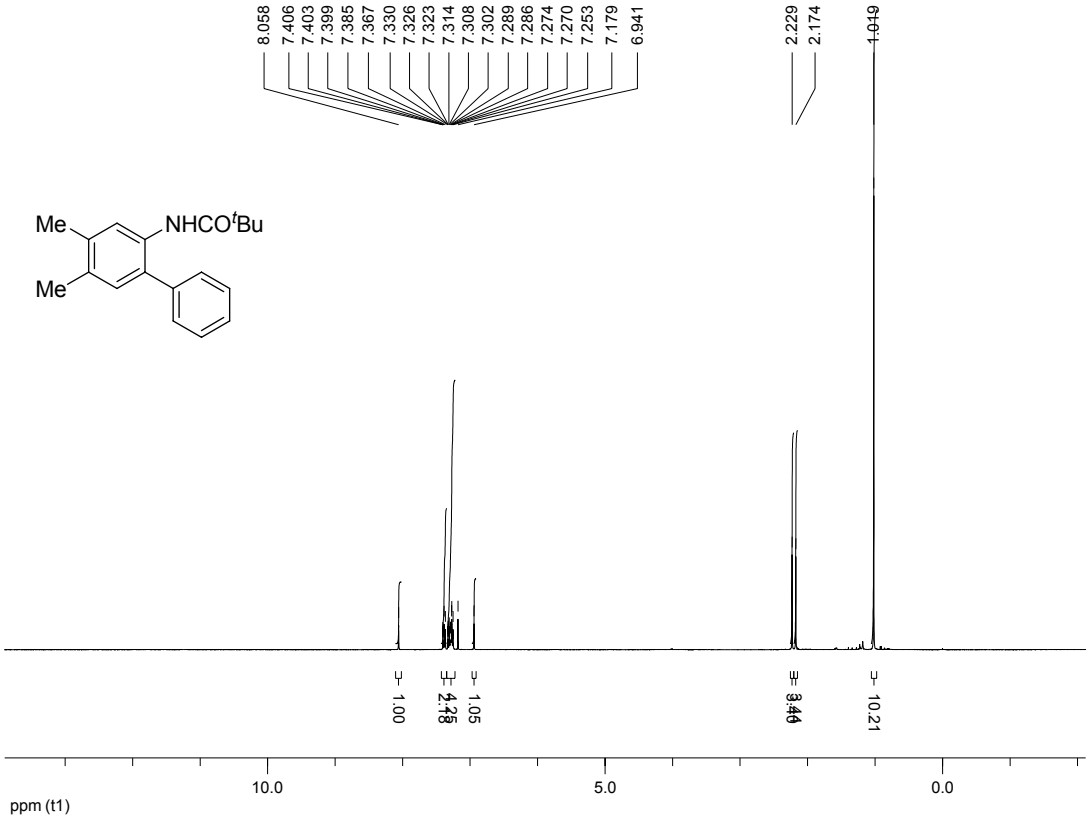
NMR spectra of compound **2t**

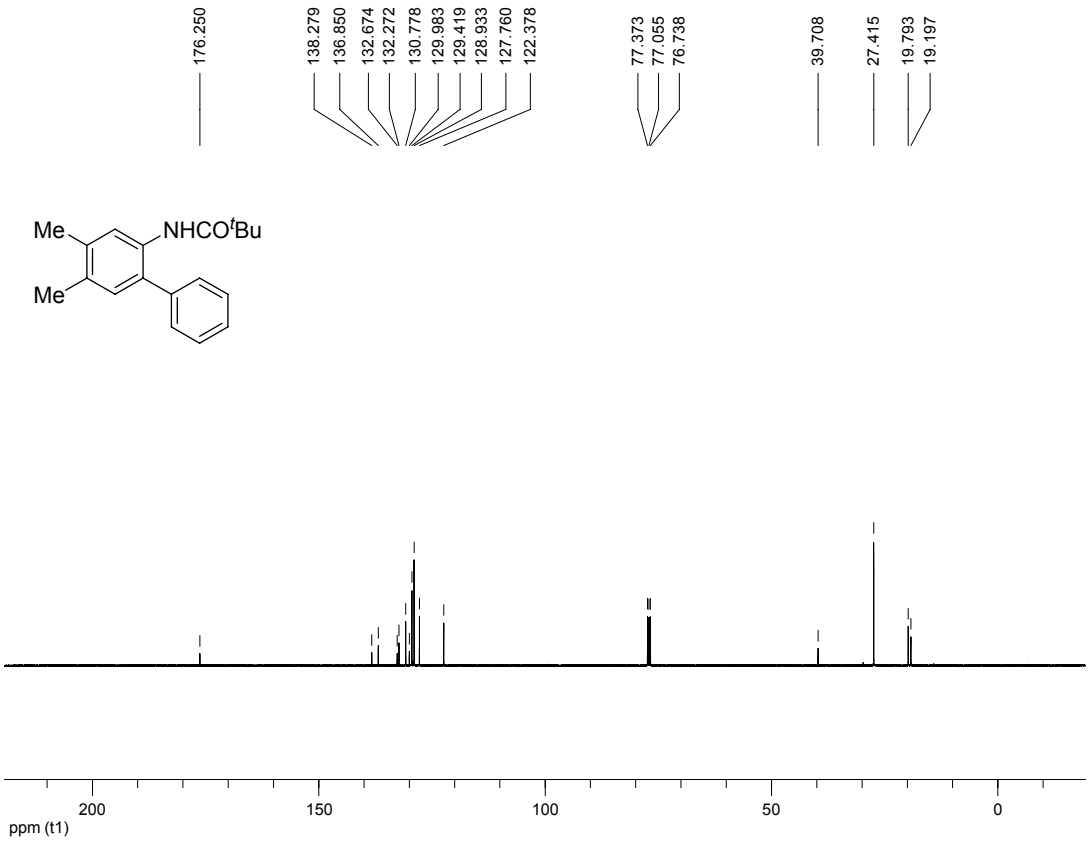


NMR spectra of compound **2u**

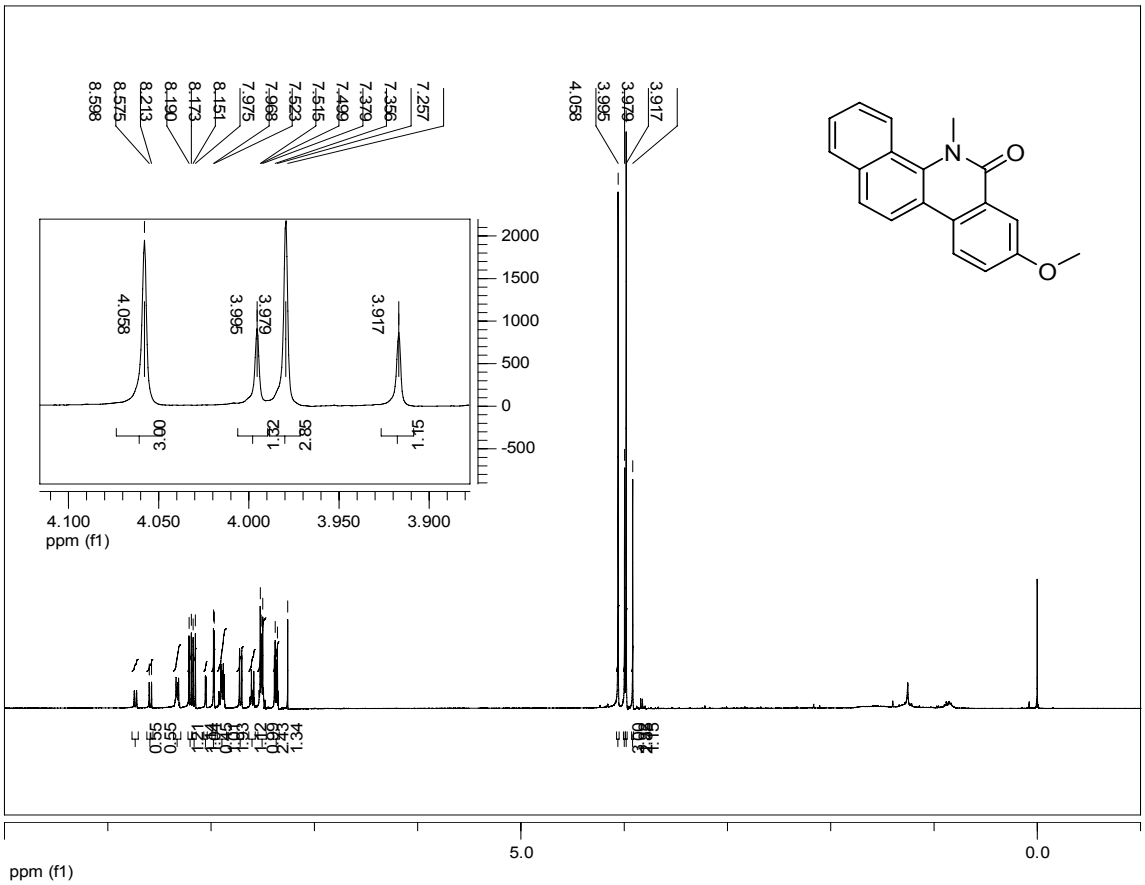


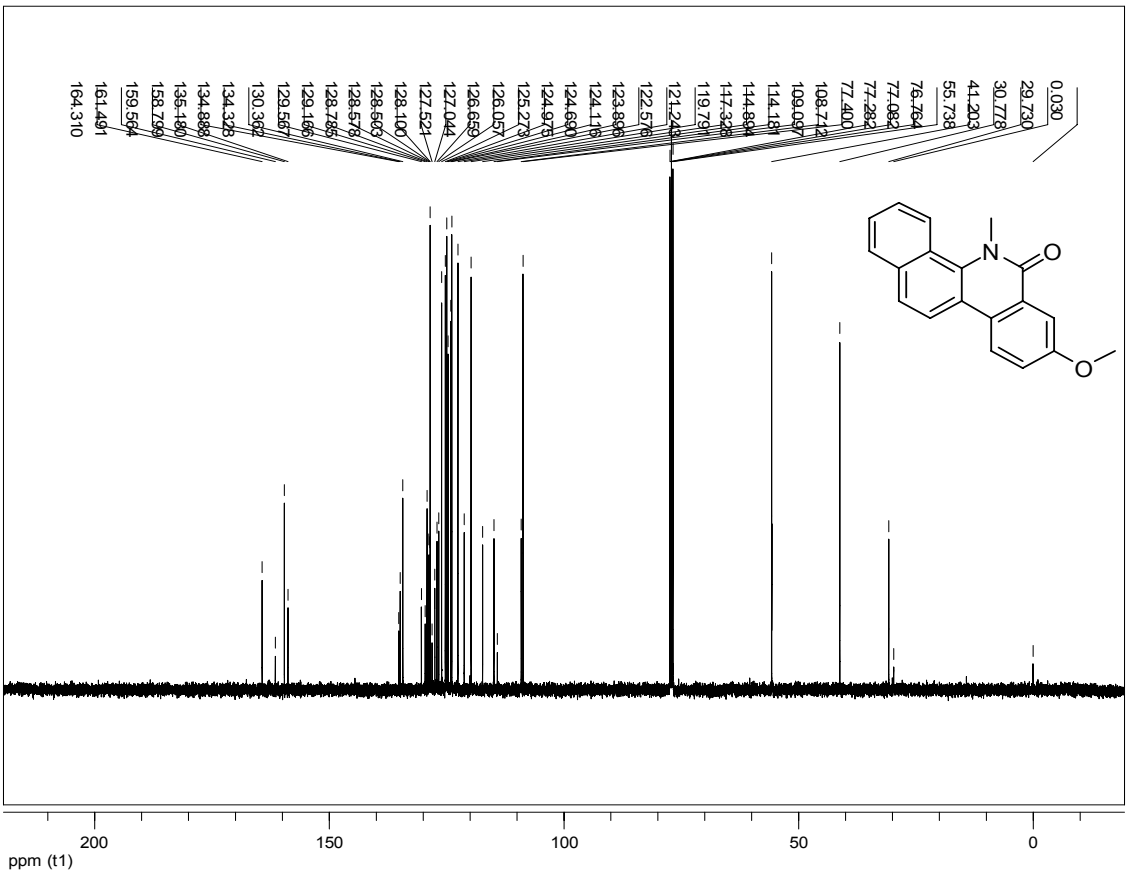
NMR spectra of compound **2x**



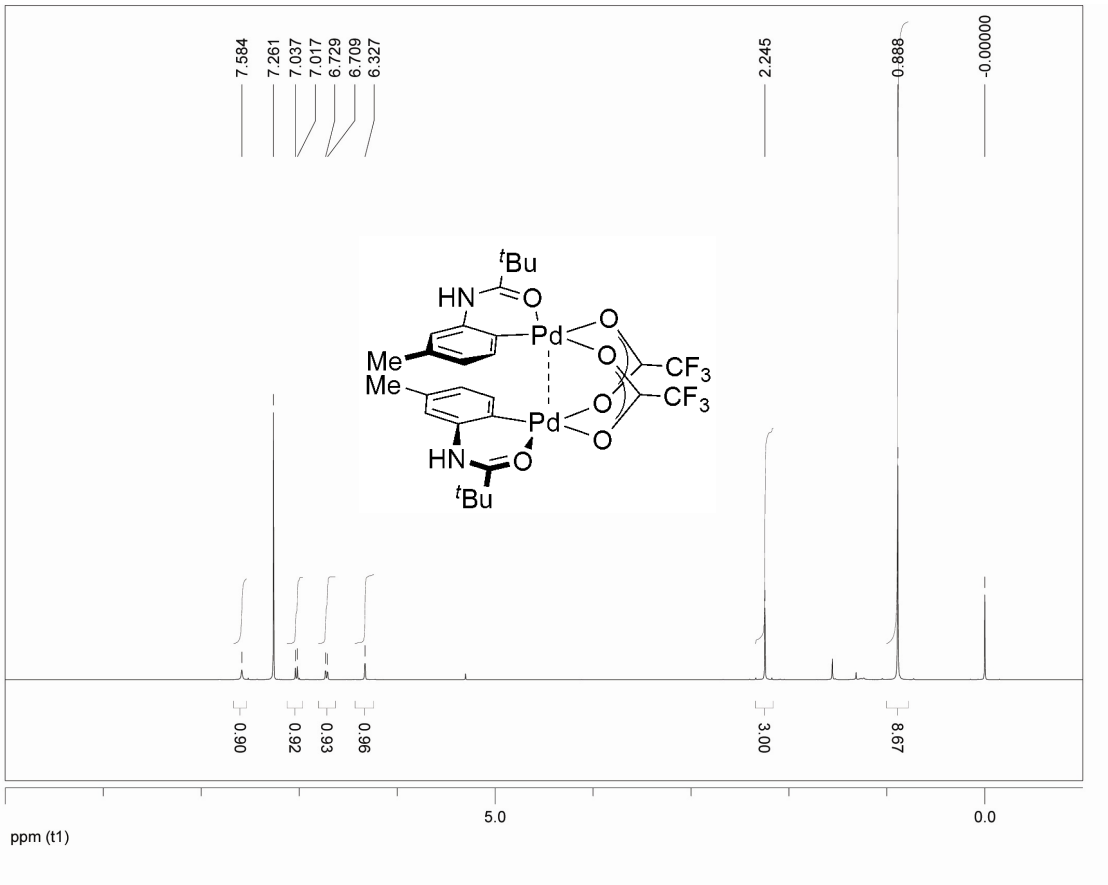


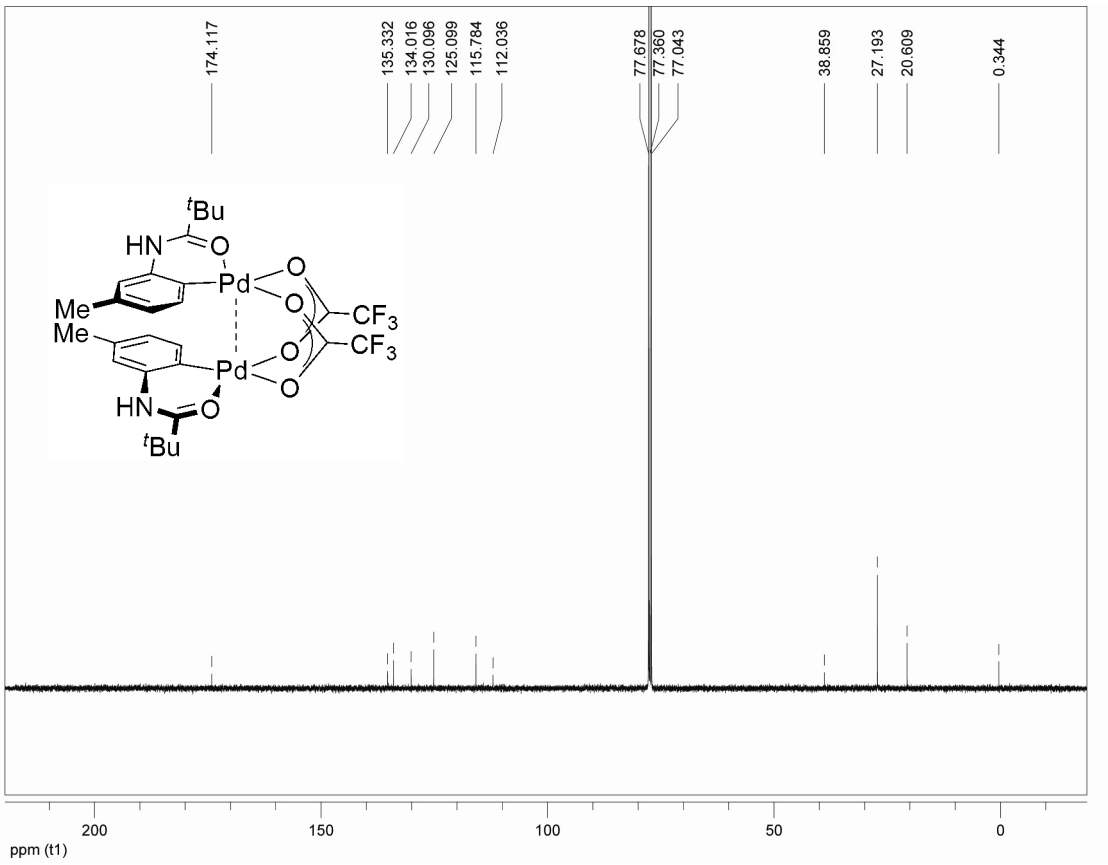
NMR spectra of compound **2aa**



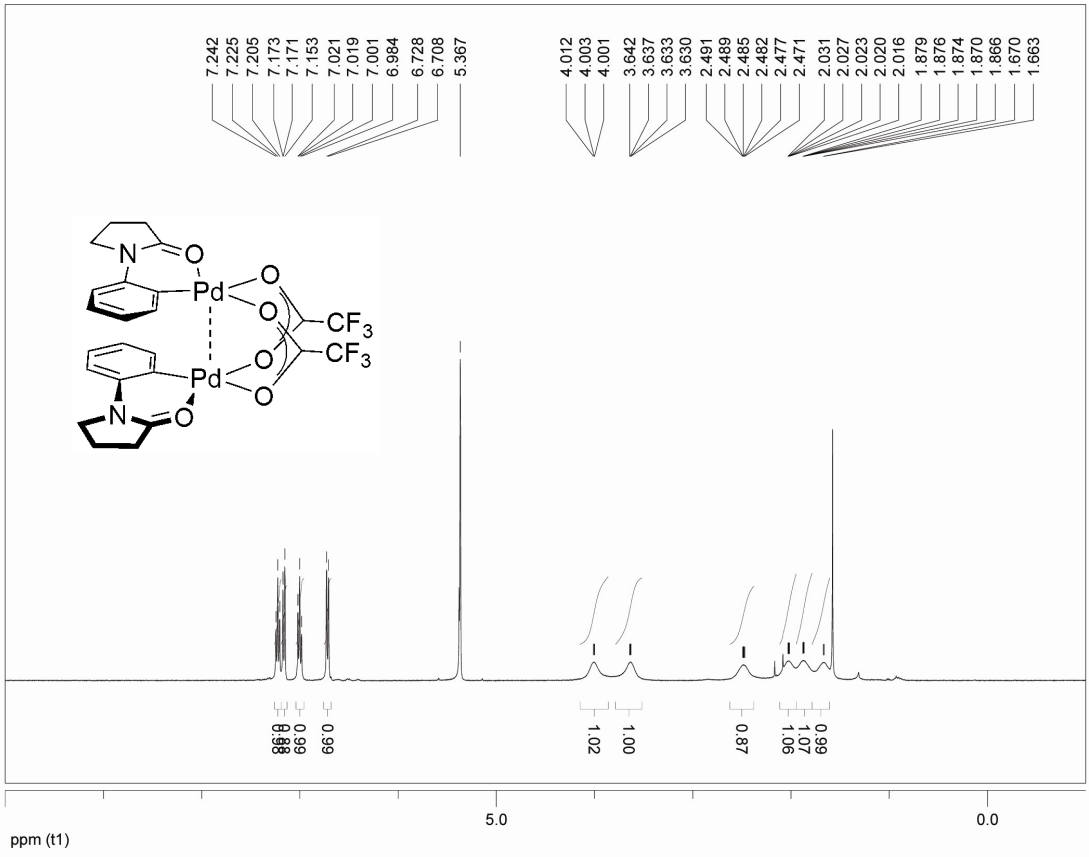


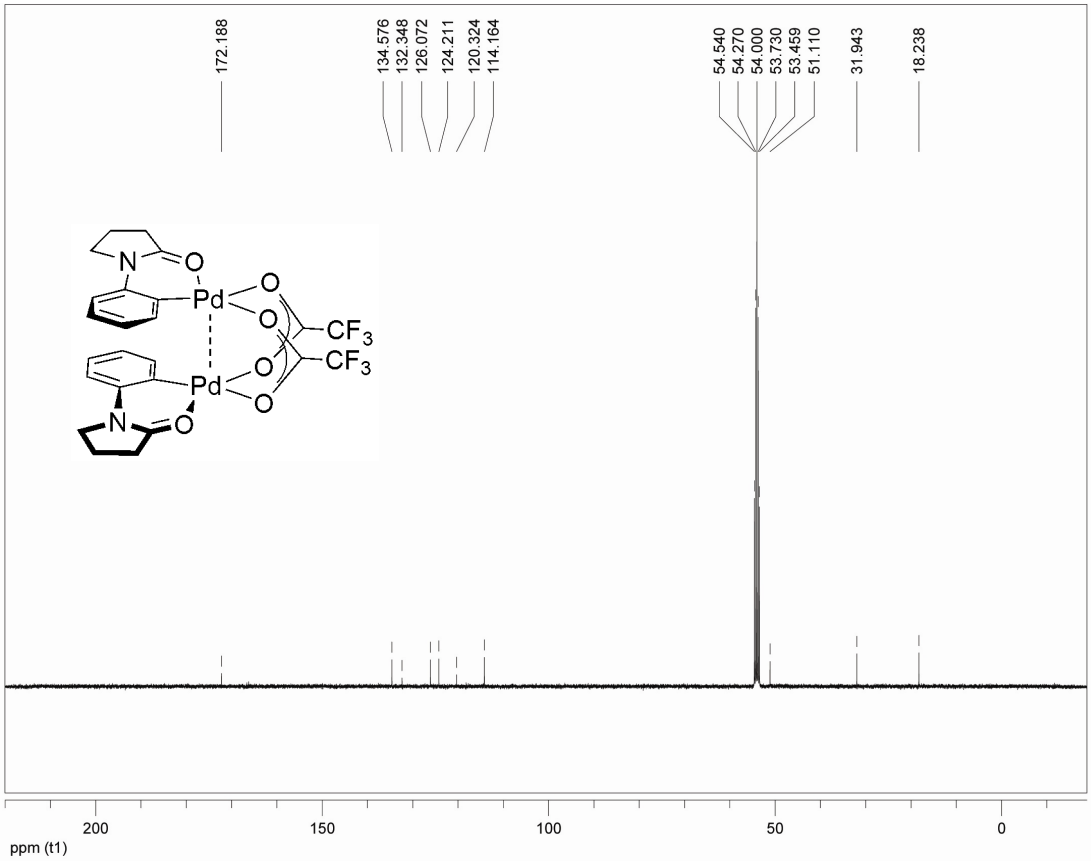
NMR spectra of compound **3a**





NMR spectra of compound **3b**





6. Crystallographic data for bimetallic Pd complex 3a

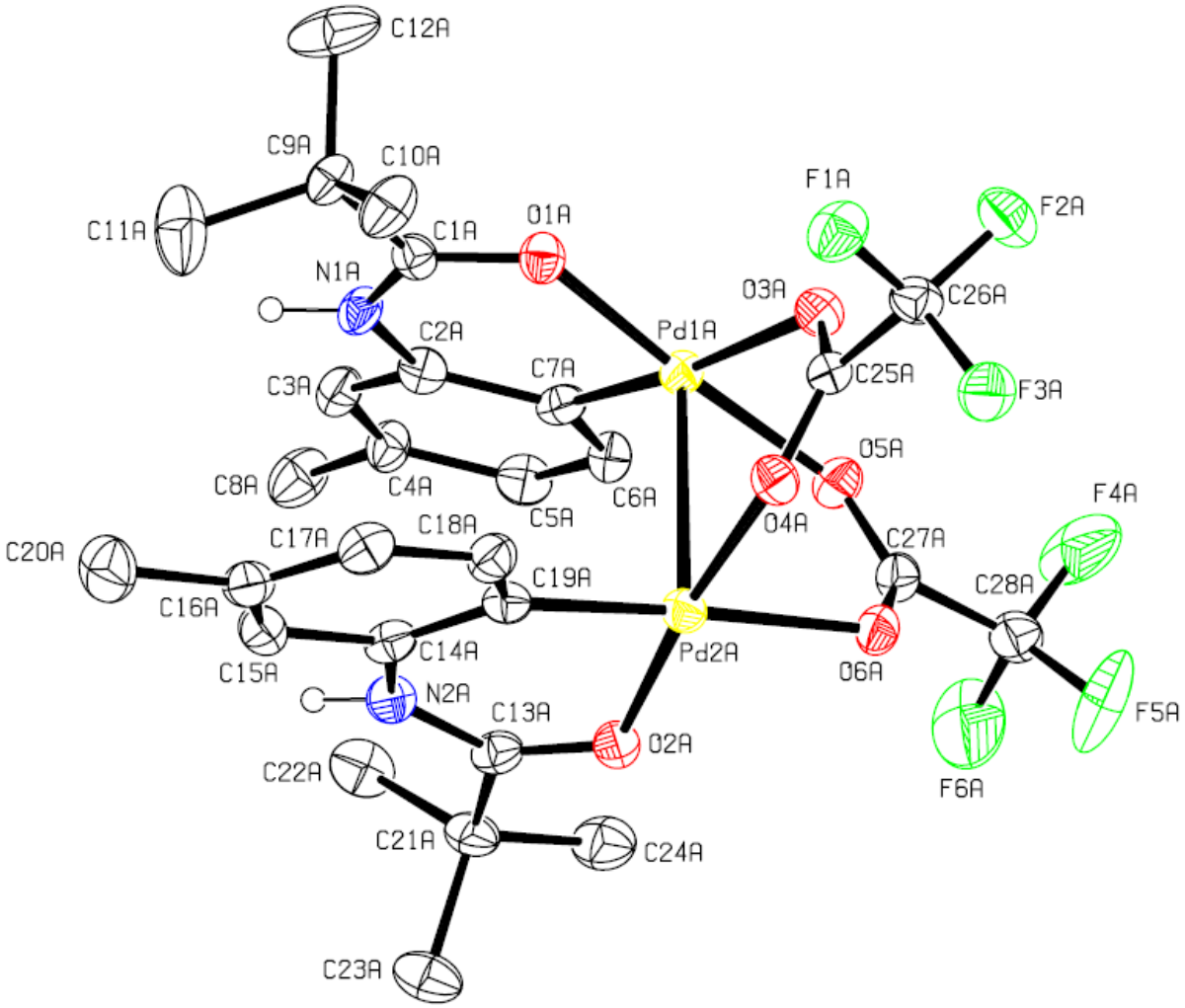


Table 1. Crystal data and structure refinement for k1031a.

Identification code	k1031a	
Empirical formula	C29 H34 Cl2 F6 N2 O6 Pd2	
Formula weight	904.28	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 33.6360(3) Å	α= 90°.
	b = 11.4193(5) Å	β= 90°.
	c = 18.0125(9) Å	γ = 90°.
Volume	6918.6(5) Å^3	
Z	8	
Density (calculated)	1.736 Mg/m^3	

Absorption coefficient	1.269 mm^{-1}
F(000)	3600
Crystal size	0.28 x 0.15 x 0.08 mm^3
Theta range for data collection	2.57 to 27.53°.
Index ranges	-43<=h<=39, -10<=k<=14, -23<=l<=23
Reflections collected	38514
Independent reflections	14407 [R(int) = 0.0622]
Completeness to theta = 27.53°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.894 and 0.719
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14407 / 1 / 863
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0546, wR2 = 0.1166
R indices (all data)	R1 = 0.0898, wR2 = 0.1359
Absolute structure parameter	-0.01(3)
Largest diff. peak and hole	1.039 and -0.963 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for k1031a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1A)	4349(1)	452(1)	2392(1)	34(1)
Pd(2A)	4833(1)	175(1)	3747(1)	35(1)
F(1A)	3928(2)	-3215(5)	3748(3)	60(1)
F(2A)	3456(1)	-1945(5)	3826(3)	62(2)
F(3A)	3861(2)	-2179(5)	4743(3)	58(2)
F(4A)	3661(2)	3343(7)	3703(5)	126(4)
F(5A)	3932(2)	3010(7)	4711(4)	103(3)
F(6A)	4218(3)	3990(6)	3908(6)	122(3)
O(1A)	4509(2)	-984(5)	1833(3)	39(1)
O(2A)	5170(2)	1591(5)	3606(3)	40(1)
O(3A)	3992(2)	-725(5)	3093(3)	38(1)
O(4A)	4448(2)	-1181(5)	3971(3)	40(1)
O(5A)	4145(2)	1885(5)	2995(3)	43(1)
O(6A)	4379(2)	1367(6)	4123(3)	41(1)
N(1A)	4971(2)	-201(6)	1078(4)	38(2)
N(2A)	5621(2)	791(6)	2812(4)	40(2)
C(1A)	4794(2)	-1108(7)	1377(4)	35(2)
C(2A)	4886(2)	999(7)	1148(5)	36(2)
C(3A)	5069(3)	1750(8)	630(5)	43(2)
C(4A)	5004(2)	2940(8)	626(5)	39(2)
C(5A)	4746(2)	3388(8)	1150(5)	45(2)
C(6A)	4553(2)	2657(8)	1660(5)	40(2)
C(7A)	4622(2)	1458(7)	1684(4)	35(2)
C(8A)	5218(3)	3771(9)	103(5)	57(3)
C(9A)	4898(2)	-2356(7)	1148(5)	38(2)
C(10A)	4866(3)	-3132(9)	1829(6)	57(3)
C(11A)	5331(3)	-2421(11)	855(8)	85(4)
C(12A)	4613(4)	-2715(10)	543(7)	86(4)
C(13A)	5443(3)	1701(7)	3136(5)	38(2)
C(14A)	5575(2)	-406(7)	2994(5)	36(2)
C(15A)	5875(2)	-1151(8)	2734(5)	46(2)
C(16A)	5881(3)	-2325(9)	2912(5)	46(2)
C(17A)	5574(3)	-2757(8)	3362(5)	46(2)

C(18A)	5274(3)	-2006(8)	3601(5)	43(2)
C(19A)	5264(2)	-829(8)	3416(4)	35(2)
C(20A)	6206(3)	-3141(9)	2612(7)	67(3)
C(21A)	5592(2)	2926(8)	2968(5)	43(2)
C(22A)	5696(3)	3058(9)	2142(5)	55(3)
C(23A)	5962(3)	3150(9)	3443(6)	56(3)
C(24A)	5271(3)	3801(9)	3176(6)	58(3)
C(25A)	4118(2)	-1246(7)	3656(5)	36(2)
C(26A)	3834(3)	-2162(8)	3988(5)	43(2)
C(27A)	4194(2)	1985(8)	3680(5)	41(2)
C(28A)	3991(3)	3082(9)	4009(5)	48(2)
Pd(1B)	6823(1)	2001(1)	2294(1)	39(1)
Pd(2B)	7386(1)	1944(1)	1059(1)	36(1)
F(1B)	6811(3)	5686(6)	664(7)	150(5)
F(2B)	6256(3)	5128(8)	980(5)	134(4)
F(3B)	6482(2)	4653(6)	-40(4)	96(2)
F(4B)	5947(2)	-8(6)	776(3)	72(2)
F(5B)	6384(2)	-398(6)	-67(3)	68(2)
F(6B)	6364(2)	-1391(5)	943(3)	72(2)
O(1B)	7046(2)	3388(5)	2800(3)	46(2)
O(2B)	7649(2)	440(5)	1328(3)	40(1)
O(3B)	6582(2)	3272(6)	1517(3)	46(2)
O(4B)	7084(2)	3397(5)	694(3)	44(2)
O(5B)	6529(2)	695(6)	1712(3)	46(2)
O(6B)	6889(2)	896(6)	659(3)	43(2)
N(1B)	7416(2)	2479(6)	3676(4)	45(2)
N(2B)	8172(2)	1140(6)	1967(4)	39(2)
C(1B)	7293(3)	3435(8)	3323(5)	40(2)
C(2B)	7304(3)	1317(8)	3591(5)	43(2)
C(3B)	7459(3)	523(9)	4109(5)	48(2)
C(4B)	7372(3)	-638(8)	4101(5)	44(2)
C(5B)	7116(3)	-1038(8)	3556(5)	45(2)
C(6B)	6952(2)	-254(8)	3036(5)	41(2)
C(7B)	7046(2)	932(8)	3030(5)	40(2)
C(8B)	7560(3)	-1486(8)	4656(5)	55(3)
C(9B)	7443(3)	4620(8)	3558(5)	47(2)
C(10B)	7321(4)	5556(9)	3001(7)	71(3)
C(11B)	7902(3)	4597(11)	3620(9)	92(4)

C(12B)	7259(5)	4901(11)	4305(8)	104(5)
C(13B)	7950(2)	271(7)	1738(5)	36(2)
C(14B)	8158(2)	2356(7)	1781(5)	35(2)
C(15B)	8495(2)	3004(8)	1997(5)	40(2)
C(16B)	8516(3)	4192(8)	1837(5)	44(2)
C(17B)	8202(3)	4706(9)	1450(6)	50(2)
C(18B)	7875(3)	4033(8)	1247(5)	45(2)
C(19B)	7843(2)	2836(7)	1395(4)	36(2)
C(20B)	8868(3)	4908(9)	2058(6)	57(3)
C(21B)	8060(2)	-983(8)	1952(5)	39(2)
C(22B)	8159(3)	-1038(9)	2779(5)	49(2)
C(23B)	8424(3)	-1343(9)	1494(5)	53(2)
C(24B)	7713(2)	-1807(8)	1790(6)	49(2)
C(25B)	6770(2)	3700(8)	980(5)	44(2)
C(26B)	6575(3)	4785(9)	654(6)	51(2)
C(27B)	6617(2)	519(8)	1044(5)	43(2)
C(28B)	6323(3)	-327(10)	667(6)	54(3)
C(1S)	3676(4)	-458(13)	-415(6)	91(4)
Cl(1)	3477(1)	-1693(4)	46(2)	96(1)
Cl(2)	4096(1)	76(3)	-13(2)	87(1)
C(2S)	3939(3)	3188(11)	50(7)	74(3)
Cl(3)	3495(1)	2739(3)	-363(2)	91(1)
Cl(4)	4022(1)	4688(3)	-83(2)	88(1)

Table 3. Bond lengths [Å] and angles [°] for k1031a.

Pd(1A)-C(7A)	1.947(9)
Pd(1A)-O(1A)	1.997(6)
Pd(1A)-O(5A)	2.081(6)
Pd(1A)-O(3A)	2.201(5)
Pd(1A)-Pd(2A)	2.9515(9)
Pd(2A)-C(19A)	1.942(8)
Pd(2A)-O(2A)	1.991(5)
Pd(2A)-O(4A)	2.058(6)
Pd(2A)-O(6A)	2.157(6)
F(1A)-C(26A)	1.317(10)
F(2A)-C(26A)	1.329(9)
F(3A)-C(26A)	1.362(10)
F(4A)-C(28A)	1.274(11)
F(5A)-C(28A)	1.284(11)
F(6A)-C(28A)	1.301(11)
O(1A)-C(1A)	1.271(9)
O(2A)-C(13A)	1.256(10)
O(3A)-C(25A)	1.250(10)
O(4A)-C(25A)	1.249(9)
O(5A)-C(27A)	1.250(10)
O(6A)-C(27A)	1.233(10)
N(1A)-C(1A)	1.312(10)
N(1A)-C(2A)	1.405(10)
N(2A)-C(13A)	1.333(10)
N(2A)-C(14A)	1.414(10)
C(1A)-C(9A)	1.525(11)
C(2A)-C(3A)	1.410(12)
C(2A)-C(7A)	1.412(11)
C(3A)-C(4A)	1.376(12)
C(4A)-C(5A)	1.381(12)
C(4A)-C(8A)	1.518(12)
C(5A)-C(6A)	1.402(12)
C(6A)-C(7A)	1.390(12)
C(9A)-C(12A)	1.509(13)
C(9A)-C(10A)	1.516(13)
C(9A)-C(11A)	1.551(13)

C(13A)-C(21A)	1.516(12)
C(14A)-C(19A)	1.379(11)
C(14A)-C(15A)	1.401(11)
C(15A)-C(16A)	1.379(13)
C(16A)-C(17A)	1.402(13)
C(16A)-C(20A)	1.534(12)
C(17A)-C(18A)	1.394(12)
C(18A)-C(19A)	1.385(11)
C(21A)-C(24A)	1.517(12)
C(21A)-C(23A)	1.533(12)
C(21A)-C(22A)	1.536(13)
C(25A)-C(26A)	1.538(11)
C(27A)-C(28A)	1.545(13)
Pd(1B)-C(7B)	1.952(9)
Pd(1B)-O(1B)	1.976(6)
Pd(1B)-O(5B)	2.074(6)
Pd(1B)-O(3B)	2.174(6)
Pd(1B)-Pd(2B)	2.9233(9)
Pd(2B)-C(19B)	1.941(8)
Pd(2B)-O(2B)	1.992(6)
Pd(2B)-O(4B)	2.053(6)
Pd(2B)-O(6B)	2.178(6)
F(1B)-C(26B)	1.300(12)
F(2B)-C(26B)	1.283(11)
F(3B)-C(26B)	1.297(12)
F(4B)-C(28B)	1.332(11)
F(5B)-C(28B)	1.341(12)
F(6B)-C(28B)	1.321(11)
O(1B)-C(1B)	1.259(10)
O(2B)-C(13B)	1.266(9)
O(3B)-C(25B)	1.254(10)
O(4B)-C(25B)	1.226(10)
O(5B)-C(27B)	1.254(11)
O(6B)-C(27B)	1.227(10)
N(1B)-C(1B)	1.329(11)
N(1B)-C(2B)	1.388(11)
N(2B)-C(13B)	1.309(10)
N(2B)-C(14B)	1.430(10)

C(1B)-C(9B)	1.504(12)
C(2B)-C(3B)	1.401(12)
C(2B)-C(7B)	1.403(12)
C(3B)-C(4B)	1.357(12)
C(4B)-C(5B)	1.383(12)
C(4B)-C(8B)	1.528(12)
C(5B)-C(6B)	1.409(12)
C(6B)-C(7B)	1.391(12)
C(9B)-C(12B)	1.515(15)
C(9B)-C(10B)	1.522(14)
C(9B)-C(11B)	1.548(14)
C(13B)-C(21B)	1.529(11)
C(14B)-C(19B)	1.381(11)
C(14B)-C(15B)	1.407(11)
C(15B)-C(16B)	1.389(12)
C(16B)-C(17B)	1.394(13)
C(16B)-C(20B)	1.492(12)
C(17B)-C(18B)	1.390(12)
C(18B)-C(19B)	1.397(12)
C(21B)-C(24B)	1.527(12)
C(21B)-C(22B)	1.527(12)
C(21B)-C(23B)	1.531(12)
C(25B)-C(26B)	1.519(13)
C(27B)-C(28B)	1.538(12)
C(1S)-Cl(2)	1.701(14)
C(1S)-Cl(1)	1.768(14)
C(2S)-Cl(3)	1.745(11)
C(2S)-Cl(4)	1.752(12)

C(7A)-Pd(1A)-O(1A)	91.6(3)
C(7A)-Pd(1A)-O(5A)	91.9(3)
O(1A)-Pd(1A)-O(5A)	175.9(2)
C(7A)-Pd(1A)-O(3A)	173.6(3)
O(1A)-Pd(1A)-O(3A)	86.3(2)
O(5A)-Pd(1A)-O(3A)	90.0(2)
C(7A)-Pd(1A)-Pd(2A)	110.1(2)
O(1A)-Pd(1A)-Pd(2A)	100.37(16)
O(5A)-Pd(1A)-Pd(2A)	80.49(16)

O(3A)-Pd(1A)-Pd(2A)	76.19(15)
C(19A)-Pd(2A)-O(2A)	90.9(3)
C(19A)-Pd(2A)-O(4A)	94.9(3)
O(2A)-Pd(2A)-O(4A)	173.7(2)
C(19A)-Pd(2A)-O(6A)	176.8(3)
O(2A)-Pd(2A)-O(6A)	86.0(2)
O(4A)-Pd(2A)-O(6A)	88.1(2)
C(19A)-Pd(2A)-Pd(1A)	102.8(2)
O(2A)-Pd(2A)-Pd(1A)	96.98(16)
O(4A)-Pd(2A)-Pd(1A)	84.04(15)
O(6A)-Pd(2A)-Pd(1A)	78.50(15)
C(1A)-O(1A)-Pd(1A)	128.4(5)
C(13A)-O(2A)-Pd(2A)	125.7(5)
C(25A)-O(3A)-Pd(1A)	124.7(5)
C(25A)-O(4A)-Pd(2A)	120.9(5)
C(27A)-O(5A)-Pd(1A)	122.9(6)
C(27A)-O(6A)-Pd(2A)	121.0(5)
C(1A)-N(1A)-C(2A)	129.7(7)
C(13A)-N(2A)-C(14A)	127.0(7)
O(1A)-C(1A)-N(1A)	121.4(8)
O(1A)-C(1A)-C(9A)	117.0(7)
N(1A)-C(1A)-C(9A)	121.5(7)
N(1A)-C(2A)-C(3A)	116.4(8)
N(1A)-C(2A)-C(7A)	123.5(7)
C(3A)-C(2A)-C(7A)	120.1(8)
C(4A)-C(3A)-C(2A)	122.3(8)
C(3A)-C(4A)-C(5A)	117.6(8)
C(3A)-C(4A)-C(8A)	123.0(8)
C(5A)-C(4A)-C(8A)	119.3(8)
C(4A)-C(5A)-C(6A)	121.2(8)
C(7A)-C(6A)-C(5A)	122.0(8)
C(6A)-C(7A)-C(2A)	116.8(8)
C(6A)-C(7A)-Pd(1A)	121.5(6)
C(2A)-C(7A)-Pd(1A)	121.7(6)
C(12A)-C(9A)-C(10A)	112.4(9)
C(12A)-C(9A)-C(1A)	107.6(7)
C(10A)-C(9A)-C(1A)	108.1(7)
C(12A)-C(9A)-C(11A)	109.8(10)

C(10A)-C(9A)-C(11A)	108.3(8)
C(1A)-C(9A)-C(11A)	110.7(8)
O(2A)-C(13A)-N(2A)	123.1(8)
O(2A)-C(13A)-C(21A)	117.8(8)
N(2A)-C(13A)-C(21A)	119.0(8)
C(19A)-C(14A)-C(15A)	121.2(8)
C(19A)-C(14A)-N(2A)	123.3(7)
C(15A)-C(14A)-N(2A)	115.5(8)
C(16A)-C(15A)-C(14A)	121.6(8)
C(15A)-C(16A)-C(17A)	117.8(8)
C(15A)-C(16A)-C(20A)	121.3(9)
C(17A)-C(16A)-C(20A)	120.9(9)
C(18A)-C(17A)-C(16A)	119.7(9)
C(19A)-C(18A)-C(17A)	122.6(8)
C(14A)-C(19A)-C(18A)	117.1(8)
C(14A)-C(19A)-Pd(2A)	121.9(6)
C(18A)-C(19A)-Pd(2A)	121.0(6)
C(13A)-C(21A)-C(24A)	109.0(7)
C(13A)-C(21A)-C(23A)	108.1(7)
C(24A)-C(21A)-C(23A)	109.3(8)
C(13A)-C(21A)-C(22A)	111.0(8)
C(24A)-C(21A)-C(22A)	109.7(8)
C(23A)-C(21A)-C(22A)	109.7(8)
O(4A)-C(25A)-O(3A)	130.1(8)
O(4A)-C(25A)-C(26A)	114.5(7)
O(3A)-C(25A)-C(26A)	115.3(7)
F(1A)-C(26A)-F(2A)	109.1(7)
F(1A)-C(26A)-F(3A)	107.4(7)
F(2A)-C(26A)-F(3A)	106.5(7)
F(1A)-C(26A)-C(25A)	110.2(7)
F(2A)-C(26A)-C(25A)	112.5(7)
F(3A)-C(26A)-C(25A)	111.0(7)
O(6A)-C(27A)-O(5A)	130.8(8)
O(6A)-C(27A)-C(28A)	116.0(8)
O(5A)-C(27A)-C(28A)	113.2(8)
F(4A)-C(28A)-F(5A)	108.0(9)
F(4A)-C(28A)-F(6A)	105.4(10)
F(5A)-C(28A)-F(6A)	106.1(9)

F(4A)-C(28A)-C(27A)	114.2(8)
F(5A)-C(28A)-C(27A)	113.1(8)
F(6A)-C(28A)-C(27A)	109.5(8)
C(7B)-Pd(1B)-O(1B)	92.4(3)
C(7B)-Pd(1B)-O(5B)	94.4(3)
O(1B)-Pd(1B)-O(5B)	172.3(2)
C(7B)-Pd(1B)-O(3B)	176.8(3)
O(1B)-Pd(1B)-O(3B)	84.4(2)
O(5B)-Pd(1B)-O(3B)	88.7(2)
C(7B)-Pd(1B)-Pd(2B)	104.7(2)
O(1B)-Pd(1B)-Pd(2B)	97.01(17)
O(5B)-Pd(1B)-Pd(2B)	84.67(16)
O(3B)-Pd(1B)-Pd(2B)	76.47(15)
C(19B)-Pd(2B)-O(2B)	91.4(3)
C(19B)-Pd(2B)-O(4B)	93.8(3)
O(2B)-Pd(2B)-O(4B)	173.9(2)
C(19B)-Pd(2B)-O(6B)	177.7(3)
O(2B)-Pd(2B)-O(6B)	87.0(2)
O(4B)-Pd(2B)-O(6B)	87.6(2)
C(19B)-Pd(2B)-Pd(1B)	105.3(2)
O(2B)-Pd(2B)-Pd(1B)	97.05(16)
O(4B)-Pd(2B)-Pd(1B)	84.55(17)
O(6B)-Pd(2B)-Pd(1B)	76.51(16)
C(1B)-O(1B)-Pd(1B)	129.1(6)
C(13B)-O(2B)-Pd(2B)	128.9(6)
C(25B)-O(3B)-Pd(1B)	124.7(5)
C(25B)-O(4B)-Pd(2B)	121.4(6)
C(27B)-O(5B)-Pd(1B)	119.3(5)
C(27B)-O(6B)-Pd(2B)	125.4(6)
C(1B)-N(1B)-C(2B)	130.5(8)
C(13B)-N(2B)-C(14B)	130.1(7)
O(1B)-C(1B)-N(1B)	121.9(8)
O(1B)-C(1B)-C(9B)	118.0(8)
N(1B)-C(1B)-C(9B)	120.1(8)
N(1B)-C(2B)-C(3B)	116.4(8)
N(1B)-C(2B)-C(7B)	123.1(8)
C(3B)-C(2B)-C(7B)	120.5(9)
C(4B)-C(3B)-C(2B)	123.0(9)

C(3B)-C(4B)-C(5B)	117.6(8)
C(3B)-C(4B)-C(8B)	121.6(8)
C(5B)-C(4B)-C(8B)	120.8(9)
C(4B)-C(5B)-C(6B)	120.5(8)
C(7B)-C(6B)-C(5B)	122.2(8)
C(6B)-C(7B)-C(2B)	116.1(8)
C(6B)-C(7B)-Pd(1B)	121.7(6)
C(2B)-C(7B)-Pd(1B)	122.1(7)
C(1B)-C(9B)-C(12B)	107.7(8)
C(1B)-C(9B)-C(10B)	110.9(8)
C(12B)-C(9B)-C(10B)	109.1(9)
C(1B)-C(9B)-C(11B)	109.7(8)
C(12B)-C(9B)-C(11B)	110.3(11)
C(10B)-C(9B)-C(11B)	109.1(9)
O(2B)-C(13B)-N(2B)	121.6(8)
O(2B)-C(13B)-C(21B)	118.9(7)
N(2B)-C(13B)-C(21B)	119.4(7)
C(19B)-C(14B)-C(15B)	123.2(8)
C(19B)-C(14B)-N(2B)	121.9(7)
C(15B)-C(14B)-N(2B)	114.9(7)
C(16B)-C(15B)-C(14B)	119.9(8)
C(15B)-C(16B)-C(17B)	118.4(8)
C(15B)-C(16B)-C(20B)	121.4(8)
C(17B)-C(16B)-C(20B)	120.2(9)
C(18B)-C(17B)-C(16B)	119.9(9)
C(17B)-C(18B)-C(19B)	123.4(8)
C(14B)-C(19B)-C(18B)	115.2(8)
C(14B)-C(19B)-Pd(2B)	123.8(6)
C(18B)-C(19B)-Pd(2B)	121.0(6)
C(24B)-C(21B)-C(22B)	109.1(8)
C(24B)-C(21B)-C(13B)	110.0(7)
C(22B)-C(21B)-C(13B)	109.7(8)
C(24B)-C(21B)-C(23B)	110.1(8)
C(22B)-C(21B)-C(23B)	109.8(7)
C(13B)-C(21B)-C(23B)	108.0(7)
O(4B)-C(25B)-O(3B)	130.4(9)
O(4B)-C(25B)-C(26B)	116.1(8)
O(3B)-C(25B)-C(26B)	113.4(8)

F(2B)-C(26B)-F(3B)	105.9(9)
F(2B)-C(26B)-F(1B)	105.2(10)
F(3B)-C(26B)-F(1B)	104.6(10)
F(2B)-C(26B)-C(25B)	115.7(9)
F(3B)-C(26B)-C(25B)	112.5(8)
F(1B)-C(26B)-C(25B)	112.1(8)
O(6B)-C(27B)-O(5B)	131.4(8)
O(6B)-C(27B)-C(28B)	116.8(9)
O(5B)-C(27B)-C(28B)	111.9(8)
F(6B)-C(28B)-F(4B)	107.2(8)
F(6B)-C(28B)-F(5B)	107.4(9)
F(4B)-C(28B)-F(5B)	107.8(8)
F(6B)-C(28B)-C(27B)	110.2(8)
F(4B)-C(28B)-C(27B)	111.9(9)
F(5B)-C(28B)-C(27B)	112.1(8)
Cl(2)-C(1S)-Cl(1)	113.6(6)
Cl(3)-C(2S)-Cl(4)	111.4(7)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for k1031a. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1A)	34(1)	37(1)	30(1)	-2(1)	0(1)	1(1)
Pd(2A)	32(1)	39(1)	33(1)	0(1)	-1(1)	-1(1)
F(1A)	78(4)	43(3)	60(4)	-5(3)	10(3)	-7(3)
F(2A)	42(3)	79(4)	66(4)	10(3)	0(3)	-11(3)
F(3A)	63(3)	67(4)	44(3)	5(3)	7(3)	-11(3)
F(4A)	114(6)	139(7)	126(7)	-83(6)	-52(5)	84(5)
F(5A)	160(7)	95(6)	53(4)	7(4)	41(4)	69(5)
F(6A)	127(6)	56(5)	184(9)	-38(5)	54(6)	-18(4)
O(1A)	40(3)	37(4)	39(3)	3(3)	6(3)	0(3)
O(2A)	37(3)	38(3)	46(4)	-6(3)	3(3)	-2(3)
O(3A)	38(3)	36(4)	41(3)	4(3)	1(3)	-3(3)
O(4A)	37(3)	41(4)	42(4)	4(3)	2(2)	-2(3)
O(5A)	50(3)	47(4)	33(3)	-1(3)	1(3)	2(3)
O(6A)	39(3)	53(4)	32(3)	-4(3)	4(3)	4(3)
N(1A)	45(4)	28(4)	40(4)	-8(3)	8(4)	-1(3)
N(2A)	44(4)	40(4)	35(4)	4(3)	3(3)	-8(3)
C(1A)	32(4)	38(5)	34(5)	4(4)	-2(3)	2(4)
C(2A)	38(4)	35(5)	36(5)	5(4)	-4(4)	2(4)
C(3A)	47(5)	48(6)	35(5)	-7(4)	7(4)	-1(4)
C(4A)	44(5)	42(6)	32(5)	2(4)	9(4)	-2(4)
C(5A)	49(5)	35(5)	49(5)	5(4)	-2(4)	-5(4)
C(6A)	39(4)	43(6)	37(5)	-1(4)	6(4)	2(4)
C(7A)	40(4)	31(5)	35(5)	-6(4)	-9(4)	4(4)
C(8A)	81(7)	48(6)	41(5)	1(5)	7(5)	-4(5)
C(9A)	52(5)	30(5)	32(4)	-1(4)	6(4)	2(4)
C(10A)	80(7)	42(6)	51(6)	-7(5)	9(5)	8(5)
C(11A)	80(8)	53(7)	121(12)	6(7)	50(8)	12(6)
C(12A)	124(10)	41(7)	92(9)	-27(6)	-56(8)	21(7)
C(13A)	44(5)	31(5)	39(5)	-4(4)	-7(4)	2(4)
C(14A)	45(4)	28(5)	35(5)	-3(4)	-10(4)	8(4)
C(15A)	36(4)	48(6)	52(5)	-3(5)	0(4)	0(4)
C(16A)	42(5)	47(6)	49(6)	-12(5)	-7(4)	4(4)
C(17A)	59(6)	34(5)	44(5)	1(4)	-2(4)	0(4)

C(18A)	45(5)	46(5)	37(5)	-3(4)	-1(4)	4(4)
C(19A)	36(4)	35(5)	35(5)	-1(4)	-6(3)	-1(4)
C(20A)	56(6)	58(7)	86(8)	-6(6)	2(6)	17(5)
C(21A)	41(5)	36(5)	53(6)	-3(4)	-6(4)	-9(4)
C(22A)	59(5)	49(6)	57(7)	18(5)	-6(5)	-9(5)
C(23A)	52(5)	41(6)	77(7)	7(5)	-18(5)	-9(5)
C(24A)	64(6)	42(6)	68(7)	-6(5)	-6(5)	-6(5)
C(25A)	35(4)	39(5)	33(5)	-5(4)	-1(4)	-1(3)
C(26A)	43(5)	46(6)	40(5)	4(4)	-5(4)	-5(4)
C(27A)	38(4)	44(5)	40(5)	-4(5)	7(4)	-3(4)
C(28A)	45(5)	61(7)	39(6)	3(5)	-4(4)	-1(5)
Pd(1B)	35(1)	49(1)	32(1)	2(1)	-1(1)	-2(1)
Pd(2B)	34(1)	41(1)	34(1)	2(1)	-1(1)	-1(1)
F(1B)	129(7)	44(5)	276(13)	37(6)	-91(8)	-11(5)
F(2B)	144(7)	146(8)	112(7)	68(6)	56(6)	101(6)
F(3B)	152(7)	75(5)	59(4)	3(4)	-26(4)	45(5)
F(4B)	51(3)	91(5)	74(4)	1(4)	-19(3)	-11(3)
F(5B)	69(4)	80(5)	57(4)	-3(3)	-12(3)	-24(3)
F(6B)	99(4)	50(4)	66(4)	-1(3)	-7(4)	-15(3)
O(1B)	50(3)	49(4)	39(4)	4(3)	-4(3)	4(3)
O(2B)	32(3)	44(4)	42(3)	1(3)	-6(2)	-6(2)
O(3B)	40(3)	56(4)	44(4)	7(3)	-1(3)	12(3)
O(4B)	43(3)	44(4)	47(4)	8(3)	4(3)	-1(3)
O(5B)	42(3)	60(4)	34(3)	-1(3)	-6(3)	-12(3)
O(6B)	38(3)	53(4)	38(3)	-2(3)	-4(3)	-4(3)
N(1B)	49(4)	39(4)	47(5)	11(4)	-19(4)	0(3)
N(2B)	42(4)	33(4)	43(4)	-7(3)	-4(3)	3(3)
C(1B)	46(5)	45(6)	29(5)	-2(4)	4(4)	-3(4)
C(2B)	48(5)	40(5)	41(6)	12(4)	8(4)	3(4)
C(3B)	56(5)	58(7)	29(5)	-1(4)	-5(4)	1(5)
C(4B)	51(5)	44(6)	38(5)	5(4)	2(4)	-3(4)
C(5B)	51(5)	33(5)	51(6)	5(4)	9(4)	-7(4)
C(6B)	40(4)	52(6)	30(5)	2(4)	6(4)	-3(4)
C(7B)	37(4)	43(6)	39(5)	-1(4)	7(4)	-6(4)
C(8B)	78(7)	42(6)	47(6)	9(4)	-9(5)	9(5)
C(9B)	54(5)	40(5)	47(6)	0(4)	4(4)	5(4)
C(10B)	97(9)	37(6)	79(8)	0(6)	-20(6)	-6(6)
C(11B)	66(7)	64(8)	146(14)	-13(9)	-20(8)	-2(6)

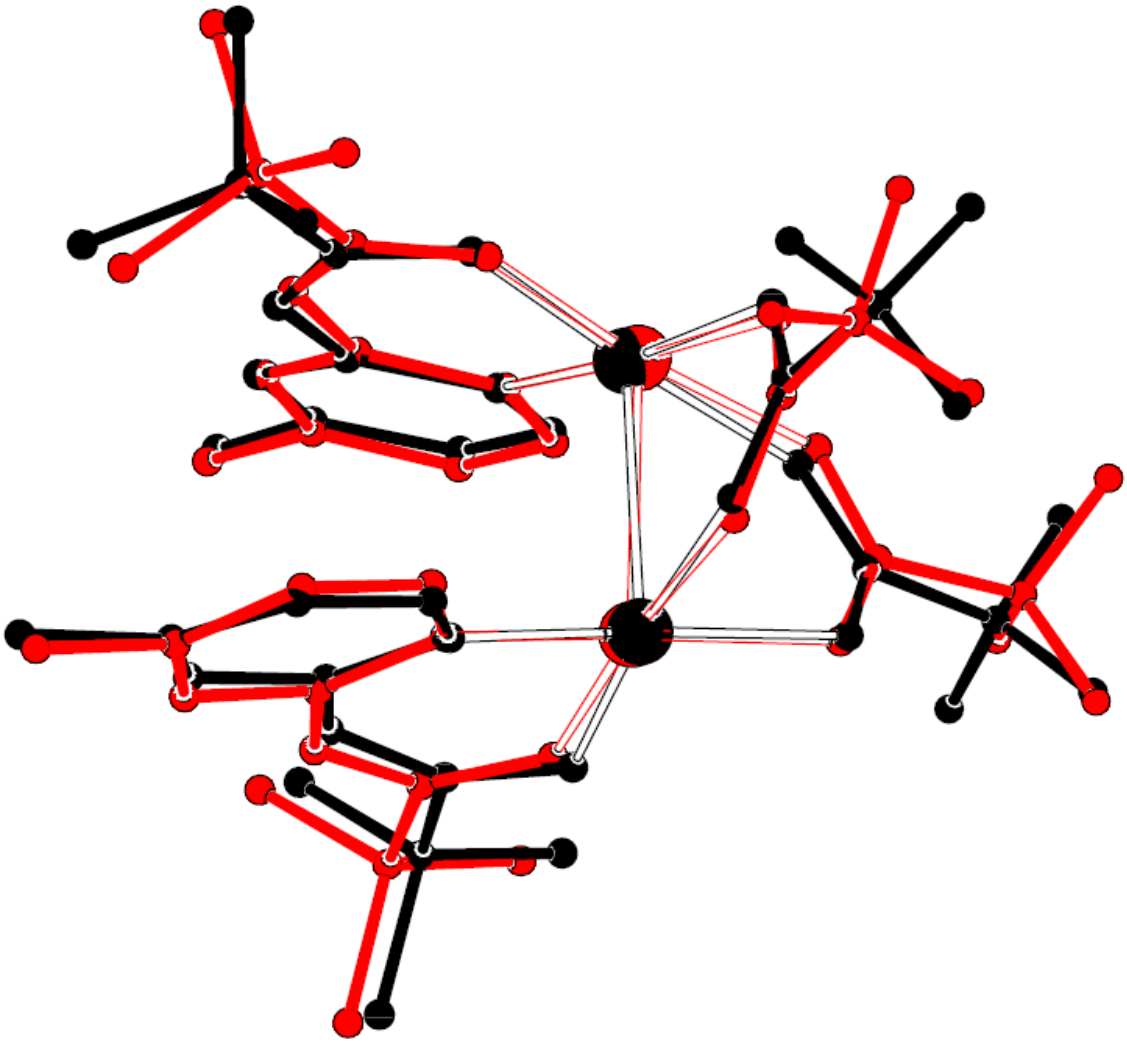
C(12B)	181(15)	51(8)	80(10)	-20(7)	40(10)	-5(9)
C(13B)	32(4)	40(5)	36(5)	3(4)	9(4)	-1(4)
C(14B)	35(4)	29(5)	42(5)	4(4)	0(4)	0(3)
C(15B)	36(4)	49(6)	36(5)	-2(4)	-2(4)	-8(4)
C(16B)	48(5)	38(5)	47(5)	-1(4)	-1(4)	-12(4)
C(17B)	49(5)	39(6)	61(7)	6(5)	-1(5)	-9(4)
C(18B)	45(5)	47(6)	42(5)	10(4)	-4(4)	1(4)
C(19B)	40(4)	35(5)	34(4)	-6(4)	4(4)	0(4)
C(20B)	53(5)	49(6)	70(7)	4(5)	-4(5)	-13(5)
C(21B)	31(4)	33(5)	54(6)	5(4)	1(4)	1(4)
C(22B)	45(5)	58(7)	45(6)	14(5)	-2(4)	-4(5)
C(23B)	60(6)	47(6)	52(6)	-4(5)	7(5)	4(5)
C(24B)	45(5)	42(6)	60(6)	0(5)	-3(4)	0(4)
C(25B)	39(4)	61(6)	32(5)	5(4)	-11(4)	-3(4)
C(26B)	55(6)	39(6)	58(7)	4(5)	-4(5)	10(5)
C(27B)	36(4)	47(6)	47(6)	-3(5)	-13(4)	-4(4)
C(28B)	47(5)	62(7)	54(7)	3(5)	-7(5)	-12(5)
C(1S)	113(10)	118(12)	41(6)	10(7)	-8(7)	29(9)
Cl(1)	71(2)	147(4)	71(2)	22(2)	13(2)	1(2)
Cl(2)	63(2)	99(3)	98(3)	26(2)	8(2)	16(2)
C(2S)	71(7)	88(10)	62(7)	15(7)	-11(6)	-19(7)
Cl(3)	83(2)	104(3)	86(2)	12(2)	-22(2)	-16(2)
Cl(4)	107(2)	73(2)	84(2)	10(2)	-5(2)	-10(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for k1031a.

	x	y	z	U(eq)
H(1AA)	5175	-369	790	45
H(2AA)	5785	953	2445	48
H(3AA)	5244	1424	271	52
H(5AA)	4698	4208	1164	54
H(6AA)	4369	2991	2000	48
H(8AA)	5379	3320	-248	85
H(8AB)	5391	4293	391	85
H(8AC)	5022	4238	-170	85
H(10A)	4595	-3093	2027	86
H(10B)	5054	-2861	2208	86
H(10C)	4929	-3942	1693	86
H(11A)	5358	-1919	417	127
H(11B)	5395	-3232	721	127
H(11C)	5514	-2154	1243	127
H(12A)	4343	-2754	746	129
H(12B)	4689	-3485	350	129
H(12C)	4621	-2138	141	129
H(15A)	6079	-840	2427	55
H(17A)	5571	-3559	3503	55
H(18A)	5067	-2314	3903	51
H(20A)	6193	-3893	2873	100
H(20B)	6467	-2782	2692	100
H(20C)	6164	-3268	2080	100
H(22A)	5465	2846	1840	82
H(22B)	5919	2540	2020	82
H(22C)	5771	3871	2040	82
H(23A)	5890	3121	3970	85
H(23B)	6071	3923	3324	85
H(23C)	6162	2548	3338	85
H(24A)	5023	3596	2922	87
H(24B)	5354	4589	3025	87
H(24C)	5229	3785	3714	87

H(1BA)	7597	2603	4018	54
H(2BA)	8359	944	2285	47
H(3BA)	7634	810	4481	57
H(5BA)	7051	-1846	3532	54
H(6BA)	6770	-546	2676	49
H(8BA)	7611	-1077	5124	83
H(8BB)	7811	-1784	4454	83
H(8BC)	7378	-2142	4745	83
H(10D)	7030	5594	2973	106
H(10E)	7429	5359	2511	106
H(10F)	7426	6317	3160	106
H(11D)	8017	4417	3133	138
H(11E)	7982	3996	3978	138
H(11F)	7997	5364	3787	138
H(12D)	6975	5061	4241	156
H(12E)	7389	5591	4518	156
H(12F)	7293	4232	4640	156
H(15B)	8707	2630	2251	48
H(17B)	8212	5513	1325	60
H(18B)	7662	4408	993	54
H(20D)	8788	5728	2117	86
H(20E)	9073	4852	1673	86
H(20F)	8974	4614	2529	86
H(22D)	7937	-714	3066	74
H(22E)	8400	-581	2876	74
H(22F)	8203	-1855	2924	74
H(23D)	8641	-788	1585	79
H(23E)	8355	-1338	966	79
H(23F)	8508	-2131	1640	79
H(24D)	7471	-1499	2023	73
H(24E)	7771	-2585	1992	73
H(24F)	7673	-1864	1252	73
H(1SA)	3736	-674	-936	109
H(1SB)	3472	168	-425	109
H(2SA)	4162	2739	-166	89
H(2SB)	3929	3017	588	89

The complex contains two independent molecules in the asymmetric unit exhibiting minor geometric differences. Shown below is a superposition of the two molecules.



7. Crystallographic data for bimetallic Pd complex 3b

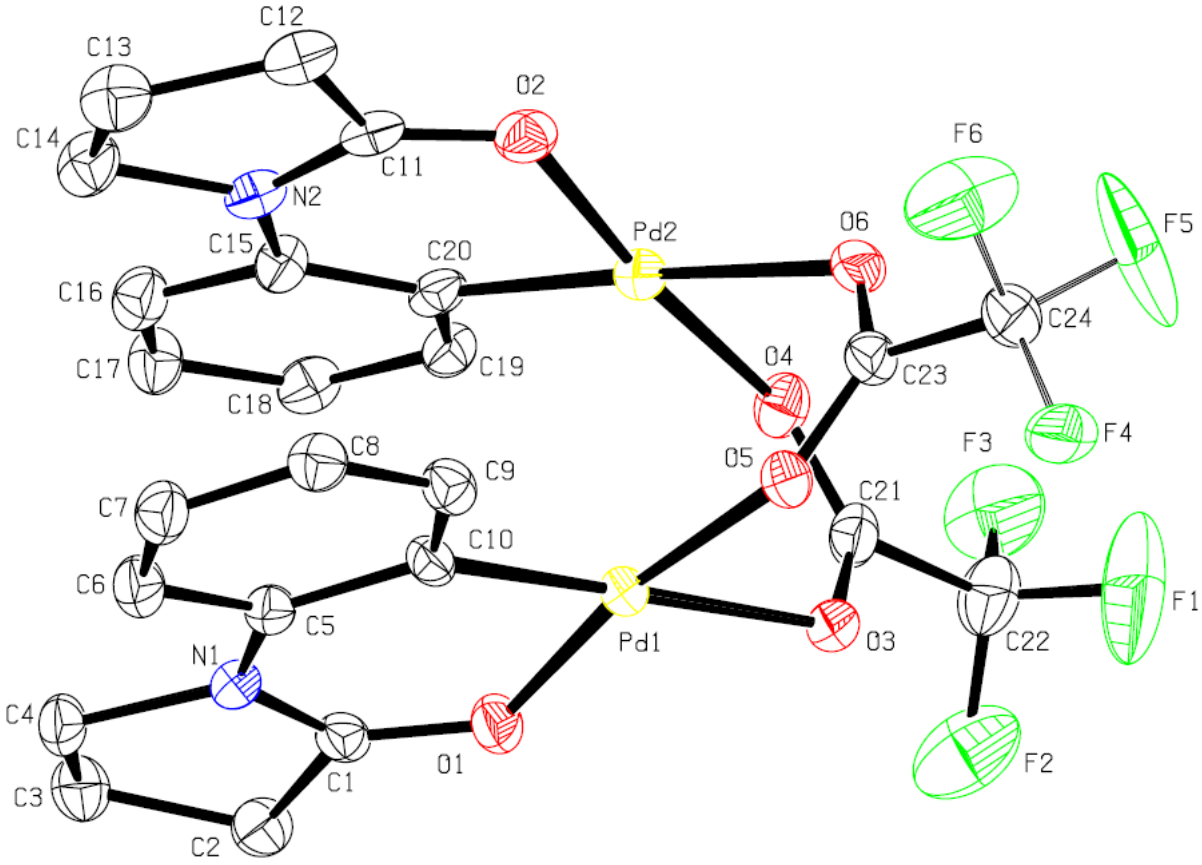


Table 1. Crystal data and structure refinement for k1035.

Identification code	k1035	
Empirical formula	C24 H20 F6 N2 O6 Pd2	
Formula weight	759.22	
Temperature	150(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 27.0838(8) Å	α= 90°.
	b = 16.8253(6) Å	β= 121.2360(15)°.
	c = 14.3465(4) Å	γ = 90°.
Volume	5589.9(3) Å^3	
Z	8	
Density (calculated)	1.804 Mg/m^3	
Absorption coefficient	1.367 mm^{-1}	
F(000)	2976	
Crystal size	0.15 x 0.09 x 0.08 mm^3	
Theta range for data collection	2.55 to 27.49°.	

Index ranges	-35<=h<=30, -21<=k<=21, -18<=l<=18
Reflections collected	19237
Independent reflections	6374 [R(int) = 0.066]
Completeness to theta = 27.49°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.899 and 0.791
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6374 / 6 / 374
Goodness-of-fit on F^2	0.983
Final R indices [I>2sigma(I)]	R1 = 0.0501, wR2 = 0.1200
R indices (all data)	R1 = 0.0928, wR2 = 0.1374
Largest diff. peak and hole	1.555 and -0.939 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for k1035. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	1128(1)	3712(1)	1677(1)	31(1)
Pd(2)	1383(1)	2404(1)	701(1)	34(1)
F(1)	-395(2)	1722(4)	668(5)	144(3)
F(2)	-767(2)	2699(4)	-388(4)	102(2)
F(3)	-540(2)	1683(3)	-947(4)	101(2)
F(4)	1610(3)	2117(3)	4646(4)	65(2)
F(5)	1481(5)	1065(4)	3743(5)	146(5)
F(6)	2270(3)	1640(6)	4493(4)	108(4)
F(4A)	1945(17)	2210(20)	4830(20)	110(14)
F(5A)	1216(7)	1590(20)	3890(20)	76(10)
F(6A)	2001(10)	1142(10)	4178(19)	41(6)
O(1)	645(2)	4402(2)	390(3)	39(1)
O(2)	2242(2)	2475(2)	1518(3)	40(1)
O(3)	366(2)	2990(2)	1097(3)	38(1)
O(4)	502(2)	2223(2)	-54(3)	40(1)
O(5)	1514(2)	2979(2)	3029(3)	36(1)
O(6)	1460(2)	1845(2)	2139(3)	40(1)
N(1)	1356(2)	5215(2)	499(3)	32(1)
N(2)	2335(2)	3461(3)	489(3)	35(1)
C(1)	823(2)	4935(3)	25(4)	34(1)
C(2)	420(2)	5356(3)	-1014(4)	41(1)
C(3)	814(2)	5826(4)	-1261(4)	46(1)
C(4)	1401(2)	5855(3)	-179(4)	39(1)
C(5)	1835(2)	5013(3)	1546(4)	32(1)
C(6)	2338(2)	5468(3)	1964(4)	42(1)
C(7)	2819(2)	5302(3)	2952(4)	42(1)
C(8)	2808(2)	4677(3)	3565(4)	39(1)
C(9)	2308(2)	4227(3)	3164(4)	35(1)
C(10)	1813(2)	4378(3)	2166(4)	31(1)
C(11)	2531(2)	2983(3)	1356(4)	35(1)
C(12)	3157(2)	3114(4)	2155(5)	48(2)
C(13)	3315(2)	3833(4)	1710(5)	49(2)
C(14)	2802(2)	3964(4)	565(5)	45(1)

C(15)	1766(2)	3448(3)	-466(4)	35(1)
C(16)	1679(2)	3922(3)	-1335(4)	42(1)
C(17)	1144(2)	3919(3)	-2300(4)	43(1)
C(18)	709(2)	3438(3)	-2406(4)	39(1)
C(19)	800(2)	2967(3)	-1535(4)	36(1)
C(20)	1323(2)	2978(3)	-548(4)	33(1)
C(21)	229(2)	2483(3)	367(5)	40(1)
C(22)	-371(3)	2136(5)	-76(6)	59(2)
C(23)	1539(2)	2244(3)	2923(4)	35(1)
C(24)	1705(2)	1773(3)	3953(4)	44(1)

Table 3. Bond lengths [Å] and angles [°] for k1035.

Pd(1)-C(10)	1.960(5)
Pd(1)-O(1)	1.991(3)
Pd(1)-O(5)	2.067(3)
Pd(1)-O(3)	2.157(4)
Pd(1)-Pd(2)	2.8779(5)
Pd(2)-C(20)	1.967(5)
Pd(2)-O(2)	1.994(4)
Pd(2)-O(4)	2.068(3)
Pd(2)-O(6)	2.178(3)
F(1)-C(22)	1.304(8)
F(2)-C(22)	1.324(8)
F(3)-C(22)	1.326(8)
F(4)-C(24)	1.286(6)
F(5)-C(24)	1.298(6)
F(6)-C(24)	1.329(6)
F(4A)-C(24)	1.306(10)
F(5A)-C(24)	1.312(10)
F(6A)-C(24)	1.267(9)
O(1)-C(1)	1.254(6)
O(2)-C(11)	1.257(6)
O(3)-C(21)	1.249(6)
O(4)-C(21)	1.252(6)
O(5)-C(23)	1.252(6)
O(6)-C(23)	1.230(6)
N(1)-C(1)	1.323(6)
N(1)-C(5)	1.426(6)
N(1)-C(4)	1.498(6)
N(2)-C(11)	1.338(7)
N(2)-C(15)	1.436(6)
N(2)-C(14)	1.479(7)
C(1)-C(2)	1.492(7)
C(2)-C(3)	1.509(7)
C(3)-C(4)	1.543(8)
C(5)-C(6)	1.398(7)
C(5)-C(10)	1.411(7)
C(6)-C(7)	1.368(7)

C(7)-C(8)	1.381(7)
C(8)-C(9)	1.389(7)
C(9)-C(10)	1.385(7)
C(11)-C(12)	1.491(7)
C(12)-C(13)	1.528(8)
C(13)-C(14)	1.520(8)
C(15)-C(20)	1.391(7)
C(15)-C(16)	1.393(7)
C(16)-C(17)	1.390(8)
C(17)-C(18)	1.373(8)
C(18)-C(19)	1.390(7)
C(19)-C(20)	1.389(7)
C(21)-C(22)	1.522(8)
C(23)-C(24)	1.525(7)

C(10)-Pd(1)-O(1)	92.49(18)
C(10)-Pd(1)-O(5)	94.66(17)
O(1)-Pd(1)-O(5)	170.93(13)
C(10)-Pd(1)-O(3)	178.51(17)
O(1)-Pd(1)-O(3)	86.15(14)
O(5)-Pd(1)-O(3)	86.75(13)
C(10)-Pd(1)-Pd(2)	100.96(14)
O(1)-Pd(1)-Pd(2)	101.72(10)
O(5)-Pd(1)-Pd(2)	82.40(10)
O(3)-Pd(1)-Pd(2)	78.75(9)
C(20)-Pd(2)-O(2)	91.51(18)
C(20)-Pd(2)-O(4)	93.80(18)
O(2)-Pd(2)-O(4)	174.01(14)
C(20)-Pd(2)-O(6)	176.19(17)
O(2)-Pd(2)-O(6)	87.76(14)
O(4)-Pd(2)-O(6)	87.11(14)
C(20)-Pd(2)-Pd(1)	98.07(14)
O(2)-Pd(2)-Pd(1)	99.77(10)
O(4)-Pd(2)-Pd(1)	82.23(10)
O(6)-Pd(2)-Pd(1)	78.38(9)
C(1)-O(1)-Pd(1)	126.4(3)
C(11)-O(2)-Pd(2)	125.4(3)
C(21)-O(3)-Pd(1)	121.1(3)

C(21)-O(4)-Pd(2)	120.4(4)
C(23)-O(5)-Pd(1)	120.6(3)
C(23)-O(6)-Pd(2)	121.1(3)
C(1)-N(1)-C(5)	127.7(4)
C(1)-N(1)-C(4)	110.9(4)
C(5)-N(1)-C(4)	121.2(4)
C(11)-N(2)-C(15)	126.2(4)
C(11)-N(2)-C(14)	111.4(4)
C(15)-N(2)-C(14)	122.1(4)
O(1)-C(1)-N(1)	126.4(5)
O(1)-C(1)-C(2)	121.1(5)
N(1)-C(1)-C(2)	112.5(4)
C(1)-C(2)-C(3)	104.1(4)
C(2)-C(3)-C(4)	105.4(4)
N(1)-C(4)-C(3)	104.0(4)
C(6)-C(5)-C(10)	119.6(5)
C(6)-C(5)-N(1)	118.3(4)
C(10)-C(5)-N(1)	122.1(4)
C(7)-C(6)-C(5)	121.7(5)
C(6)-C(7)-C(8)	119.4(5)
C(7)-C(8)-C(9)	119.3(5)
C(10)-C(9)-C(8)	122.8(5)
C(9)-C(10)-C(5)	117.1(5)
C(9)-C(10)-Pd(1)	119.6(4)
C(5)-C(10)-Pd(1)	123.3(4)
O(2)-C(11)-N(2)	126.5(5)
O(2)-C(11)-C(12)	121.8(5)
N(2)-C(11)-C(12)	111.7(5)
C(11)-C(12)-C(13)	104.5(5)
C(14)-C(13)-C(12)	105.6(5)
N(2)-C(14)-C(13)	105.3(4)
C(20)-C(15)-C(16)	120.7(5)
C(20)-C(15)-N(2)	122.8(4)
C(16)-C(15)-N(2)	116.5(4)
C(17)-C(16)-C(15)	119.7(5)
C(18)-C(17)-C(16)	120.2(5)
C(17)-C(18)-C(19)	119.7(5)
C(20)-C(19)-C(18)	121.3(5)

C(19)-C(20)-C(15)	118.2(5)
C(19)-C(20)-Pd(2)	118.8(4)
C(15)-C(20)-Pd(2)	122.8(4)
O(3)-C(21)-O(4)	130.6(5)
O(3)-C(21)-C(22)	113.6(5)
O(4)-C(21)-C(22)	115.8(6)
F(1)-C(22)-F(2)	106.4(6)
F(1)-C(22)-F(3)	109.0(6)
F(2)-C(22)-F(3)	105.7(6)
F(1)-C(22)-C(21)	111.0(6)
F(2)-C(22)-C(21)	111.7(6)
F(3)-C(22)-C(21)	112.8(5)
O(6)-C(23)-O(5)	131.0(5)
O(6)-C(23)-C(24)	115.2(5)
O(5)-C(23)-C(24)	113.8(5)
F(6A)-C(24)-F(4)	122.3(11)
F(4)-C(24)-F(5)	109.7(6)
F(6A)-C(24)-F(4A)	107(2)
F(5)-C(24)-F(4A)	133.1(18)
F(6A)-C(24)-F(5A)	107.9(16)
F(4A)-C(24)-F(5A)	100(2)
F(4)-C(24)-F(6)	104.9(5)
F(5)-C(24)-F(6)	103.8(7)
F(5A)-C(24)-F(6)	144.9(13)
F(6A)-C(24)-C(23)	120.7(10)
F(4)-C(24)-C(23)	116.0(5)
F(5)-C(24)-C(23)	112.6(5)
F(4A)-C(24)-C(23)	112.9(18)
F(5A)-C(24)-C(23)	105.8(12)
F(6)-C(24)-C(23)	108.8(5)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for k1035. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	33(1)	27(1)	35(1)	4(1)	20(1)	2(1)
Pd(2)	35(1)	32(1)	37(1)	3(1)	21(1)	3(1)
F(1)	102(4)	192(6)	121(4)	36(4)	46(4)	-75(4)
F(2)	46(3)	153(5)	95(3)	-28(3)	28(3)	-9(3)
F(3)	66(3)	107(4)	116(4)	-43(3)	37(3)	-31(3)
F(4)	98(5)	66(3)	64(3)	29(2)	65(3)	37(3)
F(5)	286(12)	61(5)	67(4)	4(3)	75(6)	-73(6)
F(6)	98(5)	171(8)	58(4)	47(4)	42(4)	71(6)
O(1)	37(2)	36(2)	43(2)	10(2)	20(2)	2(2)
O(2)	33(2)	46(2)	39(2)	8(2)	18(2)	11(2)
O(3)	35(2)	36(2)	51(2)	7(2)	27(2)	5(2)
O(4)	36(2)	45(2)	39(2)	-5(2)	20(2)	-10(2)
O(5)	40(2)	34(2)	35(2)	7(2)	21(2)	3(2)
O(6)	53(2)	33(2)	43(2)	10(2)	32(2)	10(2)
N(1)	35(2)	32(2)	37(2)	1(2)	24(2)	2(2)
N(2)	29(2)	43(3)	36(2)	-2(2)	18(2)	6(2)
C(1)	44(3)	29(3)	33(3)	1(2)	24(3)	5(2)
C(2)	40(3)	47(3)	36(3)	10(3)	19(3)	9(3)
C(3)	54(4)	46(4)	39(3)	11(3)	26(3)	5(3)
C(4)	42(3)	39(3)	43(3)	11(3)	26(3)	0(3)
C(5)	31(3)	32(3)	35(3)	5(2)	19(2)	4(2)
C(6)	44(3)	40(3)	45(3)	10(3)	26(3)	1(3)
C(7)	41(3)	41(3)	48(3)	-2(3)	26(3)	-8(3)
C(8)	35(3)	40(3)	39(3)	-2(3)	17(3)	-1(3)
C(9)	43(3)	32(3)	32(3)	2(2)	20(3)	1(2)
C(10)	40(3)	22(3)	35(3)	0(2)	22(3)	0(2)
C(11)	29(3)	42(3)	38(3)	-7(3)	19(3)	6(3)
C(12)	37(3)	58(4)	50(4)	-4(3)	23(3)	9(3)
C(13)	32(3)	58(4)	45(3)	-5(3)	11(3)	-3(3)
C(14)	36(3)	49(4)	50(3)	-11(3)	22(3)	-11(3)
C(15)	31(3)	42(3)	33(3)	2(2)	17(2)	-1(2)
C(16)	41(3)	44(3)	47(3)	-4(3)	26(3)	-8(3)
C(17)	42(3)	46(3)	39(3)	6(3)	21(3)	-3(3)

C(18)	35(3)	49(3)	33(3)	-2(3)	17(3)	3(3)
C(19)	38(3)	39(3)	39(3)	-1(2)	25(3)	0(3)
C(20)	32(3)	36(3)	38(3)	-11(2)	23(3)	-2(2)
C(21)	31(3)	45(4)	43(3)	11(3)	19(3)	-2(3)
C(22)	42(4)	72(5)	62(4)	1(4)	26(4)	-14(4)
C(23)	33(3)	33(3)	39(3)	7(3)	18(3)	3(2)
C(24)	46(4)	44(4)	39(3)	11(3)	20(3)	6(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for k1035.

	x	y	z	U(eq)
H(2A)	157	5712	-922	49
H(2B)	186	4971	-1605	49
H(3A)	661	6369	-1508	55
H(3B)	853	5561	-1835	55
H(4A)	1722	5746	-301	47
H(4B)	1463	6381	176	47
H(6A)	2346	5904	1551	50
H(7A)	3158	5614	3215	50
H(8A)	3139	4556	4254	47
H(9A)	2305	3798	3591	42
H(12A)	3386	2643	2196	58
H(12B)	3225	3226	2890	58
H(13A)	3381	4307	2170	59
H(13B)	3669	3726	1691	59
H(14A)	2686	4531	450	55
H(14B)	2897	3804	13	55
H(16A)	1983	4245	-1269	51
H(17A)	1081	4252	-2888	51
H(18A)	347	3427	-3072	47
H(19A)	499	2630	-1616	43