4-Aminoindoles as 1,4-Bisnucleophiles for Diversity-Oriented Synthesis of Tricyclic Indoles Bearing 3,4-Fused Seven-Membered Rings

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Supporting Information

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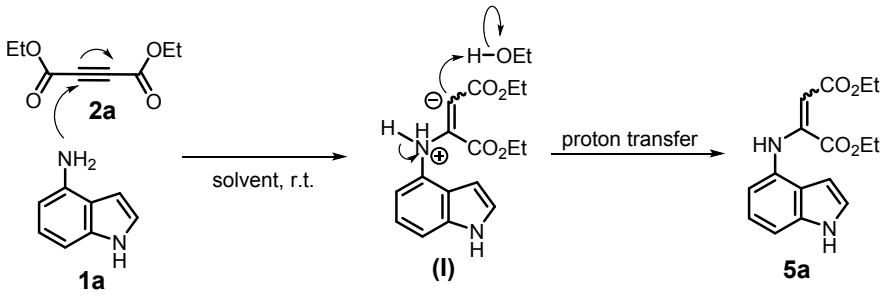
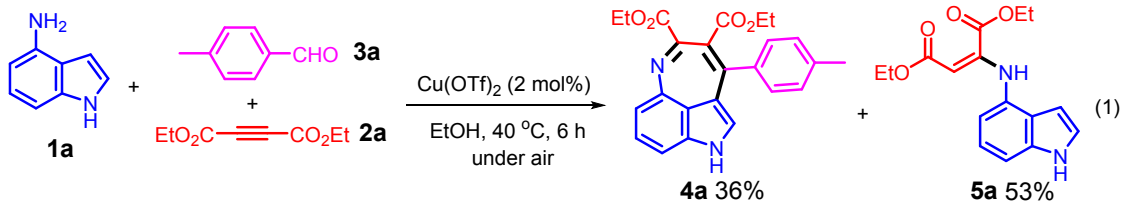


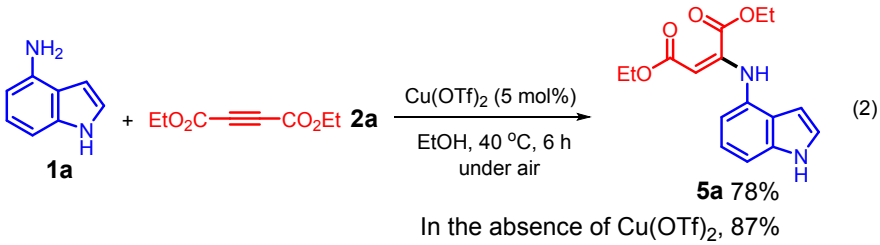
Figure S1 Plausible mechanism for the formation of **5a**

On the basis of the experimental result and previously reported works,[1] we provided the mechanism for the formation of **5a** as follows： the nitrogen atom of **1a** attacked the alkyne carbon of **2a** and formed intermediate **I**, and then an intermolecular proton transfer of the carbanion of intermediate **I** occurred, leading to the formation of **5a**.

2. Control experiments information

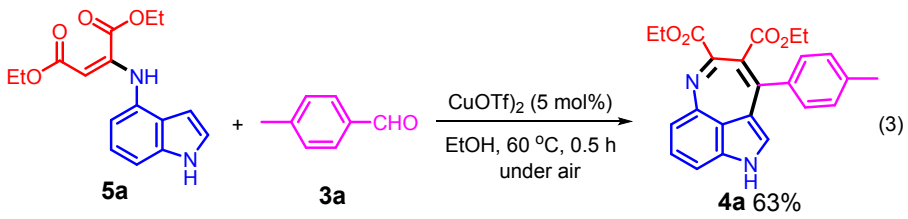


The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. **1a** (0.2 mmol) was mixed with **2a** (0.2 mmol), **3a** (0.2 mmol), and $Cu(OTf)_2$ (0.004 mmol, 2 mol%) in anhydrous ethanol (1.0 mL), the mixture was then stirred at 40 °C for 6 h. After the completion of the reaction, the mixture cooled to room temperature, and then subjected to an isolation with preparative TLC by using a mixture of petroleum ether and ethyl acetate as eluting solution (PE/EA = $4/1_{v/v}$). Compound **4a** was obtained in 36% (28.9 mg) yield, and compound **5a** was obtained in 53% yield (32.0 mg).

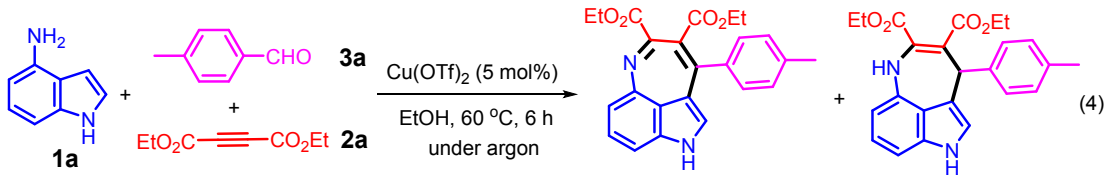


The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle

magnetic stirring. **1a** (0.2 mmol) was mixed with **2a** (0.2 mmol), and $Cu(OTf)_2$ (0.01 mmol, 5 mol%) in anhydrous ethanol (1.0 mL). The mixture was then stirred at 40 °C for 6 h. After the completion of the reaction, the mixture cooled to room temperature, and then subjected to an isolation with preparative TLC by using a mixture of petroleum ether and ethyl acetate as eluting solution (PE/EA = $4/1_{v/v}$). Compound **5a** was obtained in 78% yield (47.1 mg). Under the same conditions, compound **5a** was obtained in 87% yield (52.6 mg) without adding any catalyst.



The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. Compound **5a** (0.2 mmol) was mixed with **3a** (0.2 mmol), and $Cu(OTf)_2$ (0.01 mmol, 5 mol%) in ethanol (1.0 mL), the mixture was then stirred at 60 °C for 0.5 h. After the completion of the reaction, the mixture cooled to room temperature, and then subjected to an isolation with preparative TLC by using a mixture of petroleum ether and ethyl acetate as eluting solution (PE/EA = $4/1_{v/v}$). Compound **4a** was obtained in 63% yield (50.7 mg).

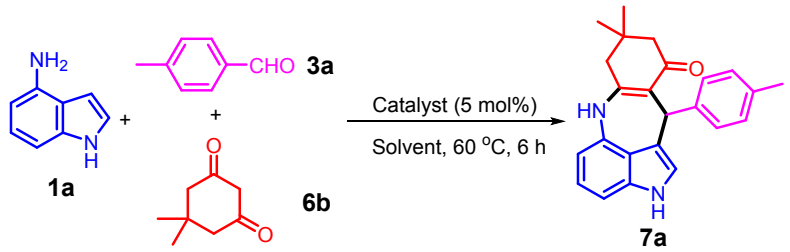


Total yield: 89%, **4a**/**5b** = 1/4

The reactions were conducted in a 10 mL of V-type flask equipped with oil bath and triangle magnetic stirring. **1a** (0.3 mmol) was mixed with **2a** (0.3 mmol), **3a** (0.2 mmol), and $Cu(OTf)_2$ (0.01 mmol, 5 mol%) in ethanol (1.0 mL). The mixture was then stirred under argon atmosphere at 60 °C for 6 h. After the completion of the reaction, the mixture cooled to room temperature, and then subjected to an isolation with preparative TLC by using a mixture of petroleum ether and ethyl acetate as eluting solution (PE/EA = $4/1_{v/v}$). The mixture of **4a** and **5b** was obtained in 89% yield (68.7 mg), and the molar ratio of **4a**/**5b** is ca. 1/4 (determined by ^{1}H NMR).

3. Condition optimization

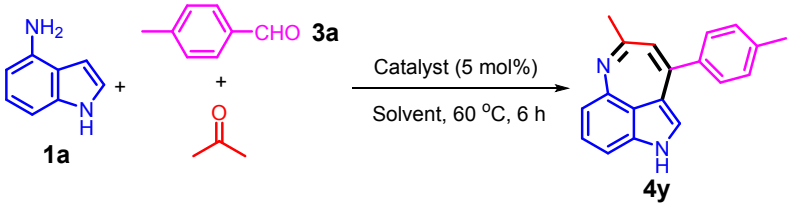
Table S1 Optimization of the three-component reaction of **1a**, **3a** and 1,3-cyclohexanediones.[a]



Entry	Catalyst	Solvent	Yield (**7a**, %)[b]
1	—	EtOH	0
2	$Cu(OTf)_2$	EtOH	0
3	$Fe(OTf)_3$	EtOH	0
4	$Al(OTf)_3$	EtOH	0
5	$Sc(OTf)_3$	EtOH	0
6	$CuCl_2$	EtOH	0
7	LiBr	EtOH	0
8	KOH	EtOH	34
9	$KF{\cdot}H_2O$	EtOH	21
10	Cs_2CO_3	EtOH	16
11	K_2CO_3	EtOH	< 10
12	Et_3N	EtOH	< 10
13	Pyridine	EtOH	< 10
14	KOH	MeCN	42
15	KOH	1,4-Dioxane	55
16	KOH	DCE	19
17	KOH	$MeNO_2$	24
18[c]	KOH	1,4-Dioxane	48
19[d]	KOH	1,4-Dioxane	52

[a] **1a**, 0.2 mmol; **3a**, 0.22 mmol; **6b**, 0.22 mmol; catalyst, 0.01 mmol; solvent, 1 mL; 60 °C; 6 h. [b] Isolated yield. [c] KOH 0.02 mmol. [d] 80 °C.

Table S2 Optimization of the three-component reaction of **1a**, **3a** and acetone.[a]

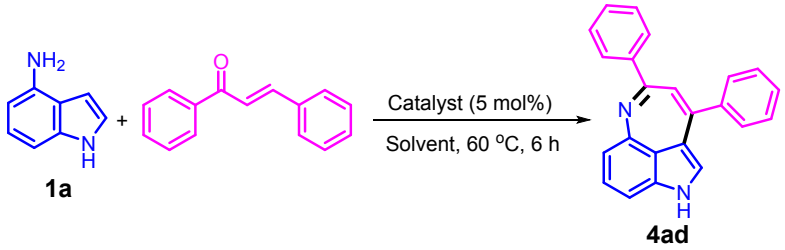


Entry	Catalyst	Solvent	Yield (**4y**, %)[b]
1	—	1,4-Dioxane	0
2	$Cu(OTf)_2$	1,4-Dioxane	17
3	$Fe(OTf)_3$	1,4-Dioxane	51
4	$Al(OTf)_3$	1,4-Dioxane	29

5	$Sc(OTf)_3$	1,4-Dioxane	33
6	$Bi(OTf)_3$	1,4-Dioxane	35
7	$Fe(OTf)_3$	1,4-Dioxane	27
8	$Fe(OTf)_3$	EtOH	35
9	$Fe(OTf)_3$	MeCN	52
10	$Fe(OTf)_3$	Toluene	21
11[c]	$Fe(OTf)_3$	1,4-Dioxane	64
12[d]	$Fe(OTf)_3$	1,4-Dioxane	63
13[e]	$Fe(OTf)_3$	1,4-Dioxane	47
14[f]	$Fe(OTf)_3$	1,4-Dioxane	78

[a] **1a**, 0.3 mmol; **3a**, 0.2 mmol; acetone, 0.3 mmol; catalyst, 0.01 mmol; solvent, 1 mL; 60 °C; 6 h. [b] Isolated yield. [c] $Fe(OTf)_3$, 0.02 mmol. [d] $Fe(OTf)_3$, 0.04 mmol. [e] $Fe(OTf)_3$, 0.02 mmol, 40 °C. [f] $Fe(OTf)_3$, 0.02 mmol, 80 °C.

Table S3 Optimization of the reaction of **1a** and chalcone.[a]

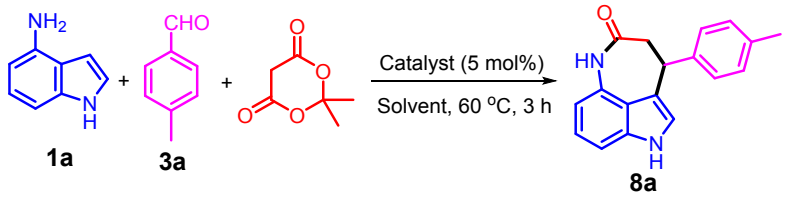


1a **4ad**

Entry	Catalyst	Solvent	Yield (**4ad**, %)[b]
1	—	1,4-Dioxane	0
2	$Cu(OTf)_2$	1,4-Dioxane	< 5
3	$Fe(OTf)_3$	1,4-Dioxane	24
4	$AlCl_3$	1,4-Dioxane	0
5	$FeCl_3$	1,4-Dioxane	0
6	$Fe(OTf)_3$	EtOH	14
7	$Fe(OTf)_3$	MeCN	21
8	$Fe(OTf)_3$	Toluene	0
9[c]	$Fe(OTf)_3$	1,4-Dioxane	36
10[d]	$Fe(OTf)_3$	1,4-Dioxane	39
11[e]	$Fe(OTf)_3$	1,4-Dioxane	47
12[f]	$Fe(OTf)_3$	1,4-Dioxane	23

[a] **1a**, 0.3 mmol; chalcone, 0.3 mmol; catalyst, 0.015 mmol; solvent, 1 mL; 60 °C; 6 h. [b] Isolated yield. [c] $Fe(OTf)_3$, 0.03 mmol. [d] $Fe(OTf)_3$, 0.06 mmol. [e] $Fe(OTf)_3$, 0.03 mmol, 80 °C. [f] $Fe(OTf)_3$, 0.03 mmol, 100 °C.

Table S4 Optimization of the three-component reaction of **1a**, **3a** and Meldrum's acid.[a]



Entry	Catalyst	Solvent	Yield (**8a**, %)[b]
1	—	EtOH	52
2	$Cu(OTf)_2$	EtOH	31
3	$Fe(OTf)_3$	EtOH	24
4	$CuBr_2$	EtOH	0
5	—	MeCN	76
6	$Cu(OTf)_2$	MeCN	22
7	$Fe(OTf)_3$	MeCN	14
8	—	1,4-Dioxane	37
9	—	Toluene	< 10
10	—	THF	0
11[c]	—	MeCN	74
12[d]	—	MeCN	78

[a] **1a**, 0.3 mmol; **3a**, 0.3 mmol; Meldrum's acid, 0.3 mmol; catalyst, 0.015 mmol; solvent, 1 mL; 60 °C; 3 h. [b] Isolated yield. [c] 80 °C. [d] 4 h.

4. Characterization data of all new compounds

Diethyl 4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4a**): yellow solid (69.9 mg, 87% yield), mp: 167–169 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.96 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.58–7.54 (m, 3H), 7.33 (d, J = 7.7 Hz, 2H), 7.19 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.39 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.05 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.4, 166.4, 154.2, 143.7, 139.2, 138.3, 137.2, 135.7, 128.9, 128.4, 125.1, 123.3, 120.3, 117.3, 116.7, 116.0, 102.2, 62.2, 61.5, 20.9, 13.9, 13.5 ppm; IR (KBr) v = 3369, 2980, 1728, 1550, 1376, 1248, 1027, 747, 501 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{23}N_2O_4^+$, $[M + H]^+$ 403.1652, found 403.1651.

Diethyl 2-((1*H*-indol-4-yl)amino)maleate (**5a**): yellow oil; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.29 (s, 1H), 9.92 (s, 1H), 7.36 (t, J = 2.8 Hz, 1H), 7.19 (d, J = 8.1 Hz, 1H), 7.00 (t, J = 7.8 Hz, 1H), 6.47–6.41 (m, 2H), 5.26 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.07 (q, J = 7.0 Hz, 2H), 1.23 (t, J = 7.0 Hz, 3H), 0.96 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 169.0, 163.9, 149.0, 136.9, 131.8, 125.4, 121.3, 121.2, 109.7, 108.3, 97.7, 91.6, 61.8, 59.7, 14.3, 13.4 ppm; IR (KBr) v = 3778, 2923, 1731, 1605, 1272, 1211, 1027, 749, 587, 482 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{16}H_{19}N_2O_4^+$, $[M + H]^+$ 303.1339, found 303.1342.

The mixture of **4a** and **5b**: yellow oil (68.7 mg, 89% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.96 (s, 1H), 11.17 (s, 4H), 7.86 (d, J = 9.0 Hz, 1H), 7.62 (s, 1H), 7.60–7.48 (m, 8H), 7.34 (s, 2H), 7.20 (s, 6H), 7.14 (d, J = 2.6 Hz, 4H), 7.04 (d, J = 7.8 Hz, 8H), 6.65 (d, J = 8.6 Hz, 8H), 6.59 (d, J = 8.6 Hz, 4H), 5.57 (d, J = 2.9 Hz, 4H), 4.47 (q, J = 7.1 Hz, 2H), 4.31 (q, J = 7.1 Hz, 8H), 4.10 (q, J = 6.8 Hz, 8H), 4.02 (t, J = 7.2 Hz, 2H), 2.40 (s, 2H), 2.20 (s, 12H), 1.35 (d, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 12H), 1.16 (t, J = 7.1 Hz, 12H), 1.06 ppm (d, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 168.0, 167.4, 166.4, 164.6, 154.2, 143.7, 141.7, 141.3, 139.8, 139.3, 138.3, 138.2, 137.2, 136.6, 135.7, 129.7, 128.9, 128.5, 125.7, 125.1, 123.5, 123.3, 120.3, 120.3, 117.3, 116.7, 116.0, 114.7, 111.1, 105.0, 102.3, 102.2, 100.2, 62.3, 61.6, 60.9, 60.3, 59.8, 51.9, 20.9, 20.6, 14.1, 14.0, 14.0, 13.9, 13.5 ppm; IR (KBr) v = 3362, 2925, 1732, 1550, 1354, 1248, 1027, 826, 750, 522 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{25}N_2O_4^+$ (**5b**), $[M + H]^+$ 405.1809, found 405.1810.

Diethyl 4-phenyl-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4b**): yellow solid (41.9 mg, 54% yield), mp: 150–152 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.99 (s, 1H), 7.89 (d, J = 9.0 Hz, 1H), 7.68–7.62 (m, 3H), 7.57 (t, J = 2.7 Hz, 1H), 7.53 (q, J = 7.0 Hz, 3H), 7.21 (s, 1H), 4.47 (q, J = 7.2 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H), 1.00 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.3, 166.4, 154.4, 143.7, 140.1, 139.4, 135.8, 128.7, 128.5, 128.3, 125.2, 123.3, 120.4, 117.3, 116.8, 116.2, 102.3, 62.3, 61.5, 13.9, 13.4 ppm; IR (KBr) v = 3380, 2980, 1717, 1549, 1246, 1213, 1017, 737, 696, 597, 499 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}N_2O_4^+$, $[M + H]^+$ 389.1496, found 389.1495.

Diethyl 4-(4-(*tert*-butyl)phenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4c**): yellow oil (54.2 mg, 61% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.97 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.65–7.60 (m, 2H), 7.58 (d, J = 7.2 Hz, 3H), 7.53 (d, J = 8.1 Hz, 2H), 7.21 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 1.36 (d, J = 7.1 Hz, 3H), 1.33 (s, 9H), 0.98 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.4, 166.4, 154.3, 151.3, 143.8, 139.3, 137.3, 135.7, 128.2, 125.1, 125.0, 123.4, 120.3, 117.3, 116. 7, 116.1, 102.3, 62.2, 61.5, 34.3, 31.1, 13.8, 13.3 ppm; IR (KBr) v = 3209, 2961, 1732, 1412, 1362, 1249, 1028, 747, 593, 447 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{27}H_{29}N_2O_4^+$, $[M + H]^+$ 445.2122, found 445.2121.

Diethyl 4-(4-methoxyphenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4d**): yellow oil (58.5 mg, 70% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.95 (s, 1H), 7.85 (d, J = 9.0 Hz, 1H), 7.62 (t, J = 9.6 Hz, 3H), 7.56 (t, J = 2.7 Hz, 1H), 7.20 (s, 1H), 7.09 (d, J = 8.3 Hz, 2H), 4.47 (q, J = 7.1 Hz, 2H), 4.16 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.09 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.5, 166.4, 159.9, 153.8, 143.7, 139.3, 135.7, 132.3, 129.9, 125.0, 123.3, 120.2, 117.3, 116.5, 115.9, 113.8, 102.2, 62.2, 61.5, 55.3, 13.9, 13.6 ppm; IR (KBr) v = 3381, 2929, 2844, 1731, 1607, 1513, 1251, 1103, 1031, 749, 557, 425 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{23}N_2O_5^+$, $[M + H]^+$ 419.1601, found 419.1601.

Diethyl 4-(4-methylthiophenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4e**): yellow oil (53.8 mg, 62% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.97 (s, 1H), 7.87 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 8.3 Hz, 3H), 7.57 (t, J = 2.7 Hz, 1H), 7.41 (d, J = 8.1 Hz, 2H), 7.20 (s, 1H), 4.47 (q, J = 7.3 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.54 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.08 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.3, 166.4, 153.7, 143.7, 139.5, 139.4, 136.3, 135.8, 129.0, 125.5, 125.2, 123.3, 120.1, 117.3, 116.8, 116.1, 102.3, 62.2, 61.6, 14.5,

13.9, 13.5 ppm; IR (KBr) v = 3380, 2982, 1730, 1592, 1494, 1249, 1141, 1027, 747, 505 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{23}N_2O_4S^+$, $[M + H]^+$ 435.1373, found 435.1365.

Diethyl 4-(4-chlorophenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4f**): yellow oil (57.4 mg, 68% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.01 (s, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.67 (t, J = 7.6 Hz, 3H), 7.64–7.55 (m, 4H), 7.20 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.05 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.1, 166.3, 153.2, 143.8, 139.6, 138.9, 135.9, 133.7, 130.3, 128.4, 125.3, 123.3, 120.1, 117.3, 117.1, 116.4, 102.3, 62.3, 61.7, 13.9, 13.5 ppm; IR (KBr) v = 3379, 2927, 1731, 1549, 1412, 1250, 1142, 1027, 778, 502 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{20}ClN_2O_4^+$, $[M + H]^+$ 423.1106, found 423.1105.

Diethyl 4-(4-(bromophenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4g**): yellow oil (49.4 mg, 53% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.01 (s, 1H), 7.90 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 8.1 Hz, 2H), 7.66–7.56 (m, 4H), 7.20 (s, 1H), 4.47 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.05 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.0, 166.3, 153.3, 143.8, 139.6, 139.2, 135.8, 131.3, 130.6, 125.3, 123.3, 122.4, 120.0, 117.3, 117.1, 116.4, 102.3, 62.3, 61.7, 13.9, 13.5 ppm; IR (KBr) v = 3381, 2927, 1730, 1588, 1489, 1250, 1142, 1027, 748, 500 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{20}BrN_2O_4^+$, $[M + H]^+$ 467.0601, found 467.0600.

Diethyl 4-(4-(ethoxycarbonyl)phenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4h**): yellow oil (74.5 mg, 81% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.03 (s, 1H), 8.12 (d, J = 8.0 Hz, 2H), 7.91 (d, J = 9.0 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.65 (d, J = 9.0 Hz, 1H), 7.59 (t, J = 2.8 Hz, 1H), 7.21 (t, J = 2.5 Hz, 1H), 4.48 (q, J = 7.0 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 4.12 (q, J = 7.1 Hz, 2H), 1.36 (td, J = 7.2, 2.3 Hz, 6H), 1.02 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.9, 166.3, 165.5, 153.4, 144.5, 143.7, 139.7, 135.9, 129.9, 129.1, 128.9, 125.4, 123.3, 120.1, 117.3, 117.2, 116.5, 102.3, 62.3, 61.7, 60.9, 14.2, 13.8, 13.4 ppm; IR (KBr) v = 3377, 2927, 1722, 1609, 1550, 1363, 1227, 1179, 872, 746, 526 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{26}H_{25}N_2O_6^+$, $[M + H]^+$ 461.1707, found 461.1706.

Diethyl 4-(4-cyanophenyl)-4,6-dihydro-3*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4i**): yellow solid (43.0 mg, 52% yield), mp: 168–170 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.04 (s, 1H), 8.01 (d, J = 7.9 Hz, 2H), 7.93 (d, J = 9.0 Hz, 1H), 7.83 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 9.0 Hz,

1H), 7.59 (t, J = 2.7 Hz, 1H), 7.20 (s, 1H), 4.48 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.02 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.7, 166.2, 152.9, 144.6, 143.7, 140.0, 135.9, 132.3, 129.5, 125.5, 123.3, 119.9, 118.7, 117.4, 117.3, 116.7, 111.3, 102.3, 62.3, 61.8, 13.8, 13.4 ppm; IR (KBr) v = 3201, 2925, 2228, 1730, 1607, 1548, 1250, 1224, 1028, 779, 539 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{20}N_3O_4^+$, $[M + H]^+$ 414.1448, found 414.1447.

Diethyl 4-(4-nitrophenyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4j**): yellow solid (34.7 mg, 40% yield), mp: 169–171 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.06 (s, 1H), 8.39 (d, J = 8.3 Hz, 2H), 7.93 (t, J = 8.6 Hz, 3H), 7.66 (d, J = 9.0 Hz, 1H), 7.60 (t, J = 2.7 Hz, 1H), 7.22 (s, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H), 1.03 ppm (t, J = 7.1 Hz, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.6, 166.2, 152.6, 147.5, 146.4, 143.8, 140.0, 136.0, 130.0, 125.5, 123.5, 123.3, 119.8, 117.6, 117.4, 116.8, 102.4, 62.4, 61.9, 13.9, 13.4 ppm; IR (KBr) v = 3389, 2927, 1729, 1602, 1520, 1347, 1250, 1027, 857, 745, 527 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{20}N_3O_6^+$, $[M + H]^+$ 434.1347, found 434.1345.

Diethyl 4-(4-trifluoromethyl)phenyl)-6*H*-azepino[4,3,2-cd]indole-2,3-dicarboxylate (**4k**): yellow solid (39.2 mg, 43% yield), mp: 126–128 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.04 (s, 1H), 7.93 (d, J = 9.1 Hz, 1H), 7.92–7.84 (m, 4H), 7.66 (d, J = 9.0 Hz, 1H), 7.59 (t, J = 2.6 Hz, 1H), 7.21 (s, 1H), 4.49 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 0.99 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.8, 166.3, 153.2, 144.1, 143.8, 139.9, 135.9, 129.0 (d, $^2J_{C\text{-}F}$ = 32 Hz), 129.4, 125.4, 125.2 (q, $^3J_{C\text{-}F}$ = 4 Hz), 124.3 (d, $^1J_{C\text{-}F}$ = 270 Hz) , 123.3, 120.0, 117.3, 117.3, 116.6, 102.3, 62.3, 61.7, 13.8, 13.2 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C) δ = -61.1 ppm; IR (KBr) v = 3379, 2984, 1730, 1615, 1551, 1324, 1128, 1028, 852, 746, 606 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{20}F_3N_2O_4^+$, $[M + H]^+$ 457.1370, found 457.1361.

Diethyl 4-(2-methoxyphenyl)-6*H*-azepino[4,3,2-cd]indole-2,3-dicarboxylate (**4l**): yellow solid (46.8 mg, 56% yield), mp: 125–127 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.97 (s, 1H), 7.88 (d, J = 9.0 Hz, 1H), 7.62–7.53 (m, 3H), 7.45 (t, J = 7.7 Hz, 1H), 7.13 (d, J = 7.4 Hz, 2H), 7.05 (d, J = 8.3 Hz, 1H), 4.46 (q, J = 7.0 Hz, 2H), 4.05 (q, J = 6.7 Hz, 2H), 3.67 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.01 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.9,

166.3, 156.2, 153.0, 144.0, 139.5, 135.7, 130.9, 130.1, 129.6, 125.1, 123.4, 121.0, 120.6, 117.4, 116.6, 116.3, 110.4, 102.2, 62.0, 61.0, 55.0, 13.9, 13.4 ppm; IR (KBr) v = 3202, 2982, 1730, 1589, 1551, 1355, 1246, 1028, 753, 599 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{23}N_2O_5^+$, $[M + H]^+$ 419.1601, found 419.1600.

Diethyl 4-(naphthalen-2-yl)-6*H*-azepino[4,3,2-cd]indole-2,3-dicarboxylate (**4m**): yellow solid (60.5 mg, 69% yield), mp: 199–201 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.02 (s, 1H), 8.18 (s, 1H), 8.06 (t, J = 6.7 Hz, 2H), 8.02–7.98 (m, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.85 (dd, J = 8.4, 1.8 Hz, 1H), 7.67 (d, J = 9.0 Hz, 1H), 7.59 (t, J = 4.6 Hz, 3H), 7.26 (s, 1H), 4.50 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H), 0.94 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.3, 166.4, 154.3, 143.3, 139.6, 137.5, 135.9, 132.8, 132.6, 128.4, 127.9, 127.9, 127.6, 126.9, 126.6, 126.4, 125.2, 123.4, 120.5, 117.4, 116.9, 116.3, 102.4, 62.3, 61.6, 13.9, 13.4 ppm; IR (KBr) v = 3381, 2980, 1727, 1550, 1243, 1021, 750, 479 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{27}H_{23}N_2O_4^+$, $[M + H]^+$ 439.1652, found 439.1644.

Diethyl 4-(furan-2-yl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4n**): yellow solid (39.3 mg, 52% yield), mp: 150–152 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.98 (s, 1H), 7.92 (s, 1H), 7.86 (d, J = 8.9 Hz, 1H), 7.64–7.56 (m, 2H), 7.30 (d, J = 2.8 Hz, 1H), 7.25 (s, 1H), 6.74 (dd, J = 3.5, 1.8 Hz, 1H), 4.47 (q, J = 7.1 Hz, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.25 ppm (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.0, 166.0, 152.4, 145.0, 143.6, 143.1, 138.7, 135.7, 125.1, 123.1, 118.8, 117.4, 116.8, 116.3, 112.4, 111.4, 102.4, 62.3, 61.7, 13.9, 13.8 ppm; IR (KBr) v = 3382, 2983, 1728, 1550, 1254, 1017, 748, 594, 437 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{21}H_{19}N_2O_5^+$, $[M + H]^+$ 379.1288, found 379.1289.

Diethyl 4-(thiophen-2-yl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4o**): yellow solid (36.2 mg, 46% yield), mp: 152–154 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.99 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 5.1 Hz, 1H), 7.64–7.56 (m, 2H), 7.38 (d, J = 3.6 Hz, 1H), 7.19 (d, J = 3.9 Hz, 2H), 4.48 (q, J = 6.9 Hz, 2H), 4.33 (q, J = 7.0 Hz, 2H), 1.36 (t, J = 7.0 Hz, 3H), 1.23 ppm (t, J = 7.0 Hz, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.3, 166.1, 146.4, 143.4, 142.8, 138.8, 135.8, 129.7, 128.3, 127.4, 125.2, 122.9, 119.2, 117.4, 116.8, 116.2, 102.2, 62.4, 62.0, 13.9, 13.6 ppm; IR (KBr) v = 3388, 2981, 1727, 1549, 1252, 1025, 748, 534 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{21}H_{19}N_2O_4S^+$, $[M + H]^+$ 395.1060, found 395.1059.

Diethyl 4-phenethyl-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4p**): yellow solid (35.8 mg,

43% yield), mp: 172–174 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.93 (s, 1H), 7.83 (d, J = 9.0 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.32–7.23 (m, 5H), 7.18 (d, J = 6.1 Hz, 1H), 4.45 (q, J = 7.1 Hz, 2H), 4.34 (q, J = 7.1 Hz, 2H), 3.44 (t, J = 6.3 Hz, 2H), 3.20–3.12 (m, 2H), 1.35 (t, J = 7.1 Hz, 3H), 1.29 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.8, 166.6, 156.4, 143.9, 141.5, 139.4, 135.7, 128.3, 125.9, 124.9, 123.0, 119.9, 117.6, 116.1, 116.0, 102.3, 62.0, 61.7, 38.1, 34.7, 13.9, 13.8 ppm; IR (KBr) v = 3369, 2982, 1721, 1555, 1242, 1019, 742, 508 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{25}N_2O_4^+$, $[M + H]^+$ 417.1809, found 417.1808.

Diethyl 4-cyclopropyl-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4q**): yellow solid (40.8 mg, 58% yield), mp: 130–132 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.85 (s, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.53 (d, J = 9.0 Hz, 1H), 7.49 (t, J = 2.7 Hz, 1H), 7.09 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 4.37 (q, J = 7.1 Hz, 2H), 2.54 (dt, J = 8.1, 3.6 Hz, 1H), 1.34 (dt, J = 8.8, 7.1 Hz, 6H), 1.27 (q, J = 3.6 Hz, 2H), 1.08 ppm (dq, J = 6.9, 3.3 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.0, 166.6, 157.4, 144.0, 138.5, 135.6, 124.7, 122.8, 120.5, 117.6, 115.6, 115.5, 102.1, 62.1, 61.8, 14.9, 13.9, 13.9, 11.0 ppm; IR (KBr) v = 3381, 2983, 1726, 1556, 1418, 1248, 1181, 1023, 865, 744, 667, 533 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{20}H_{21}N_2O_4^+$, $[M + H]^+$ 353.1496, found 353.1495.

Diethyl 8-fluoro-4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4r**): yellow oil (28.6 mg, 34% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.98 (s, 1H), 7.71 (d, J = 12.1 Hz, 1H), 7.56 (dd, J = 10.6, 5.2 Hz, 3H), 7.34 (d, J = 7.7 Hz, 2H), 7.17 (s, 1H), 4.42 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.35 (t, J = 7.0 Hz, 3H), 1.04 ppm (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 166.8, 166.6, 155.5, 152.3 (d, $^1J_{C\text{-}F}$ = 245.0 Hz), 142.6 (d, $^3J_{C\text{-}F}$ = 3.0 Hz), 138.7, 136.7, 136.6, 133.7 (d, $^2J_{C\text{-}F}$ = 14.0 Hz), 129.0, 128.4, 125.3 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 120.5, 120.4, 107.0 (d, $^3J_{C\text{-}F}$ = 15.0 Hz), 102.3, 101.1 (d, $^2J_{C\text{-}F}$ = 25.0 Hz), 62.1, 61.8, 20.9, 13.8, 13.4 ppm; ^{19}F NMR (377 MHz, DMSO-d_6, 25 °C) δ = -123.6, -123.6 ppm; IR (KBr) v = 3381, 2925, 1725, 1549, 1356, 1230, 1013, 752, 502 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{22}FN_2O_4^+$, $[M + H]^+$ 421.1558, found 421.1557.

Diethyl 8-bromo-4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4s**): yellow oil (43.2 mg, 45% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.98 (s, 1H), 8.19 (s, 1H), 7.61–7.55 (m, 3H), 7.35 (d, J = 7.8 Hz, 2H), 7.19 (s, 1H), 4.40 (q, J = 6.3, 5.8 Hz, 2H), 4.15–4.09 (m, 2H), 2.40 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.05 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz,

DMSO-d_6, 25 °C) δ = 167.1, 166.5, 154.2, 144.2, 139.2, 138.8, 136.4, 134.9, 129.0, 128.4, 126.1, 123.8, 122.6, 122.1, 114.4, 109.0, 102.7, 62.3, 61.8 , 20.9, 13.5, 13.4 ppm; IR (KBr) v = 3384, 2926, 1731, 1548, 1334, 1245, 1027, 775, 498 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{22}BrN_2O_4^+$, $[M + H]^+$ 481.0757, found 481.0756.

2,3-Diethyl 8-methyl 4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3,8-tricarboxylate (**4t**): yellow oil (47.9 mg, 52% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 12.20 (s, 1H), 8.27 (s, 1H), 7.74 (t, J = 2.8 Hz, 1H), 7.53 (d, J = 7.7 Hz, 2H), 7.34 (d, J = 7.7 Hz, 2H), 7.21 (t, J = 2.4 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.15 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 2.40 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H), 1.09 ppm (t, J = 7.1 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 168.0, 167.4, 166.0, 154.0, 144.1, 138.5, 137.0, 136.5, 133.0, 128.8, 128.4, 128.1, 126.0, 123.8, 121.4, 119.9, 114.2, 103.0, 61.9, 61.7, 52.2, 20.9, 13.5, 13.5 ppm; IR (KBr) v = 3382, 2926, 1728, 1549, 1370, 1228, 1133, 753, 499 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{26}H_{25}N_2O_6^+$, $[M + H]^+$ 461.1707, found 461.1706.

Diethyl 6-methyl-4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4u**): yellow oil (44.9 mg, 54% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 7.93 (d, J = 9.1 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 7.8 Hz, 2H), 7.53 (d, J = 2.9 Hz, 1H), 7.32 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 2.9 Hz, 1H), 4.48 (q, J = 7.1 Hz, 2H), 4.14 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 2.38 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.06 ppm (t, J = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 167.3, 166.3, 154.4, 143.5, 139.2, 138.3, 137.1, 136.0, 129.4, 128.8, 128.4, 123.6, 120.5, 117.3, 116.0, 114.9, 101.5, 62.2, 61.5, 33.1, 20.8, 13.8, 13.4 ppm; IR (KBr) v = 3380, 2981, 1732, 1543, 1295, 1107, 1026, 744, 496 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{25}N_2O_4^+$, $[M + H]^+$ 417.1809, found 417.1808.

Dimethyl 4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2,3-dicarboxylate (**4v**): yellow oil (49.4 mg, 66% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.97 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.64–7.55 (m, 4H), 7.34 (d, J = 7.7 Hz, 2H), 7.20 (s, 1H), 4.00 (s, 3H), 3.70 (s, 3H), 2.39 ppm (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 168.0, 166.9, 154.0, 143.8, 139.2, 138.4, 136.9, 135.8, 129.0, 128.4, 125.1, 123.3, 120.1, 117.4, 116.7, 116.0, 102.2, 53.3, 52.7, 20.9 ppm; IR (KBr) v = 3383, 2924, 1735, 1351, 1252, 1141, 1028, 749, 497 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{22}H_{19}N_2O_4^+$, $[M + H]^+$ 375.1339, found 375.1339.

Methyl 4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-3-carboxylate (**4w**): yellow solid (33.5 mg, 53%

yield), mp: 194–196 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.85 (s, 1H), 8.77 (s, 1H), 7.74 (q, J = 8.7 Hz, 2H), 7.55 (d, J = 7.8 Hz, 2H), 7.51 (d, J = 2.8 Hz, 1H), 7.30 (d, J = 7.7 Hz, 2H), 7.15 (s, 1H), 3.72 (s, 3H), 2.39 ppm (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 168. 4, 155.2, 143.9, 138.7, 137.8, 137.7, 136.2, 128.7, 128.6, 124.5, 123.1, 121.6, 121.2, 120.4, 115.3, 102.0, 52.2, 20.9 ppm; IR (KBr) v = 3379, 2925, 1721, 1603, 1378, 1258, 1112, 749, 585 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{20}H_{17}N_2O_2^+$, $[M + H]^+$ 317.1285, found 317.1284.

Ethyl 3-acetyl-4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole-2-carboxylate (**4x**): yellow solid (40.9 mg, 55% yield), mp: 191–193 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.95 (s, 1H), 7.86 (d, J = 9.0 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 7.3 Hz, 3H), 7.38 (d, J = 7.8 Hz, 2H), 7.20 (s, 1H), 4.40 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.05 (s, 3H), 1.31 ppm (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 203.6, 166.7, 153.2, 143.6, 139.0, 137.9, 137.0, 135.5, 129.4, 129.3, 129.0, 125.0, 123.3, 117.4, 116.6, 116.4, 102.2, 62.0, 31.3, 20.9, 13.7 ppm; IR (KBr) v = 3212, 2982, 1731, 1692, 1544, 1353, 1218, 1029, 762, 501 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{21}N_2O_3^+$, $[M + H]^+$ 373.1547, found 373.1541.

8,8-Dimethyl-11-(*p*-tolyl)-2,6,7,8,9,11-hexahydro-10*H*-benzo[6,7]azepino[4,3,2-*cd*]indol-10-one (**7a**): yellow oil (39.2 mg, 55% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.03 (s, 1H), 9.17 (s, 1H), 7.25 (t, J = 2.7 Hz, 1H), 7.05 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 8.2 Hz, 3H), 6.81 (s, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.07 (s, 1H), 2.58 (s, 2H), 2.19 (d, J = 16.2 Hz, 2H), 2.15 (s, 3H), 1.06 (s, 3H), 0.97 ppm (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 193.0, 151.5, 147.0, 135.3, 134.0, 128.4, 127.6, 126.9, 124.3, 122.9, 116.5, 114.8, 107.3, 106.7, 98.5, 50.4, 40.4, 39.5, 32.1, 29.3, 26.8, 20.5 ppm; IR (KBr) v = 3203, 2925, 1682, 1542, 1405, 1026, 755, 553 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{25}N_2O^+$, $[M + H]^+$ 357.1961, found 357.1957.

11-(4-Chlorophenyl)-8,8-dimethyl-2,6,7,8,9,11-hexahydro-10*H*-benzo[6,7]azepino[4,3,2-*cd*]indol-10-one (**7b**): yellow oil (38.4 mg, 51% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.08 (s, 1H), 9.26 (s, 1H), 7.27 (t, J = 2.8 Hz, 1H), 7.22–7.15 (m, 4H), 6.96 (d, J = 8.3 Hz, 1H), 6.83 (s, 1H), 6.77 (d, J = 8.3 Hz, 1H), 5.15 (s, 1H), 2.59 (s, 2H), 2.21 (d, J = 16.0 Hz, 1H), 2.01 (d, J = 18.0 Hz, 1H), 1.05 (s, 3H), 0.96 ppm (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 193.1, 151.8, 148.7, 135.4, 129.8, 128.9, 127.8, 127.6, 124.5, 122.9, 116.5, 114.0, 107.0, 106.8, 98.6, 50.3, 40.4, 39.4, 2.1, 29.2, 26.8 ppm; IR (KBr) v = 3278, 2927, 1602, 1487, 1259, 1026, 888,

782, 529 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{22}ClN_2O^+$, $[M + H]^+$ 377.1415, found 377.1415.

4-(8,8-Dimethyl-10-oxo-6,7,8,9,10,11-hexahydro-2*H*-benzo[6,7]azepino[4,3,2-*cd*]indol-11-yl)benzonitrile (**7c**): yellow oil (26.4 mg, 36% yield); ^1H NMR (400 MHz, $CDCl_3$, TMS, 25 °C) δ = 8.57 (s, 1H), 7.43–7.35 (m, 4H), 7.19 (t, J = 2.9 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.93 (s, 1H), 6.82 (d, J = 8.4 Hz, 1H), 6.53 (s, 1H), 5.44 (s, 1H), 2.55–2.44 (m, 2H), 2.25 (q, J = 16.4 Hz, 2H), 1.10 (s, 3H), 0.99 ppm (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25 °C) δ = 195.1, 153.9, 151.1, 135.7, 132.2, 128.6, 127.7, 124.5, 124.2, 119.5, 116.3, 114.5, 109.3, 108.6, 107.7, 97.9, 50.8, 42.2, 40.7, 32.8, 29.5, 27.4 ppm; IR (KBr) v = 3285, 2957, 2226, 1602, 1485, 1257, 1150, 887, 751, 558 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{24}H_{22}N_3O^+$, $[M + H]^+$ 368.1757, found 368.1758.

11-(*p*-Tolyl)-2,6,7,8,9,11-hexahydro-10*H*-benzo[6,7]azepino[4,3,2-*cd*]indol-10-one (**7d**): yellow oil (33.1 mg, 53% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.03 (s, 1H), 9.22 (s, 1H), 7.25 (t, J = 2.8 Hz, 1H), 7.03 (d, J = 7.7 Hz, 2H), 6.93 (d, J = 7.6 Hz, 3H), 6.80 (t, J = 6.2 Hz, 2H), 5.10 (s, 1H), 2.77 (dt, J = 17.0, 4.8 Hz, 1H), 2.67–2.59 (m, 1H), 2.25–2.17 (m, 2H), 2.15 (s, 3H), 1.95 (dd, J = 8.6, 4.1 Hz, 1H), 1.85 ppm (dd, J = 11.3, 6.2 Hz, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 193.4, 153.3, 146.9, 135.2, 134.0, 128.4, 127.6, 126.9, 124.2, 122.8, 116.4, 114.7, 108.5, 106.7, 98.5, 36.8, 27.0, 21.1, 20.5 ppm; IR (KBr) v = 3275, 2924, 1602, 1486, 1413, 1356, 1181, 1025, 762, 522 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{22}H_{21}N_2O^+$, $[M + H]^+$ 329.1648, found 329.1643.

Methyl 2,8,8-Trimethyl-11-(p-tolyl)-2,6,7,8,9,11-hexahydro-10H-benzo[6,7]azepino[4,3,2-cd]indol-10-one (**7e**): yellow solid (43.7mg, 59% yield), mp: 273–275 °C; ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 9.17 (s, 1H), 7.23 (d, J = 3.2 Hz, 1H), 7.03 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.6 Hz, 3H), 6.83 (d, J = 8.4 Hz, 1H), 6.78 (d, J = 3.2 Hz, 1H), 5.07 (s, 1H), 3.69 (s, 3H), 2.57 (s, 2H), 2.19 (d, J = 16.5 Hz, 1H), 2.15 (s, 3H), 1.98 (d, J = 8.0 Hz, 1H), 1.05 (s, 3H), 0.96 ppm (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ = 193.0, 151.4, 146.9, 135.8, 134.0, 128.5, 128.4, 127.7, 126.9, 123.0, 116.6, 115.1, 107.3, 104.9, 97.7, 50.3, 40.4, 32.5, 32.1, 29.3, 26.7, 20.5 ppm; IR (KBr) v = 3280, 2925, 1712, 1598, 1483, 1385, 1265, 1028, 758, 592 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{25}H_{27}N_2O^+$, $[M + H]^+$ 371.2118, found 371.2115.

2-Methyl-4-(*p*-tolyl)-6*H*-azepino[4,3,2-*cd*]indole (**4y**): yellow oil (42.5 mg, 78% yield); ^1H NMR

(400 MHz, DMSO-d_6, 25 °C) δ = 11.61 (s, 1H), 8.24 (d, J = 7.9 Hz, 2H), 7.87 (s, 1H), 7.68 (q, J = 8.9 Hz, 2H), 7.45 (t, J = 2.7 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7.21 (t, J = 2.4 Hz, 1H), 2.76 (s, 3H), 2.39 ppm (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 153.5, 144.7, 143.3, 138.5, 136.6, 135.0, 129.3, 126.8, 124.1, 123.8, 121.4, 116.9, 116.3, 113.7, 102.0, 20.9, 19.3 ppm; IR (KBr) v = 3257, 2922, 1596, 1361, 1092, 822, 745, 562, 478 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{19}H_{17}N_2^+$, $[M + H]^+$ 273.1386, found 273.1386.

10-(*p*-Tolyl)-2,7,8,9-tetrahydrocyclopenta[6,7]azepino[4,3,2-*cd*]indole (**4z**): yellow oil (38.2 mg, 64% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.58 (s, 1H), 7.86 (d, J = 7.7 Hz, 2H), 7.66 (d, J = 8.7 Hz, 1H), 7.52 (d, J = 8.7 Hz, 1H), 7.42 (t, J = 2.6 Hz, 1H), 7.34 (d, J = 7.7 Hz, 2H), 7.12 (s, 1H), 3.31 (t, J = 7.5 Hz, 2H), 3.25 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 2.19 ppm (p, J = 7.4 Hz, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 152.4, 151.3, 142.5, 137.9, 137.5, 134.5, 131.3, 128.8, 128.6, 123.9, 123.5, 119.5, 117.4, 114.0, 101.8 , 33.3, 31.2, 24.7, 20.9 ppm; IR (KBr) v = 3220, 2924, 1602, 1367, 1026, 825, 749, 563, 485 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{21}H_{19}N_2^+$, $[M + H]^+$ 299.1543, found 299.1542.

11-(*p*-Tolyl)-7,8,9,10-tetrahydro-2*H*-benzo[6,7]azepino[4,3,2-*cd*]indole (**4aa**): yellow oil (42.5 mg, 68% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.54 (s, 1H), 7.66 (s, 2H), 7.46 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 2.6 Hz, 1H), 7.29 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 2.4 Hz, 1H), 3.20 (t, J = 6.6 Hz, 2H), 2.71 (t, J = 6.1 Hz, 2H), 2.39 (s, 3H), 1.90 (q, J = 6.4, 6.0 Hz, 2H), 1.74–1.65 ppm (m, 2H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 157.7, 141.8, 140.9, 138.8 136.8, 134.4, 128.9, 128.5, 125.1, 124.1, 123.6, 120.9, 115.8, 113.7, 101.6, 28.3, 25.9, 22.6, 22.1, 20.9 ppm; IR (KBr) v = 3189, 2926, 1510, 1363, 1115, 1019, 743, 575, 442 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{22}H_{21}N_2^+$, $[M + H]^+$ 313.1699, found 313.1699.

11-(*p*-Tolyl)-2,7,8,10-tetrahydropyrano[3',4':6,7]azepino[4,3,2-*cd*]indole (**4ab**): yellow oil (50.3 mg, 80% yield); ^1H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.63 (s, 1H), 7.73–7.62 (m, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.43 (t, J = 2.7 Hz, 1H), 7.32 (d, J = 7.7 Hz, 2H), 7.07 (s, 1H), 4.72 (s, 2H), 4.08 (t, J = 5.9 Hz, 2H), 3.24 (t, J = 5.9 Hz, 2H), 2.40 ppm (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6, 25 °C) δ = 154.4, 141.5, 139.2, 137.5, 137.2, 134.7, 128.7, 128.7, 124.0, 123.9, 123.3, 120.3, 115.6, 114.2, 101.7, 66.4, 64.0, 25.1, 20.9 ppm; IR (KBr) v = 3217, 2924, 1594, 1361, 1115, 1026, 879, 754, 580, 465 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{21}H_{19}N_2O^+$, $[M + H]^+$ 315.1492, found 315.1486.

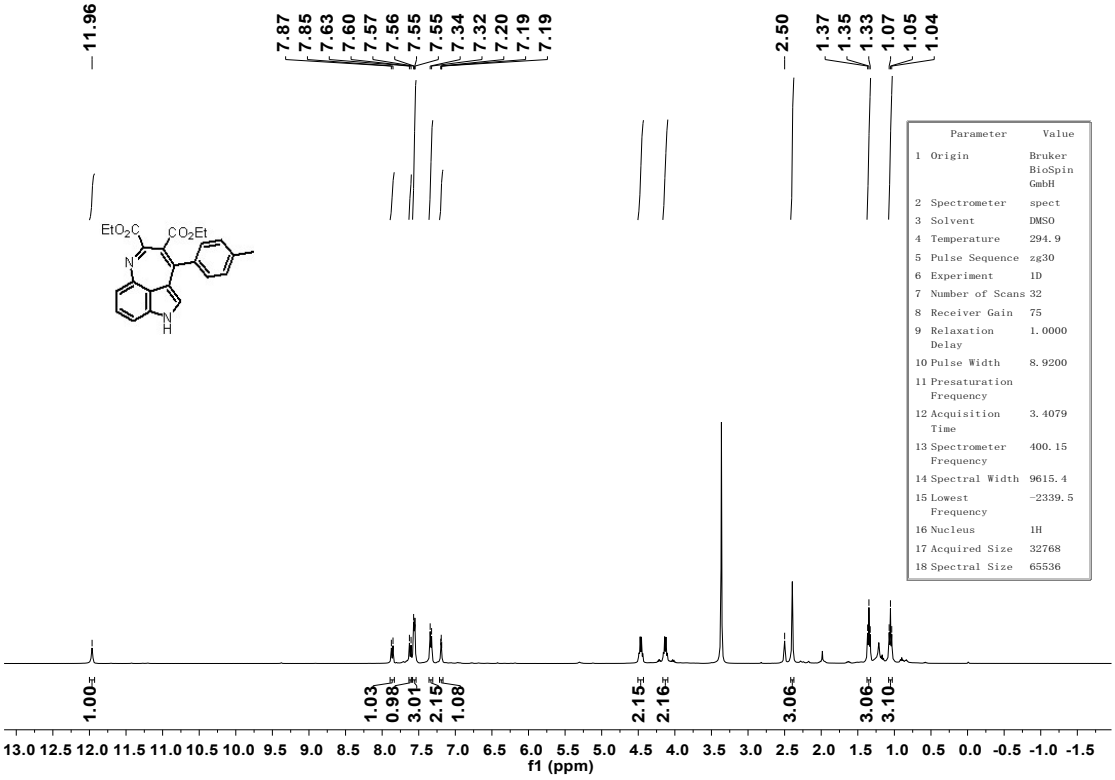
12-(*p*-Tolyl)-2,7,8,9,10,11-hexahydrocyclohepta[6,7]azepino[4,3,2-*cd*]indole (**4ac**): yellow oil (34.6 mg, 53% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.54 (s, 1H), 7.86 (d, J = 9.1 Hz, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.39 (t, J = 6.9 Hz, 3H), 7.31 (d, J = 7.6 Hz, 2H), 7.02 (s, 1H), 3.34 (s, 2H), 2.98–2.89 (m, 2H), 2.40 (s, 3H), 1.85 (q, J = 5.8 Hz, 2H), 1.71 (p, J = 5.4 Hz, 2H), 1.59 ppm (p, J = 5.5 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 156.8, 149.3, 141.7, 139.4, 136.6, 134.3, 130.7, 129.0, 128.5, 124.1, 123.5, 120.4, 116.5, 114.0, 101.8, 31.3, 30.0, 28.0, 27.1, 26.2, 20.8 ppm; IR (KBr) v = 3216, 2921, 1507, 1359, 1003, 759, 577, 485 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{23}N_2^+$, $[M + H]^+$ 327.1856, found 327.1850.

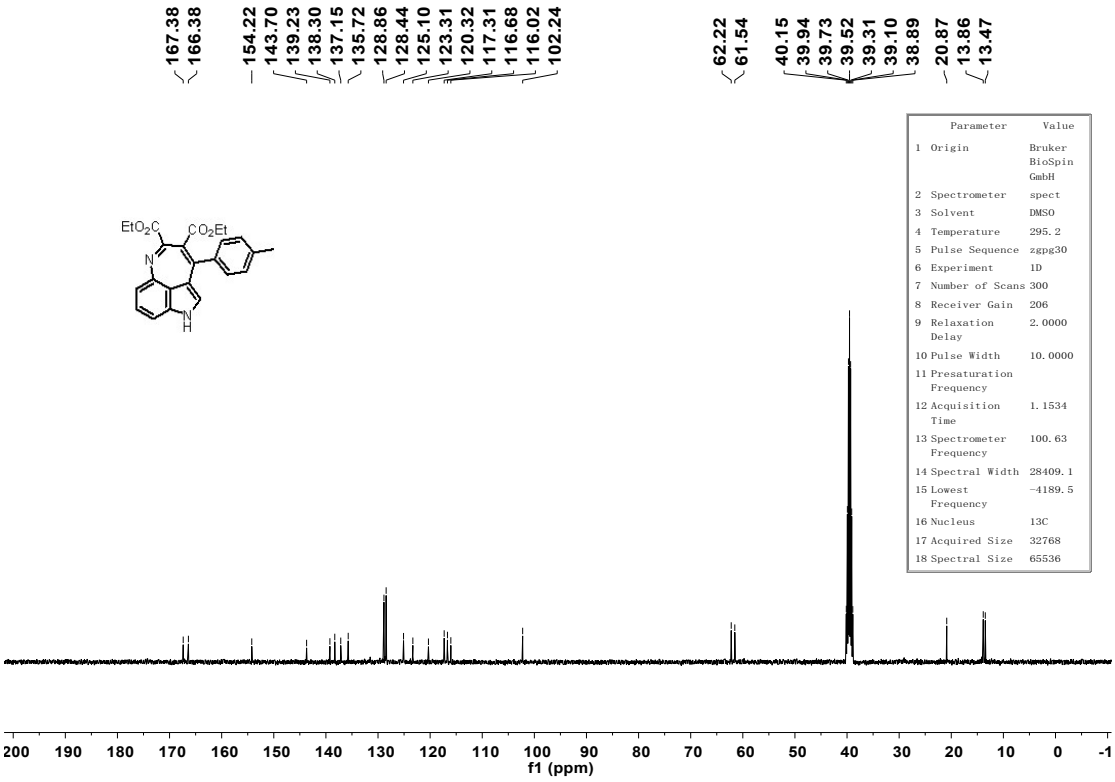
2,4-Diphenyl-6*H*-azepino[4,3,2-*cd*]indole (**4ad**): colorless oil (45.1 mg, 47% yield); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.70 (s, 1H), 8.40 (d, J = 7.6 Hz, 2H), 7.89 (s, 1H), 7.64 (q, J = 6.8, 4.9 Hz, 4H), 7.60 (s, 1H), 7.58 (d, J = 3.0 Hz, 1H), 7.55 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 8.4 Hz, 3H), 7.30 ppm (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 153.6, 148.7, 144.0, 139.2, 139.0, 134.9, 129.6, 129.1, 128.7, 128.6, 128.2, 127.1, 124.1, 119.9, 118.1, 115.9, 114.5, 102.1 ppm; IR (KBr) v = 3224, 2924, 1557, 1407, 1364, 1027, 876, 746, 699, 602 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{23}H_{17}N_2^+$, $[M + H]^+$ 321.1386, found 321.1380.

4-(*p*-Tolyl)-1,3,4,6-tetrahydro-2*H*-azepino[4,3,2-*cd*]indol-2-one (**8a**): black solid (63.0 mg, 76% yield), mp: 106–108 °C; ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ = 11.08 (s, 1H), 10.26 (s, 1H), 7.26 (t, J = 2.7 Hz, 1H), 7.09–7.01 (m, 4H), 6.98 (d, J = 8.2 Hz, 1H), 6.84 (s, 1H), 6.70 (d, J = 8.2 Hz, 1H), 4.28 (t, J = 5.7 Hz, 1H), 2.91 (dd, J = 15.8, 6.5 Hz, 1H), 2.69 (dd, J = 15.8, 5.3 Hz, 1H), 2.24 ppm (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6, 25 °C) δ = 169.7, 140.9, 136.1, 135.4, 129.5, 129.0, 127.2, 124.6, 121.6, 117.1, 114.6, 105.7, 98.8, 40.7, 39.2, 20.6 ppm; IR (KBr) v = 3214, 2924, 1671, 1590, 1495, 1377, 1026, 749, 501 cm^{-1}; HRMS (ESI, TOF) m/z: calcd for $C_{18}H_{17}N_2O^+$, $[M + H]^+$ 277.1335, found 277.1338.

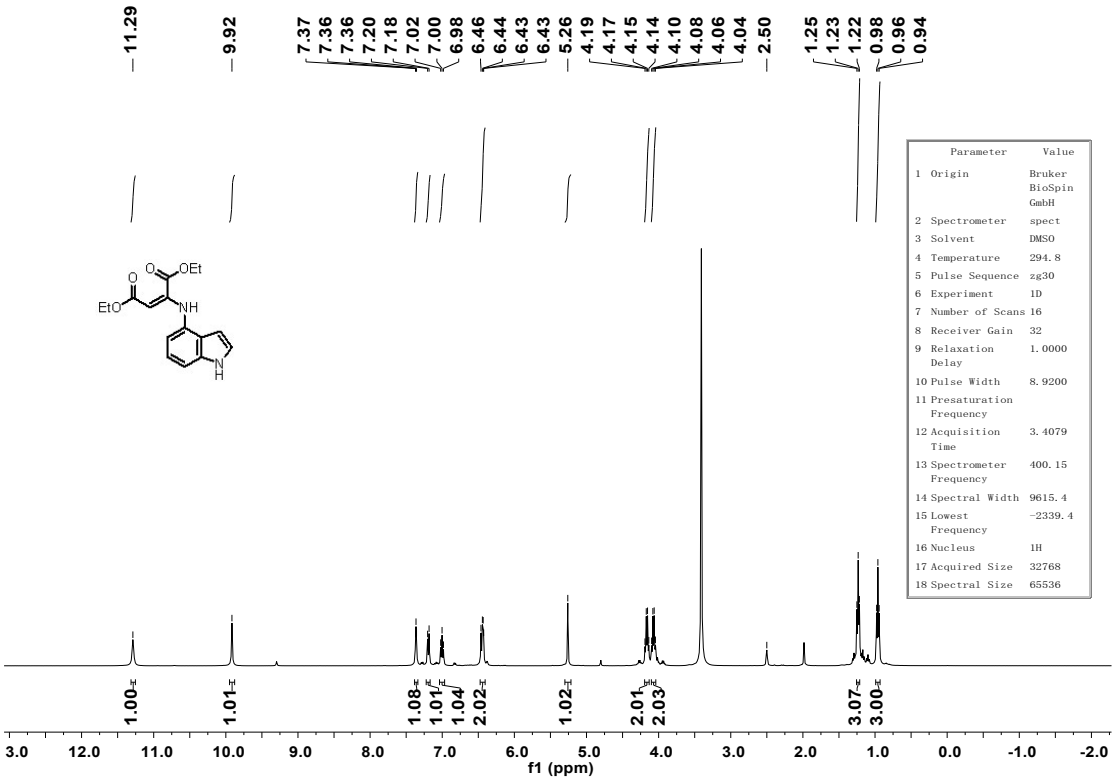
5. ^{1}H NMR and ^{13}C NMR spectra

4a





5a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5 Pulse Sequence zg30
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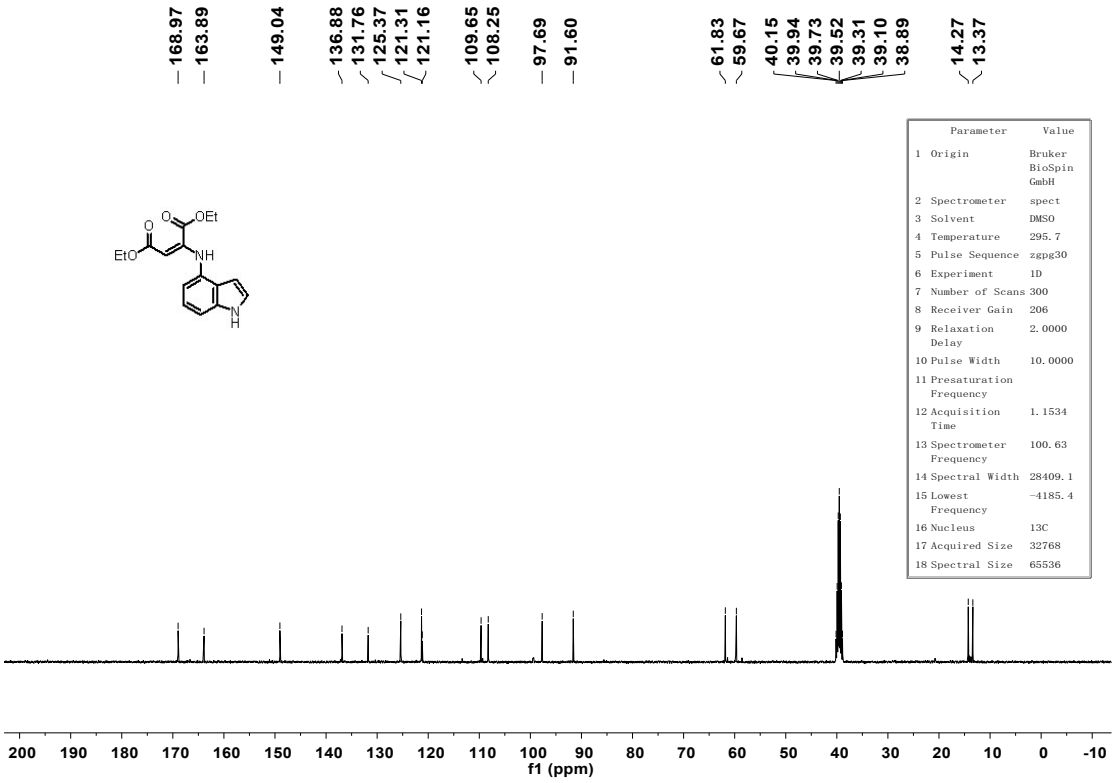
3.00
f1 (ppm)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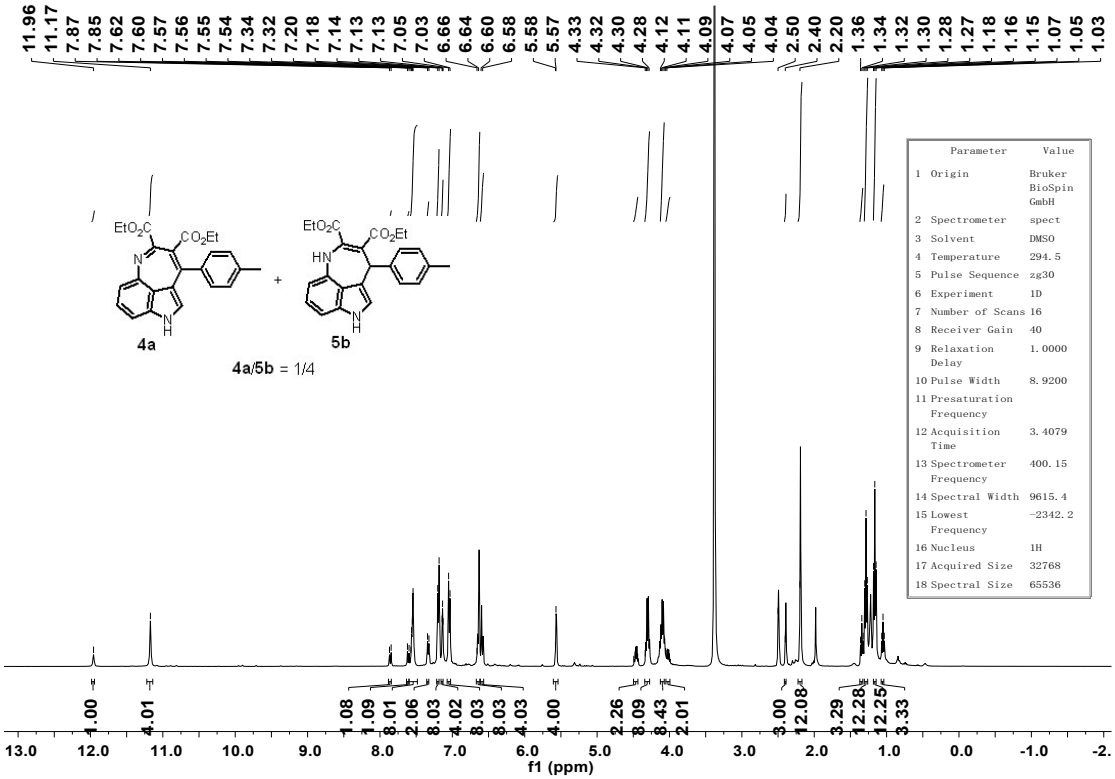
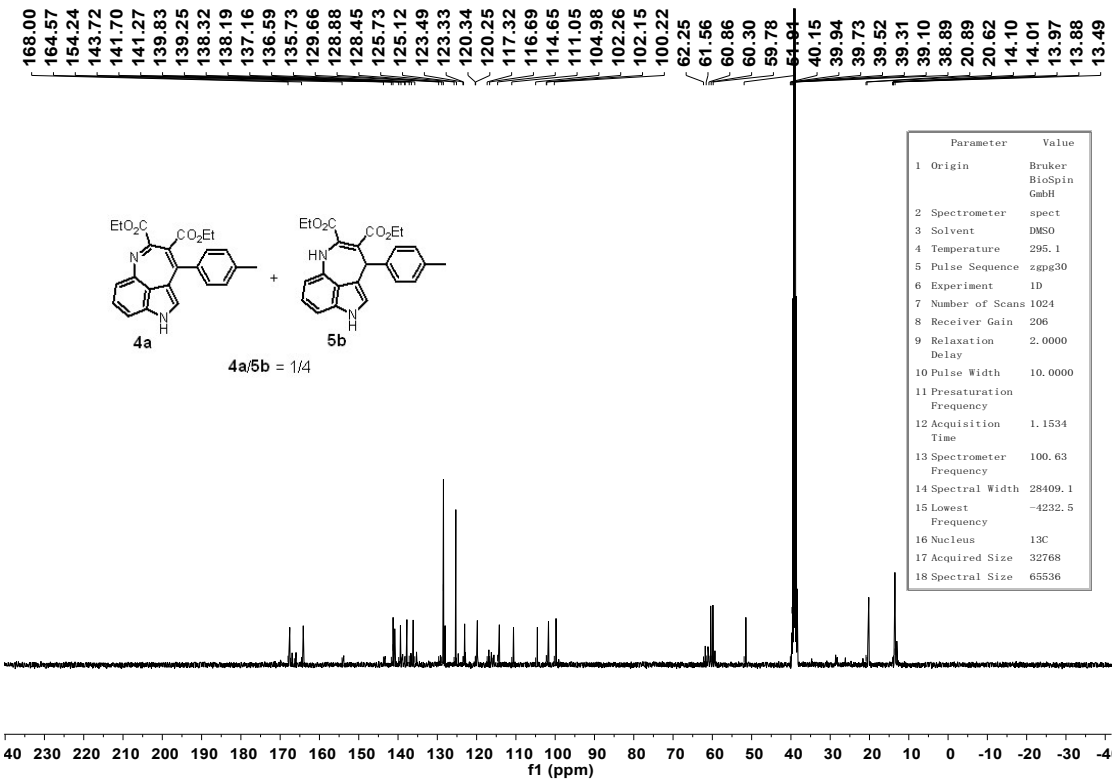
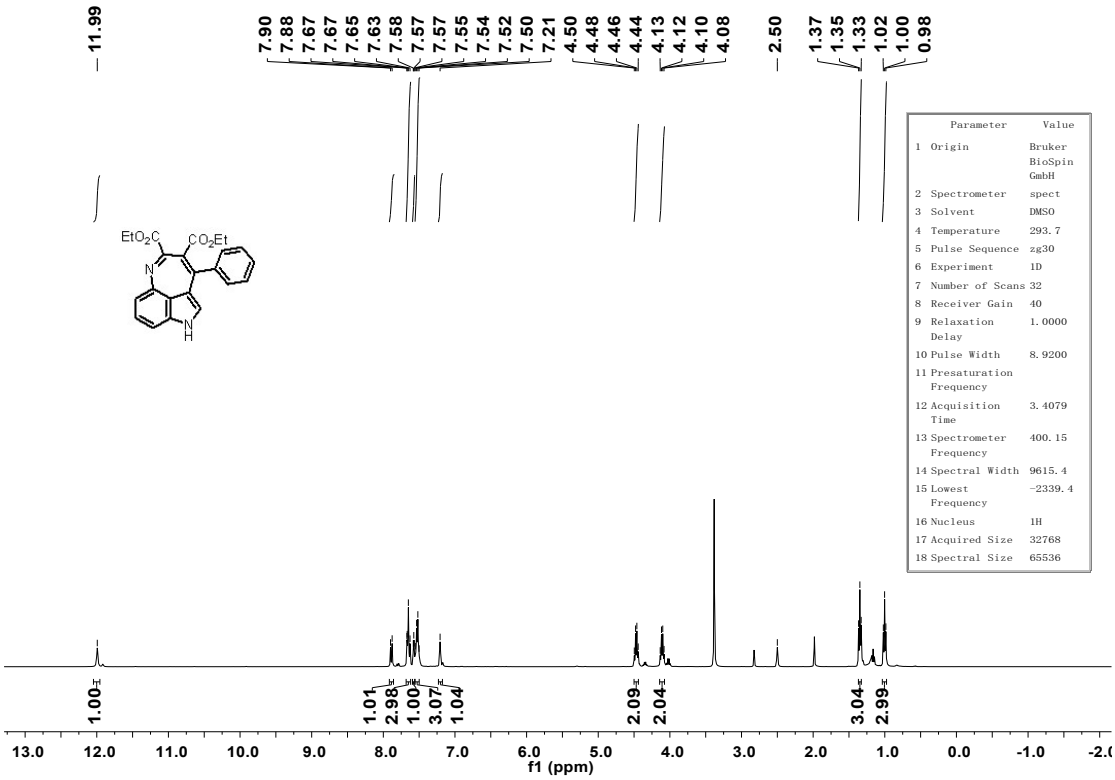
the mixture of 4a and 5b





4b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4.44
4.13
4.12
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2 Spectrometer spect
3 Solvent DMSO
4 Temperature 293.7
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6 Experiment 1D
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10.0
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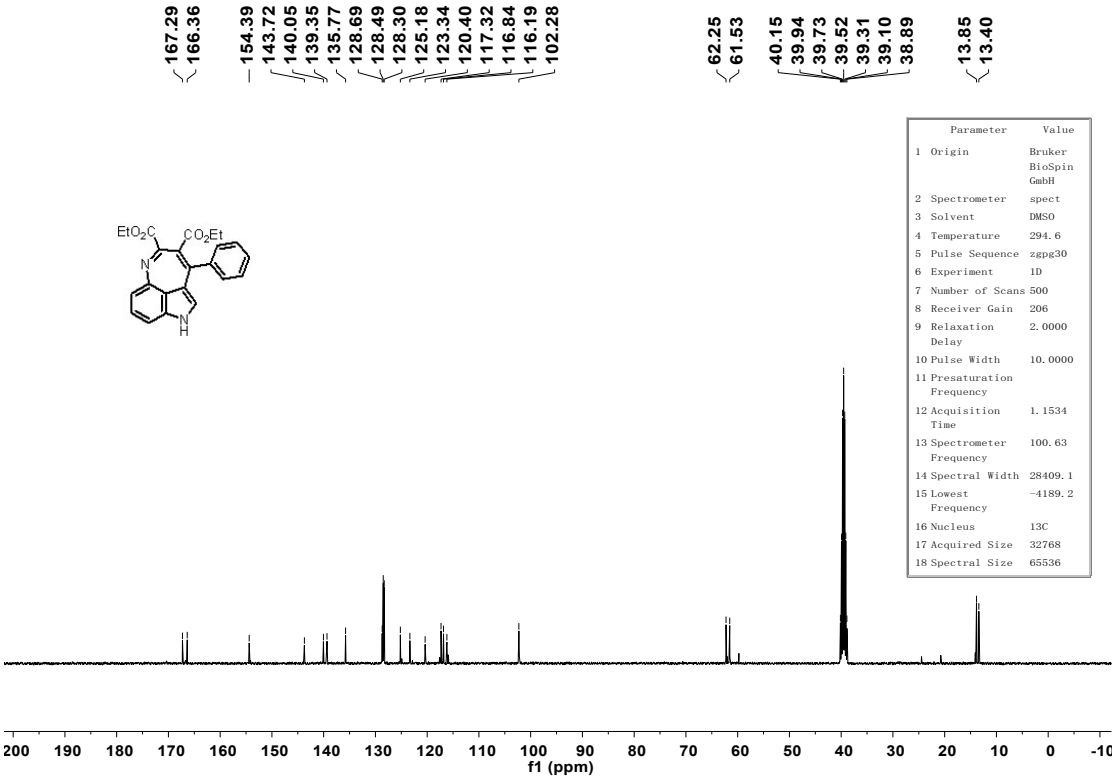
-1.0
f1 (ppm)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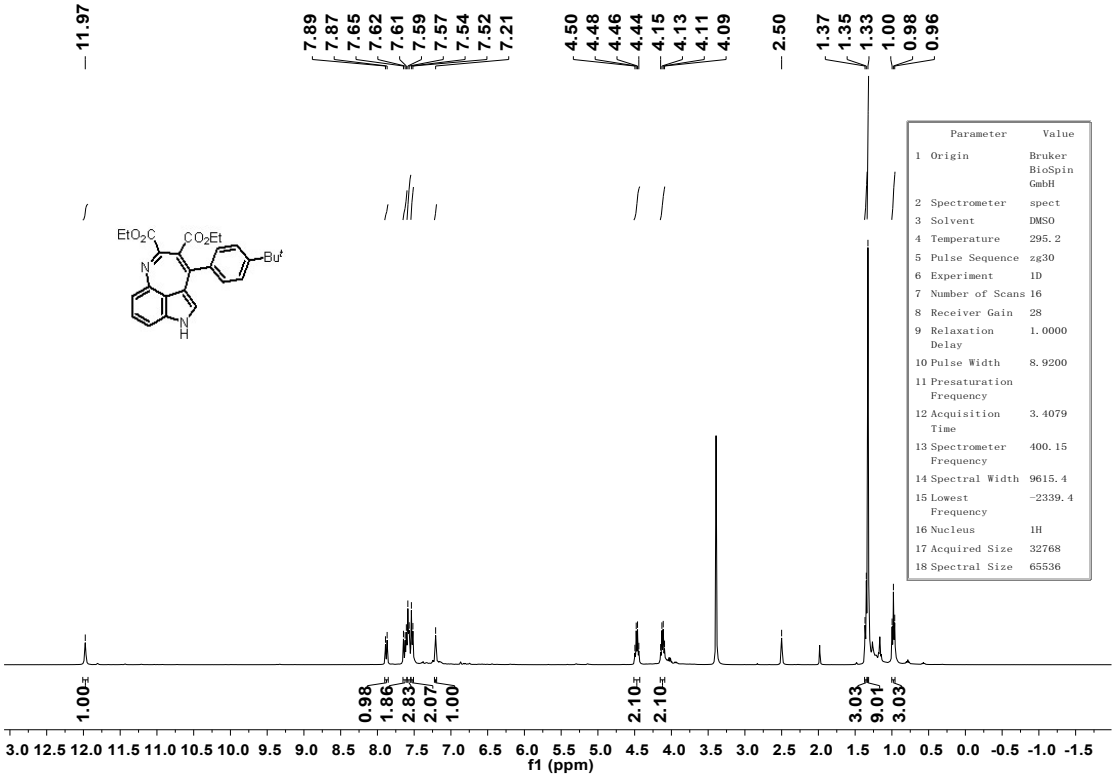
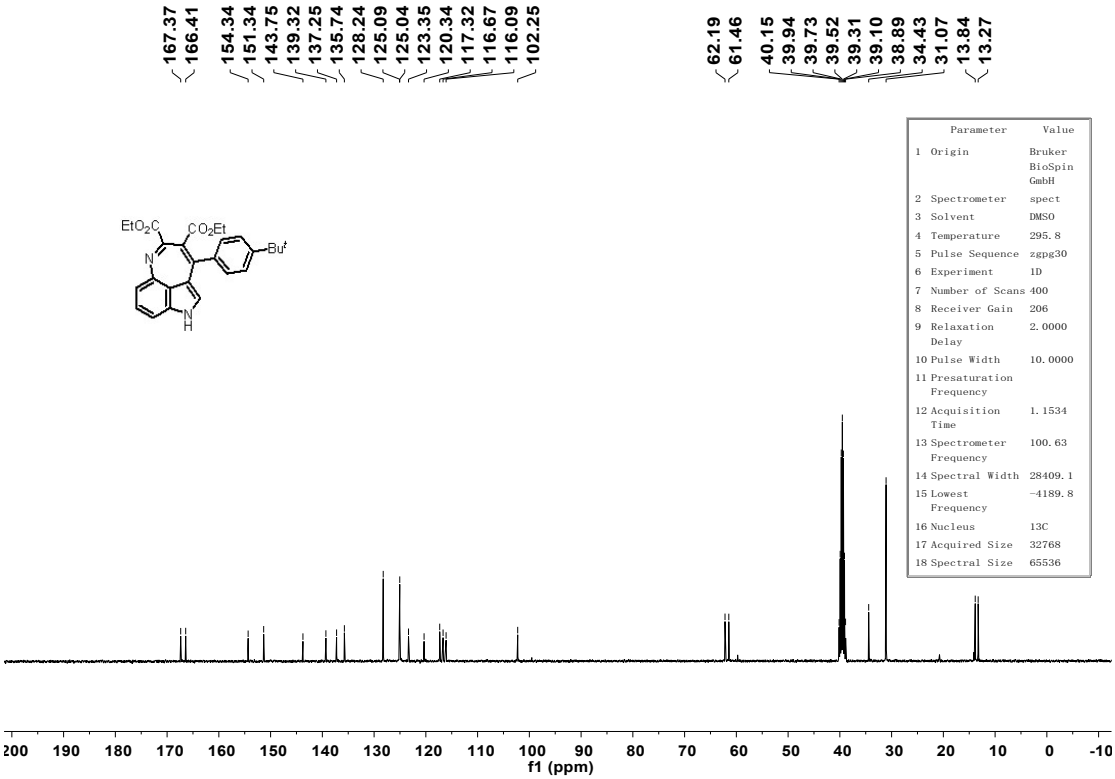
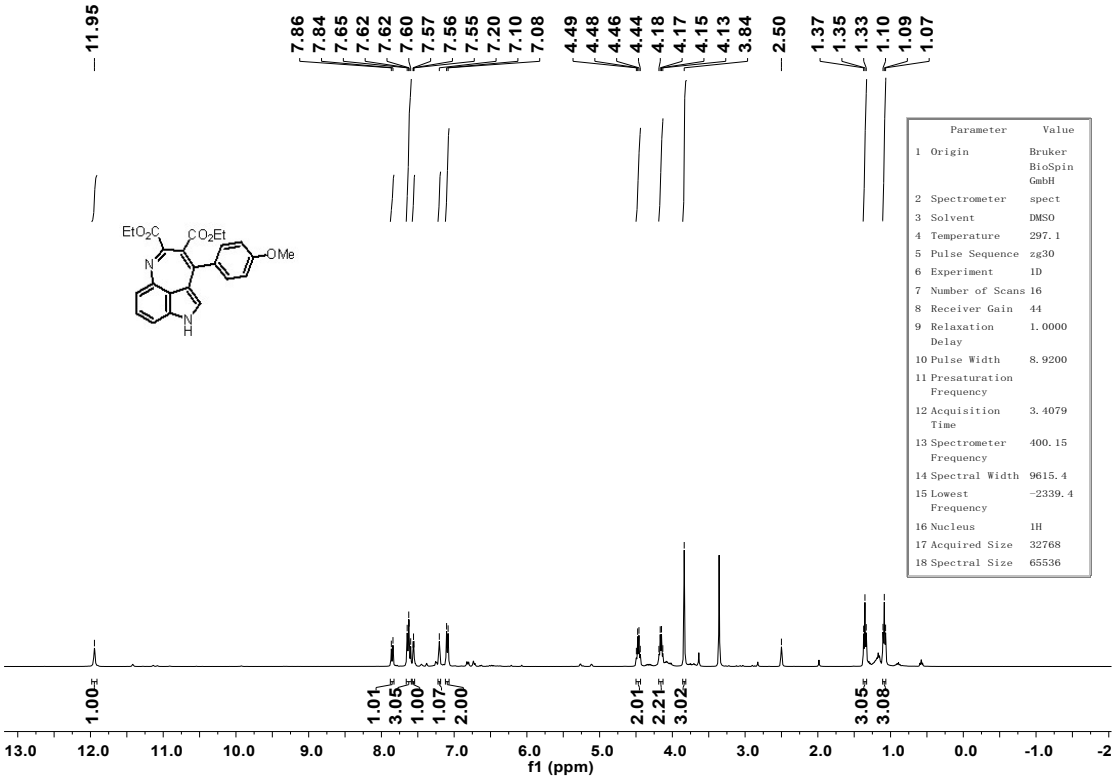
143.72
140.05
139.35
135.77
128.69
128.49
128.30
125.18
123.34
120.40
117.32
116.84
116.19
102.28
62.25
61.53
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.85
13.40
EtO2C
CO2Et
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.6
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4189.2
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

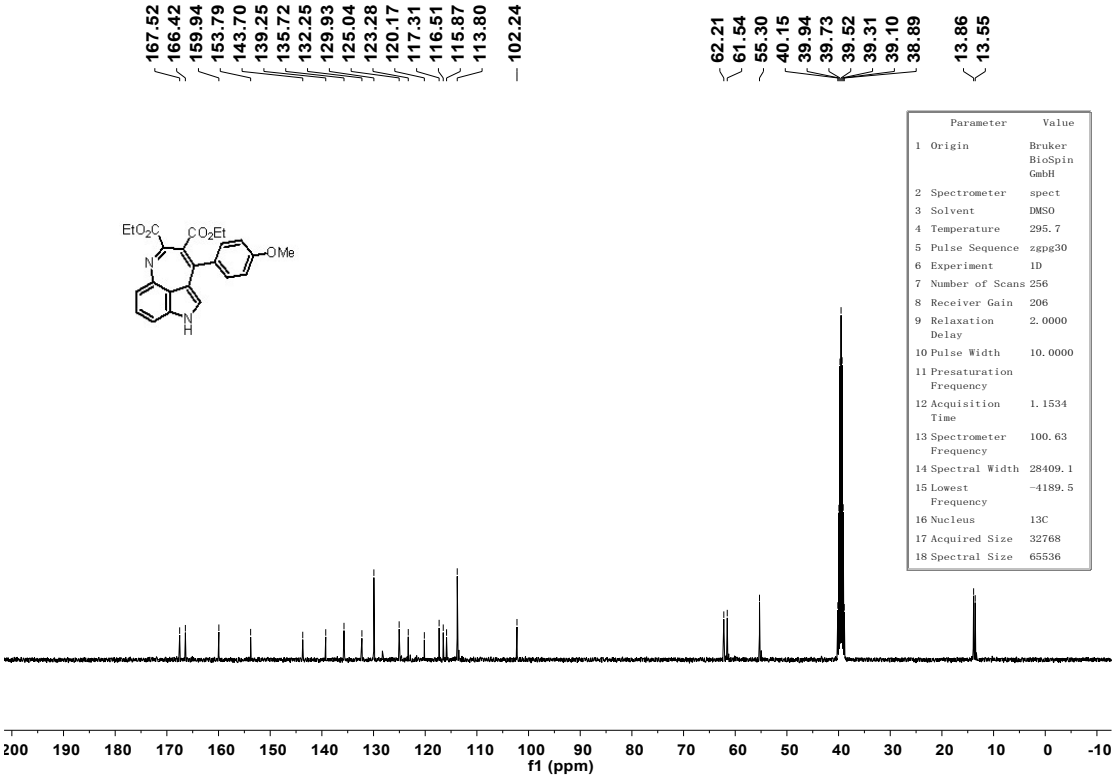
4c


11.97
7.89
7.87
7.65
7.62
7.61
7.59
7.57
7.54
7.52
7.21
4.50
4.48
4.46
4.44
4.15
4.13
4.11
4.09
2.50
1.37
1.35
1.33
1.00
0.98
0.96
EtO2C
CO2Et
But
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 28
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
0.98
1.86
2.83
2.07
1.00
2.10
2.10
3.03
9.01
3.03
f1 (ppm)

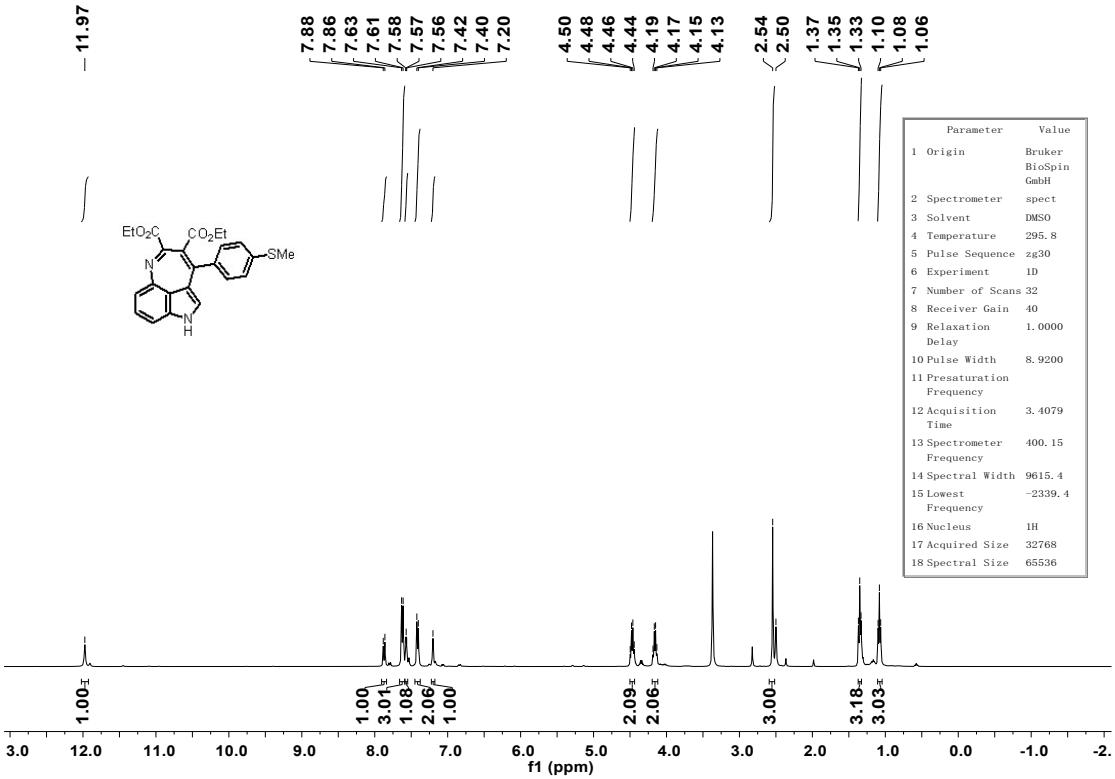

167.37
166.41
154.34
151.34
143.75
139.32
137.25
135.74
128.24
125.09
125.04
123.35
120.34
117.32
116.67
116.09
102.25
62.19
61.46
40.15
39.94
39.73
39.52
39.31
39.10
38.89
34.43
31.07
13.84
13.27
EtO2C
CO2Et
But
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.8
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4189.8
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

4d

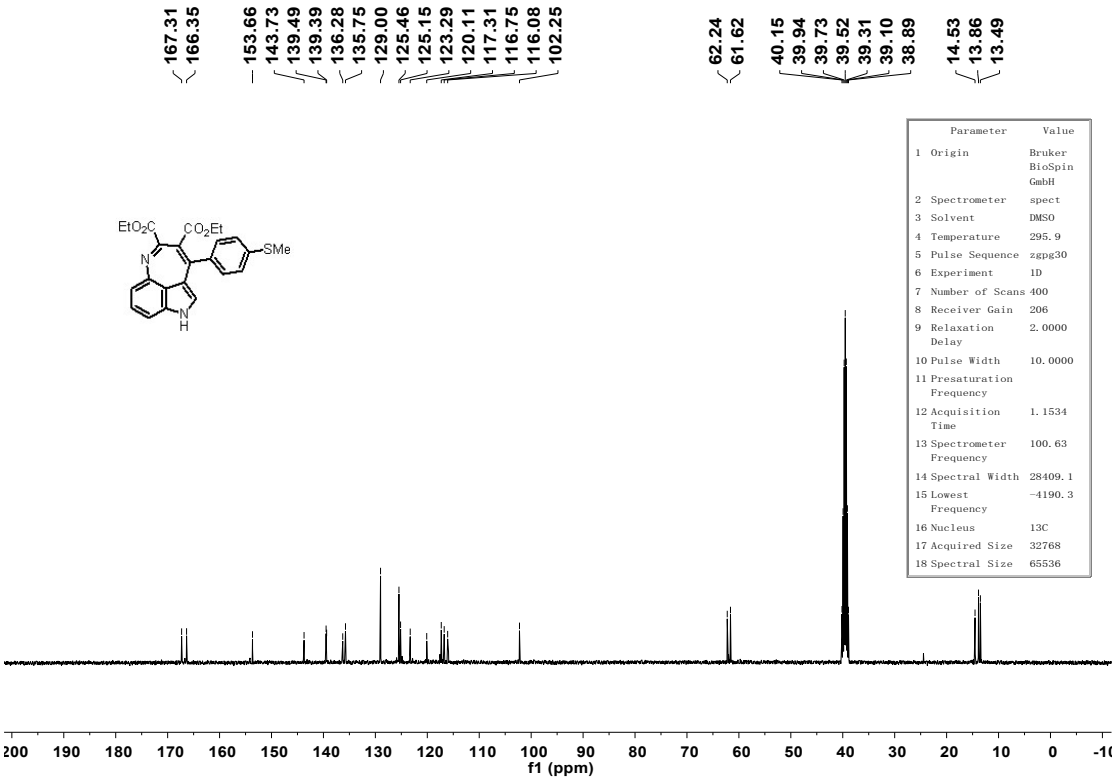

11.95
7.86
7.84
7.65
7.62
7.62
7.60
7.57
7.56
7.55
7.20
7.10
7.08
4.49
4.48
4.46
4.44
4.18
4.17
4.15
4.13
3.84
2.50
1.37
1.35
1.33
1.10
1.09
1.07
EtO2C
CO2Et
OMe
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 297.1
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 44
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.01
3.05
1.00
1.07
2.00
2.01
2.21
3.02
3.05
3.08
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2
f1 (ppm)


167.52
166.42
159.94
153.79
143.70
139.25
135.72
132.25
129.93
125.04
123.28
120.17
117.31
116.51
115.87
113.80
102.24
62.21
61.54
55.30
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.86
13.55
EtO2C
CO2Et
OMe
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 256
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4189.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4e

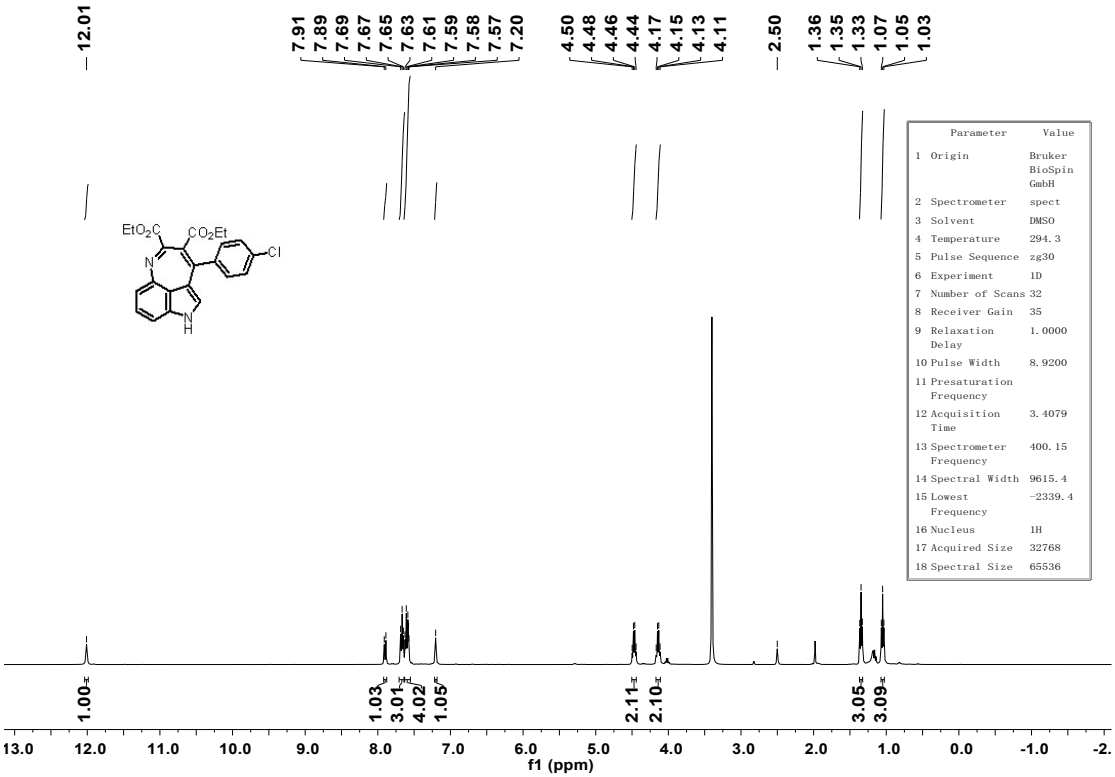


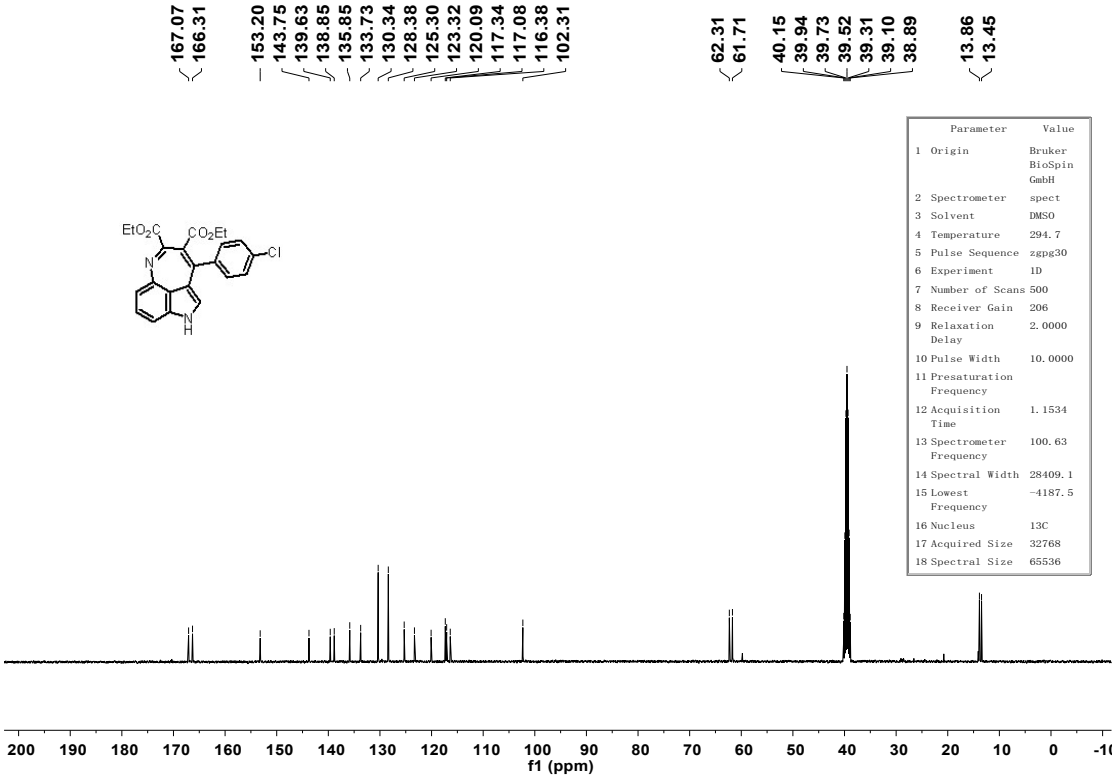
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	295.8
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	32
8	Receiver Gain	40
9	Relaxation Delay	1.0000
10	Pulse Width	8.9200
11	Presaturation Frequency	
12	Acquisition Time	3.4079
13	Spectrometer Frequency	400.15
14	Spectral Width	9615.4
15	Lowest Frequency	-2339.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



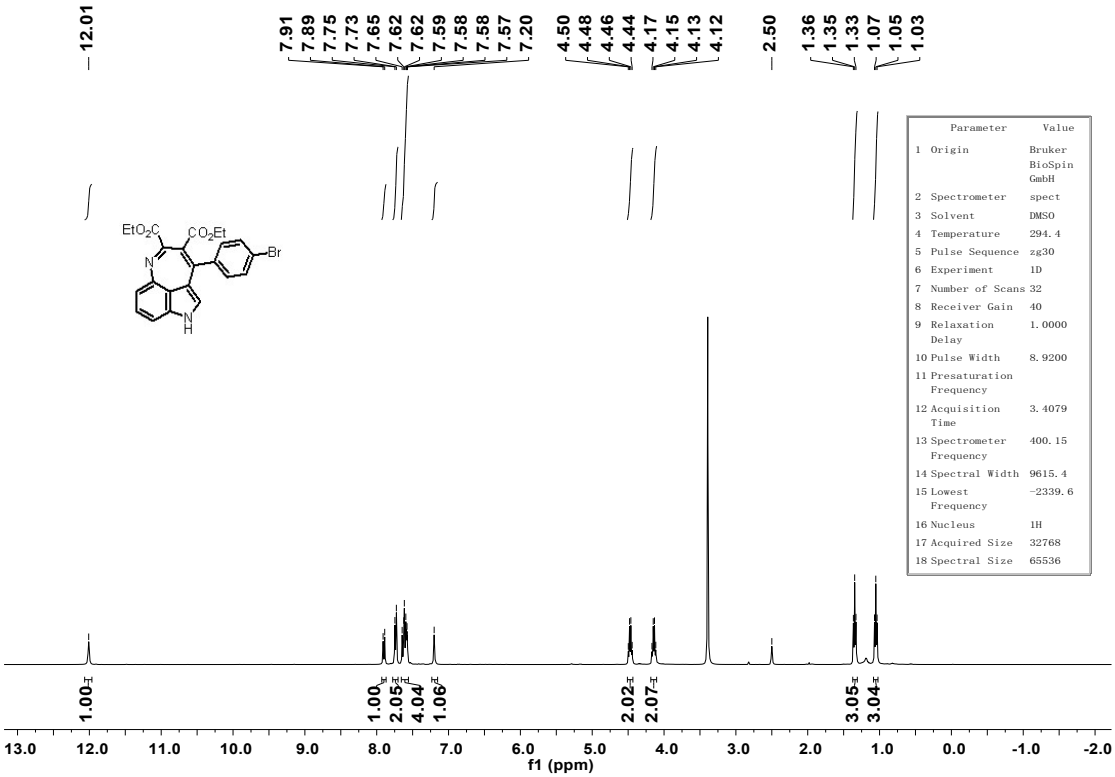
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	295.9
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	400
8	Receiver Gain	206
9	Relaxation Delay	2.0000
10	Pulse Width	10.0000
11	Presaturation Frequency	
12	Acquisition Time	1.1534
13	Spectrometer Frequency	100.63
14	Spectral Width	28409.1
15	Lowest Frequency	-4190.3
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

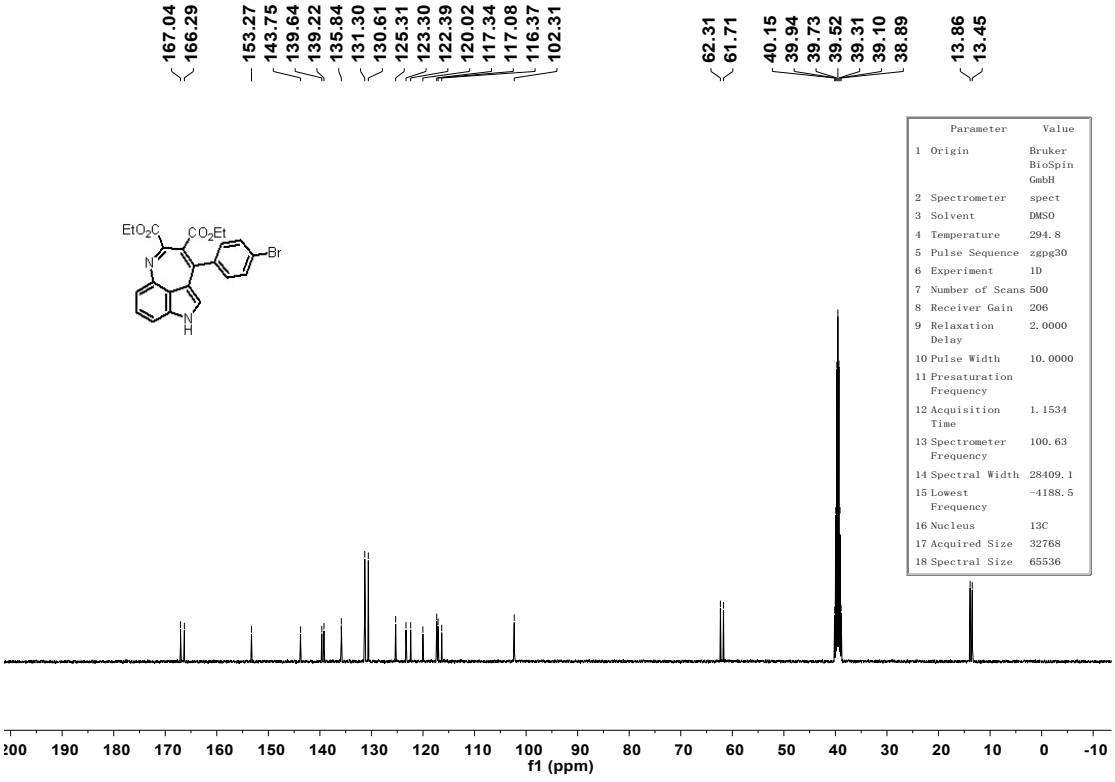
4f


12.01
7.91 7.89 7.69 7.67 7.65 7.63 7.61 7.59 7.58 7.57 7.20
4.50 4.48 4.46 4.44 4.17 4.15 4.13 4.11
2.50
1.36 1.35 1.33 1.07 1.05 1.03
EtO2C CO2Et
N
Cl
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 35
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00 1.03 3.01 4.02 1.05 2.11 2.10 3.05 3.09
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.
f1 (ppm)

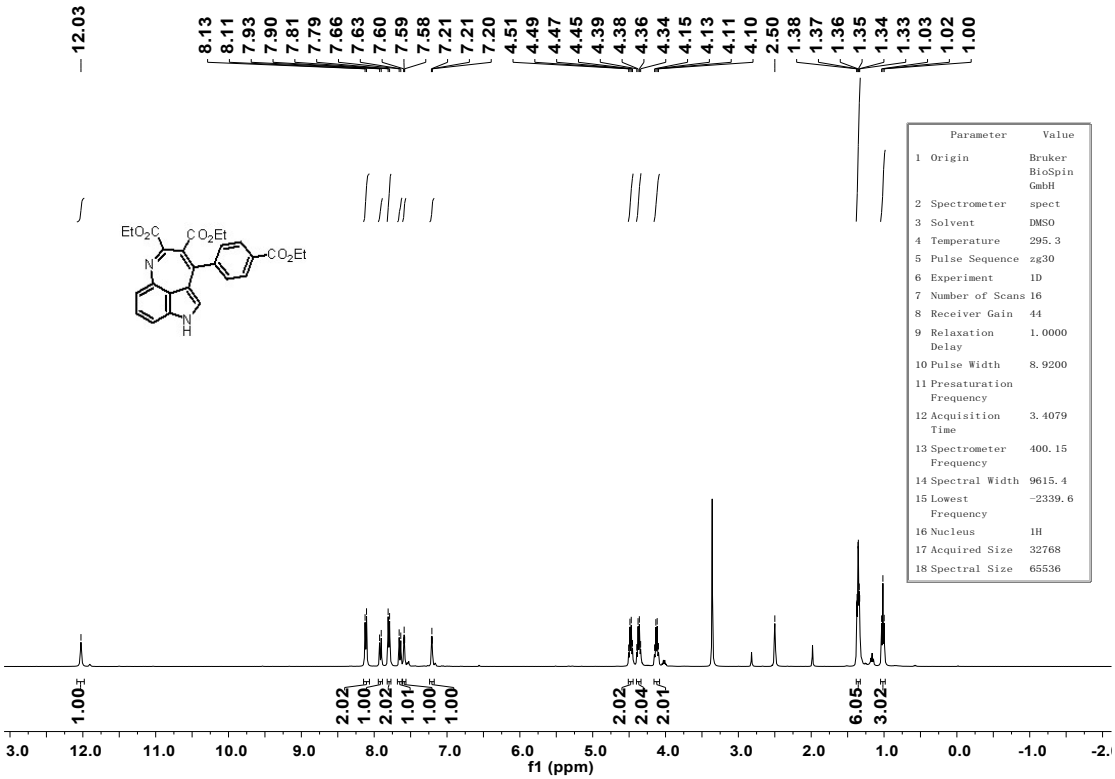

167.07 166.31
153.20 143.75 139.63 138.85 135.85 133.73 130.34 128.38 125.30 123.32 120.09 117.34 117.08 116.38 102.31
62.31 61.71
40.15 39.94 39.73 39.52 39.31 39.10 38.89
13.86 13.45
EtO2C CO2Et
N
Cl
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4187.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

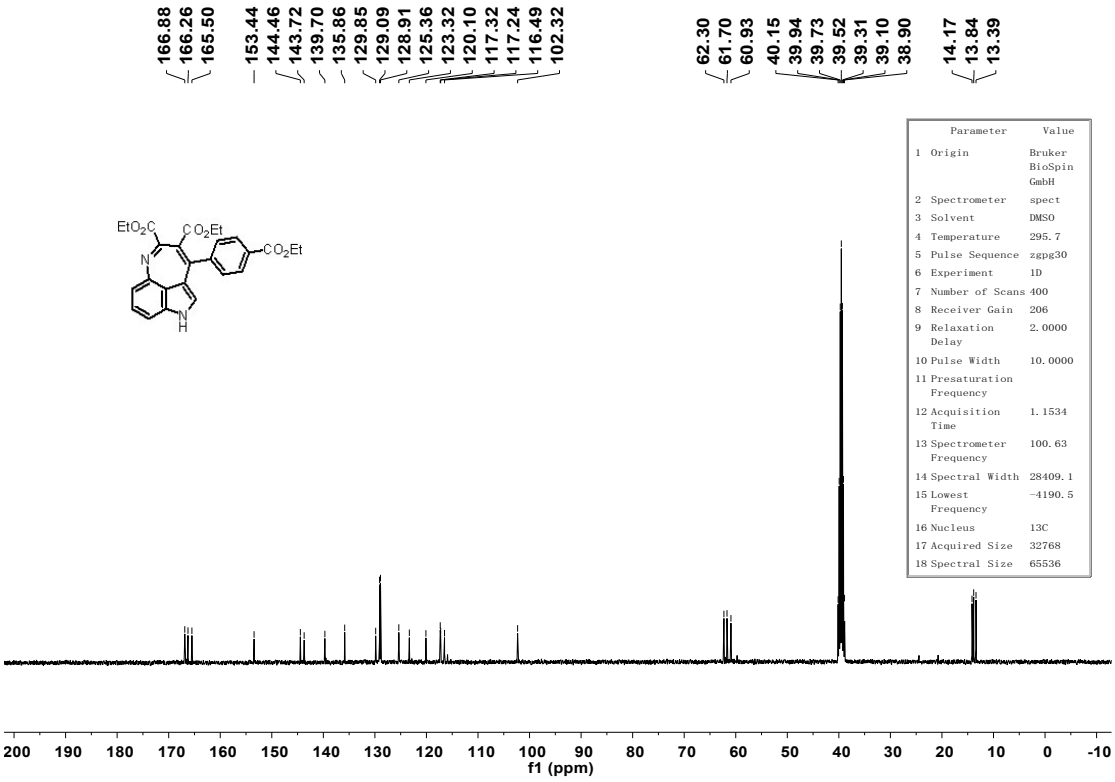
4g


12.01
7.91
7.89
7.75
7.73
7.65
7.62
7.62
7.59
7.58
7.58
7.57
7.20
4.50
4.48
4.46
4.44
4.17
4.15
4.13
4.12
2.50
1.36
1.35
1.33
1.07
1.05
1.03
EtO2C
CO2Et
Br
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.4
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 40
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.6
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.00
2.05
4.04
1.06
2.02
2.07
3.05
3.04
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

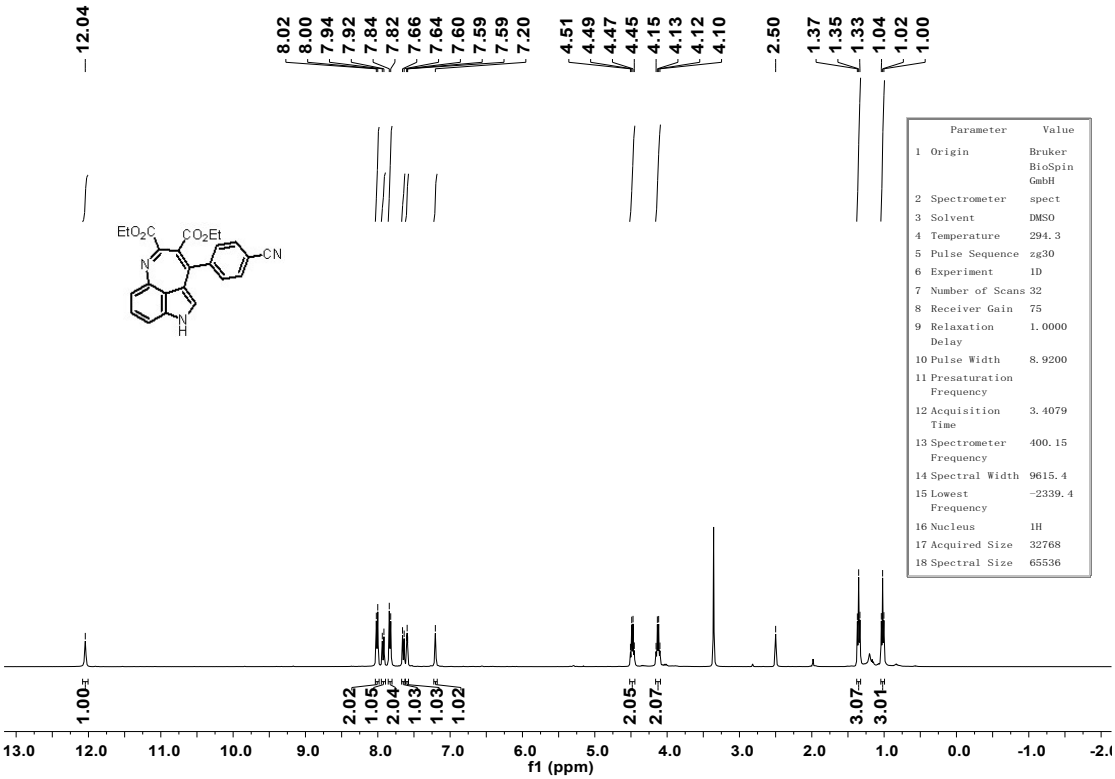

167.04
166.29
153.27
143.75
139.64
139.22
135.84
131.30
130.61
125.31
123.30
122.39
120.02
117.34
117.08
116.37
102.31
62.31
61.71
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.86
13.45
EtO2C
CO2Et
Br
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.8
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4188.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

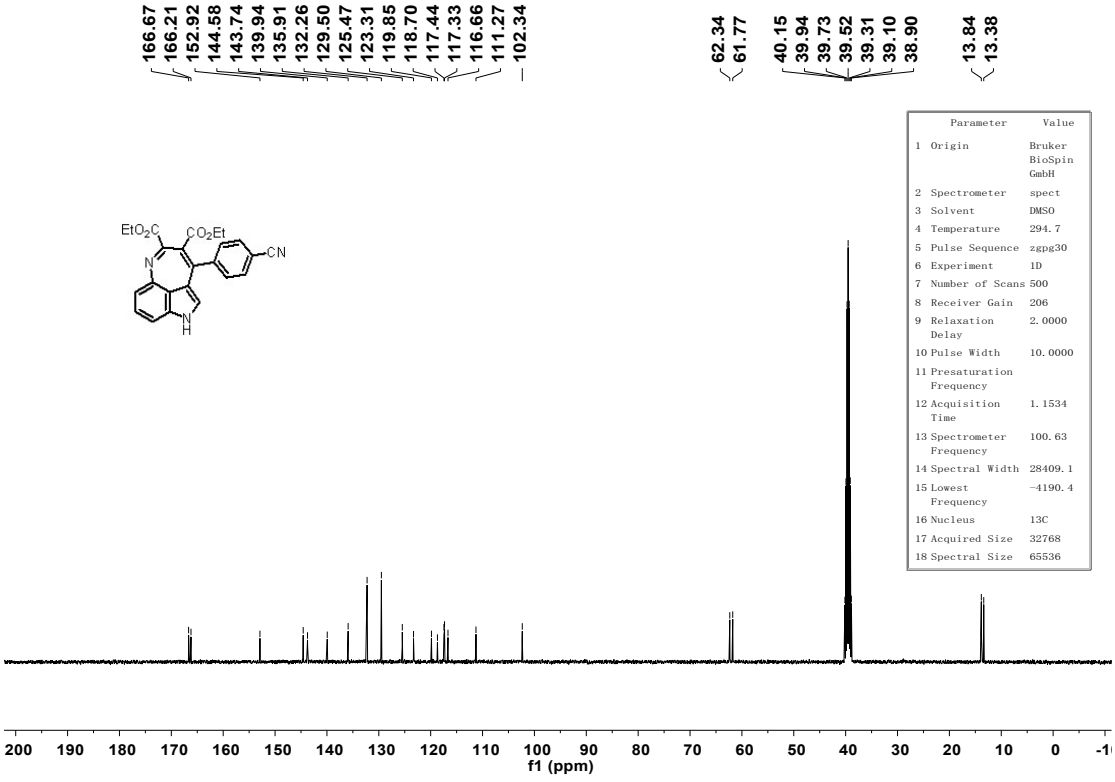
4h


12.03
8.13 8.11 7.93 7.90 7.81 7.79 7.66 7.63 7.60 7.59 7.58 7.21 7.21 7.20 4.51 4.49 4.47 4.45 4.39 4.38 4.36 4.34 4.15 4.13 4.11 4.10 2.50 1.38 1.37 1.36 1.35 1.34 1.33 1.03 1.02 1.00
EtO2C CO2Et CO2Et
N
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 44
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.6
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00 2.02 1.00 2.02 1.01 1.00 1.00 2.02 2.04 2.01 6.05 3.02
3.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

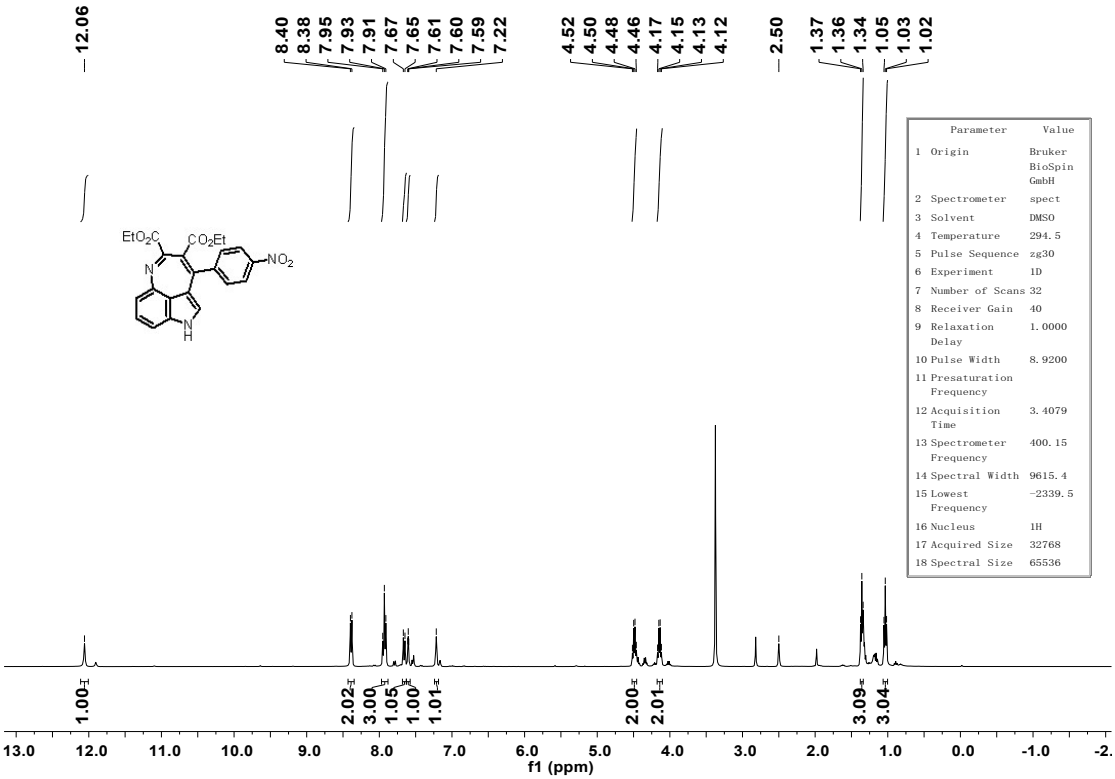

166.88 166.26 165.50 153.44 144.46 143.72 139.70 135.86 129.85 129.09 128.91 125.36 123.32 120.10 117.32 117.24 116.49 102.32
62.30 61.70 60.93 40.15 39.94 39.73 39.52 39.31 39.10 38.90 14.17 13.84 13.39
EtO2C CO2Et CO2Et
N
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

4i


12.04
8.02
8.00
7.94
7.92
7.84
7.82
7.66
7.64
7.60
7.59
7.59
7.20
4.51
4.49
4.47
4.45
4.15
4.13
4.12
4.10
2.50
1.37
1.35
1.33
1.04
1.02
1.00
EtO2C
CO2Et
CN
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
2.02
1.05
2.04
1.03
1.02
2.05
2.07
3.07
3.01
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


166.67
166.21
152.92
144.58
143.74
139.94
135.91
132.26
129.50
125.47
123.31
119.85
118.70
117.44
117.33
116.66
111.27
102.34
62.34
61.77
40.15
39.94
39.73
39.52
39.31
39.10
38.90
13.84
13.38
EtO2C
CO2Et
CN
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.4
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4j


12.06
8.40
8.38
7.95
7.93
7.91
7.67
7.65
7.61
7.60
7.59
7.22
4.52
4.50
4.48
4.46
4.17
4.15
4.13
4.12
2.50
1.37
1.36
1.34
1.05
1.03
1.02
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 40
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.5
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
2.02
3.00
1.05
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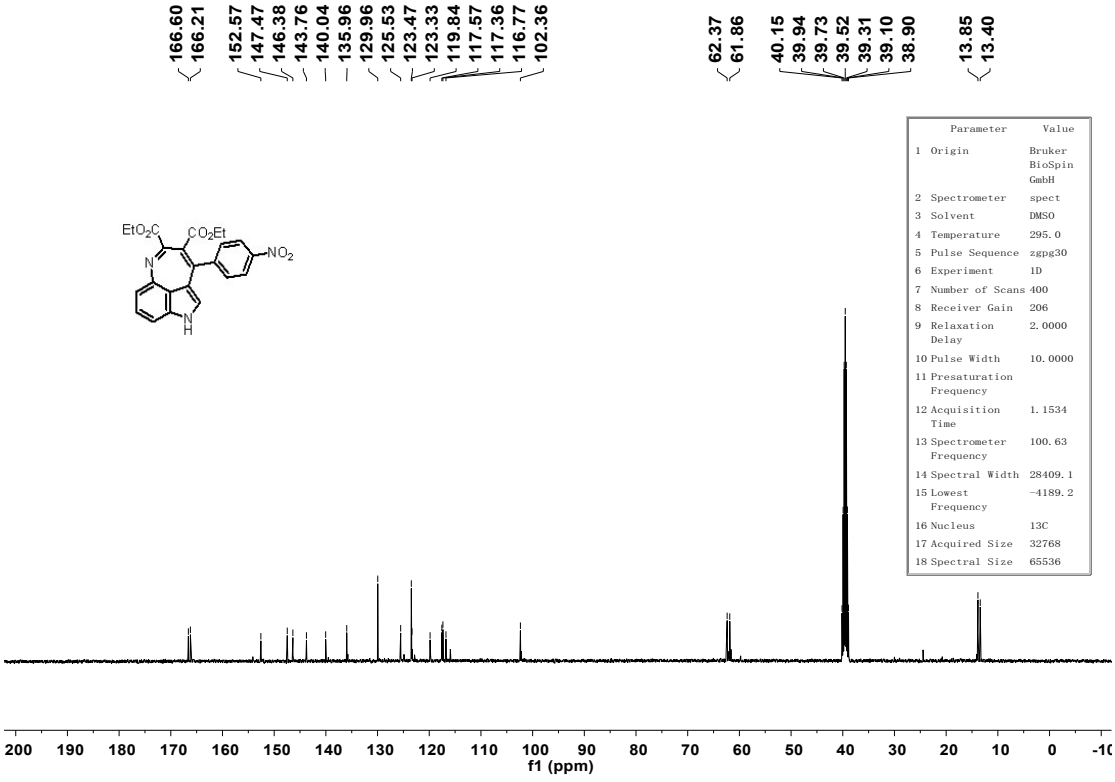
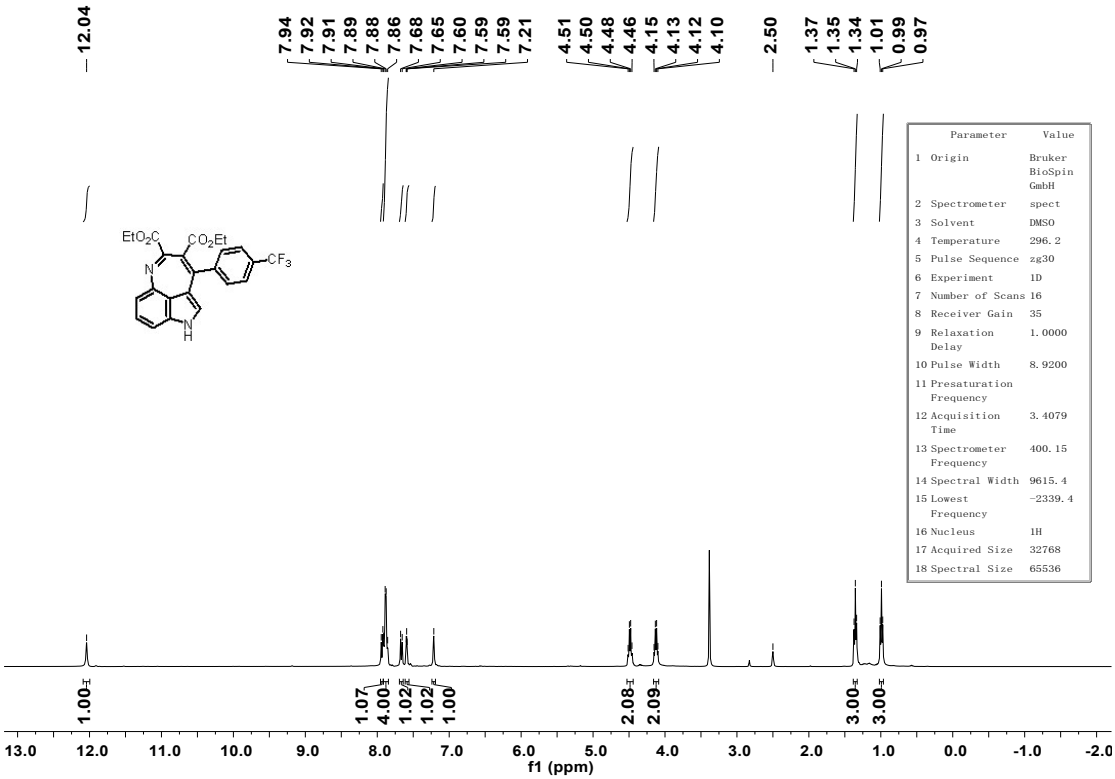
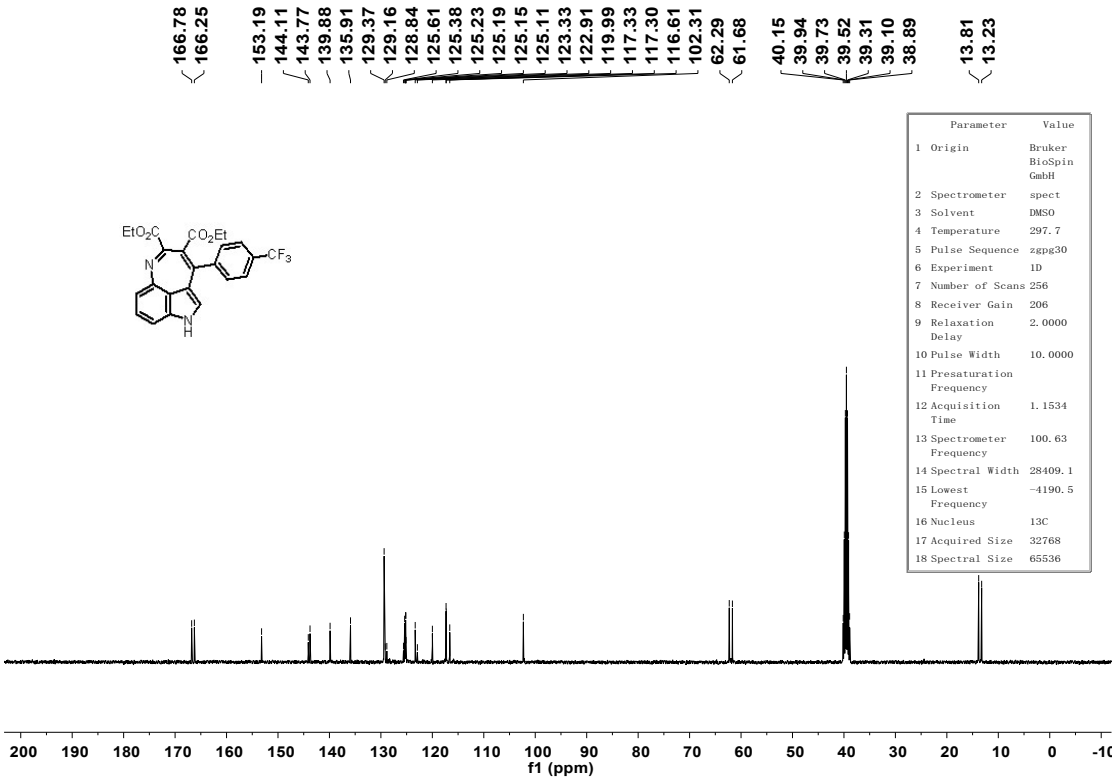
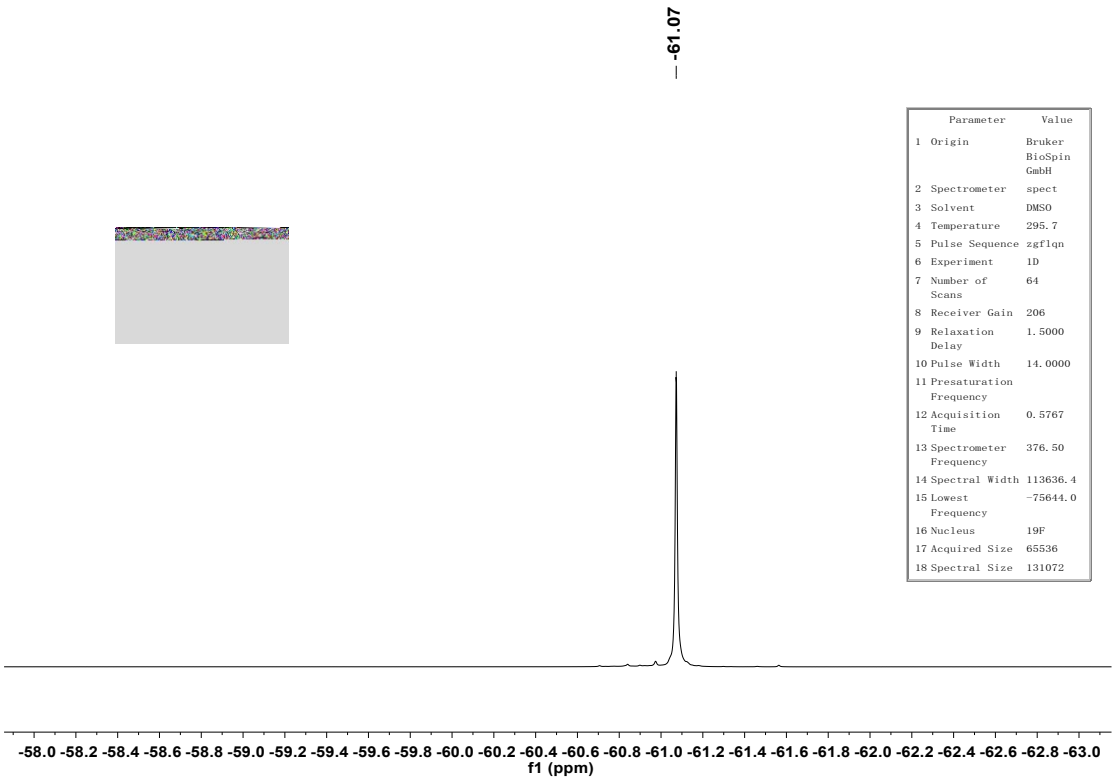
1.01
2.00
2.01
3.09
3.04
f1 (ppm)


166.60
166.21
152.57
147.47
146.38
143.76
140.04
135.96
129.96
125.53
123.47
123.33
119.84
117.57
117.36
116.77
102.36
62.37
61.86
40.15
39.94
39.73
39.52
39.31
39.10
38.90
13.85
13.40
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.0
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4189.2
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

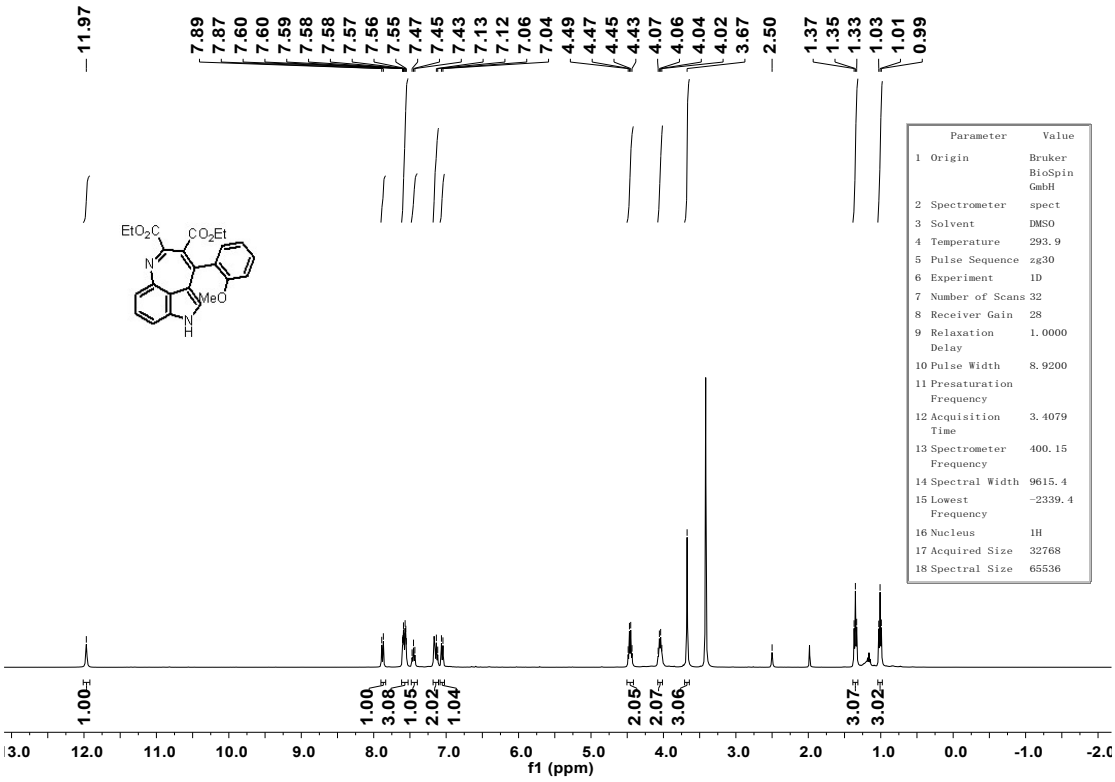
4k

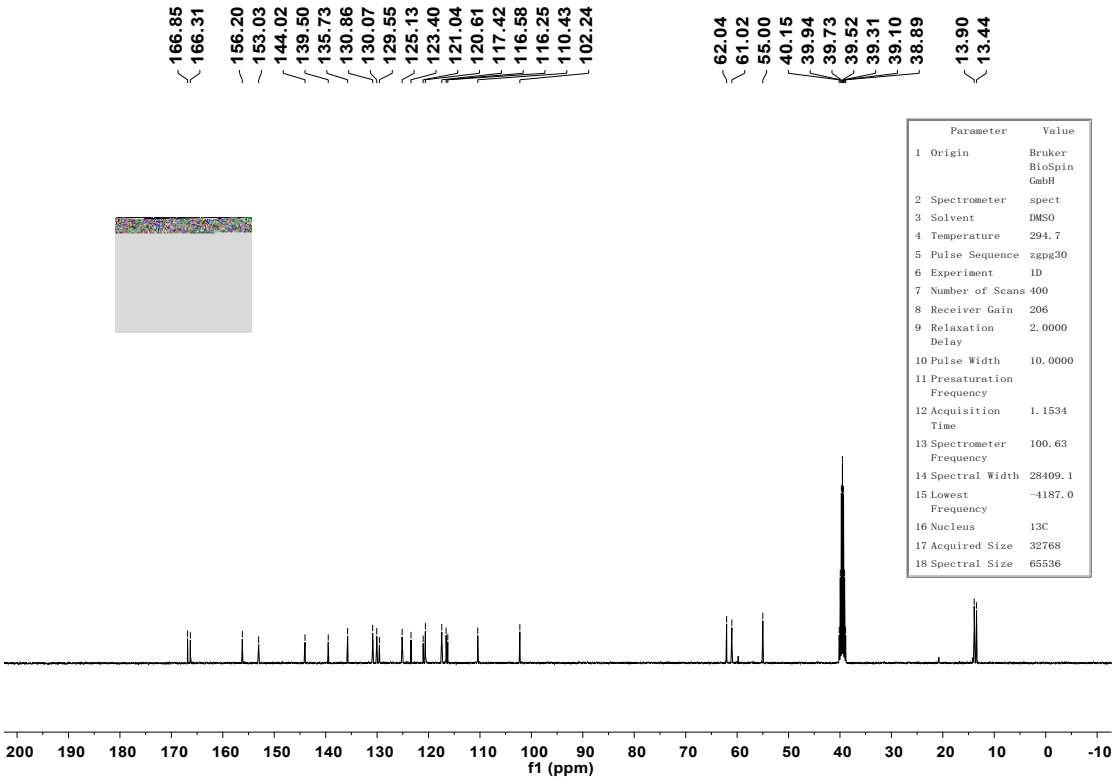

12.04
7.94
7.92
7.91
7.89
7.88
7.86
7.68
7.65
7.60
7.59
7.59
7.21
4.51
4.50
4.48
4.46
4.15
4.13
4.12
4.10
2.50
1.37
1.35
1.34
1.01
0.99
0.97
EtO2C
CO2Et
CF3
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 35
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.07
4.00
1.02
1.02
1.00
2.08
2.09
3.00
3.00
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


166.78
166.25
153.19
144.11
143.77
139.88
135.91
129.37
129.16
128.84
125.61
125.38
125.23
125.19
125.15
125.11
123.33
122.91
119.99
117.33
117.30
116.61
102.31
62.29
61.68
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.81
13.23
EtO2C
CO2Et
CF3
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 297.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 256
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

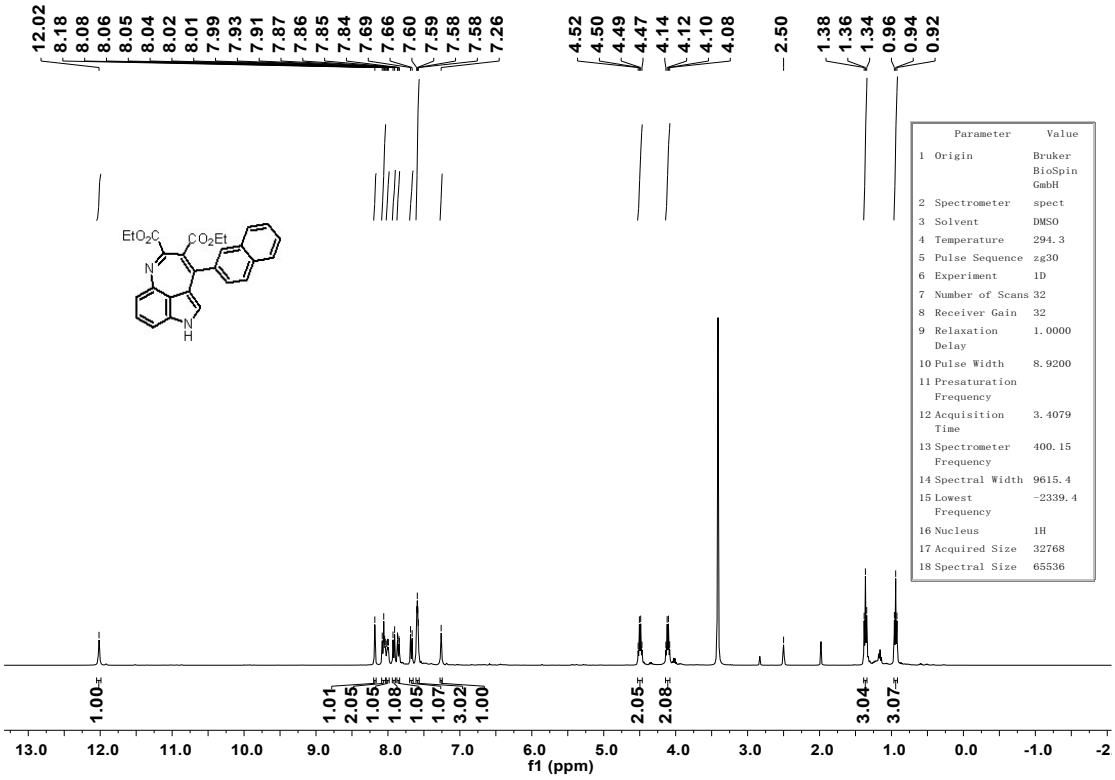

-61.07
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.7
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 64
8 Receiver Gain 206
9 Relaxation Delay 1.5000
10 Pulse Width 14.0000
11 Presaturation Frequency
12 Acquisition Time 0.5767
13 Spectrometer Frequency 376.50
14 Spectral Width 113636.4
15 Lowest Frequency -75644.0
16 Nucleus 19F
17 Acquired Size 65536
18 Spectral Size 131072
-58.0 -58.2 -58.4 -58.6 -58.8 -59.0 -59.2 -59.4 -59.6 -59.8 -60.0 -60.2 -60.4 -60.6 -60.8 -61.0 -61.2 -61.4 -61.6 -61.8 -62.0 -62.2 -62.4 -62.6 -62.8 -63.0
f1 (ppm)

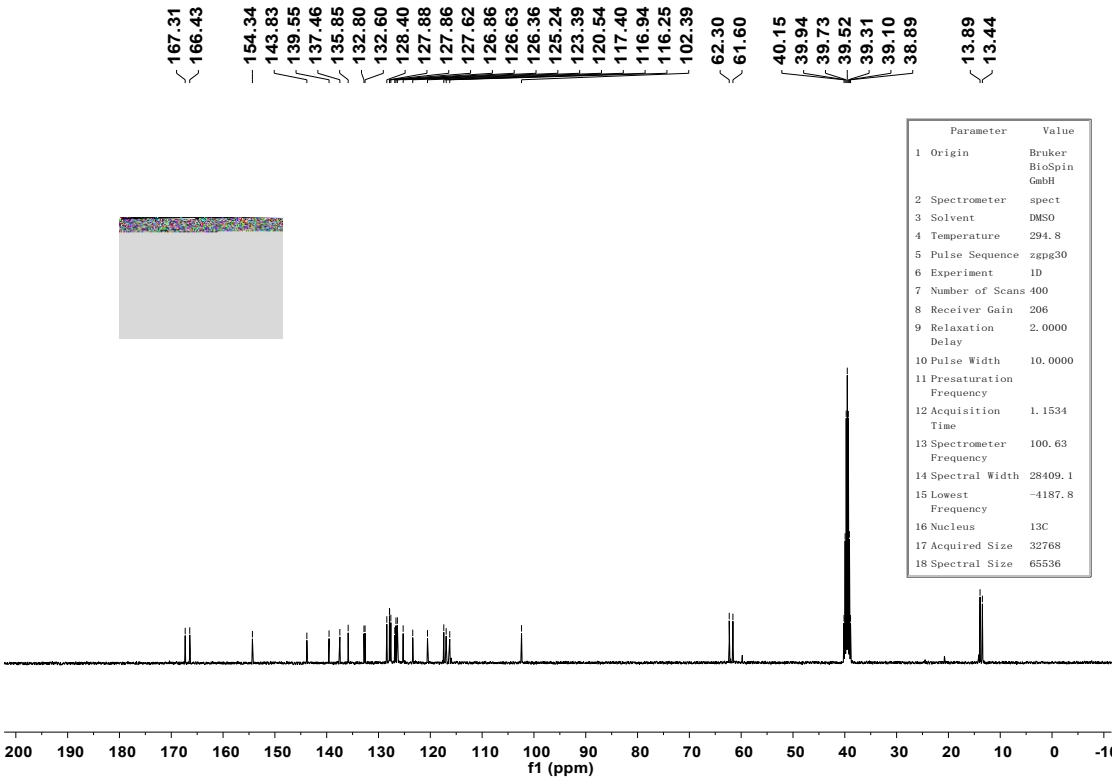
4l


11.97
7.89 7.87 7.60 7.60 7.59 7.58 7.58 7.57 7.56 7.55 7.47 7.45 7.43 7.13 7.12 7.06 7.04
4.49 4.47 4.45 4.43 4.07 4.06 4.04 4.02 3.67
2.50
1.37 1.35 1.33 1.03 1.01 0.99
EtO2C CO2Et
N
MeO
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 293.9
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 28
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00 1.00 3.08 1.05 2.02 1.04 2.05 2.07 3.06 3.07 3.02
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

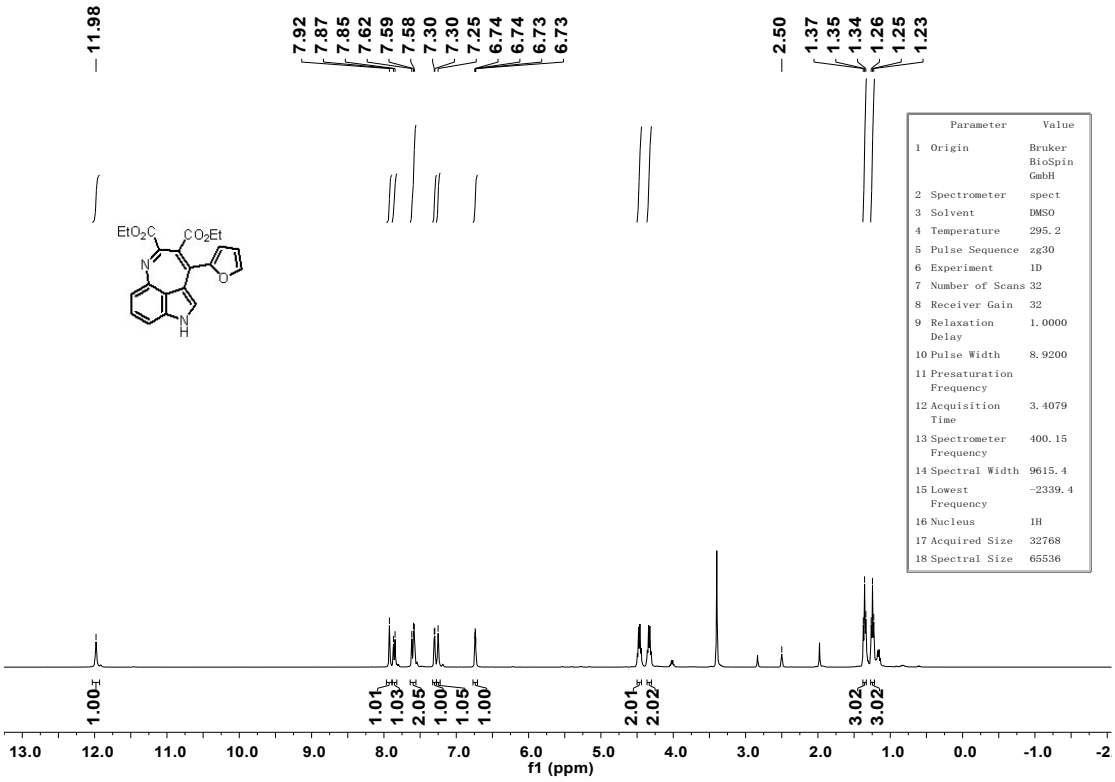

166.85
166.31
156.20
153.03
144.02
139.50
135.73
130.86
130.07
129.55
125.13
123.40
121.04
120.61
117.42
116.58
116.25
110.43
102.24
62.04
61.02
55.00
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.90
13.44
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4187.0
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

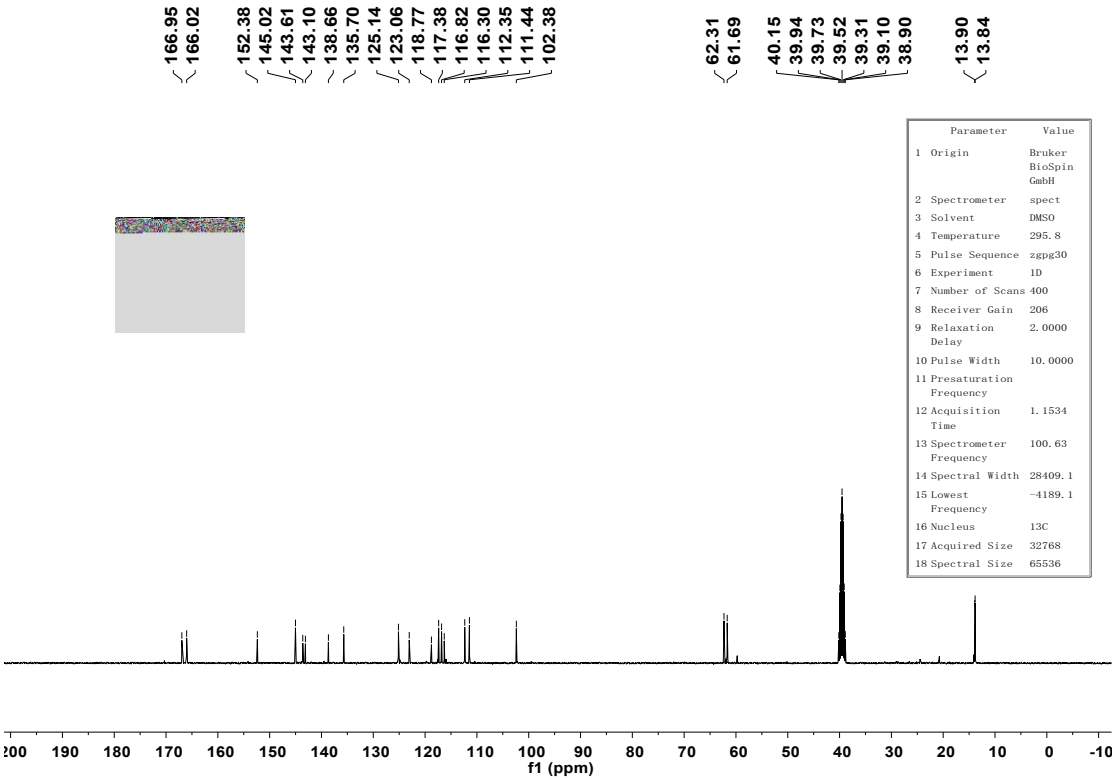
4m


12.02
8.18
8.08
8.06
8.05
8.04
8.02
8.01
7.99
7.93
7.91
7.87
7.86
7.85
7.84
7.69
7.66
7.60
7.59
7.58
7.58
7.26
4.52
4.50
4.49
4.47
4.14
4.12
4.10
4.08
2.50
1.38
1.36
1.34
0.96
0.94
0.92
EtO2C
CO2Et
N
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 32
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.01
2.05
1.05
1.08
1.05
1.07
3.02
1.00
2.05
2.08
3.04
3.07
f1 (ppm)

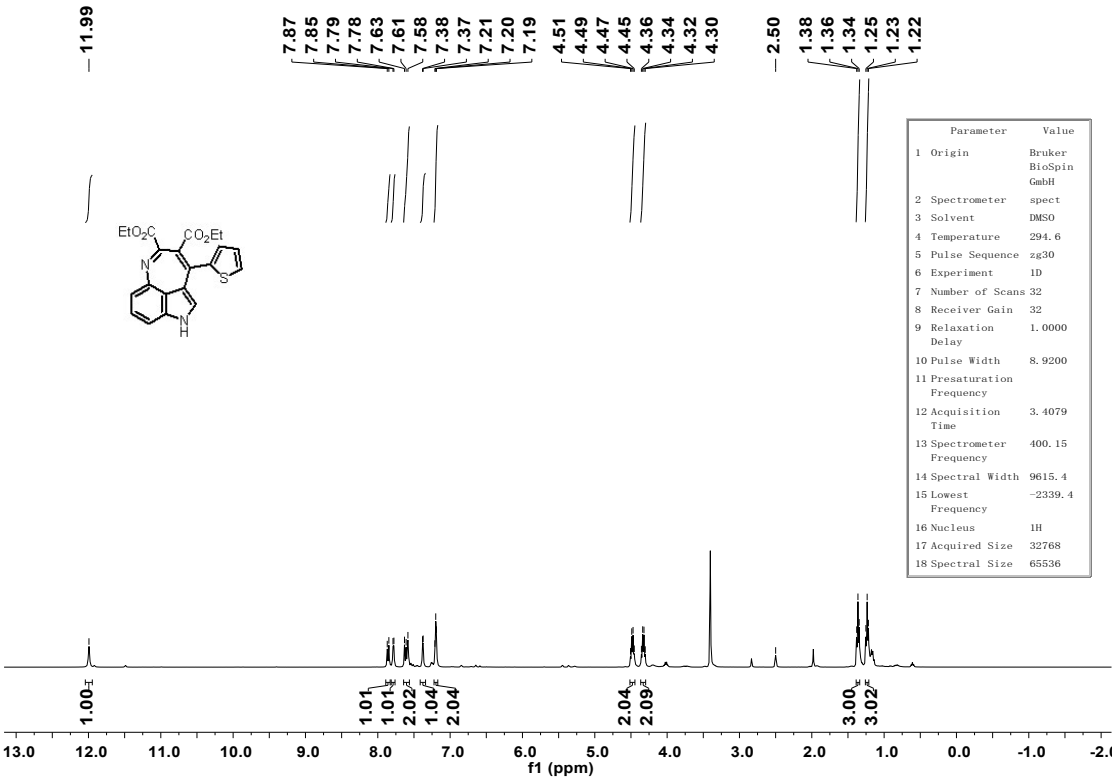

167.31
166.43
154.34
143.83
139.55
137.46
135.85
132.80
132.60
128.40
127.88
127.86
127.62
126.86
126.63
126.36
125.24
123.39
120.54
117.40
116.94
116.25
102.39
62.30
61.60
40.15
39.94
39.73
39.52
39.31
39.10
38.89
13.89
13.44
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.8
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4187.8
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

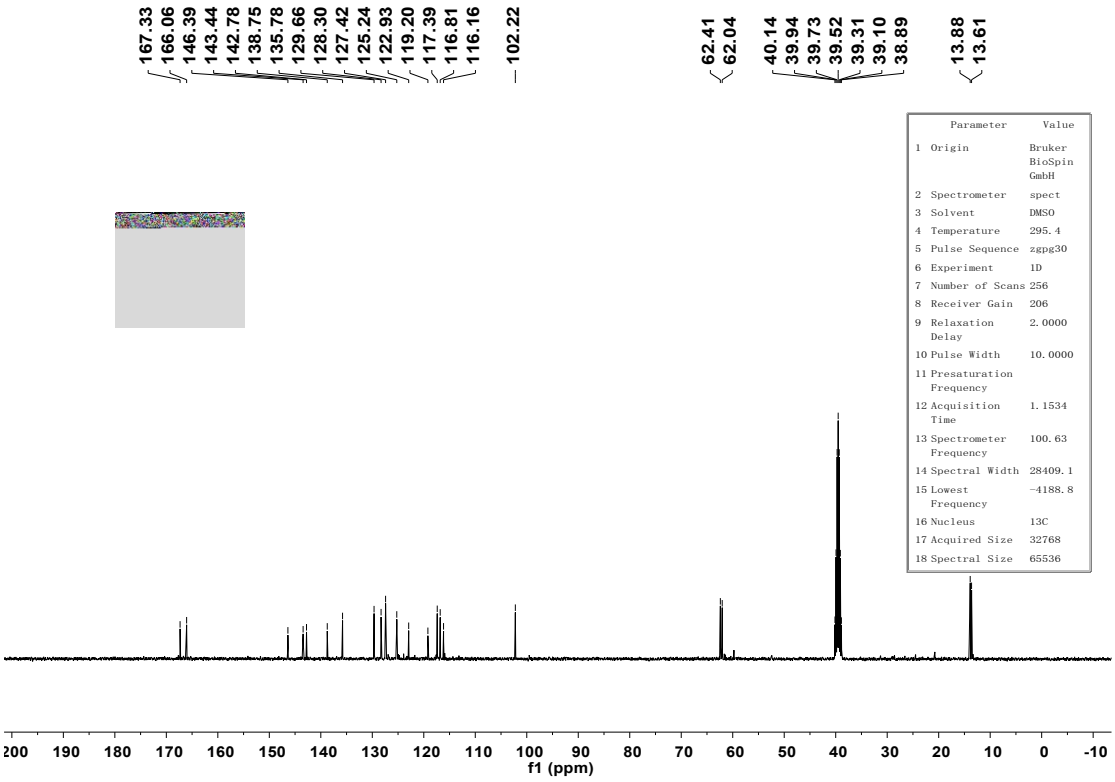
4n


11.98
7.92
7.87
7.85
7.62
7.59
7.58
7.30
7.30
7.25
6.74
6.74
6.73
6.73
2.50
1.37
1.35
1.34
1.26
1.25
1.23
EtO2C
CO2Et
N
O
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 32
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.01
1.03
2.05
1.00
1.05
1.00
2.01
2.02
3.02
3.02
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)


166.95
166.02
152.38
145.02
143.61
143.10
138.66
135.70
125.14
123.06
118.77
117.38
116.82
116.30
112.35
111.44
102.38
62.31
61.69
40.15
39.94
39.73
39.52
39.31
39.10
38.90
13.90
13.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.8
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4189.1
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

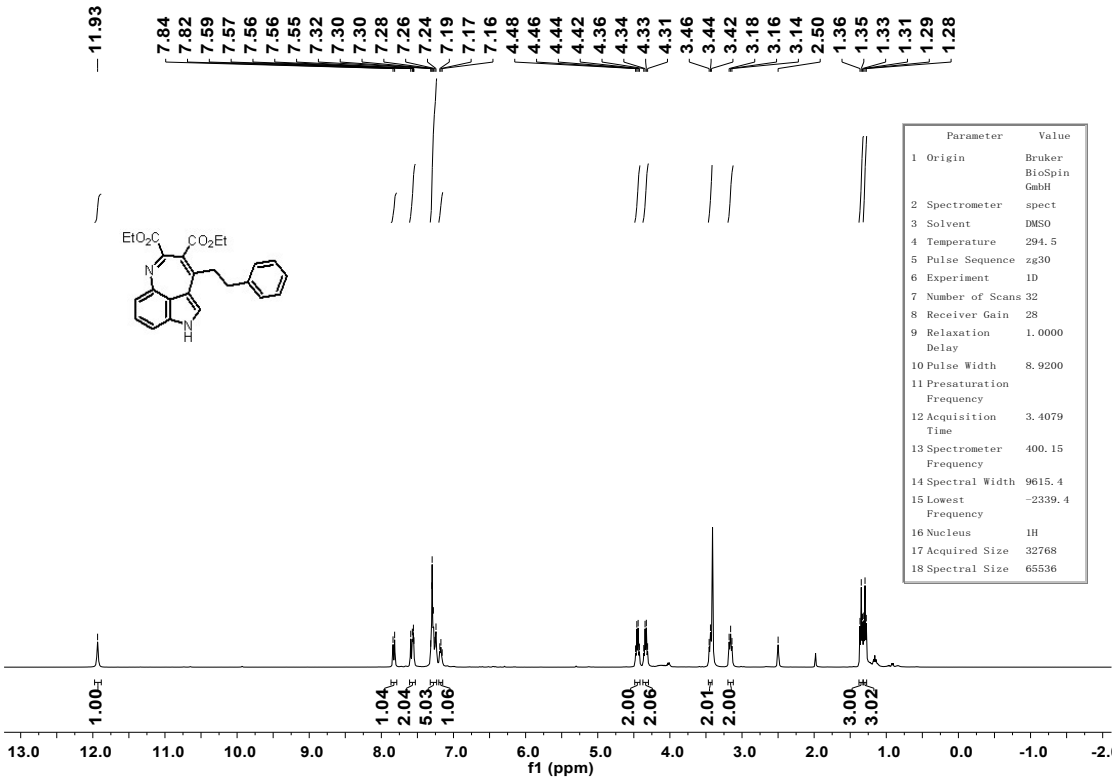
4o


11.99
7.87
7.85
7.79
7.78
7.63
7.61
7.58
7.38
7.37
7.21
7.20
7.19
4.51
4.49
4.47
4.45
4.36
4.34
4.32
4.30
2.50
1.38
1.36
1.34
1.25
1.23
1.22
EtO2C
CO2Et
N
S
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.6
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 32
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.01
1.01
2.02
1.04
2.04
2.04
2.09
3.00
3.02
f1 (ppm)

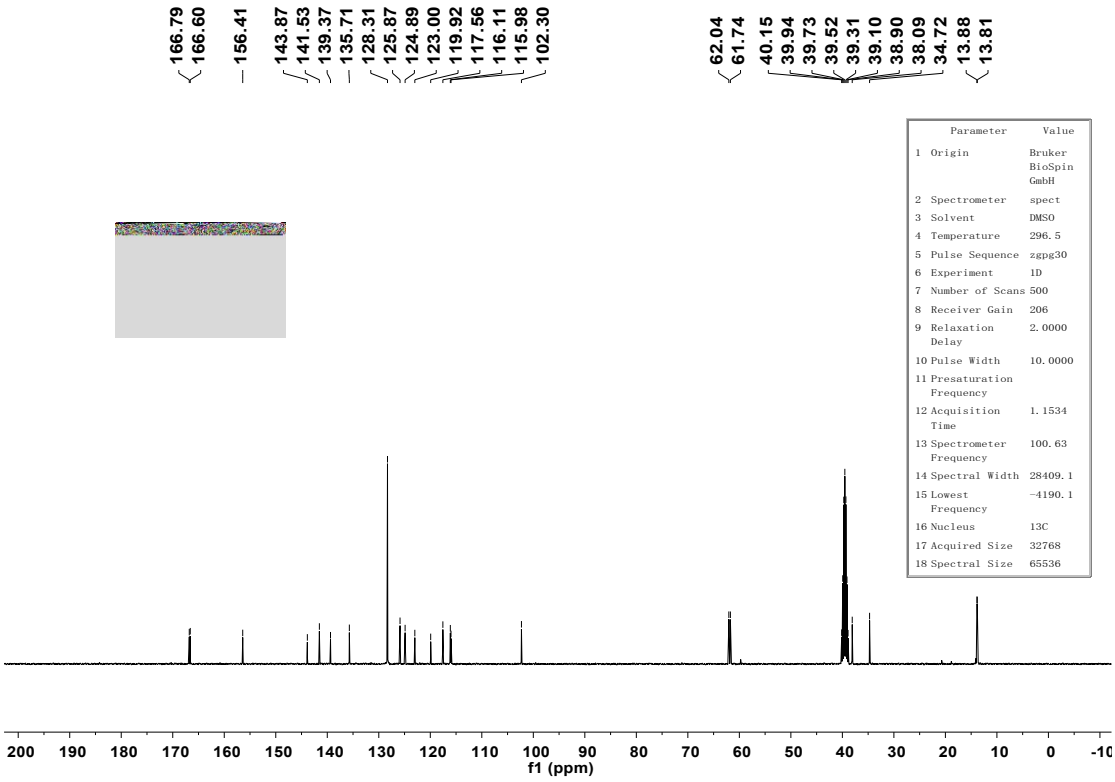


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	295.4
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	256
8	Receiver Gain	206
9	Relaxation Delay	2.0000
10	Pulse Width	10.0000
11	Presaturation Frequency	
12	Acquisition Time	1.1534
13	Spectrometer Frequency	100.63
14	Spectral Width	28409.1
15	Lowest Frequency	-4188.8
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

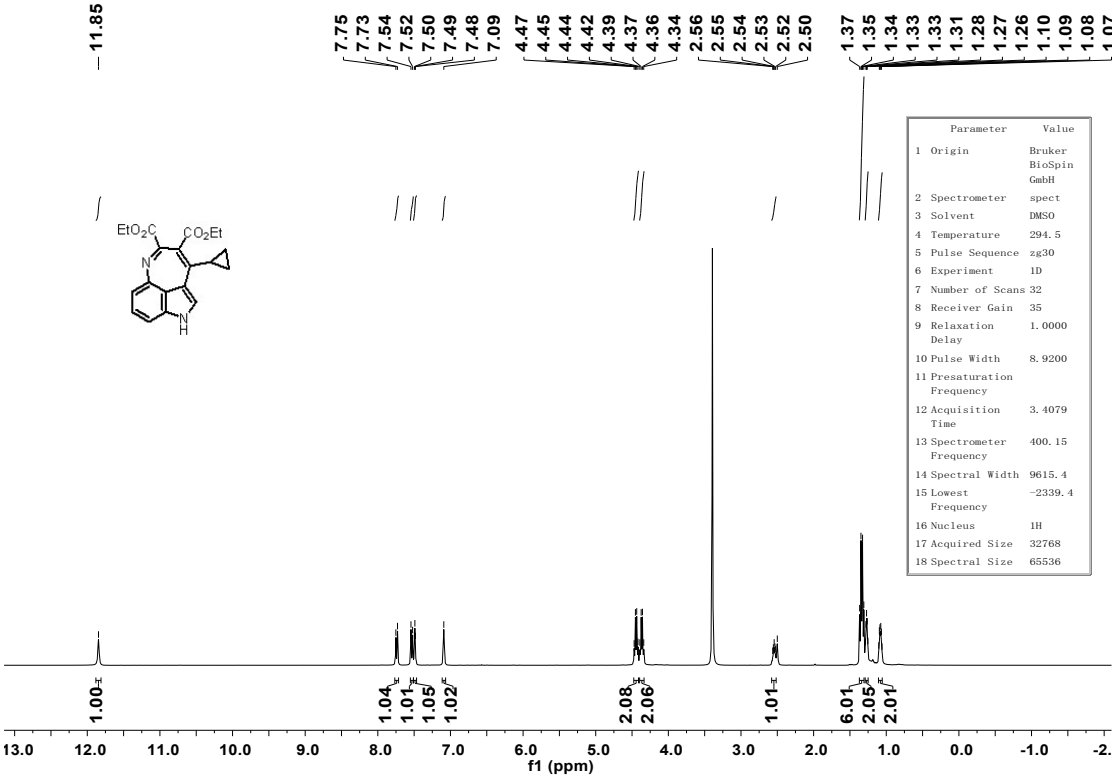
4p

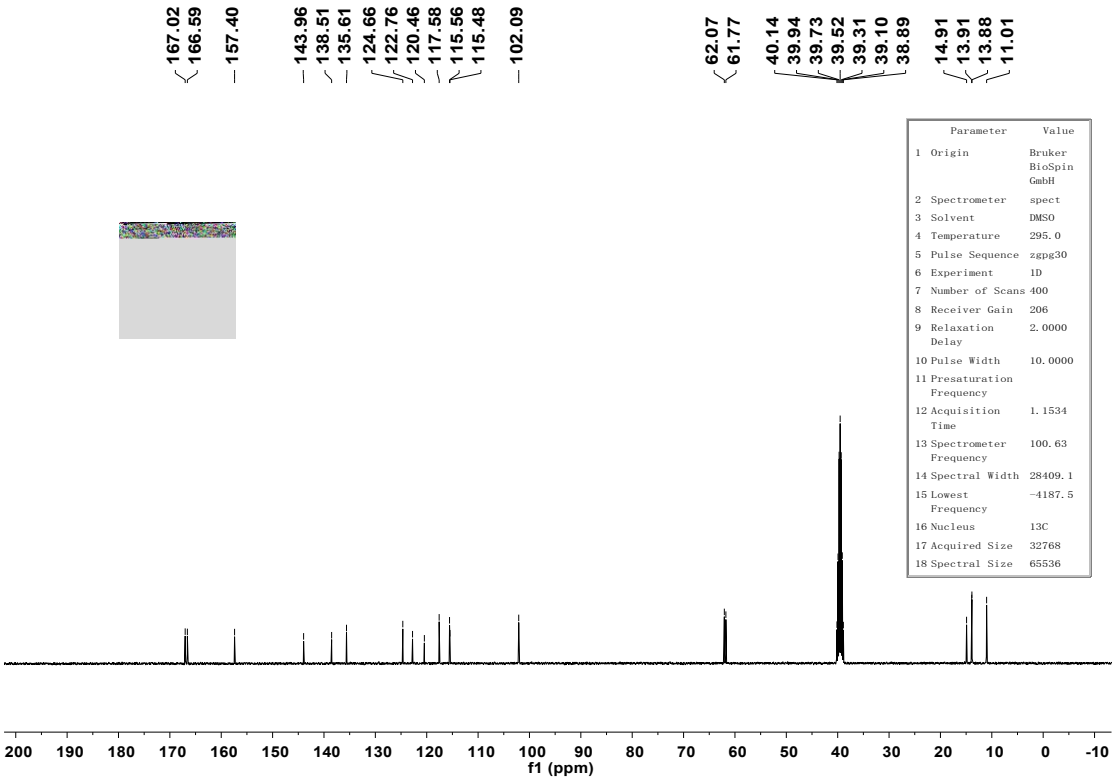


	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	294.5
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	32
8	Receiver Gain	28
9	Relaxation Delay	1.0000
10	Pulse Width	8.9200
11	Presaturation Frequency	
12	Acquisition Time	3.4079
13	Spectrometer Frequency	400.15
14	Spectral Width	9615.4
15	Lowest Frequency	-2339.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536

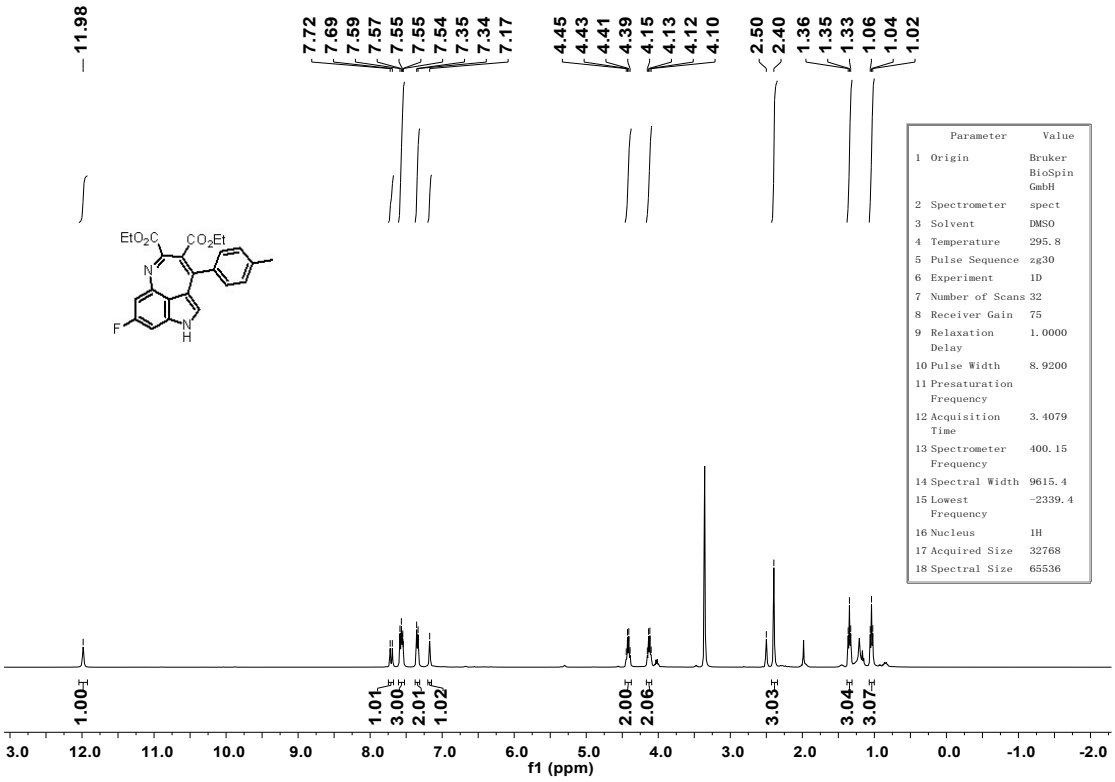

166.79
166.60
156.41
143.87
141.53
139.37
135.71
128.31
125.87
124.89
123.00
119.92
117.56
116.11
115.98
102.30
62.04
61.74
40.15
39.94
39.73
39.52
39.31
39.10
38.90
38.09
34.72
13.88
13.81
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.5
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.1
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

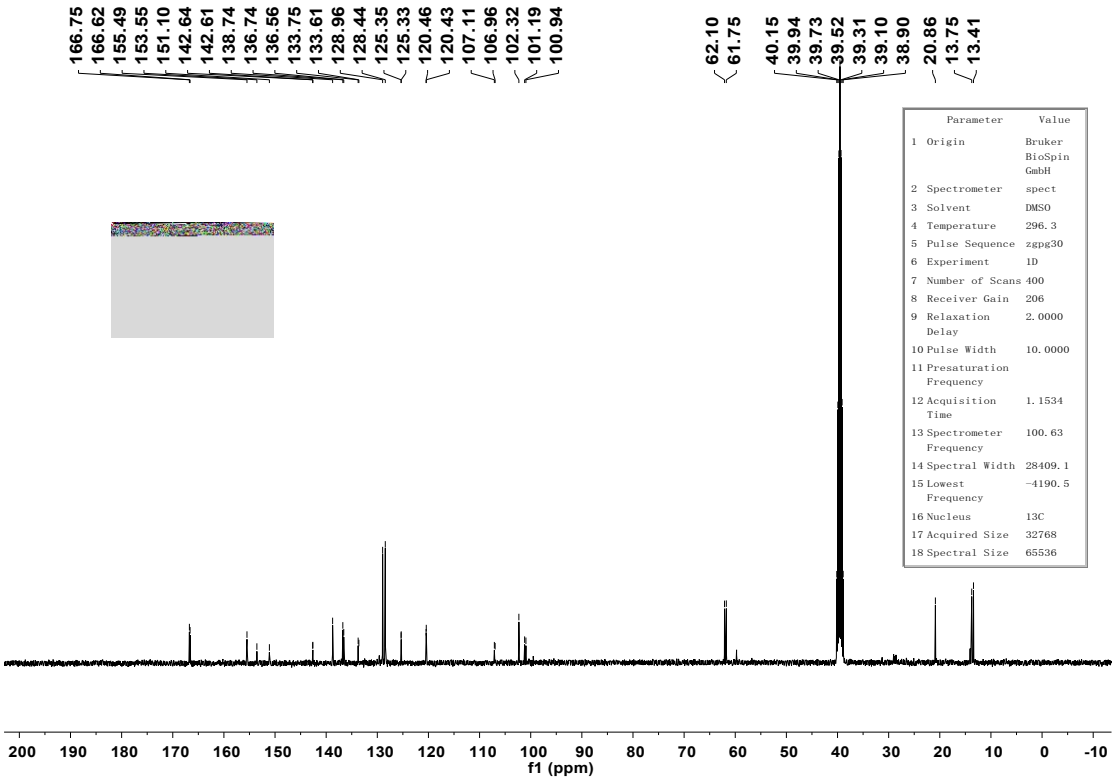
4q

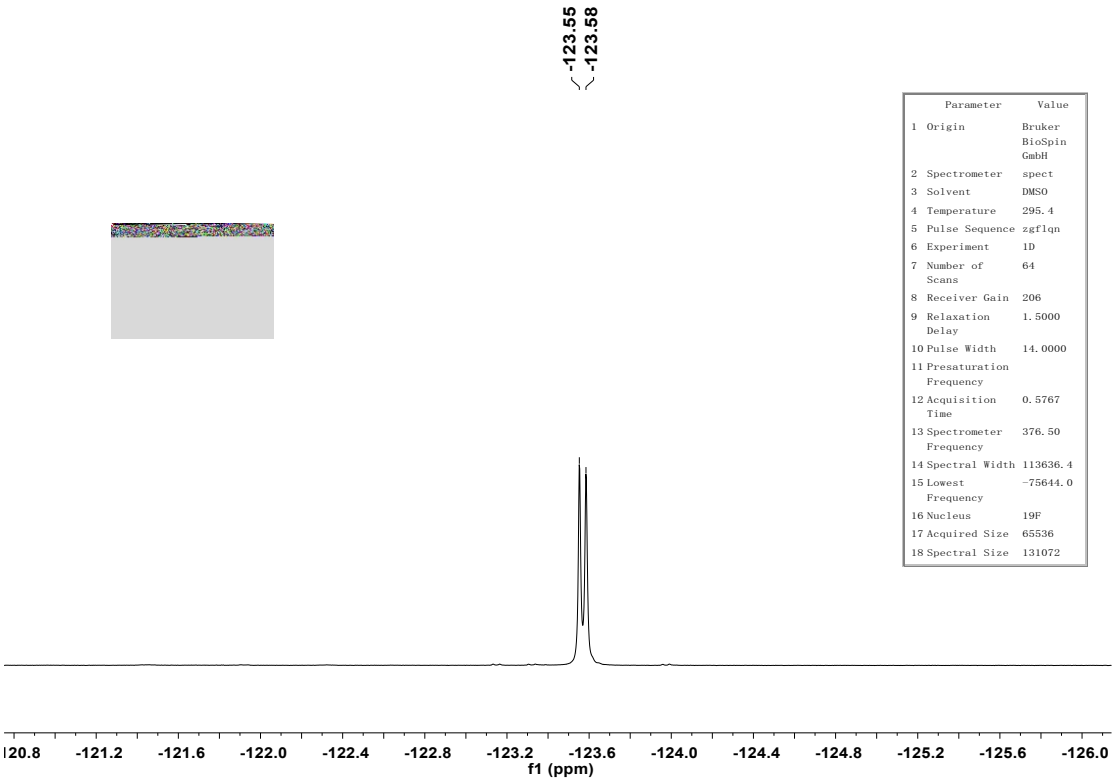

11.85
7.75
7.73
7.54
7.52
7.50
7.49
7.48
7.09
4.47
4.45
4.44
4.42
4.39
4.37
4.36
4.34
2.56
2.55
2.54
2.53
2.52
2.50
1.37
1.35
1.34
1.33
1.33
1.31
1.28
1.27
1.26
1.10
1.09
1.08
1.07
EtO2C
CO2Et
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 35
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.04
1.01
1.05
1.02
2.08
2.06
1.01
6.01
2.05
2.01
f1 (ppm)


167.02
166.59
157.40
143.96
138.51
135.61
124.66
122.76
120.46
117.58
115.56
115.48
102.09
62.07
61.77
40.14
39.94
39.73
39.52
39.31
39.10
38.89
14.91
13.91
13.88
11.01
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.0
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4187.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

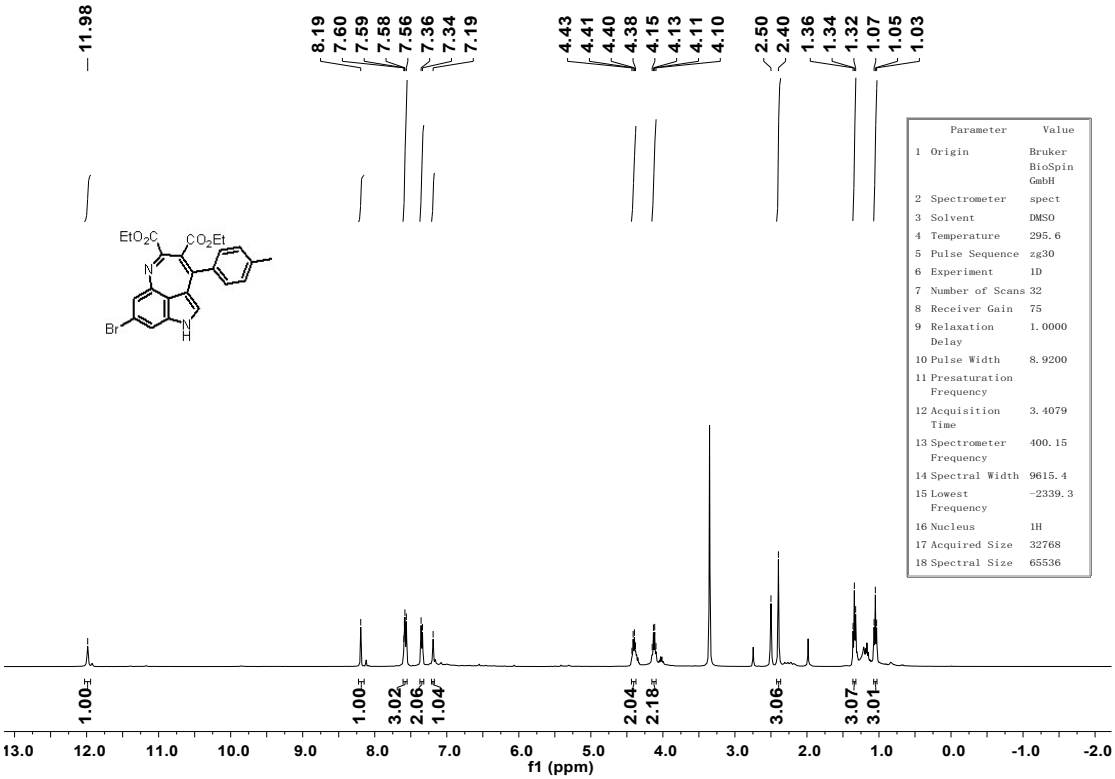
4r

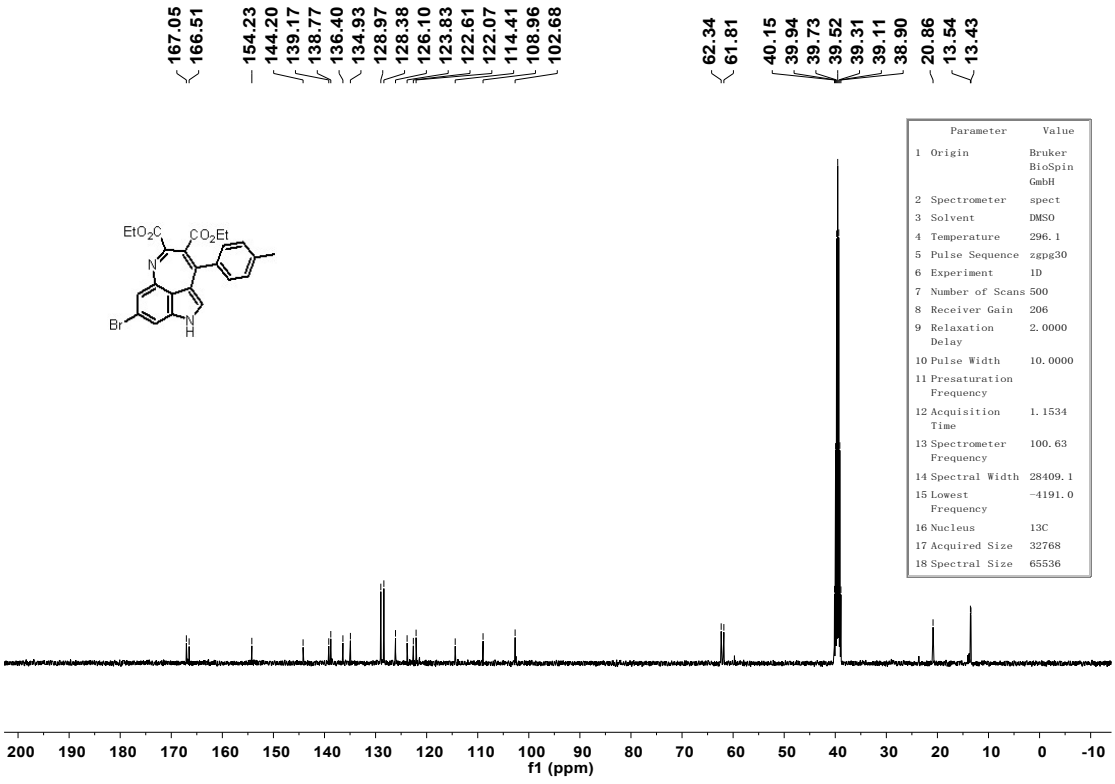

11.98
7.72
7.69
7.59
7.57
7.55
7.55
7.54
7.35
7.34
7.17
4.45
4.43
4.41
4.39
4.15
4.13
4.12
4.10
2.50
2.40
1.36
1.35
1.33
1.06
1.04
1.02
EtO2C
CO2Et
N
F
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.01
3.00
2.01
1.02
2.00
2.06
3.03
3.04
3.07
3.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)


166.75
166.62
155.49
153.55
151.10
142.64
142.61
138.74
136.74
136.56
133.75
133.61
128.96
128.44
125.35
125.33
120.46
120.43
107.11
106.96
102.32
101.19
100.94
62.10
61.75
40.15
39.94
39.73
39.52
39.31
39.10
38.90
20.86
13.75
13.41
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.3
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

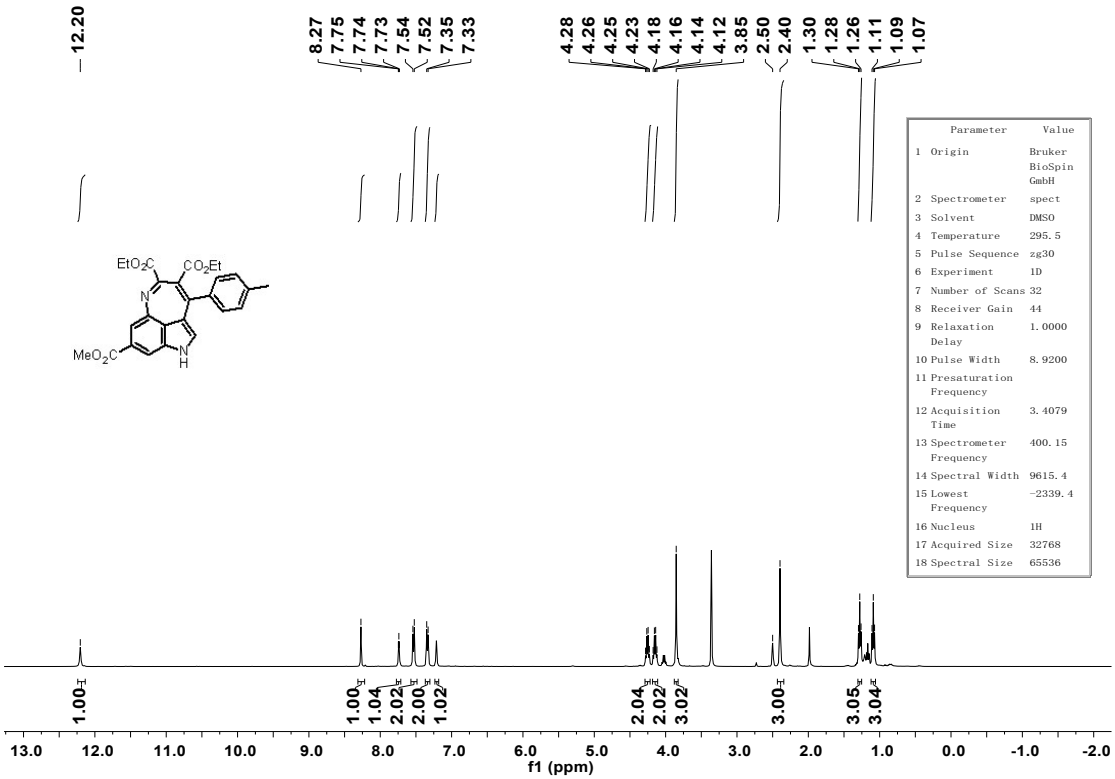

-123.55
-123.58
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.4
5 Pulse Sequence zgflqn
6 Experiment 1D
7 Number of Scans 64
8 Receiver Gain 206
9 Relaxation Delay 1.5000
10 Pulse Width 14.0000
11 Presaturation Frequency
12 Acquisition Time 0.5767
13 Spectrometer Frequency 376.50
14 Spectral Width 113636.4
15 Lowest Frequency -75644.0
16 Nucleus 19F
17 Acquired Size 65536
18 Spectral Size 131072
-120.8 -121.2 -121.6 -122.0 -122.4 -122.8 -123.2 -123.6 -124.0 -124.4 -124.8 -125.2 -125.6 -126.0
f1 (ppm)

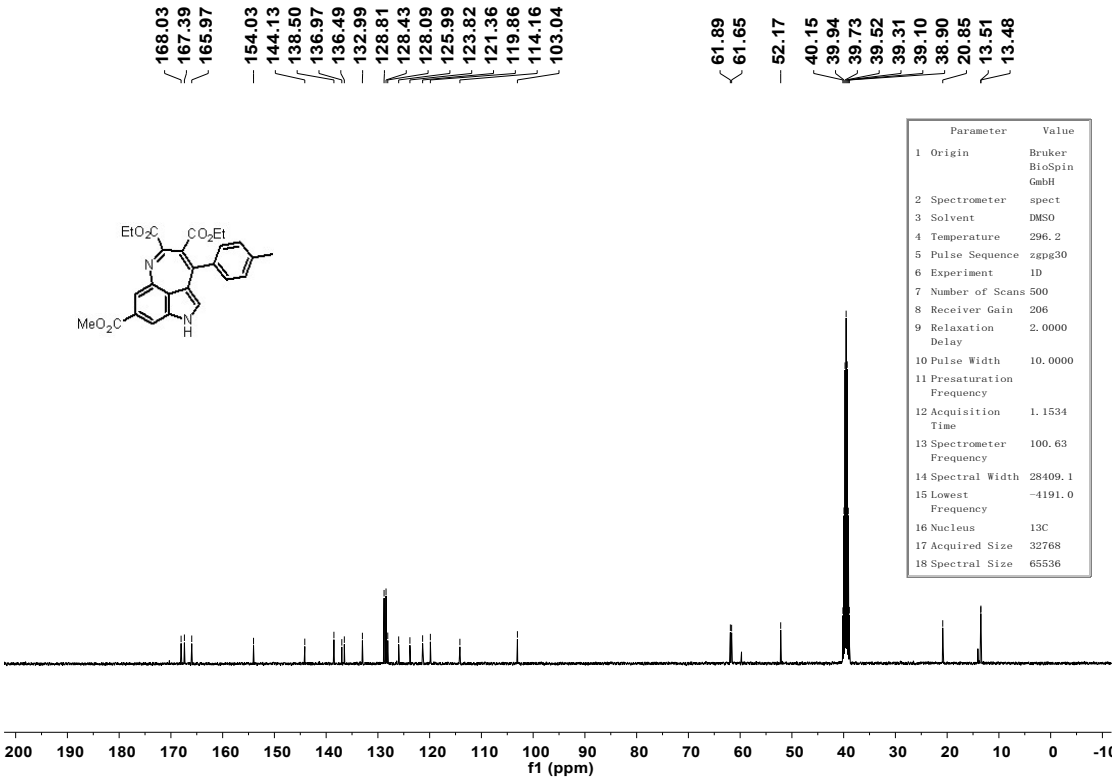
4s


11.98
8.19
7.60
7.59
7.58
7.56
7.36
7.34
7.19
4.43
4.41
4.40
4.38
4.15
4.13
4.11
4.10
2.50
2.40
1.36
1.34
1.32
1.07
1.05
1.03
EtO2C
CO2Et
Br
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.6
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.3
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.00
3.02
2.06
1.04
2.04
2.18
3.06
3.07
3.01
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

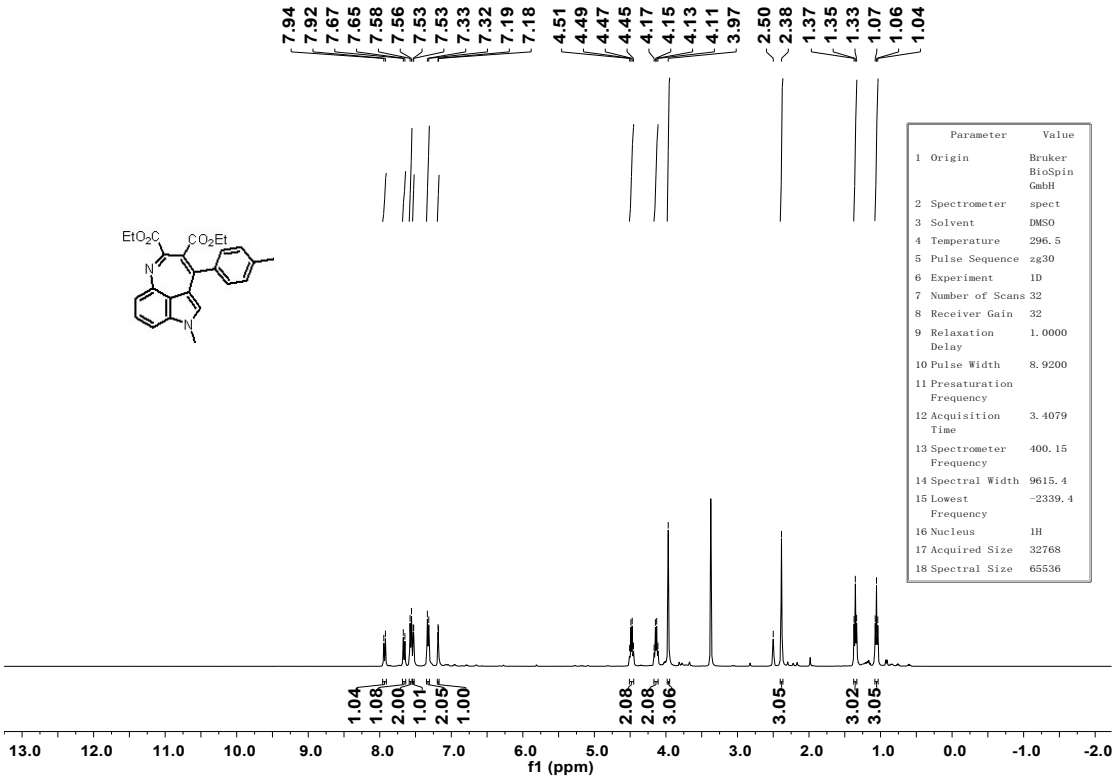

167.05
166.51
154.23
144.20
139.17
138.77
136.40
134.93
128.97
128.38
126.10
123.83
122.61
122.07
114.41
108.96
102.68
62.34
61.81
40.15
39.94
39.73
39.52
39.31
39.11
38.90
20.86
13.54
13.43
EtO2C
CO2Et
Br
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.1
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.0
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

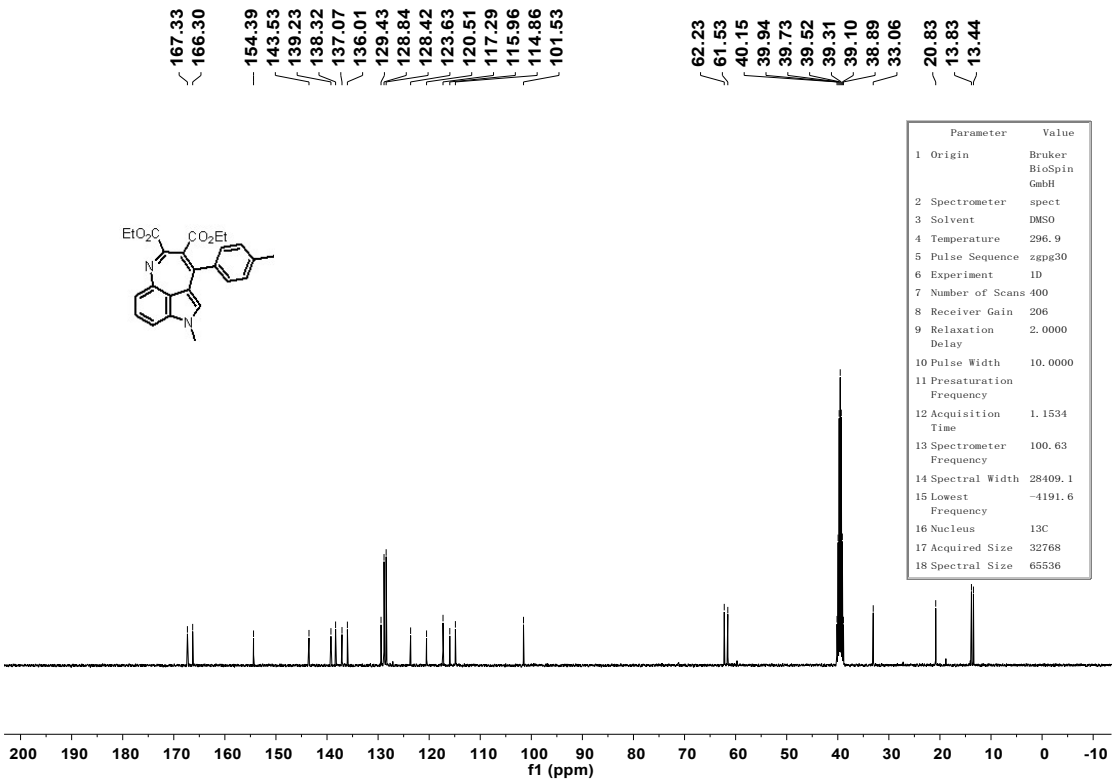
4t


12.20
8.27
7.75
7.74
7.73
7.54
7.52
7.35
7.33
4.28
4.26
4.25
4.23
4.18
4.16
4.14
4.12
3.85
2.50
2.40
1.30
1.28
1.26
1.11
1.09
1.07
EtO2C
CO2Et
MeO2C
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 44
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.00
1.04
2.02
2.00
1.02
2.04
2.02
3.02
3.00
3.05
3.04
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
-2.0
f1 (ppm)

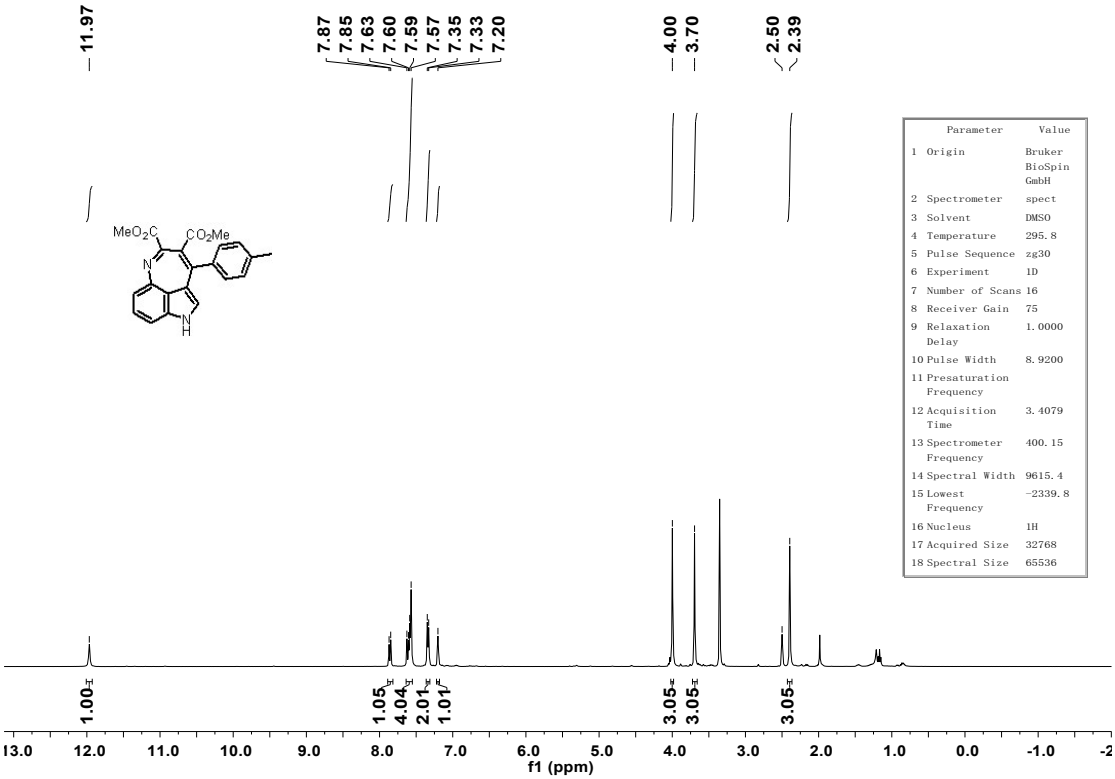

168.03
167.39
165.97
154.03
144.13
138.50
136.97
136.49
132.99
128.81
128.43
128.09
125.99
123.82
121.36
119.86
114.16
103.04
61.89
61.65
52.17
40.15
39.94
39.73
39.52
39.31
39.10
38.90
20.85
13.51
13.48
EtO2C
CO2Et
MeO2C
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.0
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

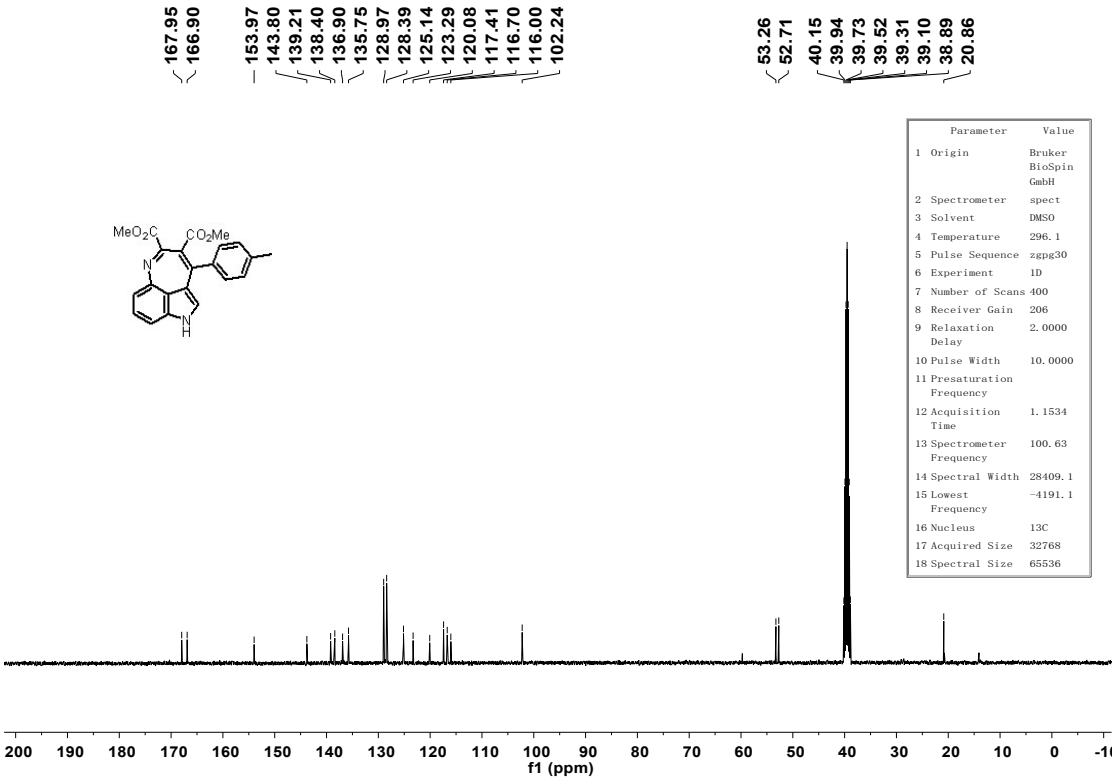
4u


7.94 7.92 7.67 7.65 7.58 7.56 7.53 7.53 7.33 7.32 7.19 7.18 4.51 4.49 4.47 4.45 4.17 4.15 4.13 4.11 3.97 2.50 2.38 1.37 1.35 1.33 1.07 1.06 1.04
EtO2C CO2Et
N
N
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 32
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.04 1.08 2.00 1.01 2.05 1.00 2.08 2.03 3.06 3.05 3.02 3.05
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

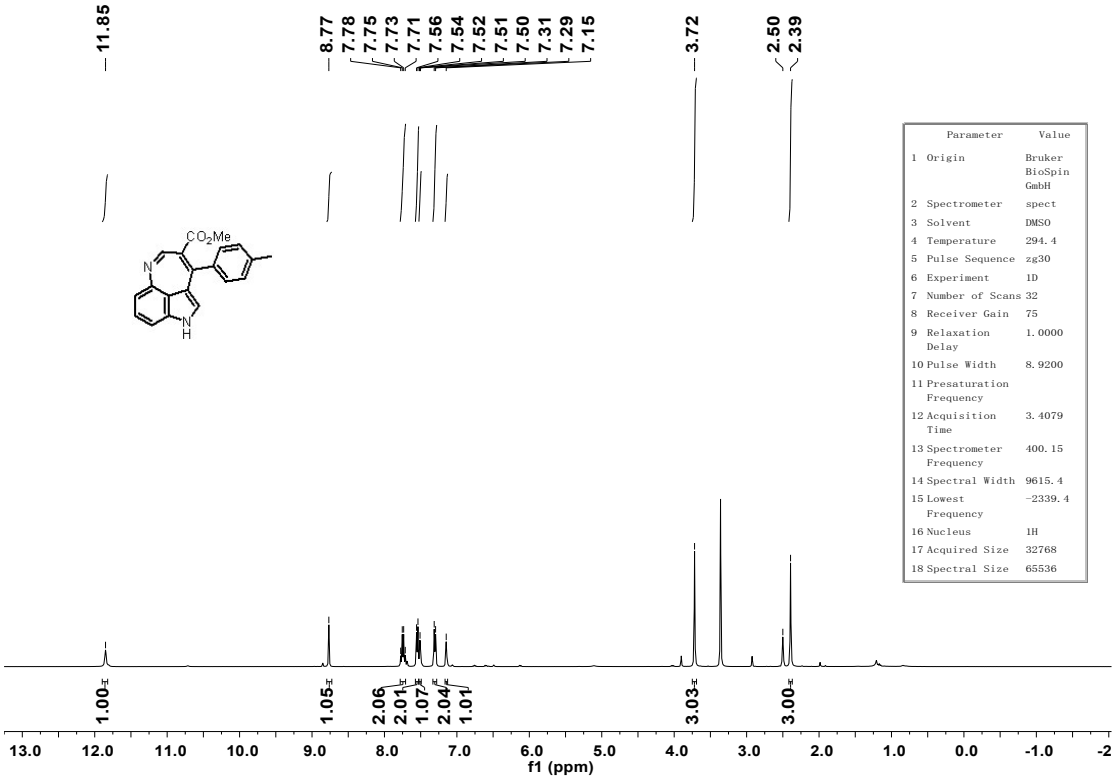

167.33 166.30 154.39 143.53 139.23 138.32 137.07 136.01 129.43 128.84 128.42 123.63 120.51 117.29 115.96 114.86 101.53 62.23 61.53 40.15 39.94 39.73 39.52 39.31 39.10 38.89 33.06 20.83 13.83 13.44
EtO2C CO2Et
N
N
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.9
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.6
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

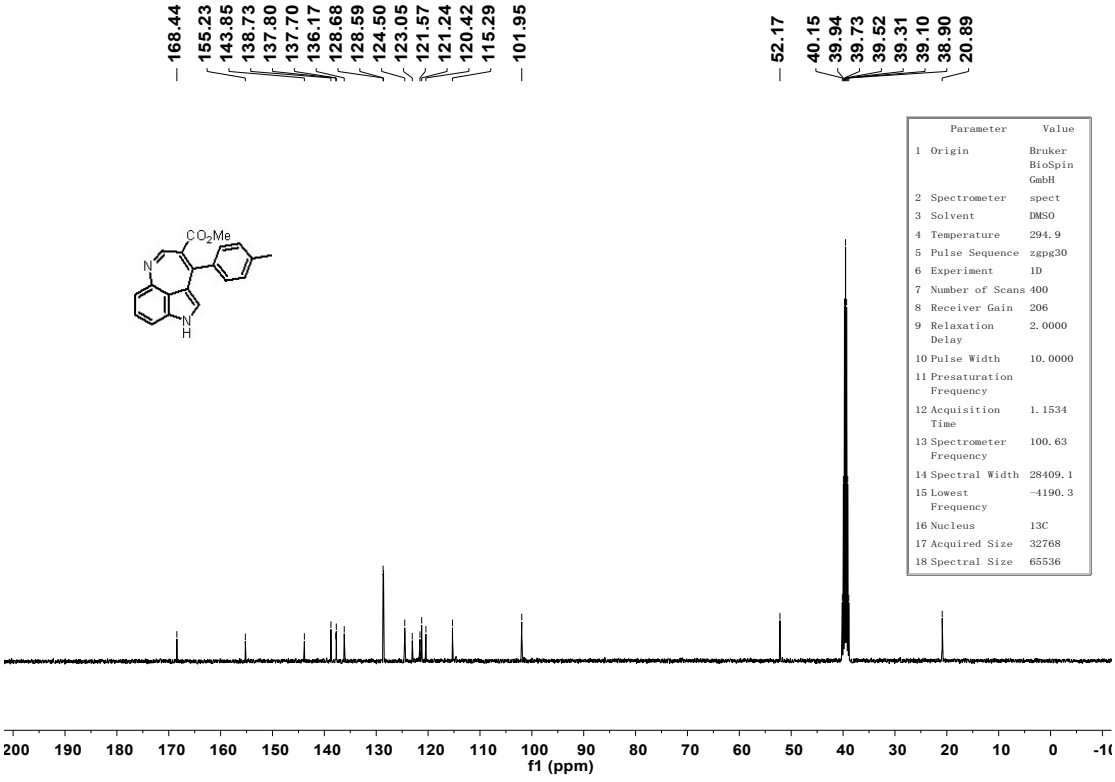
4v


11.97
7.87
7.85
7.63
7.60
7.59
7.57
7.35
7.33
7.20
4.00
3.70
2.50
2.39
MeO2C
CO2Me
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.8
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.05
4.04
2.01
1.01
3.05
3.05
3.05
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

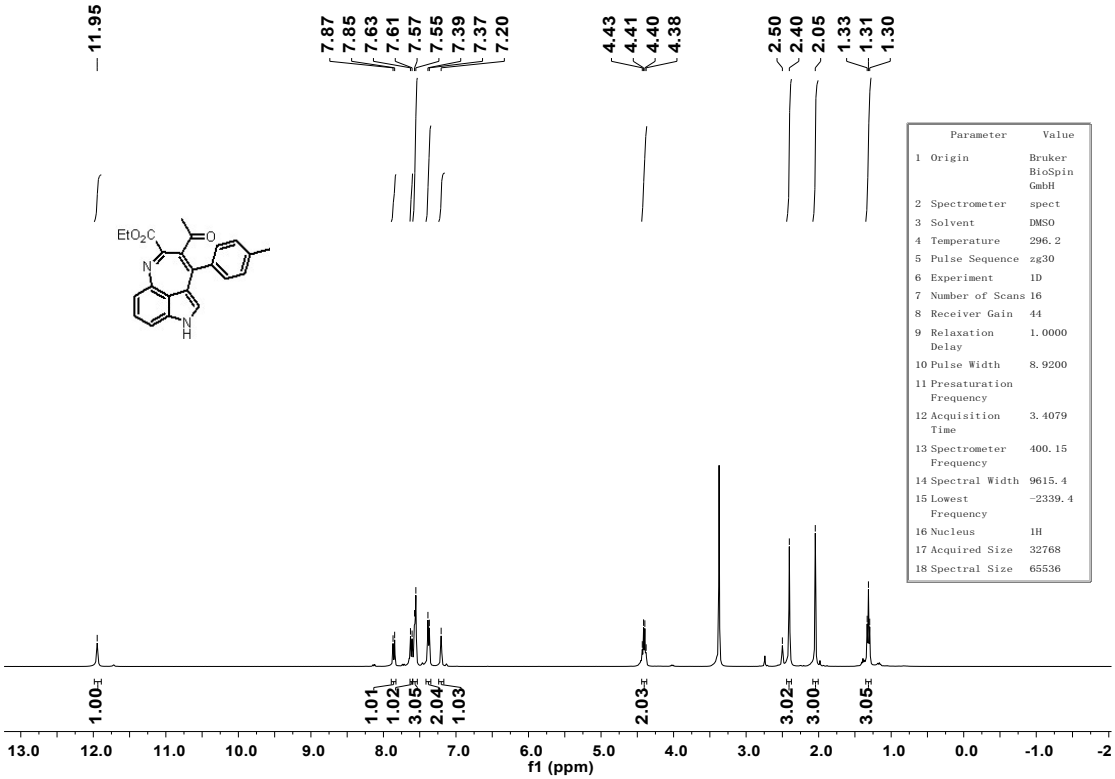

167.95
166.90
153.97
143.80
139.21
138.40
136.90
135.75
128.97
128.39
125.14
123.29
120.08
117.41
116.70
116.00
102.24
53.26
52.71
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.86
MeO2C
CO2Me
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.1
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.1
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4w

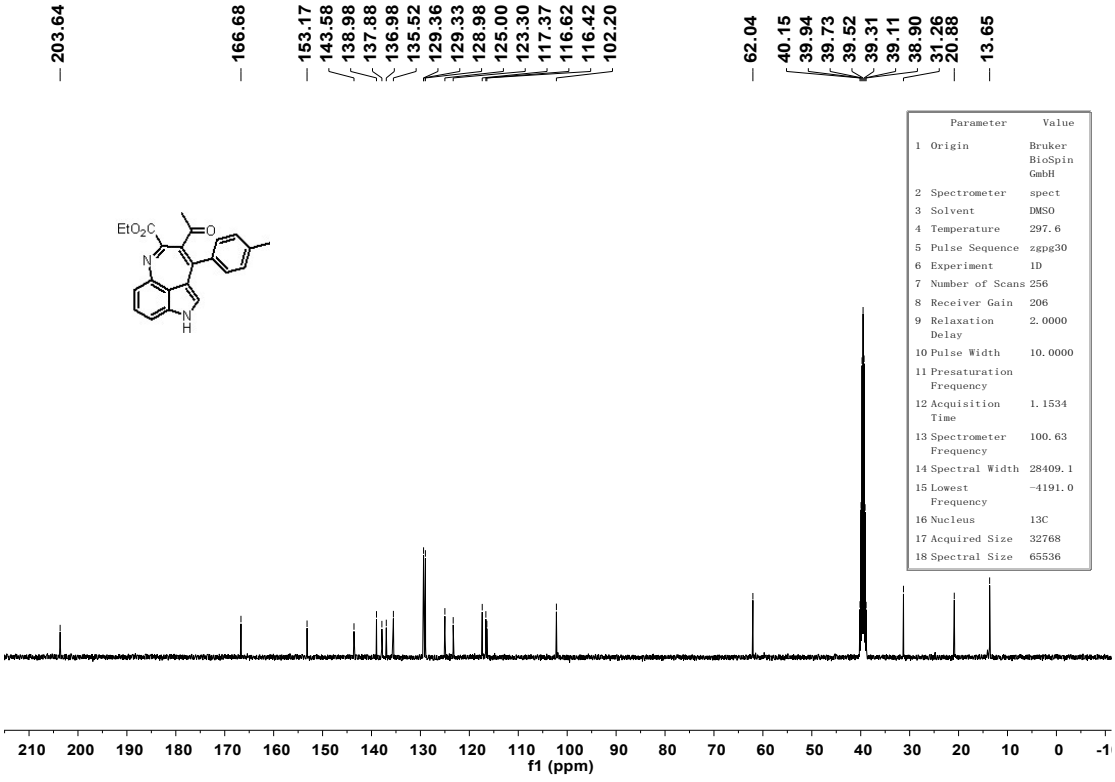

11.85
8.77
7.78
7.75
7.73
7.71
7.56
7.54
7.52
7.51
7.50
7.31
7.29
7.15
3.72
2.50
2.39
CO2Me
N
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.4
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.05
2.06
2.01
1.07
2.04
1.01
3.03
3.00
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


168.44
155.23
143.85
138.73
137.80
137.70
136.17
128.68
128.59
124.50
123.05
121.57
121.24
120.42
115.29
101.95
52.17
40.15
39.94
39.73
39.52
39.31
39.10
38.90
20.89
CO2Me
N
N
H
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.9
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.3
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4x

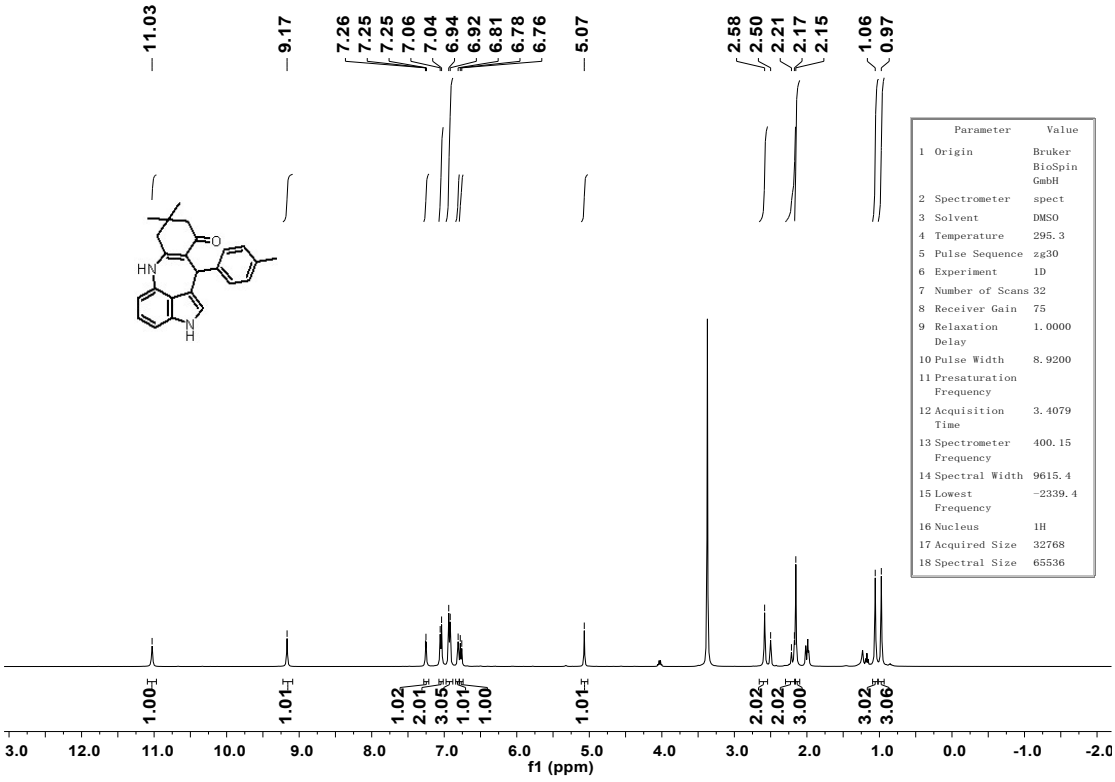


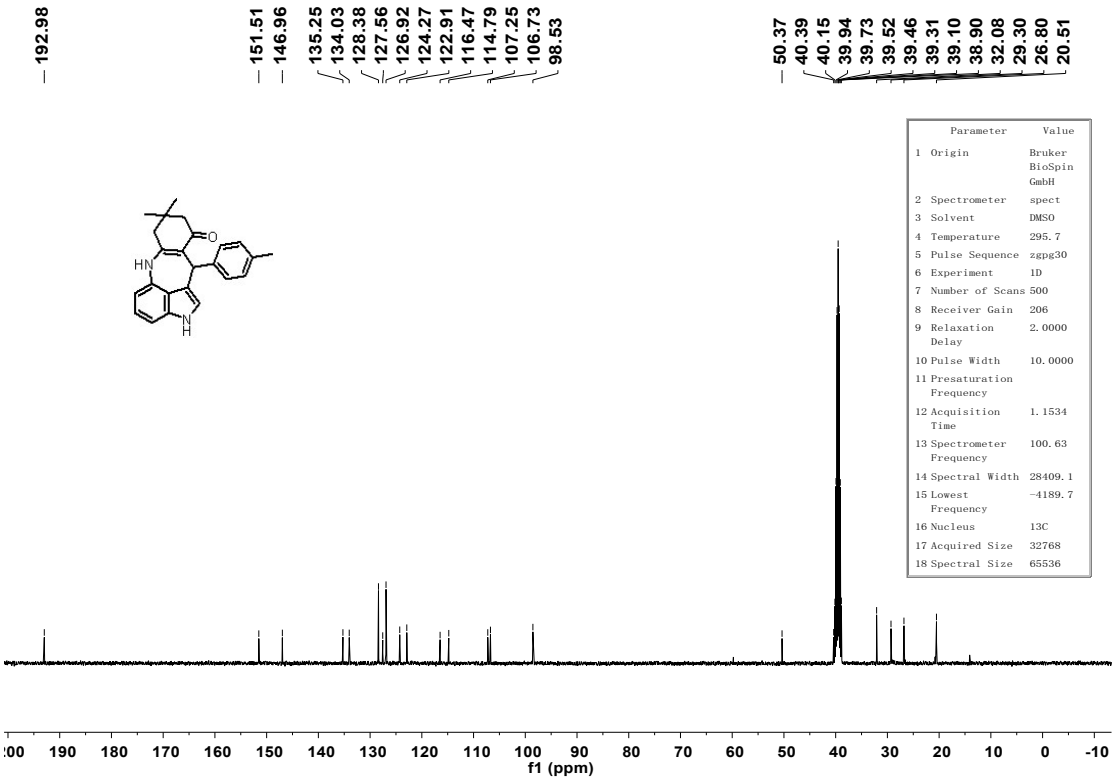
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	296.2
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	44
9	Relaxation Delay	1.0000
10	Pulse Width	8.9200
11	Presaturation Frequency	
12	Acquisition Time	3.4079
13	Spectrometer Frequency	400.15
14	Spectral Width	9615.4
15	Lowest Frequency	-2339.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



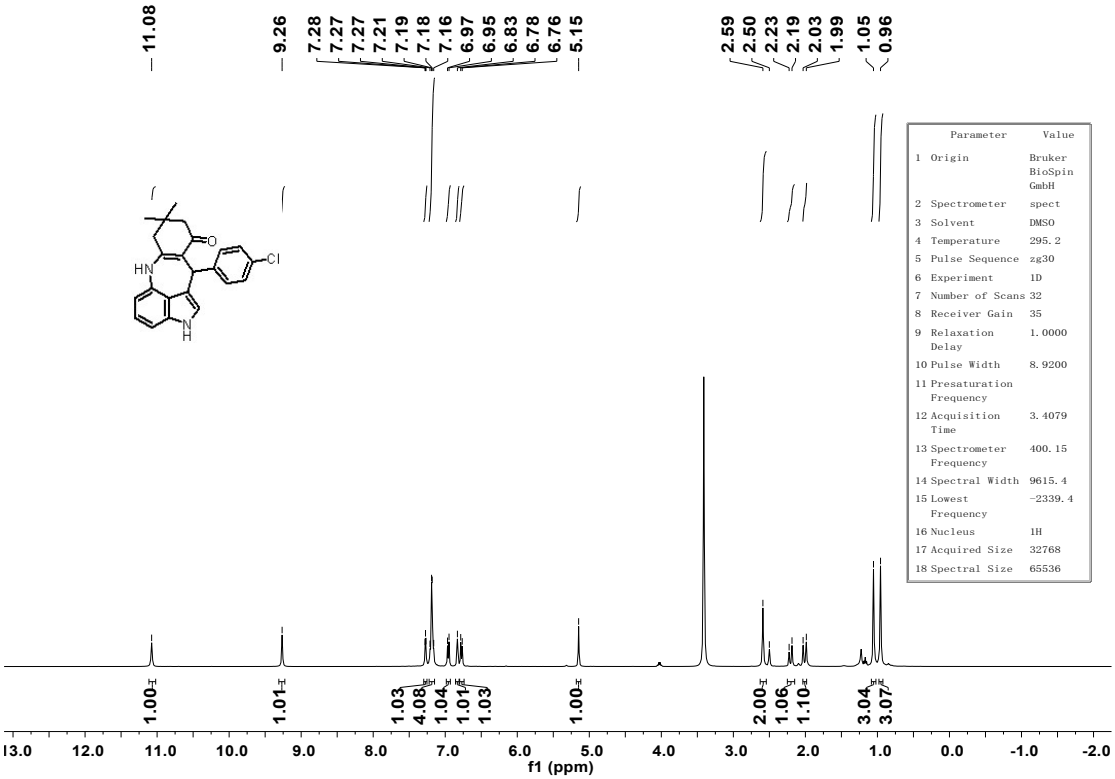
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	297.6
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	256
8	Receiver Gain	206
9	Relaxation Delay	2.0000
10	Pulse Width	10.0000
11	Presaturation Frequency	
12	Acquisition Time	1.1534
13	Spectrometer Frequency	100.63
14	Spectral Width	28409.1
15	Lowest Frequency	-4191.0
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

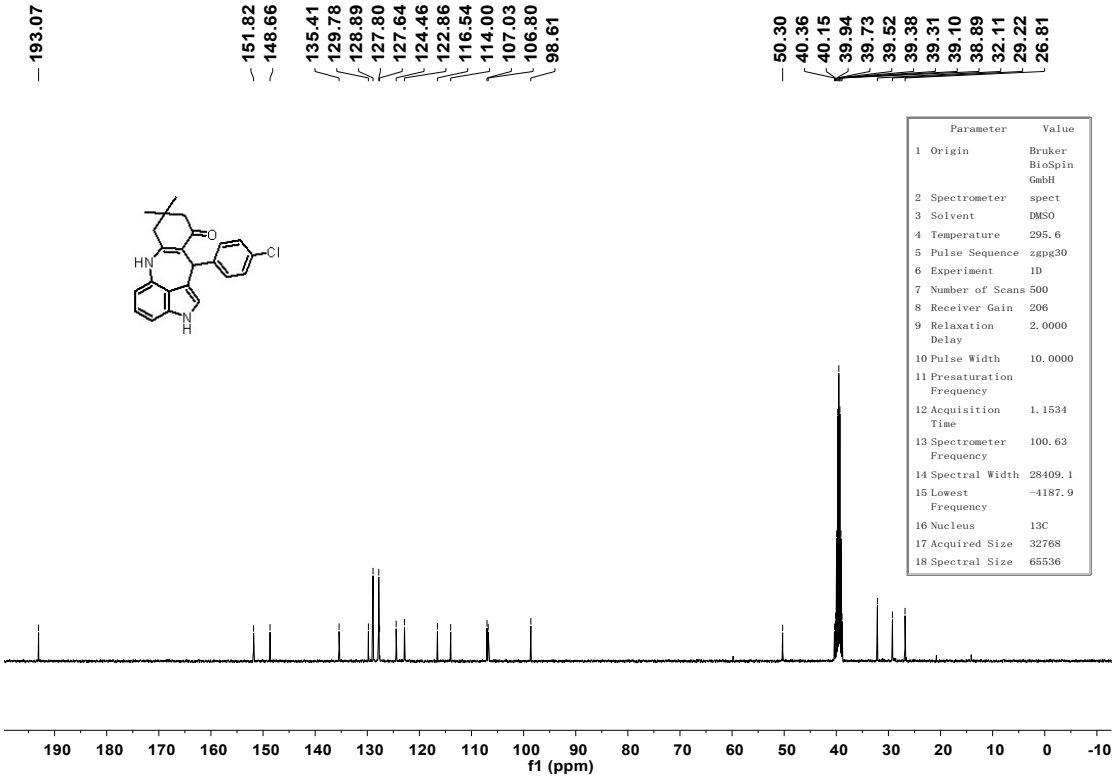
7a


11.03
9.17
7.26
7.25
7.25
7.06
7.04
6.94
6.92
6.81
6.78
6.76
5.07
2.58
2.50
2.21
2.17
2.15
1.06
0.97
1.00
1.01
1.02
2.01
3.05
1.01
1.00
1.01
2.02
2.02
3.00
3.02
3.06
f1 (ppm)
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.3
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536

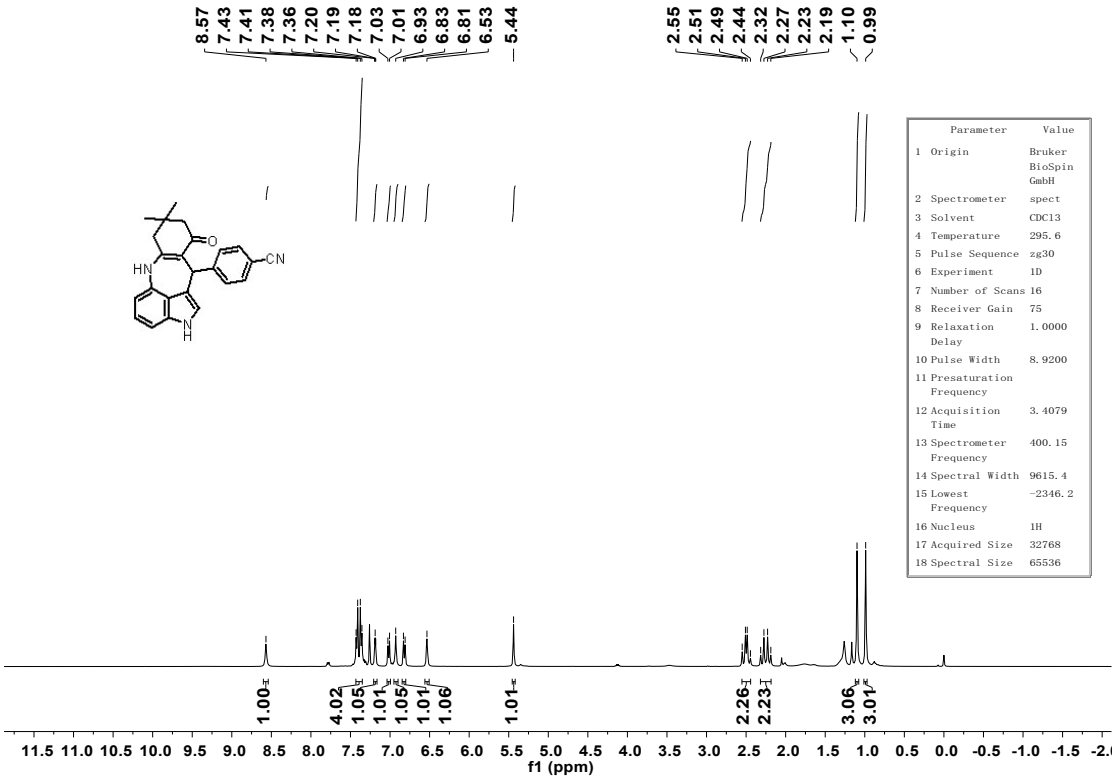

192.98
151.51
146.96
135.25
134.03
128.38
127.56
126.92
124.27
122.91
116.47
114.79
107.25
106.73
98.53
50.37
40.39
40.15
39.94
39.73
39.52
39.46
39.31
39.10
38.90
32.08
29.30
26.80
20.51
f1 (ppm)
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4189.7
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536

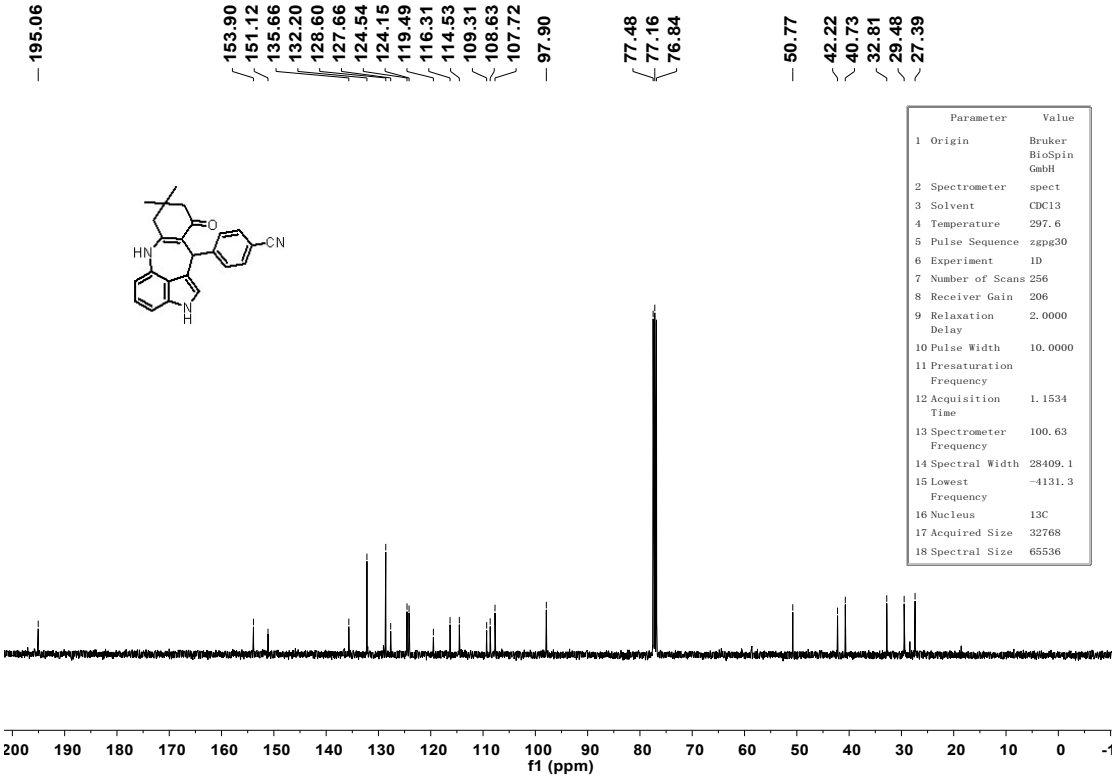
7b


11.08
9.26
7.28
7.27
7.27
7.21
7.19
7.18
7.16
6.97
6.95
6.83
6.78
6.76
5.15
2.59
2.50
2.23
2.19
2.03
1.99
1.05
0.96
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 35
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.01
1.03
4.08
1.04
1.01
1.03
1.00
2.00
1.06
1.10
3.04
3.07
f1 (ppm)

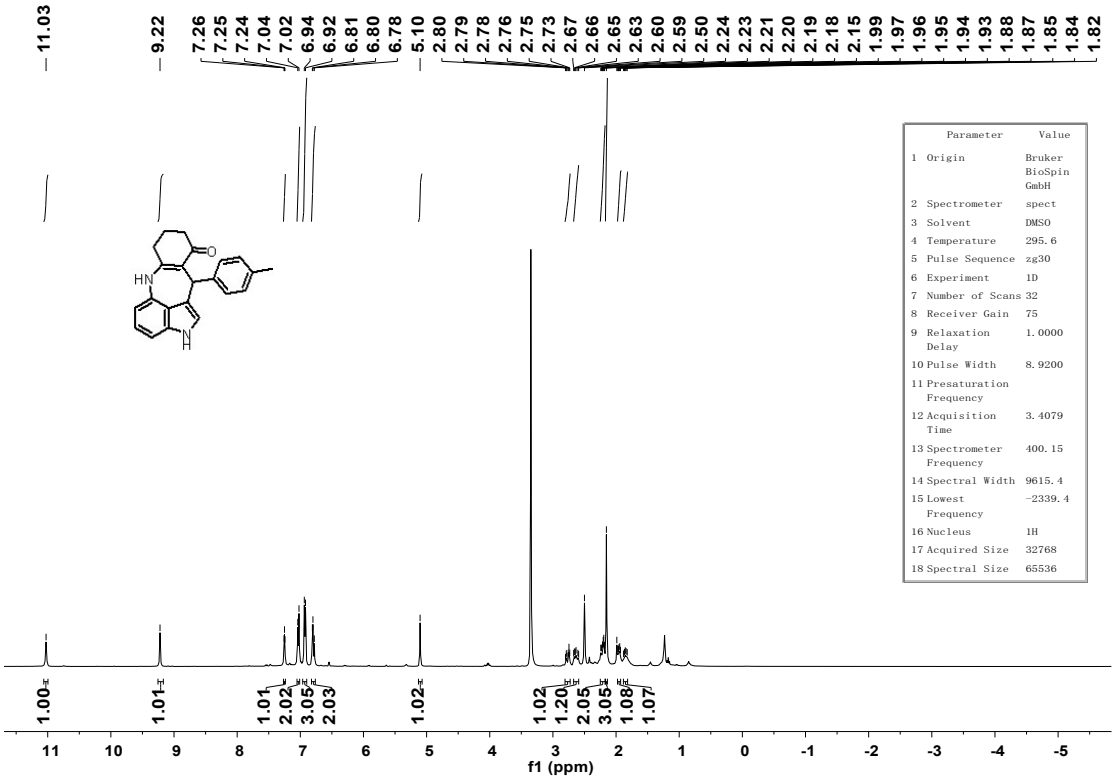

193.07
151.82
148.66
135.41
129.78
128.89
127.80
127.64
124.46
122.86
116.54
114.00
107.03
106.80
98.61
50.30
40.36
40.15
39.94
39.73
39.52
39.38
39.31
39.10
38.89
32.11
29.22
26.81
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.6
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4187.9
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

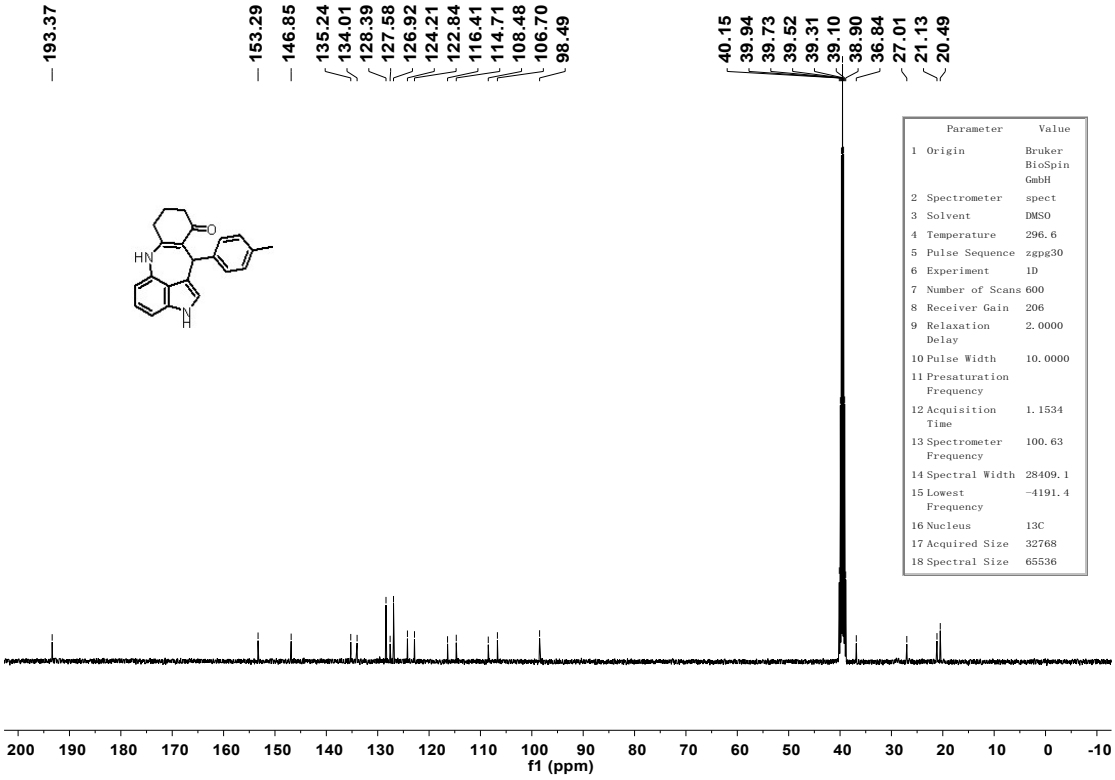
7c


8.57
7.43
7.41
7.38
7.36
7.20
7.19
7.18
7.03
7.01
6.93
6.83
6.81
6.53
5.44
2.55
2.51
2.49
2.44
2.32
2.27
2.23
2.19
1.10
0.99
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 295.6
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2346.2
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
4.02
1.05
1.01
1.05
1.01
1.06
1.01
2.26
2.23
3.06
3.01
f1 (ppm)

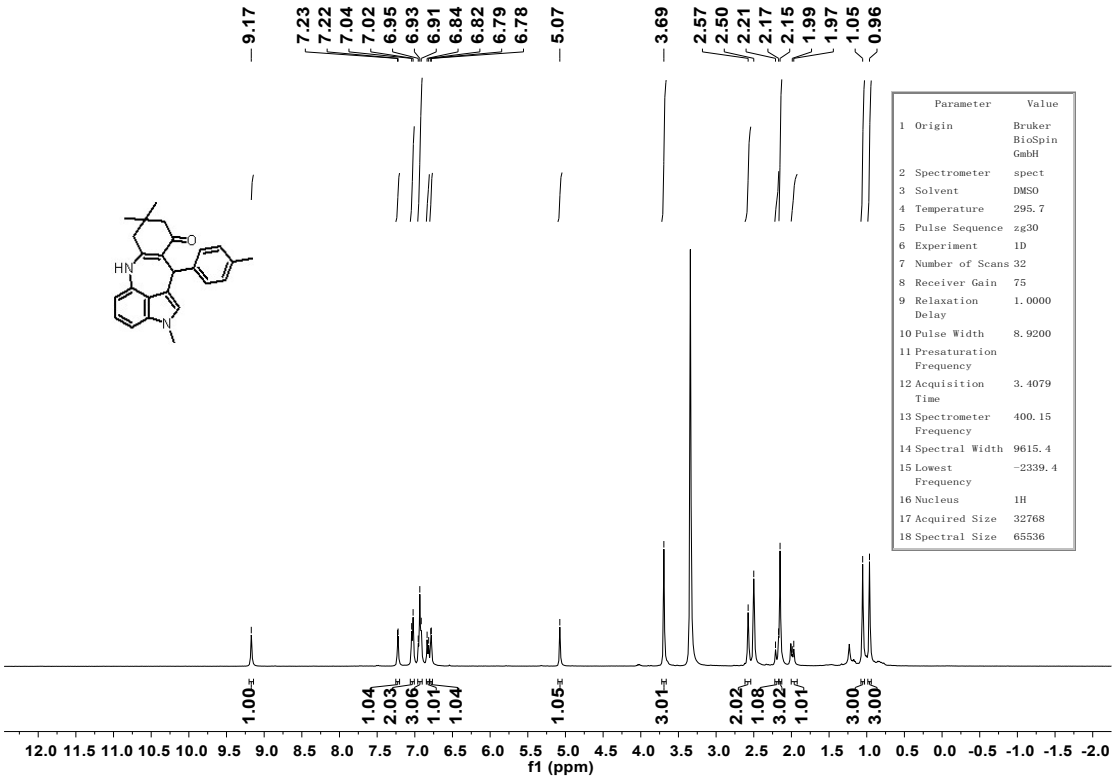

195.06
153.90
151.12
135.66
132.20
128.60
127.66
124.54
124.15
119.49
116.31
114.53
109.31
108.63
107.72
97.90
77.48
77.16
76.84
50.77
42.22
40.73
32.81
29.48
27.39
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent CDCl3
4 Temperature 297.6
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 256
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4131.3
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

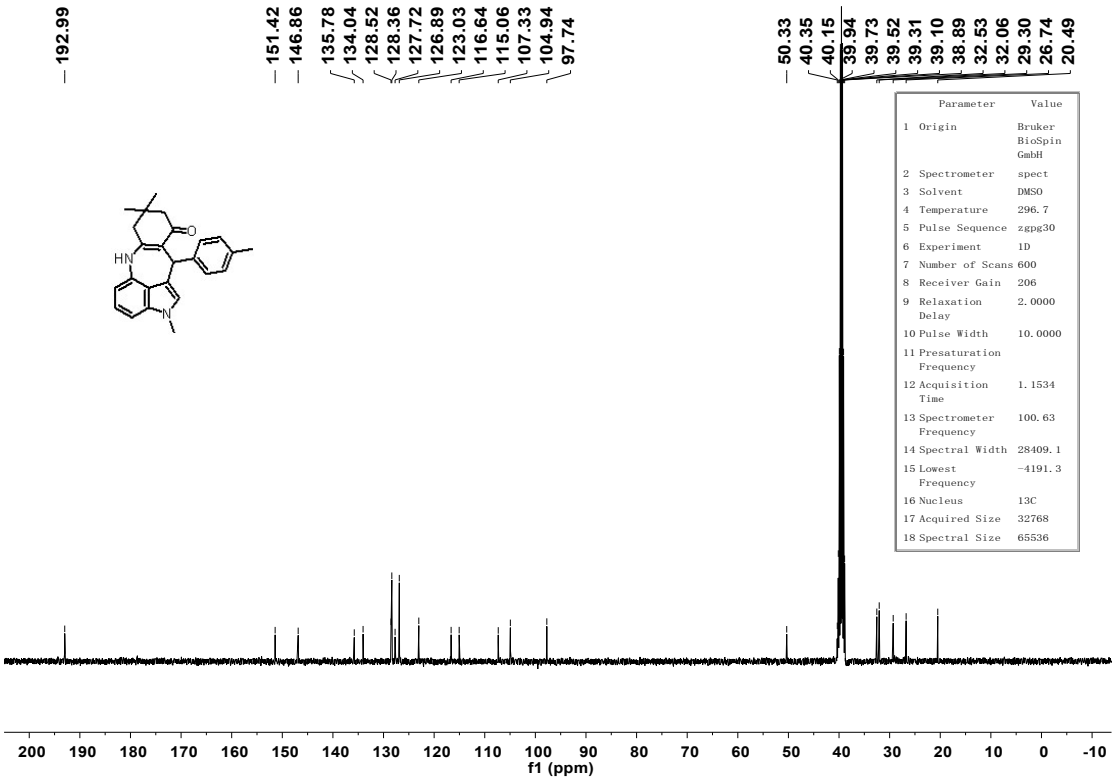
7d


11.03
9.22
7.26 7.25 7.24 7.04 7.02 6.94 6.92 6.81 6.80 6.78
5.10
2.80 2.79 2.78 2.76 2.75 2.73 2.67 2.66 2.65 2.63 2.60 2.59 2.50 2.24 2.23 2.21 2.20 2.19 2.18 2.15 1.99 1.97 1.96 1.95 1.94 1.93 1.88 1.87 1.85 1.84 1.82
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.6
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00 1.01 1.01 2.02 3.05 2.03 1.02 1.02 1.20 2.05 3.05 1.08 1.07
f1 (ppm)

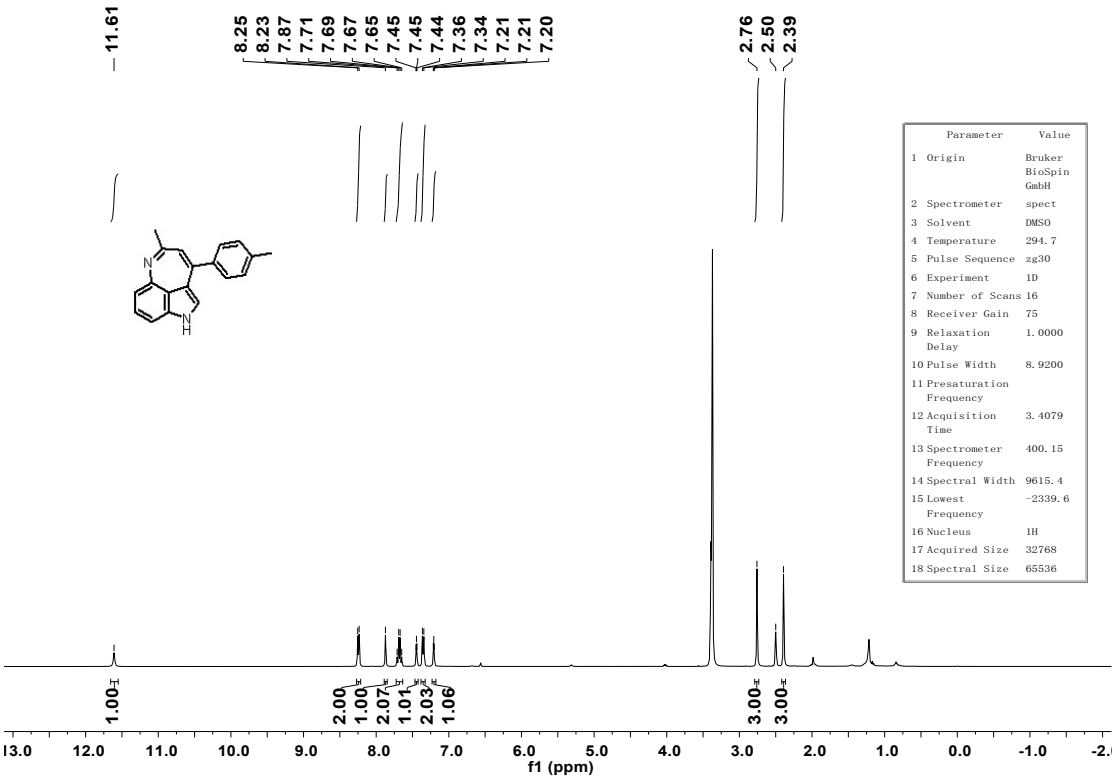

193.37
153.29 146.85 135.24 134.01 128.39 127.58 126.92 124.21 122.84 116.41 114.71 108.48 106.70 98.49
40.15 39.94 39.73 39.52 39.31 39.10 38.90 36.84 27.01 21.13 20.49
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.6
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 600
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.4
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

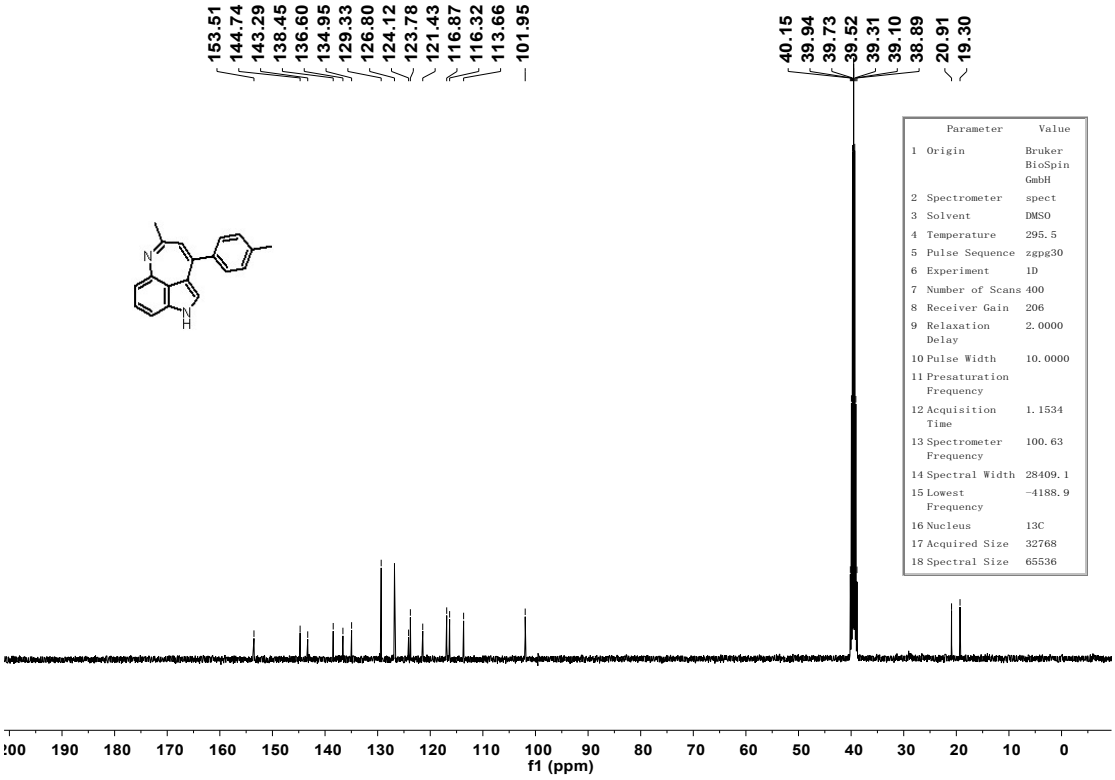
7e


9.17
7.23
7.22
7.04
7.02
6.95
6.93
6.91
6.84
6.82
6.79
6.78
5.07
3.69
2.57
2.50
2.21
2.17
2.15
1.99
1.97
1.05
0.96
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.04
2.03
3.06
1.01
1.04
1.05
3.01
2.02
1.08
3.02
1.01
3.00
3.00
f1 (ppm)

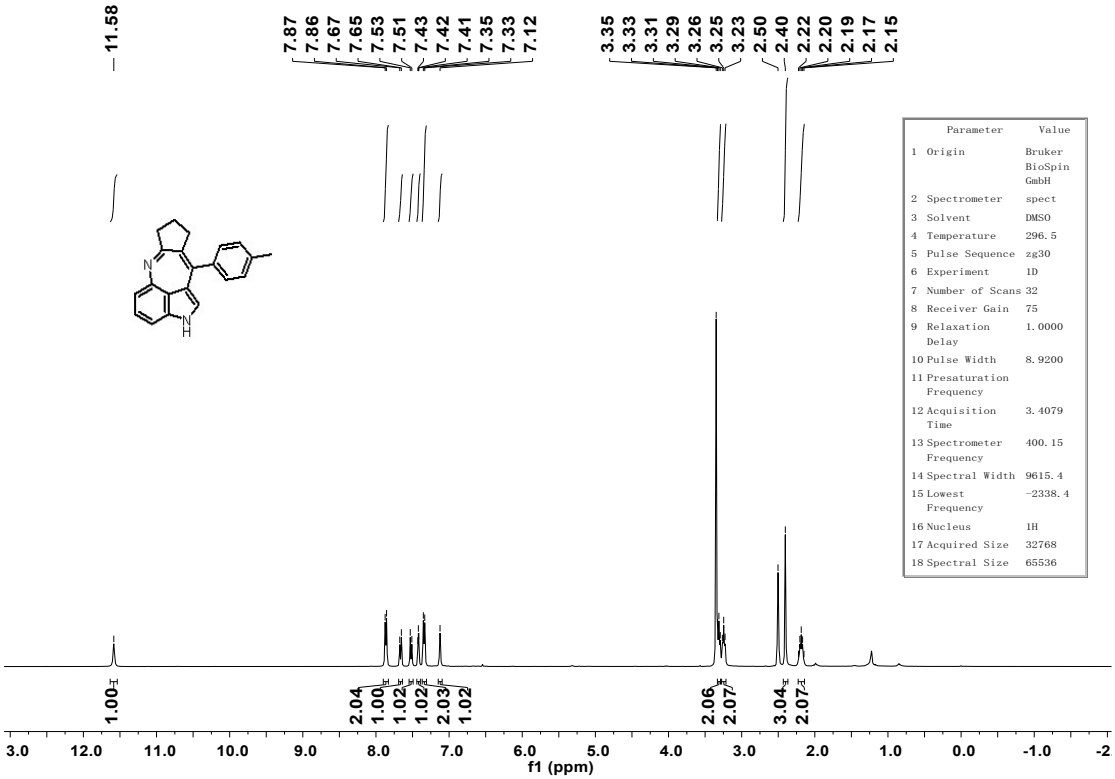

192.99
151.42
146.86
135.78
134.04
128.52
128.36
127.72
126.89
123.03
116.64
115.06
107.33
104.94
97.74
50.33
40.35
40.15
39.94
39.73
39.52
39.31
39.10
38.89
32.53
32.06
29.30
26.74
20.49
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.7
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 600
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.3
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

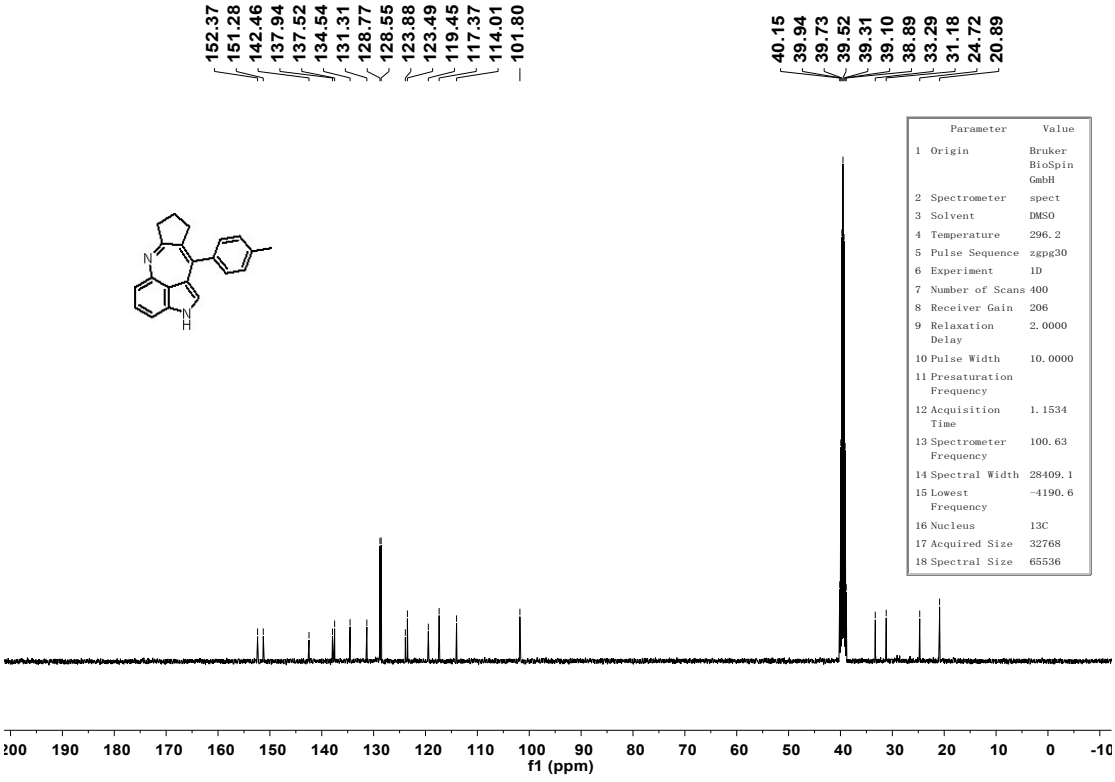
4y


11.61
8.25
8.23
7.87
7.71
7.69
7.67
7.65
7.45
7.45
7.44
7.36
7.34
7.21
7.21
7.20
2.76
2.50
2.39
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.6
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
2.00
1.00
2.07
1.01
2.03
1.06
3.00
3.00
f1 (ppm)

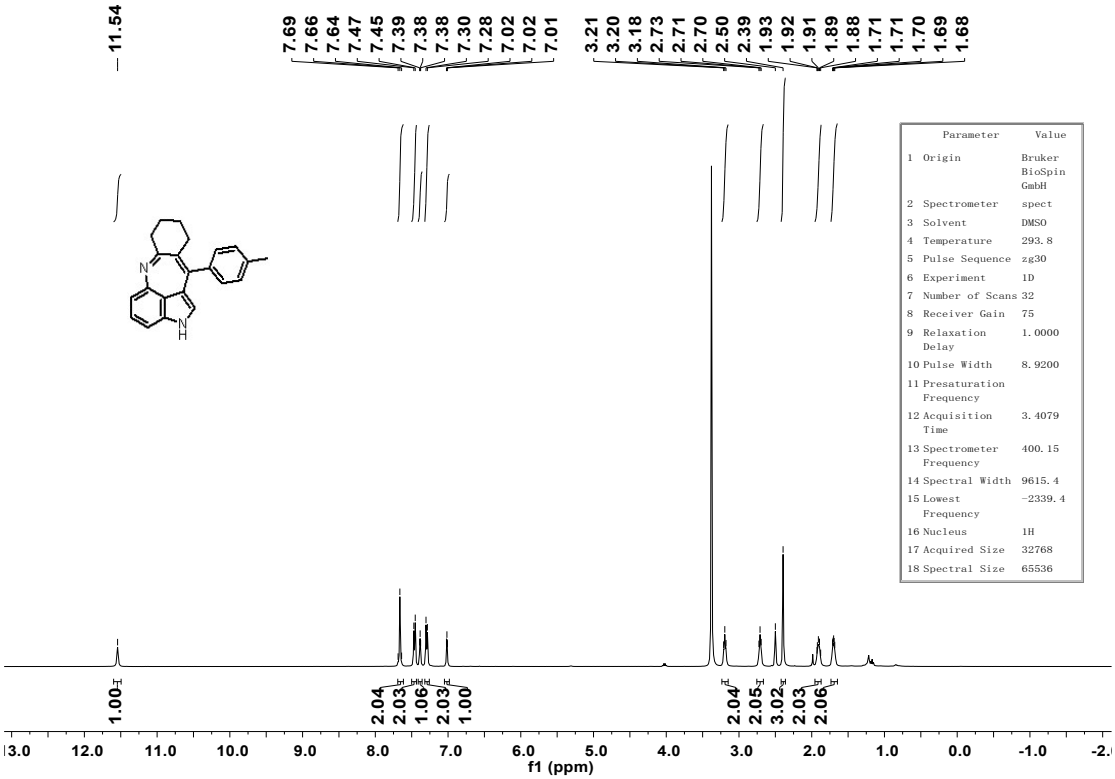

153.51
144.74
143.29
138.45
136.60
134.95
129.33
126.80
124.12
123.78
121.43
116.87
116.32
113.66
101.95
40.15
39.94
39.73
39.52
39.31
39.10
38.89
20.91
19.30
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.5
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4188.9
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

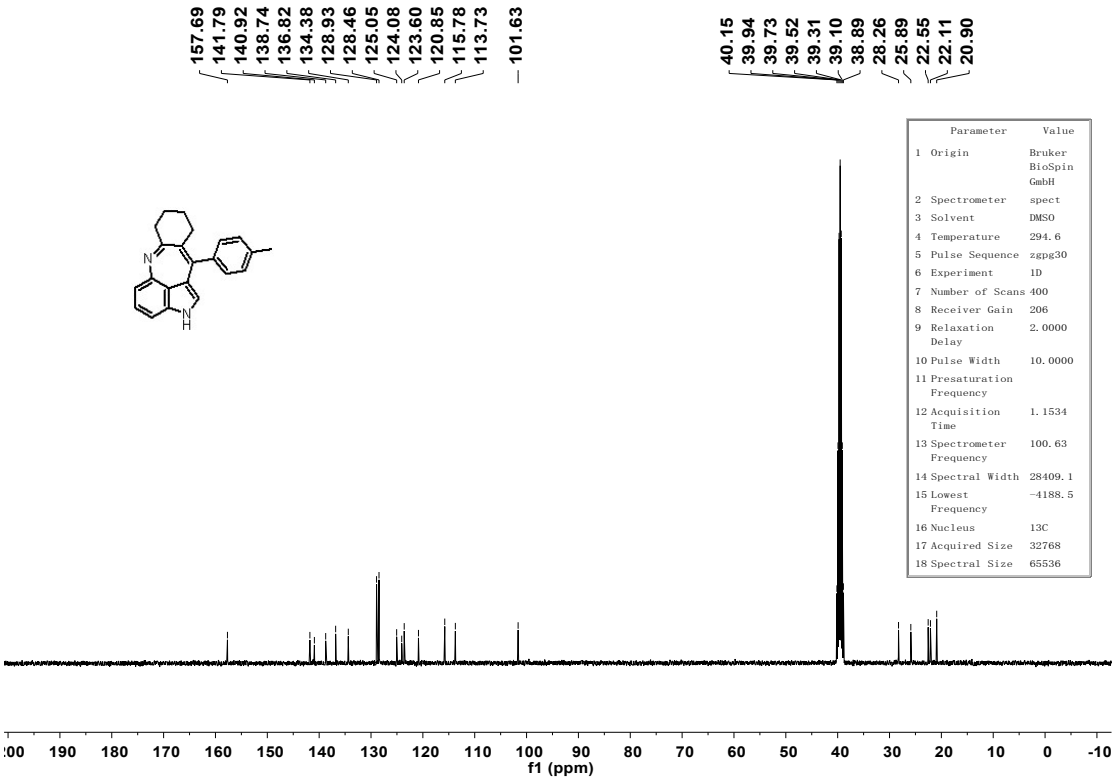
4z


11.58
7.87
7.86
7.67
7.65
7.53
7.51
7.43
7.42
7.41
7.35
7.33
7.12
3.35
3.33
3.31
3.29
3.26
3.25
3.23
2.50
2.40
2.22
2.20
2.19
2.17
2.15
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.5
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2338.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
2.04
1.00
1.02
1.02
2.03
1.02
2.06
2.07
3.04
2.07
f1 (ppm)

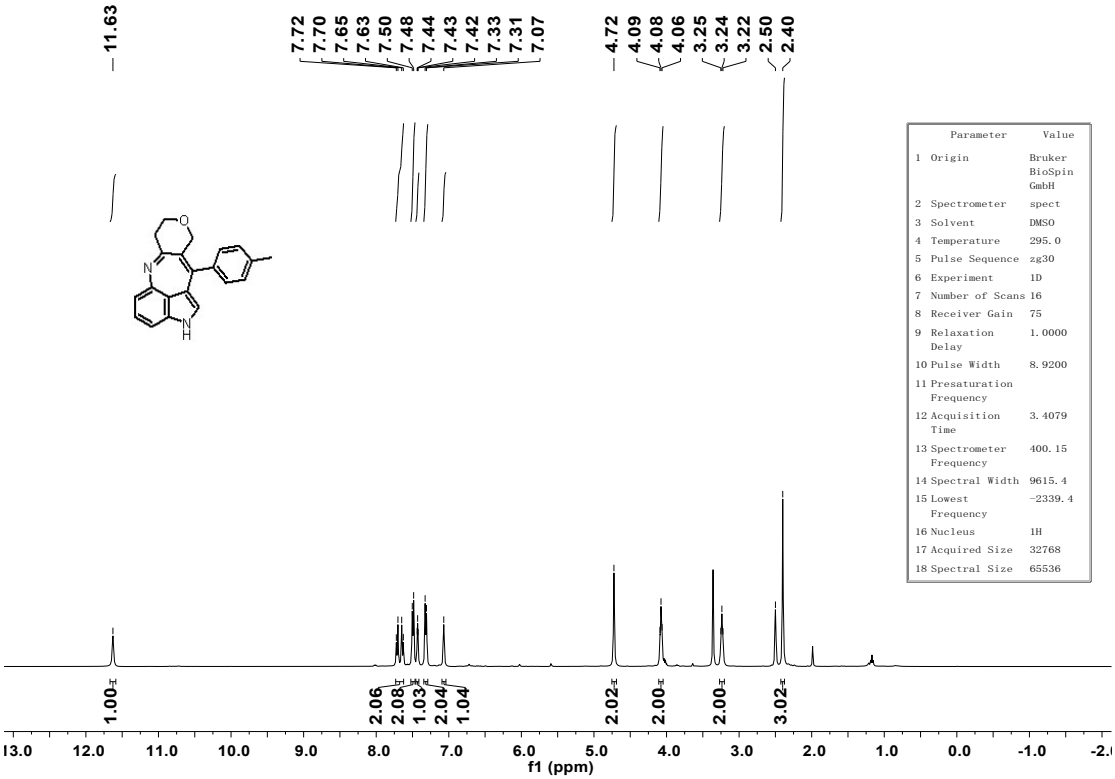

152.37
151.28
142.46
137.94
137.52
134.54
131.31
128.77
128.55
123.88
123.49
119.45
117.37
114.01
101.80
40.15
39.94
39.73
39.52
39.31
39.10
38.89
33.29
31.18
24.72
20.89
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.2
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4190.6
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

4aa

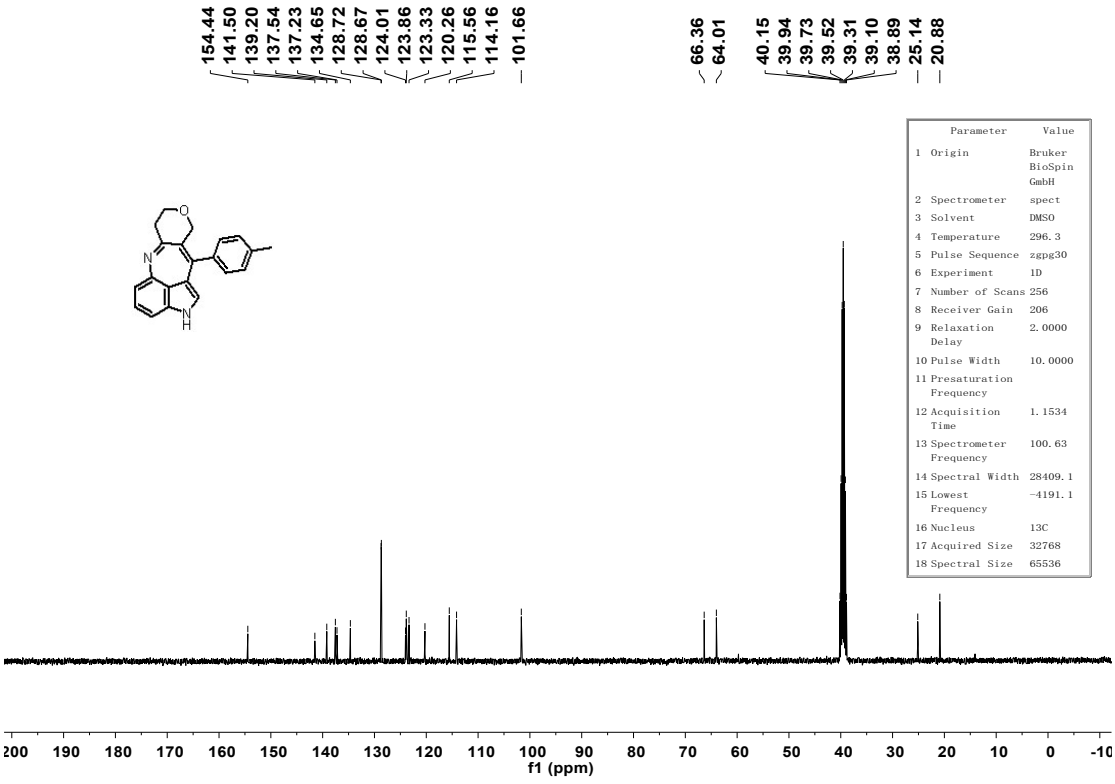

11.54
7.69
7.66
7.64
7.47
7.45
7.39
7.38
7.38
7.30
7.28
7.02
7.02
7.01
3.21
3.20
3.18
2.73
2.71
2.70
2.50
2.39
1.93
1.92
1.91
1.89
1.88
1.71
1.71
1.70
1.69
1.68
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 293.8
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
2.04
2.03
1.06
2.03
1.00
2.04
2.05
3.02
2.03
2.06
f1 (ppm)


157.69
141.79
140.92
138.74
136.82
134.38
128.93
128.46
125.05
124.08
123.60
120.85
115.78
113.73
101.63
40.15
39.94
39.73
39.52
39.31
39.10
38.89
28.26
25.89
22.55
22.11
20.90
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 294.6
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4188.5
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

4ab

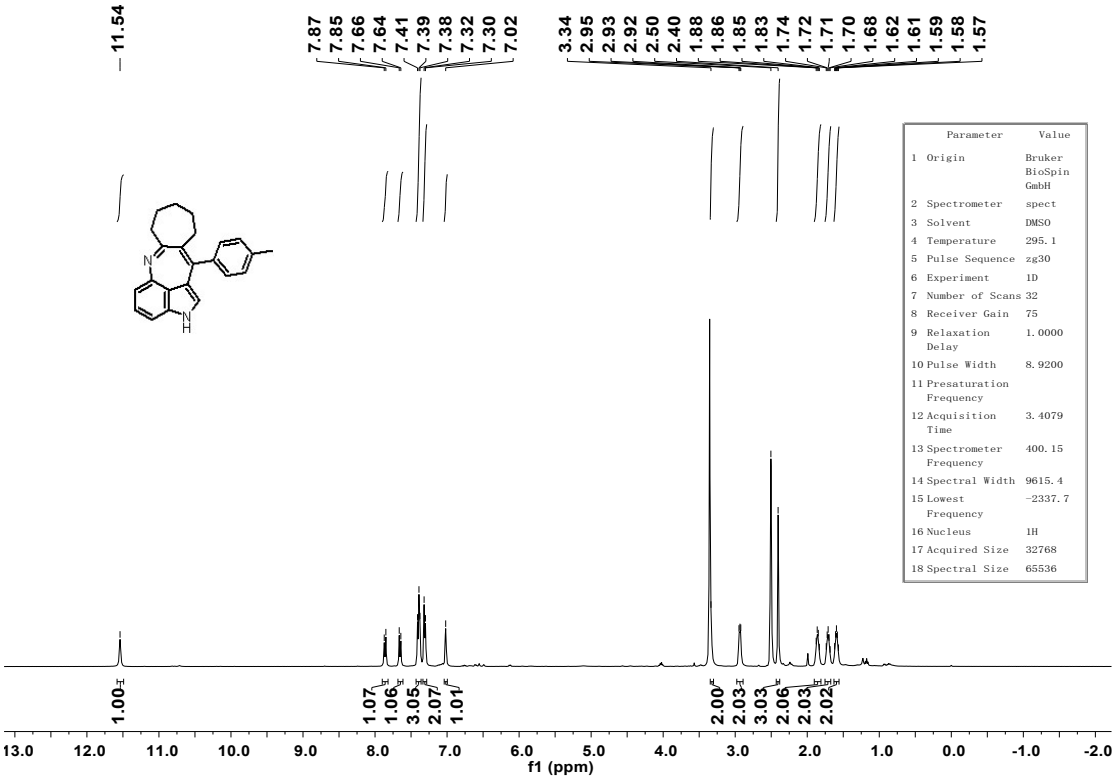


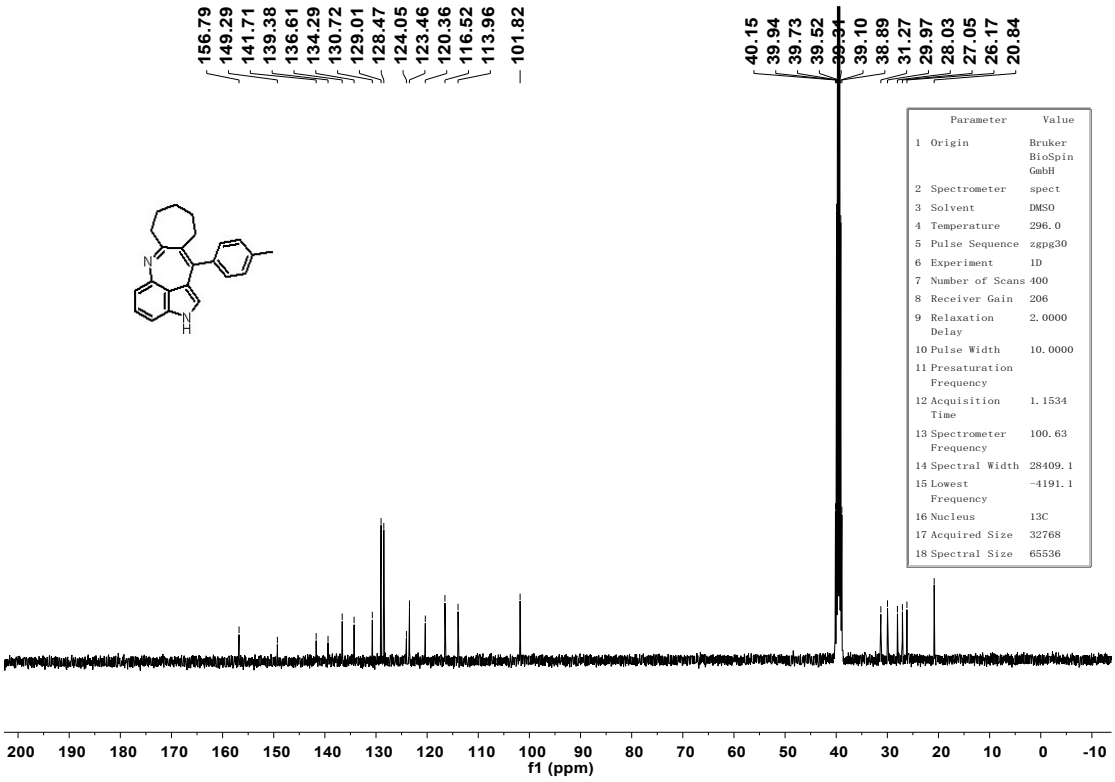
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	295.0
5	Pulse Sequence	zg30
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	75
9	Relaxation Delay	1.0000
10	Pulse Width	8.9200
11	Presaturation Frequency	
12	Acquisition Time	3.4079
13	Spectrometer Frequency	400.15
14	Spectral Width	9615.4
15	Lowest Frequency	-2339.4
16	Nucleus	1H
17	Acquired Size	32768
18	Spectral Size	65536



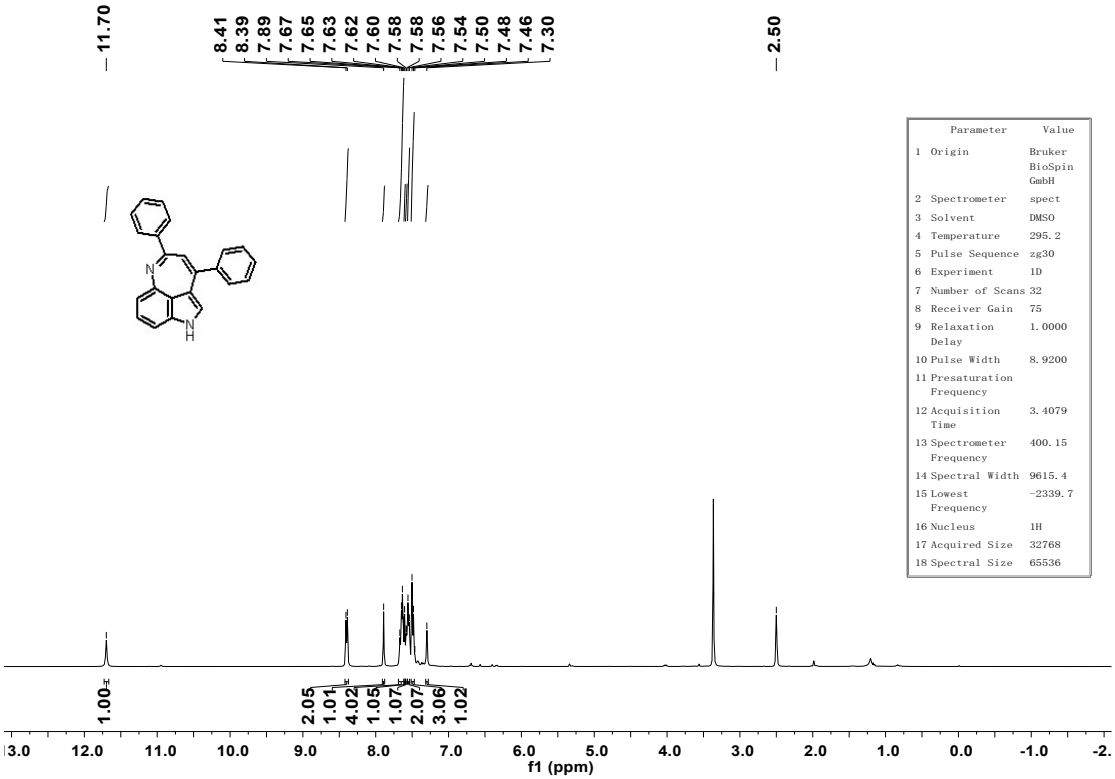
	Parameter	Value
1	Origin	Bruker BioSpin GmbH
2	Spectrometer	spect
3	Solvent	DMSO
4	Temperature	296.3
5	Pulse Sequence	zgpg30
6	Experiment	1D
7	Number of Scans	256
8	Receiver Gain	206
9	Relaxation Delay	2.0000
10	Pulse Width	10.0000
11	Presaturation Frequency	
12	Acquisition Time	1.1534
13	Spectrometer Frequency	100.63
14	Spectral Width	28409.1
15	Lowest Frequency	-4191.1
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

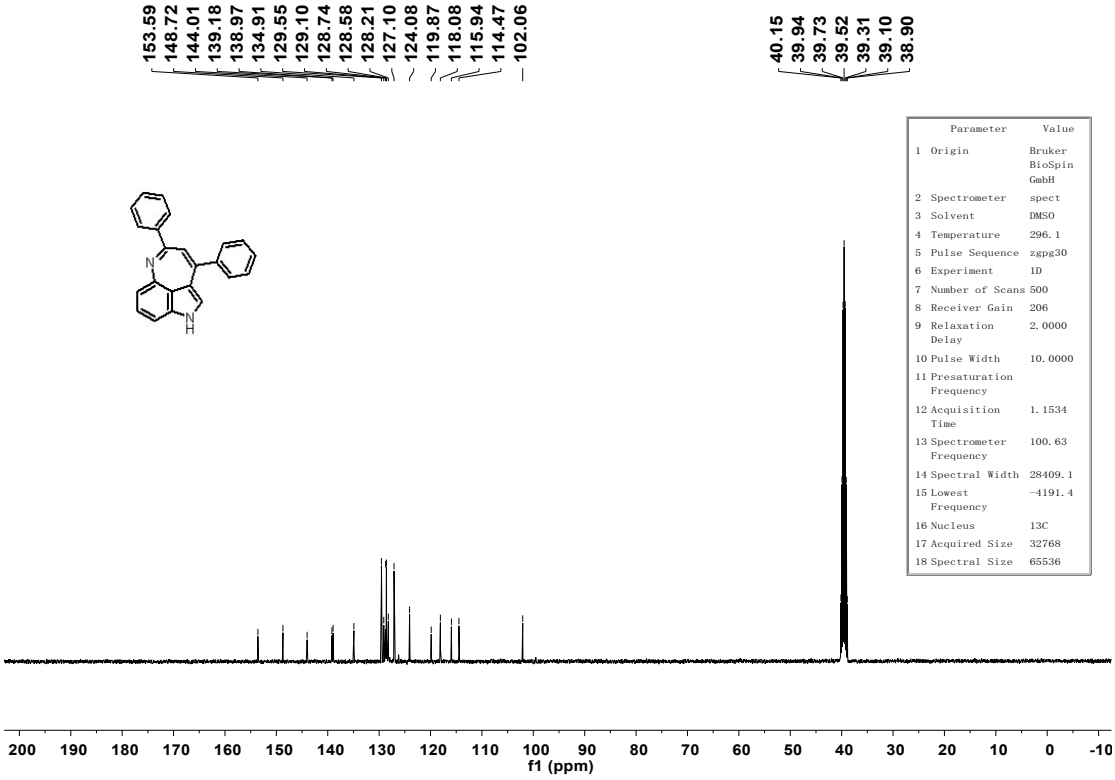
4ac


11.54
7.87
7.85
7.66
7.64
7.41
7.39
7.38
7.32
7.30
7.02
3.34
2.95
2.93
2.92
2.50
2.40
1.88
1.86
1.85
1.83
1.74
1.72
1.71
1.70
1.68
1.62
1.61
1.59
1.58
1.57
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.1
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2337.7
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.07
1.06
3.05
2.07
1.01
2.00
2.03
3.03
2.06
2.03
2.02
13.0 12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0 -2.0
f1 (ppm)

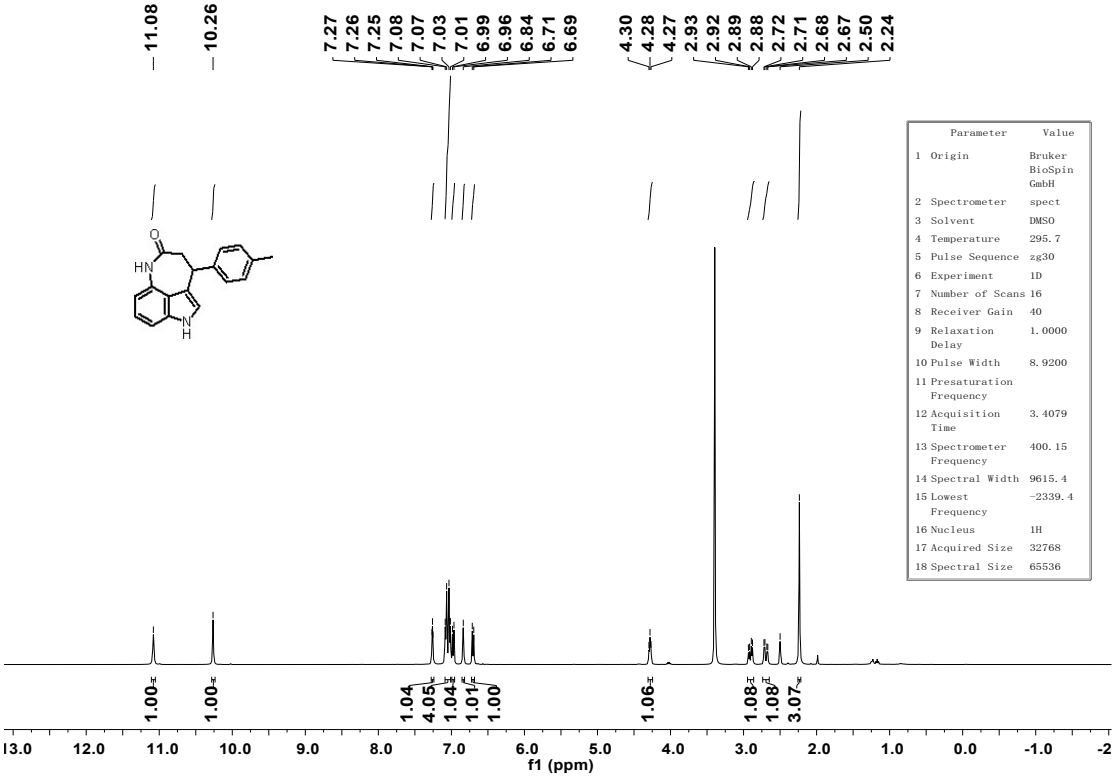

156.79
149.29
141.71
139.38
136.61
134.29
130.72
129.01
128.47
124.05
123.46
120.36
116.52
113.96
101.82
40.15
39.94
39.73
39.52
39.31
39.10
38.89
31.27
29.97
28.03
27.05
26.17
20.84
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.0
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.1
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

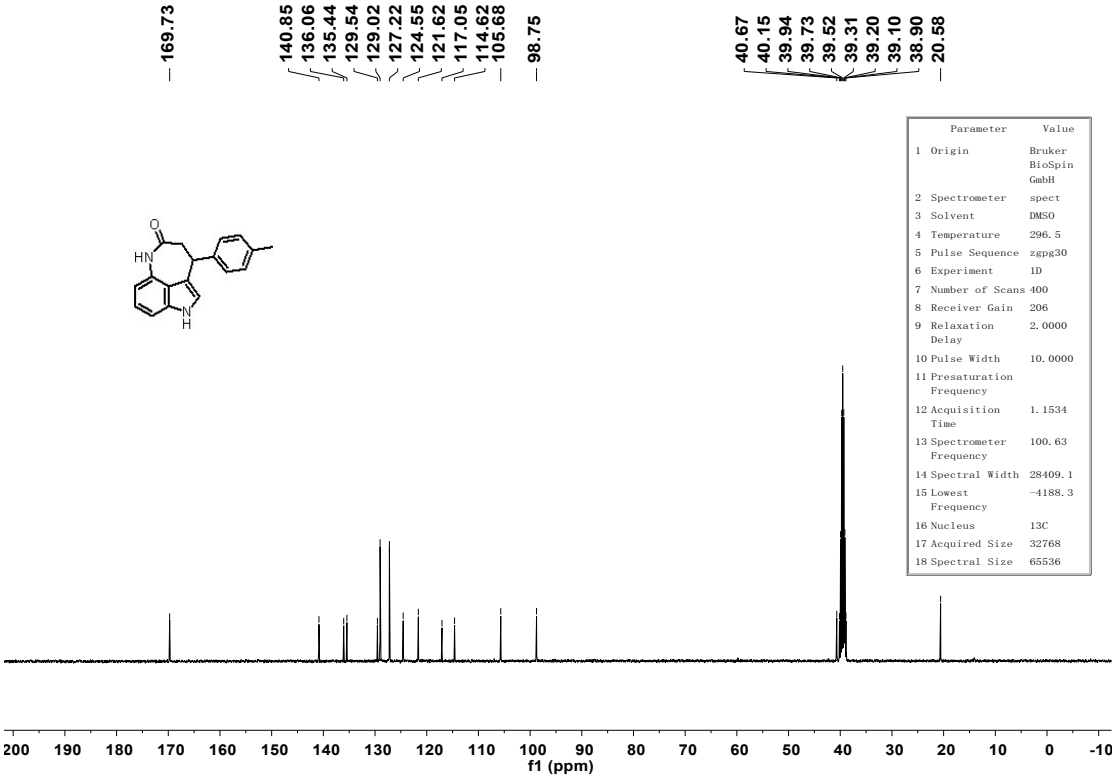
4ad


11.70
8.41
8.39
7.89
7.67
7.65
7.63
7.62
7.60
7.58
7.58
7.56
7.54
7.50
7.48
7.46
7.30
2.50
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.2
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 32
8 Receiver Gain 75
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.7
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
2.05
1.01
4.02
1.05
1.07
2.07
3.06
1.02
f1 (ppm)


153.59
148.72
144.01
139.18
138.97
134.91
129.55
129.10
128.74
128.58
128.21
127.10
124.08
119.87
118.08
115.94
114.47
102.06
40.15
39.94
39.73
39.52
39.31
39.10
38.90
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.1
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 500
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4191.4
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

8a


11.08
10.26
7.27
7.26
7.25
7.08
7.07
7.03
7.01
6.99
6.96
6.84
6.71
6.69
4.30
4.28
4.27
2.93
2.92
2.89
2.88
2.72
2.71
2.68
2.67
2.50
2.24
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 295.7
5 Pulse Sequence zg30
6 Experiment 1D
7 Number of Scans 16
8 Receiver Gain 40
9 Relaxation Delay 1.0000
10 Pulse Width 8.9200
11 Presaturation Frequency
12 Acquisition Time 3.4079
13 Spectrometer Frequency 400.15
14 Spectral Width 9615.4
15 Lowest Frequency -2339.4
16 Nucleus 1H
17 Acquired Size 32768
18 Spectral Size 65536
1.00
1.00
1.04
4.05
1.04
1.01
1.00
1.06
1.08
1.08
3.07
f1 (ppm)


169.73
140.85
136.06
135.44
129.54
129.02
127.22
124.55
121.62
117.05
114.62
105.68
98.75
40.67
40.15
39.94
39.73
39.52
39.31
39.20
39.10
38.90
20.58
Parameter Value
1 Origin Bruker BioSpin GmbH
2 Spectrometer spect
3 Solvent DMSO
4 Temperature 296.5
5 Pulse Sequence zgpg30
6 Experiment 1D
7 Number of Scans 400
8 Receiver Gain 206
9 Relaxation Delay 2.0000
10 Pulse Width 10.0000
11 Presaturation Frequency
12 Acquisition Time 1.1534
13 Spectrometer Frequency 100.63
14 Spectral Width 28409.1
15 Lowest Frequency -4188.3
16 Nucleus 13C
17 Acquired Size 32768
18 Spectral Size 65536
f1 (ppm)

6. References

(1) (a) H. Imoto, K. Nohmi, K. Kizaki, S. Watase, K. Matsukawa, S. Yamamoto, M. Mitsuishi and K. Naka, *RSC Adv*., 2015, **5**, 94344; (b) D. Ramanathan and K. Pitchumani, *Eur. J. Org. Chem.*, 2015, **2015**, 463; (c) W. Wu, Y. Guo, X. Xu, Z. Zhou, X. Zhang, B. Wu and W. Yi, *Org. Chem. Front.*, 2018, **5**, 1713; (d) Q. Zhu, H. Jiang, J. Li, M, Zhang, X. Wang and C. Qi, *Tetrahedron*, 2009, **65**, 4604.