

Isoselenazole Synthesis by Rh-catalyzed Direct Annulation of Benzimidates with Sodium Selenite

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1. Additional Data

Table S1. Optimization study 1 ^[a]

entry	additive	1a (eq.)	Bz ₂ O (eq.)	2a yield ^[b]	3 yield ^[b]
1	-	1.0	2.0	58% (54%)	18%
2	MS 4 Å (25 mg)	1.0	2.0	40%	8%
3	Se (1.0 eq.)	1.0	2.0	51%	6%
4	LiOBz (1.0 eq.)	1.0	2.0	44%	4%
5	BzOH (1.0 eq.)	1.0	2.0	53%	7%
6	AcOH	1.0	2.0	62%	14%
7	H ₂ O	1.0	2.0	18%	22%
8 ^[c]	AcOH	1.0	2.0	54%	6%
9 ^[d]	-	1.0	2.0	55%	10%
10 ^[d]	-	1.0	4.0	65%	8%
11 ^[d]	AcOH	1.0	4.0	71%	2%
12	AcOH	1.0	4.0	57%	4%
13	AcOH (5 eq.)	1.0	4.0	64%	4%
14	-	1.5	2.0	52%	20%
15	-	1.5	3.0	74%	12%
16	AcOH	1.5	3.0	84% (82%)	8%
17	AcOH (4.0 eq.)	1.5	3.0	80%	8%
18	AcOH	1.2	2.4	67%	8%
19	AcOH	1.2	3.0	72%	6%
20	AcOH	1.5	4.0	81%	5%
21	AcOH	1.5	2.0	61%	15%
22	AcOH	1.7	3.4	72%	10%
23	HCOOH	1.5	3.0	8%	50%
24	EtCOOH	1.5	3.0	59%	10%
25	PivOH	1.5	3.0	54%	5%
26	TFA	1.5	3.0	73%	4%

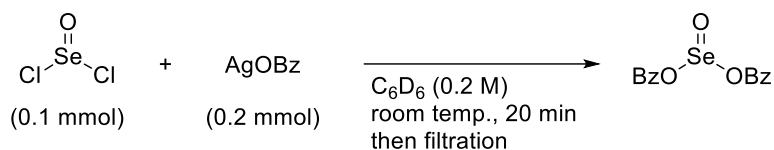
[a] Reaction conditions: **1a**, Na₂SeO₃ (0.1 mmol), [Cp*Rh(MeCN)₃][SbF₆]₂ (0.004 mmol), Bz₂O and additive (0.2 mmol) in PhCF₃ (0.5 mL) at 100 °C for 14 h under N₂. All reagents were premixed at rt for 15 min. [b] NMR yield with CH₂Br₂ as internal standard. Numbers in parathesis are isolated yield. Yield of **2a** was based on Na₂SeO₃ and yield of **3a** was based on **1a**. [c] PhCF₃ (0.3 mL). [d] Na₂SeO₃ (2 eq.).

Table S2. Optimization study 2 ^[a]

entry	temp	solvent	catalyst	2a yield ^[b]	3 yield ^[b]
1	100 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	84% (82%)	8%
2	90 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	68%	13%
3	80 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	45%	17%
4 ^c	80 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	69%	7%
5	60 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	21%	6%
6 ^[c]	60 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	25%	6%
7	100 °C	TCE	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	50%	12%
8	100 °C	toluene	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	65%	16%
9	100 °C	PhCl	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	76%	8%
10	100 °C	1,4-dioxane	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	84% (80%)	13%
11	100 °C	DMF	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	51%	15%
12	100 °C	<i>t</i> -AmOH	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	34%	9%
13	100 °C	TFE	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	40%	14%
14	100 °C	MeCN	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	80%	9%
15	100 °C	CPME	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	54%	33%
16	100 °C	2-MeTHF	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	79%	8%
17	100 °C	DME	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂	71%	8%
18	100 °C	PhCF ₃	[Cp [*] RhCl ₂] ₂	51%	23%
19 ^[d]	100 °C	PhCF ₃	[Cp [*] RhCl ₂] ₂ /AgOTf	58%	25%
20 ^[d]	100 °C	PhCF ₃	[Cp [*] IrCl ₂] ₂ /AgSbF ₆	27%	35%
21 ^[d]	100 °C	PhCF ₃	[Cp ^E RhCl ₂] ₂ /AgSbF ₆	16%	33%
22 ^[d]	100 °C	PhCF ₃	Cp [*] Co(CO)I ₂ /AgSbF ₆	n.d.	54%
23 ^[d]	100 °C	PhCF ₃	[Ru(cymene)Cl ₂] ₂ /AgSbF ₆	6%	39%
24	100 °C	PhCF ₃	Rh ₂ (OAc) ₄	2%	36%
25 ^[e]	100 °C	PhCF ₃	Rh(cod)BF ₄ /dppbz	2%	31%
26	100 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂ (1.0 mol%)	35%	28%
27	100 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂ (2.0 mol%)	55%	22%
28	100 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂ (5.0 mol%)	80%	5%
29	100 °C	PhCF ₃	[Cp [*] Rh(MeCN) ₃][SbF ₆] ₂ (7.5 mol%)	68%	5%

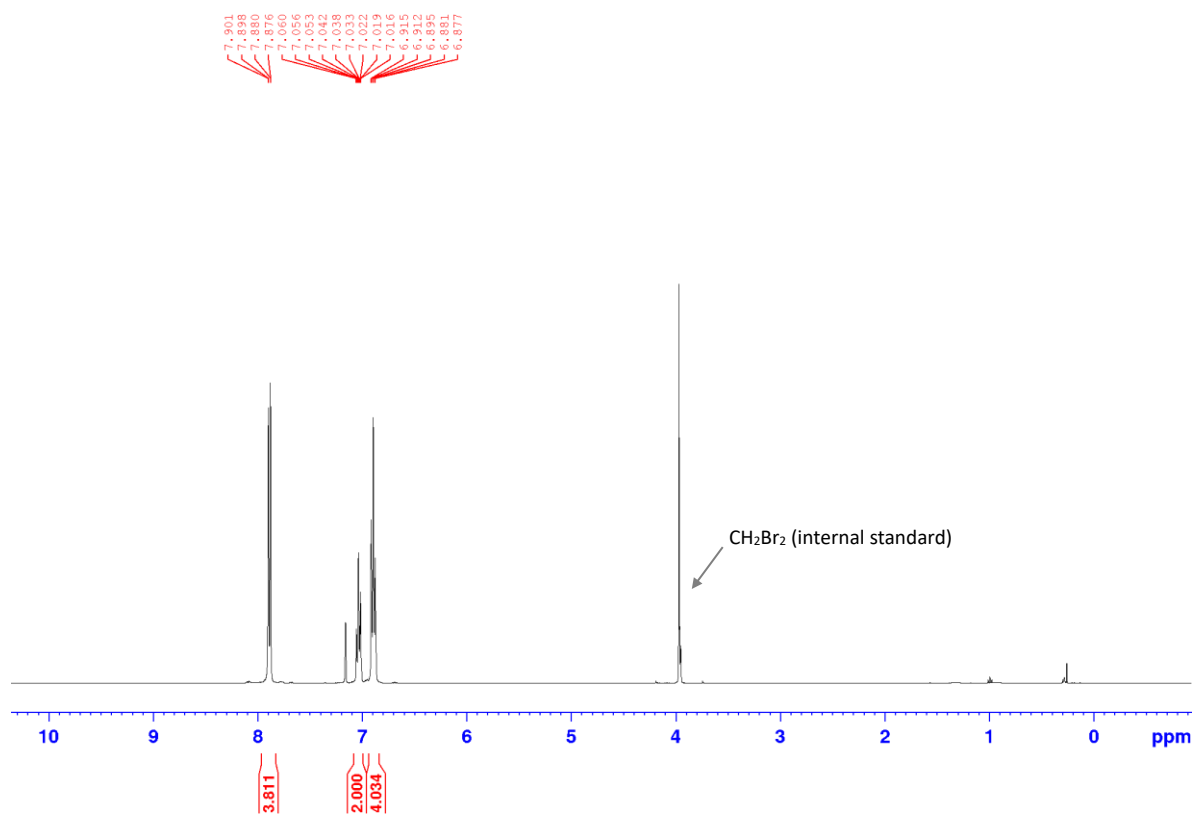
[a] Reaction conditions: **1a** (0.15 mmol), Na₂SeO₃ (0.1 mmol), catalyst (0.004 mmol, based on metal ion), Bz₂O (0.3 mmol) and AcOH (0.2 mmol) in PhCF₃ (0.5 mL) at 100 °C for 14 h under N₂. All reagents were premixed at rt for 15 min. [b] NMR yield with CH₂Br₂ as internal standard. Numbers in parathesis are isolated yield. Yield of **2** was based on Na₂SeO₃ and yield of **3** was based on **1a**. [c] Without AcOH. [d] Silver salt (15 mol%). [e] With dppbz (4.0 mol%).

In situ formation of $\text{SeO}(\text{OBz})_2$

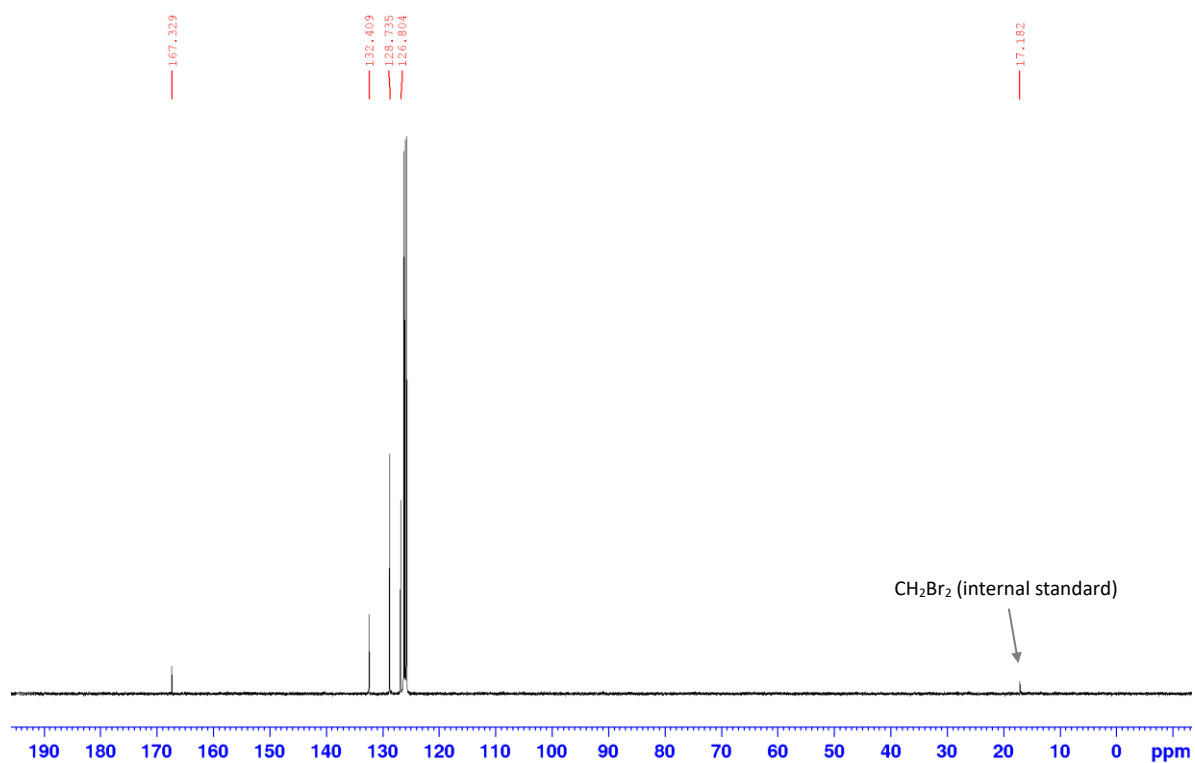


In glove box, to a glass vial were added silver benzoate (45.8 mg, 0.2 mmol) and C_6D_6 (0.5 mL). SeOCl_2 (16.6 mg, 0.1 mmol) was added dropwise, and the mixture was stirred for 20 minutes. The resulting suspension was filtered through a membrane filter eluting with C_6D_6 (0.2 mL). The filtrate was transferred to an NMR tube with an internal standard CH_2Br_2 : ^1H NMR (400 MHz, C_6D_6) δ 7.90-7.87 (m, 4H), 7.06-7.01 (m, 2H), 6.92-6.87 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6) δ 167.3, 132.4, 128.7, 126.8 (one peak may overlapped).

^1H NMR of the filtrate (400 MHz, C_6D_6)

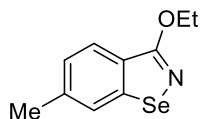


^{13}C NMR of the filtrate (100 MHz, C_6D_6)



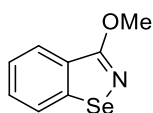
3. Product Identification Data

3-ethoxy-6-methylbenzo[*d*][1,2]selenazole (**2a**)



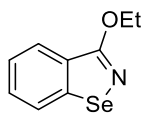
Purified by preparative TLC (*n*-hexane/EtOAc = 3/1), white solid (19.8 mg, 82% yield), m.p. 64.3-65.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.59 (s, 1H), 7.18 (dd, *J* = 8.0, 0.8 Hz, 1H), 4.57 (q, *J* = 7.2 Hz, 2H), 2.46 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 149.8, 139.7, 127.3, 126.6, 125.1, 124.0, 63.6, 21.8, 14.8; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₂NOSe 242.0079; Found 242.0077.

3-methoxybenzo[*d*][1,2]selenazole (**2b**)



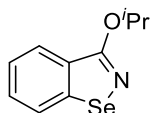
Known compound.¹ Purified by preparative TLC (*n*-hexane/EtOAc = 3/1), colorless oil (15.5 mg, 73% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (ddd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 7.83 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.51 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.40 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 4.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.3, 149.5, 129.00, 128.98, 125.4, 124.9, 124.0, 55.1.

3-ethoxybenzo[*d*][1,2]selenazole (**2c**)



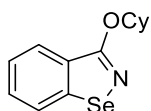
Known compound.¹ Purified by preparative TLC (*n*-hexane/EtOAc = 10/1), colorless oil (16.5 mg, 73% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (ddd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 7.83 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.40 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 4.60 (q, *J* = 7.2 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 149.4, 129.4, 129.1, 125.6, 124.9, 124.1, 63.8, 14.9.

3-isopropoxybenzo[*d*][1,2]selenazole (**2d**)



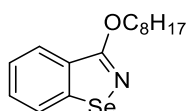
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless oil (17.2 mg, 72% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.88 (ddd, *J* = 8.0, 1.2, 0.8 Hz, 1H), 7.82 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.49 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.39 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 5.44 (septet, *J* = 6.0 Hz, 1H), 1.46 (d, *J* = 6.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 149.3, 129.9, 129.0, 125.7, 124.8, 124.0, 70.8, 22.4; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₂NOSe 242.0079; Found 242.0077.

3-(cyclohexyloxy)benzo[*d*][1,2]selenazole (**2e**)



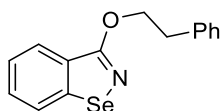
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless oil (23.2 mg, 83% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.49 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.42–7.35 (m, 1H), 5.20 (tt, *J* = 8.8, 4.0 Hz, 1H), 2.18–2.07 (m, 2H), 1.89–1.77 (m, 2H), 1.73–1.55 (m, 3H), 1.54–1.41 (m, 2H), 1.41–1.30 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 149.3, 130.0, 129.0, 125.8, 124.8, 124.0, 75.7, 32.0, 25.8, 24.0; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₃H₁₆NOSe 282.0392; Found 282.0388.

3-(octyloxy)benzo[*d*][1,2]selenazole (**2f**)



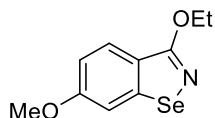
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless oil (22.1 mg, 71% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (ddd, *J* = 8.0, 1.2, 0.4 Hz, 1H), 7.83 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.50 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.40 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 4.53 (t, *J* = 6.8 Hz, 2H), 1.94–1.77 (m, 2H), 1.55–1.44 (m, 2H), 1.43–1.18 (m, 8H), 0.89 (t, *J* = 6.8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 149.4, 129.4, 129.1, 125.6, 124.9, 124.1, 68.1, 32.0, 29.5, 29.4, 29.2, 26.2, 22.8, 14.3; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₅H₂₂NOSe 312.0861; Found 312.0867.

3-phenethoxybenzo[*d*][1,2]selenazole (**2g**)



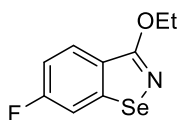
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless oil (20.8 mg, 69% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (ddd, *J* = 8.0, 0.8, 0.4 Hz, 1H), 7.82 (dt, *J* = 8.0, 0.8 Hz, 1H), 7.49 (ddd, *J* = 8.0, 7.2, 1.2 Hz, 1H), 7.39 (ddd, *J* = 8.0, 7.2, 0.8 Hz, 1H), 7.34–7.29 (m, 4H), 7.26–7.21 (m, 1H), 4.75 (t, *J* = 6.8 Hz, 2H), 3.19 (t, *J* = 6.8 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 149.5, 138.4, 129.3, 129.2, 129.1, 128.6, 126.6, 125.6, 125.0, 124.1, 68.4, 35.7; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₅H₁₄NOSe 304.0235; Found 304.0234.

3-ethoxy-6-methoxybenzo[*d*][1,2]selenazole (**2h**)



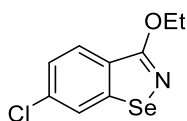
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless crystal (19.5 mg, 76% yield), m.p. 95.6–97.0 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.8 Hz, 1H), 7.33–7.18 (m, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 161.0, 151.4, 126.3, 123.3, 114.5, 106.7, 63.6, 55.8, 14.9; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₂NO₂Se 258.0028; Found 258.0029.

3-ethoxy-6-fluorobenzo[*d*][1,2]selenazole (**2i**)



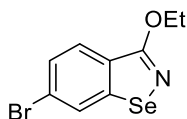
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), white solid (19.4 mg, 79% yield), m.p. 72.0–73.7 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.8 Hz, 1H), 7.33–7.18 (m, 1H), 6.96 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.56 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 1.48 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6 (d, *J* = 252.6 Hz), 163.3, 151.03 (d, *J* = 9.5 Hz), 127.05 (d, *J* = 9.9 Hz), 126.06 (d, *J* = 1.5 Hz), 113.94 (d, *J* = 24.6 Hz), 110.62 (d, *J* = 25.0 Hz), 64.0, 14.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -111.4; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₉H₉FNOSe 245.9828; Found 245.9830.

6-chloro-3-ethoxybenzo[*d*][1,2]selenazole (**2j**)



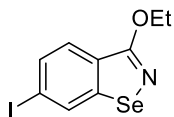
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), white solid (20.8 mg, 80% yield), m.p. 83.2–84.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 2.0 Hz, 1H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.36 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 150.7, 136.2, 128.0, 126.4, 125.9, 123.8, 64.0, 14.8; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₉H₉ClNOSe 261.9532; Found 261.9535.

6-bromo-3-ethoxybenzo[*d*][1,2]selenazole (**2k**)



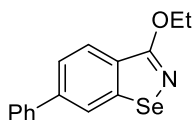
Known compound.¹ Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), white solid (22.4 mg, 73% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.98 (d, *J* = 1.6 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.51 (dd, *J* = 8.4, 1.6 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 151.1, 128.5, 128.3, 126.8, 126.6, 124.5, 64.0, 14.8.

3-ethoxy-6-iodobenzo[*d*][1,2]selenazole (**2l**)



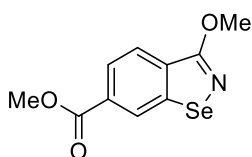
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), white solid (23.3 mg, 66% yield), m.p. 106.3–107.3 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, *J* = 1.2, 0.4 Hz, 1H), 7.70 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.59 (dd, *J* = 8.4, 0.4 Hz, 1H), 4.57 (q, *J* = 7.2 Hz, 2H), 1.48 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 151.4, 134.0, 132.7, 128.8, 126.7, 96.6, 64.0, 14.8; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₉H₉INOSe 353.8889; Found 353.8881.

3-ethoxy-6-phenylbenzo[*d*][1,2]selenazole (**2m**)



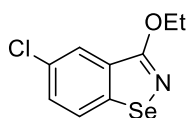
Known compound.¹ Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless oil (25.4 mg, 84% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, *J* = 1.6, 0.8 Hz, 1H), 7.93 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.69–7.61 (m, 2H), 7.61 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.51–7.45 (m, 2H), 7.43–7.37 (m, 1H), 4.61 (q, *J* = 7.2 Hz, 2H), 1.51 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 150.2, 142.4, 140.4, 129.1, 128.4, 128.1, 127.7, 125.7, 124.7, 122.4, 63.8, 14.9.

methyl 3-methoxybenzo[d][1,2]selenazole-6-carboxylate (**2n**)



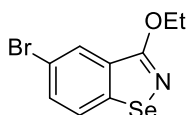
Purified by preparative TLC (*n*-hexane/EtOAc = 3/1) and GPC (CHCl₃), white solid (19.8 mg, 73% yield), m.p. 124.5–125.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.53 (dd, *J* = 1.2, 0.4 Hz, 1H), 8.06 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.92 (dd, *J* = 8.4, 0.8 Hz, 1H), 4.19 (s, 3H), 3.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.7, 164.0, 149.6, 131.8, 130.6, 126.1, 125.7, 125.4, 55.5, 52.7; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₀NO₃Se 271.9820; Found 271.9821.

5-chloro-3-ethoxybenzo[d][1,2]selenazole (**2o**)



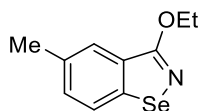
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1), white solid (20.7 mg, 79% yield), m.p. 74.1–75.1 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.87 (dd, *J* = 2.0, 0.4 Hz, 1H), 7.73 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.45 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 147.6, 131.5, 130.7, 129.5, 125.4, 125.0, 64.1, 14.8; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₉H₉ClNOSe 261.9532; Found 261.9530.

5-bromo-3-ethoxybenzo[d][1,2]selenazole (**2p**)



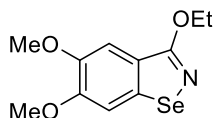
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1), white solid (22.3 mg, 73% yield), m.p. 94.0–94.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.03 (dd, *J* = 2.0, 0.4 Hz, 1H), 7.68 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.58 (dd, *J* = 8.4, 2.0 Hz, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 1.49 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.9, 148.2, 132.1, 131.1, 128.5, 125.4, 119.0, 64.1, 14.8; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₉H₉BrNOSe 305.9027; Found 305.9025.

5-methyl-3-ethoxybenzo[d][1,2]selenazole (**2q**)



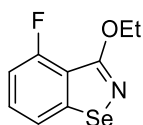
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), colorless oil (16.4 mg, 68% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.84–7.61 (m, 2H), 7.40–7.28 (m, 1H), 4.59 (q, *J* = 7.2 Hz, 2H), 2.47 (s, 3H), 1.49 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 146.3, 135.0, 130.8, 129.7, 125.5, 123.7, 63.7, 21.2, 14.9; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₀H₁₂NOS₂ 242.0079, Found 242.0078.

3-ethoxy-5,6-dimethoxybenzo[d][1,2]selenazole (**2r**)



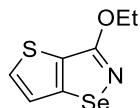
Purified by preparative TLC (*n*-hexane/EtOAc = 3/1) and GPC (CHCl₃), white solid (18.0 mg, 63% yield), m.p. 131.9–132.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.25 (s, 1H), 7.23 (s, 1H), 4.58 (q, *J* = 7.2 Hz, 2H), 3.969 (s, 3H), 3.968 (s, 3H), 1.50 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 151.8, 148.3, 142.5, 122.2, 106.0, 105.2, 63.7, 56.3, 56.2, 14.9; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₁₁H₁₄NO₃Se 288.0133; Found 288.0130.

3-ethoxy-4-fluorobenzo[d][1,2]selenazole (**2s**)



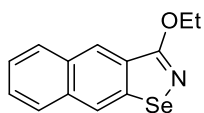
Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), white solid (9.5 mg, 39% yield), m.p. 65.6–66.6 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.42 (td, *J* = 8.0, 4.8 Hz, 1H), 7.04 (ddd, *J* = 10.4, 8.0, 0.8 Hz, 1H), 4.59 (q, *J* = 7.2 Hz, 2H), 1.50 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.56 (d, *J* = 5.2 Hz), 160.62 (d, *J* = 261.1 Hz), 152.72 (d, *J* = 2.4 Hz), 130.23 (d, *J* = 7.5 Hz), 119.94 (d, *J* = 4.6 Hz), 118.17 (d, *J* = 15.3 Hz), 111.45 (d, *J* = 20.3 Hz), 64.2, 14.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -114.4; HRMS (APCI) *m/z*: [M+H]⁺ Calcd for C₉H₉FNOS₂ 245.9828; Found 245.9826.

3-ethoxythieno[2,3-*d*][1,2]selenazole (**2t**)



Known compound.¹ Purified by preparative TLC (*n*-hexane/EtOAc = 10/1), white solid (10.7 mg, 46% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 4.8 Hz, 1H), 7.29–7.22 (m, 1H), 4.54 (q, *J* = 7.2 Hz, 2H), 1.46 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 153.6, 133.1, 128.7, 122.1, 64.2, 14.9.

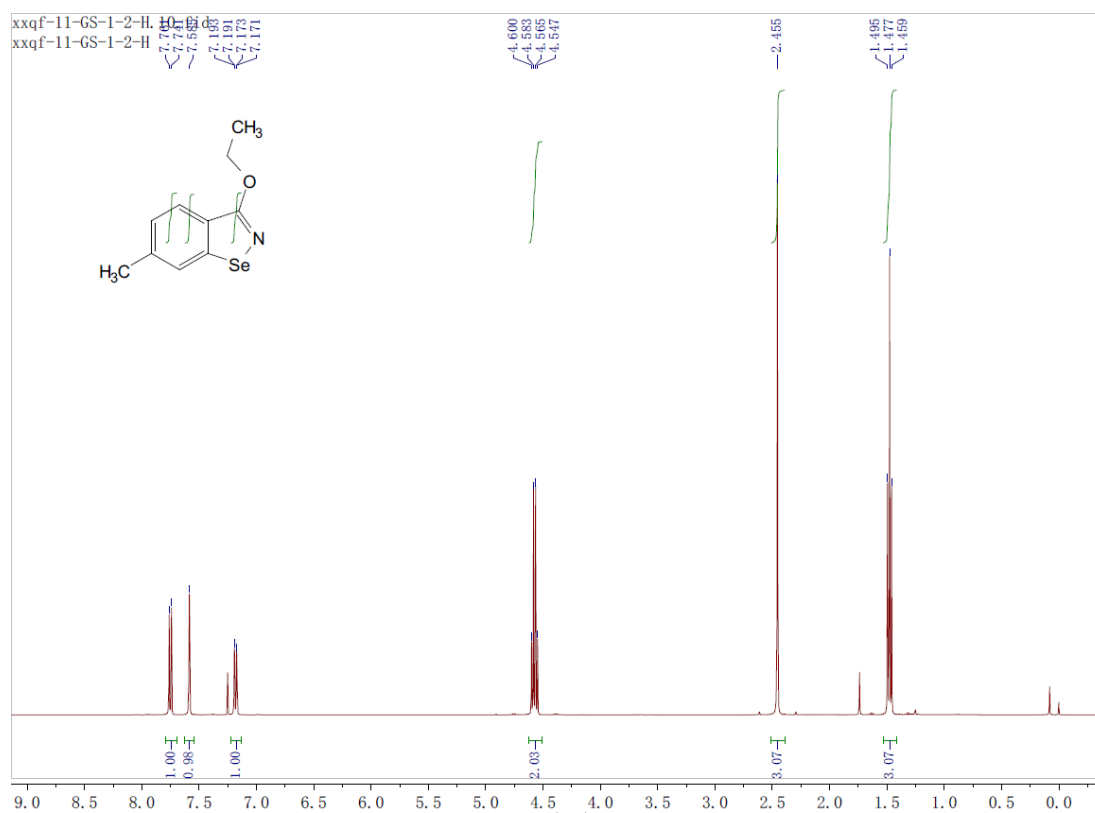
3-ethoxynaphtho[2,3-*d*][1,2]selenazole (**2u**)



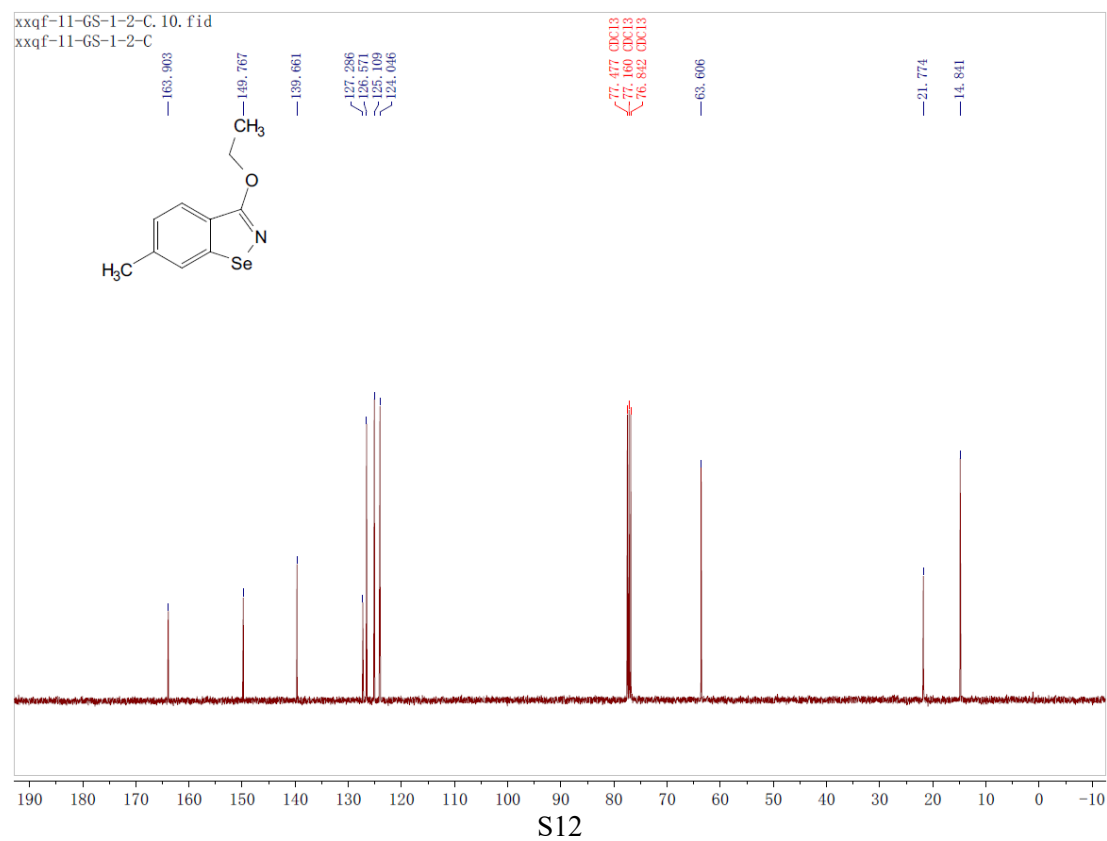
Known compound.¹ Purified by preparative TLC (*n*-hexane/EtOAc = 10/1) and GPC (CHCl₃), white solid (21.6 mg, 78% yield); ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 8.21 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.59 (ddd, *J* = 8.0, 6.4, 1.2 Hz, 1H), 7.50 (ddd, *J* = 8.4, 6.8, 1.2 Hz, 1H), 4.66 (q, *J* = 7.2 Hz, 2H), 1.54 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 142.8, 133.7, 130.8, 129.4, 129.0, 127.8, 127.3, 125.7, 125.4, 122.2, 64.0, 14.9.

3. Copy of NMR Spectra

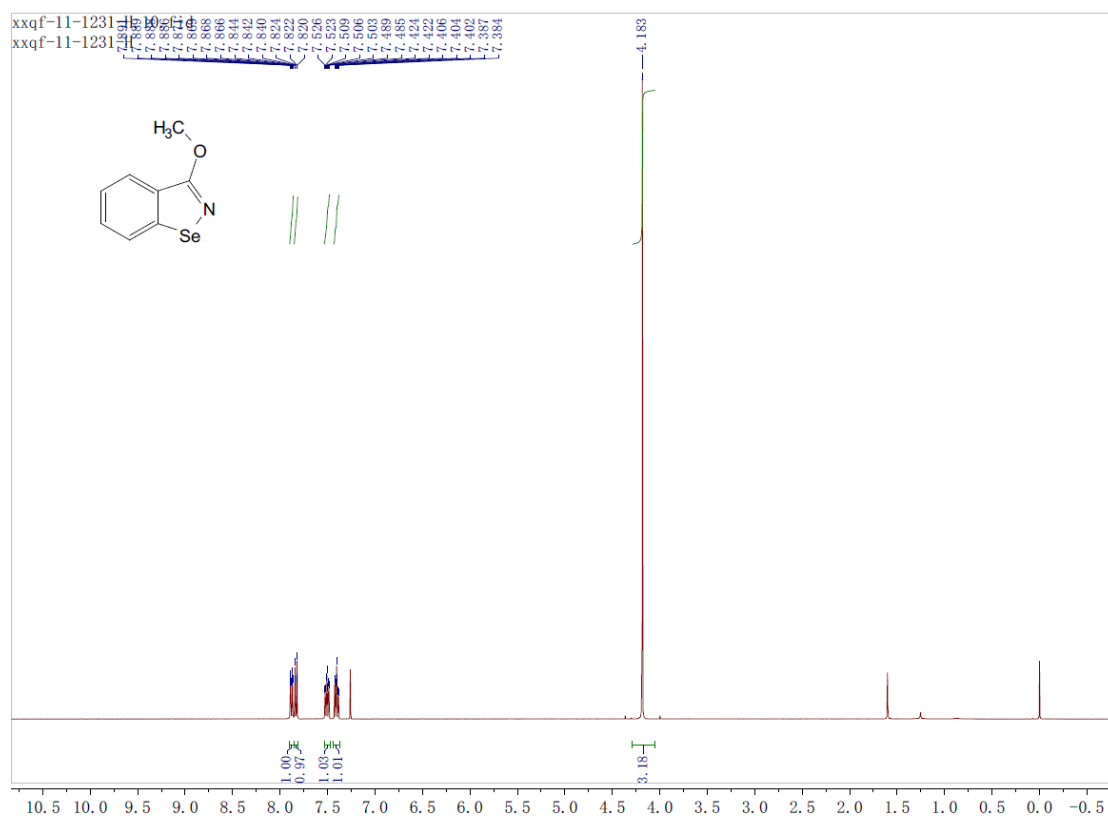
^1H NMR of **2a** (400 MHz, CDCl_3)



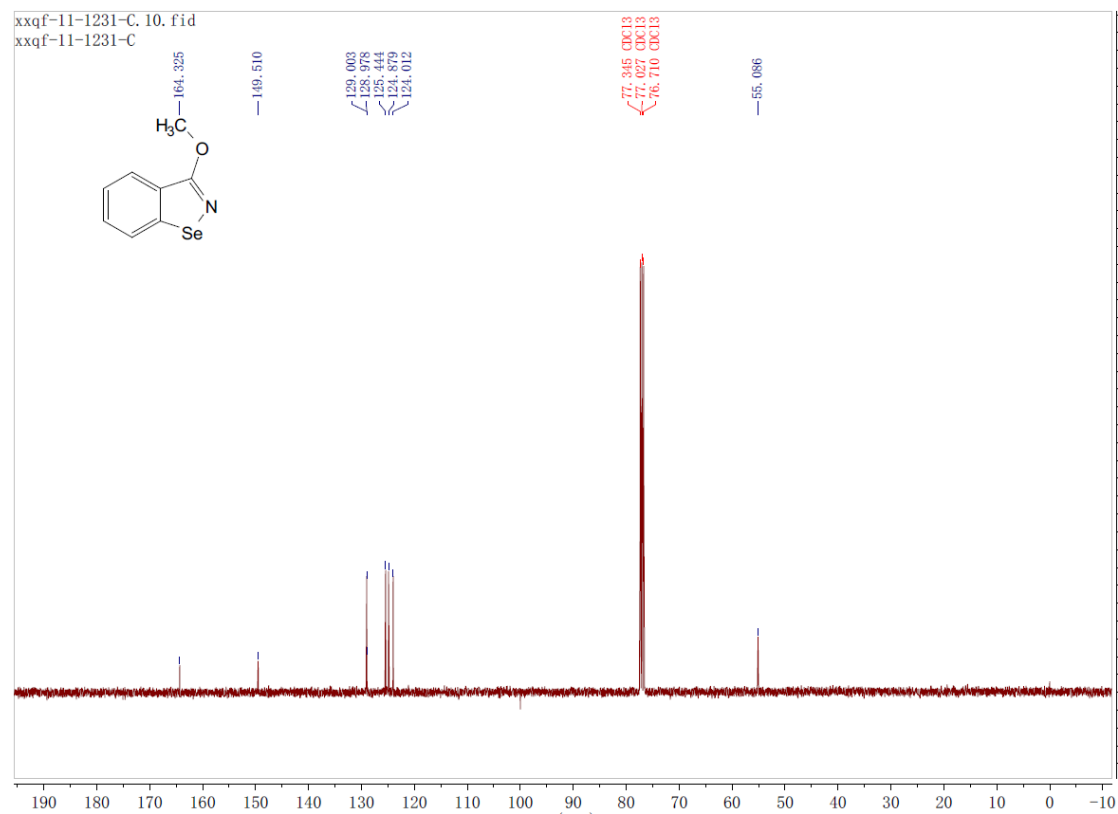
^{13}C NMR of **2a** (100 MHz, CDCl_3)



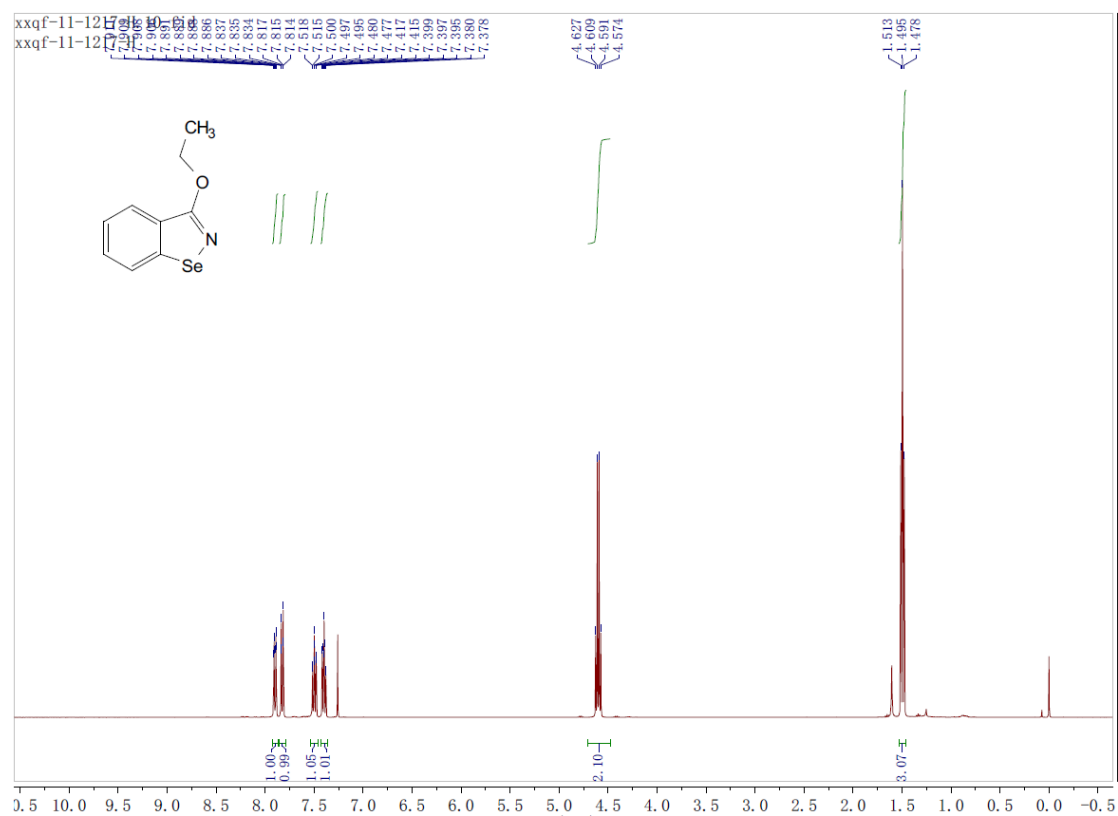
^1H NMR of **2b** (400 MHz, CDCl_3)



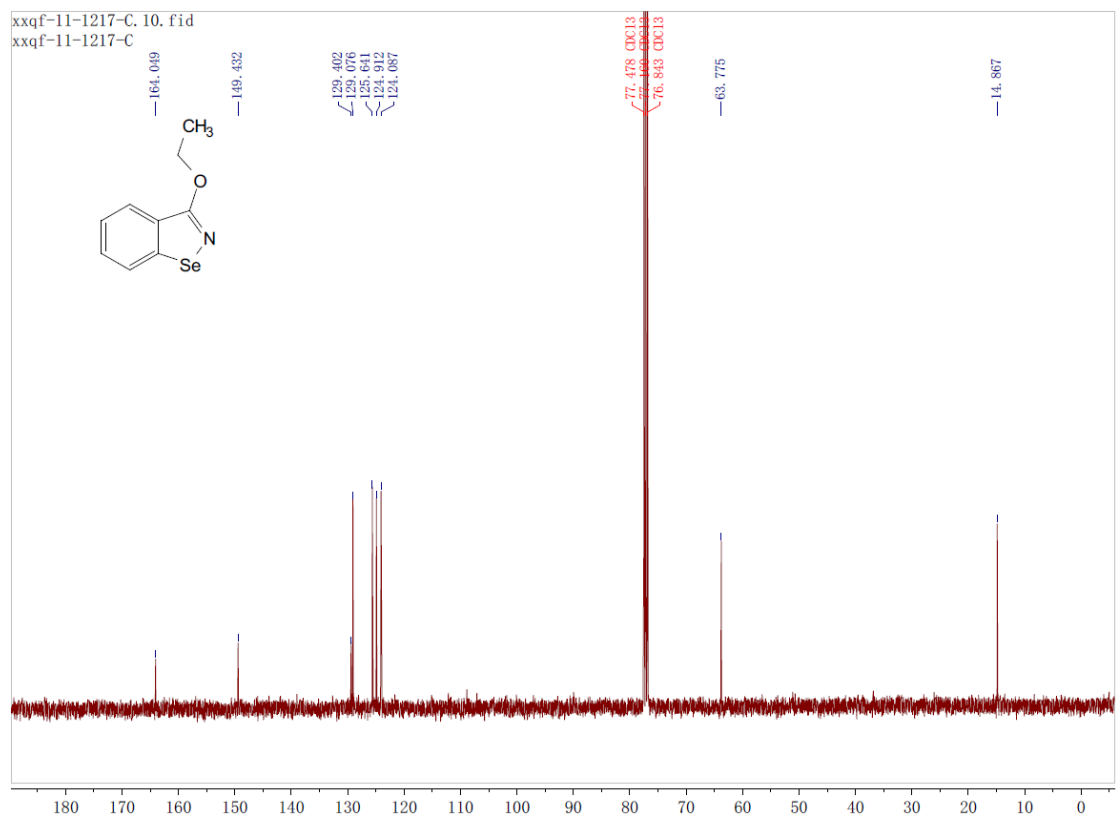
^{13}C NMR of **2b** (100 MHz, CDCl_3)

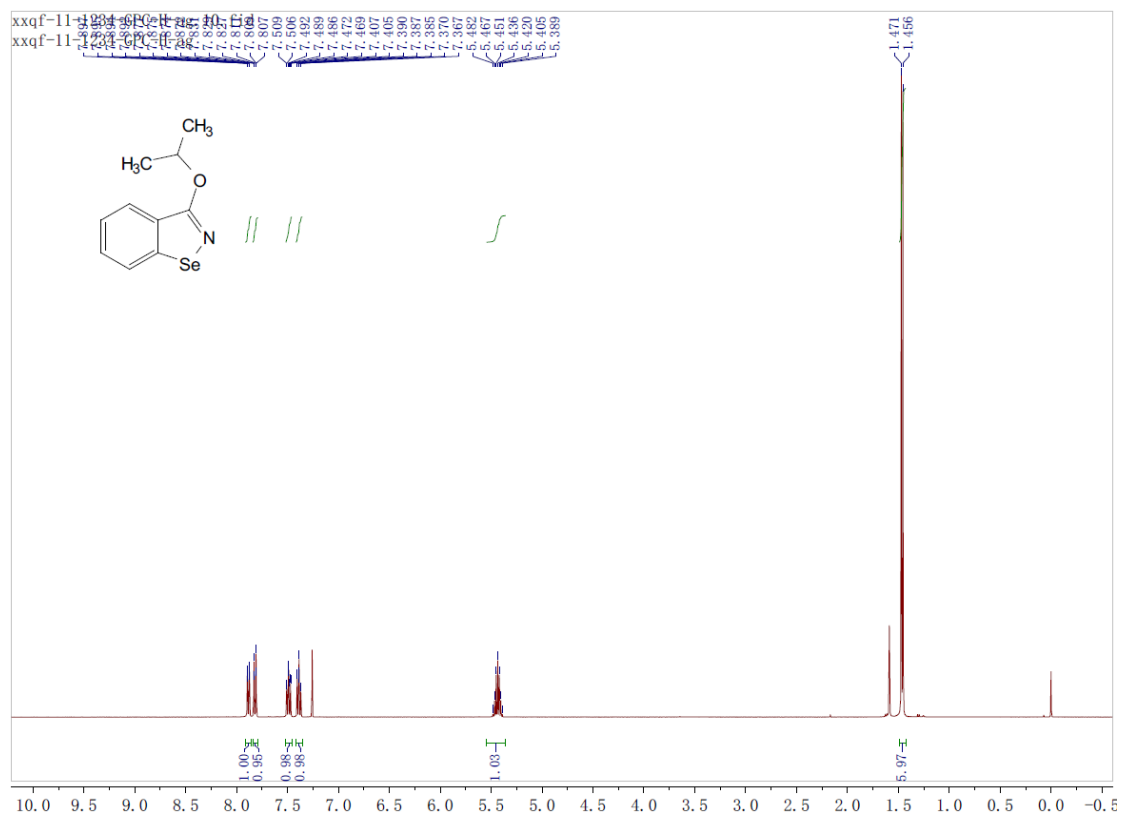
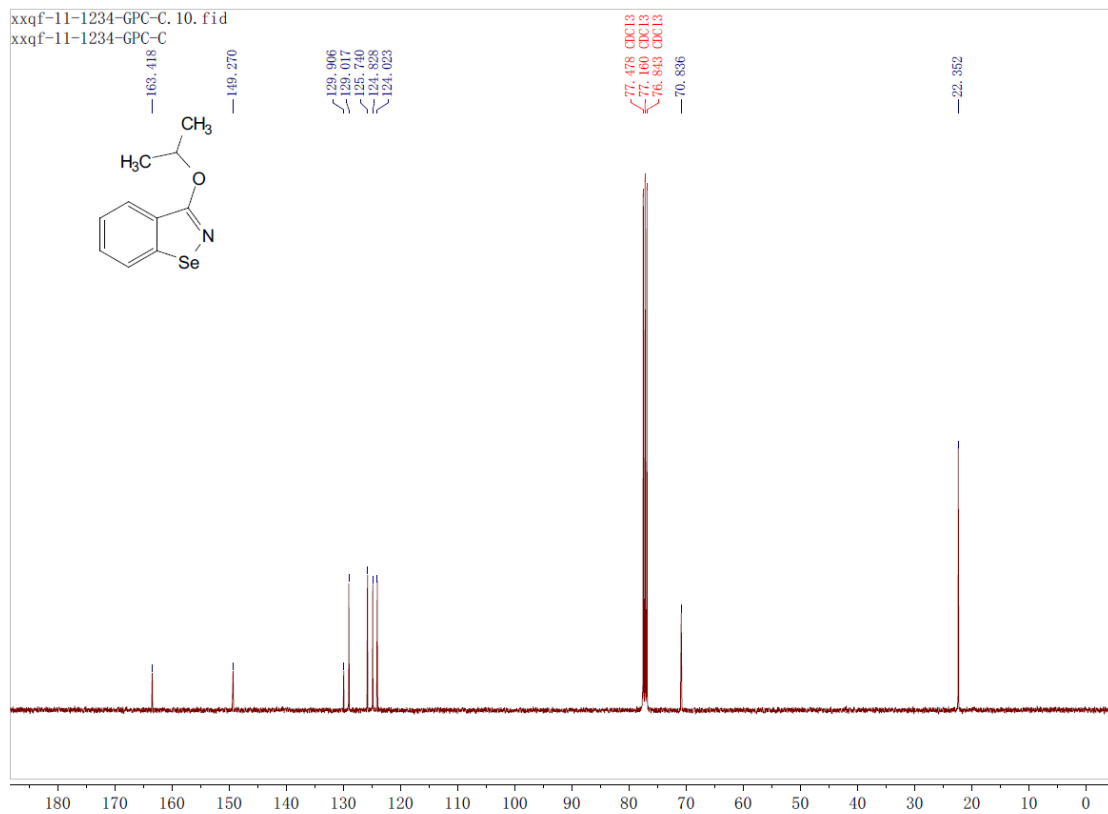


^1H NMR of **2c** (400 MHz, CDCl_3)

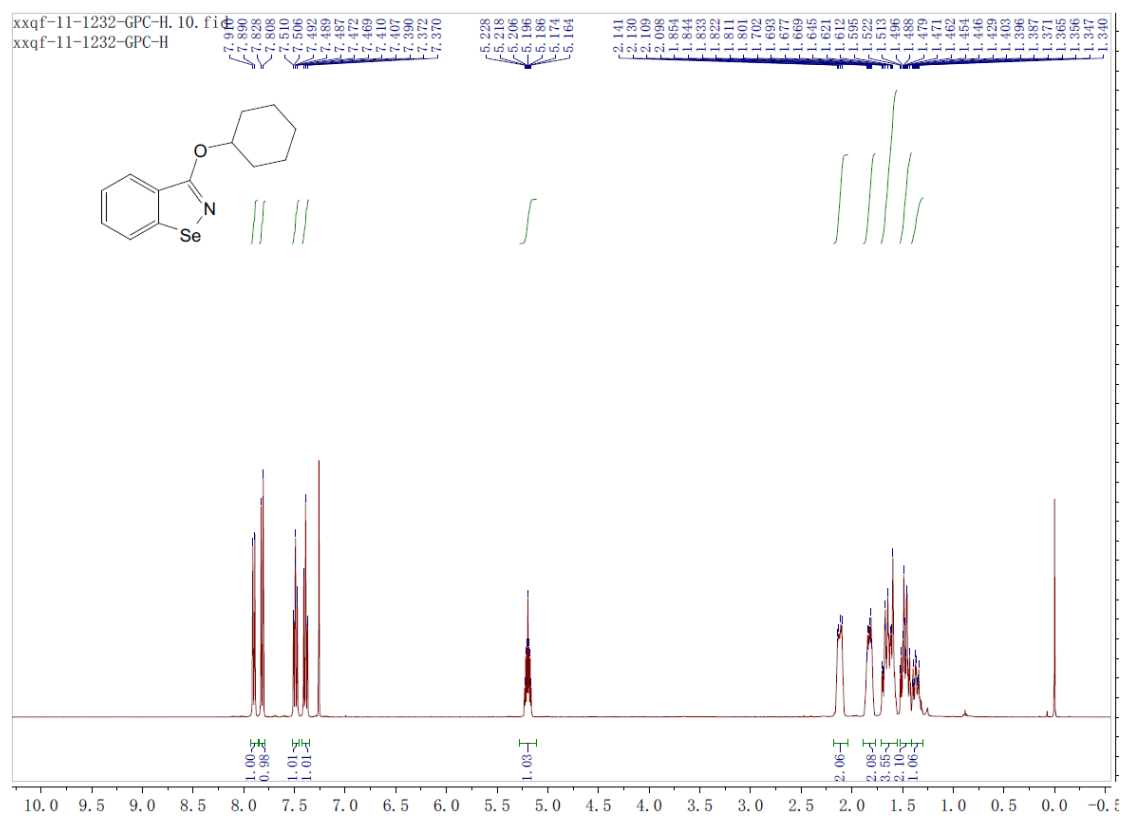


^{13}C NMR of **2c** (100 MHz, CDCl_3)

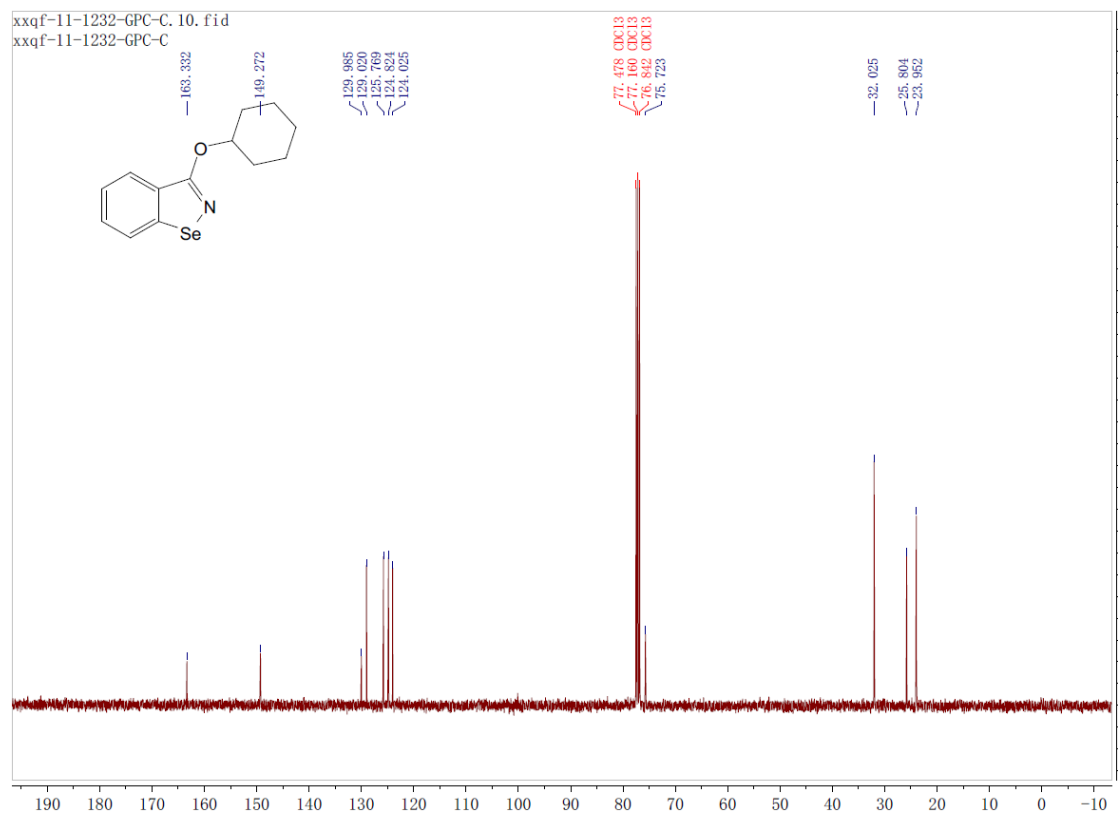


¹H NMR of **2d** (400 MHz, CDCl₃) ^{13}C NMR of **2d** (100 MHz, CDCl_3)

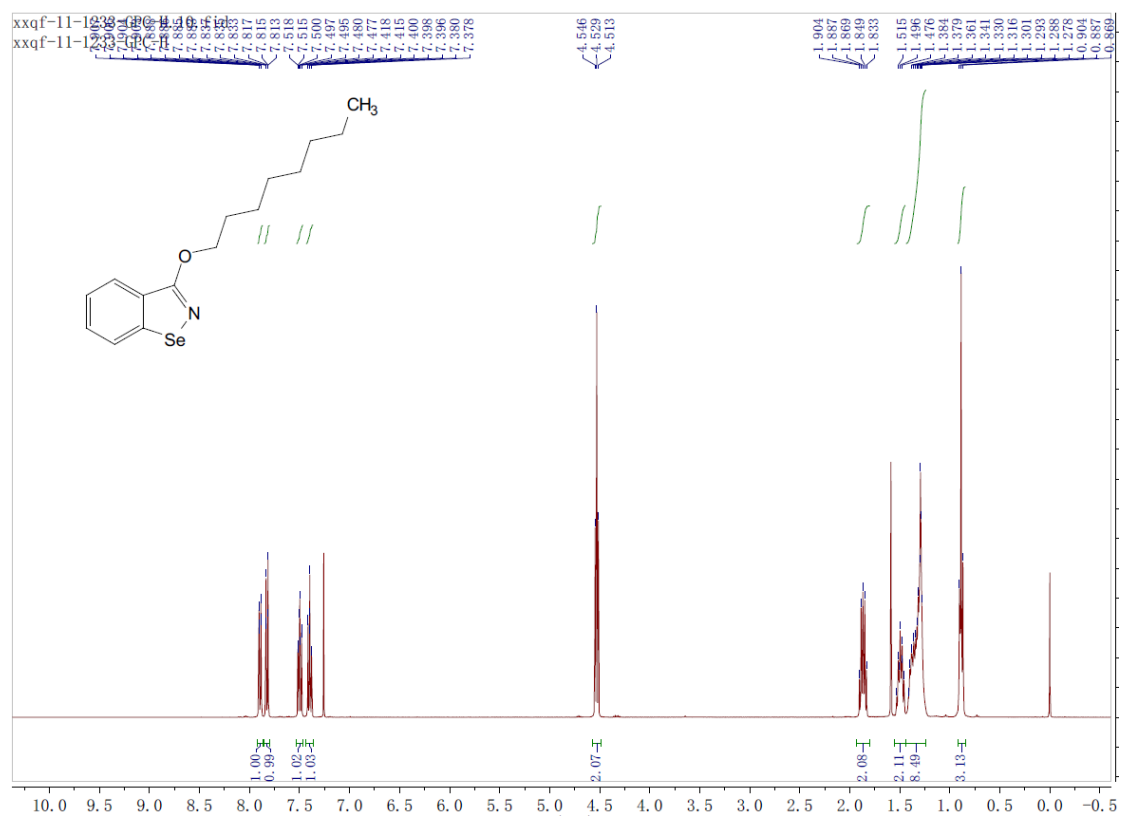
^1H NMR of **2e** (400 MHz, CDCl_3)



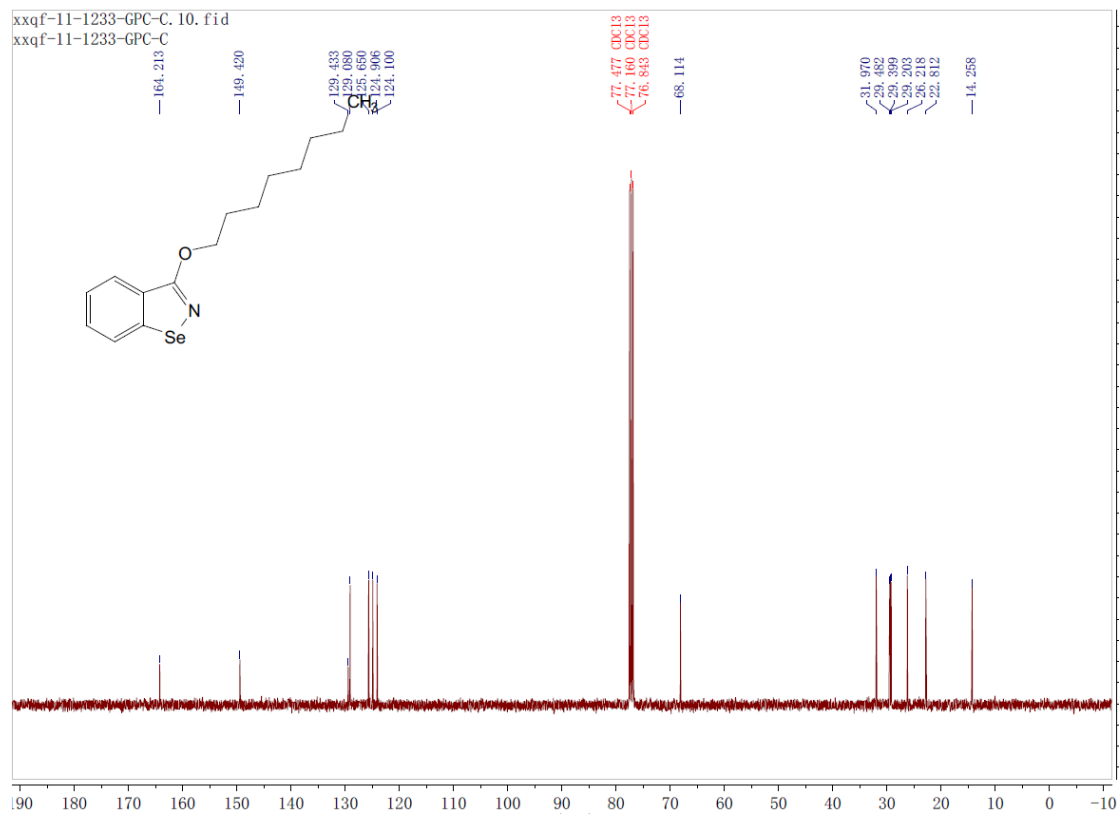
^{13}C NMR of **2e** (100 MHz, CDCl_3)



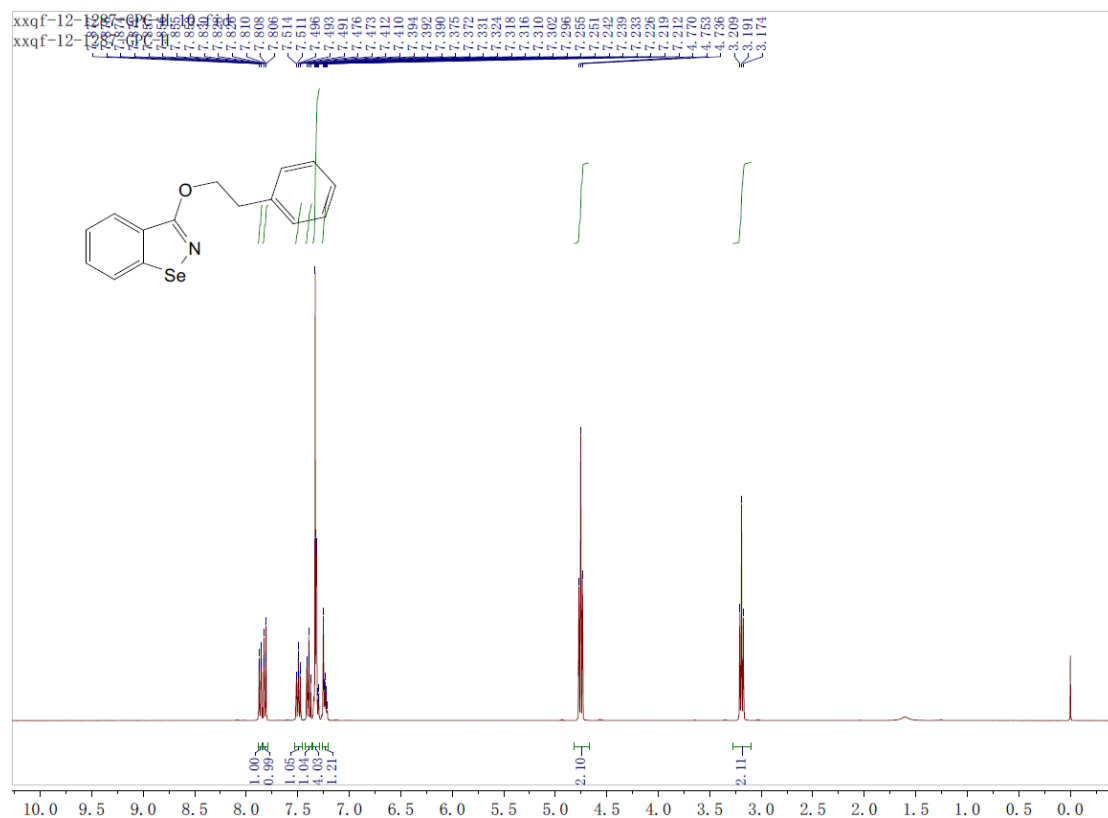
^1H NMR of **2f** (400 MHz, CDCl_3)



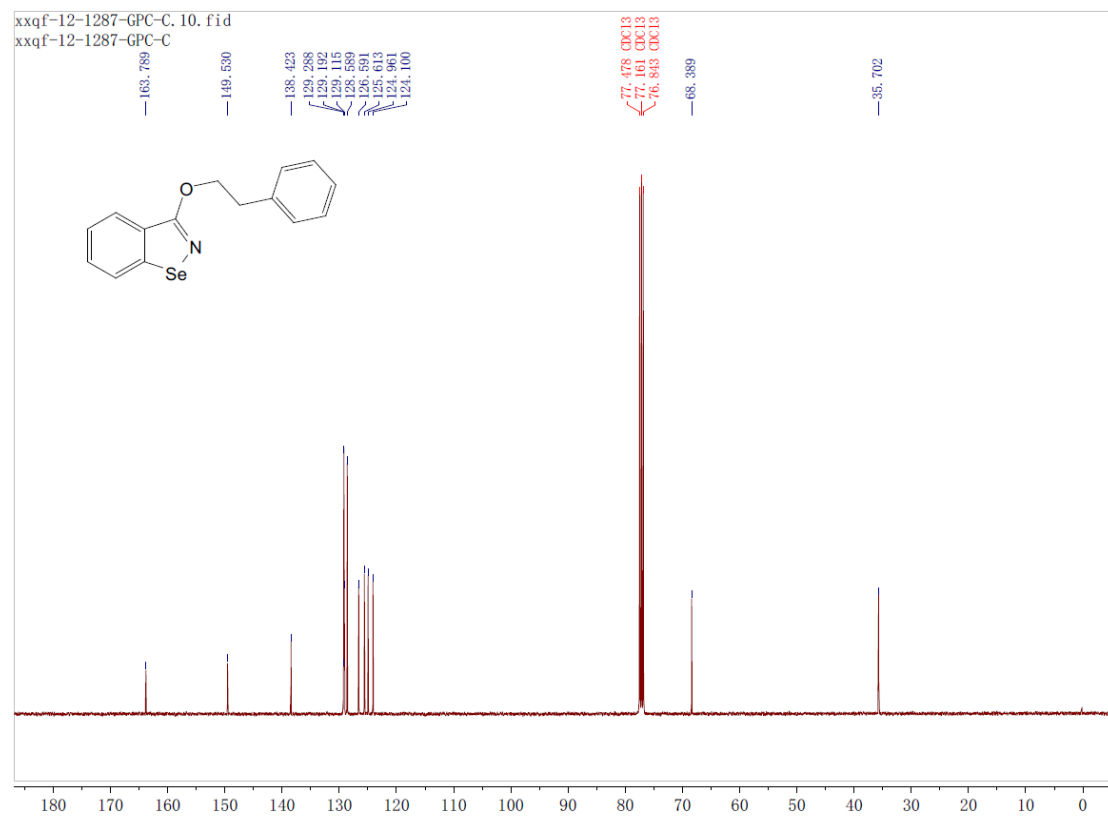
^{13}C NMR of **2f** (100 MHz, CDCl_3)



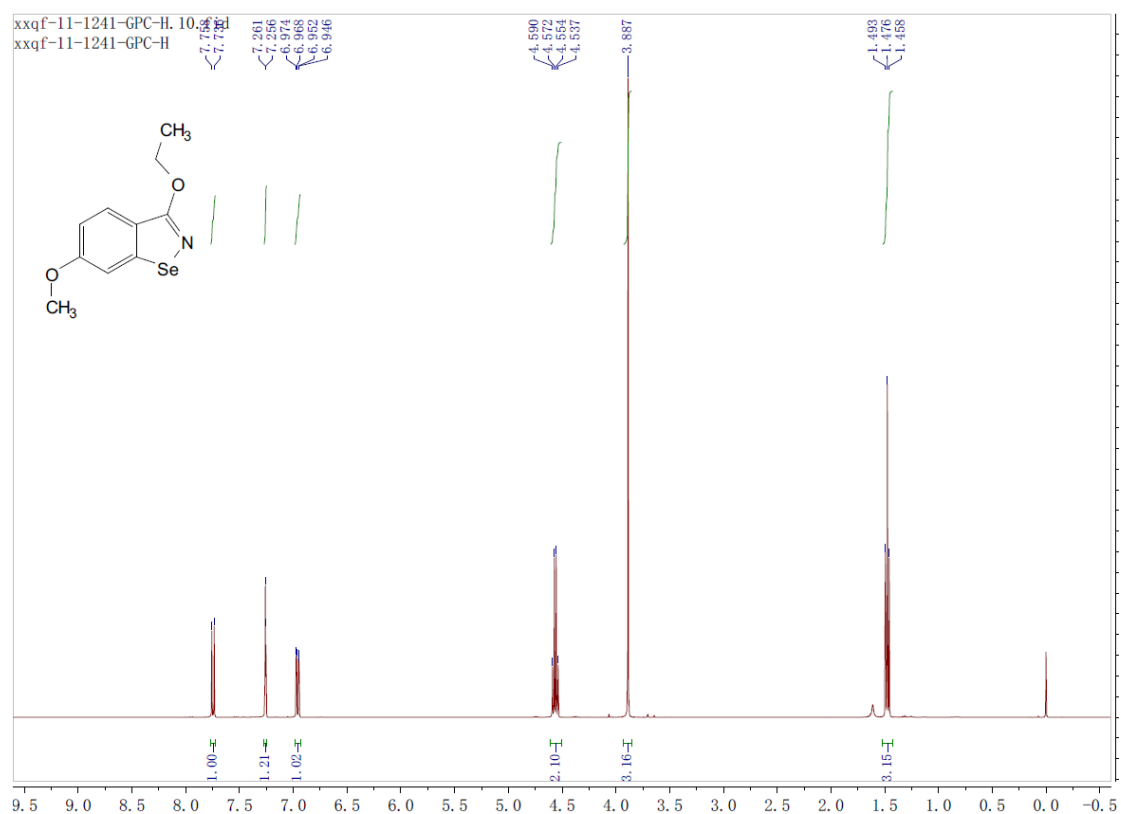
^1H NMR of **2g** (400 MHz, CDCl_3)



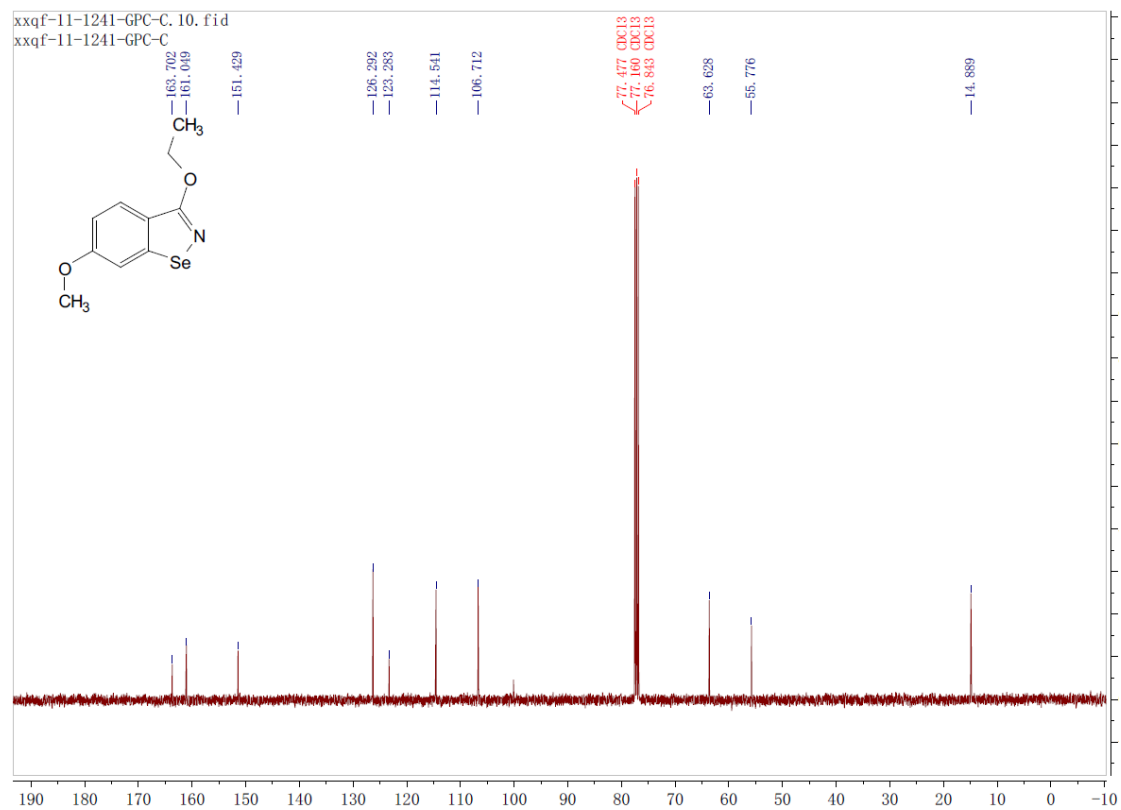
^{13}C NMR of **2g** (100 MHz, CDCl_3)

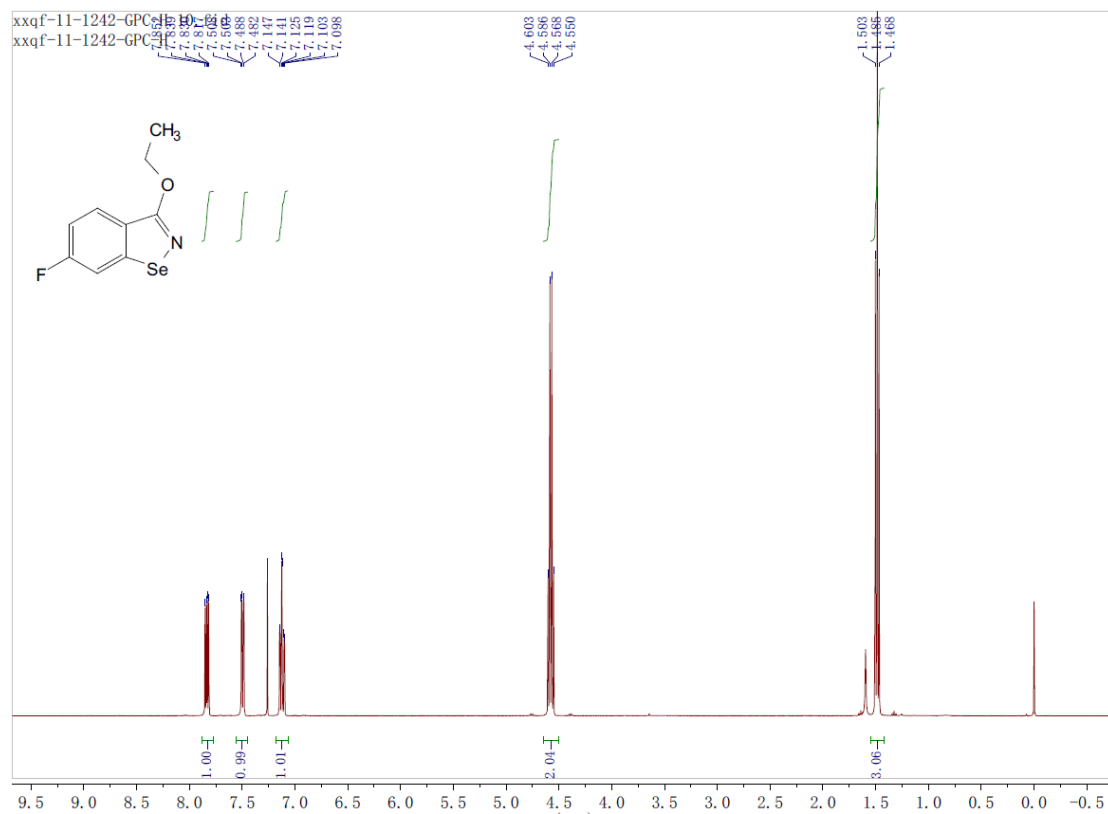
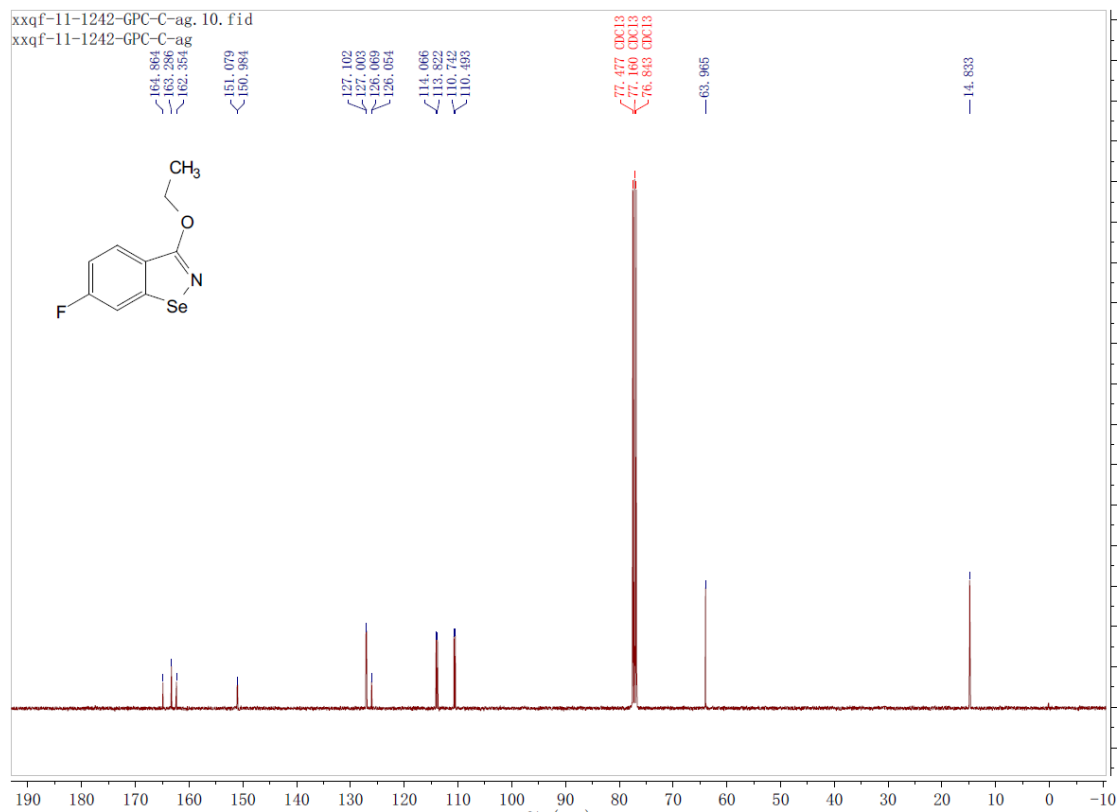


^1H NMR of **2h** (400 MHz, CDCl_3)

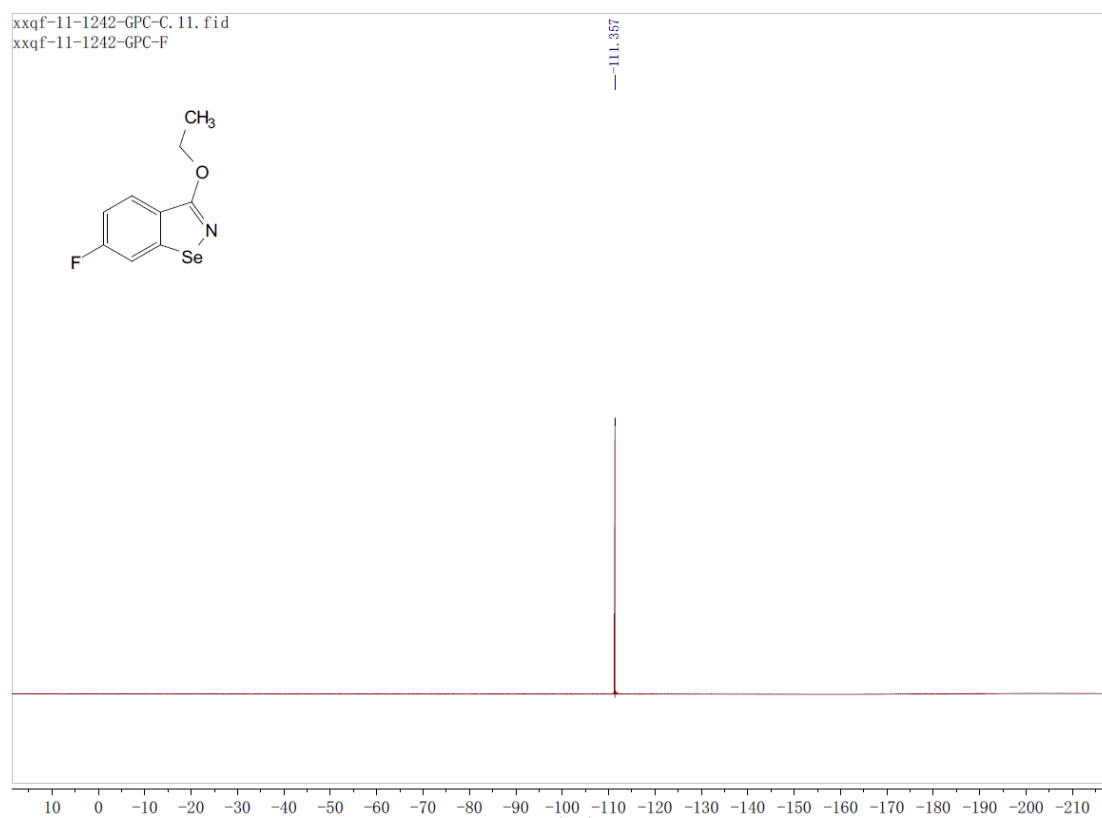


^{13}C NMR of **2h** (100 MHz, CDCl_3)

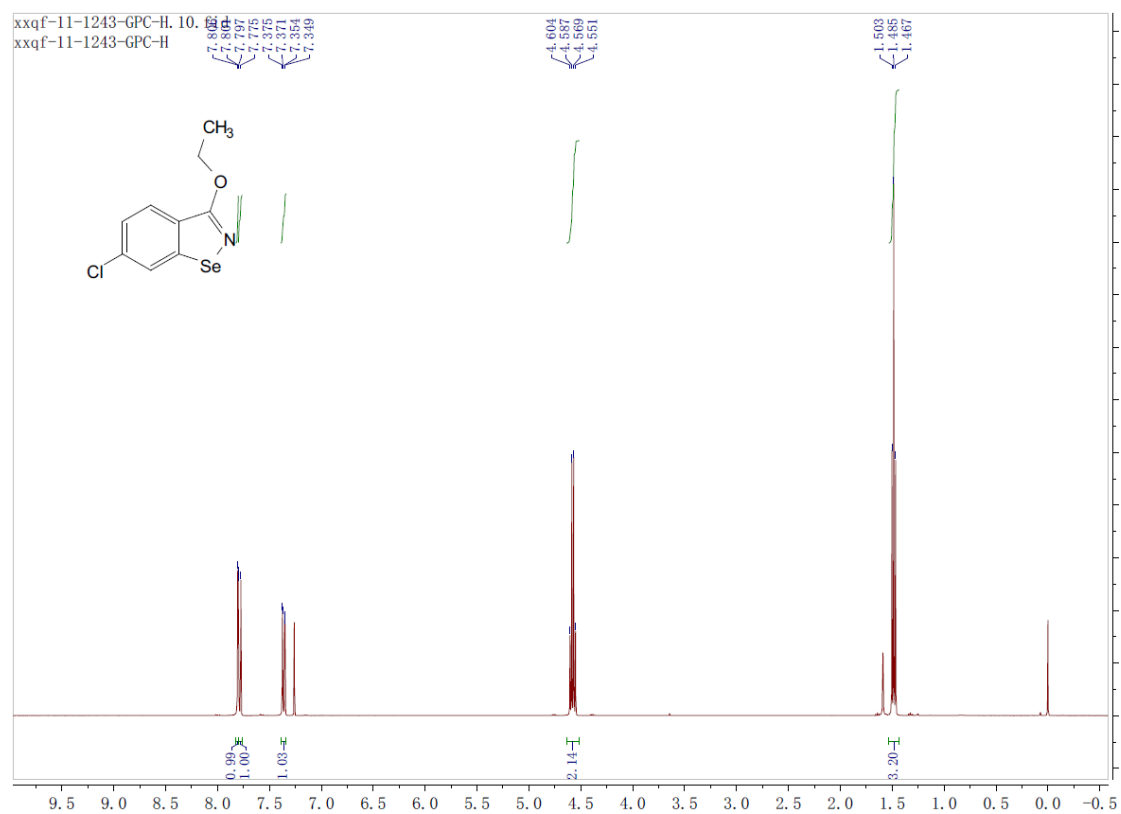


¹H NMR of **2i** (400 MHz, CDCl₃) ^{13}C NMR of **2i** (100 MHz, CDCl_3)

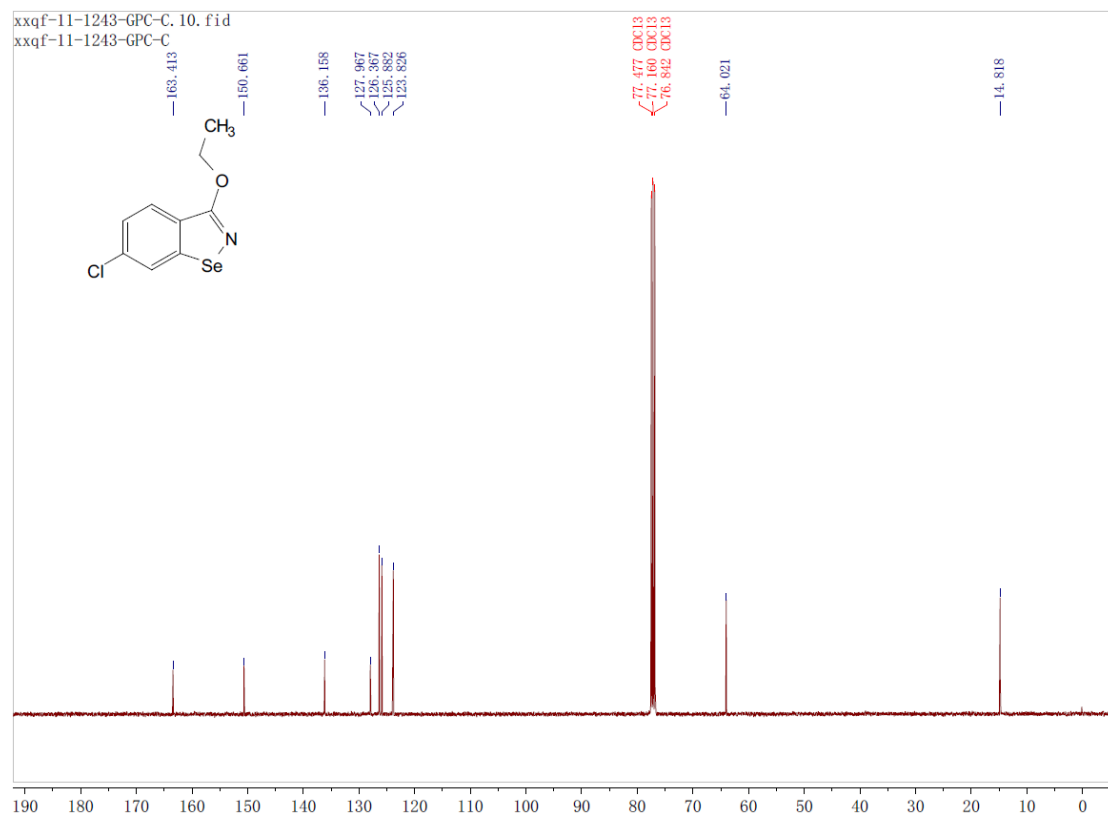
^{19}F NMR of **2i** (376 MHz, CDCl_3)



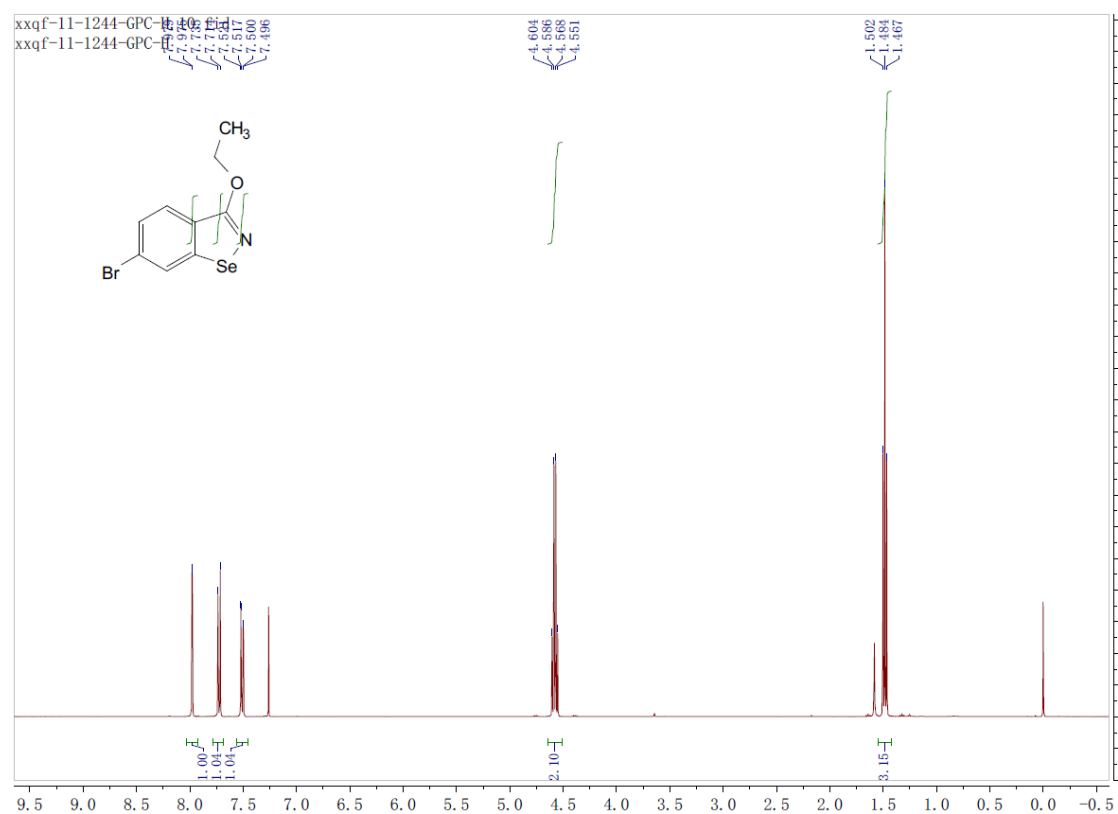
^1H NMR of **2j** (400 MHz, CDCl_3)



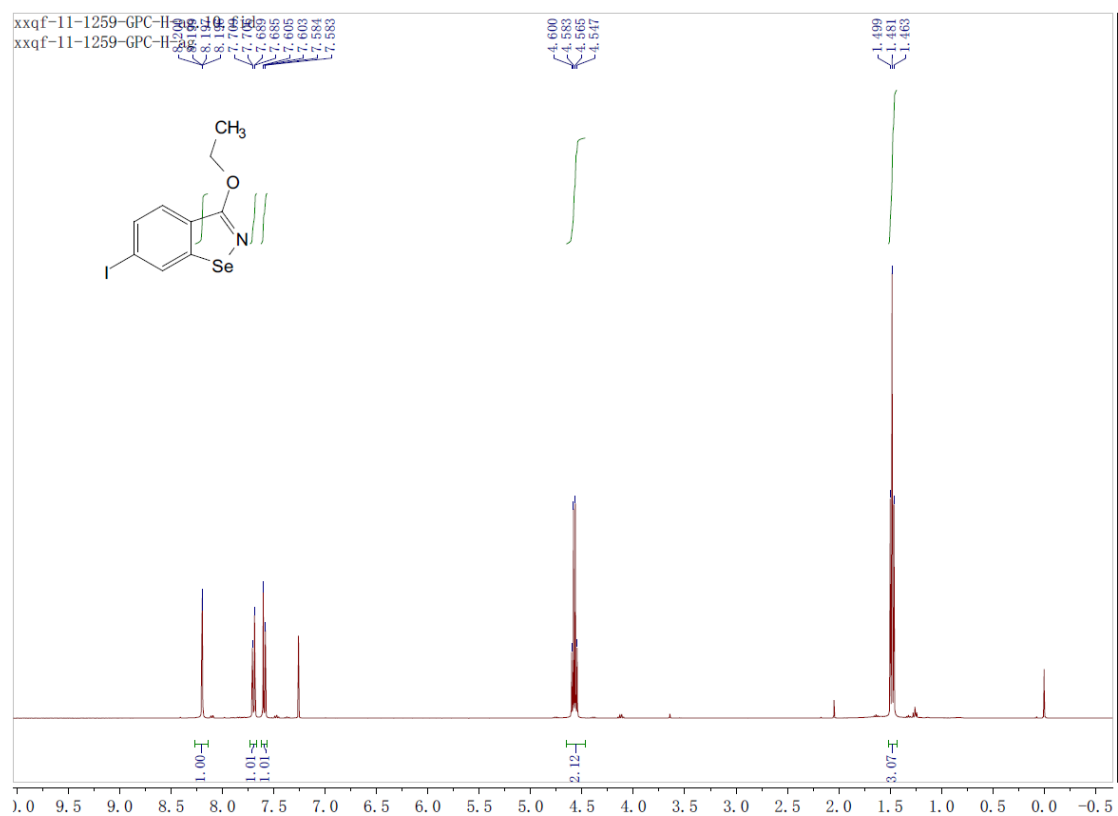
^{13}C NMR of **2j** (100 MHz, CDCl_3)



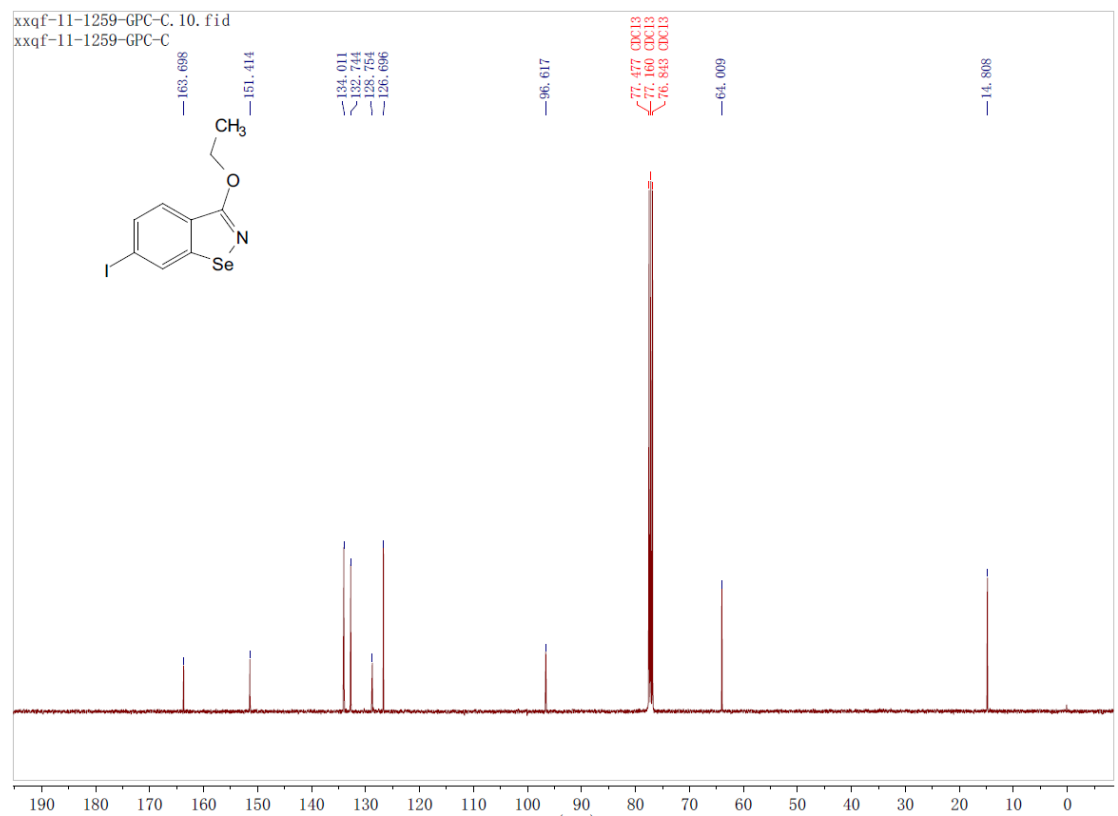
^1H NMR of **2k** (400 MHz, CDCl_3)

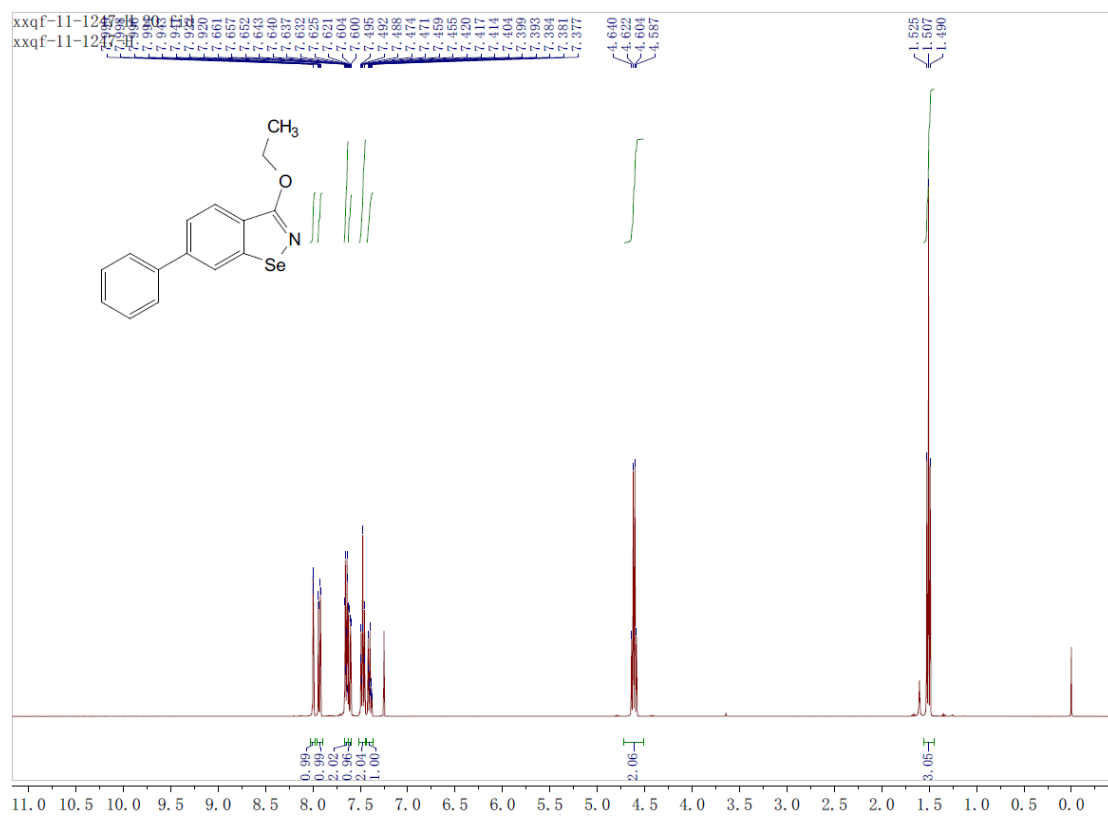
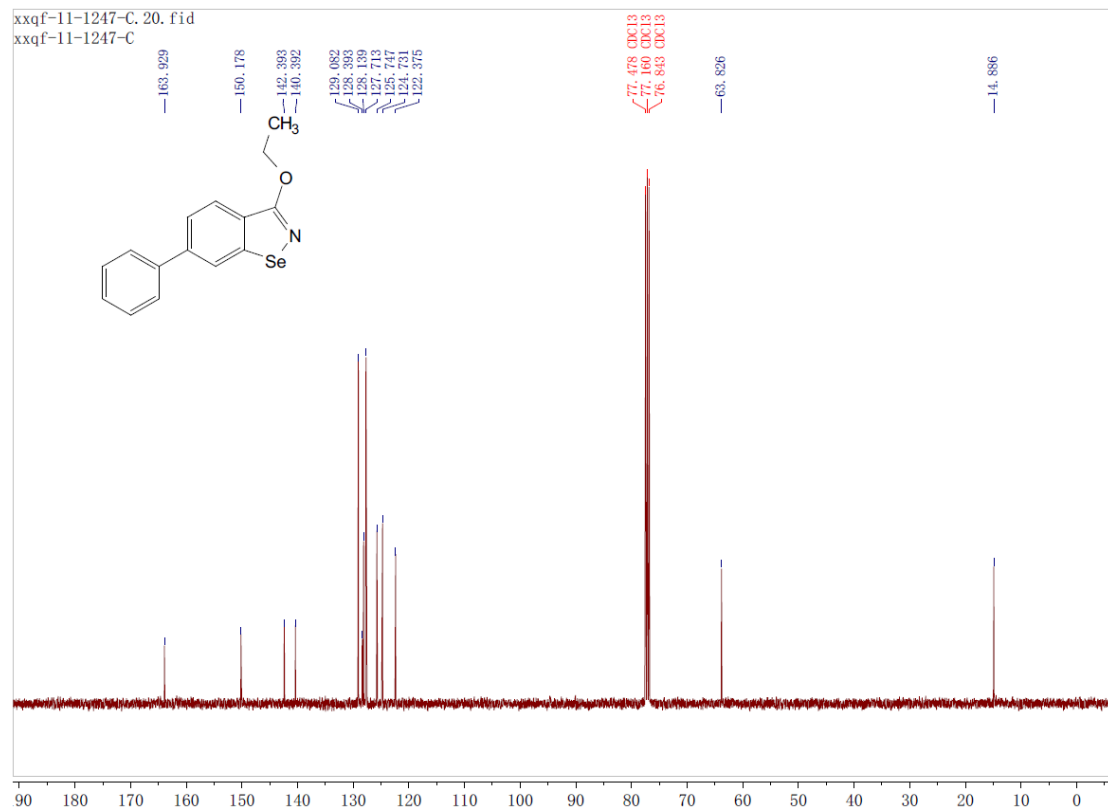


^1H NMR of **2I** (400 MHz, CDCl_3)

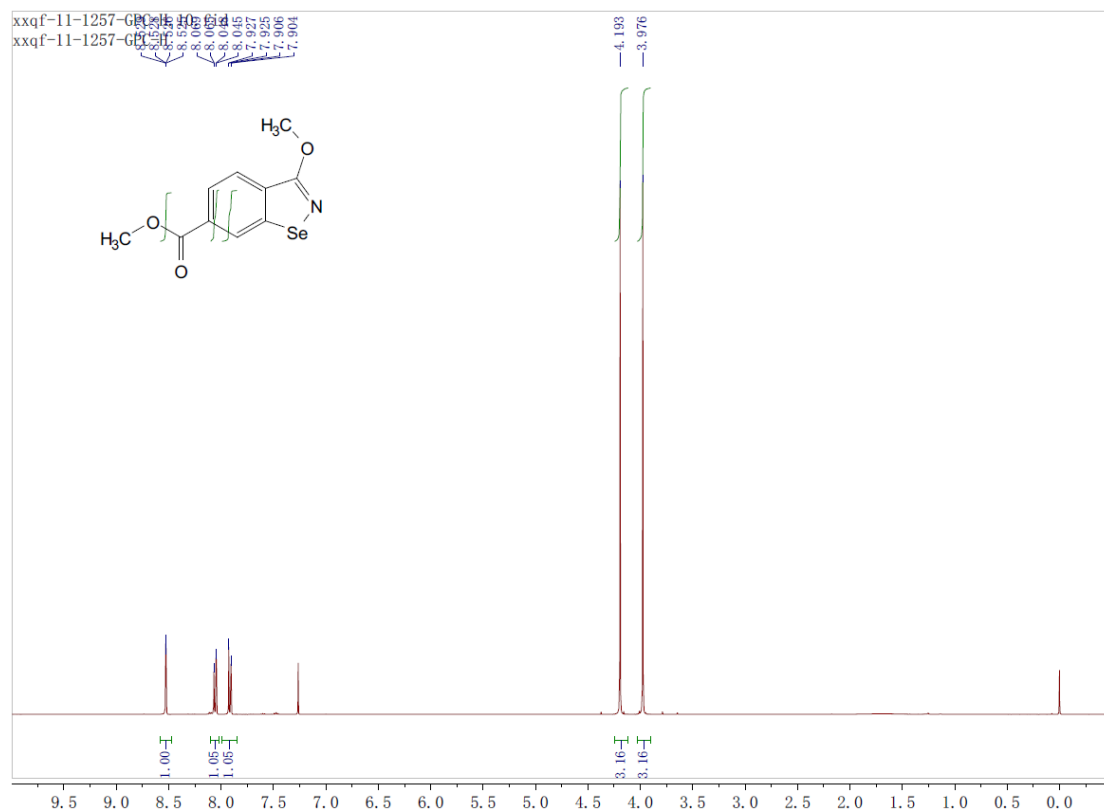


^{13}C NMR of **2I** (100 MHz, CDCl_3)

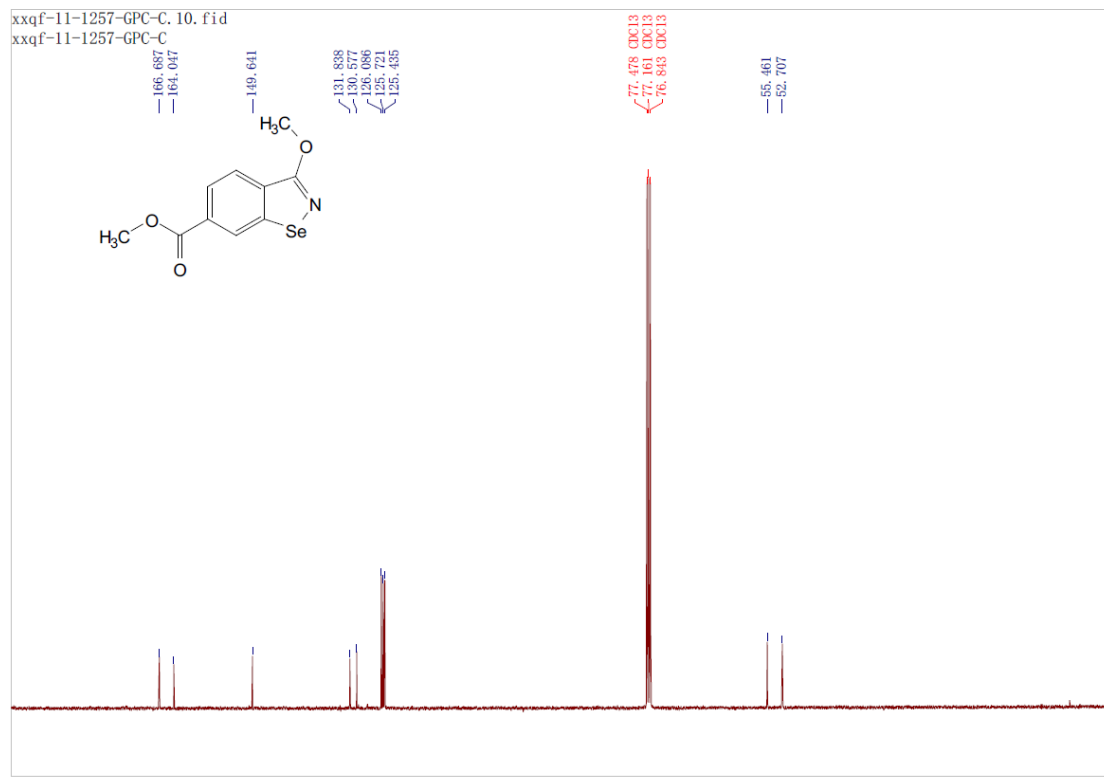


¹H NMR of **2m** (400 MHz, CDCl₃) ^{13}C NMR of **2m** (100 MHz, CDCl_3)

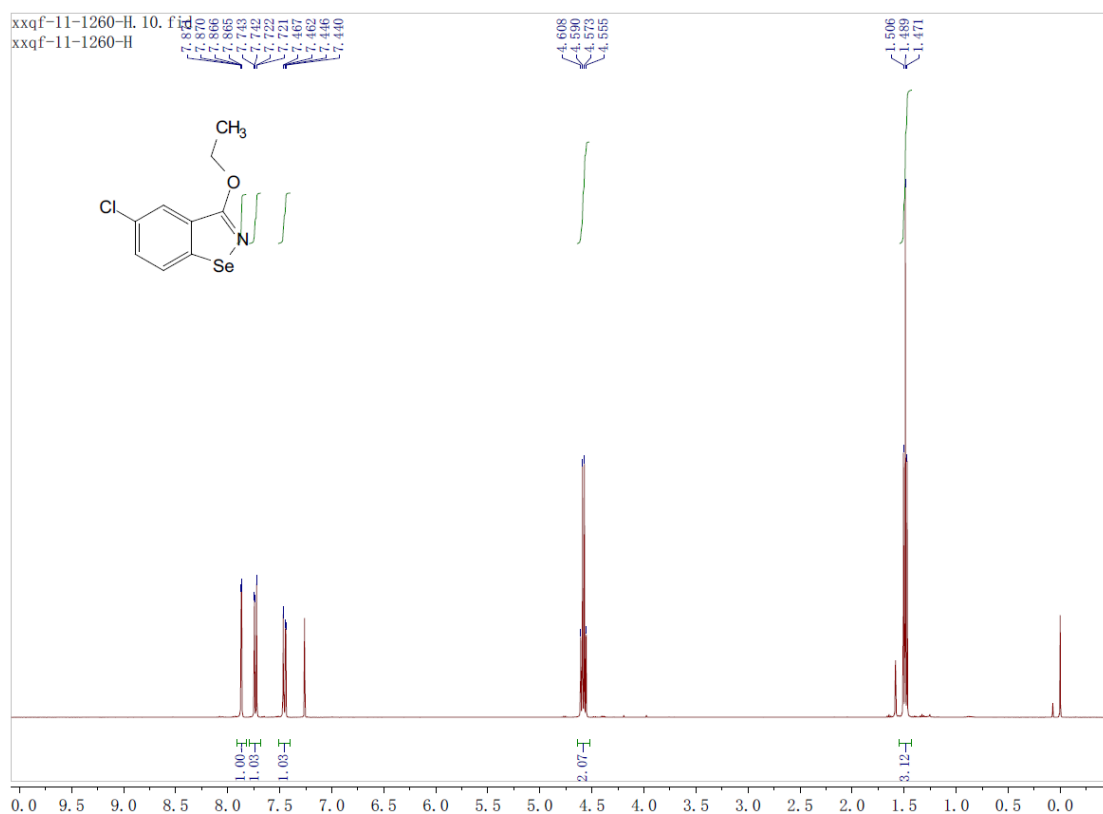
^1H NMR of **2n** (400 MHz, CDCl_3)



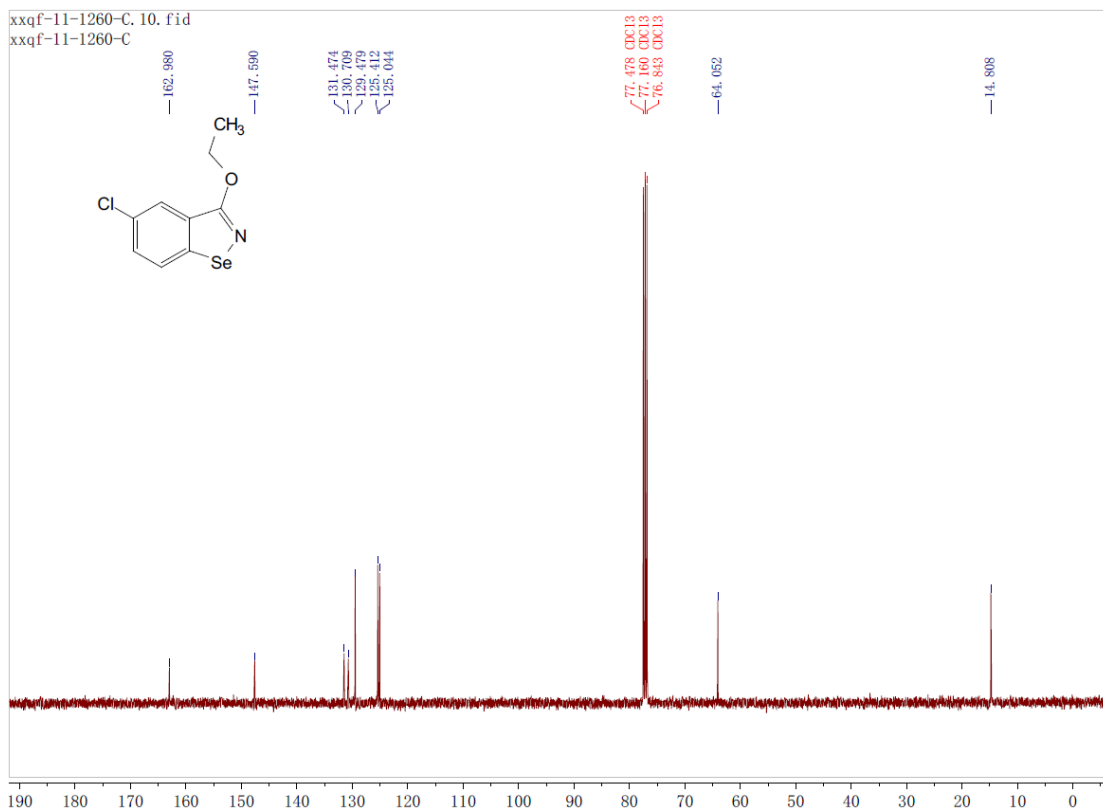
^{13}C NMR of **2n** (100 MHz, CDCl_3)



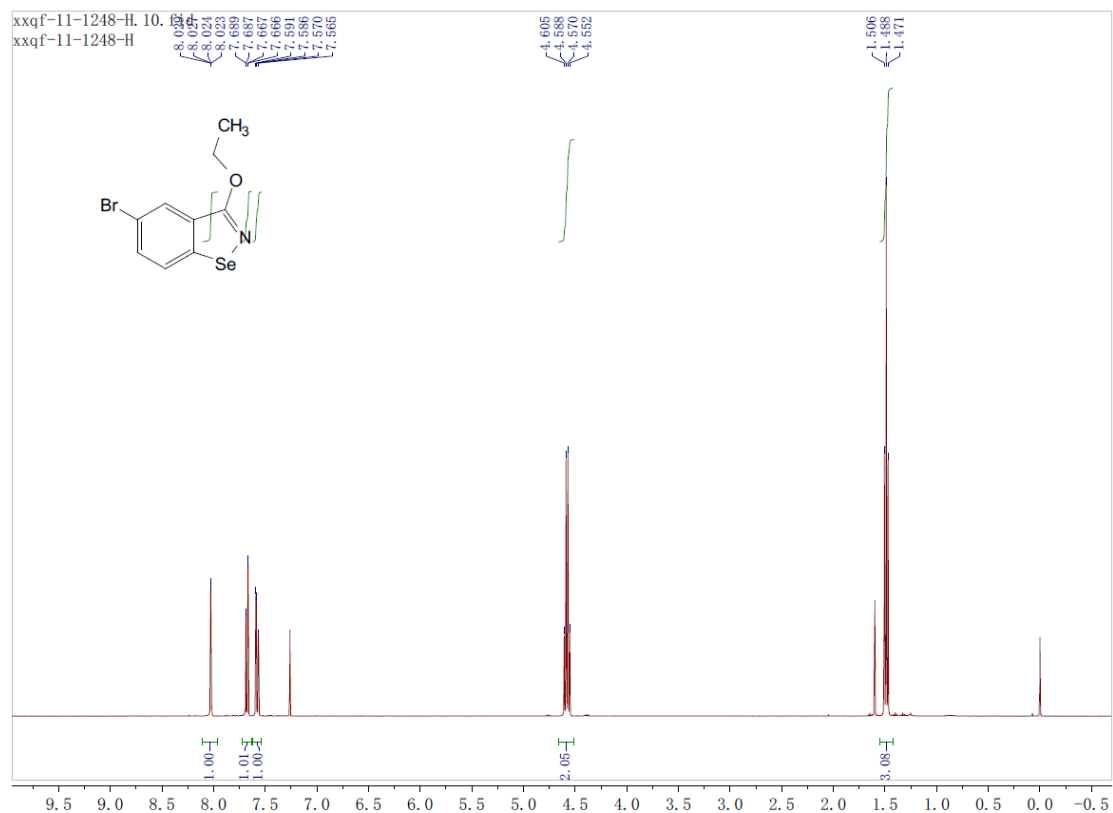
^1H NMR of **2o** (400 MHz, CDCl_3)



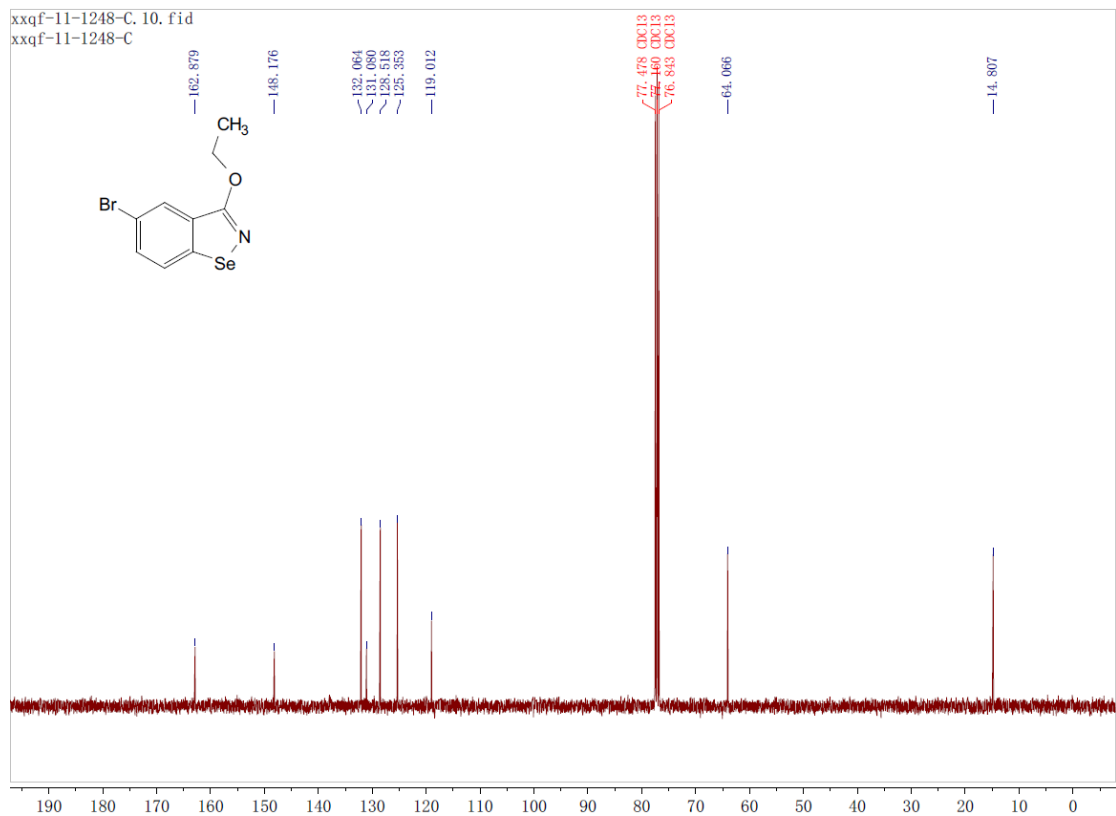
^{13}C NMR of **2o** (100 MHz, CDCl_3)



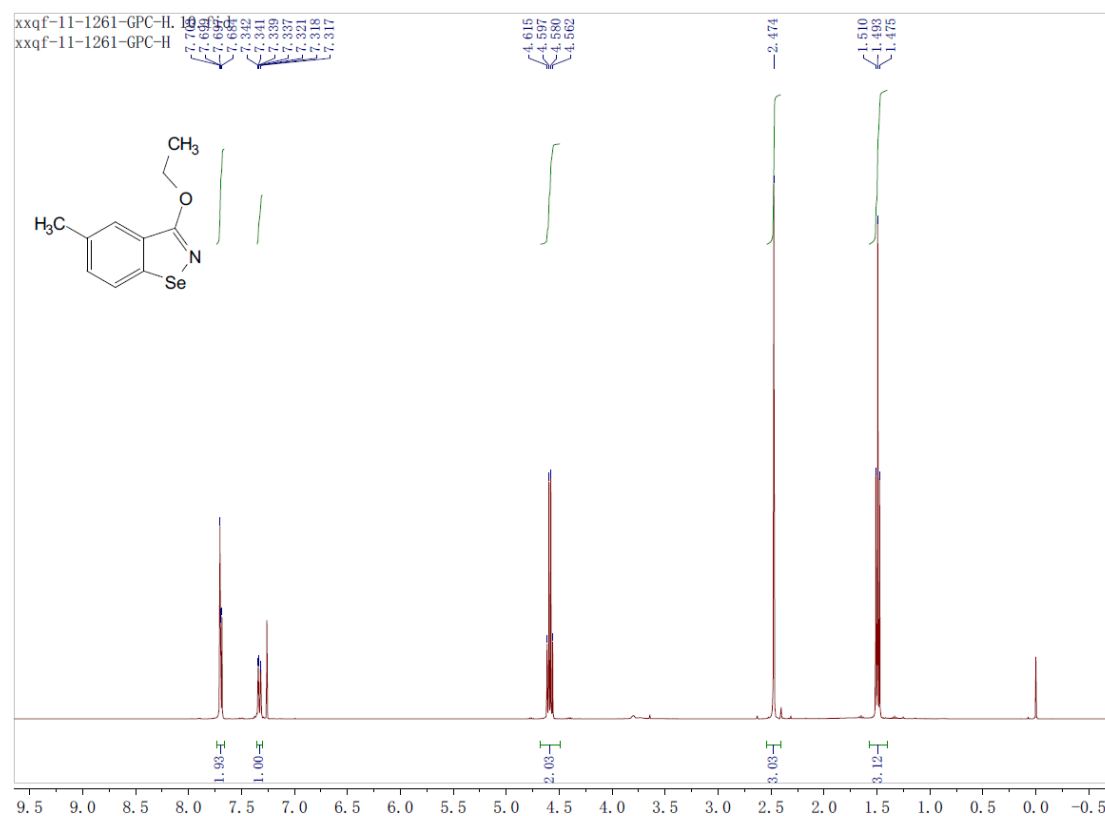
^1H NMR of **2p** (400 MHz, CDCl_3)



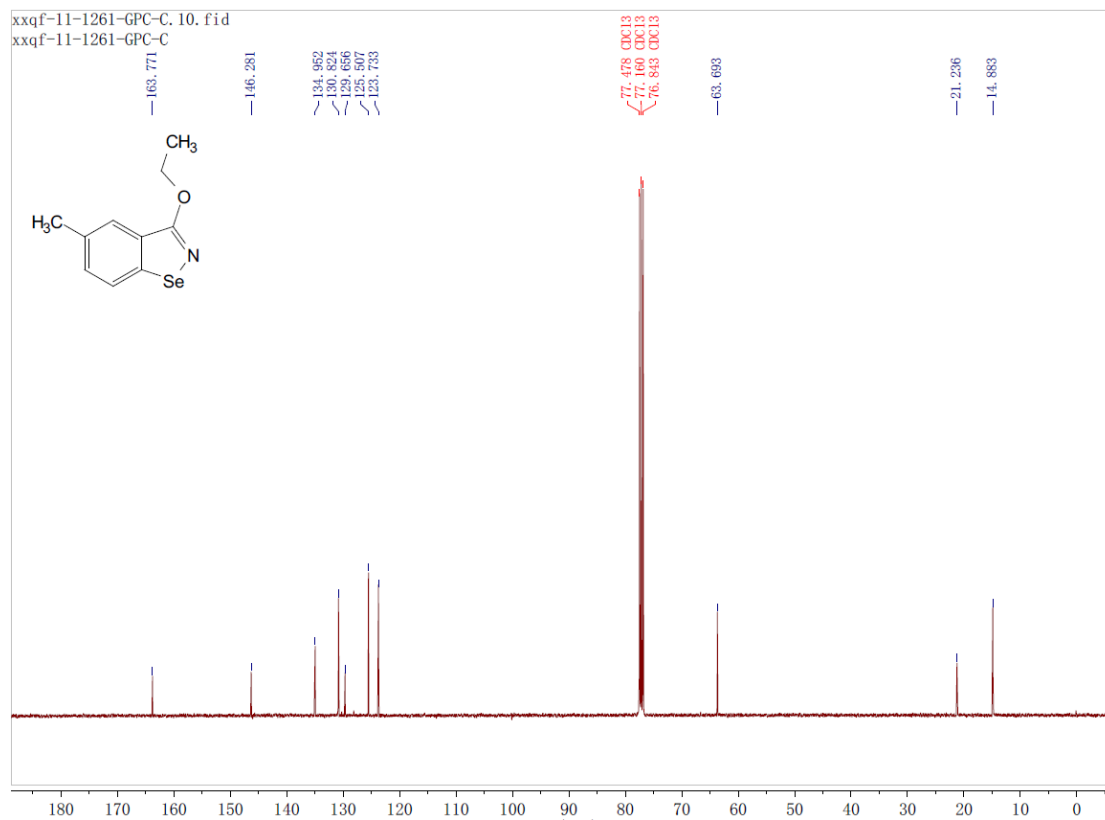
^{13}C NMR of **2p** (100 MHz, CDCl_3)



¹H NMR of **2q** (400 MHz, CDCl₃)



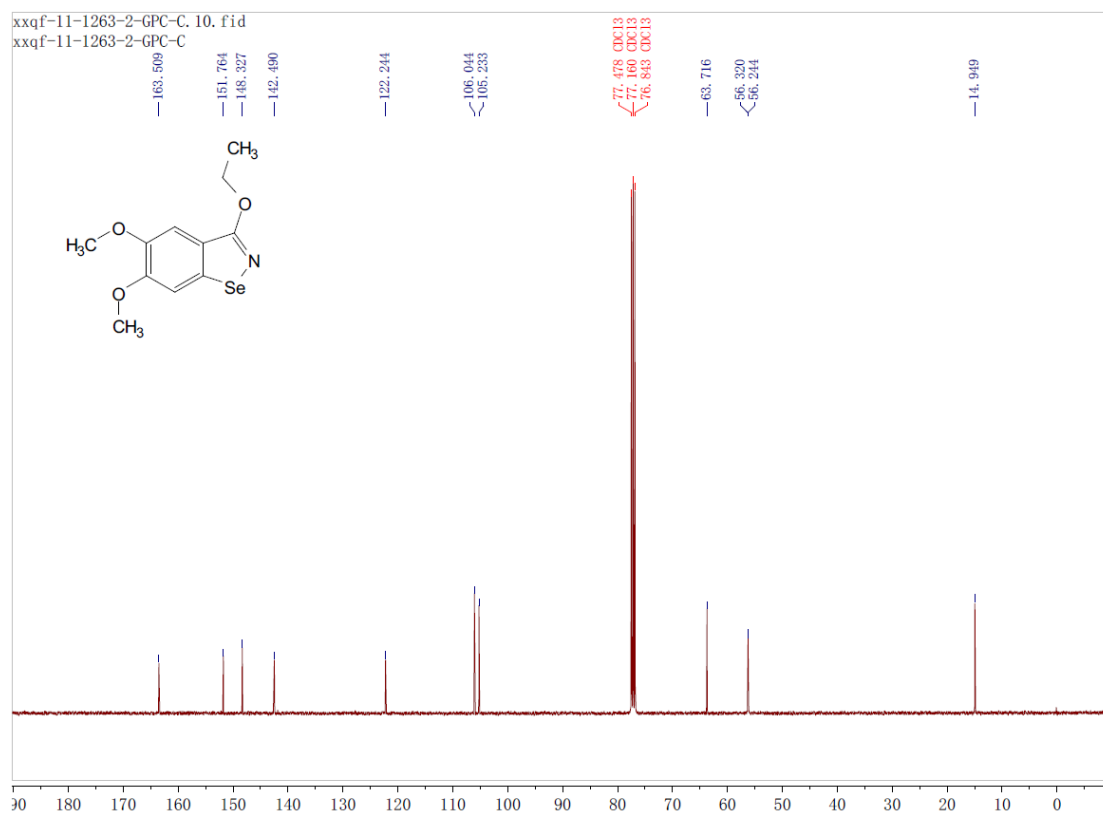
¹³C NMR of **2q** (100 MHz, CDCl₃)

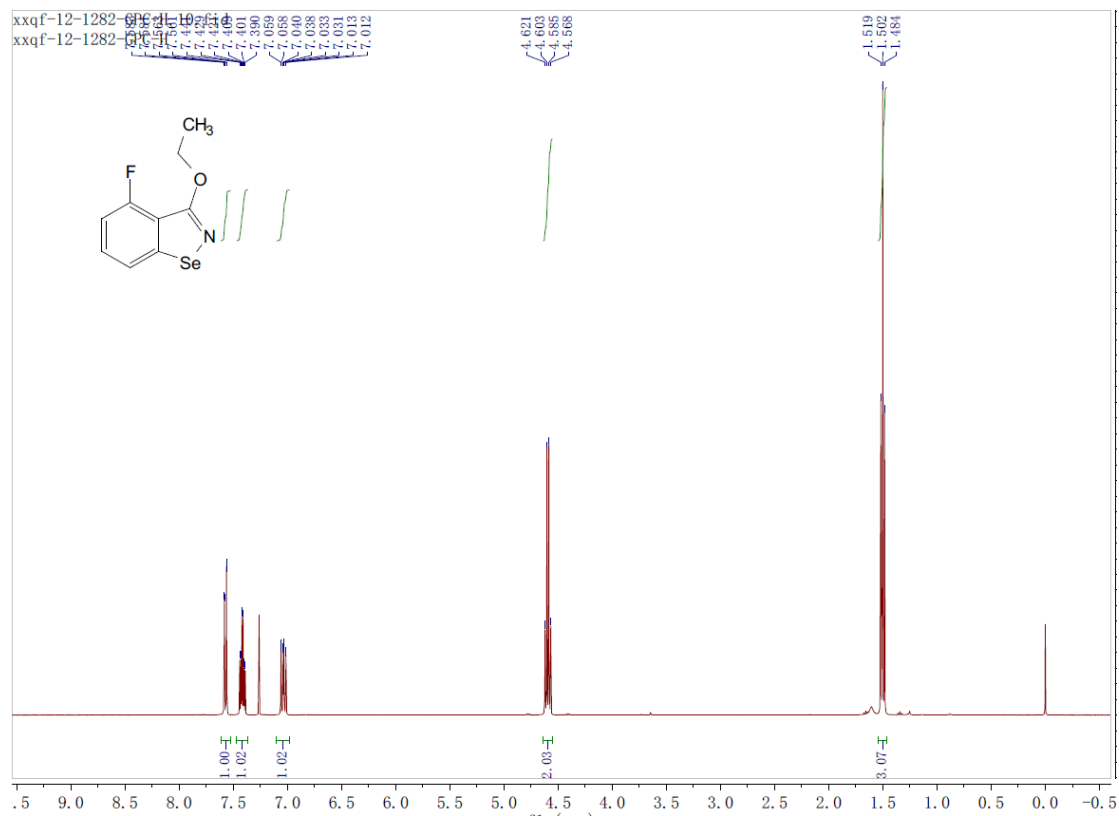
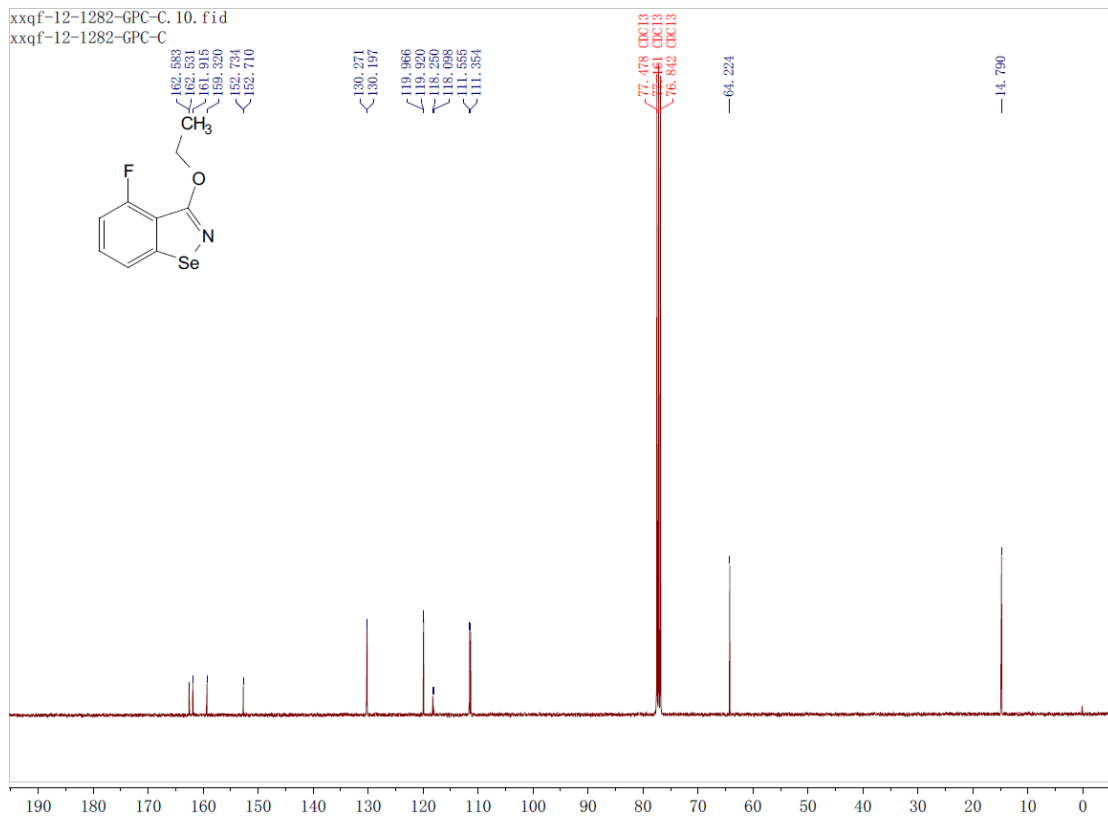


^1H NMR of **2r** (400 MHz, CDCl_3)

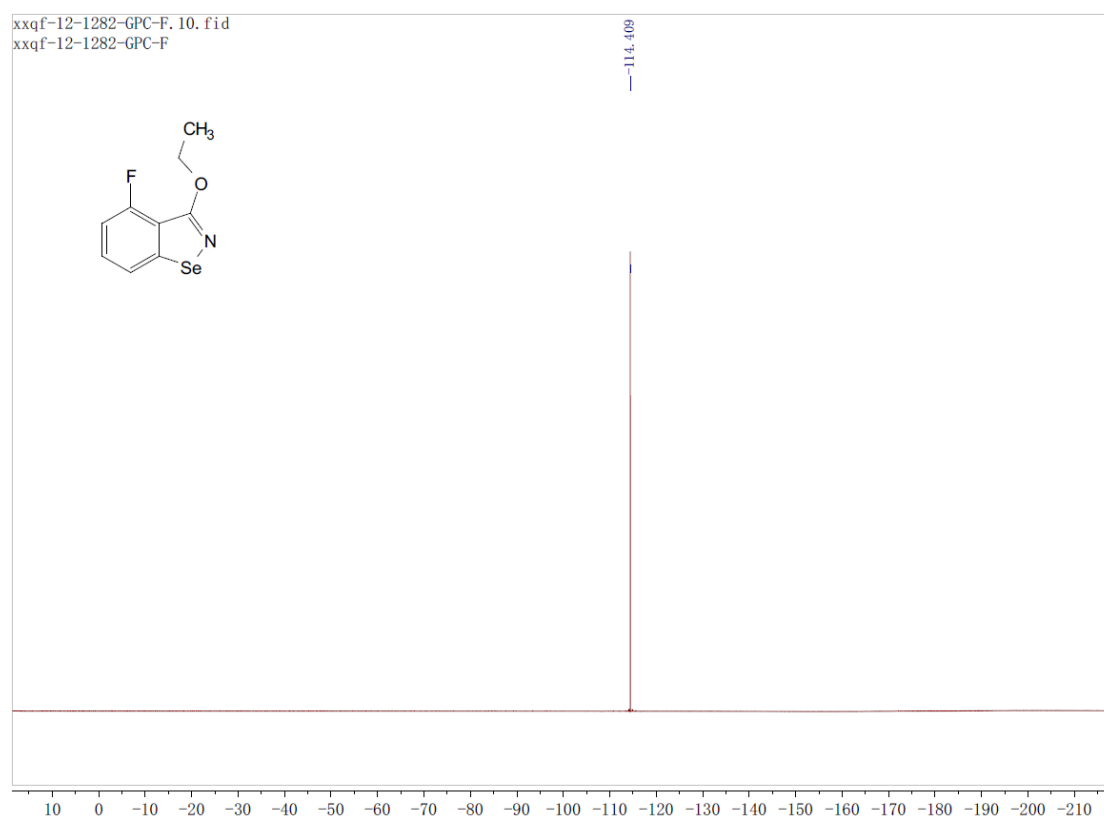


^{13}C NMR of **2r** (100 MHz, CDCl_3)

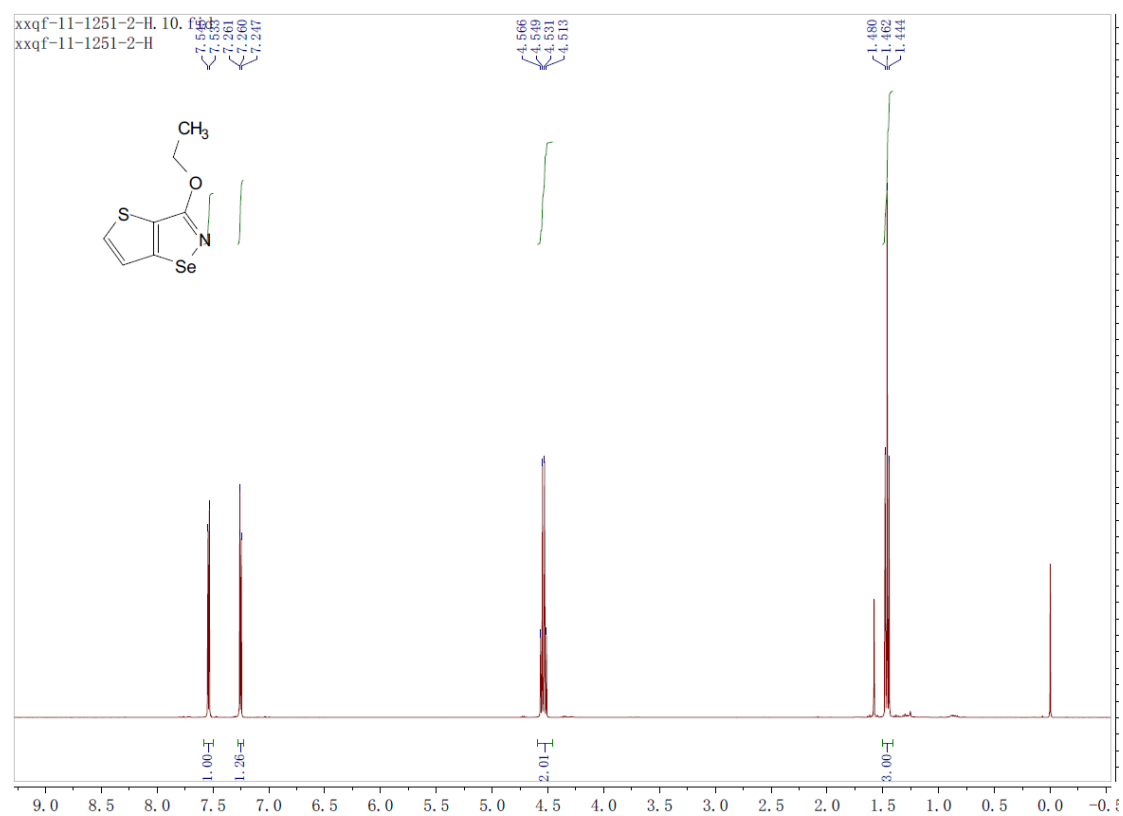


¹H NMR of **2s** (400 MHz, CDCl₃) ^{13}C NMR of **2s** (100 MHz, CDCl_3)

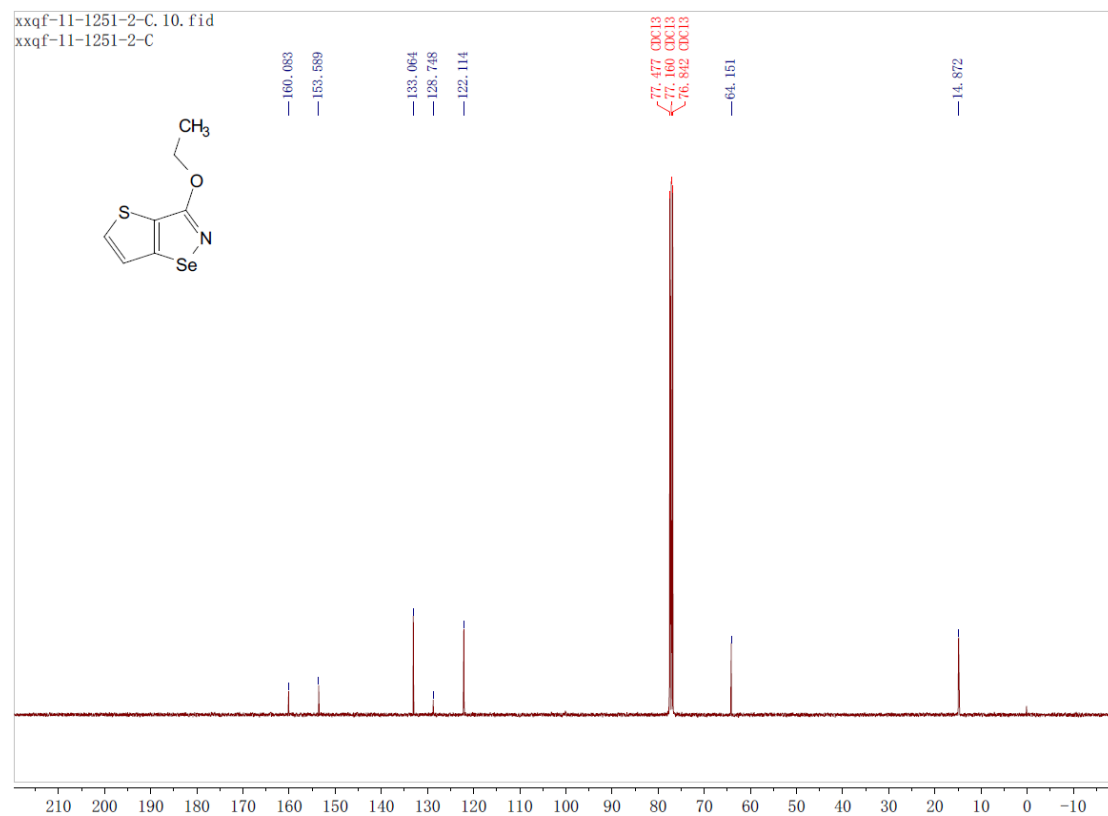
^{19}F NMR of **2s** (376 MHz, CDCl_3)



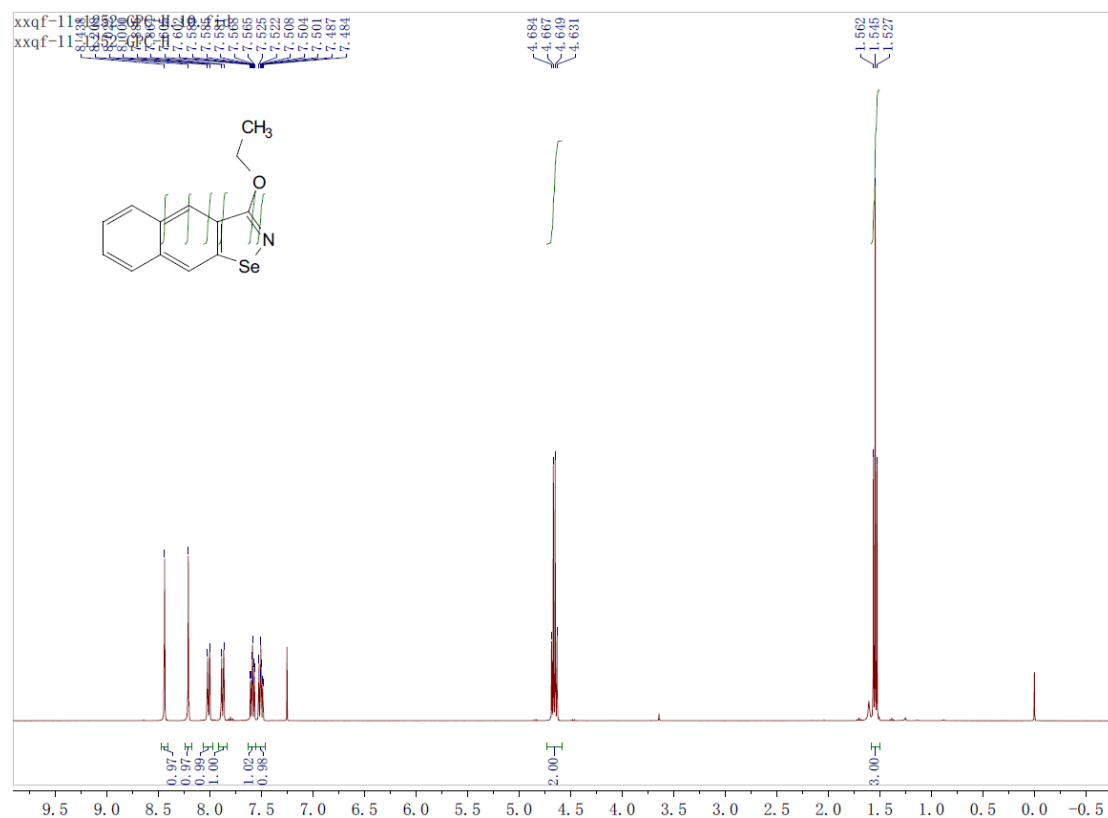
^1H NMR of **2t** (400 MHz, CDCl_3)



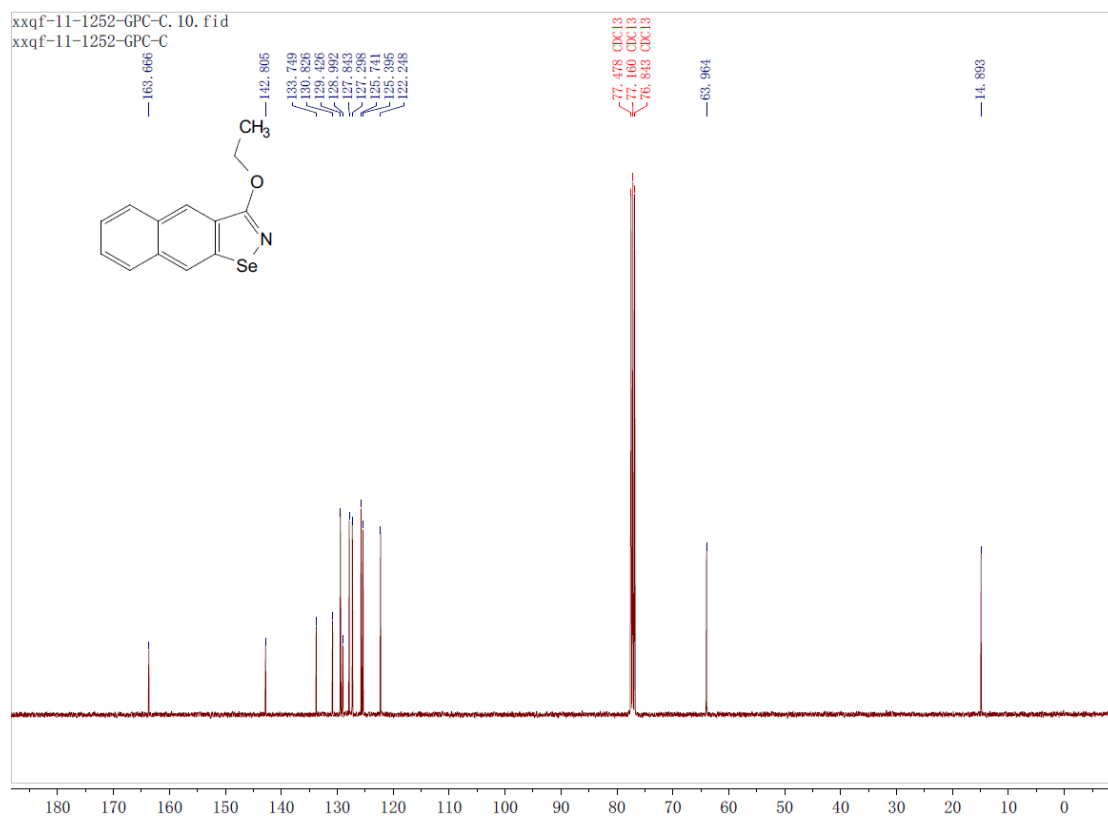
^{13}C NMR of **2t** (100 MHz, CDCl_3)



^1H NMR of **2u** (400 MHz, CDCl_3)



^{13}C NMR of **2u** (100 MHz, CDCl_3)



4. References

- ¹ Moon, S.; Nishii, Y.; Miura, M. Synthesis of Isothiazoles and Isoselenazoles through Rhodium-Catalyzed Oxidative Annulation with Elemental Sulfur and Selenium. *Org. Lett.* **2021**, *23*, 49–53.