

Ligand-Enabled Meta-Selective C–H Arylation of Nosyl Protected Phenethylamines,

Benzylamines and 2-Aryl Anilines

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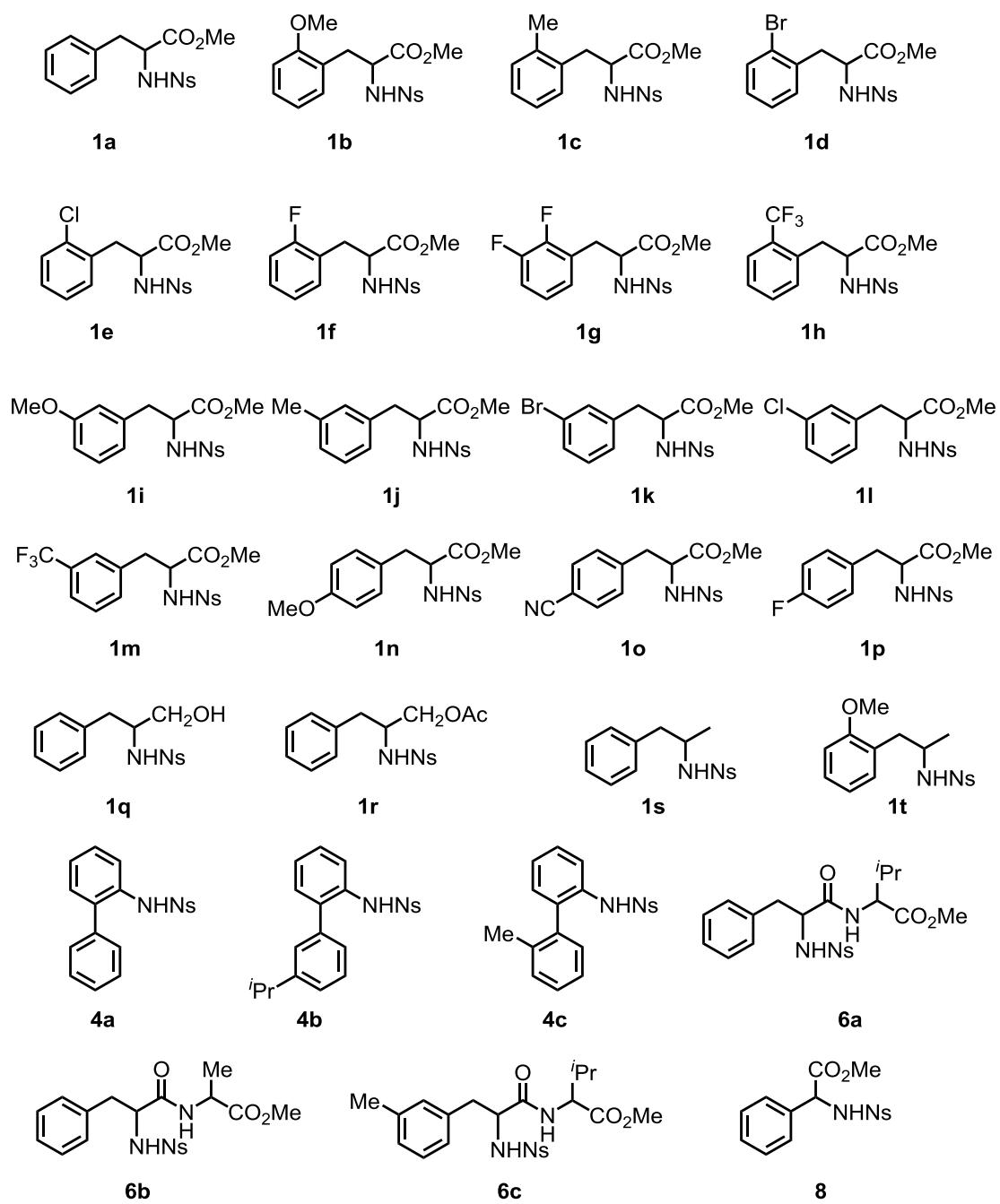
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1. General Information

Amines, aryl halides and pyridine ligands were obtained from the commercial sources or synthesized following literature procedures. Pd(OAc)₂ was obtained from Strem. AgOAc was purchased from Sigma-Aldrich. Solvents were obtained from Sigma-Aldrich, Alfa-Aesar and Acros and used directly without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light and Vogel's permanganate. ¹H NMR was recorded on Varian (400 MHz) or Bruker DRX-500 instrument (500 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.0 ppm of tetramethylsilane or 2.05 ppm of acetone-*d*. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad. Coupling constants, *J*, were reported in Hertz unit (Hz). ¹³C NMR spectra were recorded on Varian (100 MHz), Bruker DRX-500 instrument (125 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to either the center line of a triplet at 77.00 ppm of chloroform-*d* or 206.26 ppm singlet of acetone-*d*. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2. Structures of Substrates



3. Experimental Section

3.1 Optimization of Reaction Conditions

Table 1. Investigation of Directing Groups to Direct *meta*-C-H Arylation^{a,b}

1 + **2a** → **3**

Ar = *o*-CO₂MePh

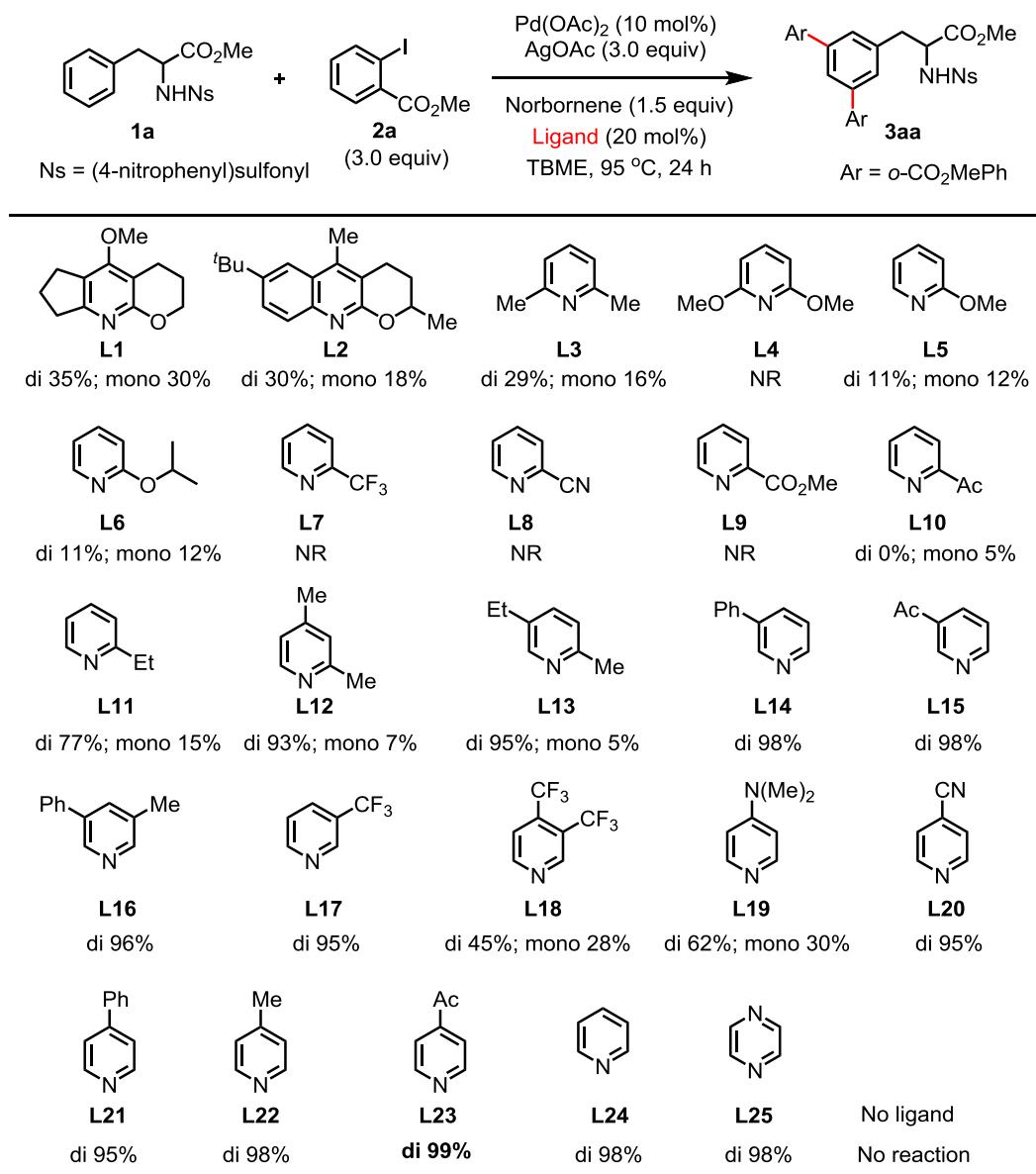
Ligand

DG =				
	di 28%; mono <5%	di 13%; mono 22%	di 9%; mono 29%	di 35%; mono 30%
DG =				
	di 32%; mono 30%	di 30%; mono 20%	di 32%; mono 15%	di 32%; mono 18%
DG =	Acetyl (Ac)	Trifluoroacetyl (Tfa)	<i>tert</i> -Butyloxycarbonyl (<i>t</i> -Boc)	Carbobenzoyl (Cbz)
	di 0%; mono 0%	di 0%; mono 0%	di 0%; mono 0%	di 0%; mono 0%

^aReaction conditions: 0.1 mmol of phenethylamine **1**, 3.0 equiv of methyl 2-iodobenzoate **2a**, 10 mol% of Pd(OAc)₂, 20 mol% of ligand, 1.5 equiv of 2-norbornene, 3.0 equiv of AgOAc, 1.0 mL of TBME, 95 °C, under air, 24 h. ^bYields of the mono- and di-products were determined by ¹H NMR using dibromomethane as an internal standard.

Table 2. Screening of Ligands for *meta*-C-H Arylation of Phenethylamine-Derived Sulfamide

1a^{a,b}



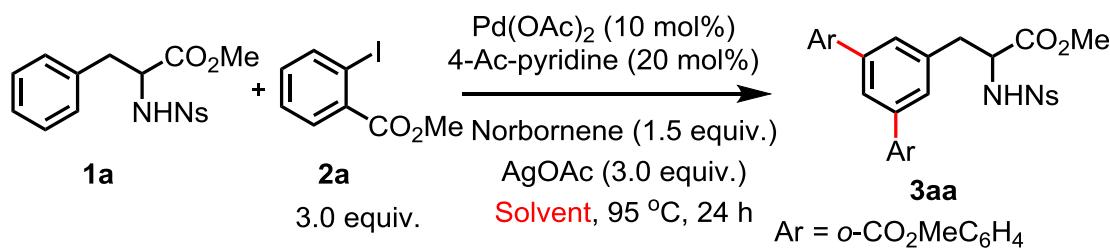
^aReaction conditions: 0.1 mmol of phenethylamine **1a**, 3.0 equiv of methyl 2-iodobenzoate **2a**, 10 mol% of Pd(OAc)₂, 20 mol% of ligand, 1.5 equiv of norbornene, 3.0 equiv of AgOAc, 1.0 mL of TBME, 95 °C, under air, 24 h. ^bYields of the mono- and di-products were determined by ¹H NMR using dibromomethane as an internal standard.

Table 3. Screening of oxidant

entry	oxidant	yield (%) of di-	yield (%) of mono-
1	AgOAc	99	1
2	AdCO ₂ Ag	97	3
3	PhCO ₂ Ag	89	11
4	Ag ₂ CO ₃	74	16
5	Ag ₂ O	6	16
6	AgOTs	0	0
7		74	20

^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

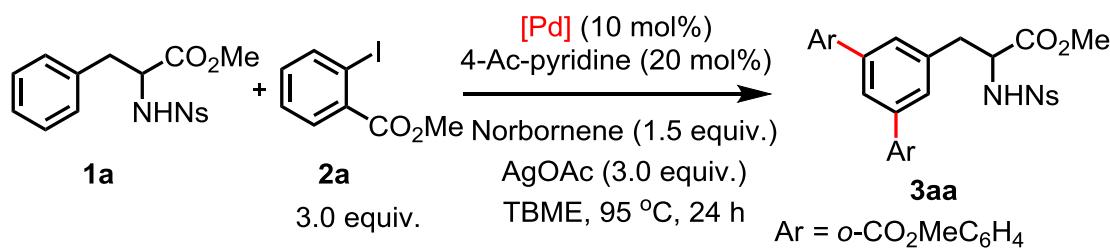
Table 4. Screening of solvent



Entry	Solvent	Yield (%) ^a of di-/mono-/SM
1	TBME	99/1/0
2	iPr ₂ O	88/12/0
3	DCE	84/10/6
4	THF	80/20/0
5	Toluene	98/0/0
6	PhCF ₃	98/2/0
7	EtOAc	90/10/0
8	MeCN	44/38/20
9	1,4-Dioxane	78/13/9
10	tBuOH	42/40/18

^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

Table 5. Screening of [Pd] catalyst



Entry	[Pd]	Yield (%) ^a of di-/mono-/SM
1	Pd(OAc) ₂	99/1/0
2	Pd(O ₂ CEt) ₂	98/2/0
3	PdI ₂	98/2/0
4	Pd(TFA) ₂	80/12/8
5	PdCl ₂ (CH ₃ CN) ₂	90/10/0
6	PdCl ₂ (allyl) ₂	64/32/4
7	Pd(PPh ₃) ₂ Cl ₂	90/10/0
8	Pd(acac) ₂	60/30/10
9	Pd(OPiv) ₂	0/4/96
10	---	0/0/100

^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

Table 6. Screening the loading of Pd(OAc)₂

1a	2a	Pd(OAc) ₂ (x mol%)	4-Ac-pyridine (20 mol%)	Norbornene (1.5 equiv.)		3aa	Ar = o-CO ₂ MeC ₆ H ₄
3.0 equiv.	3.0 equiv.	AgOAc (3.0 equiv.)	TBME, 95 °C				
Entry	x	Time (h)	Yield (%) ^a of di-/mono-/SM				
1	0	48	0/0/100				
2	2.5	48	48/42/10				
3	5	24	85/15/0				
4	10	12	99/1/0				

^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

Table 7. Screening the loading of 2-Norbornene.

		Pd(OAc) ₂ (10 mol%) 4-Ac-pyridine (20 mol%) Norbornene (<i>y</i> equiv.) AgOAc (3.0 equiv.) TBME, 95 °C, 24 h	
1a	2a	3.0 equiv.	3aa Ar = o-CO ₂ MeC ₆ H ₄
Entry	<i>y</i>	Yield (%) ^a of di-/mono-/SM	
1	1.5	99/1/0	
2	1.0	99/1/0	
3	0.5	99/1/0	
4	0.4	99/1/0	
5	0.3	99/1/0	
6	0.2	99/1/0	
7	0.1	69/24/7	
8	0	0/0/0	

^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

Table 8. Screening the equivalents of AgOAc

		Pd(OAc) ₂ (10 mol%) 4-Ac-pyridine (20 mol%) Norbornene (1.5 equiv.) AgOAc (<i>x</i> equiv.) TBME, 95 °C, 24 h	
1a	2a	3.0 equiv.	3aa Ar = o-CO ₂ MeC ₆ H ₄
Entry	<i>x</i>	Yield (%) ^a of di-/mono-/SM	
1	0	0/0/100	
2	2.0	55/33/12	
3	2.5	88/12/0	
4	3.0	99/1/0	

^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

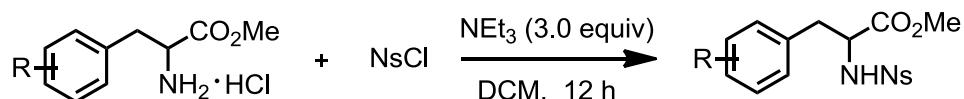
Table 9. Screening the reaction temperature

Entry	T (°C)	Time (h)	Yield (%) ^a of di-/mono-/SM
1	25	72	10/20/70
2	60	48	95/3/2
3	80	12	99/1/0
4	95	12	99/1/0
5	110	12	99/0/0

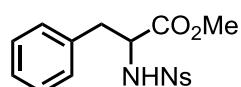
^a Yields of products were based on phenylalanine **1a** and determined by ¹H NMR using dibromomethane as internal standard.

3.2 Substrates Preparation

Synthesis of *N*-Nosyl amino acid methyl esters **1a-p** according to the reported procedures.¹



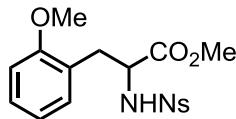
4-Nitrobenzenesulfonyl chloride (NsCl, 1.0 mmol, 1.0 equiv) was added to a cooled (0 °C) solution of amino acid methyl ester hydrochloride (1.0 mmol, 1.0 equiv) and triethylamine (TEA, 3.0 mmol, 3.0 equiv) in DCM (5 mL). After being stirred at room temperature for 12 h, the reaction mixture was poured into H₂O. The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The residue was subjected to column chromatography (EtOAc/hexanes = 1:2) to give **1a-p**.



methyl 2-(4-nitrophenoxy)sulfonamido)-3-phenylpropanoate **1a¹**

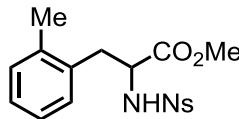
¹H NMR (500 MHz, acetone-*d*₆) δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 9.0 Hz, 2H), 7.43 (d, *J* = 9.5

Hz, 1H, N-H), 7.18-7.14 (m, 5H), 4.26 (dt, $J = 5.5, 9.5$ Hz, 1H), 3.53 (s, 3H), 3.10 (dd, $J = 5.5, 13.5$ Hz, 1H), 2.91 (dd, $J = 9.5, 13.5$ Hz, 1H); ^{13}C NMR (125 MHz, acetone- d_6) 171.89, 150.67, 147.55, 137.08, 130.17, 129.19, 128.88, 127.61, 124.94, 58.67, 52.50, 39.16.



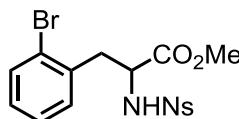
methyl 3-(2-methoxyphenyl)-2-(4-nitrophenylsulfonamido)propanoate 1b

^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.73 (d, $J = 9.0$ Hz, 2H), 7.16 (dt, $J = 1.5, 8.0$ Hz, 1H), 6.98 (dd, $J = 1.5, 7.5$ Hz, 1H), 6.78 (dt, $J = 1.0, 8.0$ Hz, 1H), 6.69 (dd, $J = 1.0, 8.0$ Hz, 1H), 5.77 (d, $J = 8.5$ Hz, 1H, N-H), 4.30-4.25 (m, 1H), 3.75 (s, 3H), 3.65 (s, 3H), 3.05 (dd, $J = 5.0, 14.0$ Hz, 1H), 2.94 (dd, $J = 9.5, 14.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) 171.71, 157.19, 149.62, 145.63, 131.25, 128.79, 127.90, 123.85, 123.49, 120.76, 110.36, 56.11, 55.31, 52.52, 33.70. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_7\text{S} [\text{M}-\text{H}]^-$: 393.0762. found: 393.0760.



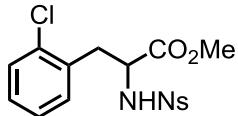
methyl 2-(4-nitrophenylsulfonamido)-3-(o-tolyl)propanoate 1c

^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.8$ Hz, 2H), 7.09 (t, $J = 7.6$ Hz, 1H), 7.03-6.98 (m, 2H), 6.95 (d, $J = 7.2$ Hz, 1H), 5.56 (d, $J = 9.6$ Hz, 1H, N-H), 4.24-4.18 (m, 1H), 3.64 (s, 3H), 3.13 (dd, $J = 5.6, 14.0$ Hz, 1H), 2.89 (dd, $J = 9.2, 14.0$ Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) 171.68, 149.77, 145.42, 136.38, 133.38, 130.64, 130.16, 128.00, 127.48, 126.13, 124.01, 56.37, 52.77, 36.57, 19.22. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_6\text{S} [\text{M}-\text{H}]^-$: 377.0813. found: 377.0812.



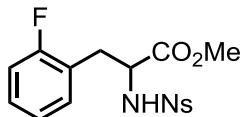
methyl 3-(2-bromophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1d

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.14-7.13 (m, 2H), 7.05-7.00 (m, 1H), 5.92 (d, *J* = 9.6 Hz, 1H, N-H), 4.42-4.36 (m, 1H), 3.69 (s, 3H), 3.25 (dd, *J* = 4.8, 13.6 Hz, 1H), 2.98 (dd, *J* = 10.0, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 171.60, 149.71, 145.30, 134.77, 132.89, 131.92, 128.95, 127.99, 127.55, 124.46, 123.98, 55.58, 52.92, 39.00. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄BrN₂O₆S [M-H]⁻: 440.9761. found: 440.9764.



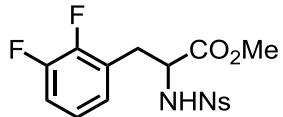
methyl 3-(2-chlorophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1e

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 9.2 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.19-7.09 (m, 4H), 5.65 (br, 1H, N-H), 4.38-4.34 (m, 1H), 3.68 (s, 3H), 3.24 (dd, *J* = 5.2, 13.6 Hz, 1H), 2.99 (dd, *J* = 9.6, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 171.52, 149.77, 145.37, 134.09, 133.06, 131.85, 129.59, 128.81, 128.01, 126.95, 124.01, 55.58, 52.90, 36.75. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄ClN₂O₆S [M-H]⁻: 397.0267. found: 397.0267.



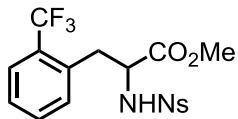
methyl 3-(2-fluorophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1f

¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 7.22-7.17 (m, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.91 (t, *J* = 9.2 Hz, 1H), 5.48 (br, 1H, N-H), 4.27 (t, *J* = 6.8 Hz, 1H), 3.64 (s, 3H), 3.11 (dd, *J* = 5.6, 14.0 Hz, 1H), 3.02 (dd, *J* = 8.0, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 171.09, 161.09 (d, *J* = 244.3 Hz), 149.90, 145.52, 131.76 (d, *J* = 4.0 Hz), 129.38 (d, *J* = 8.1 Hz), 128.13, 124.30 (d, *J* = 3.6 Hz), 124.11, 122.02 (d, *J* = 15.4 Hz), 115.39 (d, *J* = 21.8 Hz), 55.98, 52.87, 32.86. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄FN₂O₆S [M-H]⁻: 381.0562. found: 381.0564.



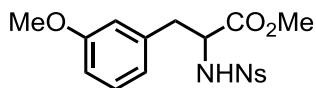
methyl 3-(2,3-difluorophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1g

¹H NMR (500 MHz, acetone-*d*₆) δ 8.32 (d, *J* = 8.5 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.57 (d, *J* = 10.0 Hz, 1H, N-H), 7.15-7.02 (m, 3H), 4.33 (dt, *J* = 5.5, 9.5 Hz, 1H), 3.56 (s, 3H), 3.23 (dd, *J* = 5.0, 14.0 Hz, 1H), 3.00 (dd, *J* = 9.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, acetone-*d*₆) 171.47, 151.39 (dd, *J* = 12.8, 244.3 Hz), 151.26, 150.34 (dd, *J* = 13.0, 244.5 Hz), 148.02, 129.37, 128.35 (t, *J* = 3.2 Hz), 127.31 (d, *J* = 11.6 Hz), 125.78 (dd, *J* = 4.7, 6.7 Hz), 125.47, 117.39 (d, *J* = 17.1 Hz), 57.54, 53.20, 33.09. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₃F₂N₂O₆S [M-H]⁻: 399.0468. found: 399.0468.



methyl 2-(4-nitrophenylsulfonamido)-3-(2-(trifluoromethyl)phenyl)propanoate 1h

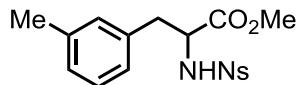
¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 10.0 Hz, 1H), 5.49 (d, *J* = 9.0 Hz, 1H, N-H), 4.29-4.25 (m, 1H), 3.64 (s, 3H), 3.19 (dd, *J* = 5.5, 14.0 Hz, 1H), 3.05 (dd, *J* = 7.0, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) 170.75, 150.03, 145.32, 135.93, 132.85, 130.98 (q, *J* = 32.2 Hz), 129.18, 128.16, 126.02 (q, *J* = 4.0 Hz), 124.26 (q, *J* = 4.0 Hz), 124.21, 123.76 (q, *J* = 270.7 Hz), 56.87, 52.91, 39.00. HRMS (ESI-TOF) *m/z* Calcd for C₁₇H₁₄F₃N₂O₆S [M-H]⁻: 431.0530 found: 431.0530.



methyl 3-(3-methoxyphenyl)-2-(4-nitrophenylsulfonamido)propanoate 1i

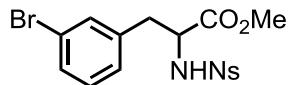
¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.71 (dd, *J* = 2.0, 8.0 Hz, 1H), 6.63 (d, *J* = 7.5 Hz, 1H), 6.51 (s, 1H), 5.62 (d, *J* = 9.0 Hz, 1H, N-H), 4.25-4.23 (m, 1H), 3.70 (s, 3H), 3.66 (s, 3H), 3.08 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.88 (dd, *J* = 8.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) 171.24, 159.60, 149.75, 145.46, 136.41, 129.67, 128.04, 123.99, 121.51, 115.04, 112.35, 57.11, 55.01, 52.75, 38.96. HRMS (ESI-TOF) *m/z* Calcd

for C₁₇H₁₇N₂O₇S [M-H]⁻: 393.0762. found: 393.0761.



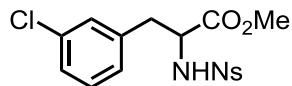
methyl 2-(4-nitrophenylsulfonamido)-3-(m-tolyl)propanoate 1j

¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.82 (s, 1H), 5.55 (d, *J* = 9.6 Hz, 1H, N-H), 4.26-4.21 (m, 1H), 3.64 (s, 3H), 3.07 (dd, *J* = 5.2, 14.0 Hz, 1H), 2.90 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.23 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) 171.26, 149.77, 145.51, 138.30, 134.77, 129.94, 128.57, 128.09, 128.03, 126.24, 123.98, 57.19, 52.67, 38.95, 21.19. HRMS (ESI-TOF) *m/z* Calcd for C₁₇H₁₇N₂O₆S [M-H]⁻: 377.0813. found: 377.0815.



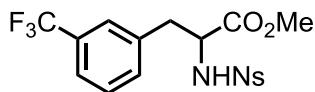
methyl 3-(3-bromophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1k

¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.32 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.13 (s, 1H), 7.09 (t, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 5.46 (d, *J* = 9.0 Hz, 1H, N-H), 4.26-4.21 (m, 1H), 3.67 (s, 3H), 3.09 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.90 (dd, *J* = 8.0, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) 170.88, 149.99, 145.34, 137.24, 132.27, 130.50, 130.22, 128.09, 127.99, 124.20, 122.68, 56.98, 52.94, 38.75. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄BrN₂O₆S [M-H]⁻: 440.9761. found: 440.9758.



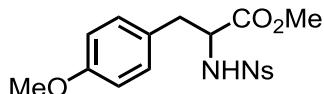
methyl 3-(3-chlorophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1l

¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.83 (d, *J* = 8.8 Hz, 2H), 7.14-7.13 (m, 2H), 6.99-6.97 (m, 2H), 5.85 (br, 1H, N-H), 4.24 (br, 1H), 3.67 (s, 3H), 3.10 (dd, *J* = 4.8, 14.0 Hz, 1H), 2.89 (dd, *J* = 8.0, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) 171.05, 149.83, 145.31, 137.09, 134.27, 129.87, 129.22, 127.97, 127.52, 127.39, 124.09, 57.01, 52.85, 38.51. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄ClN₂O₆S [M-H]⁻: 397.0267. found: 397.0269.



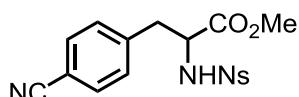
methyl 2-((4-nitrophenyl)sulfonamido)-3-(3-(trifluoromethyl)phenyl)propanoate 1m

¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 5.50 (d, *J* = 9.0 Hz, 1H, N-H), 4.29-4.25 (m, 1H), 3.64 (s, 3H), 3.19 (dd, *J* = 5.2, 14.0 Hz, 1H), 3.06 (dd, *J* = 7.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.69, 150.03, 145.27, 135.85, 132.87, 130.99 (q, *J* = 32.1 Hz), 129.19, 128.18, 126.03 (q, *J* = 3.6 Hz), 124.31 (q, *J* = 3.6 Hz), 124.24, 123.76 (q, *J* = 270.7 Hz), 55.81, 52.94, 39.04. . HRMS (ESI-TOF) *m/z* Calcd for C₁₇H₁₄F₃N₂O₆S [M-H]⁻: 431.0530 found: 431.0530.



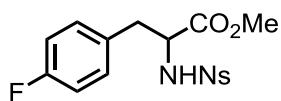
methyl 3-(4-methoxyphenyl)-2-(4-nitrophenylsulfonamido)propanoate 1n²

¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 6.95 (d, *J* = 9.0 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.42 (d, *J* = 9.5 Hz, 1H, N-H), 4.24-4.19 (m, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 3.06 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.90 (dd, *J* = 7.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.19, 158.92, 149.83, 145.63, 130.31, 128.20, 126.60, 124.05, 114.03, 57.27, 55.13, 52.70, 38.34.



methyl 3-(4-cyanophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1o

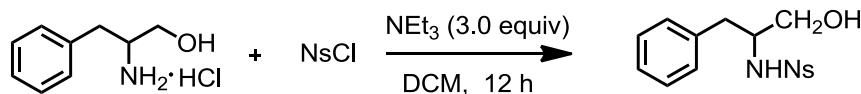
¹H NMR (400 MHz, acetone-*d*₆) δ 8.32 (d, *J* = 9.2 Hz, 2H), 7.93 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 9.2 Hz, 1H, N-H), 7.42 (d, *J* = 8.4 Hz, 2H), 4.39-4.33 (m, 1H), 3.54 (s, 3H), 3.23 (dd, *J* = 5.2, 13.6 Hz, 1H), 3.03 (dd, *J* = 9.2, 13.6 Hz, 1H); ¹³C NMR (100 MHz, acetone-*d*₆) δ 171.57, 151.85, 147.60, 143.03, 132.97, 131.47, 129.09, 125.07, 119.16, 111.64, 58.15, 53.76, 39.10. HRMS (ESI-TOF) *m/z* Calcd for C₁₇H₁₄N₃O₆S [M-H]⁻: 388.0609. found: 388.0610.



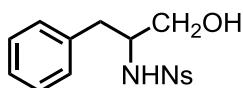
methyl 3-(4-fluorophenyl)-2-(4-nitrophenylsulfonamido)propanoate 1p

¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.06-7.03 (m, 2H), 6.88 (t, *J* = 7.5 Hz, 2H), 5.84 (d, *J* = 9.0 Hz, 1H, N-H), 4.26-4.22 (m, 1H), 3.61 (s, 3H), 3.10 (dd, *J* = 5.5, 14.0 Hz, 1H), 2.96 (dd, *J* = 7.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) 171.01, 161.93 (d, *J* = 244.5 Hz), 149.82, 145.44, 130.81 (d, *J* = 8.1 Hz), 130.62 (d, *J* = 3.5 Hz), 128.10, 124.05, 115.36 (d, *J* = 21.0 Hz), 57.07, 52.65, 38.11. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₄FN₂O₆S [M-H]⁻: 381.0562. found: 381.0560.

Synthesis of *N*-Nosyl 2-amino-3-phenylpropan-1-ol 1q.



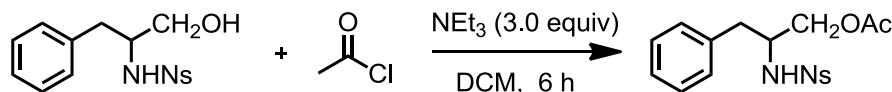
4-Nitrobenzenesulfonyl chloride (NsCl, 1.0 mmol, 1.0 equiv) was added to a cooled (0°C) solution of 2-amino-3-phenylpropan-1-ol hydrochloride (1.0 mmol, 1.0 equiv) and triethylamine (TEA, 3.0 mmol, 3.0 equiv) in DCM (5 mL). After being stirred at room temperature for 12 h, the reaction mixture was poured into H₂O. The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The residue was subjected to column chromatography (EtOAc/hexanes = 1:1) to give **1q**.



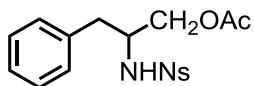
N-(1-hydroxy-3-phenylpropan-2-yl)-4-nitrobenzenesulfonamide 1q³

¹H NMR (400 MHz, Acetone-*d*₆) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.09-7.08 (m, 5H), 6.85 (d, *J* = 7.6 Hz, 1H, N-H), 4.03 (t, *J* = 5.2 Hz, 1H), 3.63-3.51 (m, 3H), 2.97 (dd, *J* = 5.2, 14.0 Hz, 1H), 2.66 (dd, *J* = 8.0, 14.0 Hz, 1H); ¹³C NMR (100 MHz, Acetone-*d*₆) δ 150.40, 148.20, 139.12, 130.146, 129.00, 128.691, 126.88, 124.87, 65.08, 58.93, 38.38.

Synthesis of *N*-Nosyl 2-amino-3-phenylpropyl acetate 1r.



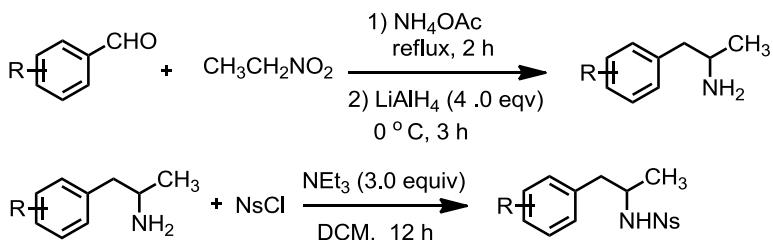
Acetyl chloride (AcCl, 0.5mmol, 1.0 equiv) was added to a cooled (0°C) solution of **1q** (0.5 mmol, 1.0 equiv) and triethylamine (TEA, 3.0 mmol, 3.0 equiv) in DCM (2.5 mL). After being stirred at room temperature for 6 h, the reaction mixture was poured into H_2O . The organic layer was separated, dried over anhydrous Na_2SO_4 , filtered and concentrated under vacuum. The residue was subjected to column chromatography (EtOAc/hexanes = 1:2) to give **1r**.



2-(4-nitrophenylsulfonamido)-3-phenylpropyl acetate **1r**

^1H NMR (500 MHz, CDCl_3) δ 8.13 (d, $J = 8.5$ Hz, 2H), 7.75 (d, $J = 8.5$ Hz, 2H), 7.30-7.11 (m, 3H), 6.98 (d, $J = 6.0$ Hz, 2H), 5.38 (d, $J = 8.5$ Hz, 1H, N-H), 4.15-4.08 (m, 2H), 3.78-3.76 (m, 1H), 2.85 (dd, $J = 6.0, 14.0$ Hz, 1H), 2.67 (dd, $J = 8.5, 14.0$ Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) 171.85, 149.63, 145.99, 136.06, 129.07, 128.64, 127.80, 126.92, 124.09, 65.67, 54.84, 38.29, 22.72. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_6\text{S} [\text{M}-\text{H}]$: 377.0813. found: 377.0811.

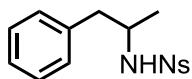
Synthesis of N-Nosyl 1-phenylpropan-2-amine **1s** and N-Nosyl 1-(2-methoxyphenyl)propan-2-amine **1t**.⁴



A solution of the corresponding arylaldehyde (~0.2 M) in nitroethane and ammonium acetate (0.85 equiv) was refluxed for 2 h, then concentrated under vacuum. The crude oil was diluted with THF and slowly added to an ice-cold solution of LiAlH_4 (4 equiv, ~0.5 M) in THF. After the addition, the solution was refluxed for 3 h and allowed to cool to room temperature. H_2O (1.3 g/g LiAlH_4) was slowly added under vigorous stirring, followed by 15% aqueous NaOH (1.3 g/g LiAlH_4), followed again by H_2O (3.25 g/g LiAlH_4). After stirring vigorously for 10 minutes the white precipitate was collected on a filter. The white solid was washed with diethyl ether and the combined filtrates dried and concentrated to yield the 1-(aryl)propan-2-amine. The amines were immediately used in the following step.

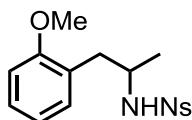
4-Nitrobenzenesulfonyl chloride (NsCl, 1.0 mmol, 1.0 equiv) was added to a cooled (0°C) solution of 1-(aryl)propan-2-amine (1.0 mmol, 1.0 equiv) and triethylamine (TEA, 3.0 mmol, 3.0 equiv) in DCM (5 mL). After being stirred at room temperature for 12 h, the reaction mixture was poured

into H₂O. The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The residue was subjected to column chromatography (EtOAc/hexanes =1:2) to give **1s** and **1t**.



4-nitro-N-(1-phenylpropan-2-yl)benzenesulfonamide **1s**⁴

¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.76 (d, *J* = 9.0 Hz, 2H), 7.16-7.14 (m, 3H), 6.97 (dd, *J* = 2.0, 7.5 Hz, 2H), 4.79 (d, *J* = 8.0 Hz, 1H, N-H), 3.59-3.54 (m, 1H), 2.75 (dd, *J* = 5.5, 14.0 Hz, 1H), 2.60 (dd, *J* = 8.0, 14.0 Hz, 1H), 1.24 (d, *J* = 5.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 149.63, 146.23, 130.90, 129.12, 128.57, 127.88, 126.80, 124.09, 51.99, 43.36, 22.37.

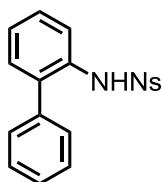


N-(1-(2-methoxyphenyl)propan-2-yl)-4-nitrobenzenesulfonamide **1t**

¹H NMR (500 MHz, CDCl₃) δ 8.03 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.70 (t, *J* = 7.5 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 1H), 5.22 (br, 1H, N-H), 3.76 (s, 3H), 3.48-3.43 (m, 1H), 2.71 (dd, *J* = 10.0, 14.0 Hz, 1H), 2.57 (dd, *J* = 4.0, 14.0 Hz, 1H), 1.35 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 156.82, 149.40, 145.78, 130.97, 128.31, 127.64, 125.86, 123.80, 121.09, 110.59, 55.49, 52.19, 37.30, 23.59. HRMS (ESI-TOF) *m/z* Calcd for C₁₆H₁₇N₂O₅S [M-H]⁻: 349.0864. found: 349.0868.

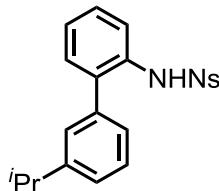
Synthesis of substrate 2-aryl N-nosylaniline **4a-c**⁵⁻⁶

4-Nitrobenzenesulfonyl chloride (NsCl, 1.0 mmol, 1.0 equiv) was added to a solution of 2-aryl aniline (1.0 mmol, 1.0 equiv) in pyridine (5 mL). After being stirred at 140 °C for 0.5 h, the reaction mixture was cooled to room temperature and poured into H₂O. The organic layer was separated, dried over anhydrous Na₂SO₄, filtered and concentrated under vacuum. The residue was purified using ethyl acetate/hexanes (1:2) as the eluent to give the substrates **4a-c**.⁵⁻⁶



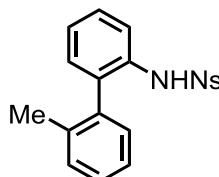
N-([1,1'-biphenyl]-2-yl)-4-nitrobenzenesulfonamide 4a⁵

This compound was prepared according to the procedure in reference 5.



N-(3'-isopropyl-[1,1'-biphenyl]-2-yl)-4-nitrobenzenesulfonamide 4b

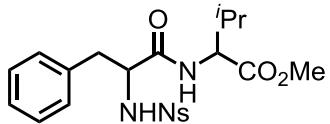
¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.69 (d, *J* = 9.2 Hz, 2H), 7.36 (t, *J* = 8.4 Hz, 1H), 7.25-7.19 (m, 3H), 7.14 (d, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 6.78 (s, 1H), 6.64-6.62 (m, 1H), 2.87-2.80 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 150.08, 150.03, 144.63, 136.78, 134.88, 132.40, 130.52, 129.16, 128.70, 128.26, 126.72, 126.28, 125.96, 125.93, 124.01, 122.13, 33.99, 23.86. HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₁₉N₂O₄S [M-H]⁻: 395.1071. found: 395.1069.



N-(3'-methyl-[1,1'-biphenyl]-2-yl)-4-nitrobenzenesulfonamide 4c

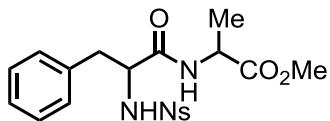
¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 1H), 7.36 (dt, *J* = 1.5, 8.0 Hz, 1H), 7.30 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.18 (dt, *J* = 1.0, 7.5 Hz, 1H), 7.11 (dt, *J* = 1.0, 7.5 Hz, 1H), 7.04 (dd, *J* = 1.5, 8.0 Hz, 1H), 6.51 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.40 (s, 1H), 1.84 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 150.20, 144.79, 136.36, 135.67, 133.07, 132.89, 130.85, 130.34, 129.18, 128.89, 128.79, 128.44, 126.41, 125.48, 124.13, 120.77, 19.46. HRMS (ESI-TOF) *m/z* Calcd for C₁₉H₁₅N₂O₄S [M-H]⁻: 367.0758. found: 367.0759.

Synthesis *N*-nosyl-dipeptides according to the reported procedures.⁴



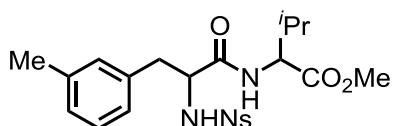
methyl 3-methyl-2-(2-(4-nitrophenylsulfonamido)-3-phenylpropanamido)butanoate 6a

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 9.0 Hz, 2H), 7.75 (d, *J* = 9.0 Hz, 2H), 7.19-7.14 (m, 3H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.53 (d, *J* = 8.5 Hz, 1H, N-H), 5.63 (d, *J* = 7.5 Hz, 1H, N-H), 4.38 (q, *J* = 4.5 Hz, 1H), 4.01-3.97 (m, 1H), 3.73 (s, 3H), 3.12 (dd, *J* = 5.5, 14.0 Hz, 1H), 2.89 (dd, *J* = 8.5, 14.0 Hz, 1H), 2.10-2.04 (m, 1H), 0.81 (q, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 171.89, 169.55, 149.93, 144.59, 135.33, 129.03, 128.97, 128.23, 127.42, 124.20, 58.65, 57.28, 39.23, 31.17, 18.73, 17.45. HRMS (ESI-TOF) *m/z* Calcd for C₂₁H₂₄N₃O₇S [M-H]⁻: 462.1340. found: 462.1341.



methyl 2-(2-(4-nitrophenylsulfonamido)-3-phenylpropanamido)propanoate 6b⁴

¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.18-7.11 (m, 3H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.74 (br, 1H, N-H), 6.05 (br, 1H, N-H), 4.48-4.43 (m, 1H), 4.05-4.03 (m, 1H), 3.73 (s, 3H), 3.08 (dd, *J* = 5.5, 14.5 Hz, 1H), 2.94-2.89 (m, 1H), 1.32 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 172.65, 169.67, 149.85, 145.12, 135.34, 129.19, 128.75, 128.11, 127.26, 124.15, 58.41, 52.62, 48.38, 38.88, 18.10.

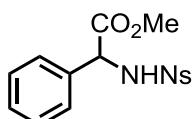


methyl 3-methyl-2-(2-(4-nitrophenylsulfonamido)-3-(m-tolyl)propanamido)butanoate 6c

¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 9.6 Hz, 2H), 7.76 (d, *J* = 9.6 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 7.5 Hz, 1H), 6.82 (s, 1H), 6.81 (d, *J* = 7.5 Hz, 1H, N-H), 6.25 (br, 1H, N-H), 4.42 (dd, *J* = 5.0, 9.0 Hz, 1H), 4.07 (dd, *J* = 6.0, 9.0 Hz, 1H), 3.72 (s, 3H), 3.10 (dd, *J* = 6.0, 14.0 Hz, 1H), 2.85 (dd, *J* = 9.0, 14.0 Hz, 1H), 2.16 (s, 3H), 2.11-2.08 (m, 1H), 0.82 (q, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 171.94, 170.05, 149.69, 144.80, 138.41, 135.43, 129.76, 128.68, 128.07, 127.87, 126.08, 123.95, 58.80, 57.23, 52.22, 38.91, 31.16, 21.04, 18.64, 17.42. HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₂₆N₃O₇S [M-H]⁻: 476.1497. found: 476.1500.

Synthesis of methyl 2-(4-nitrophenylsulfonamido)-2-phenylacetate according to the reported procedure.⁵

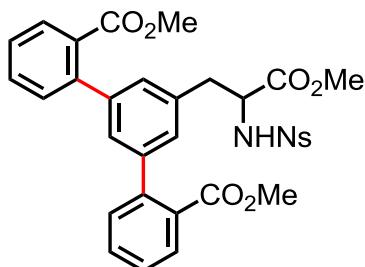
Under an nitrogen atmosphere, a round-bottom flask was charged with phenylglycine methyl ester hydrochloric acid salt (0.01 mol), pyridine (1.0 ml) and DCM (20 ml). The mixture was stirred and cooled to 0 °C. Then *p*-nitrobenzenesulfonyl chloride (0.011 mol) in DCM (20 ml) was added into the mixture slowly. The mixture was warmed to room temperature and further stirred for 30 min. The reaction mixture was diluted with DCM and washed with hydrochloric acid (1 M) and water. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated in vacuo. The product was recrystallized from ethyl acetate/hexanes to give white crystals, which was dried under high vacuum.



methyl 2-(4-nitrophenylsulfonamido)-2-phenylacetate 8

¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.8 Hz, 2H), 7.27-7.14 (m, 5H), 6.10 (br, 1H, N-H), 5.19 (d, *J* = 6.8 Hz, 1H), 3.65 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.09, 149.72, 146.03, 134.46, 128.95, 128.89, 128.19, 127.34, 123.86, 59.52, 53.32. HRMS (ESI-TOF) *m/z* Calcd for C₁₅H₁₃N₂O₆S [M-H]⁻: 349.0500. found: 349.0504.

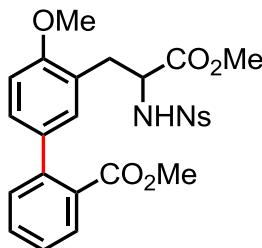
3.3 General Procedure for *meta*-C(sp²)-H Arylation of Substituted Phenethylamines (Tables 3 and 4). Substrate **1** (0.10 mmol), Pd(OAc)₂ (0.01 mmol, 2.2 mg), and AgOAc (0.30 mmol, 50.0 mg) were weighed in air and placed in a sealed tube (10 mL) with a magnetic stir bar. To the reaction mixture, 4-acetylpyridine (0.02 mmol, 2.2 μL), norbornene (0.02 mmol, 1.9 mg), aryl halide **2** (0.3 mmol), and TBME (1.0 mL) were added. The reaction mixture was heated to 80 °C for 12 to 24 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and the resulting residue purified by preparative TLC using an eluent of hexanes/ethyl acetate(2/1 to 4/1) to give the desired products **3**.



dimethyl

5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1':3',1''-terphenyl]-2,2''-dicarbonylate 3aa

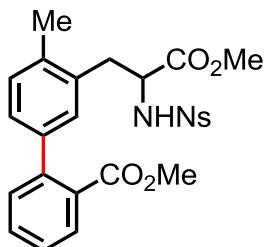
^1H NMR (500 MHz, CDCl_3) δ 8.22 (d, $J = 9.0$ Hz, 2H), 7.98 (d, $J = 9.0$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 7.5$ Hz, 2H), 7.42 (t, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.12 (s, 1H), 6.98 (s, 2H), 5.80 (d, $J = 9.0$ Hz, 1H, N-H), 4.42–4.38 (m, 1H), 3.73 (s, 6H), 3.55 (s, 3H), 3.19 (dd, $J = 6.0, 14.0$ Hz, 1H), 3.12 (dd, $J = 5.5, 14.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.67, 168.45, 149.86, 146.08, 142.02, 141.59, 133.57, 131.49, 130.71, 130.20, 130.16, 128.41, 128.29, 127.66, 127.51, 124.07, 56.89, 52.55, 52.16, 38.90. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{32}\text{H}_{27}\text{N}_2\text{O}_{10}\text{S}$ [M-H] $^-$: 631.1392. found: 631.1389.



methyl

4'-methoxy-3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carbonylate 3ba

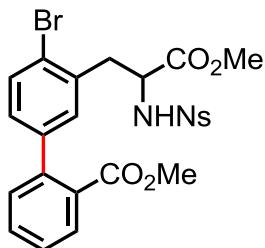
^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 8.5$ Hz, 2H), 7.85–7.83 (m, 3H), 7.51 (dt, $J = 1.5, 7.5$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 1H), 7.25 (d, $J = 7.5$ Hz, 1H), 7.15 (dd, $J = 2.5, 8.5$, 1H), 6.99 (d, $J = 2.5$, 1H), 6.72 (d, $J = 8.5, 1$ H), 5.72 (d, $J = 8.0$, 1H, N-H), 4.33–4.29 (m, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 3.63 (s, 3H), 3.07 (dd, $J = 5.0, 13.5$ Hz, 1H), 3.00 (dd, $J = 8.5, 13.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.56, 168.62, 156.64, 149.70, 145.79, 141.75, 133.68, 131.77, 131.46, 130.70, 130.06, 128.73, 128.22, 127.06, 123.89, 122.76, 109.99, 55.75, 55.37, 52.49, 52.19, 33.81. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_9\text{S}$ [M-H] $^-$: 527.1130. found: 527.1133.



methyl

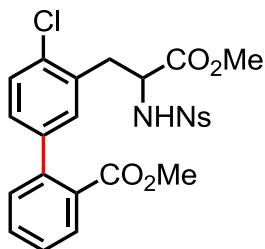
3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-4'-methyl-[1,1'-biphenyl]-2-carboxylate 3ca

¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.87-7.83 (m, 3H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.10-7.04 (m, 2H), 6.99 (s, 1H), 5.60 (br, 1H, N-H), 4.23 (t, *J* = 6.0 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 3.17 (dd, *J* = 5.6, 14.0 Hz, 1H), 2.97 (dd, *J* = 8.8, 14.0 Hz, 1H), 2.20 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.52, 168.59, 149.80, 145.51, 142.07, 139.11, 135.39, 132.66, 131.50, 130.72, 130.50, 130.48, 130.07, 130.05, 128.25, 127.56, 127.27, 124.03, 55.97, 52.72, 52.23, 36.42, 18.90. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₃N₂O₈S [M-H]⁻: 511.1181. found: 511.1178.



methyl 4'-bromo-3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3da

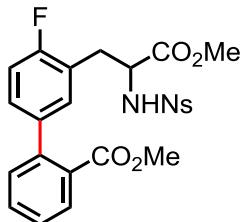
¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 2.0 Hz, 1H), 7.02 (dd, *J* = 2.0, 8.0 Hz, 1H), 5.70 (d, *J* = 9.2 Hz, 1H, N-H), 4.43-4.36 (m, 1H), 3.77 (s, 3H), 3.66 (s, 3H), 3.26 (dd, *J* = 5.2, 14.0 Hz, 1H), 3.04 (dd, *J* = 9.6, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 171.34, 168.08, 149.83, 145.40, 141.08, 140.95, 133.99, 132.56, 132.13, 131.78, 130.66, 130.38, 129.72, 129.11, 128.35, 127.83, 124.05, 123.36, 55.30, 52.88, 52.30, 38.91. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₀BrN₂O₈S [M-H]⁻: 575.0129. found: 575.0131.



methyl

4'-chloro-3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3ea

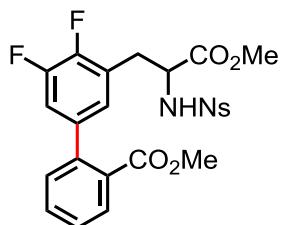
¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 6.8 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.13 (s, 1H), 7.10 (dd, *J* = 2.0, 8.4 Hz, 1H), 5.72 (br, 1H, N-H), 4.40-4.37 (m, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.25 (dd, *J* = 5.6, 14.0 Hz, 1H), 3.07 (dd, *J* = 8.8, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 171.29, 168.10, 149.84, 145.46, 141.12, 140.29, 133.10, 132.22, 132.12, 131.75, 130.71, 130.36, 129.77, 129.21, 128.89, 128.30, 127.79, 124.04, 55.27, 52.84, 52.28, 36.64. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₀ClN₂O₈S [M-H]⁻: 531.0634. found: 531.0630.



methyl

4'-fluoro-3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3fa

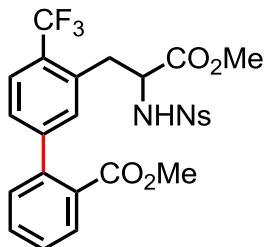
¹H NMR (400 MHz, CDCl₃) δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.94-7.90 (m, 3H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.26 (d, *J* = 7.6 Hz, 1H), 7.16-7.12 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 1H), 6.93 (t, *J* = 8.8 Hz, 1H), 5.63 (d, *J* = 9.6 Hz, 1H, N-H), 4.37-4.32 (m, 1H), 3.76 (s, 3H), 3.61 (s, 3H), 3.16-3.06 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.88, 168.15, 160.46 (d, ¹J_{CF} = 245.0 Hz), 149.90, 145.71, 141.42, 137.49 (d, ³J_{CF} = 4.6 Hz), 132.17 (d, ⁴J_{CF} = 4.3 Hz), 131.66, 130.81, 130.32, 129.87, 129.32 (d, ³J_{CF} = 8.3 Hz), 128.27, 127.59, 124.11, 121.16 (d, ²J_{CF} = 16.1 Hz), 114.99 (d, ²J_{CF} = 22.3 Hz), 55.73, 52.80, 52.21, 32.82. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₀FN₂O₈S [M-H]⁻: 515.0930. found: 515.0934.



methyl

3',4'-difluoro-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3ga

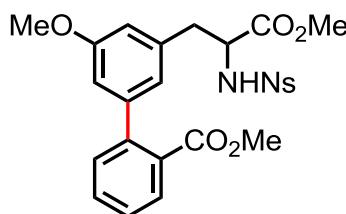
¹H NMR (500 MHz, acetone-D₆) δ 8.33 (d, *J* = 9.0 Hz, 2H), 7.99 (d, *J* = 9.0 Hz, 2H), 7.85 (dd, *J* = 1.0, 8.0 Hz, 1H), 7.64 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.56 (br, 1H, N-H), 7.53 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.41 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.12-7.08 (m, 1H), 7.03 (d, *J* = 6.0 Hz, 1H), 4.40-4.36 (m, 1H), 3.71 (s, 3H), 3.58 (s, 3H), 3.28 (dd, *J* = 5.5, 14.0 Hz, 1H), 3.04 (dd, *J* = 9.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, acetone-D₆) δ 171.59, 168.80, 150.92, 150.49 (dd, *J* = 12.5, 244 Hz), 149.23 (dd, *J* = 12.5, 244 Hz), 147.61, 141.00, 138.92, 132.51, 131.78, 131.74, 130.82, 129.14, 128.92, 128.05, 126.40 (d, *J* = 12.5 Hz), 125.13, 117.16 (d, *J* = 18.7 Hz), 56.97, 52.87, 52.53, 32.90. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₁₉F₂N₂O₈S [M-H]⁻: 533.0836. found: 533.0839.



methyl

3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate 3ha

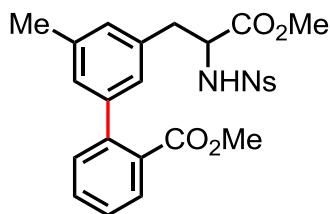
¹H NMR (500 MHz, CDCl₃) δ 8.20 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.60-7.57 (m, 2H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.30-7.26 (m, 3H), 5.56 (d, *J* = 9.5 Hz, 1H, N-H), 4.33-4.28 (m, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.34 (dd, *J* = 5.5, 14.5 Hz, 1H), 3.07 (dd, *J* = 9.5, 15.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.22, 167.92, 149.92, 145.53, 145.28, 140.99, 133.21, 132.44, 131.90, 130.78, 130.49, 129.76, 128.32, 128.21, 127.76, 127.69, 126.46 (q, *J* = 270 Hz), 126.15 (q, *J* = 7.2 Hz), 124.08, 56.62, 52.86, 52.30, 35.84. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₀F₃N₂O₈S [M-H]⁻: 565.0898. found: 565.0900.



methyl

3'-methoxy-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3ia

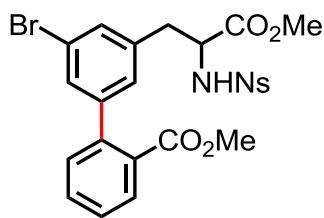
¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.87 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.53 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.42 (dt, *J* = 1.5, 7.6 Hz, 1H), 7.28 (dd, *J* = 1.5, 7.5 Hz, 1H), 6.70 (s, 1H), 6.61 (s, 1H), 6.43 (s, 1H), 5.66 (d, *J* = 8.5 Hz, 1H, N-H), 4.29-4.25 (m, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H), 3.08 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.97 (dd, *J* = 7.5, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 171.02, 168.42, 159.47, 149.80, 145.60, 142.95, 142.06, 135.61, 131.49, 130.55, 130.13, 130.03, 128.27, 127.51, 124.00, 122.31, 113.46, 112.75, 56.95, 55.10, 52.69, 52.24, 38.83. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₃N₂O₉S [M-H]⁻: 527.1130. found: 527.1131.



methyl

3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate 3ja

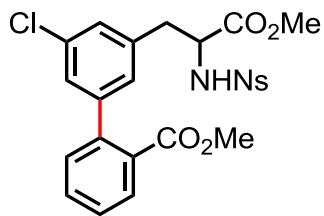
¹H NMR (400 MHz, CDCl₃) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 1H), 7.52 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 6.99 (s, 1H), 6.83 (s, 1H), 6.76 (s, 1H), 5.63 (d, *J* = 8.8 Hz, 1H, N-H), 4.32-4.26 (m, 1H), 3.75 (s, 3H), 3.60 (s, 3H), 3.08 (dd, *J* = 5.2, 14.0 Hz, 1H), 3.00 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.25 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.98, 168.48, 149.80, 145.74, 142.34, 141.58, 138.17, 134.06, 131.48, 130.67, 130.08, 130.00, 128.55, 128.28, 128.19, 127.33, 126.96, 123.99, 57.01, 52.57, 52.17, 38.80, 21.21. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₃N₂O₈S [M-H]⁻: 511.1181. found: 511.1182.



methyl

3'-bromo-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3ka

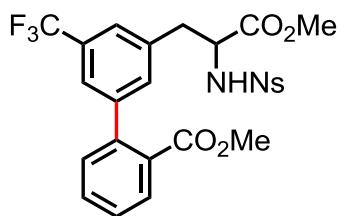
¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 9.0 Hz, 2H), 7.95-7.92 (m, 3H), 7.55 (dt, *J* = 1.5, 8.0 Hz, 1H), 7.46 (dt, *J* = 1.0, 8.0 Hz, 1H), 7.31 (s, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 5.65 (br, 1H, N-H), 4.30 (br, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 3.09 (dd, *J* = 5.0, 14.0 Hz, 1H), 3.00 (dd, *J* = 7.0, 14.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 170.68, 167.87, 150.00, 145.57, 143.57, 140.98, 136.22, 131.83, 130.71, 130.57, 130.49, 130.35, 129.62, 128.85, 128.23, 128.01, 124.19, 122.19, 56.87, 52.82, 52.32, 38.58. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₀BrN₂O₈S [M-H]⁻: 575.0129. found: 575.0130.



methyl

3'-chloro-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3la

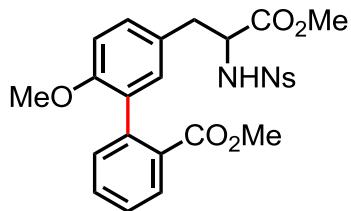
¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.15 (s, 1H), 6.95 (s, 1H), 6.90 (s, 1H), 5.74 (d, *J* = 7.6 Hz, 1H, N-H), 4.30-4.27 (m, 1H), 3.78 (s, 3H), 3.63 (s, 3H), 3.10 (dd, *J* = 4.8, 14.0 Hz, 1H), 3.00 (dd, *J* = 7.2, 14.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 170.73, 167.90, 149.94, 145.54, 143.32, 141.02, 136.06, 134.01, 131.79, 130.65, 130.43, 129.66, 128.32, 128.20, 127.96, 127.64, 127.45, 124.14, 56.84, 52.79, 52.28, 38.55. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₀ClN₂O₈S [M-H]⁻: 531.0634. found: 531.0624.



methyl

3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate 3ma

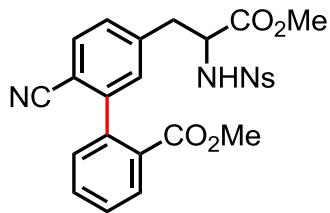
¹H NMR (500 MHz, CDCl₃) δ 8.25 (d, *J* = 9.0 Hz, 2H), 7.99 (d, *J* = 7.5 Hz, 1H), 7.94 (d, *J* = 8.8 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.31 (s, 1H), 7.29 (d, *J* = 7.5 Hz, 1H), 7.22 (s, 1H), 5.76 (d, *J* = 9.5 Hz, 1H, N-H), 4.39-4.35 (m, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 3.21-3.14 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 170.48, 167.77, 149.98, 145.66, 145.66, 142.53, 141.13, 135.12, 133.51, 131.99, 130.84, 130.78 (q, *J* = 31.9 Hz), 130.69, 129.54, 128.23, 128.18, 124.50 (q, *J* = 3.8 Hz), 124.36 (q, *J* = 3.8 Hz), 123.74 (q, *J* = 270 Hz), 56.78, 52.74, 52.28, 38.90. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₀F₃N₂O₈S [M-H]⁻: 565.0898. found: 565.0902.



methyl

2'-methoxy-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3na

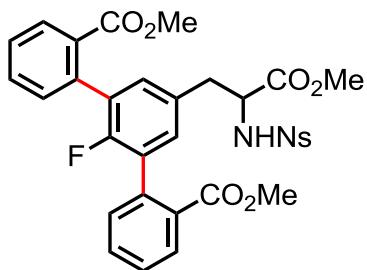
¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.53 (dt, *J* = 1.2, 7.0 Hz, 1H), 7.40 (dt, *J* = 1.2, 7.4 Hz, 1H), 7.21 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.4 Hz, 1H), 6.92 (s, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 5.46 (br, 1H, N-H), 4.28 (m, 1H), 3.71 (s, 3H), 3.67 (s, 3H), 3.60 (s, 3H), 3.11-2.98 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 171.10, 168.22, 155.45, 149.87, 145.73, 138.30, 131.62, 131.24, 131.14, 130.67, 129.44, 129.31, 128.33, 127.37, 126.45, 124.15, 110.35, 57.09, 55.25, 52.65, 51.82, 38.37. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₃N₂O₉S [M-H]⁻: 527.1130. found: 527.1130.



methyl

2'-cyano-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 3oa

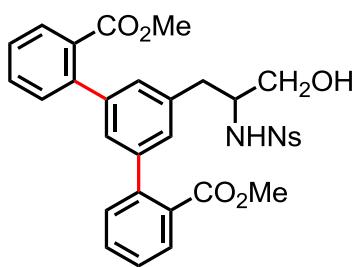
¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 9.2 Hz, 2H), 8.14-8.12 (m, 1H), 7.97 (d, *J* = 8.8 Hz, 2H), 7.65-7.59 (m, 2H), 7.54 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.28 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.17-7.14 (m, 2H), 5.71 (br, 1H, N-H), 4.38 (br, 1H), 3.78 (s, 3H), 3.55 (s, 3H), 3.19 (br, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.20, 166.77, 150.07, 145.69, 139.27, 132.56, 132.35, 130.98, 129.00, 128.44, 128.30, 124.25, 117.58, 111.43, 56.34, 52.83, 52.33, 39.24. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₀N₃O₈S [M-H]⁻: 522.0977. found: 522.0980.



dimethyl

2'-fluoro-5'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 3pa

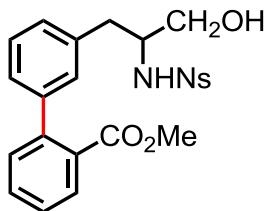
¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 8.8 Hz, 2H), 8.01-7.96 (m, 4H), 7.55 (dt, *J* = 1.2, 7.6 Hz, 2H), 7.45 (dt, *J* = 1.2, 7.6 Hz, 2H), 7.27 (dd, *J* = 1.6, 8.8 Hz, 2H), 6.97 (d, *J* = 6.4 Hz, 2H), 5.88 (br, 1H, N-H), 4.39 (br, 1H), 3.74 (s, 6H), 3.54 (s, 3H), 3.19-3.08 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 170.66, 167.56, 155.31 (d, ¹J_{CF} = 244.6 Hz), 149.92, 146.02, 136.13, 131.78, 131.35, 130.87, 130.45, 130.28, 129.42 (d, ³J_{CF} = 3.9 Hz), 129.07 (d, ²J_{CF} = 17.4 Hz), 128.31, 128.09, 124.16, 56.85, 52.58, 52.15, 38.44. HRMS (ESI-TOF) *m/z* Calcd for C₃₂H₂₆FN₂O₁₀S [M-H]⁻: 649.1298. found: 649.1293.



dimethyl

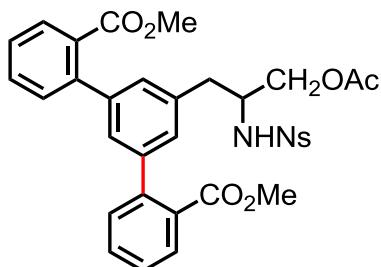
5'-(3-hydroxy-2-(4-nitrophenylsulfonamido)propyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 3qa(di)

¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 8.5 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 6.97 (s, 2H), 5.62 (d, *J* = 7.5 Hz, 1H, N-H), 3.71 (s, 6H), 3.63-3.59 (m, 3H), 2.89-2.87 (m, 2H), 2.43 (br, 1H, OH); ¹³C NMR (125 MHz, CDCl₃) δ 168.71, 149.79, 146.49, 141.91, 141.45, 135.48, 131.55, 130.69, 130.22, 130.09, 128.55, 128.26, 127.53, 127.11, 124.21, 63.50, 56.50, 52.20, 37.86. HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₂₇N₂O₉S [M-H]⁻: 603.1443. found: 603.1445.



methyl 3'-(3-hydroxy-2-(4-nitrophenylsulfonamido)propyl)-[1,1'-biphenyl]-2-carboxylate 3qa(mono)

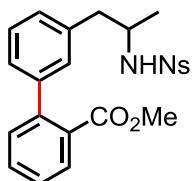
¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 9.0 Hz, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.16-7.12 (m, 2H), 7.00 (s, 1H), 6.91 (d, *J* = 6.5 Hz, 1H), 5.25 (d, *J* = 7.5 Hz, 1H, N-H), 3.75 (s, 3H), 3.70-3.54 (m, 3H), 2.89 (dd, *J* = 6.0, 14.0 Hz, 1H), 2.76 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.19 (br, 1H, OH); ¹³C NMR (125 MHz, CDCl₃) δ 168.59, 149.78, 145.94, 142.23, 141.59, 135.91, 131.64, 130.73, 130.15, 129.99, 129.88, 128.53, 128.26, 127.65, 127.50, 126.95, 124.19, 64.25, 56.88, 52.24, 37.87. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₁N₂O₇S [M-H]⁻: 469.1075. found: 469.1075.



dimethyl

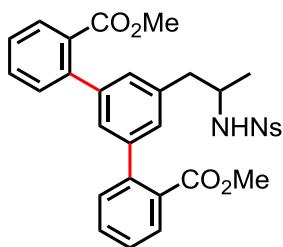
**5'-(3-acetoxy-2-(4-nitrophenylsulfonamido)propyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate
3ra**

^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 8.5$ Hz, 2H), 7.96 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 2H), 7.52 (t, $J = 7.5$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 2H), 7.27 (d, $J = 7.5$ Hz, 2H), 7.13 (s, 1H), 6.98 (s, 2H), 5.51 (d, $J = 8.0, 1$ H, N-H), 4.10-4.03 (m, 2H), 3.91-3.87 (m, 1H), 3.71 (s, 6H), 2.93-2.83 (m, 2H), 1.97 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.59, 168.50, 149.77, 146.65, 141.89, 141.56, 134.56, 131.51, 130.67, 130.21, 130.12, 128.54, 128.16, 127.53, 127.33, 124.18, 64.86, 53.85, 52.13, 38.10, 20.65. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{33}\text{H}_{29}\text{N}_2\text{O}_{10}\text{S}$ [M-H] $^-$: 645. found ESI-MS: 645.



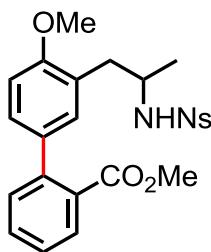
methyl 3'-(2-(4-nitrophenylsulfonamido)propyl)-[1,1'-biphenyl]-2-carboxylate3sa(mono) 3sa (mono)

^1H NMR (500 MHz, CDCl_3) δ 8.18 (d, $J = 9.0$ Hz, 2H), 7.89-7.86 (m, 3H), 7.53 (dt, $J = 1.5, 8.0$ Hz, 1H), 7.43 (dt, $J = 1.5, 7.5$ Hz, 1H), 7.27 (dd, $J = 1.5, 7.5$ Hz, 1H), 7.17-7.15 (m, 2H), 6.99 (s, 1H), 6.93-6.91 (m, 1H), 4.91 (d, $J = 7.5$ Hz, 1H, N-H), 3.73 (s, 3H), 3.61-3.53 (m, 1H) 2.81 (dd, $J = 5.5, 14.0$ Hz, 1H), 2.65 (dd, $J = 7.5, 14.0$ Hz, 1H), 1.22 (d, $J = 6.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.50, 149.68, 146.46, 142.30, 141.53, 136.09, 131.55, 130.69, 130.13, 130.08, 129.82, 128.35, 128.14, 127.91, 127.43, 126.87, 124.14, 52.18, 51.48, 43.08, 21.94. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{23}\text{H}_{21}\text{N}_2\text{O}_6\text{S}$ [M-H] $^-$: 453.1126. found: 453.1129.



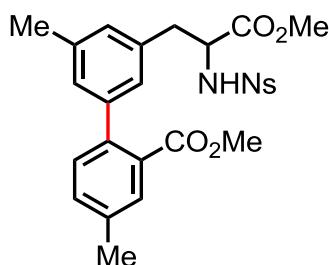
**dimethyl 5'-(2-(4-nitrophenylsulfonamido)propyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate
3sa(di)**

¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.5 Hz, 2H), 7.14 (s, 1H), 6.95 (s, 2H), 5.17 (d, *J* = 7.5, 1H, N-H), 3.72-3.67 (m, 7H), 2.86 (dd, *J* = 5.5, 13.5 Hz, 1H), 2.71 (dd, *J* = 6.5, 14.0 Hz, 1H), 1.18 (d, *J* = 6.5 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.56, 149.71, 146.91, 142.05, 141.39, 135.30, 131.51, 130.70, 130.25, 130.13, 128.72, 128.20, 127.51, 127.06, 124.17, 52.17, 50.99, 42.83, 21.38. HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₂₇N₂O₈S [M-H]⁻: 587.1494. found: 587.1500.



**methyl 4'-methoxy-3'-(2-(4-nitrophenylsulfonamido)propyl)-[1,1'-biphenyl]-2-carboxylate
3ta**

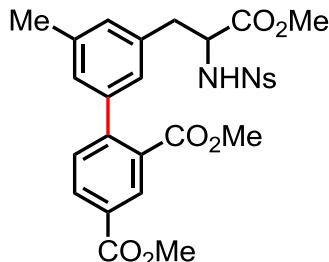
¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 7.5, 1H), 6.91 (s, 1H), 6.66 (d, *J* = 8.5, 1H), 5.26 (d, *J* = 6.0 Hz, 1H, N-H), 3.75 (s, 3H), 3.70 (s, 3H), 3.56-3.52 (m, 1H), 2.72-2.62 (m, 2H), 1.32 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.66, 156.38, 149.46, 146.13, 141.64, 133.75, 131.61, 131.47, 130.58, 130.10, 130.06, 128.15, 128.08, 127.06, 125.05, 123.81, 110.10, 55.35, 52.17, 51.18, 37.83, 23.20. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₃N₂O₇S [M-H]⁻: 483.1231. found: 483.1235.



methyl

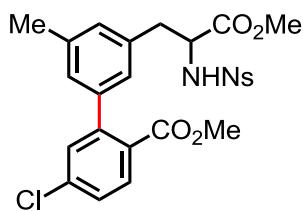
3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-4,5'-dimethyl-[1,1'-biphenyl]-2-carboxylate 3jb

^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 9.0$ Hz, 2H), 7.90 (d, $J = 8.5$ Hz, 2H), 7.69 (d, $J = 2.0$ Hz, 1H), 7.33 (dd, $J = 2.0, 8.0$ Hz, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 6.97 (s, 1H), 6.79 (s, 1H), 6.73 (s, 1H), 5.55 (d, $J = 5.0$ Hz, 1H, N-H), 4.30–4.28 (m, 1H), 3.74 (s, 3H), 3.60 (s, 3H), 3.06 (dd, $J = 5.0, 14.0$ Hz, 1H), 3.00 (dd, $J = 7.0, 13.5$ Hz, 1H), 2.42 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.97, 168.67, 149.83, 145.78, 141.59, 139.52, 138.15, 137.29, 133.96, 132.23, 130.60, 129.79, 128.38, 128.30, 128.27, 127.04, 124.01, 57.00, 52.58, 52.14, 38.83, 21.24, 20.93. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{26}\text{H}_{25}\text{N}_2\text{O}_8\text{S} [\text{M}-\text{H}]^-$: 525.1337. found: 525.1338.



dimethyl 3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-methyl-[1,1'-biphenyl]-2,4-dicarboxylate 3jc

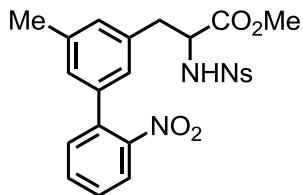
^1H NMR (500 MHz, CDCl_3) δ 8.22 (d, $J = 8.5$ Hz, 2H), 8.05 (d, $J = 8.0$ Hz, 1H), 7.93–7.89 (m, 4H), 7.00 (s, 1H), 6.84 (s, 1H), 6.82 (s, 1H), 5.63 (d, $J = 8.5$ Hz, 1H, N-H), 4.31–4.29 (m, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 3.61 (s, 3H), 3.09 (dd, $J = 5.0, 14.0$ Hz, 1H), 3.01 (dd, $J = 7.0, 13.5$ Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.93, 167.98, 166.01, 149.84, 145.72, 142.24, 140.53, 138.39, 134.49, 134.12, 132.51, 131.62, 130.00, 129.09, 128.26, 128.21, 128.15, 126.77, 124.03, 57.02, 52.60, 52.47, 52.44, 38.86, 21.21. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{25}\text{N}_2\text{O}_{10}\text{S} [\text{M}-\text{H}]^-$: 569.1235. found: 569.1236.



methyl

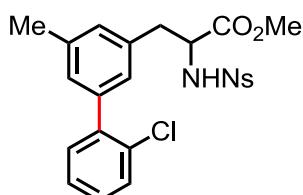
5-chloro-3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate 3jd

¹H NMR (500 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.85 (d, *J* = 8.5 Hz, 1H), 7.38 (dd, *J* = 2.5, 8.5 Hz, 1H), 7.26 (s, 1H), 6.97 (s, 1H), 6.83 (s, 1H), 6.79 (s, 1H), 5.64 (d, *J* = 8.5 Hz, 1H, N-H), 4.32-4.28 (m, 1H), 3.75 (s, 3H), 3.59 (s, 3H), 3.08 (dd, *J* = 5.0, 14.0 Hz, 1H), 3.02 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.26 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.87, 167.43, 149.85, 145.76, 144.33, 140.30, 138.34, 137.60, 134.23, 131.67, 130.80, 129.06, 128.28, 128.20, 128.04, 127.44, 126.87, 124.02, 56.97, 52.56, 52.29, 38.83, 21.20. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₂ClN₂O₈S [M-H]⁻: 545.0791. found ESI-MS: 545.



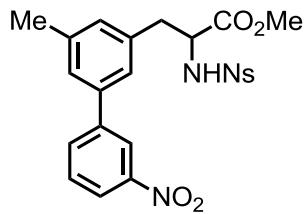
methyl 3-(5-methyl-2'-nitro-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3je

¹H NMR (400 MHz, CDCl₃) δ 8.23 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.92 (dd, *J* = 2.0, 8.8 Hz, 2H), 7.84 (dd, *J* = 1.2, 8.0 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.88 (s, 1H), 6.81 (s, 1H), 5.58 (d, *J* = 8.8 Hz, 1H, N-H), 4.31-4.26 (m, 1H), 3.60 (s, 3H), 3.08 (dd, *J* = 5.2, 14.0 Hz, 1H), 3.00 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.27 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.94, 149.90, 149.06, 138.88, 137.82, 135.78, 135.19, 132.35, 131.72, 129.80, 128.31, 128.27, 127.66, 125.95, 124.07, 56.89, 52.73, 38.90, 21.20. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₀N₃O₈S [M-H]⁻: 498.0977. found: 498.0977.



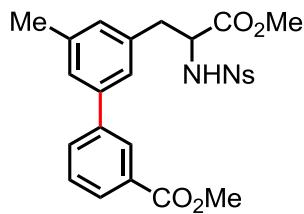
methyl 3-(2'-chloro-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jf

¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 1.5 Hz, 1H), 7.35-7.31 (m, 3H), 7.20 (s, 1H), 7.00 (s, 1H), 6.85 (s, 1H), 5.40 (d, *J* = 9.5 Hz, 1H, N-H), 4.32-4.28 (m, 1H), 3.66 (s, 3H), 3.14 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.95 (dd, *J* = 8.0, 13.5 Hz, 1H), 2.31 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.16, 149.83, 145.53, 142.20, 140.12, 139.05, 135.55, 134.73, 130.07, 129.54, 128.08, 127.53, 127.01, 126.86, 125.04, 125.00, 123.98, 57.17, 52.82, 39.13, 21.32. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₀ClN₂O₆S [M-H]⁻: 487.0736. found: 487.0736.



methyl 3-(5-methyl-3'-nitro-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jg

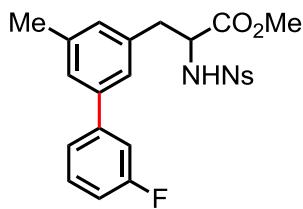
¹H NMR (500 MHz, CDCl₃) δ 8.32 (s, 1H), 8.21-8.17 (m, 3H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.29 (s, 1H), 7.10 (s, 1H), 6.94 (s, 1H), 5.41 (br, 1H, N-H), 4.32 (br, 1H), 3.66 (s, 3H), 3.18 (dd, *J* = 5.0, 14.0 Hz, 1H), 3.01 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.03, 149.90, 148.71, 145.54, 142.12, 139.41, 139.00, 135.89, 132.77, 130.29, 129.84, 128.15, 126.94, 125.17, 124.04, 122.25, 121.73, 57.05, 52.87, 39.14, 21.36. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₀N₃O₈S [M-H]⁻: 498.0977. found: 498.0976.



methyl 3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-methyl-[1,1'-biphenyl]-3-carboxylate 3jh

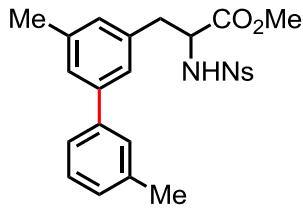
¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 8.5 Hz, 2H), 8.12 (s, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.80

(d, $J = 7.5$ Hz, 2H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 8.0$ Hz, 1H), 7.26 (s, 1H), 7.06 (s, 1H), 6.87 (s, 1H), 5.53 (d, $J = 9.0$ Hz, 1H, N-H), 4.33-4.28 (m, 1H), 3.96 (s, 3H), 3.67 (s, 3H), 3.15 (dd, $J = 5.0, 13.5$ Hz, 1H), 2.95 (dd, $J = 7.5, 14.0$ Hz, 1H), 2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.22, 166.95, 149.77, 145.56, 140.57, 140.37, 139.02, 135.64, 131.19, 130.72, 129.44, 128.96, 128.56, 128.04, 127.96, 126.83, 125.05, 123.95, 57.24, 52.81, 52.25, 39.06, 21.32. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_8\text{S}$ [M-H] $^-$: 511.1181. found: 511.1181.



methyl 3-(3'-fluoro-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3ji

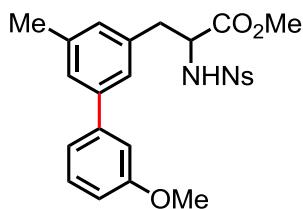
^1H NMR (500 MHz, CDCl_3) δ 8.15 (d, $J = 8.5$ Hz, 2H), 7.81 (d, $J = 8.5$ Hz, 2H), 7.40-7.35 (m, 1H), 7.25 (d, $J = 8.5$ Hz, 1H), 7.21 (s, 1H), 7.17 (m, 1H), 7.05-7.01 (m, 2H), 6.85 (s, 1H), 5.45 (d, $J = 9.0$ Hz, 1H, N-H), 4.32-4.28 (m, 1H), 3.66 (s, 3H), 3.14 (dd, $J = 5.0, 14.0$ Hz, 1H), 2.95 (dd, $J = 8.0, 14.0$ Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.20, 163.14 (d, $^1J_{CF} = 244.7$ Hz), 149.82, 145.53, 142.62 (d, $^3J_{CF} = 7.5$ Hz), 140.23, 139.01, 135.53, 130.32 (d, $^3J_{CF} = 7.5$ Hz), 129.51, 128.07, 126.83, 125.03, 123.97, 122.46, 114.33 (d, $^2J_{CF} = 21.2$ Hz), 113.74 (d, $^2J_{CF} = 22.8$ Hz), 57.18, 52.81, 39.10, 21.31. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{23}\text{H}_{20}\text{FN}_2\text{O}_6\text{S}$ [M-H] $^-$: 471.1032. found: 471.1031.



methyl 3-(3',5-dimethyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jj

^1H NMR (500 MHz, CDCl_3) δ 8.12 (d, $J = 9.0$ Hz, 2H), 7.77 (d, $J = 9.0$ Hz, 2H), 7.32-7.25 (m, 3H), 7.22 (s, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 7.01 (s, 1H), 6.79 (s, 1H), 5.32 (d, $J = 9.0$ Hz, 1H, N-H), 4.31-4.26 (m, 1H), 3.67 (s, 3H), 3.13 (dd, $J = 5.0, 14.0$ Hz, 1H), 2.92 (dd, $J = 8.0, 14.0$ Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 171.26, 149.78, 145.51, 141.70, 140.26, 138.77, 138.47, 135.28, 128.81, 128.75, 128.32, 128.05, 127.61, 126.91, 125.04, 123.94, 57.29, 52.80, 39.18, 21.50, 21.34. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{24}\text{H}_{23}\text{N}_2\text{O}_6\text{S}$ [M-H] $^-$: 467.1282.

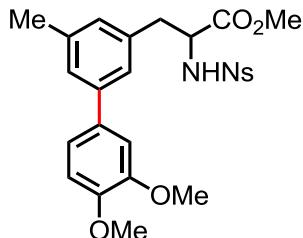
found: 467.1285.



methyl

3-(3'-methoxy-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jk

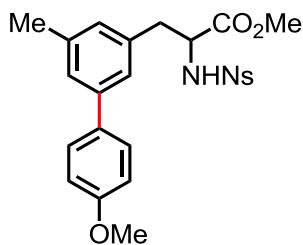
¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 1H), 7.22 (s, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.02 (s, 1H), 6.99 (s, 1H), 6.89 (dd, *J* = 2.5, 8.5 Hz, 1H), 6.81 (s, 1H), 5.42 (d, *J* = 8.5 Hz, 1H, N-H), 4.31-4.27 (m, 1H), 3.87 (s, 3H), 3.67 (s, 3H), 3.13 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.93 (dd, *J* = 8.0, 13.5 Hz, 1H), 2.29 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.27, 159.97, 149.77, 145.52, 141.79, 141.36, 138.80, 135.34, 129.84, 129.05, 128.03, 126.88, 125.07, 123.96, 119.29, 112.77, 57.23, 55.31, 52.79, 39.09, 21.32. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₃N₂O₇S [M-H]⁻: 483.1231. found: 483.1234



methyl

3-(3',4'-dimethoxy-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jl

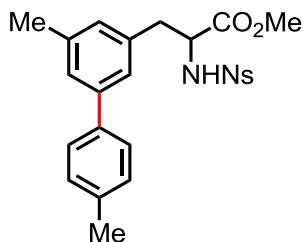
¹H NMR (500 MHz, CDCl₃) δ 8.13 (d, *J* = 9.0 Hz, 2H), 7.78 (d, *J* = 9.0 Hz, 2H), 7.17 (s, 1H), 7.03-7.02 (m, 3H), 6.92 (d, *J* = 9.0 Hz, 1H), 6.76 (s, 1H), 5.47 (d, *J* = 9.0 Hz, 1H, N-H), 4.32-4.28 (m, 1H), 3.96 (s, 3H), 3.92 (s, 3H), 3.67 (s, 3H), 3.14 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.93 (dd, *J* = 8.5, 14.0 Hz, 1H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.29, 149.74, 149.24, 148.84, 145.53, 141.30, 138.75, 135.33, 133.25, 128.40, 127.99, 126.45, 124.73, 123.91, 119.13, 111.51, 110.15, 57.24, 56.00, 55.97, 52.77, 39.05, 21.32. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₅N₂O₈S [M-H]⁻: 513.1337. found: 513.1335.



methyl

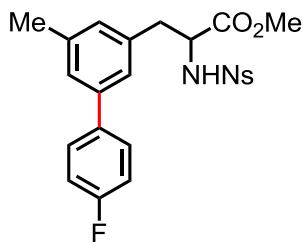
3-(4'-methoxy-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jm

¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 9.0 Hz, 2H), 7.77 (d, *J* = 9.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.17 (s, 1H), 6.97 (s, 1H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.75 (s, 1H), 5.40 (d, *J* = 8.5 Hz, 1H, N-H), 4.30-4.26 (m, 1H), 3.85 (s, 3H), 3.67 (s, 3H), 3.12 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.91 (dd, *J* = 8.0, 13.5 Hz, 1H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.30, 159.34, 149.75, 145.52, 141.10, 138.76, 135.30, 132.73, 128.26, 128.01, 127.83, 126.38, 124.55, 123.92, 114.28, 57.28, 55.35, 52.79, 39.11, 21.34. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₃N₂O₇S [M-H]⁻: 483.1231. found: 483.1234.



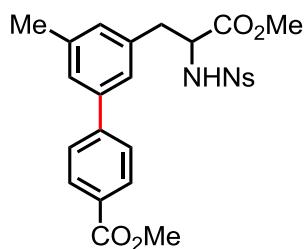
methyl 3-(4',5-dimethyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jn

¹H NMR (400 MHz, CDCl₃) δ 8.10 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 8.8 Hz, 2H), 7.20 (s, 1H), 7.00 (s, 1H), 6.77 (s, 1H), 5.45 (d, *J* = 9.2 Hz, 1H, N-H), 4.31-4.25 (m, 1H), 3.67 (s, 3H), 3.12 (dd, *J* = 4.8, 14.0 Hz, 1H), 2.91 (dd, *J* = 8.4, 14.0 Hz, 1H), 2.39 (s, 3H), 2.28 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.34, 149.72, 145.48, 141.41, 138.75, 137.41, 137.31, 135.31, 129.54, 128.58, 127.99, 126.61, 124.77, 123.91, 57.29, 52.79, 39.05, 21.32, 21.06. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₃N₂O₆S [M-H]⁻: 467.1282. found: 467.1280.



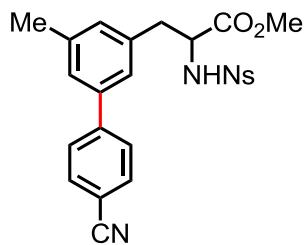
methyl 3-(4'-fluoro-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jo

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 8.5 Hz, 2H), 7.45-7.42 (m, 2H), 7.17 (s, 1H), 7.10 (t, *J* = 8.5 Hz, 2H), 7.00 (s, 1H), 6.81 (s, 1H), 5.43 (d, *J* = 9.0 Hz, 1H, N-H), 4.31-4.27 (m, 1H), 3.66 (s, 3H), 3.13 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.94 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.30 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.21, 162.55 (d, *J* = 245.2 Hz), 149.81, 145.54, 140.56, 138.92, 136.46 (d, *J* = 3.0 Hz), 135.44, 128.90, 128.43 (d, *J* = 7.8 Hz), 128.07, 126.75, 124.96, 123.95, 115.72 (d, *J* = 21.1 Hz), 57.20, 52.79, 39.12, 21.32. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₂₀FN₂O₆S [M-H]⁻: 471.1032. found: 471.1032.



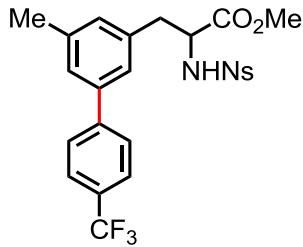
methyl 3'-(3-methoxy-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-methyl-[1,1'-biphenyl]-4-carboxylate 3jp

¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 9.0 Hz, 2H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.26 (s, 1H), 7.09 (s, 1H), 6.87 (s, 1H), 5.49 (d, *J* = 9.0 Hz, 1H, N-H), 4.33-4.28 (m, 1H), 3.94 (s, 3H), 3.65 (s, 3H), 3.15 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.97 (dd, *J* = 8.0, 13.5 Hz, 1H), 2.32 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.15, 166.87, 149.82, 145.55, 144.76, 140.31, 139.05, 135.61, 130.14, 129.79, 129.15, 128.06, 127.00, 126.78, 125.26, 123.96, 57.18, 52.79, 52.16, 39.11, 21.32. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₃N₂O₈S [M-H]⁻: 511.1181. found: 511.1185.



methyl 3-(4'-cyano-5-methyl-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jq

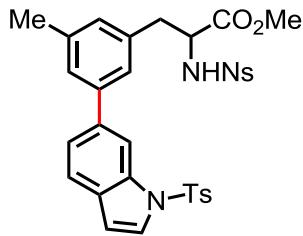
¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 7.09 (s, 1H), 6.91 (s, 1H), 5.53 (d, *J* = 9.0 Hz, 1H, N-H), 4.33-4.28 (m, 1H), 3.64 (s, 3H), 3.17 (dd, *J* = 5.0, 13.5 Hz, 1H), 2.99 (dd, *J* = 7.5, 14.0 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.07, 149.87, 145.52, 144.89, 139.49, 139.28, 135.84, 132.64, 130.31, 128.10, 127.52, 126.97, 125.30, 124.00, 118.77, 111.15, 57.07, 52.82, 39.08, 21.32. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₀N₃O₆S [M-H]: 478.1078. found: 478.1074.



methyl

3-(5-methyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)-2-(4-nitrophenylsulfonamido)propanoate 3jr

¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.23 (s, 1H), 7.09 (s, 1H), 6.88 (s, 1H), 5.60 (m, *J* = 9.0 Hz, 1H, N-H), 4.32-4.28 (m, 1H), 3.65 (s, 3H), 3.16 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.95 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.31 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.25, 149.78, 145.46, 143.84, 140.00, 139.12, 135.69, 129.81, 129.54 (q, *J* = 32.5 Hz), 128.04, 127.15, 126.94, 125.75 (q, *J* = 3.7 Hz), 125.28, 124.17 (q, *J* = 270.6 Hz), 123.97, 57.16, 52.83, 38.98, 21.29.

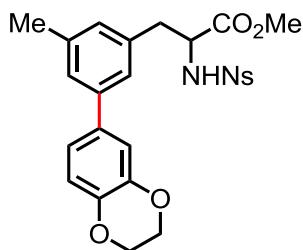


methyl

3-(3-methyl-5-(1-tosyl-1H-indol-6-yl)phenyl)-2-(4-nitrophenylsulfonamido)propanoate 3js

¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 9.0 Hz, 2H), 8.02 (d, *J* = 8.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 1.5 Hz, 1H), 7.59 (d, *J* = 3.5 Hz, 1H), 7.42 (dd, *J* = 1.5, 8.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.04 (s, 1H), 6.78 (s, 1H), 6.69 (d, *J* = 1.5 Hz, 1H), 5.39 (d, *J* = 9.0 Hz, 1H, N-H), 4.31-4.26 (m, 1H), 3.65 (s, 3H), 3.13 (dd, *J* = 5.0, 14.0 Hz, 1H), 2.93 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.34 (s, 3H), 2.28 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.22, 149.78, 145.53,

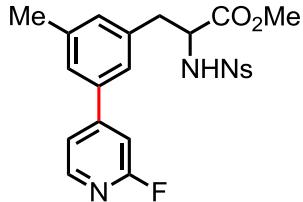
145.02, 141.61, 138.83, 135.89, 135.38, 135.28, 134.32, 131.32, 129.93, 128.65, 128.04, 127.07, 126.82, 125.31, 123.92, 123.80, 119.58, 113.81, 109.18, 57.27, 52.79, 39.18, 21.33. HRMS (ESI-TOF) m/z Calcd for $C_{32}H_{28}N_3O_8S_2$ [M-H] $^-$: 646.1323. found: 646.1323.



methyl

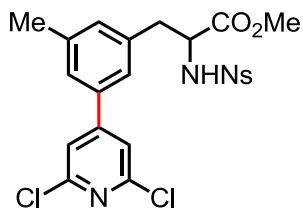
3-(3-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-5-methylphenyl)-2-(4-nitrophenylsulfonamido)propanoate 3jt

1H NMR (500 MHz, $CDCl_3$) δ 8.13 (dd, $J = 2.0, 9.0$ Hz, 2H), 7.77 (dd, $J = 2.0, 9.0$ Hz, 2H), 7.16 (s, 1H), 6.96-6.89 (m, 4H), 6.76 (s, 1H), 5.30 (d, $J = 9.0$ Hz, 1H, N-H), 4.30-4.26 (m, 5H), 3.68 (s, 3H), 3.11 (dd, $J = 5.0, 14.0$ Hz, 1H), 2.90 (dd, $J = 8.0, 14.0$ Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.27, 149.79, 145.50, 143.73, 143.38, 140.88, 138.79, 135.26, 133.74, 128.49, 128.05, 126.46, 124.52, 123.97, 119.78, 117.63, 115.53, 64.46, 64.42, 57.23, 52.82, 39.13, 21.35. HRMS (ESI-TOF) m/z Calcd for $C_{25}H_{23}N_2O_8S$ [M-H] $^-$: 511.1181. found: 511.1179.



methyl 3-(3-(2-fluoropyridin-4-yl)-5-methylphenyl)-2-(4-nitrophenylsulfonamido)propanoate 3ju

1H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, $J = 5.5$ Hz, 1H), 8.21 (d, $J = 8.5$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 2H), 7.32 (d, $J = 8.5$ Hz, 1H), 7.28 (s, 1H), 7.14 (s, 1H), 7.05 (s, 1H), 6.98 (s, 1H), 5.55 (d, $J = 9.0$ Hz, 1H, N-H), 4.34-4.30 (m, 1H), 3.63 (s, 3H), 3.18 (dd, $J = 5.0, 14.0$ Hz, 1H), 2.97 (dd, $J = 7.5, 14.0$ Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.94, 164.47 (d, $J = 236.7$ Hz), 153.46 (d, $J = 7.8$ Hz), 149.93, 148.10 (d, $J = 15.2$ Hz), 145.53, 139.49, 137.40, 136.02, 131.39, 128.14, 126.80, 125.16, 124.05, 119.33, 106.95 (d, $J = 31.2$ Hz), 56.99, 52.84, 39.10, 21.32. HRMS (ESI-TOF) m/z Calcd for $C_{22}H_{19}FN_3O_6S$ [M-H] $^-$: 472.0984. found: 472.0980.



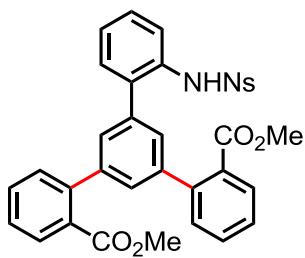
methyl

**3-(3-(2,6-dichloropyridin-4-yl)-5-methylphenyl)-2-(4-nitrophenylsulfonamido)propanoate
3jv**

¹H NMR (500 MHz, CDCl₃) δ 8.24 (d, *J* = 8.5 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.39 (s, 2H), 7.26 (s, 1H), 7.11 (s, 1H), 7.01 (s, 1H), 5.42 (br, 1H, N-H), 4.32-4.30 (m, 1H), 3.62 (s, 3H), 3.18 (dd, *J* = 5.0, 14.0 Hz, 1H), 3.02 (dd, *J* = 7.5, 14.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.84, 153.34, 151.10, 149.99, 145.45, 139.73, 136.19, 136.14, 131.93, 128.18, 126.86, 125.21, 124.11, 120.63, 56.88, 52.87, 39.10, 21.31. HRMS (ESI-TOF) *m/z* Calcd for C₂₂H₁₈Cl₂N₃O₆S [M-H]⁻: 522.0299. found: 522.0305.

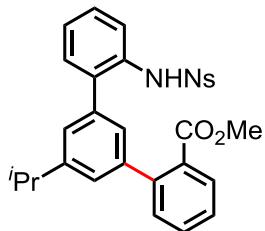
3.4 General Procedure for *meta*-C(sp²)-Harylation of 2-Aryl Anilines (Tables 5).

The starting material **4** (0.10mmol), Pd(OAc)₂ (0.01mmol, 2.2 mg), and AgOAc (0.30mmol, 50.0 mg) were weighed in air and placed in a sealed tube (10 mL) with a magnetic stir bar. To the reaction mixture, 4-acetylpyridine (0.02 mmol, 2.2 μL), norbornene (0.15 mmol, 14.0 mg), aryl iodide **2** (0.3mmol), and TBME (1.0 mL) were added. The reaction mixture was heated to 80 °C for 24 hours under vigorous stirring.Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and the resulting residue purified by preparative TLC using an eluent of hexanes/ethyl acetate (2/1 to 4/1) to give the desired products **5**.



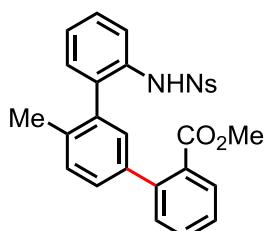
**dimethyl 5'-(2-(4-nitrophenylsulfonamido)phenyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate
5a**

¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.48-7.45 (m, 3H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.25-7.23 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.60 (s, 2H), 3.82 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.48, 149.62, 144.64, 141.51, 141.44, 135.89, 135.36, 133.31, 131.83, 130.42, 130.39, 129.95, 129.92, 128.91, 128.33, 128.07, 127.88, 127.83, 126.11, 124.53, 123.71, 52.44. HRMS (ESI-TOF) *m/z* Calcd for C₃₄H₂₅N₂O₈S [M-H]⁻: 621.1337. found: 621.1340.



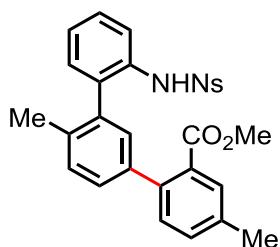
methyl 5'-isopropyl-2''-(4-nitrophenylsulfonamido)-[1,1':3',1''-terphenyl]-2-carboxylate 5b

¹H NMR (500 MHz, CDCl₃) δ 7.95-7.92 (m, 3H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.28-7.15 (m, 5H), 6.66 (s, 1H), 6.41 (s, 1H), 3.83 (s, 3H), 2.83-2.80 (m, 1H), 1.23 (d, *J* = 6.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 168.43, 149.94, 149.81, 144.78, 142.30, 141.36, 136.17, 135.27, 133.00, 131.76, 130.58, 130.28, 130.19, 129.82, 128.74, 128.29, 127.71, 126.73, 126.08, 125.96, 125.78, 123.79, 123.56, 52.50, 33.90, 23.85. HRMS (ESI-TOF) *m/z* Calcd for C₂₉H₂₅N₂O₆S [M-H]⁻: 529.1439. found: 529.1441.



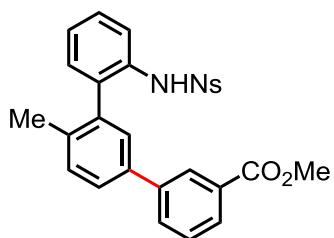
methyl 4'-methyl-2''-(4-nitrophenylsulfonamido)-[1,1':3',1''-terphenyl]-2-carboxylate 5c

¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.87-7.84 (m, 3H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.26-7.20 (m, 4H), 7.09 (d, *J* = 7.5 Hz, 1H), 6.92 (s, 1H), 6.31 (s, 1H), 3.83 (s, 3H), 1.75 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.61, 149.85, 144.98, 141.78, 138.83, 135.48, 135.21, 133.73, 133.18, 131.79, 130.59, 130.44, 130.28, 130.12, 129.86, 129.76, 128.79, 128.42, 128.32, 127.68, 125.70, 123.81, 123.40, 103.42, 52.49, 19.31. HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₂₁N₂O₆S [M-H]⁻: 501.1126. found: 501.1126.



methyl 4,4'-dimethyl-2''-(4-nitrophenylsulfonamido)-[1,1':3',1''-terphenyl]-2-carboxylate 5d

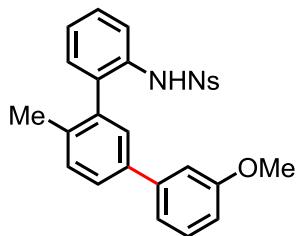
¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.70 (s, 1H), 7.64 (d, *J* = 9.0 Hz, 2H), 7.40 (dt, *J* = 1.5, 7.5 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.21 (s, 2H), 7.12-7.08 (m, 2H), 6.82 (br, 1H), 6.18 (s, 1H), 3.80 (s, 3H), 2.48 (s, 3H), 1.77 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 168.87, 149.86, 144.88, 138.78, 137.81, 135.26, 135.21, 133.82, 133.21, 132.47, 130.69, 130.54, 130.27, 130.09, 129.82, 129.69, 128.79, 128.47, 128.30, 125.72, 123.81, 123.33, 52.40, 20.94, 19.30. HRMS (ESI-TOF) *m/z* Calcd for C₂₈H₂₃N₂O₆S [M-H]⁻: 515.1282. found: 515.1279.



methyl 4'-methyl-2''-(4-nitrophenylsulfonamido)-[1,1':3',1''-terphenyl]-3-carboxylate 5e

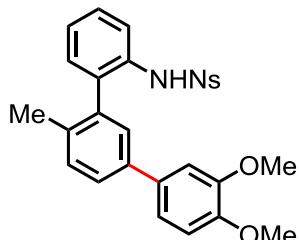
¹H NMR (500 MHz, CDCl₃) δ 8.07-8.05 (m, 2H), 7.92 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.65 (d, *J* = 9.0 Hz, 2H), 7.60 (d, *J* = 7.5 Hz, 1H), 7.56 (dd, *J* = 2.0, 8.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.43 (dt, *J* = 2.0, 7.5 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.13 (dd, *J* = 1.0, 7.5 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 6.30 (s, 1H), 3.97 (s, 3H), 1.96 (s, 3H); ¹³C NMR (125

MHz, CDCl₃) ¹³C NMR (126 MHz, DMSO) δ 166.76, 149.95, 144.47, 140.03, 138.22, 136.37, 135.99, 133.09, 133.02, 131.48, 130.97, 130.90, 130.25, 129.13, 129.08, 128.81, 128.22, 127.81, 127.67, 127.47, 125.80, 124.02, 121.30, 52.32, 19.21. HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₂₁N₂O₆S [M-H]⁻: 501.1126. found: 501.1128.



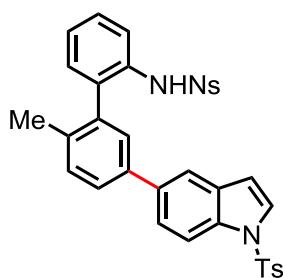
N-(3''-methoxy-6'-methyl-[1,1':3',1''-terphenyl]-2-yl)-4-nitrobenzenesulfonamide 5f

¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.50 (dd, *J* = 1.5, 8.0 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.34-7.31 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 6.5 Hz, 1H), 6.95-6.91 (m, 2H), 6.88 (s, 1H), 6.38 (s, 1H), 3.87 (s, 3H), 1.96 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 160.11, 150.01, 144.39, 141.23, 139.15, 136.07, 135.46, 133.38, 133.05, 131.28, 130.15, 130.04, 128.98, 128.15, 127.88, 127.43, 125.79, 124.03, 121.45, 118.99, 113.05, 112.37, 55.29, 19.17. HRMS (ESI-TOF) *m/z* Calcd for C₂₆H₂₁N₂O₅S [M-H]⁻: 473.1177. found: 473.1189.



N-(3'',4''-dimethoxy-6'-methyl-[1,1':3',1''-terphenyl]-2-yl)-4-nitrobenzenesulfonamide 5g

¹H NMR (400 MHz, CDCl₃) δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.48 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 6.97 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 1H), 6.84 (dd, *J* = 1.6, 8.0 Hz, 1H), 6.39 (s, 1H), 6.30 (s, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 1.92 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 149.99, 149.37, 149.01, 144.42, 139.20, 136.02, 134.75, 133.40, 133.06, 132.64, 131.25, 130.18, 128.94, 128.18, 127.49, 127.13, 125.73, 124.02, 121.34, 118.95, 111.56, 109.96, 56.04, 56.00, 19.12. HRMS (ESI-TOF) *m/z* Calcd for C₂₇H₂₃N₂O₆S [M-H]⁻: 503.1282. found: 503.1285.

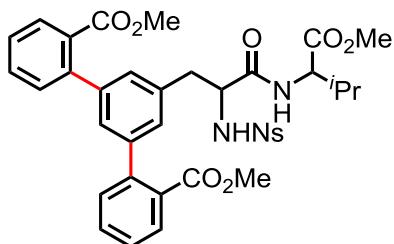


N-(2'-methyl-5'-(1-tosyl-1H-indol-6-yl)-[1,1'-biphenyl]-2-yl)-4-nitrobenzenesulfonamide 5h

¹H NMR (500 MHz, CDCl₃) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.86-7.83 (m, 4H), 7.78 (d, *J* = 8.5 Hz, 1H), 7.63-7.61 (m, 3H), 7.52-7.50 (m, 2H), 7.40-7.35 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.26-7.23 (m, 4H), 7.11 (dd, *J* = 1.5, 7.5 Hz, 1H), 6.67 (d, *J* = 3.5 Hz, 1H), 6.54 (s, 1H), 6.35 (s, 1H), 2.32 (s, 3H), 1.92 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 149.95, 145.00, 144.42, 139.43, 136.13, 135.27, 135.22, 135.02, 134.38, 133.27, 133.01, 131.40, 131.35, 130.26, 129.90, 128.94, 128.22, 127.88, 127.66, 127.29, 126.92, 125.71, 123.91, 123.50, 121.14, 119.26, 113.93, 108.94, 21.53, 19.11. HRMS (ESI-TOF) *m/z* Calcd for C₃₄H₂₆N₃O₆S₂ [M-H]⁻: 636.1269. found: 636.1279.

3.5 General Procedure for *meta*-C(sp²)-H Arylation of β -Aryl Dipeptides 6 (Tables 5).

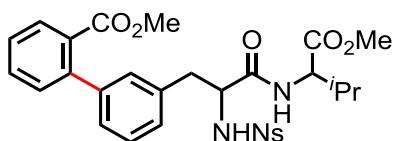
The starting material **6** (0.10 mmol), Pd(OAc)₂ (0.01 mmol, 2.2 mg), and AgOAc (0.30 mmol, 50.0 mg) were weighed in air and placed in a sealed tube (10 mL) with a magnetic stir bar. To the reaction mixture, 4-acetylpyridine (0.02 mmol, 2.2 μ L), norbornene (0.02 mmol, 1.9 mg), aryl iodide **2** (0.3mmol), and TBME (1.0 mL) were added. The reaction mixture was heated to 80 °C for 24 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and the resulting residue purified by preparative TLC using an eluent of hexanes/ethyl acetate (2/1 to 4/1) to give the desired products **7**.



dimethyl

5'-(3-((1-methoxy-3-methyl-1-oxobutan-2-yl)amino)-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 7a(di)

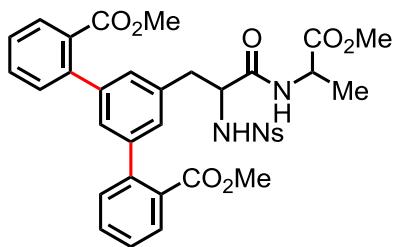
¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.94 (d, *J* = 9.0 Hz, 2H), 7.90 (d, *J* = 7.0 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.0 Hz, 2H), 7.25 (d, *J* = 7.5 Hz, 2H), 7.18 (s, 1H), 6.99 (d, *J* = 1.0 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.91 (d, *J* = 6.0 Hz, 1H, N-H), 4.34-4.32 (m, 1H), 4.06-4.02 (m, 1H), 3.79 (s, 6H), 3.64 (s, 3H), 3.13-3.04 (m, 2H), 2.04-2.00 (m, 1H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.78, 169.69, 168.53, 149.94, 145.00, 141.84, 141.43, 133.97, 131.66, 130.65, 130.35, 129.96, 128.63, 128.57, 127.62, 124.19, 58.75, 57.41, 52.31, 52.03, 39.24, 31.05, 18.71, 17.74. HRMS (ESI-TOF) *m/z* Calcd for C₃₇H₃₆N₃O₁₁S [M-H]⁻: 730.2076. found: 730.2075.



methyl

3'-(3-((1-methoxy-3-methyl-1-oxobutan-2-yl)amino)-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 7a(mono)

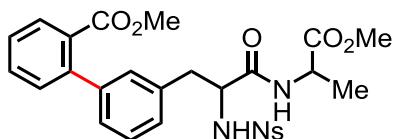
¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 9.0 Hz, 2H), 7.96 (d, *J* = 7.5 Hz, 1H), 8.87 (d, *J* = 8.5 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.13-7.09 (m, 2H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 5.68 (d, *J* = 6.5 Hz, N-H), 4.37-4.35 (m, 1H), 3.99-3.94 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.12 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.95 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.08-2.02 (m, 1H), 0.83 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.83, 169.64, 168.31, 149.96, 144.63, 142.45, 141.51, 134.36, 131.92, 130.85, 130.56, 130.36, 129.45, 128.82, 128.57, 127.60, 127.50, 127.33, 124.20, 58.86, 57.37, 52.41, 52.13, 39.24, 31.14, 18.77, 17.61. HRMS (ESI-TOF) *m/z* Calcd for C₂₉H₃₀N₃O₉S [M-H]⁻: 596.1708. found: 596.1710.



dimethyl

5'-(3-((1-methoxy-1-oxopropan-2-yl)amino)-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 7b(di)

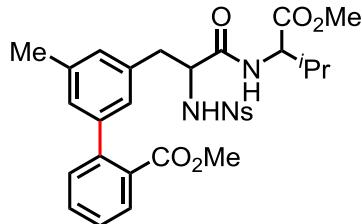
^1H NMR (500 MHz, CDCl_3) δ 8.20 (d, $J = 9.0$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 2H), 7.89 (dd, $J = 1.5, 8.0$ Hz, 2H), 7.52 (dt, $J = 1.5, 7.5$ Hz, 2H), 7.42 (dt, $J = 1.5, 7.5$ Hz, 2H), 7.28 (dd, $J = 1.5, 7.5$ Hz, 2H), 7.11 (s, 1H), 7.00 (d, $J = 1.5$ Hz, 2H), 6.75 (d, $J = 7.5$ Hz, 1H, N-H), 6.10 (d, $J = 7.5$ Hz, 1H, N-H), 4.35-4.32 (m, 1H), 4.17-4.14 (m, 1H), 3.75 (s, 6H), 3.60 (s, 3H), 3.25 (dd, $J = 5.0, 14.0$ Hz, 1H), 2.98 (dd, $J = 7.0, 14.0$ Hz, 1H), 1.15 (d, $J = 7.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.40, 169.17, 168.50, 149.98, 145.68, 142.05, 141.44, 133.97, 131.65, 130.75, 130.24, 129.91, 128.72, 128.46, 127.57, 124.24, 58.04, 52.37, 52.25, 48.33, 38.88, 17.81. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{35}\text{H}_{32}\text{N}_3\text{O}_{11}\text{S} [\text{M}-\text{H}]^-$: 702.1763. found: 702.1769.



methyl

3'-(3-((1-methoxy-1-oxopropan-2-yl)amino)-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxylate 7b(mono)

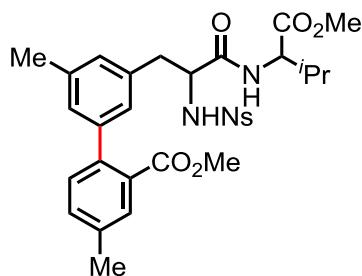
^1H NMR (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.5$ Hz, 2H), 7.93-7.90 (m, 3H), 7.55 (dt, $J = 1.5, 7.5$ Hz, 1H), 7.44 (dt, $J = 1.5, 8.0$ Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 5.0$ Hz, 2H), 7.06 (s, 1H), 6.95-6.93 (m, 1H), 6.72 (d, $J = 7.0$ Hz, 1H, N-H), 5.91 (d, $J = 7.5$ Hz, 1H, N-H), 4.41-4.38 (m, 1H), 4.08-4.03 (m, 1H), 3.78 (s, 3H), 3.68 (s, 3H), 3.05 (d, $J = 6.5$ Hz, 2H), 1.24 (d, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 172.45, 169.29, 168.39, 149.96, 145.27, 141.51, 134.41, 131.79, 130.79, 130.35, 130.05, 129.59, 128.60, 128.44, 127.93, 127.54, 127.31, 124.22, 58.24, 52.47, 52.30, 48.32, 38.94, 17.97. HRMS (ESI-TOF) m/z Calcd for $\text{C}_{27}\text{H}_{26}\text{N}_3\text{O}_9\text{S} [\text{M}-\text{H}]^-$: 568.1395. found: 568.1395.



methyl

3'-(3-((1-methoxy-3-methyl-1-oxobutan-2-yl)amino)-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-5'-methyl-[1,1'-biphenyl]-2-carboxylate 7c

¹H NMR (500 MHz, CDCl₃) δ 8.16 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.00 (s, 1H), 6.90 (s, 1H), 6.81 (d, *J* = 8.5 Hz, 1H), 6.69 (s, 1H), 5.79 (d, *J* = 6.5 Hz, N-H), 4.39-4.36 (m, 1H), 3.95-3.91 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.07 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.89 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.16 (s, 3H), 2.08-2.04 (m, 1H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.80, 169.74, 168.38, 149.87, 144.61, 141.43, 138.61, 134.36, 131.80, 130.75, 130.43, 129.54, 128.59, 128.29, 128.10, 127.45, 127.44, 124.02, 59.01, 57.33, 52.37, 52.09, 39.16, 31.13, 21.06, 18.66, 17.49. HRMS (ESI-TOF) *m/z* Calcd for C₃₀H₃₂N₃O₉S [M-H]⁻: 610.1865. found: 610.1863.



methyl

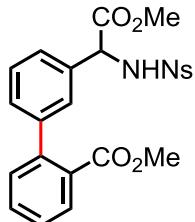
3'-(3-((1-methoxy-3-methyl-1-oxobutan-2-yl)amino)-2-(4-nitrophenylsulfonamido)-3-oxopropyl)-4,5'-dimethyl-[1,1'-biphenyl]-2-carboxylate 7d

¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.73 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.97 (s, 1H), 6.86 (s, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 6.66 (s, 1H), 5.78 (d, *J* = 6.0 Hz, N-H), 4.39-4.37 (m, 1H), 3.94-3.90 (m, 1H), 3.85 (s, 3H), 3.70 (s, 3H), 3.07 (dd, *J* = 7.0, 14.0 Hz, 1H), 2.88 (dd, *J* = 8.0, 14.0 Hz, 1H), 2.44 (s, 3H), 2.15 (s, 3H), 2.09-2.03 (m, 1H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 171.84, 169.78, 168.57, 149.86, 144.56, 141.39, 139.58, 138.55, 137.41, 134.32, 132.52, 130.90, 130.63, 129.36, 128.59, 128.14, 128.10, 127.42, 124.03, 58.99, 57.32, 52.31, 52.09, 39.11, 31.13, 21.05, 20.92, 18.67, 17.49. HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₃₄N₃O₉S [M-H]⁻: 624.2021.

found: 624.2022.

3.6 General Procedure for *meta*-C(sp²)–H Arylation of Benzylamine **8** (Scheme 2).

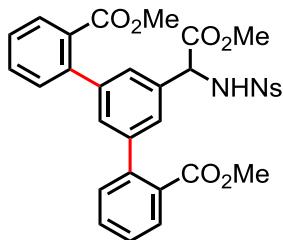
Benzylamine **8** (0.10 mmol), Pd(OAc)₂ (0.01 mmol, 2.2 mg), and AgOAc (0.30 mmol, 50.0 mg) were weighed in air and placed in a sealed tube (10 mL) with a magnetic stir bar. To the reaction mixture, pyridine (0.02 mmol, 1.6 µL), norbornene (0.15 mmol, 14.0 mg), aryl iodide **2** (0.3 mmol), and TBME (1.0 mL) were added. The reaction mixture was heated to 80 °C for 24 hours under vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and filtered through a pad of celite. The filtrate was concentrated *in vacuo*, and the resulting residue purified by preparative TLC using an eluent of hexanes/ethyl acetate(2/1 to 4/1) to give the desired products **9**.



methyl

**3'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-[1,1'-biphenyl]-2-carboxylate
9a(mono)**

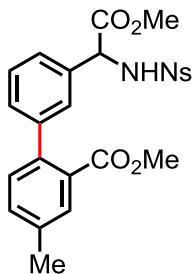
¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 3H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.21-7.16 (m, 3H), 7.13-7.09 (m, 2H), 6.24 (d, *J* = 6.8 Hz, 1H, N-H), 5.24 (d, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 3.66 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.02, 168.40, 149.72, 146.00, 141.97, 141.21, 134.29, 131.38, 130.47, 129.92, 128.84, 128.59, 128.25, 127.60, 125.93, 123.94, 59.46, 53.29, 52.02. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₁₉N₂O₈S [M-H]⁻: 483.0868. found: 483.0867.



dimethyl

5'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 9a(di)

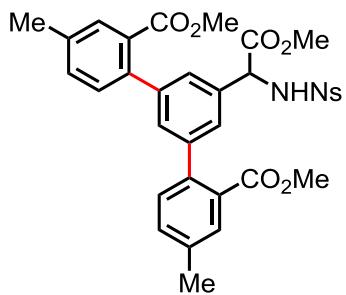
¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.8 Hz, 2H), 7.82-7.79 (m, 4H), 7.49 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.21 (s, 1H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.04 (s, 2H), 6.27 (d, *J* = 6.8 Hz, 1H, N-H), 5.27 (d, *J* = 6.4 Hz, 1H), 3.69 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 169.94, 168.45, 149.73, 145.98, 141.78, 140.96, 133.99, 131.35, 130.56, 130.46, 129.92, 128.86, 128.34, 127.67, 126.34, 123.98, 59.41, 53.31, 52.02. HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₂₅N₂O₁₀S [M-H]⁻: 617.1235. found: 617.1236.



methyl

3'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-4-methyl-[1,1'-biphenyl]-2-carboxylate 9b(mono)

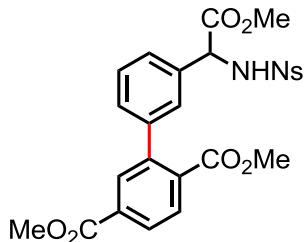
¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 8.8 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.63 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.19 (d, *J* = 5.0 Hz, 2H), 7.08-7.05 (m, 3H), 6.03 (d, *J* = 7.0 Hz, 1H, N-H), 5.22 (d, *J* = 7.0 Hz, 1H), 3.67 (s, 6H), 2.42 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.05, 168.60, 149.77, 146.06, 142.01, 138.38, 137.69, 134.20, 132.12, 130.47, 130.41, 130.29, 128.93, 128.59, 128.26, 127.67, 125.78, 123.97, 59.48, 53.35, 52.00, 20.92. HRMS (ESI-TOF) *m/z* Calcd for C₂₄H₂₁N₂O₈S [M-H]⁻: 497.1024. found: 497.1030.



dimethyl

5'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-4,4''-dimethyl-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 9b(di)

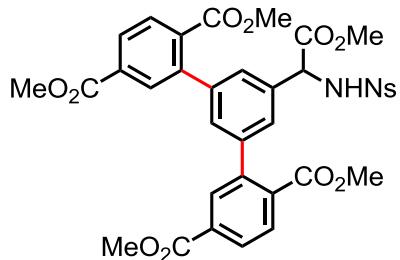
¹H NMR (500 MHz, CDCl₃) δ 8.11 (d, *J* = 8.5 Hz, 2H), 7.80 (d, *J* = 9.0 Hz, 2H), 7.60 (s, 2H), 7.29 (d, *J* = 9.0 Hz, 1H), 7.16 (s, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.98 (s, 2H), 6.23 (d, *J* = 5.0 Hz, 1H, N-H), 5.26 (s, 1H), 3.69 (s, 3H), 3.68 (s, 6H), 2.41 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 169.99, 168.70, 149.71, 146.03, 141.69, 138.13, 137.65, 133.83, 132.04, 130.39, 130.35, 128.89, 128.32, 126.18, 123.97, 59.45, 53.27, 51.96, 20.88. HRMS (ESI-TOF) *m/z* Calcd for C₃₃H₂₉N₂O₁₀S [M-H]⁻: 645.1548. found: 645.1554.



dimethyl

3'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-[1,1'-biphenyl]-2,5-dicarboxylate 9c(mono)

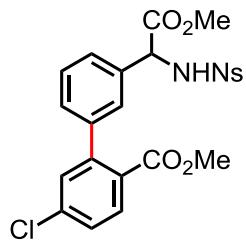
¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 9.0 Hz, 2H), 8.06 (dd, *J* = 1.8, 8.5 Hz, 1H), 7.87 -7.81 (m, 4H), 7.25-7.23 (m, 2H), 7.14-7.13 (m, 2H), 6.05 (br, 1H, N-H), 5.24 (s, 1H), 3.97 (s, 3H), 3.72 (s, 3H), 3.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.96, 167.82, 165.91, 149.79, 145.99, 141.27, 140.98, 134.65, 134.50, 132.58, 131.39, 129.94, 128.90, 128.79, 128.55, 128.26, 128.23, 127.53, 126.41, 124.00, 59.41, 53.39, 52.56, 52.35. HRMS (ESI-TOF) *m/z* Calcd for C₂₅H₂₁N₂O₁₀S [M-H]⁻: 541.0922 found: 541.0935.



tetramethyl

5'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-[1,1':3',1"-terphenyl]-2,2",5,5"-tetracarboxylate 9c(di)

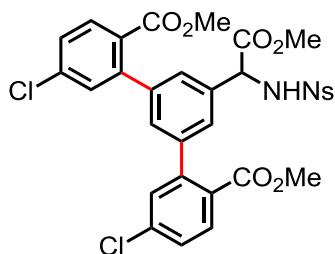
¹H NMR (500 MHz, CDCl₃) δ 8.18 (d, *J* = 9.0 Hz, 2H), 8.07 (dd, *J* = 1.8, 8.5 Hz, 2H), 7.87 - 7.83 (m, 6H), 7.23 (s, 1H), 7.11 (s, 2H), 6.05 (br, 1H, N-H), 5.28 (s, 1H), 3.97 (s, 6H), 3.76 (s, 6H), 3.72 (s, 3H), 2.63 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 169.85, 167.81, 165.83, 149.86, 145.92, 141.01, 140.85, 134.70, 134.59, 132.65, 131.33, 130.02, 128.97, 128.74, 128.33, 126.71, 124.11, 59.31, 53.49, 52.57, 52.42. HRMS (ESI-TOF) *m/z* Calcd for C₃₅H₂₉N₂O₁₄S [M-H]⁻: 733.1345. found: 733.1344.



methyl

5-chloro-3'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-[1,1'-biphenyl]-2-carboxylate 9d (mono)

¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, *J* = 9.0 Hz, 2H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.40 (dd, *J* = 2.0, 8.5 Hz, 1H), 7.24-7.17 (m, 3H), 7.13-7.11 (m, 2H), 6.02 (d, *J* = 6.5 Hz, 1H, N-H), 5.23 (d, *J* = 6.5 Hz, 1H), 3.70 (s, 3H), 3.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.98, 167.30, 149.87, 145.99, 143.29, 140.87, 137.61, 134.61, 131.55, 130.67, 128.90, 128.70, 128.31, 127.79, 127.52, 126.35, 124.08, 59.38, 53.42, 52.19. HRMS (ESI-TOF) *m/z* Calcd for C₂₃H₁₈ClN₂O₈S [M-H]⁻: 517.0478. found: 517.0480.



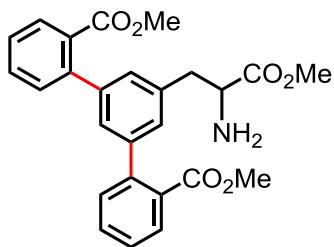
dimethyl

5,5''-dichloro-5'-(2-methoxy-1-(4-nitrophenylsulfonamido)-2-oxoethyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 9d(di)

¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.40 (dd, *J* = 2.0, 8.5 Hz, 2H), 7.16-7.10 (m, 3H), 7.09 (d, *J* = 1.2, 2H), 6.08 (d, *J* = 6.5 Hz, 1H, N-H), 5.27 (d, *J* = 6.5 Hz, 1H), 3.71 (s, 6H), 3.70 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 169.88, 167.27, 149.92, 145.94, 142.85, 140.74, 137.68, 134.58, 131.62, 130.65, 128.93, 128.71, 128.40, 127.95, 126.62, 124.19, 59.25, 53.48, 52.23. HRMS (ESI-TOF) *m/z* Calcd for C₃₁H₂₃Cl₂N₂O₁₀S [M-H]⁻: 685.0456. found: 685.685.0452.

3.7 Procedure for deprotection (Scheme 4).

4-Methoxybenzenethiol (PMP-SH, 4.0 mmol, 4.0 equiv) and potassium carbonate (4.0 mmol, 4.0 equiv) were added to a solution of diarylation product **3aa** (1.0 mmol, 1.0 equiv) in MeCN (8.0 mL) and DMSO (0.3 mL). After being stirred at room temperature for 12 h the reaction mixture was diluted with EtOAc, washed with H₂O and brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under vacuum. The residue was purified by column chromatography on silica gel (eluent: EtOAc/hexanes = 1: 1) to give **10** in 94% yield.



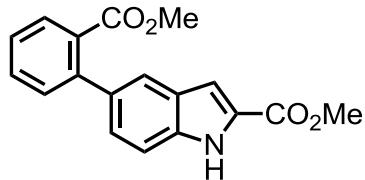
dimethyl 5'-(2-amino-3-methoxy-3-oxopropyl)-[1,1':3',1''-terphenyl]-2,2''-dicarboxylate 10

¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 4H), 7.16 (s, 1H), 7.13 (s, 2H), 3.79-3.76 (m, 1H), 3.71 (s, 3H), 3.68 (s, 6H), 3.17 (dd, *J* = 5.2, 13.6 Hz, 1H), 2.92 (dd, *J* = 8.0, 13.6 Hz, 1H), 1.64 (br, 2H, NH₂); ¹³C NMR (100 MHz, CDCl₃) δ

175.04, 168.75, 141.88, 141.33, 136.54, 131.10, 130.75, 130.55, 129.68, 128.17, 127.15, 126.75, 55.73, 51.85, 51.84, 40.95. HRMS (ESI-TOF) m/z Calcd for $C_{26}H_{26}NO_6 [M+H]^+$: 448.1755. found: 448.1758.

3.8 Procedure for Application (Scheme 5).

The starting material **3da** (1.0 mmol, 57.6 mg), CuI (0.01 mmol, 1.9 mg), CsOAc (2.0 mmol, 38.4 mg), and DMSO (2 mL) were added in a sealed tube (10 mL) under N_2 with a magnetic stir bar. The reaction mixture was heated to 90 °C for 36 hours with vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, diluted with ethyl acetate and saturated NH_4Cl , the organic layer was washed with brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using an eluent of hexanes/ethyl acetate (8/1) to give the desired product **11**.



methyl 5-(2-(methoxycarbonyl)phenyl)-1H-indole-2-carboxylate 11

1H NMR (500 MHz, $CDCl_3$) δ 9.02 (br, 1H, NH), 7.82 (dd, $J = 1.0, 9.0$ Hz, 1H), 7.64 (s, 1H), 7.53 (dt, $J = 1.5, 7.5$ Hz, 1H), 7.44-7.38 (m, 3H), 7.28 (dd, $J = 1.5, 8.5$ Hz, 1H), 7.24 (d, $J = 1.0$ Hz, 1H), 3.95 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.40, 162.33, 142.83, 136.14, 134.24, 131.17, 131.09, 129.71, 127.63, 127.47, 126.83, 126.66, 121.87, 111.38, 109.06, 52.03, 51.95. HRMS (ESI-TOF) m/z Calcd for $C_{18}H_{16}NO_4 [M+H]^+$: 310.1074. found: 310.1070.

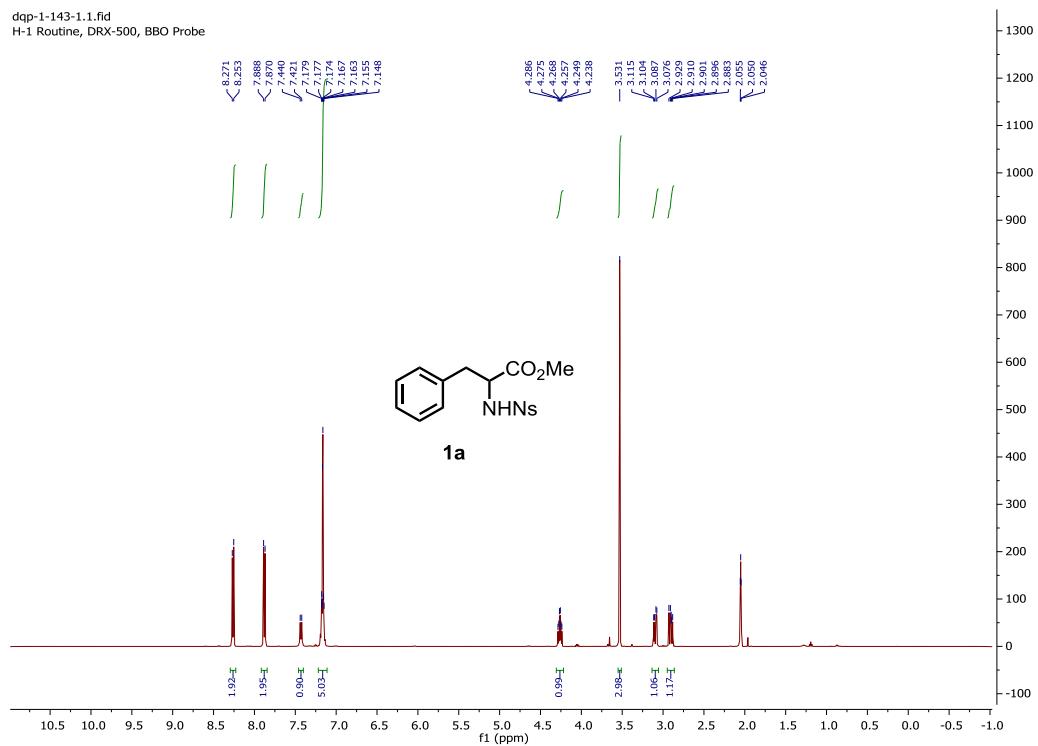
4. References:

- (1) Di Gioia, M. L.; Leggio, A.; Le Pera, A.; Liguori, A.; Napoli, A.; Siciliano, C.; Sindona,

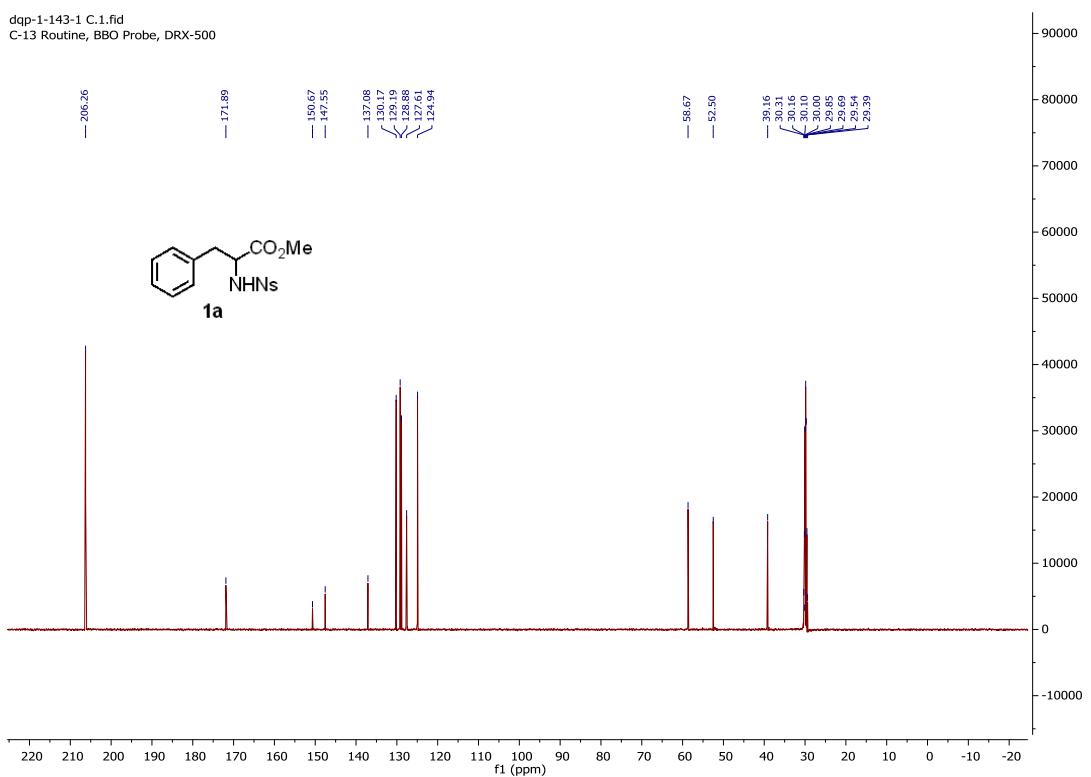
G. J. Org. Chem. 2003, 68, 7416.

- (2) Yang, X.; Zhai, H.; Li, Z. Org. Lett. 2008, 10, 2457.
- (3) Norsikian, S.; Beretta, M.; Cannillo, A.; Martin, A.; R., P.; Beau, J.-M. Chem. Comm. 2015, 51, 9991.
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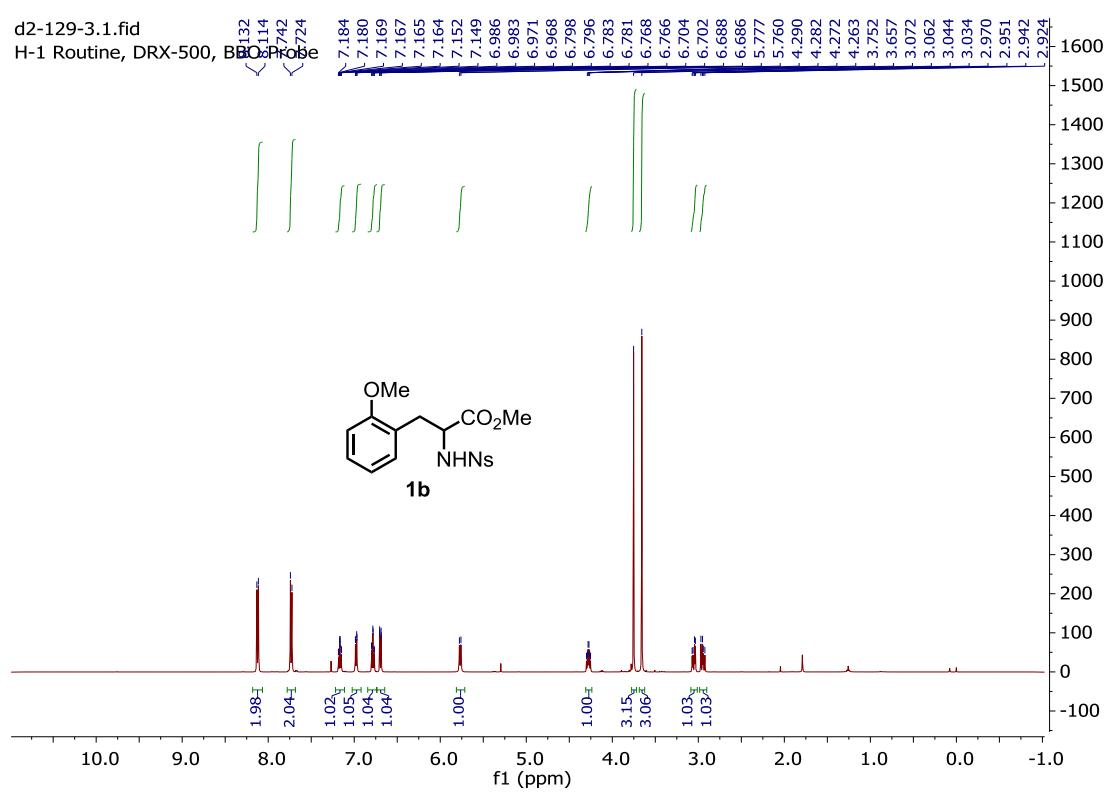
5. ^1H and ^{13}C NMR Spectra

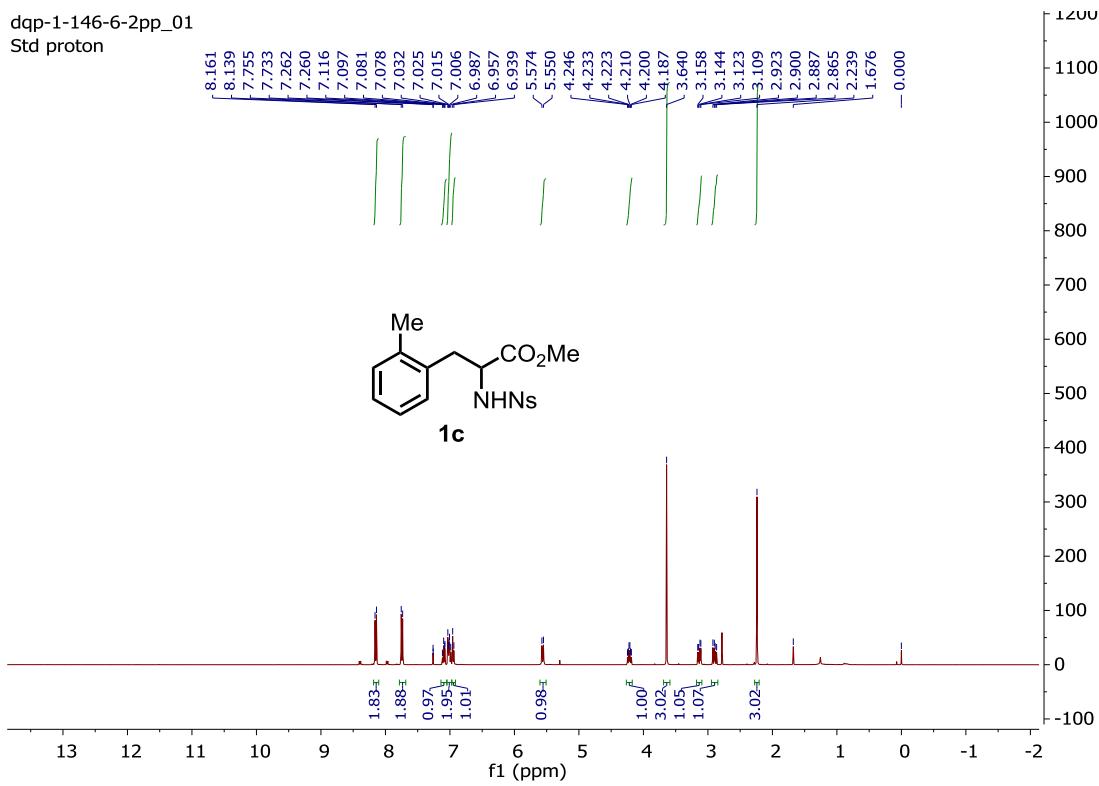
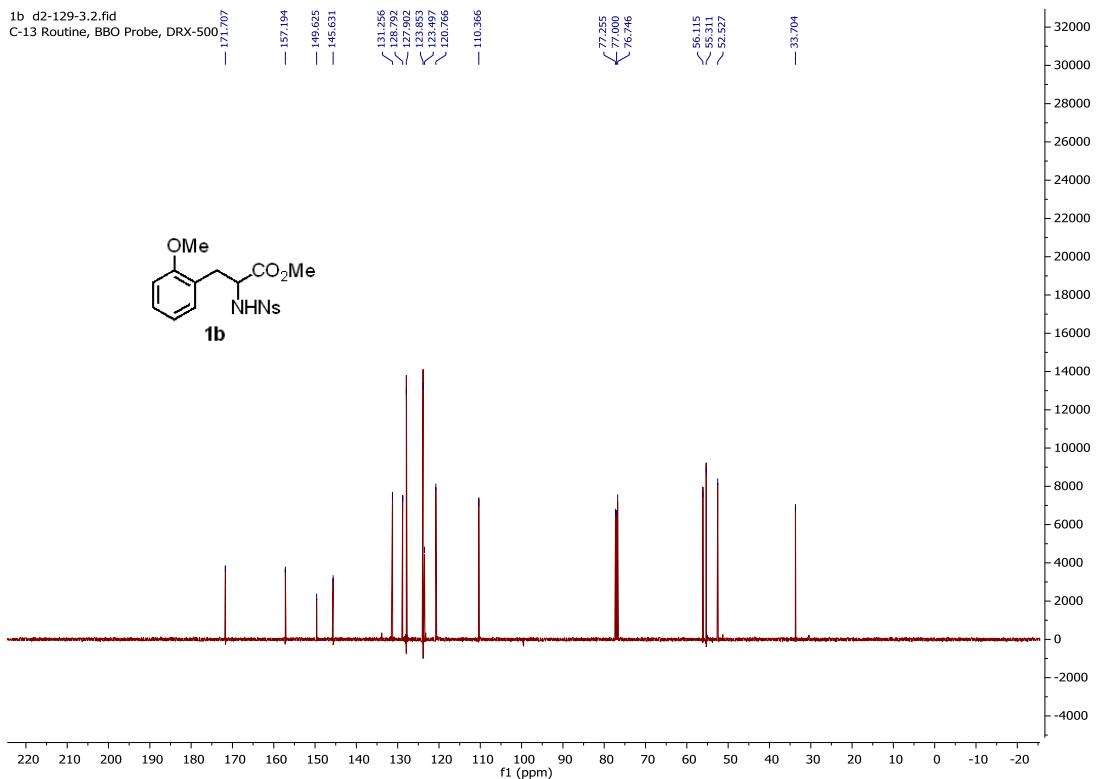


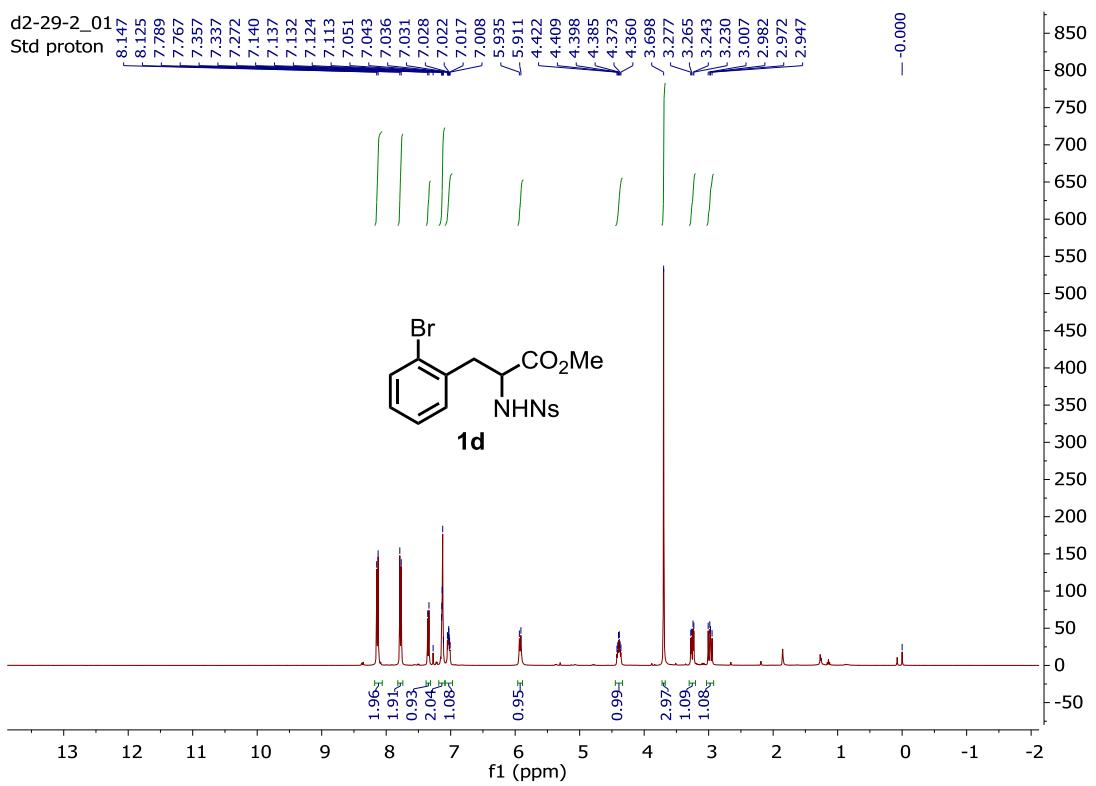
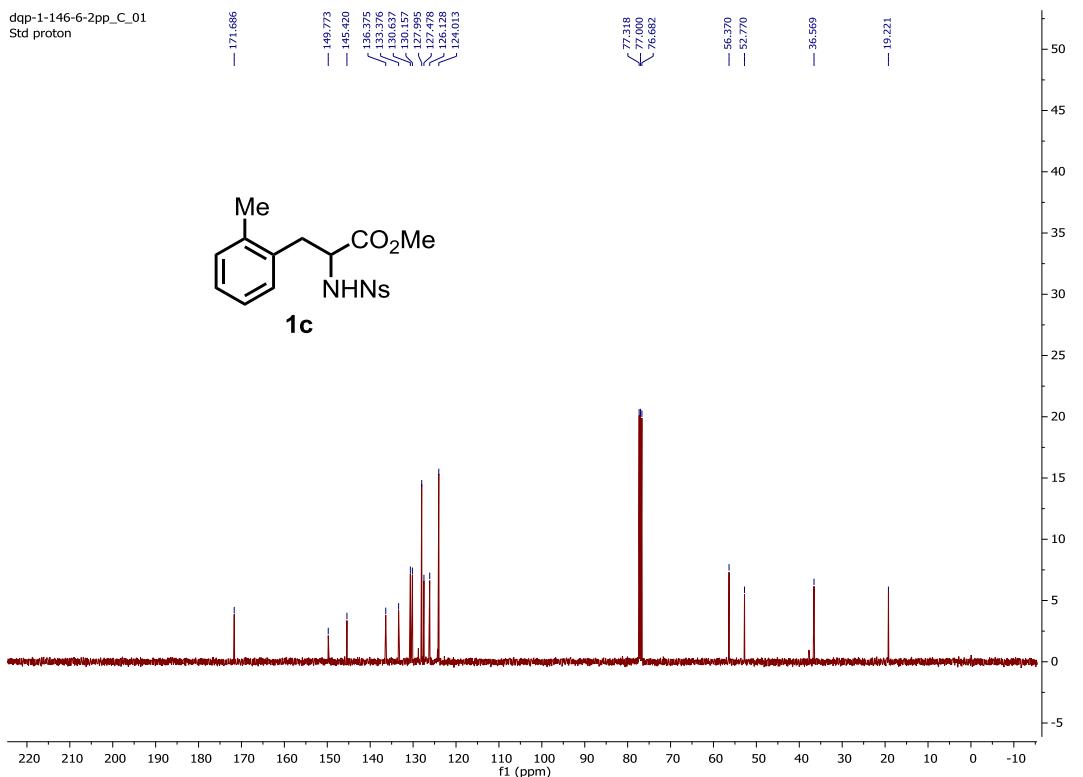
dqp-1-143-1.C.1.fid
C-13 Routine, BBO Probe, DRX-500



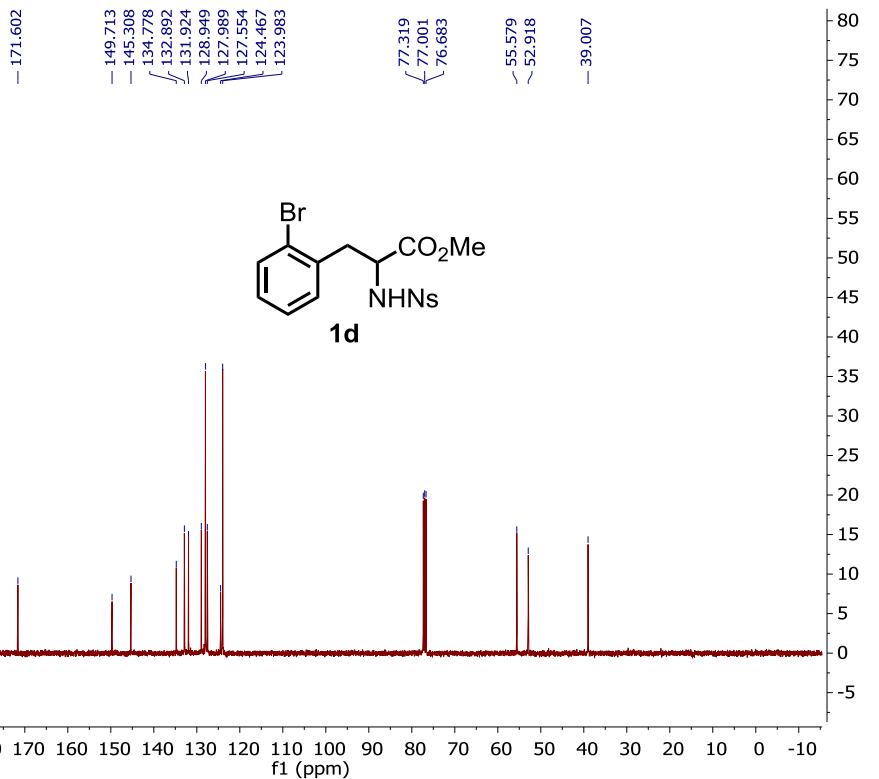
d2-129-3.1.fid
H-1 Routine, DRX-500, BBO Probe



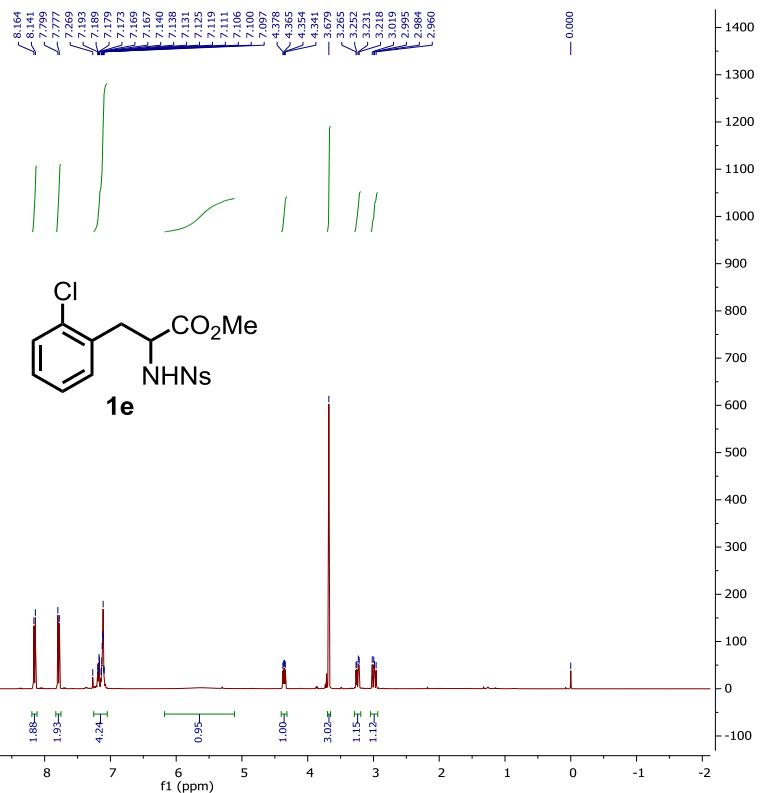




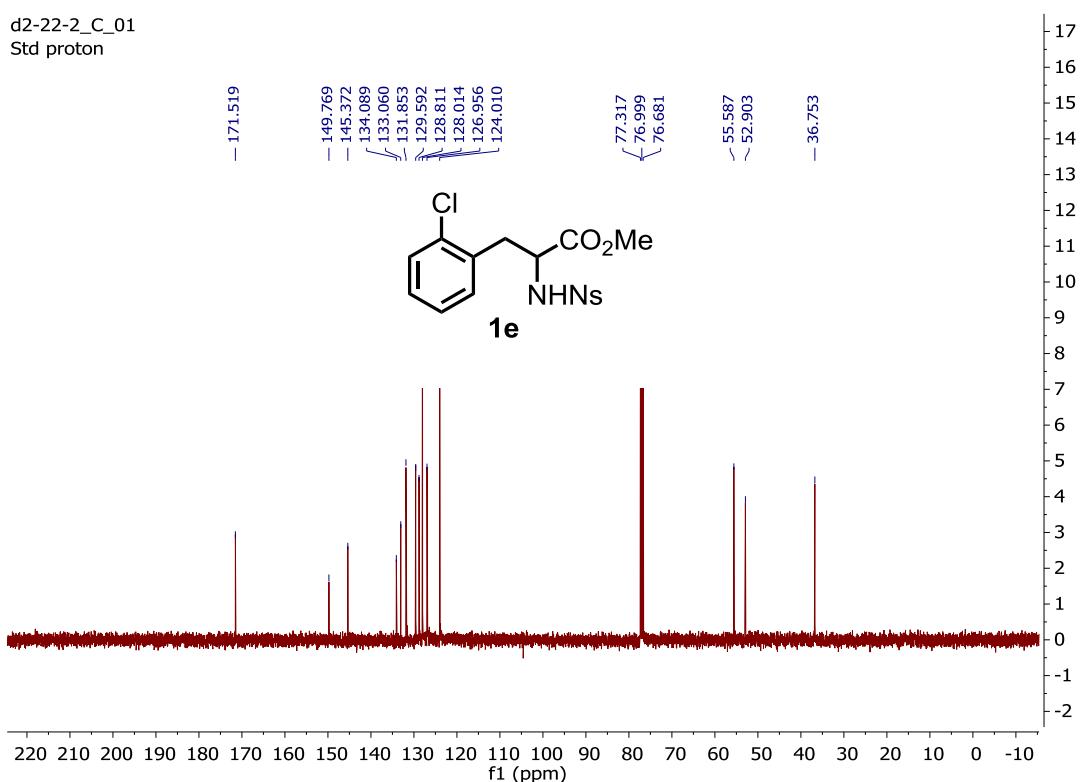
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Std proton



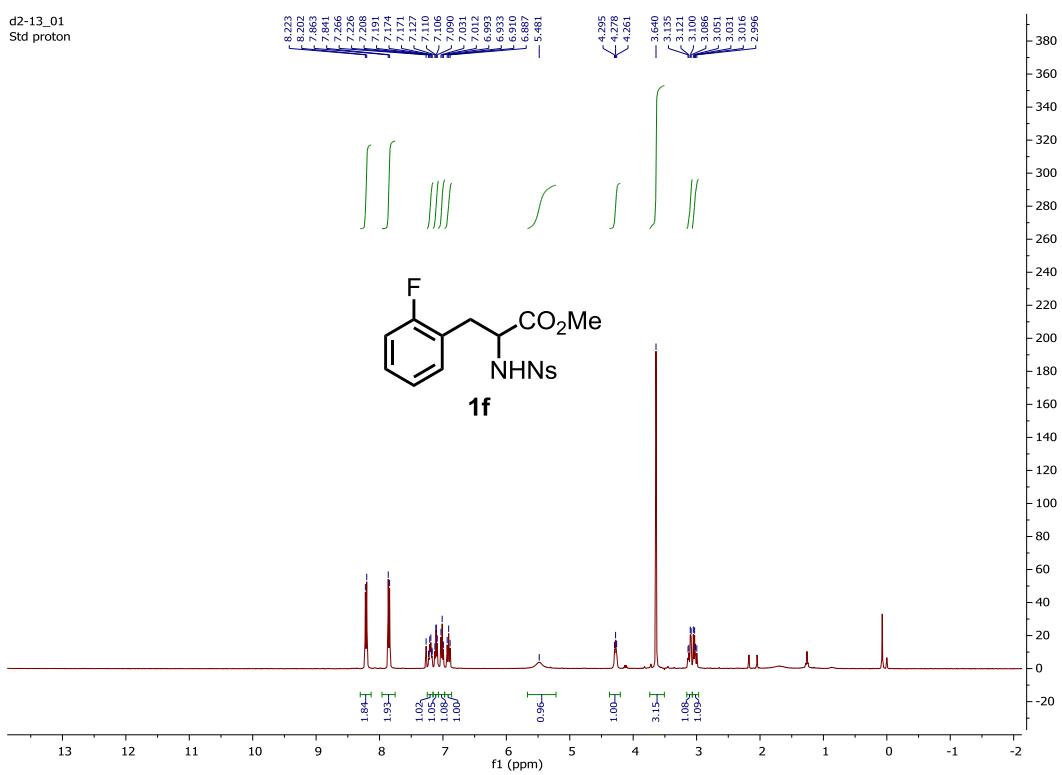
d2-22-2_01
Std proton



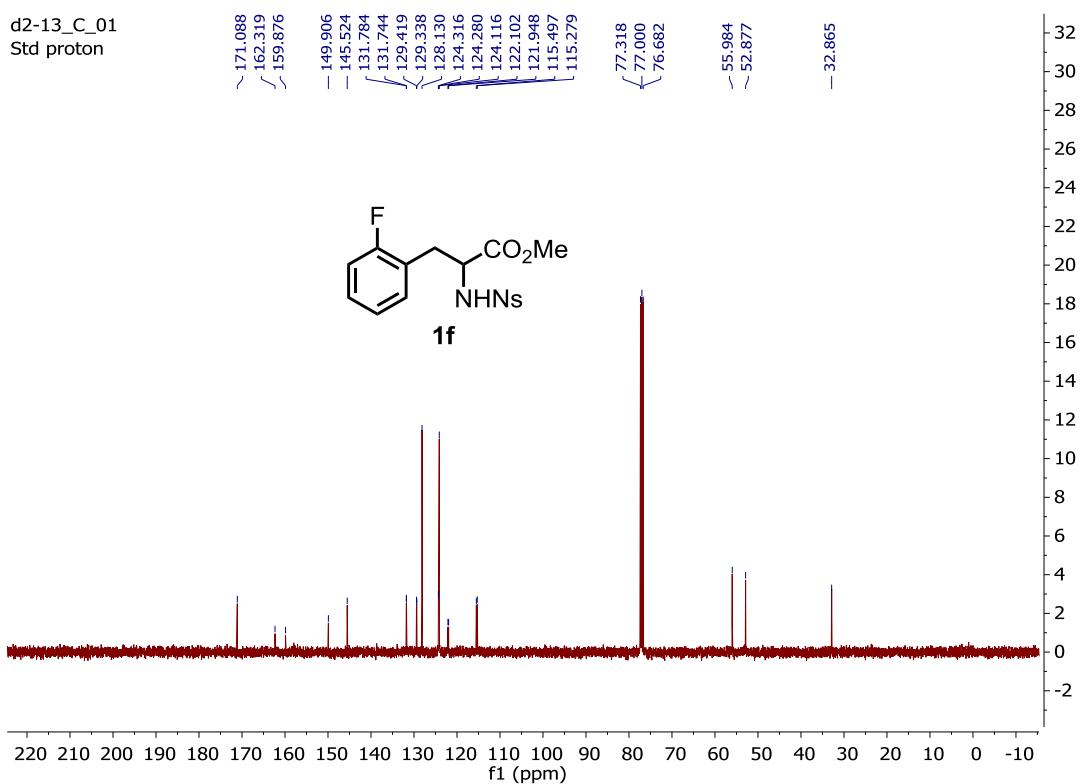
d2-22-2_C_01
Std proton



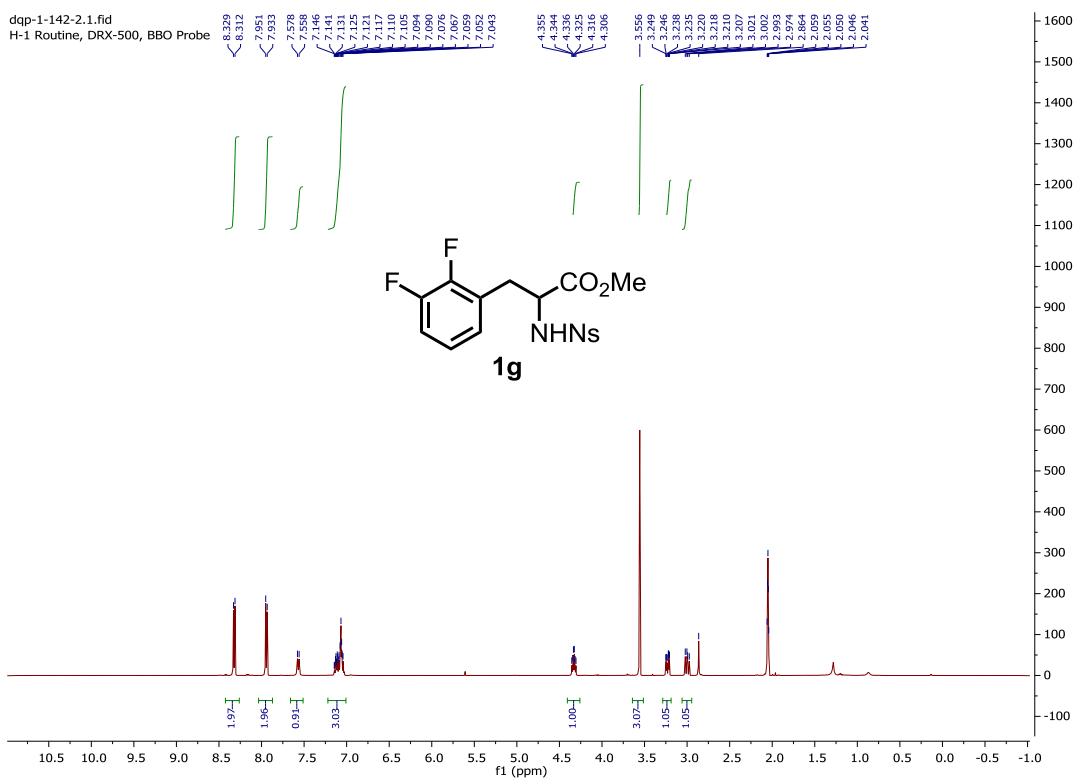
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Std proton

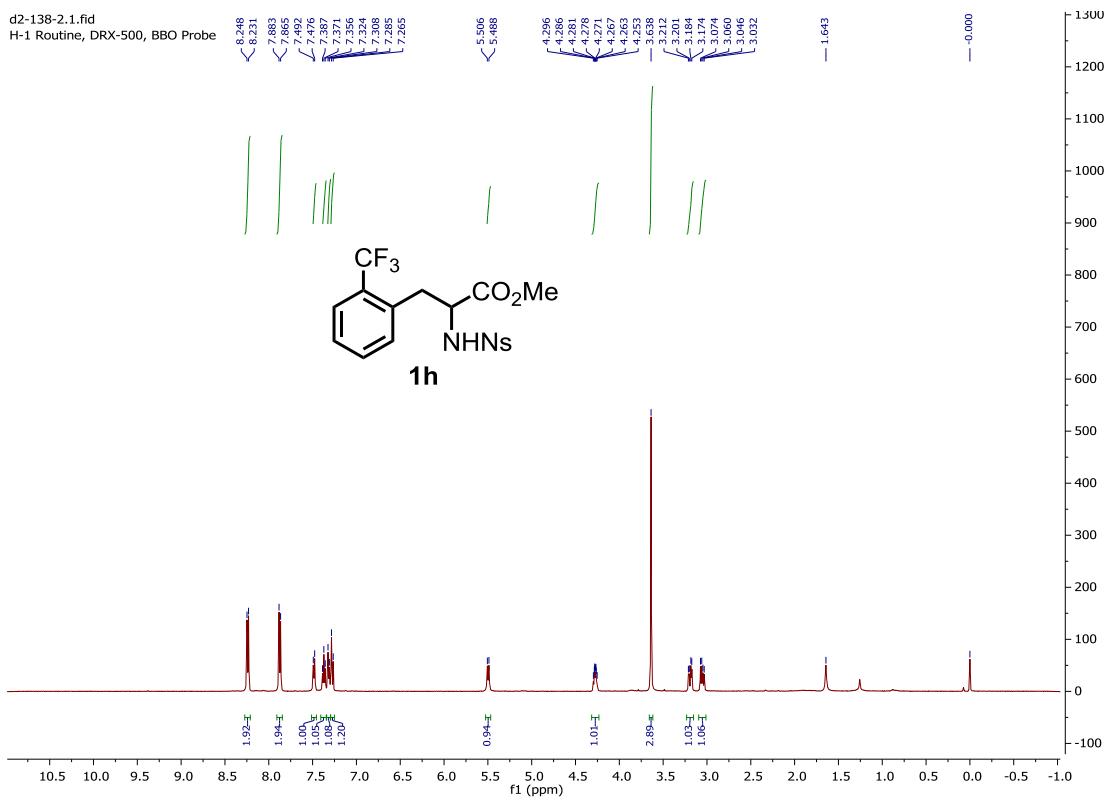
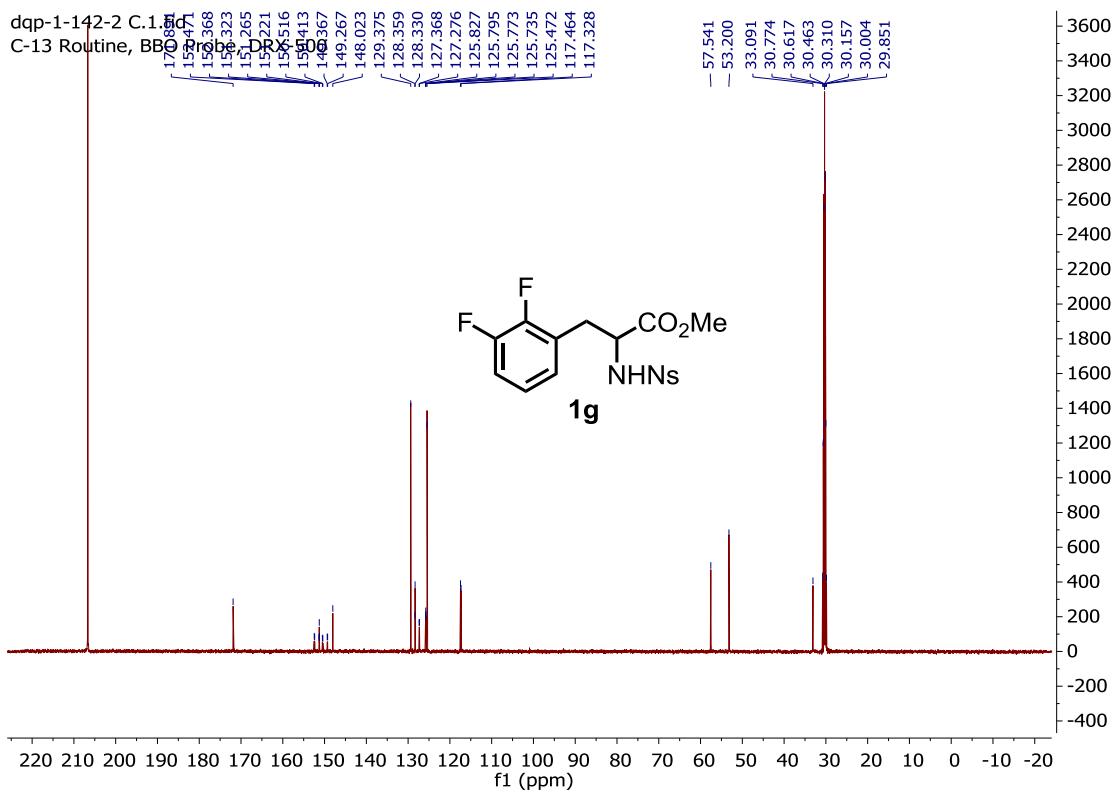


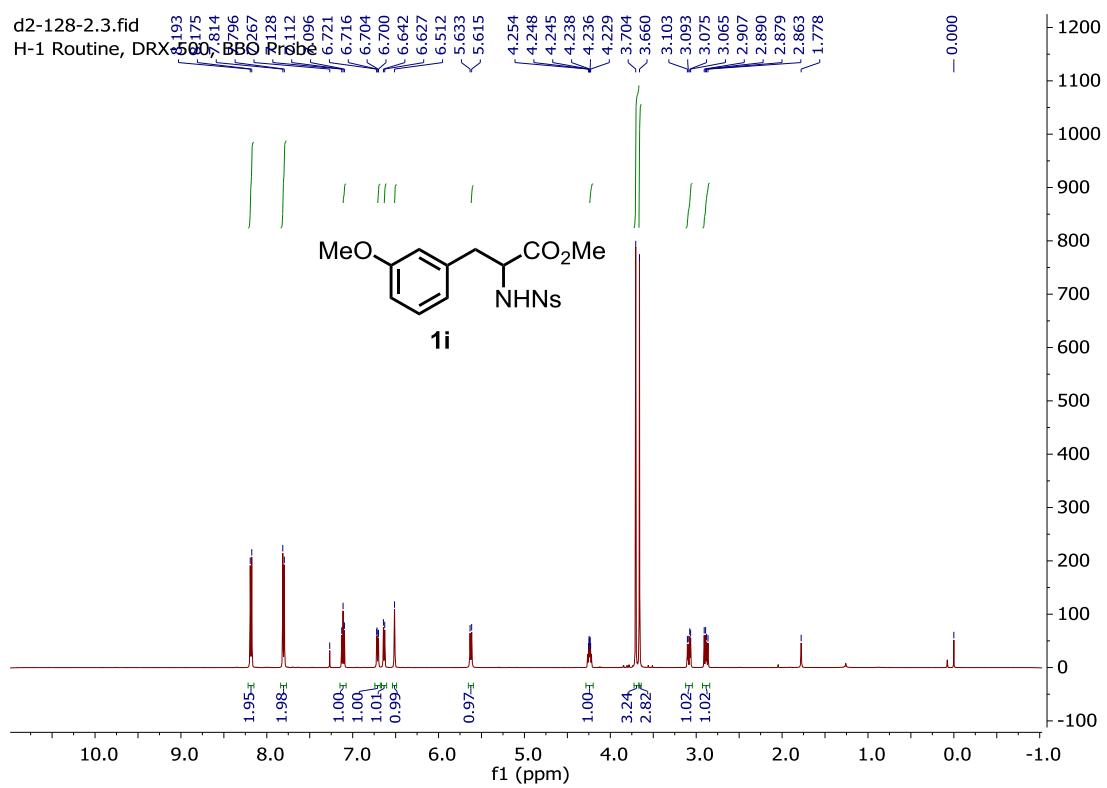
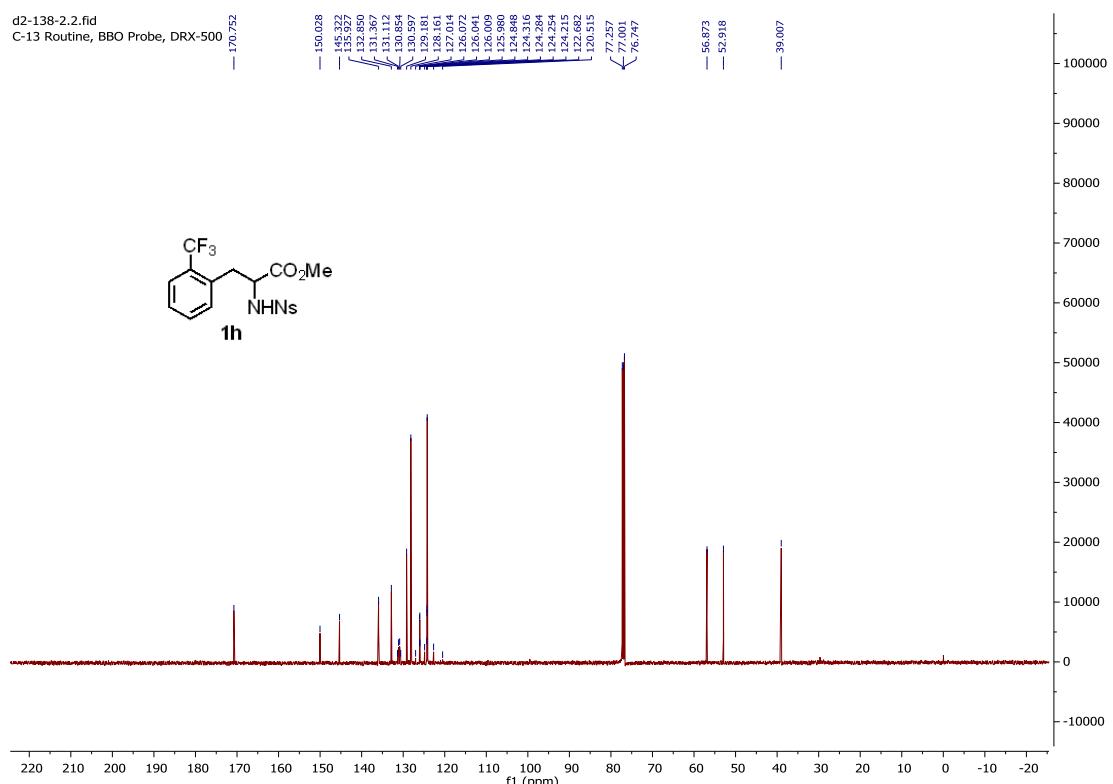
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Std proton

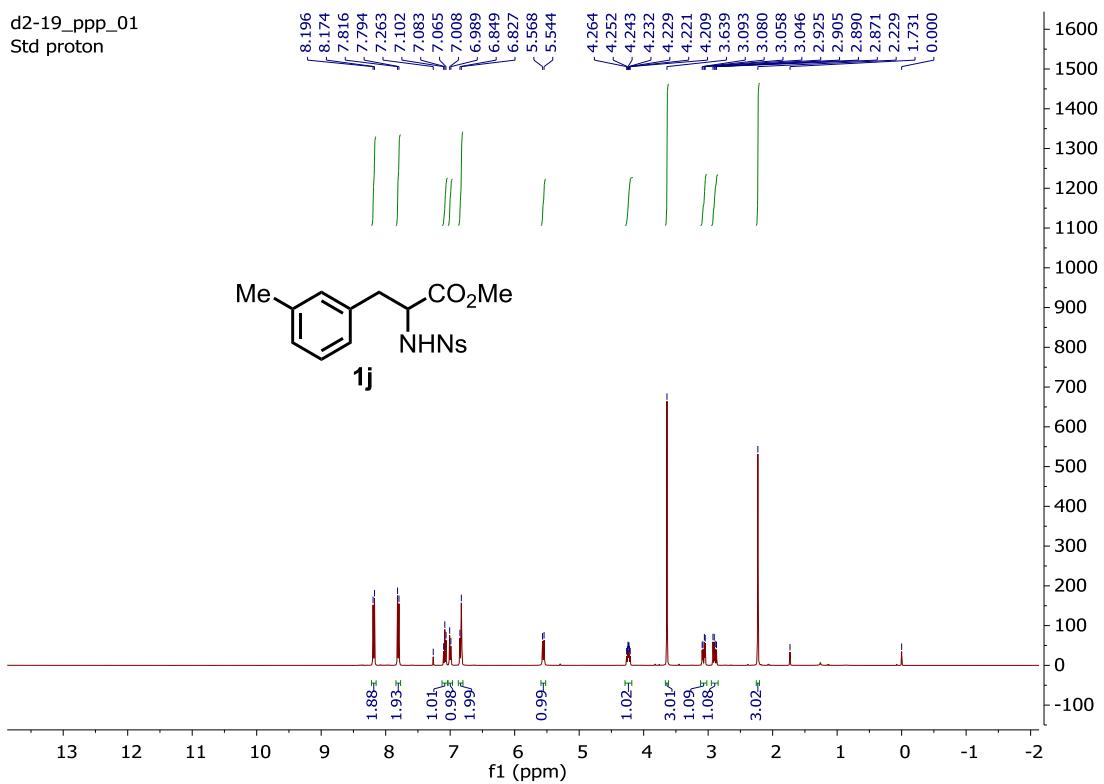
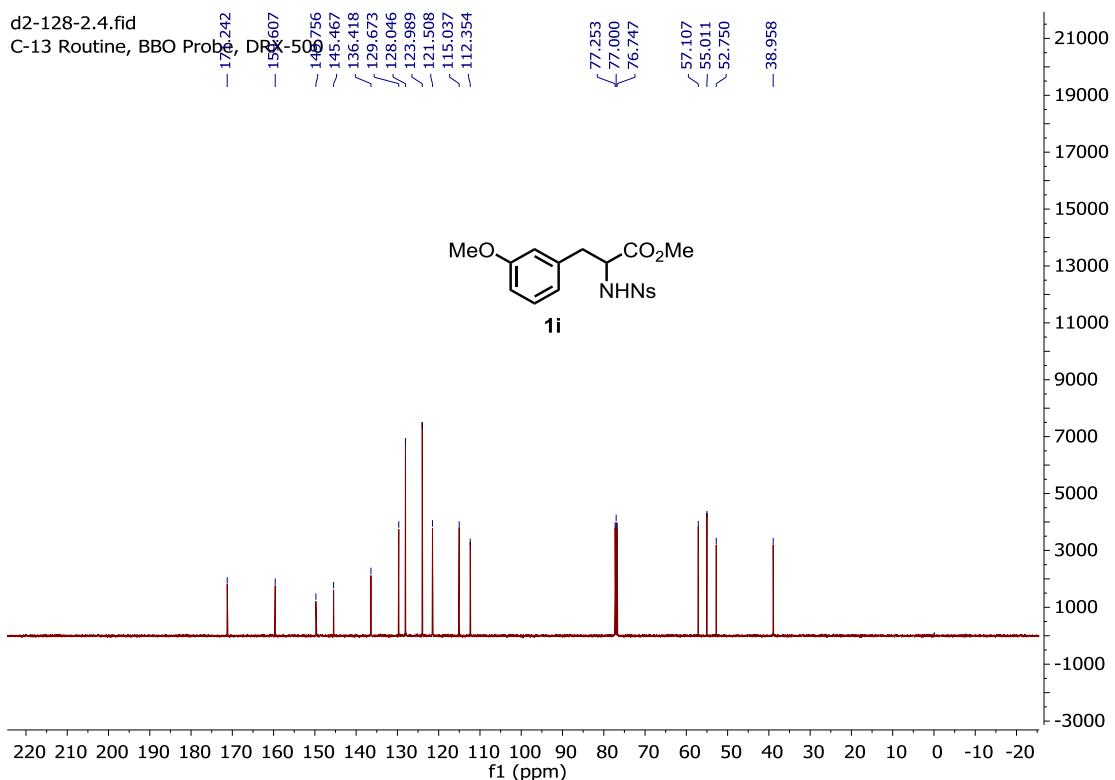


dqp-1-142-2.1.fid
H-1 Routine, DRX-500, BBO Probe

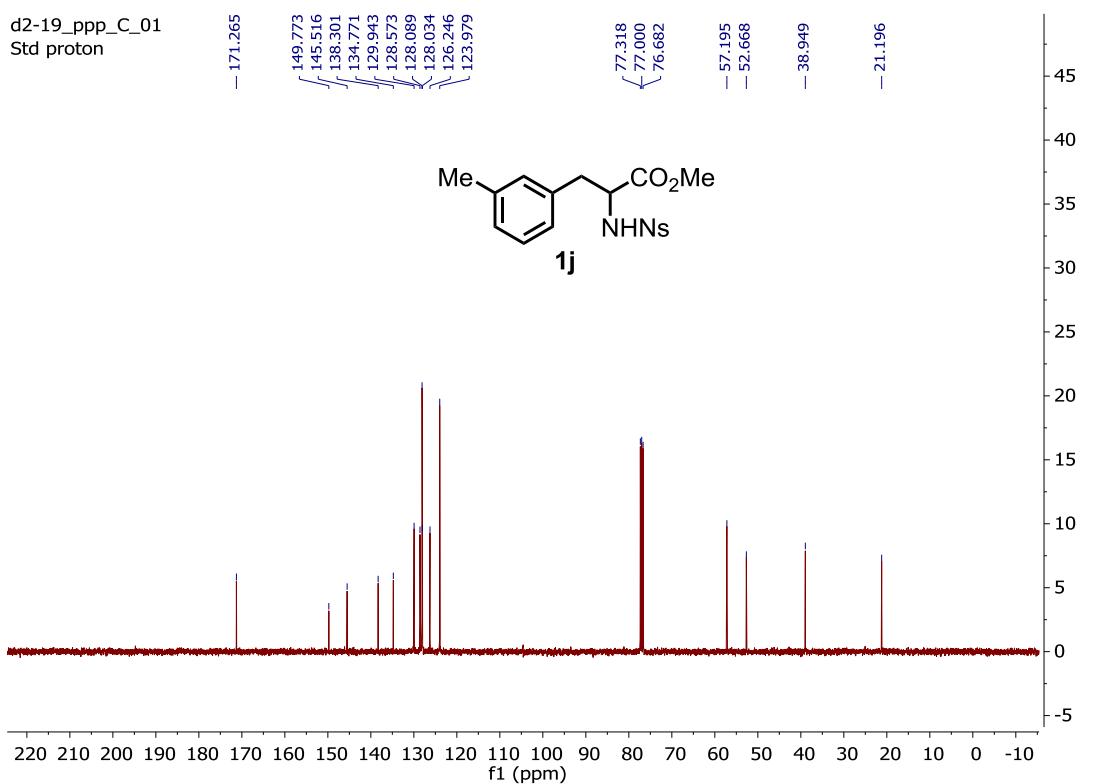




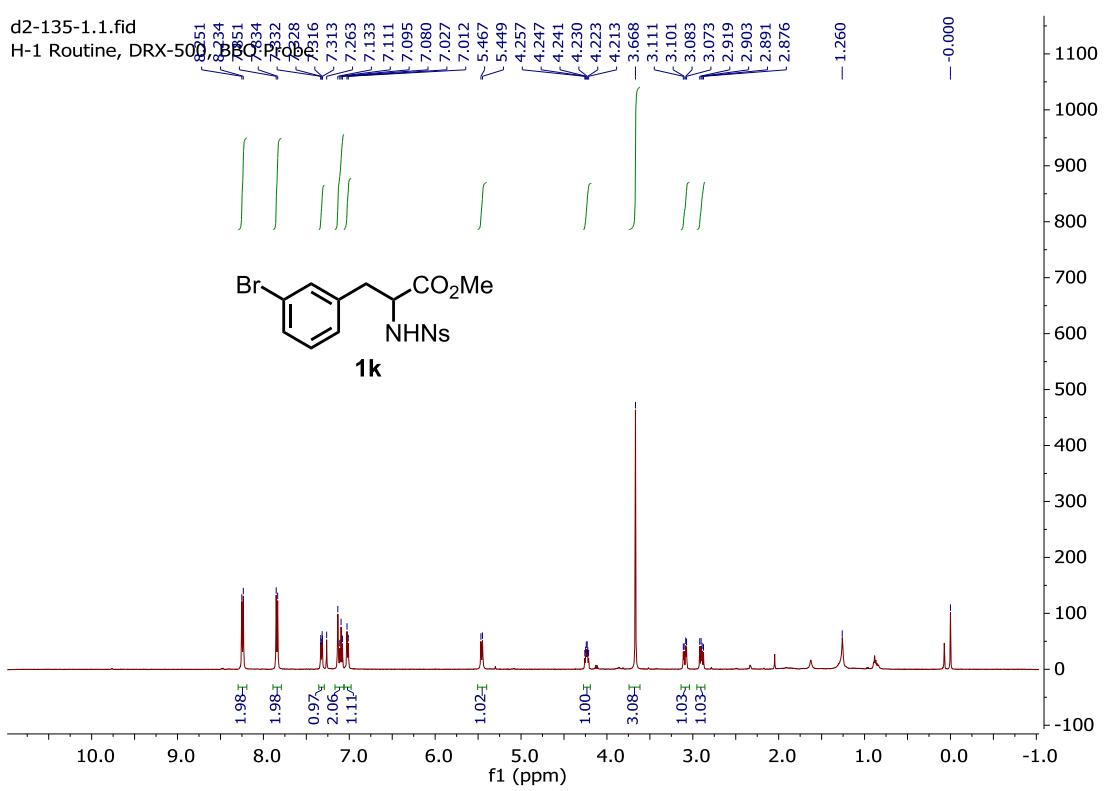


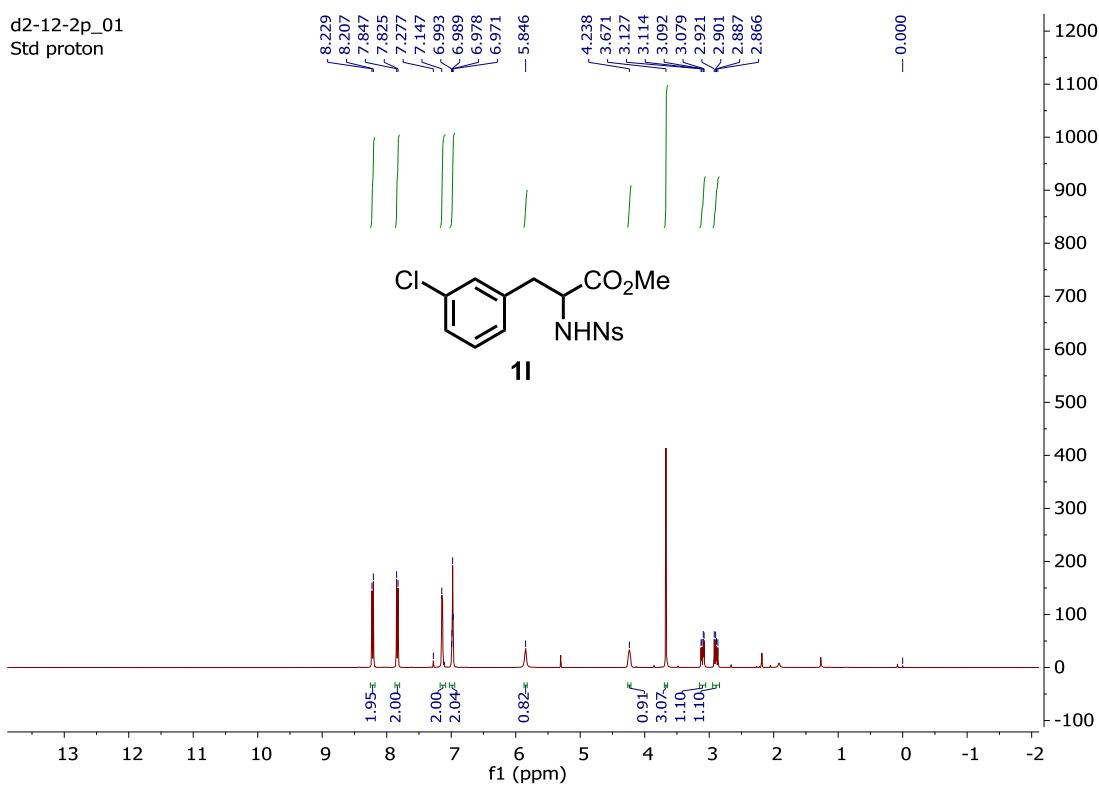
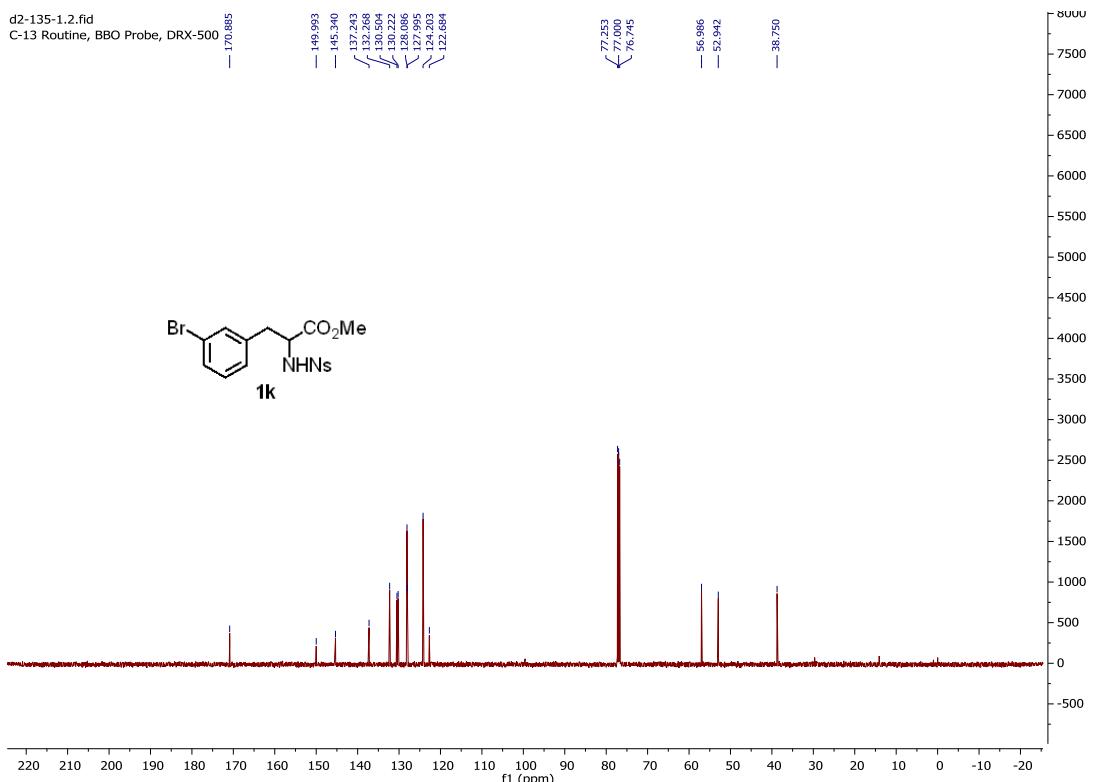


d2-19_ppp_C_01
Std proton

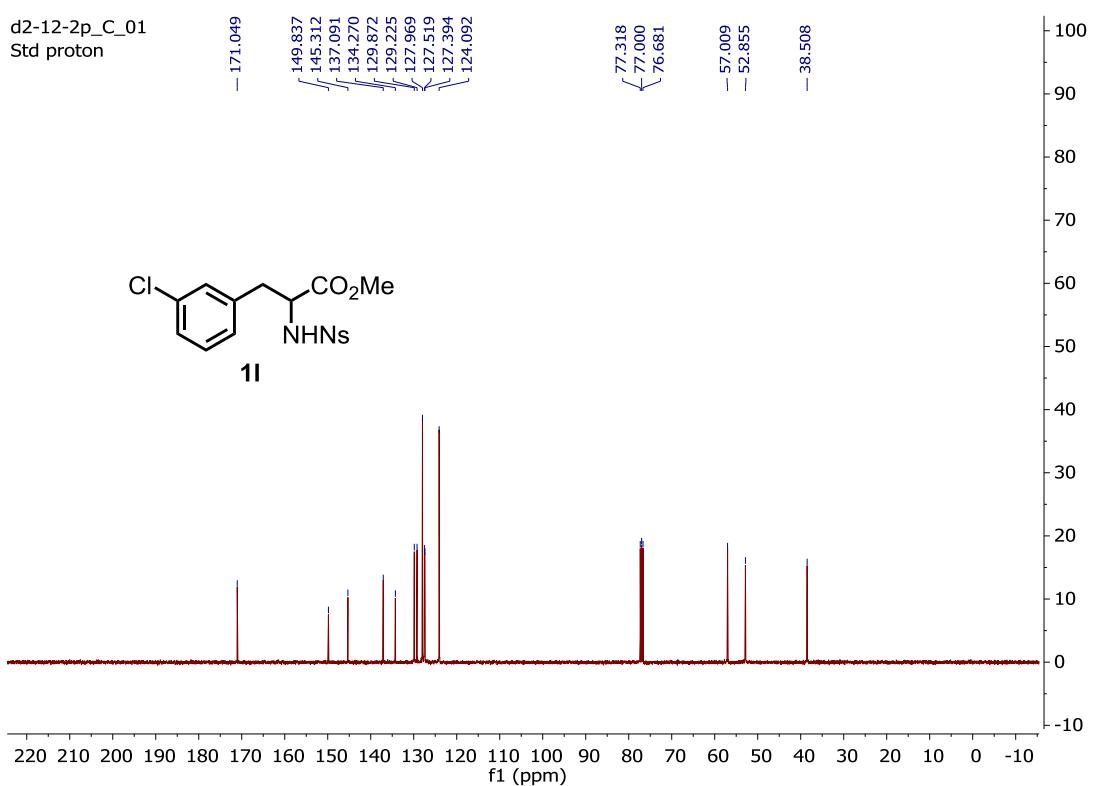


d2-135-1.1.fid
H-1 Routine, DRX-500

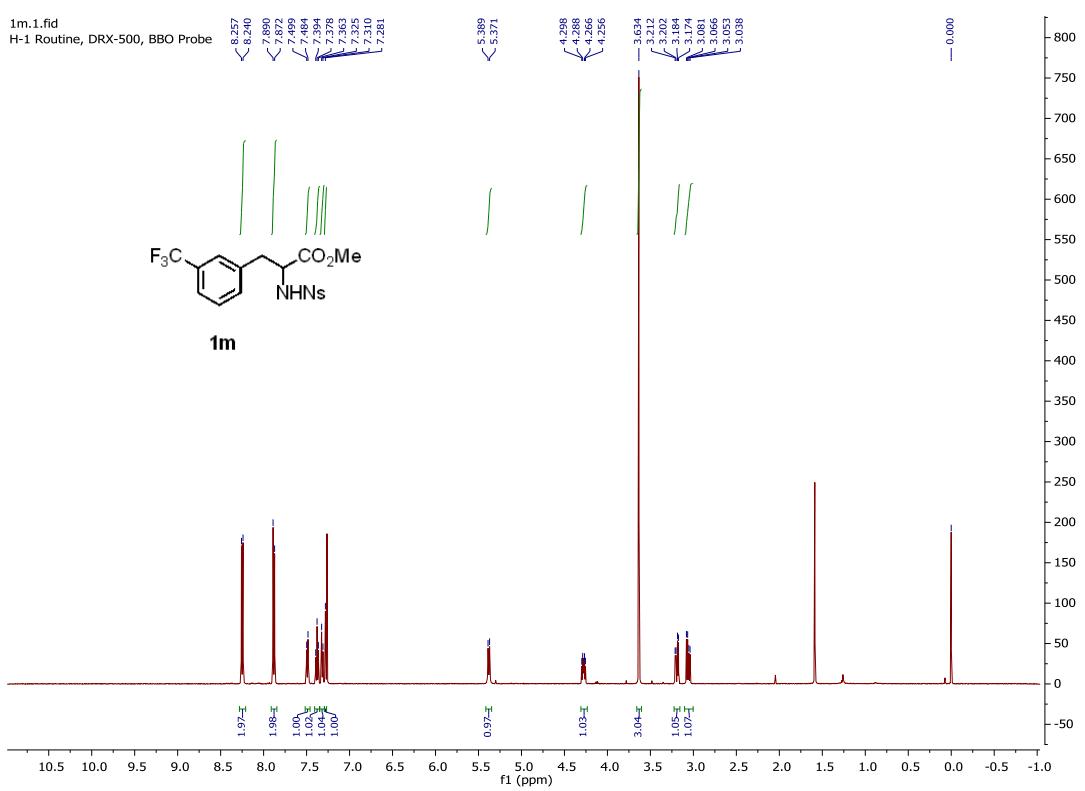


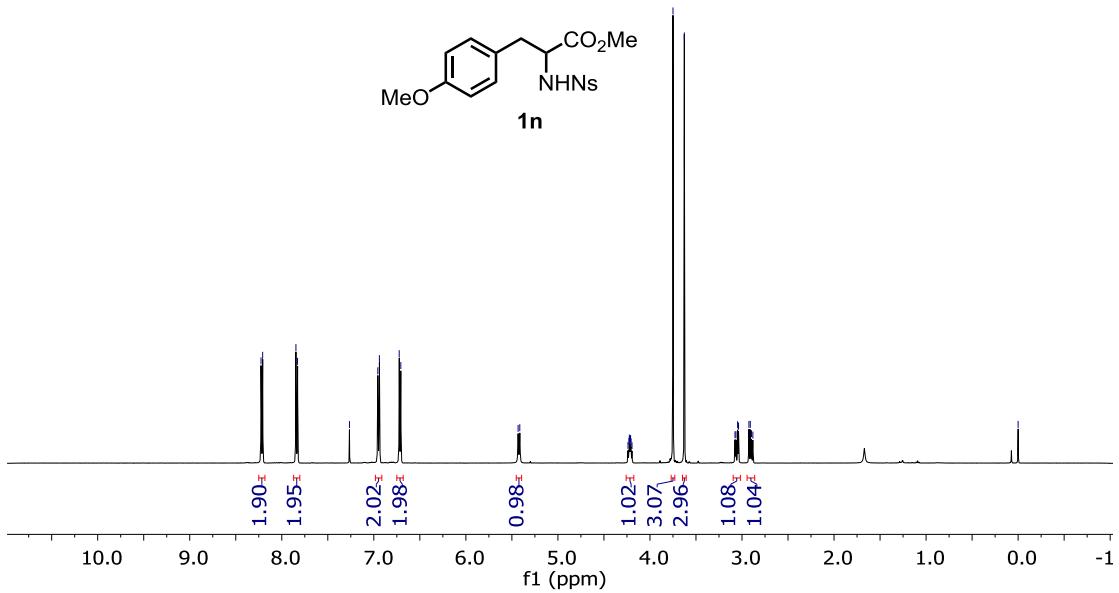
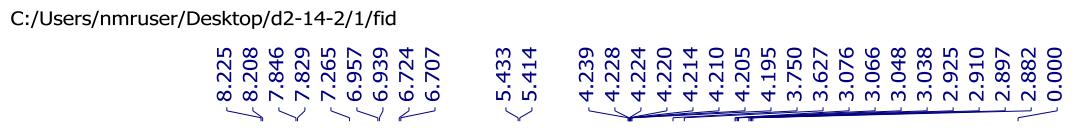
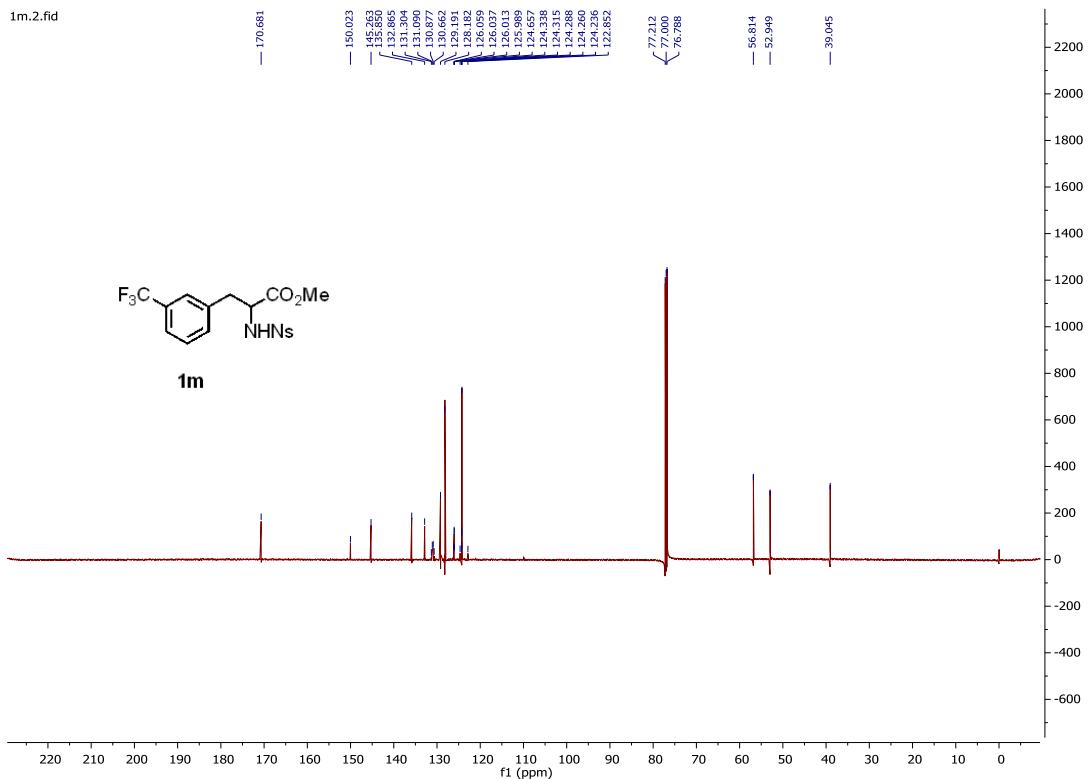


d2-12-2p_C_01
Std proton

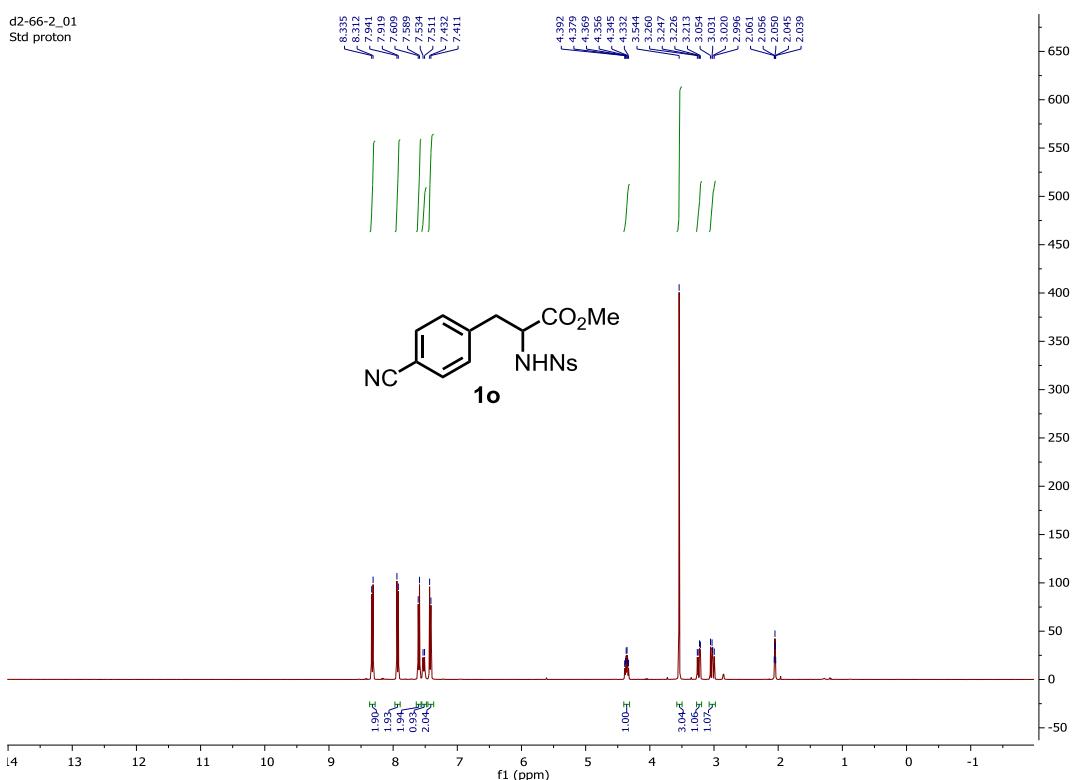
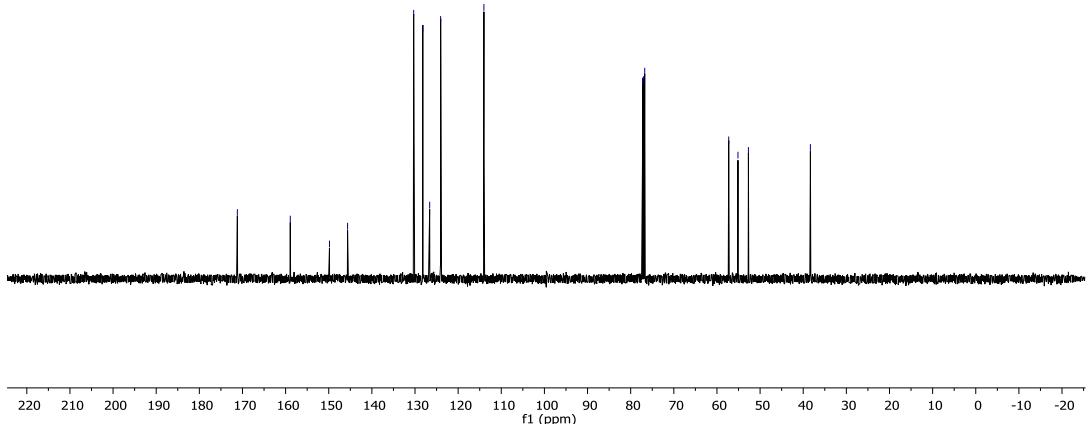
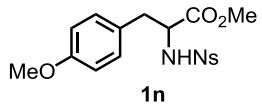


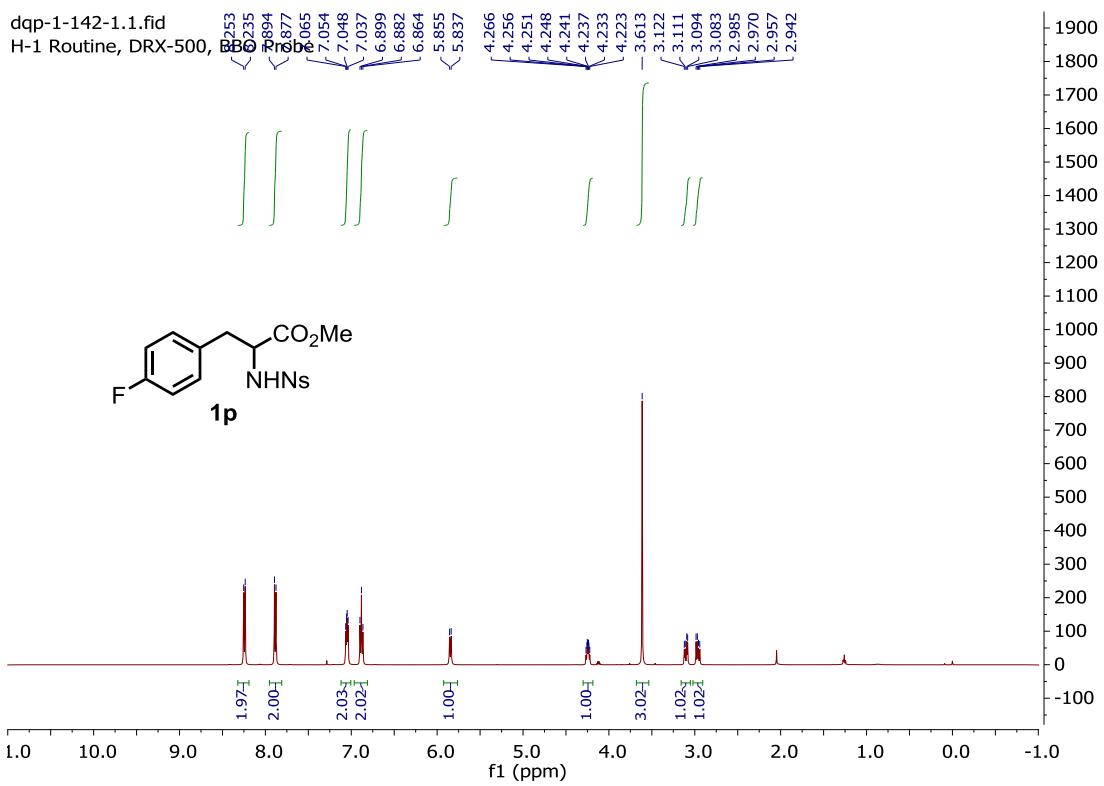
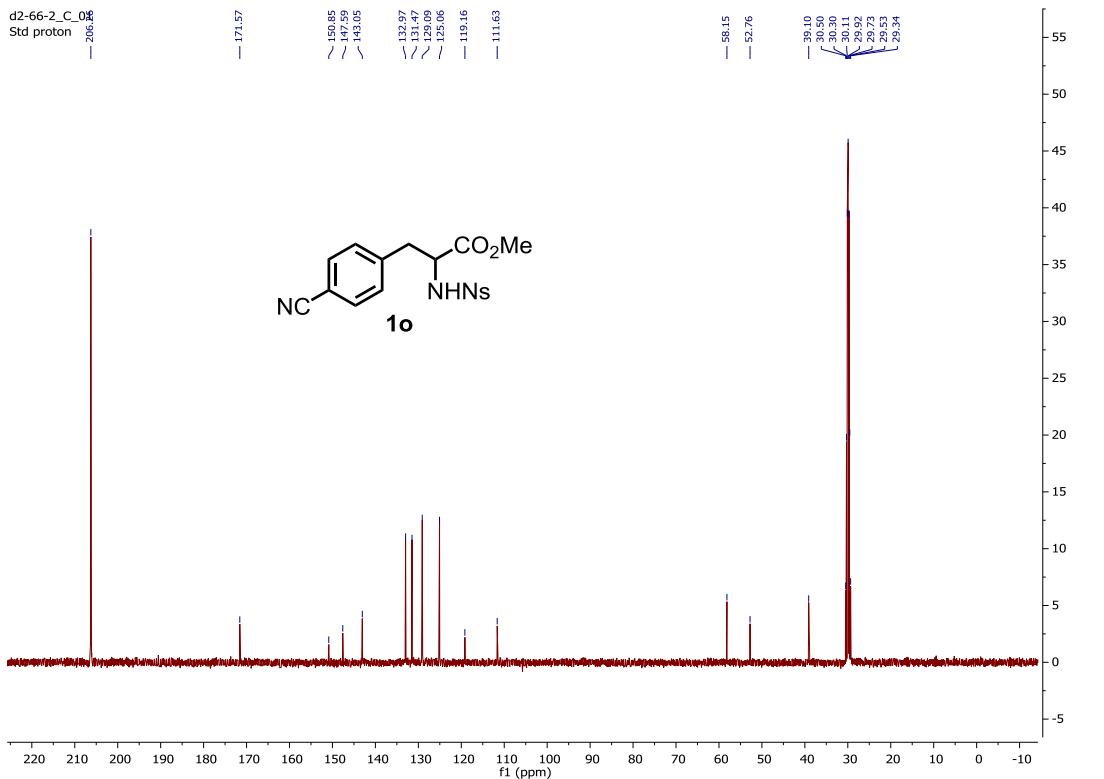
1m.fid
H-1 Routine, DRX-500, BBO Probe

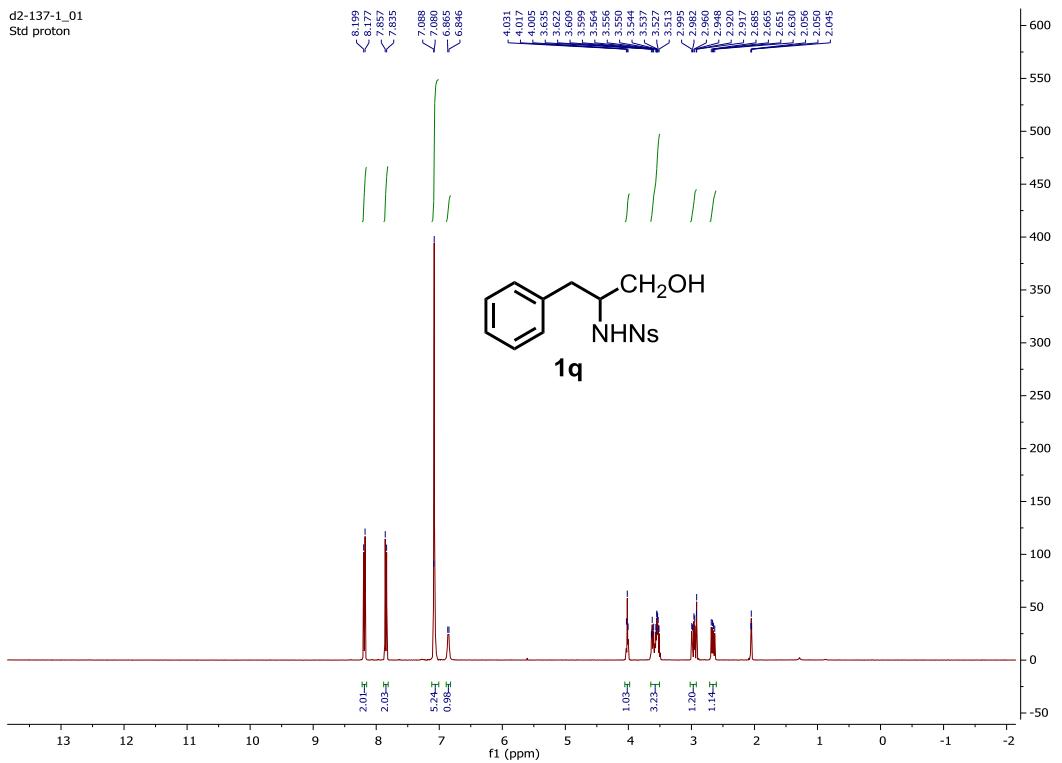
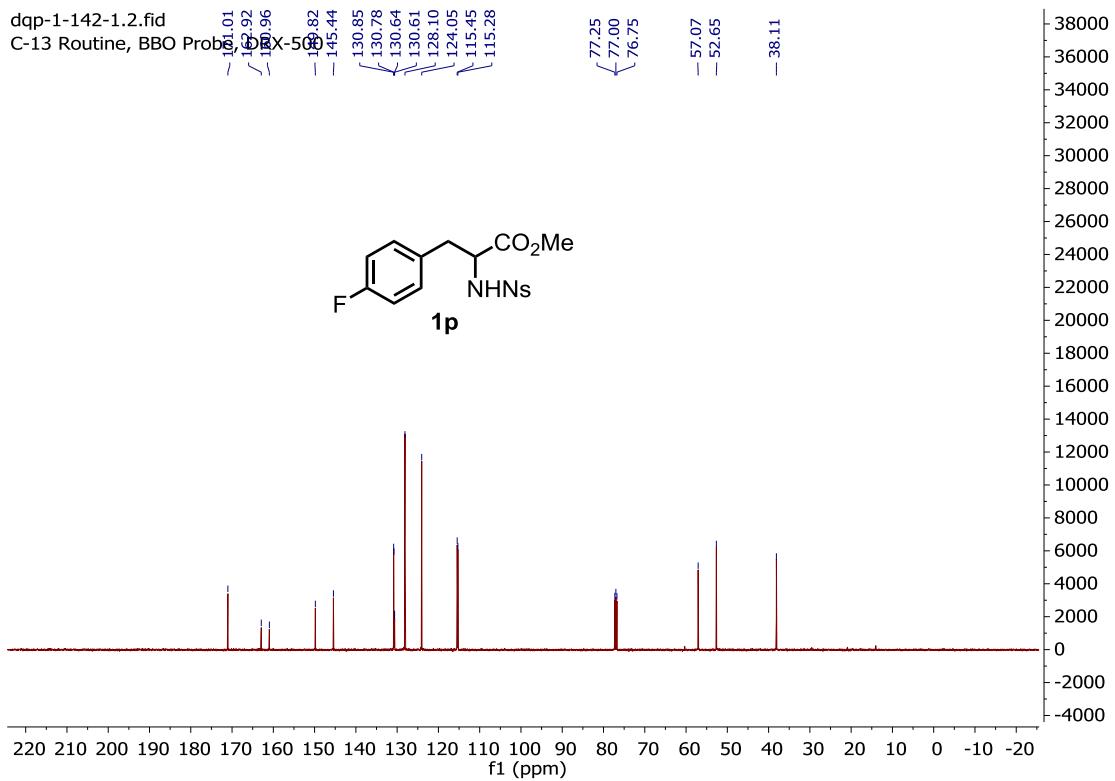




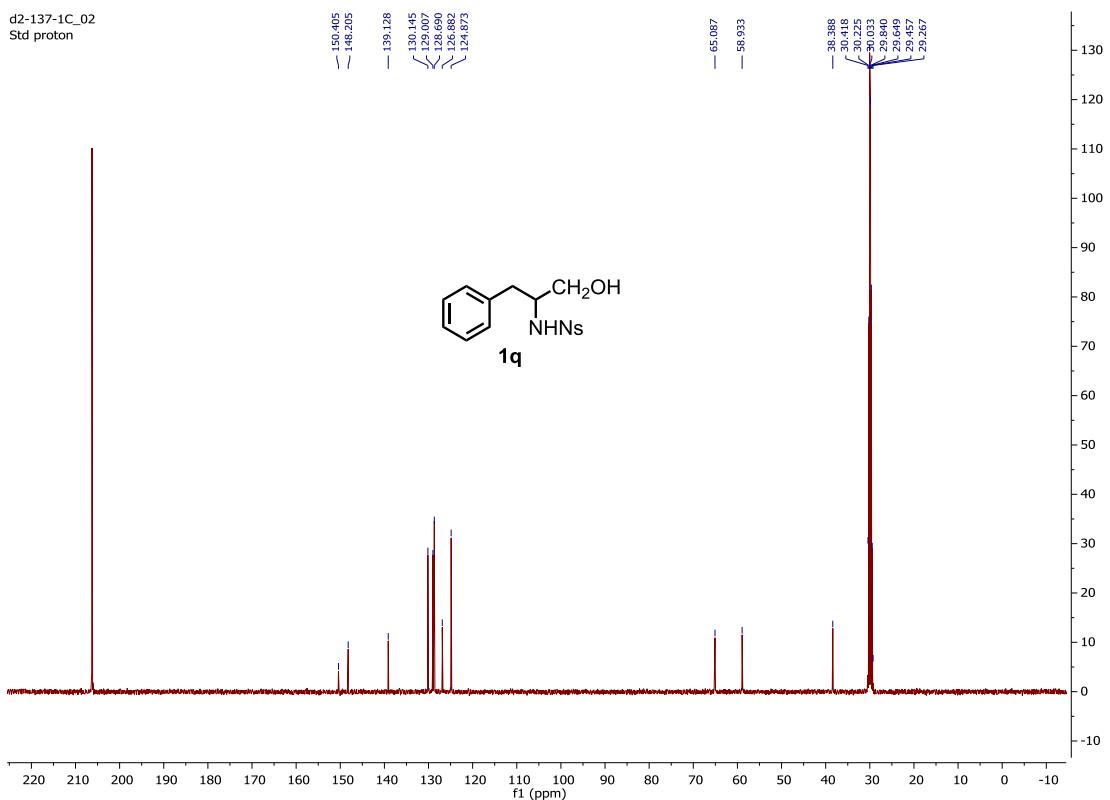
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-145.63
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-114.03





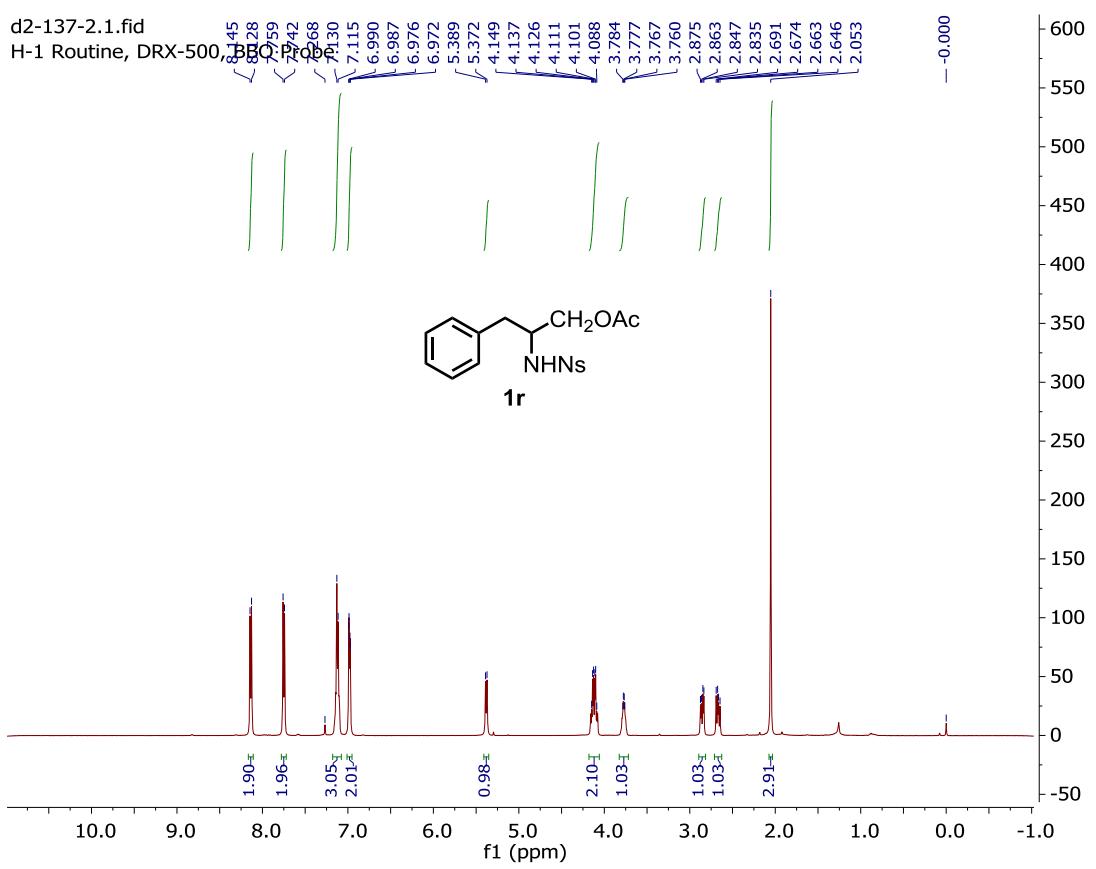


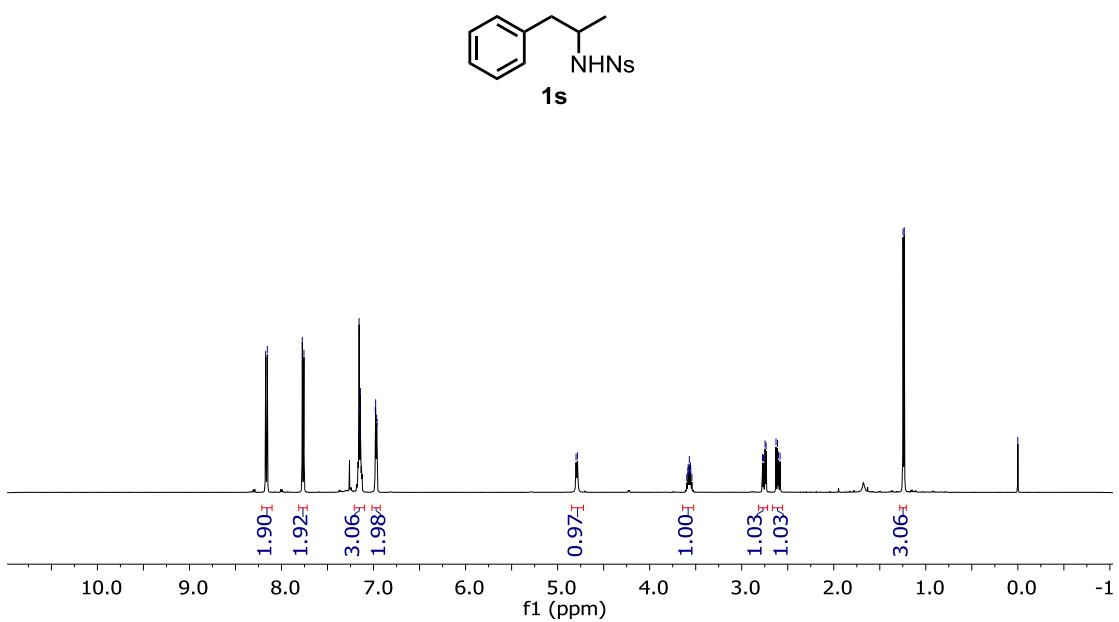
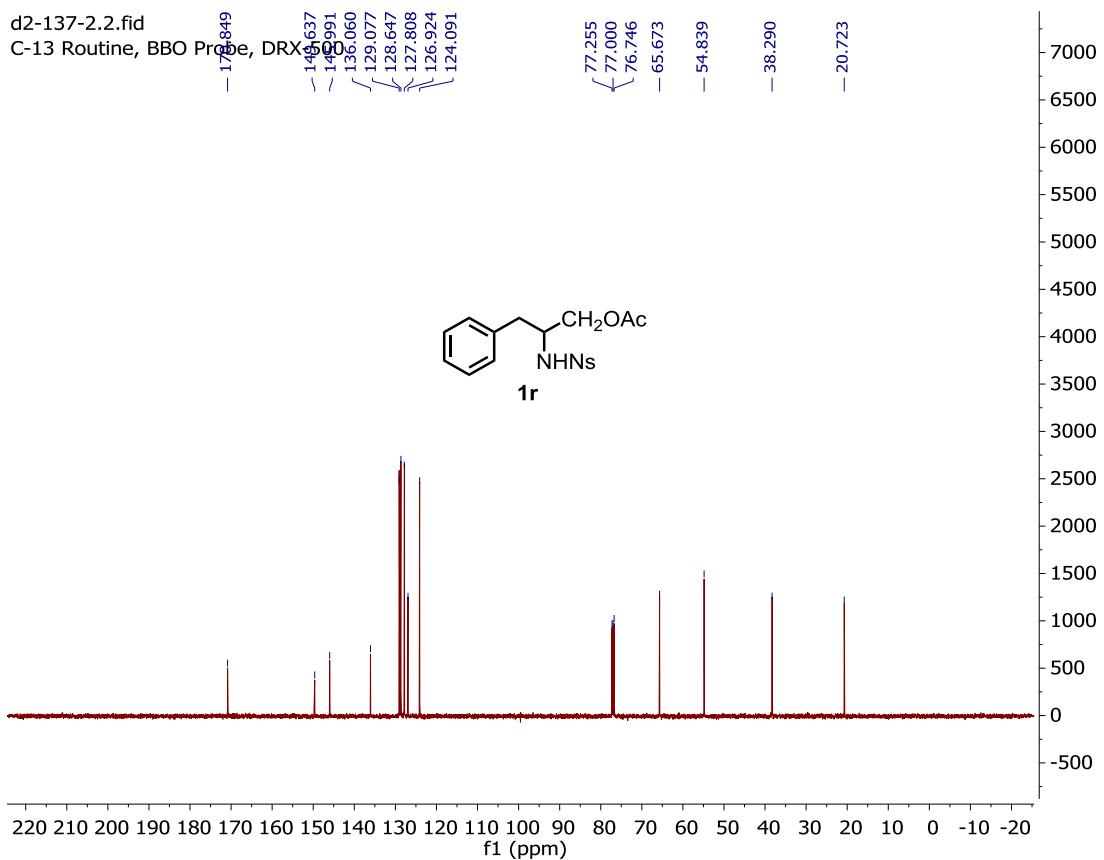
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Std proton



d2-137-2.1.fid

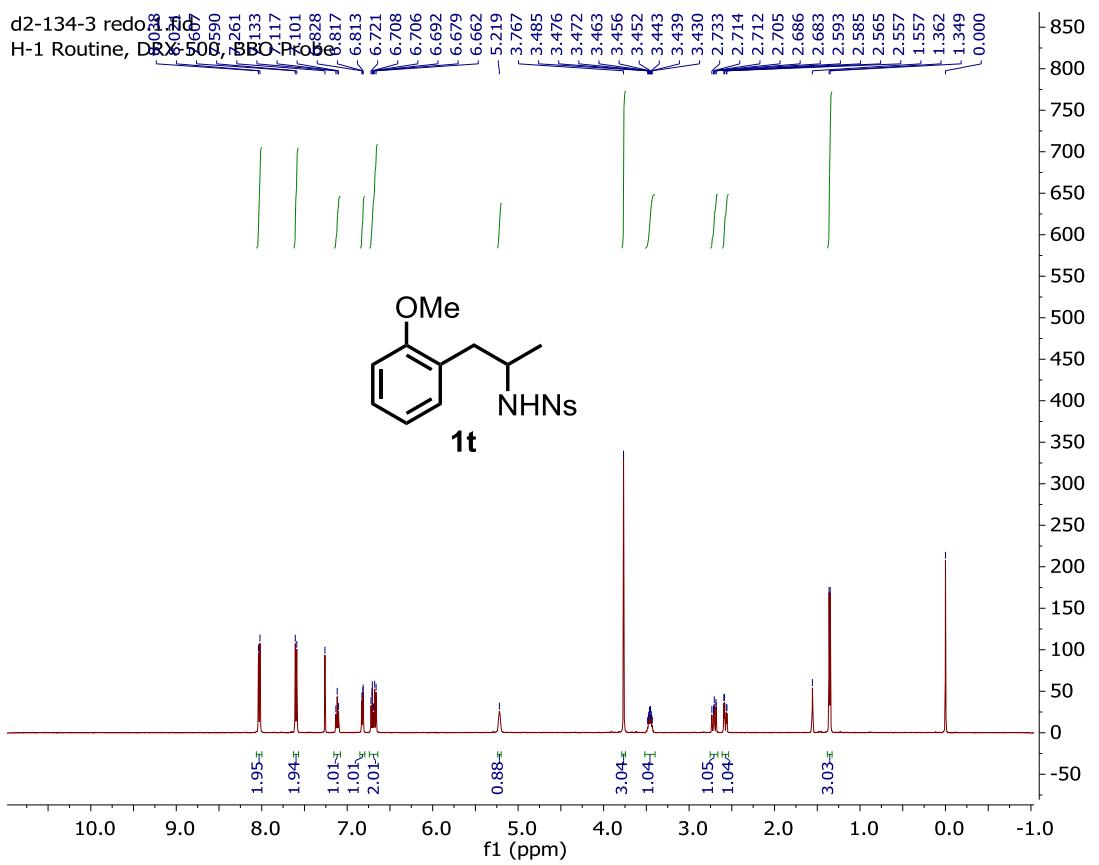
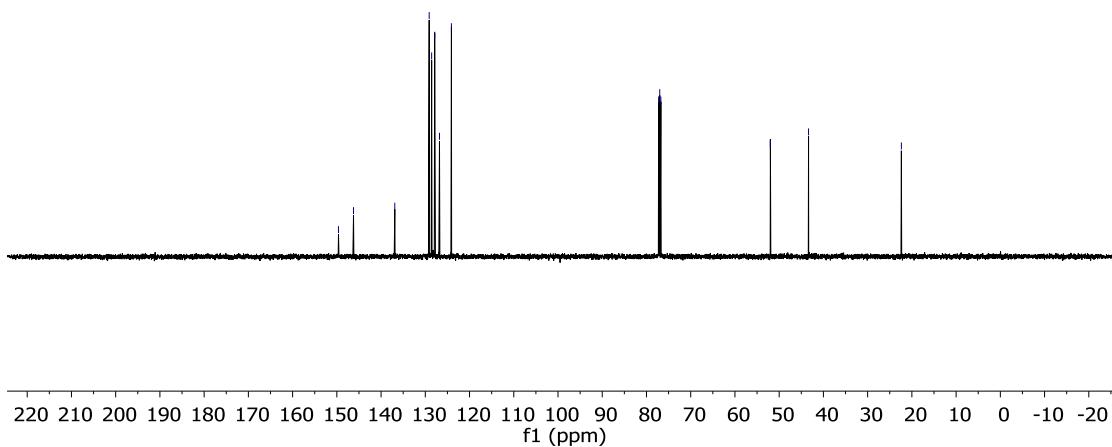
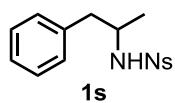
H-1 Routine, DRX-500,

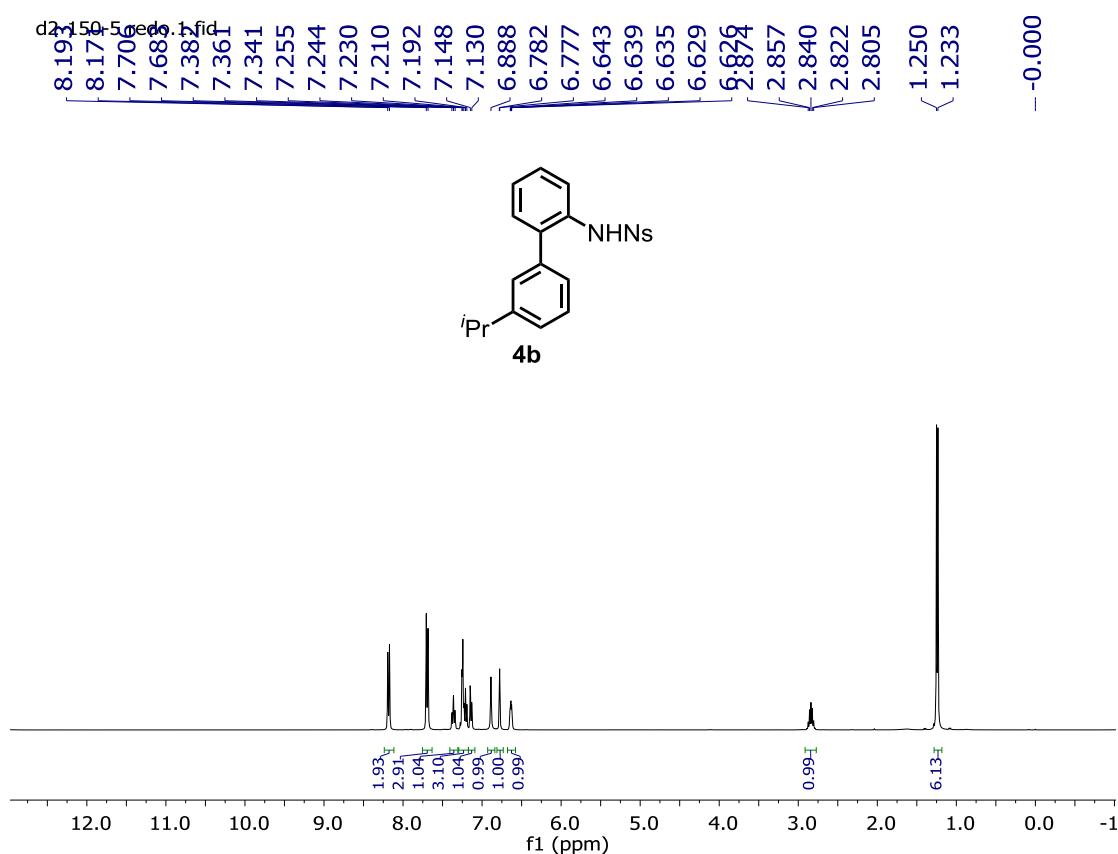
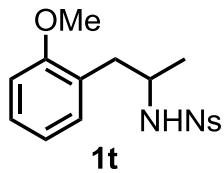
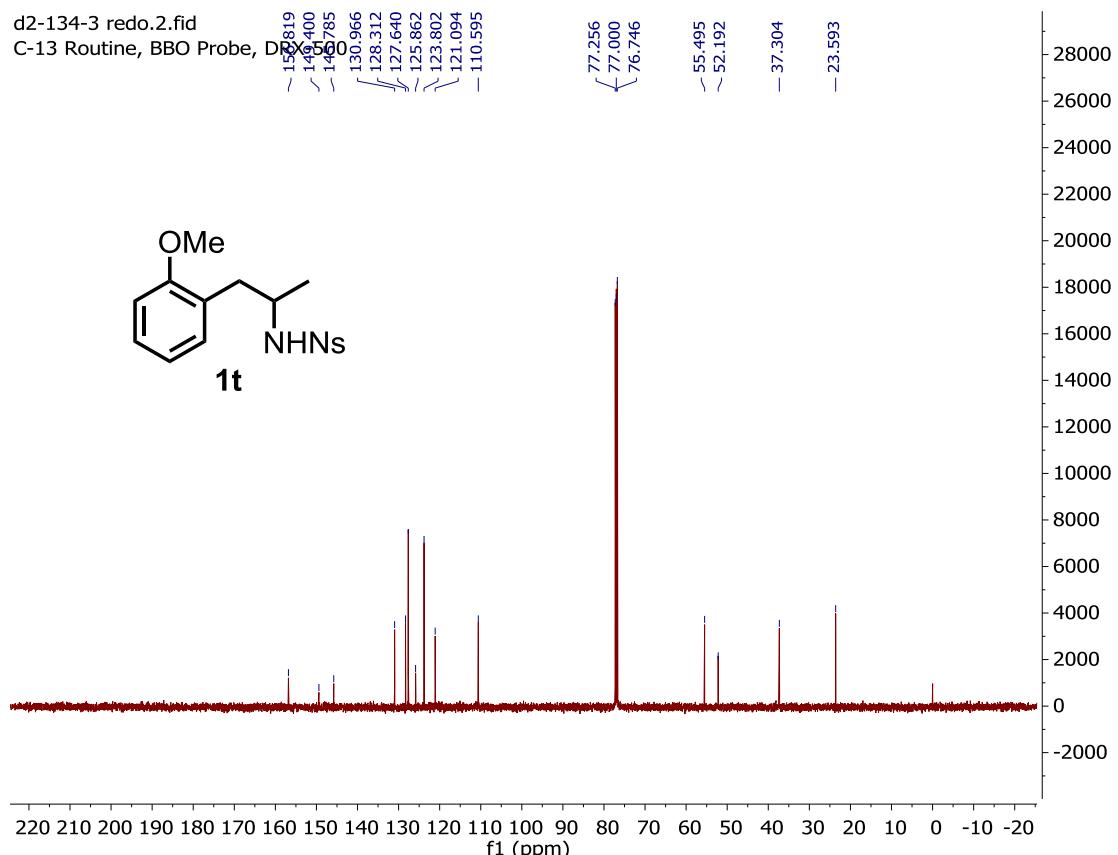


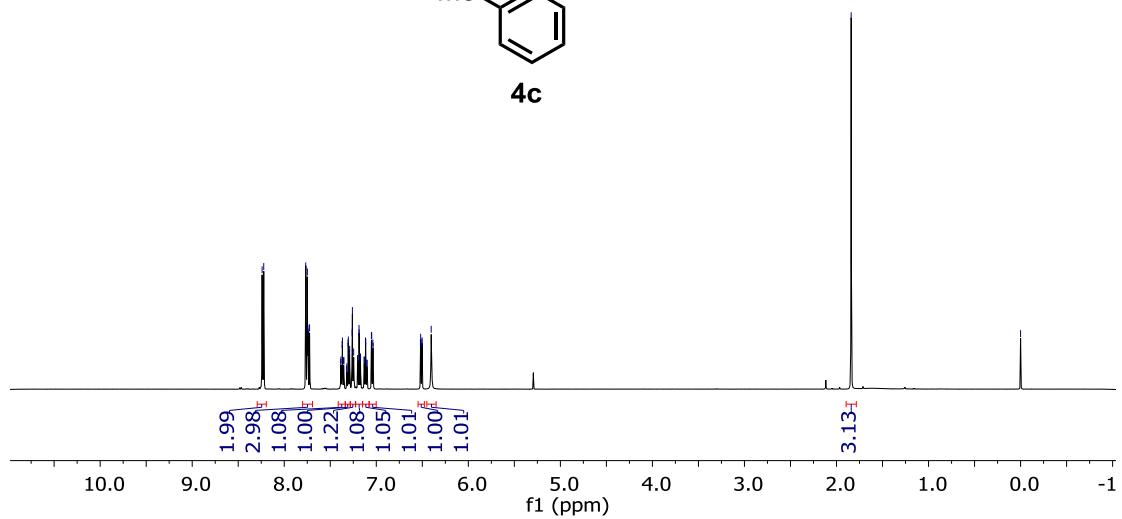
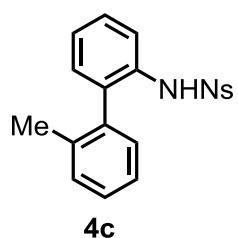
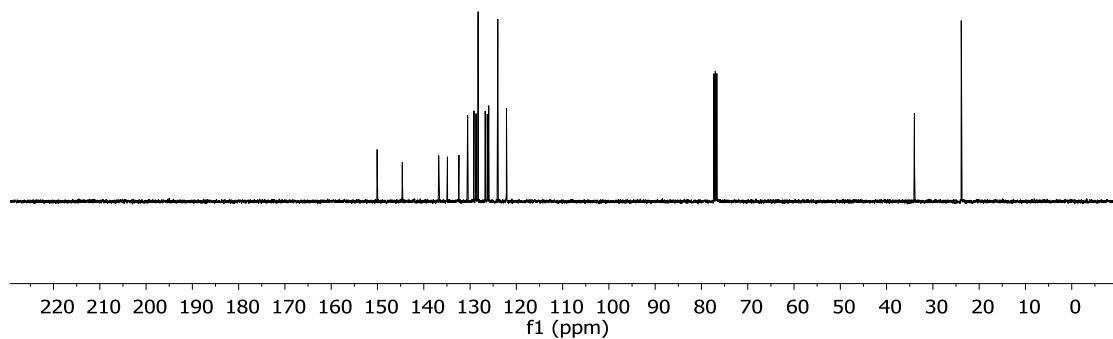
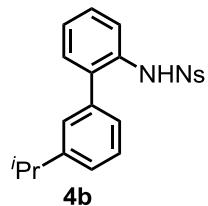
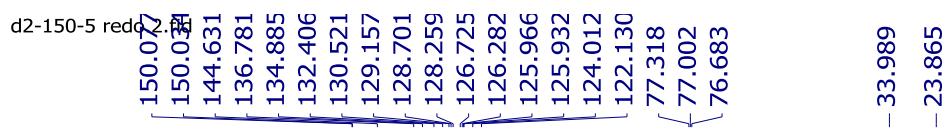


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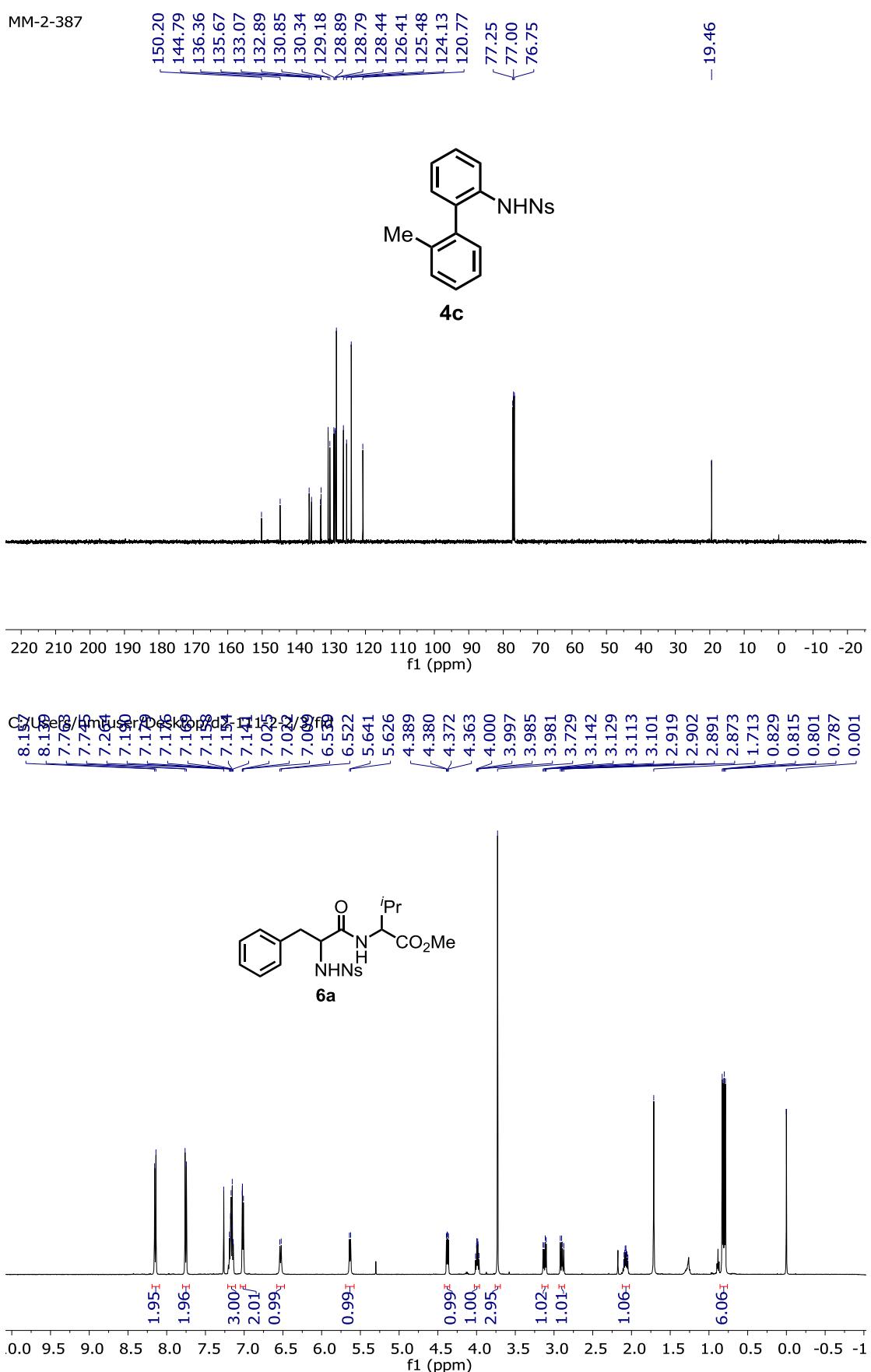
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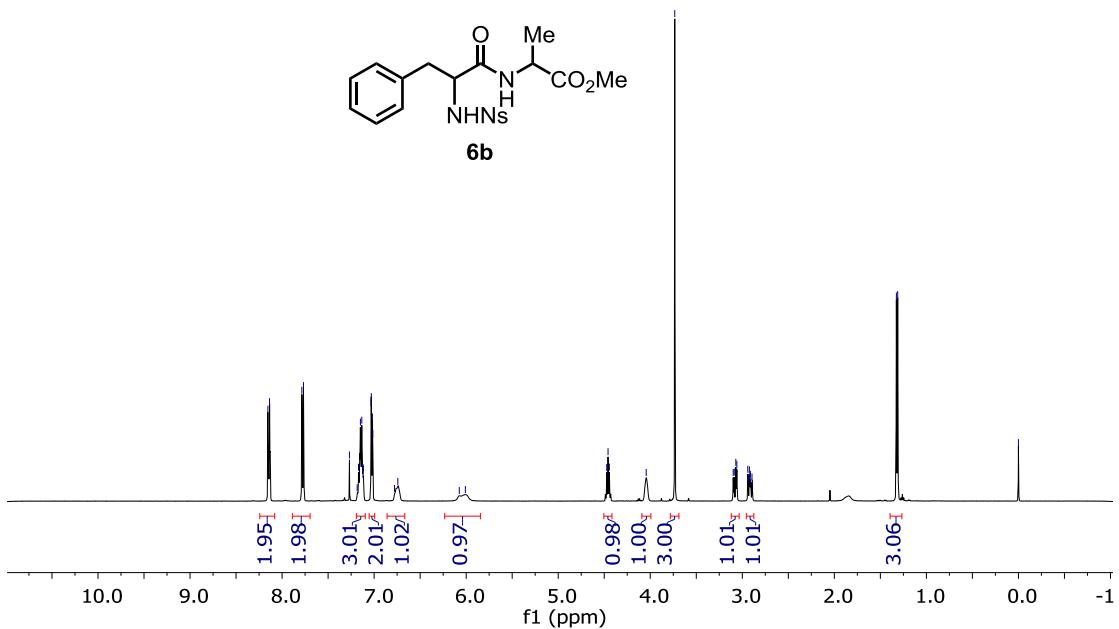
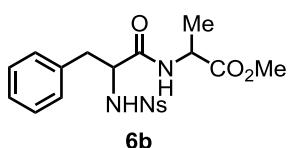
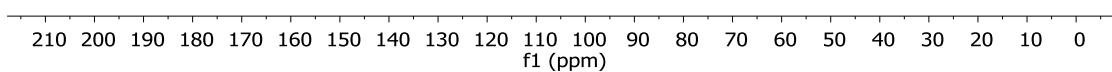
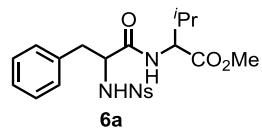
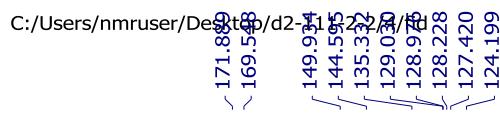




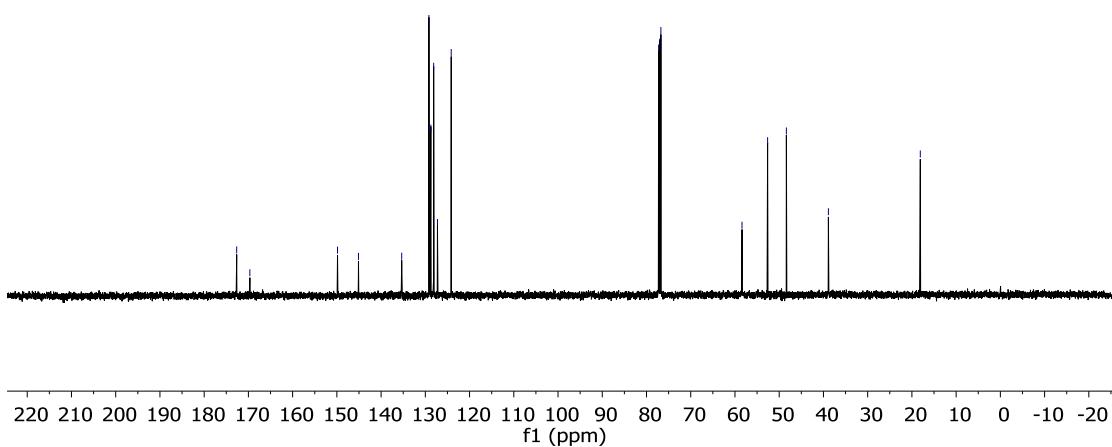
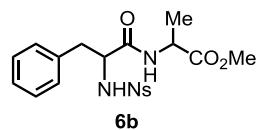


MM-2-387



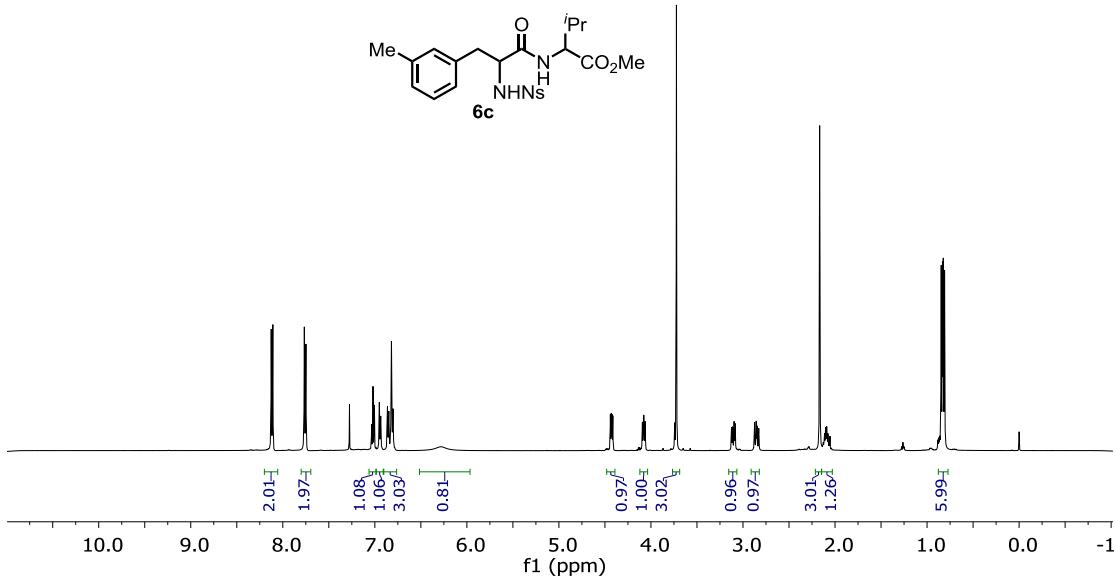


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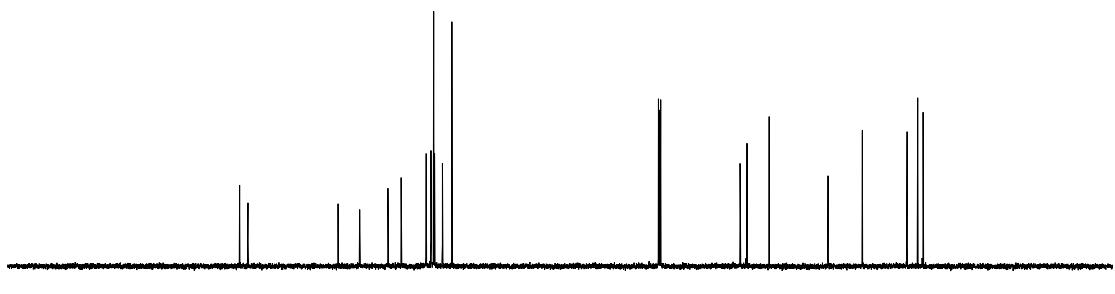
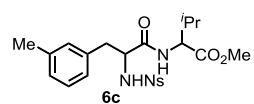
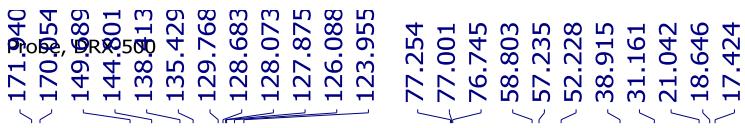
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1H proton DQX3020 Prodigy

Peak Label	Chemical Shift (ppm)
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8.10	7.74
8.05	7.27
8.03	7.03
8.02	7.02
8.01	7.00
7.95	6.93
7.91	6.86
7.88	6.86
7.85	6.84
7.82	6.82
7.80	6.80
7.78	4.44
7.76	4.43
7.74	4.42
7.72	4.41
7.70	4.09
7.68	4.08
7.66	4.07
7.64	4.06
7.62	3.72
7.60	3.09
7.58	3.08
7.56	2.87
7.54	2.85
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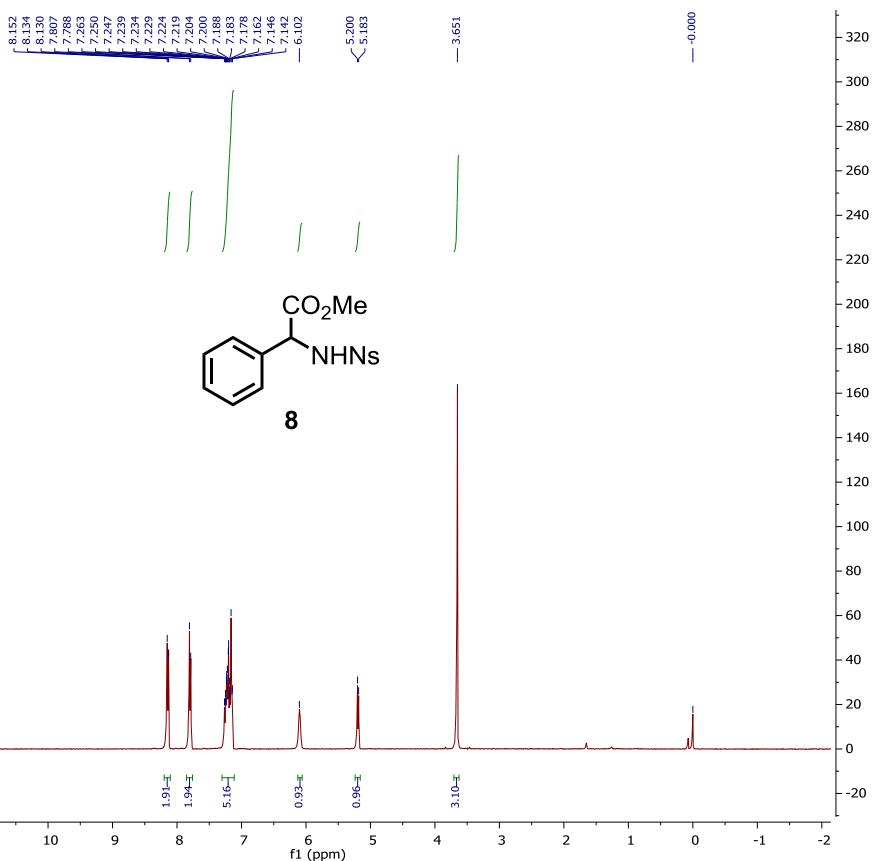


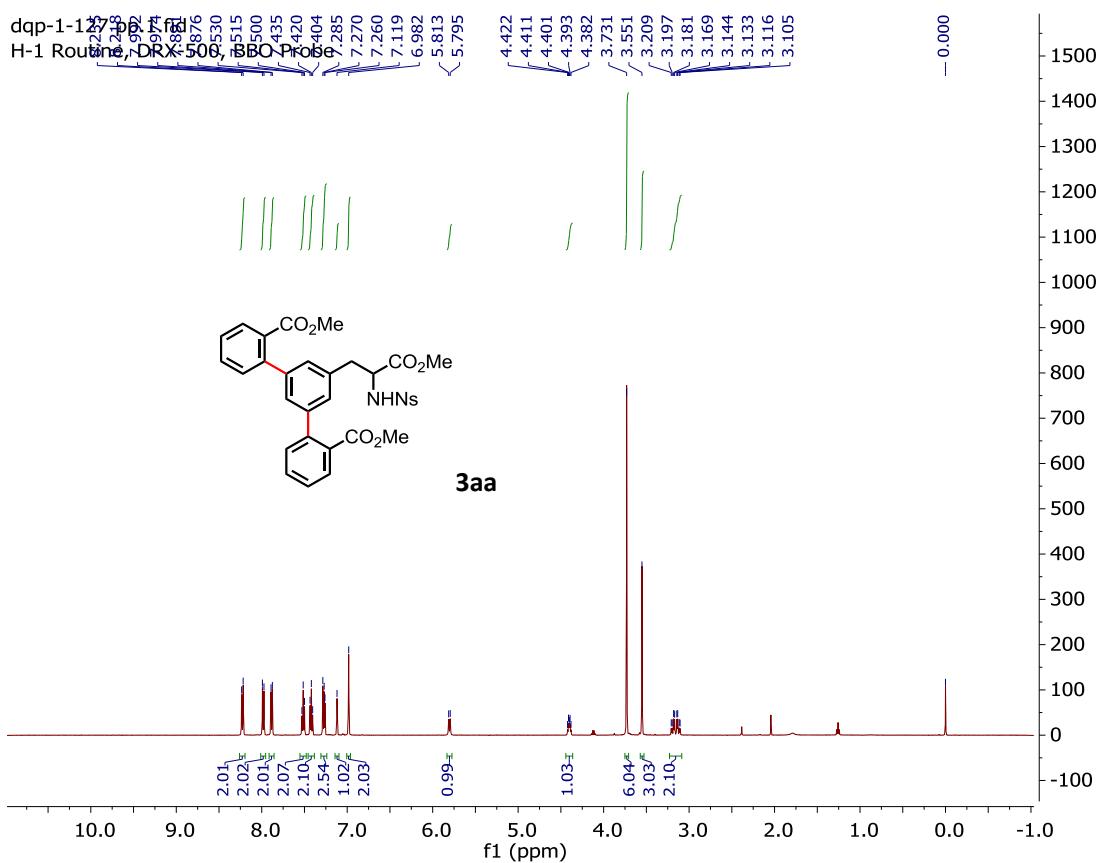
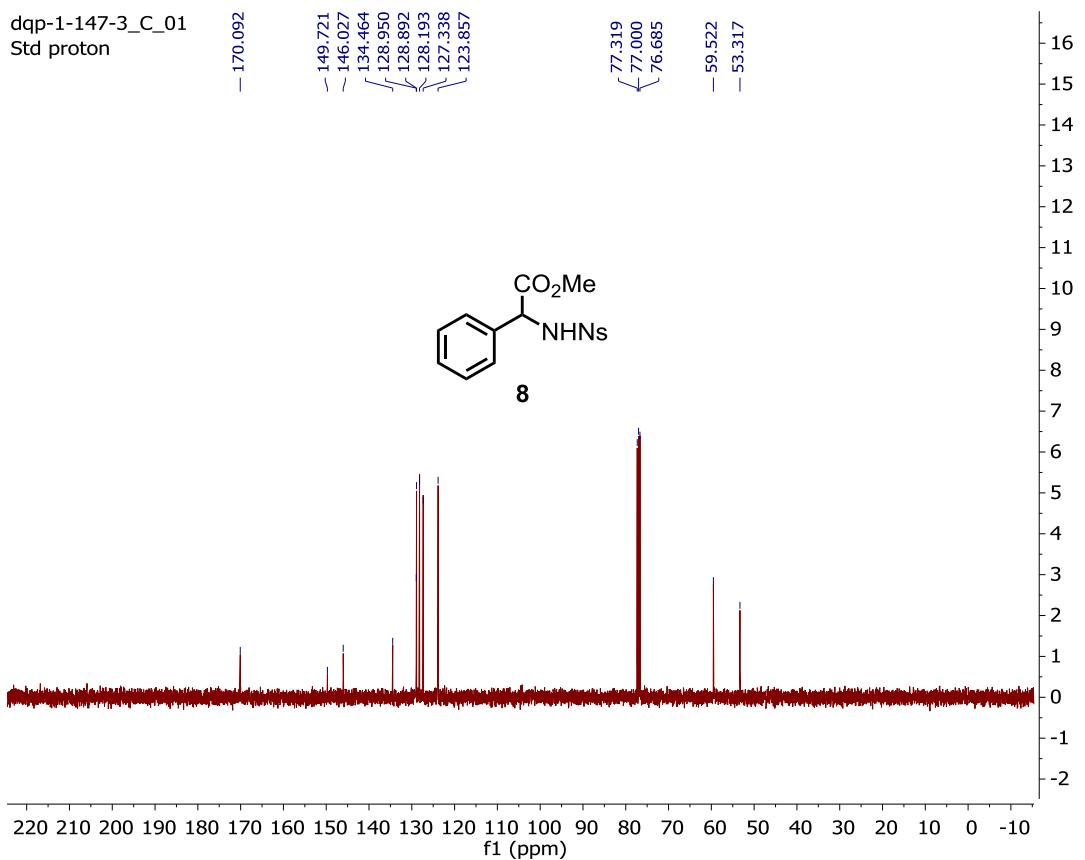
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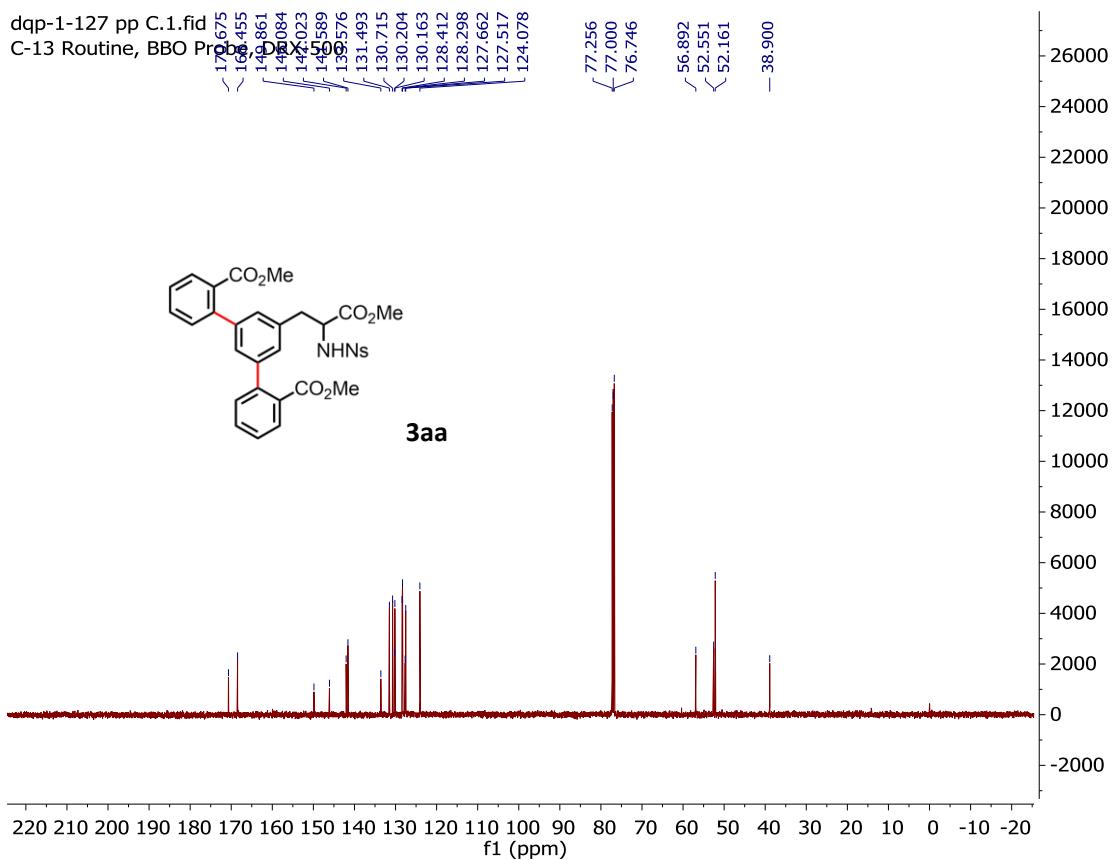
C-13 Routine, BBO



220 210 20







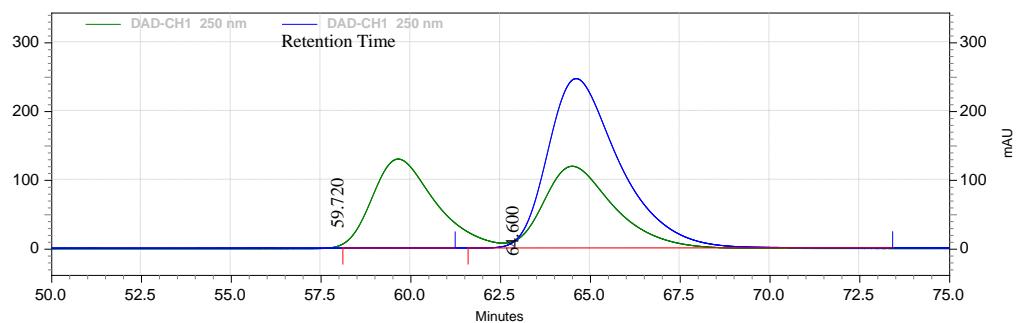
Area % Report

Data File: C:\EZChrom
 Elite\Enterprise\Projects\Default\Data\DPQ\114-2-D-p-20%-0.5mL-ADH

Method: C:\EZChrom Elite\Enterprise\Projects\Default\Method\A 75 min without fc 0.5 ml per min.met

Acquired: 6/4/2015 6:08:22 PM

Printed: 8/27/2015 10:23:44 PM

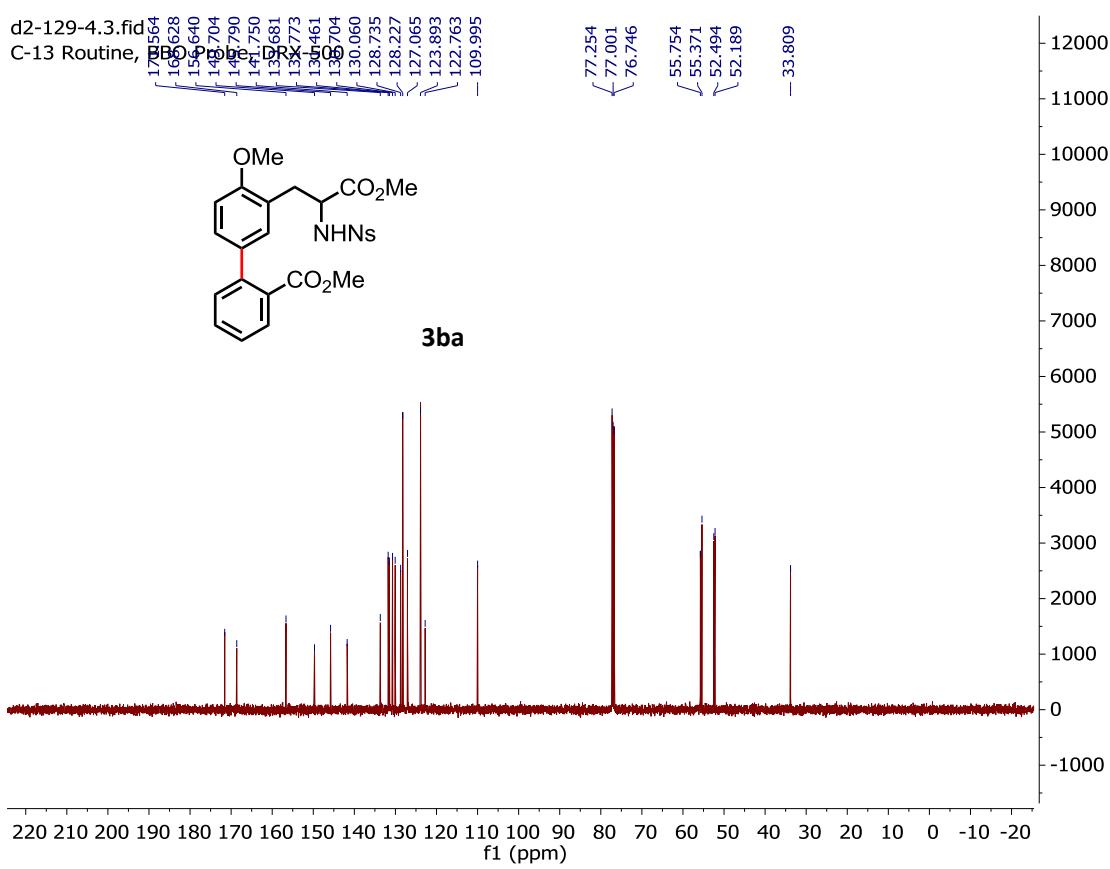
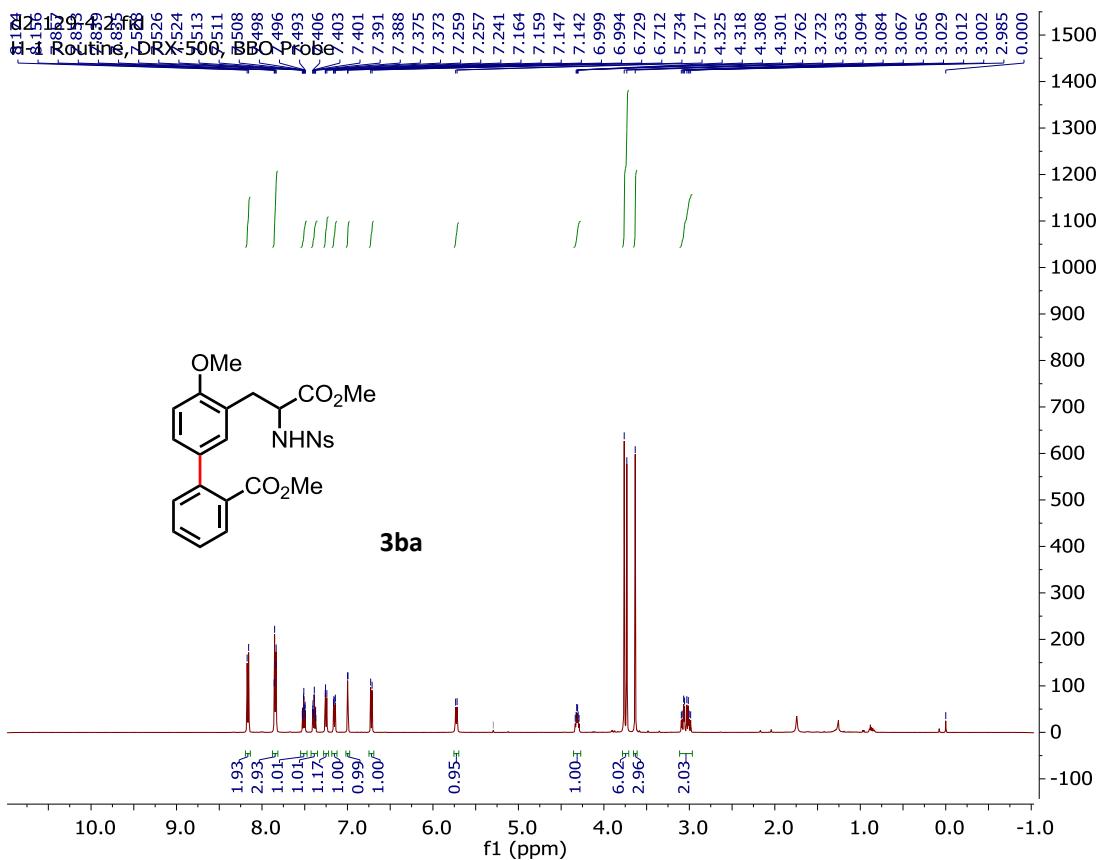


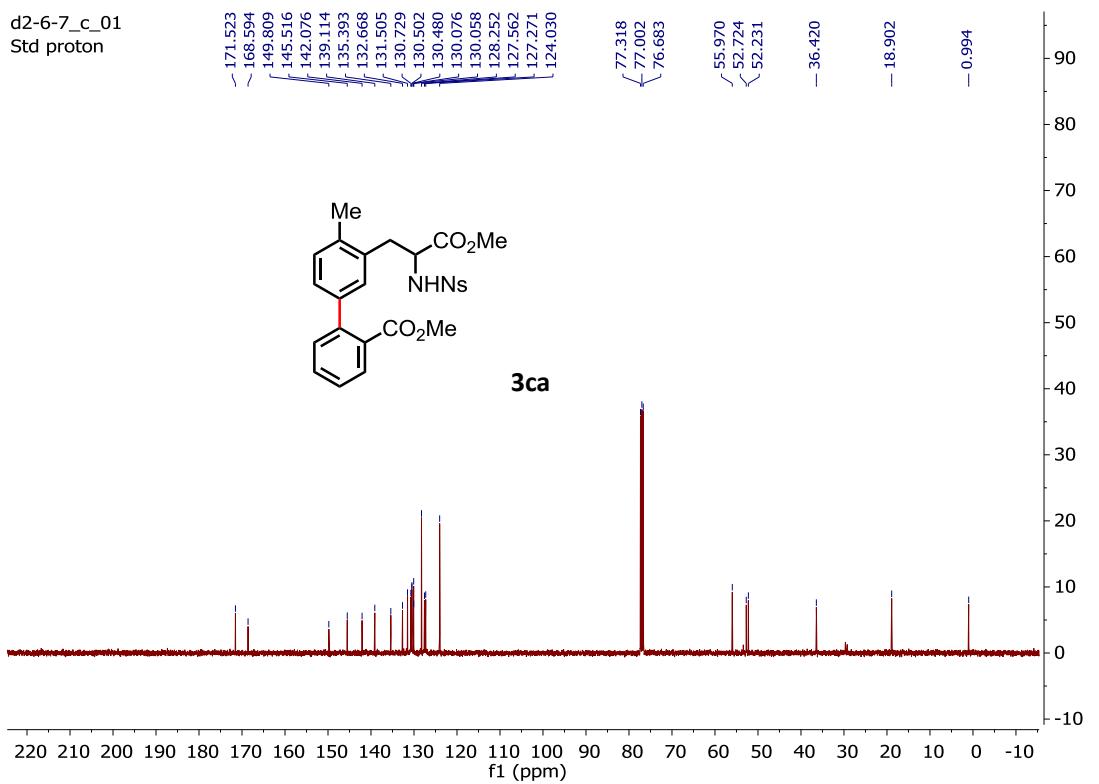
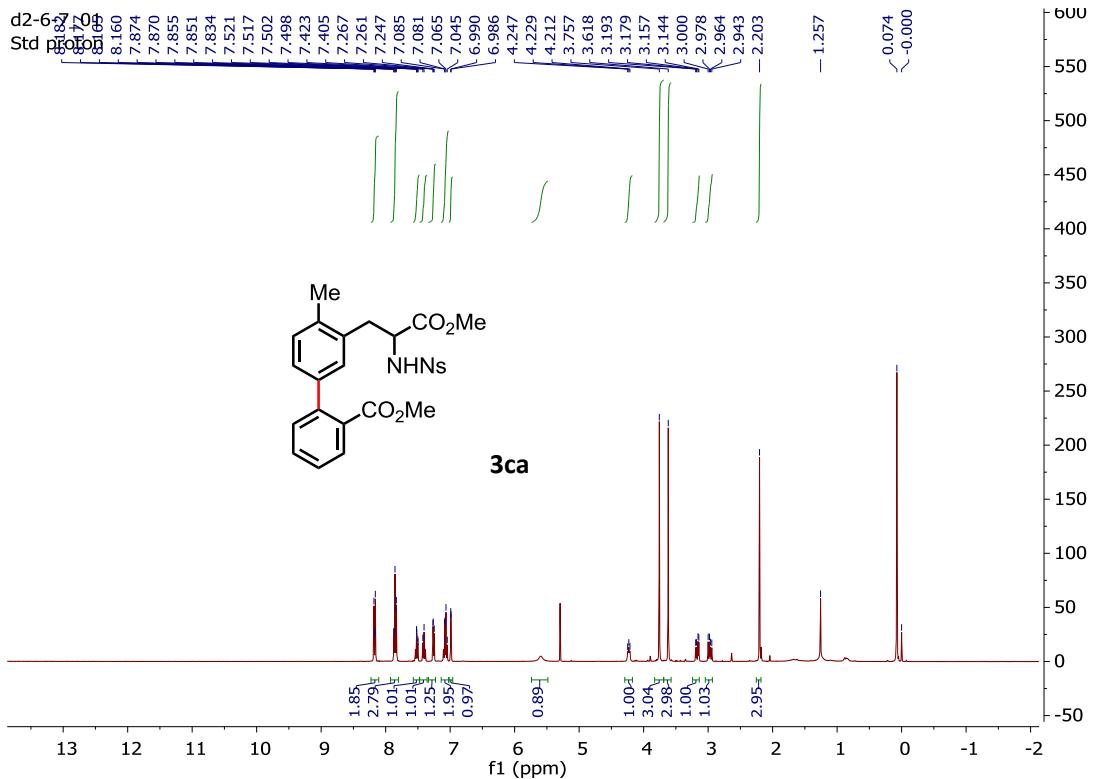
DAD-CH1 250

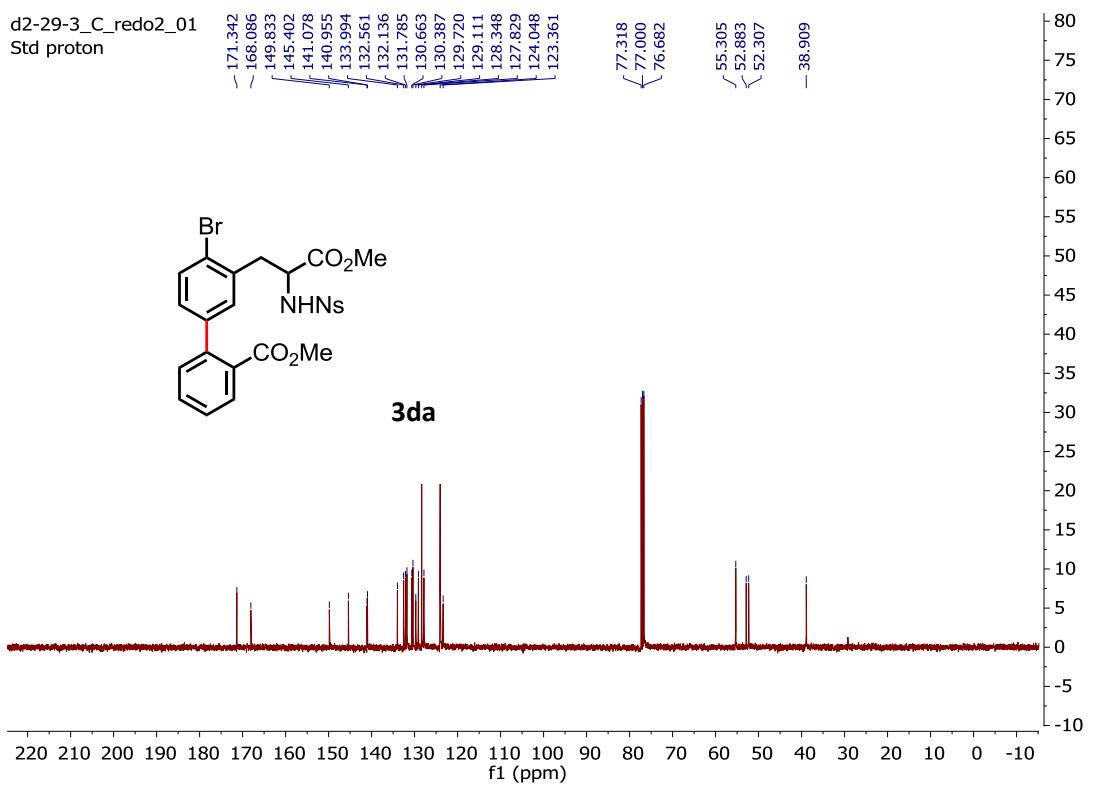
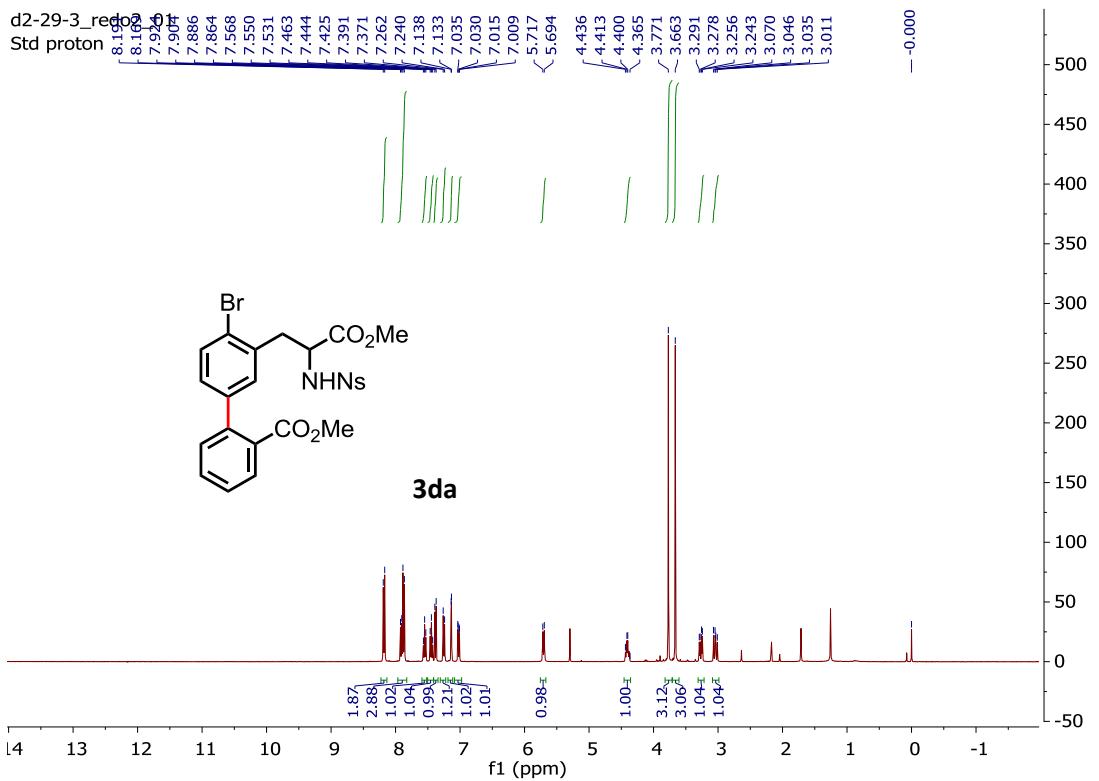
nm Results

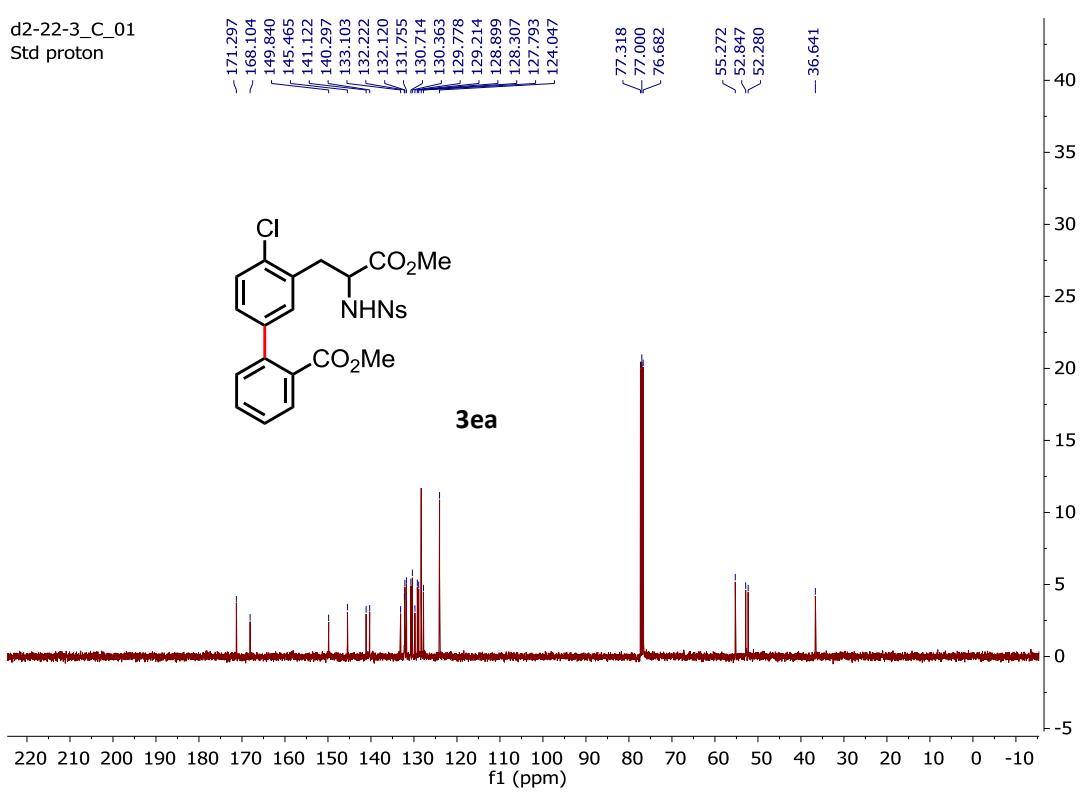
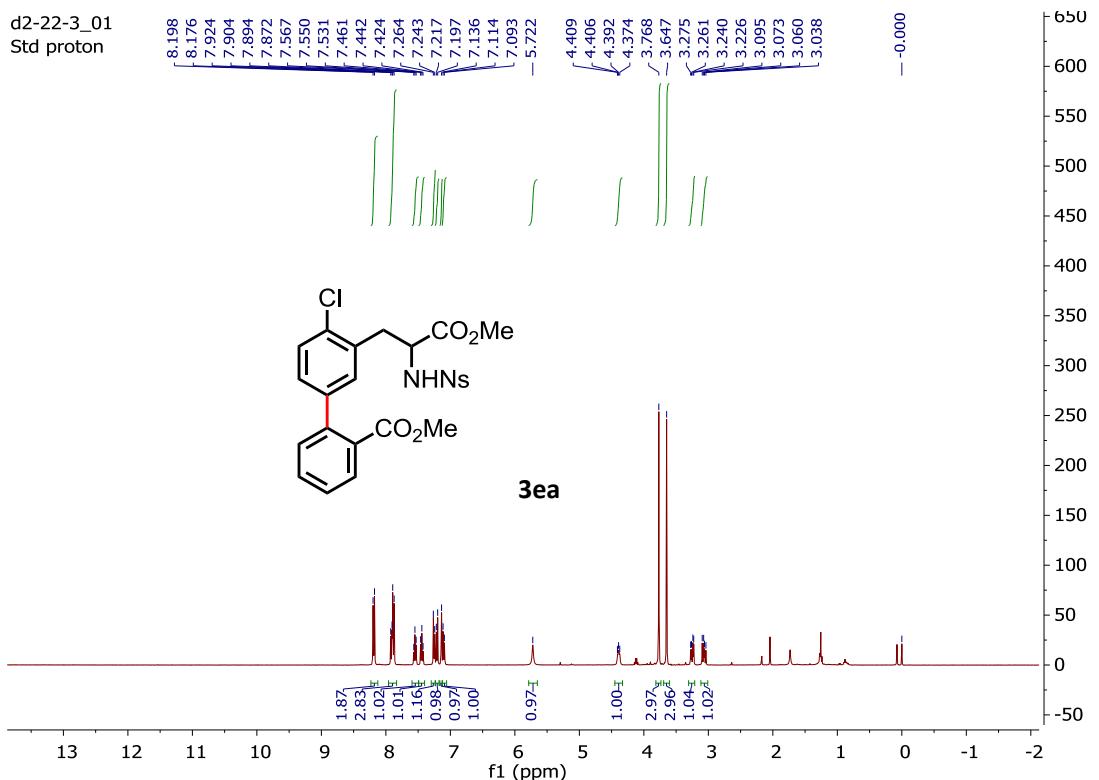
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64.600	137108036	99.98	984748	99.96

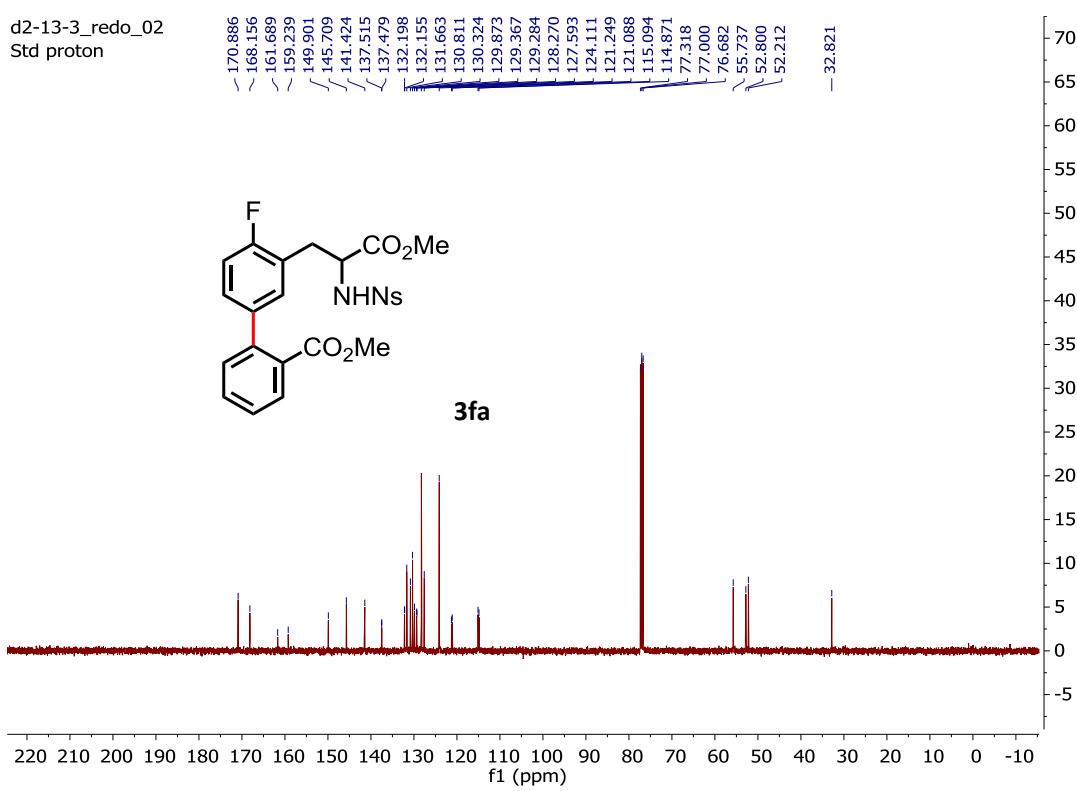
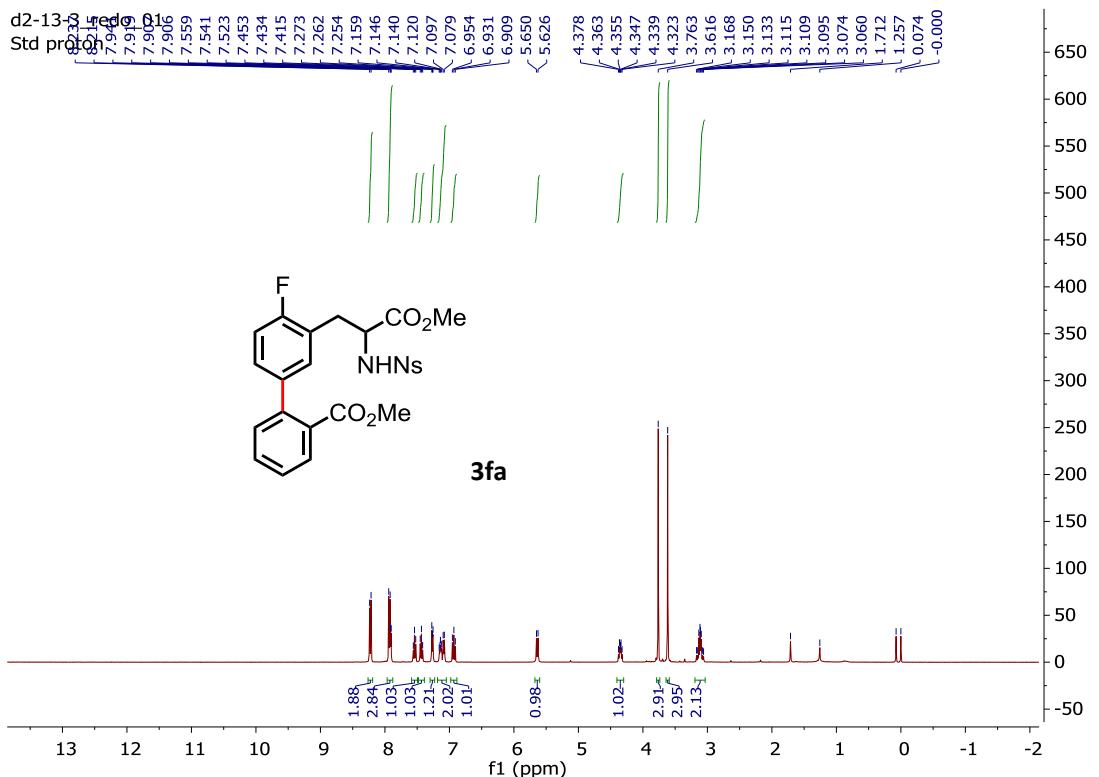
Totals	137140633	100.00	985124	100.00
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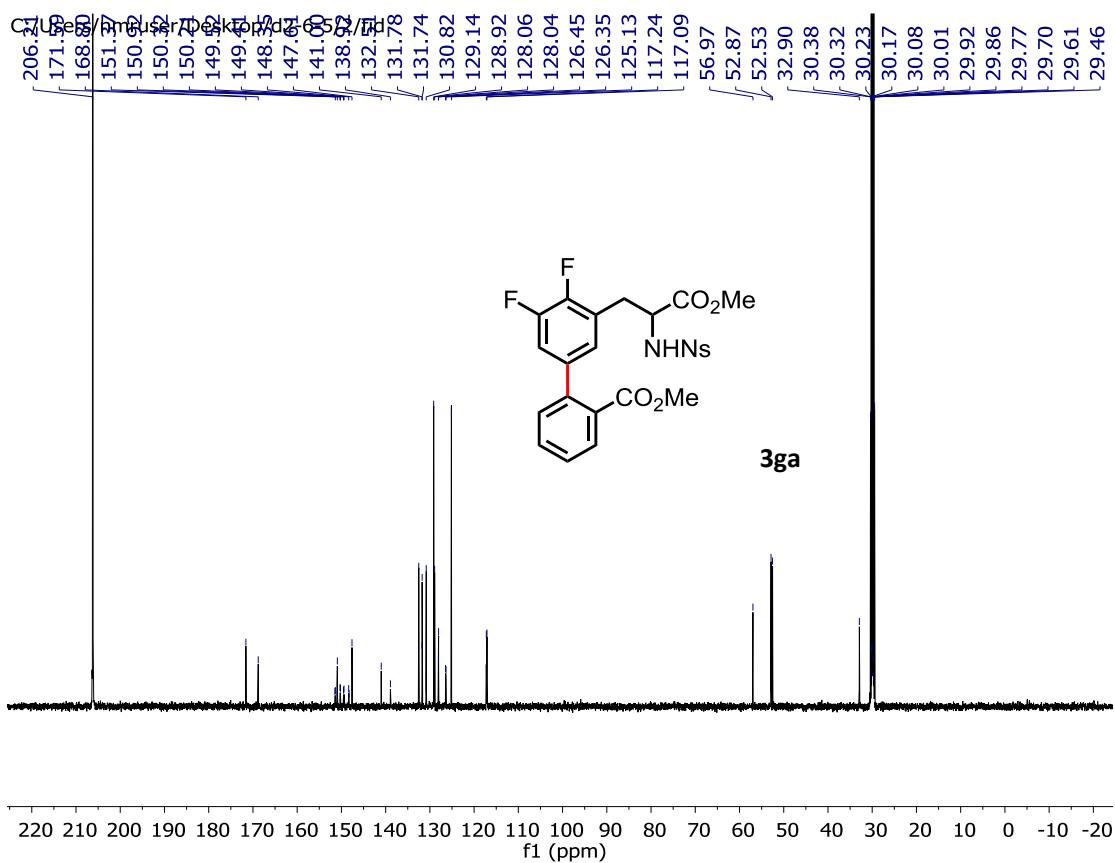
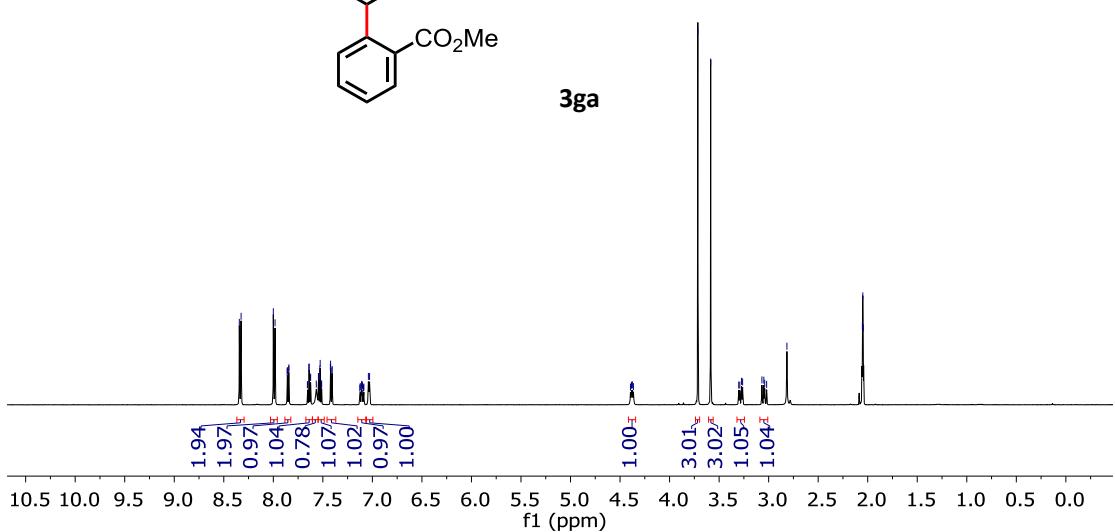


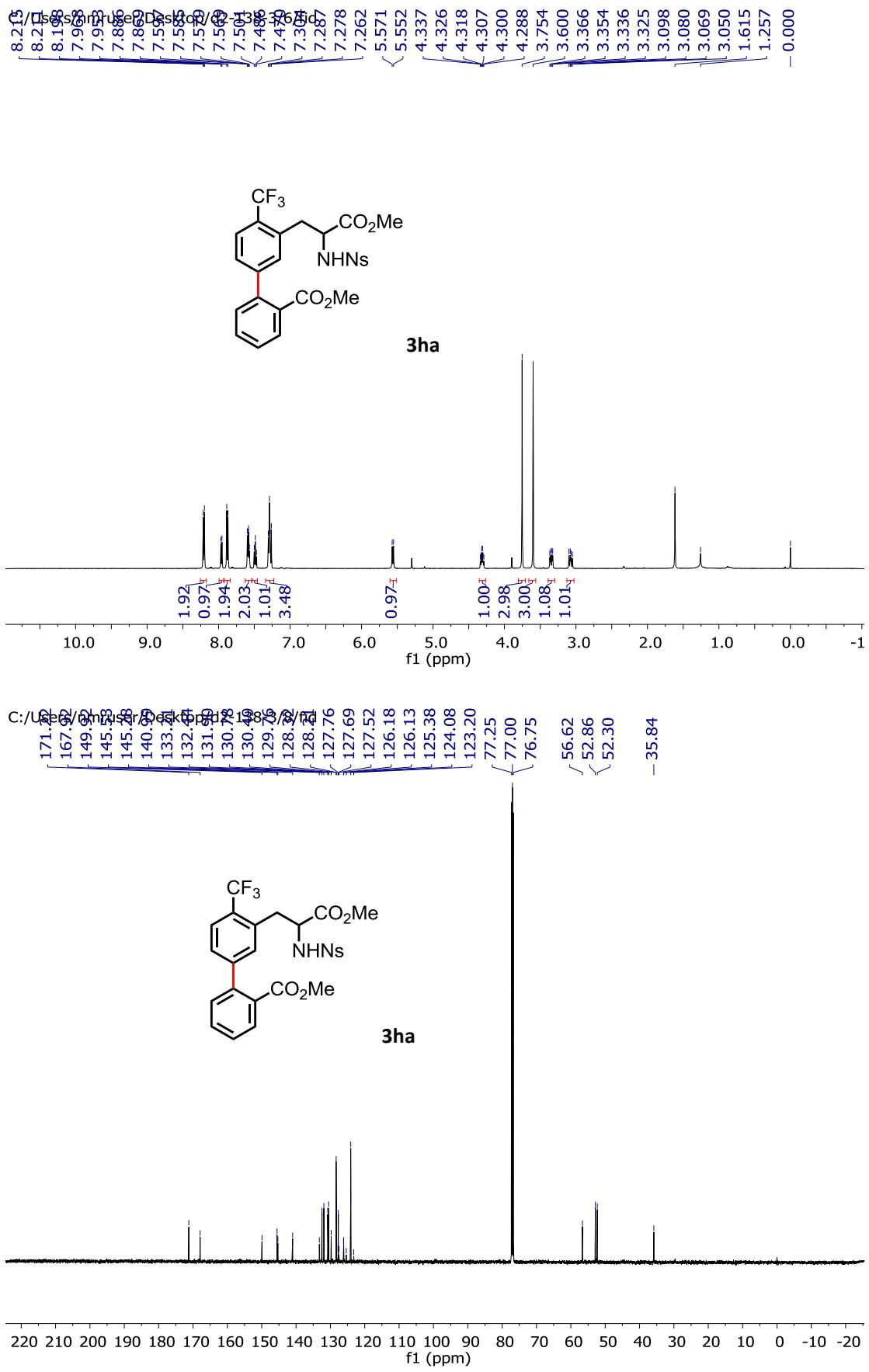


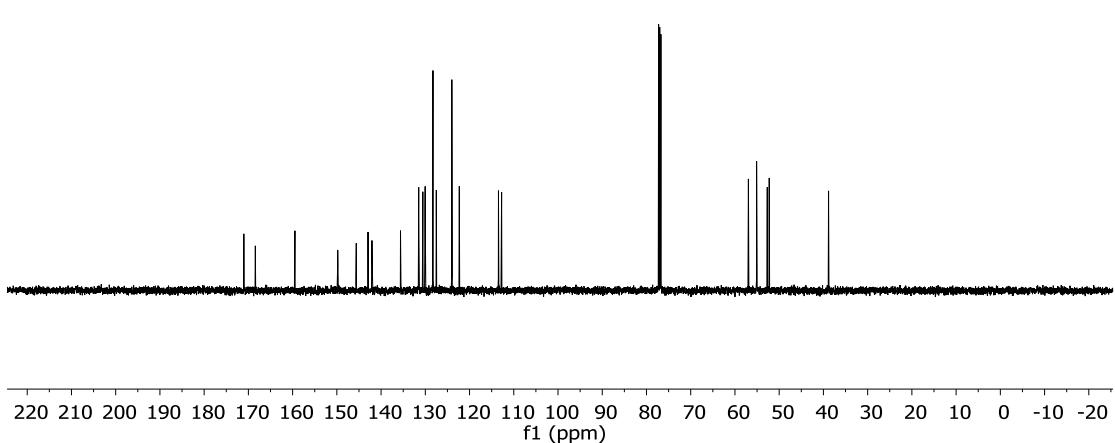
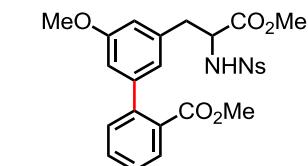
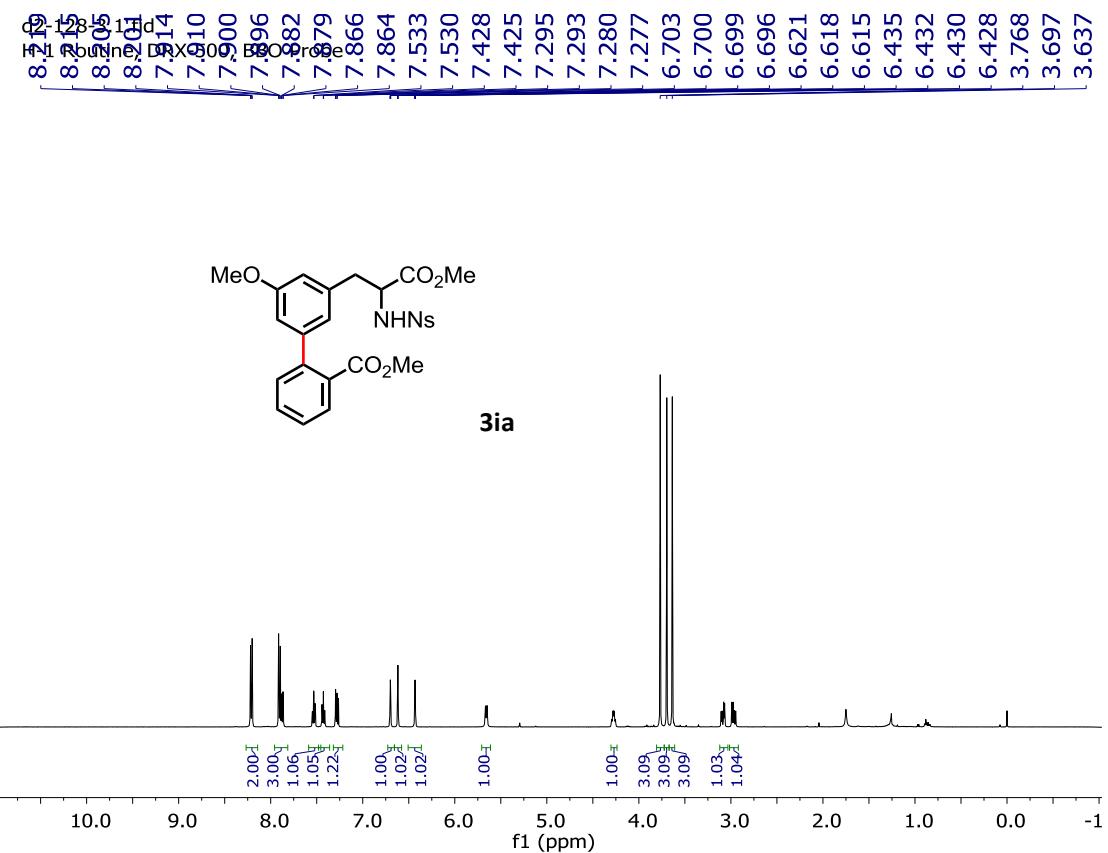


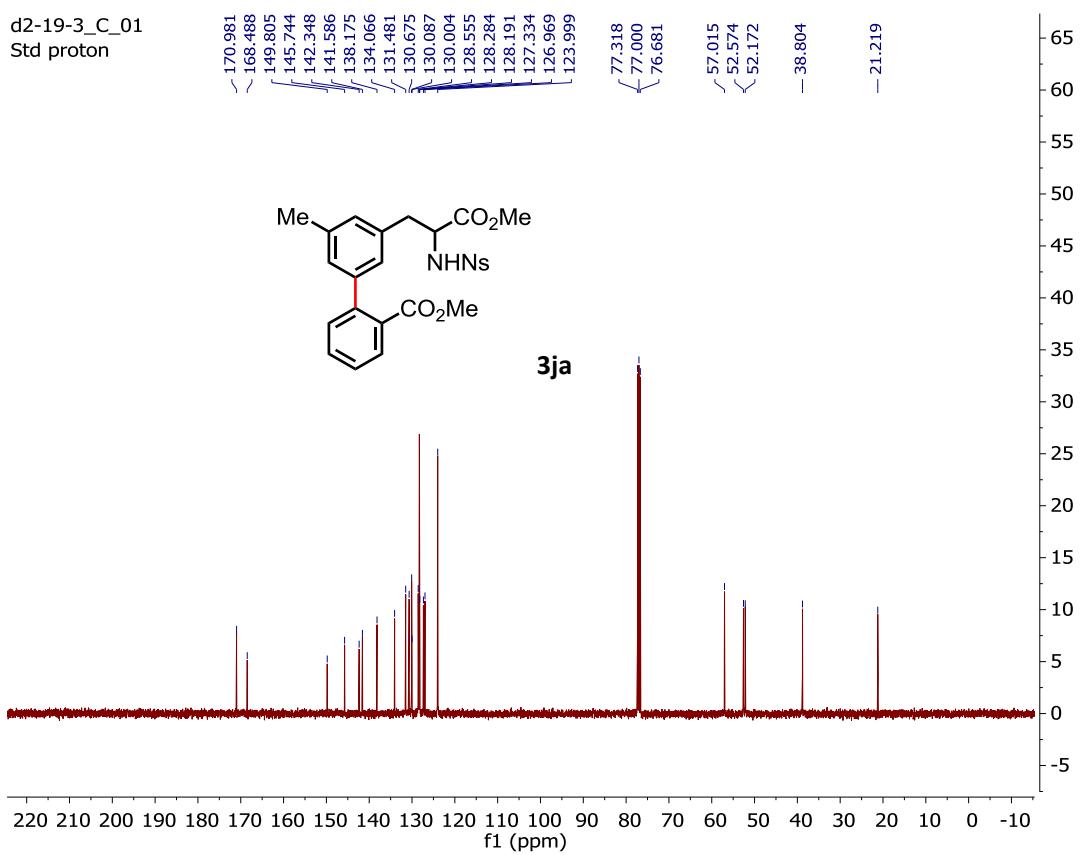
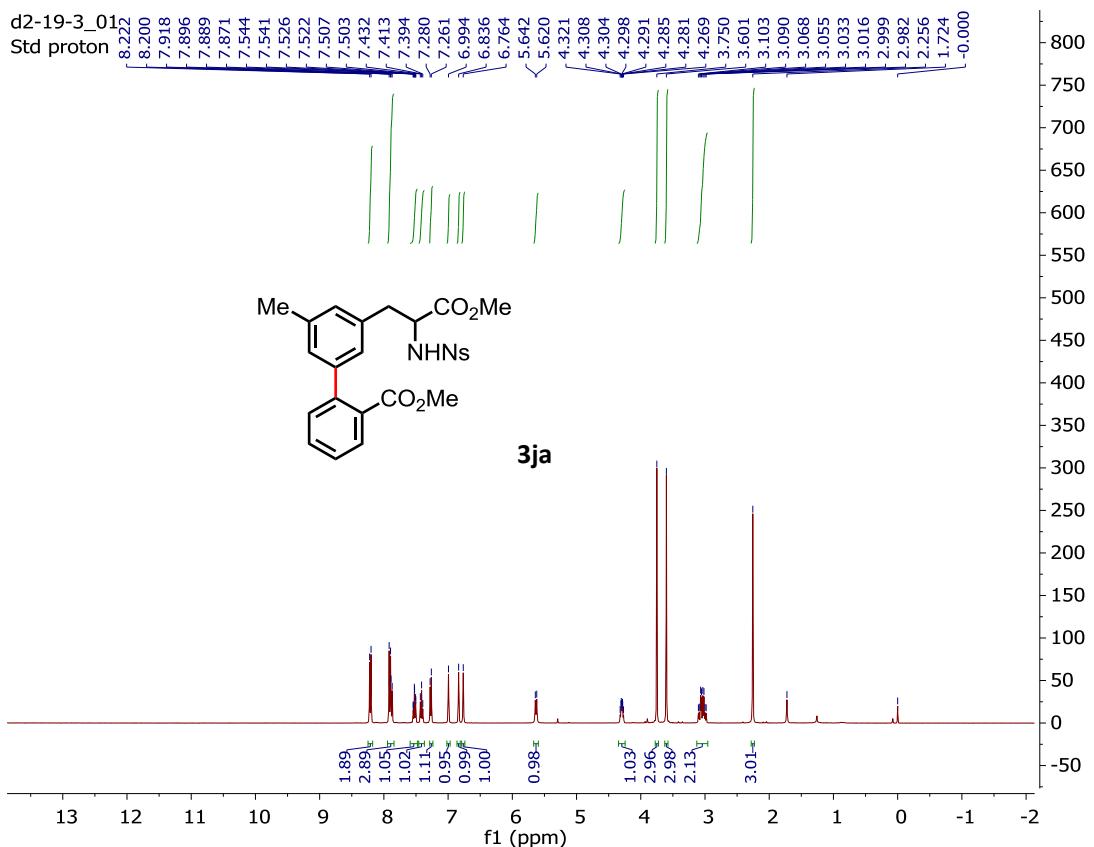


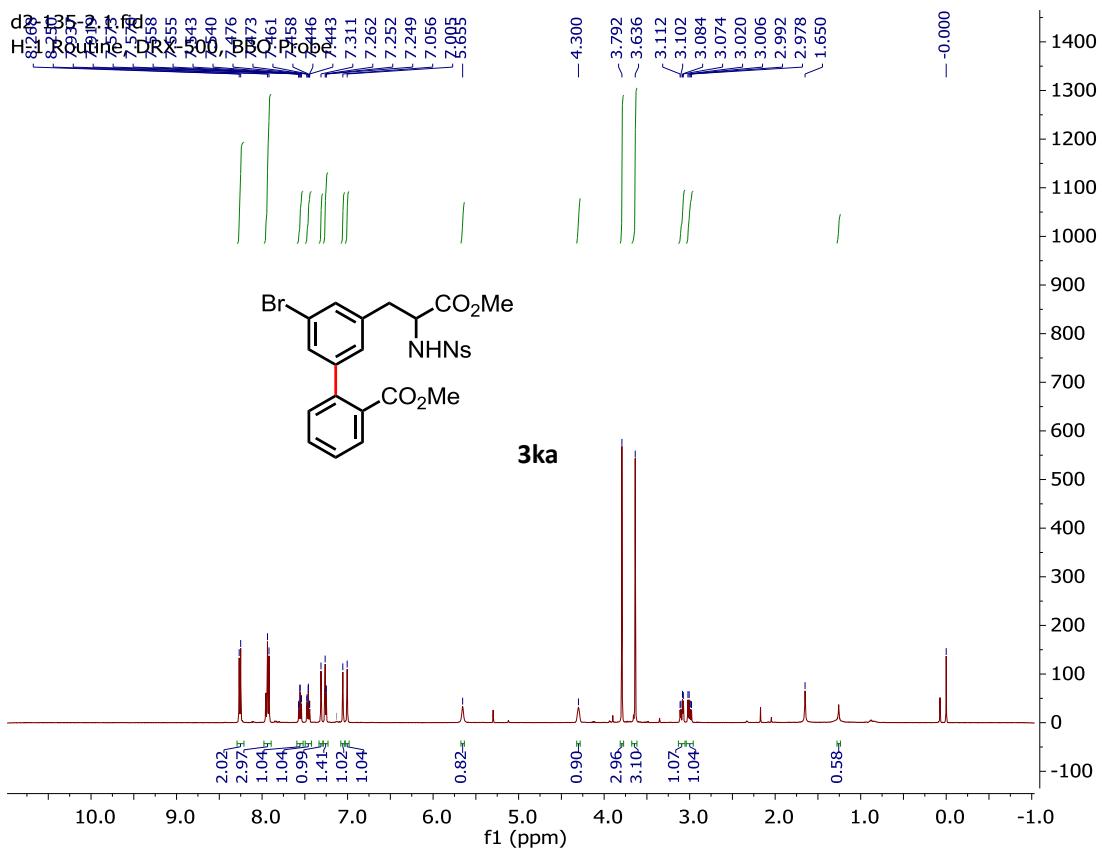


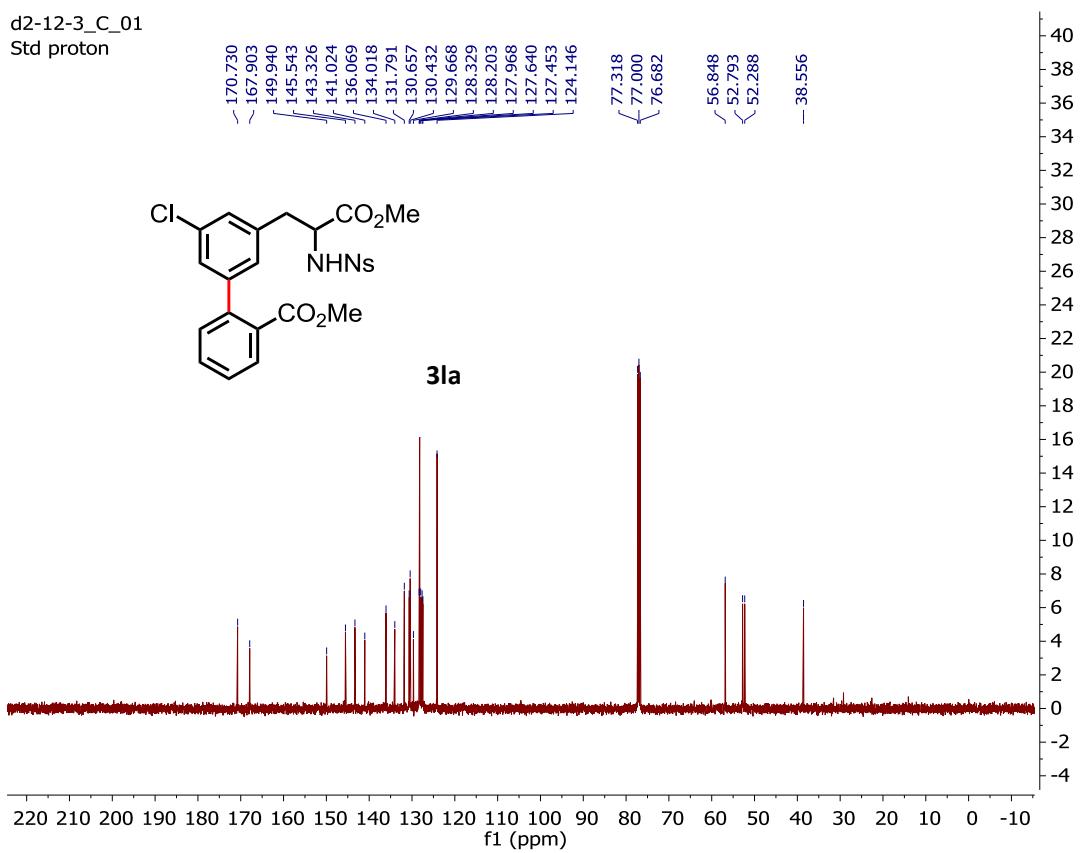
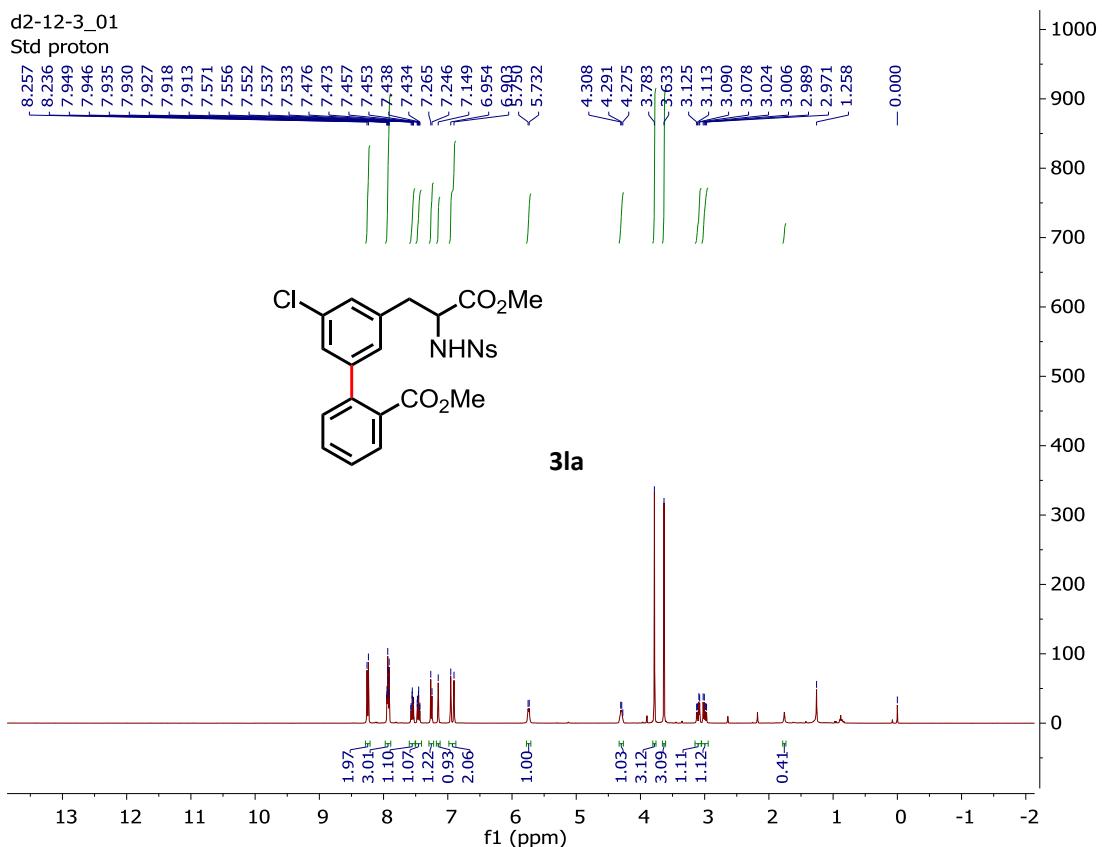




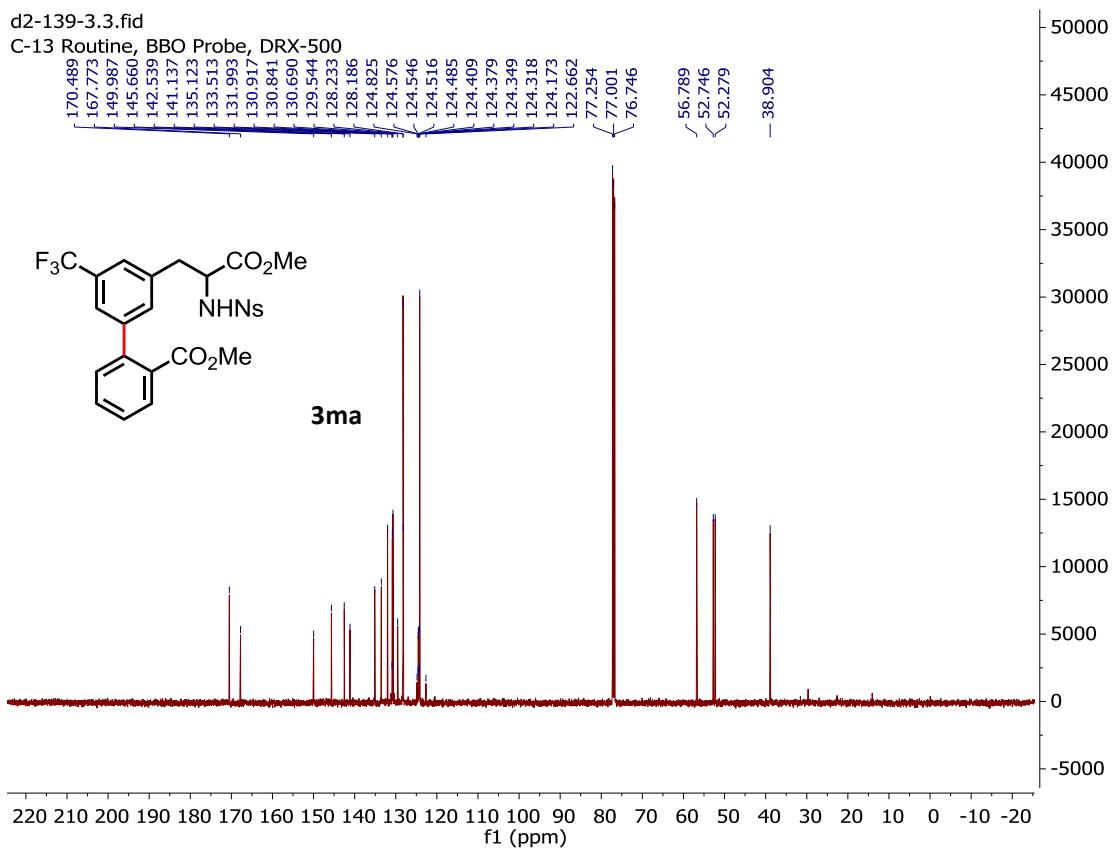
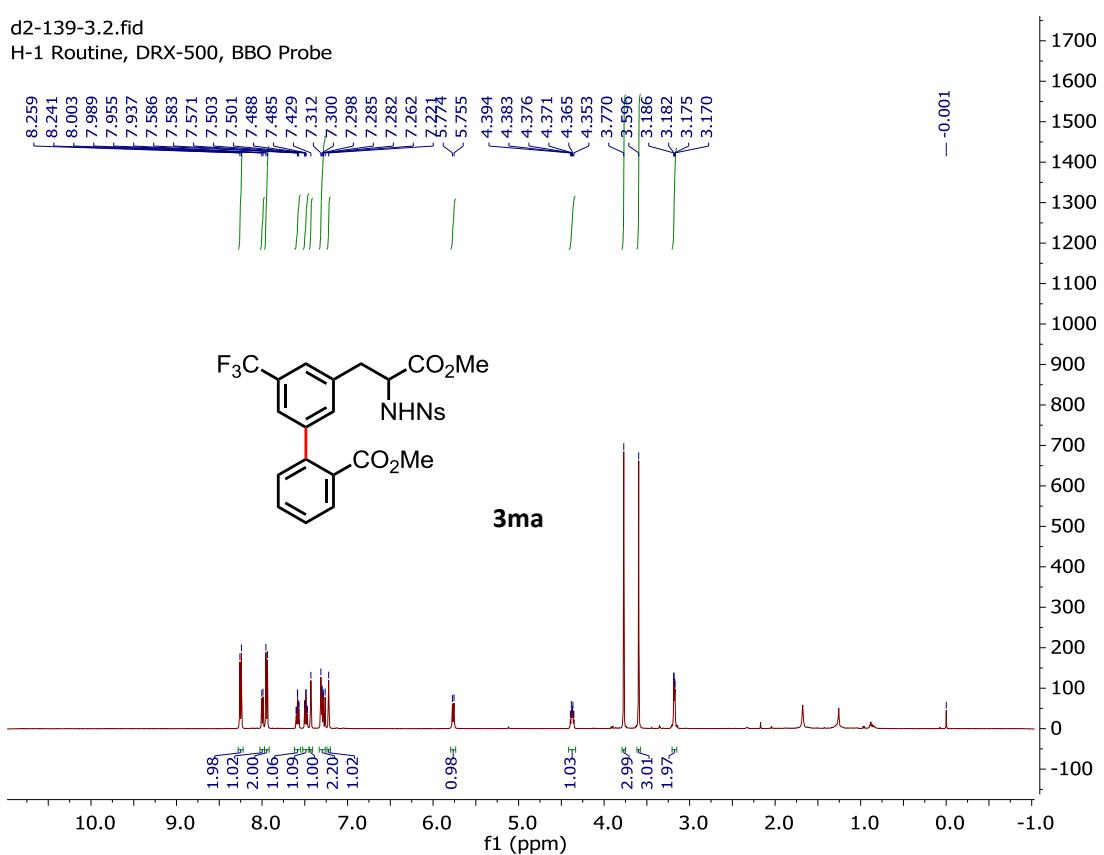


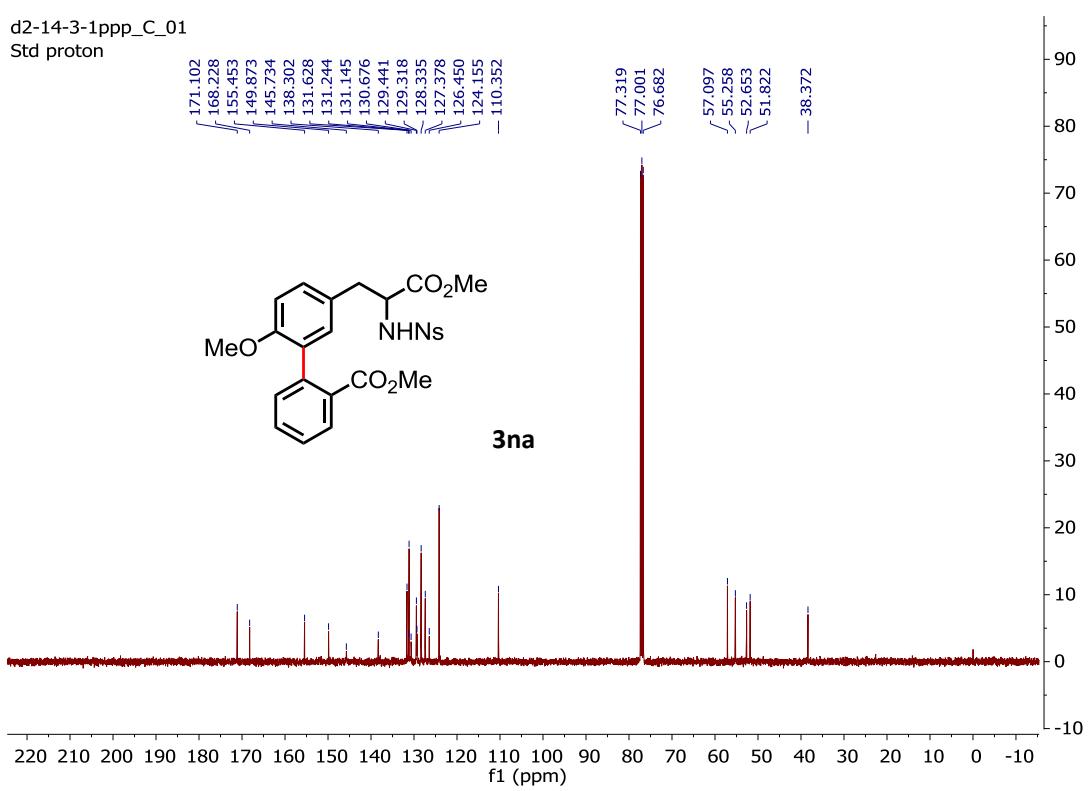
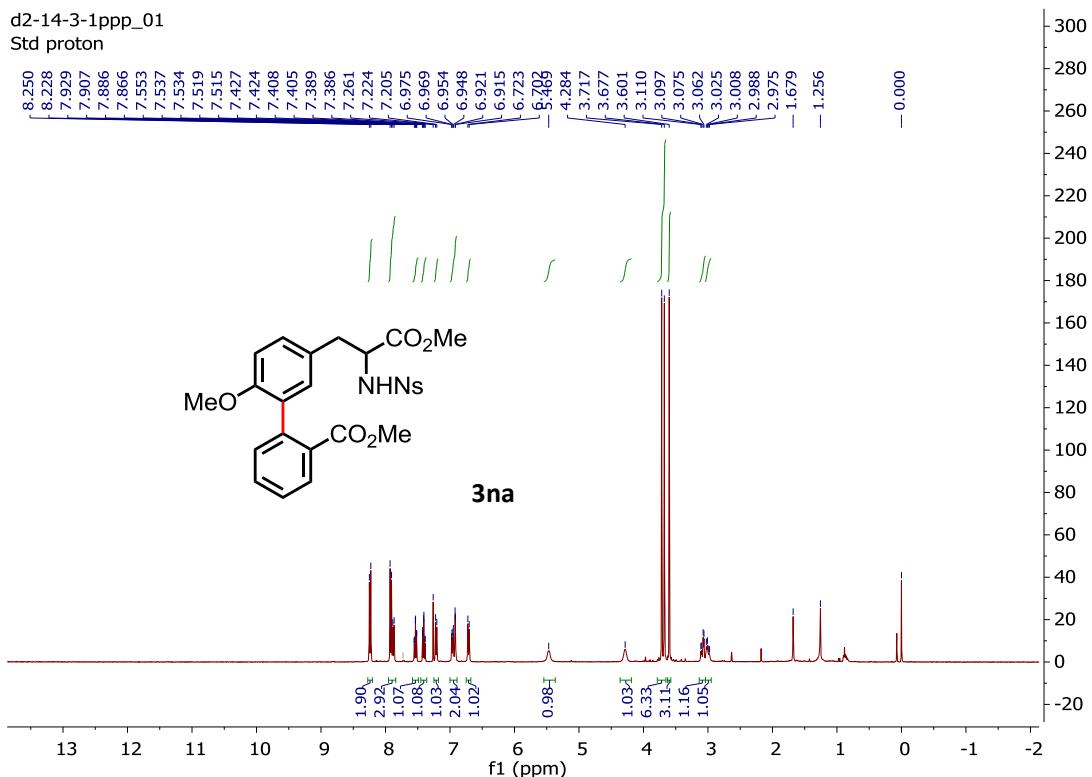


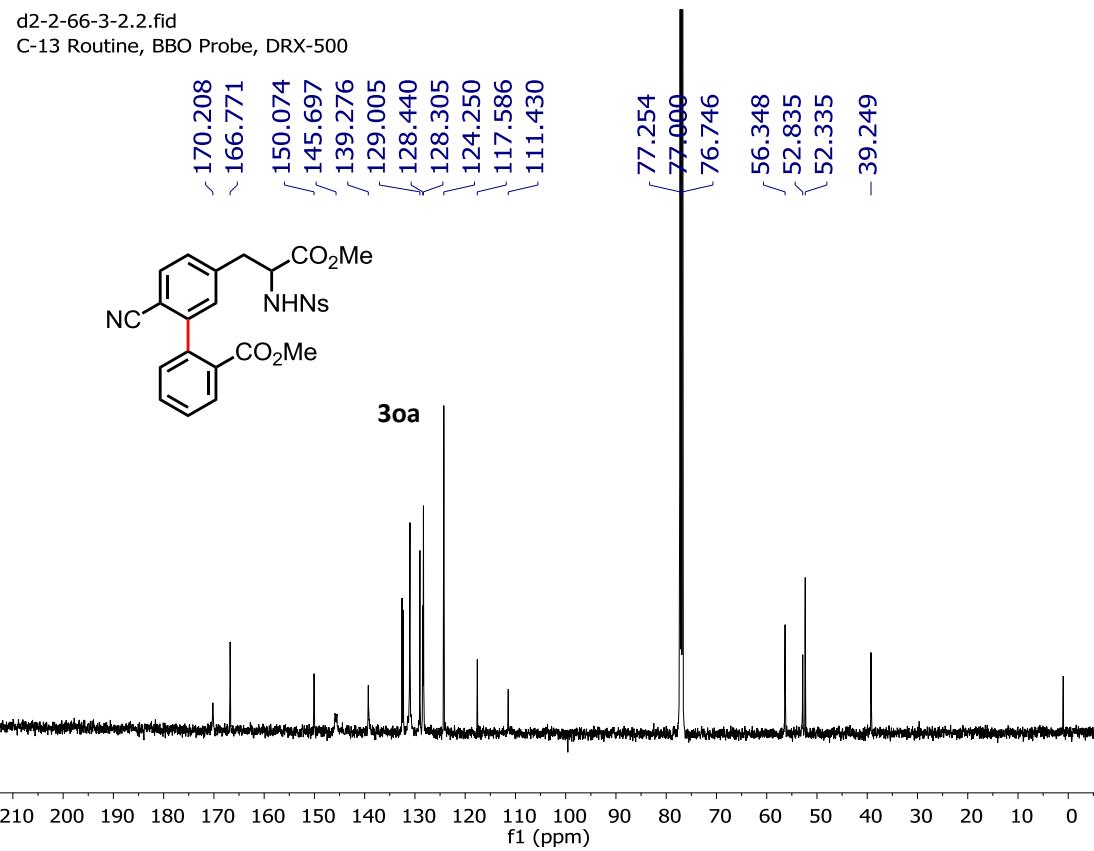
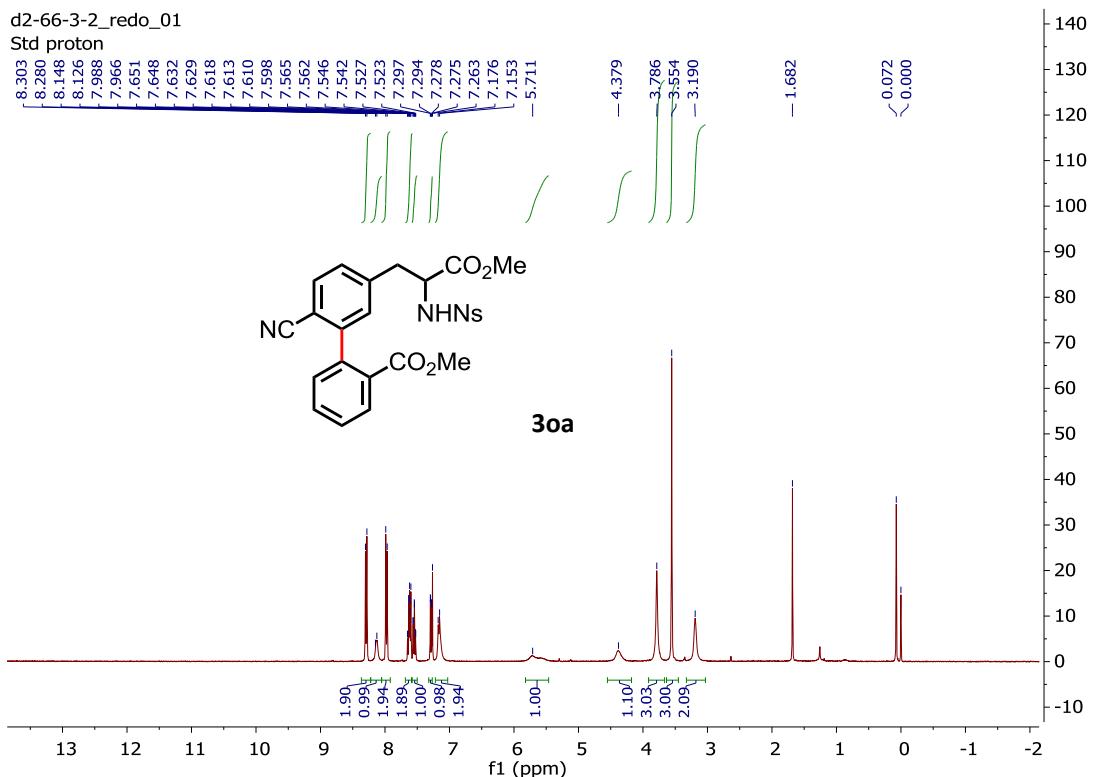




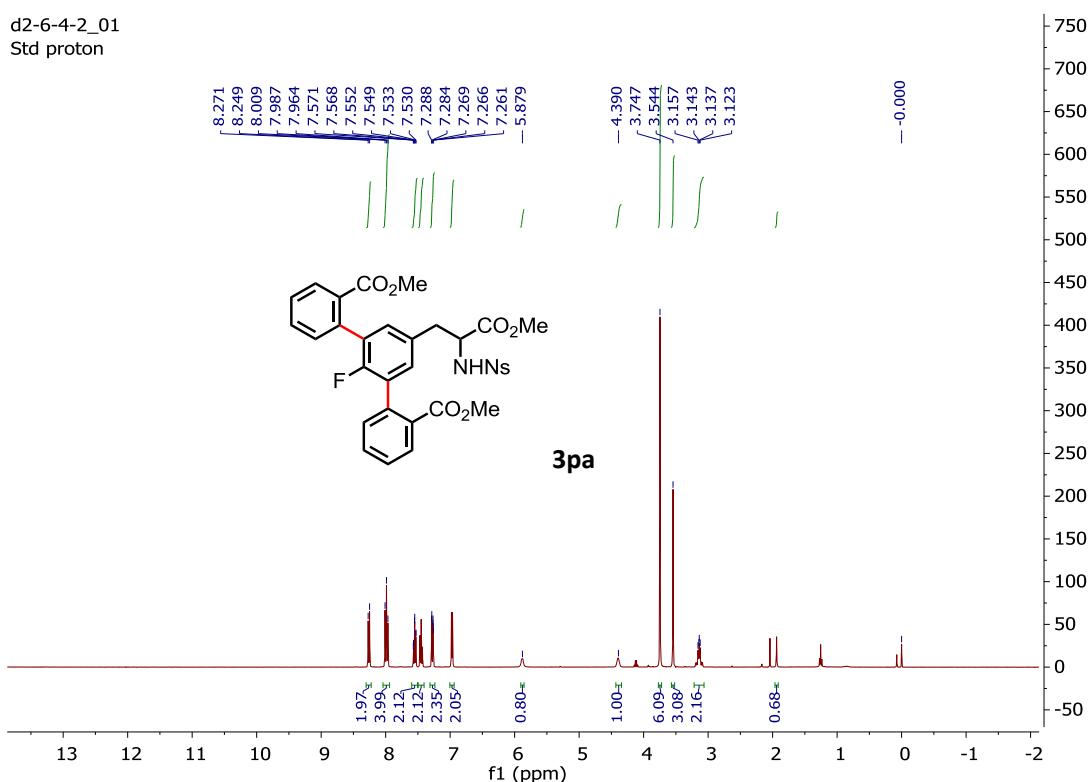
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H-1 Routine, DRX-500, BBO Probe



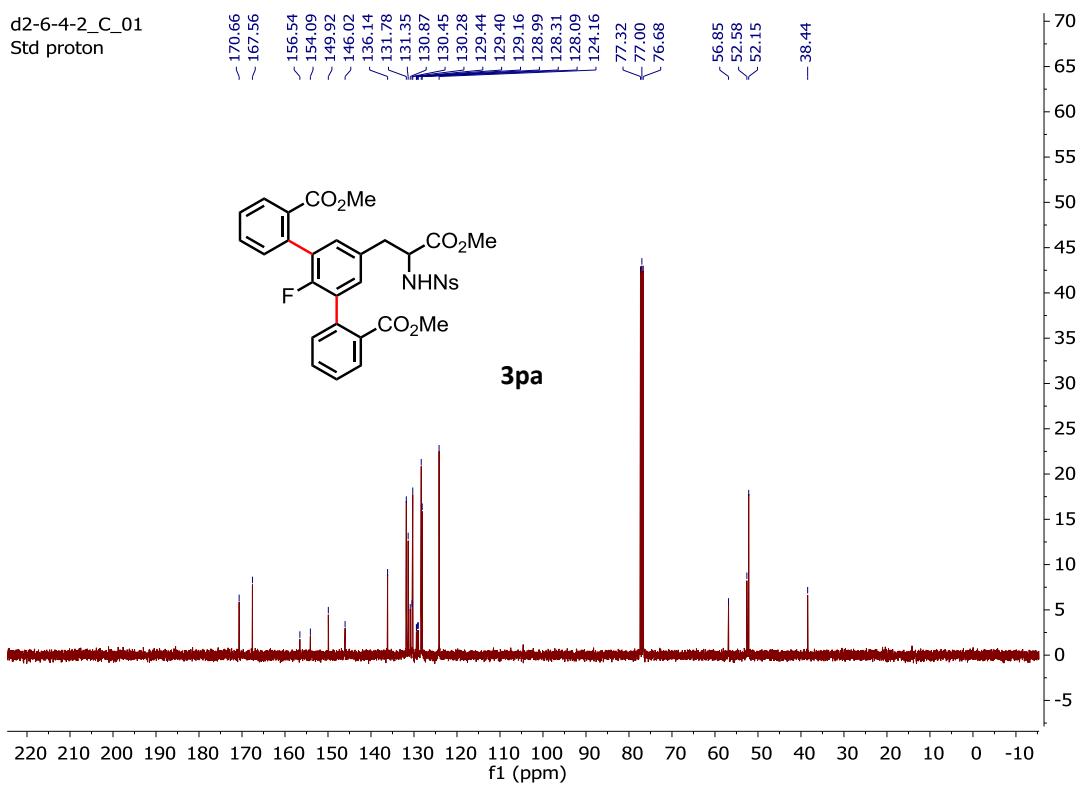




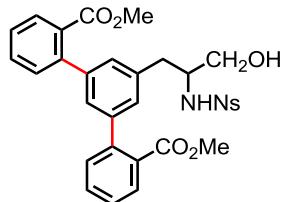
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Std proton



d2-6-4-2_C_01
Std proton

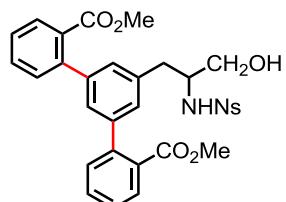


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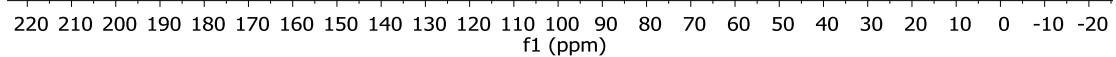


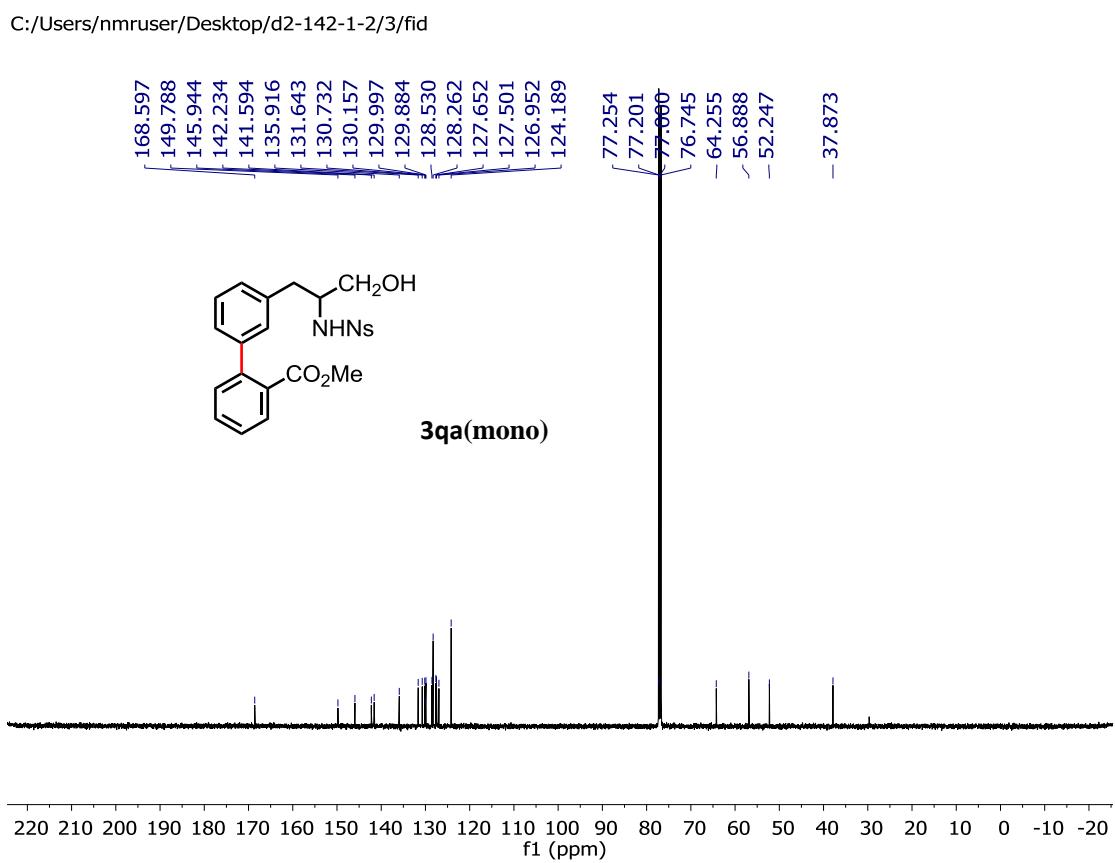
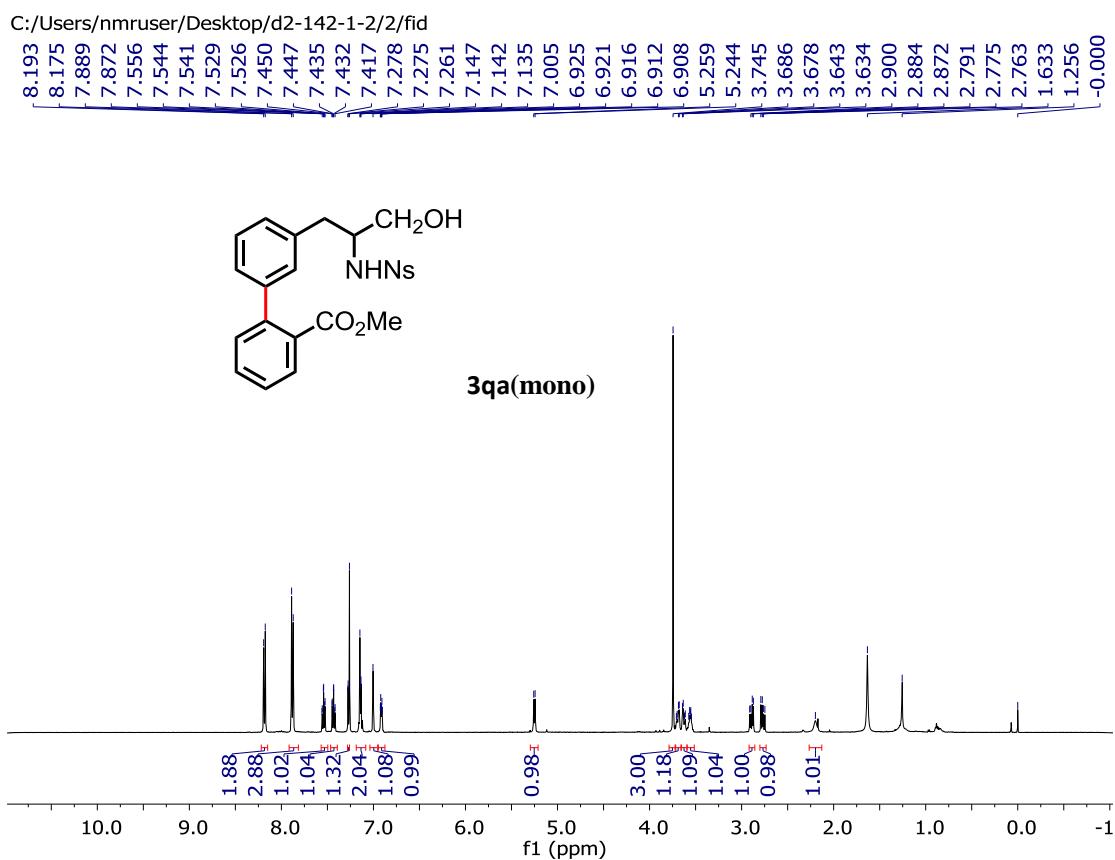
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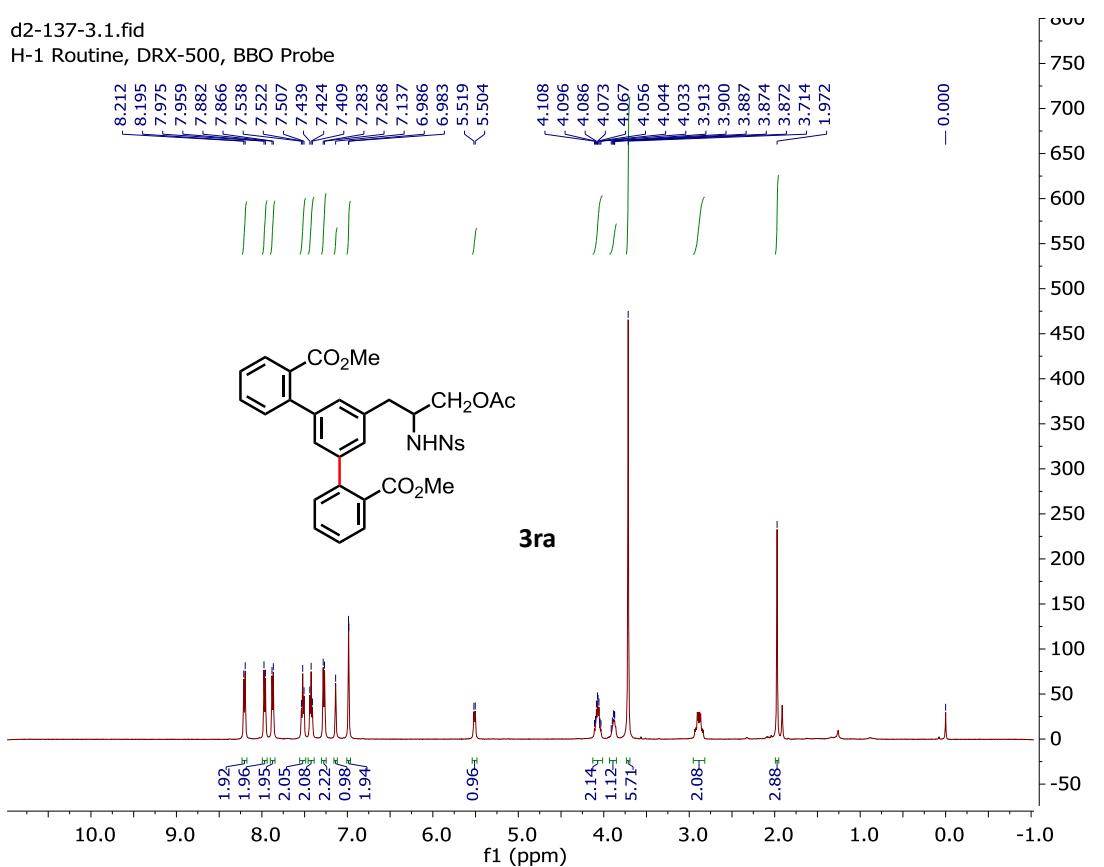


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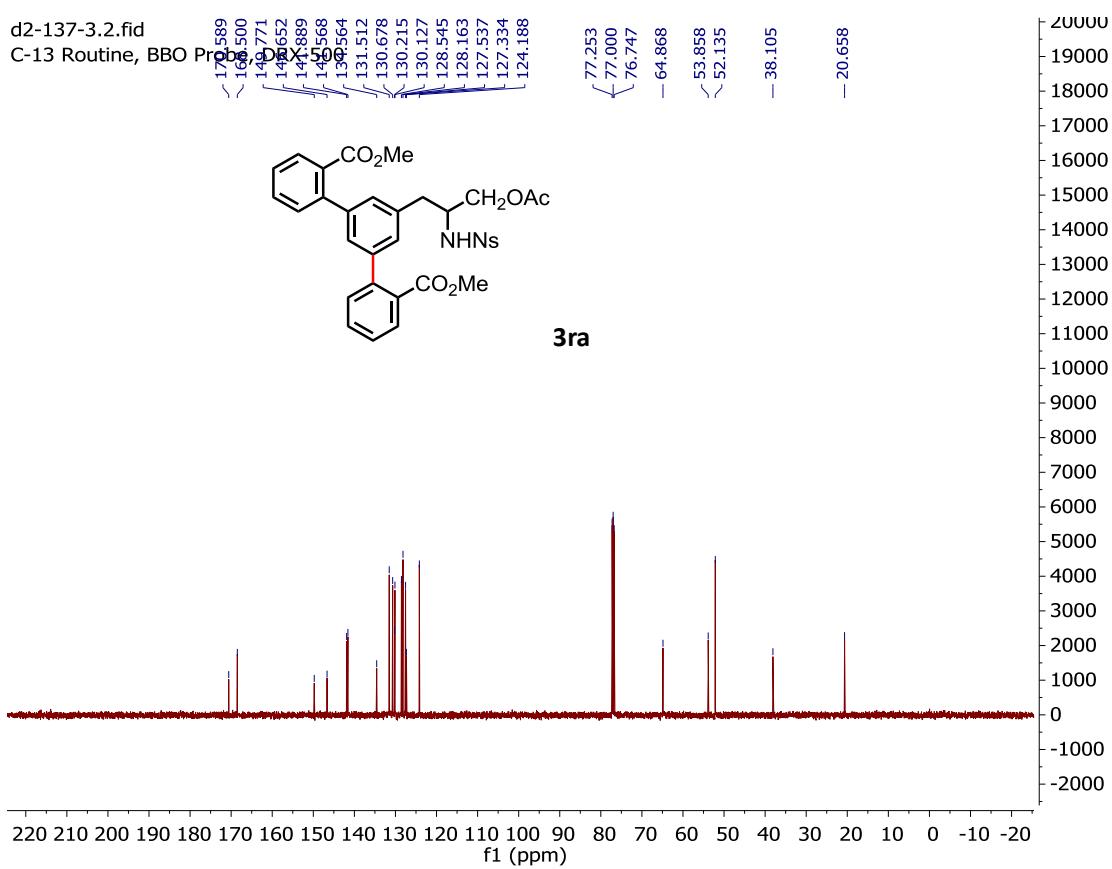




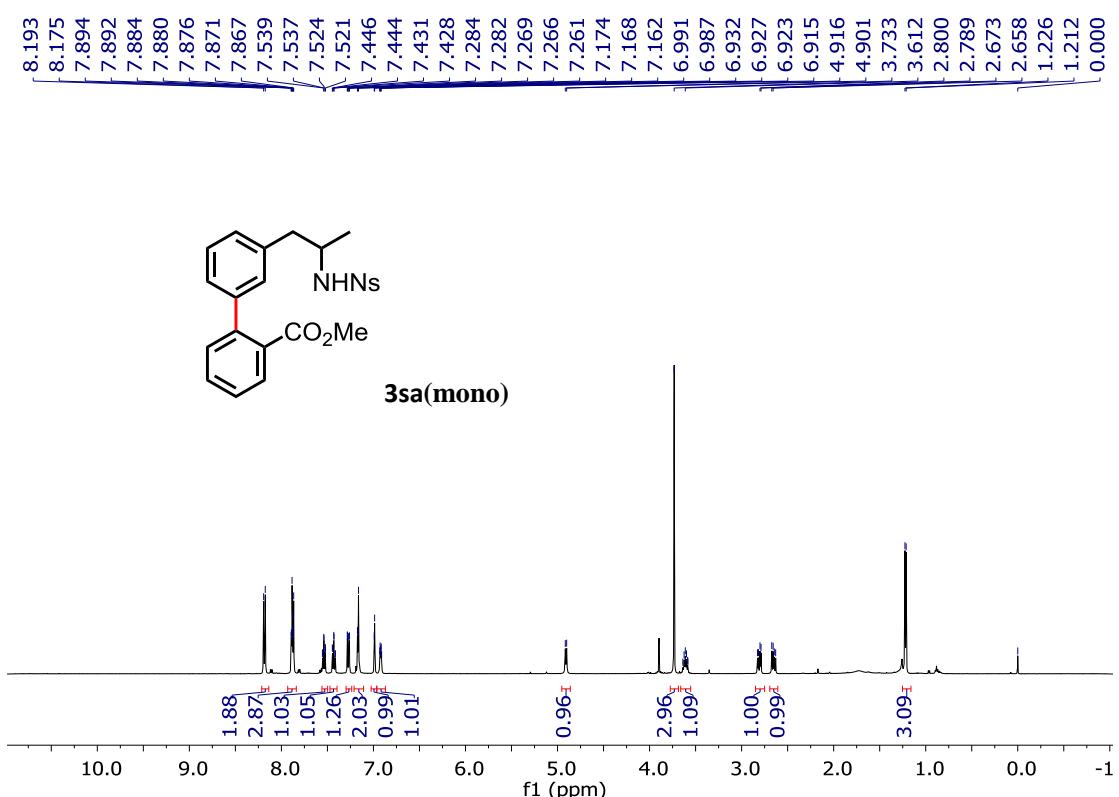
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H-1 Routine, DRX-500, BBO Probe



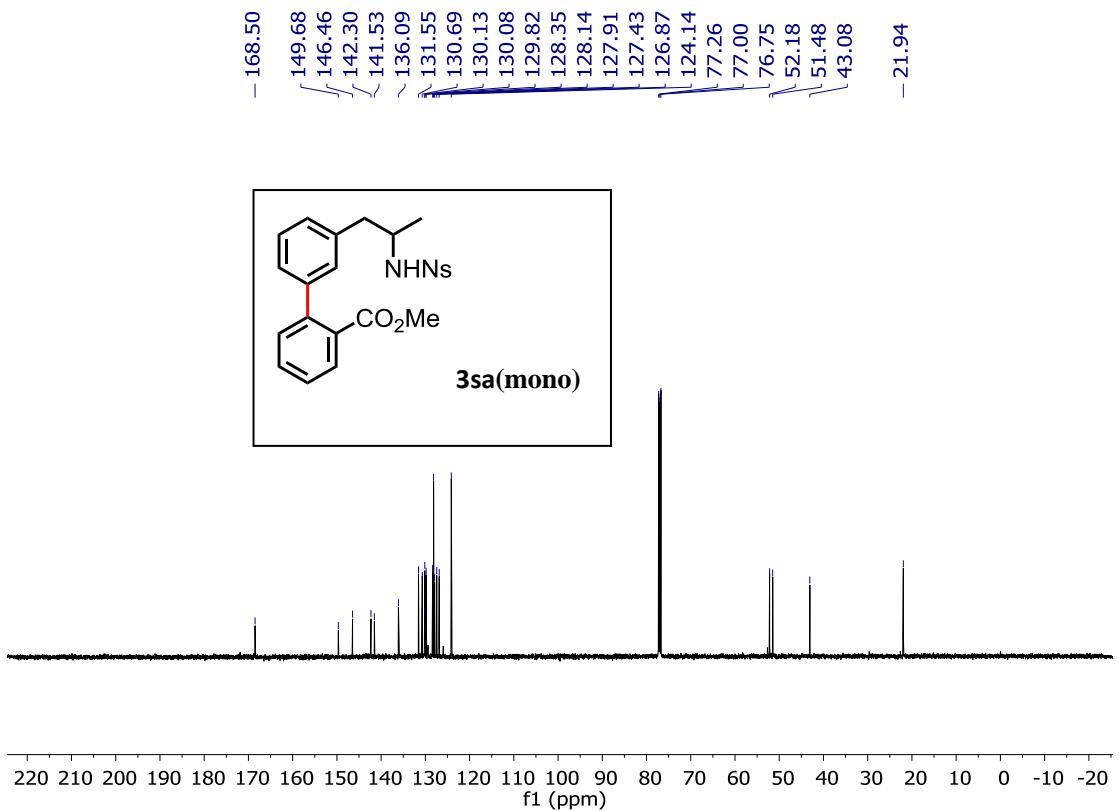
d2-137-3.2.fid
C-13 Routine, BBO Probe



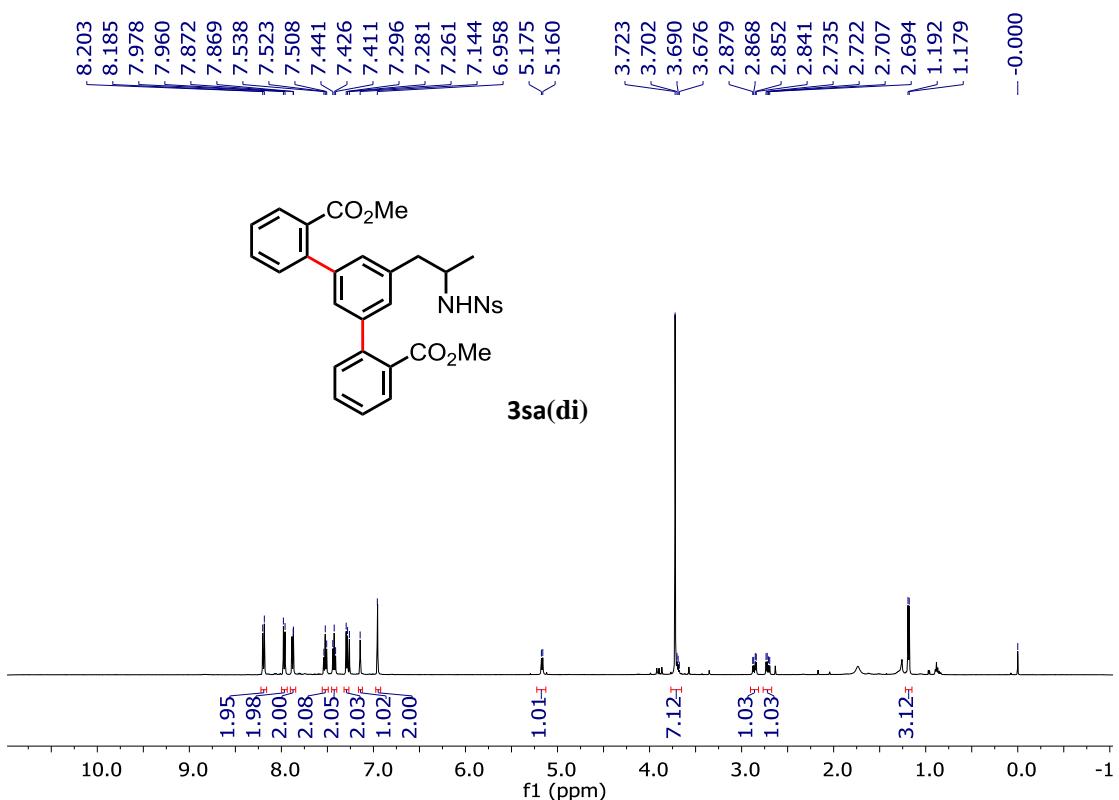
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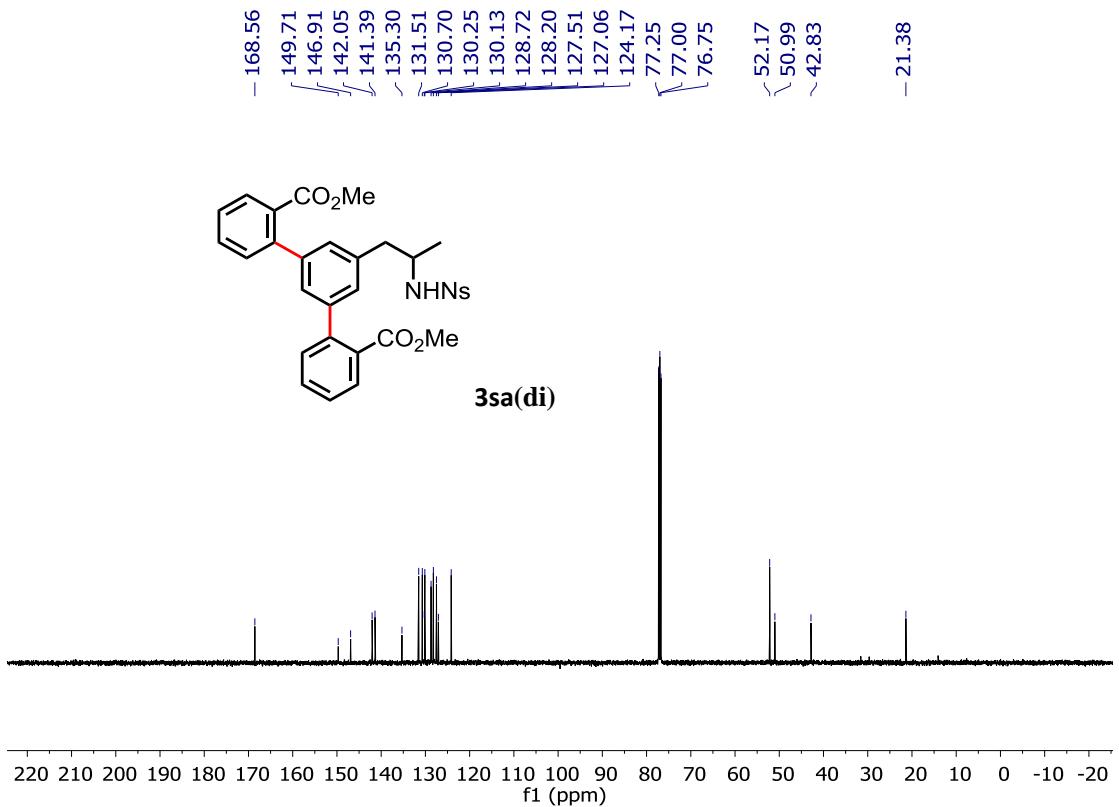
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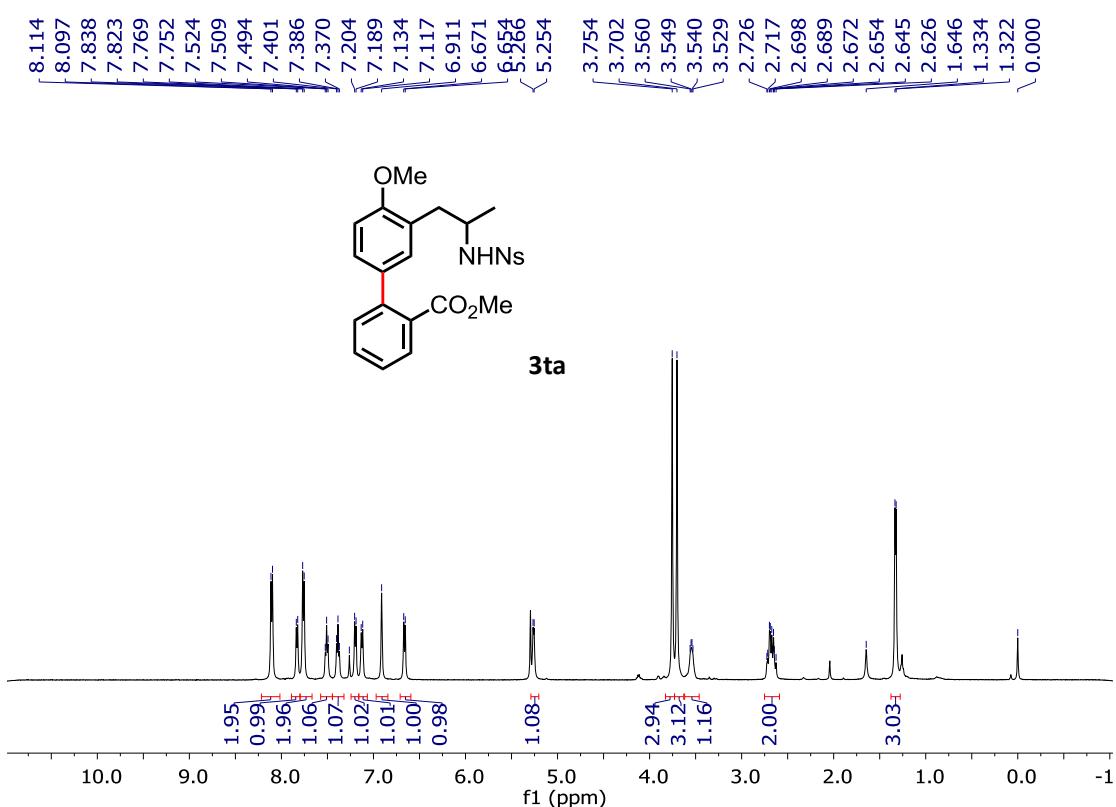
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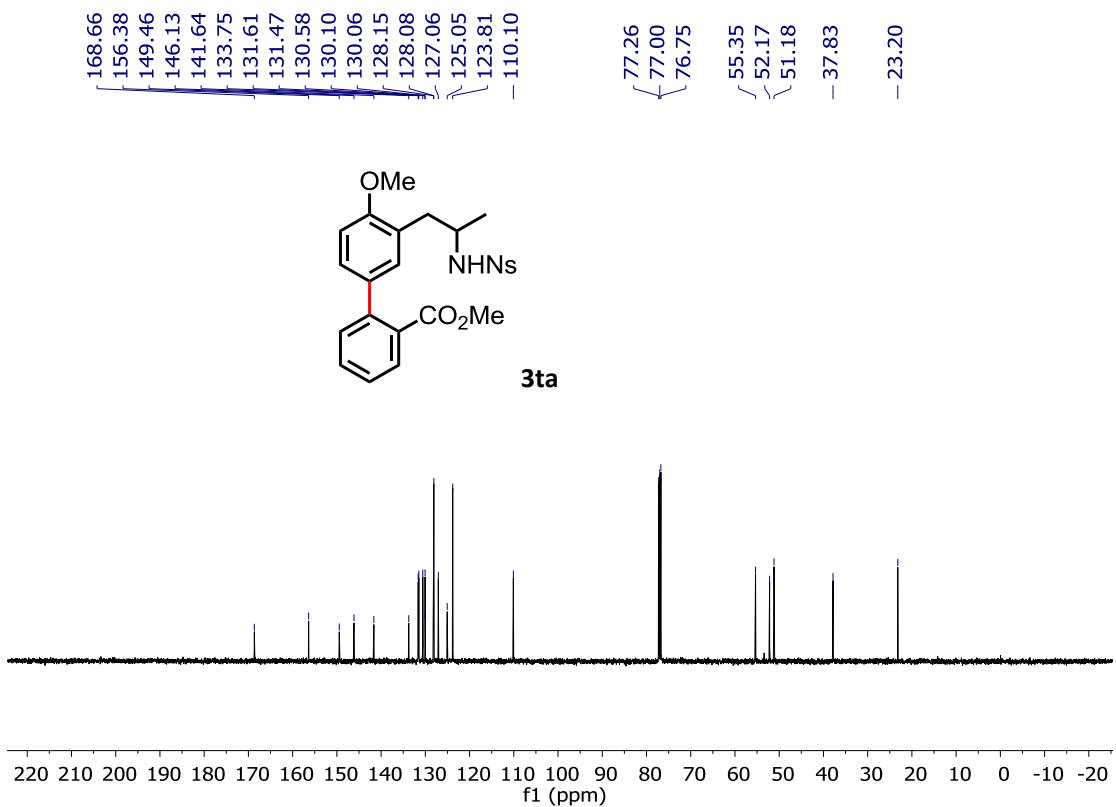
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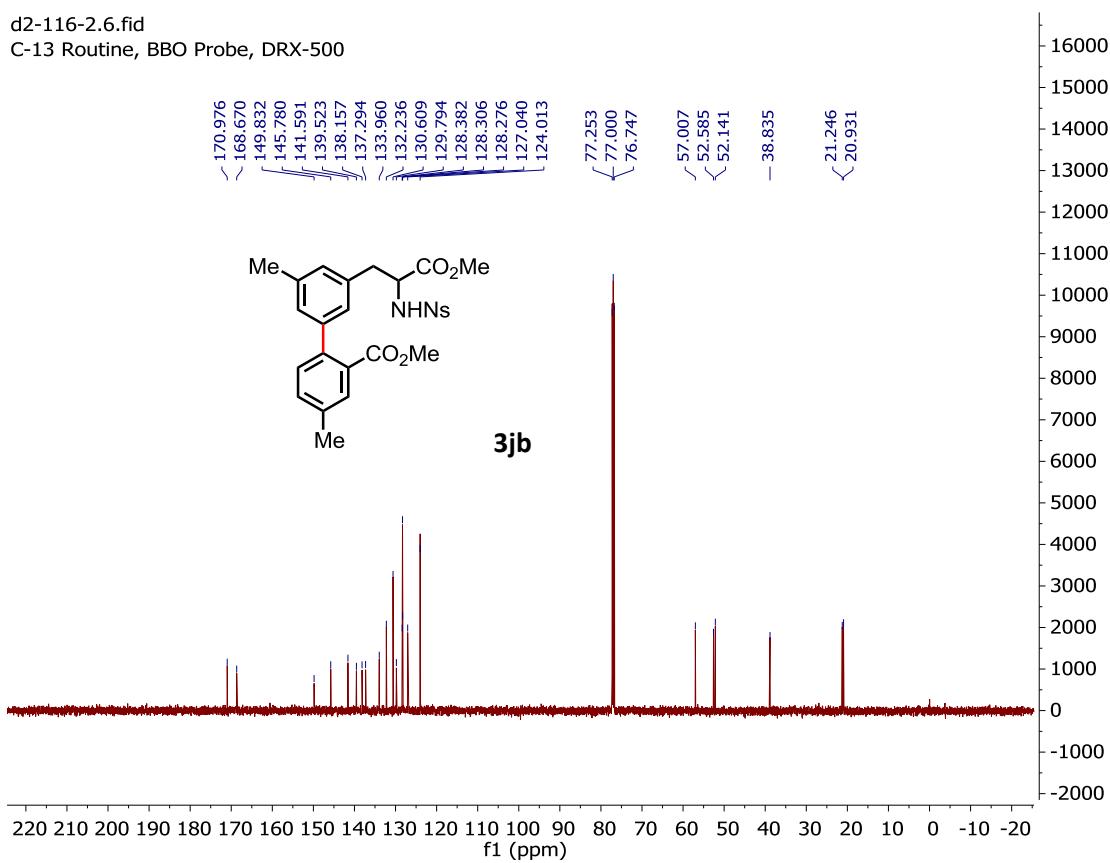
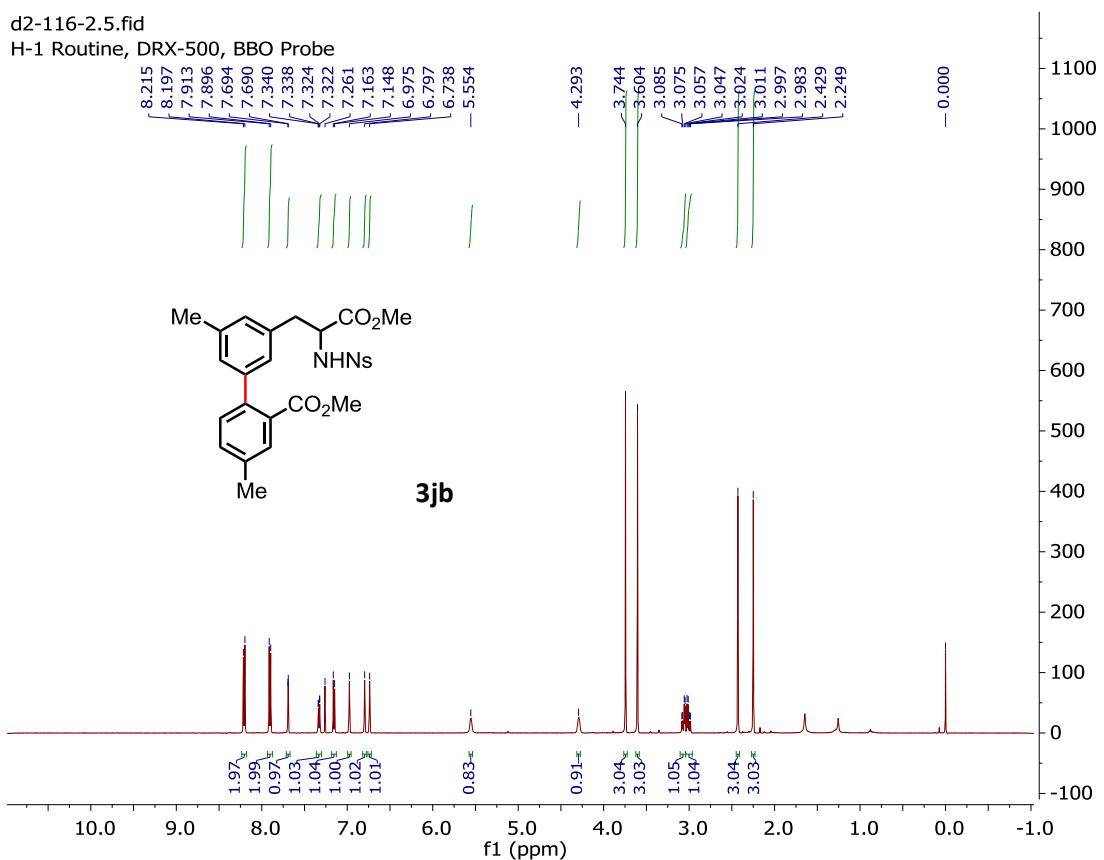


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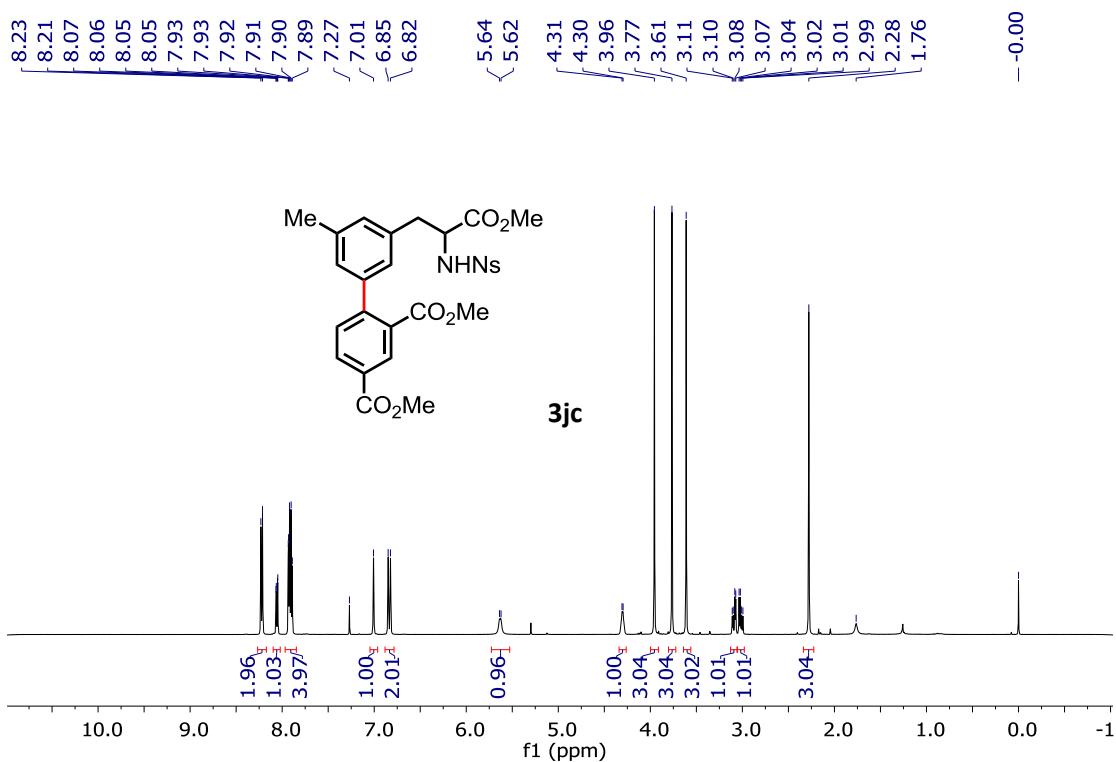


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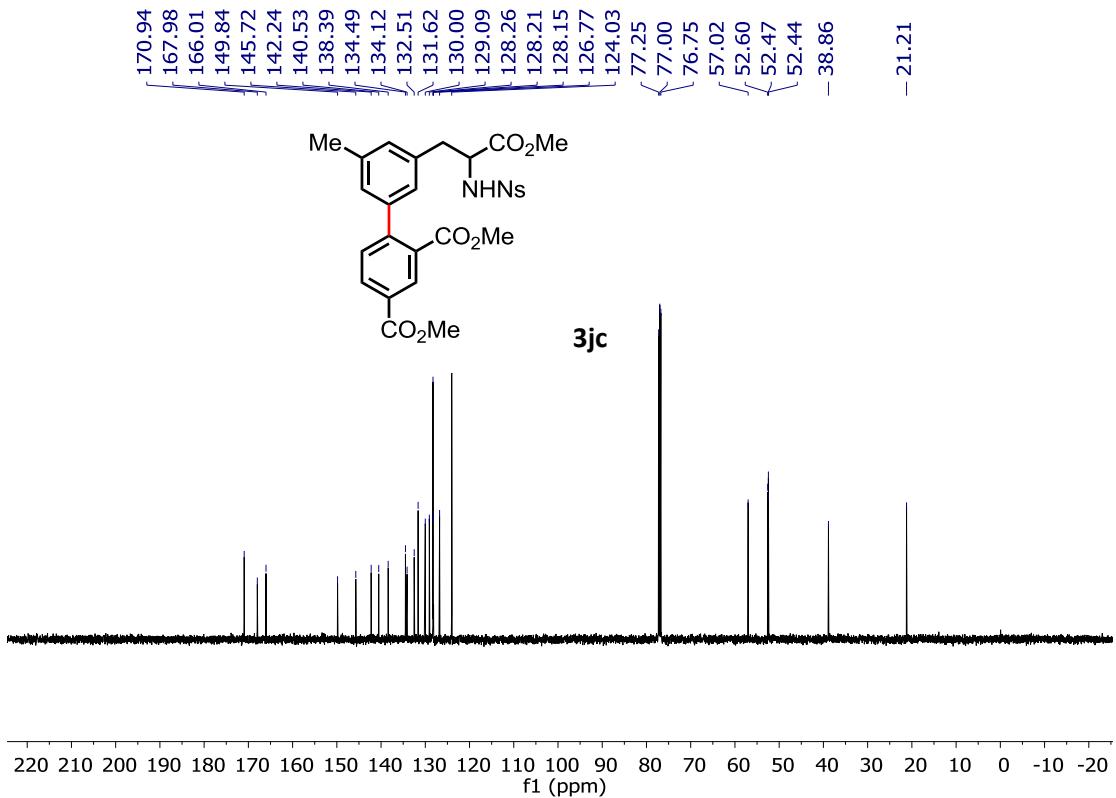




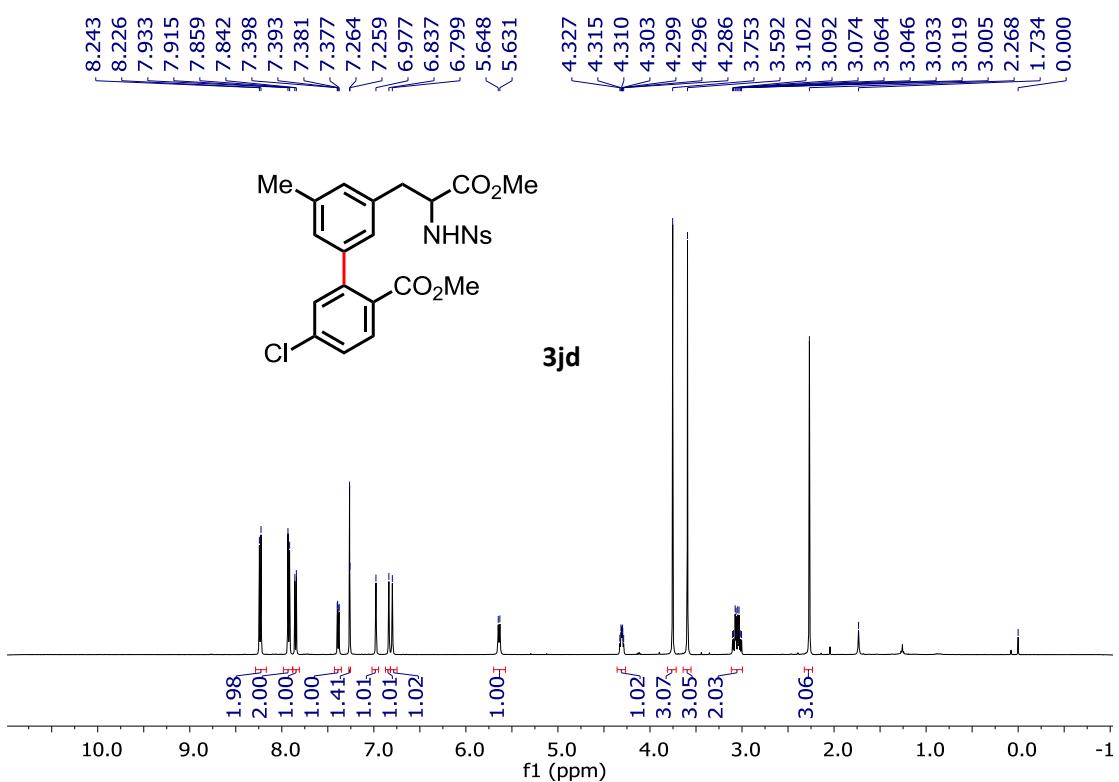
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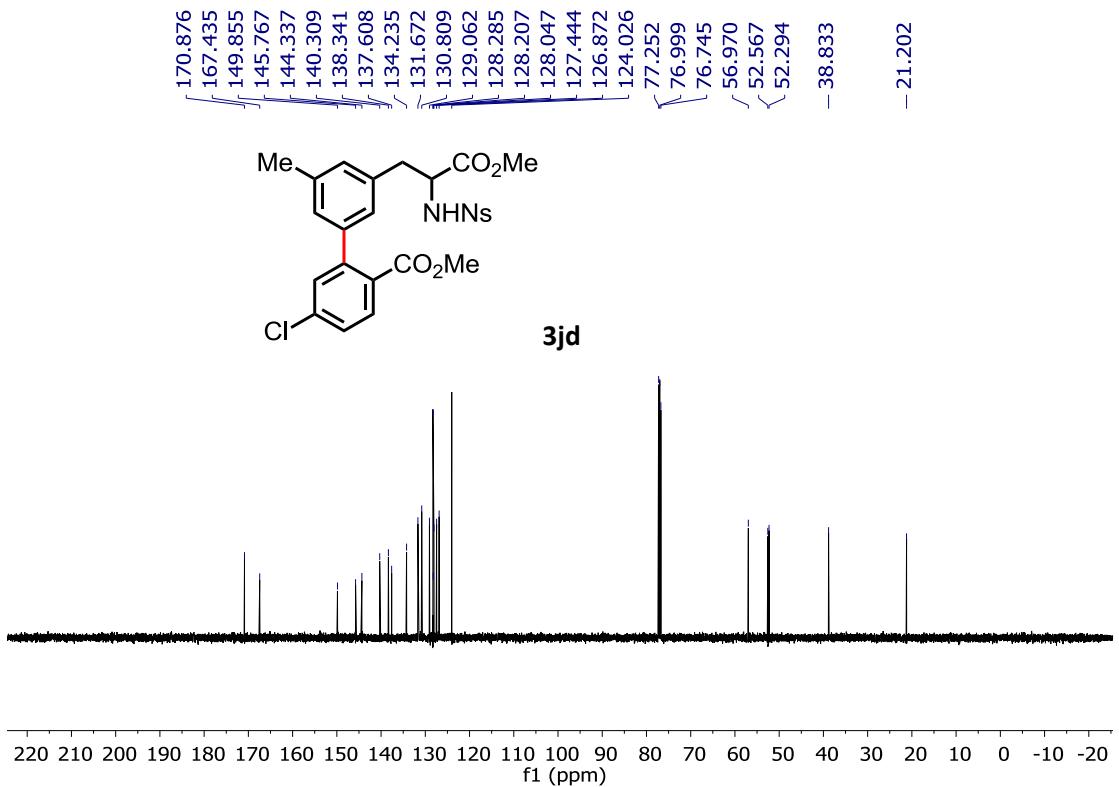
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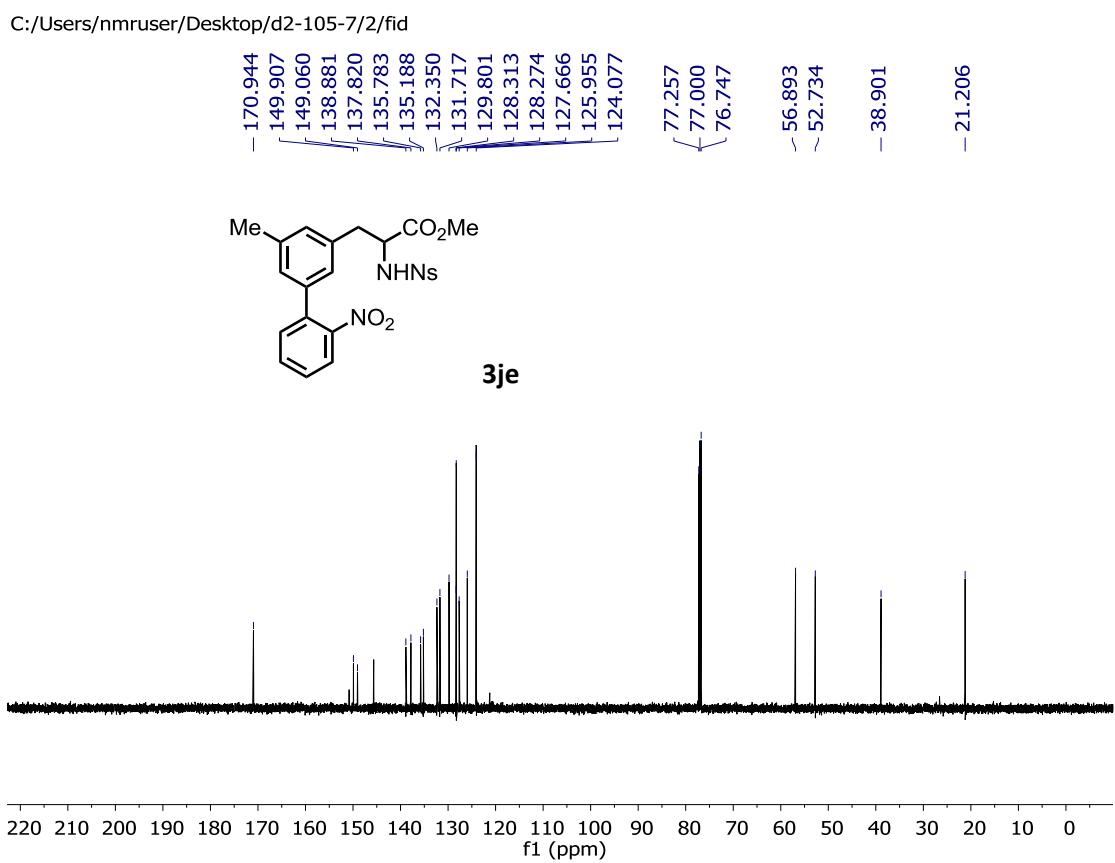
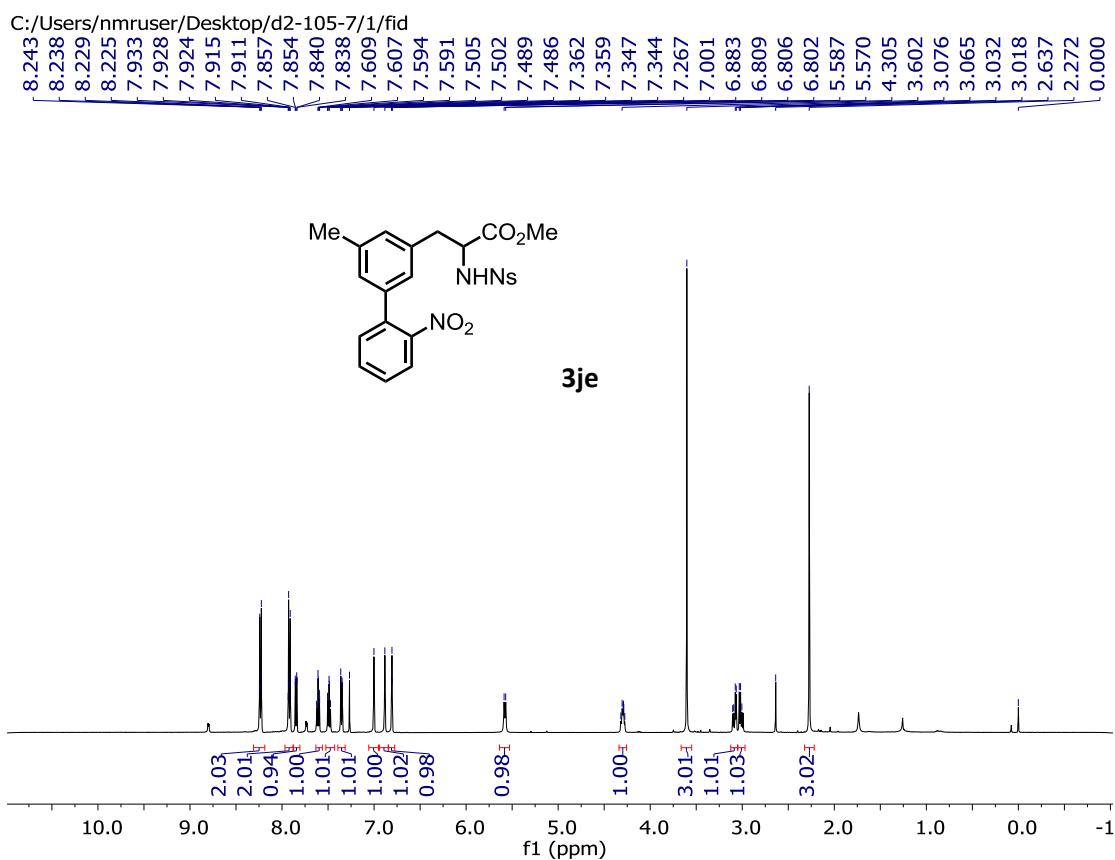


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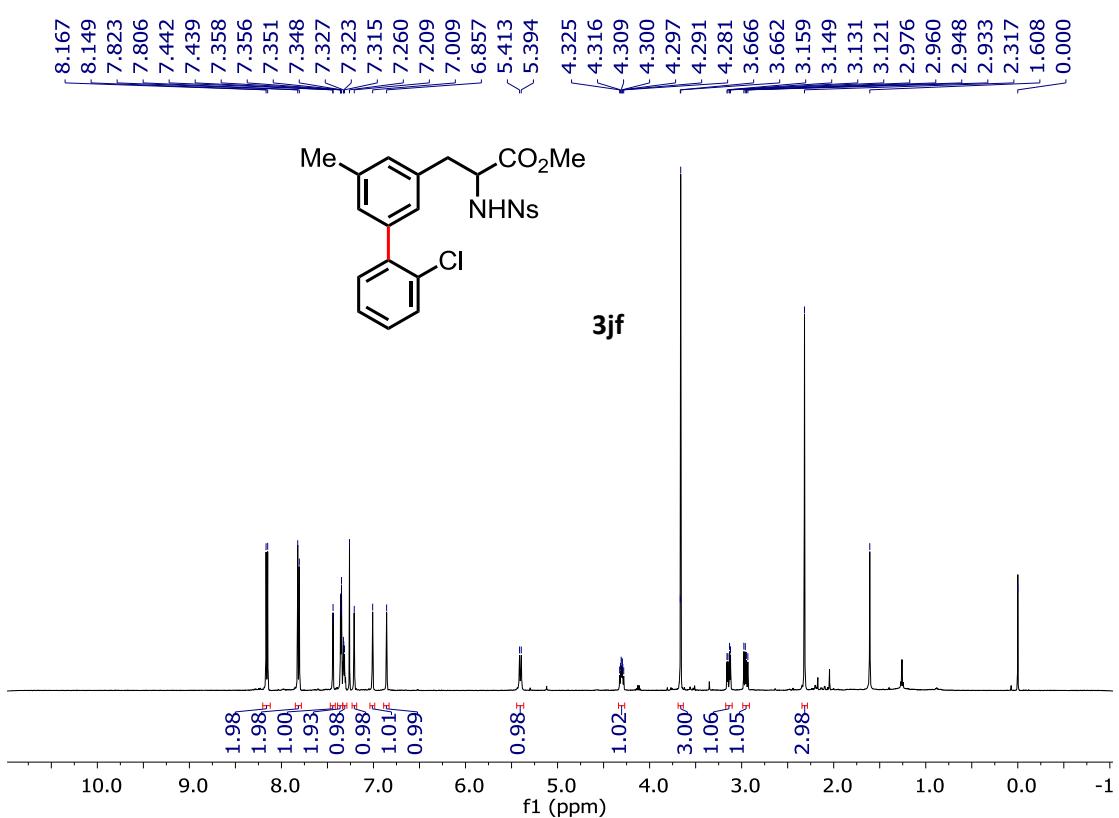


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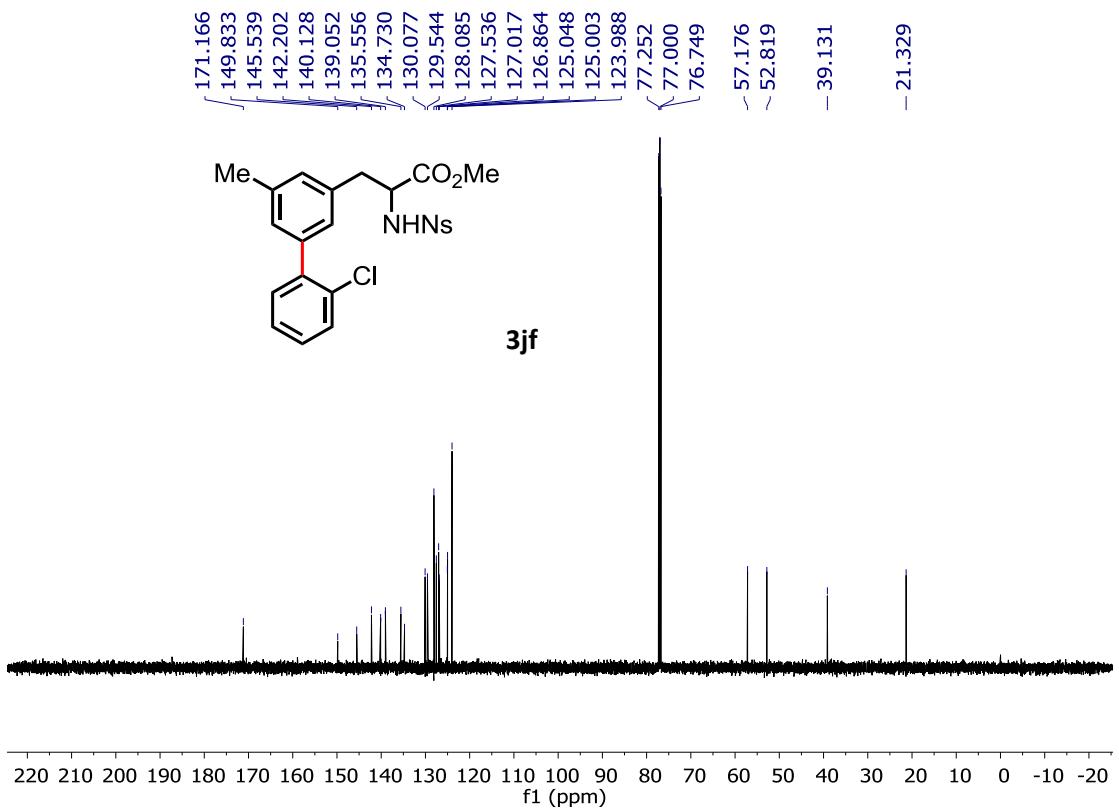




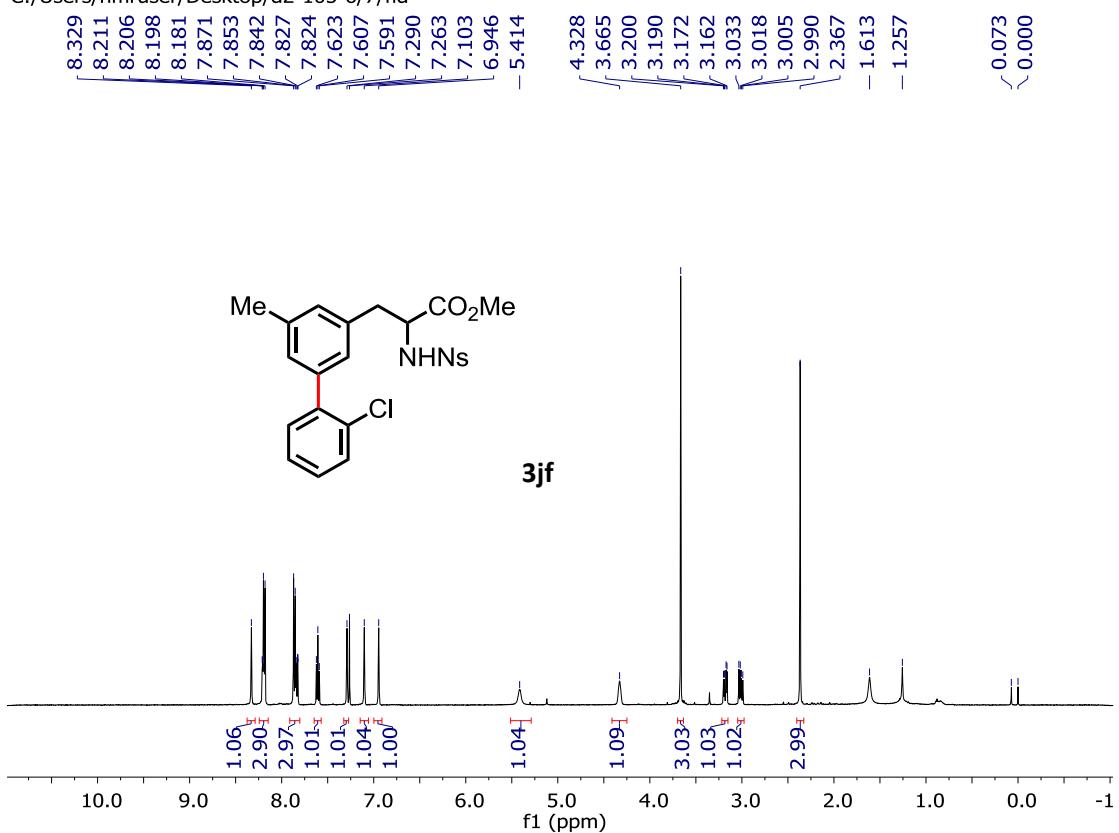
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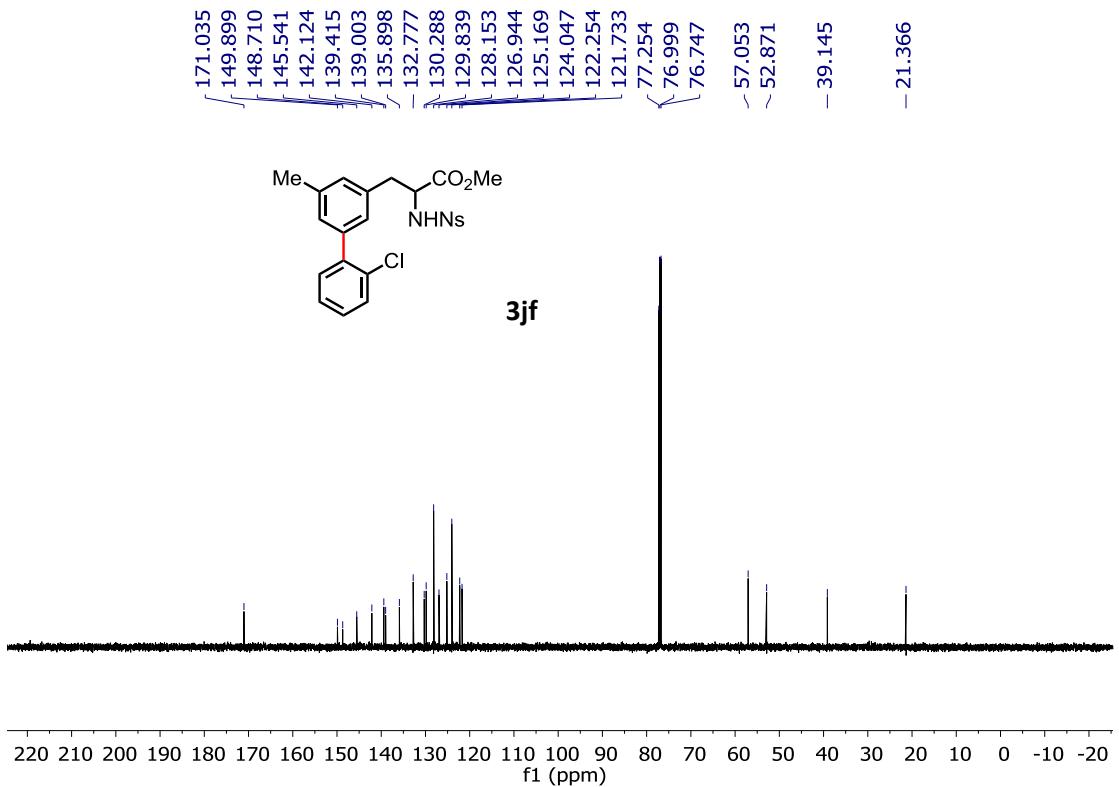
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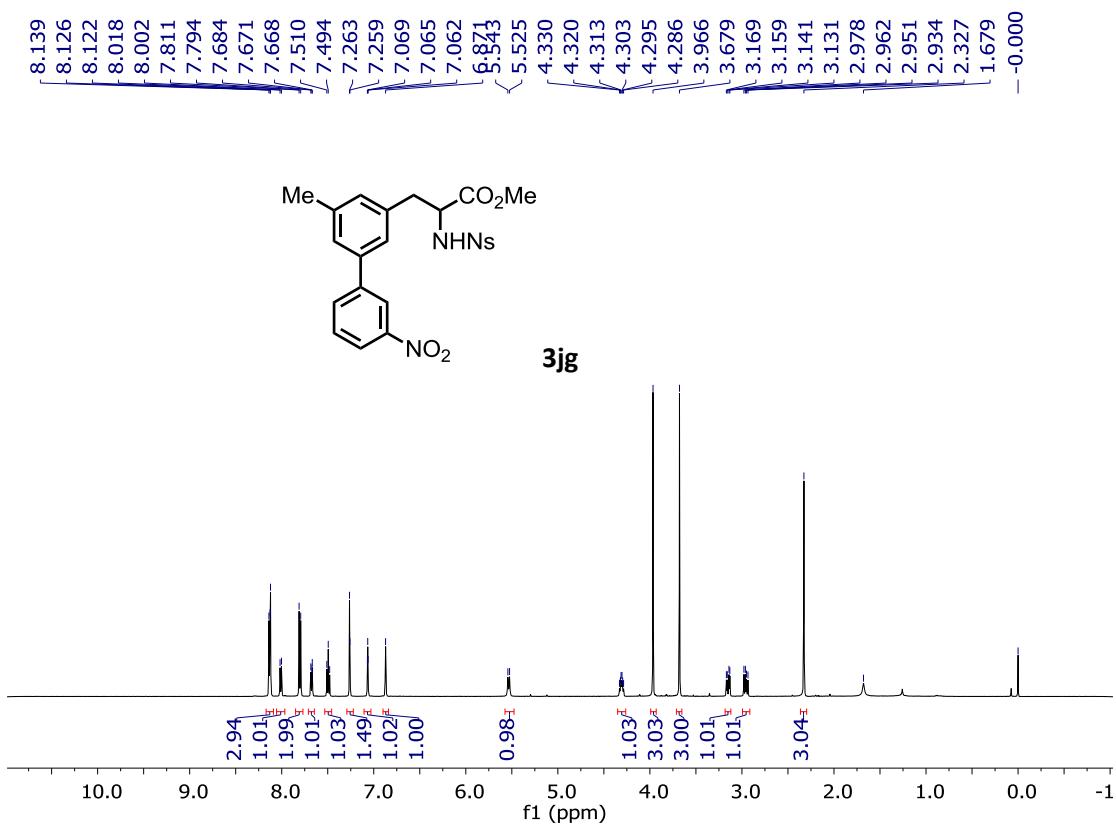
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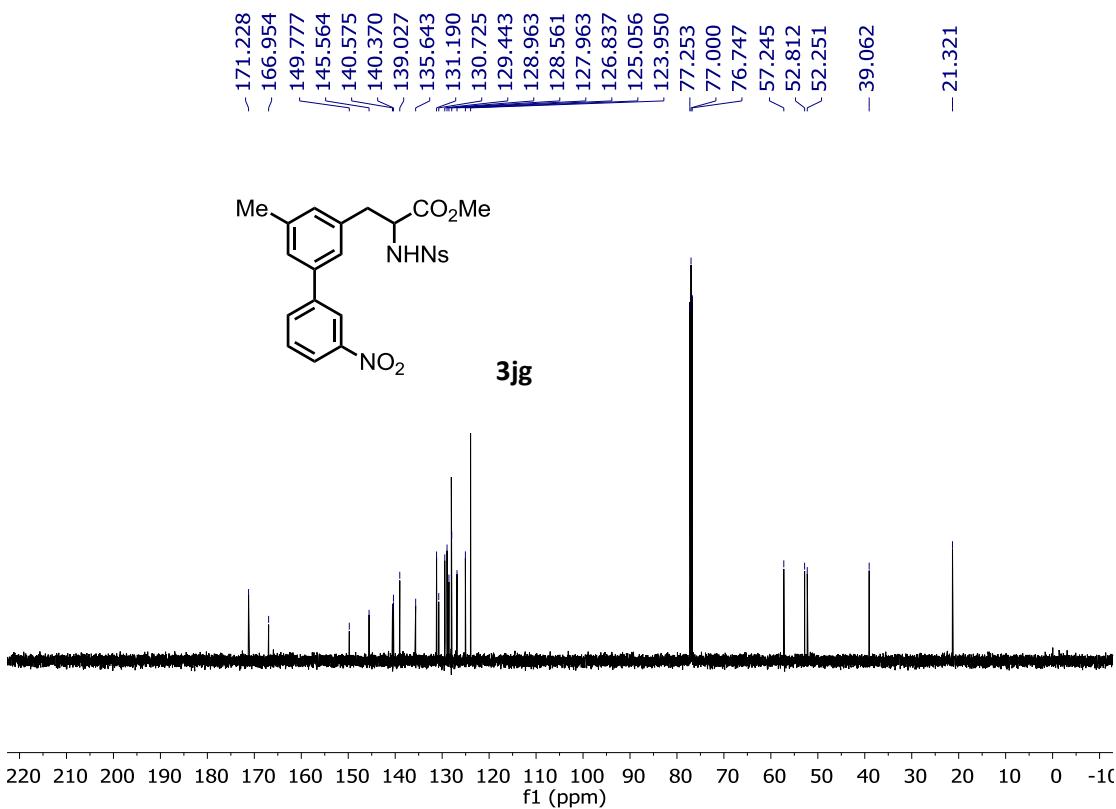
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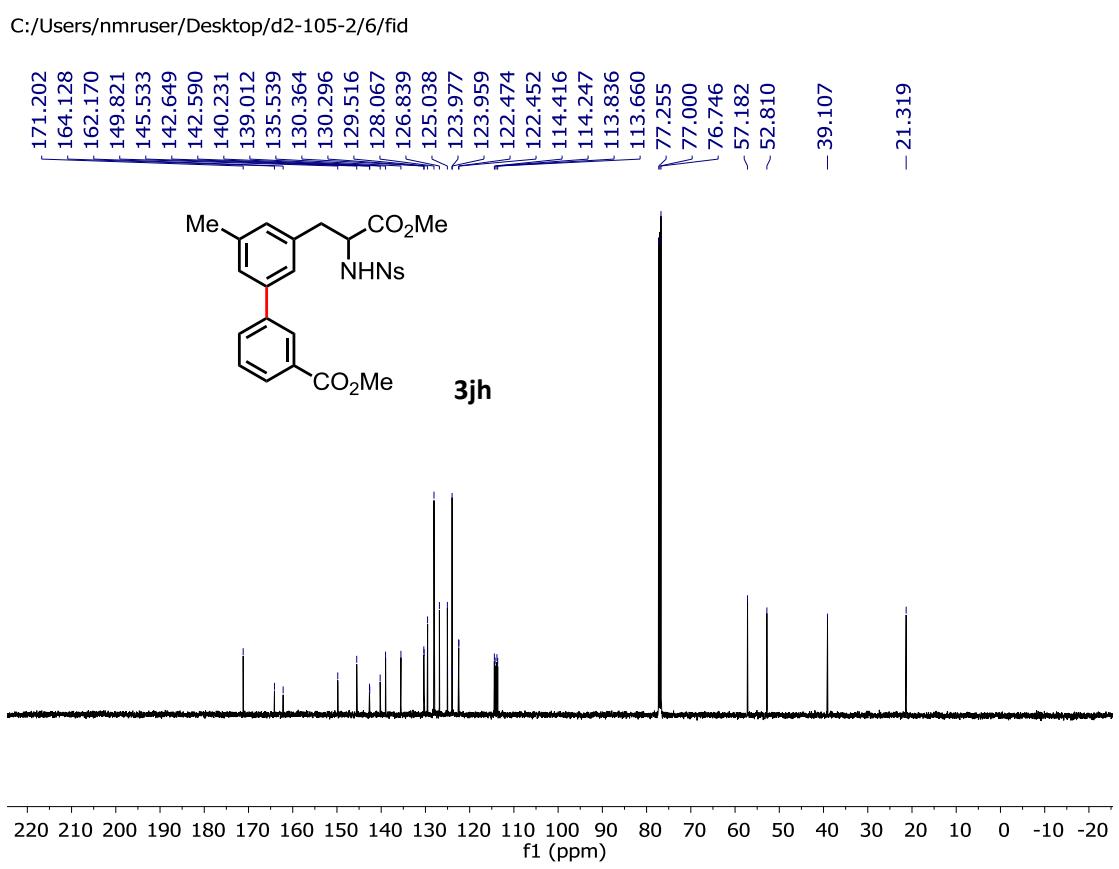
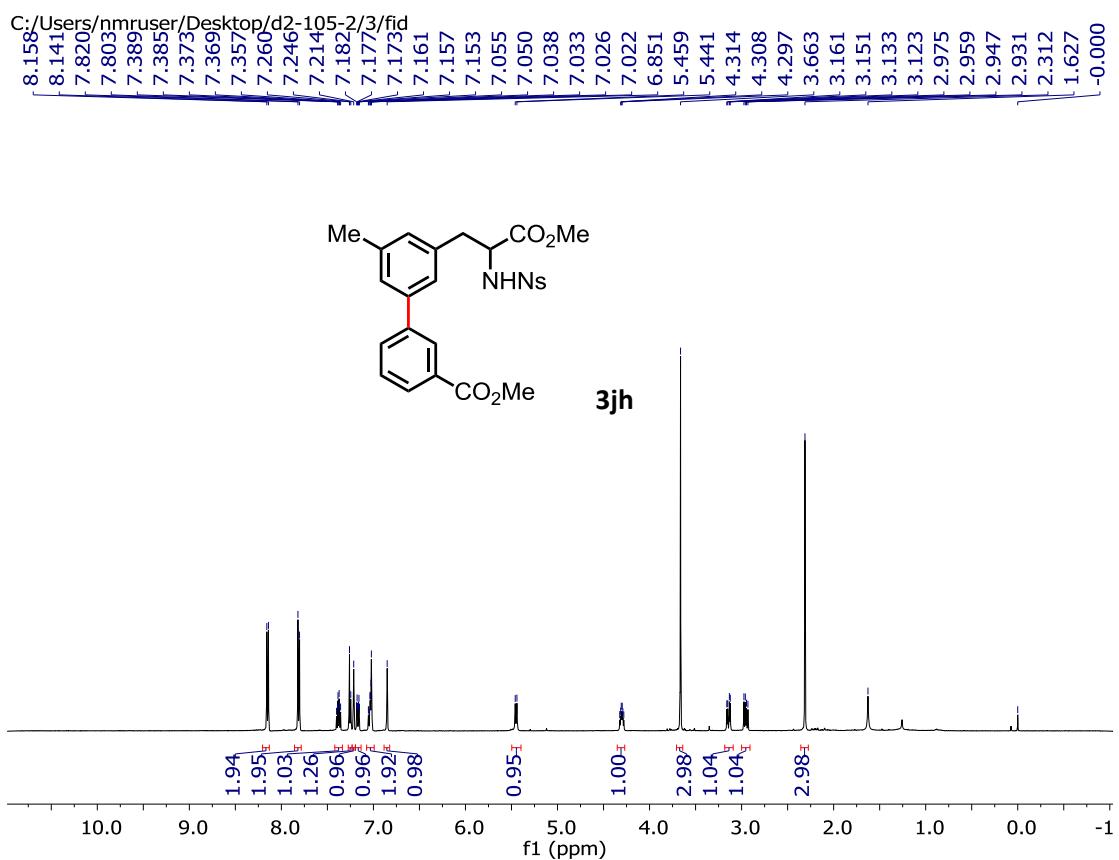


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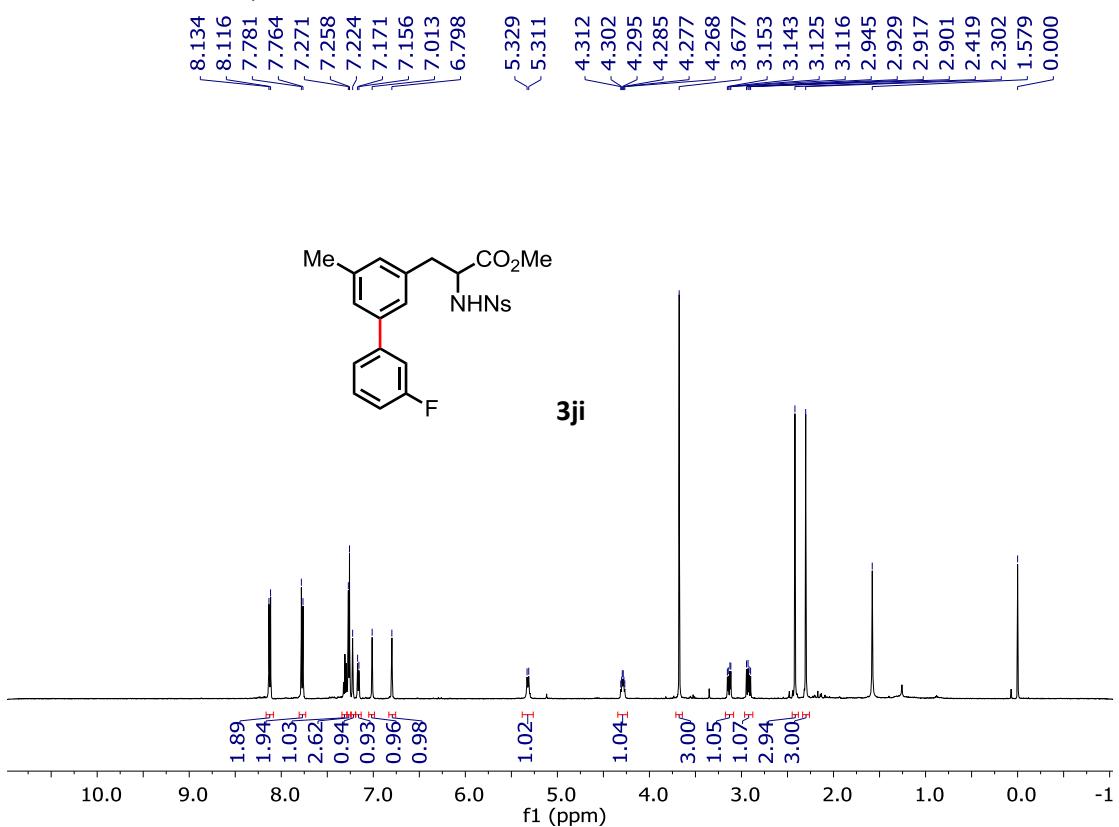


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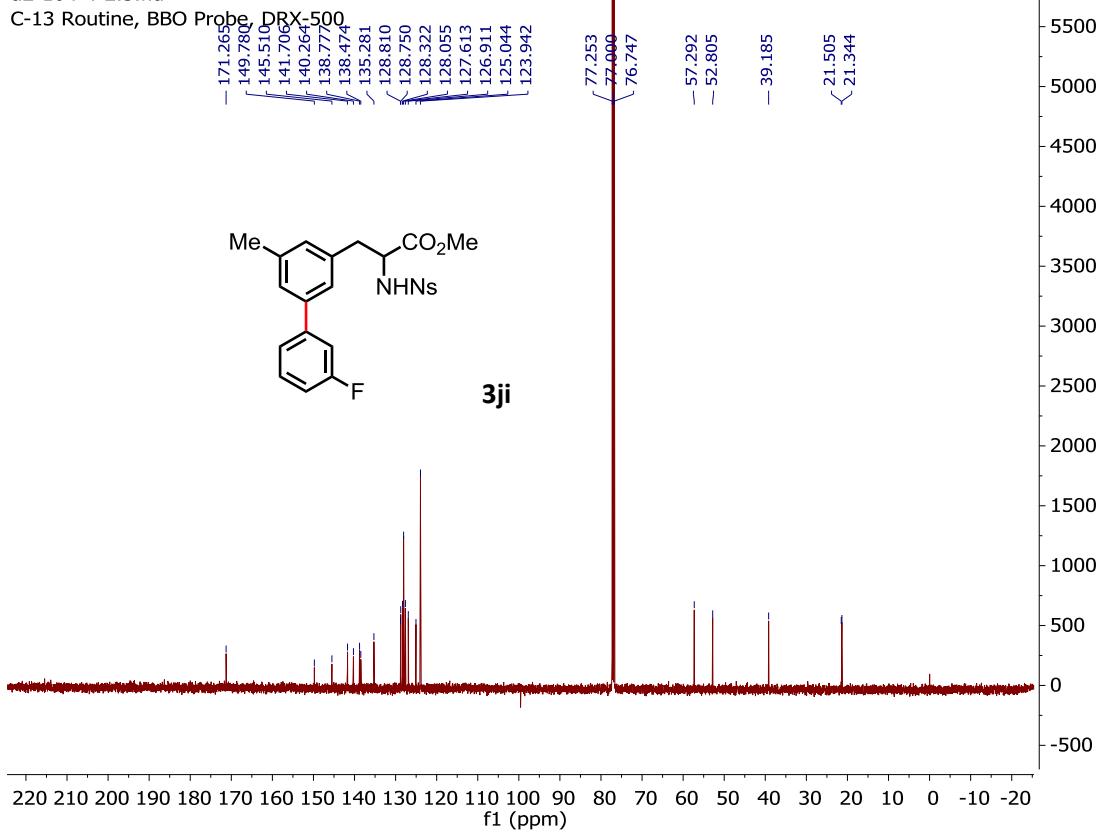


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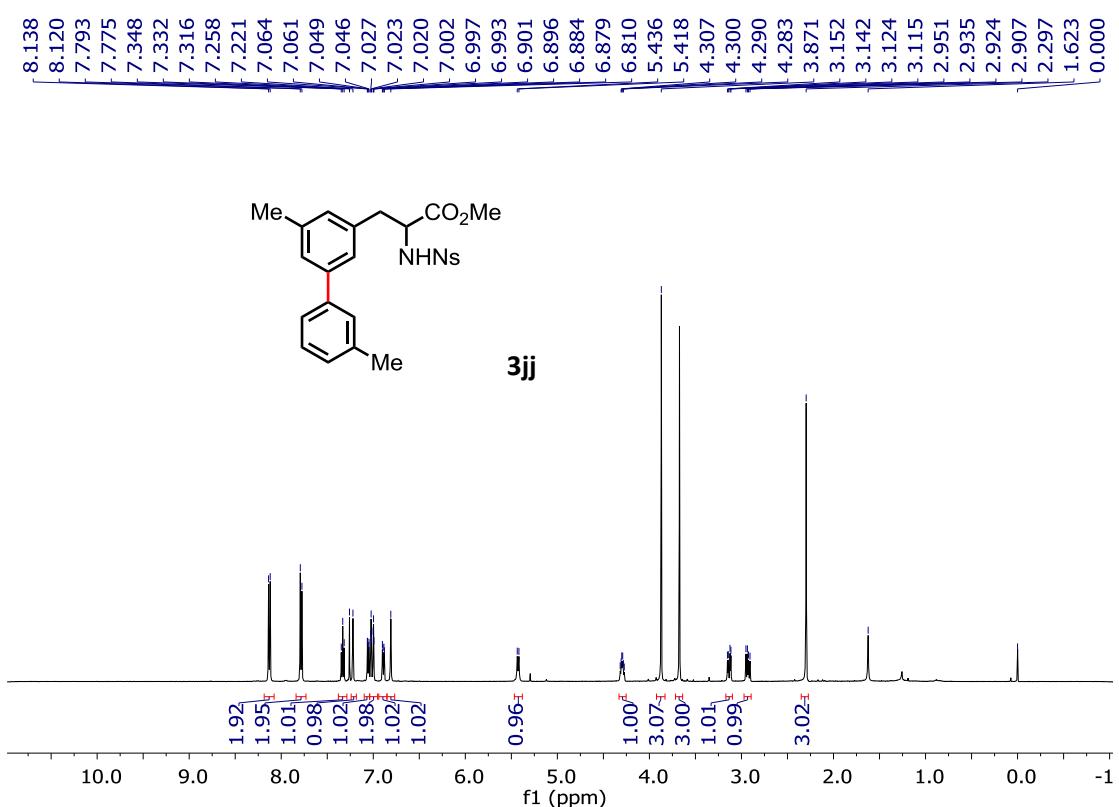


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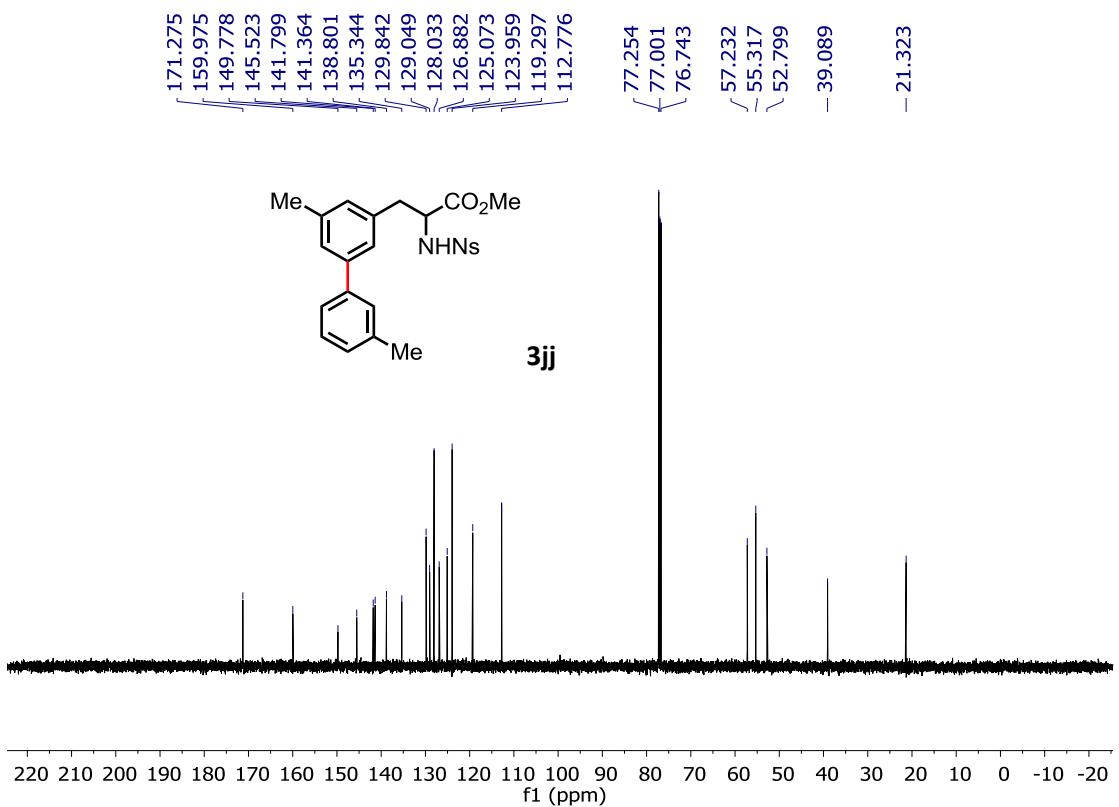
C-13 Routine, BBO Probe, DRX-500



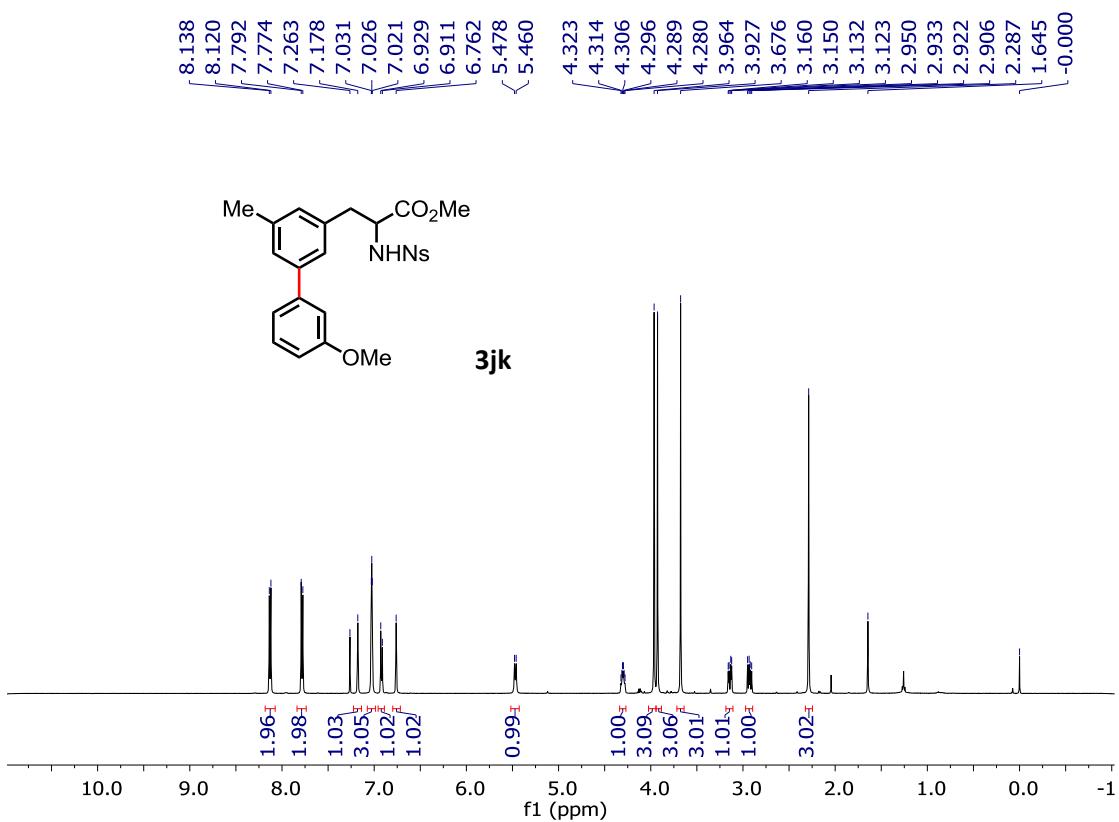
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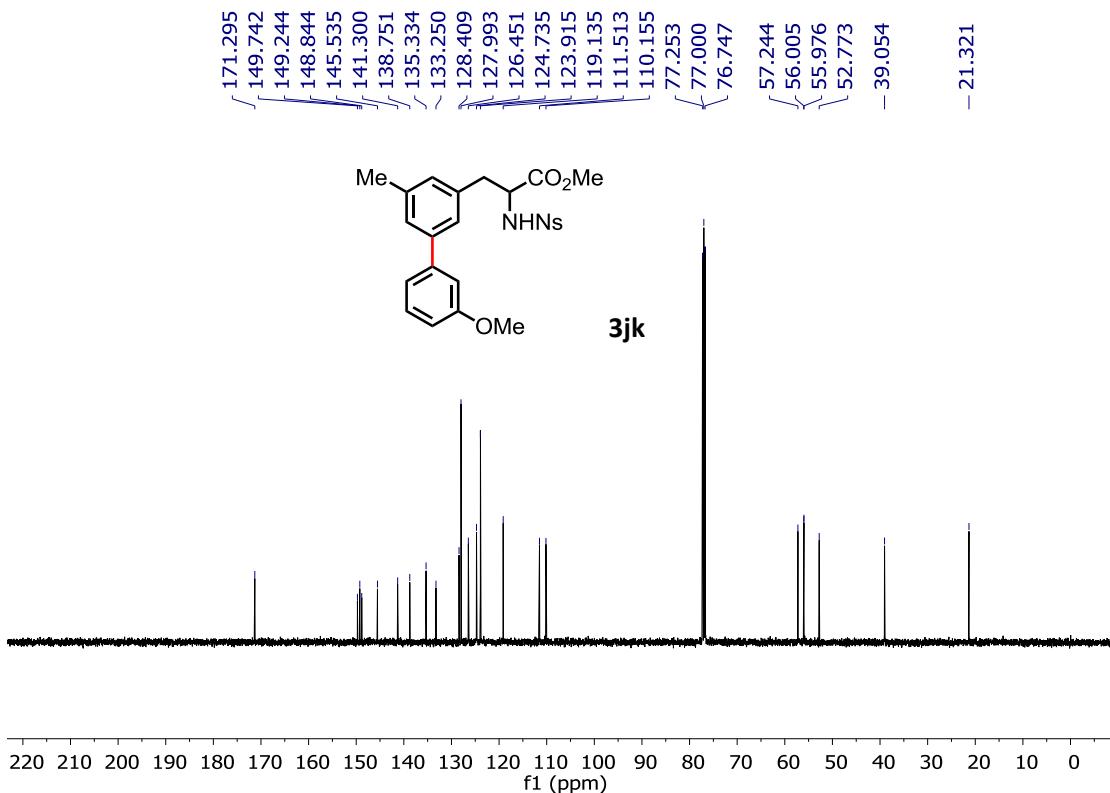
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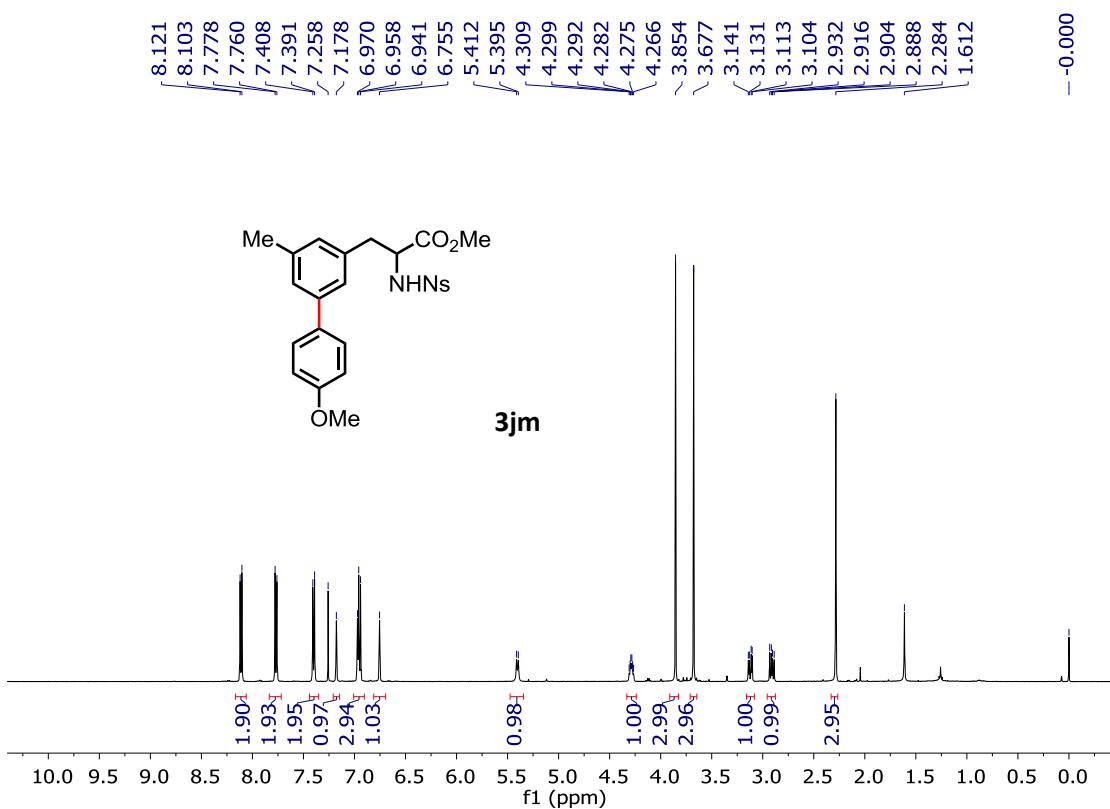
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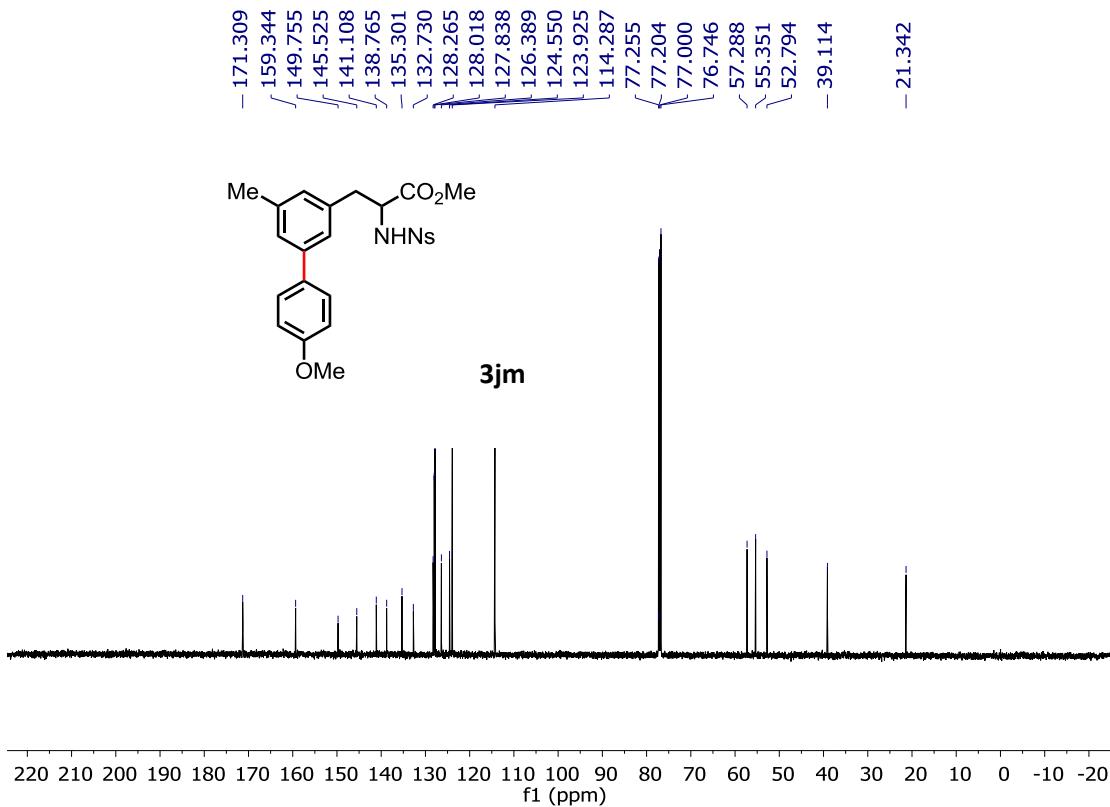
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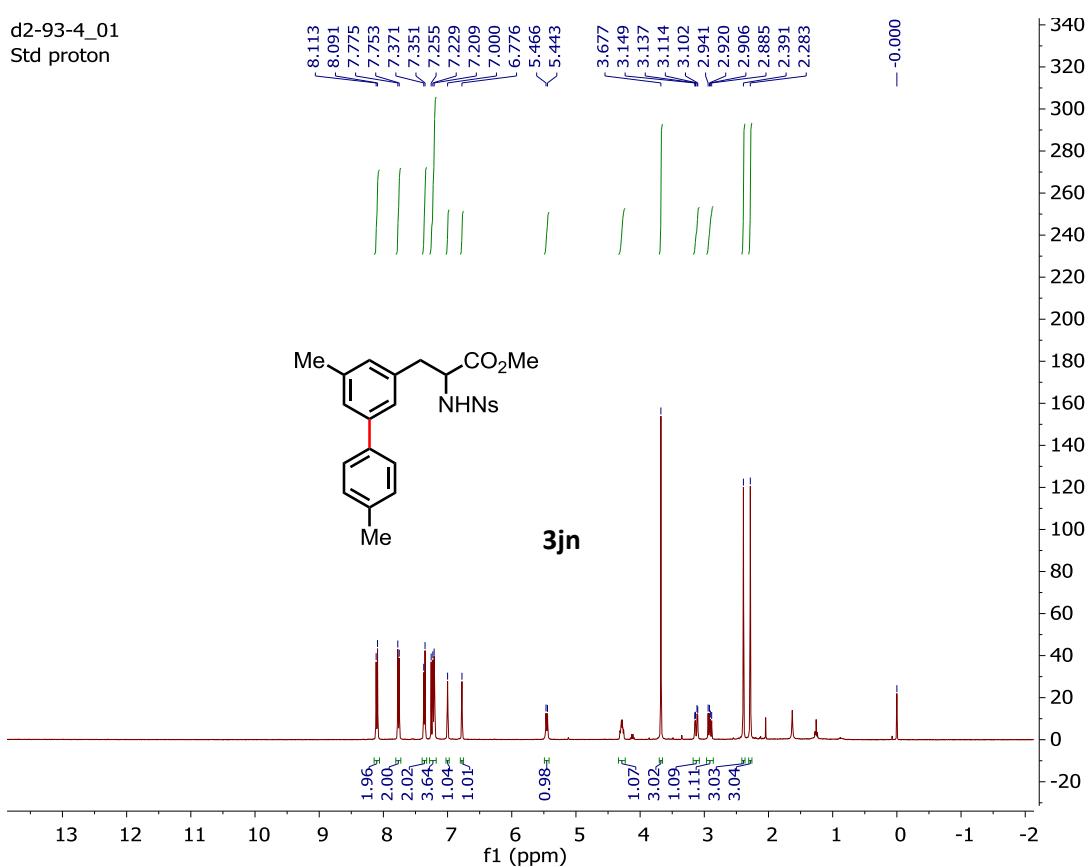
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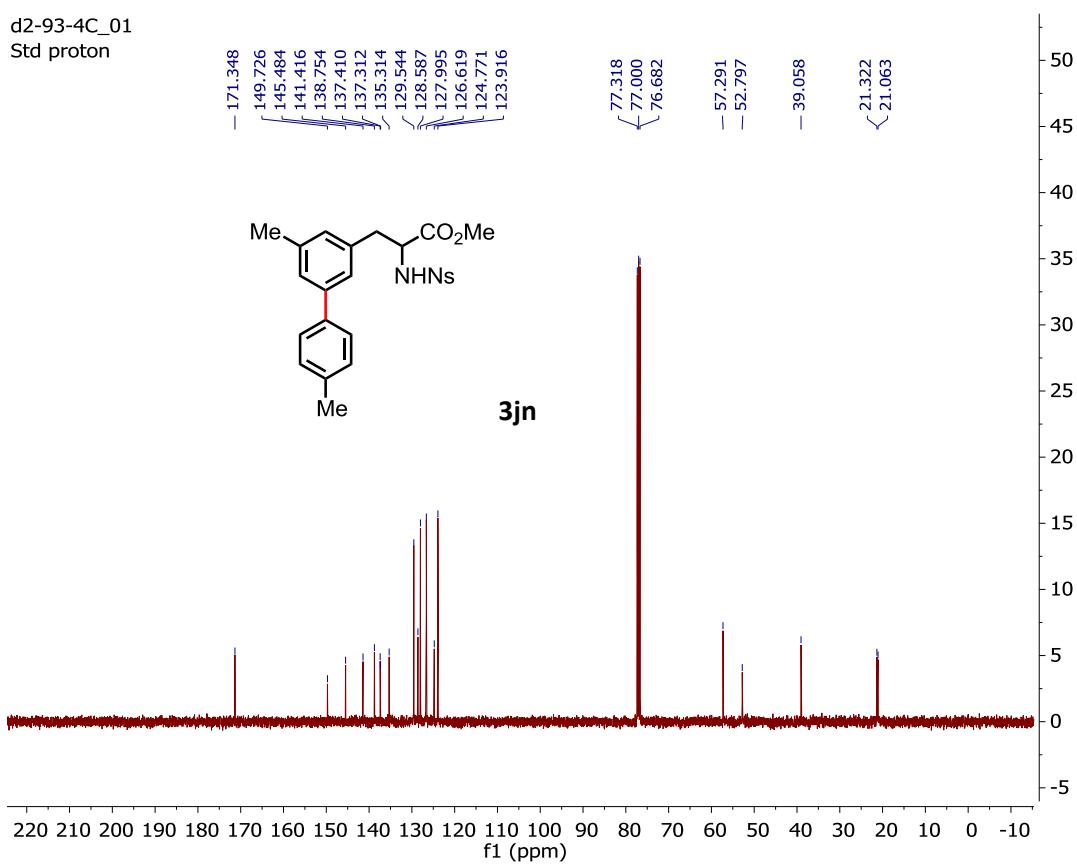
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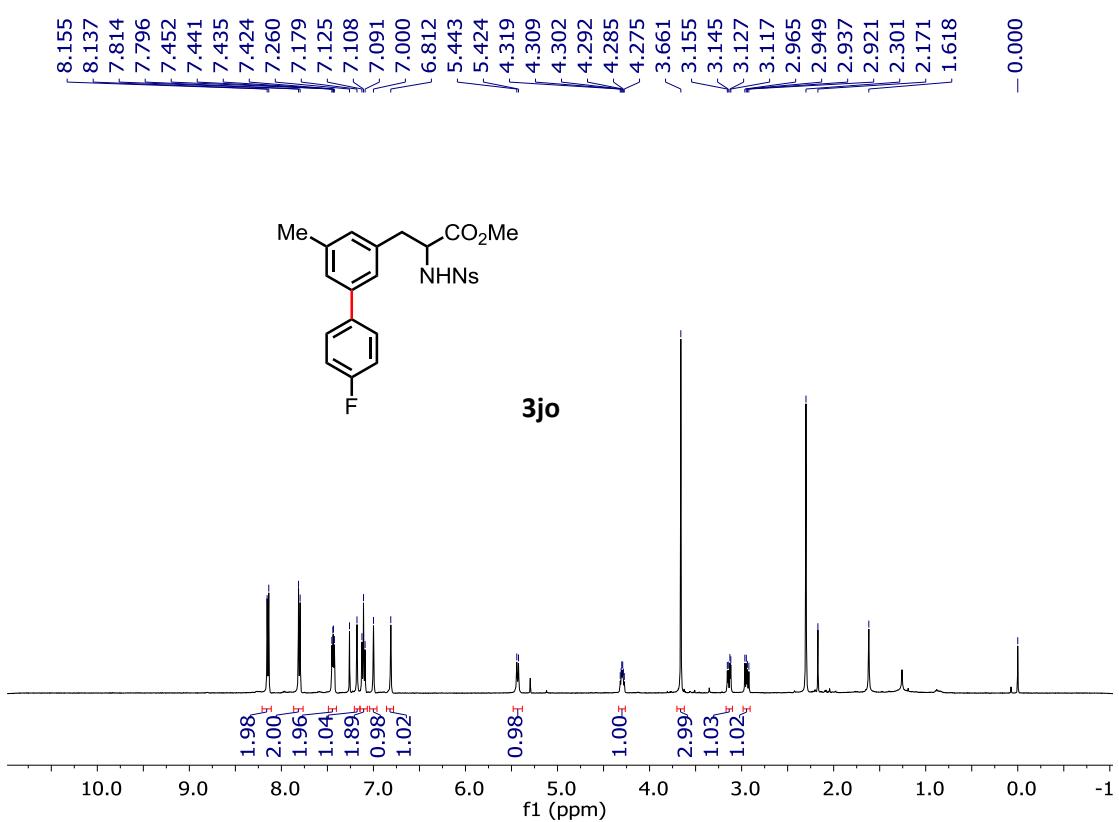
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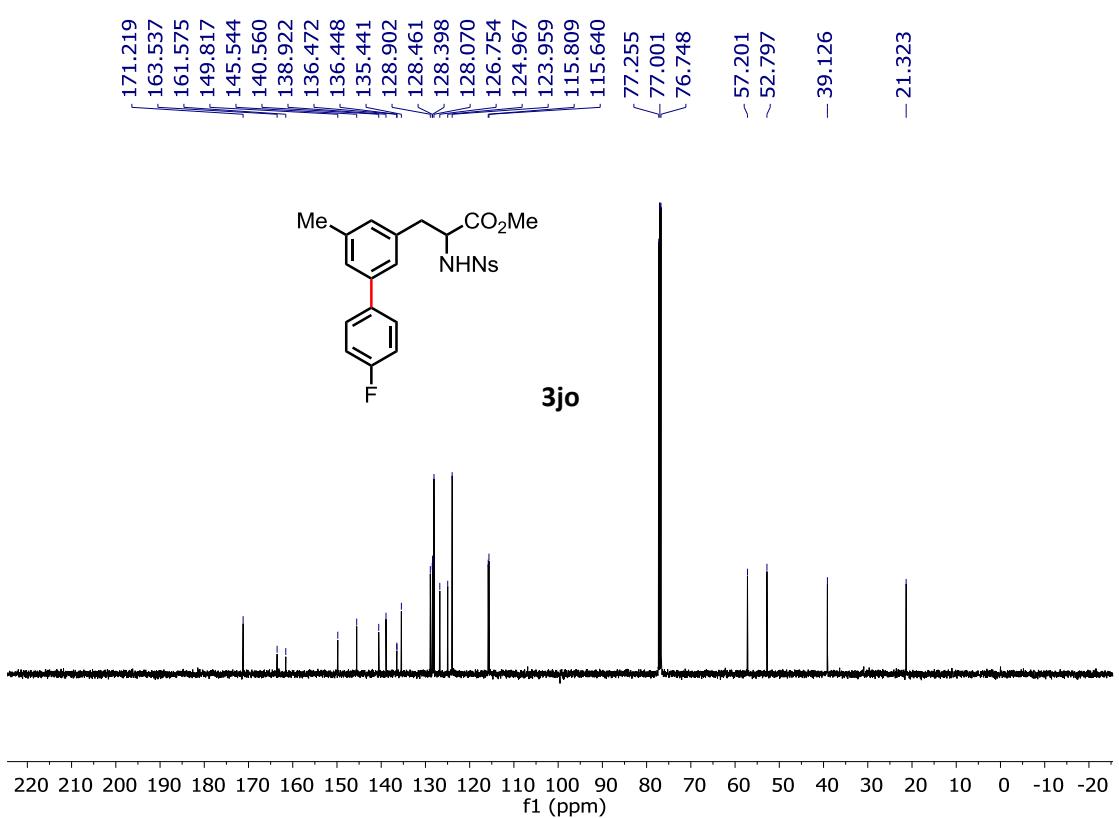
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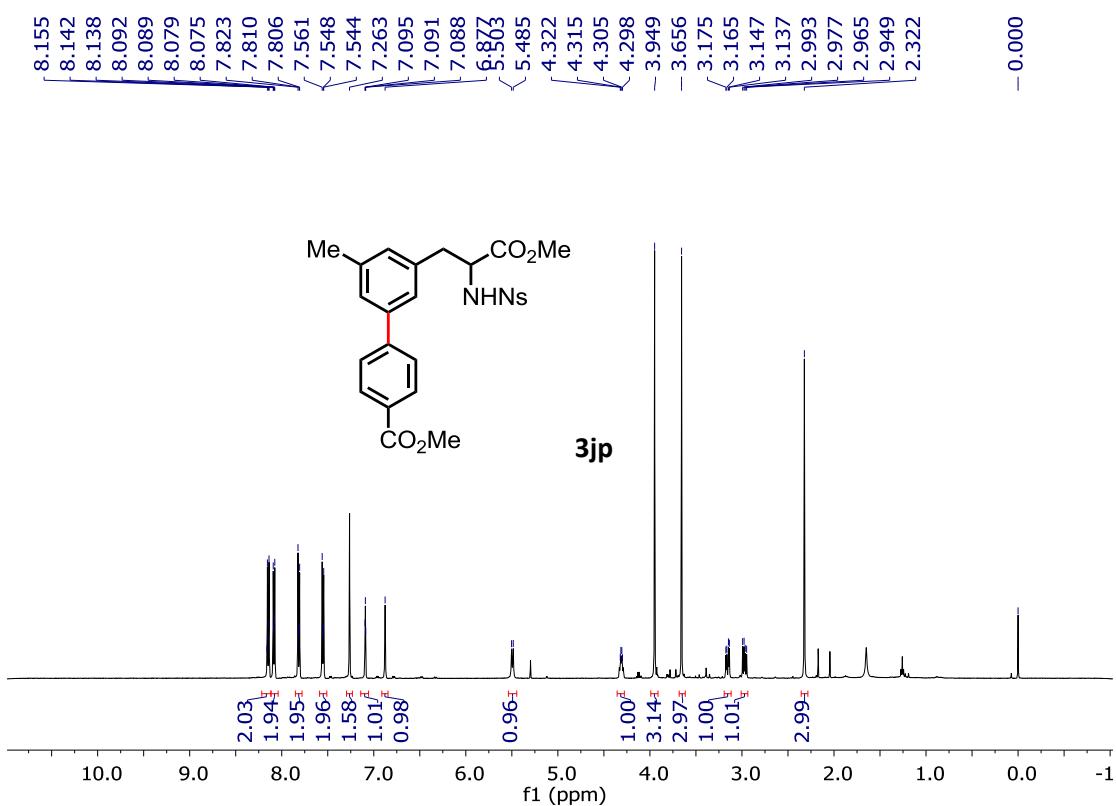
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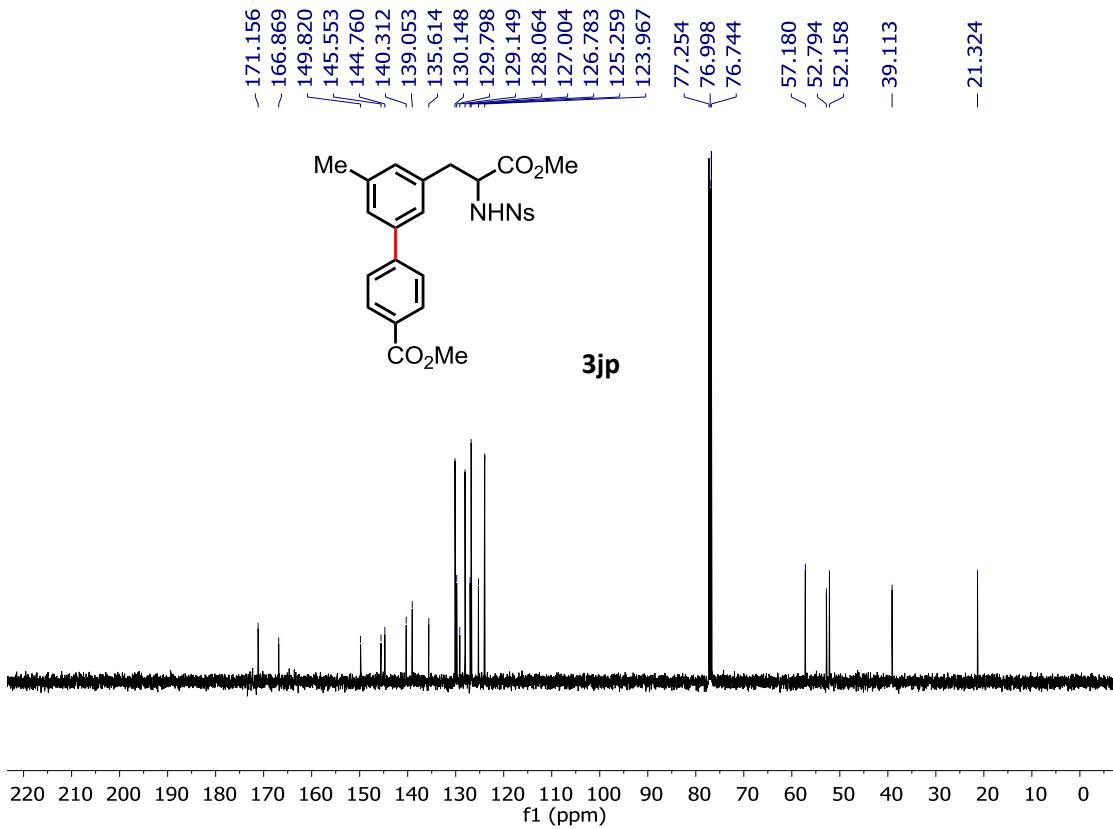
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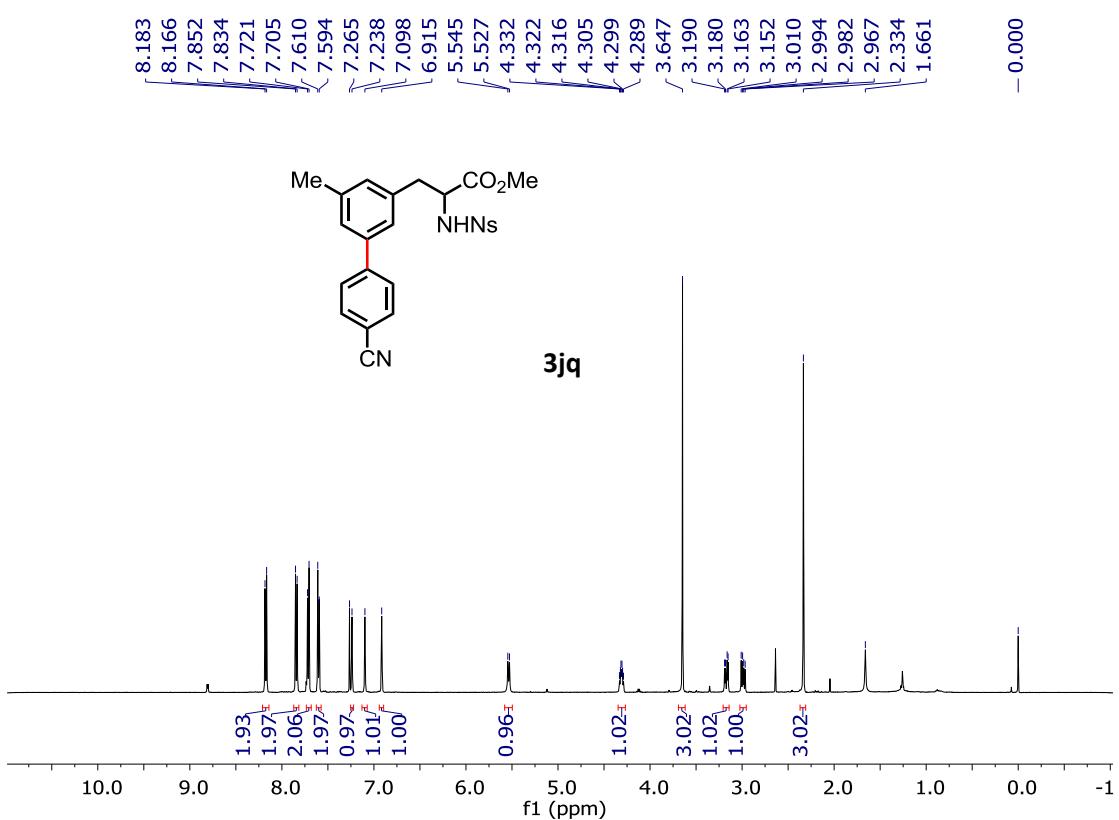
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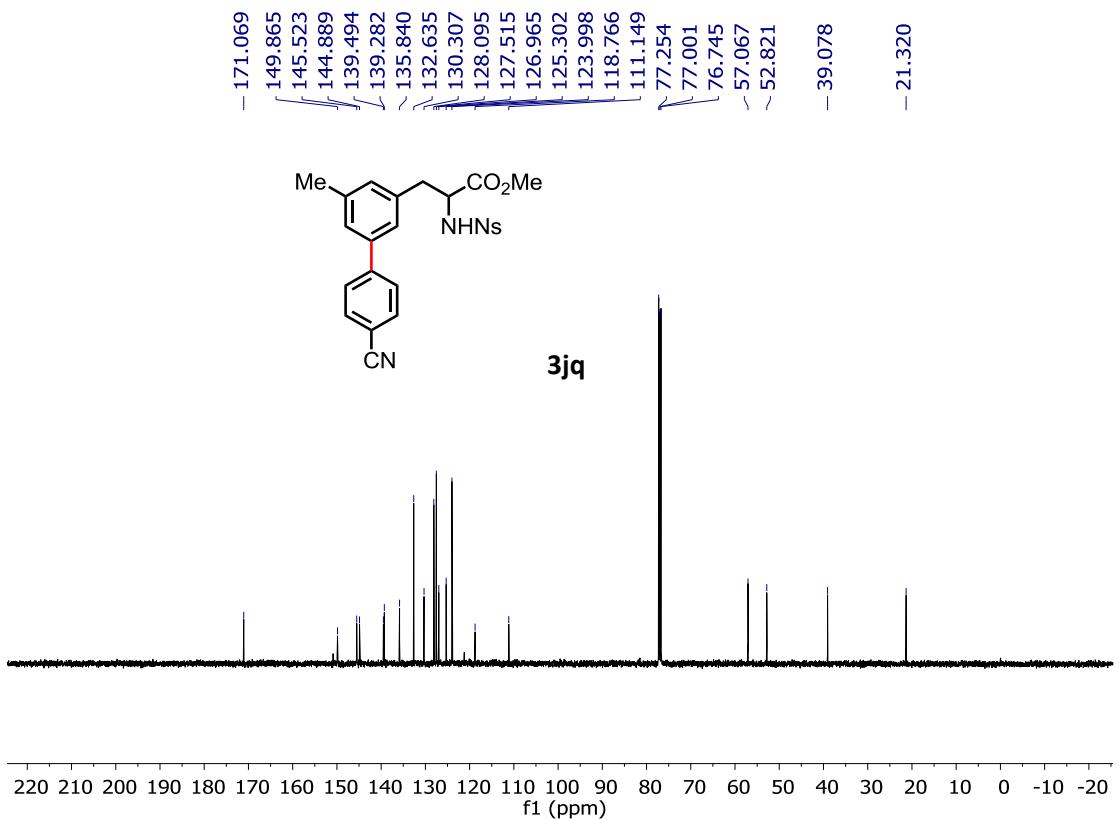
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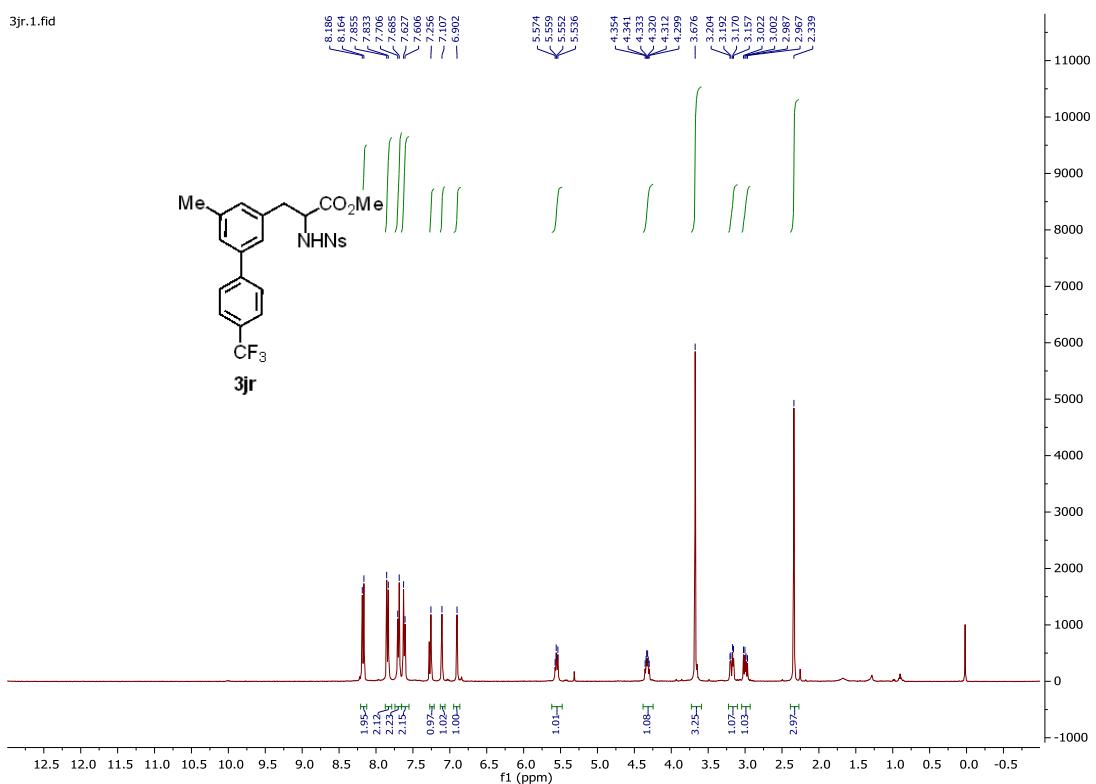
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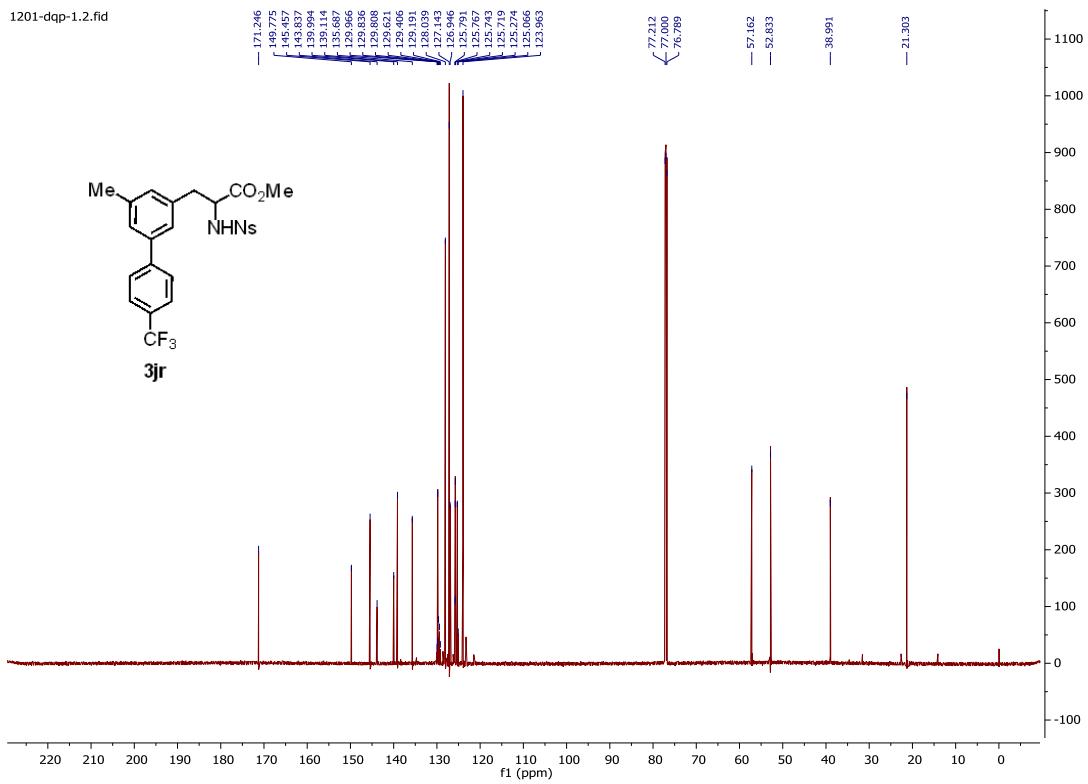
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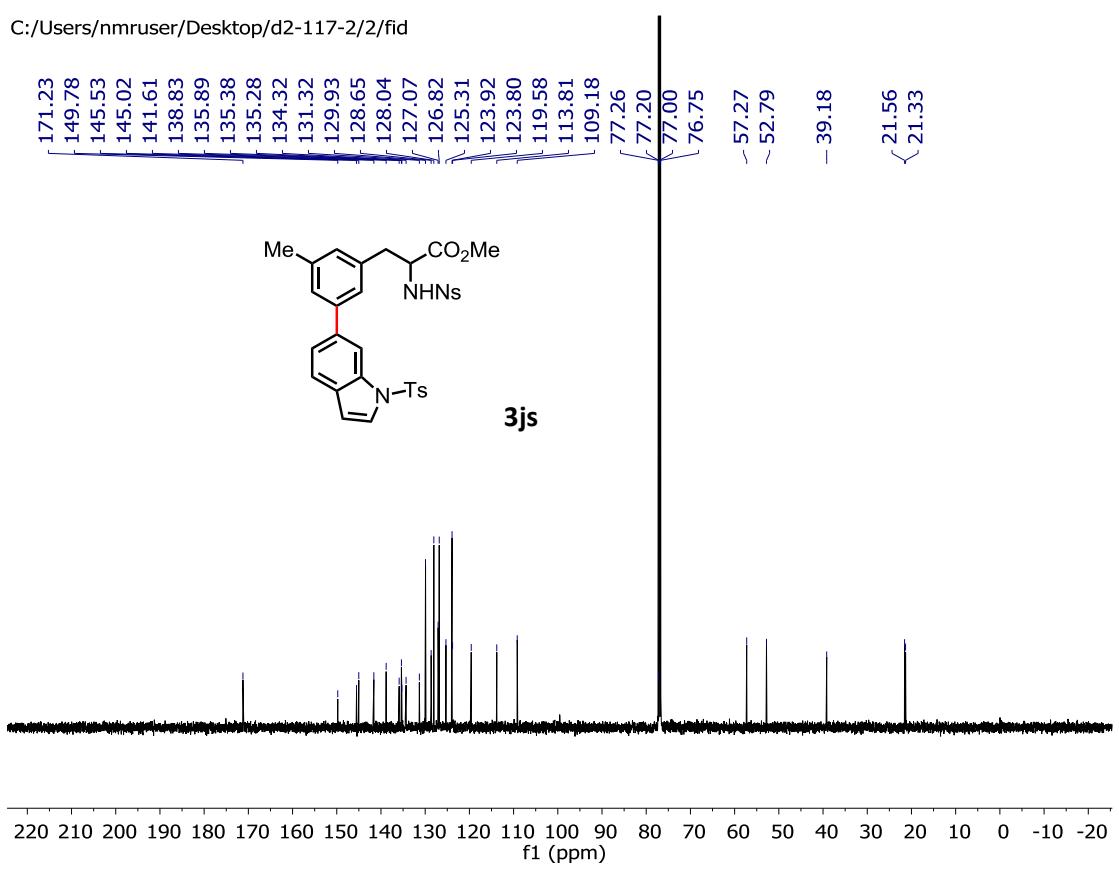
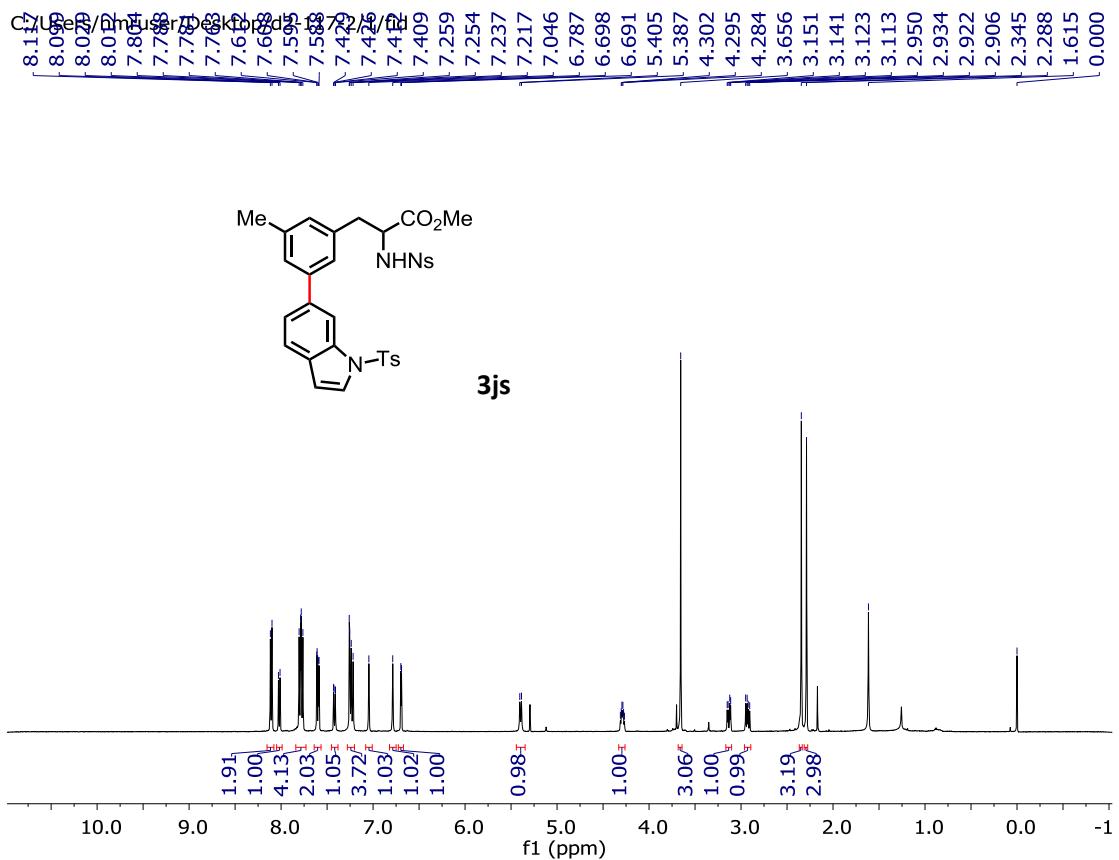


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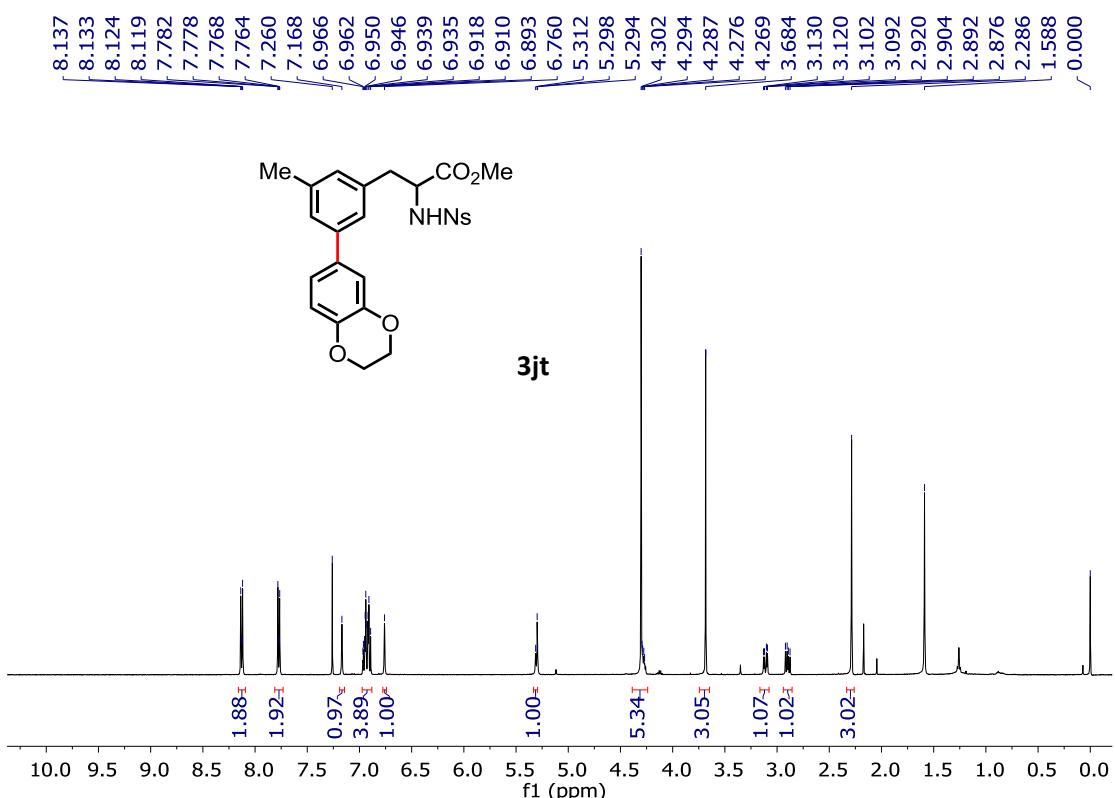


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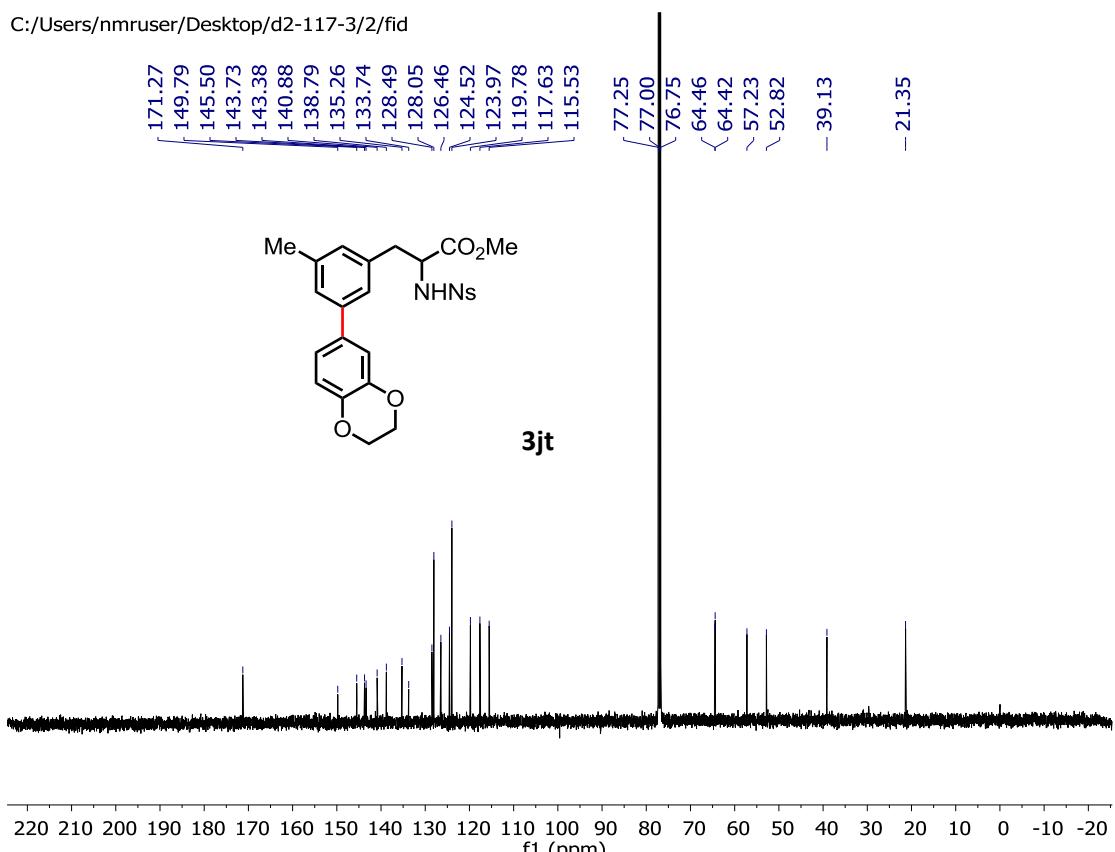




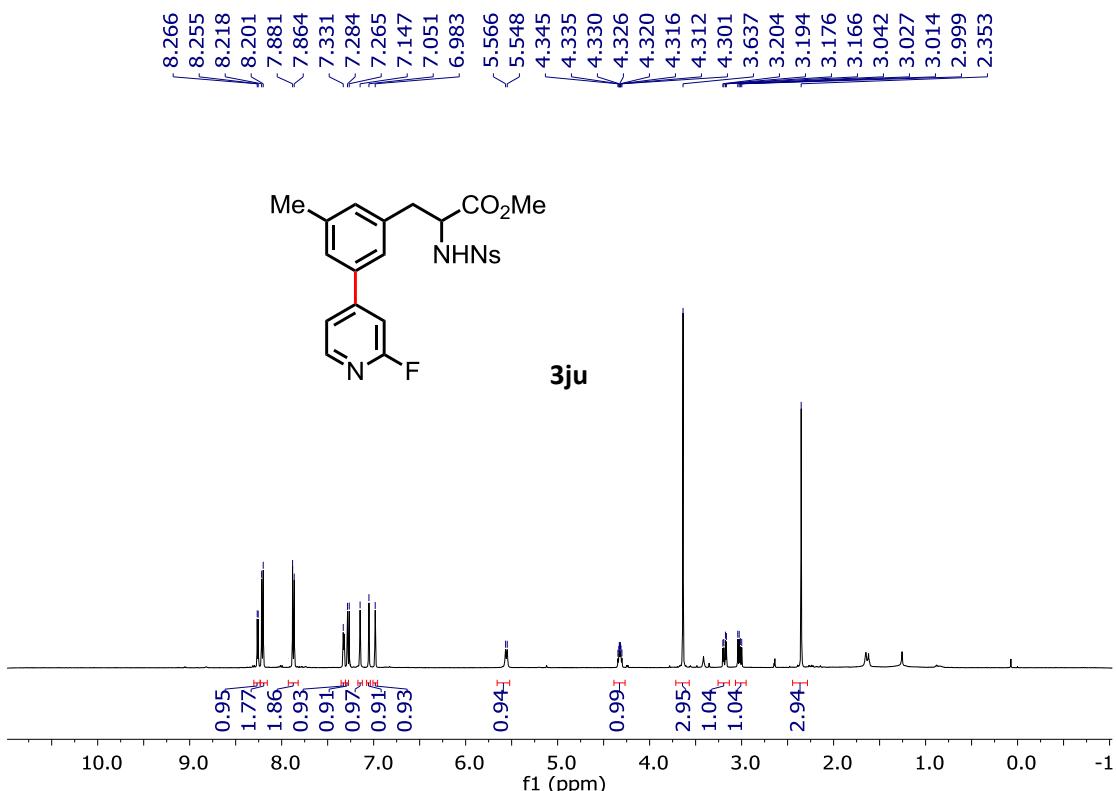
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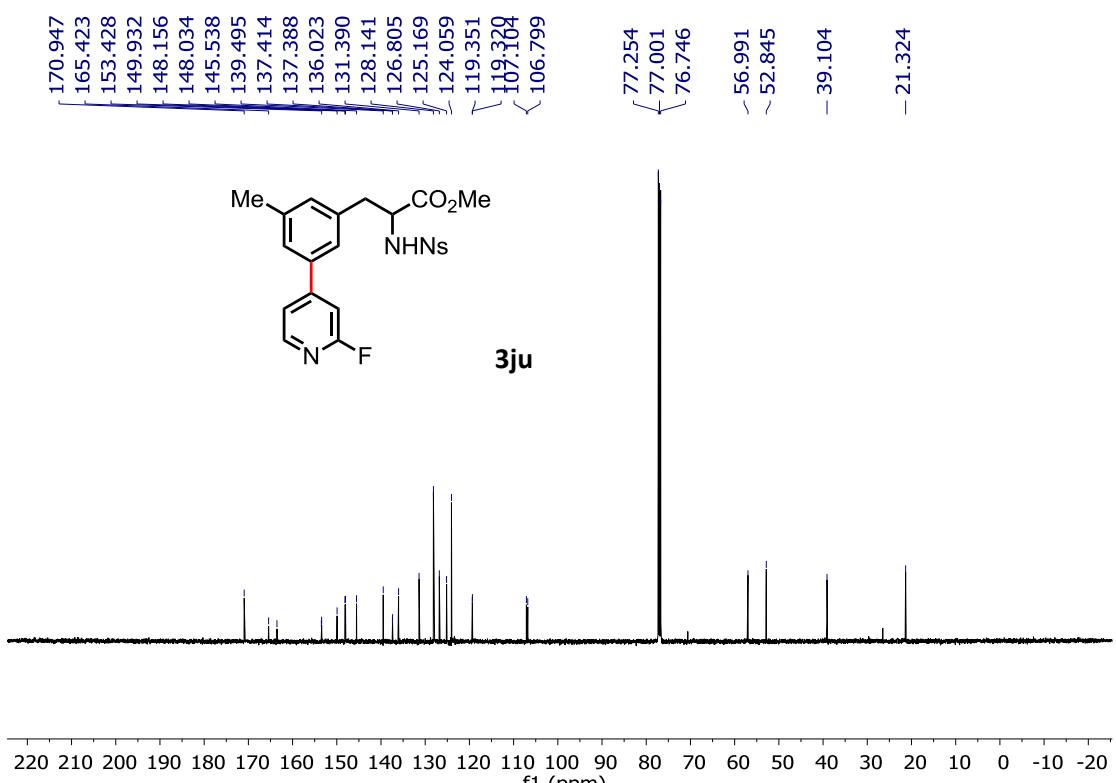
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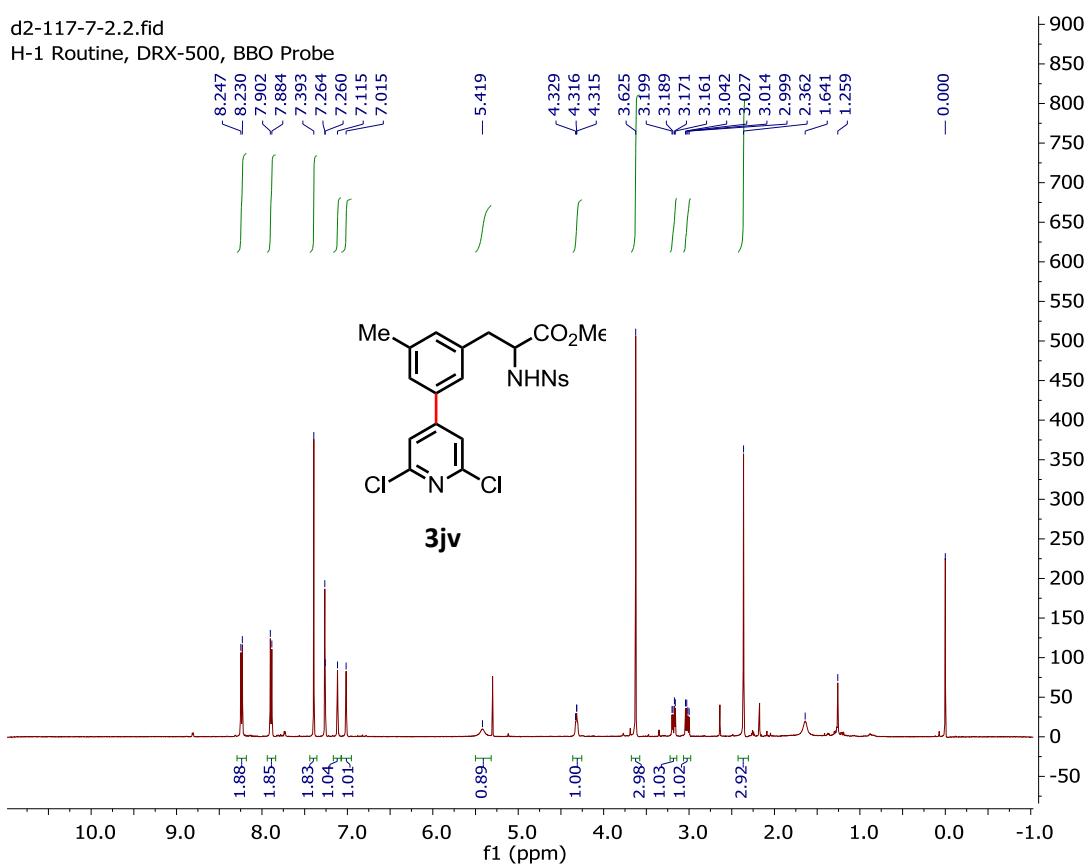


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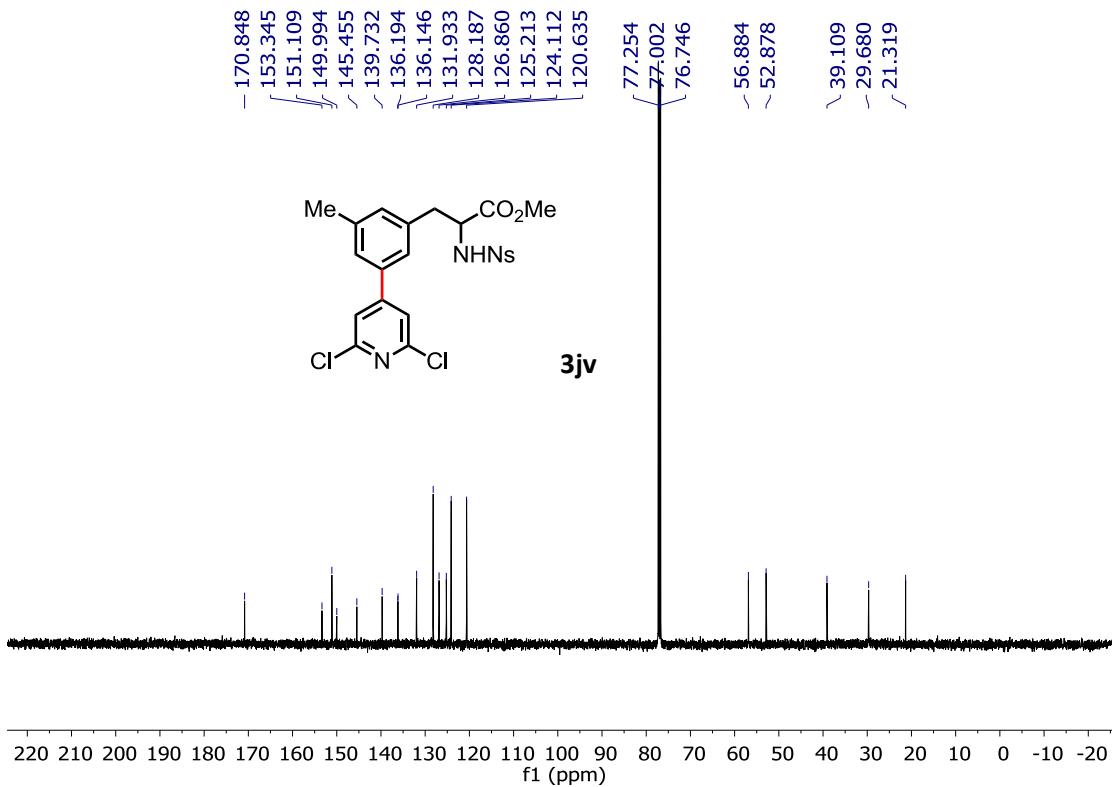


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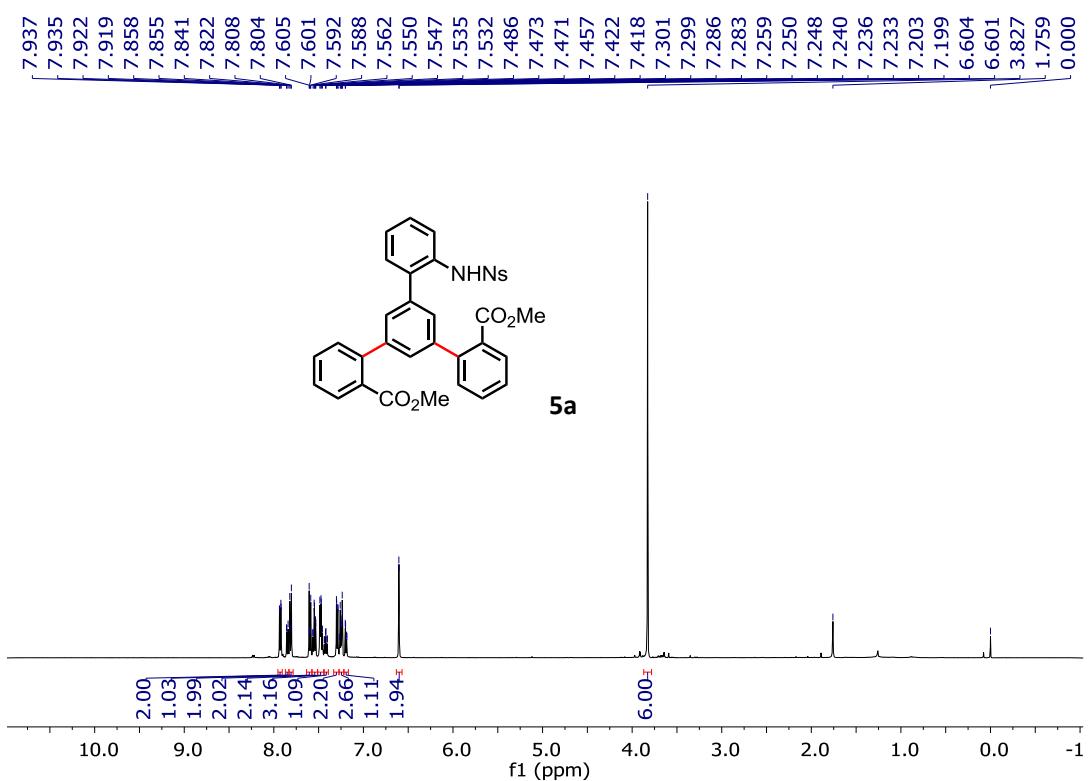
H-1 Routine, DRX-500, BBO Probe



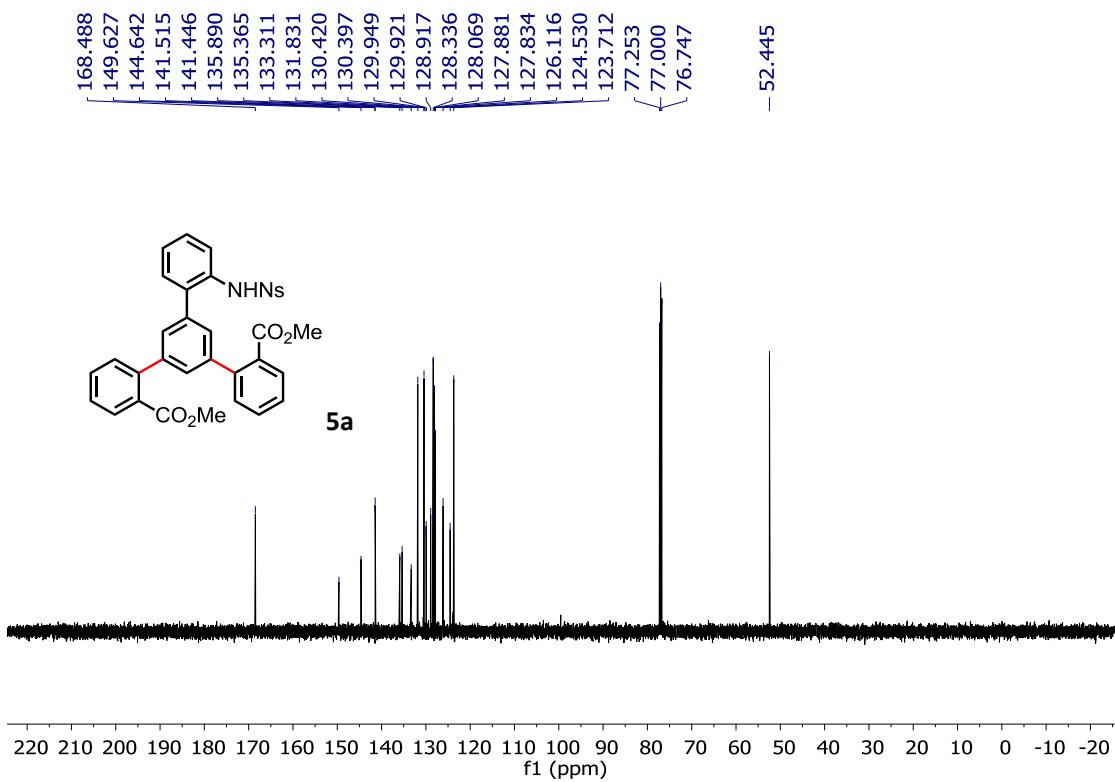
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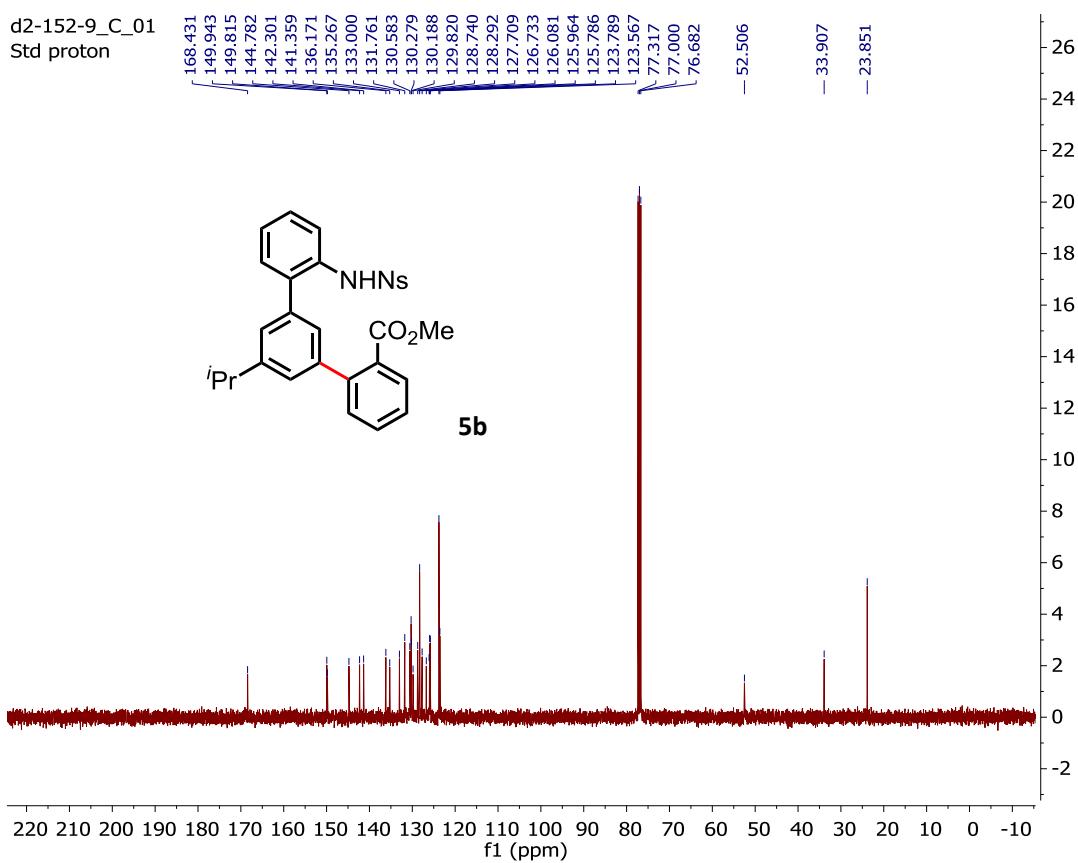
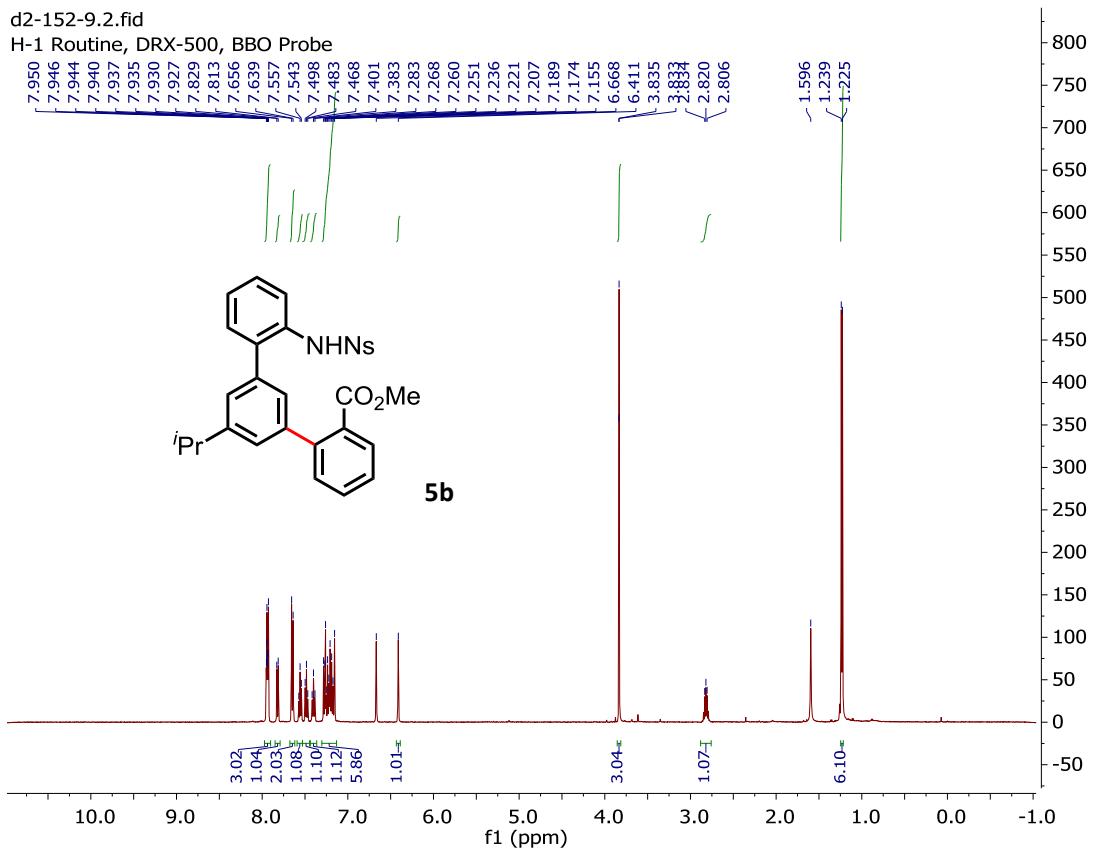


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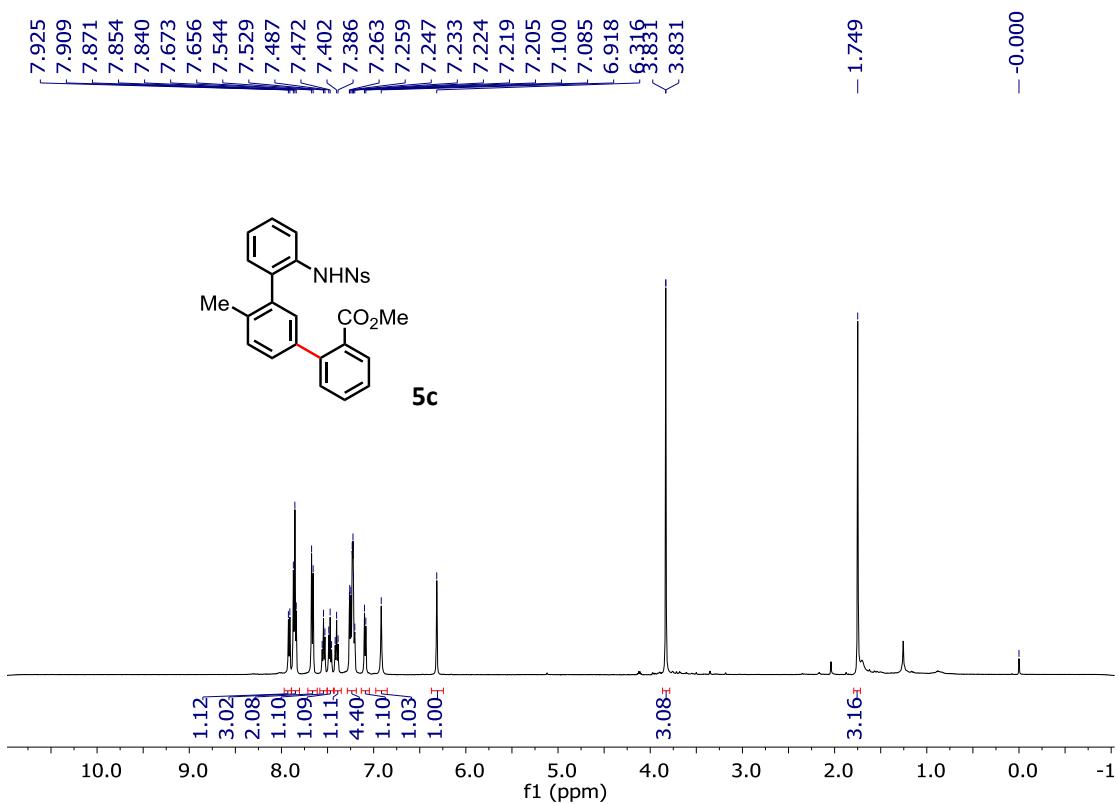


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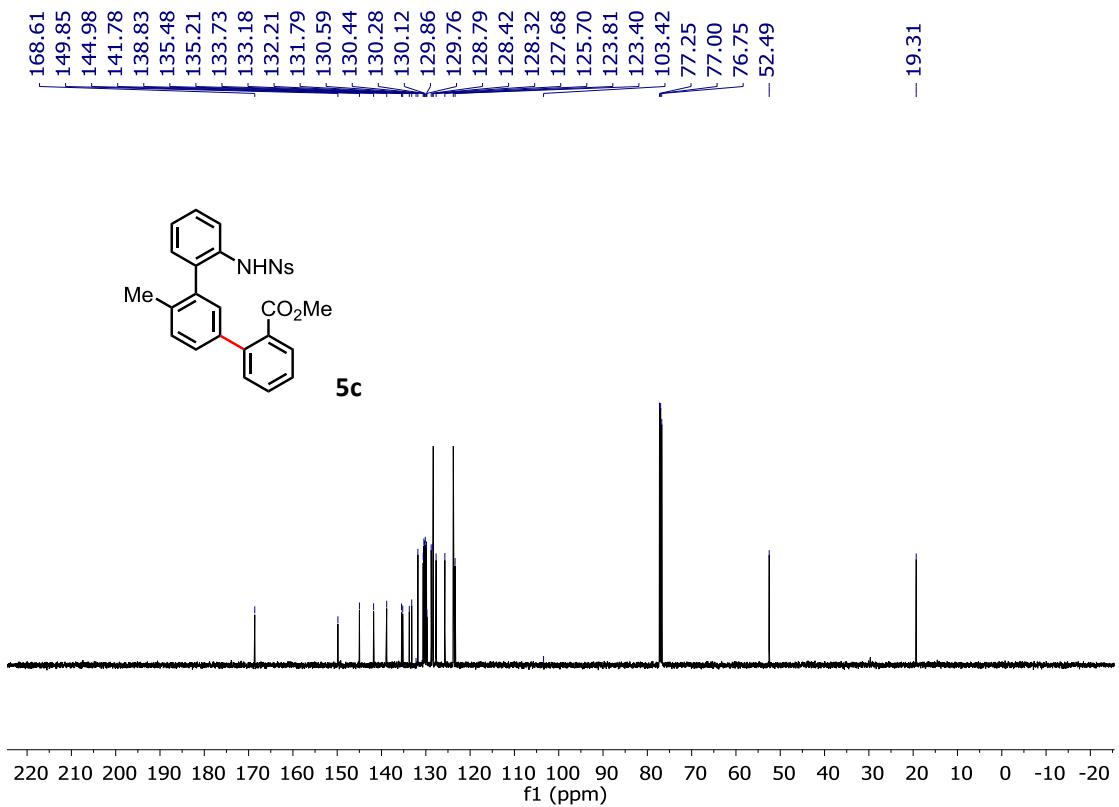


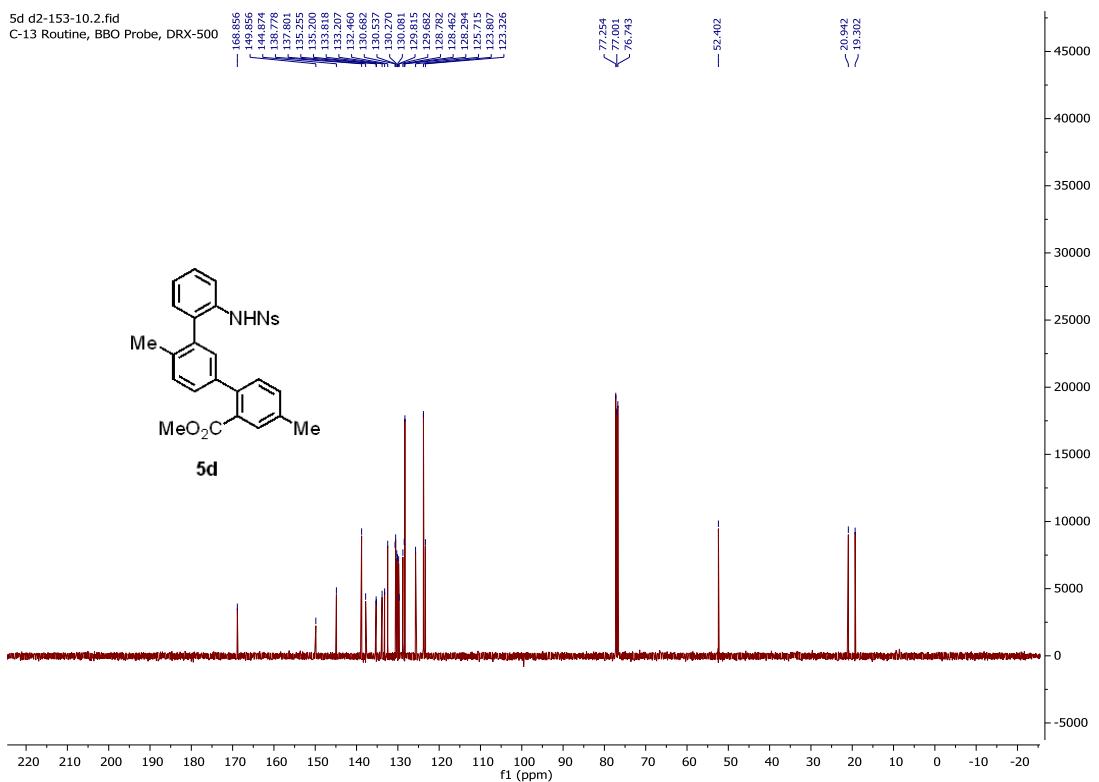
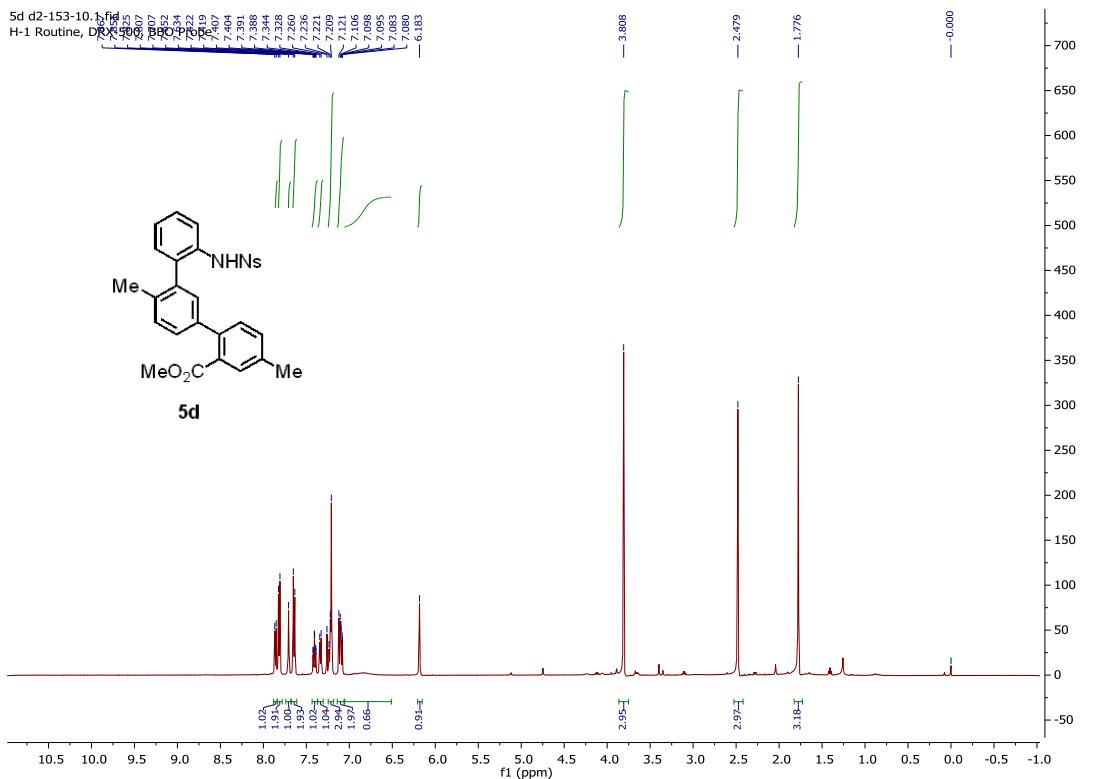


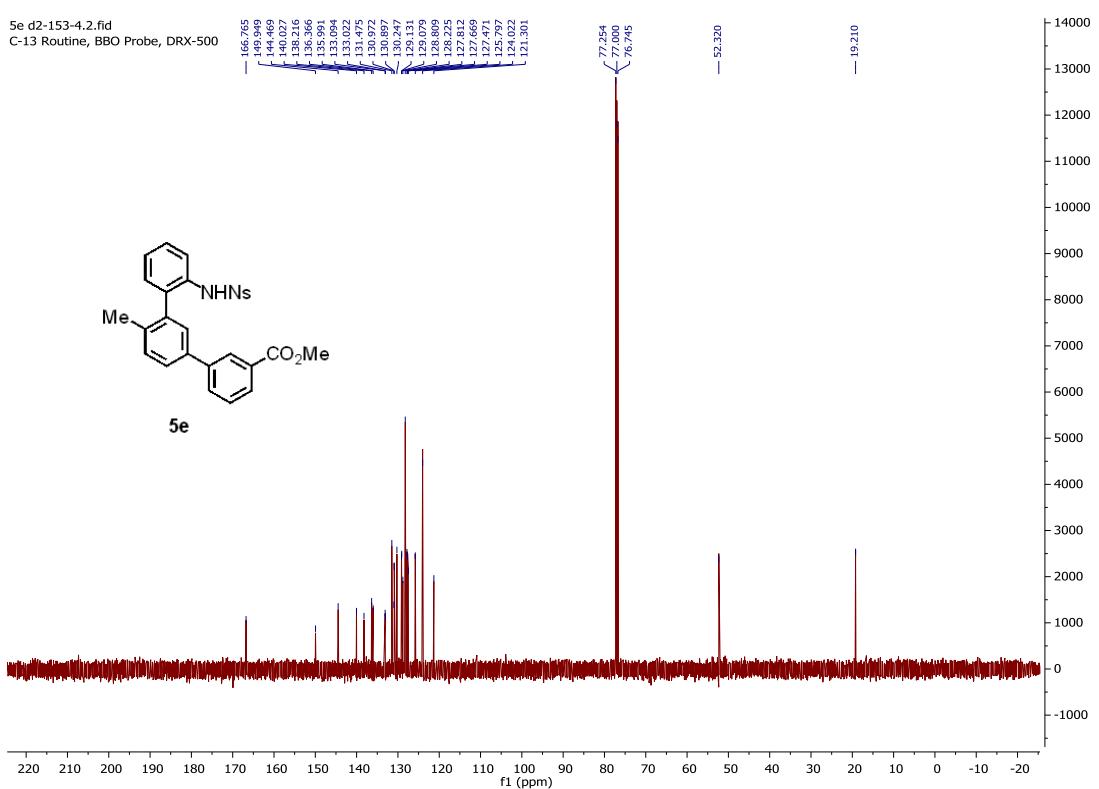
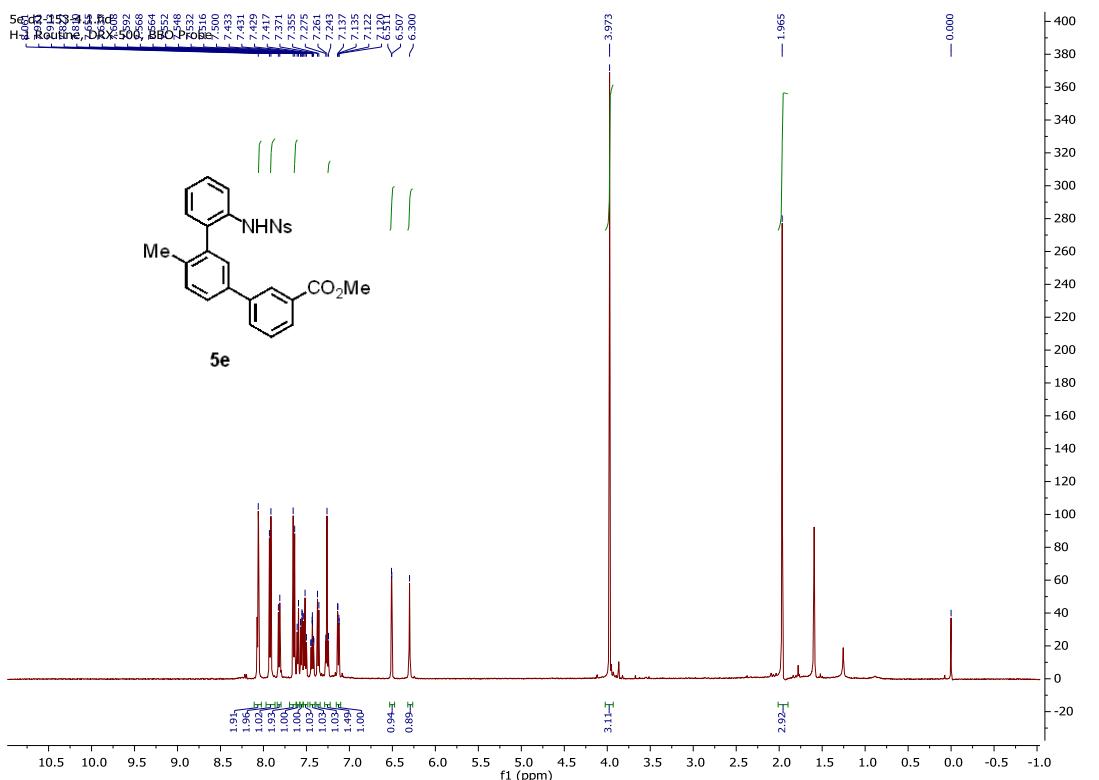
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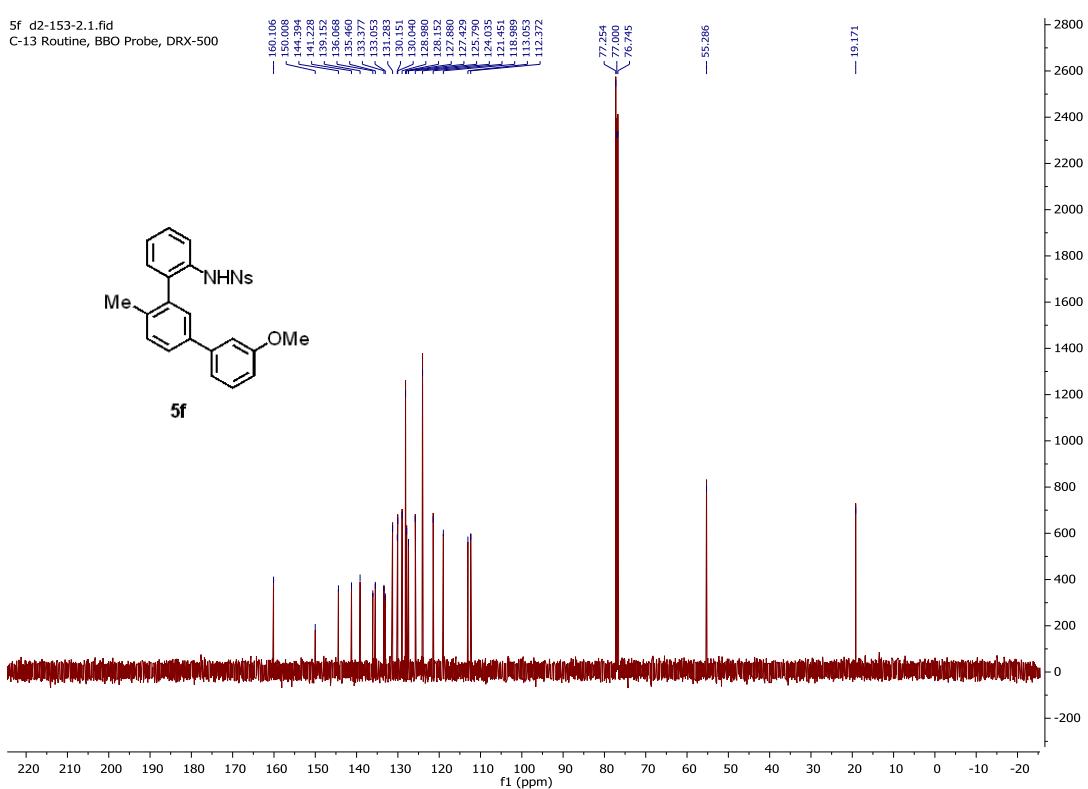
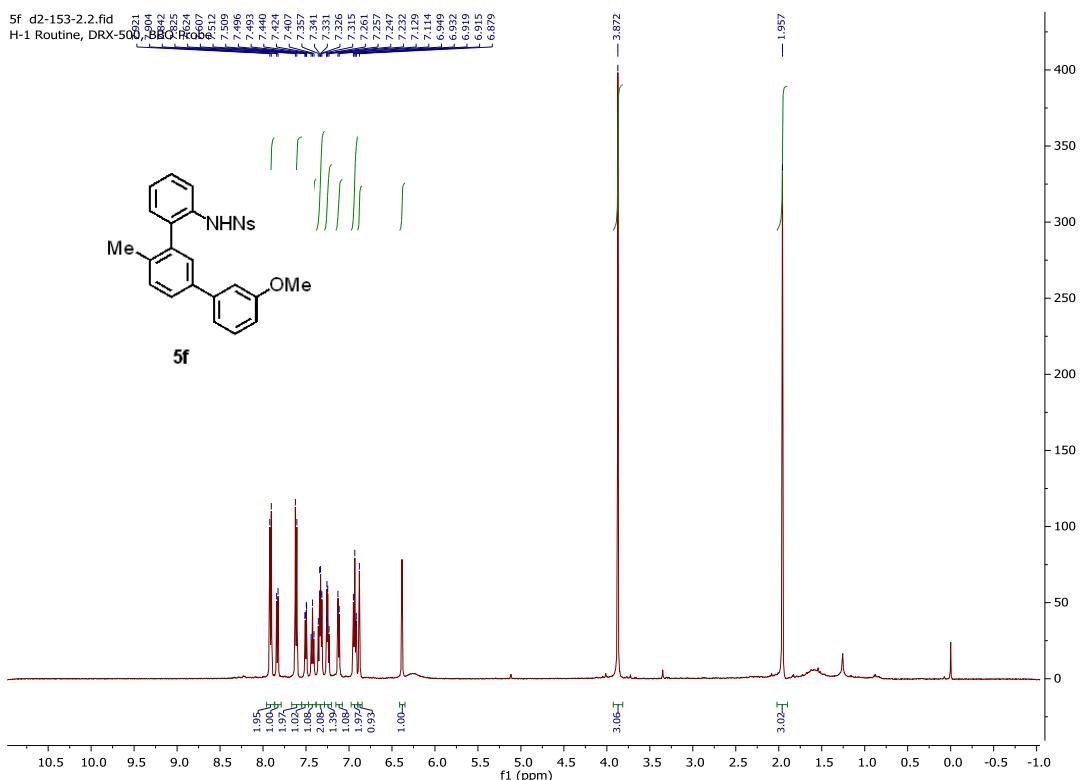


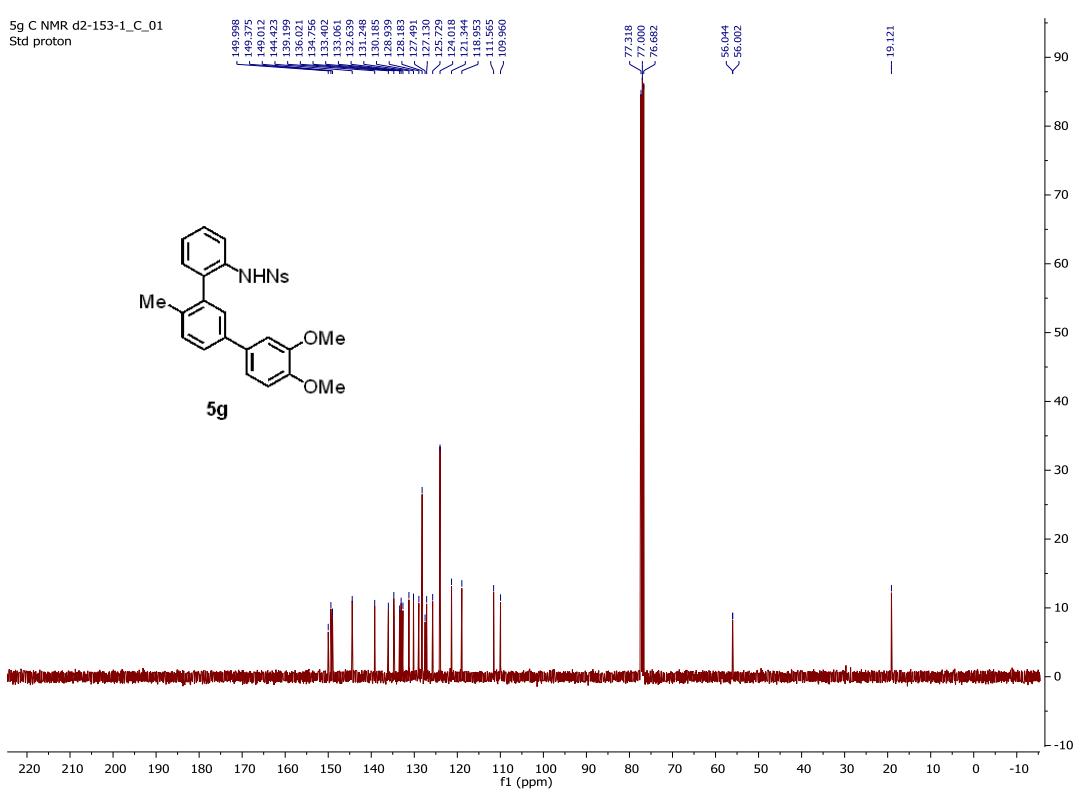
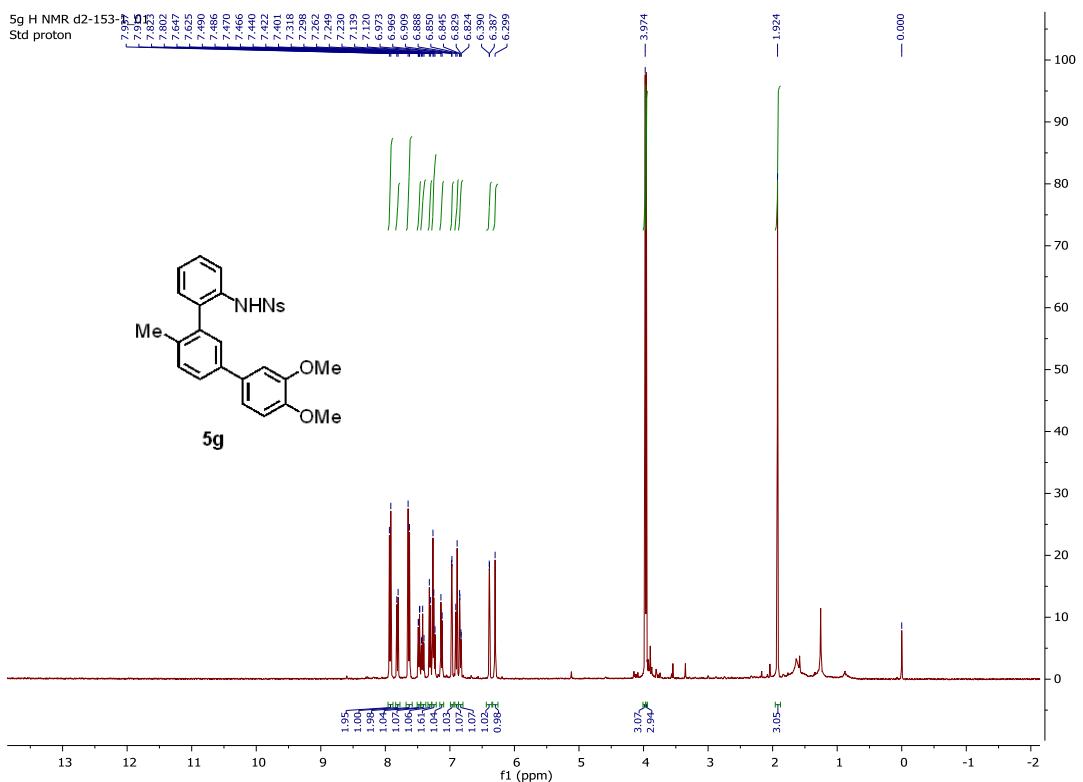
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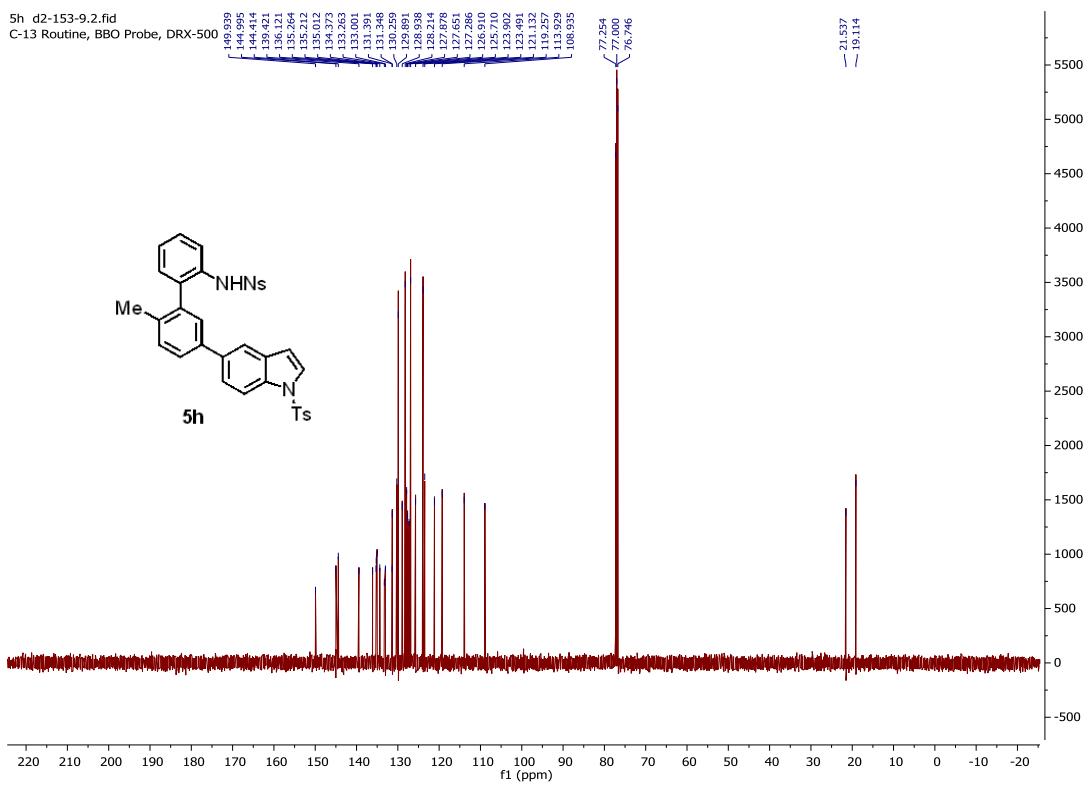
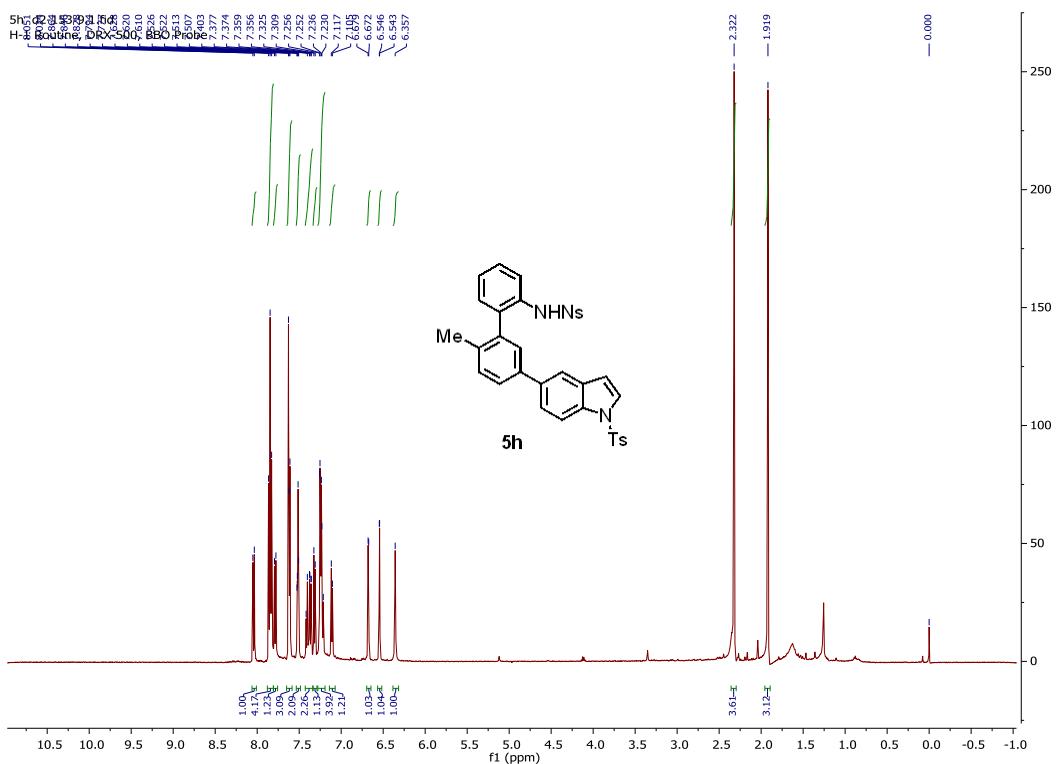


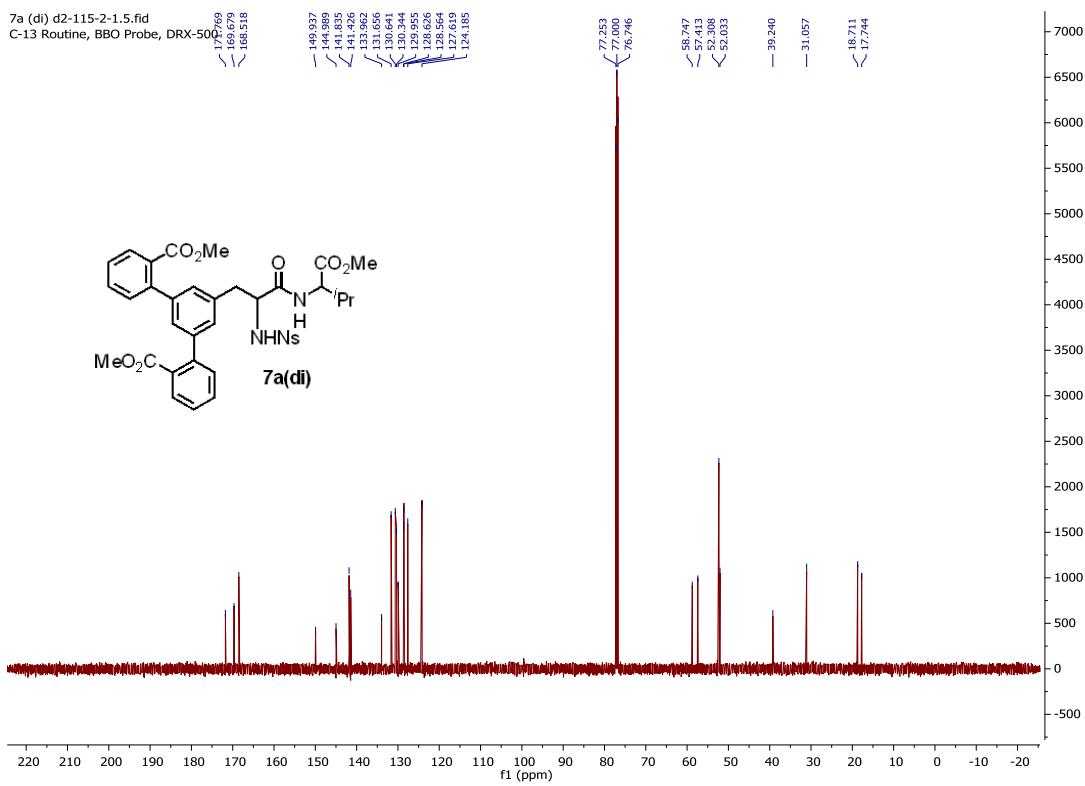
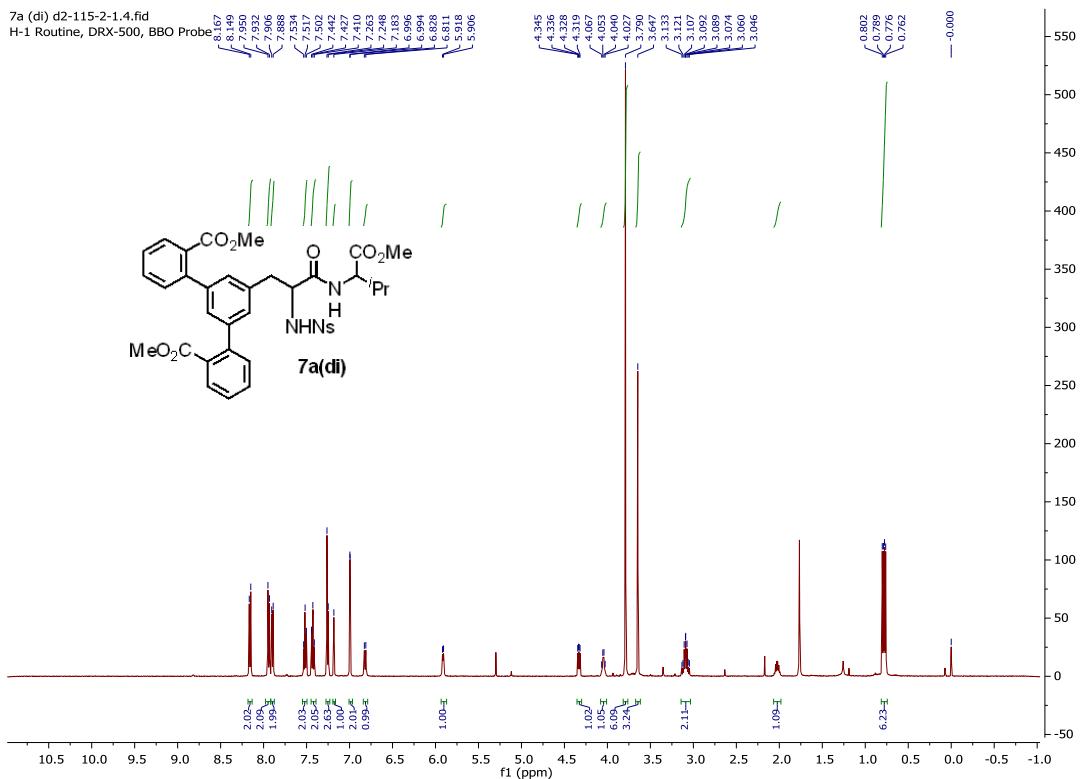


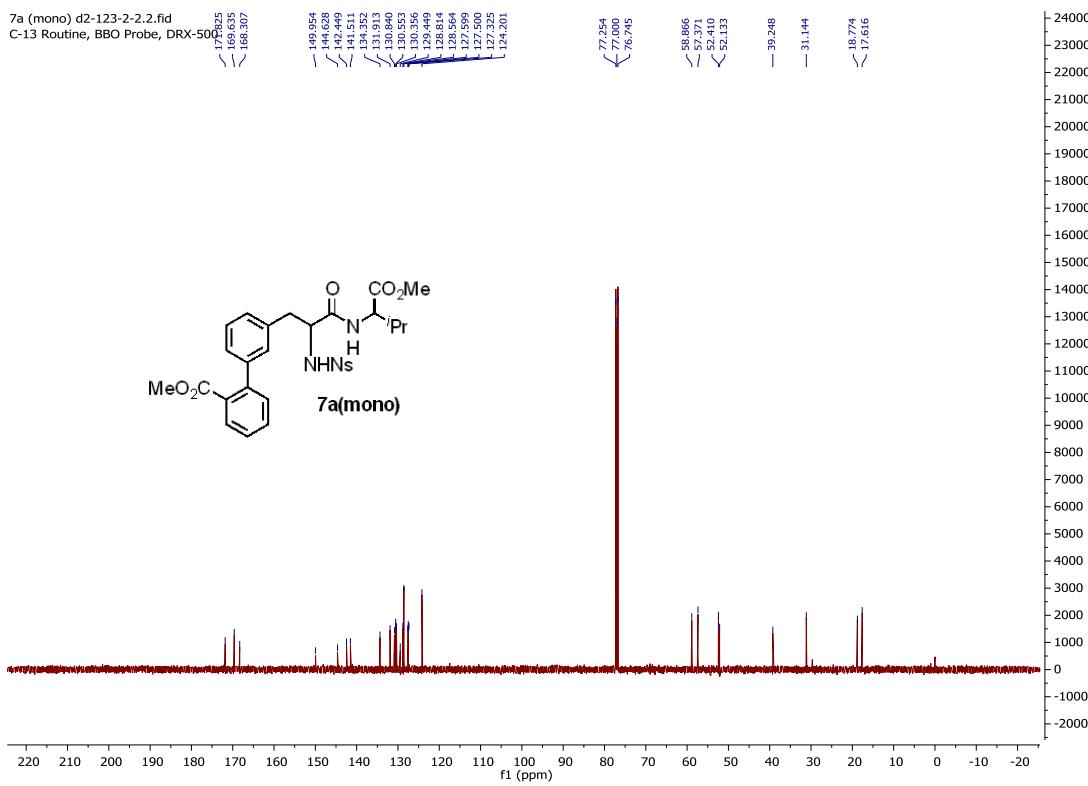
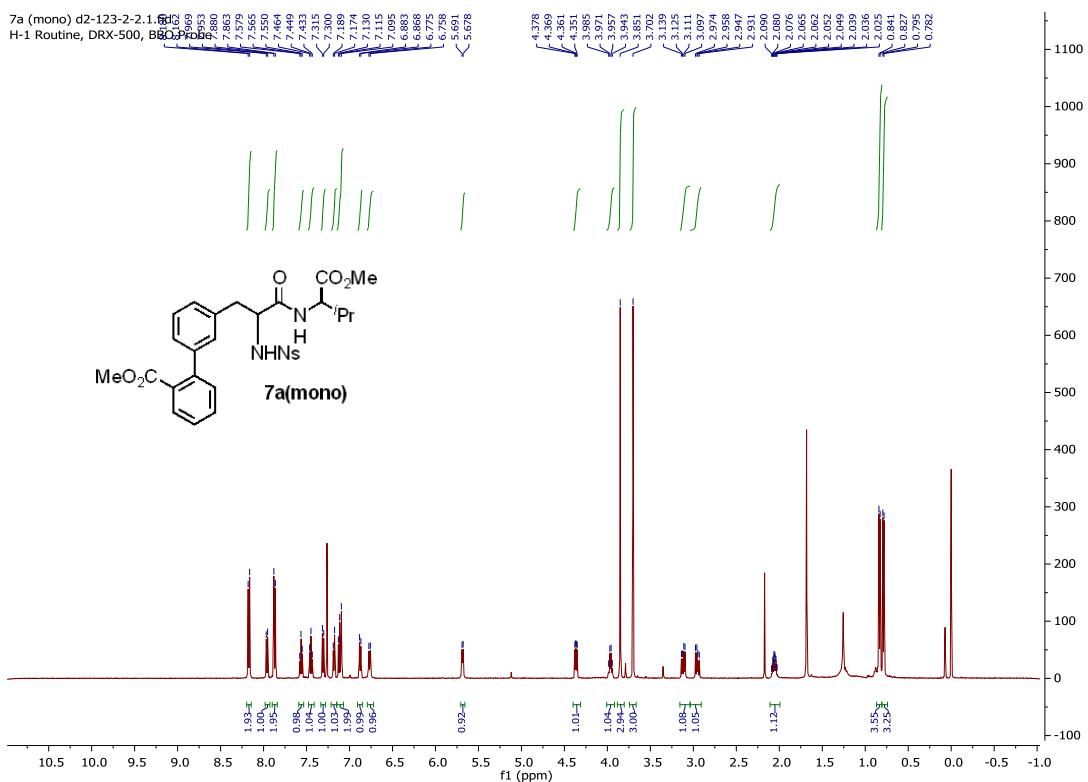


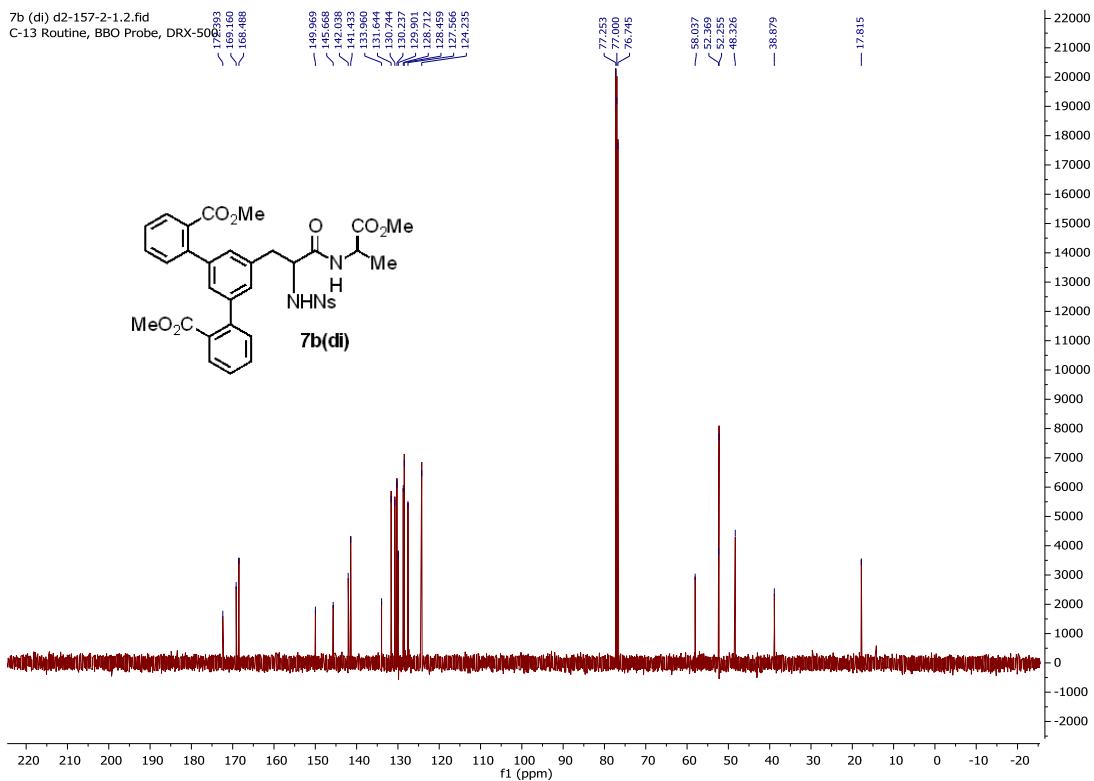
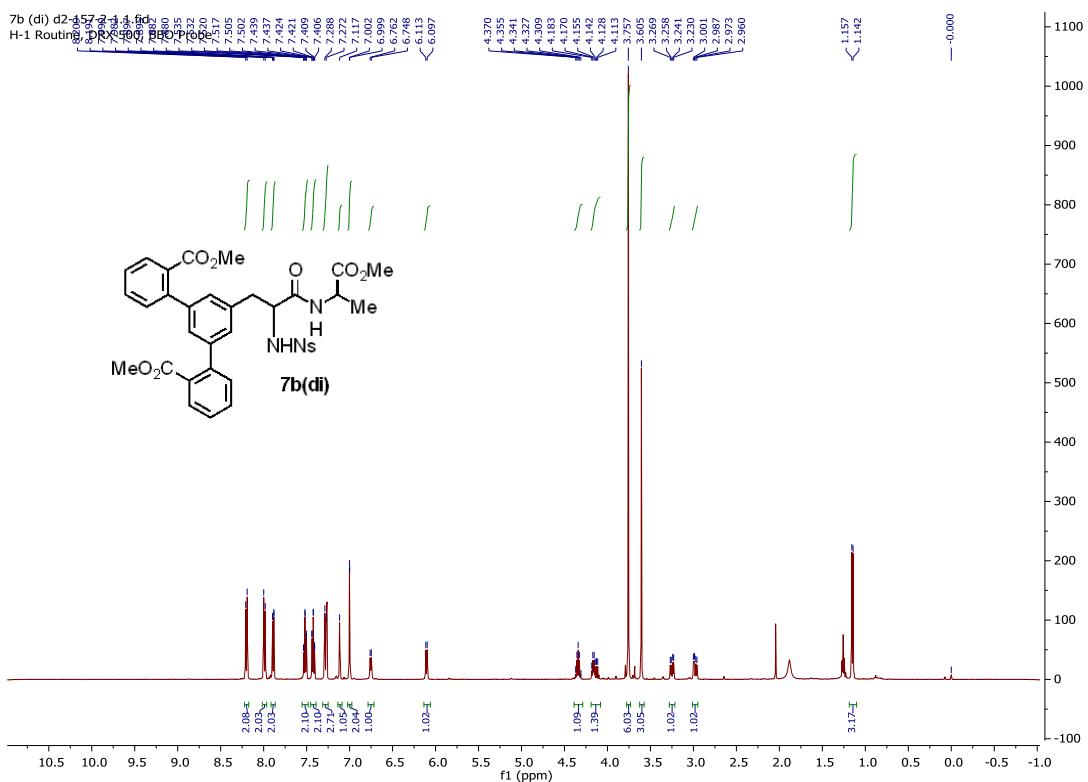


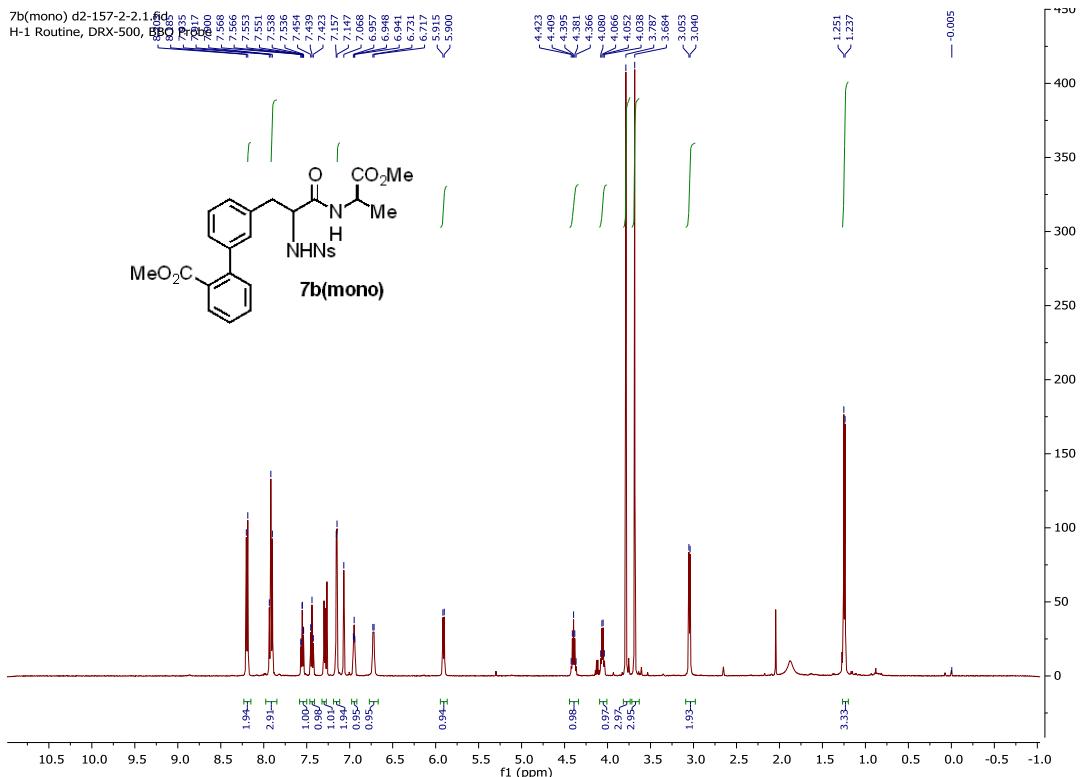


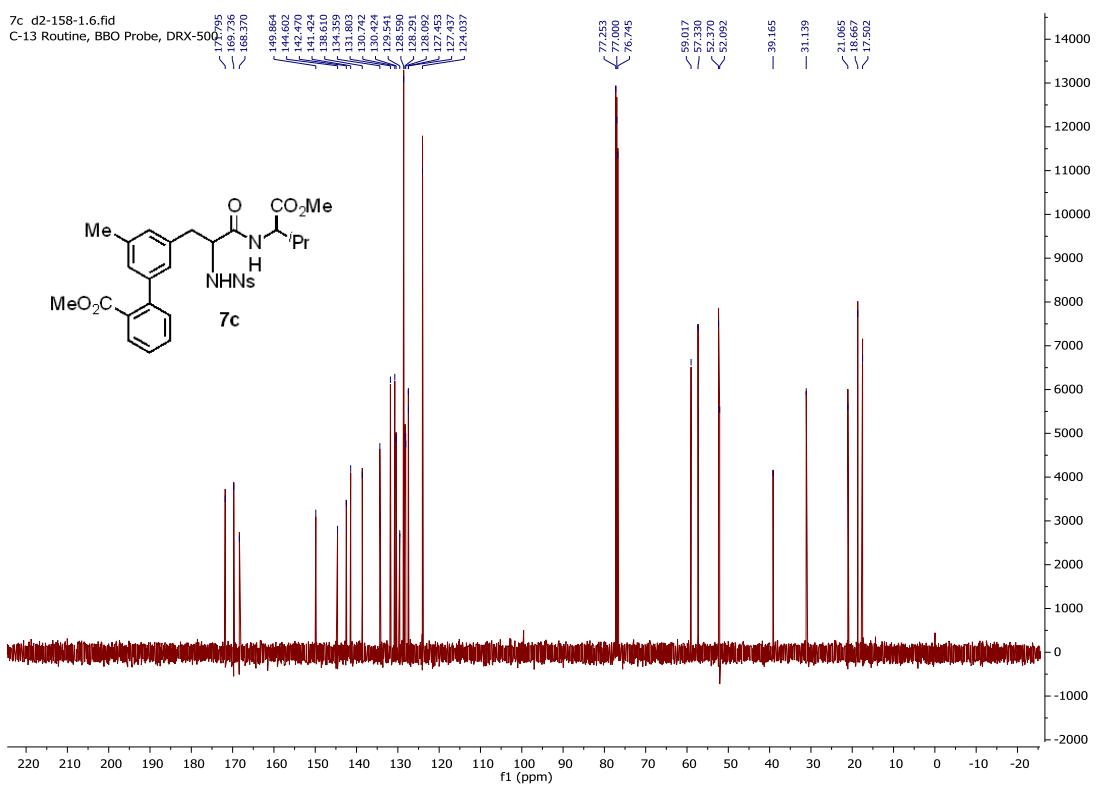
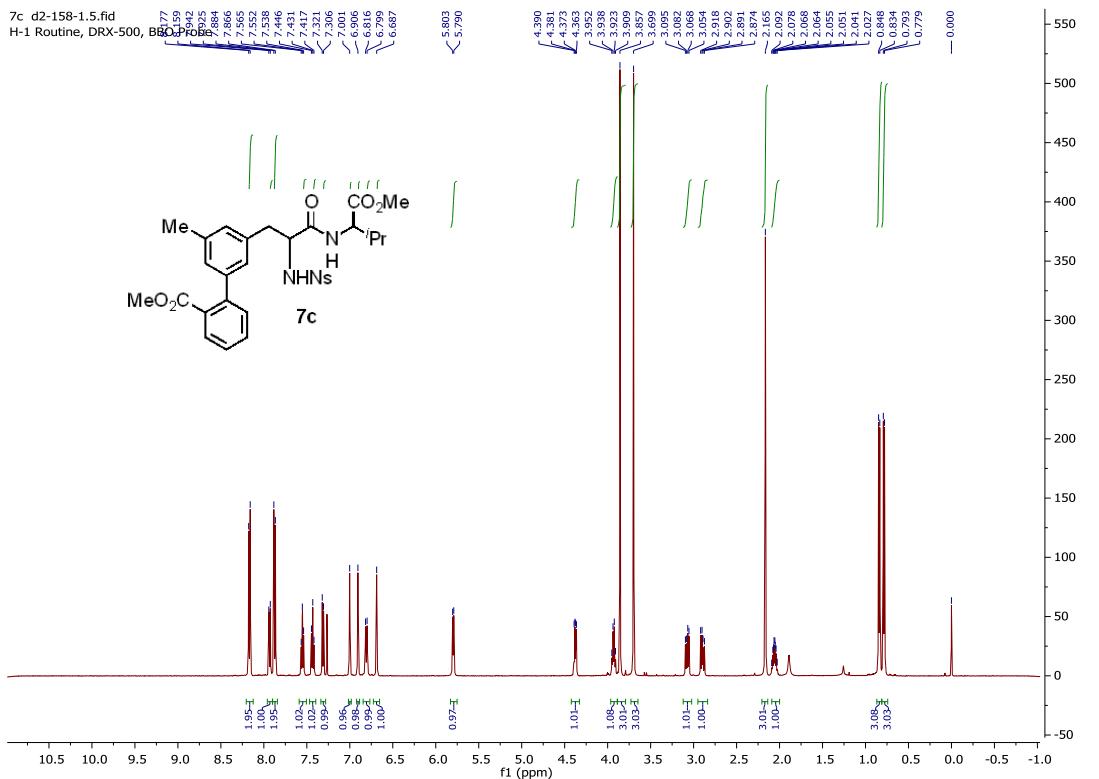


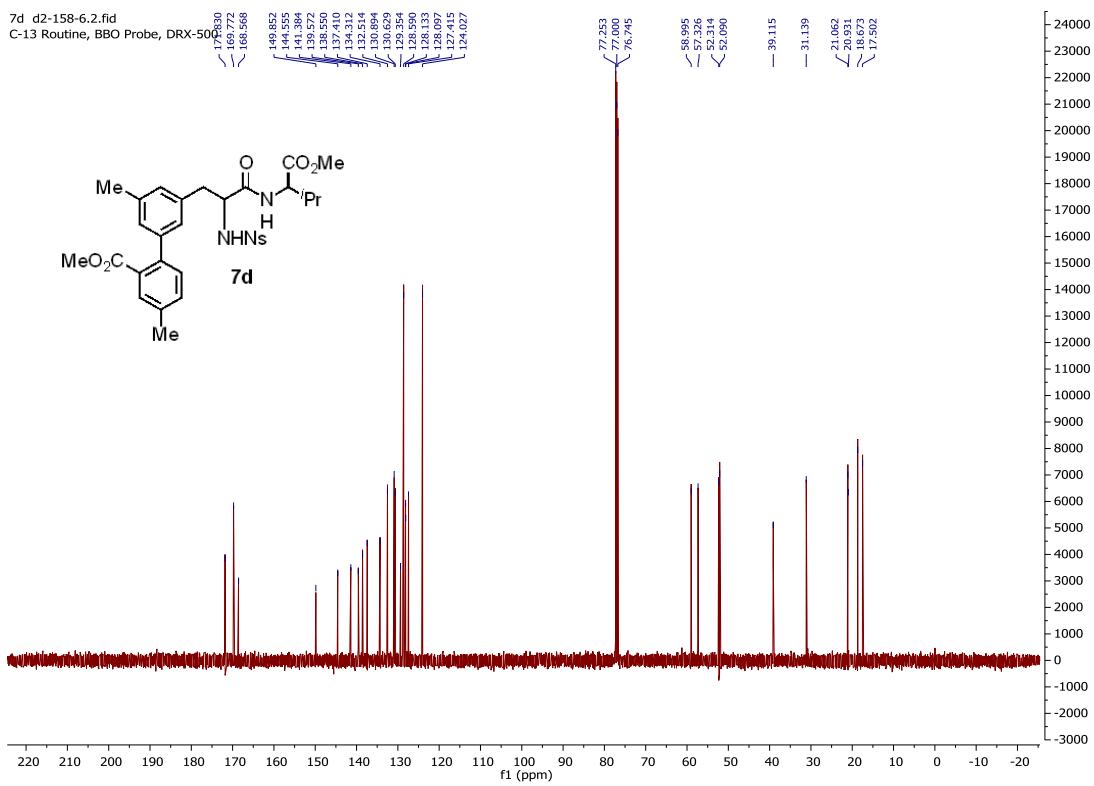
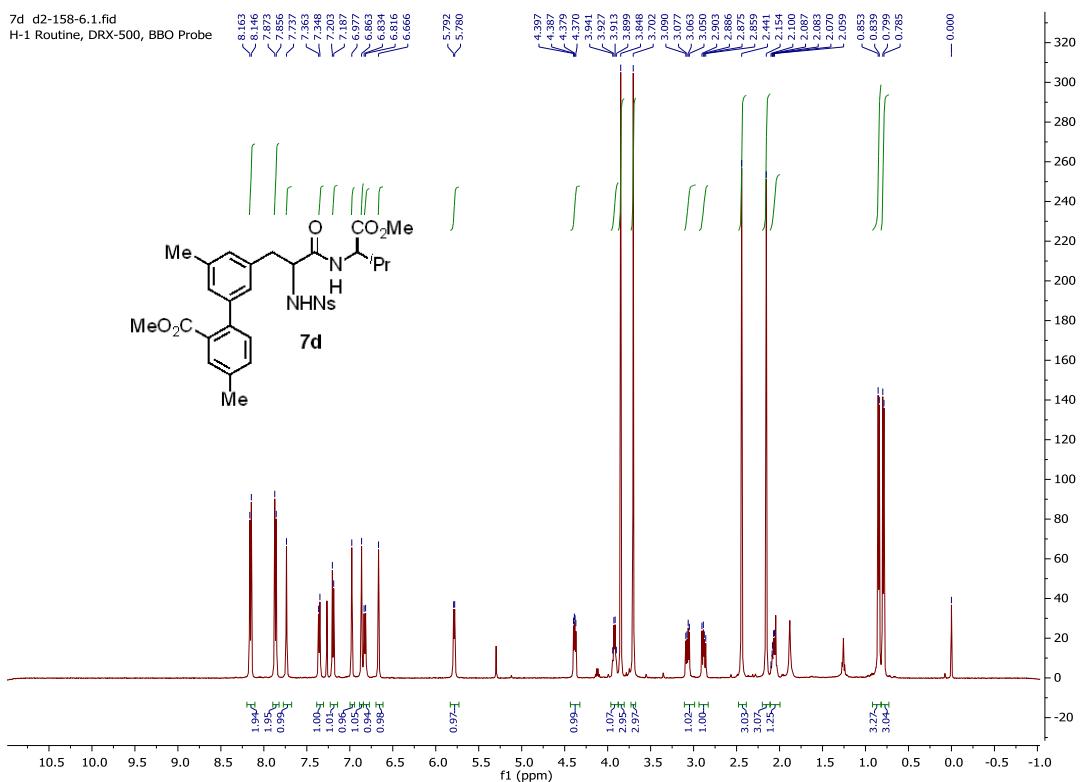


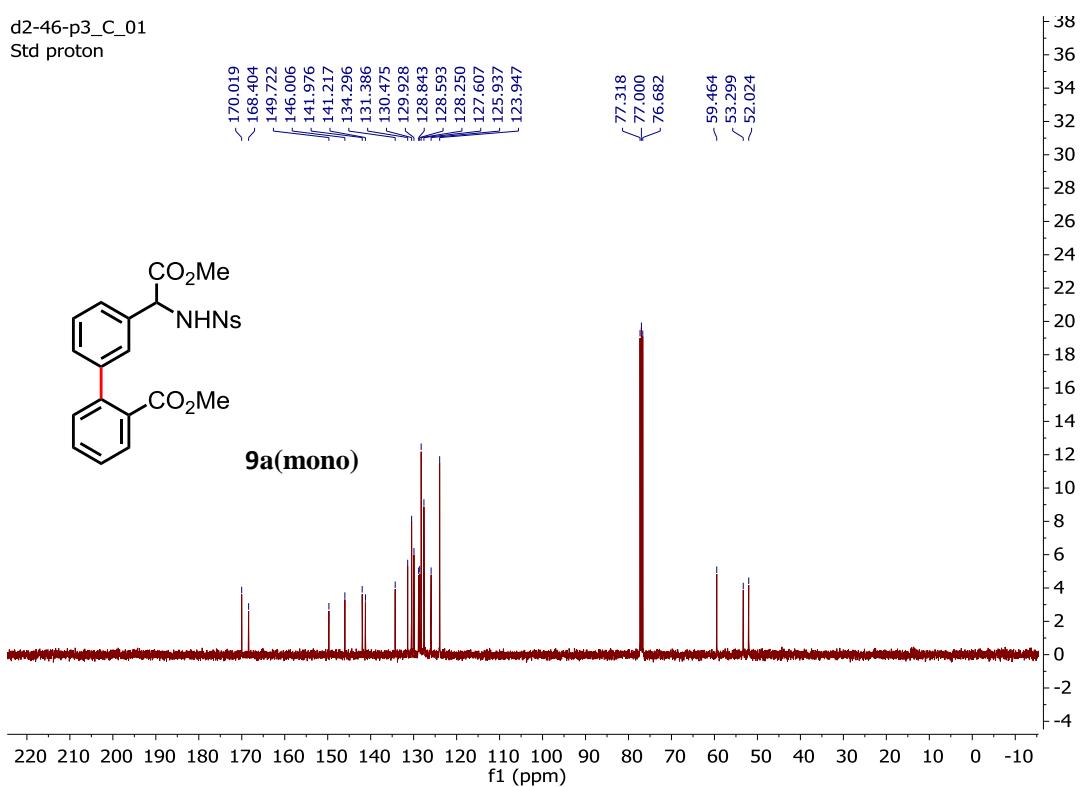
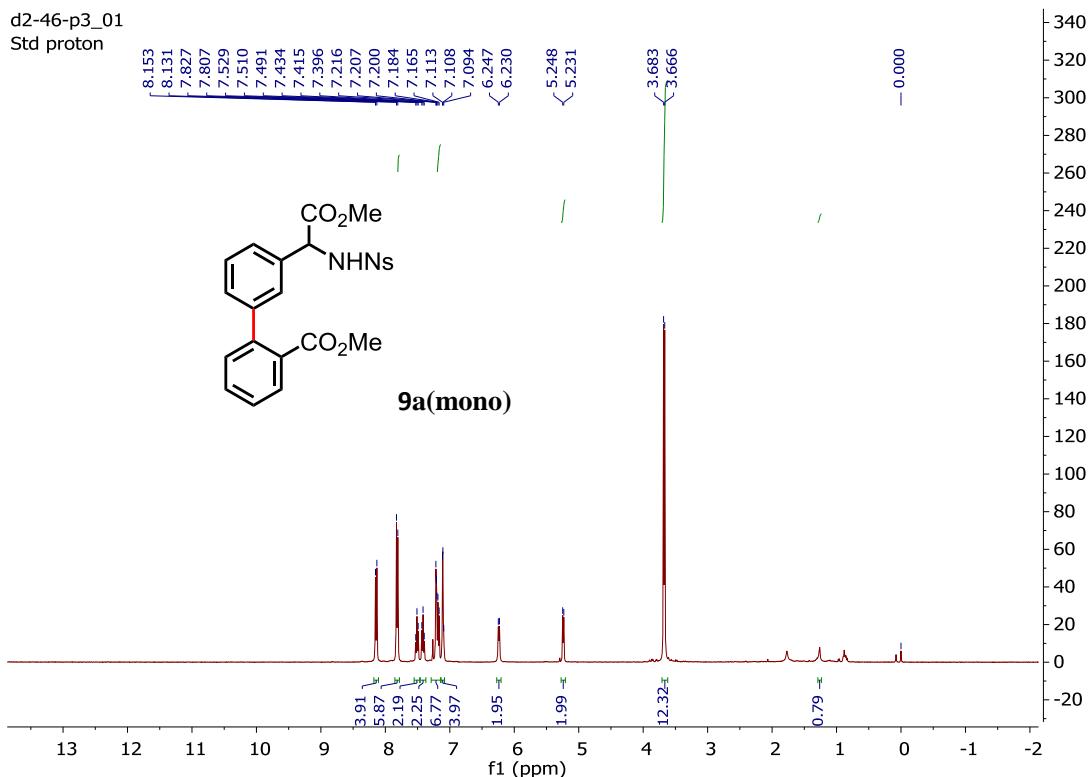




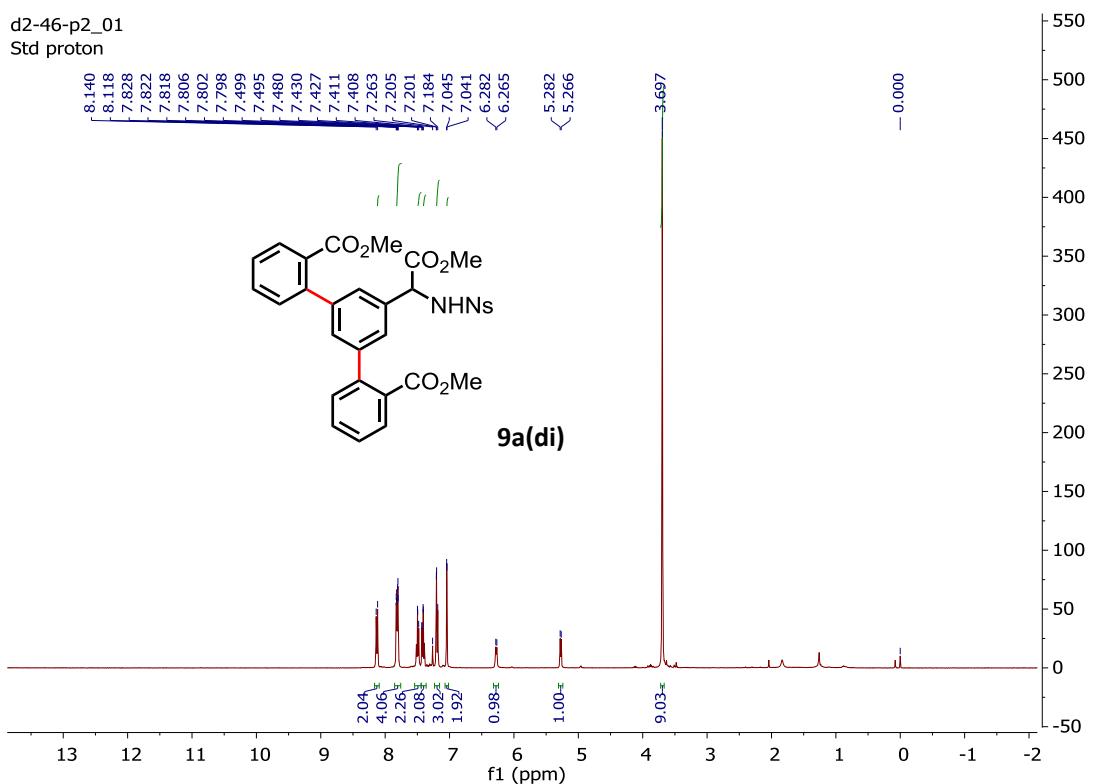




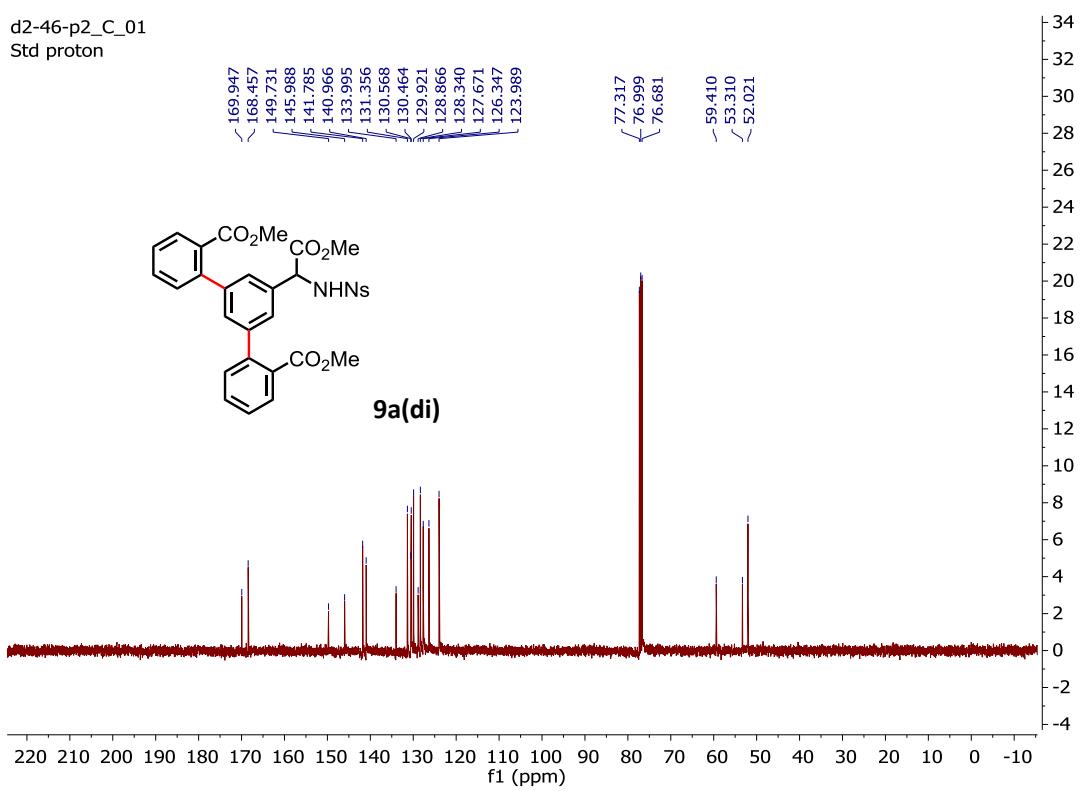




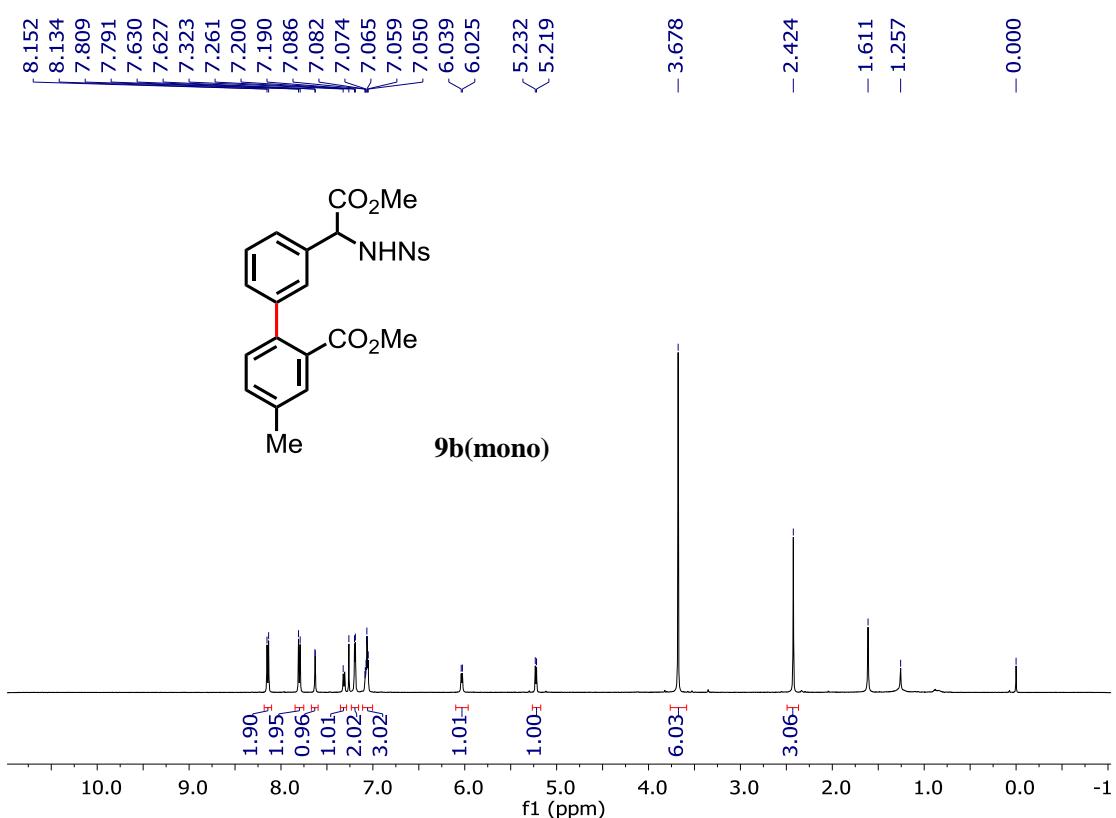
d2-46-p2_01
Std proton



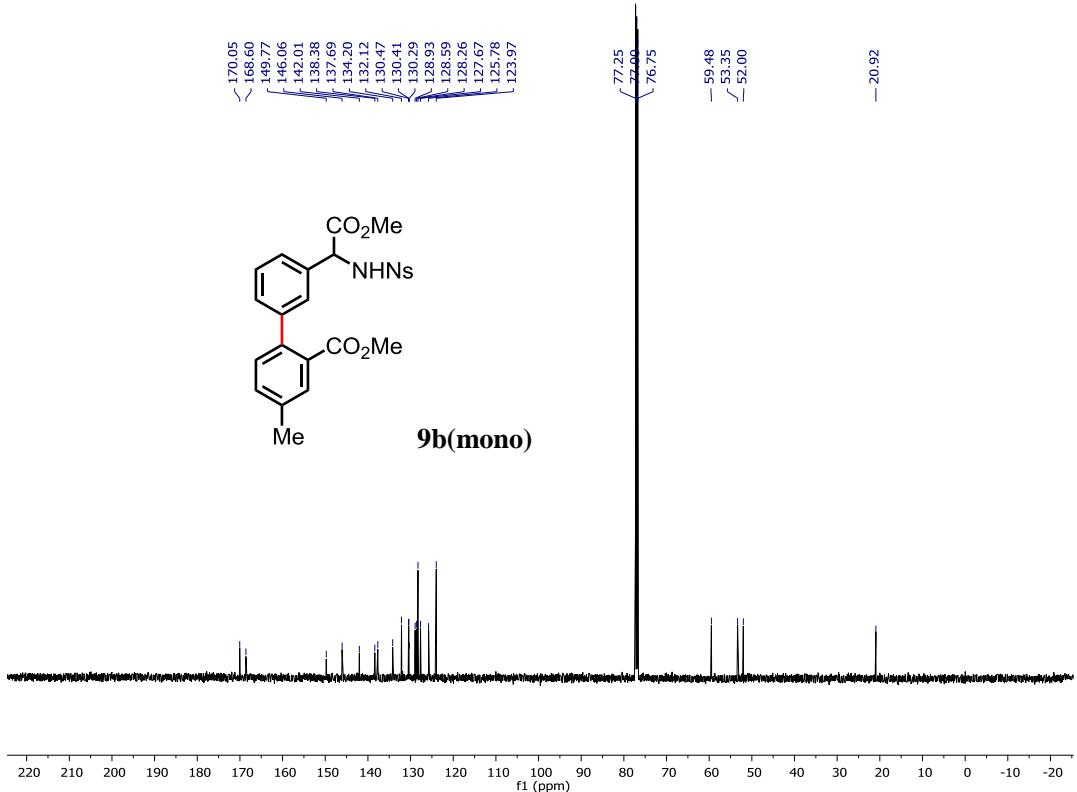
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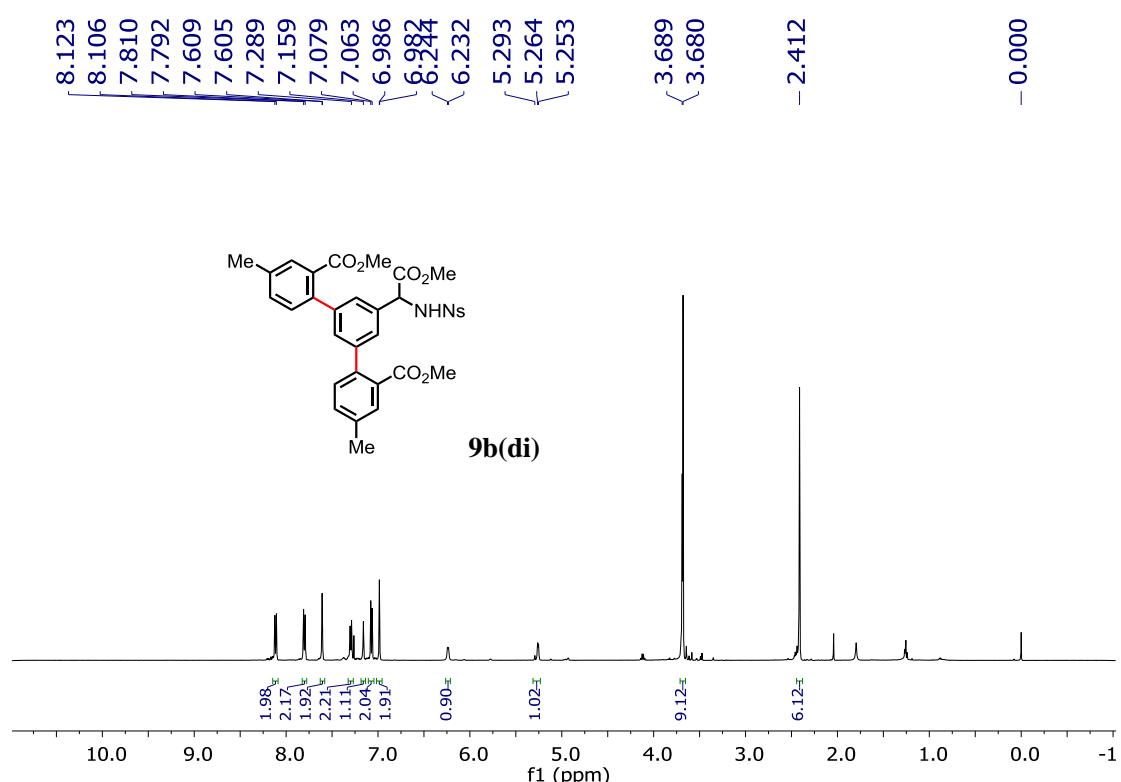
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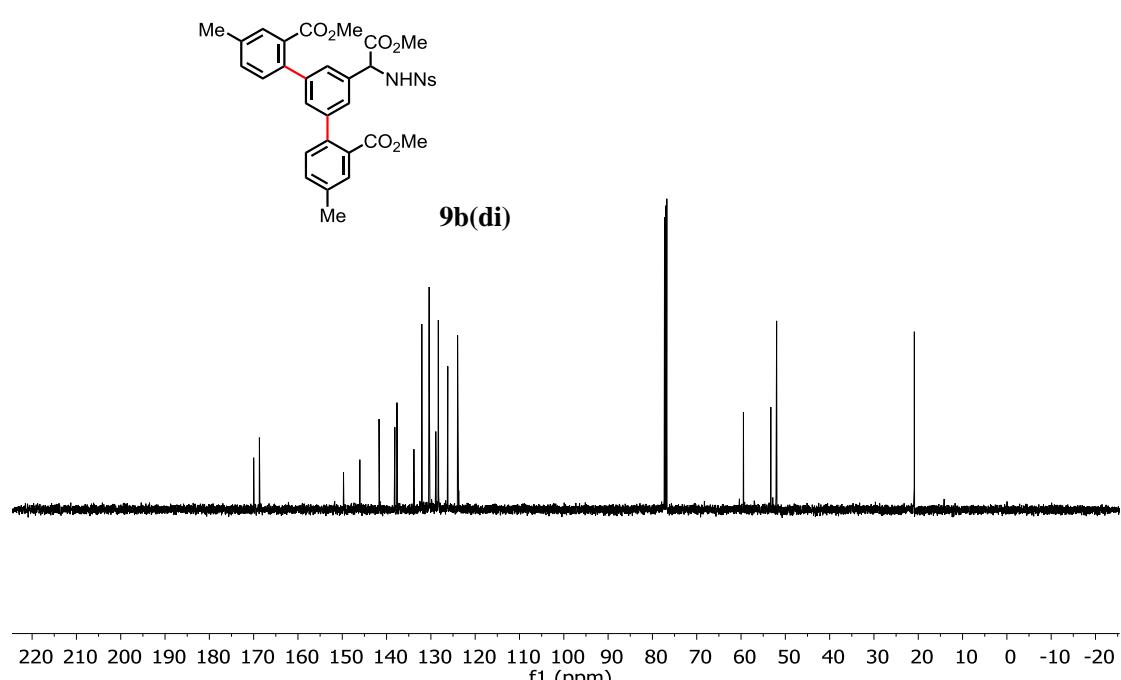
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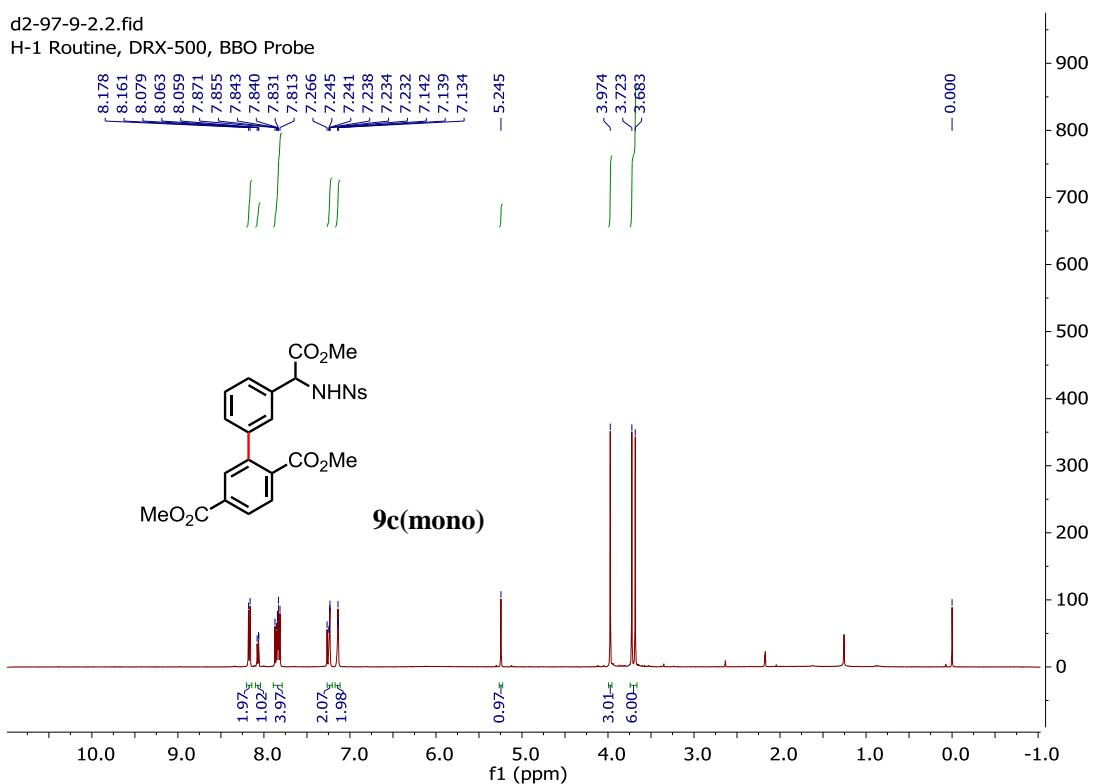
d2-97-11-1.1.fid
H-1 Routine, DRX-500, BBO Probe



d2-97-11-1.1.fid
C-13 Routine, BBO Probe, DRX-500



d2-97-9-2.2.fid
H-1 Routine, DRX-500, BBO Probe



d2-97-9-2.3.fid
C-13 Routine, BBO Probe, DRX-500

