

High yielding, versatile and practical [Rh(III)Cp*]-catalyzed *ortho*-bromination and iodination of arenes

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1. General Information

Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flame-dried glassware. Reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. CH₂Cl₂ was purified by distillation over CaH₂, Et₂O by distillation over Sodium and transferred under Argon. Anhydrous 1,2-dichloroethane and DMF was purchased from Acros Organics and stored over molecular sieves under argon.

Commercially available chemicals were obtained from Acros Organics, Aldrich Chemical Co., Strem Chemicals, Alfa Aesar, ABCR and TCI Europe and used as received unless otherwise stated.

NMR-spectra were recorded on a Bruker ARX-300, AV-300, AV-400 MHz or a Varian Unity Plus 600 or 500 INOVA. Chemical shifts (δ) are quoted in ppm downfield of tetramethylsilane and were referenced to the solvent peak (for CDCl₃, ¹H NMR: 7.26 ppm, ¹³C NMR: 77.16 ppm, for DMSO-*d*₆, ¹H NMR: 2.50 ppm, ¹³C NMR: 39.52 ppm and for CD₂Cl₄, ¹H NMR 5.91 ppm). Coupling constants (*J*) are quoted in Hz. ¹H- and ¹³C-peak attributions were determined by DEPT, ¹H-¹H gCOSY, ¹H-¹³C gHSQC, ¹H-¹³C gHMBC or by analogy. To describe the multiplicities of the signals, the following abbreviations were used: s: singlet, bs: broad signal, d: doublet, t: triplet, q: quartet, m: multiplet,

Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (ν) of recorded IR-signals are quoted in cm⁻¹.

ESI mass spectra were recorded on a Bruker Daltonics MicroTof.

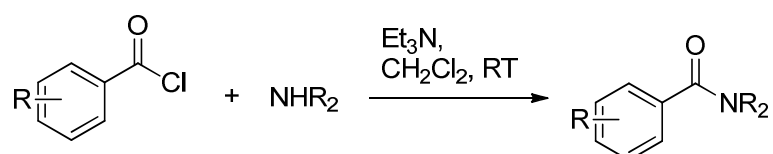
Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished with short wave UV light and/or KMnO₄ staining solution followed by gentle heating.

Flash column chromatography was performed on Merck silica gel (40-63 mesh) by using standard laboratory techniques. Solvents used for flash column chromatography were distilled before use.

2. Substrate preparation

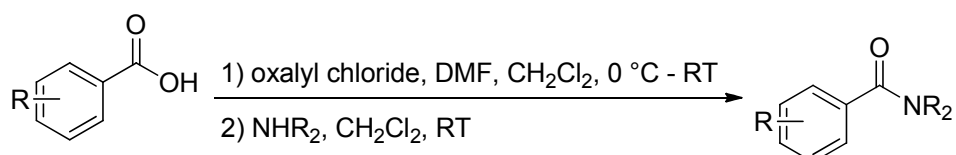
The benzamide substrates were prepared from commercially available acyl chlorides or acids using General Procedure A or B.

General Procedure A^[1]



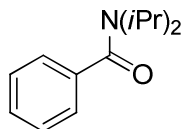
To a round bottom-flask equipped with a magnetic stir bar were added under argon the amine (1.10 equiv), Et₃N (1.25 equiv) and dichloromethane (0.5M). The acyl chloride (1.00 equiv) was added in one portion and the reaction mixture was stirred at room temperature until completion (typically 30 min). The mixture was diluted with dichloromethane and washed successively with 1N HCl and brine. The organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel.

General Procedure B^[2]



To a round bottom-flask equipped with a magnetic stir bar were added under argon the carboxylic acid (1.00 equiv), DMF (1.50 equiv) and dichloromethane (0.5M). The mixture was cooled to 0 °C and the oxalyl chloride (0.98 equiv) was added in few portions. The reaction was allowed to stir at room temperature until completion (typically 1 – 4 h). Separately, the solution of the amine (2.25 equiv) in dichloromethane (0.5M) was prepared under argon. The solution of the acyl chloride was added in one portion to the solution of the amine and the reaction was stirred at room temperature until the TLC control showed

completion of the reaction. The mixture was filtered through a pad of silica gel, washed successively with 2N NaOH, brine, 1N HCl and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel.



Chemical Formula: C₁₃H₁₉NO

Exact Mass: 205,1467

Molecular Weight: 205,2961

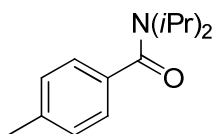
(1) *N,N*-diisopropylbenzamide: From benzoyl chloride and diisopropylamine using General Procedure A on 20 mmol scale. Product purified by SiO₂ gel column chromatography (65 x 200 mm, pentane/EtOAc = 8/2). 92% isolated yield (white solid).

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.41-7.27 (m, 5H, aromatic protons), 3.78 (bs, 1H, CH(CH₃)₂), 3.58 (bs, 1H, CH(CH₃)₂), 1.49 (bs, 6H, CH(CH₃)₂), (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 171.12 (s, C_q, CO), 138.98 (s, C_q), 128.69 (s, CH), 128.52 (s, CH), 125.65 (s, CH), 50.85 (bs, CH), 45.92 (bs, CH), 20.79 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 228.1359 [(C₁₃H₁₉NO)Na]⁺, measured 228.1361.

ATR-FTIR: ν = 2969, 1625, 1441, 1371, 1339, 706.



Chemical Formula: C₁₄H₂₁NO

Exact Mass: 219,1623

Molecular Weight: 219,3226

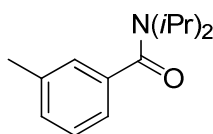
(2) *N,N*-diisopropyl-4-methylbenzamide: From 4-methylbenzoyl chloride and diisopropylamine using General Procedure A on a 25 mmol scale. Product purified by SiO₂ gel column chromatography (65 x 140 m, pentane/EtOAc = 9/1). 92% isolated yield (white solid).

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.22-7.14 (m, 4H, aromatic protons), 3.75 (bs, 1H, CH(CH₃)₂), 3.61 (bs, 1H, CH(CH₃)₂), 2.35 (s, 3H, ArCH₃), 1.40 (bs, 6H, CH(CH₃)₂), 1.23 (bs, 6H, CH(CH₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 171.31 (s, C_q , $\underline{\text{CO}}$), 138.58 (s, C_q), 136.21 (s, C_q), 129.10 (s, CH), 125.74 (s, CH), 51.80 (bs, CH), 45.85 (bs, CH), 21.41 (s, CH_3 , ArCH_3), 20.85 (s, 4 x CH_3).

ESI H.R. mass spectrometry: m/z calc. 242.1515 $[(\text{C}_{14}\text{H}_{21}\text{NO})\text{Na}]^+$, measured 242.1515.

ATR-FTIR: ν = 3035, 3004, 2977, 2962, 2929, 1621, 1444, 1369, 1338, 1037, 828.



Chemical Formula: $\text{C}_{14}\text{H}_{21}\text{NO}$

Exact Mass: 219,1623

Molecular Weight: 219,3226

(3) *N,N*-diisopropyl-3-methylbenzamide: From 3-methylbenzoic acid and diisopropylamine using a slightly modified General Procedure B.

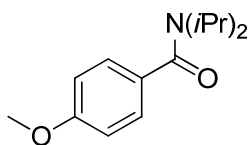
To a round bottom-flask equipped with a magnetic stir bar were added under argon 3-methylbenzoic acid (2.72 g, 20.0 mmol, 1.00 equiv), DMF (2.3 mL, 30 mmol, 1.5 equiv) and THF (40 mL). The mixture was cooled to 0 °C and the oxalyl chloride (1.68 mL, 19.6 mmol, 0.98 equiv) was added in few portions. The reaction was allowed to stir at room temperature for 1 h. Separately, the solution of diisopropylamine (6.35 mL, 45.0 mmol, 2.25 equiv) in dichloromethane (25 mL) was prepared under argon. The solution of acyl chloride was added in one portion to the solution of amine and the reaction was stirred at room temperature for 1 h. The mixture was diluted with EtOAc and filtered through a pad of silica gel. The volatiles were removed under vacuum, the residue was dissolved in EtOAc and washed successively with 2N NaOH, brine, 1N HCl and brine. The organic phase was dried over MgSO_4 , filtered and evaporated under reduced pressure. The product was purified by SiO_2 gel column chromatography (65 x 220 mm, pentane/EtOAc = 19/1). 67% isolated yield (white solid).

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.22 (dd, J = 7.5 and 7.5 Hz, 1H, aromatic proton), 7.13 (d, J = 7.5 Hz, 1H, aromatic proton), 7.10 (s, 1H, aromatic proton), 7.06 (d, J = 7.5 Hz, 1H, aromatic proton), 3.81 (bs, 1H, $\underline{\text{CH}}(\text{CH}_3)_2$), 3.50 (bs, 1H, $\underline{\text{CH}}(\text{CH}_3)_2$), 2.33 (s, 3H, ArCH_3), 1.49 (bs, 6H, 2 x $\underline{\text{CH}}(\text{CH}_3)_2$), 1.13 (bs, 6H, 2 x $\underline{\text{CH}}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 171.21 (s, C_q , $\underline{\text{CO}}$), 138.95 (s, C_q), 138.24 (s, C_q), 129.29 (s, CH), 128.26 (s, CH), 126.24 (s, CH), 122.44 (s, CH), 50.80 (s, CH), 45.64 (s, CH), 21.39 (s, CH_3 , ArCH_3), 20.72 (s, 4 x CH_3).

ESI H.R. mass spectrometry: m/z calc. 242.1515 $[(\text{C}_{14}\text{H}_{21}\text{NO})\text{Na}]^+$, measured 242.1515.

ATR-FTIR: ν = 2967, 2930, 1627, 1445, 1339, 785.



Chemical Formula: $C_{14}H_{21}NO_2$

Exact Mass: 235,1572

Molecular Weight: 235,3220

(4) *N,N*-diisopropyl-4-methoxybenzamide: From 4-methoxybenzoic acid and diisopropylamine using slightly modified General Procedure B.

To a round bottom-flask equipped with a magnetic stir bar were added under argon carboxylic 4-methoxybenzoic acid (3.04 g, 20.0 mmol, 1.00 equiv), DMF (2.3 mL, 30 mmol, 1.5 equiv) and THF (40 mL). The mixture was cooled to 0 °C and the oxalyl chloride (1.68 mL, 19.6 mmol, 0.98 equiv) was added in few portions. The reaction was allowed to stir at room temperature for 1 h. Separately, the solution of diisopropylamine (6.35 mL, 45.0 mmol, 2.25 equiv) in dichloromethane (25 mL) was prepared under argon. The solution of acyl chloride was added in one portion to the solution of amine and the reaction was stirred at room temperature over night. The mixture was diluted with EtOAc and filtered through a pad of silica gel. The volatiles were removed under reduced pressure. The product was purified by SiO_2 gel column chromatography (50 x 130 mm, pentane/EtOAc = 8/2). 33% isolated yield (colorless viscous oil).

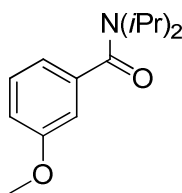
1H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.23-7.20 (m, 2H, aromatic protons), 6.84-6.80 (m, 2H, aromatic protons), 3.75 (s, 3H, \underline{CH}_3), 3.69 (bs, 2H, 2 x $\underline{CH}(CH_3)_2$), 1.27 (bs, 12H, 2 x $\underline{CH}(CH_3)_2$).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ (ppm): 171.21 (s, C_q , \underline{CO}), 160.10 (s, C_q), 131.16 (s, C_q), 127.66 (s, CH), 113.82 (s, CH), 55.42 (s, $O-\underline{CH}_3$), 20.94 (s, 4 x CH_3).

Note: 2 x $\underline{CH}(CH_3)_2$ are not visible.

ESI H.R. mass spectrometry: m/z calc. 258.1465 [$(C_{14}H_{21}NO_2)Na$] $^+$, measured 258.1473.

ATR-FTIR: ν = 2967, 2934, 1624, 1609, 1337, 1249, 1030.



Chemical Formula: C₁₄H₂₁NO₂

Exact Mass: 235,1572

Molecular Weight: 235,3220

(5) *N,N*-diisopropyl-3-methoxybenzamide: From 3-methoxybenzoyl chloride and diisopropylamine using General Procedure A on 25 mmol scale. Product purified by SiO₂ gel column chromatography (65 x 220 mm, pentane/EtOAc = 85/15 → 80/20). 93% isolated yield (yellowish solid).

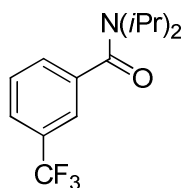
¹H NMR (500.1 MHz, CDCl₃) δ (ppm): 7.25-7.22 (m, 1H, aromatic proton), 6.87-6.80 (m, 3H, aromatic protons), 3.77 (s, 3H, O-CH₃), 3.77 (bs, 1H, CH(CH₃)₂), 3.48 (bs, 1H, CH(CH₃)₂), 1.49 (bs, 6H, CH(CH₃)₂), 1.12 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (125.6 MHz, CDCl₃) δ (ppm): 170.69 (s, C_q, C=O), 159.62 (s, C_q), 140.18 (s, C_q), 129.57 (s, CH), 117.67 (s, CH), 114.51 (s, CH), 111.00 (s, CH), 55.30 (s, CH₃, OCH₃), 20.71 (s, 4 x CH₃).

Note: 2 x CH(CH₃)₂ are not visible.

ESI H.R. mass spectrometry: m/z calc. 258.1465 [(C₁₄H₂₁NO₂)Na]⁺, measured 258.1474.

ATR-FTIR: ν = 2968, 1622, 1439, 1340, 1032.



Chemical Formula: C₁₄H₁₈F₃NO

Exact Mass: 273,1340

Molecular Weight: 273,2940

(6) *N,N*-diisopropyl-3-(trifluoromethyl)benzamide: From 3-(trifluoromethyl)benzoyl chloride and diisopropylamine using General Procedure A on 15 mmol scale. Product purified by SiO₂ gel column chromatography (45 x 210 mm, pentane/EtOAc = 19/1 → 9/1). 82% isolated yield (white solid).

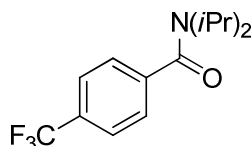
^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.62-7.60 (m, 1H, aromatic proton), 7.56 (s, 1H, aromatic proton), 7.52-7.44 (m, 2H, aromatic protons), 3.67 (bs, 1H, $\text{CH}(\text{CH}_3)_2$), 3.59 (bs, 1H, $\text{CH}(\text{CH}_3)_2$), 1.51 (bs, 6H, $\text{CH}(\text{CH}_3)_2$), 1.17 (bs, 6H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 169.45 (s, C_q , C=O), 139.66 (s, C_q), 131.07 (q, $^2J_{\text{FC}} = 30.6$ Hz, C_q , CCF_3), 129.18 (s, CH), 129.05 (s, CH), 125.56 (q, $^3J_{\text{FC}} = 3.7$ Hz, CH), 123.90 (q, $^1J_{\text{FC}} = 272.4$ Hz, C_q , CF_3), 122.8 (q, $^3J_{\text{FC}} = 3.7$ Hz, CH), 51.13 (bs, CH), 46.24 (bs, CH), 20.74 (s, 4 x CH_3).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282.4 MHz, CDCl_3) δ (ppm): - 62.81 (s).

ESI H.R. mass spectrometry: m/z calc. 296.1233 [$(\text{C}_{14}\text{H}_{18}\text{F}_3\text{NO})\text{Na}]^+$, measured 296.1235.

ATR-FTIR: $\nu = 2974, 1626, 1311, 1164, 1131$.



Chemical Formula: $\text{C}_{14}\text{H}_{18}\text{F}_3\text{NO}$

Exact Mass: 273,1340

Molecular Weight: 273,2940

(7) *N,N*-diisopropyl-4-(trifluoromethyl)benzamide. From 4-(trifluoromethyl)benzoyl chloride and diisopropylbenzamide using General Procedure A on 20 mmol scale. Product purified by SiO_2 gel column chromatography (65 x 200 mm, pentane/EtOAc = 17/3). 95% isolated yield (colorless oil).

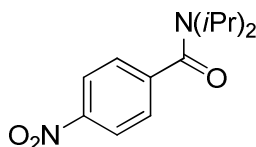
^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.63 (d, $J = 7.9$ Hz, 2H, aromatic protons), 7.40 (d, $J = 7.9$ Hz, 2H, aromatic protons), 3.69 (bs, 1H, $\text{CH}(\text{CH}_3)_2$), 3.54 (bs, 1H, $\text{CH}(\text{CH}_3)_2$), 1.52 (bs, 6H, $\text{CH}(\text{CH}_3)_2$), 1.13 (bs, 6H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 169.59 (s, C_q , C=O), 142.37 (s, C_q), 130.76 (q, $^2J_{\text{FC}} = 32.9$ Hz, C_q , CCF_3), 126.03 (s, CH), 125.71 (q, $^3J_{\text{FC}} = 3.8$ Hz, CH), 123.47 (q, $^1J_{\text{FC}} = 273.5$ Hz, C_q , CF_3), 51.12 (bs, CH), 46.15 (bs, CH), 20.69 (s, 4 x CH_3).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282.4 MHz, CDCl_3) δ (ppm): - 62.77 (s).

ESI H.R. mass spectrometry: m/z calc. 296.1233 [$(\text{C}_{14}\text{H}_{18}\text{F}_3\text{NO})\text{Na}]^+$, measured 296.1225.

ATR-FTIR: $\nu = 2973, 2936, 1635, 1323, 1127$.



Chemical Formula: C₁₃H₁₈N₂O₃

Exact Mass: 250,1317

Molecular Weight: 250,2936

(8) *N,N*-diisopropyl-4-nitrobenzamide: From 4-nitrobenzoyl chloride and diisopropylamine using General Procedure A on a 5 mmol scale. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 1/1). 92% isolated yield (yellow solid).

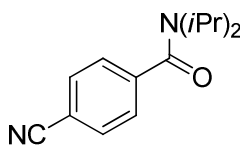
R_f (pentane/EtOAc = 5/5): 0.66.

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 8.25 (d, *J* = 8.6 Hz, 2H, aromatic protons), 7.46 (d, *J* = 8.6 Hz, 2H, aromatic protons), 3.65 (bs, 1H, CH(CH₃)₂), 3.56 (bs, 1H, CH(CH₃)₂), 1.54 (bs, 6H, CH(CH₃)₂), 1.15 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 168.69 (s, C_q, CO), 147.87 (s, C_q), 144.96 (s, C_q), 126.69 (s, CH), 124.14 (s, CH), 51.24 (bs, CH), 46.32 (bs, CH), 20.73 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 273.1210 [(C₁₃H₁₈N₂O₃)Na]⁺, measured 273.1207.

ATR-FTIR: ν = 3003, 2968, 2930, 1630, 1519, 1440, 1342, 1156, 1036, 868, 828.



Chemical Formula: C₁₄H₁₈N₂O

Exact Mass: 230,1419

Molecular Weight: 230,3055

(9) 4-cyano-*N,N*-diisopropylbenzamide: From 4-cyanobenzoic acid and diisopropylamine using a slightly modified General Procedure B.

To a round bottom-flask equipped with a magnetic stir bar were added under argon 4-cyanobenzoic acid (734 mg, 5.00 mmol, 1.00 equiv), DMF (2 drops) and CH₂Cl₂ (15 mL). The mixture was cooled to 0 °C and the oxalyl chloride (761 μL, 6.00 mmol, 1.20 equiv) was added in few portions. The reaction was allowed to stir at room temperature for 5 h. The CH₂Cl₂ and the volatiles were removed under reduces pressure. In a separate flame-dried flask under Argon, a solution of diisopropylamine (843 μL, 6.00 mmol, 1.20 equiv) and

triethylamine (901 μ L, 6.50 mmol, 1.30 equiv) in CH_2Cl_2 (7 mL) is cooled down to 0°C and the crude acid chloride is dissolved in CH_2Cl_2 (3 mL) and added dropwise herein. The mixture is then stirred at room-temperature for 4 h, washed successively two times with 1N HCl and brine. The organic layer was dried over MgSO_4 , filtered and evaporated under reduced pressure. The product was purified by SiO_2 gel column chromatography (30 x 100 mm, pentane/EtOAc = 8/2 \rightarrow 7/3). 53% isolated yield (white solid).

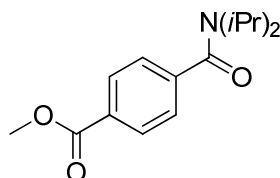
R_f (pentane/EtOAc = 8/2): 0.45.

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.69 (d, J = 8.6 Hz, 2H, aromatic protons), 7.40 (d, J = 8.6 Hz, 2H, aromatic protons), 3.65 (bs, 1H, $\text{CH}(\text{CH}_3)_2$), 3.56 (bs, 1H, $\text{CH}(\text{CH}_3)_2$), 1.52 (bs, 6H, $\text{CH}(\text{CH}_3)_2$), 1.15 (bs, 6H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 168.96 (s, C_q , CO), 143.16 (s, C_q), 132.65 (s, CH), 126.46 (s, CH), 118.42 (s, C_q), 112.67 (s, C_q), 51.12 (bs, CH), 46.16 (bs, CH), 20.75 (s, 4 x CH_3).

ESI H.R. mass spectrometry: m/z calc. 253.1311 $[(\text{C}_{14}\text{H}_{18}\text{N}_2\text{O})\text{Na}]^+$, measured 253.1318.

ATR-FTIR: ν = 2968, 2930, 1625, 1446, 1372, 1342, 1214, 1037, 836.



Chemical Formula: $\text{C}_{15}\text{H}_{21}\text{NO}_3$

Exact Mass: 263,1521

Molecular Weight: 263,3321

(10) Methyl 4-(diisopropylcarbamoyl)benzoate. From mono-Methyl terephthalate and diisopropylamine using a slightly modified General Procedure B.

To a round bottom-flask equipped with a magnetic stir bar were added under argon mono-Methyl terephthalate (900 mg, 5.00 mmol, 1.00 equiv), DMF (2 drops) and CH_2Cl_2 (15 mL). The mixture was cooled to 0°C and the oxalyl chloride (514 μ L, 6.00 mmol, 1.20 equiv) was added in few portions. The reaction was allowed to stir at room temperature for 3 h. The CH_2Cl_2 and the volatiles were removed under reduced pressure. In a separate flame-dried flask under Argon, a solution of diisopropylamine (843 μ L, 6.00 mmol, 1.20 equiv) and triethylamine (901 μ L, 6.50 mmol, 1.30 equiv) in CH_2Cl_2 (7 mL) is cooled down to 0°C and the crude acid chloride is dissolved in CH_2Cl_2 (3 mL) and added dropwise herein. The

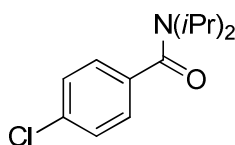
mixture is then stirred at room-temperature for 3 h, washed successively two times with 1N HCl and brine. The organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure. The product was purified by SiO₂ gel column chromatography (30 x 110 mm, pentane/EtOAc = 9/1). 88% isolated yield (colorless liquid).

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 8.05 (d, *J* = 8.4 Hz, 2H, aromatic protons), 7.36 (d, *J* = 8.4 Hz, 2H, aromatic protons), 3.92 (s, 3H, OCH₃), 3.73 (bs, 1H, CH(CH₃)₂), 3.52 (bs, 1H, CH(CH₃)₂), 1.53 (bs, 6H, CH(CH₃)₂), 1.13 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 170.07 (s, C_q, CO), 166.65 (s, C_q, CO), 143.24 (s, C_q), 130.32 (s, C_q), 130.04 (s, CH), 125.67 (s, CH), 52.38 (s, CH₃, OCH₃), 51.05 (bs, CH), 46.11 (bs, CH), 20.76 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 286.1414 [(C₁₅H₂₁NO₃)Na]⁺, measured 286.1409.

ATR-FTIR: ν = 2994, 2970, 1724, 1628, 1505, 1436, 1336, 1282, 1117, 1037, 1016, 745, 718.



Chemical Formula: C₁₃H₁₈ClNO

Exact Mass: 239,1077

Molecular Weight: 239,7411

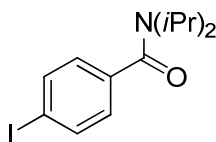
(11) 4-chloro-*N,N*-diisopropylbenzamide: From 4-chlorobenzoyl chloride and diisopropylamine using General Procedure A on a 5 mmol scale. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 9/1). 84% isolated yield (white solid).

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.37-7.33 (m, 2H, aromatic protons), 7.26-7.23 (m, 2H, aromatic protons), 3.71 (bs, 1H, CH(CH₃)₂), 3.59 (bs, 1H, CH(CH₃)₂), 1.47 (bs, 6H, CH(CH₃)₂), 1.18 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 170.01 (s, C_q, CO), 137.37 (s, C_q), 134.70 (s, C_q), 128.84 (s, CH), 127.25 (s, CH), 51.00 (bs, CH), 46.10 (bs, CH), 20.81 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 262.0969 [(C₁₃H₁₈ClNO)Na]⁺, measured 262.0967.

ATR-FTIR: ν = 2986, 2967, 2929, 1618, 1595, 1435, 1369, 1337, 1154, 1089, 1038, 1012, 825, 740.



Chemical Formula: C₁₃H₁₈INO

Exact Mass: 331,0433

Molecular Weight: 331,1926

(12) 4-iodo-*N,N*-diisopropylbenzamide: From 4-iodobenzoic acid and diisopropylamine using a slightly modified General Procedure B.

To a round bottom-flask equipped with a magnetic stir bar were added under argon 4-iodobenzoic acid (580 mg, 2.30 mmol, 1.00 equiv), DMF (2 drops) and CH₂Cl₂ (7 mL). The mixture was cooled to 0 °C and the oxalyl chloride (236 µL, 2.76 mmol, 1.20 equiv) was added in few portions. The reaction was allowed to stir at room temperature for 3 h. The CH₂Cl₂ and the volatiles were removed under reduced pressure. In a separate flame-dried flask under Argon, a solution of diisopropylamine (387 µL, 2.76 mmol, 1.20 equiv) and triethylamine (414 µL, 2.99 mmol, 1.30 equiv) in CH₂Cl₂ (3 mL) is cooled down to 0°C and the crude acid chloride is dissolved in CH₂Cl₂ (2 mL) and added dropwise herein. The mixture is then stirred at room-temperature for 3 h, washed successively two times with 1N HCl and brine. The organic layer was dried over MgSO₄, filtered and evaporated under reduced pressure. The product was purified by SiO₂ gel column chromatography (30 x 100 mm, pentane/EtOAc = 7/3). 89% isolated yield (white solid).

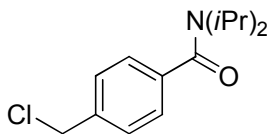
R_f (pentane/EtOAc = 8/2): 0.47.

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.72 (d, *J* = 8.3 Hz, 2H, aromatic protons), 7.05 (d, *J* = 8.3 Hz, 2H, aromatic protons), 3.74 (bs, 1H, CH(CH₃)₂), 3.54 (bs, 1H, CH(CH₃)₂), 1.48 (bs, 6H, CH(CH₃)₂), 1.16 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 170.11 (s, C_q, CO), 138.39 (s, C_q), 137.72 (s, CH), 127.57 (s, CH), 94.58 (s, C_q), 51.2 (bs, CH), 46.17 (bs, CH), 20.82 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 354.0325 [(C₁₃H₁₈INO)Na]⁺, measured 354.0320.

ATR-FTIR: ν = 2973, 2930, 1618, 1586, 1440, 1367, 1340, 1008, 820.



Chemical Formula: C₁₄H₂₀ClNO

Exact Mass: 253,1233

Molecular Weight: 253,7677

(13) 4-(chloromethyl)-*N,N*-diisopropylbenzamide: From 4-(chloromethyl)benzoyl chloride and diisopropylamine using General Procedure A on a 5 mmol scale. Product purified by SiO₂ gel column chromatography (30 x 160 mm, pentane/EtOAc = 8/2). 90% isolated yield (white solid).

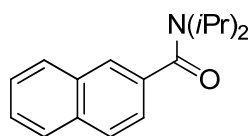
R_f (pentane/EtOAc = 8/2): 0.38.

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.40 (d, *J* = 8.1 Hz, 2H, aromatic protons), 7.30 (d, *J* = 8.1 Hz, 2H, aromatic protons), 4.59 (s, 2H, benzylic protons), 3.79 (bs, 1H, CH(CH₃)₂), 3.54 (bs, 1H, CH(CH₃)₂), 1.50 (bs, 6H, CH(CH₃)₂), 1.16 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 170.54 (s, C_q, CO), 139.05 (s, C_q), 137.97 (s, C_q), 128.83 (s, CH), 126.18 (s, CH), 51.07 (bs, CH), 46.14 (bs, CH), 45.91 (s, CH₂), 20.75 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 276.1126 [(C₁₄H₂₀ClNO)Na]⁺, measured 276.1126.

ATR-FTIR: ν = 2970, 1620, 1440, 1369, 1339, 1035, 797, 672.



Chemical Formula: C₁₇H₂₁NO

Exact Mass: 255.1623

Molecular Weight: 255.3547

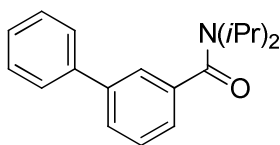
(14) *N,N*-diisopropyl-2-naphthamide. From 2-naphthoyl chloride and diisopropylamine using General Procedure A on 20 a mmol scale. Product purified by SiO₂ gel column chromatography (65 x 200 mm, pentane/EtOAc = 17/3 → 16/4). 92% isolated yield (white solid).

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.87-7.81 (m, 4H, aromatic protons), 7.52-7.48 (m, 2H, aromatic protons), 7.43 (dd, *J* = 8.4 and 1.6 Hz, 1H, aromatic proton), 3.84 (bs, 1H, CH(CH₃)₂), 3.63 (bs, 1H, CH(CH₃)₂), 1.55 (bs, 6H, CH(CH₃)₂), 1.19 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 171.01 (s, C_q, CO), 136.33 (s, C_q), 133.17 (s, C_q), 132.97 (s, C_q), 128.31 (s, CH), 128.25 (s, CH), 127.79 (s, CH), 126.57 (s, 2 x CH), 124.84 (s, CH), 123.47 (s, CH), 50.93 (bs, CH), 46.04 (bs, CH), 20.79 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 278.1515 [(C₁₇H₂₁NO)Na]⁺, measured 278.1516.

ATR-FTIR: ν = 2966, 2932, 1612, 1545, 1340, 1220, 1029, 850, 739, 688.



Chemical Formula: C₁₉H₂₃NO

Exact Mass: 281,1780

Molecular Weight: 281,3920

(15) N,N-diisopropyl-[1,1'-biphenyl]-3-carboxamide: From Biphenyl-3-carbonyl chloride and diisopropylamine using General Method A on a 4.6 mmol scale. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 9/1). 95% isolated yield (colorless oil).

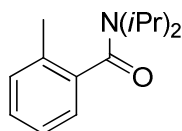
R_f (pentane/EtOAc = 8/2): 0.56.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.63-7.52 (m, 3H, aromatic protons), 7.56-7.53 (t, *J* = 1.5 Hz, 1H, aromatic proton), 7.48-7.41 (m, 3H, aromatic protons), 7.40-7.33 (m, 1H, aromatic proton), 7.29 (dt, *J* = 7.5 and 1.4 Hz, 1H, aromatic proton), 3.90 (bs, 1H, CH(CH₃)₂), 3.57 (bs, 1H, CH(CH₃)₂), 1.55 (bs, 6H, CH(CH₃)₂), 1.18 (bs, 6H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 171.01 (s, C_q, C=O), 141.58 (s, C_q), 140.64 (s, C_q), 139.52 (s, C_q), 129.01 (s, CH), 128.93 (s, CH), 127.67 (s, CH), 127.48 (s, CH), 127.26 (s, CH), 124.47 (s, CH), 124.43 (s, CH), 51.00 (bs, CH), 46.05 (bs, CH), 20.85 (s, 4 x CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 282.1852 [(C₁₉H₂₃NO)H]⁺, measured 282.1864.

ATR-FTIR: ν = 2968, 2932, 1627, 1439, 1337, 1036.



Chemical Formula: C₁₄H₂₁NO

Exact Mass: 219,1623

Molecular Weight: 219,3226

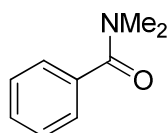
(16) N,N-diisopropyl-2-methylbenzamide: From 2-methylbenzoyl chloride and diisopropylamine using General Method A on a 20 mmol scale. Product purified by SiO₂ gel column chromatography (65 x 200 mm, pentane/EtOAc = 10/1). 93% isolated yield (white solid).

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.25-7.18 (m, 2H, aromatic protons), 7.18-7.12 (m, 1H, aromatic proton), 7.11-7.05 (m, 1H, aromatic proton), 3.72-3.58 (m, 1H, CH(CH₃)₂), 3.58-3.42 (m, 1H, CH(CH₃)₂), 2.31 (s, CH₃, ArCH₃), 1.57 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.11 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.07 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 170.75 (s, C_q , $\underline{\text{C}}\text{O}$), 138.72 (s, C_q), 133.66 (s, C_q), 130.43 (s, CH), 128.11 (s, CH), 125.83 (s, CH), 124.72 (s, CH), 50.84 (s, $\underline{\text{C}}\text{H}$, $\text{CH}(\text{CH}_3)_2$), 45.80 (s, CH, $\underline{\text{C}}\text{H}(\text{CH}_3)_2$), 21.00 (s, CH_3), 20.84 (s, CH_3), 20.80 (s, CH_3), 20.65 (s, CH_3), 18.88 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 242.1515 $[(\text{C}_{14}\text{H}_{21}\text{NO})\text{Na}]^+$, measured 242.1514.

ATR-FTIR: ν = 3015, 2965, 2936, 1618, 1442, 1371, 1342, 1033, 765, 730.



Chemical Formula: $\text{C}_9\text{H}_{11}\text{NO}$

Exact Mass: 149.0841

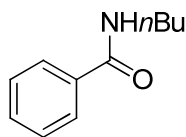
Molecular Weight: 149.1897

(17) *N,N*-dimethylbenzamide: From benzoyl chloride and dimethylamine (40% solution in water) using General Method A on a 25 mmol scale. Product purified by SiO_2 gel column chromatography (65 x 200 mm, pentane/EtOAc = 5/5 \rightarrow 3/7). 95% isolated yield (white solid).

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.46-7.26 (m, 5H, aromatic protons), 2.99 (bs, 6H, $\underline{\text{C}}\text{H}_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 171.51 (s, C_q , $\underline{\text{C}}\text{O}$), 136.27 (s, C_q), 129.42 (s, CH), 128.26 (s, CH), 126.29 (s, CH), 39.50 (bs, CH_3), 39.29 (bs, CH_3).

ESI H.R. mass spectrometry: m/z calc. 172.0733 $[(\text{C}_9\text{H}_{11}\text{NO})\text{Na}]^+$, measured 172.0732.



Chemical Formula: $\text{C}_{11}\text{H}_{15}\text{NO}$

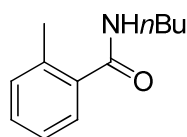
Exact Mass: 177.1154

Molecular Weight: 177.2429

(18) *N*-butylbenzamide: Benzoyl chloride (4.71 mL, 40.7 mmol, 1.67 equiv) is added dropwise to a solution of *n*-butylamine (2.40 mL, 24.4 mmol, 1.00 equiv) in 1M NaOH (50 mL). The mixture is stirred overnight, the aqueous layer saturated with brine and extracted with EtOAc (3 x 25 mL). The organic layers are dried over MgSO_4 and the solvent is removed under reduced pressure. Product purified by SiO_2 gel column chromatography (65 x 200 mm, pentane/EtOAc = 85/15 \rightarrow 80/10). 99% isolated yield (colorless oil).

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.78-7.74 (m, 2H, aromatic protons), 7.44-7.36 (m, 1H, aromatic proton), 7.36-7.29 (m, 2H, aromatic proton), 6.91 (bs, 1H, NH), 3.41-3.32 (m, 2H, NCH_2), 1.59-1.45 (m, 2H, NCH_2CH_2), 1.39-1.26 (m, 2H, CH_2CH_3), 0.90-0.84 (m, 3H, CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 167.77 (s, C_q , C=O), 134.77 (s, C_q), 131.16 (s, CH), 128.36 (s, CH), 126.97 (s, CH), 39.84 (s, CH_2), 31.65 (s, CH), 20.13 (s, CH_2), 13.75 (s, CH_3).



Chemical Formula: $\text{C}_{12}\text{H}_{17}\text{NO}$

Exact Mass: 191,1310

Molecular Weight: 191,2695

(19) *N*-butyl-2-methylbenzamide: From 2-methylbenzoyl chloride and *n*-Butylamine using a slightly modified General Procedure A.

Et_3N (901 μL , 6.50 mmol, 1.30 equiv), *n*-Butylamine (593 μL , 6.0 mmol, 1.20 equiv) were added in CH_2Cl_2 (7 mL) in a flamed dried flask under Argon and cooled to 0 $^\circ\text{C}$. The 2-methylbenzoyl chloride (651 μL , 5.00 mmol, 1.00 equiv) is dissolved in CH_2Cl_2 (3 mL) and added slowly to the reaction mixture, which is allowed to warm up to room temperature after addition. The mixture is stirred for 2.5 hours, then washed successively two times with 1N HCl and brine, dried over MgSO_4 and concentrated under reduced pressure. The product was purified by SiO_2 gel column chromatography (30 x 130 mm, pentane/EtOAc = 7/3). 100% isolated yield (white solid).

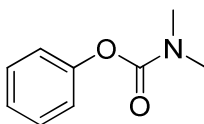
R_f (pentane/EtOAc = 6/4): 0.48.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.37-7.26 (m, 2H, aromatic protons), 7.24-7.15 (m, 2H, aromatic protons), 5.77 (bs, 1H, NH), 3.43 (q, J = 6.6 Hz, 2H, NCH_2), 2.43 (s, CH_3 , ArCH_3), 1.64-1.52 (m, 2H, NCH_2CH_2), 1.48-1.34 (m, 2H, CH_2CH_3), 0.96 (t, J = 7.3 Hz, 3H, CH_2CH_3).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 170.25 (s, C_q , C=O), 136.89 (s, C_q), 135.97 (s, C_q), 131.02 (s, CH), 129.80 (s, CH), 126.69 (s, CH), 125.78 (s, CH), 39.65 (s, NCH_2), 31.85 (s, CH_2 , NCH_2CH_2), 20.25 (s, CH_2 , CH_2CH_3), 19.84 (s, CH_3 , ArCH_3), 13.90 (s, CH_3 , CH_2CH_3).

ESI H.R. mass spectrometry: m/z calc. 214.1202 [$(\text{C}_{12}\text{H}_{17}\text{NO})\text{Na}$] $^+$, measured 214.1210.

ATR-FTIR: ν = 3285, 2952, 2930, 2870, 1639, 1538, 1313, 1153, 720.



Chemical Formula: C₉H₁₁NO₂

Exact Mass: 165,0790

Molecular Weight: 165,1891

(26) Phenyl dimethylcarbamate: HNMe₂·HCl (408 mg, 5.00 mmol, 1.00 equiv) and K₂CO₃ (1.52 g, 11.0 mmol, 2.20 equiv) were added to a flame dried flask under Argon in Et₂O (50 mL). The solution is cooled down to 0 °C and Phenyl chloroformate (783 mg, 5.00 mmol, 1.00 equiv) is added carefully with a syringe. After addition, the solution is allowed to warm up to room temperature and stirred for 3 more hours. The reaction mixture is washed successively with H₂O and brine, dried over MgSO₄ and concentrated under reduced pressure. The product was purified by SiO₂ gel column chromatography (30 x 200 mm, pentane/EtOAc = 8/2 → 3/1). 67% isolated yield (white solid).

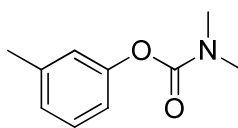
R_f (pentane/EtOAc = 5/5): 0.57.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.39-7.31 (m, 2H, aromatic protons), 7.22-7.16 (m, 1H, aromatic proton), 7.14-7.09 (m, 2H, aromatic protons), 3.10 (s, 3H, CH₃), 3.02 (s, 3H, CH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 155.04 (s, C_q, OCO), 151.64 (s, C_q), 129.32 (s, CH), 125.26 (s, CH), 121.87 (s, CH), 36.80 (s, CH₃), 36.56 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 188.0682 [(C₉H₁₁NO₂)Na]⁺, measured 188.0688.

ATR-FTIR: ν = 2933, 1706, 1481, 1387, 1199, 1164, 749.



Chemical Formula: C₁₀H₁₃NO₂

Exact Mass: 179,0946

Molecular Weight: 179,2157

(27) *m*-tolyl dimethylcarbamate: *meta*-Cresol (525 μL, 5.00 mmol, 1.00 equiv) was added to a flame dried flask in DMF (25 mL). NaH (60% dispersion, 6.50 mmol, 1.30 equiv) was added slowly, the solution was stirred for 15 min at room temperature and dimethylcarbamoyl chloride (546 μL, 5.00 mmol, 1.00 equiv) was added. After stirring for 30 more minutes at room temperature, the reaction mixture is carefully quenched with ice and extracted into Et₂O. The organic layer is washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The product was purified by SiO₂ gel column chromatography (30 x 150 mm, pentane/EtOAc = 9/1). 100% isolated yield (colorless solid).

R_f (pentane/EtOAc = 5/5): 0.57.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.23 (t, *J* = 7.6 Hz, 1H, aromatic proton), 7.00 (dt, *J* = 7.6 and 0.9 Hz, 1H, aromatic proton), 6.95-6.88 (m, 2H, aromatic protons), 3.09 (s, 3H, N(CH₃)), 3.01 (s, 3H, N(CH₃)), 2.35 (s, 3H, ArCH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 155.17 (s, C_q, OCO), 151.54 (s, C_q), 139.44 (s, C_q), 129.05 (s, CH), 126.10 (s, CH), 122.52 (s, CH), 118.80 (s, CH), 36.78 (s, N(CH₃)), 36.56 (s, N(CH₃)), 21.43 (s, CH₃, ArCH₃).

ESI H.R. mass spectrometry: *m/z* calc. 202.0383 [(C₁₀H₁₃NO₂)Na]⁺, measured 202.0845.

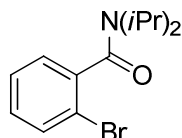
ATR-FTIR: ν = 2927, 1717, 1485, 1383, 1244, 1163, 789.

3. Catalysis

General Procedure:

To a flame-dried screw-capped test tube equipped with a magnetic stir bar were added under argon [RhCp*Cl₂]₂ (6.2 mg, 0.01 mmol), AgSbF₆ (13.7 mg, 0.04 mmol) and PivOH (112.3 mg, 1.1 mmol). 1,2-DCE (5 mL), the substrate (**1-26**) (1.0 mmol) and NXS (1.1 eq.) were added. The closed tube is added to a pre-heated oil-bath and stirred for 16h. The mixture was then allowed to cool down to room temperature, diluted with EtOAc (20 mL) and filtered through a short pad of silica gel and eluted with EtOAc (100 mL). After removing the solvent under reduced pressure, the product was purified by flash chromatography.

4. Product purification and characterization



Chemical Formula: $C_{13}H_{18}BrNO$

Exact Mass: 283,0572

Molecular Weight: 284,1921

(1-Br) 2-bromo-*N,N*-diisopropylbenzamide: From **1** and NBS at 60 °C using the General Procedure. Product purified by SiO_2 gel column chromatography (30 x 130 mm, pentane/EtOAc = 8/2). 99% isolated yield (white solid).

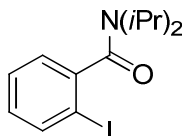
R_f (pentane/EtOAc = 8/2): 0.51.

1H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 7.57-7.51 (m, 1H, aromatic proton), 7.35-7.27 (m, 1H, aromatic proton), 7.23-7.14 (m, 2H, aromatic protons), 3.66-3.44 (m, 2H, $CH(CH_3)_2$), 1.57 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.56 (d, $J = 6.8$ Hz, 3H, $CH(CH_3)_2$), 1.23 (d, $J = 6.7$ Hz, 3H, $CH(CH_3)_2$), 1.05 (d, $J = 6.7$ Hz, 3H, $CH(CH_3)_2$).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ (ppm): 168.29 (s, C_q , \underline{CO}), 140.24 (s, C_q), 132.95 (s, CH), 129.57 (s, CH), 127.66 (s, CH), 126.68 (s, CH), 119.03 (s, C_q), 51.28 (s, CH), 46.09 (s, CH), 20.90 (s, CH_3), 20.79 (s, CH_3), 20.73 (s, CH_3), 20.19 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 306.0464 [$(C_{13}H_{18}BrNO)Na$] $^+$, measured 306.0461.

ATR-FTIR: $\nu = 2976, 2929, 1628, 1439, 1370, 1340, 1211, 1020, 772$.



Chemical Formula: $C_{13}H_{18}INO$

Exact Mass: 331,0433

Molecular Weight: 331,1926

(1-I) 2-iodo-*N,N*-diisopropylbenzamide: From **1** and NIS at 60 °C using the general procedure. Product purified by SiO_2 gel column chromatography (30 x 110 mm, pentane/EtOAc = 9/1). 98% isolated yield (white solid).

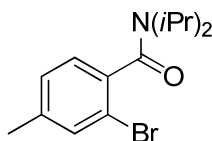
R_f (pentane/EtOAc = 8/2): 0.66.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.80 (ddd, *J* = 8.0, 1.1 and 0.4 Hz, 1H, aromatic proton), 7.34 (dt, *J* = 7.5 and 1.1 Hz, 1H, aromatic proton), 7.13 (ddd, *J* = 7.6, 1.7 and 0.4 Hz, 1H, aromatic proton), 7.02 (ddd, *J* = 8.0, 7.4 and 1.7 Hz, 1H, aromatic proton). 3.64-3.44 (m, 2H, CH(CH₃)₂), 1.59 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.26 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.05 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 169.93 (s, C_q, CO), 144.32 (s, C_q), 139.41 (s, CH), 129.55 (s, CH), 128.31 (s, CH), 125.92 (s, CH), 92.37 (s, C_q), 51.34 (s, CH), 46.09 (s, CH), 20.86 (s, 2 x CH₃), 20.75 (s, CH₃), 20.15 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 354.0325 [(C₁₃H₁₈INO)Na]⁺, measured 354.0316.

ATR-FTIR: ν = 2994, 2967, 1619, 1436, 1340, 1210, 1012, 772.



Chemical Formula: C₁₄H₂₀BrNO

Exact Mass: 297.0728

Molecular Weight: 298.2187

(2-Br) 2-bromo-N,N-diisopropyl-4-methylbenzamide: From **2** and NBS at 60 °C. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 9/1). 98% isolated yield (white solid).

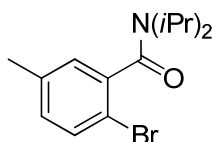
R_f (pentane/EtOAc = 8/2): 0.52.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.37 (s, 1H, aromatic proton), 7.11 (d, *J* = 7.7 Hz, 1H, aromatic proton), 7.05 (d, *J* = 7.7 Hz, 1H, aromatic proton), 3.68-3.43 (m, 2H, CH(CH₃)₂), 2.32 (s, 3H, ArCH₃), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.55 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.22 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.04 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 168.67 (s, C_q, CO), 139.81 (s, C_q), 137.42 (s, C_q), 133.30 (s, CH), 128.39 (s, CH), 126.42 (s, CH), 118.78 (s, C_q), 51.28 (s, CH), 46.25 (s, CH), 21.02 (s, CH₃), 20.92 (s, CH₃), 20.81 (s, CH₃), 20.71 (s, CH₃), 20.21 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 320.0620 [(C₁₄H₂₀BrNO₃)Na]⁺, measured 320.0617.

ATR-FTIR: ν = 2993, 2969, 2933, 1628, 1437, 1369, 1337, 1046, 1028, 832, 809.



Chemical Formula: C₁₄H₂₀BrNO

Exact Mass: 297,0728

Molecular Weight: 298,2187

(3-Br) 2-bromo-N,N-diisopropyl-5-methylbenzamide: From **3** and NBS at 60 °C. Product purified by SiO₂ gel column chromatography (30 x 110 mm, pentane/EtOAc = 9/1). 98% isolated yield (colorless oil).

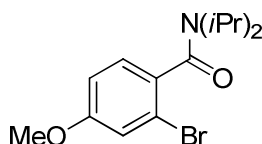
R_f (pentane/EtOAc = 8/2): 0.57.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.40 (d, *J* = 8.3 Hz, 1H, aromatic proton), 7.01-6.96 (m, 2H, aromatic protons), 3.69-3.43 (m, 2H, CH(CH₃)₂), 2.29 (s, 3H, ArCH₃), 1.57 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.55 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.23 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.06 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 168.46 (s, C_q, CO), 139.98 (s, C_q), 137.75 (s, C_q), 132.62 (s, CH), 130.42 (s, CH), 127.24 (s, CH), 115.54 (s, C_q), 51.25 (s, CH), 46.04 (s, CH), 21.00 (s, CH₃), 20.95 (s, CH₃), 20.77 (s, CH₃), 20.70 (s, CH₃), 20.19 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 320.0620 [(C₁₄H₂₀BrNO₃)Na]⁺, measured 320.0618.

ATR-FTIR: ν = 2994, 2961, 2930, 1627, 1442, 1370, 1339, 1210, 1024, 832, 805.



Chemical Formula: C₁₄H₂₀BrNO₂

Exact Mass: 313,0677

Molecular Weight: 314,2181

(4-Br) 2-bromo-N,N-diisopropyl-4-methoxybenzamide: From **4** and NBS at 60 °C. Product purified by SiO₂ gel column chromatography (25 x 350 mm, pentane/EtOAc = 8/2). 95% isolated yield (white solid).

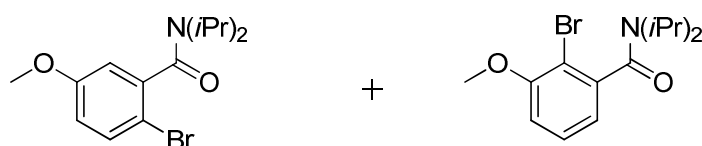
R_f (pentane/EtOAc = 8/2): 0.24.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.07 (d, *J* = 8.5 Hz, 1H, aromatic proton), 7.06 (d, *J* = 2.4 Hz, 1H, aromatic proton), 6.83 (dd, *J* = 8.4 and 2.4 Hz, 1H, aromatic proton), 3.77 (s, 3H, OCH₃), 3.68-3.42 (m, 2H, CH(CH₃)₂), 1.54 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.53 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.20 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.03 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 168.41 (s, C_q , C=O), 159.74 (s, C_q), 132.74 (s, C_q), 127.35 (s, CH), 119.52 (s, C_q), 118.01 (s, CH), 113.73 (s, CH), 55.63 (s, CH_3 , OCH_3), 51.24 (s, CH), 45.99 (s, CH), 20.89 (s, CH_3), 20.74 (s, CH_3), 20.70 (s, CH_3), 20.18 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 336.0570 $[(\text{C}_{13}\text{H}_{20}\text{BrNO}_2)\text{Na}]^+$, measured 336.0571.

ATR-FTIR: ν = 2966, 2934, 1621, 1601, 1435, 1339, 1040, 858, 802, 594.



Chemical Formula: $\text{C}_{14}\text{H}_{20}\text{BrNO}_2$

Exact Mass: 313.0677

Molecular Weight: 314.2181

(5a-Br) 2-bromo-*N,N*-diisopropyl-5-methoxybenzamide + (5b-Br) 2-bromo-*N,N*-diisopropyl-3-methoxybenzamide: From **5** and NBS at 60 °C. Product purified by SiO_2 gel column chromatography (30 x 300 mm, pentane/EtOAc = 85/15 \rightarrow 80/20). 44% isolated yield (white solid) for **5a-Br** and 54% isolated yield (white solid) for **5b-Br**.

2-bromo-*N,N*-diisopropyl-5-methoxybenzamide (5a-Br)

R_f (pentane/EtOAc = 8/2): 0.18.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.40 (d, J = 8.8 Hz, 1H, aromatic proton), 6.73 (dd, J = 8.8 and 3.0 Hz, 1H, aromatic proton), 6.69 (d, J = 3.0 Hz, 1H, aromatic proton), 3.77 (s, 3H, OCH_3), 3.66-3.45 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.56 (d, J = 6.8 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.55 (d, J = 6.7 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.23 (d, J = 6.7 Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.06 (d, J = 6.7 Hz, 3H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 168.03 (s, C_q , C=O), 159.12 (s, C_q), 140.84 (s, C_q), 133.72 (s, CH), 115.74 (s, CH), 112.02 (s, CH), 109.26 (s, C_q), 55.69 (s, CH_3 , OCH_3), 51.25 (s, CH), 46.06 (s, CH), 21.00 (s, CH_3), 20.79 (s, CH_3), 20.63 (s, CH_3), 20.13 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 336.0570 $[(\text{C}_{14}\text{H}_{20}\text{BrNO}_2)\text{Na}]^+$, measured 336.0561.

ATR-FTIR: ν = 3076, 2996, 2933, 1627, 1456, 1339, 1289, 1033, 828.

2-bromo-*N,N*-diisopropyl-3-methoxybenzamide (5b-Br)

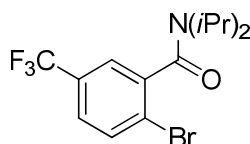
R_f (pentane/EtOAc = 8/2): 0.29.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.27 (dd, $J = 8.2$ and 7.6 Hz, 1H, aromatic proton), 6.84 (dd, $J = 8.2$ and 1.3 Hz, 1H, aromatic proton), 6.77 (dd, $J = 7.6$ and 1.3 Hz, 1H, aromatic proton), 3.89 (s, 3H, OCH_3), 3.64-3.44 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.57 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.55 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.04 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 168.08 (s, C_q , CO), 156.17 (s, C_q), 141.83 (s, C_q), 128.88 (s, CH), 118.50 (s, CH), 111.19 (s, CH), 108.57 (s, C_q), 56.45 (s, CH_3 , OCH_3), 51.23 (s, CH), 46.04 (s, CH), 20.87 (s, CH_3), 20.76 (s, CH_3), 20.73 (s, CH_3), 20.18 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 336.0570 $[(\text{C}_{14}\text{H}_{20}\text{BrNO}_2)\text{Na}]^+$, measured 336.0568.

ATR-FTIR: $\nu = 3077, 2988, 2963, 1625, 1426, 1342, 1271, 1028, 786$.



Chemical Formula: $\text{C}_{14}\text{H}_{17}\text{BrF}_3\text{NO}$

Exact Mass: 351,0446

Molecular Weight: 352,1901

(6-Br) 2-bromo-*N,N*-diisopropyl-5-(trifluoromethyl)benzamide: From **6** and NBS at 120°C , using a slightly modified general procedure with 2 equiv of NBS and 48h reaction time. Product purified by SiO_2 gel column chromatography (30 x 160 mm, pentane/EtOAc = 20/1). 70% isolated yield (white solid).

R_f (pentane/EtOAc = 9/1): 0.62.

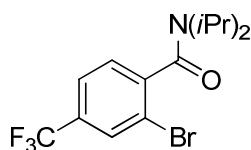
^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.69 (d, $J = 8.3$ Hz, 1H, aromatic proton), 7.46-7.43 (m, 1H, aromatic proton), 7.42-7.40 (m, 1H, aromatic proton), 3.60-3.46 (m, 2H, $\text{CH}(\text{CH}_3)_2$), 1.58 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.57 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.25 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 166.83 (s, C_q , CO), 140.95 (s, C_q), 133.73 (s, CH), 130.36 (q, $^2J_{FC} = 33.3$ Hz, C_q), 126.30 (q, $^3J_{FC} = 3.6$ Hz, CH), 123.65 (q, $^3J_{FC} = 3.8$ Hz, CH), 123.61 (q, $^1J_{FC} = 272.4$ Hz, C_q , ArCF_3), 123.18 (q, $^4J_{FC} = 1.6$ Hz, C_q), 51.50 (s, CH), 46.38 (s, CH), 20.88 (s, CH_3), 20.77 (s, CH_3), 20.69 (s, CH_3), 20.13 (s, CH_3).

$^{19}\text{F}\{^1\text{H}\}$ NMR (282.4 MHz, CDCl_3) δ (ppm): -62.83 (s).

ESI H.R. mass spectrometry: m/z calc. 374.0338 $[(\text{C}_{14}\text{H}_{17}\text{BrF}_3\text{NO})\text{Na}]^+$, measured 374.0336.

ATR-FTIR: $\nu = 3072, 2977, 2934, 1632, 1313, 1128, 1077, 1025, 904, 846$.



Chemical Formula: C₁₄H₁₇BrF₃NO

Exact Mass: 351,0446

Molecular Weight: 352,1901

(7-Br) 2-bromo-*N,N*-diisopropyl-4-(trifluoromethyl)benzamide: From **7** and NBS at 120°C, using a slightly modified general procedure with 2 equiv of NBS and 24h reaction time. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 9/1). 93% isolated yield (white solid).

R_f (pentane/EtOAc = 9/1): 0.39.

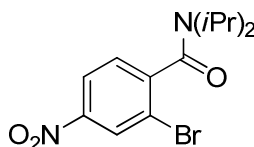
¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.82 (s, 1H, aromatic proton), 7.59 (d, *J* = 7.9 Hz, 1H, aromatic proton), 7.30 (d, *J* = 7.9 Hz, 1H, aromatic proton), 3.61-3.46 (m, 2H, CH(CH₃)₂), 1.57 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.25 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.08 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 167.03 (s, C_q, C=O), 143.58 (s, C_q), 131.80 (q, ²*J*_{FC} = 33.3 Hz, C_q), 130.13 (q, ³*J*_{FC} = 3.9 Hz, CH), 127.12 (s, CH), 127.77 (q, ³*J*_{FC} = 3.7 Hz, CH), 123.03 (q, ¹*J*_{FC} = 272.8 Hz, C_q, ArCF₃), 119.48 (s, C_q), 51.47 (s, CH), 46.36 (s, CH), 20.91 (s, CH₃), 20.74 (s, CH₃), 20.71 (s, CH₃), 20.12 (s, CH₃).

¹⁹F{¹H} NMR (282.4 MHz, CDCl₃) δ (ppm): -62.83 (s).

ESI H.R. mass spectrometry: *m/z* calc. 374.0338 [(C₁₄H₁₇BrF₃NO)Na]⁺, measured 374.0334.

ATR-FTIR: ν = 2974, 2936, 2877, 1637, 1441, 1319, 1170, 1074, 1028, 837, 706.



Chemical Formula: C₁₃H₁₇BrN₂O₃

Exact Mass: 328,0423

Molecular Weight: 329,1897

(8-Br) 2-bromo-*N,N*-diisopropyl-4-nitrobenzamide: From **8** and NBS at 120°C, using a slightly modified general procedure with 2 equiv of NBS and 24h reaction time. Product purified by SiO₂ gel column chromatography (30 x 90 mm, pentane/EtOAc = 8/2). 87% isolated yield (white solid).

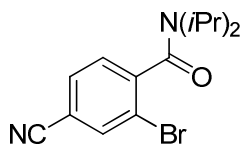
R_f (pentane/EtOAc = 8/2): 0.48.

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 8.44 (d, *J* = 2.1 Hz, 1H, aromatic proton), 8.22 (dd, *J* = 8.4 and 2.2 Hz, 1H, aromatic proton), 7.36 (d, *J* = 8.4 Hz, 1H, aromatic proton), 3.61-3.41 (m, 2H, CH(CH₃)₂), 1.57 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.26 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.09 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 166.31 (s, C_q, C=O), 147.79 (s, C_q), 145.99 (s, C_q), 128.39 (s, CH), 127.33 (s, CH), 123.02 (s, CH), 119.74 (s, C_q), 51.55 (s, CH), 46.49 (s, CH), 20.91 (s, CH₃), 20.74 (s, CH₃), 20.67 (s, CH₃), 20.08 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 351.0315 [(C₁₃H₁₇BrN₂O₃)Na]⁺, measured 351.0322.

ATR-FTIR: ν = 3097, 2968, 2931, 2874, 1701, 1642, 1527, 1438, 1356, 1338, 1211, 1027, 827.



Chemical Formula: C₁₄H₁₇BrN₂O

Exact Mass: 308,0524

Molecular Weight: 309,2016

(9-Br) 2-bromo-4-cyano-*N,N*-diisopropylbenzamide: From **9** and NBS at 120°C, using a slightly modified general procedure with 2 equiv of NBS and 48h reaction time. Product purified by SiO₂ gel column chromatography (30 x 210 mm, pentane/EtOAc = 9/1 → 8/3). 70% isolated yield (yellow solid).

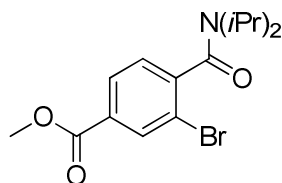
R_f (pentane/EtOAc = 7/3): 0.51.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 8.84 (d, *J* = 1.5 Hz, 1H, aromatic proton), 7.63 (dd, *J* = 7.9 and 1.5 Hz, 1H, aromatic proton), 7.28 (d, *J* = 7.9 Hz, 1H, aromatic proton), 3.61-3.41 (m, 2H, CH(CH₃)₂), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.55 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.25 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.08 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 166.43 (s, C_q, C=O), 144.49 (s, C_q), 136.37 (s, CH), 131.46 (s, CH), 127.28 (s, CH), 119.73 (s, C_q), 117.01 (s, C_q), 113.59 (s, C_q), 51.52 (s, CH), 46.43 (s, CH), 20.91 (s, CH₃), 20.74 (s, CH₃), 20.66 (s, CH₃), 20.07 (s, CH₃).

ESI H.R. mass spectrometry: m/z calc. 331.0416 $[(C_{14}H_{17}BrN_2O)Na]^+$, measured 331.0418.

ATR-FTIR: ν = 2984, 2967, 2933, 1632, 1441, 1374, 1339, 1215, 1048, 1030, 921, 837.



Chemical Formula: $C_{15}H_{20}BrNO_3$

Exact Mass: 341,0627

Molecular Weight: 342,2282

(10-Br) methyl 3-bromo-4-(diisopropylcarbamoyl)benzoate: From **10** and NBS at 70 °C. Product purified by SiO_2 gel column chromatography (30 x 120 mm, pentane/EtOAc = 8/2). 94% isolated yield (colorless oil).

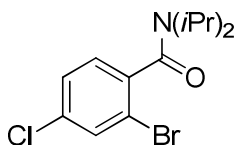
R_f (pentane/EtOAc = 7/3): 0.59.

1H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 8.22 (dd, J = 1.6 and 0.4 Hz, 1H, aromatic proton), 7.98 (dd, J = 7.9 and 1.6 Hz, 1H, aromatic proton), 7.25 (dd, J = 7.9 and 0.4 Hz, 1H, aromatic proton), 3.91 (s, 3H, OCH_3), 3.60-3.43 (m, 2H, $CH(CH_3)_2$), 1.57 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.55 (d, J = 6.8 Hz, 3H, $CH(CH_3)_2$), 1.23 (d, J = 6.7 Hz, 3H, $CH(CH_3)_2$), 1.06 (d, J = 6.7 Hz, 3H, $CH(CH_3)_2$).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ (ppm): 167.44 (s, C_q , \underline{CO}), 165.40 (s, C_q , \underline{CO}), 144.18 (s, C_q), 134.19 (s, CH), 131.41 (s, C_q), 128.92 (s, CH), 126.66 (s, CH), 119.11 (s, C_q), 52.64 (s, CH_3 , OCH_3), 51.38 (s, CH), 46.25 (s, CH), 20.87 (s, CH_3), 20.72 (s, CH_3), 20.70 (s, CH_3), 20.12 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 342.0699 $[(C_{15}H_{20}BrNO_3)H]^+$, measured 342.0696.

ATR-FTIR: ν = 2971, 2935, 1725, 1635, 1435, 1339, 1284, 1243, 1109, 1028, 771.



Chemical Formula: $C_{13}H_{17}BrClNO$

Exact Mass: 317,0182

Molecular Weight: 318,6372

(11-Br) 2-bromo-4-chloro-N,N-diisopropylbenzamide: From **11** and NBS at 80 °C. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 9/1). 96% isolated yield (white solid).

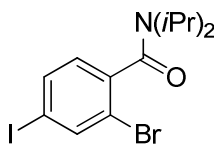
R_f (pentane/EtOAc = 9/1): 0.32.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.57 (d, *J* = 1.9 Hz, 1H, aromatic proton), 7.31 (dd, *J* = 8.2 and 1.9 Hz, 1H, aromatic proton), 7.11 (d, *J* = 8.2 Hz, 1H, aromatic proton), 3.66-3.43 (m, 2H, CH(CH₃)₂), 1.56 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.54 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.23 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.06 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 167.37 (s, C_q, CO), 138.77 (s, C_q), 134.63 (s, C_q), 132.73 (s, CH), 128.06 (s, CH), 127.55 (s, CH), 119.65 (s, C_q), 51.36 (s, CH), 46.24 (s, CH), 20.96 (s, CH₃), 20.76 (s, 2 x CH₃), 20.18 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 340.0074 [(C₁₃H₁₇BrClNO)Na]⁺, measured 340.0076.

ATR-FTIR: ν = 2978, 2933, 1629, 1437, 1970, 1339, 1028, 822.



Chemical Formula: $C_{13}H_{17}BrINO$

Exact Mass: 408,9538

Molecular Weight: 410,0886

(12-Br) 2-bromo-4-iodo-N,N-diisopropylbenzamide: From **12** and NBS at 70 °C. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 9/1). 93% isolated yield (white solid).

R_f (pentane/EtOAc = 8/2): 0.63.

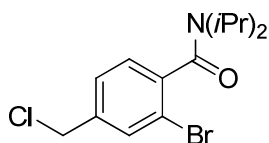
¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.92 (d, *J* = 1.6 Hz, 1H, aromatic proton), 7.65 (dd, *J* = 8.0 and 1.6 Hz, 1H, aromatic proton), 6.91 (d, *J* = 8.0 Hz, 1H, aromatic proton), 3.62-3.44

(m, 2H, CH(CH₃)₂), 1.55 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.54 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.23 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.06 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 167.44 (s, C_q, C=O), 140.96 (s, CH), 139.72 (s, C_q), 136.76 (s, CH), 127.95 (s, CH), 119.91 (s, C_q), 93.67 (s, C_q), 51.36 (s, CH), 46.22 (s, CH), 20.93 (s, CH₃), 20.74 (s, 2 x CH₃), 20.15 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 431.9430 [(C₁₃H₁₇BrINO)Na]⁺, measured 431.9422.

ATR-FTIR: ν = 2982, 2963, 2931, 1620, 1574, 1435, 1368, 1338, 1024, 846, 829.



Chemical Formula: C₁₄H₁₉BrClNO

Exact Mass: 331.0339

Molecular Weight: 332.6638

(13-Br) 2-bromo-4-(chloromethyl)-N,N-diisopropylbenzamide: From **13** and NBS at 60°C, using a slightly modified general procedure with 2.5 mol% of [RhCp*Cl₂]₂ and 10 mol% AgSbF₆. Product purified by SiO₂ gel column chromatography (30 x 110 mm, pentane/EtOAc = 8/2). 87% isolated yield (white solid).

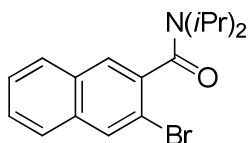
R_f (pentane/EtOAc = 8/2): 0.32

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.59 (d, *J* = 1.7 Hz, 1H, aromatic proton), 7.34 (dd, *J* = 7.8 and 1.7 Hz, 1H, aromatic proton), 7.16 (d, *J* = 7.8 Hz, 1H, aromatic proton), 4.53 (s, 2H, benzylic protons), 3.65-3.44 (m, 2H, CH(CH₃)₂), 1.57 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.55 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.23 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.06 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 167.81 (s, C_q, C=O), 140.17 (s, C_q), 139.02 (s, C_q), 132.96 (s, CH), 127.86 (s, CH), 126.92 (s, CH), 119.21 (s, C_q), 51.35 (s, CH), 46.18 (s, CH), 44.90 (s, CH₂), 20.93 (s, CH₃), 20.76 (s, CH₃), 20.75 (s, CH₃), 20.17 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 332.0422 [(C₁₄H₁₉BrClNO)H]⁺, measured 332.0409.

ATR-FTIR: ν = 2987, 2968, 2934, 1623, 1442, 1371, 1640, 1208, 1190, 1156, 1029, 815.



Chemical Formula: $C_{17}H_{20}BrNO$

Exact Mass: 333,0728

Molecular Weight: 334,2508

(14-Br) 3-bromo-N,N-diisopropyl-2-naphthamide: From **14** and NBS at 60 °C. Product purified by SiO₂ gel column chromatography (35 x 320 mm, pentane/EtOAc = 90/10 → 65/15). 85% isolated yield (white solid).

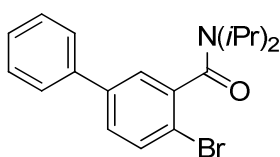
R_f (pentane/EtOAc = 8/2): 0.45.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 8.08 (s, 1H, aromatic proton), 7.82-7.72 (m, 2H, aromatic protons), 7.66 (s, 1H, aromatic proton), 7.54-7.49 (m, 2H, aromatic protons), 3.71-3.50 (m, 2H, CH(CH₃)₂), 1.63 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.62 (d, *J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.24 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.07 (d, *J* = 6.7 Hz, 3H, CH(CH₃)₂).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 168.29 (s, C_q, CO), 137.66 (s, C_q), 133.87 (s, C_q), 131.99 (s, C_q), 131.68 (s, CH), 120.01 (s, CH), 127.37 (s, CH), 127.02 (s, CH), 126.97 (s, CH), 125.58 (s, CH), 116.65 (s, C_q), 51.40 (s, CH), 46.19 (s, CH), 20.92 (s, CH₃), 20.88 (s, CH₃), 20.54 (s, CH₃), 20.15 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 356.0620 [(C₁₇H₂₀BrNO)Na]⁺, measured 356.0621.

ATR-FTIR: ν = 3046, 2993, 2972, 1629, 1464, 1338, 1041, 898, 750.



Chemical Formula: $C_{19}H_{22}BrNO$

Exact Mass: 359,0885

Molecular Weight: 360,2881

(15-Br) 4-bromo-N,N-diisopropyl-[1,1'-biphenyl]-3-carboxamide: From **15** and NBS at 60 °C. Product purified by SiO₂ gel column chromatography (30 x 180 mm, pentane/EtOAc = 8/2). 81% isolated yield (white solid).

R_f (pentane/EtOAc = 8/2): 0.75.

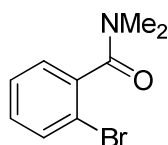
¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.61 (d, *J* = 8.2 Hz, 1H, aromatic proton), 7.58-7.52 (m, 2H, aromatic protons), 7.48-7.34 (m, 5H, aromatic protons), 3.76-3.47 (m, 2H,

$\text{CH}(\text{CH}_3)_2$), 1.60 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.59 (d, $J = 6.8$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.26 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$), 1.08 (d, $J = 6.7$ Hz, 3H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 168.24 (s, C_q , C=O), 140.98 (s, C_q), 140.57 (s, C_q), 139.57 (s, C_q), 133.34 (s, CH), 129.08 (s, CH), 128.32 (s, CH), 128.05 (s, CH), 127.13 (s, CH), 125.21 (s, CH), 118.03 (s, C_q), 51.38 (s, CH), 46.18 (s, CH), 21.05 (s, CH_3), 20.84 (s, CH_3), 20.76 (s, CH_3), 20.22 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 382.0777 $[(\text{C}_{19}\text{H}_{22}\text{BrNO})\text{Na}]^+$, measured 382.0771.

ATR-FTIR: $\nu = 2967, 2932, 2874, 1624, 1440, 1338, 1023, 758$.



Chemical Formula: $\text{C}_9\text{H}_9\text{BrNO}$

Exact Mass: 226.9946

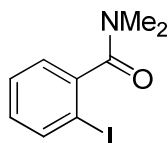
Molecular Weight: 228.0858

(17-Br) 2-bromo-N,N-dimethylbenzamide: From **16** and NBS at 70 °C using a slightly modified general procedure with 24 h reaction time. Product purified by SiO_2 gel column chromatography (35 x 350 mm, toluene/EtOAc = 4/6). 86% isolated yield (white solid).

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.56-7.51 (m, 1H, aromatic proton), 7.36-7.29 (m, 1H, aromatic proton), 7.25-7.17 (m, 2H, aromatic protons), 3.10 (s, 3H, $\text{N}(\text{CH}_3)_2$), 2.82 (s, 3H, $\text{N}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 169.22 (s, C_q , C=O), 138.55 (s, C_q), 132.72 (s, CH), 130.20 (s, CH), 127.76 (s, CH), 127.71 (s, CH), 119.1 (s, C_q), 38.22 (s, CH_3), 34.67 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 249.9838 $[(\text{C}_9\text{H}_9\text{BrNO})\text{Na}]^+$, measured 249.9387.



Chemical Formula: $\text{C}_9\text{H}_9\text{INO}$

Exact Mass: 274.9807

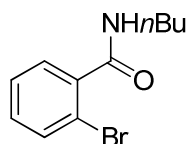
Molecular Weight: 275.0863

(17-I) 2-iodo-*N,N*-dimethylbenzamide: From **16** and NIS at 90 °C using a slightly modified general procedure with 24 h reaction time and 1.6 equiv of NIS. Product purified by SiO₂ gel column chromatography (35 x 350 mm, toluene/EtOAc = 5/5). 75% isolated yield (white solid).

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.79-7.74 (m, 1H, aromatic proton), 7.37-7.31 (m, 1H, aromatic proton), 7.19-7.14 (m, 1H, aromatic proton), 7.05-6.98 (m, 1H, aromatic proton), 3.10-3.07 (m, 3H, N(CH₃)), 2.80-2.78 (m, 3H, N(CH₃)).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 170.71 (s, C_q, C=O), 142.73 (s, C_q), 139.02 (s, CH), 130.08 (s, CH), 128.41 (s, CH), 127.00 (s, CH), 92.39 (s, C_q), 38.43 (s, CH₃), 34.71 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 249.9838 [(C₉H₁₀BrNO)Na]⁺, measured 249.9387.



Chemical Formula: C₁₁H₁₄BrNO

Exact Mass: 255,0259

Molecular Weight: 256,1390

(18-Br) *N*-butyl-2-bromobenzamide: From **17** and NBS at 60 °C using the general procedure. Product purified by SiO₂ gel column chromatography (30 x 90 mm, pentane/EtOAc = 8/2). 80% isolated yield (white solid).

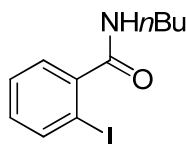
R_f (pentane/EtOAc = 8/2): 0.48.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 7.55 (dd, *J* = 7.9 and 1.3 Hz, 1H, aromatic proton), 7.47 (dd, *J* = 7.5 and 1.8 Hz, 1H, aromatic proton), 7.31 (td, *J* = 7.5 and 1.3 Hz, 1H, aromatic proton), 7.23 (td, *J* = 7.9 and 1.8 Hz, 1H, aromatic proton), 6.01 (bs, 1H, NH), 3.42 (td, *J* = 7.1 and 5.8 Hz, 2H, NCH₂), 1.64-1.53 (m, 2H, NCH₂CH₂), 1.48-1.34 (m, 2H, CH₂CH₃), 0.94 (t, *J* = 7.3 Hz, 3H, CH₃).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 167.71 (s, C_q, C=O), 138.19 (s, C_q), 133.35 (s, CH), 131.16 (s, CH), 129.59 (s, CH), 127.59 (s, CH), 119.30 (s, C_q), 39.92 (s, CH₂, NCH₂), 31.53 (s, CH₂, NCH₂CH₂), 20.25 (s, CH₂, CH₂CH₃), 13.86 (s, CH₃, CH₂CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 278.0151 [(C₁₁H₁₄BrNO)Na]⁺, measured 278.0151.

ATR-FTIR: ν = 3263, 2956, 2931, 2870, 1636, 1548, 1430, 1312, 1021, 765.



Chemical Formula: C₁₁H₁₄INO

Exact Mass: 303,0120

Molecular Weight: 303,1394

(18-I) N-butyl-2-iodobenzamide: From **17** and NIS at 60 °C using the general procedure. Product purified by SiO₂ gel column chromatography (30 x 130 mm, pentane/EtOAc = 8/2). 78% isolated yield (white solid).

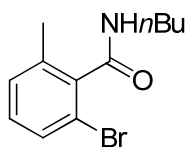
R_f (pentane/EtOAc = 6/4): 0.55.

¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.82 (dd, *J* = 7.9 Hz, 1H, aromatic proton), 7.35-7.32 (m, 2H, aromatic protons), 7.09-7.02 (m, 1H, aromatic proton), 5.92 (bs, 1H, NH), 3.41 (td, *J* = 7.2 and 5.8 Hz, 2H, NCH₂), 1.64-1.54 (m, 2H, NCH₂CH₂), 1.48-1.36 (m, 2H, CH₂CH₃), 0.94 (t, *J* = 7.3 Hz, 3H, CH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 169.49 (s, C_q, CO), 142.61 (s, C_q), 139.85 (s, CH), 131.04 (s, CH), 128.32 (s, CH), 128.22 (s, CH), 92.54 (s, C_q), 39.92 (s, CH₂, NCH₂), 31.51 (s, CH₂, NCH₂CH₂), 20.28 (s, CH₂, CH₂CH₃), 13.86 (s, CH₃, CH₂CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 326.0012 [(C₁₁H₁₄INO)Na]⁺, measured 326.0012.

ATR-FTIR: ν = 3269, 2926, 2866, 1635, 1545, 1426, 1310, 1258, 1012, 681.



Chemical Formula: C₁₂H₁₆BrNO

Exact Mass: 269,0415

Molecular Weight: 270,1655

(19-Br) 2-bromo-N-butyl-6-methylbenzamide: From **18** and NBS at 60°C, using a slightly modified general procedure with 2.5 mol% of [RhCp*Cl₂]₂, 10 mol% AgSbF₆ and 1.5 equiv of NBS. Product purified by SiO₂ gel column chromatography (30 x 120 mm, pentane/EtOAc = 7/3). 87% isolated yield (white solid).

R_f (pentane/EtOAc = 6/4): 0.64.

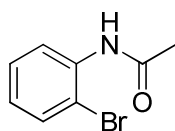
¹H NMR (400.1 MHz, CDCl₃) δ (ppm): 7.38-7.33 (m, 1H, aromatic proton), 7.14-7.06 (m, 2H, aromatic protons), 5.76 (bs, 1H, NH), 3.45 (td, *J* = 7.2 and 5.9 Hz, 2H, NCH₂), 2.35 (s,

3H, ArCH₃), 1.65-1.56 (m, 2H, NCH₂CH₂), 1.47-1.37 (m, 2H, CH₂CH₃), 0.95 (t, 3H, CH₂CH₃).

¹³C{¹H} NMR (100.6 MHz, CDCl₃) δ (ppm): 168.21 (s, C_q, C=O), 139.04 (s, C_q), 137.30 (s, C_q), 130.11 (s, CH), 130.04 (s, CH), 129.20 (s, CH), 119.51 (s, C_q), 39.67 (s, CH₂), 31.54 (s, CH₂), 20.30 (s, CH₂), 19.68 (s, CH₃), 13.86 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 292.0307 [(C₁₂H₁₆BrNO)Na]⁺, measured 292.0303.

ATR-FTIR: ν = 3254, 3079, 2954, 2930, 2871, 1638, 1550, 1439, 1306, 1179, 844, 774.



Chemical Formula: C₈H₈BrNO

Exact Mass: 212.9789

Molecular Weight: 214.0592

(20-Br) N-(2-bromophenyl)acetamide: From Acetanilide and NBS at 60 °C using the general procedure. Product purified by SiO₂ gel column chromatography (30 x 110 mm, pentane/EtOAc = 3/1). 89% isolated yield (white solid).

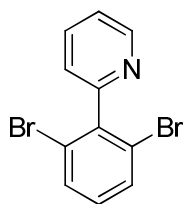
R_f (pentane/EtOAc = 8/2): 0.44.

¹H NMR (300.1 MHz, CDCl₃) δ (ppm): 8.31 (d, *J* = 8.0 Hz, 1H, aromatic proton), 7.62 (bs, 1H, NH), 7.52 (dd, *J* = 8.0 and 1.2 Hz, 1H, aromatic proton), 7.34-7.27 (m, 1H, aromatic proton), 7.01-6.93 (m, 1H, aromatic proton), 2.23 (s, 3H, CH₃).

¹³C{¹H} NMR (75.5 MHz, CDCl₃) δ (ppm): 168.37 (s, C_q, C=O), 135.78 (s, C_q), 132.30 (s, CH), 128.48 (s, CH), 125.29 (s, CH), 122.08 (s, CH), 113.35 (s, C_q), 24.98 (s, CH₃).

ESI H.R. mass spectrometry: *m/z* calc. 235.9681 [(C₈H₈BrNO)Na]⁺, measured 235.9681.

ATR-FTIR: ν = 3280, 1659, 1528, 1438, 1296, 1027, 760.



Chemical Formula: $C_{11}H_7Br_2N$

Exact Mass: 310,8945

Molecular Weight: 312,9880

(21-Br) 2-(2,6-dibromophenyl)pyridine: From 2-Phenylpyridine and NBS at 60 °C using a slightly modified general procedure with 2.2 equiv NBS. Product purified by SiO_2 gel column chromatography (30 x 100 mm, pentane/EtOAc = 6/1). 73% isolated yield (orange solid).

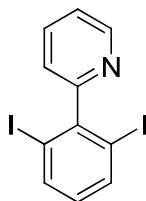
R_f (pentane/EtOAc = 8/2): 0.63.

1H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 8.74 (ddd, J = 4.9, 1.7 and 1.0 Hz, 1H, aromatic proton), 7.81 (td, J = 7.7 and 1.8 Hz, 1H, aromatic proton), 7.62 (d, J = 8.1 Hz, 2H, aromatic protons), 7.34 (ddd, J = 7.6, 4.9 and 1.2 Hz, 1H, aromatic proton), 7.30 (dt, J = 7.8 and 1.0 Hz, 1H, aromatic proton), 7.11 (t, J = 8.1 Hz, 1H, aromatic proton).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ (ppm): 158.76 (s, C_q), 149.54 (s, CH), 141.80 (s, C_q), 136.63 (s, CH), 131.96 (s, CH), 130.72 (s, CH), 124.73 (s, CH), 128.85 (s, C_q), 126.16 (s, CH).

ESI H.R. mass spectrometry: m/z calc. 333.8837 [$(C_{11}H_7Br_2N)Na$] $^+$, measured 333.8838.

ATR-FTIR: ν = 3072, 1591, 1546, 1415, 1185, 990, 778, 746, 720.



Chemical Formula: $C_{11}H_7I_2N$

Exact Mass: 406,8668

Molecular Weight: 406,9889

(21-I) 2-(2,6-diiodophenyl)pyridine: From 2-Phenylpyridine and NIS at 60 °C using a slightly modified general procedure with 2.2 equiv NIS. Product purified by SiO_2 gel column chromatography (30 x 100 mm, pentane/EtOAc = 9/1). 88% isolated yield (white solid).

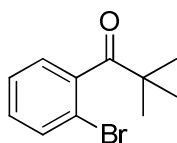
R_f (pentane/EtOAc = 9/1): 0.57.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 8.75 (d, $J = 4.8$ Hz, 1H, aromatic proton), 7.92 (d, $J = 7.9$ Hz, 2H, aromatic protons), 7.82 (td, $J = 7.7$ and 1.6 Hz, 1H, aromatic proton), 7.35 (ddd, $J = 7.6$, 4.9 and 0.9 Hz, 1H, aromatic proton), 7.25 (d, $J = 7.7$ Hz, 1H, aromatic proton), 6.74 (t, $J = 7.9$ Hz, 1H, aromatic proton).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 164.30 (s, C_q), 149.40 (s, CH), 148.33 (s, C_q), 139.13 (s, CH), 136.79 (s, CH), 131.29 (s, CH), 124.22 (s, CH), 123.38 (s, CH), 90.05 (s, C_q).

ESI H.R. mass spectrometry: m/z calc. 407.8741 $[(\text{C}_{11}\text{H}_7\text{I}_2\text{N})\text{H}]^+$, measured 407.8734.

ATR-FTIR: $\nu = 3076, 1587, 1566, 1539, 1476, 1413, 1192, 993, 779, 766, 742, 689$.



Chemical Formula: $\text{C}_{11}\text{H}_{13}\text{BrO}$

Exact Mass: 240.0150

Molecular Weight: 241.1243

(22-Br) 1-(2-bromophenyl)-2,2-dimethylpropan-1-one: From 2,2-Dimethylpropiophenone and NBS at 120 °C. Product purified by SiO_2 gel column chromatography (30 x 140 mm, pentane/EtOAc = 50/1). 78% isolated yield (colorless oil).

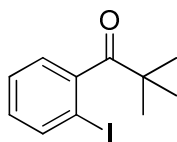
R_f (pentane/EtOAc = 19/1): 0.6.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.57 (ddd, $J = 7.9, 1.2$ and 0.4 Hz, 1H, aromatic proton), 7.32 (td, $J = 7.5$ and 1.2 Hz, 1H, aromatic proton), 7.23 (ddd, $J = 7.9, 7.5$ and 1.2 Hz, 1H, aromatic proton), 7.13 (ddd, $J = 7.5, 1.8$ and 0.4 Hz, 1H, aromatic proton), 1.28 (s, 9H, $(\text{CH}_3)_3$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 212.16 (s, C_q , C=O), 142.73 (s, C_q), 133.15 (s, CH), 130.01 (s, CH), 126.68 (s, CH), 126.15 (s, CH), 117.96 (s, C_q), 45.12 (s, C_q , $\text{C}(\text{CH}_3)_3$), 27.22 (s, CH_3 , $\text{C}(\text{CH}_3)_3$).

ESI H.R. mass spectrometry: m/z calc. 263.0042 $[(\text{C}_{11}\text{H}_{13}\text{BrO})\text{Na}]^+$, measured 263.0038.

ATR-FTIR: $\nu = 2970, 2905, 2870, 1695, 1464, 1195, 1055, 963, 753, 735$.



Chemical Formula: $C_{11}H_{13}IO$

Exact Mass: 288,0011

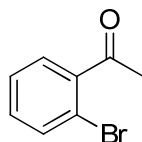
Molecular Weight: 288,1248

(22-I) 1-(2-iodophenyl)-2,2-dimethylpropan-1-one: From 2,2-Dimethylpropiophenone and NIS at 120°C using a modified procedure where 5 x 0.5 equiv of NIS were added in periodical times over a total time of 52 h. Product purified by SiO_2 gel column chromatography (30 x 300 mm, toluene/EtOAc = 80/1). 53% isolated yield (colorless oil).

R_f (toluene/EtOAc = 20/1): 0.53.

1H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.83 (d, $J = 8.0$ Hz, 1H, aromatic proton), 7.35 (t, $J = 7.5$ Hz, 1H, aromatic proton), 7.12-7.07 (m, 1H, aromatic proton), 7.07-7.03 (m, 1H, aromatic proton), 1.30 (s, 9H, $C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ (ppm): 213.09 (s, C_q , \underline{CO}), 146.87 (s, C_q), 139.67 (s, CH), 130.04 (s, CH), 127.51 (s, CH), 125.48 (s, CH), 90.08 (s, C_q), 44.85 (s, C_q , $\underline{C(CH_3)_3}$), 27.41 (s, CH_3 , $C(\underline{CH_3})_3$).



Chemical Formula: C_8H_7BrO

Exact Mass: 197,9680

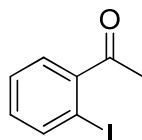
Molecular Weight: 199,0446

(23-Br) 1-(2-bromophenyl)ethanone: From Acetophenone and NBS at 120°C, using a slightly modified general procedure with 2.5 mol% of $[RhCp^*Cl_2]_2$, 10 mol% $AgSbF_6$, 2.2 equiv of NBS, 1.1 equiv $Cu(OAc)_2$ instead of PivOH and 21 h reaction time. Product purified by SiO_2 gel column chromatography (35 x 350 mm, toluene). 50% isolated yield (colorless liquid).

1H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 7.90 (dd, $J = 7.9$ and 1.3 Hz, 1H, aromatic proton), 7.45 (dd, $J = 7.5$ and 1.9 Hz, 1H, aromatic proton), 7.35 (td, $J = 7.5$ and 1.4 Hz, 1H, aromatic proton), 7.28 (td, $J = 7.6$ and 1.9 Hz, 1H, aromatic proton), 2.62 (s, 3H, $\underline{CH_3}$).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ (ppm): 201.44 (s, C_q , \underline{CO}), 141.50 (s, C_q), 133.91 (s, CH), 131.88 (s, CH), 128.99 (s, CH), 127.53 (s, CH), 119.96 (s, CH), 30.41 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 220.9572 $[(C_8H_7BrO)Na]^+$, measured 220.9575.



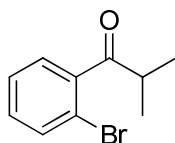
Chemical Formula: C_8H_7IO
Exact Mass: 245,9542
Molecular Weight: 246,0451

(23-I) 1-(2-Iodophenyl)ethanone: From Acetophenone and NIS at 120 °C, using a slightly modified general procedure with 2.5 mol% of $[RhCp^*Cl_2]_2$, 10 mol% $AgSbF_6$, 1.4 equiv of NIS, 2.2 equiv $Cu(OAc)_2$ instead of PivOH and 22 h reaction time. Product purified by SiO_2 gel column chromatography (35 x 350 mm). 62% isolated yield (colorless liquid).

1H NMR (400.1 MHz, $CDCl_3$) δ (ppm): 7.93 (dd, $J = 8.0$ and 1.1 Hz, 1H, aromatic proton), 7.46 (dd, $J = 7.7$ and 1.8 Hz, 1H, aromatic proton), 7.40 (td, $J = 7.5$ and 1.4 Hz, 1H, aromatic proton), 7.11 (td, $J = 7.6$ and 1.8 Hz, 1H, aromatic proton), 2.61 (s, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (100.6 MHz, $CDCl_3$) δ (ppm): 201.78 (s, C_q , \underline{CO}), 144.00 (s, C_q), 140.87 (s, CH), 131.83 (s, CH), 128.33 (s, CH), 128.07 (s, CH), 90.96 (s, C_q), 29.51 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 268.9434 $[(C_8H_7IO)Na]^+$, measured 268.9436.



Chemical Formula: $C_{10}H_{11}BrO$
Exact Mass: 225,9993
Molecular Weight: 227,0977

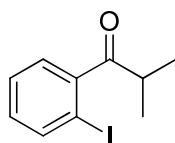
(24-Br) 1-(2-bromophenyl)-2-methylpropan-1-one: From Isobutyrophenone and NBS at 120 °C, using a slightly modified general procedure with 2.5 mol% of $[RhCp^*Cl_2]_2$, 10 mol% $AgSbF_6$, 1.1 equiv of NBS, 2.2 equiv $Cu(OAc)_2$ instead of PivOH and 21 h reaction time. Product purified by SiO_2 gel column chromatography (35 x 350 mm, toluene). 73% isolated yield (colorless oil).

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.61-7.53 (m, 1H, aromatic proton), 7.36-7.30 (m, 1H, aromatic proton), 7.29-7.22 (m, 2H, aromatic protons), 3.38-3.22 (m, 1H, $\text{CH}(\text{CH}_3)_2$), 1.18 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 208.78 (s, C_q , C=O), 142.05 (s, C_q), 133.44 (s, CH), 131.15 (s, CH), 128.17 (s, CH), 127.33 (s, CH), 118.70 (s, C_q), 40.25 (s, $\text{CH}(\text{CH}_3)_2$), 18.19 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 245.9885 $[(\text{C}_{10}\text{H}_{11}\text{BrO})\text{Na}]^+$, measured 248.9884.

ATR-FTIR: $\nu = 2972, 2932, 2873, 1701, 1464, 1428, 1217, 1052, 977, 737$.



Chemical Formula: $\text{C}_{10}\text{H}_{11}\text{IO}$

Exact Mass: 273.9855

Molecular Weight: 274.0982

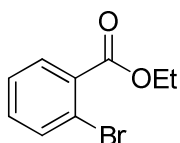
(24-I) 1-(2-iodophenyl)-2-methylpropan-1-one: From Isobutyrophenone and NIS at 120 °C, using a slightly modified general procedure with 2.5 mol% of $[\text{RhCp}^*\text{Cl}_2]_2$, 10 mol% AgSbF_6 , 1.1 equiv of NIS, 2.2 equiv $\text{Cu}(\text{OAc})_2$ instead of PivOH and 21 h reaction time. Product purified by SiO_2 gel column chromatography (35 x 350 mm, toluene). 61% isolated yield (yellow oil).

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.87 (dd, $J = 7.9$ and 1.1 Hz, 1H, aromatic proton), 7.38 (td, $J = 7.5$ and 1.1 Hz, 1H, aromatic proton), 7.25 (dd, $J = 7.6$ and 1.8 Hz, 1H, aromatic proton), 7.09 (ddd, $J = 7.9, 7.4$ and 1.7 Hz, 1H, aromatic proton), 3.29 (hept, $J = 6.9$ Hz, 1H, $\text{CH}(\text{CH}_3)_2$), 1.19 (d, $J = 6.9$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 209.23 (s, C_q , C=O), 145.34 (s, C_q), 140.21 (s, CH), 131.21 (s, CH), 127.95 (s, CH), 127.61 (s, CH), 91.40 (s, C_q), 39.72 (s, $\text{CH}(\text{CH}_3)_2$), 18.28 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 296.9747 $[(\text{C}_{10}\text{H}_{11}\text{IO})\text{Na}]^+$, measured 296.9748.

ATR-FTIR: $\nu = 2971, 2931, 2872, 1697, 1460, 1217, 1017, 975, 733$.



Chemical Formula: $C_9H_9BrO_2$

Exact Mass: 227,9786

Molecular Weight: 229,0706

(25-Br) Ethyl 2-bromobenzoate: From Ethyl benzoate and NBS at 120 °C, using a slightly modified general procedure with 2.5 mol% of $[RhCp^*Cl_2]_2$, 10 mol% $AgSbF_6$, 2.0 equiv of NBS were added in four portions (1 x 0.8 mmol, 3 x 0.4 mmol), 1.1 equiv $Cu(OAc)_2$ instead of PivOH and 21 h reaction time . Product purified by SiO_2 gel column chromatography (35 x 350 mm, pentane/EtOAc = 99/1). 60% isolated yield (colorless liquid).

1H NMR (300.1 MHz, $CDCl_3$) δ (ppm): 7.78-7.73 (m, 1H, aromatic proton), 7.65-7.61 (m, 1H, aromatic proton), 7.37-7.26 (m, 2H, aromatic proton), 4.38 (q, $J = 7.1$ Hz, 2H, OCH_2), 1.38 (t, 3H, CH_3).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ (ppm): 166.29 (s, C_q , \underline{CO}), 134.29 (s, CH), 132.57 (s, C_q), 132.46 (s, CH), 131.20 (s, CH), 127.19 (s, CH), 121.56 (s, C_q), 61.69 (s, CH_2), 14.27 (s, CH_3).

ESI H.R. mass spectrometry: m/z calc. 250.9678 $[(C_9H_9BrO_2)Na]^+$, measured 250.9677.

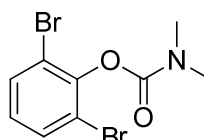


Chemical Formula: $C_9H_{10}BrNO_2$

Exact Mass: 242,9895

Molecular Weight: 244,0852

+



Chemical Formula: $C_9H_9Br_2NO_2$

Exact Mass: 320,9000

Molecular Weight: 322,9813

(26a-Br) 2-bromophenyl dimethylcarbamate + (26b-Br) 2,6-dibromophenyl dimethylcarbamate: From **25** and NBS at 120°C, using a slightly modified general procedure with 2.5 mol% of $[RhCp^*Cl_2]_2$, 10 mol% $AgSbF_6$, 2.0 equiv of NBS, 2.2 equiv $Cu(OAc)_2$ instead of PivOH and 48h reaction time . Product purified by SiO_2 gel column chromatography (30 x 200 mm, pentane/EtOAc = 8/2). 35% isolated yield (colorless oil) for 25a-Br and 49% isolated yield (yellow solid) for 25b-Br.

2-bromophenyl dimethylcarbamate (26a-Br)

R_f (pentane/EtOAc = 5/5): 0.74.

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.58 (dd, $J = 8.0$ and 1.6 Hz, 1H, aromatic proton), 7.31 (ddd, $J = 8.1$, 7.4 and 1.6 Hz, 1H, aromatic proton), 7.22 (dd, $J = 8.1$ and 1.6 Hz, 1H, aromatic proton), 7.08 (ddd, $J = 8.0$, 7.4 and 1.6 Hz, 1H, aromatic proton), 3.16 (s, 3H, $\text{N}(\text{CH}_3)$), 3.03 (s, 3H, $\text{N}(\text{CH}_3)$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 153.87 (s, C_q , C=O), 148.95 (s, C_q), 133.19 (s, CH), 128.42 (s, CH), 126.84 (s, CH), 124.31 (s, CH), 116.54 (s, C_q), 36.98 (s, CH_3 , $\text{N}(\text{CH}_3)$), 36.70 (s, CH_3 , $\text{N}(\text{CH}_3)$).

ESI H.R. mass spectrometry: m/z calc. 265.9787 $[(\text{C}_9\text{H}_{10}\text{BrNO}_2)\text{Na}]^+$, measured 265.9790.

ATR-FTIR: $\nu = 2935, 1723, 1471, 1383, 1217, 1151, 1047, 747$.

2,6-dibromophenyl dimethylcarbamate (26b-Br)

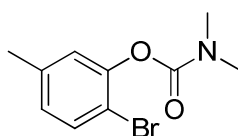
R_f (pentane/EtOAc = 5/5): 0.72.

^1H NMR (400.1 MHz, CDCl_3) δ (ppm): 7.54 (d, $J = 8.1$ Hz, 2H, aromatic protons), 6.97 (t, $J = 8.1$ Hz, 1H, aromatic proton), 3.19 (s, 3H, $\text{N}(\text{CH}_3)$), 3.06 (s, 3H, $\text{N}(\text{CH}_3)$).

$^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz, CDCl_3) δ (ppm): 152.45 (s, C_q , C=O), 148.81 (s, C_q), 132.39 (s, CH), 127.82 (s, CH), 118.63 (s, C_q), 37.17 (s, CH_3 , $\text{N}(\text{CH}_3)$), 36.81 (s, CH_3 , $\text{N}(\text{CH}_3)$).

ESI H.R. mass spectrometry: m/z calc. 345.8872 $[(\text{C}_9\text{H}_9\text{Br}_2\text{NO}_2)\text{Na}]^+$, measured 345.8871.

ATR-FTIR: $\nu = 2948, 1728, 1432, 1381, 1321, 1151, 845$.



Chemical Formula: $\text{C}_{10}\text{H}_{12}\text{BrNO}_2$

Exact Mass: 257.0051

Molecular Weight: 258.1118

(27-Br) 2-bromo-5-methylphenyl dimethylcarbamate: From **26** and NBS at 120°C , using a slightly modified general procedure with 2.5 mol% of $[\text{RhCp}^*\text{Cl}_2]_2$, 10 mol% AgSbF_6 , 1.5 equiv of NBS, 2.2 equiv $\text{Cu}(\text{OAc})_2$ instead of PivOH and 24h reaction time. Product purified by SiO_2 gel column chromatography (30 x 140 mm, pentane/EtOAc = 7/3). 76% isolated yield (yellow oil).

R_f (pentane/EtOAc = 5/5): 0.73.

^1H NMR (300.1 MHz, CDCl_3) δ (ppm): 7.43 (d, $J = 8.2$ Hz, 1H, aromatic proton), 7.04-7.02 (m, 1H, aromatic proton), 6.91-6.87 (m, 1H, aromatic proton), 3.15 (s, 3H, $\text{N}(\text{CH}_3)$), 3.03 (s, 3H, $\text{N}(\text{CH}_3)$), 2.31 (s, 3H, ArCH_3).

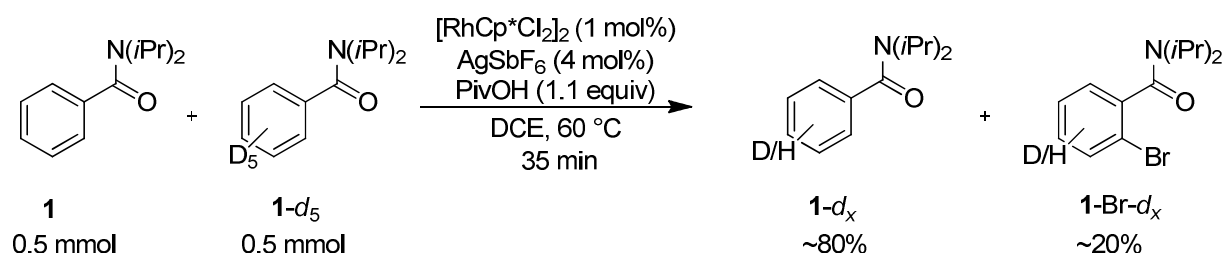
$^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl_3) δ (ppm): 154.00 (s, C_q , CO), 148.57 (s, C_q), 138.82 (s, C_q), 132.67 (s, CH), 127.75 (s, CH), 124.90 (s, CH), 112.98 (s, C_q), 36.96 (s, CH_3 , $\text{N}(\text{CH}_3)$), 36.68 (s, CH_3 , $\text{N}(\text{CH}_3)$), 21.07 (s, CH_3 , ArCH_3).

ESI H.R. mass spectrometry: m/z calc. 279.9944 $[(\text{C}_{10}\text{H}_{12}\text{BrNO}_2)\text{Na}]^+$, measured 279.9936.

ATR-FTIR: $\nu = 2926, 1723, 1479, 1378, 1236, 1161, 1037, 806$.

5. Mechanistic Experiments

5.1 KIE intermolecular competition experiment



To a flame-dried screw-capped flask equipped with a magnetic stir bar were added under argon $[\text{RhCp}^*\text{Cl}_2]_2$ (6.2 mg, 0.01 mmol), AgSbF_6 (13.7 mg, 0.04 mmol) and PivOH (112.3 mg, 1.1 mmol). DCE (5 mL), the benzamide **1**, **1-d₅** (each 0.5 mmol) and NBS (1 mmol, 1.0 equiv) were added. The closed tube is added to an pre-heated oil-bath (60 °C) and stirred for 35 min. The mixture was then diluted with EtOAc (20 mL) and filtered through a pad of silica gel and eluted with EtOAc (100 mL). After removing the solvent under reduced pressure, the product and starting material were separated by SiO_2 gel column chromatography (30 x 300 mm, toluene/EtOAc = 9/1). The product and the reisolated starting material were submitted for ESI H.R. analysis to determine the deuteration grade.

1-Br-d_x (measured for $[(\text{C}_{13}\text{H}_{18-x}\text{D}_x\text{BrNO})\text{H}]^+$):

D-level	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
percentage	78,73	0,25	0,68	1,83	18,52	0,00

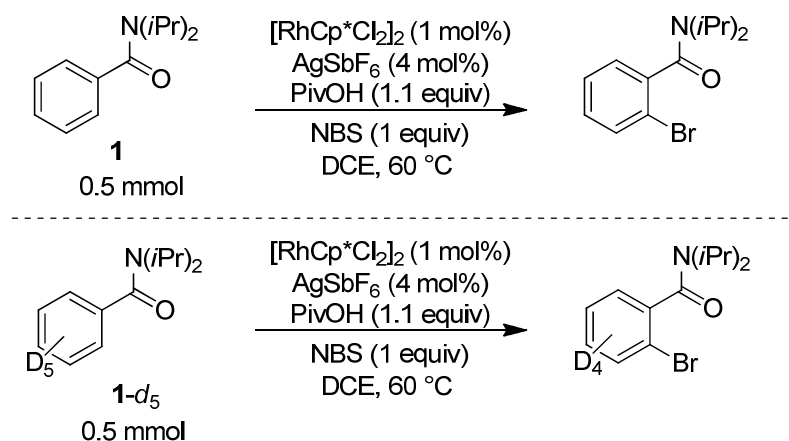
$$\underline{\text{KIE}} = 78.7 / (18.5+1.8) = \mathbf{3.9}.$$

1-d_x (measured for [(C₁₃H_{19-x}D_xNO)H]⁺):

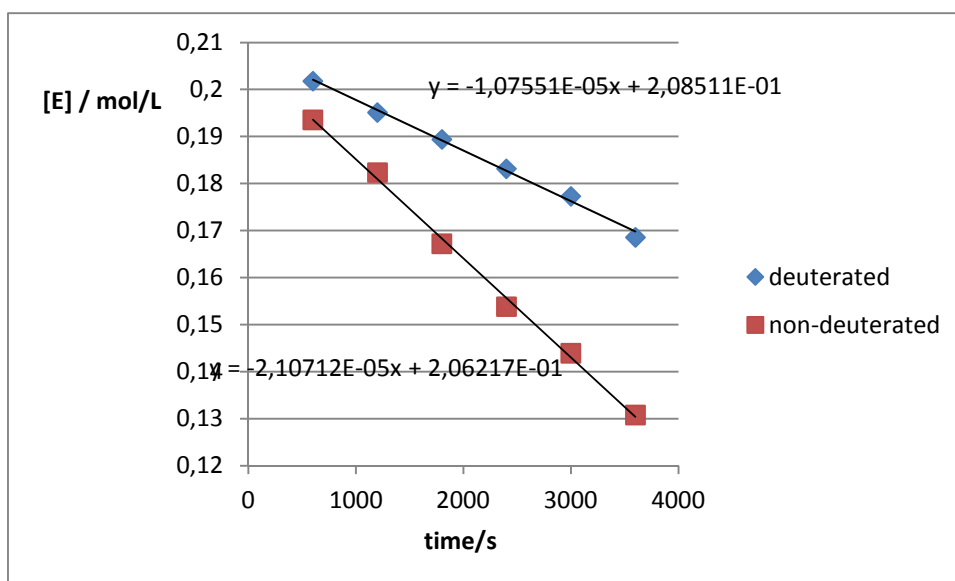
D-level	D ₀	D ₁	D ₂	D ₃	D ₄	D ₅
percentage	41,36	1,47	0,00	2,49	18,34	36,33

Important quantities of unreacted **1-d₅** underwent D/H scrambling.

5.2 KIE initial rate constants

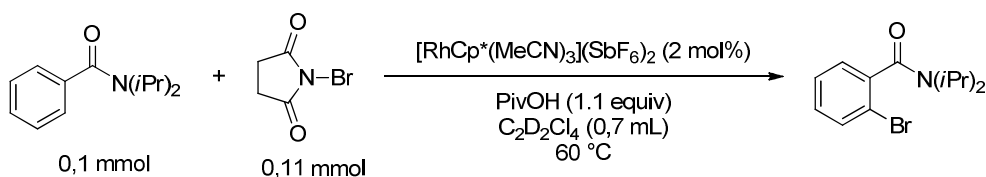


To a flame-dried screw-capped flask equipped with a magnetic stir bar were added under argon [RhCp*Cl₂]₂ (3.1 mg, 0.0050 mmol), AgSbF₆ (6.9 mg, 0.020 mmol) and PivOH (56.2 mg, 0.550 mmol). DCE (2.5 mL), the benzamide **1** or **1-d₅** (0.5 mmol), NBS (0.55 mmol, 1.1 equiv) and an internal standard (1,3,5-Tri-tert-butylbenzene, 123.18 mg) were added. The closed tube is added to an pre-heated oil-bath (60 °C) and stirred. For one hour, every ten minutes an aliquot (~20 µl) is collected and submitted to GC analysis to determine the conversion.

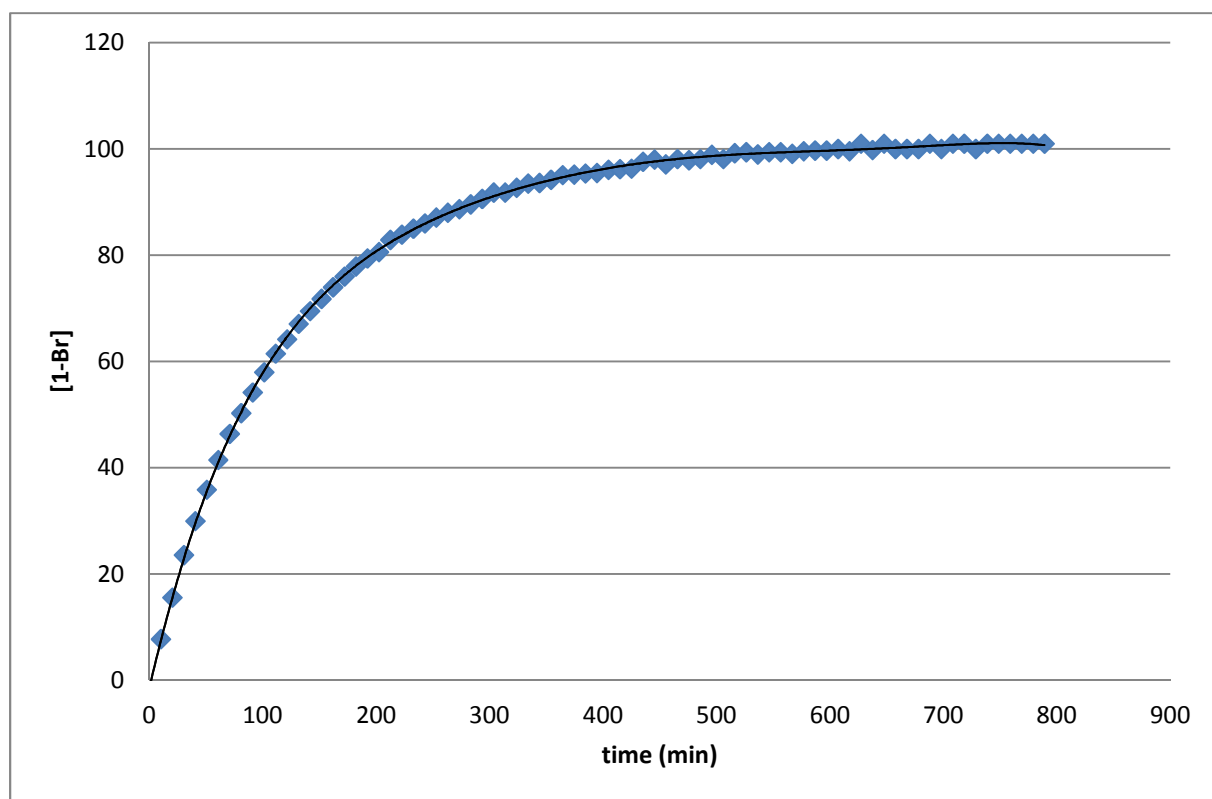


$$\frac{k_H}{k_D} = \frac{2.107 \cdot 10^{-5} \frac{\text{mol}}{\text{L} \cdot \text{s}}}{1.076 \cdot 10^{-5} \frac{\text{mol}}{\text{L} \cdot \text{s}}} \approx 2$$

5.3 NMR Experiments



The flame dried Schlenk tube was charged with $[\text{RhCp}^*(\text{MeCN})_3](\text{SbF}_6)_2$ (1.7 mg, 2 mol%), substrate **1** (20.5 mg, 0,10 mmol) and PivOH (11.2 mg, 0.11 mmol). The Schlenk was filled with argon and 0.7 mL of $\text{C}_2\text{D}_2\text{Cl}_4$ were added. The mixture was stirred at room temperature. After 15 min the reaction mixture was transferred to an NMR tube prefilled with Argon. The initial NMR spectrum was acquired at 60°C . Then NBS (19.6 mg, 0.11 mmol) was added. The kinetic was followed by NMR at 60°C . The results are presented as a time dependence of the concentration of product **1-Br**.

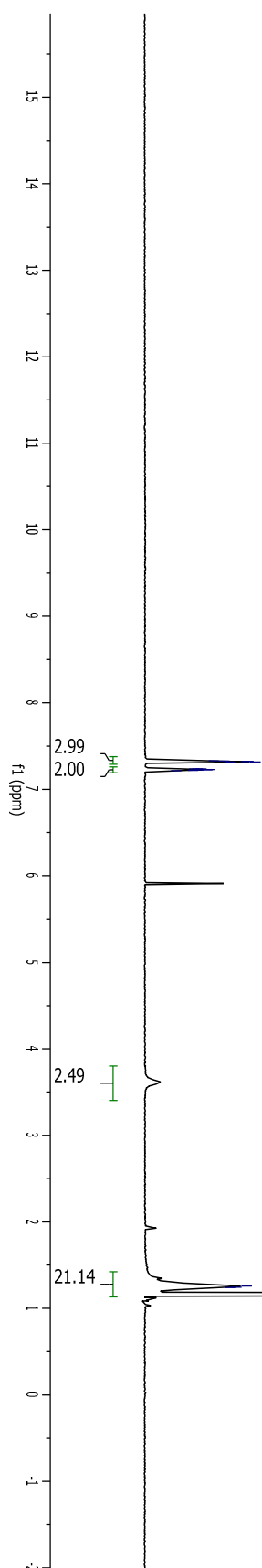
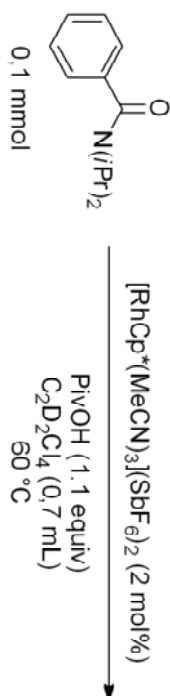


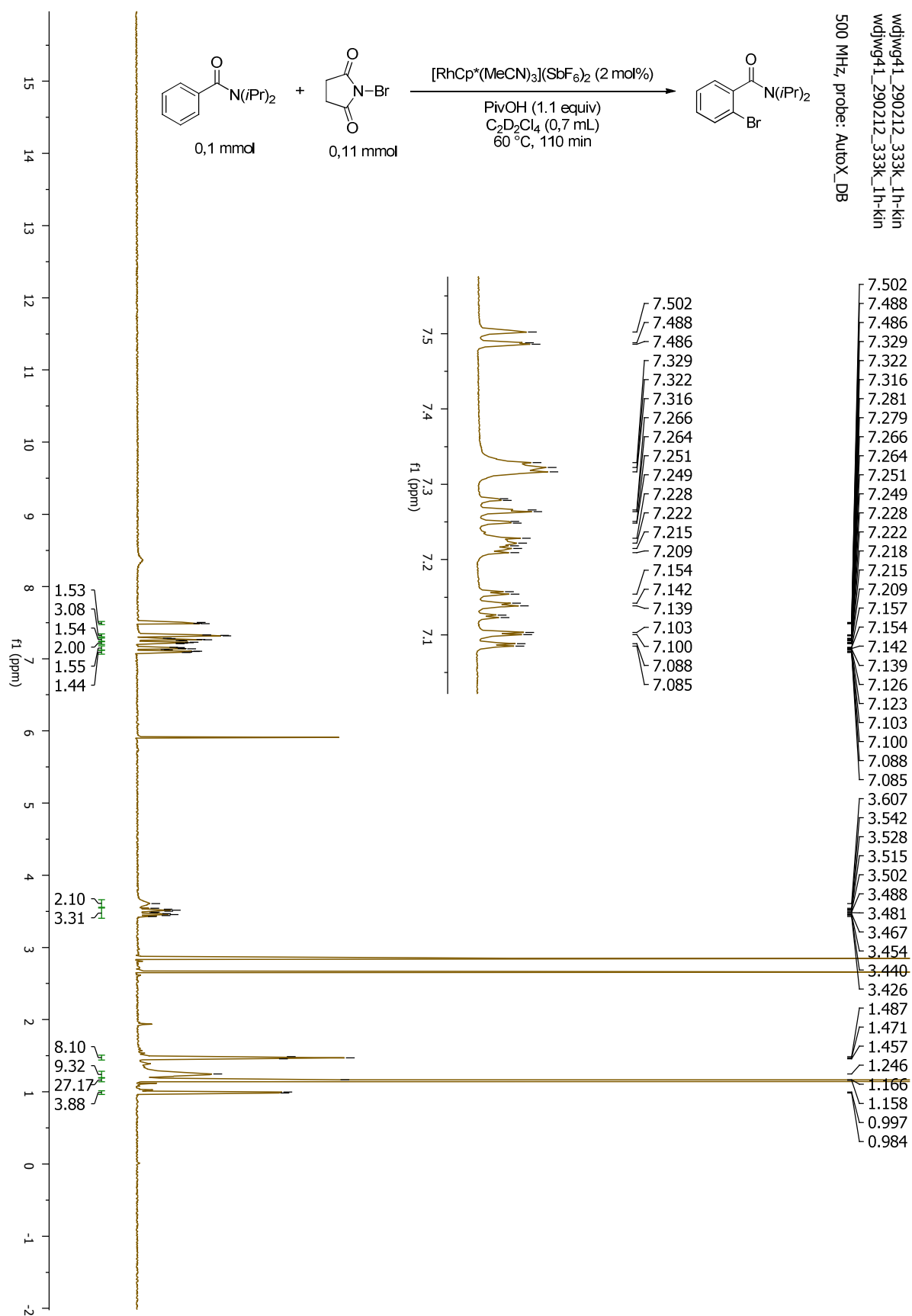
wdjwg41_280212_333k_1h
wdjwg41_280212_333k_1h
500 MHz, probe: AutoX_DB

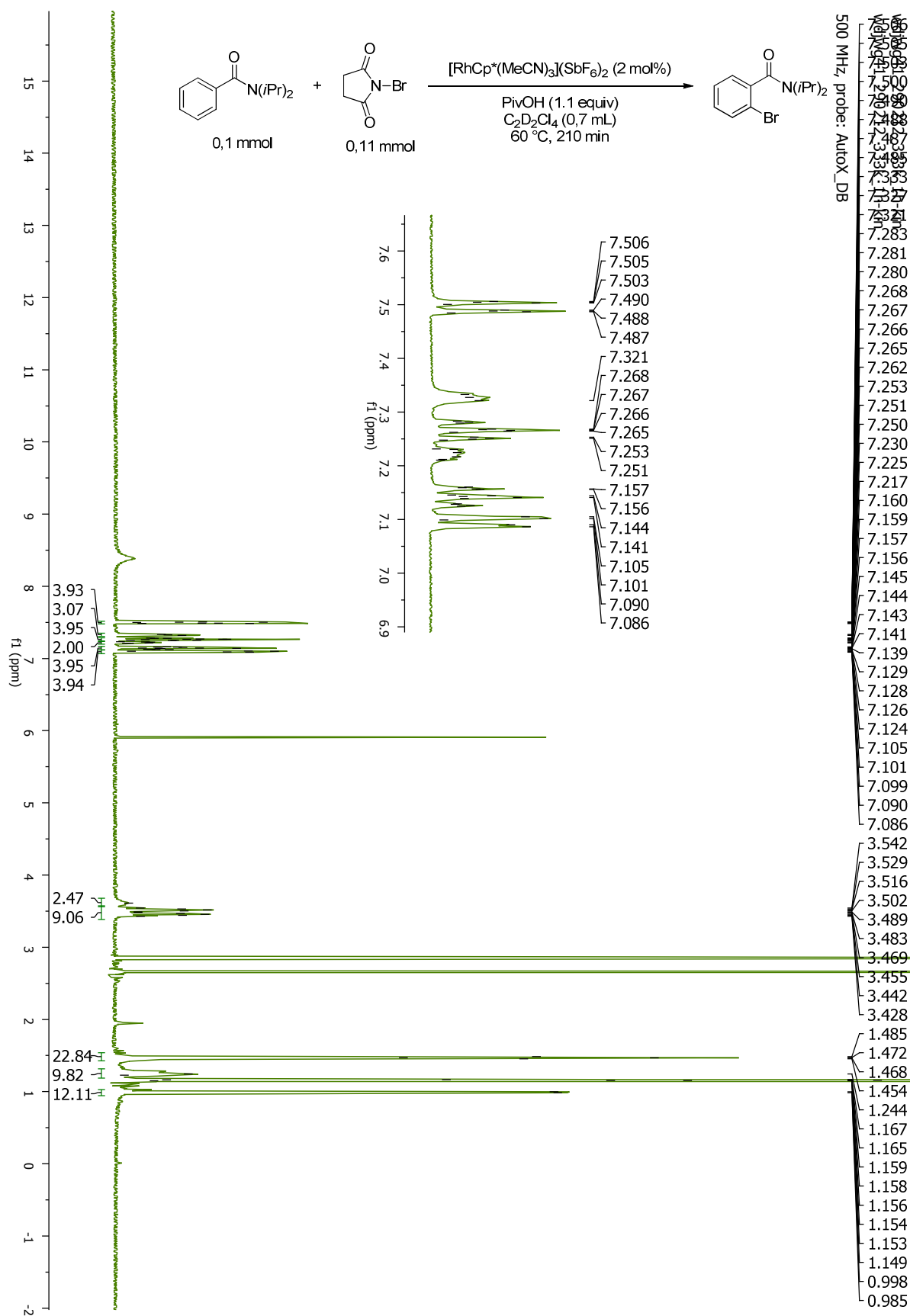
7.331
7.328
7.324
7.321
7.318
7.315
7.237
7.236
7.234
7.232
7.229
7.227
7.221
7.217
7.214

1.258
1.246
1.242
1.165
1.163
1.161

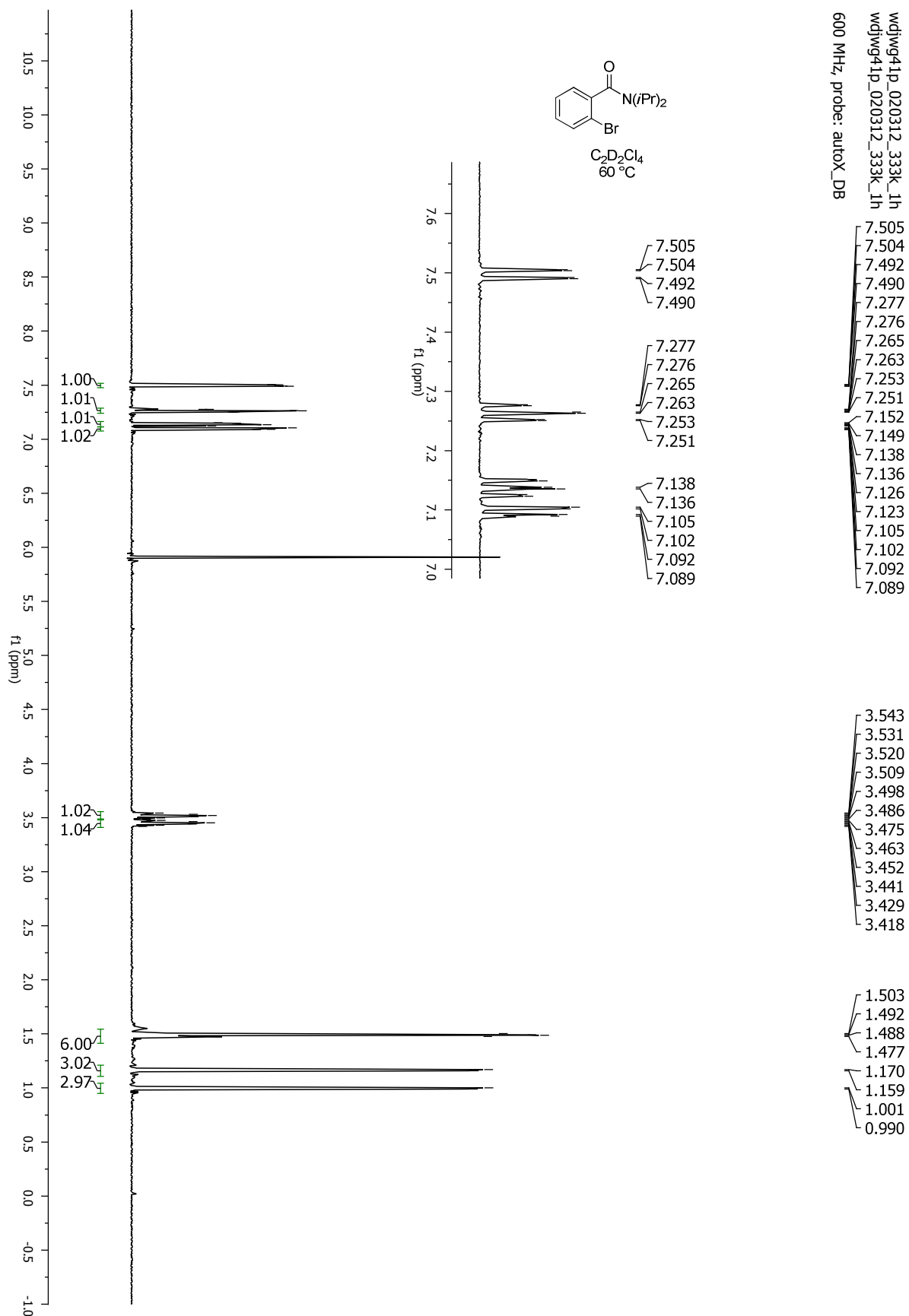
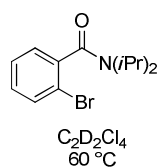
Initial spectrum in absence of NBS







wjdwg41p_020312_333k_1h
 wjdwg41p_020312_333k_1h
 600 MHz, probe: autoX_DB



6. References

- [1] G. Barbe, A. Charette, *J. Am. Chem. Soc.* **2008**, *130*, 18-19.
- [2] Modified procedure from: T. Besset, N. Kuhl, F. W. Patureau, F. Glorius, *Chem. Eur. J.* **2011**, *17*, 7167-7171.

7. Spectra

