Enantioselective Michael Reactions of β, β-Disubstituted Nitroalkenes: A New Approach to $\beta^{2,2}$-Amino Acids with Hetero-Quaternary Stereocenters

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Contents

1. General methods

Proton and carbon nuclear magnetic resonance (^{1}H & ^{13}C NMR) spectra were recorded on Varian-Mercury 400/600 (400/600 MHz) spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual solvent signals ($CHCl_3$, 7.26 ppm for ^{1}H NMR, $CDCl_3$, 77.0 ppm for ^{13}C NMR). Data are reported as follows: chemical shift (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dd = doublet of triplets, m = multiplet, br = broad signal), coupling constants (Hz). Mass spectra were measured on a Finnigan Trace MS spectrometer. Elementary analyses were taken on a Vario EL III elementary analysis instrument. Chromatographic purification of products was accomplished using nitrogen-forced-flow chromatography according to the method of Still.[1] The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC. Optical rotations were measured with JASCO P-1020 polarimeter.

2. Materials

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[2] Flash chromatography was conducted using 60 silica (mesh 230-400). β-nitroacrylates **2**[3] and acid-base bifuntional organocatalysis **4, 9-12**[4] were prepared according to literature procedures.

[1] Still, W. C.; Kahn, M.; Mitra, A. J. *J. Org. Chem.* **1978**, *43*, 2923.

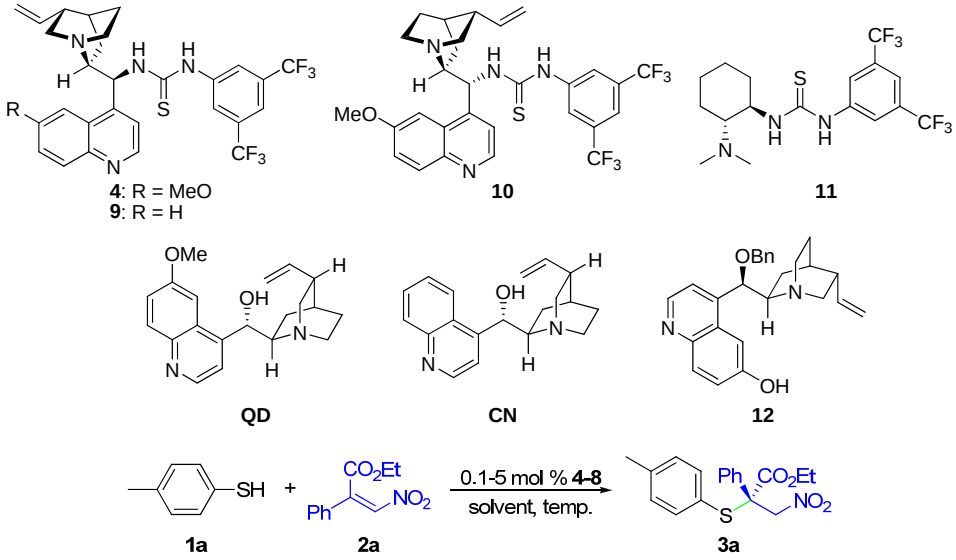
[2] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals, 4th ed.*; Pergamon Press: Oxford, 1997.

[3] a) Creary, X. *J. Org. Chem.* **1987**, *52*, 5026; b) Christensen, C.; Juhl, K.; Hazell, R. G.; Jørgensen, K. A. *J. Org. Chem.* **2002**, *67*, 4875; c) Martin, N. J. A.; Cheng, X.; List, B. *J. Am. Chem. Soc.* **2008**, *130*, 13862.

[4] a) Okino, T.; Hoashi, Y.; Takemoto, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12672; b) Li, H.; Wang, Y.; Tang, L.; Deng, L. *J. Am. Chem. Soc.* **2004**, *126*, 9906; c) Vakulya, B.; Varga, S.; Csámpai, A.; Soós, T. *Org. Lett.* **2005**, *7*, 1967; d) Li, B.; Jiang, L.; Liu, M.; Chen, Y.; Ding, L.; Wu, Y. *Synlett* **2005**, 603; e) McCooey, S. H.; Connon, S. J. *Angew. Chem. Int. Ed.* **2005**, *44*, 6367; f) Ye, J.; Dixon, D. J.; Hynes, P. S. *Chem. Commun.* **2005**, 4481.

3. Reaction Optimization and Result Summary

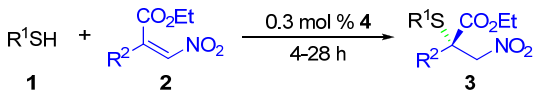
Table 1. Conjugated addition of *p*-thiocresol **1a** to (*E*)-α-phenyl-β-nitroacrylate **2a** by means of selected bifunctional organocatalysts under various conditions.[a]



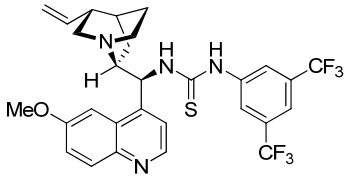
entry	catalyst	solvent	time	yield (%)[b]	ee (%)[c]
1	**4**			96	75
2	**9**			95	70
3	**10**			96	-66
4	**11**	toluene	< 5 min	97	-72
5	**QD**			93	33
6	**CN**			95	27
7	**12**			95	-40
8		xylenes	< 5 min	94	77
9		benzene	< 5 min	98	80
10		DCM	< 5 min	96	74
11		DCE	< 5 min	93	71
12		$CHCl_3$	< 5 min	90	78
13		Et_2O	< 5 min	95	78
14	**4**	CH_3CN	< 5 min	87	11
15		DMF	2 h	83	0
16		benzene	< 5 min	96	87[d]
17		benzene	< 5 min	95	88[e]
18		benzene	20 min	95	89[f]
19		benzene	5 h	93	88[g]
20		benzene-Et_2O	4 h	98	92[f,h]

[a] Unless noted, reactions were carried out with **1a** (0.22 mmol), **2a** (0.20 mmol) and **4-8** (5 mol %) in 1.0 mL of solvent at 8 °C. [b] Isolated yield. [c] Determined by chiral HPLC. [d] 1.0 mol % of **4**. [e] 0.5 mol % of **4**. [f] 0.3 mol % of **4**. [g] 0.1 mol % of **4**. [h] 0.5 mL of benzene and 0.5 mL of Et_2O at -25 °C.

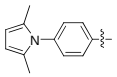
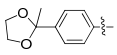
Table 2. Conjugated addition of various thiols **1** to β-nitroacrylates **2** with organocatalyst **4**.[a]



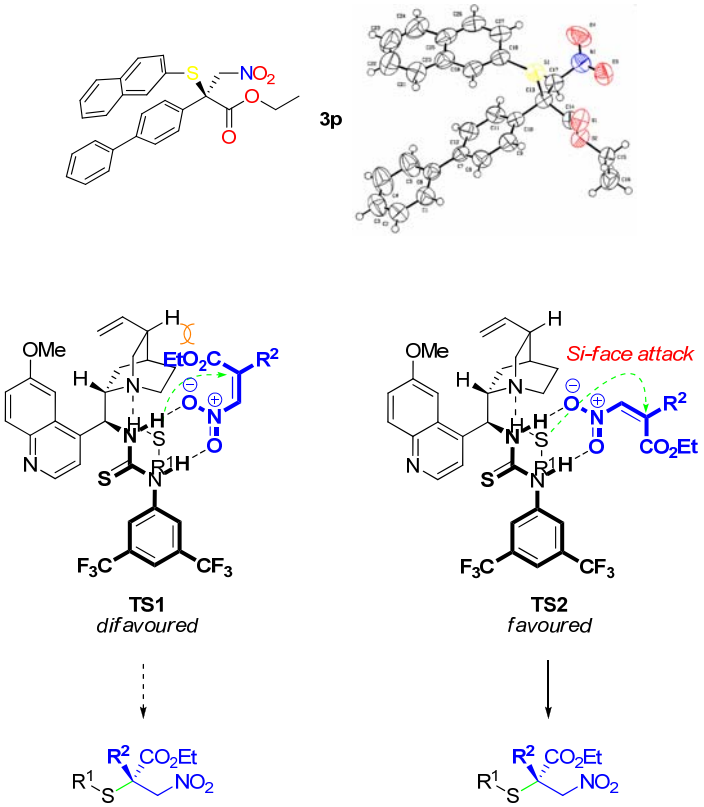
1 2 3



4

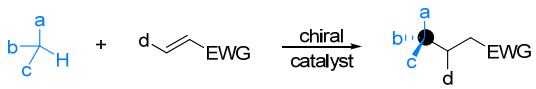
entry	R^1	R^2		yield (%)[b]	ee (%)[c]	method
1	4-$CH_3C_6H_5$ (**1a**)		**3a**	98	92	A
2	2-$CH_3C_6H_5$ (**1b**)		**3b**	94	93	C
3	3-$CH_3C_6H_5$ (**1c**)		**3c**	97	89	A
4	4-$CH_3OC_6H_5$ (**1d**)	C_6H_5 (**2a**)	**3d**	92	91	A
5	4-^{t}BuC_6H_5 (**1e**)		**3e**	93	92	A
6	4-FC_6H_5 (**1f**)		**3f**	92	90	A
7	4-ClC_6H_5 (**1g**)		**3g**	95	88	A
8	C_6H_5 (**1h**)		**3h**	94	92	A
9	3,5-$(CH_3)_2C_6H_5$ (**1i**)		**3i**	89	91	A
10	2-naphthyl (**1j**)		**3j**	97	93	A
11	4-CH_3OBn (**1k**)		**3k**	90	87[d]	A
12		2-$CH_3C_6H_4$ (**2b**)	**3l**	99	92	D
13		3-$CH_3OC_6H_4$ (**2c**)	**3m**	93	90	B
14		4-TBSO$CH_2C_6H_4$ (**2d**)	**3n**	93	90	C
15		4-$C_6H_5C_6H_4$ (**2e**)	**3o**	97	94[e]	C
16		3, 5-$Me_2C_6H_3$ (**2f**)	**3p**	100	92	C
17	2-naphthyl (**1l**)	 (**2g**)	**3q**	99	92	C
18		 (**2h**)	**3r**	95	98	C
19		 (**2i**)	**3s**	98	94	C
20		2-thienyl (**2j**)	**3t**	93	92	A
21		*c*-hex (**2k**)	**3u**	90	95[f]	C

[a] **Method A**: 1.0 mL of benzene-Et_2O (v/v = 1/1) at -25 °C. **Method B**: 1.0 mL of toluene at -25 °C. **Method C**: 1.0 mL of toluene at -45 °C. **Method D**: 1.0 mL of toluene at -60 °C. [b] Isolated yield. [c] Determined by chiral HPLC. [d] 3.0 equiv. of thiol and 10 mol % **4** were used after 96 h. [e] Absolute configuration of **3p** was determined to be *S* by X-ray analysis and we assume for assigning the absolute configuration of **3a-t** the same approach of thiols to the *si*-face in **TS2** (see Scheme 1). [f] The β-nitroacrylate **2k** has a *E*-configuration opposite to β-nitroacrylates **2a-2j**, thus the absolute configuration of **3u** could not be assigned by analogy like **3a-t**.



Scheme 1. Proposed transition state for the observed stereo-outcome.

4. Additional References and Acknowledgments



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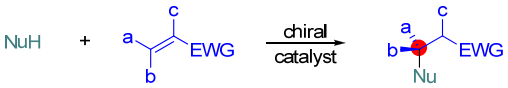
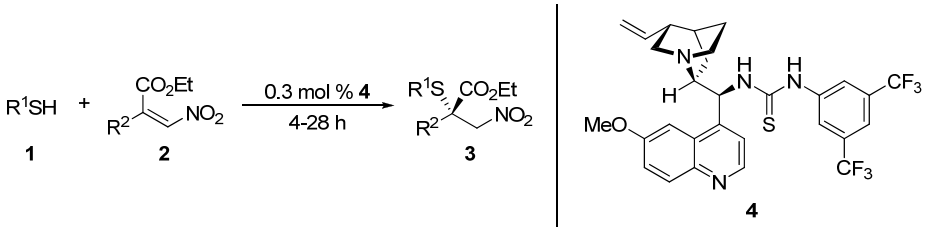


Impressive advances in this endeavor have focused on metal catalyzed procedures with copper and rhodium being the most prevalent, pioneered by **Hoveyda** *and* **Alexakis** *independently.* See: copper-catalyzed asymmetric conjugate addition of zinc reagents: (a) Wu, J.; Mampreian, D. M.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 4584. (b) Hird, A. W.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2005**, *127*, 14988. (c) Fillion, E.; Wilsily, A. *J. Am. Chem. Soc.* **2006**, *128*, 2774. (d) Wilsily, A.; Fillion, E. *Org. Lett.* **2008**, *10*, 2801. Copper-catalyzed asymmetric conjugate addition of Grignard reagents: (e) Martin, D.; Kehrli, S. d'Augustin, M.; Clavier, H. Mauduit, M.; Alexakis, A. *J. Am. Chem. Soc.* **2006**, *128*, 8416. copper-catalyzed asymmetric conjugate addition of aluminum reagents: (f) d'Augustin, M.; Palais, L.; Alexakis, A. *Angew. Chem. Int. Ed.* **2005**, *44*, 1376. (g) d'Augustin, M.; Alexakis, A. *Chem. Eur. J.* **2007**, *13*, 9647. (h) Fuchs, N.; d'Augustin, M.; Humam, M.; Alexakis, A.; Taras, R.; Gladiali, S. *Tetrahedron: Asymmetry* **2005**, *16*, 3143. (i) Hawner, C.; Li, K.; Cirriez, V.; Alexakis, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 8211. (j) May, T. L.; Brown, M. K. Hoveyda, A. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 7358. Rhodium-catalyzed asymmetric conjugate addition of organoboronic acids: (k) Mauleón, P.; Carretero, J. C. *Chem. Commun.* **2005**, 4961. (l) Shintani, R.; Duan, W.-L.; Hayashi, T. *J. Am. Chem. Soc.* **2006**, *128*, 5628. Other sporadic examples: (m) Emori, E.; Arai, T.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1998**, *120*, 4043. (n) Mitchell, C. E. T.; Brenner S. E.; Ley, S. V. *Chem. Commun.* **2005**, 5346.

For additional interesting examples on catalytic asymmetric sulfa-Michael reactions, see: (a) Hiemstra H.; Hans Wynberg, H. *J. Am. Chem. Soc.* **1981**, 103, 417. (b) Nishimura, K.; Ono, M.; Nagaoka, Y.; Tomioka, K. *J. Am. Chem. Soc.* **1997**, *119*, 12974. (c) Emori, E.; Arai, T.; Sasai, H.; Shibasaki, M. J. Am. Chem. Soc. **1998**, 120, 4043. (d) Kanemasa, S.; Oderaotoshi, Y.; Wada, E. J. Am. Chem. Soc. **1999**, 121, 8675. (e) Li, B.; Jiang, L.; Liu, M.; Chen, Y.; Ding, L.; Wu, Y. *Synlett* **2005**, 603. (f) Marigo, M.; Schulte, T.; Franzén, J.; Jørgensen, K. *J. Am. Chem. Soc.* **2005**, *127*, 15710. (g) Abe, A. M. M.; Sauerland, S. J. K.; Koskinen, A.M. P. *J. Org. Chem.* **2007**, *72*, 5411. (h) Leow, D.; Lin, S.; Chittimlla, S. K.; Fu, X.; Tan, C.-H. *Angew. Chem. Int. Ed.* **2008**, *47*, 5641. (i) Ricci, P.; Carlone, A.; Bartoli, G.; Bosco, M.; Sambri, L.; Melchiorre, P. *Adv. Synth. Catal.* **2008**, *350*, 49.

Additional Acknowledgments. We are grateful to the National Science Foundation of China (20672040) and the Program for New Century Excellent Talents in University (NCET-05-0672) for support of this research. We also thank Dr. Vy M. Dong at University of Toronto and Dr. Howard Alper at the University of Ottawa for helpful advice.

5. Experimental Procedures and Characterizations



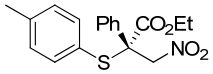
Method A. Thiol **1** (0.22 mmol) was added to a solution of β-nitroacrylates **2** (0.2 mmol) and organocatalyst **4** (0.0006 mmol, 71 μL of the catalyst solution) in 0.5 mL of benzene and 0.5 mL of benzene and 0.5 mL of ether at -25 °C. After completed (monitored by TLC analysis), the desired product **3** was purified by flash column chromatography.

Method B. Thiol **1** (0.22 mmol) was added to a solution of β-nitroacrylates **2** (0.2 mmol) and organocatalyst **4** (0.0006 mmol, 71 μL of the catalyst solution) in 1.0 mL of toluene at -25 °C. After completed (monitored by TLC analysis), the desired product **3** was purified by flash column chromatography.

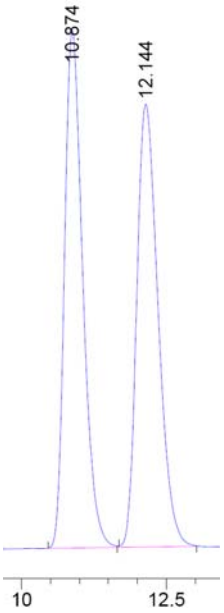
Method C. Thiol **1** (0.22 mmol) was added to a solution of β-nitroacrylates **2** (0.2 mmol) and organocatalyst **4** (0.0006 mmol, 71 μL of the catalyst solution) in 1.0 mL of toluene at -45 °C. After completed (monitored by TLC analysis), the desired product **3** was purified by flash column chromatography.

Method D. Thiol **1** (0.22 mmol) was added to a solution of β-nitroacrylates **2** (0.2 mmol) and organocatalyst **4** (0.0006 mmol, 71 μL of the catalyst solution) in 1.0 mL of toluene at -60 °C. After completed (monitored by TLC analysis), the desired product **3** was purified by flash column chromatography.

*Note: The catalyst solution was prepared by dissolving 50 mg **4** in 10 mL of benzene.*



(*S*)-Ethyl 3-nitro-2-phenyl-2-(*p*-tolylthio)propanoate (3a). Prepared according to method A as a colorless oil (98% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35-7.30 (m, 5H), 7.10 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 5.20 (d, J = 14.4 Hz, 1H), 5.00 (d, J = 14.4 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 2.31 (s, 3H), 1.22 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 140.7, 137.2, 135.8, 129.7, 128.5, 127.1, 125.1, 78.8, 62.6, 60.4, 21.2, 13.7; *Anal. Calcd.* for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; Found: C, 62.53; H, 5.60; N, 4.16; $[\alpha]_D^{14}$ = -53.7 (c = 1.8, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 10.23 min, t_{major} = 11.30 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
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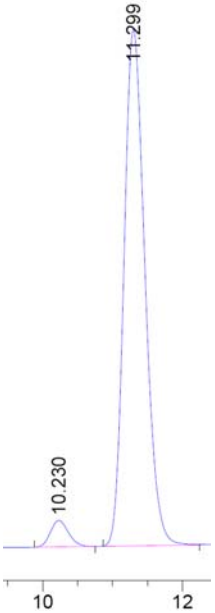
2	12.144	BB	0.3974	1.84217e4	720.36670	50.0156



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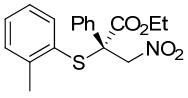
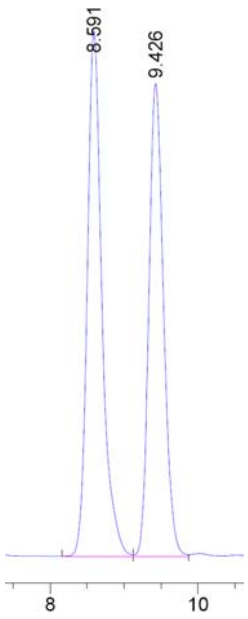


(*S*)-Ethyl 3-nitro-2-phenyl-2-(*o*-tolylthio)propanoate (3b). Prepared according to method C as a colorless solid (94% yield, 93% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.36 (m, 2H), 7.34-7.32 (m, 3H), 7.29-7.20 (m, 3H), 7.11 (t, J = 7.2 Hz, 1H), 5.21 (d, J = 14.8 Hz, 1H), 5.12 (d, J = 14.8 Hz, 1H), 4.24-4.19 (m, 2H), 2.23 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.8, 144.7, 138.3, 135.5, 130.8, 130.5, 129.2, 128.5, 128.4, 127.9, 127.3, 126.3, 78.8, 62.5, 60.0, 20.7, 13.6; *Anal. Calcd.* for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; Found: C, 62.47; H, 5.50; N, 4.13; $[\alpha]_D^{14}$ = -29.6 (c = 2.4, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 8.79 min, t_{major} = 9.68 min).



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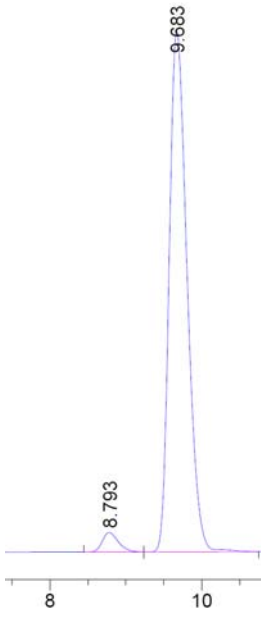

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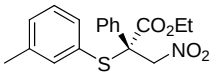
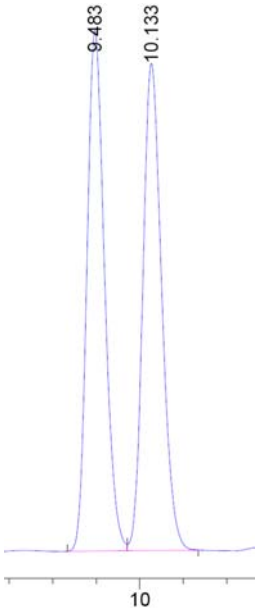
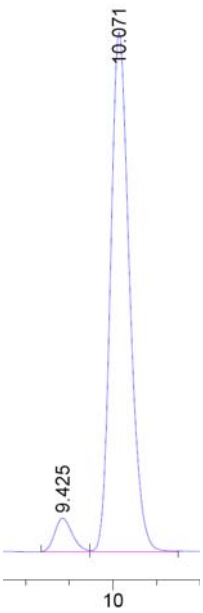
1	8.793	BP	0.2576	972.57434	60.43526	3.3798
2	9.683	VB	0.2635	2.78031e4	1675.28455	96.6202



(*S*)-Ethyl 3-nitro-2-phenyl-2-(*m*-tolylthio)propanoate (3c). Prepared according to method A as a colorless solid (97% yield, 88% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33 (br, 5H), 7.24-7.14 (m, 2H), 7.06 (d, J = 7.2 Hz, 1H), 6.98 (s, 1H), 5.21 (d, J = 14.0 Hz, 1H), 5.01 (d, J = 14.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.24 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm)

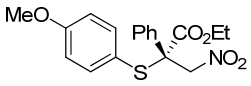


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.483	BV	0.2176	1.02218e4	728.44409	49.9310
2	10.133	VB	0.2322	1.02500e4	681.85974	50.0690

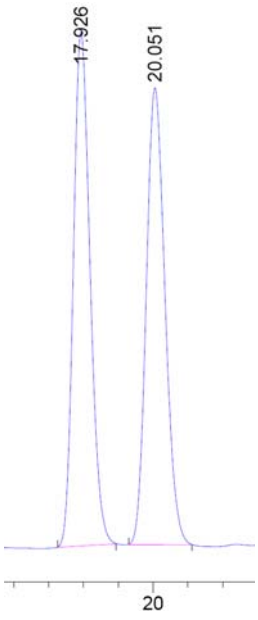


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.425	BV	0.2151	326.12479	23.38941	5.6283
2	10.071	VB	0.2339	5468.25342	363.26312	94.3717

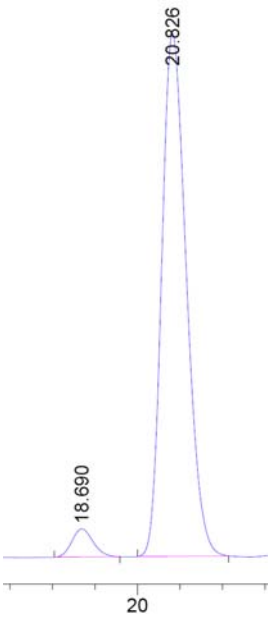
168.9, 138.8, 137.9, 135.8, 134.2, 131.0, 128.7, 128.4, 127.1, 78.7, 76.7, 62.6, 60.4, 21.0, 13.7; *Anal. Calcd.* for $C_{18}H_{19}NO_4S$: C, 62.59; H, 5.54; N, 4.06; Found: C, 62.63; H, 5.47; N, 4.00; $[\alpha]_D^{14}$ = -66.1 (c = 1.6, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 9.43 min, t_{major} = 10.07 min).



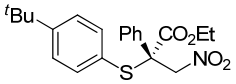
(*S*)-Ethyl 2-(4-methoxyphenylthio)-3-nitro-2-phenylpropanoate (3d). Prepared according to method A as a colorless solid (92% yield, 91% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33 (br, 5H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 5.20 (d, *J* = 14.4 Hz, 1H), 5.00 (d, *J* = 14.4 Hz, 1H), 4.26 (q, *J* = 14.4 Hz, 1H), 3.79 (s, 3H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 161.3, 138.9, 135.8, 129.1, 128.8, 128.5, 128.4, 127.1, 125.2, 119.2, 114.4, 78.7, 62.6, 60.5, 55.3, 13.8; *Anal. Calcd.* for $C_{18}H_{19}NO_5S$: C, 59.82; H, 5.30; N, 3.88; Found: C, 59.76; H, 5.41; N, 3.79; $[\alpha]_D^{14}$ = -78.6 (c = 2.1, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 18.69 min, t_{major} = 20.83 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.926	BB	0.5155	4825.92334	145.34041	50.0017
2	20.051	BB	0.5827	4825.58838	129.22639	49.9983

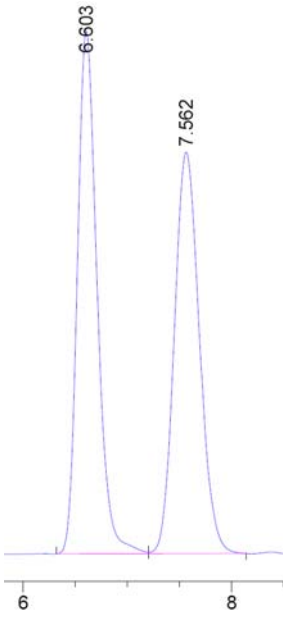


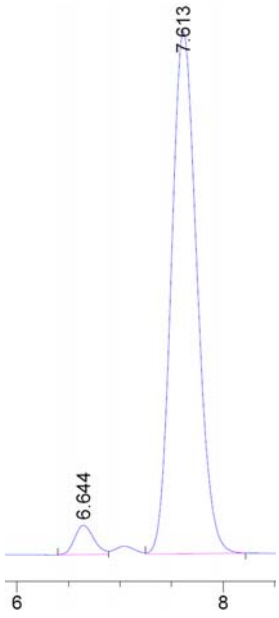
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.690	PB	0.5337	710.00092	20.56935	4.4347
2	20.826	BB	0.6259	1.53000e4	382.03021	95.5653



(*S*)-Ethyl 2-(4-*tert*-butylphenylthio)-3-nitro-2-phenylpropanoate (3e). Prepared according to method A as a colorless solid (93% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.39-7.24 (m, 7H), 7.18 (d, *J* = 8.4 Hz, 2H), 5.20 (d, *J* = 14.0 Hz, 1H), 5.04 (d, *J* = 14.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.20 (s, 9H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 153.8, 137.0, 135.7, 128.4, 127.2, 126.1, 126.3, 79.0, 62.5, 60.3, 34.7, 31.1, 13.7; *Anal. Calcd.* for

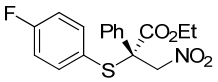
$C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61; Found: C, 65.13; H, 6.54; N, 3.50; $[\alpha]_D^{14}$ = -99.2 (c = 1.5, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 6.64 min, t_{major} = 7.61 min).



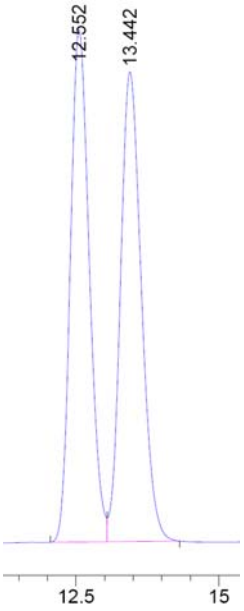


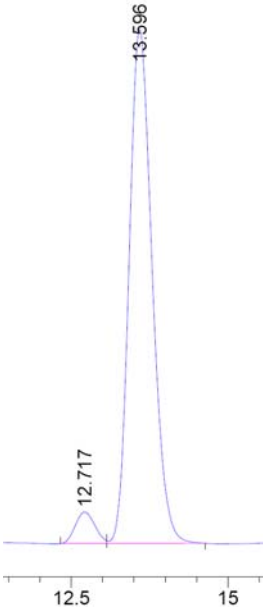
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.603	BV	0.2023	3773.49438	288.09488	50.5647
2	7.562	VB	0.2602	3689.21631	221.10059	49.4353

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.644	BV	0.2006	249.24336	19.24874	4.0898
2	7.613	VB	0.2673	5845.00879	340.43518	95.9102



(*S*)-Ethyl 2-(4-fluorophenylthio)-3-nitro-2-phenylpropanoate (3f). Prepared according to method A as a colorless solid (92% yield, 90% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33-7.31 (m, 3H), 7.27-7.24 (m, 2H), 7.16-7.13 (m, 2H), 6.94-6.89 (m, 2H), 5.25 (d, J = 14.4 Hz, 1H), 4.98 (d, J = 14.4 Hz, 1H), 4.30-4.26 (m, 2H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm)

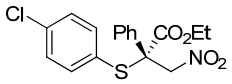




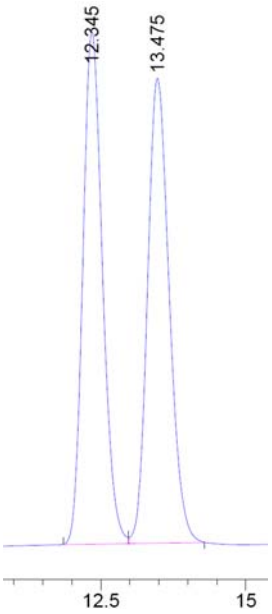
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.552	BV	0.3574	5875.19922	255.24550	49.7577
2	13.442	VB	0.3933	5932.41357	234.03619	50.2423

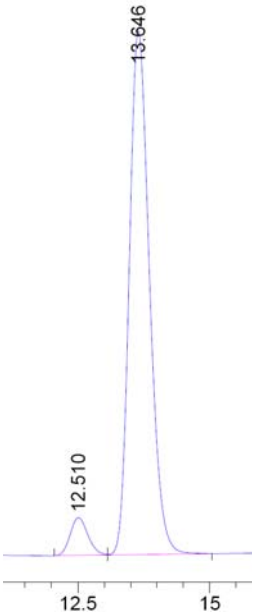
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.717	PV	0.3477	132.95528	6.09507	4.9231
2	13.596	VB	0.3954	2567.71094	99.12200	95.0769

168.8, 165.2, 162.7, 139.5, 139.4, 135.6, 128.6, 126.9, 124.0, 116.2, 116.0, 78.6, 62.9, 60.9, 13.7; *Anal. Calcd.* for $C_{17}H_{16}FNO_4S$: C, 58.44; H, 4.62; N, 4.01; Found: C, 58.51; H, 4.55; N, 4.00; $[\alpha]_D^{14}$ = -108.8 (c = 2.2, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 12.72 min, t_{major} = 13.60 min).



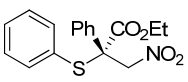
(*S*)-Ethyl 2-(4-chlorophenylthio)-3-nitro-2-phenylpropanoate (3g). Prepared according to method A as a colorless solid (95% yield, 88% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34-7.32 (m, 3H), 7.26-7.25 (m, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 5.26 (d, J = 14.0 Hz, 1H), 4.96 (d, J = 14.0 Hz, 1H), 4.33-4.25 (m, 2H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.7, 138.5, 136.8, 135.5, 129.1, 128.7, 127.1, 126.7, 78.5, 62.9, 61.0, 13.8; *Anal. Calcd.* for C17H16ClNO4S: C, 55.81; H, 4.41; N, 3.83; Found: C, 55.87; H, 4.35; N, 3.86; $[\alpha]_D^{14}$ = -119.6 (c = 2.8, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 12.51 min, t_{major} = 13.65 min).





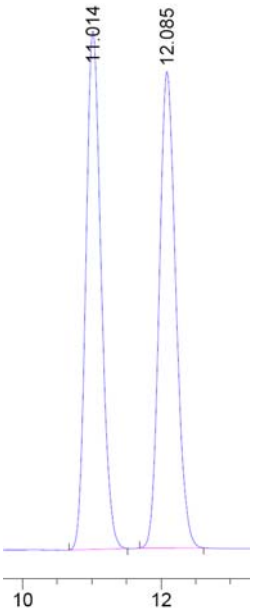
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.345	BV	0.3638	3072.23218	131.04211	49.8989
2	13.475	VB	0.4018	3084.68188	118.86951	50.1011

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.510	PV	0.3624	353.10913	15.13593	5.9731
2	13.646	VB	0.4110	5558.54443	209.84142	94.0269

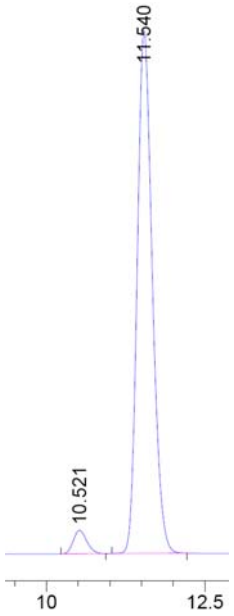


(*S*)-Ethyl 3-nitro-2-phenyl-2-(phenylthio)propanoate (3h). Prepared according to method A as a colorless solid (94% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.35 (m, 1H), 7.32 (br, 5H), 7.26-7.20 (m, 4H), 5.23 (d, J = 14.4 Hz, 1H), 5.02 (d, J = 14.4 Hz, 1H), 4.26 (q, J = 7.2 Hz,

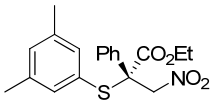
2H), 1.22 (t, J = 7.22Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.8, 137.3, 135.7, 130.3, 128.9, 128.7, 128.6, 127.0, 78.8, 62.7, 60.6, 13.7; *Anal. Calcd.* for $C_{17}H_{17}NO_4S$: C, 61.61; H, 5.17; N, 4.23; Found: C, 61.55; H, 5.24; N, 4.17; $[\alpha]_D^{14}$ = -87.9 (c = 2.3, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 10.52 min, t_{major} = 11.54 min).



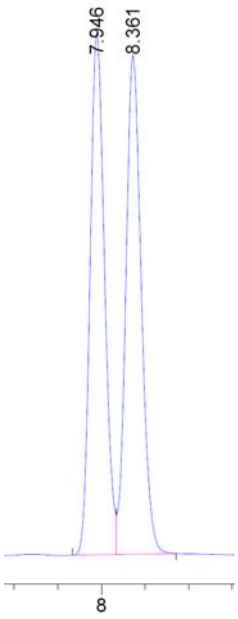
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.014	BB	0.2372	2479.25244	161.66653	49.9895
2	12.085	BB	0.2573	2480.29321	148.59248	50.0105

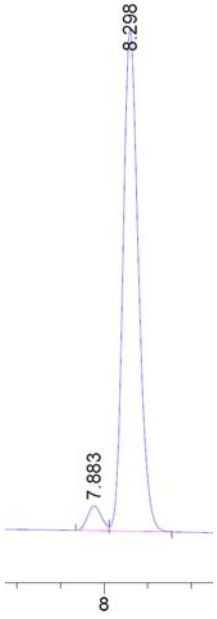


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.521	BB	0.2277	637.83398	43.17952	3.8720
2	11.540	BB	0.2551	1.58353e4	959.71222	96.1280



(*S*)-Ethyl 2-(3,5-dimethylphenylthio)-3-nitro-2-phenylpropanoate (3i). Prepared according to

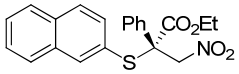




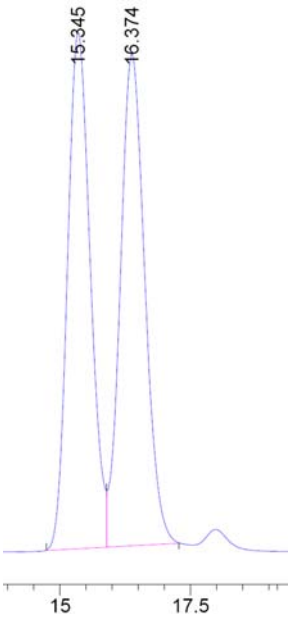
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.946	BV	0.1781	3239.64941	281.07730	49.5471
2	8.361	VB	0.1883	3298.86890	268.87646	50.4529

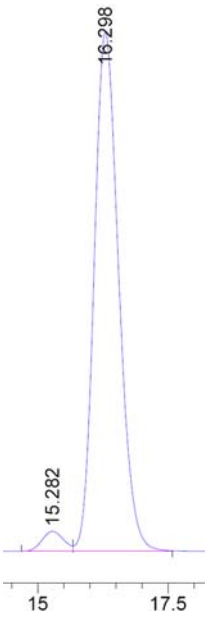
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.883	BV	0.1723	232.11989	20.81488	4.3211
2	8.298	VB	0.1899	5139.64551	418.39890	95.6789

method A as a colorless solid (89% yield, 91% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.34 (br, 5H), 7.25 (s, 1H), 7.00 (s, 1H), 6.82 (s, 1H), 5.19 (d, J = 14.4 Hz, 1H, 5.01 (d, J = 14.4 Hz, 1H, 4.25 (q, J = 7.2 Hz, 2H), 2.21 (s, 6H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 169.0, 138.5, 135.9, 134.9, 132.0, 128.4, 128.0, 127.0, 78.8, 62.6, 60.2, 21.0, 13.7; *Anal. Calcd.* for $C_{19}H_{21}NO_4S$: C, 63.49; H, 5.89; N, 3.90; Found: C, 63.53; H, 5.81; N, 3.93; $[\alpha]_D^{14}$ = -56.3 (c = 2.7, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 7.88 min, t_{major} = 8.30 min).



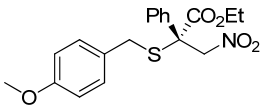
(*S*)-Ethyl 2-(naphthalen-2-ylthio)-3-nitro-2-phenylpropanoate (3j). Prepared according to method A as a colorless solid (97% yield, 93% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.66 (m, 4H), 7.54-7.51 (m, 2H), 7.33 (br, 5H), 7.15 (d, J = 8.4 Hz, 1H, 5.27 (d, J = 14.4 Hz, 1H), 5.03 (d, J = 14.4 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 138.0, 135.8, 133.5, 133.1, 132.9, 129.3, 128.6, 128.4, 128.0, 127.8, 127.5, 127.1, 126.6, 125.9, 78.7, 62.8, 60.8, 13.7; *Anal. Calcd.* for $C_{21}H_{19}NO_4S$: C, 66.12; H, 5.02; N, 3.67; Found: C, 66.01; H, 5.14; N, 3.62; $[\alpha]_D^{14}$ = -120.7 (c = 2.8, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 15.28 min, t_{major} = 16.30 min).



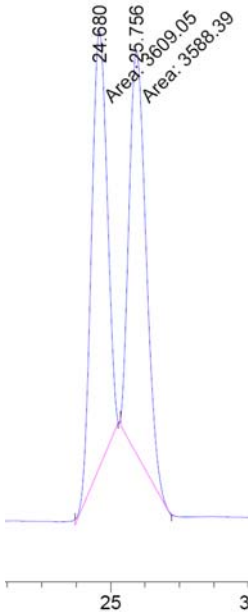


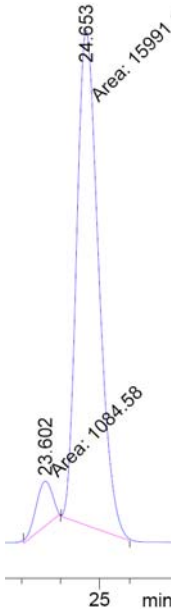
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.345	BV	0.4693	2615.00781	86.47776	49.3439
2	16.374	VB	0.5026	2684.55078	82.34914	50.6561

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.282	BV	0.4511	300.56757	10.47904	3.2804
2	16.298	VB	0.5049	8861.96777	272.27737	96.7196



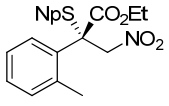
(*S*)-Ethyl 2-(4-methoxybenzylthio)-3-nitro-2-phenylpropanoate (3k). Prepared according to method A as a colorless solid (98% yield, 87% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.58 (d, J = 7.6 Hz, 2H), 7.43-7.33 (m, 3H), 7.08 (d, J = 8.4 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 5.09 (q, J = 14.4 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 3.78 (s, 3H), 3.64 (d, J = 12.0 Hz, 1H), 3.44 (d, J = 12.0 Hz, 1H), 1.33 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 169.0, 168.9, 134.9, 130.3, 128.8, 128.5, 128.0, 127.2, 114.0, 79.8, 62.6, 58.0, 55.2, 34.7, 13.9; *Anal. Calcd.* for $C_{19}H_{21}NO_5S$: C, 60.78; H, 5.64; N, 3.73; Found: C, 60.71; H, 5.68; N, 3.68; $[\alpha]_D^{20}$ = -24.0 (c = 3.1, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 23.60 min, t_{major} = 24.65 min).



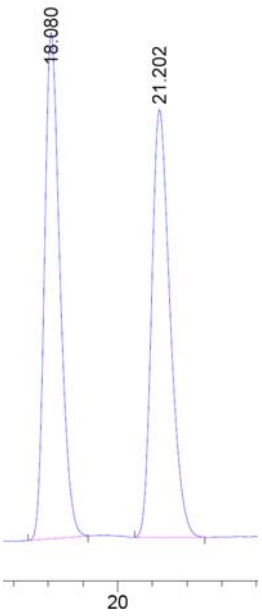


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.680	MM	0.5214	3609.05200	115.35874	50.1435
2	25.756	MM	0.5662	3588.39087	105.62514	49.8565

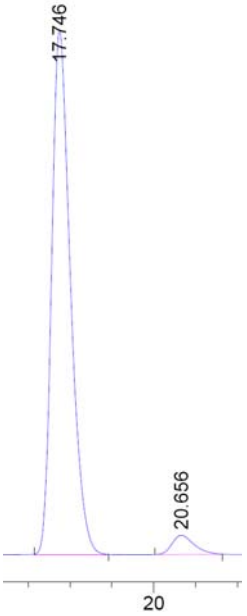
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.602	MM	0.4829	1084.57690	37.43455	6.3516
2	24.653	MM	0.6504	1.59911e4	409.78400	93.6484



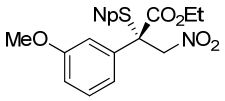
(*S*)-Ethyl 2-(naphthalen-2-ylthio)-3-nitro-2-*o*-tolylpropanoate (3l). Prepared according to method A as a colorless solid (99% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82-7.80 (m, 2H), 7.74-7.67 (m, 2H), 7.54-7.51 (m, 2H), 7.24-7.22 (m, 2H, 7.18-7.12 (m, 3H), 5.24 (d, J = 14.0 Hz, 1H), 5.01 (d, J = 14.0 Hz, 1H), 4.24 (q, J = 7.2 Hz, 2H), 2.35 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 169.1, 138.6, 138.0, 133.5, 133.1, 132.9, 132.7, 130.0, 129.2, 128.4, 127.7, 127.6, 127.0, 126.6, 126.1, 78.8, 62.7, 60.6, 21.0, 13.7; *Anal. Calcd.* for $C_{22}H_{21}NO_4S$: C, 66.82; H, 5.35; N, 3.54; Found: C, 66.77; H, 5.43; N, 3.48; $[\alpha]_D^{20}$ = -86 (c = 4.3, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{major} = 17.75 min, t_{minor} = 20.66 min).



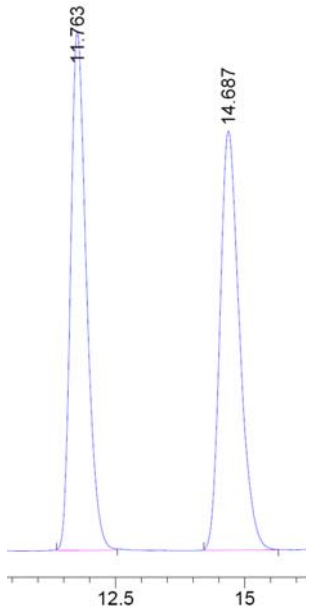
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.080	PB	0.4723	2882.40137	92.97725	49.7859
2	21.202	PB	0.5641	2907.19312	78.58620	50.2141



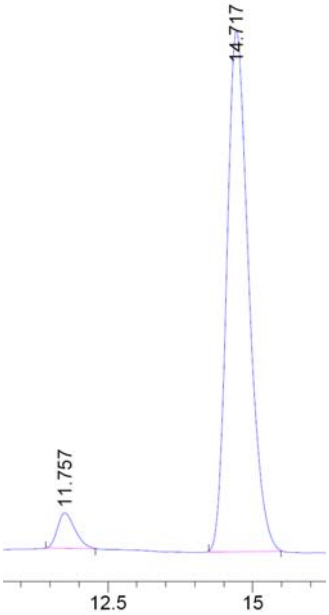
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.746	BB	0.4691	1.23812e4	399.73547	95.7707
2	20.656	BB	0.5600	546.76044	14.77011	4.2293



(*S*)-Ethyl 2-(3-methoxyphenyl)-2-(naphthalen-2-ylthio)-3-nitropropanoate (3m). Prepared according to method A as a colorless solid (93% yield, 90% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.67 (m, 4H), 7.56-7.52 (m, 2H), 7.23-7.17 (m, 2H), 6.94 (s, 1H), 6.87-6.85 (m, 2H),

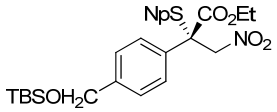


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.763	BB	0.3245	3461.03833	162.28273	50.1534
2	14.687	BB	0.3993	3439.86157	131.08998	49.8466

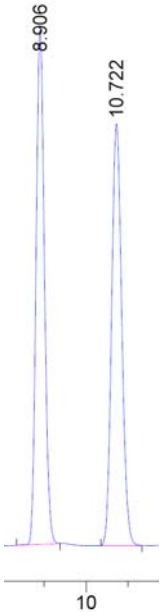


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.757	BB	0.3218	199.89014	9.47829	5.1705
2	14.717	BB	0.4003	3666.11401	139.91043	94.8295

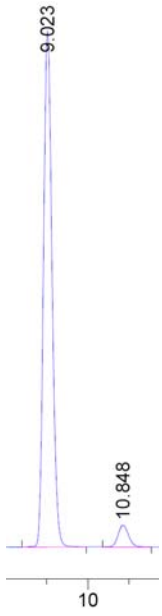
5.25 (d, J = 14.0 Hz, 1H), 5.00 (d, J = 14.0 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 3.76 (s, 3H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 159.6, 138.0, 137.3, 133.6, 133.2, 132.8, 129.5, 128.4, 128.0, 127.6, 126.6, 126.0, 119.2, 114.0, 113.5, 78.8, 62.8, 60.8, 55.3, 13.7; *Anal. Calcd.* for $C_{22}H_{21}NO_5S$: C, 64.22; H, 5.14; N, 3.40; Found: C, 64.27; H, 5.18; N, 3.26; $[\alpha]_D^{20}$ = -108 (c = 3.7, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 210 nm, t_{minor} = 11.76 min, t_{major} = 14.72 min).



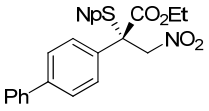
(*S*)-Ethyl 2-(4-((tert-butyldimethylsilyloxy)methyl)phenyl)-2-(naphthalen-2- ylthio)-3-nitro-propanoate (3n). Prepared according to method A as a colorless oil (93% yield, 90% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (br, 2H), 7.72 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.55-7.46 (m, 2H), 7.36-7.22 (m, 4H), 7.15 (d, J = 8.8 Hz, 1H), 5.25 (d, J = 14.4 Hz, 1H), 5.02 (d, J = 14.4 Hz, 1H), 4.73 (s, 2H), 4.25 (q, J = 7.2 Hz, 2H), 1.19 (t, J = 7.2 Hz, 3H), 0.95 (s, 9H), 0.11 (s, 6H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 169.0, 142.0, 138.0, 134.3, 133.5, 133.1, 132.9, 128.3, 128.0, 127.7, 127.5, 127.0, 126.8, 126.6, 126.1, 126.0, 78.8, 64.3, 62.7, 61.8, 60.7, 25.9, 18.3, 13.7, 5.3; *Anal. Calcd.* for $C_{28}H_{35}NO_5SSi$: C, 63.97; H, 6.71; N, 2.66; Found: C, 64.01; H, 6.63; N, 2.57; $[\alpha]_D^{20}$ = -132 (c = 3.8, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{major} = 9.02 min, t_{minor} = 10.85 min).



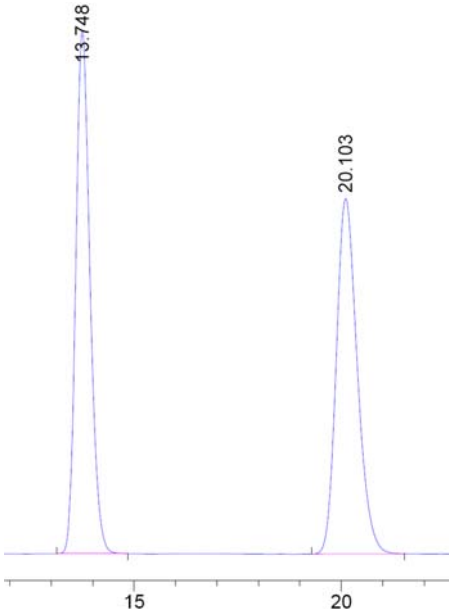
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.906	BB	0.2138	1351.74878	98.62769	49.9957
2	10.722	BB	0.2606	1351.98145	80.87231	50.0043



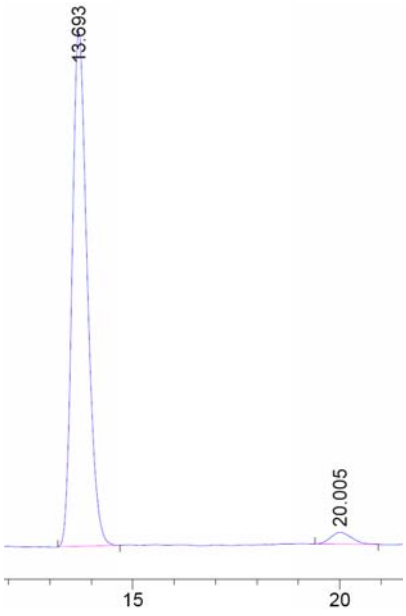
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.023	BB	0.2237	1.23015e4	859.99127	95.0792
2	10.848	BB	0.2728	636.66016	36.34771	4.9208



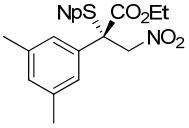
(*S*)-Ethyl 2-(biphenyl-4-yl)-2-(naphthalen-2-ylthio)-3-nitropropanoate (3o). Prepared according to method A as a colorless solid (97% yield, 94% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82-7.68 (m, 4H), 7.59-7.52 (m, 5H), 7.50-7.37 (m, 6H), 7.20 (d, J = 8.4 Hz, 1H), 5.30 (d, J = 13.6 Hz, 1H), 5.08 (d, J = 13.6 Hz, 1H), 4.31-4.25 (m, 2H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 141.3, 140.0, 138.1, 134.7, 133.5, 133.1, 132.9, 128.8, 128.4, 128.0, 127.7, 127.6, 127.1, 127.0, 126.7, 125.9, 78.7, 62.8, 60.6, 13.7; *Anal. Calcd.* for $C_{27}H_{23}NO_4S$: C, 70.88; H, 5.07; N, 3.06; Found: C, 70.81; H, 5.14; N, 3.01; $[\alpha]_D^{20}$ = -212 (>99% ee, c = 1.0, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 210 nm, t_{major} = 13.69 min, t_{minor} = 20.00 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.748	BB	0.3663	1.11818e4	470.19257	49.9204
2	20.103	BB	0.5392	1.12174e4	319.46091	50.0796

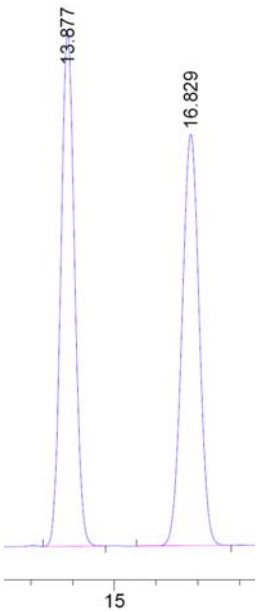


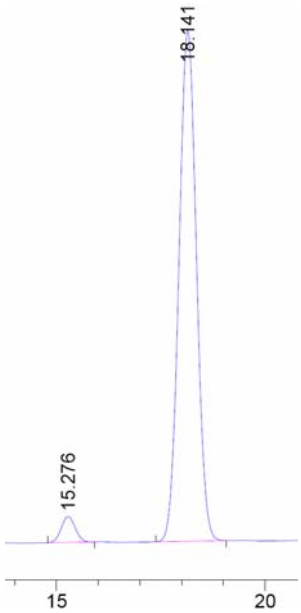
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.693	PB	0.3881	3898.46924	154.19540	96.8552
2	20.005	PB	0.5466	126.58085	3.55393	3.1448



(*S*)-Ethyl 2-(3,5-dimethylphenyl)-2-(naphthalen-2-ylthio)-3-nitropropanoate (3p). Prepared according to method A as a colorless oil (100% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.67 (m, 4H), 7.55-7.48 (m, 2H), 7.17-7.10 (m, 1H), 6.95 (s, 1H), 6.88 (s, 2H), 5.23 (d, J = 14.0 Hz, 1H), 4.98 (d, J = 14.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 2.24 (s, 6H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 169.1, 138.2, 138.1, 135.6, 133.6, 133.1, 133.0, 130.2, 128.2, 128.0, 127.5, 126.6, 126.2, 124.7, 78.8, 62.7, 61.0, 21.3, 13.7; *Anal. Calcd.* for $C_{23}H_{23}NO_4S$: C, 67.46; H, 5.66; N, 3.42; Found: C, 67.41; H, 5.69; N, 3.38; $[\alpha]_D^{20}$ = -62 (c = 1.5, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol =

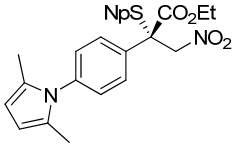
95/5, 1 mL/min, 210 nm, t_{minor} = 15.28 min, t_{major} = 18.14 min).



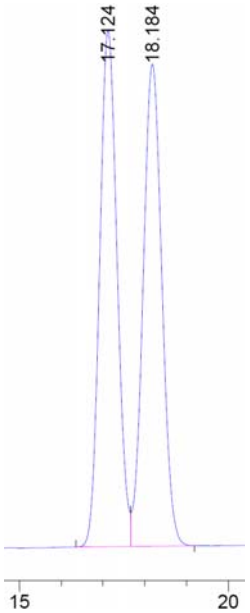


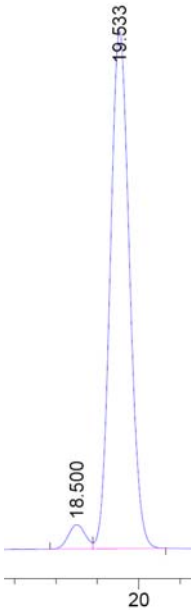
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.877	VB	0.3572	1.14347e4	499.78659	50.0261
2	16.829	PB	0.4496	1.14228e4	400.03421	49.9739

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.276	BP	0.3654	422.06076	18.08885	3.9198
2	18.141	BB	0.4532	1.03454e4	356.90814	96.0802



(*S*)-Ethyl 2-(4-(2,5-dimethyl-1*H*-pyrrol-1-yl)phenyl)-2-(naphthalen-2-ylthio) -3-nitropropanoate (3q). Prepared according to method A as a colorless oil (99% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.86 (s, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.73 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 8.4 Hz, 1H), 7.54-7.50 (m, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.19-7.17 (m, 1H), 7.13 (d, J

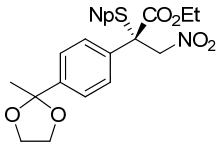




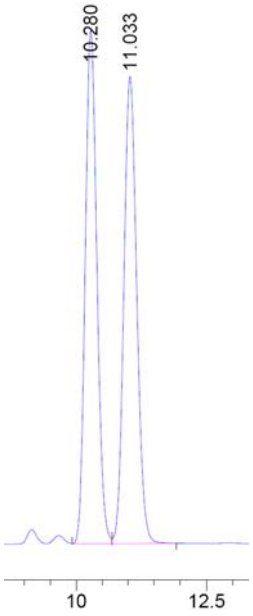
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.124	BV	0.4545	6314.20508	217.90326	49.8771
2	18.184	VB	0.4860	6345.32031	203.56908	50.1229

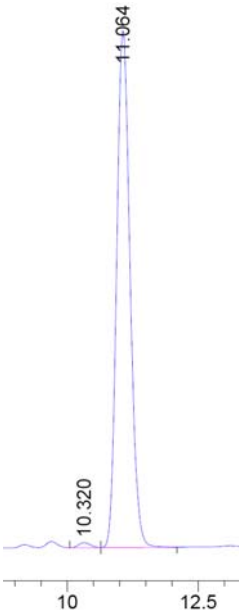
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.500	BV	0.4495	654.94397	22.84564	4.0143
2	19.533	VB	0.5040	1.56603e4	486.08722	95.9857

= 8.8 Hz, 2H), 5.90 (s, 2H), 5.31 (d, *J* = 14.4 Hz, 1H), 5.15 (d, *J* = 14.4 Hz, 1H), 4.37-4.29 (m, 2H), 2.00 (s, 6H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.7, 144.5, 138.9, 138.1, 135.0, 133.5, 133.0, 132.7, 128.5, 128.4, 128.0, 127.7, 127.5, 126.7, 125.7, 106.0, 78.8, 62.9, 60.4, 13.7, 12.9; *Anal. Calcd.* for $C_{27}H_{26}N_2O_4S$: C, 68.33; H, 5.52; N, 5.90; Found: C, 68.37; H, 5.46; N, 5.93; $[\alpha]_D^{20}$ = -168 (c = 4.2, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 18.50 min, t_{major} = 19.53 min).



(*S*)-Ethyl 2-(4-(2-methyl-1,3-dioxolan-2-yl)phenyl)-2-(naphthalen-2-ylthio) -3-nitropropanoate (3r). Prepared according to method A as a white solid (95% yield, 98% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.81-7.66 (m, 4H), 7.55-7.49 (m, 2H), 7.41-7.31 (m, 4H), 7.21-7.20 (m, 1H), 5.26 (d, *J* = 14.0 Hz, 1H), 5.09 (d, *J* = 14.0 Hz, 1H), 4.27-4.24 (m, 2H), 4.03 (br, 2H), 3.72-3.70 (m, 2H), 1.62 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 168.9, 143.8. 138.1, 135.1, 133.5, 133.1, 132.9, 128.4, 127.9, 127.6, 127.2, 126.7, 126.0, 125.5, 108.4, 79.0, 64.4, 62.8, 60.5, 27.5, 13.7; *Anal. Calcd.* for $C_{25}H_{25}NO_6S$: C, 64.22; H, 5.39; N, 3.00; Found: C, 64.29; H, 5.42; N, 2.96; $[\alpha]_D^{20}$ = -102 (c = 1.0, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 210 nm, t_{minor} = 10.32 min, t_{major} = 11.06 min).





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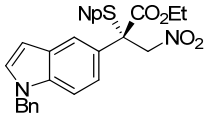
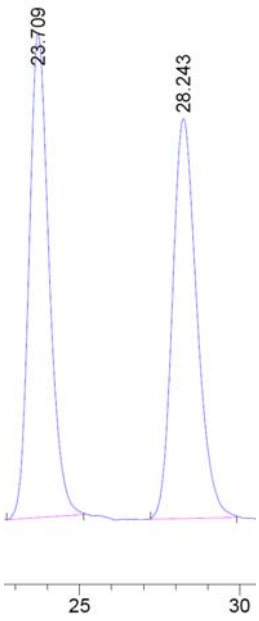
1	10.280	VV	0.2405	4396.52441	283.69858	49.8327
2	11.033	VB	0.2671	4426.04590	258.01492	50.1673

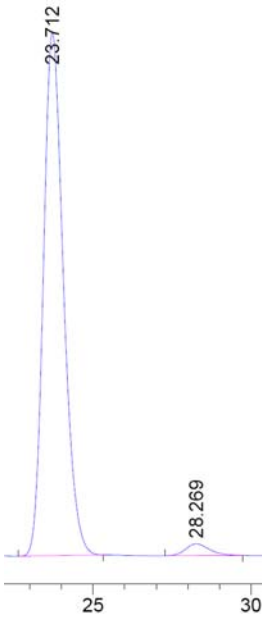
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.320	VV	0.2551	69.84647	4.26587	0.9474
2	11.064	VB	0.2772	7302.69385	410.90964	99.0526



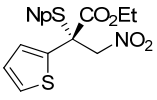
(*S*)-Ethyl 2-(1-benzyl-1H-indol-5-yl)-2-(naphthalen-2-ylthio)-3-nitropro- panoate (3s). Prepared according to method A as an offwhite solid (98% yield, 94% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.76 (d, J = 8.0 Hz, 1H), 7.72 (s, 1H), 7.62-7.57 (m, 2H), 7.50-7.45 (m, 3H), 7.34-7.26 (m, 6H), 7.15-7.07 (m, 4H), 6.44 (d, J = 3.2 Hz, 1H, 5.36-5.33 (m, 3H), 5.04 (d, J = 14.0 Hz, 1H), 4.26 (q, J = 7.2 Hz, 2H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 169.6, 137.9, 137.1, 135.8, 133.4, 133.1, 133.0, 129.3, 128.8, 128.3, 128.1, 128.0, 127.7, 127.5, 127.3, 126.7, 126.6, 126.4, 121.0, 119.6, 102.3, 79.2, 62.6, 61.5, 50.1, 13.8; *Anal. Calcd.* for $C_{30}H_{26}N_2O_4S$: C, 70.57; H, 5.13; N, 5.49; Found: C, 70.63; H, 5.10; N, 5.43; $[\alpha]_D^{20}$ = -241 (c = 3.6, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 80/20, 1 mL/min, 210 nm, t_{major} = 23.71 min, t_{minor} = 28.27 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.709	VB	0.6656	1659.52112	38.19462	49.8819
2	28.243	BB	0.8076	1667.37891	31.53456	50.1181

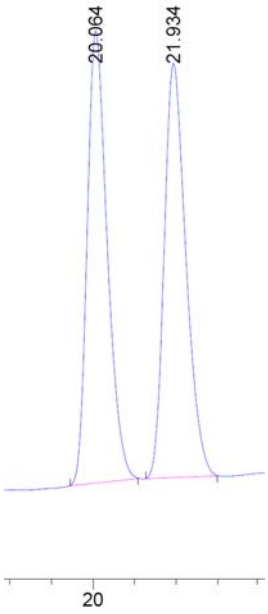


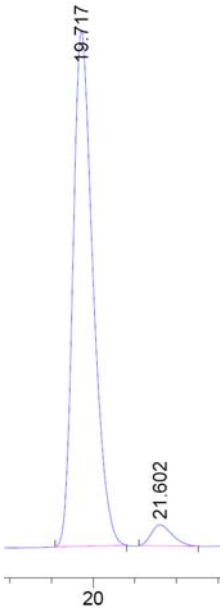
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.712	VB	0.6727	2.29362e4	523.60925	97.3117
2	28.269	BB	0.7829	633.62109	11.87058	2.6883



(*S*)-Ethyl 2-(naphthalen-2-ylthio)-3-nitro-2-(thiophen-2-yl)propanoate (3t). Prepared according to method A as a yellow oil (93% yield, 92% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (s, 1H), 7.84 (d, J = 7.6 Hz, 1H), 7.80-7.75 (m, 2H), 7.58-7.54 (m, 2H), 7.37-7.31 (m, 2H), 6.98-6.88 (m, 2H), 5.25 (s, 2H), 4.30-4.24 (m, 1H), 4.20-4.12 (m, 1H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 167.9, 137.9, 137.5, 133.7, 133.1, 132.6, 128.6, 128.0, 127.8, 127.7, 127.6, 126.9, 126.7, 126.2, 126.0, 79.1, 62.8, 56.9, 13.6; *Anal. Calcd.* for $C_{19}H_{17}NO_4S_2$: C, 58.90; H, 4.42; N, 3.61; Found: C, 58.97; H, 4.36; N, 3.55; $[\alpha]_D^{20}$ = -17 (c = 3.9, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210

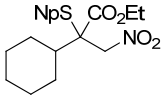
nm, t_{major} = 19.72 min, t_{minor} = 21.50 min).



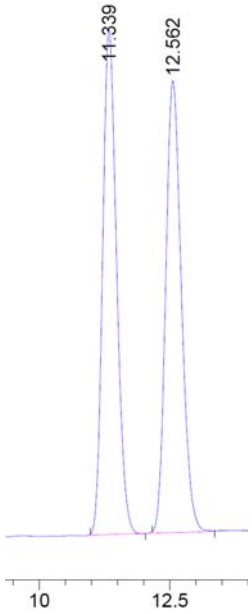


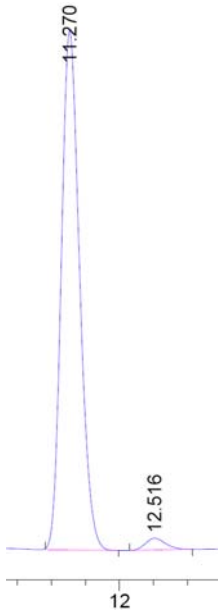
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.064	BB	0.5094	1786.94177	53.45599	50.1470
2	21.934	BB	0.5529	1776.46619	48.96375	49.8530

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.717	BB	0.5059	6195.87744	185.62605	95.9082
2	21.602	BB	0.5202	264.33673	7.55739	4.0918



(*S*)-Ethyl 2-cyclohexyl-2-(naphthalen-2-ylthio)-3-nitropropanoate (3v). Prepared according to method A as a colorless oil (28 h, 90% yield, 95% ee). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (s, 1H), 7.88-7.82 (m, 3H, 7.59-7.53 (m, 3H), 4.97 (d, J = 13.6 Hz, 1H), 4.56 (d, J = 13.6 Hz, 1H), 4.30-4.20 (m, 2H), 2.34 (br, 1H), 1.84-1.65 (m, 6H), 1.38-1.13 (m, 7H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm)



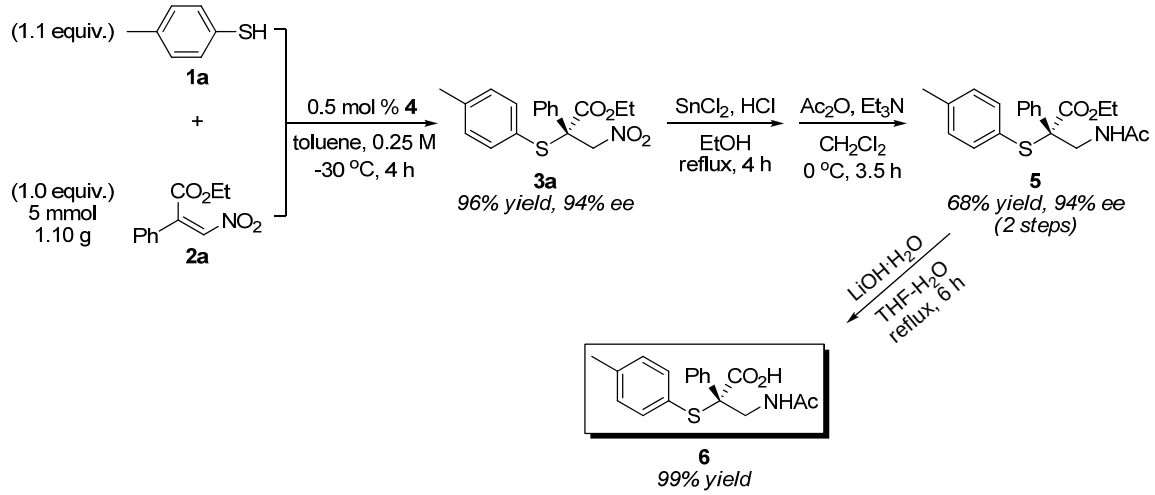


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.339	BP	0.2924	2586.37524	139.22182	49.8265
2	12.562	BB	0.3249	2604.38672	124.84502	50.1735

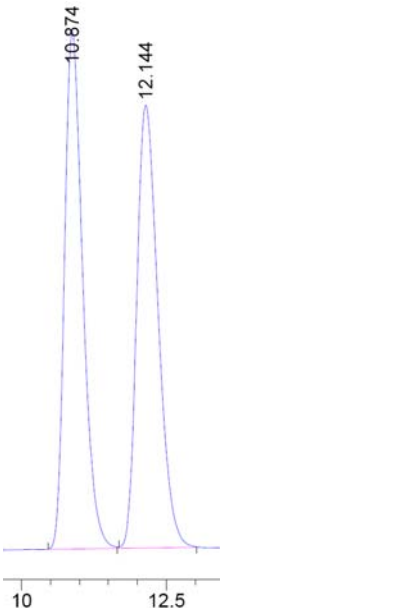
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.270	BP	0.2924	2299.86133	123.81800	97.5374
2	12.516	PB	0.3230	58.06568	2.80509	2.4626

169.2, 138.5, 133.5, 133.3, 128.6, 128.0, 127.6, 127.5, 126.7, 126.0, 77.7, 62.1, 61.8, 42.2, 28.5, 28.0, 26.6, 26.5, 26.0, 13.9; *Anal. Calcd.* for $C_{21}H_{25}NO_4S$: C, 65.09; H, 6.50; N, 3.61; Found: C, 65.13; H, 6.53; N, 3.54; $[\alpha]_D^{20}$ = 10 (c = 2.1, $CHCl_3$); the enantiomeric excess was determined by chiral HPLC (Chiralpak AD column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{major} = 11.27 min, t_{minor} = 12.52 min).

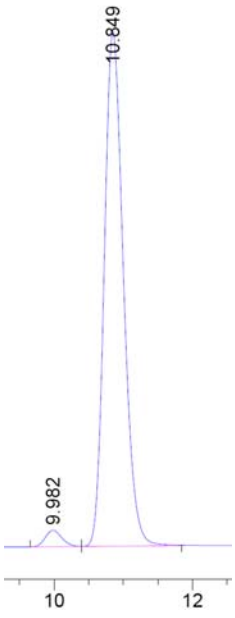
6. Catalytic Asymmetric Synthesis of $\beta^{2,2}$-Amino Acid 6 and Dipeptide 8



(*S*)-Ethyl 3-nitro-2-phenyl-2-(*p*-tolylthio)propanoate (3a). A 50-mL round-bottomed flash equipped with a magnetic stirring bar were sequentially charged with catalyst 4 (0.5 mol %, 15.4 mg), toluene (20 mL) and α-phenyl-β-nitroacrylate 2a (5.15 mmol, 1.14 g). The mixture was stirred at romm temperature for 15 min and cooled to -30 °C for 25 min. *p*-Thiocresol **1a** (0.70 g) was then added in two portions. After 4 h, the crude reaction mixture was loaded on silica gel column chromatography (petroleum ether/ethyl acetate = 15:1) to afford the pure product **3a** as a colorless oil in 98 % yield with 94 % ee. The enantiomeric excess was determined by chiral HPLC (Chiralpak AS column: hexane/2-propanol = 95/5, 1 mL/min, 210 nm, t_{minor} = 9.98 min, t_{major} = 10.85 min).



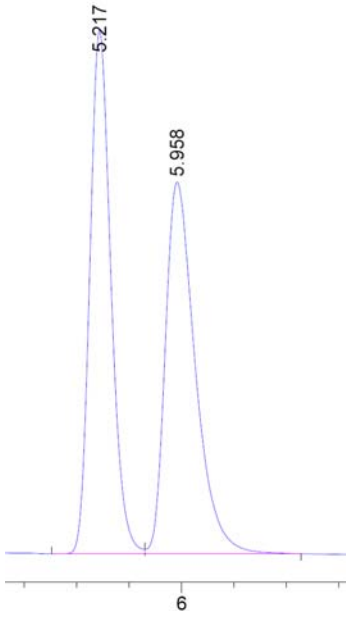
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.874	BB	0.3366	1.84102e4	842.05469	49.9844
2	12.144	BB	0.3974	1.84217e4	720.36670	50.0156



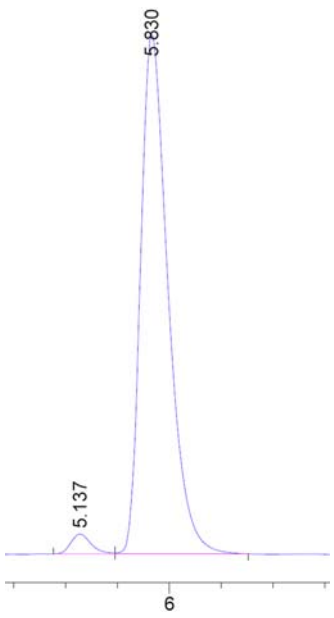
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.982	BV	0.2620	225.85446	13.51215	2.7138
2	10.849	VB	0.2990	8096.53076	422.96777	97.2862

(*S*)-Ethyl 3-acetamido-2-phenyl-2-(*p*-tolylthio)propanoate (5). To a two-necked 50-mL flask were sequentially added 3.79 g (20 mmol) of anhydrous tin(II) chloride in Glove Box and a solution of **3a** (0.69 g, 2.0 mmol) in 25 mL of EtOH containing (20 mmol HCl, prepared from 20 mmol of

acetic chloride at 0 °C) under nitrogen atmosphere. The reaction mixture was heated to reflux for 4 h. It was then cooled to 0 °C, quenched with sat. NH_4Cl and basified with $NH_3 \cdot H_2O$. Dichloromethane was added and vigorously stirred for 10 min. The white suspension was suction filtrated over Celit. The aqueous phase was extracted with CH_2Cl_2 and the combined organic phase was dried over Na_2SO_4. After suction filtration and concentration, the residue was dissolved in 20 mL of CH_2Cl_2 and cooled to 0 °C, Et_3N (0.6 mL) and Ac_2O (0.4 mL) were sequentially added. After stirred at RT for 3.5 h, the mixture was concentrated and the residue was subjected to silica gel column chromatography (PE/acetone = 3:1) to afford the pure product **5** as a colorless oil (68 % yield over two steps, 94 % ee). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.32-7.28 (m, 5H), 7.12 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.4 Hz, 2H), 6.05 (br, 1H), 4.25-4.18 (m, 2H), 4.17-4.14 (m, 1H), 3.64-3.61 (m, 1H), 2.31 (s, 3H), 1.91 (s, 3H), 1.22 (t, J = 7.8 Hz, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 120.9, 169.5, 139.5, 136.9, 136.4, 129.1, 127.8, 127.5, 126.9, 125.4, 63.5, 61.6, 43.1, 22.6, 20.7, 13.4; *Anal. Calcd.* for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92; Found: C, 66.27; H, 6.40; N, 3.78; MS (EI) *m/z* 357 (M^+); the enantiomeric excess was determined by chiral HPLC (Chiralpak OD column: hexane/2-propanol = 70/30, 1 mL/min, 210 nm, t_{minor} = 5.14 min, t_{major} = 5.83 min).

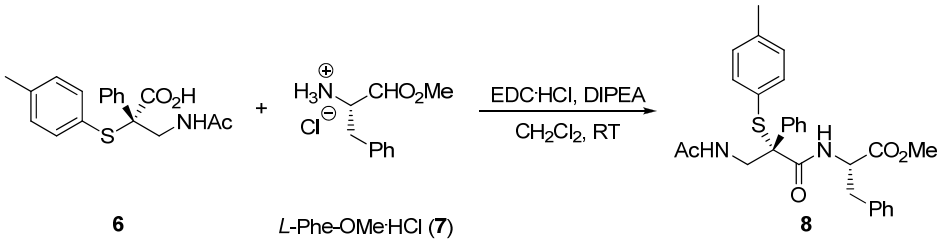


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.217	VV	0.2154	2888.39600	206.73929	49.7245
2	5.958	VB	0.3032	2920.39746	146.92853	50.2755



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.137	BV	0.2106	57.62789	4.21023	2.7855
2	5.830	VB	0.2800	2011.18909	109.40812	97.2145

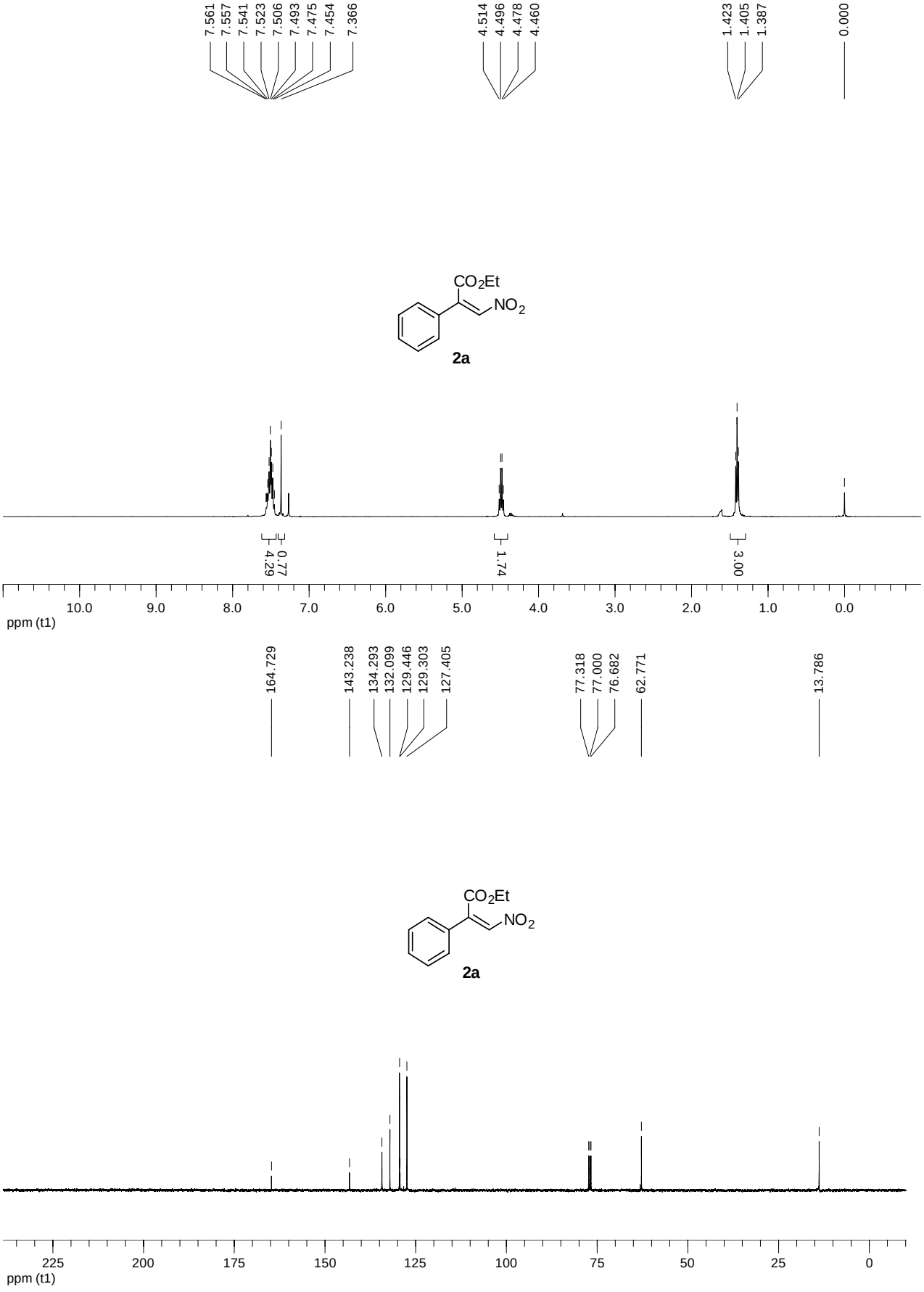
(*S*)-3-Acetamido-2-phenyl-2-(*p*-tolylthio)propanoic acid (6). $LiOH \cdot H_2O$ (0.57 g, 10.0 equiv.) was added to a stirred solution of **5** (0.49 g) in 20 mL of THF-H_2O (v/v = 4/1) at RT. The reaction mixture was heated to reflux for 5-6 h. After cooling, the the reaction mixture was acidified with ice-cold 1 N HCl and extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4. Suction filtration, concentration and dried *in vavuo* afforded 0.45 g of the desired product **6** as a white solid (99 % yield). ^{1}H NMR (400 MHz, DMSO) δ (ppm) 13.3 (br, 1H), 7.60 (br, 1H), 7.32-7.19 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.87-3.82 (m, 1H), 3.59-3.54 (m, 1H), 2.27 (s, 3H), 1.80 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 172.1, 169.4, 139.4, 138.2, 136.7, 129.4, 127.9, 127.5, 127.4, 126.4, 63.9, 42.6, 22.6, 20.8; MS (EI) *m/z* 329 (M^+); $[\alpha]_D^{25}$ = -107.0 (c = 0.8, EtOH).

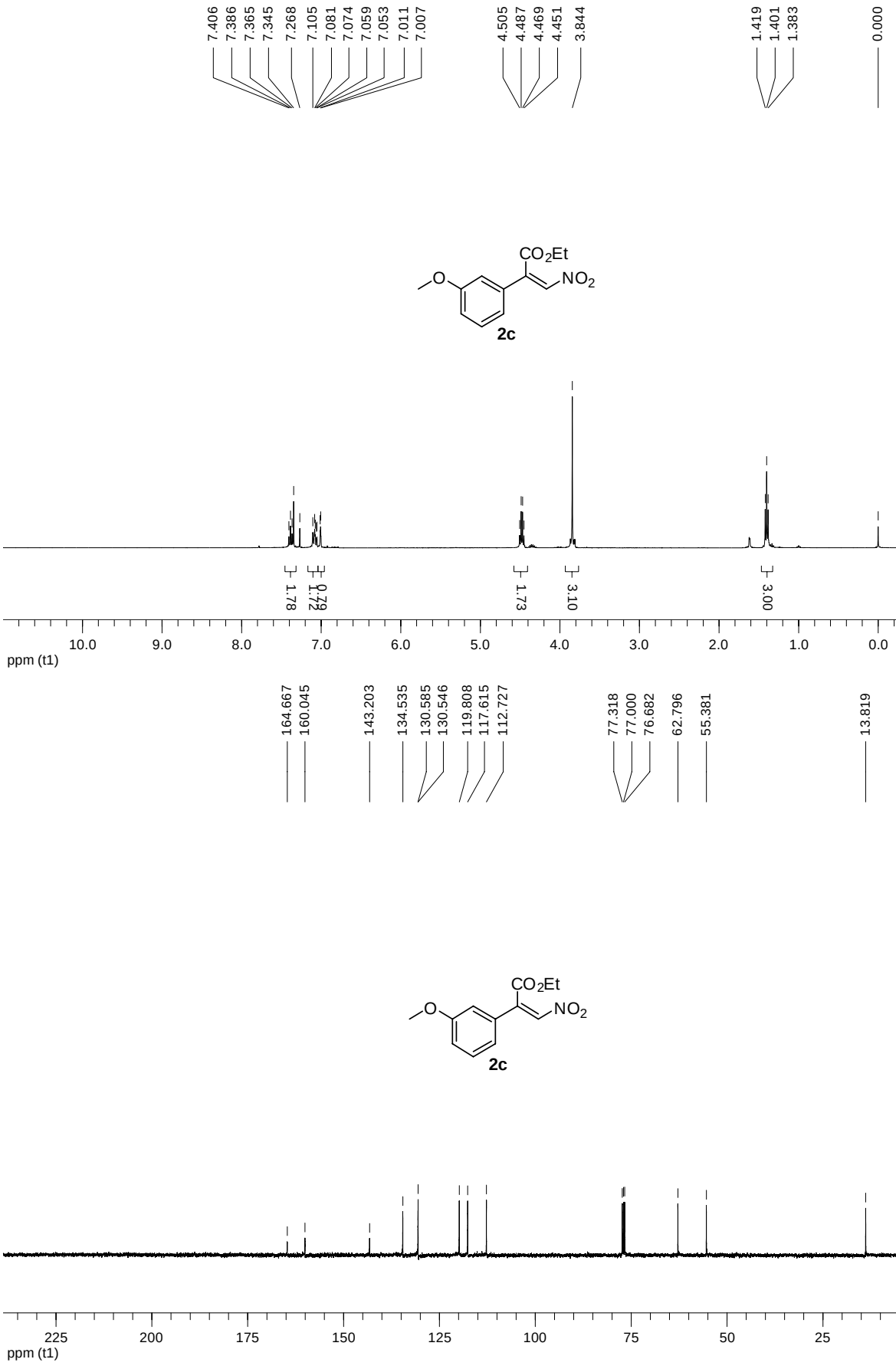


6 *L*-Phe-OMe·HCl (**7**) **8**

(*S*)-Methyl 2-((*S*)-3-acetamido-2-phenyl-2-(*p*-tolylthio)propanamido)-3-phenyl- propanoate (8). To a solution of **6** (410 mg, 1.25 mmol) in dry CH_2Cl_2 (15 mL) were sequentially added *L*-Phe-OMe·HCl (320 mg, 1.2 equiv.), EDC·HCl (360 mg, 1.5 equiv.), DIEA (330 μL, 1.5 equiv.). The mixture was stirred at RT for 12 h, then diluted with CH_2Cl_2, acidified with 10% citric acid and extracted with CH_2Cl_2. The combined organic layers were washed with sat. $NaHCO_3$ dried over Na_2SO_4, filtered and concentrated. The residue was purified via column chromatography eluting with PE/acetone to afford pure product **8** as an amorphous white solid (535 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.34 (m, 2H), 7.31-7.22 (m, 5H), 7.14-7.12 (m, 2H), 6.99-6.98 (m, 2H), 6.91 (br, 1H), 6.89 (d, J = 8.4 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.42 (br, 1H), 4.82-4.76 (m, 1H), 4.29-4.23 (m, 1H), 3.78 (s, 3H), 3.78-3.37 (m, 1H), 3.36-3.21 (m, 1H), 3.20-3.00 (m, 1H), 2.98 (s, 3H), 1.59 (s, 3H); ^{13}C NMR(100 MHz, $CDCl_3$) δ (ppm) 172.5, 171.7, 169.6, 139.6, 136.8, 136.1, 135.4, 129.5, 128.9, 128.2, 128.1, 128.0, 127.4, 125.6, 63.3, 54.3, 52.5, 45.4, 37.3, 23.0, 21.1; MS (EI) *m/z* 490(M^+), $[\alpha]_D^{25}$ = -12.7. (c = 1.0, $CHCl_3$).

7. NMR Spectra of 2, 3, 5, 6 and 8

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NO2
O
2c
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1.73
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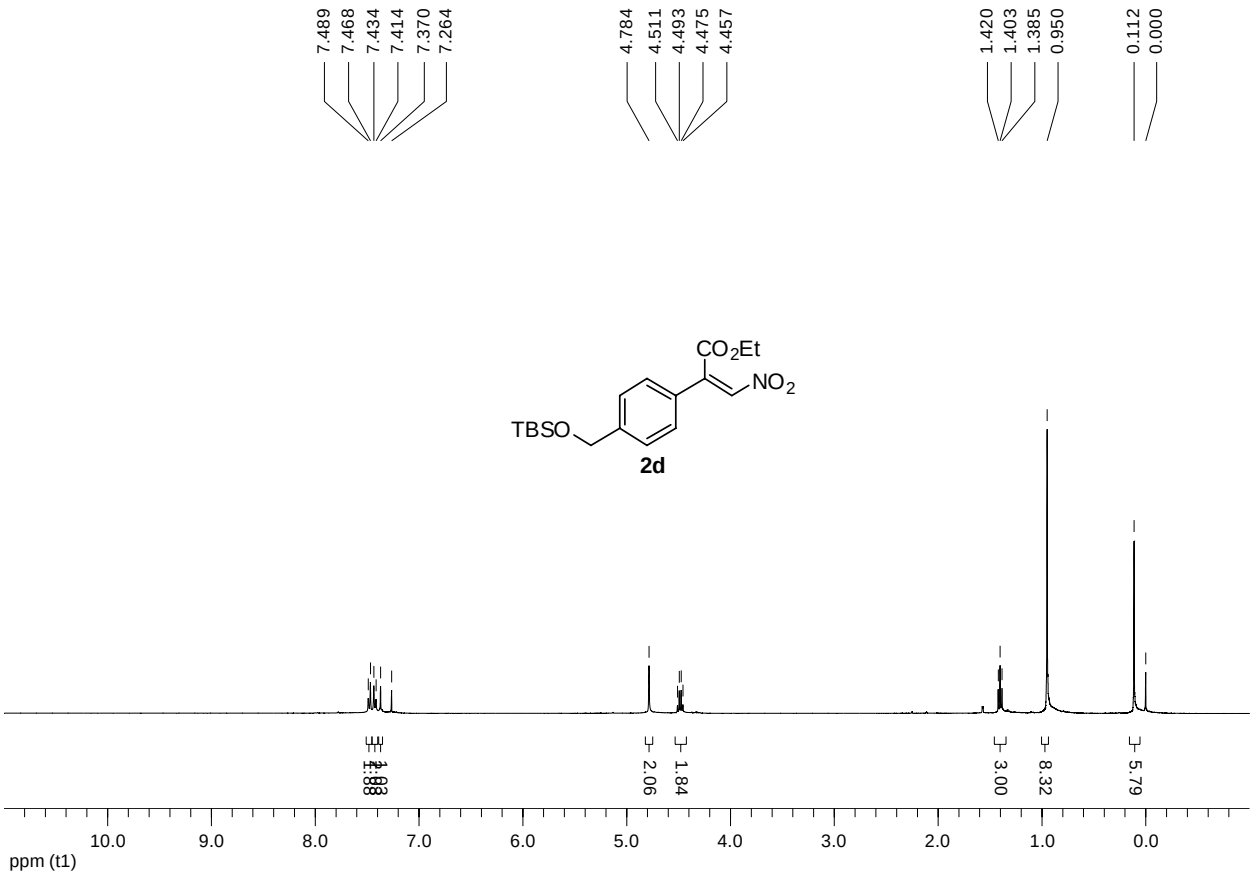
ppm (t1)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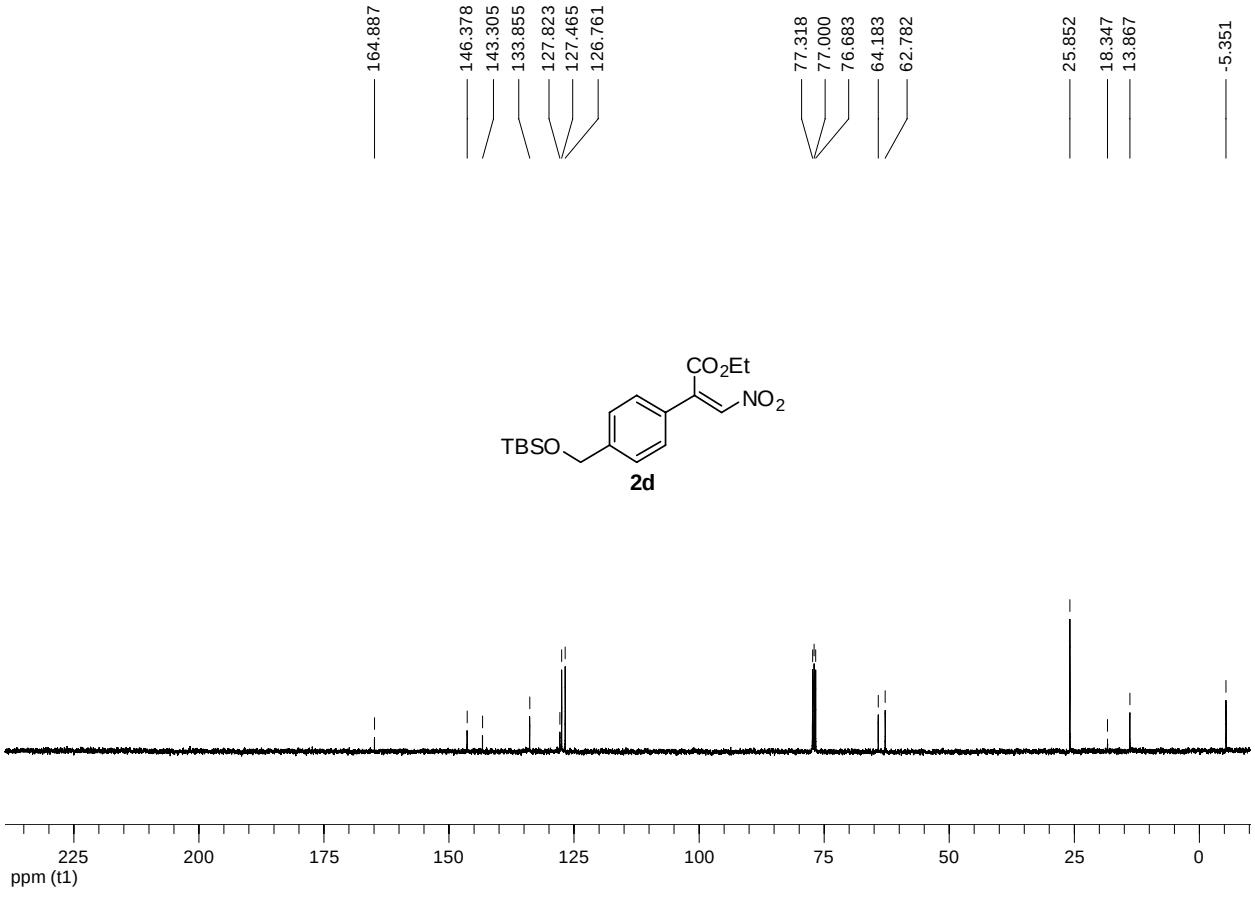
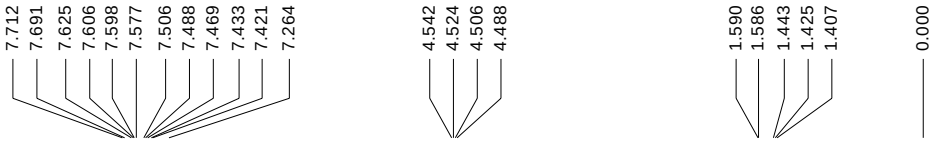
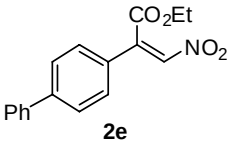
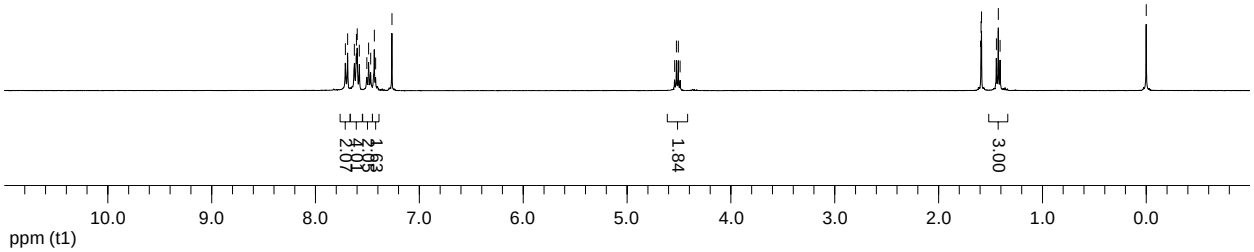
1.385
0.950
0.112
0.000
CO2Et
NO2
TBSO
2d
2.06
1.84
3.00
8.32
5.79
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

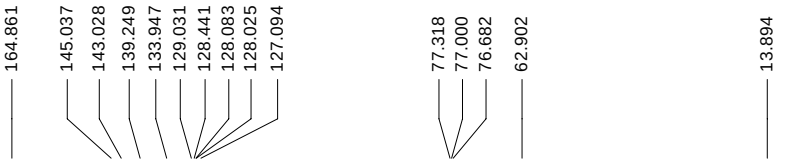

164.887
146.378
143.305
133.855
127.823
127.465
126.761
77.318
77.000
76.683
64.183
62.782
25.852
18.347
13.867
-5.351
CO2Et
NO2
TBSO
2d
225
200
175
150
125
100
75
50
25
0
ppm (t1)

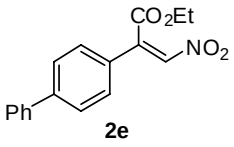

7.712
7.691
7.625
7.606
7.598
7.577
7.506
7.488
7.469
7.433
7.421
7.264
4.542
4.524
4.506
4.488
1.590
1.586
1.443
1.425
1.407
0.000


CO2Et
NO2
Ph

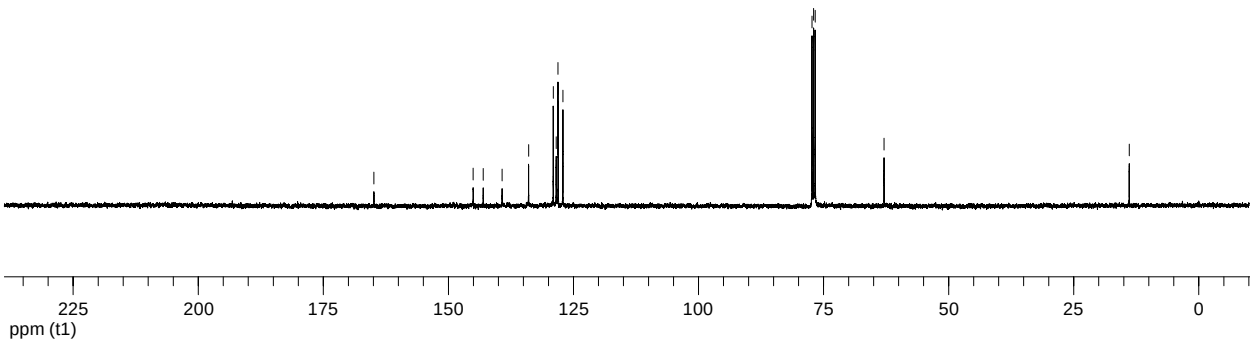
2e

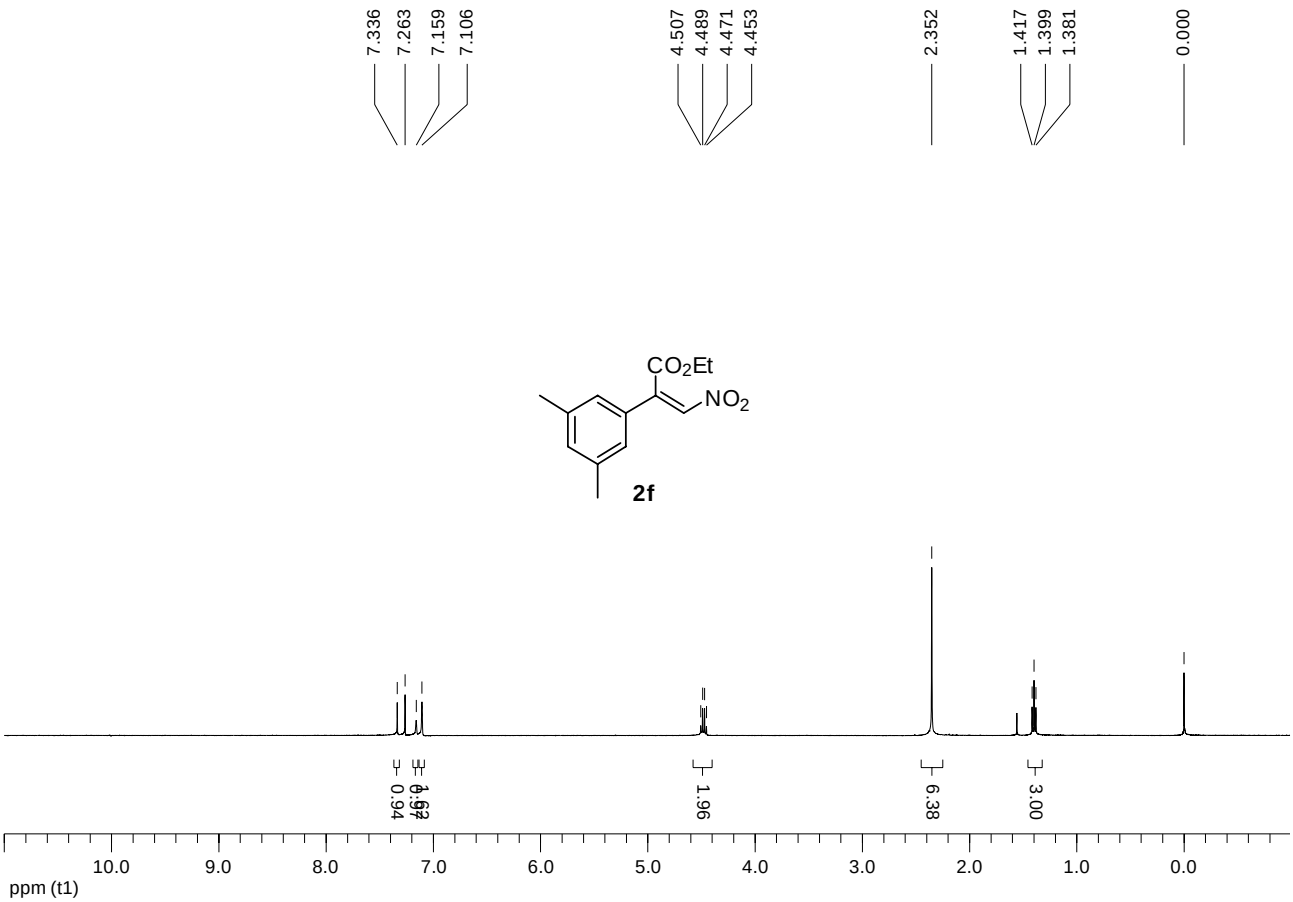

2.07
1.84
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

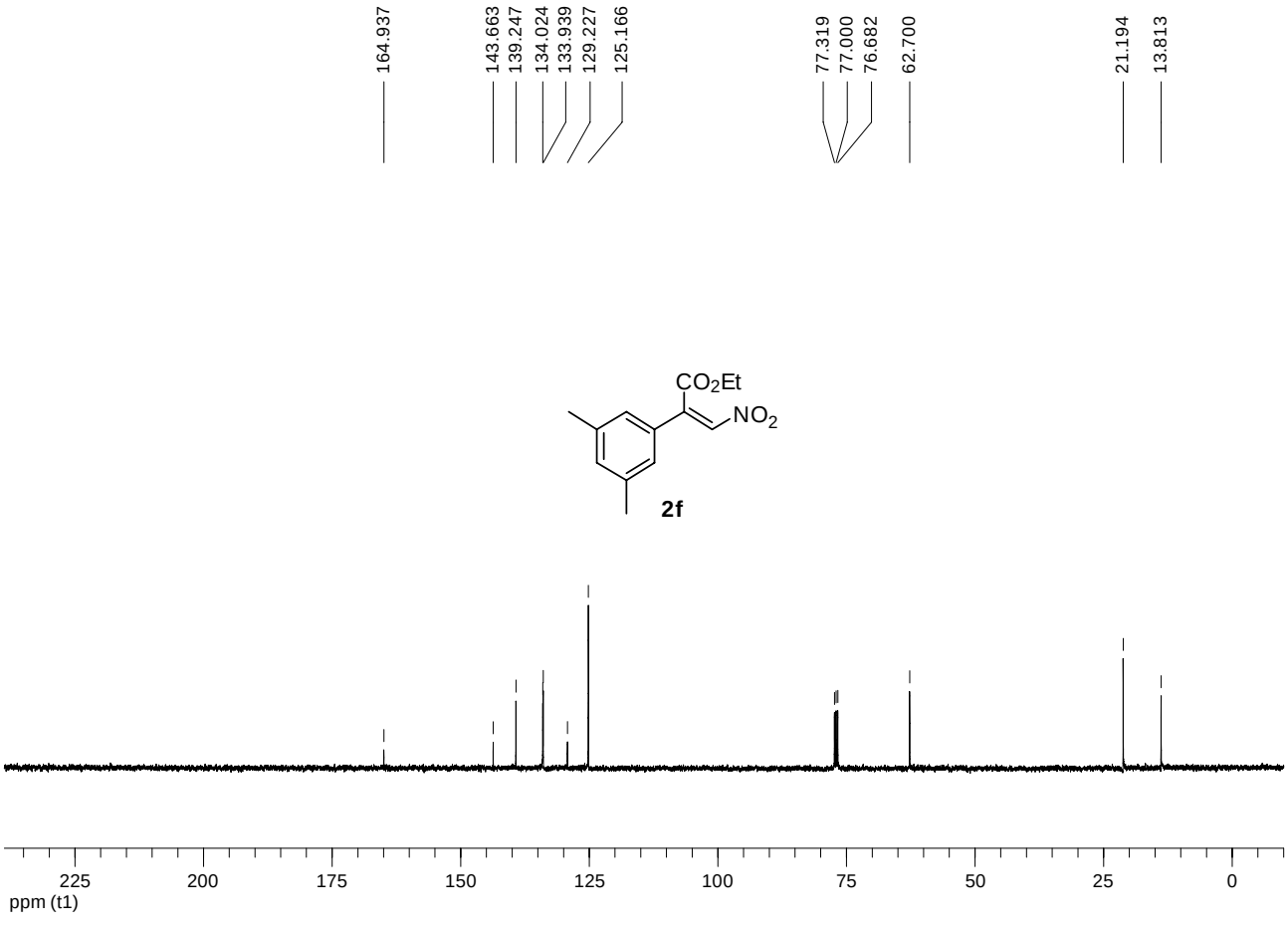

164.861
145.037
143.028
139.249
133.947
129.031
128.441
128.083
128.025
127.094
77.318
77.000
76.682
62.902
13.894


CO2Et
NO2
Ph

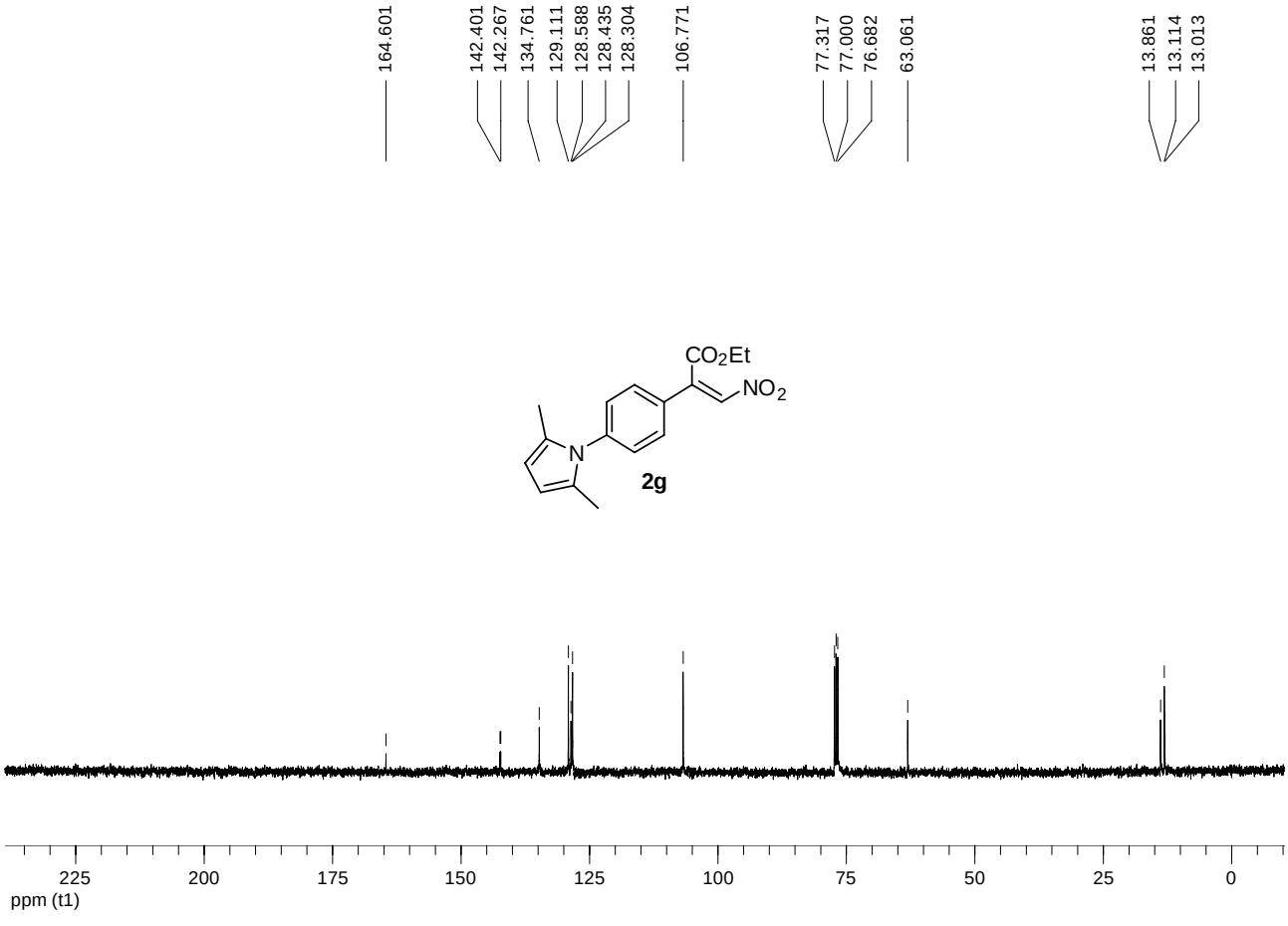
2e

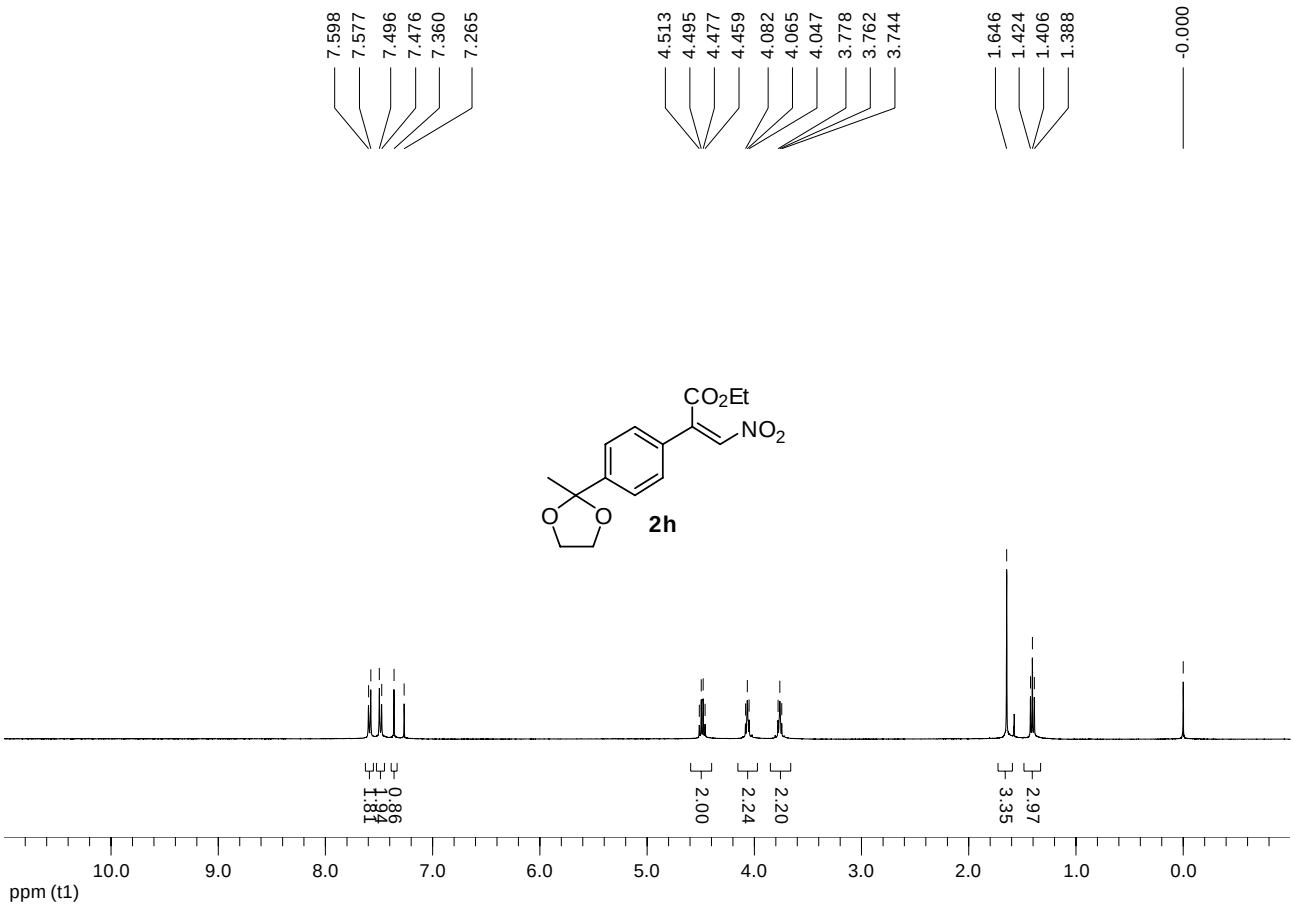

225
200
175
150
125
100
75
50
25
0
ppm (t1)

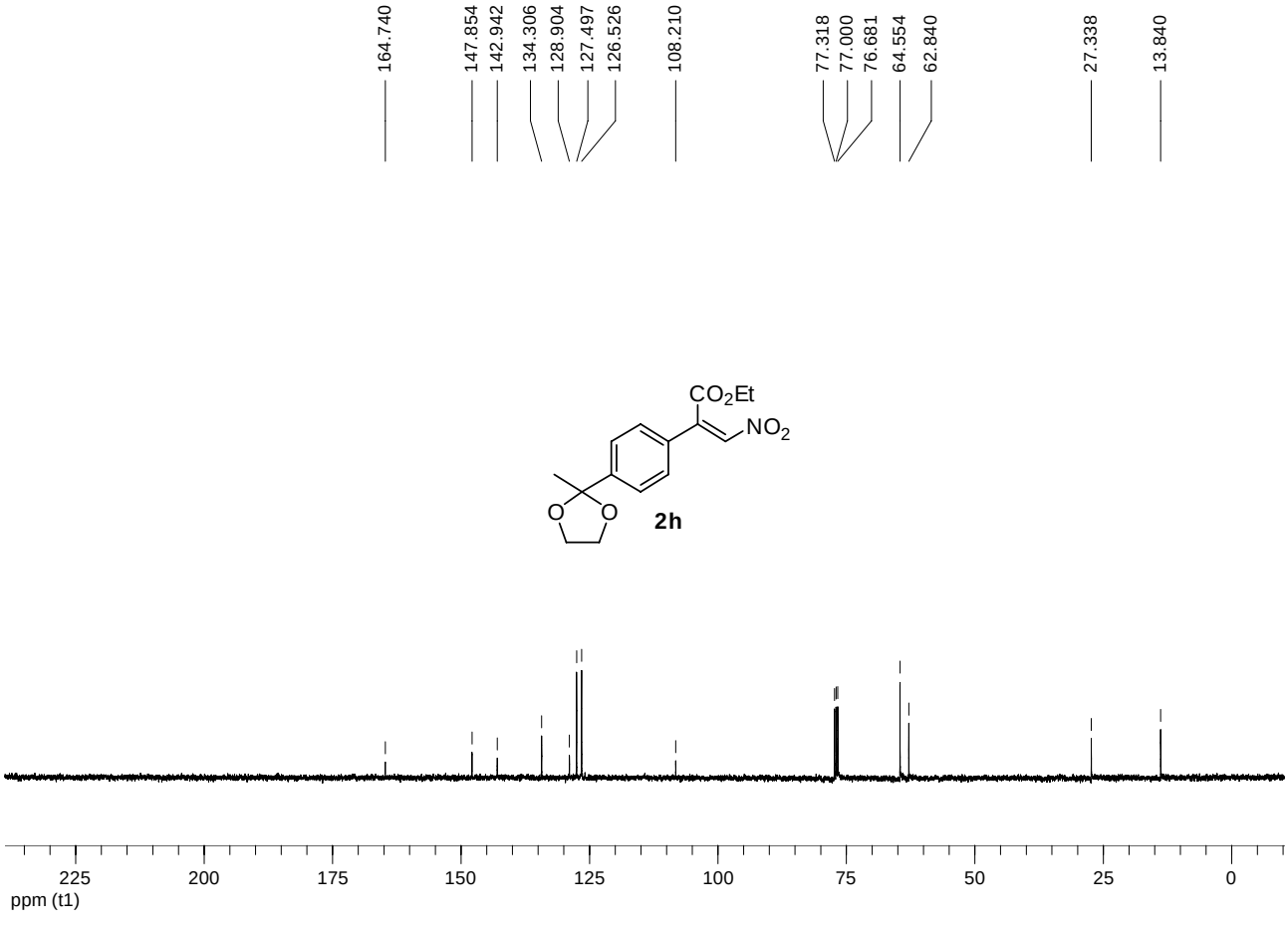

7.336
7.263
7.159
7.106
4.507
4.489
4.471
4.453
2.352
1.417
1.399
1.381
0.000
CO2Et
NO2
2f
0.94
1.96
6.38
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

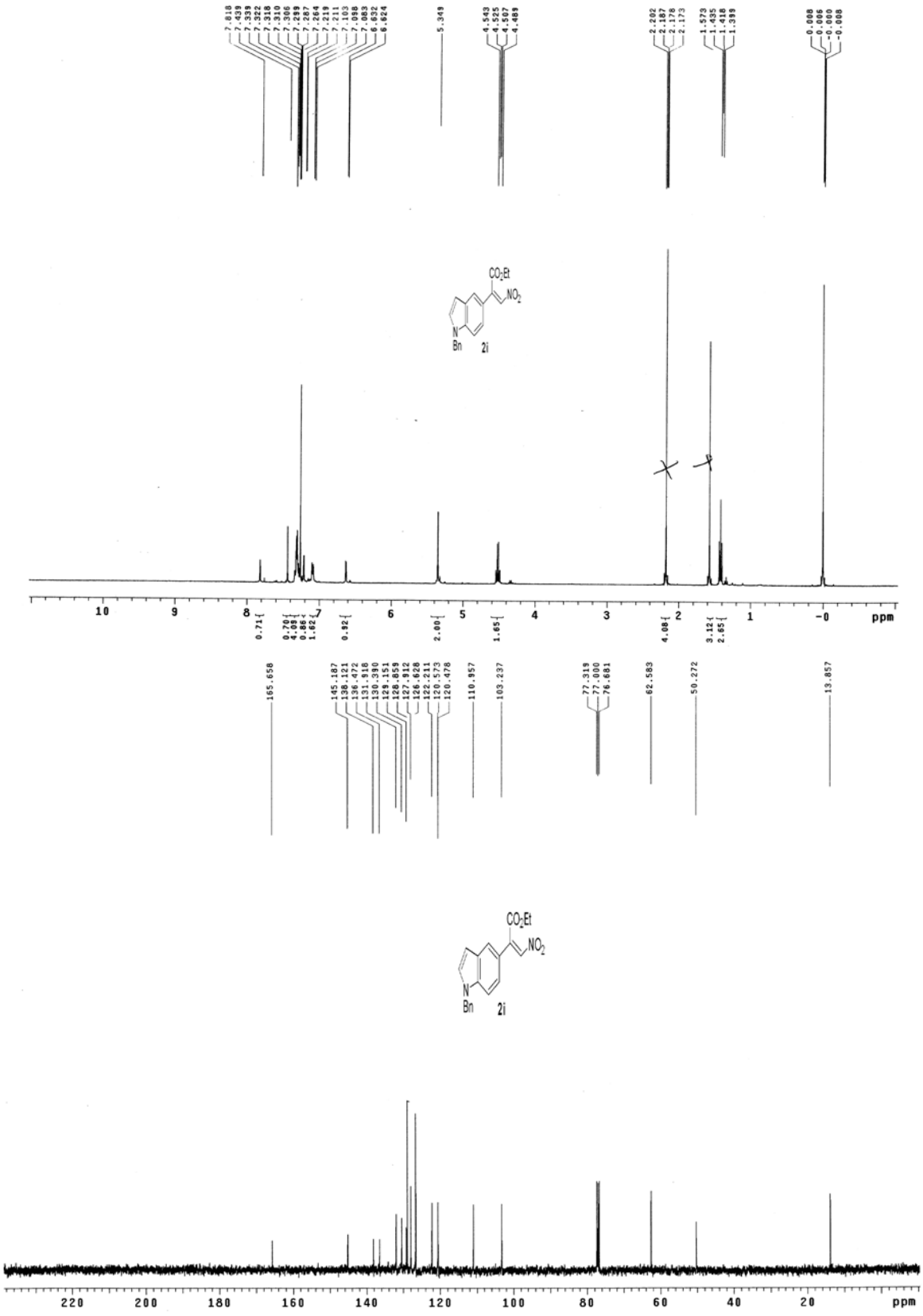

164.937
143.663
139.247
134.024
133.939
129.227
125.166
77.319
77.000
76.682
62.700
21.194
13.813
CO2Et
NO2
2f
225
200
175
150
125
100
75
50
25
0
ppm (t1)

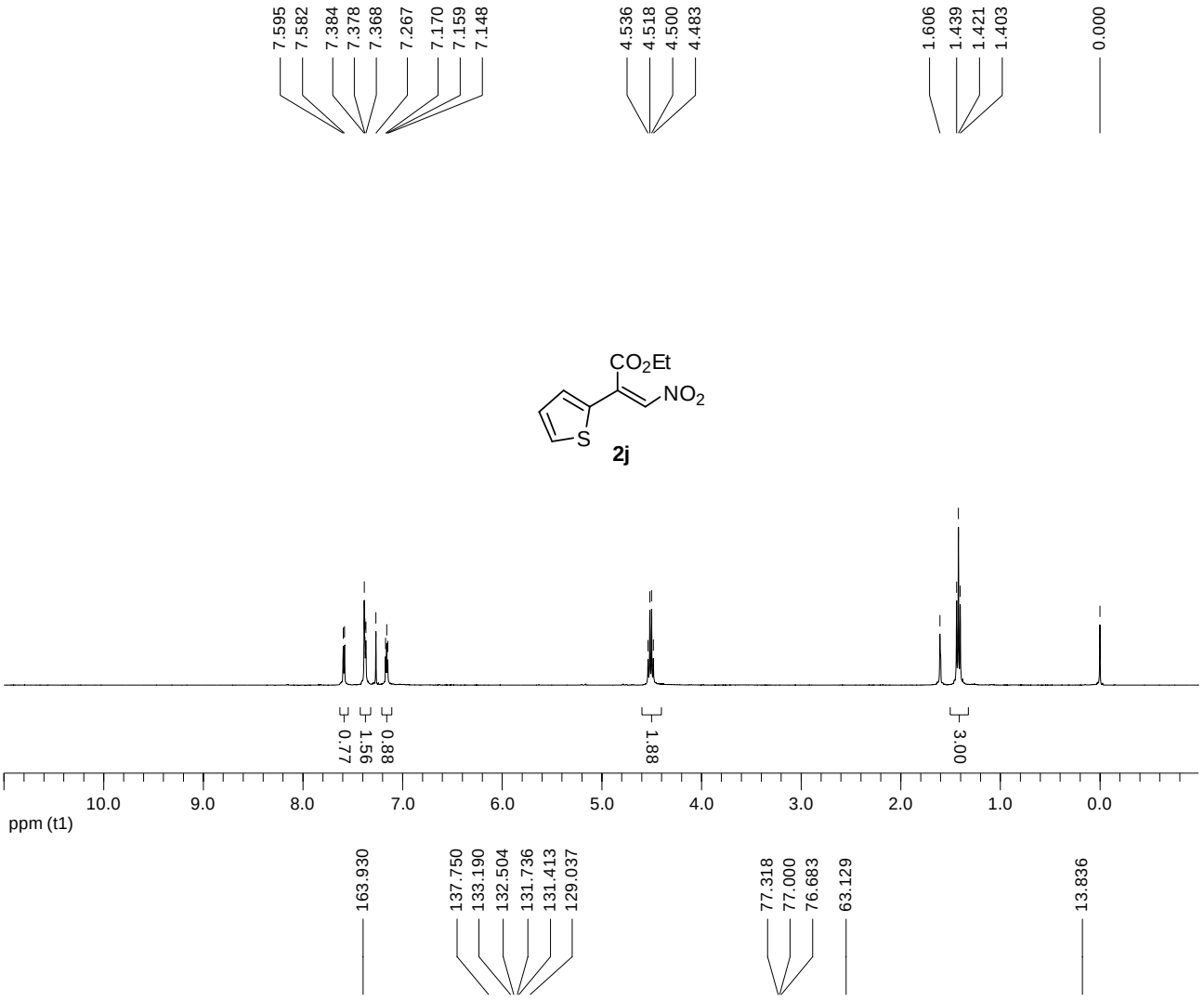

7.625
7.604
7.412
7.338
7.316
7.263
5.939
4.547
4.529
4.511
4.493
2.084
2.060
1.558
1.453
1.435
1.417
0.000
CO2Et
NO2
N
2g
2.03
0.94
1.00
1.70
1.93
6.45
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

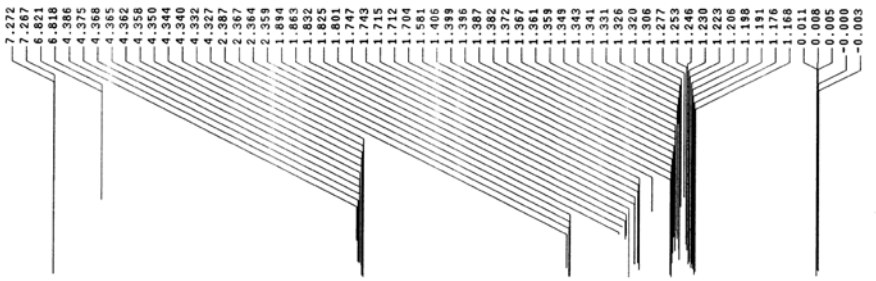

164.601
142.401
142.267
134.761
129.111
128.588
128.435
128.304
106.771
77.317
77.000
76.682
63.061
13.861
13.114
13.013
CO2Et
NO2
N
2g
225
200
175
150
125
100
75
50
25
0
ppm (t1)

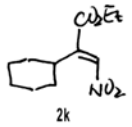

7.598
7.577
7.496
7.476
7.360
7.265
4.513
4.495
4.477
4.459
4.082
4.065
4.047
3.778
3.762
3.744
1.646
1.424
1.406
1.388
-0.000
CO2Et
NO2
O
O
2h
1.81
1.84
0.86
2.00
2.24
2.20
3.35
2.97
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


164.740
147.854
142.942
134.306
128.904
127.497
126.526
108.210
77.318
77.000
76.681
64.554
62.840
27.338
13.840
CO2Et
NO2
O
O
2h
225
200
175
150
125
100
75
50
25
0
ppm (t1)

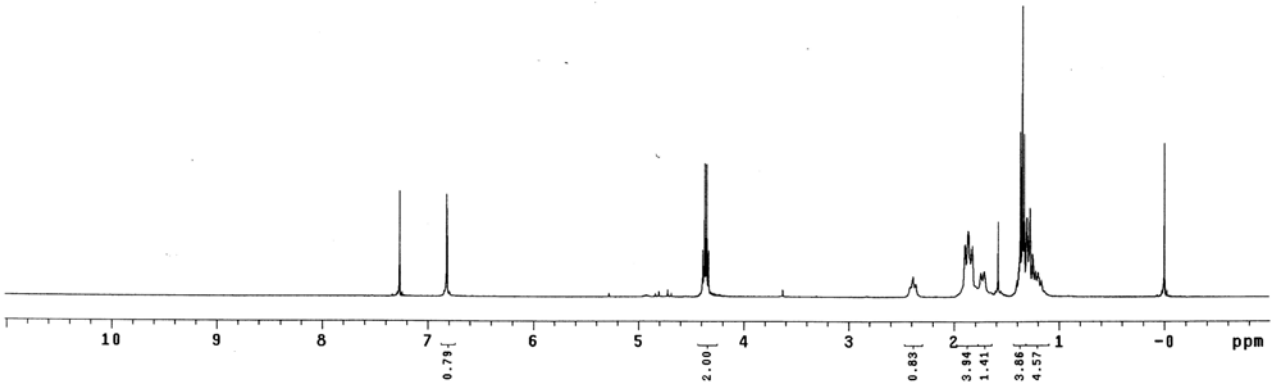

7.818
7.439
7.339
7.322
7.318
7.310
7.306
7.289
7.287
7.264
7.219
7.211
7.103
7.098
7.083
6.832
6.824
5.349
4.543
4.525
4.507
4.489
2.202
2.187
2.178
2.173
1.573
1.435
1.418
1.399
0.008
0.006
0.000
-0.008
CO2Et
NO2
N
Bn
2i
ppm
165.658
145.187
138.121
136.472
131.318
130.380
129.151
128.854
127.912
126.628
122.211
120.573
120.478
110.957
103.237
77.319
77.000
76.681
62.583
50.272
13.857

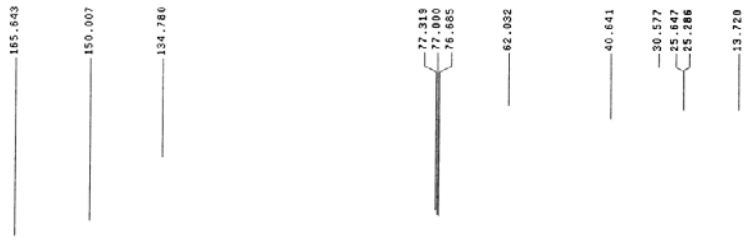

7.595
7.582
7.384
7.378
7.368
7.267
7.170
7.159
7.148
4.536
4.518
4.500
4.483
1.606
1.439
1.421
1.403
0.000
CO2Et
NO2
S
2j
0.77
1.56
0.88
1.88
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
163.930
137.750
133.190
132.504
131.736
131.413
129.037
77.318
77.000
76.683
63.129
13.836
CO2Et
NO2
S
2j
225
200
175
150
125
100
75
50
25
0
ppm (t1)

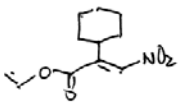

7.272
7.267
6.821
6.818
4.386
4.375
4.368
4.365
4.362
4.358
4.350
4.344
4.340
4.332
4.327
2.387
2.367
2.364
2.359
1.894
1.863
1.832
1.825
1.801
1.747
1.743
1.715
1.712
1.704
1.581
1.406
1.399
1.396
1.387
1.382
1.372
1.367
1.361
1.359
1.349
1.343
1.341
1.331
1.326
1.320
1.306
1.277
1.253
1.246
1.230
1.223
1.205
1.198
1.191
1.176
1.168
0.011
0.008
0.005
0.000
-0.003

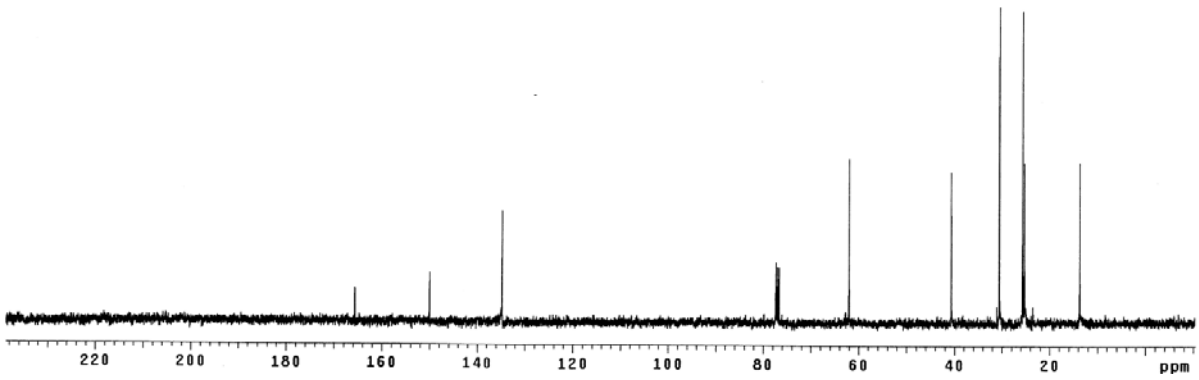

CO2Et
NO2

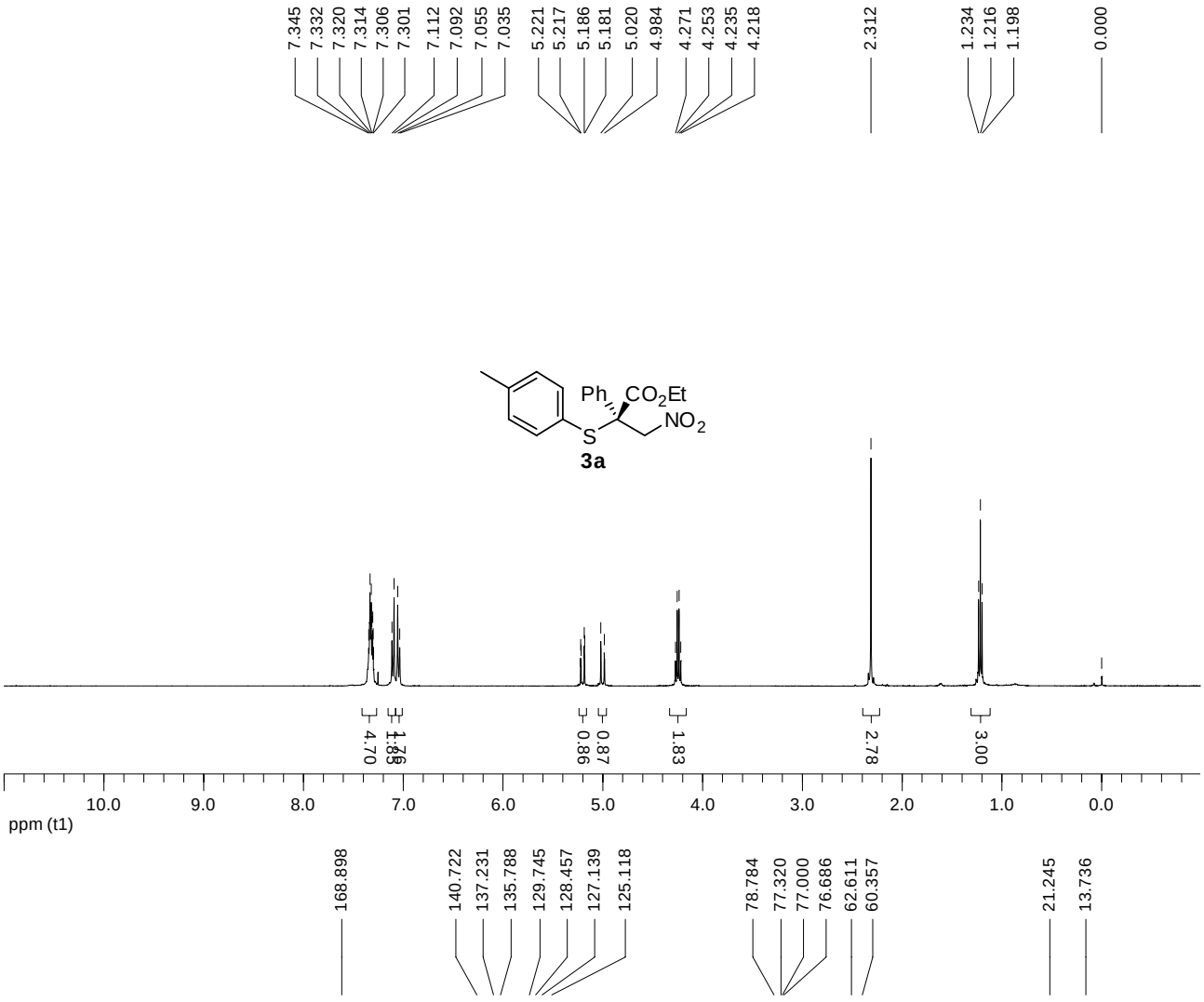
2k

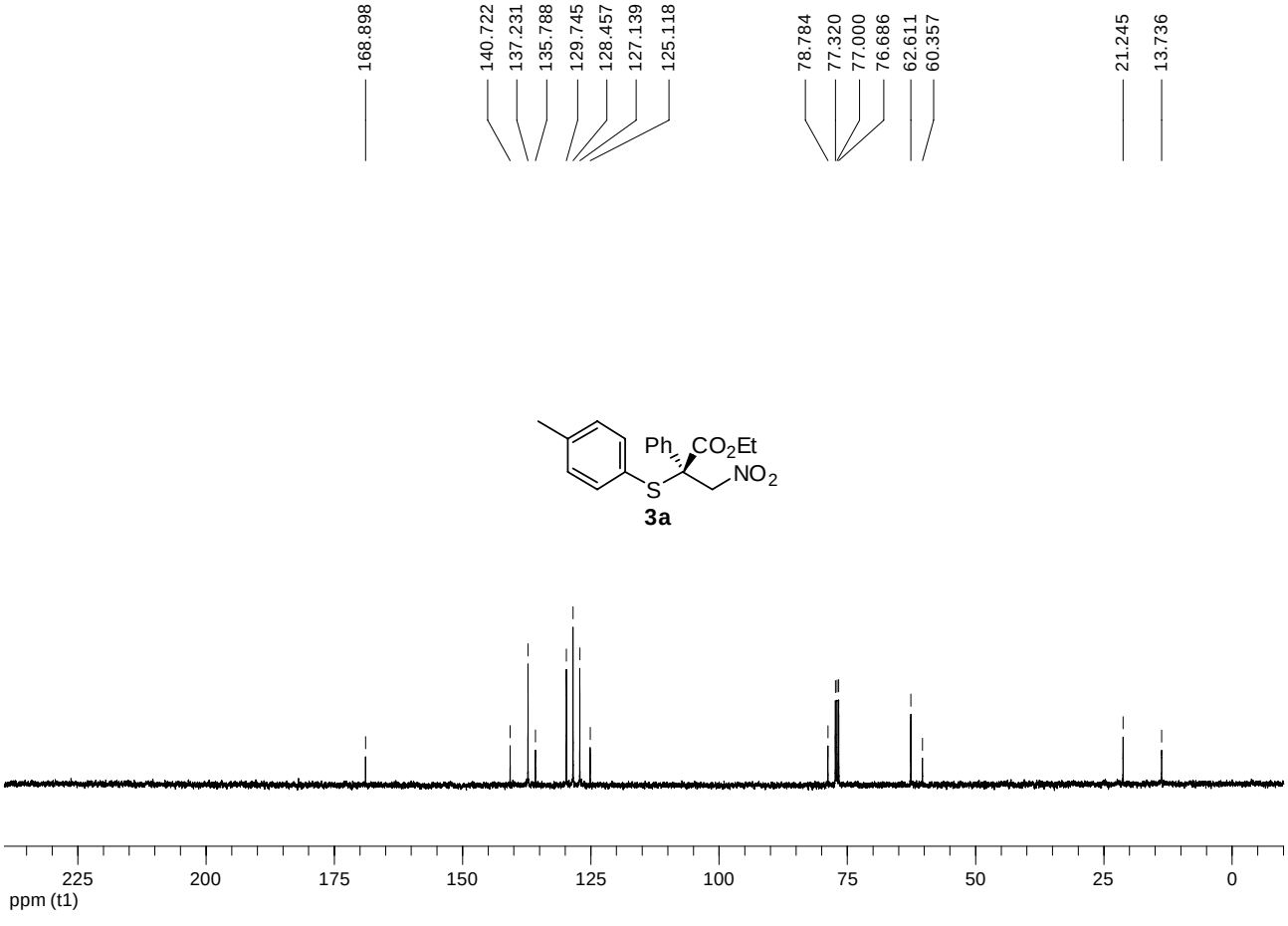

10
9
8
7
6
5
4
3
2
1
-0
ppm
0.79
2.00
0.83
3.84
1.41
3.86
4.57

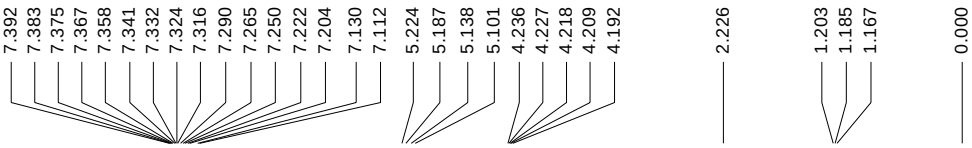

165.643
150.007
134.786
77.319
77.000
76.685
62.032
40.641
30.577
25.647
25.286
13.720

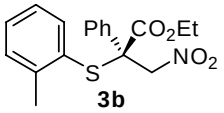

NO2
O
O


220
200
180
160
140
120
100
80
60
40
20
ppm

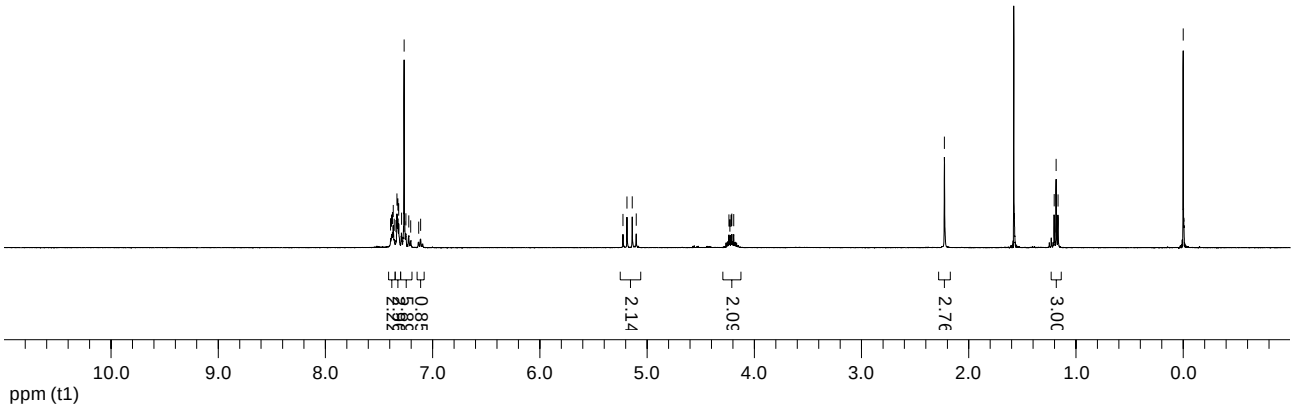

7.345
7.332
7.320
7.314
7.306
7.301
7.112
7.092
7.055
7.035
5.221
5.217
5.186
5.181
5.020
4.984
4.271
4.253
4.235
4.218
2.312
1.234
1.216
1.198
0.000
Ph
CO2Et
NO2
S
3a
4.70
1.89
1.86
0.86
0.87
1.83
2.78
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

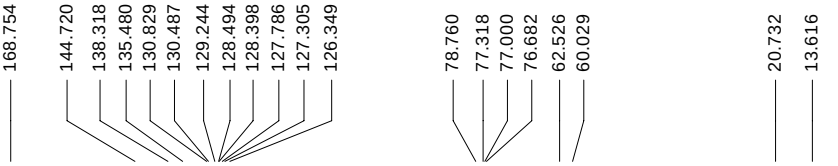

168.898
140.722
137.231
135.788
129.745
128.457
127.139
125.118
78.784
77.320
77.000
76.686
62.611
60.357
21.245
13.736
Ph
CO2Et
NO2
S
3a
225
200
175
150
125
100
75
50
25
0
ppm (t1)

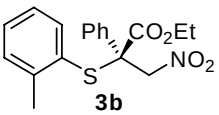

7.392
7.383
7.375
7.367
7.358
7.341
7.332
7.324
7.316
7.290
7.265
7.250
7.222
7.204
7.130
7.112
5.224
5.187
5.138
5.101
4.236
4.227
4.218
4.209
4.192
2.226
1.203
1.185
1.167
0.000


Ph
CO2Et
NO2
S

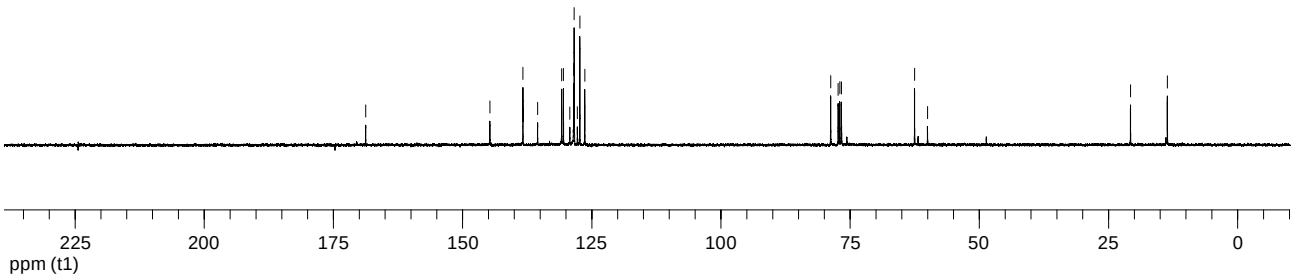
3b

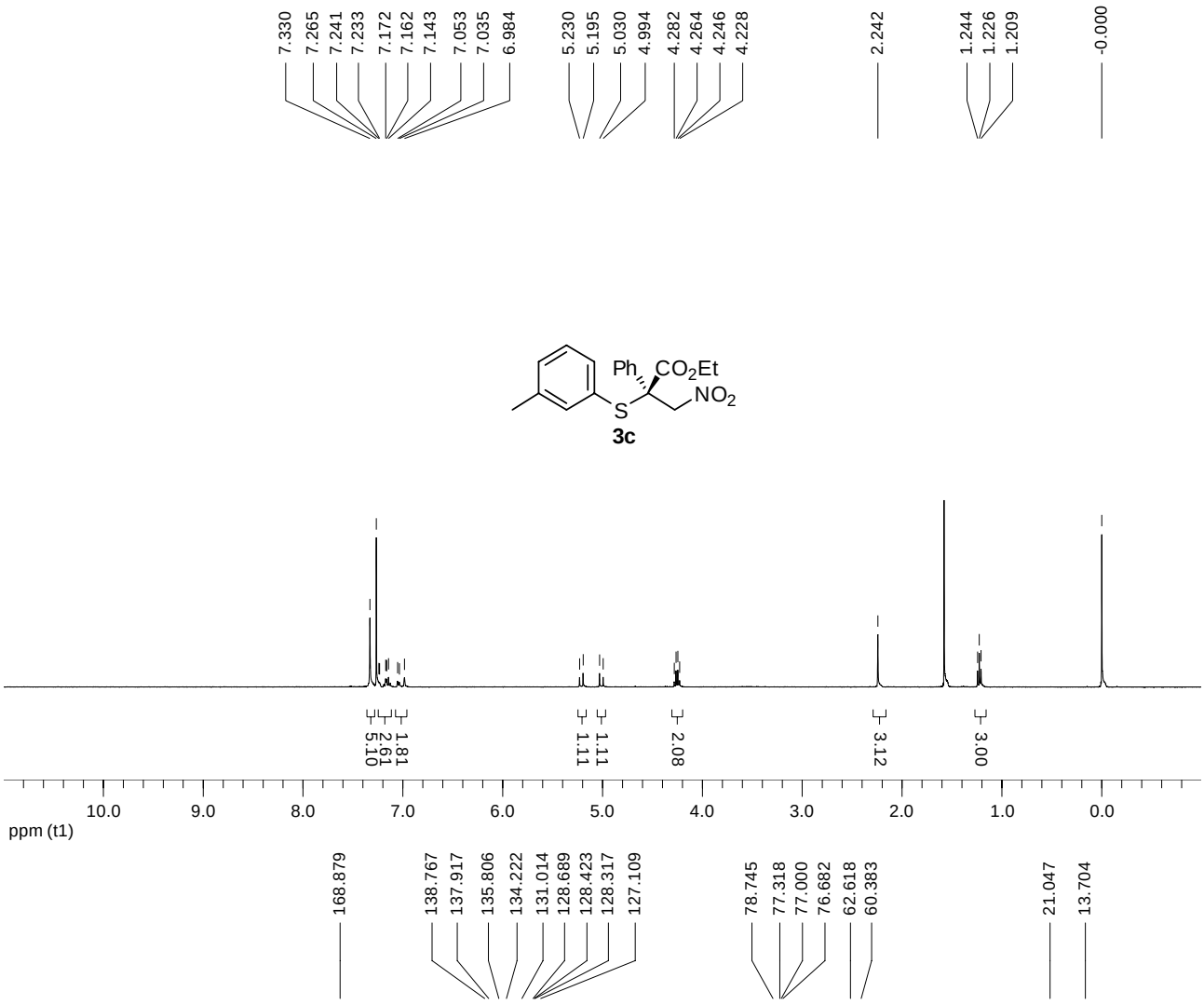

2.14
2.00
2.76
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

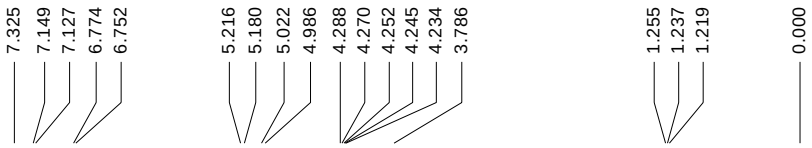

168.754
144.720
138.318
135.480
130.829
130.487
129.244
128.494
128.398
127.786
127.305
126.349
78.760
77.318
77.000
76.682
62.526
60.029
20.732
13.616

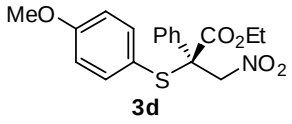

Ph
CO2Et
NO2
S

3b

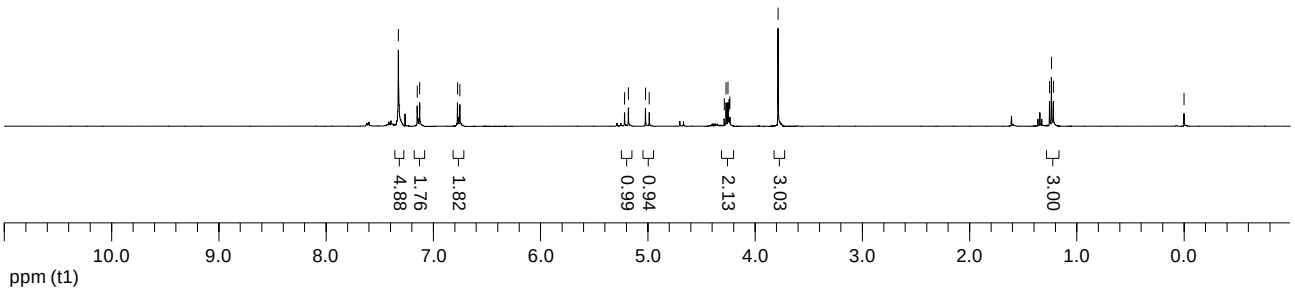

225
200
175
150
125
100
75
50
25
0
ppm (t1)

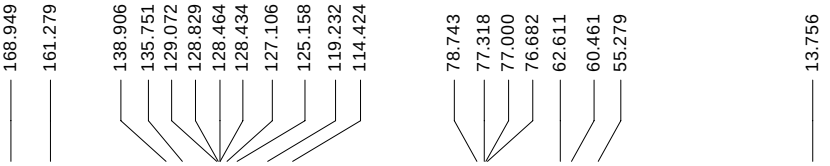

7.330
7.265
7.241
7.233
7.172
7.162
7.143
7.053
7.035
6.984
5.230
5.195
5.030
4.994
4.282
4.264
4.246
4.228
2.242
1.244
1.226
1.209
-0.000
Ph
CO2Et
NO2
S
3c
5.10
2.01
1.81
1.11
1.11
2.08
3.12
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
168.879
138.767
137.917
135.806
134.222
131.014
128.689
128.423
128.317
127.109
78.745
77.318
77.000
76.682
62.618
60.383
21.047
13.704
225
200
175
150
125
100
75
50
25
0
ppm (t1)

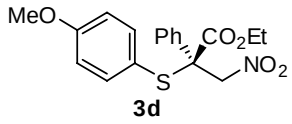

7.325
7.149
7.127
6.774
6.752
5.216
5.180
5.022
4.986
4.288
4.270
4.252
4.245
4.234
3.786
1.255
1.237
1.219
0.000


MeO
Ph
CO2Et
NO2
S

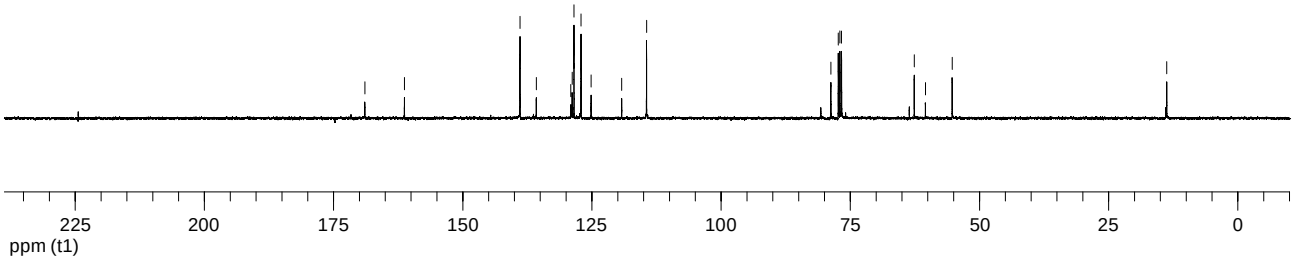
3d

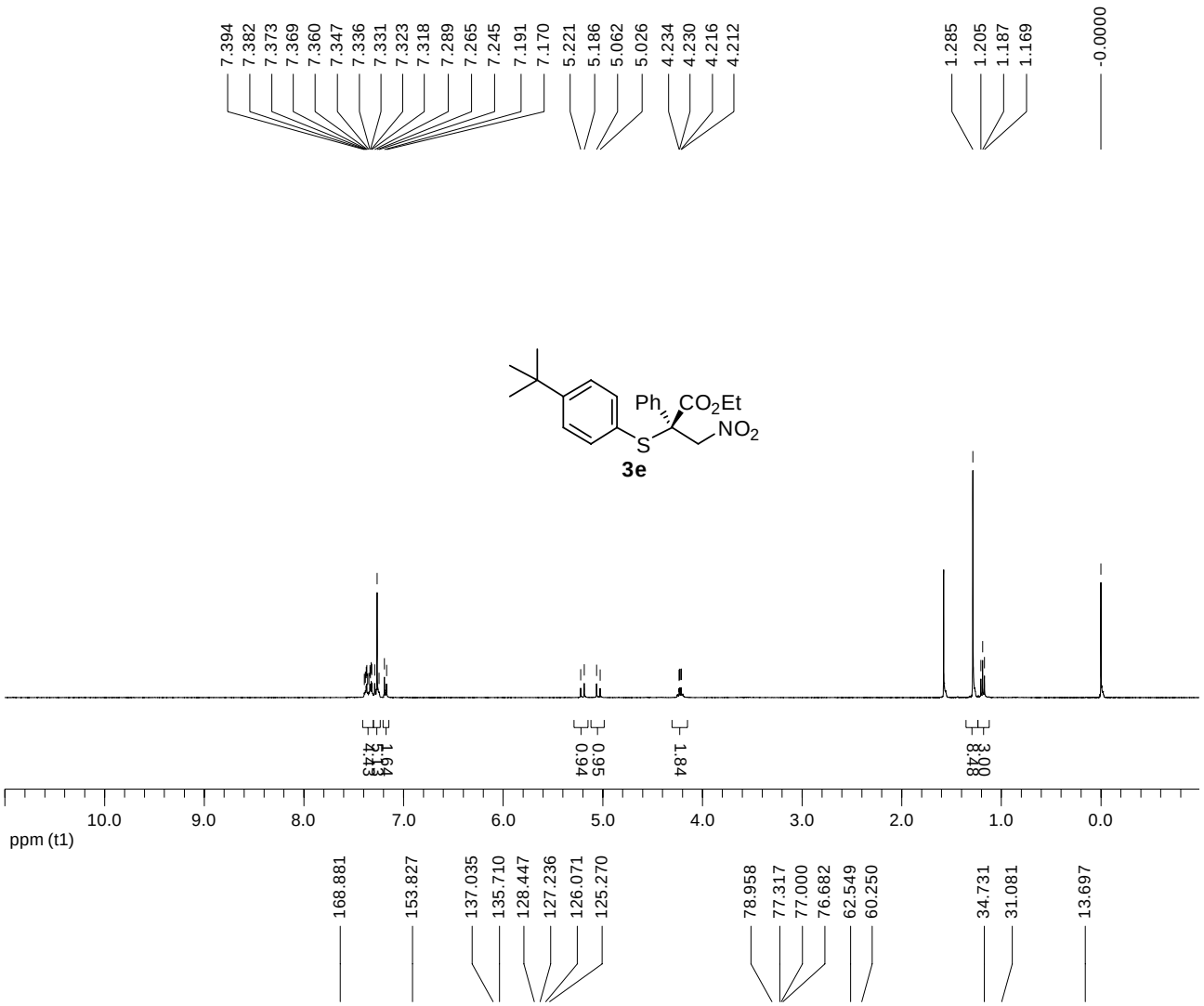

4.88
1.76
1.82
0.99
0.94
2.13
3.03
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


168.949
161.279
138.906
135.751
129.072
128.829
128.464
128.434
127.106
125.158
119.232
114.424
78.743
77.318
77.000
76.682
62.611
60.461
55.279
13.756


MeO
Ph
CO2Et
NO2
S

3d


225
200
175
150
125
100
75
50
25
0
ppm (t1)


7.394
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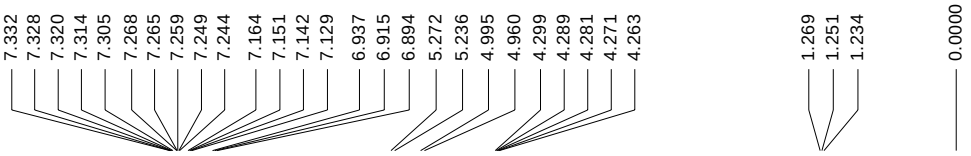
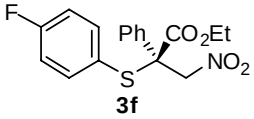
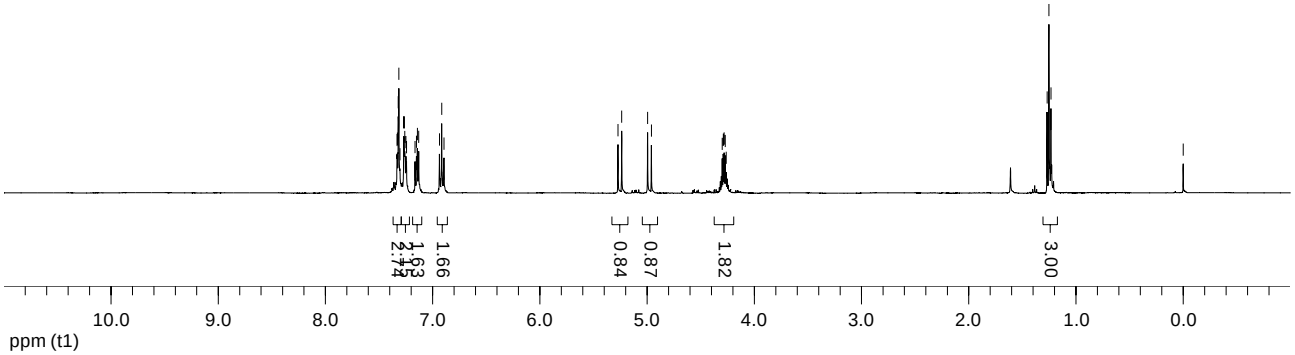
7.373
7.369
7.360
7.347
7.336
7.331
7.323
7.318
7.289
7.265
7.245
7.191
7.170
5.221
5.186
5.062
5.026
4.234
4.230
4.216
4.212
1.285
1.205
1.187
1.169
-0.0000
Ph
CO2Et
NO2
S
3e
1.43
4.43
0.94
0.95
1.84
8.48
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)
168.881
153.827
137.035
135.710
128.447
127.236
126.071
125.270
78.958
77.317
77.000
76.682
62.549
60.250
34.731
31.081
13.697
Ph
CO2Et
NO2
S
3e
225
200
175
150
125
100
75
50
25
0
ppm (t1)


7.332
7.328
7.320
7.314
7.305
7.268
7.265
7.259
7.249
7.244
7.164
7.151
7.142
7.129
6.937
6.915
6.894
5.272
5.236
4.995
4.960
4.299
4.289
4.281
4.271
4.263
1.269
1.251
1.234
0.0000


F
Ph
CO2Et
NO2
S

3f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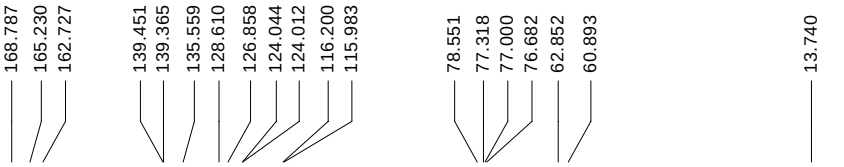
2.63
1.66
0.84
0.87
1.82
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


168.787
165.230
162.727
139.451
139.365
135.559
128.610
126.858
124.044
124.012
116.200
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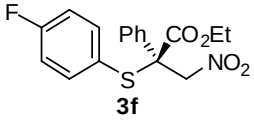
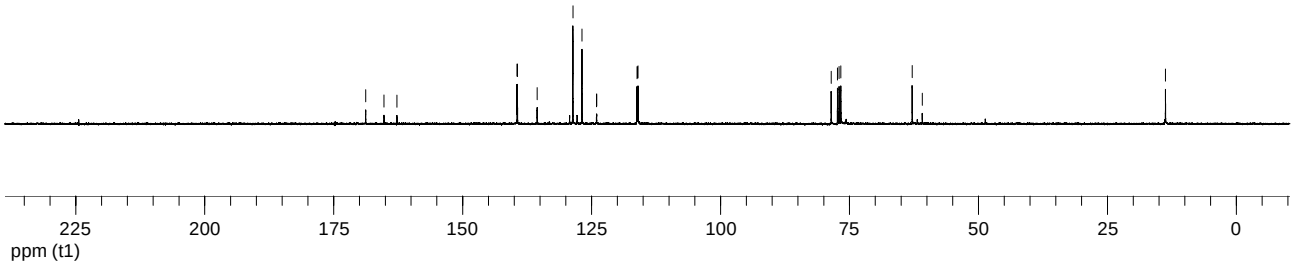
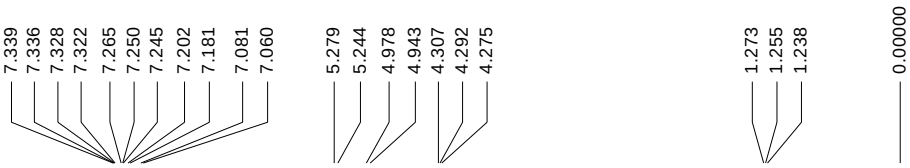
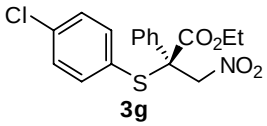
78.551
77.318
77.000
76.682
62.852
60.893
13.740


F
Ph
CO2Et
NO2
S

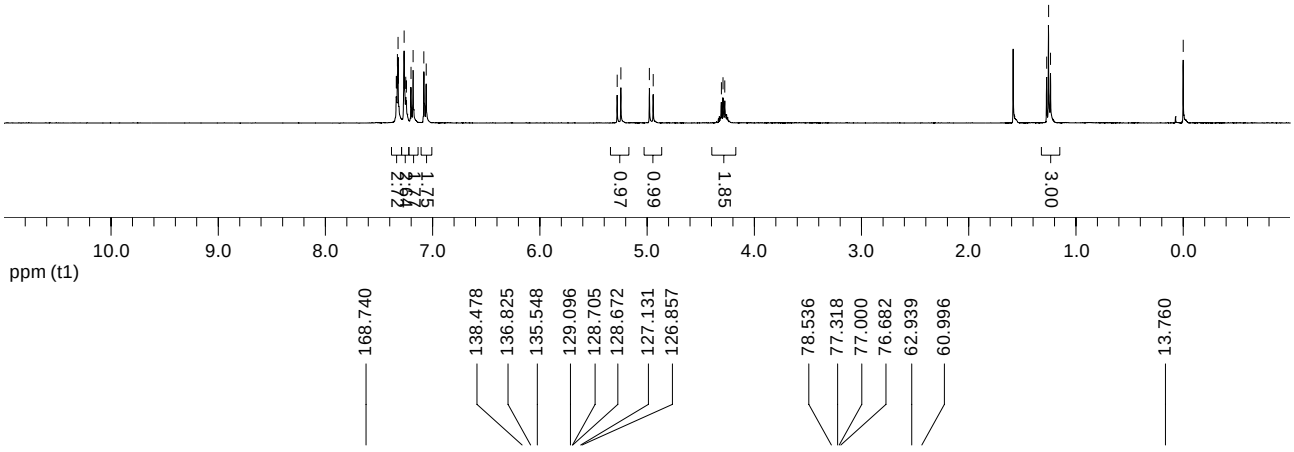
3f


225
200
175
150
125
100
75
50
25
0
ppm (t1)

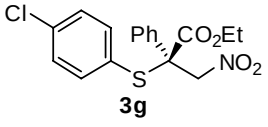

7.339
7.336
7.328
7.322
7.265
7.250
7.245
7.202
7.181
7.081
7.060
5.279
5.244
4.978
4.943
4.307
4.292
4.275
1.273
1.255
1.238
0.00000


Cl
Ph
CO2Et
NO2
S

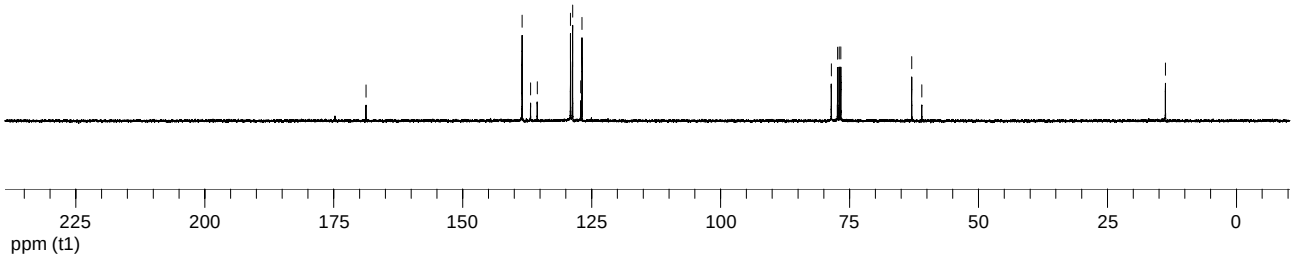
3g

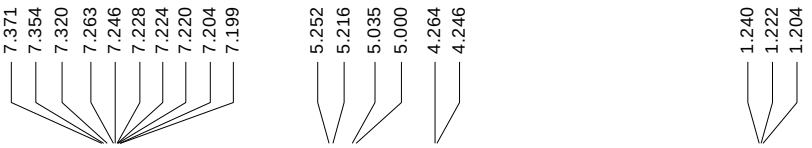

2.72
2.64
1.75
0.97
0.99
1.85
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

168.740
138.478
136.825
135.548
129.096
128.705
128.672
127.131
126.857
78.536
77.318
77.000
76.682
62.939
60.996
13.760


Cl
Ph
CO2Et
NO2
S

3g


225
200
175
150
125
100
75
50
25
0
ppm (t1)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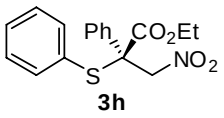
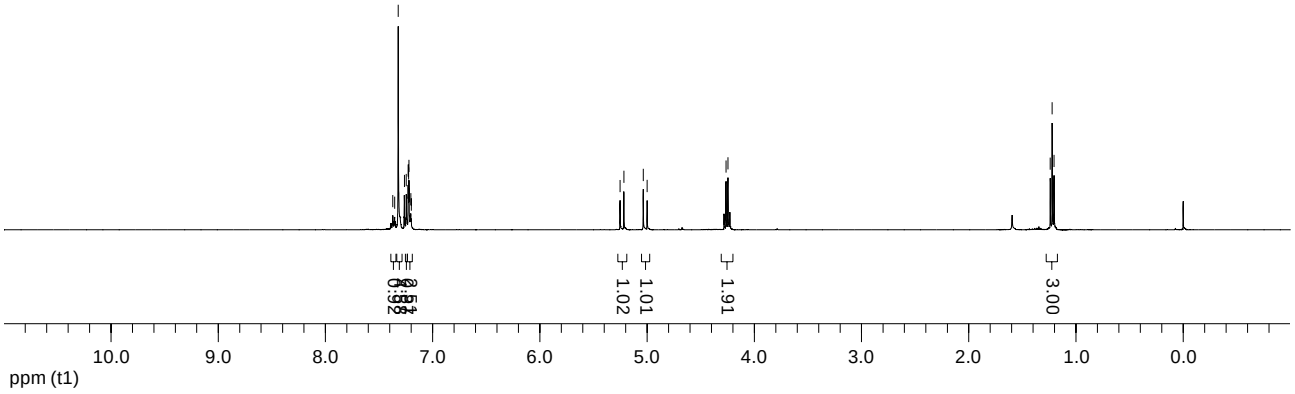
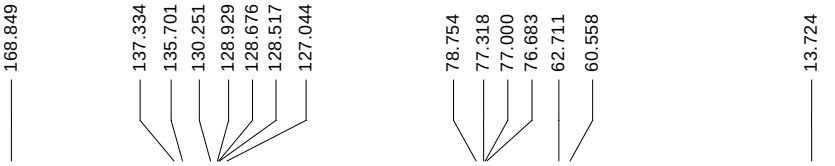
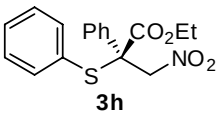
7.263
7.246
7.228
7.224
7.220
7.204
7.199
5.252
5.216
5.035
5.000
4.264
4.246
1.240
1.222
1.204


Ph
CO2Et
NO2
S

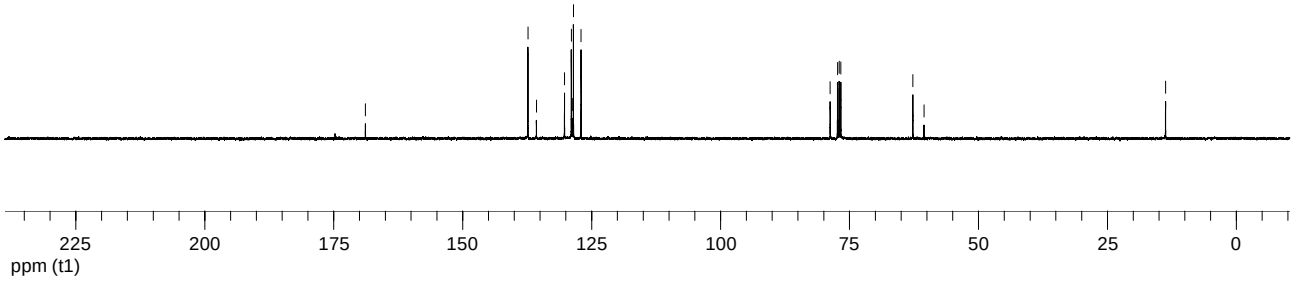
3h

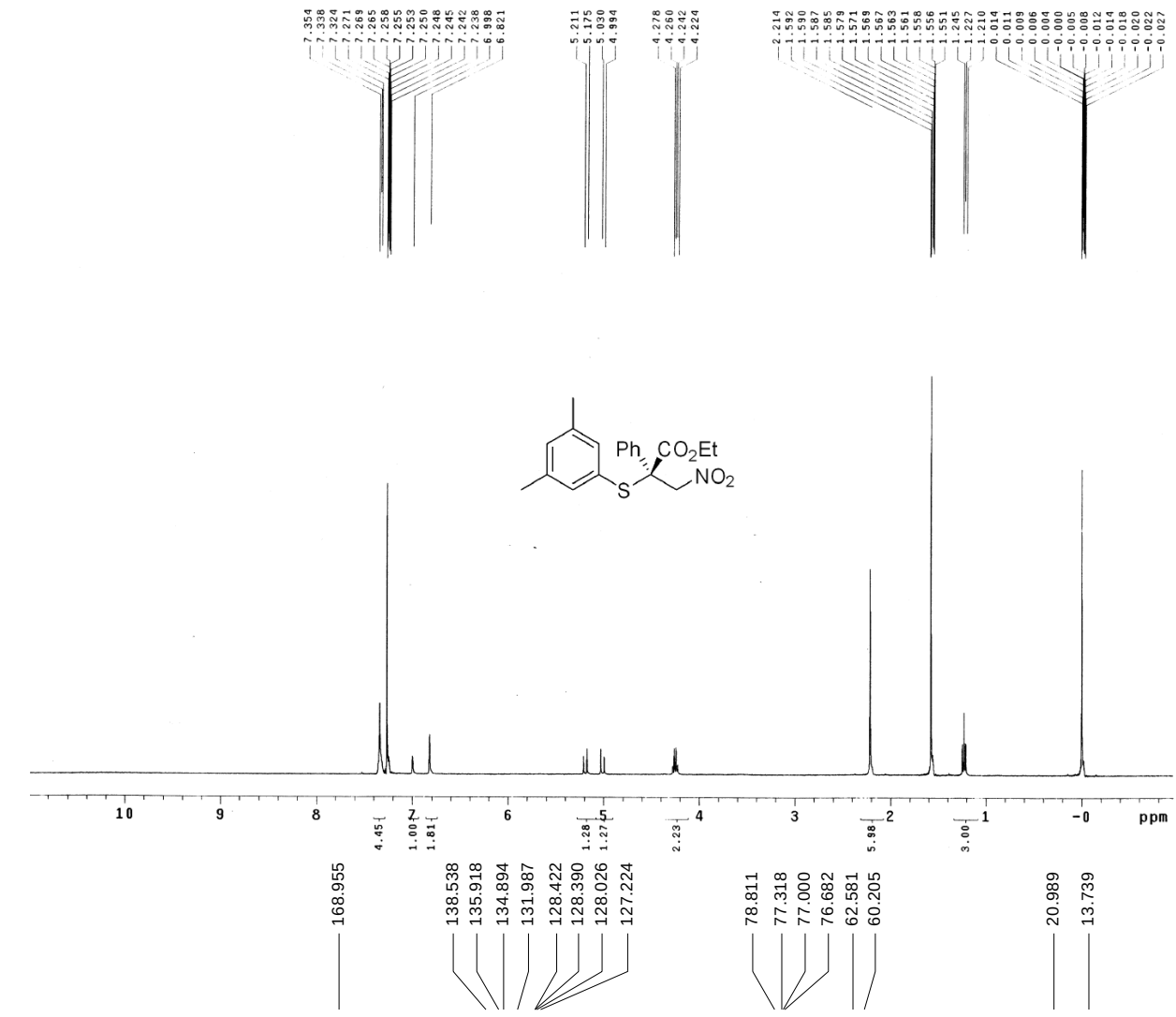

1.92
1.02
1.01
1.91
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


168.849
137.334
135.701
130.251
128.929
128.676
128.517
127.044
78.754
77.318
77.000
76.683
62.711
60.558
13.724


Ph
CO2Et
NO2
S

3h


225
200
175
150
125
100
75
50
25
0
ppm (t1)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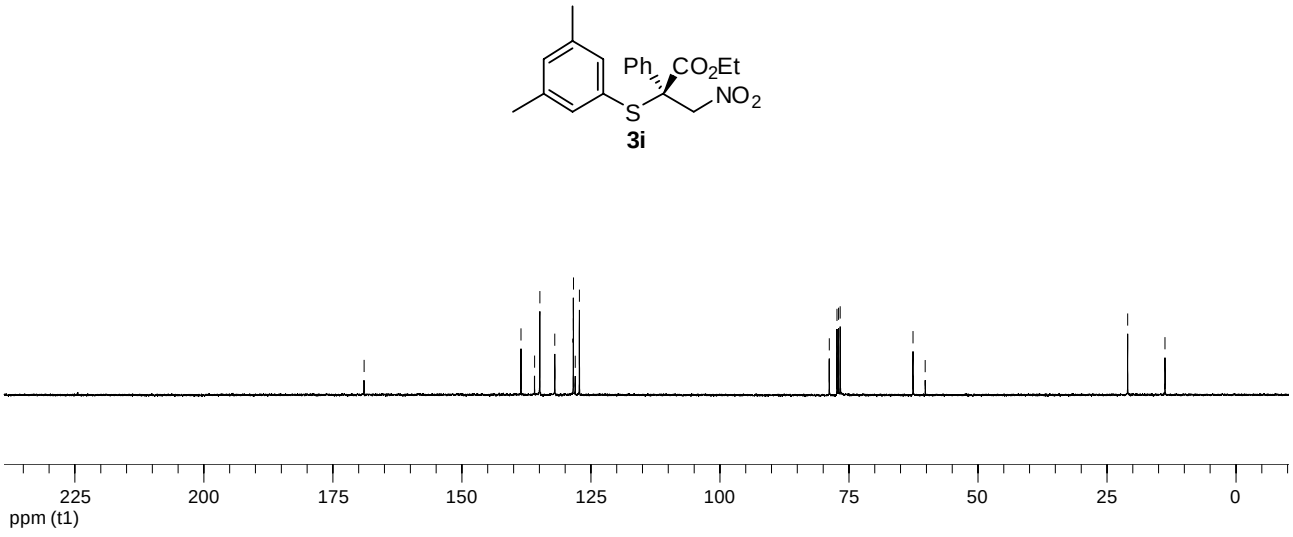
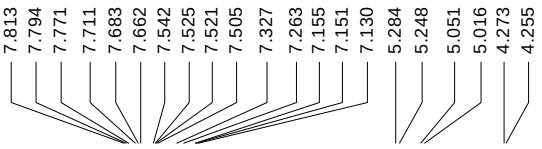
7.324
7.271
7.269
7.265
7.258
7.255
7.253
7.250
7.248
7.245
7.242
7.238
6.998
6.821
5.211
5.175
5.030
4.994
4.278
4.260
4.242
4.224
2.214
1.592
1.590
1.587
1.585
1.579
1.571
1.569
1.567
1.563
1.561
1.558
1.556
1.551
1.245
1.227
1.210
0.014
0.011
0.009
0.006
0.004
0.000
-0.005
-0.008
-0.012
-0.014
-0.018
-0.020
-0.022
-0.027
Ph
CO2Et
NO2
S
10
9
8
7
6
5
4
3
2
1
-0
ppm
4.45
1.00
1.81
1.28
1.27
2.23
5.98
3.00
168.955
138.538
135.918
134.894
131.987
128.422
128.390
128.026
127.224
78.811
77.318
77.000
76.682
62.581
60.205
20.989
13.739


Ph
CO2Et
NO2
S
225
200
175
150
125
100
75
50
25
0
ppm (t1)

3i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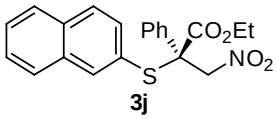
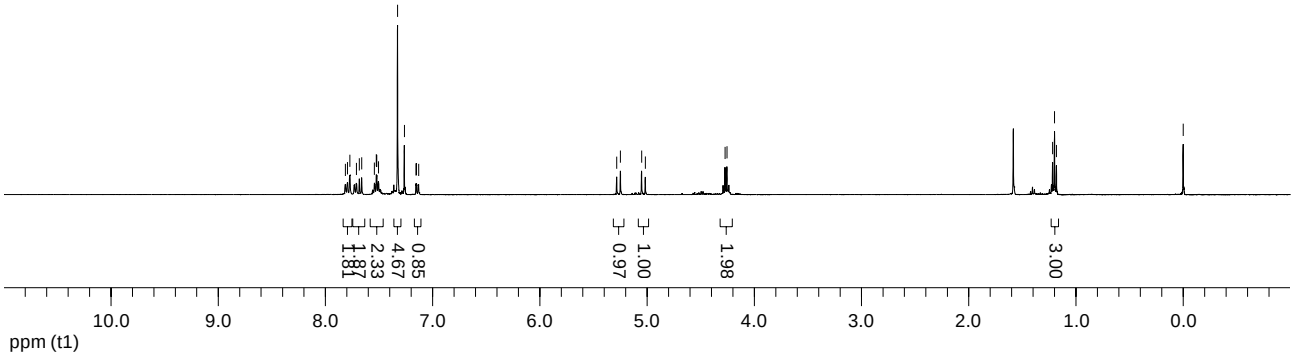
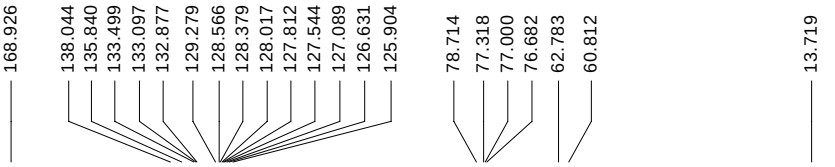
7.771
7.711
7.683
7.662
7.542
7.525
7.521
7.505
7.327
7.263
7.155
7.151
7.130
5.284
5.248
5.051
5.016
4.273
4.255
1.218
1.200
1.182
0.000


Ph
CO2Et
NO2
S

3j


1.87
1.87
2.33
4.67
0.85
0.97
1.00
1.98
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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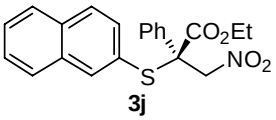
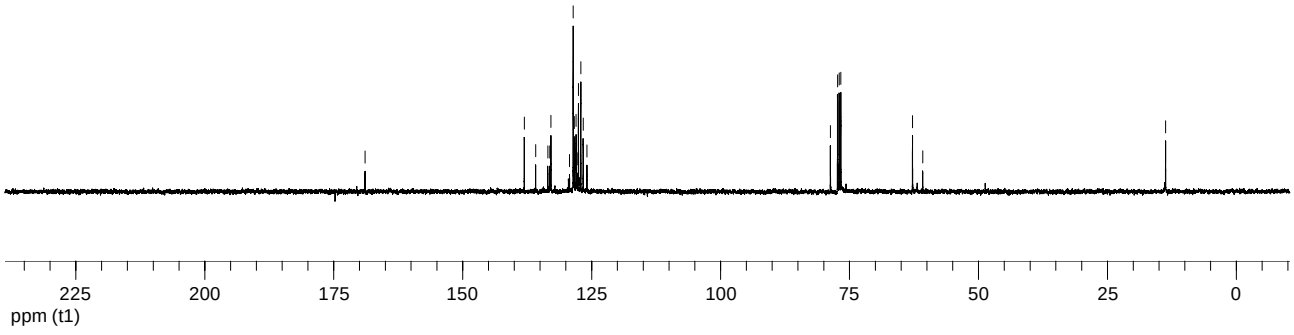
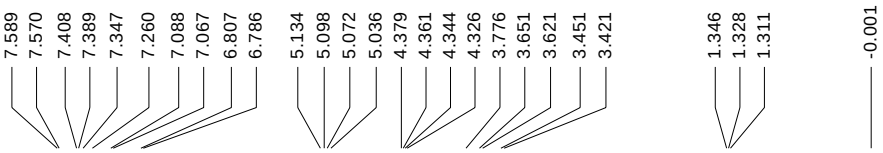
133.097
132.877
129.279
128.566
128.379
128.017
127.812
127.544
127.089
126.631
125.904
78.714
77.318
77.000
76.682
62.783
60.812
13.719


Ph
CO2Et
NO2
S

3j


225
200
175
150
125
100
75
50
25
0
ppm (t1)


7.589
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7.408
7.389
7.347
7.260
7.088
7.067
6.807
6.786
5.134
5.098
5.072
5.036
4.379
4.361
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3.776
3.651
3.621
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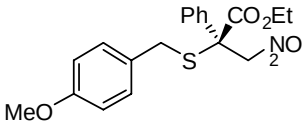
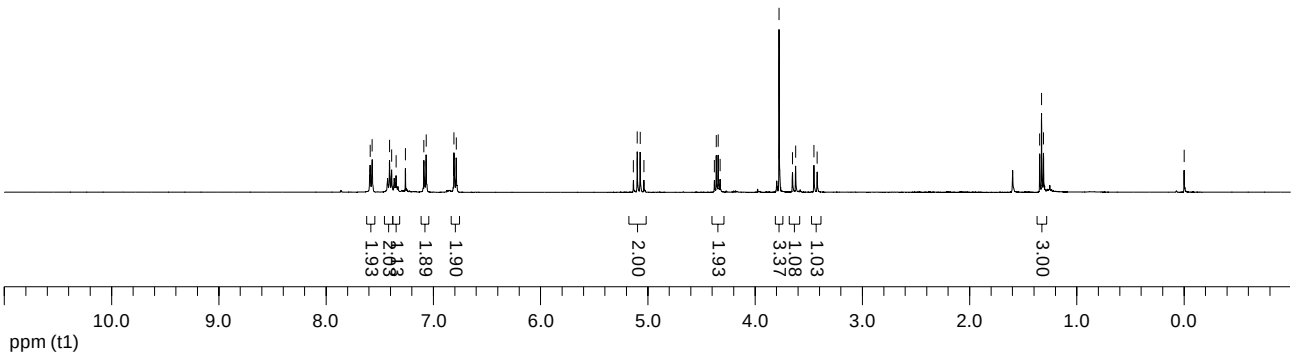
3.421
1.346
1.328
1.311
-0.001


Ph
CO2Et
NO2
S
MeO

3k


1.93
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1.89
1.90
2.00
1.93
3.37
1.80
1.03
3.00
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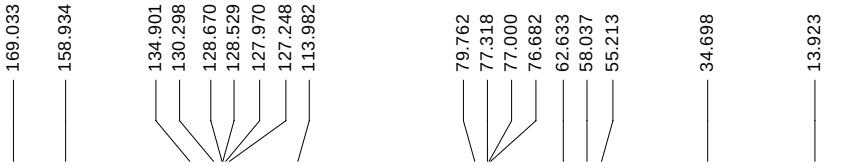
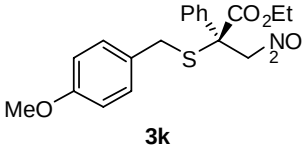
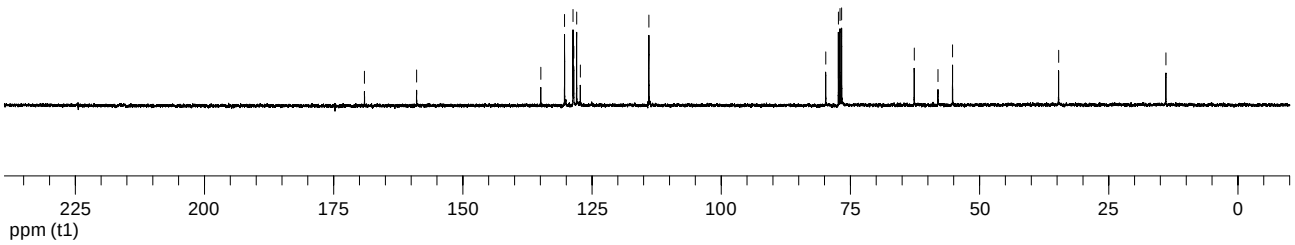
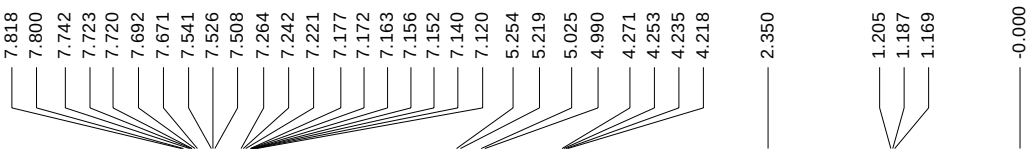
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)


169.033
158.934
134.901
130.298
128.670
128.529
127.970
127.248
113.982
79.762
77.318
77.000
76.682
62.633
58.037
55.213
34.698
13.923


Ph
CO2Et
NO2
S
MeO

3k


225
200
175
150
125
100
75
50
25
0
ppm (t1)


7.818
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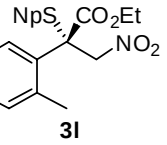
7.508
7.264
7.242
7.221
7.177
7.172
7.163
7.156
7.152
7.140
7.120
5.254
5.219
5.025
4.990
4.271
4.253
4.235
4.218
2.350
1.205
1.187
1.169
-0.000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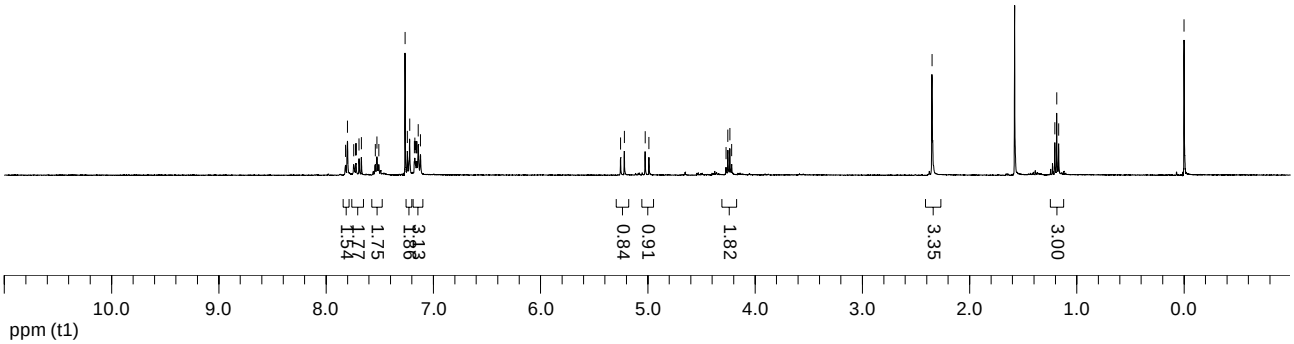
CO2Et
NO2

3l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0.84
0.91
1.82
3.35
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7.0
6.0
5.0
4.0
3.0
2.0
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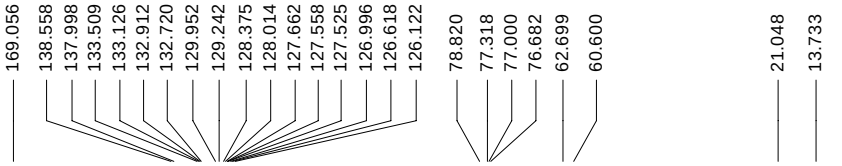
0.0
ppm (t1)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128.014
127.662
127.558
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126.996
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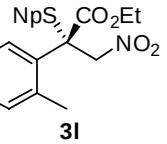
126.122
78.820
77.318
77.000
76.682
62.699
60.600
21.048
13.733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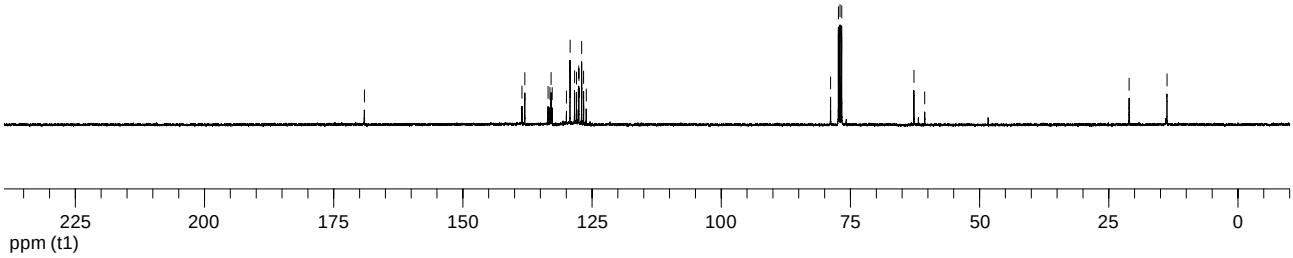
CO2Et
NO2

3l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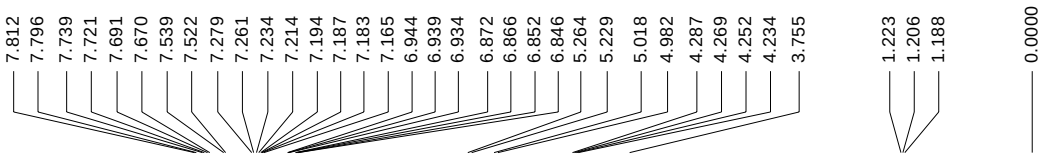
175
150
125
100
75
50
25
0
ppm (t1)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7.670
7.539
7.522
7.279
7.261
7.234
7.214
7.194
7.187
7.183
7.165
6.944
6.939
6.934
6.872
6.866
6.852
6.846
5.264
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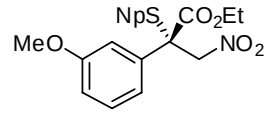
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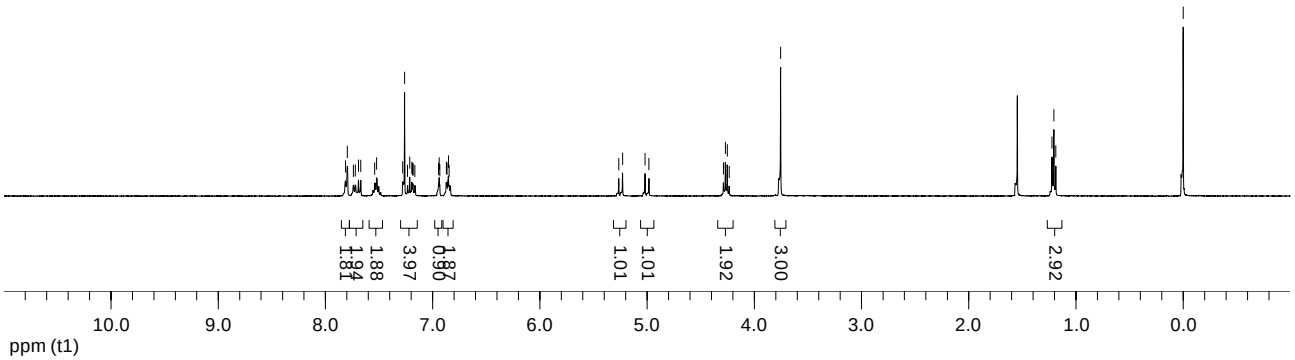
CO2Et
MeO
NO2

3m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1.00
1.01
1.01
1.92
3.00
2.92
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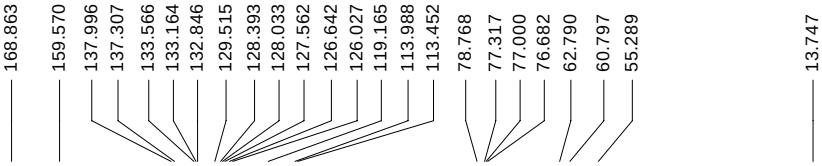
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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129.515
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127.562
126.642
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77.000
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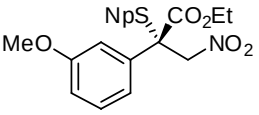
62.790
60.797
55.289
13.747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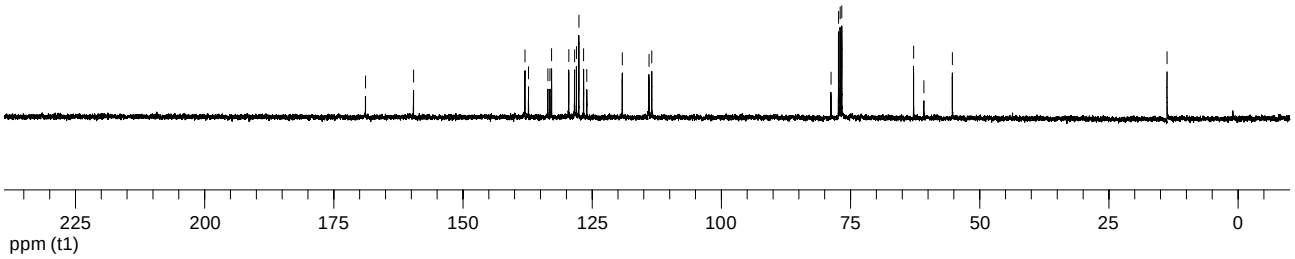
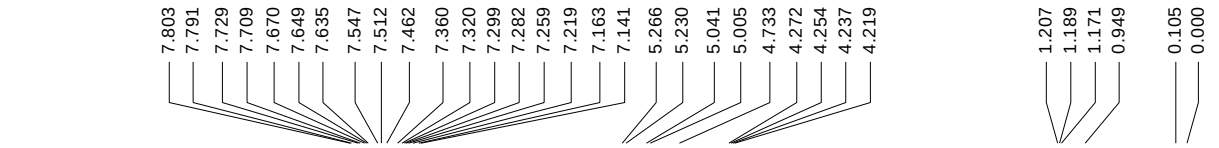
CO2Et
MeO
NO2

3m


225
200
175
150
125
100
75
50
25
0
ppm (t1)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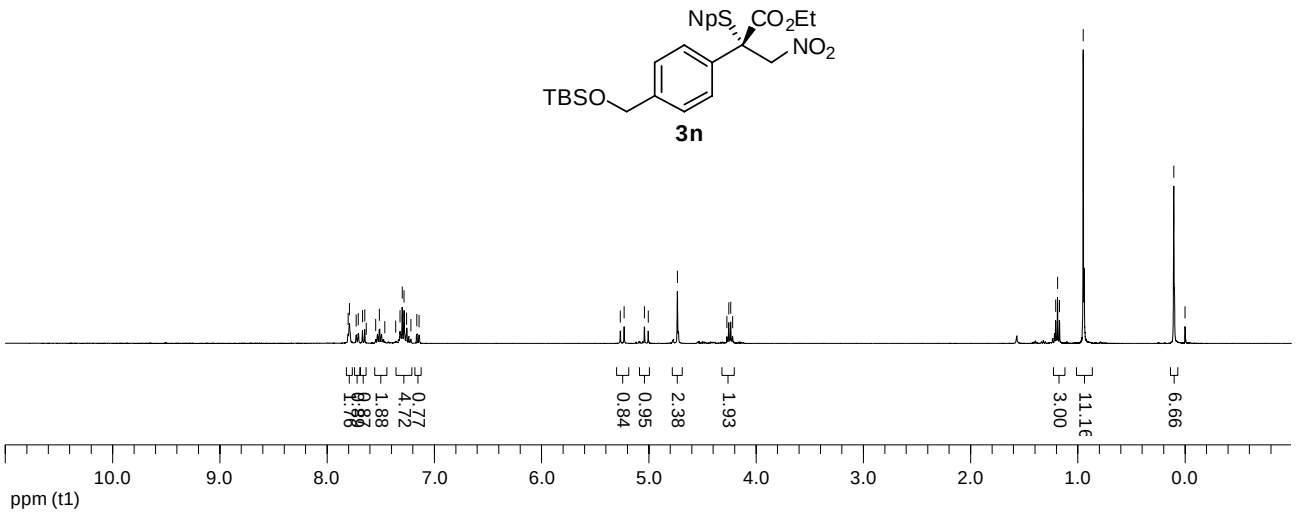
7.729
7.709
7.670
7.649
7.635
7.547
7.512
7.462
7.360
7.320
7.299
7.282
7.259
7.219
7.163
7.141
5.266
5.230
5.041
5.005
4.733
4.272
4.254
4.237
4.219
1.207
1.189
1.171
0.949
0.105
0.000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CO2Et
NO2
TBSO
3n
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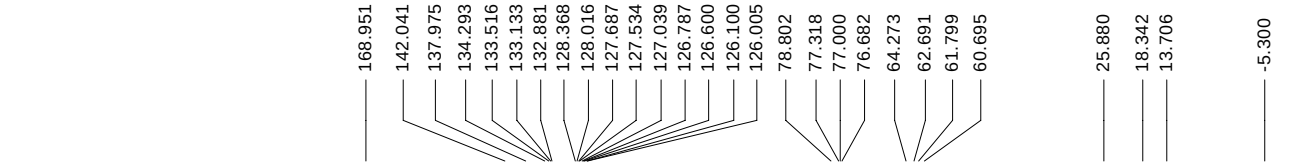
1.88
2.38
0.84
0.95
1.93
3.00
11.16
6.66
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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133.516
133.133
132.881
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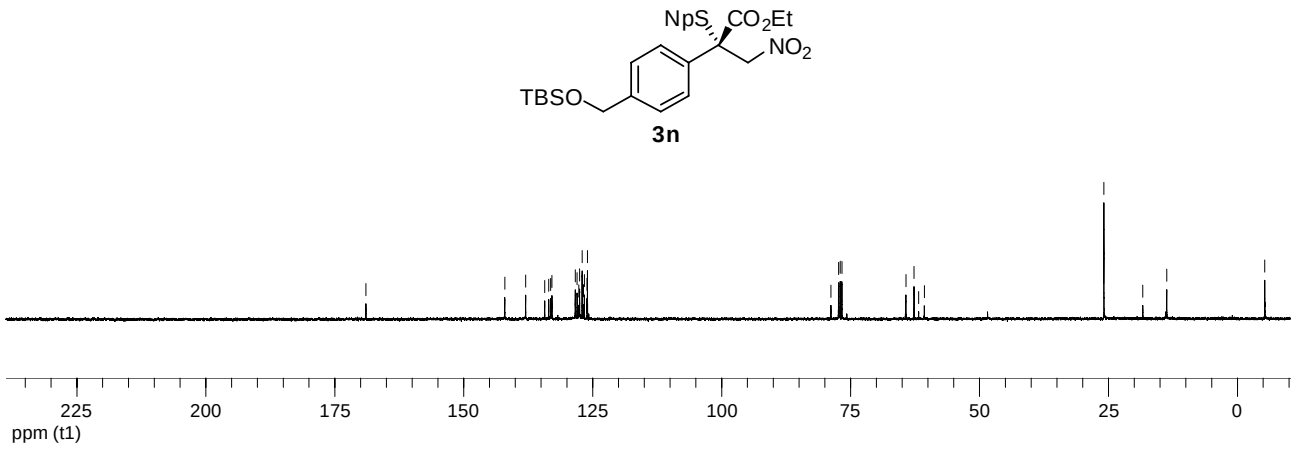
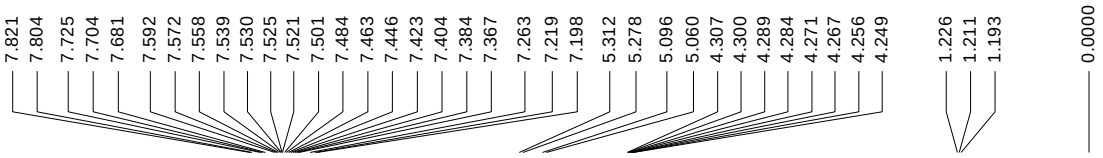
128.016
127.687
127.534
127.039
126.787
126.600
126.100
126.005
78.802
77.318
77.000
76.682
64.273
62.691
61.799
60.695
25.880
18.342
13.706
-5.300


NpS
CO2Et
NO2
TBSO
3n
225
200
175
150
125
100
75
50
25
0
ppm (t1)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7.592
7.572
7.558
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7.530
7.525
7.521
7.501
7.484
7.463
7.446
7.423
7.404
7.384
7.367
7.263
7.219
7.198
5.312
5.278
5.096
5.060
4.307
4.300
4.289
4.284
4.271
4.267
4.256
4.249
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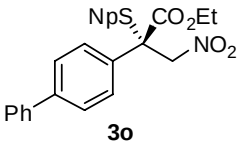
1.211
1.193
0.0000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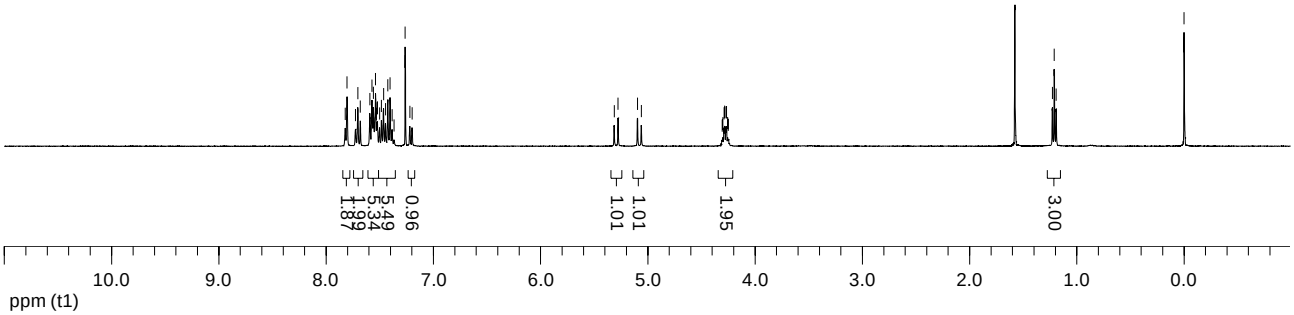
CO2Et
NO2
Ph

3o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5.34
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0.96
1.01
1.01
1.95
3.00
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9.0
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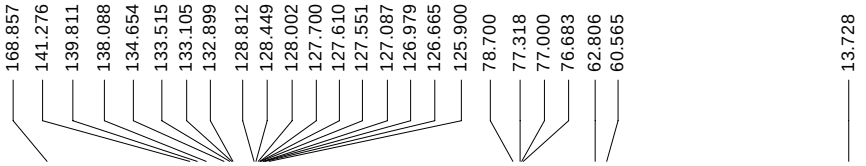
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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133.105
132.899
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128.449
128.002
127.700
127.610
127.551
127.087
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126.665
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78.700
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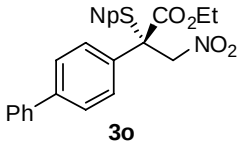
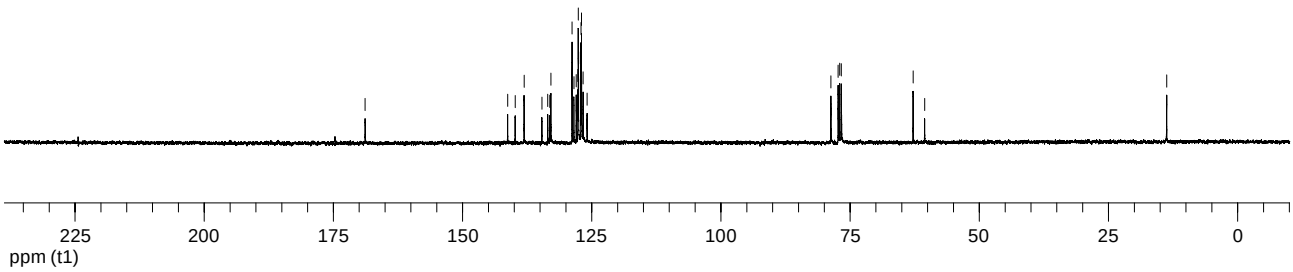
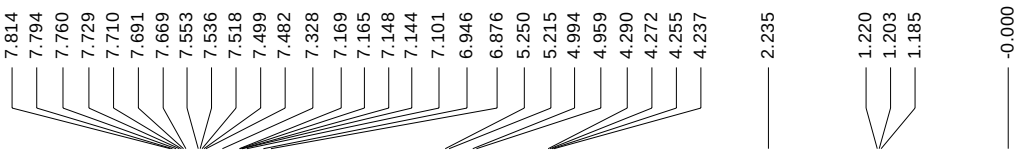
77.000
76.683
62.806
60.565
13.728


NpS
CO2Et
NO2
Ph

3o


225
200
175
150
125
100
75
50
25
0
ppm (t1)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7.760
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7.710
7.691
7.669
7.553
7.536
7.518
7.499
7.482
7.328
7.169
7.165
7.148
7.144
7.101
6.946
6.876
5.250
5.215
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4.290
4.272
4.255
4.237
2.235
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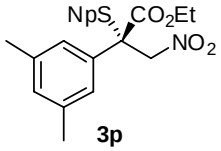
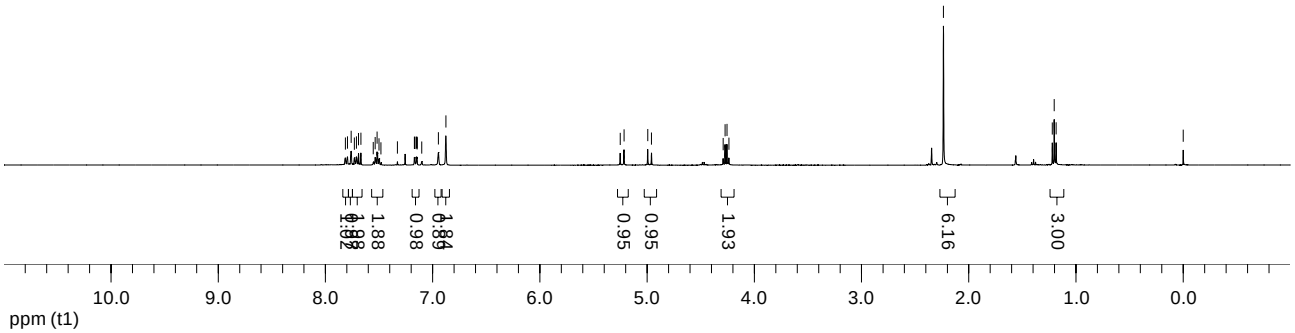
1.203
1.185
-0.000


NpS
CO2Et
NO2

3p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0.95
1.93
6.16
3.00
10.0
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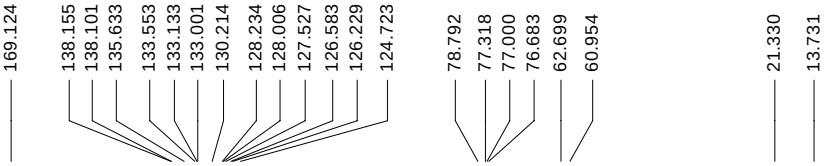
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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133.133
133.001
130.214
128.234
128.006
127.527
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124.723
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77.318
77.000
76.683
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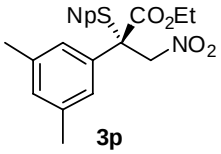
60.954
21.330
13.731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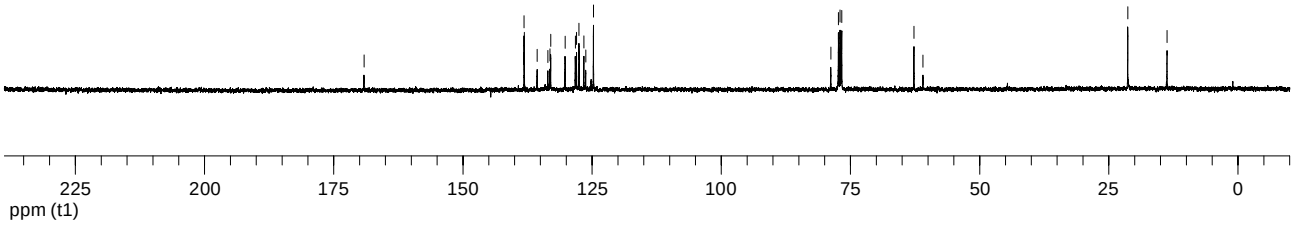
CO2Et
NO2

3p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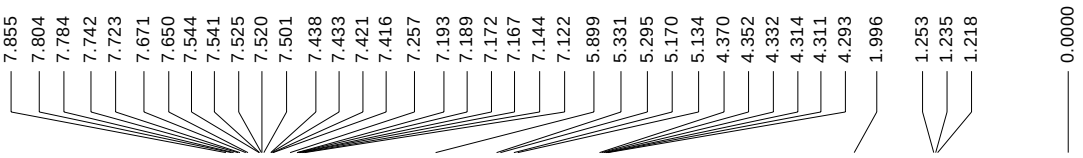
200
175
150
125
100
75
50
25
0
ppm (t1)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7.544
7.541
7.525
7.520
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7.433
7.421
7.416
7.257
7.193
7.189
7.172
7.167
7.144
7.122
5.899
5.331
5.295
5.170
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4.332
4.314
4.311
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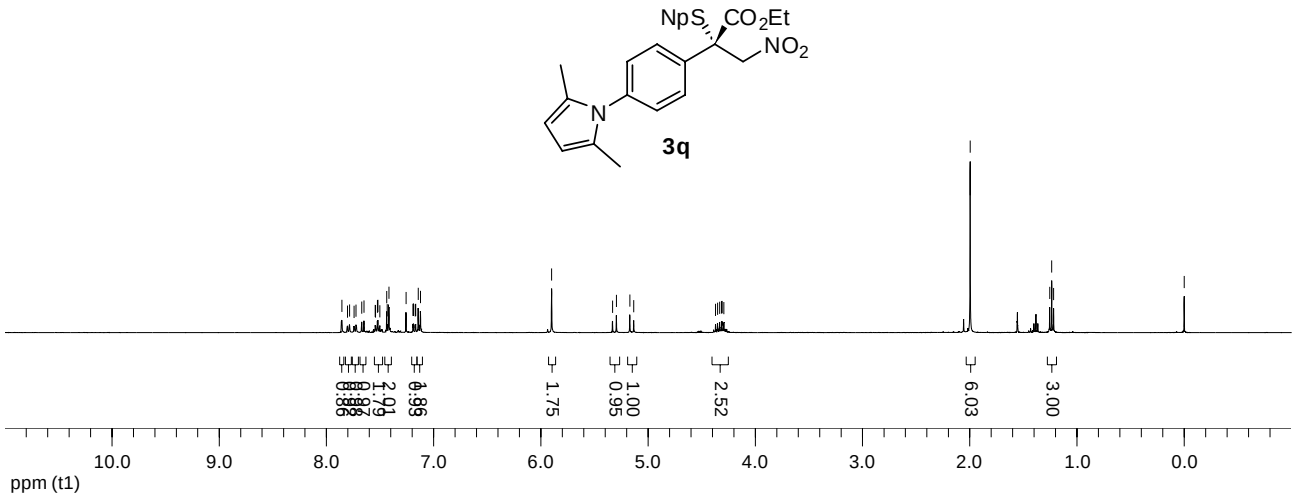
1.253
1.235
1.218
0.0000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CO2Et
NO2
N
3q
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1.75
1.00
0.95
2.52
6.03
3.00
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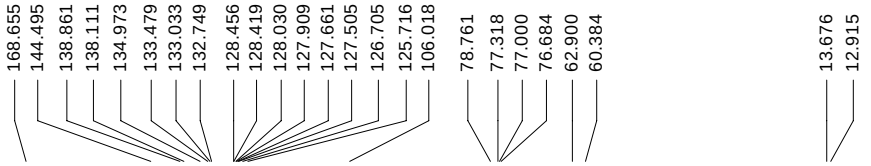
2.0
1.0
0.0
ppm (t1)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132.749
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128.419
128.030
127.909
127.661
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76.684
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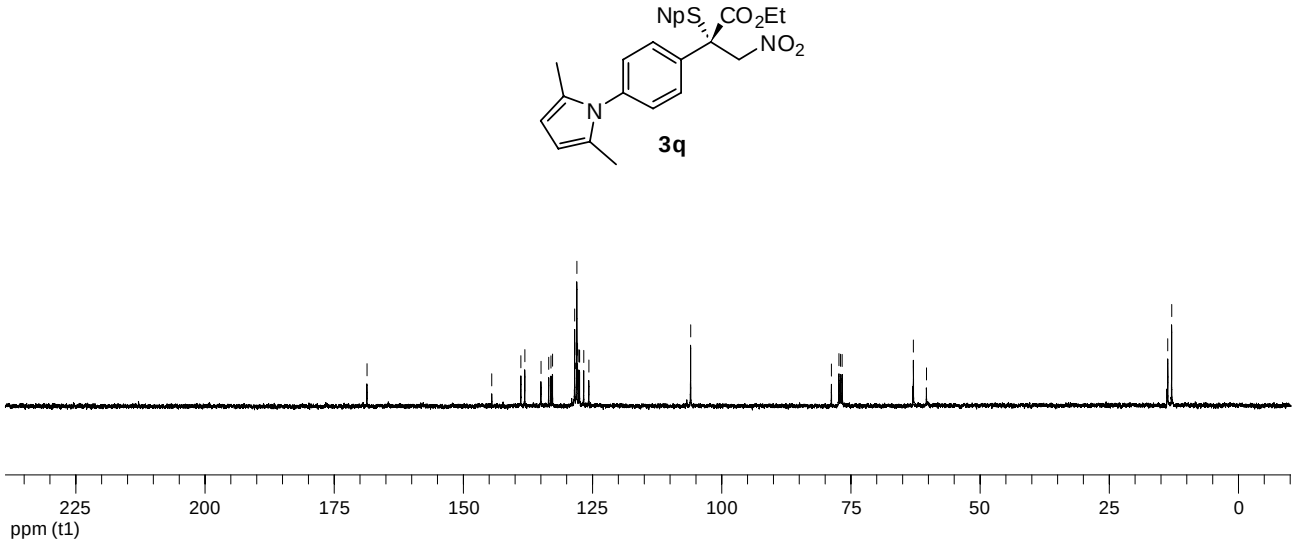
13.676
12.915


NpS
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NO2
N
3q
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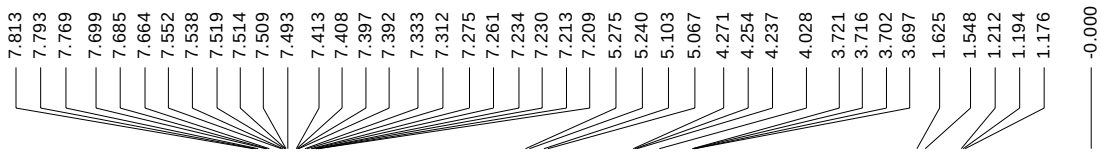
200
175
150
125
100
75
50
25
0
ppm (t1)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7.793
7.769
7.699
7.685
7.664
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7.538
7.519
7.514
7.509
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7.408
7.397
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7.275
7.261
7.234
7.230
7.213
7.209
5.275
5.240
5.103
5.067
4.271
4.254
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4.028
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3.697
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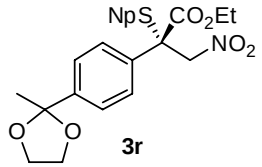
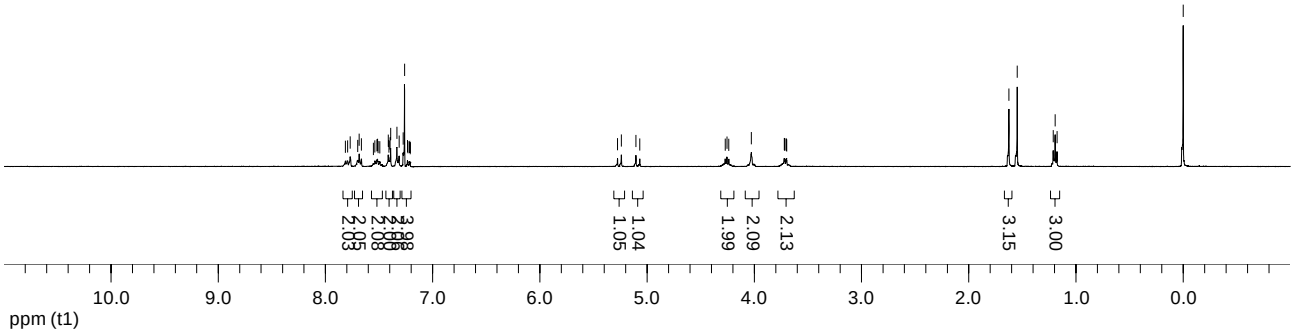
1.548
1.212
1.194
1.176
-0.000


NpS
CO2Et
NO2
O
O

3r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1.04
1.99
2.09
2.13
3.15
3.00
10.0
9.0
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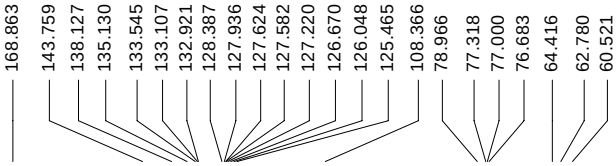
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)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133.107
132.921
128.387
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127.624
127.582
127.220
126.670
126.048
125.465
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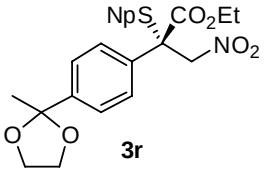
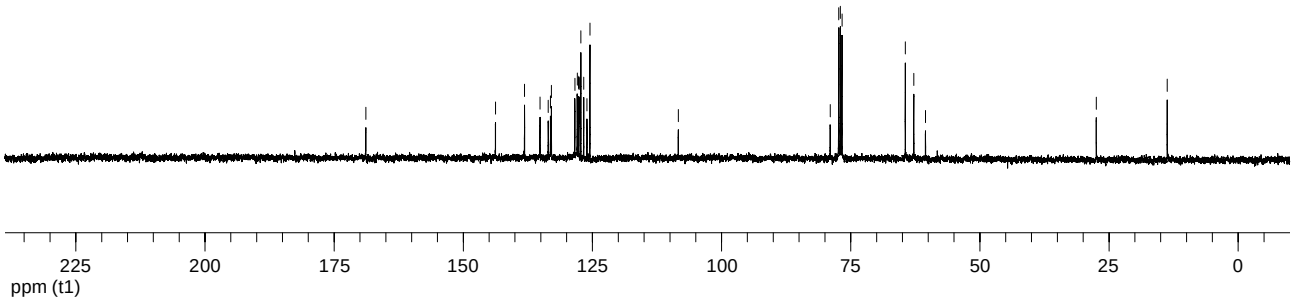
78.966
77.318
77.000
76.683
64.416
62.780
60.521
27.458
13.733


NpS
CO2Et
NO2
O
O

3r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200
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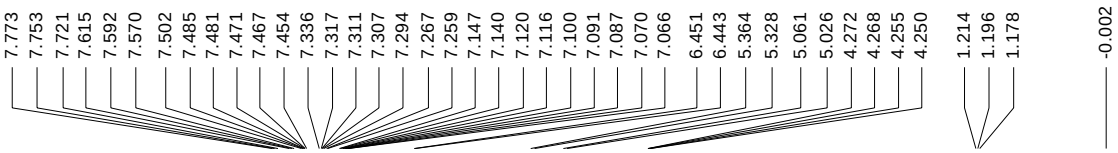
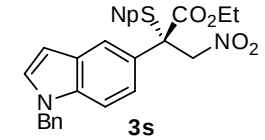
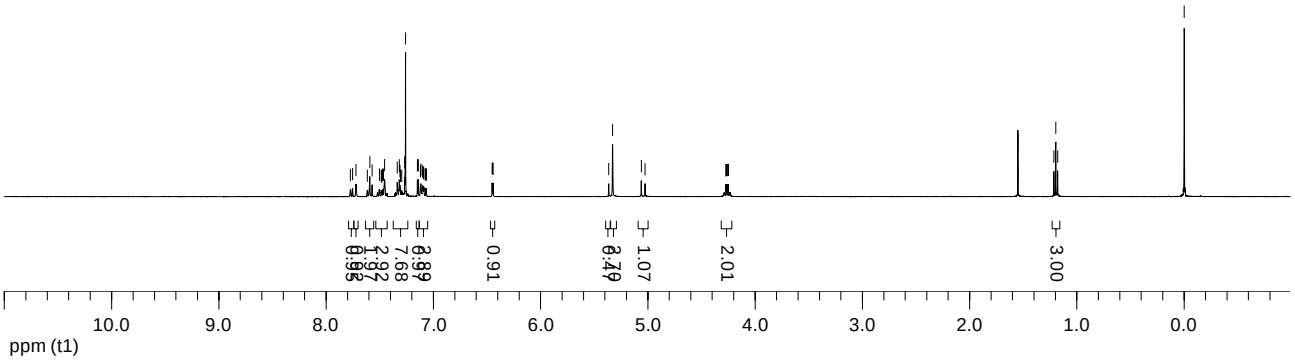
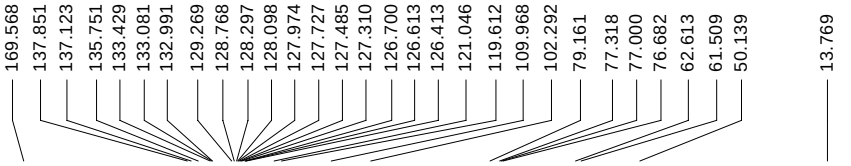
125
100
75
50
25
0
ppm (t1)

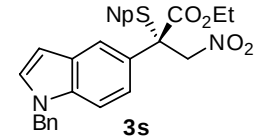

7.773
7.753
7.721
7.615
7.592
7.570
7.502
7.485
7.481
7.471
7.467
7.454
7.336
7.317
7.311
7.307
7.294
7.267
7.259
7.147
7.140
7.120
7.116
7.100
7.091
7.087
7.070
7.066
6.451
6.443
5.364
5.328
5.061
5.026
4.272
4.268
4.255
4.250
1.214
1.196
1.178
-0.002


NpS
CO2Et
NO2
N
Bn

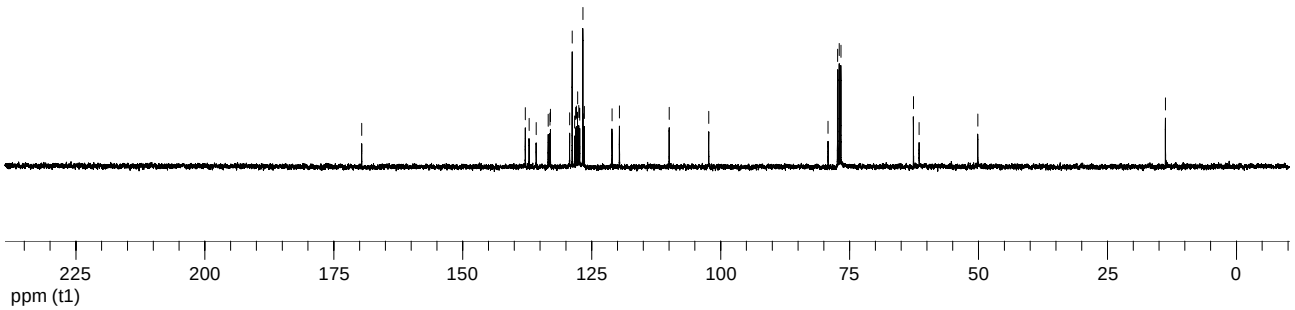
3s

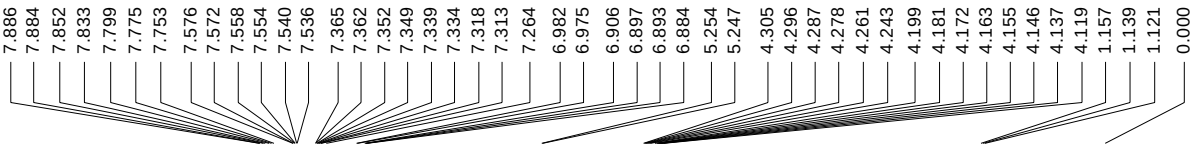

0.91
0.79
1.07
2.01
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

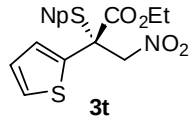

169.568
137.851
137.123
135.751
133.429
133.081
132.991
129.269
128.768
128.297
128.098
127.974
127.727
127.485
127.310
126.700
126.613
126.413
121.046
119.612
109.968
102.292
79.161
77.318
77.000
76.682
62.613
61.509
50.139
13.769


NpS
CO2Et
NO2
N
Bn

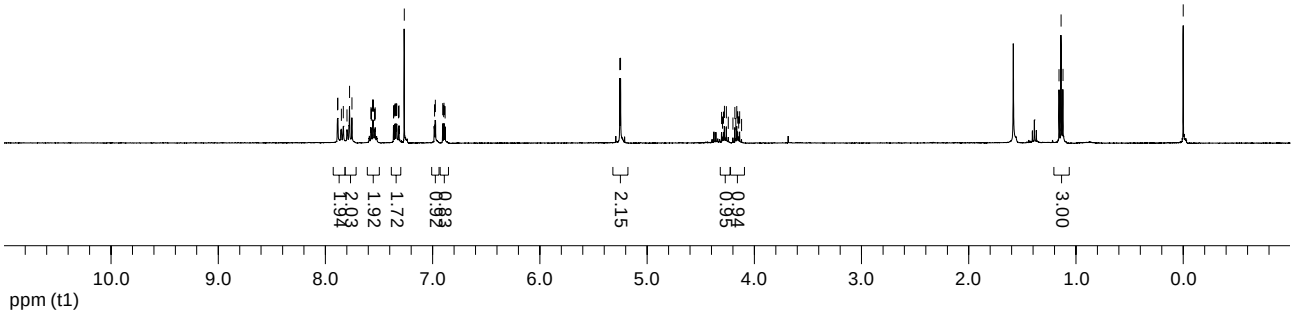
3s

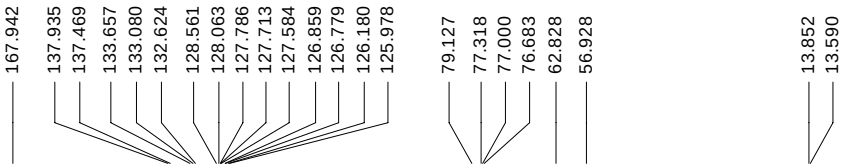

225
200
175
150
125
100
75
50
25
0
ppm (t1)

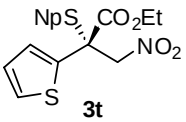

7.886
7.884
7.852
7.833
7.799
7.775
7.753
7.576
7.572
7.558
7.554
7.540
7.536
7.365
7.362
7.352
7.349
7.339
7.334
7.318
7.313
7.264
6.982
6.975
6.906
6.897
6.893
6.884
5.254
5.247
4.305
4.296
4.287
4.278
4.261
4.243
4.199
4.181
4.172
4.163
4.155
4.146
4.137
4.119
1.157
1.139
1.121
0.000


NpS
CO2Et
NO2
S

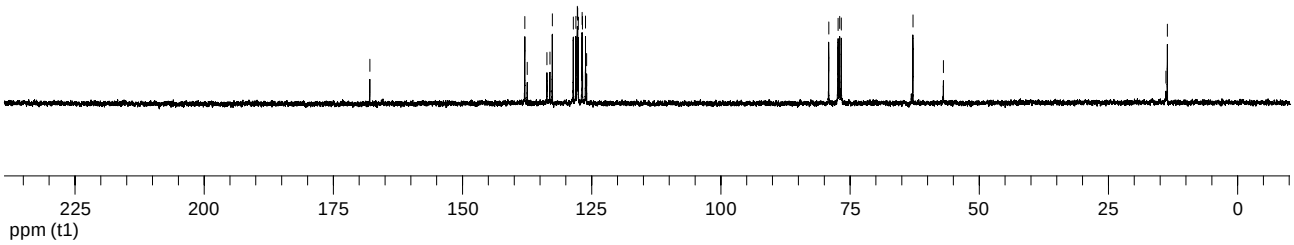
3t

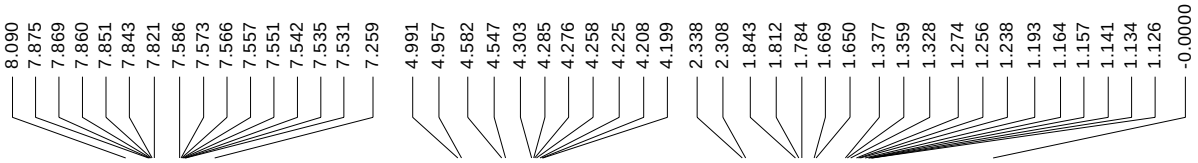

1.03
2.03
1.92
1.72
0.92
0.88
2.15
0.95
0.94
3.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (t1)

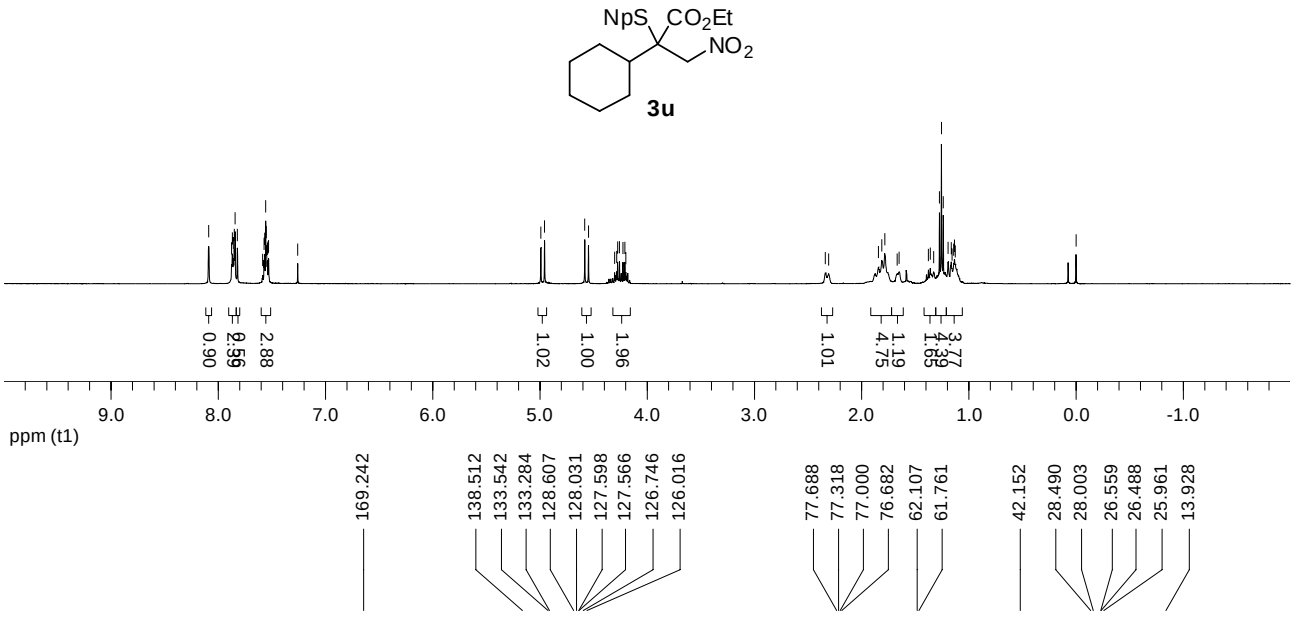

167.942
137.935
137.469
133.657
133.080
132.624
128.561
128.063
127.786
127.713
127.584
126.859
126.779
126.180
125.978
79.127
77.318
77.000
76.683
62.828
56.928
13.852
13.590


NpS
CO2Et
NO2
S

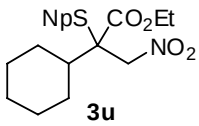
3t

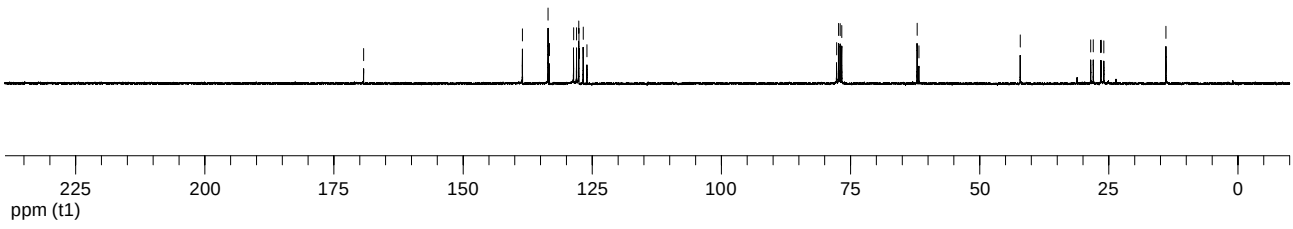

225
200
175
150
125
100
75
50
25
0
ppm (t1)

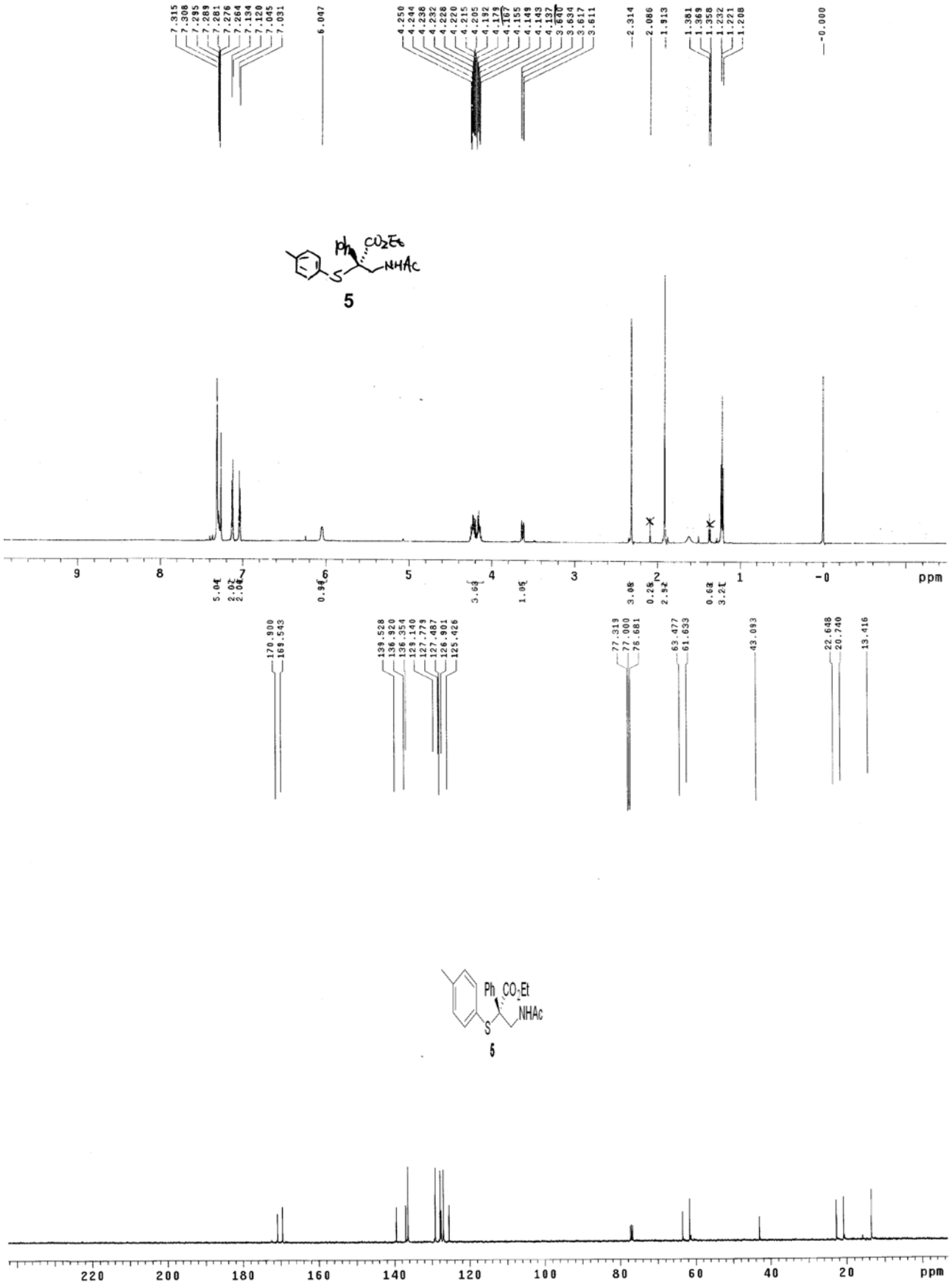

8.090
7.875
7.869
7.860
7.851
7.843
7.821
7.586
7.573
7.566
7.557
7.551
7.542
7.535
7.531
7.259
4.991
4.957
4.582
4.547
4.303
4.285
4.276
4.258
4.225
4.208
4.199
2.338
2.308
1.843
1.812
1.784
1.669
1.650
1.377
1.359
1.328
1.274
1.256
1.238
1.193
1.164
1.157
1.141
1.134
1.126
-0.0000

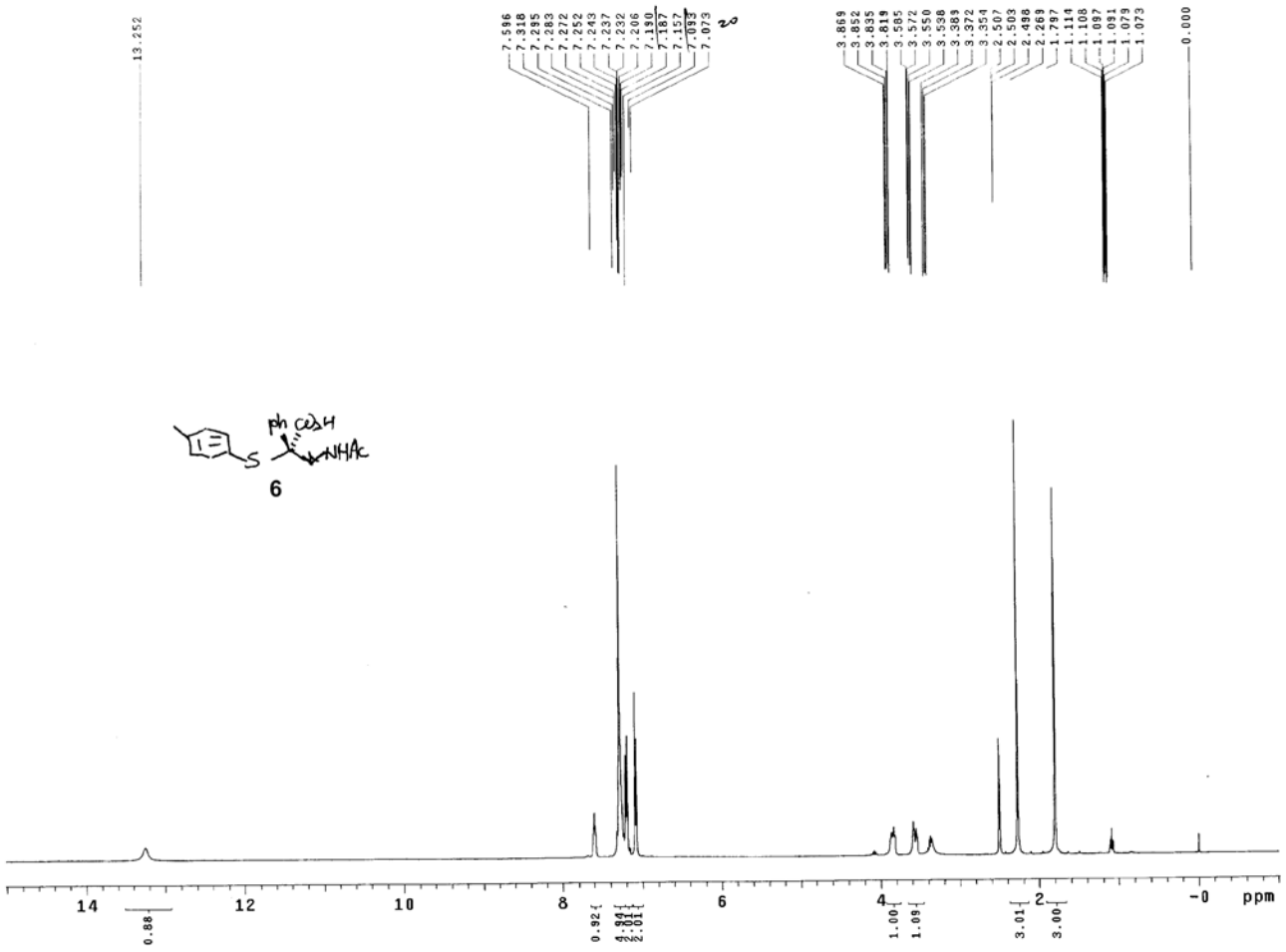

NpS
CO2Et
NO2
3u
0.90
0.96
0.95
2.88
1.02
1.00
1.96
1.01
1.19
4.75
1.85
1.69
3.77
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
ppm (t1)

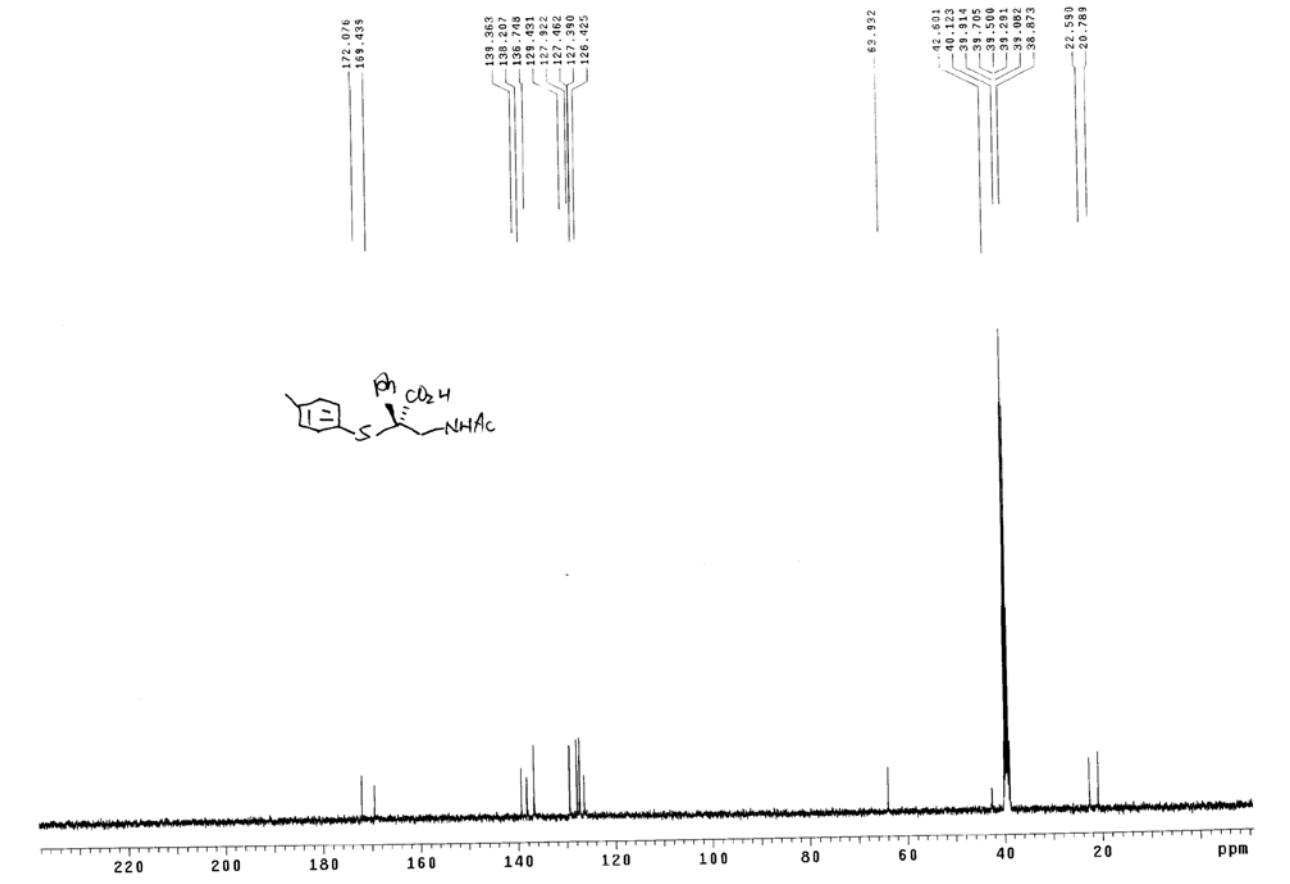
169.242
138.512
133.542
133.284
128.607
128.031
127.598
127.566
126.746
126.016
77.688
77.318
77.000
76.682
62.107
61.761
42.152
28.490
28.003
26.559
26.488
25.961
13.928

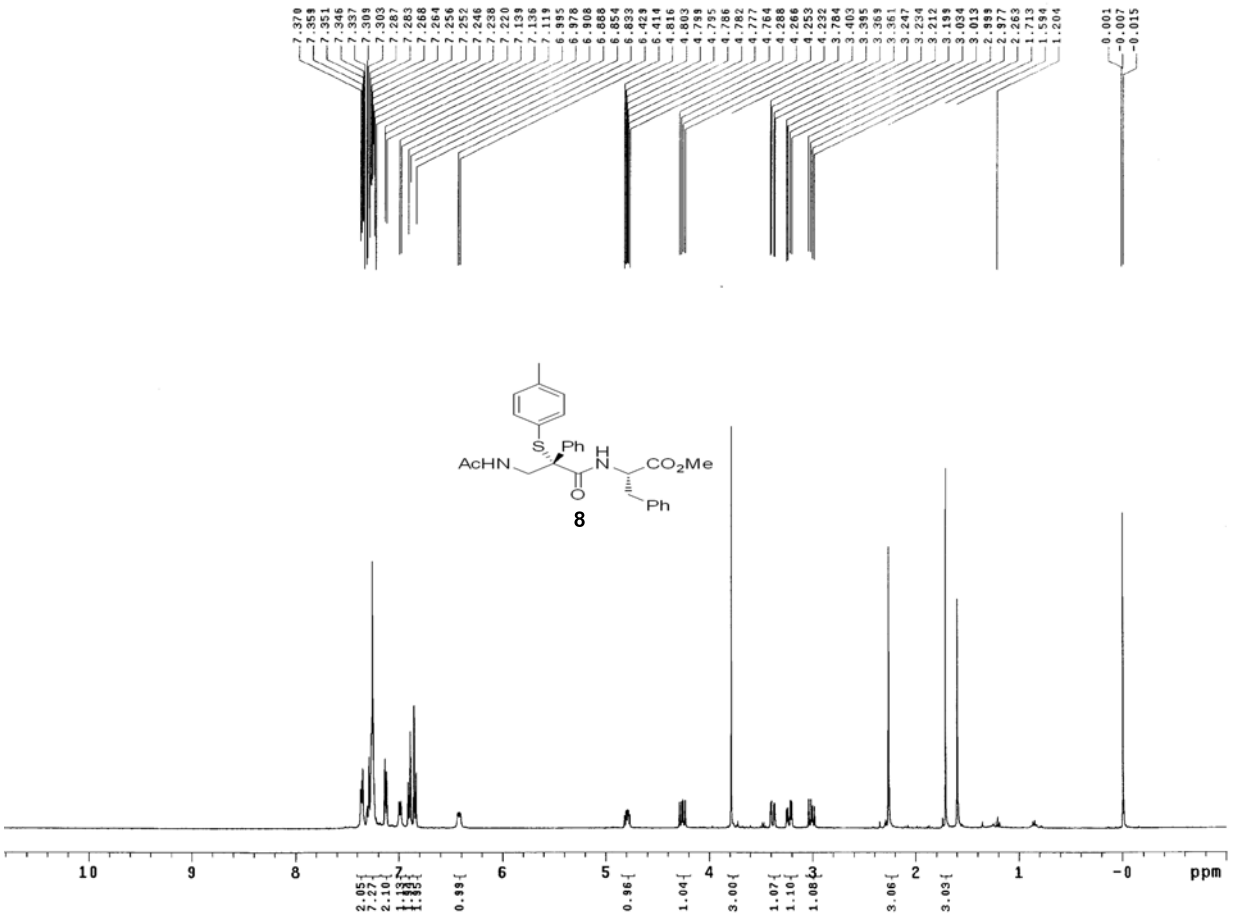

NpS
CO2Et
NO2
3u

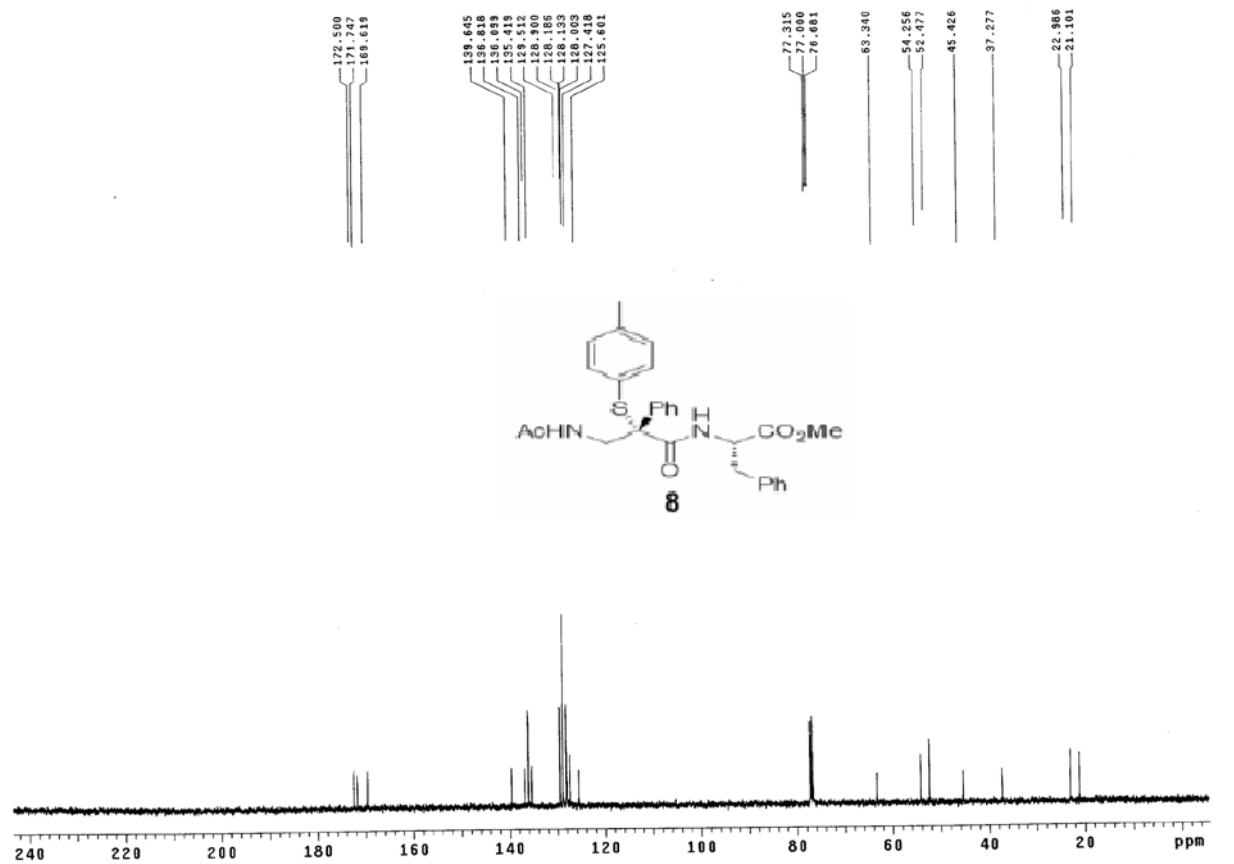

225
200
175
150
125
100
75
50
25
0
ppm (t1)


7.315
7.308
7.295
7.289
7.281
7.276
7.264
7.134
7.120
7.045
7.031
6.047
4.250
4.244
4.238
4.232
4.228
4.220
4.215
4.205
4.192
4.179
4.167
4.155
4.149
4.143
4.137
3.640
3.634
3.617
3.611
2.314
2.086
1.913
1.381
1.369
1.358
1.232
1.221
1.208
0.000
Ph
CO2Et
NHAc
S
5
ppm
170.900
169.543
139.528
136.920
136.354
129.140
127.779
127.487
126.901
125.426
77.319
77.000
76.681
63.477
61.633
43.093
22.648
20.740
13.416
Ph
CO2Et
NHAc
S
5
ppm


13.252
7.586
7.318
7.295
7.283
7.272
7.252
7.243
7.237
7.232
7.206
7.190
7.187
7.157
7.093
7.073
3.869
3.852
3.835
3.819
3.585
3.572
3.550
3.538
3.389
3.372
3.354
2.507
2.503
2.498
2.269
1.797
1.114
1.108
1.097
1.091
1.079
1.073
0.000
Ph
CO2H
NHAc
6
14
12
10
8
6
4
2
-0
ppm
0.88
0.92
4.04
2.01
1.00
1.09
3.01
3.00


172.076
169.439
139.363
138.207
136.748
129.431
127.922
127.462
127.390
126.425
63.932
42.601
40.123
39.914
39.705
39.500
39.291
39.082
38.873
22.590
20.789
Ph
CO2H
NHAc
220
200
180
160
140
120
100
80
60
40
20
ppm


AcHN
S
Ph
H
N
CO2Me
O
Ph
8
ppm


AcHN
S
Ph
H
N
CO2Me
O
Ph
8
ppm