

Supporting Information

De Novo Synthesis of Inherently Chiral Heteracalix[4]aromatics from Enantioselective Macrocyclization Enabled by Chiral Phosphoric Acid-catalyzed Intramolecular S_NAr Reaction

Xing-Chi Li,^[a] Ying Cheng,^{*[a]} Xu-Dong Wang,^[b] Shuo Tong,^{*[c]} and Mei-Xiang Wang^{*[c]}

^[a] College of Chemistry, Beijing Normal University, Beijing 100875, China

^[b] Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

^[c] Key Laboratory of Bioorganic Phosphorous and Chemical Biology (MOE), Department of Chemistry, Tsinghua University, Beijing 100084, China

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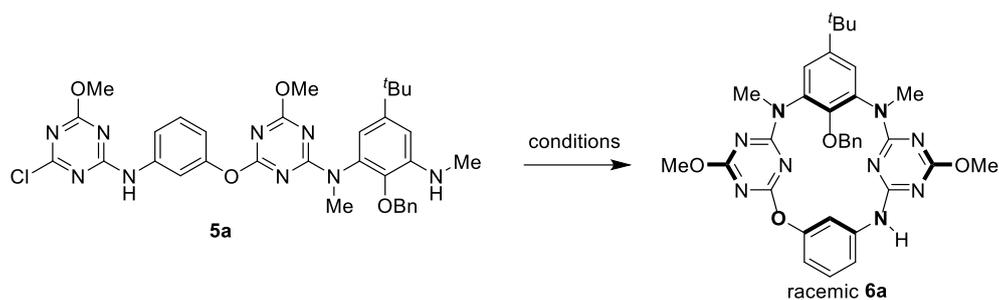
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1. General Information

Commercially available chemical reagents were used without further purification. Anhydrous solvents were prepared according to standard procedures. Melting points were uncorrected. ^1H NMR (400 and 600 MHz) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 and 150 MHz) were recorded in the indicated solvents using JEOL NMR spectrometers. Coupling constants (J values) are reported in Hz. IR spectra were recorded using an AVATAR 360 FT-IR spectrometer. High resolution mass spectral analysis (HRMS) was performed on a LCT Premier XE (ESI). Column chromatography was performed using 200-300 mesh silica gel eluted with the solvents as indicated in experiments. The starting materials 2,4,6-trichloro-1,3,5-triazine, 3-aminophenol and substituted 3-aminophenols **1**, 4-(*t*-butyl)-2,6-dinitrophenol are commercially available.

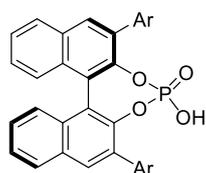
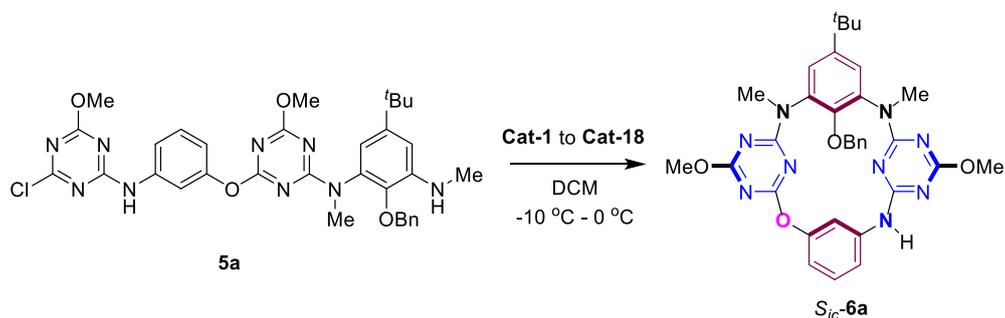
2. Optimization of reaction conditions for the formation of macrocycles **6**

Table S1. Formation of racemic 6a from macrocyclization of 5a under basic and acidic conditions.



Entry	Base or Acid (equiv.)	Solvent ($c = 2.5 \times 10^{-3}$ M)	Temp. ($^{\circ}\text{C}$)	Time (h)	Yield (%)
1	DIPEA (2.0)	acetone	rt	12	9
2	Et_3N (2.0)	acetone	rt	12	7
3	K_2CO_3 (2.0)	acetone	rt	12	11
4	Cs_2CO_3 (2.0)	acetone	rt	12	trace
5	DIPEA (2.0)	DCM	rt	12	12
6	K_2CO_3 (2.0)	DCM	rt	12	8
7	Cs_2CO_3 (2.0)	CH_3CN	rt	12	8
8	Cs_2CO_3 (2.0)	CH_3CN	reflux	12	15
9	$\text{CH}_3\text{CO}_2\text{H}$ (0.5)	DCM	rt	12	68
10	$\text{CF}_3\text{CO}_2\text{H}$ (0.5)	DCM	rt	12	73
11	<i>p</i> -TsOH (0.5)	DCM	rt	12	71
12	HCl (1.0)	DCM	rt	12	66
13	$\text{CF}_3\text{CO}_2\text{H}$ (1.0)	DCM	rt	12	73
14	$\text{CF}_3\text{CO}_2\text{H}$ (2.0)	DCM	rt	12	76

Table S2. Screening of chiral phosphoric acid catalysts.



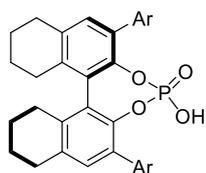
Cat-1, Ar = Ph

Cat-2, Ar = 4-Ph-C₆H₄

Cat-3, Ar = 4-NO₂-C₆H₄

Cat-4, Ar = 2,4,6-(*i*Pr)₃-C₆H₂

Cat-5, Ar = 9-Anthryl

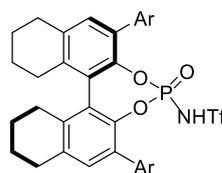


Cat-6, Ar = 4-Ph-C₆H₄

Cat-7, Ar = 4-NO₂-C₆H₄

Cat-8, Ar = 4-Cl-C₆H₄

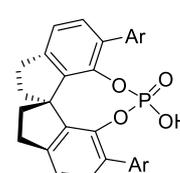
Cat-9, Ar = 4-MeO-C₆H₄



Cat-10, Ar = 4-NO₂-C₆H₄

Cat-11, Ar = 4-Cl-C₆H₄

Cat-12, Ar = 4-MeO-C₆H₄



Cat-13, Ar = Ph

Cat-14, Ar = 1-Naphthyl

Cat-15, Ar = 2-Naphthyl

Cat-16, Ar = 9-Anthryl

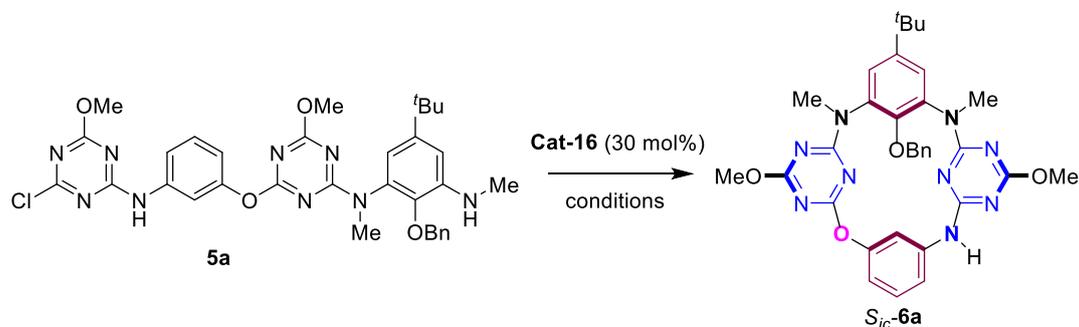
Cat-17, Ar = 9-Phenanthryl

Cat-18, Ar = 2-Pyrenyl

Entry	Catalyst (30 mol%)	Solvent (<i>c</i> = 2.5 × 10 ⁻³ M)	Temp. (°C)	Time (h)	Yield (%)	<i>ee.</i> (%)
1	Cat-1	DCM	0	12	21	10
2	Cat-2	DCM	0	12	59	24
3	Cat-3	DCM	-10	12	32	17
4	Cat-4	DCM	0	12	10	20
5	Cat-5	DCM	0	12	48	2
6	Cat-6	DCM	0	12	25	31
7	Cat-7	DCM	-10	12	29	16
8	Cat-8	DCM	-10	12	18	25
9	Cat-9	DCM	-10	12	16	16
10	Cat-10	DCM	0	12	59	2
11	Cat-11	DCM	0	12	trace	7
12	Cat-12	DCM	0	12	16	14
13	Cat-13	DCM	0	12	24	38
14	Cat-14	DCM	0	12	30	11
15	Cat-15	DCM	0	12	22	4
16	Cat-16	DCM	0	12	48	34

17	Cat-17	DCM	0	12	29	20
18	Cat-18	DCM	0	12	14	11

Table S3. Optimization of Cat-16 catalyzed macrocyclization reaction of 5a.



Entry	Solvent ($c = 2.5 \times 10^{-3}$ M)	Additive	Temp. (°C)	Time (h)	Yield (%)	ee. (%)
1	DCM	-	0	12	48	34
2	DCE	-	0	12	50	47
3	CHCl ₃	-	0	12	48	64
4	CHCl ₃	-	-30	24	17	85
5	CCl ₄	-	0	12	16	86
6	toluene	-	0	12	10	64
7	xylenes	-	0	12	11	68
8	acetone	-	0	12	7	33
9	CH ₃ CN	-	0	12	trace	48
10	benzene	-	0	12	21	64
11	CCl ₄	-	0	24	23	86
12	CCl ₄	-	0	36	31	86
13	CCl ₄	-	0	72	37	85
14	CCl ₄	-	-10	24	14	87
15	CCl ₄	-	10	24	33	83
16	CCl ₄	-	20	24	40	78
17	CCl ₄	-	30	24	64	72
18 ^[a]	CCl ₄	-	0	24	15	86
19 ^[b]	CCl ₄	-	0	24	21	85
20 ^[c]	CCl ₄	-	0	24	15	87
21	CCl ₄	3 Å M.S. ^[d]	0	24	19	88
22	CCl ₄	4 Å M.S. ^[d]	0	24	19	88

23	CCl ₄	5Å M.S. ^[d]	0	24	26	87
24	CCl ₄	3Å M.S. ^[e]	0	24	27	87
25	CCl ₄	4Å M.S. ^[e]	0	24	28	88
26	CCl ₄	5Å M.S. ^[e]	0	24	26	86
27	CCl ₄	Ag ₂ CO ₃ (1.0 equiv.) ^[f]	0	12	20	88
28	CCl ₄	CH ₃ CO ₂ Ag (1.0 equiv.) ^[f]	0	24	N.R.	
29	CCl ₄	K ₂ CO ₃ (0.6 equiv.) ^[g]	0	72	38	87
30	CCl ₄	K ₂ CO ₃ (1.0 equiv.) ^[g]	0	72	31	90
31	CCl ₄ : Cl ₂ CHCHCl ₂ (13 : 7 mL)	-	0	24	52	15
32	CCl ₄ : CHCl ₃ (13 : 7 mL)	-	0	24	54	76
33	CCl ₄ : CHCl ₃ (13 : 7 mL)	-	-30	24	21	90
34	CCl ₄ : cyclohexane (13 : 7 mL)	-	0	24	12	90
35	CCl ₄ : cyclohexane (13 : 7 mL)	-	0	48	19	90
36	CCl ₄ : cyclohexane (13 : 7 mL)	-	0	72	24	90
37	CCl ₄ : cyclohexane (13 : 7 mL)	-	10	24	33	88
38	CCl ₄ : CHCl ₃ (13 : 7 mL)	K ₂ CO ₃ (0.6 equiv.) ^[g]	-30	72	30	92
39	CCl ₄ : cyclohexane (13 : 7 mL)	K ₂ CO ₃ (0.6 equiv.) ^[f]	0	72	6	90
40	CCl ₄ : cyclohexane (13 : 7 mL)	K ₂ CO ₃ (0.6 equiv.) ^[g]	0	72	36	93
41	CCl ₄ : cyclohexane (13 : 7 mL)	K ₂ CO ₃ (1.0 equiv.) ^[g]	0	72	28	92
42	1,2-dichloroethane	K ₂ CO ₃ (0.6 equiv.)	0	72	84	41

^[a] Catalyst loading is 20 mol%.

^[b] Concentration of **5a** is 5.0×10⁻³ M.

^[c] Concentration of **5a** is 2.5×10⁻² M.

^[d] Non-activated molecular sieve (30 mg), **5a** and **Cat-16** were mixed in a reaction vial.

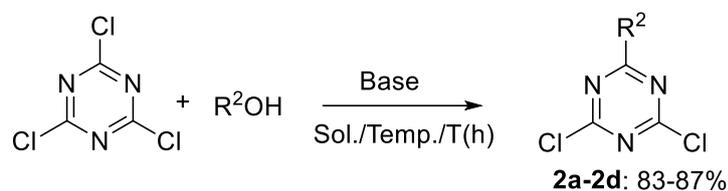
^[e] Activated molecular sieve (30 mg), **5a** and **Cat-16** were mixed in a reaction vial.

[^f] K₂CO₃ or silver salt, **5a** and **Cat-16** were mixed in a reaction vial.

[^g] K₂CO₃ was added after 12 h.

3. Synthesis of 6-substituted 2,4-dichloro-1,3,5-triazines (monomers)

3.1 Preparation of 6-alkoxy-2,4-dichloro-1,3,5-triazines **2a-2d**



R ² OH,	Base,	Sol.	Temp.	T(h)	Product
MeOH,	NaHCO ₃ ,	MeOH,	0°C	4	2a , R ² = OMe
EtOH,	NaHCO ₃ ,	EtOH,	rt	4	2b , R ² = OEt
ⁱ PrOH,	NaHCO ₃ ,	ⁱ PrOH,	rt	4	2c , R ² = OPr ^{<i>i</i>}
BnOH,	DIPEA,	CH ₂ Cl ₂ ,	rt	2	2d , R ² = OBn

Scheme S1

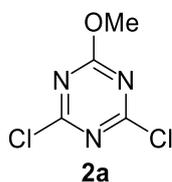
- A. In a flask that was cooled in an ice bath, 2,4,6-trichloro-1,3,5-triazine (9.22 g, 50 mmol) and NaHCO₃ (4.62 g, 55 mmol) were mixed with an alcohol (methanol, ethanol or isopropanol) (50 mL). The resulting mixture was stirred for 4h at 0 °C or for 4h at room temperature (see Scheme S1). The reaction was quenched by the addition of ice water (100 mL) and the resulting mixture was stirred for 5 min. 2,4-Dichloro-6-methoxy-1,3,5-triazine **2a** was then precipitated from the mixture. After being filtrated, washed with ice water (2×50 mL) and dried under vacuum, the product **2a** was obtained in 83% yield. 2,4-Dichloro-6-ethoxy-1,3,5-triazine **2b** and 2,4-dichloro-6-isopropoxy-1,3,5-triazine **2c** were isolated from the mixture by extraction with ethyl acetate (200×2 mL). The organic layer was washed with saturated aqueous sodium chloride (50×3 mL) and was dried over anhydrous Na₂SO₄. After removal of Na₂SO₄ and solvents, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 10:1) to give products **2b** in 87% and **2c** in 83% yields.
- B. At 0 °C, a solution of phenylmethanol (4.33g, 40 mmol) and DIPEA (5.69 g, 44 mmol) in CH₂Cl₂ (40 mL) was added dropwise in 30 min to the solution of 2,4,6-trichloro-1,3,5-triazine (7.38 g, 40 mmol) in dichloromethane (70 mL) cooled in an ice bath. The resulting mixture was stirred for 2 h at room temperature. The reaction mixture was then washed with aqueous HCl (1M, 110 mL) and saturated aqueous NaCl (50×2 mL). The organic layer was dried over anhydrous Na₂SO₄ and concentrated under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and chloroform (PE:CHCl₃ = 1:1) to give product **2d** in 87% yield.

3.2 Preparation of 2,4-dichloro-6-(4-methoxyphenyl)-1,3,5-triazine **2e** and 2,4-dichloro-6-methyl-1,3,5-triazine **2f**

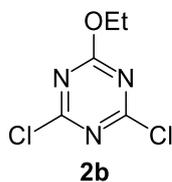


Scheme S2

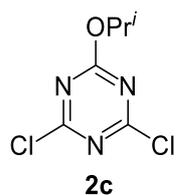
Under the protection of nitrogen atmosphere, the Grignard reagent (*p*-methoxyphenyl)magnesium bromide or methylmagnesium bromide (50 mmol, 50 mL, 1.0 mol/L in THF) was added dropwise in 1h to the solution of 2,4,6-trichloro-1,3,5-triazine (9.22 g, 50 mmol) in dry THF (30 mL) which was cooled at - 20 °C. The resulting mixture was stirred for another 1 h at - 20 °C. The reaction solution was concentrated, and then aqueous HCl (1M, 100 mL) was added. The resulting mixture was extracted with dichloromethane (50×2 mL). The combined organic layer was washed with saturated aqueous NaCl (30×3 mL) and dried over anhydrous Na₂SO₄. After removal of solvent under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 15:1) to give products **2e** (64%) and **2f** (68%), respectively.



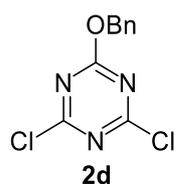
2,4-Dichloro-6-methoxy-1,3,5-triazine 2a:^[1] white solid, 7.43 g (from 50 mmol 2,4,6-trichloro-1,3,5-triazine), 83% yield, mp 90 - 91 °C. ¹H NMR (600 MHz, Acetone-*d*₆) δ (ppm): 4.13 (s, 3H). ¹³C NMR (150 MHz, Acetone-*d*₆) δ (ppm): 172.7, 172.6, 57.3. IR (KBr) ν 1510, 1488 cm⁻¹.



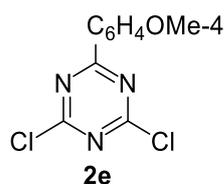
2,4-Dichloro-6-ethoxy-1,3,5-triazine 2b:^[2] white solid, 8.36 (from 50 mmol 2,4,6-trichloro-1,3,5-triazine), 87% yield, mp 31 - 32 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 4.54 (q, $J = 7.2$ Hz, 2H), 1.43 (t, $J = 7.2$ Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 172.6, 171.0, 66.7, 14.0. IR (KBr) ν 1545, 1508 cm⁻¹.



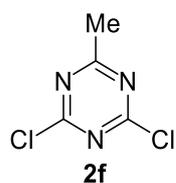
2,4-Dichloro-6-isopropoxy-1,3,5-triazine 2c:^[2] colorless oil, 8.60 g (from 50 mmol 2,4,6-trichloro-1,3,5-triazine), 83% yield. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 5.40 (hept, *J* = 6.0 Hz, 1H), 1.41 (d, *J* = 6.0 Hz, 6H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ (ppm): 172.4, 171.2, 75.1, 21.4. IR (KBr) ν 1543, 1504, 1458 cm⁻¹.



2-(Benzyloxy)-4,6-dichloro-1,3,5-triazine 2d:^[3] white solid, 8.87 g (from 40 mmol 2,4,6-trichloro-1,3,5-triazine), 87% yield, mp 87 - 88 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 7.53 (dd, *J* = 8.0, 2.0 Hz, 2H), 7.45 - 7.39 (m, 3H), 5.57 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.7, 171.0, 133.9, 129.2, 128.9, 128.8, 71.9. IR (KBr) ν 1537, 1510, 1499 cm⁻¹.



2,4-Dichloro-6-(4-methoxyphenyl)-1,3,5-triazine 2e: white solid, 8.20 g (from 50 mmol 2,4,6-trichloro-1,3,5-triazine), 64% yield, mp 129 - 130 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.46 (d, *J* = 6.6 Hz, 2H), 6.99 (d, *J* = 6.6 Hz, 2H), 3.91 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 174.3, 171.8, 165.3, 132.4, 125.2, 114.6, 55.8. IR (KBr) ν 1607, 1543, 1479 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₀H₈Cl₂N₃O: 256.0038; Found: 256.0036.



2,4-Dichloro-6-methyl-1,3,5-triazine 2f: white solid, 5.55 g (from 50 mmol 2,4,6-trichloro-1,3,5-triazine), 68% yield, mp 94 - 95 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 2.67 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 180.9, 171.8, 25.5. IR (KBr) ν : 1524, 1496 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₄H₄Cl₂N₃: 161.9631; Found: 161.9635.

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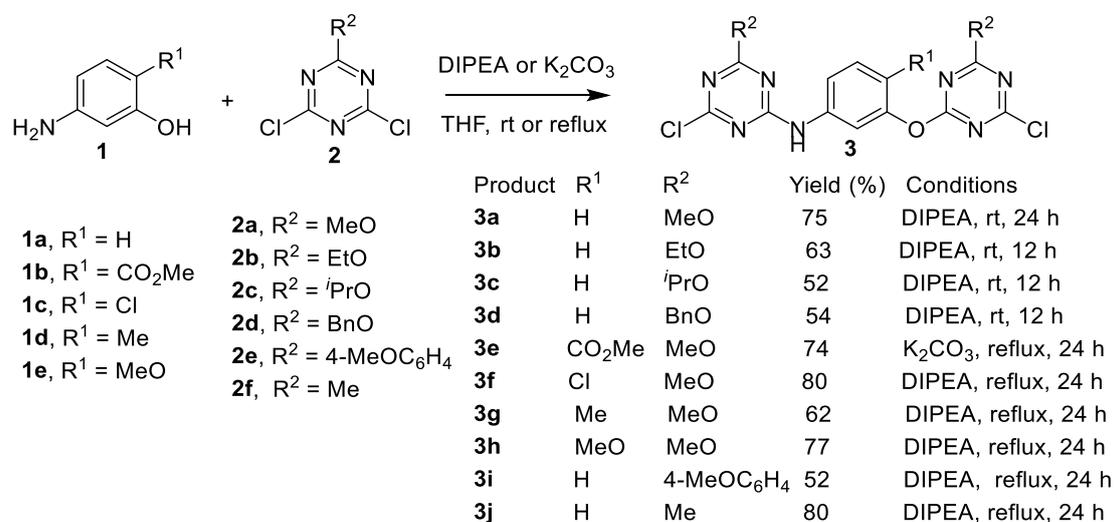
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[2]. S. Yrjölä, T. Kalliokoski, T. Laitinen, A. Poso, T. Parkkari, T. Nevalainen, Discovery of novel cannabinoid receptor ligands by a virtual screening approach: Further development of 2,4,6-trisubstituted 1,3,5-triazines as CB₂ agonists. *Eur. J. Pharm. Sci.* **2013**, *48*, 9 - 20.

[3]. H. Fujita, N. Hayakawa, M. Kunishima, Study of the reactivities of acid-catalyzed *O*-benzylating reagents based on structural isomers of 1,3,5-triazine. *J. Org. Chem.* **2015**, *80*, 11200-11205.)

4. Synthesis of *N*-(3-((6-(alkoxy, alkyl, aryl)-4-chloro-1,3,5-triazin-2-yl)oxy)phenyl)-6-(alkoxy, alkyl, aryl)-4-chloro-1,3,5-triazin-2-amine (trimers)



Scheme S3

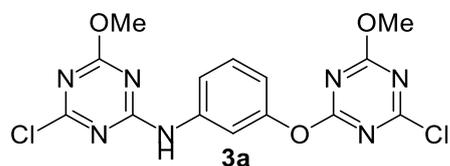
A. Preparation of compounds **3a-3d** and **3f-3j**

At ambient temperature, 2,4-dichloro-6-substituent-1,3,5-triazines **2** (4.8 mmol) were dissolved in THF (20 mL) in a flask. The solution of 3-aminophenols **1** (2 mmol) and DIPEA (5.0 mmol, 646.2 mg) in THF (20 mL) was added dropwise in 30 min into the flask. The resulting mixture was stirred for 12-24h at room temperature or for 24h in refluxing THF (see Scheme S3). After filtrating diisopropylethylammonium chloride salt, the reaction solution was concentrated under reduced pressure. The products **3a-3d** and **3f-3j** were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA from 4:1 to 2:1 for **3a-3d**, **3f**, and **3h-3j**; PE:EA = 4:1 for **3g**).

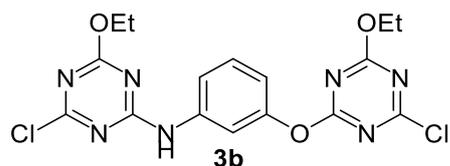
B. Preparation of compound **3e**

At ambient temperature, methyl 4-aminosalicylate **1b** (2 mmol), 2,4-dichloro-6-methoxy-1,3,5-triazine **2a** (864.0 mg, 4.8 mmol), K₂CO₃ (691.1 mg, 5.0 mmol) and THF (40 mL) were added into a flask. The resulting mixture was stirred for 24 h in refluxing solvent. The inorganic salts were filtrated and washed with dichloromethane (10 mL). The solvents of combined filtrate was evaporated under reduced pressure and the residue was dissolved in dichloromethane (200 mL). The

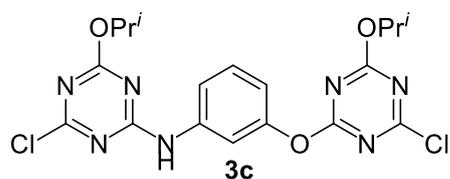
resulting solution was washed with saturated aqueous NaCl (30 × 3 mL) and was dried over anhydrous Na₂SO₄. After removal of Na₂SO₄ and dichloromethane, the residue was recrystallized in a mixture of dichloromethane and petroleum ether to give product **3e** in 74% yield.



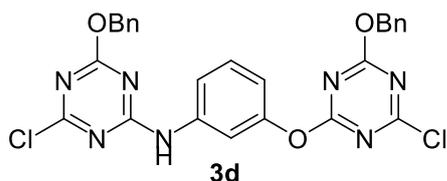
N-(3-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)oxy)phenyl)-4-chloro-6-methoxy-1,3,5-triazin-2-amine 3a: white solid, 604.6 mg, 75% yield, mp 148 - 149 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.62 (s, 1H), 7.86 (brs, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 8.4 Hz, 1H), 7.09 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.01 (s, 3H), 3.99 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 173.5, 172.9, 172.2, 171.6, 171.1, 165.2, 151.8, 138.4, 130.2, 118.7, 117.6, 114.1, 56.5, 55.9. IR (KBr) ν: 3353 (w), 3287 (w), 1613, 1559 cm⁻¹. HRMS (TOF-ESI) *m/z* [M + H]⁺ calcd for C₁₄H₁₂Cl₂N₇O₃: 396.0373; Found: 396.0376.



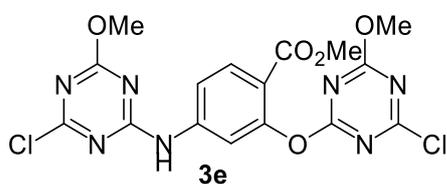
N-(3-((4-Chloro-6-ethoxy-1,3,5-triazin-2-yl)oxy)phenyl)-4-chloro-6-ethoxy-1,3,5-triazin-2-amine 3b: white solid, 533.1 mg, 63% yield, mp 122 - 123 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.56 (s, 1H), 7.83 (brs, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.07 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.46 - 4.38 (m, 4H), 1.344 (t, *J* = 6.8 Hz, 3H), 1.337 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ (ppm): 173.2, 173.13, 173.06, 171.7, 171.2, 166.3, 152.7, 140.2, 130.5, 119.2, 117.7, 114.6, 66.1, 65.0, 14.3, 14.1. IR (KBr) ν: 3356 (w), 3290 (w), 1613, 1557, 1538 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd for C₁₆H₁₆Cl₂N₇O₃: 424.0686; Found: 424.0689.



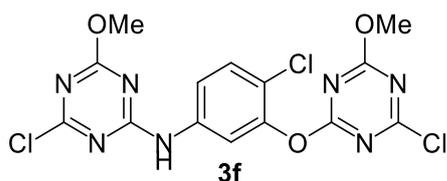
N-(3-((4-Chloro-6-isopropoxy-1,3,5-triazin-2-yl)oxy)phenyl)-4-chloro-6-isopropoxy-1,3,5-triazin-2-amine 3c: white solid, 469.1 mg, 52% yield, mp 78 - 79 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.51 (s, 1H), 7.82 (brs, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.06 (dd, *J* = 8.0, 2.4 Hz, 1H), 5.29 - 5.19 (m, 2H), 1.33 (d, *J* = 5.6 Hz, 6H), 1.32 (d, *J* = 6.0 Hz, 6H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ (ppm): 173.2, 173.0, 172.5, 171.1, 166.1, 152.6, 140.1, 130.4, 119.0, 117.6, 114.4, 73.9, 72.5, 21.6, 21.4. IR (KBr) ν: 3356 (w), 3291 (w), 1616, 1557, 1533 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₈H₂₀Cl₂N₇O₃: 452.0999; Found: 452.1003.



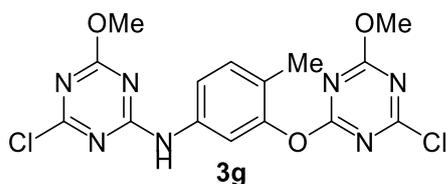
***N*-(3-((4-(Benzyloxy)-6-chloro-1,3,5-triazin-2-yl)oxy)phenyl)-4-(benzyloxy)-6-chloro-1,3,5-triazin-2-amine 3d**: white solid, 590.9 mg, 54% yield, mp 71 - 72 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.66 (brs, 1H), 7.83 (brs, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.44 - 7.31 (m, 10H), 7.08 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 2H), 5.40 (s, 2H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ (ppm): 173.3, 173.0, 171.6, 171.2, 166.2, 152.6, 140.1, 136.3, 135.6, 130.5, 129.3, 129.1, 128.9, 128.7, 119.4, 117.8, 114.8, 71.2, 70.3. IR (KBr) ν: 3356, 3195, 1657, 1588, 1545 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₂₆H₂₀Cl₂N₇O₃: 548.0999; Found: 548.0997.



Methyl 4-((4-chloro-6-methoxy-1,3,5-triazin-2-yl)amino)-2-((4-chloro-6-methoxy-1,3,5-triazin-2-yl)oxy)benzoate 3e: white solid, 670.5 mg, 74% yield, mp 216 - 218 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.90 (brs, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.97 (s, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 4.03 (s, 3H), 4.00 (s, 3H), 3.72 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ (ppm): 172.4, 171.9, 171.8, 171.0, 170.0, 165.0, 163.7, 151.1, 143.9, 132.5, 118.0, 116.7, 114.3, 56.4, 55.7, 52.2. IR (KBr) ν: 3280 (w), 3171 (w), 1697, 1619, 1562 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₆H₁₄Cl₂N₇O₅: 454.0427; Found: 454.0429.

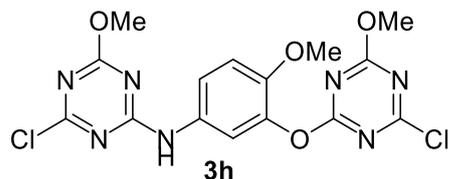


***N*-(4-Chloro-3-((4-chloro-6-methoxy-1,3,5-triazin-2-yl)oxy)phenyl)-4-chloro-6-methoxy-1,3,5-triazin-2-amine 3f**: white solid, 687.0 mg, 80% yield, mp 172 - 173 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.72 (s, 1H), 8.00 (s, 1H), 7.76 (d, *J* = 9.2 Hz, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 4.03 (s, 3H), 3.99 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ (ppm): 172.6, 172.1, 171.1, 169.8, 164.9, 146.9, 138.4, 130.5, 120.0, 115.6, 56.6, 55.6. IR (KBr) ν: 3358, 3288, 1611, 1560 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₄H₁₁Cl₃N₇O₃: 429.9983; Found: 429.9986.

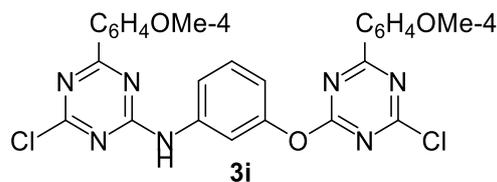


***N*-(3-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)oxy)-4-methylphenyl)-4-chloro-6-methoxy-**

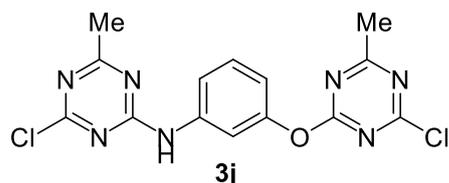
1,3,5-triazin-2-amine 3g: white solid, 507.2 mg, 62% yield, mp 185 - 186 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.54 (brs, 1H), 7.76 (brs, 1H), 7.60 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 2.15 (s, 3H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ (ppm): 173.9, 173.4, 172.9, 172.4, 171.1, 166.3, 150.9, 137.9, 132.0, 126.5, 119.8, 115.2, 56.5, 55.8, 15.6. IR (KBr) ν: 3356 (w), 3286 (w), 1610, 1559, 1540 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₅H₁₄Cl₂N₇O₃: 410.0529; Found: 410.0535.



***N*-(3-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)oxy)-4-methoxyphenyl)-4-chloro-6-methoxy-1,3,5-triazin-2-amine 3h**: white solid, 655.0 mg, 77% yield, mp 164 - 166 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.43 (s, 1H), 7.78 (s, 1H), 7.66 (d, *J* = 9.6 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.81 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆, 60 °C) δ (ppm): 172.4, 171.7, 171.4, 170.8, 169.4, 164.7, 147.1, 139.4, 131.0, 120.0, 115.5, 113.4, 56.14, 56.05, 55.1. IR (KBr) ν: 3361, 3288, 1613, 1563, 1509 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₅H₁₄Cl₂N₇O₄: 426.0478; Found: 426.0474.



***N*-(3-((4-Chloro-6-(4-methoxyphenyl)-1,3,5-triazin-2-yl)oxy)phenyl)-4-chloro-6-(4-methoxyphenyl)-1,3,5-triazin-2-amine 3i**: white solid, 570.9 mg, 52% yield, mp 90 - 92 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.68 (brs, 1H), 8.37 - 8.33 (m, 4H), 8.02 (br, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.17 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.99 (br, 2H), 3.90 (s, 3H), 3.88 (s, 3H). ¹³C NMR (100 MHz, Acetone-*d*₆) δ (ppm): 175.5, 173.1, 172.3, 165.6, 165.5, 164.8, 153.1, 140.5, 140.4, 132.2, 131.7, 130.7, 127.7, 126.8, 119.3, 119.2, 117.7, 115.1, 114.8, 56.0, 55.8. IR (KBr) ν: 3391, 3318, 1608, 1570, 1544 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₂₆H₂₀Cl₂N₇O₃: 548.0999; Found: 548.1005.

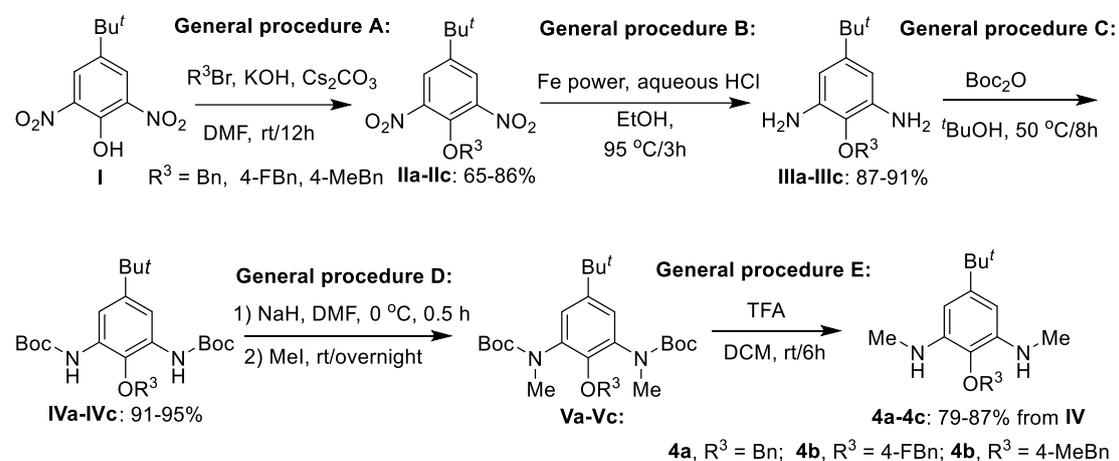


***N*-(3-((4-Chloro-6-methyl-1,3,5-triazin-2-yl)oxy)phenyl)-4-chloro-6-methyl-1,3,5-triazin-2-amine 3j**: white solid, 580.4 mg, 80% yield, mp 113 - 114 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 9.57 (brs, 1H), 7.86 (brs, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 2.52 (s, 3H), 2.42 (s, 3H). ¹³C NMR (150 MHz, benzene-*d*₆) δ (ppm): 181.5, 172.9,

171.4, 164.3, 152.3, 139.0, 129.9, 128.4, 118.21, 117.2, 113.9, 24.9. IR (KBr) ν : 3384, 3278, 1610, 1566, 1543 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{14}\text{H}_{12}\text{Cl}_2\text{N}_7\text{O}$: 364.0474; Found: 364.0478.

5. Synthesis of N^1, N^3 -dimethyl-2-benzyloxy-5-(*t*-butyl)benzene-1,3-diamines (monomers)

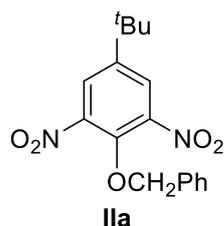
The compounds **4** were prepared based on the reported method for the preparation of **4a** [4]. (Ref. [4]. Tong, S.; Li, J. -T.; Liang, D. -D.; Zhang, Y. -E.; Feng, Q. -Y.; Zhang, X.; Zhu, J. -P.; Wang, M. -X. Catalytic enantioselective synthesis and switchable chiroptical property of inherently chiral macrocycles. *J. Am. Chem. Soc.* **2020**, *142*, 14432–14436.)



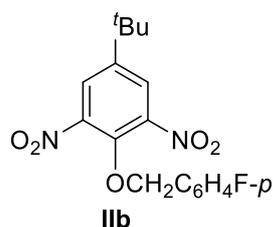
Scheme S4

General procedure A:

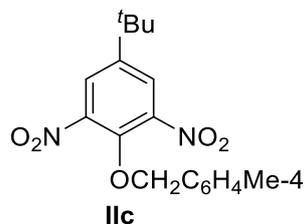
At ambient temperature, 4-(*t*-butyl)-2,6-dinitrophenol **I** (7.21 g, 30 mmol), KOH (3.37 g, 60 mmol) and Cs_2CO_3 (977.5 mg, 3 mmol) were mixed in a flask. The flask was then evacuated and backfilled with nitrogen gas. Under the protection of N_2 atmosphere, the solution of benzyl bromides (90 mmol) in dry DMF (250 mL) was added to flask. The resulting reaction mixture was kept stirring at room temperature for 12 h until the starting material was consumed completely (monitored by TLC). The reaction mixture was added water (100 mL) and then was extracted with ethyl acetate (200×3 mL). The combined organic layer was washed with saturated aqueous NaCl (200×3 mL) and dried over anhydrous Na_2SO_4 . After filtration of Na_2SO_4 and evaporation of solvents under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 20:1) to give 2-benzyloxy-5-(*t*-butyl)-1,3-dinitrobenzenes **IIa-IIIc**.



2-(Benzyloxy)-5-(*t*-butyl)-1,3-dinitrobenzene IIa: yellow solid, 8.49 g, 86% yield, mp 98 - 99 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.06 (s, 2H), 7.48 (dd, *J* = 8.4, 2.4 Hz, 2H), 7.42-7.38 (m, 3H), 5.20 (s, 2H), 1.39 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 149.0, 145.5, 143.5, 134.9, 129.2, 129.1, 128.8, 126.4, 79.1, 35.3, 30.9. IR (KBr) ν: 1561, 1533 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+Na]⁺ calcd. for C₁₇H₁₈N₂O₅Na: 353.1107; Found: 353.1106.



5-(*t*-Butyl)-2-((4-fluorobenzyl)oxy)-1,3-dinitrobenzene IIb: white solid, 6.78 g, 65% yield, mp 93 - 94 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.06 (s, 2H), 7.47 (dd, *J* = 9.0, 5.4 Hz, 2H), 7.08 (t, *J* = 8.4 Hz, 2H), 5.16 (s, 2H), 1.39 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 163.3 (d, *J* = 246.0 Hz), 149.2, 145.6, 143.4, 131.3 (d, *J* = 9.0 Hz), 130.9 (d, *J* = 3.0 Hz), 126.5, 115.7 (d, *J* = 22.5 Hz), 78.3, 35.4, 30.9. IR (KBr) ν: 1601, 1533, 1514 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+Na]⁺ calcd. for C₁₇H₁₇FN₂O₅Na: 371.1013; Found: 371.1020.

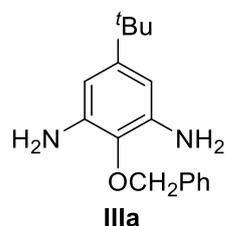


5-(*t*-Butyl)-2-((4-methylbenzyl)oxy)-1,3-dinitrobenzene IIc: white solid, 8.86 g, 86% yield, mp 67 - 69 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 8.04 (s, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.16 (s, 2H), 2.37 (s, 3H), 1.39 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 148.8, 145.6, 143.6, 139.1, 131.9, 129.5, 129.4, 126.3, 79.2, 35.4, 31.0, 21.4. IR (KBr) ν: 1620, 1539, 1521 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+Na]⁺ calcd. for C₁₈H₂₀N₂O₅Na: 367.1264; Found: 367.1261.

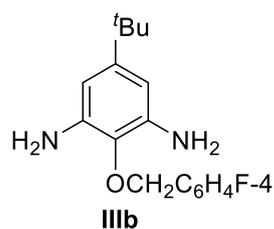
General procedure B:

At ambient temperature, the 2-benzyloxy-5-(*t*-butyl)-1,3-dinitrobenzenes **II** (6 mmol), ethanol (50 mL), water (10 mL) and concentrated HCl (12 M, 0.3 mL) were mixed in a test tube, and then iron powder (7 g) was added portionwise with stirring. The resulting mixture was heated for 3h at 95 °C or for 5h at 60 °C in an oil bath (see Scheme S4). After being cooled to room temperature, the

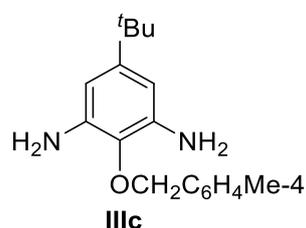
solids in reaction mixture were filtrated and washed with DCM (20 mL). The combined filtrate was concentrated under reduced pressure. The residue was dissolved in DCM (200 mL) and this solution was washed with saturated aqueous solution of sodium chloride (30 × 2 mL). The organic layer was dried over anhydrous sodium sulfate. After filtration of Na₂SO₄ and removal of DCM, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 10:1) to give 2-benzyloxy-5-(*t*-butyl)benzene-1,3-diamines **IIIa-IIIc**.



2-(Benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine IIIa: white solid, 1.47 g, 91% yield, mp 111 - 112 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.49 (d, *J* = 6.6 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.2 Hz, 1H), 6.26 (s, 2H), 4.90 (s, 2H), 3.75 (brs, 4H), 1.25 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 148.5, 139.4, 138.0, 132.3, 128.8, 128.3, 128.2, 104.4, 73.1, 34.4, 31.5. IR (KBr) ν: 3447, 3354, 3340, 1613, 1595 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₇H₂₃N₂O: 271.1804; Found: 271.1813.



5-(*t*-Butyl)-2-((4-fluorobenzyl)oxy)benzene-1,3-diamine IIIb: white solid, 1.50 g, 87% yield, mp 106 - 107 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.45 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.25 (s, 2H), 4.87 (s, 2H), 3.67 (brs, 4H), 1.27 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 162.7 (d, *J* = 244.5 Hz), 148.5, 139.4, 133.8, 132.0, 130.0 (d, *J* = 7.5 Hz), 115.6 (d, *J* = 22.5 Hz), 104.2, 72.3, 34.4, 31.5. IR (KBr) ν: 3454, 3367, 1610 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₇H₂₂FN₂O: 289.1710; Found: 289.1711.

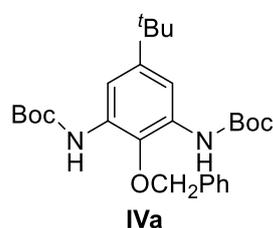


5-(*t*-Butyl)-2-((4-methylbenzyl)oxy)benzene-1,3-diamine IIIc: pale yellow solid, 1.50 g, 88% yield, mp 126 - 127 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.38 (d, *J* = 6.6 Hz, 2H), 7.22 (d, *J* = 6.6 Hz, 2H), 6.25 (s, 2H), 4.86 (s, 2H), 3.68 (brs, 4H), 2.39 (s, 3H), 1.27 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 148.4, 139.5, 138.1, 135.0, 132.3, 129.4, 128.3, 104.2, 73.0, 34.4, 31.5, 21.4.

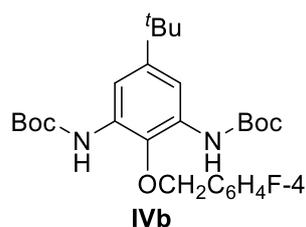
IR (KBr) ν : 3463, 3374, 1610 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}$: 285.1961; Found: 285.1963.

General procedure C:

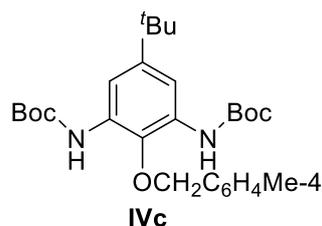
2-Benzyloxy-5-(*t*-butyl)benzene-1,3-diamines **III** (3 mmol), Boc_2O (2.60 g, 12 mmol) and *t*-BuOH (50 mL) were mixed in a flask. The mixture was warmed for 8 h at 50 °C oil bath temperature. Then solvent was evaporated under vacuum and the residue was dissolved in DCM (50 mL). The resulting solution was washed with saturated aqueous NaHCO_3 (30×2 mL) and saturated aqueous NaCl (30×2 mL). After being dried and removal of solvent, the di(*t*-butyl) 1,3-(2-benzyloxy-5-(*t*-butyl)phenylene)dicarbamates **IVa-IVc** were isolated by chromatography on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 10:1).



Di(*t*-butyl) (2-(benzyloxy)-5-(*t*-butyl)-1,3-phenylene)dicarbamate IVa: white solid, 1.31 g, 93% yield, m p 128 - 129 °C. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 7.75 (brs, 2H), 7.44 - 7.40 (m, 5H), 6.75 (brs, 2H), 4.81 (s, 2H), 1.51 (s, 18H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 152.7, 148.5, 136.4, 134.6, 131.1, 129.11, 129.06, 128.8, 110.9, 80.5, 76.1, 35.2, 31.6, 28.5. IR (KBr) ν : 3424, 3330, 1732, 1699, 1605 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{27}\text{H}_{39}\text{N}_2\text{O}_5$: 471.2853; Found: 471.2849.



Di(*t*-butyl) (5-(*t*-butyl)-2-((4-fluorobenzyl)oxy)-1,3-phenylene)dicarbamate IVb: white solid, 1.39g, 95% yield, mp 129 - 130 °C. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 7.73 (brs, 2H), 7.38 (dd, $J = 8.4, 5.4$ Hz, 2H), 7.10 (t, $J = 8.4$ Hz, 2H), 6.66 (s, 2H), 4.79 (s, 2H), 1.51 (s, 18H), 1.33 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 163.2 (d, $J = 246.0$ Hz), 152.7, 148.7, 134.4, 132.4 (d, $J = 4.5$ Hz), 131.1, 130.9 (d, $J = 9.0$ Hz), 116.1 (d, $J = 21.0$ Hz), 111.0, 80.6, 75.4, 35.2, 31.6, 28.5. IR (KBr) ν : 3428, 3332, 1732, 1700, 1604 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{27}\text{H}_{38}\text{FN}_2\text{O}_5$: 489.2759; Found: 489.2763.



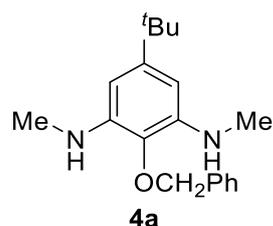
Di(*t*-butyl) (5-(*t*-butyl)-2-((4-methylbenzyl)oxy)-1,3-phenylene)dicarbamate IVc: white solid, 1.32 g, 91% yield, mp 143 - 144 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.74 (brs, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.2 Hz, 2H), 6.74 (s, 2H), 4.77 (s, 2H), 2.39 (s, 3H), 1.51 (s, 18H), 1.33 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 152.7, 148.5, 138.9, 134.6, 133.5, 131.2, 129.8, 129.0, 110.8, 80.4, 76.0, 35.2, 31.6, 28.5, 21.4. IR (KBr) ν: 3422, 3330, 1732, 1700, 1605, 1552 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₂₈H₄₁N₂O₅: 485.3009; Found: 485.2997.

General procedure D:

At 0 °C, the 1,3-(2-benzyloxy-5-(*t*-butyl)phenylene)dicarbamates **IVa-IVc** (3 mmol) was added to a stirred suspension of NaH (12 mmol, 480 mg of 60% dispersion in mineral oil). The mineral oil was removed by washing with *n*-hexane in dry DMF (30 mL). After being stirred at 0 °C for 0.5 h, MeI (1.70 g, 12 mmol) was added dropwise. The resulting mixture was then stirred at room temperature until the starting material was consumed completely (monitored by TLC). The reaction was quenched with ice water and the mixture was extracted with DCM (100 × 3 mL). The combined organic layers were washed with saturated aqueous NaCl (100 × 5 mL) and dried over anhydrous Na₂SO₄. After filtration and concentration under vacuo, the crude di(*t*-butyl) 1,3-(2-benzyloxy-5-(*t*-butyl)phenylene)bis(methylcarbamates) **Va-Vc** were obtained, which were used for next step without further purification.

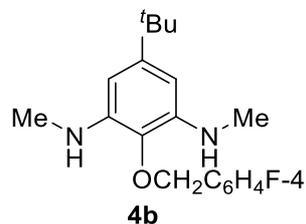
General procedure E:

The above obtained crude products **Va-Vc**, DCM (30 mL) and TFA (6 mL) were mixed in a flask. The mixture was stirred at room temperature for 6 h. Solvent was removed under vacuum and the residue was dissolved in DCM (50 mL). The resulting solution was washed with saturated aqueous Na₂CO₃ solution and brine, and dried over anhydrous Na₂SO₄. After solvent evaporation, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 20:1) to give *N*¹,*N*³-dimethyl-2-benzyloxy-5-(*t*-butyl)benzene-1,3-diamines **4a-4c**.

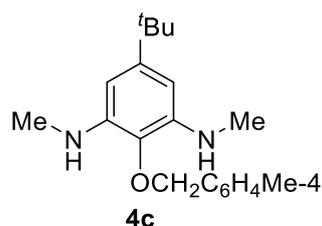


***N*¹,*N*³-Dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine 4a⁴:** red solid, 781.6 mg, 87%

yield, mp 46 - 47 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.51 (d, *J* = 5.2 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.23 (s, 2H), 4.87 (s, 2H), 4.03 (br, 2H), 2.87 (s, 6H), 1.39 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 148.5, 141.8, 138.1, 131.0, 128.7, 128.1, 127.9, 98.6, 72.6, 35.0, 31.7, 31.0. IR (KBr) ν: 3426, 1597, 1535 cm⁻¹.

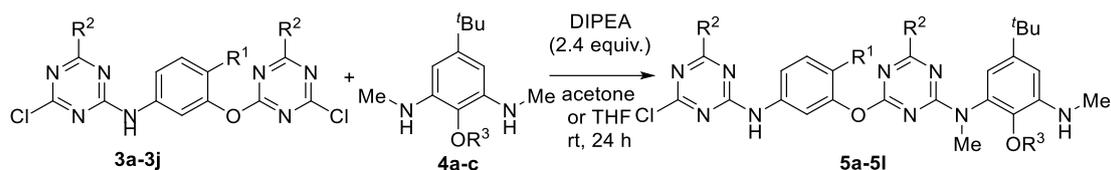


***N*¹,*N*³-Dimethyl-2-((4-fluorobenzyl)oxy)-5-(*t*-butyl)benzene-1,3-diamine 4b:** red solid, 816.7 mg, 86% yield, mp 79 - 80 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.42 (dd, *J* = 8.4, 5.4 Hz, 2H), 7.09 (t, *J* = 8.4 Hz, 2H), 6.19 (s, 2H), 4.79 (s, 2H), 2.83 (s, 6H), 1.33 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 162.7 (d, *J* = 244.5 Hz), 148.7, 141.7, 133.9 (d, *J* = 3.0 Hz), 131.0, 129.9 (d, *J* = 9.0 Hz), 115.6 (d, *J* = 21.0 Hz), 98.8, 72.0, 35.0, 31.7, 31.0. IR (KBr) ν: 3426, 1598, 1535 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₁₉H₂₆FN₂O: 317.2023; Found: 317.2027.



***N*¹,*N*³-Dimethyl-2-((4-methylbenzyl)oxy)-5-(*t*-butyl)benzene-1,3-diamine 4c:** red solid, 740.1 mg, 79% yield, mp 63 - 64 °C. ¹H NMR (600 MHz, CDCl₃) δ (ppm): 7.44 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 6.28 (s, 2H), 4.87 (s, 2H), 4.11 (brs, 2H), 2.91 (s, 6H), 2.47 (s, 3H), 1.44 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 148.4, 141.8, 137.8, 135.1, 131.0, 129.3, 128.0, 98.4, 72.6, 34.9, 31.7, 30.9, 21.3. IR (KBr) ν: 3424, 1597, 1534 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₂₀H₂₉N₂O: 313.2274; Found: 313.2279.

6. Synthesis of *N*¹-(4-(3-((6-(alkoxy, alkyl, aryl)-4-chloro-1,3,5-triazin-2-yl)amino)phenoxy)-6-(alkoxy, alkyl, aryl)-1,3,5-triazin-2-yl)-*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamines (tetramers)

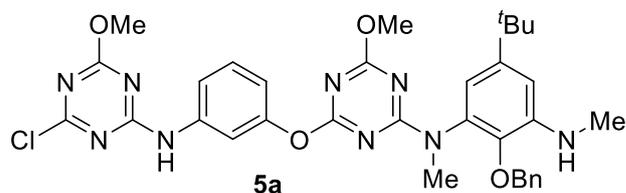


5	5a ^a	5b ^a	5c ^a	5d ^a	5e ^a	5f ^a	5g ^a	5h ^a	5i ^a	5j ^a	5k ^b	5l ^a
R ¹	H	H	H	H	H	H	CO ₂ Me	Cl	Me	MeO	H	H
R ²	MeO	EtO	ⁱ PrO	BnO	MeO	MeO	MeO	MeO	MeO	MeO	4-MeOC ₆ H ₄	Me
R ³	Bn	Bn	Bn	Bn	4-FBn	4-MeBn	Bn	Bn	Bn	Bn	Bn	Bn
yield	86	76	73	73	85	82	86	81	94	78	67	78

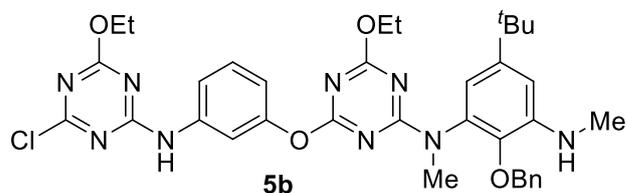
^a The reaction solvent was acetone. ^b The reaction solvent was THF.

Scheme S5

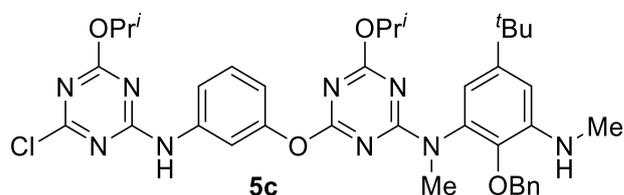
In a flask, trimers **3** (0.5 mmol), *N*¹,*N*³-dimethyl-5-(*t*-butyl)-2-(benzyloxy)benzene-1,3-diamine **4** (0.5 mmol), DIPEA (1.2 mmol, 2.4 equiv.) and acetone or THF (20 mL) were added successively (Note: Acetone was employed as the solvent for all reactions, except the one between **3i** and **4a** which was conducted in THF due to the low solubility of **3i** in acetone). The resulting mixture was stirred for 24h at ambient temperature. Then the reaction was stopped by removal of solvent under vacuum. The residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA from 6:1 to 3:1 for **5a-5d**; PE:EA from 3:1 to 2:1 for **5e-5l**) to give products **5** in 67-94% yields.



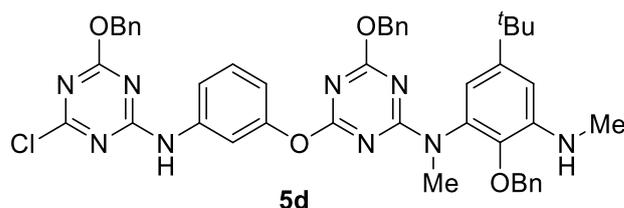
*N*¹-(4-(3-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)amino)phenoxy)-6-methoxy-1,3,5-triazin-2-yl)-*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine **5a**: white solid, 282.0 mg, 86% yield, mp 83 - 84 °C. ¹H NMR (400 MHz, CDCl₃) (two rotamers 0.5:0.5) δ (ppm): 7.61 - 7.49 (m, 2H), 7.38 - 7.26 (m, 6.5H), 7.21 - 7.17 (m, 1.5H), 7.02 (d, *J* = 7.2 Hz, 0.5H), 6.88 (d, *J* = 7.2 Hz, 0.5H), 6.78 (br, 0.5H), 6.72 (br, 0.5H), 6.62 (br, 0.5H), 6.54 (br, 0.5H), 4.75 (s, 1H), 4.69 (s, 1H), 4.01 (s, 1.5H), 4.00 (s, 1.5H), 3.97 (s, 1.5H), 3.68 (s, 1.5H), 3.46 (s, 1.5H), 3.39 (s, 1.5H), 2.82 (s, 3H), 1.30 (s, 4.5H), 1.24 (s, 4.5H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.6, 172.0, 171.9, 171.4, 170.9, 170.6, 167.73, 167.66, 165.08, 165.05, 152.4, 152.3, 148.4, 148.0, 138.1, 137.5, 136.9, 136.8, 135.8, 129.4, 129.0, 128.4, 128.24, 128.16, 127.9, 117.9, 114.6, 75.3, 55.5, 54.8, 54.6, 37.9, 37.8, 34.74, 34.68, 31.34, 31.27. IR (KBr) ν : 1574, 1481 cm⁻¹. HRMS (APCI) *m/z* [M+H]⁺ calcd. for C₃₃H₃₇ClN₉O₄: 658.2652; Found: 658.2647.



N*¹-(4-(3-((4-Chloro-6-ethoxy-1,3,5-triazin-2-yl)amino)phenoxy)-6-ethoxy-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine **5b*: white solid, 261.3 mg, 76% yield, mp 75 - 76 °C. ¹H NMR (400 MHz, CDCl₃) (two rotamers 0.5:0.5) δ (ppm): 8.42 - 8.36 (br, 0.5H), 8.11 - 8.00 (br, 0.5H), 7.60 (s, 0.5H), 7.36 (brs, 0.5H), 7.27-7.17 (m, 6.5H), 7.13-7.09 (m, 0.5H), 6.93 (d, *J* = 7.6 Hz, 0.5H), 6.83 (d, *J* = 8.0 Hz, 0.5H), 6.67 (s, 0.5H), 6.61 (s, 0.5H), 6.54 (s, 0.5H), 6.49 (s, 0.5H), 4.72 (s, 1H), 4.68 (s, 1H), 4.44-4.31 (m, 3H), 4.10-4.05 (m, 1H), 3.44 (s, 1.5H), 3.39 (s, 1.5H), 2.79 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 1.5H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.27 (s, 4.5H), 1.22 (s, 4.5H), 1.12 (t, *J* = 7.2 Hz, 1.5H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.0, 171.3, 170.7, 170.5, 167.72, 167.65, 165.0, 164.9, 152.4, 152.3, 148.1, 147.7, 142.8, 139.6, 139.5, 138.2, 137.4, 137.1, 135.4, 135.3, 129.2, 128.8, 128.4, 128.1, 128.03, 127.95, 127.8, 117.8, 117.7, 117.5, 114.6, 114.4, 113.9, 113.5, 107.7, 107.2, 74.8, 74.6, 64.6, 63.6, 63.4, 37.9, 37.8, 34.60, 34.58, 31.4, 31.3, 14.3, 14.1, 14.0. IR (KBr) ν: 1599, 1574, 1560 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₃₅H₄₀ClN₉O₄: 686.2965; Found: 686.2955.

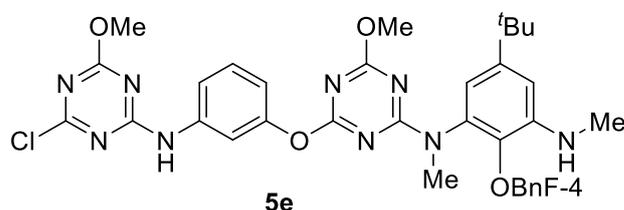


N*¹-(4-(3-((4-Chloro-6-isopropoxy-1,3,5-triazin-2-yl)amino)phenoxy)-6-isopropoxy-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)-benzene-1,3-diamine **5c*: white solid, 260.1 mg, 73% yield, mp 86 - 87 °C. ¹H NMR (400 MHz, CDCl₃) (two rotamers 0.5:0.5) δ (ppm): 8.06 (s, 0.5H), 7.81 (s, 0.5H), 7.57 (s, 0.5H), 7.43 (brs, 0.5H), 7.33-7.27 (m, 6.5H), 7.21-7.15 (m, 1.5H), 6.98 (d, *J* = 7.6 Hz, 0.5H), 6.87 (d, *J* = 6.8 Hz, 0.5H), 6.70 (br, 0.5H), 6.62 (s, 0.5H), 6.53 (s, 0.5H), 6.49 (s, 0.5H), 5.36 - 5.30 (m, 0.5H), 5.24 (br, 1H), 4.90 - 4.84 (m, 0.5H), 4.73 (s, 1H), 4.69 (s, 1H), 3.46 (s, 1.5H), 3.41 (s, 1.5H), 2.82 (s, 3H), 1.39 (d, *J* = 6.4 Hz, 3H), 1.35 - 1.32 (m, 6H), 1.30 (s, 4.5H), 1.24 (s, 4.5H), 1.15 (d, *J* = 6.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 172.1, 171.8, 171.1, 170.8, 167.94, 167.89, 165.3, 165.2, 152.7, 152.6, 148.3, 147.9, 143.1, 139.7, 138.2, 137.5, 137.4, 135.7, 135.5, 129.5, 129.0, 128.6, 128.3, 128.1, 128.0, 118.1, 117.7, 117.5, 114.7, 114.5, 113.7, 107.8, 107.3, 74.9, 74.8, 72.5, 71.1, 71.0, 38.0, 37.9, 34.8, 31.5, 31.4, 22.0, 21.73, 21.69. IR (KBr) ν: 1574, 1526 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₃₇H₄₅ClN₉O₄: 714.3277; Found: 714.3273.

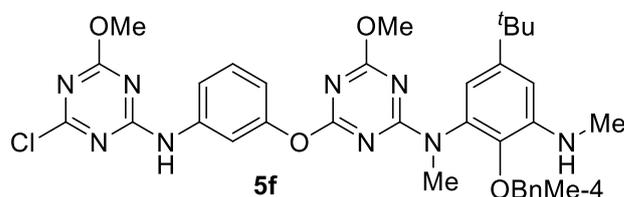


N*¹-(4-(Benzyloxy)-6-(3-((4-(benzyloxy)-6-chloro-1,3,5-triazin-2-yl)amino)phenoxy)-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine **5d*: white solid,

294.2 mg, 73% yield, mp 78 - 79 °C. ¹H NMR (400 MHz, CDCl₃) (two rotamers 0.63:0.37) δ (ppm): 8.27 (brs, 0.63H), 8.01 (brs, 0.37H), 7.50 - 7.13 (m, 13H), 7.19 - 7.13 (m, 5H), 6.96 (d, *J* = 7.6 Hz, 2H), 6.75 (s, 1H), 6.64 (s, 0.63H), 6.53 (s, 0.37H), 5.42 - 5.28 (m, 2.74H), 5.10 (d, *J* = 12.0 Hz, 0.63H), 5.00 (d, *J* = 12.0 Hz, 0.63H), 4.70 (brs, 0.74H), 4.46 (d, *J* = 10.8 Hz, 0.63H), 4.33 (d, *J* = 11.2 Hz, 0.63 H), 3.47 (s, 1.1H), 3.40 (s, 1.9H), 2.92 (s, 1.9H), 2.82 (s, 1.1H), 1.37 (s, 5.7H), 1.25 (s, 3.3H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.1, 172.0, 171.2, 170.8, 167.8, 167.7, 165.2, 165.0, 152.5, 152.4, 148.3, 148.1, 140.1, 138.1, 137.3, 137.2, 136.1, 136.0, 135.53, 135.45, 135.2, 129.4, 129.1, 128.9, 128.6, 128.54, 128.47, 128.44, 128.23, 128.16, 128.12, 128.0, 127.9, 127.8, 118.2, 118.0, 114.8, 108.2, 107.3, 75.0, 74.5, 70.0, 69.3, 69.2, 38.1, 37.6, 34.9, 34.7, 31.6, 31.4. IR (KBr) ν 3273, 1605, 1578 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₄₅H₄₅ClN₉O₄: 810.3278; Found: 810.3155.

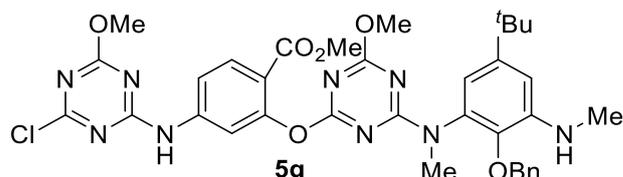


***N*¹-(4-(3-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)amino)phenoxy)-6-methoxy-1,3,5-triazin-2-yl)-*N*³-dimethyl-5-(*t*-butyl)-2-((4-fluorobenzyl)oxy)benzene-1,3-diamine 5e**: white solid, 286.1 mg, 85% yield, mp 89 - 90 °C. ¹H NMR (400 MHz, CDCl₃) (two rotamers 0.5:0.5) δ (ppm): 8.26 (br, 0.5H), 7.96 (br, 0.5H), 7.58 (s, 0.5H), 7.43 (br, 0.5H), 7.29 - 7.22 (m, 3.5H), 7.15 - 7.12 (m, 1.5H), 7.00 - 6.90 (m, 2.5H), 6.84 (d, *J* = 7.6 Hz, 0.5H), 6.68 (brs, 0.5H), 6.62 (s, 0.5H), 6.56 (s, 0.5H), 6.49 (s, 0.5H), 4.69 (s, 1H), 4.64 (s, 1H), 3.97 (s, 1.5H), 3.92 (s, 3H), 3.65 (s, 1.5H), 3.43 (s, 1.5H), 3.37 (s, 1.5H), 2.80 (s, 3H), 1.28 (s, 4.5H), 1.23 (s, 4.5H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 172.7, 172.1, 172.0, 171.5, 170.9, 167.9, 167.8, 165.2, 163.44, 163.42, 161.81, 161.78, 152.5, 148.5, 148.1, 140.0, 138.1, 137.5, 135.7, 135.5, 133.1, 130.1, 130.0, 129.9, 129.8, 129.5, 129.1, 118.1, 117.9, 117.7, 115.4, 115.3, 114.7, 114.4, 74.3, 74.2, 55.6, 54.9, 54.6, 37.92, 37.86, 34.80, 34.76, 31.5, 31.4. IR (KBr) ν: 1568, 1562, 1533 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₃₃H₃₆ClFN₉O₄: 676.2557; Found: 676.2561.

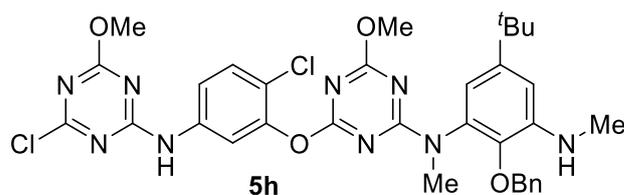


***N*¹-(4-(3-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)amino)phenoxy)-6-methoxy-1,3,5-triazin-2-yl)-*N*³-dimethyl-5-(*t*-butyl)-2-((4-methylbenzyl)oxy)benzene-1,3-diamine 5f**: white solid, 274.1 mg, 82% yield, mp 88 - 82 °C. ¹H NMR (600 MHz, CDCl₃) (two rotamers 0.5:0.5) δ (ppm): 8.15 (s, 0.5H), 7.91 (brs, 0.5H), 7.60 (s, 0.5H), 7.43 (br, 0.5H), 7.32 - 7.26 (m, 2.5H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 0.5H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.07 (s, 2H), 6.98 (d, *J* = 7.8 Hz, 0.5H), 6.85 (d, *J* = 8.4 Hz, 0.5H), 6.72 (brs, 0.5H), 6.66 (brs, 0.5H), 6.59 (s, 0.5H), 6.51 (s, 0.5H),

4.69 (s, 1H), 4.65 (s, 1H), 3.99 (s, 1.5H), 3.95 (brs, 1.5H), 3.93 (s, 1.5H), 3.66 (s, 1.5H), 3.46 (s, 1.5H), 3.40 (s, 1.5H), 2.80 (s, 3H), 2.32 (s, 1.5H), 2.29 (s, 1.5H), 1.29 (s, 4.5H), 1.23 (s, 4.5H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 172.8, 172.1, 172.0, 170.9, 167.9, 167.8, 165.3, 152.7, 148.4, 147.9, 138.2, 138.0, 137.4, 135.7, 134.2, 129.7, 129.3, 129.2, 129.1, 128.4, 128.2, 118.3, 117.8, 114.7, 75.1, 74.9, 55.6, 54.9, 54.6, 37.94, 37.88, 34.83, 34.78, 31.5, 31.4, 21.32, 21.26. IR (KBr) ν: 1576, 1559, 1539 cm⁻¹. HRMS (TOF-ESI) m/z [M+H]⁺ calcd. for C₃₄H₃₉ClN₉O₄: 672.2813; Found: 672.2811.

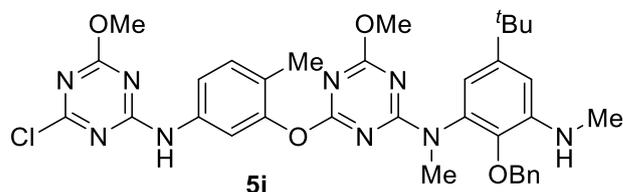


Methyl 2-((4-((2-(Benzyloxy)-5-(*t*-butyl)-3-(methylamino)phenyl)(methylamino)-6-methoxy-1,3,5-triazin-2-yl)oxy)-4-((4-chloro-6-methoxy-1,3,5-triazin-2-yl)amino)benzoate 5g: white solid, 307.6 mg, 86% yield, mp 93 - 94 °C. ¹H NMR (400 MHz, CDCl₃) (two rotamers 0.57:0.43) δ (ppm): 7.95 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 0.57H), 7.78 (s, 0.43H), 7.60 (s, 0.43H), 7.49 (d, *J* = 6.4 Hz, 0.57H), 7.41 (d, *J* = 6.4 Hz, 0.43H), 7.35 - 7.26 (m, 6.57H), 6.64 - 6.57 (m, 1.57H), 6.44 (s, 0.43H), 4.72 - 4.68 (m, 1.57H), 4.63 - 4.60 (m, 0.43H), 4.00 - 3.97 (m, 4.3H), 3.68 (s, 1.7H), 3.65 (s, 1.7H), 3.54 (s, 1.3H), 3.42 (s, 3H), 2.81 (s, 1.7H), 2.77 (s, 1.3H), 1.30 (s, 5.1H), 1.20 (s, 3.9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.5, 172.3, 171.9, 171.8, 167.8, 165.0, 164.5, 152.5, 148.0, 147.9, 143.1, 142.7, 142.0, 139.9, 139.3, 137.5, 137.2, 135.4, 135.3, 132.4, 132.3, 128.62, 128.55, 128.4, 128.3, 128.2, 128.1, 118.7, 118.5, 117.1, 116.9, 115.33, 115.26, 114.1, 113.4, 107.6, 107.0, 75.0, 74.7, 55.7, 54.9, 54.7, 52.1, 52.0, 38.1, 38.0, 34.8, 34.7, 31.6, 31.4. IR (KBr) ν: 1724, 1601, 1572, 1565 cm⁻¹. HRMS (TOF-ESI) m/z [M+H]⁺ Calcd. for C₃₅H₃₉ClN₉O₆: 716.2706; Found: 716.2711.

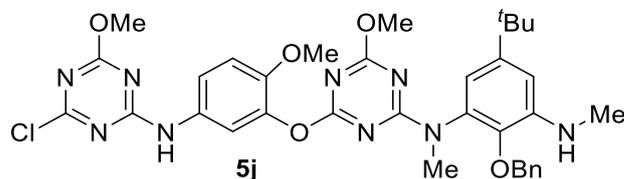


***N*¹-(4-(2-Chloro-5-((4-chloro-6-methoxy-1,3,5-triazin-2-yl)amino)phenoxy)-6-methoxy-1,3,5-triazin-2-yl)-*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine 5h:** white solid, 280.5 mg, 81% yield, mp 104 - 106 °C. ¹H NMR (600 MHz, CDCl₃) (two rotamers 0.55:0.45) δ (ppm): 8.35 - 8.25 (br, 0.55H), 8.09 (br, 0.45H), 7.67 (brs, 0.55H), 7.40 (brs, 0.45H), 7.32 - 7.27 (m, 6.55H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.19 (d, *J* = 9.0 Hz, 0.45H), 6.63 (s, 0.55H), 6.61 (s, 0.45H), 6.58 (s, 0.55H), 6.48 (s, 0.45H), 4.74 - 4.66 (m, 2H), 3.98 (s, 1.65H), 3.96 (s, 1.35H), 3.91 (s, 1.35H), 3.65 (s, 1.65H), 3.44 (s, 1.35H), 3.41 (s, 1.65H), 2.82 (s, 1.65H), 2.77 (s, 1.35H), 1.30 (s, 4.95H), 1.23 (s, 4.05H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 172.5, 171.8, 171.4, 170.9, 170.7, 167.8, 167.7, 165.0, 164.9, 148.2, 148.1, 147.9, 142.8, 139.9, 139.4, 137.3, 137.0, 135.3, 135.2, 130.0,

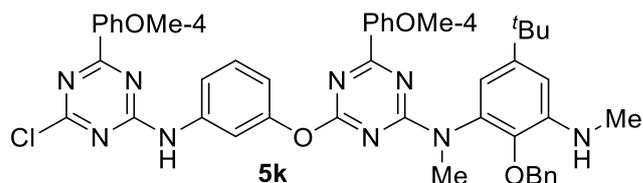
129.7, 128.48, 128.45, 128.3, 128.0, 127.7, 122.4, 122.3, 119.0, 116.3, 114.0, 108.0, 107.3, 74.9, 74.7, 55.6, 54.9, 54.7, 38.1, 37.9, 34.7, 34.6, 31.4, 31.3. IR (KBr) ν : 1602, 1572, 1560 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{33}\text{H}_{36}\text{Cl}_2\text{N}_9\text{O}_4$: 692.2261; Found: 692.2253.



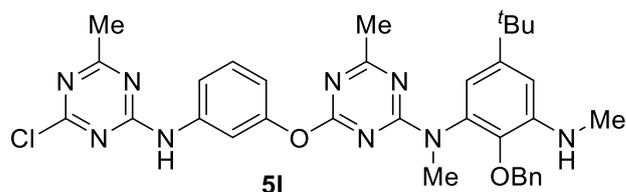
***N*¹-(4-(5-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)amino)-2-methylphenoxy)-6-methoxy-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine 5i**: white solid, 315.5 mg, 94% yield, mp 85 - 86 °C. ¹H NMR (400 MHz, CDCl_3) (two rotamers 0.5:0.5) δ (ppm): 8.30 (br, 0.5H), 8.02 (br, 0.5H), 7.41 (s, 1H), 7.26- 7.17 (m, 7H), 7.05 (d, J = 8.4 Hz, 0.5H), 6.96 (d, J = 8.0 Hz, 0.5H), 6.63 (s, 1H), 6.57 (s, 0.5H), 6.47 (s, 0.5H), 4.72 - 4.64 (m, 2H), 3.94 (s, 1.5H), 3.91 (s, 1.5H), 3.87 (s, 1.5H), 3.62 (s, 1.5H), 3.42 (s, 1.5H), 3.38 (s, 1.5H), 2.80 (s, 1.5H), 2.76 (s, 1.5H), 2.18 (s, 1.5H), 2.03 (s, 1.5 H), 1.28 (s, 4.5 H), 1.22 (s, 4.5H). ¹³C NMR (100 MHz, CDCl_3) δ (ppm): 172.6, 171.9, 171.8, 171.4, 171.1, 170.5, 167.8, 165.1, 150.6, 148.1, 147.9, 142.8, 139.9, 139.4, 137.3, 137.2, 135.9, 135.43, 135.36, 135.3, 131.0, 130.7, 128.5, 128.23, 128.18, 127.8, 126.9, 118.4, 118.0, 115.1, 114.9, 114.1, 113.6, 107.9, 107.3, 74.8, 74.7, 55.5, 54.8, 54.6, 38.1, 37.9, 34.8, 34.7, 31.5, 31.4, 16.0, 15.9. IR (KBr) ν : 1597, 1572, 1560 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ Calcd. For $\text{C}_{34}\text{H}_{39}\text{ClN}_9\text{O}_4^+$ 672.2808; Found: 672.2812.



***N*¹-(4-(5-((4-Chloro-6-methoxy-1,3,5-triazin-2-yl)amino)-2-methoxyphenoxy)-6-methoxy-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine 5j**: white solid, 267.3 mg, 78% yield, mp 98 - 99 °C. ¹H NMR (600 MHz, CDCl_3) (two rotamers 0.6:0.4) δ (ppm): 8.09 - 8.00 (br, 0.6H), 7.85 - 7.82 (br, 0.4H), 7.33 (s, 0.6H), 7.28 (d, J = 9.0 Hz, 0.6H), 7.23- 7.09 (m, 6.8H), 6.80 (d, J = 8.4 Hz, 0.6H), 6.68 (d, J = 9.0 Hz, 0.4H), 6.57 (brs, 1H), 6.52 (s, 0.6H), 6.43 (s, 0.4H), 4.66 (s, 1.2H), 4.62 (s, 0.8H), 3.87 (s, 3H), 3.84 (s, 1.2H), 3.68 (s, 1.8H), 3.55 (s, 1.8H), 3.54 (s, 1.2H), 3.33 (s, 3H), 2.73 (s, 1.8H), 2.72 (s, 1.2H), 1.22 (s, 5.4H), 1.14 (s, 3.6H). ¹³C NMR (100 MHz, CDCl_3) δ (ppm): 172.3, 171.8, 171.7, 171.24, 171.15, 170.4, 170.2, 167.6, 164.82, 164.75, 148.3, 148.2, 147.8, 147.5, 142.8, 140.7, 140.5, 139.8, 139.0, 137.3, 137.0, 135.3, 135.1, 130.3, 129.7, 128.3, 128.1, 127.8, 127.5, 119.3, 118.9, 116.7, 113.9, 113.3, 112.1, 107.4, 106.8, 74.5, 74.4, 55.9, 55.3, 54.9, 54.6, 54.4, 38.0, 37.7, 34.6, 34.4, 31.3, 31.2. IR (KBr) ν : 1601, 1575, 1509 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{34}\text{H}_{39}\text{ClN}_9\text{O}_5$: 688.2757; Found: 688.2761.

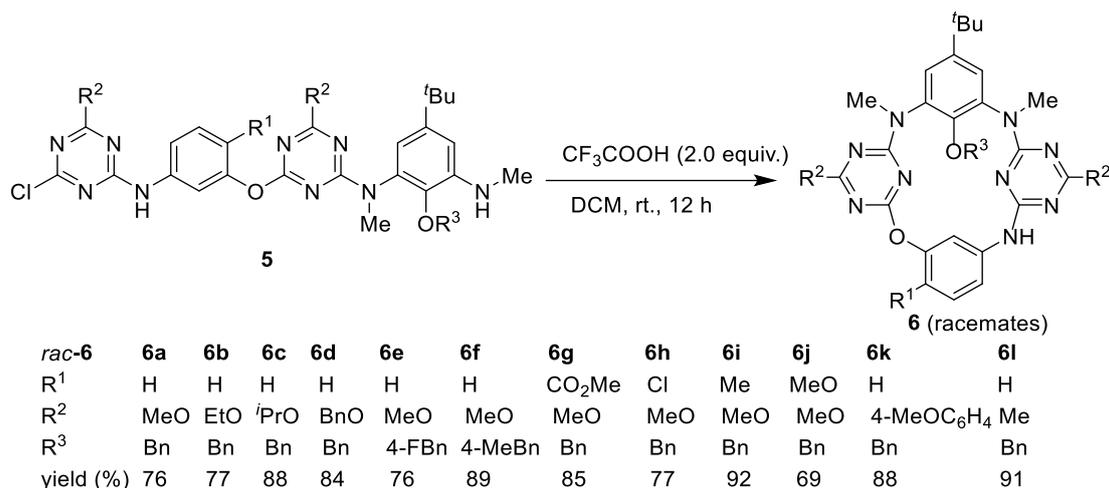


N*¹-(4-(3-((4-Chloro-6-(4-methoxyphenyl)-1,3,5-triazin-2-yl)amino)phenoxy)-6-(4-methoxyphenyl)-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine **5k*: white solid, 271.4 mg, 67% yield, mp 108 - 110 °C. ¹H NMR (600 MHz, CDCl₃) (two rotamers 0.55:0.45) δ (ppm): 8.49 (d, *J* = 8.4 Hz, 1H), 8.36 - 8.30 (m, 2H), 8.16 (d, *J* = 8.4 Hz, 1H), 7.84 (br, 0.45H), 7.72 (br, 0.55H), 7.62 (brs 1H), 7.47 - 7.42 (m, 1.45H), 7.24 - 7.11 (m, 5.55H), 7.00 - 6.96 (m, 2H), 6.91 (d, *J* = 9.6 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.73 (brs, 0.55H), 6.68 (brs, 1H), 6.56 (s, 0.45H), 4.71 (s, 1H), 4.69 (s, 1H), 3.88 (s, 1.65H), 3.83 (s, 1.35H), 3.82 (s, 1.35H), 3.79 (s, 1.65H), 3.62 (s, 1.65H), 3.41 (s, 1.35H), 2.83 (s, 3H), 1.34 (s, 4.95H), 1.26 (s, 4.05H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 172.9, 172.6, 172.0, 171.4, 170.4, 167.2, 167.1, 164.3, 163.8, 163.1, 162.9, 153.0, 152.8, 148.2, 147.7, 138.3, 137.7, 137.2, 135.8, 135.7, 131.7, 131.1, 130.7, 129.3, 128.9, 128.7, 128.4, 128.3, 128.2, 127.9, 127.0, 126.8, 125.9, 117.9, 117.3, 114.2, 113.9, 113.7, 113.5, 75.0, 74.6, 55.4, 55.3, 37.9, 37.4, 34.70, 34.66, 31.5, 31.4. IR (KBr) ν : 1601, 1545 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₄₅H₄₅ClN₉O₄: 810.3277; Found: 810.3273.



N*¹-(4-(3-((4-Chloro-6-methyl-1,3,5-triazin-2-yl)amino)phenoxy)-6-methyl-1,3,5-triazin-2-yl)-*N*¹,*N*³-dimethyl-2-(benzyloxy)-5-(*t*-butyl)benzene-1,3-diamine **5l*: white solid, 244.0 mg, 78% yield, mp 109 - 111 °C. ¹H NMR (600 MHz, CDCl₃) (two rotamers 0.65:0.35) δ (ppm): 7.58 - 7.49 (m, 2H), 7.41 - 7.27 (m, 5.35H), 7.19 (t, *J* = 8.4 Hz, 1H), 7.15-7.13 (m, 1.65H), 7.04 (d, *J* = 7.8 Hz, 0.35H), 6.90 (d, *J* = 7.8 Hz, 0.65H), 6.74 (brs, 0.65H), 6.62 (s, 0.35H), 6.52 (s, 0.35H), 6.48 (s, 0.35H), 4.72 (s, 0.7H), 4.64 (s, 1.3H), 3.50 (s, 1.95H), 3.29 (s, 1.05H), 2.83 (s, 1.05H), 2.82 (s, 1.95H), 2.49 (s, 3H), 2.48 (s, 1.95H), 2.27 (s, 1.05H), 1.31 (s, 3.15H), 1.23 (s, 5.85H). ¹³C NMR (150 MHz, CDCl₃) δ (ppm): 178.4, 177.9, 170.4, 169.4, 166.9, 166.7, 164.1, 152.5, 148.3, 147.9, 143.1, 139.6, 137.4, 137.1, 135.5, 129.2, 128.9, 128.4, 128.1, 128.0, 127.8, 125.9, 118.1, 117.5, 114.5, 114.1, 113.7, 113.2, 107.5, 107.0, 74.8, 74.4, 37.7, 34.6, 31.4, 31.3, 25.6, 25.4. IR (KBr) ν : 1647, 1566, 1543 cm⁻¹. HRMS (TOF-ESI) *m/z* [M+H]⁺ calcd. for C₃₃H₃₇ClN₉O₂: 626.2753; Found: 626.2754.

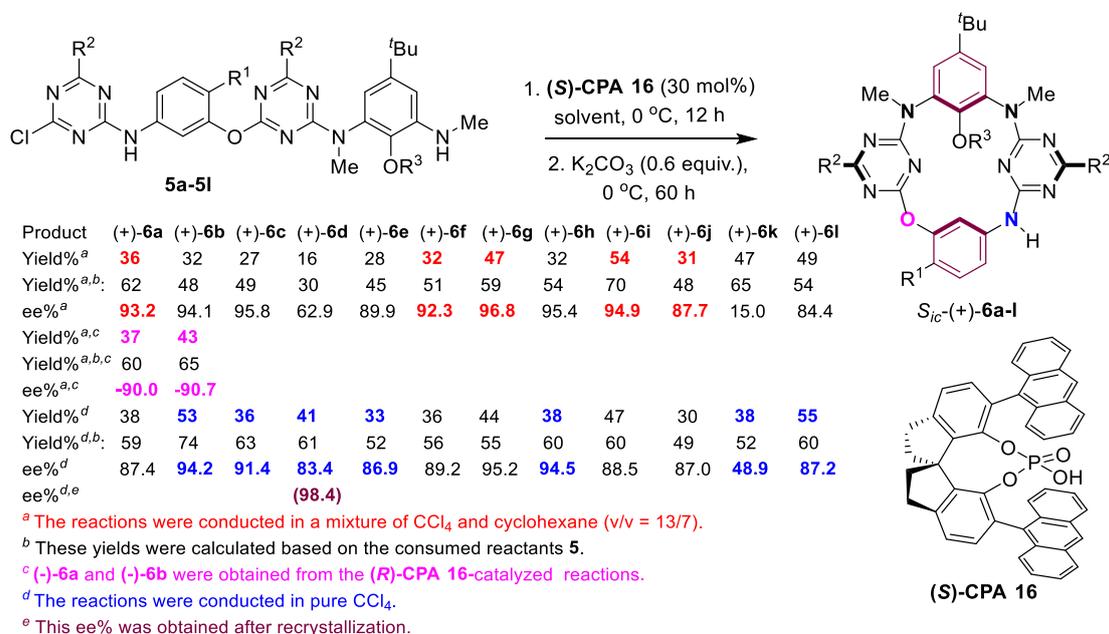
7. Synthesis of racemic macrocycles **6**



Scheme S6

The tetramers **5** (0.1 mmol), CF₃CO₂H (0.2 mmol) and DCM (40 mL) were mixed in a flask. The mixture was stirred at room temperature for 12 h until the starting material was consumed completely. The reaction solution was washed with saturated aqueous NaHCO₃ (10×2 mL). The organic layer was dried over anhydrous Na₂SO₄. After removal of solvent, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA from 5:1 to 2:1) to give the racemic macrocycles **6** in 69-92% yields.

8. Enantioselective synthesis of inherently chiral macrocycles **6**



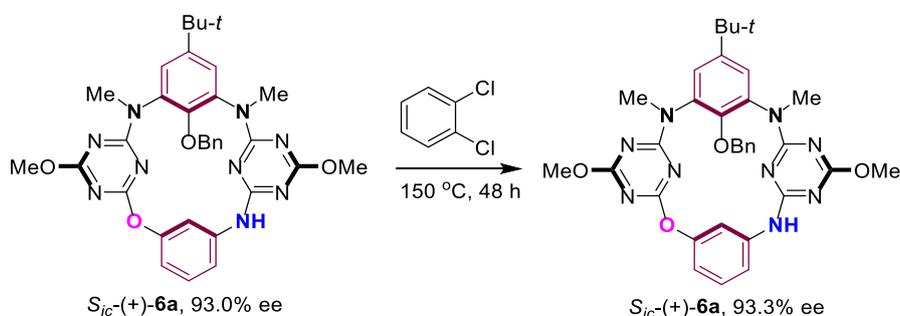
Scheme S7

7.1 General procedure:

In a test tube that was cooled at 0 °C, the tetramers **5** (0.05 mmol), chiral phosphoric acid (S)-CPA-

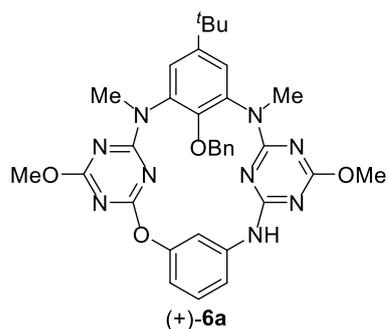
16 (10.0 mg, 30 mol%), tetrachloromethane (13 mL) and cyclohexane (7 mL) (or sole tetrachloromethane, 20 mL) were added successively with stirring. The reaction mixture was stirred for 12 h at 0 °C. Then K₂CO₃ (4.1 mg, 0.03 mmol) was added and the resulting mixture was stirred for another 60h at 0 °C. The solids in reaction mixture were suction filtrated quickly and washed with dichloromethane (5 mL) that was precooled at 0 °C. The combined filtrate was washed with cool saturated aqueous NaHCO₃ (10 mL). The organic layer was dried over anhydrous Na₂SO₄. After removal of Na₂SO₄ and solvents, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA from 3:1 to 2:1). The optically active macrocycles (+)-**6** were isolated in 16-54% yields with 15.0-96.8% ee from the reactions in the mixture of tetrachloromethane and cyclohexane (~2:1), or in 30-55% yields with 48.9-95.2% ee from the reactions in tetrachloromethane.

7.2 Stability of inherent chirality of compound **6a**



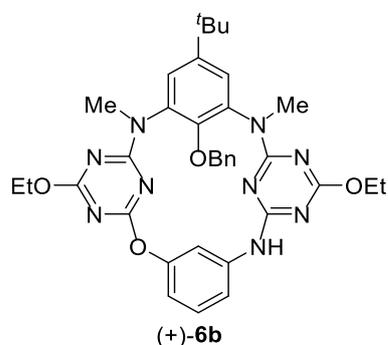
Scheme S8

Inherent chirality of heteracalix[4](het)arenes **6** were found very stable. For example, no racemization took place after heating *S*_{ic}-(+)-**6a** at 150 °C for 48 h in *o*-dichlorobenzene (Scheme S8).

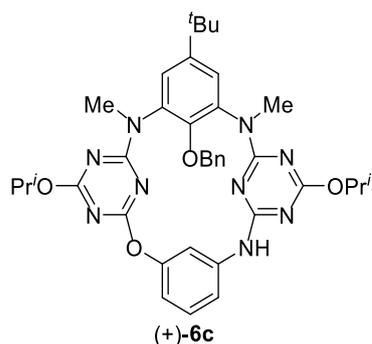


*S*_{ic}-(+)-**7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **6a**: white solid, 11.2 mg, 36% yield and 93.2% ee from the reaction in the mixture of tetrachloromethane and cyclohexane (v:v = 13:7), [α]_D²⁵ = +38.0 ° (c = 0.1, CH₂Cl₂), mp 99 - 101 °C. ¹H NMR (400 MHz, Acetone-*d*₆) δ (ppm): 8.12 (s, 1H), 7.26 - 7.22 (m, 3H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.08 (dd, *J* = 7.2, 2.0 Hz, 2H), 7.02 (d, *J* = 2.4 Hz, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 6.90 - 6.89 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.80 (dd, *J* = 8.0, 2.4 Hz, 1H),**

4.73 (d, $J = 12.0$ Hz, 1H), 4.62 (d, $J = 12.0$ Hz, 1H), 3.94 (s, 3H), 3.87 (s, 3H), 3.38 (s, 3H), 3.36 (s, 3H), 1.17 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.1, 171.7, 171.6, 168.4, 167.9, 166.9, 152.6, 150.0, 148.0, 138.5, 137.9, 137.8, 136.9, 129.4, 128.4, 127.6, 126.9, 126.4, 125.3, 125.0, 123.7, 120.3, 74.0, 54.8, 54.1, 37.2, 36.4, 34.3, 31.3. IR (KBr) ν : 3225 (w), 1667, 1582, 1543 cm^{-1} . HRMS (APCI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{36}\text{N}_9\text{O}_4$: 622.2885; Found: 622.2872.

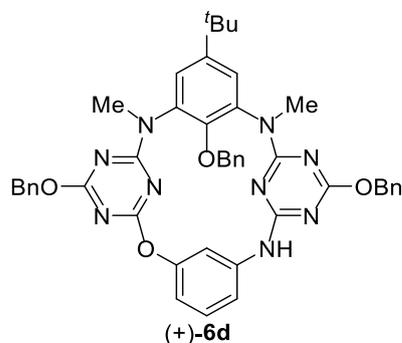


Sic*(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-diethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **6b*: white solid, 17.2 mg, 53% yield and 94.2% ee from the reaction in tetrachloromethane, $[\alpha]_{\text{D}}^{25} = +94.2^\circ$ ($c = 0.2$, CH_2Cl_2), mp 98 - 99 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.46 (s, 1H), 7.25 - 7.22 (m, 3H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.09 (dd, $J = 7.6, 1.6$ Hz, 2H), 7.02 (d, $J = 2.4$ Hz, 1H), 7.00 (d, $J = 2.4$ Hz, 1H), 6.90 - 6.86 (m, 2H), 6.80 (dd, $J = 8.0, 2.0$ Hz, 1H), 4.73 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 4.41 (q, $J = 7.2$ Hz, 2H), 4.32 (qd, $J = 7.2, 1.6$ Hz, 2H), 3.38 (s, 3H), 3.35 (s, 3H), 1.38 (t, $J = 7.2$ Hz, 3H), 1.29 (t, $J = 7.2$ Hz, 3H), 1.17 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 172.5, 171.6, 171.0, 168.4, 167.8, 166.8, 152.5, 149.9, 147.9, 138.6, 137.9, 137.8, 137.0, 129.3, 128.4, 127.7, 127.0, 126.4, 125.3, 125.0, 123.7, 120.2, 74.0, 63.8, 62.8, 37.3, 36.4, 34.3, 31.3, 14.6. IR (KBr) ν : 3210 (w), 1667, 1574, 1551 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{35}\text{H}_{40}\text{N}_9\text{O}_4$: 650.3197; Found: 650.3203.

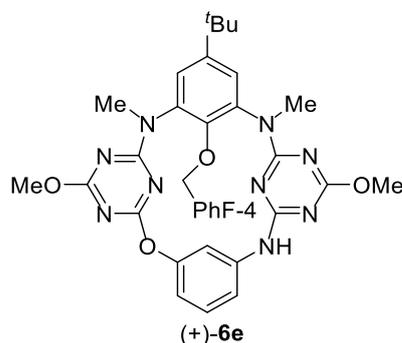


Sic*(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-diisopropoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **6c*: white solid, 12.2 mg, 36% yield, 91.4% ee from the reaction in tetrachloromethane, $[\alpha]_{\text{D}}^{25} = +61.5^\circ$ ($c = 0.2$, CH_2Cl_2), mp 91 - 92 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.11 (s, 1H), 7.24 - 7.23 (m, 3H), 7.18 (t, $J = 8.0$ Hz, 1H), 7.08 (dd, $J = 7.6, 2.0$ Hz, 2H), 7.02 (d, $J = 2.4$ Hz, 1H), 7.00 (d, $J = 2.4$ Hz, 1H), 6.90 - 6.88 (m, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.79 (dd, $J = 8.0, 2.0$ Hz, 1H), 5.34 - 5.24 (m, 2H), 4.72 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 3.37 (s, 3H), 3.35 (s, 3H), 1.37 (d, $J = 2.0$ Hz, 3H), 1.36 (d, $J =$

2.0 Hz, 3H), 1.32 (d, $J = 6.4$ Hz, 6H), 1.17 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 172.2, 171.7, 170.5, 168.5, 167.9, 166.8, 152.6, 150.0, 147.9, 138.7, 138.0, 137.8, 137.1, 129.3, 128.4, 127.7, 127.1, 126.4, 125.3, 125.1, 123.8, 120.2, 74.0, 70.9, 69.8, 37.3, 36.4, 34.3, 31.3, 22.11, 22.08. IR (KBr) ν : 3217 (w), 1574, 1535 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{37}\text{H}_{44}\text{N}_9\text{O}_4$: 678.3510; Found: 678.3512.

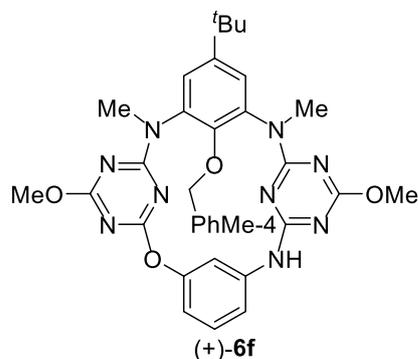


Sic-(+)-1⁶,5⁶,7²-Tris(benzyloxy)-7⁵-(*t*-butyl)-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzacyclooctaphane **6d**: white solid, 15.9 mg, 41% yield and 83.4% ee from the reaction in tetrachloromethane (98.4% ee after recrystallization), $[\alpha]_{\text{D}}^{25} = +32.0^\circ$ ($c = 0.2$, CH_2Cl_2) for 83 % ee, $[\alpha]_{\text{D}}^{25} = +50.5^\circ$ ($c = 0.2$, CH_2Cl_2) for 98 % ee, mp 101 - 103 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.24 (s, 1H), 7.54 (d, $J = 6.8$ Hz, 2H), 7.50 (d, $J = 6.8$ Hz, 2H), 7.45 - 7.34 (m, 6H), 7.21 - 7.17 (m, 4H), 7.07 - 7.05 (m, 2H), 7.02 (d, $J = 2.8$ Hz, 1H), 7.00 (d, $J = 2.8$ Hz, 1H), 6.91 - 6.90 (m, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.81 (dd, $J = 8.0, 2.4$ Hz, 1H), 5.45 (s, 2H), 5.40 (s, 2H), 4.70 (d, $J = 11.6$ Hz, 1H), 4.60 (d, $J = 11.6$ Hz, 1H), 3.39 (s, 3H), 3.37 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 172.5, 171.7, 170.9, 168.5, 167.9, 166.9, 152.6, 149.9, 148.0, 138.6, 137.9, 137.7, 137.0, 136.9, 136.3, 129.4, 128.6, 128.52, 128.49, 128.4, 128.32, 128.29, 128.1, 127.7, 127.0, 126.4, 125.3, 125.0, 123.7, 120.2, 74.1, 69.3, 68.4, 37.3, 36.5, 34.4, 31.3. IR (KBr) ν : 3217, 1667, 1582, 1543 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{45}\text{H}_{44}\text{N}_9\text{O}_4$: 774.3551; Found: 774.3543.

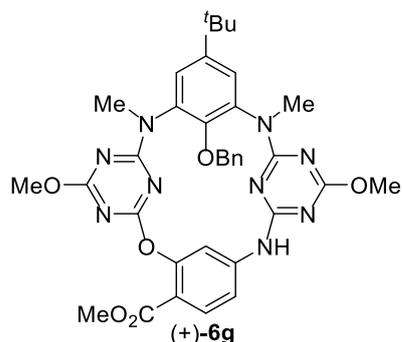


Sic-(+)-7⁵-(*t*-Butyl)-7²-((4-fluorobenzyl)oxy)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzacyclooctaphane **6e**: white solid, 10.5 mg, 33% yield and 86.9% ee from the reaction in tetrachloromethane, $[\alpha]_{\text{D}}^{25} = +37.5^\circ$ ($c = 0.2$, CH_2Cl_2), mp 96 - 98 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.21 (s, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.15 - 7.11 (m, 2H), 7.02 - 6.97 (m, 4H), 6.91 - 6.90 (m, 1H), 6.86 (d, $J = 8.0$ Hz, 1H), 6.80 (dd, $J = 8.0, 1.6$ Hz, 1H),

4.72 (d, $J = 11.6$ Hz, 1H), 4.62 (d, $J = 11.6$ Hz, 1H), 3.95 (s, 3H), 3.87 (s, 3H), 3.38 (s, 3H), 3.35 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.1, 171.7, 171.4, 168.3, 167.8, 166.7, 162.3 (d, $J = 245.0$ Hz), 152.5, 149.8, 148.2, 138.4, 137.7, 136.8, 133.7 (d, $J = 3.0$ Hz), 129.5, 128.6 (d, $J = 8.0$ Hz), 126.4, 125.3, 125.0, 123.6, 120.4, 115.3 (d, $J = 21.0$ Hz), 73.3, 54.9, 54.2, 37.2, 36.4, 34.4, 31.3. IR (KBr) ν : 3223 (w), 1612, 1579, 1534 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{35}\text{FN}_9\text{O}_4$: 640.2790; Found: 640.2800.

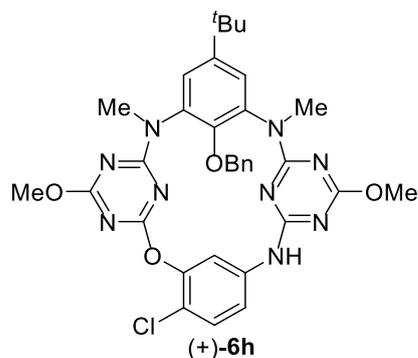


***Sic*-(+)-7⁵-(*t*-Butyl)-7²-((4-methylbenzyl)oxy)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triazina-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane 6f**: white solid, 10.2 mg, 32% yield and 92.3% ee from the reaction in tetrachloromethane and cyclohexane ($v:v = 13:7$), $[\alpha]_{\text{D}}^{25} = +65.5^\circ$ ($c = 0.2$, CH_2Cl_2), mp 89 - 91 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.12 (s, 1H), 7.19 (t, $J = 8.0$ Hz, 1H), 7.05 (d, $J = 8.0$ Hz, 2H), 7.01 (d, $J = 2.8$ Hz, 1H), 6.99 (d, $J = 2.4$ Hz, 1H), 6.96 (d, $J = 8.0$ Hz, 2H), 6.88 - 6.85 (m, 2H), 6.80 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.67 (d, $J = 11.6$ Hz, 1H), 4.56 (d, $J = 11.6$ Hz, 1H), 3.95 (s, 3H), 3.88 (s, 3H), 3.37 (s, 3H), 3.36 (s, 3H), 2.28 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.0, 171.6, 171.3, 168.4, 167.8, 166.6, 152.5, 150.0, 147.9, 138.4, 137.8, 137.4, 136.9, 134.8, 129.4, 129.1, 127.1, 126.3, 125.3, 125.0, 123.7, 120.3, 74.0, 54.9, 54.2, 37.2, 36.4, 34.3, 31.3, 21.2. IR (KBr) ν : 3231 (w), 1613, 1579, 1534 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{34}\text{H}_{38}\text{N}_9\text{O}_4$: 636.3041; Found: 636.3023.

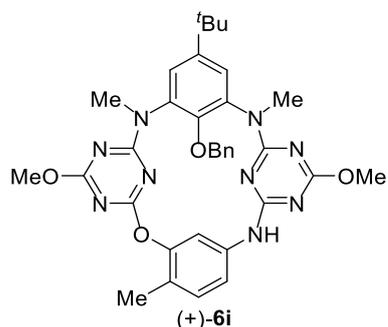


***Sic*-(+)-Methyl 7²-(benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triazina-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane-3⁶-carboxylate 6g**: white solid, 16.0 mg, 47% yield and 96.8% ee from the reaction in tetrachloromethane and cyclohexane ($v:v = 13:7$), $[\alpha]_{\text{D}}^{25} = +74.5^\circ$ ($c = 0.2$, CH_2Cl_2), mp 77 - 78 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 7.81 (s, 1H), 7.77 (d, $J = 7.8$ Hz, 1H), 7.24 - 7.19 (m, 3H), 7.02 (d, $J = 1.2$ Hz, 1H), 7.01 (d, $J = 1.2$ Hz, 1H), 6.90

(dd, $J = 8.4, 1.8$ Hz, 1H), 6.82-6.81 (m, 3H), 4.58 (d, $J = 11.4$ Hz, 1H), 4.47 (d, $J = 12.0$ Hz, 1H), 4.02 (s, 3H), 3.86 (s, 3H), 3.76 (s, 3H), 3.37 (s, 3H), 3.34 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.2, 171.8, 171.5, 168.3, 167.8, 166.8, 164.6, 152.5, 150.0, 148.0, 143.0, 137.8, 137.7, 137.1, 131.9, 128.4, 127.6, 126.8, 126.2, 125.5, 125.3, 125.1, 121.7, 74.0, 54.9, 54.1, 52.2, 37.1, 36.4, 34.3, 31.2. IR (KBr) ν : 3217 (w), 1728, 1589, 1543 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{35}\text{H}_{38}\text{N}_9\text{O}_6$: 680.2939; Found: 680.2933.

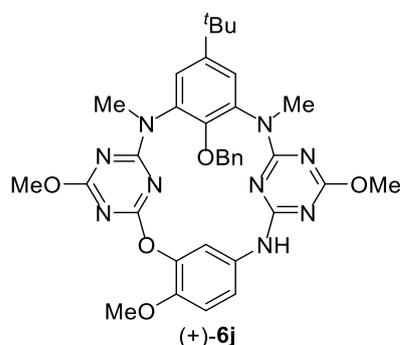


***Sic*(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-3⁶-chloro-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane 6h**: white solid, 12.3 mg, 38% yield and 94.5% ee from the reaction in tetrachloromethane, $[\alpha]_{\text{D}}^{25} = +42^\circ$ ($c = 0.2$, CH_2Cl_2), mp 109 - 111 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.14 (s, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 7.23- 7.20 (m, 3H), 7.06 (dd, $J = 7.6, 2.4$ Hz, 2H), 7.03 (d, $J = 2.4$ Hz, 1H), 7.01 (d, $J = 2.4$ Hz, 1H), 7.00 (d, $J = 2.8$ Hz, 1H), 6.89 (dd, $J = 8.4, 2.0$ Hz, 1H), 4.67 (d, $J = 11.6$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.38 (s, 3H), 3.34 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.3, 171.6, 171.1, 168.3, 167.8, 167.2, 150.0, 148.6, 148.1, 137.82, 137.80, 137.3, 136.9, 130.0, 128.4, 127.7, 126.9, 126.8, 126.4, 126.1, 125.5, 125.4, 74.0, 55.0, 54.2, 37.1, 36.4, 34.4, 31.3. IR (KBr) ν : 3221 (w), 1612, 1582, 1537 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{35}\text{ClN}_9\text{O}_4$: 656.2495; Found: 656.2499.

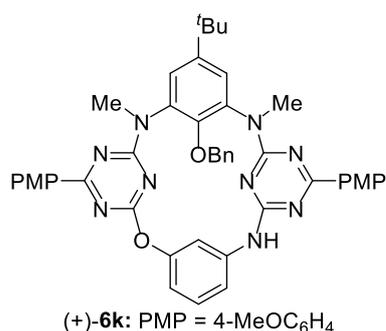


***Sic*(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-3⁶,6,8-trimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane 6i**: white solid, 17.2 mg, 54% yield and 94.9% ee from the reaction in tetrachloromethane and cyclohexane ($v:v = 13:7$), $[\alpha]_{\text{D}}^{25} = +47.0^\circ$ ($c = 0.2$, CH_2Cl_2), mp 90 - 91 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.01 (s, 1H), 7.25 - 7.20 (m, 3H), 7.07-7.02 (m, 3H), 7.02 (d, $J = 2.8$ Hz, 1H), 6.97 (d, $J = 2.4$ Hz, 1H), 6.76 - 6.74 (m, 2H),

4.64 (d, $J = 12.0$ Hz, 1H), 4.53 (d, $J = 12.0$ Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.36 (s, 3H), 3.33 (s, 3H), 2.02 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.1, 171.5, 171.3, 168.4, 167.7, 167.2, 150.8, 150.0, 147.8, 138.0, 137.8, 136.9, 136.1, 130.8, 129.4, 128.3, 127.5, 126.8, 126.3, 125.8, 125.3, 123.4, 74.0, 54.9, 54.1, 37.0, 36.3, 34.3, 31.3, 15.7. IR (KBr) ν : 3225 (w), 1582, 1543 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{34}\text{H}_{38}\text{N}_9\text{O}_4$: 636.3041; Found: 636.3045.

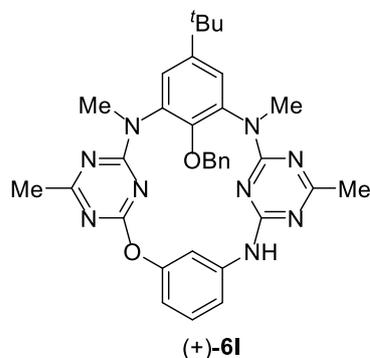


Sic*-(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,3⁶,5⁶-trimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **6j*: white solid, 10.2 mg, 31% yield and 87.7% ee from the reaction in tetrachloromethane and cyclohexane ($v:v = 13:7$), $[\alpha]_{\text{D}}^{25} = +64.0^\circ$ ($c = 0.2$, CH_2Cl_2), mp 115 - 116 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 7.92 (s, 1H), 7.23 - 7.20 (m, 3H), 7.05 (dd, $J = 7.6, 2.0$ Hz, 2H), 7.01 (d, $J = 2.4$ Hz, 1H), 6.97 (d, $J = 2.4$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 6.82 - 6.77 (m, 2H), 4.71 (d, $J = 12.0$ Hz, 1H), 4.54 (d, $J = 12.0$ Hz, 1H), 3.93 (s, 3H), 3.87 (s, 3H), 3.70 (s, 3H), 3.35 (s, 3H), 3.32 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.2, 171.63, 171.58, 168.4, 167.8, 167.5, 150.7, 150.1, 147.7, 141.3, 137.9, 137.2, 130.3, 128.4, 127.6, 126.8, 126.6, 126.4, 125.1, 124.8, 112.1, 73.9, 56.1, 54.9, 54.1, 37.2, 36.3, 34.4, 31.4. IR (KBr) ν : 3223 (w), 1612, 1580, 1534 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{34}\text{H}_{38}\text{N}_9\text{O}_5$: 652.2990; Found: 652.2996.



Sic*-(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-bis(4-methoxyphenyl)-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **6k*: white solid, 14.8 mg, 38% yield and 48.9% ee from the reaction in tetrachloromethane, $[\alpha]_{\text{D}}^{25} = +40.5^\circ$ ($c = 0.2$, CH_2Cl_2), mp 126 - 128 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.49 (d, $J = 8.8$ Hz, 2H), 8.45 (d, $J = 8.8$ Hz, 2H), 8.23 (s, 1H), 7.24 (t, $J = 8.0$ Hz, 1H), 7.11-7.07 (m, 4H), 7.05 - 6.98 (m, 8H), 6.92 (d, $J = 8.0$ Hz, 1H), 6.87 (dd, $J = 8.0, 2.4$ Hz, 1H), 4.79 (d, $J = 11.6$ Hz, 1H), 4.69 (d, $J = 11.6$ Hz, 1H), 3.92 (s,

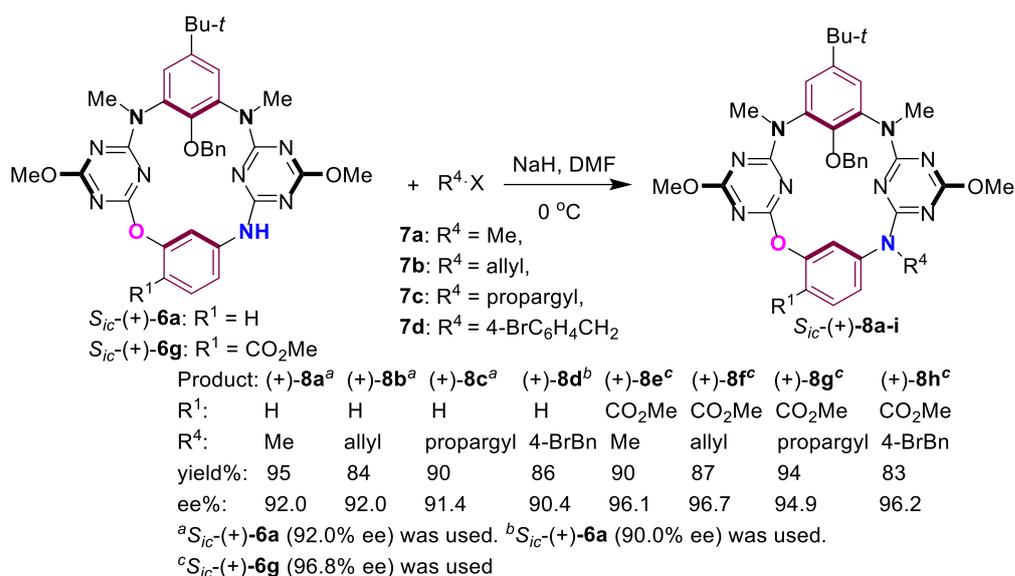
3H), 3.90 (s, 3H), 3.56 (s, 3H), 3.53 (s, 3H), 1.20 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.2, 171.1, 171.0, 167.7, 166.9, 166.1, 163.1, 162.6, 152.6, 150.2, 148.0, 138.6, 138.0, 137.6, 137.0, 130.8, 130.2, 129.7, 129.5, 128.8, 128.3, 127.6, 127.0, 126.4, 125.4, 124.8, 123.8, 120.4, 113.71, 113.66, 74.1, 55.53, 55.50, 37.2, 36.4, 34.4, 31.3. IR (KBr) ν : 3228 (w), 1609, 1590, 1557, 1518 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{45}\text{H}_{44}\text{N}_9\text{O}_4$: 774.3510; Found: 774.3514.



***Sic*-(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶,6,8-tetramethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane 6I**: white solid, 16.2 mg, 55% yield and 87.2% ee from the reaction in tetrachloromethane, $[\alpha]_{\text{D}}^{25} = +48.0^\circ$ ($c = 0.2$, CH_2Cl_2), mp 97 - 99 $^\circ\text{C}$. ^1H NMR (400 MHz, Acetone- d_6) δ (ppm): 8.12 (s, 1H), 7.24 - 7.22 (m, 3H), 7.19 (d, $J = 8.0$ Hz, 1H), 7.04 - 7.02 (m, 3H), 6.98 (d, $J = 2.4$ Hz, 1H), 6.89 - 6.87 (m, 1H), 6.85 (d, $J = 8.0$ Hz, 1H), 6.79 (dd, $J = 8.0$, 1.2 Hz, 1H), 4.68 (d, $J = 12.0$ Hz, 1H), 4.57 (d, $J = 12.0$ Hz, 1H), 3.40 (s, 3H), 3.37 (s, 3H), 2.35 (s, 3H), 2.23 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 178.7, 175.6, 170.6, 167.5, 166.5, 165.4, 152.6, 150.0, 148.2, 138.6, 137.9, 137.8, 136.9, 129.5, 128.4, 127.6, 126.9, 126.3, 125.3, 125.1, 123.7, 120.4, 74.0, 37.2, 36.4, 34.4, 31.3, 25.8, 25.6. IR (KBr) ν : 3215, 1574, 1533 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{33}\text{H}_{36}\text{N}_9\text{O}_2$: 590.2986; Found: 590.2990.

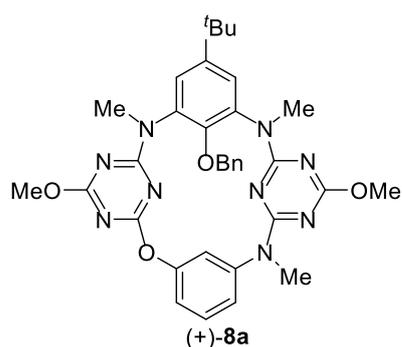
9. Functionalization of macrocyclic compounds *Sic*-(+)-6a and *Sic*-(+)-6g

9.1 Synthesis of *N*-alkyl substituted macrocycles 8



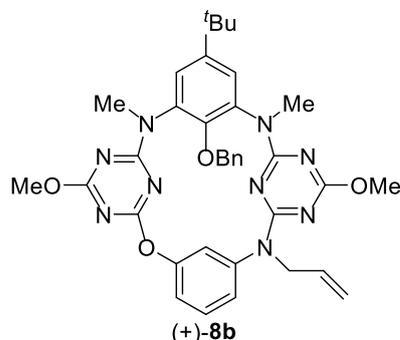
Scheme S9

Under the protection of nitrogen atmosphere, a solution of macrocycles **6** ((+)-**6a**: 90.0% ee or 92.0% ee; (+)-**6g**: 96.8% ee) (0.05 mmol) in dry DMF (2 mL) was added to the NaH (0.1 mmol, 4 mg of 60% dispersion in mineral oil. The mineral oil was removed by washing with *n*-hexane) in a test tube that was cooled in an ice bath. The resulting mixture was stirred for 0.5 h at 0 °C, and then the haloalkanes **7** (0.15 mmol) (**7a**: iodomethane; **7b**: 3-bromoprop-1-ene; **7c**: 3-bromoprop-1-yne; **7d**: *p*-bromobenzyl bromide) were added to it. The reaction mixture was stirred for another 0.5 h at 0 °C. The reaction was quenched with ice water and the mixture was extracted with DCM (30 × 2 mL). The combined organic layers were washed with saturated aqueous NaCl (30 × 3 mL) and dried over anhydrous Na₂SO₄. After filtration and concentration under vacuo, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 4:1) to give the chiral macrocycles **8** in 83-95% yields with 90.4-96.7% ee.

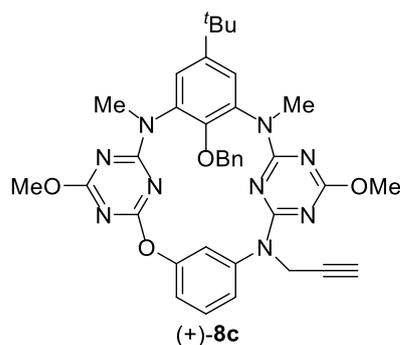


$S_{ic}-(+)$ -**7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-4,6,8-trimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **8a**: white solid, 30.1 mg, 95% yield, 92.0% ee, $[\alpha]_D^{25} = +73.0^\circ$ ($c = 0.2$, CH₂Cl₂), mp 80 – 81 °C. ¹H NMR (600 MHz, Acetone-*d*₆) δ (ppm): 7.24 - 7.19 (m, 4H), 7.03 (dd, $J = 7.2, 1.8$ Hz, 2H), 6.97 (d, $J = 2.4$ Hz, 1H), 6.95 (d, $J = 2.4$ Hz, 1H), 6.91 - 6.89 (m, 1H), 6.82 - 6.80 (m, 2H), 4.62 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 12.0$ Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.34 (s, 3H), 3.324 (s, 3H), 3.317 (s, 3H), 1.20 (s, 9H). ¹³C NMR (100**

MHz, CDCl₃) δ (ppm): 173.0, 171.9, 171.2, 168.2, 167.1, 166.5, 153.0, 149.8, 147.7, 145.9, 137.8, 136.9, 130.0, 128.3, 127.5, 126.7, 126.4, 124.9, 124.7, 122.3, 120.6, 73.8, 54.9, 54.1, 37.6, 36.9, 36.4, 34.3, 31.4. IR (KBr) ν : 1574, 1535 cm⁻¹. HRMS (TOF-ESI) m/z [M+H]⁺ calcd. for C₃₄H₃₈N₉O₄: 636.3041; Found: 636.3019.

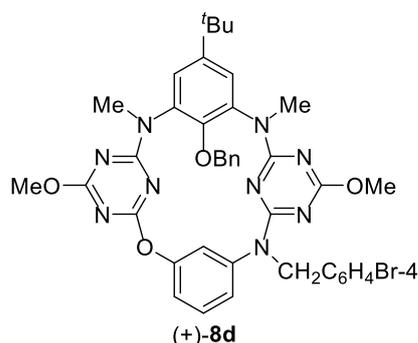


Sic-(+)-4-Allyl-7²-(benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **8b**: white solid, 27.7 mg, 84% yield, 92.0% ee, $[\alpha]_D^{25} = +83.0^\circ$ ($c = 0.2$, CH₂Cl₂), mp 64 – 65 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.26 - 7.19 (m, 3H), 7.10 (t, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 8.0$ Hz, 2H), 6.84 (d, $J = 2.4$ Hz, 1H), 6.80 - 6.75 (m, 3H), 6.56 (t, $J = 2.0$ Hz, 1H), 5.92 - 5.82 (m, 1H), 5.06 (d, $J = 10$ Hz, 1H), 5.03 (d, $J = 15.6$ Hz, 1H), 4.55 (d, $J = 12.0$ Hz, 1H), 4.44 - 4.37 (m, 2H), 4.28 (dd, $J = 14.8, 6.4$ Hz, 1H), 3.98 (s, 3H), 3.94 (s, 3H), 3.35 (s, 3H), 3.33 (s, 3H), 1.15 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 173.0, 171.9, 171.2, 168.1, 167.3, 166.3, 152.8, 149.8, 147.7, 144.3, 137.9, 136.8, 133.6, 129.7, 128.3, 127.4, 126.6, 126.4, 125.8, 124.9, 123.2, 120.7, 117.8, 73.7, 54.8, 54.0, 52.5, 36.9, 36.4, 34.3, 31.3. IR (KBr) ν : 1589 cm⁻¹. HRMS (TOF-ESI) m/z [M+H]⁺ calcd. for C₃₆H₄₀N₉O₄: 662.3197; Found: 662.3195.

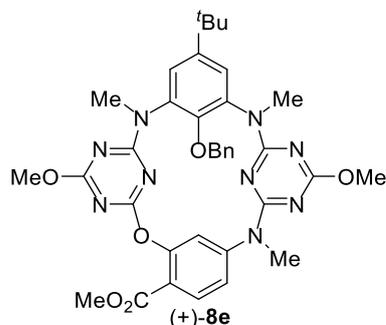


Sic-(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-4-(prop-2-yn-1-yl)-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **8c**: white solid, 29.6 mg, 90% yield, 91.4% ee, $[\alpha]_D^{25} = +72.5^\circ$ ($c = 0.2$, CH₂Cl₂), mp 79 – 80 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.26 - 7.19 (m, 3H), 7.14 (t, $J = 8.0$ Hz, 1H), 6.98 (d, $J = 6.0$ Hz, 2H), 6.92 (d, $J = 7.6$ Hz, 1H), 6.84 - 6.80 (m, 3H), 6.72 (t, $J = 2.0$ Hz, 1H), 4.65 (d, $J = 17.6$ Hz, 1H), 4.53 (d, $J = 8$ Hz, 1H), 4.49 (d, $J = 13.6$ Hz, 1H), 4.40 (d, $J = 11.6$ Hz, 1H), 4.00 (s, 3H), 3.96 (s, 3H), 3.35 (s, 3H), 3.32 (s, 3H), 2.16 (s, 1H), 1.15 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 173.0, 172.0, 171.3, 168.1, 167.4, 166.2, 152.9, 149.8, 147.7, 143.6, 137.83, 137.78, 136.8, 129.8, 128.3, 127.4, 126.6, 126.3,

125.7, 125.0, 123.2, 121.2, 79.8, 73.8, 71.9, 54.9, 54.2, 38.9, 36.9, 36.5, 34.3, 31.3. IR (KBr) ν : 3294, 1605 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{36}\text{H}_{38}\text{N}_9\text{O}_4$: 660.3041; Found: 660.3035.

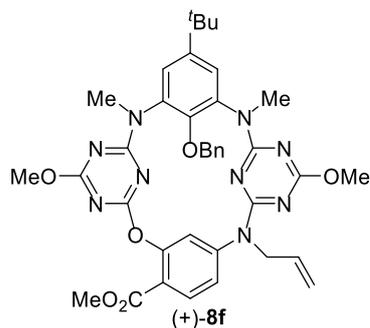


***Sic*-(+)-7²-(Benzyloxy)-4-(4-bromobenzyl)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane 8d**: white solid, 33.8 mg, 86% yield, 90.4% ee, $[\alpha]_{\text{D}}^{25} = +57^\circ$ ($c = 0.2$, CH_2Cl_2), mp 105 - 106 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.34 (d, $J = 8.4$ Hz, 2H), 7.27 - 7.23 (m, 3H), 7.08 (d, $J = 8$ Hz, 2H), 7.05 (t, $J = 8$ Hz, 1H), 6.96 (d, $J = 7.6$ Hz, 2H), 6.86 (d, $J = 2.4$ Hz, 1H), 6.80 (d, $J = 2.0$ Hz, 1H), 6.75 (d, $J = 8.4$ Hz, 1H), 6.59 (d, $J = 8.0$ Hz, 1H), 6.40 (t, $J = 2.4$ Hz, 1H), 4.96 ($J = 15.2$ Hz, 1H), 4.90 (d, $J = 15.2$ Hz, 1H), 4.54 (d, $J = 11.6$ Hz, 1H), 4.39 (d, $J = 11.6$ Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H), 3.36 (s, 3H), 3.35 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.0, 171.9, 171.3, 168.1, 167.4, 166.7, 152.9, 149.8, 147.7, 143.9, 137.84, 137.77, 137.1, 136.8, 131.5, 130.3, 129.8, 128.3, 127.5, 126.5, 126.3, 125.9, 125.0, 123.0, 121.4, 120.9, 73.7, 54.9, 54.2, 52.6, 36.9, 36.6, 34.3, 31.3. IR (KBr) ν : 1574, 1535 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{40}\text{H}_{41}\text{BrN}_9\text{O}_4$: 790.2459; Found: 790.2452.

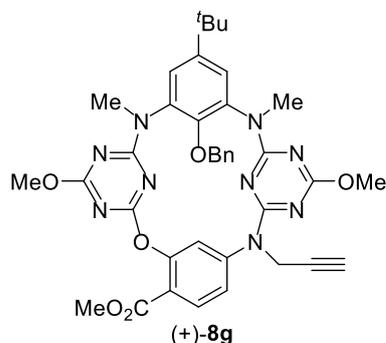


***Sic*-(+)-Methyl 7²-(benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-4,6,8-trimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane-3⁶-carboxylate 8e**: white solid, 31.1 mg, 90% yield, 96.1% ee, $[\alpha]_{\text{D}}^{25} = +45.5^\circ$ ($c = 0.2$, CH_2Cl_2), mp 78 - 79 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.80 (d, $J = 8.4$ Hz, 1H), 7.27 - 7.21 (m, 3H), 6.99 (dd, $J = 8.0, 2.0$ Hz, 2H), 6.88 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.83 (d, $J = 2.8$ Hz, 1H), 6.78 (d, $J = 2.4$ Hz, 1H), 6.70 (d, $J = 2.0$ Hz, 1H), 4.51 (d, $J = 11.6$ Hz, 1H), 4.39 (d, $J = 11.6$ Hz, 1H), 4.03 (s, 3H), 3.98 (s, 3H), 3.77 (s, 3H), 3.37 (s, 3H), 3.353 (s, 3H), 3.347 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.2, 171.9, 171.1, 168.1, 166.9, 166.4, 164.3, 153.2, 149.9, 149.8, 147.8, 137.8, 137.7, 137.0, 132.7, 128.4, 127.6, 126.7, 126.2, 125.2, 125.1, 124.0, 121.9, 73.8, 55.0, 54.2, 52.2, 37.1, 36.8, 36.6, 34.3, 31.3. IR (KBr)

ν : 1728, 1605 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{36}\text{H}_{40}\text{N}_9\text{O}_6$: 694.3096; Found: 694.3105.

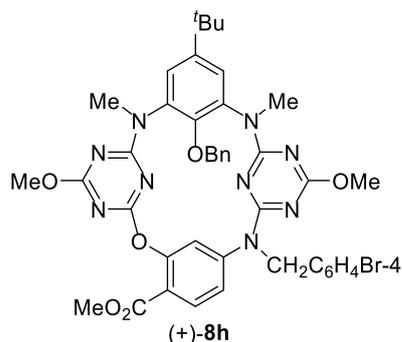


***S*_{ic}-(+)-Methyl 4-allyl-7²-(benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-dithiazina-3,7(1,3)-dibenzenacyclooctaphane-3⁶-carboxylate 8f**: white solid, 31.3 mg, 87% yield, 96.7% ee, $[\alpha]_{\text{D}}^{25} = +48.0^\circ$ ($c = 0.2$, CH_2Cl_2), mp 76 - 77 $^\circ\text{C}$. ^1H NMR (600 MHz, CDCl_3) δ (ppm): 7.76 (d, $J = 8.4$ Hz, 1H), 7.25 - 7.19 (m, 3H), 6.97 (d, $J = 6.0$ Hz, 2H), 6.85 - 6.83 (m, 2H), 6.77 (d, $J = 2.4$ Hz, 1H), 6.67 (d, $J = 1.8$ Hz, 1H), 5.90 - 5.84 (m, 1H), 5.09 (d, $J = 10.2$ Hz, 1H), 5.05 (d, $J = 17.4$ Hz, 1H), 4.49 (d, $J = 11.4$ Hz, 1H), 4.42 (dd, $J = 15.0, 6.0$ Hz, 1H), 4.40 (d, $J = 12.0$ Hz, 1H), 4.33 (dd, $J = 15.6, 6.6$ Hz, 1H), 4.03 (s, 3H), 3.96 (s, 3H), 3.76 (s, 3H), 3.35 (s, 3H), 3.34 (s, 3H), 1.15 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ (ppm): 173.2, 171.9, 171.0, 168.1, 166.8, 166.0, 164.3, 153.1, 149.8, 148.2, 147.8, 137.8, 137.7, 137.0, 133.2, 132.4, 128.4, 127.6, 126.6, 126.2, 126.1, 125.3, 124.9, 122.0, 118.4, 73.8, 55.0, 54.3, 52.3, 52.2, 36.81, 36.75, 34.3, 31.3. IR (KBr) ν : 1728, 1582 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{38}\text{H}_{42}\text{N}_9\text{O}_6$: 720.3252; Found: 720.3290.



***S*_{ic}-(+)-Methyl 7²-(benzyloxy)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-4-(prop-2-yn-1-yl)-2-oxa-4,6,8-triaza-1,5(2,4)-dithiazina-3,7(1,3)-dibenzenacyclooctaphane-3⁶-carboxylate 8g**: white solid, 33.7 mg, 94% yield, 94.9% ee, $[\alpha]_{\text{D}}^{25} = +41.0^\circ$ ($c = 0.2$, CH_2Cl_2), mp 85 - 86 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.80 (d, $J = 8.4$ Hz, 1H), 7.27 - 7.21 (m, 3H), 6.99 - 6.98 (m, 3H), 6.84 (d, $J = 2.4$ Hz, 1H), 6.83 (d, $J = 2.8$ Hz, 1H), 6.78 (d, $J = 2.4$ Hz, 1H), 4.68 (dd, $J = 17.6, 2.4$ Hz, 1H), 4.54 (dd, $J = 17.6, 2.4$ Hz, 1H), 4.47 (d, $J = 12.0$ Hz, 1H), 4.40 (d, $J = 11.6$ Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.77 (s, 3H), 3.36 (s, 3H), 3.33 (s, 3H), 2.20 (t, $J = 2.4$ Hz, 1H), 1.16 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.2, 172.0, 171.2, 168.1, 167.1, 166.0, 164.3, 153.1, 149.9, 147.9, 147.5, 137.8, 137.7, 137.0, 132.5, 128.4, 127.6, 126.7, 126.2, 126.1, 125.4, 125.0,

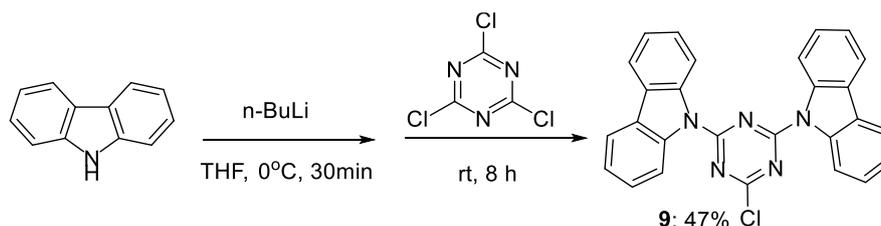
122.5, 79.4, 73.9, 72.4, 55.0, 54.3, 52.3, 38.5, 36.8, 36.7, 34.3, 31.3. IR (KBr) ν : 3287 (w), 2376 (w), 1728, 1605, 1589 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{38}\text{H}_{40}\text{N}_9\text{O}_6$: 718.3096; Found: 718.3095.



Sic-(+)-7²-(Benzyloxy)-4-(4-bromobenzyl)-7⁵-(*t*-butyl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane-3⁶-carboxylate 8h: white solid, 35.2 mg, 83% yield, 96.2% ee, $[\alpha]_{\text{D}}^{25} = +48.0^\circ$ ($c = 0.2$, CH_2Cl_2), mp 90 - 91 $^\circ\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.70 (d, $J = 8.4$ Hz, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.27 - 7.23 (m, 3H), 7.07 (d, $J = 8.0$ Hz, 2H), 6.95 (d, $J = 6.4$ Hz, 2H), 6.84 (s, 1H), 6.76 (s, 1H), 6.64 (d, $J = 8.0$ Hz, 1H), 6.50 (s, 1H), 4.97 (d, $J = 15.2$ Hz, 1H), 4.91 (d, $J = 14.8$ Hz, 1H), 4.48 (d, $J = 11.6$ Hz, 1H), 4.38 (d, $J = 11.6$ Hz, 1H), 4.02 (s, 3H), 3.97 (s, 3H), 3.75 (s, 3H), 3.35 (s, 6H), 1.14 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ (ppm): 173.2, 171.9, 171.4, 168.0, 167.3, 166.6, 164.2, 153.1, 149.8, 148.0, 147.8, 137.8, 137.7, 136.9, 136.7, 132.4, 131.7, 130.4, 128.3, 127.6, 126.6, 126.4, 126.1, 125.3, 124.8, 122.2, 121.7, 73.8, 55.0, 54.3, 52.2, 36.8, 36.7, 34.3, 31.3. IR (KBr) ν 1733, 1614, 1579, 1562 cm^{-1} . HRMS (TOF-ESI) m/z $[M+H]^+$ calcd. for $\text{C}_{42}\text{H}_{43}\text{BrN}_9\text{O}_6$: 848.2514; Found: 850.2483.

9.2 Synthesis of 4,6-di(carbazolyl)triazinyl substituted macrocycle 10

Preparation of 6-chloro-9,9'-di(carbazolyl)-1,3,5-triazine 9^[5]:

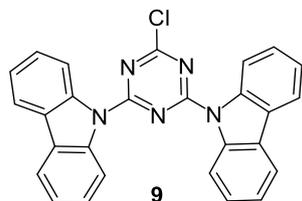


Scheme S10

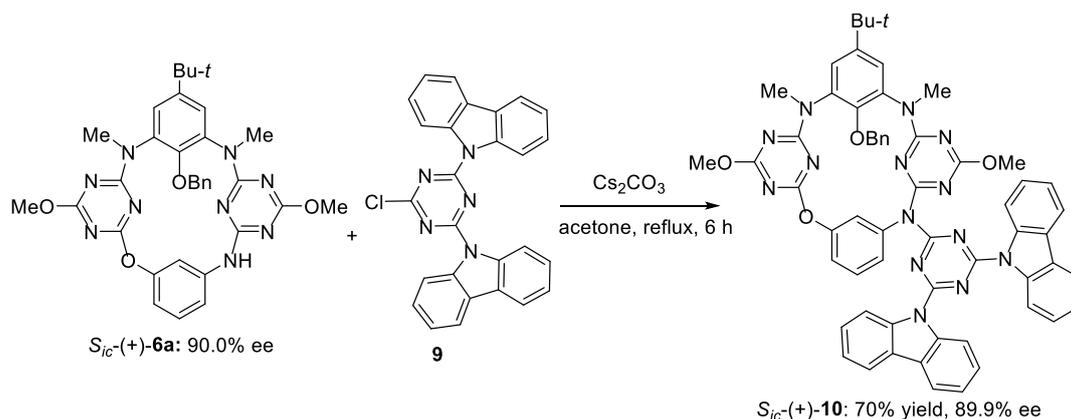
Under the argon atmosphere, the solution of *n*-BuLi in THF (6.6 mmol, 2.75 mL, 2.4 mol/L in THF) was added dropwise in 1 h into the solution of 9H-carbazole (1.10 g, 6.6 mmol) in dry THF (20 mL) that was cooled in an ice bath. The resulting mixture was stirred for 30 min and then was added dropwise into the solution of 2,4,6-trichloro-1,3,5-triazine (553.2 mg, 3 mmol) in dry THF (10 mL) at 0 $^\circ\text{C}$. The mixture was stirred for 8h at ambient temperature. Then the reaction was quenched with water (30 mL) and the mixture was extracted with DCM (20 \times 2 mL). The combined organic layer was washed with saturated aqueous NaCl (30 \times 3 mL) and dried over anhydrous Na_2SO_4 . After

filtration and removal of solvents under vacuo, the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 5:1) to give 6-chloro-9,9'-di(carbazolyl)-1,3,5-triazine **9** in 47% yield.

(Ref. [5]: C. Li, X. Fan, C. Han, H. Xu, Ternary phosphine oxide host featuring thermally activated delayed fluorescence for blue PHOLEDs with > 20% EQE and extremely low Roll-offs. *J. Mater. Chem. C*, **2018**, *6*, 6747-6754.)

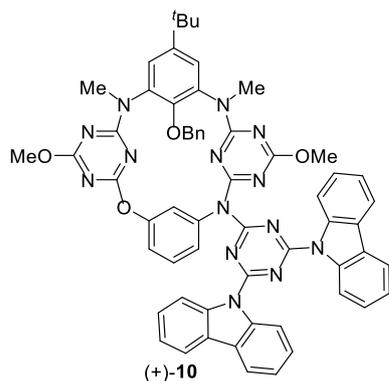


6-Chloro-9,9'-di(carbazolyl)-1,3,5-triazine **9**^[5]: pale yellow solid, 628.6 mg, 47% yield, mp = 230 - 231 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.93 (d, *J* = 8.4 Hz, 4H), 8.06 (d, *J* = 7.6 Hz, 4H), 7.52 (t, *J* = 7.2 Hz, 4H), 7.45 (t, *J* = 7.6 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ(ppm): 170.7, 164.1, 138.6, 127.4, 127.0, 124.2, 119.9, 118.0. IR (KBr) ν 1551, 1512, 1420 cm⁻¹.



Scheme S11

At ambient temperature, the macrocyclic compound (+)-**6a** (18.6 mg, 0.03 mmol, 90.0% ee), 9,9'-(6-chloro-1,3,5-triazine-2,4-diyl)bis(carbazole) **9** (16.1 mg, 0.036 mmol), Cs₂CO₃ (19.5 mg, 0.06 mmol) and acetone (2 mL) were added successively into a flask. The resulting mixture was stirred for 6h in refluxing acetone. After the reaction mixture being cooled to room temperature, the inorganic salts were filtrated and washed with ethyl acetate (5 mL). The combined filtrate was concentrated under vacuo and the residue was chromatographed on a silica gel column eluting with a mixture of petroleum ether and ethyl acetate (PE:EA = 4:1) to give the chiral macrocycles (+)-**10** in 70% yields with 90% ee.



***S*_{ic}-(+)-7²-(Benzyloxy)-7⁵-(*t*-butyl)-4-(4,6-di(carbazol-9-yl)-1,3,5-triazin-2-yl)-1⁶,5⁶-dimethoxy-6,8-dimethyl-2-oxa-4,6,8-triaza-1,5(2,4)-ditriazina-3,7(1,3)-dibenzenacyclooctaphane **10**:** white solid, 21.6 mg, 70% yield, 89.9% ee, $[\alpha]_{\text{D}}^{25} = +138.0^{\circ}$ ($c = 0.2$, CH_2Cl_2), mp 169 - 171 °C. ¹H NMR (400 MHz, CDCl_3) δ (ppm): 8.73 (brs, 4H), 8.03 (dd, $J = 6.0, 3.2$ Hz, 4H), 7.38 (dd, $J = 6.0, 3.2$ Hz, 8H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.18 (t, $J = 8.0$ Hz, 2H), 7.11 (t, $J = 6.8$ Hz, 2H), 7.06 - 7.02 (m, 4H), 6.97 (dd, $J = 6.8, 2.4$ Hz, 2H), 4.65 (d, $J = 12.0$ Hz, 1H), 4.52 (d, $J = 12.0$ Hz, 1H), 4.17 (s, 3H), 4.01 (s, 3H), 3.46 (s, 3H), 3.44 (s, 3H), 1.25 (s, 9H). ¹³C NMR (100 MHz, CDCl_3) δ (ppm): 173.1, 172.1, 171.7, 168.1, 167.9, 167.3, 167.2, 164.3, 153.7, 149.8, 148.0, 143.4, 138.9, 137.7, 137.1, 136.9, 130.2, 128.3, 127.4, 127.0, 126.7, 126.4, 126.0, 125.3, 123.3, 123.2, 121.5, 119.5, 117.7, 73.9, 54.9, 54.8, 36.94, 36.90, 34.4, 31.4. IR (KBr) ν : 1574, 1535 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{60}\text{H}_{51}\text{N}_{14}\text{O}_4$: 1031.4212; Found: 1031.4203.

10. Crystal data and structure refinements for products (±)-6a, (±)-6d, (±)-6j, *S*_{ic}-(+)-6b, (±)-8d and *S*_{ic}-(+)-8a

Single crystals of compounds (±)-6a (CCDC: 2303849), (±)-6d (CCDC: 2303851), (±)-6j (CCDC 2303853), and *S*_{ic}-(+)-8a (CCDC: 2304021) were obtained by slow evaporation of the solution of the corresponding compounds in dichloromethane and *n*-hexane. Single crystals of compound *S*_{ic}-(+)-6b (CCDC: 2304020) that was recrystallized from THF and methanol was obtained by slow evaporation of the solution in dichloromethane and *n*-hexane. Single crystals of compound (±)-8d (CCDC: 2304018) were obtained by slow evaporation of the solution of (±)-8d in chloroform and *n*-hexane. Crystallographic data of compounds (±)-6a, (±)-6d, (±)-6j, *S*_{ic}-(+)-6b, (±)-8d and *S*_{ic}-(+)-8a were collected on a XtaLAB Synergy R, DW system, HyPix diffractometer equipped with graphite monochromatized $\text{CuK}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at 100 K. The crystal data and structure refinement results are listed in the Table S4-S9.

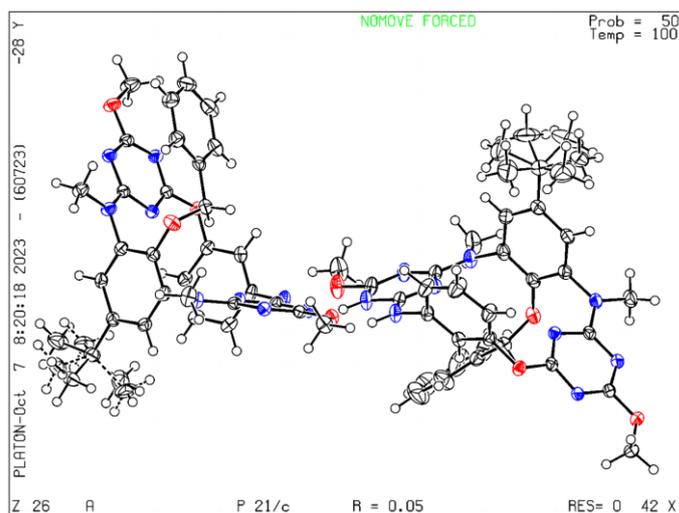
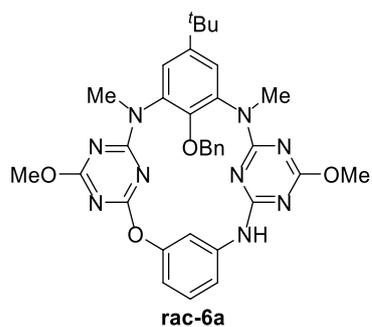


Figure S1. X-ray molecular structure of (\pm)-**6a**. The ellipsoid contour probability level is 50%.

Table S4. Crystal data and structure refinement for (\pm)-**6a**

Identification code	A
Empirical formula	C ₃₃ H ₃₅ N ₉ O ₄
Formula weight	621.70
Temperature/K	100.15
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	19.0635(2)
b/Å	15.8724(2)
c/Å	21.4307(2)
α /°	90
β /°	91.9570(10)
γ /°	90
Volume/Å ³	6480.79(12)
Z	8

$\rho_{\text{calc}}/\text{cm}^3$	1.274
μ/mm^{-1}	0.711
F(000)	2624.0
Crystal size/ mm^3	$0.2 \times 0.1 \times 0.05$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2θ range for data collection/ $^\circ$	4.638 to 124.998
Index ranges	$-21 \leq h \leq 21, -17 \leq k \leq 18, -24 \leq l \leq 24$
Reflections collected	56351
Independent reflections	10348 [$R_{\text{int}} = 0.0388, R_{\text{sigma}} = 0.0254$]
Data/restraints/parameters	10348/90/883
Goodness-of-fit on F^2	1.027
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0472, wR_2 = 0.1293$
Final R indexes [all data]	$R_1 = 0.0542, wR_2 = 0.1355$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.68/-0.57
CCDC No.	2303849

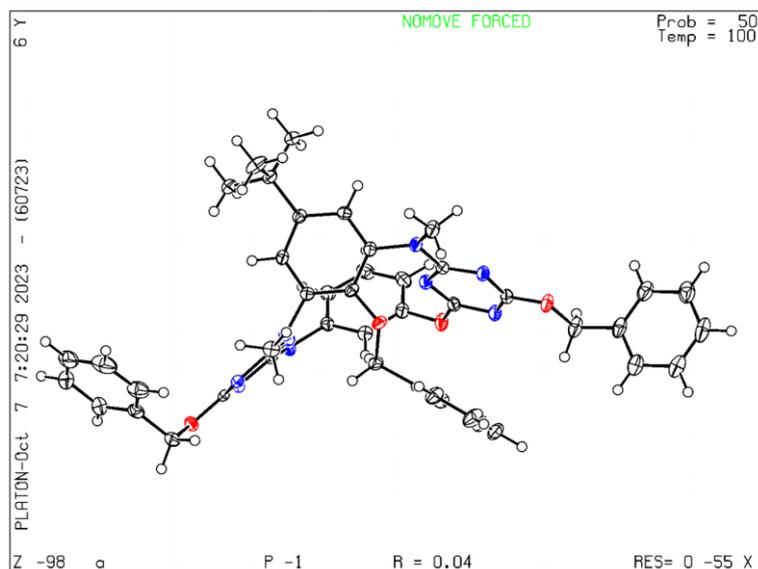
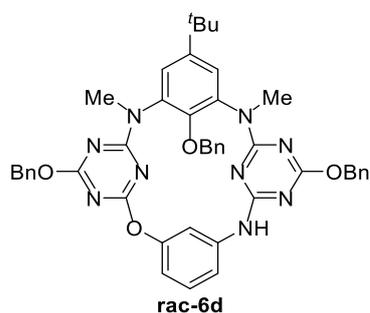


Figure S2. X-ray molecular structure of (\pm)-**6d**. The ellipsoid contour probability level is 50%.

Table S5. Crystal data and structure refinement for (\pm)-**6d**

Identification code	a
Empirical formula	C ₄₅ H ₄₃ N ₉ O ₄
Formula weight	773.88
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	10.0108(2)
b/Å	12.9368(3)
c/Å	17.2186(4)
α /°	105.174(2)
β /°	98.881(2)
γ /°	107.685(2)
Volume/Å ³	1983.04(8)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.296
μ/mm^{-1}	0.691
F(000)	816.0
Crystal size/mm ³	0.2 × 0.1 × 0.05
Radiation	CuK α (λ = 1.54184)
2 Θ range for data collection/°	5.498 to 124.978
Index ranges	-11 ≤ h ≤ 9, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	33123
Independent reflections	6323 [R _{int} = 0.0219, R _{sigma} = 0.0120]
Data/restraints/parameters	6323/0/524
Goodness-of-fit on F ²	0.999
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0365, wR ₂ = 0.0922
Final R indexes [all data]	R ₁ = 0.0373, wR ₂ = 0.0928
Largest diff. peak/hole / e Å ⁻³	0.49/-0.39
CCDC No.	2303851

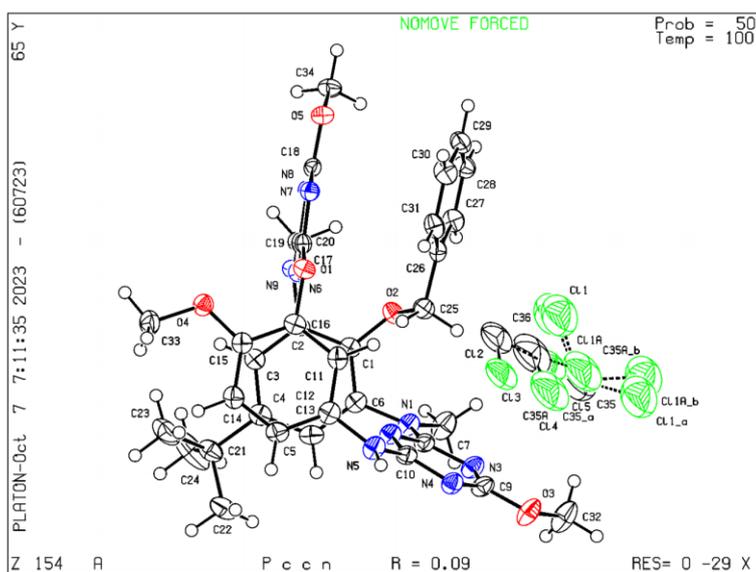
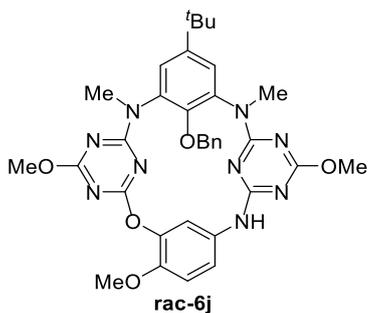
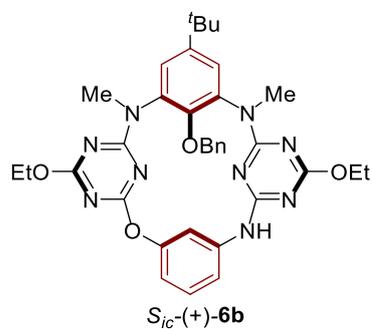


Figure S3. X-ray molecular structure of (±)-**6j**. The ellipsoid contour probability level is 50%.

Table S6. Crystal data and structure refinement for (±)-**6j**

Identification code	A
Empirical formula	$C_{34.5}H_{38}N_9O_5Cl$
Formula weight	694.19
Temperature/K	100.15
Crystal system	orthorhombic
Space group	Pccn
a/Å	14.2497(2)
b/Å	36.7753(5)
c/Å	14.4950(2)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	7595.92(18)

Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.214
μ/mm^{-1}	1.311
F(000)	2920.0
Crystal size/ mm^3	$0.2 \times 0.1 \times 0.05$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	6.652 to 125
Index ranges	$-14 \leq h \leq 16, -42 \leq k \leq 40, -10 \leq l \leq 16$
Reflections collected	34722
Independent reflections	6052 [$R_{\text{int}} = 0.0408, R_{\text{sigma}} = 0.0280$]
Data/restraints/parameters	6052/68/475
Goodness-of-fit on F^2	1.202
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0857, wR_2 = 0.2538$
Final R indexes [all data]	$R_1 = 0.0893, wR_2 = 0.2575$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	2.02/-0.79
CCDC No.	2303853



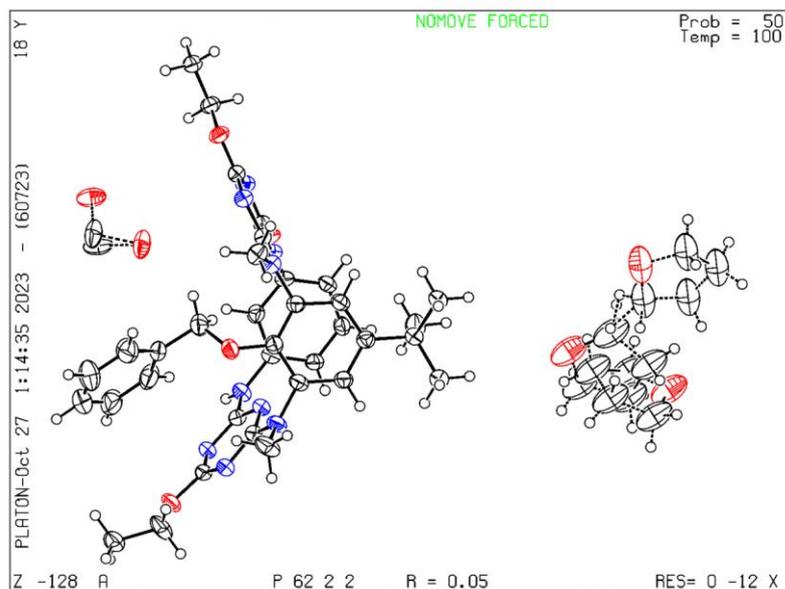


Figure S4. X-ray molecular structure of $S_{ic}(+)$ -**6b**. The ellipsoid contour probability level is 50%.

Table S7. Crystal data and structure refinement for $S_{ic}(+)$ -**6b**

Identification code	A
Empirical formula	$C_{36.25}H_{42}N_9O_{4.5}$
Formula weight	675.79
Temperature/K	100.15
Crystal system	hexagonal
Space group	$P6_222$
$a/\text{\AA}$	17.07750(10)
$b/\text{\AA}$	17.07750(10)
$c/\text{\AA}$	48.3005(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	120
Volume/ \AA^3	12199.18(16)
Z	12
$\rho_{\text{calc}}/\text{cm}^3$	1.104
μ/mm^{-1}	0.611
F(000)	4302.0
Crystal size/ mm^3	$0.2 \times 0.2 \times 0.05$
Radiation	$\text{CuK}\alpha$ ($\lambda = 1.54184$)
2θ range for data collection/ $^\circ$	7.008 to 124.982

Index ranges	-17 ≤ h ≤ 19, -19 ≤ k ≤ 19, -55 ≤ l ≤ 55
Reflections collected	238456
Independent reflections	6484 [R _{int} = 0.1015, R _{sigma} = 0.0210]
Data/restraints/parameters	6484/137/482
Goodness-of-fit on F ²	1.097
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0539, wR ₂ = 0.1485
Final R indexes [all data]	R ₁ = 0.0572, wR ₂ = 0.1518
Largest diff. peak/hole / e Å ⁻³	0.72/-0.21
Flack parameter	-0.03(7)
CCDC No.	2304020

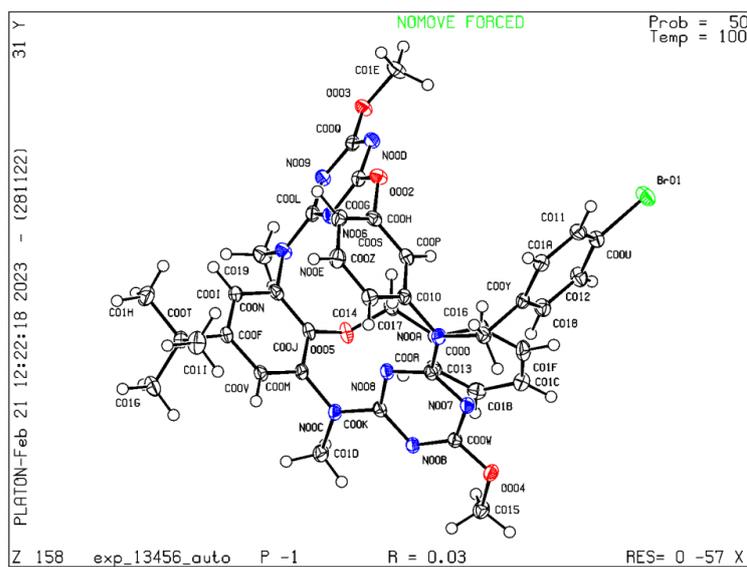
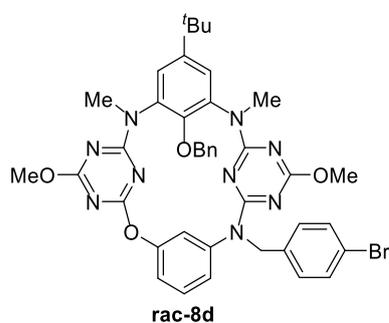
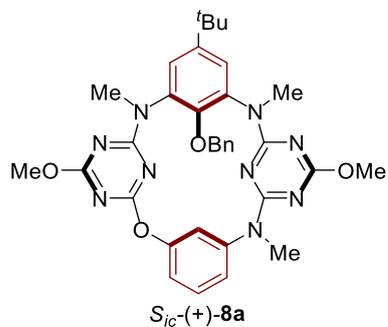


Figure S5. X-ray molecular structure of (±)-**8d**. The ellipsoid contour probability level is 50%.

Table S8. Crystal data and structure refinement for (±)-**8d**

Identification code	exp_13456_auto
Empirical formula	C ₄₀ H ₄₀ BrN ₉ O ₄
Formula weight	790.72

Temperature/K	99.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	11.19970(10)
b/Å	11.6776(2)
c/Å	15.8142(3)
α /°	74.250(2)
β /°	73.2240(10)
γ /°	70.731(2)
Volume/Å ³	1833.45(6)
Z	2
$\rho_{\text{calc}}/\text{cm}^3$	1.432
μ/mm^{-1}	1.985
F(000)	820.0
Crystal size/mm ³	0.01 × 0.01 × 0.01
Radiation	Cu K α (λ = 1.54184)
2 Θ range for data collection/°	8.178 to 152.86
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	79604
Independent reflections	7356 [R_{int} = 0.0542, R_{sigma} = 0.0192]
Data/restraints/parameters	7356/0/494
Goodness-of-fit on F ²	1.033
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0313, wR_2 = 0.0801
Final R indexes [all data]	R_1 = 0.0325, wR_2 = 0.0808
Largest diff. peak/hole / e Å ⁻³	0.26/-0.59
CCDC No.	2304018



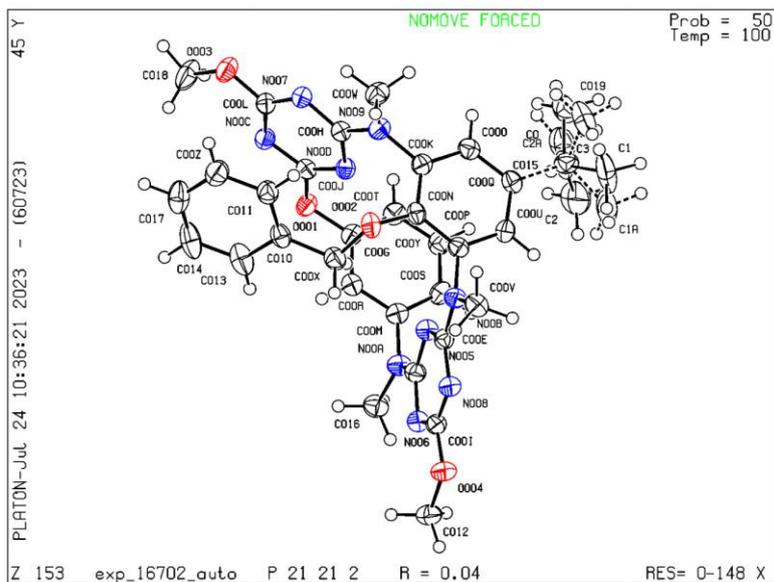


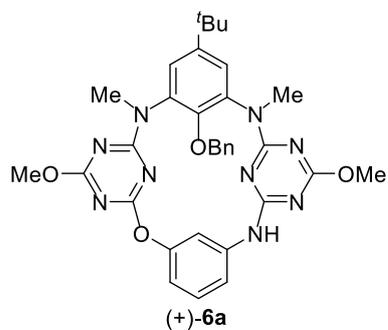
Figure S6. X-ray molecular structure of $S_{ic}-(+)$ -**8a**. The ellipsoid contour probability level is 50%.

Table S9. Crystal data and structure refinement for $S_{ic}-(+)$ -**8a**

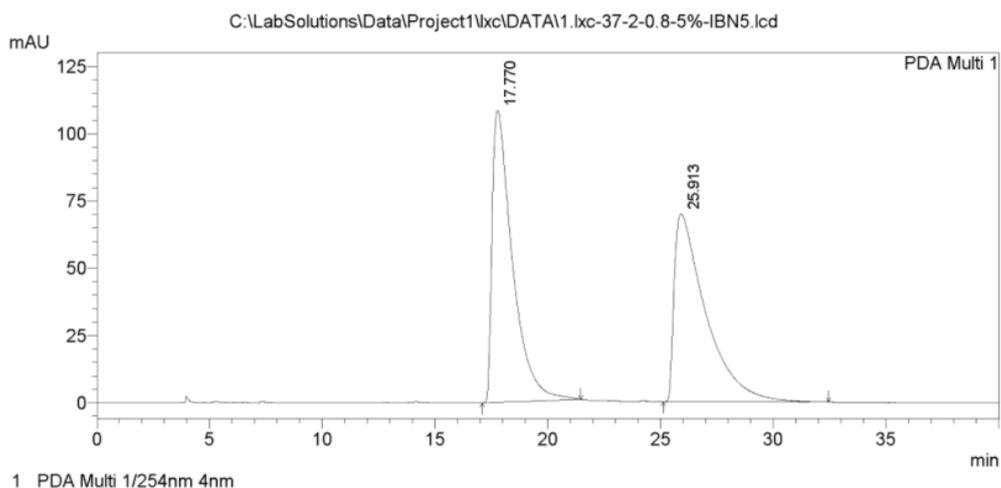
Identification code	exp_16702_auto
Empirical formula	$C_{34}H_{37}N_9O_4$
Formula weight	635.731
Temperature/K	99.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12$
$a/\text{\AA}$	24.6160(7)
$b/\text{\AA}$	13.0934(5)
$c/\text{\AA}$	9.9979(3)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3222.39(18)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.310
μ/mm^{-1}	0.727
$F(000)$	1348.6
Crystal size/ mm^3	$0.15 \times 0.1 \times 0.05$
Radiation	Cu $K\alpha$ ($\lambda = 1.54184$)

2 Θ range for data collection/ $^{\circ}$	7.18 to 154.18
Index ranges	-30 \leq h \leq 26, -16 \leq k \leq 16, -12 \leq l \leq 12
Reflections collected	27752
Independent reflections	6548 [$R_{\text{int}} = 0.0522$, $R_{\text{sigma}} = 0.0321$]
Data/restraints/parameters	6548/20/472
Goodness-of-fit on F^2	1.041
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0420$, $wR_2 = 0.1057$
Final R indexes [all data]	$R_1 = 0.0466$, $wR_2 = 0.1141$
Largest diff. peak/hole / e \AA^{-3}	0.20/-0.23
Flack parameter	-0.07(7)
CCDC No.	2304021

11. HPLC spectra of products 6, 8 and 10

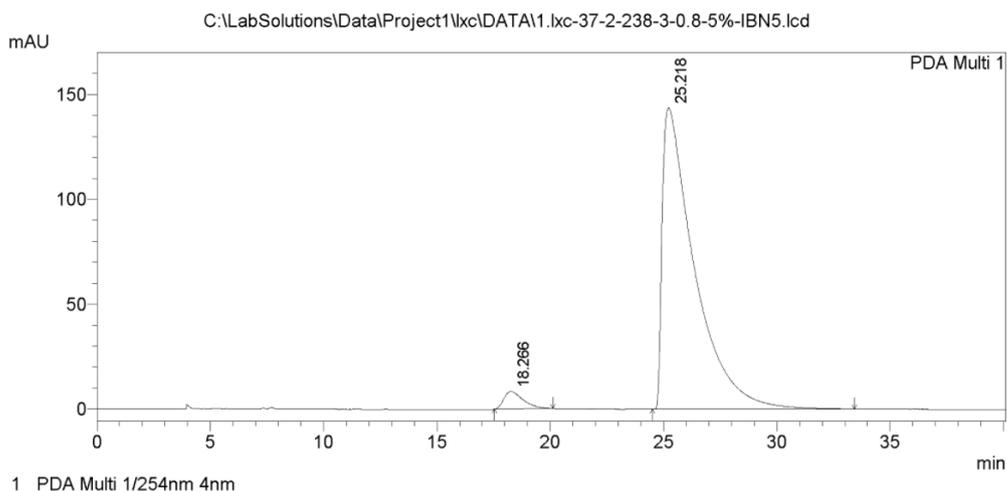


HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.8 mL/min, 254 nm, 25 $^{\circ}$ C, 93.2% ee.



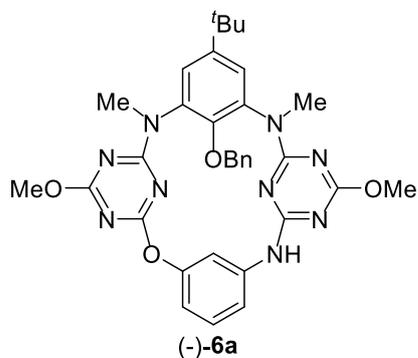
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PeakTable

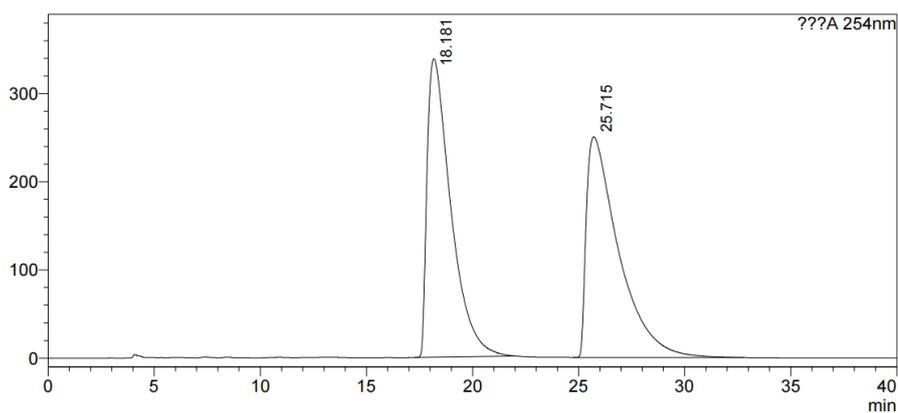
Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.266	499011	8343	3.401	5.487
2	25.218	14172651	143695	96.599	94.513
Total		14671662	152038	100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.8 mL/min, 254 nm, 25 °C, 90.0% ee.

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mV



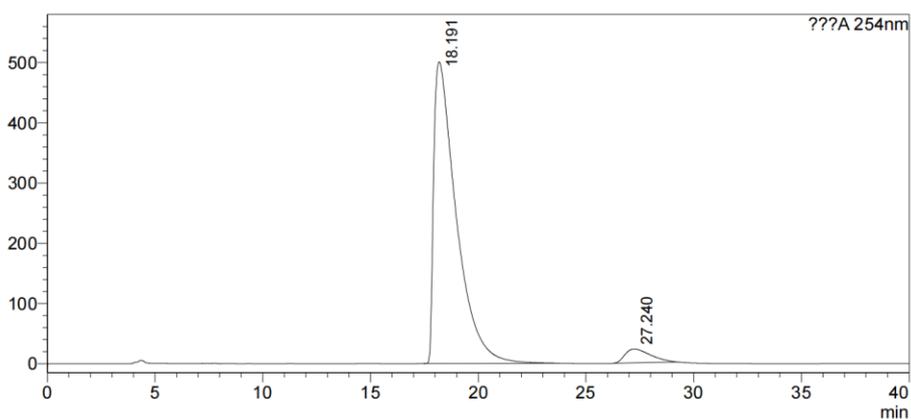
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??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	18.181	26363809	338620	49.843	49.843	57.493
2	25.715	26530110	250352	50.157	50.157	42.507
Total		52893919	588972		100.000	100.000

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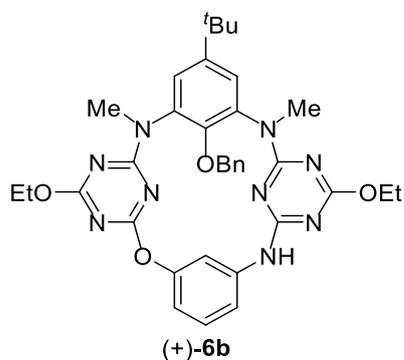
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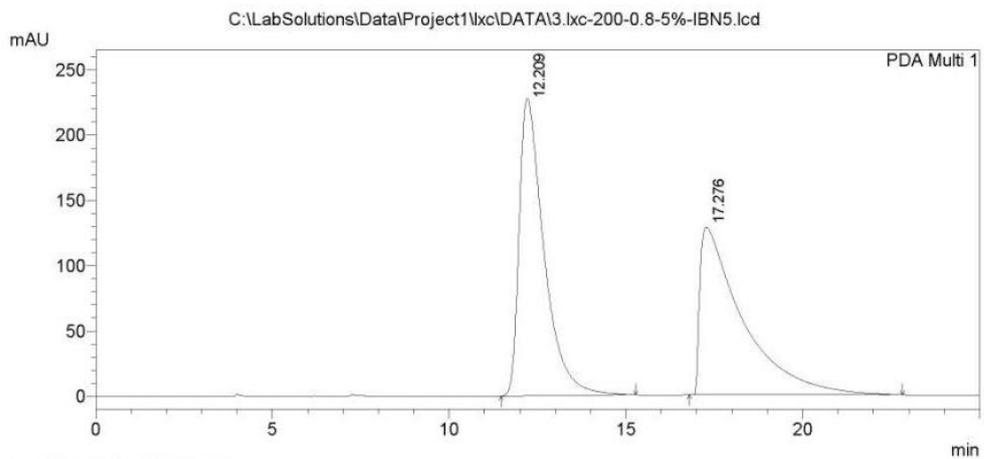
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??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	18.191	36404785	500734	95.007	95.007	95.596
2	27.240	1913088	23070	4.993	4.993	4.404
Total		38317873	523804		100.000	100.000



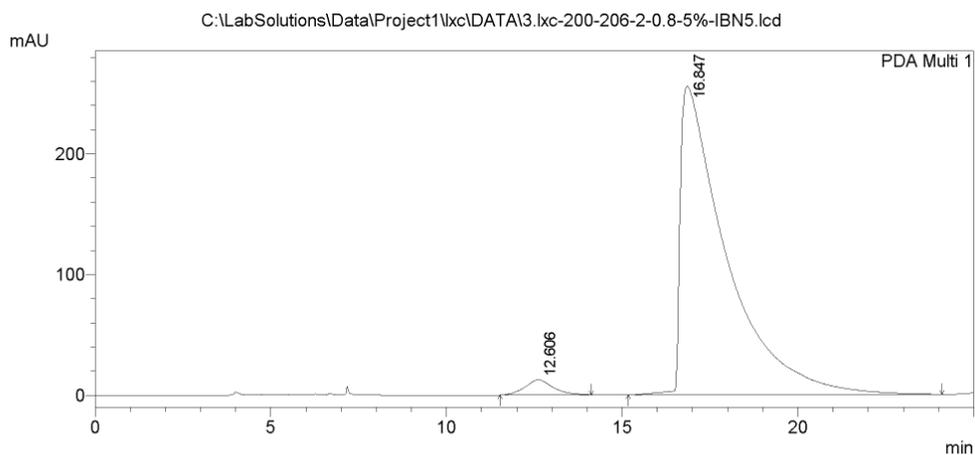
HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.8 mL/min, 254 nm, 25 °C, 94.2% ee.



PeakTable

PDA Ch1 254nm 4nm

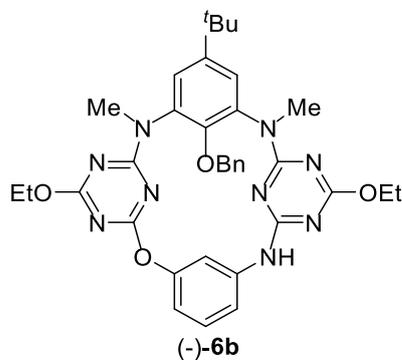
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.209	11085827	227700	50.685	63.972
2	17.276	10786122	128237	49.315	36.028
Total		21871948	355936	100.000	100.000



PeakTable

PDA Ch1 254nm 4nm

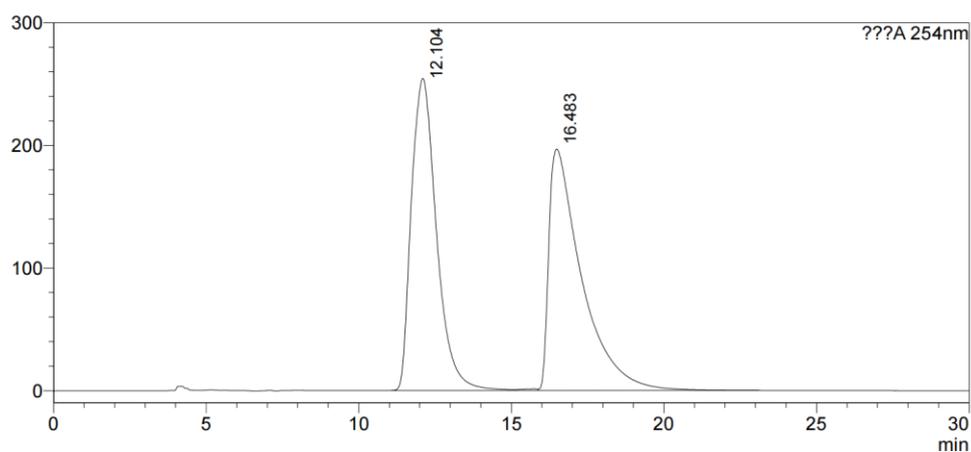
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1	12.606	690701	12509	2.881	4.670
2	16.847	23282296	255348	97.119	95.330
Total		23972997	267857	100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.8 mL/min, 254 nm, 25 °C, 90.7% ee.

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mV



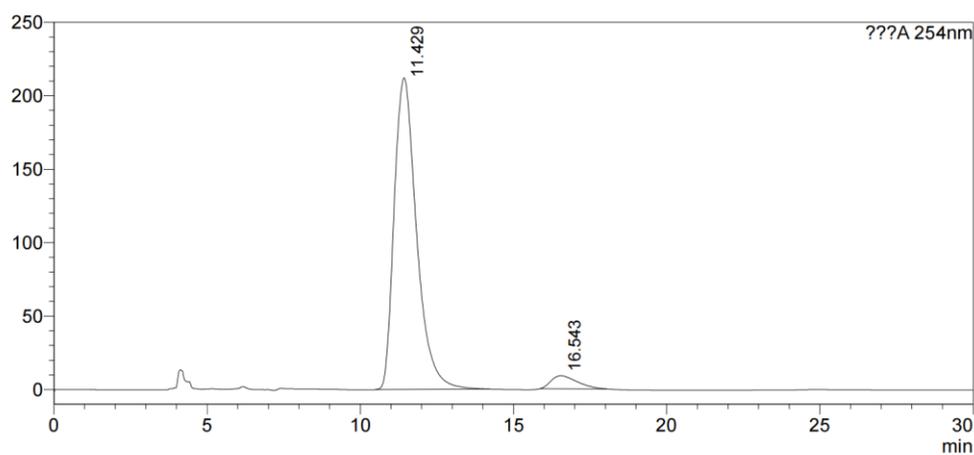
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??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.104	14620789	254581	49.902	49.902	56.403
2	16.483	14678460	196776	50.098	50.098	43.597
Total		29299249	451358		100.000	100.000

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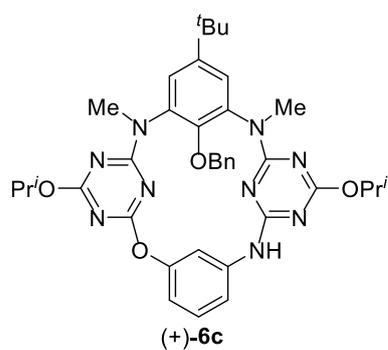
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??A 254nm

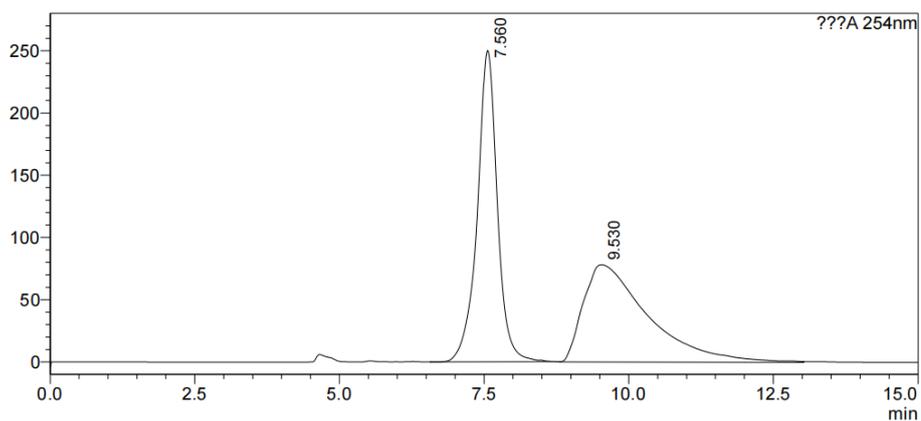
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	11.429	10841988	212152	95.374	95.374	95.986
2	16.543	525832	8872	4.626	4.626	4.014
Total		11367820	221024		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.8 mL/min, 254 nm, 25 °C, 91.4% ee.

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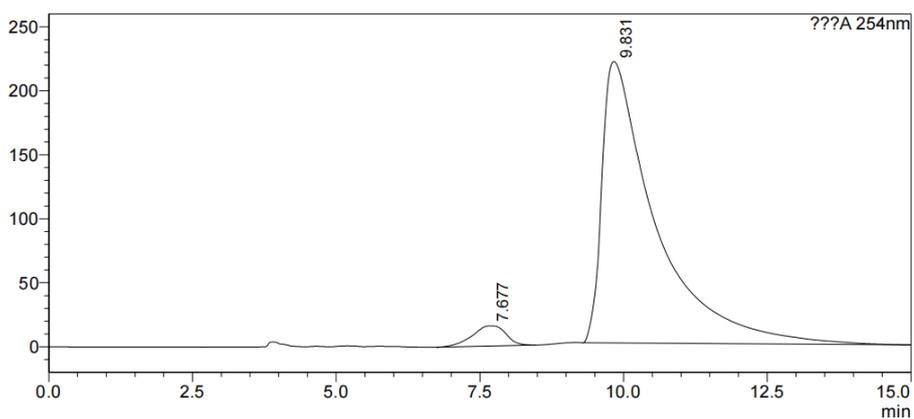
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??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	7.560	6030646	250090	49.851	49.851	76.220
2	9.530	6066809	78025	50.149	50.149	23.780
Total		12097455	328115		100.000	100.000

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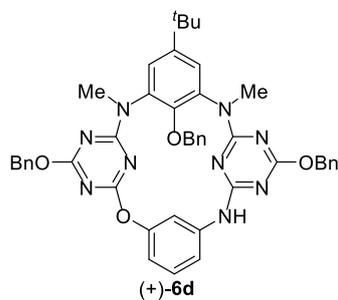
mV



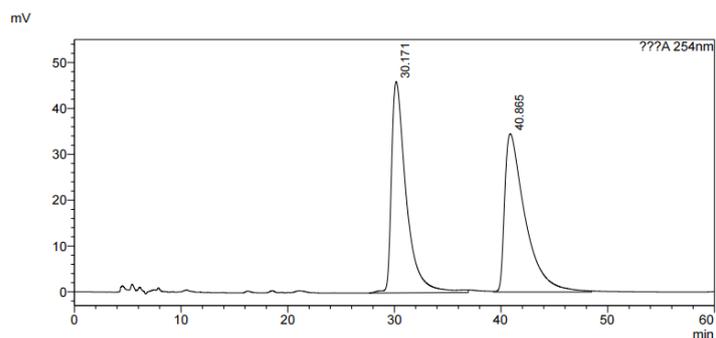
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??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	7.677	641603	15728	4.289	4.289	6.679
2	9.831	14318499	219780	95.711	95.711	93.321
Total		14960102	235508		100.000	100.000

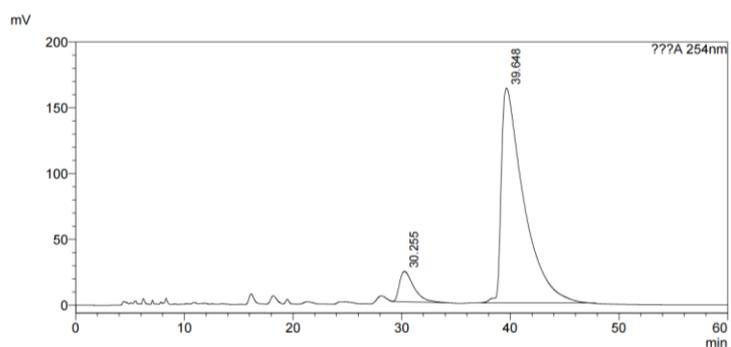


HPLC: IBN5 column, Hexane : *i*-PrOH = 93 : 7, flow rate 0.7 mL/min, 254 nm, 25 °C, 83.4% ee (98.4% ee after recrystallization).



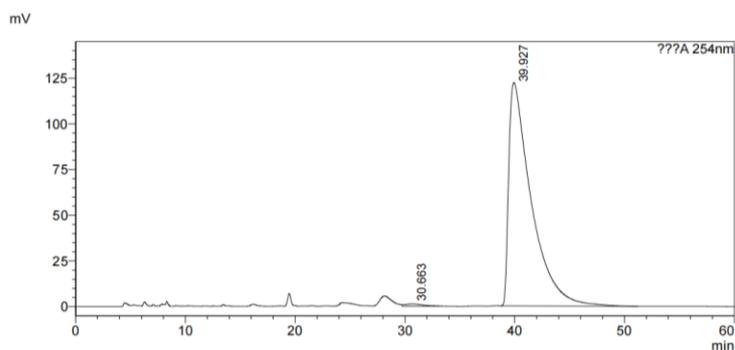
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	30.171	4469341	46111	49.179	49.179	57.191
2	40.865	4618528	34516	50.821	50.821	42.809
Total		9087869	80627		100.000	100.000



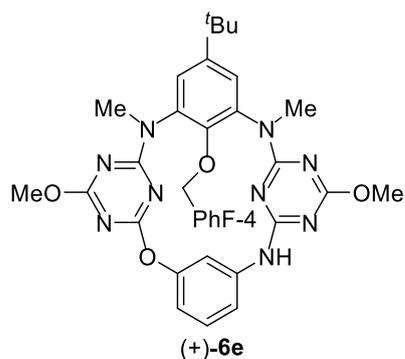
<Peak Table>

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	30.255	2136265	23090	8.320	8.320	12.383
2	39.648	23540791	163378	91.680	91.680	87.617
Total		25677056	186468		100.000	100.000



<Peak Table>

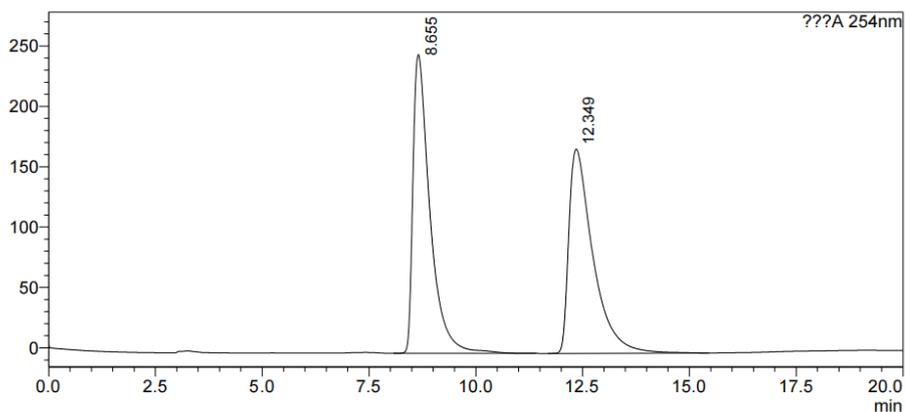
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	30.663	140356	1201	0.800	0.800	0.974
2	39.927	17399479	122124	99.200	99.200	99.026
Total		17539834	123325		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 90 : 10, flow rate 1.0 mL/min, 254 nm, 25 °C, 86.9% ee.

<Chromatogram>

mV



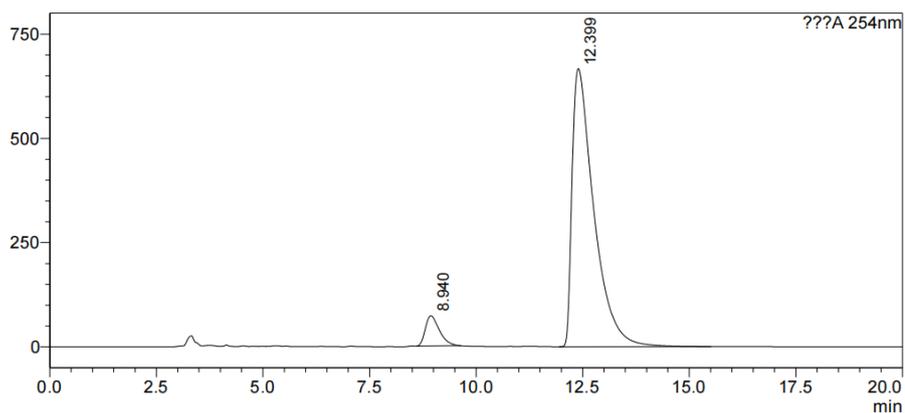
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	8.655	6848463	247368	50.787	50.787	59.394
2	12.349	6636226	169119	49.213	49.213	40.606
Total		13484689	416486		100.000	100.000

<Chromatogram>

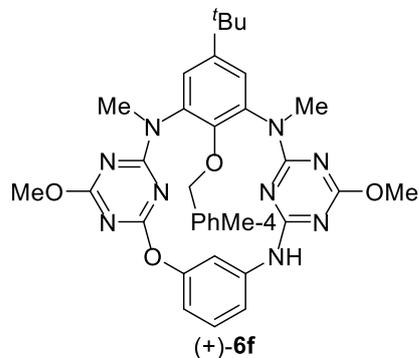
mV



<Peak Table>

??A 254nm

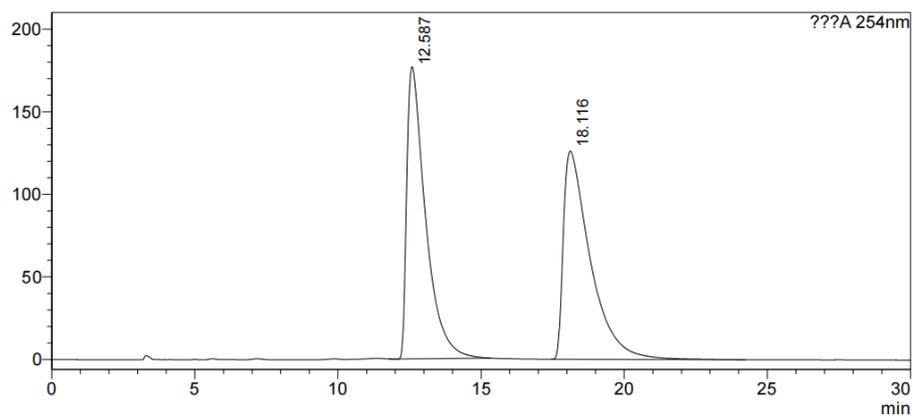
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	8.940	1658297	72426	6.532	6.532	9.795
2	12.399	23728215	667030	93.468	93.468	90.205
Total		25386513	739456		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 1.0 mL/min, 254 nm, 25 °C, 92.3% ee.

<Chromatogram>

mV



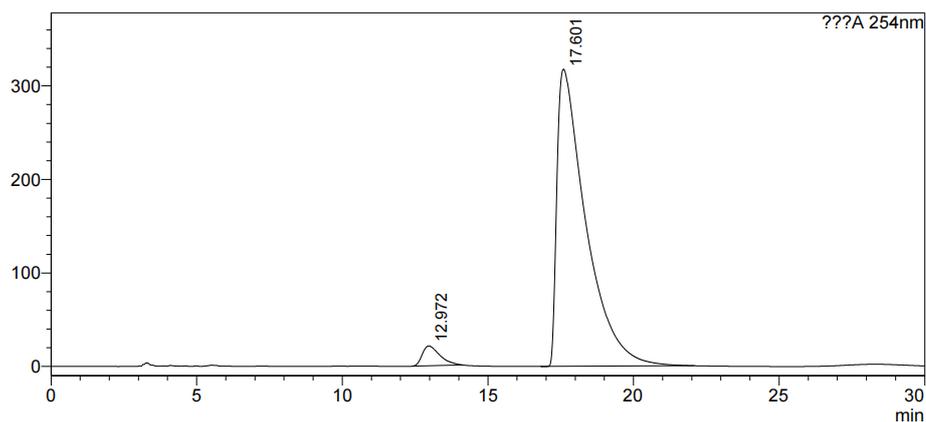
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.587	8070201	176607	49.386	49.386	58.369
2	18.116	8270971	125964	50.614	50.614	41.631
Total		16341173	302571		100.000	100.000

<Chromatogram>

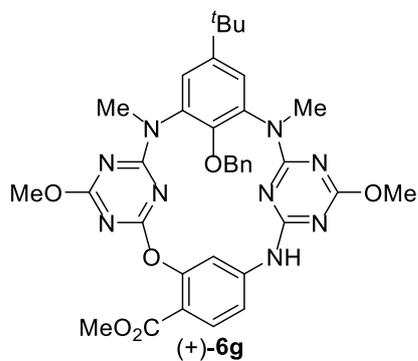
mV



<Peak Table>

??A 254nm

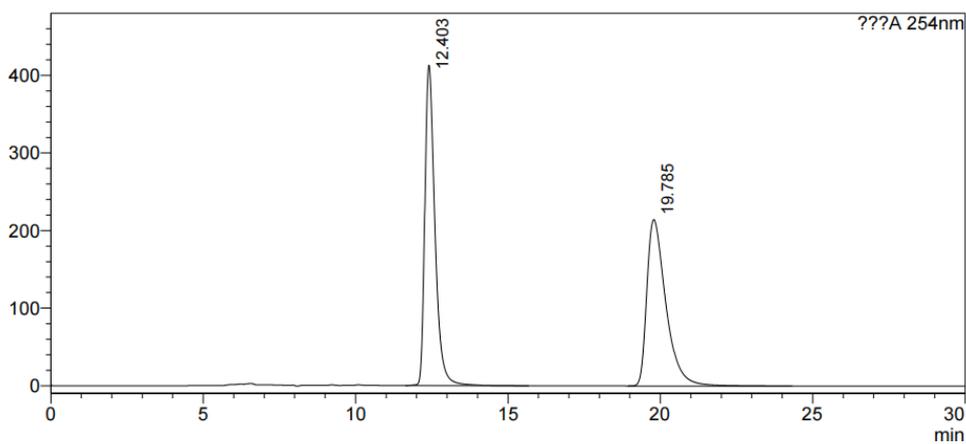
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.972	882509	21045	3.873	3.873	6.211
2	17.601	21902163	317798	96.127	96.127	93.789
Total		22784672	338843		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 80 : 20, flow rate 0.5 mL/min, 254 nm, 25 °C, 96.8% ee.

<Chromatogram>

mV



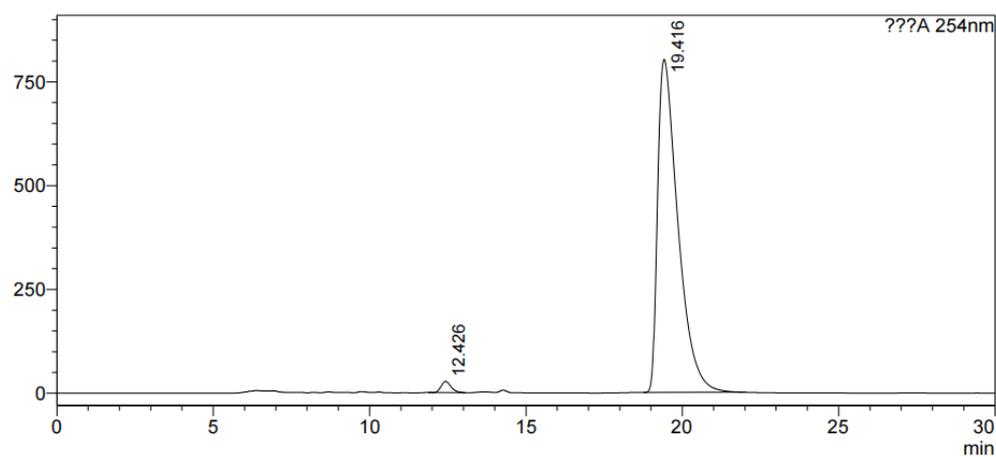
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.403	9432405	413258	50.193	50.193	65.830
2	19.785	9359960	214508	49.807	49.807	34.170
Total		18792365	627765		100.000	100.000

<Chromatogram>

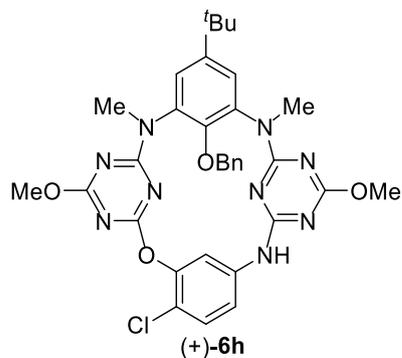
mV



<Peak Table>

??A 254nm

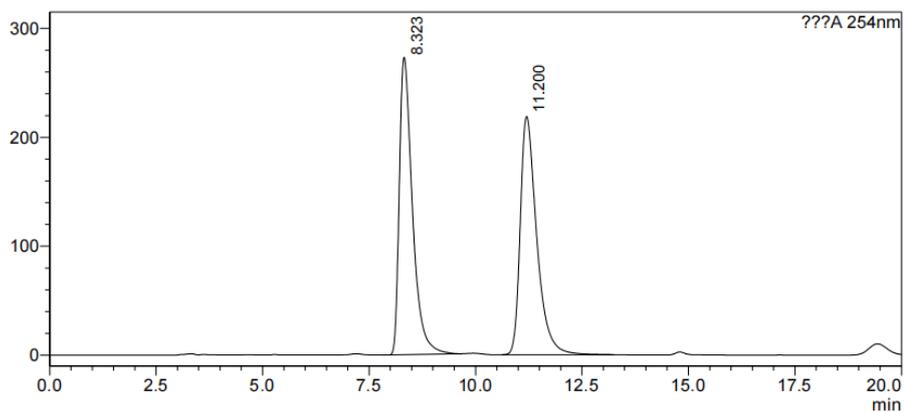
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.426	586773	26682	1.589	1.589	3.221
2	19.416	36345351	801812	98.411	98.411	96.779
Total		36932124	828494		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 90 : 10, flow rate 1.0 mL/min, 254 nm, 25 °C, 94.5% ee.

<Chromatogram>

mV

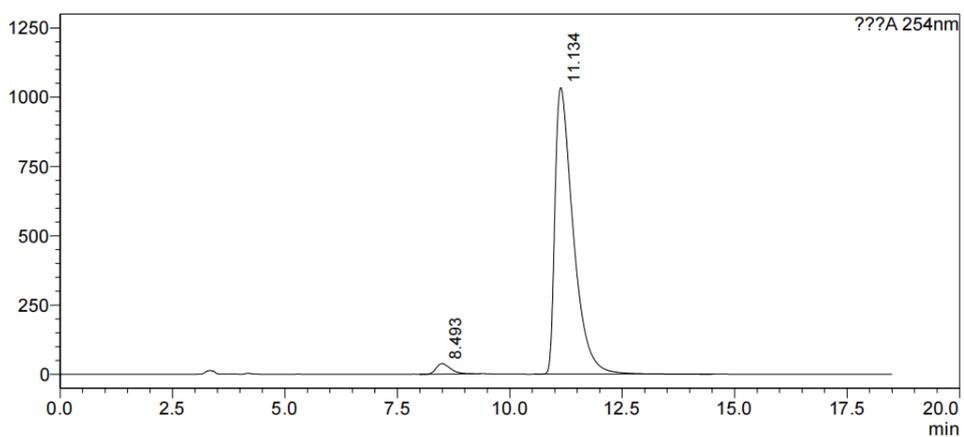


<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	8.323	5866043	273120	49.874	49.874	55.513
2	11.200	5895599	218877	50.126	50.126	44.487
Total		11761642	491997		100.000	100.000

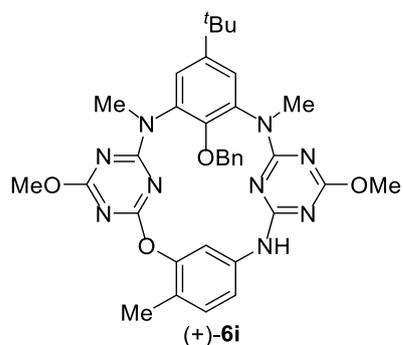
mV



<Peak Table>

??A 254nm

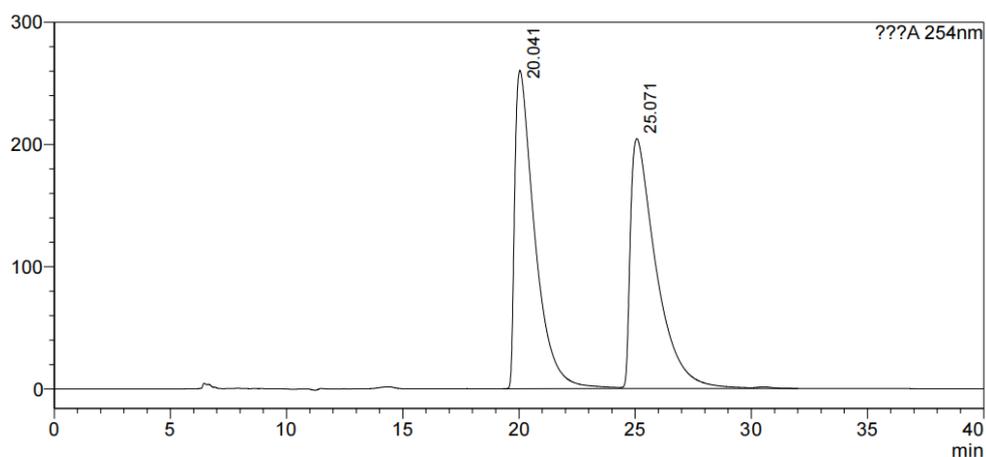
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	8.493	826179	37486	2.742	2.742	3.498
2	11.134	29306221	1034214	97.258	97.258	96.502
Total		30132400	1071700		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.5 mL/min, 254 nm, 25 °C, 94.9% ee.

<Chromatogram>

mV



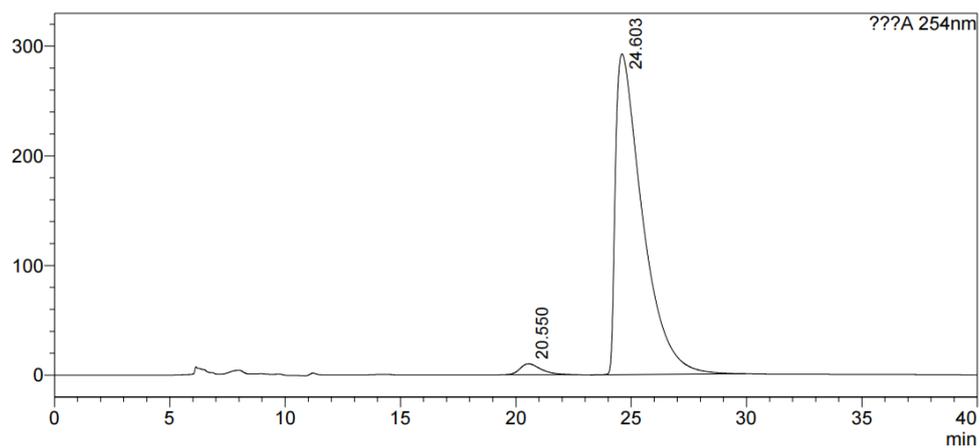
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.041	15631203	260501	49.775	56.011
2	25.071	15772829	204588	50.225	43.989
Total		31404032	465089	100.000	100.000

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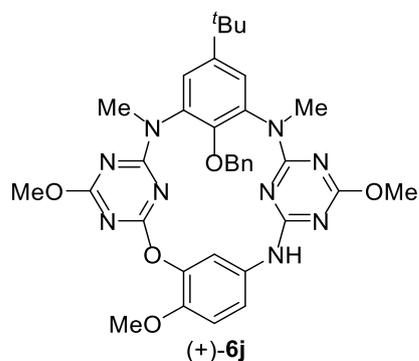
mV



<Peak Table>

??A 254nm

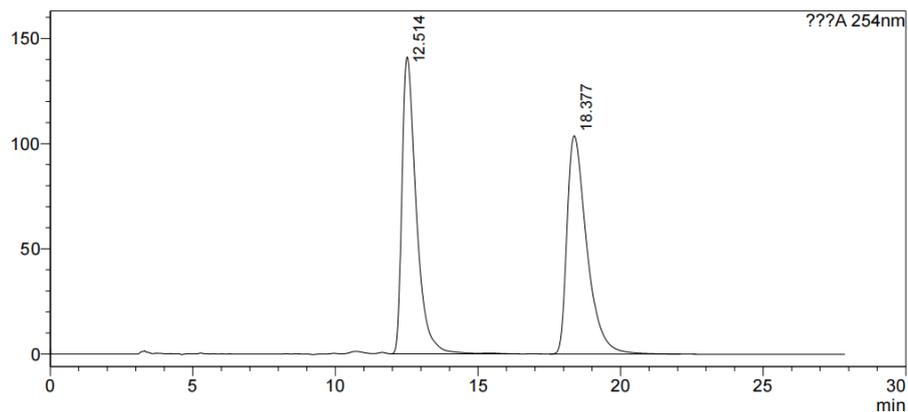
Peak#	Ret. Time	Area	Height	Area%	Height%
1	20.550	628675	9883	2.574	3.268
2	24.603	23795736	292552	97.426	96.732
Total		24424411	302435	100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 90 : 10, flow rate 1.0 mL/min, 254 nm, 25 °C, 87.7% ee.

<Chromatogram>

mV



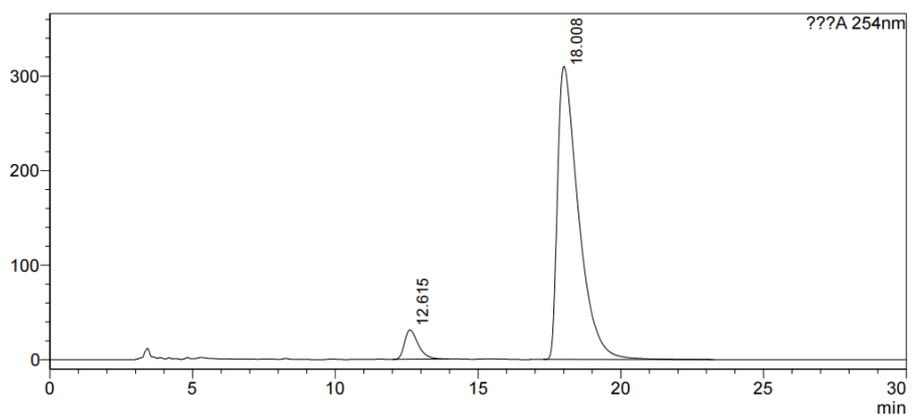
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.514	4942848	141155	49.540	49.540	57.623
2	18.377	5034617	103810	50.460	50.460	42.377
Total		9977465	244964		100.000	100.000

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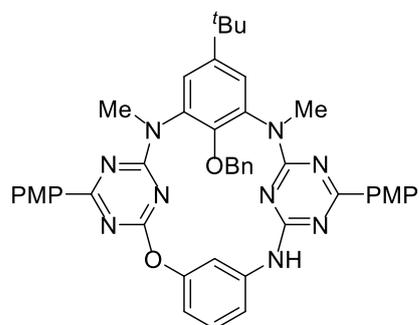
mV



<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.615	1042057	31175	6.160	6.160	9.137
2	18.008	15873670	310033	93.840	93.840	90.863
Total		16915727	341208		100.000	100.000

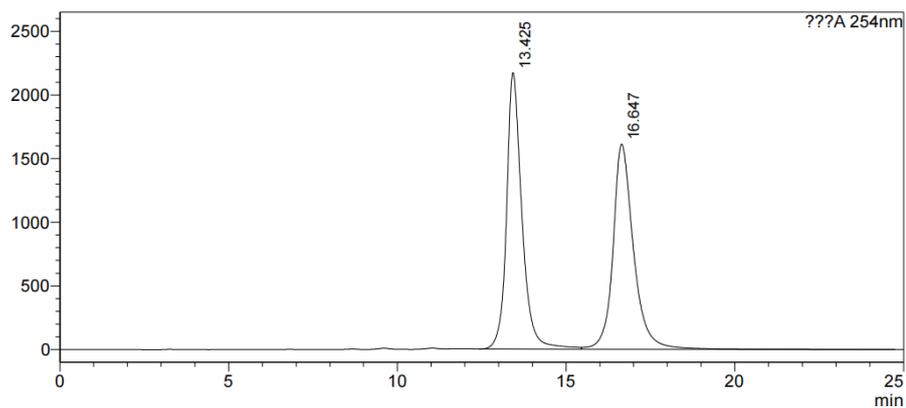


(+)-6k: PMP = 4-MeOC₆H₄

HPLC: IA column, Hexane : *i*-PrOH = 94 : 6, flow rate 1.0 mL/min, 254 nm, 25 °C, 48.9% ee.

<Chromatogram>

mV



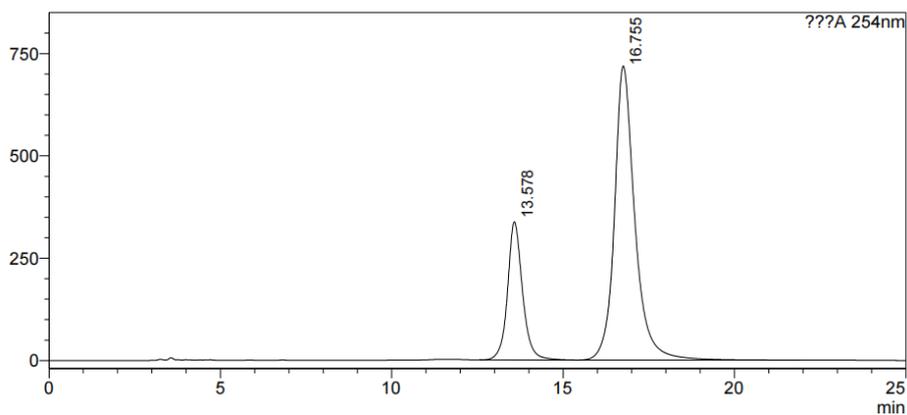
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	13.425	68995960	2171826	50.209	50.209	57.391
2	16.647	68422291	1612441	49.791	49.791	42.609
Total		137418251	3784268		100.000	100.000

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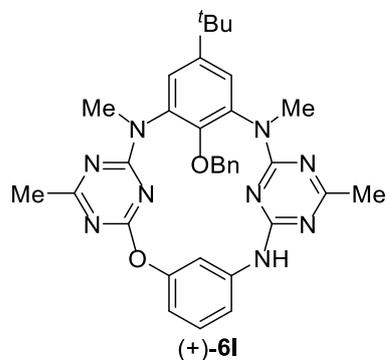
mV



<Peak Table>

??A 254nm

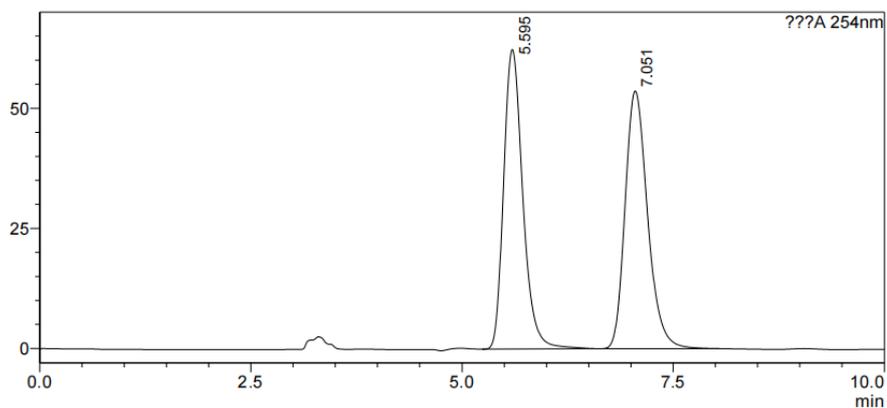
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	13.578	10284990	337793	25.564	25.564	31.974
2	16.755	29946970	718654	74.436	74.436	68.026
Total		40231960	1056447		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 92 : 8, flow rate 1.0 mL/min, 254 nm, 25 °C, 87.2% ee.

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mV



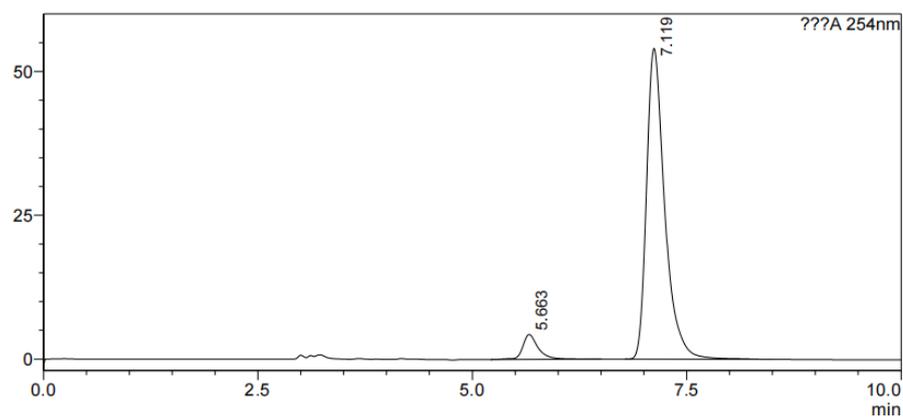
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	5.595	986770	62323	49.708	49.708	53.738
2	7.051	998344	53652	50.292	50.292	46.262
Total		1985114	115975		100.000	100.000

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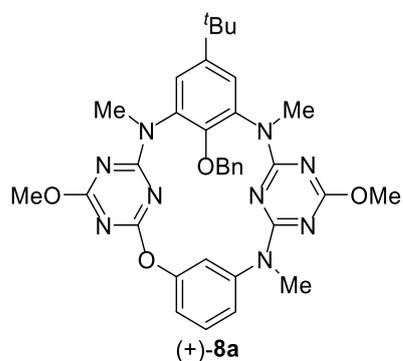
mV



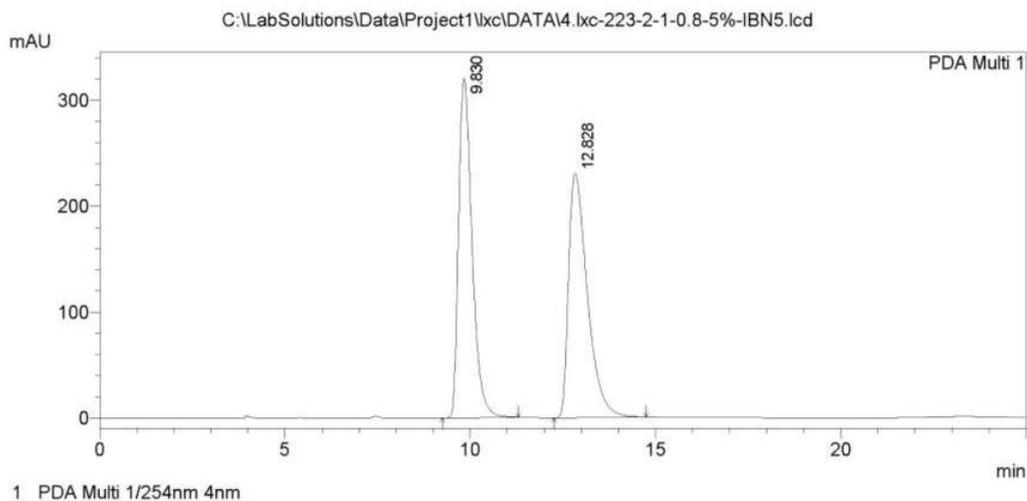
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???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	5.663	54963	4323	6.409	6.409	7.405
2	7.119	802590	54050	93.591	93.591	92.595
Total		857553	58373		100.000	100.000

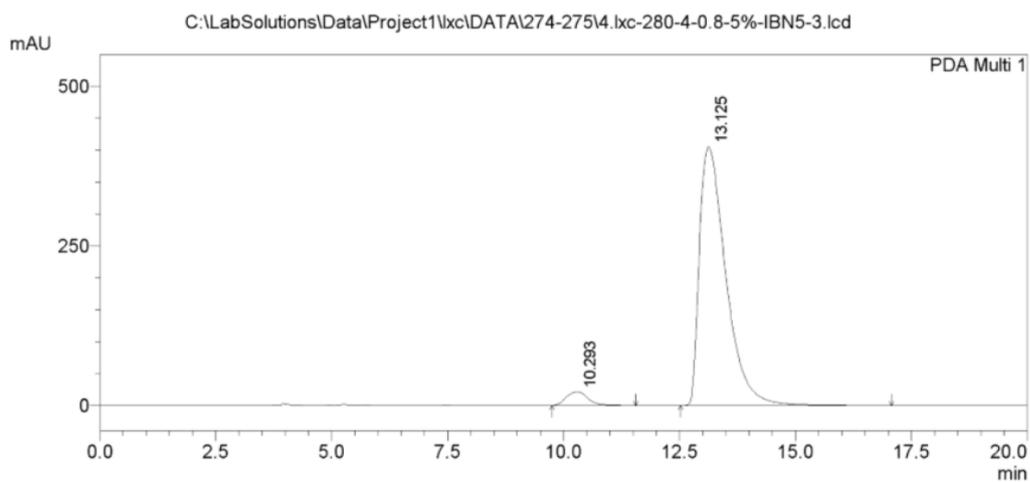


HPLC: IBN5 column, Hexane : i-PrOH = 95 : 5, flow rate 0.8 mL/min, 25 °C, 254 nm, 92% ee.



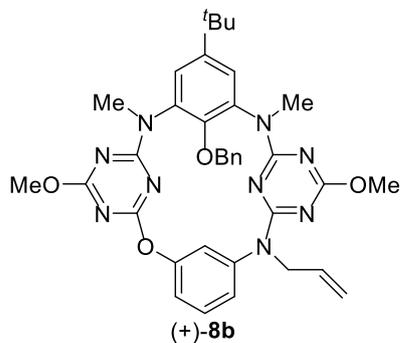
PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.830	8090858	319969	49.911	58.130
2	12.828	8119605	230464	50.089	41.870
Total		16210463	550433	100.000	100.000

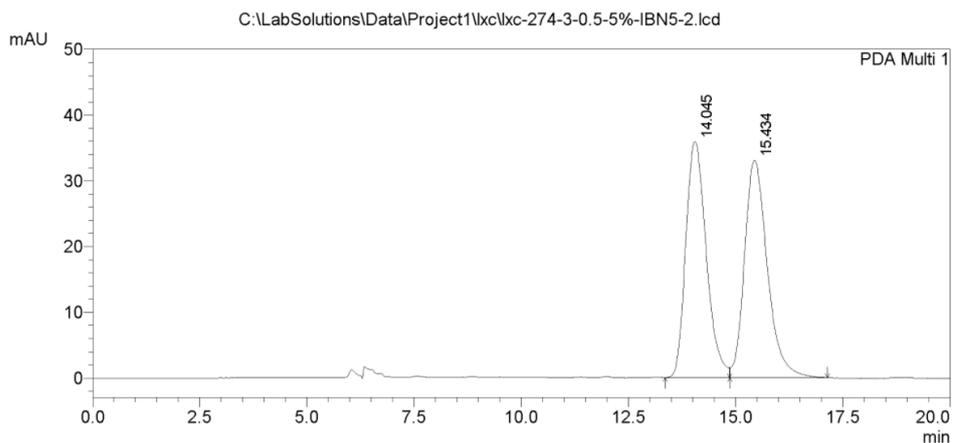


PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.293	676973	21172	4.024	4.963
2	13.125	16144744	405405	95.976	95.037
Total		16821716	426577	100.000	100.000



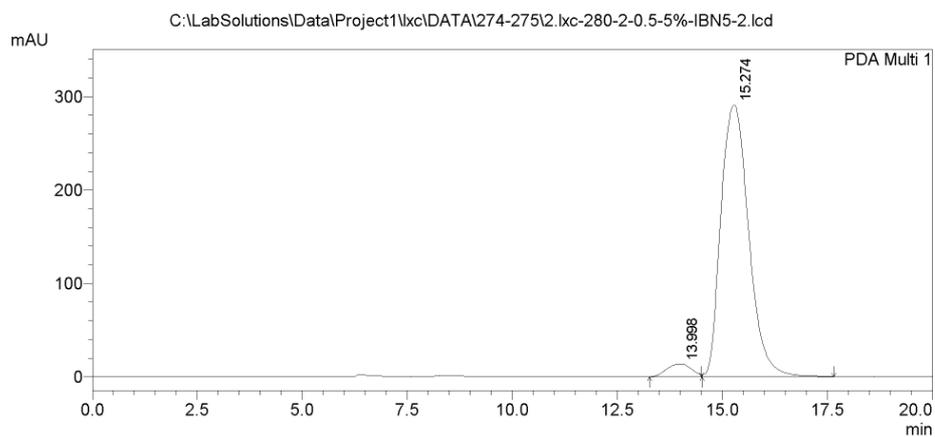
HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.5 mL/min, 254 nm, 25 °C, 92% ee.



PeakTable

PDA Ch1 254nm 4nm

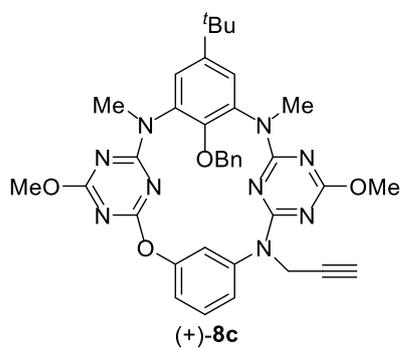
Peak#	Ret. Time	Area	Height	Area %	Height %
1	14.045	1199761	35956	49.364	52.068
2	15.434	1230687	33101	50.636	47.932
Total		2430448	69057	100.000	100.000



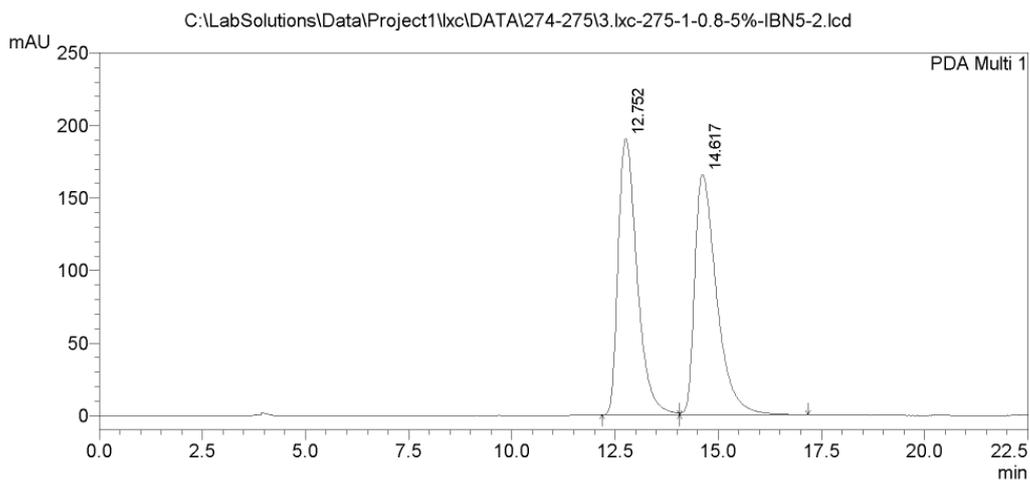
PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.998	557019	13735	3.985	4.504
2	15.274	13420118	291183	96.015	95.496
Total		13977137	304917	100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 95 : 5, flow rate 0.8 mL/min, 25 °C, 254 nm, 94.1% ee.

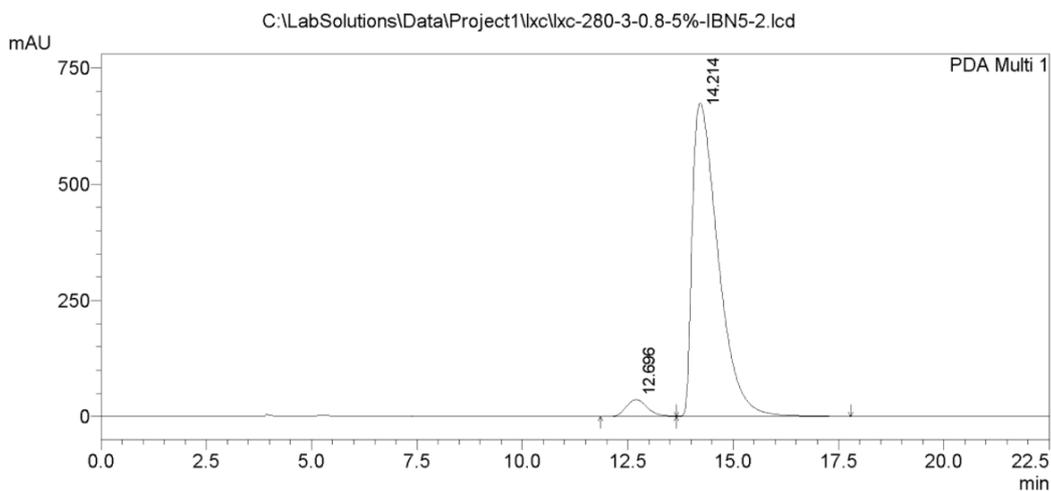


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.752	6045929	190612	49.615	53.495
2	14.617	6139641	165708	50.385	46.505
Total		12185570	356320	100.000	100.000

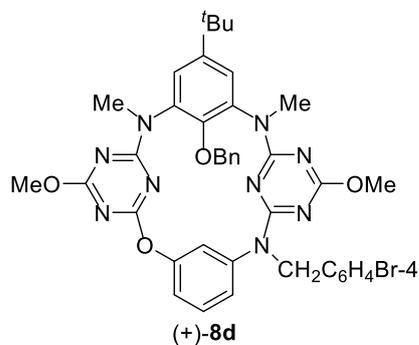


1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

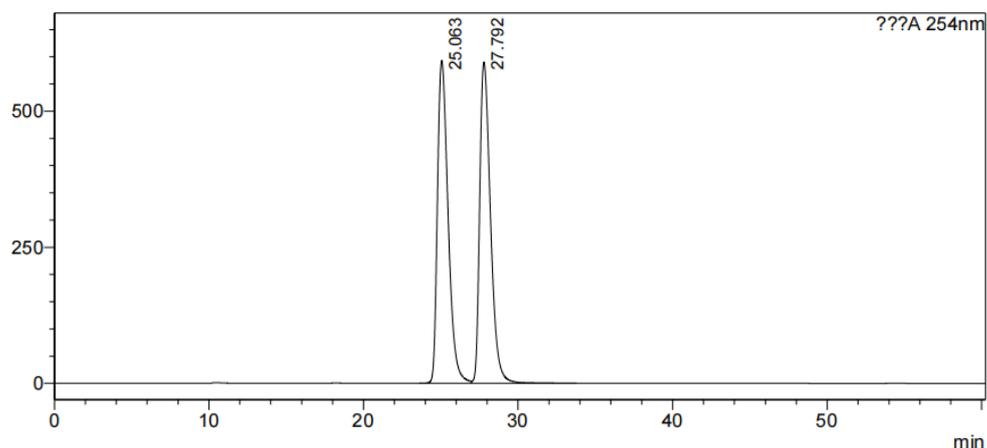
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.696	1297097	36556	4.294	5.137
2	14.214	28908931	675065	95.706	94.863
Total		30206028	711621	100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 94 : 6, flow rate 0.3 mL/min, 254 nm, 25 °C, 90.4% ee.

<Chromatogram>

mV



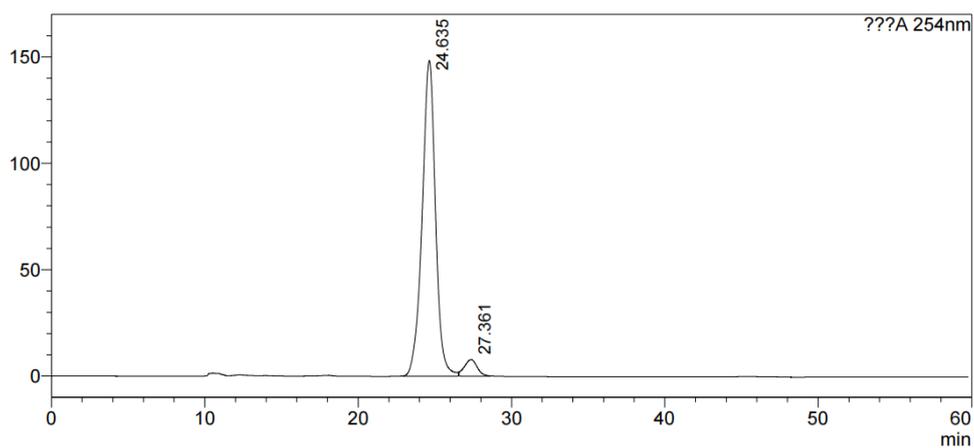
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	25.063	28544349	593173	49.869	49.869	50.127
2	27.792	28694708	590161	50.131	50.131	49.873
Total		57239057	1183333		100.000	100.000

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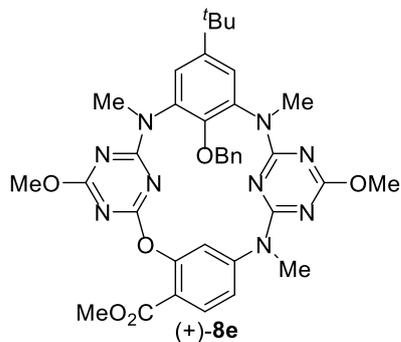
mV



<Peak Table>

??A 254nm

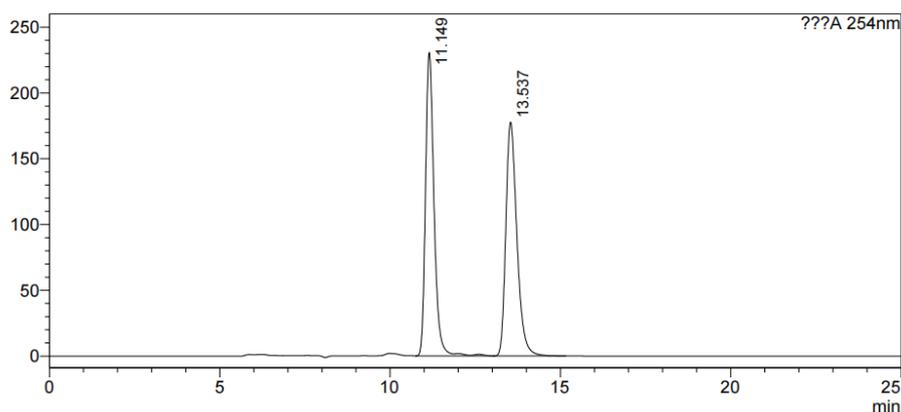
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	24.635	8966530	148450	95.183	95.183	95.002
2	27.361	453812	7810	4.817	4.817	4.998
Total		9420342	156260		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 80 : 20, flow rate 0.5 mL/min, 254 nm, 25 °C, 96.1% ee.

<Chromatogram>

mV



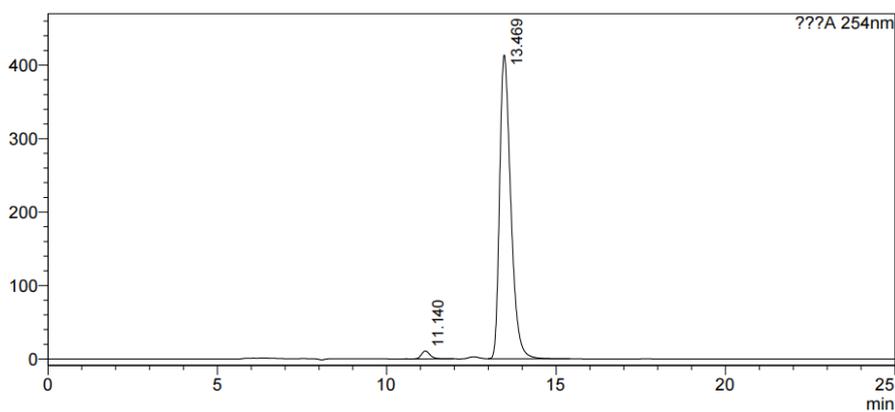
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	11.149	4041970	230232	50.233	50.233	56.450
2	13.537	4004515	177622	49.767	49.767	43.550
Total		8046485	407854		100.000	100.000

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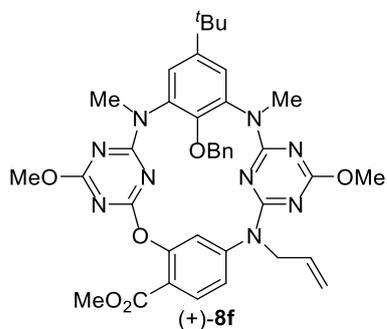
mV



<Peak Table>

??A 254nm

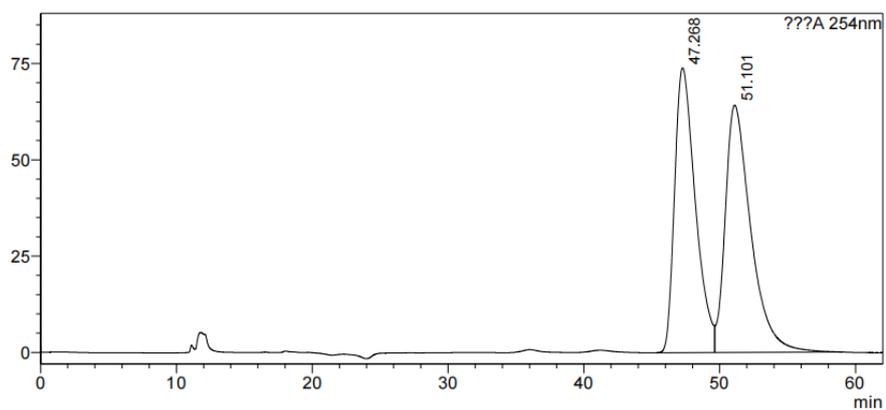
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	11.140	186777	10667	1.929	1.929	2.513
2	13.469	9498246	413756	98.071	98.071	97.487
Total		9685023	424423		100.000	100.000



HPLC: IBN5 column, Hexane: *i*-PrOH = 97 : 3, flow rate 0.3 mL/min, 254 nm, 25 °C, 96.7% ee.

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mV



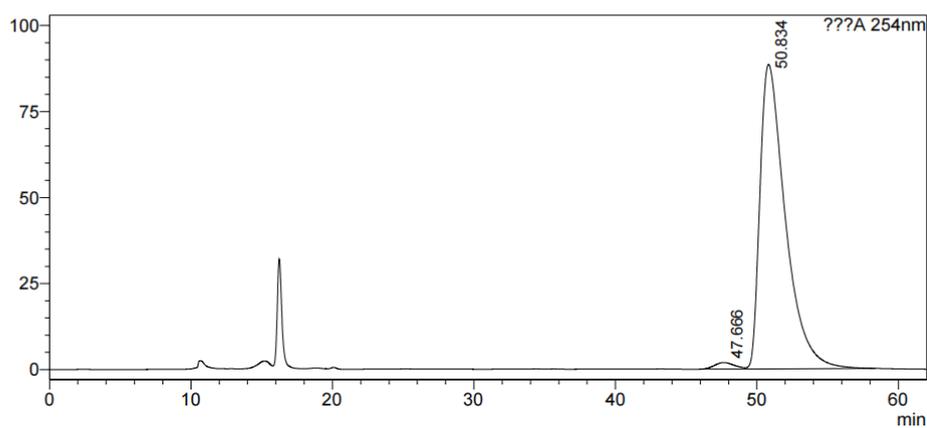
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	47.268	7848929	73936	48.209	48.209	53.539
2	51.101	8431996	64161	51.791	51.791	46.461
Total		16280925	138097		100.000	100.000

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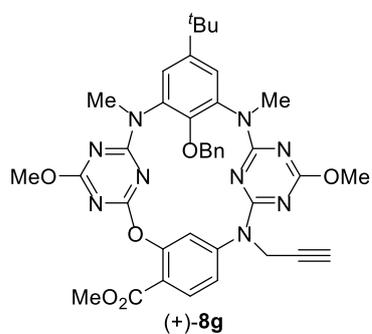
mV



<Peak Table>

??A 254nm

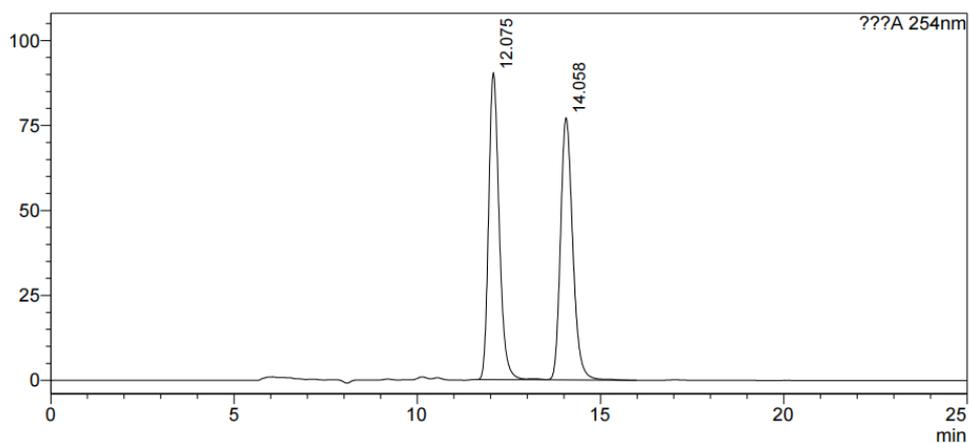
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	47.666	187565	1919	1.671	1.671	2.122
2	50.834	11038407	88509	98.329	98.329	97.878
Total		11225972	90429		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 80 : 20, flow rate 0.5 mL/min, 254 nm, 25 °C, 94.9% ee.

<Chromatogram>

mV



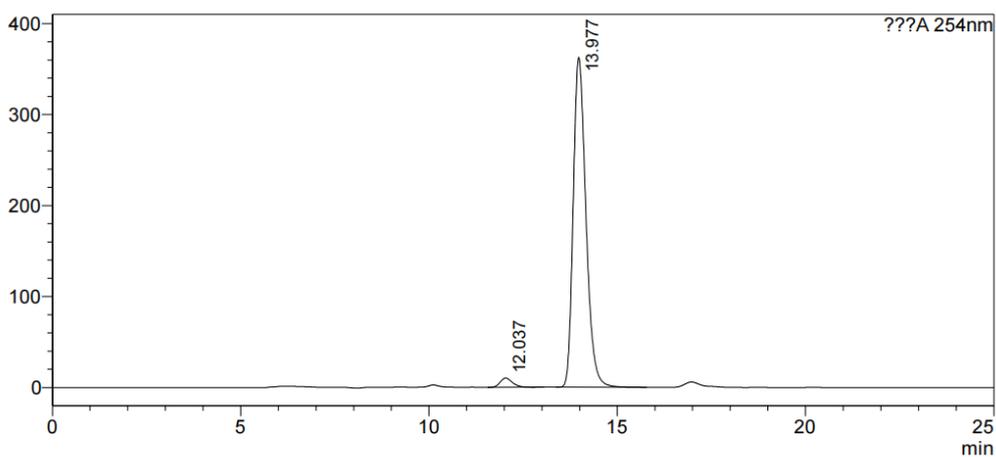
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.075	1804438	90243	50.273	50.273	53.932
2	14.058	1784813	77085	49.727	49.727	46.068
Total		3589251	167327		100.000	100.000

<Chromatogram>

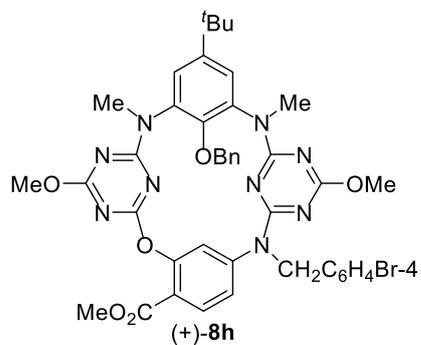
mV



<Peak Table>

??A 254nm

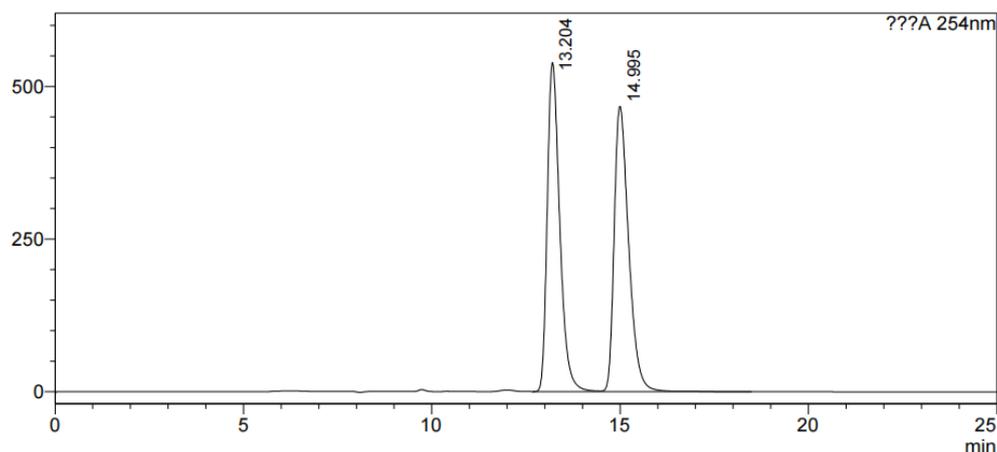
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	12.037	224716	10021	2.575	2.575	2.692
2	13.977	8501223	362202	97.425	97.425	97.308
Total		8725939	372223		100.000	100.000



HPLC: IBN5 column, Hexane : *i*-PrOH = 80 : 20, flow rate 0.5 mL/min, 254 nm, 25 °C, 96.2% ee.

<Chromatogram>

mV



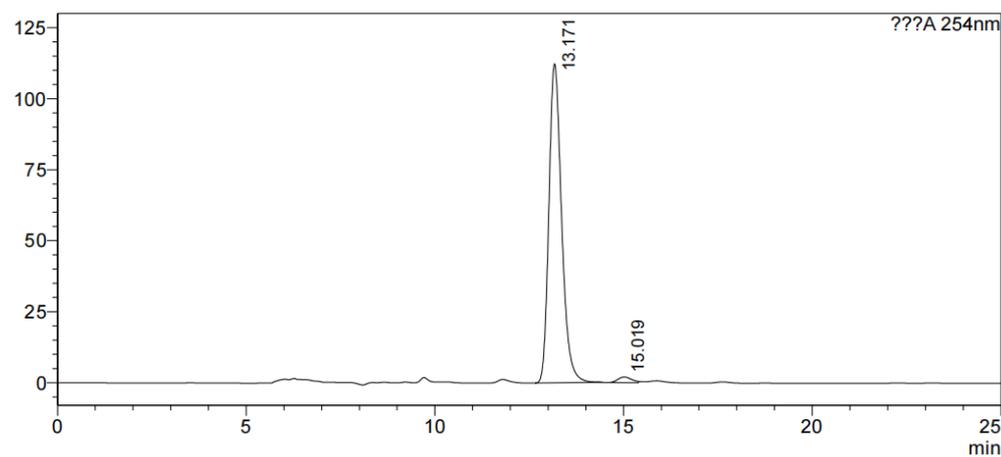
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	13.204	12426750	538893	49.811	49.811	53.550
2	14.995	12521053	467437	50.189	50.189	46.450
Total		24947803	1006330		100.000	100.000

<Chromatogram>

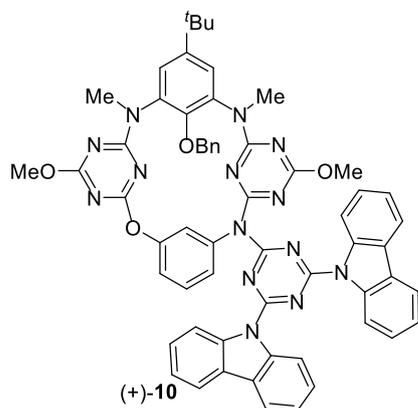
mV



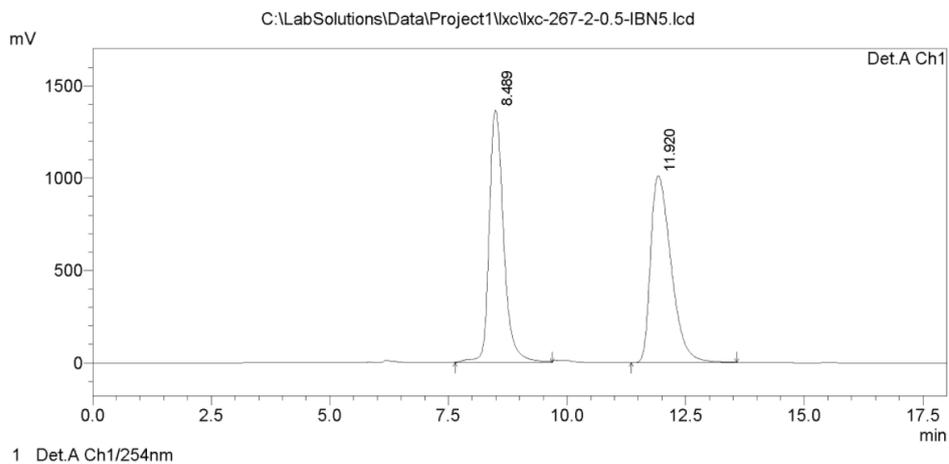
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	13.171	2637208	112357	98.099	98.099	98.242
2	15.019	51108	2011	1.901	1.901	1.758
Total		2688316	114368		100.000	100.000



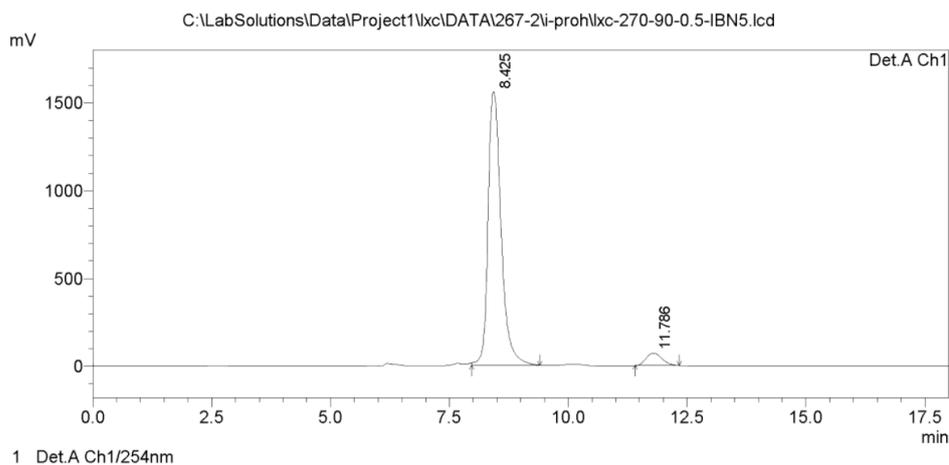
HPLC: IBN5 column, Hexane : *i*-PrOH : CH₂Cl₂ = 80 : 5 : 15, flow rate 0.5 mL/min, 254 nm, 25 °C, 89.9% ee.



检测器 A Ch1 254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.489	28932135	1366782	48.819	57.460
2	11.920	30331878	1011890	51.181	42.540
Total		59264013	2378672	100.000	100.000



检测器 A Ch1 254nm

PeakTable

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.425	29748768	1560192	94.971	95.738
2	11.786	1575167	69459	5.029	4.262
Total		31323935	1629651	100.000	100.000

12. Copies of CD spectra of compounds 6a-6l, 8a-8h and 10.

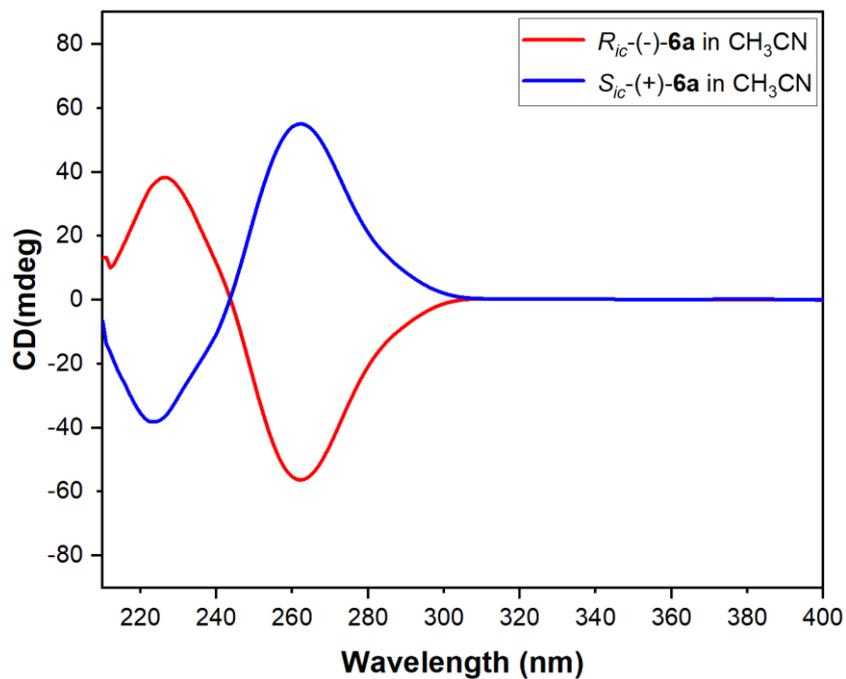


Figure S7. CD spectrum of R_{ic} -(-)-**6a** and S_{ic} -(+)-**6a** in CH_3CN ($5.00 \times 10^{-5} \text{ M}$) at 25°C .

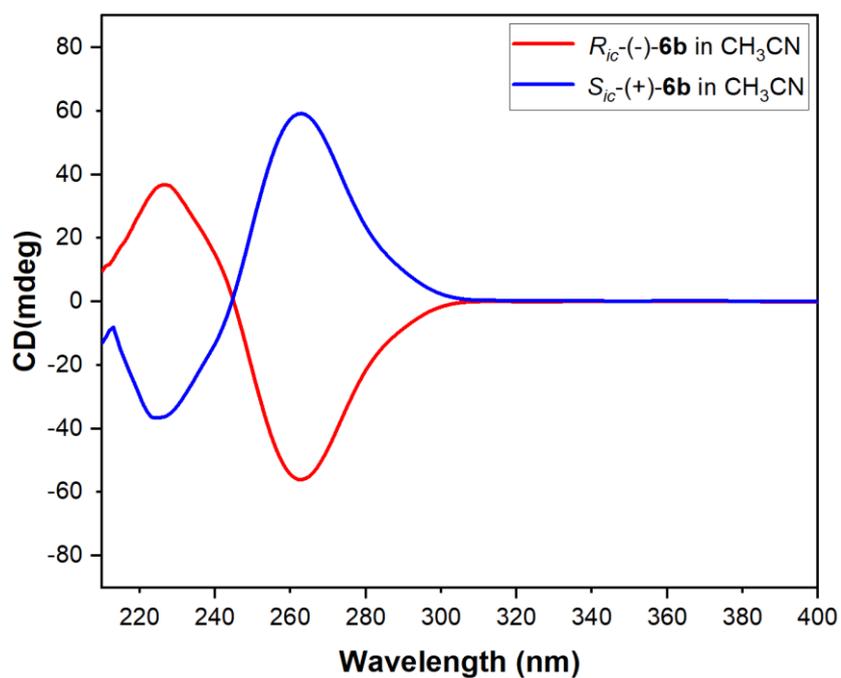


Figure S8. CD spectrum of R_{ic} -(-)-**6b** and S_{ic} -(+)-**6b** in CH_3CN ($5.00 \times 10^{-5} \text{ M}$) at 25°C .

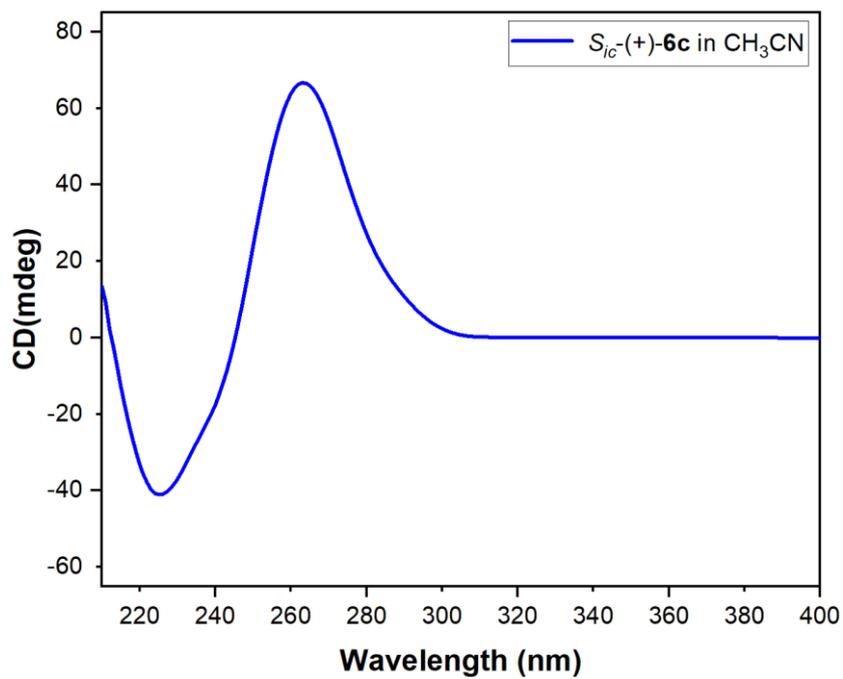


Figure S9. CD spectrum of $S_{ic}-(+)-6c$ in CH_3CN (5.25×10^{-5} M) at 25 °C.

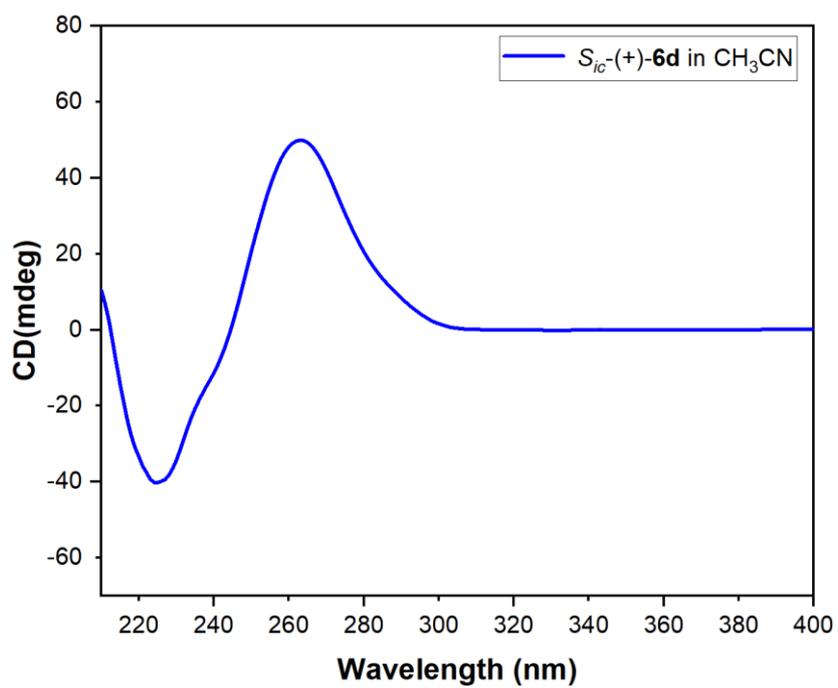


Figure S10. CD spectrum of $S_{ic}-(+)-6d$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

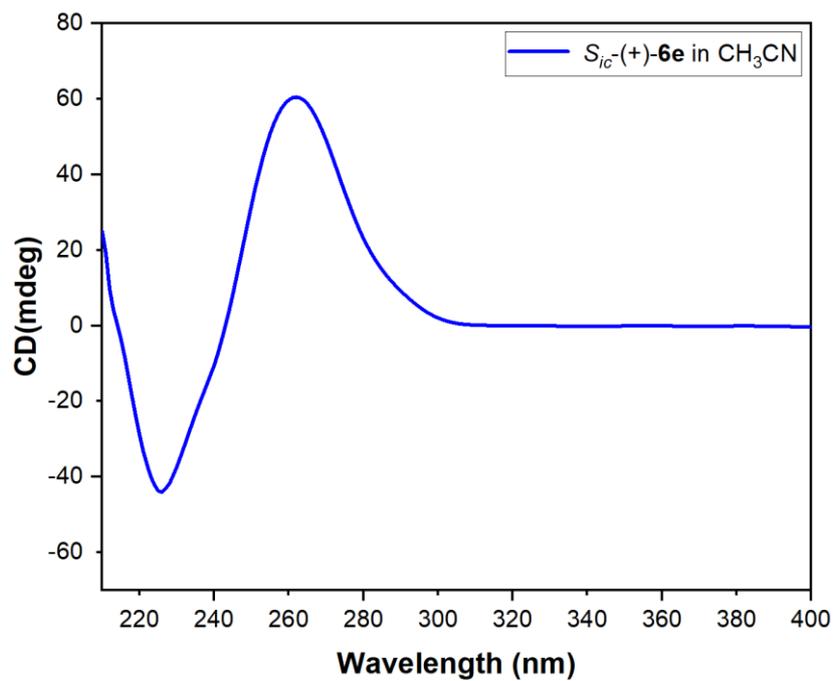


Figure S11. CD spectrum of $S_{ic}-(+)-6e$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

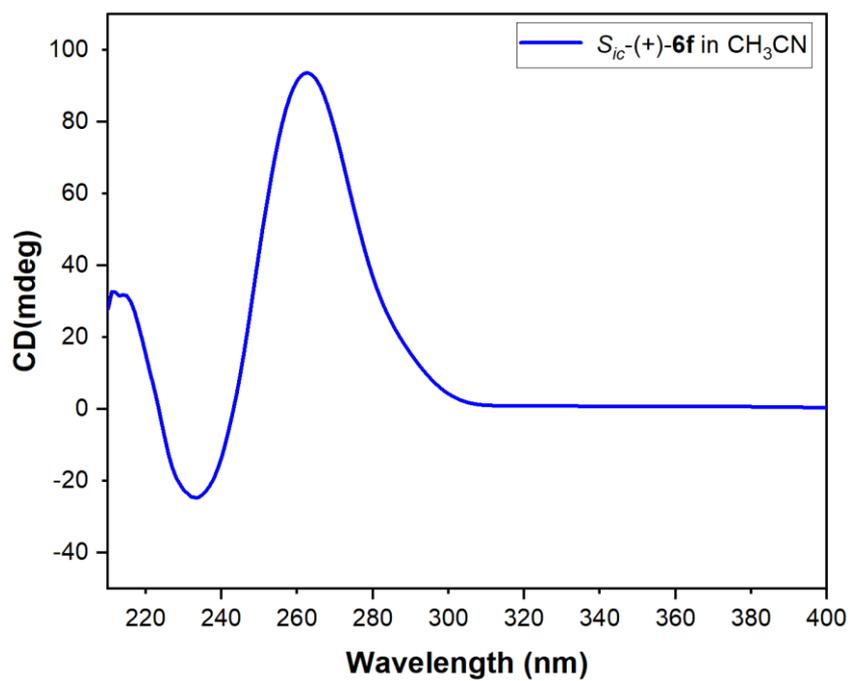


Figure S12. CD spectrum of $S_{ic}-(+)-6f$ in CH_3CN (5.65×10^{-5} M) at 25 °C.

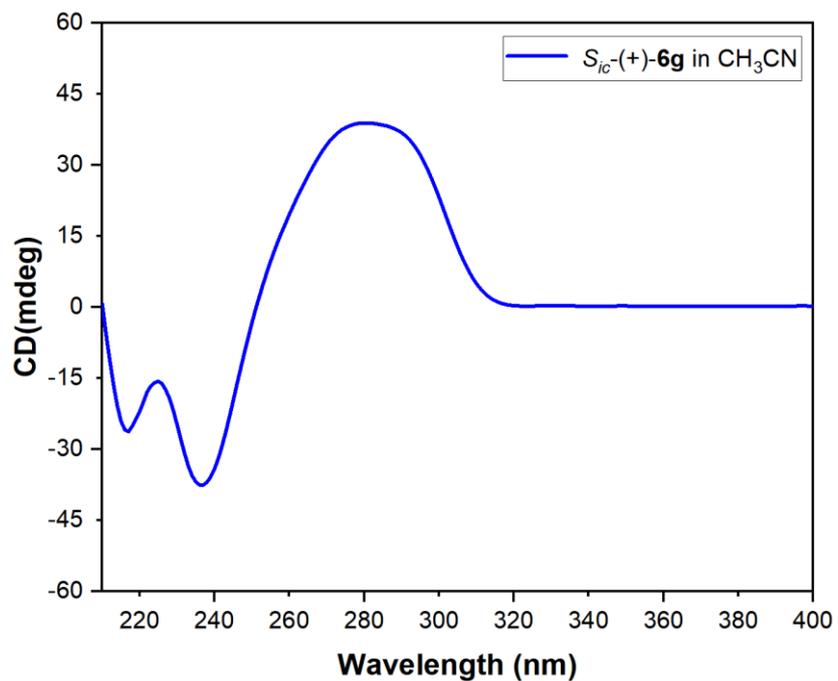


Figure S13. CD spectrum of $S_{ic}-(+)-6g$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

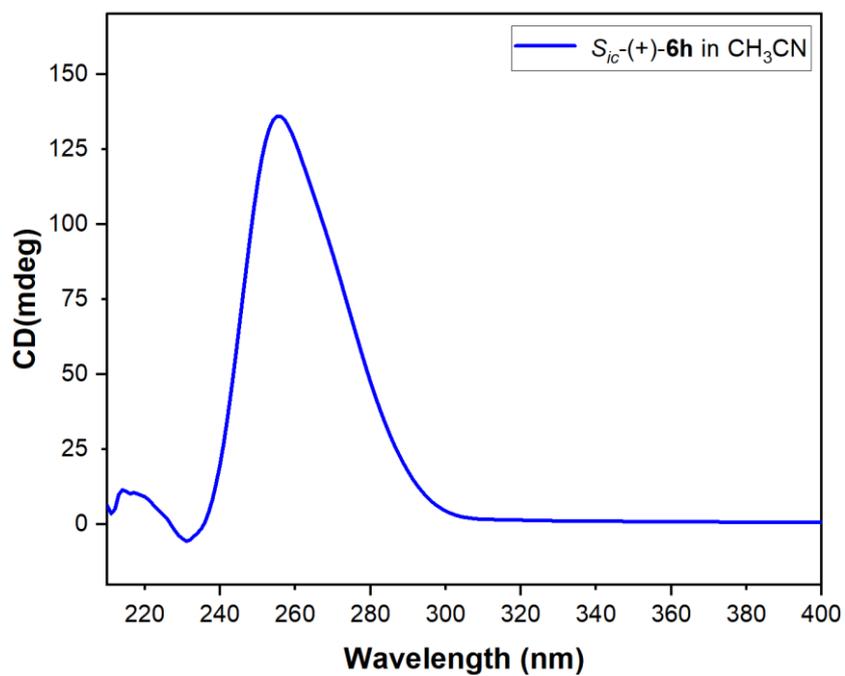


Figure S14. CD spectrum of $S_{ic}-(+)-6h$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

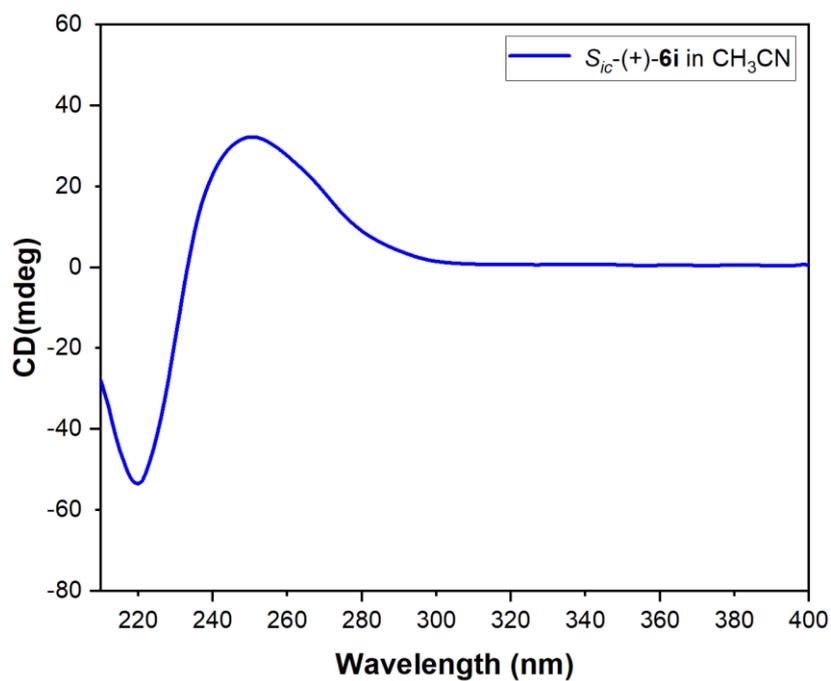


Figure S15. CD spectrum of $S_{ic}-(+)-6i$ in CH_3CN (5.05×10^{-5} M) at 25 °C.

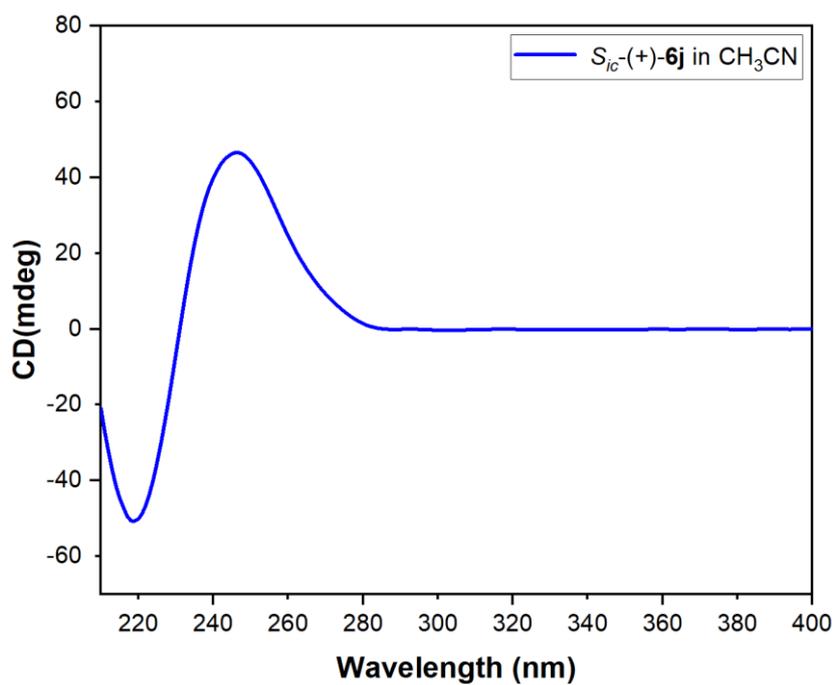


Figure S16. CD spectrum of $S_{ic}-(+)-6j$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

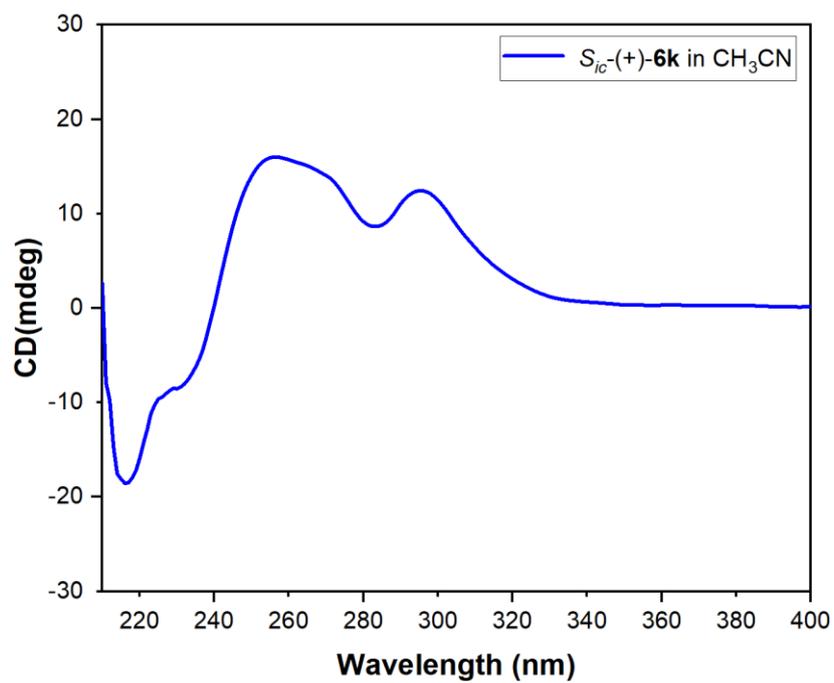


Figure S17. CD spectrum of $S_{ic}-(+)-6k$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

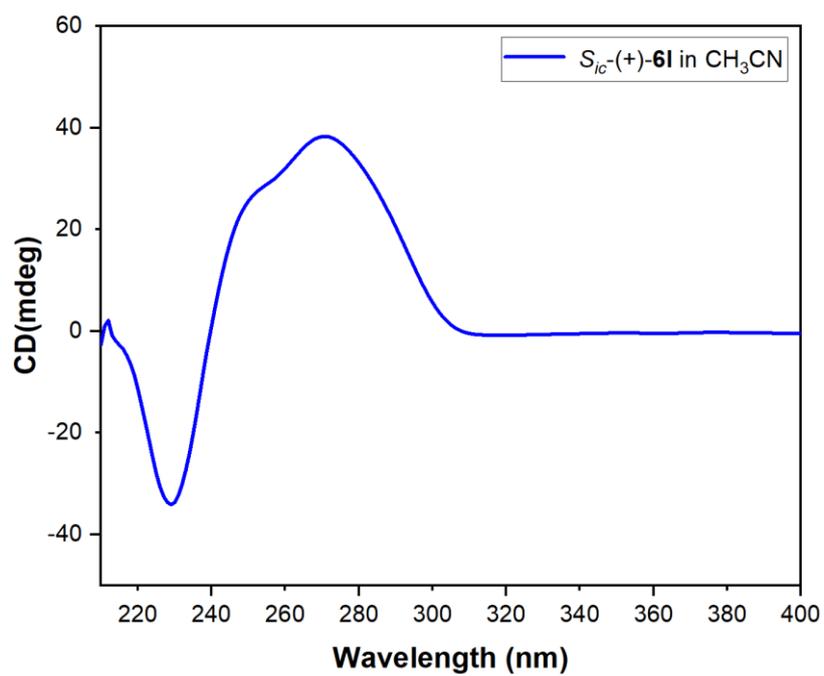


Figure S18. CD spectrum of $S_{ic}-(+)-6l$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

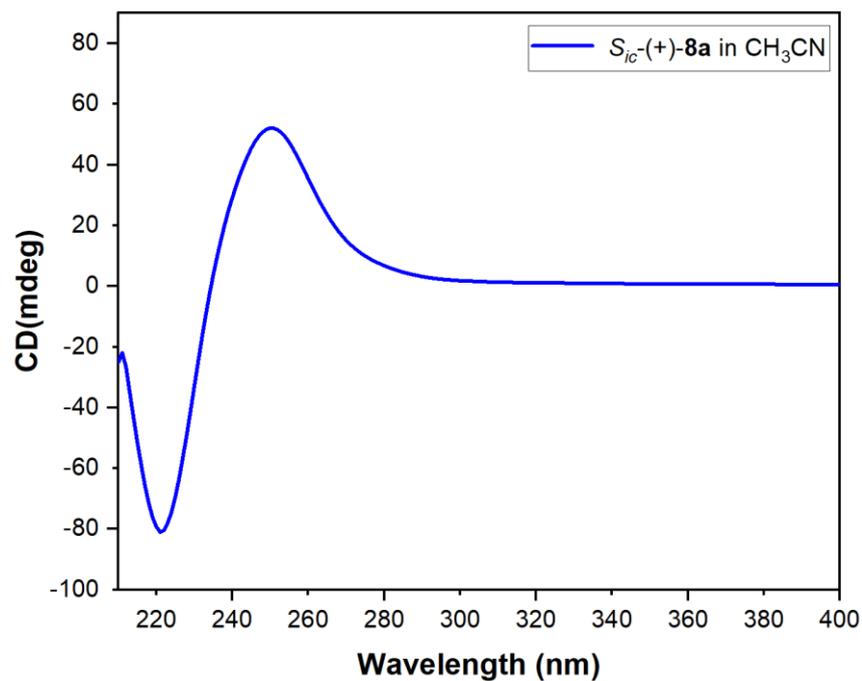


Figure S19. CD spectrum of $S_{ic}-(+)-8a$ in CH_3CN (5.11×10^{-5} M) at 25 °C.

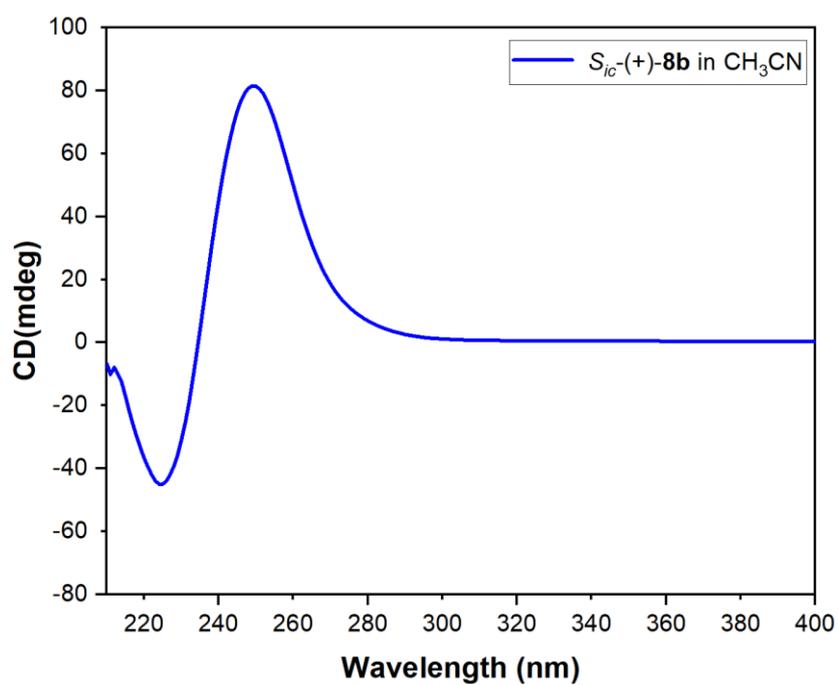


Figure S20. CD spectrum of $S_{ic}-(+)-8b$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

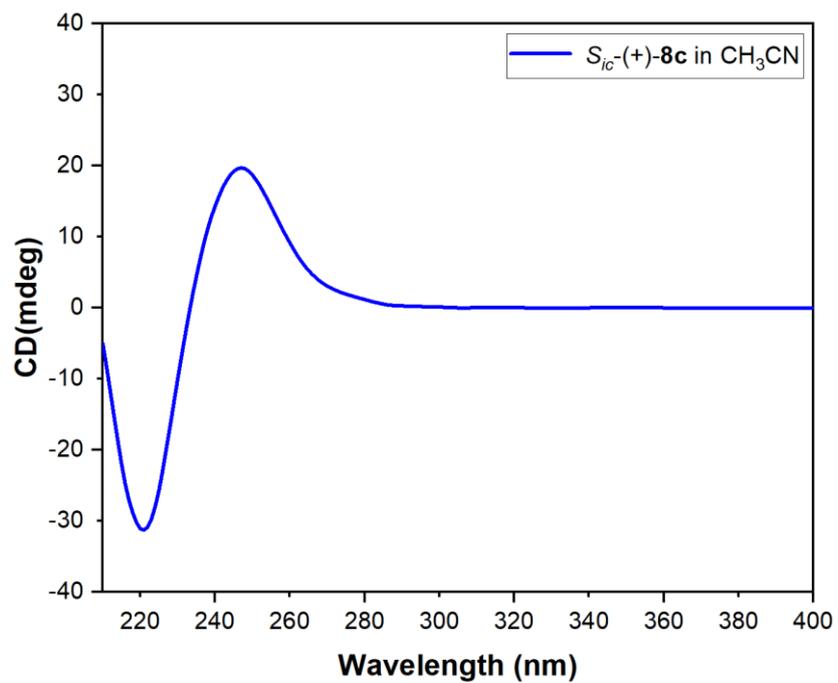


Figure S21. CD spectrum of $S_{ic}-(+)-8c$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

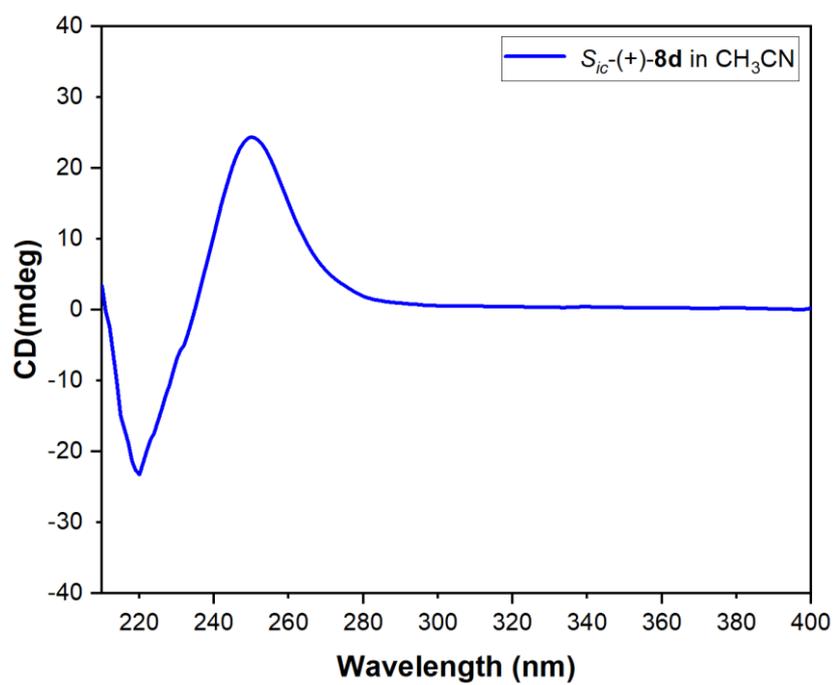


Figure S22. CD spectrum of $S_{ic}-(+)-8d$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

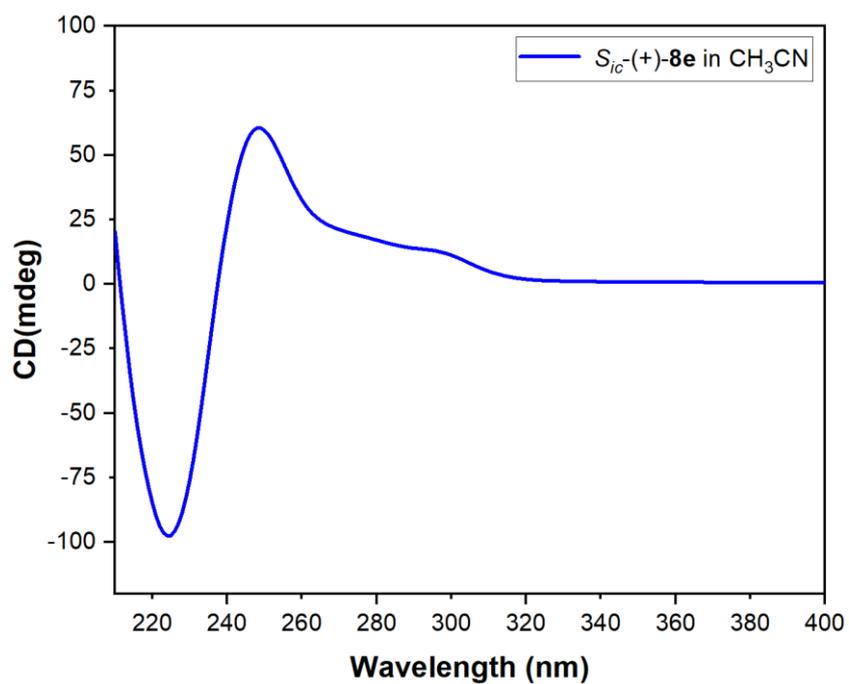


Figure S23. CD spectrum of $S_{ic}-(+)-8e$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

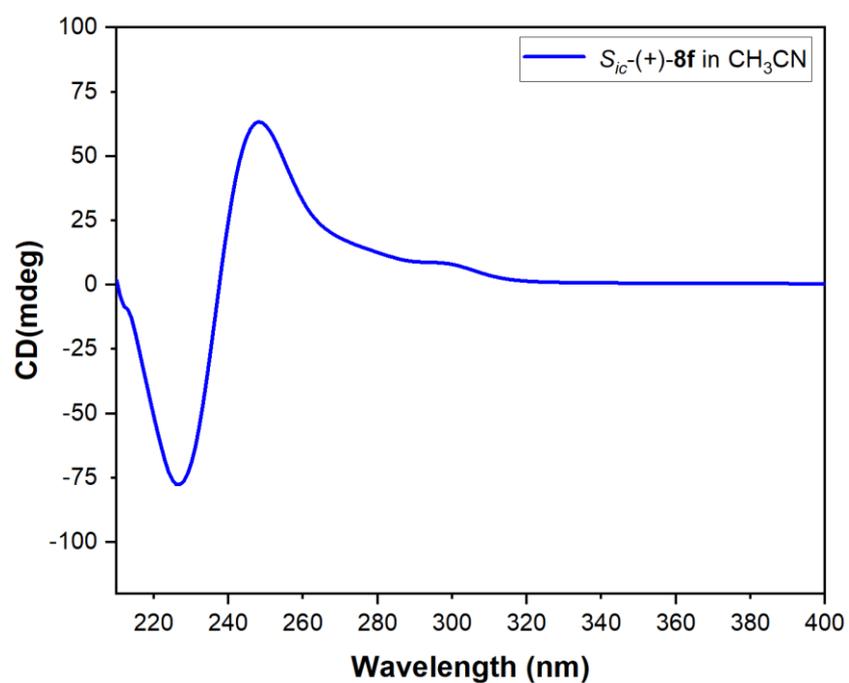


Figure S24. CD spectrum of $S_{ic}-(+)-8f$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

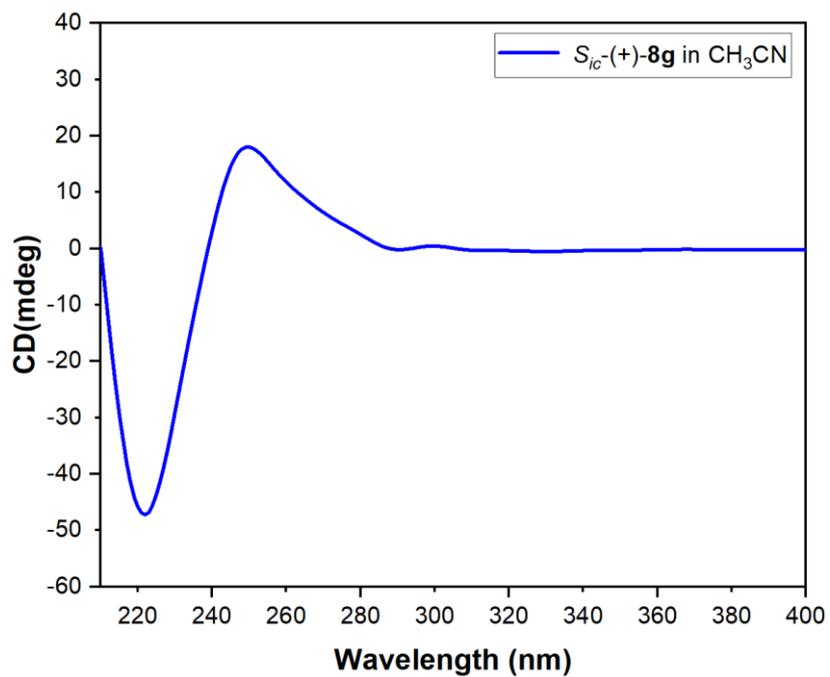


Figure S25. CD spectrum of $S_{ic}-(+)-8g$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

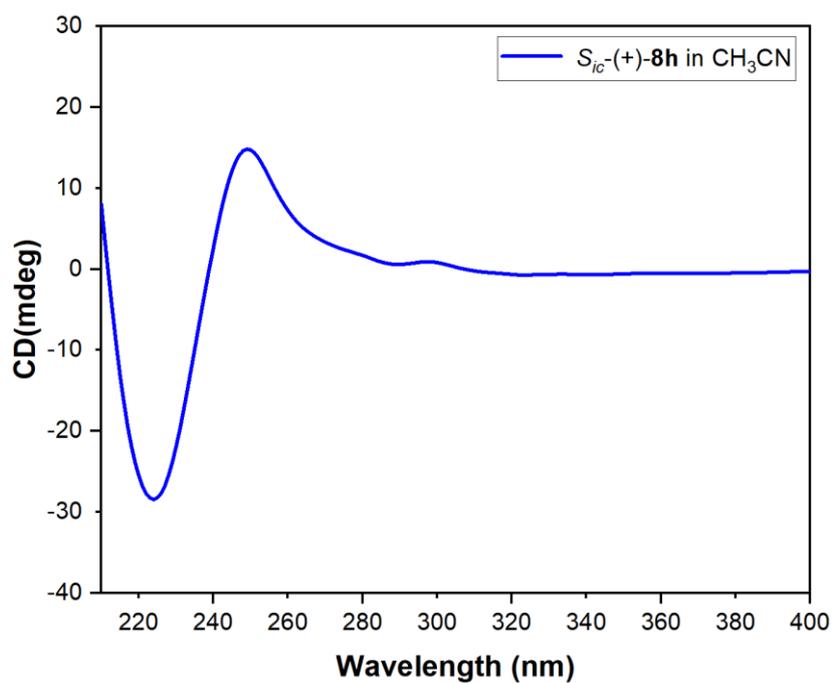


Figure S26. CD spectrum of $S_{ic}-(+)-8h$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

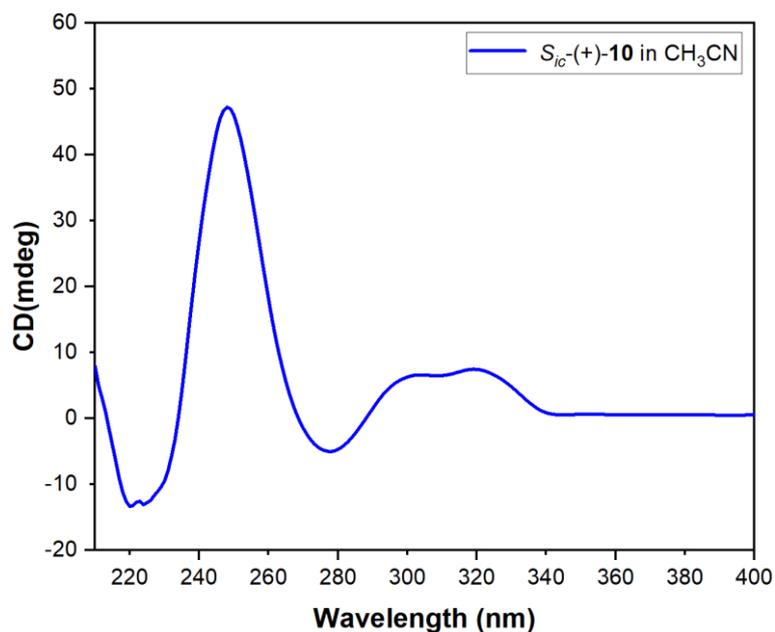


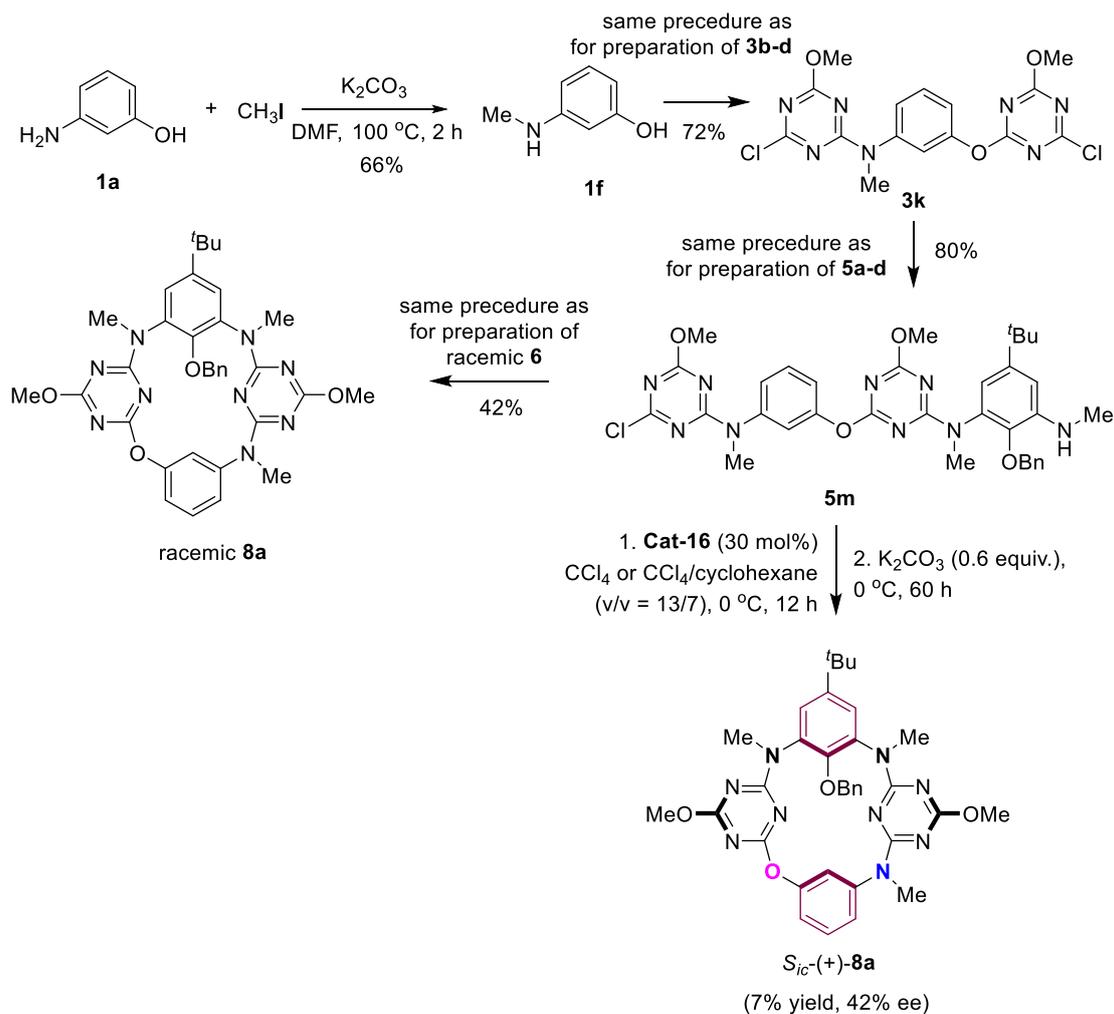
Figure S27. CD spectrum of $S_{ic}-(+)-10$ in CH_3CN (5.00×10^{-5} M) at 25 °C.

Table S10. g_{abs} values of compounds **6a-6l**, **8a-8h** and **10**.

compound	λ_{CD} [nm] ^[a]	g_{abs}
$S_{ic}-(+)-6a$	263	2.30×10^{-3}
$R_{ic}(-)-6a$	263	-2.30×10^{-3}
$S_{ic}-(+)-6b$	262	2.17×10^{-3}
$R_{ic}(-)-6b$	262	-2.14×10^{-3}
$S_{ic}-(+)-6c$	264	2.64×10^{-3}
$S_{ic}-(+)-6d$	263	2.36×10^{-3}
$S_{ic}-(+)-6e$	263	1.83×10^{-3}
$S_{ic}-(+)-6f$	262	2.21×10^{-3}
$S_{ic}-(+)-6g$	285	1.54×10^{-3}
$S_{ic}-(+)-6h$	256	2.02×10^{-3}
$S_{ic}-(+)-6i$	250	1.41×10^{-3}
$S_{ic}-(+)-6j$	247	2.06×10^{-3}
$S_{ic}-(+)-6k$	257	3.10×10^{-4}
$S_{ic}-(+)-6l$	271	1.24×10^{-3}
$S_{ic}-(+)-8a$	251	2.35×10^{-3}
$S_{ic}-(+)-8b$	250	2.15×10^{-3}
$S_{ic}-(+)-8c$	247	1.56×10^{-3}
$S_{ic}-(+)-8d$	250	1.19×10^{-3}
$S_{ic}-(+)-8e$	248	1.73×10^{-3}
$S_{ic}-(+)-8f$	248	1.77×10^{-3}
$S_{ic}-(+)-8g$	249	1.25×10^{-3}
$S_{ic}-(+)-8h$	249	1.16×10^{-3}
$S_{ic}-(+)-10$	319	1.96×10^{-4}

^[a]The wavelength corresponding to the first Cotton effect.

13. Result of a control experiment



To a solution of **1a** (1.09 g, 10 mmol) and K_2CO_3 (1.38 g, 10 mmol, 1.0 equiv) in DMF (10 mL) at room temperature was added CH_3I (1.42 g, 10 mmol, 1.0 equiv) and the resulting mixture was kept stirring for 2 h. After filtration through a celite pad and washing with ethyl acetate (3 X 10 mL), the filtrate was concentrated to dryness. The residue was dissolved in ethyl acetate (20 mL) and washed with saline (3 X 10 mL). The organic phase was dried over anhydrous Na_2SO_4 . After removal of organic solvent, the residue was chromatographed with silica gel using a mixture of petroleum ether and ethyl acetate (v/v = 4/1) as an eluent to give product **1f** as brown oil, 812.0 mg, 66% yield. $^1\text{H NMR}$ (600 MHz, CDCl_3) δ (ppm): 7.04 (t, $J = 7.8$ Hz, 1H), 6.24 (d, $J = 7.8$ Hz, 2H), 6.08 (s, 1H), 5.04 (brs, 2H), 2.74 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm): 156.8, 150.1, 130.3, 106.2, 105.9, 100.9, 31.1. IR (KBr) ν 3410, 3333, 1612, 1504 cm^{-1} .

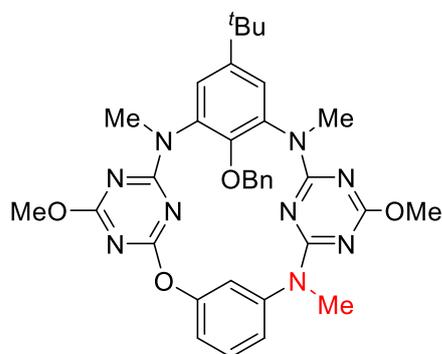
Following the same synthetic procedure for **3b-d**, product **3k** was obtained as white solid, 589.0 mg, 72% yield, m.p. = 152 - 153 $^\circ\text{C}$. $^1\text{H NMR}$ (400 MHz, CDCl_3) δ (ppm): 7.48 (t, $J = 8.4$ Hz, 1H), 7.25 - 7.22 (m, 1H), 7.15 - 7.12 (m, 2H), 4.03 (s, 3H), 3.84 (br, 3H), 3.55 (s, 3H). $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ (ppm): 173.4, 172.9, 172.1, 170.9, 166.5, 151.7, 144.2, 130.2, 124.4, 120.1, 120.0, 56.5, 55.4, 38.7. IR (KBr) ν : 1566 cm^{-1} . HRMS (TOF-ESI) m/z $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{N}_7\text{O}_3$: 410.0529; Found: 410.0535.

Following the same synthetic procedure for **5a-d**, product **5m** was obtained as white solid, 268.5

mg, 80% yield, m.p. = 70 - 72 °C. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.44 (t, J = 8.4 Hz, 0.57H), 7.30 - 7.17 (m, 8H), 7.07 - 7.00 (m, 1.43H), 6.61 (s, 0.57H), 6.55 (s, 0.43H), 6.54 (s, 0.57H), 6.45 (s, 0.43H), 4.72 - 4.66 (m, 2H), 4.12 - 3.98 (m, 3H), 3.79 - 3.70 (m, 3H), 3.54 (s, 1.7H), 3.44 (s, 1.3H), 3.37 (s, 3H), 2.81 (s, 1.7H), 2.79 (s, 1.3H), 1.30 (s, 5.1H), 1.24 (s, 3.9H). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 172.5, 172.0, 171.9, 171.1, 167.7, 166.3, 166.1, 152.4, 152.3, 148.2, 148.1, 143.6, 143.2, 136.9, 136.8, 135.8, 135.7, 129.7, 129.2, 128.4, 128.2, 128.1, 128.0, 127.8, 123.4, 123.0, 120.6, 120.4, 119.8, 75.3, 55.2, 54.8, 54.6, 38.6, 38.0, 37.7, 34.74, 34.65, 31.3, 31.2. IR (KBr) ν: 1744, 1574 cm⁻¹. HRMS (TOF-ESI) m/z [M+H]⁺ calcd. for C₃₄H₃₉CIN₉O₄: 672.2808; Found: 672.2796.

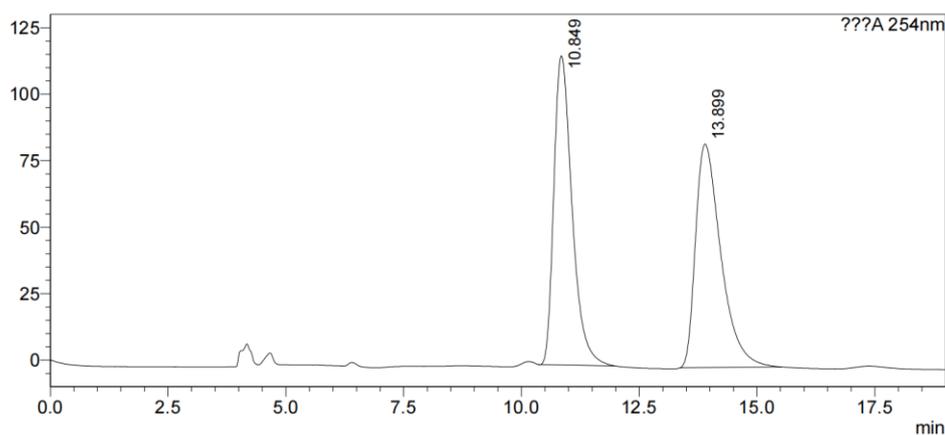
Following the same synthetic procedure for racemic **6**, racemic product **8a** was obtained as white solid, 27.0 mg, 42% yield.

Following the same catalytic enantioselective reaction of **5**, *S_{ic}*-**8a** was obtained in 7% yield and 42% ee.



<Chromatogram>

mV



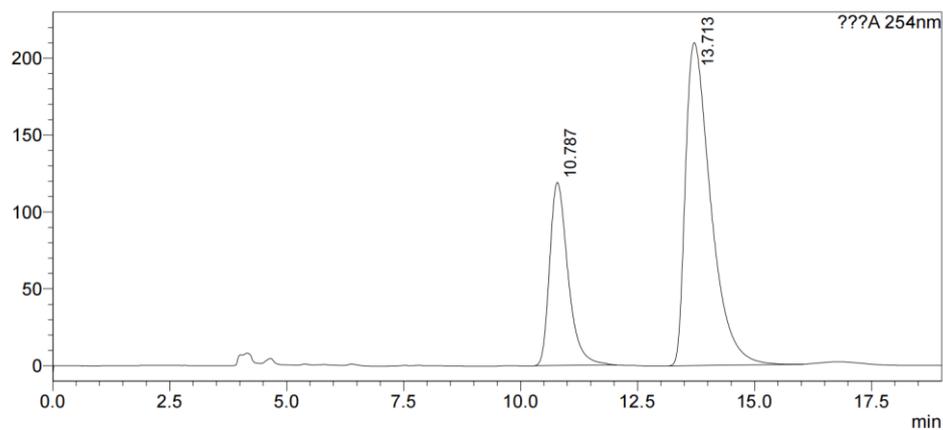
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	10.849	3125169	116302	49.810	49.810	58.050
2	13.899	3149065	84045	50.190	50.190	41.950
Total		6274234	200347		100.000	100.000

<Chromatogram>

mV



<Peak Table>

??A 254nm

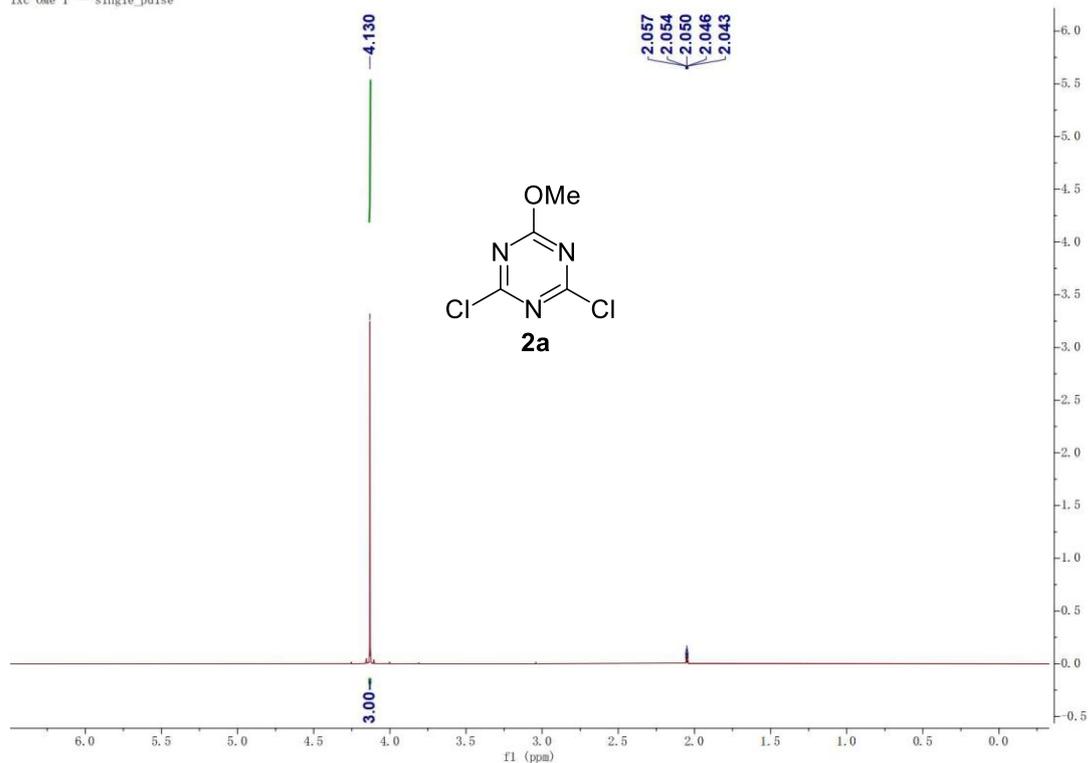
Peak#	Ret. Time	Area	Height	Conc.	Area%	Height%
1	10.787	3254294	119035	29.127	29.127	36.182
2	13.713	7918627	209953	70.873	70.873	63.818
Total		11172921	328988		100.000	100.000

HPLC analysis of racemic sample of **8a** (top) and enantioenriched sample of *S_{ic}*-**8a** (bottom).

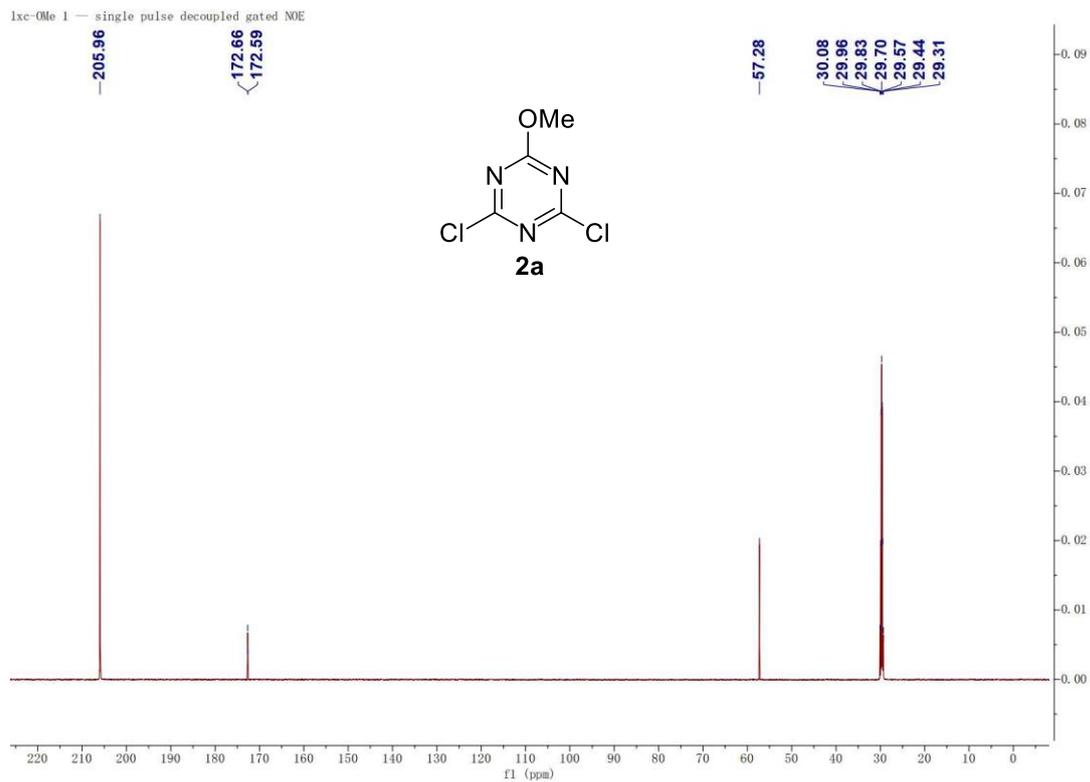
14. ¹H and ¹³C NMR spectra of all products

2a: ¹H NMR, 600 MHz, acetone-*d*₆

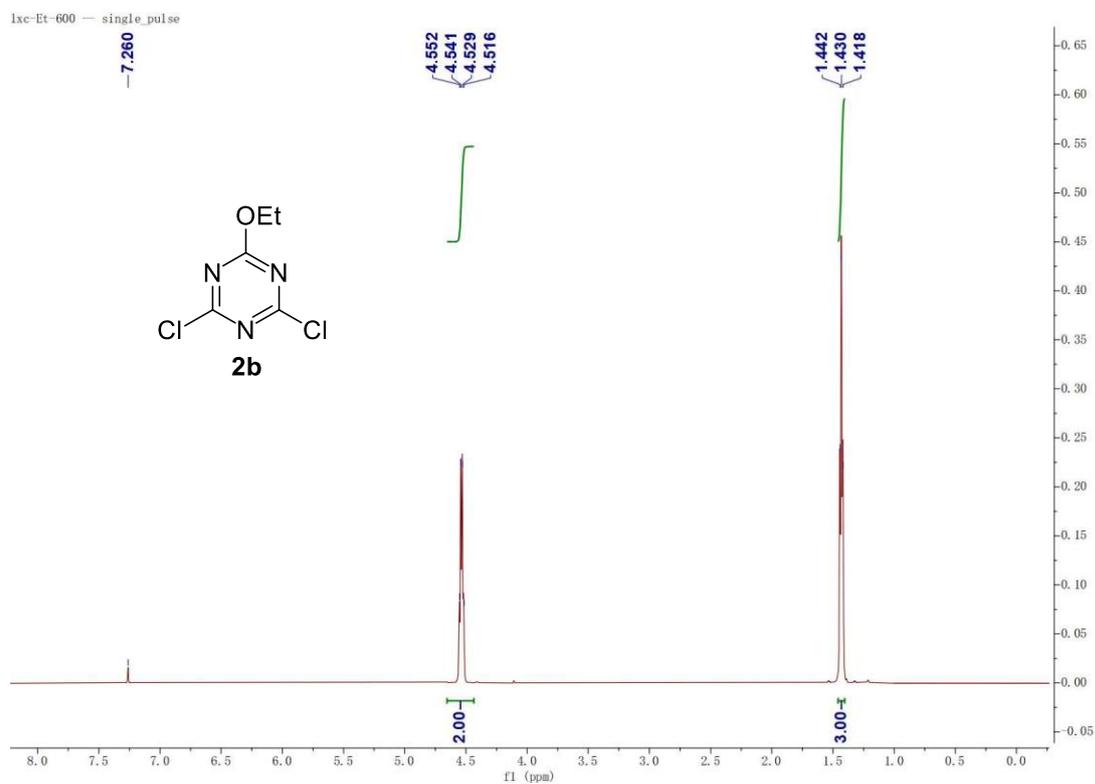
1xc-0Me 1 - single_pulse



2a: ¹³C NMR, 150 MHz, acetone-*d*₆

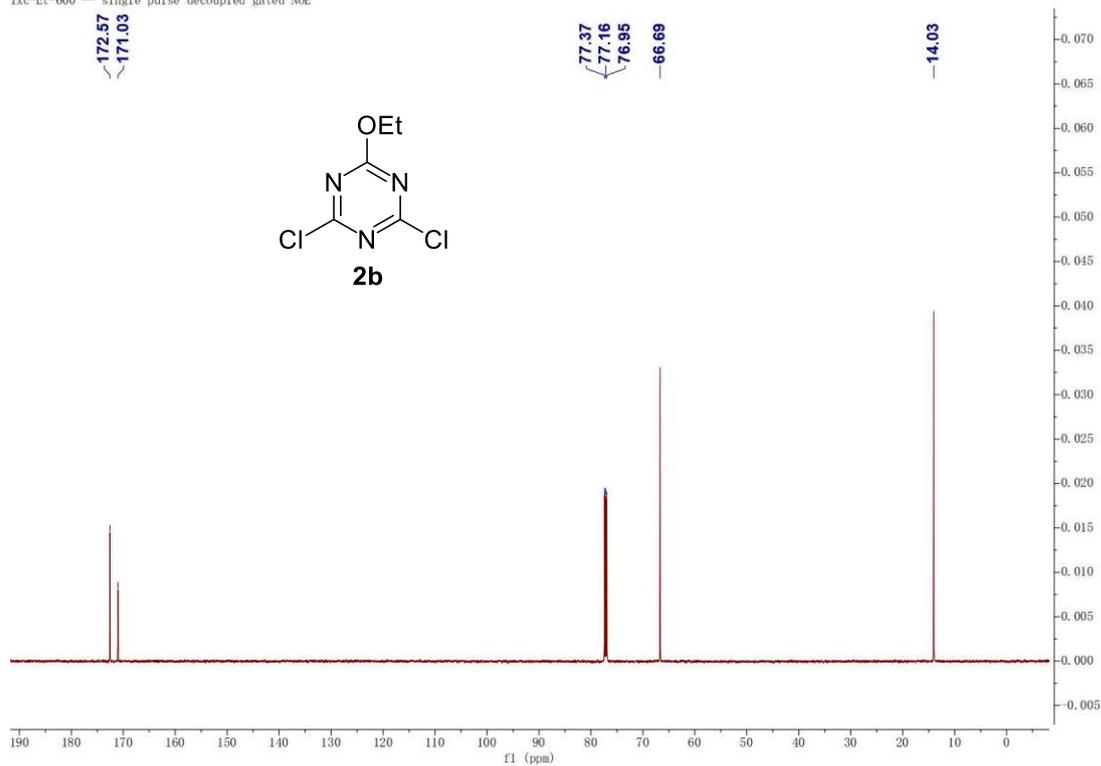


2b: ^1H NMR, 600 MHz, CDCl_3

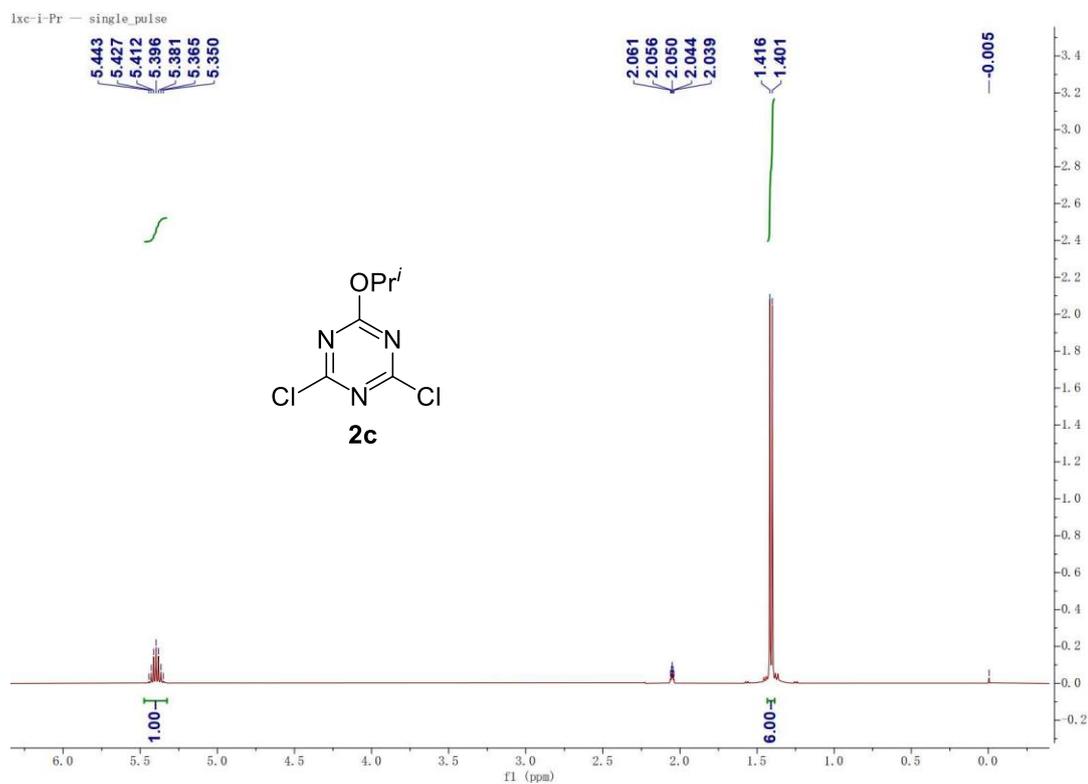


2b: ^{13}C NMR, 150 MHz, CDCl_3

lxc-Et-600 — single pulse decoupled gated NOE

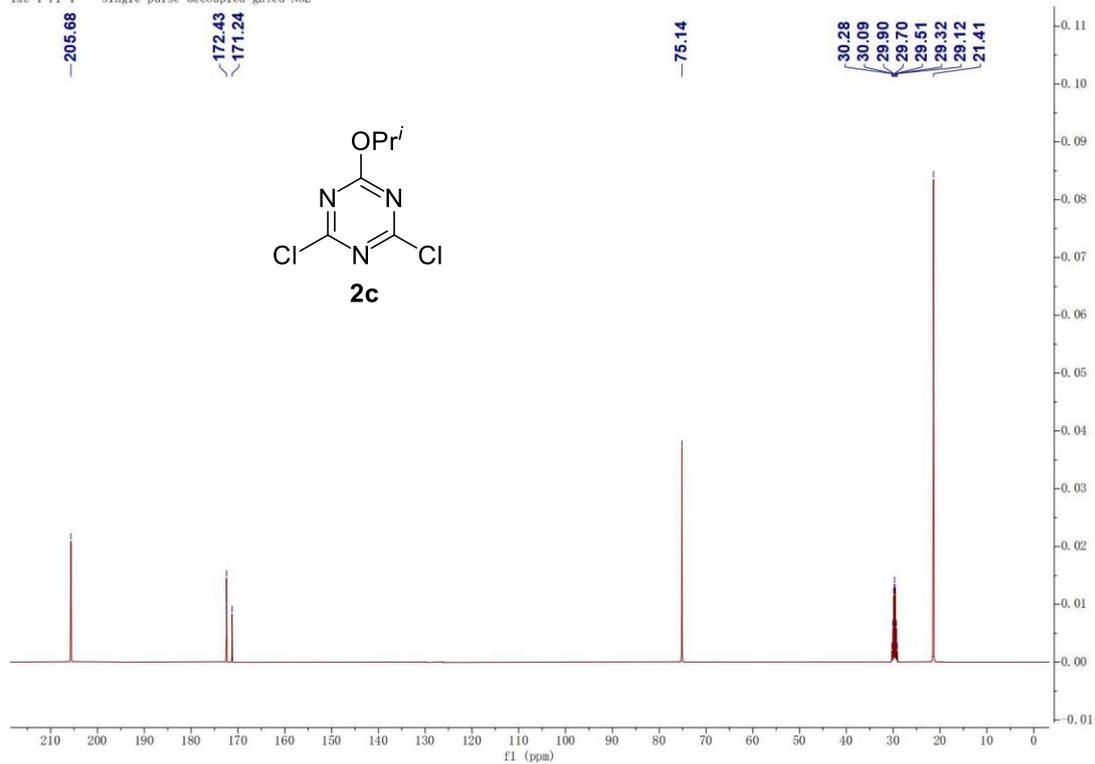


2c: ¹H NMR, 400 MHz, acetone-*d*₆



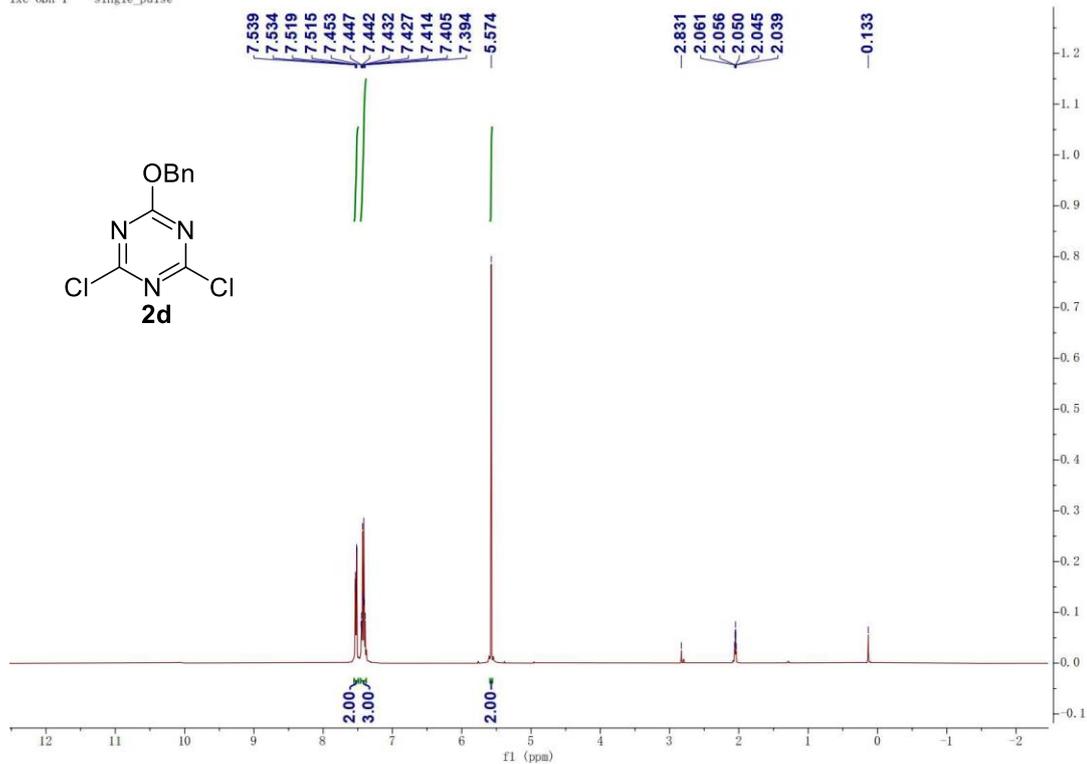
2c: ¹³C NMR, 100 MHz, acetone-*d*₆

lxc-i-Pr 1 — single pulse decoupled gated NOE



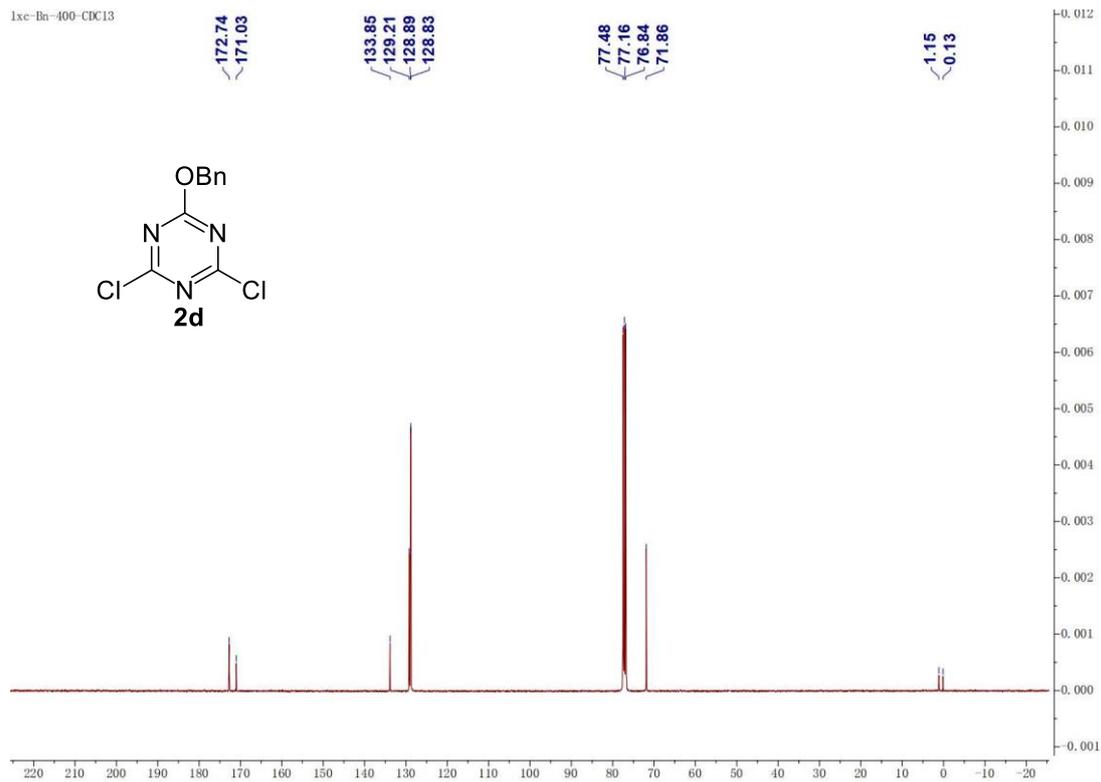
4d: ¹H NMR, 400 MHz, acetone-*d*₆

lxc-OBn 1 — single_pulse



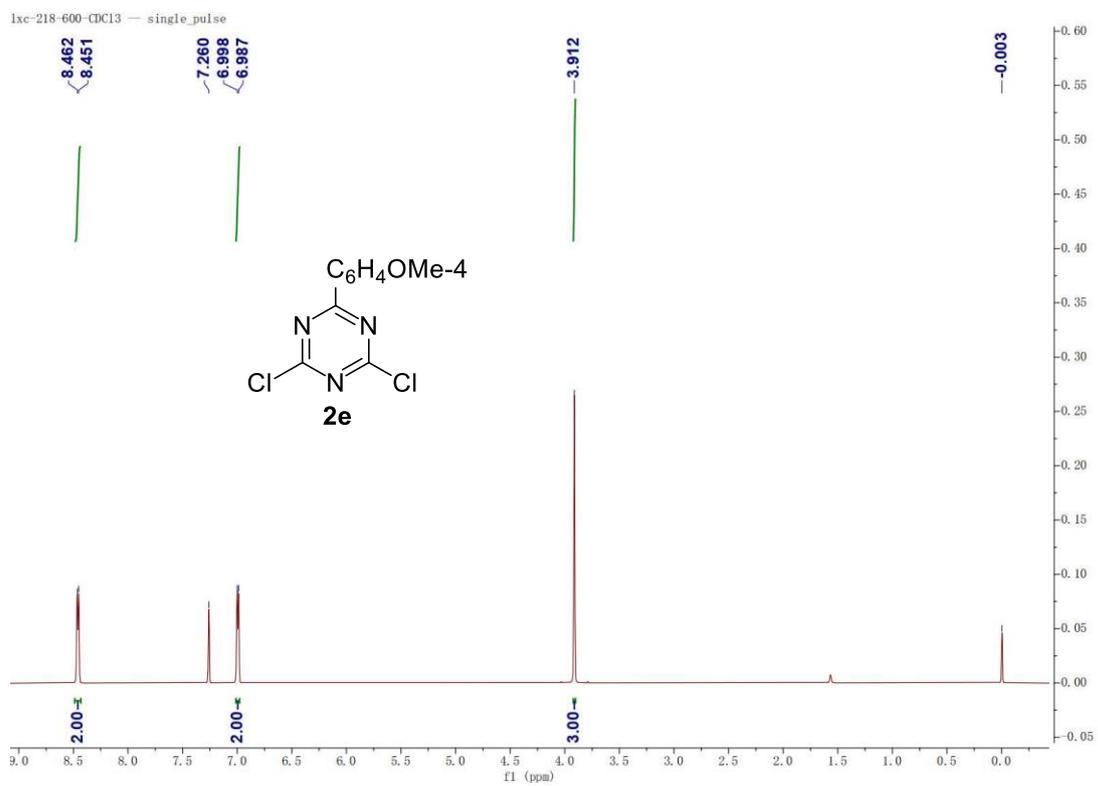
2d: ¹³C NMR, 100 MHz, CDCl₃

1xc-Bn-400-CDCl3

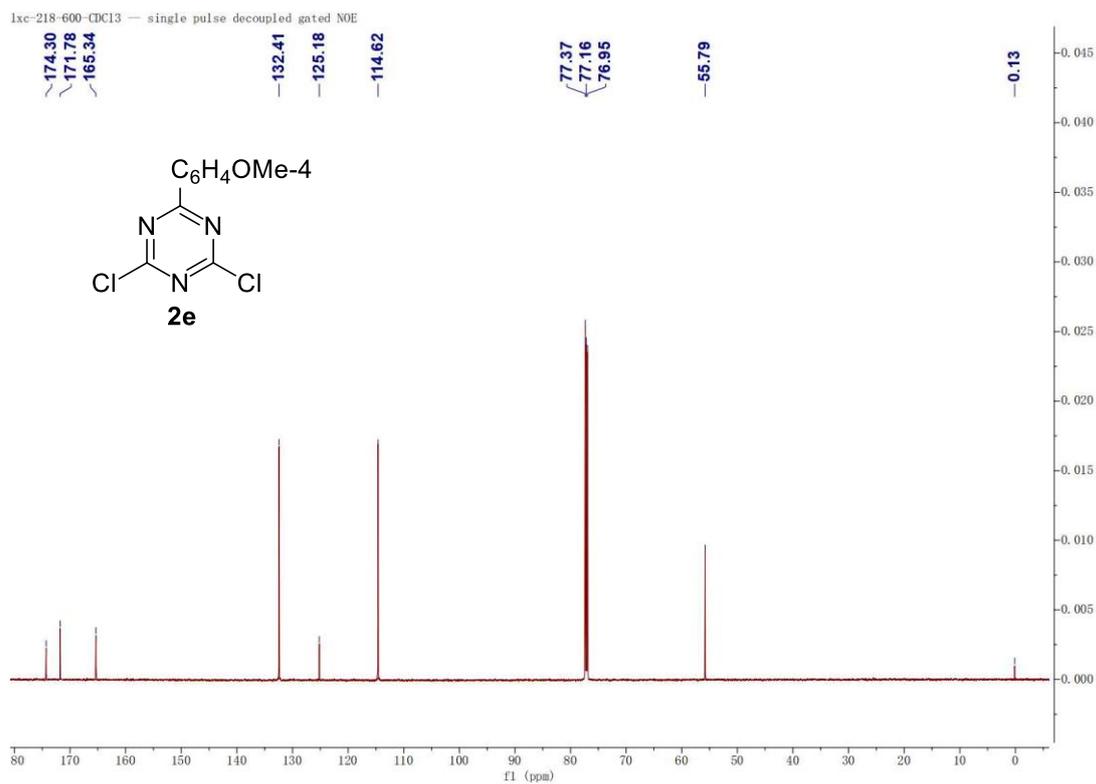


2e: ¹H NMR, 600 MHz, CDCl₃

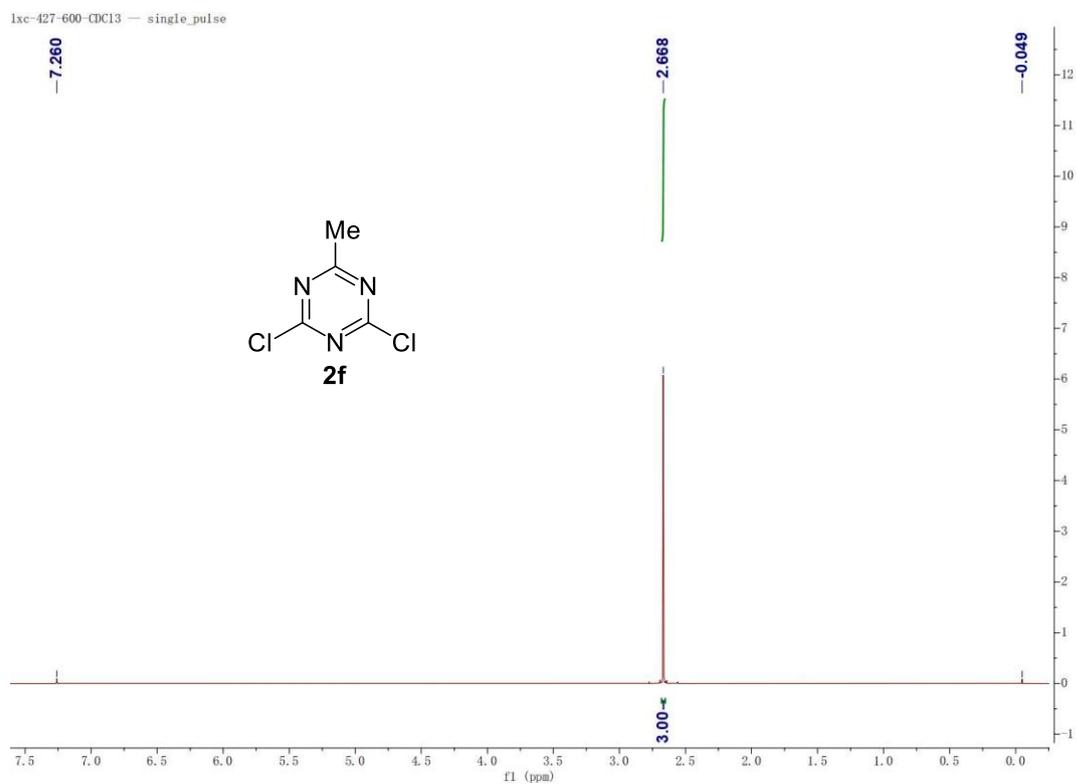
1xc-218-600-CDCl3 - single_pulse



2e: ¹³C NMR, 150 MHz, CDCl₃

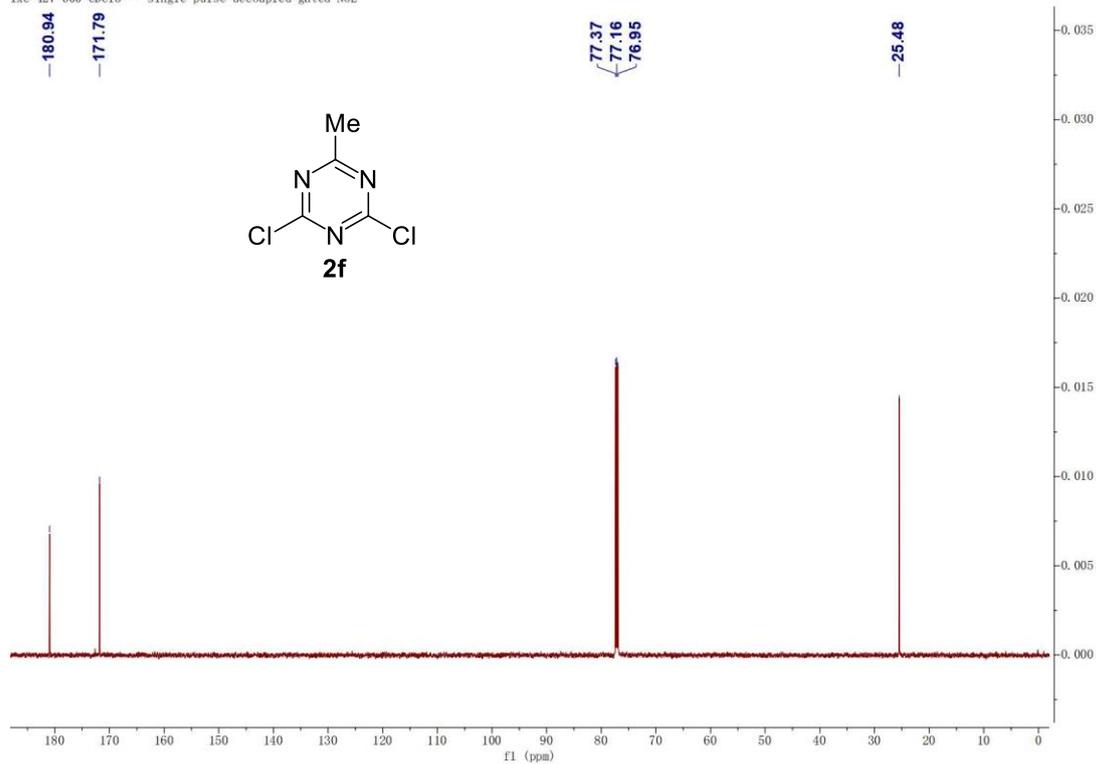


2f: ^1H NMR, 600 MHz, CDCl_3



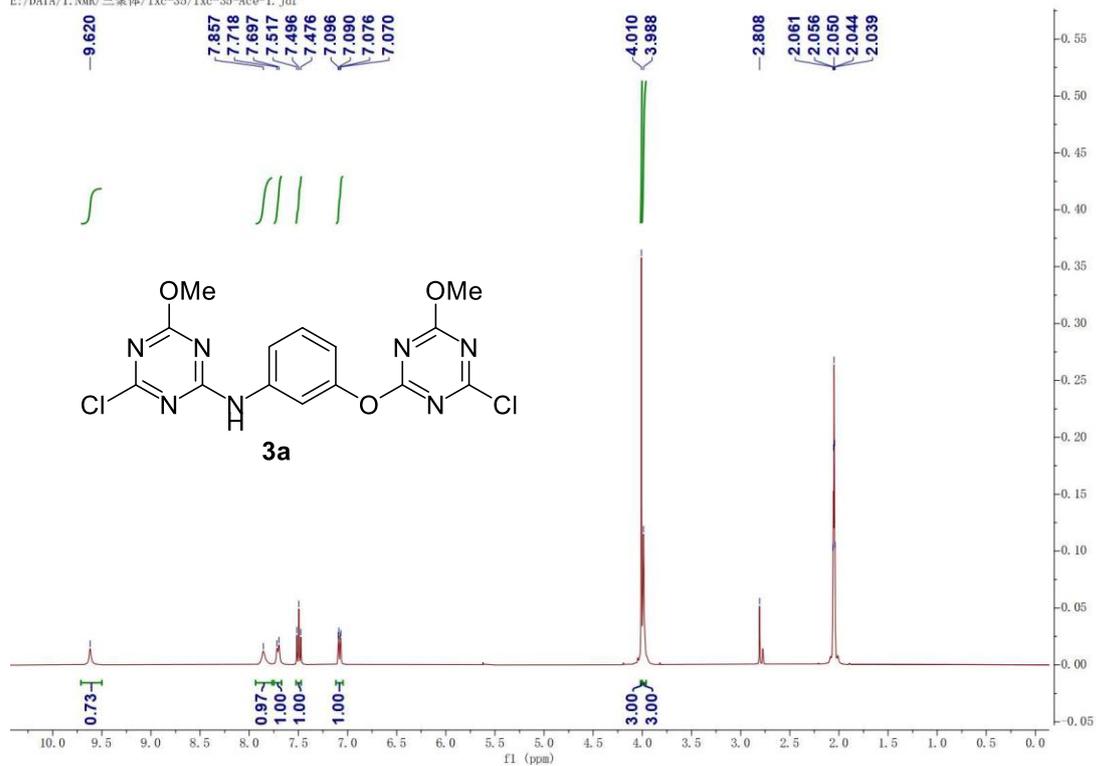
2f: ^{13}C NMR, 150 MHz, CDCl_3

lxc-427-600-CDCl3 — single pulse decoupled gated NOE



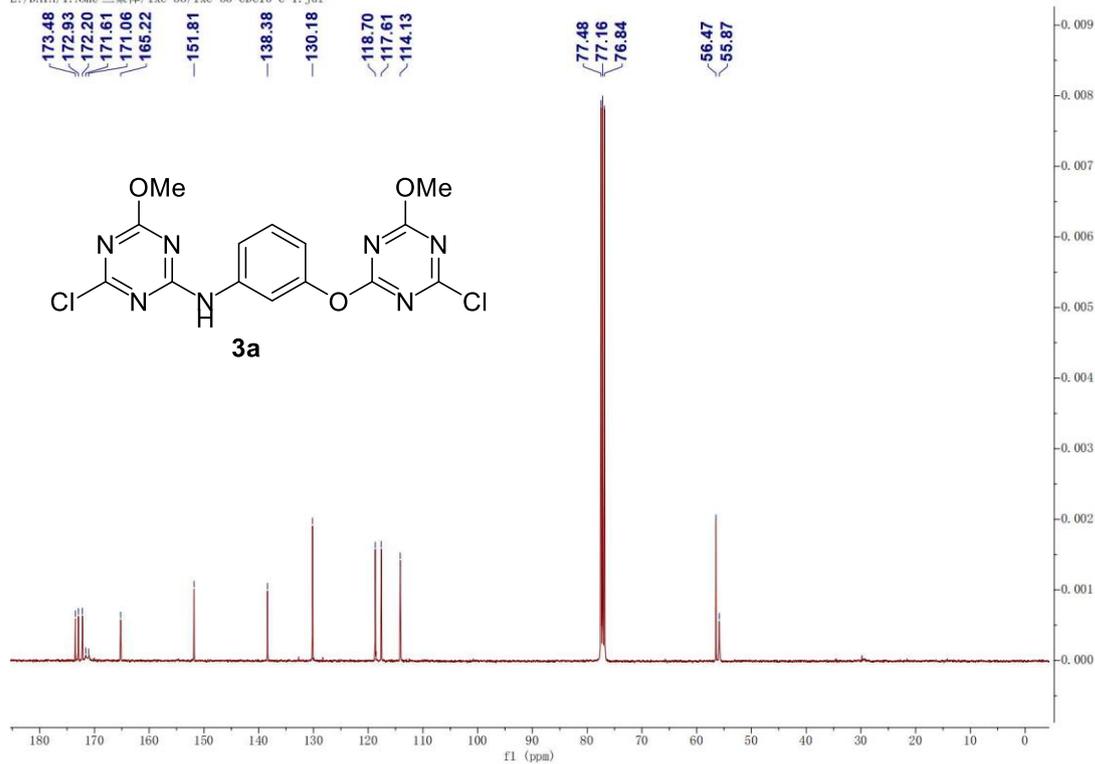
3a: ¹H NMR, 400 MHz, acetone-*d*₆

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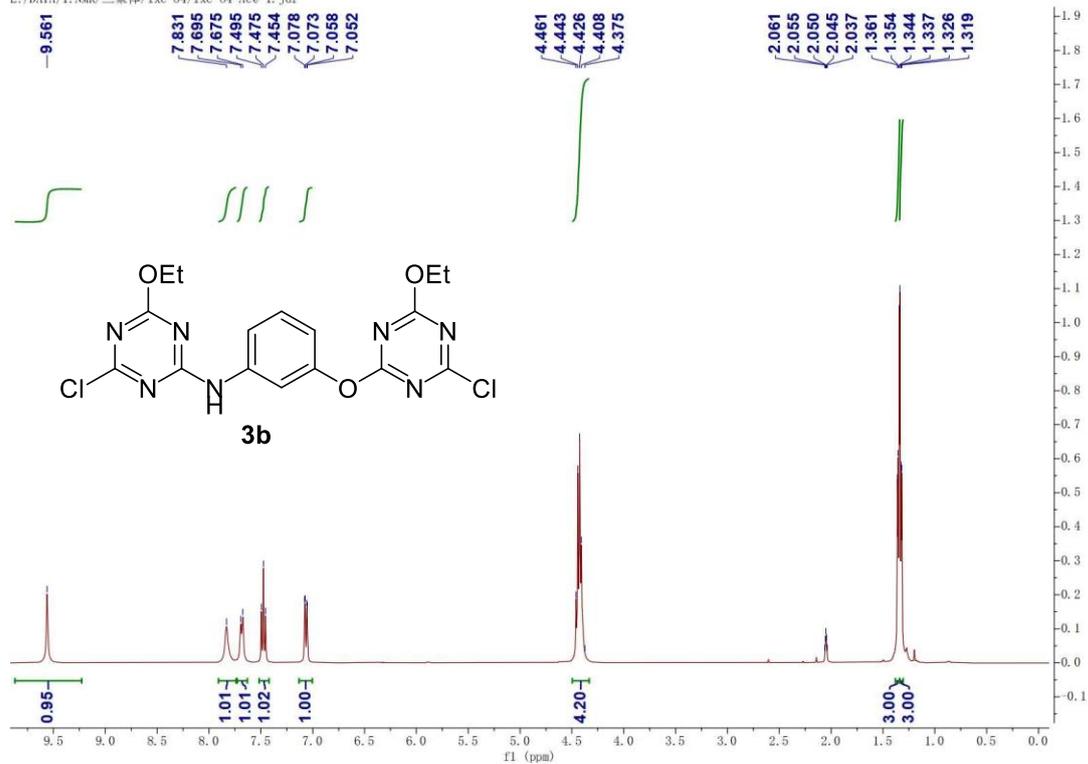
3a: ¹³C NMR, 100 MHz, CDCl₃

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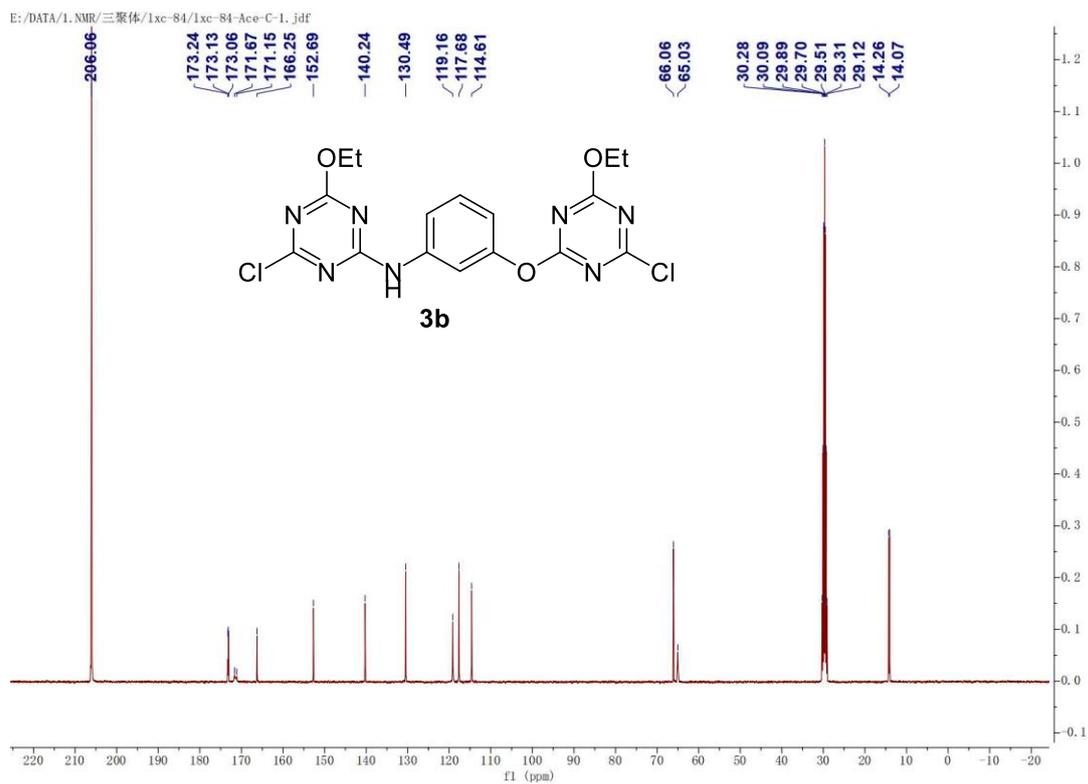


3b: ¹H NMR, 400 MHz, acetone-*d*₆

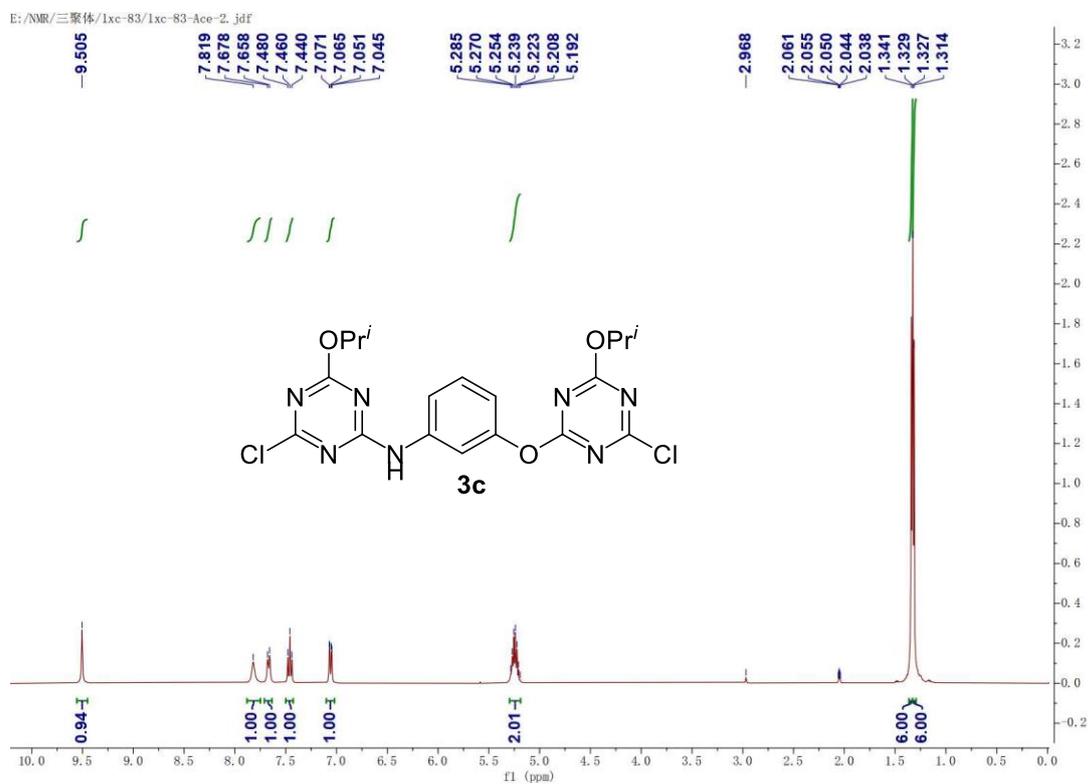
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3b: ¹³C NMR, 100 MHz, acetone-*d*₆

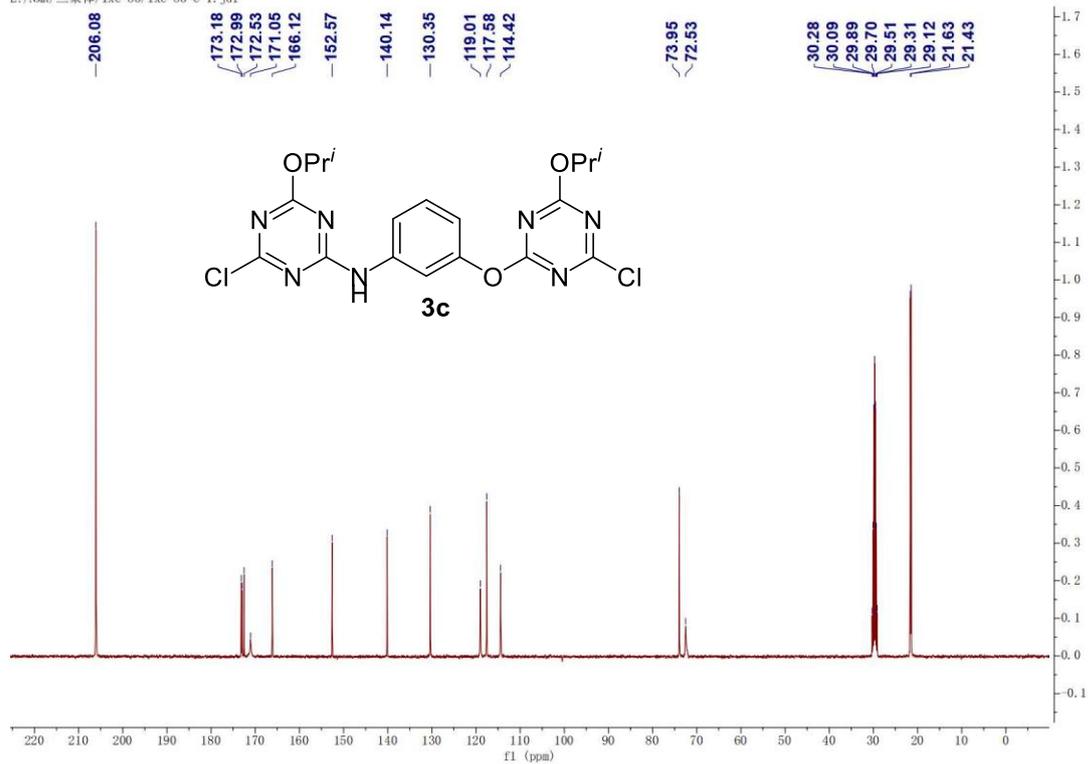


3c: ¹H NMR, 400 MHz, acetone-*d*₆



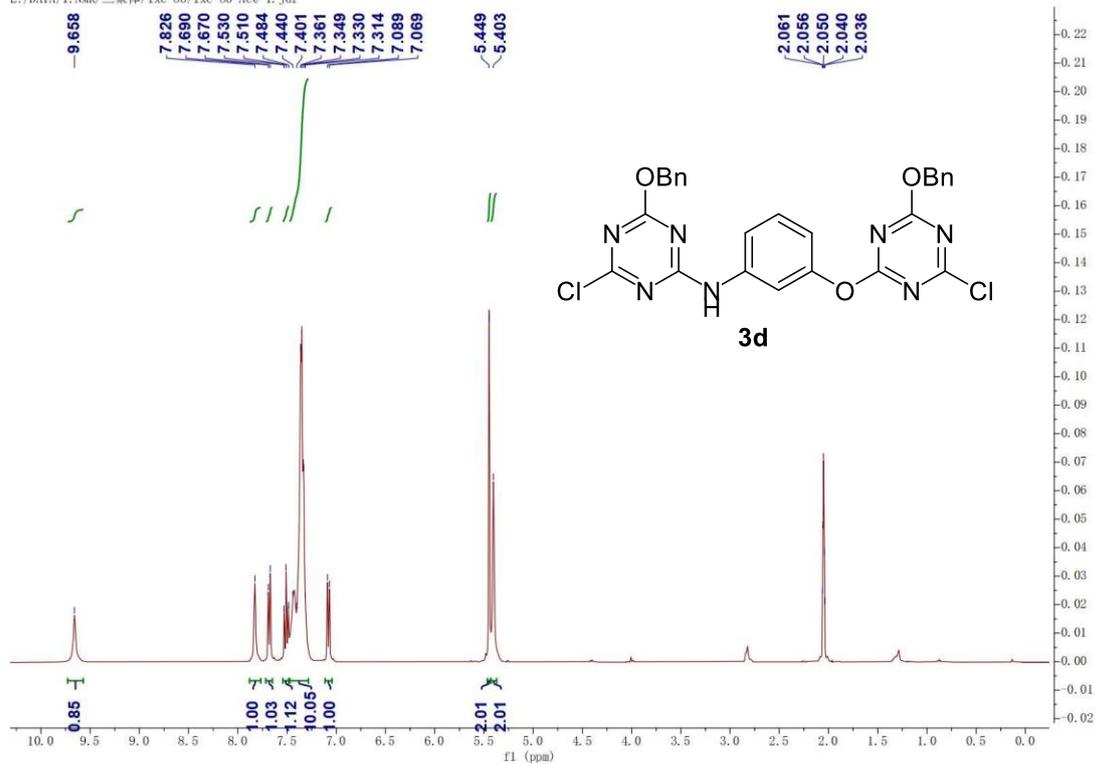
3c: ¹³C NMR, 100 MHz, acetone-*d*₆

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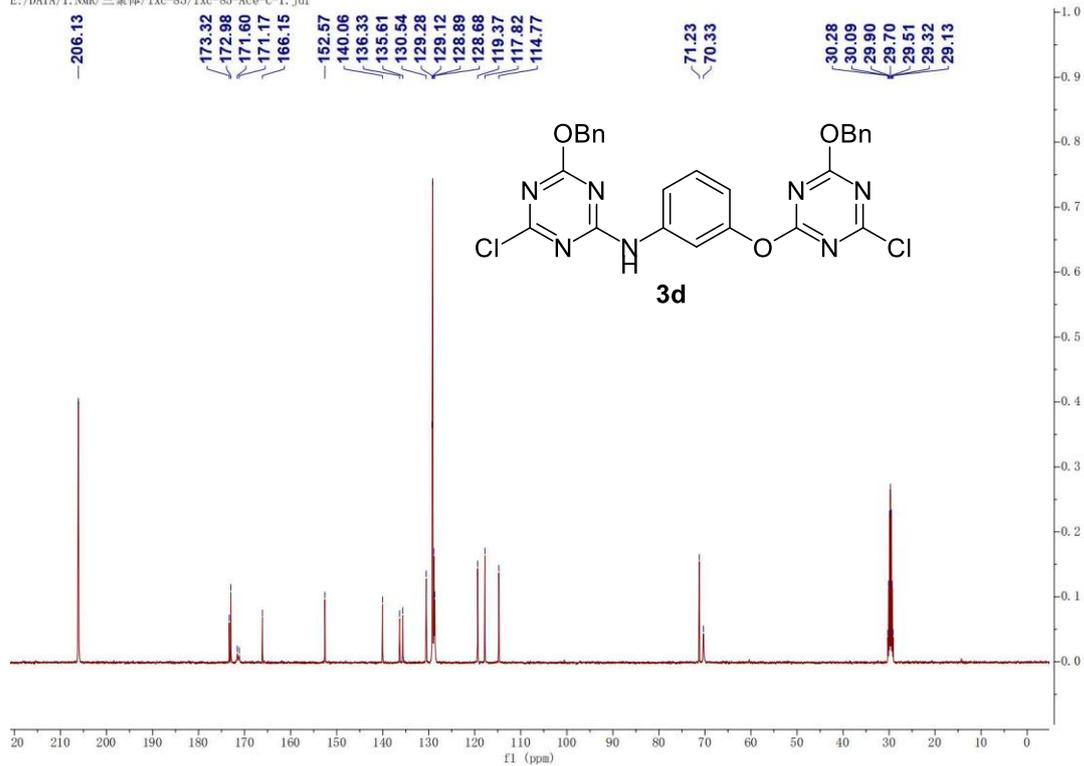
3d: ^1H NMR, 400 MHz, acetone- d_6

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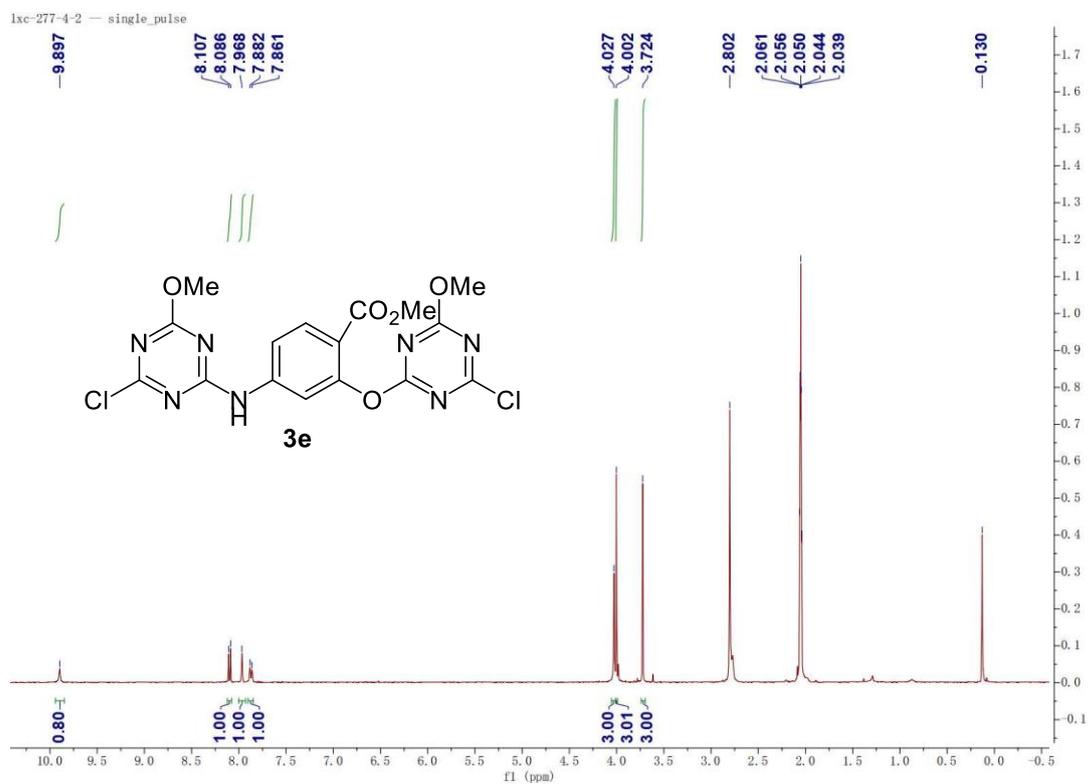


3d: ^{13}C NMR, 100 MHz, acetone- d_6

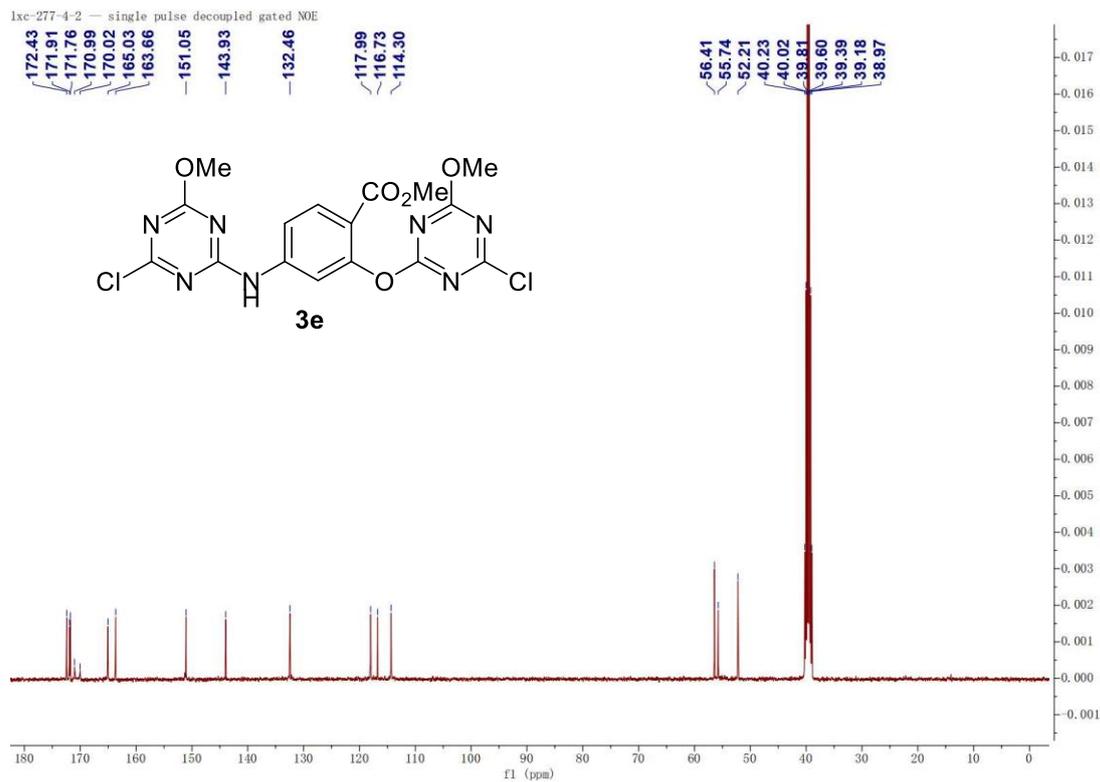
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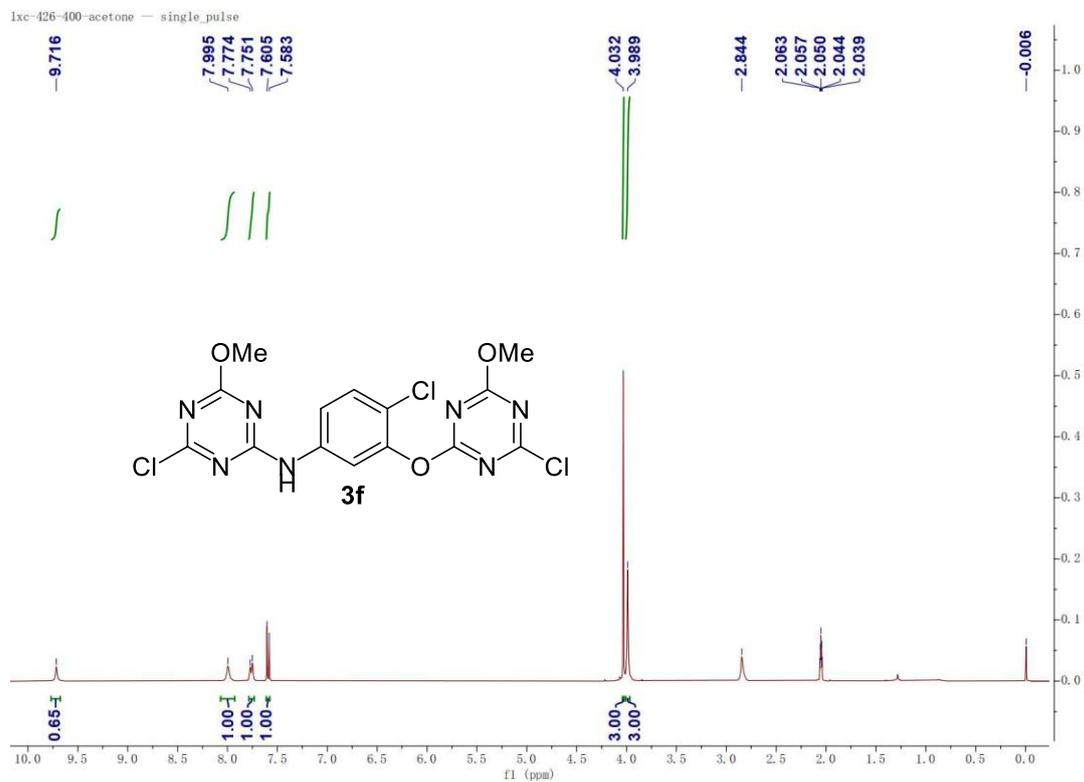
3e: ¹H NMR, 400 MHz, acetone-*d*₆



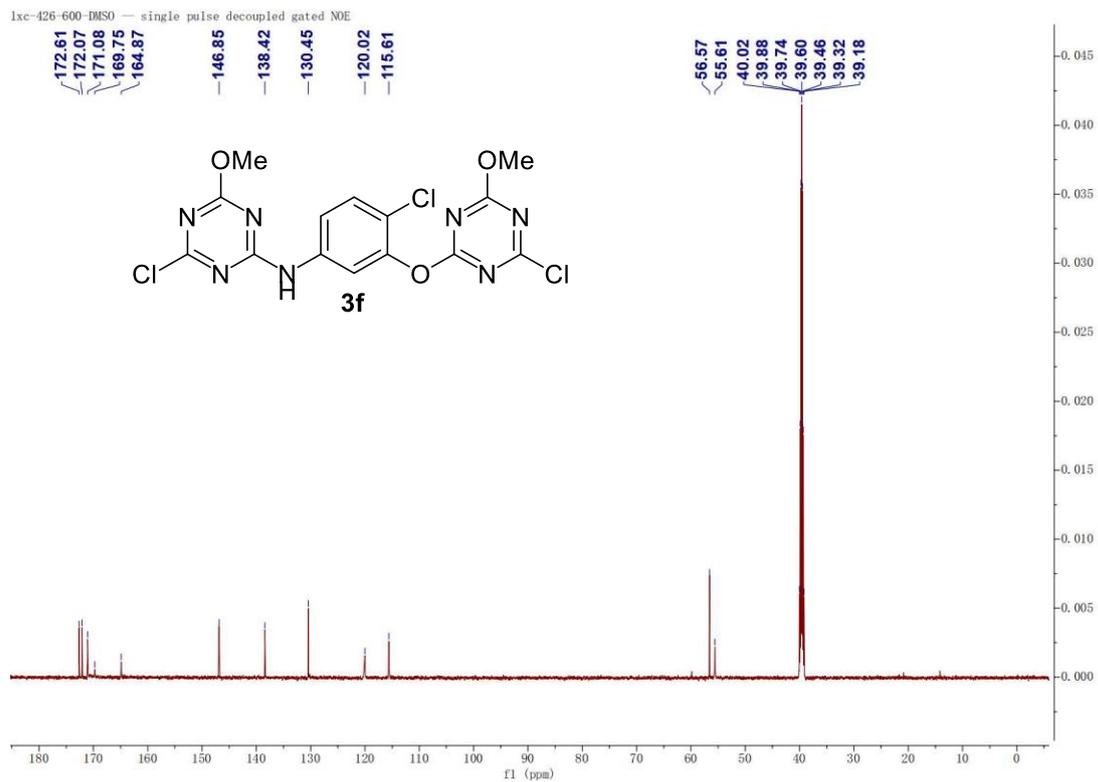
3e: ¹³C NMR, 100 MHz, DMSO-*d*₆



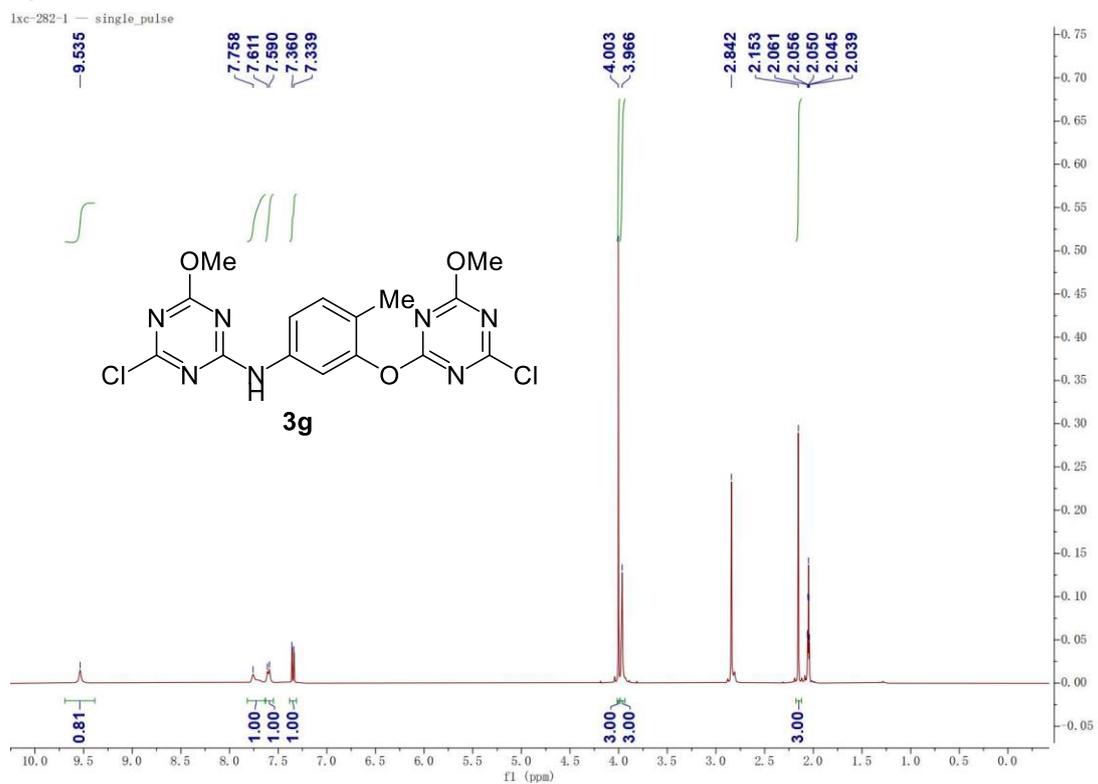
3f: ¹H NMR, 400 MHz, acetone-*d*₆



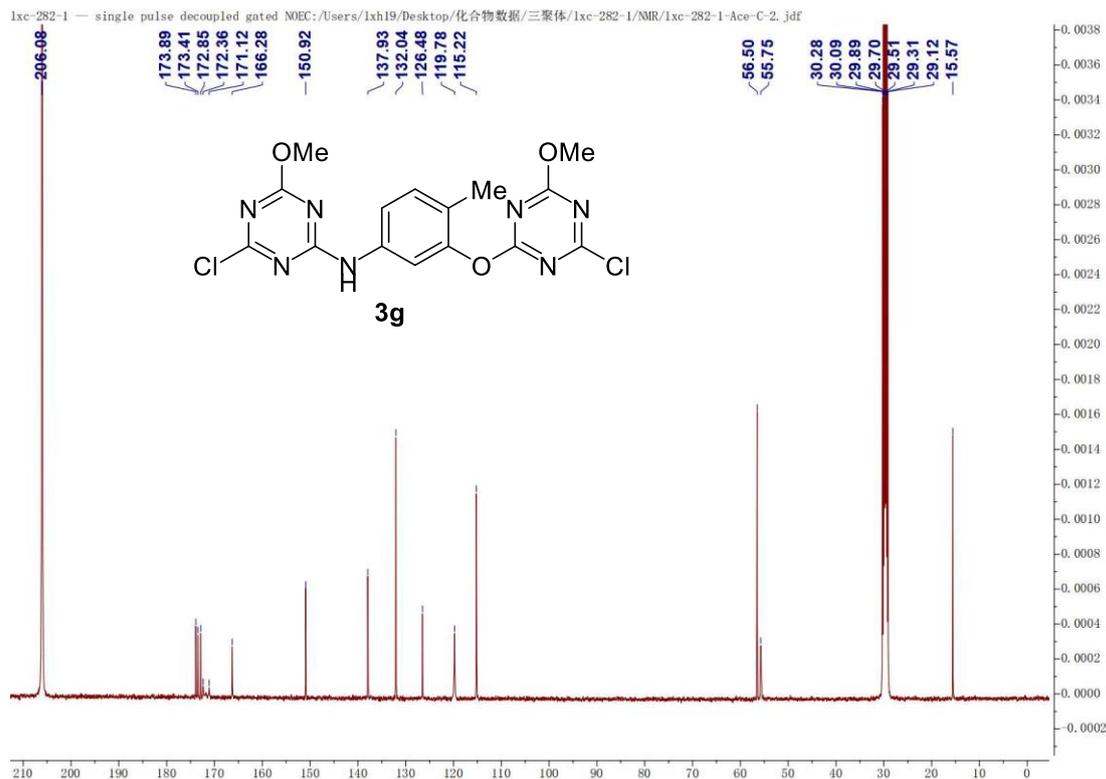
3f: ¹³C NMR, 150 MHz, DMSO-*d*₆



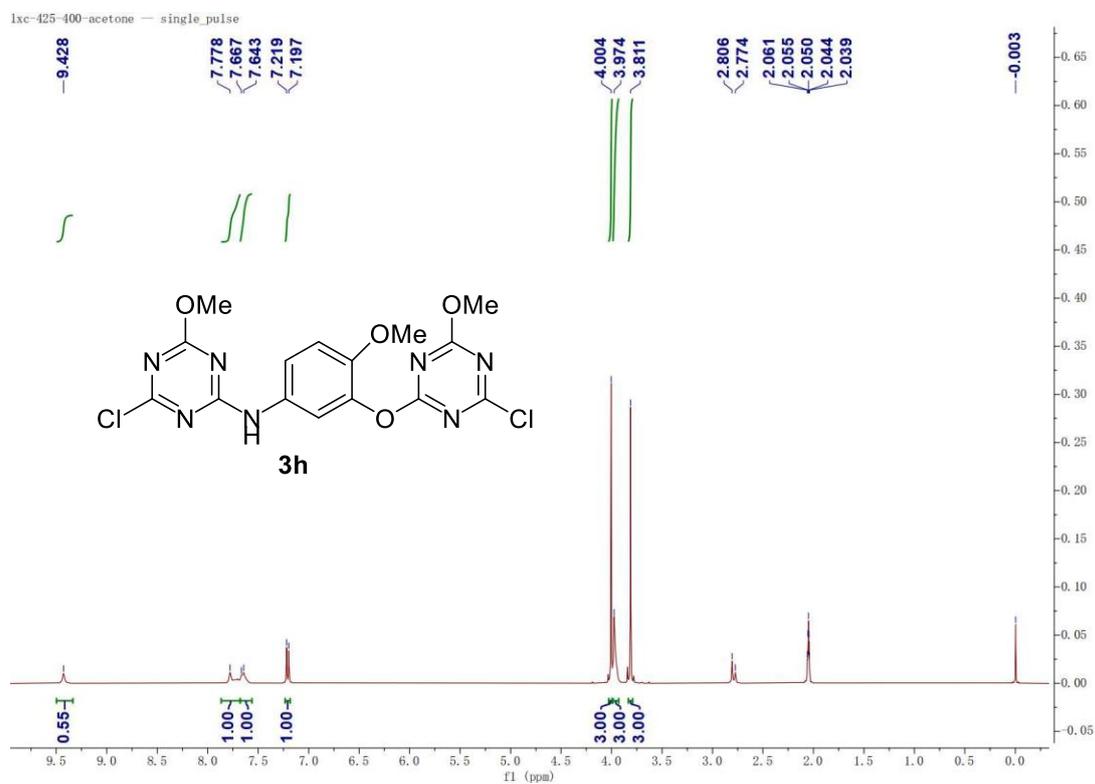
3g: ¹H NMR, 400 MHz, acetone-*d*₆



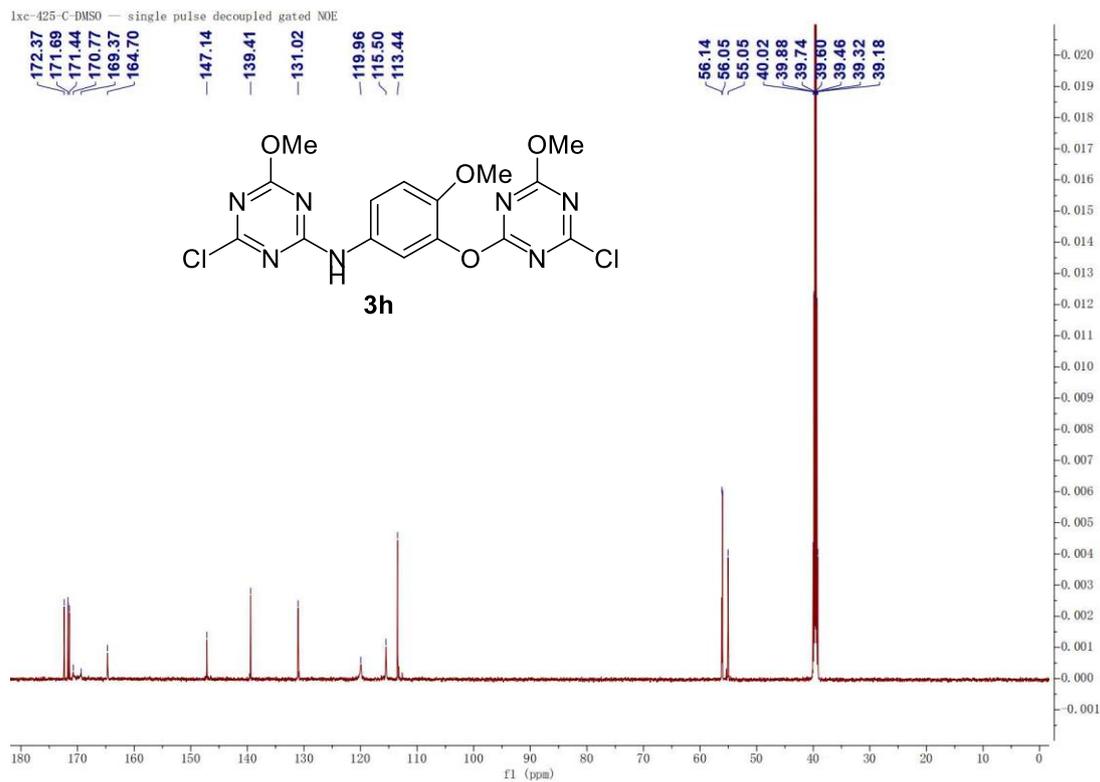
3g: ¹³C NMR, 100 MHz, acetone-*d*₆



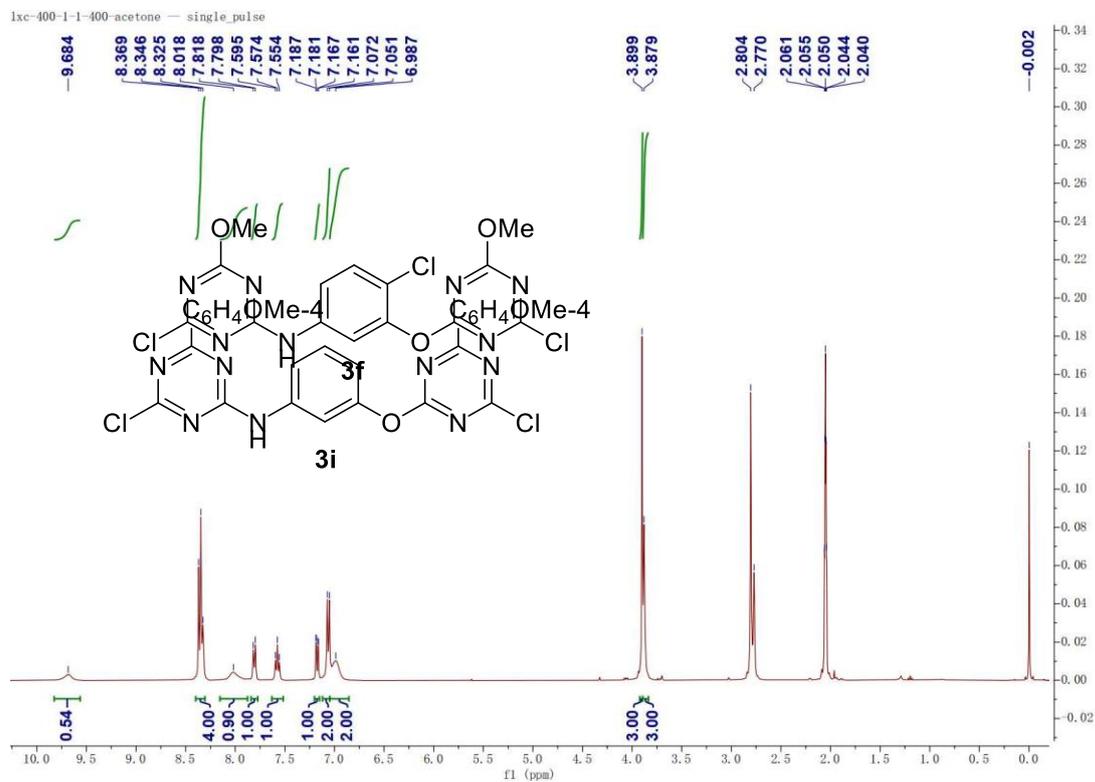
3h: ^1H NMR, 400 MHz, acetone- d_6



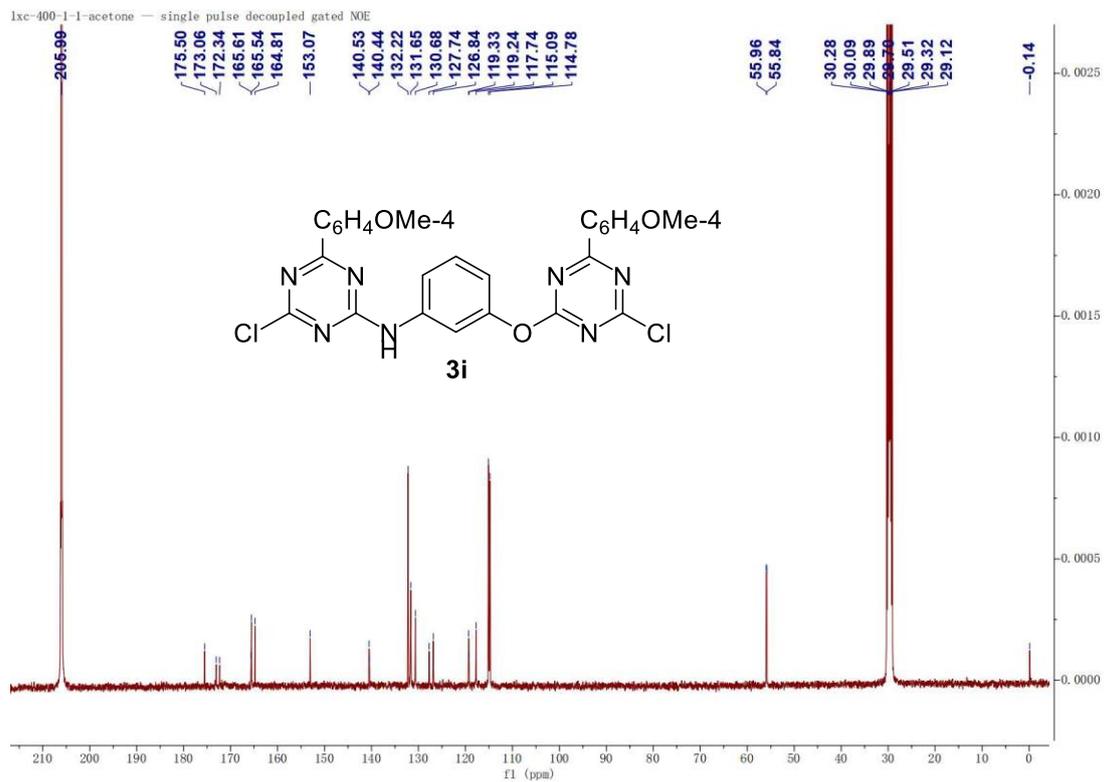
3h: ^{13}C NMR, 150 MHz, DMSO- d_6 , 60 °C



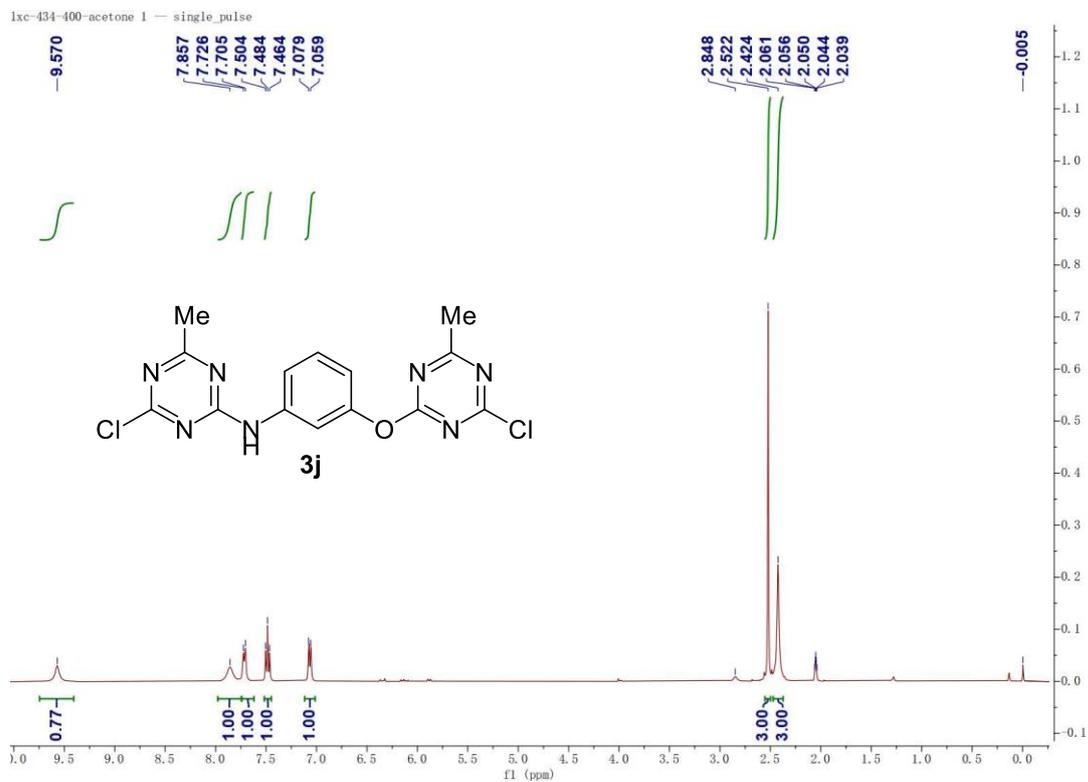
3i: ^1H NMR, 400 MHz, acetone- d_6



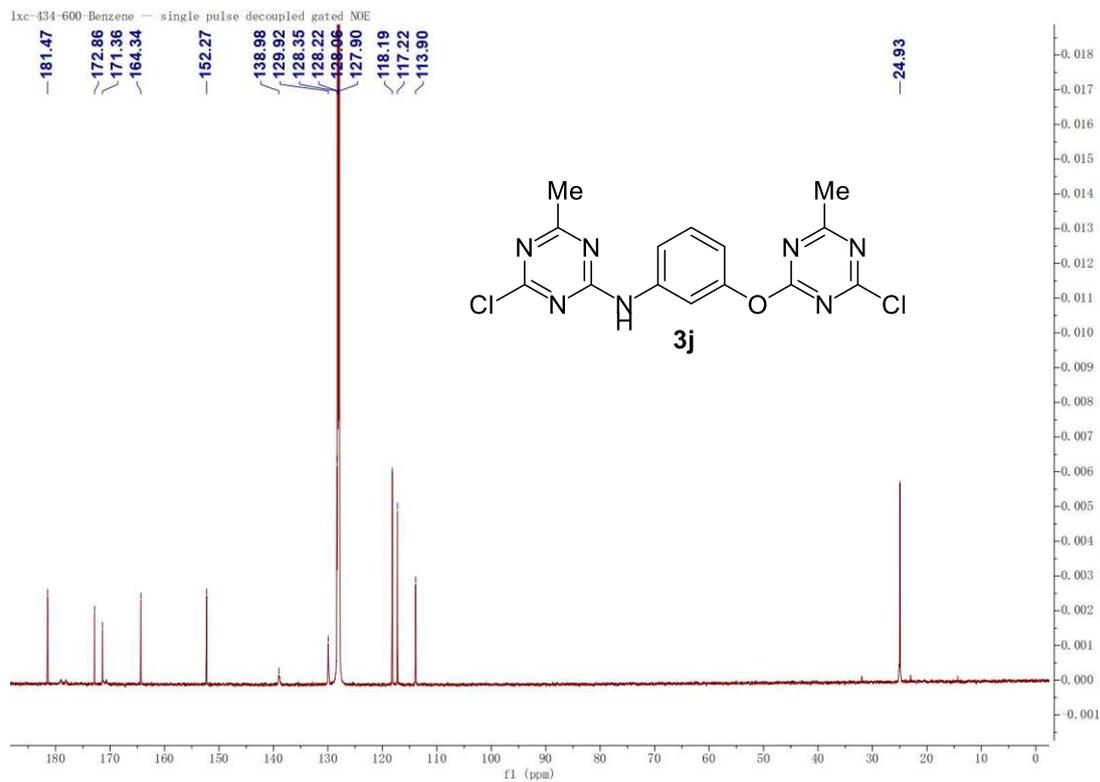
3i: ^{13}C NMR, 150 MHz, acetone- d_6



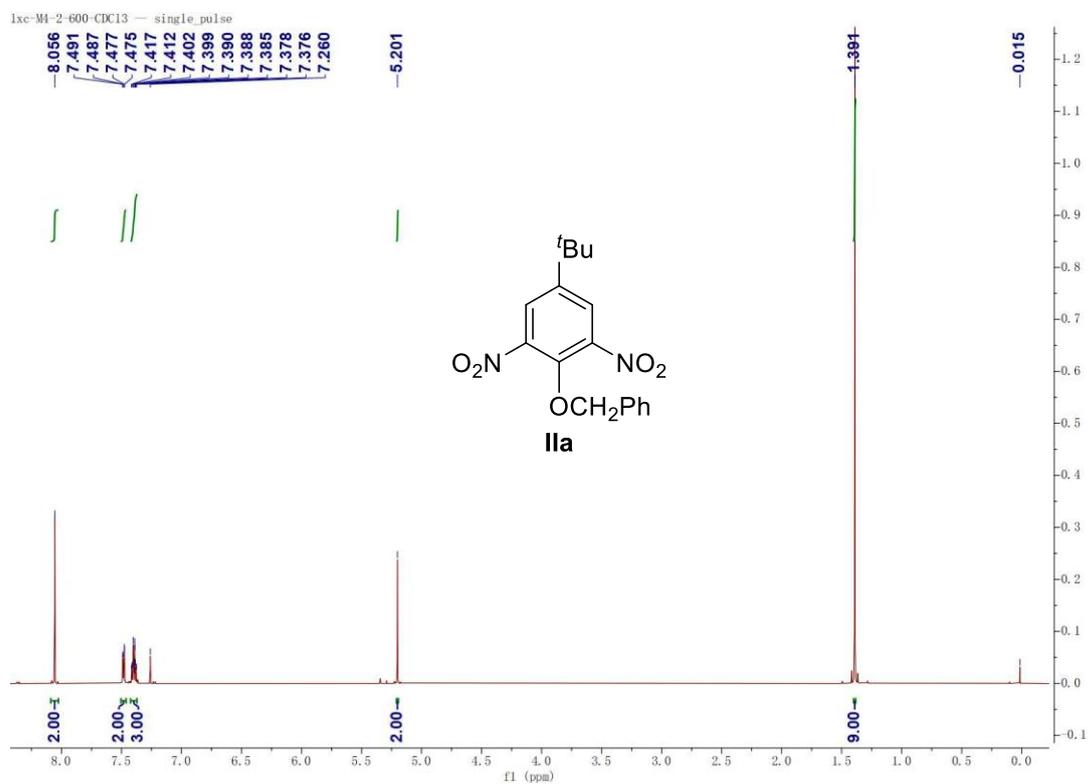
3j: ¹H NMR, 400 MHz, acetone-*d*₆



3j: ¹³C NMR, 150 MHz, benzene-*d*₆

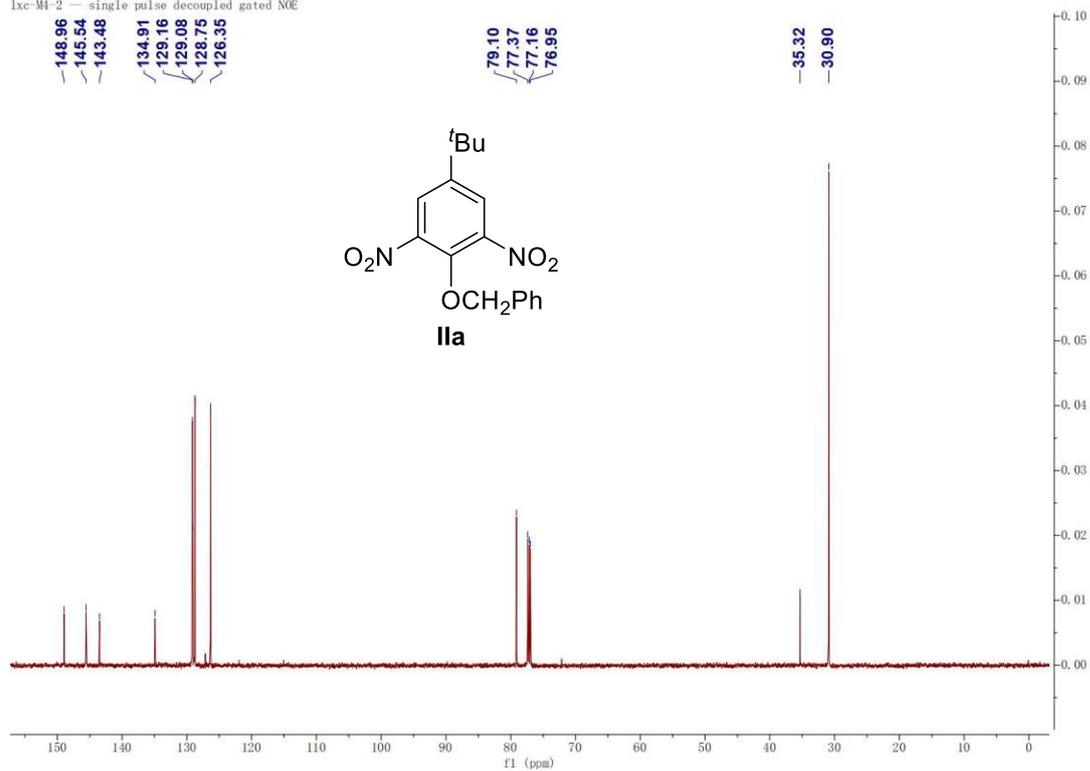


IIa: ^1H NMR, 600 MHz, CDCl_3



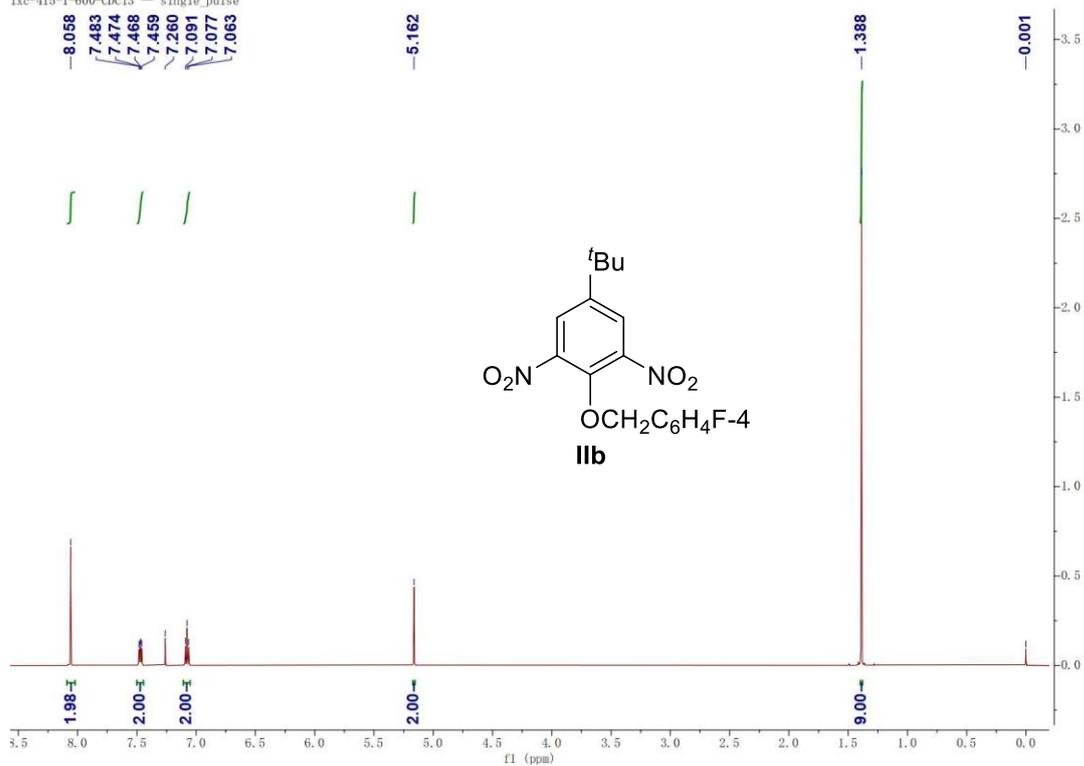
IIa: ^{13}C NMR, 150 MHz, CDCl_3

lxc-M4-2 - single pulse decoupled gated NOE

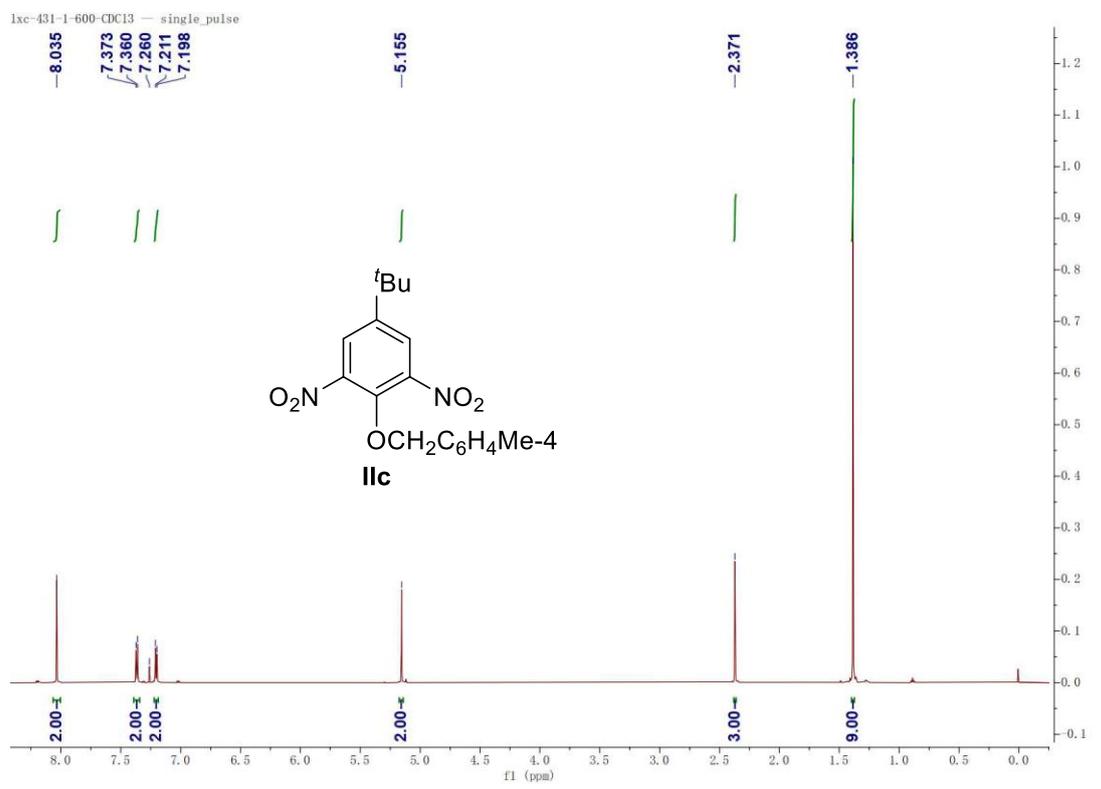
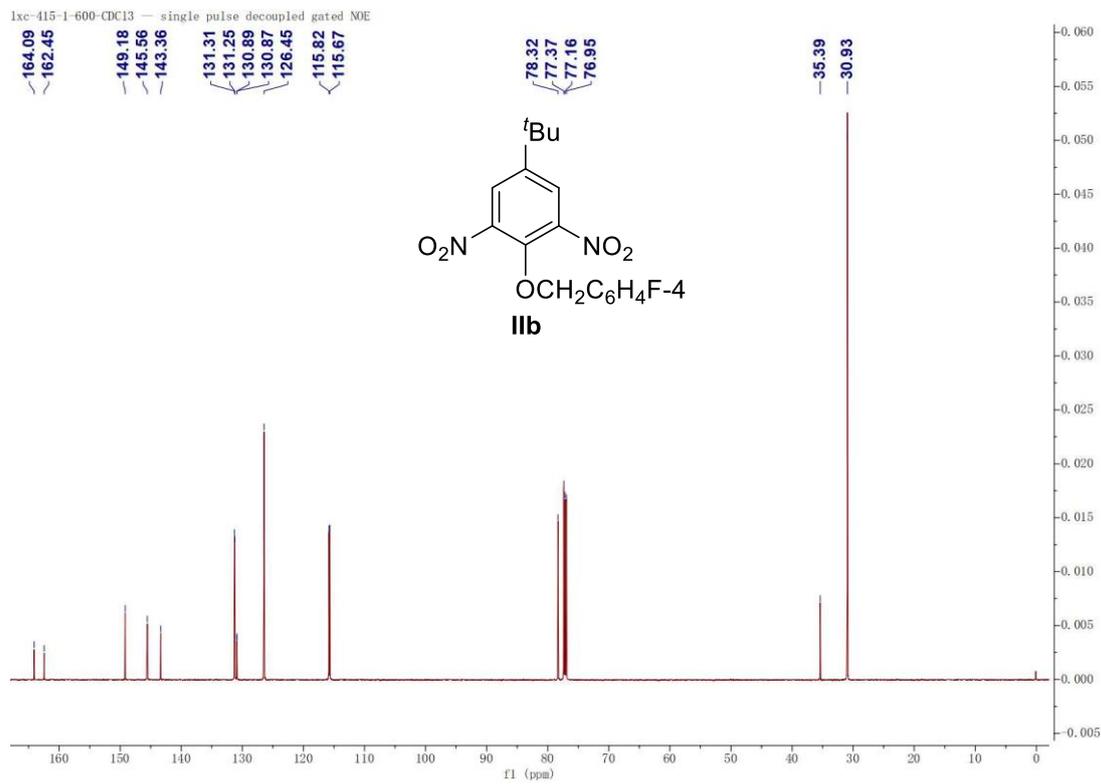


IIb: ^1H NMR, 600 MHz, CDCl_3

lxc-415-1-600- CDCl_3 - single_pulse

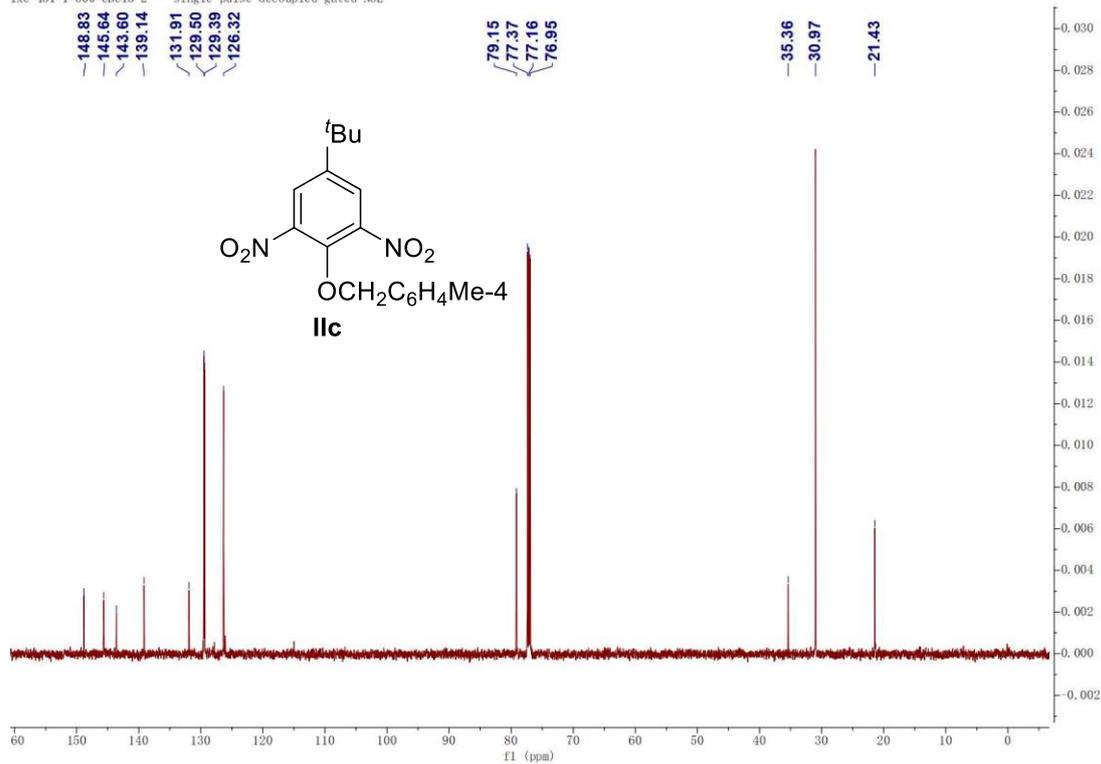


IIb: ^{13}C NMR, 150 MHz, CDCl_3



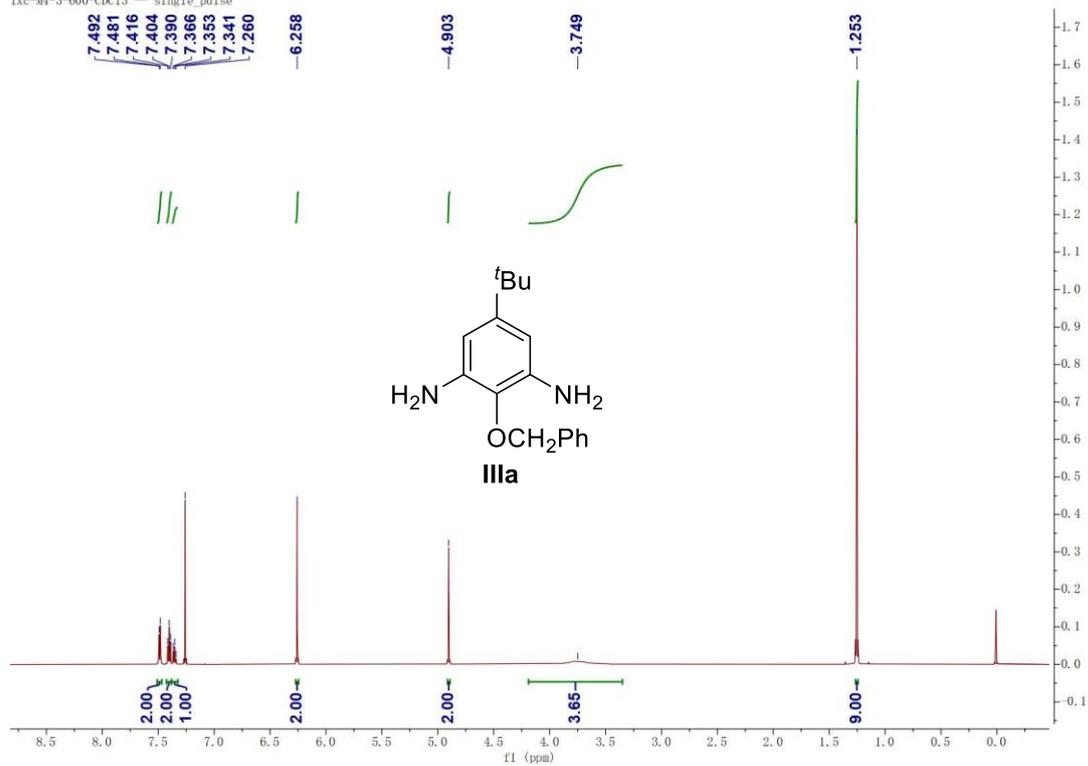
IIc: ^{13}C NMR, 150 MHz, CDCl_3

1xc-431-1-600-CDCl3 2 - single pulse decoupled gated NDE



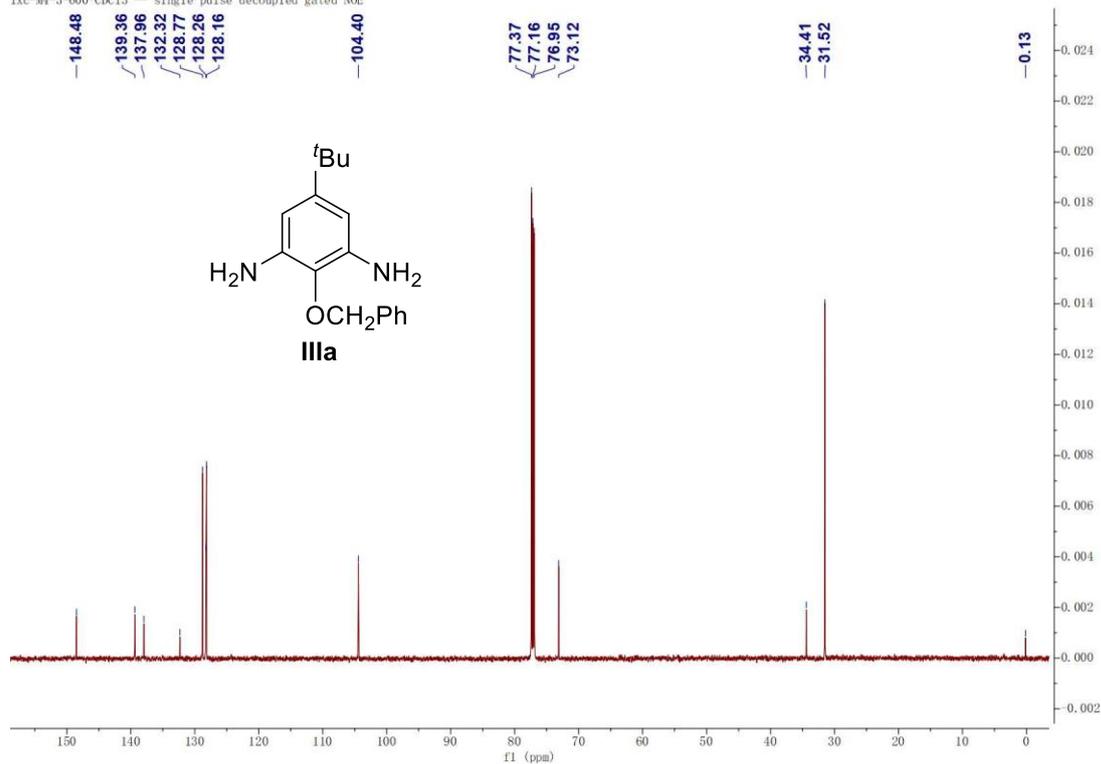
IIIa: ^1H NMR, 600 MHz, CDCl_3

1xc-M-3-600-CDCl3 - single pulse



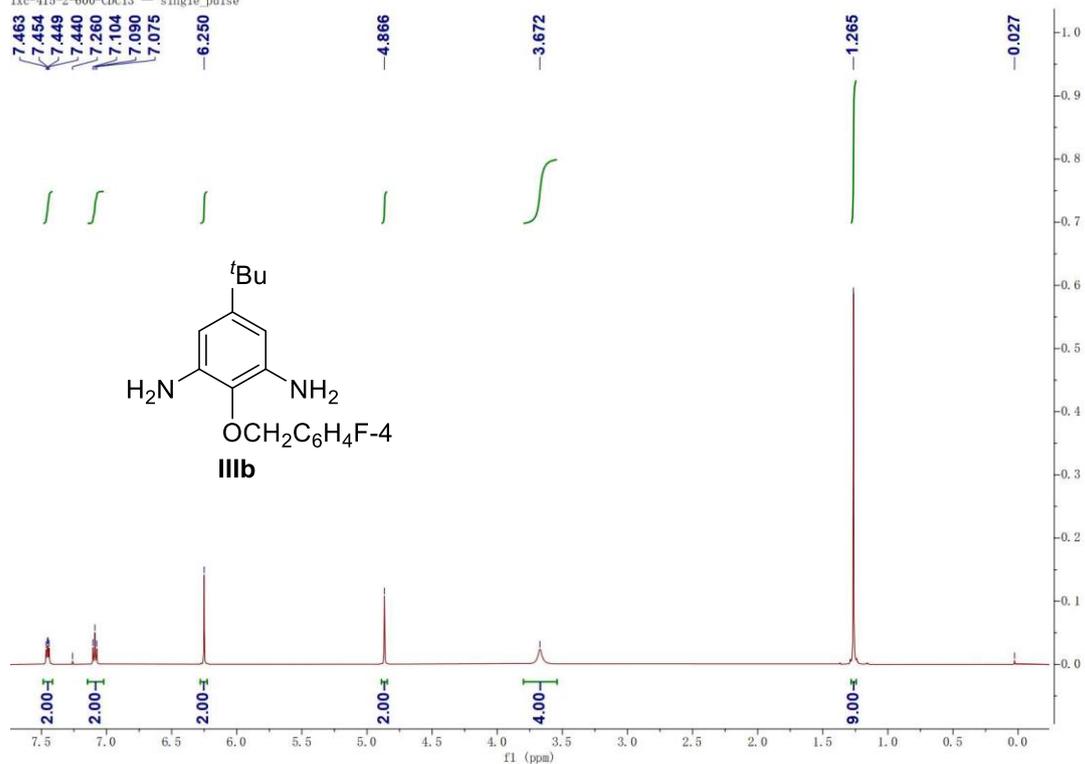
IIIa: ^{13}C NMR, 150 MHz, CDCl_3

lxc-M-3-600-CDCl3 — single pulse decoupled gated NOE



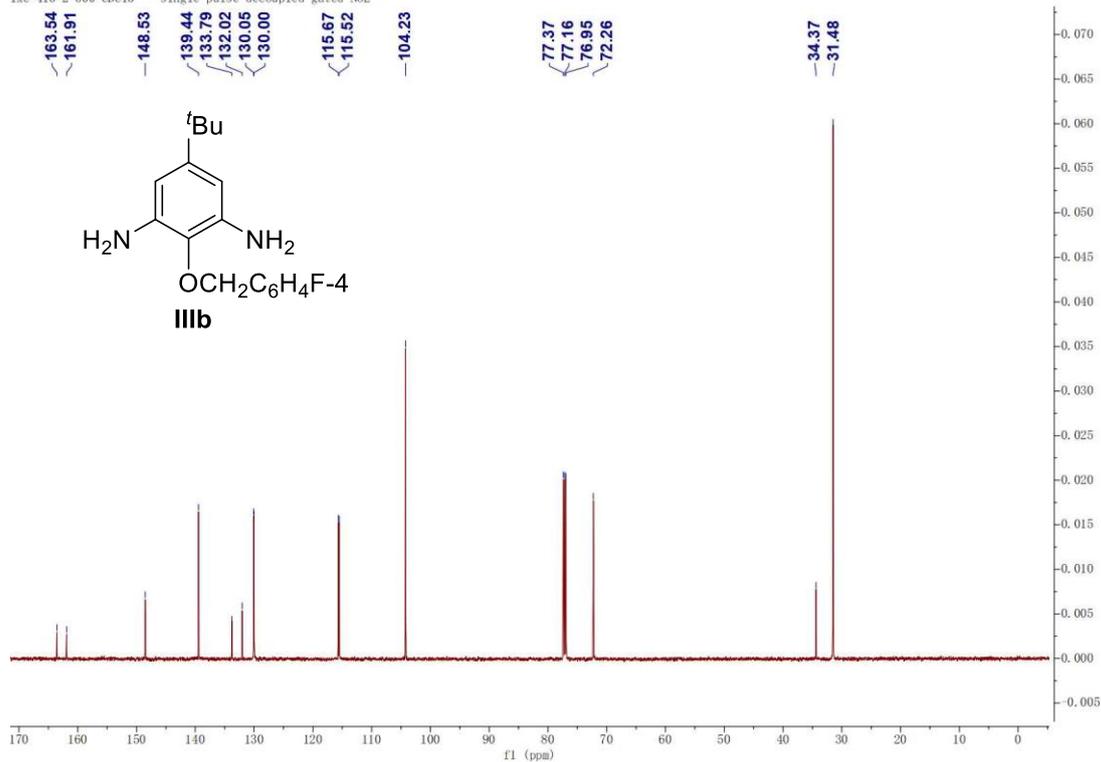
IIIb: ^1H NMR, 600 MHz, CDCl_3

lxc-415-2-600-CDCl3 — single_pulse



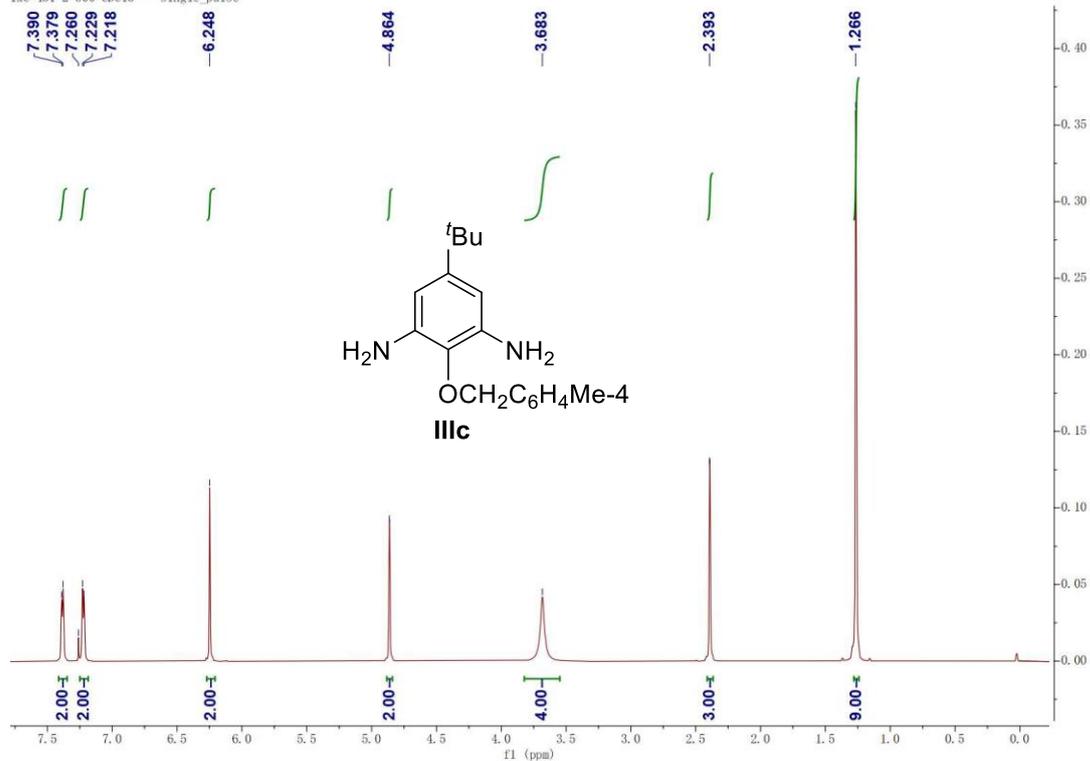
IIIb: ^{13}C NMR, 100 MHz, CDCl_3

lxc-415-2-600- CDCl_3 — single pulse decoupled gated NOE



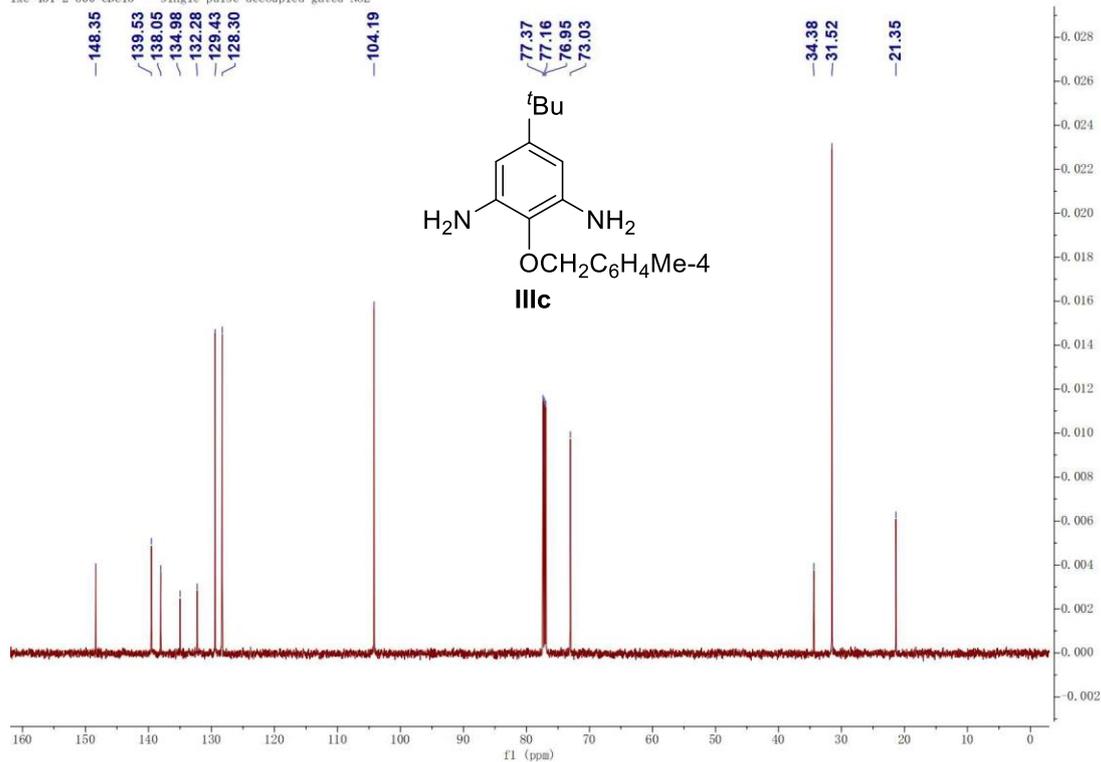
IIIc: ^1H NMR, 600 MHz, CDCl_3

lxc-431-2-600- CDCl_3 — single_pulse



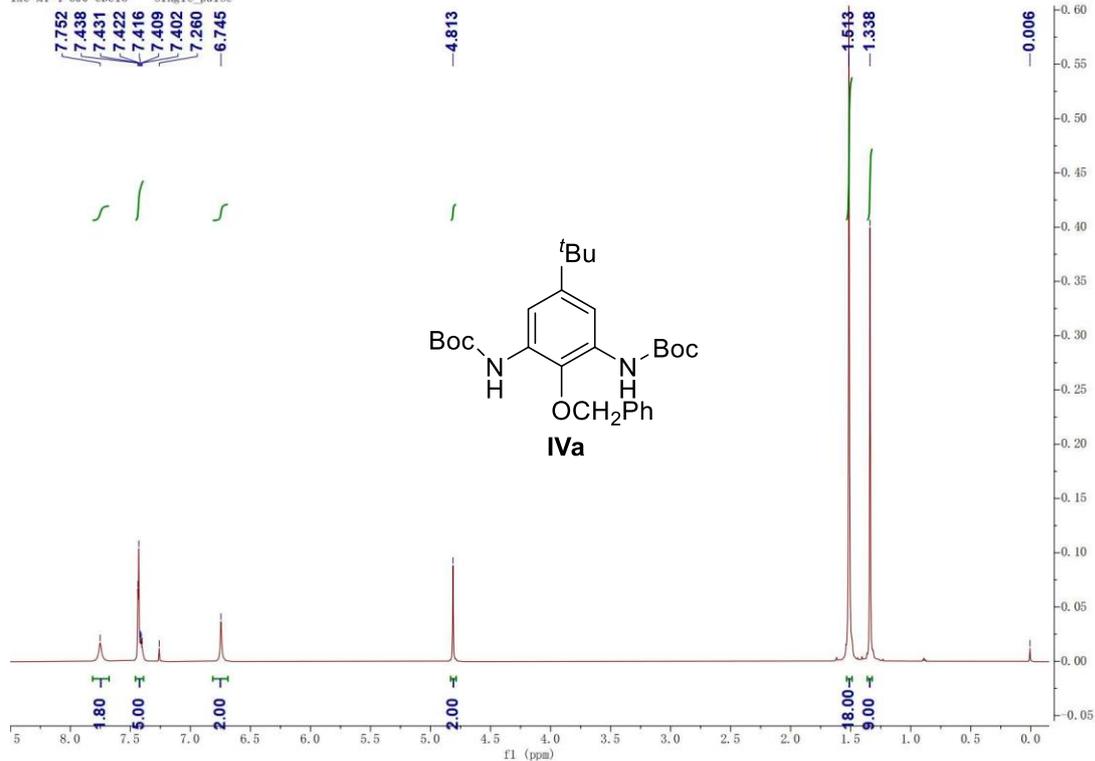
IIIc: ^{13}C NMR, 150 MHz, CDCl_3

lxc-431-2-600- CDCl_3 — single pulse decoupled gated NOE



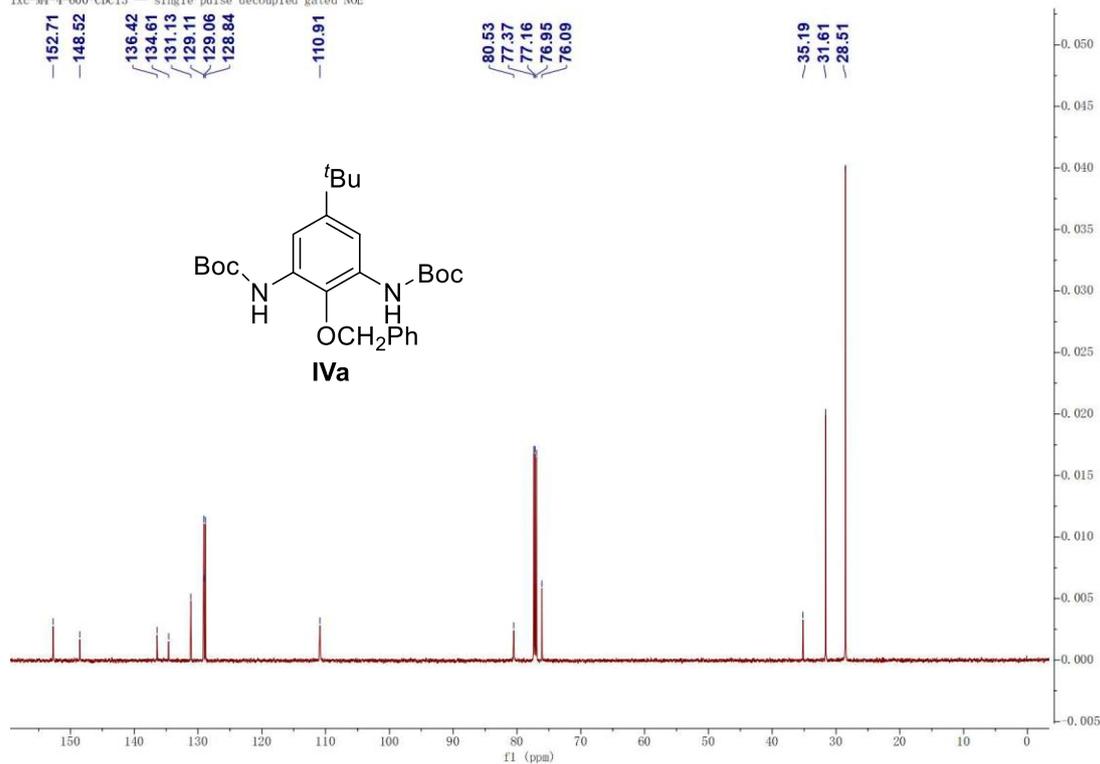
IVa: ^1H NMR, 600 MHz, CDCl_3

lxc-M4-4-600- CDCl_3 — single pulse



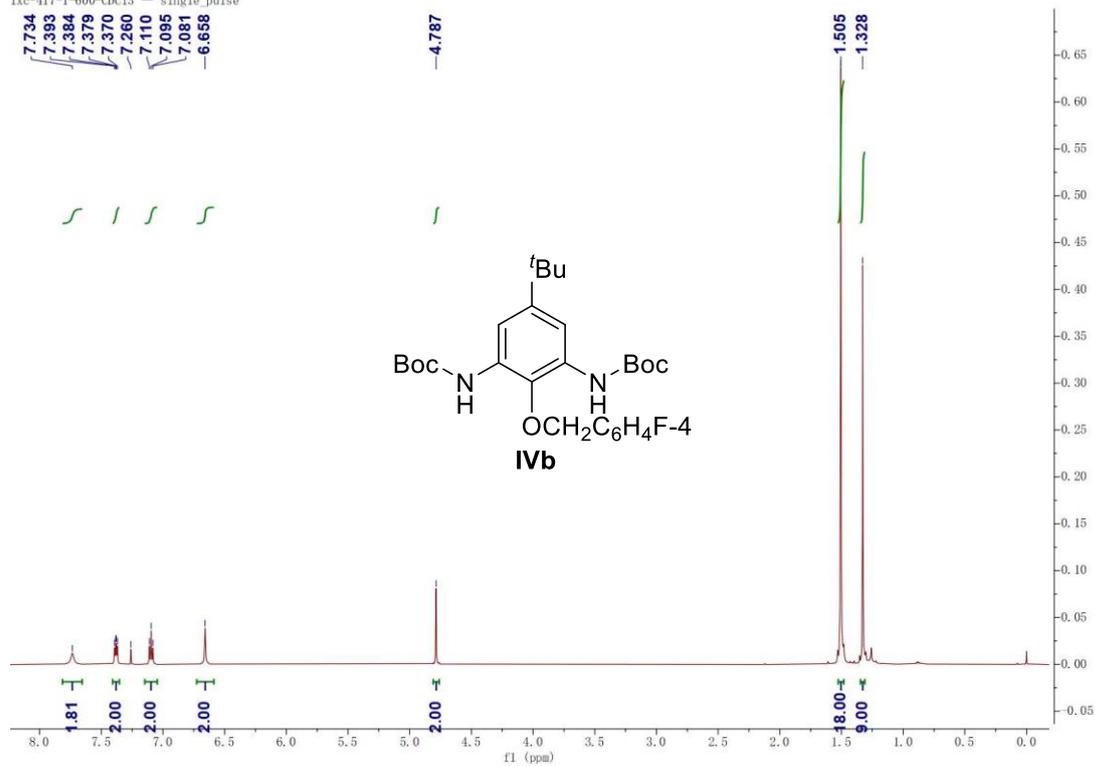
IVa: ^{13}C NMR, 150 MHz, CDCl_3

lxc-M4-4-600-CDCl3 -- single pulse decoupled gated NOE



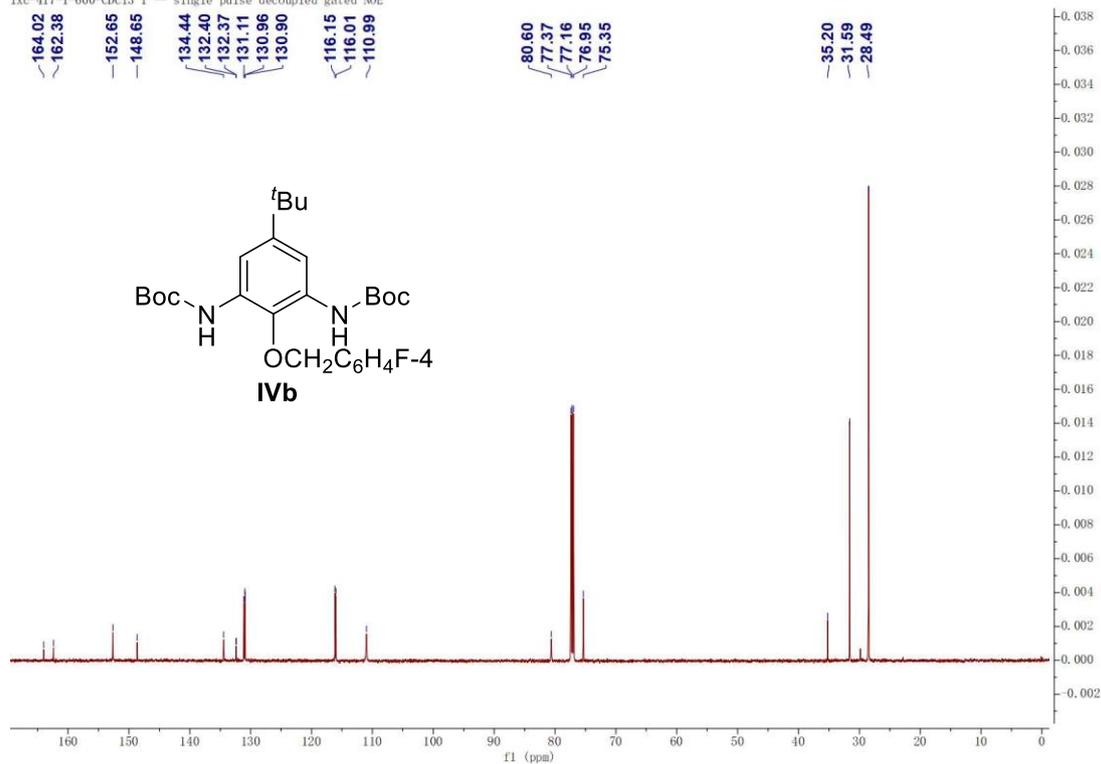
IVb: ^1H NMR, 600 MHz, CDCl_3

lxc-417-1-600-CDCl3 -- single_pulse



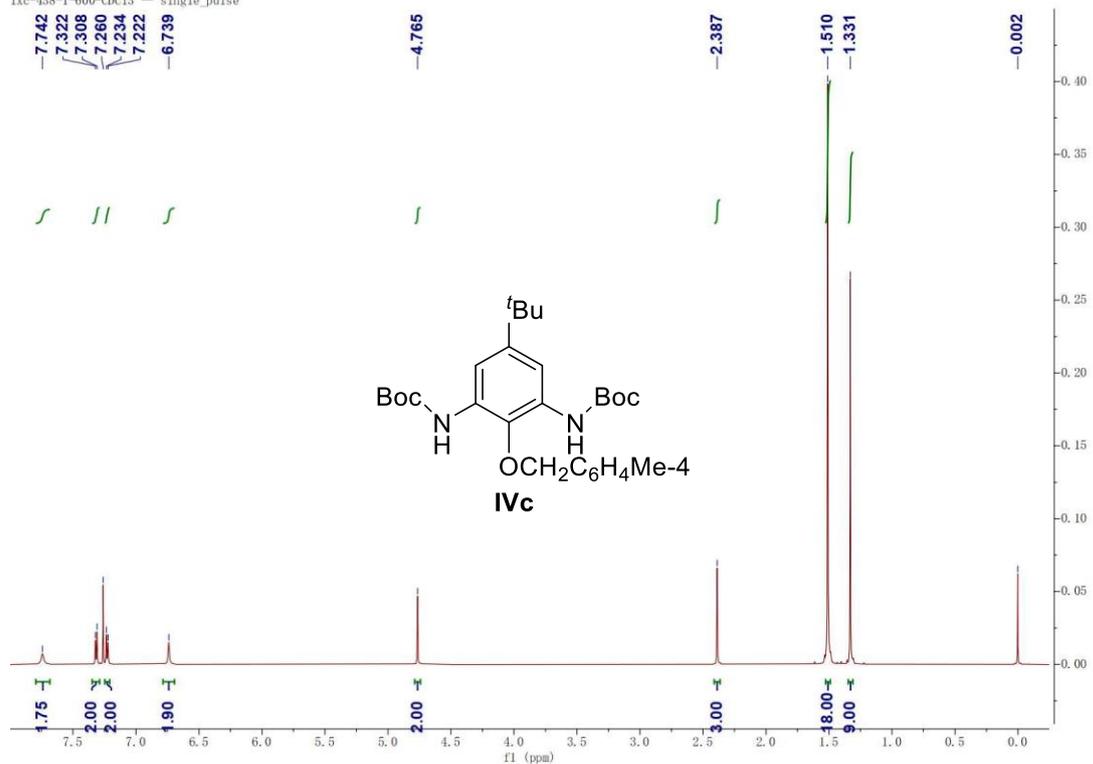
IVb: ^{13}C NMR, 150 MHz, CDCl_3

lxc-417-1-600- CDCl_3 1 — single pulse decoupled gated NOE



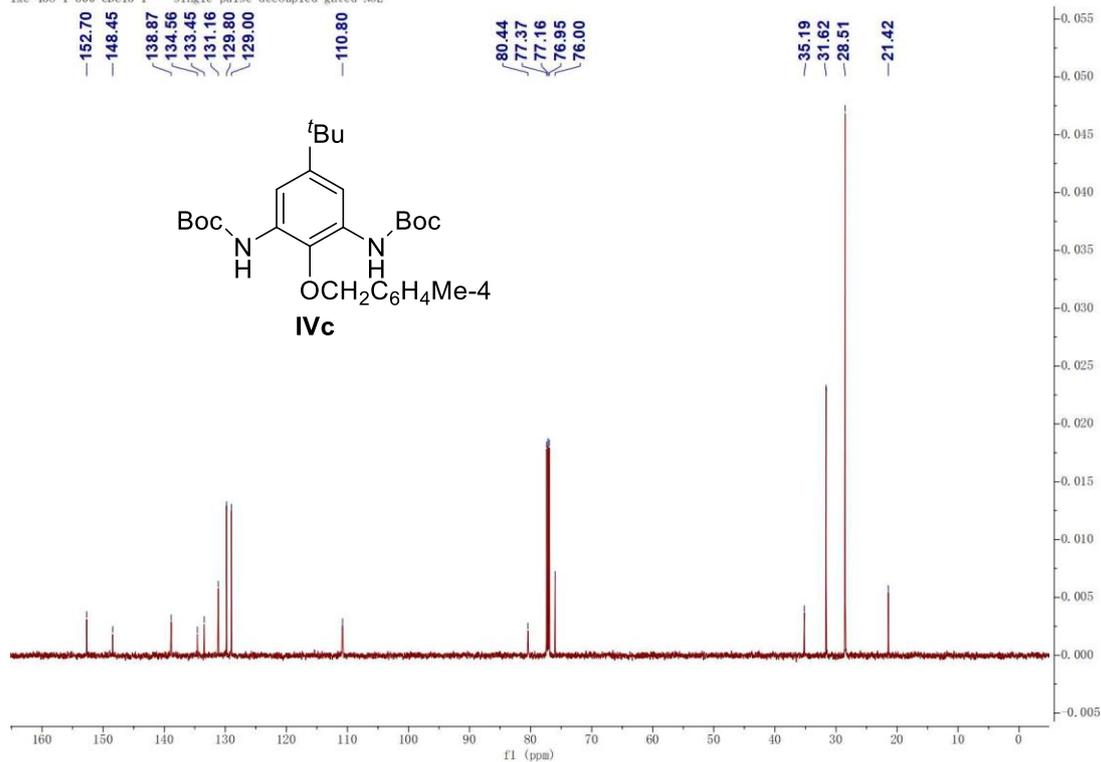
IVc: ^1H NMR, 600 MHz, CDCl_3

lxc-438-1-600- CDCl_3 — single_pulse



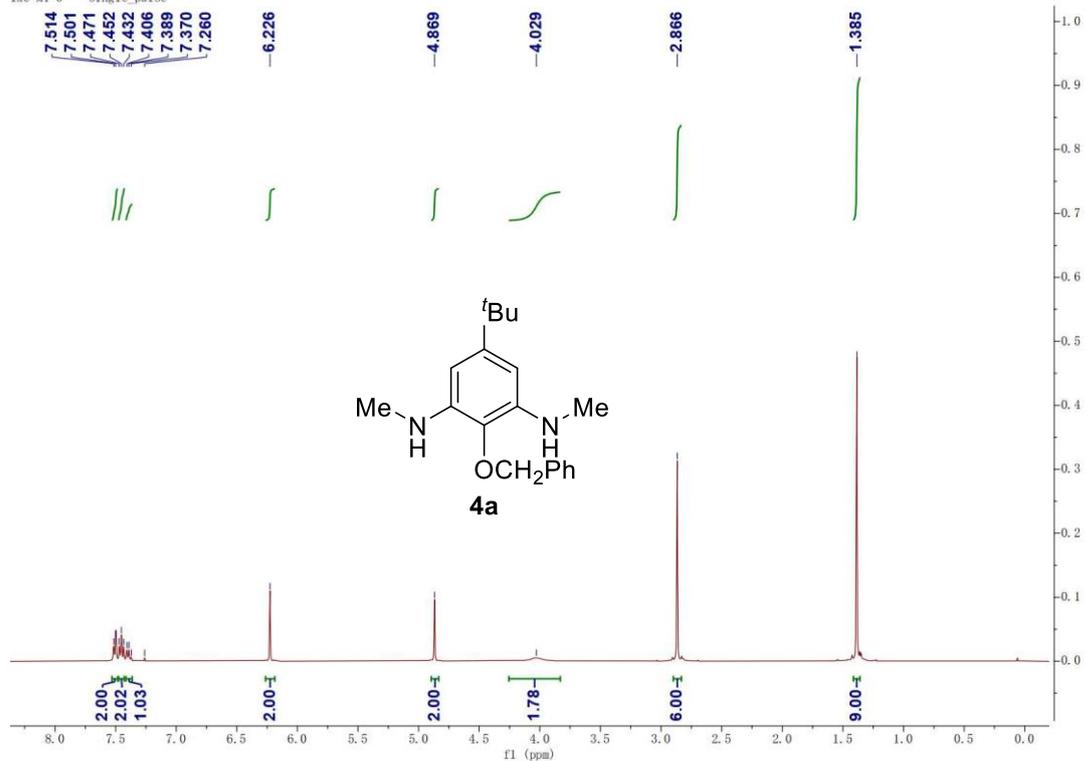
IVc: ^{13}C NMR, 150 MHz, CDCl_3

lxc-438-1-600- CDCl_3 1 - single pulse decoupled gated NOE



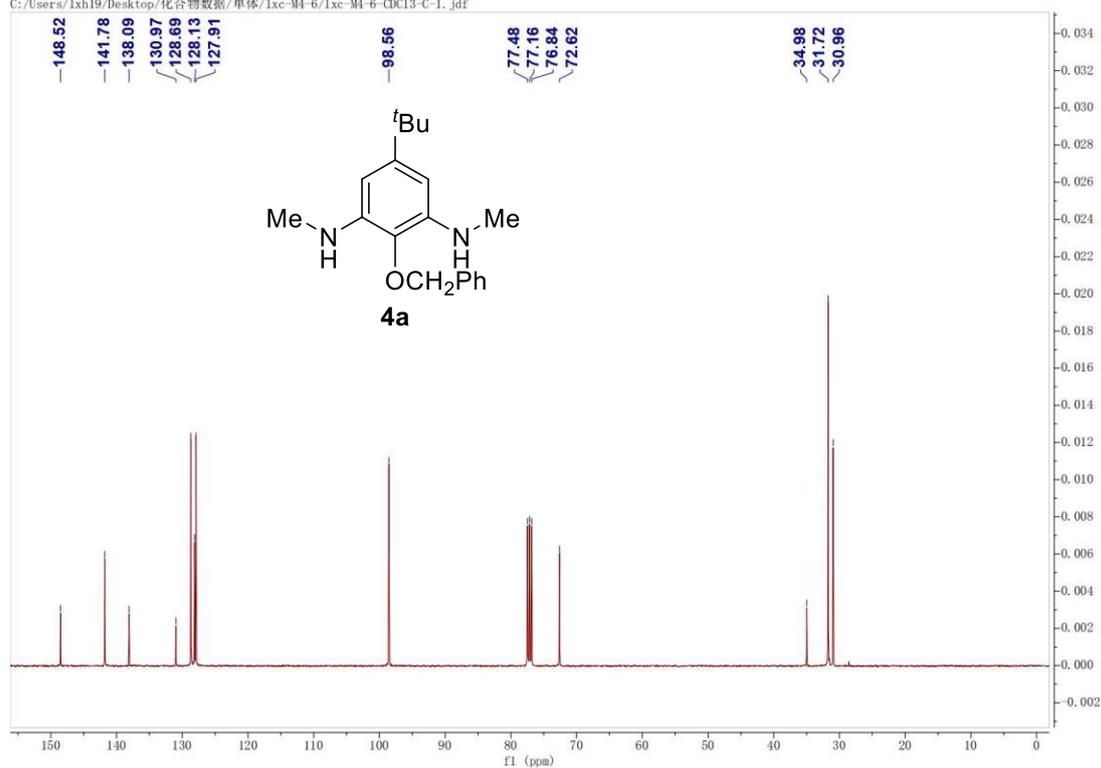
4a: ^1H NMR, 400 MHz, CDCl_3

lxc-M4-6 - single pulse



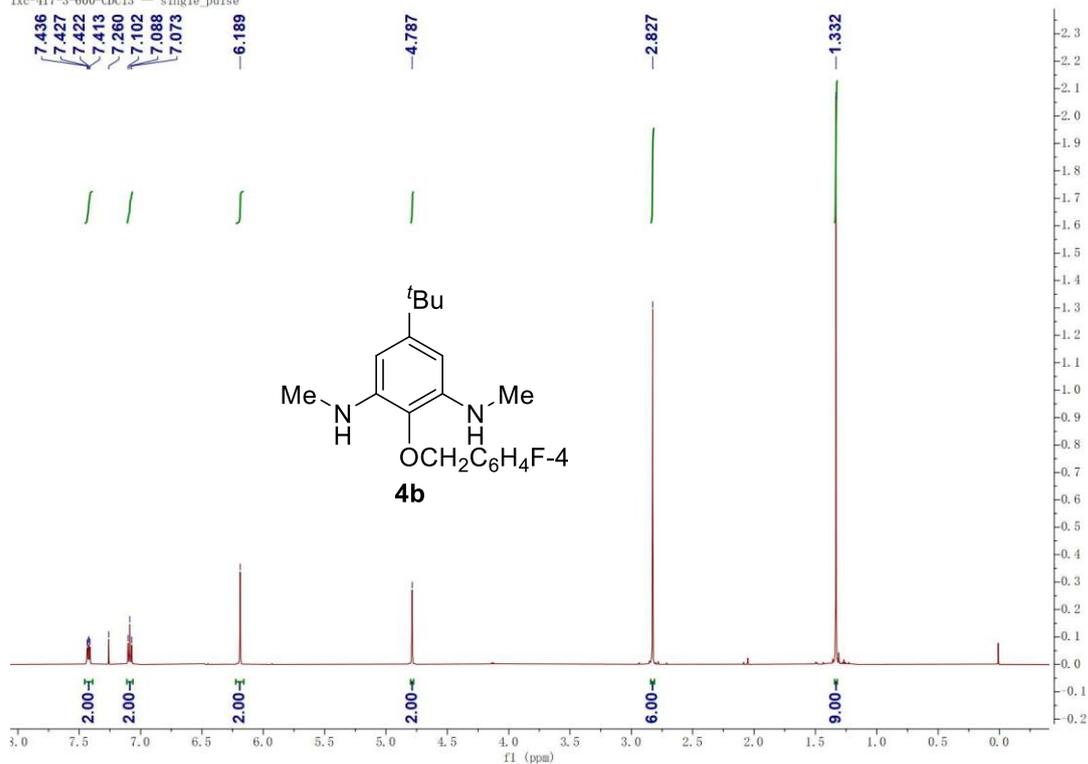
4a: ^{13}C NMR, 100 MHz, CDCl_3

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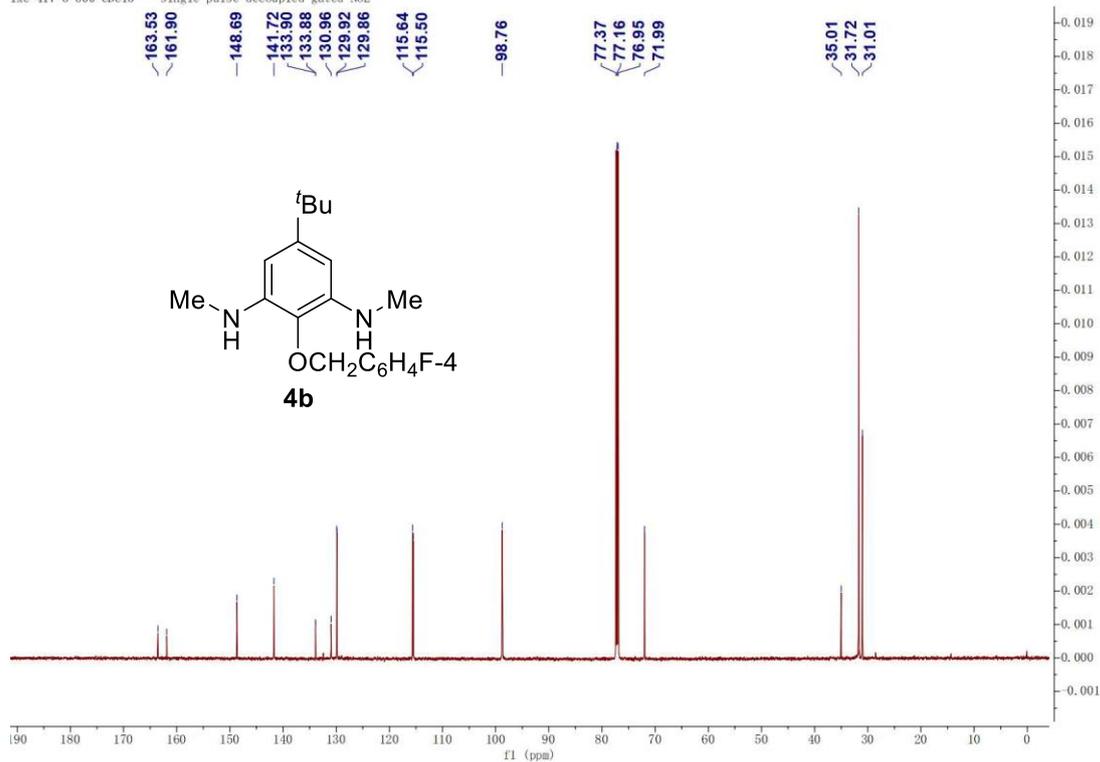
4b: ^1H NMR, 600 MHz, CDCl_3

lxc-417-3-600-CDCl3 -- single_pulse



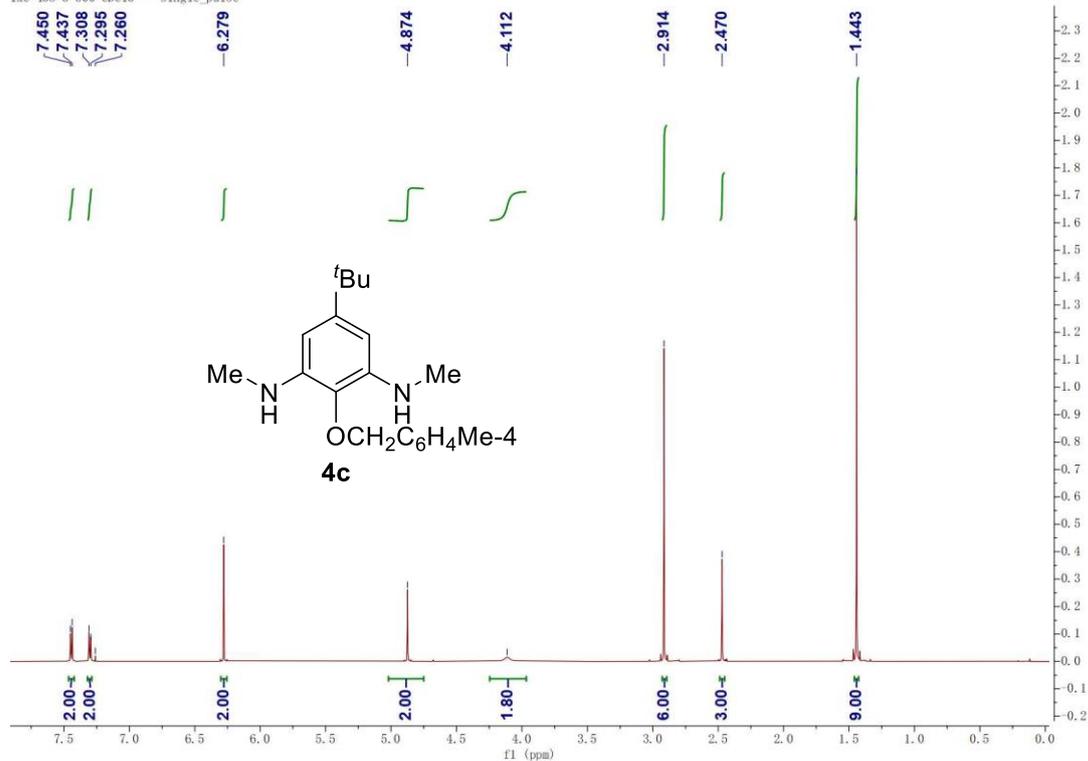
4b: ^{13}C NMR, 150 MHz, CDCl_3

lxc-417-3-600- CDCl_3 — single pulse decoupled gated NOE



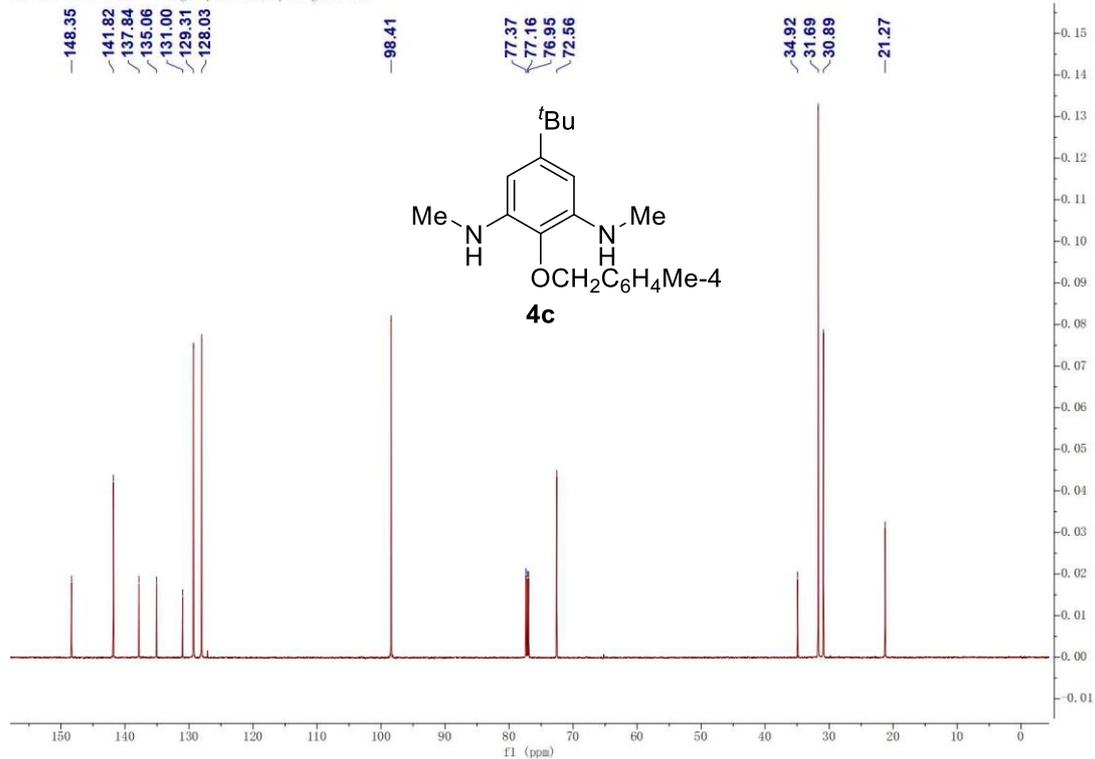
4c: ^1H NMR, 600 MHz, CDCl_3

lxc-438-3-600- CDCl_3 — single_pulse



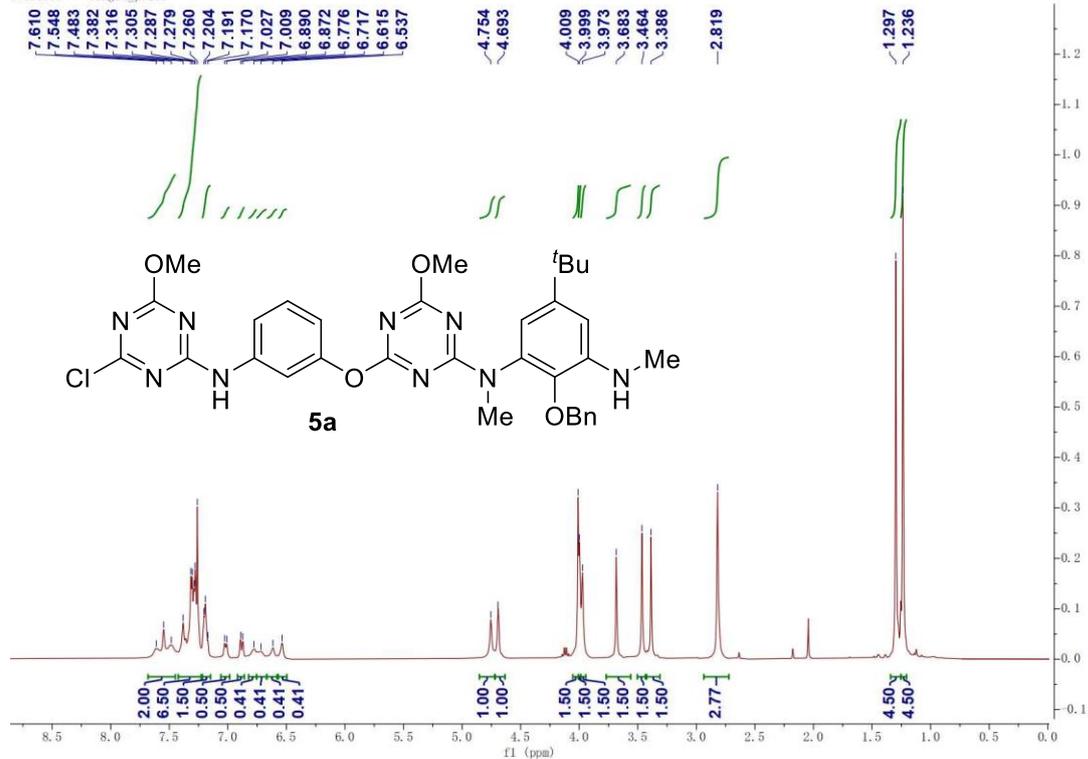
4c: ^{13}C NMR, 150 MHz, CDCl_3

lxc-438-3-600- CDCl_3 — single pulse decoupled gated NOE



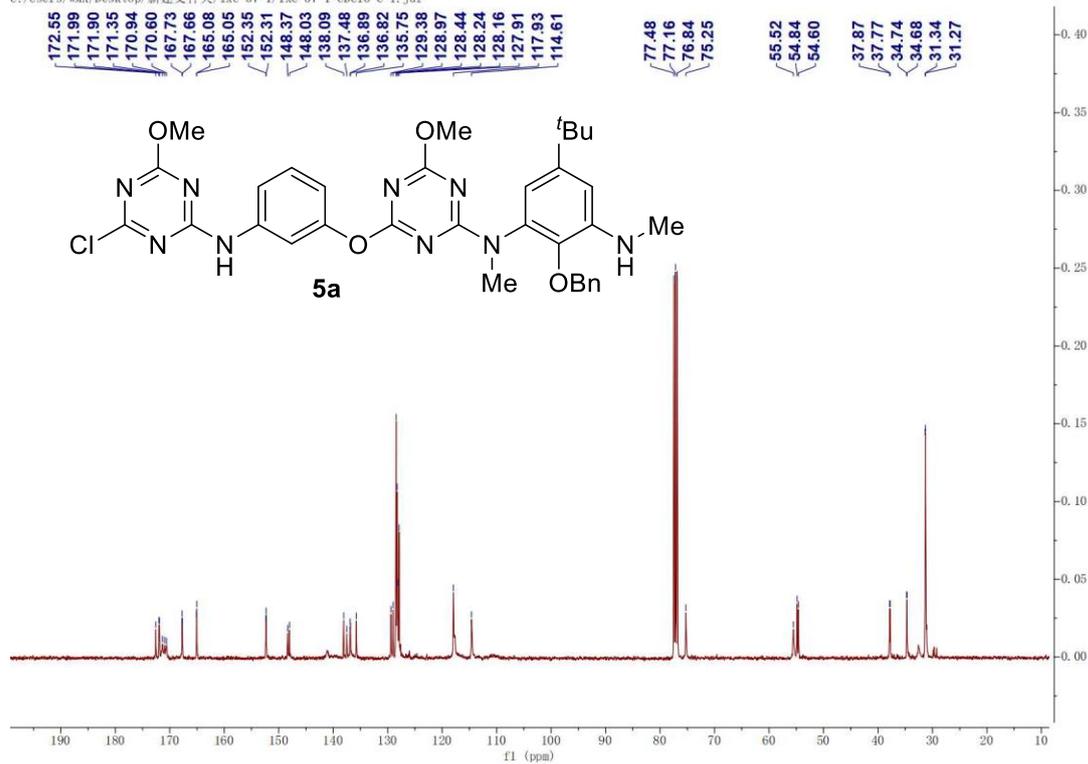
5a: ^1H NMR, 600 MHz, CDCl_3

S#650565 — single pulse



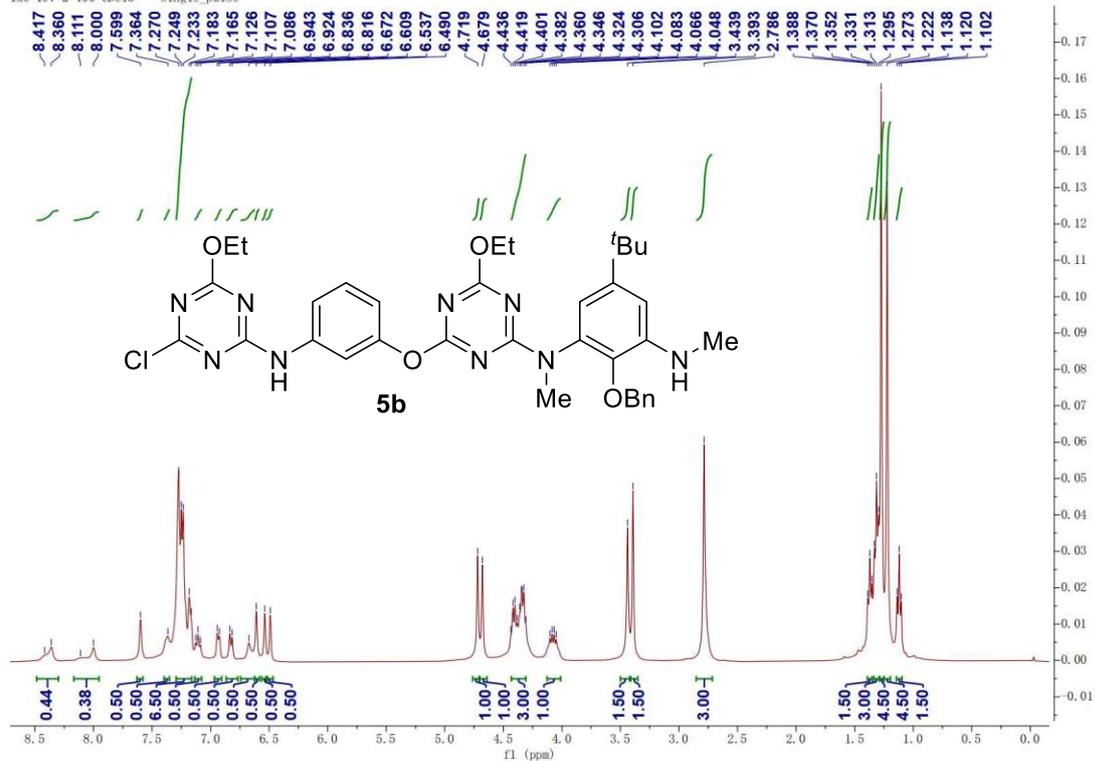
5a: ^{13}C NMR, 100 MHz, CDCl_3

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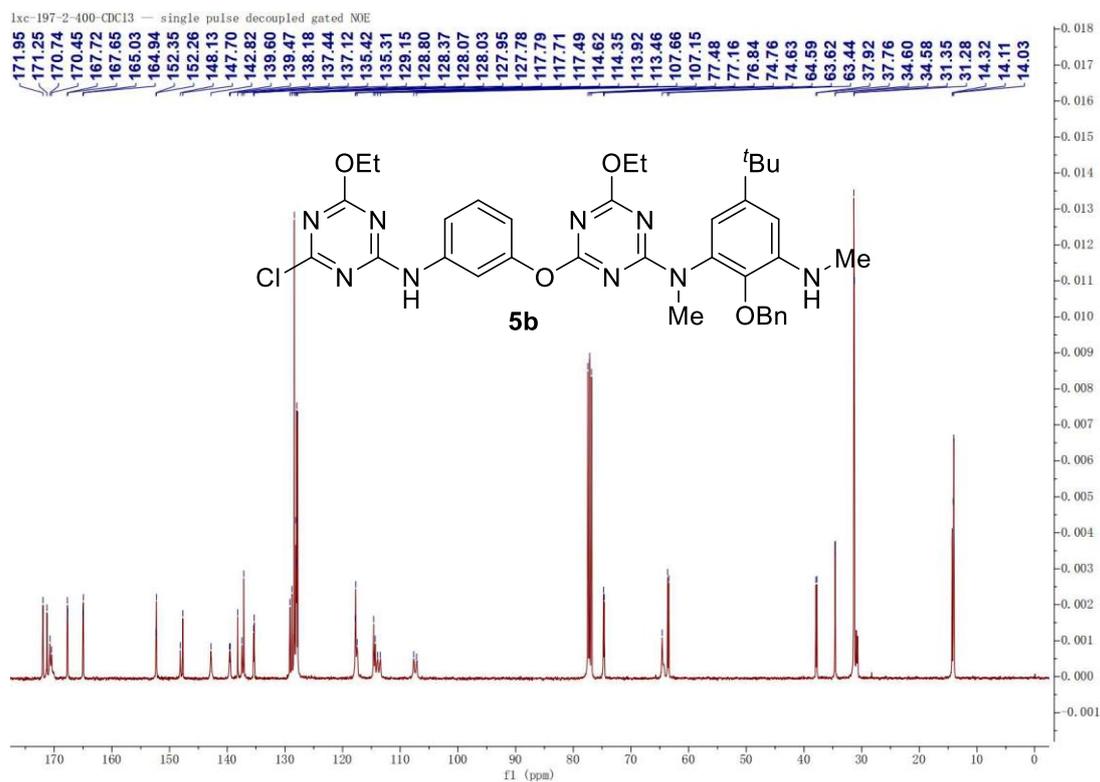


5b: ^1H NMR, 400 MHz, CDCl_3

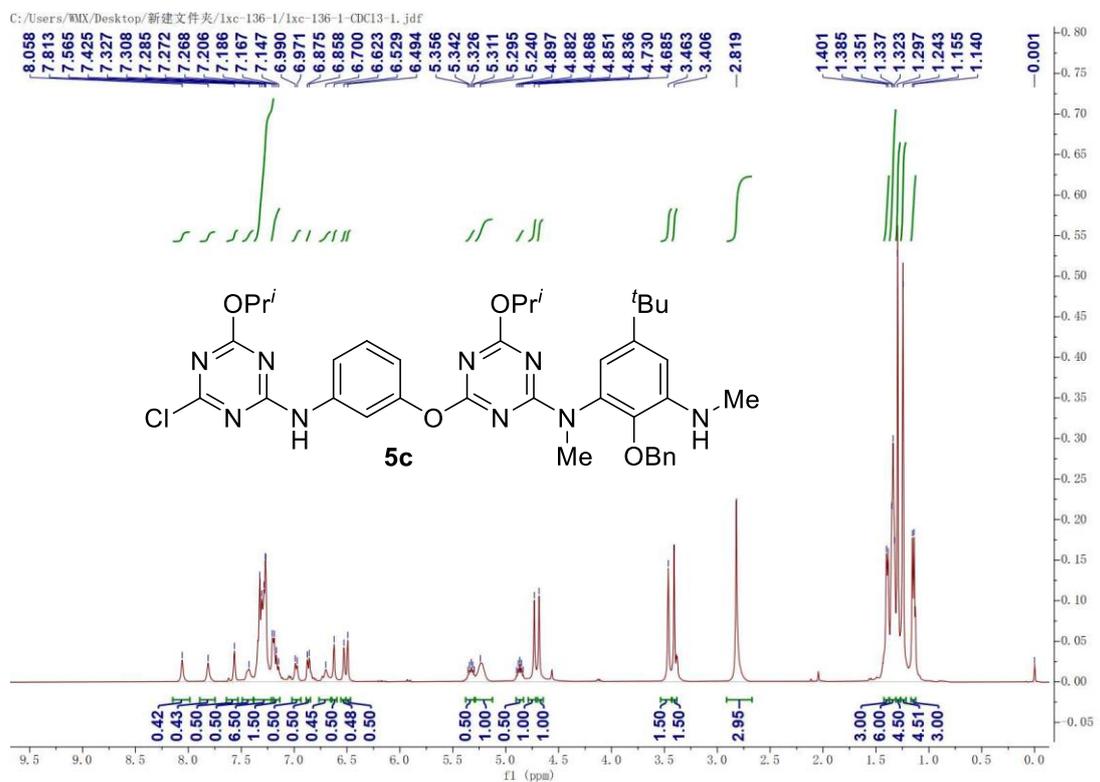
1xc-197-2-400-CDCl3 -- single_pulse



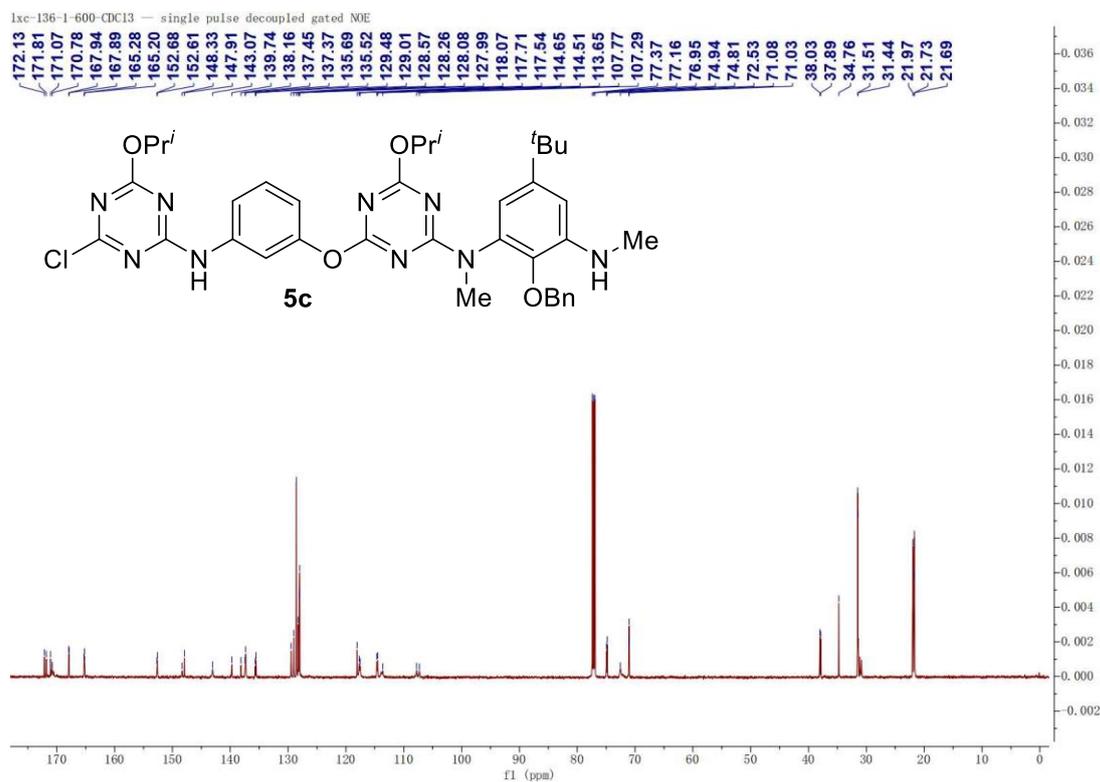
5b: ^{13}C NMR, 100 MHz, CDCl_3



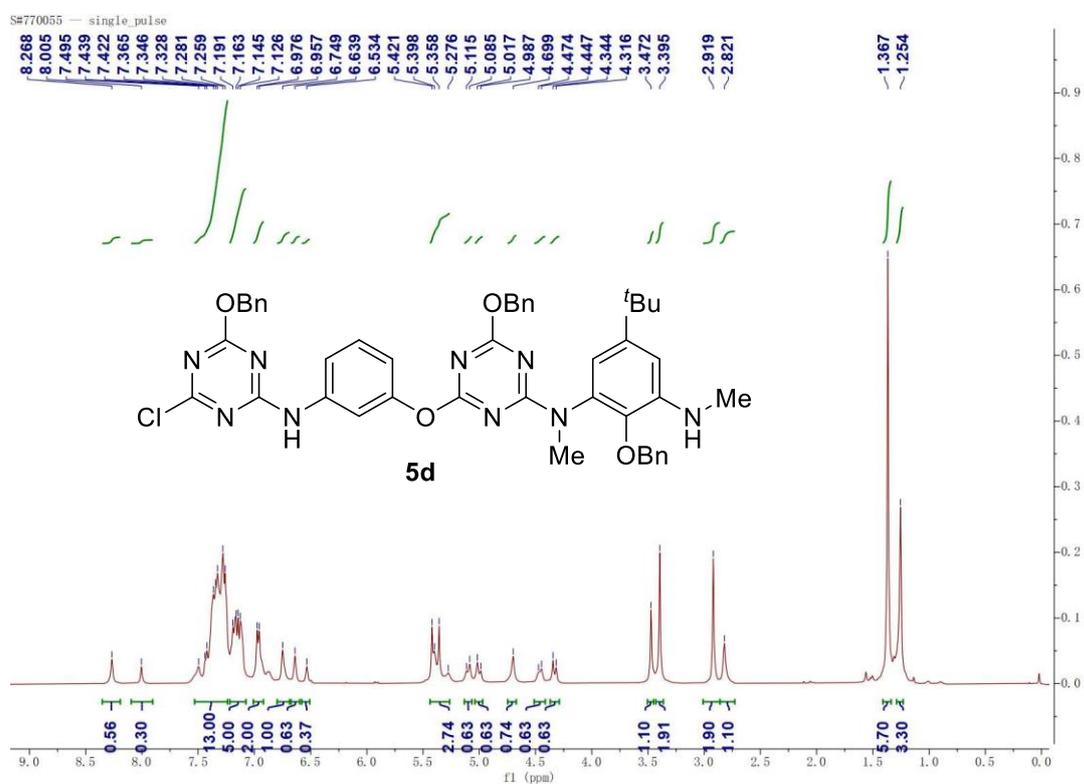
5c: ^1H NMR, 400 MHz, CDCl_3



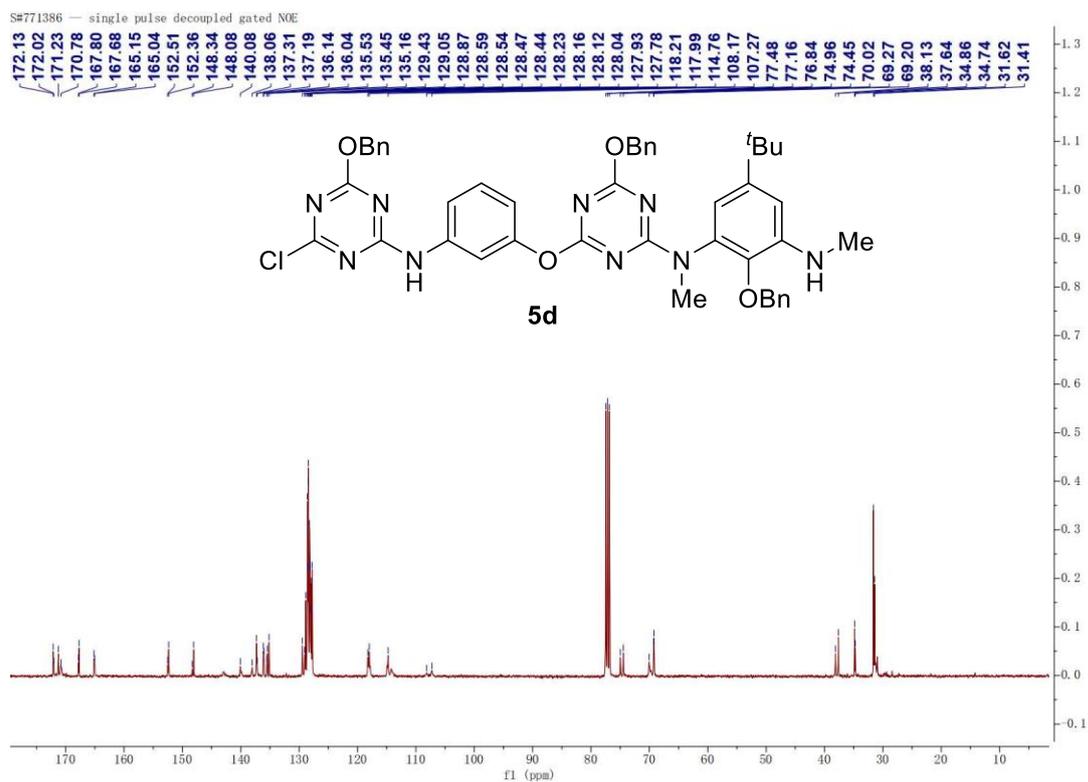
5c: ^{13}C NMR, 150 MHz, CDCl_3



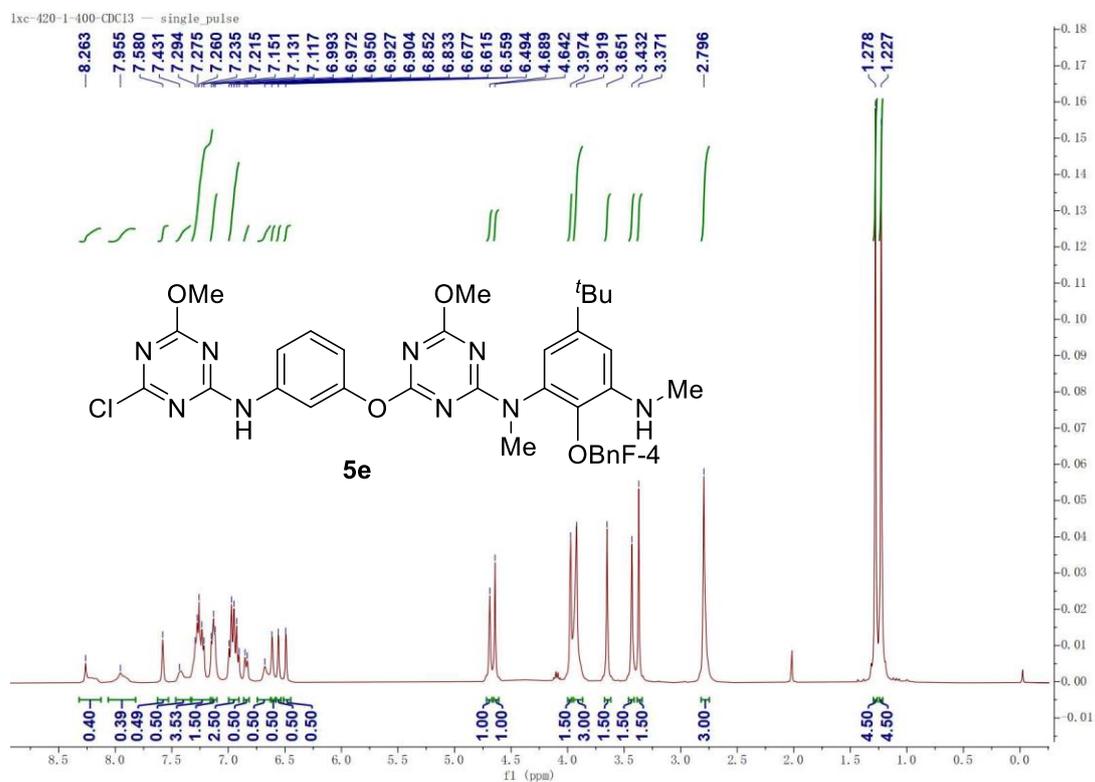
5d: ^1H NMR, 400 MHz, CDCl_3



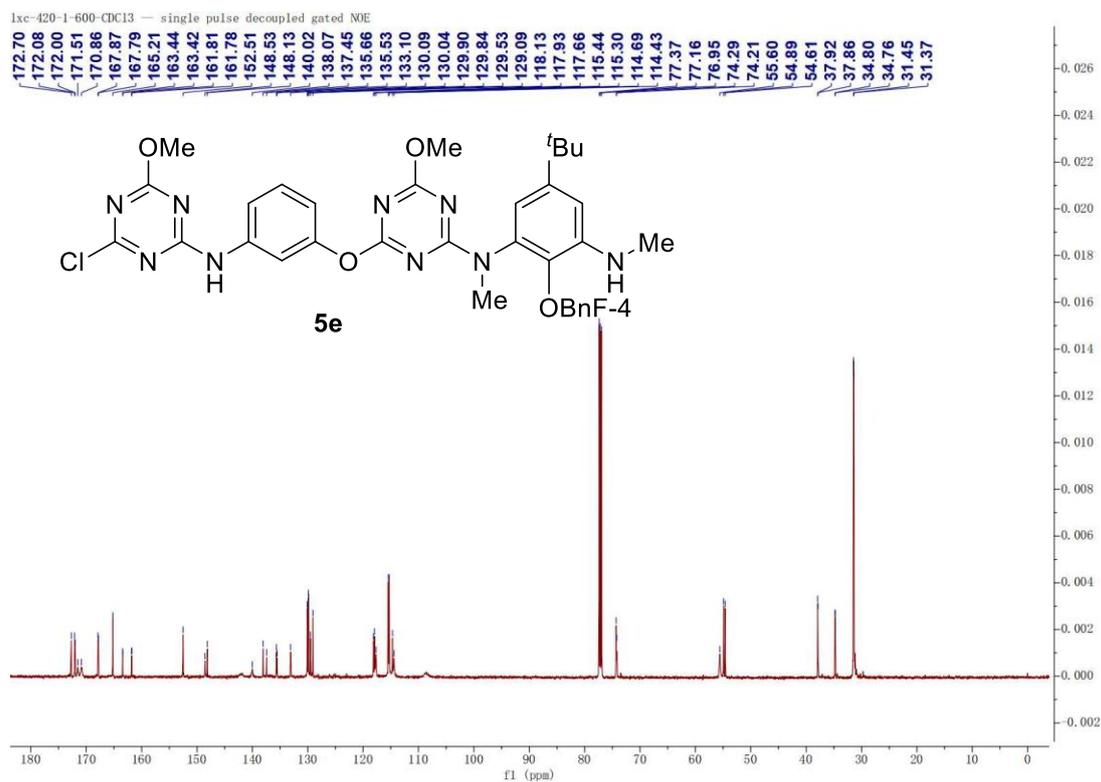
5d: ^{13}C NMR, 100 MHz, CDCl_3



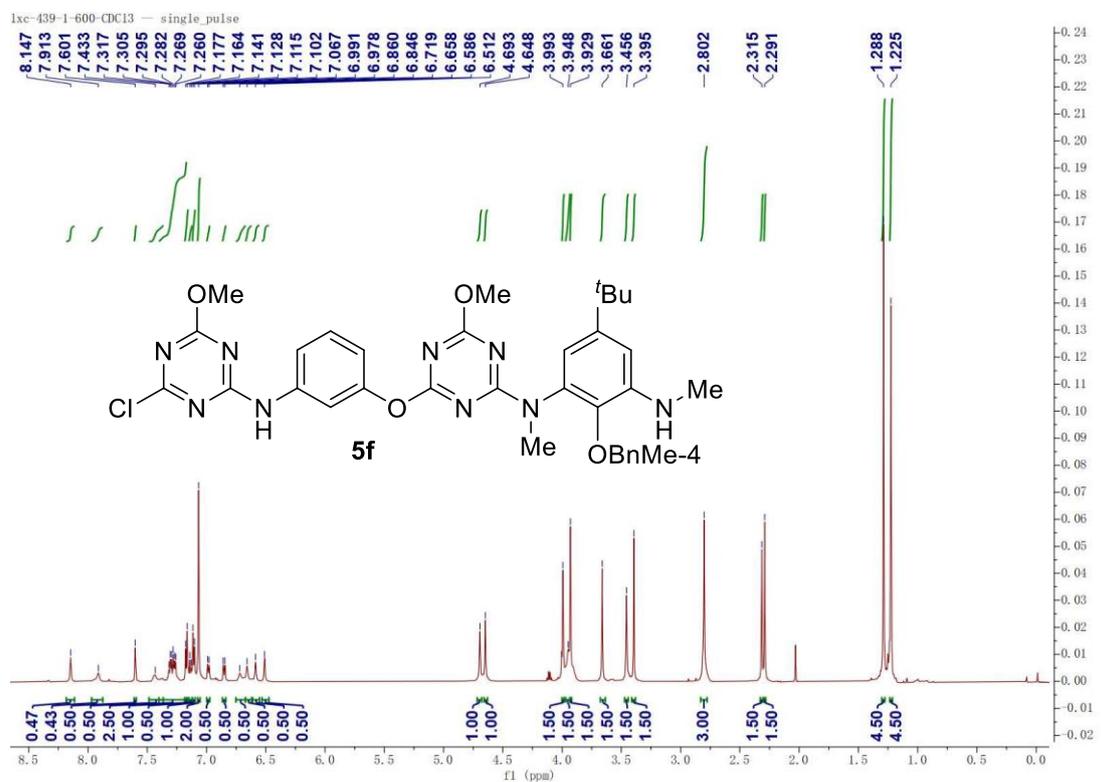
5e: ^1H NMR, 400 MHz, CDCl_3



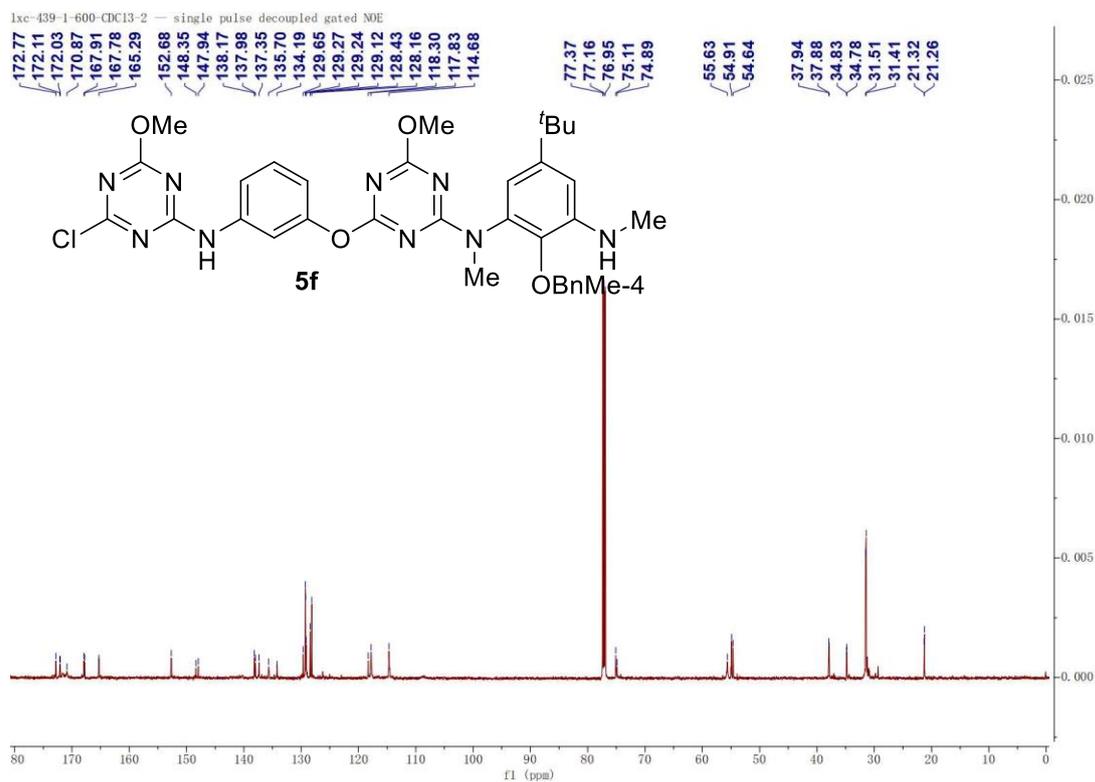
5e: ^{13}C NMR, 150 MHz, CDCl_3



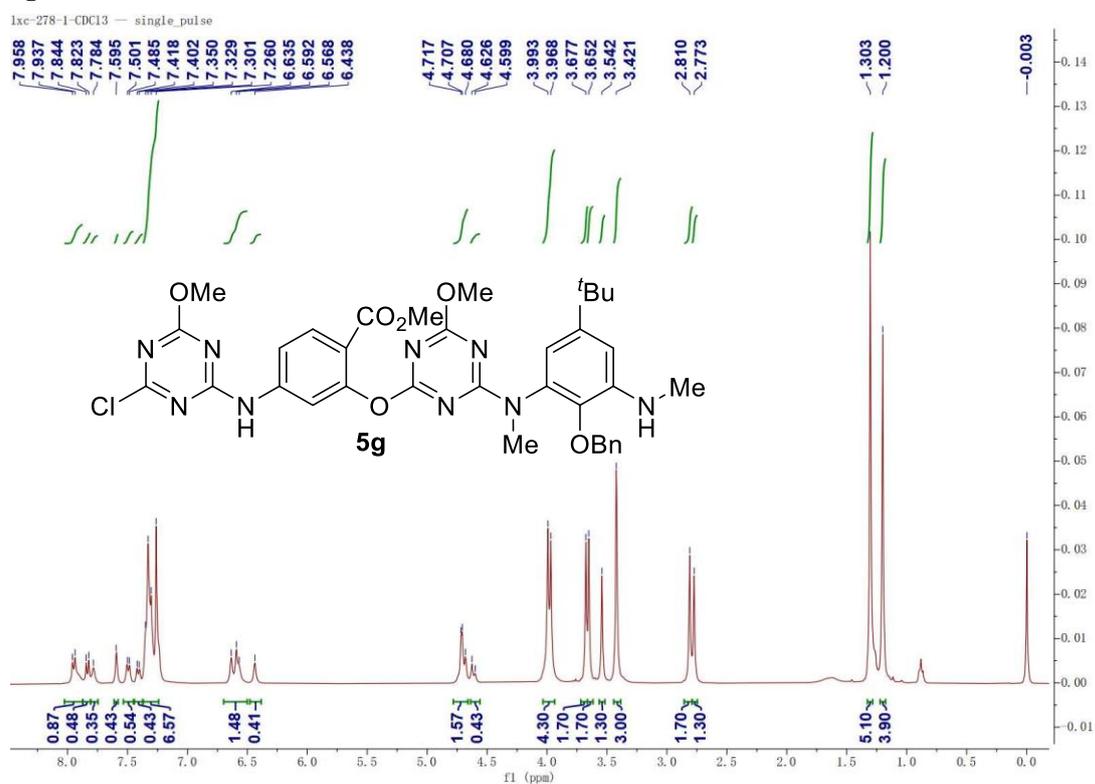
5f: ^1H NMR, 600 MHz, CDCl_3



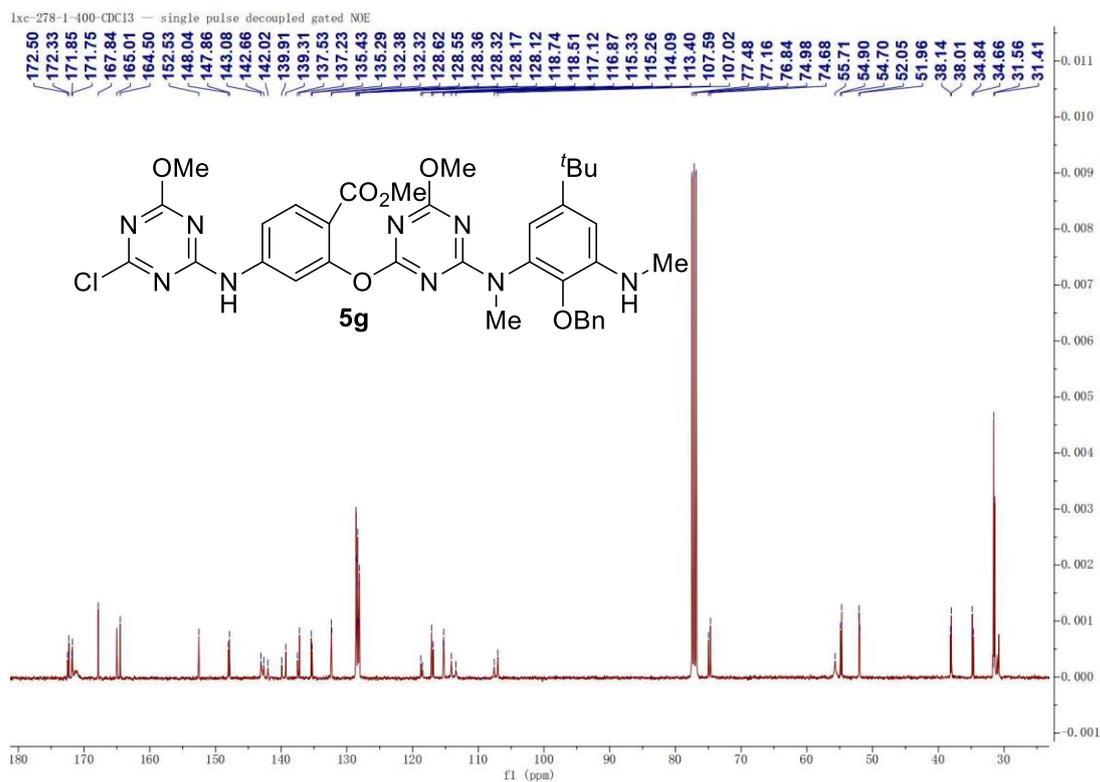
5f: ^{13}C NMR, 150 MHz, CDCl_3



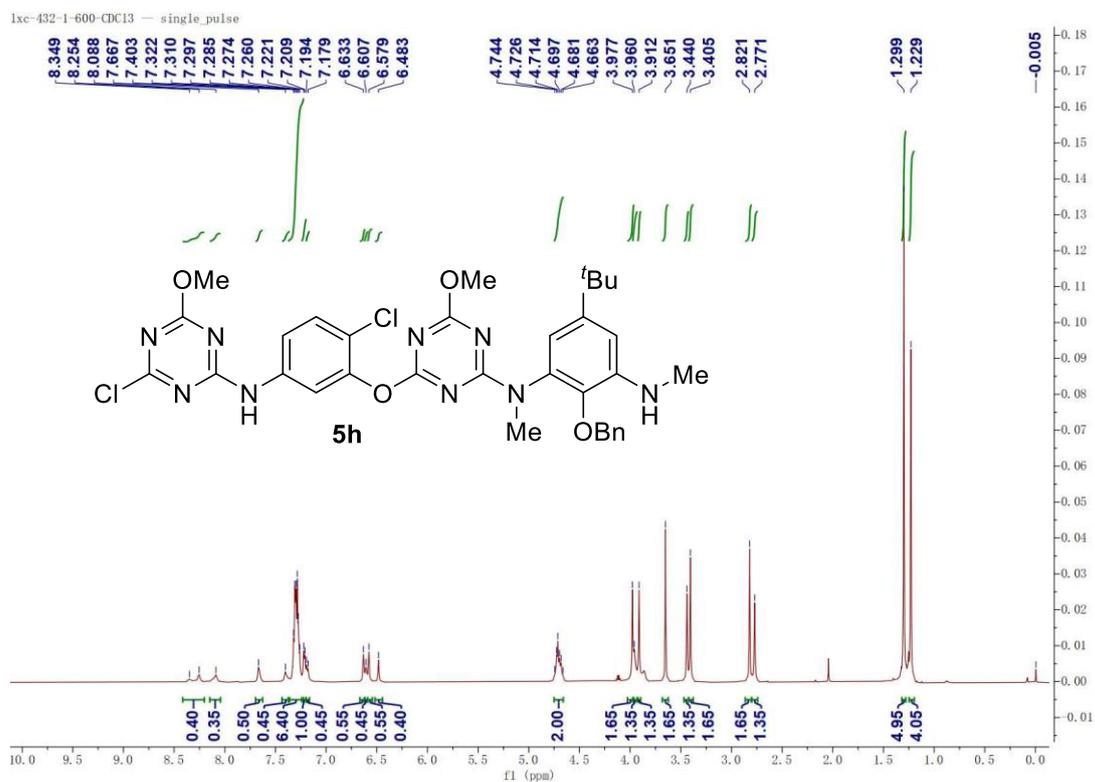
5g: ^1H NMR, 400 MHz, CDCl_3



5g: ^{13}C NMR, 100 MHz, CDCl_3

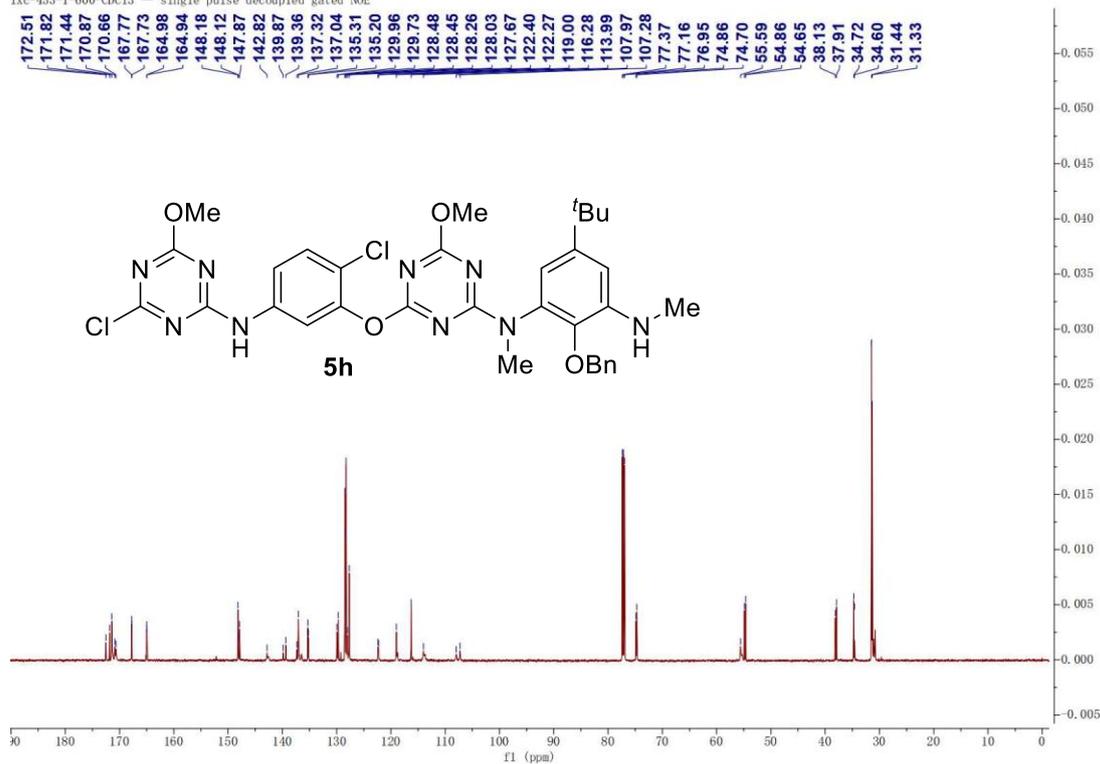


5h: ^1H NMR, 600 MHz, CDCl_3



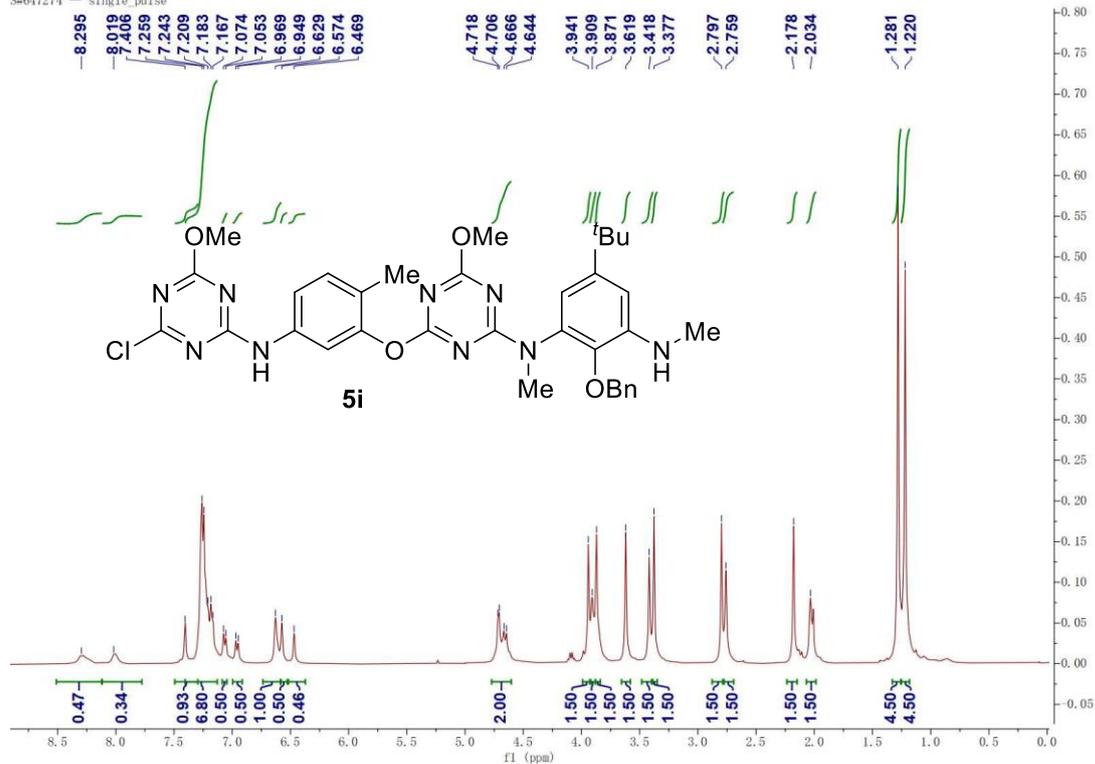
5h: ^{13}C NMR, 150 MHz, CDCl_3

lxc-433-1-600- CDCl_3 — single pulse decoupled gated NOE

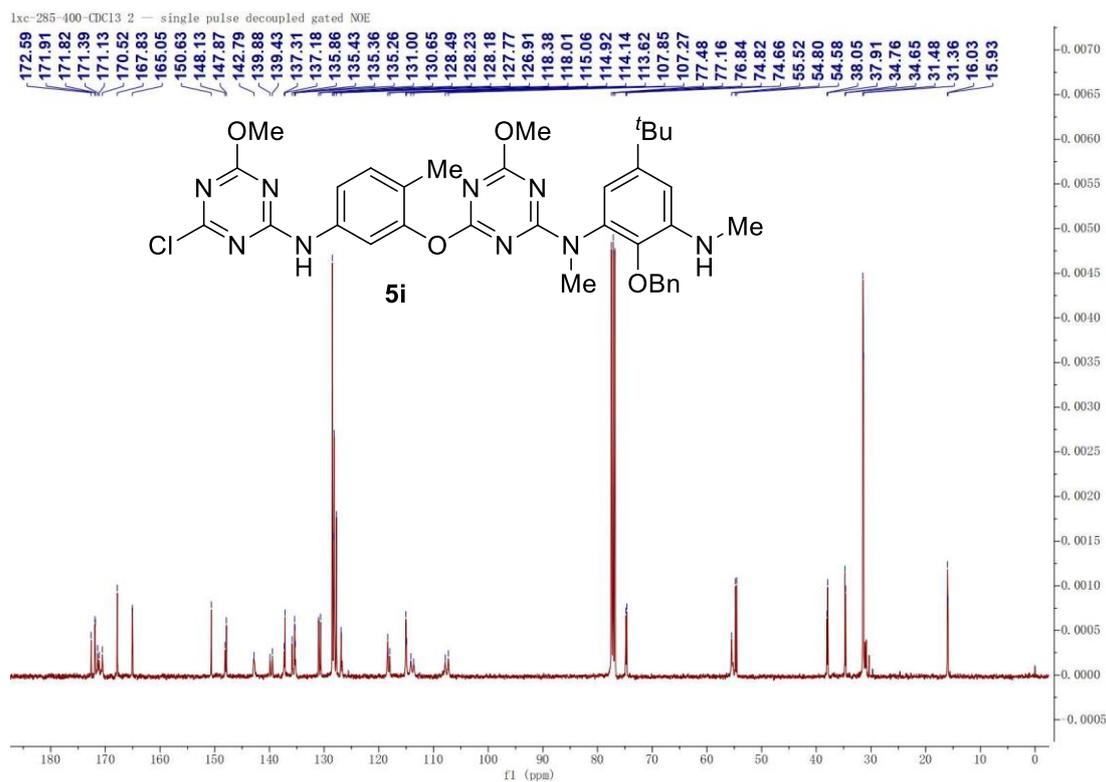


5i: ^1H NMR, 400 MHz, CDCl_3

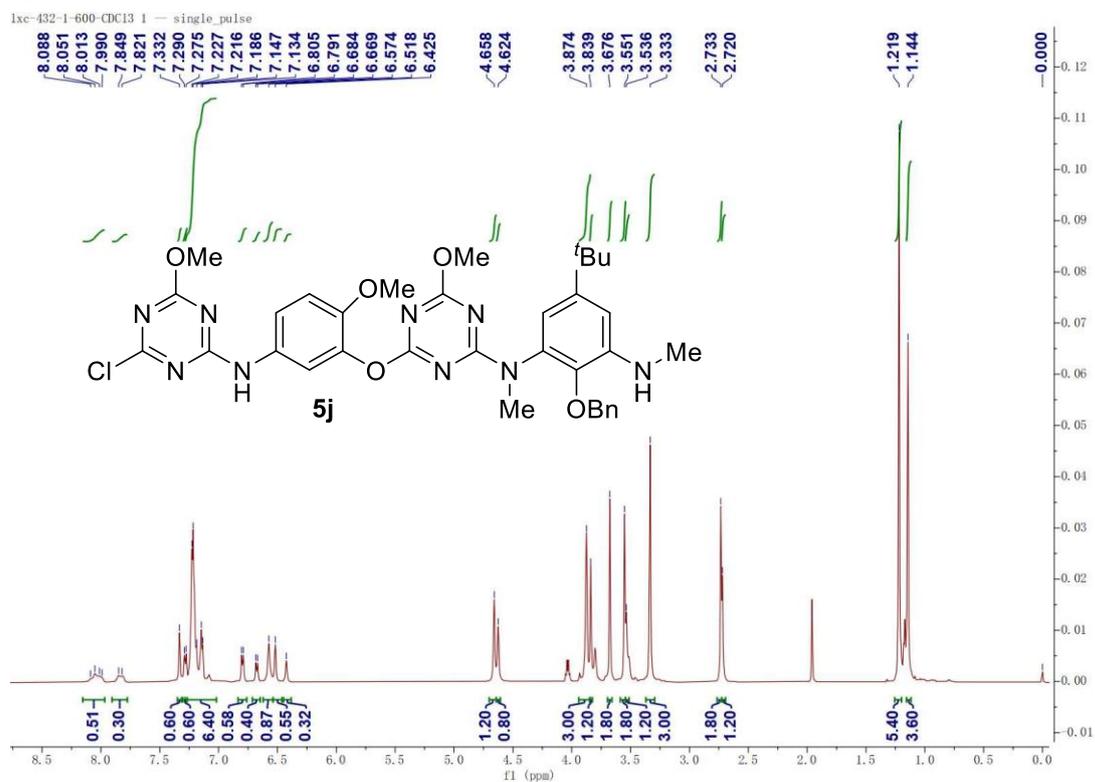
S#647274 — single pulse



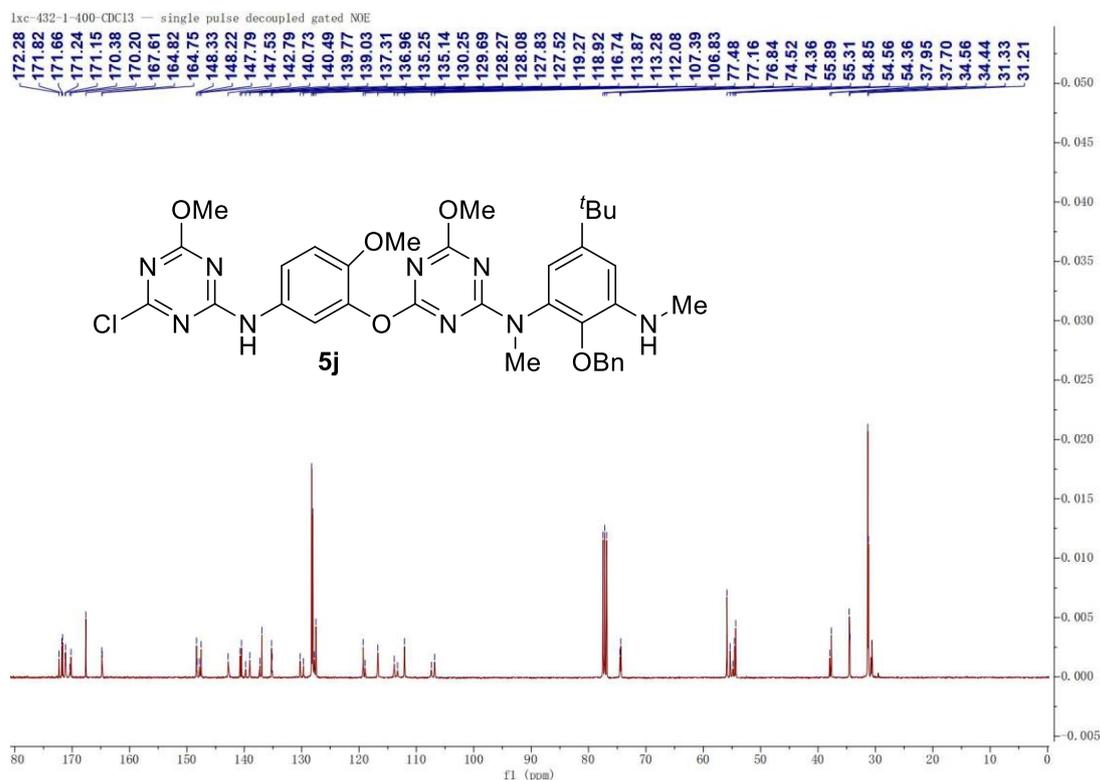
5i: ^{13}C NMR, 100 MHz, CDCl_3



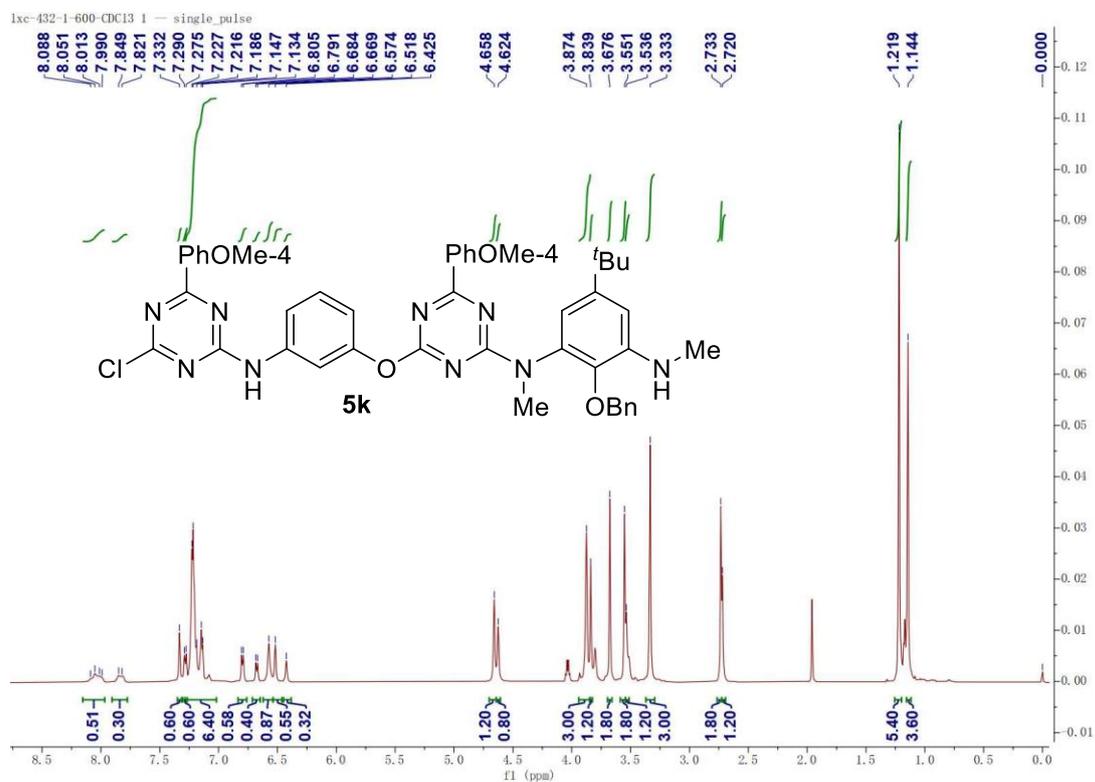
5j: ^1H NMR, 400 MHz, CDCl_3



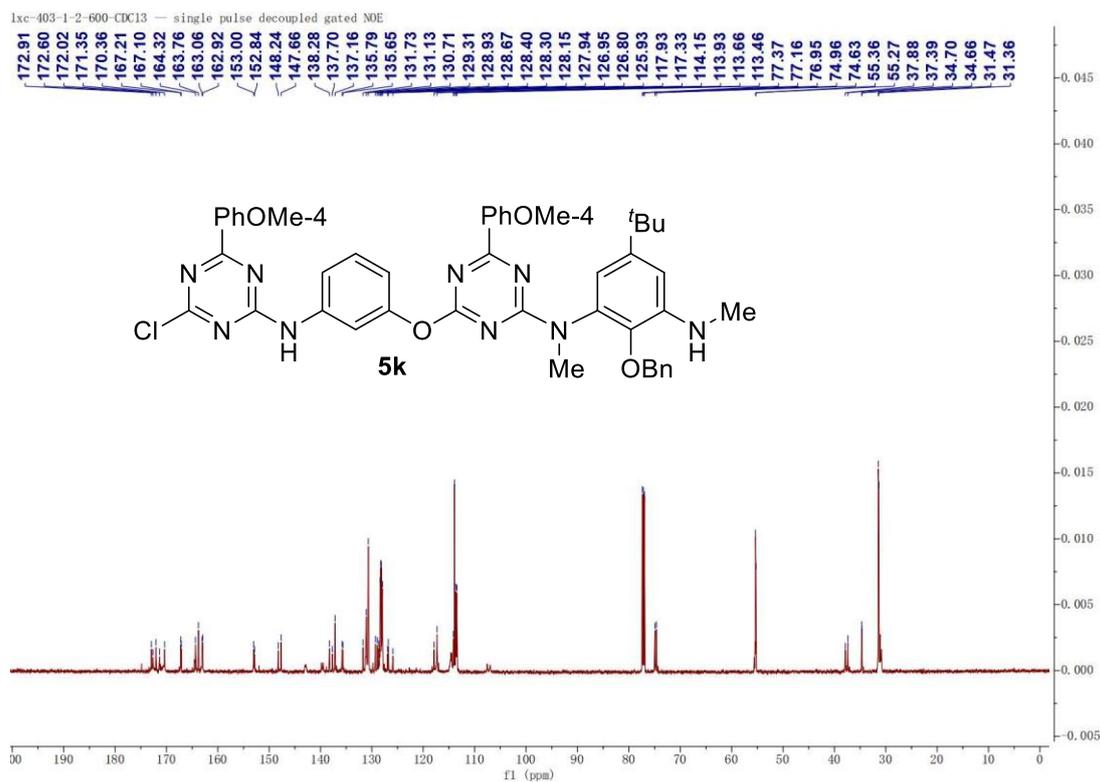
5j: ^{13}C NMR, 100 MHz, CDCl_3



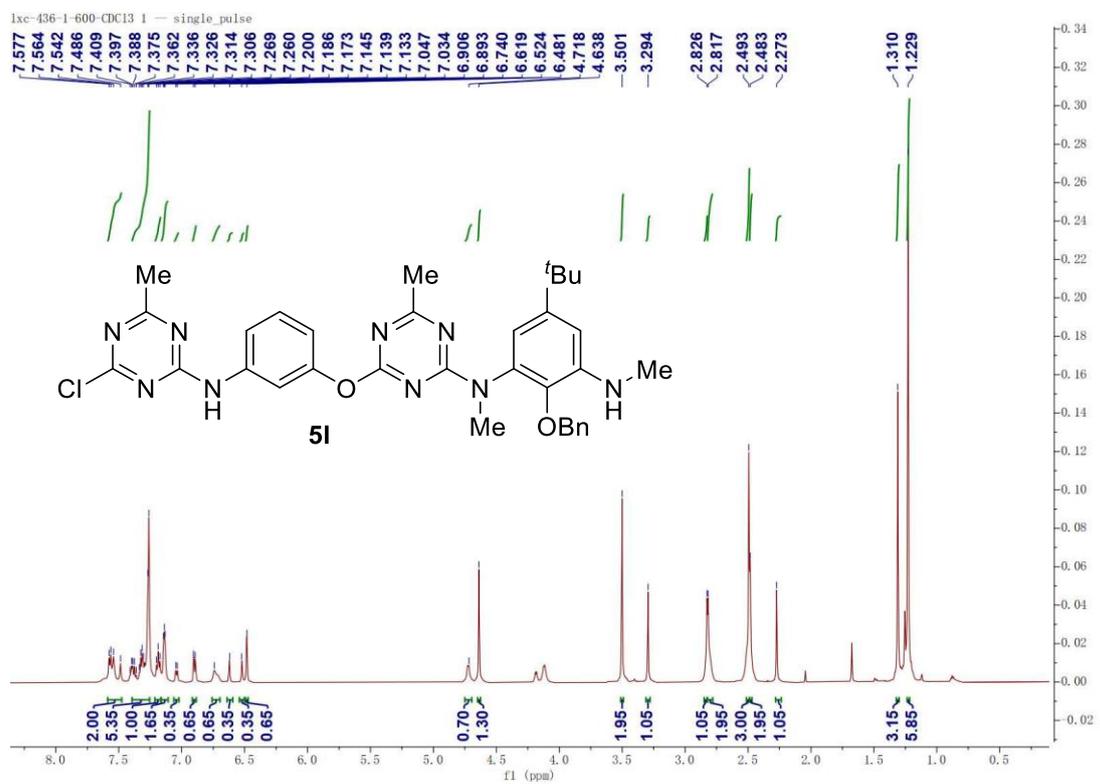
5k: ^1H NMR, 400 MHz, CDCl_3



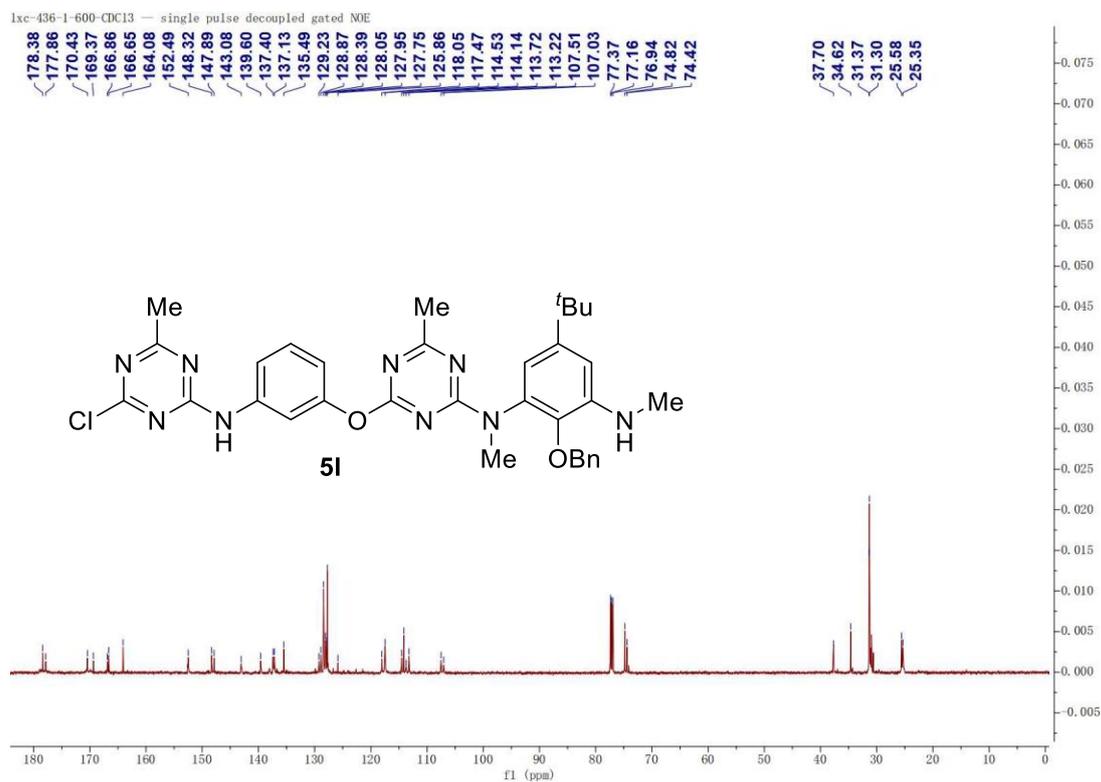
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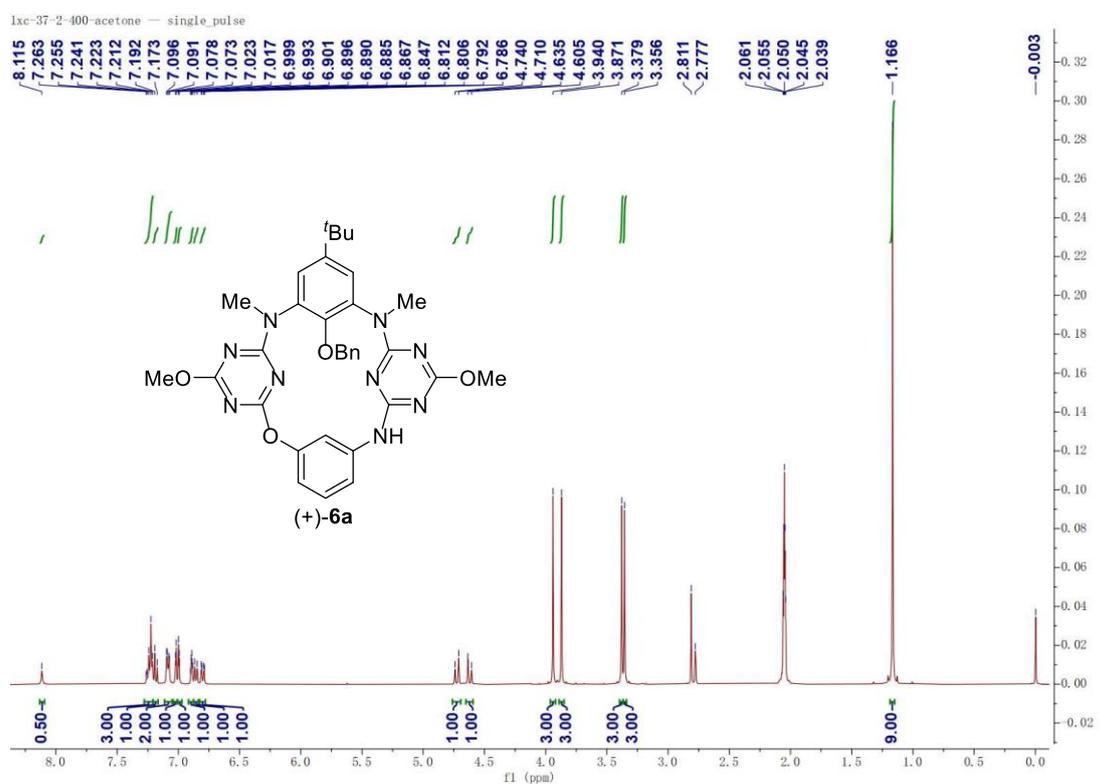
5l: ^1H NMR, 600 MHz, CDCl_3



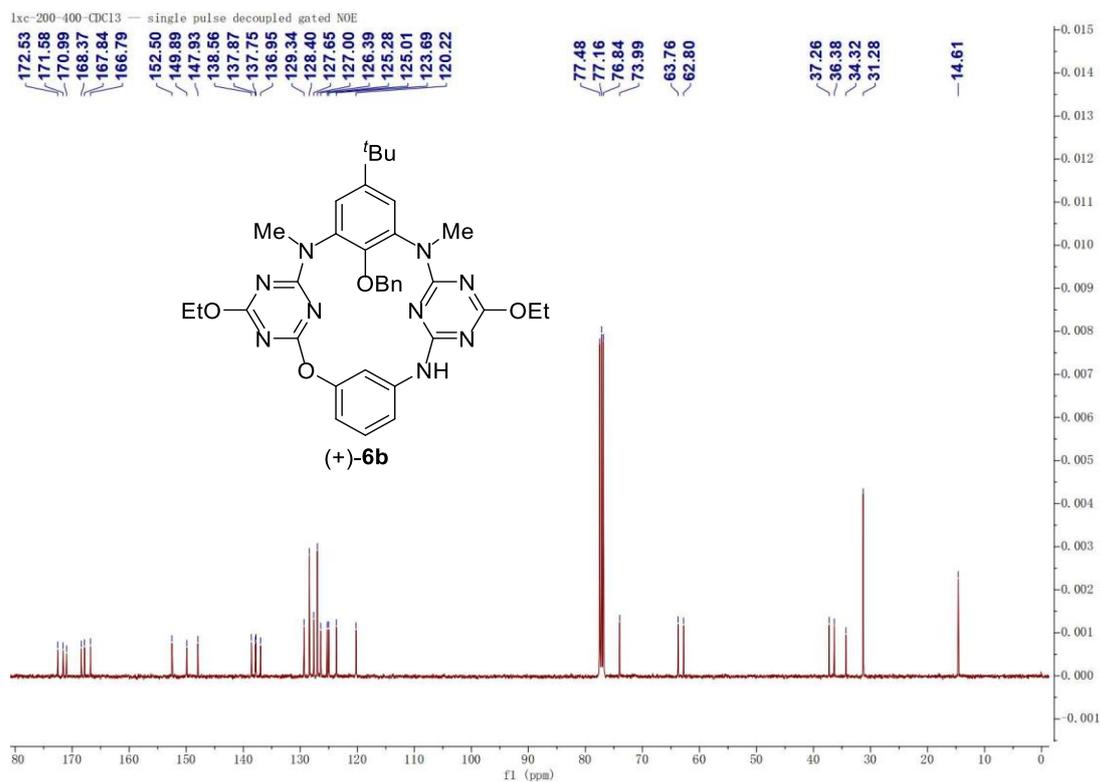
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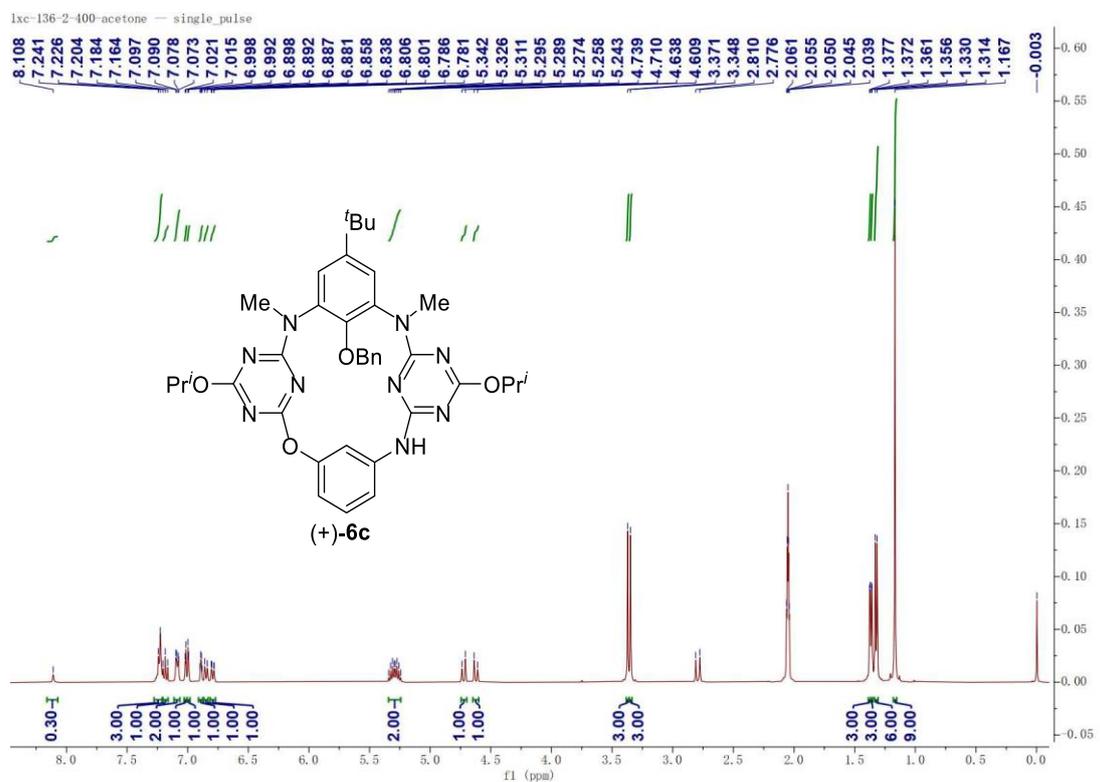
6a: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



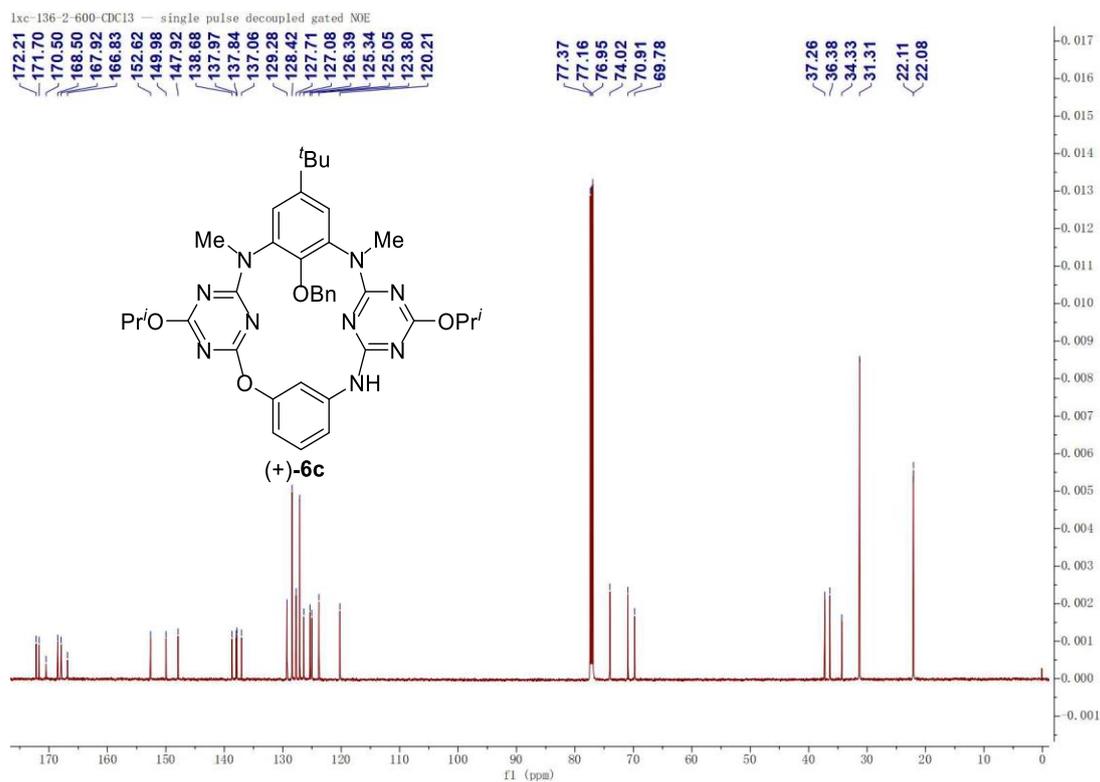
6b: ^{13}C NMR, 100 MHz, CDCl_3



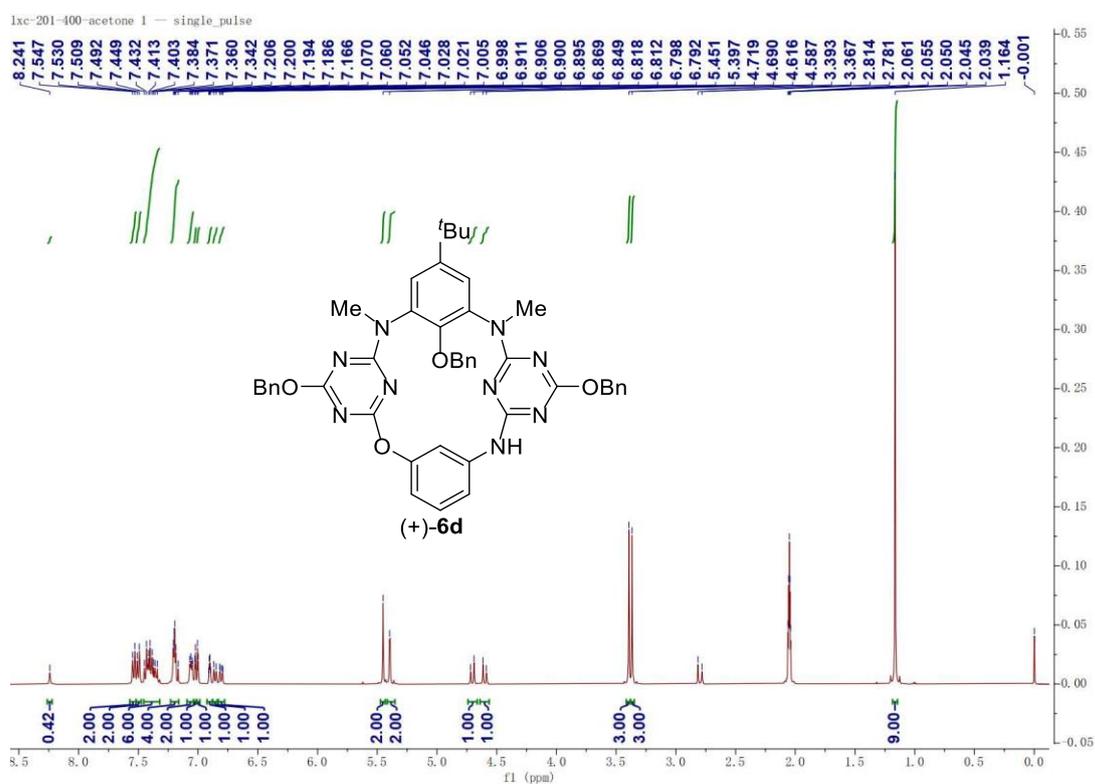
6c: ^1H NMR, 600 MHz, $\text{acetone-}d_6$



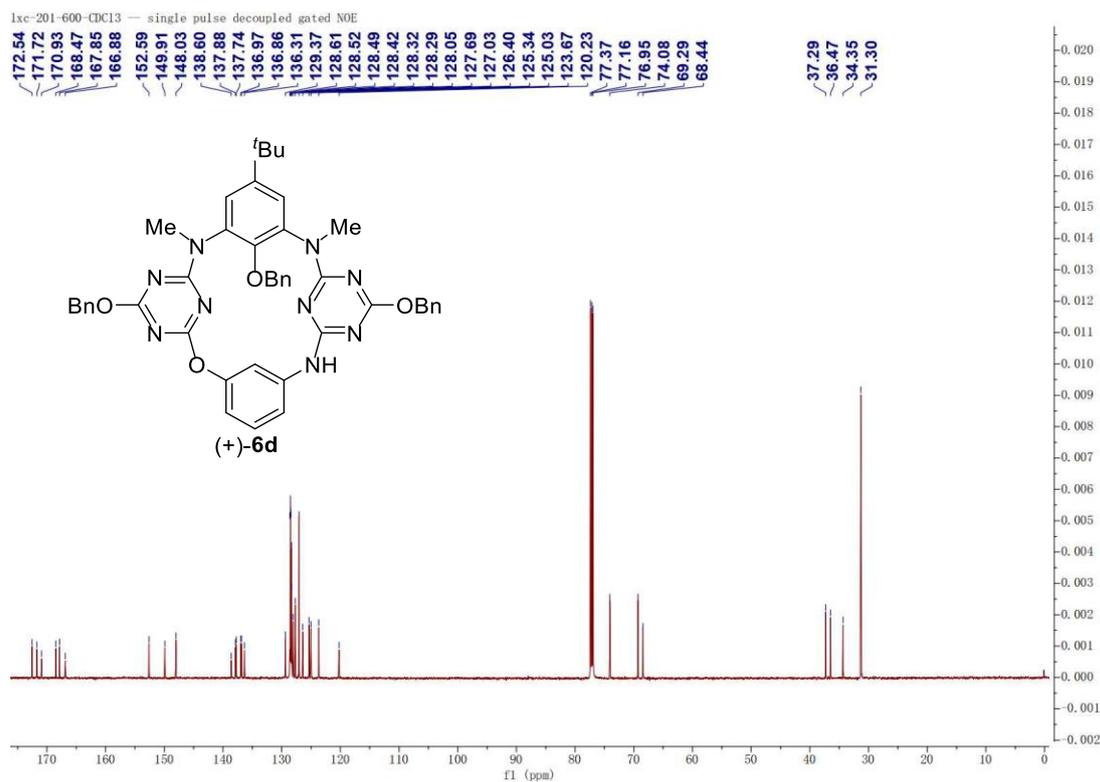
6c: ^{13}C NMR, 150 MHz, CDCl_3



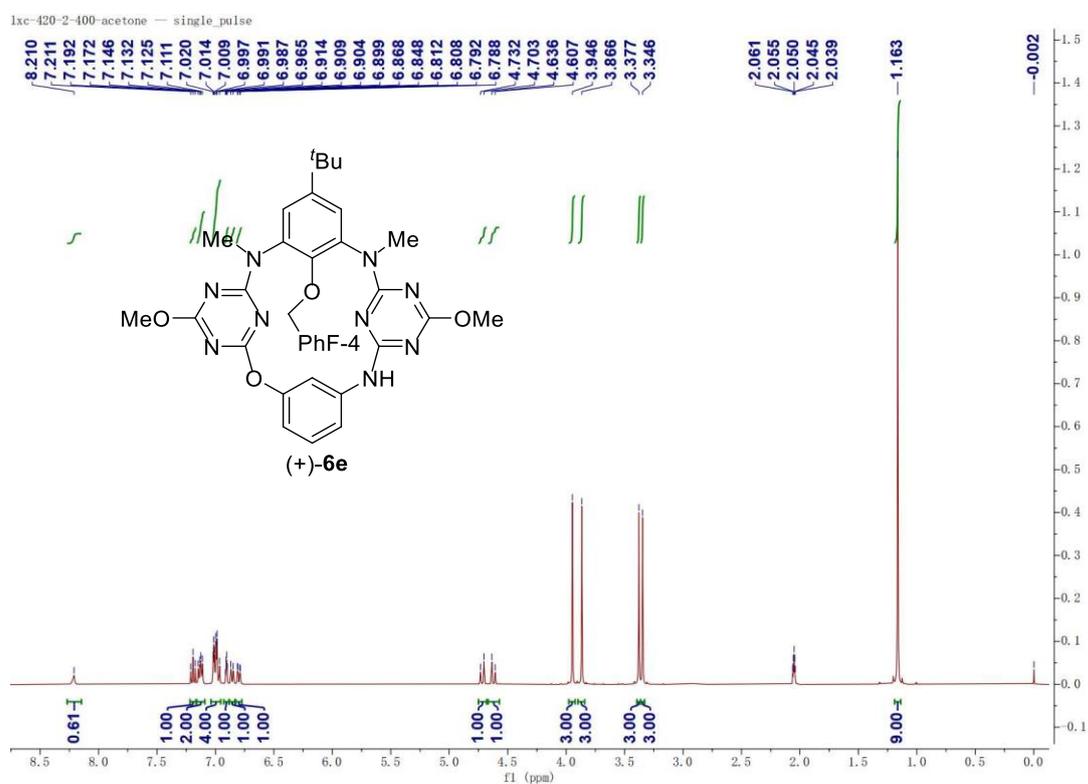
6d: ^1H NMR, 400 MHz, acetone- d_6



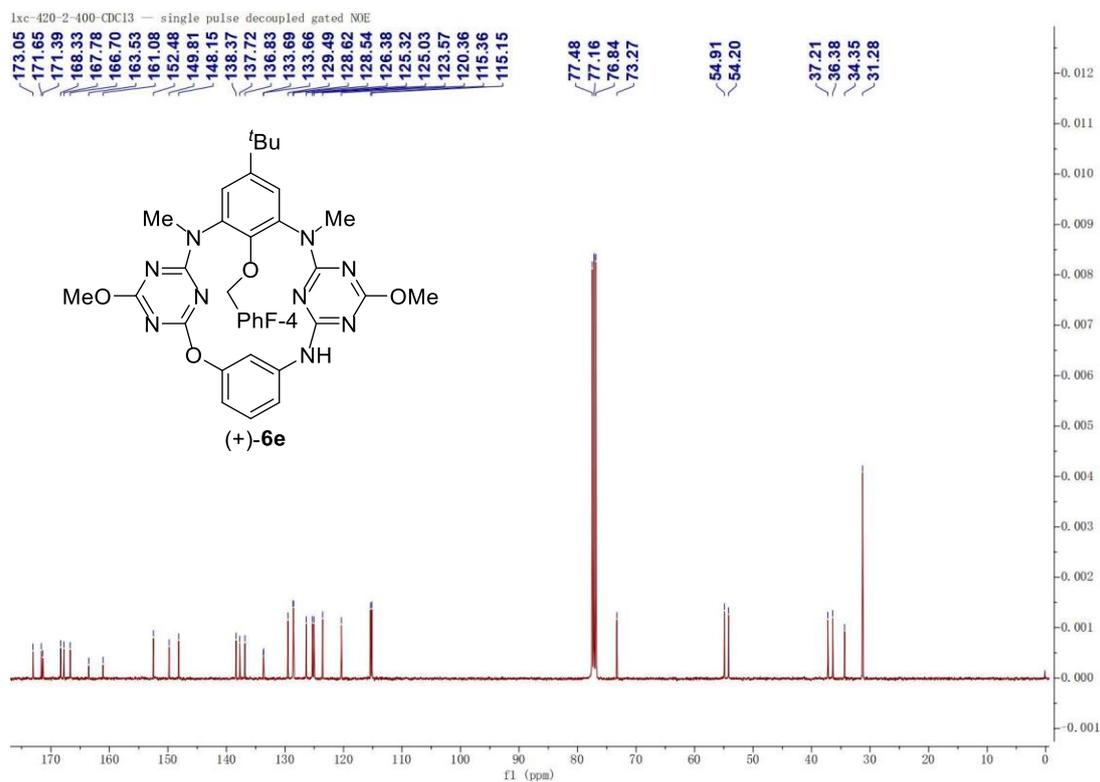
6d: ^{13}C NMR, 150 MHz, CDCl_3



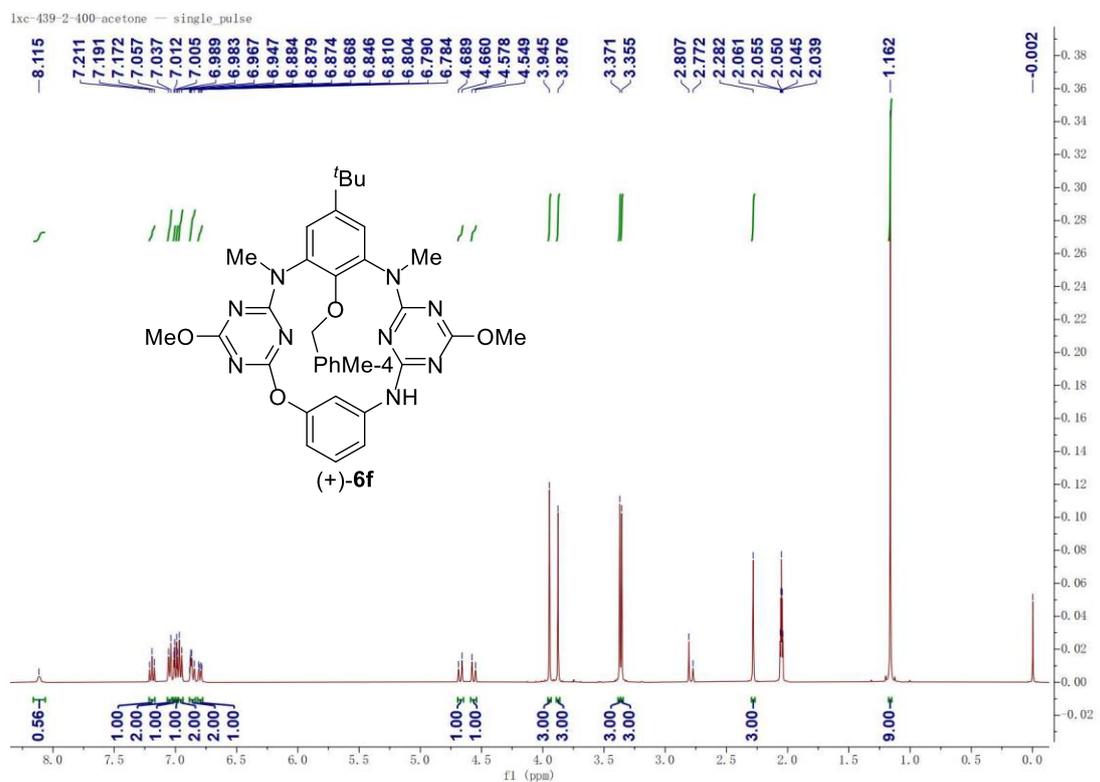
6e: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



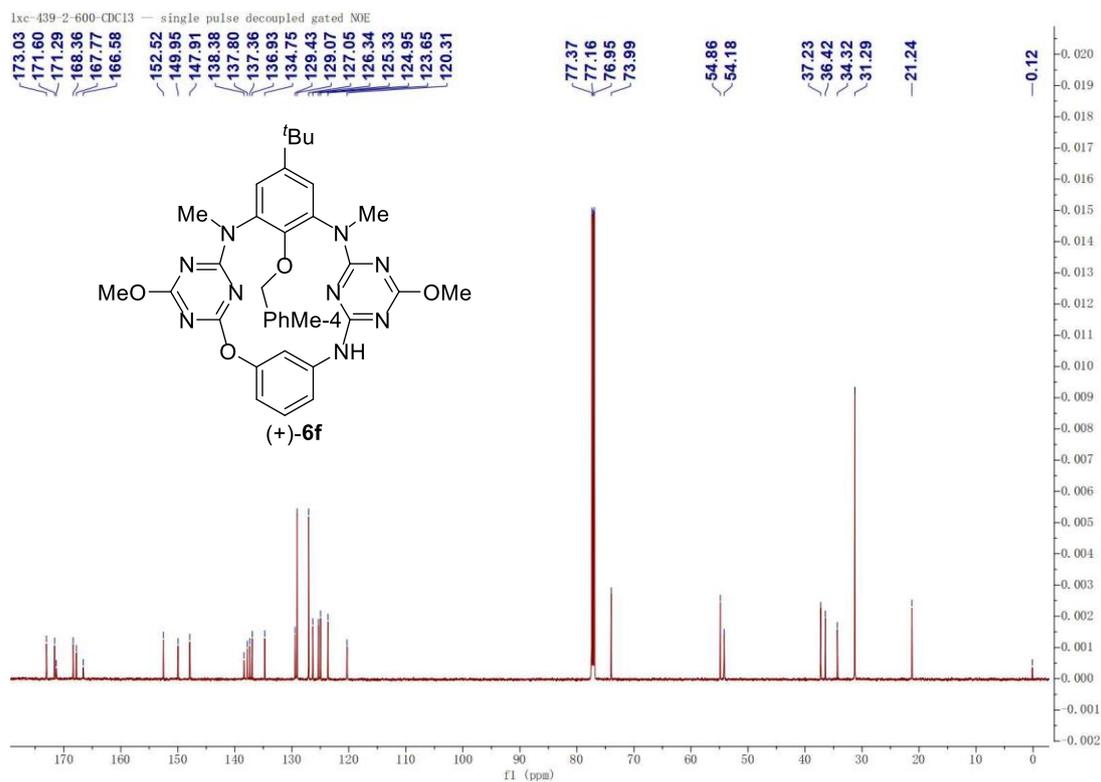
6e: ^{13}C NMR, 100 MHz, CDCl_3



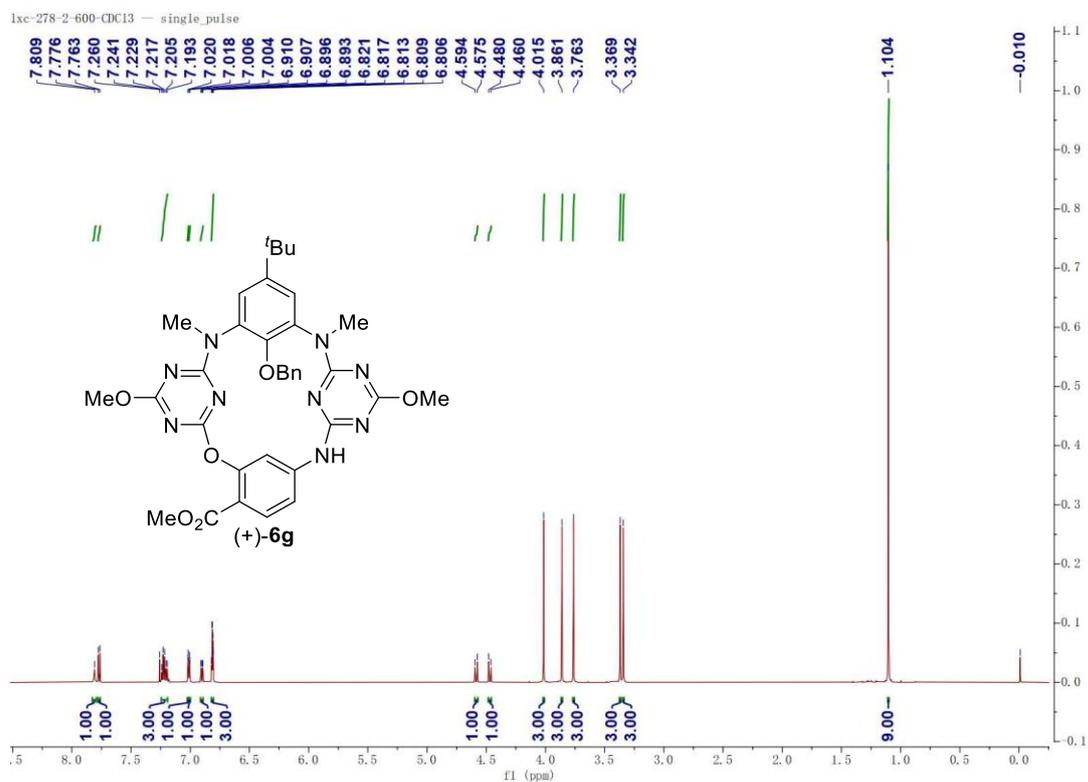
6f: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



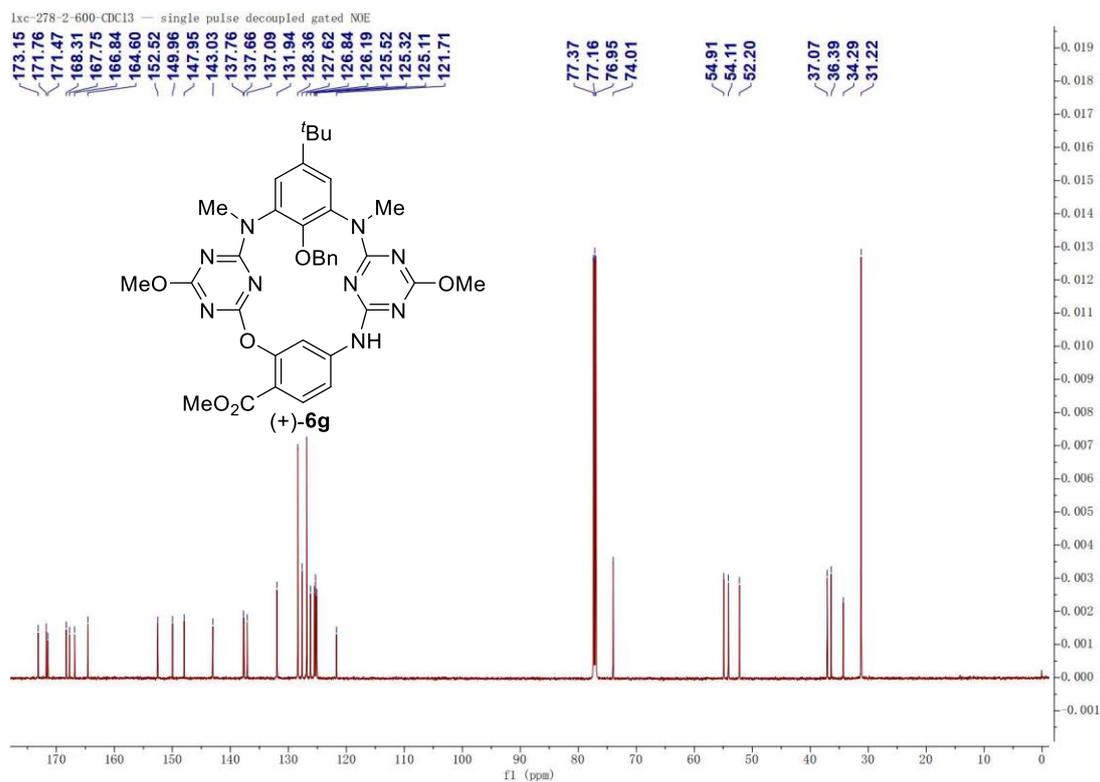
6f: ^{13}C NMR, 150 MHz, CDCl_3



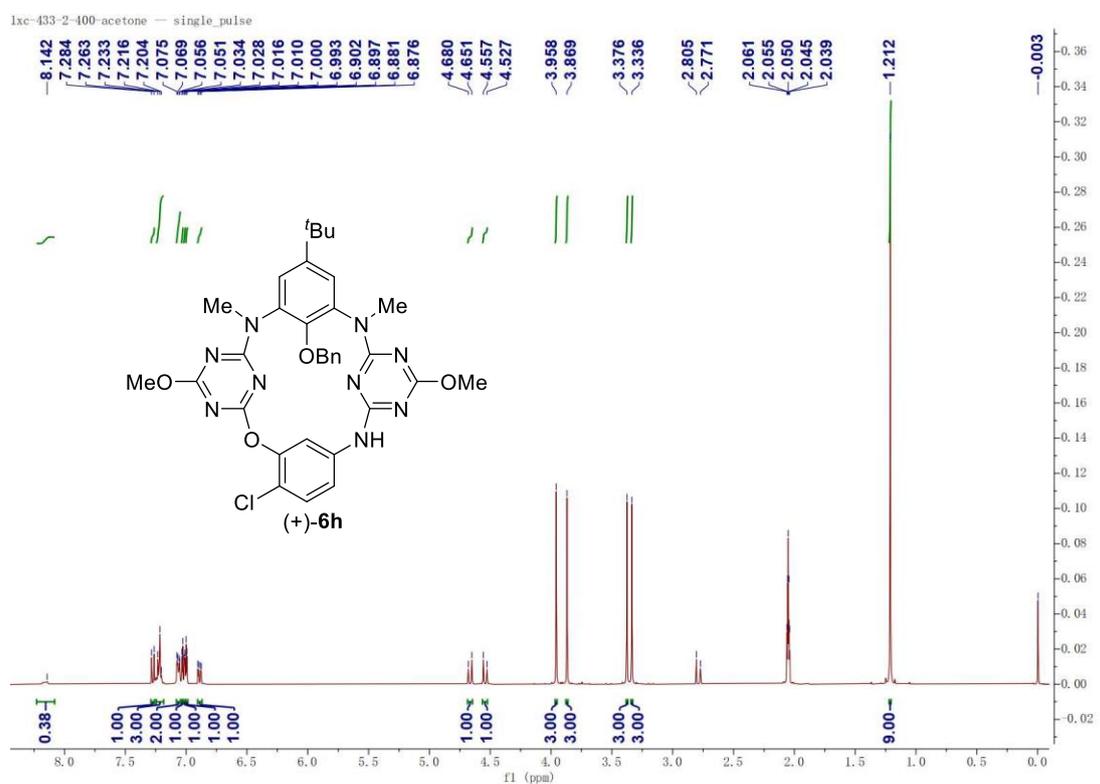
6g: ^1H NMR, 600 MHz, CDCl_3



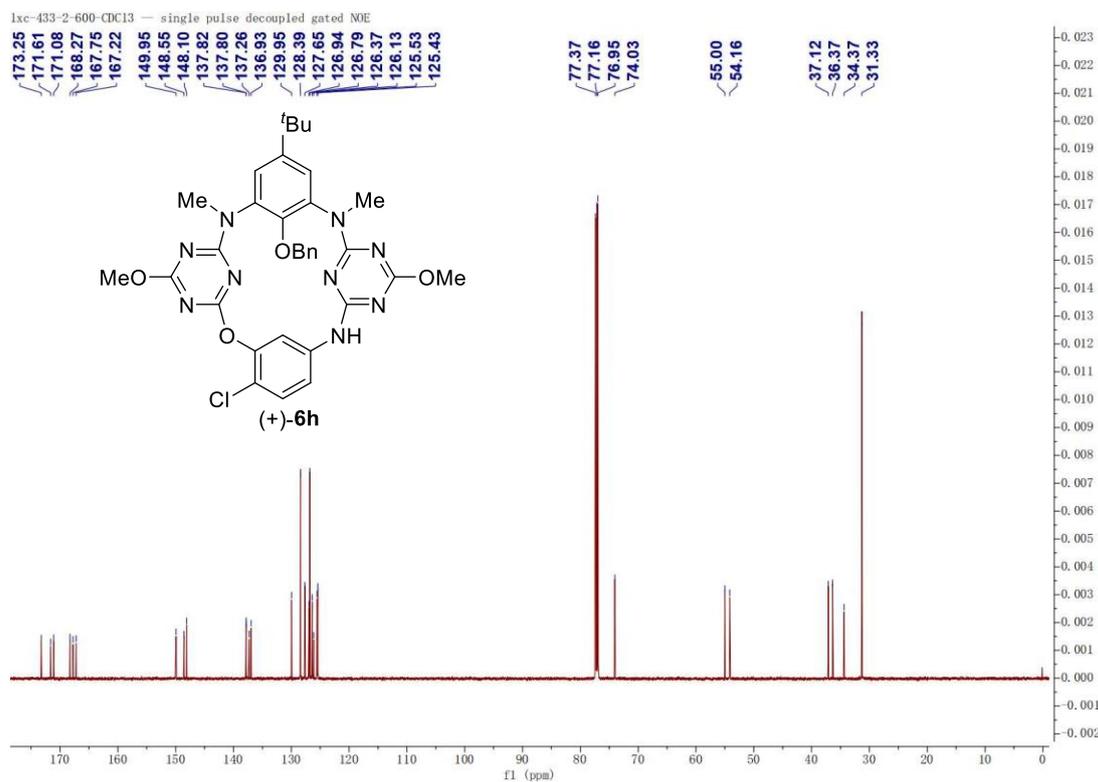
6g: ^{13}C NMR, 150 MHz, CDCl_3



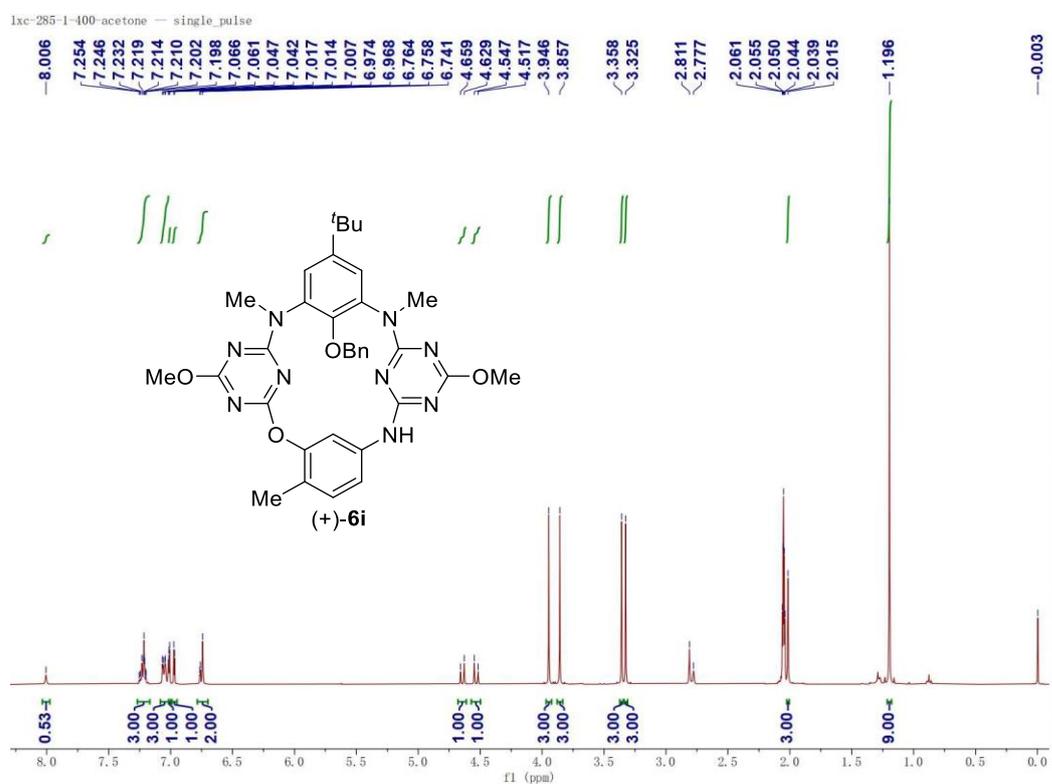
6h: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



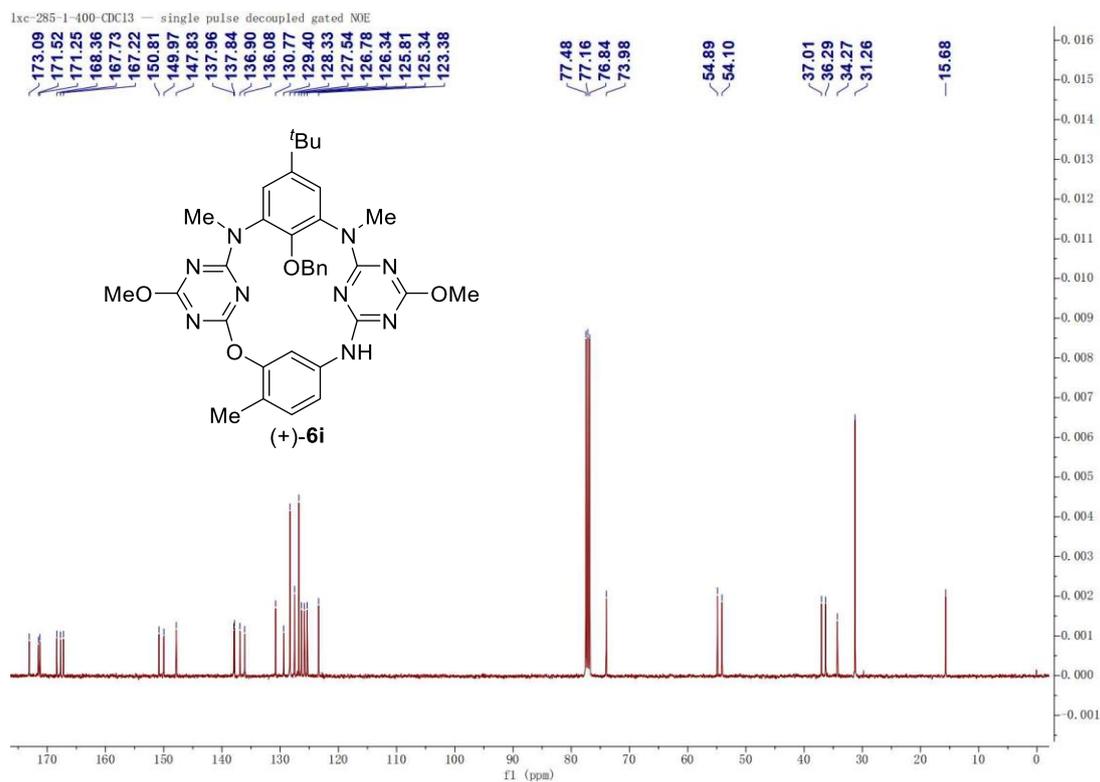
6h: ^{13}C NMR, 150 MHz, CDCl_3



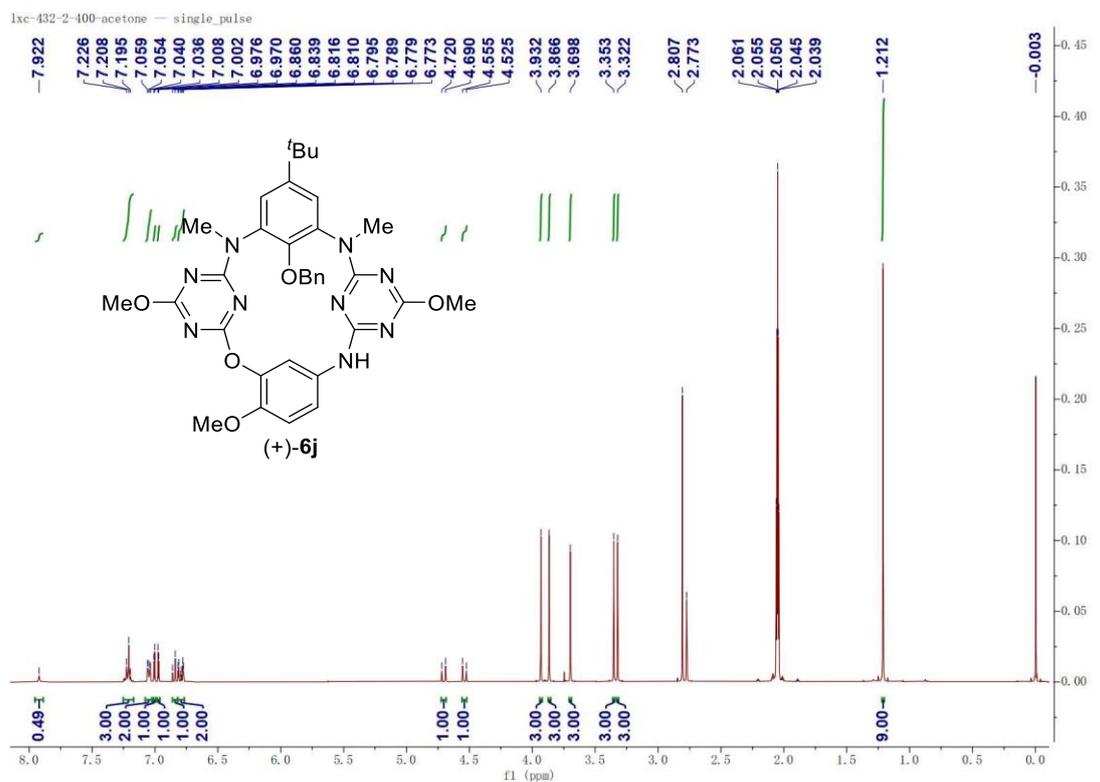
6i: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



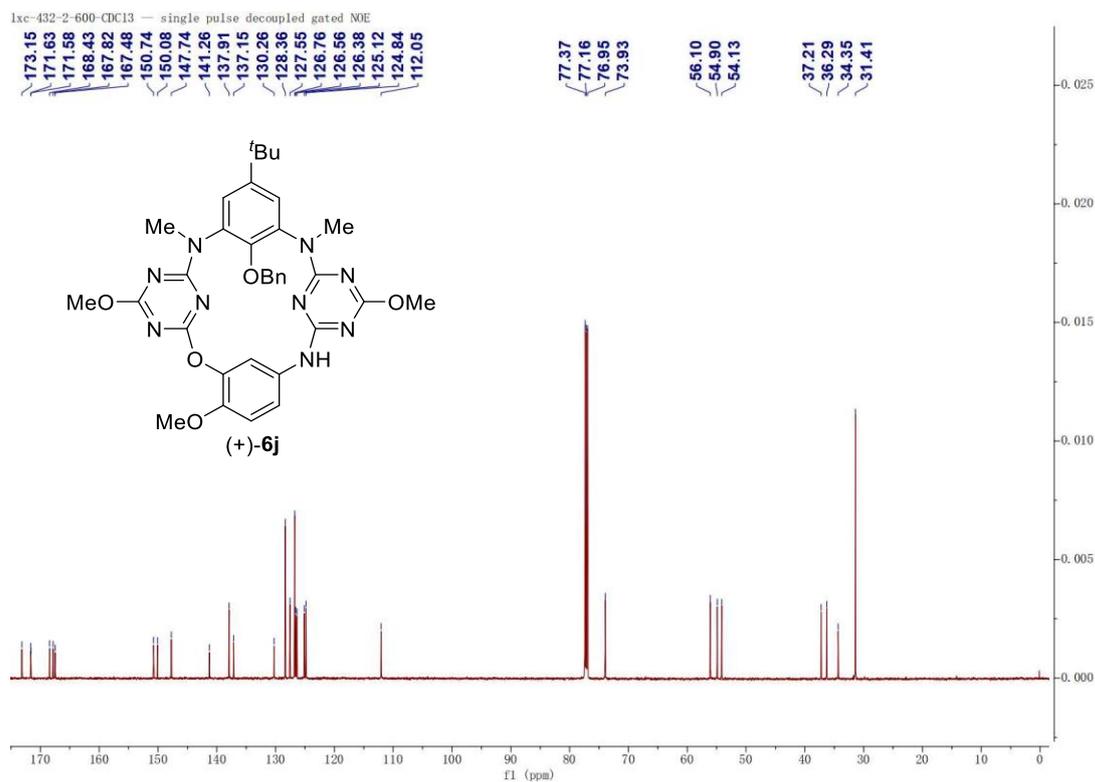
6i: ^{13}C NMR, 100 MHz, CDCl_3



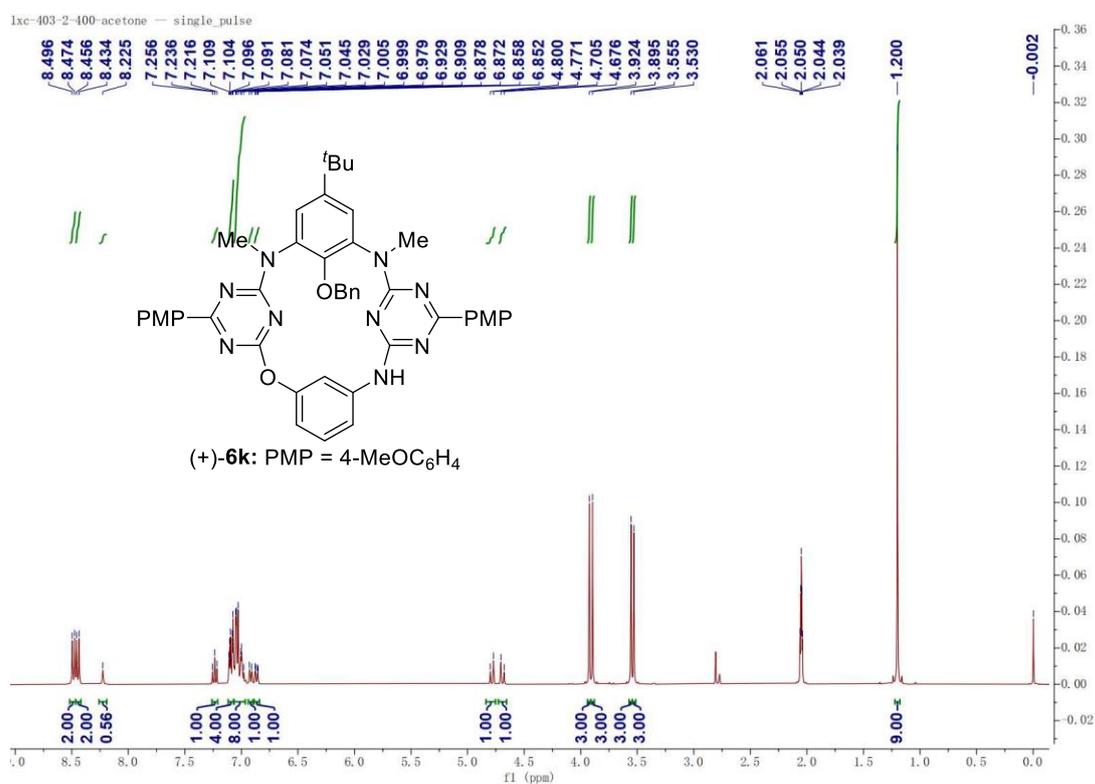
6j: ^1H NMR, 400 MHz, acetone- d_6



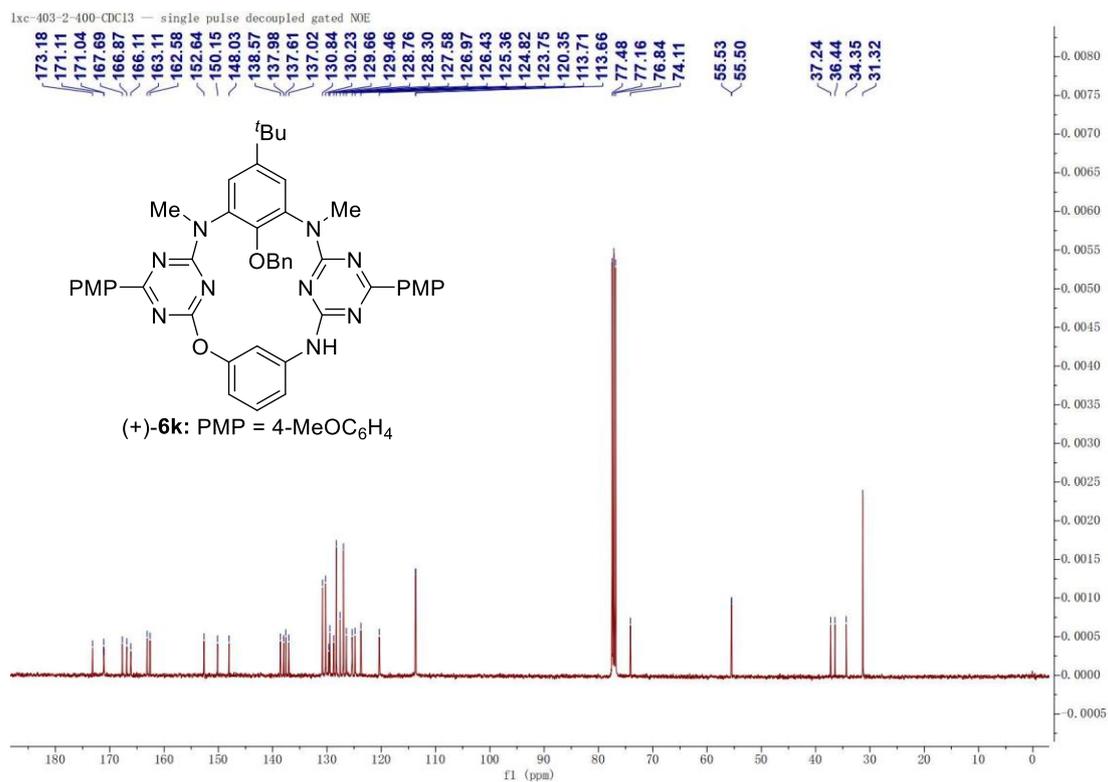
6j: ^{13}C NMR, 150 MHz, CDCl_3



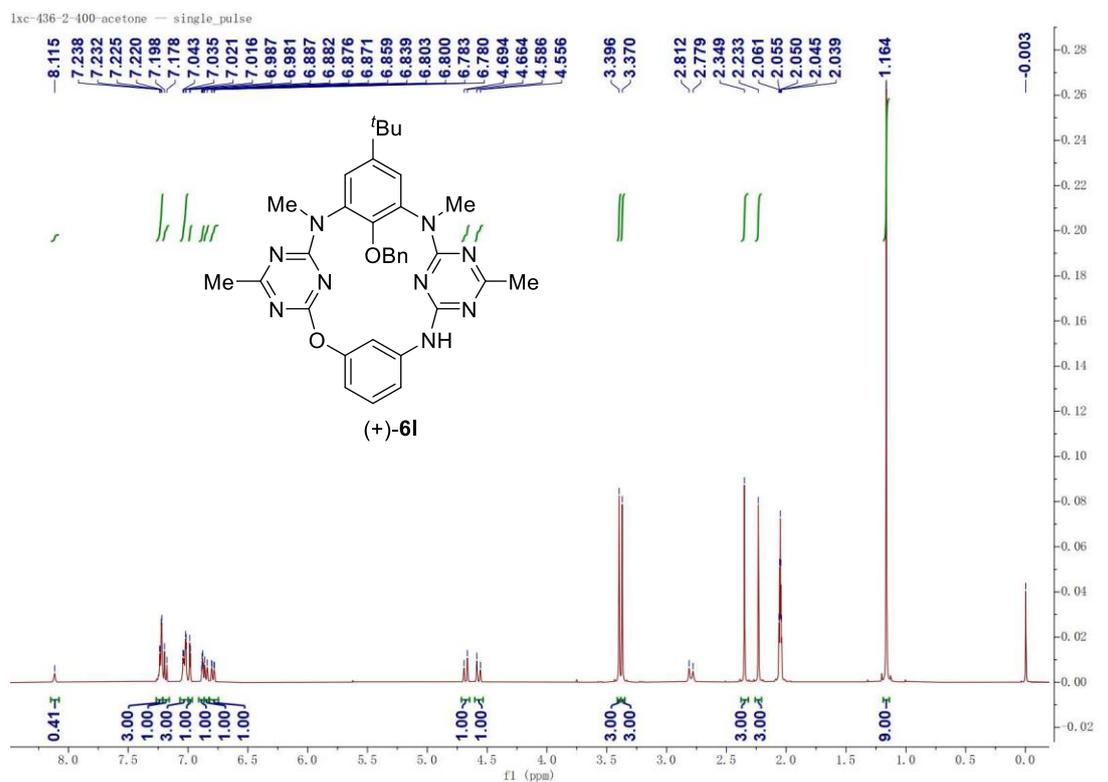
6k: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



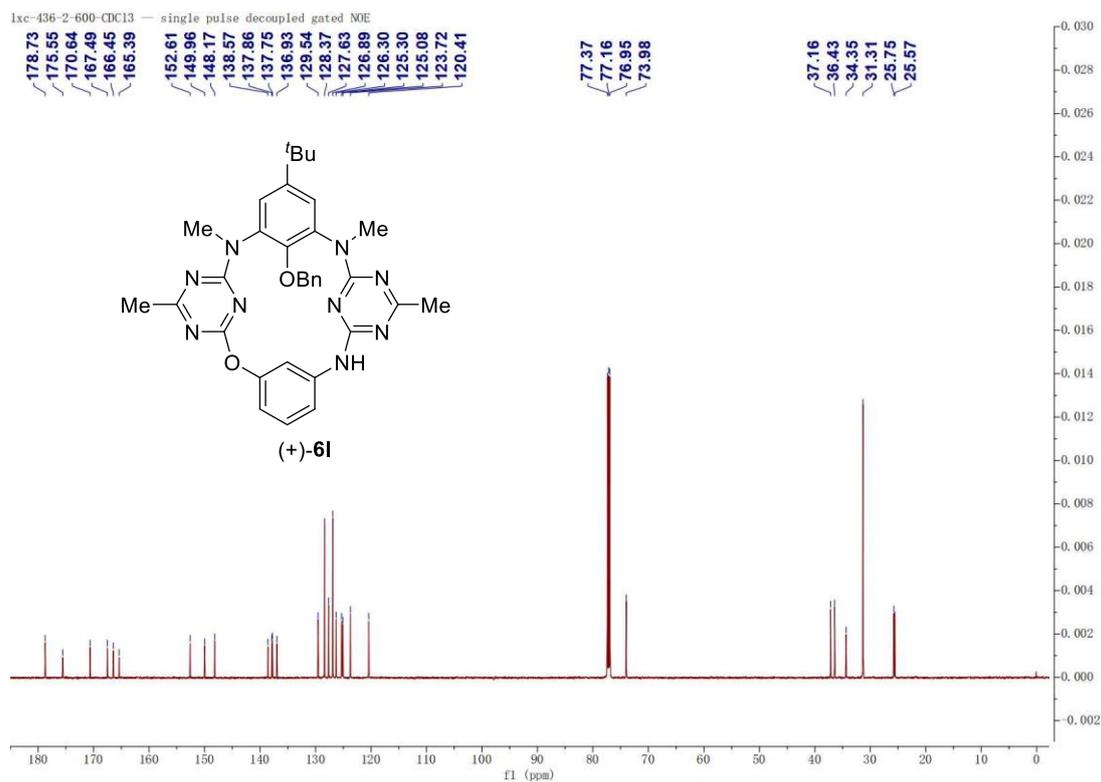
6k: ^{13}C NMR, 100 MHz, CDCl_3



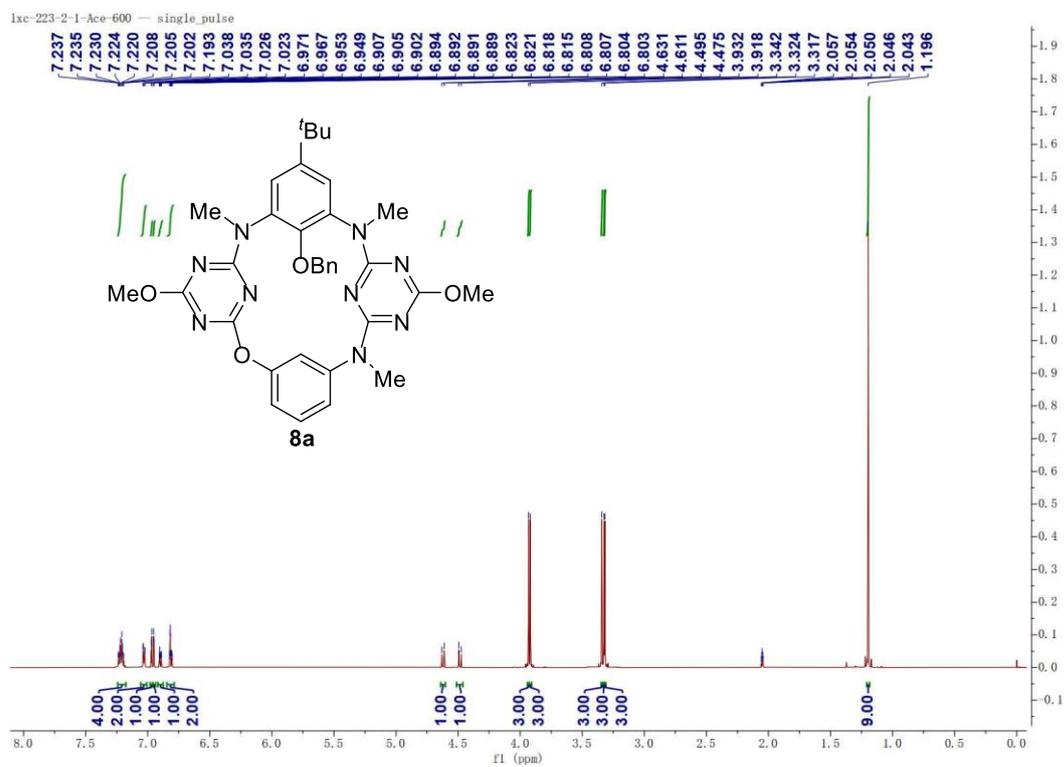
6l: ^1H NMR, 400 MHz, $\text{acetone-}d_6$



6l: ^{13}C NMR, 150 MHz, CDCl_3

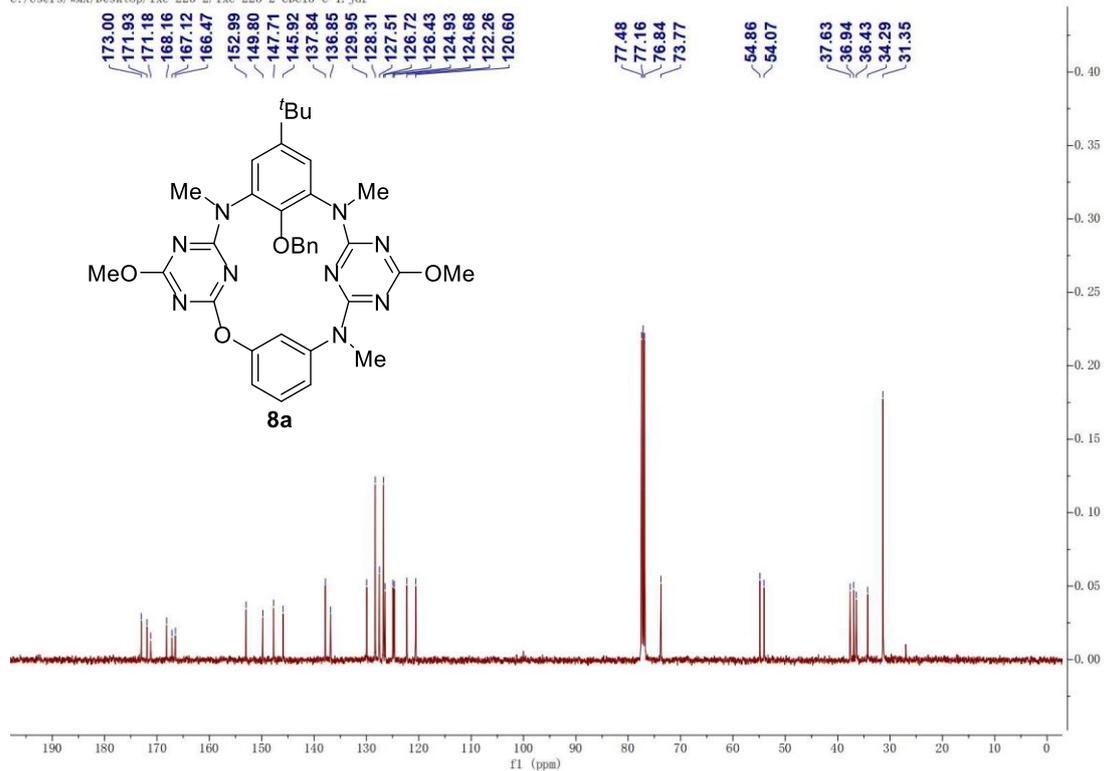


8a: ^1H NMR, 600 MHz, CDCl_3



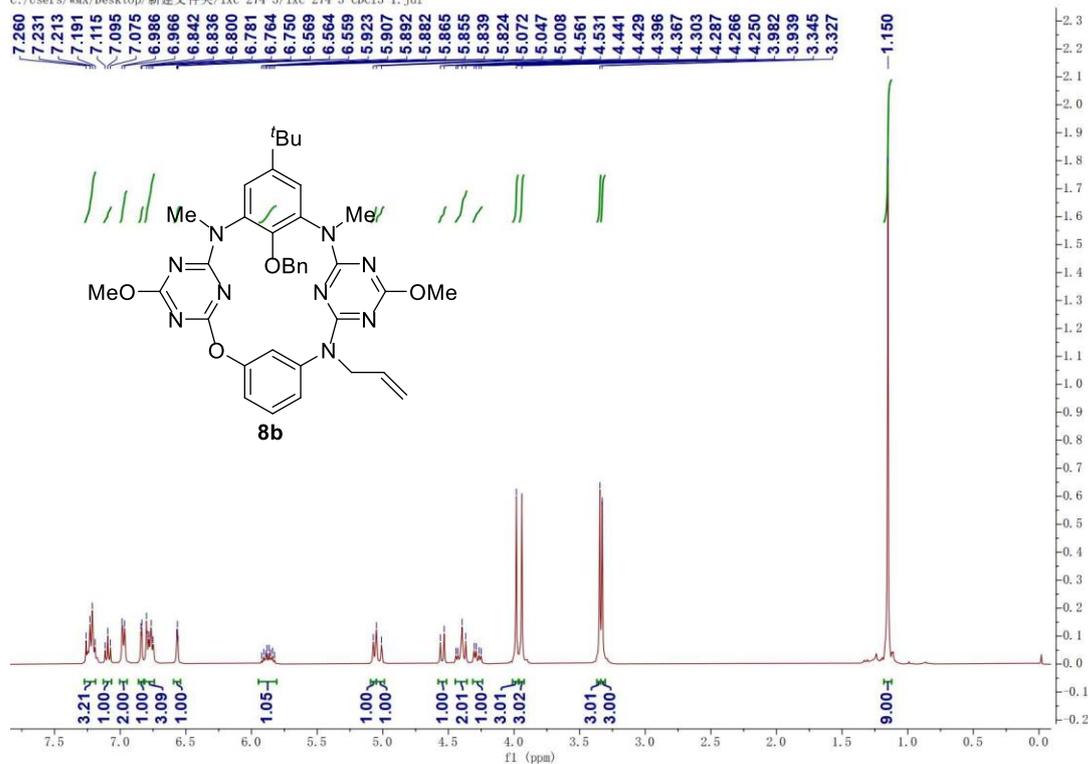
8a: ^{13}C NMR, 100 MHz, CDCl_3

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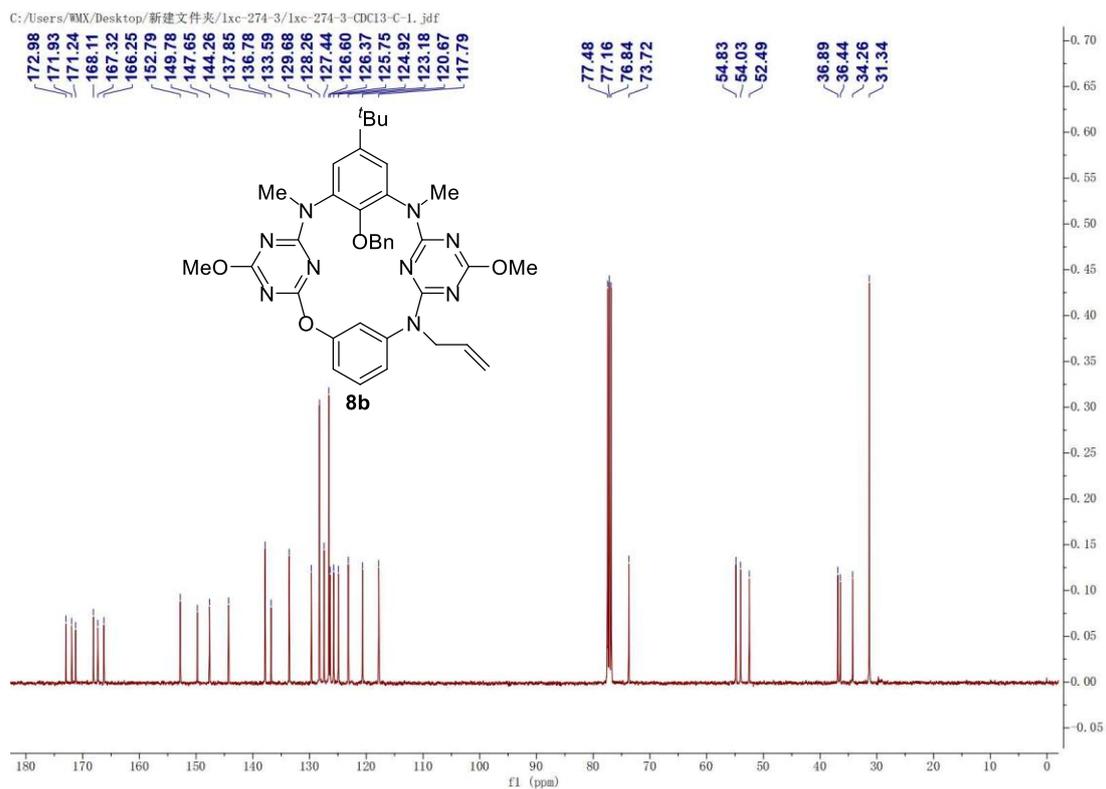


8b: ^1H NMR, 600 MHz, CDCl_3

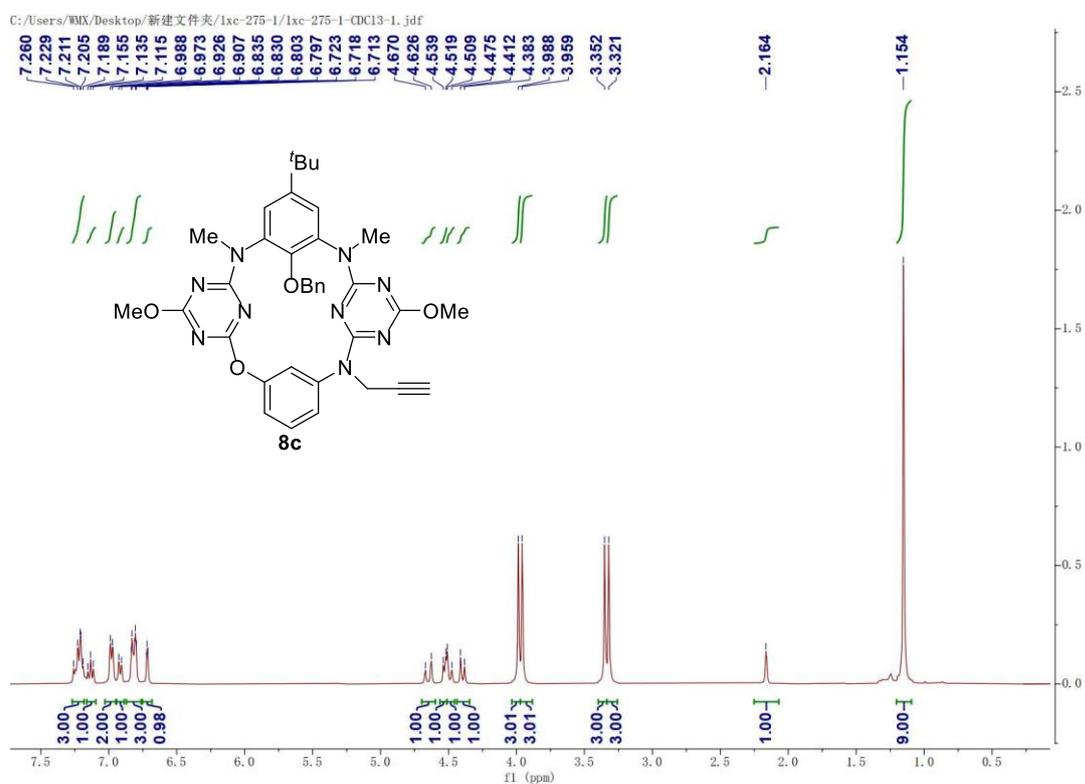
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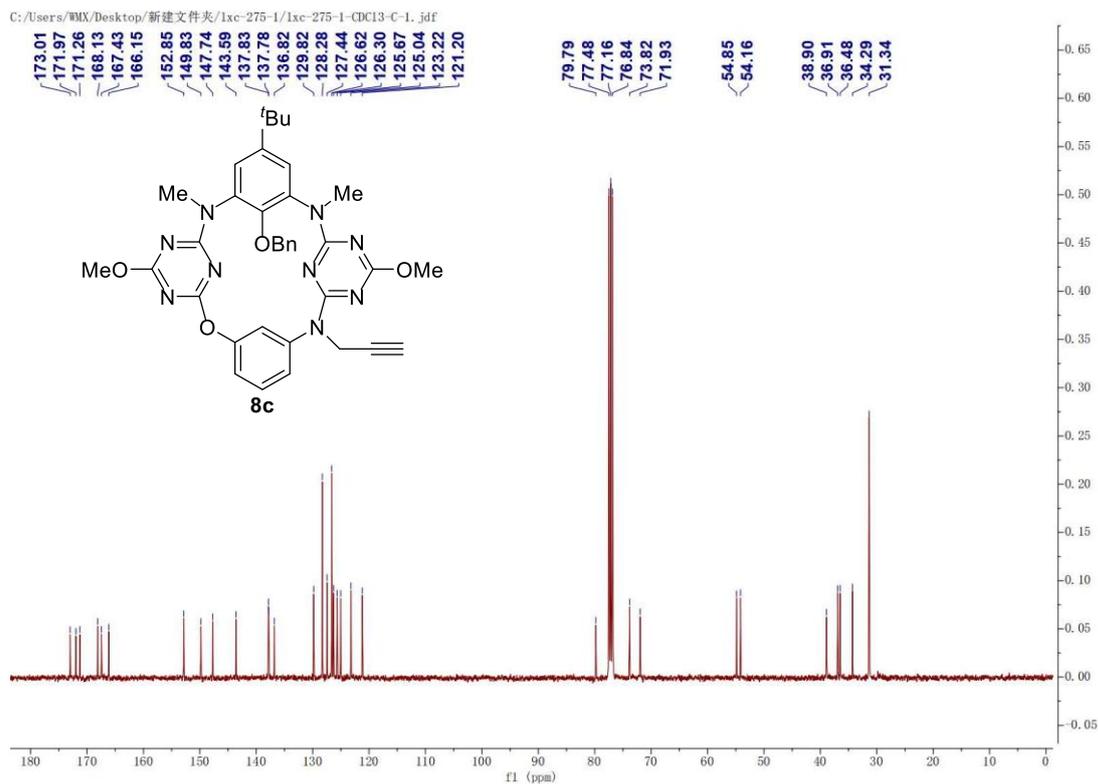
8b: ^{13}C NMR, 100 MHz, CDCl_3



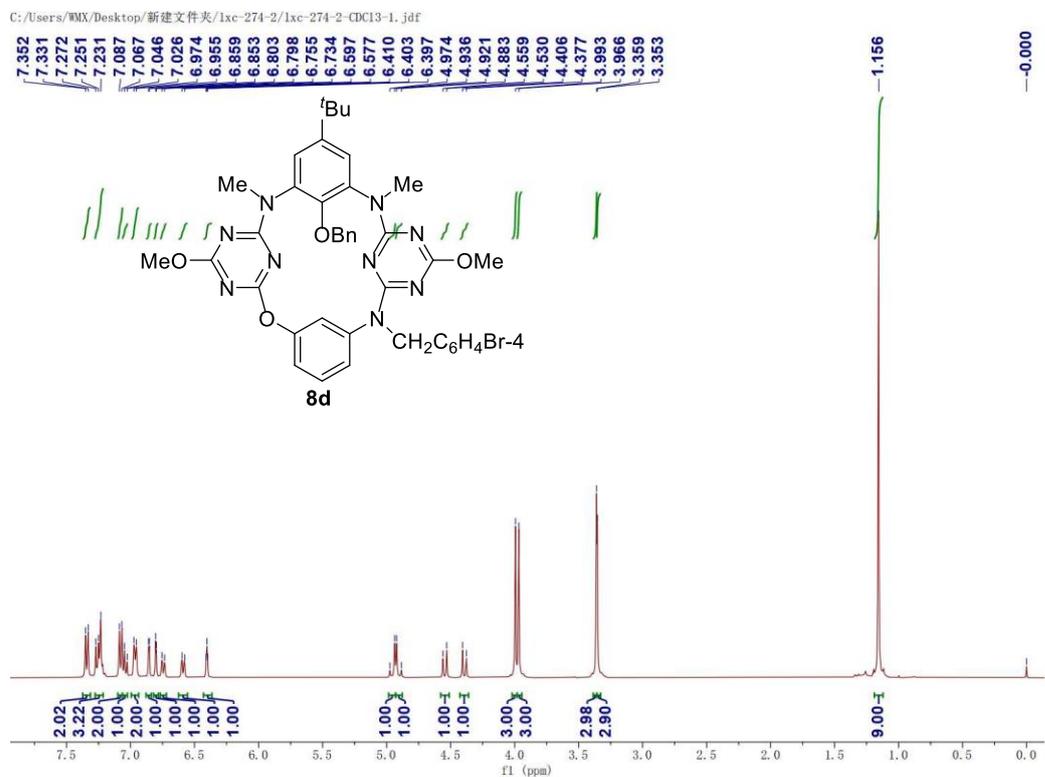
8c: ^1H NMR, 400 MHz, CDCl_3



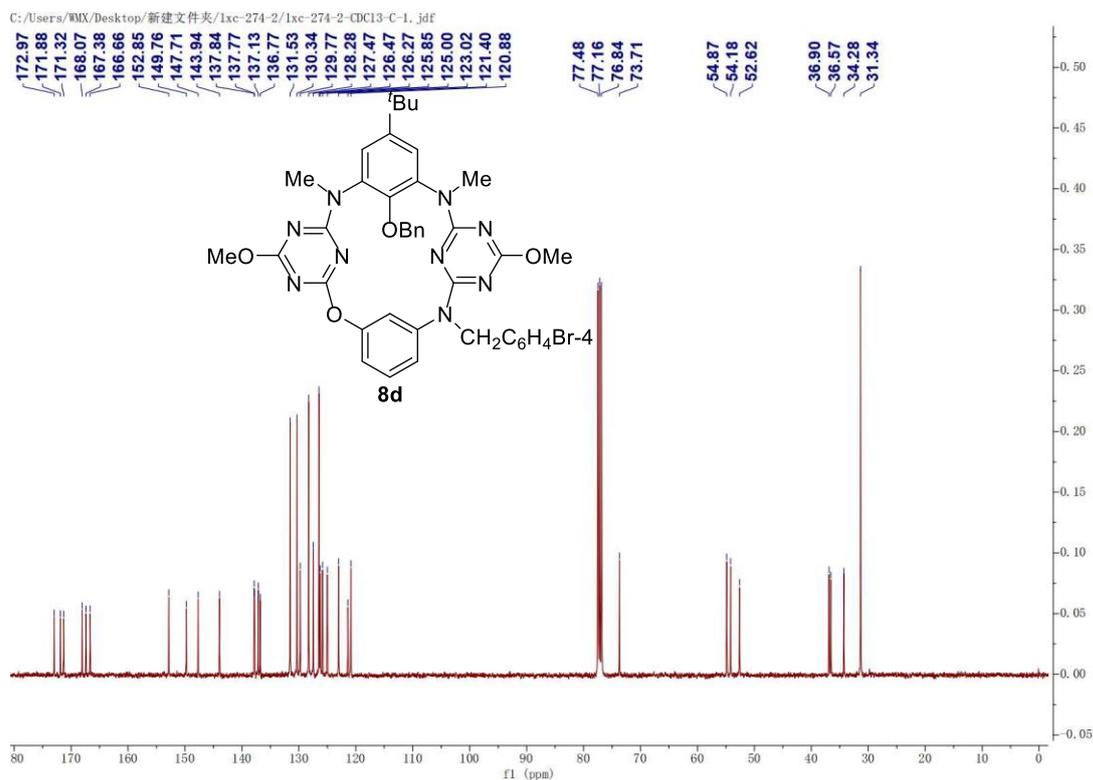
8c: ^{13}C NMR, 100 MHz, CDCl_3



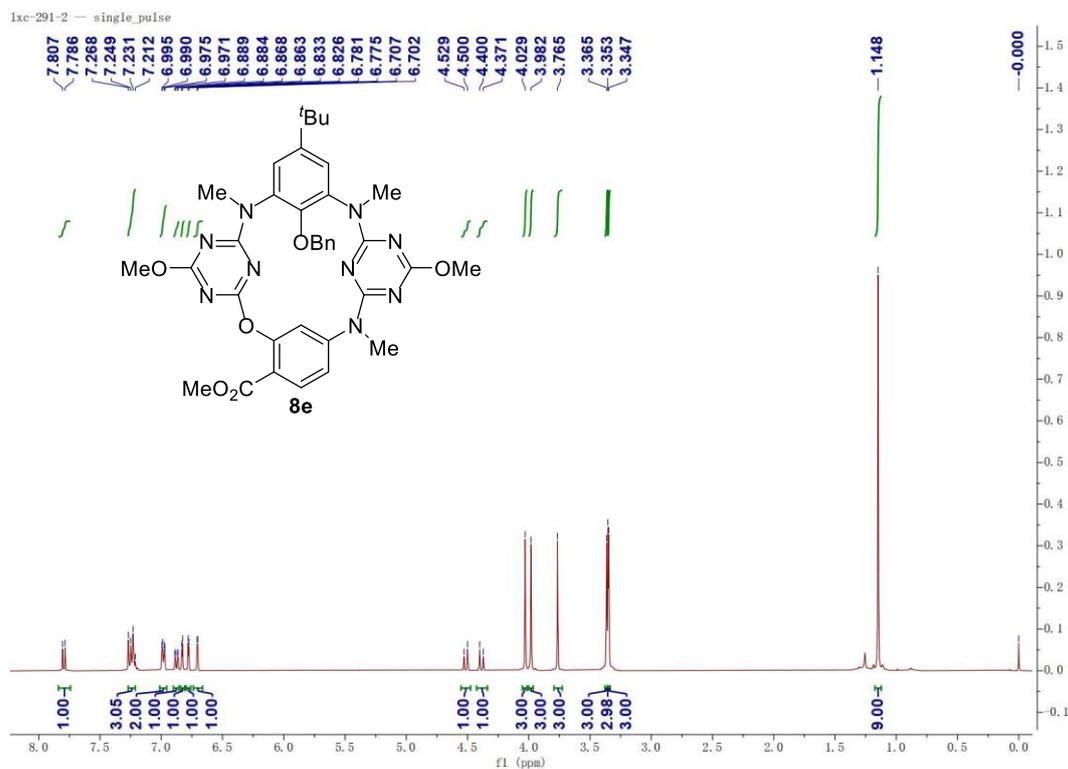
8d: ¹H NMR, 400 MHz, CDCl₃



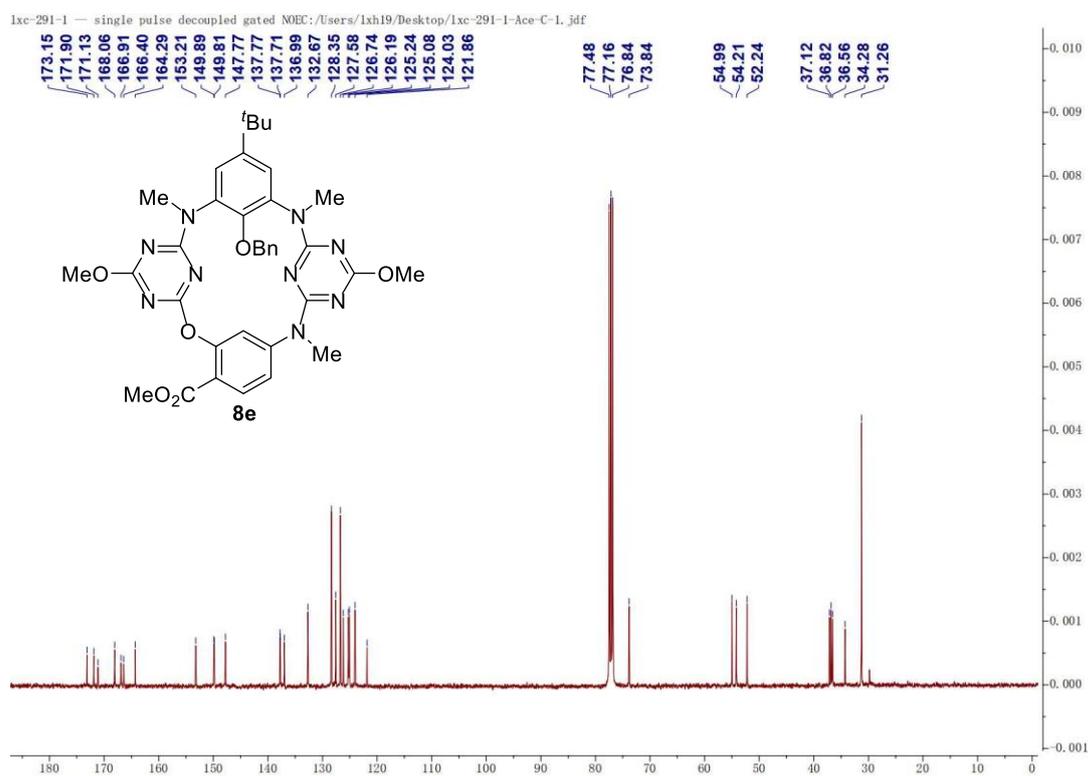
8d: ^{13}C NMR, 100 MHz, CDCl_3



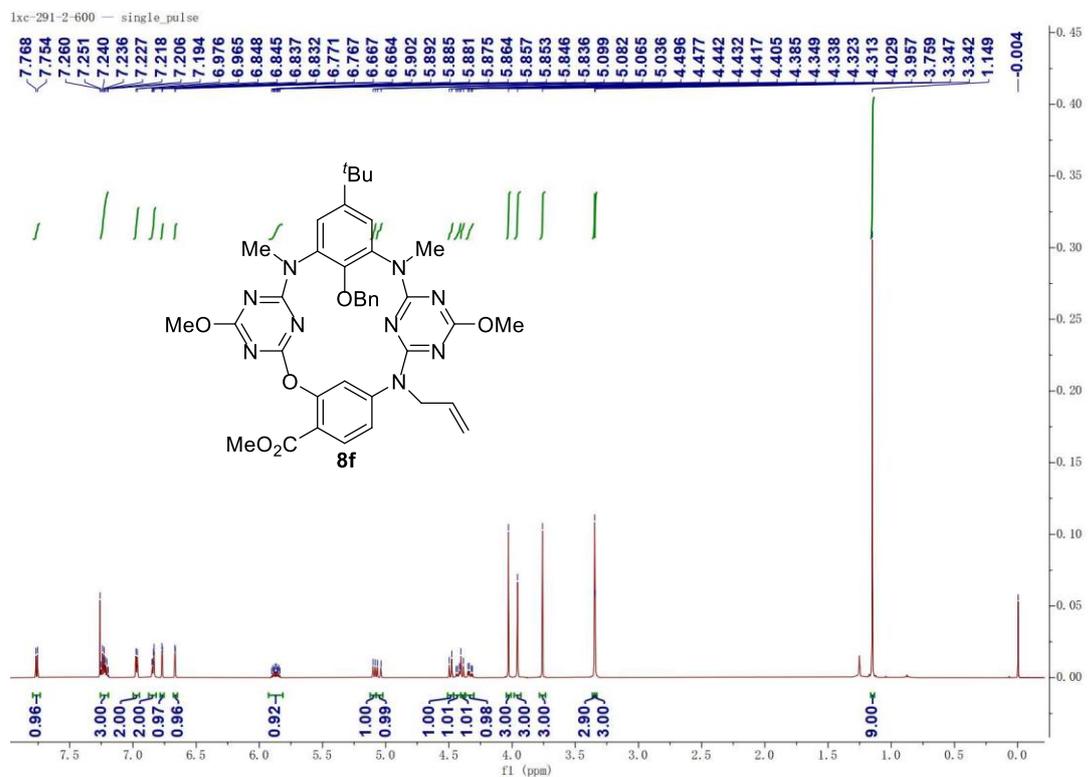
8e: ^1H NMR, 400 MHz, CDCl_3



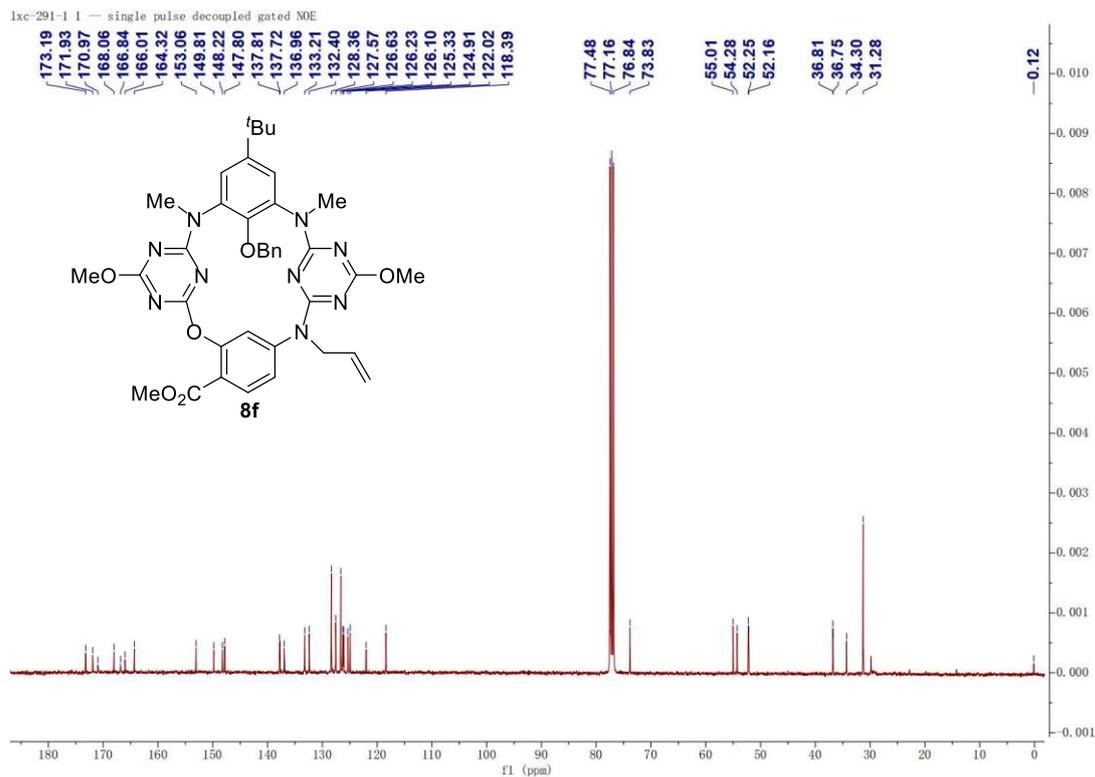
8e: ^{13}C NMR, 100 MHz, CDCl_3



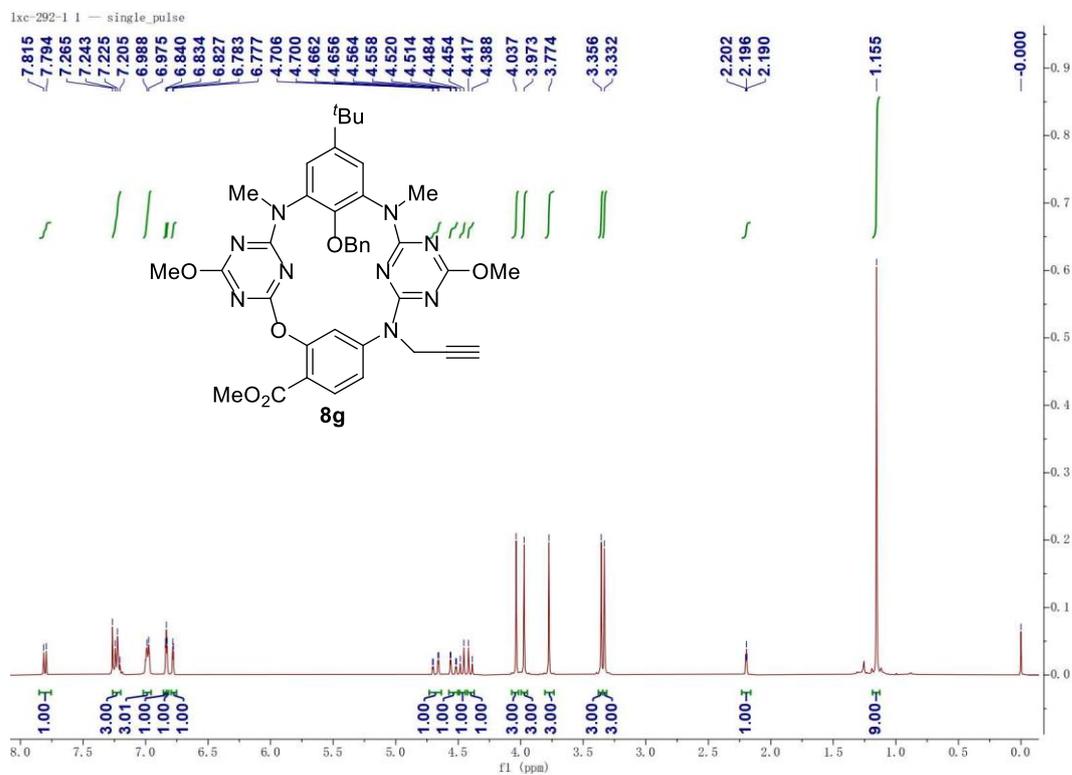
8f: ^1H NMR, 600 MHz, CDCl_3



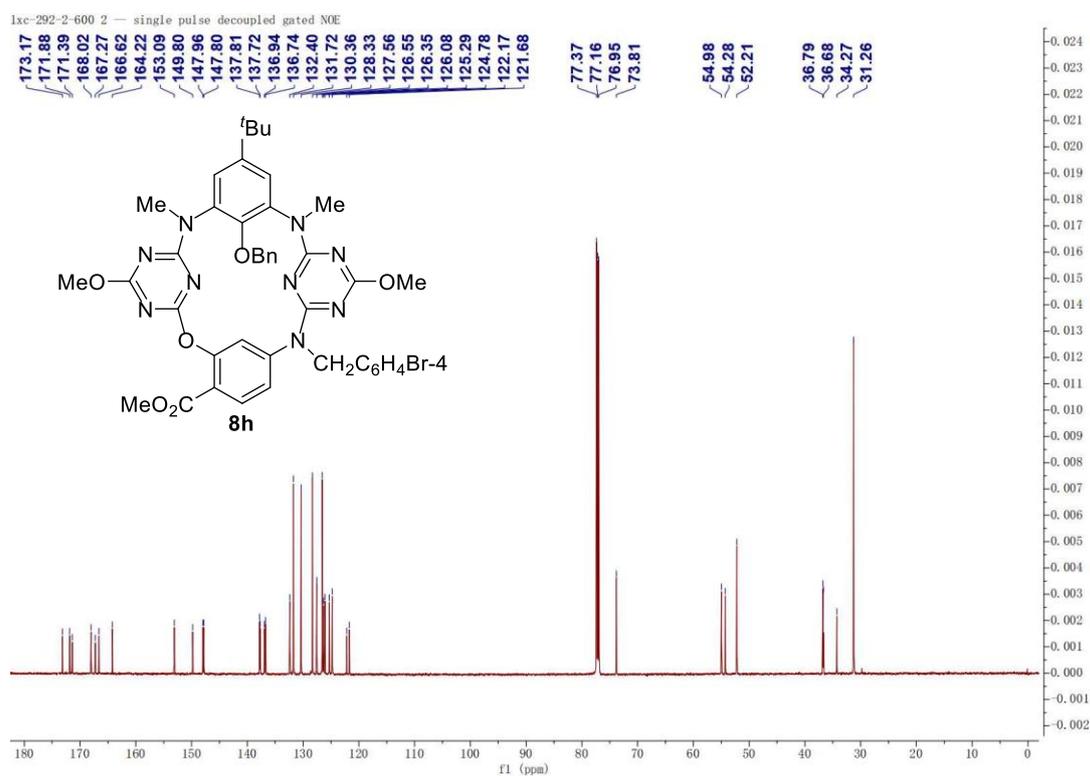
8f: ^{13}C NMR, 100 MHz, CDCl_3



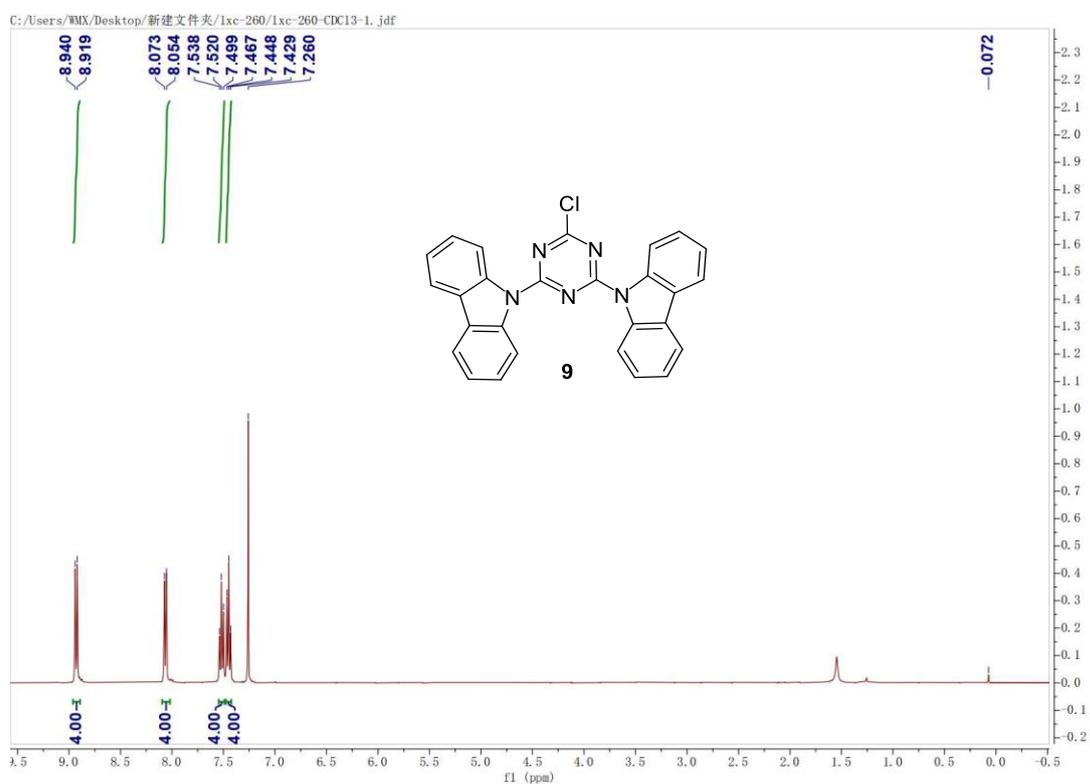
8g: ¹H NMR, 400 MHz, CDCl₃



8h: ^{13}C NMR, 150 MHz, CDCl_3

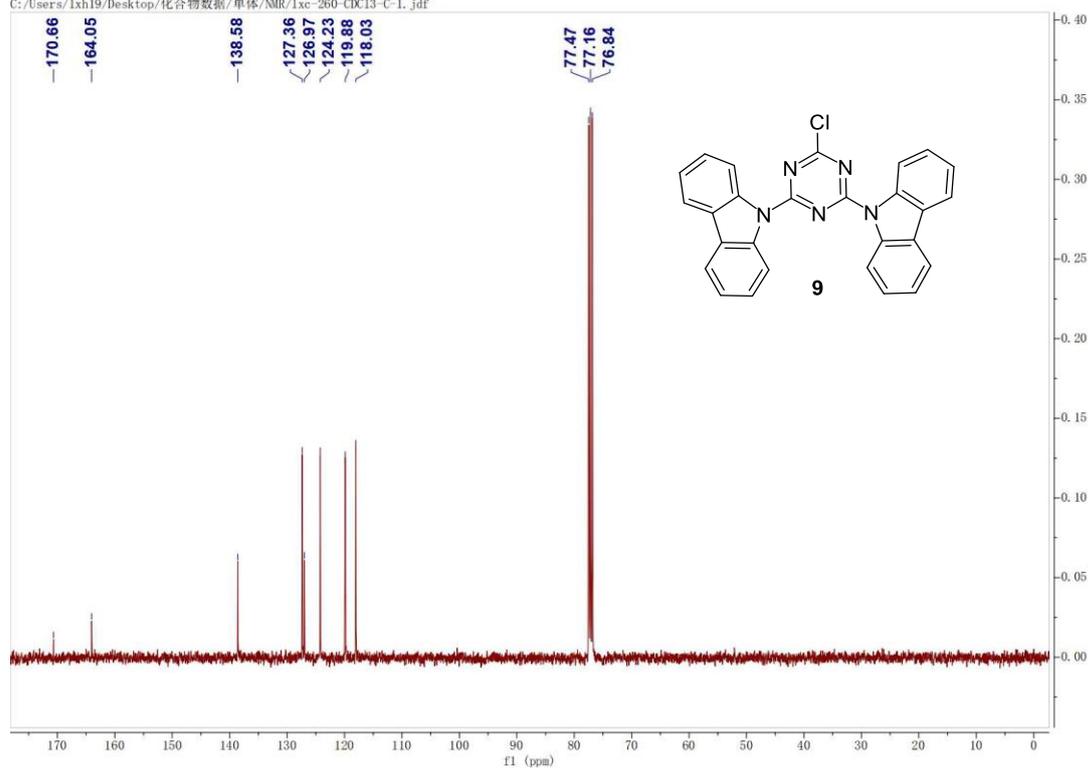


9: ^1H NMR, 400 MHz, CDCl_3



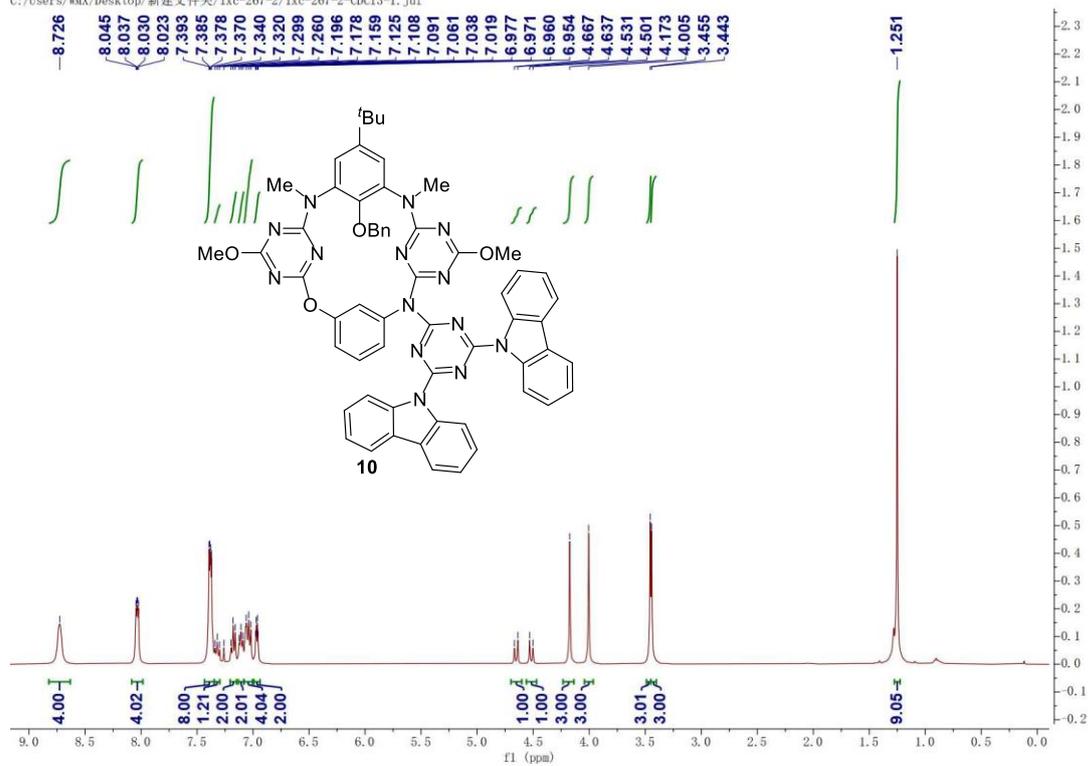
9: ^{13}C NMR, 100 MHz, CDCl_3

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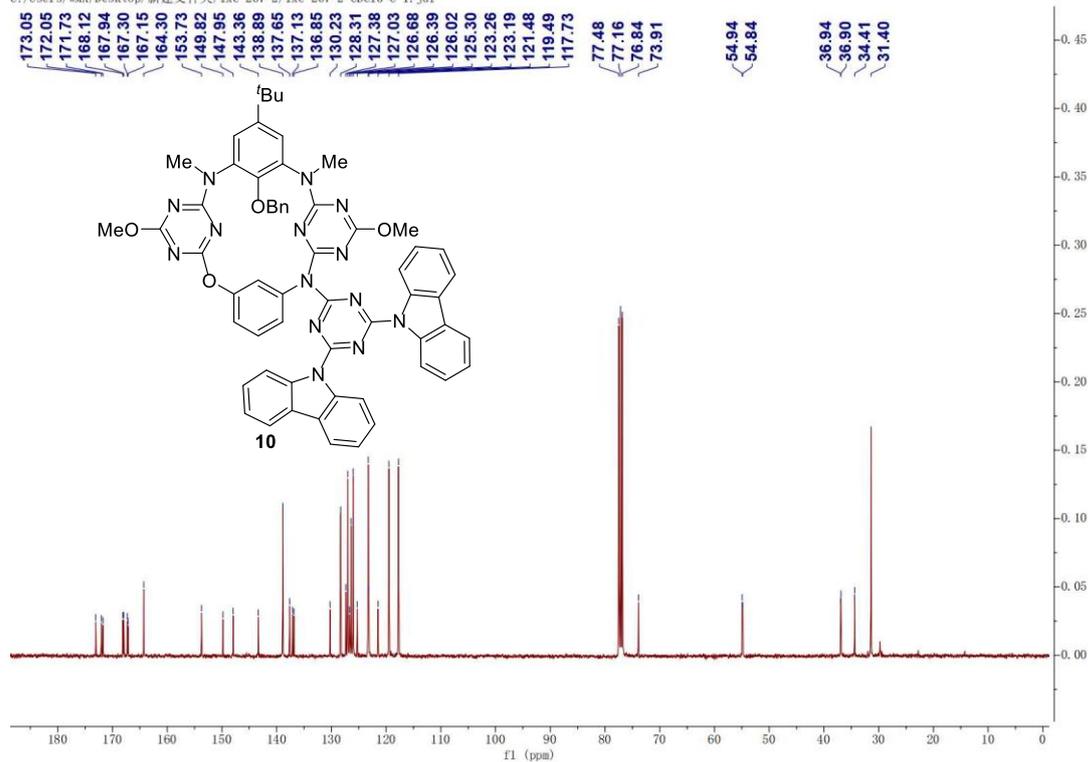
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10: ^{13}C NMR, 100 MHz, CDCl_3

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15. Details of theoretical calculations

Mechanism of catalytic enantioselective macrocyclization

All geometrical optimizations were carried out with the Gaussian16 suite of program at the M06-2X/6-31G(d,p) level.

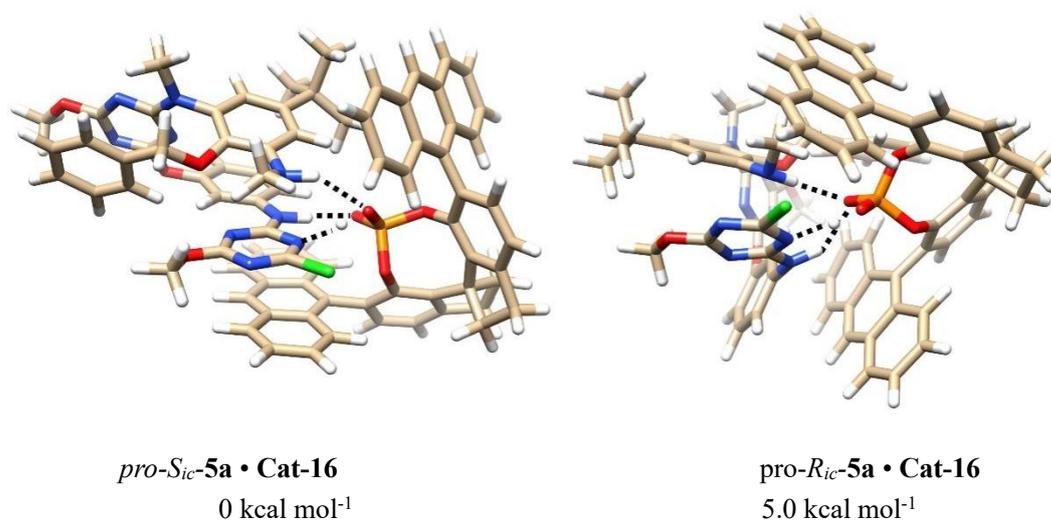


Figure S28. Optimized structures (at M06-2X/6-31G(d,p) level) of complexes between **Cat-16** and substrate **5a** which lead to the formation of *Sic-6a* (left) and *Ric-6a* (right), respectively. The zero point energy suggests that complex *pro-Sic-5a•Cat-16* (left) was favored. This was in line with

observed enantioselectivity.

Geometrical coordinates of the optimized structures

Table S10 Cartesian coordinates:

pro-S_{ic}-5a•Cat-16

C	6.88890900	0.64274700	1.67649100
C	7.79131800	-0.45324400	2.19153300
C	7.12632800	-1.71323600	1.61492700
C	6.09164800	0.16761500	0.62884200
H	6.31095800	-2.03222500	2.27307700
C	6.51164100	-1.24732900	0.26290900
C	5.55159300	-2.29175700	-0.27162600
C	6.24384600	-3.22607400	-1.04428500
C	7.60047800	-1.28020700	-0.84609300
C	7.66400800	-2.76048800	-1.27465400
C	5.60200800	-4.37075200	-1.49831800
C	4.19295100	-2.45644200	-0.05334700
C	3.50823700	-3.59236400	-0.50434700
C	4.25439000	-4.55533600	-1.19922900
H	3.74066200	-5.44788900	-1.54290800
H	6.13605800	-5.11147400	-2.08571600
C	5.11720500	1.00273400	0.09613300
C	6.76496300	1.94630600	2.13545100
C	5.81921100	2.78043900	1.54816200
H	5.70515300	3.80506200	1.88901500
C	4.96917700	2.32392300	0.53418100
H	7.38760700	2.30887200	2.94765700
C	2.31928800	-3.60236300	2.19864100
C	1.52020700	-3.82273800	1.02874000
C	1.76511700	-3.58946200	3.44423000
C	2.04781100	-3.79726900	-0.28106000
C	0.12341100	-4.10048900	1.22351000
C	0.36799400	-3.81081000	3.62557100
H	2.39146500	-3.40647300	4.31123200
C	1.20403600	-4.04885600	-1.38857000
C	-0.68329400	-4.39770700	0.12724600
C	-0.42210000	-4.06927300	2.54676900
H	-0.05756300	-3.77058700	4.62318900
C	1.65322600	-3.95774600	-2.74799200
C	-0.17142100	-4.40063100	-1.16896900
H	-1.73658700	-4.61880700	0.28515200
H	-1.48811500	-4.25013800	2.66370500
C	0.82958400	-4.28385400	-3.78565800
H	2.65716600	-3.60024900	-2.94410900

C	-1.00375100	-4.73137800	-2.28505900
C	-0.51402100	-4.70062600	-3.55442300
H	1.19365300	-4.20356800	-4.80527700
H	-2.04042300	-4.99215800	-2.09132800
H	-1.15357500	-4.94731600	-4.39565200
H	3.38524200	-3.44246200	2.08706600
C	2.68630300	3.25511800	2.10260700
C	2.92968200	3.76027600	0.78201200
C	1.68566100	3.76533100	2.87777100
C	3.96253100	3.26369000	-0.03938100
C	2.07280100	4.80388000	0.29366100
C	0.83426800	4.80221100	2.38710900
H	1.52475200	3.36763900	3.87635100
C	4.11241800	3.73961900	-1.35825500
C	2.27134400	5.30824200	-0.99102500
C	1.02314500	5.29960100	1.13332100
H	0.03311100	5.18011400	3.01480000
C	5.11850000	3.24457100	-2.25011800
C	3.24630900	4.78062800	-1.83621900
H	1.63753100	6.11473400	-1.35164300
H	0.37709600	6.07972700	0.73985700
C	5.22786100	3.72220700	-3.52219000
H	5.79589400	2.47288500	-1.90201700
C	3.39796100	5.25854900	-3.17619200
C	4.35215800	4.74171800	-3.99883500
H	5.99053100	3.32465200	-4.18380600
H	2.72655400	6.04059700	-3.52022700
H	4.45541000	5.10430900	-5.01627000
H	3.29934600	2.43953100	2.46952200
O	4.25204300	0.51871100	-0.88332200
O	3.50638400	-1.43311600	0.59281200
P	2.94375800	-0.27563100	-0.39160600
O	2.17018400	-0.80118700	-1.53589500
O	2.21946800	0.66988200	0.61821900
H	8.81225500	-0.32988500	1.80979200
H	7.85330600	-0.46407600	3.28287400
H	7.25976000	-0.66610400	-1.68648100
H	8.55869600	-0.88338000	-0.49895800
H	8.36960500	-3.32593400	-0.65401600
H	7.97828800	-2.88639900	-2.31415400
O	-8.90585700	0.01789200	-1.70228200
O	-4.87740100	-1.88974200	-2.54993400
O	-3.31019500	-1.58140700	3.12886300
O	-3.67717000	1.29306800	2.08549700

N	-2.00382000	-1.36938700	1.34121500
N	-1.16356500	-0.90090100	3.52583900
N	-7.06604700	1.14430800	-1.11825200
N	-4.94243500	0.12514600	-1.46411800
N	-0.52832100	-1.16197900	-0.45773700
H	0.44494800	-1.01468600	-0.73202900
N	-5.12373900	2.14011100	-0.36939800
N	-6.90987800	-1.01654400	-2.12489500
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C	-0.02634500	-0.62885500	2.92513500
C	-5.73497000	1.10721100	-1.00520600
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H	-3.44876500	2.66648400	-2.27461900
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H	-3.53268300	-1.86793200	-4.74831600
C	-9.51059500	-1.15937000	-2.22480100
H	-9.23254700	-2.03294000	-1.63018600
H	-9.20280100	-1.33127300	-3.25817600
C	-0.93898800	2.36607200	-0.02745300
H	0.13861700	2.45885600	0.09611700
C	-3.69654600	2.16658000	-0.23024700
C	-1.52821600	-1.57660300	-3.95427900
H	-1.04047000	-1.58478100	-4.92382900
C	-0.68491300	2.86288100	-2.51324000
C	-5.90259200	3.34382200	-0.09912200
H	-6.32389000	3.75131500	-1.02298800
H	-5.23847700	4.08174000	0.35104500
H	-6.73319700	3.11493300	0.57552600
C	0.73043400	2.27910700	-2.38247300
H	1.28954400	2.71102800	-1.54621700

H	1.30401700	2.49167400	-3.29110200
H	0.69742400	1.19294300	-2.24537200
C	-1.32256400	2.28244700	-3.78396300
H	-1.49811800	1.20779900	-3.67781300
H	-0.65383100	2.44363900	-4.63572900
H	-2.27438100	2.76523300	-4.02347600
C	-0.60545400	4.39290400	-2.64153600
H	-1.59519500	4.81599500	-2.84300000
H	0.06968600	4.67865400	-3.45719700
H	-0.23228000	4.82983700	-1.71156400
C	-4.95704100	1.68987100	2.54368700
H	-5.18255600	2.71365400	2.22526700
H	-4.88224700	1.70490200	3.63994700
C	-1.62832700	2.42831300	3.56444300
H	-2.28141000	1.68237400	4.02252200
H	-2.20825600	3.34829100	3.40072100
H	-0.82013500	2.64658500	4.26743900
C	-3.57175200	-1.33014100	4.50598600
H	-4.62470100	-1.57164400	4.64223800
H	-3.38495400	-0.27978300	4.74212500
H	-0.06624600	2.21002200	2.24657400
Cl	1.26857000	-0.06734500	3.94174800
H	-10.58370000	-0.98200800	-2.16770600
H	-2.94115200	-1.95549400	5.14132700
C	-6.05768800	0.73876100	2.12773100
C	-7.39026800	1.10139700	2.32844400
C	-5.76192600	-0.50014200	1.55924000
C	-8.41969800	0.24208000	1.95703800
H	-7.62590200	2.06883600	2.76822800
C	-6.79383000	-1.36249900	1.19353400
H	-4.72488600	-0.77037100	1.38826400
C	-8.12301000	-0.99468100	1.39041400
H	-9.45252300	0.54288800	2.09900400
H	-6.55626200	-2.31895500	0.73695400
H	-8.92516300	-1.66414500	1.09513100
H	7.81098200	-2.55621700	1.48801200
H	1.45539900	0.15645600	1.08376900

Table S11 Cartesian coordinates:

pro-R_{ic}-5a•Cat-16

O	-5.96301700	-3.38229300	-3.33121300
O	-5.14579700	-2.11944100	0.92698400
O	-2.43505800	4.16998800	3.26125100
O	-2.12001100	0.23907200	-1.45659300

N	-1.73492300	2.01713800	3.03816100
N	-0.23523800	3.86015000	2.95465700
N	-5.30790000	-1.27420200	-2.97079200
N	-4.82753100	-0.57305000	-0.73714700
N	-0.98112600	-0.07461600	2.46537900
H	-0.32525200	-0.59536400	1.88327200
N	-4.60981400	0.87103300	-2.52766100
N	-5.54935600	-2.79802200	-1.15893100
N	-0.69623100	2.08049000	0.07440900
N	0.57655200	1.65144500	2.62045200
C	-1.45195000	3.30006900	3.08243400
C	-5.14905500	-1.79142200	-0.37446400
C	-4.34492500	-1.49804700	1.86475600
C	-2.29851200	-0.58374100	2.67029300
C	-5.60149800	-2.45885500	-2.44298000
C	0.70385700	2.96655700	2.76352800
C	-4.91769300	-0.36437700	-2.06736100
C	-3.06533100	-1.01157900	1.59110300
H	-2.67015100	-0.97164100	0.57940700
C	-4.48206400	3.04930300	-1.43332700
H	-5.47069500	3.25972600	-1.83095000
C	-0.70884100	1.21937500	2.70834300
C	-2.78161700	-0.63416000	3.97827800
H	-2.14162700	-0.30271200	4.78869400
C	-3.78910000	4.00347200	-0.67595700
C	-2.66427100	1.47413200	-1.19366200
C	-1.96027700	2.40545500	-0.42516400
C	-4.85395400	-1.53726100	3.15616500
H	-5.85066400	-1.93549100	3.30878500
C	-6.26231500	-4.67997300	-2.82578400
H	-5.39154100	-5.11203700	-2.32604500
H	-7.08881700	-4.63908100	-2.11366600
C	-2.53387300	3.66018000	-0.17660600
H	-1.96779700	4.35526700	0.43661800
C	-3.92805800	1.80163000	-1.68913600
C	-4.06527400	-1.10134000	4.21591600
H	-4.45240500	-1.14008800	5.22865100
C	-4.42794700	5.37242600	-0.42223500
C	-4.69468100	1.13962400	-3.95979500
H	-5.66955800	0.83442000	-4.34082900
H	-4.55259900	2.20966200	-4.10810500
H	-3.92617000	0.58646500	-4.51197600
C	-3.54909600	6.26172700	0.46336200
H	-2.58727900	6.47511600	-0.01327300

H	-4.05419000	7.21660900	0.63741200
H	-3.34820300	5.80097600	1.43605500
C	-5.78864800	5.18907100	0.27002700
H	-5.66986500	4.67970600	1.23083600
H	-6.25229800	6.16422400	0.45262400
H	-6.47773600	4.59812100	-0.33938700
C	-4.63957400	6.08424400	-1.76929100
H	-5.30094900	5.51123800	-2.42574900
H	-5.09166500	7.06905400	-1.61044300
H	-3.68545300	6.22244600	-2.28672600
C	-1.11091400	0.25160000	-2.47702300
H	-1.50010200	0.81167300	-3.33991300
H	-0.20404400	0.75822200	-2.12245400
C	0.40775400	2.91738200	-0.38590600
H	0.44649100	2.98528300	-1.48127900
H	0.32566700	3.93032700	0.02145900
H	1.35454000	2.49551400	-0.02982900
C	-3.76023100	3.63159200	3.28596100
H	-4.41247200	4.49057200	3.43920600
H	-3.97913600	3.13561600	2.33584500
H	-0.48511300	1.09400900	-0.06506900
Cl	2.32341500	3.56998600	2.65429300
H	-6.53532500	-5.27209100	-3.69780000
H	-3.86909800	2.91047100	4.09796700
C	-0.79393600	-1.16717000	-2.85868100
C	0.52654400	-1.61355400	-2.88963900
C	-1.82366800	-2.03893200	-3.21722400
C	0.81432100	-2.91996900	-3.27791900
H	1.32656400	-0.93736100	-2.59945400
C	-1.53620600	-3.34685100	-3.59679800
H	-2.85250200	-1.68847200	-3.20377600
C	-0.21513000	-3.79216300	-3.62297100
H	1.84434300	-3.26070300	-3.29281200
H	-2.34569300	-4.01535700	-3.87649000
H	0.01135500	-4.81388800	-3.91250300
C	6.59736500	-0.95463000	-0.86348100
C	7.30170400	-2.27961600	-0.68882500
C	6.13356800	-3.23047100	-0.37957600
C	5.21560000	-1.14113100	-0.98312200
H	5.90402400	-3.20265500	0.69097500
C	4.93188400	-2.62168900	-1.15508800
C	3.63256700	-3.29344900	-0.76788100
C	3.43631800	-4.42550200	-1.56283500
C	5.02015000	-3.03577600	-2.65252900

C	4.44876100	-4.46465400	-2.68415700
C	2.39480400	-5.30149400	-1.29413000
C	2.72532200	-2.99255000	0.23799100
C	1.66287900	-3.85405800	0.53812000
C	1.53898500	-5.01865400	-0.23705700
H	0.72467900	-5.69707500	-0.00517800
H	2.24084500	-6.18849900	-1.90154800
C	4.37874700	-0.03094000	-1.01384100
C	7.14986200	0.31622500	-0.90862600
C	6.30255300	1.40706500	-1.05362300
H	6.71325500	2.40962900	-1.11828000
C	4.90735200	1.26616800	-1.07857500
H	8.22377900	0.45932200	-0.83827200
C	2.49187100	-3.46294600	3.37042500
C	1.11235300	-3.53280600	2.98516700
C	2.85668700	-3.31803900	4.67590400
C	0.68515100	-3.64732200	1.64355300
C	0.13211900	-3.53683200	4.03800000
C	1.87528800	-3.24729300	5.70765800
H	3.90843700	-3.26038300	4.93690000
C	-0.69266800	-3.77394100	1.34642100
C	-1.20560100	-3.78308300	3.73405400
C	0.55618800	-3.36579800	5.39430200
H	2.18763000	-3.11943700	6.73892200
C	-1.20474000	-3.76531300	0.00509900
C	-1.63270500	-3.94712300	2.41723700
H	-1.93091700	-3.86176800	4.54089400
H	-0.20603400	-3.34658900	6.16850300
C	-2.51333600	-4.06715800	-0.24179300
H	-0.54350200	-3.50083900	-0.81531500
C	-2.98422900	-4.30114800	2.11069100
C	-3.40567500	-4.39887900	0.81922200
H	-2.88572900	-4.04224400	-1.26142000
H	-3.66894400	-4.47188200	2.93705200
H	-4.43587500	-4.64583200	0.58628900
H	3.25808400	-3.52874500	2.60793900
C	5.08256800	3.39433600	0.91153100
C	4.27864300	3.54551600	-0.26727200
C	5.29966100	4.44200800	1.75828300
C	4.08516000	2.50223500	-1.20197400
C	3.65198800	4.81911700	-0.48407800
C	4.71142200	5.71726700	1.51073200
H	5.90711200	4.29883200	2.64617500
C	3.23285400	2.69335300	-2.31129900

C	2.82604400	4.99821700	-1.59268000
C	3.89791900	5.89001100	0.43278300
H	4.89464500	6.53621200	2.19832400
C	2.97358100	1.67269500	-3.28454300
C	2.59146300	3.96555300	-2.49831900
H	2.34995300	5.96326200	-1.75121600
H	3.41760600	6.84588300	0.24434700
C	2.09623900	1.87597400	-4.30924900
H	3.48155700	0.71934100	-3.20040300
C	1.69943700	4.14851000	-3.60312800
C	1.43987300	3.13206600	-4.47115100
H	1.90175900	1.07613900	-5.01691600
H	1.21961100	5.11649600	-3.71788000
H	0.74837300	3.27462400	-5.29507200
H	5.49767000	2.42013200	1.14111500
O	2.99454200	-0.20695100	-1.01233600
O	2.90177900	-1.81260100	0.95854600
P	2.20931000	-0.47950800	0.37303800
O	0.75232800	-0.58798500	0.12868700
O	2.68007100	0.61234100	1.38070100
H	7.82508200	-2.57161300	-1.60727300
H	8.04780900	-2.24692900	0.10963600
H	4.37728800	-2.36583000	-3.23582600
H	6.03653200	-2.95748600	-3.04763300
H	5.22749400	-5.21215700	-2.49063300
H	3.99277700	-4.71910000	-3.64573000
H	6.32395900	-4.26980100	-0.66005700
H	1.89418400	0.96699400	1.93732500