

Supporting Information

Cp^{*}Co^{III}-catalyzed Dehydrative C-H Allylation of 6-Arylpurines and Aromatic Amides Using Allyl Alcohols in Fluorinated Alcohols

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Experimental Section

General: Reported melting points were uncorrected. Infrared (IR) spectra were recorded on a JASCO FT/IR-5300 spectrophotometer and absorbance bands are reported in wave numbers (cm^{-1}). NMR spectra were recorded on JEOL JNM-ECS400 spectrometers operating at 391.78 MHz for ^1H NMR and 98.52 MHz for ^{13}C NMR, JOEL JNM-ECX400 spectrometers, operating at 395.88 MHz for ^1H NMR and 99.55 MHz for ^{13}C NMR, and JNM-ECA500 spectrometers, operating at 500.16 MHz for ^1H NMR and 125.77 MHz for ^{13}C NMR. Chemical shifts in CDCl_3 , were reported in the scale relative to TMS (0.00 ppm for ^1H NMR), CHCl_3 (7.26 ppm for ^1H NMR), CDCl_3 (77.0 ppm for ^{13}C NMR), and CD_3CN (118.26 ppm for ^{13}C NMR) as an internal reference, respectively. ESI mass spectra were measured on JEOL JMS-T100LCP spectrometer. Column chromatography was performed with silica gel Kanto Silica gel 60 N (40-50 mesh) or Yamazen YFLC AI-580 using Universal Column SiOH.

1,1,1,3,3,3-Hexafluoropropan-2-ol, 1,2-dichloroethane (CaH_2), and 2,2,2-trifluoroethanol (CaSO_4 and NaHCO_3) were distilled from the indicated reagents, purged with argon for over 30 min, and stored over activated molecular sieves 3A or 4A under argon atmosphere before use. Commercially available THF, toluene, MeOH (Wako Ltd., deoxidized grade) were used without further manipulation unless otherwise stated. $\text{Cp}^*\text{Co}(\text{CO})\text{I}_2$ was synthesized according to the literature.^[1] All benzamide derivatives **4** were prepared from corresponding benzoic acid or benzoyl chloride and *tert*-butylamine. Purine derivatives **1** were prepared from commercially available 6-chloropurine according to the literature^{[2][3][4]}. Allyl alcohol was distilled from dried K_2CO_3 under argon atmosphere. All other reagents were commercially available and used as received.

- [1] Sun, B.; Yoshino, T.; Matsunaga, S.; Kanai, M. *Adv. Synth. Catal.* **2014**, *356*, 1491.
- [2] Havelková, M.; Dvořák, D.; Hocek, M. *Synthesis* **2001**, *11*, 1704.
- [3] Hocek, M.; Holý, A.; Votruba, I.; Dvořáková, D. *J. Med. Chem.* **2000**, *43*, 1817.
- [4] Wang, D.-C.; Niu, H.-Y.; Qu, G.-R.; Liang, L.; Wei, X.-J.; Zhang, Y.; Guo, H.-M. *Org. Biomol. Chem.* **2011**, *9*, 7663.

General Procedure of Cp^{*}Co^{III}-Catalyzed C-H Allylation of Purine Derivatives (Table 2)

To a dried screw-capped vial were added purine derivative **1** (0.30 mmol), Cp^{*}Co(CO)I₂ (7.1 mg, 0.015 mmol, 5 mol %), AgOTf (7.7 mg, 0.030 mmol, 10 mol %), AgOAc (5.0 mg, 0.030 mmol, 10 mol %), and TFE (3.0 mL) under argon atmosphere in a glovebox. Allyl alcohol **2** (31 µL, 0.45 mmol, 1.5 eq) was then added to the vial. The vial was capped, taken out of the glovebox, and the mixture was heated at 60 °C for 8 h with stirring. After the mixture was cooled to room temperature and diluted with CH₂Cl₂, saturated EDTA · 2Na *aq.* was added. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ three times. The organic layers were dried over Na₂SO₄. After filtration and evaporation, the obtained crude mixture was purified by silica gel column chromatography (AcOEt/hexane) to give a corresponding product **3**.

Gram-scale Synthesis of **3b**

To a flame-dried 100 mL Schlenk flask were added 9-benzyl-6-phenyl-9*H*-purine (1.0 g, 3.5 mmol), Cp^{*}Co(CO)I₂ (83.1 mg, 0.175 mmol, 5 mol %), AgOTf (89.7 mg, 0.35 mmol, 10 mol %), and AgOAc (58.3 mg, 0.35 mmol, 10 mol %) in a glovebox. The flask was charged with TFE (35 mL) and allyl alcohol **2a** (356 µL, 5.2 mmol, 1.5 eq). The flask was taken out of the glovebox, and the mixture was heated at 60 °C for 8 h with stirring under argon atmosphere. After the mixture was cooled to room temperature, diluted with CH₂Cl₂, and transferred to a separatory funnel, saturated EDTA · 2Na *aq.*(ca. 100 mL) was added. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂(100 mL x 2). The organic layers were dried over Na₂SO₄. After filtration and evaporation, the obtained crude mixture was purified by silica gel column chromatography (AcOEt/hexane = 2/1) to give **3b** (1.08 g, 95%).

Table S1. Optimization of Reaction Conditions for Benzamide **4d^a**

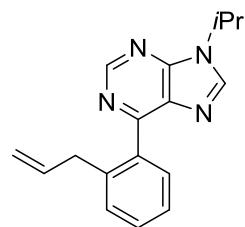
entry	Ag salt (Y mol %)	solvent (Z M)	allyl alcohol (X equiv)	temp. (°C)	time (h)	yield ^b (%)
1	AgOTf (10)	TFE (0.1)	1.5	60	8	41
2	AgNTf ₂ (10)	TFE (0.1)	1.5	60	8	45
3	AgNTf ₂ (20)	TFE (0.1)	1.5	60	8	48
4	AgNTf ₂ (20)	TFE (0.1)	1.5	80	24	57
5	AgNTf ₂ (20)	TFE (0.1)	3.0	80	24	69
6	AgNTf ₂ (20)	HFIP (1)	3.0	80	24	71 (67 ^c)

^aThe reactions were run using **4d** (0.10 mmol) and **2a** (X equiv) under indicated conditions. ^bDetermined by ¹H NMR analysis of the crude mixture using dibenzyl ether as an internal standard. ^cIsolated yield after silica gel column chromatography at 0.30 mmol scale.

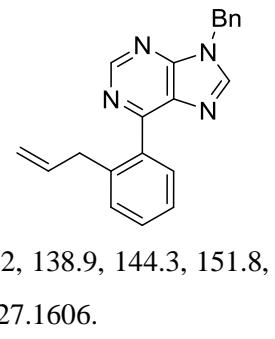
General Procedure of Cp*Co^{III}-Catalyzed C-H Allylation of Benzamide Derivatives (Table 3)

To a dried screw-capped vial were added benzamide derivative **4** (0.30 mmol), Cp*Co(CO)I₂ (7.1 mg, 0.015 mmol, 5 mol %), AgNTf₂ (23.3 mg, 0.060 mmol, 20 mol %), AgOAc (5.0 mg, 0.030 mmol, 10 mol %), and HFIP (0.3 mL) under argon atmosphere in a glovebox. Allyl alcohol **2** (61 μ L, 0.90 mmol, 3.0 eq) was then added to the vial. The vial was capped, taken out of the glovebox, and the mixture was heated at 80 °C for 24 h with stirring. The workup was the same as above.

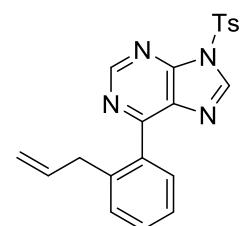
6-(2-allylphenyl)-9-isopropyl-9H-purine (3a**):** a colorless oil (65.4 mg, 78%); IR (neat) ν 2978, 1582, 1329, 1216, 764, 649 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 1.70 (d, *J* = 7.0 Hz, 6H), 3.63 (d, *J* = 6.3 Hz, 2H), 4.84-4.90 (m, 2H), 5.00 (sept, *J* = 7.0 Hz, 1H), 5.87 (ddt, *J* = 17.2, 10.4, 6.3 Hz, 1H), 7.36-7.46 (m, 3H), 7.69 (d, *J* = 7.7 Hz, 1H), 8.15 (s, 1H), 9.04 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 22.4, 37.6, 47.3, 115.4, 126.1, 129.6, 130.1, 130.8, 132.5, 134.7, 137.3, 138.8, 142.2, 151.3, 151.7, 158.5; HRMS (ESI): *m/z* calculated for C₁₇H₁₉N₄⁺ [M+H⁺]: 279.1604, found: 279.1603.



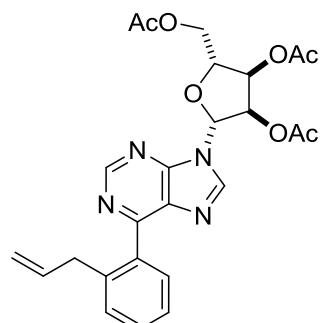
6-(2-allylphenyl)-9-benzyl-9*H*-purine (3b**):** a colorless oil (86.9 mg, 89%); IR (neat) ν 3062, 3032, 1583, 1504, 1455, 1402, 1327, 1213, 924, 763, 727, 699, 650 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 3.64 (d, *J* = 6.6 Hz, 2H), 4.83-4.87 (m, 2H), 5.46 (s, 2H), 5.85 (ddt, *J* = 17.2, 10.3, 6.6 Hz, 1H), 7.33-7.44 (m, 8H), 7.71 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.05 (s, 1H), 9.07 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 37.7, 47.2, 115.4, 126.1, 127.8, 128.5, 129.0, 129.7, 130.2, 130.9, 132.0, 134.6, 135.0, 137.2, 138.9, 144.3, 151.8, 152.2, 158.6; HRMS (ESI): *m/z* calculated for C₂₁H₁₉N₄⁺ [M+H⁺]: 327.1604, found: 327.1606.



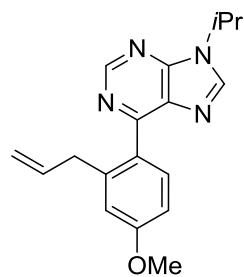
6-(2-allylphenyl)-9-(*p*-tolylsulfonyl)-9*H*-purine (3c**):** a colorless solid (74.7 mg, 64%); mp 127.0-128.5 °C; IR (neat) ν 3065, 1581, 1387, 1362, 1194, 1180, 1153, 1089, 670, 578 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 2.45 (s, 3H), 3.56 (d, *J* = 6.6 Hz, 2H), 4.80-4.86 (m, 2H), 5.81 (ddt, *J* = 17.2, 9.2, 6.6 Hz, 1H), 7.35-7.47 (m, 5H), 7.60 (d, *J* = 7.4 Hz, 1H), 8.23 (d, *J* = 8.6 Hz, 2H), 8.53 (s, 1H), 9.12 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.8, 37.5, 115.7, 126.2, 128.7, 130.2, 130.4, 130.9, 132.5, 133.5, 133.7, 137.0, 137.0, 139.0, 141.6, 147.1, 150.3, 153.6, 159.9; HRMS (ESI): *m/z* calculated for C₂₁H₁₉O₂N₄S⁺ [M+H⁺]: 391.1223, found: 391.1223.



6-(2-allylphenyl)-9-((2*R*,3*R*,4*R*,5*R*)-3,4-diacetoxy-5-(acetoxymethyl)tetrahydrofuran-2-yl)-9*H*-purine (3d**):** a pale yellow amorphous (130.9 mg, 88%); IR (neat) ν 2979, 1748, 1584, 1373, 1223, 1099, 1048, 762 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 2.08 (s, 3H), 2.10 (s, 3H), 2.14 (s, 3H), 3.60 (d, *J* = 6.9 Hz, 2H), 4.38 (dd, *J* = 13.2, 5.2 Hz, 1H), 4.44-4.47 (m, 2H), 4.83-4.88 (m, 2H), 5.71 (dd, *J* = 5.4, 4.6 Hz, 1H), 5.84 (ddt, *J* = 16.6, 9.7, 6.9 Hz, 1H), 6.00 (dd, *J* = 5.4, 5.4 Hz, 1H), 6.27 (d, *J* = 4.6 Hz, 1H), 7.34-7.44 (m, 3H), 7.66 (dd, *J* = 7.4, 1.1 Hz, 1H), 8.22 (s, 1H), 9.03 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 20.3, 20.4, 20.6, 37.6, 62.9, 70.4, 73.0, 80.2, 86.4, 115.6, 126.2, 129.9, 130.2, 130.9, 132.8, 134.3, 137.1, 138.9, 142.8, 151.2, 152.3, 159.2, 169.3, 169.5, 170.2; HRMS (ESI): *m/z* calculated for C₂₅H₂₆N₄NaO₇⁺ [M+Na⁺]: 517.1694, found: 517.1695.

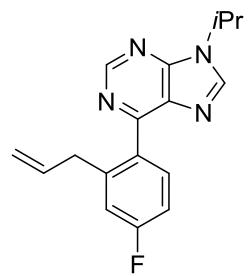


6-(2-allyl-4-methoxyphenyl)-9-isopropyl-9*H*-purine (3e**):** a colorless oil (77.0 mg, 83%); IR (neat) ν 2977, 2935, 1605, 1579, 1506, 1450, 1329, 1217, 648 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 1.64 (d, *J* = 6.9 Hz, 6H), 3.66 (d, *J* = 6.3 Hz, 2H), 3.82 (s, 3H), 4.87-4.96 (m, 3H), 5.85 (ddt, *J* = 16.6, 10.3, 6.3 Hz, 1H), 6.87-6.90 (m, 2H), 7.73 (d, *J* = 8.0 Hz, 1H), 8.10 (s, 1H), 8.96 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 22.4, 37.8, 47.2, 55.2, 111.4, 115.6, 115.9, 127.3, 132.4, 132.7, 137.2,

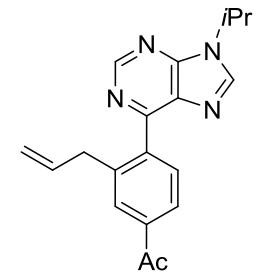


141.1, 141.8, 151.2, 151.6, 158.2, 160.6; HRMS (ESI): m/z calculated for $C_{18}H_{21}N_4O^+$ [M+H $^+$]: 309.1710, found: 309.1711.

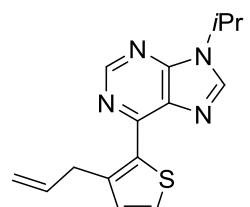
6-(2-allyl-4-fluorophenyl)-9-isopropyl-9*H*-purine (3f**):** a colorless oil (61.8 mg, 70%); IR (neat) ν 2979, 1589, 1503, 1330, 1216, 970, 809, 648 cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz) δ 1.66 (d, $J = 6.9$ Hz, 6H), 3.61 (d, $J = 6.9$ Hz, 2H), 4.88-4.99 (m, 3H), 5.83 (ddt, $J = 16.6, 9.7, 6.9$ Hz, 1H), 7.04 (ddd, $J = 8.5, 8.5, 2.5$ Hz, 1H), 7.09 (dd, $J = 10.0, 2.5$ Hz, 1H), 7.70 (dd, $J = 8.5, 6.3$ Hz, 1H), 8.13 (s, 1H), 9.00 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.5, 37.6, 47.4, 113.1 (d, $^2J_{CF} = 30.9$ Hz), 116.3, 116.9 (d, $^2J_{CF} = 21.6$ Hz), 130.8 (d, $^4J_{CF} = 2.4$ Hz), 132.7 (d, $^3J_{CF} = 46.8$ Hz), 133.0, 136.4, 142.1 (d, $^3J_{CF} = 8.4$ Hz), 142.3, 151.4, 151.7, 157.5, 163.5 (d, $^1J_{CF} = 248.3$ Hz); HRMS (ESI): m/z calculated for $C_{17}H_{18}FN_4^+$ [M+H $^+$]: 297.1510, found: 297.1511.



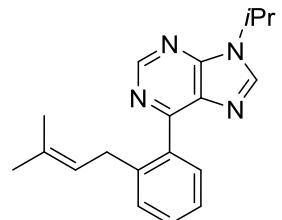
6-(4-acetyl-2-allylphenyl)-9-isopropyl-9*H*-purine (3g**):** a colorless oil (89.0 mg, 93%); IR (neat) ν 2979, 1685, 1578, 1392, 1329, 1216, 931, 756, 648 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 1.68 (d, $J = 7.0$ Hz, 6H), 2.63 (s, 3H), 3.65 (d, $J = 6.7$ Hz, 2H), 4.84-4.92 (m, 2H), 4.98 (sept, $J = 7.0$ Hz, 1H), 5.83 (ddt, $J = 16.6, 9.9, 6.7$ Hz, 1H), 7.77 (d, $J = 8.1$ Hz, 1H), 7.93 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.97 (s, 1H), 8.16 (s, 1H), 9.03 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.4, 26.7, 37.5, 47.4, 116.2, 126.0, 129.9, 131.1, 132.4, 136.4, 137.5, 139.1, 139.5, 142.7, 151.4, 151.6, 157.1, 197.9; HRMS (ESI): m/z calculated for $C_{19}H_{21}N_4O^+$ [M+H $^+$]: 321.1710, found: 321.1712.



6-(3-allylthiophene-2-yl)-9-isopropyl-9*H*-purine (3h**):** a colorless oil (50.2 mg, 59%); IR (neat) ν 3075, 2977, 2931, 1577, 1446, 1327, 1218, 917, 831, 647 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 1.67 (d, $J = 6.7$ Hz, 6H), 4.11 (d, $J = 6.5$ Hz, 2H), 4.97 (sept, $J = 6.7$ Hz, 1H), 5.04 (dd, $J = 10.1, 1.8$ Hz, 1H), 5.11 (ddt, $J = 17.1, 1.8, 1.8$ Hz, 1H), 6.08 (ddt, $J = 17.1, 10.1, 6.5$ Hz, 1H), 7.09 (d, $J = 5.1$ Hz, 1H), 7.57 (d, $J = 5.1$ Hz, 1H), 8.18 (s, 1H), 8.96 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 22.5, 34.9, 47.2, 115.4, 129.8, 130.3, 130.8, 131.2, 137.1, 141.4, 143.9, 151.3, 151.6, 151.7; HRMS (ESI): m/z calculated for $C_{15}H_{17}N_4S^+$ [M+H $^+$]: 285.1168, found: 285.1171.

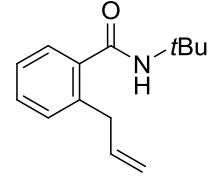


9-isopropyl-6-(2-(3-methylbut-2-en-1-yl)phenyl)-9*H*-purine (3i**):** a colorless oil (71.7 mg, 78%); IR (neat) ν 2978, 2928, 1583, 1329, 1216, 934, 762, 649 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 1.43 (s, 3H), 1.56 (s, 3H), 1.68 (d, $J = 6.8$ Hz, 6H), 3.53 (d, $J = 7.2$ Hz, 2H), 4.98 (sept, $J = 6.8$ Hz, 1H), 5.14 (t, $J = 7.2$ Hz,

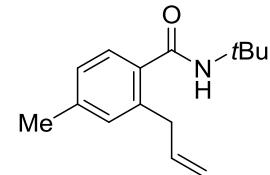


1H), 7.32-7.43 (m, 3H), 7.63 (d, $J = 6.3$ Hz, 1H), 8.15 (s, 1H), 9.04 (s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 17.4, 22.4, 25.4, 32.1, 47.3, 123.2, 125.8, 129.5, 129.8, 130.4, 131.9, 132.6, 134.7, 140.5, 142.1, 151.2, 151.8, 158.9; HRMS (ESI): m/z calculated for $\text{C}_{19}\text{H}_{23}\text{N}_4^+$ [M+H $^+$]: 307.1917, found: 307.1917.

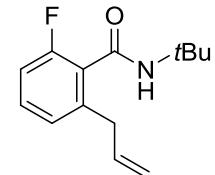
2-allyl-N-(tert-butyl)benzamide (5a): a colorless solid (35.3 mg, 54%); mp 62.5-63.0 °C; IR (KBr) ν 3284, 2966, 1631, 1551, 1361, 1324, 1224, 921, 740 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.44 (s, 9H), 3.55 (d, $J = 6.3$ Hz, 2H), 4.99 (dd, $J = 17.1, 1.7$ Hz, 1H), 5.08 (dd, $J = 10.2, 1.7$ Hz, 1H), 5.71 (brs, 1H), 6.03 (ddt, $J = 17.1, 10.2, 6.3$ Hz, 1H), 7.2-7.24 (m, 2H), 7.31-7.37 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 28.7, 37.3, 51.8, 116.0, 126.2, 127.1, 129.6, 130.3, 136.8, 137.6, 137.7, 169.3; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{19}\text{NNaO}^+$ [M+Na $^+$]: 240.1359, found: 240.1361.



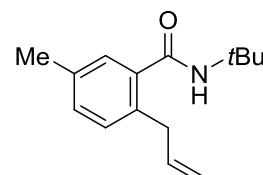
2-allyl-N-(tert-butyl)-4-methylbenzamide (5b): a colorless solid (33.2 mg, 48%); mp 77.4-77.8 °C; IR (KBr) ν 3267, 2972, 1639, 1542, 1323, 1225, 822 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.44 (s, 9H), 2.33 (s, 3H), 3.53 (d, $J = 6.3$ Hz, 2H), 5.01 (ddt, $J = 16.6, 1.7, 1.7$ Hz, 1H), 5.07 (ddt, $J = 9.7, 1.7, 1.7$ Hz, 1H), 5.64 (brs, 1H), 6.02 (ddt, $J = 16.6, 9.7, 6.3$ Hz, 1H), 7.02 (s, 1H), 7.03 (d, $J = 6.9$ Hz, 1H), 7.27 (d, $J = 6.9$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 21.2, 28.8, 37.3, 51.6, 115.9, 126.8, 127.1, 131.0, 135.0, 137.0, 137.8, 139.5, 169.4; HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{21}\text{NNaO}^+$ [M+Na $^+$]: 254.1515, found: 254.1517.



2-allyl-N-(tert-butyl)-6-fluorobenzamide (5c): a colorless solid (49.9 mg, 71%); mp 77.3-78.0 °C; IR (KBr) ν 3283, 3077, 2970, 2928, 1647, 1558, 1456, 1363, 1322, 1252, 1223, 985, 803, 762 cm^{-1} ; ^1H NMR (CDCl_3 , 500 MHz) δ 1.46 (s, 9H), 3.48 (d, $J = 6.6$ Hz, 2H), 5.04 (ddt, $J = 16.9, 1.7, 1.7$ Hz, 1H), 5.08 (ddt, $J = 10.6, 1.7, 1.7$ Hz, 1H), 5.67 (brs, 1H), 5.96 (ddt, $J = 16.9, 10.6, 6.6$ Hz, 1H), 6.90-6.93 (m, 1H), 6.99-7.00 (m, 1H), 7.23-7.27 (m, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 28.7, 36.9 (d, $^4J_{\text{CF}} = 2.4$ Hz), 52.1, 113.4 (d, $^2J_{\text{CF}} = 21.6$ Hz), 116.3, 125.3 (d, $^4J_{\text{CF}} = 2.4$ Hz), 125.9 (d, $^2J_{\text{CF}} = 18.0$ Hz), 130.1 (d, $^3J_{\text{CF}} = 8.3$ Hz), 136.7, 139.8 (d, $^3J_{\text{CF}} = 2.4$ Hz), 159.0 (d, $^1J_{\text{CF}} = 245.9$ Hz), 164.1; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{18}\text{FNNaO}^+$ [M+Na $^+$]: 258.1265, found: 258.1264.

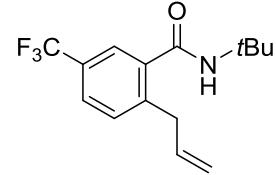


2-allyl-N-(tert-butyl)-5-methylbenzamide (5d): a colorless solid (46.5 mg, 67%); mp 66.5-66.9 °C; IR (KBr) ν 3250, 2977, 2957, 1635, 1545, 1450, 1326, 1223, 913, 822 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.44 (s, 9H), 2.33 (s, 3H), 3.50 (d, $J = 6.3$ Hz, 2H), 4.98 (ddt, $J = 16.9, 1.8, 1.8$ Hz, 1H), 5.06 (ddt, $J = 10.2, 1.8, 1.8$ Hz, 1H), 5.65 (brs, 1H), 6.02 (ddt, $J = 16.9, 10.2, 6.3$ Hz, 1H), 7.09 (d, $J = 7.7$ Hz, 1H), 7.14 (d, $J = 7.7$ Hz, 1H), 7.18

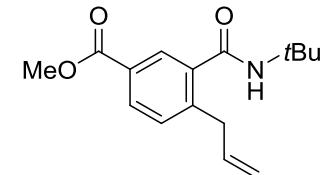


(s, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.8, 28.7, 36.9, 51.7, 115.8, 127.7, 130.2, 130.3, 133.7, 135.9, 137.6, 137.9, 169.5; HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{21}\text{NNaO}^+ [\text{M}+\text{Na}^+]$: 254.1515, found: 254.1516.

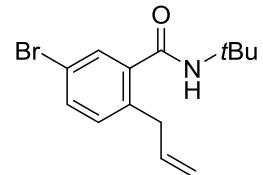
2-allyl-N-(*tert*-butyl)-5-(trifluoromethyl)benzamide (5e): a colorless solid (40.8 mg, 48%); mp 93.0-93.7 °C; IR (KBr) ν 3297, 3084, 2979, 2929, 1643, 1550, 1343, 1308, 1146, 1126 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.46 (s, 9H), 3.58 (d, $J = 6.3$ Hz, 2H), 5.01 (ddt, $J = 17.0, 1.8, 1.4$ Hz, 1H), 5.13 (ddt, $J = 10.2, 1.8, 1.4$ Hz, 1H), 5.72 (brs, 1H), 6.00 (ddt, $J = 17.0, 10.2, 6.3$ Hz, 1H), 7.34 (brd, $J = 8.1$ Hz, 1H), 7.57 (brd, $J = 8.1$ Hz, 1H), 7.60 (brs, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 28.7, 37.2, 52.2, 116.9, 123.8 (q, $^1J_{\text{CF}} = 273.1$ Hz), 124.1 (q, $^3J_{\text{CF}} = 3.8$ Hz), 126.2 (q, $^3J_{\text{CF}} = 3.9$ Hz), 128.7 (q, $^2J_{\text{CF}} = 32.4$ Hz), 130.9, 136.6, 138.3, 141.2, 167.9; HRMS (ESI): m/z calculated for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{NNaO}^+ [\text{M}+\text{Na}^+]$: 308.1233, found: 308.1234.



Methyl 4-allyl-3-(*tert*-butylcarbamoyl)benzoate (5f): a colorless oil (51.4 mg, 62%); IR (KBr) ν 3330, 2961, 2926, 1726, 1652, 1260, 1224 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.46 (s, 9H), 3.60 (d, $J = 6.3$ Hz, 2H), 3.92 (s, 3H), 5.02 (dd, $J = 17.1, 1.7$ Hz, 1H), 5.11 (dd, $J = 10.4, 1.7$ Hz, 1H), 5.73 (brs, 1H), 6.00 (ddt, $J = 17.1, 10.4, 6.3$ Hz, 1H), 7.30 (d, $J = 8.1$ Hz, 1H), 7.97 (dd, $J = 8.1, 1.8$ Hz, 1H), 8.01 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 28.7, 37.3, 52.0, 52.1, 116.6, 128.1, 128.1, 130.4, 130.4, 136.6, 137.8, 142.7, 166.4, 168.3; HRMS (ESI): m/z calculated for $\text{C}_{16}\text{H}_{21}\text{NNaO}_3^+ [\text{M}+\text{Na}^+]$: 298.1414, found: 298.1414.



2-allyl-5-bromo-N-(*tert*-butyl)benzamide (5g): a colorless solid (52.1 mg, 59%); mp 131.3-132.0 °C; IR (KBr) ν 3293, 2966, 1639, 1547 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.44 (s, 9H), 3.48 (d, $J = 5.9$ Hz, 2H), 4.98 (ddt, $J = 16.8, 1.8, 1.4$ Hz, 1H), 5.09 (ddt, $J = 10.0, 1.8, 1.4$ Hz, 1H), 5.66 (brs, 1H), 5.97 (ddt, $J = 16.8, 10.0, 6.3$ Hz, 1H), 7.08 (d, $J = 8.2$ Hz, 1H), 7.44 (dd, $J = 8.2, 1.8$ Hz, 1H), 7.48 (d, $J = 1.8$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 28.7, 36.7, 52.0, 116.4, 119.8, 129.9, 132.1, 132.5, 136.0, 137.0, 139.5, 167.6; HRMS (ESI): m/z calculated for $\text{C}_{14}\text{H}_{18}\text{BrNNaO}^+ [\text{M}+\text{Na}^+]$: 318.0464, found: 318.0465.

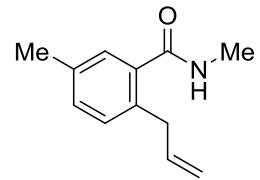


2-allyl-N-(*tert*-butyl)-5-iodobenzamide (5h): a colorless solid (61.4 mg, 60%); mp 128.8-129.2 °C; IR (KBr) ν 3292, 2968, 1639, 1546, 1450, 1319, 1222 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 1.42 (s, 9H), 3.45 (d, $J = 6.3$ Hz, 2H), 4.97 (ddt, $J = 17.3, 1.8, 1.8$ Hz, 1H), 5.07 (ddt, $J = 10.1, 1.8, 1.3$ Hz, 1H), 5.68 (brs, 1H), 5.96 (ddt, $J = 17.3, 10.1, 6.3$ Hz, 1H), 6.94 (d, $J = 8.1$ Hz, 1H), 7.62 (dd, $J = 8.1, 2.0$ Hz, 1H), 7.65 (d, $J = 2.0$ Hz, 1H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 28.7, 36.8, 52.0, 91.1, 116.5, 132.2, 135.7, 136.6, 136.9, 138.4, 139.8, 167.5;

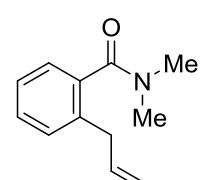


HRMS (ESI): m/z calculated for $C_{14}H_{18}INNaO^+ [M+Na^+]$: 366.0325, found: 366.0330.

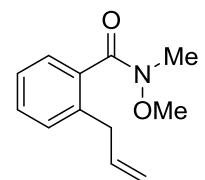
2-allyl-N,5-dimethylbenzamide (5i): a colorless solid (25.6 mg, 45%); mp 136-137 °C; IR (KBr) ν 3291, 3076, 2944, 1635, 1550, 1409, 1323, 913 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 2.32 (s, 3H), 2.96 (d, J = 5.2 Hz, 3H), 3.50 (d, J = 6.3 Hz, 2H), 4.99 (dd, J = 16.7, 1.7 Hz, 1H), 5.05 (dd, J = 9.9, 1.7 Hz, 1H), 5.83 (brs, 1H), 6.00 (ddt, J = 16.7, 9.9, 6.3 Hz, 1H), 7.12 (d, J = 8.0 Hz, 1H), 7.16 (d, J = 8.0 Hz, 1H), 7.21 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.8, 26.5, 37.1, 115.6, 127.9, 130.3, 130.6, 134.2, 135.9, 136.4, 138.0, 170.7; HRMS (ESI): m/z calculated for $C_{12}H_{16}NO^+ [M+H^+]$: 190.1226, found: 190.1229.

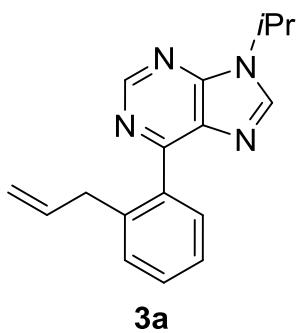


2-allyl-N,N-dimethylbenzamide (5j): a colorless oil (17.7 mg, 31%); IR (KBr) ν 2927, 1636, 1507, 1395, 1267, 1068 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz) δ 2.81 (s, 3H), 3.11 (s, 3H), 3.39 (brs, 2H), 5.04-5.09 (m, 2H), 5.91 (ddt, J = 17.2, 10.3, 6.3 Hz, 1H), 7.16 (dd, J = 7.4, 1.1 Hz, 1H), 7.21-7.28 (m, 2H), 7.31 (ddd, J = 7.4, 7.4, 1.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 34.6, 37.3, 38.8, 116.1, 126.0, 126.3, 128.9, 129.8, 136.4, 136.5, 136.5, 171.3; HRMS (ESI): m/z calculated for $C_{12}H_{16}NO^+ [M+H^+]$: 190.1226, found: 190.1228.

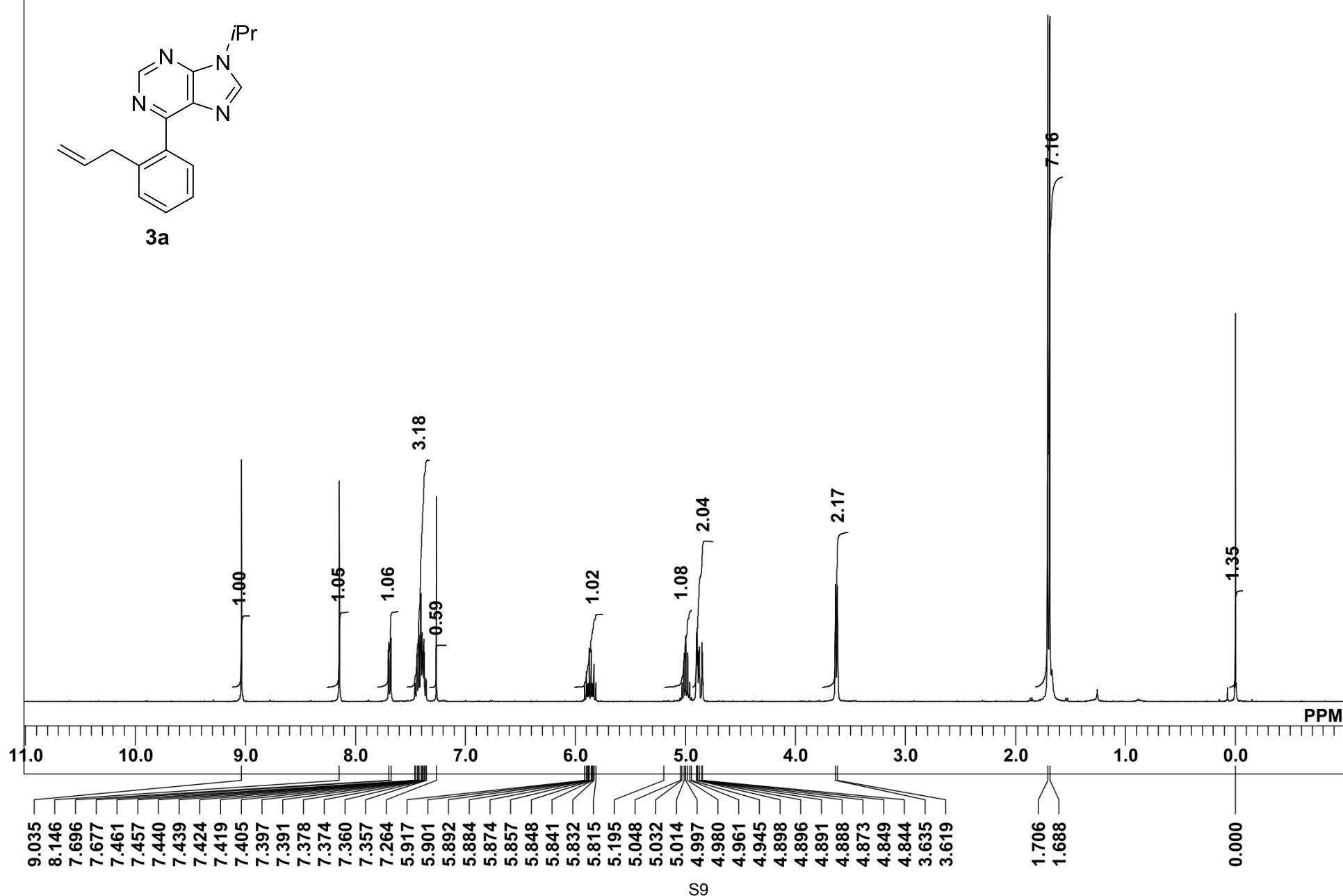


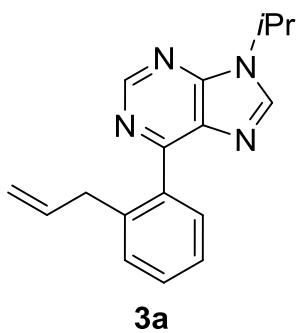
2-allyl-N-methoxy-N-methylbenzamide (7): a colorless oil (26.8 mg, 44%); IR (neat) ν 2975, 2934, 1651, 1378, 988 cm^{-1} ; 1H NMR ($CDCl_3$, 400 MHz, 50 °C) δ 3.26 (s, 3H), 3.44 (d, J = 6.5 Hz, 2H), 3.52 (s, 3H), 5.04-5.11 (m, 1H), 5.94 (ddt, J = 16.8, 10.0, 6.5 Hz, 1H), 7.20-7.34 (m, 4H); ^{13}C NMR (CD_3CN , 100 MHz, 50 °C) δ 34.0 (brs), 38.2, 61.7, 116.7, 127.0, 127.6, 130.4, 130.6, 136.9, 138.1, 138.4, 170.9 (brs); HRMS (ESI): m/z calculated for $C_{12}H_{15}O_2NNa^+ [M+Na^+]$: 228.0995, found: 228.0997.



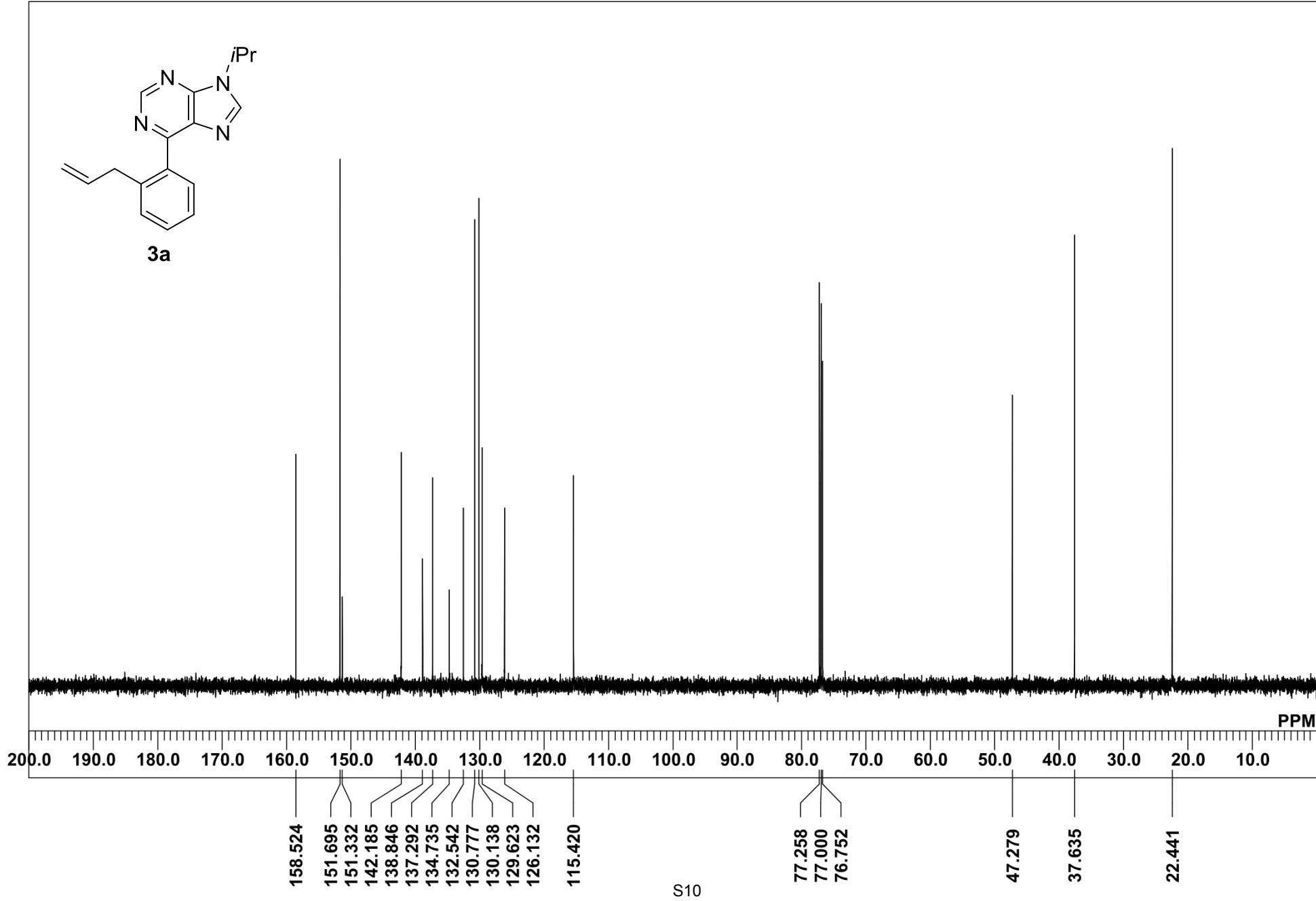


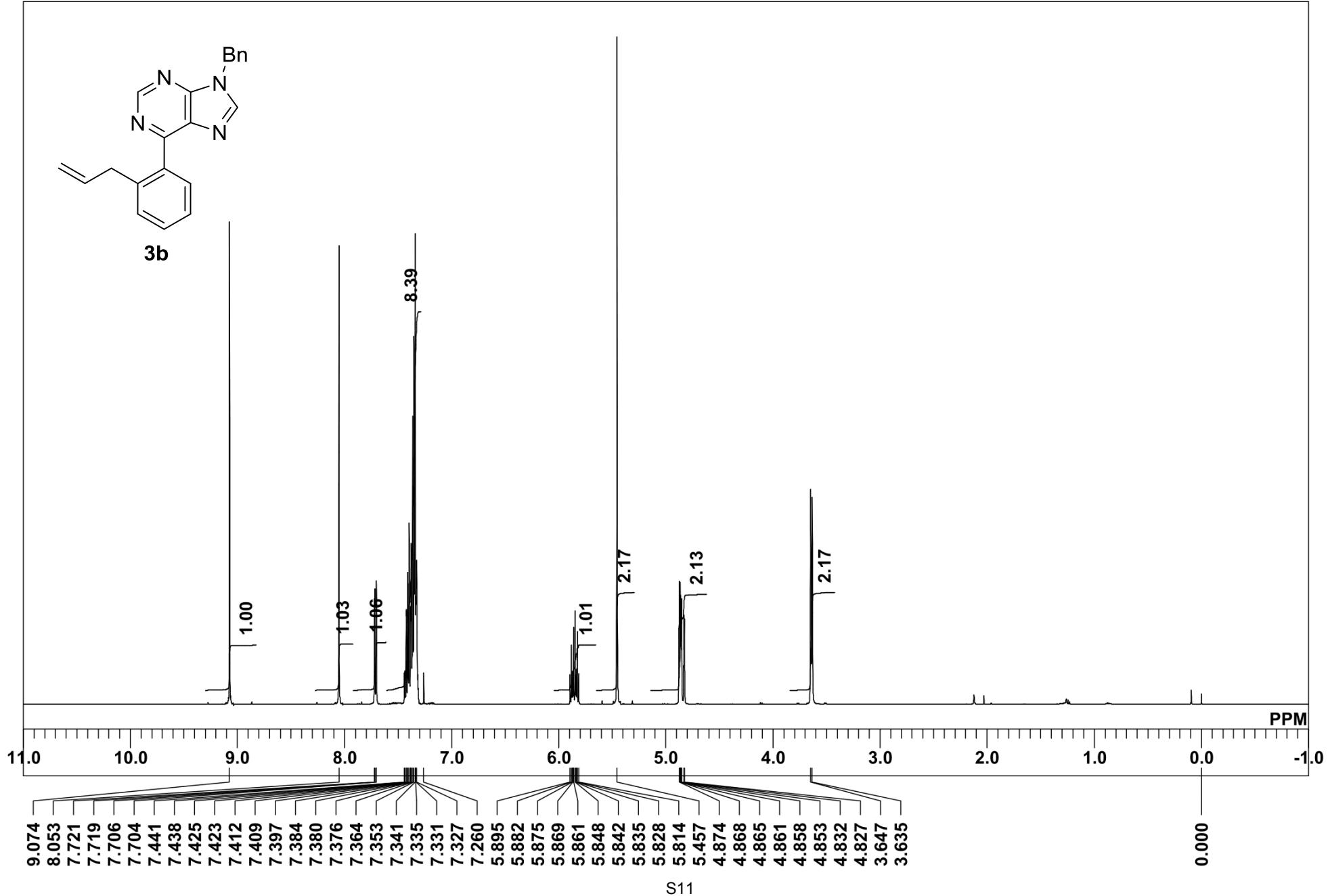
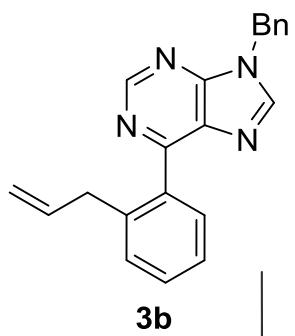
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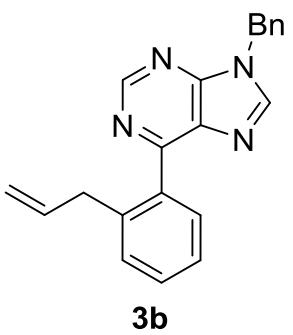




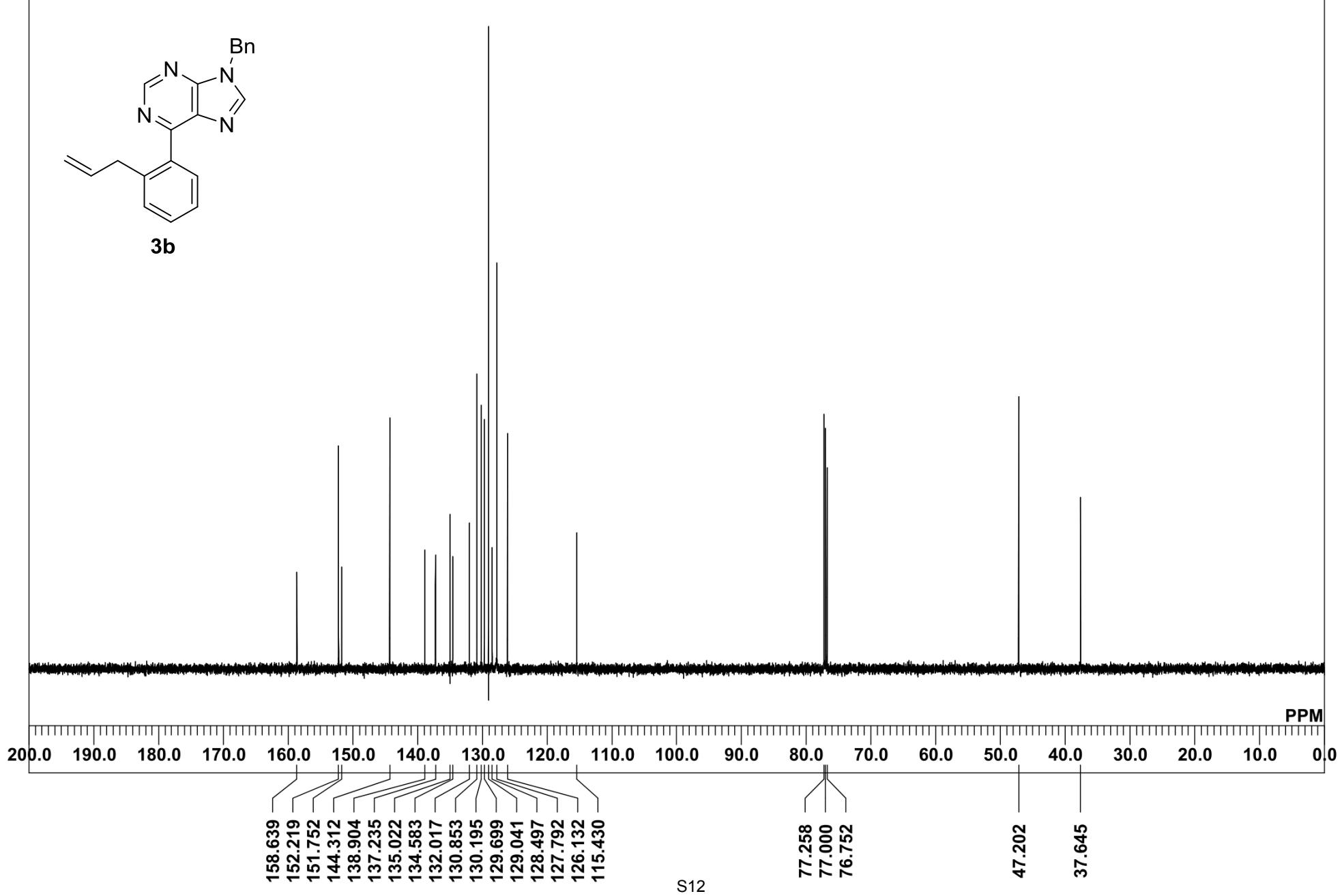
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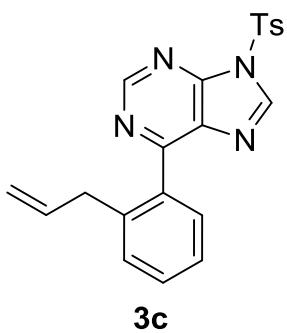




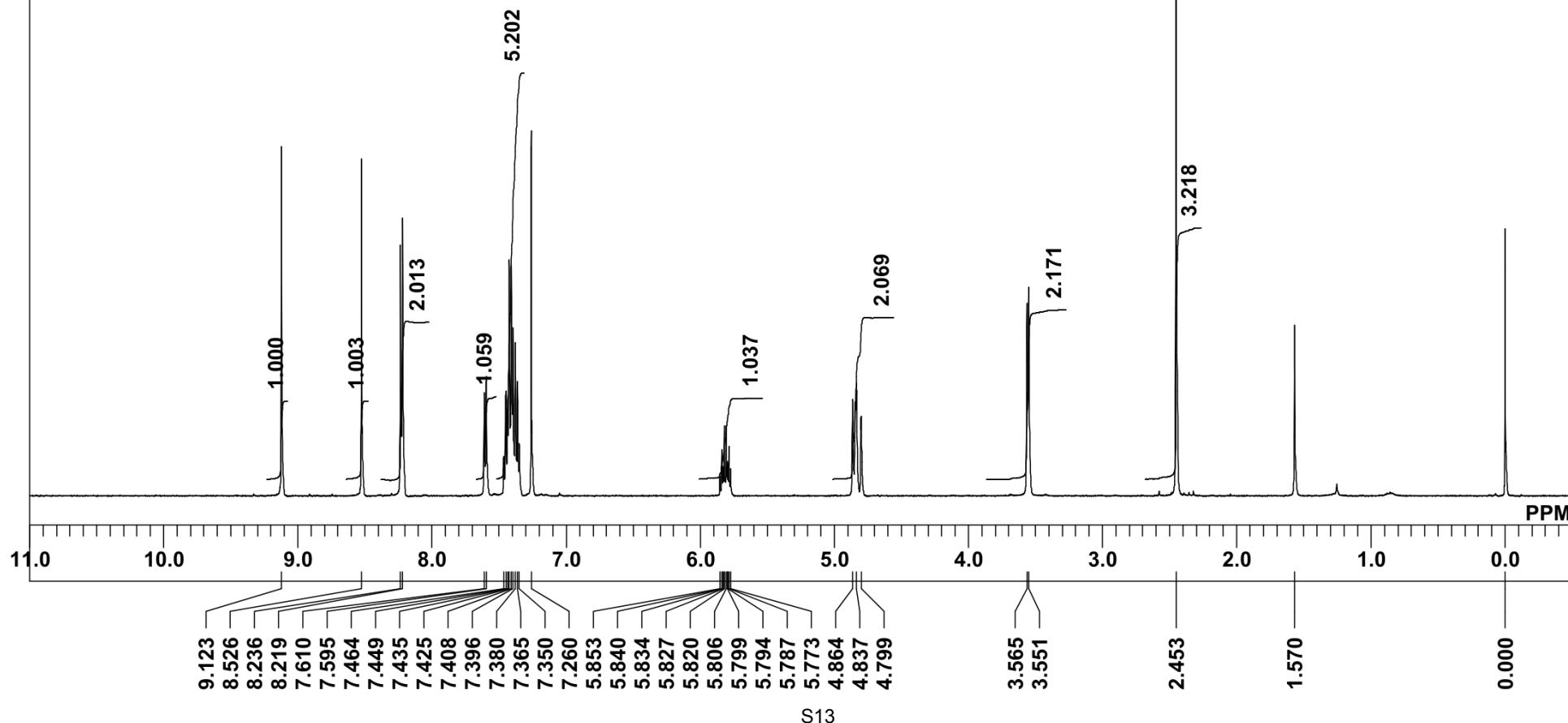


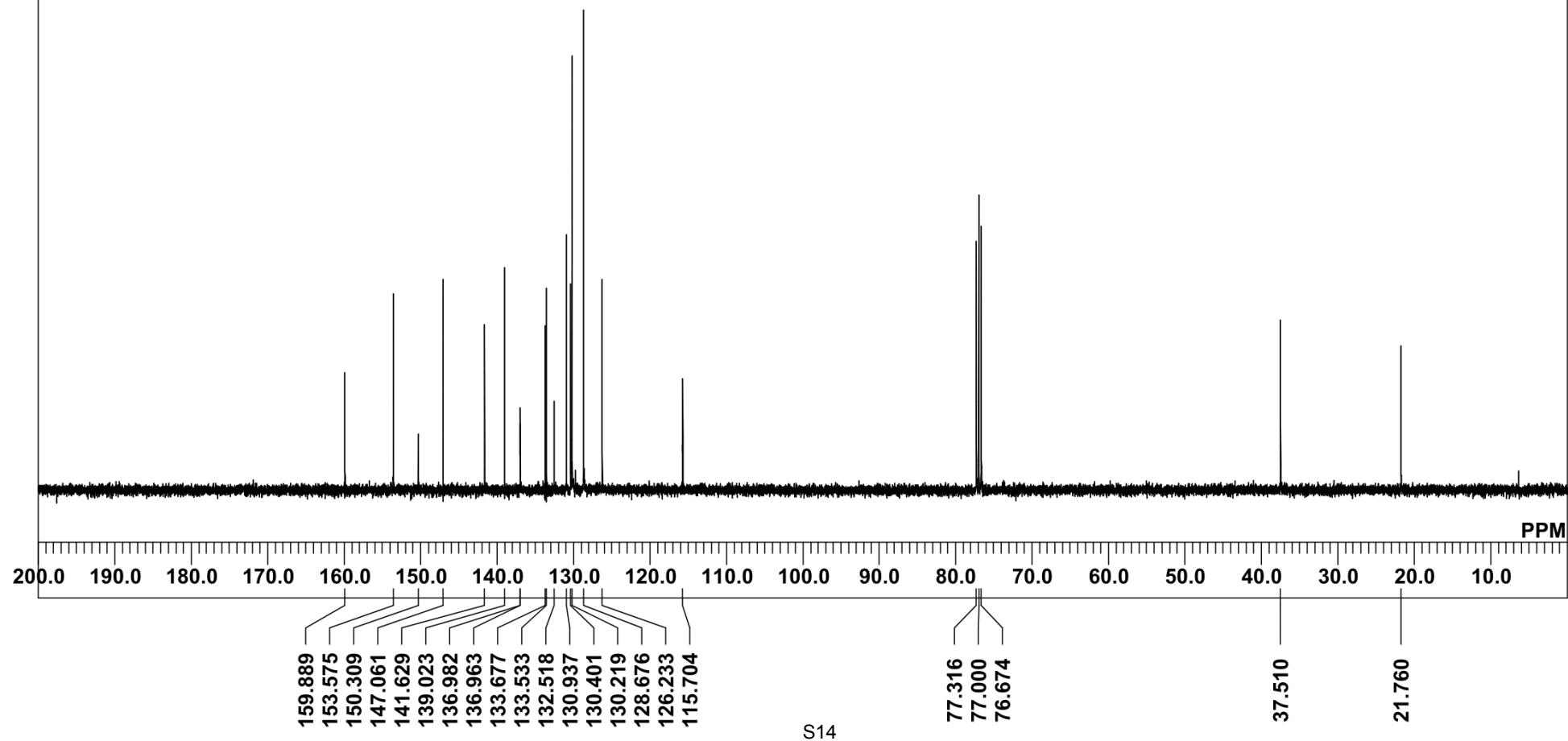
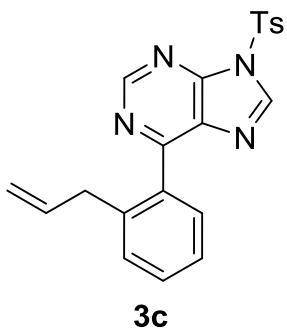
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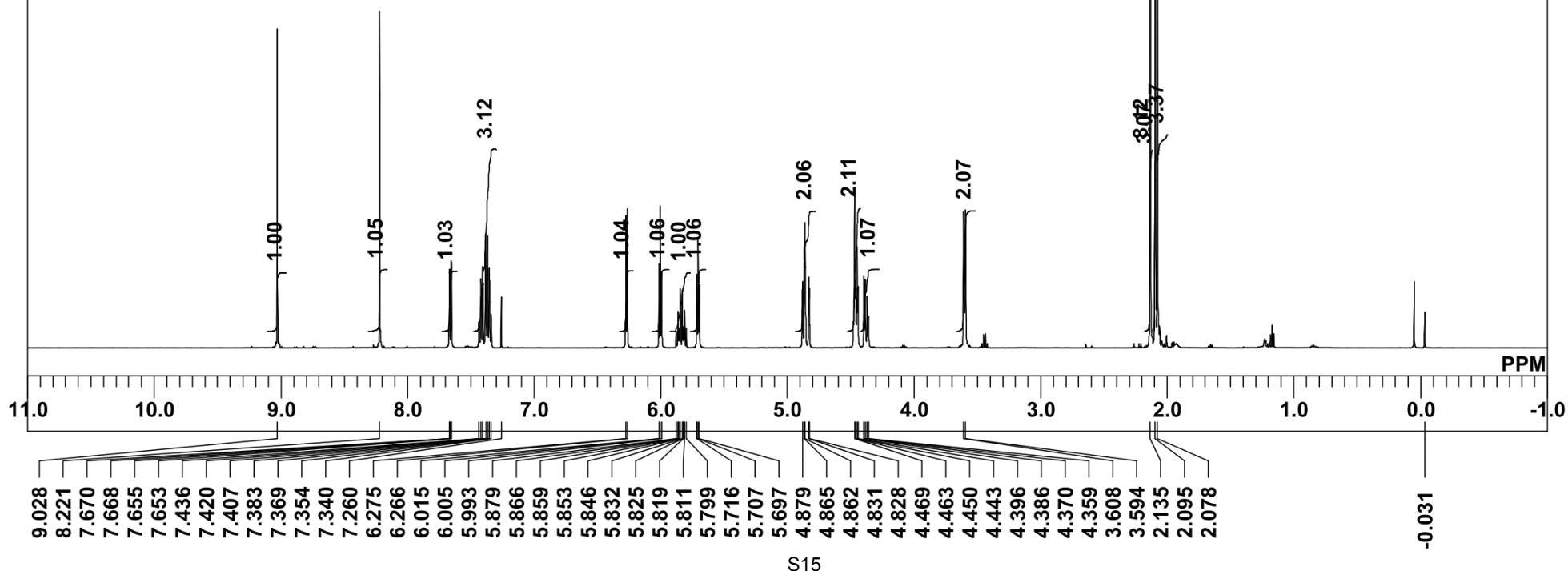
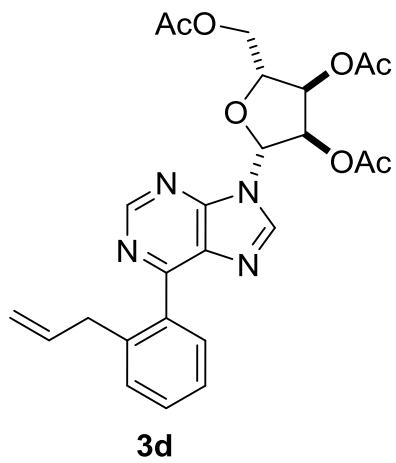


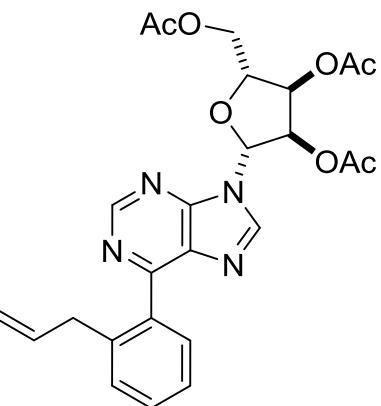
3c



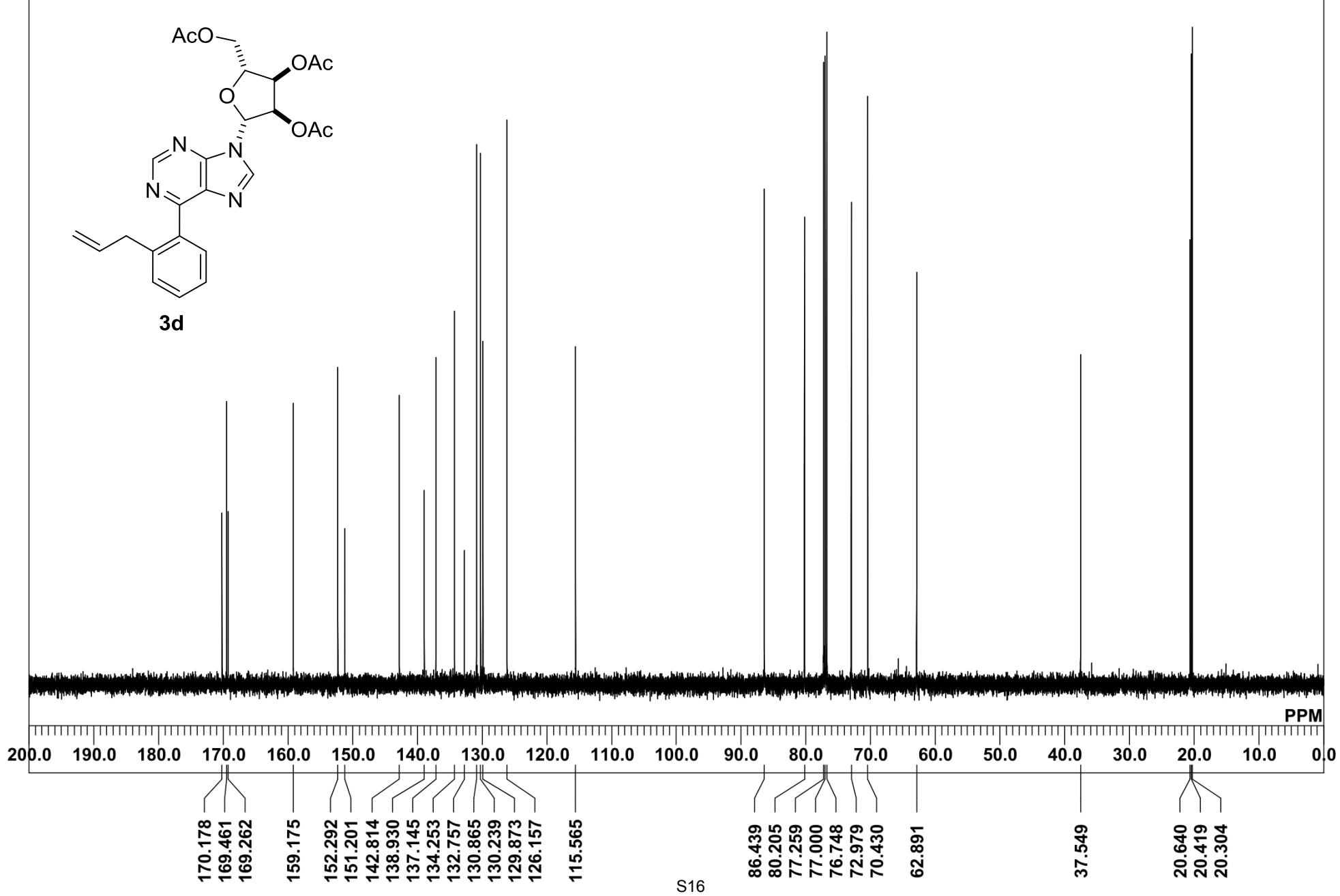


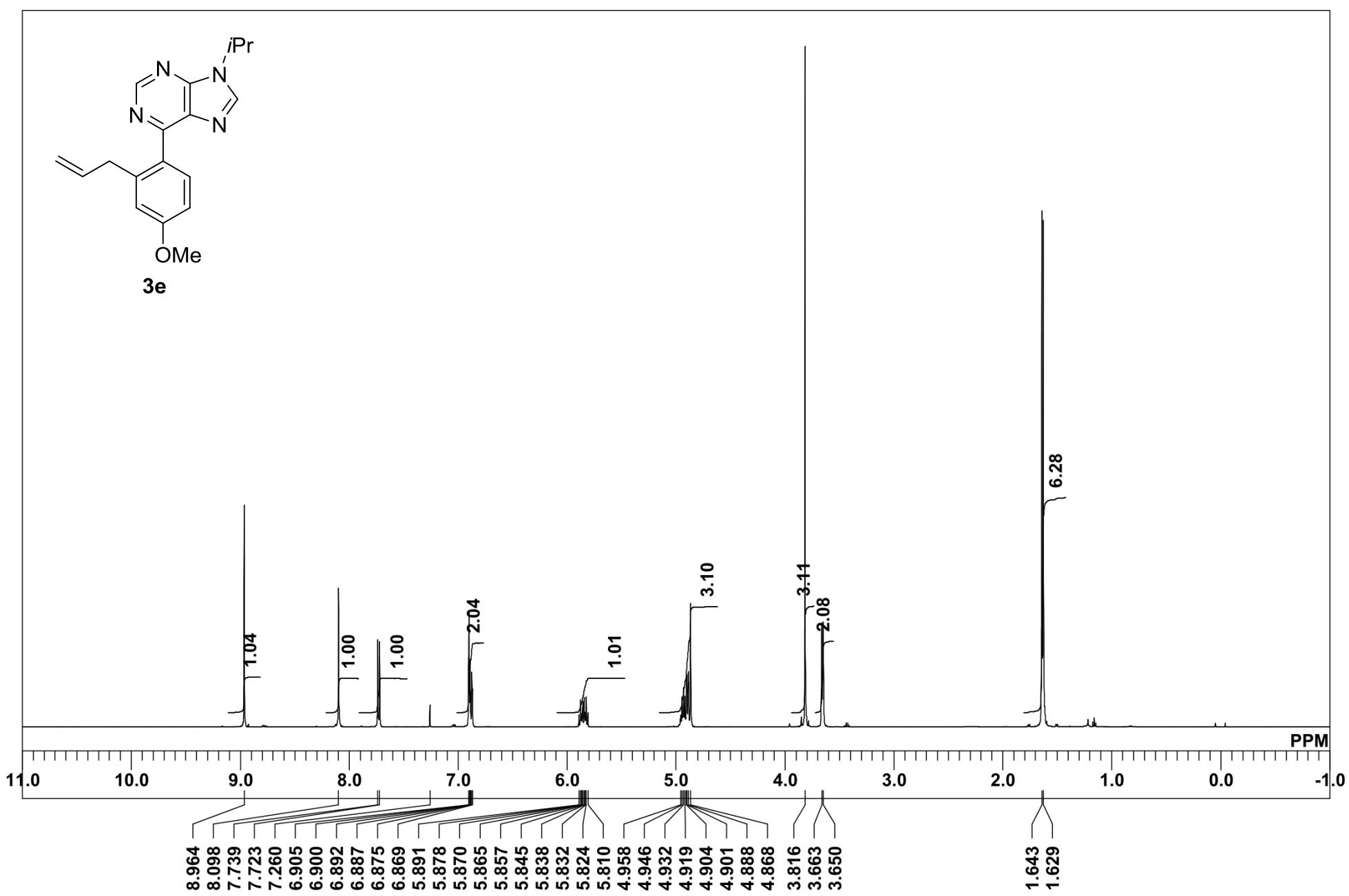
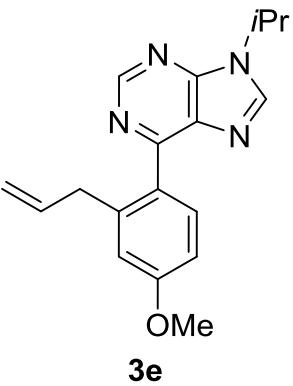
S14

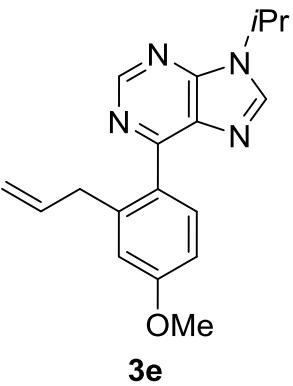




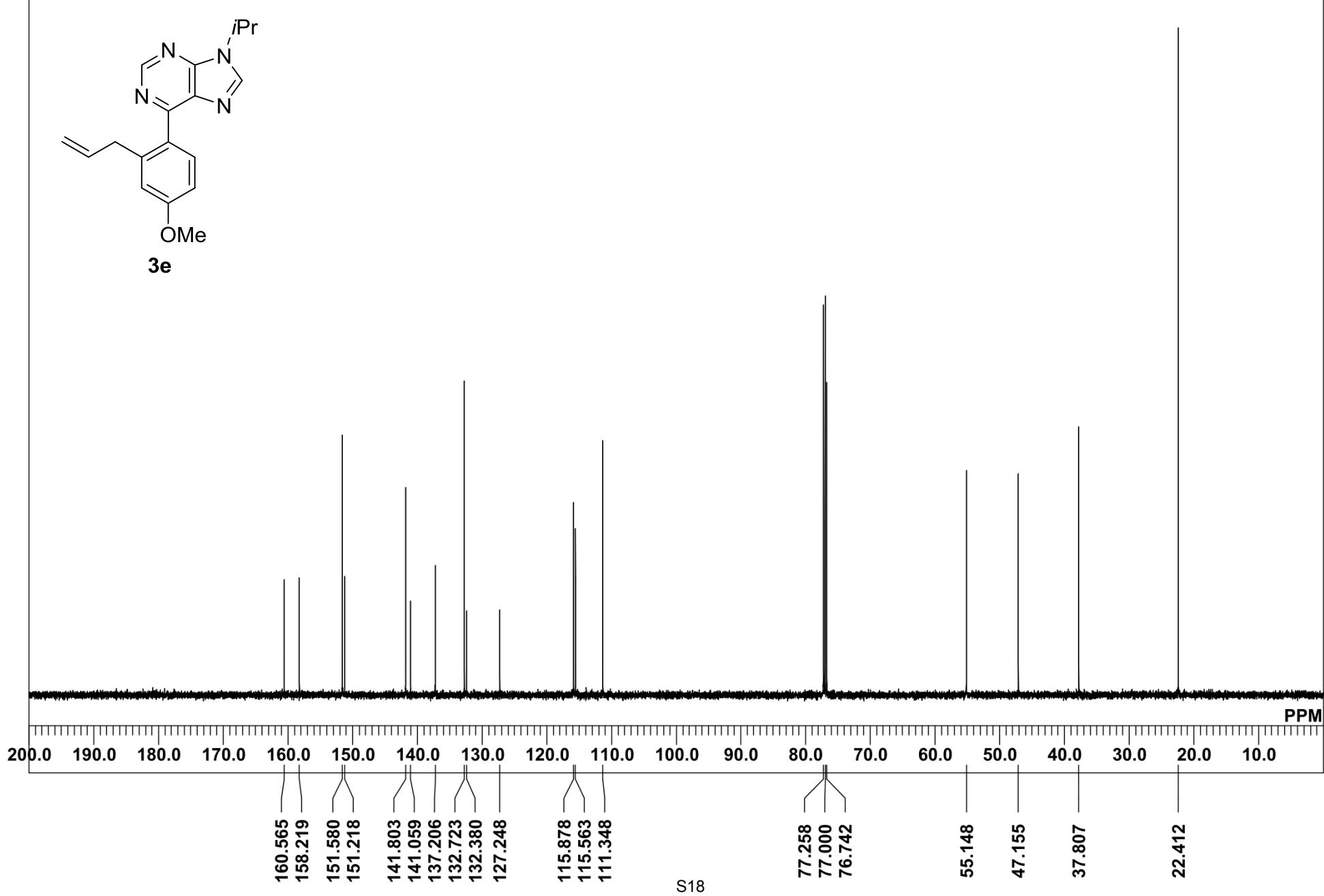
3d

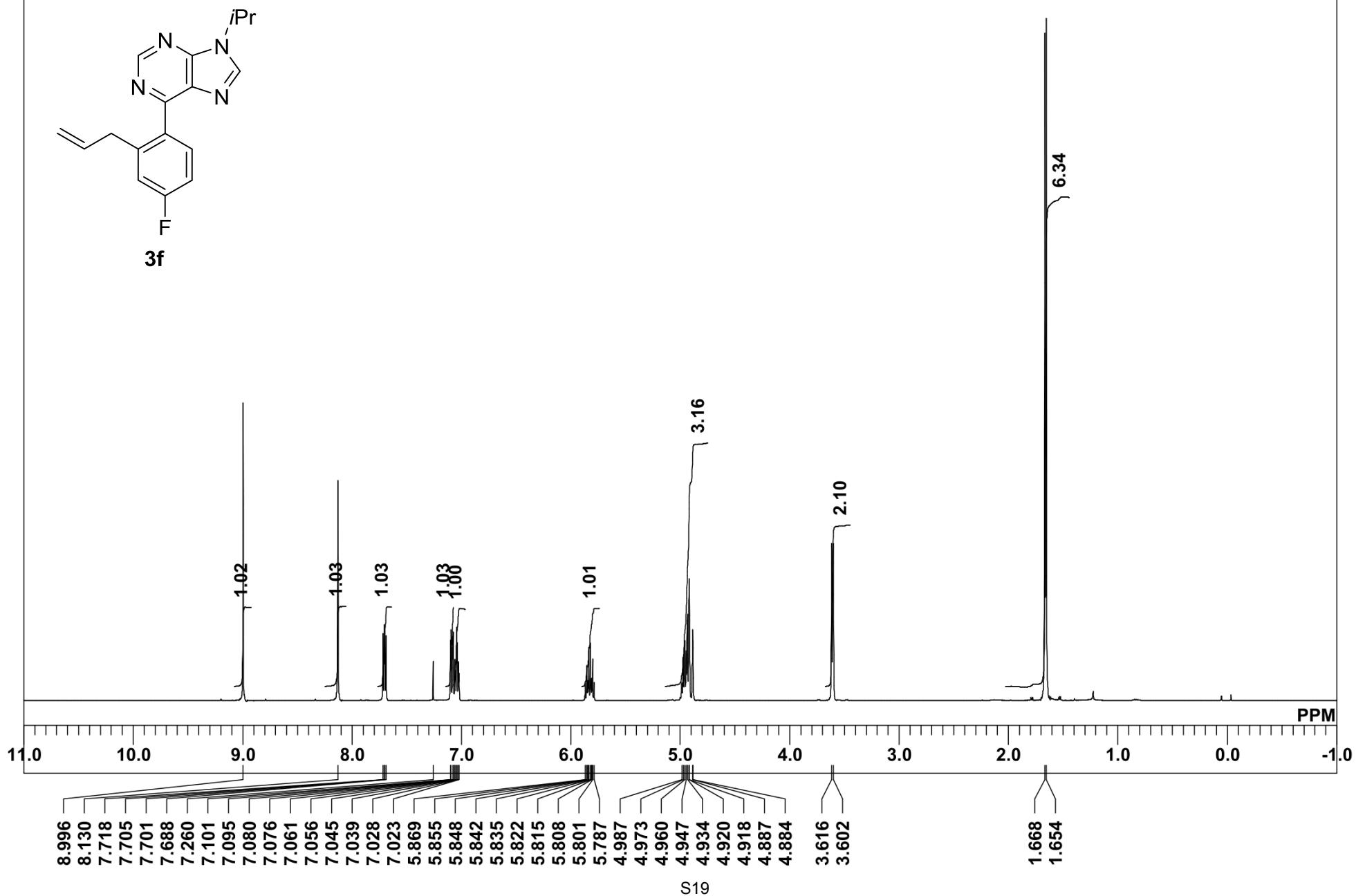
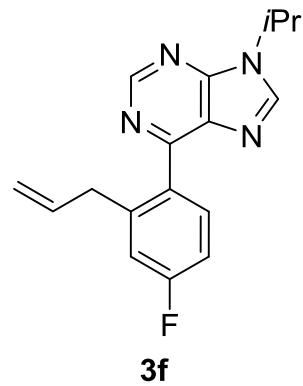


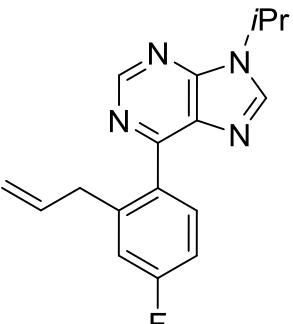




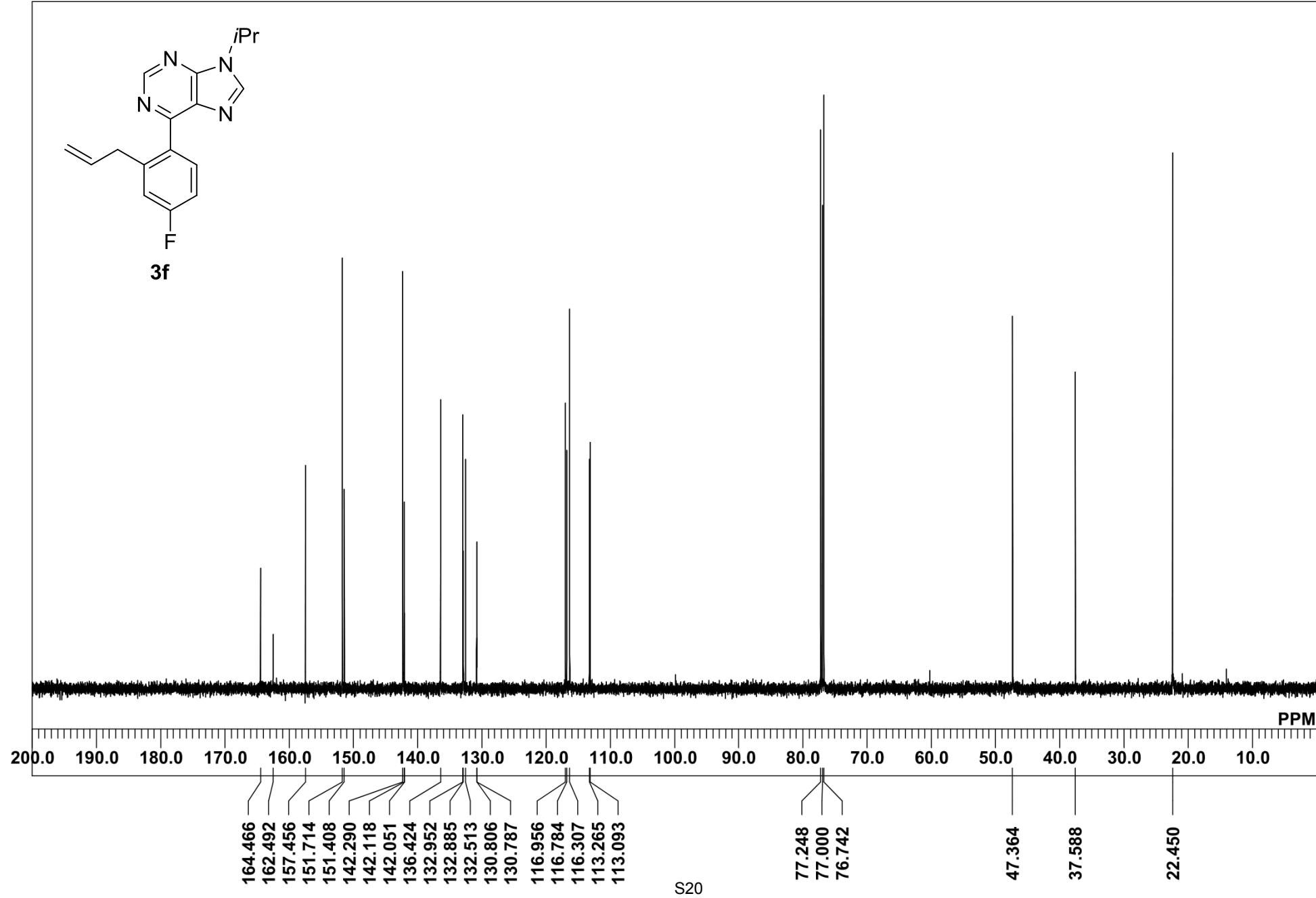
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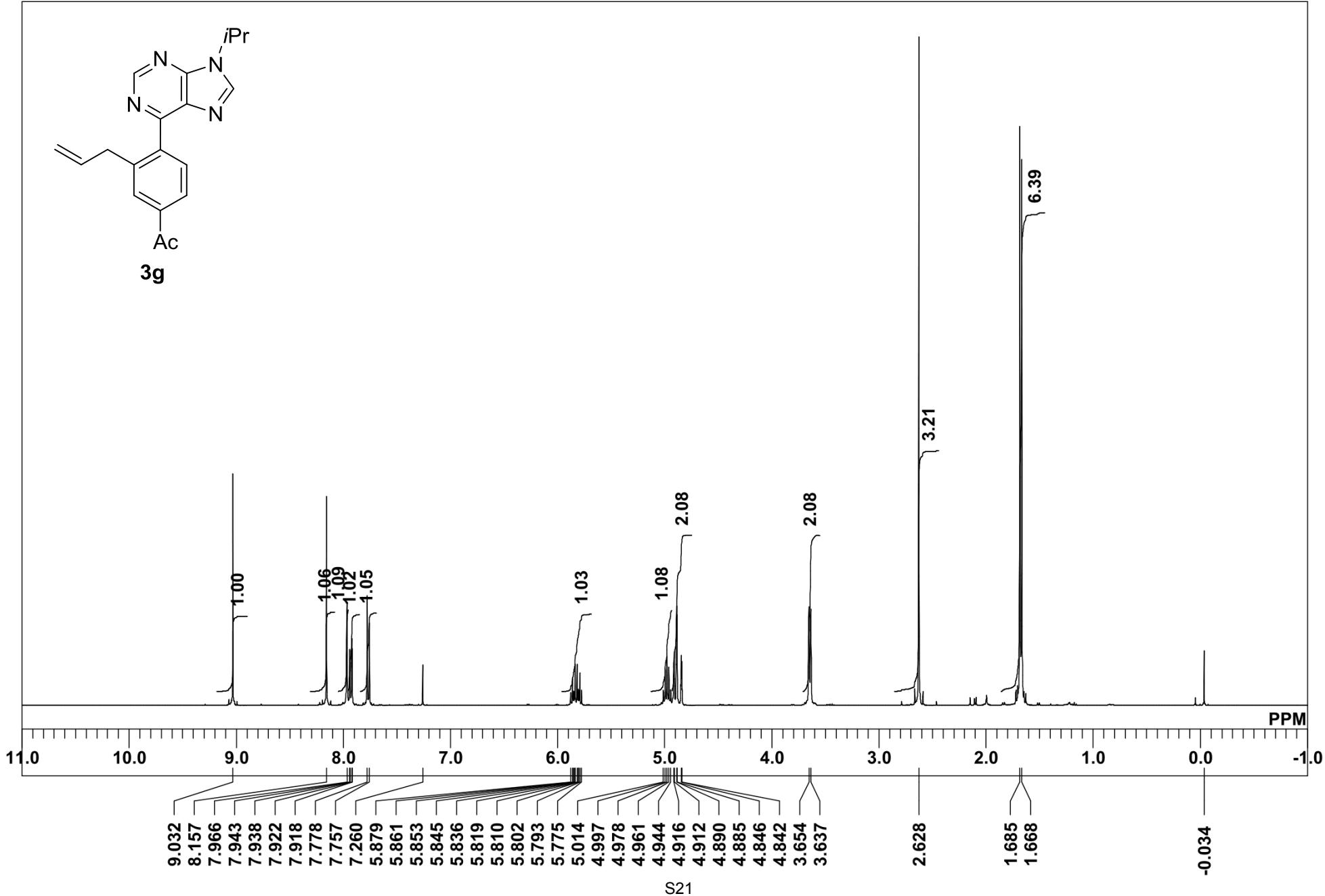
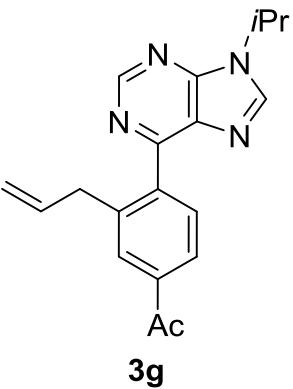


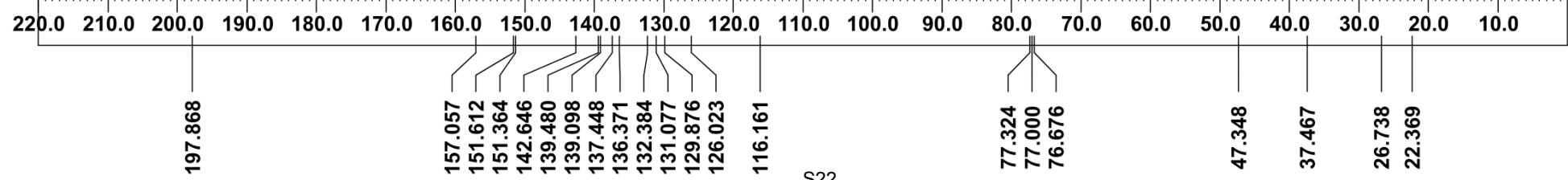
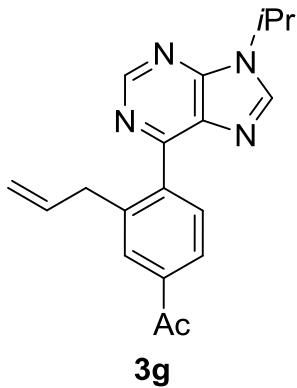




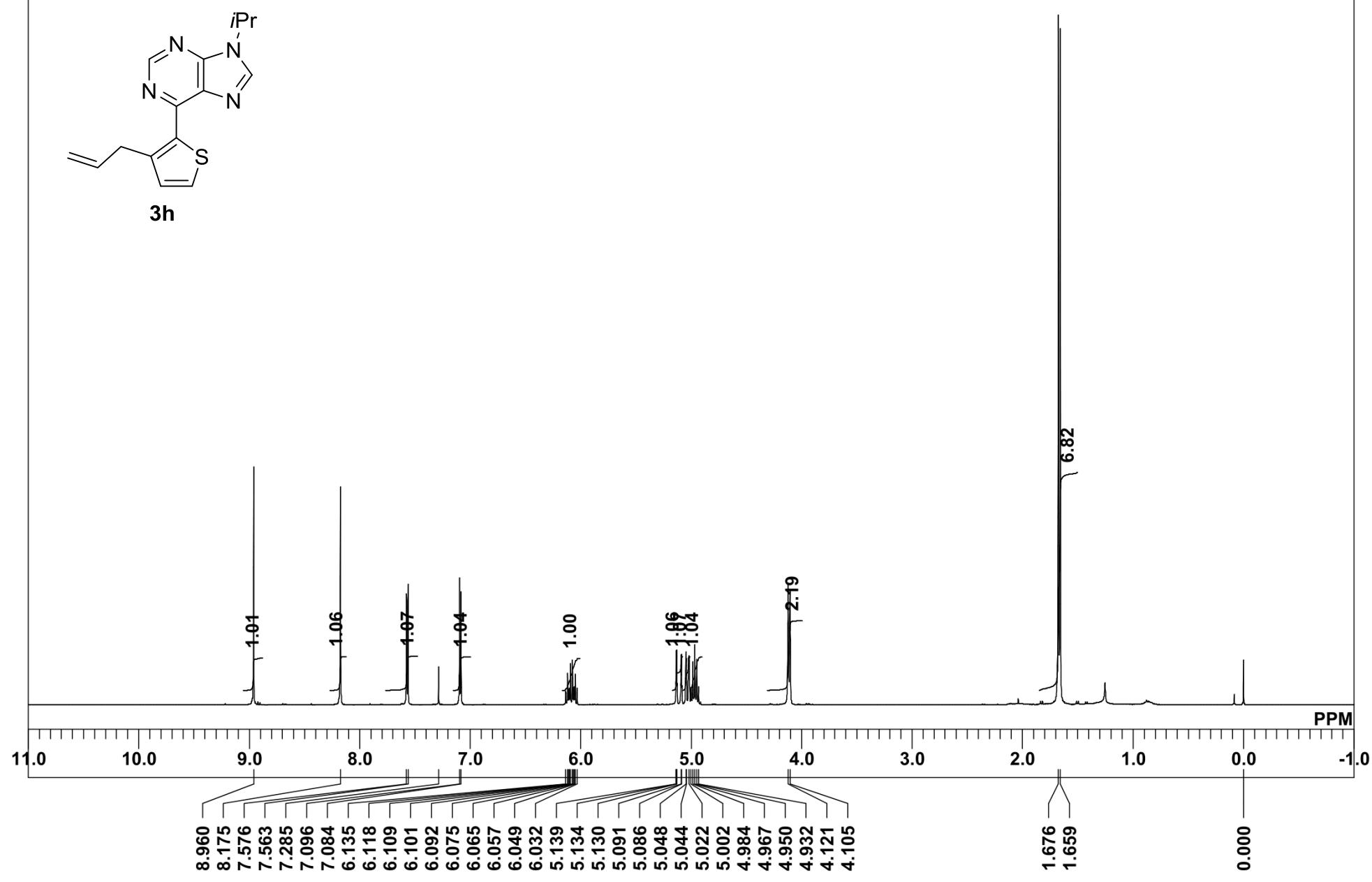
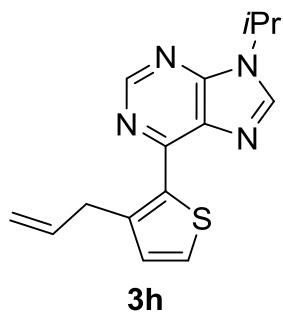
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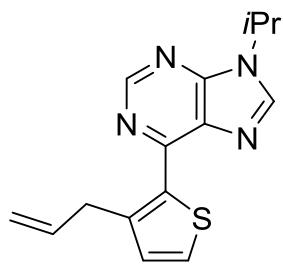




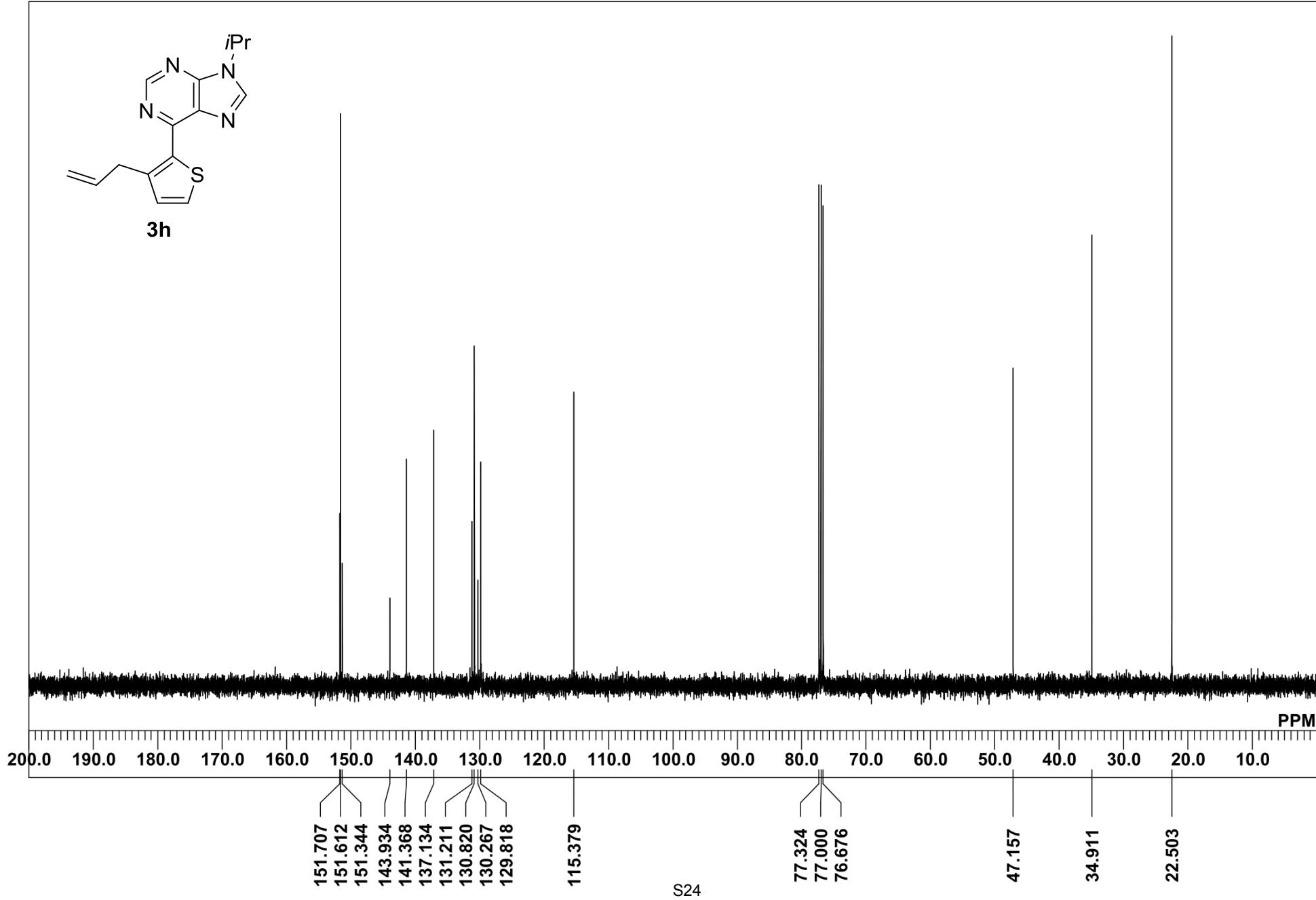


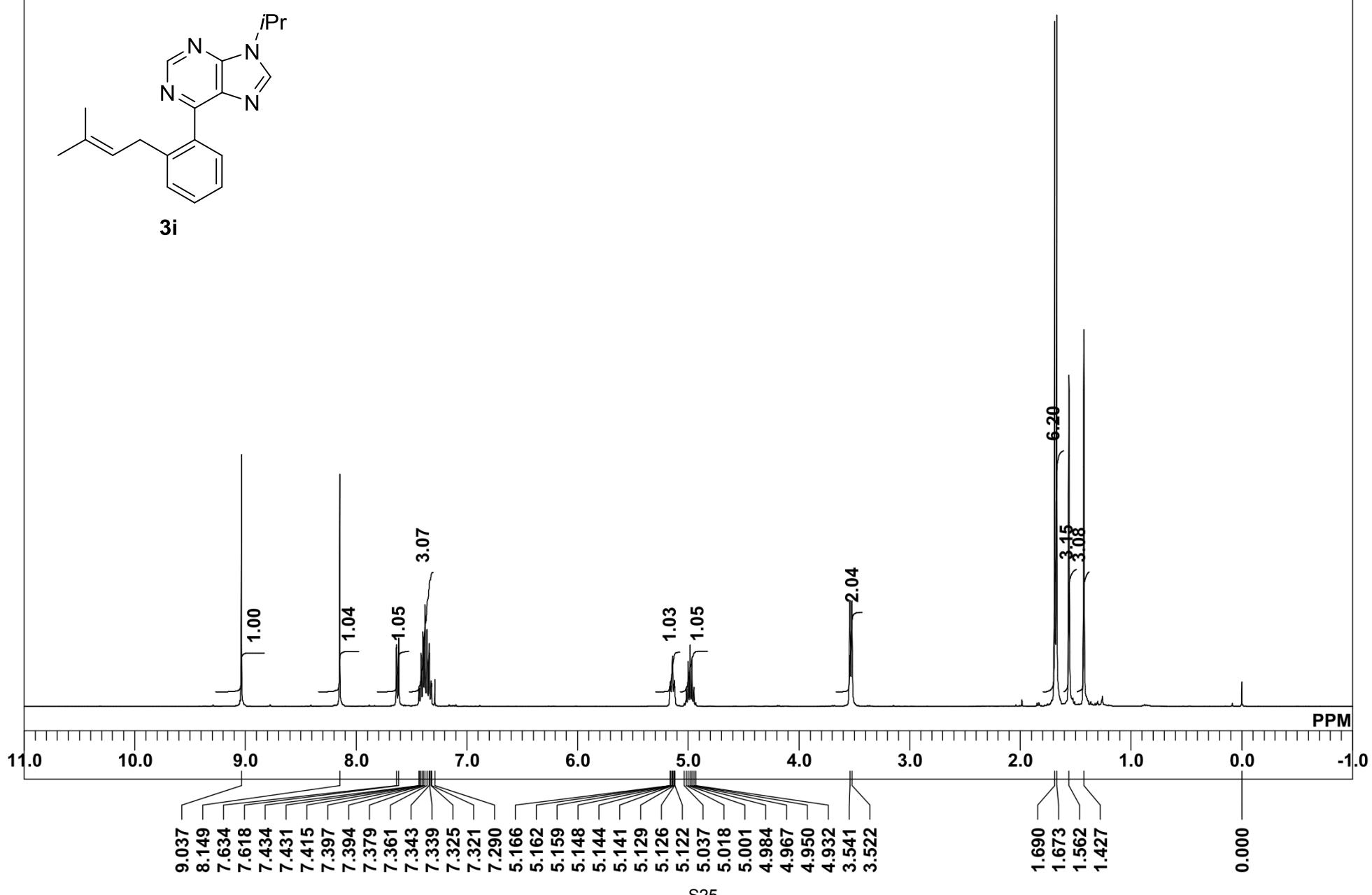
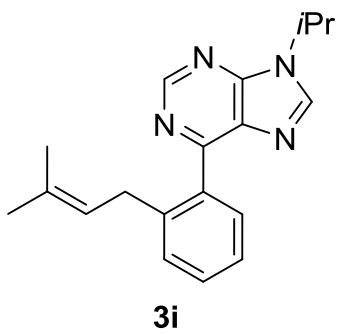
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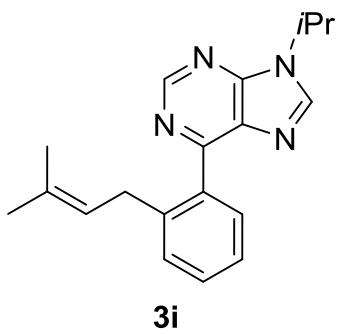




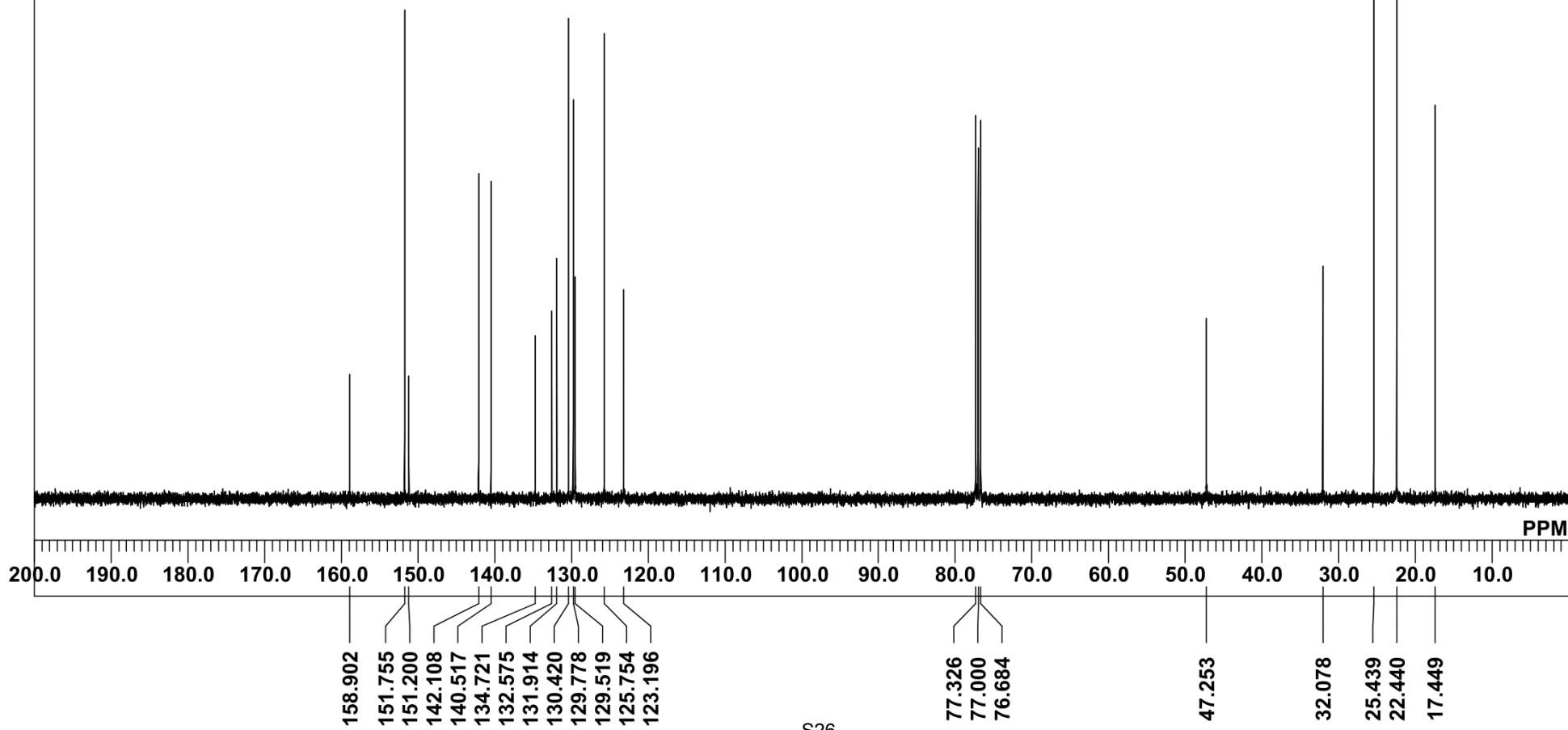
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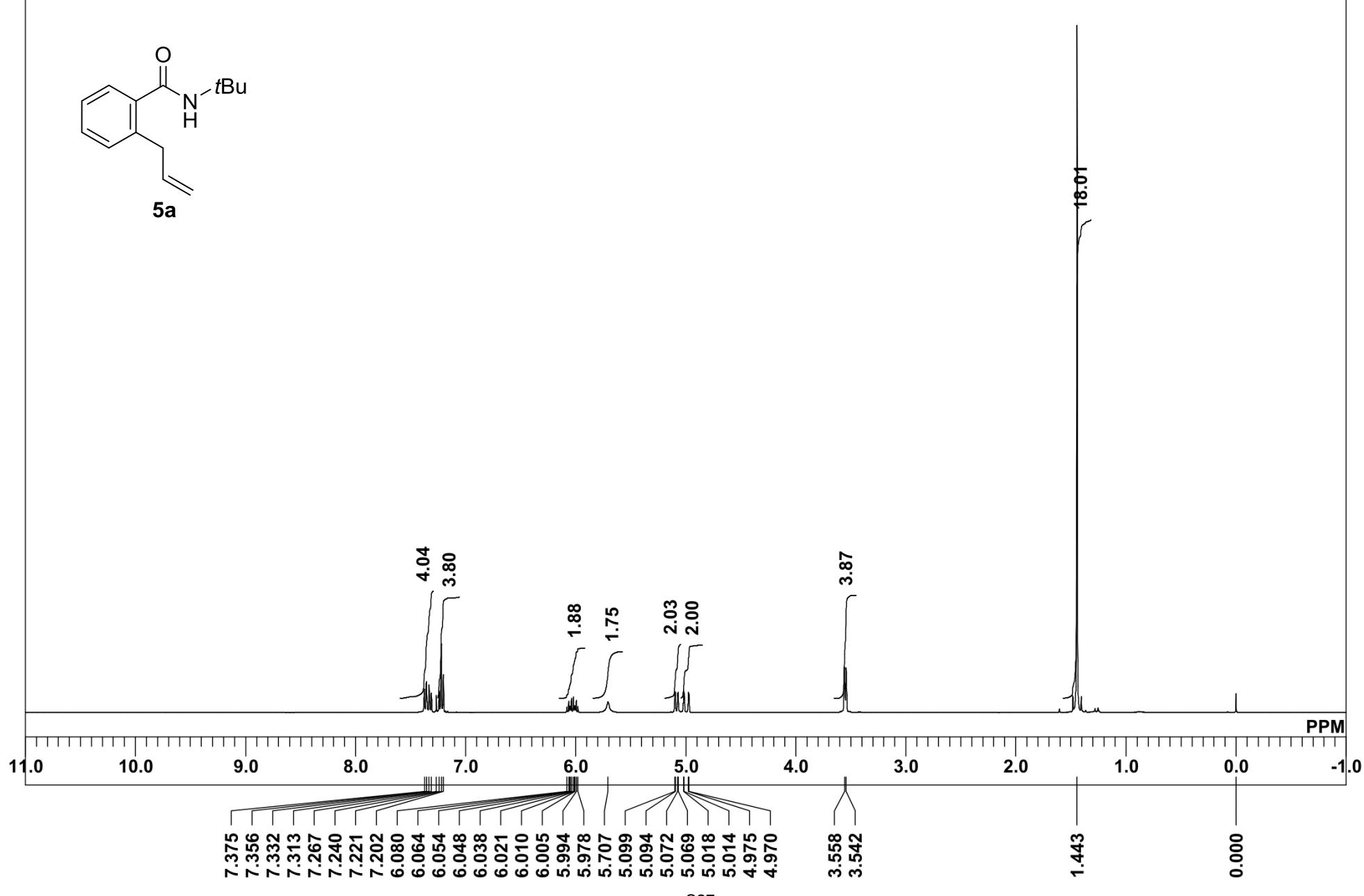
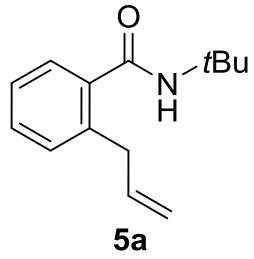


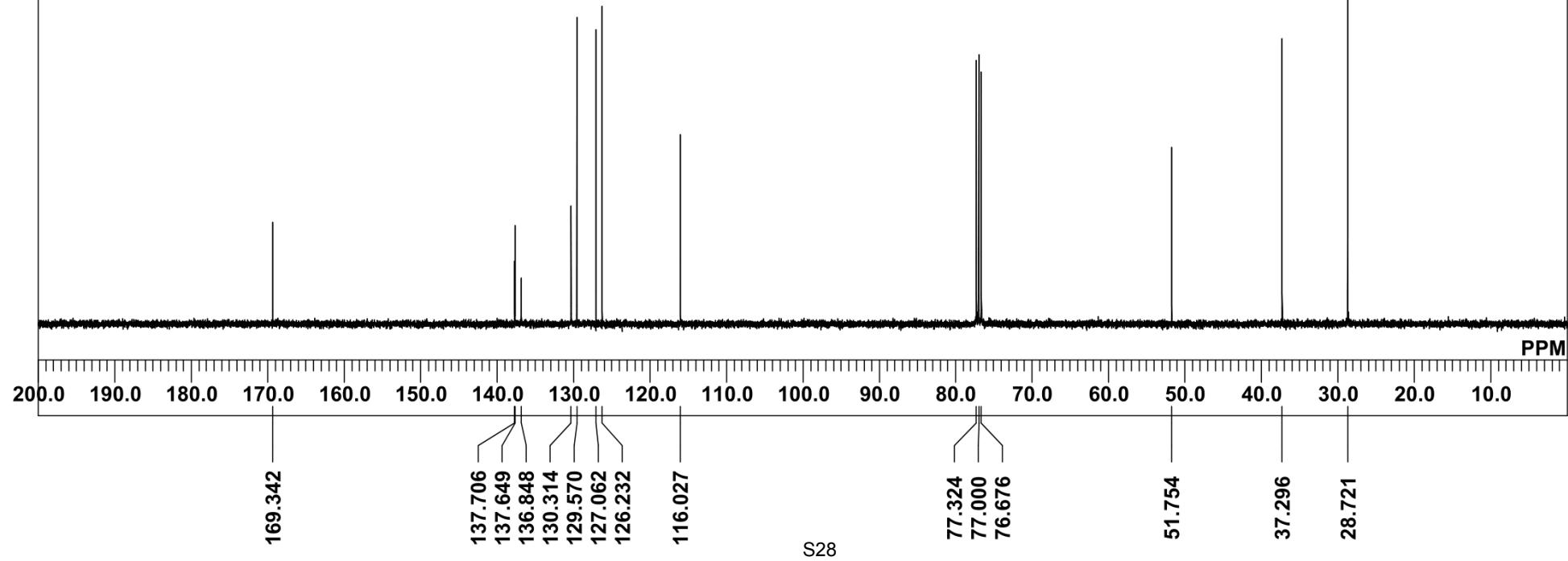
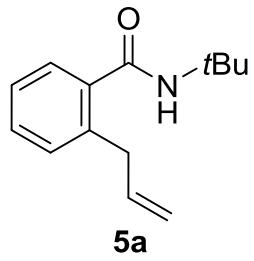




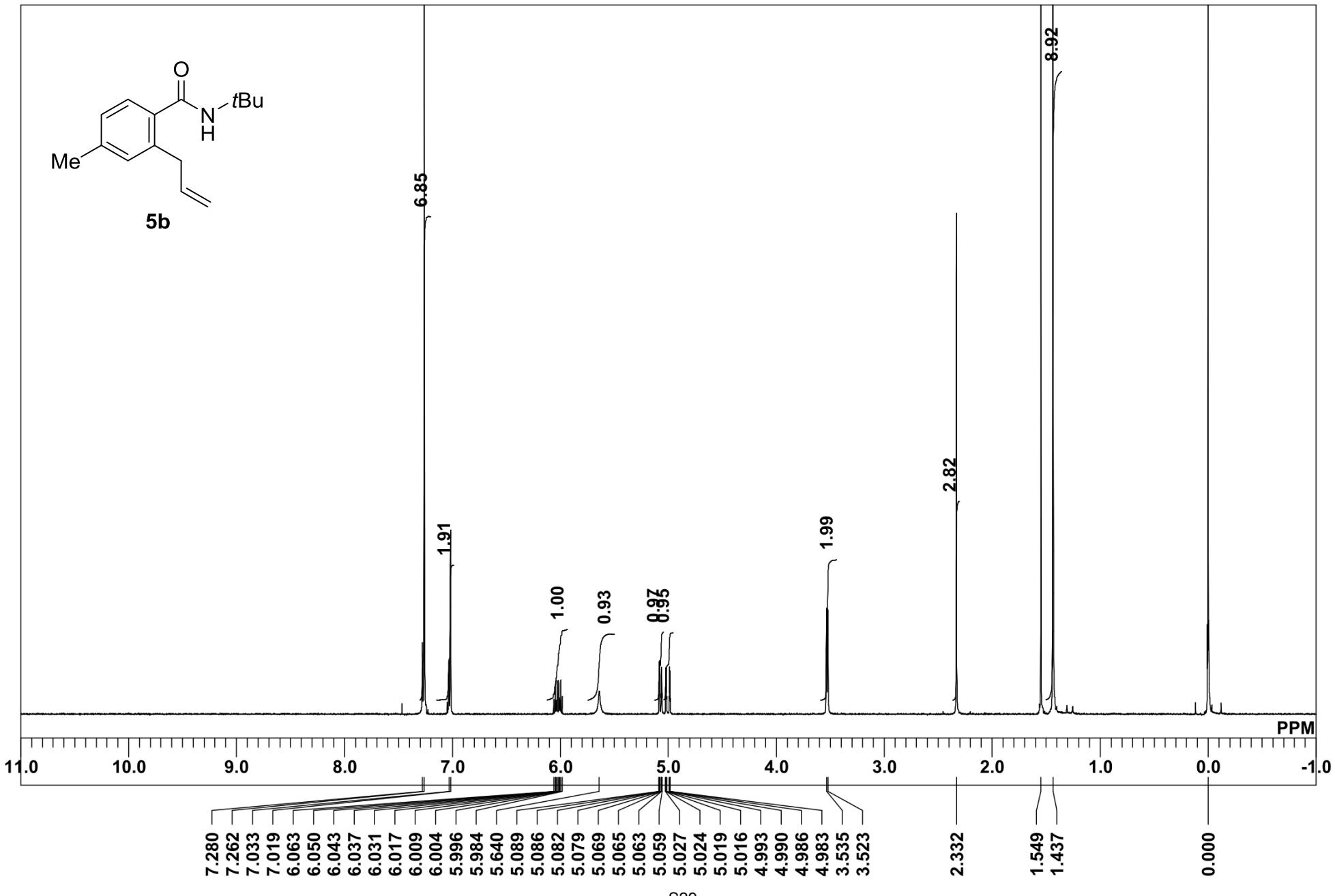
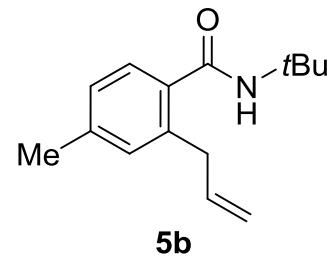
3i

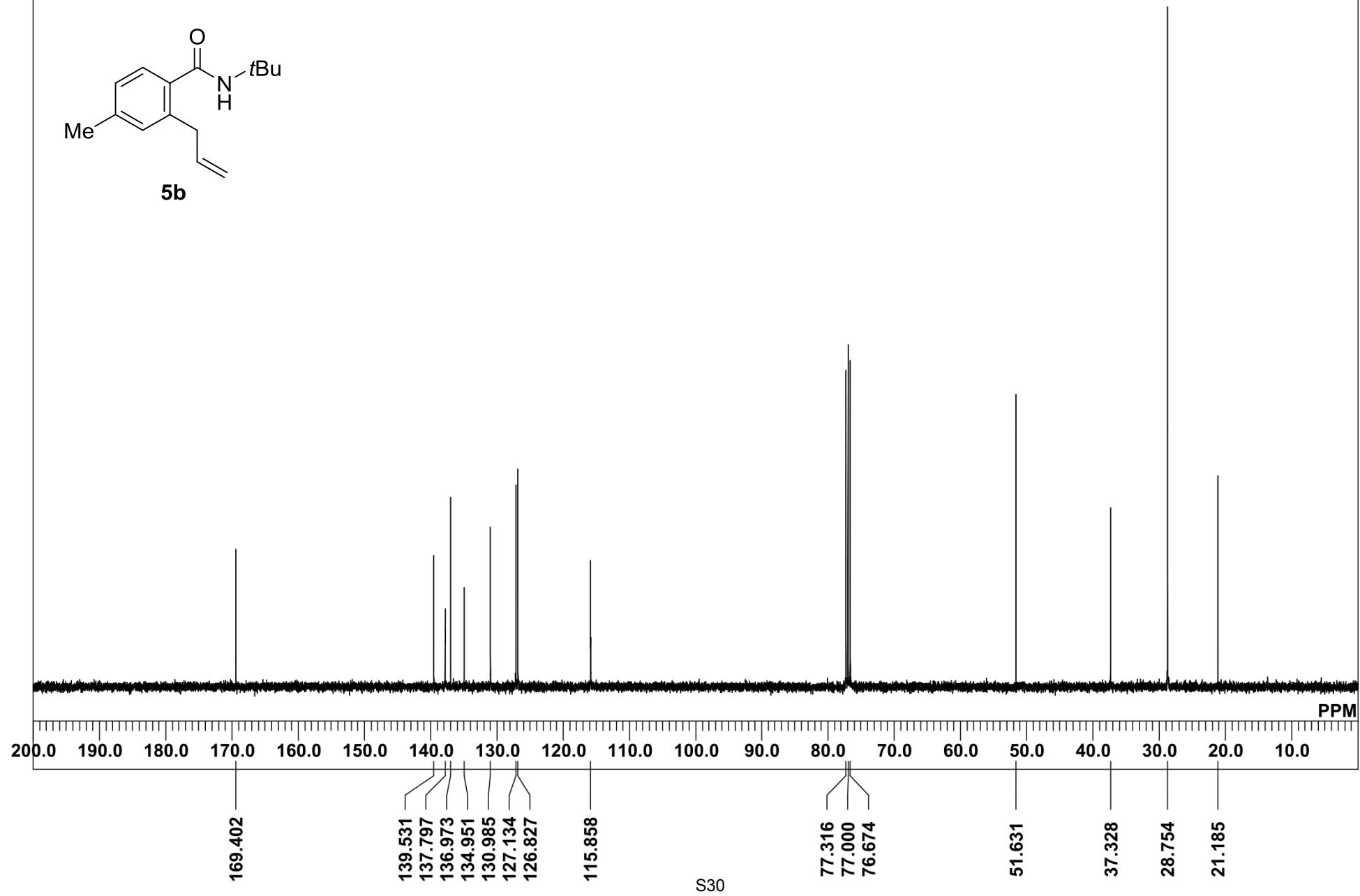
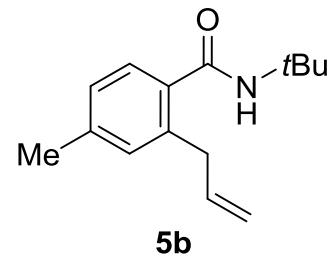


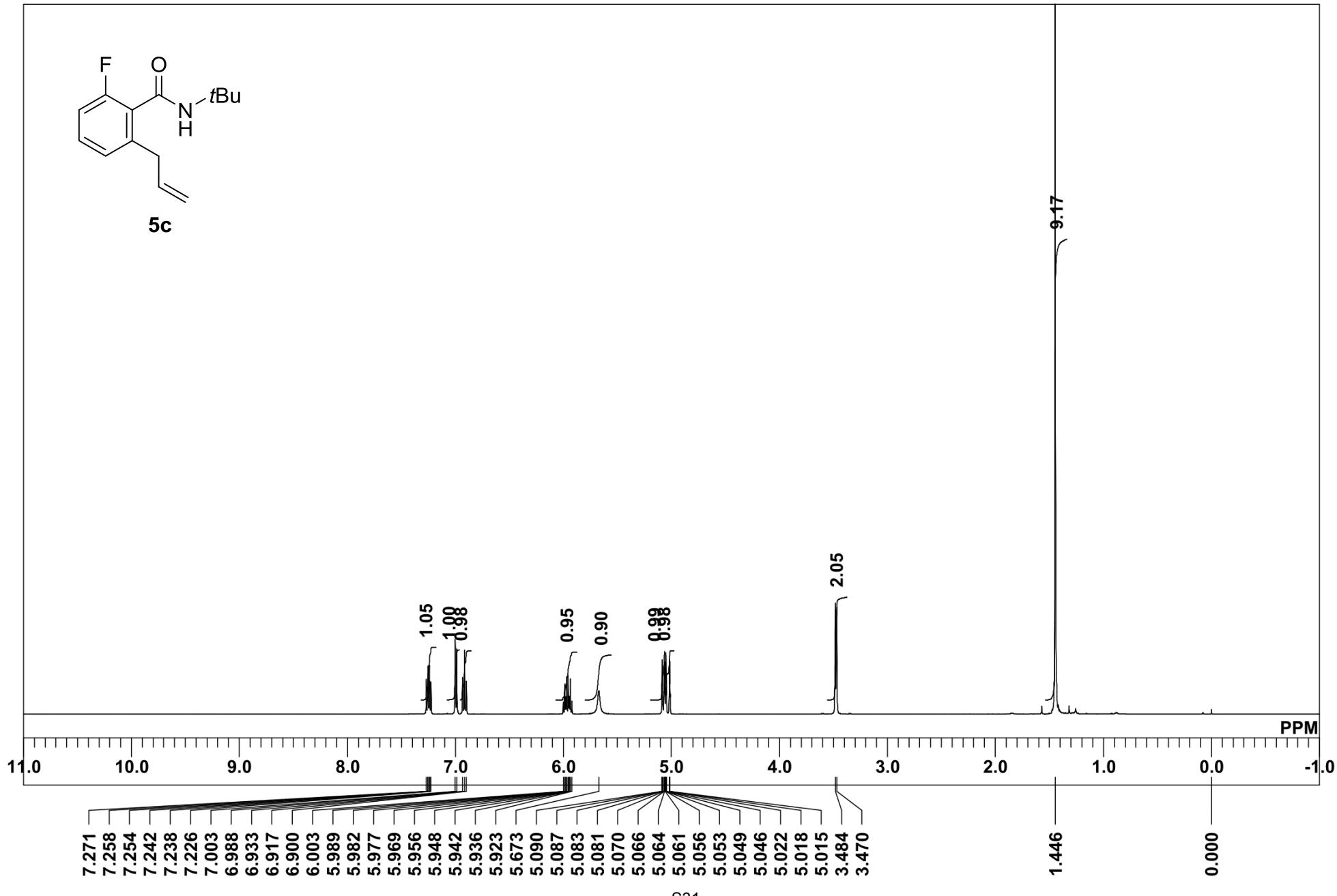
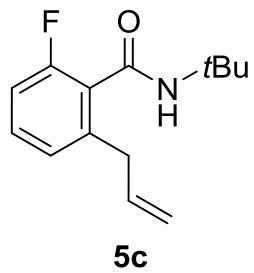


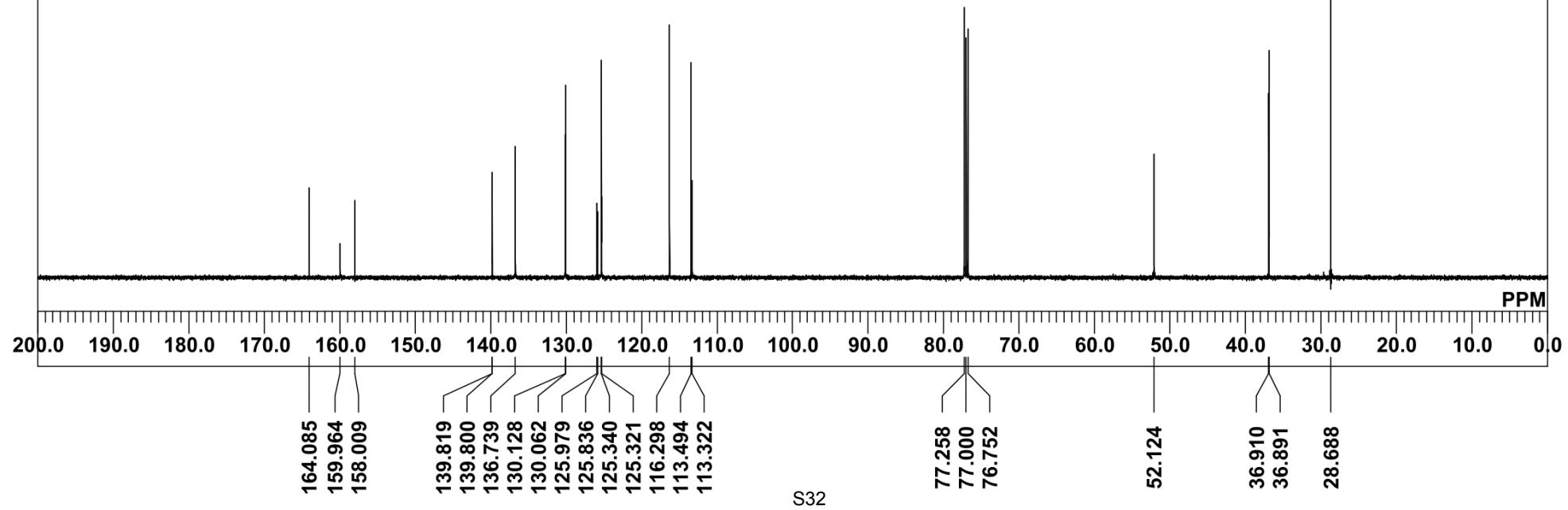
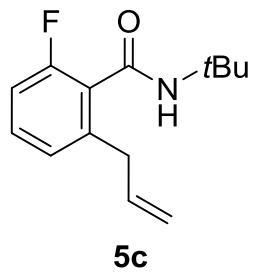


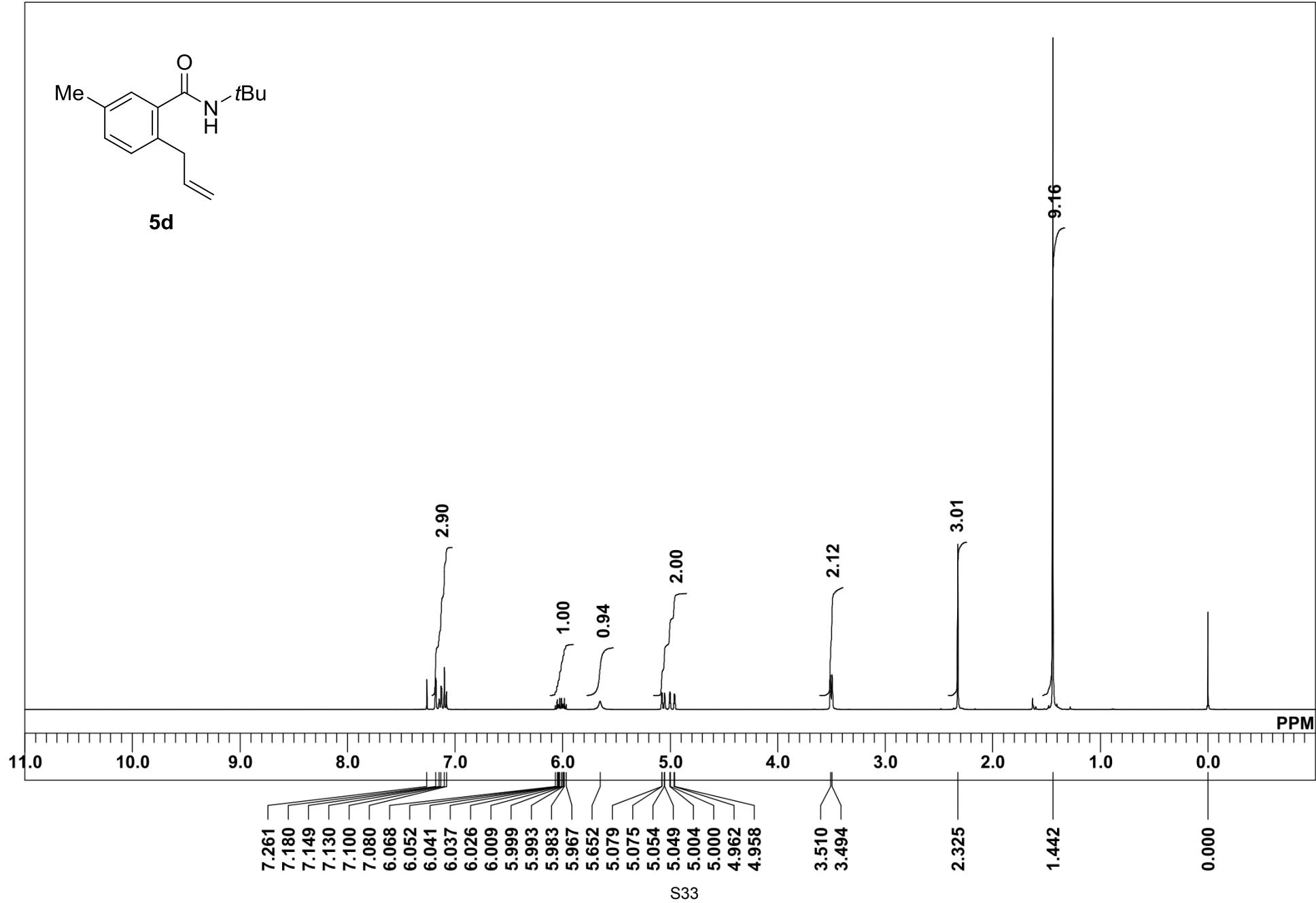
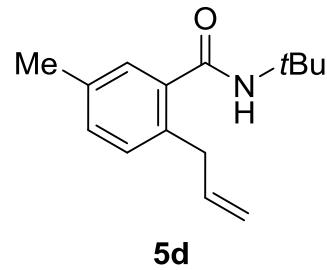
S28

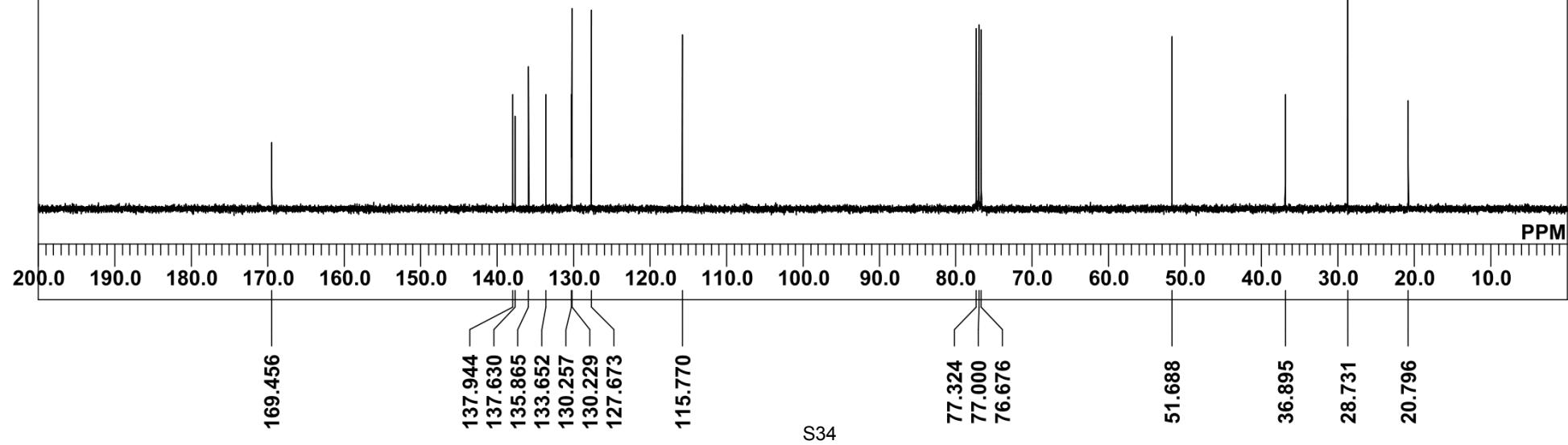
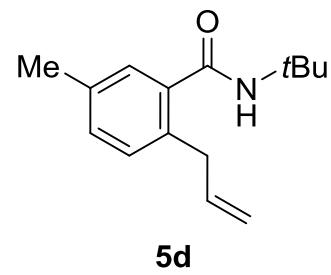


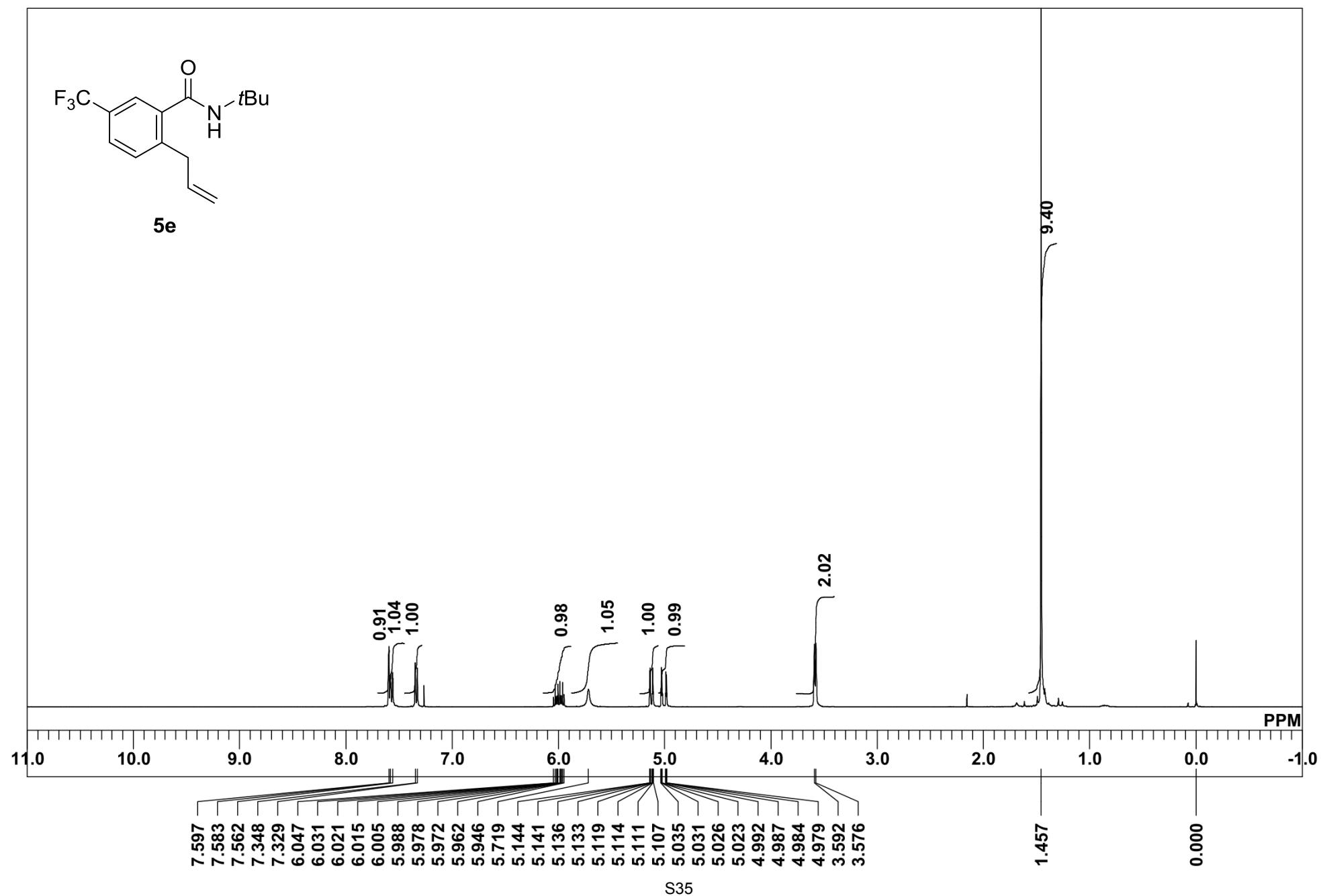
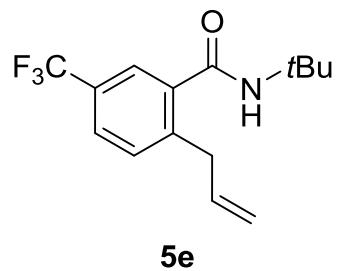


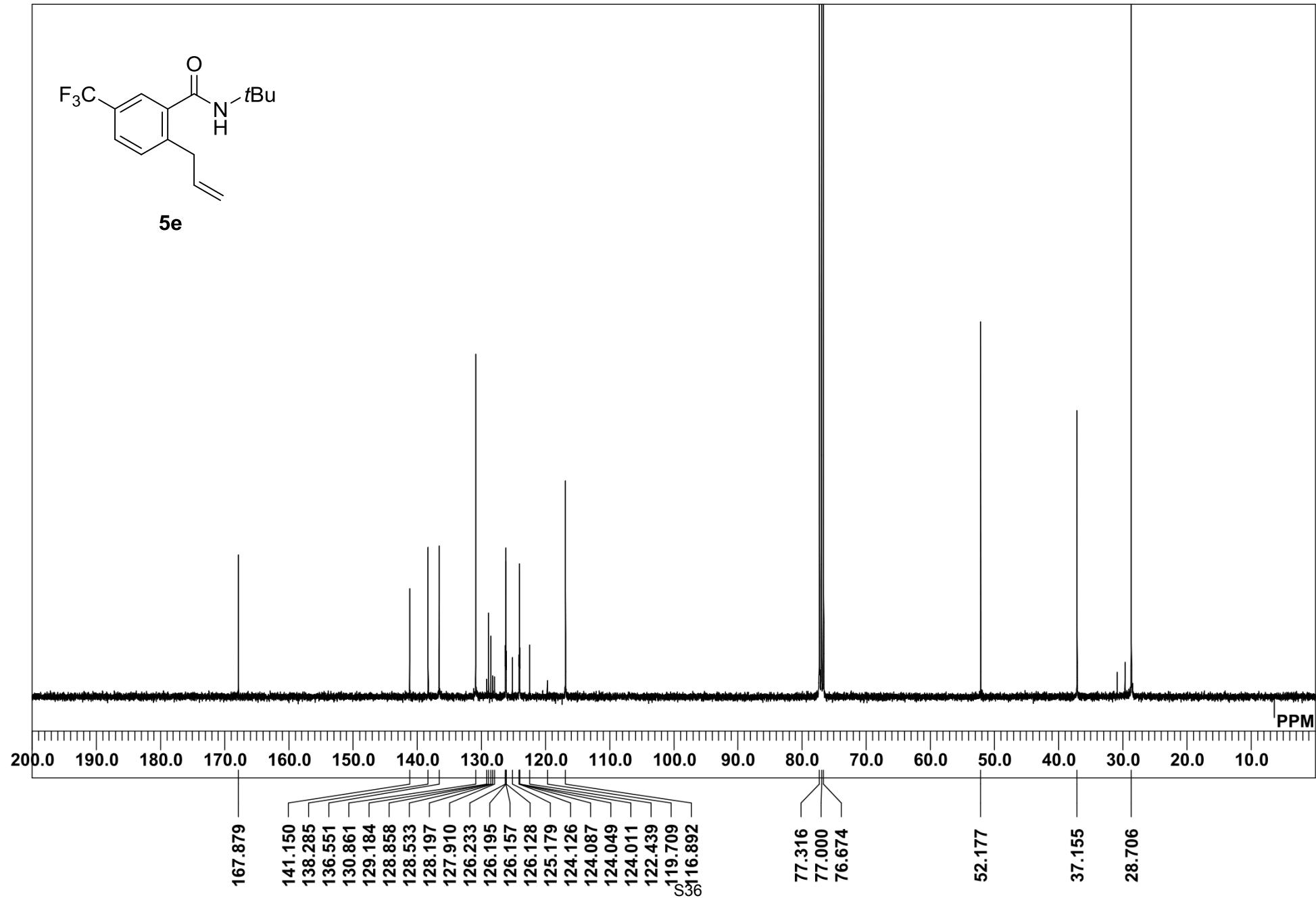
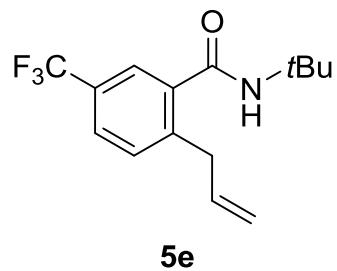


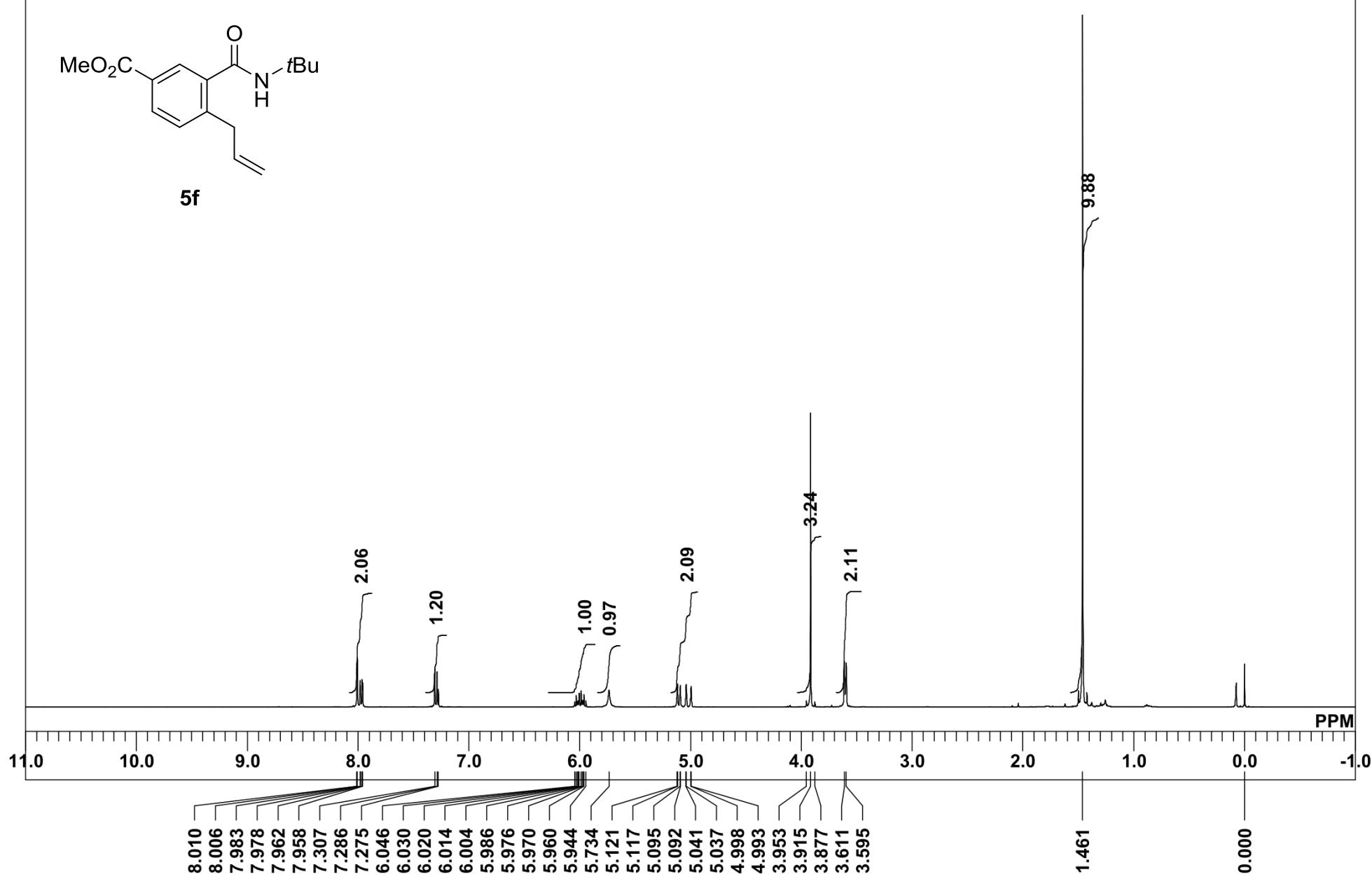
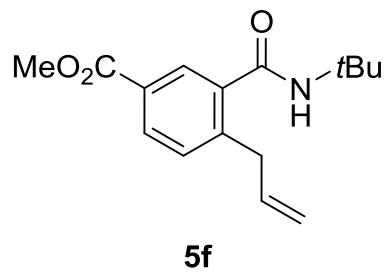


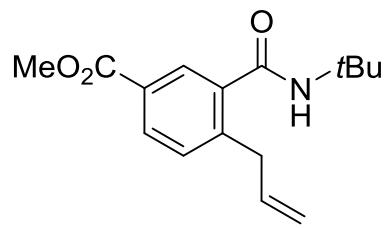




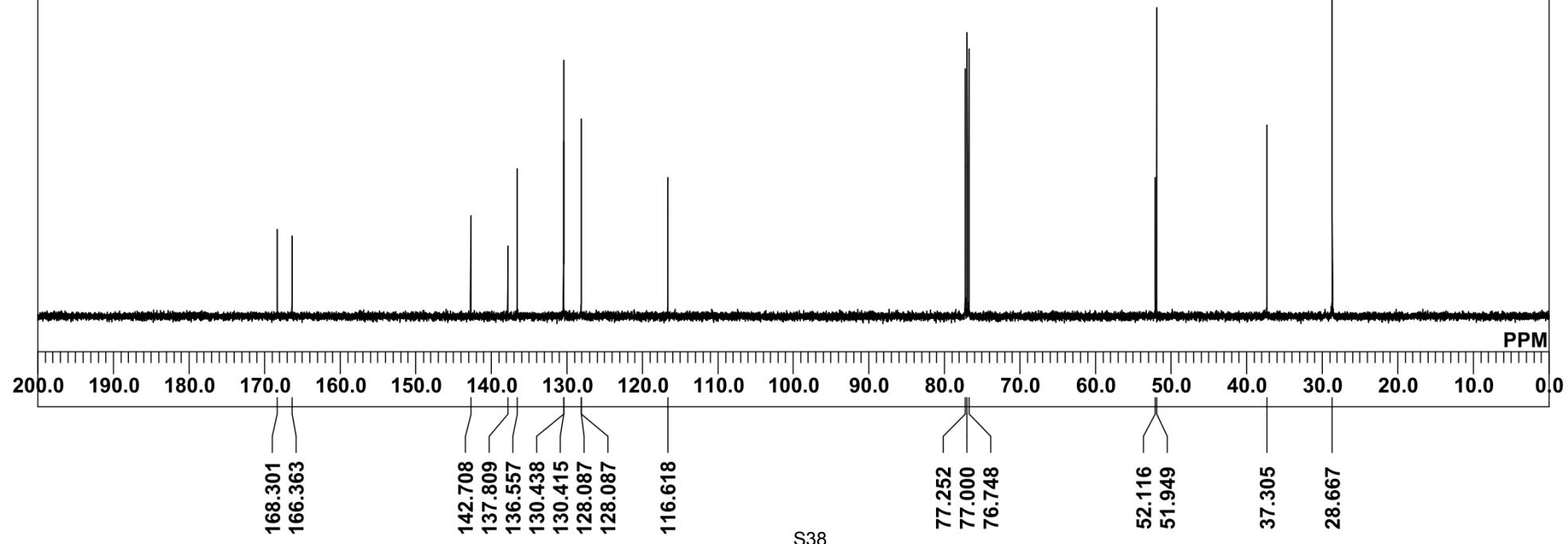


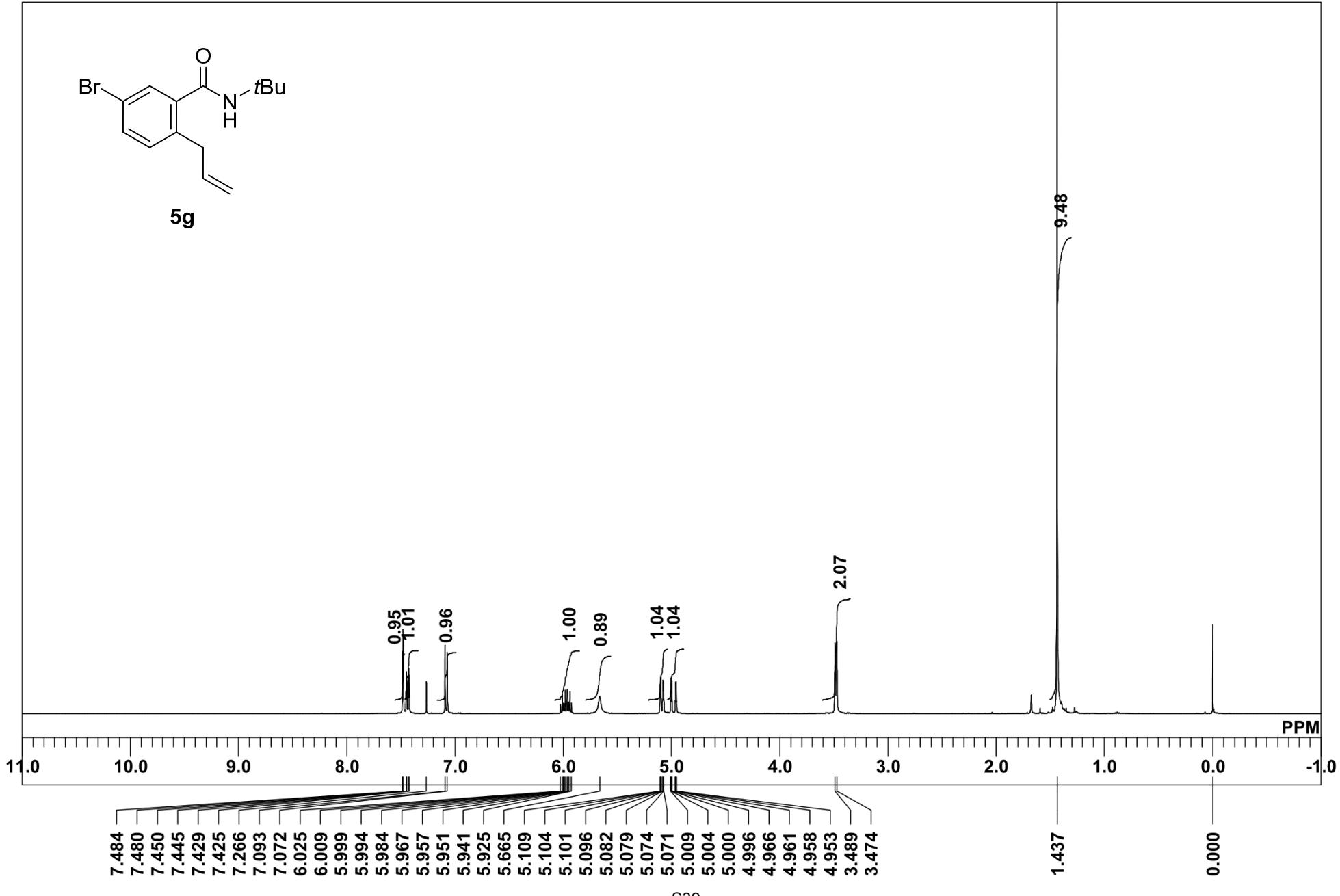
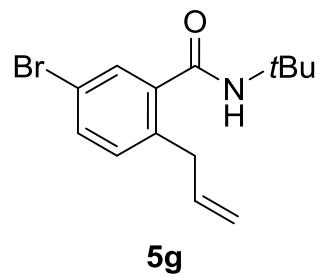


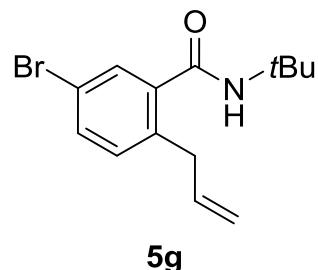




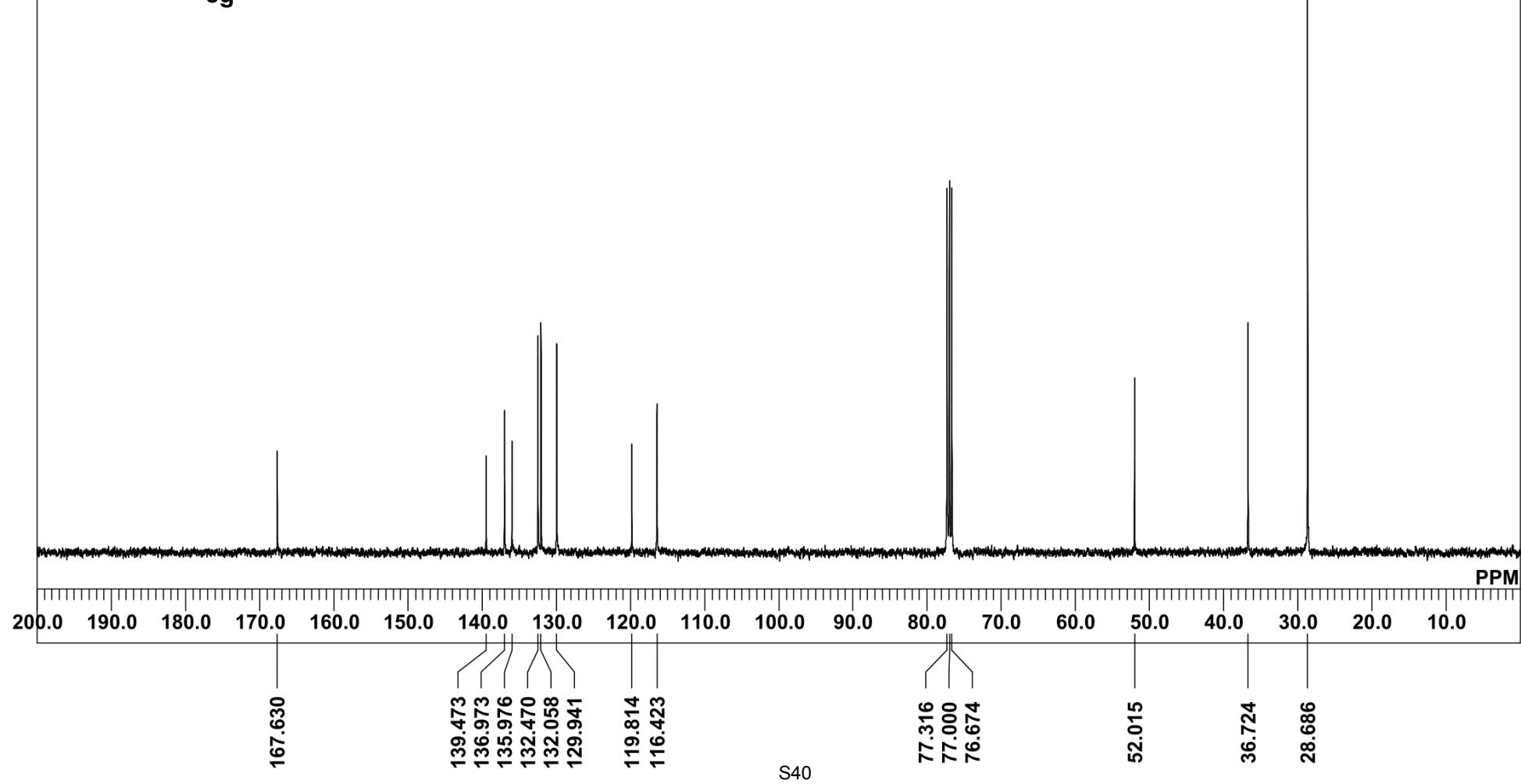
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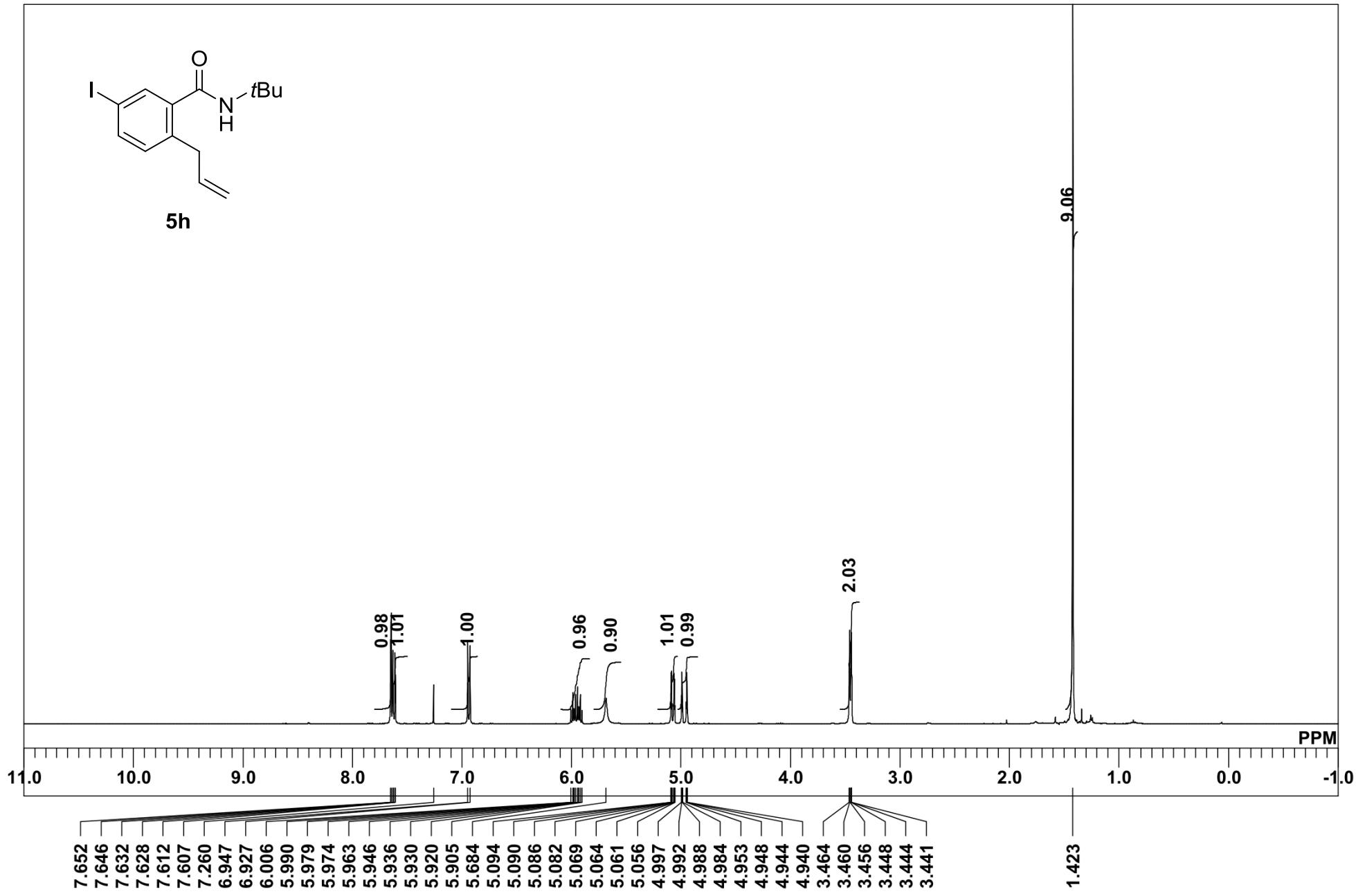
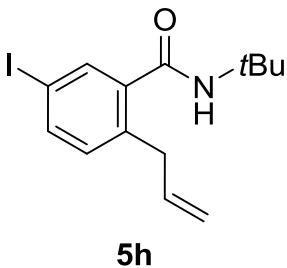


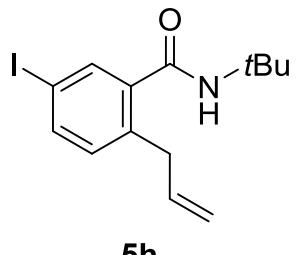




5g







5h

