Electronic Supplementary Material (ESI) for ChemComm.
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Supporting Information

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General Considerations

All reactions were carried out with commercial solvents and reagents that were used as received. For NaDT photochemical reactions, degassing of the solvent was carried out via several freeze/pump/thaw cycles. Flash chromatography was carried out with Geduran® Si60 silica gel (Merck). Concentration and removal of trace solvents was done via a Büchi rotary evaporator using dry ice/acetone condenser, and vacuum applied from an aspirator or Büchi V-500 pump. All reagents and starting materials were purchased from Sigma Aldrich, Alfa Aesar, TCI America, and/or Strem, and were used without further purification. All solvents were purchased from Sigma Aldrich, EMD, Anachemia, Caledon, Fisher, or ACP and used without further purification, unless otherwise specified. Nuclear magnetic resonance (NMR) spectra were recorded using chloroform-*d* ($CDCl_3$), acetonitrile-*d*$_3$ (CD_3CN), DMSO-*d*$_6$ or methanol-*d*$_4$ (MeOD). Signal positions (δ) are given in parts per million from tetramethylsilane (δ 0) and were measured relative to the signal of the solvent (^{1}H NMR: $CDCl_3$: δ 7.26, CD_3CN: δ 1.96, DMSO-*d*$_6$: δ 2:50, MeOD: δ 3.31; ^{13}C NMR: $CDCl_3$: δ 77.16, CD_3CN: δ 118.26, DMSO-*d*$_6$: δ 39.52, MeOD: δ 49.00). Coupling constants (*J* values) are given in Hertz (Hz) and are reported to the nearest 0.1 Hz. ^{1}H NMR spectral data are tabulated in the order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet), coupling constants, number of protons. NMR spectra were recorded on a Bruker Avance 600 equipped with a QNP, Bruker 500 (500 MHz), or Bruker 400 (400 MHz). Assignments of ^{1}H and ^{13}C NMR spectra are based on analysis of ^{1}H-, ^{1}H COSY, HSQC, and HMBC spectra, where applicable. 1,3,5-Tris(trifluoromethyl)benzene was added to the crude reaction mixtures and used as an internal standard. Yields were then calculated following analysis of quantitative ^{19}F NMR spectra. Highresolution mass spectra were performed on an Agilent 6210 TOF LC/MS, Bruker MaXis Impact TOF LC/MS, or Bruker microTOF-II LC mass spectrometer.

General Procedure A

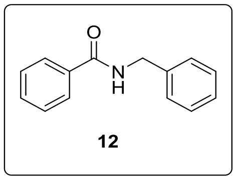
To a solution of the aldehyde in CH_3CN (0.1 - 0.3 M) was added NFSI (1.1 equiv.) and NaDT (2.5 mol %). The resulting mixture was degassed via 3 x freeze/pump/thaw cycles. The reaction was irradiated with a long-wave UV (~365 nm) for 3 hours. The formation of the acyl fluoride intermediate was characterized by ^{19}F NMR spectroscopy. *N*, *N*–Diisopropylethylamine (2.0 equiv.) and benzylamine (2.0 equiv.) were then added to the reaction mixture and the resulting solution was stirred for an additional 2 hours. The reaction mixture was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was dried over $MgSO_4$, filtered, and concentrated under reduced pressure and the crude reaction product was purified by column chromatography as indicated.

General Procedure B

To a solution of alcohol (1 equiv.) in CH_3CN (0.1 M) was added NFSI (2.5 equiv.) and NaDT (2.0 mol %). The resulting mixture was degassed via 3 x freeze/pump/thaw cycles. The reaction was irradiated with UV-light (~365 nm) for 16 hours. The formation of the acyl fluoride intermediate was characterized by ^{19}F-NMR spectroscopy. *N*, *N*-Diisopropylethylamine (2 equiv.) and benzylamine (2 equiv.) were then added to the reaction mixture and the resulting solution was stirred for an additional 3 hours. The reaction mixture was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure and the crude reaction product was purified by flash column chromatography.

Preparation of Compound **12**

Following General Procedure **A**, a solution of benzaldehyde (0.106 g, 1.0 mmol), NFSI (0.378 g, 1.2 mmol), and NaDT (61.1 mg, 0.025 mmol) in 3 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **11** was characterized by ^{19}F-NMR spectroscopy (δ = 17 ppm, CD_3CN, ^{19}F NMR yield = 79%). *N*, *N*-Diisopropylethylamine (0.348 mL, 2.0 mmol) and benzylamine (0.218 mL, 2.0 mmol) were then added to the reaction mixture and the resulting mixture was stirred for an additional 2 hours. Purification of crude amide **12** by flash chromatography (pentane-EtOAc 9:1) afforded amide **12** (0.166 g, 79% yield). Spectral data recorded on amide **12** were in complete agreement with that previously reported.[1]


12

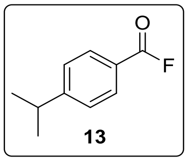
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.76-7.83 (m, 2H), 7.27-7.54 (m, 8H), 6.39 (br s, 1H), 4.66 (d, *J* = 5.6 Hz, 2H); **^{13}C NMR** (75 MHz, DMSO-*d*$_6$): δ 166.2, 139.7, 134.3, 131.2, 128.30, 128.26, 127.21, 127.16, 126.7, 42.6; HRMS (ESI) calcd for $[C_{14}H_{14}NO]^+$: 212.1070; found 212.1088.

[1] Kosal, A. D.; Wilson, E. E.; Ashfeld, B. L. *Angew. Chem. Int. Ed.* **2012**, *51*, 12036

Preparation of Compound **13** and **13a**

Following General Procedure **A**, a solution of 4-isopropylbenzaldehyde (0.074 g, 0.5 mmol), NFSI (0.189 g, 0.6 mmol), and NaDT (31.7 mg, 0.013 mmol) in 5.0 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **13** was characterized by ^{19}F-NMR spectroscopy (δ = 16 ppm, CD_3CN, ^{19}F NMR yield = 43%). The reaction mixture was then concentrated and purified by flash chromatography (pentane-Et_2O) to afford an analytical sample of **13**. In a separate identical experiment, *N*, *N*-diisopropylethylamine (0.174 mL, 1.0 mmol) and benzylamine (0.107 mL, 1.0 mmol) were directly added to the crude reaction mixture which was stirred for an additional 2 hours. Purification of crude amide **13a** by flash chromatography (pentane:EtOAc = 90:10) afforded amide **13a** (0.053 g, 42% yield). Spectral data recorded on amide **13a** were in complete agreement with that previously reported.[2]

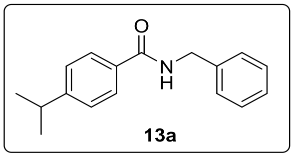
Compound **13**



13

^{1}H NMR (600 MHz, CD_2Cl_2): δ 7.96 (d, 2H), 7.40 (d, 2H), 3.00 (septet, J = 7.0 Hz, 1H), 1.27 (d, J = 7.0 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 157.9, 157.8 (d, J = 343.0 Hz), 127.7 (d, J = 0.8 Hz), 122.6 (d, J = 61.5 Hz), 34.8, 23.6; **^{19}F NMR** (470 MHz, CD_2Cl_2): δ 16.8.

Compound **13a**



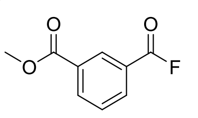
13a

IR (neat): υ = 3315, 2960, 2930, 2875, 1635, 1539, 1308, 697 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.34-7.37 (m, 4H), 7.27-7.32 (m, 3H), 6.33 (br s, 1H), 4.66 (d, *J* = 5.6 Hz, 2H), 2.95 (septet, *J* = 6.5 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H); **^{13}C NMR** (125 MHz, $CDCl_3$): δ 167.4, 152.9, 138.5, 132.0, 128.8, 128.0, 127.6, 127.3, 126.7, 44.1, 34.2, 23.9; HRMS (ESI$^+$) calcd for $[C_{17}H_{20}NO]^+$ 254.1539, found 254.1514.

[2]Das, J.; Banerjee, D. *J. Org. Chem*. **2018**, *83*, 3378

Preparation of Compound **14**

Following General Procedure **A**, a solution of methyl 3-formylbenzoate (0.082 g, 0.50 mmol), NFSI (0.173 g, 0.55 mmol), and NaDT (24.0 mg) in 0.5 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **14** was characterized by ^{19}F-NMR spectroscopy (δ = 18 ppm, CD_3CN, ^{19}F NMR yield = 60%). The reaction mixture was then concentrated and purified by flash chromatography (pentane-Et_2O) to afford **14**.



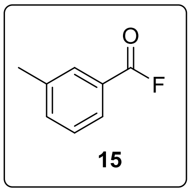
14

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.71 (s, 1H), 8.37 (d, J = 7.8 Hz, 1H), 8.24 (d, J = 7.8 Hz, 1H), 7.64 (dd, J = 7.8 Hz, 1H), 3.98 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 165.6, 156.8 (d, J = 345.5 Hz), 136.2, 135.5 (d, J = 4.1 Hz), 132.6 (d, J = 3.4 Hz), 131.6, 129.5, 125.7 (d, J = 62.7 Hz), 52.8; **^{19}F NMR** (470 MHz, $CDCl_3$): δ 19.2

Preparation of Compound **15**

Following General Procedure **A**, a solution of 3-methylbenzaldehyde (0.050 g, 0.42 mmol), NFSI (0.145 g, 0.46 mmol), and NaDT (26.0 mg) in 2.1 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride **15** was characterized by ^{19}F-NMR spectroscopy (δ = 17 ppm, CD_3CN, ^{19}F NMR = 69%). The reaction mixture was then concentrated and purified by flash chromatography (pentane-Et_2O) to afford **15**. In a separate identical experiment, *N*, *N*-diisopropylethylamine (0.146 mL, 0.84 mmol) and benzylamine (0.092 mL, 0.84 mmol) were directly added to the crude reaction mixture which was left to stir for 2 hours. Purification of crude amide **15a** by flash chromatography (pentane-EtOAc 70:30) afforded amide **15a** (0.058 g, 62% yield). Spectral data recorded on amide **15a** were in complete agreement with that previously reported.[3]

Compound **15**

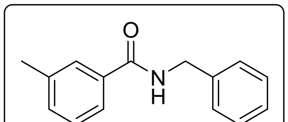


15

^{1}H NMR (600 MHz, CD_2Cl_2): *δ* 7.86 (s, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.51 (d, J = 7.6 Hz, 1H), 7.41 (dd, J = 7.6 Hz, 1H), 2.43 (s, 3H); **^{13}C NMR** (150 MHz, CD_2Cl_2): *δ* 157.8 (d, J = 345.0 Hz), 139.2, 136.3, 132.0 (d, J = 4.1 Hz), 129.1 (d, J = 0.8 Hz), 128.8 (d, J = 3.8 Hz), 125.0 (d, J = 60.1 Hz), 21.4; **^{19}F NMR** (470 MHz, CD_2Cl_2): *δ* 18.3

[3]Birrell, J. A.; Desrosiers, J.-N.; Jacobsen, E. N. *J. Am. Chem. Soc*. **2011**, *133*, 1387.

Compound **15a**



15a

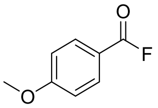
IR (neat): *υ* = 3310, 1640, 1538, 743.7, 697 cm^{-1}; **^{1}H NMR** (600 MHz, $CDCl_3$): *δ* 7.61 (s, 1H), 7.56 (m, 1H), 7.34 (m, 7H) 1H), 6.35 (br s), 4.66 (d, *J* = 5.3 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): *δ* 167.7, 138.6, 138.4, 134.5, 132.4, 128.9, 128.6, 128.1, 127.8, 127.8, 124.0, 44.3, 21.5; HRMS (EI$^+$) calcd for $[C_{15}H_{16}NO]^+$ 226.1226, found 216.1205.

Kulkarni, ,S. S.; Xiangdong, H.; Manetsch, R. *Chem. Commun*. **2013**, *49*, 1193

Preparation of Compound **16**

Following General Procedure **A**, a solution of p-anisaldehyde (0.050 mL, 0.41 mmol), NFSI (0.130 g, 0.41 mmol), and NaDT (25.0 mg, 0.010 mmol) in 2.7 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **16** was characterized by ^{19}F-NMR spectroscopy (δ = 16 ppm, CD_3CN). The reaction mixture was then concentrated and purified by flash chromatography (pentane-Et_2O) to afford **16**. Spectral data recorded on acyl fluoride **16** were in complete agreement with that previously reported.[4] In a separate identical experiment, *N*, *N*-diisopropylethylamine (0.142 mL, 0.82 mmol) and benzylamine (0.090 mL, 0.82 mmol) were directly added to the crude reaction mixture which was left to stir for 2 hours. Purification of crude amide **16a** by flash chromatography (pentane-EtOAc 30:70) afforded amide **16a** (0.038 g, 38% yield). Spectral data recorded on amide **16a** were in complete agreement with that previously reported.[5]

Compound **16**

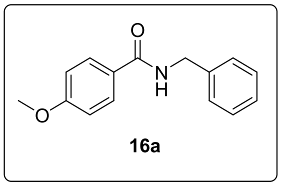


16

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.99 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): *δ* 165.4, 157.5 (d, J = 340.2 Hz), 133.9 (d, J = 4.1 Hz), 117.0 (d, J = 61.7 Hz), 114.6 (d, J = 0.8 Hz), 55.8; **^{19}F NMR** (470 MHz, $CDCl_3$): *δ* 16.0

[4]Cismesia, M. A.; Ryan, S. J.; Bland, D. C.; Sanford, M. S. *J. Org, Chem*. **2017**, *82*, 5020

Compound **16a**

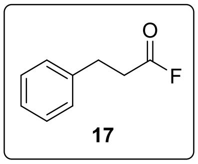

16a

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.76 (dd, *J* = 8.8 Hz, 2H), 7.36 (m, 4H), 7.30 (m, 2H), 6.92 (d, *J* = 8.8, 2H), 6.28 (br s, 1H), 4.65 (d, J = 5.6 Hz, 2H), 3.85 (s, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$): *δ* 167.0, 162.4, 138.5, 128.9, 128.9, 128.1 127.8, 126.7, 113.9, 55.6, 44.2; HRMS (EI^+) calcd for $[C_{15}H_{16}NO_2]^+$ 242.1176, found 242.1150.

[5] Lundbreg, H.; Tinnis, F.; Adolfsson, H. *Chem. Eur. J.* **2012**, *18*, 3822

Preparation of Compound **17**

Following General Procedure **A**, a solution of hydrocinnamaldehyde (0.134 g, 1.0 mmol), NFSI (0.346 g, 1.1 mmol), and NaDT (46.0 mg, 0.020) in 10.0 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate was characterized by ^{19}F-NMR spectroscopy (δ = 43 ppm, CD_3CN, ^{19}F NMR yield = 51%). The reaction mixture was then concentrated and purified by flash chromatography (pentane-Et_2O) to afford **17**. Spectral data recorded on acyl fluoride **17** were in complete agreement with that previously reported.[6]

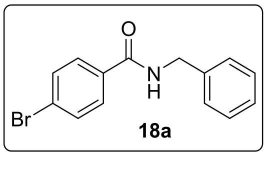

17

^{1}H NMR (600 MHz, $CDCl_3$): *δ* 7.32-7.22 (m, 5H), 3.00 (t, J = 8.0 Hz, 2H), 2.83 (t, J = 8.0 Hz, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$): *δ* 162.8 (d, J = 360.2 Hz), 139.1, 128.9, 128.4, 127.0, 34.0 (d, J = 50.9 Hz), 30.2 (d, J = 2.8 Hz); ^{19}F-NMR (470 MHz, $CDCl_3$): δ 45.3.

[6] L'Heureux, A.; Beaulieu, F.; Bennett, C.; Bill, D. R.; Clayton, S.; LaFlamme, F.; Mirmehrabi, M.; Tadayon, S.; Tovell, D.; Couturier, M. *J. Org. Chem.* **2010**, *75*, 3401.

Preparation of Compound **18a**

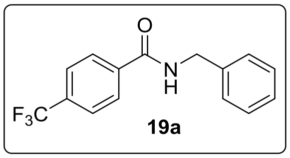
Following General Procedure **A**, a solution of 4-bromobenzaldehyde (0.050 g, 0.27 mmol), NFSI (0.085 g, 0.27 mmol), and NaDT (0.016 g, 0.27 mmol) in 1.35 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **18** was characterized by ^{19}F-NMR spectroscopy (δ = 17 ppm, CD_3CN, ^{19}F NMR yield = 40%). *N*, *N*-Diisopropylethylamine (0.094 mL, 0.54 mmol) and benzylamine (0.059 mL, 0.54 mmol) were then added to the reaction mixture and the resulting reaction mixture was stirred for an additional 2 hours. Purification of crude amide **18a** by flash chromatography (pentane-EtOAc 95:5) afforded amide **18a** (0.031 g, 40% yield). Spectral data recorded on amide **18a** were in complete agreement with that previously reported.[7]


18a

^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.66 (d, *J* = 8.3 Hz, 2H), 7.57 (d, J = 8.3 Hz, 2H), 7.36 (m, 4H), 7.31 (m, 1H), 6.31 (br s), 4.64 (d, J = 5.7 Hz, 2H); HRMS (ESI) calcd for $[C_{14}H_{13}BrNO]^+$: 290.0175; found 290.0176.

[7] Liu, Y.; Shi, S.; Achtenhagen, M.; Liu, R.; Szostak, M. *Org. Lett.* **2017**, *1*, 1614.

Preparation of Compound **19a**

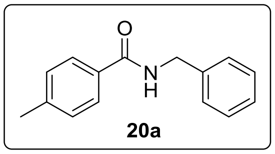

19a

Following General Procedure **A**, a solution of 4-(trifluoromethyl)benzaldehyde (0.050 g, 0.287 mmol), NFSI (0.100 g, 0.316 mmol), and NaDT (18.1 mg, 2.5 mol%) in 1.44 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **19** was characterized by ^{19}F-NMR spectroscopy (δ = 19 ppm, CD_3CN, ^{19}F NMR yield = 53%). *N*, *N*-Diisopropylethylamine (0.348 mL, 2.0 mmol) and benzylamine (0.218 mL, 2.0 mmol) were then added to the reaction mixture and the resulting mixture was stirred for an additional 2 hours. Spectral data recorded on crude amide **19a** were in complete agreement with that previously reported.[8]

[8] Sutthichat, K.; Quan, X.; Parihar, V. S.; Andersson, P. G. *J. Org. Chem*. **2015**, *80*, 11529

Preparation of Compound **20a**

Following General Procedure **A**, a solution of 4-methylbenzaldehyde (0.122 g, 1.0 mmol), NFSI (0.378 g, 2.0 mmol), and NaDT (61.1 mg, 0.025 mmol) in 3 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **20** was characterized by ^{19}F-NMR spectroscopy (δ = 16 ppm, CD_3CN, ^{19}F NMR yield = 70%). *N*, *N*-Diisopropylethylamine (0.348 mL, 2.0 mmol) and benzylamine (0.218 mL, 2.0 mmol) were then added to the reaction mixture and the resulting reaction mixture was stirred for an additional 2 hours. Purification of crude amide **20a** by flash chromatography (pentane-EtOAc 9:1) afforded amide **20a** (0.096 g, 43% yield). Spectral data recorded on crude amide **20a** were in complete agreement with that previously reported.[8]

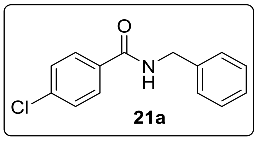

20a

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65-7.73 (m, 2H), 7.27-7.42 (m, 5H), 7.19-7.25 (m, 2H), 6.16-6.53 (m, 1H), 4.64 (d, J = 5.6 Hz, 2H), 2.39 (s, 3H); **^{13}C NMR** (75 MHz, DMSO-d_6) δ 166.0, 141.1, 139.8, 131.5, 128.8, 128.2, 127.23, 127.16, 126.7, 42.5, 20.9; HRMS (ESI) calcd for $[C_{15}H_{16}NO]^+$: 226.1226; found 226.1236.

[8] Sutthichat, K.; Quan, X.; Parihar, V. S.; Andersson, P. G. *J. Org. Chem*. **2015**, *80*, 11529

Preparation of Compound **21a**

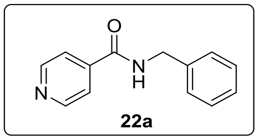
Following General Procedure **A**, a solution of 4-chlorobenzaldehyde (0.146 g, 1.0 mmol), NFSI (0.378 g, 1.2 mmol), and NaDT (61.1 mg, 0.025 mmol) in 3 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **21** was characterized by ^{19}F-NMR spectroscopy (δ = 17 ppm, CD_3CN, ^{19}F NMR yield = 67%). *N*, *N*-Diisopropylethylamine (0.348 mL, 2.0 mmol) and benzylamine (0.218 mL, 2.0 mmol) were then added to the reaction mixture and the resulting reaction mixture was stirred for an additional 2 hours. Purification of crude amide **21a** by flash chromatography (pentane-EtOAc 95:5) afforded amide **21a** (0.090 g, 37% yield). Spectral data recorded on crude amide **21a** were in complete agreement with that previously reported.[9]


21a

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.73 (d, J = 8.46 Hz, 2H), 7.28-7.42 (m, 7H), 6.34 (br s, 1H), 4.64 (d, J = 5.6 Hz, 2H); **^{13}C-NMR** (75 MHz, DMSO-d_6): δ 165.1, 139.5, 136.0, 133.0, 129.2, 128.4, 128.3, 127.2, 126.8, 42.7; HRMS (ESI) calcd for $[C_{14}H_{13}ClNO]^+$: 246.0680; found 246.0686.

[9] Green, R. A.; Pletcher, D.; Leach, S.G.; Brown, R. C. D. *Org. Lett.* **2016**, *18*, 1198

Preparation of Compound **22a**

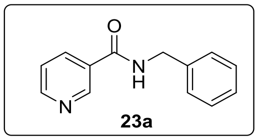


22a

Following General Procedure **A**, a solution of 4-pyridinecarboxyaldehyde (0.050 g, 0.467 mmol), NFSI (0.147 g, 0.467 mmol), and NaDT (28.0 mg, 2.5 mol%) in 3.10 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **22** was characterized by ^{19}F-NMR spectroscopy (δ = 21 ppm, CD_3CN). *N*, *N*-Diisopropylethylamine (0.163 mL, 0.934 mmol) and benzylamine (0.102 mL, 0.934 mmol) were then added to the reaction mixture and the resulting reaction mixture was stirred for an additional 2 hours. Purification of crude amide **22a** by flash chromatography (pentane-EtOAc 70:30) afforded amide **22a** (0.055 g, 55% yield). Spectral data recorded on crude amide **22a** were in complete agreement with that previously reported.[8]

[8] Sutthichat, K.; Quan, X.; Parihar, V. S.; Andersson, P. G. *J. Org. Chem.* **2015**, *80*, 11529

Preparation of Compound **23a**



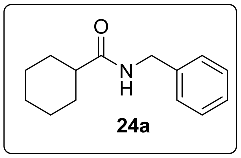
23a

Following General Procedure **A**, a solution of 4-pyridinecarboxyaldehyde (0.050 g, 0.467 mmol), NFSI (0.147 g, 0.467 mmol), and NaDT (28.0 mg, 2.5 mol%) in 3.10 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **23** was characterized by ^{19}F-NMR spectroscopy (δ = 21 ppm, CD_3CN, ^{19}F NMR yield = 37%). *N*, *N*-Diisopropylethylamine (0.163 mL, 0.934 mmol) and benzylamine (0.102 mL, 0.934 mmol) were then added to the reaction mixture and the resulting reaction mixture was stirred for an additional 2 hours. Purification of crude amide **23a** by flash chromatography (pentane-EtOAc 70:30) afforded amide **23a** (0.033 g, 33% yield). Spectral data recorded on crude amide **23a** were in complete agreement with that previously reported.[10]

[10] Orliac, A.; Pardo, D. G.; Bombrun, A.; Cossy, J. *Org. Lett.* **2013**, *15*, 902

Preparation of Compound **24a**

Following General Procedure **A**, a solution of cyclohexanecarboxaldehyde (0.050 g, 0.446 mmol), NFSI (0.155 g, 0.491 mmol), and NaDT (27.2 mg) in 3.0 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate was characterized by ^{19}F-NMR spectroscopy (δ = 35 ppm, CD_3CN, ^{19}F NMR yield = 61%). *N*, *N*-Diisopropylethylamine (0.155 mL, 0.892 mmol) and benzylamine (0.097 mL, 0.892 mmol) were then added to the reaction mixture and the resulting reaction mixture was stirred for an additional 2 hours. Purification of crude amide **24a** by flash chromatography (pentane-EtOAc 80:20) afforded amide **24a** (0.053 g, 55% yield). Spectral data recorded on crude amide **24a** were in complete agreement with that previously reported.[11]



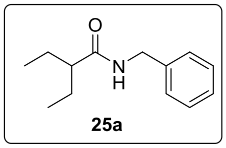
24a

IR (neat): υ = 3276, 2927, 1641, 1552, 696 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 7.2, 7.2 Hz, 2H), 7.27 (m, 3H), 5.70 (br s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 2.11(dddd, *J* = 11.9, 11.9, 3.3, 3.3 Hz, 1H), 1.89 (m, 2H), 1.80 (m, 2H), 1.67 (m, 1H), 1.47 (m, 2H), 1.25 (m, 3H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 176.0, 138.7, 128.8, 127.9, 127.6, 45.7, 43.5, 29.9, 25.9; HRMS (EI^+) calcd for $[C_{14}H_{20}NO]^+$ 218.1539, found 218.1513.

[11] Liu, Y.; Achtenhagen, M.; Liu, R.; Szostak, M. *Org. Biomol. Chem.* **2018**, *16*, 1322

Preparation of Compound **25a**

Following General Procedure **A**, a solution of 2-ethylbutanal (0.050 g, 0.50 mmol), NFSI (0.173 g, 0.55 mmol), and NaDT (32.0 mg) in 2.5 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **25** was characterized by ^{19}F-NMR spectroscopy (δ = 39 ppm, CD_3CN, ^{19}F NMR yield = 40%). *N*, *N*-Diisopropylethylamine (0.174 mL, 1.00 mmol) and benzylamine (0.109 mL, 1.00 mmol) were then added to the reaction mixture and the resulting mixture was left for an additional 2 hours. Purification of crude amide **25a** by flash chromatography (pentane-EtOAc 80:20) afforded amide **25a** (0.036 g, 35% yield). Spectral data recorded on crude amide **25a** were in complete agreement with that previously reported.[12]



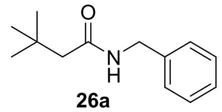
25a

IR (neat): υ = 3279, 2961, 1639, 1547, 691 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.31 (m, 5H), 5.70 (br s, 1H), 4.48 (d, *J* = 5.8, 2H), 1.87 (m, 1H), 1.65 (m, 2H), 1.50 (m, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 175.7, 138.7, 128.8, 128.0, 127.6, 51.8, 43.6, 25.9, 12.3; HRMS (EI$^+$) calcd for $[C_{13}H_{20}NO]^+$ 206.1539, found 260.1514.

[12] Lafrance, D.; Bowles, P.; Leeman, K. L.; Rafka, R. *Org. Lett.* **2011**, *13*, 2322

Preparation of Compound **26a**

Following General Procedure **A**, a solution of 3,3-dimethylbutanal (0.050 g, 0.485 mmol), NFSI (0.168 g, 0.534 mmol), and NaDT (30.0 mg) in 2.4 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **26** was characterized by ^{19}F-NMR spectroscopy (δ = 53 ppm, CD_3CN). *N*, *N*-Diisopropylethylamine (0.169 mL, 0.97 mmol) and benzylamine (0.106 mL, 0.97 mmol) were then added to the reaction mixture and the resulting mixture was left for an additional 2 hours. Purification of crude amide **26a** by flash chromatography (pentane-EtOAc 30:70) afforded amide **26a** (0.065 g, 65% yield). Spectral data recorded on crude amide **26a** were in complete agreement with that previously reported.[13]



26a

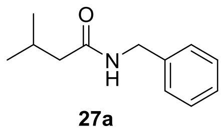
IR (neat): υ = 3293, 2953, 1641, 1543, 905, 725, 698 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.33 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.28 (m, 3H), 5.66 (br s, 1H), 4.43 (d, *J* = 5.7, 2H), 2.03 (s, 2H), 1.05 (s, 9H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 171.6, 138.6, 128.8, 128.1, 127.6, 50.8, 43.7, 31.1, 30.0; HRMS (EI$^+$) calcd for $[C_{13}H_{20}NO]^+$ 206.1539, found 206.1517.

[13] Bechara, W. S.; Khazhieva, I. S.; Rodriguez, E.; Charette, A. B. *Org. Lett.* **2015**, *17*, 1184

Preparation of Compound **27a**

Following General Procedure **A**, a solution of 3-methylbutanal (0.050 mL, 0.464 mmol), NFSI (0.161 g, 0.511 mmol), and NaDT (28.0 mg) in 2.3 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **27** was characterized by ^{19}F-NMR spectroscopy (δ = 46 ppm, CD_3CN, ^{19}F NMR yield = 55%). *N*, *N*-Diisopropylethylamine (0.161 mL, 0.928 mmol) and benzylamine (0.101 mL, 0.928 mmol) were then added to the reaction mixture and the resulting mixture was left for an additional 2 hours. Purification of crude amide **27a** by flash chromatography (pentane-

EtOAc 70:30) afforded amide **27a** (0.046 g, 52% yield). Spectral data recorded on crude amide **19a** were in complete agreement with that previously reported.[14]

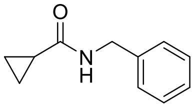

27a

IR (neat): υ = 3288, 2958, 1643, 1547, 698 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.34 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.28 (m, 3H), 5.70 (br s, 1H), 4.45 (d, *J* = 5.3 Hz, 2H), 2.15 (m, 1H), 2.09 (d, *J* = 7.0 Hz, 2H) 0.97 (d, *J* = 6.5 Hz, 6H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 172.4, 138.6, 128.9, 128.0, 127.6, 46.3, 43.7, 26.3, 22.6; HRMS (EI^{+}) calcd for $[C_{12}H_{18}NO]^{+}$ 192.1383, found 192.1364.

[14] Starkov, P.; Sheppard, T. D. *Org. Biomol. Chem.* **2011**, *9*, 1320.

Preparation of Compound **28a**

Following General Procedure **A**, a solution of cyclopropanecarbaldehyde (0.025 mL, 0.335 mmol), NFSI (0.105 g, 0.335 mmol), and NaDT (20.1 mg) in 1.6 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **28** was characterized by ^{19}F-NMR spectroscopy (δ = 31 ppm, CD_3CN, ^{19}F NMR yield = 66%). *N*, *N*-Diisopropylethylamine (0.116 mL, 0.670 mmol) and benzylamine (0.073 mL, 0.670 mmol) were then added to the reaction mixture and the resulting mixture was left for an additional 2 hours. Purification of crude amide **28a** by flash chromatography (pentane-EtOAc 80:20) afforded amide **28a** (0.053 g, 64% yield). Spectral data recorded on crude amide **28a** were in complete agreement with that previously reported.[15]

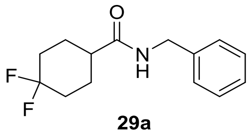

28a

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.34 (m, 2H), 7.29 (m, 3H), 5.90 (br s, 1H), 4.46 (d, *J* = 5.8 Hz, 2H), 1.35 (m, 1H), 1.01 (m, 2H), 0.75 (m, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 173.5, 138.6, 128.8, 128.0, 127.6, 44.0, 14.9, 7.4; HRMS (EI^{+}) calcd for $[C_{11}H_{14}NO]^{+}$ 176.1070, found 176.1072.

[15] Rolfe, A.; Probst, D. A.; Volpk, A.; Omar, I.; Flynn, D. L.; Hanson, P. R. *J. Org. Chem.* **2008**, *73*, 8785

Preparation of Compound **29a**

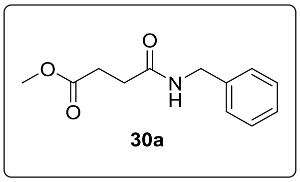
Following General Procedure **A**, a solution of 4,4-difluorocyclohexane-1-carbaldehyde (0.050 g, 0.337 mmol), NFSI (0.117 g, 0.371 mmol), and NaDT (21 mg) in 1.7 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **29** was characterized by ^{19}F-NMR spectroscopy (δ = 36 ppm, CD_3CN, ^{19}F NMR yield = 41%). *N*, *N*-Diisopropylethylamine (0.117 mL, 0.674 mmol) and benzylamine (0.074 mL, 0.674 mmol) were then added to the reaction mixture and the resulting mixture was left for an additional 2 hours. Purification of crude amide **29a** by flash chromatography (pentane-EtOAc 40:60) afforded amide **29a** (0.038 g, 44% yield).


29a

IR (neat): υ = 3296, 2950, 1647, 1110, 959, 732 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.34 (t, *J* = 7.6 Hz, 2H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.26 (m, 2H), 5.74 (br s), 4.44 (d, *J* = 5.6 Hz, 2H), 2.18 (m, 3H), 1.96 (m, 2H), 1.86 (m, 2H), 1.74 (m, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 173.9, 138.3, 129.0 (t, *J* = 24.6 Hz), 127.9, 127.8, 122.7 (t, *J* = 240.8 Hz), 43.7, 43.0, 33.0, 26.1 (t, *J* = 9.6 Hz); HRMS (EI^{+}) calcd for $[C_{14}H_{18}F_2NO]^{+}$ 254.1351, found 254.1327.

Preparation of Compound **30a**

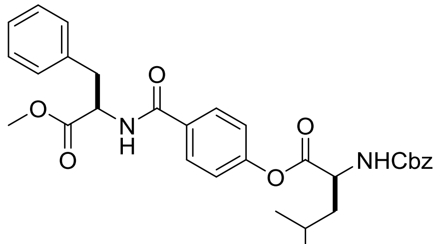
Following General Procedure **A**, a solution of methyl 4-oxobutanoate (0.050 g, 0.43 mmol), NFSI (0.150 g, 0.474 mmol), and NaDT (26.0 mg) in 2.2 mL CH_3CN was irradiated with UV-light (365 nm) for 3 hours. The formation of the acyl fluoride intermediate **30** was characterized by ^{19}F-NMR spectroscopy (δ = 42 ppm, CD_3CN). *N*, *N*-Diisopropylethylamine (0.15 mL, 0.86 mmol) and benzylamine (0.094 mL, 0.86 mmol) were then added to the reaction mixture and the resulting mixture was left for an additional 2 hours. Purification of crude amide **30a** by flash chromatography (pentane-EtOAc 50:50) afforded amide **30a** (0.045 g, 47% yield).


30a

IR (neat): υ = 3304, 2952, 1737, 1652, 1547, 1169, 700 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.33 (t, *J* = 7.3 Hz, 2H), 7.28-7.26 (m, 3H), 5.97 (br s, 1H), 4.44 (d, *J* = 5.7 Hz, 2H), 3.68 (s, 3H), 2.70 (t, *J* = 6.8 Hz ,2H), 2.51 (t, *J* = 6.8 Hz, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 173.6, 171.3, 138.2, 128.8, 127.9, 127.6, 52.0, 43.8, 31.2, 29.5; HRMS (EI$^+$) calcd for $[C_{12}H_{16}NO_3]^+$ 222.1125,

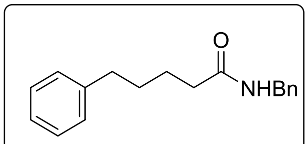
Preparation of Compound **32**

Following General Procedure **A**, to a solution of **31** (0.048 g, 0.13 mmol, 1 equiv.) in 1.3 mL of CH_3CN (0.1 M) was added NFSI (0.045 g, 0.143 mmol, 1.1 equiv.) and NaDT (6.0 mg, 2.0 mol %). The resulting mixture was degassed via 3 x freeze/pump/thaw cycles. The reaction was irradiated with UV-light (~365 nm) for 16 hours. The formation of the acyl fluoride intermediate was characterized by ^{19}F-NMR spectroscopy (δ = 18 ppm, CD_3CN). *N*, *N*-Diisopropylethylamine (0.042 g, 0.325 mmol, 2.5 equiv.) and *D*-phenylalanine methylester (0.034 g, 0.156 mmol, 1.2 equiv.) were then added to the reaction mixture and the resulting solution was left for 3 hours. The reaction mixture was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure and the crude reaction product **32** was purified by flash column chromatography (pentanes-EtoAc 70:30) to afford amide **32** (0.025 g, 36%).


32

^{1}H-NMR (600 MHz, $CDCl_3$): δ 7.74 (d, J = 8.5 Hz, 2H), 7.24-7.36 (m, 8H), 7.13 (m, 4H), 6.56 (d, J = 7.5 Hz, 1H), 5.24 (d, J = 8.6 Hz, 1H), 5.14 (s, 2H), 5.08 (m, 1H), 4.62 (m, 1H), 3.77 (s, 3H), 3.29 (dd, J = 13.9, 5.8 Hz, 1H), 3.22 (dd, J = 13.9, 5.8 Hz, 1H), 1.82 (m, 2H), 1.68 (m, 1H), 1.01 (m, 6H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 172.1, 171.6, 166.0, 156.2, 153.2, 138.2, 135.9, 131.9, 129.4, 128.8, 128.7, 128.7, 128.4, 128.3, 127.4, 121.7, 67.3, 53.7, 53.6, 52.9, 41.3, 38.0, 25.0, 23.0, 21.9; HRMS (EI$^+$) calcd for $[C_{31}H_{35}N_2O_7]^+$ 547.2431, found 547.2450.

Preparation of Compound **34**

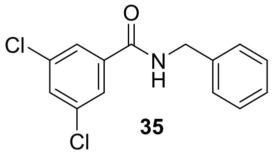

34

Following General Procedure **B**, to a solution of 5-phenylpentan-1-ol (0.082 g, 0.50 mmol, 1 equiv.) in 5.0 mL of CH_3CN (0.1 M) was added NFSI (0.472 g, 1.5 mmol, 3.0 equiv.) and NaDT (24.0 mg, 2.0 mol0%). The resulting mixture was degassed via 3 x freeze/pump/thaw cycles. The reaction was irradiated with UV-light (~365 nm) for 16 hours. *N*, *N*-Diisopropylethylamine (0.226 g, 1.75 mmol, 3.5 equiv.) and benzylamine (0.107 g, 1.00 mmol, 2 equiv.) were then added to the reaction mixture and the resulting solution was stirred for an additional 3 hours. The reaction mixture was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure and the crude reaction product **34** was purified by flash column chromatography (pentanes-EtoAc 95:5) to afford amide **34** (0.050 g, 38%). Spectral data recorded on crude amide **34** were in complete agreement with that previously reported.[16]

[16] Zhang, G.; Gao, B.; Huang, H. *Angew. Chem. Int. Ed.* **2015**, *54*, 7657.

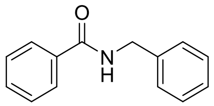
Preparation of Compound **35**

Following General Procedure **B**, to a solution of (3,5-dichlorophenyl)methanol (0.089 g, 0.50 mmol, 1 equiv.) in 5.0 mL of CH_3CN (0.1 M) was added NFSI (0.394 g, 1.25 mmol, 2.5 equiv.) and NaDT (24.0 mg, 2.0 mol %). The resulting mixture was degassed via 3 x freeze/pump/thaw cycles. The reaction was irradiated with UV-light (~365 nm) for 16 hours. The formation of the acyl fluoride intermediate was characterized by ^{19}F-NMR spectroscopy (δ = 19 ppm, CD_3CN). *N*, *N*-Diisopropylethylamine (0.174 mL, 1.00 mmol, 2 equiv.) and benzylamine (0.109 mL, 1.00 mmol, 2 equiv.) were then added to the reaction mixture and the resulting solution was left for 3 hours. The reaction mixture was then diluted with CH_2Cl_2 and washed with water and brine. The organic layer was then dried over $MgSO_4$, filtered, and concentrated under reduced pressure and the crude reaction product **35** was purified by flash column chromatography (pentanes-EtoAc 95:5) to afford amide **35** (0.068 g, 49%) as a light orange solid.

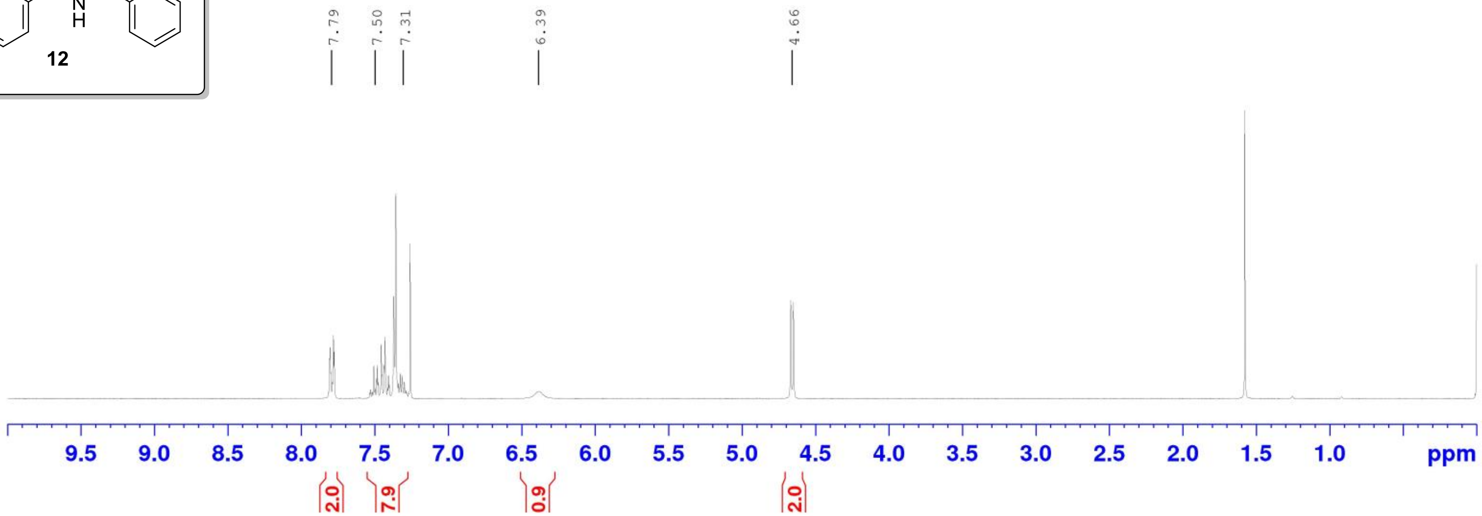

35

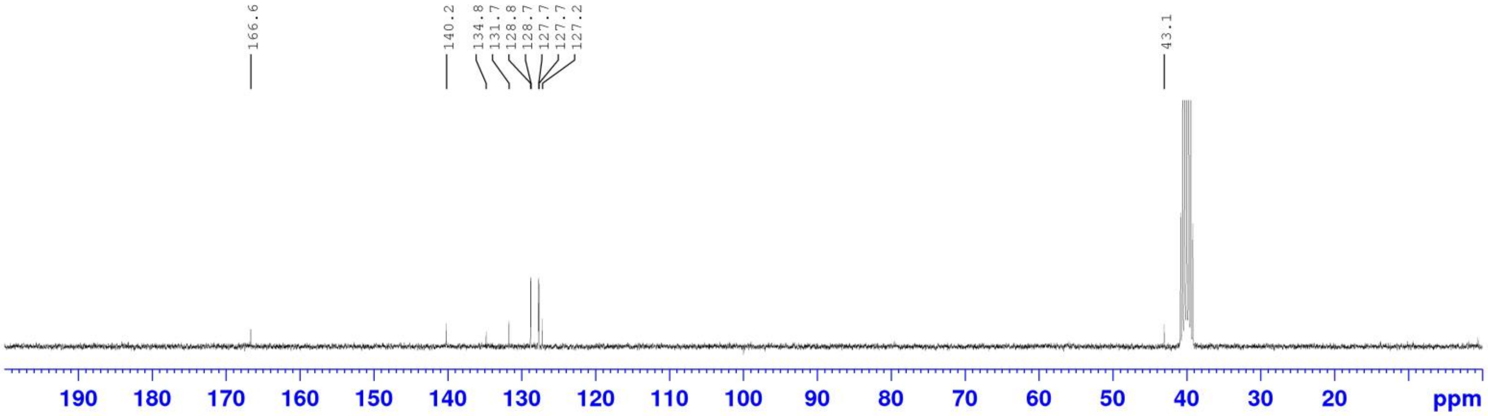
IR (neat): υ = 3310, 1645, 1566, 1542, 1163, 804, 698 cm^{-1}; **^{1}H-NMR** (600 MHz, $CDCl_3$): δ 7.64 (s, 2H), 7.48 (s, 1H), 7.34 (m, 5H), 6.33 (br s, 1H), 4.62 (d, *J* = 5.5 Hz, 2H); **^{13}C-NMR** (150 MHz, $CDCl_3$): δ 164.9, 137.6, 137.4, 135.7, 131.6, 129.1, 128.2, 128.1, 125.8, 44.6; HRMS (EI^+) calcd for $[C_{14}H_{12}Cl_2NO]^+$ 280.0290, found 280.0300.

^{1}H and ^{13}C NMR spectra of **12** recorded on 300 MHz spectrometer

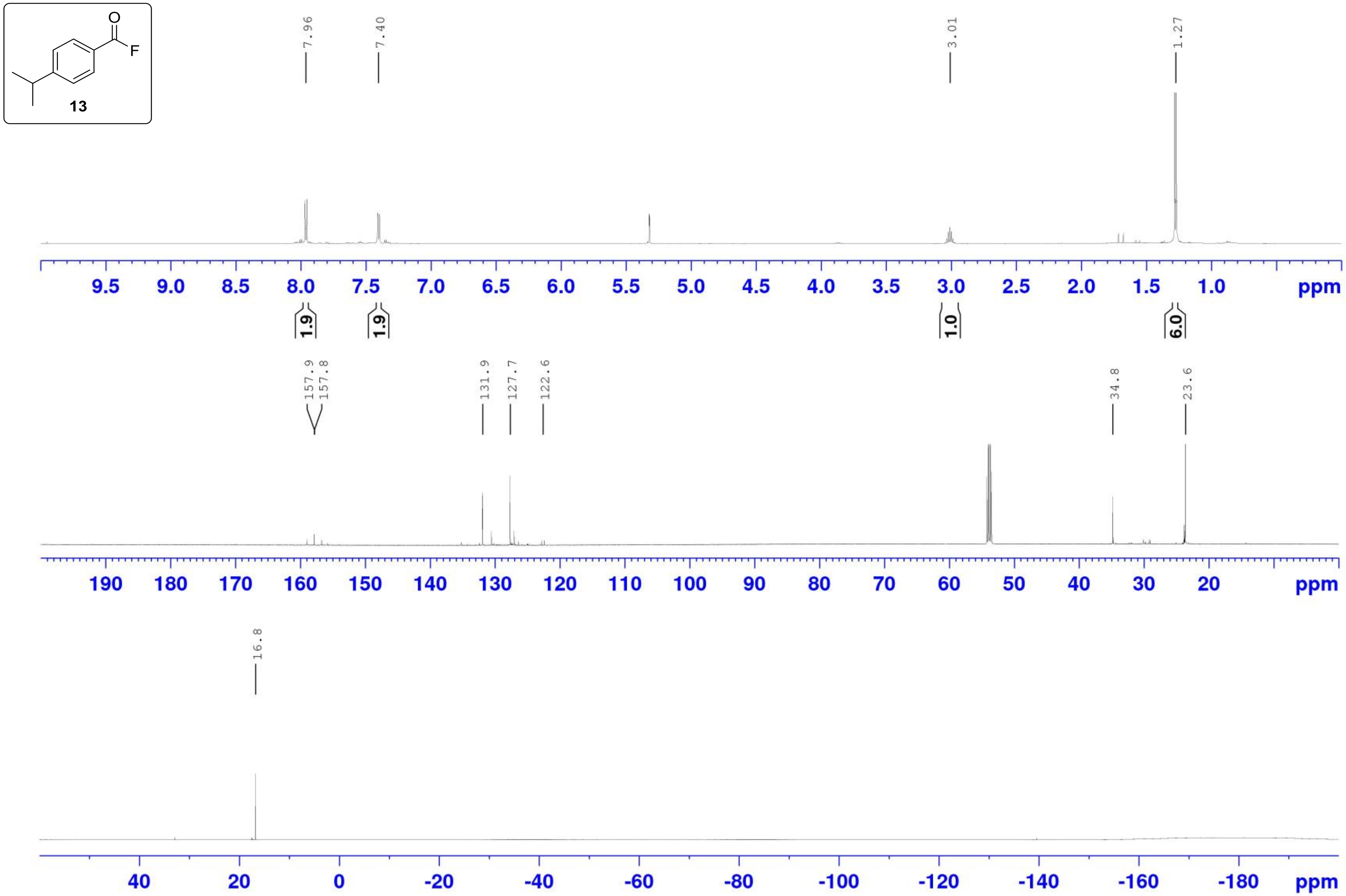


12

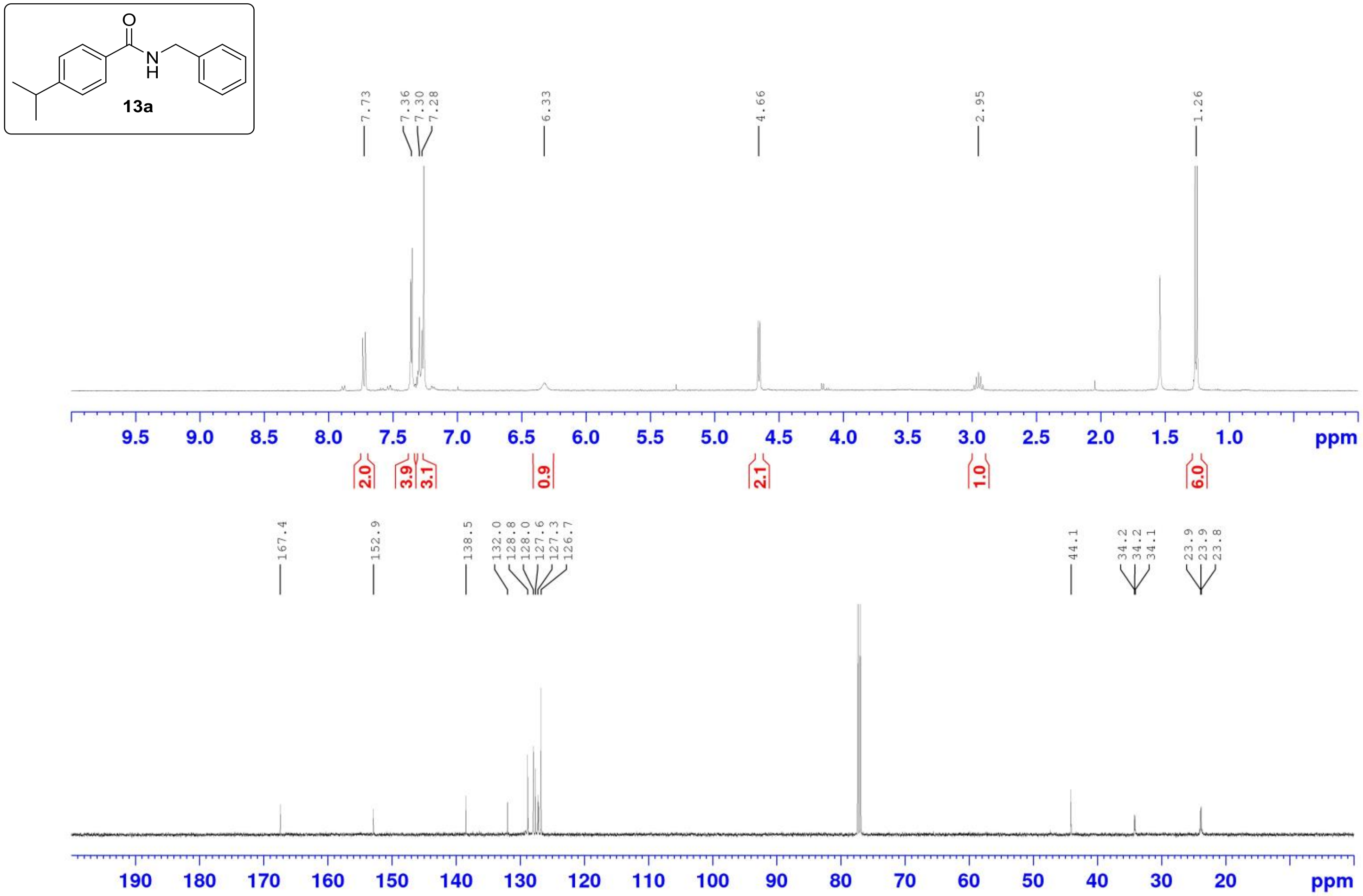




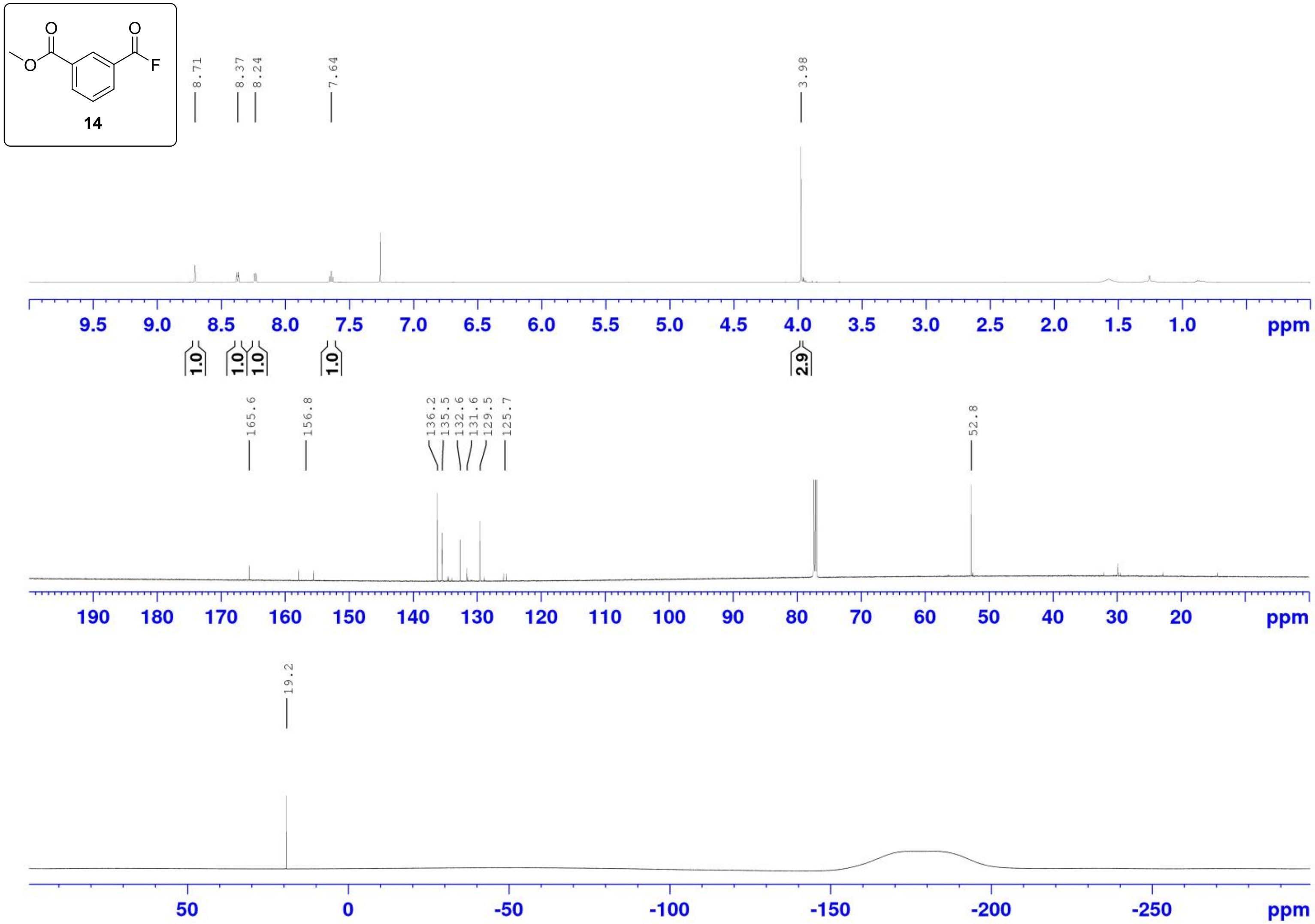
^{1}H, ^{13}C, and ^{19}F-NMR spectra of **13** recorded on a 600 MHz spectrometer



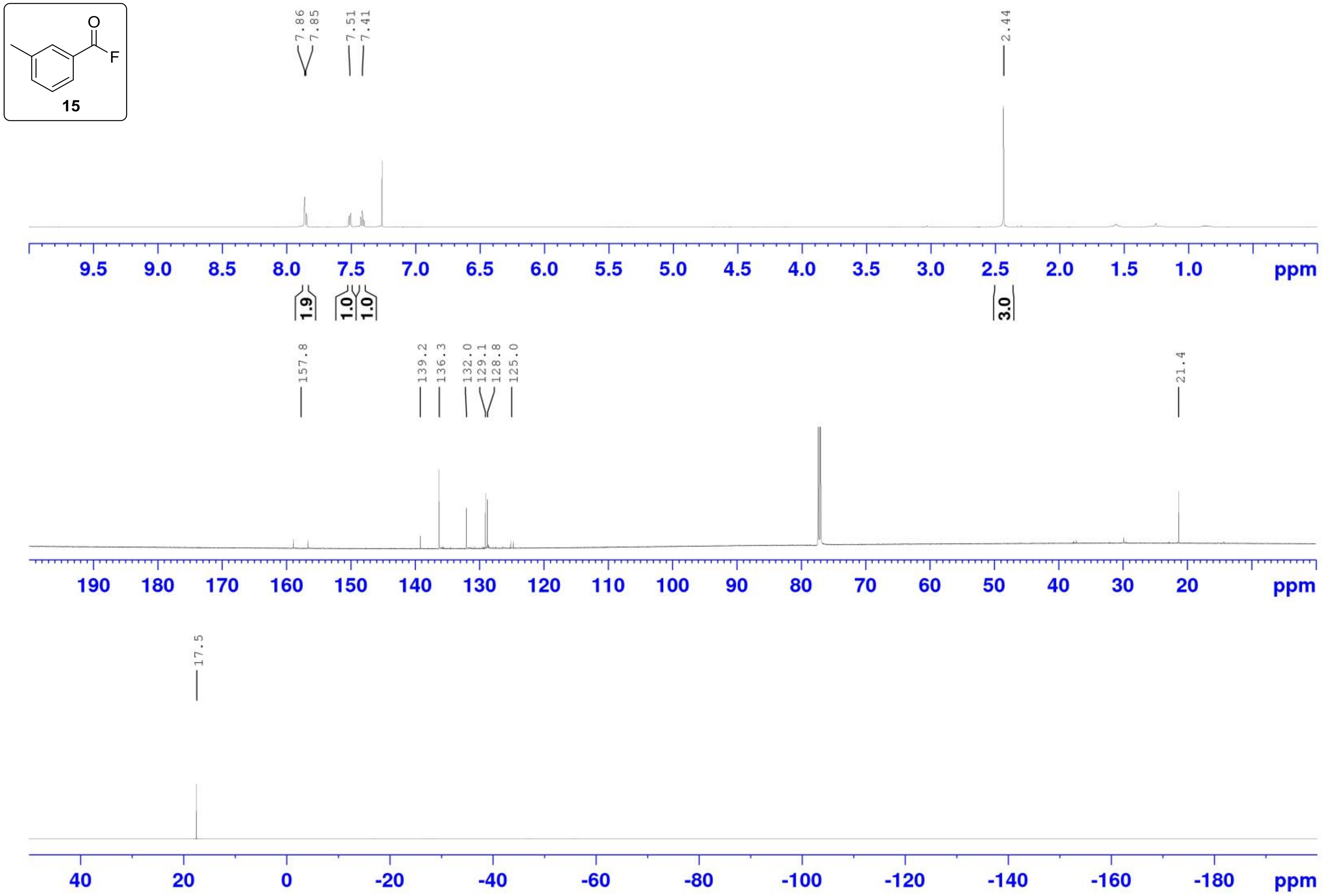
^{1}H and ^{13}C NMR spectra of **13a** recorded on a 600 MHz spectrometer



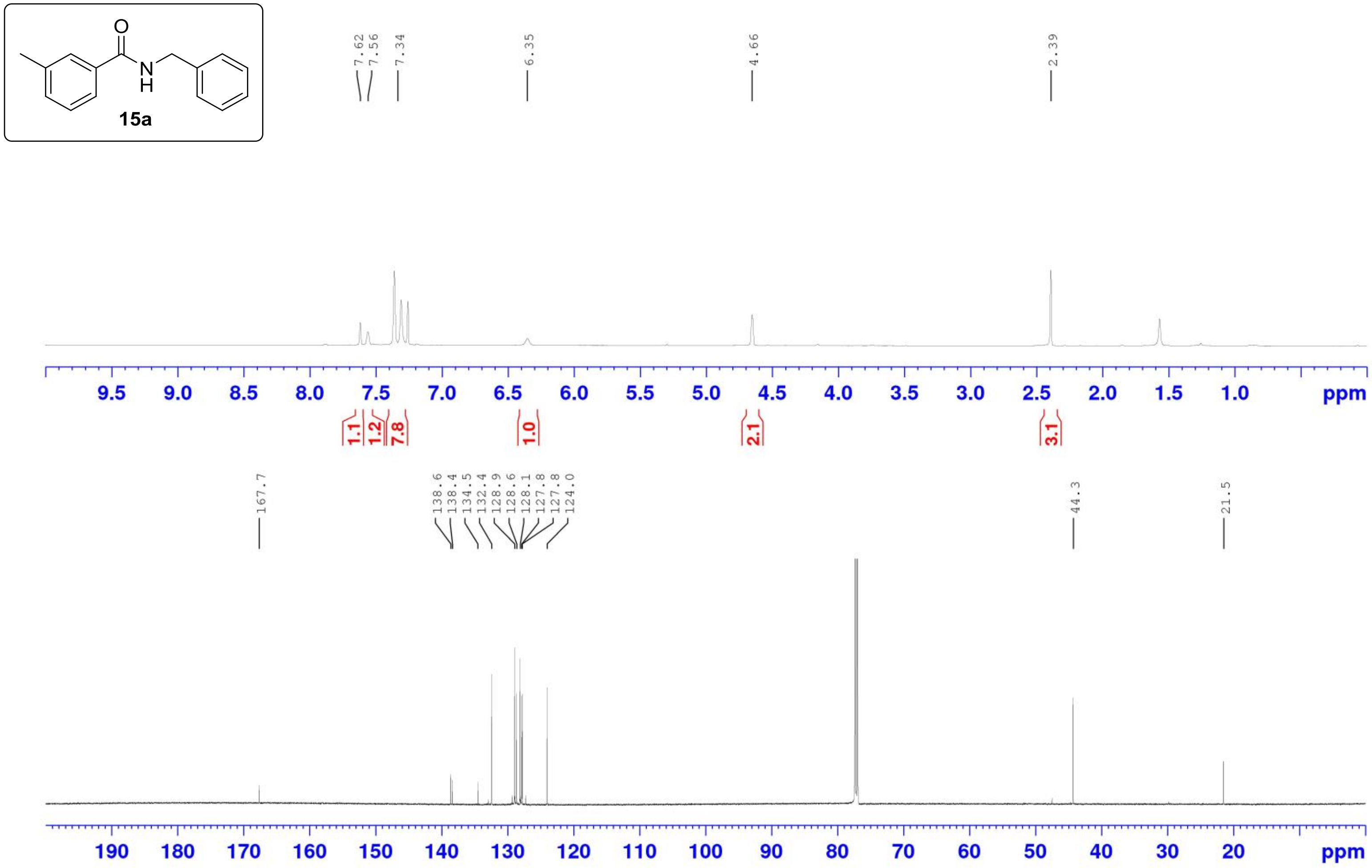
^{1}H, ^{13}C, and ^{19}F NMR spectra of **14** recorded on a 600 MHz spectrometer



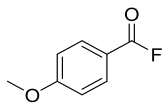
^{1}H, ^{13}C, and ^{19}F-NMR spectra of **15** recorded on a 600 MHz spectrometer



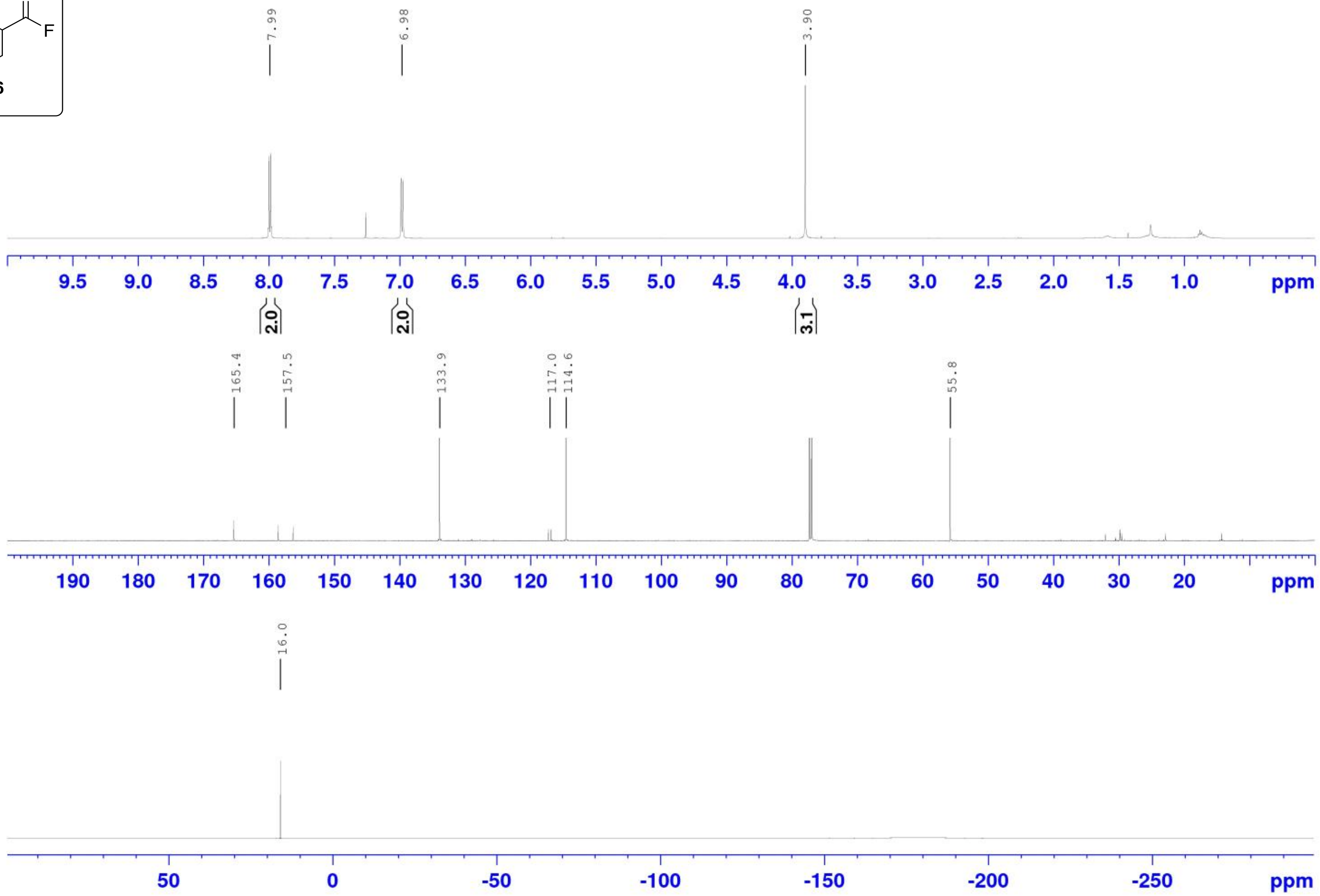
^{1}H and ^{13}C NMR spectra of **15a** recorded on a 600 MHz spectrometer



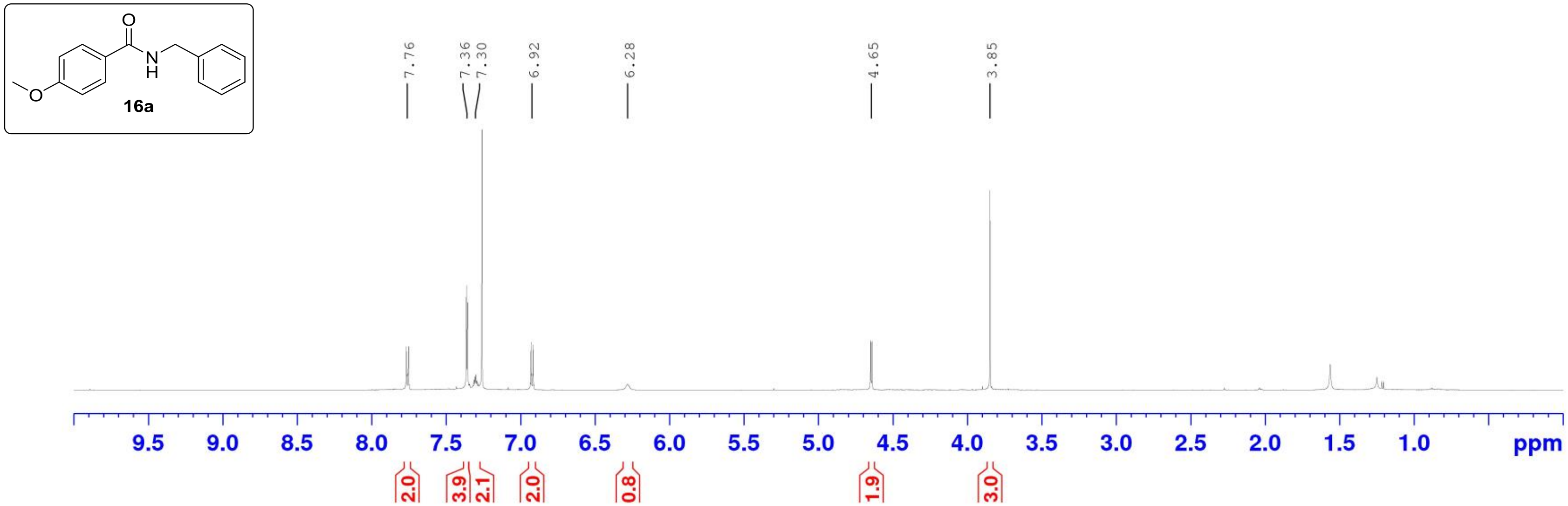
^{1}H, ^{13}C, and ^{19}F-NMR spectra of **16** recorded on a 600 MHz spectrometer

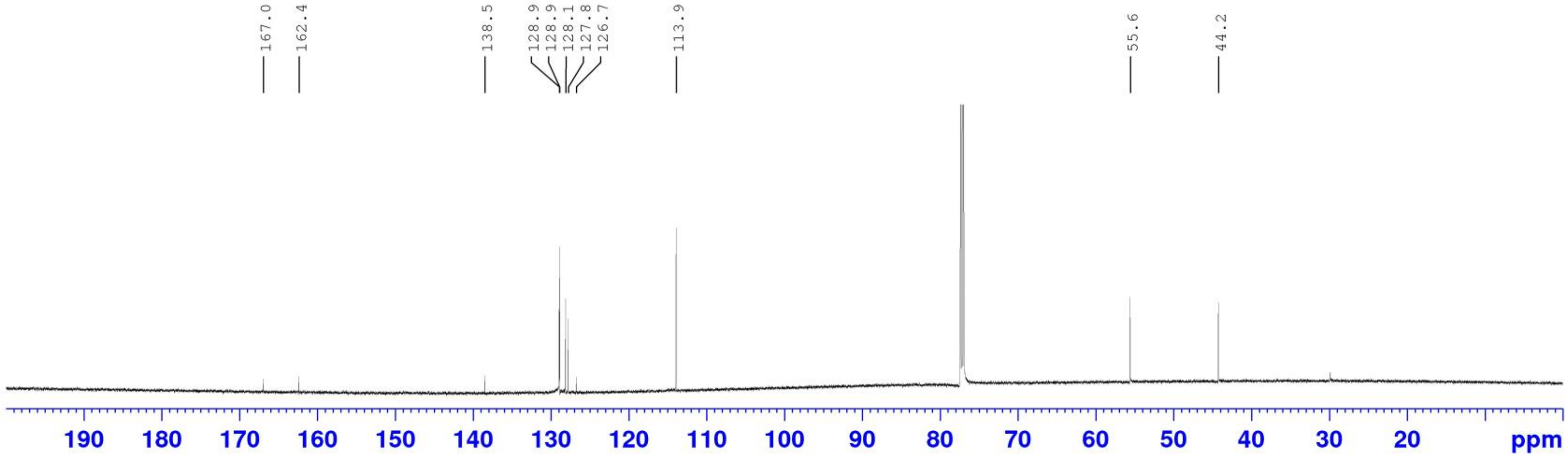


16

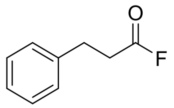


^{1}H and ^{13}C NMR spectra of **16a** recorded on a 600 MHz spectrometer

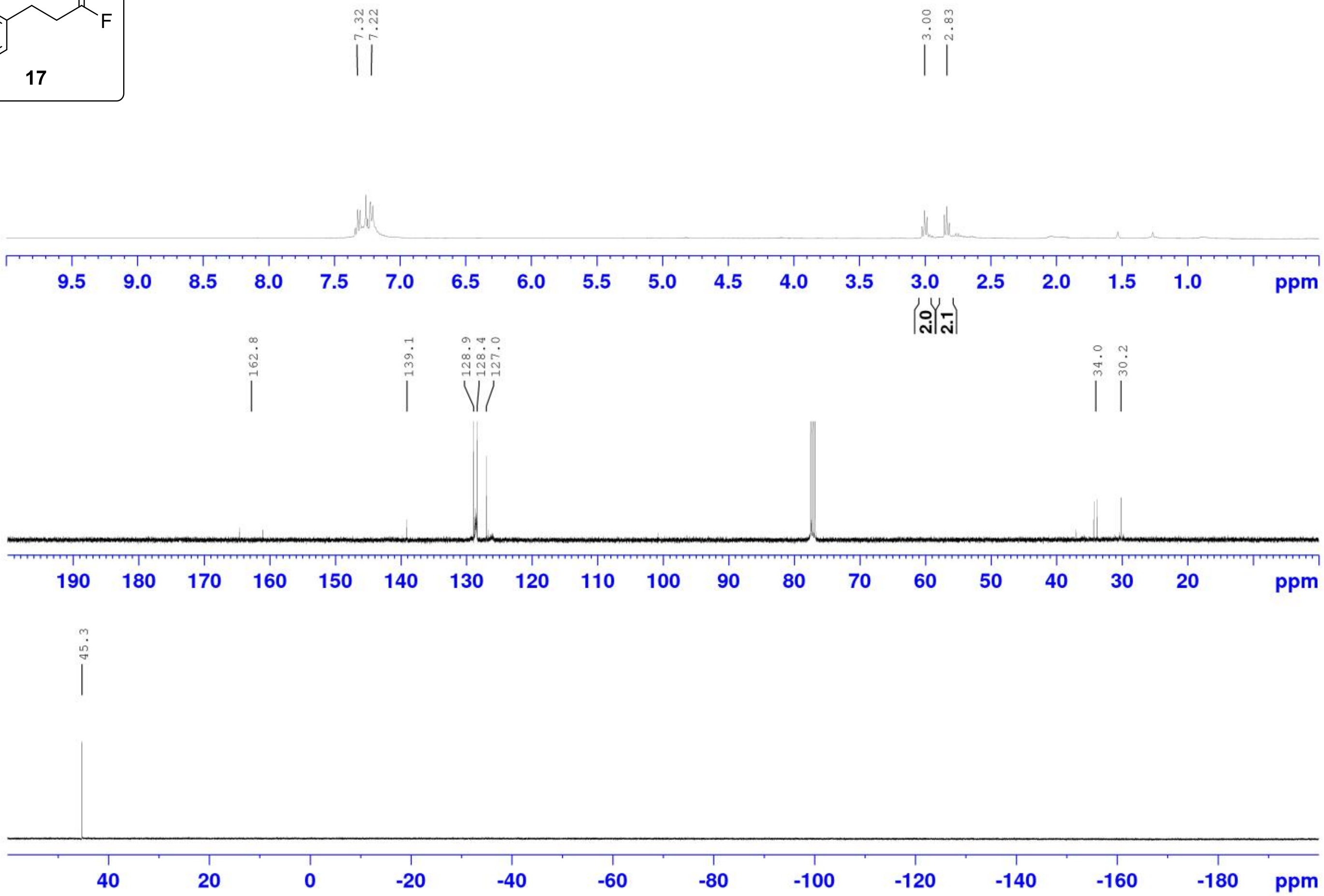

16a



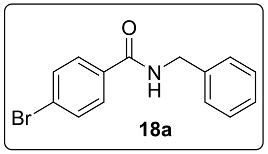
^{1}H , ^{13}C, and ^{19}F NMR spectra of **17** recorded on a 600 MHz spectrometer

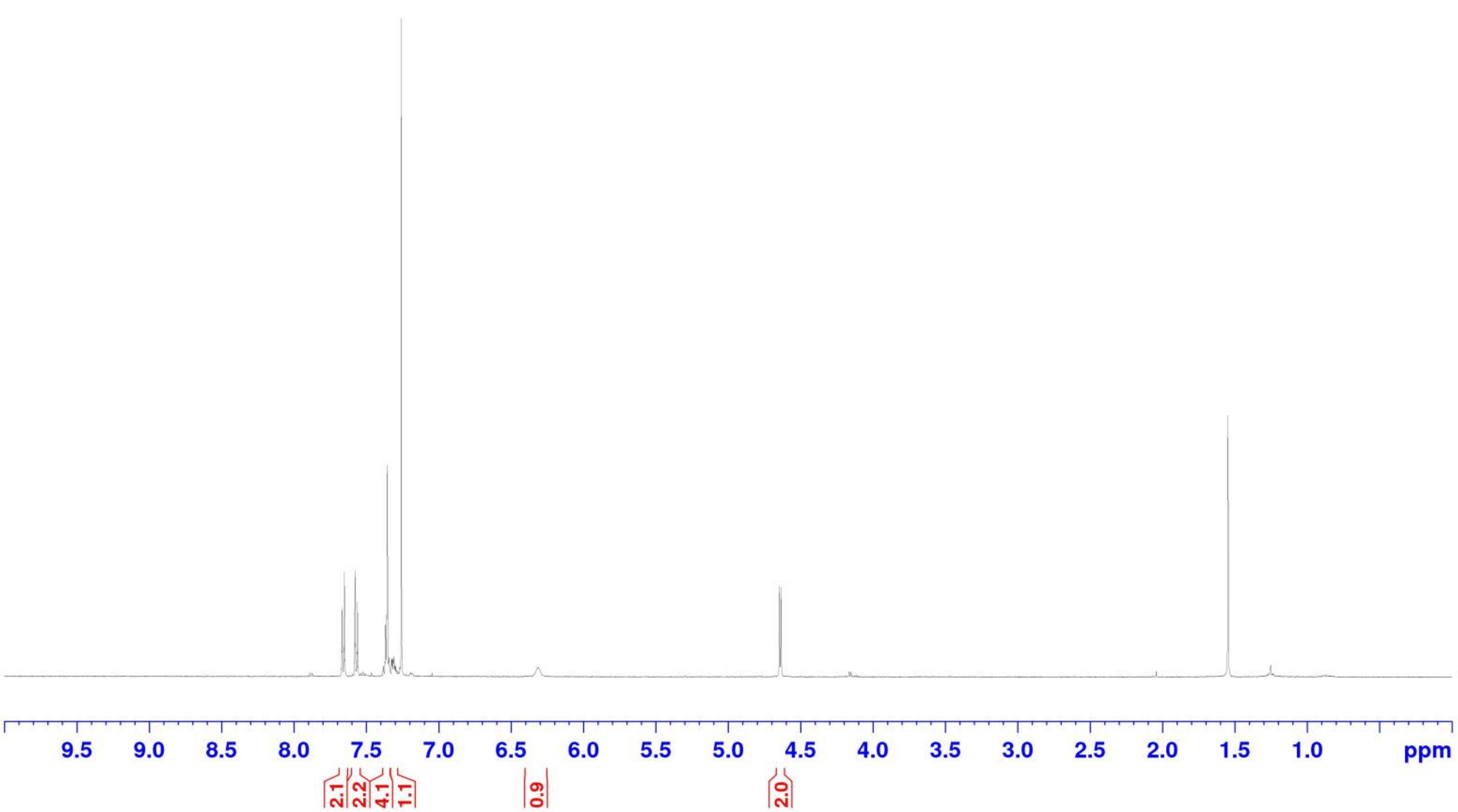


17

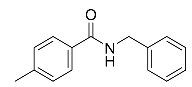


^{1}H NMR spectra of **18a** recorded on a 500 MHz spectrometer

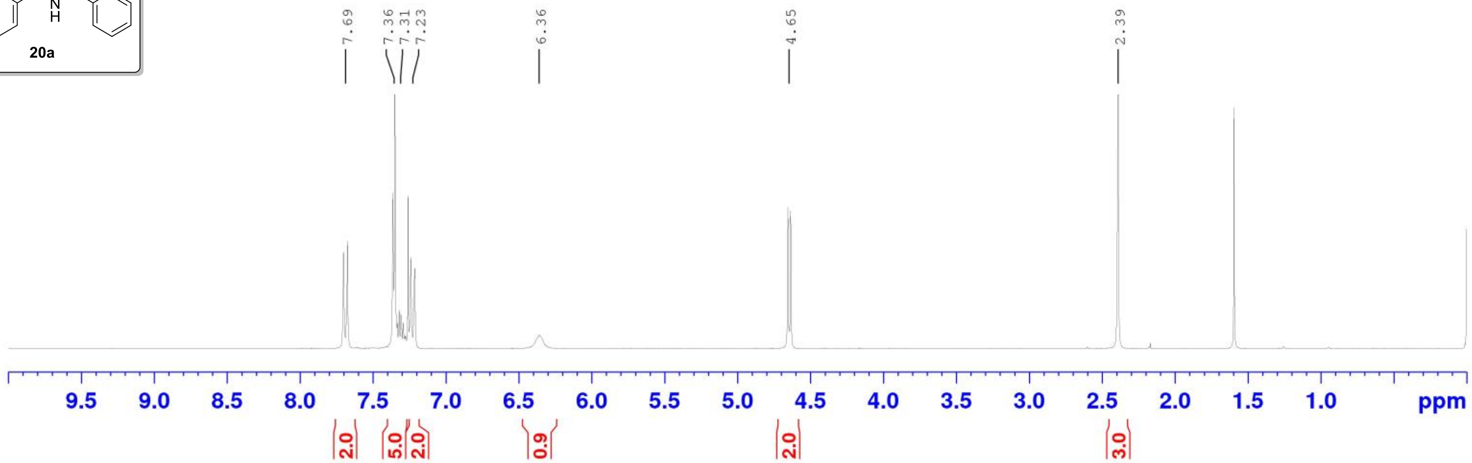

18a

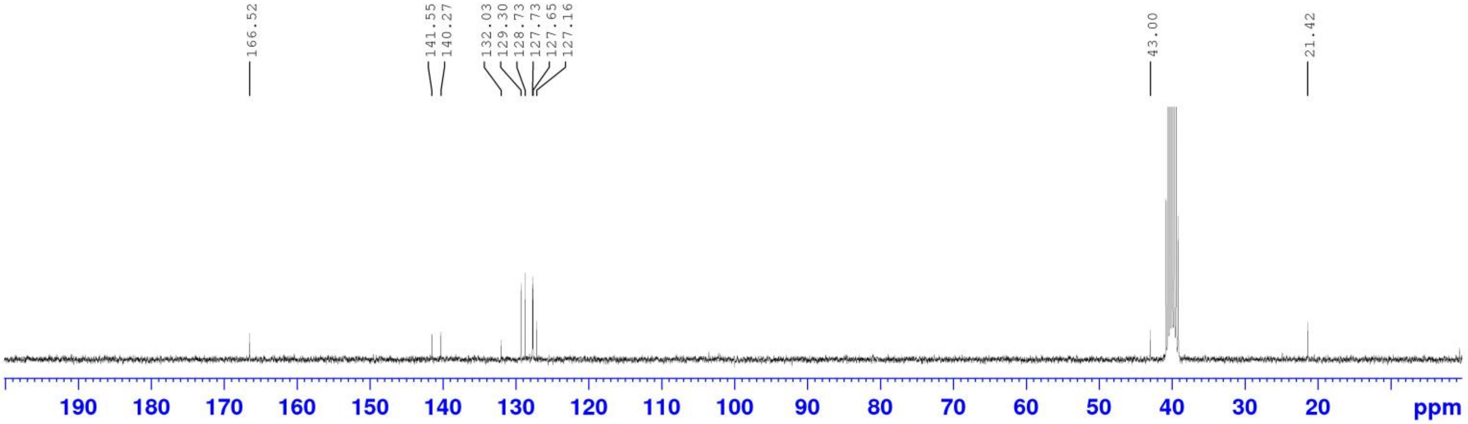


^{1}H and ^{13}C NMR spectra of **20a** recorded on a 300 MHz spectrometer

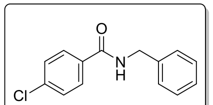


20a

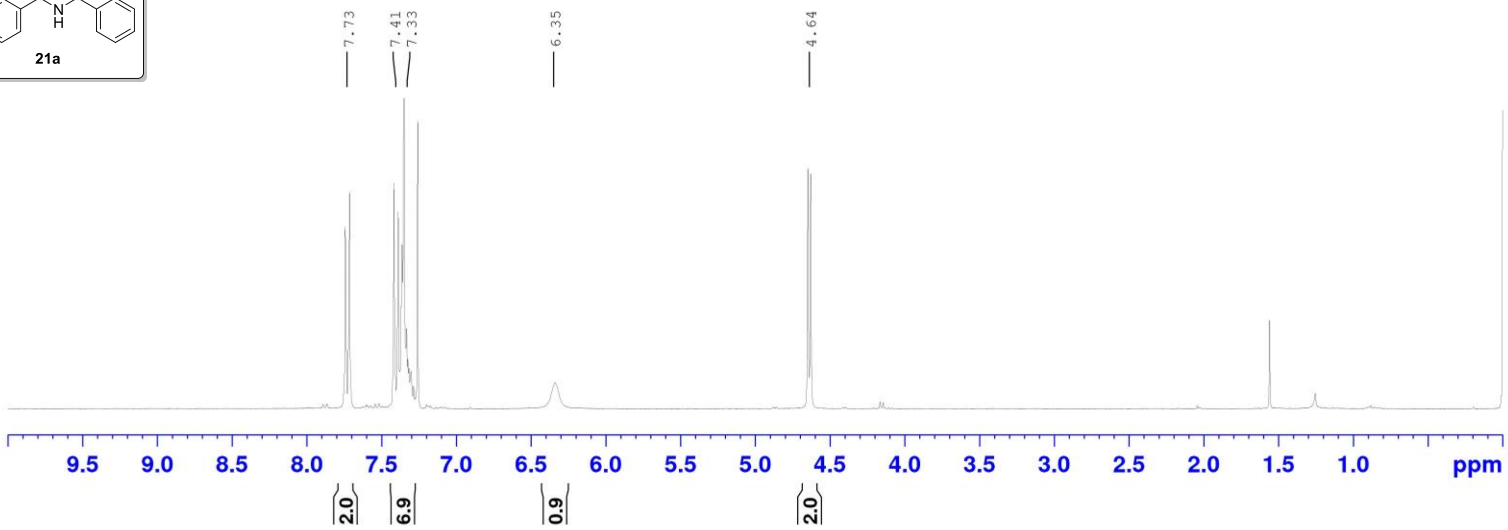


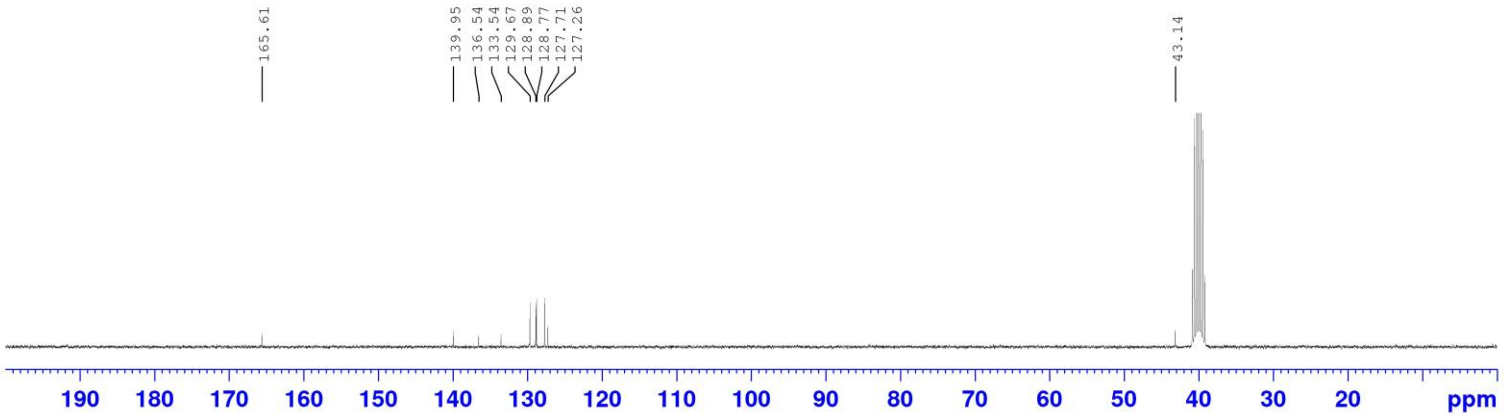


^{1}H and ^{13}C NMR spectra of **21a** recorded on a 300 MHz spectrometer

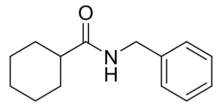


21a

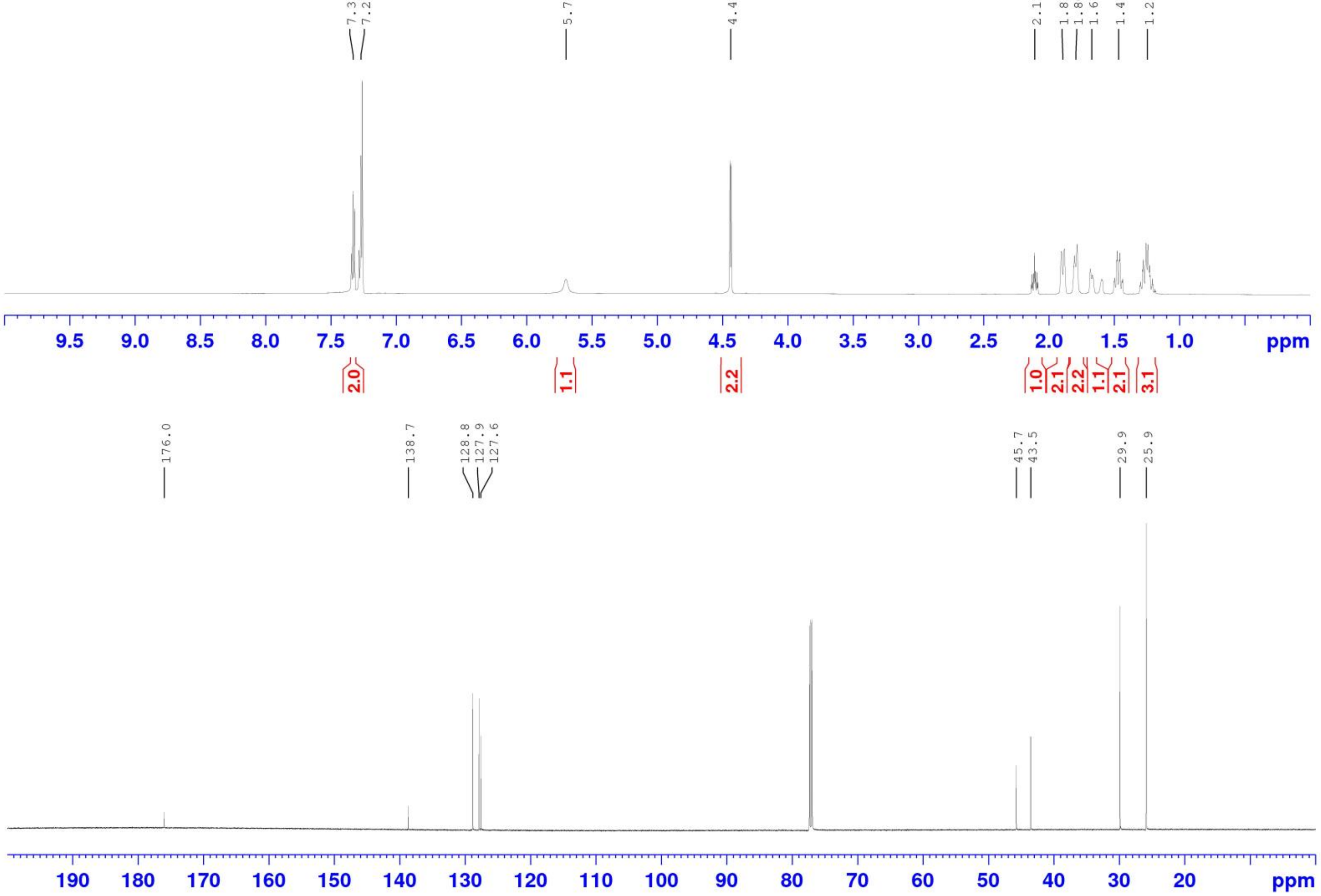




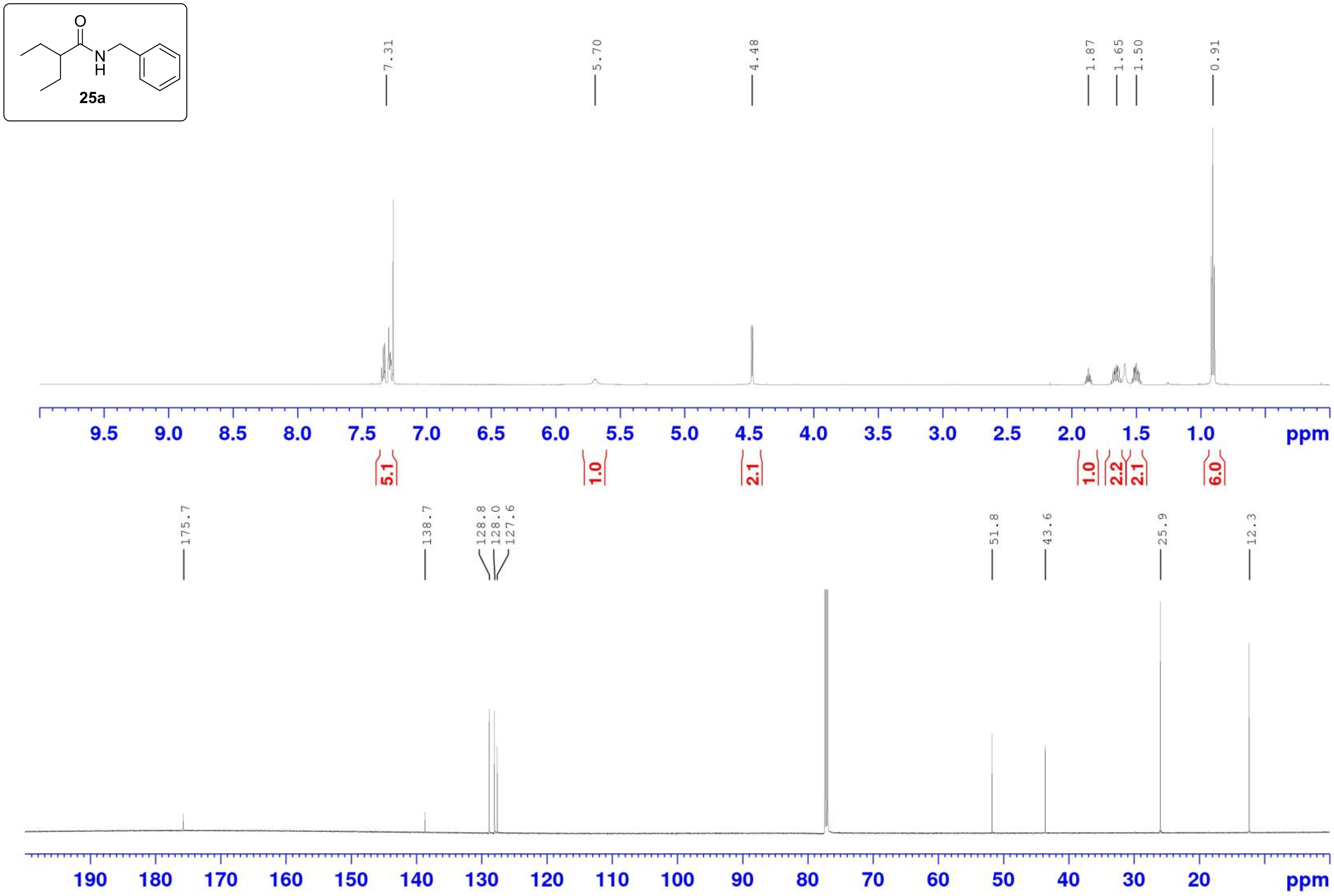
^{1}H and ^{13}C NMR spectra of **24a** recorded on a 600 MHz spectrometer



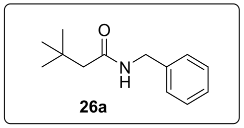
24a

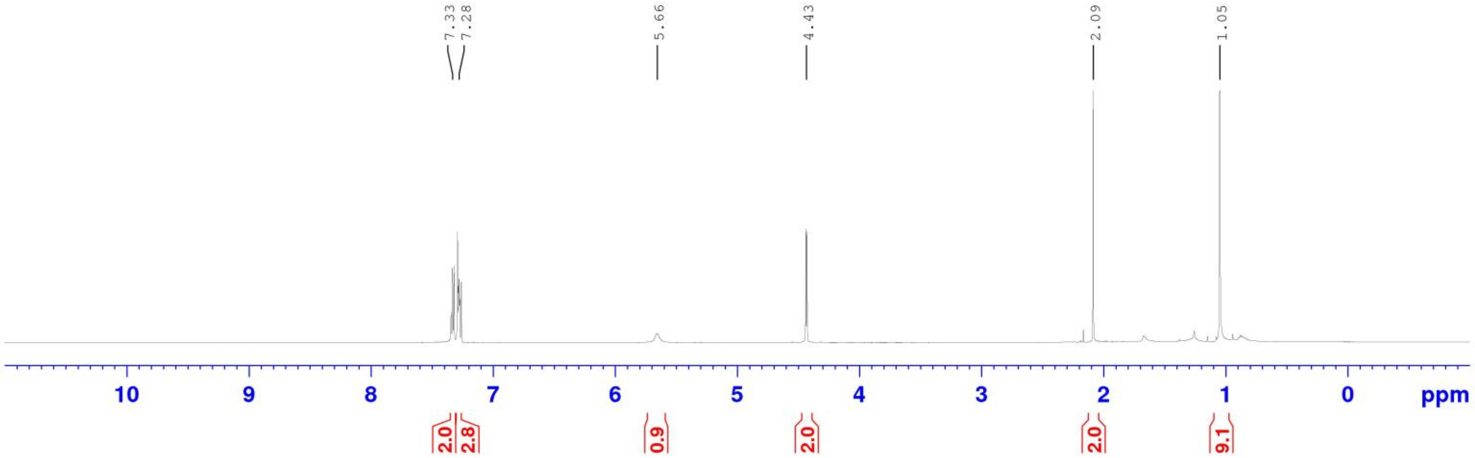


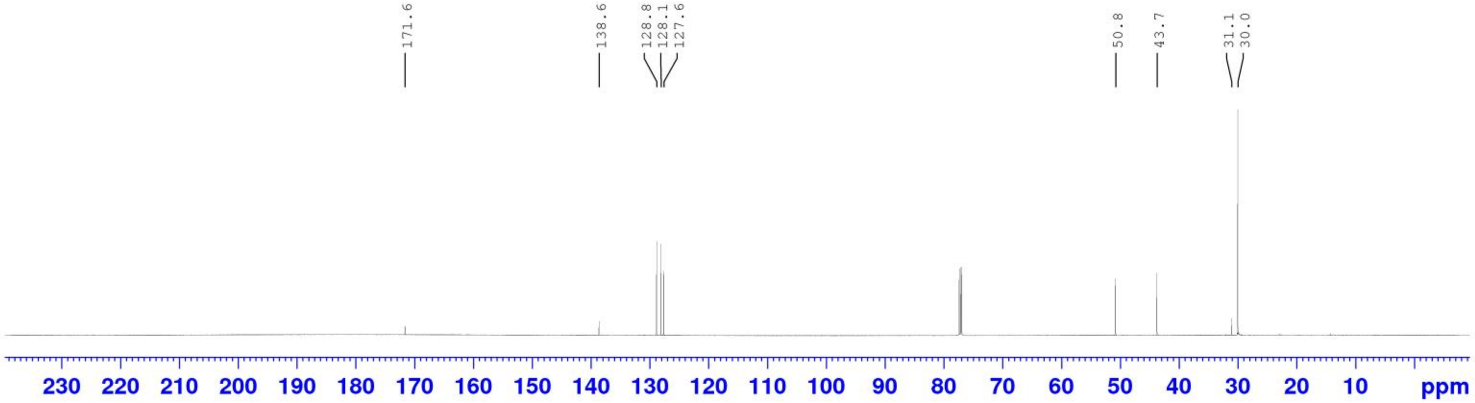
^{1}H and ^{13}C NMR spectra of **25a** recorded on a 600 MHz spectrometer



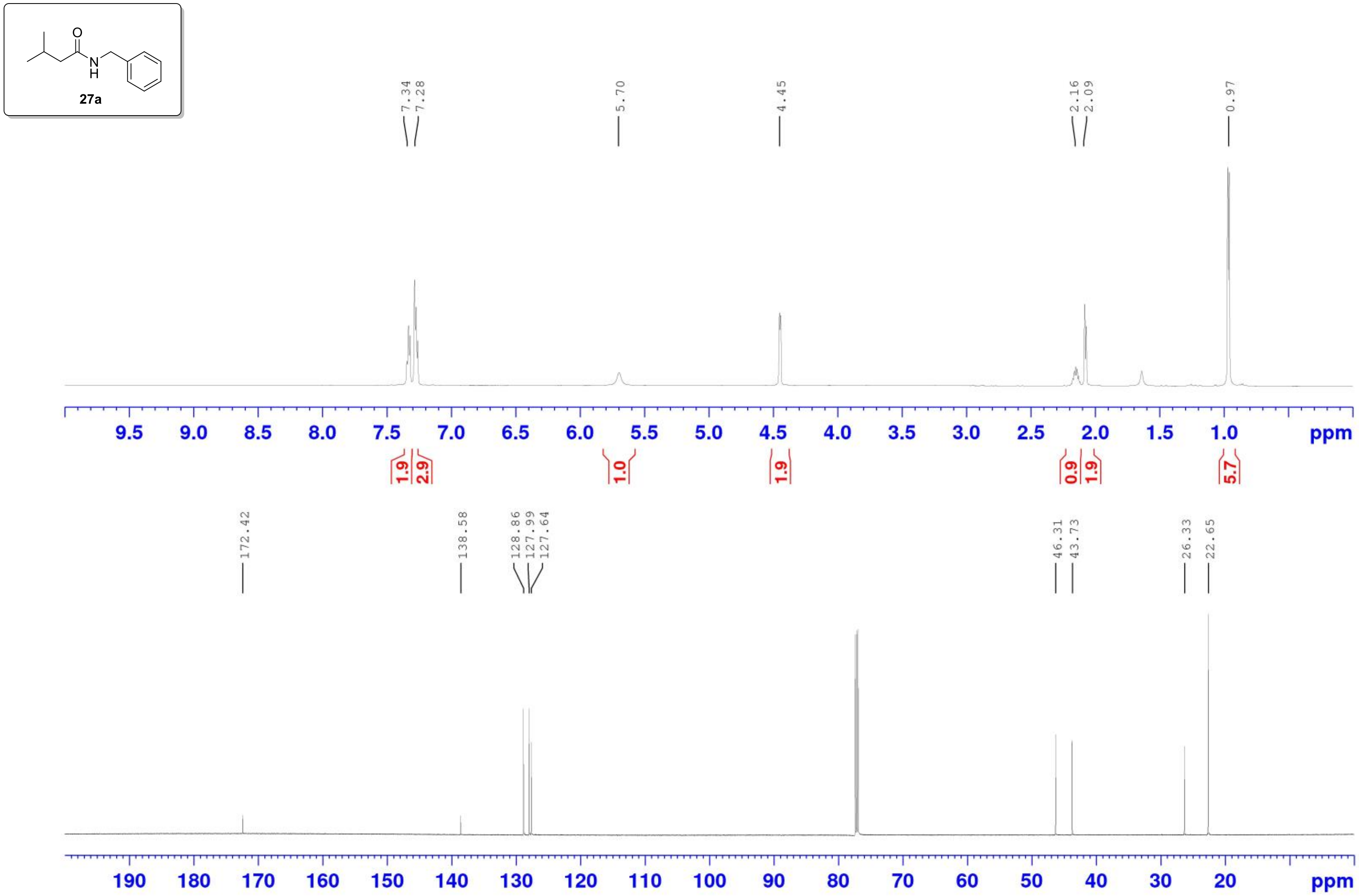
^{1}H and ^{13}C NMR spectra of **26a** recorded on 600 MHz spectrometer


26a

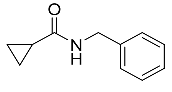




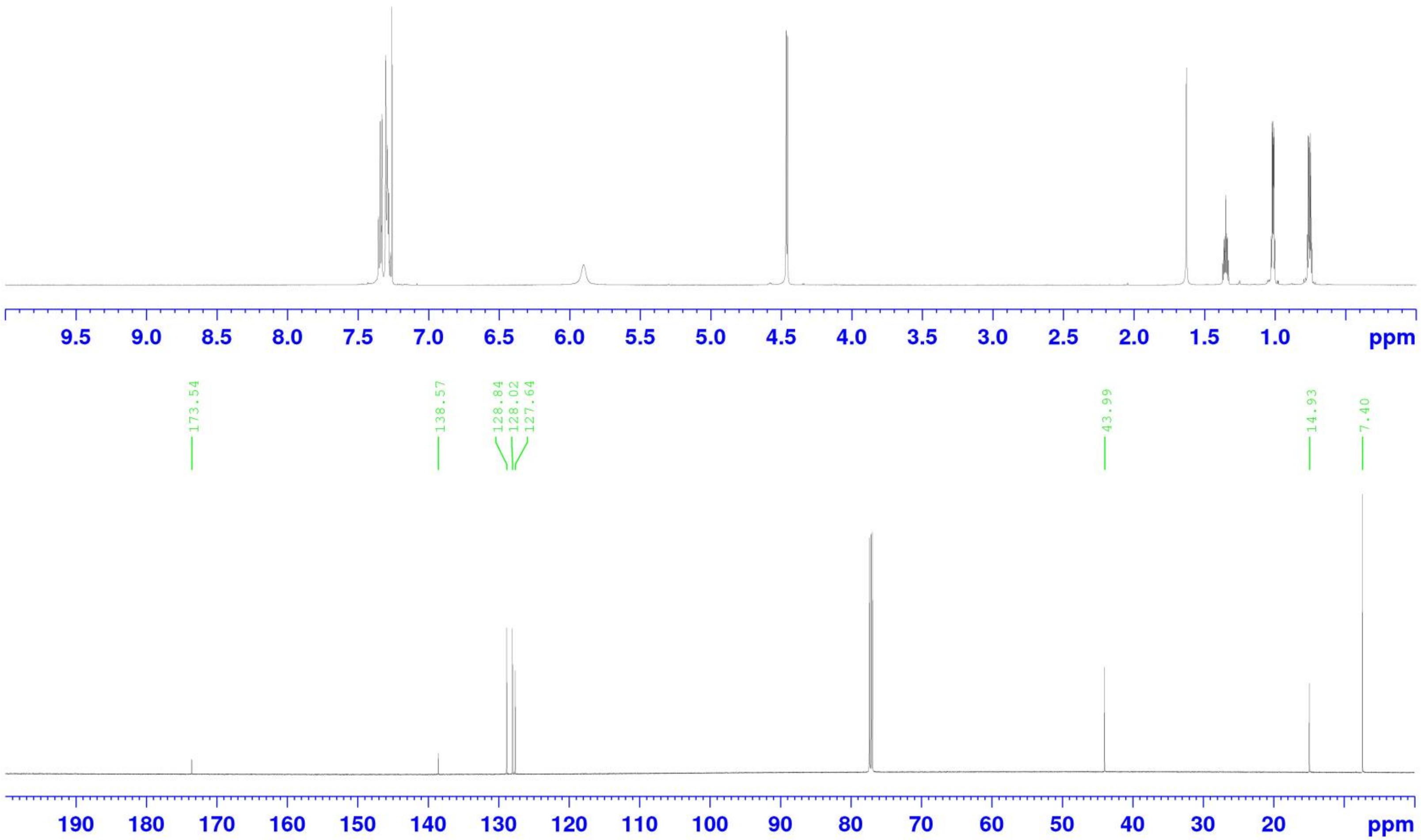
^{1}H and ^{13}C NMR spectra of **27a** recorded on 600 MHz spectrometer



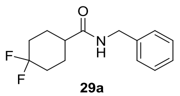
^{1}H and ^{13}C NMR spectra of **28a** recorded on a 600 MHz spectrometer



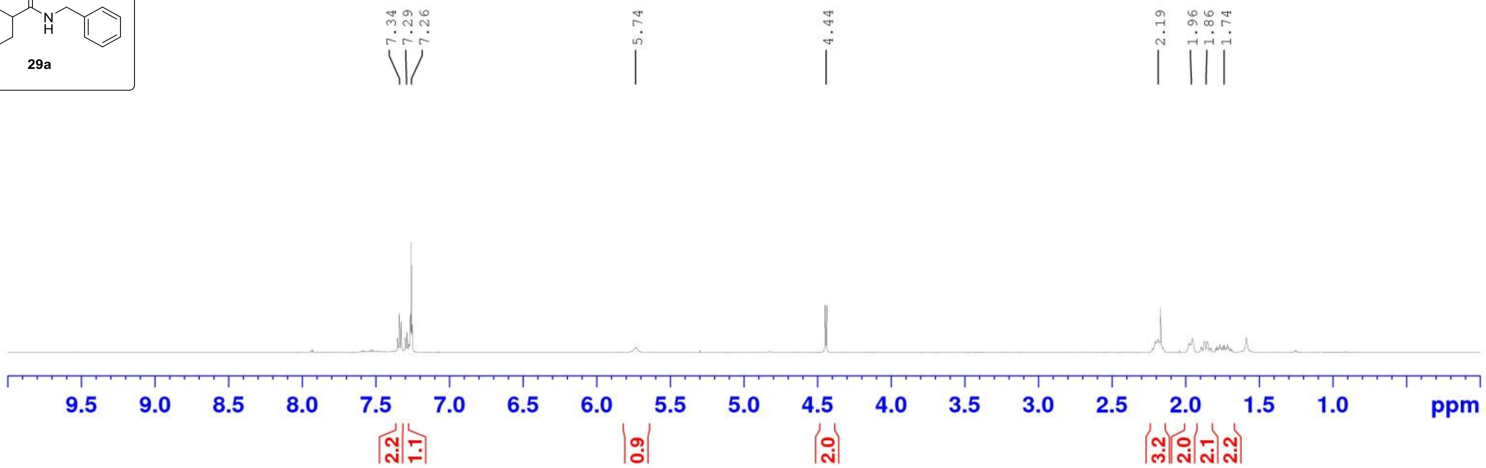
26a

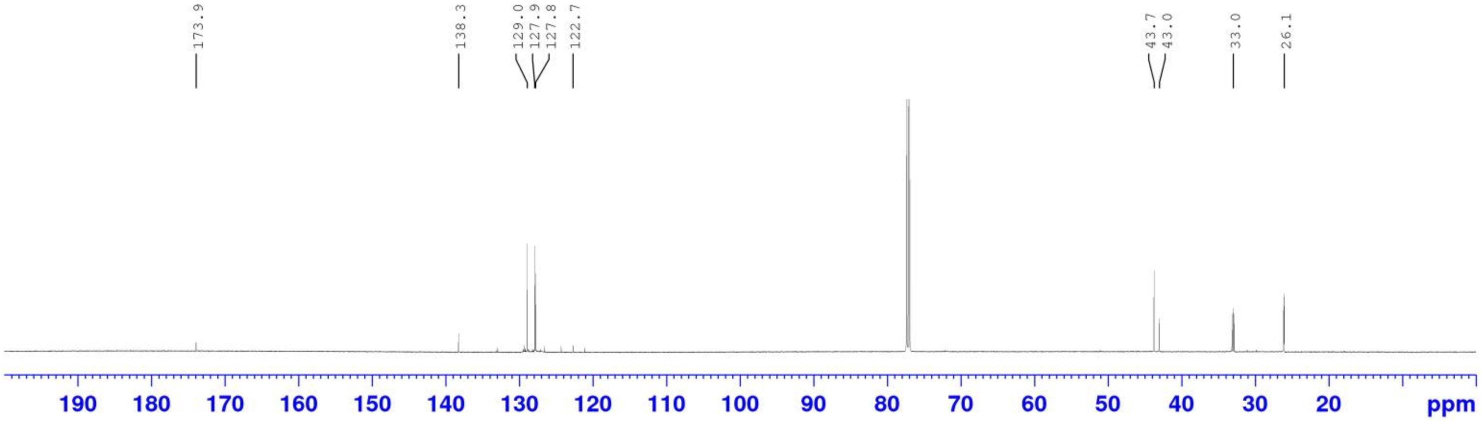


^{1}H and ^{13}C NMR spectra of **29a** recorded on a 600 MHz spectrometer

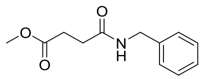


29a

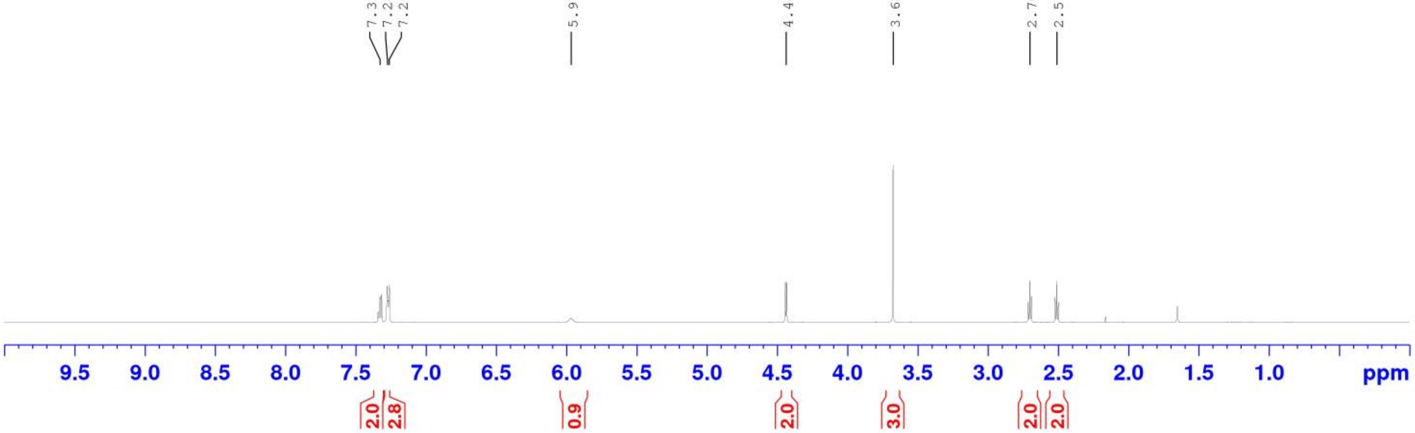


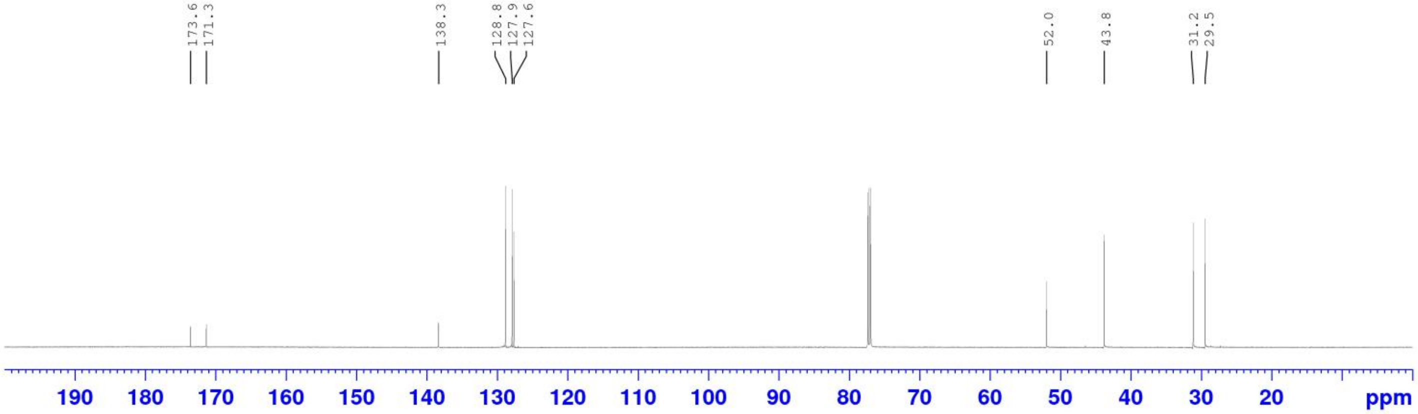


^1H and ^{13}C NMR spectra of **30a** recorded on a 600 MHz spectrometer

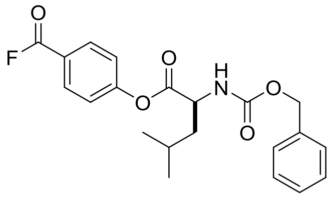


30a

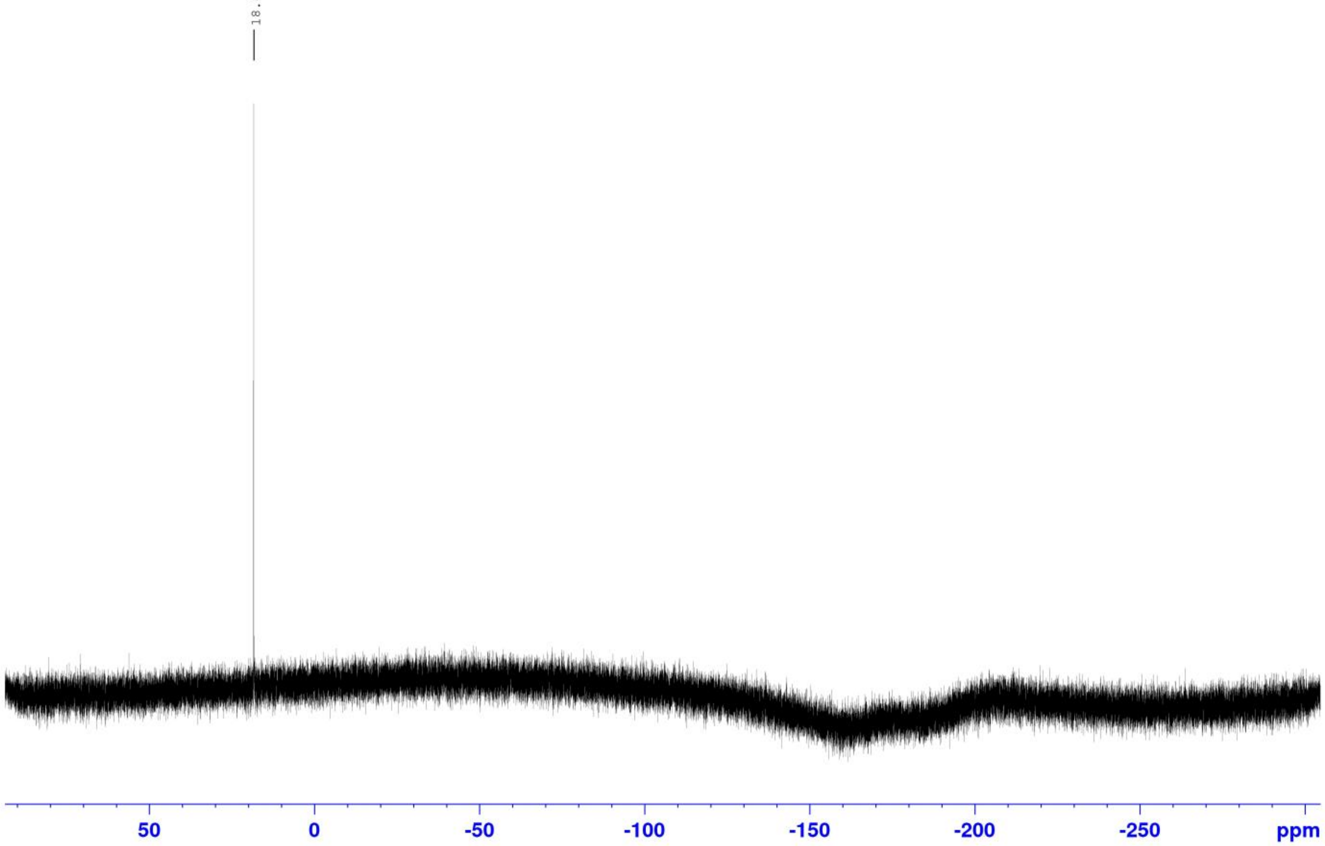




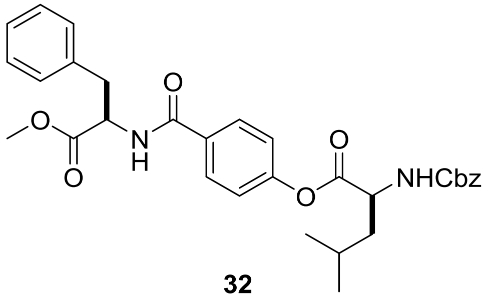
^{19}F- NMR spectra of **31** recorded on a 600 MHz spectrometer



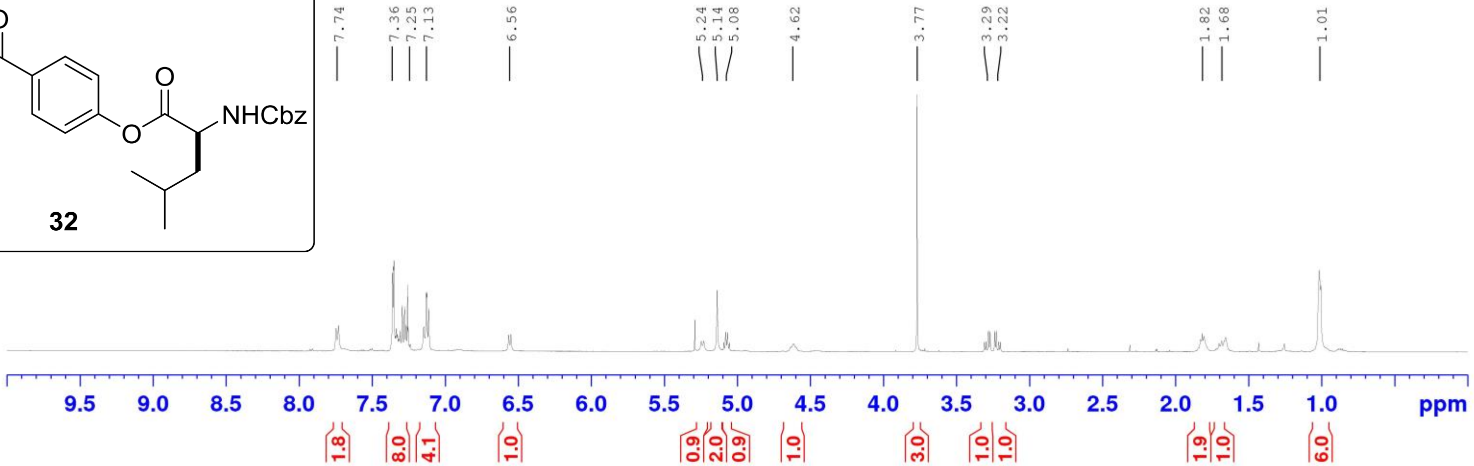
31

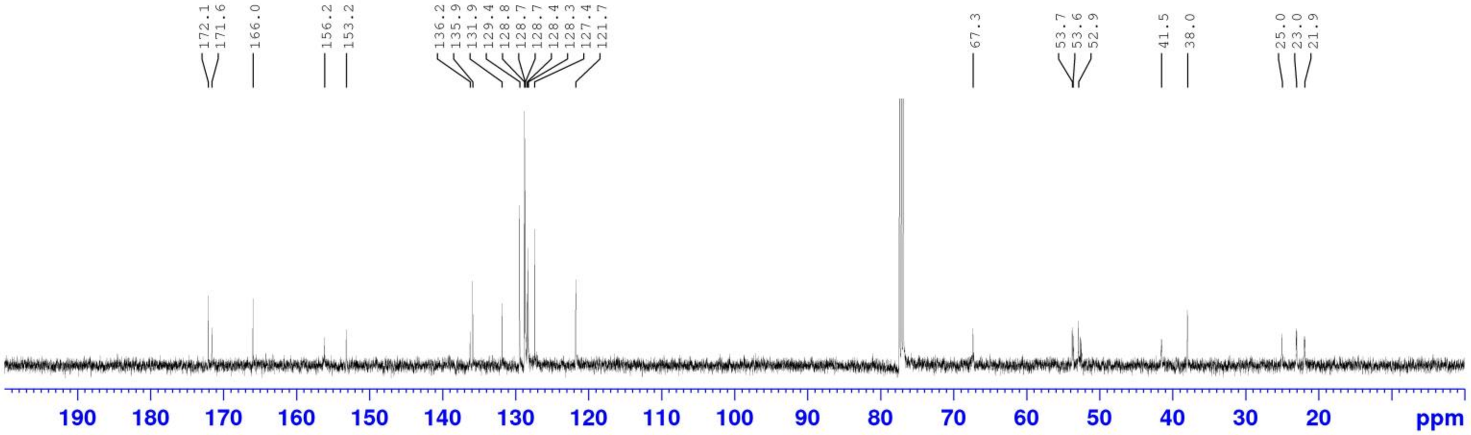


^{1}H and ^{13}C NMR spectra of **32** recorded on a 600 MHz spectrometer

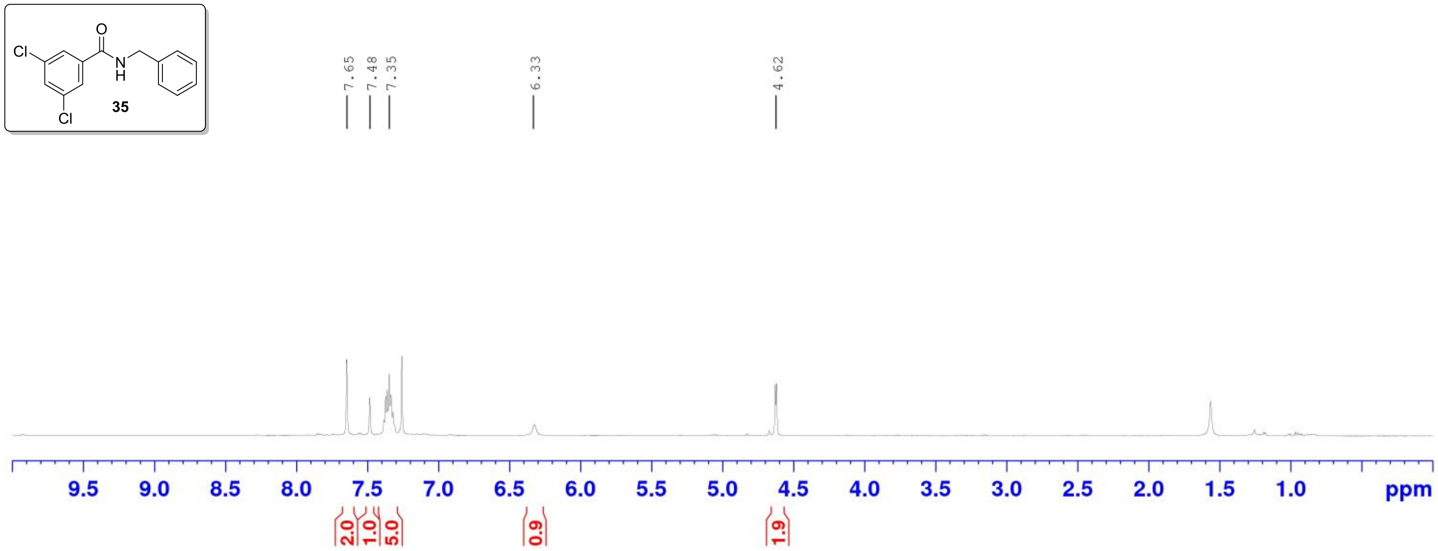


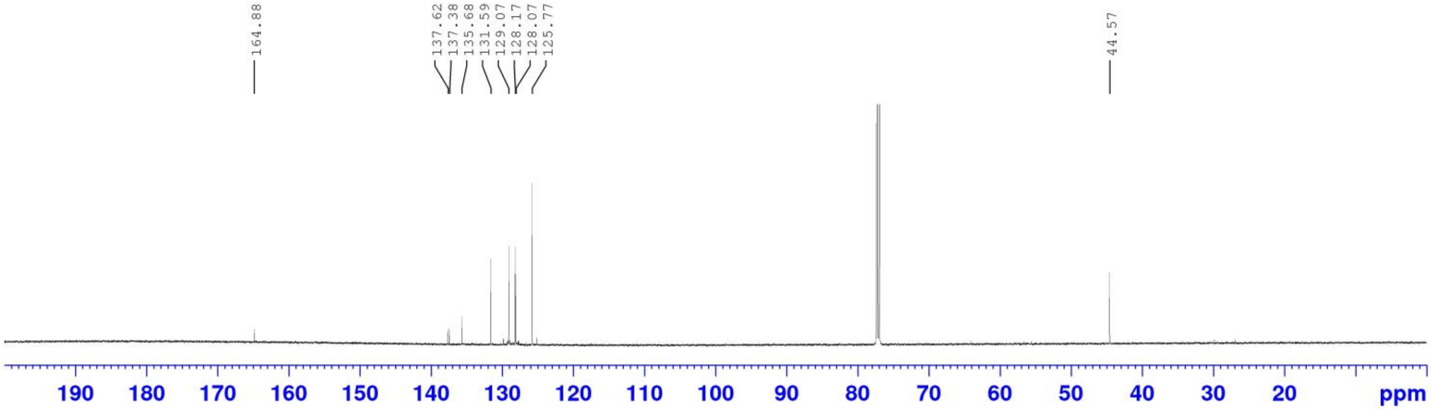
32





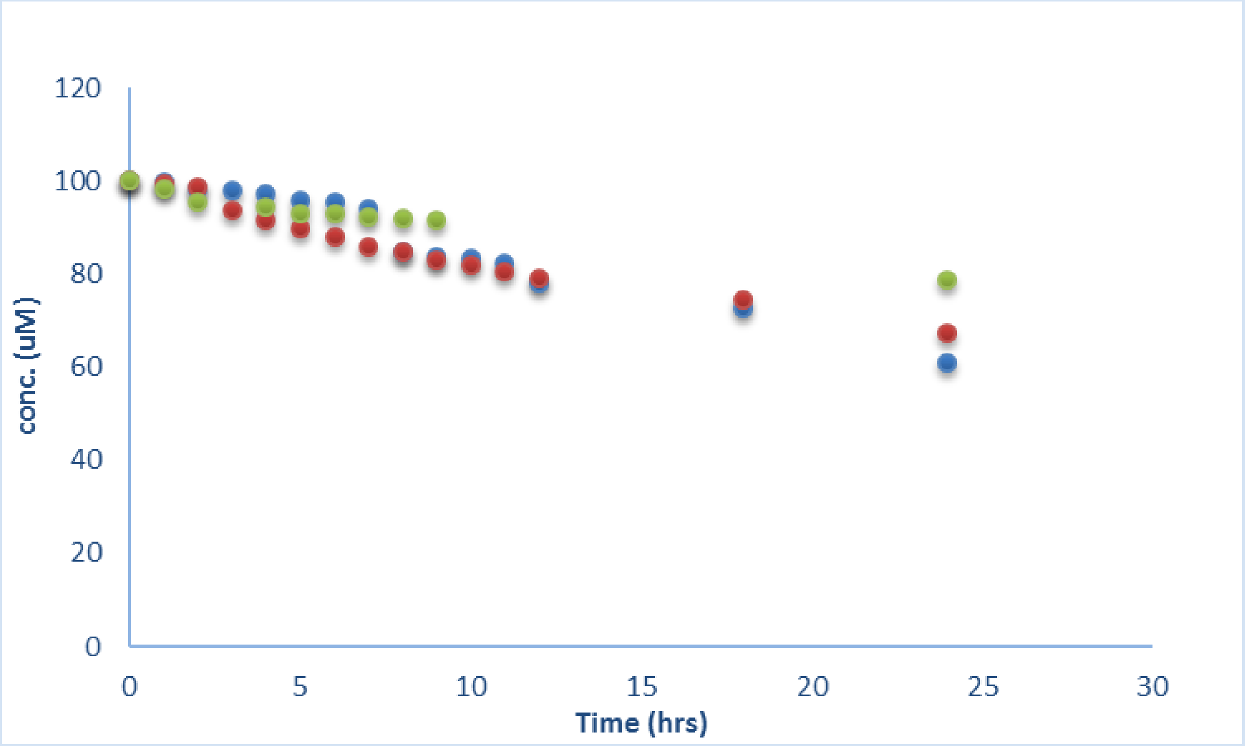
^{1}H and ^{13}C NMR spectra of **35** recorded on a 600 MHz spectrometer





Stability of Benzoyl Fluoride

***Note: Benzoyl fluoride used here was purchased from Sigma-Aldrich**



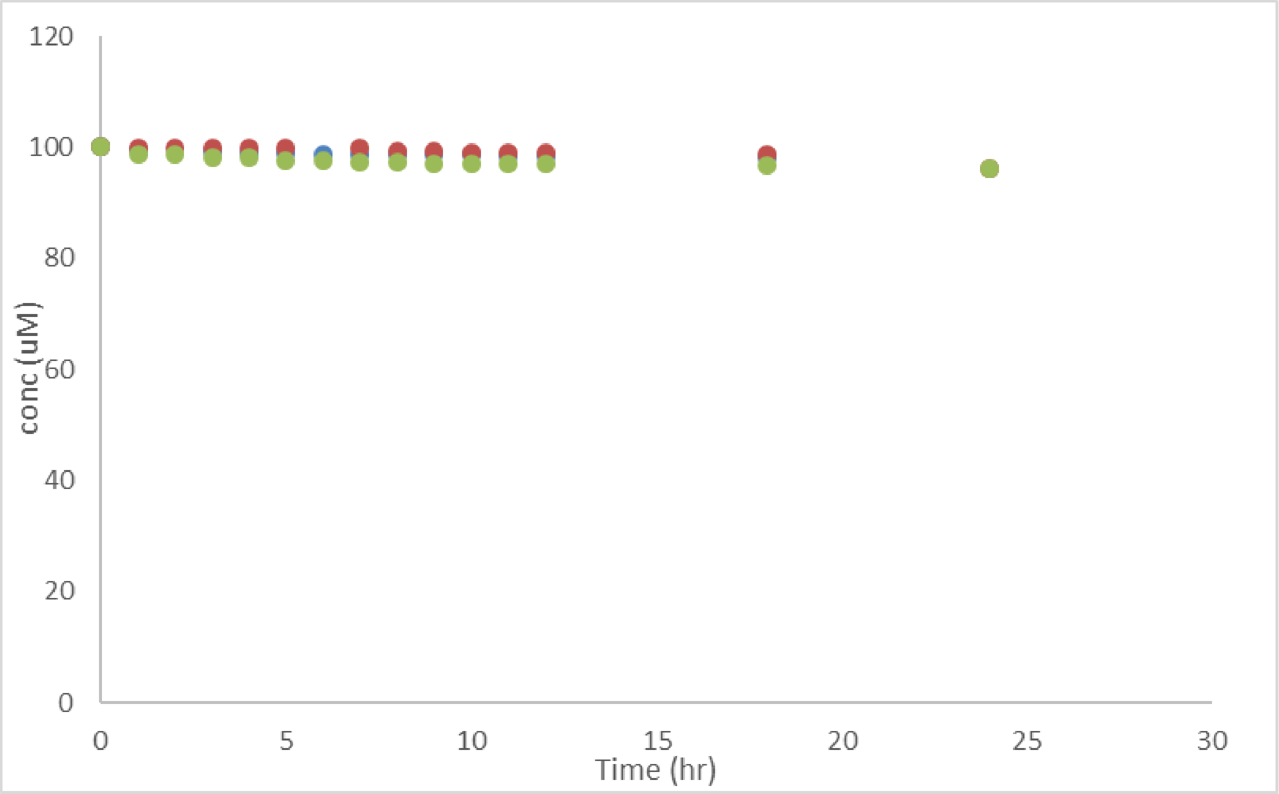
pH = 4 (blue circles), 7 (red circles), and 9 (green circles)

Benzoyl fluoride: pH = 4-> the final pH was 1.10. (ΔpH = 2.90)

Benzoyl fluoride: pH = 7 -> the final pH was 1.65. (ΔpH = 5.35)

Benzoyl fluoride: pH = 9 -> the final pH was 1.55. (ΔpH = 7.45)

Stability of Benzenesulfonyl Fluoride



pH = 4 (blue circles), 7 (red circles), and 9 (green circles)

Benzenesulfonyl fluoride: pH = 4 -> the final pH was 3.53. (ΔpH = 0.47)

Benzenesulfonyl fluoride: pH = 7 -> the final pH was 6.88. (ΔpH = 0.12)

Benzenesulfonyl fluoride: pH = 9 -> the final pH was 7.68. (ΔpH = 1.32)

Stability of benzoyl fluoride and benzenesulfonyl fluoride with and wiithout of cysteine methyl ester at pH = 4