Supporting Information

Base-controlled Dearomative [3 + 2] cycloadditions between 3-nitro-indoles and fumaric acid amide esters

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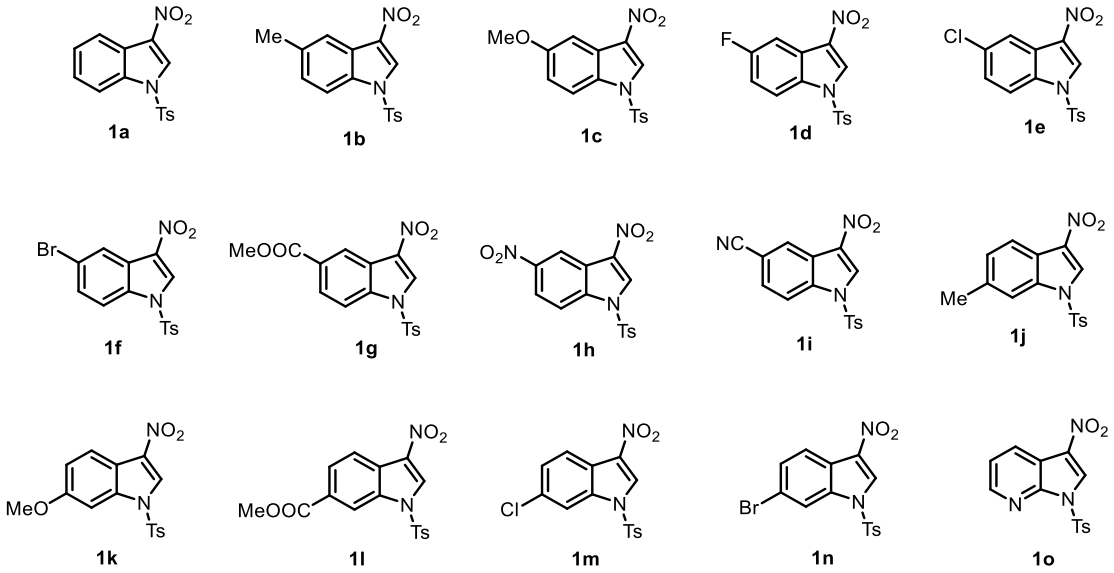
1. General Information

All reagents and all solvents were obtained from commercial suppliers and used without further purification except as indicated below. The silica gel (300-400 mesh) was used for column chromatography and TLC inspections were on silica gel GF 254 plates (0.25 mm layer thickness). NMR spectra were all recorded on a Bruker AM400 (400 MHz) spectrometer. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and chloroform-d (δ 77.16) for ^{13}C NMR. Enantioselectivities were determined by high-performance liquid chromatography (HPLC) with an Aglilent-1260 intelligent uv/vis detector (λ = 214 nm, 220nm or 254 nm) and a Daicel IB. Optical rotations were measured in $CHCl_3$ on a Pekin-Elmer 241MC automatic polarimeter. HRESIMS were recorded on an Agilent 6210 TOF LC/MS equipped with an electrospray ionization (ESI) probe operating in positive or negative ion mode.

2. General procedure

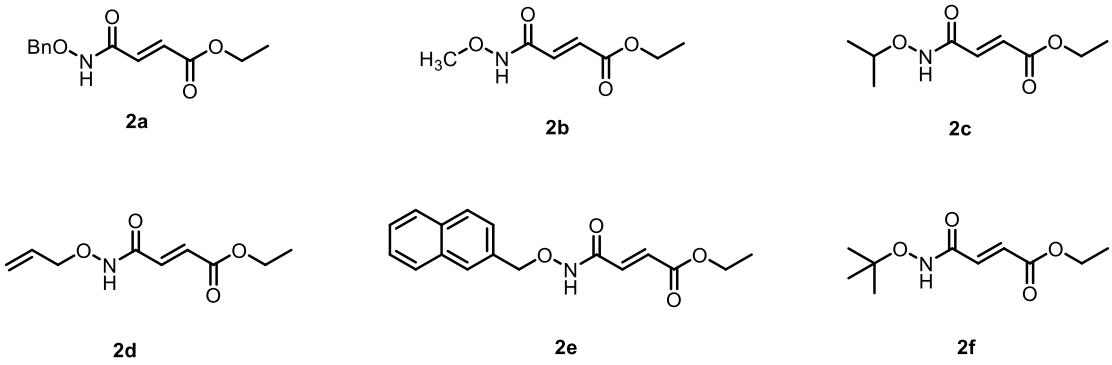
General procedure A: the synthesis of 3-Nitro-indoles 1a–o:

3-Nitro-indoles 1 were prepared according to the following representative methods reported in the literature.[1]

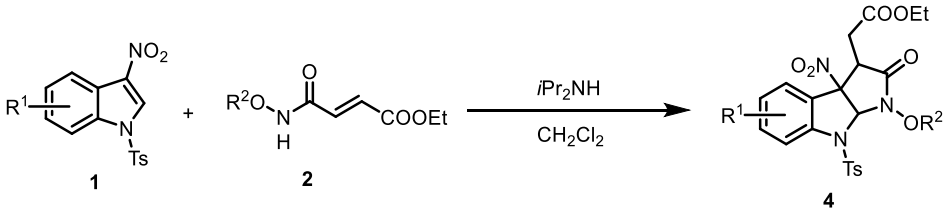


General procedure B: the synthesis of fumaric acid amide esters 2a-e:

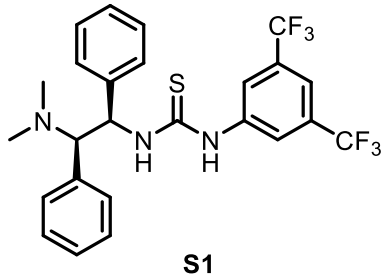
α, *β*-Unsaturated acrylamide **2** were prepared according to the following representative procedure.[2]



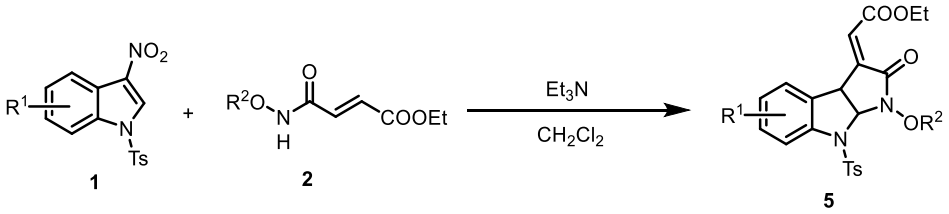
General procedure C: the synthesis of Pyrrolo[2,3-b]indole 4:



A solution of 3-Nitro-indoles **1** (0.24 mmol), fumaric acid amide esters **2** (0.20 mmol) and *i*Pr_2NH (0.01 mmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature (25 ºC) for 48 h. The mixture was concentrated under reduced pressure and the residue was purified via flash chromatograph on silica gel (EtOAc /Petrol Ether = 1/4, v/v as eluent) to afford the desired product **4**. When the *i*-Pr_2NH was replaced by catalyst **S1**, 50% ee **4a** could be obtained.



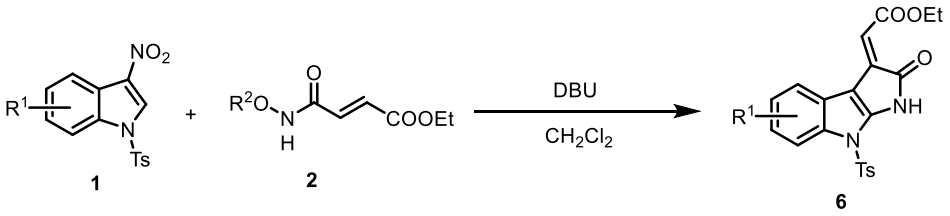
General procedure D: the synthesis of Pyrrolo[2,3-b]indole 5:



A solution of 3-Nitro-indoles **1** (0.24 mmol), fumaric acid amide esters **2** (0.20 mmol) and Et_3N (0.30 mmol) in CH_2Cl_2 (0.5 mL) was stirred at room temperature (25 ºC) for 48 h. The mixture was concentrated under reduced pressure and the residue was purified via flash chromatograph on silica gel (EtOAc/Petrol Ether = 1/4, v/v as eluent) to afford the desired

product **5**.

General procedure E: the synthesis of Pyrrolo[2,3-b]indole 6:



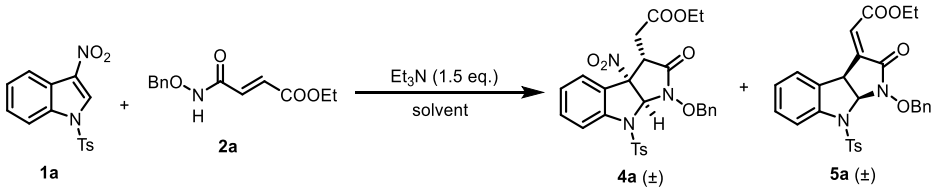
A solution of 3-Nitro-indoles **1** (0.24 mmol) and fumaric acid amide esters **2** (0.20 mmol) was dissolved in CH_2Cl_2 (2.0 mL), DBU (0.8 mmol) in CH_2Cl_2 (2.0 mL) was added dropwise to the mixture at room temperature (25 ^oC) during 20 min, keeping stirring for 3-12 h after dropping finished. The mixture was purified via flash chromatograph on silica gel (pure DCM), the collected solution was concentrated under reduced pressure to afford the desired product **6**.

References:

1. Rivinoja, D. J.; Gee, Y. S.; Gardiner, M. G.; Ryan, J. H.; Hyland, C. J. P. *ACS. Catal.* **2017**, *7*, 1053.

2. Yokosaka, T.; Hamajima, A.; Nemoto, t.; Hamada, Y. *Tetrahedron Lett.* **2012**, *53*, 1245.

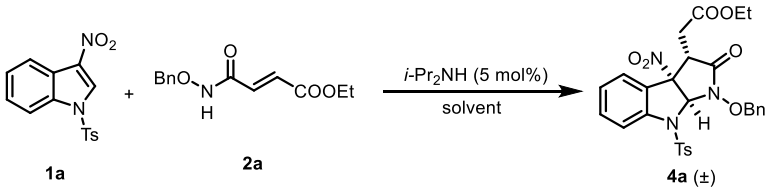
Table S1. Optimization of the reaction condition [a]



Entry	Solvent	Compound 4 [b]	Compound 5 [b] (dr) [c]
1	CH_2Cl_2	trace	77(>20:1)
2	$CHCl_3$	trace	75(>20:1)
3	MeCN	9	67(>20:1)
4	EA	19	60(>20:1)
5	toluene	trace	72(>20:1)
6	acetone	9	68(>20:1)
7	THF	trace	76(>20:1)

[a]Typical reaction conditions: **1a** (0.11 mmol), **2a** (0.10 mmol) in solvent (0.5 mL), at 25 °C for 48 h. [b]Determined by ^{1}H NMR. [c]Determined by ^{1}H NMR analysis of the crude reaction mixture before purification.

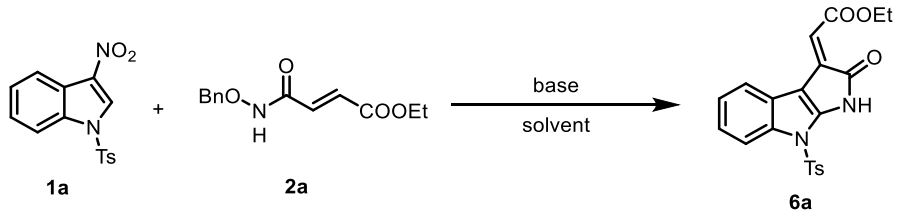
Table S2. Optimization of the reaction condition [a]



Entry	Solvent	dr[b]	Yield[c] (%)
1	CH_2Cl_2	18:1	90
2	$CHCl_3$	17:1	88
3	THF	5:1	60
4	CH_3CN	5:1	70
5	toluene	15:1	77
6	EA	16:1	60
7	DCE	8:1	82
8	actone	5:1	50

[a]Typical reaction conditions: **1a** (0.11 mmol), **2a** (0.10 mmol), in solvent (0.5 mL), at 25 °C for 48 h. [b]Determined by ^{1}H-NMR analysis of the crude reaction mixture before purification. [c]Determined by ^{1}H NMR.

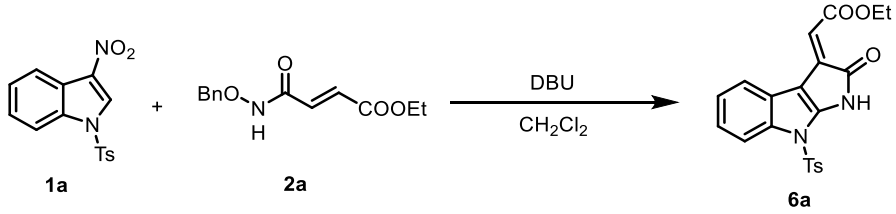
Table S3. Optimization of the reaction solvent [a]



Entry	Base	Equiv.	Solvent	Yield[b] (%)
1	DBU	1.0	CH_2Cl_2	0
2	DBU	1.2	CH_2Cl_2	<5
3	DBU	1.5	CH_2Cl_2	37
4	DBU	2.0	CH_2Cl_2	53
5	DBU	2.4	CH_2Cl_2	52
6	DBN	2.0	CH_2Cl_2	40
7	DBU	2.0	$CHCl_3$	50
8	DBU	2.0	THF	48
9	DBU	2.0	CH_3CN	34
10	DBU	2.0	toluene	44
11	DBU	2.0	ethyl acetate	44
12	DBU	2.0	DCE	<20
12	DBU	2.0	actone	35
13	DBU	2.0	DMF	50
14	K_2CO_3	2.0	DMF	<20
15	CH_3ONa	2.0	DMF	52
16	*t*-BuOK	2.0	DMF	44
17[c]	DBU	2.0	CH_2Cl_2	50

[a]Typical reaction conditions: **1a** (0.11 mmol), **2a** (0.10 mmol) in solvent (0.5 mL), at 25 °C for 1 h. [b]Determined by ^{1}H NMR. [c]The reaction was at 0 °C for 1 h.

Table S4. Optimization of the reaction condition [a]

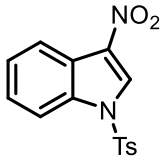


Entry	Equiv.	5a yield (%)	6a yield (%)	Dropping time (min)
1	2.0	0	54	0
2	2.0	20	58	10

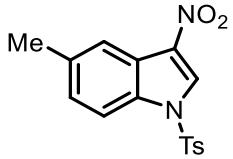
3	2.5	<10	64	10
4	2.0	34	54	60
5	2.5	24	60	60
6	3.0	16	64	60
7	3.0	0	68	20
8	3.0	0	64	10
9	4.0	0	72	60
10	4.0	0	70	30
11	4.0	0	70	20
12	4.0	0	62	10

[a]Typical reaction conditions: **1a** (0.11 mmol), **2a** (0.10 mmol) in CH_2Cl_2 (1.0 mL), DBU in CH_2Cl_2 (1.0 mL) was added dropwise to the mixture at 25 °C during 20 min, keeping stirring for 3 h after dripping finished. [b]Determined by ^{1}H-NMR.

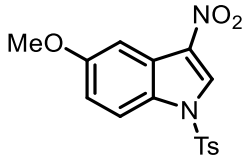
3. Analytical data of the products



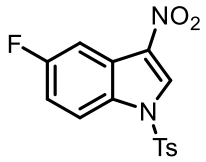
1a, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.38 – 8.14 (m, 1H), 8.06 – 7.97 (m, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.50 – 7.42 (m, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 2.40 (s, 3H).



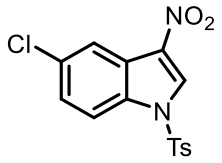
1b, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (s, 1H), 8.03 (s, 1H), 7.87 (d, *J* = 6.8 Hz, 3H), 7.41 – 7.28 (m, 3H), 2.48 (s, 3H), 2.40 (s, 3H).



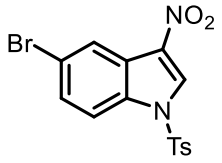
1c, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.94 – 7.82 (m, 3H), 7.68 (d, *J* = 2.4 Hz, 1H), 7.40 – 7.25 (m, 2H), 7.08 (dd, *J* = 9.2, 2.4 Hz, 1H), 3.90 (s, 3H), 2.42 (s, 3H).



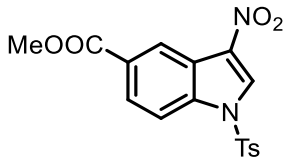
1d, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.04 – 7.79 (m, 4H), 7.35 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 9.0 Hz, 1H), 2.41 (s, 3H).



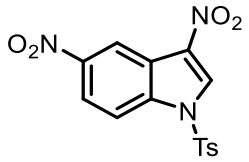
1e, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.23 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 7.0 Hz, 2H), 2.41 (s, 3H).



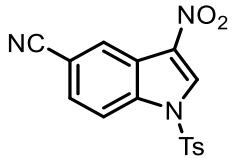
1f, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.40 (s, 1H), 7.87 (t, *J* = 7.8 Hz, 3H), 7.57 (d, *J* = 8.9 Hz, 1H), 7.35 (d, *J* = 7.9 Hz, 2H), 2.41 (s, 3H).



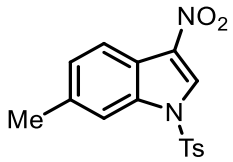
1g, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 (s, 1H), 8.62 (s, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.06 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 3.97 (s, 3H), 2.41 (s, 3H).



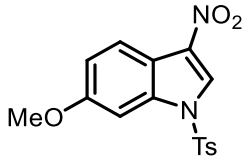
1h, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.14 (s, 1H), 8.70 (s, 1H), 8.36 (d, *J* = 9.2 Hz, 1H), 8.16 (d, *J* = 9.2 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).



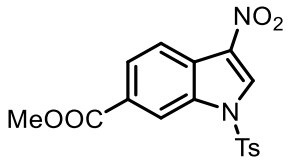
1i, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.58 (m, 2H), 8.13 (d, *J* = 8.8 Hz, 1H), 7.90 (t, *J* = 7.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).



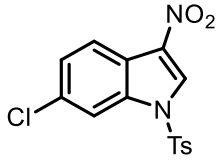
1j, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.80 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.29 (s, 1H), 2.52 (s, 3H), 2.41 (s, 3H).



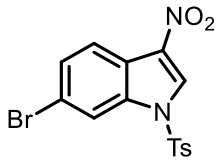
1k, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (s, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.48 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 8.8 Hz, 1H), 3.91 (s, 3H), 2.41 (s, 3H).



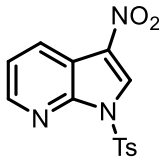
1l, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.16 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.68 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.51 (dd, *J* = 8.4, 7.6 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.89 (d, *J* = 4.4 Hz, 3H), 2.41 (s, 3H).



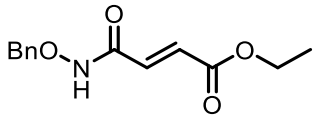
1m, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.03 (s, 1H), 7.89 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).



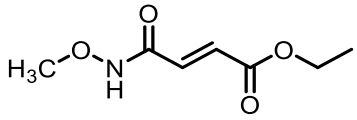
1n, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.20 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).



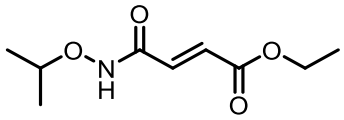
1o, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.54 (dd, *J* = 13.6, 6.4 Hz, 2H), 8.19 (d, *J* = 7.6 Hz, 2H), 7.43 (dd, *J* = 7.6, 5.0 Hz, 1H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.42 (s, 3H).



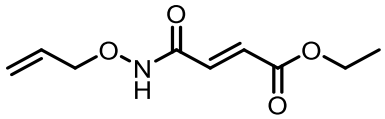
2a, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 7.44 –7.32 (m, 5H), 6.86 (s, 2H), 4.94 (s, 2H), 4.28 – 4.13 (m, 2H), 1.29 (t, *J* = 6.8 Hz, 3H).



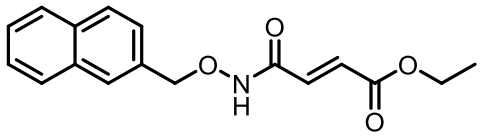
2b, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (s, 1H), 7.24 – 6.47 (m, 2H), 4.35 –4.25 (m, 2H), 4.05 – 3.71 (m, 3H), 1.37 – 1.29 (m, 3H).



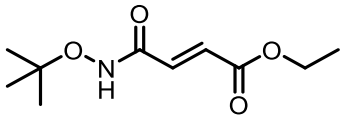
2c, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (s, 1H), 6.94 (dd, *J* = 15.6, 3.8 Hz, 2H), 4.33 – 4.18 (m, 3H), 1.37 – 1.24 (m, 9H).



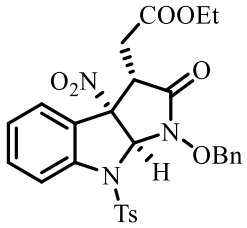
2d, ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 6.91 (d, *J* = 12.4 Hz, 2H), 6.03 – 5.93 (m, 1H), 5.49 – 5.15 (m, 2H), 4.53 (dd, *J* = 62.0, 5.6 Hz, 2H), 4.27 – 4.23 (m, 2H), 1.36 – 1.24 (m, 3H).



2e, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.93 – 7.82 (m, 4H), 7.62 – 7.46 (m, 2H), 7.02 – 6.34 (m, 2H), 5.15 (s, 22H), 4.30 – 4.18 (m, 2H), 1.38 – 1.22 (m, 3H).

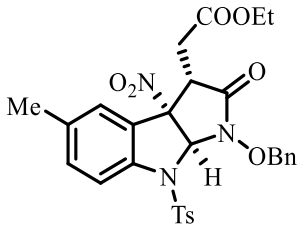


2f, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (s, 1H), 7.35 – 6.32 (m, 2H), 4.32 – 4.18 (m, 2H), 1.36 – 1.28 (m, 12H).

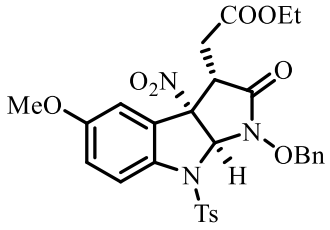


4a, white solid, m.p. = 158.8-160.9 ºC. 101mg, 89% yield, 18:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 3H), 7.62 (t, *J* = 6.4 Hz, 3H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.76 (s, 1H), 5.23 (dd, *J* = 25.4, 9.0 Hz, 2H), 4.13 (q, *J* = 7.2 Hz, 2H), 3.45 – 3.39 (m, 1H), 3.12 (dd, *J* = 18.2, 4.0 Hz, 1H), 2.94 (dd, *J* = 18.2, 6.4 Hz, 1H), 2.35 (s, 3H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.39, 165.12, 145.18, 140.62, 134.20, 133.72, 133.05, 130.30, 129.81, 120.10, 129.04, 128.41, 127.57, 126.38, 126.03, 117.38, 91.21, 80.35, 77.93, 61.69, 44.92, 33.24, 21.57, 13.98. HRMS (ESI) calcd for $C_{28}H_{27}N_3O_8S$ $[M+H]^+$: 566.1592. Found:

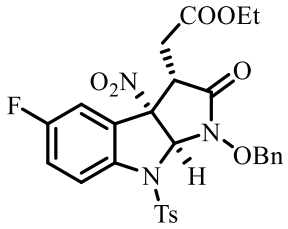
566.1597.



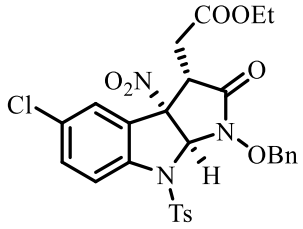
4b, white solid, m.p. = 153.0-155.1 °C. 100mg, 86% yield, 17:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J*=8.4, 2H), 7.64 – 7.60 (m, 2H), 7.59 (d, *J*=8.4, 1H), 7.43 – 7.35 (m, 4H), 7.30 (dd, *J*=8.4, 1.2, 1H), 7.18 (d, *J*=8.0, 2H), 6.73 (s, 1H), 5.22 (dd, *J*=23.2, 9.2, 2H), 4.13 (q, *J*=7.2, 2H), 3.39 (dd, *J*=6.4, 4.0, 1H), 3.11 (dd, *J*=18.0, 4.0, 1H), 2.94 (dd, *J*=18.0, 6.4, 1H), 2.36 (s, 3H), 2.35 (s, 3H), 1.25 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.53, 165.30, 145.22, 138.41, 136.48, 134.35, 134.05, 133.91, 130.46, 129.94, 129.33, 129.19, 128.58, 127.74, 126.66, 117.43, 91.41, 80.77, 78.13, 61.83, 45.07, 33.42, 21.74, 21.21, 14.15. HRMS (ESI) calcd for C29H29N3O8S $[M+H]^+$: 580.1748. Found: 580.1758.



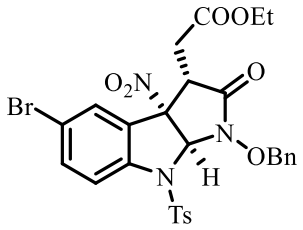
4c, white solid, m.p. = 129.1-131.8 °C. 97mg, 81% yield, 16:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 – 7.53 (m, 5H), 7.43 – 7.35 (m, 3H), 7.17 (d, *J*=8.4, 2H), 7.13 (d, *J*=2.4, 1H), 7.06 (dd, *J*=9.2, 2.8, 1H), 6.65 (s, 1H), 5.23 (q, *J*=8.8, 2H), 4.12 (q, *J*=7.2, 2H), 3.82 (s, 3H), 3.40 (dd, *J*=6.8, 4.0, 1H), 3.08 (dd, *J*=18.0, 4.0, 1H), 2.87 (dd, *J*=18.0, 6.8, 1H), 2.35 (s, 3H), 1.24 (t, *J*=7.2, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.47, 165.23, 158.36, 145.26, 134.02, 133.93, 133.89, 130.47, 129.97, 129.22, 128.58, 127.69, 119.70, 119.07, 110.92, 91.55, 81.14, 78.25, 61.82, 56.02, 45.11, 33.40, 21.74, 14.15. HRMS (ESI) calcd for C29H29N3O9S $[M+H]^+$: 596.1697. Found: 596.1698.



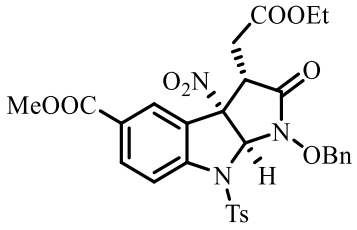
4d, white solid, m.p. = 154.3-157.1 °C. 106mg, 91% yield, 18:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (dd, *J*=8.8, 4.4, 1H), 7.63 – 7.57 (m, 4H), 7.43 – 7.34 (m, 4H), 7.21 (m, 3H), 6.65 (s, 1H), 5.22 (q, *J*=9.2, 2H), 4.12 (q, *J*=7.2, 2H), 3.37 (dd, *J*=7.2, 4.0, 1H), 3.08 (dd, *J*=18.4, 4.0, 1H), 2.87 (dd, *J*=18.4, 7.2, 1H), 2.36 (s, 3H), 1.24 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.32, 164.90, 160.47(*J* = 245.9), 145.47, 136.75, 133.68, 133.61, 130.58(*J* = 8.6), 130.34, 129.95, 129.14, 128.46, 127.47, 120.38(*J* = 23.5), 119.12(*J* = 8.3), 113.88(*J* = 25.3), 90.98, 81.02, 78.05, 61.79, 44.89, 33.18, 21.59, 13.98. ^{19}F NMR (376 MHz, CDCl3) δ -113.9 (m). HRMS (ESI) calcd for C28H26FN3O8S $[M+H]^+$: 584.1497. Found: 584.1499.



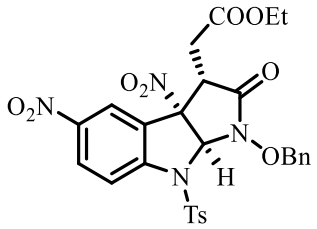
4e, pale yellow solid, m.p. = 98.9-101.3 °C. 101mg, 84% yield, 14:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (m, 6H), 7.46 (dd, *J*=8.8, 2.4, 1H), 7.42 – 7.35 (m, 3H), 7.20 (d, *J*=8.0, 2H), 6.70 (s, 1H), 5.21 (dd, *J*=24.4, 9.2, 2H), 4.12 (q, *J*=7.2, 2H), 3.37 (dd, *J*=6.4, 4.0, 1H), 3.10 (dd, *J*=18.4, 4.0, 1H), 2.93 (dd, *J*=18.4, 6.4, 1H), 2.36 (s, 3H), 1.24 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.49, 165.04, 145.68, 139.46, 133.99, 133.77, 133.43, 131.66, 130.71, 130.49, 130.15, 129.29, 128.62, 127.67, 126.80, 118.73, 91.00, 80.87, 78.12, 61.96, 44.92, 33.34, 21.77, 14.14. HRMS (ESI) calcd for C28H26ClN3O8S $[M+H]^+$: 600.1202. Found: 600.1201.



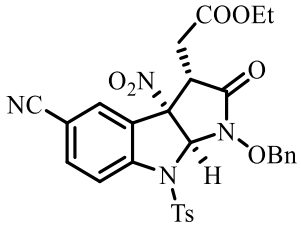
4f, yellow solid, m.p. = 128.8-132.6 °C. 103mg, 80% yield, 12:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.74 (d, *J*=1.6, 1H), 7.67 – 7.63 (m, 2H), 7.62 – 7.53 (m, 4H), 7.42 – 7.34 (m, 3H), 7.20 (d, *J*=8.0, 2H), 6.69 (s, 1H), 5.20 (dd, *J*=25.6, 8.8, 2H), 4.12 (q, *J*=7.2, 2H), 3.36 (dd, *J*=6.4, 4.0, 1H), 3.10 (dd, *J*=18.4, 4.0, 1H), 2.93 (dd, *J*=18.4, 6.4, 1H), 2.36 (s, 3H), 1.24 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.49, 165.03, 145.68, 139.96, 136.29, 134.01, 133.76, 131.00, 130.48, 130.15, 129.63, 129.28, 128.61, 127.68, 119.02, 118.82, 90.90, 80.75, 78.09, 61.96, 44.89, 33.33, 21.77, 14.14. HRMS (ESI) calcd for C28H26BrN3O8S $[M+H]^+$: 644.0697. Found: 644.0692.



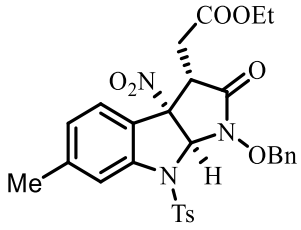
4g, white solid, m.p. = 167.3-169.5 °C. 113mg, 91% yield, 18:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (d, *J*=1.2, 1H), 8.17 (dd, *J*=8.4, 1.6, 1H), 7.75 (d, *J*=8.4, 2H), 7.69 (d, *J*=8.4, 1H), 7.60 (dd, *J*=6.4, 2.8, 2H), 7.41 – 7.33 (m, 3H), 7.21 (d, *J*=8.4, 2H), 6.88 (s, 1H), 5.21 (dd, *J*=37.2, 8.8, 2H), 4.14 (q, *J*=7.2, 2H), 3.91 (s, 3H), 3.39 (t, *J*=4.8, 1H), 3.19 (dd, *J*=18.4, 4.4, 1H), 3.07 (dd, *J*=18.4, 5.6, 1H), 2.35 (s, 3H), 1.26 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.57, 165.41, 165.11, 145.72, 144.43, 134.96, 134.29, 133.78, 130.46, 130.11, 129.57, 129.24, 128.59, 127.95, 127.83, 127.80, 116.65, 90.62, 80.70, 77.84, 61.96, 52.64, 44.78, 33.32, 21.76, 14.13. HRMS (ESI) calcd for C30H29N3O10S $[M+H]^+$: 624.1646. Found: 624.1641.



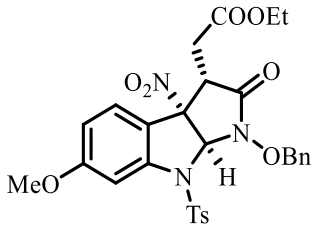
4h, yellow solid, m.p. = 180.1-183.7 ºC. 90mg, 74% yield, 16:1 dr,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J*=2.4, 1H), 8.38 (dd, *J*=8.8, 2.4, 1H), 7.78 – 7.69 (m, 3H), 7.60 (dt, *J*=9.6, 2.8, 2H), 7.43 – 7.36 (m, 3H), 7.24 (d, *J*=8.0, 2H), 6.88 (s, 1H), 5.22 (dd, *J*=37.6, 8.8, 2H), 4.16 (q, *J*=7.2, 2H), 3.42 (dd, *J*=6.0, 4.0, 1H), 3.21 (dd, *J*=18.4, 4.0, 1H), 3.08 (dd, *J*=18.4, 6.0, 1H), 2.38 (s, 3H), 1.27 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.59, 164.87, 146.25, 145.91, 145.27, 133.98, 133.61, 130.50, 130.36, 130.13, 129.37, 129.13, 128.66, 127.76, 122.75, 116.91, 90.30, 80.99, 77.87, 62.15, 44.69, 33.28, 21.81, 14.14. HRMS (ESI) calcd for $C_{28}H_{26}N_4O_{10}S$ $[M+H]^+$: 611.1442. Found: 611.1446.



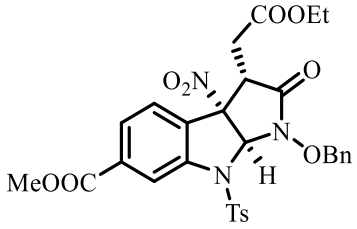
4i, white solid, m.p. = 161.6-162.4 ºC. 89mg, 75% yield, 13:1 dr,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.50 (d, *J*=2.0, 1H), 8.38 (dd, *J*=9.2, 2.4, 1H), 7.85 – 7.68 (m, 3H), 7.66 – 7.55 (m, 2H), 7.48 – 7.34 (m, 3H), 7.24 (d, *J*=8.0, 2H), 6.88 (s, 1H), 5.22 (dd, *J*=37.6, 9.2, 2H), 4.16 (q, *J*=7.2, 2H), 3.42 (dd, *J*=6.0, 4.0, 1H), 3.21 (dd, *J*=18.4, 4.0, 1H), 3.08 (dd, *J*=18.4, 6.0, 1H), 2.38 (s, 3H), 1.26 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.59, 164.87, 146.25, 145.90, 145.26, 133.98, 133.61, 130.50, 130.35, 130.12, 129.37, 129.13, 128.65, 127.75, 122.75, 116.90, 90.29, 80.98, 77.86, 62.14, 44.68, 33.28, 21.80, 14.14. HRMS (ESI) calcd for $C_{29}H_{26}N_4O_8S$ $[M+H]^+$: 591.1544. Found: 591.1565.



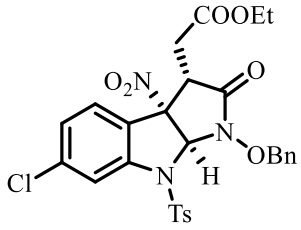
4j, white solid, m.p. = 134.1-137.6 ºC. 95mg, 82% yield, 16:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (d, *J*=8.4, 2H), 7.61 (m, 2H), 7.49 (d, *J*=8.4, 2H), 7.39 (m, 3H), 7.18 (d, *J*=8.0, 2H), 7.03 (d, *J*=8.0, 1H), 6.73 (s, 1H), 5.21 (dd, *J*=21.6, 8.8, 2H), 4.12 (q, *J*=7.2, 2H), 3.38 (dd, *J*=6.4, 4.0, 1H), 3.09 (dd, *J*=18.0, 4.0, 1H), 2.91 (dd, *J*=18.0, 6.4, 1H), 2.42 (s, 3H), 2.34 (s, 3H), 1.23 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.51, 165.35, 145.25, 144.23, 140.88, 134.50, 133.95, 130.43, 129.95, 129.14, 128.55, 127.67, 127.17, 126.55, 126.12, 117.90, 91.27, 80.81, 78.10, 61.78, 45.12, 33.42, 22.10, 21.71, 14.13. HRMS (ESI) calcd for $C_{29}H_{29}N_3O_8S$ $[M+H]^+$: 580.1748. Found: 580.1745.



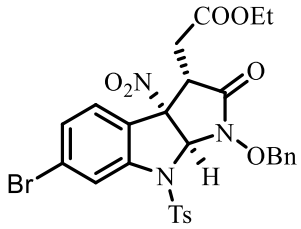
4k, white solid, m.p. = 103.6-106.3 ºC. 95mg, 80% yield, 16:1 dr,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69 (d, *J*=8.4, 2H), 7.65 – 7.59 (m, 2H), 7.50 (d, *J*=8.8, 1H), 7.43 – 7.32 (m, 3H), 7.20 (dd, *J*=5.2, 2.8, 3H), 6.81 – 6.67 (m, 2H), 5.22 (dd, *J*=23.6, 9.2, 2H), 4.12 (q, *J*=7.2, 2H), 3.86 (s, 3H), 3.37 (dd, *J*=6.4, 4.0, 1H), 3.07 (dd, *J*=18.0, 4.0, 1H), 2.89 (dd, *J*=18.0, 6.4, 1H), 2.36 (s, 3H), 1.24 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.86, 165.76, 164.13, 145.70, 142.70, 134.75, 134.28, 130.78, 130.34, 129.50, 128.90, 128.06, 127.61, 121.46, 113.20, 102.91, 91.49, 81.48, 78.45, 62.12, 56.37, 45.51, 33.78, 22.07, 14.48. HRMS (ESI) calcd for $C_{29}H_{29}N_3O_9S$ $[M+H]^+$: 596.1697. Found: 596.1698.



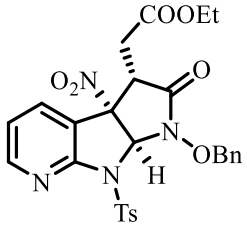
4l, white solid, m.p. = 157.2-158.6 ºC. 112mg, 90% yield, 17:1 dr,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.29 (d, *J*=1.2, 1H), 7.91 (dd, *J*=8.0, 1.2, 1H), 7.70 (m, 3H), 7.64 – 7.56 (m, 2H), 7.43 – 7.31 (m, 3H), 7.19 (d, *J*=8.0, 2H), 6.76 (s, 1H), 5.28 – 5.15 (m, 2H), 4.13 (q, *J*=7.2, 2H), 3.96 (d, *J*=11.2, 3H), 3.40 (dd, *J*=6.8, 4.0, 1H), 3.12 (dd, *J*=18.4, 4.0, 1H), 2.94 (dd, *J*=18.4, 6.8, 1H), 2.36 (s, 3H), 1.25 (t, *J*=7.2, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.53, 165.58, 165.08, 145.63, 141.15, 135.07, 134.16, 133.79, 133.20, 130.47, 130.12, 129.27, 128.61, 127.74, 127.44, 126.72, 118.43, 91.05, 80.82, 78.17, 61.95, 52.91, 44.87, 33.36, 21.74, 14.14. HRMS (ESI) calcd for $C_{30}H_{29}N_3O_{10}S$ $[M+H]^+$: 624.1646. Found: 624.1647.



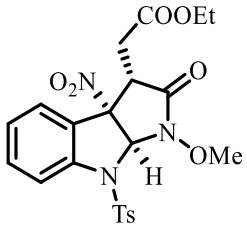
4m, white solid, m.p. = 148.1-150.5 ºC. 101mg, 84% yield, 15:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.68 (m, 3H), 7.63 – 7.52 (m, 3H), 7.42 – 7.34 (m, 3H), 7.24 – 7.16 (m, 3H), 6.70 (s, 1H), 5.21 (q, *J*=9.2, 2H), 4.12 (q, *J*=7.2, 2H), 3.37 (dd, *J*=6.8, 4.0, 1H), 3.09 (dd, *J*=18.4, 4.0, 1H), 2.91 (dd, *J*=18.4, 6.8, 1H), 2.36 (s, 3H), 1.24 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.53, 165.17, 145.71, 141.91, 139.37, 134.13, 133.79, 130.49, 130.17, 129.25, 128.60, 127.68, 127.59, 127.54, 126.50, 117.80, 90.92, 80.92, 78.12, 61.92, 44.93, 33.35, 21.75, 14.13. HRMS (ESI) calcd for $C_{28}H_{26}ClN_3O_8S$ $[M+H]^+$: 600.1202. Found: 600.1206.



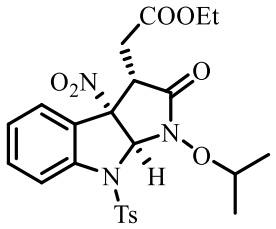
4n, white solid, m.p. = 101.5-105.7 °C. 103mg, 80% yield, 14:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (d, *J*=1.6, 1H), 7.70 (d, *J*=8.4, 2H), 7.66 – 7.56 (m, 2H), 7.52 (d, *J*=8.4, 1H), 7.47 – 7.36 (m, 4H), 7.24 (d, *J*=8.0, 2H), 6.70 (s, 1H), 5.24 (q, *J*=9.2, 2H), 4.15 (q, *J*=7.2, 2H), 3.39 (dd, *J*=6.8, 4.0, 1H), 3.12 (dd, *J*=18.4, 4.0, 1H), 2.93 (dd, *J*=18.4, 6.8, 1H), 2.39 (s, 3H), 1.26 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.53, 165.17, 145.72, 141.96, 134.12, 133.80, 130.50, 130.18, 129.42, 129.26, 128.61, 128.14, 127.79, 127.68, 127.36, 120.73, 91.00, 80.84, 78.14, 61.93, 44.89, 33.35, 21.76, 14.14. HRMS (ESI) calcd for $C_{28}H_{26}BrN_3O_8S$ $[M+H]^+$: 644.0697. Found: 644.0684.



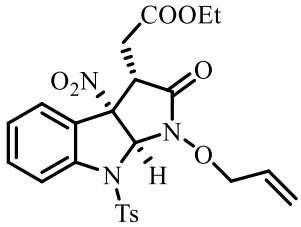
4o, white solid, m.p. = 190.0-194.1 °C. 82mg, 72% yield, 15:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.46 (dd, *J*=4.8, 1.6, 1H), 8.14 – 7.93 (m, 3H), 7.71 – 7.52 (m, 2H), 7.48 – 7.36 (m, 3H), 7.18 (d, *J*=8.0, 2H), 7.12 (m, 2H), 5.31 (d, *J*=8.8, 1H), 5.20 (d, *J*=8.8, 1H), 4.19 (q, *J*=7.2, 2H), 3.43 (dd, *J*=6.4, 4.0, 1H), 3.19 (dd, *J*=18.4, 4.0, 1H), 2.98 (dd, *J*=18.4, 6.4, 1H), 2.37 (s, 3H), 1.30 (t, *J*=7.2, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.62, 164.73, 154.22, 152.98, 145.12, 135.68, 135.60, 133.66, 130.49, 129.53, 129.32, 128.79, 128.63, 121.60, 120.14, 89.59, 77.47, 62.02, 44.82, 33.40, 21.74, 14.17. HRMS (ESI) calcd for $C_{27}H_{26}N_4O_8S$ $[M+H]^+$: 567.1544. Found: 567.1551.



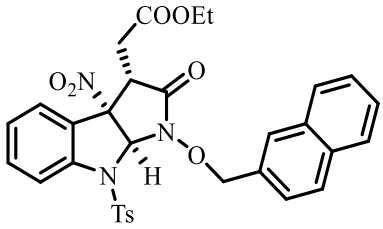
4p, white solid, m.p. = 175.7-177.4 °C. 73mg, 74% yield, 13:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.73 (d, *J*=8.4, 2H), 7.68 (d, *J*=8.4, 1H), 7.61 (d, *J*=7.6, 1H), 7.50 (t, *J*=7.6, 1H), 7.22 (t, *J*=7.6, 3H), 6.79 (s, 1H), 4.13 (q, *J*=7.2, 2H), 4.02 (s, 3H), 3.37 (dd, *J*=5.6, 4.4, 1H), 3.16 (dd, *J*=18.4, 4.0, 1H), 3.03 (dd, *J*=18.4, 5.6, 1H), 2.36 (s, 3H), 1.25 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.62, 165.05, 145.35, 140.75, 134.47, 133.28, 129.98, 129.25, 127.81, 126.32, 126.07, 117.25, 91.22, 79.86, 63.72, 61.86, 45.03, 33.30, 21.73, 14.14. HRMS (ESI) calcd for $C_{22}H_{23}N_3O_8S$ $[M+H]^+$: 490.1279. Found: 490.1288.



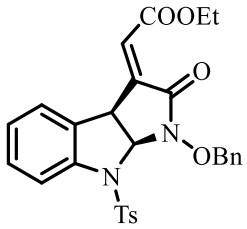
4q, white solid, m.p. = 100.9-102.4 ºC. 50mg, 52% yield, 18:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.72 (d, *J*=8.0, 1H), 7.65 (t, *J*=8.0, 3H), 7.51 (t, *J*=8.0, 1H), 7.23 (t, *J*=8.0, 1H), 7.18 (d, *J*=8.0, 2H), 6.68 (s, 1H), 4.67 (dt, *J*=12.4, 6.4, 1H), 4.13 (q, *J*=7.2, 2H), 3.42 (dd, *J*=6.4, 4.0, 1H), 3.14 (dd, *J*=18.0, 4.0, 1H), 2.94 (dd, *J*=18.0, 6.0, 1H), 2.34 (s, 3H), 1.34 (dd, *J*=8.4, 6.4, 6H), 1.25 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.58, 166.72, 145.33, 140.79, 134.30, 133.23, 129.96, 129.51, 127.72, 126.66, 126.29, 117.66, 91.39, 81.39, 79.41, 61.85, 45.12, 33.44, 21.75, 21.08, 21.03, 14.16. HRMS (ESI) calcd for C24H27N3O8S $[M+H]^+$: 518.1592. Found: 518.1597.



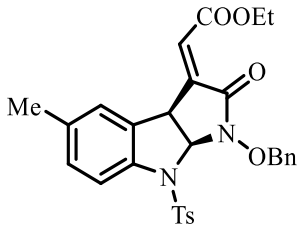
4r, white solid, m.p. = 118.0-120.3 ºC. 76mg, 74% yield, 15:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (m, 3H), 7.63 (m, 1H), 7.51 (td, *J*=8.0, 1.2, 1H), 7.26 – 7.18 (m, 3H), 6.74 (s, 1H), 6.15 (ddt, *J*=17.2, 10.0, 6.8, 1H), 5.50 – 5.16 (m, 2H), 4.72 (ddd, *J*=26.0, 10.8, 6.8, 2H), 4.14 (q, *J*=7.2, 2H), 3.41 (dd, *J*=6.4, 4.0, 1H), 3.14 (dd, *J*=18.0, 4.0, 1H), 2.96 (dd, *J*=18.0, 6.4, 1H), 2.36 (s, 3H), 1.26 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.50, 165.52, 145.36, 140.78, 134.43, 133.24, 131.59, 129.99, 129.29, 127.74, 126.57, 126.16, 121.85, 117.40, 91.33, 80.57, 77.42, 61.84, 45.08, 33.46, 21.73, 14.15. C24H25N3O8S $[M+H]^+$: 516.1435. Found:516.1445.



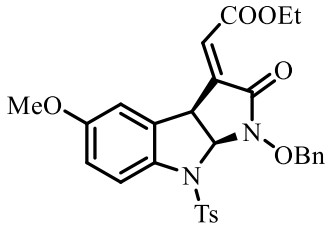
4s, white solid, m.p. = 172.4-175.3 ºC. 111mg, 90% yield, 18:1 dr, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (s, 1H), 7.82 (m, 4H), 7.66 (d, *J*=8.4, 2H), 7.60 (t, *J*=7.2, 2H), 7.55 – 7.39 (m, 3H), 7.20 (t, *J*=7.6, 1H), 7.15 (d, *J*=8.0, 2H), 6.76 (s, 1H), 5.39 (dd, *J*=21.2, 9.2, 2H), 4.12 (q, *J*=7.2, 2H), 3.40 (dd, *J*=6.4, 4.0, 1H), 3.11 (dd, *J*=18.0, 4.0, 1H), 2.94 (dd, *J*=18.0, 6.4, 1H), 2.33 (s, 3H), 1.24 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.55, 165.40, 145.33, 140.76, 134.40, 133.79, 133.25, 133.13, 131.44, 130.00, 129.97, 129.27, 128.44, 128.36, 127.83, 127.71, 126.57, 126.52, 126.17, 117.56, 91.38, 80.62, 78.19, 61.86, 45.08, 33.42, 21.71, 14.15. C32H29N3O8S $[M+H]^+$: 616.1748. Found: 616.1752.



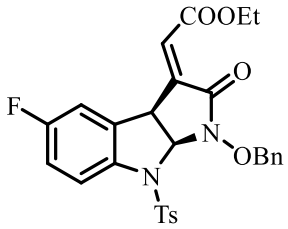
5a, white solid, m.p. = 138.8-141.3 °C. 80mg, 77% yield, dr>20:1, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.51 (m, 5H), 7.38 – 7.37 (m, 3H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.75 (s, 1H), 5.92 (d, *J* = 6.4 Hz, 1H), 5.23 (s, 2H), 4.93 (d, *J* = 6.3 Hz, 1H), 4.30 – 4.25 (m, 2H), 2.36 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.69, 160.63, 144.83, 144.26, 139.70, 134.94, 133.87, 131.20, 130.21, 129.98, 129.56, 129.02, 128.43, 126.94, 126.06, 126.03, 121.56, 118.12, 78.87, 77.47, 61.30, 43.09, 21.55, 14.04. HRMS (ESI) calcd for C28H26N2O6S $[M+H]^+$: 519.1584. Found: 519.1569.



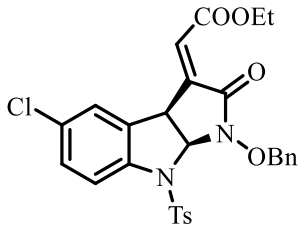
5b, white solid, m.p. = 158.5-160.7 °C. 64mg, 60% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 – 7.48 (m, 5H), 7.37 (m, 3H), 7.18 (d, *J*=8.0, 2H), 7.11 (d, *J*=8.0, 1H), 6.99 (s, 1H), 6.74 (s, 1H), 5.87 (d, *J*=6.4, 1H), 5.22 (s, 2H), 4.84 (d, *J*=6.4, 1H), 4.35 – 4.22 (m, 2H), 2.37 (s, 3H), 2.26 (s, 3H), 1.33 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.90, 160.80, 144.88, 144.60, 137.49, 136.23, 135.07, 134.07, 131.45, 130.43, 130.37, 130.13, 129.17, 128.60, 127.12, 126.60, 121.59, 118.20, 79.13, 77.94, 61.44, 43.26, 21.72, 21.29, 14.21. HRMS (ESI) calcd for $C_{29}H_{28}N_2O_6S$ $[M+H]^+$: 533.1741. Found: 533.1749.



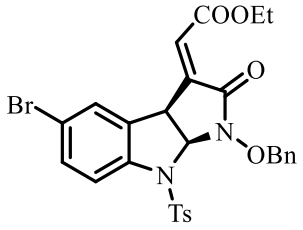
5c, white solid, m.p. = 192.7-195.6 °C. 77mg, 71% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.55 (m, 3H), 7.51 (d, *J*=8.4, 2H), 7.43 – 7.35 (m, 3H), 7.19 (d, *J*=8.4, 2H), 6.88 – 6.82 (m, 1H), 6.79 (m, 1H), 6.74 (d, *J*=1.6, 1H), 5.85 (d, *J*=6.4, 1H), 5.23 (s, 2H), 4.79 (d, *J*=6.4, 1H), 4.35 – 4.17 (m, 2H), 3.74 (s, 3H), 2.38 (s, 3H), 1.32 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.84, 160.69, 158.40, 144.90, 144.37, 134.87, 134.12, 133.24, 133.11, 130.36, 130.14, 129.17, 128.60, 127.16, 121.78, 119.53, 114.98, 111.89, 79.15, 78.26, 61.46, 55.72, 43.38, 21.72, 14.20. HRMS (ESI) calcd for $C_{29}H_{28}N_2O_7S$ $[M+H]^+$: 549.1690. Found: 549.1681.



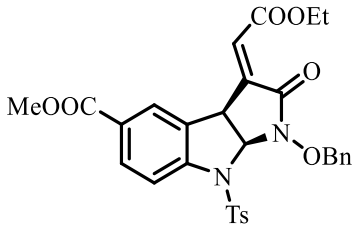
5d, m.p. = 147.3-151.8 ºC. white solid, 96mg, 90% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 – 7.46 (m, 5H), 7.37 (m, 3H), 7.20 (d, *J*=8.0, 2H), 7.00 (m, 2H), 6.73 (s, 1H), 5.87 (d, *J*=6.4, 1H), 5.23 (s, 2H), 4.84 (d, *J*=6.4, 1H), 4.39 – 4.14 (m, 2H), 2.37 (s, 3H), 1.33 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.82, 161.01(*J* = 244.4), 160.62, 145.23, 143.82, 135.93(*J* = 2.2), 134.75, 133.97, 133.67, 130.42, 130.26, 129.26, 128.63, 127.12, 122.22, 119.58(*J* = 8.6), 119.54, 116.68(*J* = 23.7), 113.80(*J* = 25.2) , 79.06, 78.19, 61.65, 43.19, 21.75, 14.19. ^{19}F NMR (376 MHz, CDCl3) δ -115.2 (m). HRMS (ESI) calcd for $C_{28}H_{25}FN_2O_6S$ $[M+H]^+$: 537.1490. Found: 537.1498.



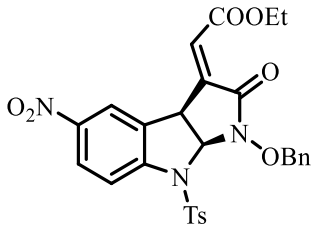
5e, white solid, m.p. = 164.5-166.6 ºC. 80mg, 73% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55 (m, 5H), 7.37 (m, 3H), 7.24 (m, 4H), 6.77 (s, 1H), 5.87 (d, *J*=6.4, 1H), 5.31 – 5.10 (m, 2H), 4.87 (d, *J*=6.4, 1H), 4.43 – 4.12 (m, 2H), 2.38 (s, 3H), 1.33 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.82, 160.64, 145.31, 143.63, 138.62, 134.87, 133.95, 133.20, 131.60, 130.44, 130.33, 129.92, 129.28, 128.65, 127.09, 126.63, 122.33, 119.22, 79.03, 77.89, 61.68, 43.08, 21.76, 14.20. HRMS (ESI) calcd for $C_{28}H_{25}ClN_2O_6S$ $[M+H]^+$: 553.1195. Found: 553.1197.



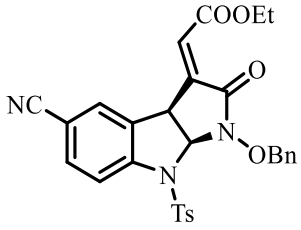
5f, white solid, m.p. = 175.5-176.6 ºC. 100mg, 84% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.56 (m, 4H), 7.46 (m, 2H), 7.37 (s, 4H), 7.22 (d, *J*=8.0, 2H), 6.78 (s, 1H), 5.87 (d, *J*=6.4, 1H), 5.27 – 5.13 (m, 2H), 4.89 (d, *J*=6.4, 1H), 4.42 – 4.15 (m, 2H), 2.39 (s, 3H), 1.34 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.80, 160.63, 145.32, 143.58, 139.13, 134.86, 133.94, 133.47, 132.82, 130.43, 130.33, 129.53, 129.27, 128.64, 127.08, 122.35, 119.57, 119.11, 79.01, 77.78, 61.68, 43.01, 21.76, 14.19. HRMS (ESI) calcd for $C_{28}H_{25}BrN_2O_6S$ $[M+H]^+$: 597.0689. Found: 597.0694.



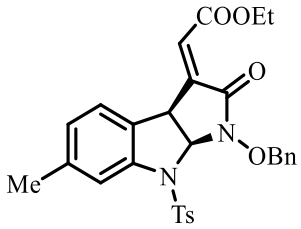
5g, white solid, m.p. = 174.5-176.2 ºC. 103mg, 89% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J*=8.4, 1H), 7.96 – 7.78 (m, 1H), 7.60 (dd, *J*=14.8, 8.0, 5H), 7.37 (s, 3H), 7.19 (d, *J*=8.0, 2H), 6.79 (s, 1H), 5.95 (d, *J*=6.4, 1H), 5.31 – 5.14 (m, 2H), 5.01 (d, *J*=6.4, 1H), 4.45 – 4.22 (m, 2H), 3.88 (s, 3H), 2.39 (s, 3H), 1.38 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.97, 165.67, 160.60, 145.22, 143.66, 143.24, 134.90, 133.71, 131.56, 131.27, 130.28, 130.15, 129.11, 128.46, 127.74, 127.70, 126.89, 122.27, 117.10, 78.69, 77.55, 61.51, 52.17, 42.62, 21.57, 14.02. HRMS (ESI) calcd for $C_{30}H_{28}N_2O_8S$ $[M+H]^+$: 577.1639. Found: 577.1646.



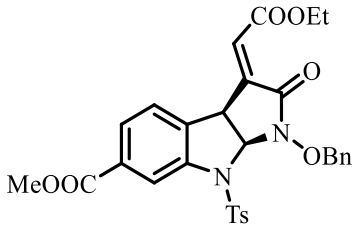
5h, white solid, m.p. = 95.5-98.5 ºC. 74mg, 66% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.27 – 8.09 (m, 2H), 7.61 (m, 5H), 7.38 (s, 3H), 7.29 – 7.18 (m, 2H), 6.85 (s, 1H), 5.99 (d, *J*=6.4, 1H), 5.27 – 5.18 (m, 2H), 5.08 (d, *J*=6.4, 1H), 4.51 – 4.16 (m, 2H), 2.39 (s, 3H), 1.38 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.85, 160.61, 145.87, 145.58, 145.33, 142.60, 134.90, 133.72, 132.43, 130.51, 129.40, 128.68, 127.09, 126.01, 123.13, 122.57, 117.08, 78.75, 77.81, 62.01, 42.62, 21.78, 14.20. HRMS (ESI) calcd for $C_{28}H_{25}N_3O_8S$ $[M+H]^+$: 564.1435. Found: 564.1431.



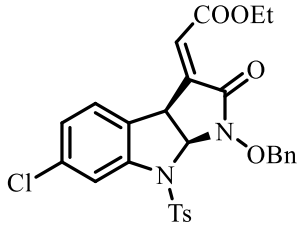
5i, white solid, m.p. = 182.3-184.1 ºC. 81mg, 75% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.61 (m, 7H), 7.38 (m, 3H), 7.31 – 7.17 (m, 2H), 6.82 (s, 1H), 5.94 (d, *J*=6.4, 1H), 5.26 – 5.17 (m, 2H), 5.01 (d, *J*=6.4, 1H), 4.47 – 4.18 (m, 2H), 2.39 (s, 3H), 1.36 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.84, 160.56, 145.76, 143.78, 143.02, 134.94, 134.17, 133.74, 132.31, 130.62, 130.48, 129.38, 128.67, 127.06, 122.83, 118.43, 117.88, 109.33, 78.79, 77.38, 61.92, 42.82, 21.78, 14.20. HRMS (ESI) calcd for $C_{29}H_{25}N_3O_6S$ $[M+H]^+$: 544.1537. Found: 544.1532.



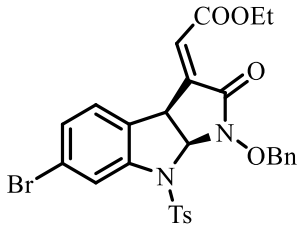
5j, white solid, m.p. = 169.1-171.1 ºC. 64mg, 60% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (m, 4H), 7.45 (s, 1H), 7.38 (m, 3H), 7.19 (d, *J*=8.0, 2H), 7.09 (d, *J*=8.0, 1H), 6.89 (d, *J*=8.0, 1H), 6.72 (s, 1H), 5.87 (d, *J*=6.4, 1H), 5.22 (s, 2H), 4.85 (d, *J*=6.4, 1H), 4.27 (q, *J*=7.2, 2H), 2.37 (s, 6H), 1.32 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.88, 160.82, 144.92, 144.65, 140.10, 139.97, 135.20, 134.07, 130.38, 130.14, 129.15, 128.60, 128.48, 127.08, 125.78, 121.51, 118.90, 79.09, 77.95, 61.42, 42.99, 21.77, 21.73, 14.21. HRMS (ESI) calcd for $C_{29}H_{28}N_2O_6S$ $[M+H]^+$: 533.1741. Found: 533.1766.



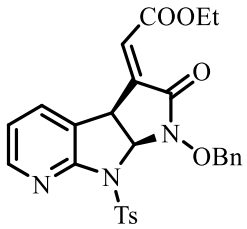
5l, white solid, m.p. = 178.9-181.0 ºC. 101mg, 88% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.78 (d, *J*=8.0, 1H), 7.57 (m, 4H), 7.36 (m, 3H), 7.31 (d, *J*=8.0, 1H), 7.19 (d, *J*=8.0, 2H), 6.77 (s, 1H), 5.94 (d, *J*=6.4, 1H), 5.22 (s, 2H), 4.98 (d, *J*=6.4, 1H), 4.43 – 4.17 (m, 2H), 3.95 (s, 3H), 2.37 (s, 3H), 1.33 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.22, 165.82, 160.67, 145.28, 143.58, 140.28, 136.21, 134.96, 133.90, 131.97, 130.41, 130.29, 129.26, 128.62, 127.69, 127.12, 126.26, 122.31, 119.03, 79.05, 77.82, 61.64, 52.61, 43.24, 21.74, 14.20. HRMS (ESI) calcd for $C_{30}H_{28}N_2O_8S$ $[M+H]^+$: 577.1639. Found: 577.1631.



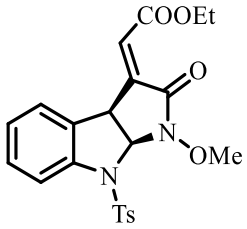
5m, white solid, m.p. = 204.5-206.9 ºC. 74mg, 67% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57 (d, *J*=8.0, 5H), 7.38 (,m, 3H), 7.22 (d, *J*=8.0, 2H), 7.16 (d, *J*=8.0, 1H), 7.04 (d, *J*=8.0, 1H), 6.76 (s, 1H), 5.87 (d, *J*=6.4, 1H), 5.22 (s, 2H), 4.86 (d, *J*=6.4, 1H), 4.27 (q, *J*=7.2, 2H), 2.39 (s, 3H), 1.32 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.85, 160.81, 145.34, 143.91, 141.04, 135.48, 134.97, 133.92, 132.11, 130.46, 130.34, 129.81, 129.26, 128.64, 127.10, 126.25, 122.07, 118.44, 78.97, 77.94, 61.60, 42.82, 21.77, 14.21. HRMS (ESI) calcd for $C_{28}H_{25}ClN_2O_6S$ $[M+H]^+$: 553.1195. Found: 553.1185.



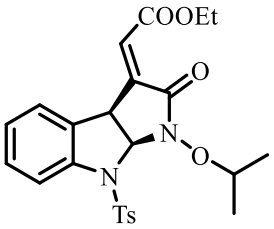
5n, white solid, m.p. = 214.2-216.0 °C. 97mg, 81% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.80 – 7.66 (s, 1H), 7.52 (m, 4H), 7.38 (m, 3H), 7.25 – 7.16 (m, 3H), 7.14 – 7.02 (m, 1H), 6.76 (s, 1H), 5.79 (m, *J*=6.4, 1H), 5.26 – 5.18 (m, 2H), 4.83 (d, *J*=6.4, 1H), 4.39 – 4.02 (m, 2H), 2.39 (s, 3H), 1.32 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.81, 160.70, 145.34, 143.78, 141.14, 134.87, 133.87, 130.45, 130.34, 129.26, 129.16, 128.62, 127.46, 127.05, 123.18, 122.08, 121.27, 78.96, 77.84, 61.59, 42.86, 21.76, 14.19. HRMS (ESI) calcd for $C_{28}H_{25}BrN_2O_6S$ $[M+H]^+$: 597.0689. Found: 597.0696.



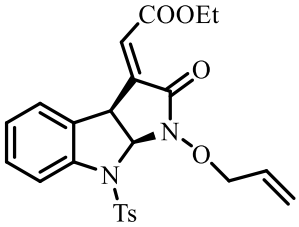
50, white solid, m.p. = 187.0-189.9 °C. 50mg, 48% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.22 (m, 1H), 7.92 (d, *J*=8.0, 2H), 7.63 (m, 1H), 7.57 (m, 2H), 7.39 (m, 3H), 7.13 (d, *J*=8.0, 2H), 7.02 – 6.85 (m, 1H), 6.79 (s, 1H), 6.31 (d, *J*=6.4, 1H), 5.32 (d, *J*=6.4, 1H), 5.18 (m, 2H), 4.38 – 4.11 (m, 2H), 2.35 (s, 3H), 1.36 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.75, 160.30, 154.20, 149.25, 144.66, 143.65, 136.46, 135.31, 133.67, 130.34, 129.51, 129.33, 128.64, 128.41, 123.43, 122.21, 119.86, 78.02, 73.73, 61.66, 41.45, 21.74, 14.27. HRMS (ESI) calcd for $C_{27}H_{25}N_3O_6S$ $[M+H]^+$: 520.1537. Found: 520.1534.



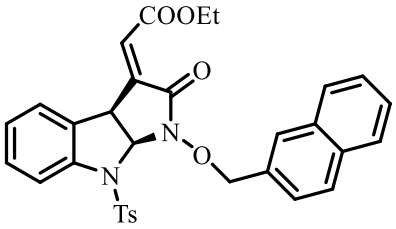
5p, white solid, m.p. = 85.5-88.5 °C. 75mg, 85% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J*=8.0, 1H), 7.61 (d, *J*=8.0, 2H), 7.34 (t, *J*=7.6, 1H), 7.28 – 7.19 (m, 3H), 7.11 (t, *J*=7.6, 1H), 6.78 (d, 1H), 6.00 (d, *J*=6.4, 1H), 5.00 (d, *J*=6.4, 1H), 4.39 – 4.22 (m, 2H), 4.05 (s, 3H), 2.40 (s, 3H), 1.34 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.84, 160.58, 145.06, 144.34, 139.84, 135.19, 131.25, 130.18, 129.81, 127.17, 126.34, 126.19, 121.94, 118.05, 64.97, 61.49, 43.24, 28.30, 21.73, 14.21. HRMS (ESI) calcd for $C_{22}H_{22}N_2O_6S$ $[M+H]^+$: 443.1271. Found: 443.1271.



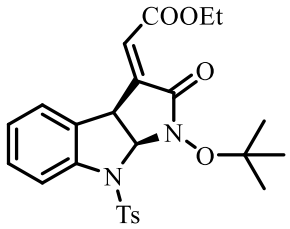
5q, white solid, m.p. = 153.3-155.7 ºC. 84mg, 89% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (d, *J*=8.0, 1H), 7.56 (d, *J*=8.0, 2H), 7.31 (t, *J*=8.0, 1H), 7.21 (m, 3H), 7.08 (t, *J*=8.0, 1H), 6.71 (s, 1H), 5.89 (d, *J*=6.4, 1H), 4.91 (d, *J*=6.4, 1H), 4.70 (m, 1H), 4.27 (q, *J*=7.2, 2H), 2.36 (s, 3H), 1.31 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.92, 161.99, 144.96, 144.50, 139.91, 135.21, 131.63, 130.14, 129.75, 127.06, 126.25, 126.23, 121.71, 118.27, 79.78, 78.17, 61.43, 43.20, 21.71, 21.18, 14.19. HRMS (ESI) calcd for $C_{24}H_{26}N_2O_6S$ $[M+H]^+$: 471.1584. Found: 471.1582.



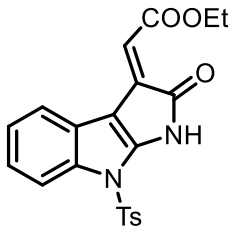
5r, white solid, m.p. = 134.2-136.5 ºC. 48mg, 51% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.63 (d, *J*=8.0, 1H), 7.60 – 7.56 (m, 2H), 7.34 – 7.28 (m, 1H), 7.21 (m, 3H), 7.08 (m, 1H), 6.74 (d, *J*=1.6, 1H), 6.25 – 6.04 (m, 1H), 5.94 (d, *J*=6.4, 1H), 5.38 – 5.24 (m, 2H), 4.95 (d, *J*=6.4, 1H), 4.73 (qd, *J*=11.2, 6.8, 2H), 4.27 (qd, *J*=7.2, 1.4, 2H), 2.37 (s, 3H), 1.32 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.71, 160.92, 144.86, 144.19, 139.68, 134.99, 131.54, 131.20, 130.00, 129.59, 126.93, 126.11, 125.99, 121.82, 121.62, 117.92, 78.08, 77.45, 61.30, 43.10, 21.57, 14.04. HRMS (ESI) calcd for $C_{24}H_{24}N_2O_6S$ $[M+H]^+$: 469.1428. Found: 469.1438.



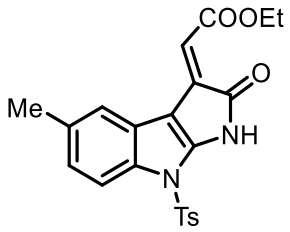
5s, white solid, m.p. = 196.4-198.7 ºC. 66mg, 58% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (s, 1H), 7.90 – 7.79 (m, 3H), 7.76 (dd, *J*=8.4, 1.6, 1H), 7.56 – 7.44 (m, 5H), 7.25 – 7.17 (m, 2H), 7.14 (d, *J*=8.0, 2H), 7.04 (t, *J*=7.2, 1H), 6.75 (d, *J*=1.6, 1H), 5.88 (d, *J*=6.4, 1H), 5.39 (s, 2H), 4.88 (d, *J*=6.4, 1H), 4.37 – 4.20 (m, 2H), 2.33 (s, 3H), 1.31 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.85, 160.93, 144.95, 144.40, 139.83, 135.14, 133.79, 133.24, 131.59, 131.34, 130.12, 129.94, 129.63, 128.48, 128.39, 127.82, 127.78, 127.07, 126.57, 126.14, 121.74, 118.30, 79.03, 77.73, 61.45, 43.28, 21.69, 14.20. HRMS (ESI) calcd for $C_{32}H_{28}N_2O_6S$ $[M+H]^+$: 569.1741. Found: 569.1750.



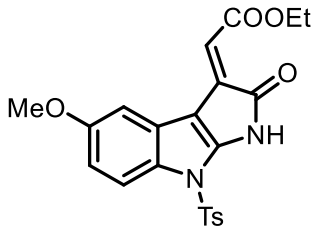
5t, white solid, m.p. = 145.9-146.9 ºC. 88mg, 91% yield, dr>20:1,^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65 (d, *J*=8.0, 1H), 7.52 (m, 2H), 7.31 (t, *J*=8.0, 1H), 7.19 (m, 3H), 7.09 (t, *J*=8.0, 1H), 6.73 (s, 1H), 5.73 (d, *J*=6.4, 1H), 4.82 (d, *J*=5.6, 1H), 4.39 – 4.18 (m, 2H), 2.35 (s, 3H), 1.49 – 1.40 s, 9H), 1.30 (t, *J*=14.8, 7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.89, 164.34, 144.84, 144.35, 140.12, 135.33, 132.22, 130.07, 129.67, 127.03, 126.39, 126.12, 121.72, 118.79, 86.81, 79.43, 61.40, 43.36, 28.30, 21.70, 14.18. HRMS (ESI) calcd for $C_{25}H_{28}N_2O_6S$ $[M+H]^+$: 485.1741. Found: 485.1738.



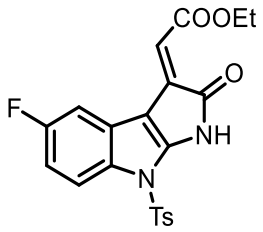
6a, red solid, m.p. no data(carbonizated), 49mg, 60% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.24 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.2 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.59 (s, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.38 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.92, 166.04, 148.59, 146.61, 135.35, 133.63, 133.49, 130.40, 127.17, 125.40, 125.30, 123.02, 122.62, 115.70, 113.26, 60.98, 21.66, 14.23. HRMS (ESI) calcd for C21H18N2O5S $[M+H]^+$: 411.1009. Found: 411.1000.



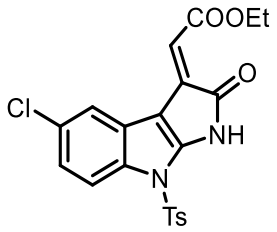
6b, red solid, m.p. no data(carbonizated), 42mg, 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.19 (s, 1H), 8.00 (s, 1H), 7.77 (d, *J*=8.4, 2H), 7.70 (d, *J*=8.4, 1H), 7.28 (d, *J*=8.4, 2H), 7.03 – 6.94 (m, 1H), 6.57 (s, 1H), 4.33 (q, *J*=7.2, 2H), 2.41 (s, 3H), 2.37 (s, 3H), 1.35 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.06, 166.19, 146.68, 135.26, 134.76, 134.68, 133.78, 133.72, 130.54, 127.33, 125.78, 125.73, 124.26, 123.04, 115.79, 113.12, 61.14, 21.86, 21.83, 14.42. HRMS (ESI) calcd for $C_{22}H_{20}N_2O_5S$ $[M+H]^+$: 425.1166. Found: 425.1172.



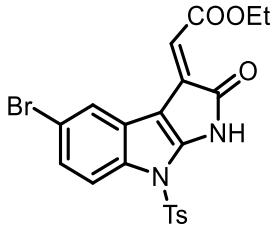
6c, red solid, m.p. no data(carbonizated), 44mg, 50% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (s, 1H), 7.88 (d, *J*=2.8, 1H), 7.78 (d, *J*=8.4, 2H), 7.73 (d, *J*=9.2, 1H), 7.31 (d, *J*=8.4, 2H), 6.77 (dd, *J*=9.2, 2.8, 1H), 6.59 (s, 1H), 4.33 (q, *J*=7.2, 2H), 3.86 (s, 3H), 2.40 (s, 3H), 1.36 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.94, 166.19, 157.94, 149.16, 146.70, 133.77, 133.66, 130.55, 129.82, 127.30, 126.90, 115.80, 114.12, 110.72, 107.05, 61.12, 55.74, 21.84, 14.41. HRMS (ESI) calcd for $C_{22}H_{20}N_2O_6S$ $[M+H]^+$: 441.1115. Found: 441.1131.



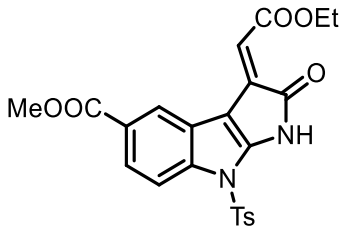
6d, red solid, m.p. no data(carbonizated), 49mg, 58% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.69 (s, 1H), 8.01 (d, *J*=8.4, 2H), 7.91 (m, 2H), 7.48 (d, *J*=8.4, 2H), 7.02 (td, *J*=9.2, 2.6, 1H), 6.27 (s, 1H), 4.26 (q, *J*=7.2, 2H), 2.36 (s, 3H), 1.27 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ 171.82, 166.05, 160.33(*J* = 236.5), 153.21, 147.50, 134.02, 133.23, 131.62, 131.23, 127.70, 126.75(*J* = 11.7), 115.12(*J* = 9.8), 113.60, 110.09(*J* = 25.3), 108.45(*J* = 27.3), 97.88, 61.24, 21.62, 14.53. ^{19}F NMR (376 MHz, CDCl3) δ -116.9 (m). HRMS (ESI) calcd for $C_{21}H_{17}FN_2O_5S$ $[M+H]^+$: 429.0915. Found: 429.0915.



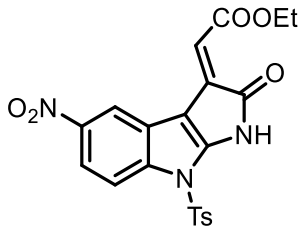
6e, red solid, m.p. no data(carbonizated), 41mg, 46% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.74 (s, 1H), 8.20 (d, *J*=2.4, 1H), 8.01 (d, *J*=8.4, 2H), 7.89 (d, *J*=8.8, 1H), 7.49 (d, *J*=8.2, 2H), 7.21 (dd, *J*=8.8, 2.2, 1H), 6.26 (s, 1H), 4.26 (d, *J*=7.2, 2H), 2.36 (s, 3H), 1.27 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.46, 165.60, 147.16, 133.52, 133.32, 132.70, 130.83, 129.69, 127.29, 126.24, 122.29, 121.13, 114.84, 113.25, 96.94, 60.85, 21.19, 14.09. HRMS (ESI) calcd for $C_{21}H_{17}ClN_2O_5S$ $[M+H]^+$: 445.0619. Found: 445.0639.



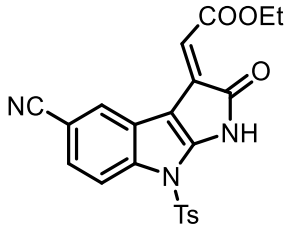
6f, red solid, m.p. no data(carbonizated), 48mg, 49% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.73 (s, 1H), 8.34 (d, *J*=2.0, 1H), 8.00 (d, *J*=8.4, 2H), 7.84 (d, *J*=8.8, 1H), 7.48 (d, *J*=8.0, 2H), 7.33 (dd, *J*=8.8, 2.0, 1H), 6.27 (s, 1H), 4.25 (q, *J*=7.2, 2H), 2.35 (s, 3H), 1.26 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 171.39, 165.59, 147.16, 133.67, 133.47, 132.69, 130.82, 127.32, 127.29, 126.60, 125.05, 124.10, 117.97, 115.22, 113.28, 96.57, 60.86, 21.18, 14.08. HRMS (ESI) calcd for $C_{21}H_{17}BrN_2O_5S$ $[M+H]^+$: 489.0114. Found: 489.0108.



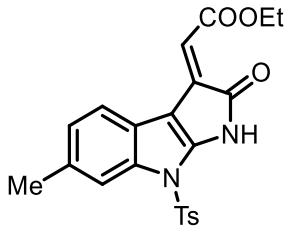
6g, red solid, m.p. no data(carbonizated), 53mg, 56% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.71 (s, 1H), 8.74 (d, *J*=1.6, 1H), 8.09 – 7.98 (m, 3H), 7.79 (dd, *J*=8.4, 1.8, 1H), 7.47 (d, *J*=8.0, 2H), 6.30 (s, 1H), 4.29 (q, *J*=7.2, 2H), 3.84 (s, 3H), 2.33 (s, 3H), 1.28 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.47, 166.26, 165.52, 152.32, 147.22, 137.38, 133.24, 132.73, 130.84, 127.33, 126.30, 124.72, 123.67, 123.01, 113.71, 113.46, 97.19, 60.85, 52.21, 21.18, 14.07. HRMS (ESI) calcd for $C_{23}H_{20}N_2O_7S$ $[M+H]^+$: 469.1064. Found: 469.1070.



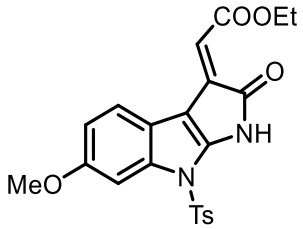
6h, red solid, m.p. no data(carbonizated), 42mg, 47% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.88 (s, 1H), 9.08 (d, *J*=2.4, 1H), 8.17 – 7.98 (m, 4H), 7.51 (d, *J*=8.2, 2H), 6.33 (s, 1H), 4.30 (q, *J*=7.2, 2H), 2.37 (s, 3H), 1.30 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.21, 165.55, 153.50, 147.52, 144.85, 137.84, 133.20, 132.54, 130.93, 127.47, 125.09, 117.71, 116.96, 114.02, 113.93, 96.98, 60.99, 21.20, 14.07. HRMS (ESI) calcd for $C_{21}H_{17}N_3O_7S$ $[M+H]^+$: 456.0860. Found: 456.0859.



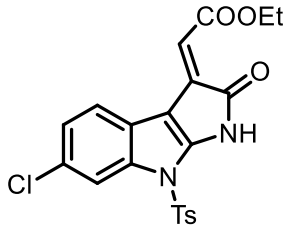
6i, red solid, m.p. no data(carbonizated), 38mg, 44% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.84 (s, 1H), 8.53 (d, *J*=1.2, 1H), 8.07 (m, 3H), 7.61 (dd, *J*=8.4, 1.6, 1H), 7.50 (d, *J*=8.4, 2H), 6.30 (s, 1H), 4.28 (q, *J*=7.2, 2H), 2.37 (s, 3H), 1.29 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.70, 166.04, 153.40, 147.87, 137.23, 133.78, 133.08, 131.35, 127.88, 126.41, 125.89, 125.49, 119.76, 114.91, 114.21, 107.93, 96.99, 61.41, 21.64, 14.52. HRMS (ESI) calcd for $C_{22}H_{17}N_3O_5S$ $[M+H]^+$: 436.0962. Found: 436.0963.



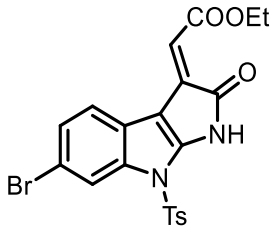
6j, red solid, m.p. no data(carbonizated), 40mg, 47% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.48 (s, 1H), 8.02 (d, *J*=8.4, 3H), 7.71 (s, 1H), 7.47 (d, *J*=8.4, 2H), 7.08 (d, *J*=8.0, 1H), 6.24 (s, 1H), 4.24 (q, *J*=7.2, 2H), 2.40 (s, 3H), 2.35 (s, 3H), 1.26 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.63, 165.52, 151.04, 146.76, 135.17, 133.70, 132.99, 132.30, 130.68, 127.15, 125.99, 122.33, 121.49, 113.56, 112.57, 97.60, 60.56, 21.19, 21.11, 14.09. HRMS (ESI) calcd for $C_{22}H_{20}N_2O_5S$ $[M+H]^+$: 425.1166. Found: 425.1156.



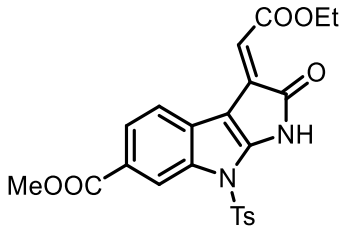
6k, red solid, m.p. no data(carbonizated), 42mg, 48% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (m, 2H), 7.78 (d, *J*=8.4, 2H), 7.41 (d, *J*=2.4, 1H), 7.29 (d, *J*=8.0, 2H), 6.88 (dd, *J*=8.0, 2.4, 1H), 6.55 (s, 1H), 4.30 (q, *J*=7.2, 2H), 3.85 (s, 3H), 2.39 (s, 3H), 1.34 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 170.74, 161.99, 156.42, 147.72, 144.02, 136.49, 136.19, 130.30, 129.77, 127.05, 126.99, 122.46, 114.79, 112.02, 99.23, 55.38, 29.32, 21.45, 14.06. HRMS (ESI) calcd for $C_{22}H_{20}N_2O_6S$ $[M+H]^+$: 441.1115. Found: 441.1118.



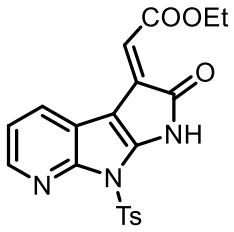
6l, red solid, m.p. no data(carbonizated), 44mg, 50% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.69 (s, 1H), 8.15 (d, *J*=8.8, 1H), 8.05 (d, *J*=8.0, 2H), 7.86 (d, *J*=1.6, 1H), 7.51 (d, *J*=8.4, 2H), 7.34 (dd, *J*=8.8, 2.0, 1H), 6.28 (s, 1H), 4.25 (q, *J*=7.2, 2H), 2.37 (s, 3H), 1.27 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.36, 165.48, 151.92, 147.16, 135.09, 133.47, 132.71, 130.85, 127.23, 126.95, 125.10, 123.64, 122.83, 113.30, 113.09, 97.05, 60.71, 21.15, 14.06. HRMS (ESI) calcd for $C_{21}H_{17}ClN_2O_5S$ $[M+H]^+$: 445.0619. Found: 445.0613.



6m, red solid, m.p. no data(carbonizated), 50mg, 51% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.70 (s, 1H), 8.10 (d, *J*=8.8, 1H), 8.03 (d, *J*=8.0, 2H), 7.98 (s, 1H), 7.51 (d, *J*=8.4, 2H), 7.46 (d, *J*=8.4, 1H), 6.28 (s, 1H), 4.25 (q, *J*=7.2, 2H), 2.37 (s, 3H), 1.24 (t, *J*=7.2, 2H). ^{13}C NMR (101 MHz, DMSO) δ = 171.38, 165.48, 151.85, 147.18, 135.37, 133.48, 132.71, 130.87, 127.87, 127.21, 123.96, 123.25, 115.78, 114.70, 113.35, 97.09, 60.72, 21.16, 14.07. HRMS (ESI) calcd for $C_{21}H_{17}BrN_2O_5S$ $[M+H]^+$: 489.0114. Found: 489.0107.

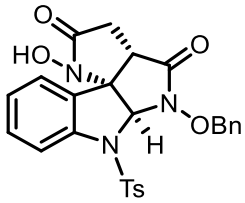


6n, red solid, m.p. no data(carbonizated). 50mg, 53% yield, ^{1}H NMR (400 MHz, DMSO) δ = 11.89 (s, 1H), 8.44 (d, *J*=1.2, 1H), 8.20 (d, *J*=8.4, 1H), 7.96 (d, *J*=8.4, 2H), 7.85 (dd, *J*=8.4, 1.6, 1H), 7.51 (d, *J*=8.0, 2H), 6.32 (s, 1H), 4.27 (q, *J*=7.2, 2H), 3.95 – 3.83 (s, 3H), 2.35 (d, *J*=5.5, 4H), 1.32 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 171.81, 166.46, 165.86, 154.12, 147.64, 134.81, 133.71, 133.17, 131.35, 129.13, 127.48, 126.32, 123.74, 121.74, 114.54, 114.34, 97.89, 61.25, 52.68, 21.59, 14.51. HRMS (ESI) calcd for $C_{23}H_{20}N_2O_7S$ $[M+H]^+$: 469.1064. Found: 469.1076.

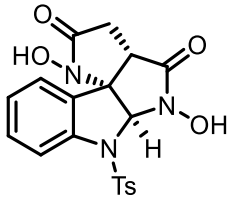


6o, orange solid, m.p. no data(carbonizated). 21mg, 26% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.58 (dd, *J*=8.0, 1.2, 1H), 8.36 (s, 1H), 8.18 (dd, *J*=4.8, 1.2, 1H), 8.10 (d, *J*=8.4, 2H), 7.33 (d, *J*=8.4, 2H), 7.20 (dd, *J*=8.0, 4.8, 1H), 6.57 (s, 1H), 4.31 (q, *J*=7.2, 2H), 2.41 (s, 2H), 1.35 (t, *J*=7.2, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.82, 166.01, 148.43, 147.99, 146.72, 141.97, 133.75, 133.56, 130.48, 130.00, 128.54, 120.72, 118.92, 115.49, 61.00, 21.74, 14.22. HRMS (ESI) calcd for $C_{20}H_{17}N_3O_5S$ $[M+H]^+$: 412.0962,

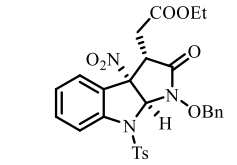
Found: 412.0958.



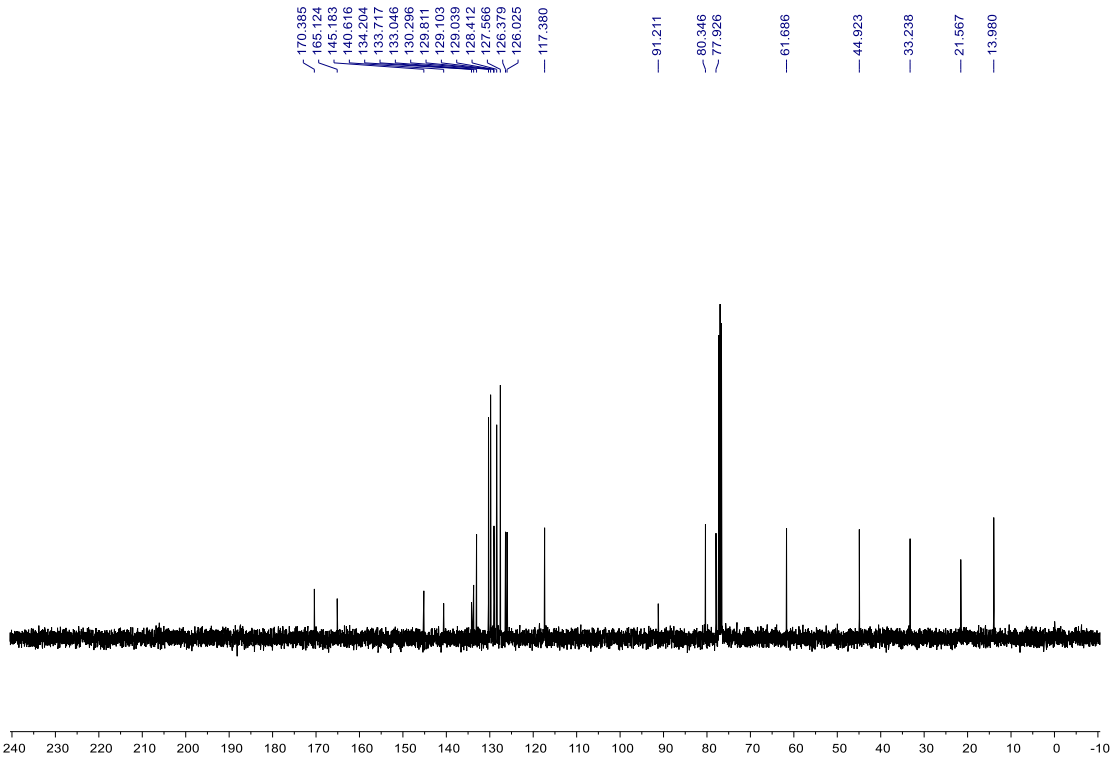
7, white solid, m.p. = 178.2-180.4 ºC. 39mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.61 (d, *J* = 3.8 Hz, 2H), 7.55 (d, *J* = 7.4 Hz, 1H), 7.35 (s, 4H), 7.08 (d, *J* = 7.8 Hz, 4H), 6.14 (s, 1H), 5.30 (d, *J* = 8.6 Hz, 1H), 5.19 (d, *J* = 8.6 Hz, 1H), 2.99 (d, *J* = 10.8 Hz, 1H), 2.93 – 2.82 (m, 1H), 2.60 (d, *J* = 17.2 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.09, 167.66, 144.85, 141.37, 133.82, 131.43, 130.34, 129.67, 129.06, 128.43, 128.15, 128.05, 125.67, 124.01, 116.61, 79.81, 78.31, 70.47, 40.49, 29.21, 21.48, 0.99. HRMS (ESI) calcd for $C_{26}H_{24}N_3O_6S$ $[M+H]^+$: 506.1386. Found: 506.1311.

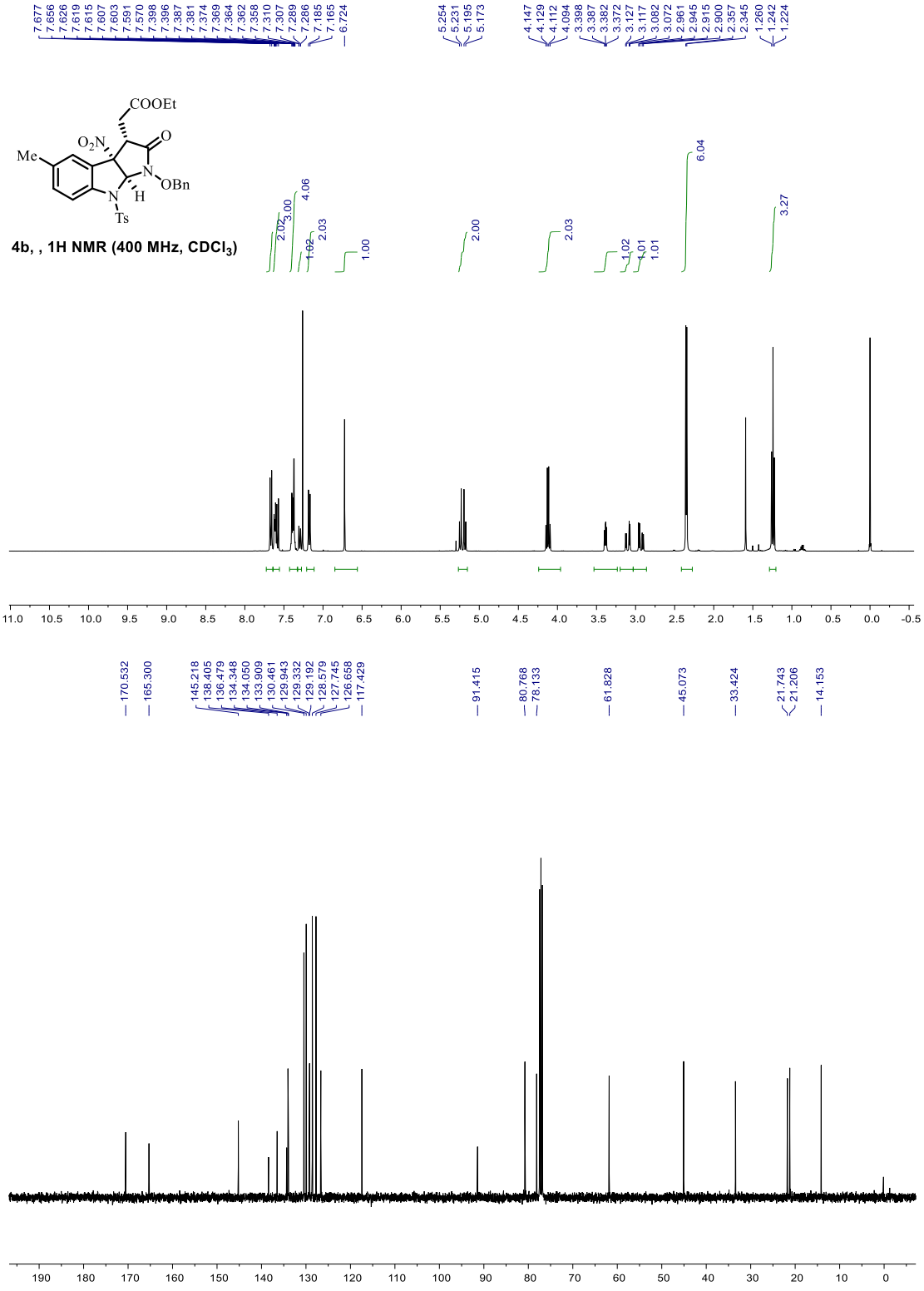


8, white solid, m.p. = 202.4-204.1 ºC. 30mg, 77% yield, ^{1}H NMR (400 MHz, DMSO) δ 10.23 (s, 1H), 9.58 (s, 1H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.41 (dd, *J* = 22.0, 7.8 Hz, 3H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 5.99 (s, 1H), 3.19 (dd, *J* = 11.2, 3.8 Hz, 1H), 2.93 (dd, *J* = 16.8, 11.6 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ 167.75, 166.78, 144.90, 141.12, 134.55, 133.62, 131.43, 130.18, 130.09, 128.43, 125.85, 125.65, 115.95, 81.41, 69.36, 29.48, 21.48. HRMS (ESI) calcd for $C_{19}H_{18}N_3O_6S$ $[M+H]^+$: 416.0916. Found: 416.0970.



4a, 1H NMR (400 MHz, $CDCl_3$)

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N
OBn
N
H
Ts
4b, , 1H NMR (400 MHz, CDCl3)
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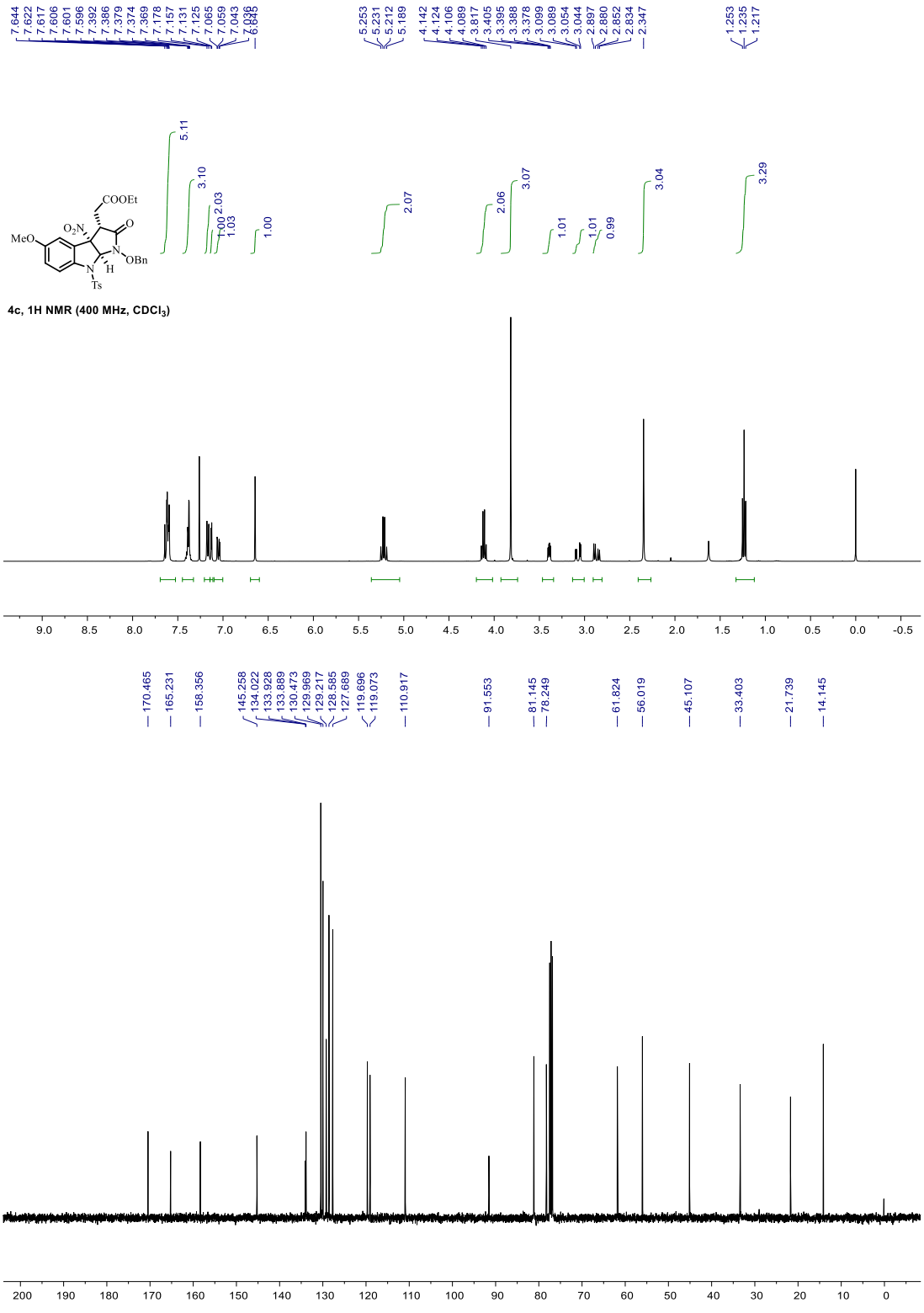
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O
N
OBn
N
H
Ts
4c, 1H NMR (400 MHz, CDCl3)
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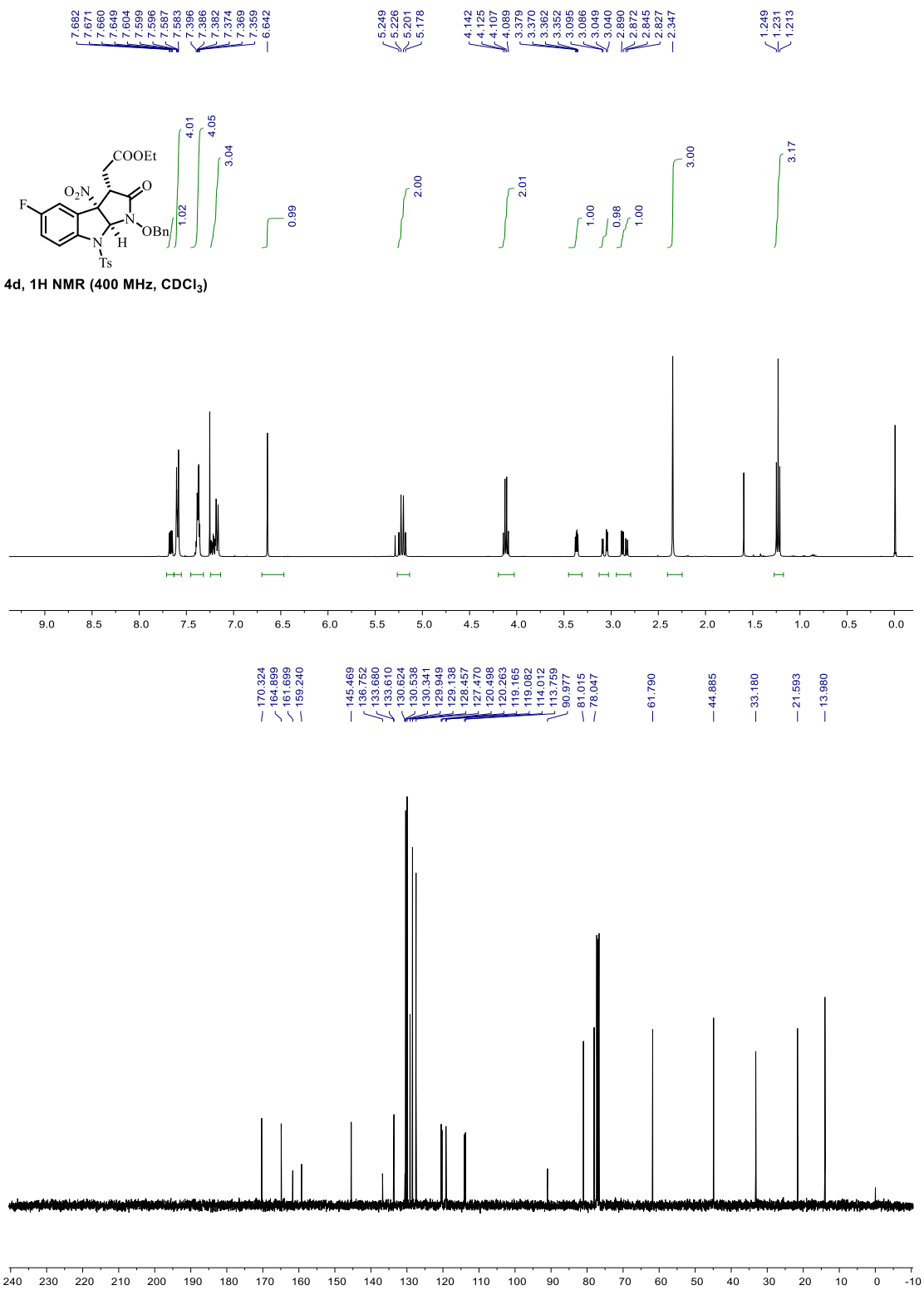

4d, 1H NMR (400 MHz, $CDCl_3$)


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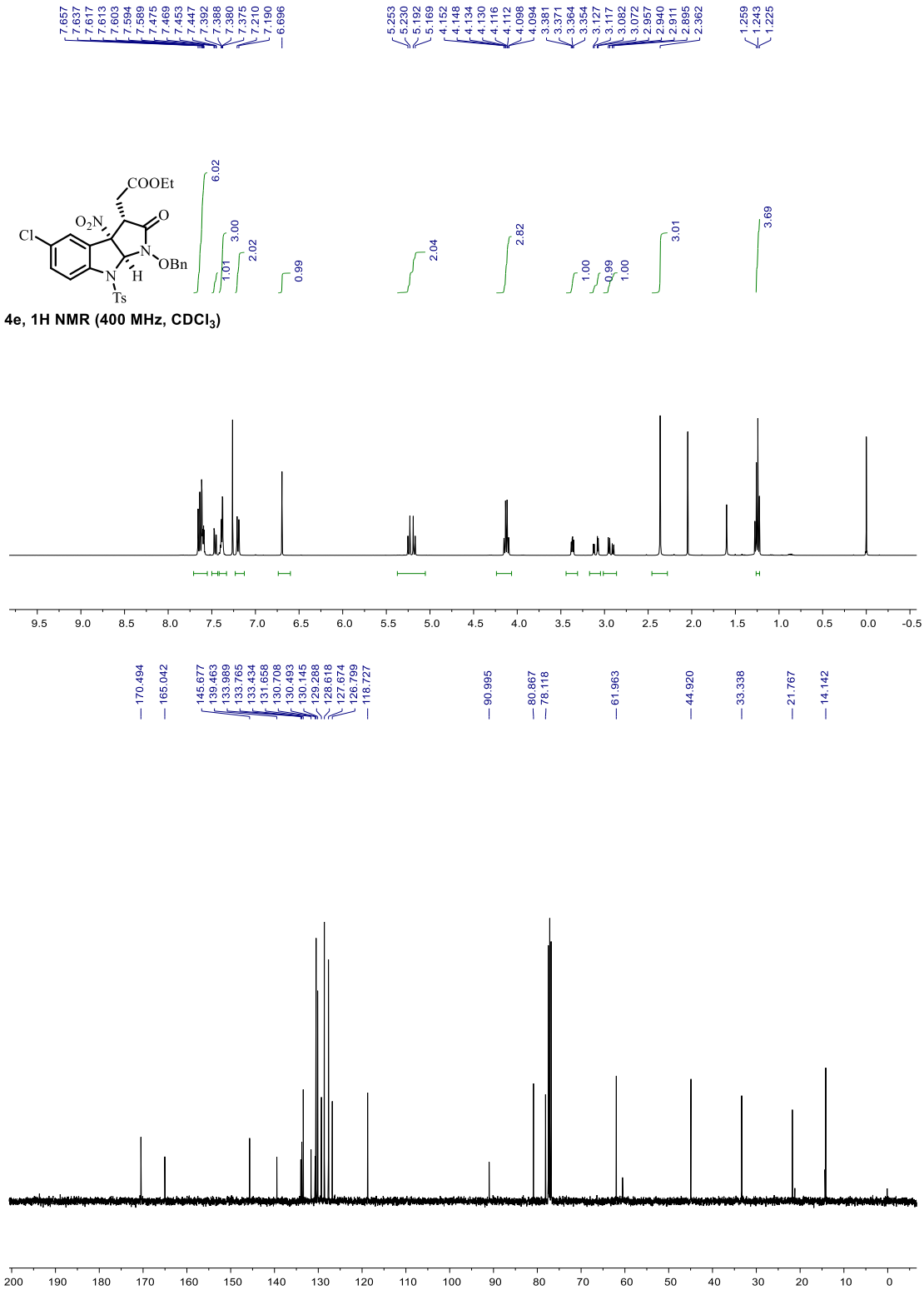
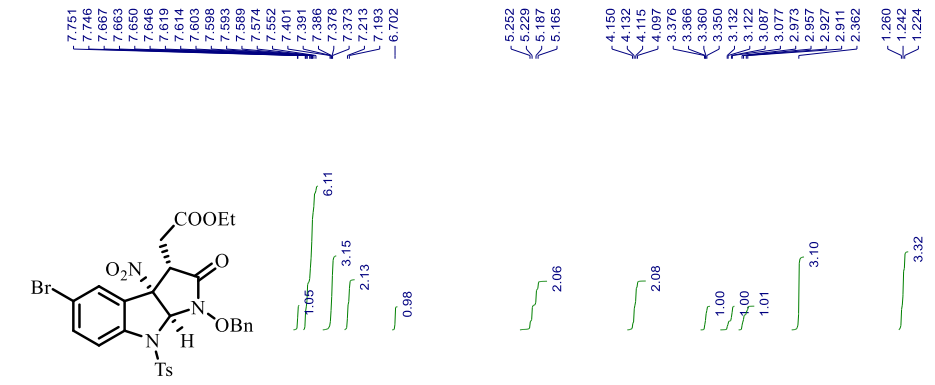
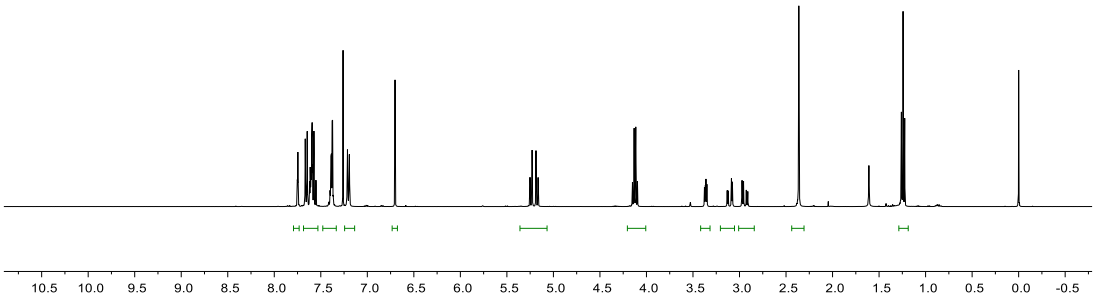
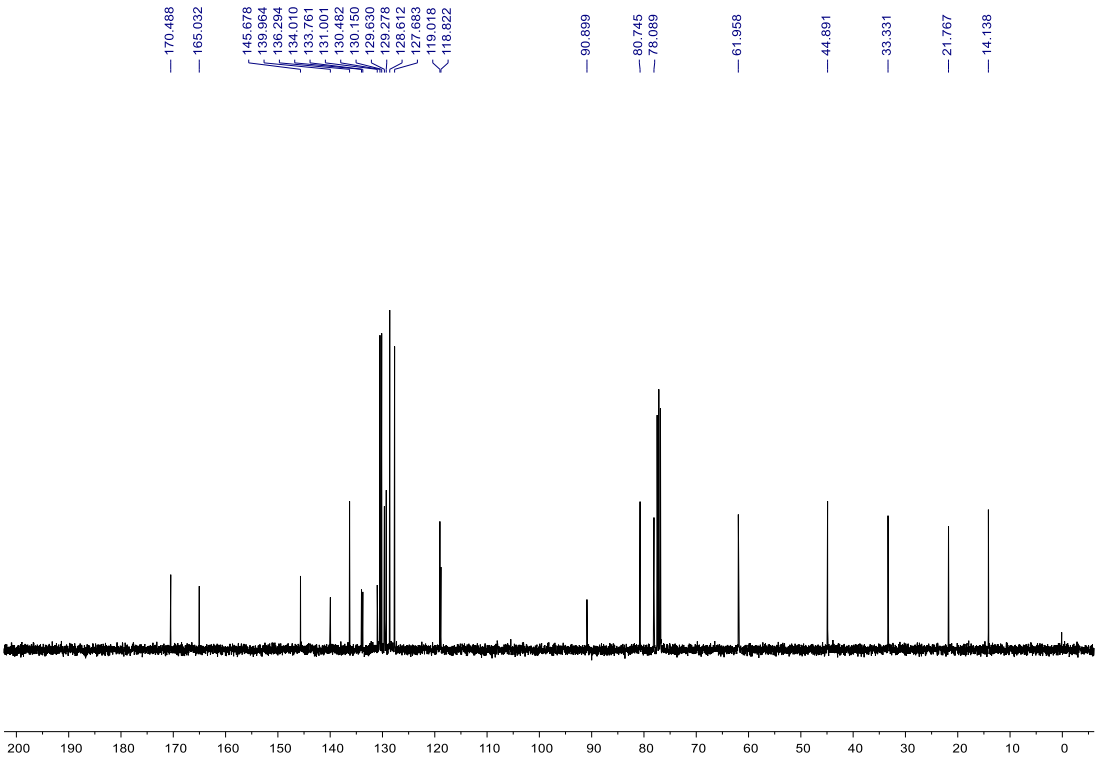


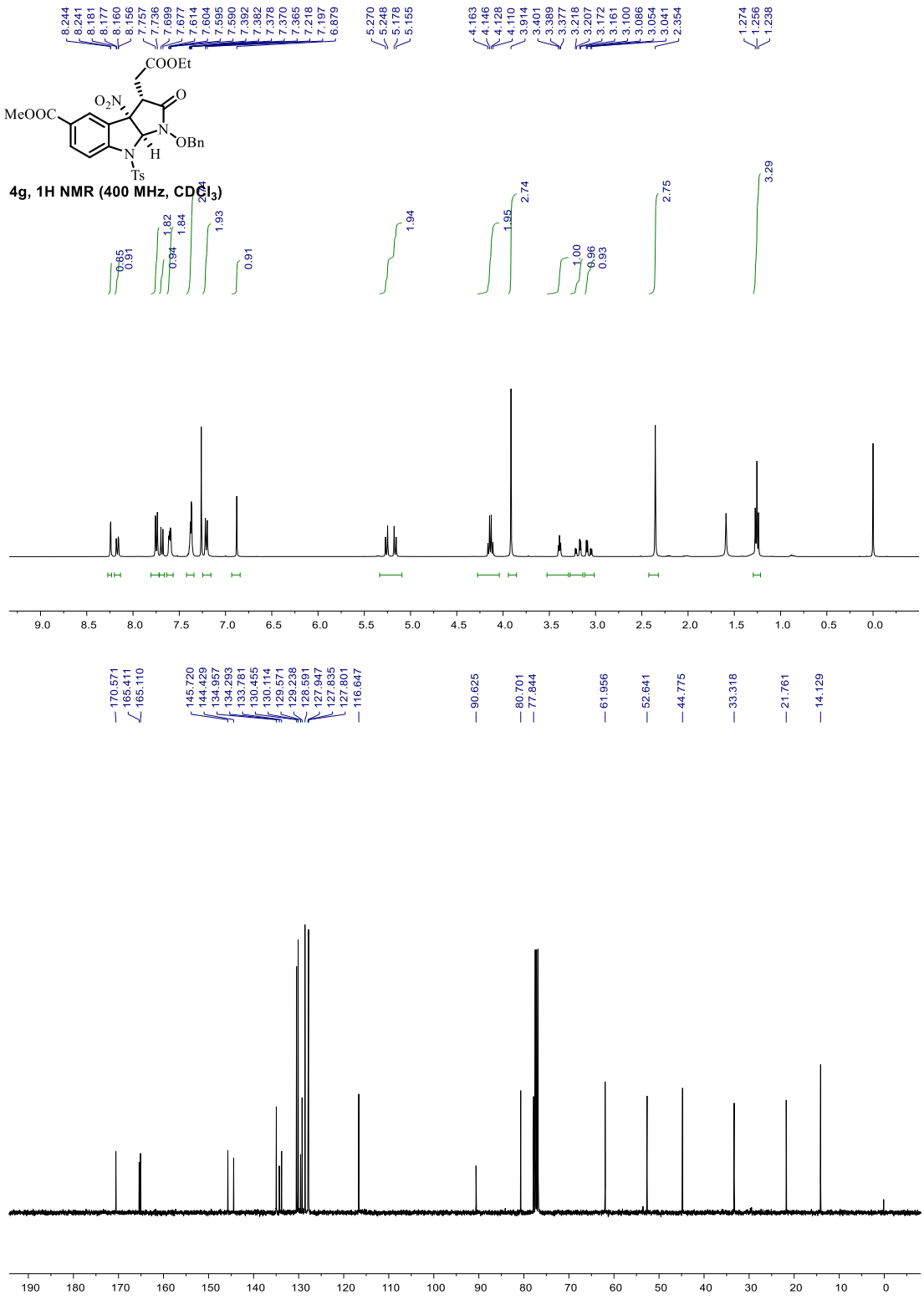
4e, 1H NMR (400 MHz, $CDCl_3$)

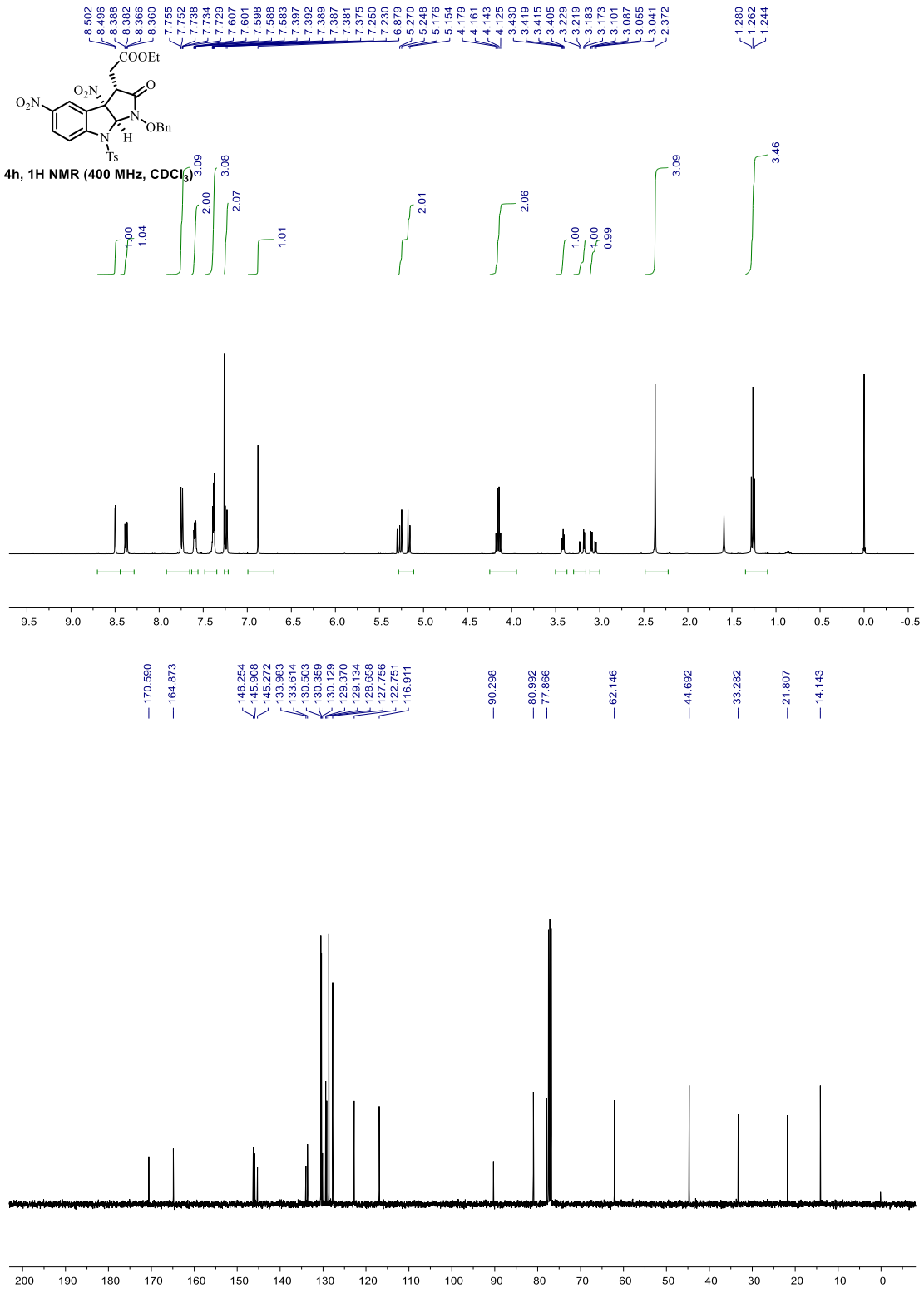


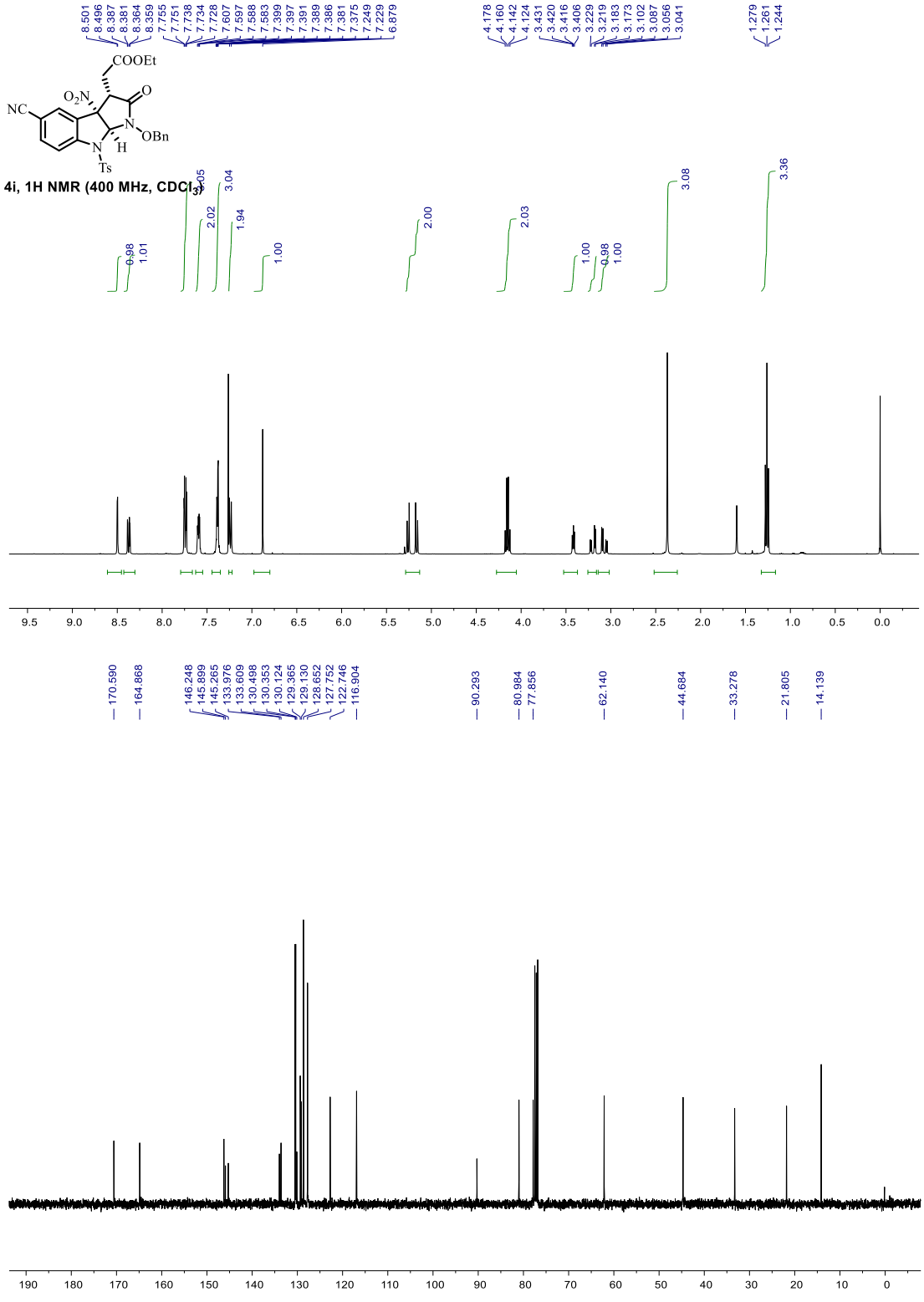
4f, 1H NMR (400 MHz, $CDCl_3$)

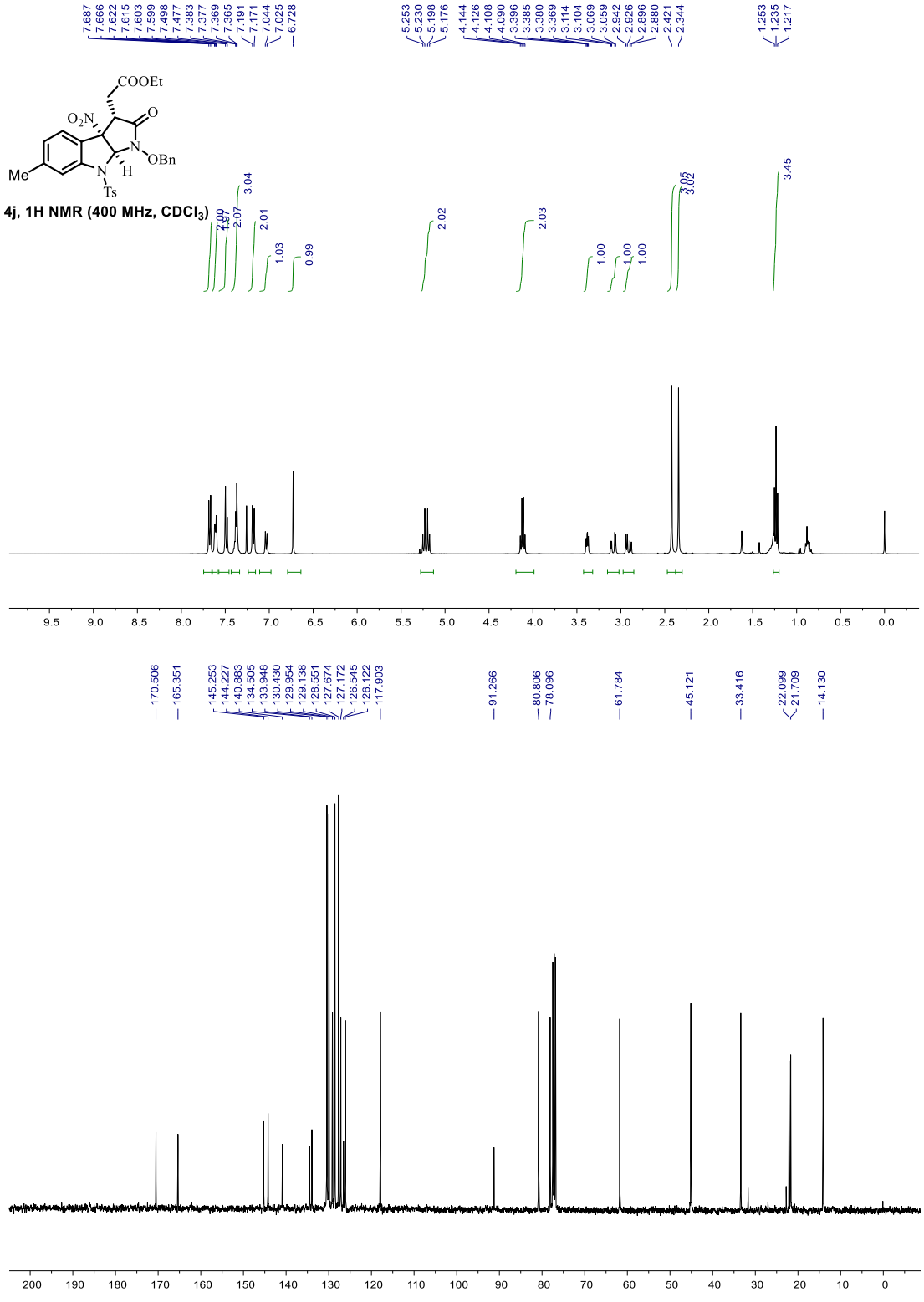


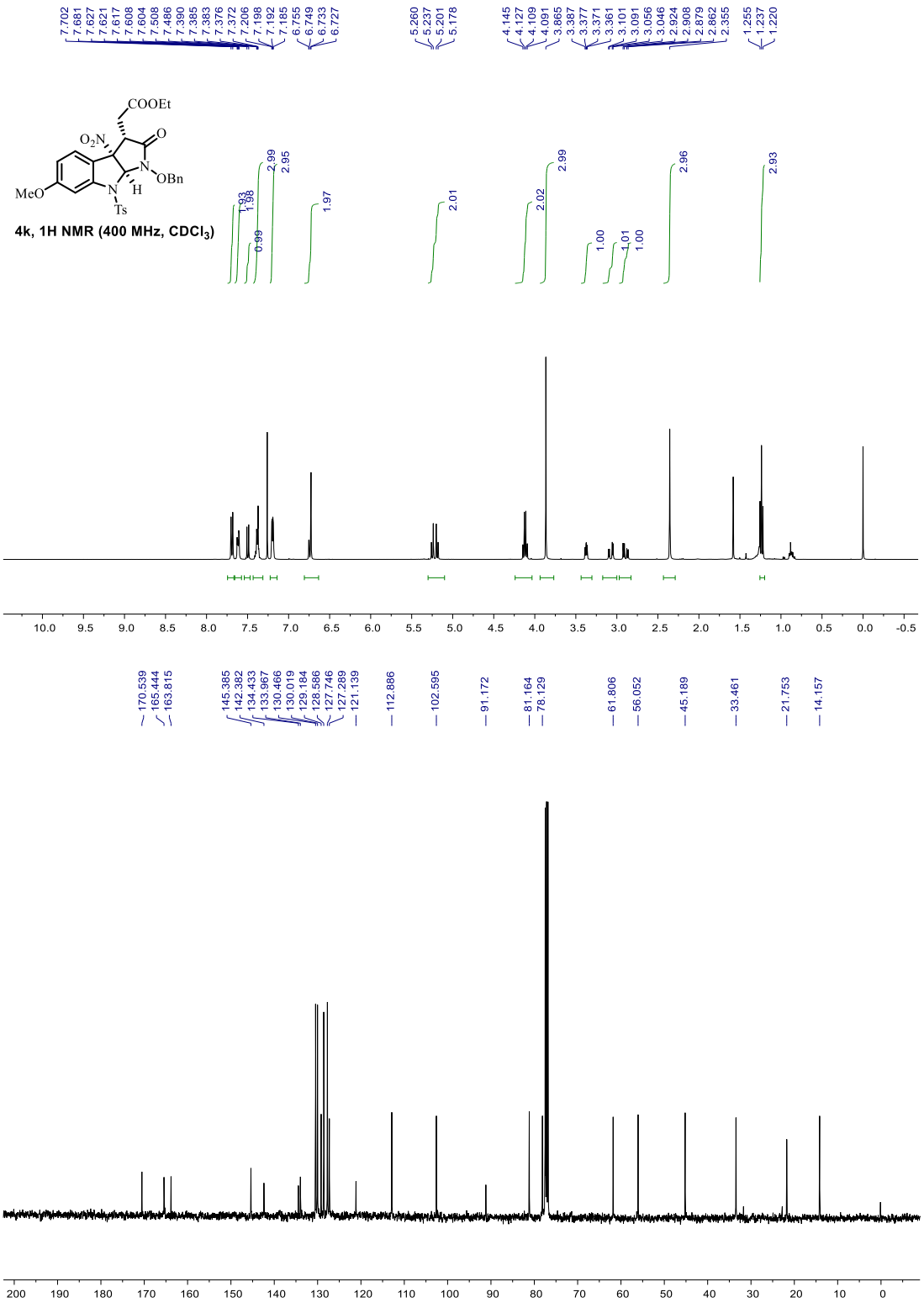



8.244
8.241
8.181
8.177
8.160
8.156
7.757
7.736
7.699
7.677
7.614
7.604
7.595
7.590
7.392
7.382
7.378
7.370
7.365
7.218
7.197
6.879
5.270
5.248
5.178
5.155
4.163
4.146
4.128
4.110
3.914
3.401
3.389
3.377
3.218
3.207
3.172
3.161
3.100
3.086
3.054
3.041
2.354
1.274
1.256
1.238
COOEt
MeOOC
O2N
O
N
OBn
N
H
Ts
4g, 1H NMR (400 MHz, CDCl3)
0.85
0.91
0.94
1.82
1.84
2.04
1.93
0.91
1.94
1.95
2.74
1.00
0.96
0.93
2.75
3.29
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.571
165.411
165.110
145.720
144.429
134.957
134.293
133.781
130.455
130.114
129.571
129.238
128.591
127.947
127.835
127.801
116.647
90.625
80.701
77.844
61.956
52.641
44.775
33.318
21.761
14.129
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


4h, 1H NMR (400 MHz, CDCl3)
COOEt
O2N
O2N
O
N
OBn
N
H
Ts
8.502
8.496
8.388
8.382
8.366
8.360
7.755
7.752
7.738
7.734
7.729
7.607
7.601
7.598
7.588
7.583
7.397
7.392
7.389
7.387
7.381
7.375
7.250
7.230
6.879
5.270
5.248
5.176
5.154
4.179
4.161
4.143
4.125
3.430
3.419
3.415
3.405
3.229
3.219
3.183
3.173
3.101
3.087
3.055
3.041
2.372
1.280
1.262
1.244
1.00
1.04
3.09
2.00
3.08
2.07
1.01
2.01
2.06
1.00
1.00
0.99
3.09
3.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
170.590
164.873
146.254
145.908
145.272
133.983
133.614
130.503
130.359
130.129
129.370
129.134
128.658
127.756
122.751
116.911
90.298
80.992
77.866
62.146
44.692
33.282
21.807
14.143
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


8.501
8.496
8.387
8.381
8.364
8.359
7.755
7.751
7.738
7.734
7.728
7.607
7.597
7.588
7.583
7.399
7.397
7.391
7.389
7.386
7.381
7.375
7.249
7.229
6.879
4.178
4.160
4.142
4.124
3.431
3.420
3.416
3.406
3.229
3.219
3.183
3.173
3.102
3.087
3.056
3.041
1.279
1.261
1.244
COOEt
O2N
NC
O
N
OBn
H
N
Ts
4i, 1H NMR (400 MHz, CDCl3)
0.98
1.01
3.05
2.02
3.04
1.94
1.00
2.00
2.03
1.00
0.98
1.00
3.08
3.36
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.590
164.868
146.248
145.899
145.265
133.976
133.609
130.498
130.353
130.124
129.365
129.130
128.652
127.752
122.746
116.904
90.293
80.984
77.856
62.140
44.684
33.278
21.805
14.139
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.687
7.666
7.622
7.615
7.603
7.599
7.498
7.477
7.383
7.377
7.369
7.365
7.191
7.171
7.044
7.025
6.728
5.253
5.230
5.198
5.176
4.144
4.126
4.108
4.090
3.396
3.385
3.380
3.369
3.114
3.104
3.069
3.059
2.942
2.926
2.896
2.880
2.421
2.344
1.253
1.235
1.217
COOEt
O2N
O
N
OBn
H
N
Ts
Me
4j, 1H NMR (400 MHz, CDCl3)
3.04
2.00
1.97
2.07
2.01
1.03
0.99
2.02
2.03
1.00
1.00
1.00
3.05
3.02
3.45
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.506
165.351
145.253
144.227
140.883
134.505
133.948
130.430
129.954
129.138
128.551
127.674
127.172
126.545
126.122
117.903
91.266
80.806
78.096
61.784
45.121
33.416
22.099
21.709
14.130
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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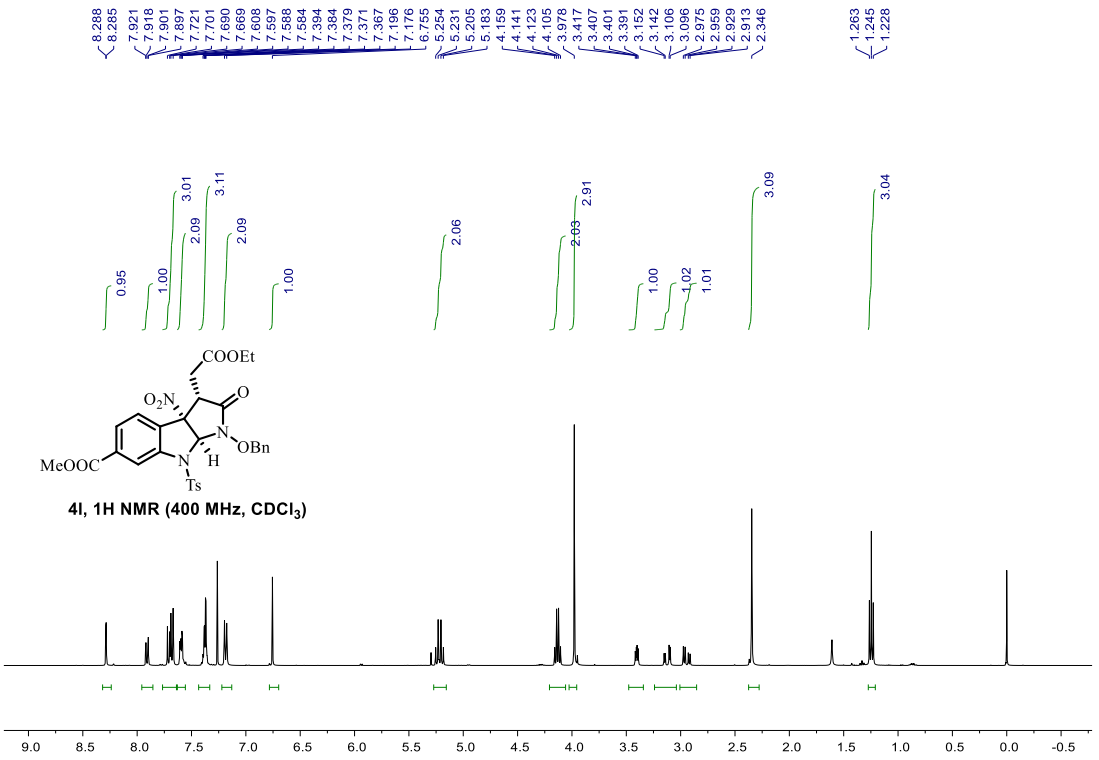
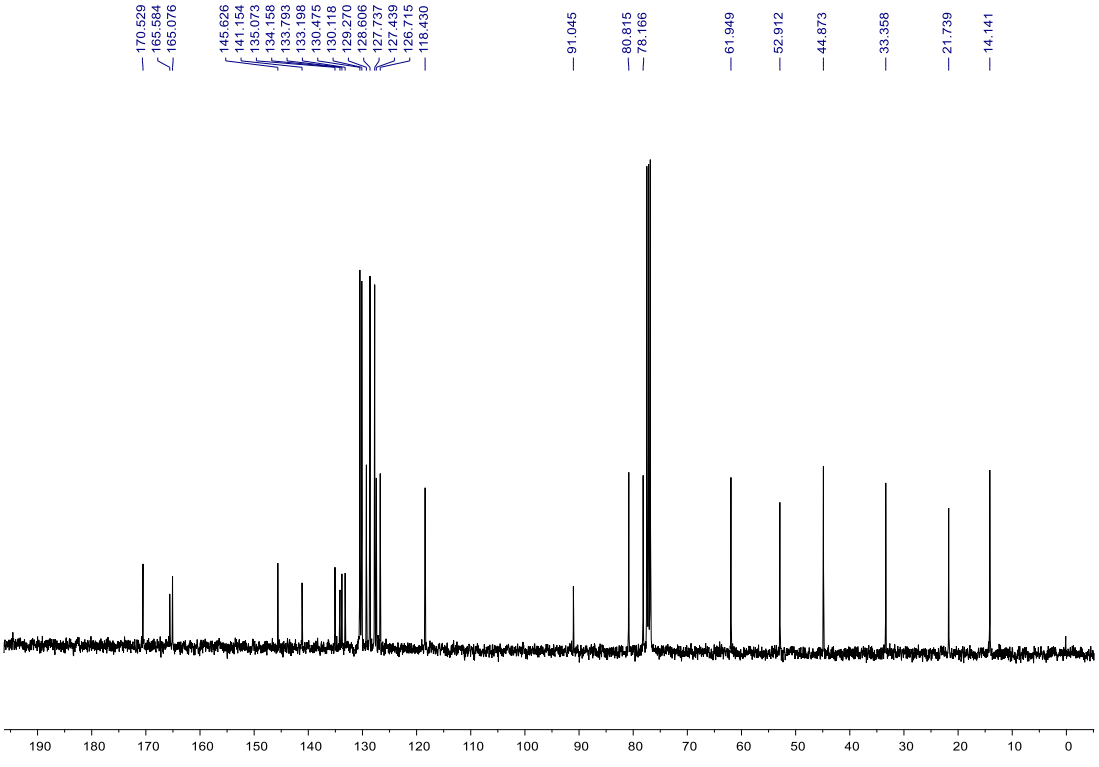
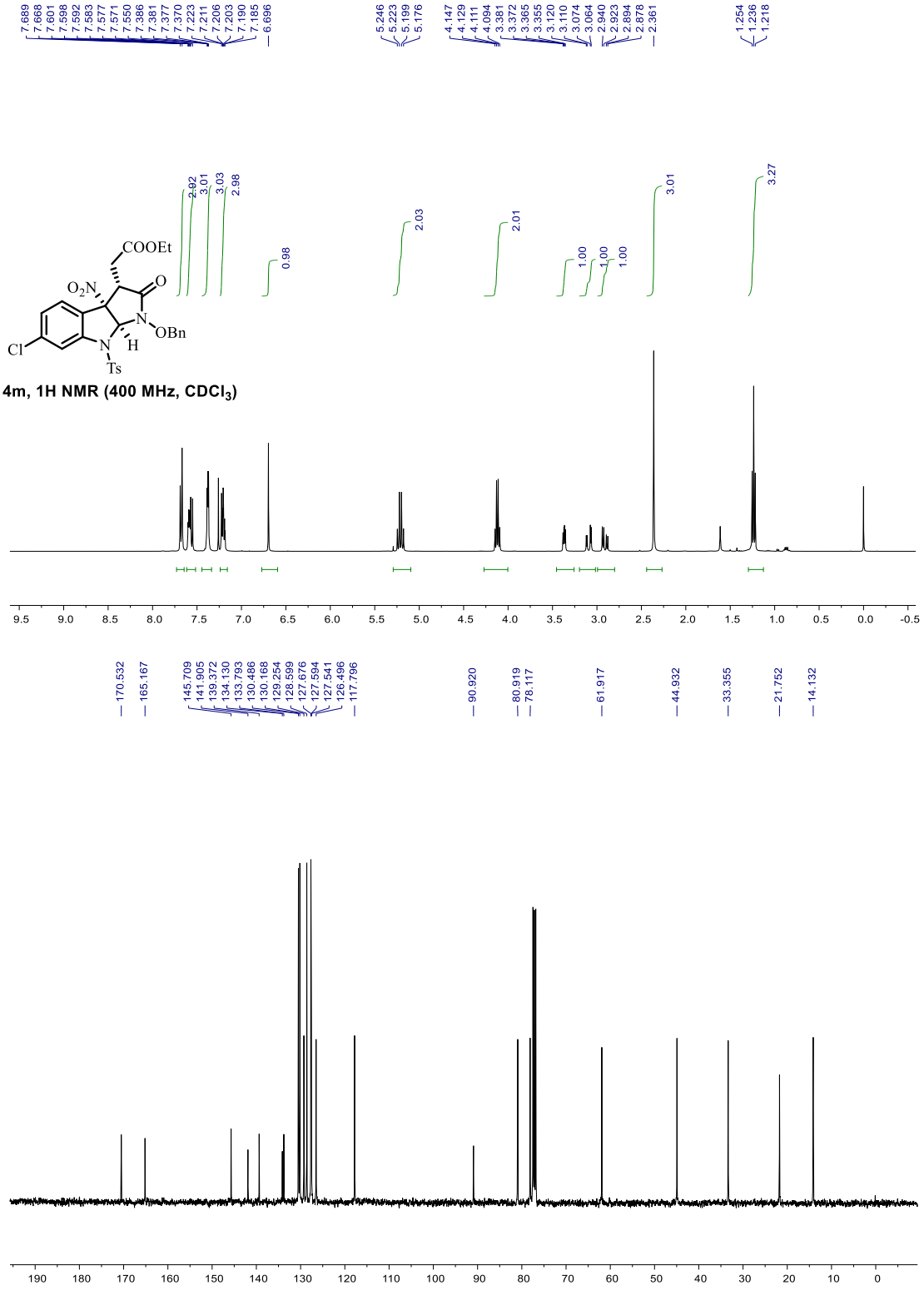
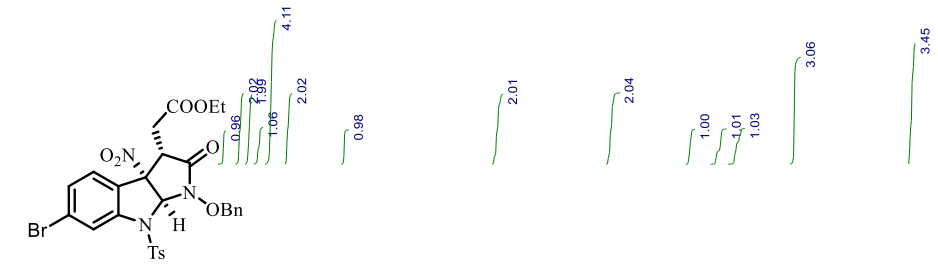
7.681
7.627
7.621
7.617
7.608
7.604
7.508
7.486
7.390
7.385
7.383
7.376
7.372
7.206
7.198
7.192
7.185
6.755
6.749
6.733
6.727
5.260
5.237
5.201
5.178
4.145
4.127
4.109
4.091
3.865
3.387
3.377
3.371
3.361
3.101
3.091
3.056
3.046
2.924
2.908
2.879
2.862
2.355
1.255
1.237
1.220
COOEt
O2N
O
N
OBn
MeO
N
H
Ts
4k, 1H NMR (400 MHz, CDCl3)
1.93
1.88
0.99
2.99
2.95
1.97
2.01
2.02
2.99
1.00
1.01
1.00
2.96
2.93
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
170.539
165.444
163.815
145.385
142.382
134.433
133.967
130.466
130.019
129.184
128.586
127.746
127.289
121.139
112.886
102.595
91.172
81.164
78.129
61.806
56.052
45.189
33.461
21.753
14.157
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

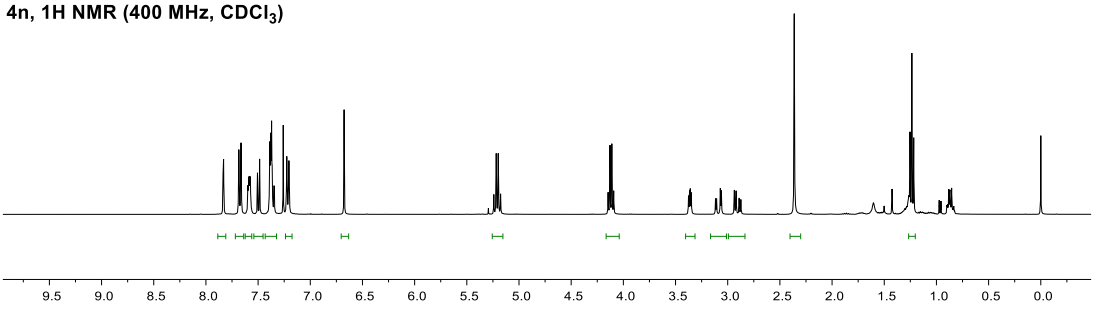

8.288
8.285
7.921
7.918
7.901
7.897
7.721
7.701
7.690
7.669
7.608
7.597
7.588
7.584
7.394
7.384
7.379
7.371
7.367
7.196
7.176
6.755
5.254
5.231
5.205
5.183
4.159
4.141
4.123
4.105
3.978
3.417
3.407
3.401
3.391
3.152
3.142
3.106
3.096
2.975
2.959
2.929
2.913
2.346
1.263
1.245
1.228
0.95
1.00
3.01
2.09
3.11
2.09
1.00
2.06
2.03
2.91
1.00
1.02
1.01
3.09
3.04
COOEt
O2N
O
N
OBn
MeOOC
N
H
Ts
4l, 1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

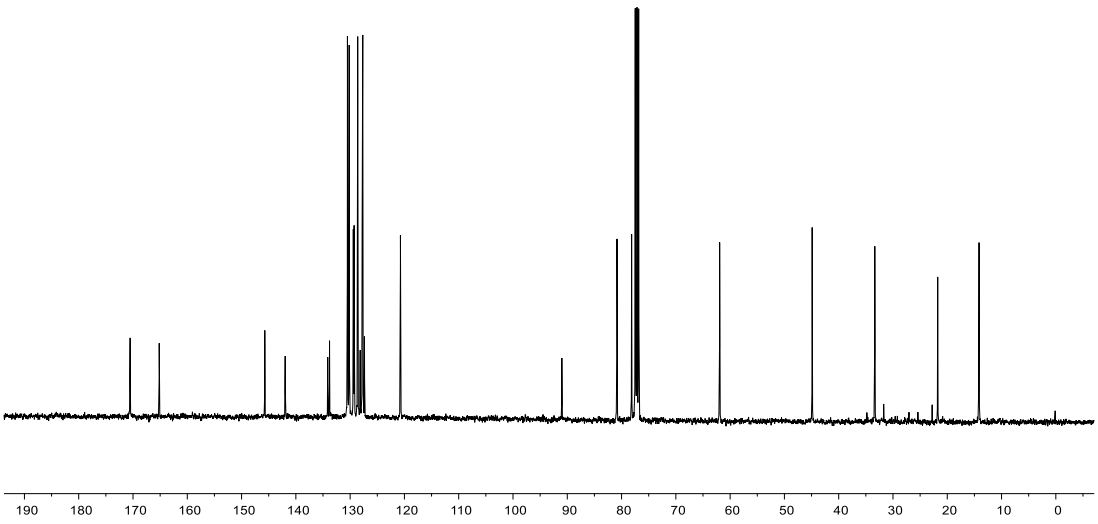

170.529
165.584
165.076
145.626
141.154
135.073
134.158
133.793
133.198
130.475
130.118
129.270
128.606
127.737
127.439
126.715
118.430
91.045
80.815
78.166
61.949
52.912
44.873
33.358
21.739
14.141
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

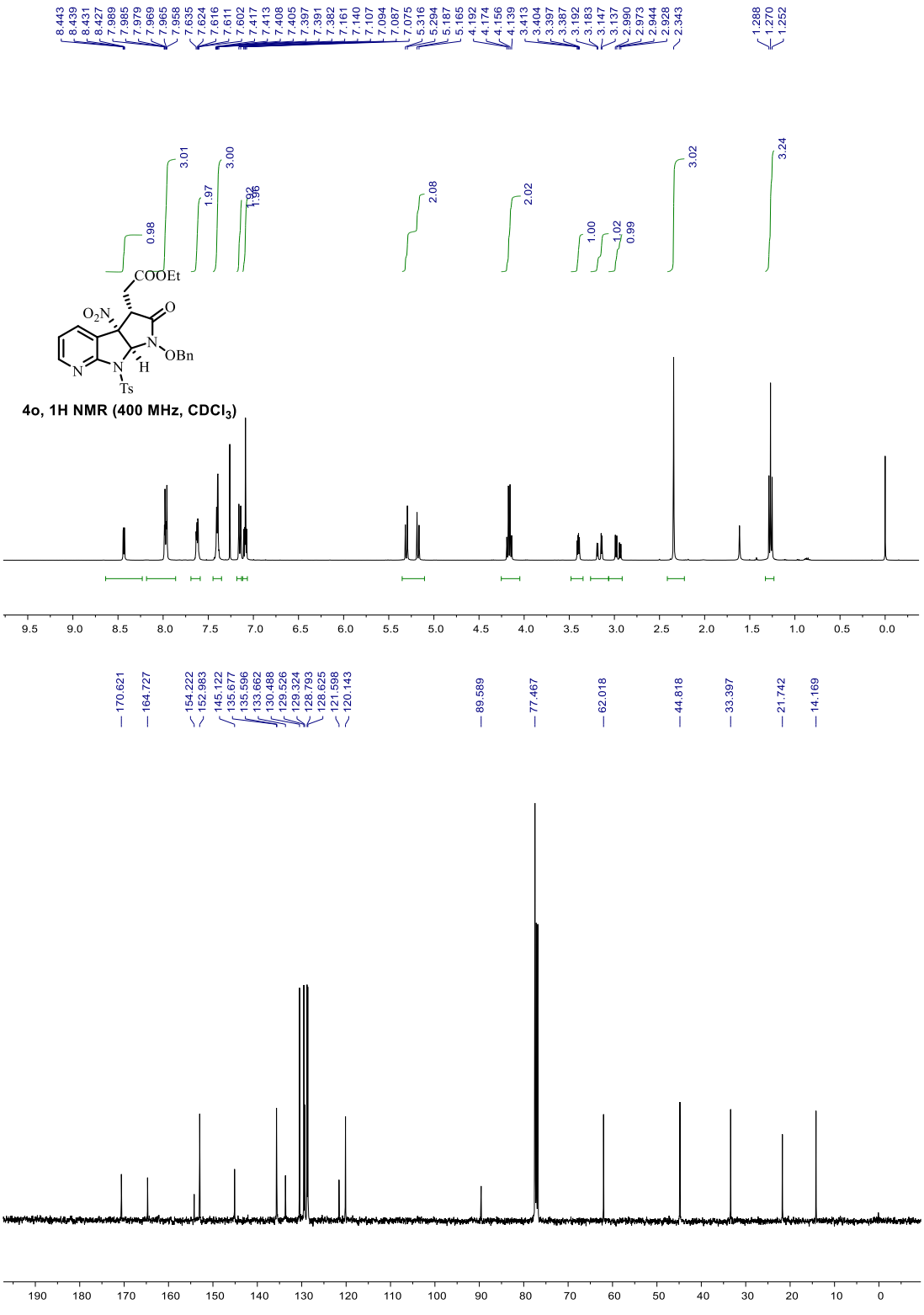

7.689
7.668
7.601
7.598
7.592
7.583
7.577
7.571
7.550
7.386
7.381
7.377
7.370
7.223
7.211
7.206
7.203
7.190
7.185
6.696
5.246
5.223
5.199
5.176
4.147
4.129
4.111
4.094
3.381
3.372
3.365
3.355
3.120
3.110
3.074
3.064
2.940
2.923
2.894
2.878
2.361
1.254
1.236
1.218
2.92
3.01
3.03
2.98
0.98
2.03
2.01
1.00
1.00
1.00
3.01
3.27
COOEt
O2N
O
N
OBn
Cl
N
H
Ts
4m, 1H NMR (400 MHz, CDCl3)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
170.532
165.167
145.709
141.905
139.372
134.130
133.793
130.486
130.168
129.254
128.599
127.676
127.594
127.541
126.496
117.796
90.920
80.919
78.117
61.917
44.932
33.355
21.752
14.132
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



4n, 1H NMR (400 MHz, $CDCl_3$)



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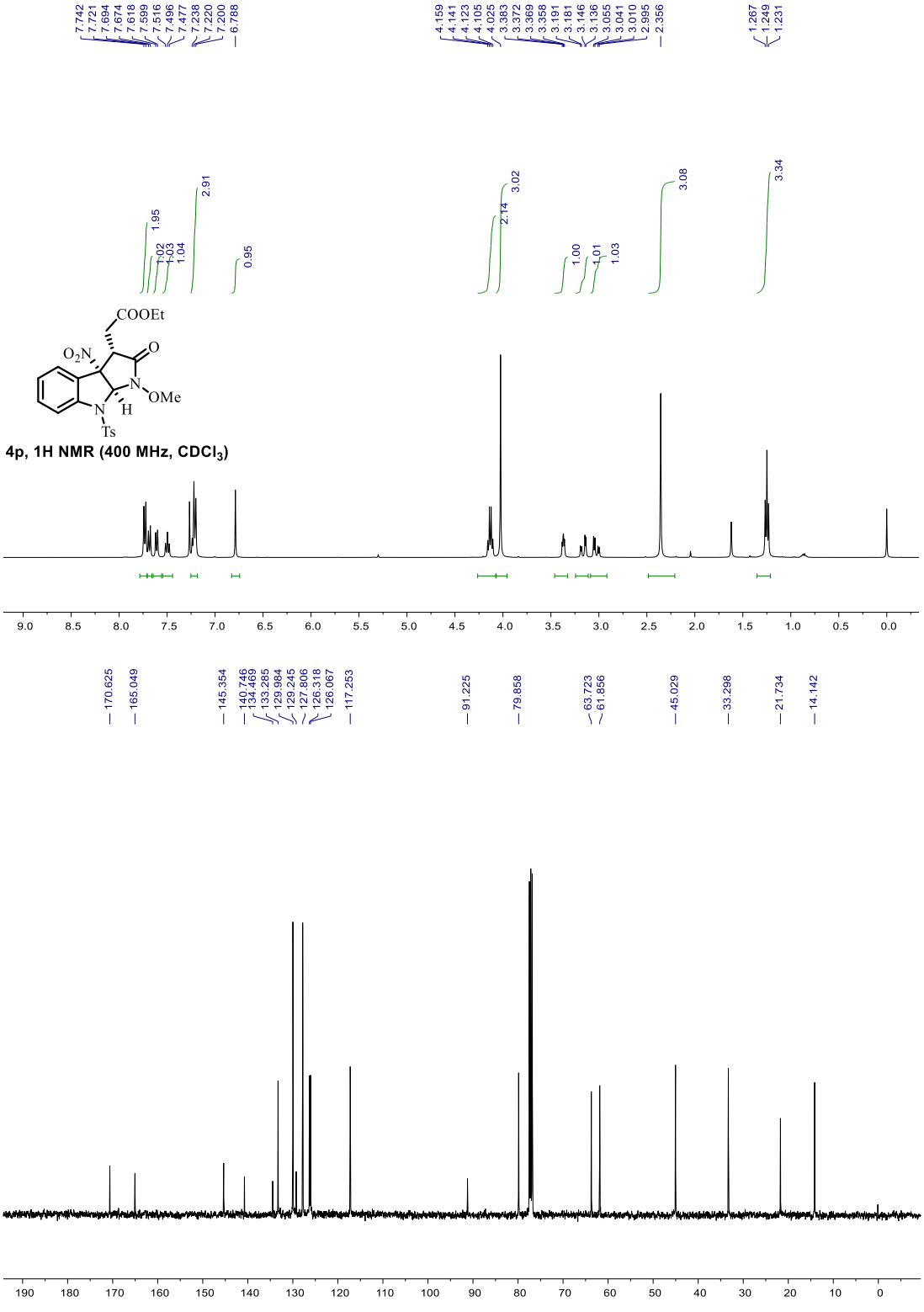
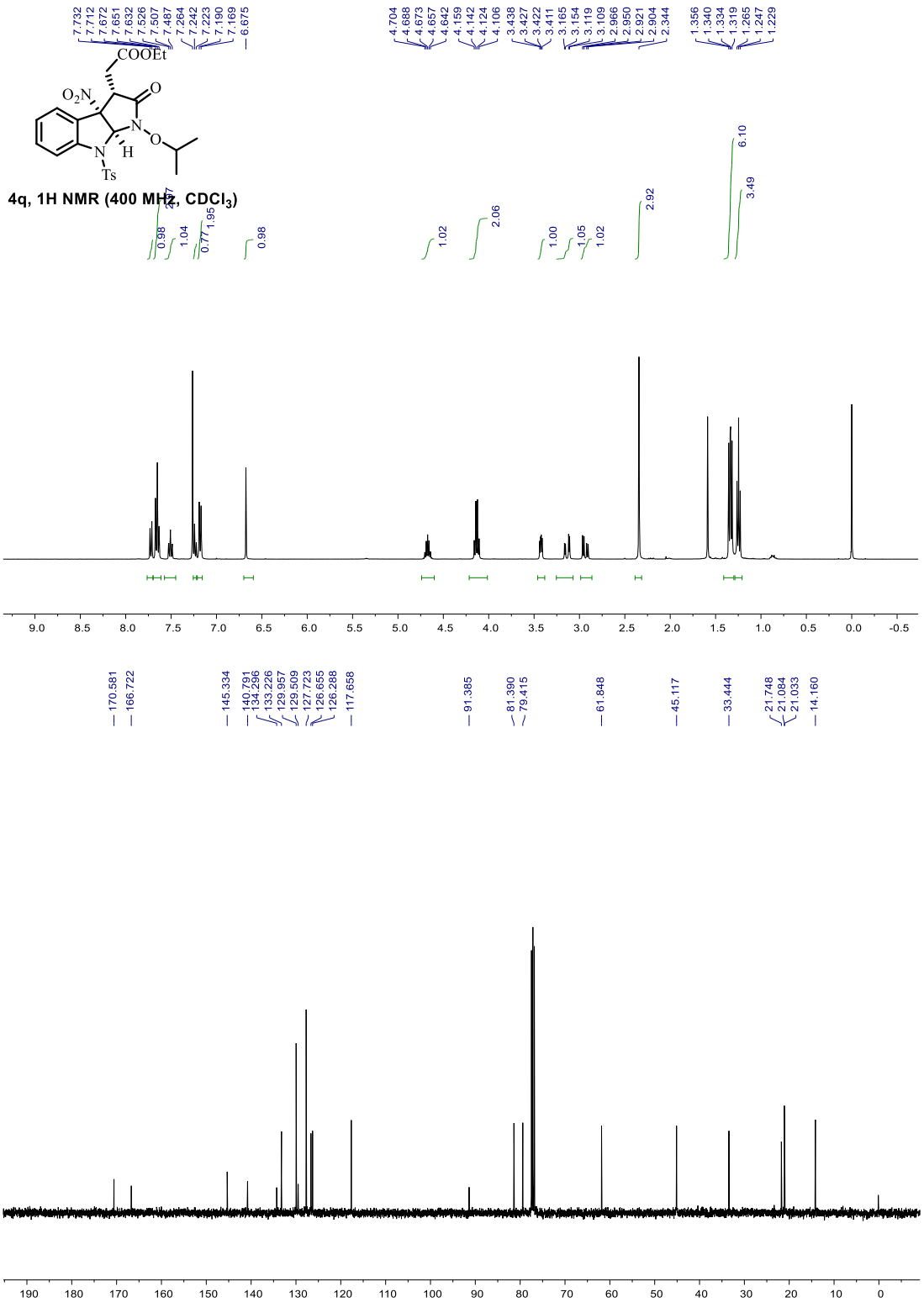
8.439
8.431
8.427
7.989
7.985
7.979
7.969
7.965
7.958
7.635
7.624
7.616
7.611
7.602
7.417
7.413
7.408
7.405
7.397
7.391
7.382
7.161
7.140
7.107
7.094
7.087
7.075
5.316
5.294
5.187
5.165
4.192
4.174
4.156
4.139
3.413
3.404
3.397
3.387
3.192
3.183
3.147
3.137
2.990
2.973
2.944
2.928
2.343
1.288
1.270
1.252
0.98
3.01
3.00
1.97
1.92
1.96
2.08
2.02
1.00
1.02
0.99
3.02
3.24
COOEt
O2N
O
N
OBn
N
H
Ts
4o, 1H NMR (400 MHz, CDCl3)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.621
164.727
154.222
152.983
145.122
135.677
135.596
133.662
130.488
129.526
129.324
128.793
128.625
121.598
120.143
89.589
77.467
62.018
44.818
33.397
21.742
14.169
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.742
7.721
7.694
7.674
7.618
7.599
7.516
7.496
7.477
7.238
7.220
7.200
6.788
4.159
4.141
4.123
4.105
4.025
3.383
3.372
3.369
3.358
3.191
3.181
3.146
3.136
3.055
3.041
3.010
2.995
2.356
1.267
1.249
1.231
1.95
1.02
1.03
1.04
2.91
0.95
3.02
2.14
1.00
1.01
1.03
3.08
3.34
COOEt
O2N
O
N
OMe
N
H
Ts
4p, 1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.625
165.049
145.354
140.746
134.469
133.285
129.984
129.245
127.806
126.318
126.067
117.253
91.225
79.858
63.723
61.856
45.029
33.298
21.734
14.142
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.732
7.712
7.672
7.651
7.632
7.526
7.507
7.487
7.264
7.242
7.223
7.190
7.169
6.675
4.704
4.688
4.673
4.657
4.642
4.159
4.142
4.124
4.106
3.438
3.427
3.422
3.411
3.165
3.154
3.119
3.109
2.966
2.950
2.921
2.904
2.344
1.356
1.340
1.334
1.319
1.265
1.247
1.229
COOEt
O2N
O
N
O
N
H
Ts
4q, 1H NMR (400 MHz, CDCl3)
0.98
1.04
0.77
1.95
0.98
1.02
2.06
1.00
1.05
1.02
2.92
6.10
3.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
170.581
166.722
145.334
140.791
134.296
133.226
129.957
129.509
127.723
126.655
126.288
117.658
91.385
81.390
79.415
61.848
45.117
33.444
21.748
21.084
21.033
14.160
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
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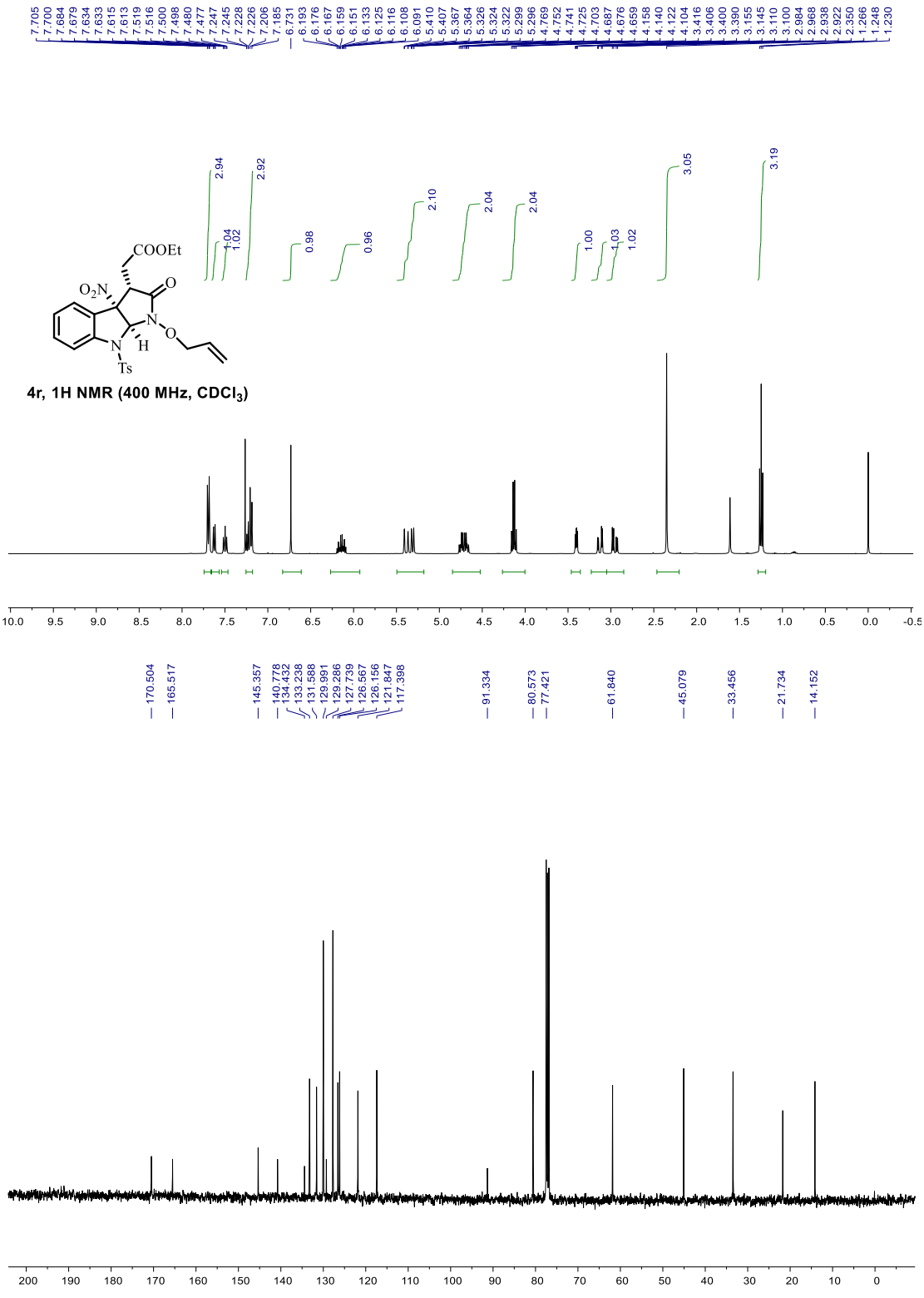
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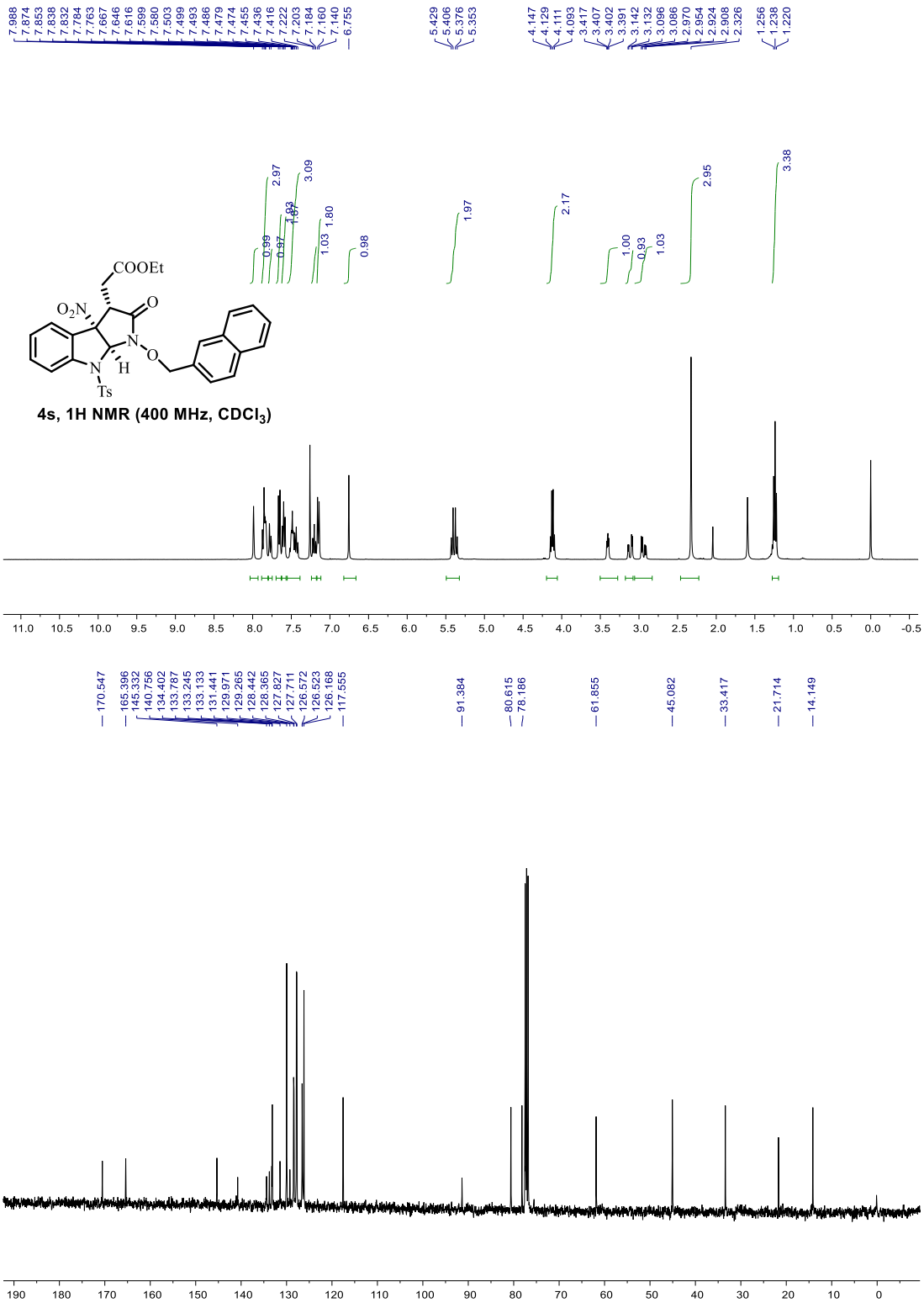
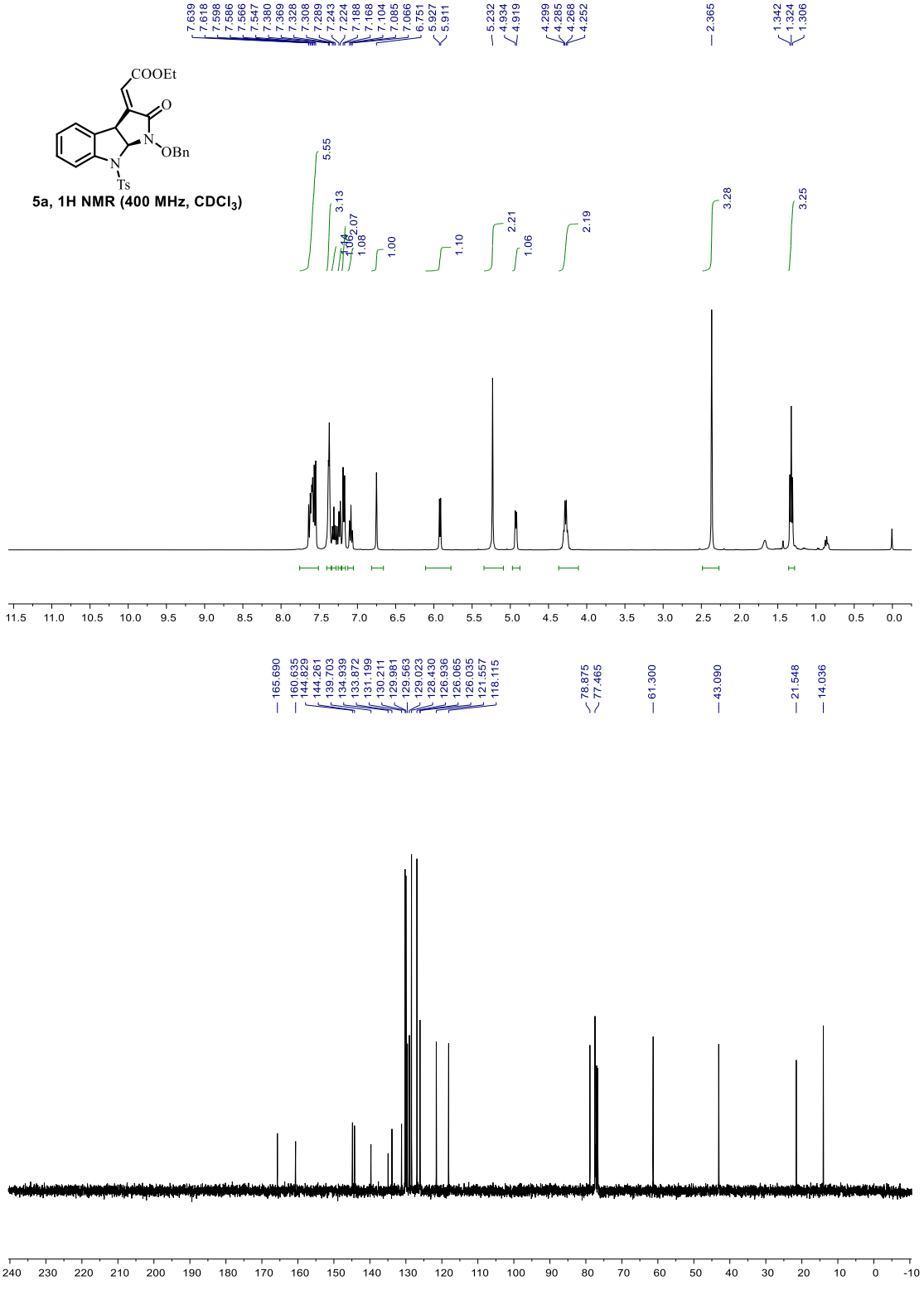
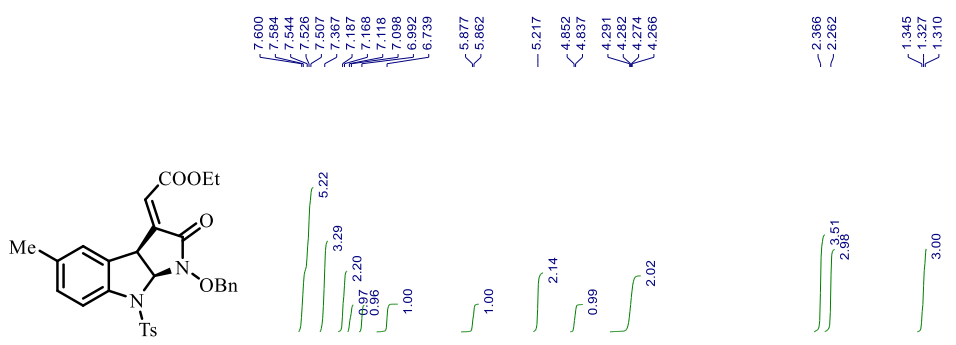
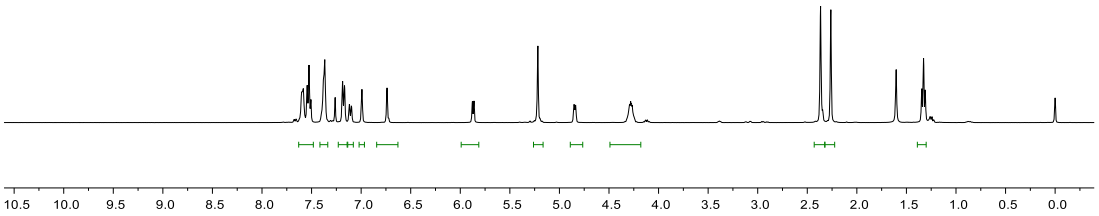
7.700
7.684
7.679
7.634
7.633
7.615
7.613
7.519
7.516
7.500
7.498
7.480
7.477
7.247
7.245
7.228
7.226
7.206
7.185
6.731
6.193
6.176
6.167
6.159
6.151
6.133
6.125
6.116
6.108
6.091
5.410
5.407
5.367
5.364
5.326
5.324
5.322
5.299
5.296
4.769
4.752
4.741
4.725
4.703
4.687
4.676
4.659
4.158
4.140
4.122
4.104
3.416
3.406
3.400
3.390
3.155
3.145
3.110
3.100
2.984
2.968
2.938
2.922
2.350
1.266
1.248
1.230
2.94
1.04
1.02
2.92
0.98
0.96
2.10
2.04
2.04
1.00
1.03
1.02
3.05
3.19
COOEt
O2N
O
N
O
N
H
Ts
4r, 1H NMR (400 MHz, CDCl3)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
170.504
165.517
145.357
140.778
134.432
133.238
131.588
129.991
129.286
127.739
126.567
126.156
121.847
117.398
91.334
80.573
77.421
61.840
45.079
33.456
21.734
14.152
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

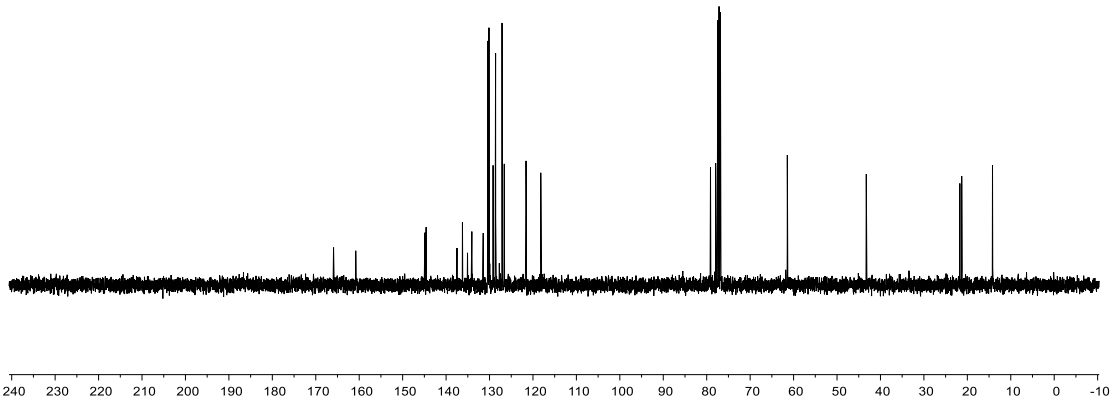

7.988
7.874
7.853
7.838
7.832
7.784
7.763
7.667
7.646
7.616
7.599
7.580
7.503
7.499
7.493
7.486
7.479
7.474
7.455
7.436
7.416
7.222
7.203
7.184
7.160
7.140
6.755
5.429
5.406
5.376
5.353
4.147
4.129
4.111
4.093
3.417
3.407
3.402
3.391
3.142
3.132
3.096
3.086
2.970
2.954
2.924
2.908
2.326
1.256
1.238
1.220
2.97
3.09
1.80
1.03
0.98
1.97
2.17
1.00
0.93
1.03
2.95
3.38
0.99
0.97
COOEt
O2N
O
N
O
N
H
Ts
4s, 1H NMR (400 MHz, CDCl3)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
170.547
165.396
145.332
140.756
134.402
133.787
133.245
133.133
131.441
129.971
129.265
128.442
128.365
127.827
127.711
126.572
126.523
126.168
117.555
91.384
80.615
78.186
61.855
45.082
33.417
21.714
14.149
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

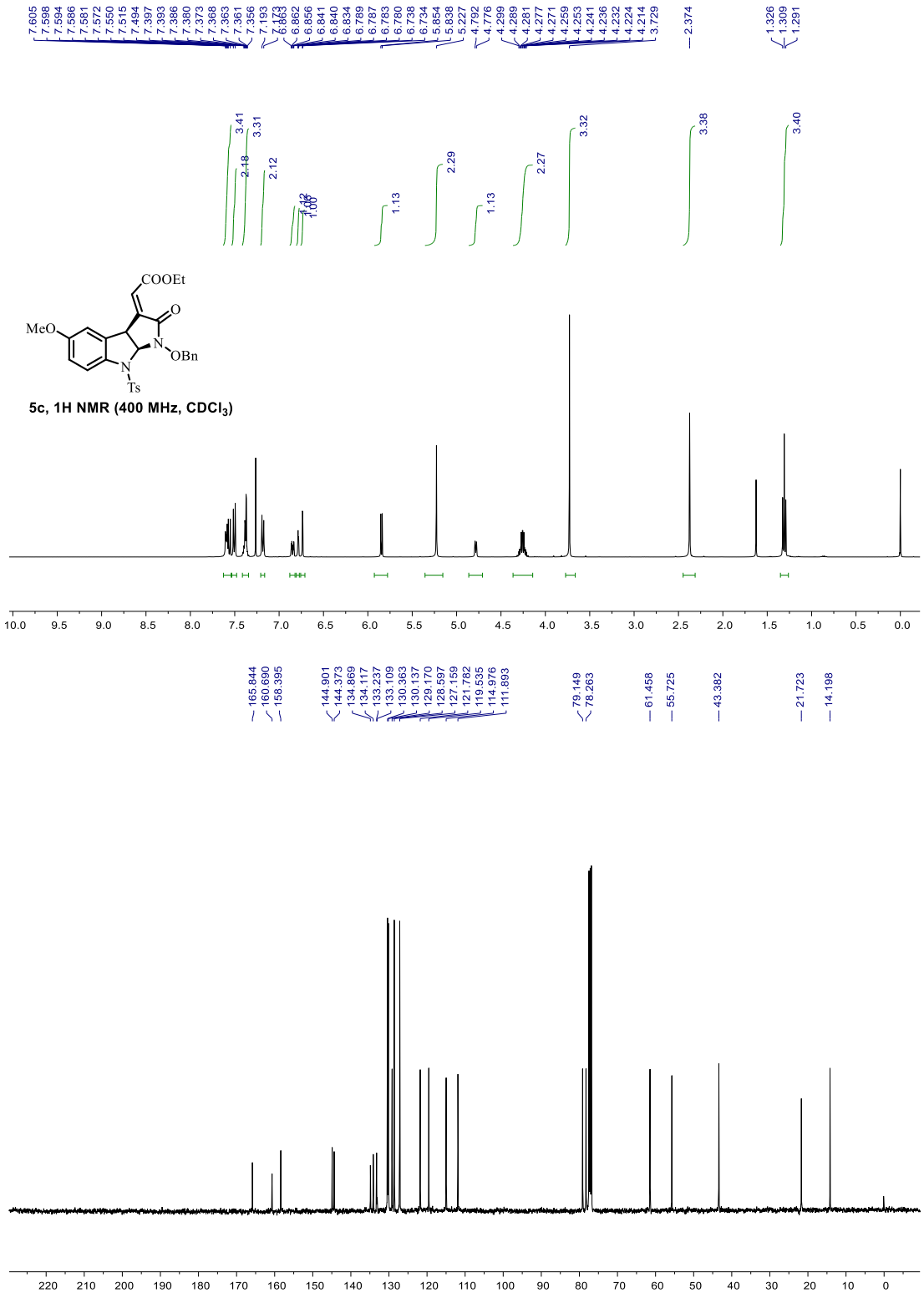

COOEt
O
N
OBn
N
Ts
5a, 1H NMR (400 MHz, CDCl3)
7.639
7.618
7.598
7.586
7.566
7.547
7.380
7.369
7.328
7.308
7.289
7.243
7.224
7.188
7.168
7.104
7.085
7.066
6.751
5.927
5.911
5.232
4.934
4.919
4.299
4.285
4.268
4.252
2.365
1.342
1.324
1.306
5.55
3.13
2.07
2.04
1.08
1.00
1.10
2.21
1.06
2.19
3.28
3.25
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
165.690
160.635
144.829
144.261
139.703
134.939
133.872
131.199
130.211
129.981
129.563
129.023
128.430
126.936
126.065
126.035
121.557
118.115
78.875
77.465
61.300
43.090
21.548
14.036
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

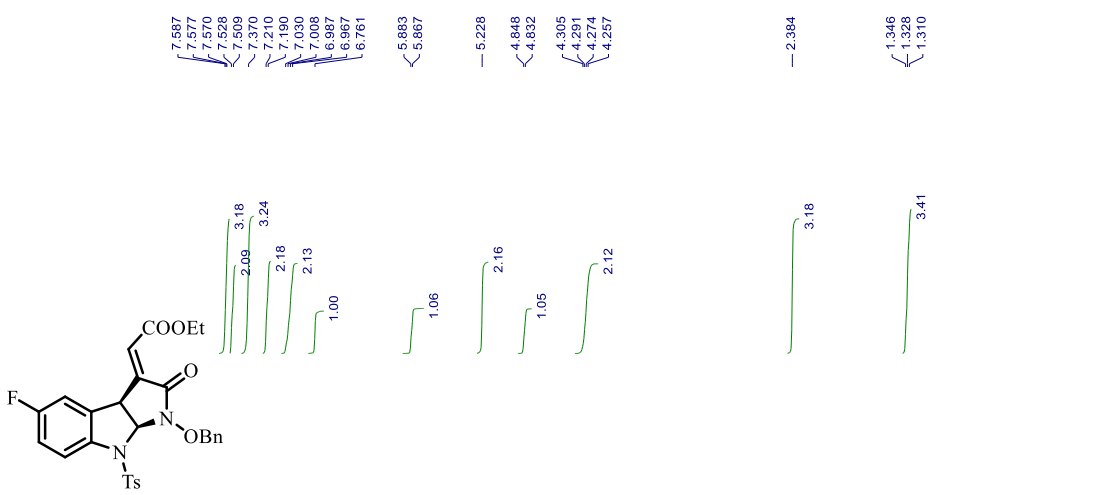


5b, 1H NMR (400 MHz, $CDCl_3$)

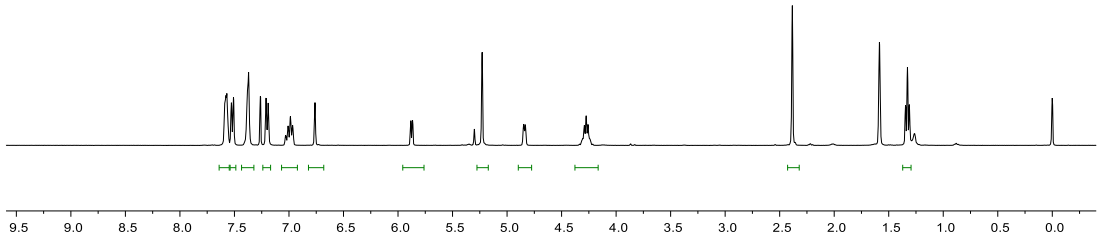


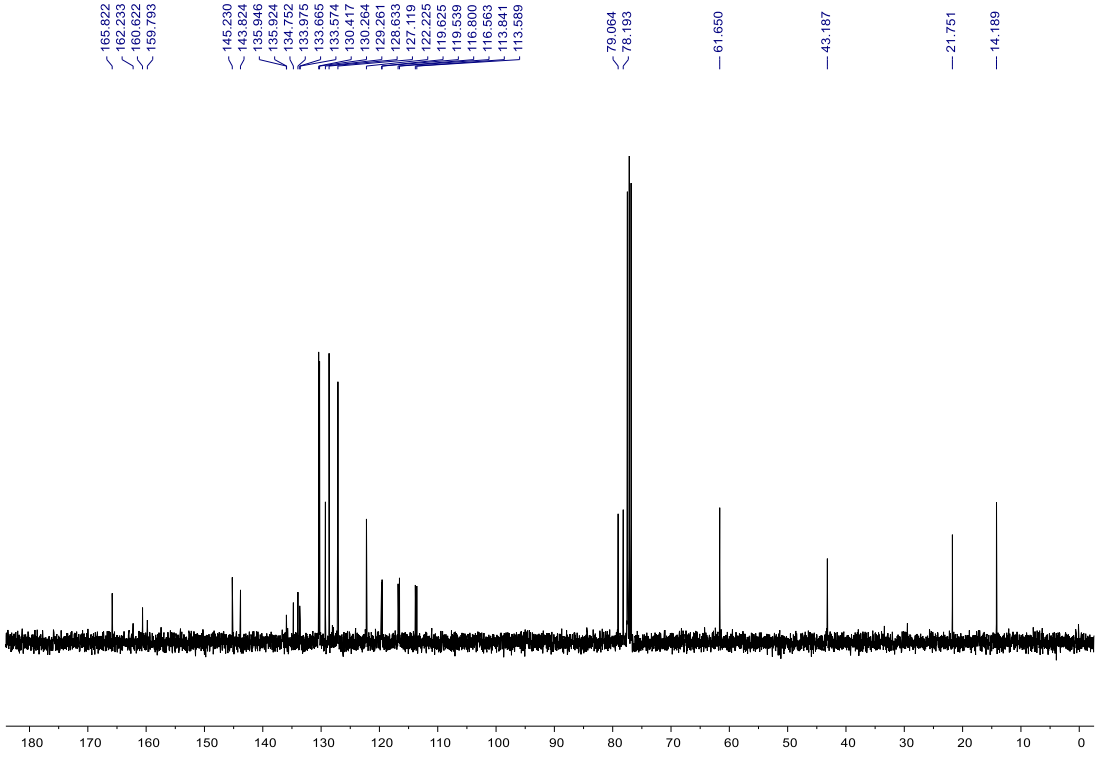


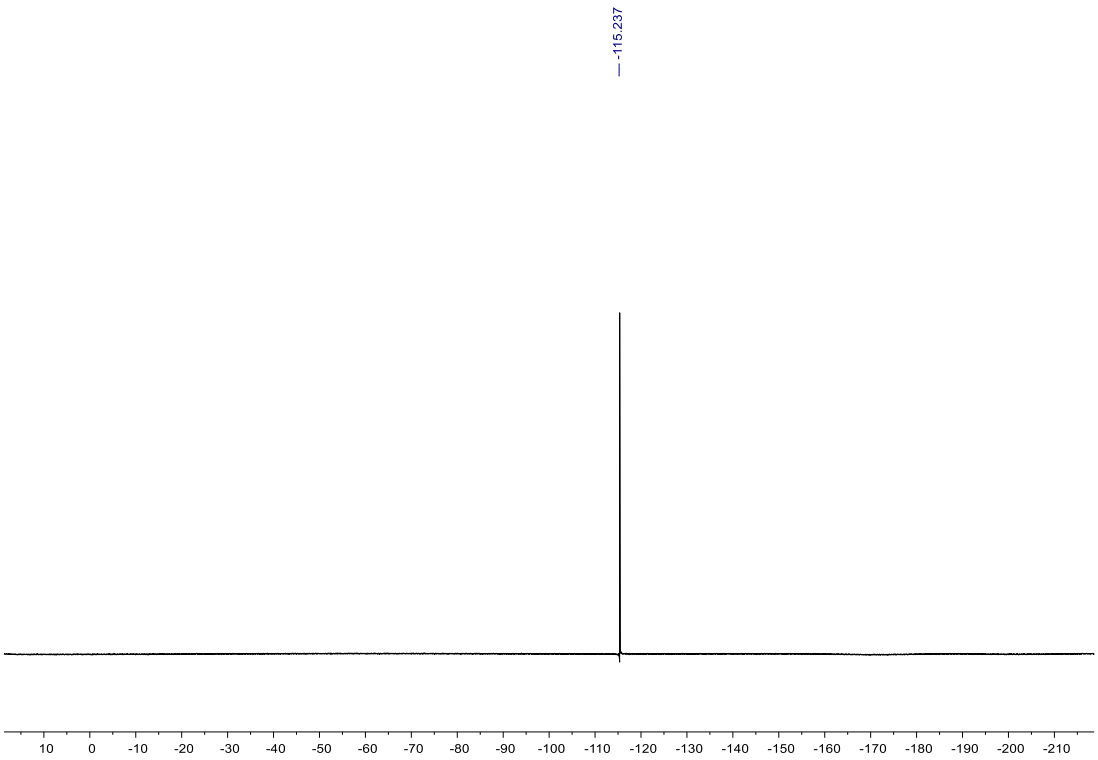

7.605
7.598
7.594
7.586
7.581
7.572
7.550
7.515
7.494
7.397
7.393
7.386
7.380
7.373
7.368
7.363
7.361
7.356
7.193
7.173
6.863
6.862
6.856
6.841
6.840
6.834
6.789
6.787
6.783
6.780
6.738
6.734
5.854
5.838
5.227
4.792
4.776
4.299
4.289
4.281
4.277
4.271
4.259
4.253
4.241
4.236
4.232
4.224
4.214
3.729
2.374
1.326
1.309
1.291
3.41
3.31
2.18
2.12
1.13
2.29
1.13
2.27
3.32
3.38
3.40
COOEt
O
MeO
N
OBn
N
Ts
5c, 1H NMR (400 MHz, CDCl3)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
165.844
160.690
158.395
144.901
144.373
134.869
134.117
133.237
133.109
130.363
130.137
129.170
128.597
127.159
121.782
119.535
114.976
111.893
79.149
78.263
61.458
55.725
43.382
21.723
14.198
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

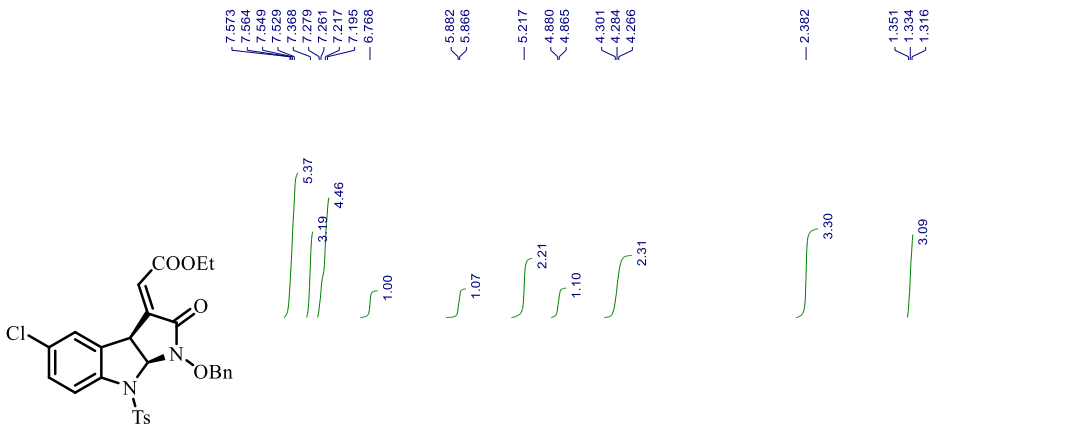


5d, 1H NMR (400 MHz, $CDCl_3$)

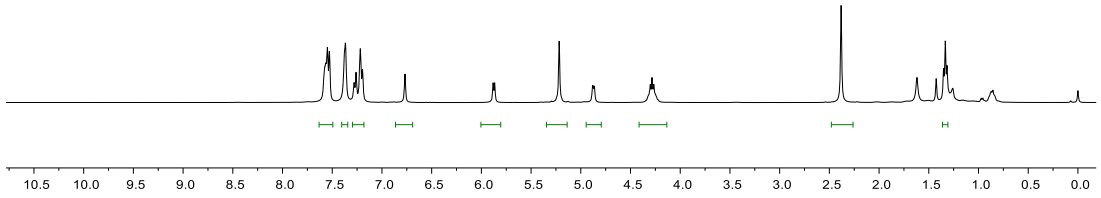


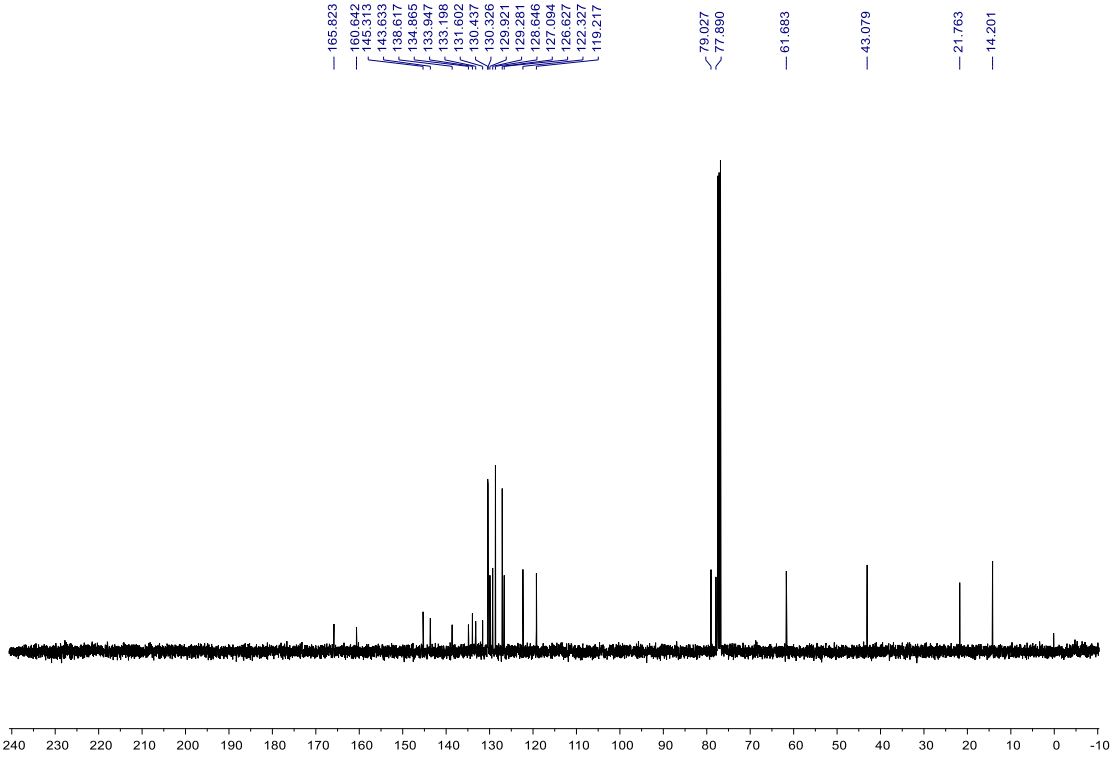


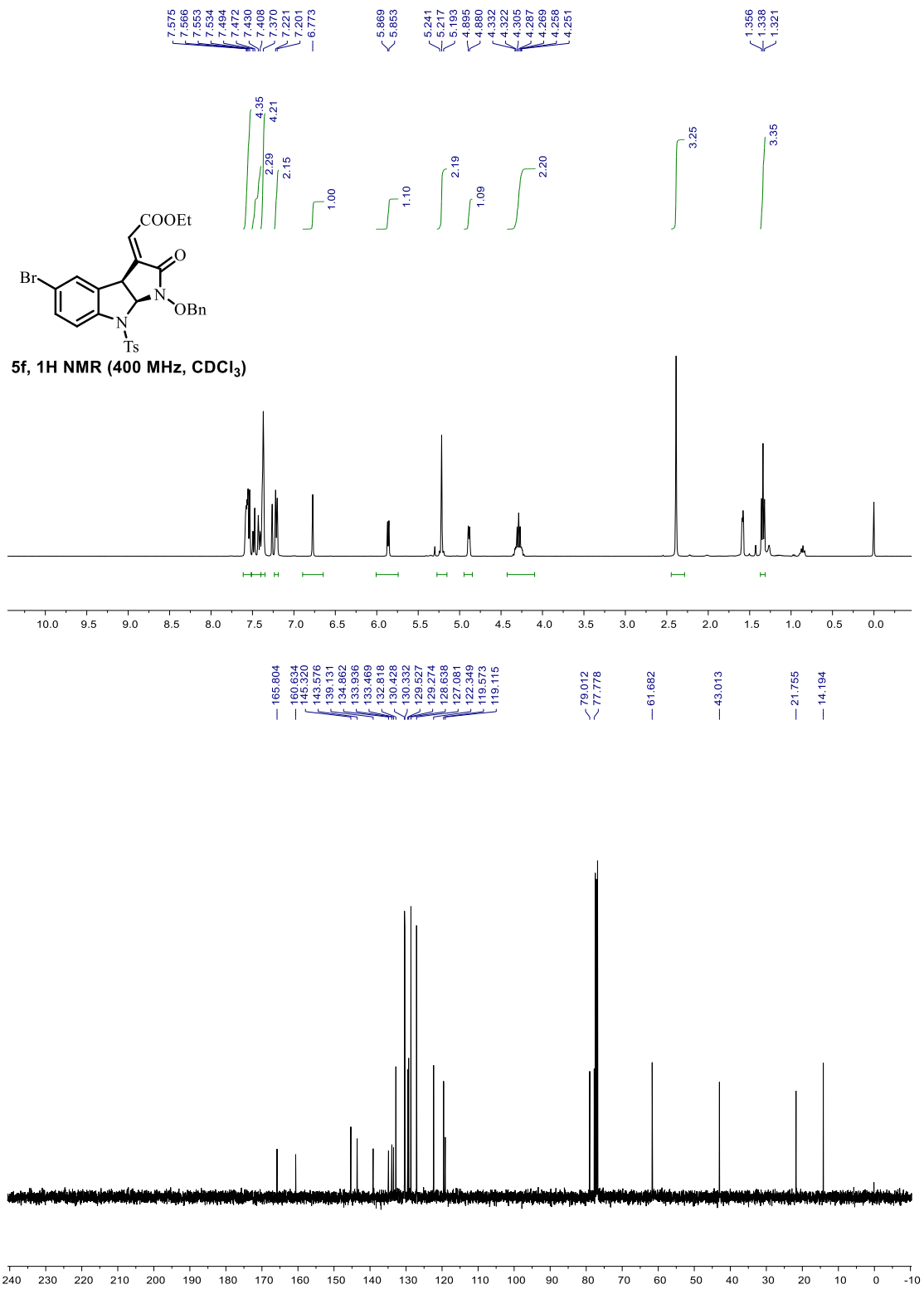

-115.237
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210



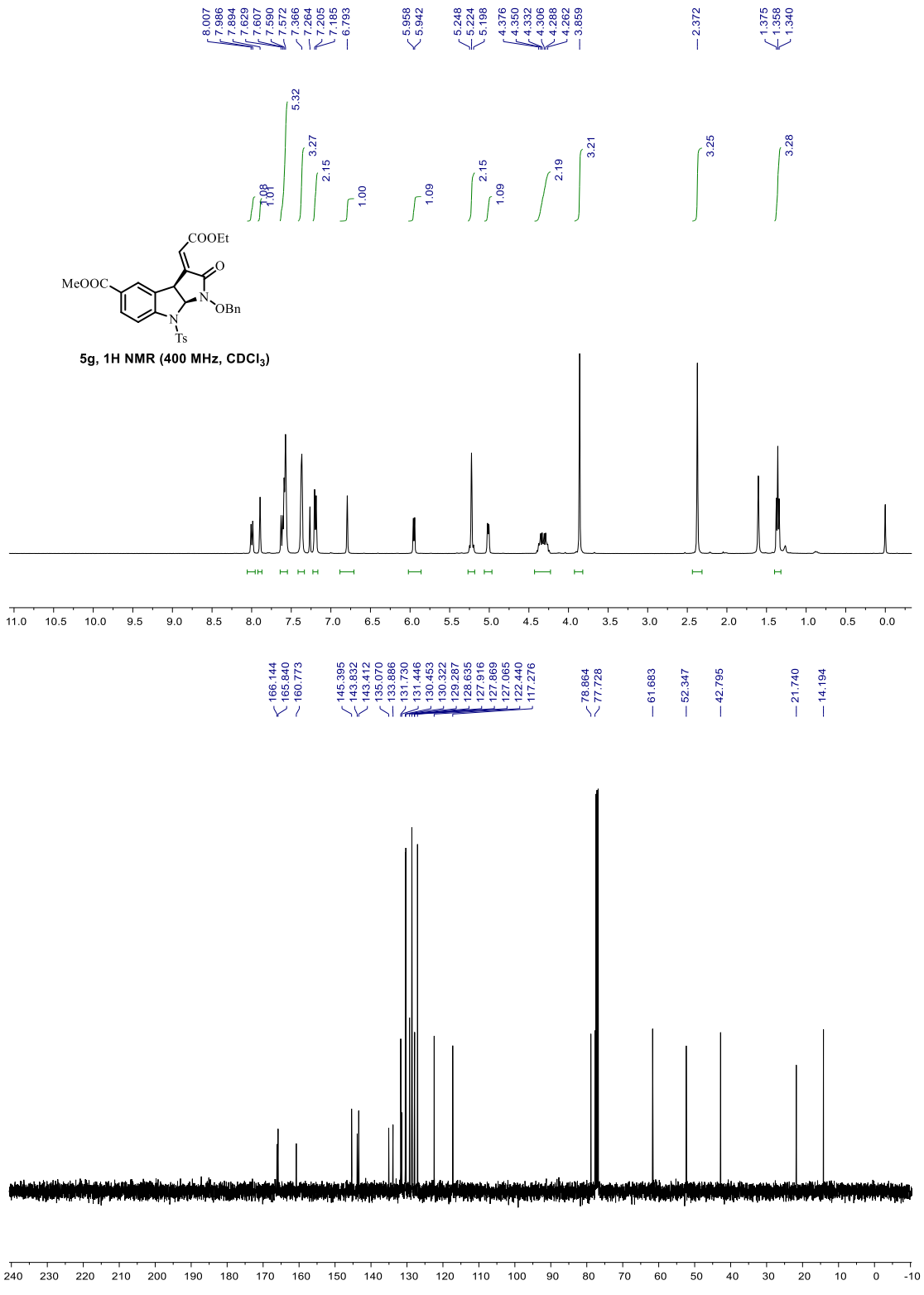
5e, 1H NMR (400 MHz, $CDCl_3$)



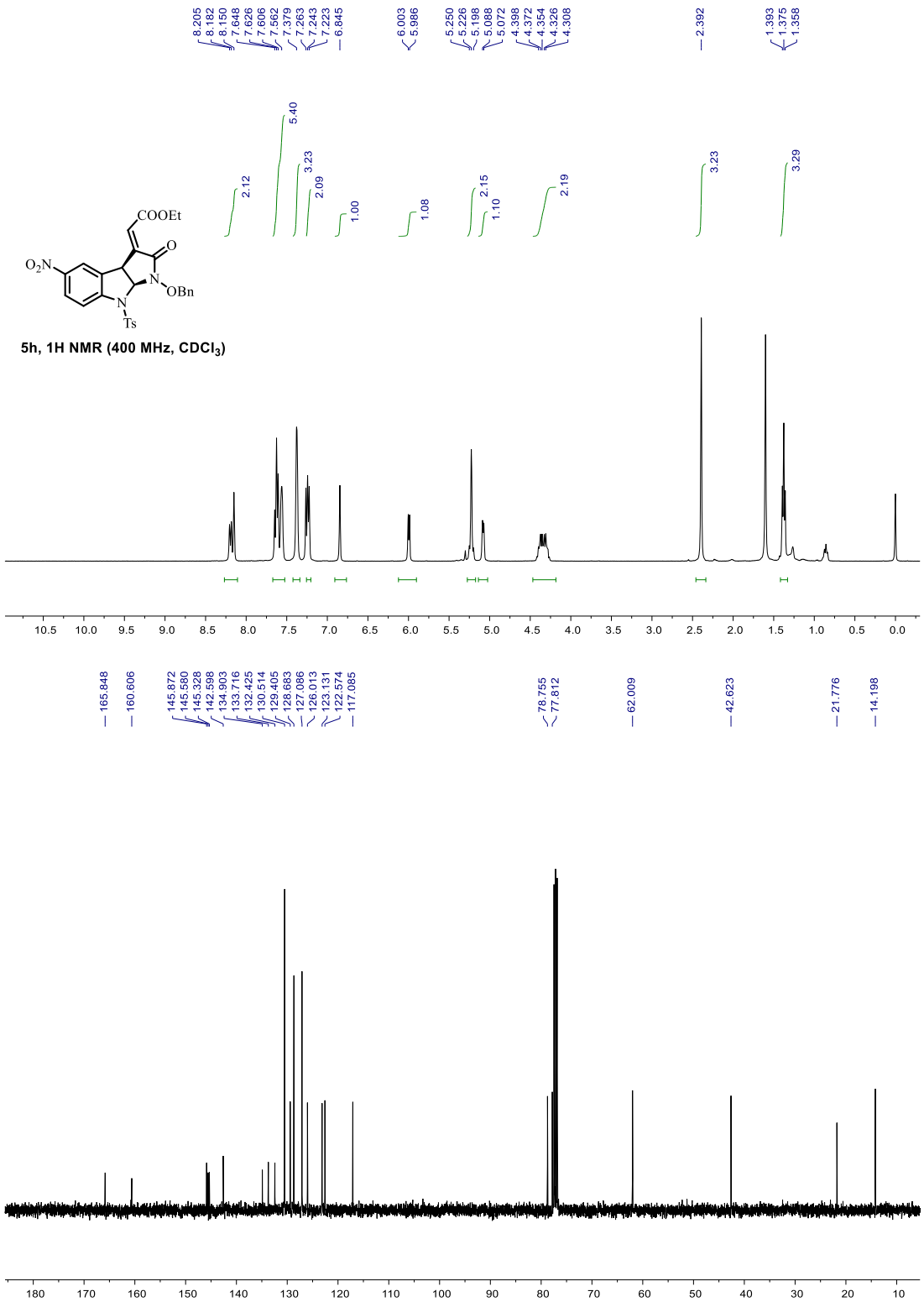


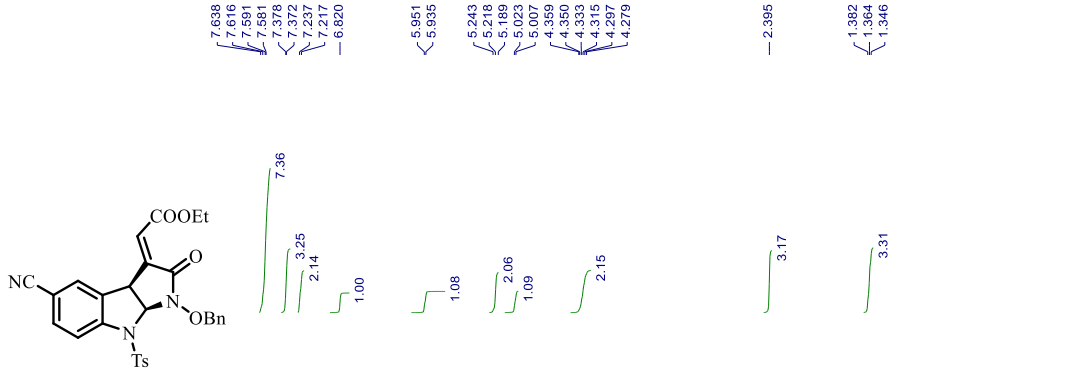


5f, 1H NMR (400 MHz, $CDCl_3$)

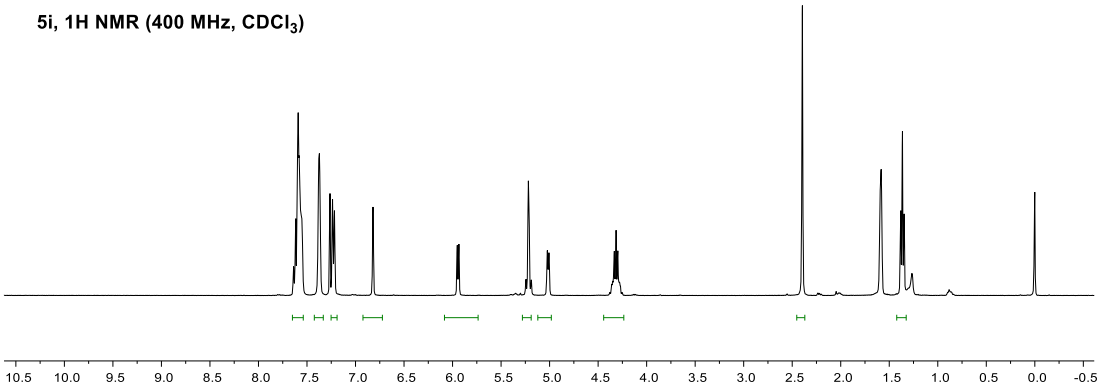


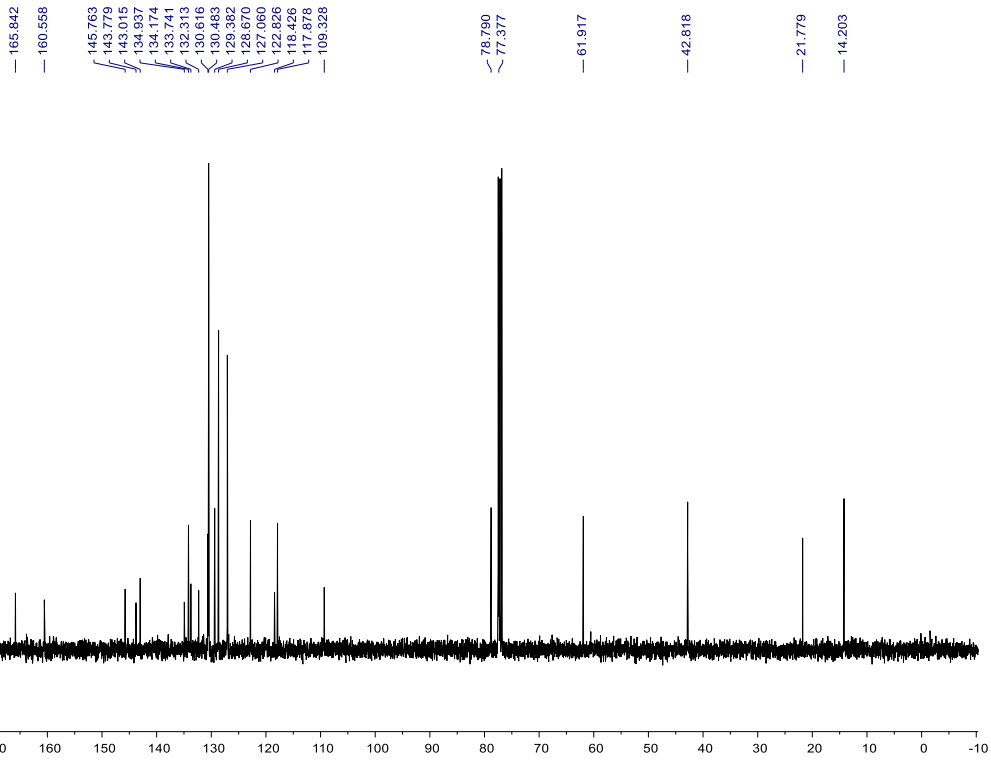
5g, 1H NMR (400 MHz, $CDCl_3$)

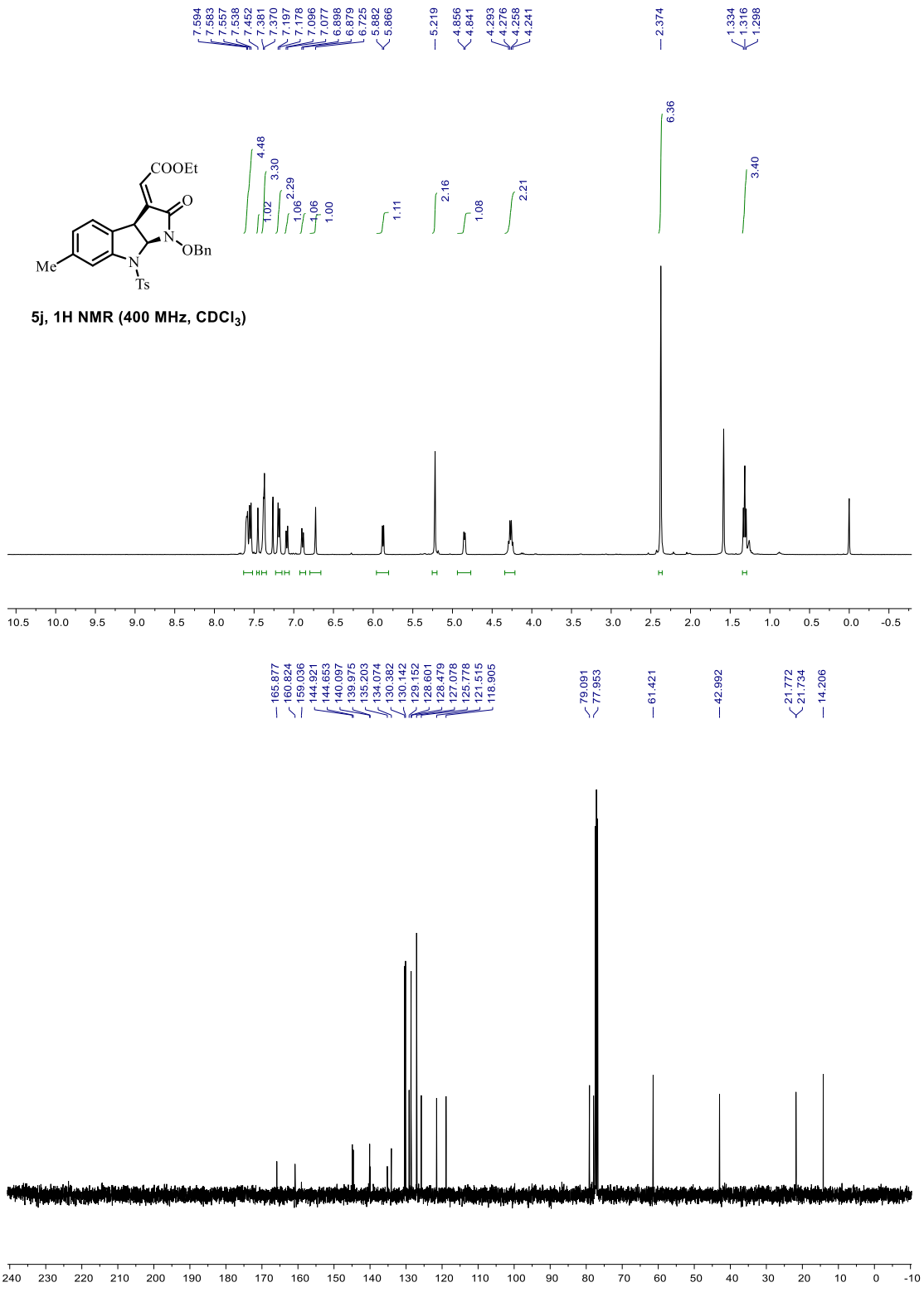

8.205
8.182
8.150
7.648
7.626
7.606
7.562
7.379
7.263
7.243
7.223
6.845
6.003
5.986
5.250
5.226
5.198
5.088
5.072
4.398
4.372
4.354
4.326
4.308
2.392
1.393
1.375
1.358
2.12
5.40
3.23
2.09
1.00
1.08
2.15
1.10
2.19
3.23
3.29
COOEt
O
O2N
N
OBn
N
Ts
5h, 1H NMR (400 MHz, CDCl3)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
165.848
160.606
145.872
145.580
145.328
142.598
134.903
133.716
132.425
130.514
129.405
128.683
127.086
126.013
123.131
122.574
117.085
78.755
77.812
62.009
42.623
21.776
14.198
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

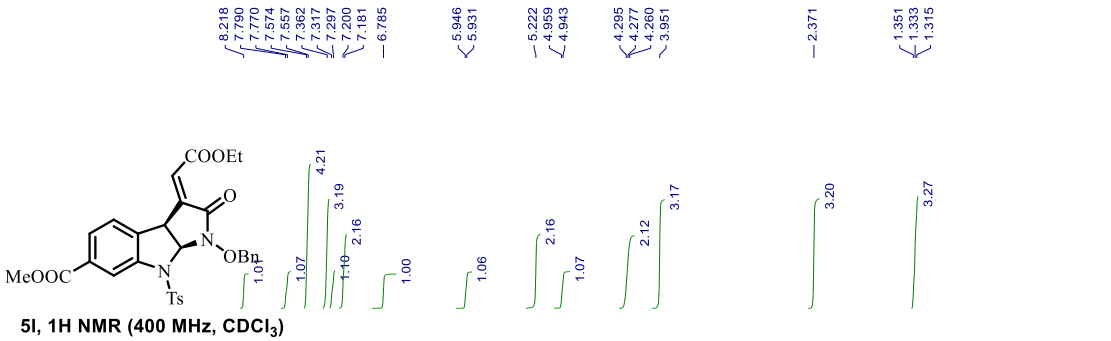


5i, 1H NMR (400 MHz, $CDCl_3$)

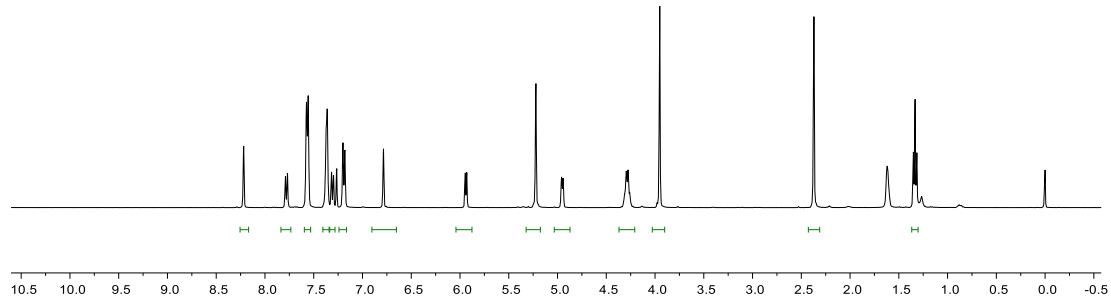


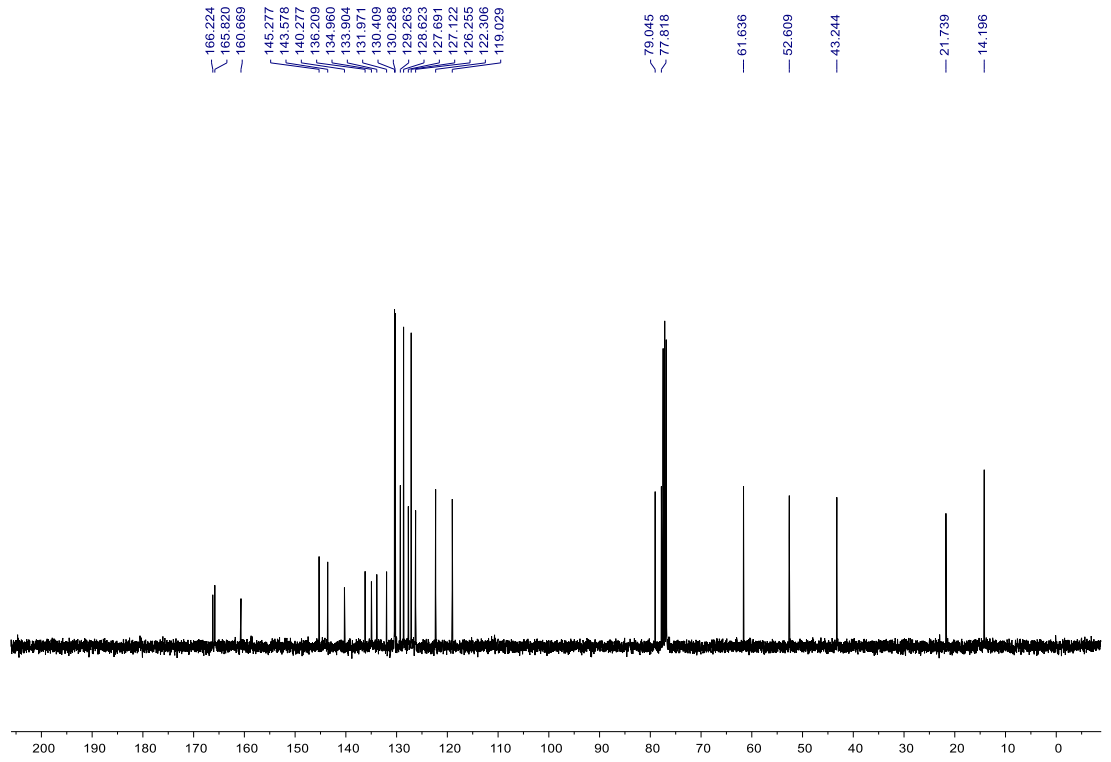


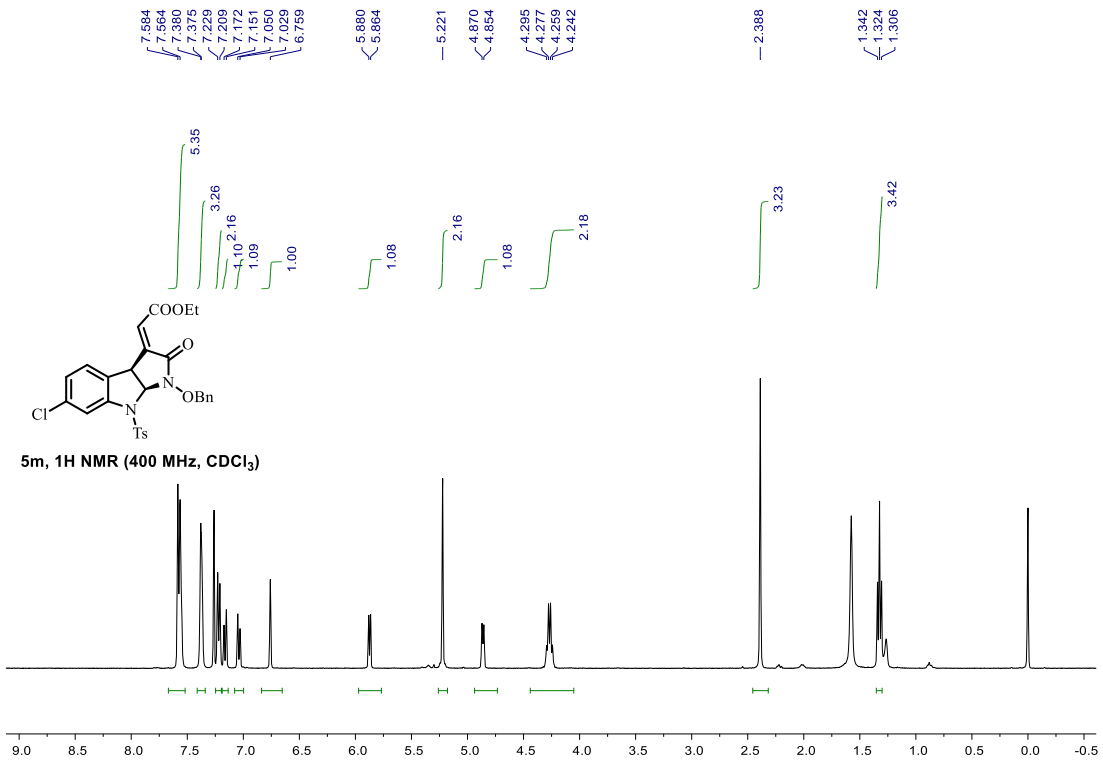

7.594
7.583
7.557
7.538
7.452
7.381
7.370
7.197
7.178
7.096
7.077
6.898
6.879
6.725
5.882
5.866
5.219
4.856
4.841
4.293
4.276
4.258
4.241
2.374
1.334
1.316
1.298
4.48
3.30
2.29
1.02
1.06
1.06
1.00
1.11
2.16
1.08
2.21
6.36
3.40
COOEt
O
N
OBn
Me
N
Ts
5j, 1H NMR (400 MHz, CDCl3)
165.877
160.824
159.036
144.921
144.653
140.097
139.975
135.203
134.074
130.382
130.142
129.152
128.601
128.479
127.078
125.778
121.515
118.905
79.091
77.953
61.421
42.992
21.772
21.734
14.206

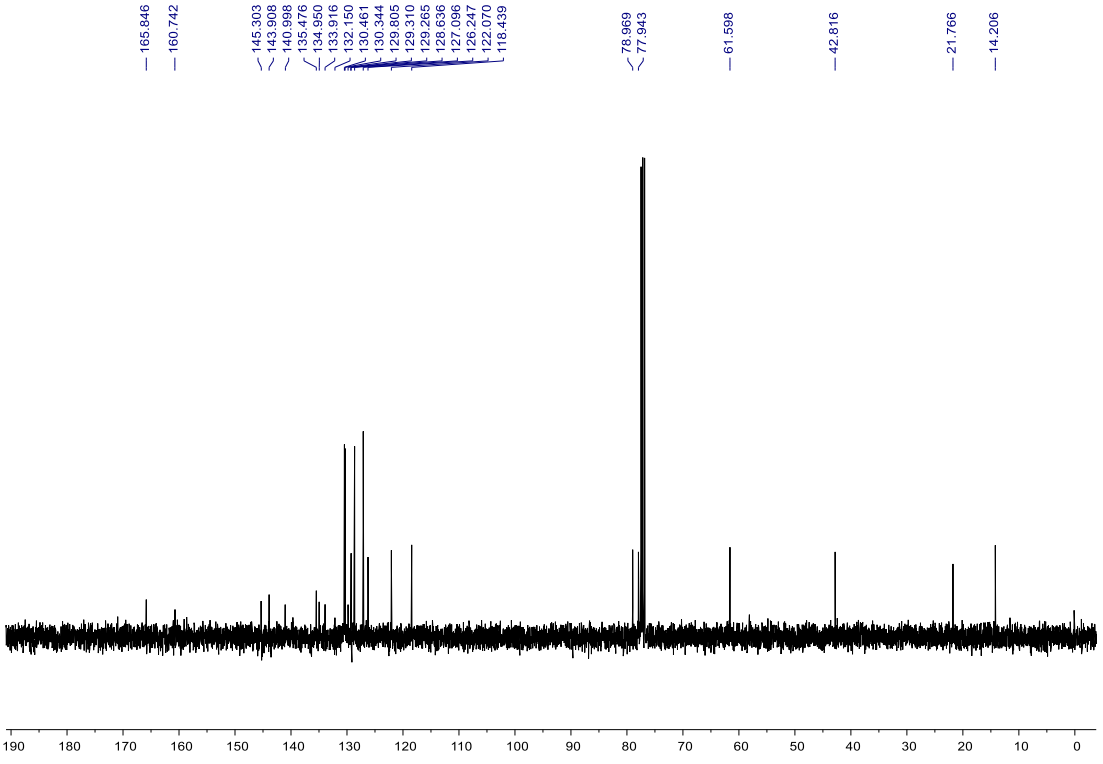


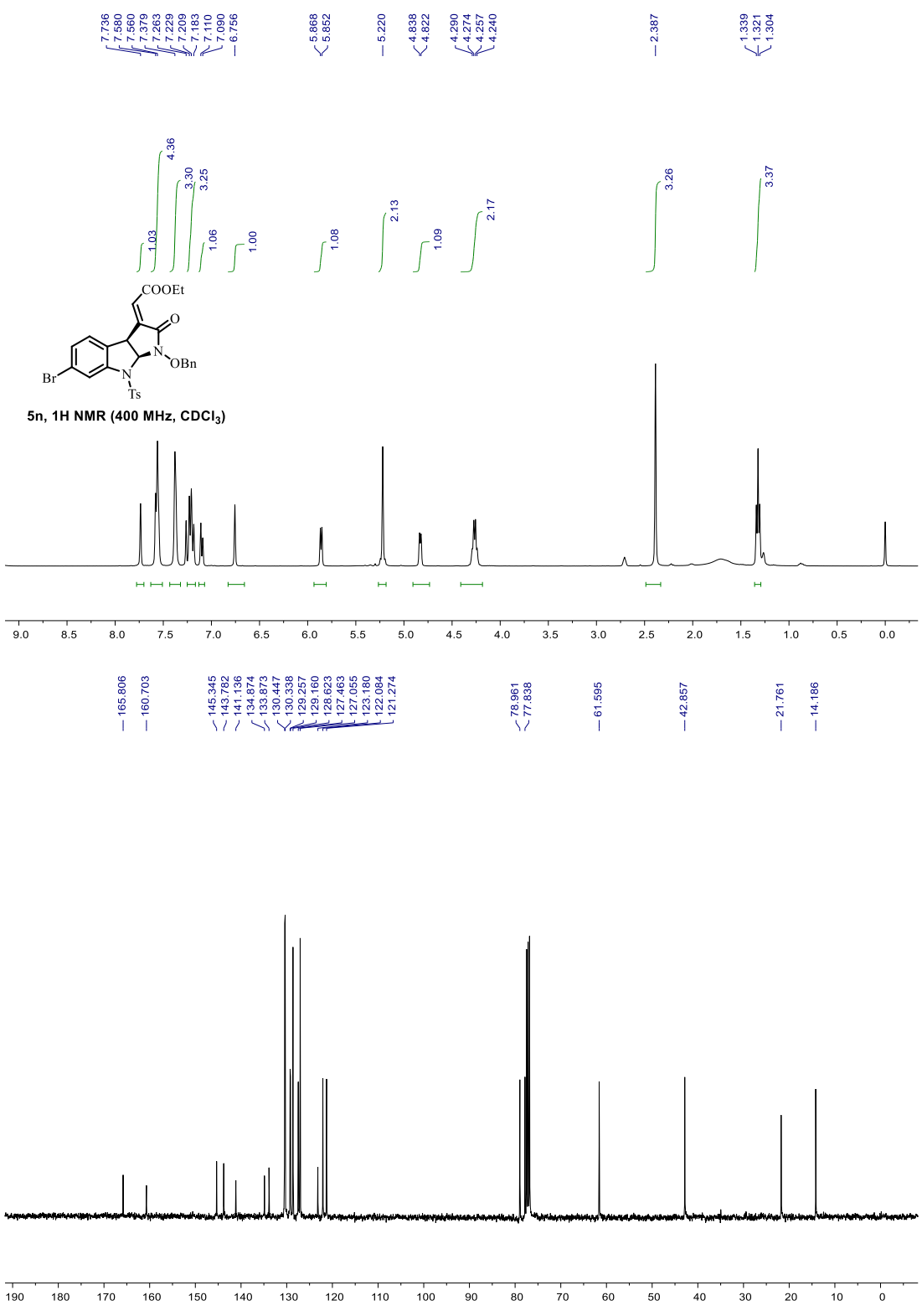
5l, 1H NMR (400 MHz, $CDCl_3$)

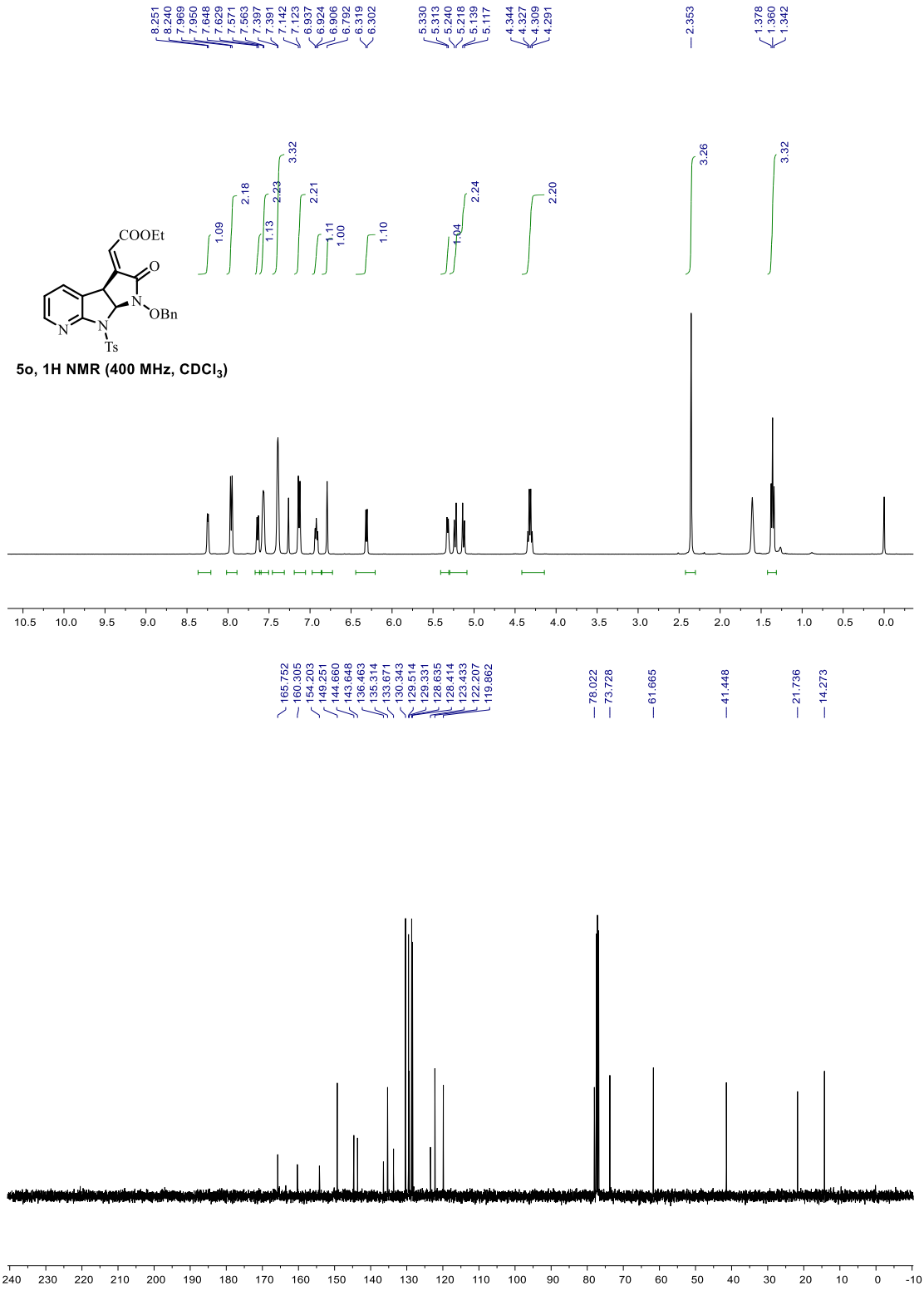


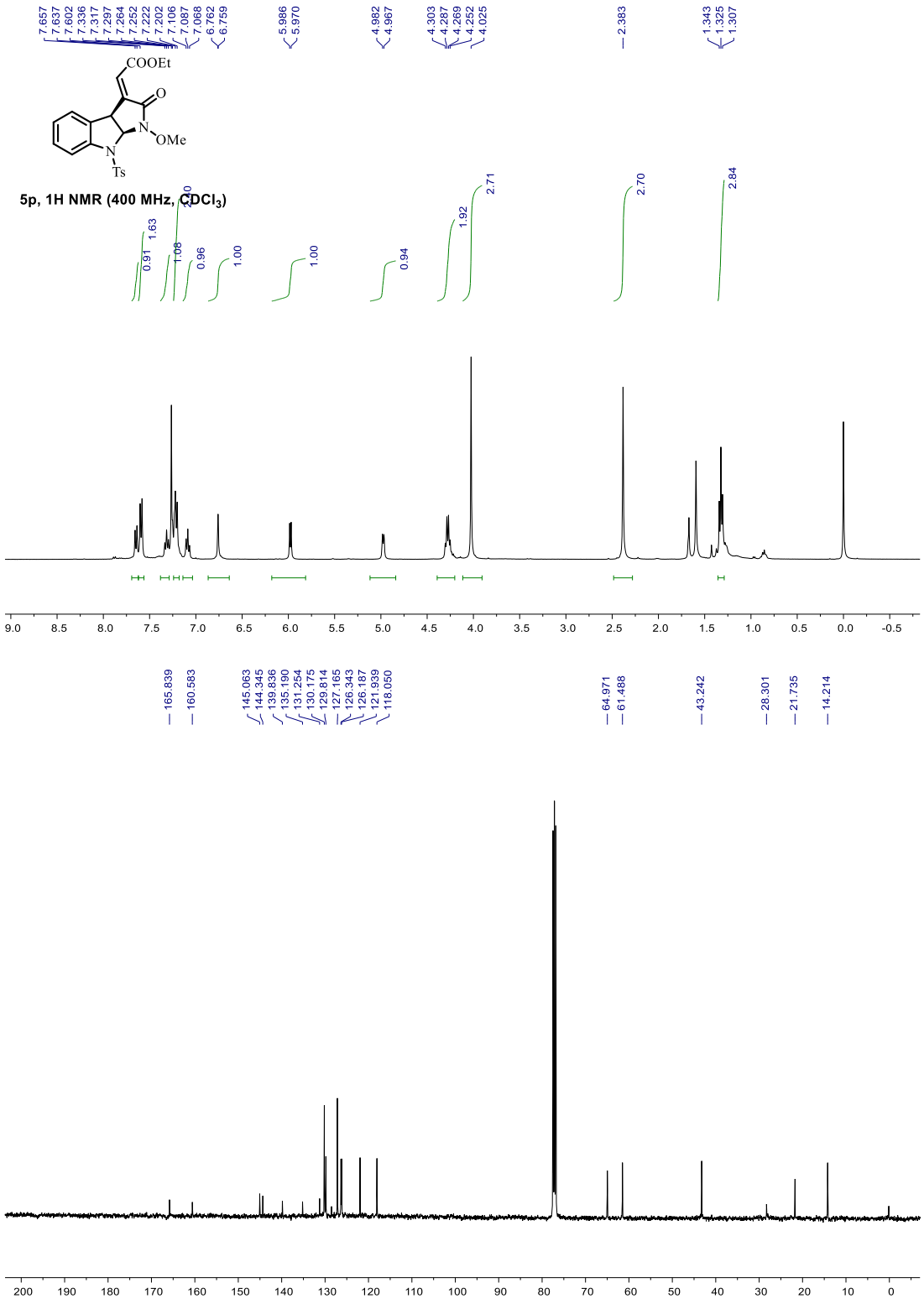


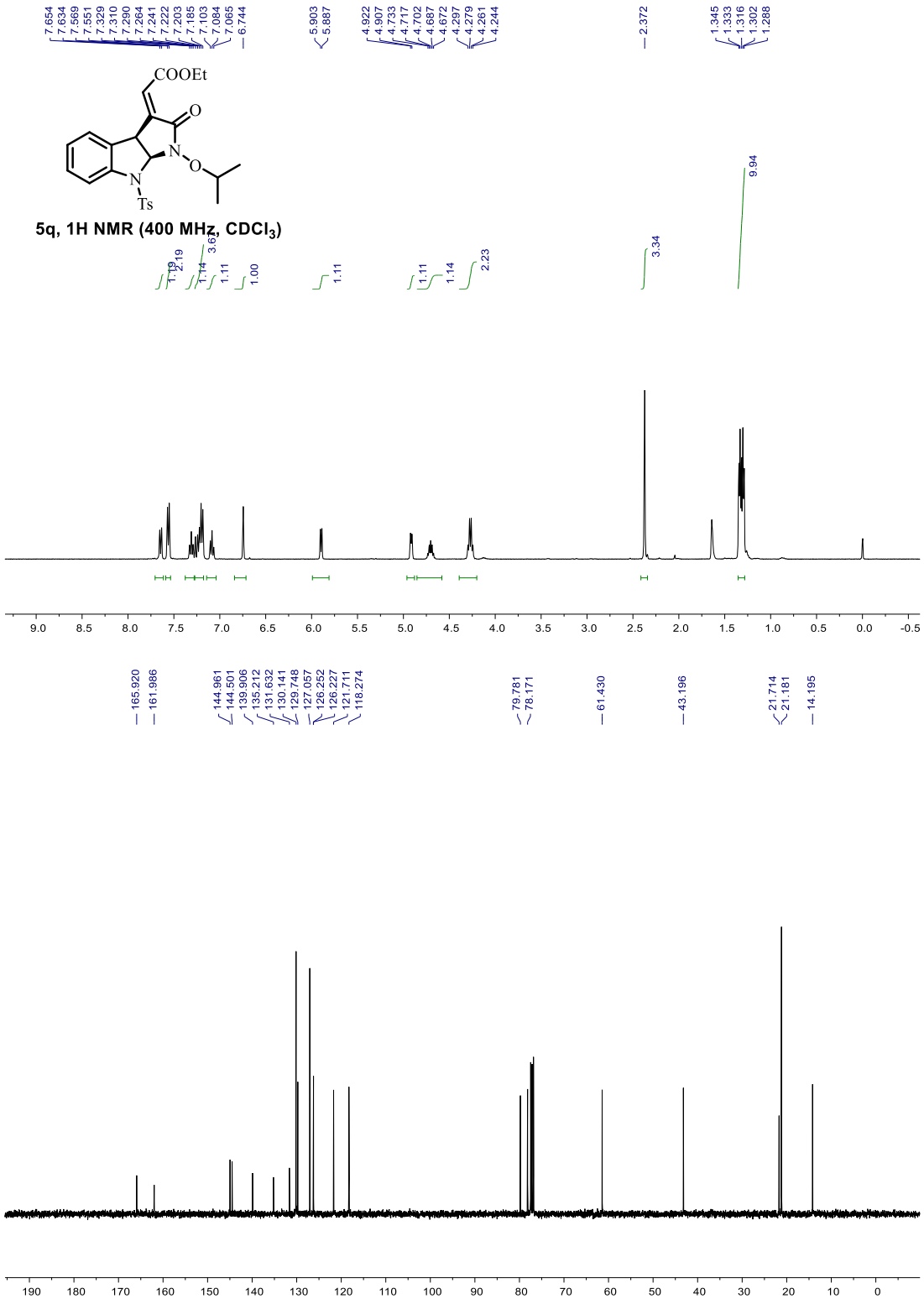

7.584
7.564
7.380
7.375
7.229
7.209
7.172
7.151
7.050
7.029
6.759
5.880
5.864
5.221
4.870
4.854
4.295
4.277
4.259
4.242
2.388
1.342
1.324
1.306
5.35
3.26
2.16
1.10
1.09
1.00
1.08
2.16
1.08
2.18
3.23
3.42
COOEt
O
N
OBn
Cl
N
Ts
5m, 1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


165.846
160.742
145.303
143.908
140.998
135.476
134.950
133.916
132.150
130.461
130.344
129.805
129.310
129.265
128.636
127.096
126.247
122.070
118.439
78.969
77.943
61.598
42.816
21.766
14.206
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

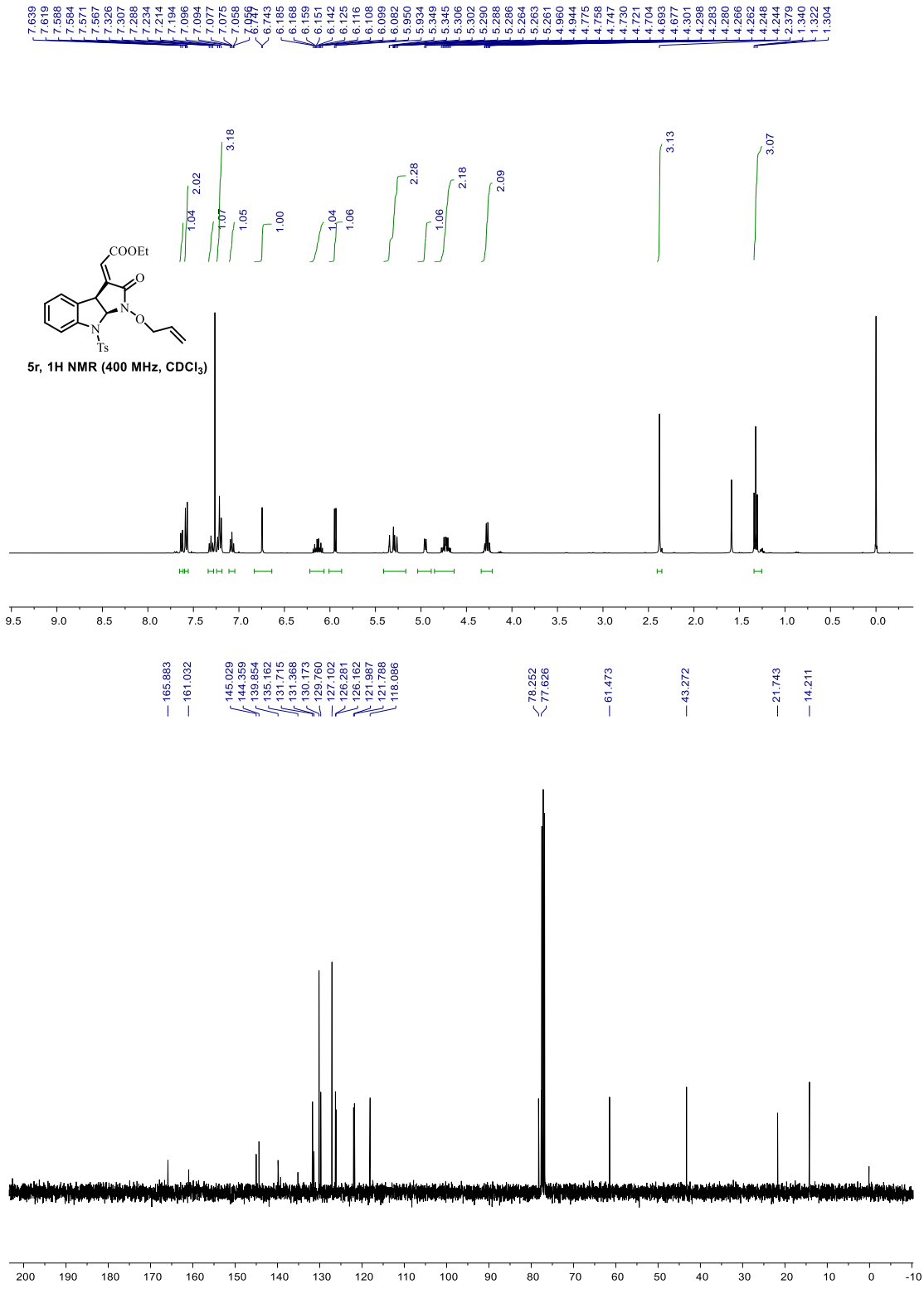

7.736
7.580
7.560
7.379
7.263
7.229
7.209
7.183
7.110
7.090
6.756
5.868
5.852
5.220
4.838
4.822
4.290
4.274
4.257
4.240
2.387
1.339
1.321
1.304
4.36
3.30
3.25
1.03
1.06
1.00
1.08
2.13
1.09
2.17
3.26
3.37
COOEt
O
N
OBn
Br
N
Ts
5n, 1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
165.806
160.703
145.345
143.782
141.136
134.874
133.873
130.447
130.338
129.257
129.160
128.623
127.463
127.055
123.180
122.084
121.274
78.961
77.838
61.595
42.857
21.761
14.186
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

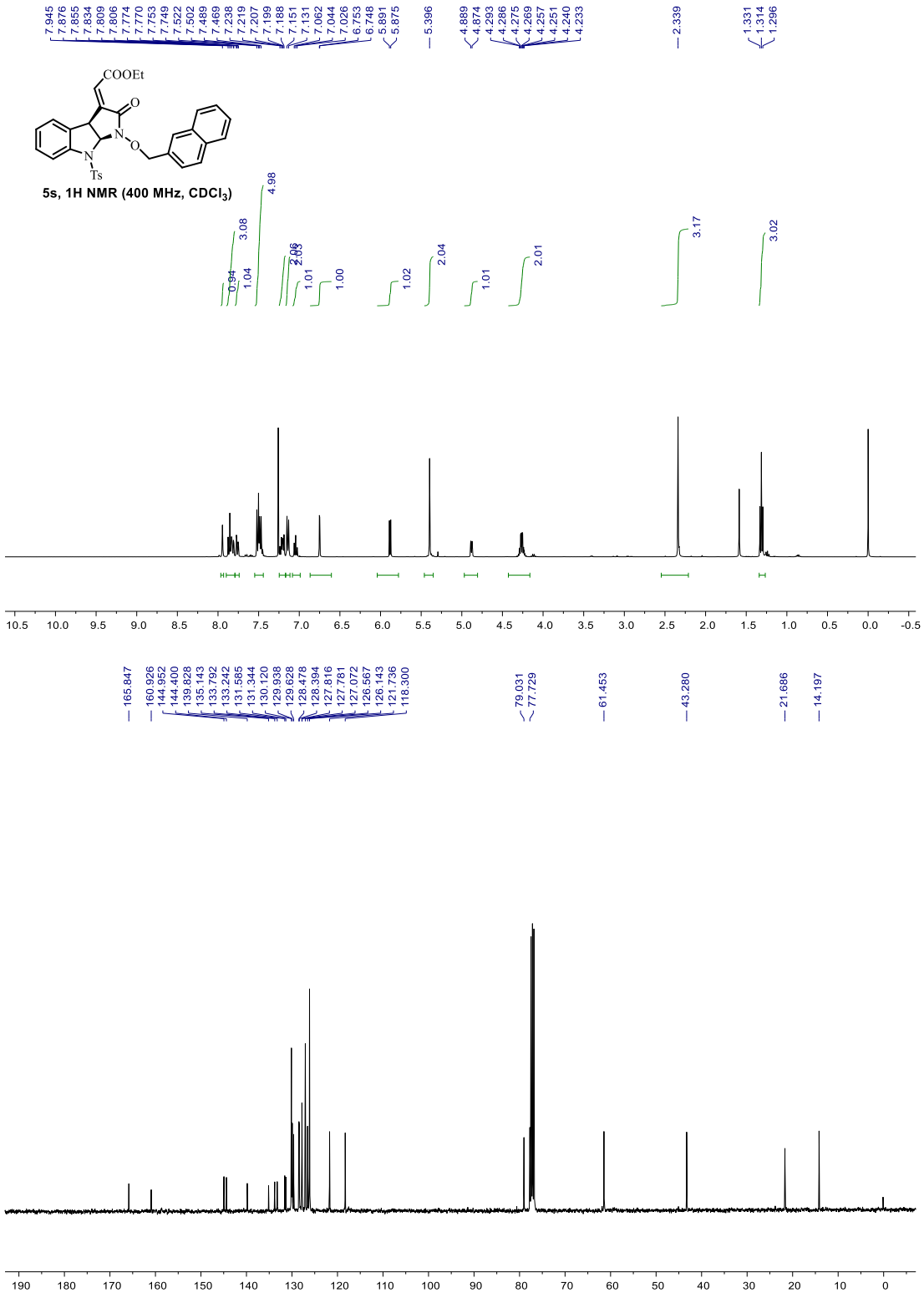

8.251
8.240
7.969
7.950
7.648
7.629
7.571
7.563
7.397
7.391
7.142
7.123
6.937
6.924
6.906
6.792
6.319
6.302
5.330
5.313
5.240
5.218
5.139
5.117
4.344
4.327
4.309
4.291
2.353
1.378
1.360
1.342
3.32
2.18
2.23
2.21
1.09
1.13
1.11
1.00
1.10
2.24
1.04
2.20
3.26
3.32
COOEt
O
N
OBn
N
N
Ts
5o, 1H NMR (400 MHz, CDCl3)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
165.752
160.305
154.203
149.251
144.660
143.648
136.463
135.314
133.671
130.343
129.514
129.331
128.635
128.414
123.433
122.207
119.862
78.022
73.728
61.665
41.448
21.736
14.273
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

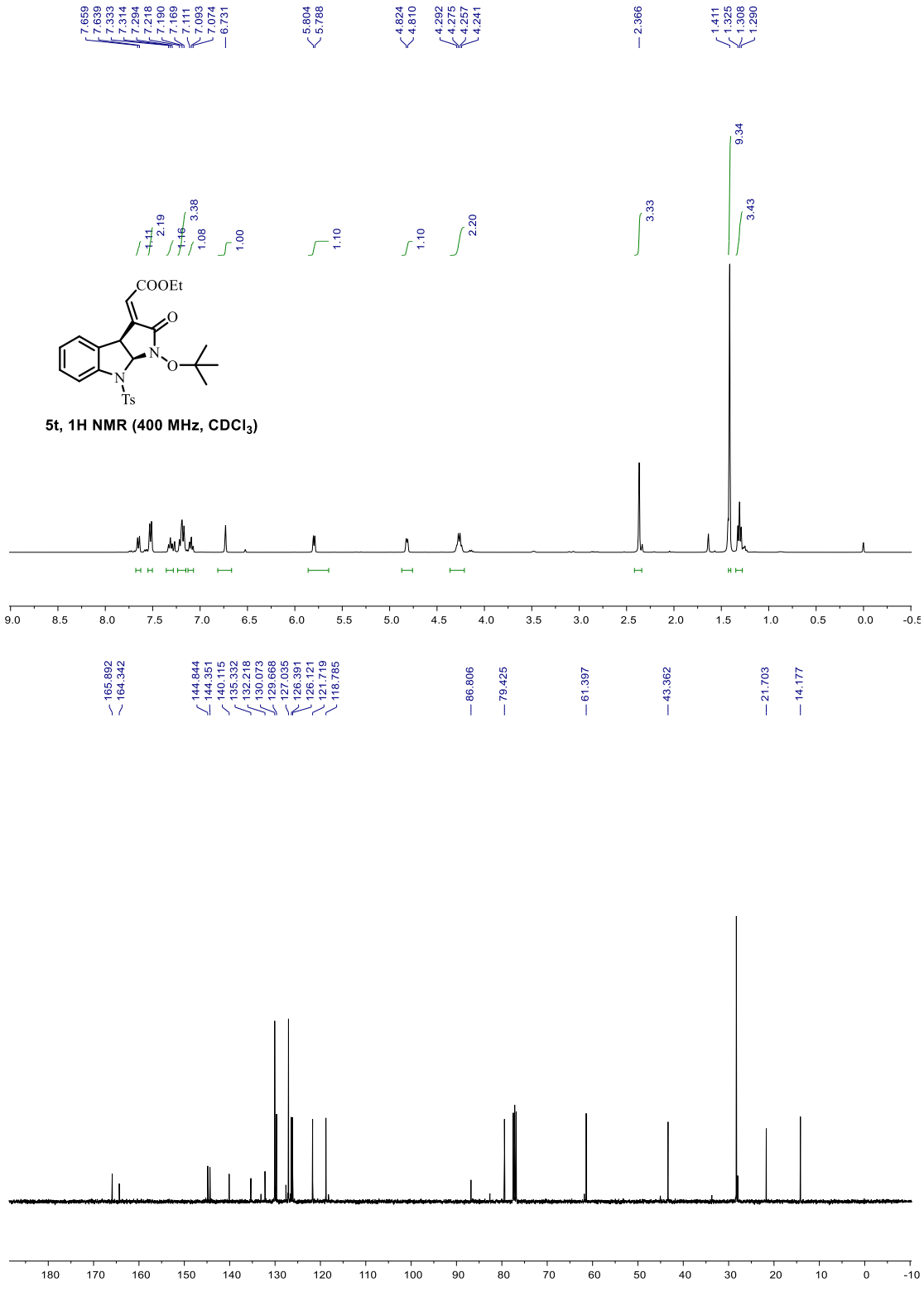

7.657
7.637
7.602
7.336
7.317
7.297
7.264
7.252
7.222
7.202
7.106
7.087
7.068
6.762
6.759
5.986
5.970
4.982
4.967
4.303
4.287
4.269
4.252
4.025
2.383
1.343
1.325
1.307
COOEt
O
N
OMe
N
Ts
5p, 1H NMR (400 MHz, CDCl3)
0.91
1.63
2.20
1.08
0.96
1.00
1.00
0.94
1.92
2.71
2.70
2.84
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
165.839
160.583
145.063
144.345
139.836
135.190
131.254
130.175
129.814
127.165
126.343
126.187
121.939
118.050
64.971
61.488
43.242
28.301
21.735
14.214
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

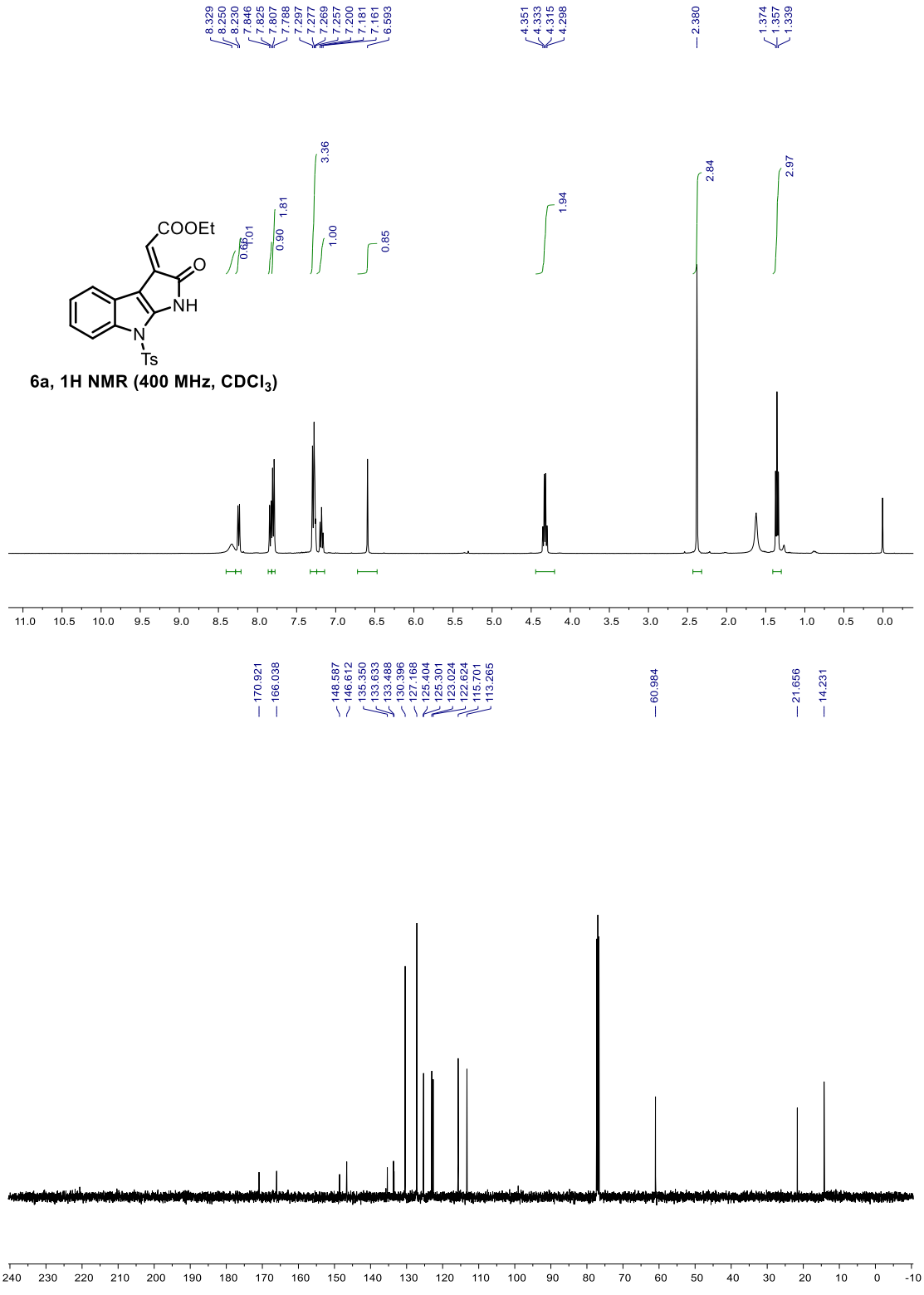


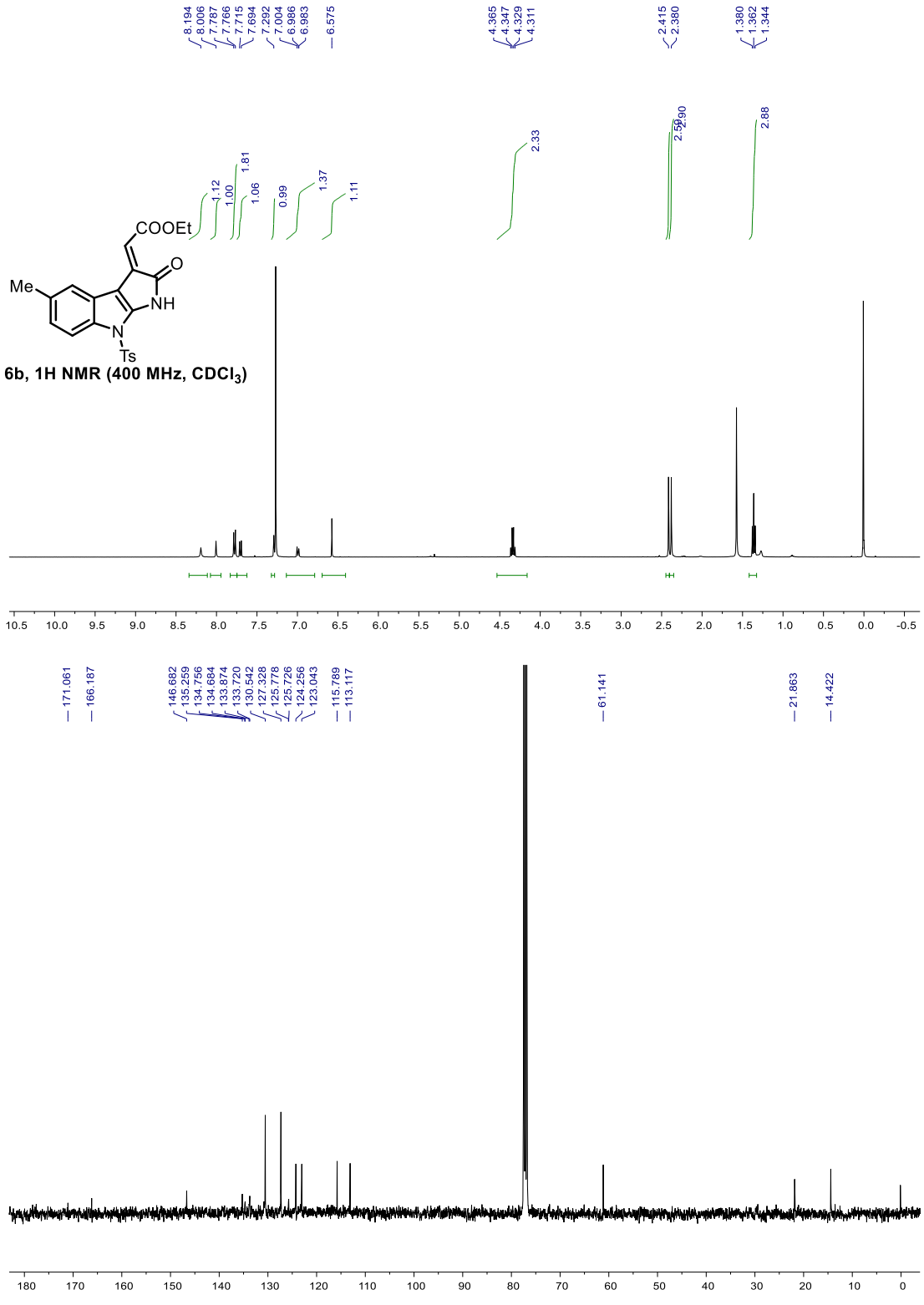
5q, 1H NMR (400 MHz, $CDCl_3$)

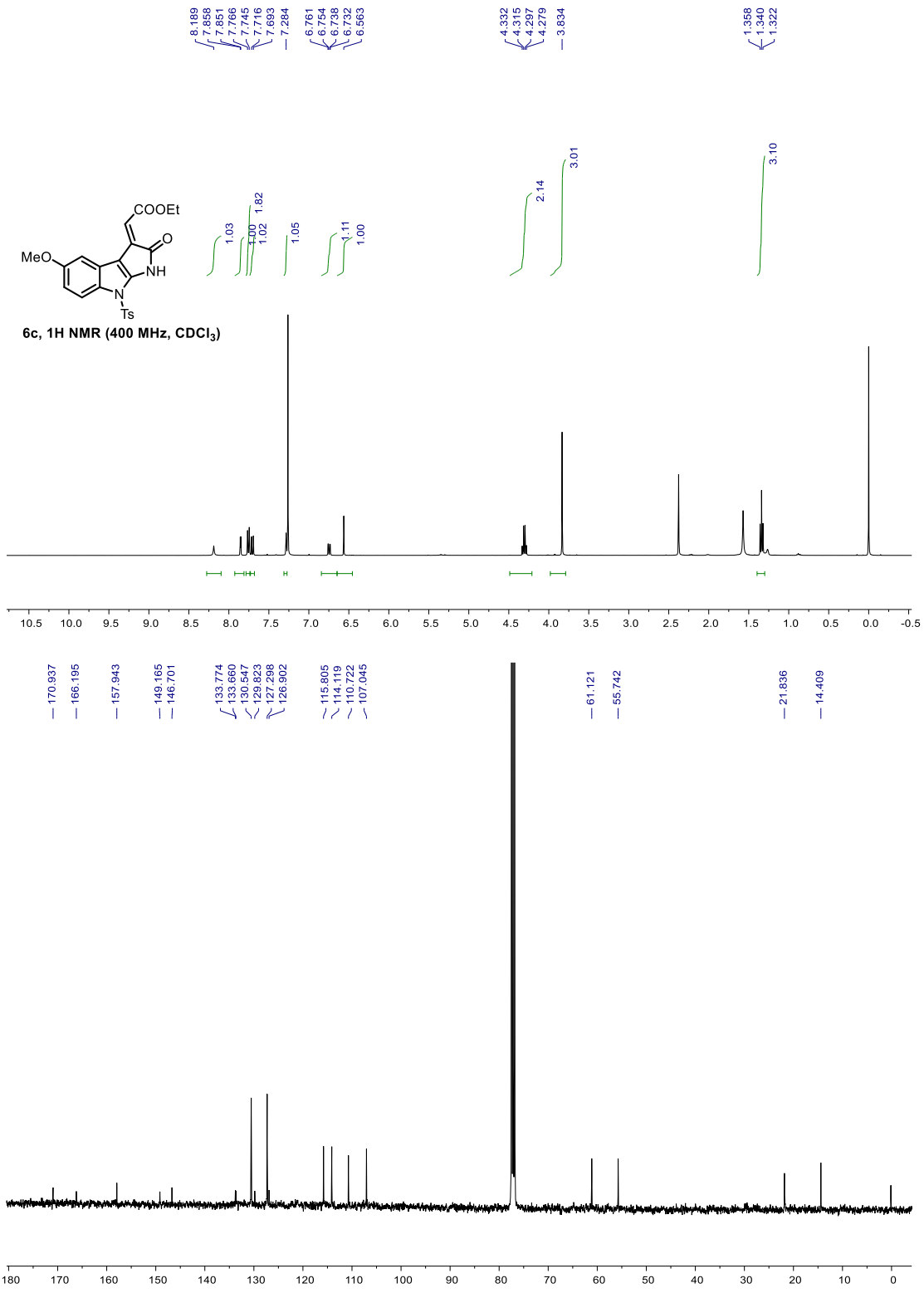

7.639
7.619
7.588
7.584
7.571
7.567
7.326
7.307
7.288
7.234
7.214
7.194
7.096
7.094
7.077
7.075
7.058
6.747
6.743
6.185
6.168
6.159
6.151
6.142
6.125
6.116
6.108
6.099
6.082
5.950
5.934
5.349
5.345
5.306
5.302
5.290
5.288
5.286
5.264
5.263
5.261
4.960
4.944
4.775
4.758
4.747
4.730
4.721
4.704
4.693
4.677
4.301
4.298
4.283
4.280
4.266
4.262
4.248
4.244
2.379
1.340
1.322
1.304
3.18
2.02
1.04
1.07
1.05
1.00
1.04
1.06
2.28
1.06
2.18
2.09
3.13
3.07
COOEt
O
N
O
N
Ts
5r, 1H NMR (400 MHz, CDCl3)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
165.883
161.032
145.029
144.359
139.854
135.162
131.715
131.368
130.173
129.760
127.102
126.281
126.162
121.987
121.788
118.086
78.252
77.626
61.473
43.272
21.743
14.211
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

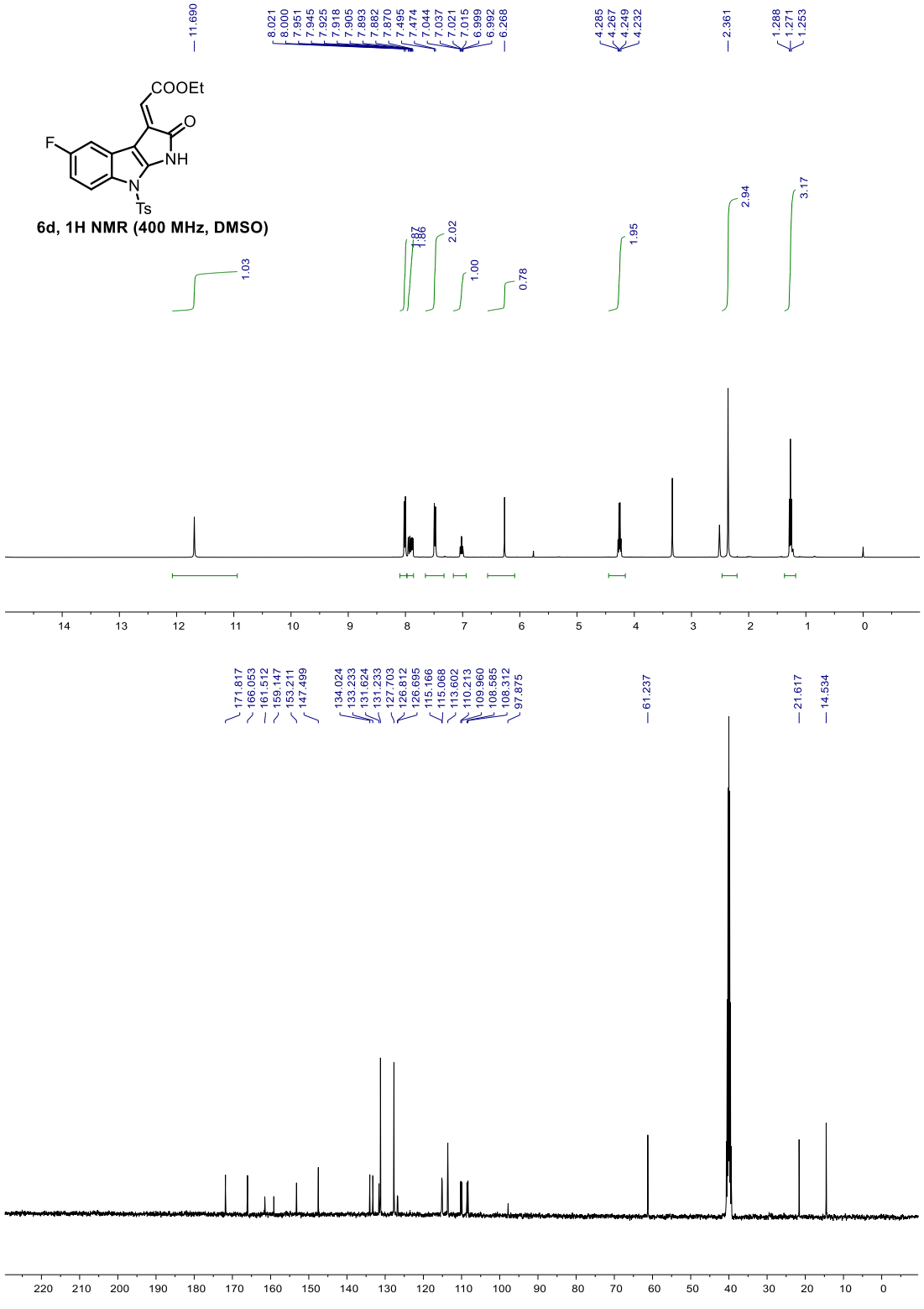

7.945
7.876
7.855
7.834
7.809
7.806
7.774
7.770
7.753
7.749
7.522
7.502
7.489
7.469
7.238
7.219
7.207
7.199
7.188
7.151
7.131
7.062
7.044
7.026
6.753
6.748
5.891
5.875
5.396
4.889
4.874
4.293
4.286
4.275
4.269
4.257
4.251
4.240
4.233
2.339
1.331
1.314
1.296
COOEt
O
N
O
N
Ts
5s, 1H NMR (400 MHz, CDCl3)
0.94
3.08
1.04
4.98
2.06
2.03
1.01
1.00
1.02
2.04
1.01
2.01
3.17
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
165.847
160.926
144.952
144.400
139.828
135.143
133.792
133.242
131.585
131.344
130.120
129.938
129.628
128.478
128.394
127.816
127.781
127.072
126.567
126.143
121.736
118.300
79.031
77.729
61.453
43.280
21.686
14.197
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.659
7.639
7.333
7.314
7.294
7.218
7.190
7.169
7.111
7.093
7.074
6.731
5.804
5.788
4.824
4.810
4.292
4.275
4.257
4.241
2.366
1.411
1.325
1.308
1.290
9.34
3.43
3.33
3.38
2.19
2.20
1.10
1.08
1.00
COOEt
O
N
O
N
Ts
5t, 1H NMR (400 MHz, CDCl3)
165.892
164.342
144.844
144.351
140.115
135.332
132.218
130.073
129.668
127.035
126.391
126.121
121.719
118.785
86.806
79.425
61.397
43.362
21.703
14.177


8.329
8.250
8.230
7.846
7.825
7.807
7.788
7.297
7.277
7.269
7.257
7.200
7.181
7.161
6.593
4.351
4.333
4.315
4.298
2.380
1.374
1.357
1.339
3.36
2.84
2.97
1.94
1.81
1.00
0.90
0.85
0.66
0.01
COOEt
O
NH
N
Ts
6a, 1H NMR (400 MHz, CDCl3)
170.921
166.038
148.587
146.612
135.350
133.633
133.488
130.396
127.168
125.404
125.301
123.024
122.624
115.701
113.265
60.984
21.656
14.231


8.194
8.006
7.787
7.766
7.715
7.694
7.292
7.004
6.986
6.983
6.575
4.365
4.347
4.329
4.311
2.415
2.380
1.380
1.362
1.344
1.12
1.00
1.81
1.06
0.99
1.37
1.11
2.33
2.50
2.90
2.88
COOEt
O
Me
NH
N
Ts
6b, 1H NMR (400 MHz, CDCl3)
171.061
166.187
146.682
135.255
134.756
134.684
133.874
133.720
130.542
127.328
125.778
125.726
124.256
123.043
115.789
113.117
61.141
21.863
14.422


8.189
7.858
7.851
7.766
7.745
7.716
7.693
7.284
6.761
6.754
6.738
6.732
6.563
4.332
4.315
4.297
4.279
3.834
1.358
1.340
1.322
COOEt
MeO
O
NH
N
Ts
1.03
1.00
1.02
1.82
1.05
1.11
1.00
2.14
3.01
3.10
6c, 1H NMR (400 MHz, CDCl3)
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
170.937
166.195
157.943
149.165
146.701
133.774
133.660
130.547
129.823
127.298
126.902
115.805
114.119
110.722
107.045
61.121
55.742
21.836
14.409
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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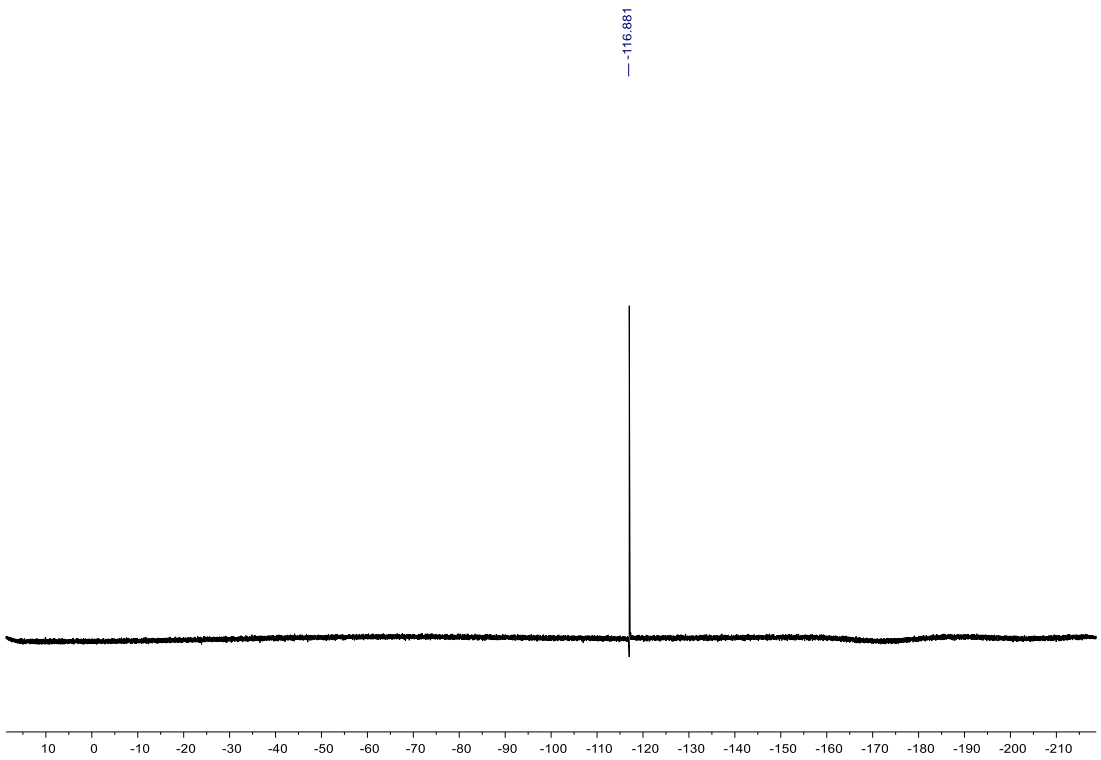
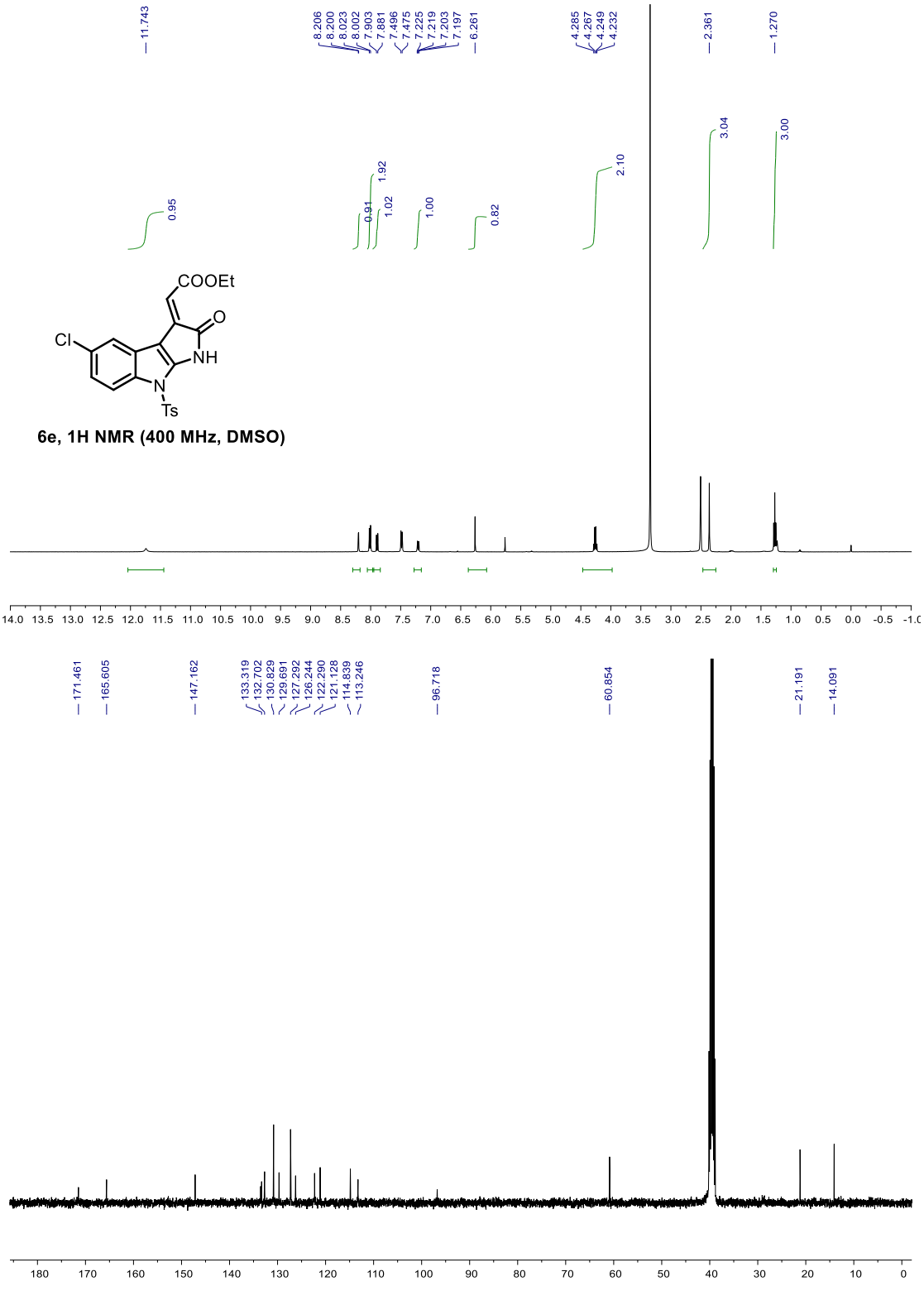
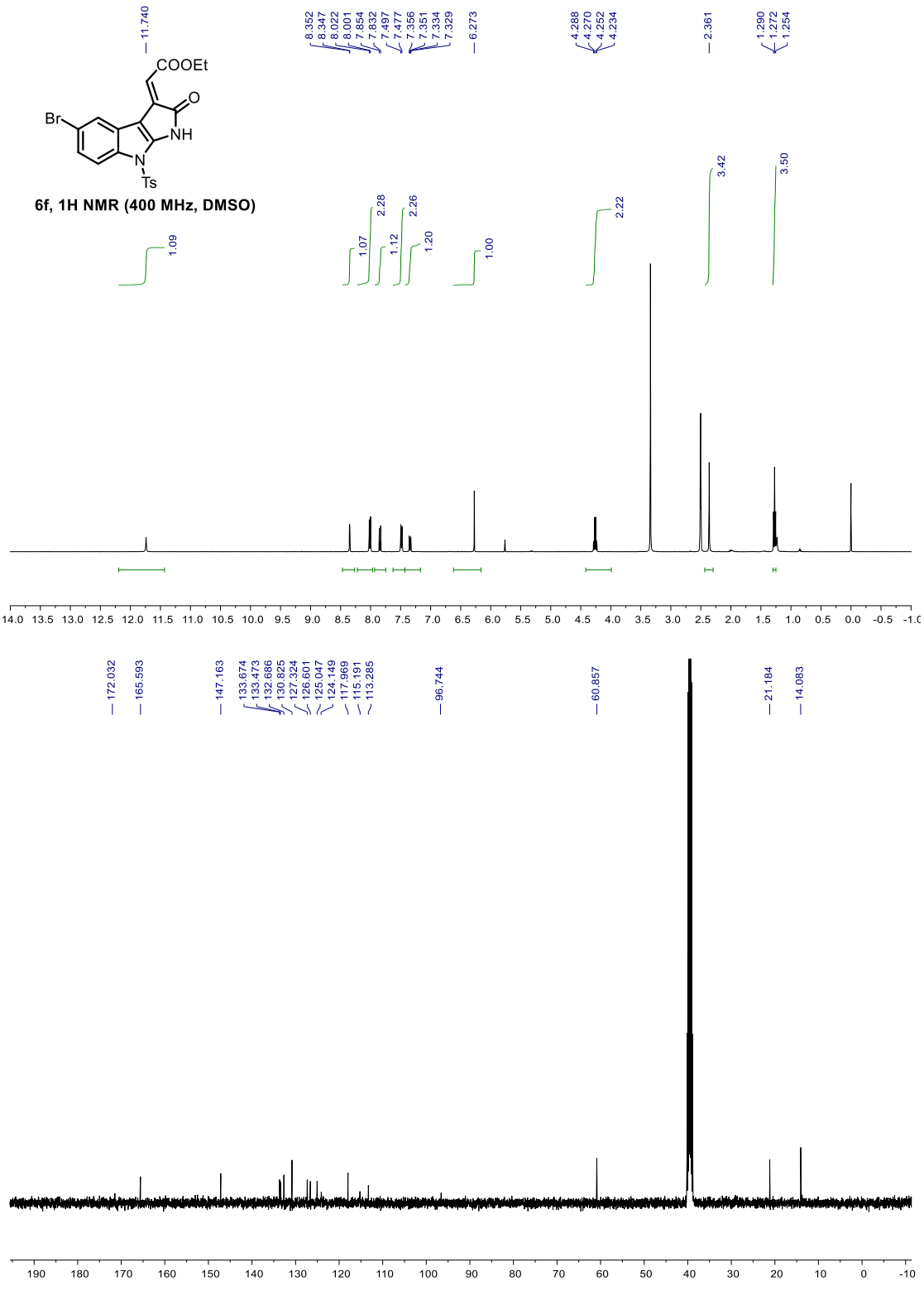
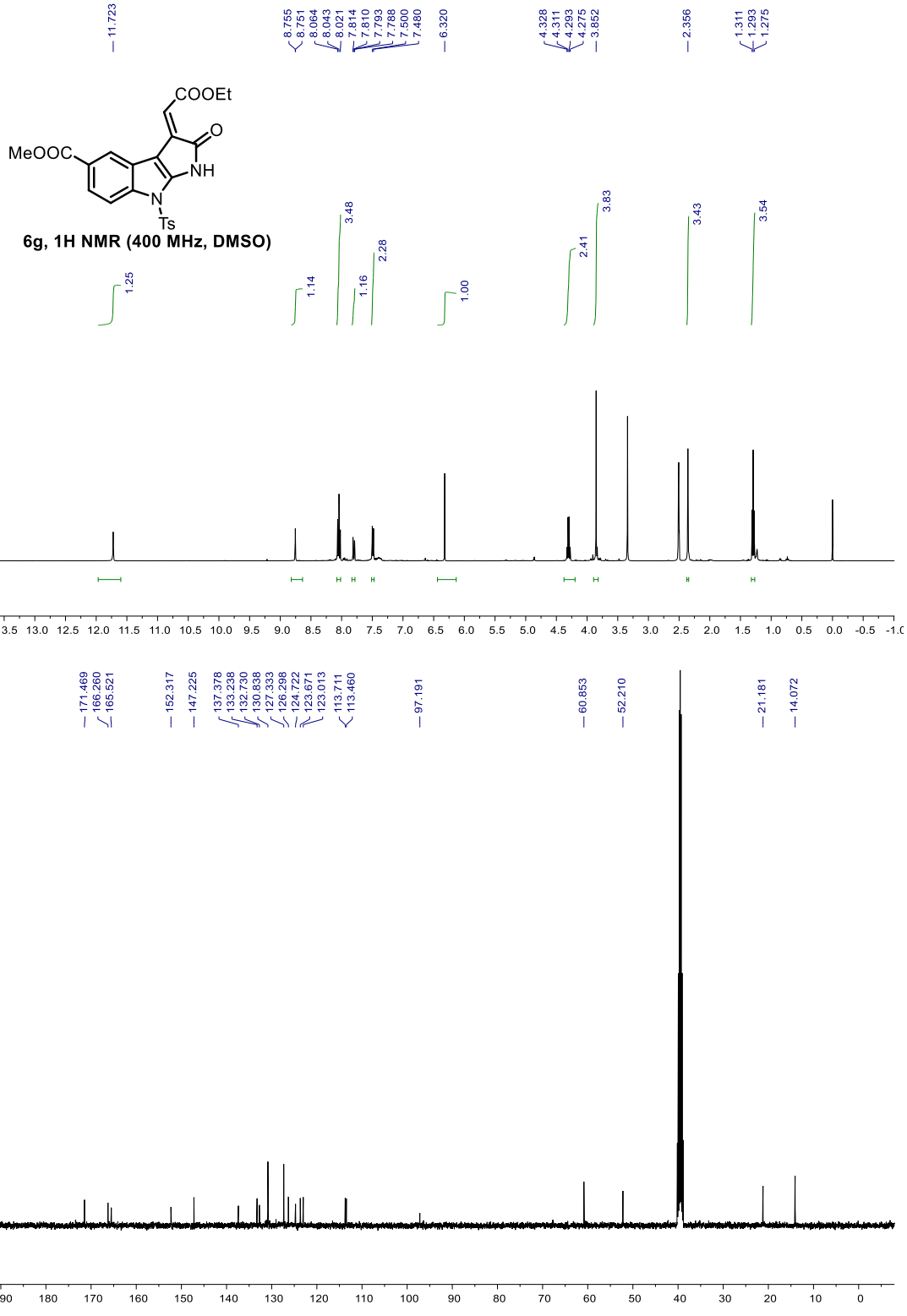
8.021
8.000
7.951
7.945
7.925
7.918
7.905
7.893
7.882
7.870
7.495
7.474
7.044
7.037
7.021
7.015
6.999
6.992
6.268
4.285
4.267
4.249
4.232
2.361
1.288
1.271
1.253
COOEt
O
F
NH
N
Ts
6d, 1H NMR (400 MHz, DMSO)
1.03
1.87
1.86
2.02
1.00
0.78
1.95
2.94
3.17
171.817
166.053
161.512
159.147
153.211
147.499
134.024
133.233
131.624
131.233
127.703
126.812
126.695
115.166
115.068
113.602
110.213
109.960
108.585
108.312
97.875
61.237
21.617
14.534

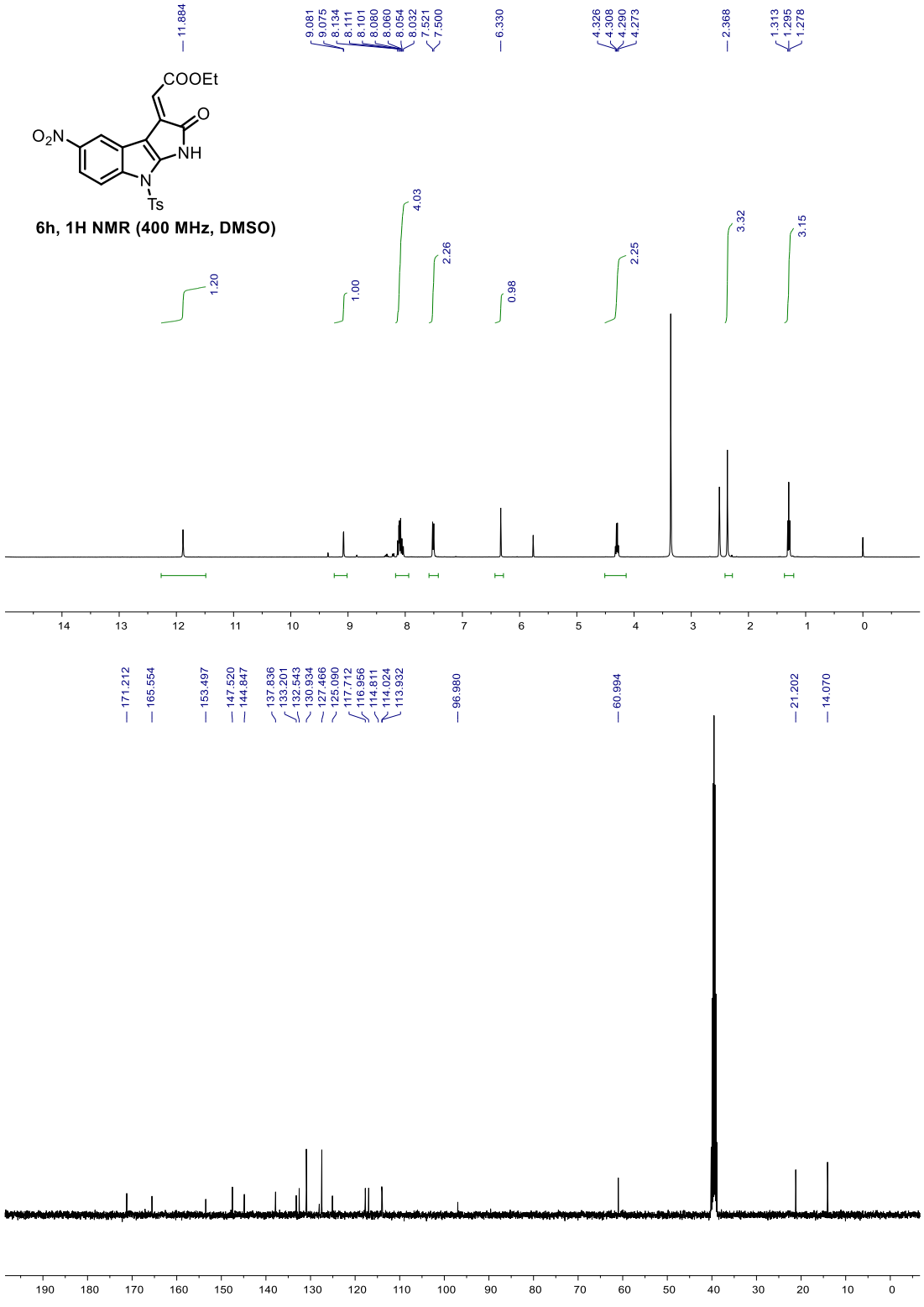

-116.881
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

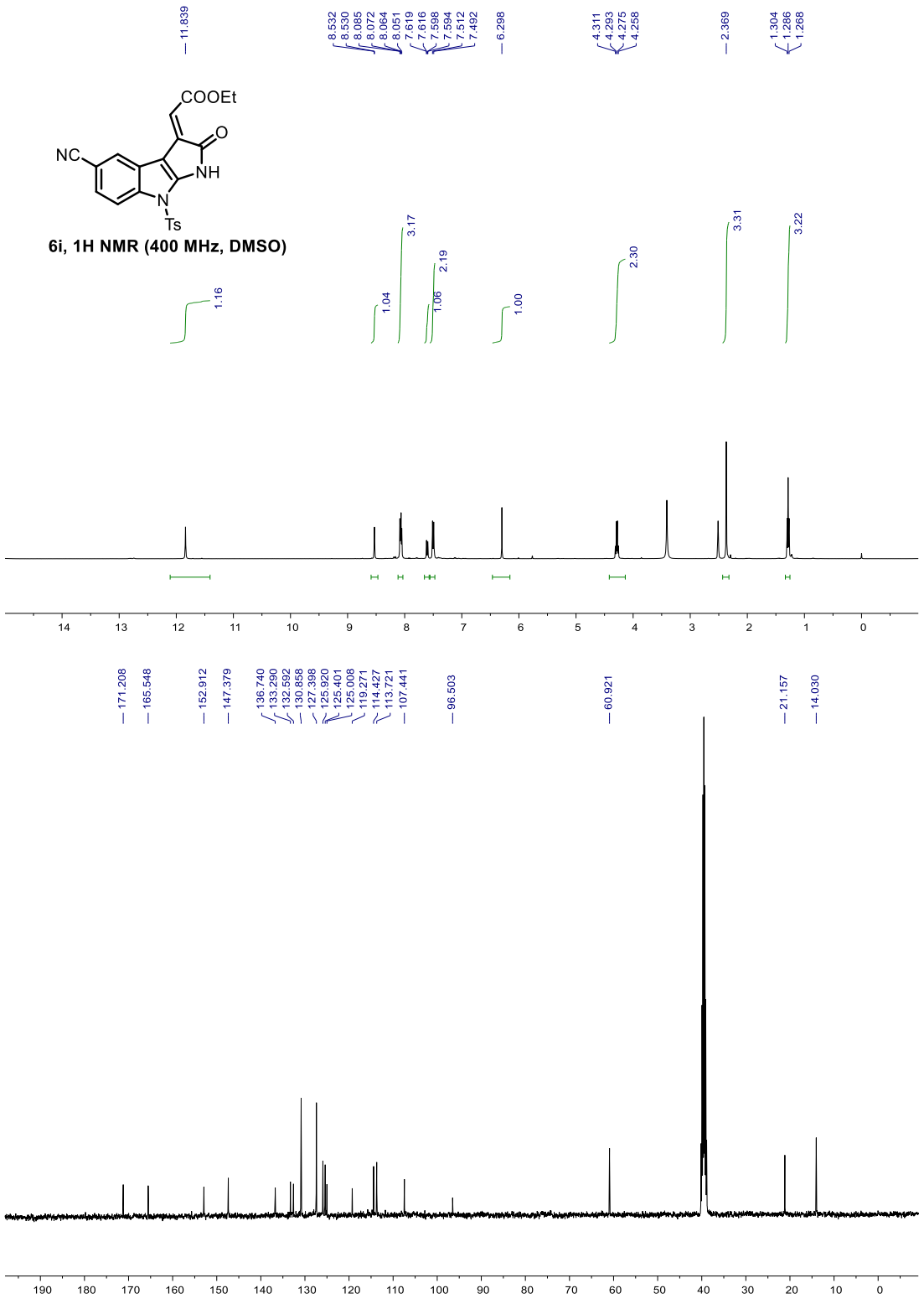


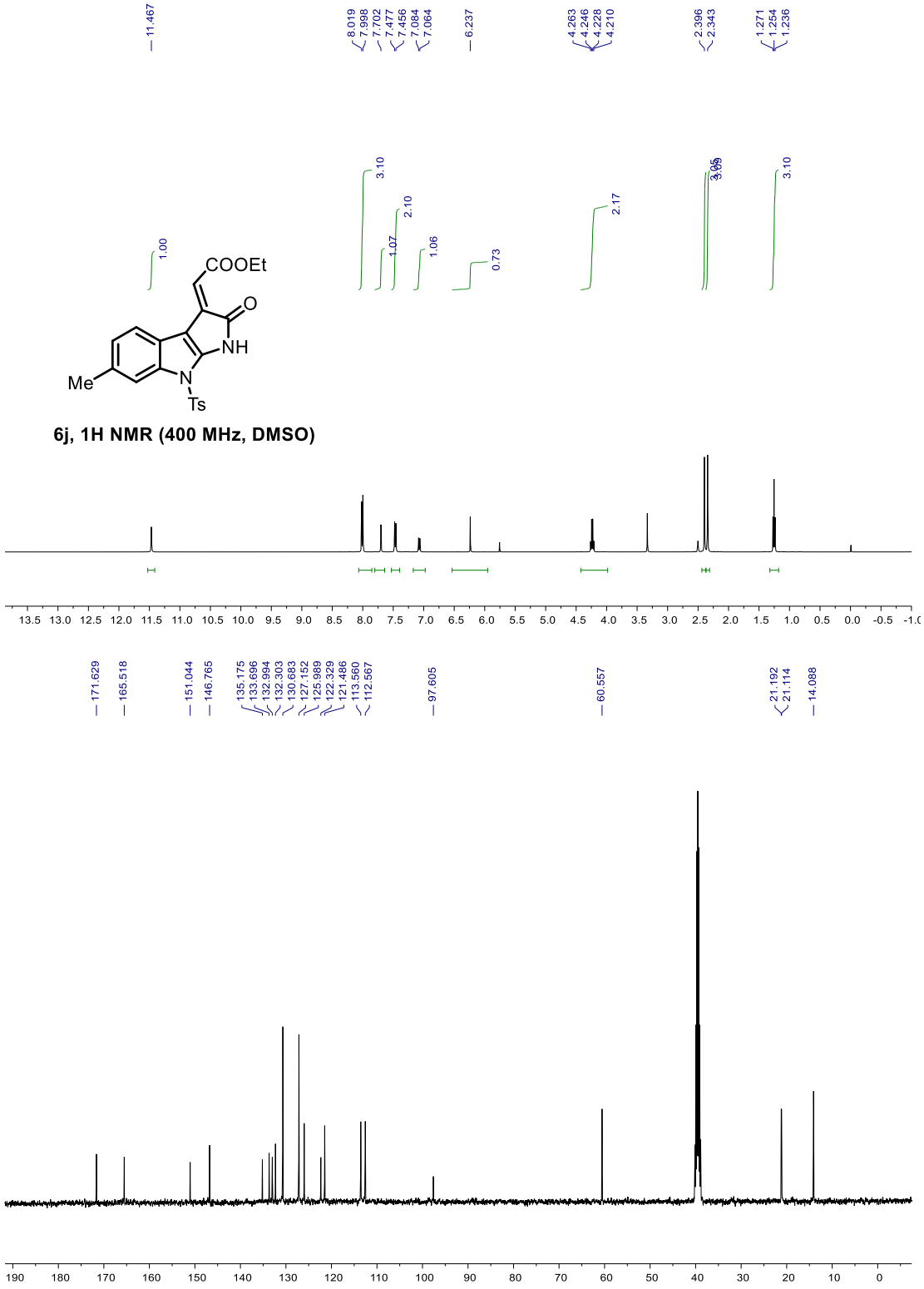
6e, 1H NMR (400 MHz, DMSO)

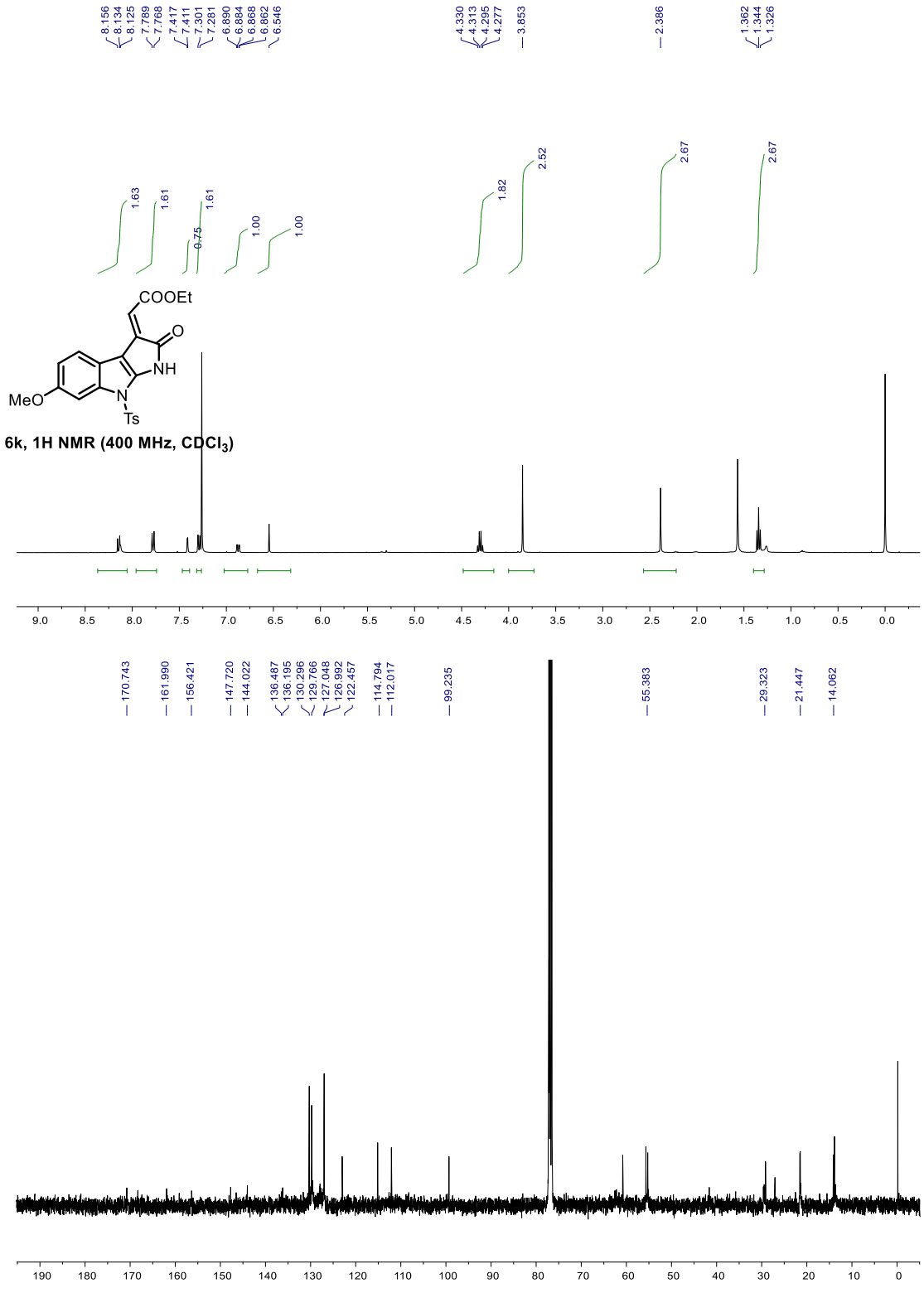

11.740
8.352
8.347
8.022
8.001
7.854
7.832
7.497
7.477
7.356
7.351
7.334
7.329
6.273
4.288
4.270
4.252
4.234
2.361
1.290
1.272
1.254
COOEt
O
Br
NH
N
Ts
6f, 1H NMR (400 MHz, DMSO)
1.09
1.07
2.28
1.12
2.26
1.20
1.00
2.22
3.42
3.50
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
172.032
165.593
147.163
133.674
133.473
132.686
130.825
127.324
126.601
125.047
124.149
117.969
115.191
113.285
96.744
60.857
21.184
14.083
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

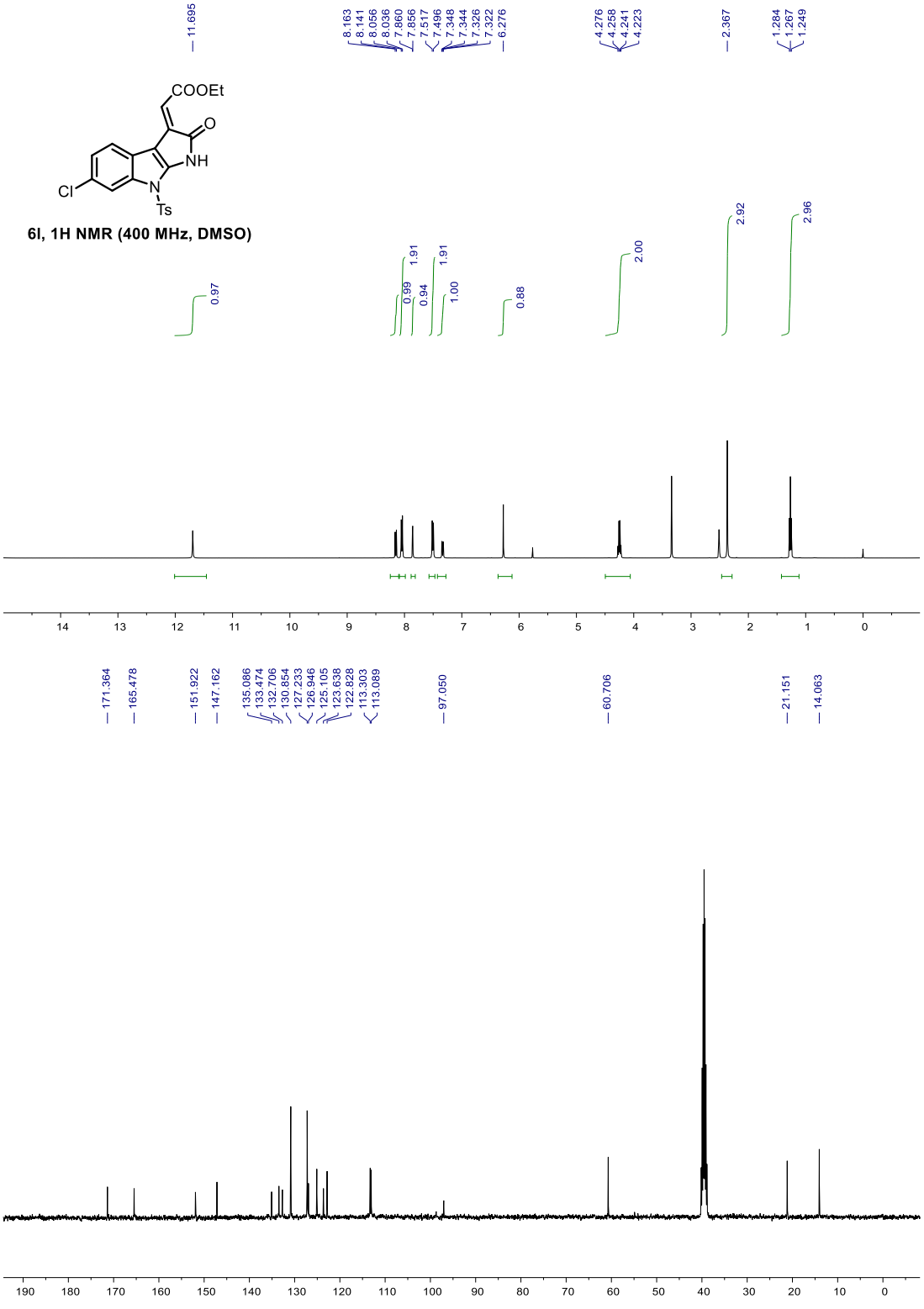

11.723
8.755
8.751
8.064
8.043
8.021
7.814
7.810
7.793
7.788
7.500
7.480
6.320
4.328
4.311
4.293
4.275
3.852
2.356
1.311
1.293
1.275
COOEt
O
MeOOC
NH
N
Ts
6g, 1H NMR (400 MHz, DMSO)
1.25
1.14
3.48
1.16
2.28
1.00
2.41
3.83
3.43
3.54
171.469
166.260
165.521
152.317
147.225
137.378
133.238
132.730
130.838
127.333
126.298
124.722
123.671
123.013
113.711
113.460
97.191
60.853
52.210
21.181
14.072

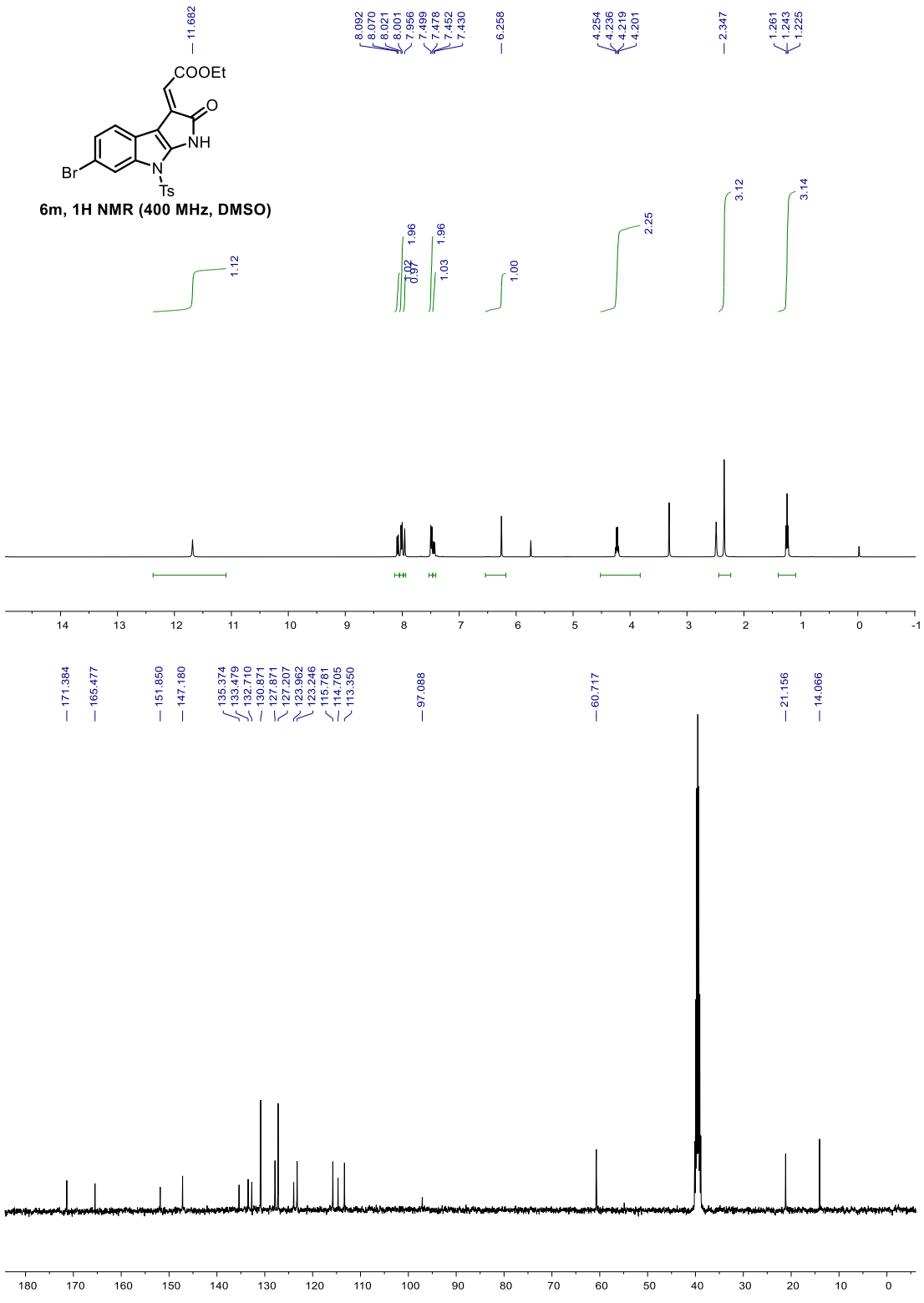

11.884
9.081
9.075
8.134
8.111
8.101
8.080
8.060
8.054
8.032
7.521
7.500
6.330
4.326
4.308
4.290
4.273
2.368
1.313
1.295
1.278
COOEt
O
O2N
NH
N
Ts
6h, 1H NMR (400 MHz, DMSO)
1.20
1.00
4.03
2.26
0.98
2.25
3.32
3.15
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
171.212
165.554
153.497
147.520
144.847
137.836
133.201
132.543
130.934
127.466
125.090
117.712
116.956
114.811
114.024
113.932
96.980
60.994
21.202
14.070
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

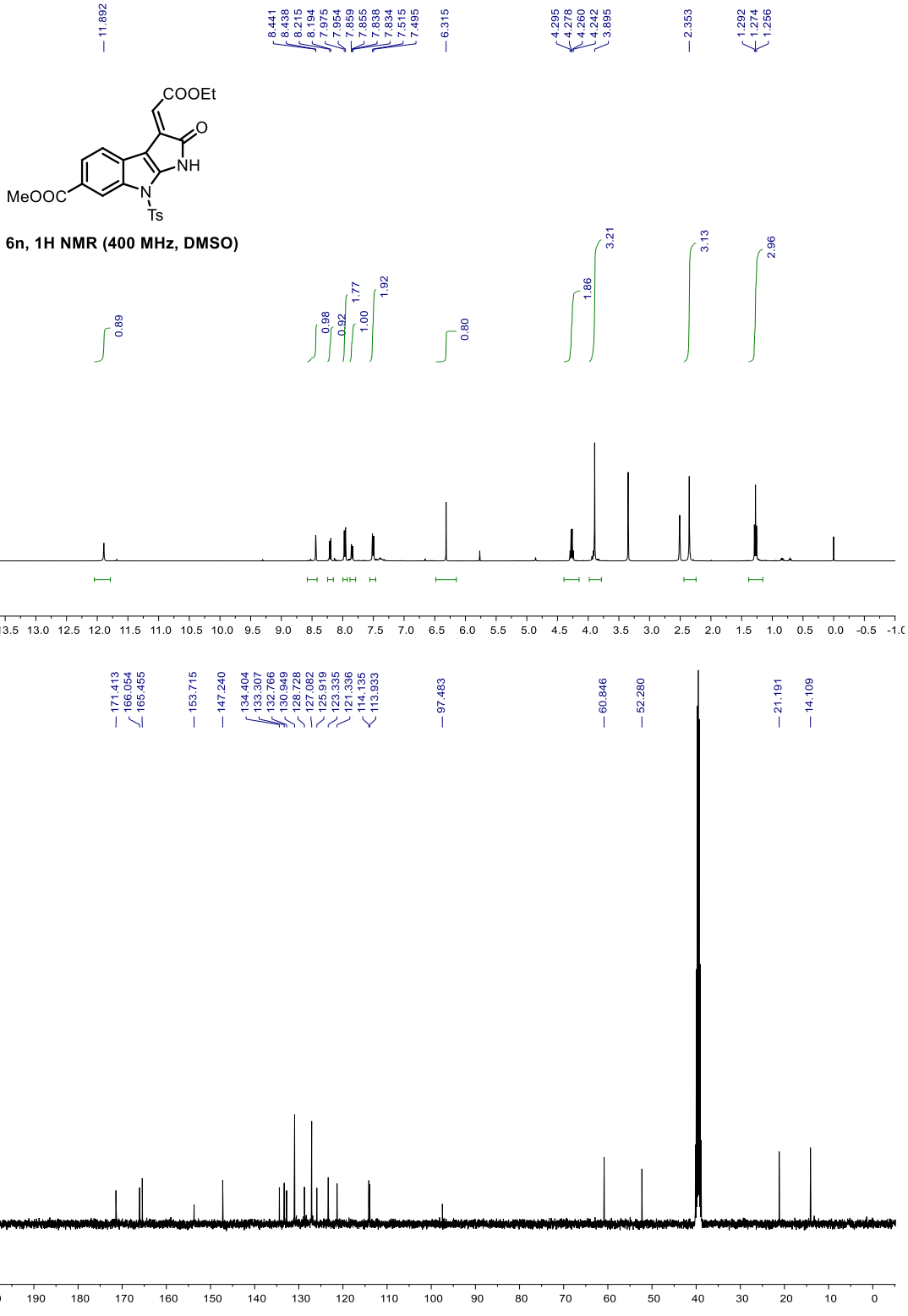

11.839
8.532
8.530
8.085
8.072
8.064
8.051
7.619
7.616
7.598
7.594
7.512
7.492
6.298
4.311
4.293
4.275
4.258
2.369
1.304
1.286
1.268
COOEt
O
NC
NH
N
Ts
6i, 1H NMR (400 MHz, DMSO)
1.16
1.04
3.17
1.06
2.19
1.00
2.30
3.31
3.22
171.208
165.548
152.912
147.379
136.740
133.290
132.592
130.858
127.398
125.920
125.401
125.008
119.271
114.427
113.721
107.441
96.503
60.921
21.157
14.030

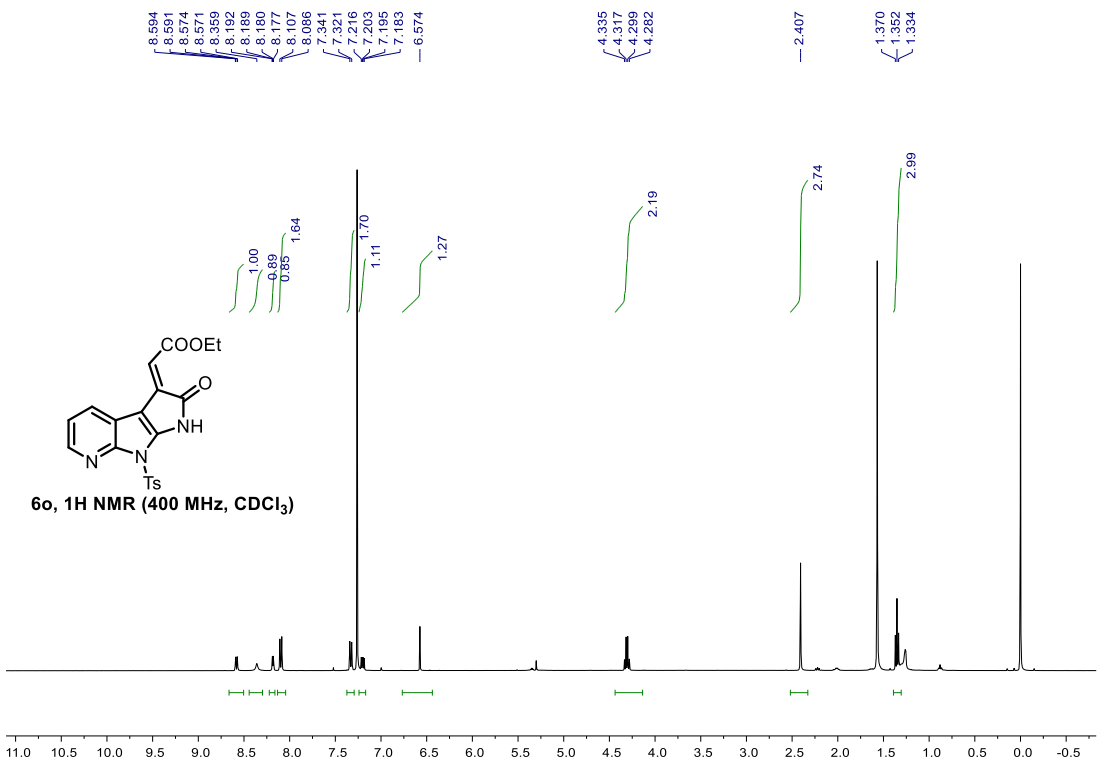

11.467
8.019
7.998
7.702
7.477
7.456
7.084
7.064
6.237
4.263
4.246
4.228
4.210
2.396
2.343
1.271
1.254
1.236
1.00
3.10
1.07
2.10
1.06
0.73
2.17
3.10
COOEt
O
NH
N
Me
Ts
6j, 1H NMR (400 MHz, DMSO)
171.629
165.518
151.044
146.765
135.175
133.696
132.994
132.303
130.683
127.152
125.989
122.329
121.486
113.560
112.567
97.605
60.557
21.192
21.114
14.088


8.156
8.134
8.125
7.789
7.768
7.417
7.411
7.301
7.281
6.890
6.884
6.868
6.862
6.546
4.330
4.313
4.295
4.277
3.853
2.386
1.362
1.344
1.326
1.63
1.61
0.75
1.61
1.00
1.00
1.82
2.52
2.67
2.67
COOEt
O
NH
MeO
N
Ts
6k, 1H NMR (400 MHz, CDCl3)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
170.743
161.990
156.421
147.720
144.022
136.487
136.195
130.296
129.766
127.048
126.992
122.457
114.794
112.017
99.235
55.383
29.323
21.447
14.062
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

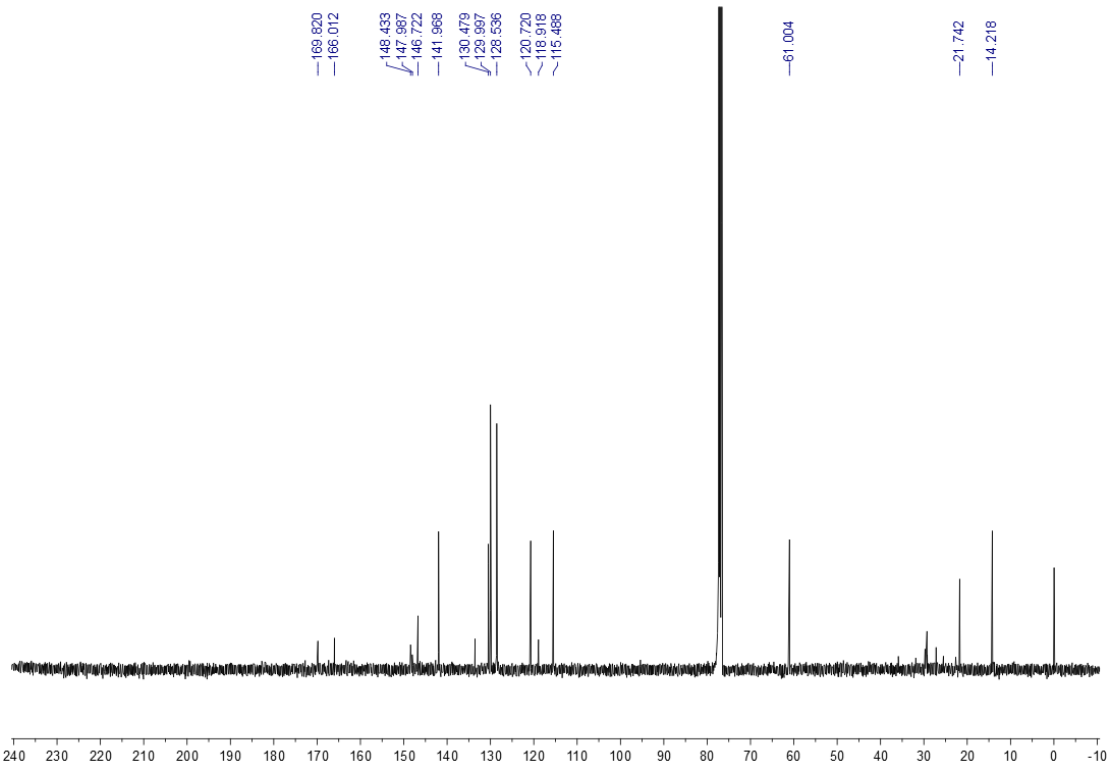

11.695
8.163
8.141
8.056
8.036
7.860
7.856
7.517
7.496
7.348
7.344
7.326
7.322
6.276
4.276
4.258
4.241
4.223
2.367
1.284
1.267
1.249
COOEt
O
NH
Cl
N
Ts
6l, 1H NMR (400 MHz, DMSO)
0.97
1.91
0.99
0.94
1.91
1.00
0.88
2.00
2.92
2.96
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
171.364
165.478
151.922
147.162
135.086
133.474
132.706
130.854
127.233
126.946
125.105
123.638
122.828
113.303
113.089
97.050
60.706
21.151
14.063
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

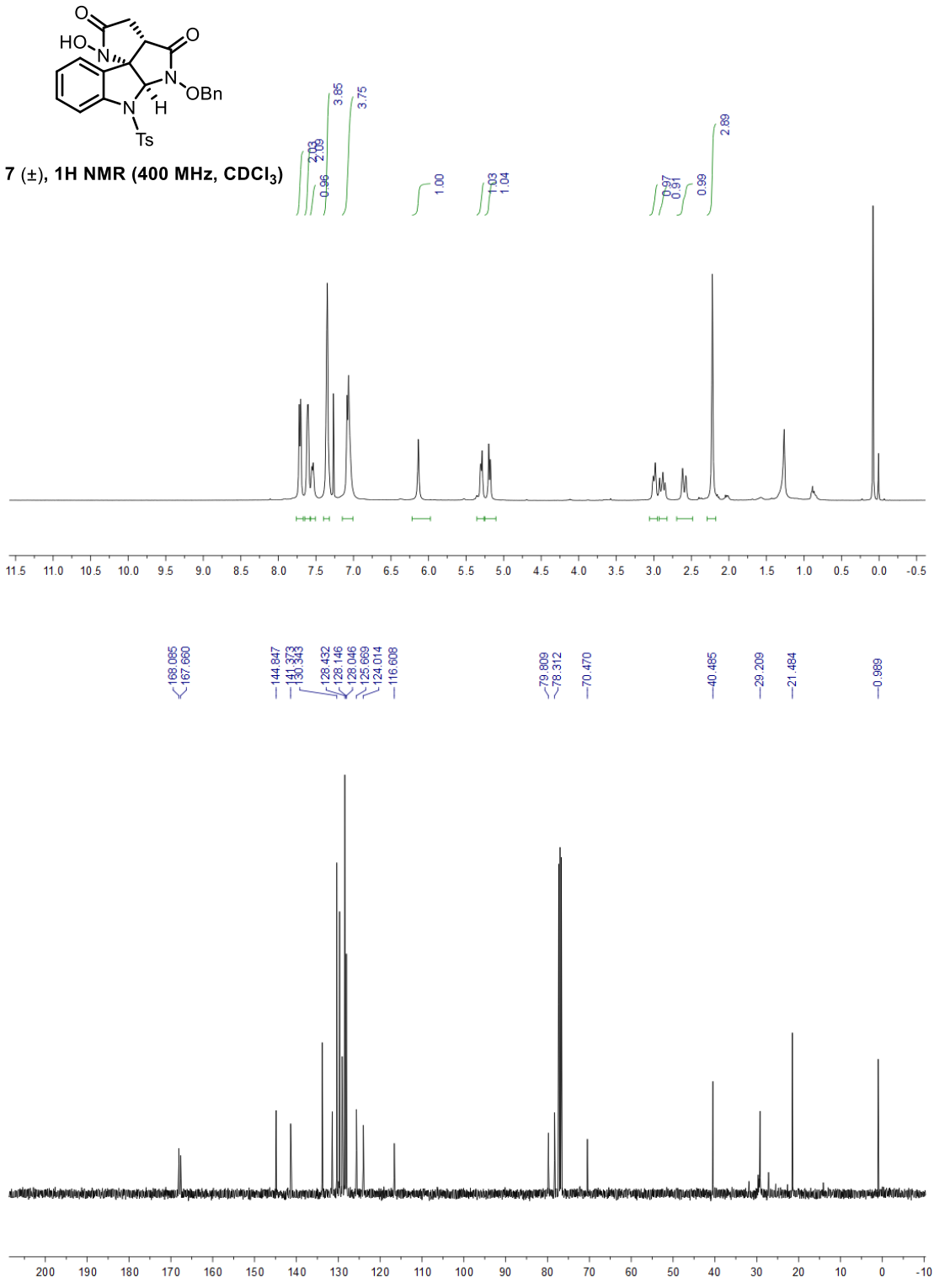

11.682
8.092
8.070
8.021
8.001
7.956
7.499
7.478
7.452
7.430
6.258
4.254
4.236
4.219
4.201
2.347
1.261
1.243
1.225
COOEt
O
NH
N
Br
Ts
6m, 1H NMR (400 MHz, DMSO)
1.12
1.96
1.97
1.03
1.96
1.00
2.25
3.12
3.14
171.384
165.477
151.850
147.180
135.374
133.479
132.710
130.871
127.871
127.207
123.962
123.246
115.781
114.705
113.350
97.088
60.717
21.156
14.066


11.892
8.441
8.438
8.215
8.194
7.975
7.954
7.859
7.855
7.838
7.834
7.515
7.495
6.315
4.295
4.278
4.260
4.242
3.895
2.353
1.292
1.274
1.256
COOEt
O
NH
MeOOC
N
Ts
6n, 1H NMR (400 MHz, DMSO)
0.89
0.98
0.92
1.77
1.00
1.92
0.80
1.86
3.21
3.13
2.96
14.0 13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
171.413
166.054
165.455
153.715
147.240
134.404
133.307
132.766
130.949
128.728
127.082
125.919
123.335
121.336
114.135
113.933
97.483
60.846
52.280
21.191
14.109
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

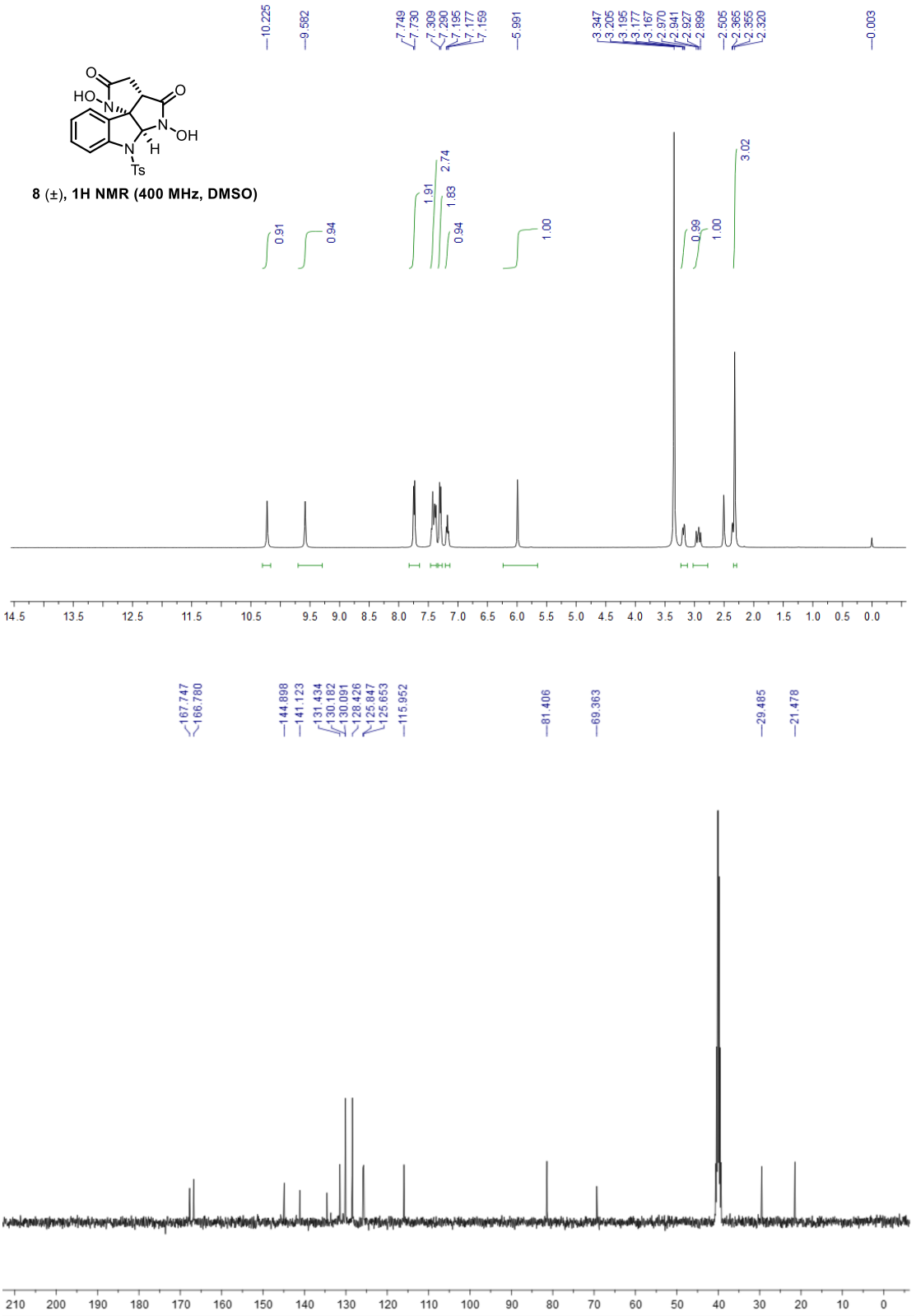


6o, 1H NMR (400 MHz, $CDCl_3$)





7 (±), **1H NMR (400 MHz, $CDCl_3$)**



8 (±), **1H NMR (400 MHz, DMSO)**

Figure S1, X-ray crystal structure of 4a (The crystal was obtained by slow evaporation of the solution of diethyl ether and hexane)

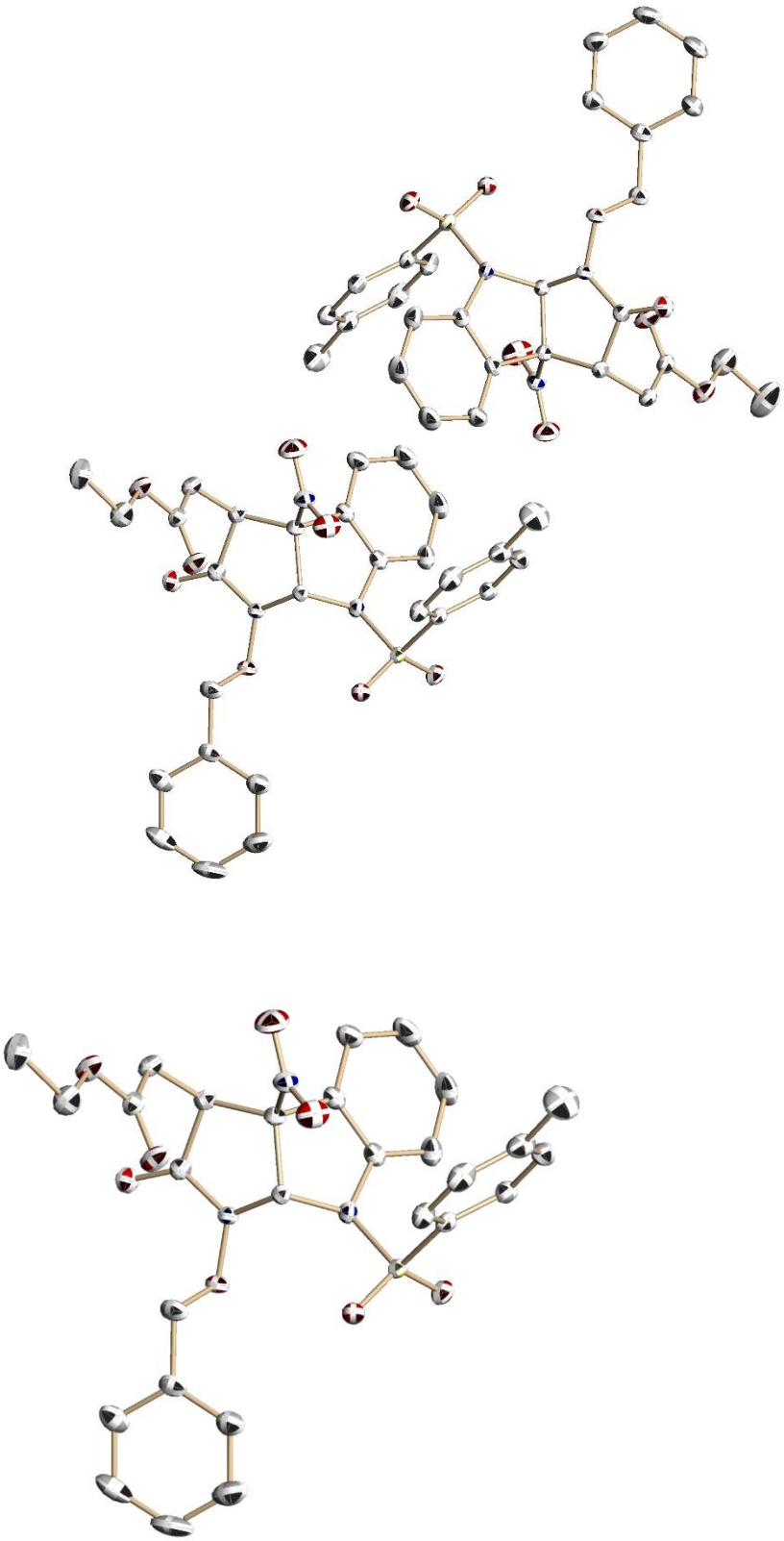


Table S4 Crystal data and structure refinement for 4a.

Identification code	20190529THZA	
Chemical formula	C56H54N6O16S2	
Formula weight	1131.17 g/mol	
Temperature	197(2) K	
Wavelength	1.54178 Å	
Crystal size	0.140 x 0.170 x 0.190 mm	
Crystal habit	clear light colourless block	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a =23.1540(14)Å	α = 90°
	b =10.2807(6)Å	β = 111.897(2)°
	c =24.2524(15)Å	γ = 90°
Volume	5356.5(6) Å3	
Z	4	
Density (calculated)	1.403 g/cm3	
Absorption coefficient	1.562 mm-1	
F(000)	2368	

Diffractometer	d8 venture
Theta range for data collection	2.25 to 72.47°
Index ranges	-28<=h<=27, -12<=k<=9, -29<=l<=29
Reflections collected	74191
Independent reflections	10542 [R(int) = 0.0272]
Coverage of independent reflections	99.1%
Absorption correction	Multi-Scan
Max. and min. transmission	0.8110 and 0.7560
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F2
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	Σ w(Fo2 - Fc2)2
Data / restraints / parameters	10542 / 0 / 725
Goodness-of-fit on F2	1.026
Δ/σmax	0.001
Final R indices	10234 data; I>2σ(I) R1 = 0.0326, wR2 = 0.0870

	all data	R1 = 0.0333, wR2 = 0.0878
Weighting scheme	w=1/[σ2(Fo2)+(0.0445P)2+2.6342P] where P=(Fo2+2Fc2)/3	
Largest diff. peak and hole	0.348 and -0.423 eÅ-3	
R.M.S. deviation from mean	0.043 eÅ-3	

Figure S2, X-ray crystal structure of 5a (The crystal was obtained by slow evaporation of the solution of diethyl ether and hexane)

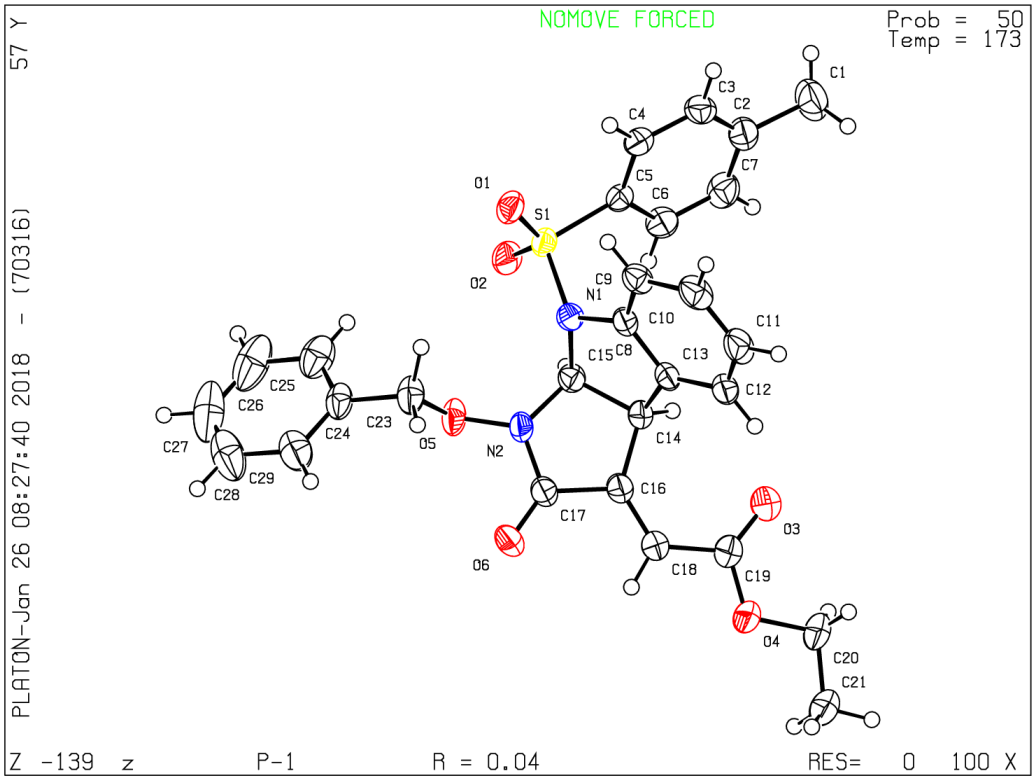


Table S5 Crystal data and structure refinement for 5a.

Identification code	z	
Empirical formula	C28 H26 N2 O6 S	
Formula weight	518.57	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.2364(5) Å	α= 107.241(2)°.
	b = 11.9238(6) Å	β= 105.874(2)°.
	c = 11.9612(6) Å	γ = 99.055(2)°.
Volume	1295.20(11) $Å^3$	
Z	2	
Density (calculated)	1.330 Mg/m^3	

Absorption coefficient	1.494 mm^{-1}
F(000)	544
Crystal size	0.260 x 0.230 x 0.200 mm^3
Theta range for data collection	4.612 to 66.639°.
Index ranges	-12<=h<=12, -14<=k<=14, -14<=l<=14
Reflections collected	16994
Independent reflections	4526 [R(int) = 0.0233]
Completeness to theta = 66.639°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.728 and 0.656
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4526 / 0 / 337
Goodness-of-fit on F^2	1.045

Figure S3, X-ray crystal structure of 6a (The crystal was obtained by slow evaporation of the solution of dichloromethane)

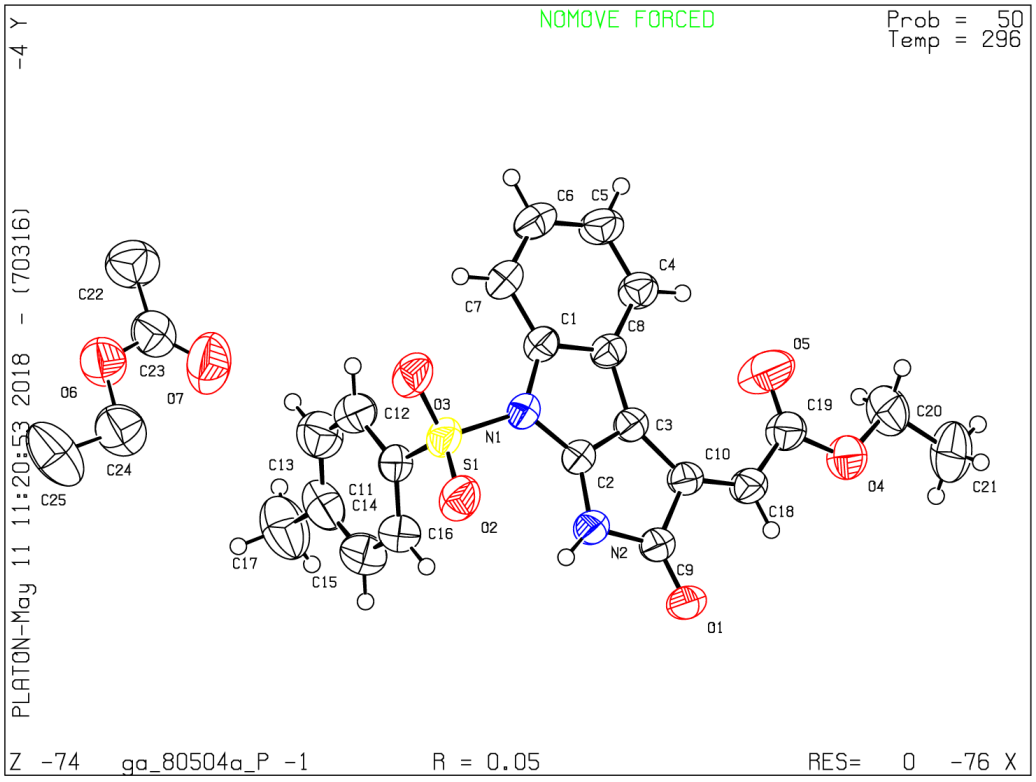


Table S6 Crystal data and structure refinement for 6a.

Identification code	ga_80504a_a
Empirical formula	C23 H22 N2 O6 S
Formula weight	454.48
Temperature	296(2) K
Wavelength	1.34138 Å

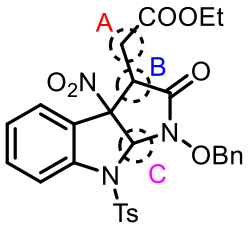
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.9808(13) Å	a= 105.673(13)°.
	b = 10.3586(15) Å	b= 95.539(11)°.
	c = 11.4372(19) Å	g = 102.695(12)°.
Volume	1095.3(3) $Å^3$	
Z	2	
Density (calculated)	1.378 Mg/m^3	
Absorption coefficient	1.096 mm^{-1}	
F(000)	476	
Crystal size	0.260 x 0.150 x 0.140 mm^3	
Theta range for data collection	3.541 to 60.667°.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	14321	
Independent reflections	5012 [R(int) = 0.0270]	
Completeness to theta = 53.594°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.902 and 0.788	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5012 / 36 / 323	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0496, wR2 = 0.1462	
R indices (all data)	R1 = 0.0586, wR2 = 0.1572	
Extinction coefficient	0.018(2)	
Largest diff. peak and hole	0.426 and -0.280 $e.Å^{-3}$	

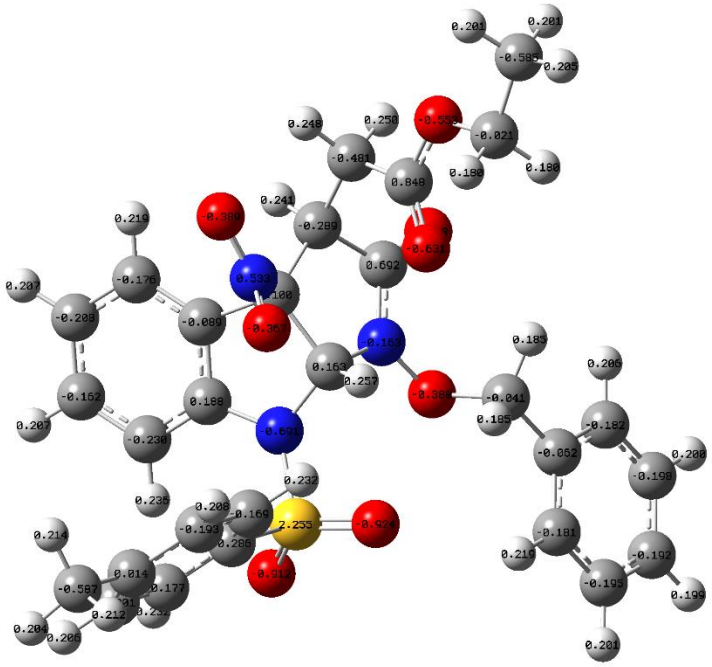
Theoretical calculation of atomic charges

The molecular geometric structures were optimized at B3LYP/6-311g(d,p) level of theory. Harmonic vibration frequency calculations at the same level were performed to verify all stationary points as local minima (with no imaginary frequency).

The natural bonding orbital (NBO) calculations were performed at the B3LYP method with 6-311g(d,p) basis set.

Compound **4a**





Intermediate I