

Supporting Information

Divergent Synthesis of α -Functionalized Amides through Selective N-O/C-C or N-O/C-C/C-N Cleavage of Aza-Cyclobutanone Oxime Esters

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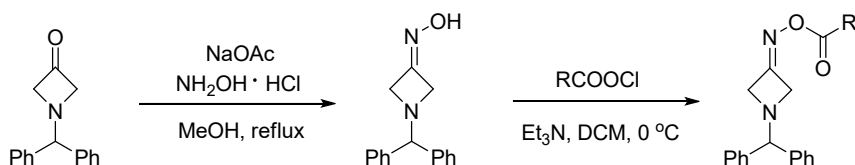
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1. General information

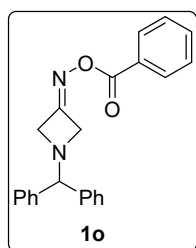
Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All reactions were carried out under an atmosphere of nitrogen and using anhydrous solvent unless otherwise noted. Fe (CAS 7439-59-6) was purchased from Macklin. Fe(OAc)₂ (CAS 3094-87-9) was purchased from Aladdin. ⁴BuNC (CAS 7188-38-7) was purchased from Aladdin. Reactions were monitored by thin-layer chromatography (TLC) using UV light as the visualizing agent and an acid solution of p-Anisaldehyde (PA) with heat as the stains. Flash column chromatography was performed using Yantai Yinlong flash silica gel (200–300 mesh). Melting points were recorded on an Electrothermal digital melting point apparatus. ¹H, ¹³C and ¹⁹F NMR spectra were recorded on Bruker 400 MHz spectrometer in CDCl₃ or DMSO-*d*₆ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet; d = doublet; t = triplet; q = quarter; p = pentet; m = multiplet; br = broad), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectroscopy (HRMS) analyses were obtained using a commercial apparatus (ESI or EI Source).

2. Preparation of aza-cyclobutanone oxime esters

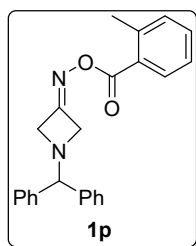


Aza-cyclobutanone oxime esters were prepared following the literature procedures.^[1-2] To a mixture of 1-benzhydrylazetid-3-one (5 mmol, 1.0 equiv) and hydrazine monohydrate (6 mmol, 1.2 equiv) in MeOH (30 mL) was added NaOAc (11 mmol, 2.2 equiv). The mixture was heated to reflux until the reaction was judged to be complete by TLC analysis. Then it was filtered through celite, the organic layers were concentrated and the resulting residue purified by silica gel column chromatography to provide 1-benzhydrylazetid-3-one oxime. To a mixture of 1-benzhydrylazetid-3-one oxime (1.0 equiv), triethylamine (2.0 equiv) and DCM (0.5M) in a 30-mL two-necked flask was added acyl chloride (1.5 equiv) at 0 °C. After 6 h, water was added to the above solution, and the mixture was diluted with diethyl ether,

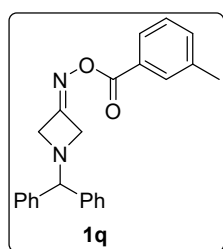
and then dried over Na_2SO_4 . The organic layers were concentrated and the resulting residue was purified by silica gel column chromatography to obtain the aza-cyclobutanone oxime esters. The product **1a** is a known compound.



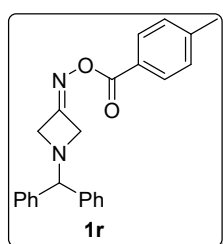
According to the general procedure, **1o** was obtained in 70% yield (0.3742 g). White solid, **mp**: 98.1 – 99.3 °C. **^1H NMR (400 MHz, CDCl_3)**: δ 7.98 – 7.95 (m, 2H), 7.56 – 7.49 (m, 1H), 7.49 – 7.42 (m, 4H), 7.39 (t, $J = 7.7$ Hz, 2H), 7.32 – 7.29 (m, 4H), 7.24 – 7.18 (m, 2H), 4.56 (s, 1H), 4.13 – 4.10 (m, 4H). **^{13}C NMR (100 MHz, CDCl_3)**: δ 163.6, 161.8, 141.6, 133.5, 129.7, 128.8, 128.6, 128.5, 127.7, 127.3, 77.3, 60.7, 60.8. **FT-IR (ATR)**: 1745.3, 1450.6, 1253.4, 749.7, 701.8 cm^{-1} . **HRMS (ESI, m/z)**: calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_2^+$, $[\text{M}+\text{H}]^+$: 357.1603, found: 357.1601.



According to the general procedure, **1p** was obtained in 65% yield (0.3611 g). White solid, **mp**: 89.2 – 90.1 °C. **^1H NMR (400 MHz, CDCl_3)**: δ 7.76 (d, $J = 7.8$ Hz, 1H), 7.47 – 7.43 (m, 4H), 7.41 – 7.37 (m, 1H), 7.33 – 7.28 (m, 4H), 7.25 – 7.18 (m, 4H), 4.56 (s, 1H), 4.13 – 4.06 (m, 4H), 2.57 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3)**: δ 164.8, 161.5, 141.7, 140.4, 132.5, 131.9, 130.4, 128.9, 128.1, 127.8, 127.4, 125.8, 77.4, 61.1, 61.0, 21.7. **FT-IR (ATR)**: 1746.9, 1455.6, 1231.2, 738.3, 697.2 cm^{-1} . **HRMS (ESI, m/z)**: calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_2^+$ $[\text{M}+\text{Na}]^+$: 393.1579, found: 393.1579.

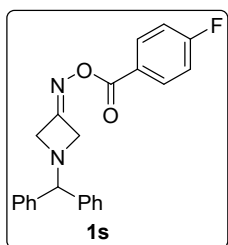


According to the general procedure, **1q** was obtained in 74% yield (0.4112 g). White solid, **mp**: 51.5 – 52.6 °C. **^1H NMR (400 MHz, CDCl_3)**: δ 7.81 – 7.74 (m, 2H), 7.48 – 7.43 (m, 4H), 7.35 – 7.24 (m, 6H), 7.23 – 7.18 (m, 2H), 4.56 (s, 1H), 4.15 – 4.06 (m, 4H), 2.34 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3)**: δ 163.8, 161.6, 141.6, 138.4, 134.3, 130.2, 128.8, 128.4(1), 128.3(6), 127.6, 127.3, 126.8, 77.2, 60.9, 60.8, 21.3. **FT-IR (ATR)**: 1743.7, 1452.6, 1264.4, 873.0, 737.1, 703.8 cm^{-1} . **HRMS (ESI, m/z)**: calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 371.1760, found: 371.1744.

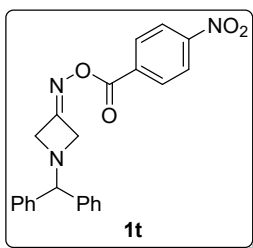


According to the general procedure, **1r** was obtained in 78% yield (0.4334 g). White solid, **mp**: 111.3 – 112.2 °C. **^1H NMR (400 MHz, CDCl_3)**: δ 7.86 (d, $J = 7.9$ Hz, 2H), 7.45 (d, $J = 7.6$ Hz, 4H), 7.31 – 7.29

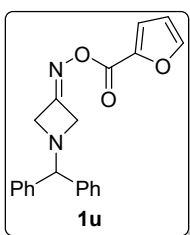
(m, 4H), 7.22 – 7.17(m, 4H), 4.55 (s, 1H), 4.11 – 4.08 (m, 4H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.6, 161.4, 144.3, 141.6, 129.7, 129.3, 128.8, 127.6, 127.3, 125.7, 77.2, 60.9, 60.8, 21.7. FT-IR (ATR): 1745.3, 1507.4, 1249.8, 742.5, 705.8 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{NaO}_2^+ [\text{M}+\text{Na}]^+$: 393.1579, found: 393.1570.



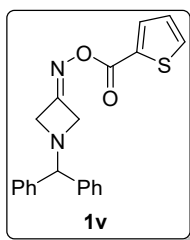
According to the general procedure, **1s** was obtained in 80% yield (0.4493 g). White solid, mp: 117.5 – 118.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.01 – 7.94 (m, 2H), 7.50 – 7.43 (m, 4H), 7.31 – 7.28 (m, 4H), 7.23 – 7.19 (m, 2H), 7.08 – 7.04 (m, 2H), 4.57 (s, 1H), 4.12 – 4.10 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.0 (d, $J = 253.5$), 162.6, 161.9, 141.6, 132.3 (d, $J = 9.4$ Hz), 128.8, 127.7, 127.3, 124.7 (d, $J = 3.0$ Hz), 115.8 (d, $J = 21.9$ Hz), 77.2, 60.9, 60.8. FT-IR (ATR): 1740.4, 1601.5, 1505.0, 1454.4, 1254.2, 847.6, 756.9, 699.3 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}_2^+ [\text{M}+\text{H}]^+$: 375.1509, found: 375.1506.



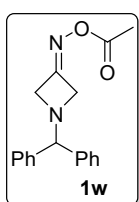
According to the general procedure, **1t** was obtained in 83% yield (0.4998 g). White solid, mp: 126.8 – 127.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 8.24 (d, $J = 8.6$ Hz, 2H), 8.13 (d, $J = 8.6$ Hz, 2H), 7.49 – 7.43 (m, 4H), 7.35 – 7.28 (m, 4H), 7.25 – 7.20 (m, 2H), 4.59 (s, 1H), 4.17 – 4.10 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.1, 161.8, 150.8, 141.4, 134.0, 130.8, 128.9, 127.8, 127.3, 123.7, 77.3, 60.9, 60.8. FT-IR (ATR): 1750.0, 1526.1, 1453.2, 1239.2, 853.4, 747.6, 706.8 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{20}\text{N}_3\text{O}_4^+ [\text{M}+\text{H}]^+$: 402.1454, found: 402.1445.



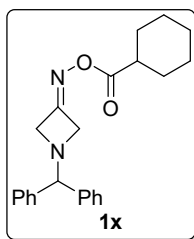
According to the general procedure, **1u** was obtained in 67% yield (0.3479 g) (*E/Z* mixture). White solid, mp: 70.0 – 71.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.69 (s, 0.41H), 7.57 (s, 1H), 7.45 (d, $J = 7.4$ Hz, 4H), 7.41 (d, $J = 3.6$ Hz, 0.49H), 7.34 – 7.26 (m, 4H), 7.25 – 7.20 (m, 2H), 7.18 (d, $J = 3.6$ Hz, 1H), 6.62 – 6.57 (m, 0.45H), 6.52 – 6.46 (m, 1H), 4.56 (s, 1H), 4.14 – 4.07 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 162.1, 156.1, 153.0, 148.6, 147.0, 143.1, 142.6, 141.6, 128.9, 127.7, 127.4, 121.8, 119.1, 112.8, 112.1, 77.3, 60.9. FT-IR (ATR): 1733.7, 1572.7, 1471.8, 1274.0, 883.4, 771.7, 743.1, 704.9 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{29}\text{N}_2\text{O}_3^+ [\text{M}+\text{H}]^+$: 347.1396, found: 347.1400.



According to the general procedure, **1v** was obtained in 63% yield (0.3425 g). White solid, **mp**: 100.5 – 101.7 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 7.83 – 7.77 (m, 1H), 7.57 – 7.51 (m, 1H), 7.49 – 7.42 (m, 4H), 7.34 – 7.27 (m, 4H), 7.25 – 7.19 (m, 2H), 7.12 – 7.03 (m, 1H), 4.56 (s, 1H), 4.13 – 4.06 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)**: δ 161.8, 159.4, 141.6, 134.4, 133.2, 131.0, 128.9, 128.0, 127.7, 127.3, 77.3, 60.9, 60.8. **FT-IR (ATR)**: 1736.4, 1245.7, 860.0, 734.0, 708.7 cm⁻¹. **HRMS (ESI, m/z)**: calcd for C₂₁H₁₉N₂O₂S⁺ [M+H]⁺: 363.1167, found: 363.1153.



According to the general procedure, **1w** was obtained in 61% yield (0.2693 g). White solid, **mp**: 81.3 – 82.5 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 7.47 – 7.41 (m, 4H), 7.34 – 7.26 (m, 4H), 7.26 – 7.17 (m, 2H), 4.53 (s, 1H), 4.06 – 3.98 (m, 4H), 2.08 (s, 3H). **¹³C NMR (100 MHz, CDCl₃)**: δ 168.1, 161.0, 141.6, 128.8, 127.7, 127.3, 77.3, 60.9, 60.8, 19.3. **FT-IR (ATR)**: 1757.5, 1228.2, 734.3, 703.7 cm⁻¹. **HRMS (ESI, m/z)**: calcd for C₁₈H₁₈N₂NaO₂⁺ [M+Na]⁺: 317.1266, found: 317.1273.



According to the general procedure, **1x** was obtained in 74% yield (0.4023 g). White solid, **mp**: 77.3 – 78.2 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 7.43 (d, *J* = 7.7 Hz, 4H), 7.31 – 7.25 (m, 4H), 7.23 – 7.15 (m, 2H), 4.52 (s, 1H), 4.05 – 3.96 (m, 4H), 2.37 – 2.25 (m, 1H), 1.91 – 1.83 (m, 2H), 1.77 – 1.67 (m, 2H), 1.64 – 1.56 (m, 1H), 1.54 – 1.39 (m, 2H), 1.30 – 1.14 (m, 3H). **¹³C NMR (75 MHz, CDCl₃)**: δ 172.6, 160.8, 141.6, 128.7, 127.5, 127.2, 77.2, 60.8, 60.7, 41.9, 28.9, 25.5, 25.3. **FT-IR (ATR)**: 1755.8, 1490.1, 1449.6, 1238.9, 745.1, 695.2 cm⁻¹. **HRMS (ESI, m/z)**: calcd for C₂₃H₂₇N₂O₂⁺ [M+H]⁺: 363.2073, found: 363.2075.

3. Experimental Procedure

General procedure for the synthesis of α-cyanomethylaminoamides derivatives (using **3a** as an illustrative example)

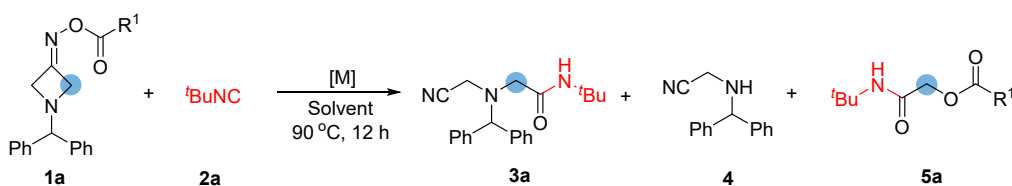
In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), Fe (0.04 mmol, 0.2 equiv). The flask was evacuated and backfilled with N₂ three times. Dioxane (1 mL) and 20 μL HCl (1 M) was then added with syringe under N₂. The system was stirred in an oil bath at 90 °C. After 12 h, it was removed from the oil bath, concentrated and the resulting residue was

purified by silica gel column chromatography (eluent: $V_{PE}/V_{EtOAc} = 5/1$) to give the desired product **3a** as a colorless oil (0.0631 g, 94% yield).

General procedure for the synthesis of α -acyloxyamides derivatives (using **5a** as an illustrative example)

In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), $Fe(OAc)_2$ (0.04 mmol, 0.2 equiv). The flask was evacuated and backfilled with N_2 three times. Dioxane (1 mL) and 20 μ L HCl (1 M) was then added with syringe under N_2 . The system was stirred in an oil bath at 90 °C. After 48 h, it was removed from the oil bath, concentrated and the resulting residue was purified by silica gel column chromatography (eluent: $V_{PE}/V_{EtOAc} = 5/1$) to give the desired product **5a** as a white solid (0.0425g, 70% yield) with the formation of **4** as a white solid (0.0373g, 84% yield).

Optimization of reaction conditions

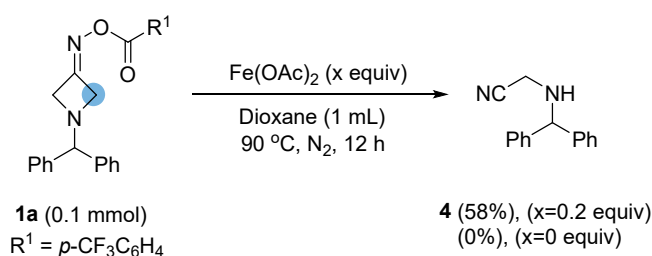


entry	catalyst	solvent	3a (%) ^b	4 (%) ^b	5a (%) ^b
1	NiBr ₂	Dioxane	42	44	trace
2	NiBr ₂	DMSO	trace	trace	trace
3	NiBr ₂	DMF	trace	trace	trace
4	NiBr ₂	Toluene	35	62	trace
5	NiBr ₂	DCM	trace	34	trace
6	NiBr ₂	EtOH	37	trace	trace
7	Ni(COD) ₂	Dioxane	6	70	43
8	FeCl ₃	Dioxane	52	40	4
9	FeCl ₂	Dioxane	47	13	10
10	FeBr ₂	Dioxane	45	15	15
11	FeSO ₄ ·7H ₂ O	Dioxane	80	11	trace
12	Fe(OAc) ₂	Dioxane	trace	87	51
13	Fe	Dioxane	94	trace	6
14	CoCl ₂	Dioxane	trace	trace	trace
15	Pd(OAc) ₂	Dioxane	trace	31	trace
16	Pd(dba) ₃	Dioxane	trace	trace	trace
17	Cu	Dioxane	18	59	45
18	CuBr	Dioxane	50	26	5
19	CuBr ₂	Dioxane	40	39	trace
20	RuCl ₃	Dioxane	45	31	trace
21	CeCl ₃	Dioxane	25	trace	trace

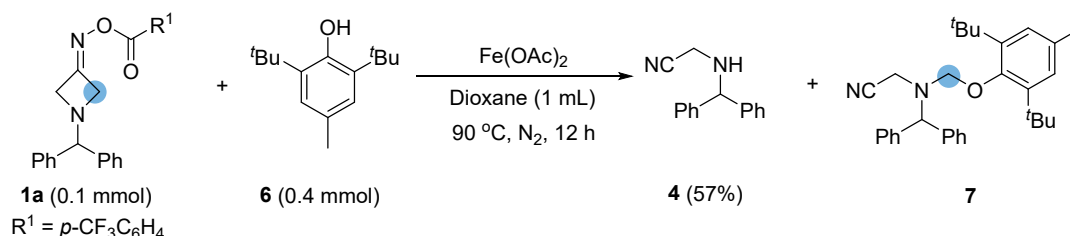
22	CrCl ₃	Dioxane	19	trace	trace
23 ^c	Fe(OAc) ₂	Dioxane	trace	79	62
24 ^d	Fe(OAc) ₂	Dioxane	trace	51	65
25^e	Fe(OAc)₂	Dioxane	trace	84	70
26 ^f	Fe(OAc) ₂	Dioxane	12	72	60
27 ^g	Fe(OAc) ₂	Dioxane	25	46	41

^aReaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), catalyst (20 mol %), 1 M HCl (20 μL), Dioxane (1 mL), 90 °C, under N₂. ^bYield of isolated product. ^c24 h. ^d48 h. ^e**2a** (0.5 mmol), 48 h. ^fFe(OAc)₂ (10 mol %), 48 h. ^gFe(OAc)₂ (5 mol %), 48 h.

Control experiments



In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.1 mmol, 1.0 equiv), Fe(OAc)₂ (0.02 mmol, 0.2 equiv). The flask was evacuated and backfilled with N₂ three times. Dioxane (1 mL) was then added with syringe under N₂. The system was stirred in an oil bath at 90 °C. After 12 h, it was removed from the oil bath, concentrated and the resulting residue was purified by silica gel column chromatography (eluent: V_{PE}/V_{EtOAc} = 10/1) to give the desired product **4** as a white solid in 58% yield.

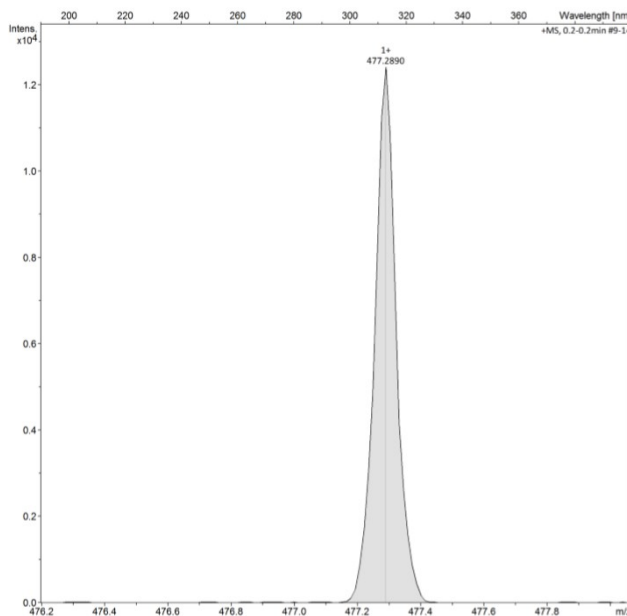


In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.1 mmol, 1.0 equiv), **6** (0.4 mmol, 4.0 equiv), Fe(OAc)₂ (0.02 mmol, 0.2 equiv). The flask was evacuated and backfilled with N₂ three times. Dioxane (1 mL) was then added with syringe under N₂. The system was stirred in an oil bath at 90 °C. After 12 h, it was removed from the oil bath, concentrated and the resulting residue was purified by silica gel column chromatography (eluent: V_{PE}/V_{EtOAc} = 10/1) to give the desired product **4** as a white solid in 57% yield with the formation of **7** identified by HRMS (**HRMS (ESI, m/z)**: calcd for C₃₁H₃₈N₂NaO⁺ [M+Na]⁺: 477.2882, found: 477.2890).

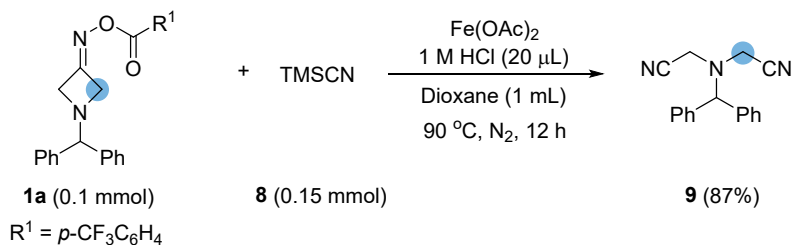
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Sample Name	LHW-112	Comment		

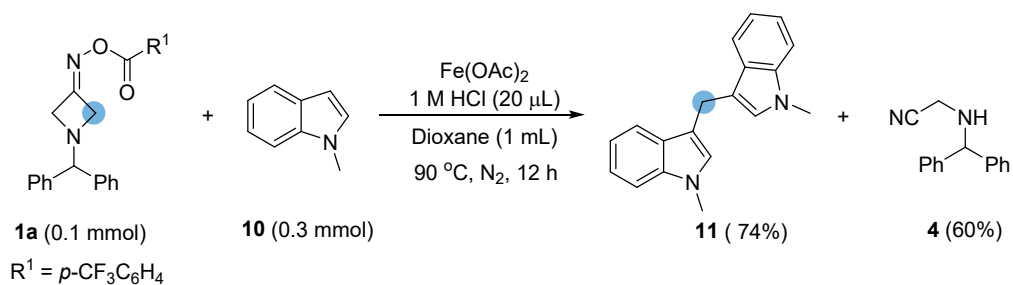
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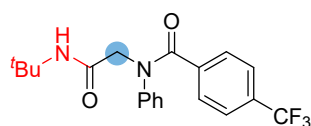
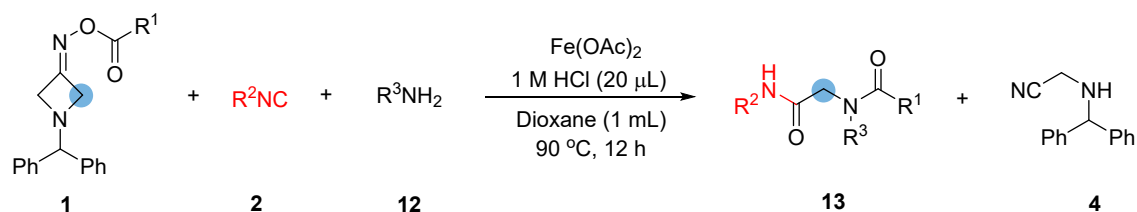


In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.1 mmol, 1.0 equiv), **8** (0.15 mmol, 1.5 equiv), Fe(OAc)₂ (0.02 mmol, 0.2 equiv). The flask was evacuated and backfilled with N₂ three times. Dioxane (1 mL) and 20 μL HCl (1 M) was then added with syringe under N₂. The system was stirred in an oil bath at 90 °C. After 12 h, it was removed from the oil bath, concentrated and the resulting residue was purified by silica gel column chromatography (eluent: V_{PE}/V_{EtOAc} = 10/1) to give the desired product **9** as a white solid in 87% yield.

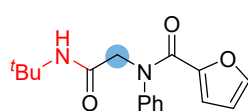


In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.1 mmol, 1.0 equiv), **10** (0.3 mmol, 3.0 equiv), $\text{Fe}(\text{OAc})_2$ (0.02 mmol, 0.2 equiv). The flask was evacuated and backfilled with N_2 three times. Dioxane (1 mL) 20 μL HCl (1 M) was then added with syringe under N_2 . The system was stirred in an oil bath at 90 $^\circ\text{C}$. After 12 h, it was removed from the oil bath, concentrated and the resulting residue was purified by silica gel column chromatography (eluent: $V_{\text{PE}}/V_{\text{EtOAc}} = 10/1$) to give the desired product **11** and **4** in 74% and 60% yield respectively.

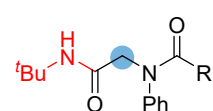
Synthetic application (using 13a as an illustrative example)



13a, 74% (97%)

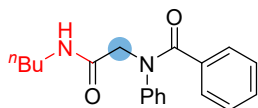


13b, 60% (74%)

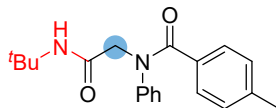


13c, $\text{R}^1 = \text{Ph}$, 85% (91%)

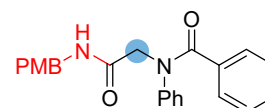
13d, $\text{R}^1 = \text{Cy}$, 31% (88%)



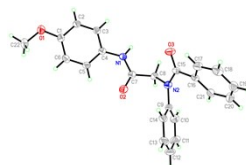
13e, 70% (92%)



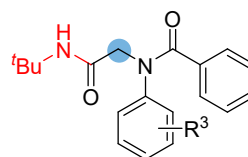
13f, 64% (94%)



13g, 36% (93%)



crystal of **13g**
CCDC 2082920



13h, $\text{R}^3 = o\text{-Me}$, 62% (90%)

13i, $\text{R}^3 = p\text{-F}$, 61% (88%)

13j, $\text{R}^3 = p\text{-Cl}$, 65% (90%)

^aReaction conditions: **1** (0.2 mmol), **2** (0.5 mmol), **3** (0.3 mmol), $\text{Fe}(\text{OAc})_2$ (20 mol %), 1 M HCl (20 μL), Dioxane (1 mL), 90 $^\circ\text{C}$, 12 h, N_2 . The numbers in parentheses are the yields of **4**.

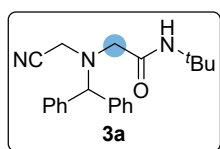
In a 5 mL test tube was equipped with a rubber septum and magnetic stir and was charged with **1a** (0.2 mmol, 1.0 equiv), **2a** (0.5 mmol, 2.5 equiv), **12a** (0.3 mmol, 1.5 equiv), $\text{Fe}(\text{OAc})_2$ (0.04 mmol, 0.2 equiv). The flask was evacuated and backfilled with N_2 three times. Dioxane (1 mL) and 20 μL HCl (1 M) was then added with syringe under N_2 . The system was stirred in an oil bath at 90 $^\circ\text{C}$. After 12 h, it was removed from the oil bath, concentrated and the resulting residue was purified by silica gel column chromatography (eluent: $V_{\text{PE}}/V_{\text{EtOAc}} = 5/1$) to give the desired product **13a** as a white solid (0.0560g, 74% yield) with the formation of **4** as a white solid (0.0431g, 97% yield).

4. References

- [1] Xia, P.-J.; Ye, Z.-P.; Hu, Y.-Z.; Song, D.; Xiang, H.-Y.; Chen, X.-Q.; Yang, H. Photocatalytic, Phosphoranyl Radical-Mediated N-O Cleavage of Strained Cycloketone Oximes. *Org. Lett.* **2019**, *21*, 2658.
- [2] Li, J.; Wang, S.-Y.; Ji, S.-J. Nickel-Catalyzed Thiolation and Selenylation of Cycloketone Oxime Esters with Thiosulfonate or Seleniumsulfonate. *J. Org. Chem.* **2019**, *84*, 16147.

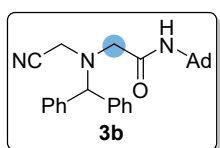
5. Analytic and characterization data for the products

2-(benzhydryl(cyanomethyl)amino)-*N*-(*tert*-butyl)acetamide (**3a**)



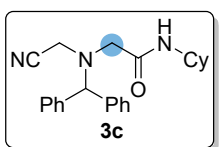
According to the general procedure, **3a** was obtained in 94% yield (63 mg). colorless oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.47 – 7.40 (m, 4H), 7.36 – 7.29 (m, 4H), 7.28 – 7.22 (m, 2H), 6.51 (s, 1H), 4.82 (s, 1H), 3.58 (s, 2H), 3.20 (s, 2H), 1.39 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 168.3, 140.3, 129.3, 128.3, 127.7, 114.9, 72.3, 55.9, 51.2, 41.6, 28.9. FT-IR (ATR): 3366.8, 2360.6, 1670.0, 1514.1, 1454.2, 1240.9, 747.3 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{21}\text{H}_{26}\text{N}_3\text{O}^+$ $[\text{M}+\text{H}]^+$: 336.2076, found: 336.2082.

N-((3*s*,5*s*,7*s*)-adamantan-1-yl)-2-(benzhydryl(cyanomethyl)amino)acetamide (**3b**)



According to the general procedure, **3b** was obtained in 95% yield (79 mg). White solid, mp: 129.1 – 130.2 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.47 – 7.40 (m, 4H), 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 2H), 6.38 (s, 1H), 4.82 (s, 1H), 3.57 (s, 2H), 3.17 (s, 2H), 2.14 – 2.08 (m, 3H), 2.05 – 2.00 (m, 6H), 1.74 – 1.68 (m, 6H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 167.8, 140.4, 129.3, 128.3, 127.7, 114.9, 72.2, 55.9, 51.9, 41.9, 41.6, 36.4, 29.5. FT-IR (ATR): 3376.4, 2366.0, 1731.4, 1514.8, 739.6, 702.6 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{27}\text{H}_{31}\text{N}_3\text{NaO}^+$ $[\text{M}+\text{Na}]^+$: 436.2365, found: 436.2368.

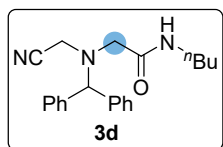
2-(benzhydryl(cyanomethyl)amino)-*N*-cyclohexylacetamide (**3c**)



According to the general procedure, **3c** was obtained in 89% yield (64 mg). White solid, mp: 126.5 – 127.6 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.49 – 7.40 (m, 4H), 7.37 – 7.28 (m, 4H), 7.28 – 7.22 (m, 2H), 6.54 (d, J = 8.5 Hz, 1H), 4.82 (s, 1H), 3.88 – 3.74 (m, 1H), 3.57 (s, 2H), 3.26 (s, 2H), 1.97 – 1.87 (m, 2H), 1.77 – 1.71 (m, 2H), 1.68 – 1.59 (m, 1H), 1.49 – 1.34 (m, 2H), 1.31 – 1.16 (m, 3H). ^{13}C

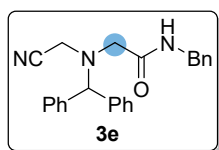
NMR (100 MHz, CDCl₃) δ 167.9, 140.3, 129.3, 128.3, 127.7, 114.8, 72.3, 55.4, 47.9, 41.6, 33.2, 25.6, 24.8. **FT-IR (ATR):** 3358.3, 2358.5, 1665.4, 1511.3, 743.1, 703.5 cm⁻¹. **HRMS (ESI, m/z):** calcd for C₂₃H₂₇N₃NaO⁺ [M+Na]⁺: 384.2052, found: 384.2044.

2-(benzhydryl(cyanomethyl)amino)-*N*-butylacetamide (3d)



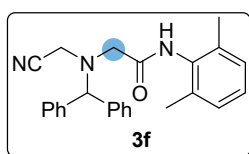
According to the general procedure, **3d** was obtained in 64% yield (43 mg). White solid, **mp**: 94.3 – 95.5 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.49 – 7.42 (m, 4H), 7.36 – 7.28 (m, 4H), 7.28 – 7.22 (m, 2H), 6.65 (t, *J* = 6.0 Hz, 1H), 4.81 (s, 1H), 3.57 (s, 2H), 3.36 – 3.26 (m, 4H), 1.60 – 1.48 (m, 2H), 1.45 – 1.32 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.8, 140.3, 129.3, 128.3, 127.7, 114.7, 72.3, 55.3, 41.7, 39.0, 31.8, 20.2, 13.9. **FT-IR (ATR):** 3338.6, 1648.4, 1523.3, 745.1, 701.3 cm⁻¹. **HRMS (ESI, m/z):** calcd for C₂₁H₂₅N₃NaO⁺ [M+Na]⁺: 358.1895, found: 358.1907.

2-(benzhydryl(cyanomethyl)amino)-*N*-benzylacetamide (3e)



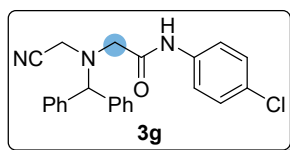
According to the general procedure, **3e** was obtained in 60% yield (44 mg). White solid, **mp**: 112.4 – 113.5 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.44 – 7.39 (m, 4H), 7.39 – 7.35 (m, 2H), 7.33 – 7.22 (m, 9H), 6.95 (t, *J* = 6.2 Hz, 1H), 4.81 (s, 1H), 4.50 (d, *J* = 5.9 Hz, 2H), 3.56 (s, 2H), 3.36 (s, 2H). **¹³C NMR (100 MHz, CDCl₃)** δ 168.9, 140.2, 138.2, 129.3, 129.0, 128.4, 127.8(4), 127.7(5), 127.6(5), 114.7, 72.4, 55.4, 43.3, 41.8. **FT-IR (ATR):** 3287.5, 2365.5, 1649.6, 1520.8, 733.6, 695.5 cm⁻¹. **HRMS (ESI, m/z):** calcd for C₂₄H₂₃N₃NaO⁺ [M+Na]⁺: 392.1739, found: 392.1749.

2-(benzhydryl(cyanomethyl)amino)-*N*-(2,6-dimethylphenyl)acetamide (3f)



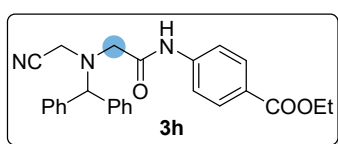
According to the general procedure, **3f** was obtained in 70% yield (54 mg). White solid, **mp**: 89.1 – 90.2 °C. **¹H NMR (400 MHz, DMSO-*d*₆)** δ 9.56 (s, 1H), 7.76 – 7.70 (m, 4H), 7.36 – 7.31 (m, 4H), 7.28 – 7.23 (m, 2H), 7.11 (s, 3H), 4.84 (s, 1H), 3.79 (s, 2H), 3.27 (s, 2H), 2.15 (s, 6H). **¹³C NMR (100 MHz, DMSO-*d*₆)** δ 167.0, 141.6, 135.6, 134.9, 128.9, 127.7(3), 127.7(1), 127.6(8), 126.7, 115.5, 71.8, 54.8, 41.5, 18.2. **FT-IR (ATR):** 3262.7, 2367.8, 1670.3, 1494.6, 771.7, 705.4 cm⁻¹. **HRMS (ESI, m/z):** calcd for C₂₅H₂₅N₃NaO⁺ [M+Na]⁺: 406.1895, found: 406.1902.

2-(benzhydryl(cyanomethyl)amino)-*N*-(4-chlorophenyl)acetamide (3g)



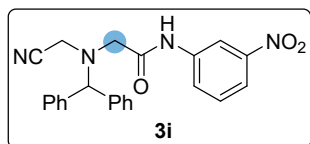
According to the general procedure, **3g** was obtained in 64% yield (51 mg). White solid, mp: 158.9 – 159.8 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.43 (s, 1H), 7.52 – 7.47 (m, 5H), 7.39 – 7.25 (m, 9H), 4.89 (s, 1H), 3.65 (s, 2H), 3.44 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.1, 139.9, 135.8, 130.0, 129.5, 129.4, 128.6, 127.8, 121.1, 114.5, 72.5, 56.1, 42.0. FT-IR (ATR): 3044.2, 2366.0, 1667.5, 1491.9, 746.2, 703.9 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{20}\text{N}_3\text{NaO}^+$ [M+Na] $^+$: 412.1193, found: 412.1194.

ethyl 4-(2-(benzhydryl(cyanomethyl)amino)acetamido)benzoate (3h)



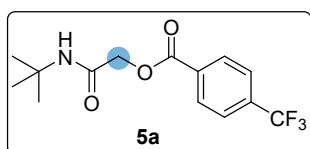
According to the general procedure, **3h** was obtained in 28% yield (24 mg). Yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.70 (s, 1H), 8.07 – 8.00 (m, 2H), 7.68 – 7.61 (m, 2H), 7.52 – 7.46 (m, 4H), 7.37 – 7.30 (m, 4H), 7.28 – 7.23 (m, 2H), 4.87 (s, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 3.68 (s, 2H), 3.47 (s, 2H), 1.39 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.4, 166.1, 141.2, 139.8, 131.0, 129.5, 128.6, 127.8, 126.6, 119.0, 114.6, 72.4, 61.1, 56.1, 41.9, 14.4. FT-IR (ATR): 3333.1, 1703.9, 1598.5, 1517.5, 746.7, 697.0 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{26}\text{H}_{25}\text{N}_3\text{NaO}_3^+$ [M+Na] $^+$: 450.1794, found: 450.1800.

2-(benzhydryl(cyanomethyl)amino)-N-(3-nitrophenyl)acetamide (3i)



According to the general procedure, **3i** was obtained in 27% yield (22 mg). Yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.74 (s, 1H), 8.37 (t, $J = 2.2$ Hz, 1H), 8.05 – 7.94 (m, 2H), 7.56 – 7.48 (m, 5H), 7.38 – 7.33 (m, 4H), 7.30 – 7.25 (m, 2H), 4.89 (s, 1H), 3.70 (s, 2H), 3.51 (s, 2H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 167.7, 148.7, 148.6, 139.8, 138.3, 130.2, 129.5, 128.6, 127.8, 125.7, 119.4, 114.6, 72.5, 56.0, 42.0. FT-IR (ATR): 3326.8, 1697.5, 1525.8, 1517.5, 737.3, 705.1 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{23}\text{H}_{20}\text{N}_4\text{NaO}_3^+$ [M+Na] $^+$: 423.1433, found: 423.1439.

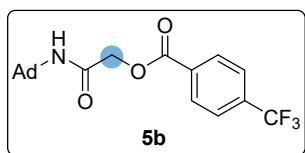
2-(tert-butylamino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5a)



According to the general procedure, **5a** was obtained in 70% yield (43 mg). White solid, mp: 134.9 – 135.8 °C. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.17 (d, $J = 8.1$ Hz, 2H), 7.74 (d, $J = 8.1$ Hz, 2H), 5.85 (s, 1H), 4.73 (s, 2H), 1.39 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 165.8, 164.3, 135.2 (q, $J = 32.8$ Hz), 132.5, 130.3, 125.8 (q, $J = 3.7$ Hz), 123.6 (q, $J = 272.8$ Hz), 64.1, 51.8, 28.9. $^{19}\text{F NMR}$ (376 MHz, CDCl_3) δ -63.24. FT-IR (ATR): 3334.0, 1719.8, 1654.3, 1507.4,

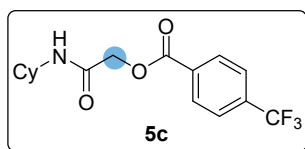
1423.7, 1125.8, 868.2 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 304.1161, found: 304.1165.

2-(adamantan-1-ylamino)-2-oxoethyl 4-(trifluoromethyl)benzoate (**5b**)



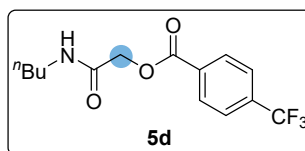
According to the general procedure, **5b** was obtained in 60% yield (46 mg). White solid, **mp**: 130.2 – 131.4 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.18 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 5.69 (s, 1H), 4.73 (s, 2H), 2.12 – 2.07 (m, 3H), 2.06 – 2.01 (m, 6H), 1.71 – 1.66 (m, 6H). **^{13}C NMR (100 MHz, CDCl_3):** δ 165.4, 164.2, 135.2 (q, J = 32.4 Hz), 132.5, 130.3, 125.8 (q, J = 3.7 Hz), 123.6 (q, J = 273.1 Hz), 64.1, 52.4, 41.7, 36.4, 29.5. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.22. **FT-IR (ATR):** 3331.2, 1725.3, 1666.0, 1507.4, 1420.4, 1129.4, 866.6 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 404.1449, found: 404.1449.

2-(cyclohexylamino)-2-oxoethyl 4-(trifluoromethyl)benzoate (**5c**)



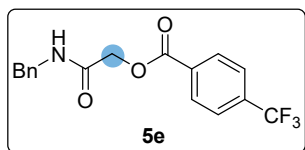
According to the general procedure, **5c** was obtained in 51% yield (34 mg). White solid, **mp**: 135.7 – 136.6 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.18 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H), 5.91 (d, J = 8.0 Hz, 1H), 4.82 (s, 2H), 3.93 – 3.80 (m, 1H), 2.00 – 1.91 (m, 2H), 1.74 – 1.61 (m, 3H), 1.46 – 1.34 (m, 2H), 1.24 – 1.12 (m, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 165.7, 164.3, 135.3 (q, J = 32.9 Hz), 132.5, 130.3, 125.9 (q, J = 3.6 Hz), 123.6 (q, J = 272.8 Hz), 64.0, 48.3, 33.1, 25.5, 24.9. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.24. **FT-IR (ATR):** 3282.3, 1724.7, 1653.7, 1420.0, 1123.8, 866.3 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{16}\text{H}_{19}\text{F}_3\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 330.1317, found: 330.1324.

2-(butylamino)-2-oxoethyl 4-(trifluoromethyl)benzoate (**5d**)



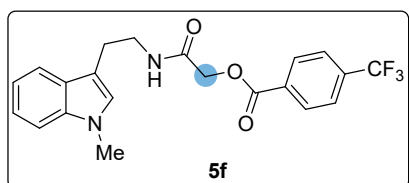
According to the general procedure, **5d** was obtained in 61% yield (37 mg). White solid, **mp**: 124.1 – 125.3 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.19 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 6.08 (s, 1H), 4.84 (s, 2H), 3.39 – 3.30 (m, 2H), 1.59 – 1.47 (m, 2H), 1.43 – 1.29 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 166.6, 164.3, 135.3 (q, J = 32.8 Hz), 132.4 (q, J = 0.7 Hz), 130.3, 125.9 (q, J = 3.7 Hz), 123.6 (q, J = 273.1 Hz), 64.0, 39.2, 31.7, 20.2, 13.8. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.24. **FT-IR (ATR):** 3288.7, 1732.5, 1653.7, 1507.3, 1457.1, 1418.7, 1124.1, 862.4 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{14}\text{H}_{17}\text{F}_3\text{NO}_3^+$ $[\text{M}+\text{H}]^+$: 304.1161, found: 304.1157.

2-(benzylamino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5e)



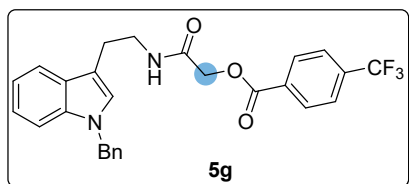
According to the general procedure, **5e** was obtained in 61% yield (41 mg). White solid, **mp**: 128.5 – 129.7 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.28 (m, 5H), 6.36 (s, 1H), 4.89 (s, 2H), 4.54 (d, *J* = 5.9 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ 166.7, 164.4, 137.7, 135.3 (q, *J* = 32.9 Hz), 132.3, 130.4, 129.0, 128.0, 127.9, 125.9 (q, *J* = 3.9 Hz), 123.6 (q, *J* = 272.9 Hz), 63.9, 43.4. **¹⁹F NMR (376 MHz, CDCl₃)** δ -63.24. **FT-IR (ATR)**: 3285.0, 1716.9, 1653.5, 1457.0, 1123.6, 861.1 cm⁻¹. **HRMS (ESI, m/z)**: calcd for C₁₇H₁₅F₃NO₃⁺ [M+H]⁺: 338.1004, found: 338.0992.

2-((2-(1-methyl-1*H*-indol-3-yl)ethyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5f)



According to the general procedure, **5f** was obtained in 58% yield (47 mg). White solid, **mp**: 102.7 – 103.8 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.27 (s, 1H), 7.23 – 7.17 (m, 1H), 7.10 – 7.02 (m, 1H), 6.84 (s, 1H), 6.20 (s, 1H), 4.79 (s, 2H), 3.68 (q, *J* = 6.3 Hz, 2H), 3.64 (s, 3H), 3.00 (t, *J* = 6.5 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ 166.7, 164.1, 137.2, 135.0 (q, *J* = 32.8 Hz), 132.2 (q, *J* = 1.6 Hz), 130.2, 127.8, 127.1, 125.7 (q, *J* = 3.7 Hz), 123.6 (q, *J* = 272.6 Hz), 122.1, 119.3, 118.8, 111.0, 109.5, 63.7, 39.7, 32.7, 25.0. **¹⁹F NMR (376 MHz, CDCl₃)** δ -63.22. **FT-IR (ATR)**: 3284.5, 1733.1, 1652.0, 1507.3, 1420.6, 1120.3, 866.2 cm⁻¹. **HRMS (ESI, m/z)**: calcd for C₂₁H₁₉F₃N₂NaO₃⁺ [M+Na]⁺: 427.1245, found: 427.1246.

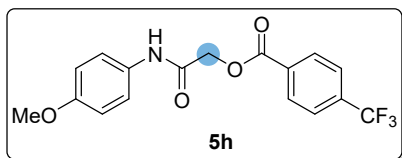
2-((2-(1-benzyl-1*H*-indol-3-yl)ethyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5g)



According to the general procedure, **5g** was obtained in 42% yield (42 mg). White solid, **mp**: 115.3 – 116.5 °C. **¹H NMR (400 MHz, CDCl₃)**: δ 7.84 (d, *J* = 8.1 Hz, 2H), 7.62 – 7.53 (m, 3H), 7.25 – 7.21 (m, 4H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.09 – 7.02 (m, 3H), 6.95 (s, 1H), 6.20 – 6.13 (m, 1H), 5.18 (s, 2H), 4.77 (s, 2H), 3.69 (q, *J* = 6.4 Hz, 2H), 3.02 (t, *J* = 6.6 Hz, 2H). **¹³C NMR (100 MHz, CDCl₃)**: δ 166.6, 164.1, 137.4, 136.8, 135.0 (q, *J* = 32.7 Hz), 132.2 (q, *J* = 1.0 Hz), 130.1, 128.9, 128.2, 127.8, 126.8, 126.4, 125.7 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 271.1 Hz), 122.3, 119.6, 118.9, 111.8, 110.0, 63.8, 50.1, 39.8, 25.1. **¹⁹F NMR (376 MHz, CDCl₃)** δ -63.18. **FT-IR (ATR)**: 3329.5,

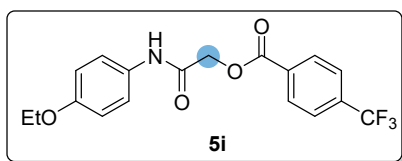
1733.8, 1688.1, 1507.3, 1456.8, 1280.7, 1126.0, 867.0 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{27}\text{H}_{23}\text{F}_3\text{N}_2\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$: 503.1558, found: 503.1545.

2-((4-methoxyphenyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5h)



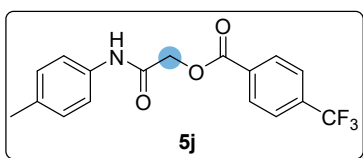
According to the general procedure, **5h** was obtained in 61% yield (43 mg). Yellow solid, **mp**: 130.9 – 132.0 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.22 (d, $J = 8.1$ Hz, 2H), 7.80 – 7.72 (m, 3H), 7.44 – 7.39 (m, 2H), 6.89 – 6.84 (m, 2H), 4.95 (s, 2H), 3.79 (s, 3H); **^{13}C NMR (100 MHz, CDCl_3):** δ 164.9, 164.4, 157.1, 135.3 (q, $J = 32.7$ Hz), 132.3, 130.4, 129.7, 125.8 (q, $J = 3.5$ Hz), 123.6 (q, $J = 271.3$ Hz), 122.4, 114.3, 64.0, 55.6; **^{19}F NMR (376 MHz, CDCl_3)** δ -63.22; **FT-IR (ATR):** 3314.6, 1733.1, 1667.9, 1508.4, 1130.0, 866.2 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 346.0773, found: 346.0777.

2-((4-ethoxyphenyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5i)



According to the general procedure, **5i** was obtained in 51% yield (37.5 mg). Yellow solid, **mp**: 130.1 – 131.3 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.22 (d, $J = 8.1$ Hz, 2H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.72 (s, 1H), 7.45 – 7.36 (m, 2H), 6.90 – 6.81 (m, 2H), 4.96 (s, 2H), 4.01 (q, $J = 7.0$ Hz, 2H), 1.40 (t, $J = 7.0$ Hz, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 164.7, 164.4, 156.6, 135.4 (q, $J = 32.7$ Hz), 132.3, 130.4, 129.5, 125.9 (q, $J = 3.6$ Hz), 123.6 (q, $J = 32.7$ Hz), 122.4, 115.0, 64.1, 63.9, 14.9. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.22. **FT-IR (ATR):** 3312.7, 1728.5, 1670.7, 1498.0, 1112.3, 864.8 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NNaO}_4^+$ $[\text{M}+\text{Na}]^+$: 346.0773, found: 346.0777.

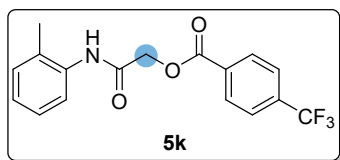
2-((4-ethoxyphenyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (5j)



According to the general procedure, **5j** was obtained in 56% yield (38 mg). Yellow solid, **mp**: 133.5 – 134.7 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.22 (d, $J = 8.1$ Hz, 2H), 7.80 – 7.72 (m, 3H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 4.96 (s, 2H), 2.32 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 164.7, 164.4, 135.4 (q, $J = 33.0$ Hz), 135.1, 134.1, 132.3, 130.4, 129.8, 125.9 (q, $J = 3.7$ Hz), 123.6 (q, $J = 272.6$ Hz), 120.5, 64.1, 21.0. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.23. **FT-IR (ATR):** 3312.7, 1731.2, 1670.7,

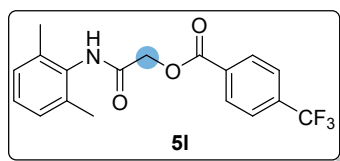
1498.0, 1112.3, 864.8 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 360.0823, found: 360.0819.

2-oxo-2-(o-tolylamino)ethyl 4-(trifluoromethyl)benzoate (**5k**)



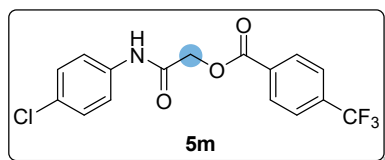
According to the general procedure, **5k** was obtained in 60% yield (41 mg). White solid, **mp**: 150.2 – 151.4 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.23 (d, $J = 8.1$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.81 – 7.72 (m, 3H), 7.26 – 7.18 (m, 2H), 7.14 – 7.08 (m, 1H), 5.01 (s, 2H), 2.25 (s, 3H). **^{13}C NMR (100 MHz, CDCl_3):** δ 164.8, 164.3, 135.5 (q, $J = 32.1$ Hz), 134.7, 132.2, 130.8, 130.3, 128.9, 127.2, 126.0 (q, $J = 3.7$ Hz), 125.9, 123.6 (q, $J = 273.9$ Hz), 123.0, 64.4, 17.7. **^{19}F NMR (376 MHz, CDCl_3)** δ -63.23. **FT-IR (ATR):** 3274.6, 1735.4, 1663.9, 1507.3, 1457.3, 1130.5, 860.6 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{17}\text{H}_{14}\text{F}_3\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 360.0823, found: 360.0819.

2-((2,6-dimethylphenyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (**5l**)



According to the general procedure, **5l** was obtained in 64% yield (45 mg). White solid, **mp**: 155.8 – 156.9 °C. **^1H NMR (400 MHz, $\text{DMSO-}d_6$):** δ 9.57 (s, 1H), 8.27 (d, $J = 8.1$ Hz, 2H), 7.95 (d, $J = 8.1$ Hz, 2H), 7.08 (s, 3H), 5.02 (s, 2H), 2.17 (s, 6H); **^{13}C NMR (100 MHz, $\text{DMSO-}d_6$):** δ 165.1, 164.5, 135.4, 134.2, 133.0(4) (q, $J = 0.7$ Hz), 133.0(3) (q, $J = 31.7$ Hz), 130.4, 127.7, 126.7, 125.8 (q, $J = 3.8$ Hz), 123.7 (q, $J = 272.7$ Hz), 63.5, 18.0. **^{19}F NMR (376 MHz, $\text{DMSO-}d_6$)** δ -61.68. **FT-IR (ATR):** 3257.9, 1733.3, 1670.2, 1415.0, 1125.9, 864.5 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{18}\text{H}_{16}\text{F}_3\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 374.0980, found: 374.0969.

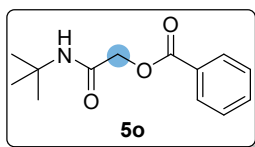
2-((4-chlorophenyl)amino)-2-oxoethyl 4-(trifluoromethyl)benzoate (**5m**)



According to the general procedure, **5m** was obtained in 24% yield (17 mg). Yellow solid, **mp**: 147.3 – 148.5 °C. **^1H NMR (400 MHz, $\text{DMSO-}d_6$):** δ 10.40 (s, 1H), 8.23 (d, $J = 8.1$ Hz, 2H), 7.94 (d, $J = 8.2$ Hz, 2H), 7.65 – 7.59 (m, 2H), 7.41 – 7.34 (m, 2H), 4.99 (s, 2H). **^{13}C NMR (100 MHz, $\text{DMSO-}d_6$):** δ 165.2, 164.4, 137.3, 133.1 (q, $J = 32.2$ Hz), 132.9, 130.3, 128.7, 127.2, 125.8 (q, $J = 3.8$ Hz), 123.7 (q, $J = 272.6$ Hz), 120.9, 63.5. **^{19}F NMR (376 MHz, $\text{DMSO-}d_6$)** δ -61.73. **FT-IR (ATR):** 3312.6, 1720.7,

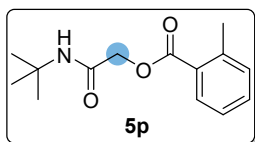
1672.5, 1490.4, 1117.4, 867.2 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{16}\text{H}_{11}\text{ClF}_3\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 380.0277, found: 380.0276.

2-(*tert*-butylamino)-2-oxoethyl benzoate (**5o**)



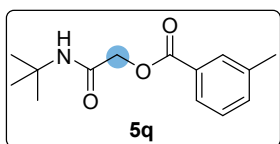
According to the general procedure, **5o** was obtained in 70% yield (33 mg). White solid, **mp**: 96.4 – 97.5 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.09 – 8.03 (m, 2H), 7.65 – 7.59 (m, 1H), 7.53 – 7.46 (m, 2H), 5.95 (s, 1H), 4.71 (s, 2H), 1.40 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 166.3, 165.3, 133.8, 129.8, 129.2, 128.8, 63.8, 51.6, 28.9. **FT-IR (ATR):** 3312.8, 1718.0, 1653.5, 1507.3, 1456.8, 1419.4, 1118.6, 704.5 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{13}\text{H}_{17}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 258.1106, found: 258.1104.

2-(*tert*-butylamino)-2-oxoethyl 2-methylbenzoate (**5p**)



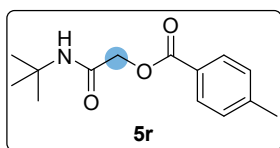
According to the general procedure, **5p** was obtained in 58% yield (29 mg). White solid, **mp**: 98.7 – 99.9 °C. **^1H NMR (400 MHz, CDCl_3):** δ 7.95 – 7.89 (m, 1H), 7.50 – 7.42 (m, 1H), 7.32 – 7.27 (m, 2H), 5.96 (s, 1H), 4.68 (s, 2H), 2.63 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 166.4, 166.0, 140.8, 132.8, 132.1, 130.6, 128.6, 126.1, 63.8, 51.6, 28.9, 21.9. **FT-IR (ATR):** 3305.2, 1635.8, 1558.1, 1507.3, 1457.0, 1247.4, 1099.3, 738.2 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 272.1263, found: 272.1268.

2-(*tert*-butylamino)-2-oxoethyl 3-methylbenzoate (**5q**)



According to the general procedure, **5q** was obtained in 73% yield (36 mg). White solid, **mp**: 93.2 – 94.5 °C. **^1H NMR (400 MHz, CDCl_3):** δ 7.90 – 7.81 (m, 2H), 7.46 – 7.40 (m, 1H), 7.40 – 7.33 (m, 1H), 5.93 (s, 1H), 4.70 (s, 2H), 2.43 (s, 3H), 1.40 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 166.4, 165.5, 138.7, 134.6, 130.4, 129.2, 128.7, 126.9, 63.8, 51.6, 28.9, 21.4. **FT-IR (ATR):** 3295.2, 1733.3, 1661.3, 1419.2, 1196.5, 944.9, 747.0 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 272.1263, found: 272.1262.

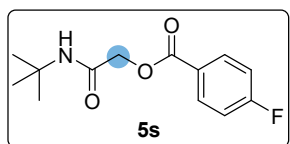
2-(*tert*-butylamino)-2-oxoethyl 4-methylbenzoate (**5r**)



According to the general procedure, **5r** was obtained in 68% yield (34 mg). White solid, **mp**: 104.2 – 105.5 °C. **^1H NMR (400 MHz, CDCl_3):** δ 7.94 (d, J = 8.3 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.93 (s, 1H), 4.69 (s, 2H), 2.44 (s, 3H), 1.39 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 166.4,

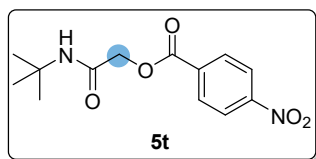
165.3, 144.7, 129.8, 129.6, 126.5, 63.7, 51.6, 28.9, 21.9. **FT-IR (ATR):** 3314.6, 1717.4, 1654.7, 1507.4, 1456.9, 1114.9, 756.5 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 272.1263, found: 272.1257.

2-(*tert*-butylamino)-2-oxoethyl 4-fluorobenzoate (**5s**)



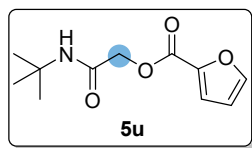
According to the general procedure, **5s** was obtained in 70% yield (36 mg). White solid, **mp**: 99.8-100.9 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.11 – 8.05 (m, 2H), 7.19 – 7.13 (m, 2H), 5.88 (s, 1H), 4.70 (s, 2H), 1.40 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 166.3 (d, $J = 256.3$ Hz), 166.1, 164.4, 132.4 (d, $J = 9.5$ Hz), 125.5 (d, $J = 3.2$ Hz), 116.0 (d, $J = 22.2$ Hz), 63.9, 51.7, 28.9. **^{19}F NMR (376 MHz, CDCl_3)** δ -104.21. **FT-IR (ATR):** 3314.35, 1720.3, 1661.3, 1507.8, 1394.2, 1116.2, 859.5 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{13}\text{H}_{16}\text{FNNaO}_3^+$ $[\text{M}+\text{Na}]^+$: 276.1012, found: 276.1016.

2-(*tert*-butylamino)-2-oxoethyl 4-nitrobenzoate (**5t**)



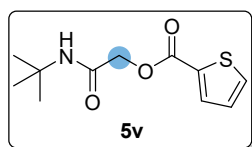
According to the general procedure, **5t** was obtained in 82% yield (46 mg). White solid, **mp**: 109.1 – 110.3 °C. **^1H NMR (400 MHz, CDCl_3):** δ 8.32 – 8.29 (m, 2H), 8.24 – 8.20 (m, 2H), 5.82 (s, 1H), 4.73 (s, 2H), 1.38 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 165.4, 163.7, 151.0, 134.7, 131.0, 123.9, 64.3, 51.9, 28.9. **FT-IR (ATR):** 3329.2, 1719.5, 1654.3, 1420.1, 1123.8, 879.3 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{13}\text{H}_{16}\text{N}_2\text{NaO}_5^+$ $[\text{M}+\text{Na}]^+$: 303.0957, found: 303.0957.

2-(*tert*-butylamino)-2-oxoethyl furan-2-carboxylate (**5u**)



According to the general procedure, **5u** was obtained in 65% yield (29 mg). White solid, **mp**: 60.8 – 61.9 °C. **^1H NMR (400 MHz, CDCl_3):** δ 7.63 (d, $J = 1.5$ Hz, 1H), 7.28 (d, $J = 3.6$ Hz, 1H), 6.59 – 6.55 (m, 1H), 5.99 (s, 1H), 4.66 (s, 2H), 1.39 (s, 9H). **^{13}C NMR (100 MHz, CDCl_3):** δ 165.9, 157.1, 147.1, 143.8, 119.3, 112.4, 63.4, 51.6, 28.9. **FT-IR (ATR):** 3312.9, 1732.8, 1670.4, 1457.1, 1127.8, 795.8, 762.7 cm^{-1} . **HRMS (ESI, m/z):** calcd for $\text{C}_{11}\text{H}_{15}\text{NNaO}_4^+$ $[\text{M}+\text{Na}]^+$: 248.0899, found: 248.0900.

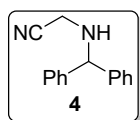
2-(*tert*-butylamino)-2-oxoethyl thiophene-2-carboxylate (**5v**)



According to the general procedure, **5v** was obtained in 71% yield (34 mg). White solid, **mp**: 86.2 – 87.5 °C. **^1H NMR (400 MHz, CDCl_3):** δ 7.91 – 7.85 (m, 1H), 7.69 – 7.61 (m, 1H), 7.20 – 7.13 (m, 1H), 5.99

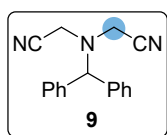
(s, 1H), 4.67 (s, 2H), 1.40 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 166.0, 160.6, 134.5, 133.4, 132.3, 128.3, 63.6, 51.6, 28.8. FT-IR (ATR): 3284.5, 1716.2, 1653.8, 1507.3, 1457.1, 1086.2, 750.8, 668.5 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{11}\text{H}_{15}\text{NNaO}_3\text{S}^+$ $[\text{M}+\text{Na}]^+$: 264.0670, found: 264.0673.

2-(benzhydrylamino)acetonitrile (4)



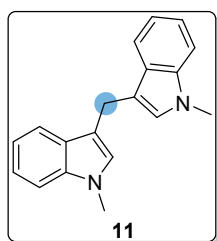
According to the general procedure, **4** was isolated from the reaction system as white powder, mp: 69.1 – 70.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.44 – 7.37 (m, 4H), 7.32 – 7.25 (m, 4H), 7.25 – 7.18 (m, 2H), 5.03 (s, 1H), 3.42 (s, 2H), 1.91 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 141.9, 128.8, 127.7, 127.2, 117.7, 65.7, 35.2. FT-IR (ATR): 3333.87, 2201.0, 1490.1 1457.6, 1130.7, 743.9 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 245.1055, found: 245.1051.

2,2'-(benzhydrylazanediy)diacetonitrile (9)



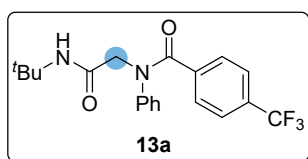
According to the general procedure, **9** was obtained in 87% yield (23 mg). White solid, mp: 142.4 – 143.6 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.49 – 7.44 (m, 4H), 7.37 – 7.32 (m, 4H), 7.29 – 7.25 (m, 2H), 4.67 (s, 1H), 3.64 (s, 4H). ^{13}C NMR (100 MHz, CDCl_3): δ 139.5, 129.6, 128.7, 127.6, 114.6, 72.0, 40.7. FT-IR (ATR): 2360.2, 1558.5, 1507.3, 1457.0, 668.3 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{17}\text{H}_{15}\text{N}_3^+$ $[\text{M}+\text{H}]^+$: 262.1344, found: 262.1341.

bis(1-methyl-1H-indol-3-yl)methane (11)



According to the general procedure, **11** was obtained in 74% yield (20 mg). White solid, mp: 86.1 – 87.2 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.61 (d, $J = 7.9$ Hz, 2H), 7.28 (s, 2H), 7.24 – 7.16 (m, 2H), 7.12 – 7.03 (m, 2H), 6.76 (s, 2H), 4.21 (s, 2H), 3.66 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 137.3, 128.1, 127.1, 121.5, 119.4, 118.7, 114.5, 109.2, 32.7, 21.1. FT-IR (ATR): 2922.8, 1471.5, 1325.1, 1236.4, 1125.9, 737.4 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{18}\text{N}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 297.1368, found: 297.1369.

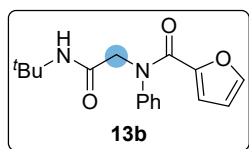
N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-phenyl-4-(trifluoromethyl)benzamide (13a)



According to the general procedure, **13a** was obtained in 74% yield (56 mg). Yellow oil. ^1H NMR (400 MHz, CDCl_3): δ 7.44 (s, 4H), 7.26 – 7.17 (m, 3H), 7.16 – 7.11 (m, 2H), 6.10 (s, 1H), 4.41 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 169.7, 167.4, 143.4, 138.8, 131.8

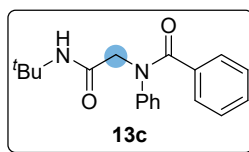
(q, $J = 32.7$ Hz), 129.6, 129.2, 127.6, 127.3, 125.0 (q, $J = 3.9$ Hz), 122.3, 55.7, 51.6, 28.9. ^{19}F NMR (376 MHz, CDCl_3) δ -63.02. FT-IR (ATR): 3315.7, 2969.6, 1636.1, 1546.6, 1493.8, 1321.2, 1125.2, 851.5, 764.0 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 379.1633, found: 379.1645.

N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-phenylfuran-2-carboxamide (13b)



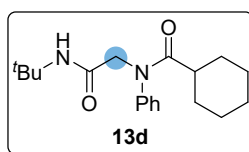
According to the general procedure, **13b** was obtained in 60% yield (36 mg). White solid, mp: 128.5 – 129.4 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.46 – 7.35 (m, 4H), 7.30 – 7.26 (m, 2H), 6.37 (s, 1H), 6.22 (dd, $J = 3.6, 1.7$ Hz, 1H), 5.78 (d, $J = 3.6$ Hz, 1H), 4.34 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 167.7, 159.9, 146.3, 145.0, 142.9, 129.9, 128.6, 128.0, 117.6, 111.3, 56.2, 51.4, 28.8. FT-IR (ATR): 3308.0, 2971.7, 1650.0, 1554.8, 1495.2, 740.3, 698.1 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{NaO}_3^+$ $[\text{M}+\text{Na}]^+$: 323.1372, found: 323.1370.

N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-phenylbenzamide (13c)



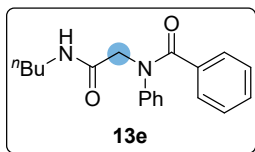
According to the general procedure, **13c** was obtained in 84% yield (53 mg). White solid, mp: 129.1 – 130.3 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.34 – 7.27 (m, 2H), 7.24 – 7.09 (m, 8H), 6.29 (s, 1H), 4.42 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 171.2, 168.0, 143.9, 135.2, 130.2, 129.4, 128.9, 128.0, 127.2, 127.1, 56.0, 51.5, 28.9. FT-IR (ATR): 3312.5, 2965.0, 1645.8, 1594.0, 1542.1, 1496.3, 1268.8, 696.0 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{NaO}_2^+$ $[\text{M}+\text{Na}]^+$: 333.1579, found: 333.1583.

N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-phenylcyclohexancarboxamide (13d)



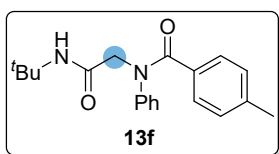
According to the general procedure, **13d** was obtained in 31% yield (20 mg). Light yellow solid, mp: 74.7 – 75.8 °C. ^1H NMR (400 MHz, CDCl_3): δ 7.44 – 7.34 (m, 3H), 7.23 – 7.19 (m, 2H), 6.38 (s, 1H), 4.14 (s, 2H), 2.29 – 2.17 (m, 1H), 1.71 – 1.64 (m, 4H), 1.59 – 1.48 (m, 3H), 1.35 (s, 9H), 1.23 – 1.13 (m, 1H), 1.04 – 0.92 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 177.5, 168.6, 143.0, 130.0, 128.4, 127.5, 55.4, 51.2, 41.4, 29.4, 28.8, 25.6, 25.5. FT-IR (ATR): 3327.8, 2926.1, 1684.1, 1632.4, 1543.8, 1492.8, 1260.6, 701.0 cm^{-1} . HRMS (ESI, m/z): calcd for $\text{C}_{19}\text{H}_{29}\text{N}_2\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 317.2229, found: 317.2228.

N-(2-(butylamino)-2-oxoethyl)-*N*-phenylbenzamide (**13e**)



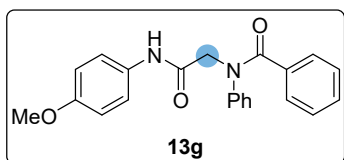
According to the general procedure, **13e** was obtained in 70% yield (43 mg). Yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.36 – 7.30 (m, 2H), 7.28 – 7.07 (m, 8H), 6.58 (s, 1H), 4.51 (s, 2H), 3.32 – 3.24 (m, 2H), 1.54 – 1.46 (m, 2H), 1.38 – 1.31 (m, 2H), 0.91 (t, $J = 7.3$ Hz, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.3, 168.7, 143.9, 135.0, 130.3, 129.4, 129.0, 127.9, 127.2, 127.1, 55.2, 39.4, 31.7, 20.1, 13.8. **FT-IR (ATR)**: 3306.6, 2957.3, 1630.5, 1595.0, 1547.8, 1492.0, 1225.6, 728.3, 695.7 cm^{-1} . **HRMS (ESI, m/z)**: calcd for $\text{C}_{19}\text{H}_{22}\text{N}_2\text{NaO}_2^+$ [$\text{M}+\text{Na}$] $^+$: 333.1579, found: 333.1587.

N-(2-(*tert*-butylamino)-2-oxoethyl)-4-methyl-*N*-phenylbenzamide (**13f**)



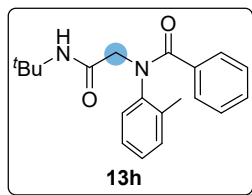
According to the general procedure, **13f** was obtained in 64% yield (42 mg). Yellow oil. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.24 – 7.19 (m, 4H), 7.17 – 7.13 (m, 1H), 7.12 – 7.08 (m, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.35 (s, 1H), 4.41 (s, 2H), 2.26 (s, 3H), 1.36 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.2, 168.1, 144.1, 140.6, 132.1, 129.4, 129.1, 128.6, 127.2, 127.0, 56.1, 51.4, 28.9, 21.5. **FT-IR (ATR)**: 3316.3, 2967.9, 1736.8, 1631.1, 1595.4, 1544.1, 1493.1, 1237.0, 829.5, 756.1, 697.9 cm^{-1} . **HRMS (ESI, m/z)**: calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{NaO}_2^+$ [$\text{M}+\text{Na}$] $^+$: 347.1735, found: 347.1743.

N-(2-((4-methoxyphenyl)amino)-2-oxoethyl)-*N*-phenylbenzamide (**13g**)



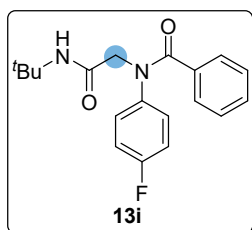
According to the general procedure, **13g** was obtained in 36% yield (26 mg). Brown solid, **mp**: 157.8 – 158.9 $^{\circ}\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.68 (s, 1H), 7.46 – 7.39 (m, 2H), 7.38 – 7.32 (m, 2H), 7.28 – 7.19 (m, 4H), 7.19 – 7.13 (m, 4H), 6.84 – 6.78 (m, 2H), 4.66 (s, 2H), 3.77 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3): δ 171.8, 166.8, 156.5, 143.8, 134.8, 134.7, 131.1, 130.5, 129.5, 129.1, 128.0, 127.4, 121.8, 114.2, 56.2, 55.6. **FT-IR (ATR)**: 3312.9, 2952.6, 1685.4, 1619.3, 1544.0, 1508.5, 831.7, 724.1, 696.6 cm^{-1} . **HRMS (ESI, m/z)**: calcd for $\text{C}_{22}\text{H}_{20}\text{N}_2\text{NaO}_3^+$ [$\text{M}+\text{Na}$] $^+$: 383.1372, found: 383.1362.

N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-(*o*-tolyl)benzamide (**13h**)



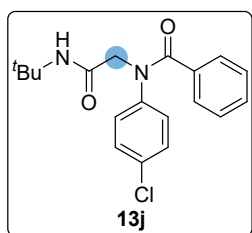
According to the general procedure, **13h** was obtained in 62% yield (40 mg). White solid, mp: 140.3 – 141.4 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.19 – 7.08 (m, 6H), 6.66 (s, 1H), 4.61 (d, *J* = 14.4 Hz, 1H), 3.98 (d, *J* = 14.5 Hz, 1H), 2.16 (s, 3H), 1.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 171.4, 167.9, 142.4, 135.0, 134.7, 131.5, 130.3, 129.0, 128.5, 128.3, 127.8, 127.2, 56.1, 51.4, 28.9, 18.0. FT-IR (ATR): 3323.5, 2963.9, 1662.3, 1651.3, 1541.6, 1221.0, 749.8, 701.0 cm⁻¹. HRMS (ESI, *m/z*): calcd for C₂₀H₂₄N₂NaO₂⁺ [*M*+Na]⁺: 347.1735, found: 347.1727.

N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-(4-fluorophenyl)benzamide (**13i**)



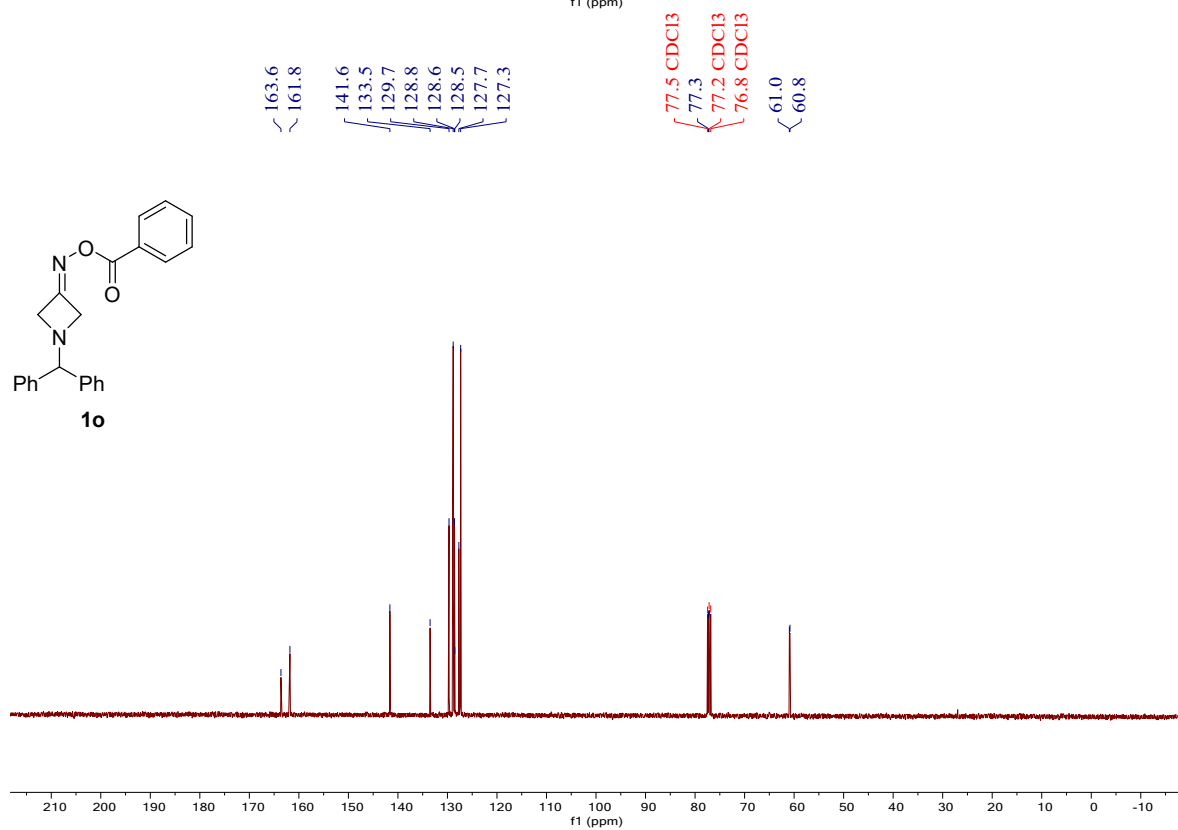
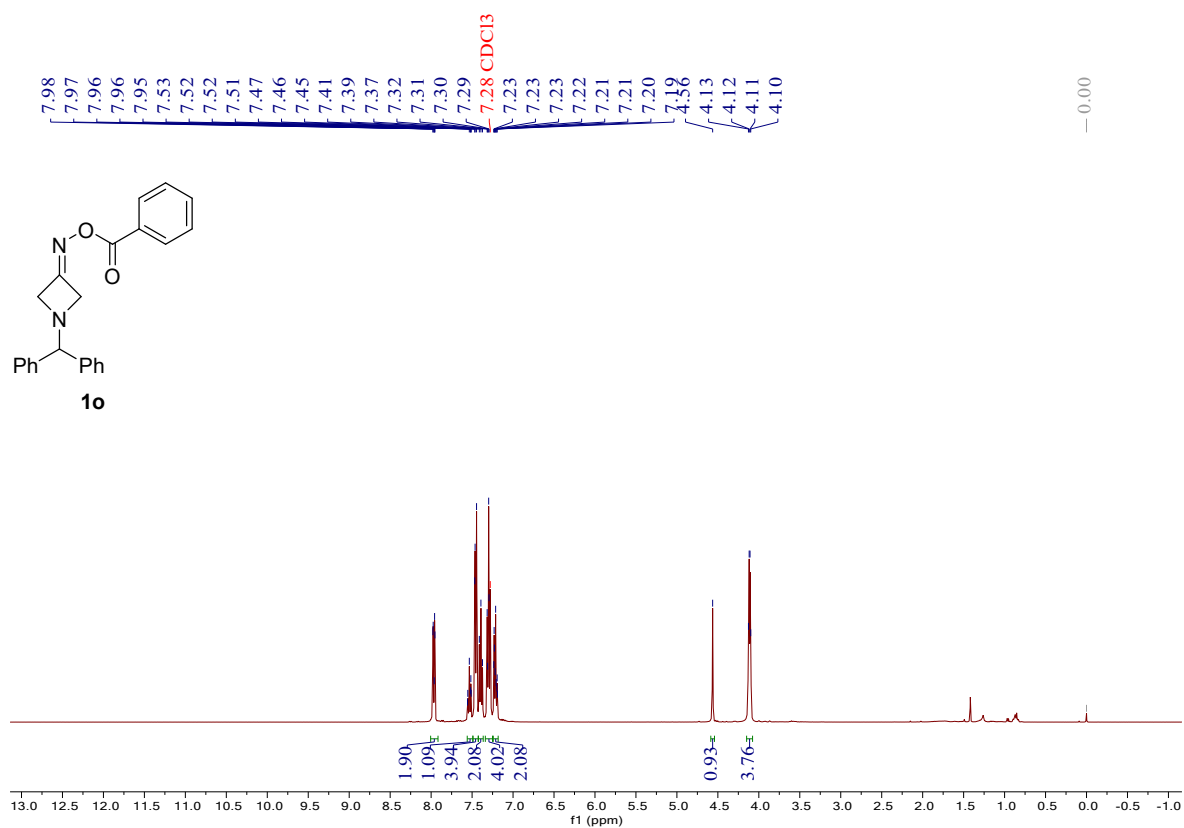
According to the general procedure, **13i** was obtained in 62% yield (40 mg). Yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.32 – 7.25 (m, 3H), 7.22 – 7.17 (m, 2H), 7.14 – 7.08 (m, 2H), 6.93 – 6.87 (m, 2H), 6.24 (s, 1H), 4.37 (s, 2H), 1.37 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 171.2, 167.8, 161.2 (d, *J* = 247.7 Hz), 140.0 (d, *J* = 3.2 Hz), 135.0, 130.2, 129.1 (d, *J* = 8.5 Hz), 128.8, 128.1, 116.2 (d, *J* = 22.8 Hz), 55.9, 51.5, 28.9. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.22. FT-IR (ATR): 3311.0, 2965.3, 1671.4, 1642.1, 1509.1, 1216.5, 845.9, 722.8, 696.2 cm⁻¹. HRMS (ESI, *m/z*): calcd for C₁₉H₂₁FN₂NaO₂⁺ [*M*+Na]⁺: 351.1485, found: 351.1475.

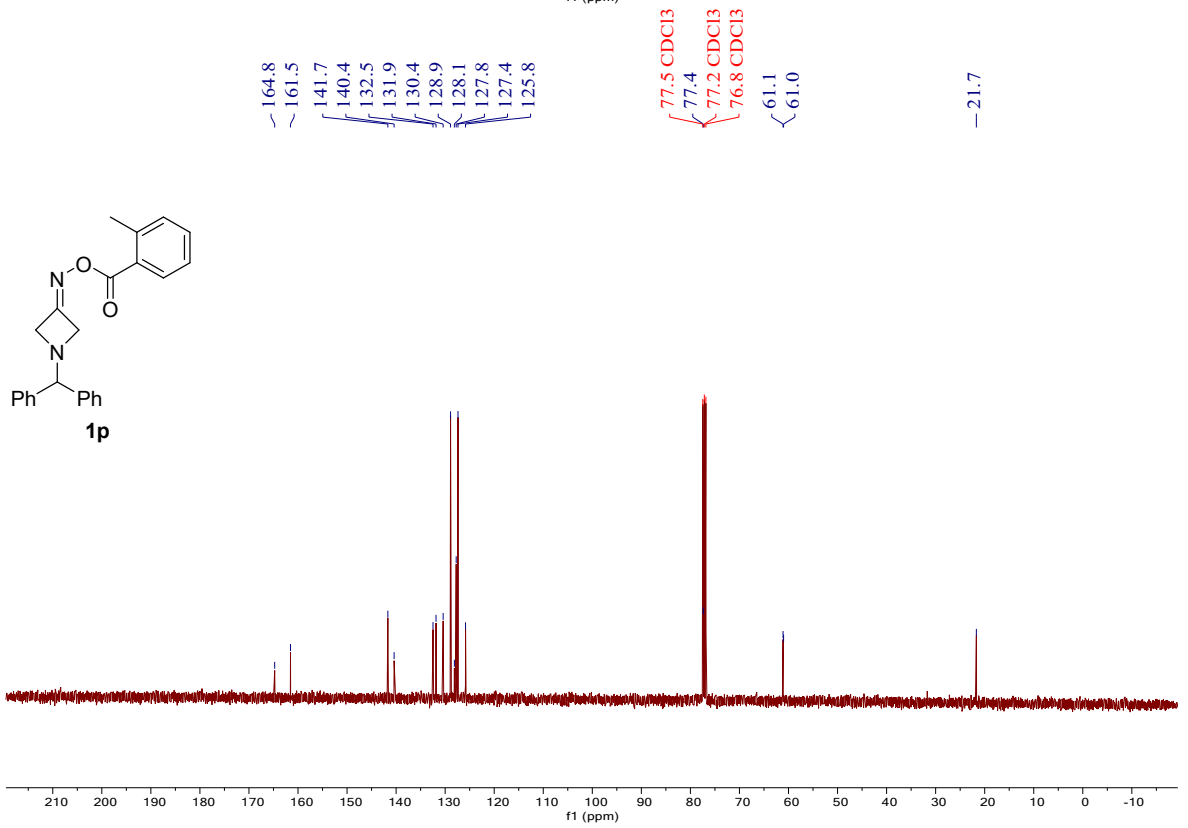
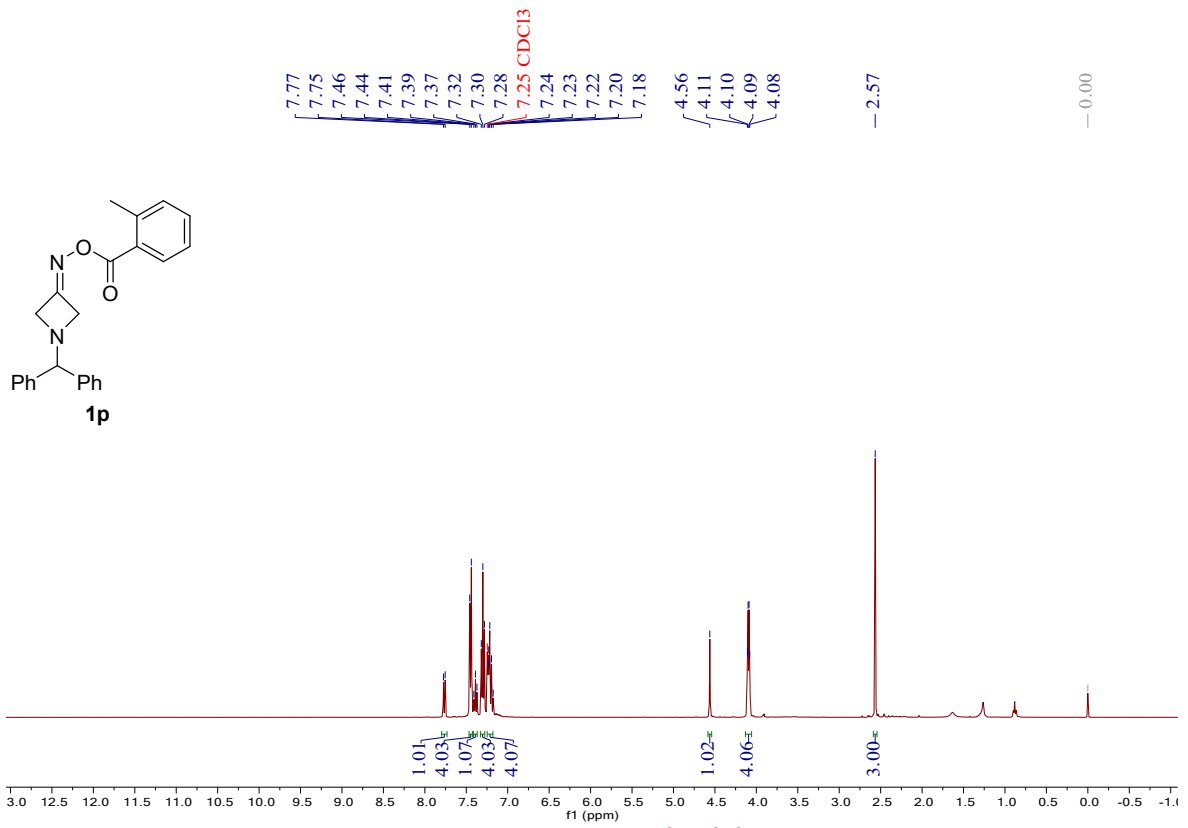
N-(2-(*tert*-butylamino)-2-oxoethyl)-*N*-(4-chlorophenyl)benzamide (**13j**)

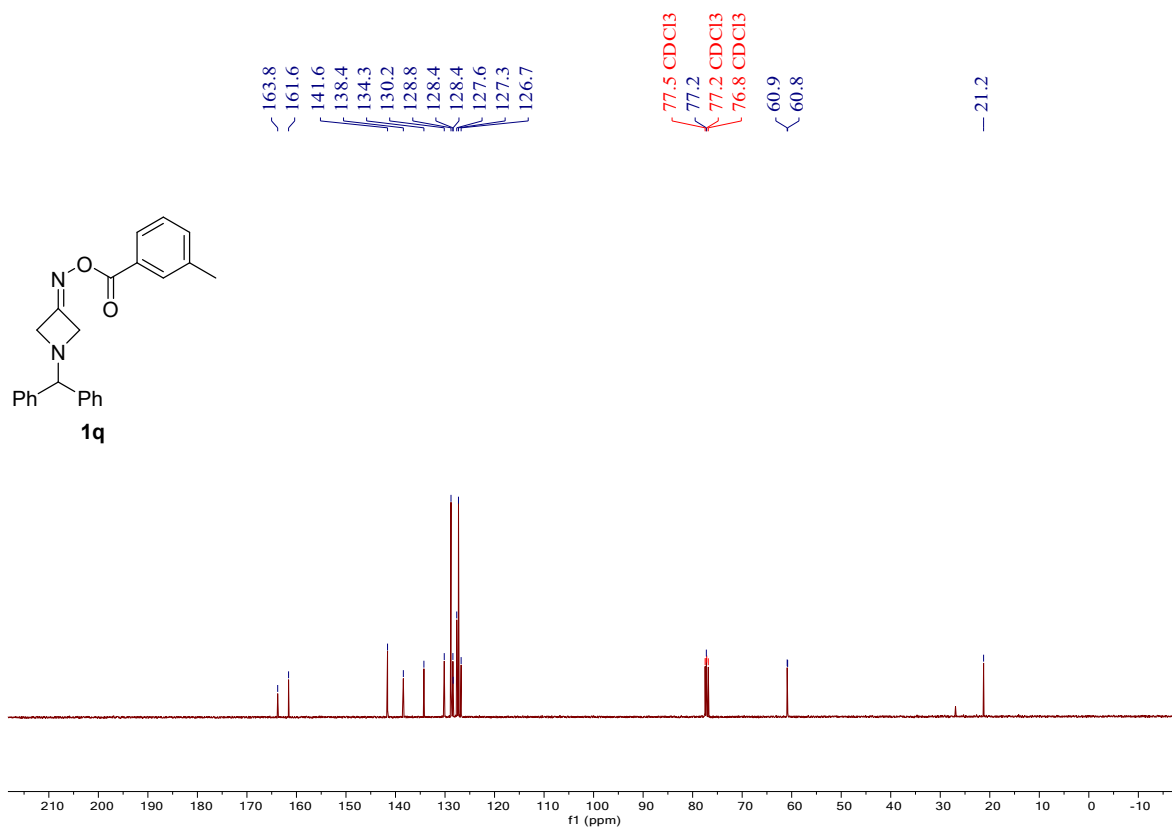
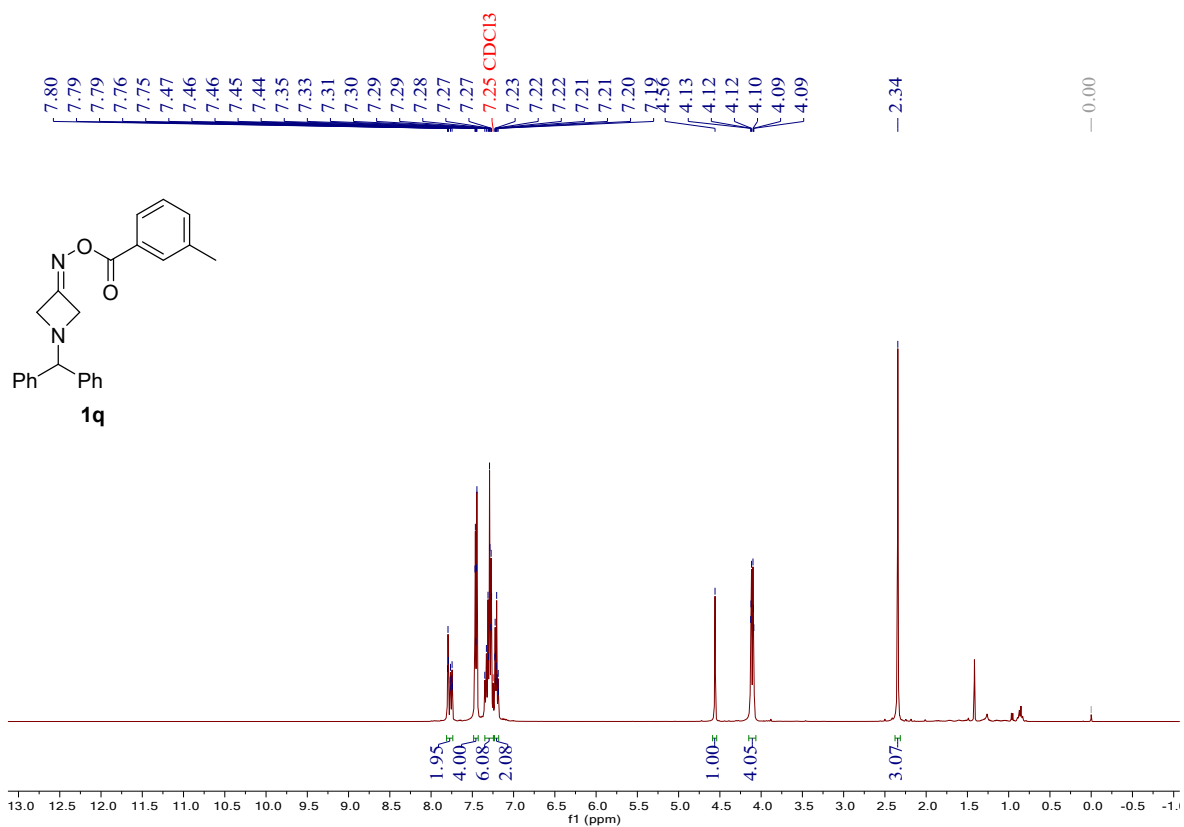


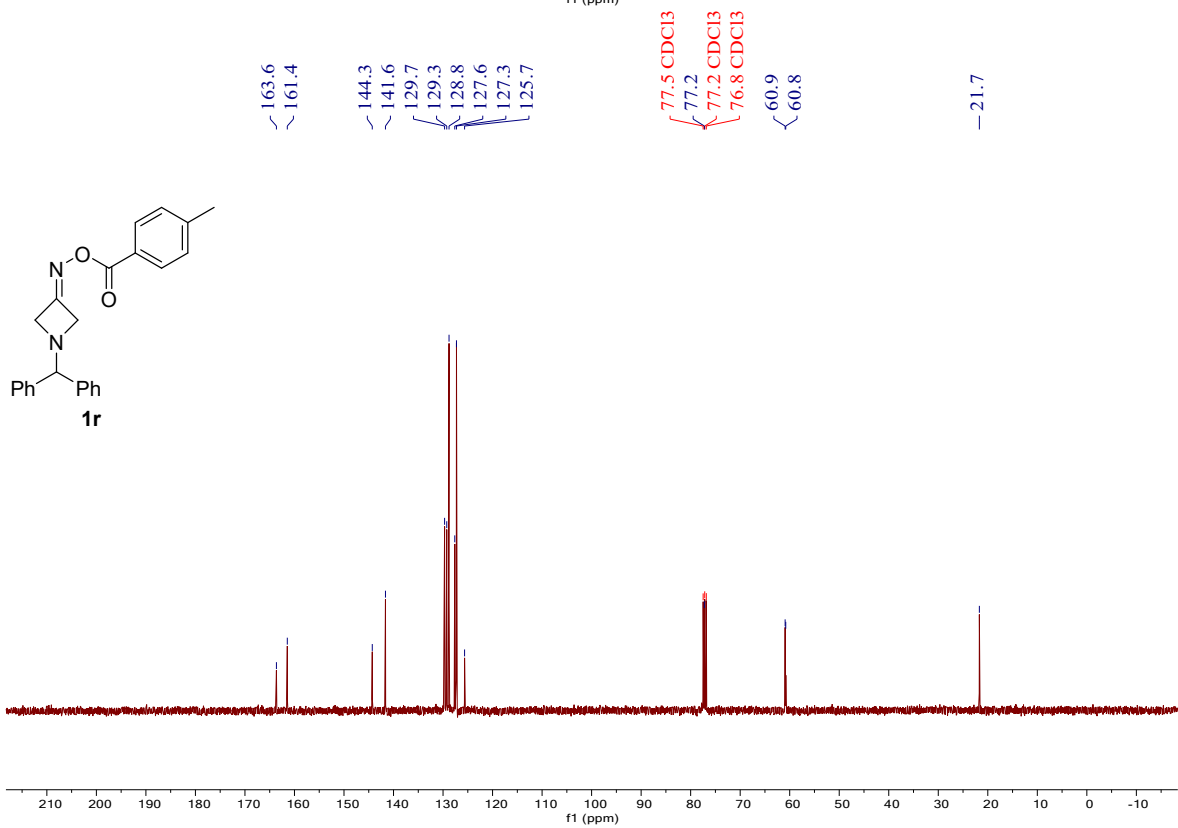
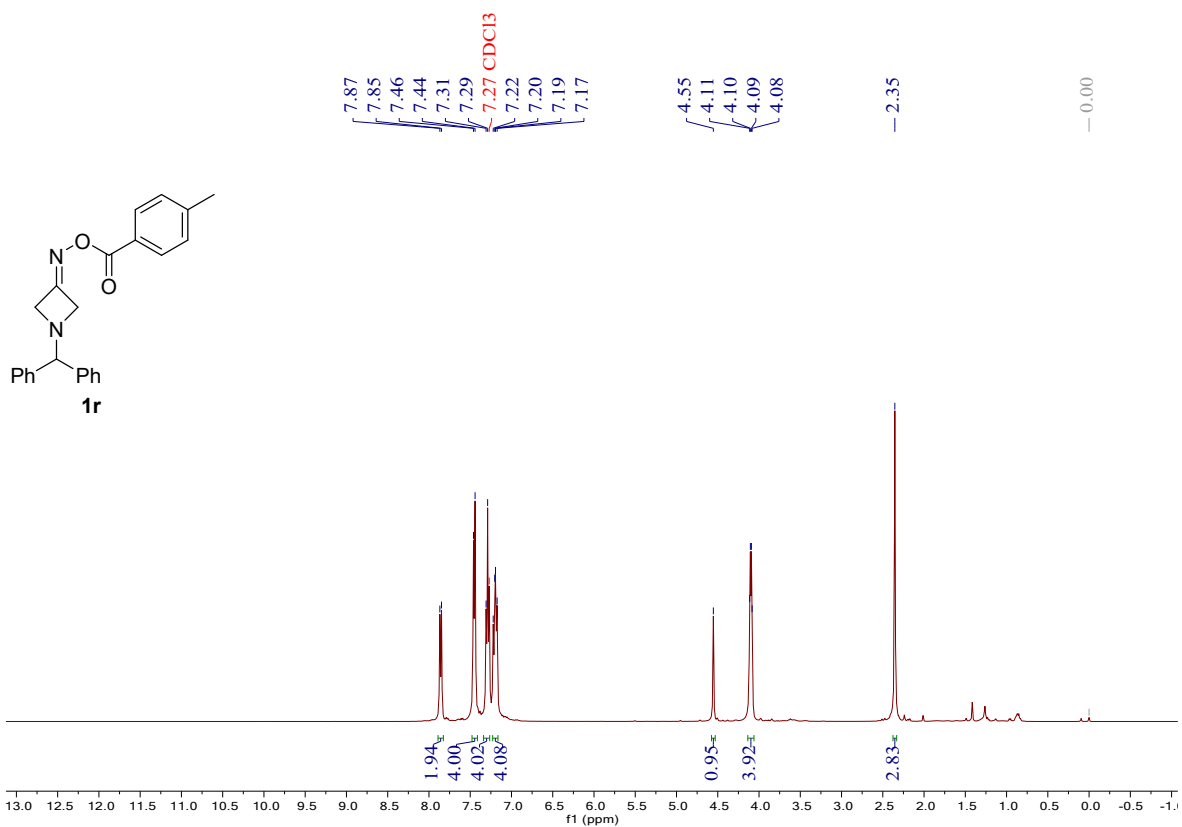
According to the general procedure, **13j** was obtained in 65% yield (45 mg). Light yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 7.33 – 7.27 (m, 3H), 7.23 – 7.15 (m, 4H), 7.10 – 7.03 (m, 2H), 6.19 (s, 1H), 4.37 (s, 2H), 1.36 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): δ 171.1, 167.7, 142.6, 134.8, 132.7, 130.4, 129.5, 128.9, 128.5, 128.1, 55.7, 51.6, 28.9. FT-IR (ATR): 3329.5, 2965.2, 1664.8, 1649.0, 1575.5, 1491.8, 1221.0, 841.4, 714.6, 698.0 cm⁻¹. HRMS (ESI, *m/z*): calcd for C₁₉H₂₁ClN₂NaO₂⁺ [*M*+Na]⁺: 367.1189, found: 367.1179.

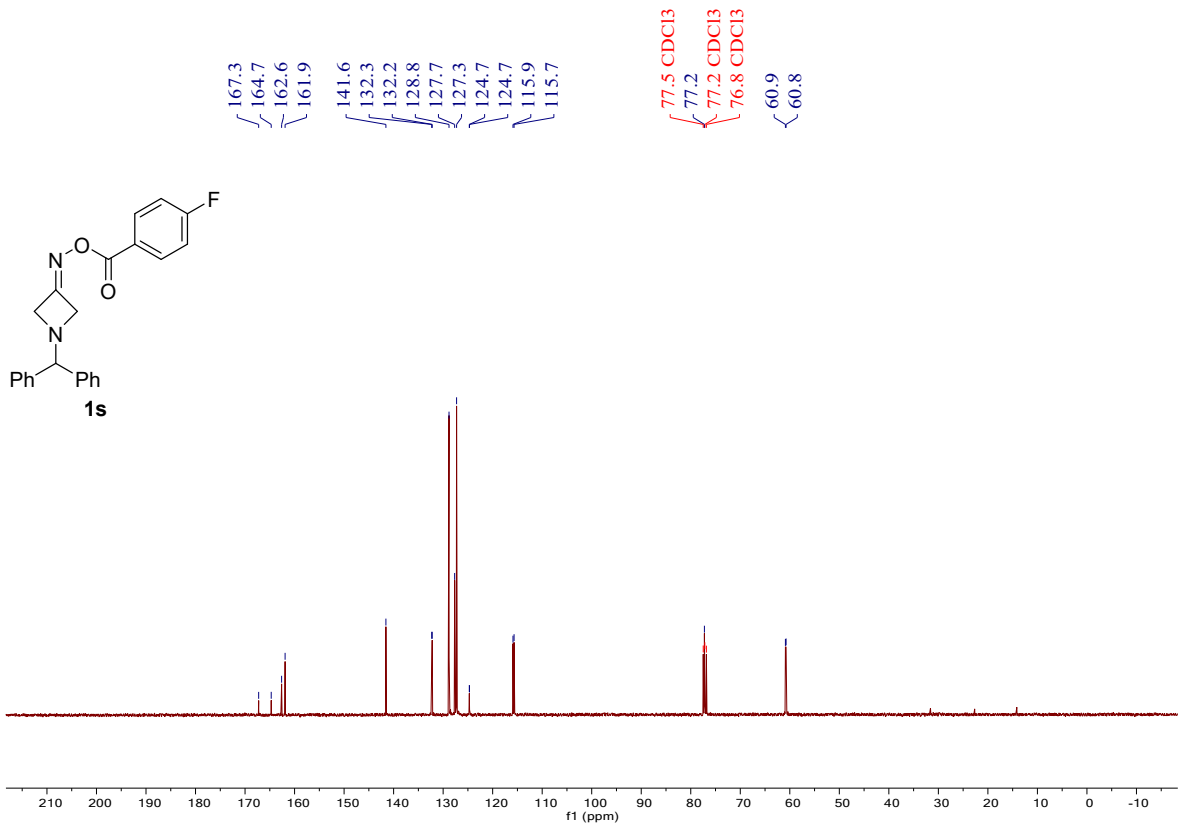
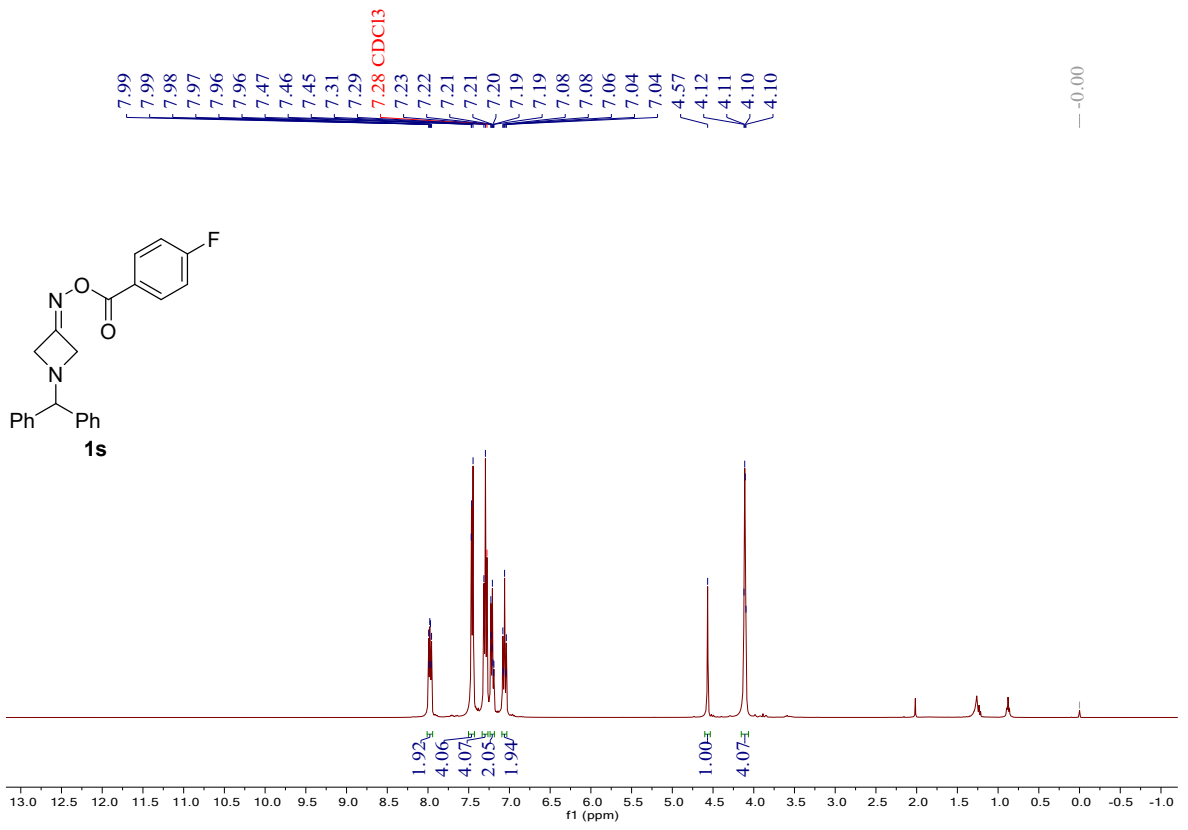
6. ^1H , ^{13}C and ^{19}F NMR spectra of new substrates and all products

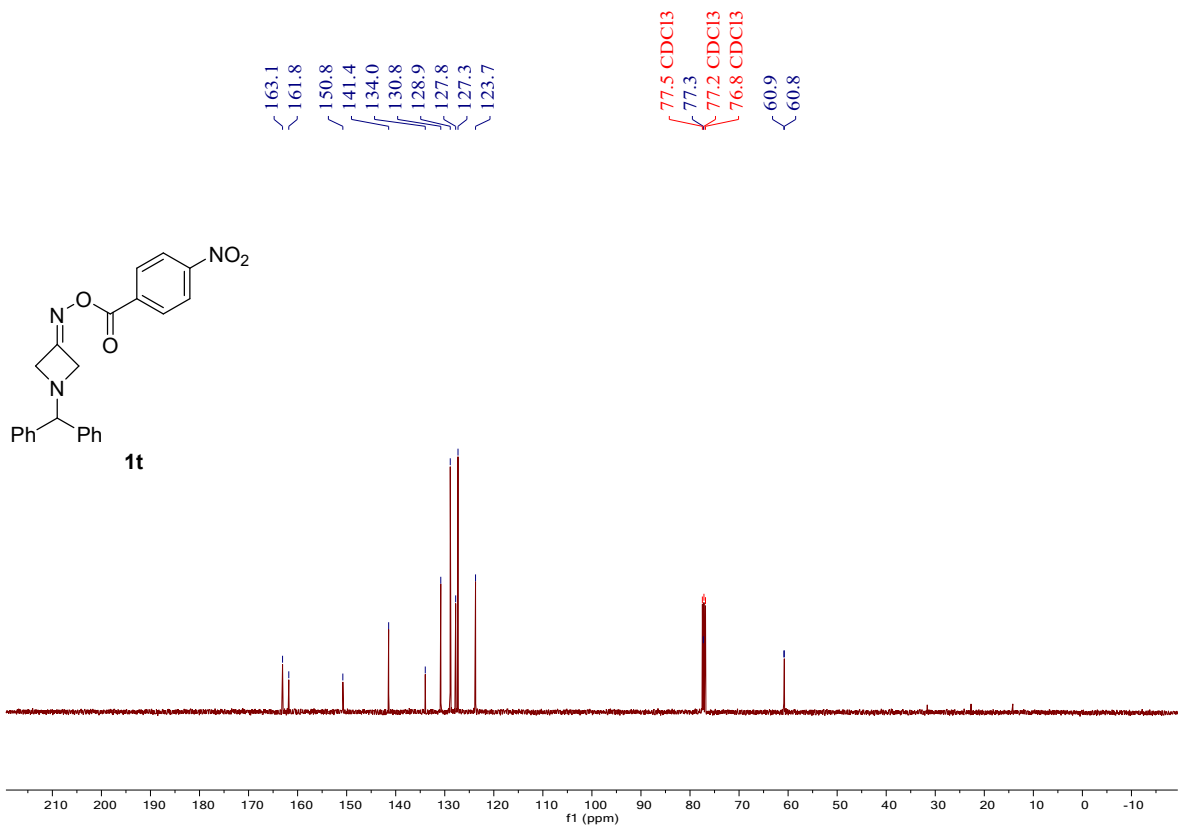
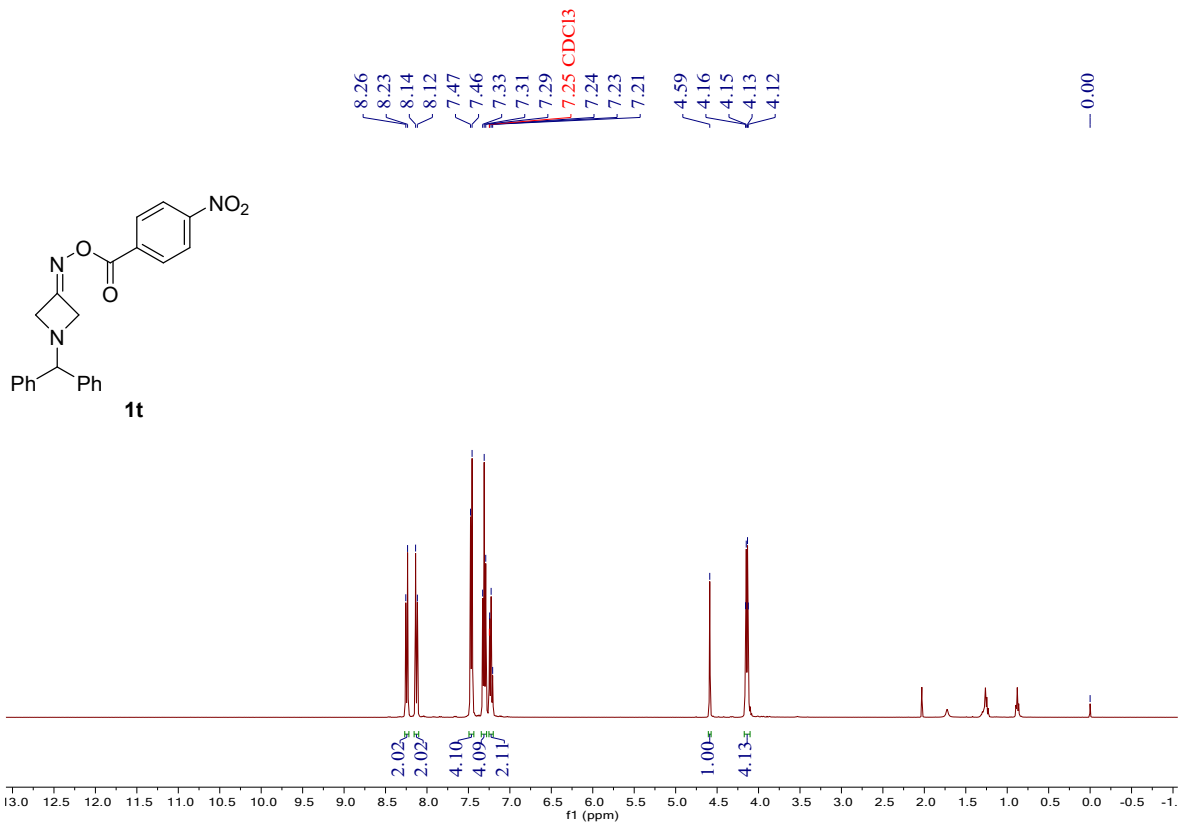


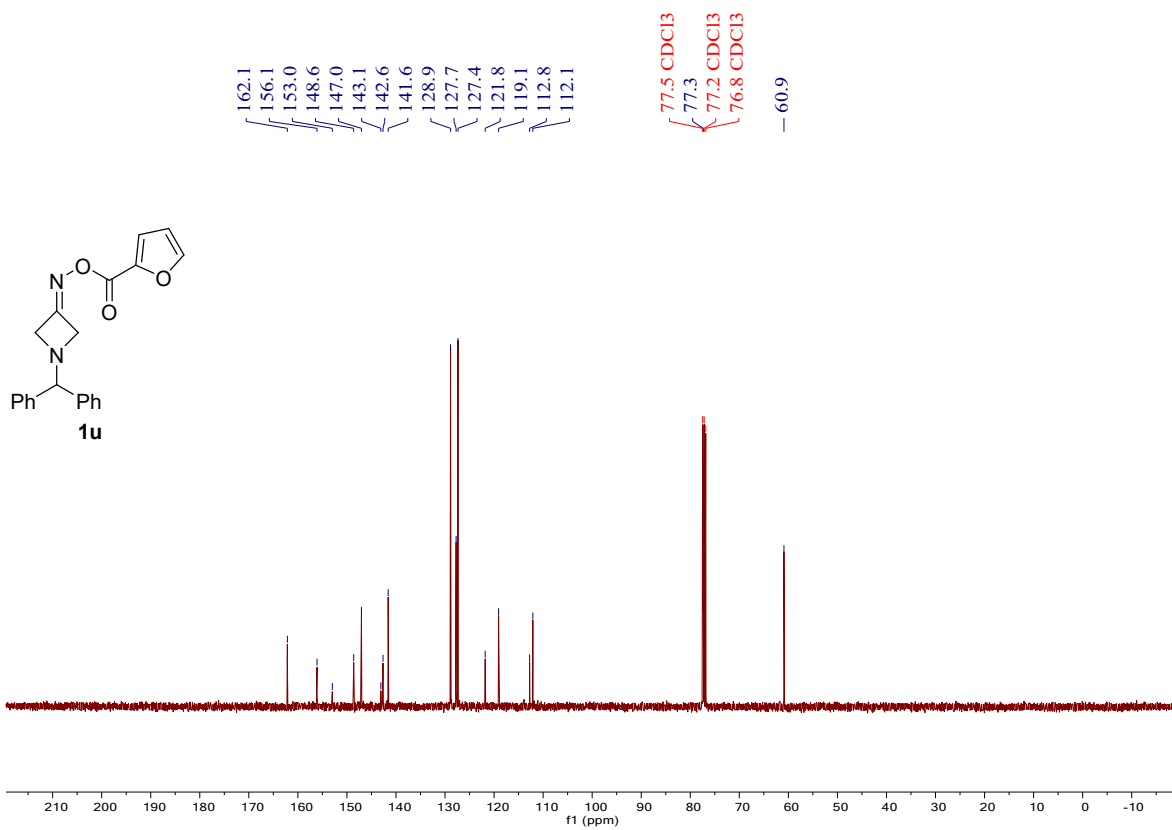
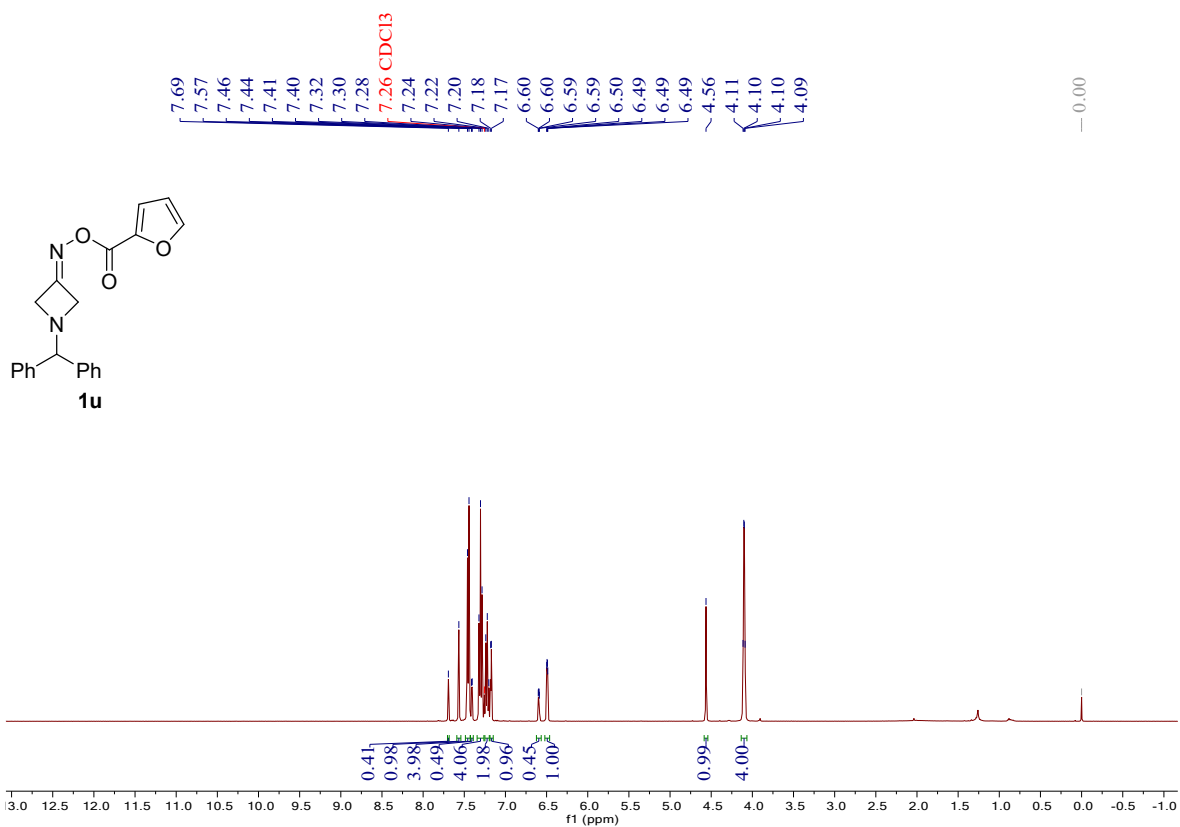


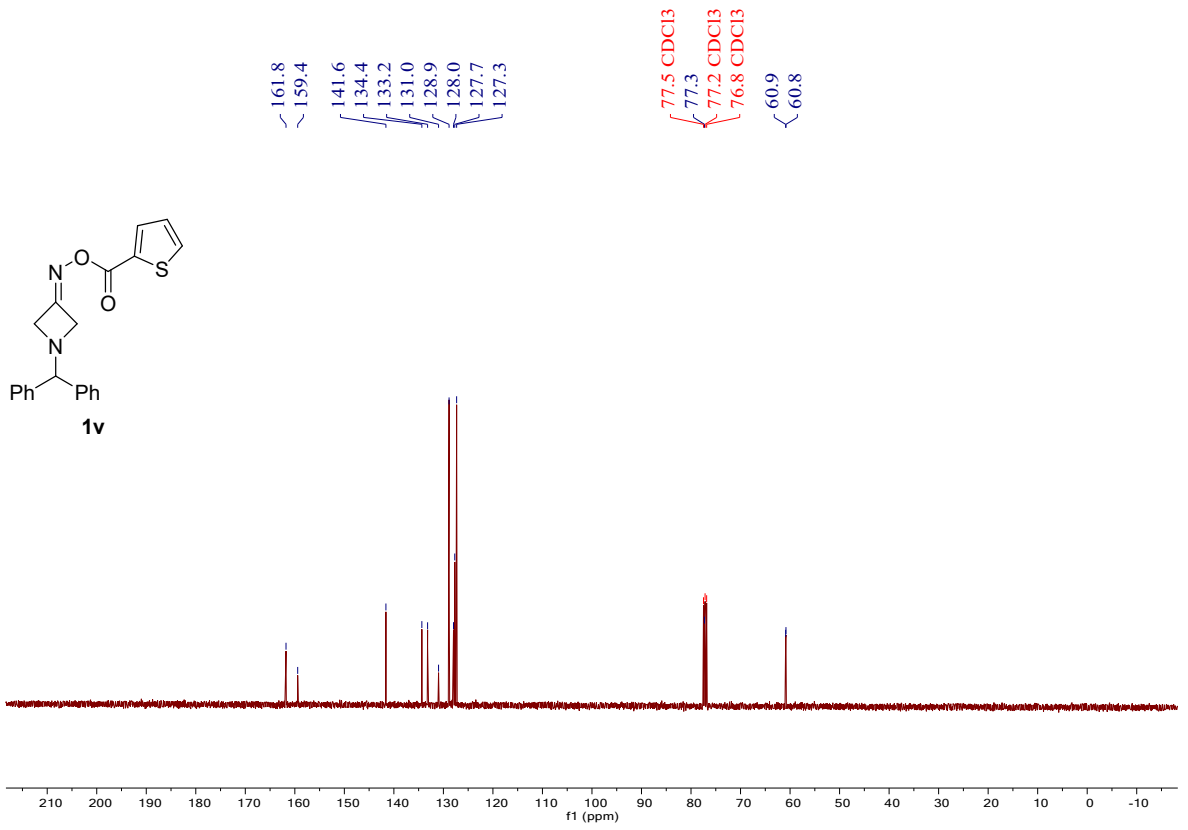
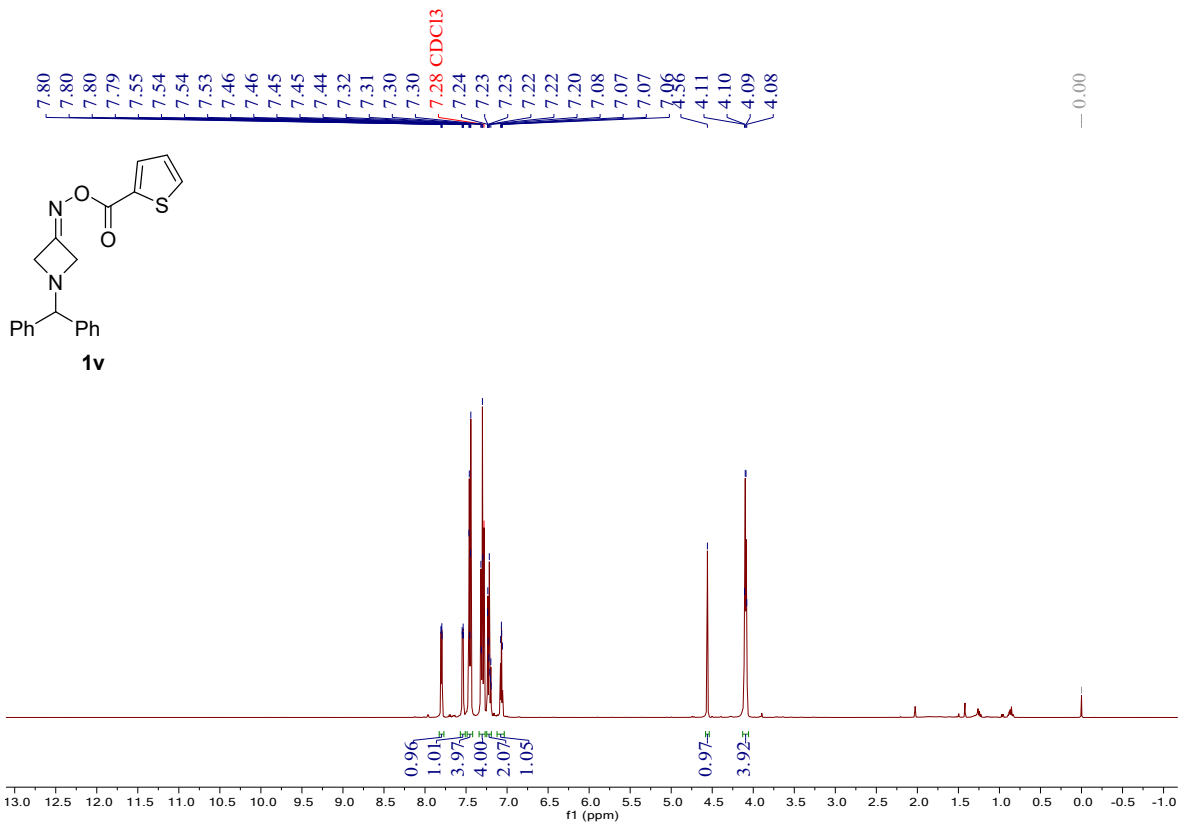


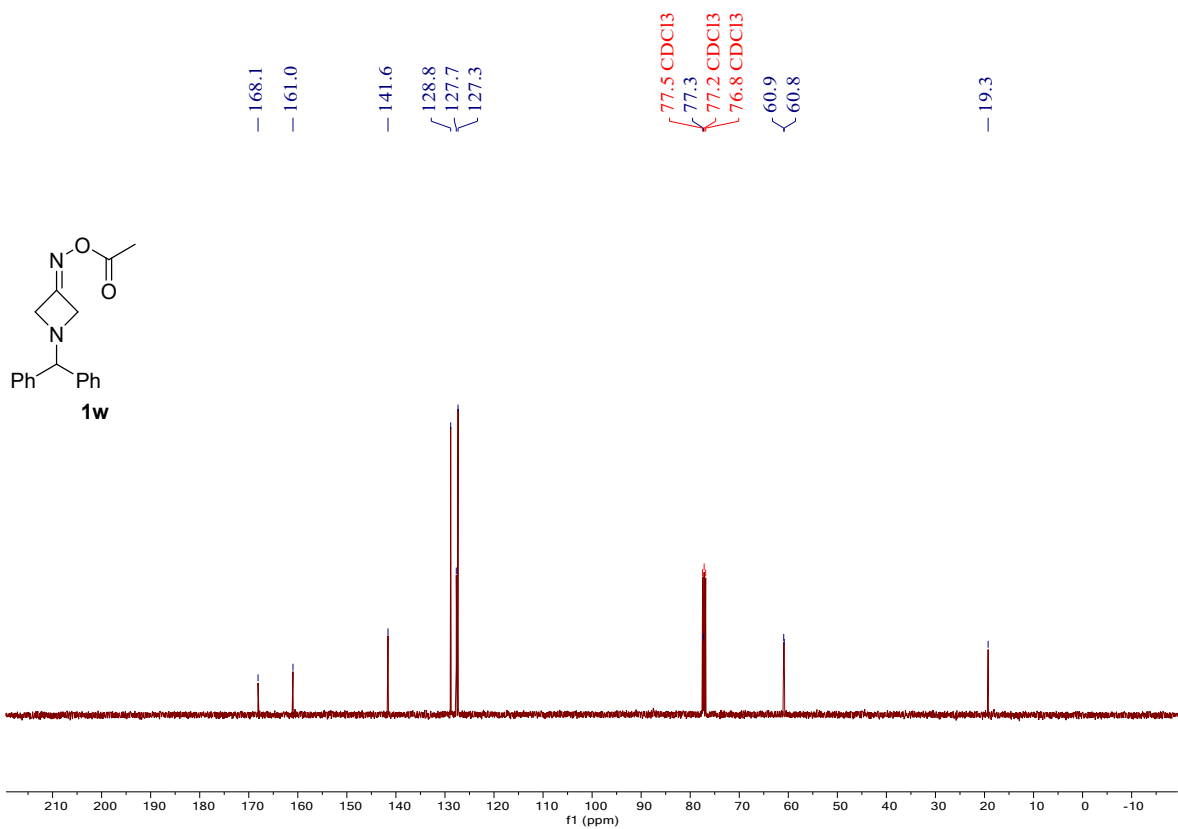
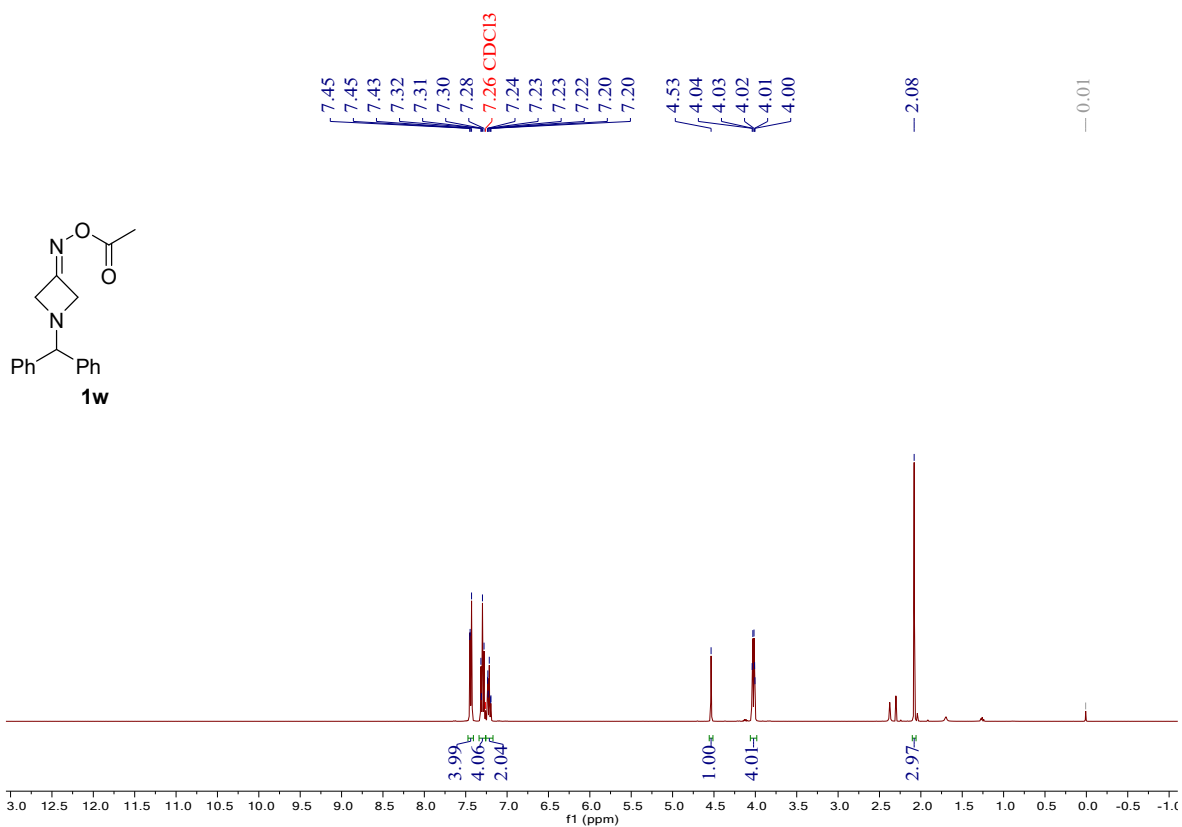


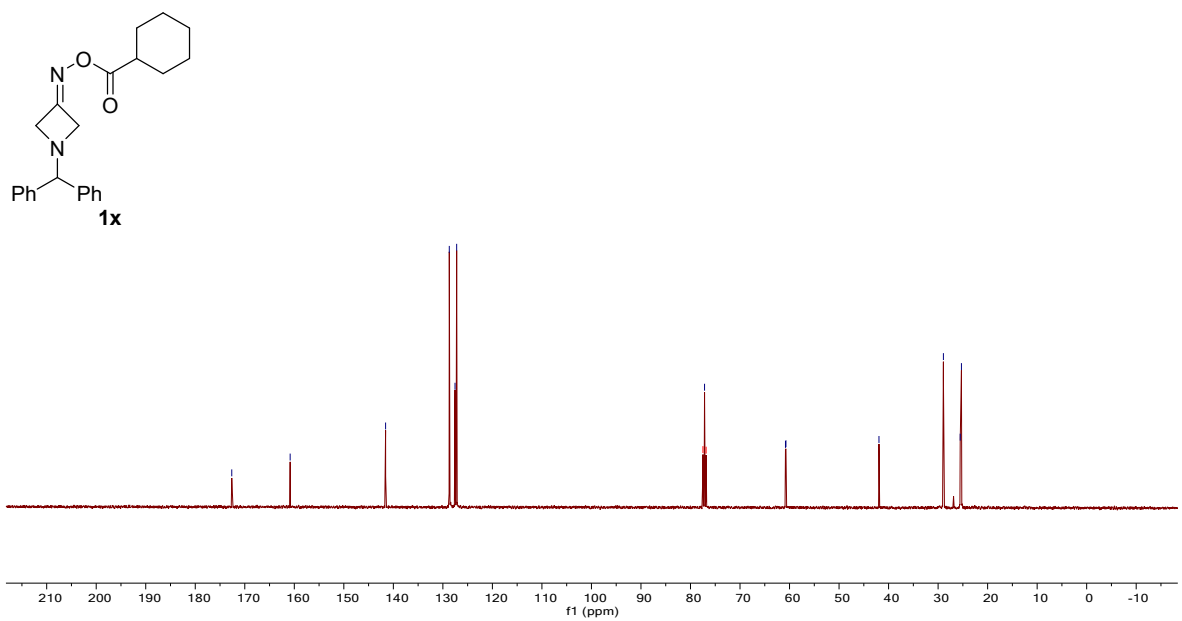
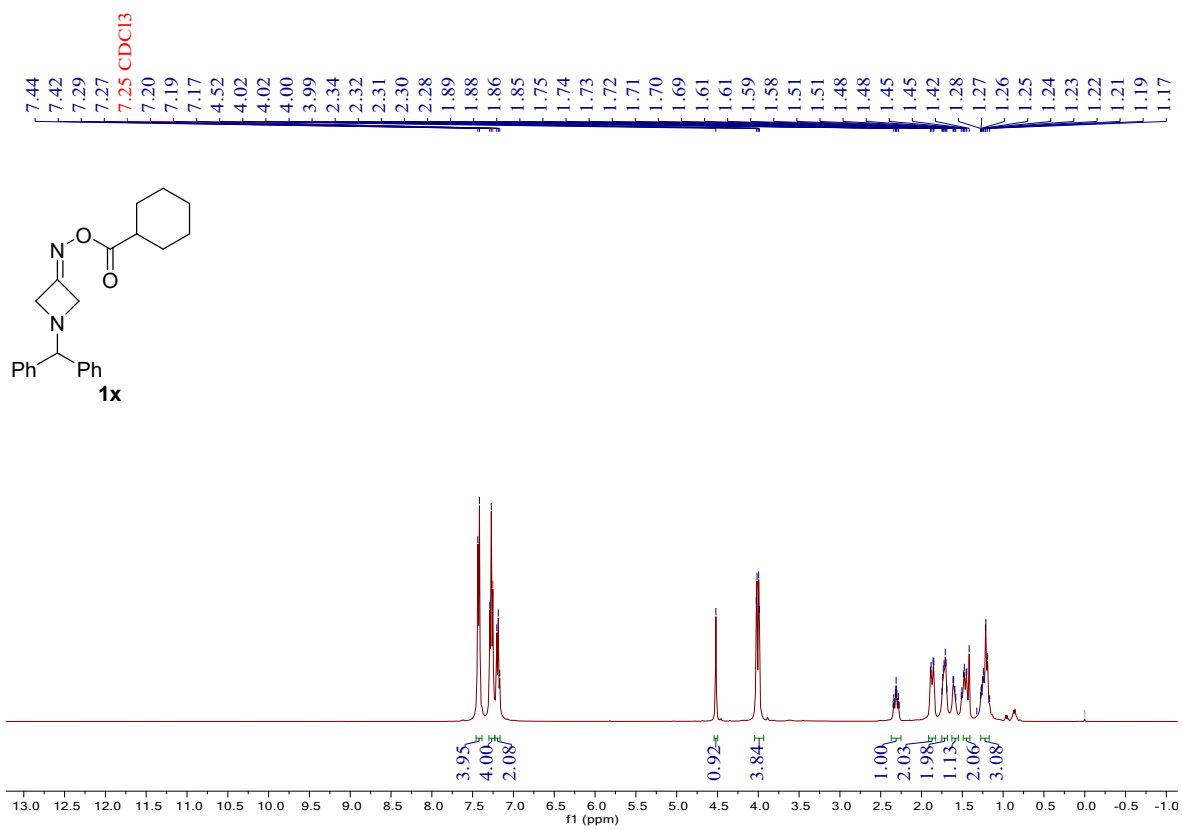


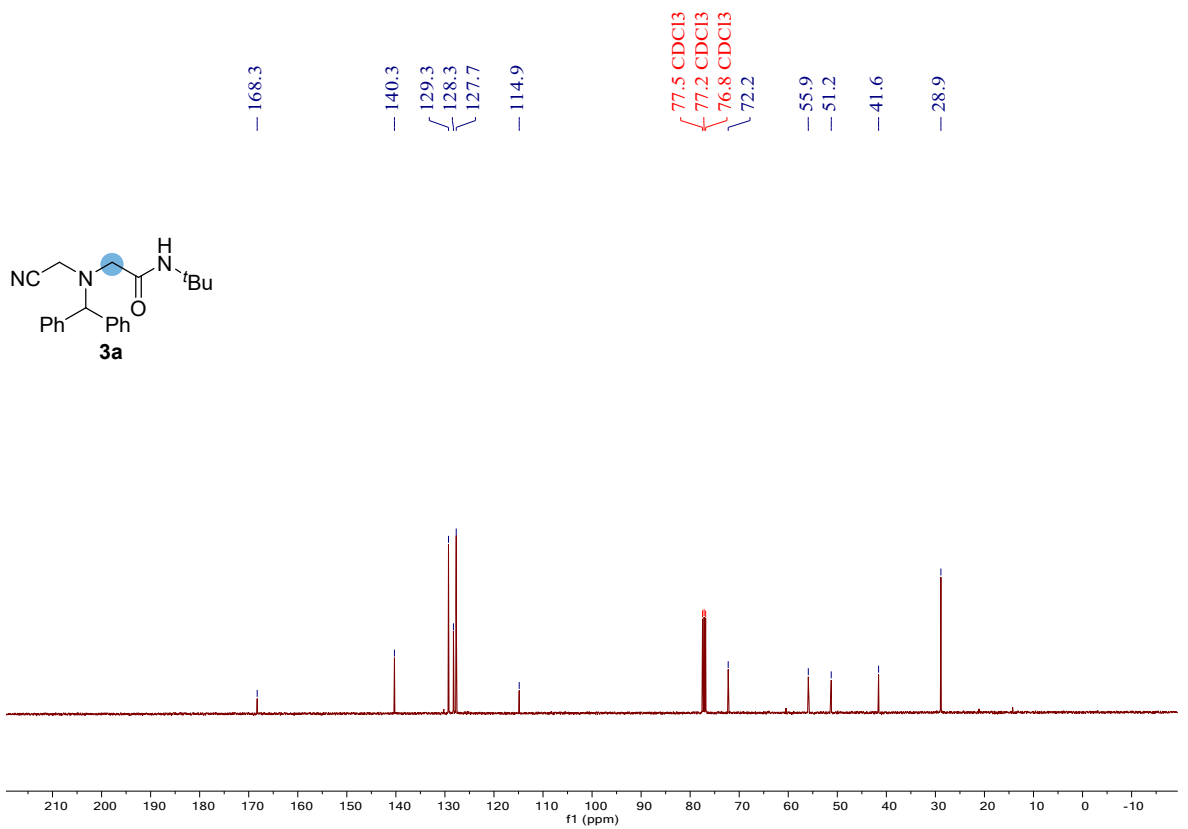
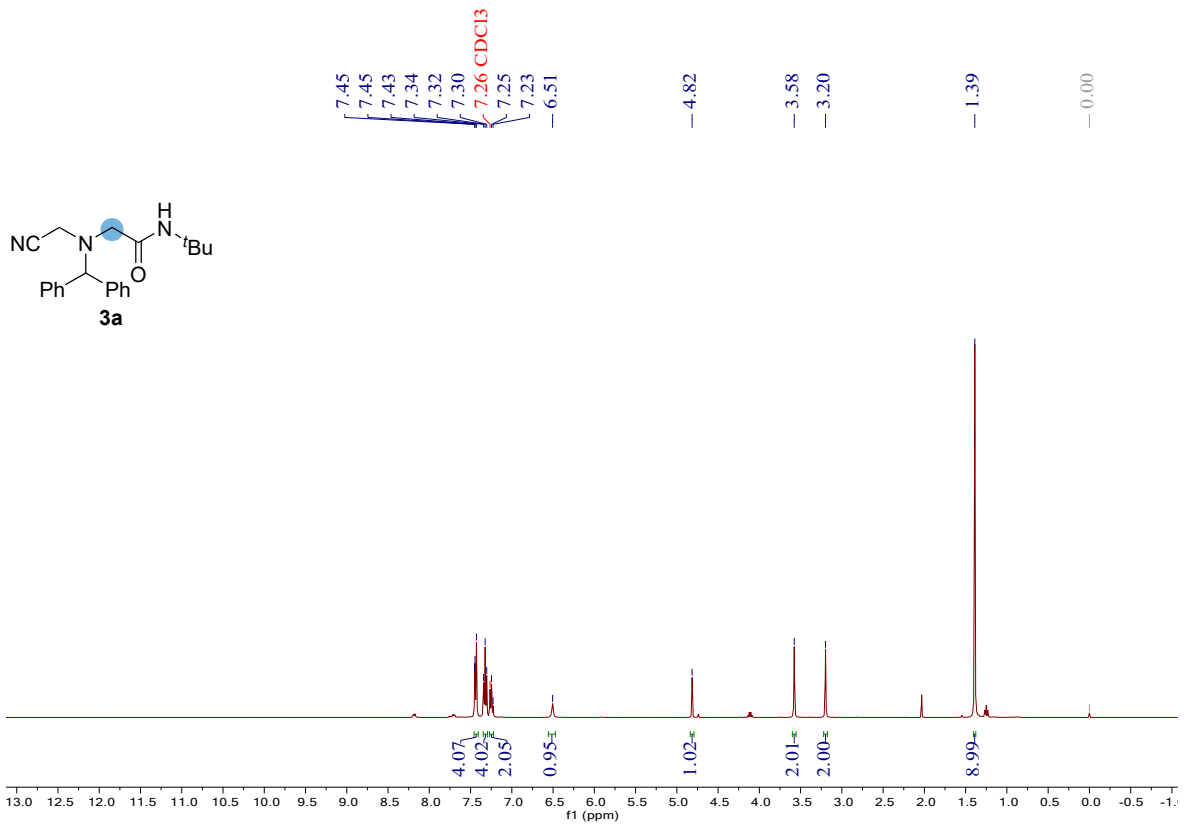


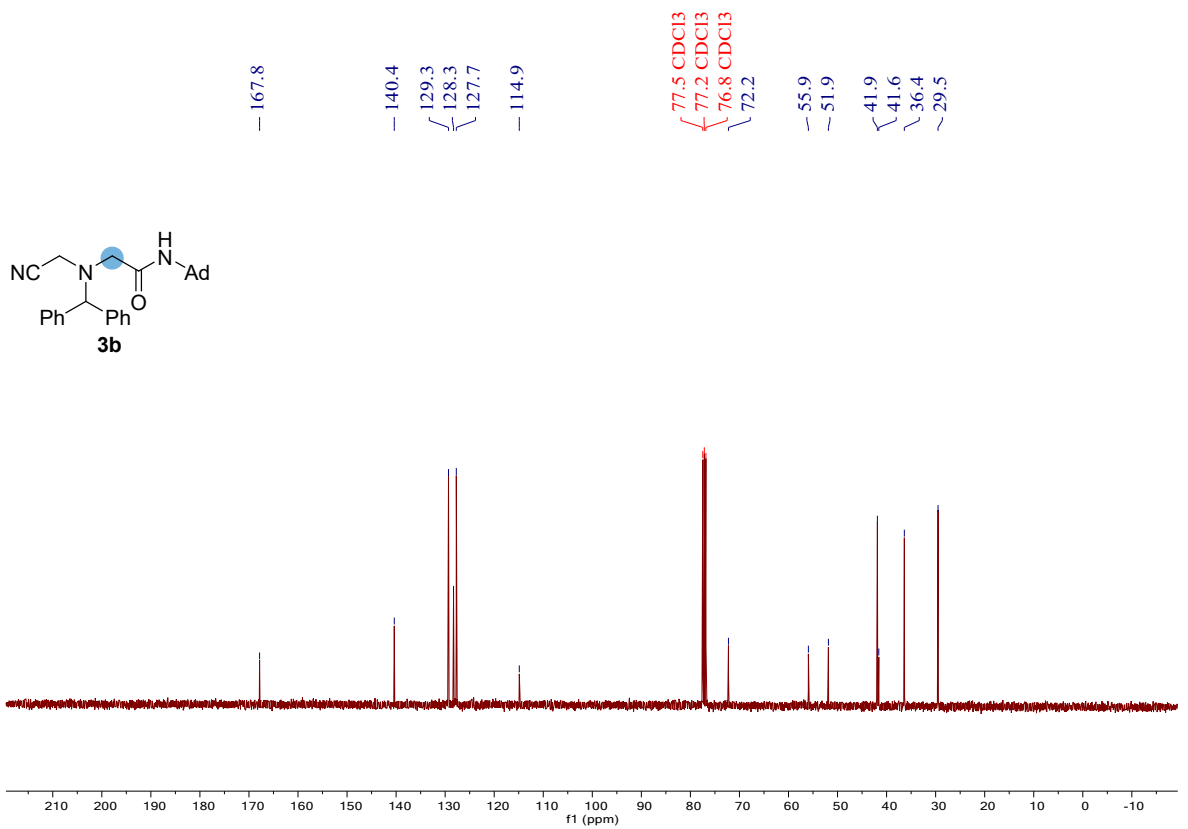
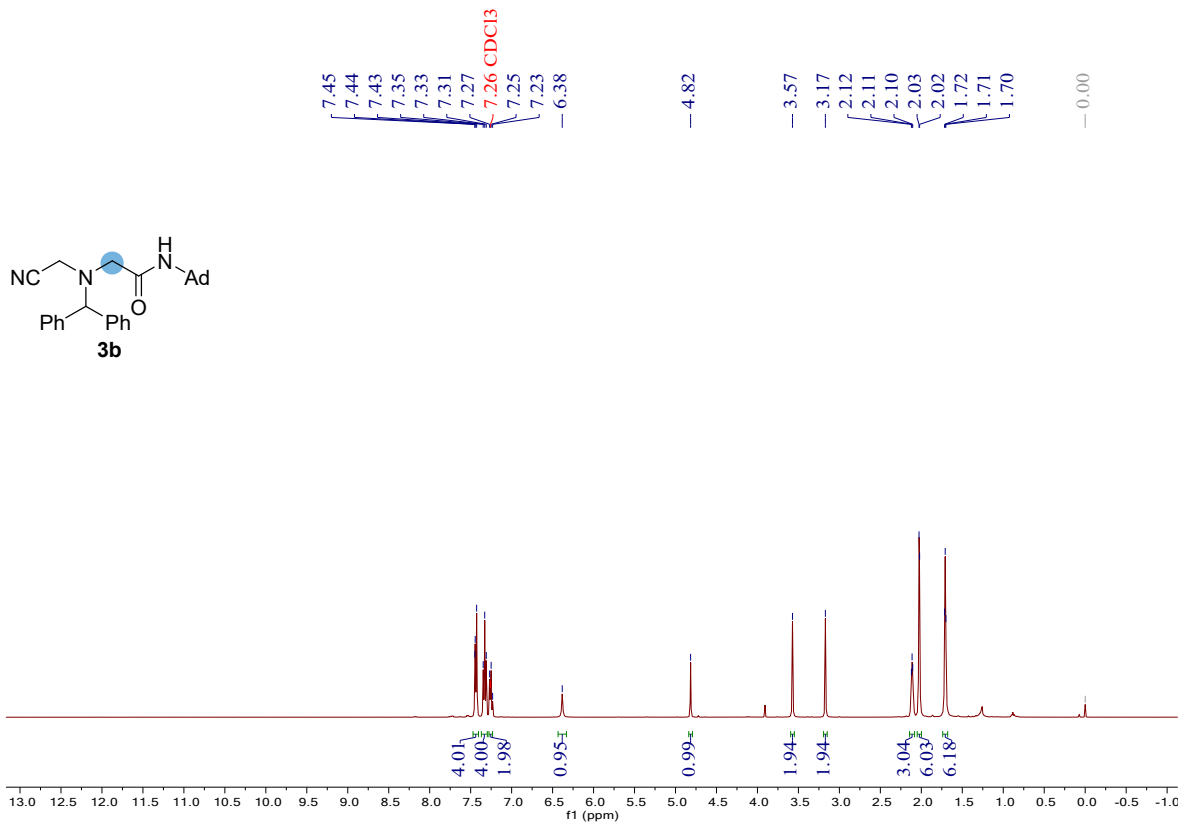


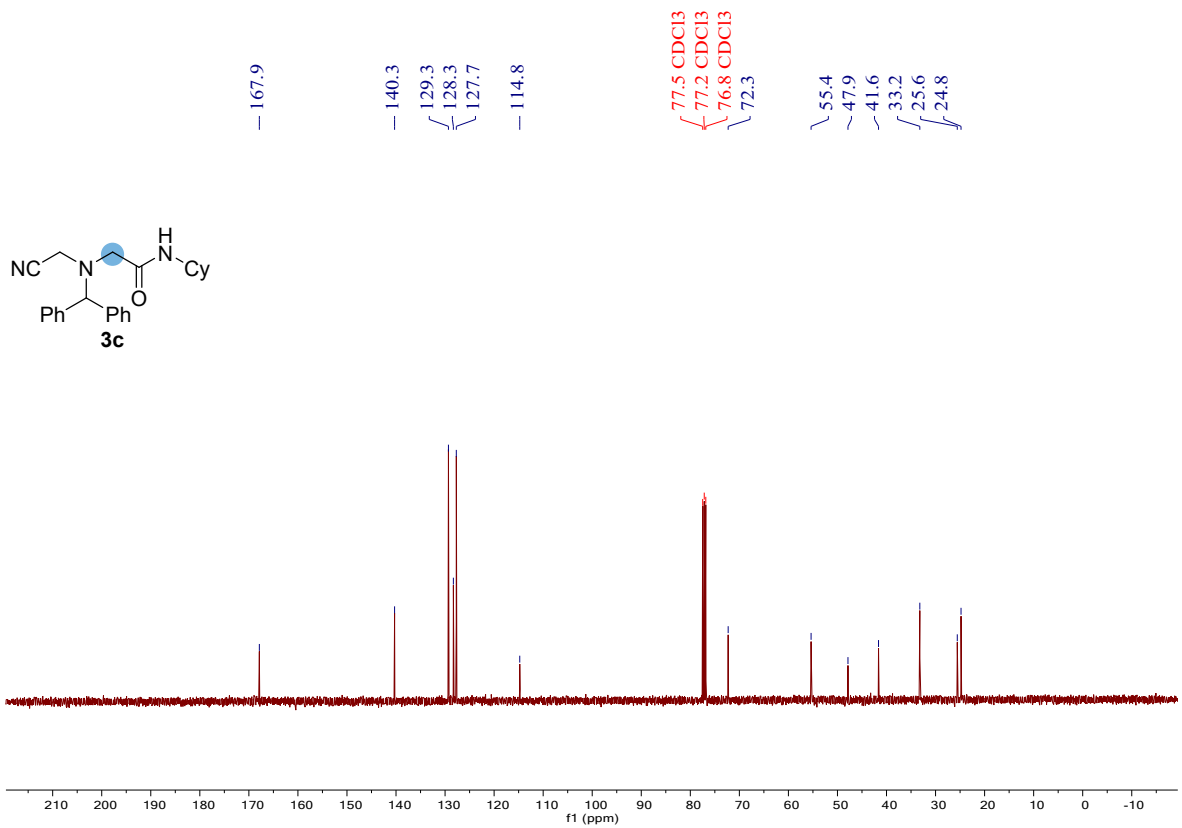
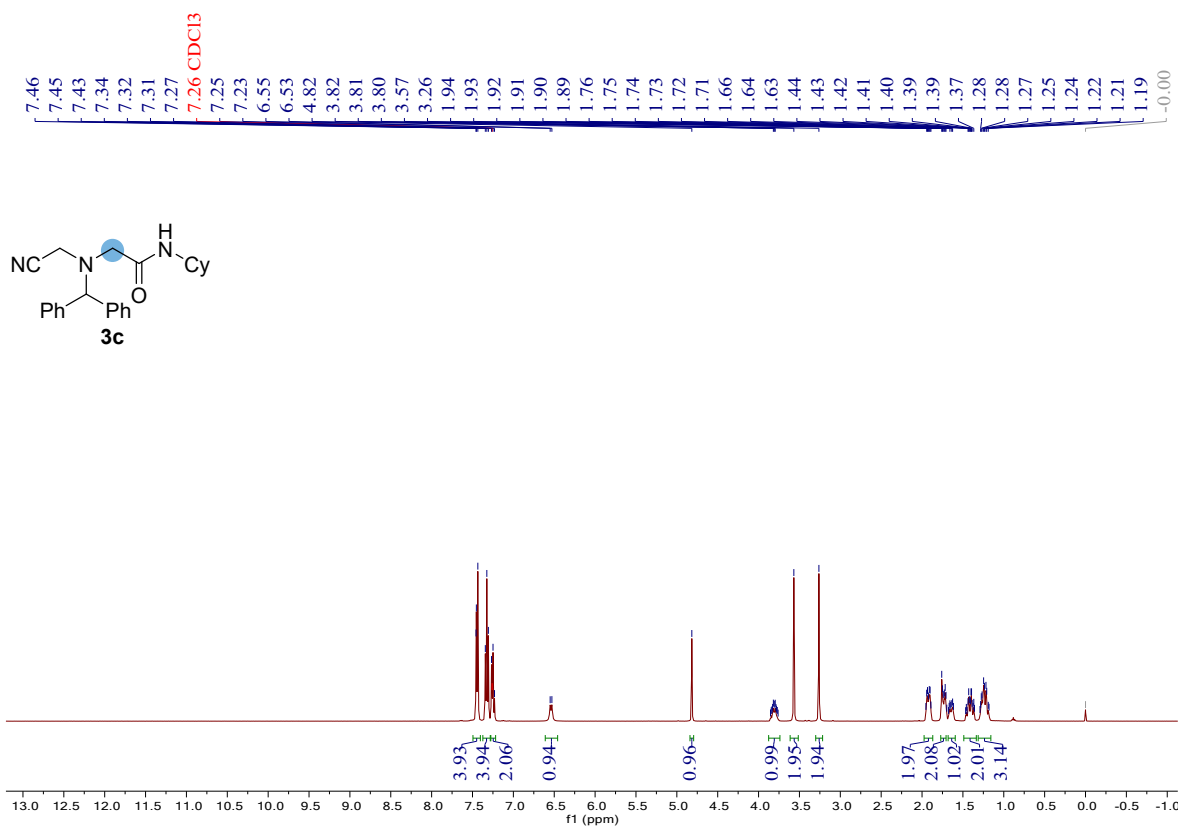


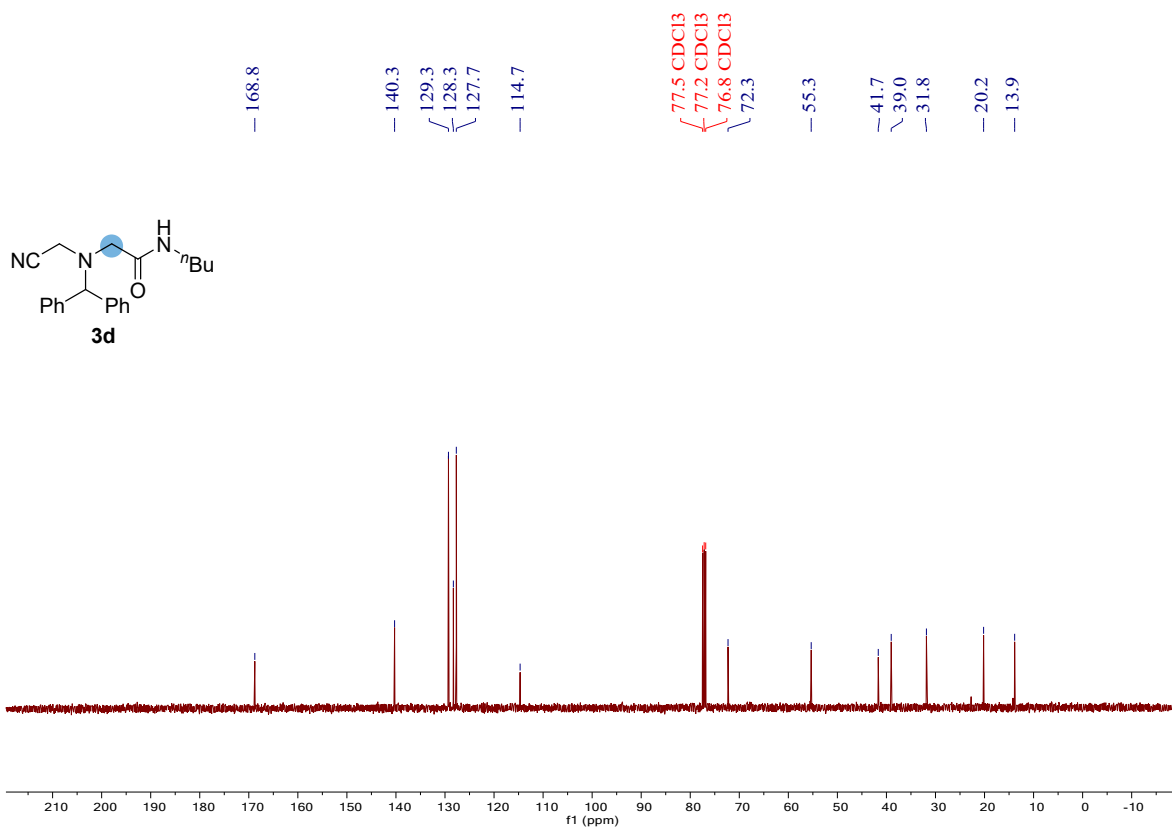
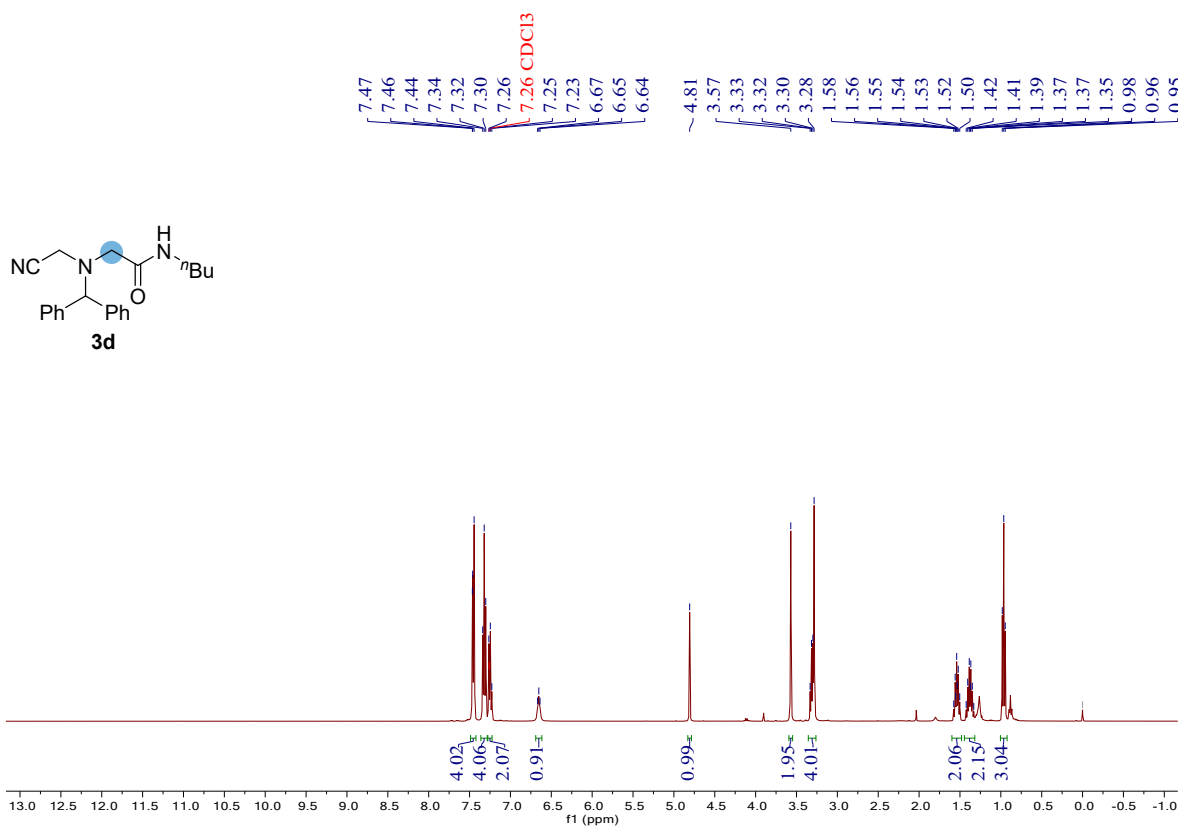


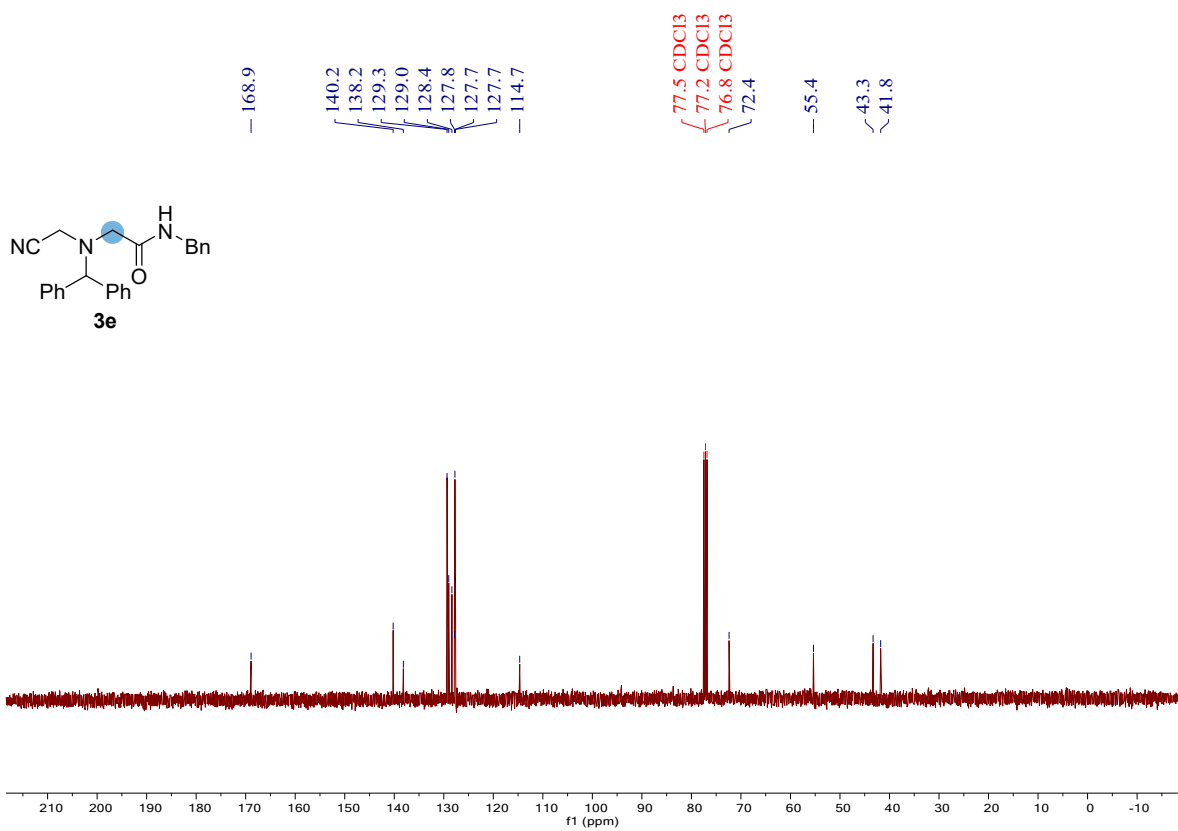
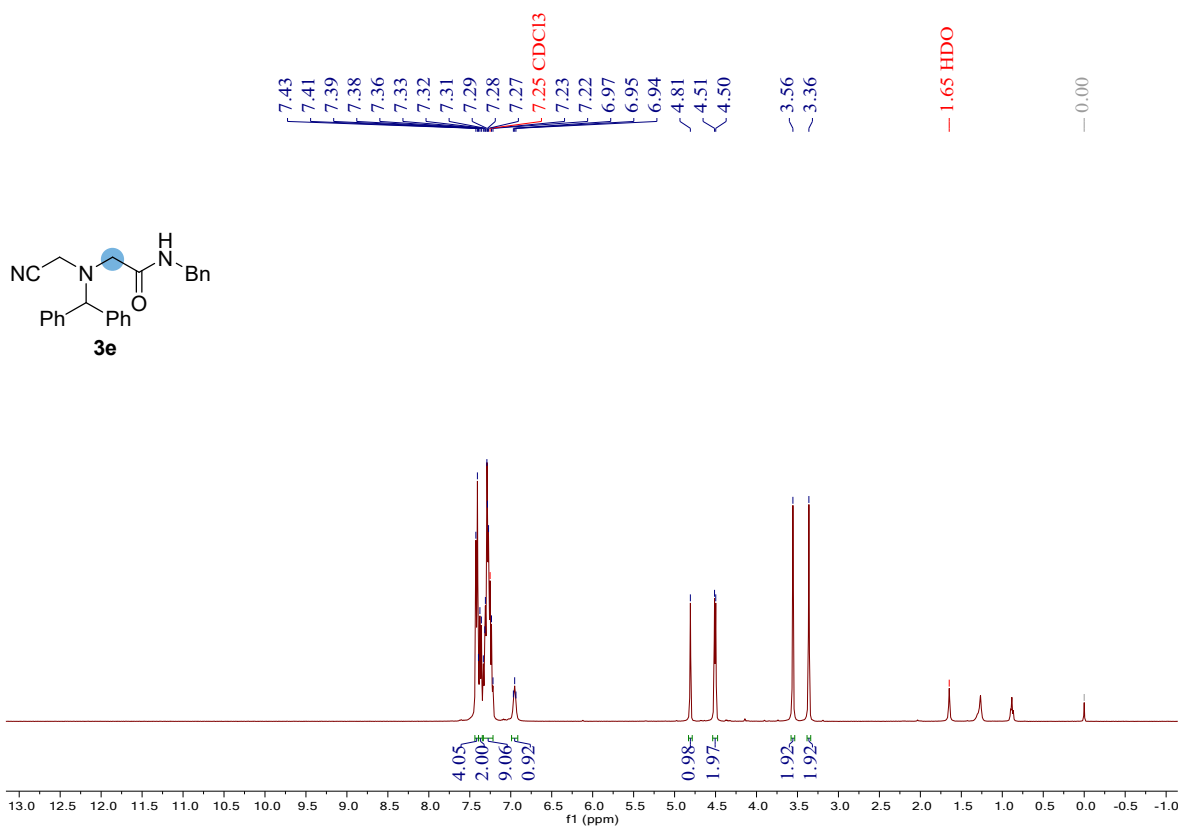


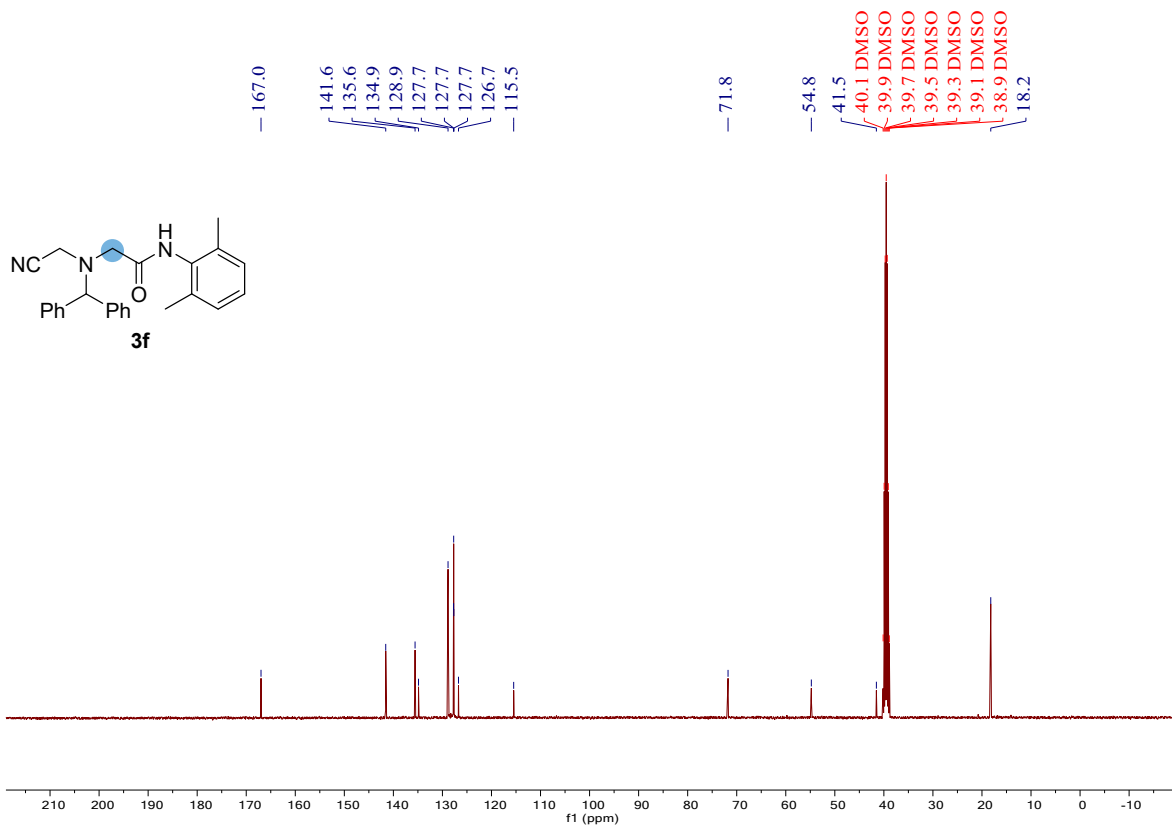
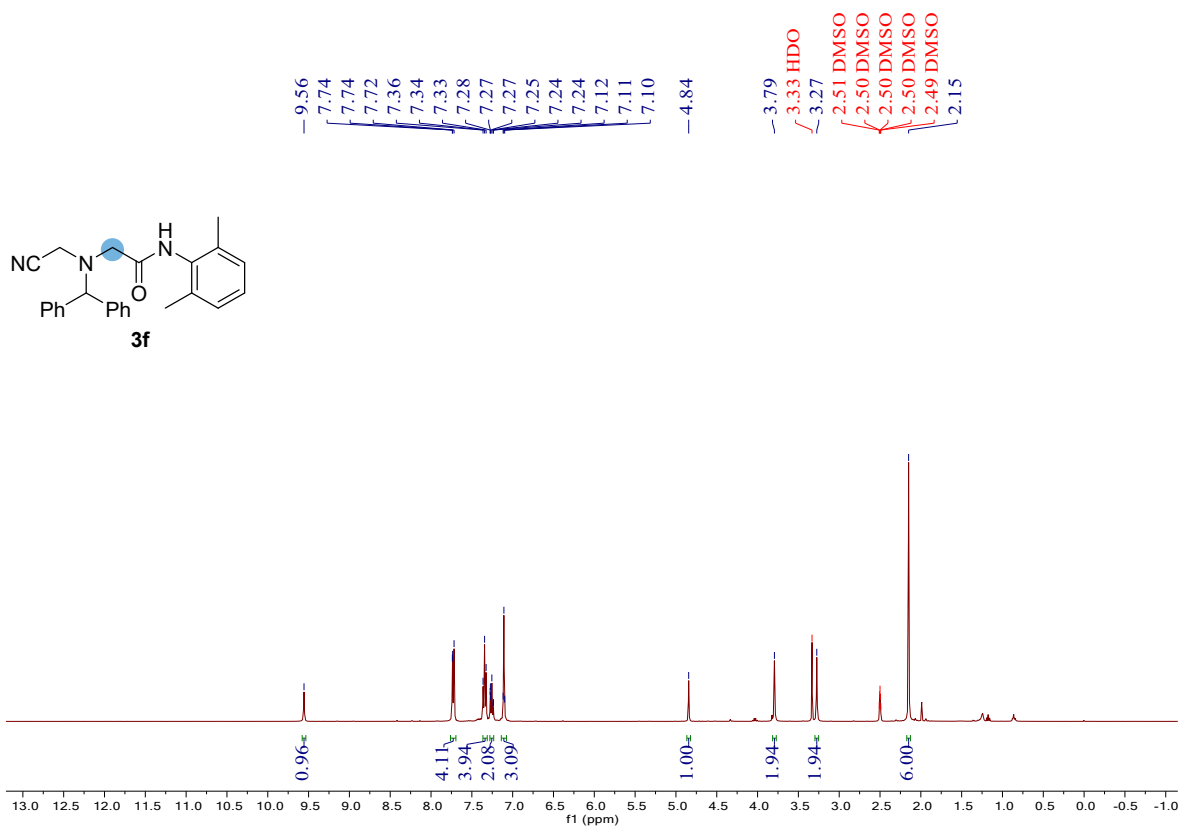


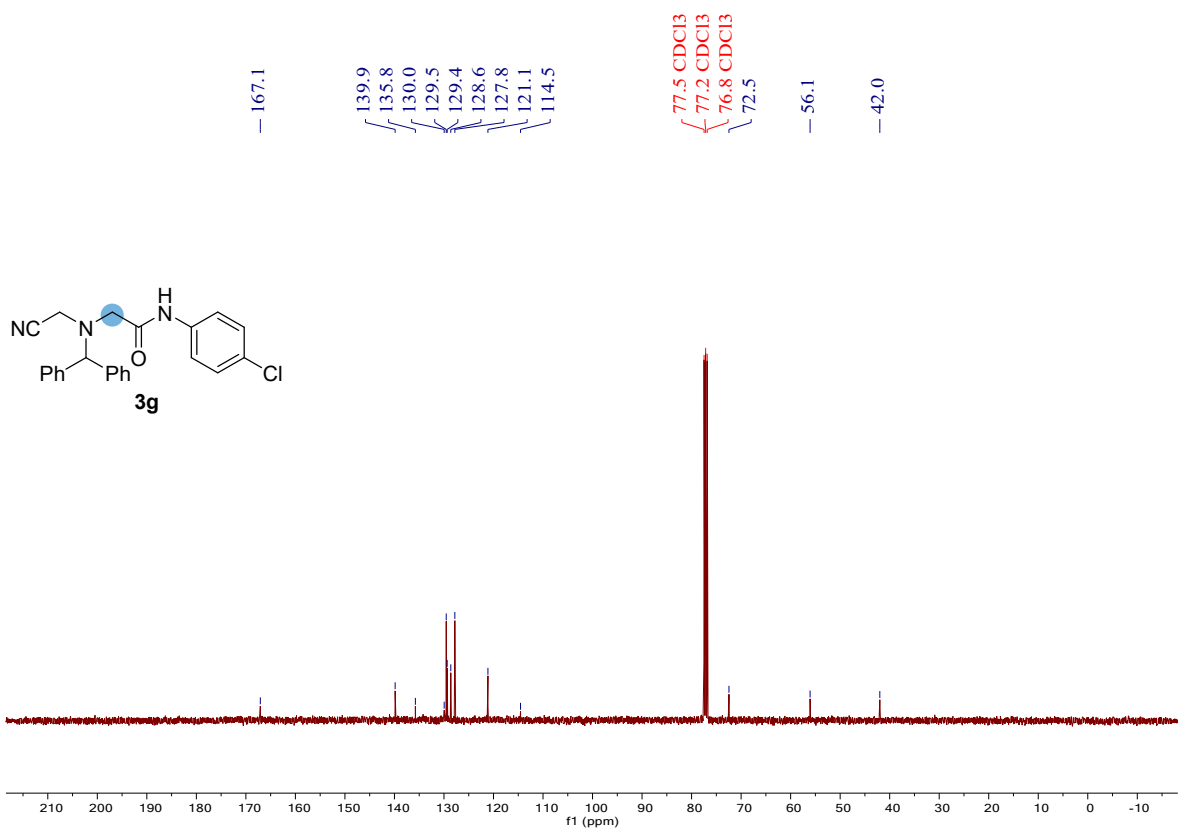
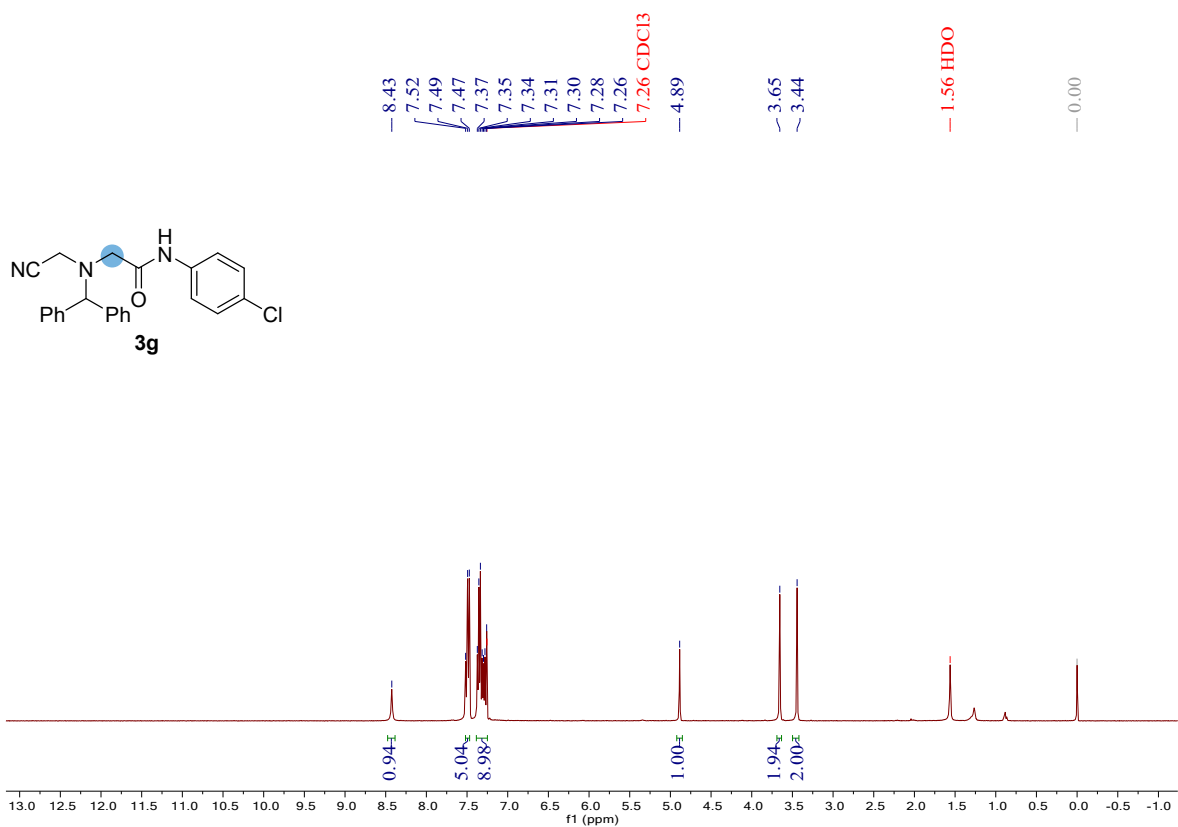


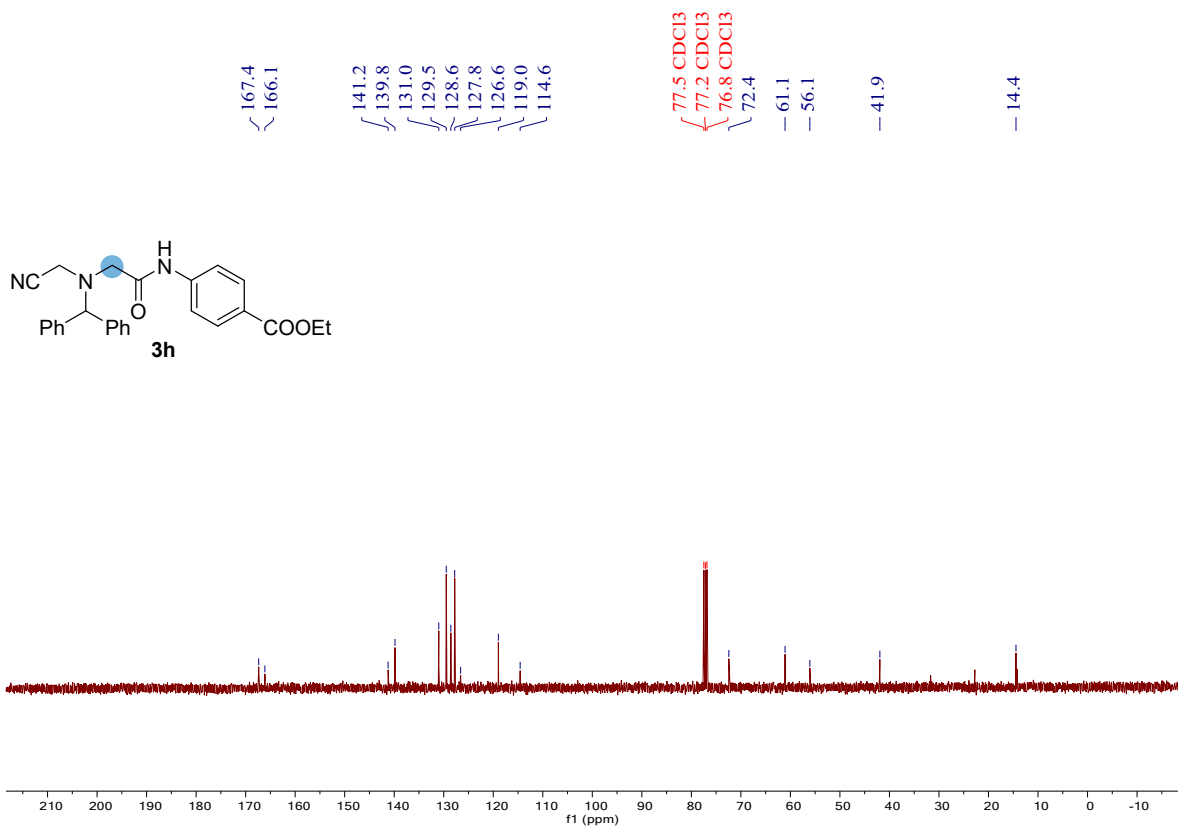
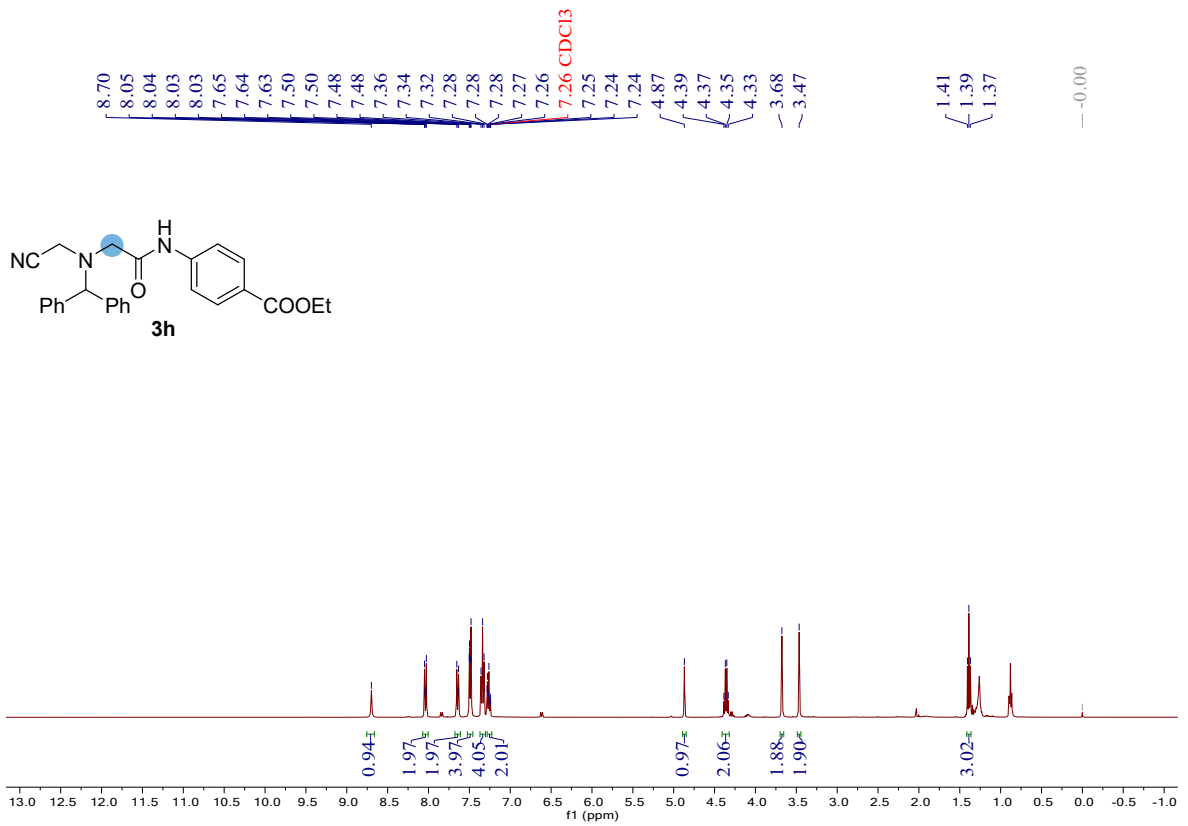


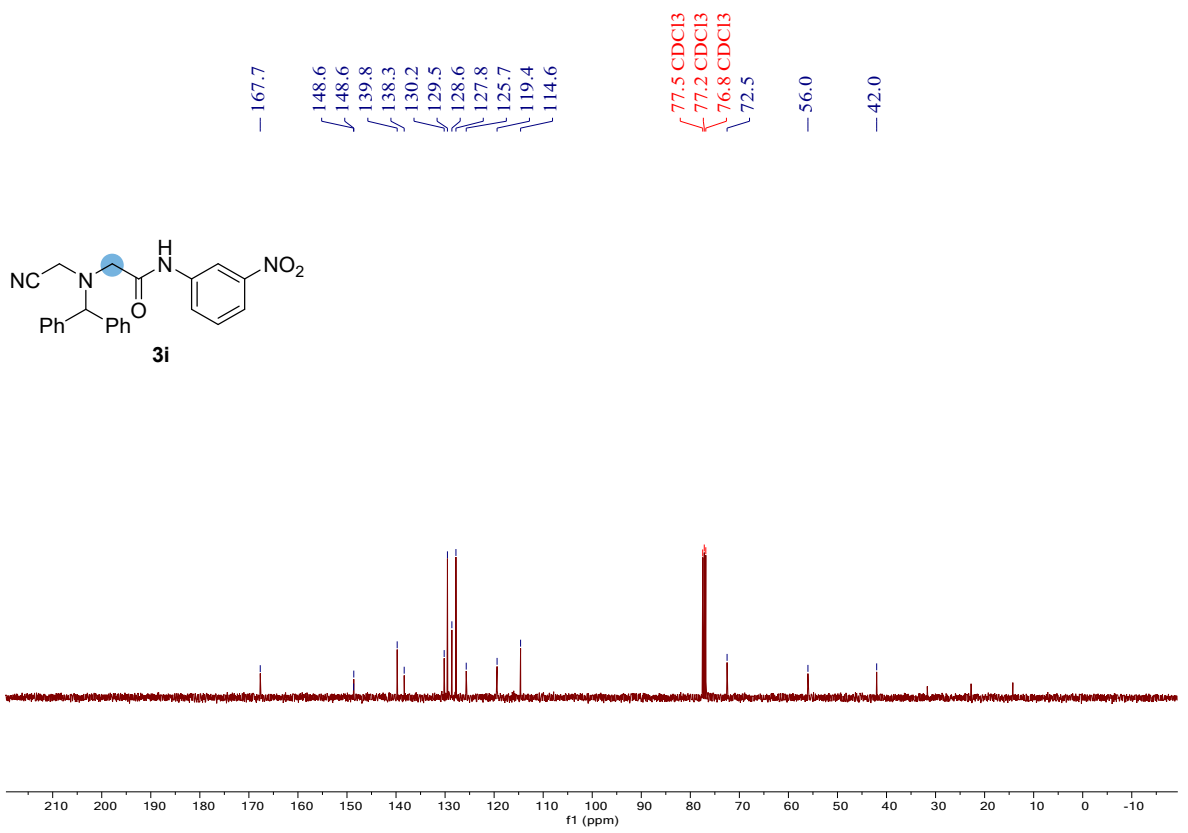
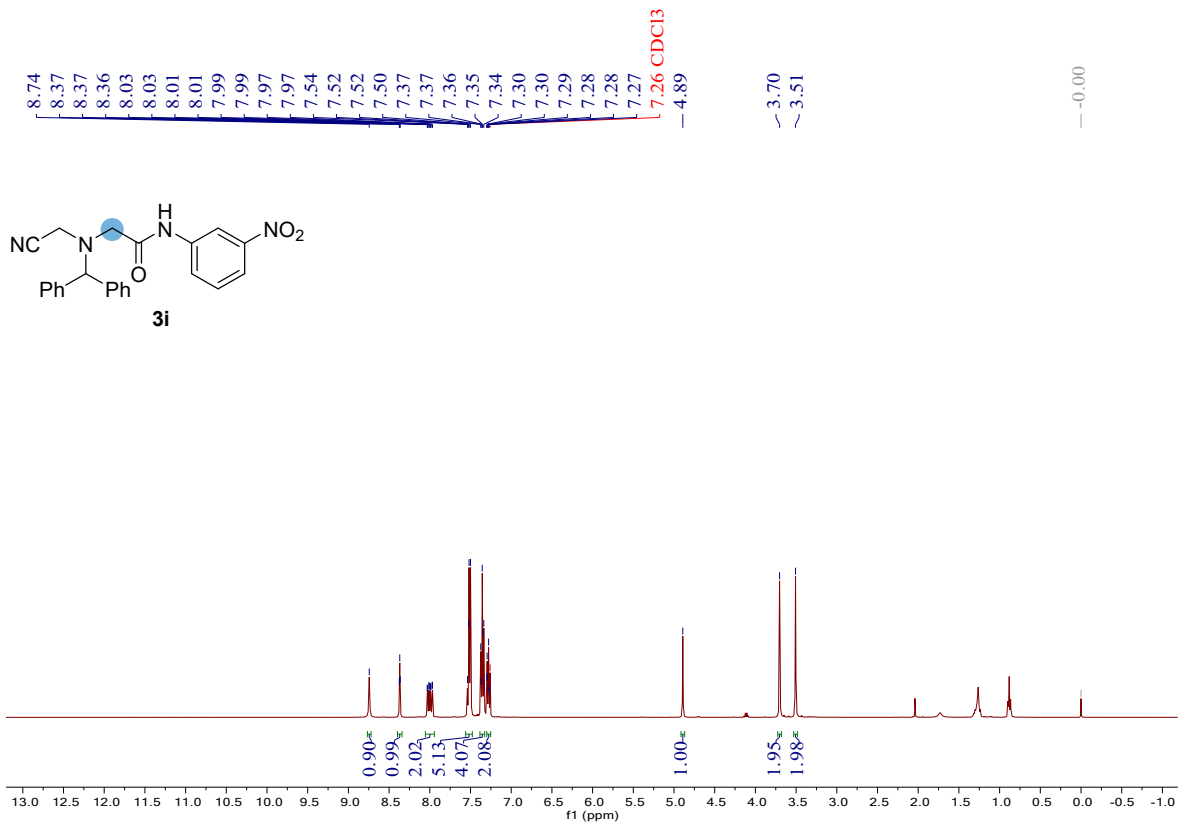


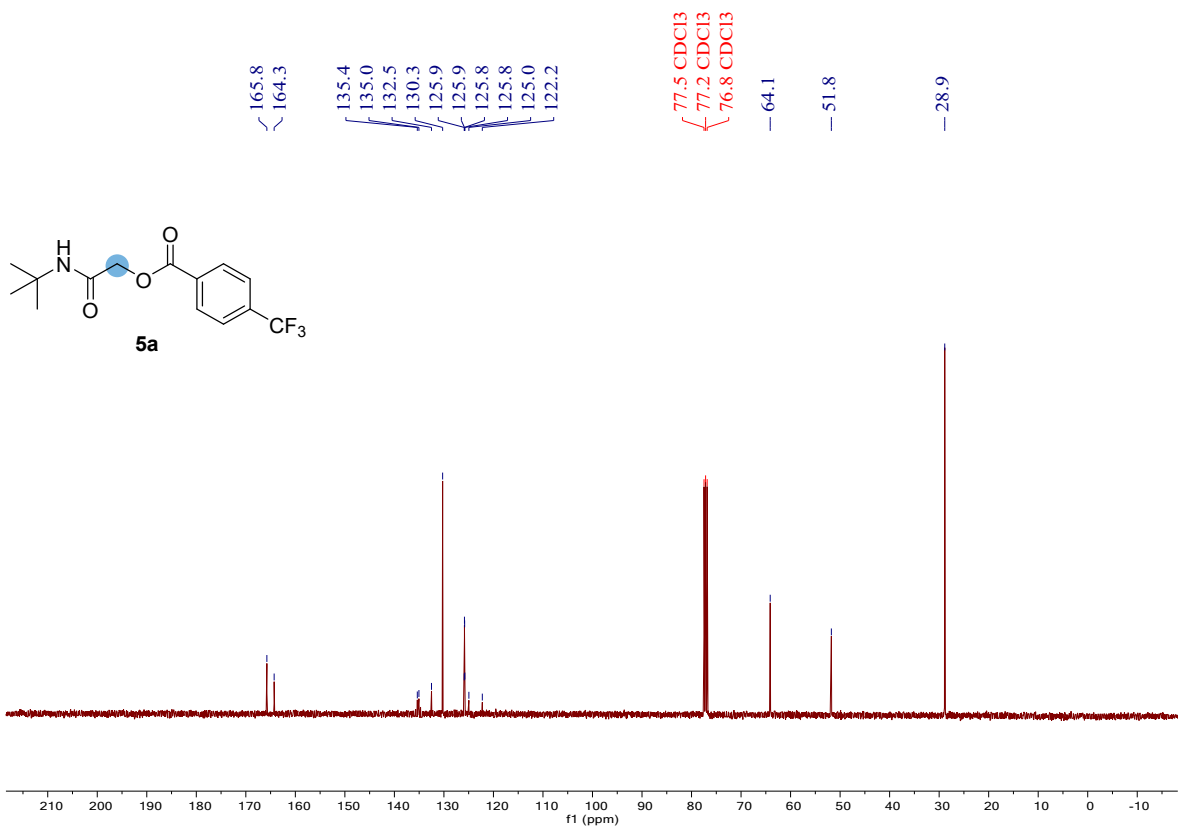
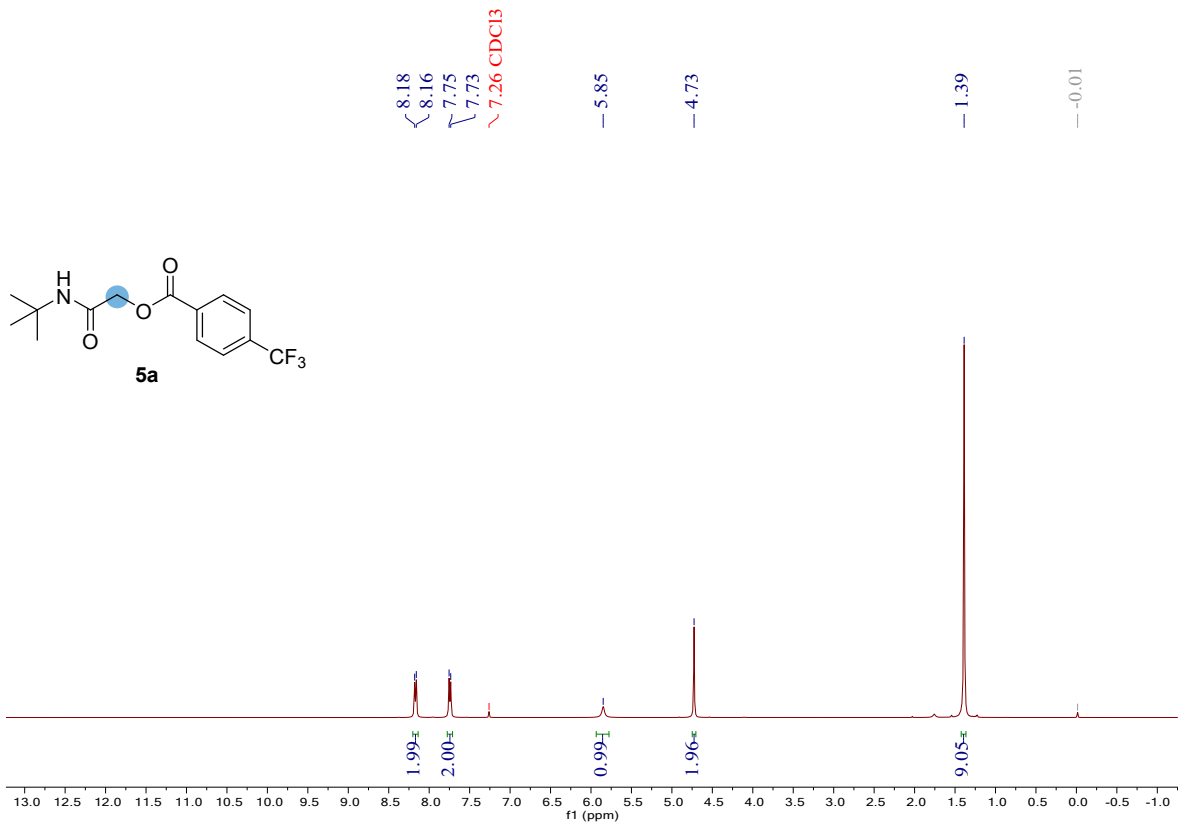


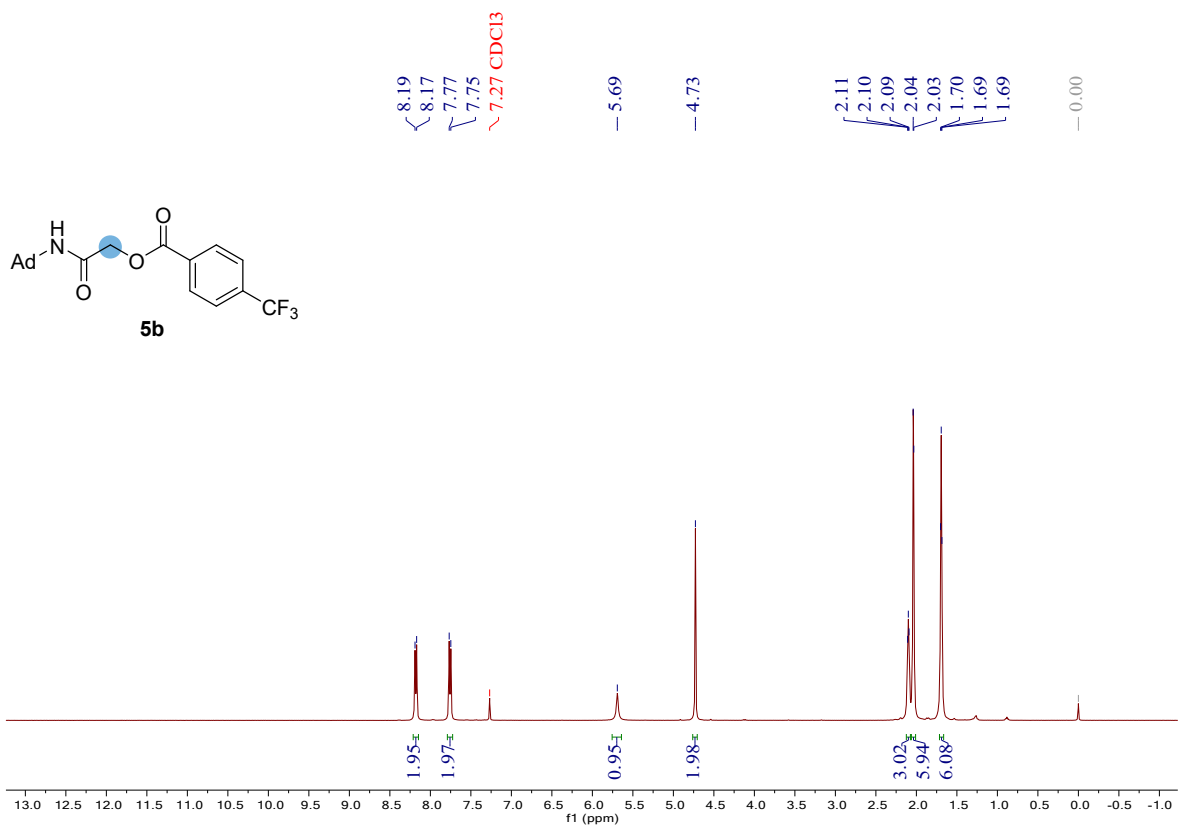
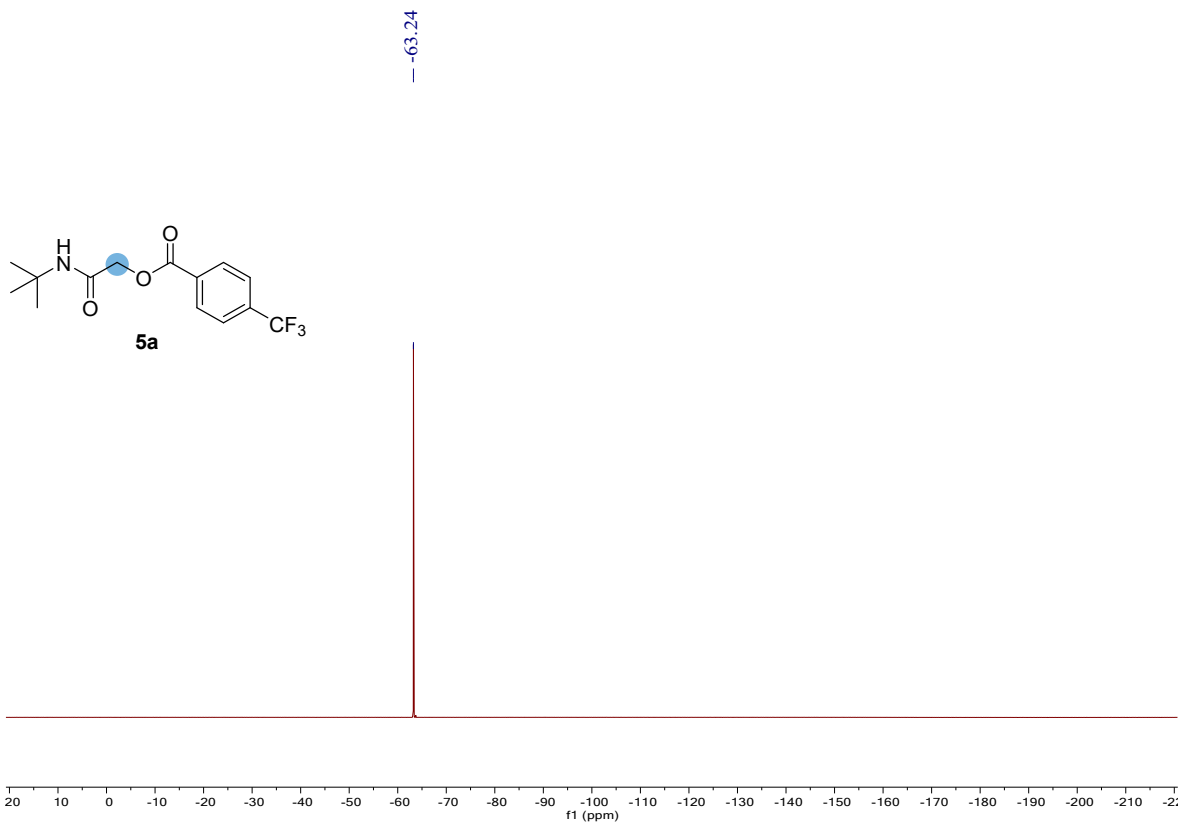


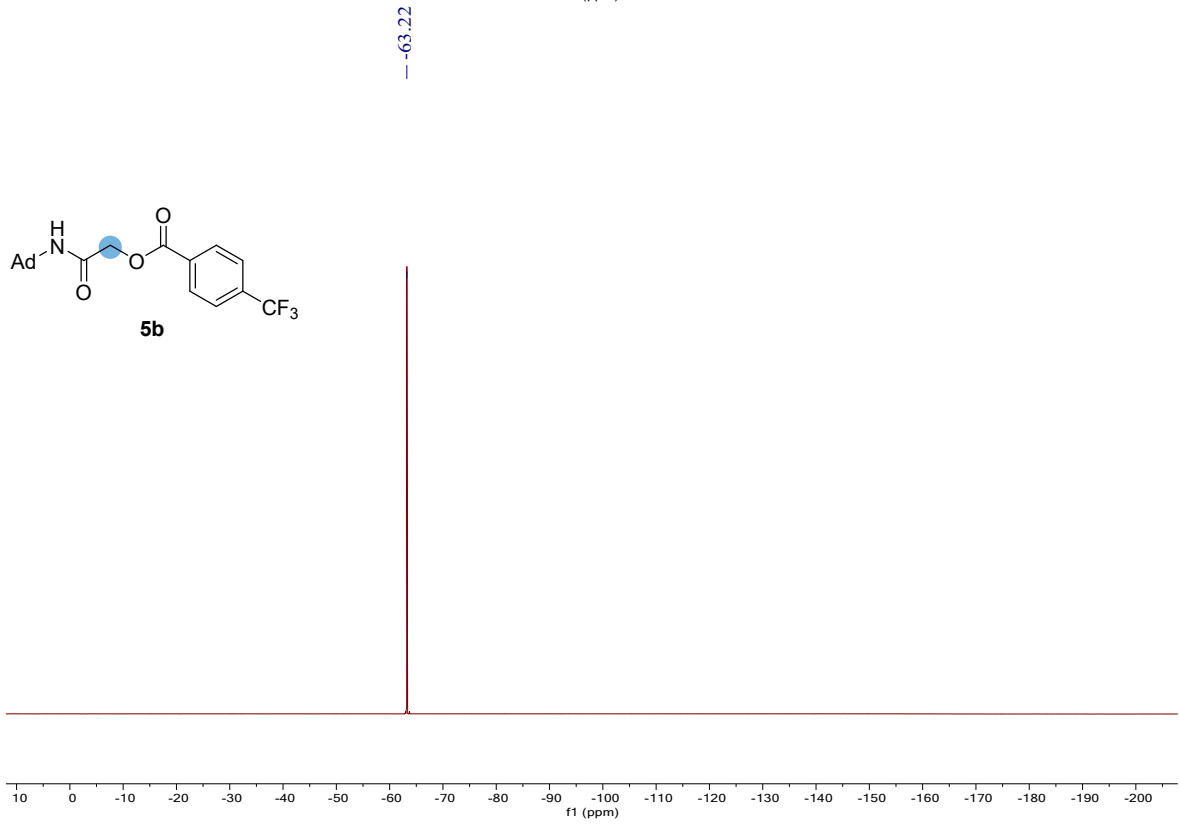
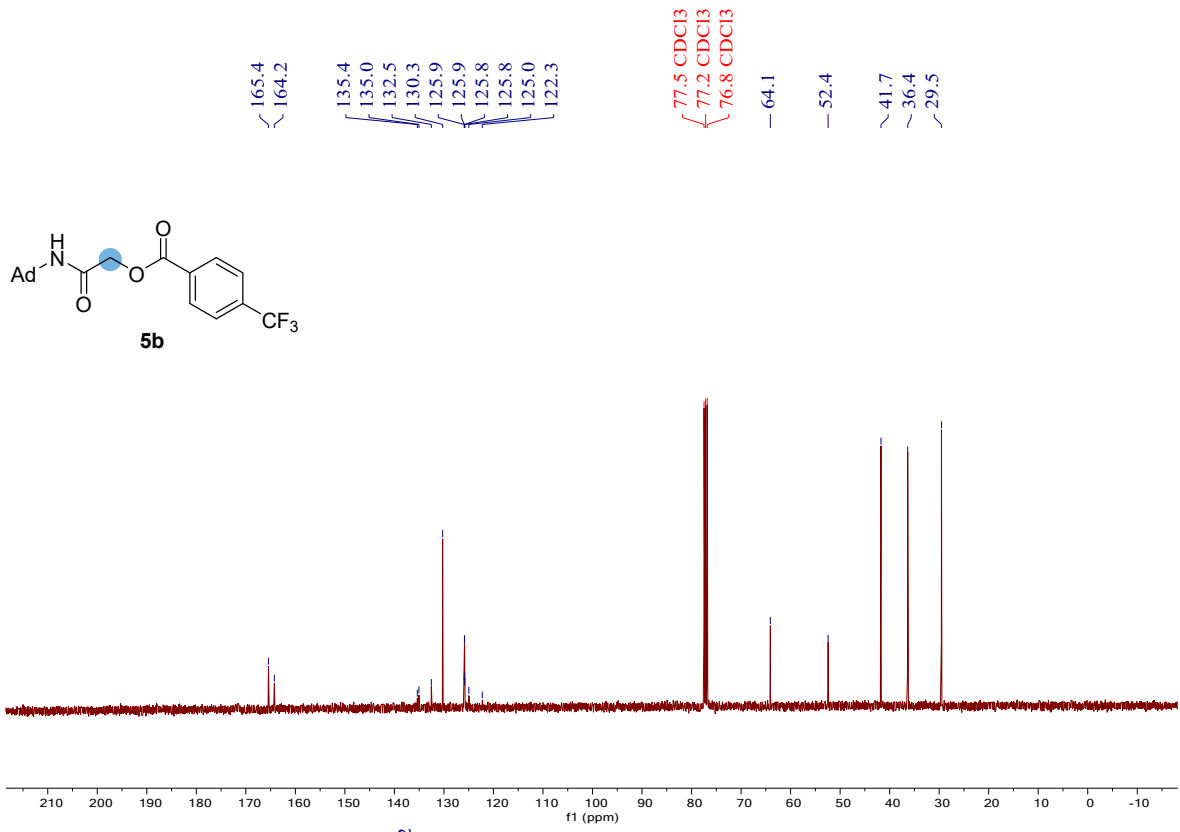


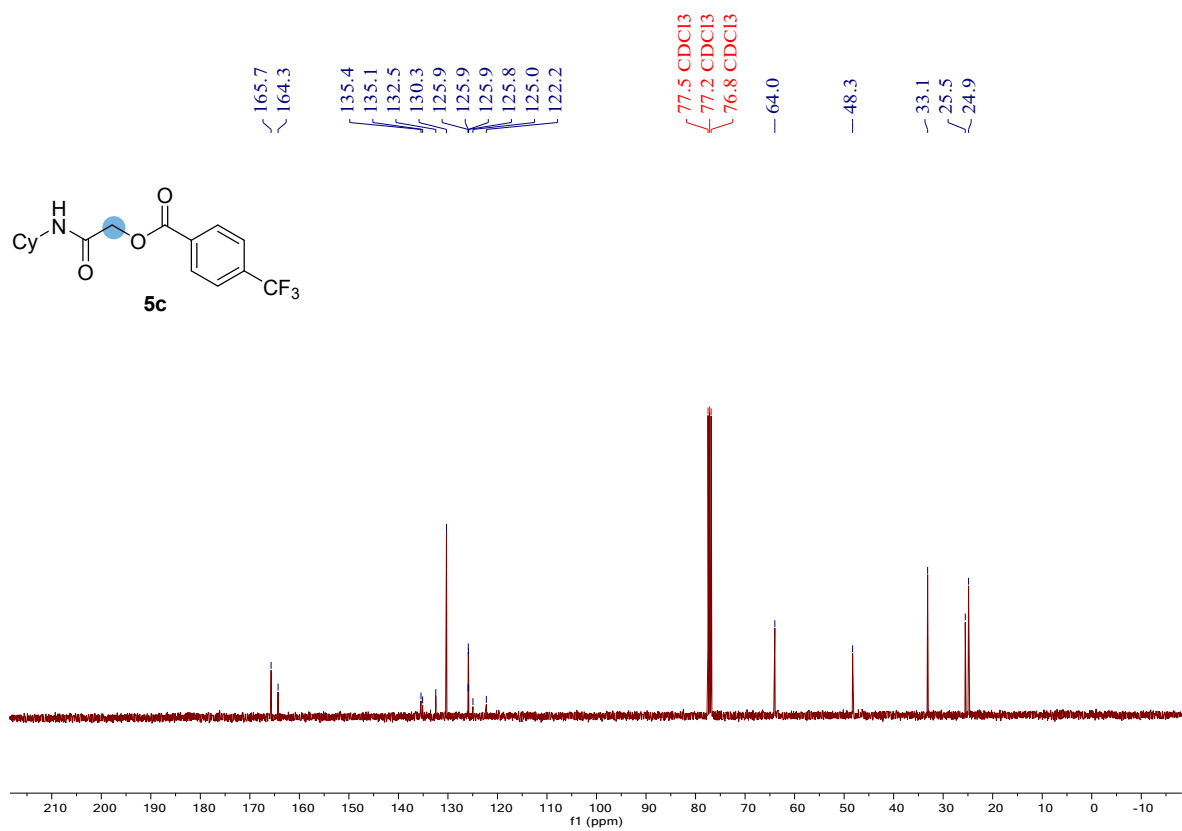
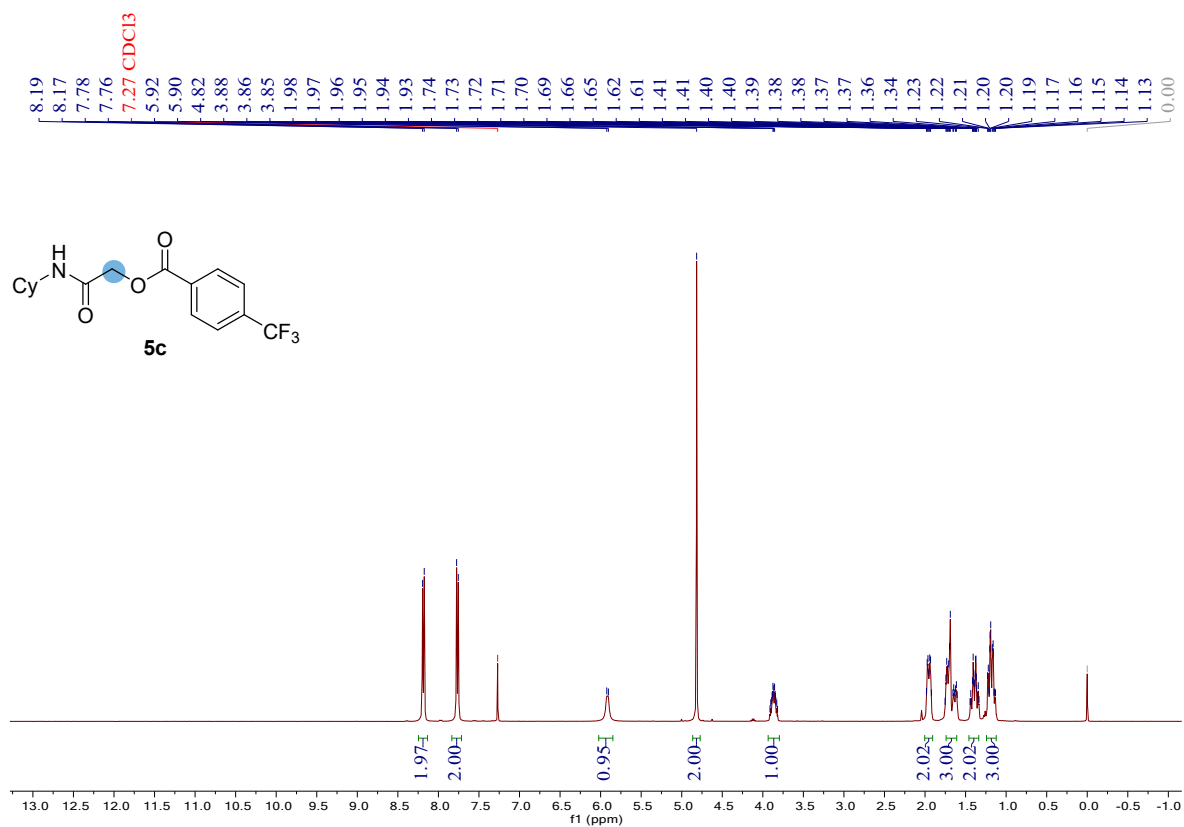


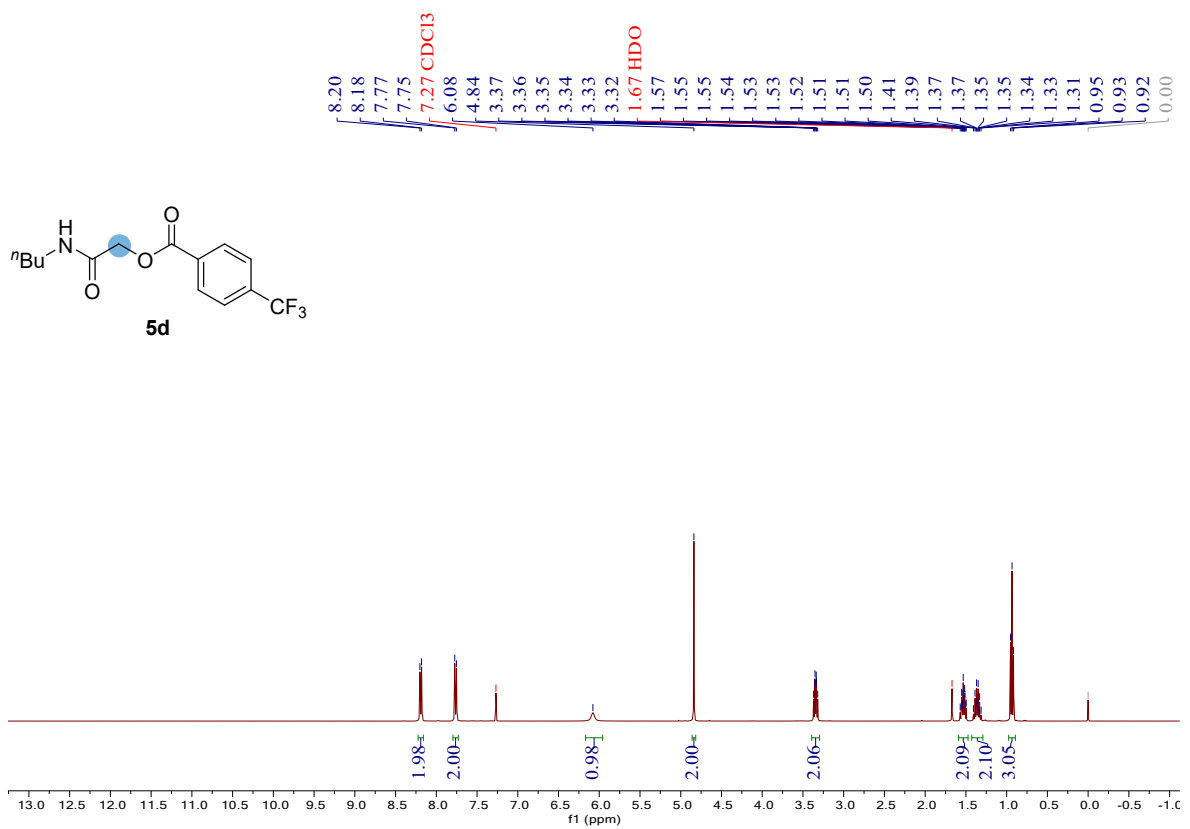
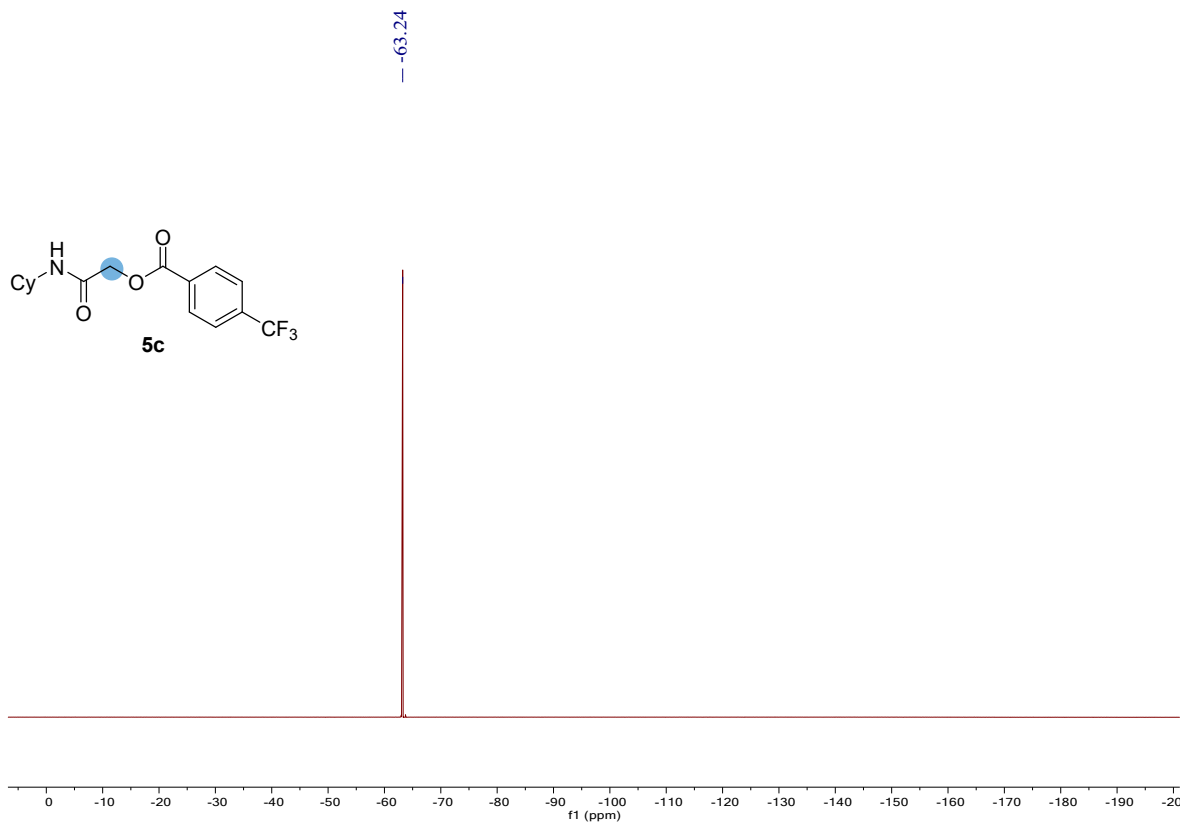


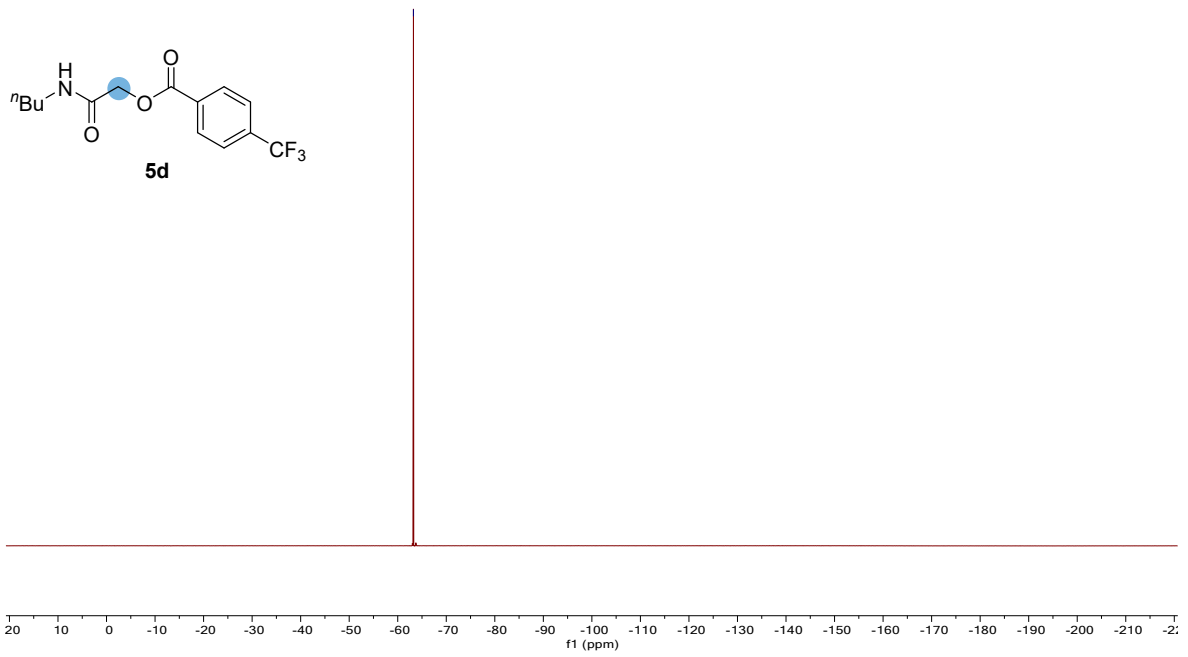
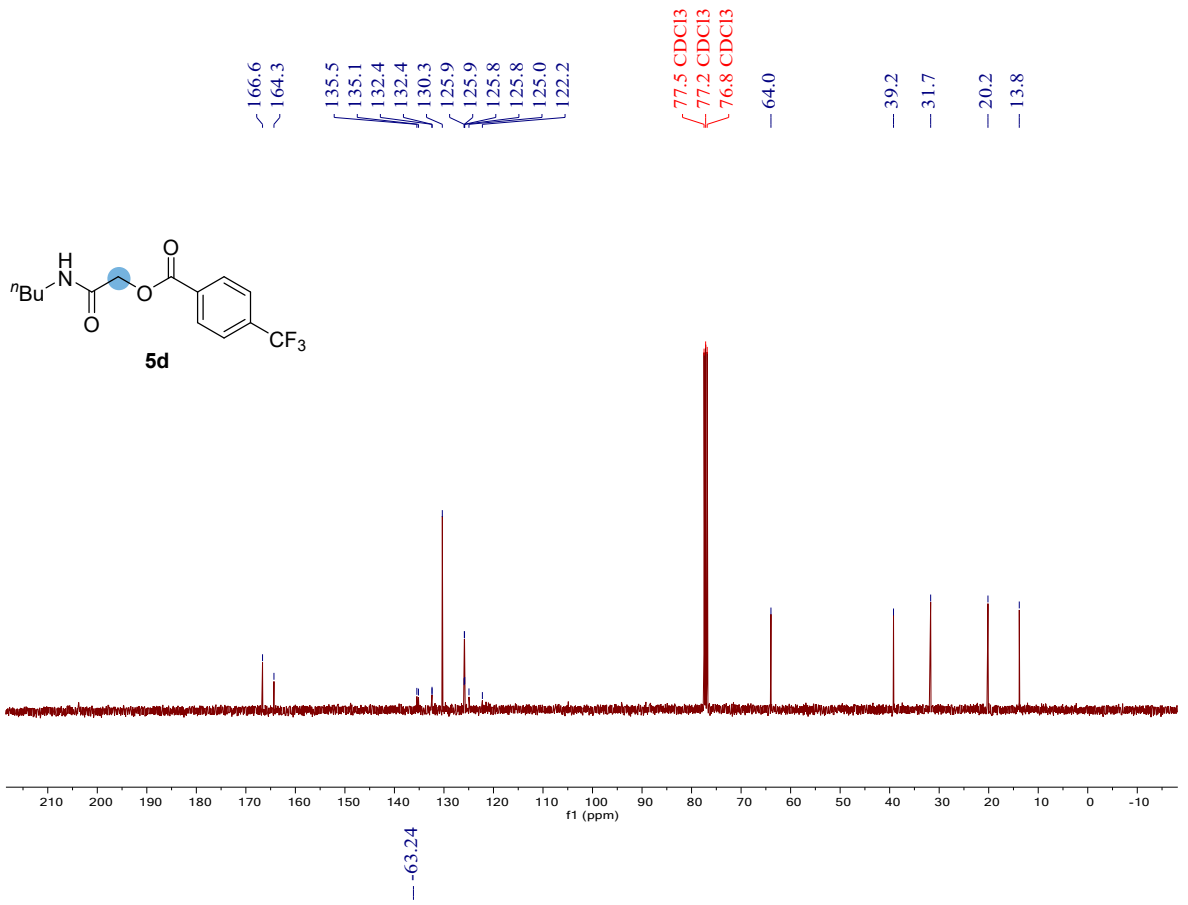


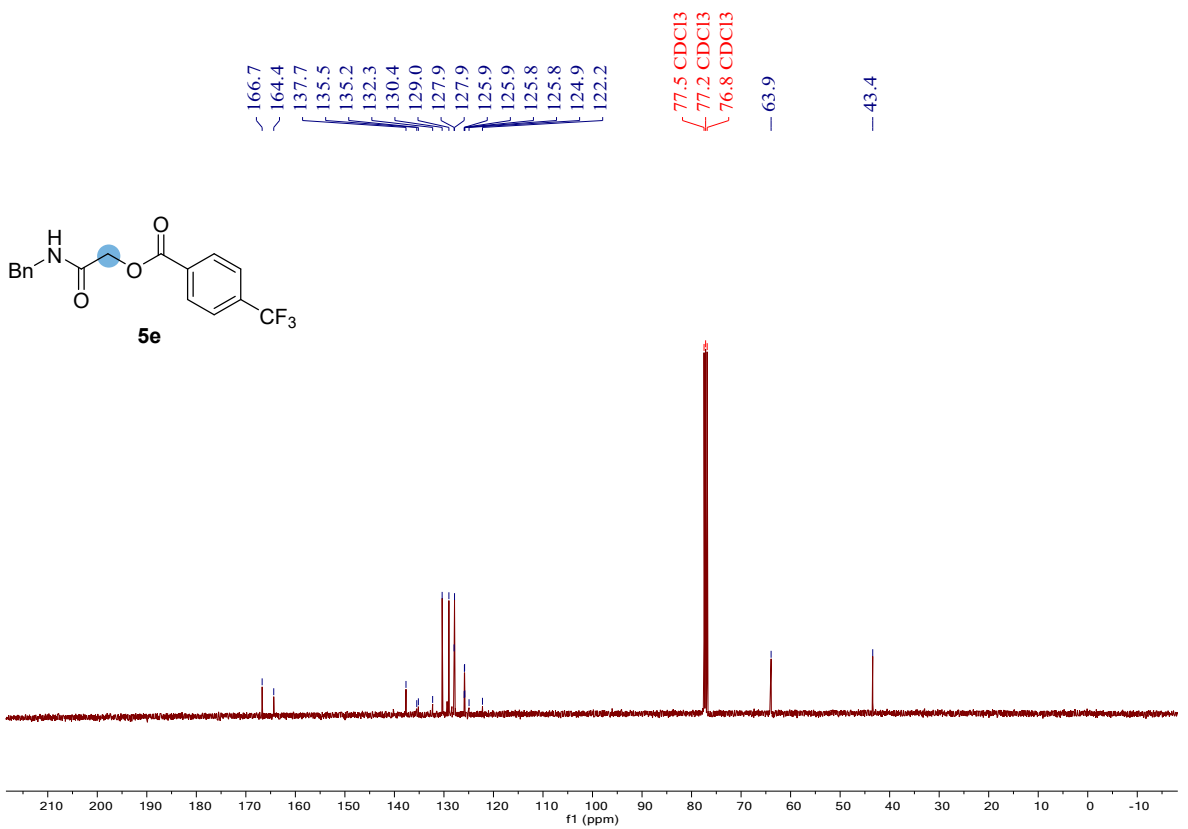
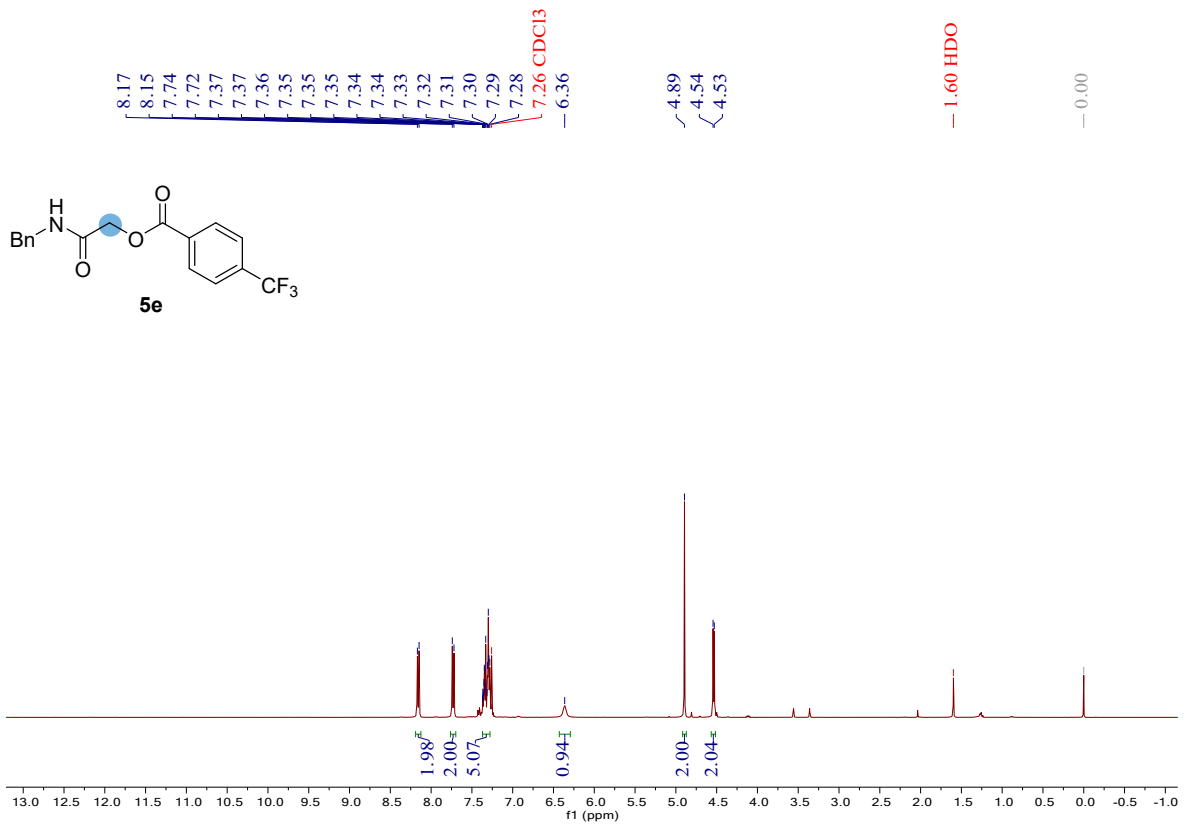


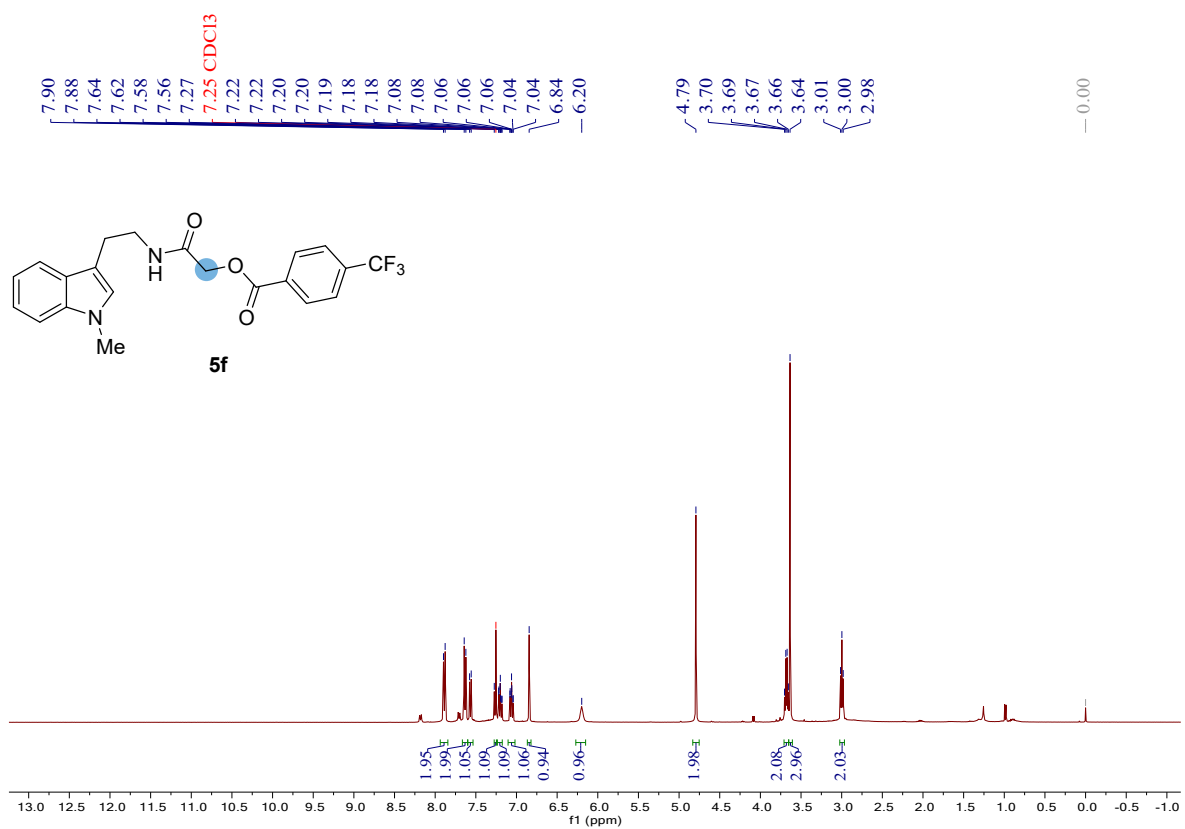
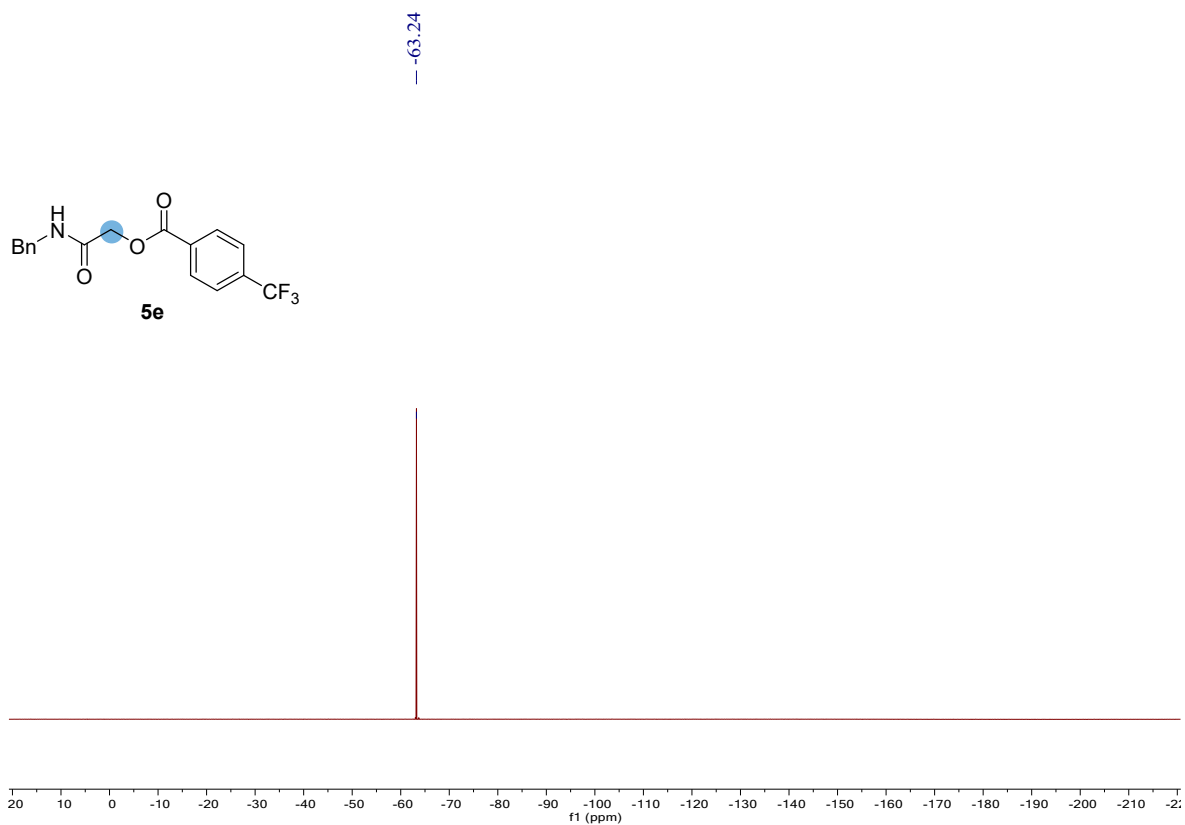


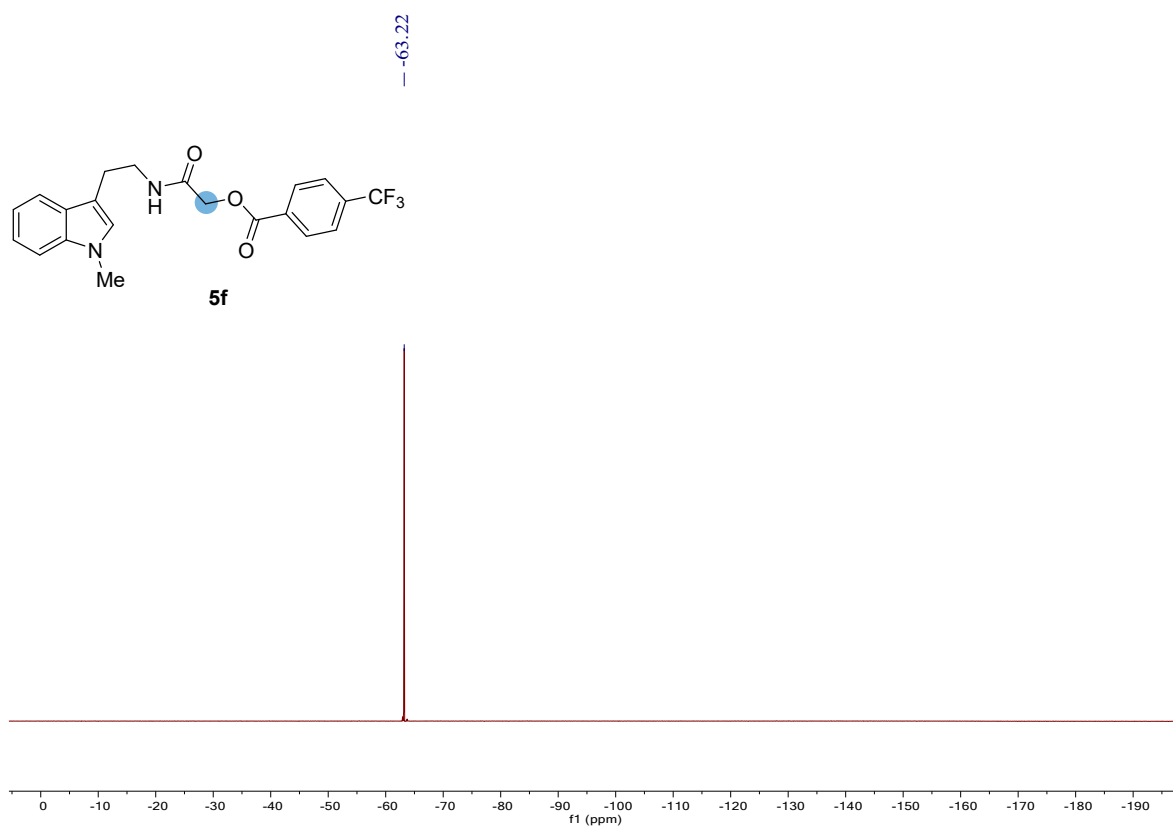
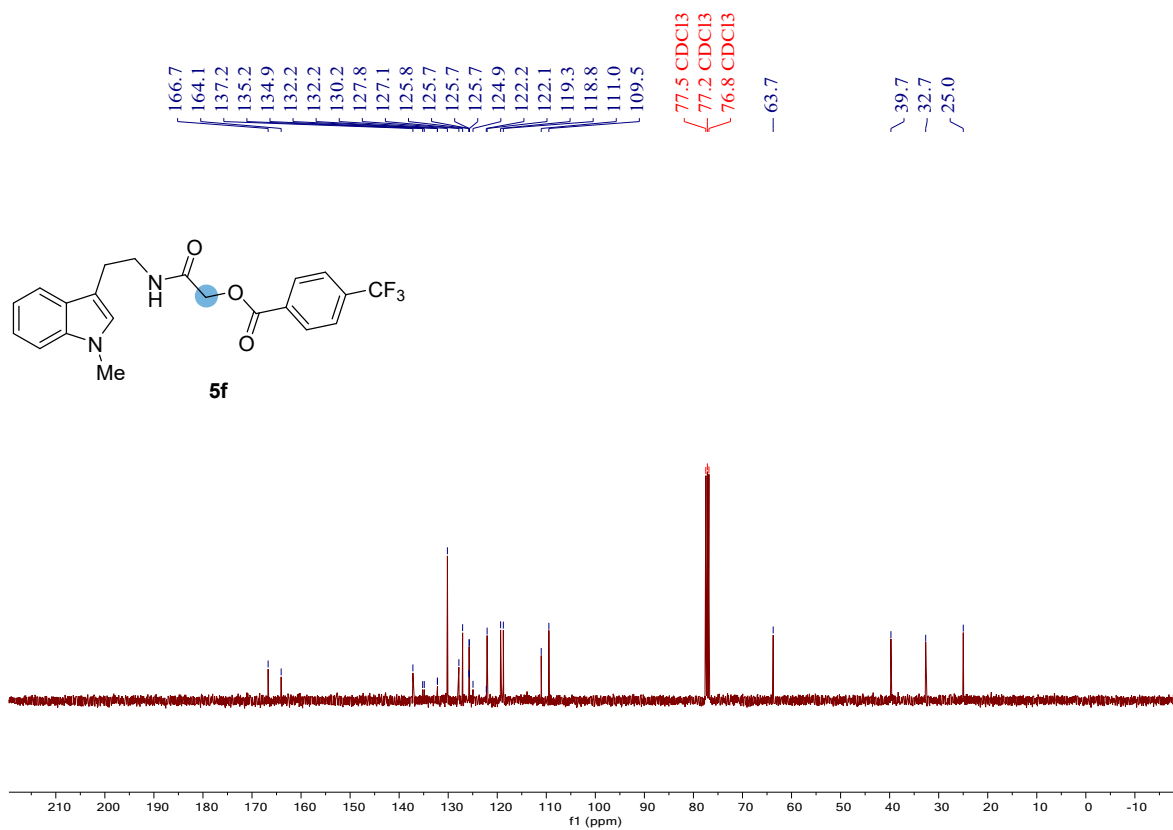


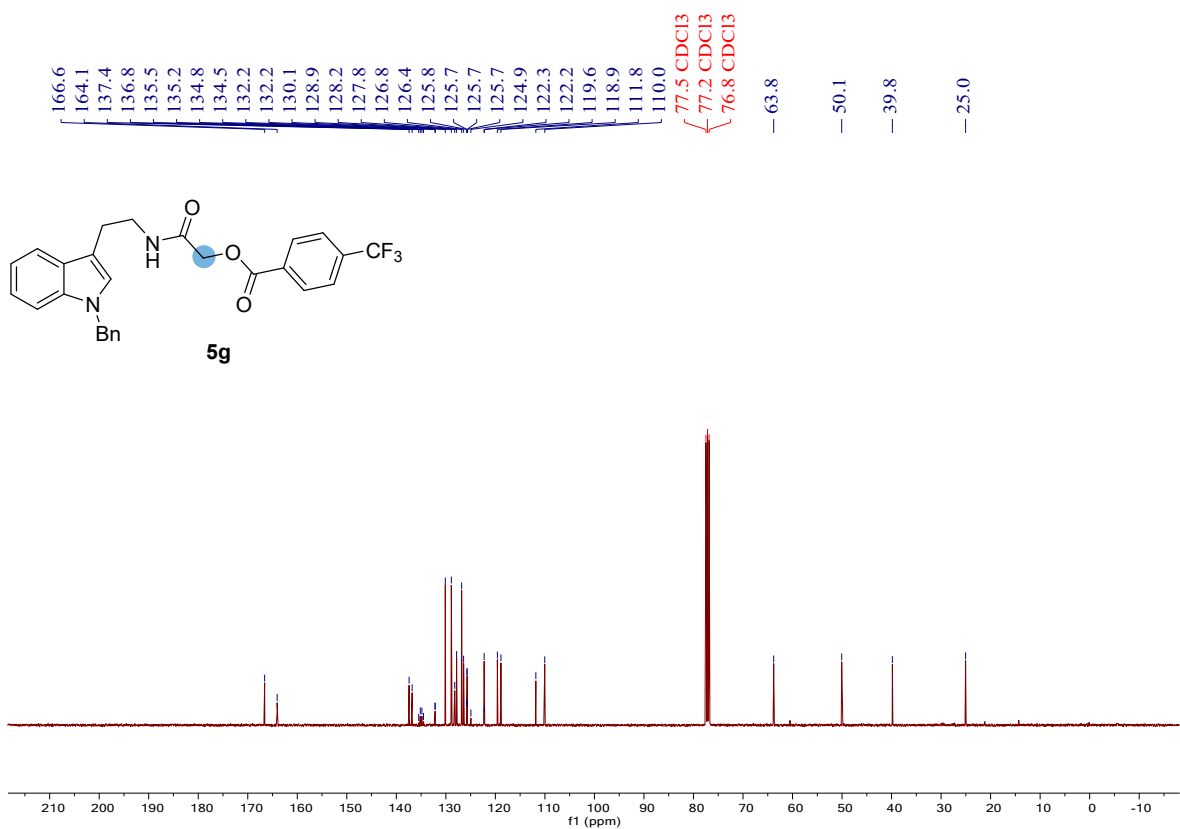
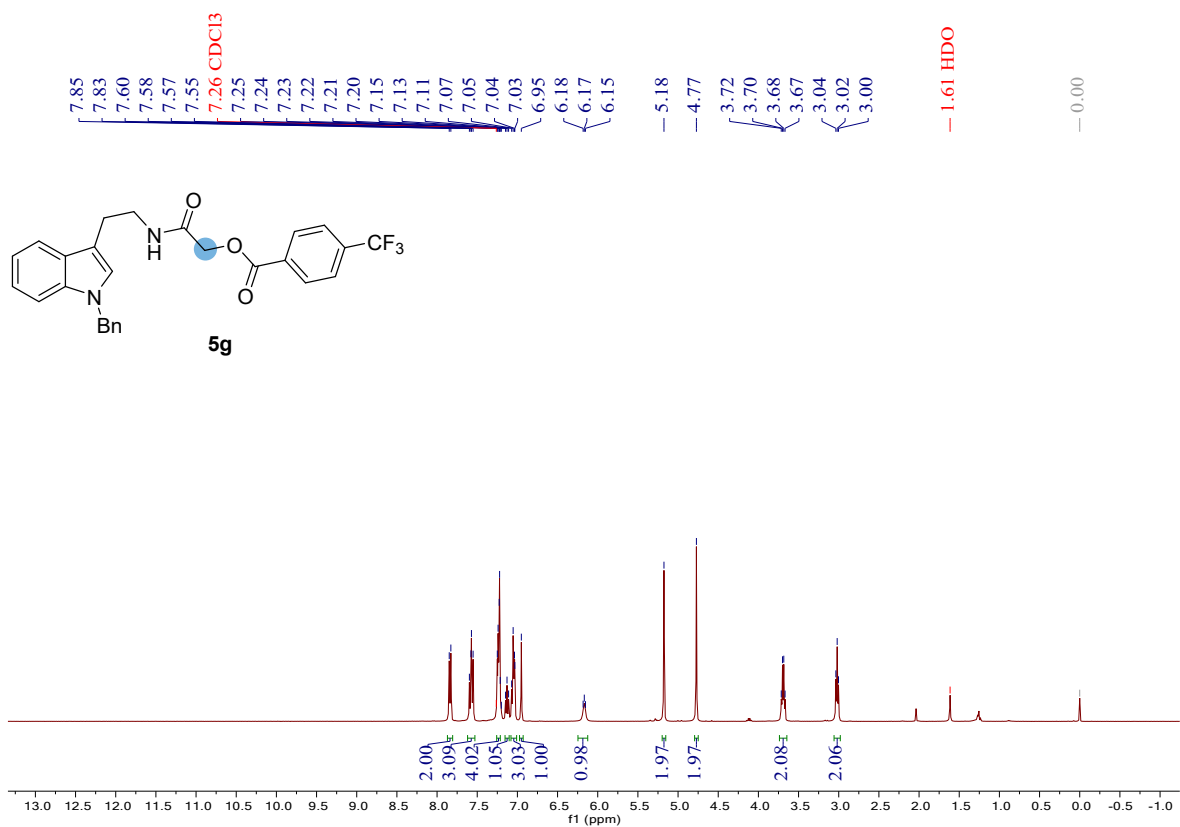


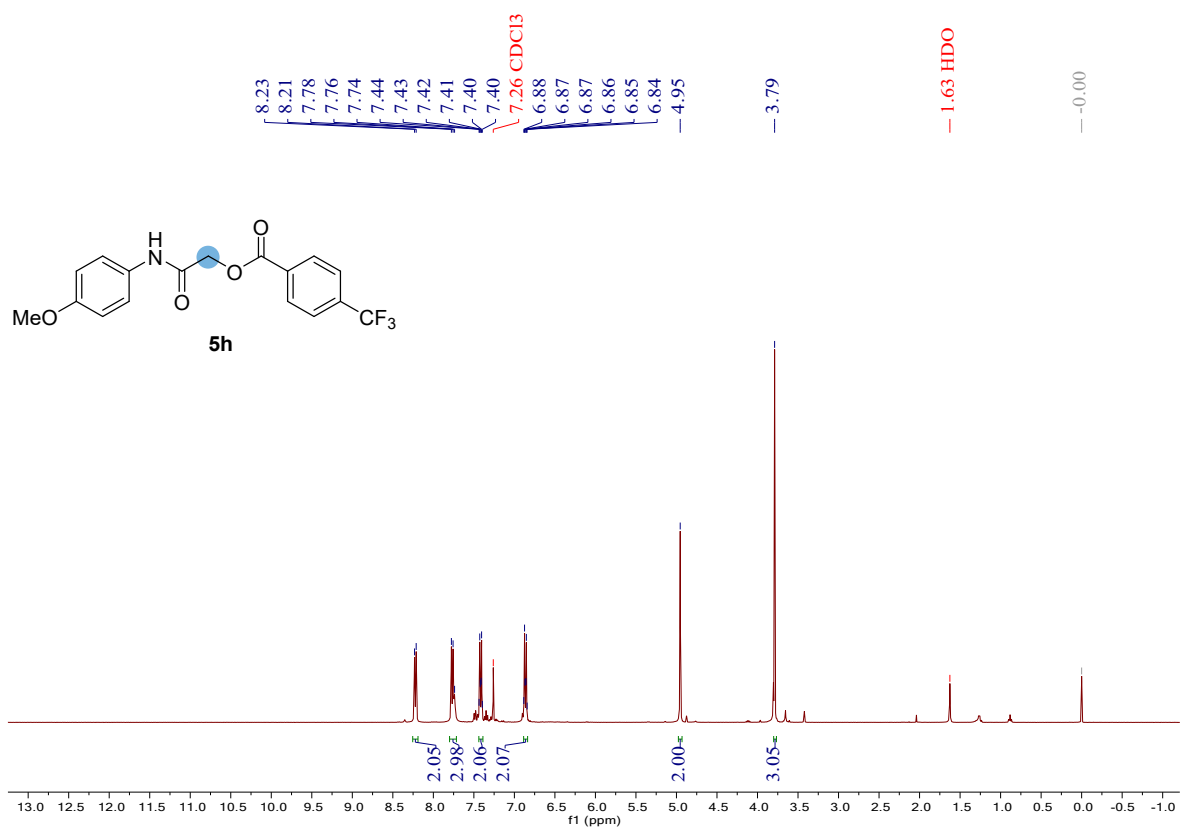
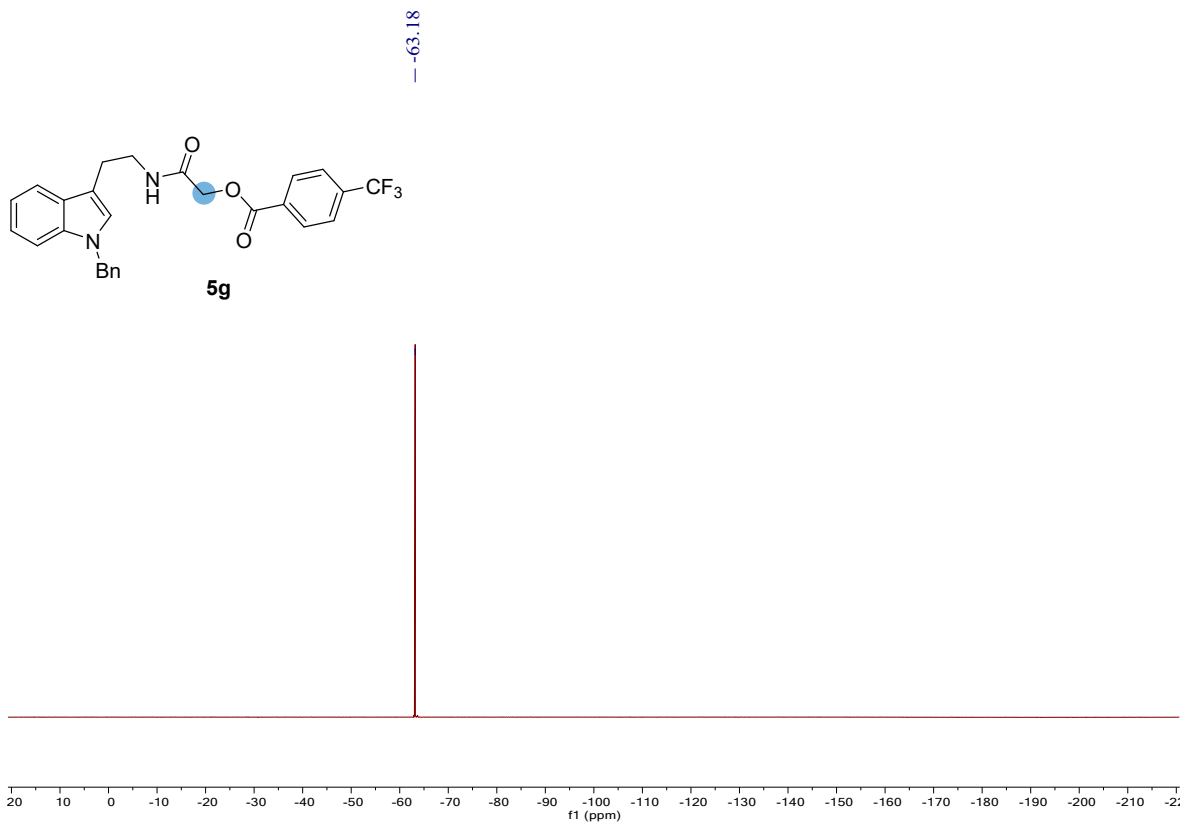


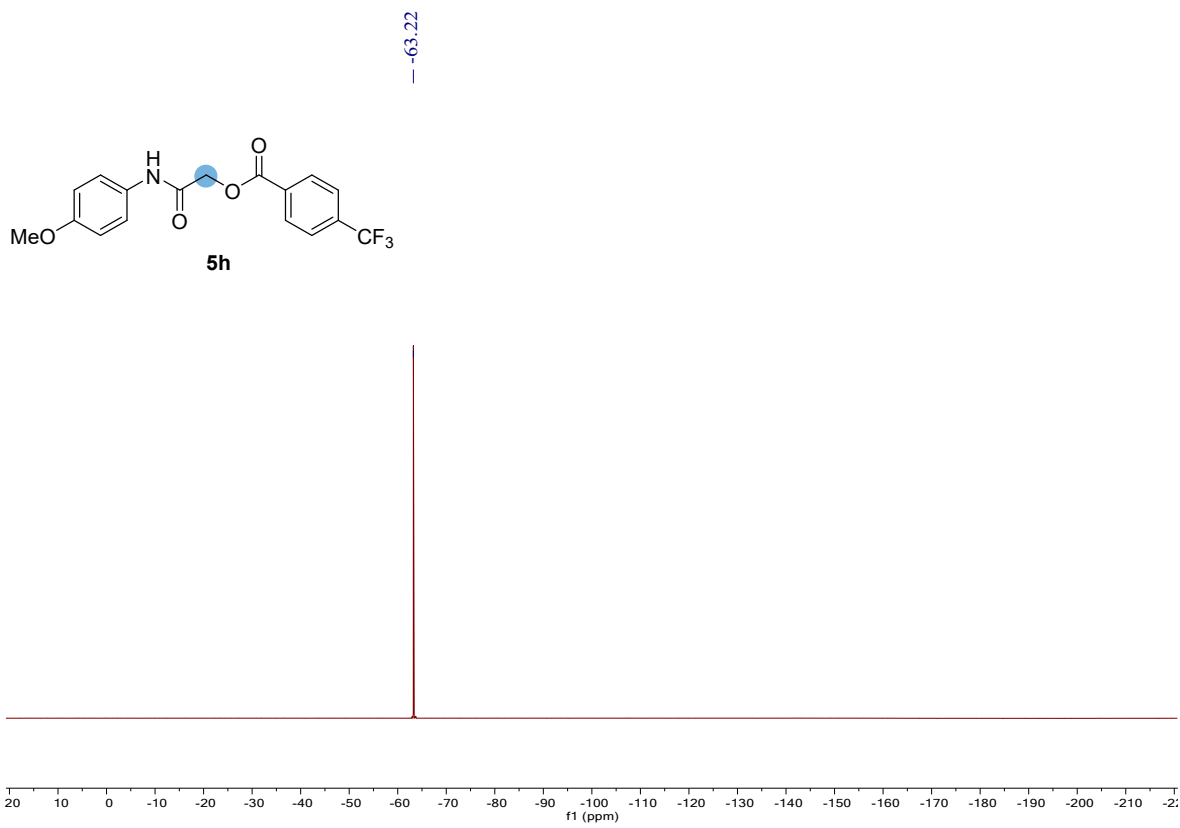
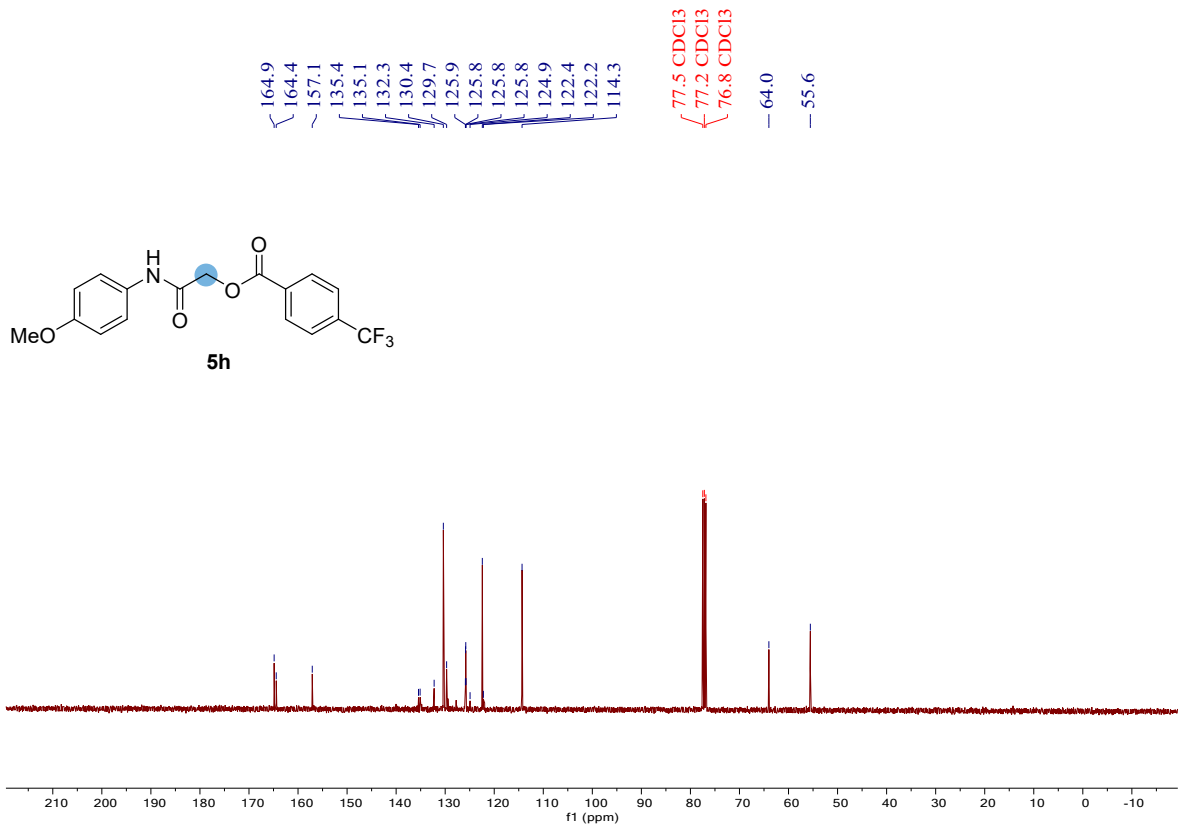


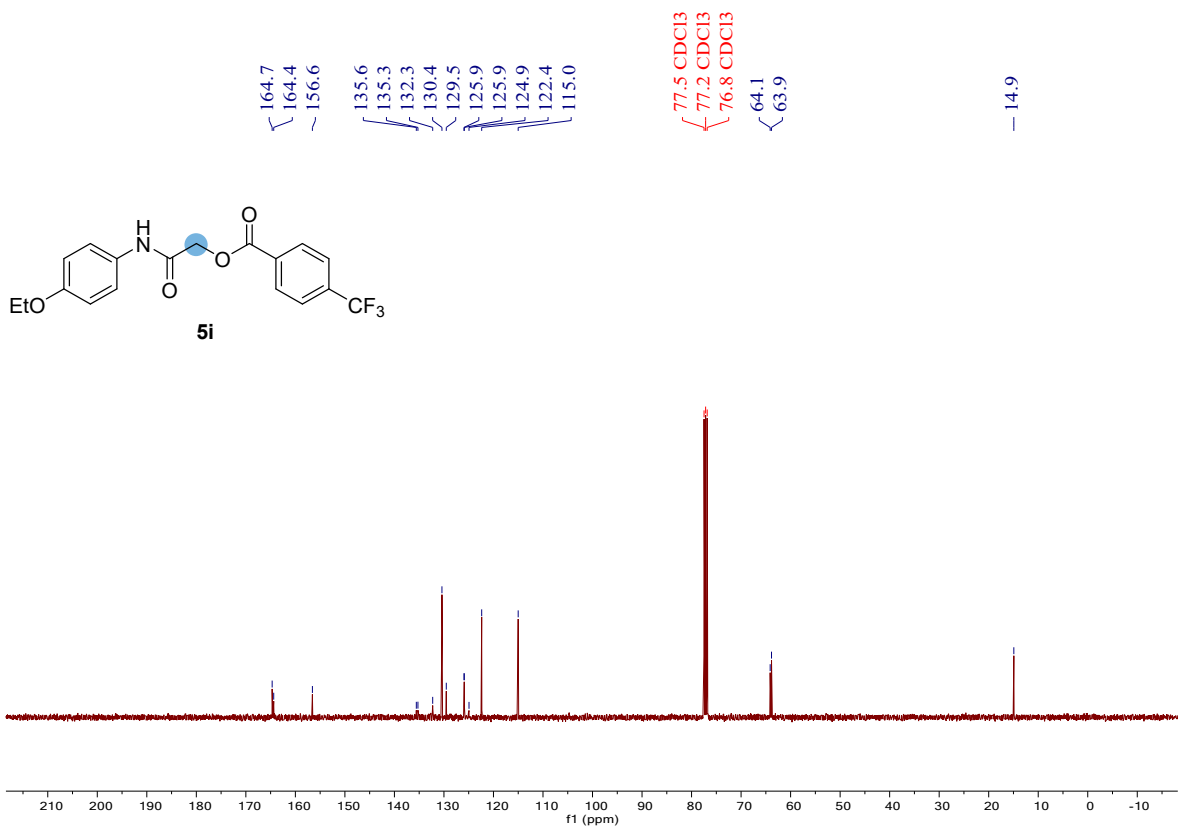
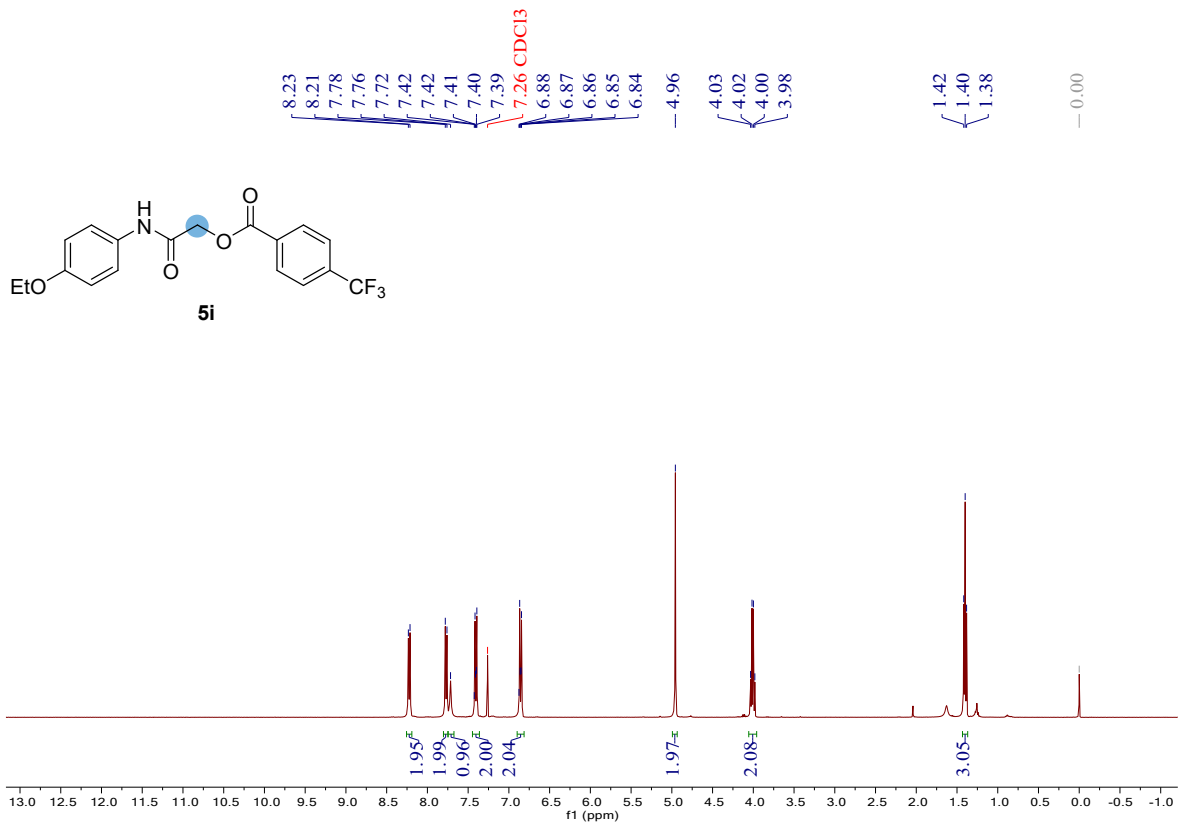


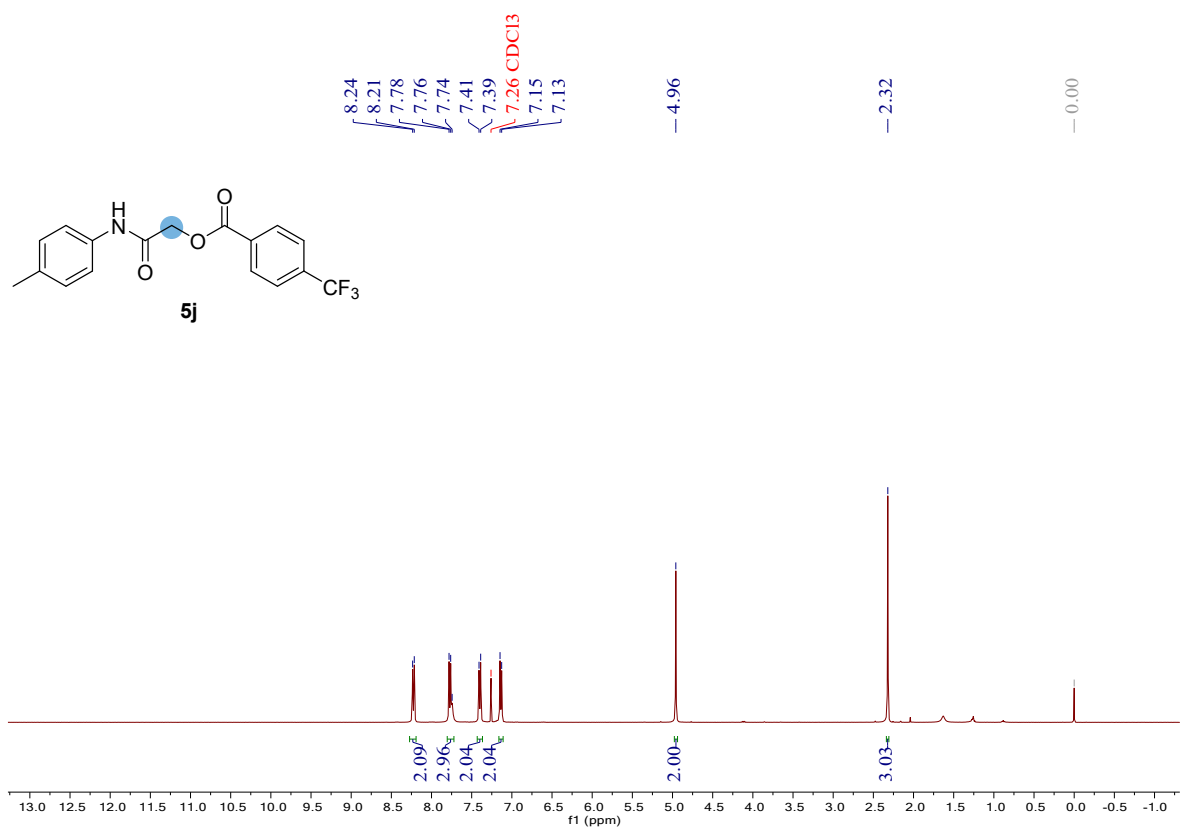
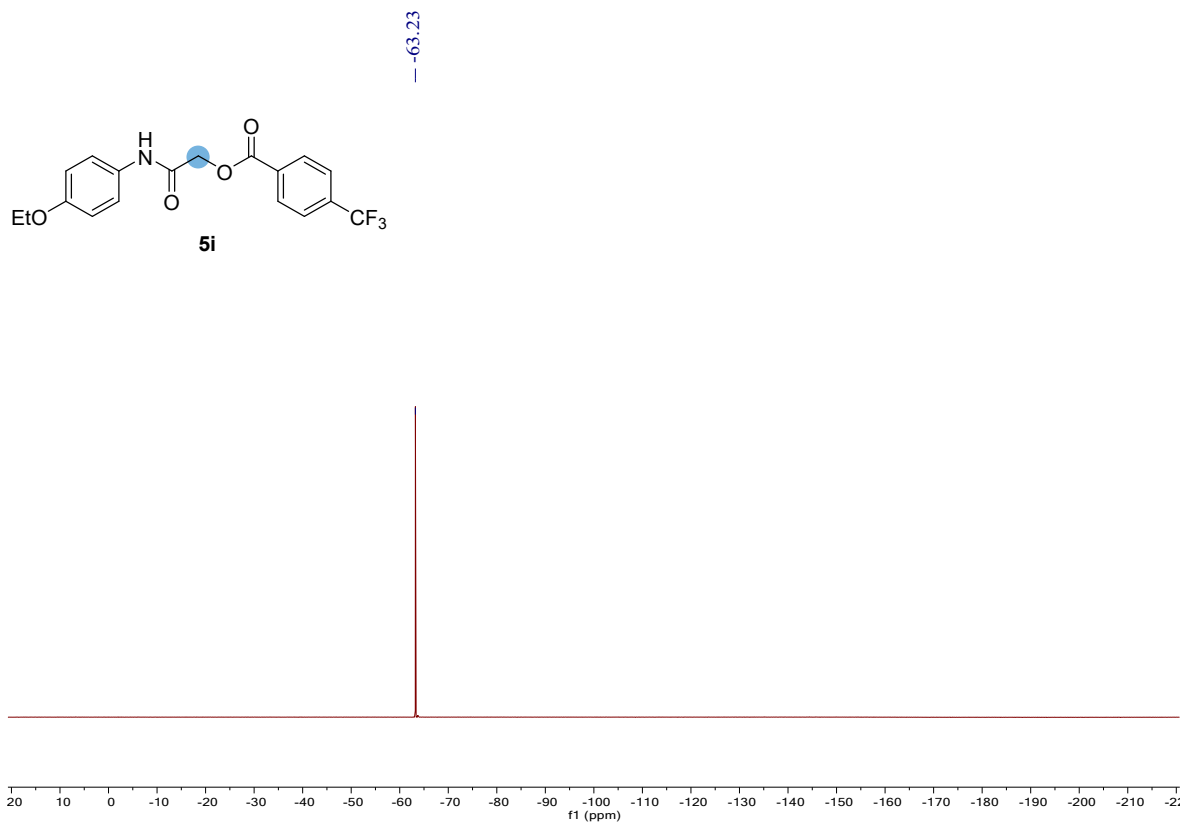


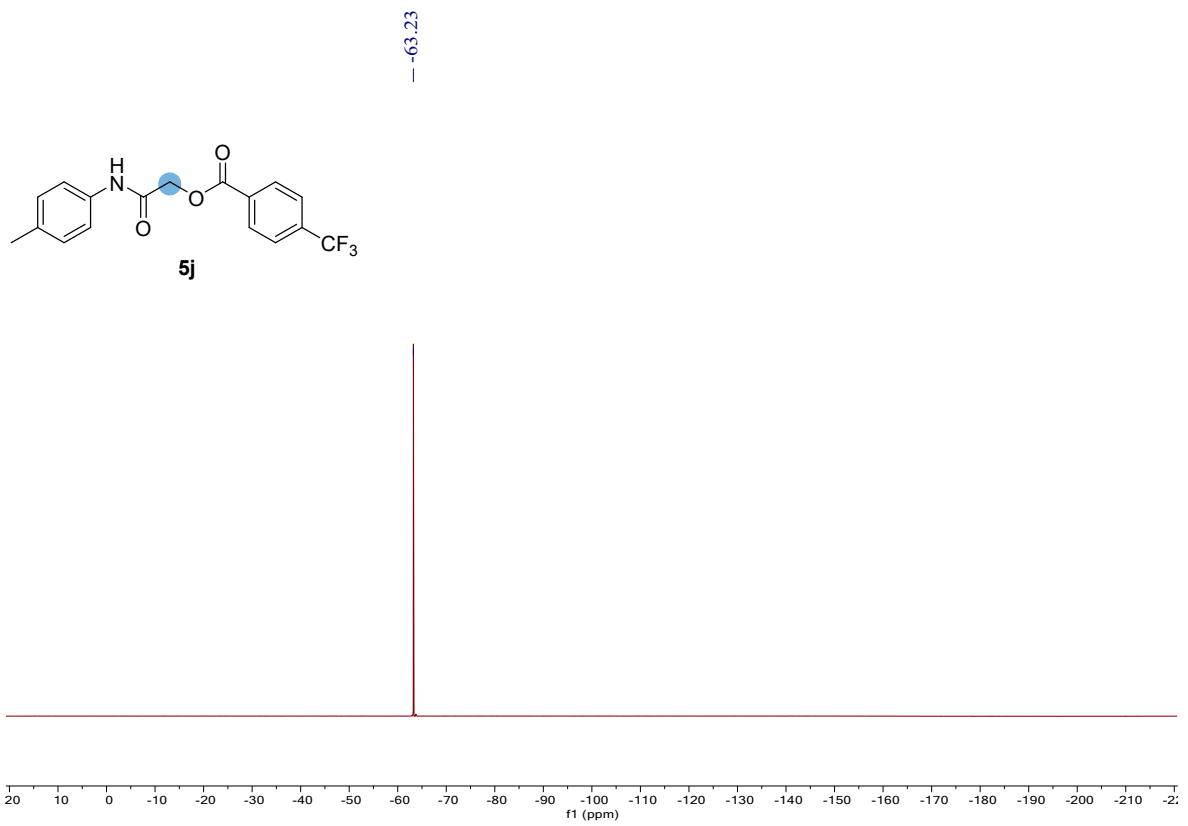
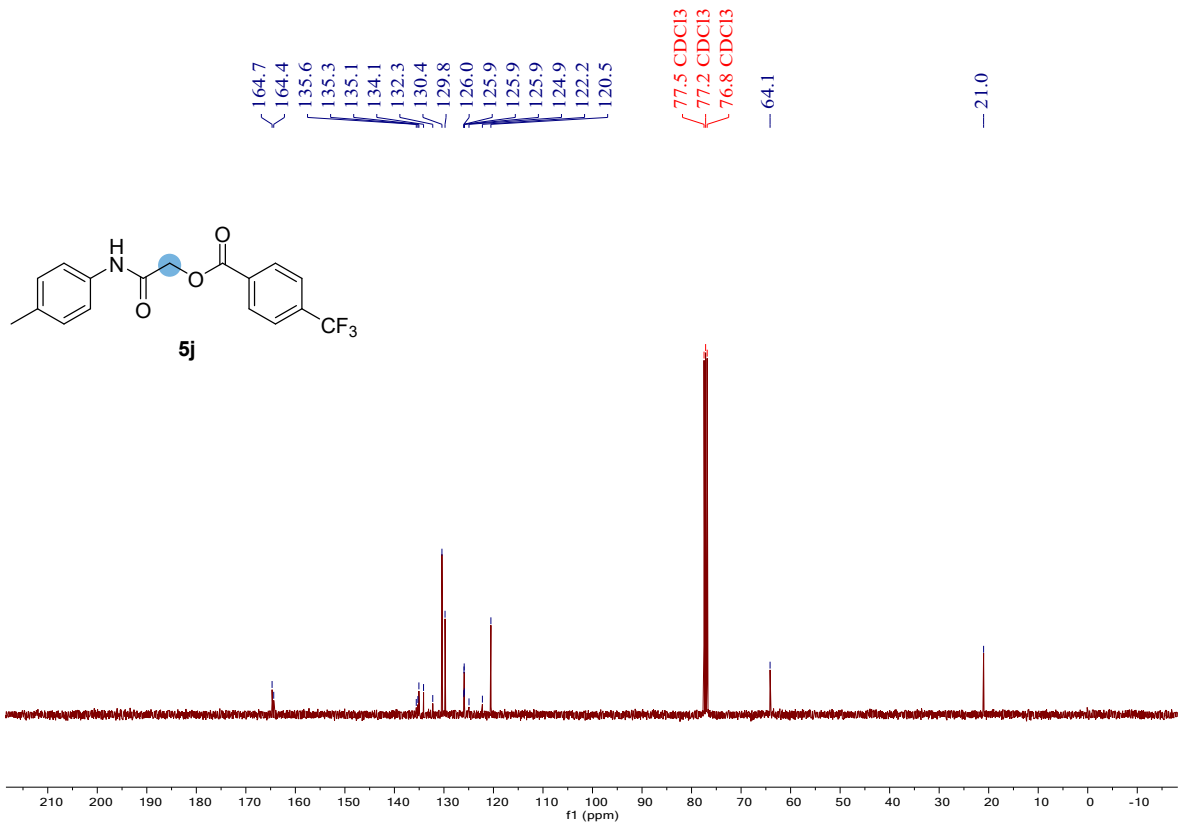


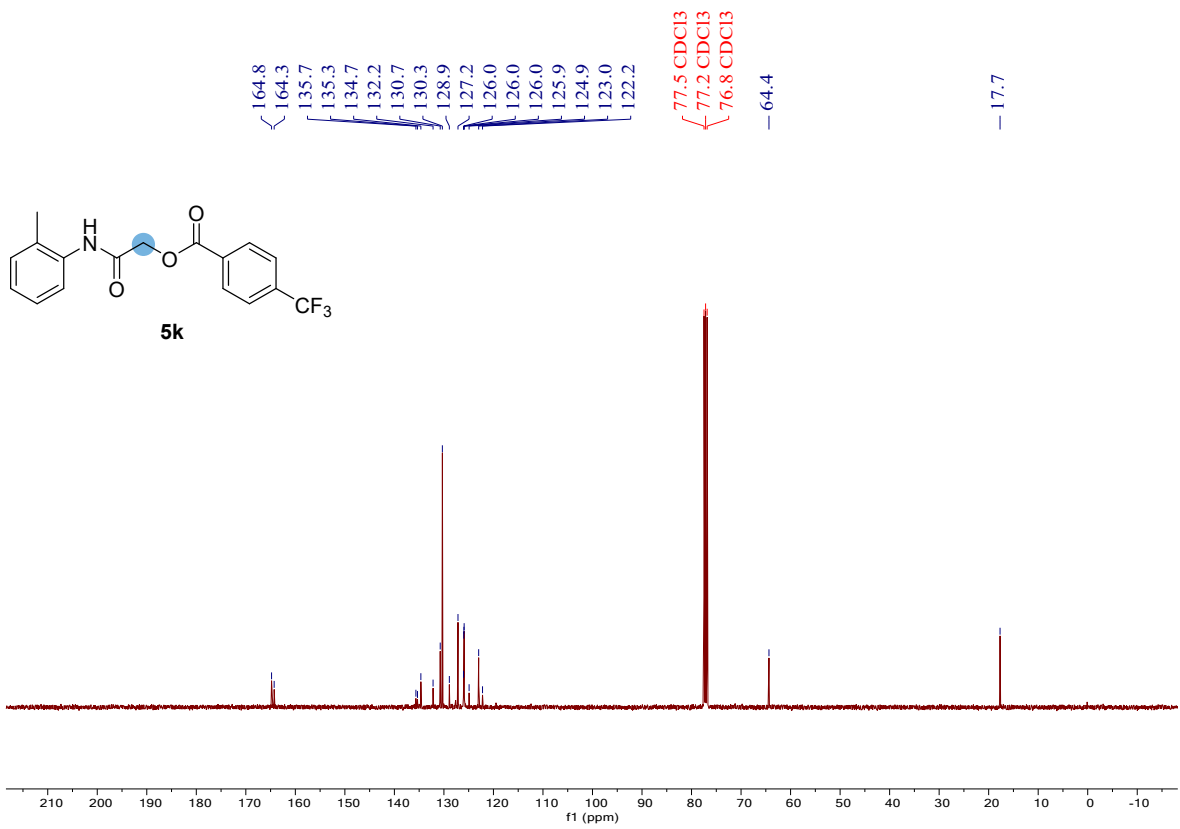
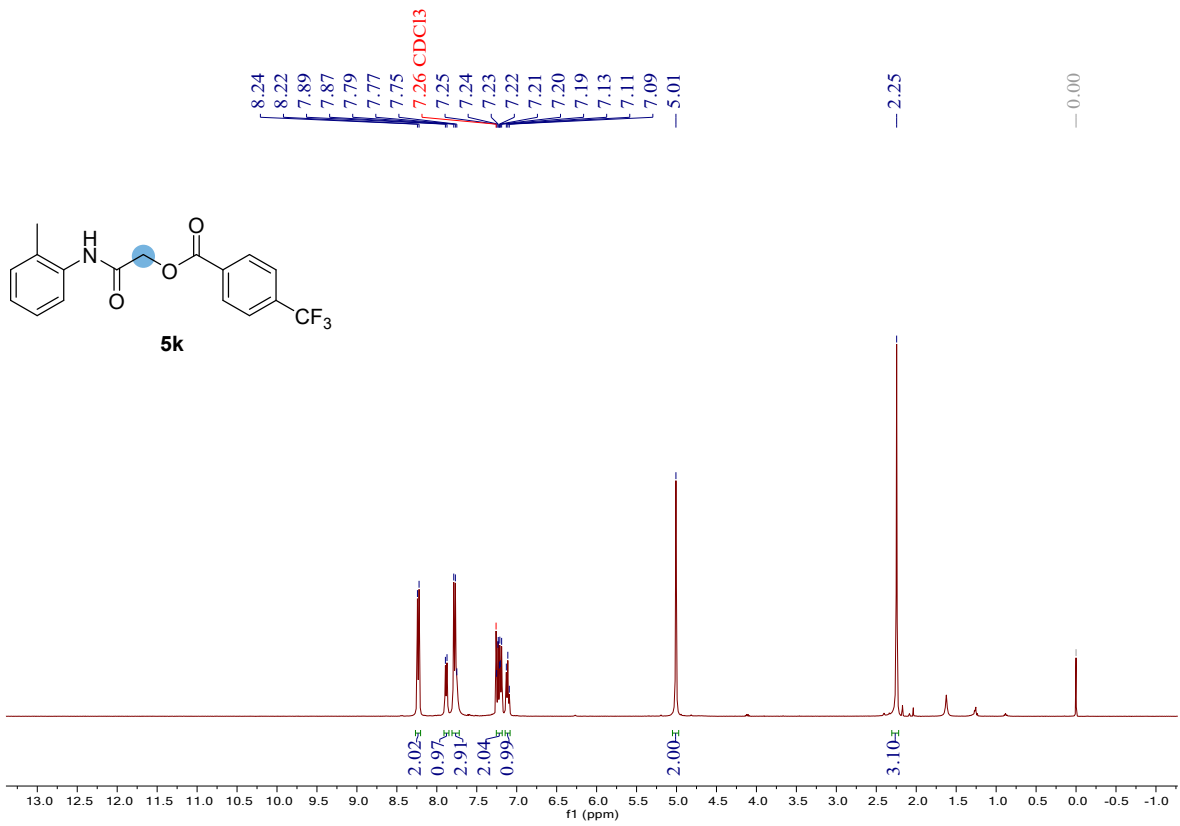


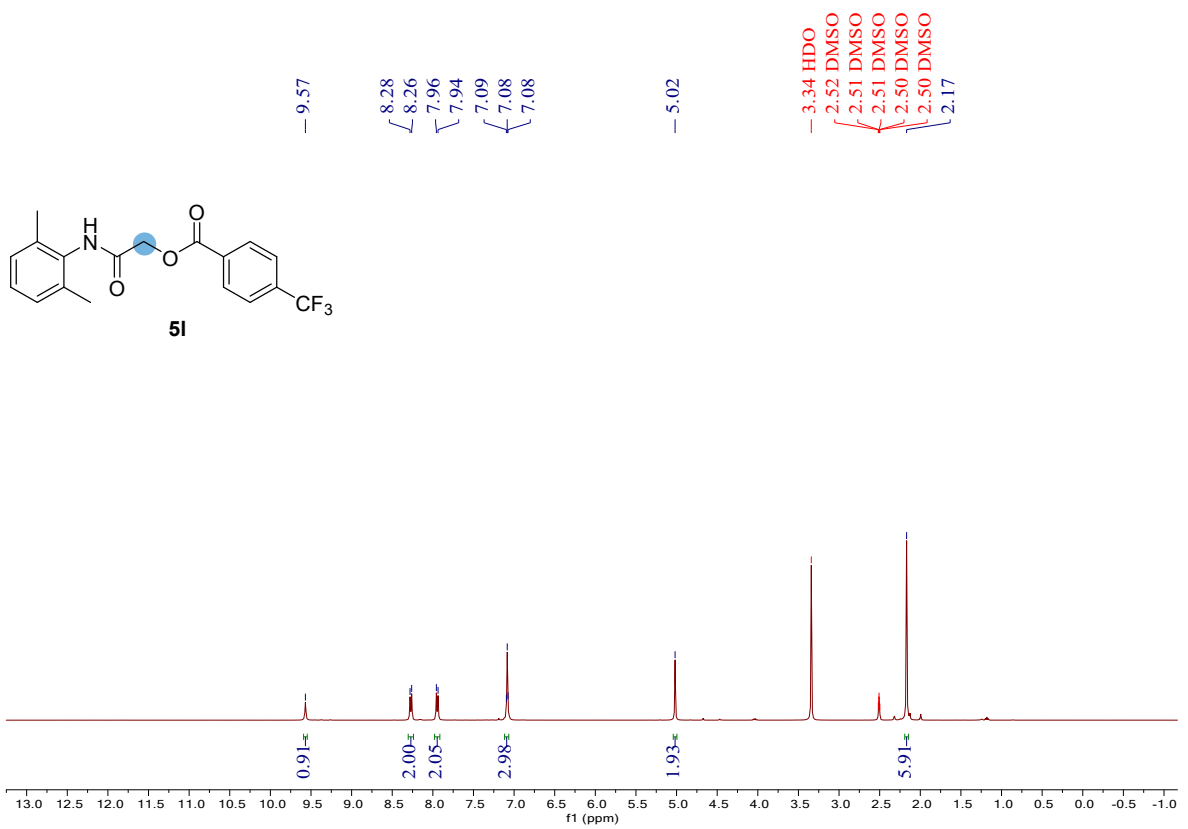
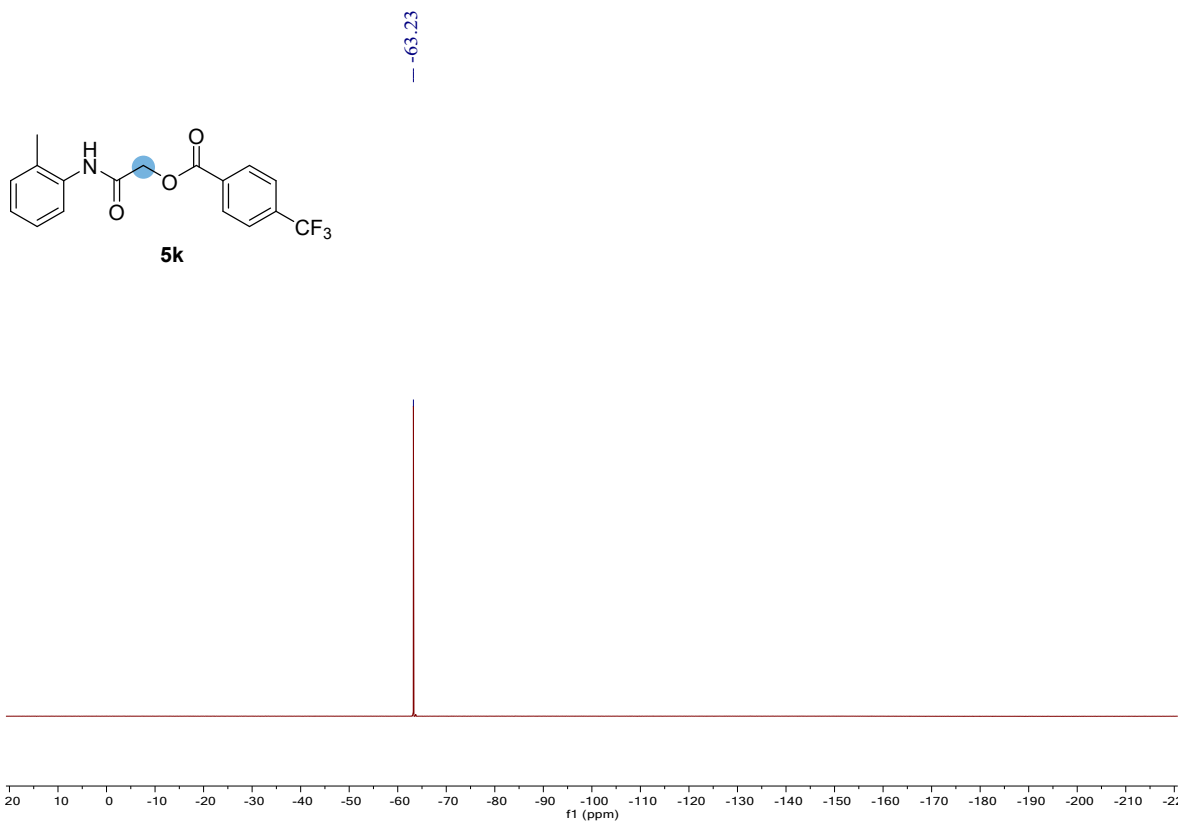


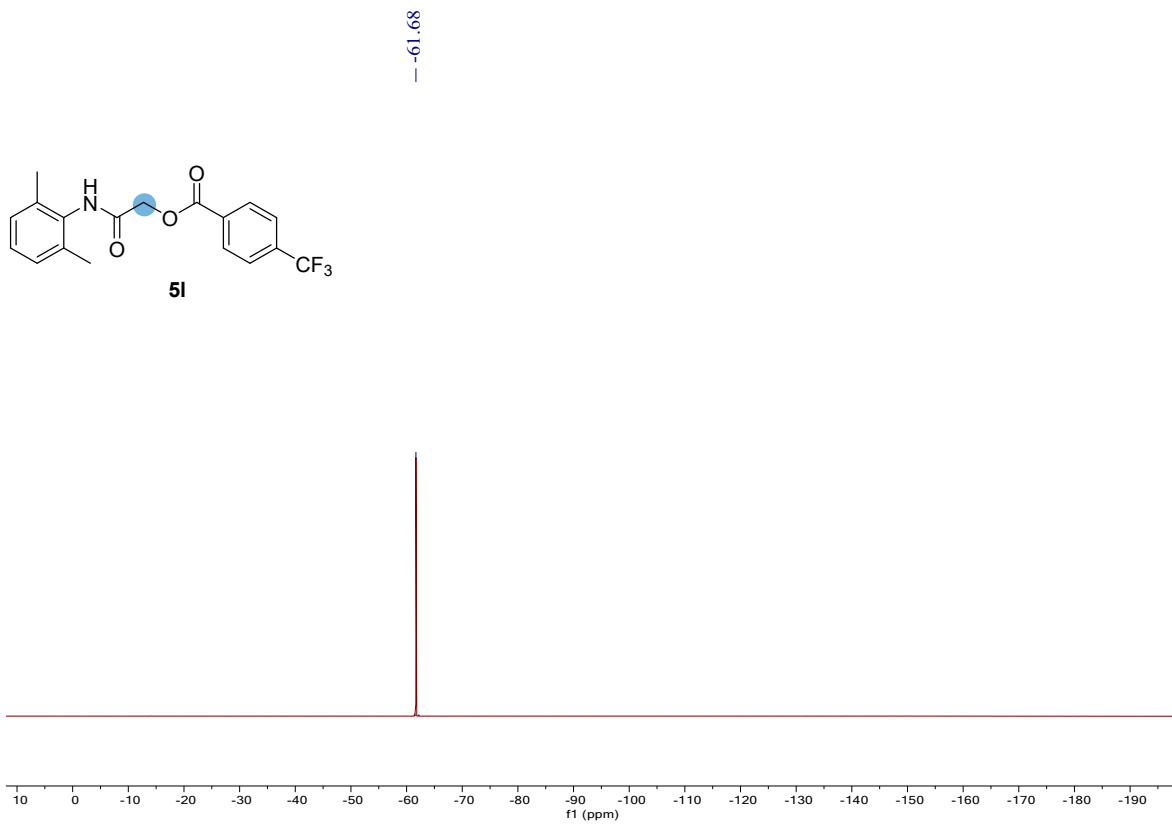
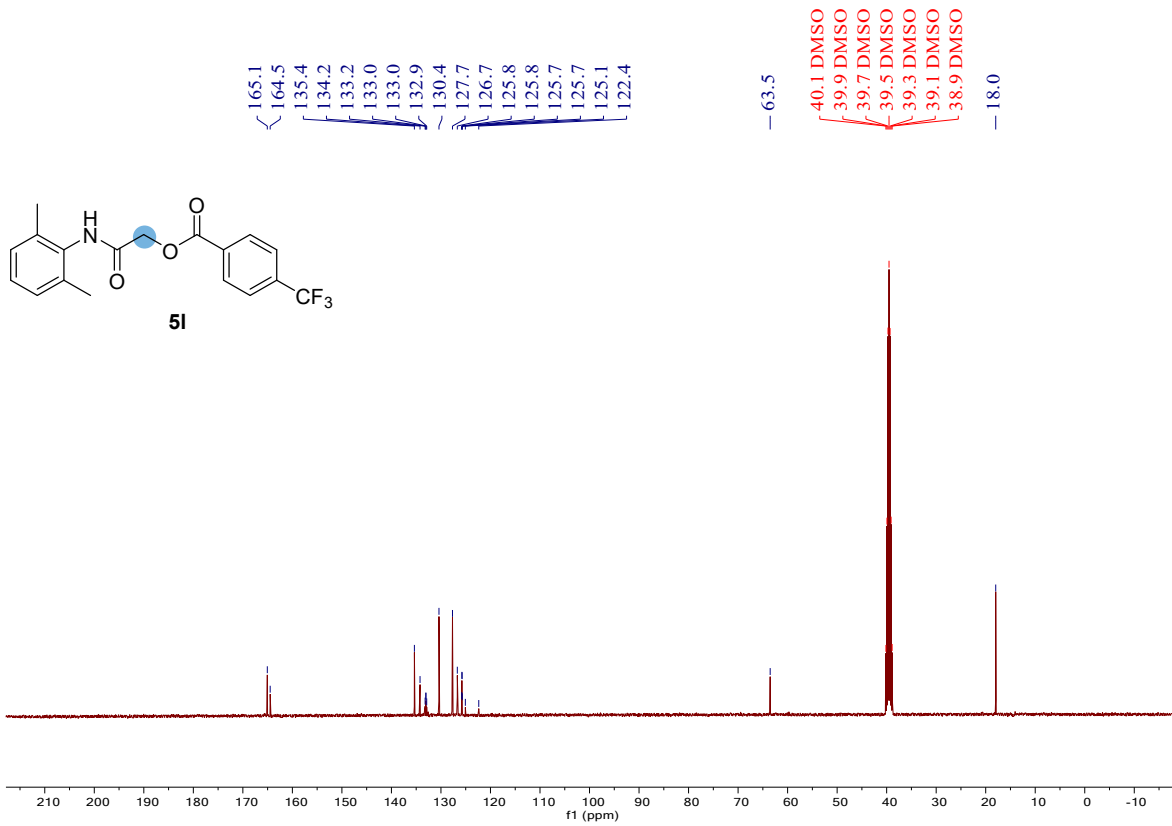


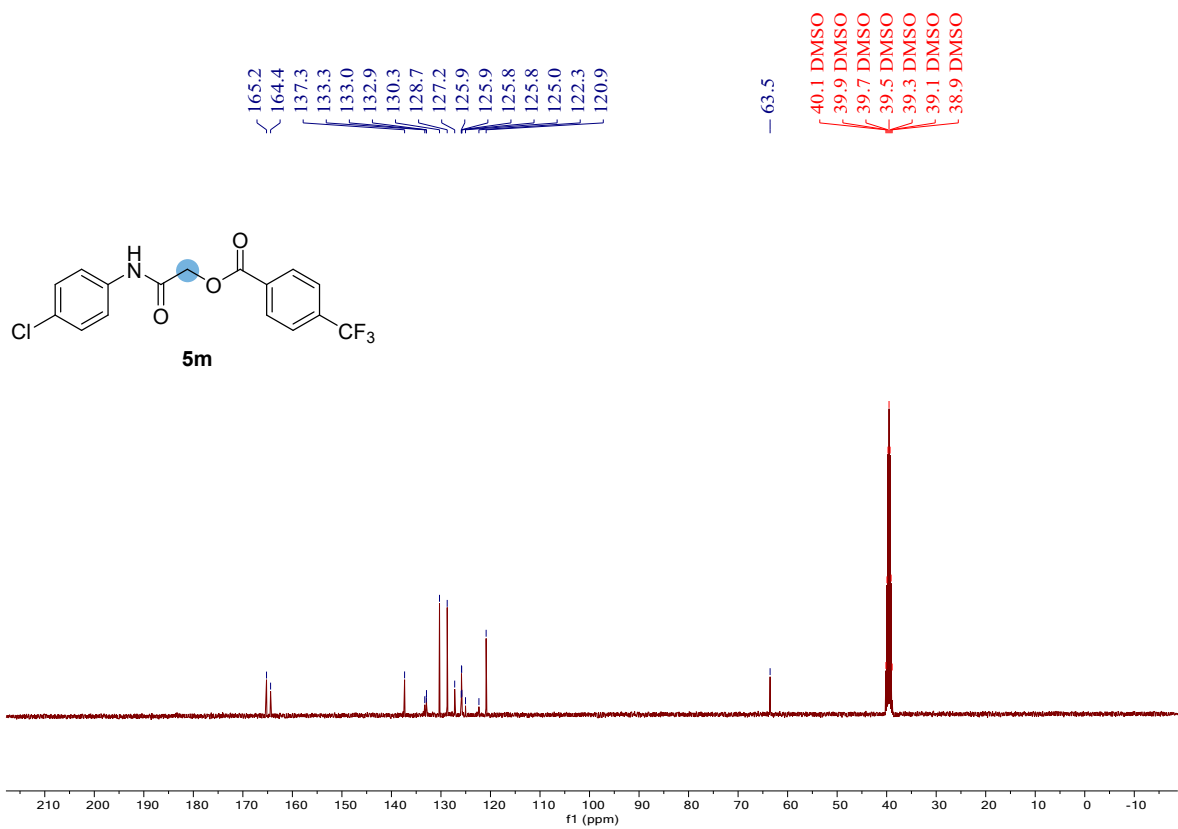
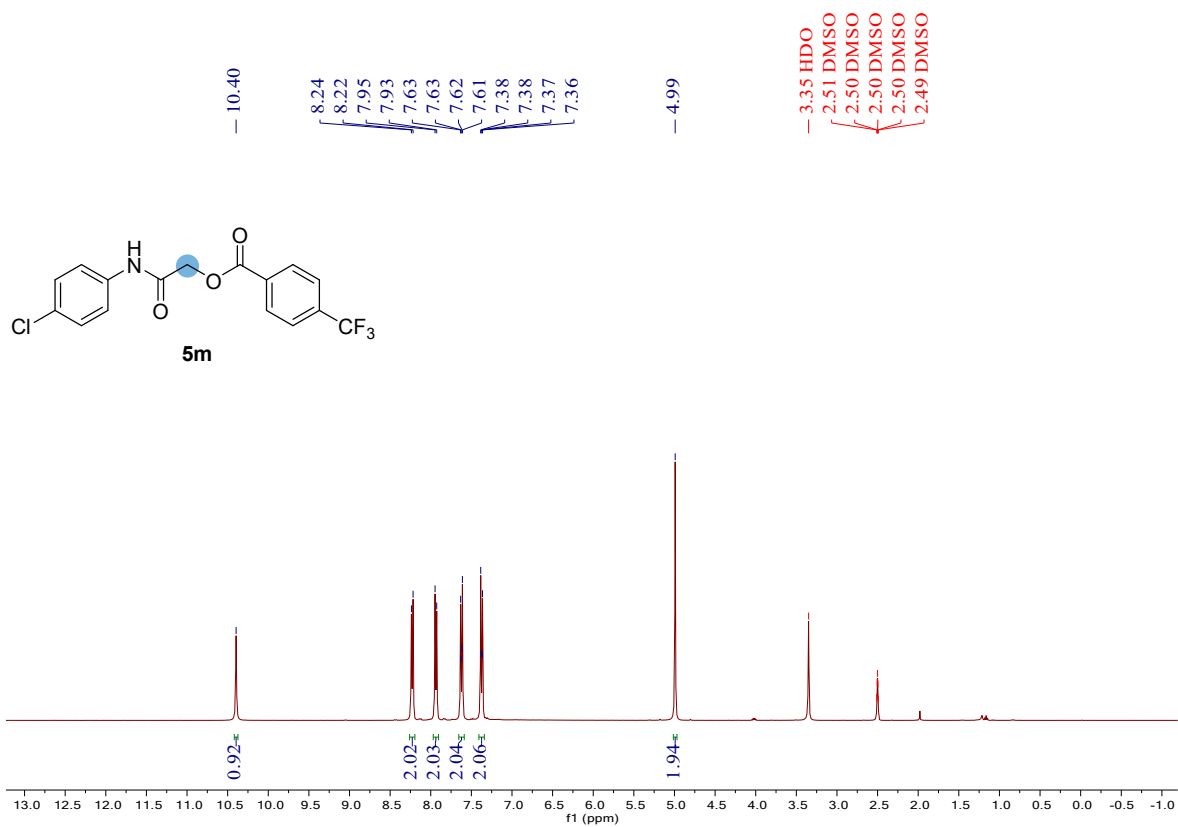


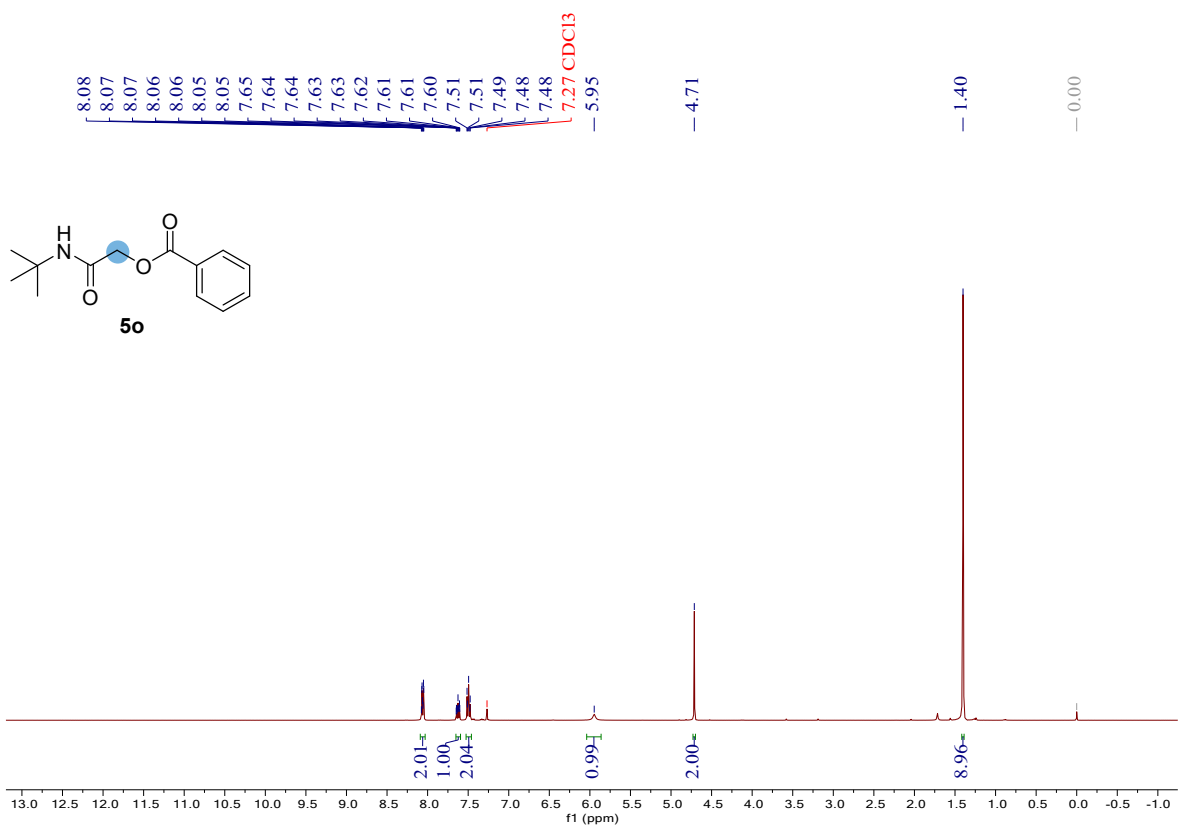
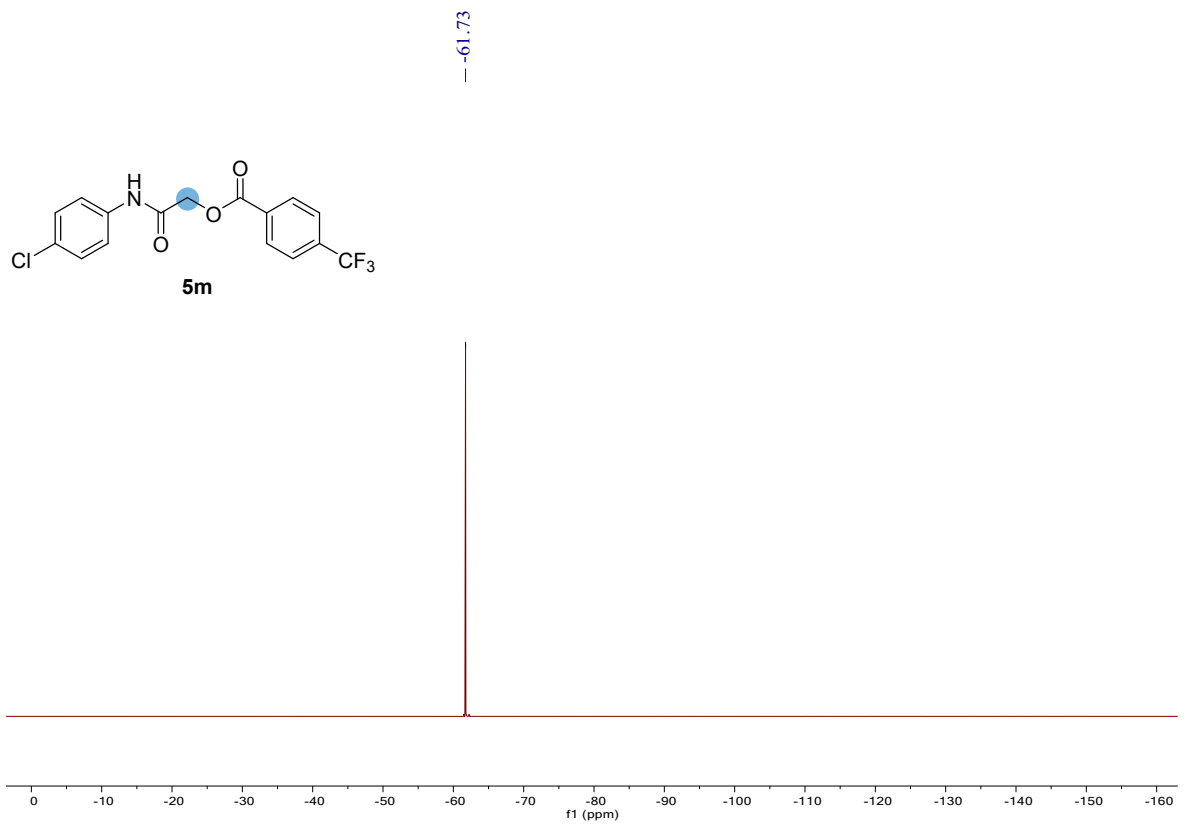


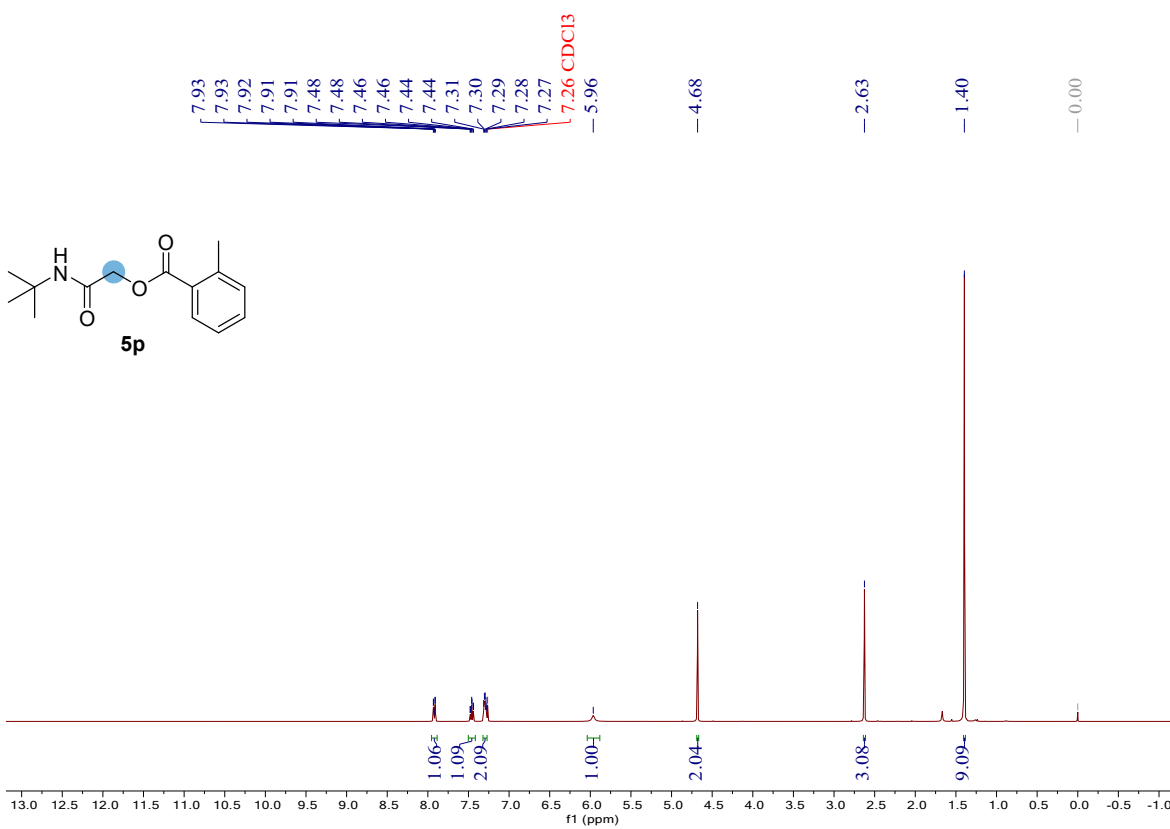
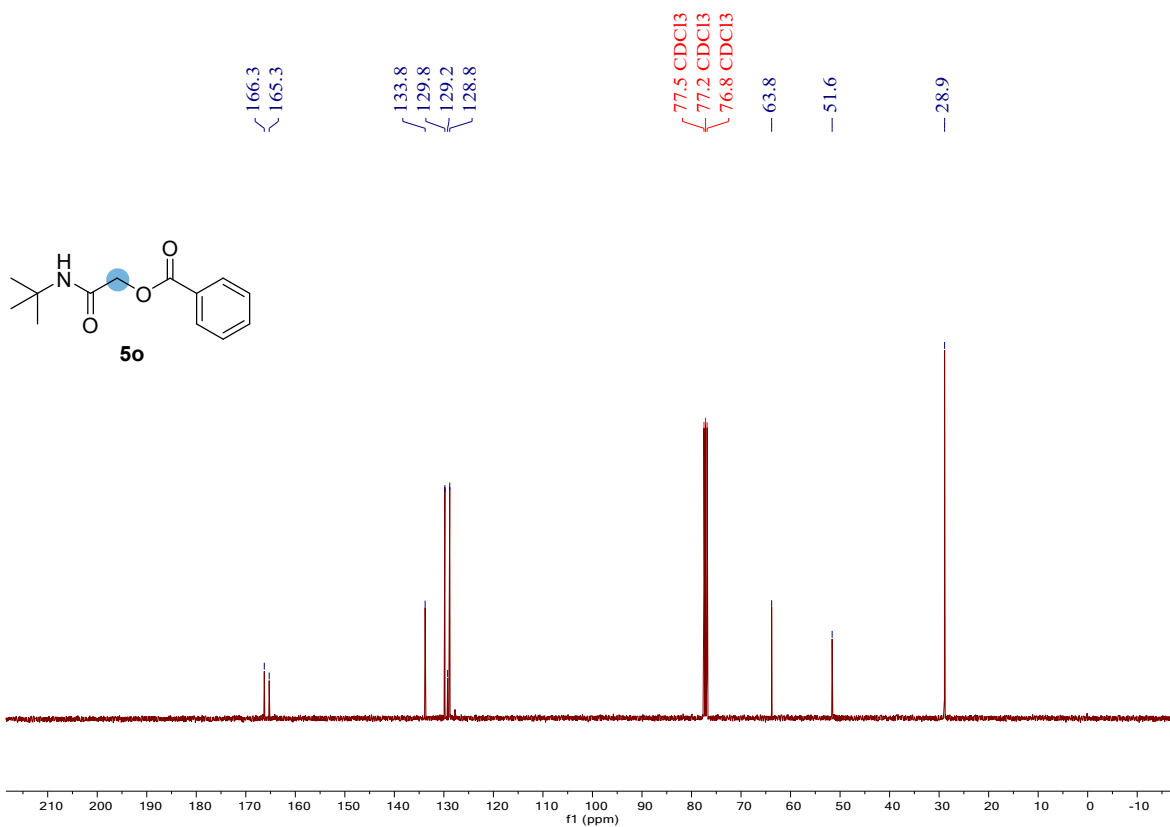


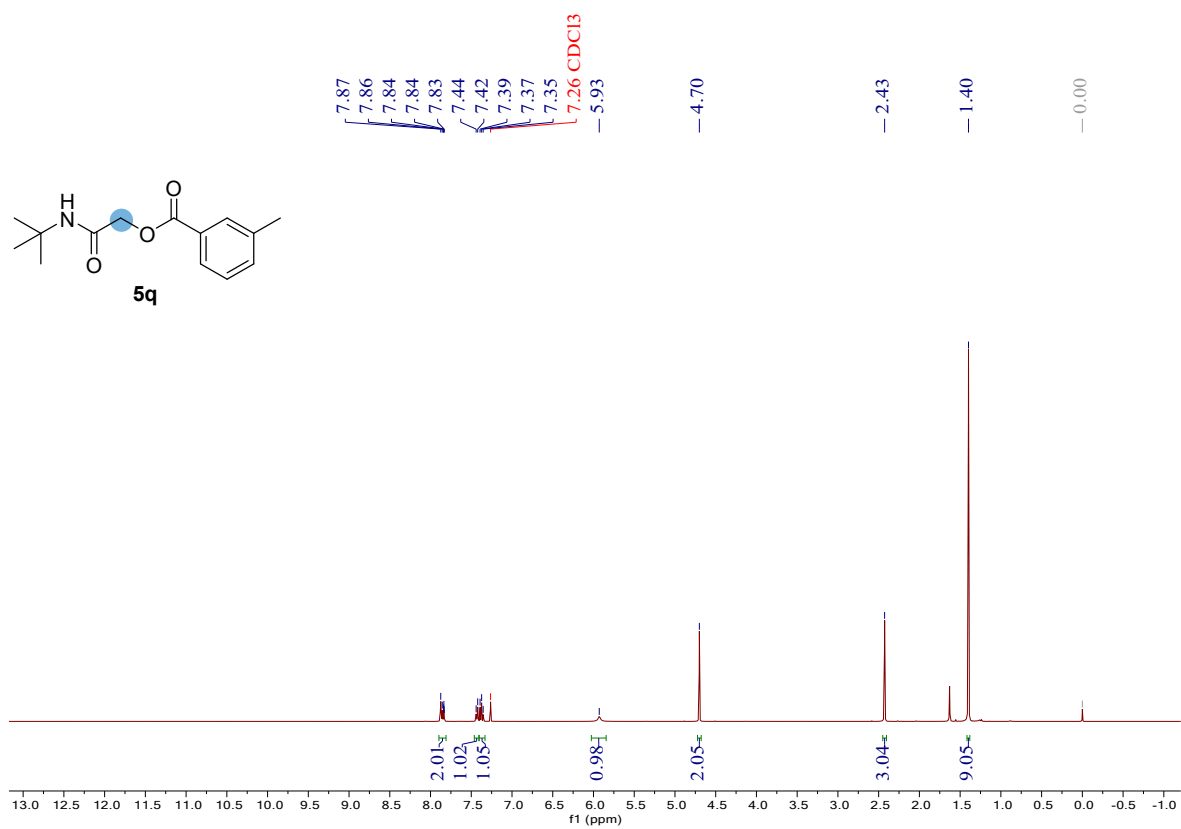
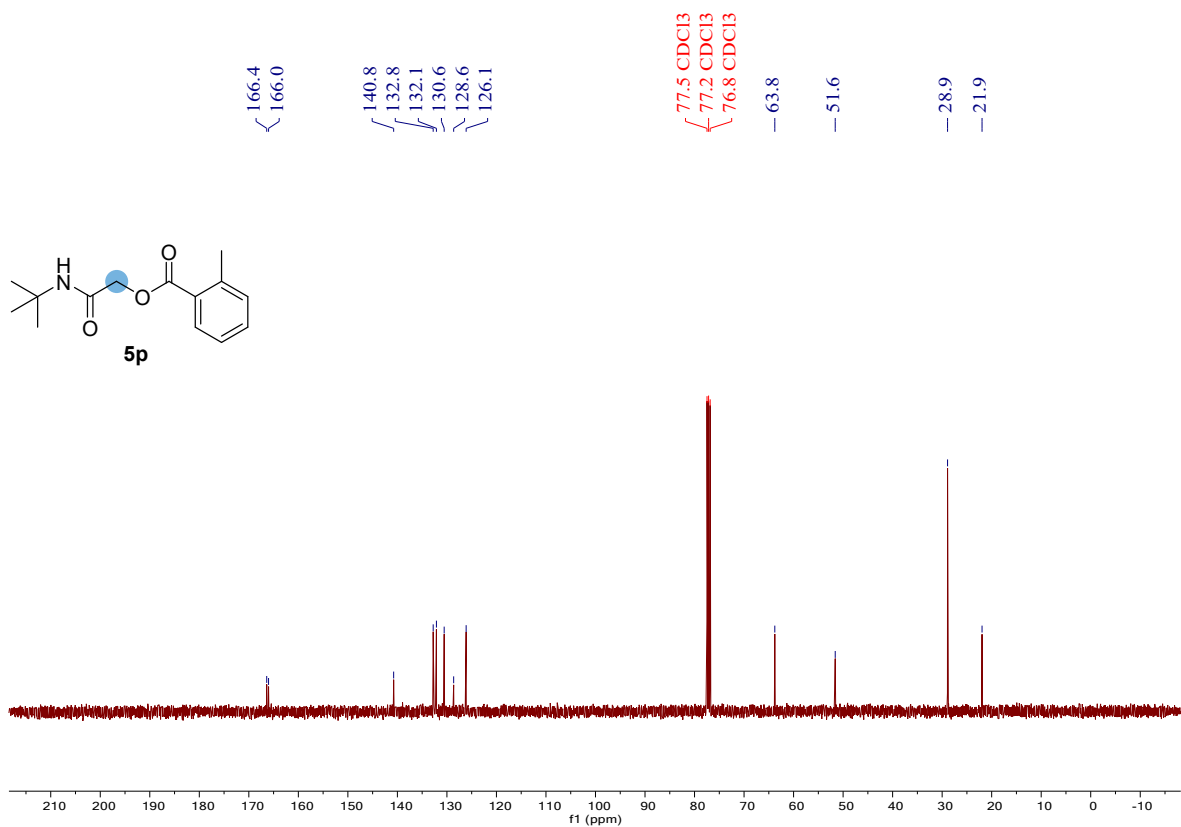


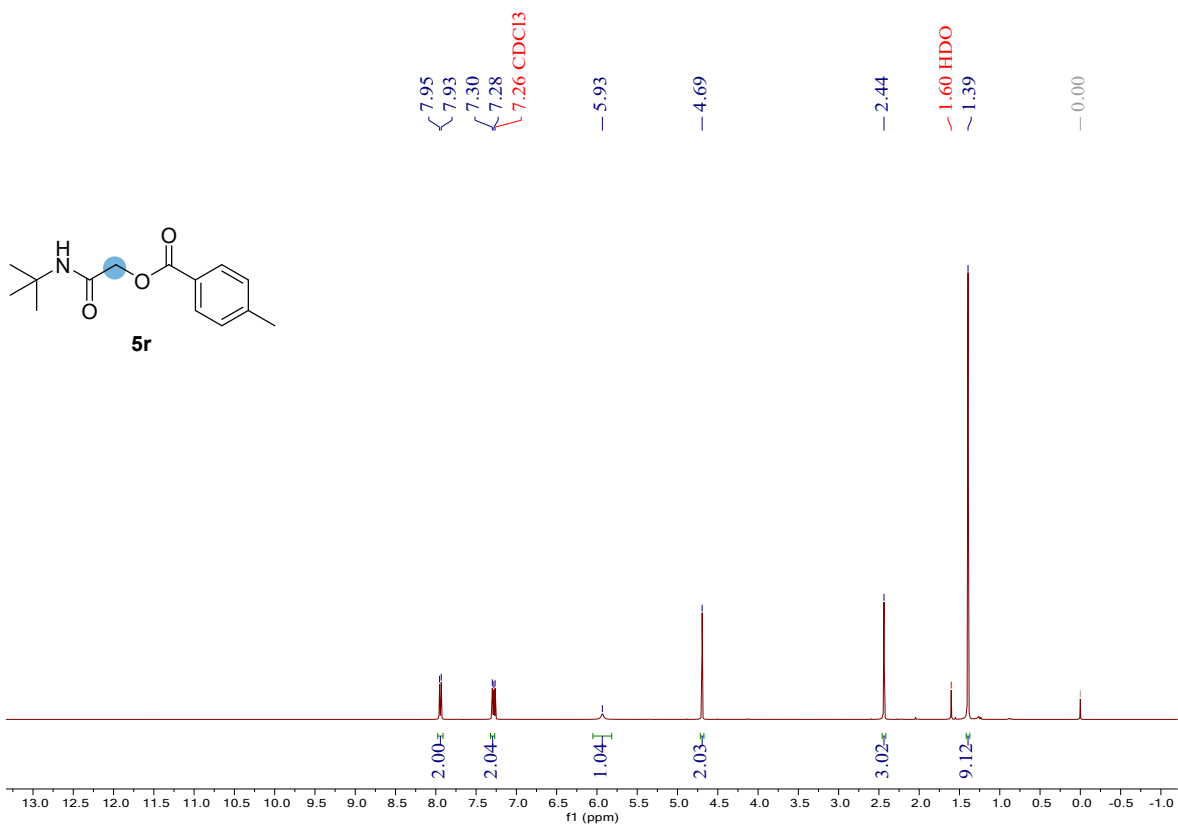
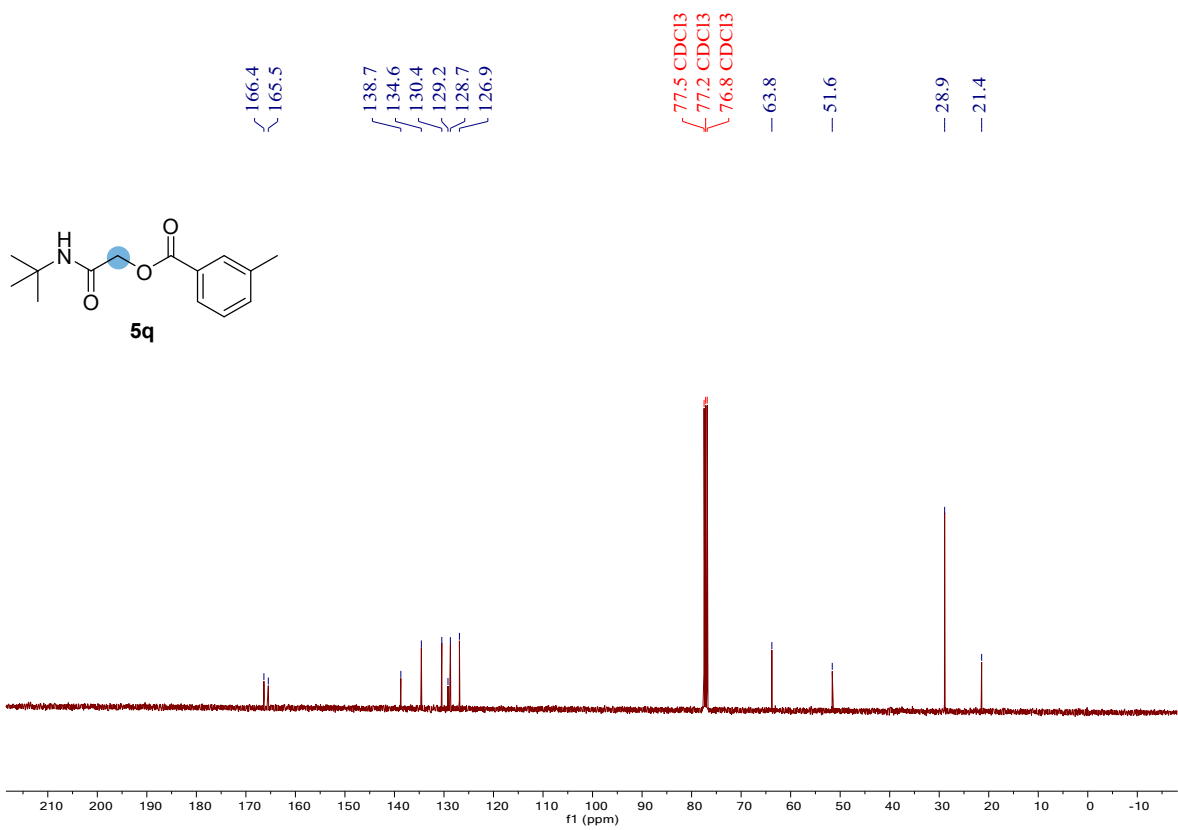


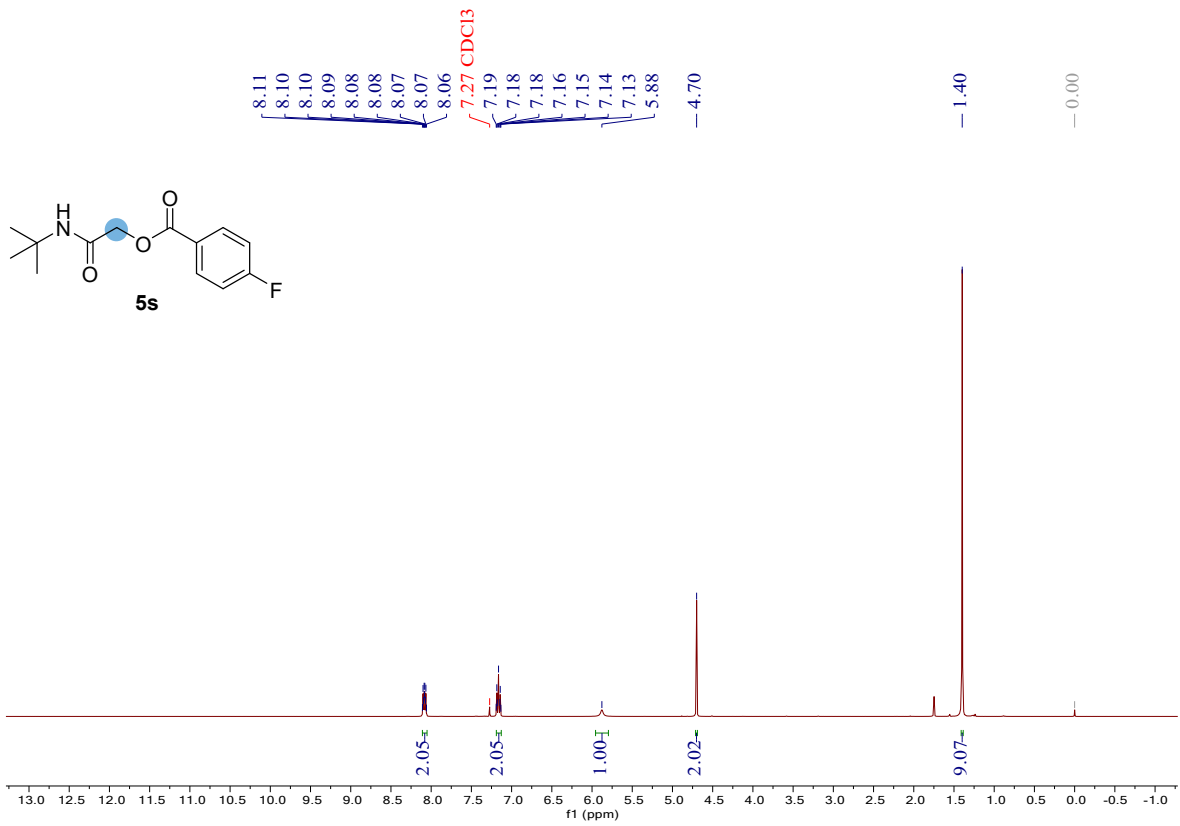
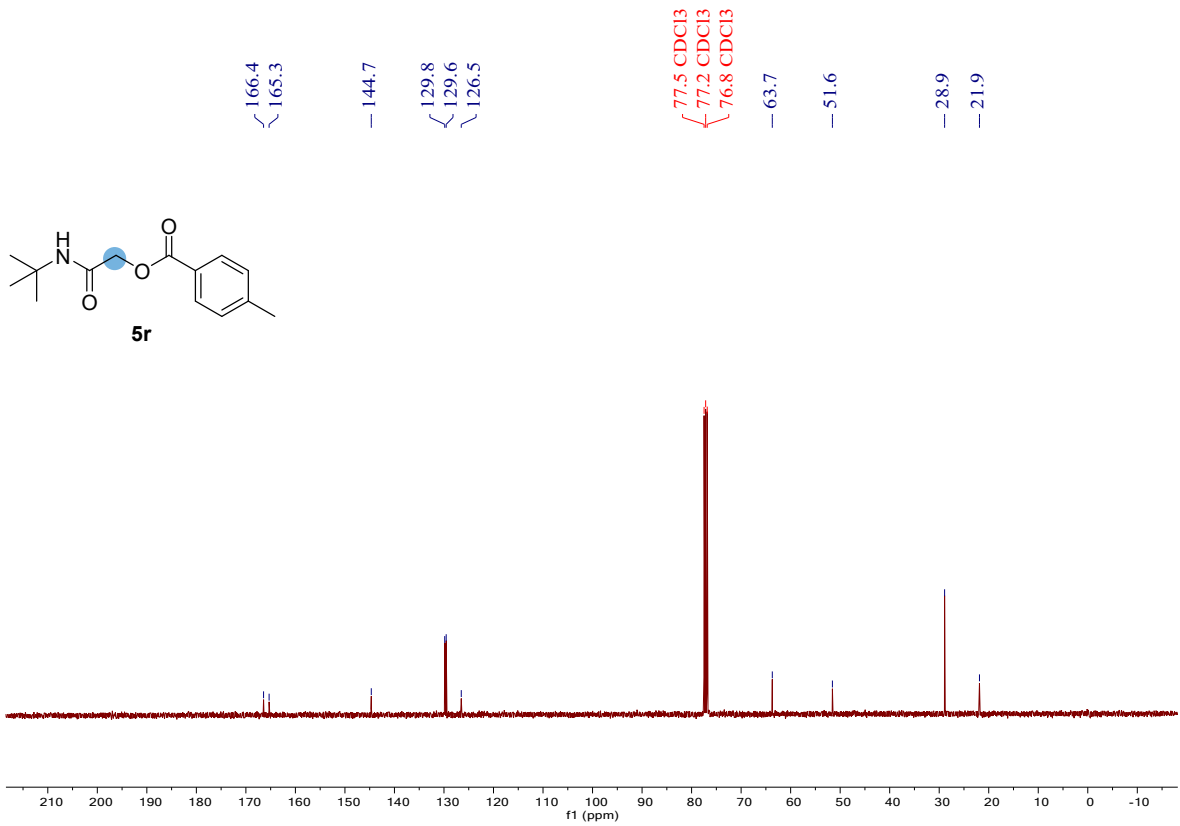


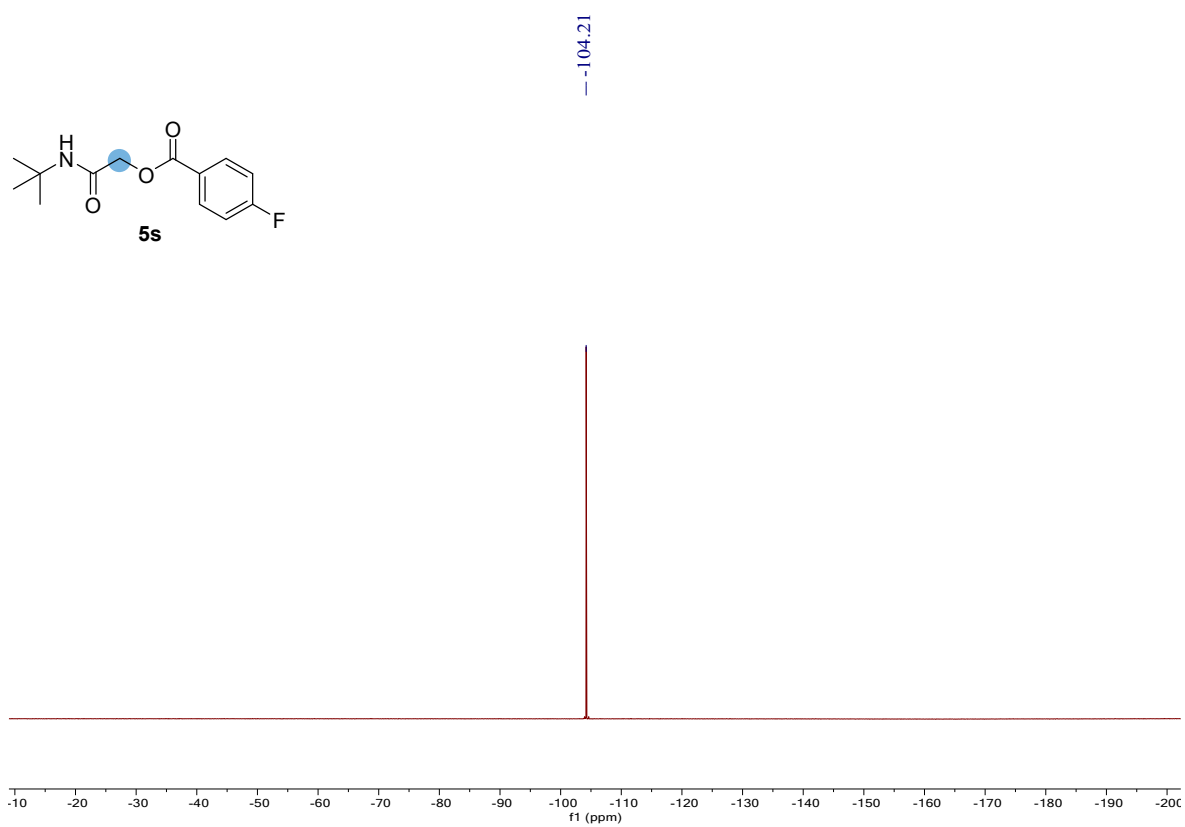
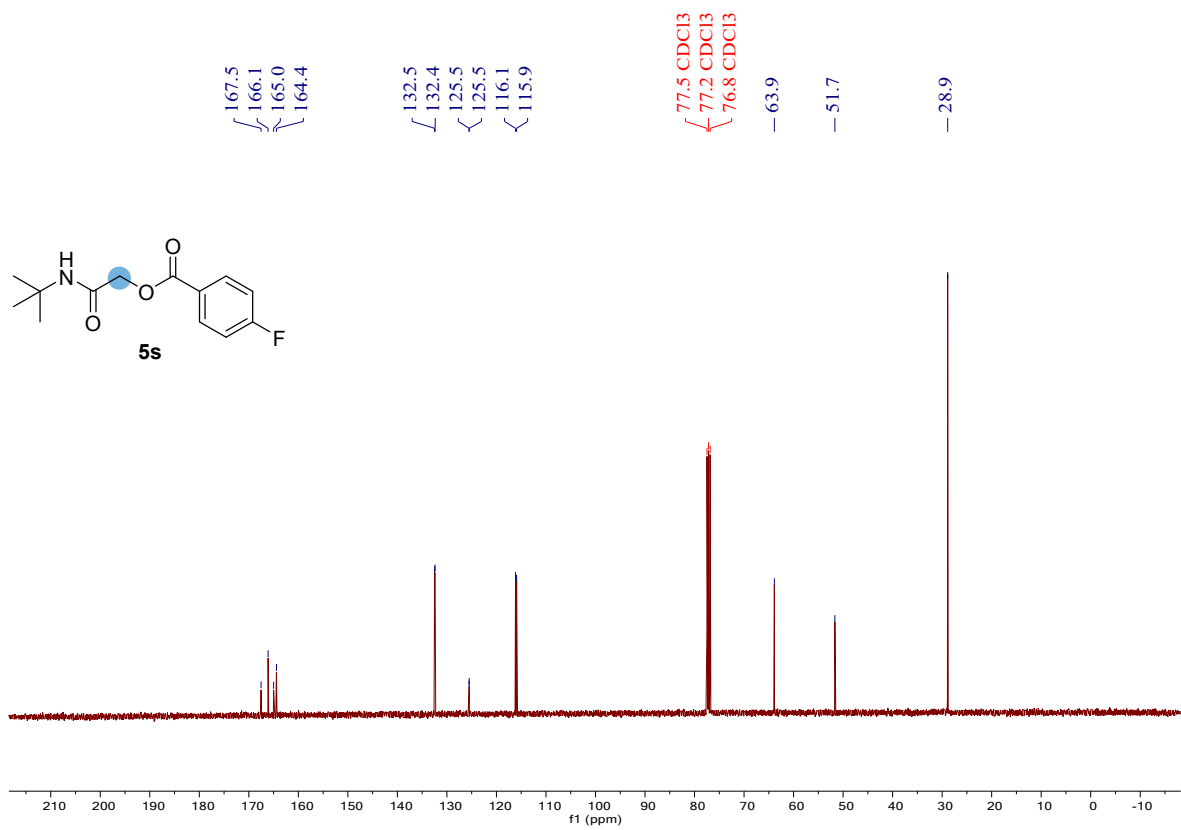


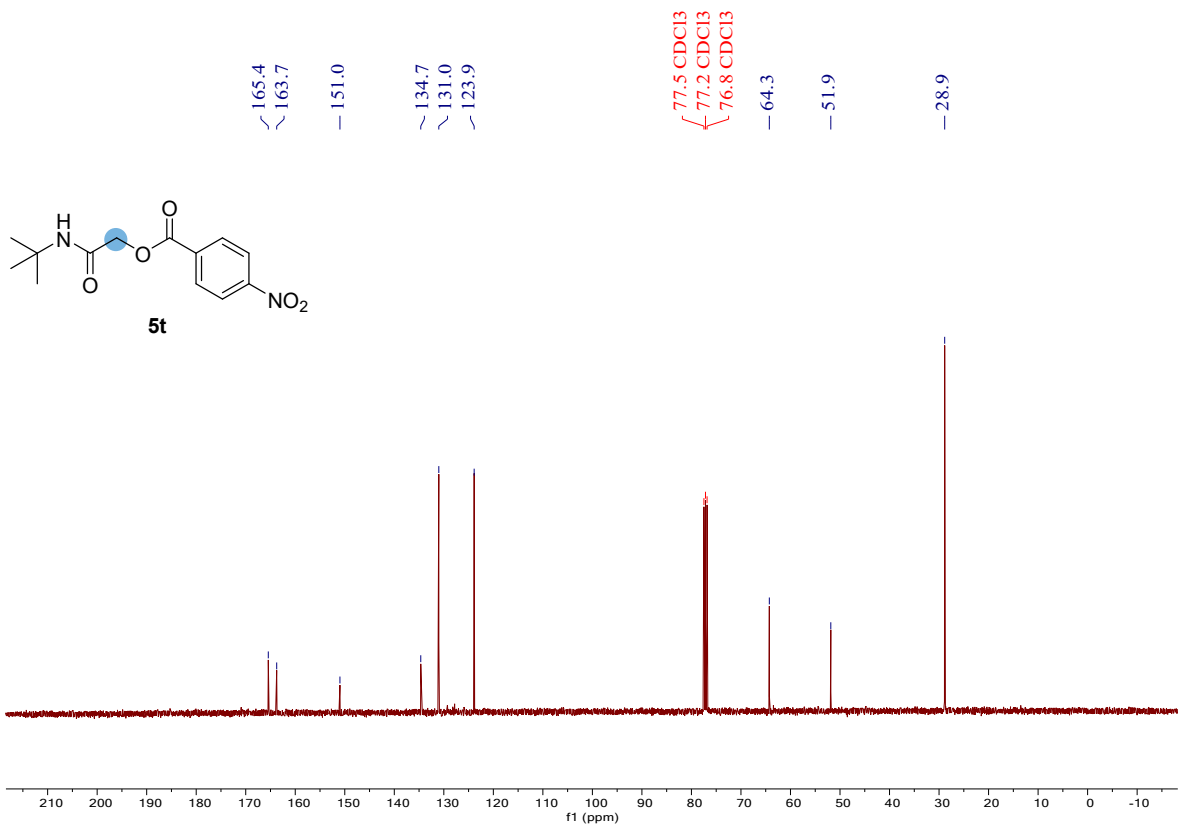
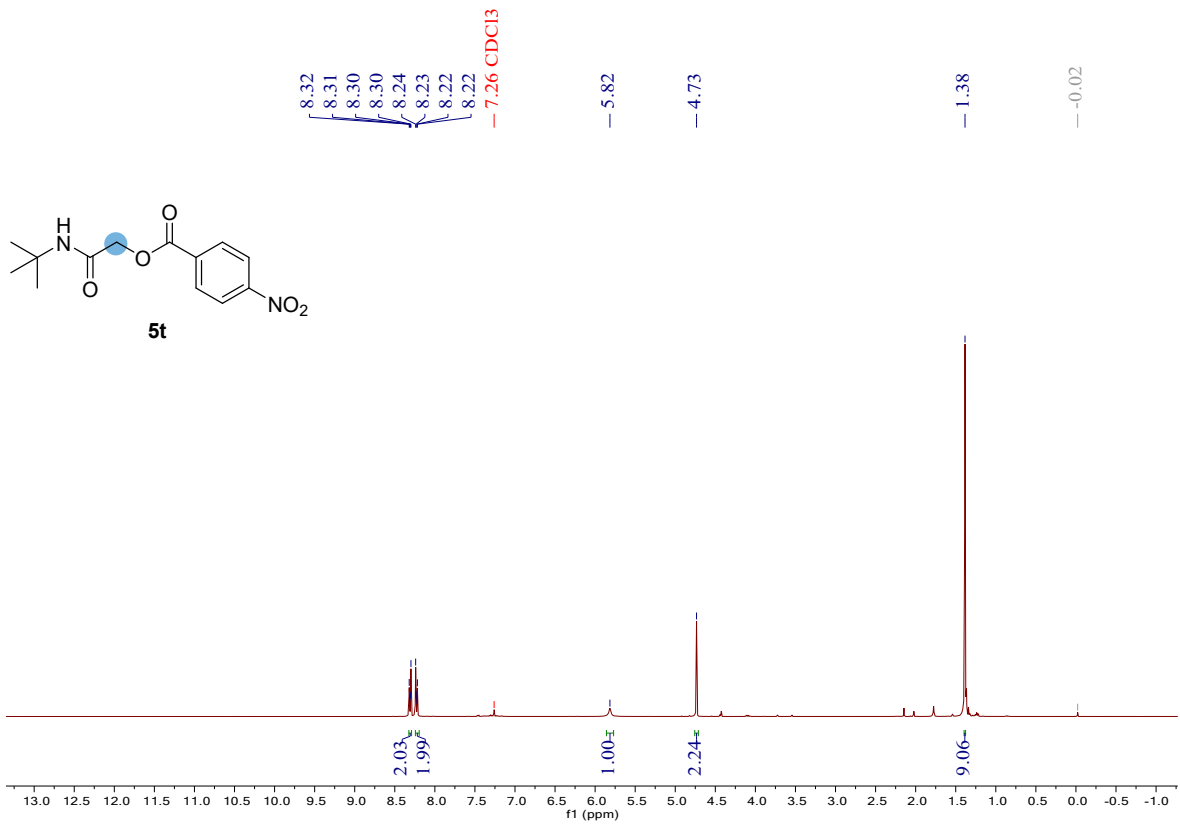


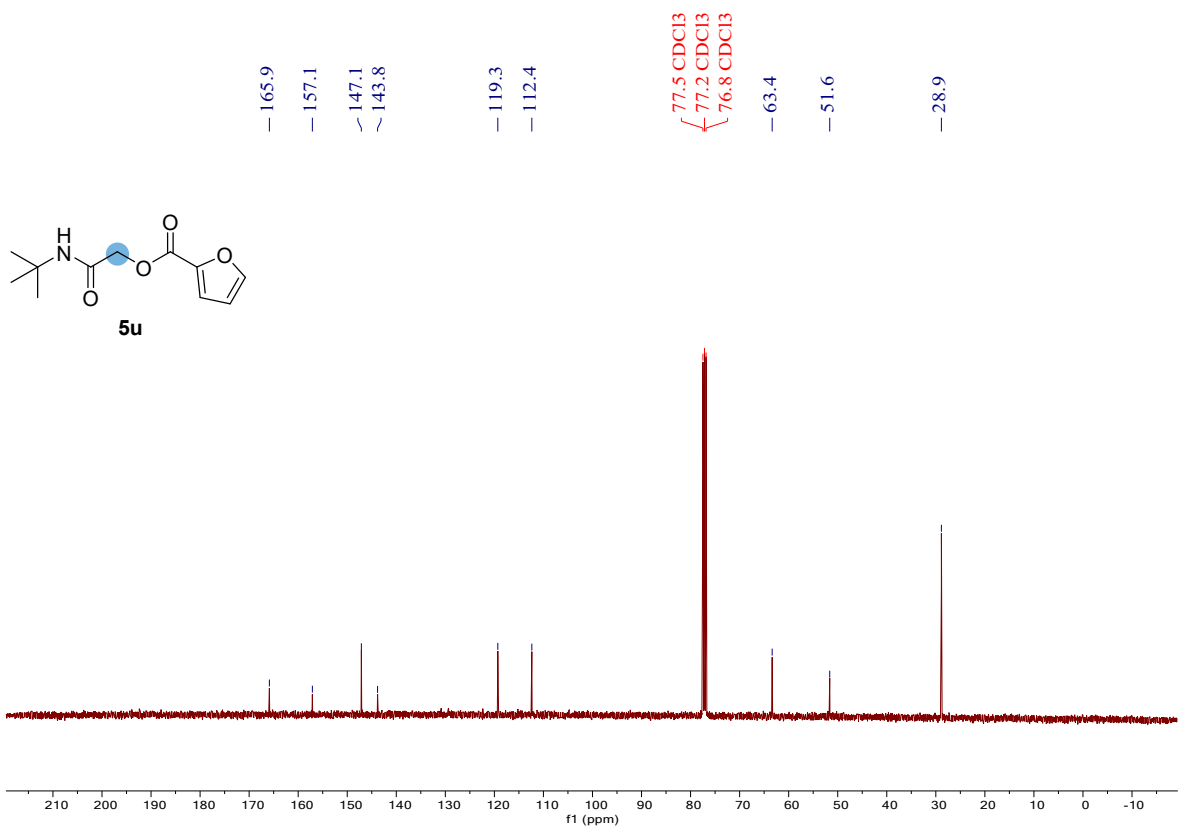
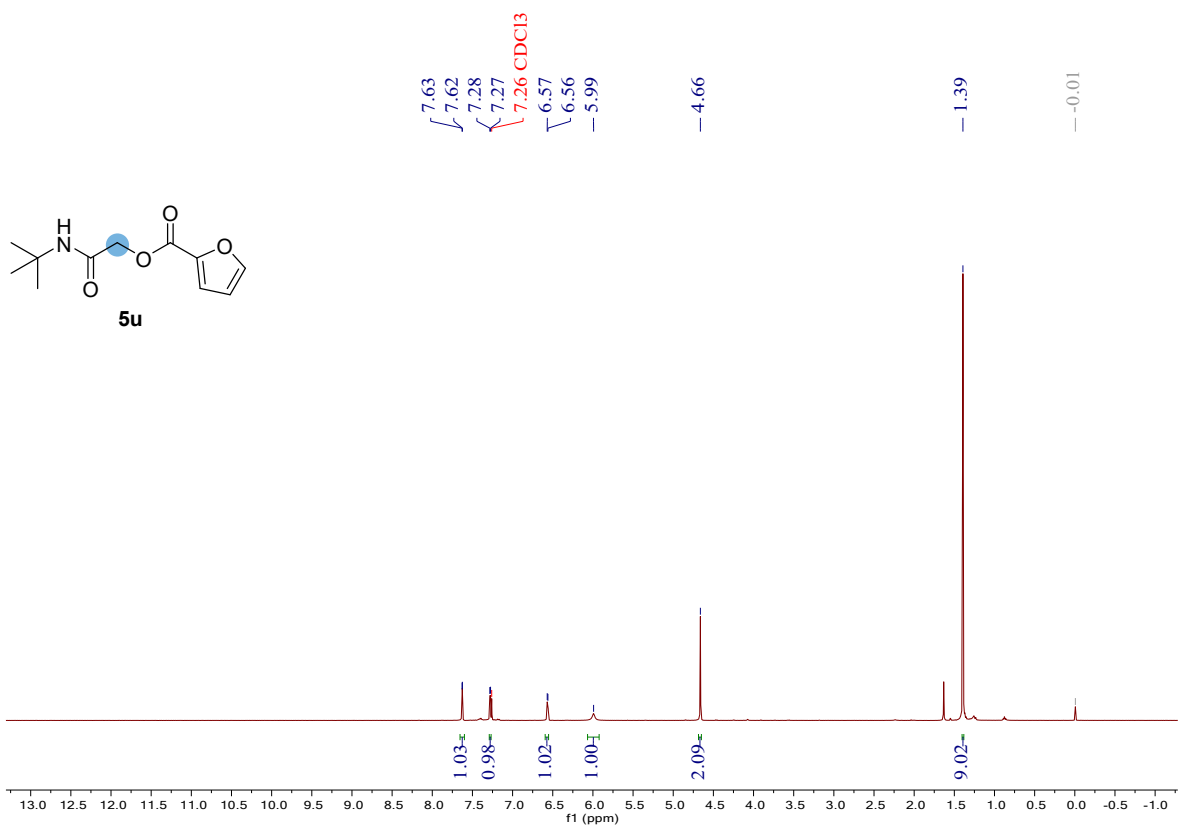


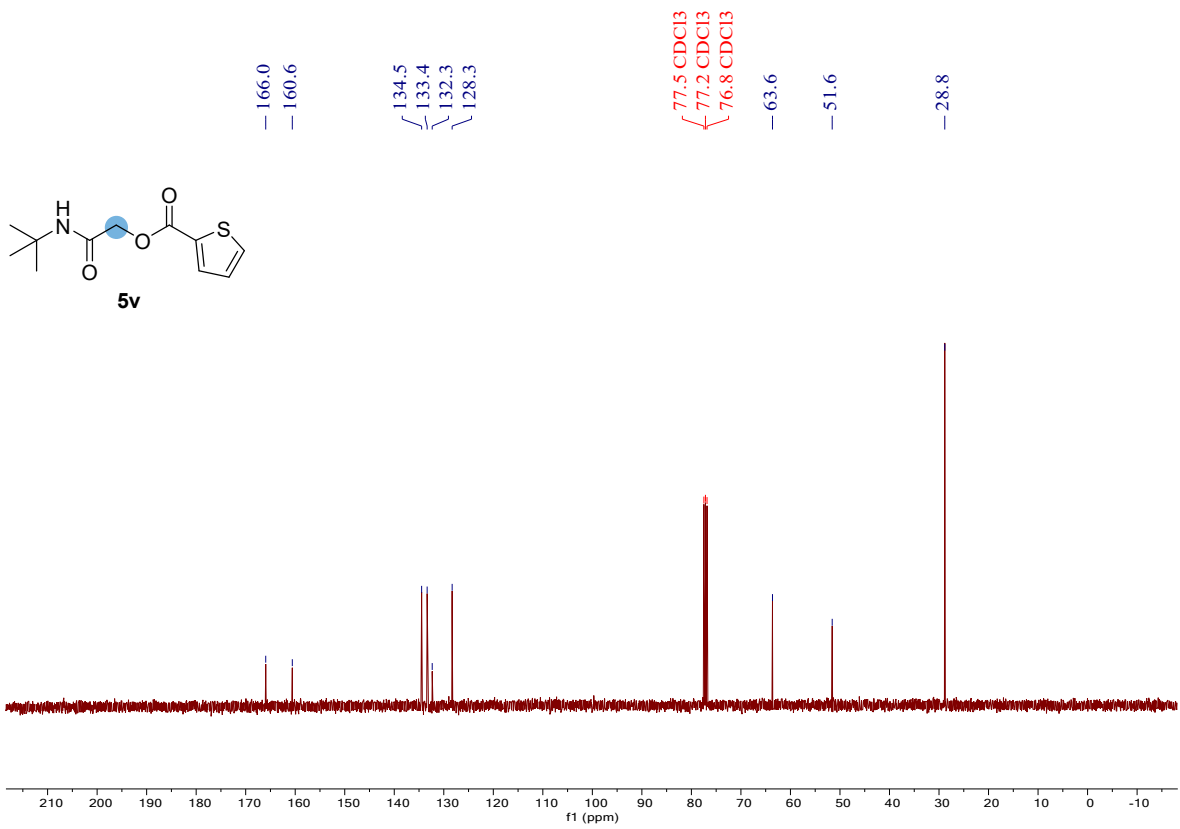
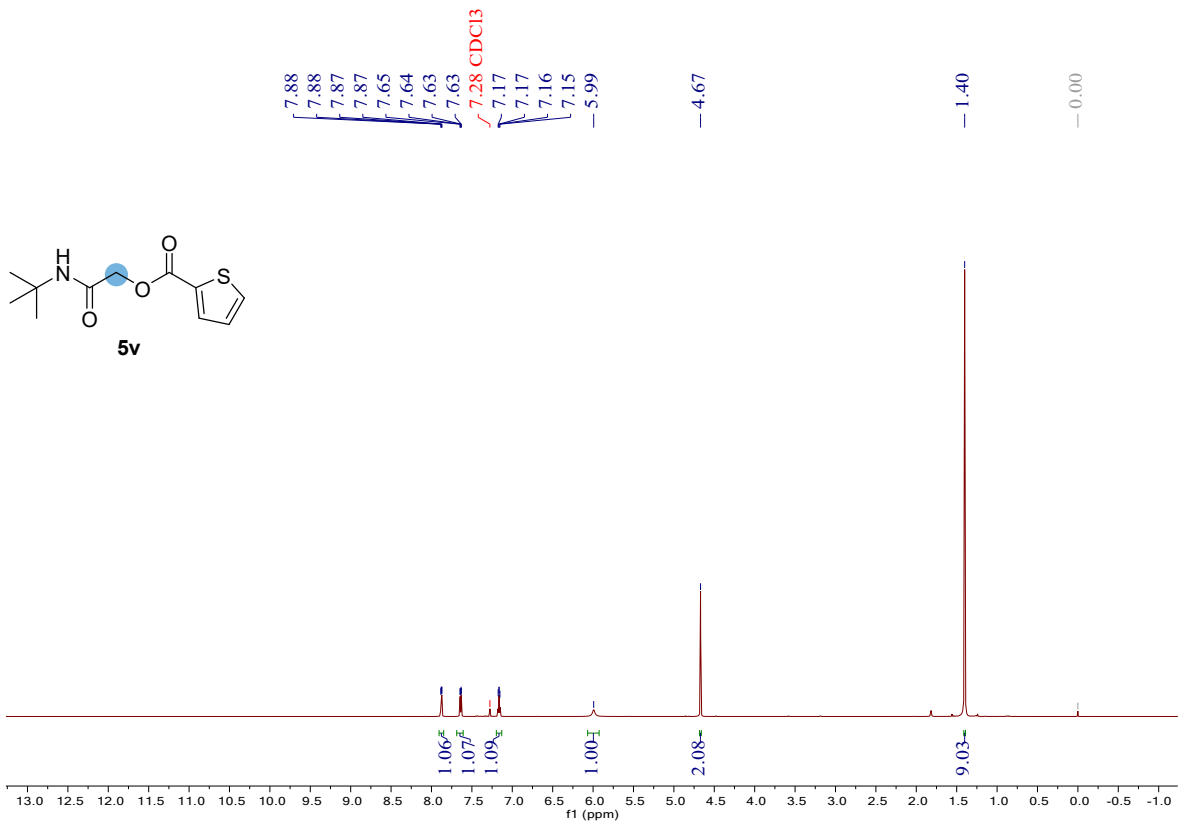


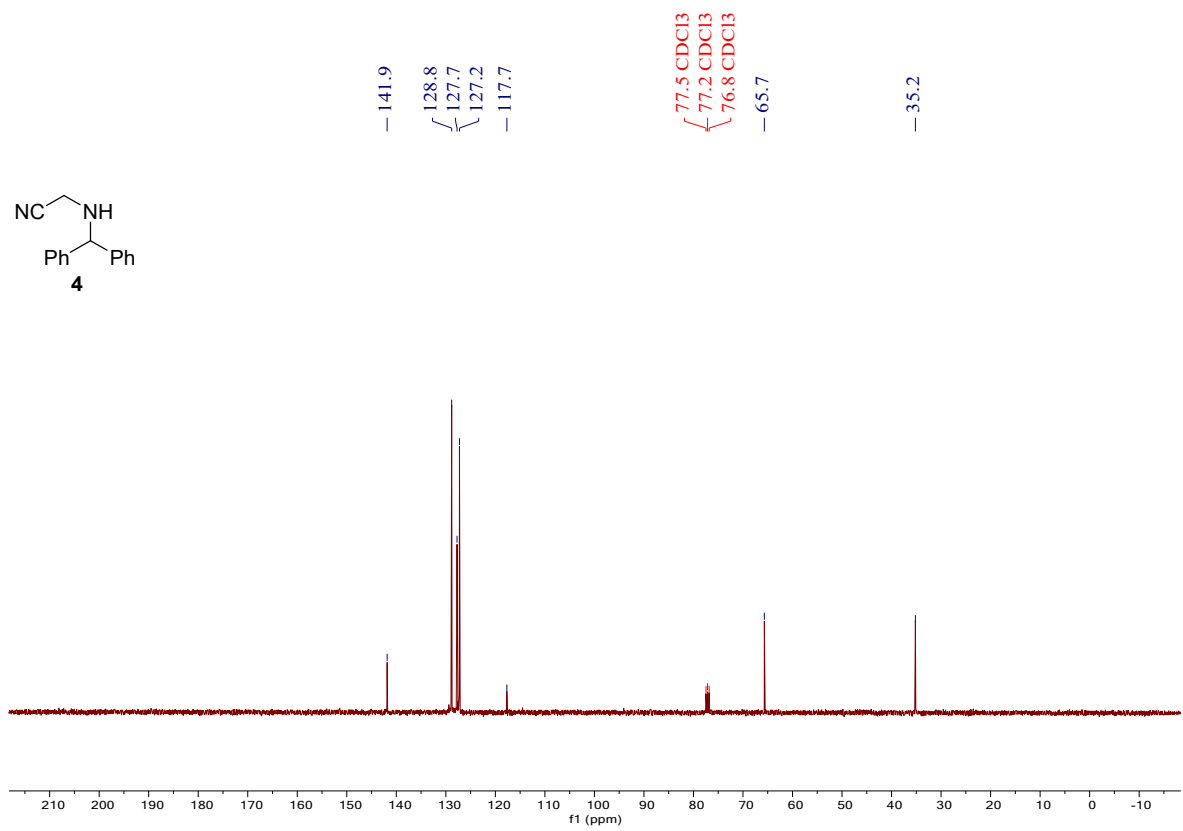
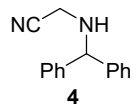
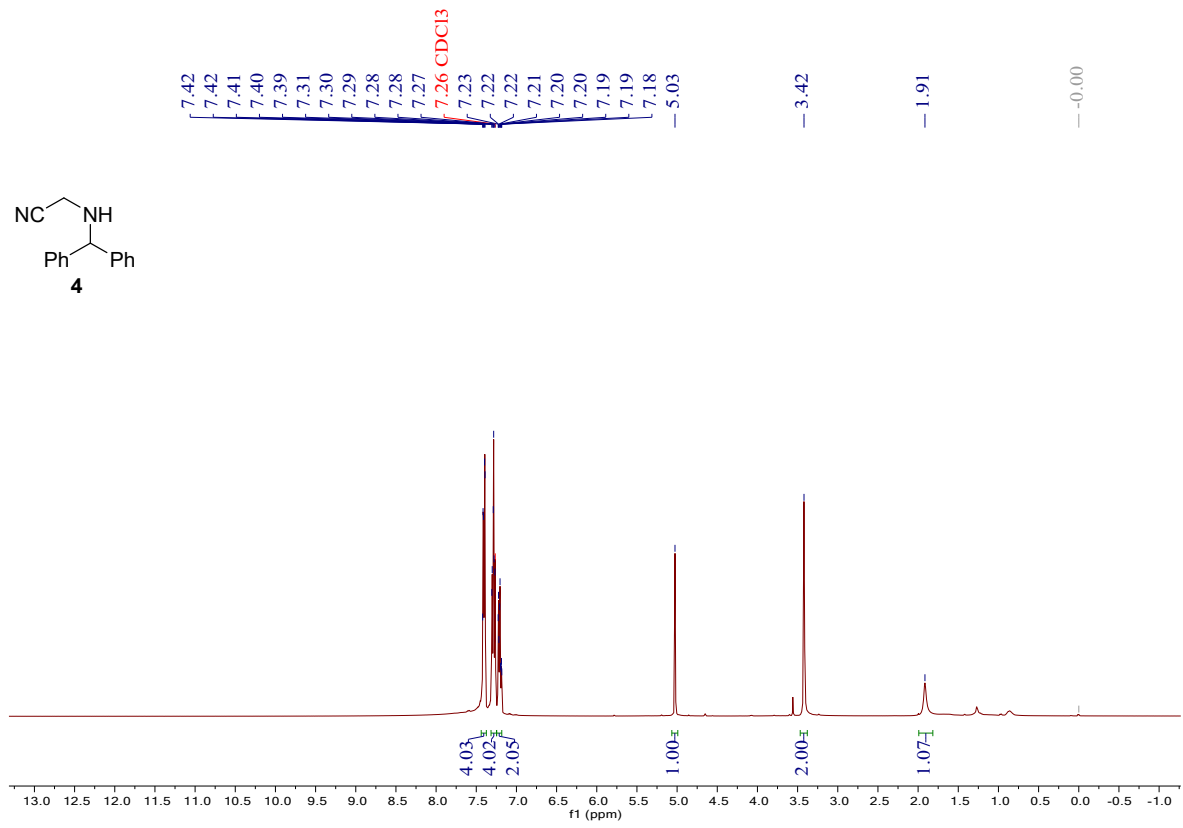
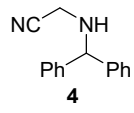


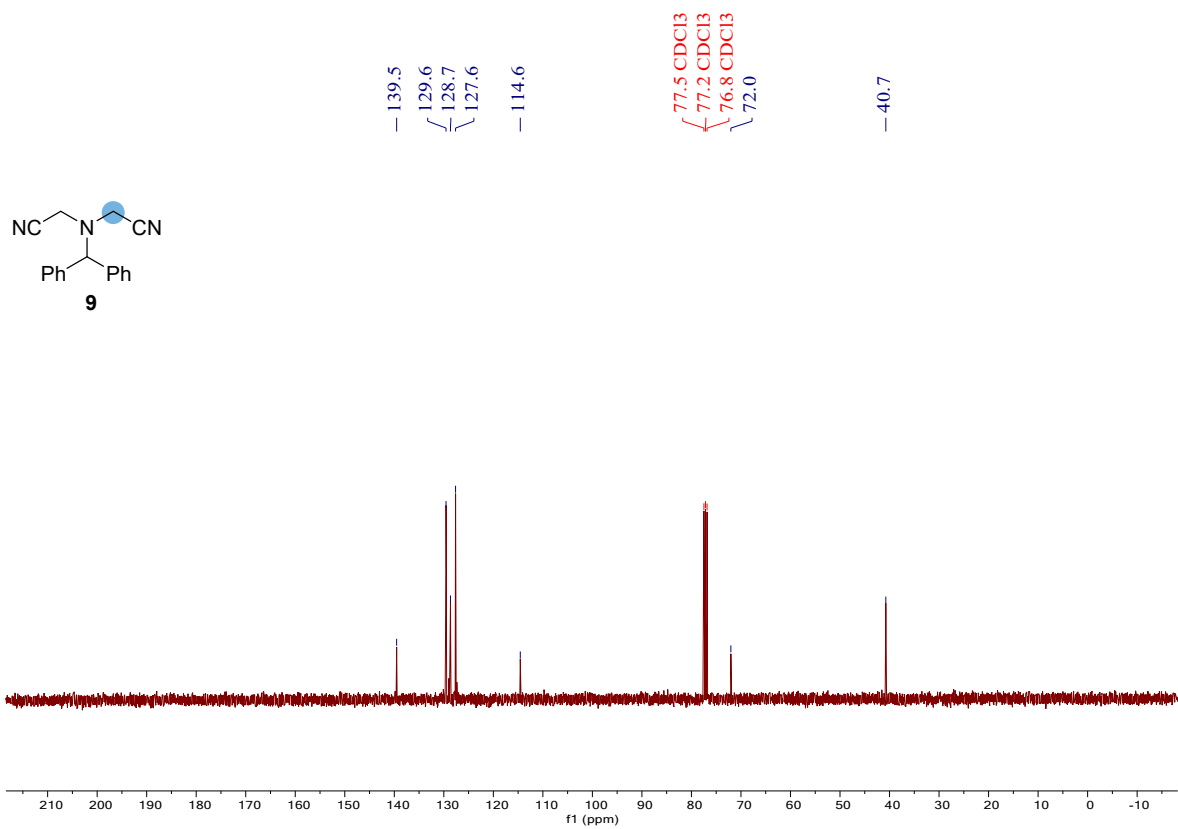
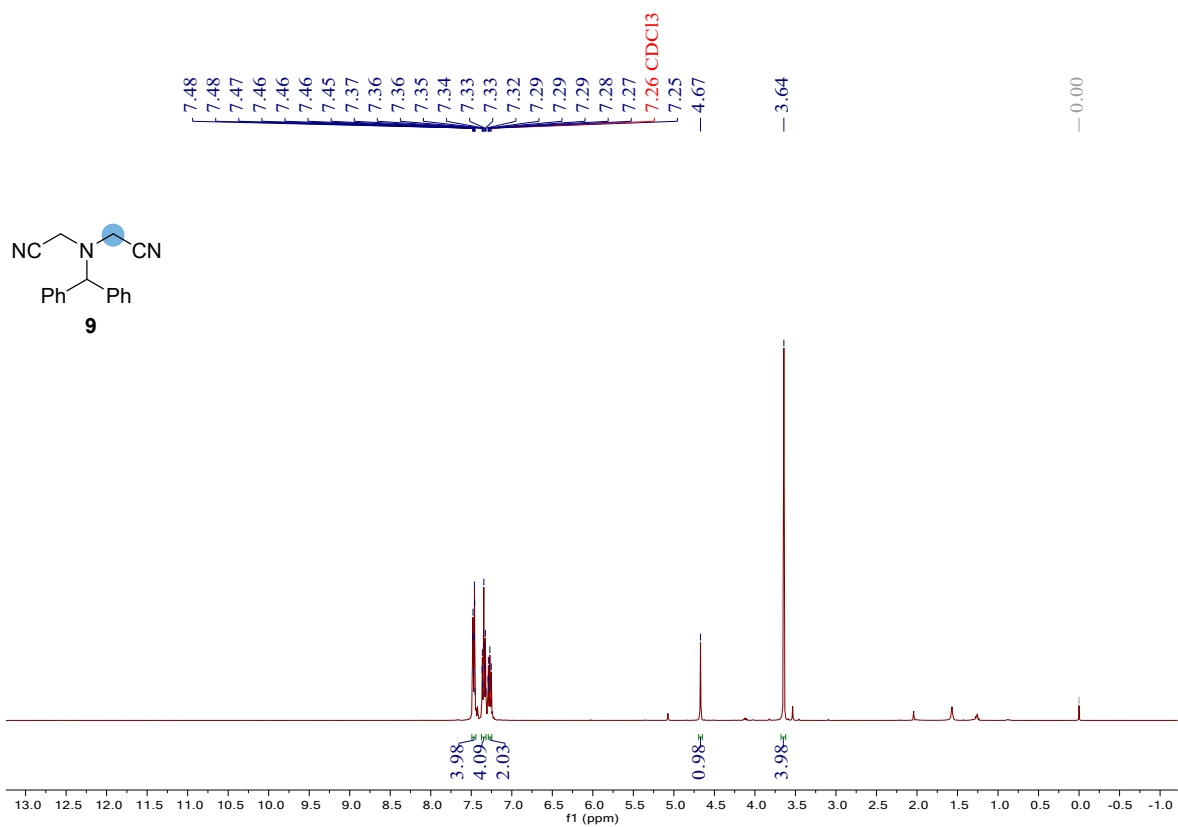


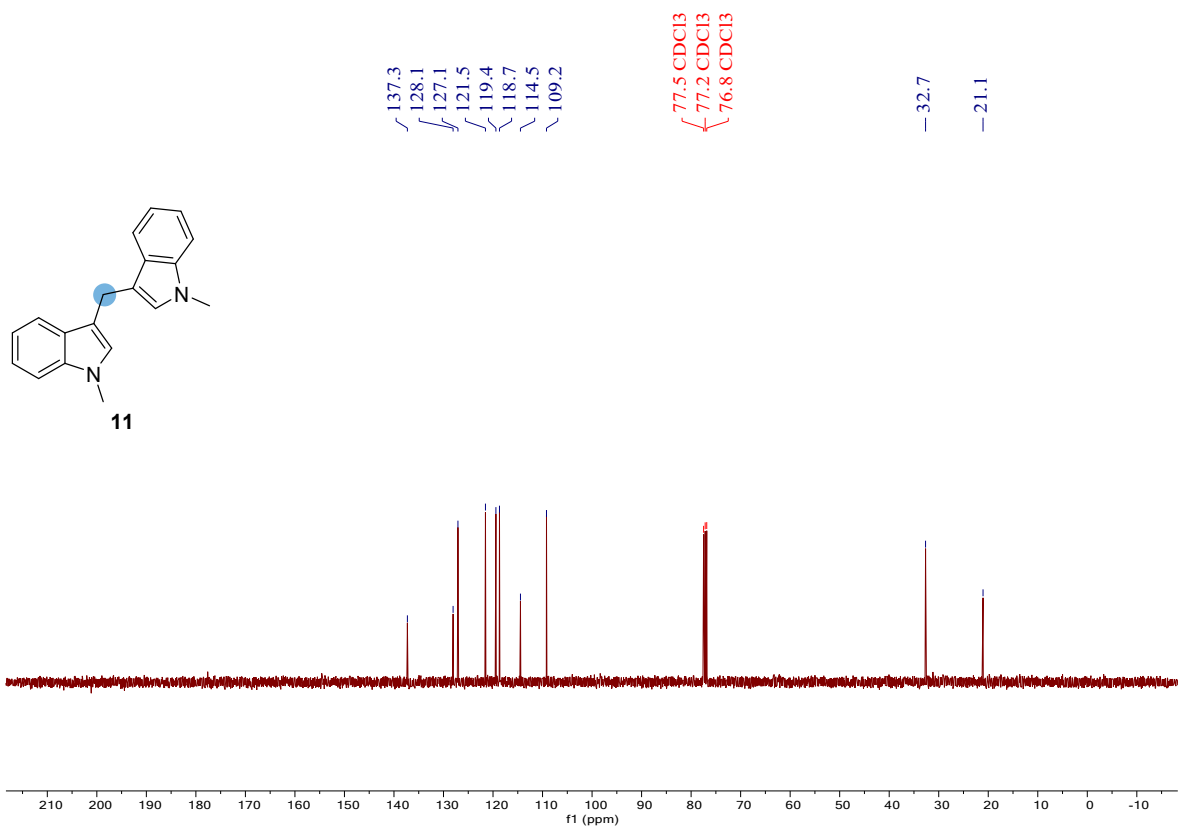
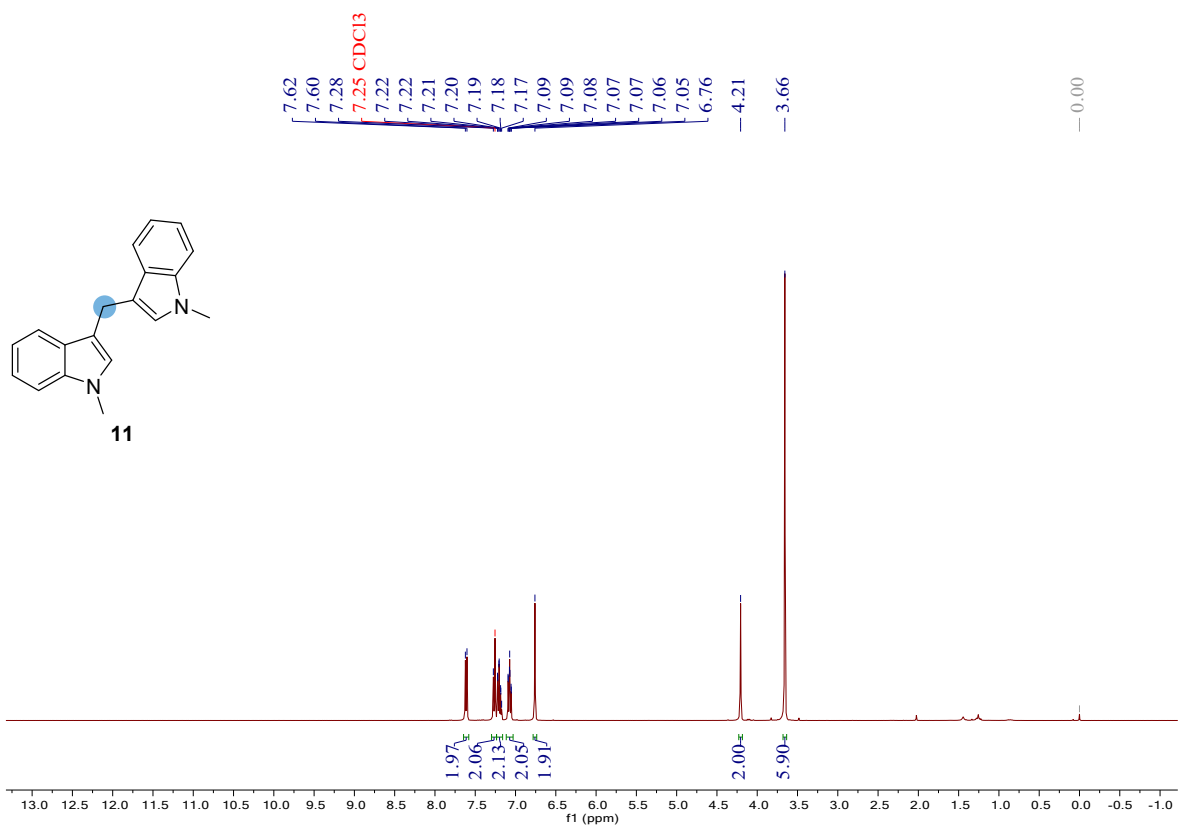


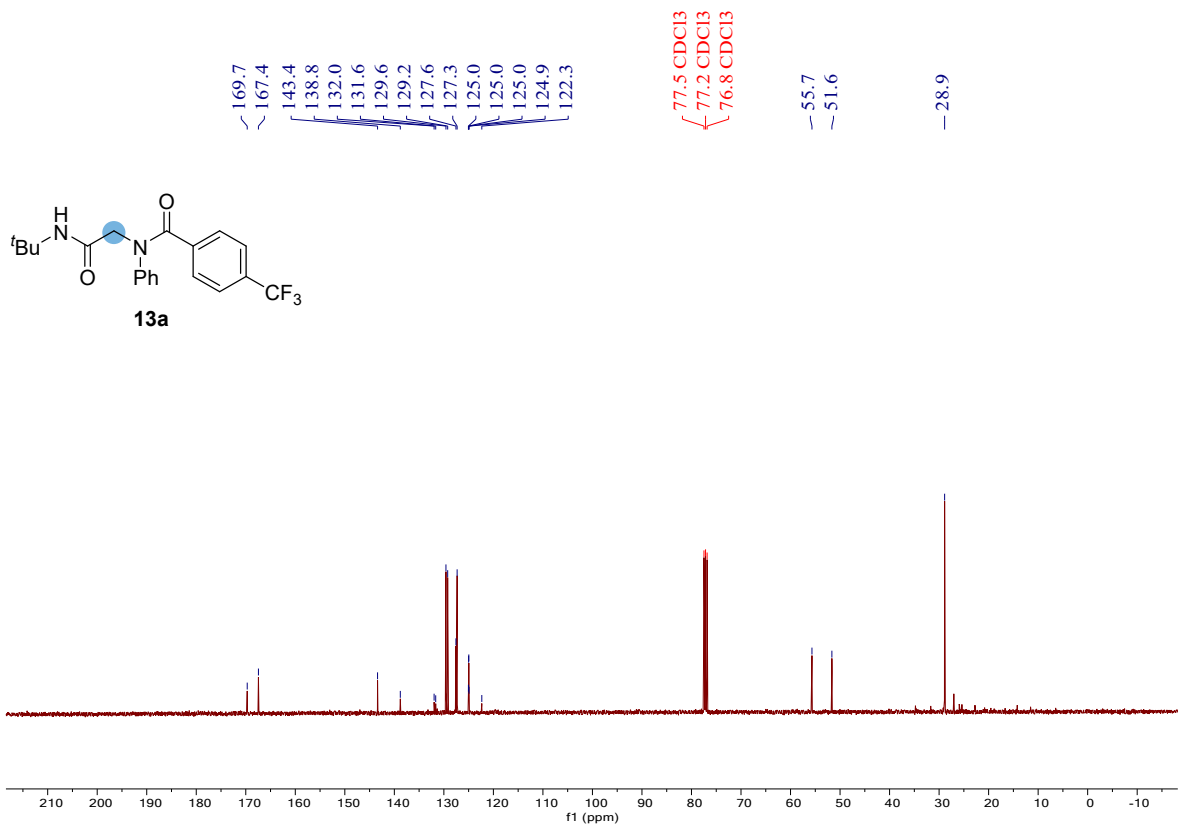
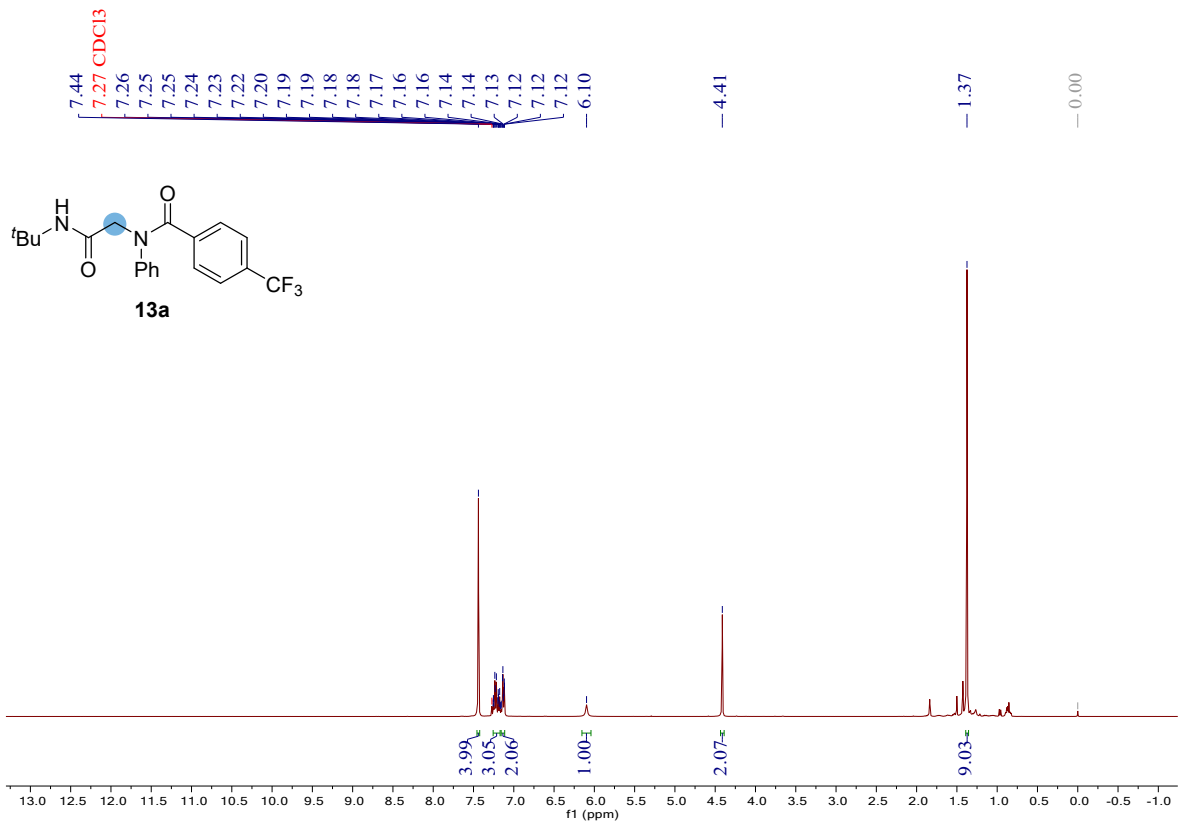


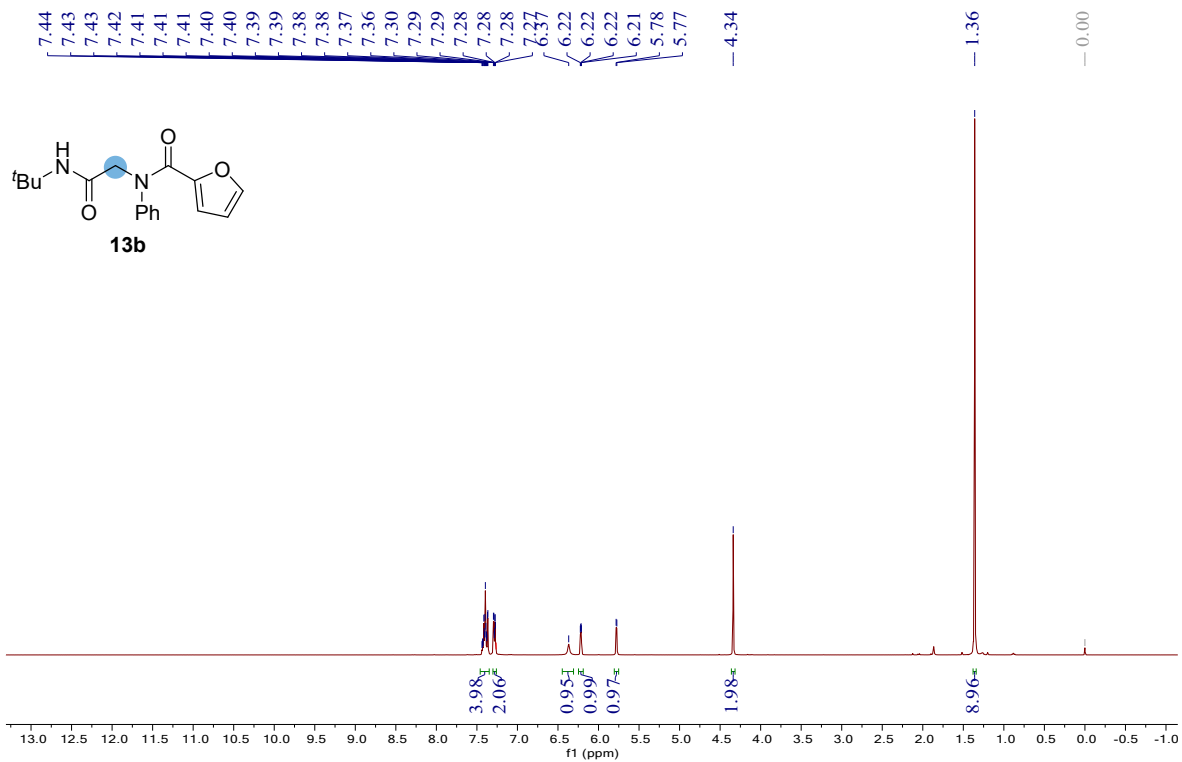
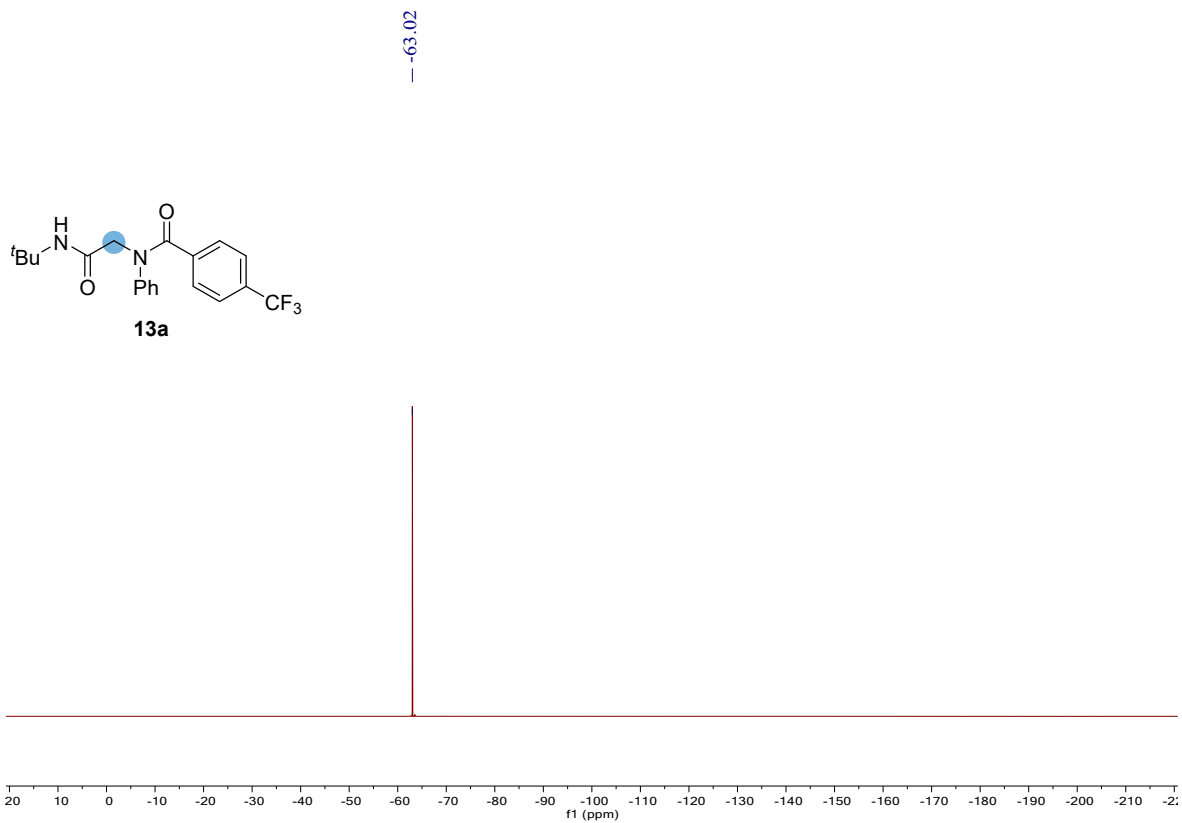


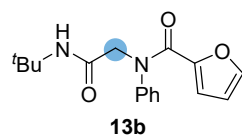










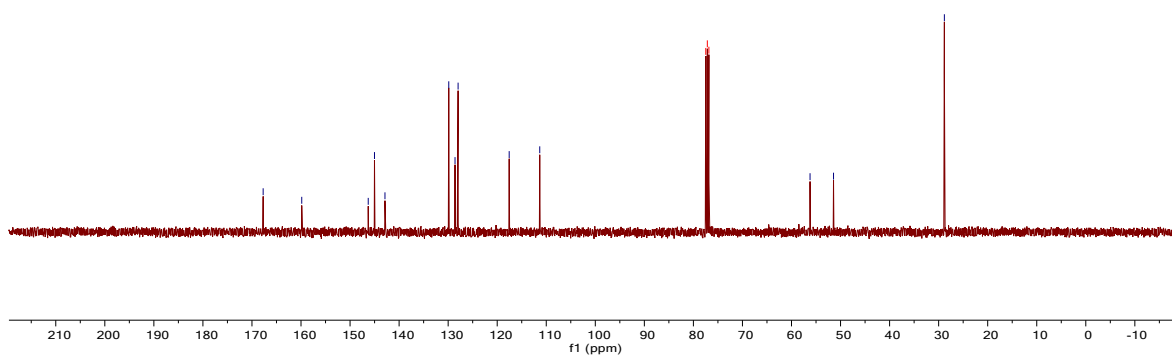


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 145.0
 142.9
 129.9
 128.6
 128.0
 -117.6
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77.5 CDCl₃
 77.2 CDCl₃
 76.8 CDCl₃

-56.2
 -51.4

-28.8

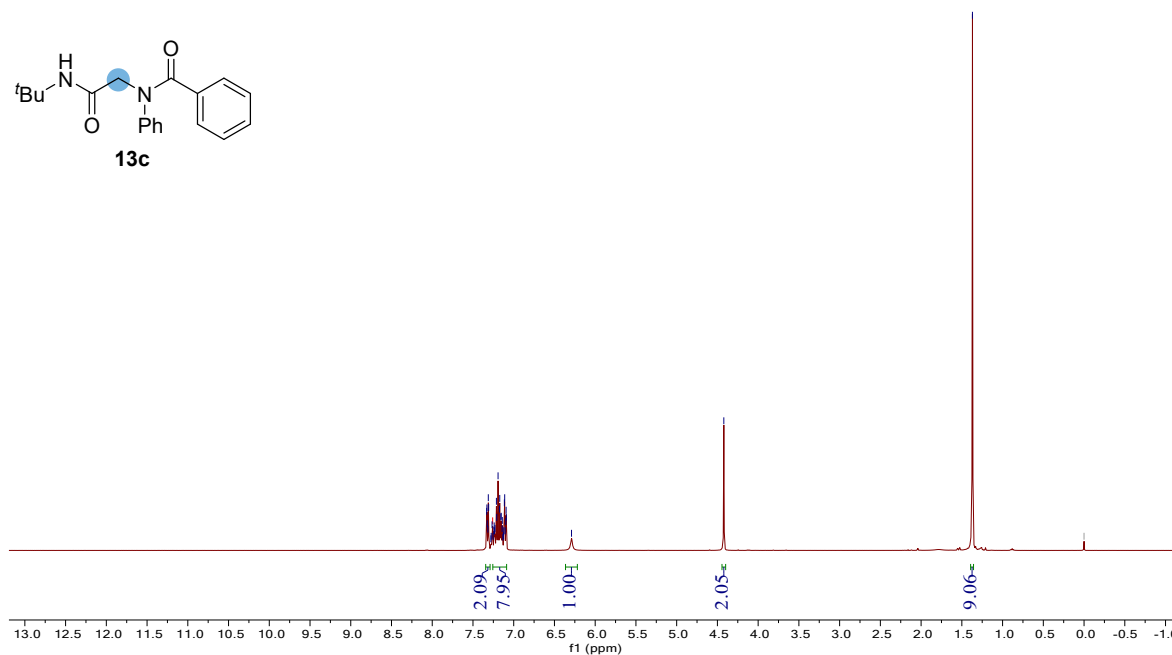
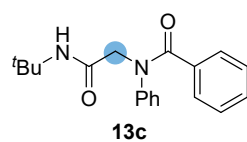


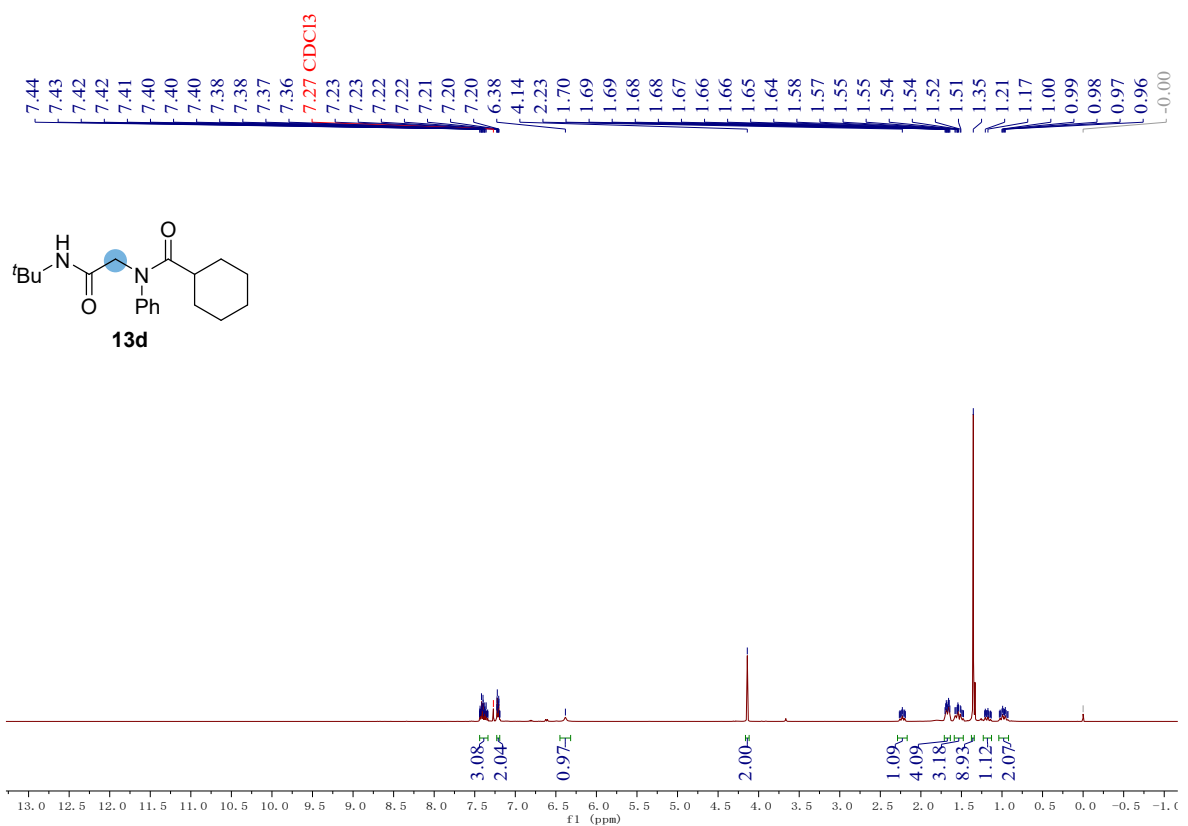
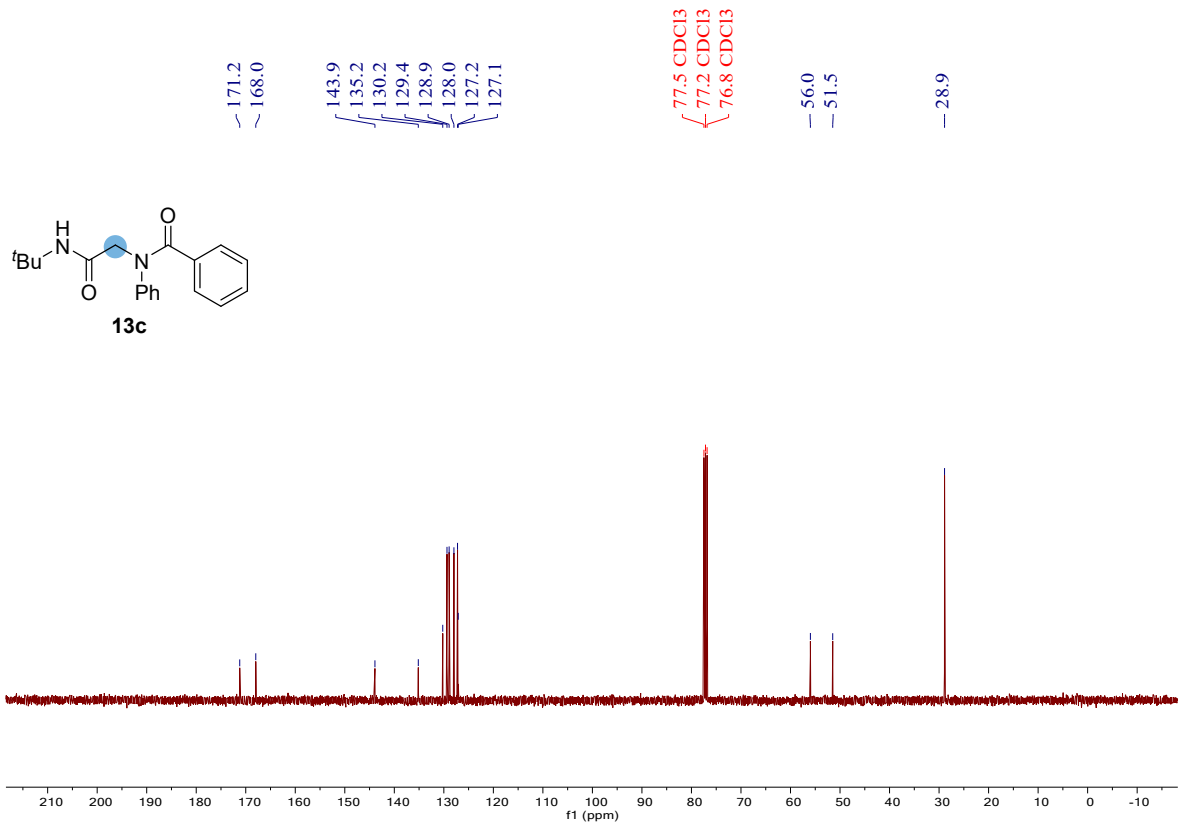
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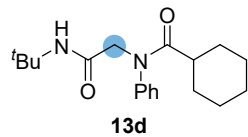
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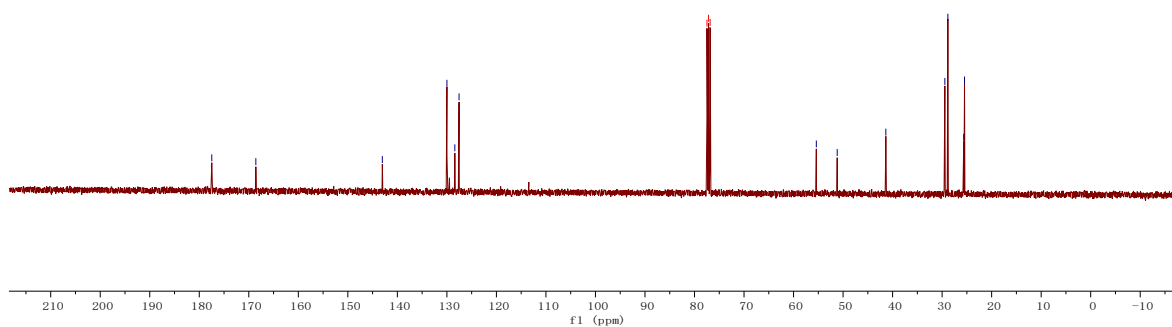


— 177.5
— 168.6

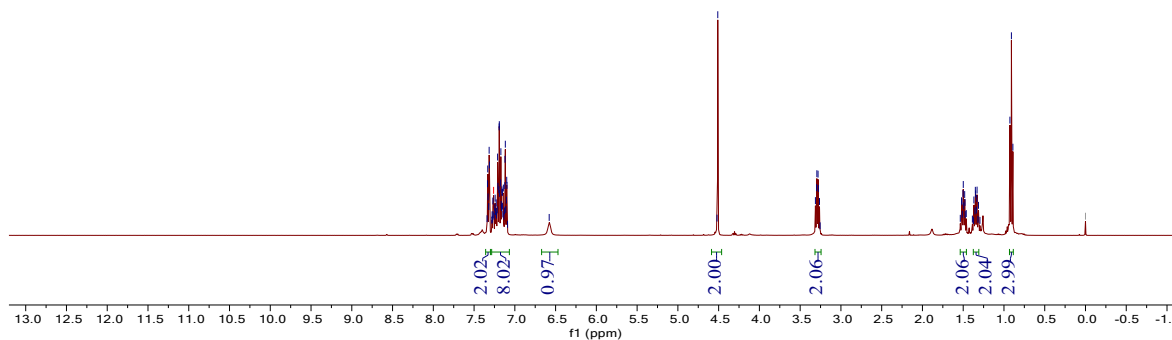
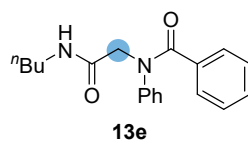
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128.4
127.5

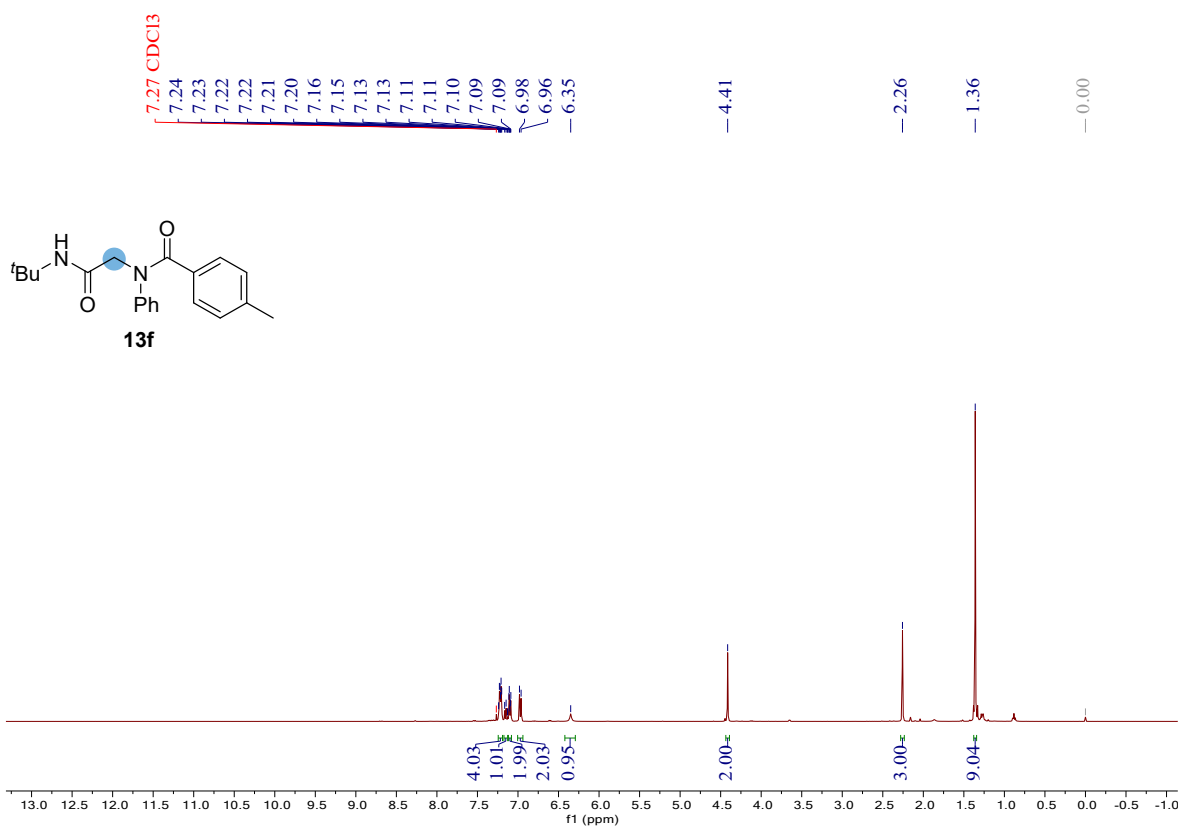
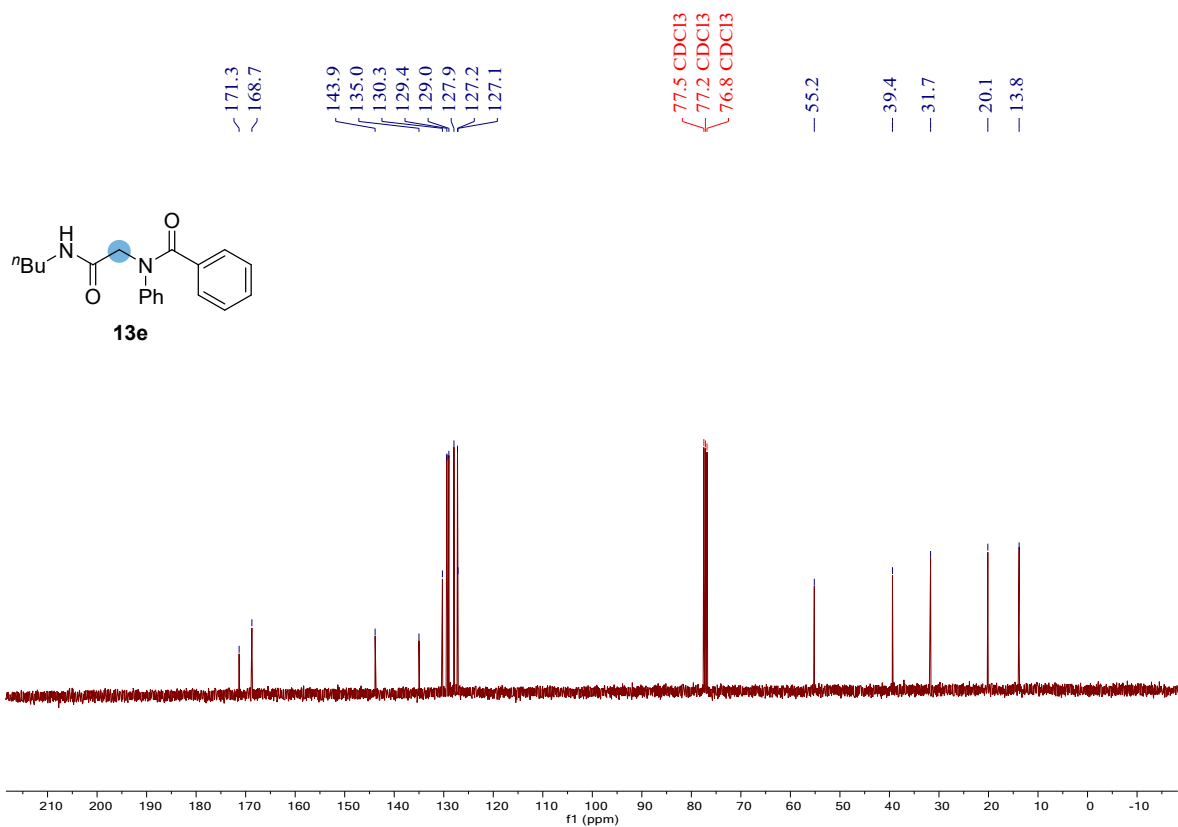
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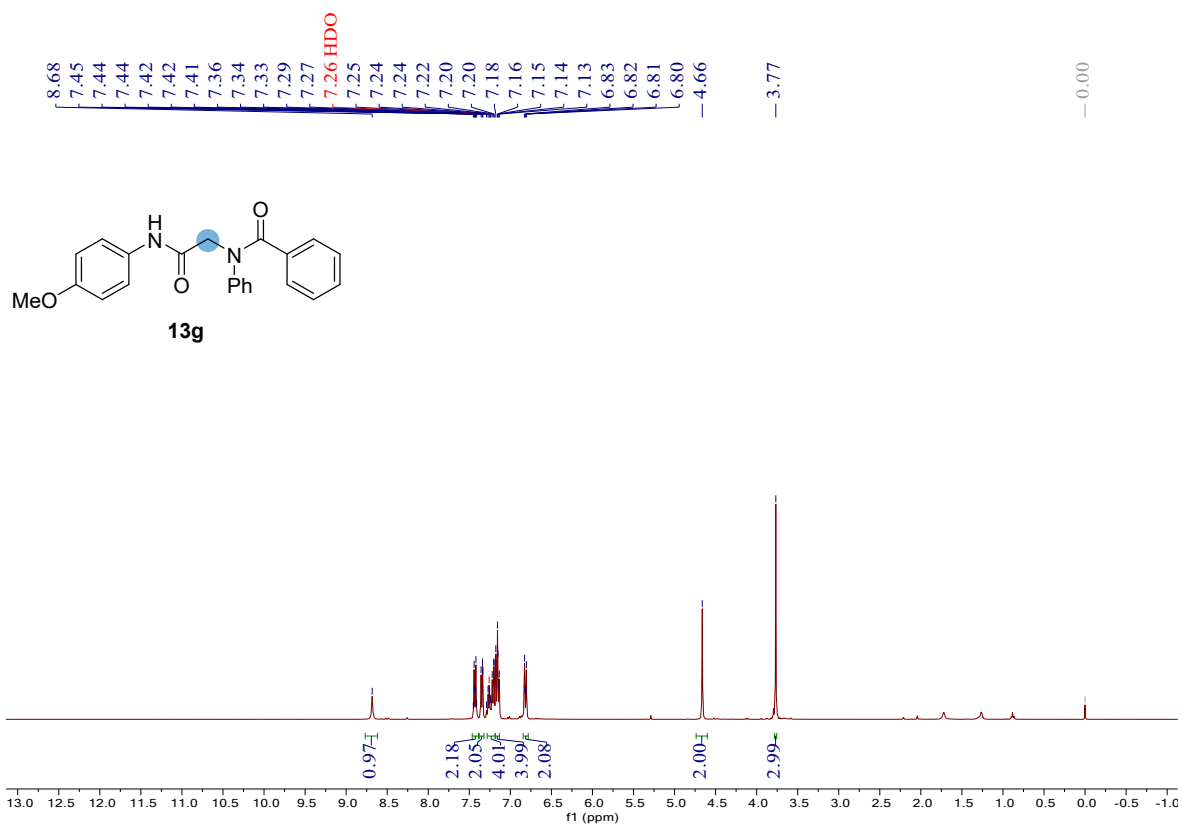
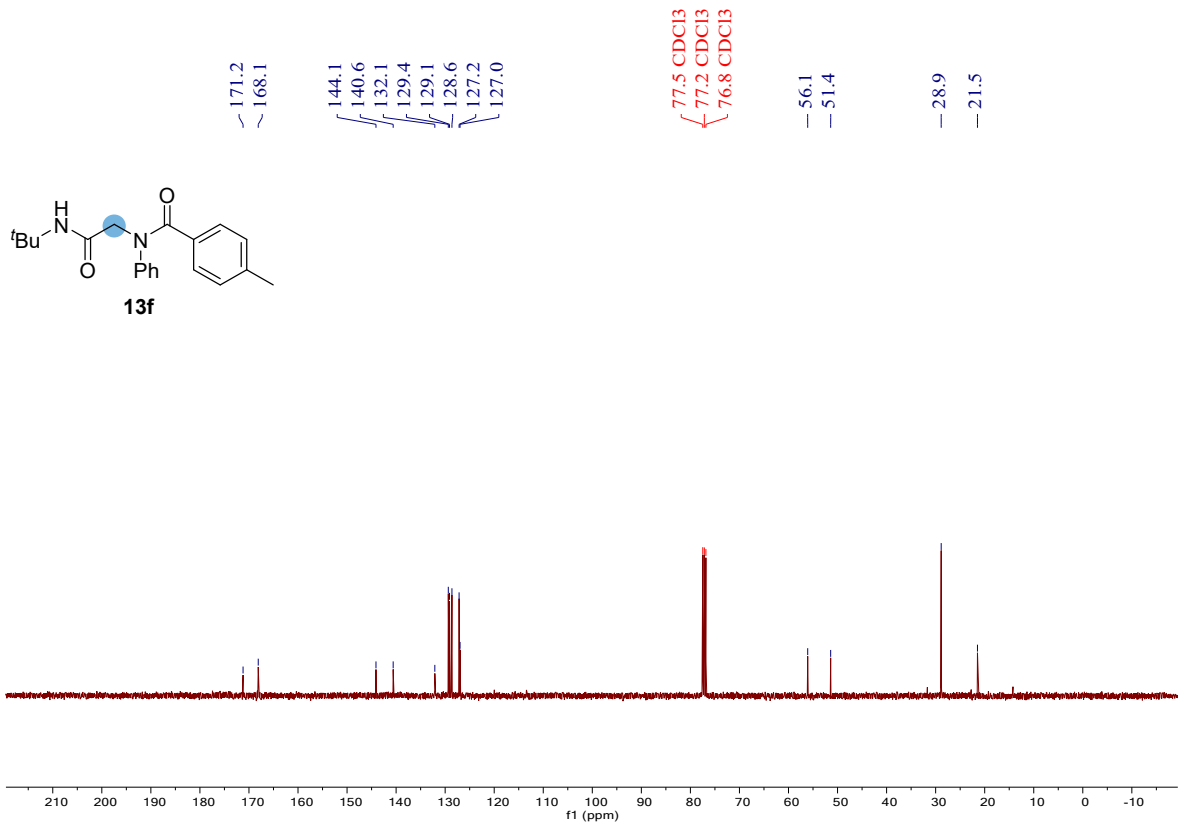
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— 51.2
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25.5

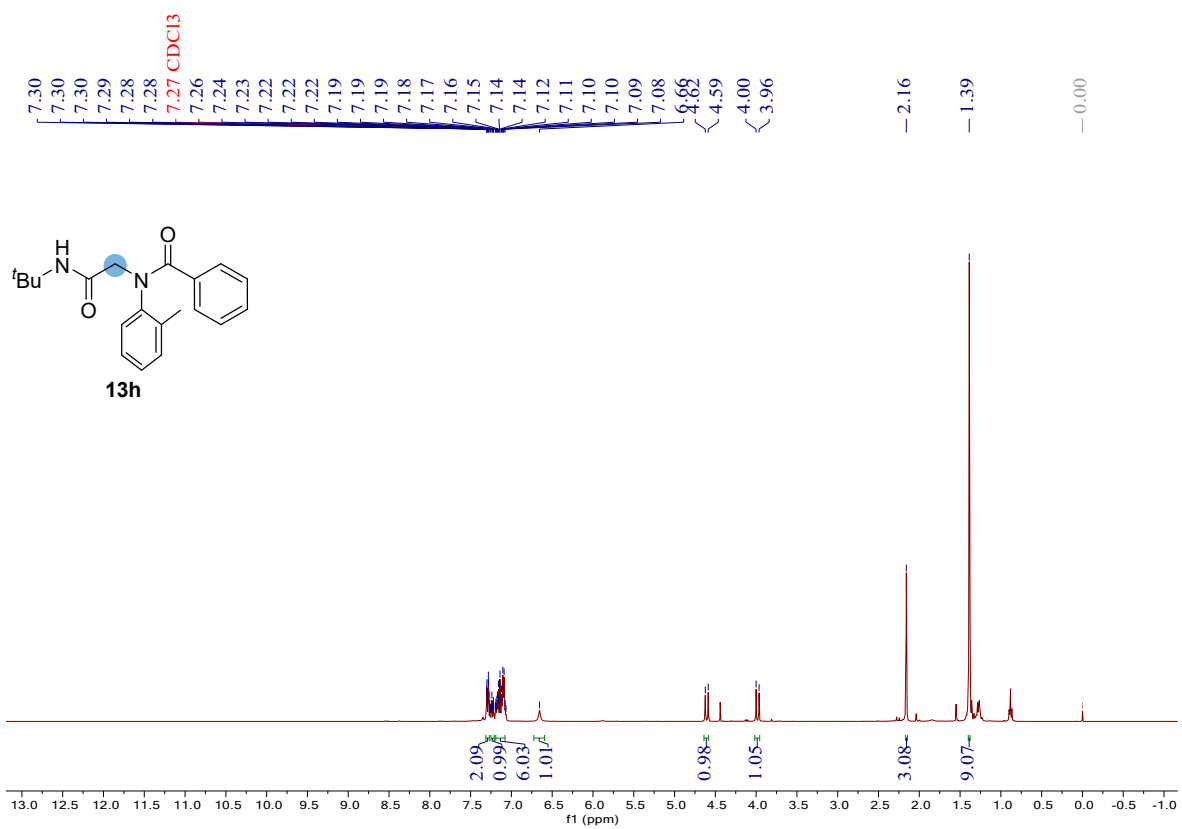
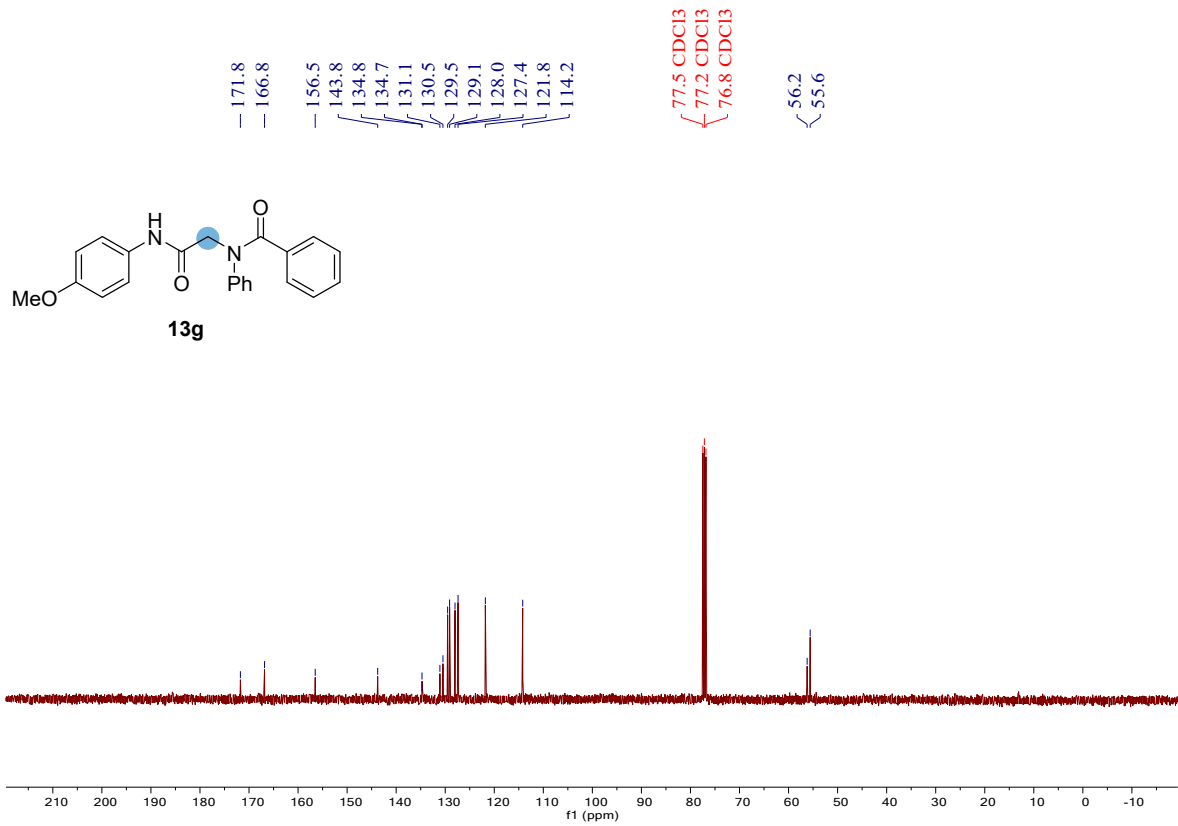


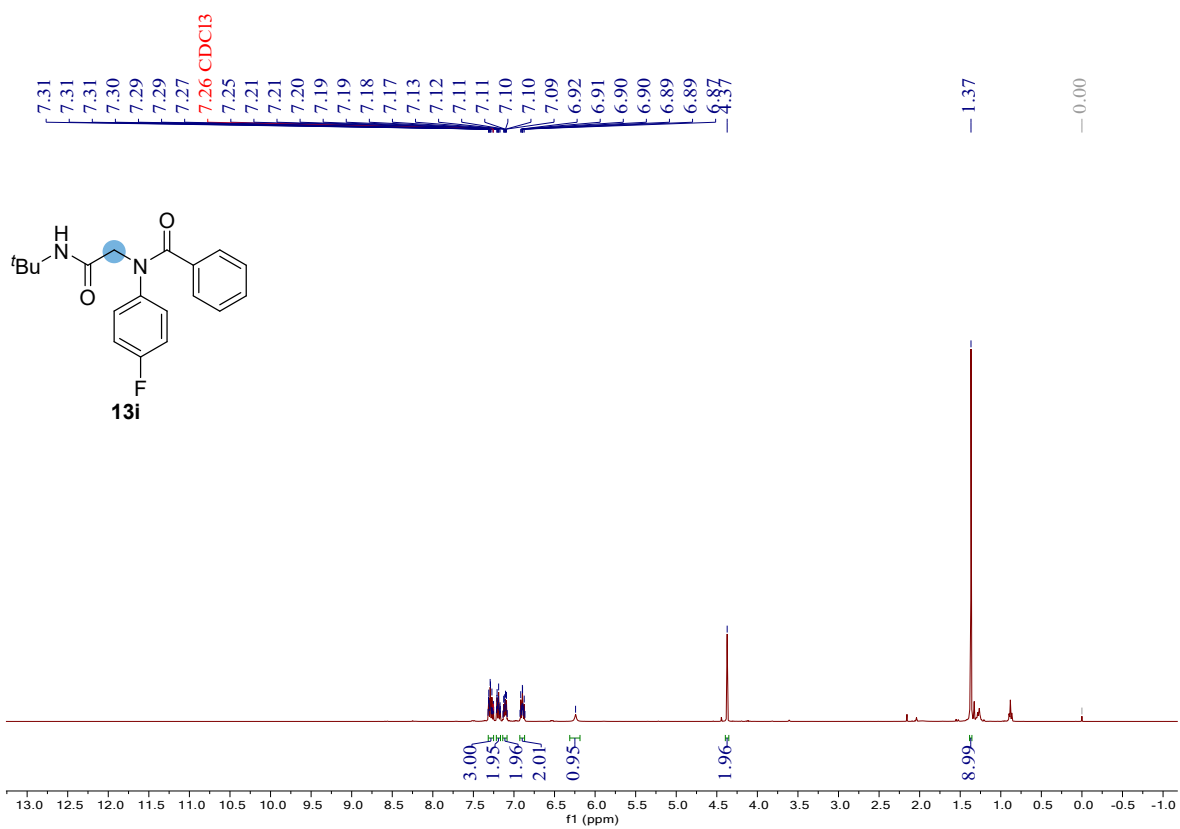
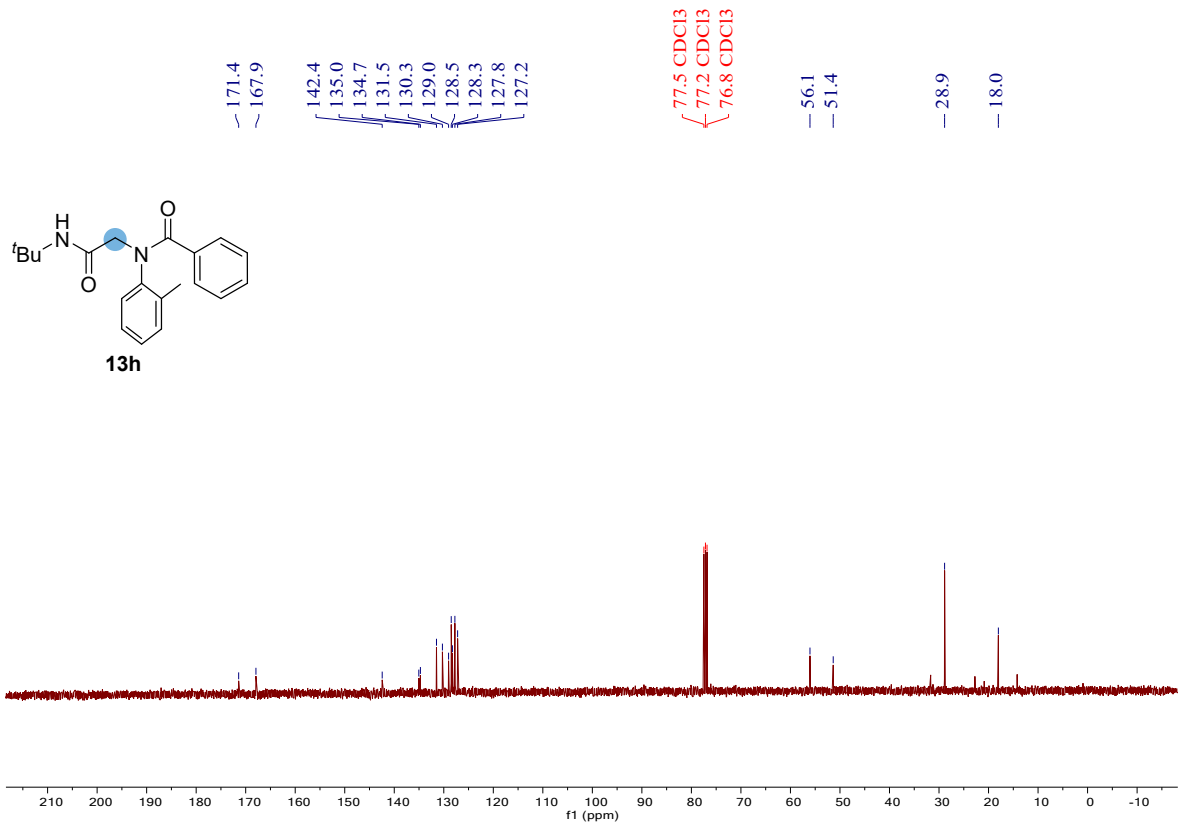
7.34
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7.26 CDCl₃
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1.33
1.31
0.93
0.91
0.89

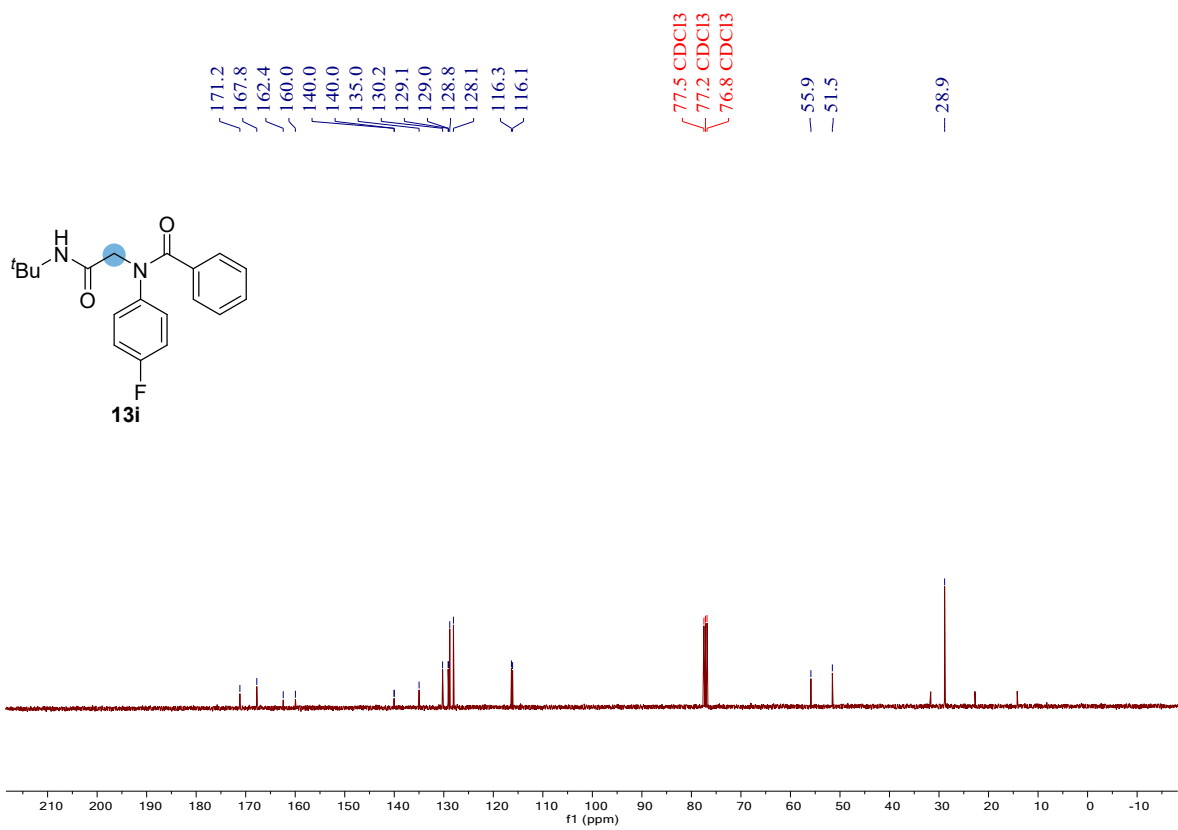


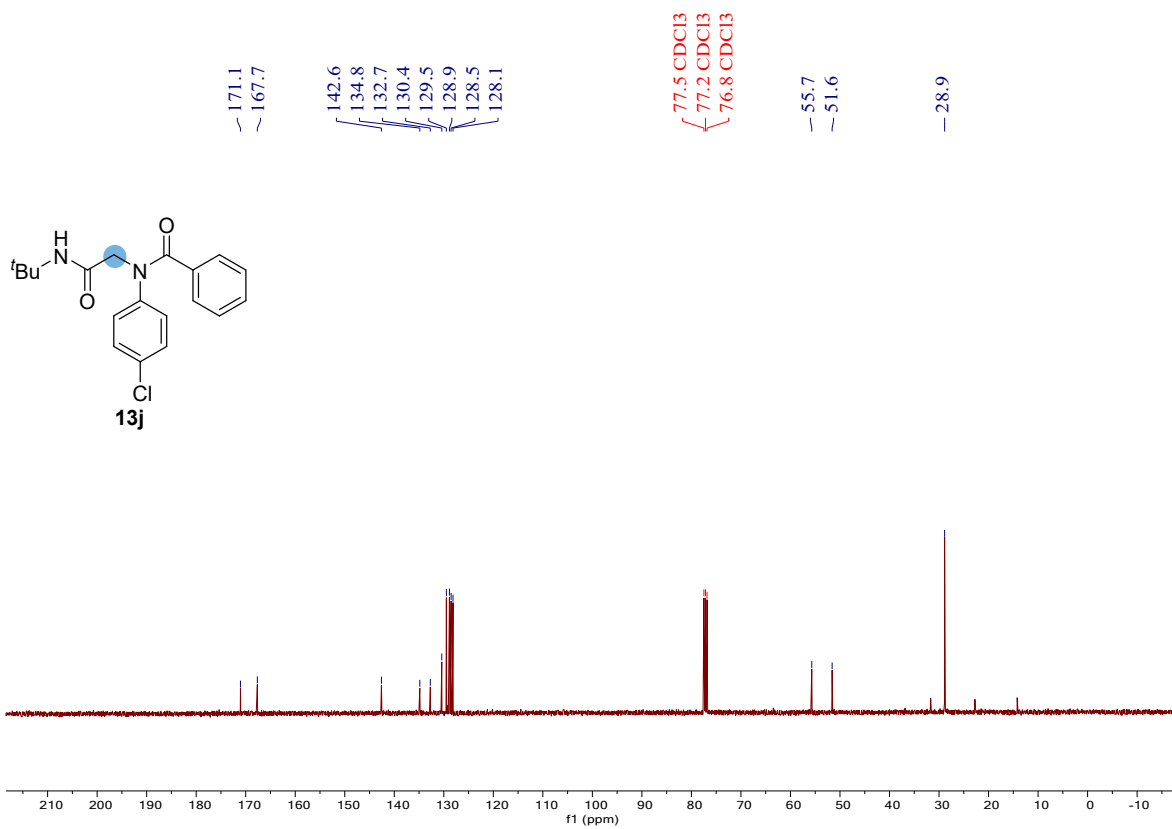
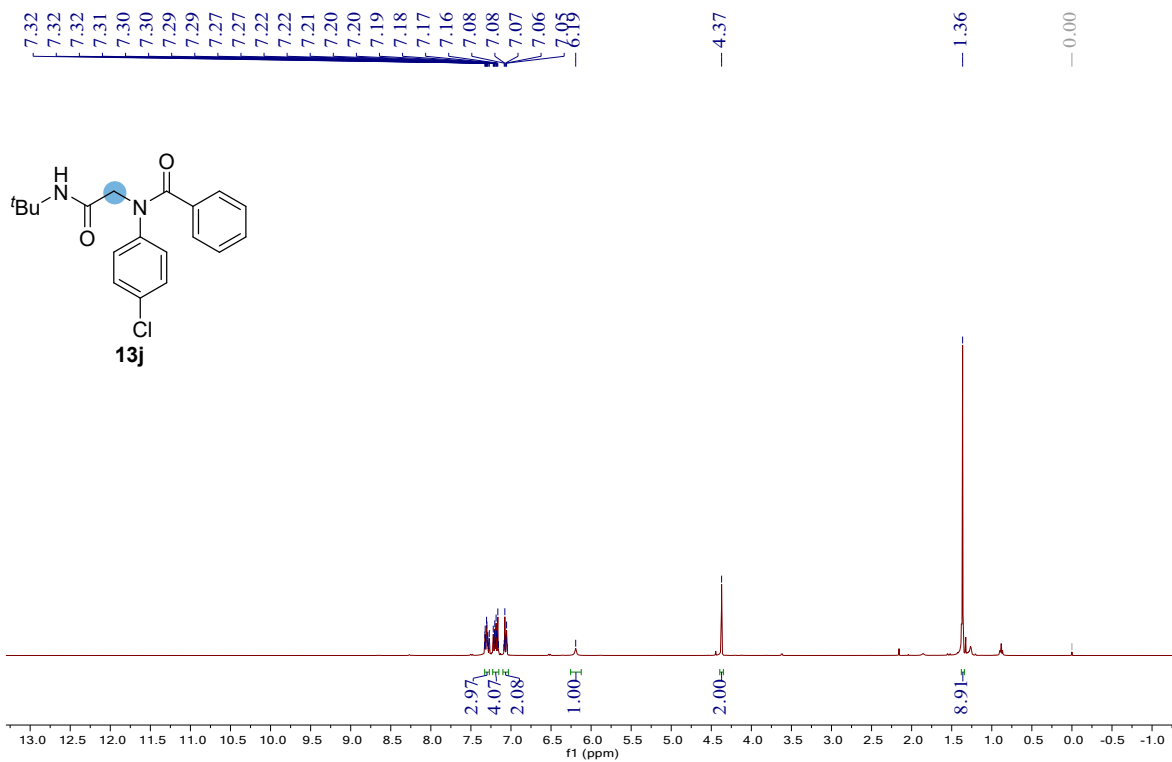






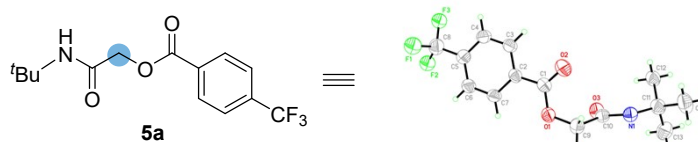






7. Crystal data and structure refinement for 5a and 13g

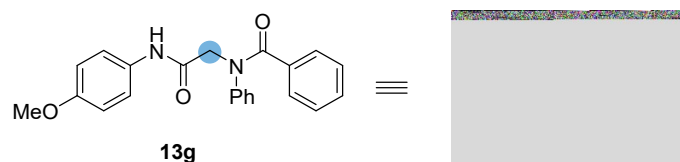
Compound **5a**: (The crystal structure of compound **5a** has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2062894). The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.)



Crystal data and structure refinement for **5a**.

Empirical formula	C ₁₄ H ₁₆ F ₃ NO ₃	
Formula weight	303.28	
Temperature/K	293	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 14.5103(9) Å	α = 90 °
	b = 10.8097(7) Å	β = 93.534(6) °
	c = 9.4091(5) Å	γ = 90 °
Volume/Å ³	1473.03(16)	
Z	4	
Density (calculated) g/cm ³	1.363	
F(000)	628	
Crystal size/mm ³	0.60 × 0.30 × 0.28	
Theta range for data collection/°	3.051 to 67.076	
Index ranges	-17 ≤ h ≤ 17, -12 ≤ k ≤ 12, -11 ≤ l ≤ 7	

Compound **13g**: (The crystal structure of compound **13g** has been deposited at the Cambridge Crystallographic Data Centre (CCDC 2082920). The data is available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.)



Crystal data and structure refinement for **13g**.

Empirical formula	C ₂₂ H ₂₀ N ₂ O ₃	
Formula weight	360.41	
Temperature/K	223	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	C 2	
Unit cell dimensions	a = 25.6297(8) Å	α = 90 °
	b = 6.39261(18) Å	β = 114.818(3) °
	c = 12.4690(3) Å	γ = 90 °
Volume/Å ³	1854.25(10)	
Z	4	
Density (calculated) g/cm ³	1.291	
F(000)	760	
Crystal size/mm ³	0.40 × 0.20 × 0.15	
Theta range for data collection/°	3.800 to 77.285	
Index ranges	-30 ≤ h ≤ 32, -7 ≤ k ≤ 8, -15 ≤ l ≤ 13	