

# Development of Azo-Based Turn-On Chemical Array System for Hydrazine Detection with Fluorescence Pattern Analysis

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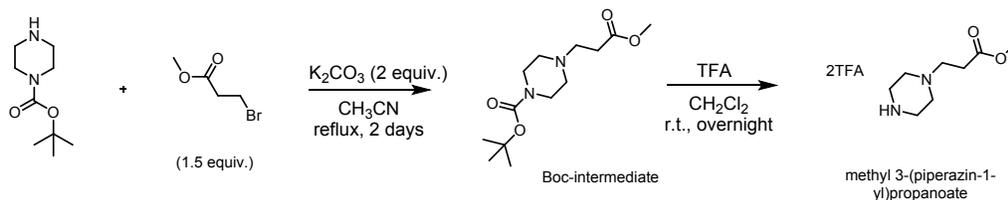
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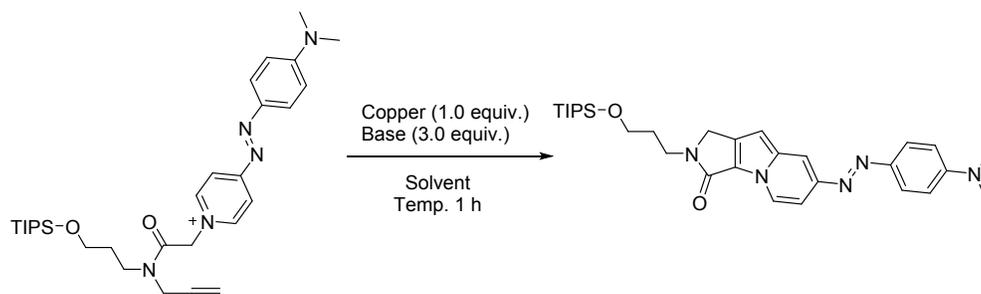
### Synthesis of methyl 3-(piperazin-1-yl)propanoate



**Boc-intermediate:** *tert*-Butyl piperazine-1-carboxylate (800 mg, 4.30 mmol), methyl 3-bromopropionate (1.08 g, 6.44 mmol), and potassium carbonate (1.19 g, 8.59 mmol) were dissolved in acetonitrile (6.5 mL). The mixture was stirred at reflux condition for 2 days. The resulting residue was washed with saturated NaHCO<sub>3</sub> aqueous solution, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude product was purified by flash column chromatography (silica gel, CH<sub>2</sub>Cl<sub>2</sub>:CH<sub>3</sub>OH=40:1) to afford **Boc-intermediate** (1.12 g, 4.11 mmol, 95.7% yield) as a transparent oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 3.69 (s, 3H), 3.41 (t, *J*=5.1 Hz, 4H), 2.70 (t, *J*=7.2 Hz, 2H), 2.51 (t, *J*=7.4 Hz, 2H), 2.40 (t, *J*=5.1 Hz, 4H), 1.46 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.8, 154.7, 79.6, 53.6, 52.7, 51.7, 51.7, 32.1, 28.4; LRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> [M+H]<sup>+</sup>: 273.18, found: 273.15.

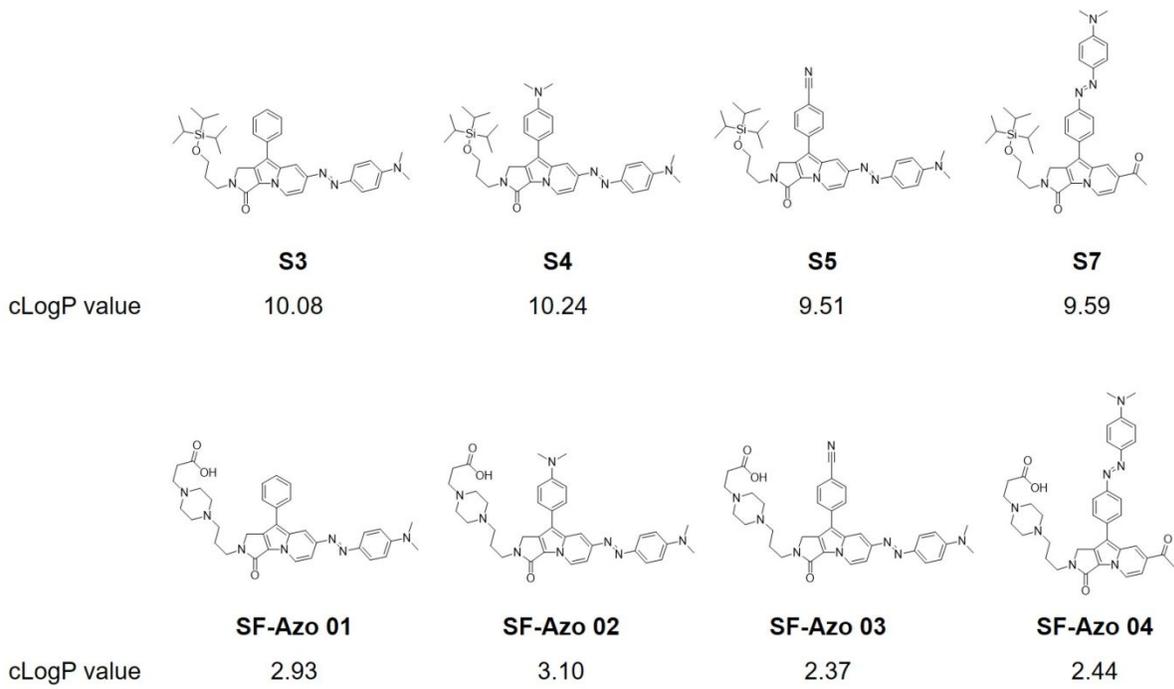
**methyl 3-(piperazin-1-yl)propanoate:** **Boc-intermediate** (583.6 mg, 2.14 mmol) and trifluoroacetic acid (TFA, 1.49 g, 13.1 mmol, 1.00 mL) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). The mixture was stirred at room temperature for overnight. Solvent was removed under the reduced pressure. Proceed to the next step without further purifications; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) δ 3.71 (s, 3H), 3.45 (t, *J*=5.5 Hz, 4H), 3.19–3.37 (m, 6H), 2.79 (t, *J*=6.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>OD) δ 172.8, 53.9, 52.6, 50.3, 42.9, 30.6; LRMS (ESI) *m/z* calcd for C<sub>8</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 173.13, found: 173.10.

**Table S1.** Reaction Condition Optimization for Intramolecular 1,3-Dipolar Cycloaddition.

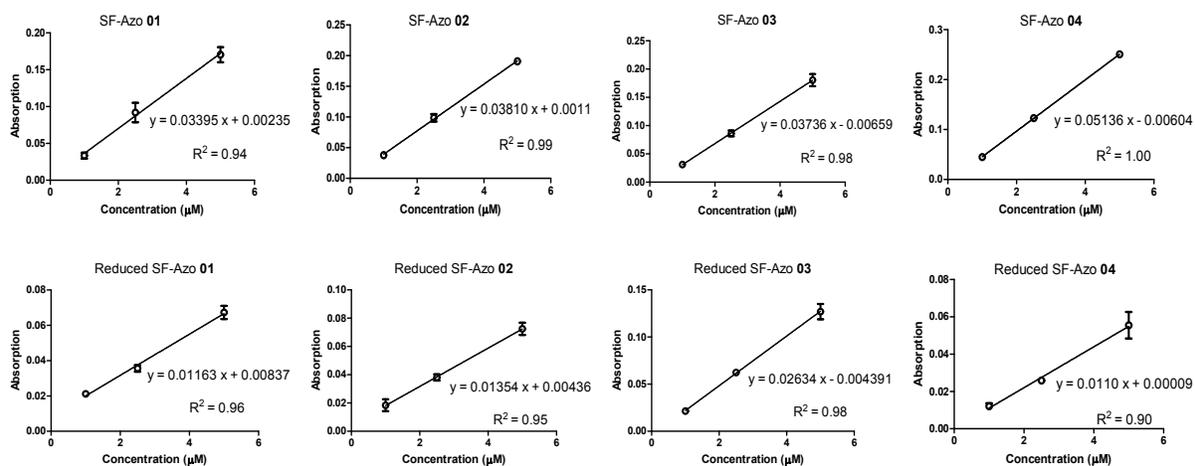


	Temp(°C)	Base	Solvent	Copper	Product Yield <sup>a</sup>
<b>1</b>	25	K <sub>2</sub> CO <sub>3</sub>	CH <sub>3</sub> CN	-	-
<b>2</b>	25	N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CN	-	-
<b>3</b>	25	N(CH <sub>2</sub> CH <sub>3</sub> ) <sub>3</sub>	CH <sub>3</sub> CN	CuI	-
<b>4</b>	25	DBU	CH <sub>3</sub> CN	-	trace
<b>5</b>	0	DBU	CH <sub>3</sub> CN	CuI	trace
<b>6</b>	25	DBU	CH <sub>3</sub> CN	CuI	6
<b>7</b>	50	DBU	CH <sub>3</sub> CN	CuI	6
<b>8</b>	80	DBU	CH <sub>3</sub> CN	CuI	20
<b>9</b>	80	DBU	1,2-dichloroethane	CuI	21
<b>10</b>	80	DBU	DMF	CuI	23
<b>11</b>	80	DBU	Toluene	CuI	21
<b>12</b>	110	DBU	Toluene	CuI	22
<b>13</b>	<b>120</b>	<b>DBU</b>	<b>DMF</b>	<b>CuI</b>	<b>30</b>
<b>14</b>	120	DBU	dryDMF	CuI	25
<b>15</b>	120	DBU	DMF	CuCN	25
<b>16</b>	120	DBU	DMF	CuCl	31
<b>17</b>	120	DBU	DMF	CuBr	22

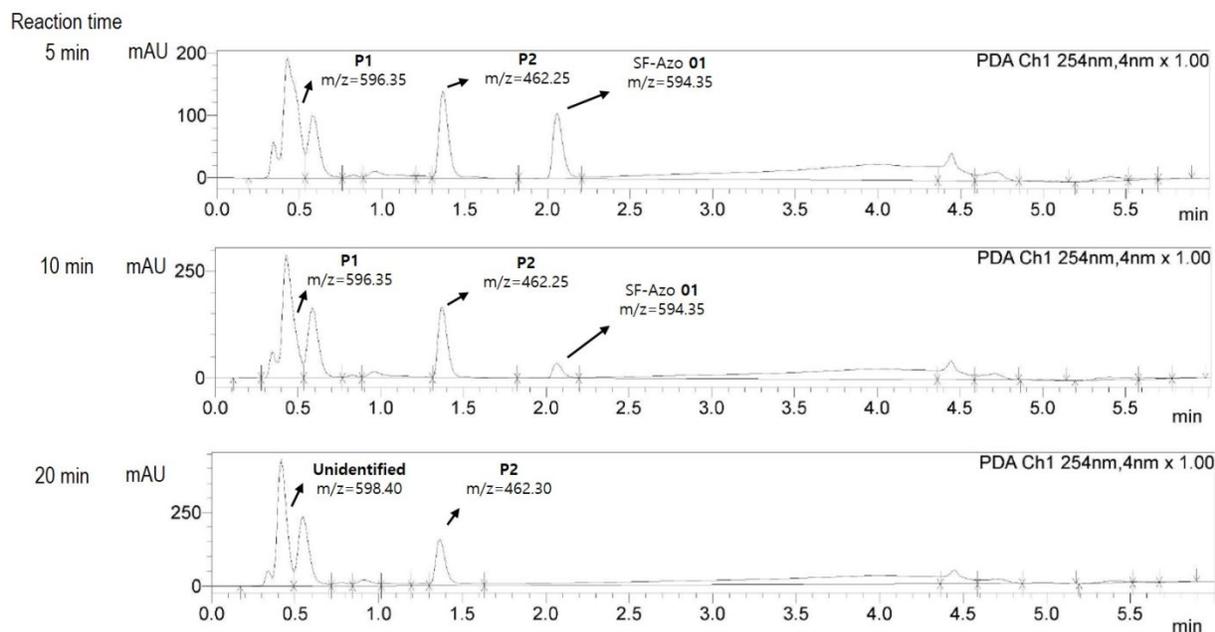
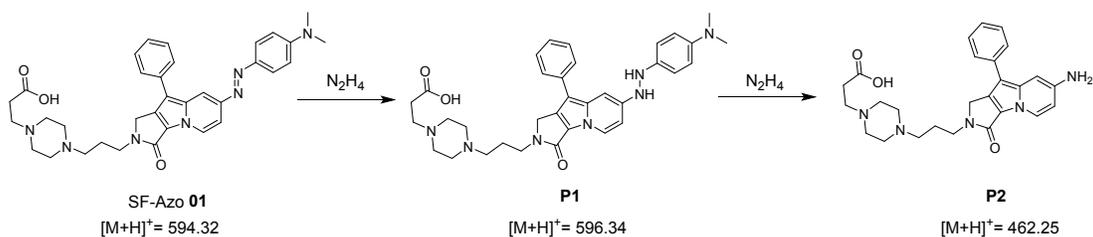
<sup>a</sup>NMR Yield estimation



**Figure S1.** Chemical structures and cLogP values for **S3**, **S4**, **S5**, **S7**, and **SF-Azo 01–04**.



**Figure S2.** The linear plots of SF-Azo concentration versus absorption intensity. Each slope represents a  $1:10^6$  scale of molar absorptivity ( $\epsilon$ ) for corresponding SF-Azo or its reduced species.



**Figure S3.** Proposed reduction structures of SF-Azo **01** and time relevant LC/MS data of hydrazine treated SF-Azo **01**. SF-Azo **01** (100  $\mu\text{M}$ ) was incubated with hydrazine monohydrate (200 mM) in methanol and water mixture (0.5 mL, v:v=1:1) at 50  $^\circ\text{C}$ . Data were measured at 5, 10, and 20 min.

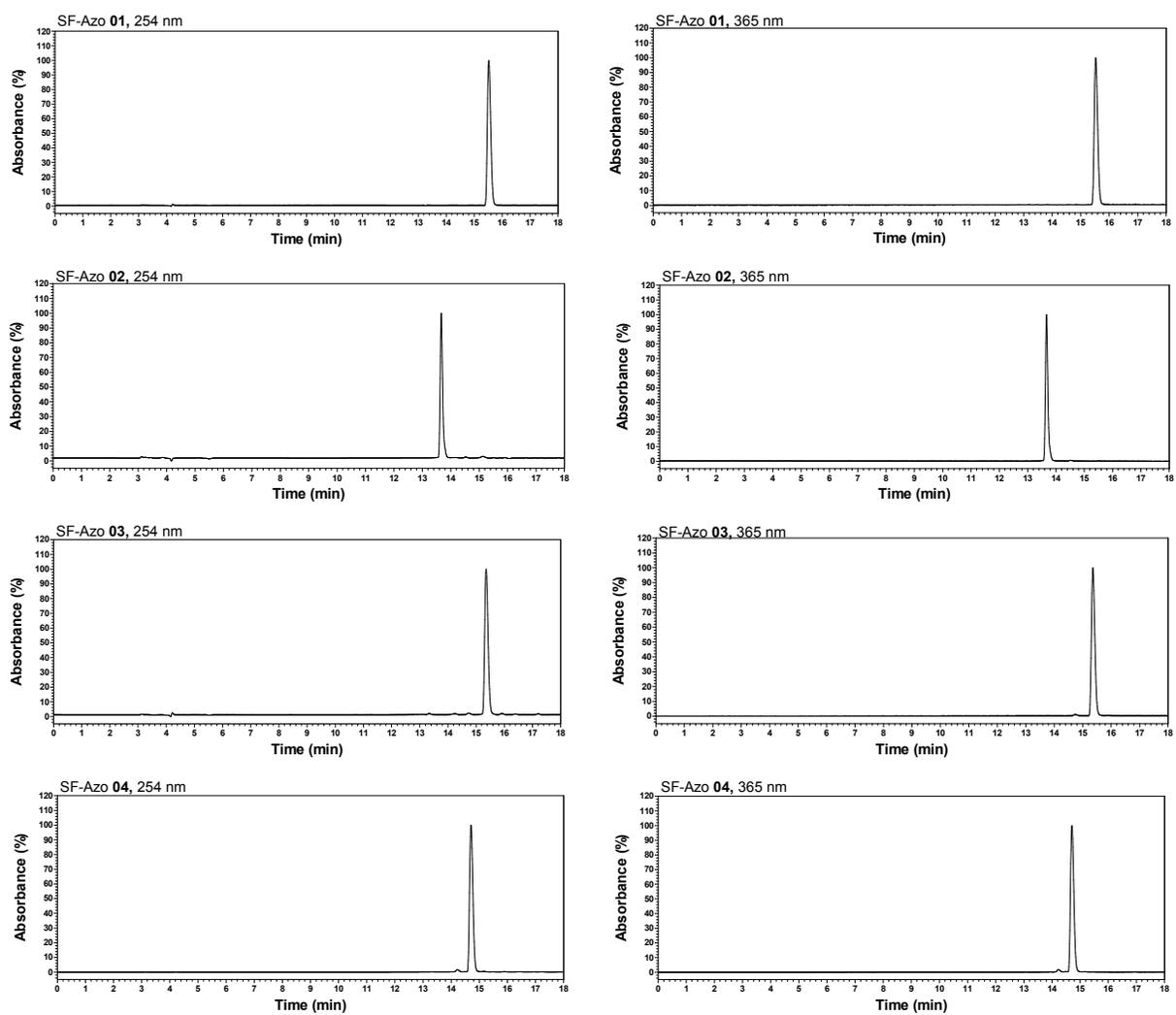


Figure S4. Purity of SF-Azo 01-04 was confirmed by HPLC analysis.

Figure S5. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound Boc-intermediate

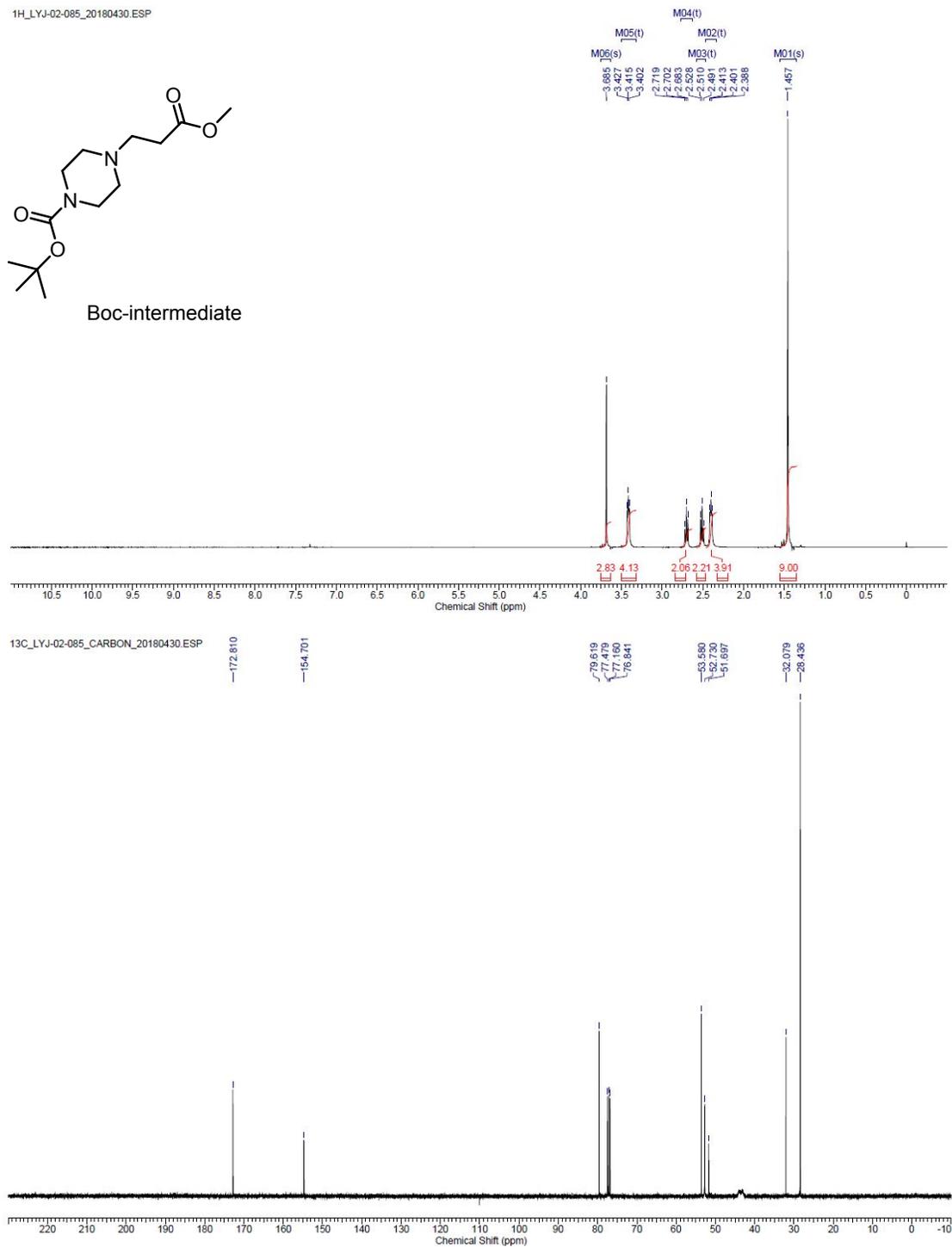




Figure S6. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound methyl 3-(piperazin-1-yl)propanoate

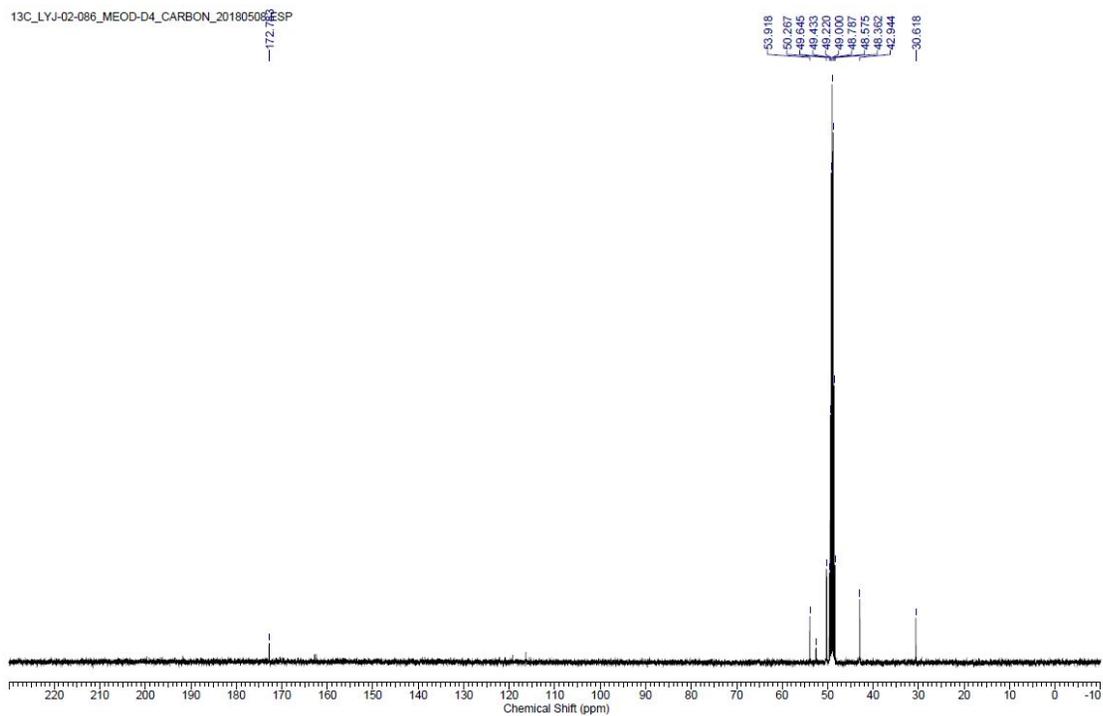
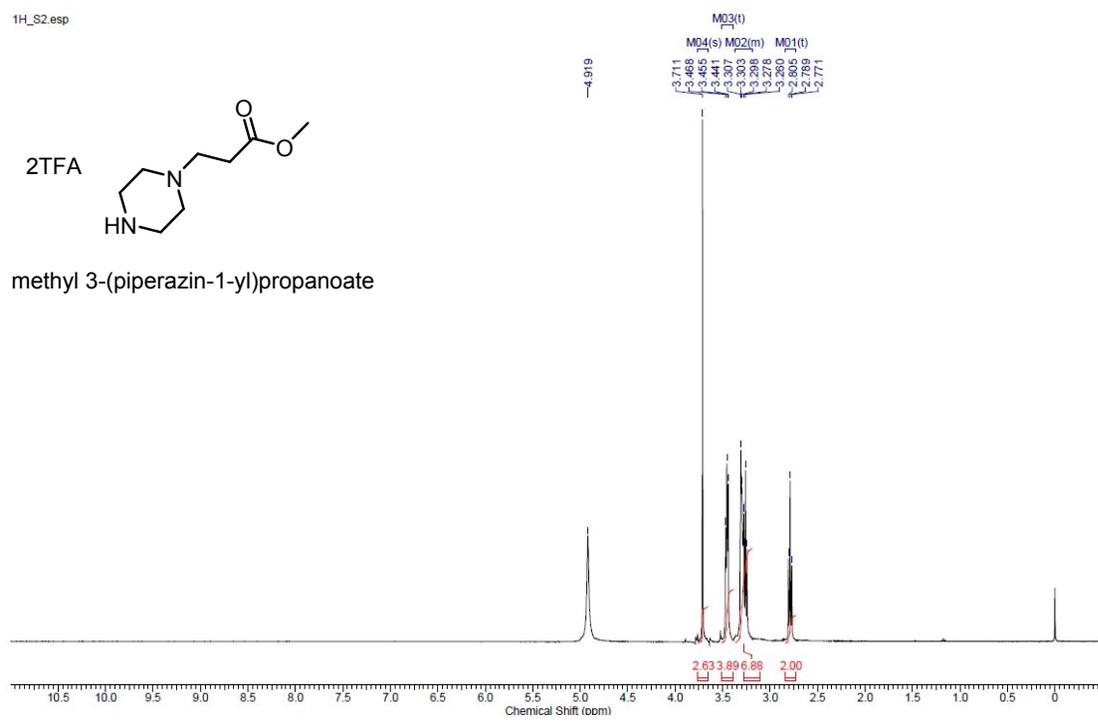


Figure S7. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S1

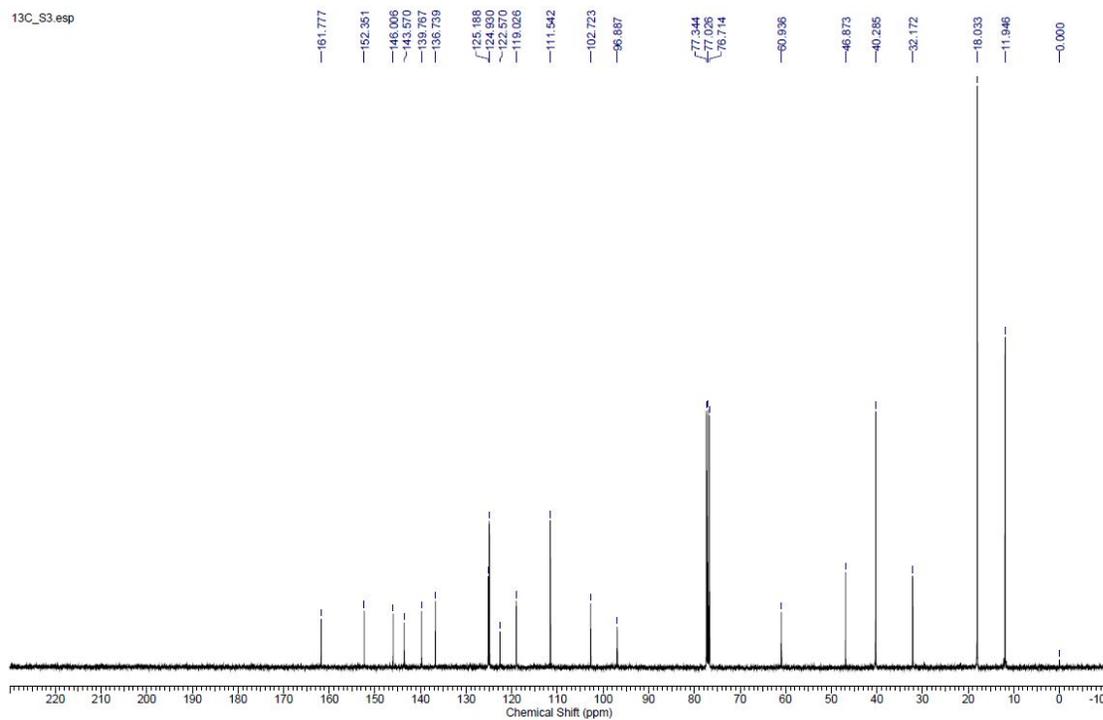
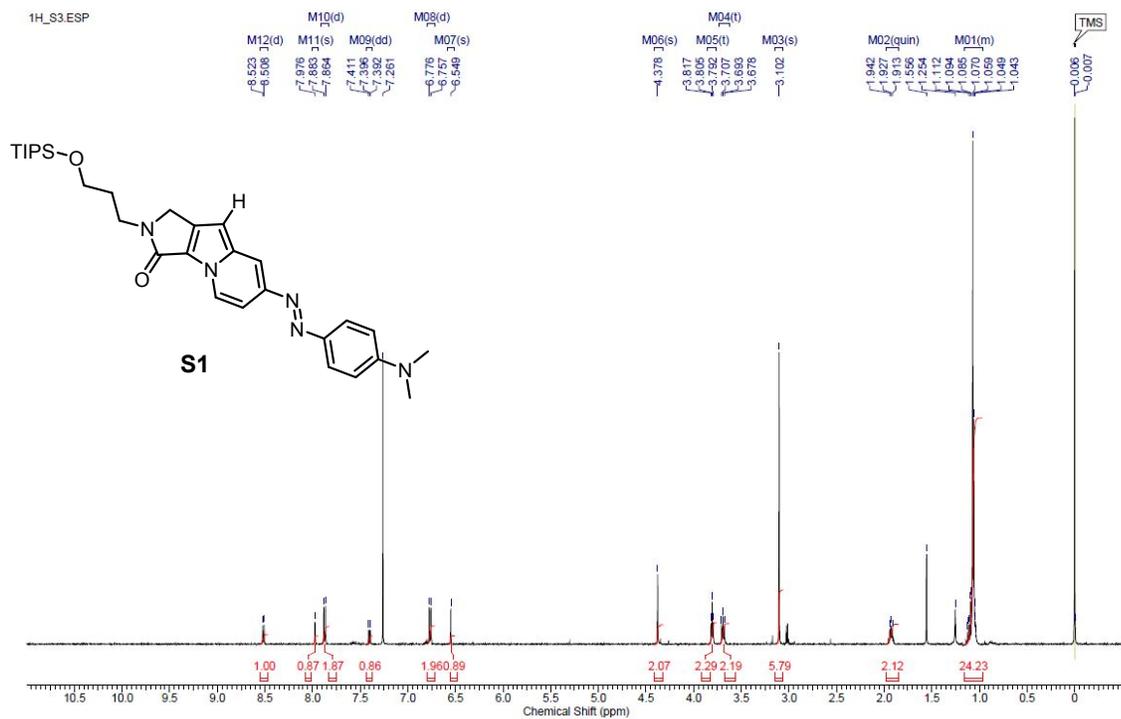


Figure S8. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S2

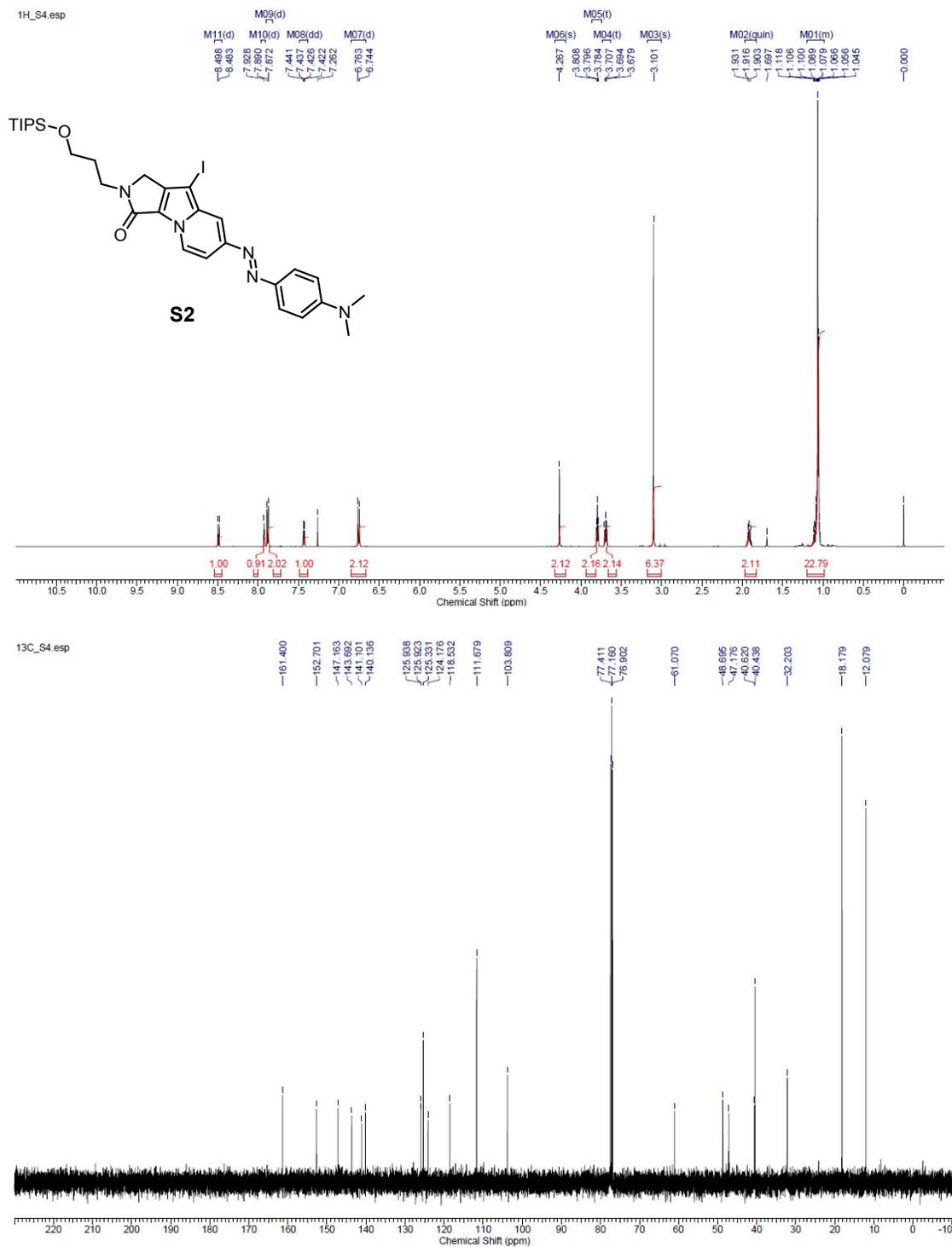
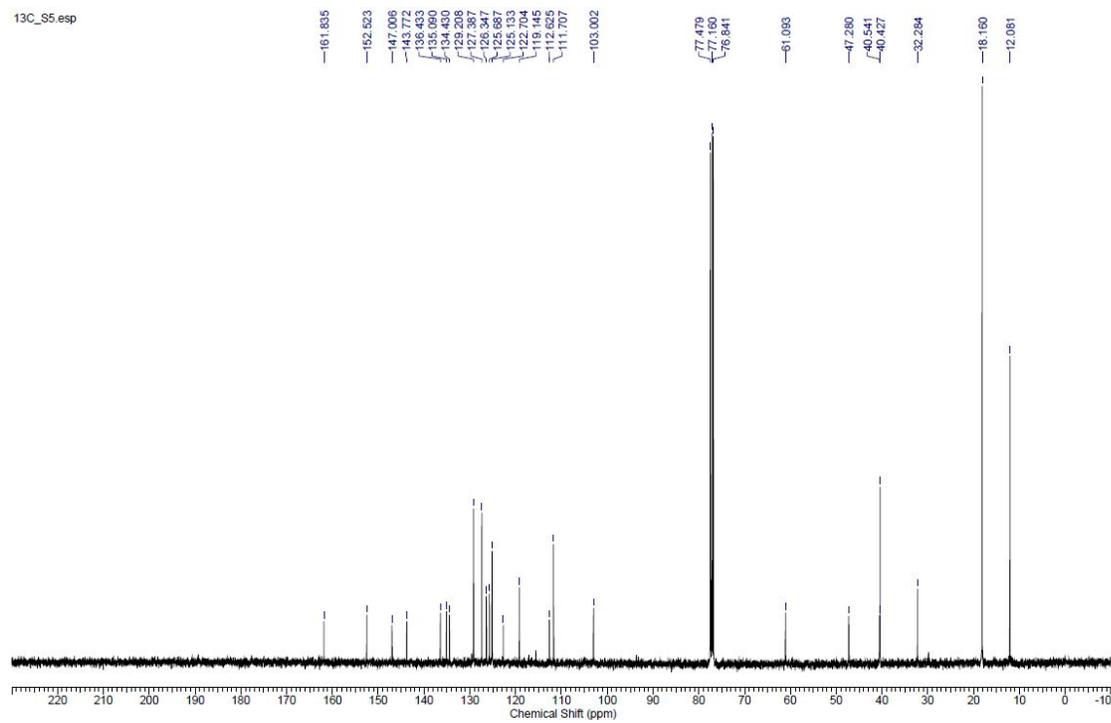
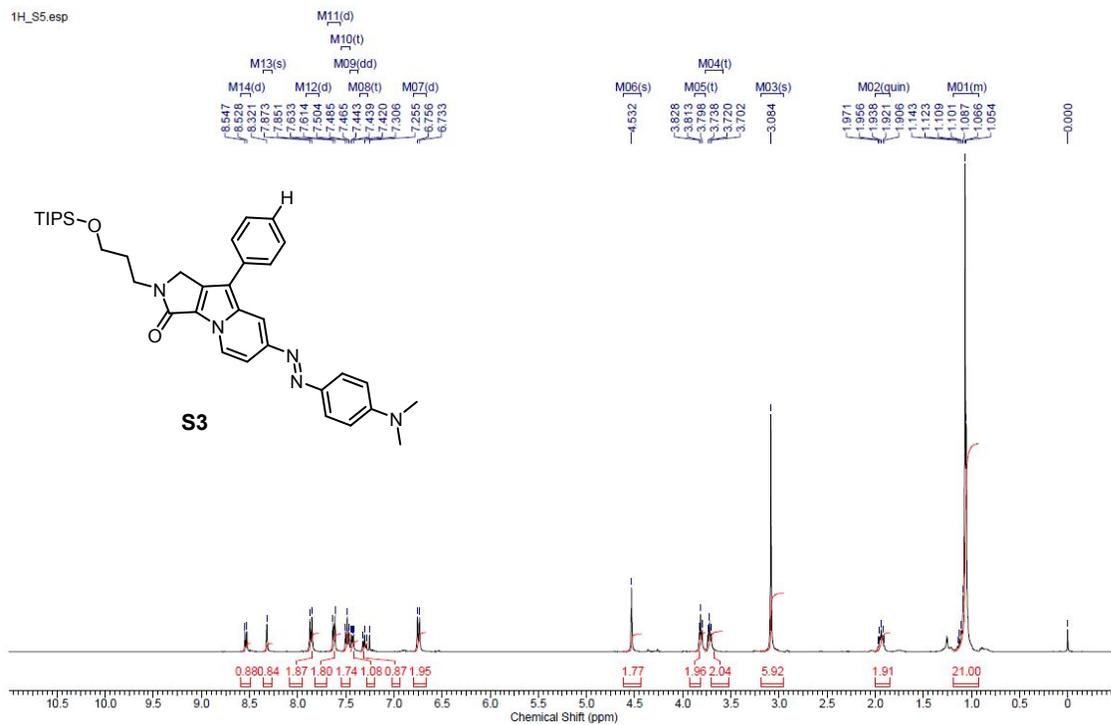


Figure S9. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S3



**Figure S10.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for compound S4

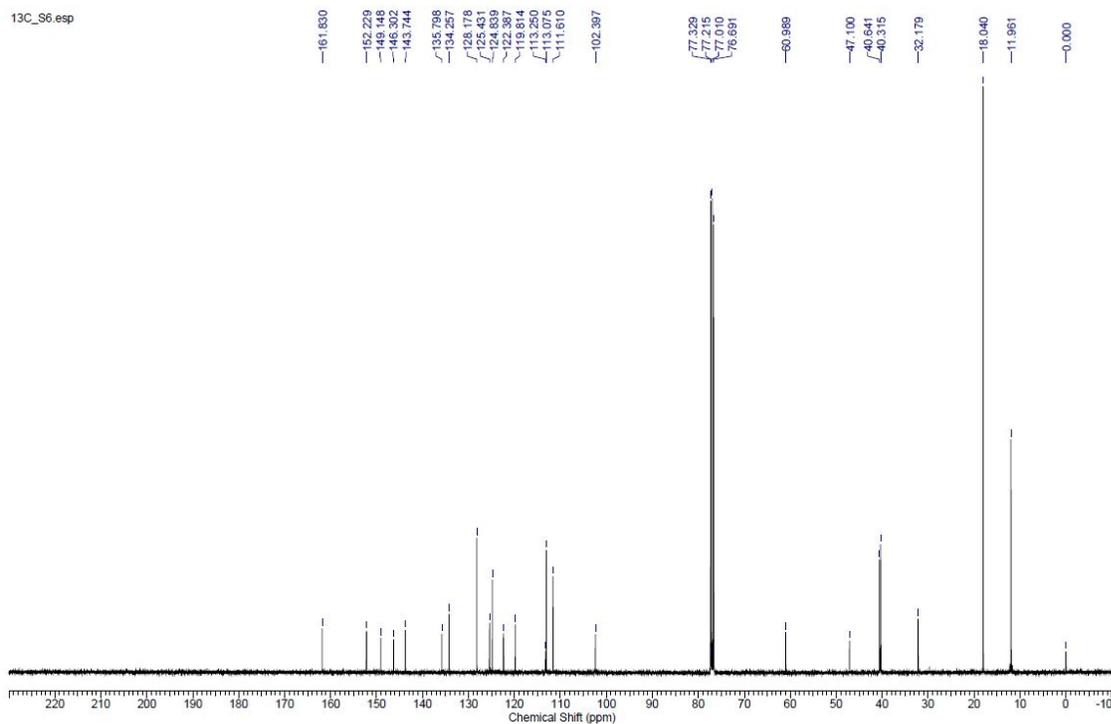
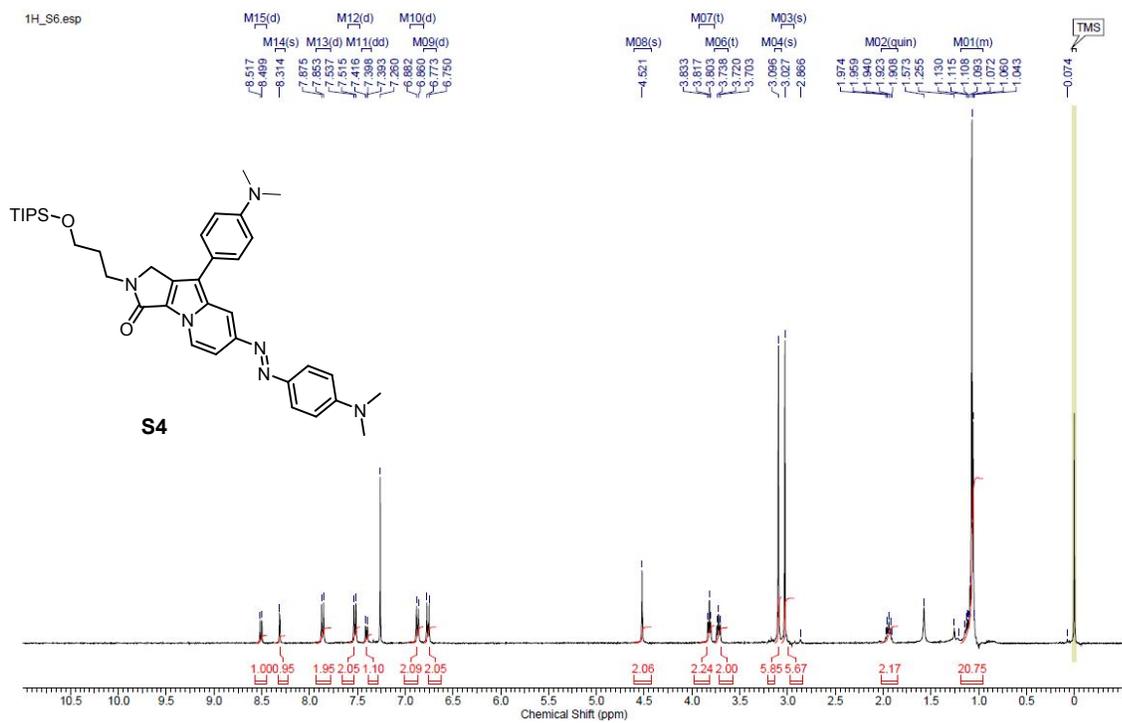


Figure S11. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S5

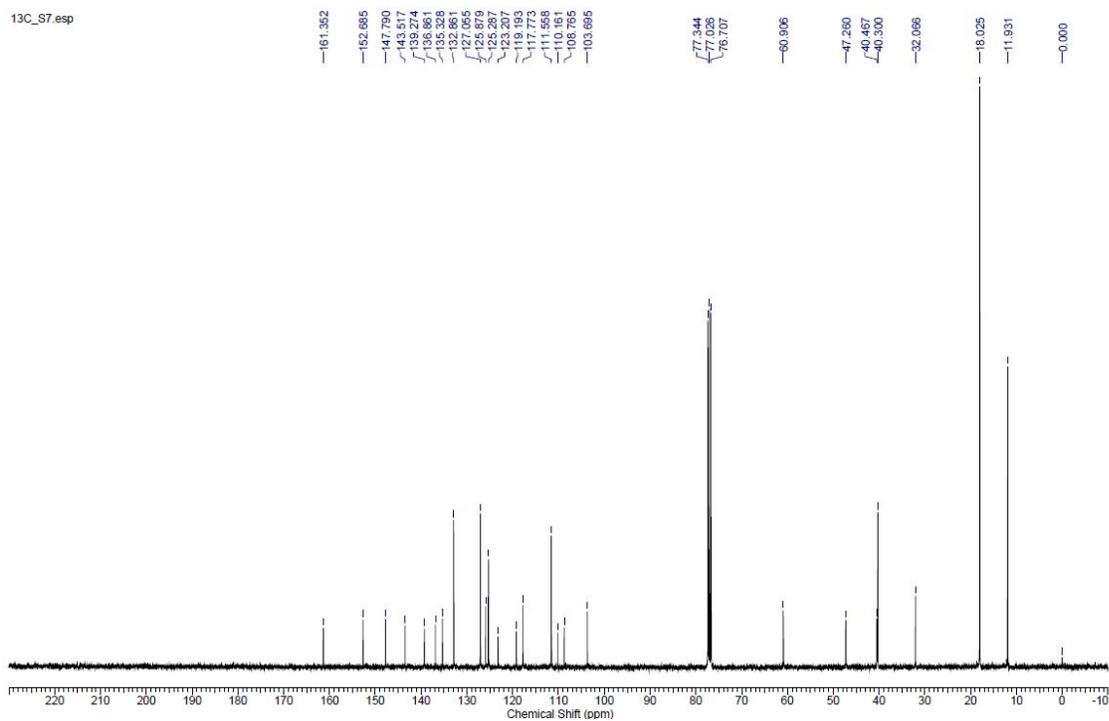
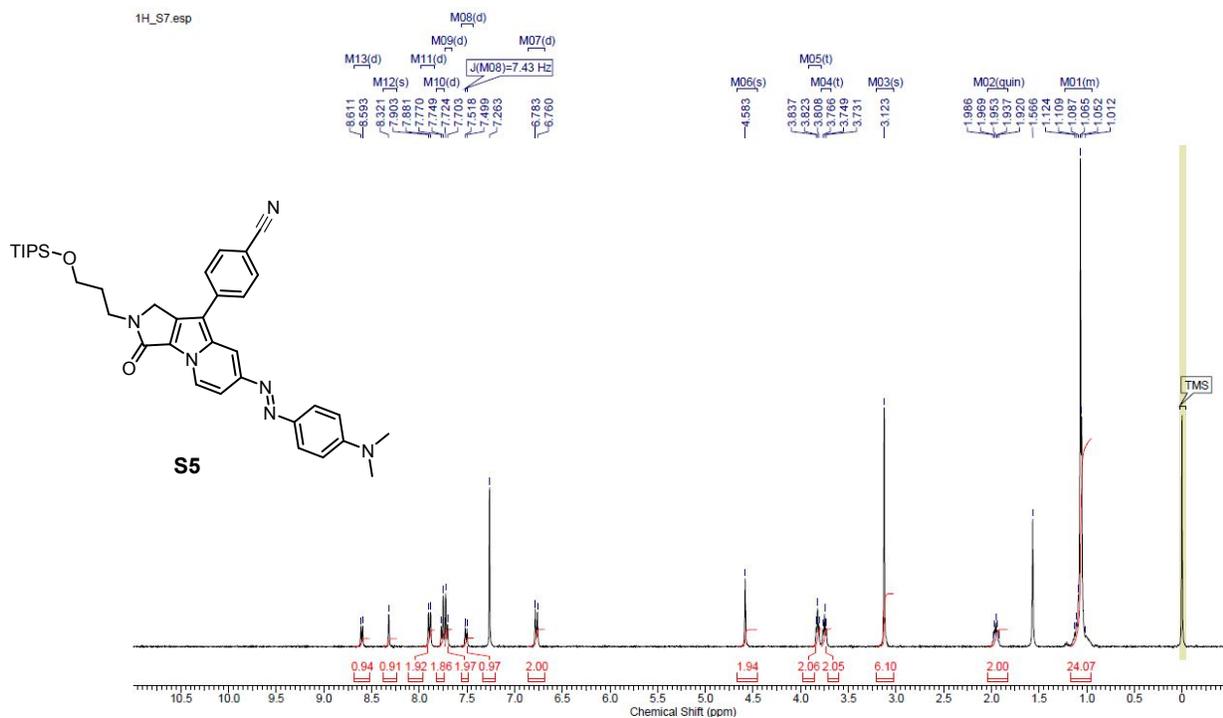


Figure S12. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S6

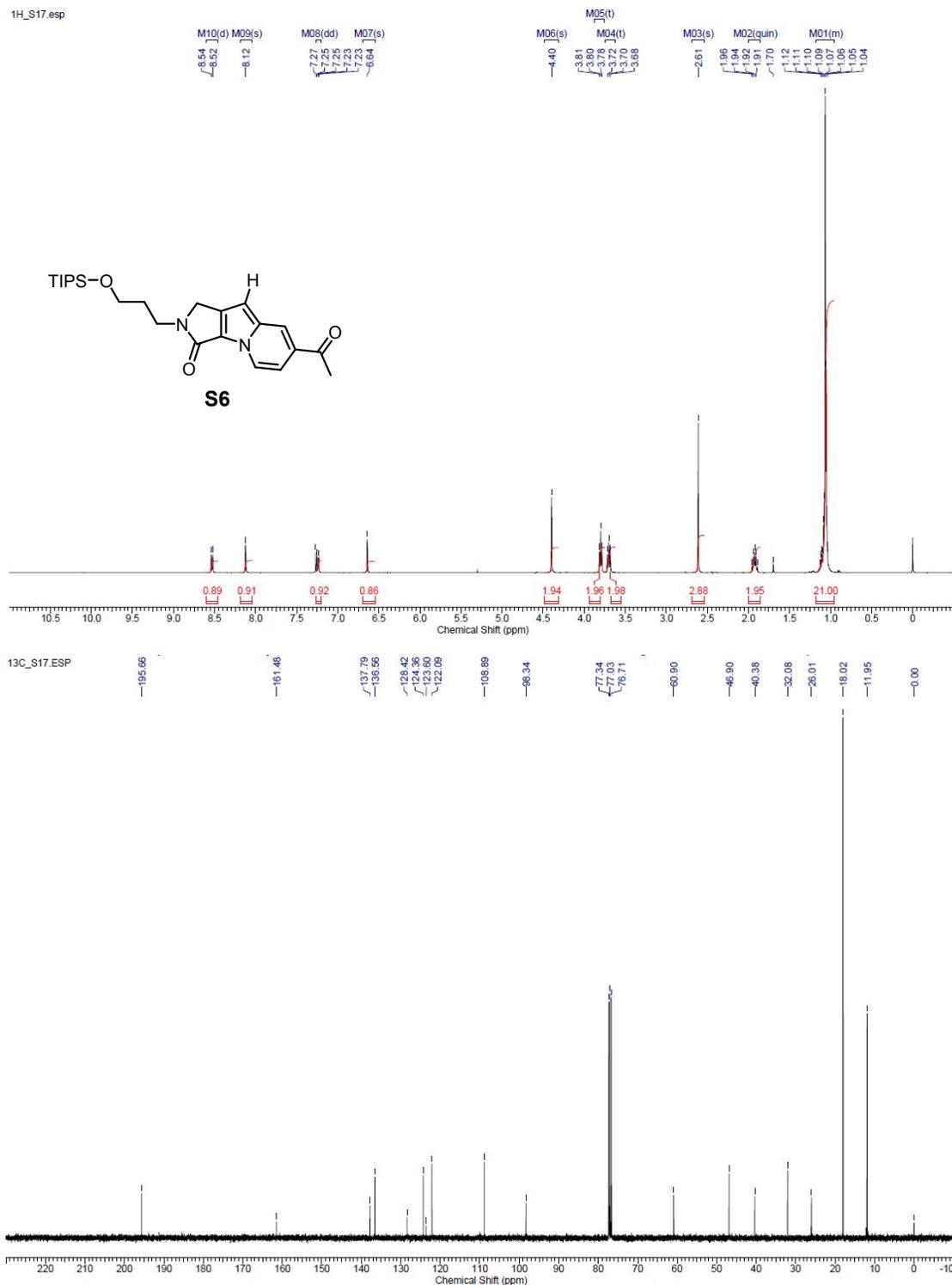


Figure S13. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S7

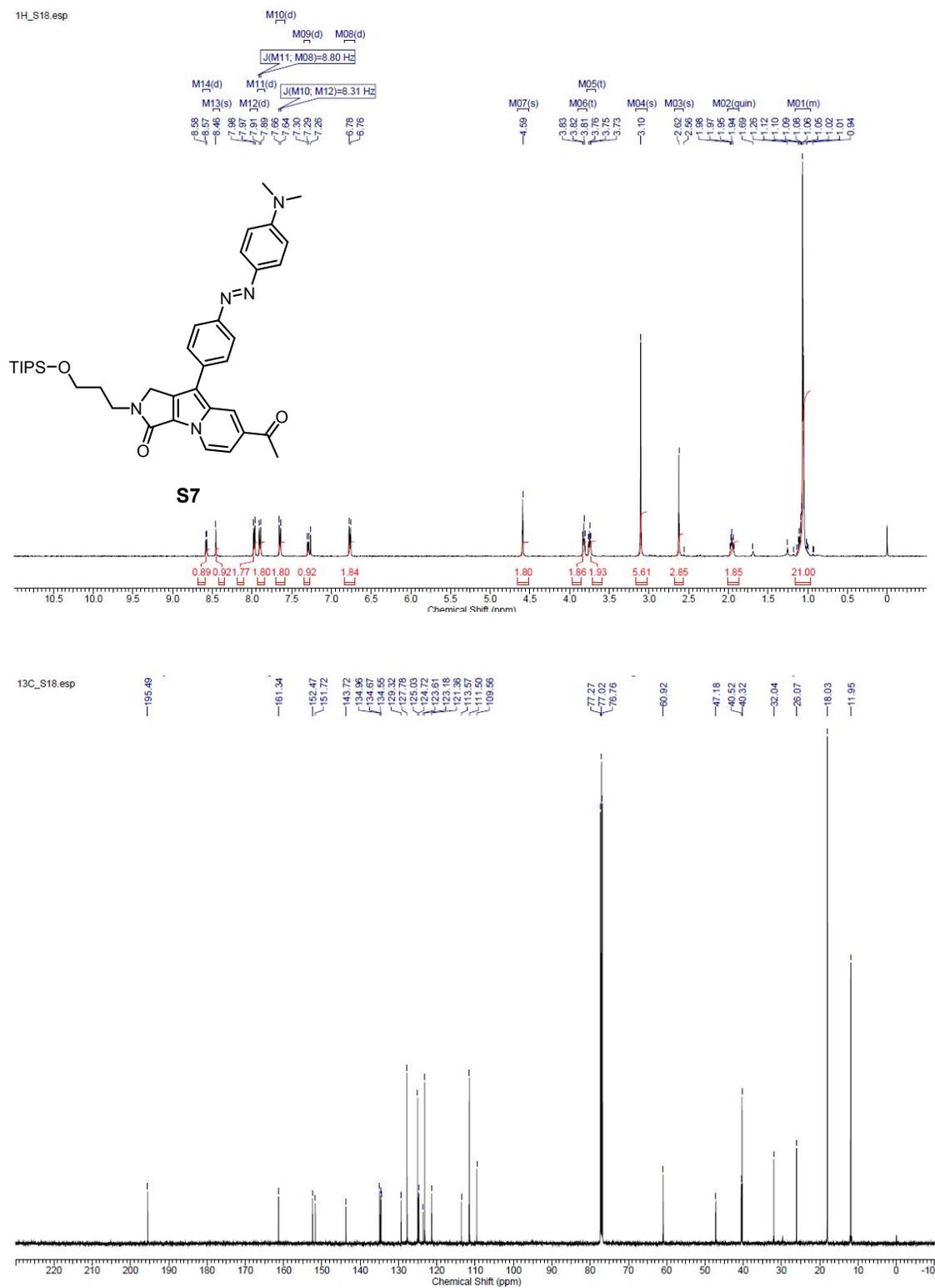


Figure S14. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S8

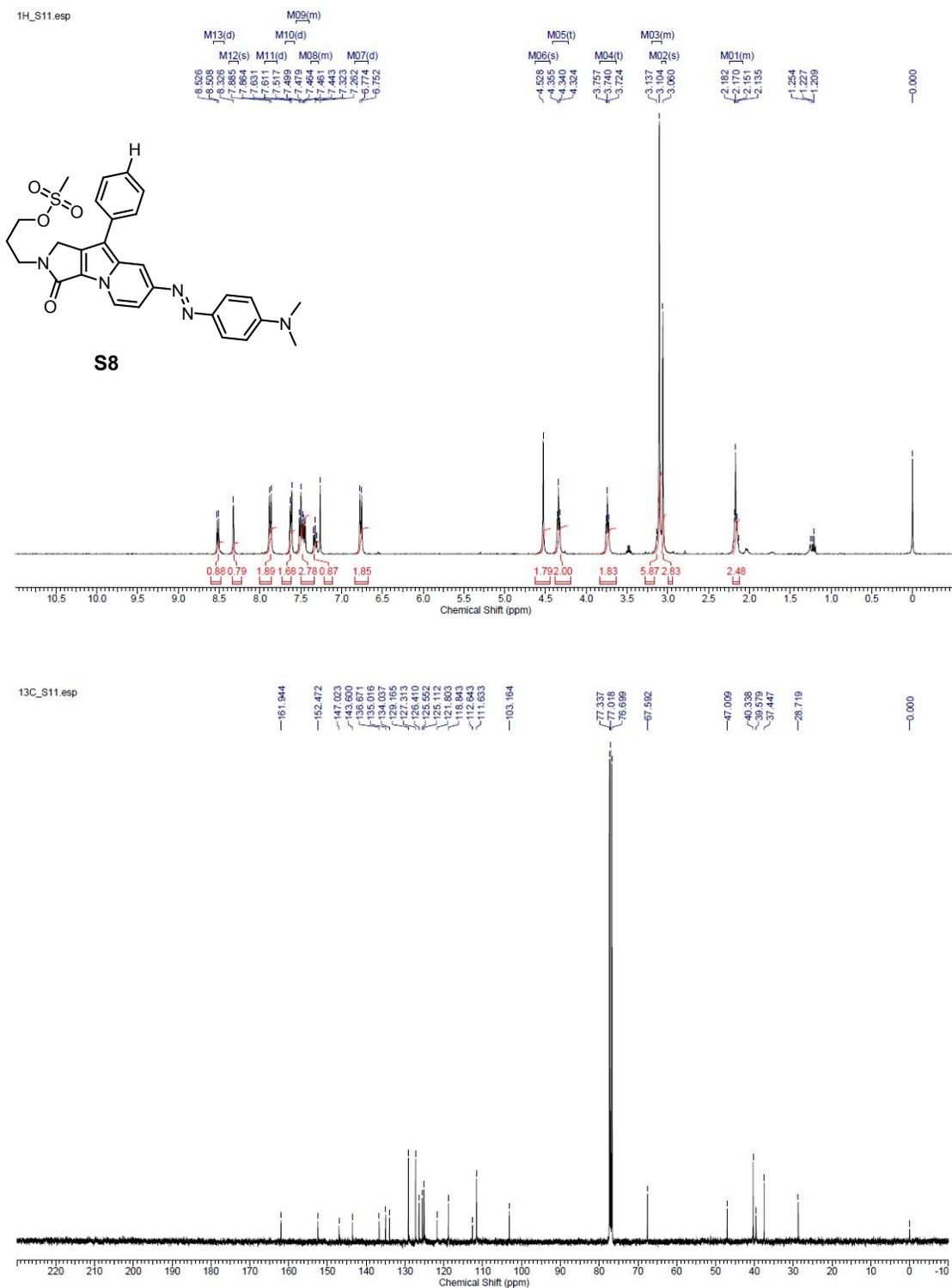


Figure S15. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S9

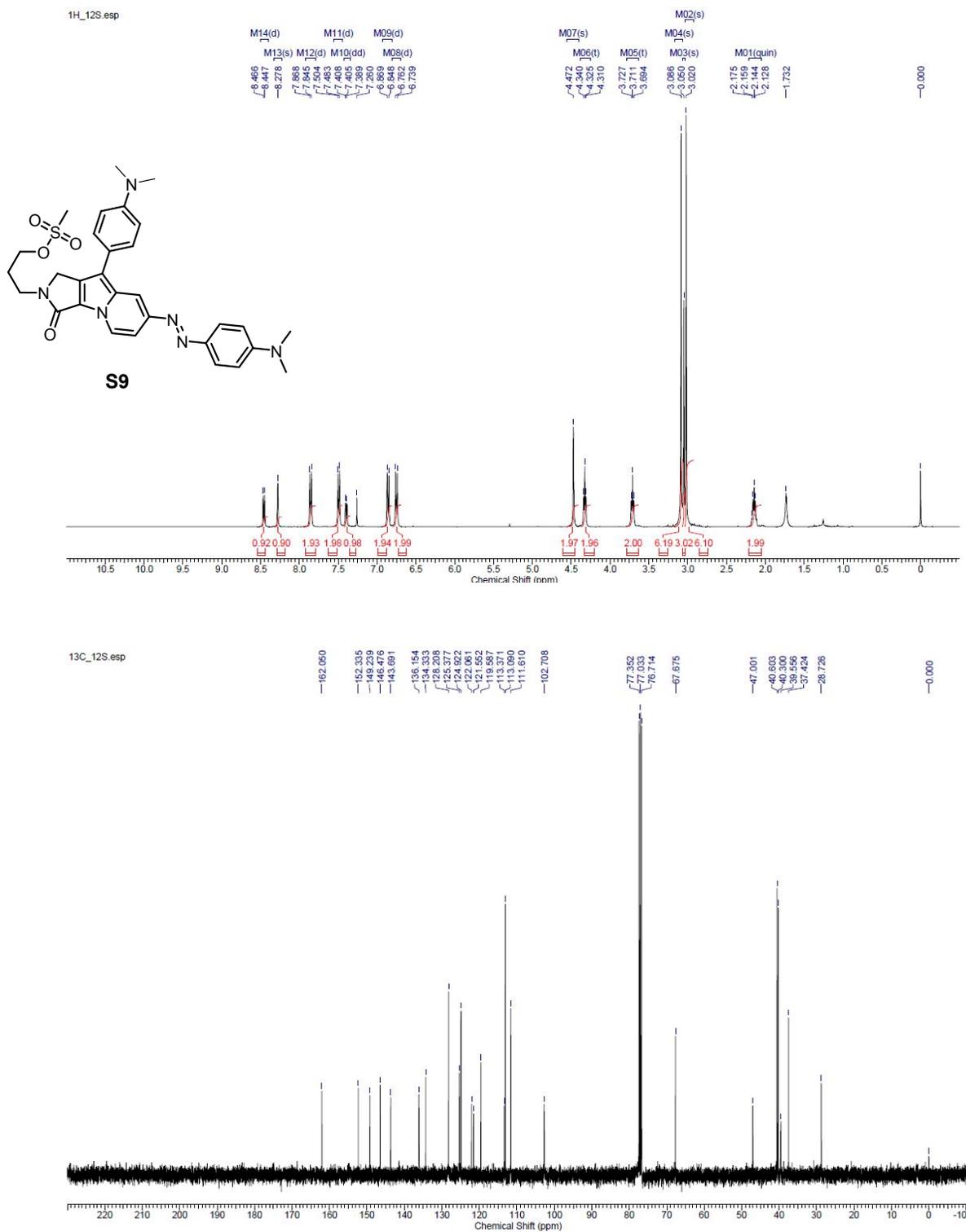


Figure S16. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S10

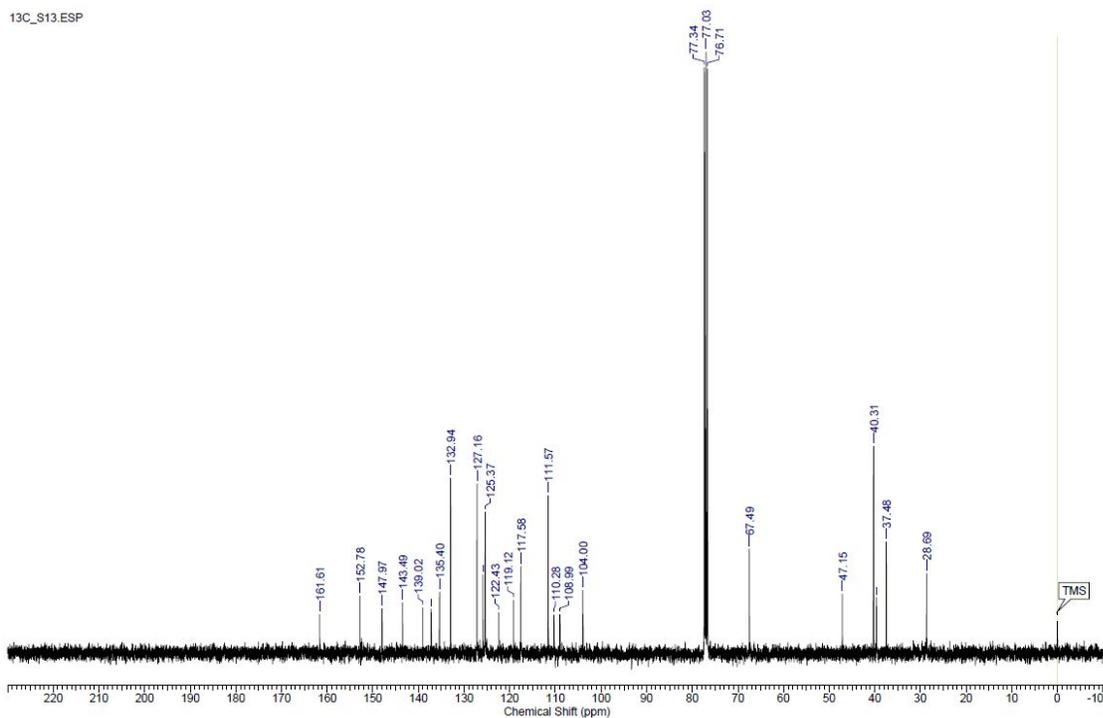
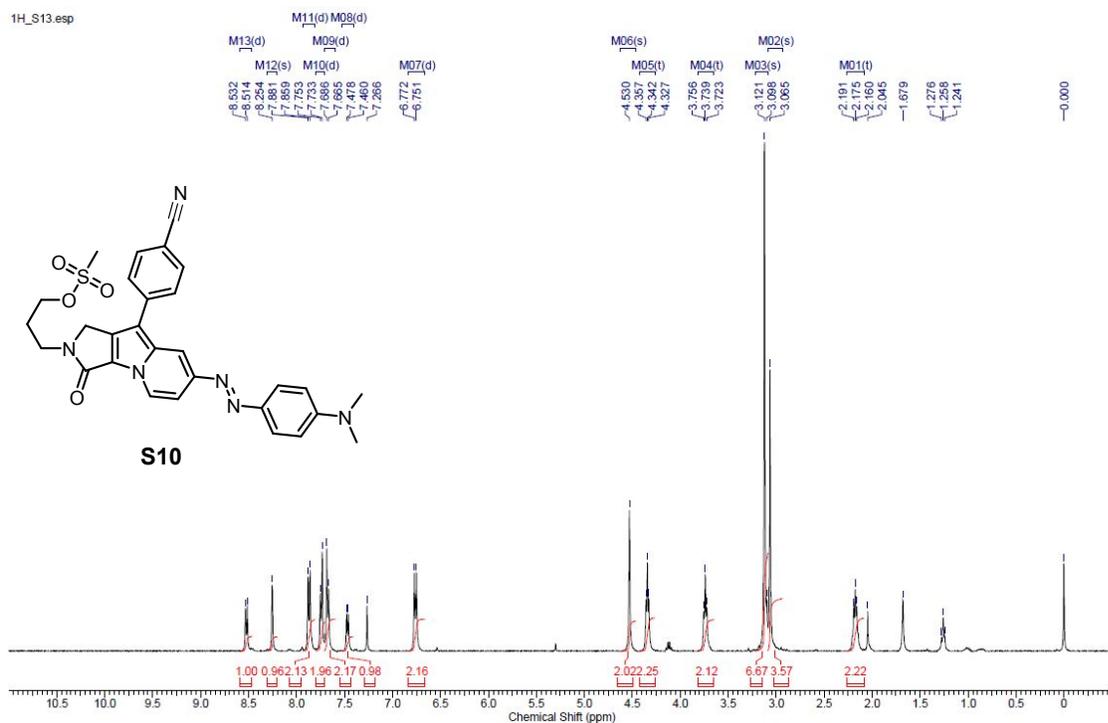


Figure S17. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S11

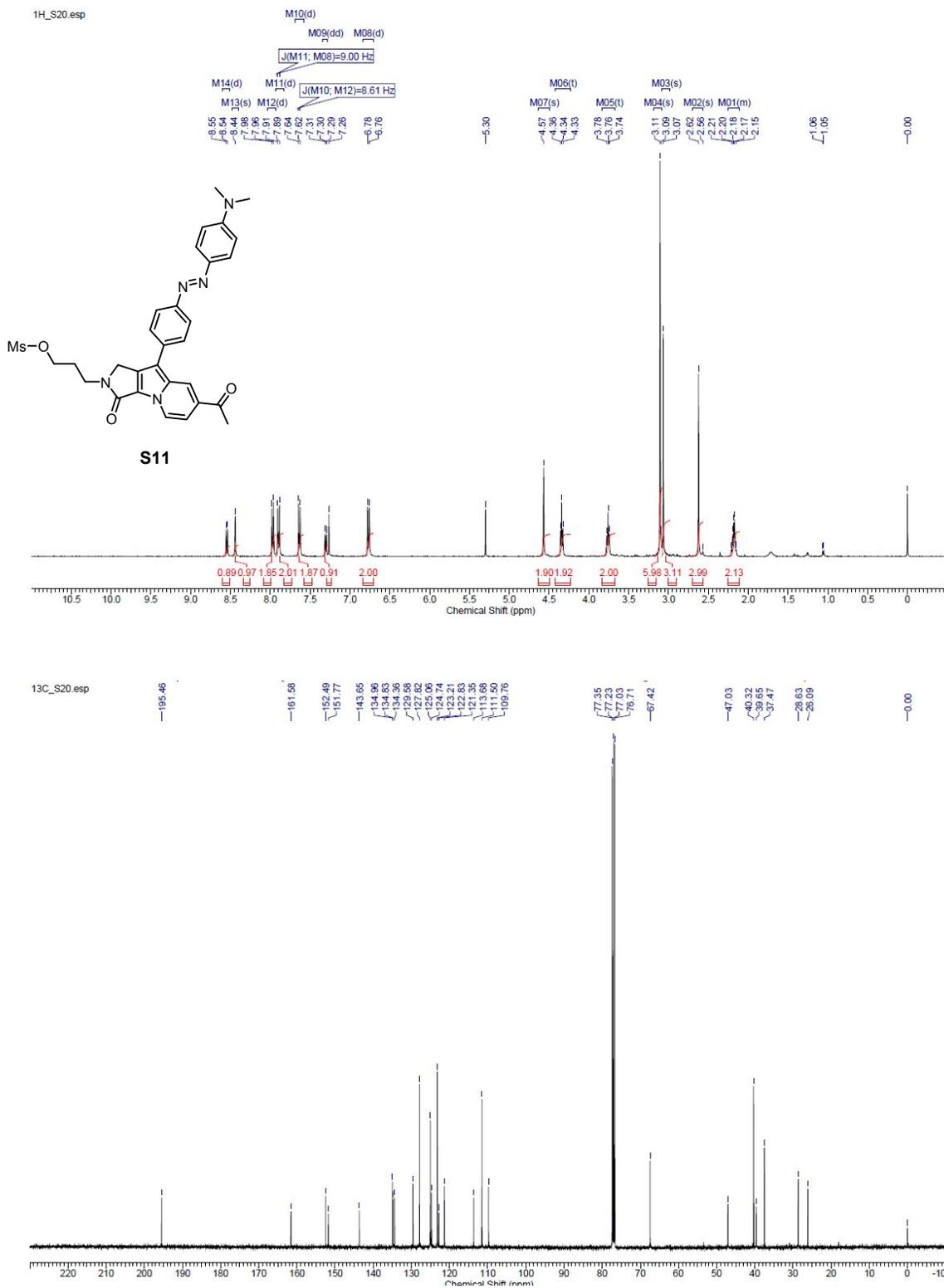


Figure S18. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S8'

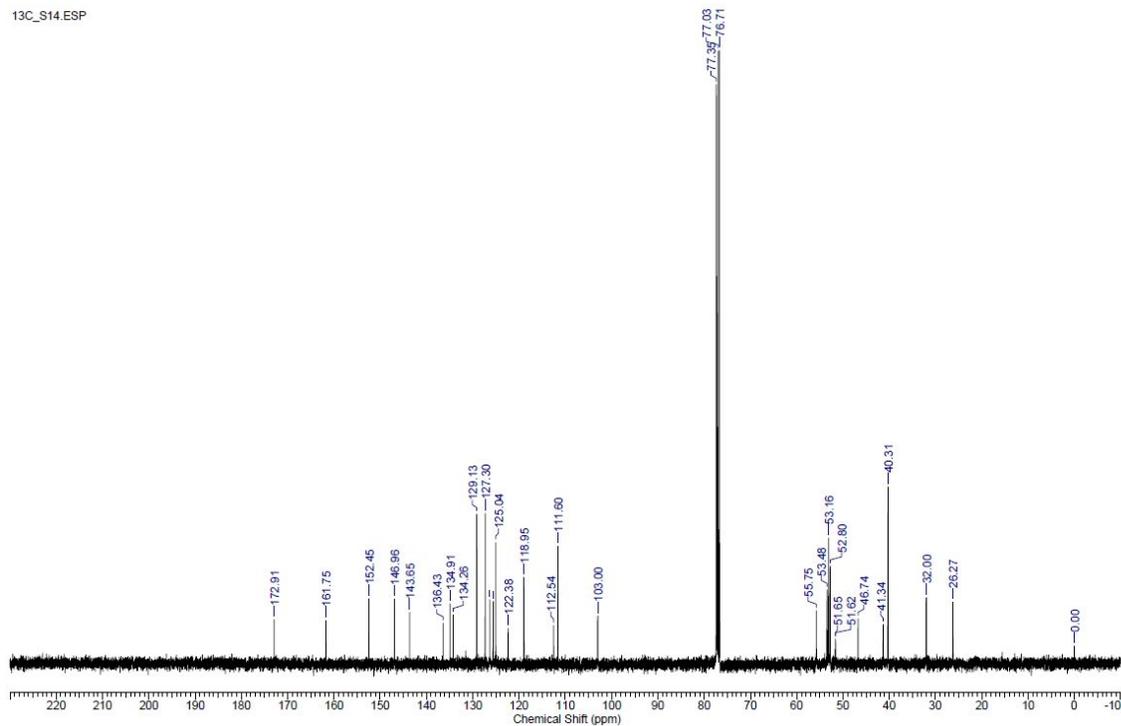
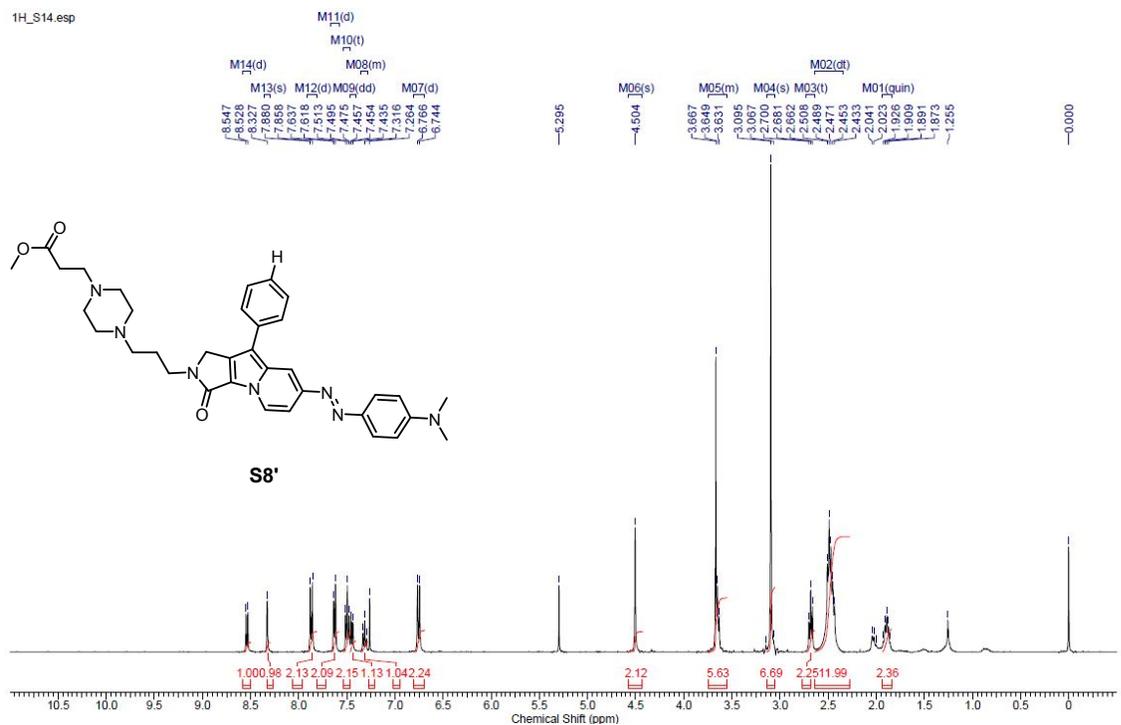


Figure S19. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S9'

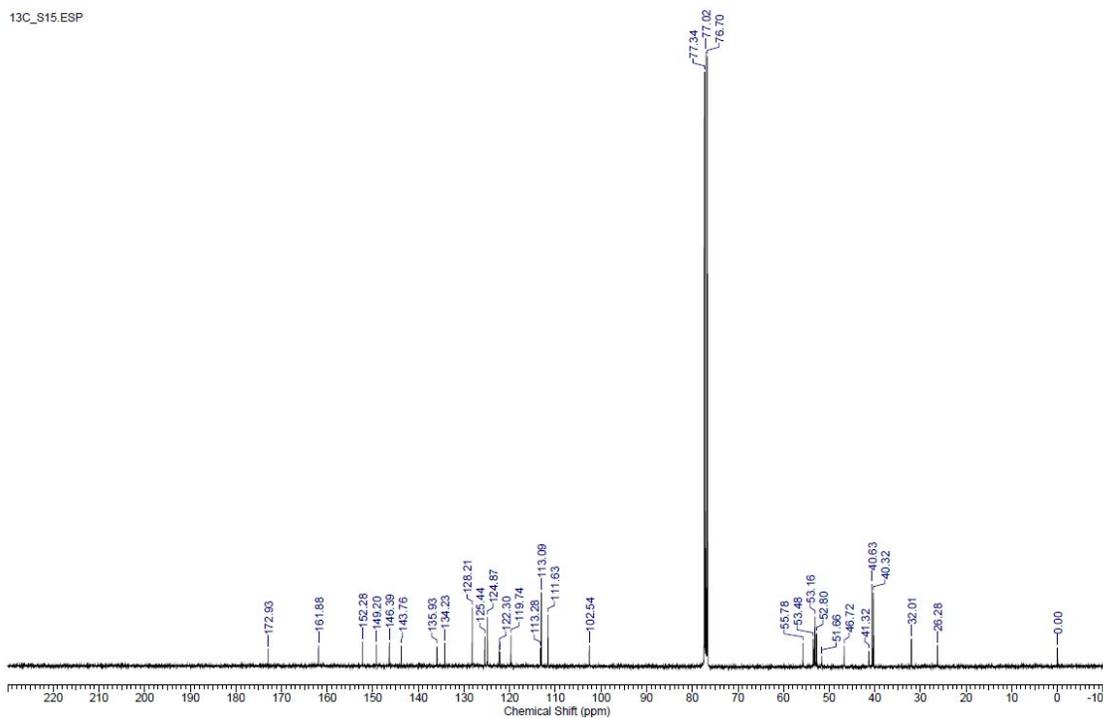
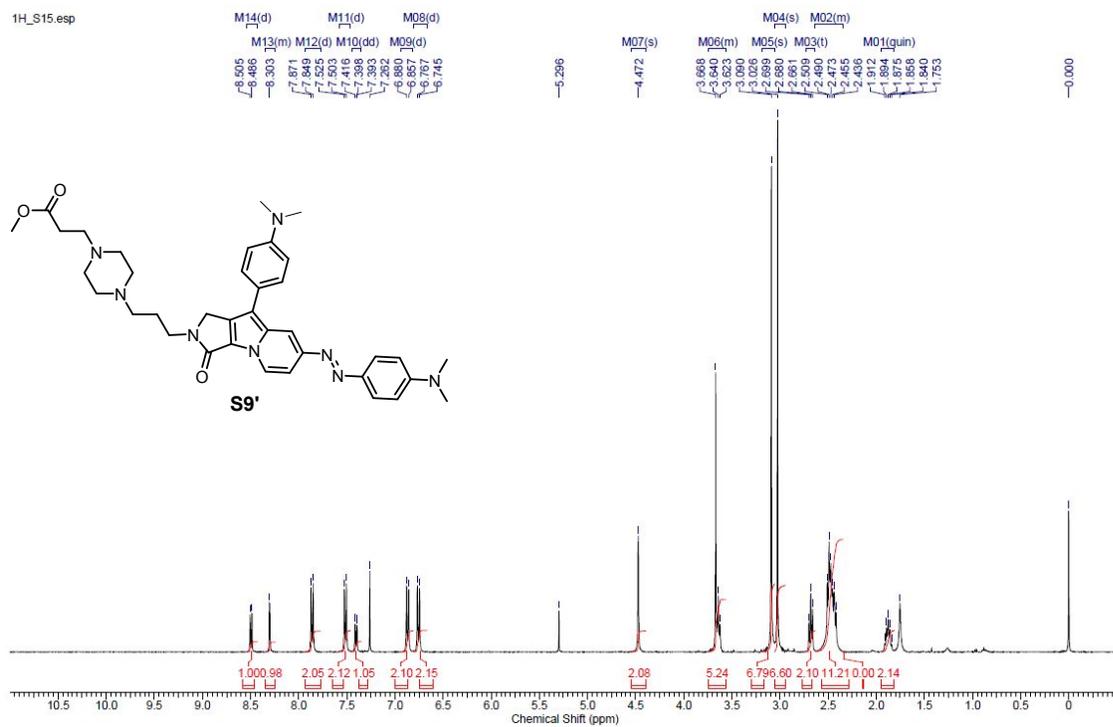


Figure S20. <sup>1</sup>H and <sup>13</sup>C NMR spectra for compound S10'

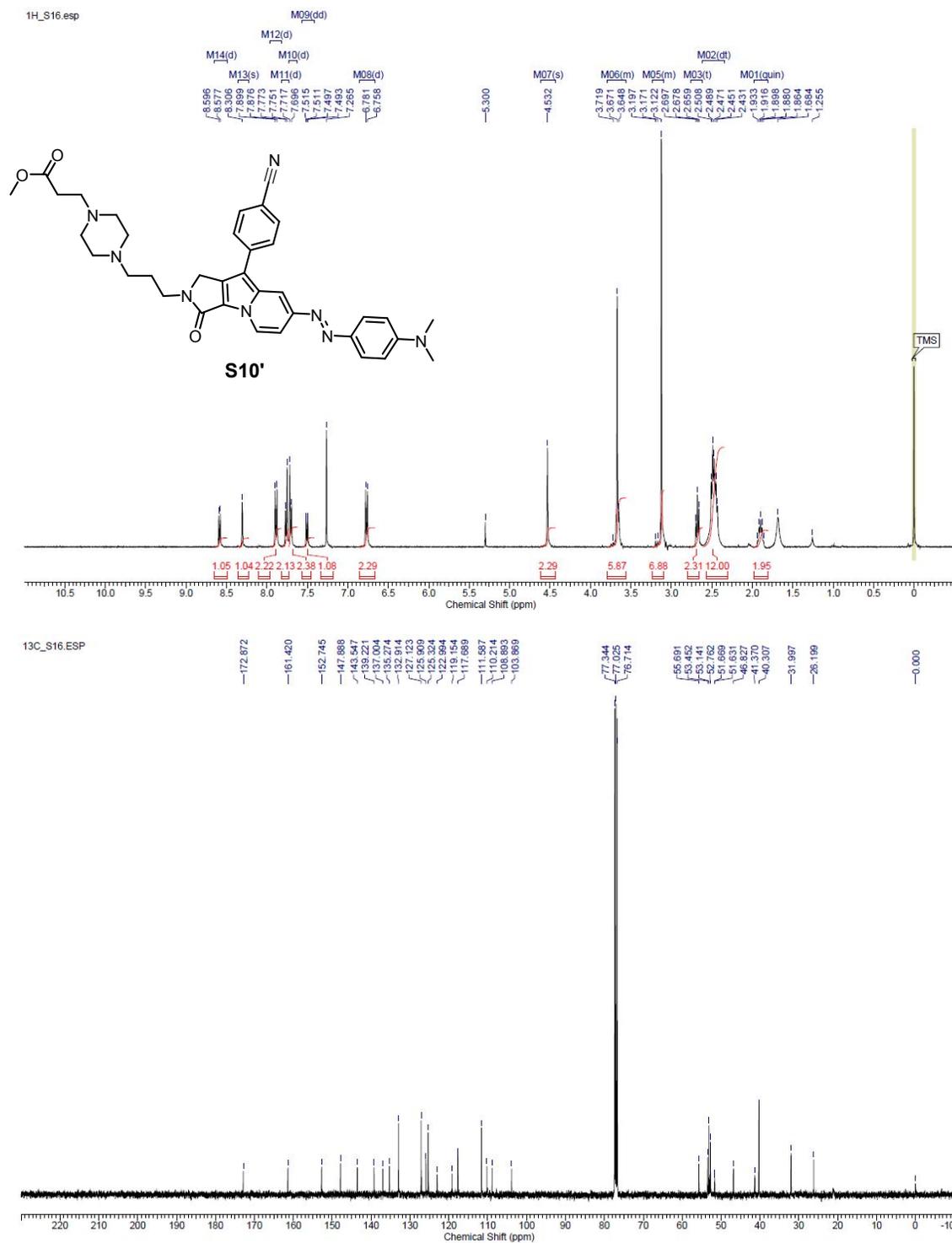


Figure S21. <sup>1</sup>H NMR spectrum for compound S11'

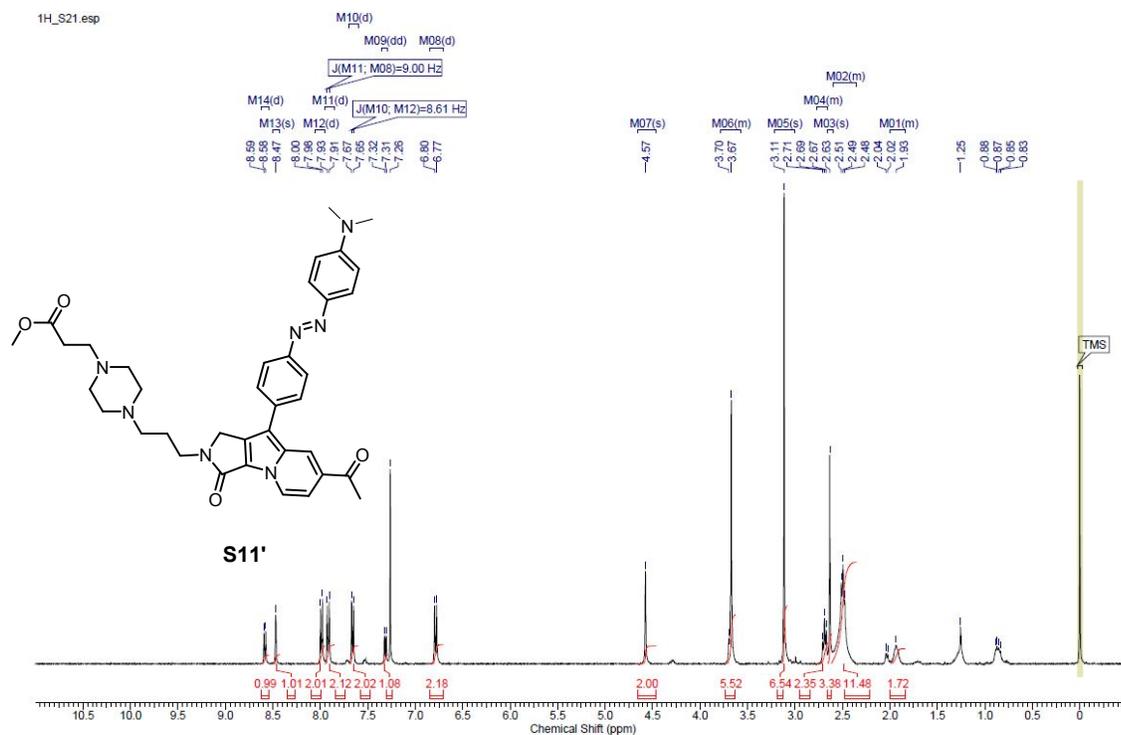
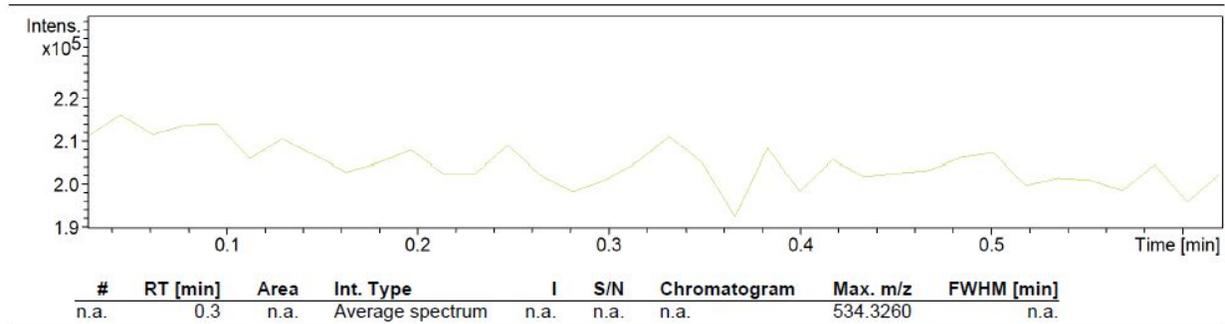


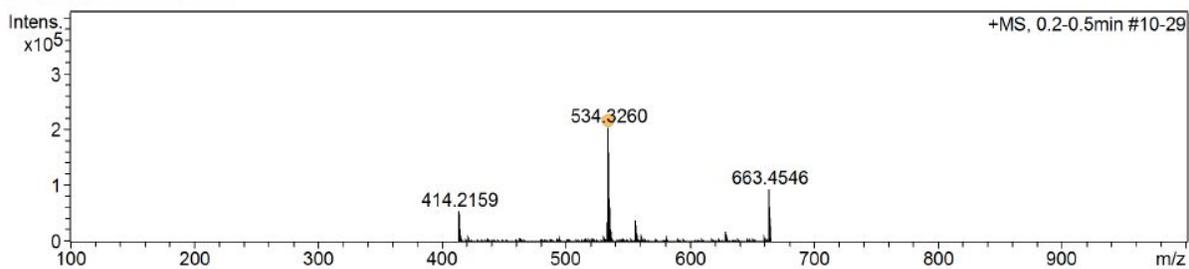
Figure S22. HRMS spectra for compound S1

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	420 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	660 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



**+MS, 0.2-0.5min #10-29**

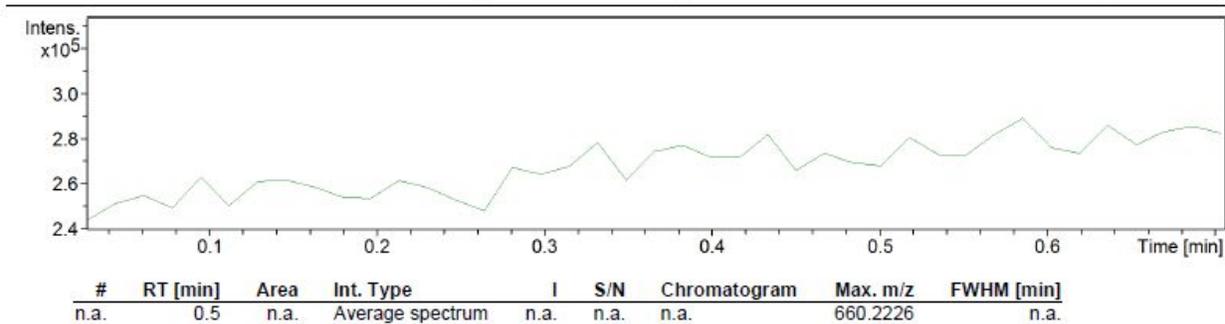


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
534.3260	1	C <sub>29</sub> H <sub>48</sub> NO <sub>6</sub> Si	534.3245	2.7	4.3	1	64.76	7.5	even	ok
	2	C <sub>30</sub> H <sub>44</sub> N <sub>5</sub> O <sub>2</sub> Si	534.3259	0.2	7.4	2	100.00	12.5	even	ok
	3	C <sub>35</sub> H <sub>44</sub> N <sub>3</sub> Si	534.3299	-7.3	28.3	3	4.31	16.5	even	ok
	4	C <sub>28</sub> H <sub>52</sub> NO <sub>3</sub> Si <sub>3</sub>	534.3250	-2.0	59.7	4	20.81	6.5	even	ok
534.3235	1	C <sub>28</sub> H <sub>45</sub> N <sub>5</sub> NaO <sub>2</sub> Si	534.3235	-4.7	4.5	1	61.71	9.5	even	ok
	2	C <sub>33</sub> H <sub>45</sub> N <sub>3</sub> NaSi	534.3275	2.8	20.0	2	100.00	13.5	even	ok

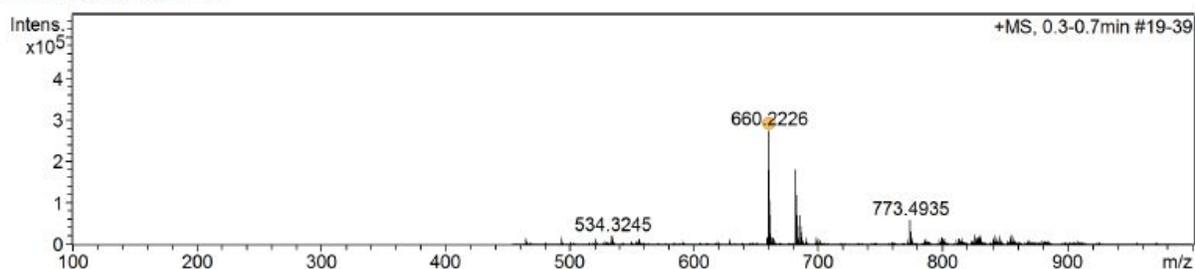
Figure S23. HRMS spectra for compound S2

**Acquisition Parameter**

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Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	460 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



**+MS, 0.3-0.7min #19-39**

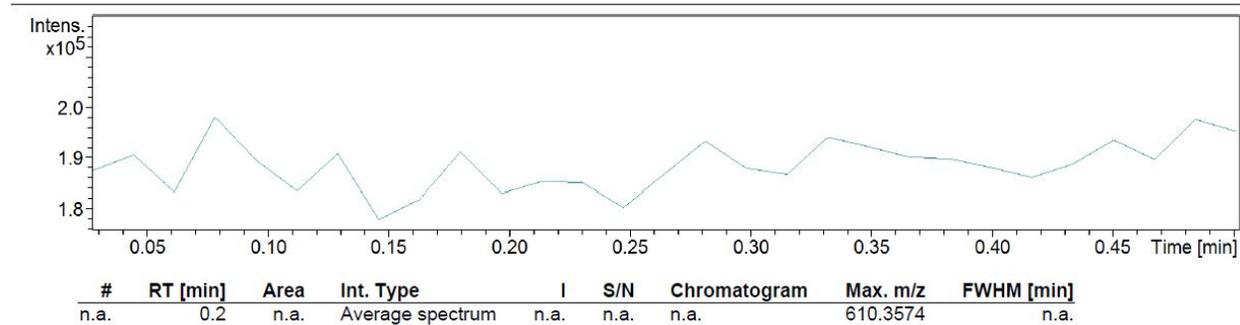


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
660.2226	1	C26H39IN11Si	660.2198	4.1	6.5	1	17.71	13.5	even	ok
	2	C29H47INO6Si	660.2212	2.1	6.8	2	62.49	7.5	even	ok
	3	C30H43IN5O2Si	660.2225	0.1	6.9	3	100.00	12.5	even	ok
	4	C22H43IN11OSi2	660.2230	-0.6	15.8	4	89.45	8.5	even	ok
	5	C21H47IN7O5Si2	660.2216	-1.4	19.6	5	63.89	3.5	even	ok
	6	C25H51INO7Si2	660.2243	2.7	21.5	6	35.86	2.5	even	ok
	7	C26H47IN5O3Si2	660.2257	-4.7	23.4	7	11.00	7.5	even	ok
	8	C35H43IN3Si	660.2265	-6.0	27.5	8	3.84	16.5	even	ok
	9	C24H47IN7OSi3	660.2189	5.5	49.2	9	3.15	7.5	even	ok
	10	C28H51INO3Si3	660.2216	1.5	60.5	10	20.28	6.5	even	ok
	11	C20H51IN7O2Si4	660.2221	-0.8	61.7	11	29.70	2.5	even	ok
	12	C24H55INO4Si4	660.2247	-3.3	71.7	12	7.16	1.5	even	ok
	13	C25H51IN5Si4	660.2261	-5.3	78.0	13	1.60	6.5	even	ok
	14	C27H55INSi5	660.2220	0.8	115.5	14	2.78	5.5	even	ok
	15	C23H59INOSi6	660.2251	-3.9	132.7	15	0.27	0.5	even	ok
	1	C28H44IN5NaO2Si	660.2201	-3.7	5.5	1	30.87	9.5	even	ok
	2	C20H44IN11NaOSi2	660.2206	3.0	16.4	2	45.42	5.5	even	ok
	3	C27H48INNaO6Si	660.2188	-5.7	17.2	3	6.55	4.5	even	ok
	4	C24H48IN5NaO3Si2	660.2233	1.1	17.8	4	100.00	4.5	even	ok

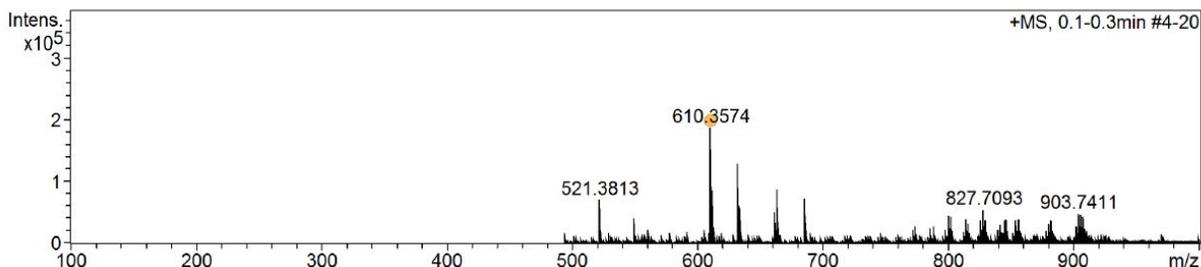
Figure S24. HRMS spectra for compound S3

Acquisition Parameter

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Scan Begin	500 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



+MS, 0.1-0.3min #4-20

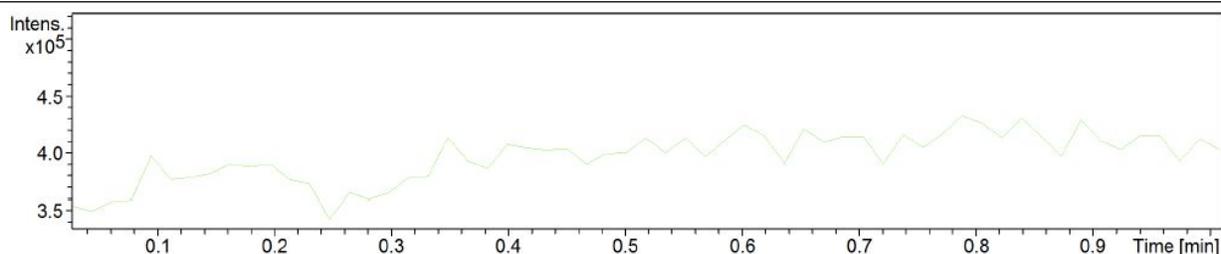


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
610.3574	1	C36H48N5O2Si	610.3572	0.4	6.6	1	100.00	16.5	even	ok
	2	C32H52N5O3Si2	610.3603	4.7	21.3	2	12.57	11.5	even	ok
	3	C30H52N7OSi3	610.3536	6.4	48.2	3	2.20	11.5	even	ok
	1	C34H49N5NaO2Si	610.3548	-4.4	8.1	1	25.60	13.5	even	ok
	2	C30H53N5NaO3Si2	610.3579	-0.8	15.2	2	100.00	8.5	even	ok

Figure S25. HRMS spectra for compound S4

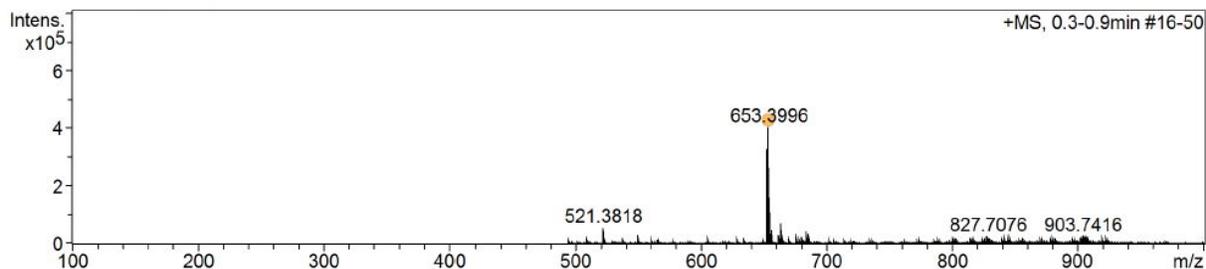
**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
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Scan Begin	500 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.6	n.a.	Average spectrum	n.a.	n.a.	n.a.	653.3996	n.a.

**+MS, 0.3-0.9min #16-50**

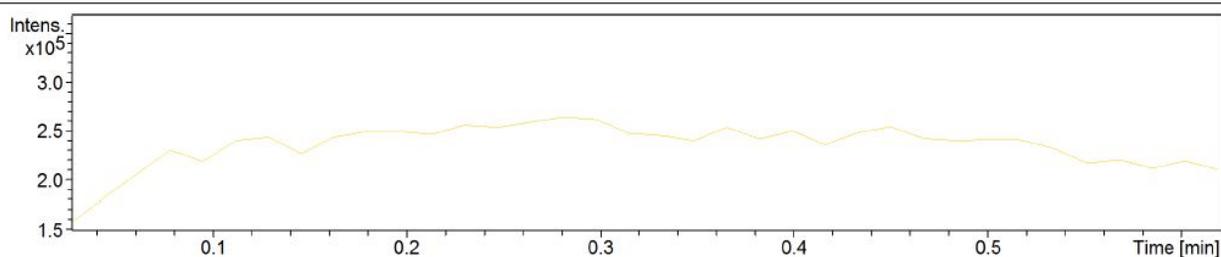


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
653.3996	1	C37H57N2O6Si	653.3980	2.3	34.3	1	63.61	11.5	even	ok
	2	C38H53N6O2Si	653.3994	0.3	44.4	2	100.00	16.5	even	ok
	3	C30H53N12O5Si2	653.3998	0.4	44.6	3	94.88	12.5	even	ok
	4	C33H61N2O7Si2	653.4012	-2.5	48.2	4	39.98	6.5	even	ok
	5	C34H57N6O3Si2	653.4025	-4.5	57.0	5	10.07	11.5	even	ok
	6	C32H57N8OSi3	653.3958	5.8	76.8	6	2.50	11.5	even	ok
	7	C36H61N2O3Si3	653.3984	1.7	88.5	7	15.36	10.5	even	ok
	8	C32H65N2O4Si4	653.4016	-3.1	104.0	8	3.99	5.5	even	ok
	9	C31H69N2OSi6	653.4020	-3.7	156.6	9	0.15	4.5	even	ok
	1	C35H58N2NaO6Si	653.3956	-6.0	23.7	1	10.23	8.5	even	ok
	2	C36H54N6NaO2Si	653.3970	3.9	33.8	2	31.59	13.5	even	ok
	3	C31H62N2NaO7Si2	653.3988	1.2	38.1	3	100.00	3.5	even	ok
	4	C32H58N6NaO3Si2	653.4001	0.9	46.4	4	88.36	8.5	even	ok
	5	C34H62N2NaO3Si3	653.3960	5.4	78.5	5	3.56	7.5	even	ok
	6	C30H66N2NaO4Si4	653.3992	0.6	94.1	6	19.69	2.5	even	ok

Figure S26. HRMS spectra for compound S5

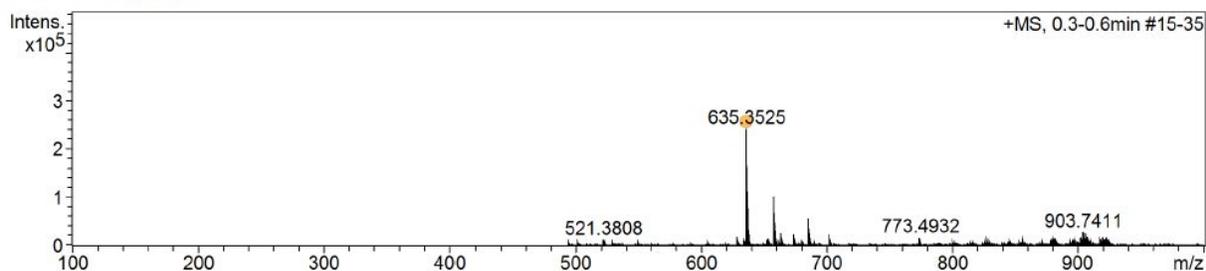
**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	500 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.4	n.a.	Average spectrum	n.a.	n.a.	n.a.	635.3525	n.a.

**+MS, 0.3-0.6min #15-35**

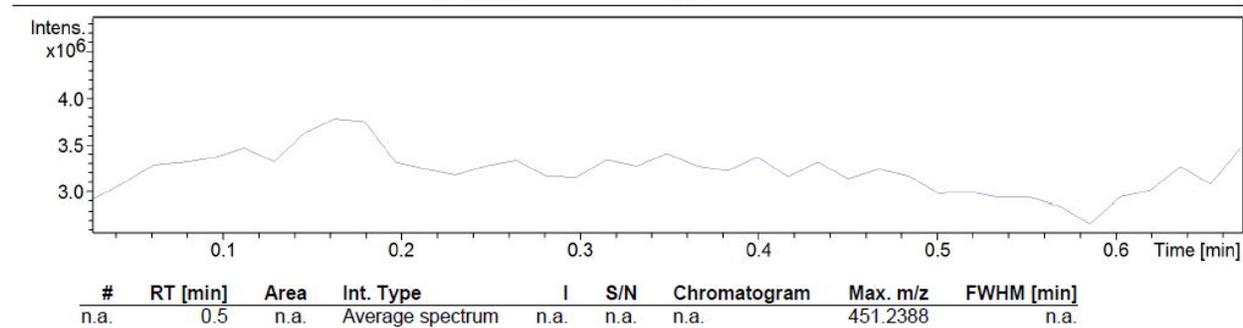


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
635.3525	1	C37H47N6O2Si	635.3524	-0.1	5.1	1	100.00	18.5	even	ok
	2	C36H51N2O6Si	635.3511	-2.2	6.7	2	48.25	13.5	even	ok
	3	C35H55N2O3Si3	635.3515	1.6	56.1	3	21.76	12.5	even	ok
	1	C35H48N6NaO2Si	635.3500	-3.9	6.6	1	100.00	15.5	even	ok

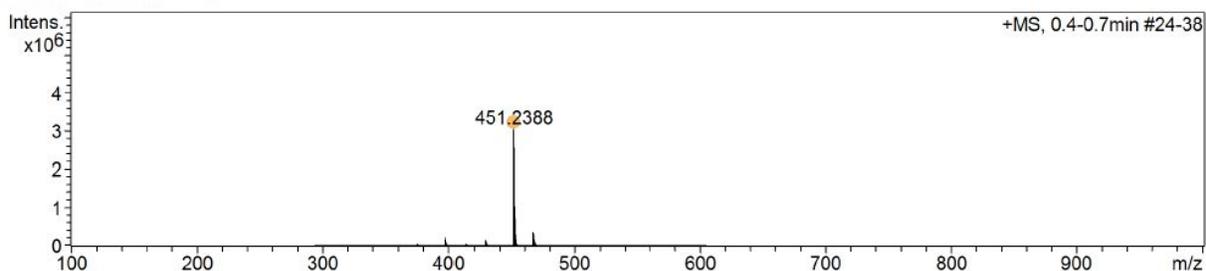
Figure S27. HRMS spectra for compound S6

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	300 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



+MS, 0.4-0.7min #24-38

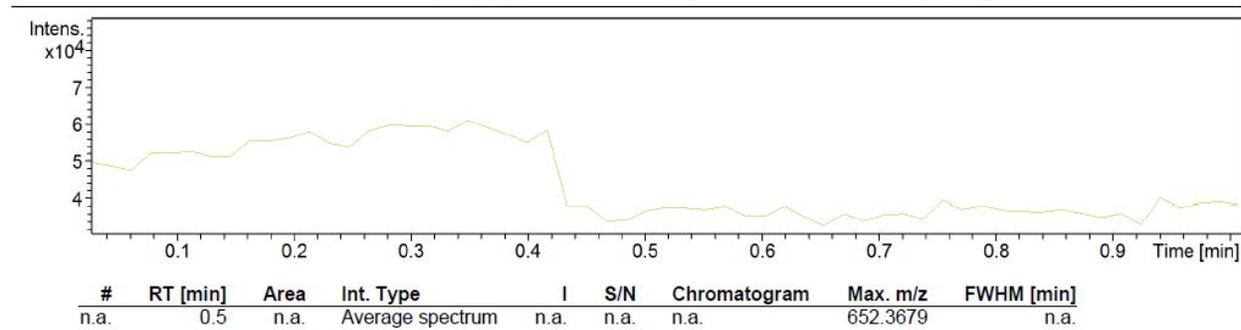


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
451.2388	1	C21H35N4O5Si	451.2371	3.8	7.5	1	55.75	7.5	even	ok
	2	C22H31N8OSi	451.2385	-0.8	17.2	2	100.00	12.5	even	ok
	3	C26H35N2O3Si	451.2411	5.2	29.8	3	21.39	11.5	even	ok
	4	C20H39N4O2Si3	451.2375	-2.8	64.9	4	20.16	6.5	even	ok
	1	C20H32N8NaOSi	451.2361	-6.1	5.9	1	21.99	9.5	even	ok
	2	C24H36N2NaO3Si	451.2387	0.2	18.5	2	100.00	8.5	even	ok
	3	C20H40N2NaO4Si2	451.2419	6.8	30.6	3	12.26	3.5	even	ok

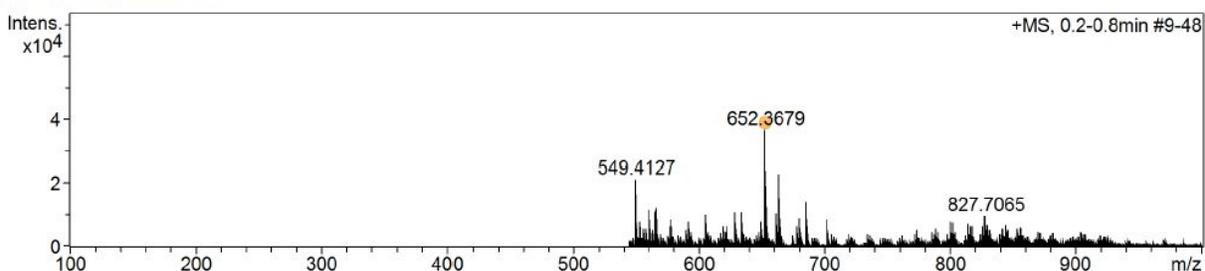
Figure S28. HRMS spectra for compound S7

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	550 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



+MS, 0.2-0.8min #9-48

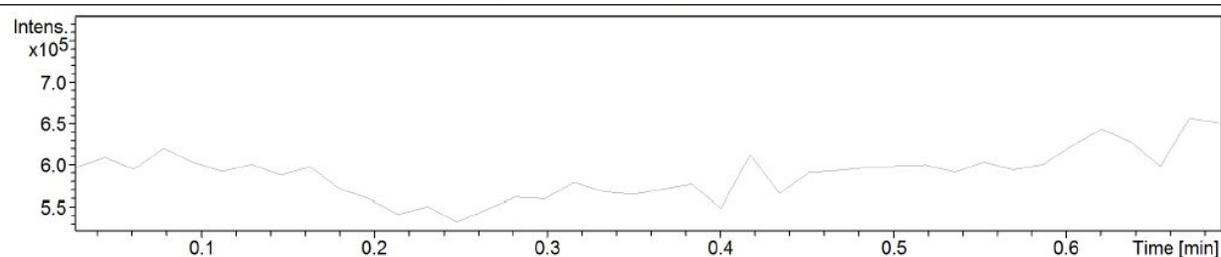


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
652.3679	1	C34H54N5O4Si2	652.3709	4.6	17.7	1	16.56	12.5	even	ok
	2	C43H50N3OSi	652.3718	-6.0	19.0	2	6.28	21.5	even	ok
	3	C30H50N11O2Si2	652.3682	0.5	25.4	3	92.87	13.5	even	ok
	4	C38H50N5O3Si	652.3677	-0.2	26.4	4	100.00	17.5	even	ok
	5	C32H54N7O2Si3	652.3641	-5.7	33.7	5	6.56	12.5	even	ok
	6	C34H46N11OSi	652.3651	-4.3	36.8	6	13.07	18.5	even	ok
	7	C33H58N5OSi4	652.3713	5.3	61.6	7	3.95	11.5	even	ok
	1	C41H51N3NaOSi	652.3694	-2.3	20.6	1	65.42	18.5	even	ok
	2	C32H55N5NaO4Si2	652.3685	-0.9	24.6	2	100.00	9.5	even	ok
	3	C36H51N5NaO3Si	652.3653	3.9	35.1	3	21.25	14.5	even	ok
	4	C31H59N5NaOSi4	652.3689	-1.6	53.6	4	43.88	8.5	even	ok

Figure S29. HRMS spectra for SF-Azo 01

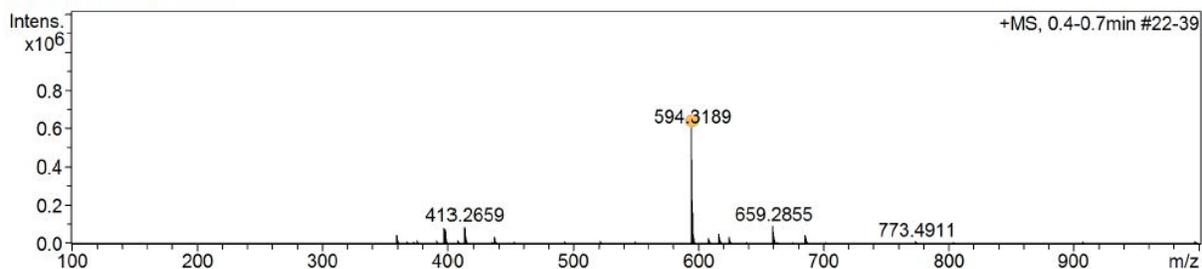
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.5	n.a.	Average spectrum	n.a.	n.a.	n.a.	594.3189	n.a.

+MS, 0.4-0.7min #22-39

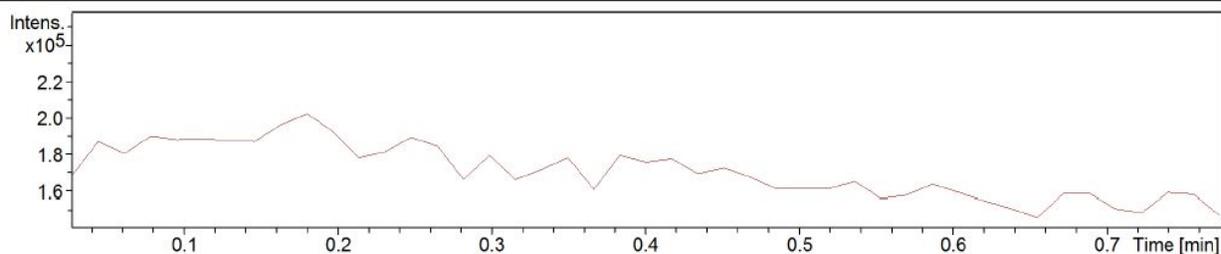


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
594.3189	1	C30H36N13O	594.3160	4.9	3.7	1	17.86	19.5	even	ok
	2	C33H44N3O7	594.3174	-2.6	4.7	2	52.31	13.5	even	ok
	3	C34H40N7O3	594.3187	0.4	9.7	3	100.00	18.5	even	ok
	4	C38H44NO5	594.3214	4.2	22.8	4	18.18	17.5	even	ok
	5	C39H40N5O	594.3227	6.4	33.9	5	3.67	22.5	even	ok
	6	C45H40N	594.3155	5.7	61.0	6	2.55	26.5	even	ok
	1	C32H41N7NaO3	594.3163	-4.4	2.1	1	22.92	15.5	even	ok
	2	C36H45NNaO5	594.3190	0.1	11.3	2	100.00	14.5	even	ok
	3	C31H45N3NaO7	594.3150	6.7	13.7	3	4.68	10.5	even	ok
	4	C37H41N5NaO	594.3203	2.4	22.2	4	39.70	19.5	even	ok

Figure S30. HRMS spectra for SF-Azo 02

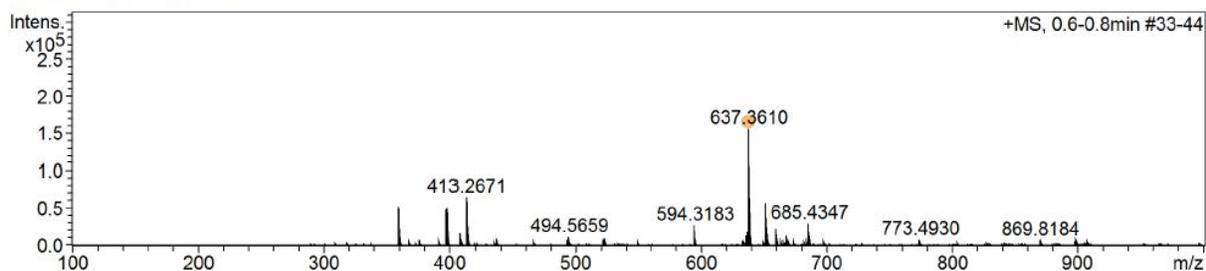
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.7	n.a.	Average spectrum	n.a.	n.a.	n.a.	637.3610	n.a.

+MS, 0.6-0.8min #33-44

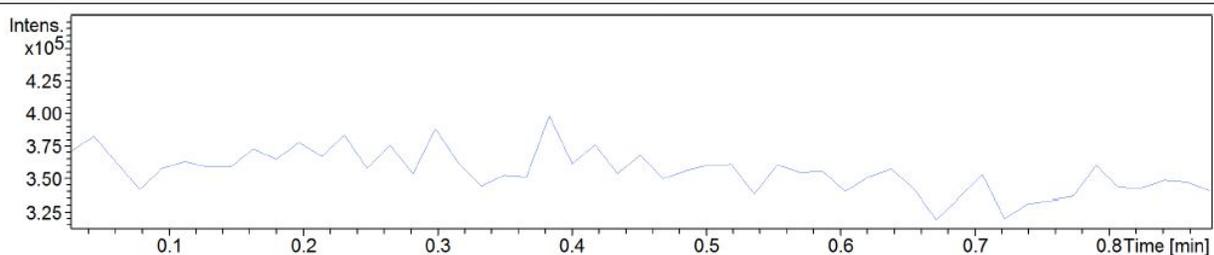


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
637.3610	1	C35H49N4O7	637.3596	2.2	4.3	1	53.55	13.5	even	ok
	2	C32H41N14O	637.3582	4.3	4.9	2	18.46	19.5	even	ok
	3	C36H45N8O3	637.3609	-0.1	8.9	3	100.00	18.5	even	ok
	4	C34H53O11	637.3582	4.3	15.4	4	15.34	8.5	even	ok
	5	C40H49N2O5	637.3636	4.1	22.1	5	15.31	17.5	even	ok
	6	C41H45N6O	637.3649	-6.2	33.3	6	2.97	22.5	even	ok
	7	C47H45N2	637.3577	5.1	60.7	7	2.76	26.5	even	ok
	1	C34H46N8NaO3	637.3585	3.9	2.9	1	26.45	15.5	even	ok
	2	C38H50N2NaO5	637.3612	-0.3	10.4	2	100.00	14.5	even	ok
	3	C33H50N4NaO7	637.3572	-6.0	14.3	3	5.61	10.5	even	ok
	4	C39H46N6NaO	637.3625	-2.4	21.5	4	38.38	19.5	even	ok

Figure S31. HRMS spectra for SF-Azo 03

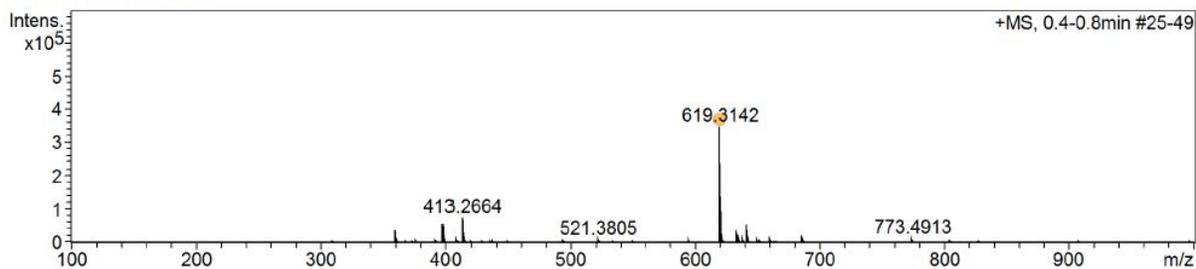
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



#	RT [min]	Area	Int. Type	I	S/N	Chromatogram	Max. m/z	FWHM [min]
n.a.	0.6	n.a.	Average spectrum	n.a.	n.a.	n.a.	619.3142	n.a.

+MS, 0.4-0.8min #25-49

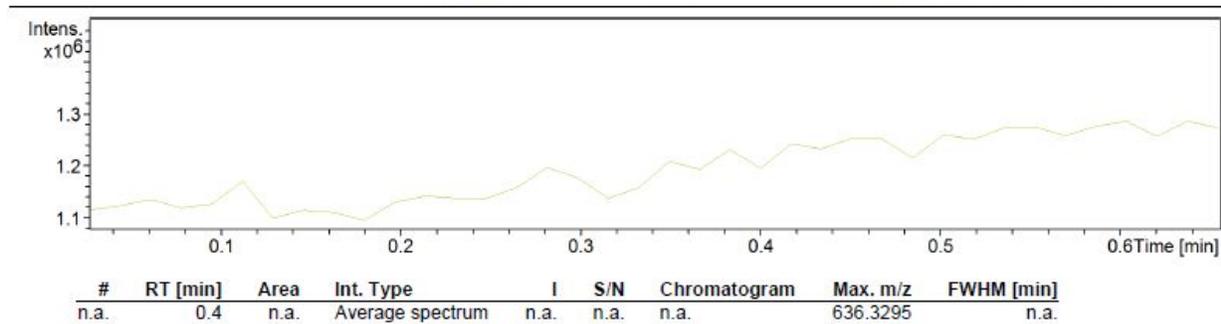


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
619.3142	1	C34H43N4O7	619.3126	-2.5	3.4	1	53.02	15.5	even	ok
	2	C31H35N14O	619.3113	-4.6	5.5	2	17.27	21.5	even	ok
	3	C35H39N8O3	619.3140	-0.3	8.9	3	100.00	20.5	even	ok
	4	C33H47O11	619.3113	-4.6	14.8	4	14.66	10.5	even	ok
	5	C39H43N2O5	619.3166	-4.0	21.9	5	17.79	19.5	even	ok
	6	C40H39N6O	619.3180	6.2	33.2	6	3.56	24.5	even	ok
	7	C46H39N2	619.3108	-5.5	60.4	7	2.60	28.5	even	ok
619.3142	1	C33H40N8NaO3	619.3116	4.2	3.2	1	22.66	17.5	even	ok
	2	C37H44N2NaO5	619.3142	0.1	10.2	2	100.00	16.5	even	ok
	3	C32H44N4NaO7	619.3102	-6.4	14.0	3	4.71	12.5	even	ok
	4	C38H40N6NaO	619.3156	2.3	21.5	4	39.23	21.5	even	ok

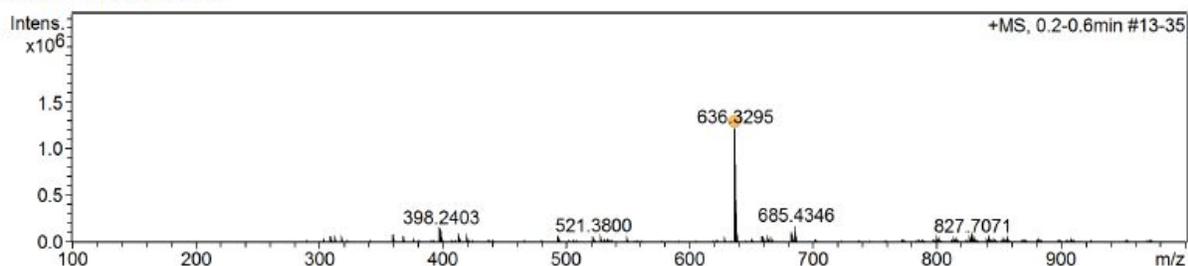
Figure S32. HRMS spectra for SF-Azo 04

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4000 V	Set Dry Heater	200 °C
Scan Begin	100 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



**+MS, 0.2-0.6min #13-35**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
636.3295	1	C32H38N13O2	636.3266	-4.6	11.7	1	20.55	20.5	even	ok
	2	C35H46N3O8	636.3279	-2.5	13.2	2	59.88	14.5	even	ok
	3	C36H42N7O4	636.3293	0.4	24.1	3	100.00	19.5	even	ok
	4	C25H42N13O7	636.3325	-4.6	26.0	4	14.86	11.5	even	ok
	5	C41H42N5O2	636.3333	5.9	48.5	5	3.41	23.5	even	ok
	1	C33H47N3NaO8	636.3255	6.3	2.8	1	19.58	11.5	even	ok
	2	C34H43N7NaO4	636.3269	4.2	12.6	2	65.72	16.5	even	ok
	3	C27H47N7NaO9	636.3327	5.1	25.0	3	28.99	7.5	even	ok
	4	C26H51N3NaO13	636.3314	3.0	36.5	4	70.72	2.5	even	ok
	5	C39H43N5NaO2	636.3309	2.2	36.8	5	100.00	20.5	even	ok