

Supporting Information

ortho-Ethynyl Group Assisted Regioselective and Diastereoselective [2+2] Cross-Photocycloaddition of Alkenes under Photocatalyst-, Additive-, and Solvent-free Conditions

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Table of Contents

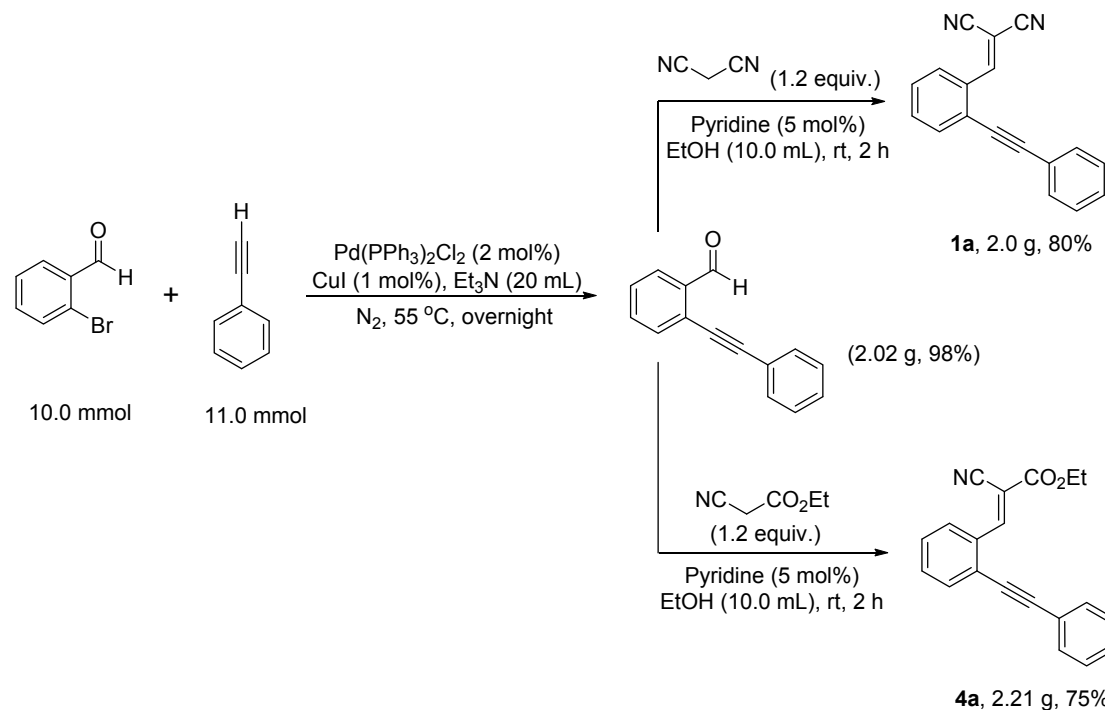
1.	General considerations.....	S3
2.	General procedures for the synthesis of substrates and products.....	S3
3.	X-Ray single crystal diffraction analysis of the products.....	S12
4.	Further optimization of the reaction conditions	S24
5.	Mechanistic investigations.....	S25
6.	The possible stereoisomers of [2+2]-cycloaddition products.....	S32
7.	DFT calculations for the [2+2] cross-cycloaddition of 1a and 2a	S33
8.	Characterization data for the products.....	S76
9.	¹ H NMR, ¹³ C NMR and ¹⁹ F NMR spectra of the products.....	S111
10.	HRMS spectra for the products.....	S177

1. General considerations

All ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on a 600 MHz or 400 MHz Bruker FT-NMR spectrometers (600/150/564 MHz, or 400/100/376 MHz, respectively). All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, J , are reported in Hertz (Hz). High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). The chemicals and solvents were purchased from commercial suppliers either Aldrich (USA), or Shanghai Chemical Company (P. R. China). Products were purified by flash chromatography on 200–300 mesh silica gels, SiO_2 .

2. General procedures for the synthesis of substrates and products

2.1 Representative procedure for the synthesis of 1a and 4a



To a solution of 2-bromobenzaldehyde (1.85 g, 10.0 mmol) and ethynylbenzene (1.124g, 11.0 mmol) in Et₃N (20.0 mL) was added Pd(PPh₃)₂Cl₂ (140 mg, 2.0% mol) and CuI (20 mg, 1.0% mol). The mixture was stirred at 55 °C for overnight. It was then quenched with water and washed with ethyl acetate. After removal of solvent, the crude residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 100:1, v/v) to afford the desired product 2-(phenylethynyl)benzaldehyde (2.02 g, 98% yield).

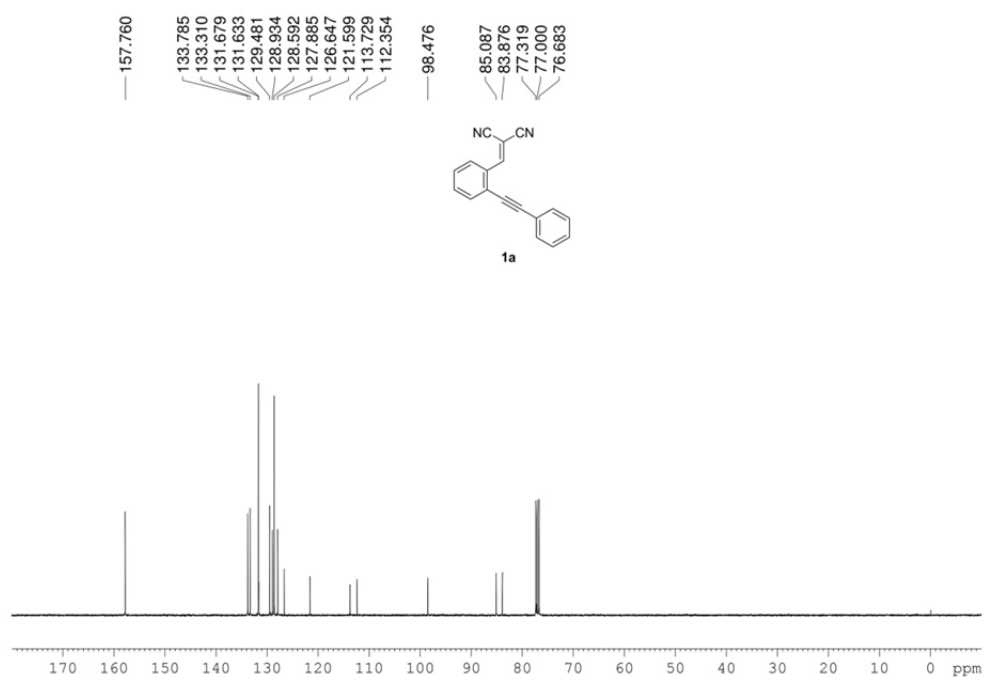
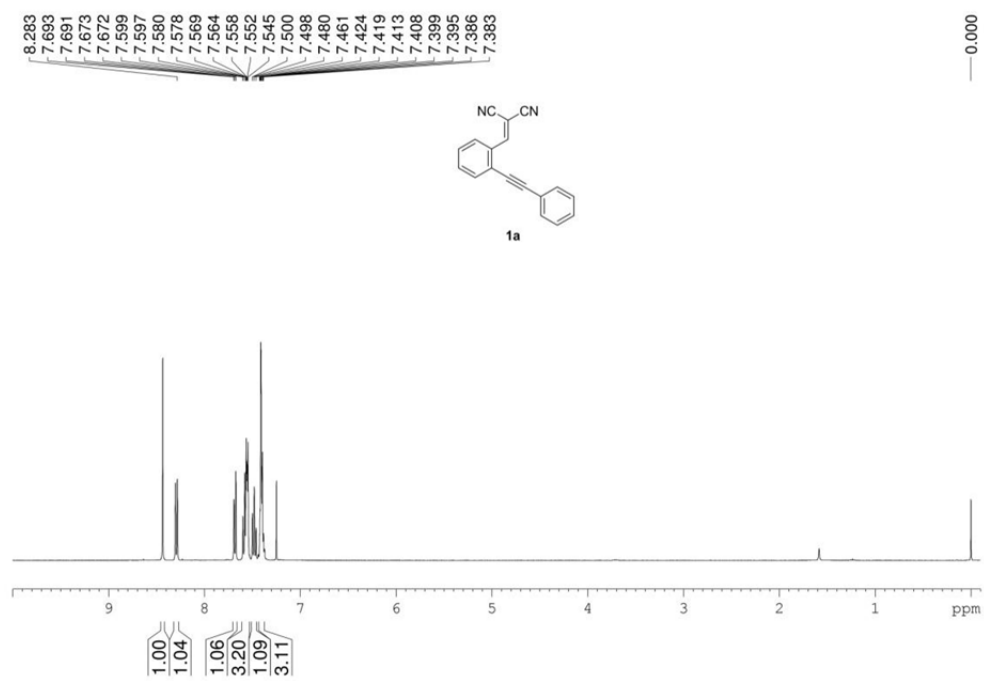
To a solution of 2-(phenylethynyl)benzaldehyde (2.02 g, 9.8 mmol) and malononitrile (780 mg, 11.8 mmol) in EtOH (10.0 mL) at room temperature was added pyridine (39 mg, 5% mol) under air. The reaction mixture was stirred at room temperature for 2 h, then mixed solution was suction filtered and washed with ethanol to afford the desired product **1a** (yellow solid, 2.0 g, 80% yield).

To a solution of 2-(phenylethynyl)benzaldehyde (2.02 g, 9.8 mmol) and ethyl 2-cyanoacetate (1.34 g, 11.8 mmol) in EtOH (10.0 mL) at room temperature was added pyridine (39 mg, 5% mol) under air. The reaction mixture was stirred at room temperature for 2 h, then mixed solution was suction filtered and washed with ethanol to afford the desired product **4a** (yellow solid, 2.21 g, 75% yield).

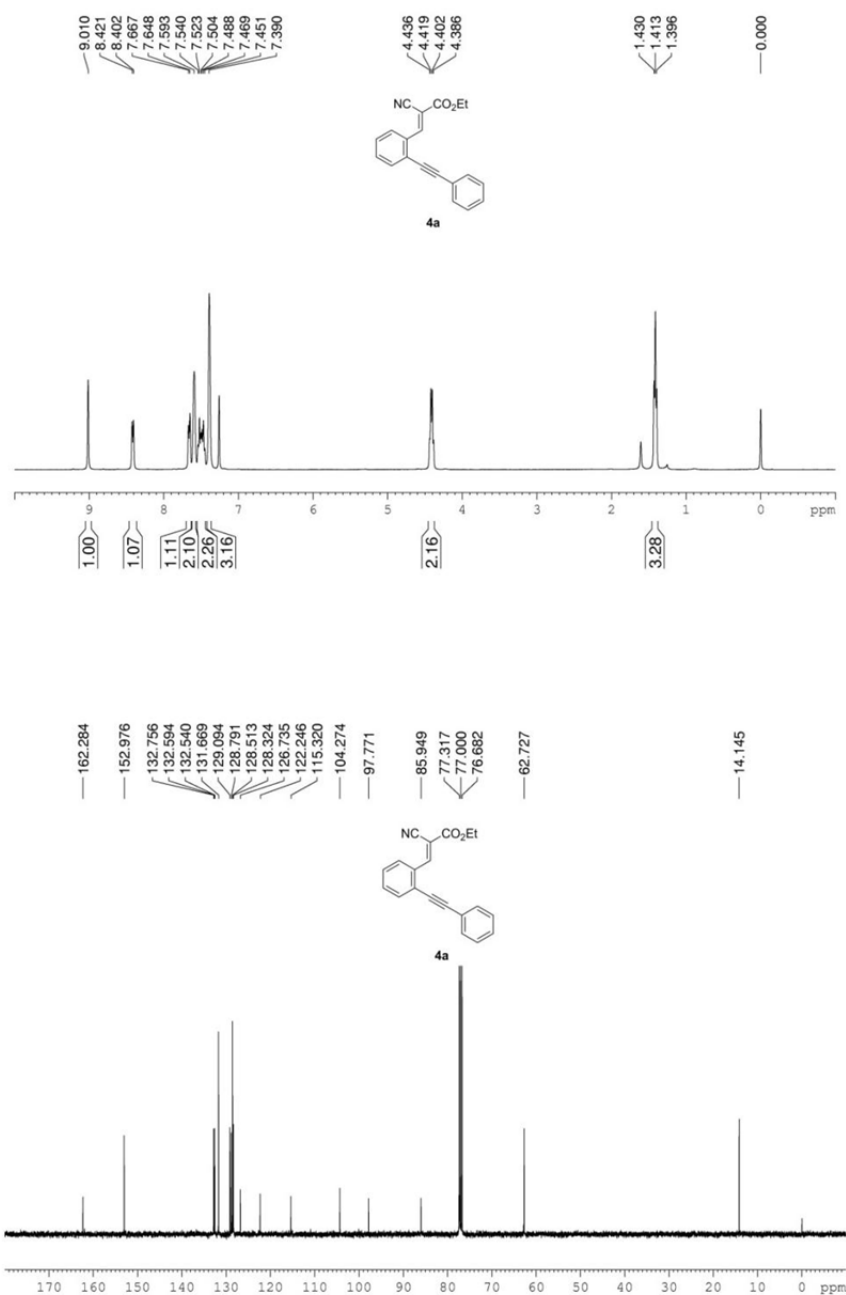
2-(2-(Phenylethynyl)benzylidene)malononitrile (1a): Yellow solid. m.p. 105.7–106.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.44 (s, 1H), 8.30–8.28 (m, 1H), 7.69–7.67 (m, 1H), 7.60–7.54 (m, 3H), 7.50–7.46 (m, 1H), 7.42–7.38 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 157.8, 133.8, 133.3, 131.7, 131.6, 129.5, 128.9,

128.6, 127.9, 126.6, 121.6, 113.7, 112.4, 98.5, 85.1, 83.9. HRMS (ESI) $[M+H]^+$

Calcd. for $[C_{18}H_{11}N_2]^+$: 255.0917, Found: 255.0920.

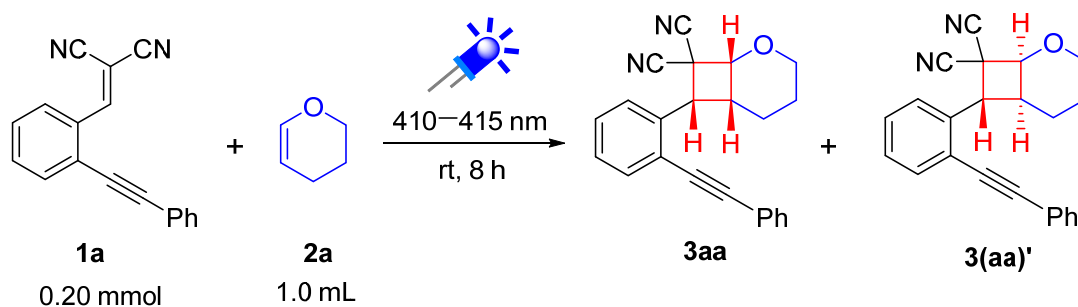


Ethyl (*E*)-2-cyano-3-(2-(phenylethynyl)phenyl)acrylate (4a): Yellow solid. m.p. 56.2–58.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.01 (s, 1H), 8.42–8.40 (m, 1H), 7.67–7.65 (m, 1H), 7.59 (s, 2H), 7.54–7.45 (m, 2H), 7.39 (s, 3H), 4.44–4.39 (m, 2H), 1.41 (t, *J* = 8.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 153.0, 132.8, 132.6, 132.5, 131.7, 129.1, 128.8, 128.5, 128.3, 126.7, 122.2, 115.3, 104.3, 97.8, 85.9, 62.7, 14.1. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₀H₁₅NNaO₂]⁺: 324.0995, Found: 324.0999.



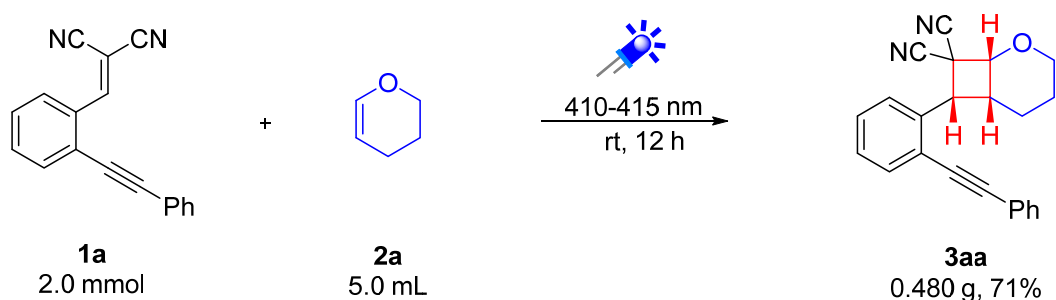
2.2 Representative procedure for *ortho*-ethynyl group assisted regioselective and diastereoselective [2+2] cross-photocycloaddition of alkenes

2.2.1 Synthesis of **3aa** and **3(aa)'** in 0.20 mmol scale



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.9 mg, 0.20 mmol), 3,4-dihydro-2*H*-pyran (**2a**, 1.0 mL). The reaction vessel was exposed to blue LED (410–415 nm, 3 W) irradiation at room temperature in air with stirring for 8 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1, V/V) to give the product **3aa** (54 mg, 79% yield) and product **3(aa)'** (8 mg, 11% yield).

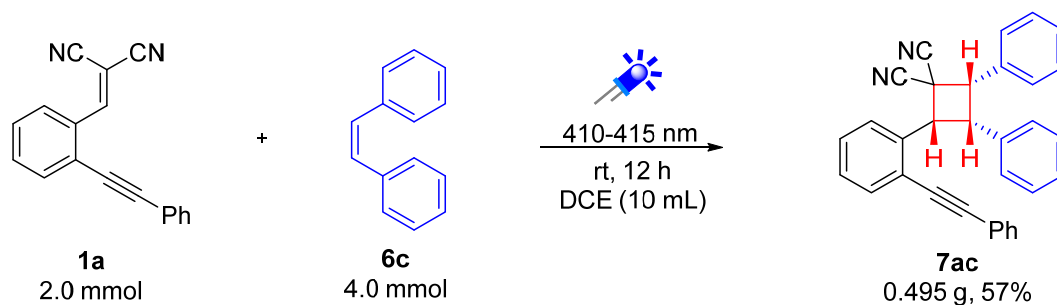
2.2.2 Synthesis of **3aa** in 2.0 mmol scale



A 20.0 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 0.520 g, 2.0 mmol) and 3,4-dihydro-2*H*-pyran (**2a**, 5.0 mL). The reaction vessel was exposed to LED (410–415 nm, 3 W) irradiation at room temperature in air with stirring for 12 h. After

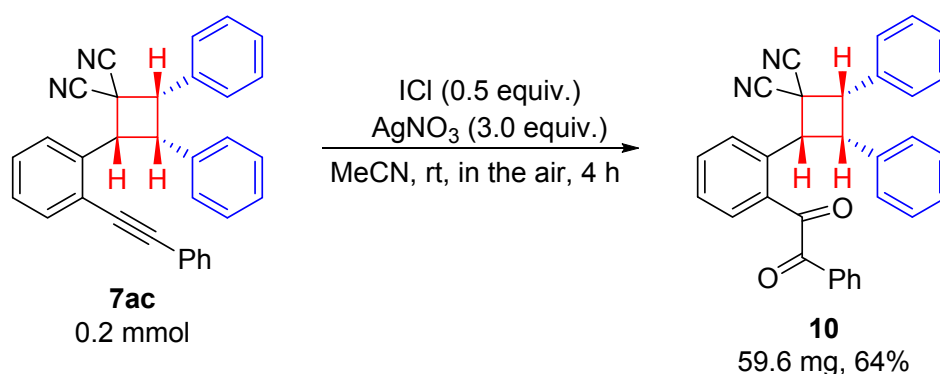
completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give the desired product **3aa** (0.480 g, 71% yield).

2.2.3 Synthesis of **7ac** in 2.0 mmol scale



A 20 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 0.509 g, 2.0 mmol), (*Z*)-1,2-diphenylethene (**6c**, 0.721 g, 4.0 mmol) and DCE (10.0 mL). The reaction vessel was exposed to LED (410–415 nm) irradiation at room temperature in air with stirring for 12 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1) to give the desired product **7ac** (0.495 g, 57% yield).

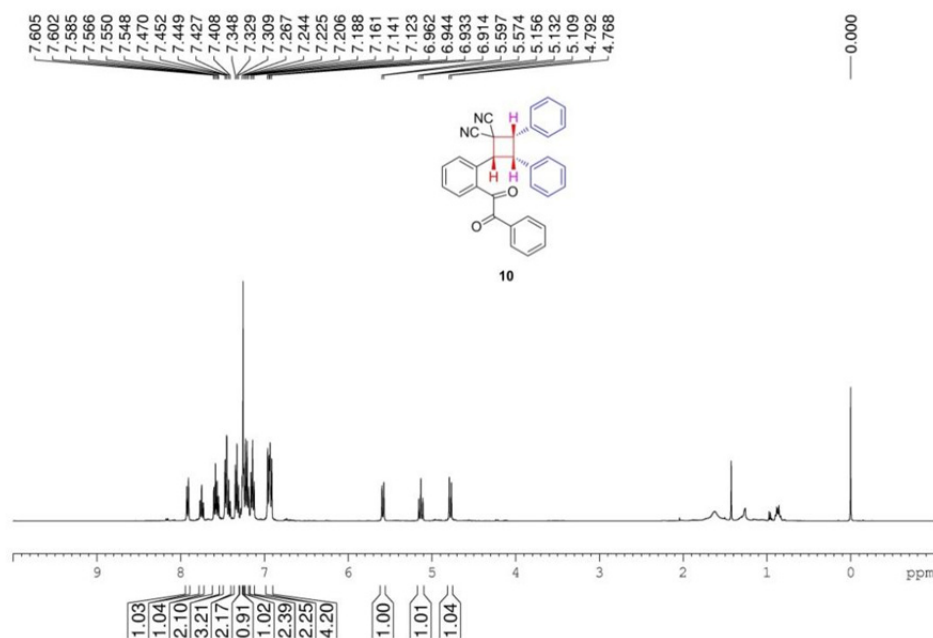
2.3.1 Further transformations of **7ac** into compound **10**

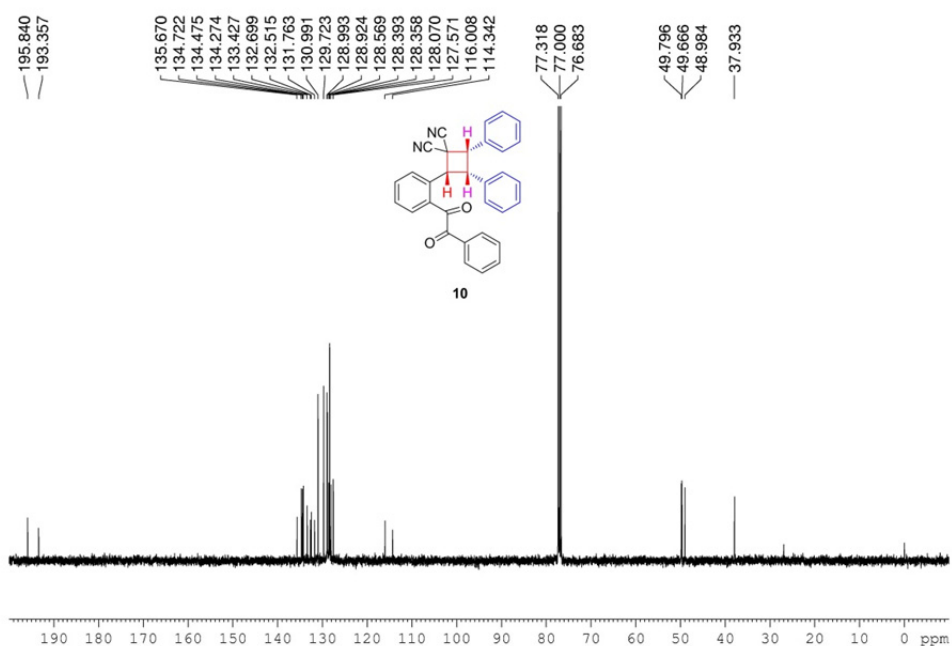


According to a reported procedure (see: W. Yang, Y. Chen, Y. Yao, X. Yang, Q. Lin, D. Yang, *J. Org. Chem.* **2019**, *84*, 11080–11090), a 5 mL oven-dried reaction

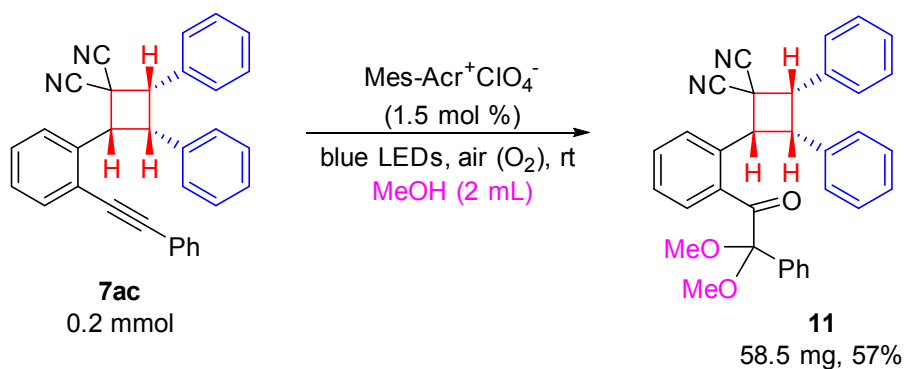
vessel equipped with a magnetic stirrer bar was charged with (\pm)-(*2S,3S,4R*)-2,3-diphenyl-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (**7ac**, 86.9 mg, 0.2 mmol), ICl (16.3 mg, 0.10 mmol), AgNO₃ (101.9 mg, 0.60 mmol) and MeCN (2.0 mL). The reaction vessel was exposed to room temperature in air with stirring for 4 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 10:1, V/V) to give the product **10** (59.6 mg, 64% yield).

(\pm)-(*2R,3S,4S*)-2-(2-(2-Oxo-2-phenylacetyl)phenyl)-3,4-diphenylcyclobutane-1,1-dicarbonitrile (10**):** Brown oil. ¹H NMR (400 MHz, CDCl₃) δ 7.93–7.91 (m, 1H), 7.77–7.73 (m, 1H), 7.61–7.55 (m, 2H), 7.47–7.41 (m, 3H), 7.35–7.31 (m, 2H), 7.27–7.24 (m, 2H), 7.23–7.19 (m, 2H), 7.16–7.12 (m, 2H), 6.96–6.91 (m, 4H), 5.58 (d, *J* = 9.2 Hz, 1H), 5.13 (t, *J* = 9.6 Hz, 1H), 4.78 (d, *J* = 9.6 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 193.4, 135.7, 134.7, 134.5, 134.3, 133.4, 132.7, 132.5, 131.8, 131.0, 129.7, 129.0, 128.9, 128.6, 128.39, 128.36, 128.1, 127.6, 116.0, 114.3, 49.8, 49.7, 49.0, 37.9. HRMS (ESI) [M+Na]⁺ Calcd. for [C₃₂H₂₂N₂NaO₂]⁺: 489.1573, Found: 489.1573.





2.3.2 Further transformations of 7ac into compound 11

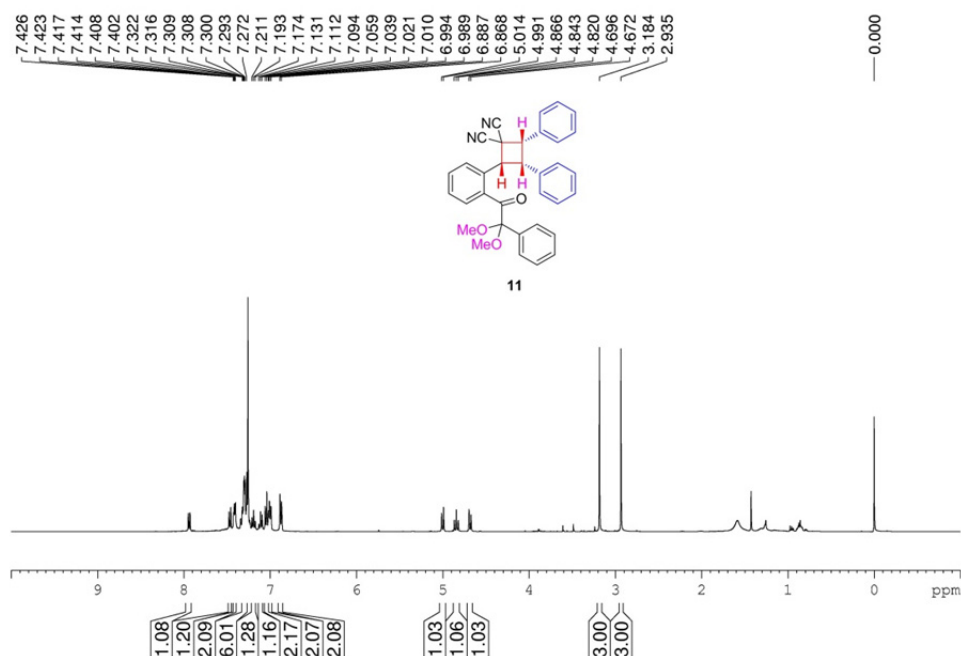


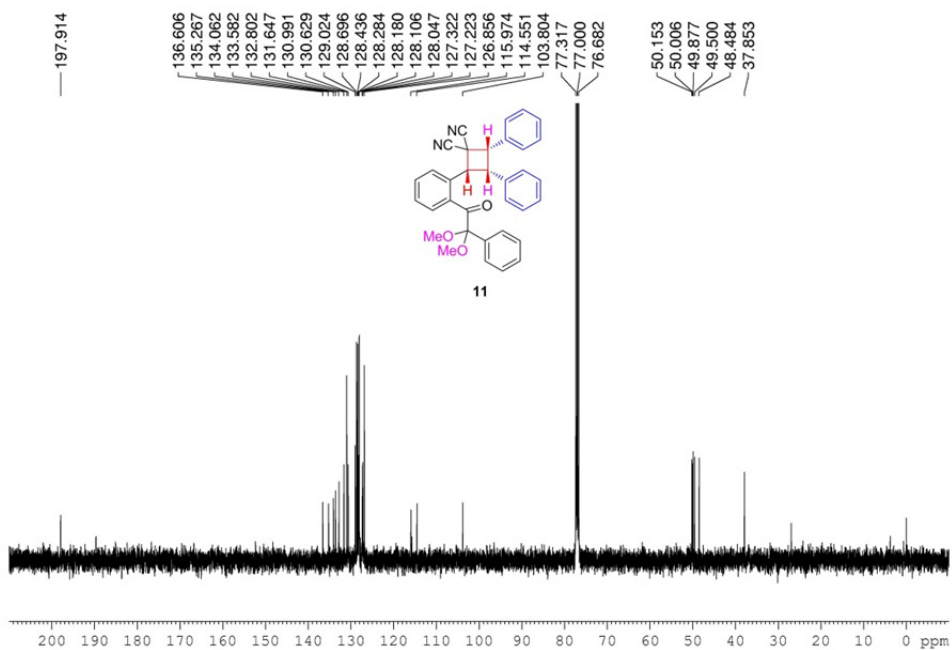
According to a reported procedure (see: W.-L. Lei, B. Yang, Q.-B. Zhang, P.-F. Yuan, L.-Z. Wu, Q. Liu, *Green Chem.* **2018**, *20*, 5479–5483), a 5.0 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with (±)-(2*S*,3*S*,4*R*)-2,3-diphenyl-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (**7ac**, 86.9 mg, 0.2 mmol), 9-mesityl-10-methylacridinium perchlorate (1.3 mg, 1.5 mol%) and MeOH (2.0 mL). The reaction vessel was exposed to LED (450–455 nm, 3 W)

irradiation at room temperature in air with stirring for 3 h. After completion of the reaction, the mixture was concentrated to yield the crude product, which was further purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 20:1, V/V) to give the product **11** (58.5 mg, 57% yield).

(±)-(2*R*,3*S*,4*S*)-2-(2-(2,2-Dimethoxy-2-phenylacetyl)phenyl)-3,4-diphenyl

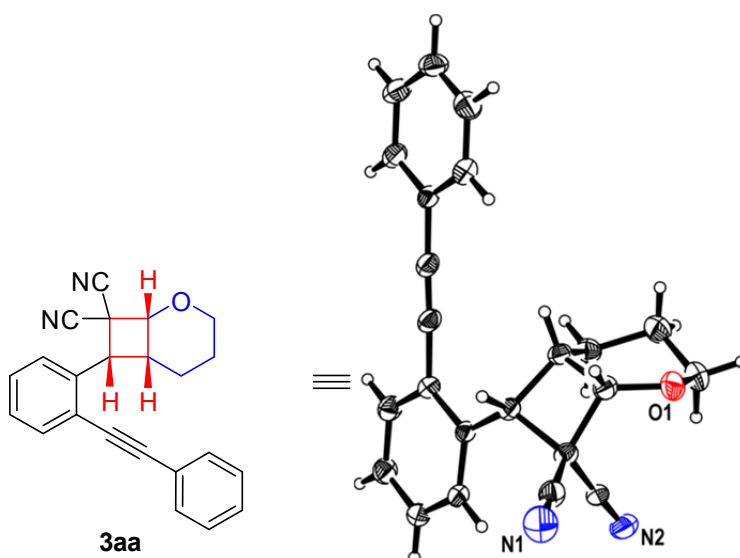
cyclobutane-1,1-dicarbonitrile (11): Brown oil. ^1H NMR (400 MHz, CDCl_3) δ 7.95–7.93 (m, 1H), 7.48–7.46 (m, 1H), 7.43–7.40 (m, 2H), 7.32–7.27 (m, 6H), 7.21–7.17 (m, 1H), 7.13–7.09 (m, 1H), 7.06–7.02 (m, 2H), 7.01–6.99 (m, 2H), 6.89–6.87 (m, 2H), 5.00 (d, $J = 9.2$ Hz, 1H), 4.84 (t, $J = 9.2$ Hz, 1H), 4.68 (d, $J = 9.6$ Hz, 1H), 3.18 (s, 3H), 2.94 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.9, 136.6, 135.3, 134.1, 133.6, 132.8, 131.6, 131.0, 129.0, 128.7, 128.4, 128.3, 128.2, 128.1, 128.0, 127.3, 127.2, 126.8, 116.0, 114.5, 103.8, 50.1, 50.0, 49.9, 49.5, 48.5, 37.8. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{34}\text{H}_{28}\text{N}_2\text{NaO}_3]^+$: 535.1992, Found: 535.1995.





3. X-Ray single crystal diffraction analysis of the products

3.1 X-Ray single crystal diffraction analysis of 3aa (CCDC: 2035710)



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 1

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No syntax errors found.

[CIF dictionary](#)

[Interpreting this report](#)

Datablock: 1

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=7.6019(8) b=26.579(3) c=9.0787(10)
 alpha=90 beta=98.982(2) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1811.9(3)	1811.9(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C23 H18 N2 O	?
Sum formula	C23 H18 N2 O	C23 H18 N2 O
Mr	338.39	338.39
Dx, g cm-3	1.240	1.241
Z	4	4
Mu (mm-1)	0.077	0.077
F000	712.0	712.0
F000'	712.27	
h, k, lmax	9, 31, 10	9, 31, 10
Nref	3176	3174
Tmin, Tmax	0.985, 0.990	
Tmin'	0.979	

Correction method= Not given

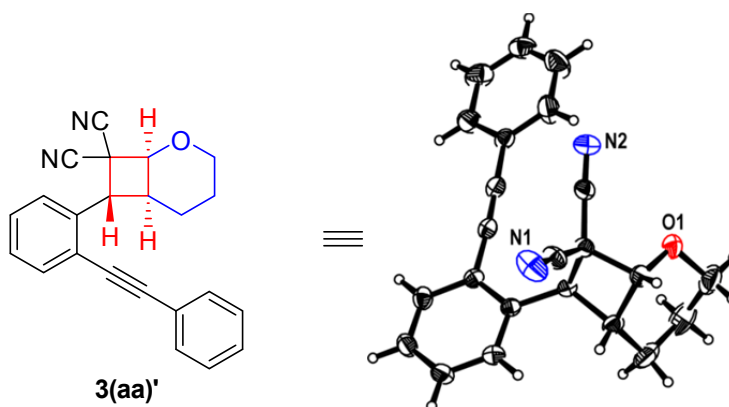
Data completeness= 0.999 Theta(max)= 24.990

R(reflections)= 0.0459(1970) wR2(reflections)= 0.1308(3174)

S = 0.915 Npar= 235

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test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

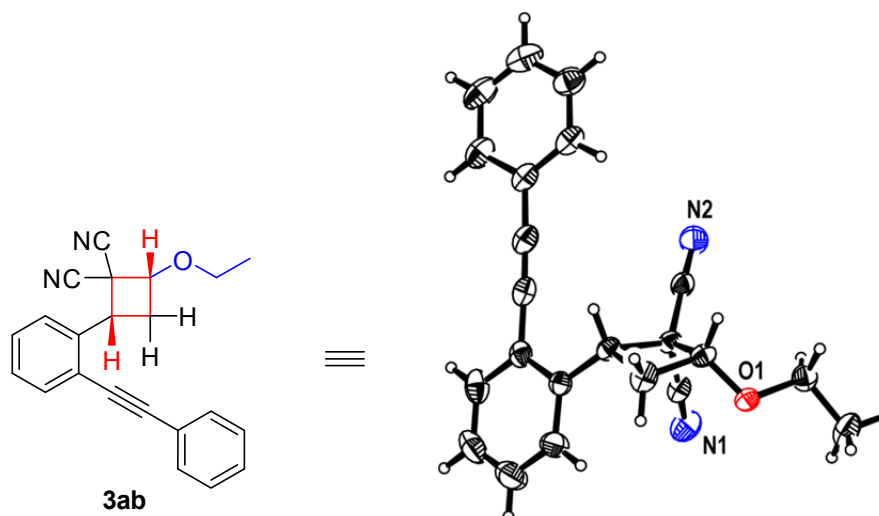
3.2 X-Ray single crystal diffraction analysis of 3(aa)' (CCDC: 2035711)



Datablock: 1

Bond precision:	C-C = 0.0030 Å	Wavelength=0.71073	
Cell:	a=11.6258 (16)	b=11.1970 (16)	c=15.042 (2)
	alpha=90	beta=110.329 (2)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1836.1 (4)	1836.1 (4)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C23 H18 N2 O	?	
Sum formula	C23 H18 N2 O	C23 H18 N2 O	
Mr	338.39	338.39	
Dx, g cm ⁻³	1.224	1.224	
Z	4	4	
Mu (mm ⁻¹)	0.076	0.076	
F000	712.0	712.0	
F000'	712.27		
h, k, lmax	13, 13, 17	13, 13, 17	
Nref	3229	3221	
Tmin, Tmax	0.980, 0.985		
Tmin'	0.980		
Correction method=	Not given		
Data completeness=	0.998	Theta(max)= 24.998	
R(reflections)=	0.0454 (2445)	wR2(reflections)= 0.1401 (3221)	
S =	0.873	Npar= 236	

3.3 X-Ray single crystal diffraction analysis of 3ab (CCDC: 2035712)



Datablock: 1

Bond precision: C-C = 0.0027 Å

Wavelength=0.71073

Cell: a=12.2425 (11)
alpha=90

b=7.5829 (7)
beta=101.893 (2)

c=20.0771 (19)
gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1823.8 (3)	1823.8 (3)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C22 H18 N2 O	?
Sum formula	C22 H18 N2 O	C22 H18 N2 O
Mr	326.38	326.38
Dx, g cm ⁻³	1.189	1.189
Z	4	4
Mu (mm ⁻¹)	0.074	0.074
F000	688.0	688.0
F000'	688.26	
h, k, lmax	14, 9, 23	14, 9, 23
Nref	3199	3194
Tmin, Tmax	0.978, 0.979	
Tmin'	0.978	

Correction method= Not given

Data completeness= 0.998

Theta(max)= 24.999

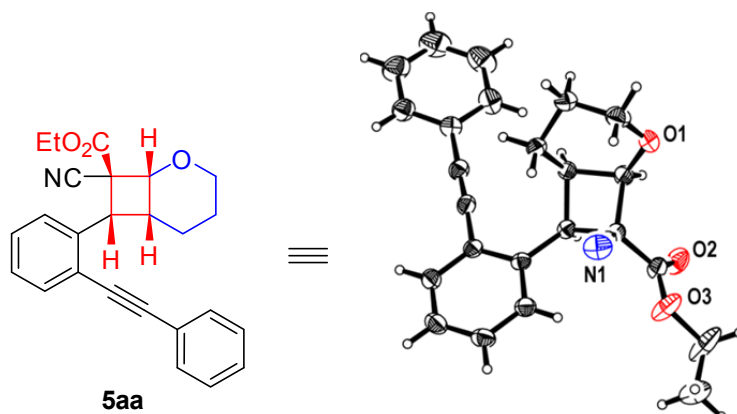
R(reflections)= 0.0424 (2321)

wR2(reflections)= 0.1160 (3194)

S = 1.050

Npar= 227

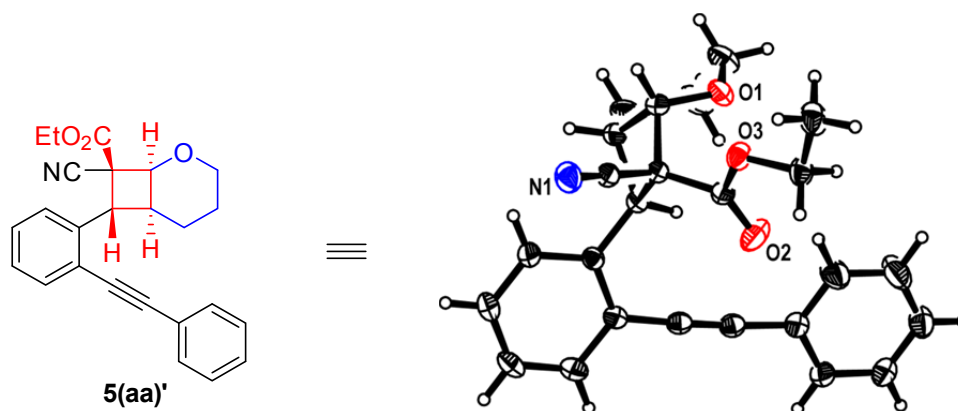
3.4 X-Ray single crystal diffraction analysis of 5aa (CCDC: 2035713)



Datablock: 1

Bond precision:	C-C = 0.0032 Å	Wavelength=0.71073	
Cell:	a=11.0334 (12) alpha=90	b=8.2617 (9) beta=94.328 (2)	c=23.153 (3) gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	2104.5 (4)	2104.5 (4)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C ₂₅ H ₂₃ N O ₃	?	
Sum formula	C ₂₅ H ₂₃ N O ₃	C ₂₅ H ₂₃ N O ₃	
Mr	385.44	385.44	
Dx, g cm ⁻³	1.217	1.217	
Z	4	4	
Mu (mm ⁻¹)	0.080	0.080	
F ₀₀₀	816.0	816.0	
F ₀₀₀ '	816.37		
h, k, lmax	13, 9, 27	13, 9, 27	
Nref	3699	3696	
Tmin, Tmax	0.979, 0.983		
Tmin'	0.979		
Correction method=	Not given		
Data completeness=	0.999	Theta (max)= 24.994	
R(reflections)=	0.0480 (2516)	wR2(reflections)=	0.1367 (3696)
S =	1.069	Npar=	263

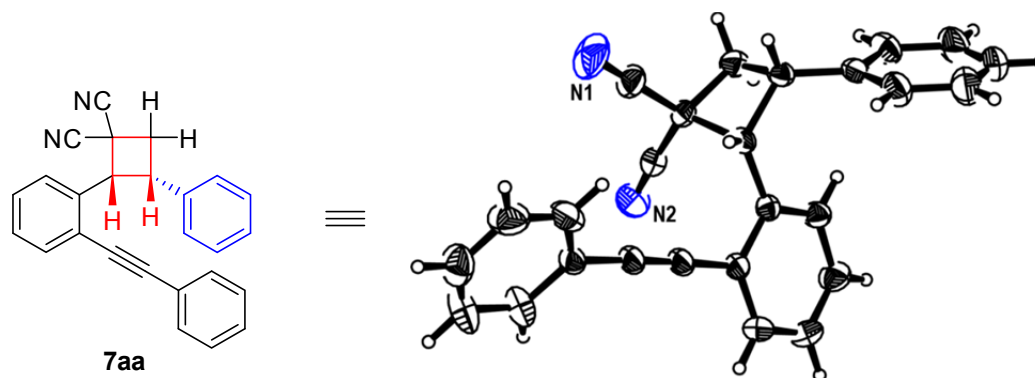
3.5 X-Ray single crystal diffraction analysis of 5(aa)' (CCDC: 2045867)



Datablock: 1

Bond precision:	C-C = 0.0023 Å	Wavelength=0.71073	
Cell:	a=11.9742 (8)	b=12.1683 (8)	c=15.4294 (11)
	alpha=90	beta=109.162 (1)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	2123.6 (3)	2123.6 (3)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C ₂₅ H ₂₃ N O ₃	?	
Sum formula	C ₂₅ H ₂₃ N O ₃	C ₂₅ H ₂₃ N O ₃	
Mr	385.44	385.44	
Dx, g cm ⁻³	1.206	1.206	
Z	4	4	
Mu (mm ⁻¹)	0.079	0.079	
F000	816.0	816.0	
F000'	816.37		
h, k, lmax	14, 14, 18	14, 14, 18	
Nref	3746	3737	
Tmin, Tmax	0.980, 0.984		
Tmin'	0.980		
Correction method=	Not given		
Data completeness=	0.998	Theta(max)= 24.996	
R(reflections)=	0.0407 (2801)	wR2(reflections)= 0.1142 (3737)	
S =	0.970	Npar= 263	

3.6 X-Ray single crystal diffraction analysis of 7aa (CCDC: 2035714)



Datablock: 1

Bond precision: C-C = 0.0032 Å

Wavelength=0.71073

Cell: a=19.398(3)

b=10.0574(15)

c=21.725(4)

alpha=90

beta=107.917(6)

gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	4032.9(11)	4032.9(11)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C ₂₆ H ₁₈ N ₂	?
Sum formula	C ₂₆ H ₁₈ N ₂	C ₂₆ H ₁₈ N ₂
Mr	358.42	358.42
Dx, g cm ⁻³	1.181	1.181
Z	8	8
Mu (mm ⁻¹)	0.069	0.069
F000	1504.0	1504.0
F000'	1504.52	
h, k, lmax	22, 11, 25	22, 11, 25
Nref	3533	3505
Tmin, Tmax	0.982, 0.985	
Tmin'	0.982	

Correction method= Not given

Data completeness= 0.992

Theta(max)= 24.996

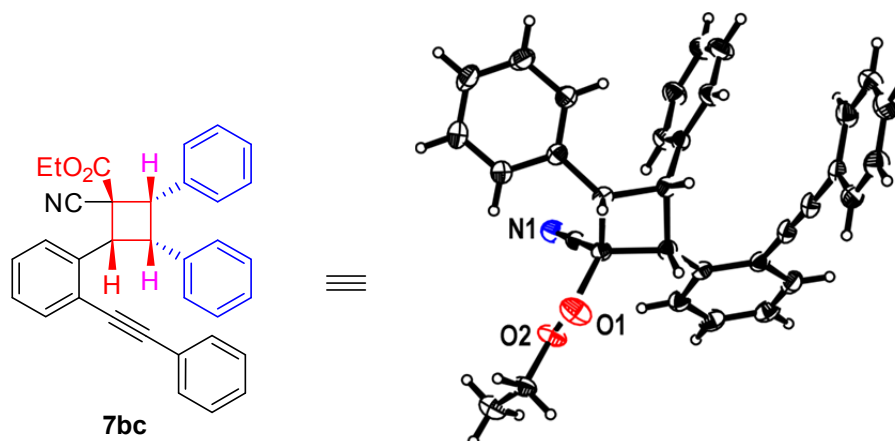
R(reflections)= 0.0456(1704)

wR2(reflections)= 0.0918(3505)

S = 0.846

Npar= 253

3.7 X-Ray single crystal diffraction analysis of 7bc (CCDC: 2035715)



Datablock: 1

Bond precision: C-C = 0.0023 Å

Wavelength=0.71073

Cell: a=9.9610 (12)
alpha=70.640 (2)

b=11.2201 (14)
beta=86.203 (2)

c=12.7264 (16)
gamma=74.814 (2)

Temperature: 296 K

	Calculated	Reported
Volume	1294.7 (3)	1294.7 (3)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C34 H27 N O2	?
Sum formula	C34 H27 N O2	C34 H27 N O2
Mr	481.57	481.56
Dx, g cm ⁻³	1.235	1.235
Z	2	2
Mu (mm ⁻¹)	0.076	0.076
F000	508.0	508.0
F000'	508.21	
h, k, lmax	11, 13, 15	11, 13, 15
Nref	4554	4524
Tmin, Tmax	0.977, 0.983	
Tmin'	0.977	

Correction method= Not given

Data completeness= 0.993

Theta(max)= 24.999

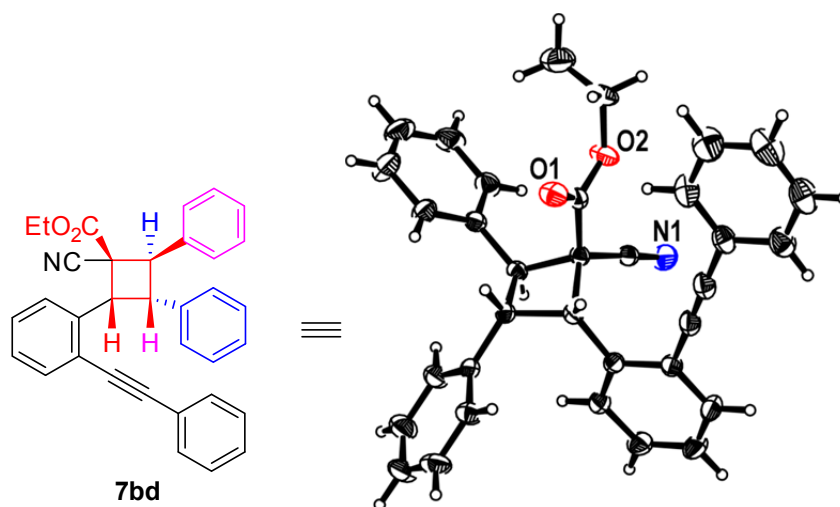
R(reflections)= 0.0395 (3568)

wR2(reflections)= 0.1214 (4524)

S = 0.953

Npar= 334

3.8 X-Ray single crystal diffraction analysis of 7bd (CCDC: 2035716)



Datablock: 1

Bond precision: C-C = 0.0026 Å

Wavelength=0.71073

Cell: a=10.6954(13)

b=23.526(3)

c=11.3878(13)

alpha=90

beta=108.403(2)

gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	2718.9(6)	2718.8(6)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C ₃₄ H ₂₇ N O ₂	?
Sum formula	C ₃₄ H ₂₇ N O ₂	C ₃₄ H ₂₇ N O ₂
Mr	481.57	481.56
Dx, g cm ⁻³	1.176	1.176
Z	4	4
Mu (mm ⁻¹)	0.072	0.072
F ₀₀₀	1016.0	1016.0
F ₀₀₀ '	1016.42	
h, k, lmax	12, 27, 13	12, 27, 13
Nref	4790	4787
Tmin, Tmax	0.979, 0.983	
Tmin'	0.979	

Correction method= Not given

Data completeness= 0.999

Theta(max)= 24.999

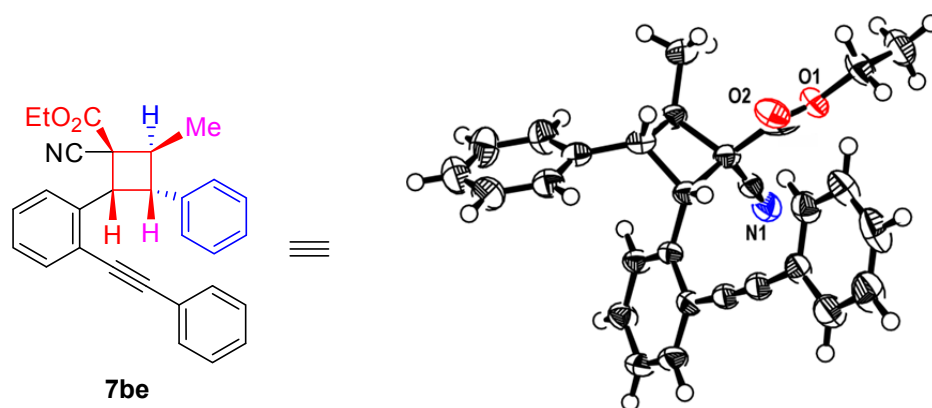
R(reflections)= 0.0426(3440)

wR2(reflections)= 0.1141(4787)

S = 1.044

Npar= 334

3.9 X-Ray single crystal diffraction analysis of 7be (CCDC: 2035717)



Datablock: 1

Bond precision: C-C = 0.0032 Å Wavelength=0.71073

Cell: a=17.274 (2) b=17.574 (2) c=17.610 (2)
 alpha=90 beta=119.159 (2) gamma=90

Temperature: 100 K

	Calculated	Reported
Volume	4668.4 (9)	4668.7 (10)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C29 H25 N O2	?
Sum formula	C29 H25 N O2	C58 H50 N2 O4
Mr	419.50	839.00
Dx, g cm ⁻³	1.194	1.194
Z	8	4
Mu (mm ⁻¹)	0.074	0.074
F000	1776.0	1776.0
F000'	1776.74	
h,k,lmax	20,20,20	20,20,20
Nref	8216	8195
Tmin,Tmax	0.981,0.982	
Tmin'	0.981	

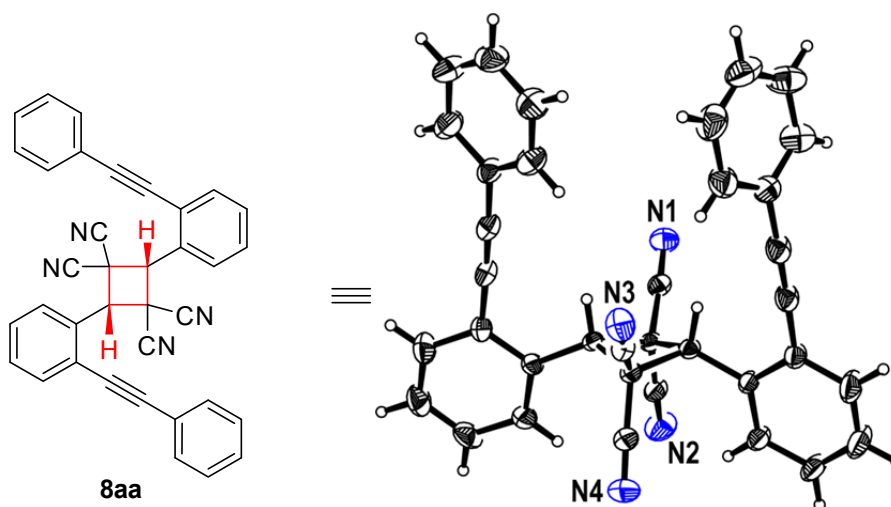
Correction method= Not given

Data completeness= 0.997 Theta(max) = 25.000

R(reflections)= 0.0476 (4844) wR2(reflections)= 0.1258 (8195)

S = 0.811 Npar= 581

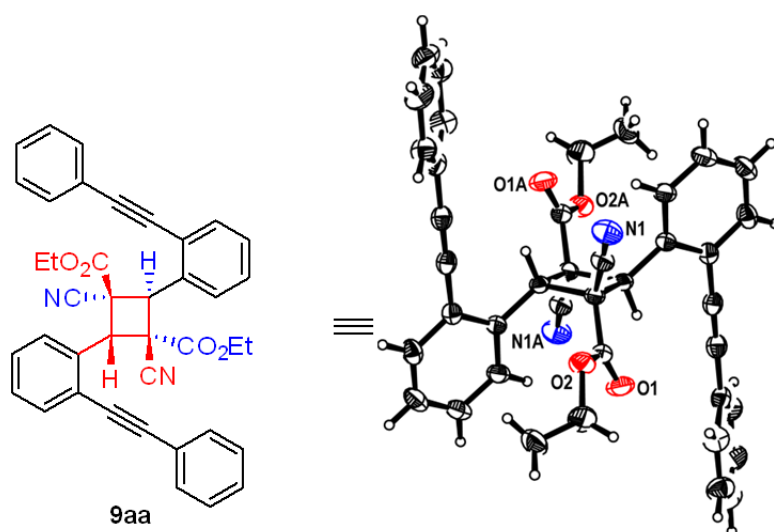
3.10 X-Ray single crystal diffraction analysis of 8aa (CCDC: 2035718)



Datablock: 1

Bond precision:	C-C = 0.0047 Å	Wavelength=0.71073	
Cell:	a=10.4403 (13) alpha=90	b=21.619 (3) beta=100.287 (3)	c=25.312 (3) gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	5621.3 (12)	5621.2 (12)	
Space group	P 21/c	P 21/c	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C ₃₆ H ₂₀ N ₄	C ₃₆ H ₂₀ N ₄	
Sum formula	C ₃₆ H ₂₀ N ₄	C ₃₆ H ₂₀ N ₄	
Mr	508.56	508.56	
Dx, g cm ⁻³	1.202	1.202	
Z	8	8	
Mu (mm ⁻¹)	0.072	0.072	
F000	2112.0	2112.0	
F000'	2112.73		
h, k, lmax	12, 25, 30	12, 25, 30	
Nref	10022	10008	
Tmin, Tmax	0.975, 0.980	0.898, 0.908	
Tmin'	0.975		
Correction method=	# Reported T Limits: Tmin=0.898 Tmax=0.908		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.999	Theta(max)= 25.099	
R(reflections)=	0.0593 (5296)	wR2(reflections)= 0.1756 (10008)	
S =	1.004	Npar= 709	

3.11 X-Ray single crystal diffraction analysis of 9aa (CCDC: 2035719)

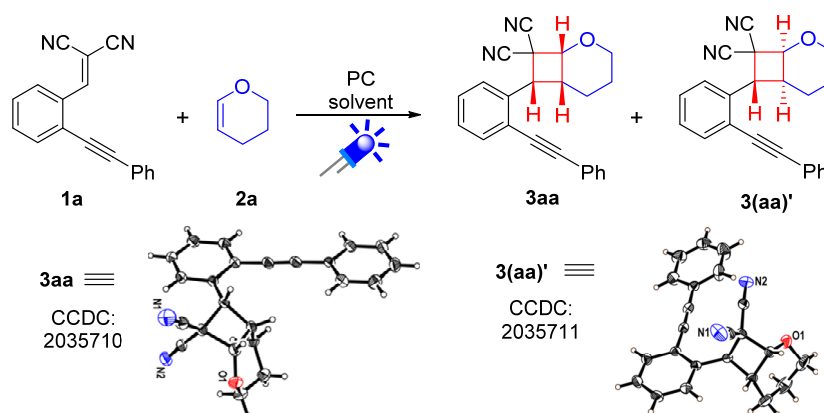


Datablock: 1

Bond precision:	C-C = 0.0024 Å	Wavelength=0.71073	
Cell:	a=11.2244 (19)	b=12.002 (2)	c=11.899 (2)
	alpha=90	beta=93.971 (3)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	1599.1 (5)	1599.0 (5)	
Space group	P 21/n	P 21/n	
Hall group	-P 2yn	-P 2yn	
Moiety formula	C40 H28 N2 O4	?	
Sum formula	C40 H28 N2 O4	C20 H14 N O2	
Mr	600.64	300.32	
Dx, g cm ⁻³	1.247	1.247	
Z	2	4	
Mu (mm ⁻¹)	0.081	0.081	
F000	628.0	628.0	
F000'	628.28		
h, k, lmax	13, 14, 14	13, 14, 14	
Nref	2982	2973	
Tmin, Tmax	0.978, 0.979		
Tmin'	0.978		
Correction method= Not given			
Data completeness=	0.997	Theta(max)= 25.497	
R(reflections)=	0.0465 (2220)	wR2(reflections)= 0.1511 (2973)	
S =	0.930	Npar= 220	

4. Further optimization of the reaction conditions (Table S1)

Table S1. Optimization of the photocatalyst and time on the reaction^a



entry	photocatalyst (PC)	2a (equiv.)	light source (nm)	solvent	time (h)	yield (%) ^b 3aa/3(aa)' ^c
1	<i>fac</i> -Ir(ppy) ₃	2.0	380–385	DCE	8	27/4
2	Ru(bpy) ₃ Cl ₂	2.0	450–455	DCE	8	29/4
3	Mes-Acr ⁺ ClO ₄ ⁻	2.0	420–425	DCE	8	28/4
4	TPPT	2.0	410–415	DCE	8	35/5
5	rose bengal	2.0	530–535	DCE	8	28/4
6	eosin Y	2.0	530–535	DCE	8	15/trace
7	–	55 (1.0 mL)	410–415	–	8	79/11
8	–	55 (1.0 mL)	410–415	–	2	29/4
9	–	55 (1.0 mL)	410–415	–	4	43/6
10	–	55 (1.0 mL)	410–415	–	6	64/9
11	–	55 (1.0 mL)	410–415	–	10	79/11
12	–	55 (1.0 mL)	410–415	–	12	79/11
13	–	55 (1.0 mL)	410–415	–	20	72/10

^aReaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), PC (2.5 mol%), DCE (1.0 mL), room temperature, air, under LED irradiation for the time indicated in Table S1. ^bYield of isolated product. TPPT = 2,4,6-triphenylpyrylium tetrafluoroborate.

5. Mechanistic investigations

5.1 The UV/Vis absorption spectra of **1a**, **1a'**, **1a''** and **1-III**

The UV/Vis absorption spectra of 2-(2-(phenylethynyl)benzylidene) malononitrile **1a** (0.1 M, 0.05 M, 0.025 M), 2-(3-(phenylethynyl)benzylidene) malononitrile **1a'** (0.1 M, 0.05 M, 0.025 M) and 2-(4-(phenylethynyl)benzylidene) malononitrile **1a''** (0.1 M, 0.05 M, 0.025 M) in 1,2-dichloroethane were recorded in 1 cm path quartz cuvettes by using a UV-Visible U-4100 spectrophotometer. The obtained charge-transfer bands in UV/vis absorption spectra were shown in Figures S1, S2, and S3. In addition, the UV/Vis absorption spectra comparison of **1-III** in 1,2-dichloroethane was shown in Figure S4.

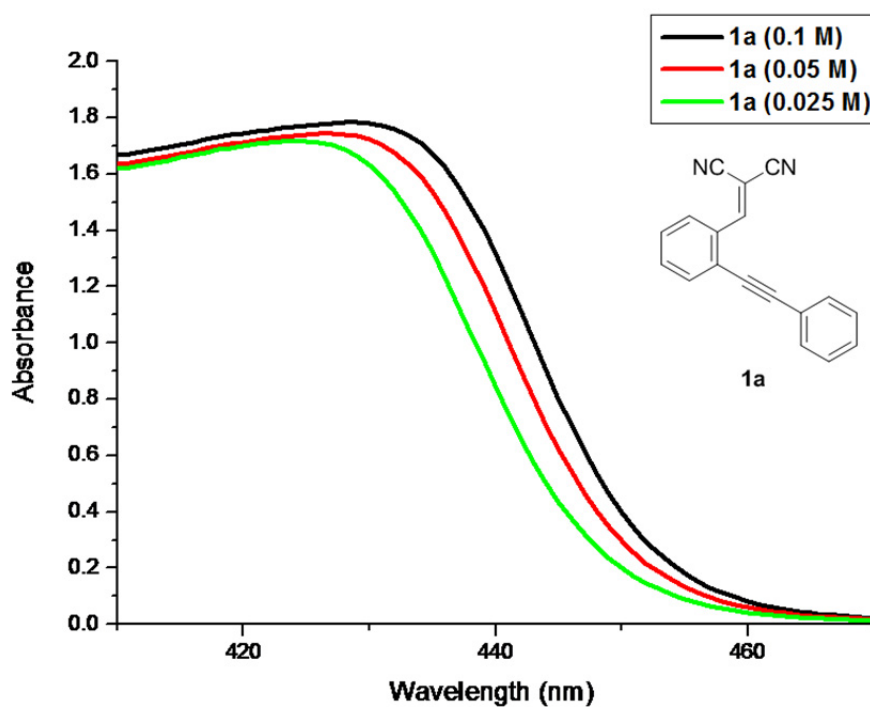


Figure S1. Absorption spectra of **1a** in DCE

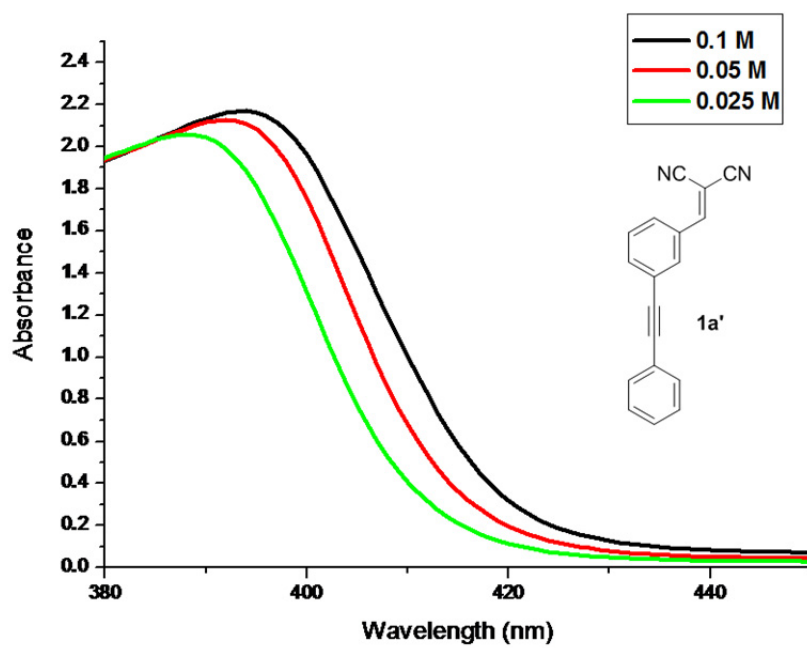


Figure S2. Absorption spectra of 1a' in DCE

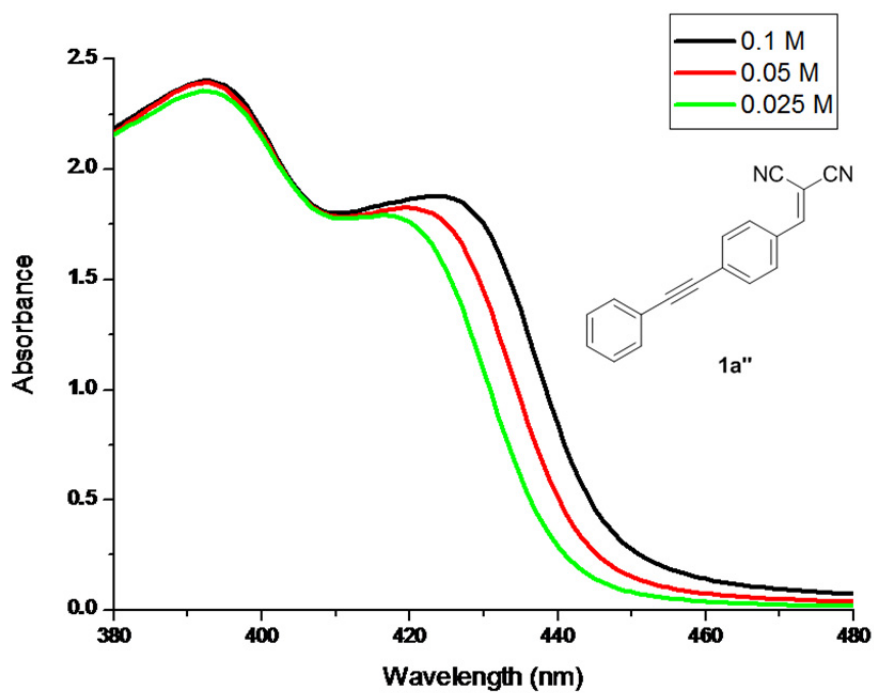


Figure S3. Absorption spectra of 1a'' in DCE

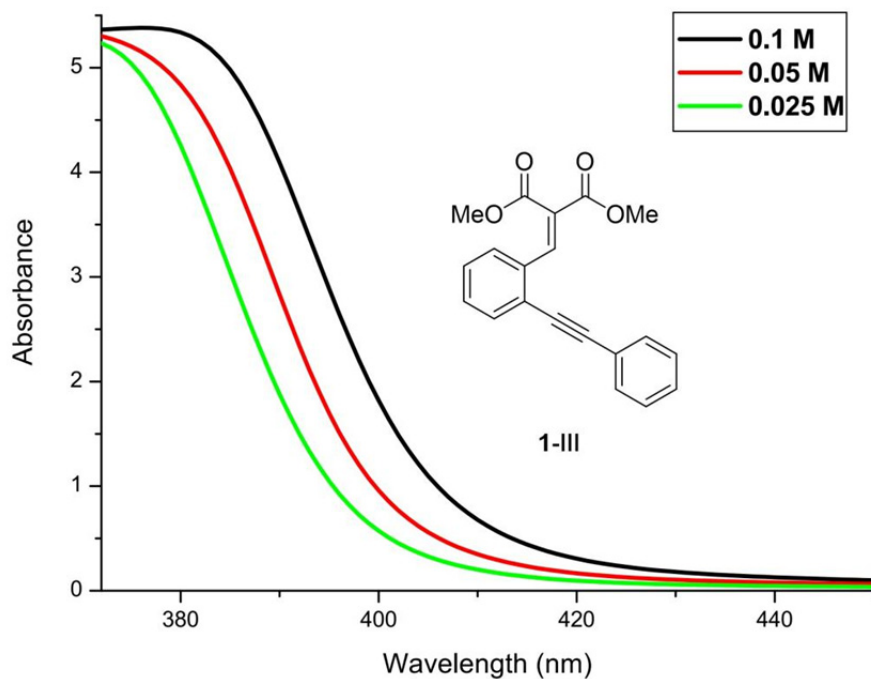


Figure S4. Absorption spectra of **1-III** in DCE

5.2 Fluorescence quenching experiment of **1a** with **2a**

To further elucidate the possible reaction pathway, fluorescence quenching experiment was performed. The fluorescence emission intensity was recorded on the Cary Eclipse Fluorescence Spectrometer with the excitation wavelength was fixed at 380 nm, and the fluorescence quenching result of 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.9 mg, 0.20 mmol in 2.0 mL DCE) by the addition of 3,4-dihydro-2*H*-pyran (**2a**, 2.0 equiv., 4.0 equiv. and 6.0 equiv.) was shown in Figure S5.

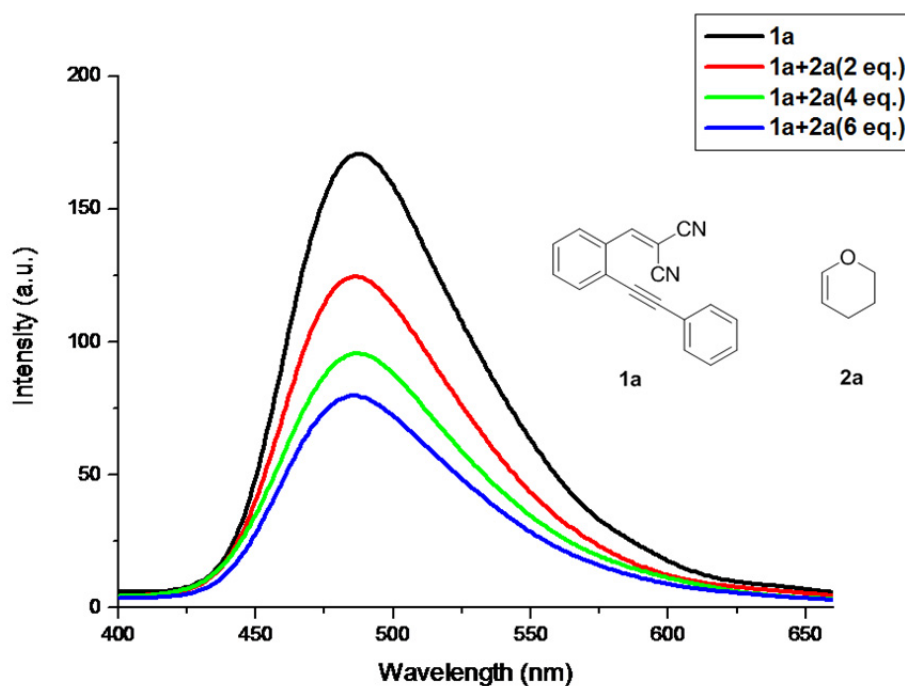


Figure S5. Fluorescence quenching experiment of **1a** with **2a**

5.3 Cyclic voltammetry measurements of **1a** and **2a** under visible light irradiation

Cyclic voltammetry measurements of **1a** and **2a** were performed in a three-electrode cell system under air at room temperature. The working electrode was a steady glassy carbon disk electrode, the counter electrode a platinum wire. The reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution, and separated from reaction by a salt bridge. DCE (5.0 mL) containing 0.25 M *n*-Bu₄NBF₆ was poured into the electrochemical cell in the samples of **1a** (0.50 mmol), **2a** (0.50 mmol), and **1a/2a** (0.50 mmol/0.50 mmol), respectively. Under the irradiation of blue LED (410–415 nm, 3 W) for 1 h, the samples were scanned at rate of 0.1 V/s ranging from 1.0 V to 4.0 V, and the corresponding cyclic voltammetry curves were recorded, as shown in Figure S6. It can be seen from Figure S6 that

there is no redox process between **1a** and **2a** under the present reaction conditions.

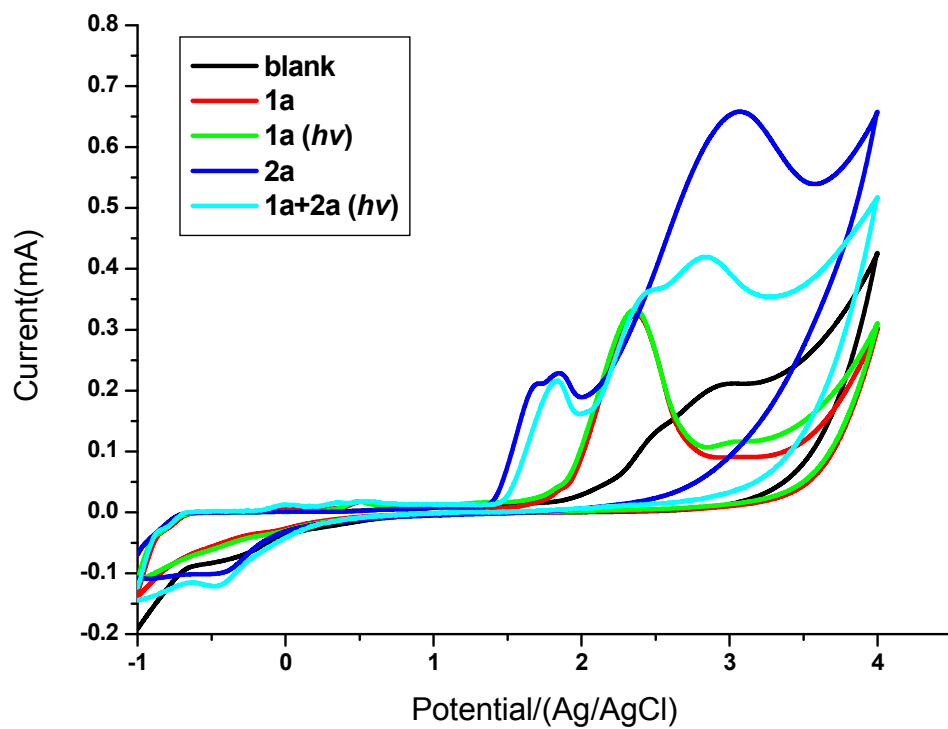
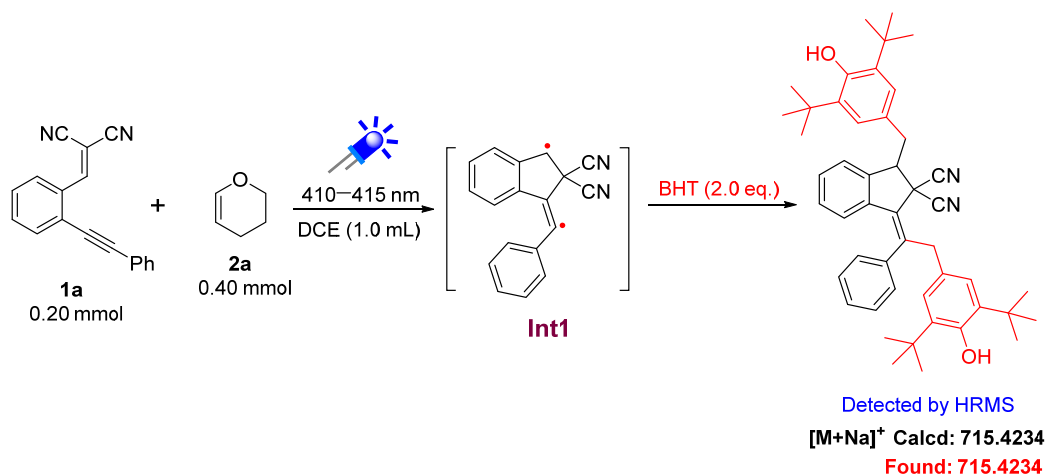


Figure S6. Cyclic voltammetry curves

5.4 The trapping experiments of key intermediates

5.4.1 The trapping experiment of key intermediate **Int1** using BHT



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.9 mg, 0.20 mmol), 3,4-dihydro-2*H*-pyran (**2a**, 0.40 mmol) in DCE (1.0 mL), and 2,6-di-*tert*-butyl-4-methylphenol (BHT, 88.2 mg, 0.40 mmol) as a free-radical trapping reagent was added. The reaction vessel was exposed to blue LED (410–415 nm, 3 W) irradiation at room temperature in air with stirring for 8 h. After the reaction, their corresponding adduct was detected by HRMS analysis (Figure S7).

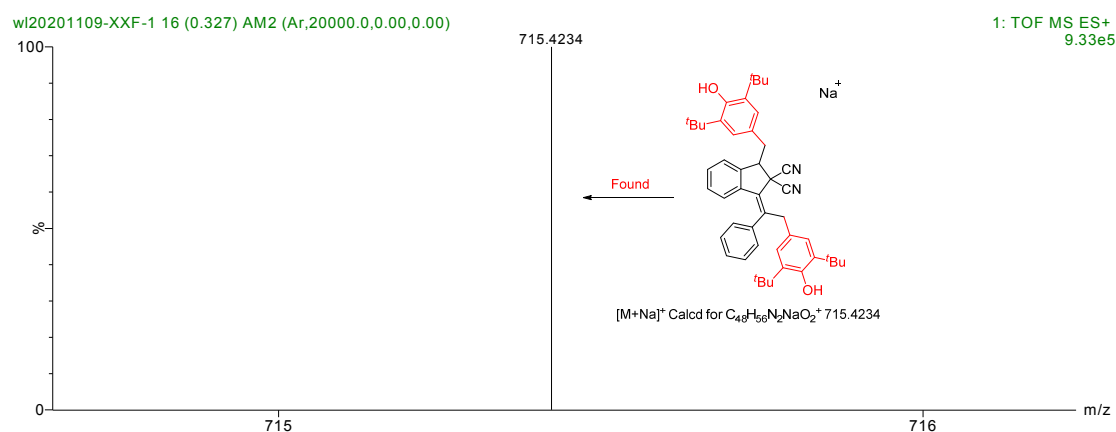
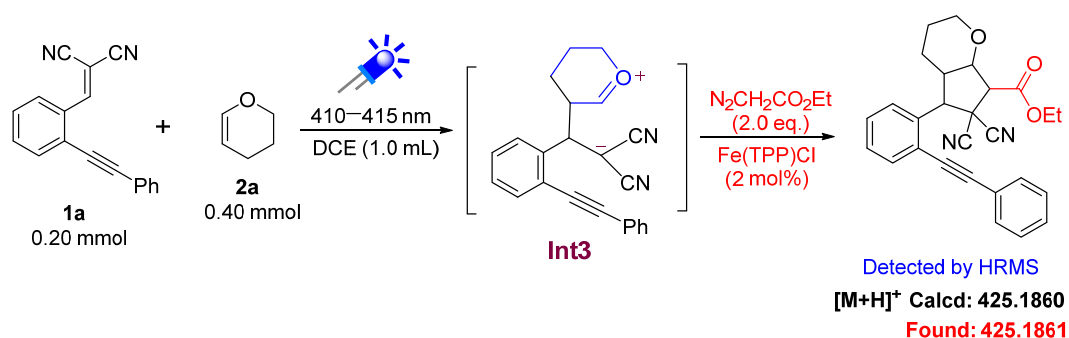


Figure S7. HRMS analysis of the **Int1** adduct with BHT

5.4.2 The trapping experiment of key intermediate **Int3** using ethyl diazoacetate



A 5 mL oven-dried reaction vessel equipped with a magnetic stirrer bar was charged with 2-(2-(phenylethynyl)benzylidene)malononitrile (**1a**, 50.9 mg, 0.20 mmol), 3,4-dihydro-2*H*-pyran (**2a**, 33.6 mg, 0.40 mmol) in DCE (1.0 mL), and ethyl diazoacetate (0.40 mmol) with Fe(TPP)Cl (0.0040 mmol, 2 mol%) as a carbanion capturing agent was added. The reaction vessel was exposed to blue LED (410–415 nm, 3 W) irradiation at room temperature in air with stirring for 8 h. After the reaction, their corresponding adduct was detected by HRMS analysis (Figure S8).

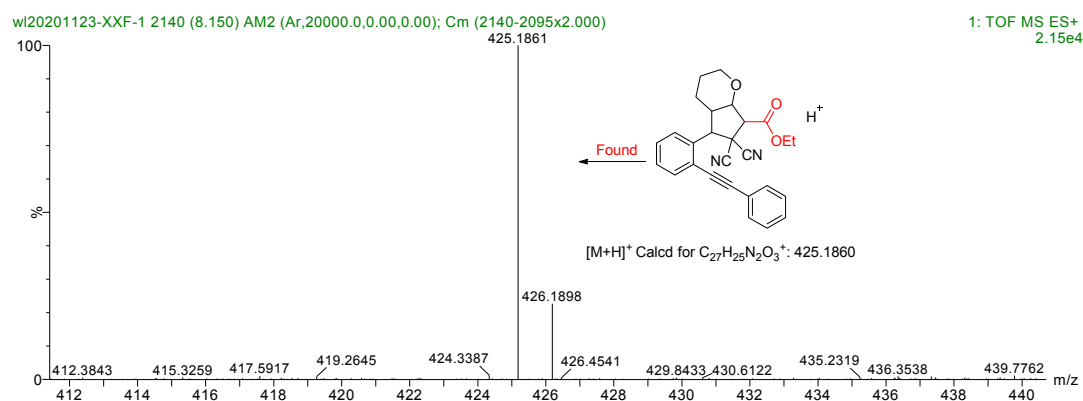
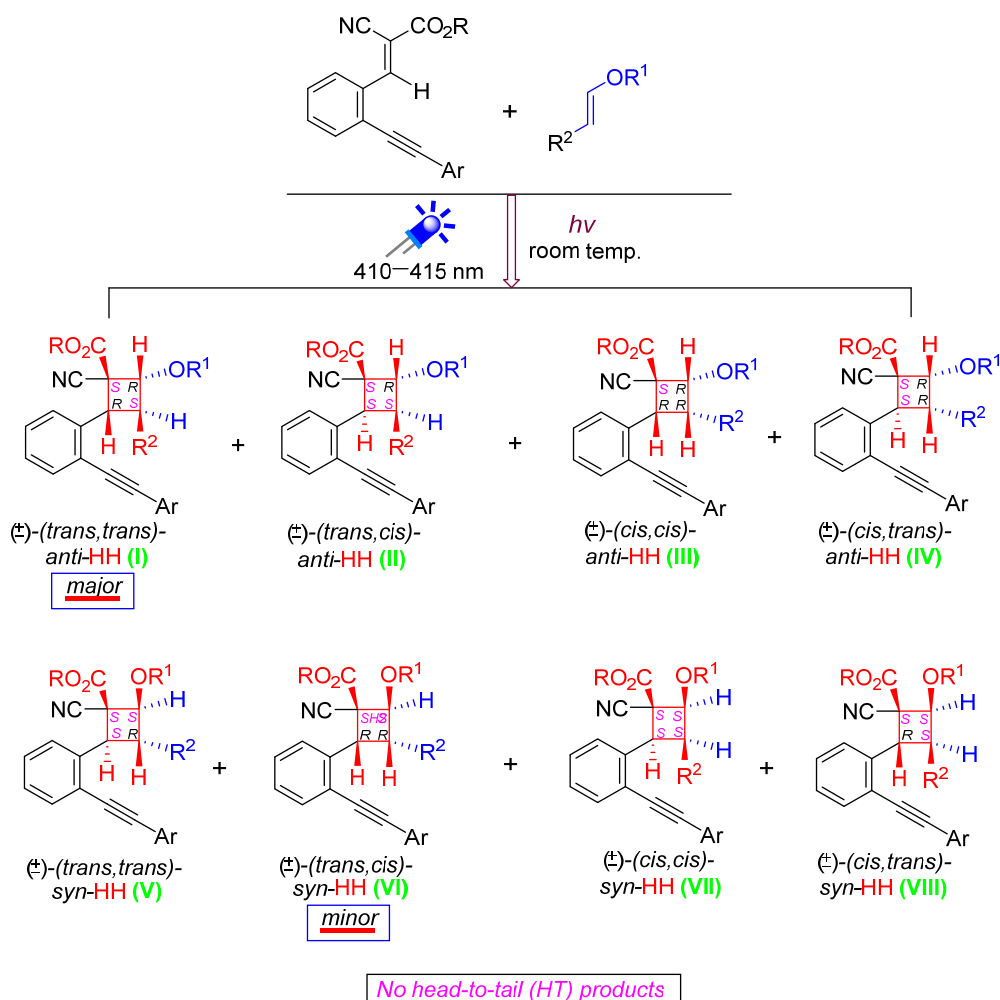


Figure S8. HRMS analysis of the **Int3** adduct with ethyl diazoacetate

6. The possible stereoisomers of [2+2]-cycloaddition products

In theory, a crossed [2+2] cycloaddition of two different asymmetric chain olefins can yield sixteen head-to-head and sixteen head-to-tail stereoisomers (Scheme S1). As outlined above, the major products in all cases were found to be the (\pm)-(*trans,trans*)-*anti*-head-to-head (**I**) isomer derived from an electron-poor and an electron-rich olefin. Importantly, only head-to-head isomers were found and no head-to-tail isomers were observed, illustrating the regioselectivity of the reaction. Moreover, among the isolated head-to-head isomers, **I** was obtained in the majority and (\pm)-(*trans,cis*)-*syn*-head-to-head (**VI = I'**) was isolated in the minority with good diastereoselectivity, demonstrating almost no geometric isomerization of the olefins during the [2+2]-cycloaddition.

Scheme S1. The possible stereoisomers of [2+2]-cycloaddition products



7. DFT calculations for the [2+2] cross-cycloaddition of 1a and 2a

All density functional theory (DFT) calculations were carried out using the M06-D3 functional^[1] (with Grimme's D3 dispersion^[2]) and performed in the Gaussian 16 program.^[3] The def2-SVP^[4] basis set was used for geometry optimization. Analytical frequency calculations were implemented on all the optimized structures at the same level of theory, to identify all the stationary point as minima (zero imaginary frequency) or transition states (one imaginary frequency) and to obtain Gibbs free energy corrections at 298 K. The final and solvation energies for the fully optimized structures in the dichloromethane were calculated by employing the SMD continuum solvation model^[5] with the larger def2-TZVPP^[6] basis set. The basis set information is downloaded from the website.^[7]

References

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7.1 Computational structures

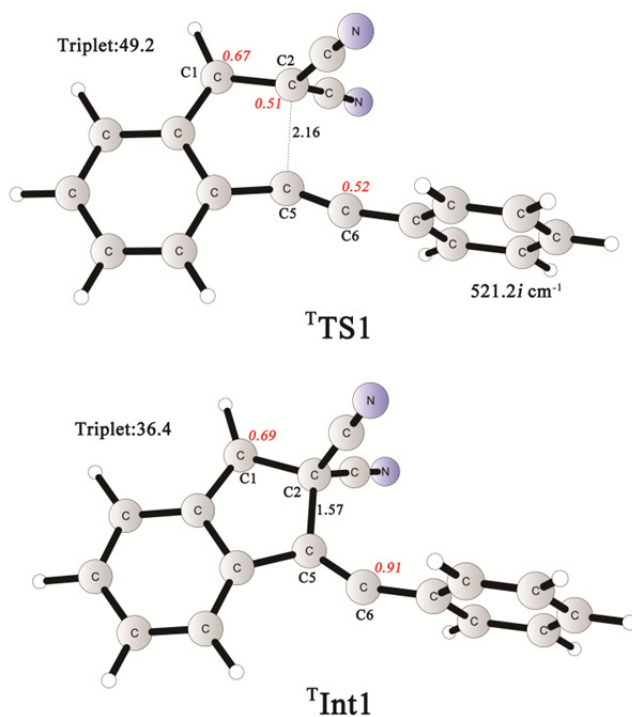


Figure S9. Optimized structures of TS1 , Int1 (Distances are given in Å. Spin densities on selected atoms are indicated in red italics. Superscripts indicate the multiplicity of the structures)

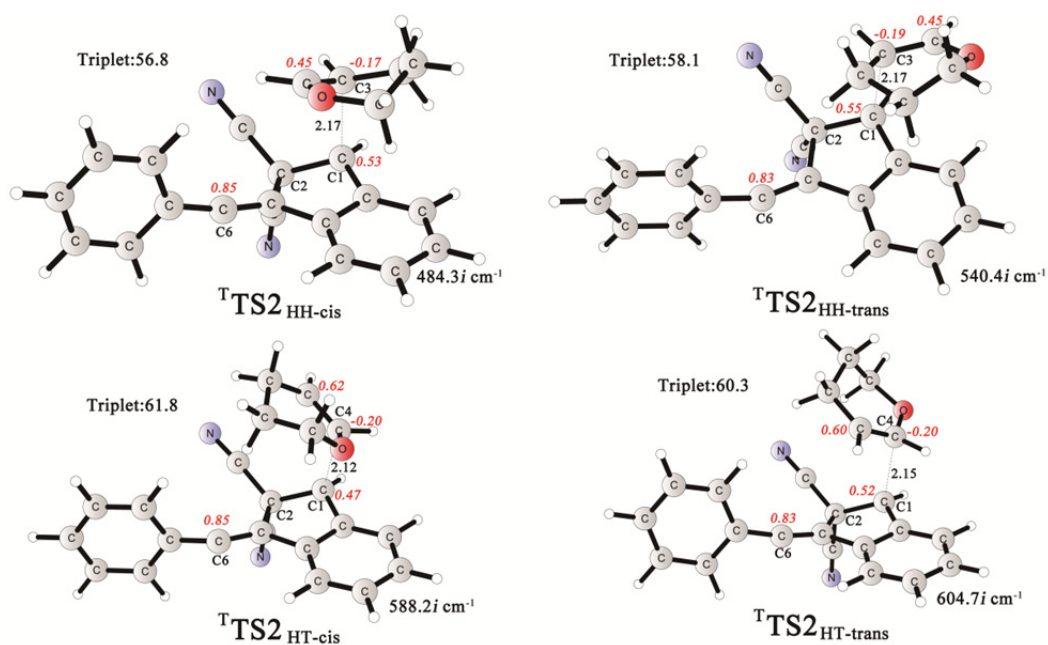


Figure S10. Optimized structures of $\text{TS2}_{\text{HH-cis}}$, $\text{TS2}_{\text{HH-trans}}$, $\text{TS2}_{\text{HT-cis}}$ and $\text{TS2}_{\text{HT-trans}}$ (Distances are given in Å. Spin densities on selected atoms are indicated in red italics)

Superscripts indicate the multiplicity of the structures. The imaginary frequencies for transition states are also shown.

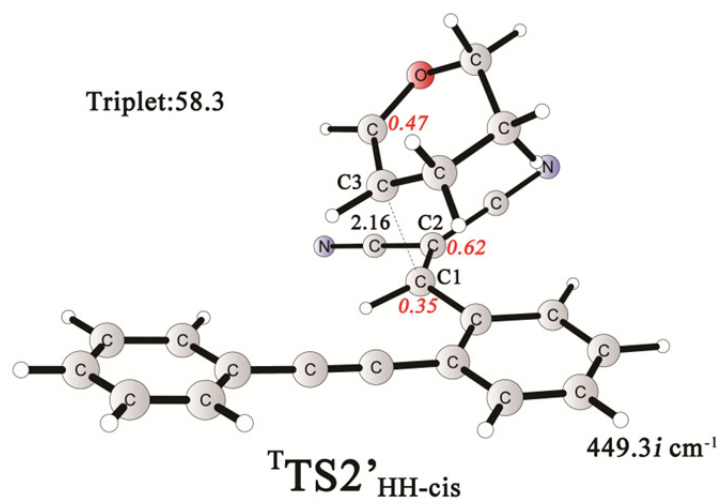


Figure S11. Optimized structures of $\text{TS2}'_{\text{HH-cis}}$ (Distances are given in Å. Spin densities on selected atoms are indicated in red italics. Superscripts indicate the multiplicity of the structures)

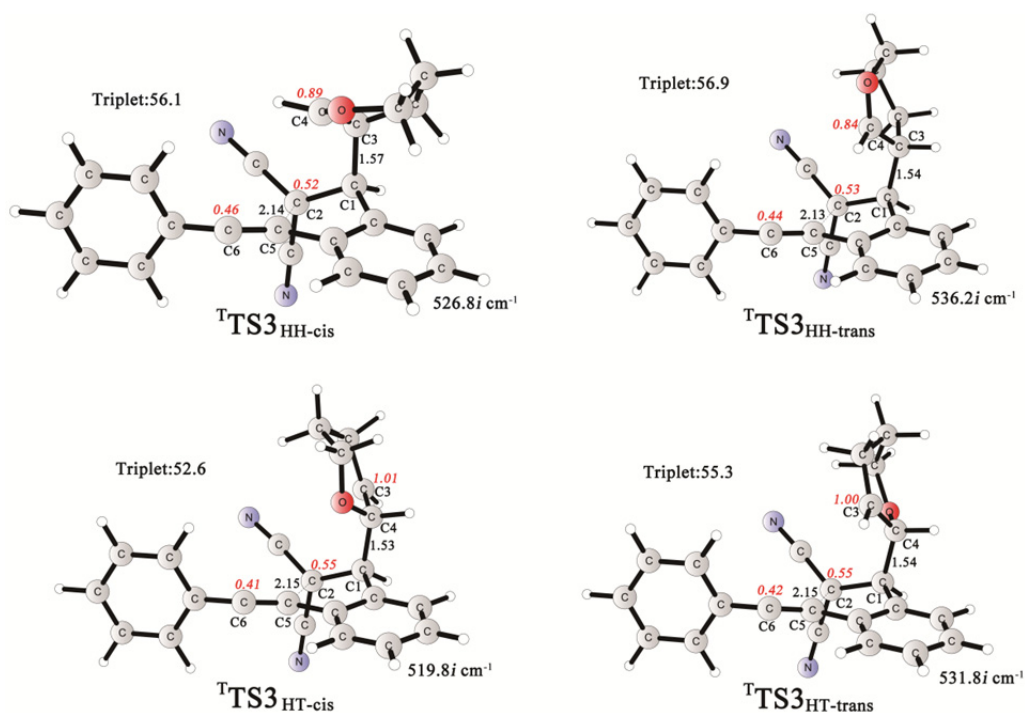
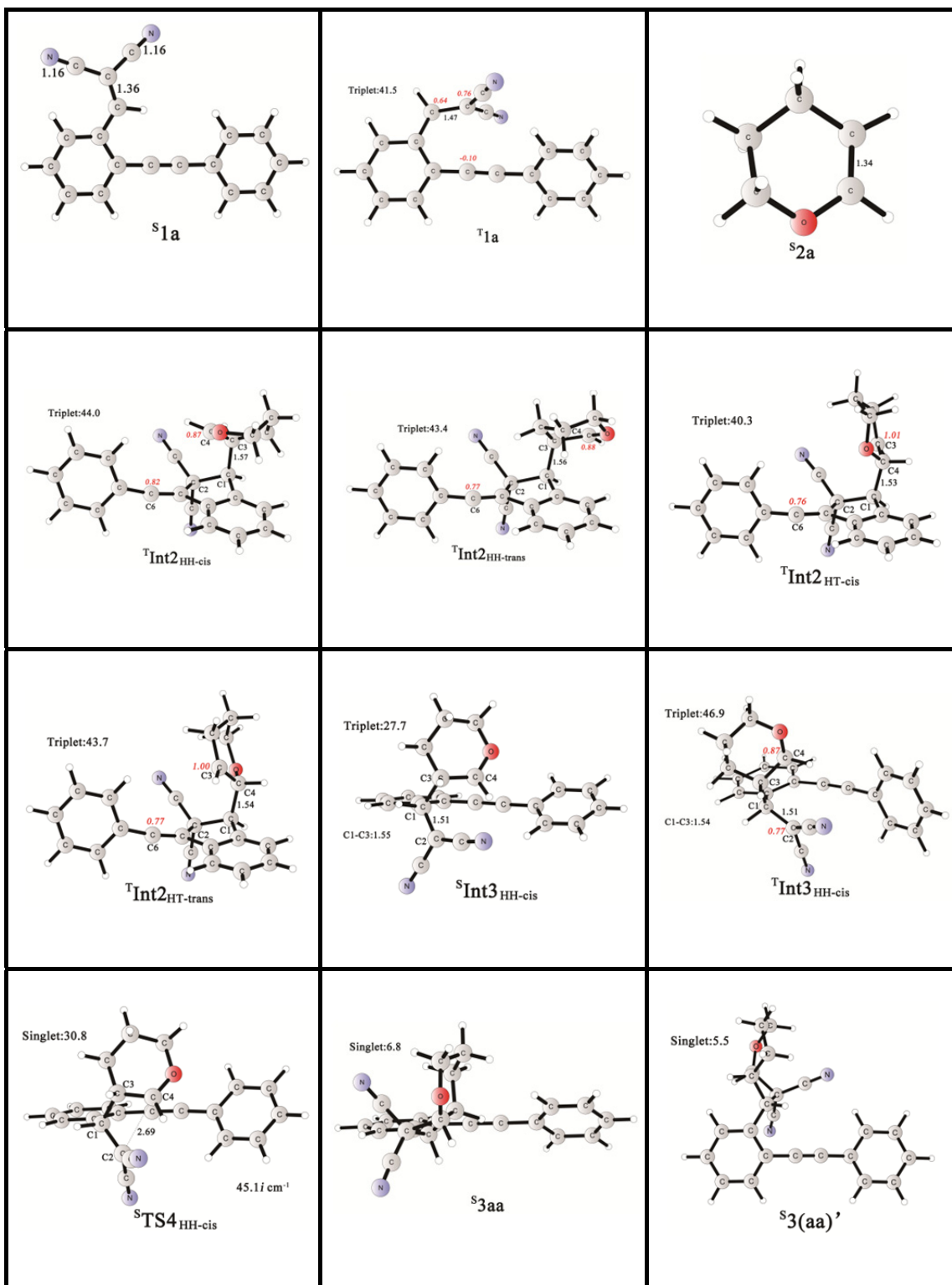


Figure S12. Optimized structures of $\text{TS3}_{\text{HH-cis}}$, $\text{TS3}_{\text{HH-trans}}$, $\text{TS3}_{\text{HT-cis}}$ and $\text{TS}_{\text{HT-trans}}$ (Distances are given in Å. Spin densities on selected atoms are indicated in red italics. Superscripts indicate the multiplicity of the structures. The imaginary frequencies for transition states are also shown.)



6.2 Calculated energies (Table S2)

Table S2. Calculated energies in Hartree and imaginary frequencies

Stationary point	Geometry optimization energy	Gibbs energy correction energy	Large basis energy	Imaginary frequencies
^S 1a	-800.1491078	0.17435	-801.0534516	
^T 1a	-800.0825673	0.170151	-800.9831834	
^S 2a	-270.1541718	0.093198	-270.4654954	
^T TS1	-800.0722321	0.17202	-800.9727379	521.2 <i>i</i>
^T Int1	-800.0975839	0.172406	-800.9935537	
^T TS2 _{HH-cis}	-1070.251336	0.28926	-1071.450099	484.3 <i>i</i>
^T TS2' _{HH-cis}	-1070.239978	0.286748	-1071.445166	449.3 <i>i</i>
^T TS2 _{HH-trans}	-1070.248466	0.287897	-1071.44677	540.4 <i>i</i>
^T TS2 _{HT-cis}	-1070.243688	0.288427	-1071.441337	588.2 <i>i</i>
^T TS2 _{HT-trans}	-1070.245195	0.287819	-1071.443048	604.7 <i>i</i>
^T Int2 _{HH-cis}	-1070.275993	0.291296	-1071.472514	
^T Int2 _{HH-trans}	-1070.279219	0.291778	-1071.473968	
^T Int2 _{HT-cis}	-1070.280389	0.289309	-1071.476434	
^T Int2 _{HT-trans}	-1070.277859	0.291104	-1071.47283	
^T TS3 _{HH-cis}	-1070.250967	0.289948	-1071.451959	526.8 <i>i</i>
^T TS3 _{HH-trans}	-1070.249982	0.290511	-1071.451208	536.2 <i>i</i>
^T TS3 _{HT-cis}	-1070.255044	0.288265	-1071.455761	519.8 <i>i</i>
^T TS3 _{HT-trans}	-1070.252336	0.288225	-1071.451575	531.8 <i>i</i>
^S Int3 _{HH-cis}	-1070.273872	0.293507	-1071.500684	
^T Int3 _{HH-cis}	-1070.264610	0.290353	-1071.467087	
^S TS4 _{HH-cis}	-1070.272697	0.29469	-1071.497068	45.1 <i>i</i>
^S 3aa	-1070.337302	0.296885	-1071.537505	
^S 3(aa)'	-1070.33925	0.296702	-1071.539326	

6.3 Cartesian coordinates of optimized structures

^s1a E(opt)= -800.1491078 hartree

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z
1	6	0	3.497300	-2.531861	0.000063
2	6	0	3.250627	-1.167458	0.000114
3	6	0	1.936990	-0.664936	0.000122
4	6	0	0.852643	-1.592901	0.000082
5	6	0	1.124938	-2.969589	0.000025
6	6	0	2.432174	-3.434822	0.000015
7	1	0	0.284511	-3.668495	-0.000010
8	1	0	2.624765	-4.511185	-0.000028
9	1	0	4.097770	-0.478978	0.000161
10	6	0	-0.500095	-1.154292	0.000092
11	6	0	-1.656238	-0.769512	0.000091
12	6	0	-2.998197	-0.292650	0.000015
13	6	0	-3.256352	1.089651	-0.000012
14	6	0	-4.077422	-1.192820	-0.000030
15	6	0	-4.565148	1.555505	-0.000082
16	1	0	-2.416172	1.791051	0.000023
17	6	0	-5.382838	-0.717788	-0.000100
18	1	0	-3.874004	-2.267335	-0.000007
19	6	0	-5.629950	0.654809	-0.000126
20	1	0	-4.756724	2.632003	-0.000102
21	1	0	-6.217424	-1.424423	-0.000134

22	1	0	-6.658956	1.025167	-0.000182
23	1	0	4.528132	-2.894667	0.000064
24	6	0	1.617142	0.745204	0.000188
25	1	0	0.543676	0.966838	0.000383
26	6	0	2.411357	1.855027	0.000025
27	6	0	1.780891	3.142933	0.000138
28	6	0	3.842218	1.858165	-0.000303
29	7	0	1.248772	4.174643	0.000239
30	7	0	5.003254	1.875933	-0.000534

¹1a E(opt)= -800.0825673 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.734161	-1.005588	-0.138835
2	6	0	4.113850	0.216947	0.003836
3	6	0	2.694566	0.338671	0.023555
4	6	0	1.916922	-0.863252	-0.127318
5	6	0	2.577223	-2.091875	-0.264771
6	6	0	3.964772	-2.172324	-0.271039
7	1	0	1.970416	-2.994834	-0.374521
8	1	0	4.453058	-3.144035	-0.382843
9	1	0	4.710156	1.128467	0.112144
10	6	0	0.497346	-0.835093	-0.138794
11	6	0	-0.723723	-0.856317	-0.152904
12	6	0	-2.147860	-0.820196	-0.140112
13	6	0	-2.844175	0.052563	-0.995283

14	6	0	-2.869342	-1.644261	0.741323
15	6	0	-4.232811	0.096223	-0.961284
16	1	0	-2.283832	0.695308	-1.681103
17	6	0	-4.257102	-1.594143	0.764475
18	1	0	-2.322769	-2.316322	1.408721
19	6	0	-4.941227	-0.724681	-0.085032
20	1	0	-4.767508	0.779140	-1.627108
21	1	0	-4.811782	-2.236088	1.454484
22	1	0	-6.034056	-0.686226	-0.062395
23	1	0	5.825841	-1.065218	-0.146750
24	6	0	2.132033	1.614254	0.199773
25	6	0	0.694692	1.926313	0.273544
26	1	0	2.819753	2.466100	0.299180
27	6	0	-0.002352	2.331129	-0.886424
28	6	0	0.021012	1.931040	1.515872
29	7	0	-0.514549	1.921623	2.552062
30	7	0	-0.560764	2.646556	-1.861104

^s2a E(opt)= -270.1541718 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.838587	-1.039830	-0.323980
2	6	0	0.535344	-1.206578	0.291770
3	6	0	0.901208	1.065299	-0.083398
4	6	0	-0.398089	1.356272	0.063121
5	6	0	-1.443051	0.283944	0.126008

S40

6	1	0	0.454666	-1.189800	1.398726
7	1	0	1.008829	-2.157420	0.004108
8	1	0	-0.730803	-1.049945	-1.423871
9	1	0	-1.478050	-1.896525	-0.055760
10	1	0	-1.854807	0.191953	1.150633
11	1	0	-2.305231	0.550466	-0.510746
12	1	0	1.675465	1.830482	-0.199354
13	1	0	-0.688986	2.409846	0.095730
14	8	0	1.422247	-0.180462	-0.112574

[‡]TS1 E(opt)= -800.0722321 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.144317	-1.575206	0.147180
2	6	0	3.685869	-0.330752	0.505544
3	6	0	2.888974	0.820805	0.425880
4	6	0	1.571908	0.745529	-0.007268
5	6	0	0.986586	-0.520629	-0.398071
6	6	0	1.835735	-1.670650	-0.291268
7	7	0	0.773488	1.891934	-0.025785
8	6	0	-0.503955	1.981287	-0.572055
9	6	0	-1.099517	0.713889	-0.939904
10	6	0	-0.348058	-0.557078	-0.822648
11	8	0	-1.066283	3.074157	-0.674747
12	6	0	-2.135554	-2.111608	0.088724
13	6	0	-3.118905	-0.966116	0.388776

S41

14	6	0	-2.500847	0.300468	0.950847
15	6	0	-1.576066	0.313131	1.952972
16	1	0	3.755777	-2.470579	0.211157
17	1	0	4.713172	-0.253259	0.846304
18	1	0	3.296552	1.786060	0.716768
19	1	0	1.438222	-2.640782	-0.567767
20	1	0	1.182827	2.779562	0.234003
21	1	0	-1.953094	0.776261	-1.606573
22	1	0	-2.711244	-3.008515	-0.169847
23	1	0	-1.559277	-2.360873	0.987105
24	1	0	-3.672550	-0.720930	-0.525716
25	1	0	-3.871888	-1.322714	1.106397
26	1	0	-3.004067	1.234253	0.710946
27	1	0	-1.232537	1.249317	2.379665
28	1	0	-1.093761	-0.592051	2.306490
29	6	0	-1.151037	-1.800902	-1.067512
30	1	0	-0.511235	-2.672779	-1.227846
31	1	0	-1.737745	-1.672771	-1.989796

^TInt1 E(opt)= -800.0975839 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.591280	-1.232494	0.000379
2	6	0	4.193523	0.090751	0.001226
3	6	0	2.807786	0.388674	0.000761
4	6	0	1.861571	-0.683496	-0.000561

S42

5	6	0	2.281058	-2.009495	-0.001412
6	6	0	3.647336	-2.280762	-0.000940
7	1	0	1.540695	-2.815822	-0.002401
8	1	0	3.995459	-3.317363	-0.001594
9	6	0	2.153093	1.623363	0.001459
10	1	0	4.928357	0.900619	0.002251
11	6	0	0.509409	-0.147509	-0.000607
12	6	0	-0.662832	-0.749480	-0.001086
13	6	0	-2.056906	-0.752656	-0.000782
14	6	0	-2.780544	-0.761461	1.222486
15	6	0	-2.781627	-0.759473	-1.223389
16	6	0	-4.164771	-0.768124	1.211607
17	1	0	-2.224845	-0.744519	2.164704
18	6	0	-4.165873	-0.766147	-1.211229
19	1	0	-2.226823	-0.740967	-2.166104
20	6	0	-4.864248	-0.773298	0.000490
21	1	0	-4.712228	-0.762706	2.158267
22	1	0	-4.714160	-0.759172	-2.157397
23	1	0	-5.957804	-0.777161	0.000991
24	6	0	0.651339	1.414009	0.000449
25	6	0	0.021894	1.967958	-1.207207
26	7	0	-0.460041	2.377888	-2.177681
27	6	0	0.020203	1.966662	1.207760
28	7	0	-0.463195	2.375603	2.177921
29	1	0	2.606225	2.616289	0.002462
30	1	0	5.657625	-1.475767	0.000726

^TTS2_{HH-cis} E(opt)= -1070.251336 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.315942	-1.729492	-1.914916
2	6	0	-3.215288	-1.492967	-0.547912
3	6	0	-1.961735	-1.175245	-0.001256
4	6	0	-0.827834	-1.132139	-0.847433
5	6	0	-0.936628	-1.359985	-2.215297
6	6	0	-2.189868	-1.655430	-2.748176
7	1	0	-0.044183	-1.317284	-2.848012
8	1	0	-2.295226	-1.849335	-3.819122
9	6	0	-1.604414	-0.772930	1.333089
10	6	0	-0.939810	1.980256	0.607330
11	6	0	-2.480751	2.141648	-1.161016
12	1	0	-2.580259	1.093095	-1.502422
13	1	0	-4.097055	-1.572729	0.096292
14	6	0	0.365768	-0.818441	-0.059199
15	6	0	1.575468	-0.488732	-0.442170
16	6	0	2.877147	-0.037180	-0.543296
17	6	0	3.145473	1.361660	-0.610769
18	6	0	3.976634	-0.941253	-0.598995
19	6	0	4.446552	1.818349	-0.716414
20	1	0	2.302546	2.059261	-0.580525
21	6	0	5.269381	-0.460719	-0.705214
22	1	0	3.777627	-2.015372	-0.546880
23	6	0	5.515665	0.915886	-0.764208
24	1	0	4.638590	2.894158	-0.761734
25	1	0	6.105332	-1.165267	-0.739803

26	1	0	6.541370	1.285848	-0.846796
27	6	0	-1.874999	1.376520	1.433390
28	6	0	-3.516988	2.459320	-0.106436
29	1	0	-3.397368	3.516112	0.194086
30	1	0	-4.525460	2.361510	-0.539347
31	8	0	-1.162796	2.340022	-0.661627
32	6	0	-3.341050	1.545873	1.101985
33	1	0	-3.866139	1.965291	1.976240
34	1	0	-3.825037	0.573082	0.903085
35	1	0	-1.590513	1.368694	2.491609
36	1	0	0.090409	2.173698	0.921119
37	1	0	-2.570388	2.791805	-2.043525
38	6	0	-0.088030	-0.958416	1.432353
39	6	0	0.191794	-2.338577	1.864739
40	7	0	0.388282	-3.433979	2.188707
41	6	0	0.617503	-0.031138	2.322038
42	7	0	1.185075	0.705667	3.012508
43	1	0	-2.216524	-1.036886	2.203384
44	1	0	-4.287145	-1.988874	-2.346454

^tTS2'_{HH-cis} E(opt)= -1070.239978 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.452553	3.367550	-0.487463
2	6	0	-2.341202	2.010158	-0.755095
3	6	0	-1.098436	1.348054	-0.699457

S45

4	6	0	0.051462	2.129208	-0.361052
5	6	0	-0.083736	3.499828	-0.095811
6	6	0	-1.324542	4.120953	-0.153321
7	1	0	0.813623	4.070364	0.160260
8	1	0	-1.413734	5.189995	0.056727
9	6	0	-0.923827	-0.070560	-0.921575
10	6	0	-1.350457	-2.265293	0.903576
11	6	0	-3.055983	-1.575285	2.410239
12	1	0	-2.690818	-1.936675	3.391539
13	1	0	-3.241837	1.453306	-1.025591
14	6	0	1.329158	1.513691	-0.258644
15	6	0	2.404292	0.946518	-0.160562
16	6	0	3.640138	0.248398	-0.043935
17	6	0	3.736049	-1.090595	-0.464798
18	6	0	4.775510	0.875696	0.497559
19	6	0	4.935794	-1.780693	-0.341956
20	1	0	2.856116	-1.578005	-0.897515
21	6	0	5.971567	0.178603	0.615445
22	1	0	4.701715	1.917051	0.823482
23	6	0	6.055948	-1.149622	0.198151
24	1	0	4.998917	-2.820663	-0.674358
25	1	0	6.849325	0.676170	1.037592
26	1	0	6.999452	-1.694606	0.292174
27	6	0	-0.652389	-1.047151	0.991386
28	6	0	-2.629217	-0.143896	2.183290
29	1	0	-3.135216	0.260433	1.289513
30	1	0	-2.969335	0.468306	3.033707
31	8	0	-2.560452	-2.473413	1.416456
32	6	0	-1.120919	-0.060118	2.016451

33	1	0	-0.798307	0.964340	1.768849
34	1	0	-0.616493	-0.303849	2.973482
35	1	0	0.426733	-1.106841	0.809837
36	1	0	-0.987381	-3.115613	0.317341
37	1	0	-4.149297	-1.689617	2.390644
38	6	0	-1.933313	-0.973945	-1.475405
39	6	0	-3.308634	-0.931825	-1.162867
40	7	0	-4.437982	-0.901163	-0.868453
41	6	0	-1.490388	-2.061181	-2.262911
42	7	0	-1.078017	-2.956269	-2.887528
43	1	0	0.080280	-0.341877	-1.267393
44	1	0	-3.434075	3.846158	-0.547552

^TTS2_{HH-trans} E(opt)= -1070.248466 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.060824	2.725311	-0.540880
2	6	0	2.898782	1.756384	0.442240
3	6	0	1.657266	1.112928	0.562301
4	6	0	0.594860	1.477858	-0.295475
5	6	0	0.765680	2.445966	-1.280773
6	6	0	2.007519	3.066378	-1.402837
7	1	0	-0.071394	2.713646	-1.933800
8	1	0	2.160044	3.834145	-2.166404
9	6	0	1.279326	0.025375	1.428118
10	6	0	3.532827	-1.633965	0.874855

11	6	0	4.114723	-1.556292	-1.397897
12	1	0	4.264625	-2.642172	-1.564195
13	1	0	3.727235	1.485088	1.103648
14	6	0	-0.604530	0.710671	0.038684
15	6	0	-1.788070	0.653519	-0.528144
16	6	0	-3.111100	0.231674	-0.631086
17	6	0	-3.459255	-0.902440	-1.413935
18	6	0	-4.145418	0.936893	0.043071
19	6	0	-4.779335	-1.307270	-1.506720
20	1	0	-2.663039	-1.455952	-1.921071
21	6	0	-5.460064	0.515904	-0.063697
22	1	0	-3.878529	1.803021	0.656266
23	6	0	-5.786023	-0.602262	-0.838111
24	1	0	-5.034023	-2.188663	-2.101992
25	1	0	-6.246184	1.059732	0.467765
26	1	0	-6.826693	-0.929122	-0.916059
27	6	0	2.183171	-1.787123	0.624556
28	6	0	2.695196	-1.164431	-1.738238
29	1	0	2.593890	-0.069454	-1.648997
30	1	0	2.487939	-1.415450	-2.791152
31	8	0	4.441963	-1.268945	-0.043898
32	6	0	1.716612	-1.867070	-0.806739
33	1	0	0.701135	-1.452367	-0.928385
34	1	0	1.623733	-2.934495	-1.085118
35	1	0	1.622516	-2.361608	1.370502
36	1	0	3.954005	-1.674422	1.885475
37	1	0	4.852682	-1.016702	-2.009327
38	6	0	-0.249757	-0.086339	1.342476
39	6	0	-0.859495	0.625123	2.476361

40	7	0	-1.322554	1.216361	3.359505
41	6	0	-0.772880	-1.457100	1.292495
42	7	0	-1.177093	-2.540414	1.222145
43	1	0	1.724311	-0.086298	2.422525
44	1	0	4.024412	3.232837	-0.643785

[†]TS2_{HT-cis} E(opt)= -1070.243688 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.725227	-2.387769	-0.935839
2	6	0	-3.485991	-1.606986	0.187336
3	6	0	-2.191641	-1.119513	0.411654
4	6	0	-1.157050	-1.441448	-0.493888
5	6	0	-1.403585	-2.217458	-1.622922
6	6	0	-2.696057	-2.686541	-1.841638
7	1	0	-4.731443	-2.774998	-1.120544
8	1	0	-0.586611	-2.455161	-2.312078
9	1	0	-2.910640	-3.302396	-2.719478
10	6	0	-1.730489	-0.174462	1.399703
11	6	0	-1.794129	2.696707	1.001408
12	6	0	-0.663184	2.632533	-1.186786
13	1	0	-0.176482	3.238065	-1.968454
14	1	0	-4.296172	-1.364878	0.882866
15	6	0	0.103219	-0.855839	-0.041292
16	6	0	1.295135	-0.817343	-0.593493
17	6	0	2.662106	-0.551435	-0.618336

18	6	0	3.181215	0.608987	-1.253553
19	6	0	3.573673	-1.455105	-0.006028
20	6	0	4.543922	0.850732	-1.260997
21	1	0	2.486038	1.309998	-1.724957
22	6	0	4.933509	-1.195444	-0.025402
23	1	0	3.177644	-2.346284	0.490490
24	6	0	5.427290	-0.046496	-0.651344
25	1	0	4.930123	1.752776	-1.744005
26	1	0	5.623132	-1.892655	0.458841
27	1	0	6.502526	0.152560	-0.661034
28	6	0	-2.540320	1.605074	0.567288
29	6	0	-1.991837	2.120897	-1.694699
30	1	0	-1.875853	1.501238	-2.598221
31	1	0	-2.649395	2.975694	-1.955919
32	1	0	-3.447394	1.331851	1.123996
33	1	0	-1.871892	2.981470	2.055894
34	1	0	0.002049	1.771037	-0.990152
35	6	0	-0.200437	-0.276925	1.383407
36	6	0	0.213977	-1.299725	2.359859
37	7	0	0.524095	-2.125124	3.112573
38	6	0	0.561563	0.944926	1.660597
39	7	0	1.227934	1.867685	1.876638
40	1	0	-2.200041	-0.111348	2.388788
41	6	0	-0.869918	3.429201	0.091800
42	8	0	-2.663836	1.305174	-0.750296
43	1	0	0.091408	3.627585	0.597320
44	1	0	-1.294993	4.426739	-0.146472

[‡]TS2_{HT-trans} E(opt)= -1070.245195 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.076856	-3.307363	-1.089405
2	6	0	-3.188946	-2.216323	-0.233964
3	6	0	-2.028346	-1.526264	0.142860
4	6	0	-0.775672	-1.946707	-0.356344
5	6	0	-0.669718	-3.033600	-1.218651
6	6	0	-1.829343	-3.714560	-1.582214
7	1	0	-3.975423	-3.859345	-1.379985
8	1	0	0.312723	-3.342664	-1.590164
9	1	0	-1.767230	-4.577416	-2.251019
10	6	0	-1.893123	-0.311463	0.912370
11	6	0	-1.494011	1.454012	-1.314712
12	6	0	-1.776203	3.858607	-0.841352
13	1	0	-1.247169	4.811642	-0.682131
14	1	0	-4.166249	-1.904340	0.149000
15	6	0	0.279245	-1.071072	0.157314
16	6	0	1.538986	-0.948671	-0.186616
17	6	0	2.838360	-0.481544	-0.292397
18	6	0	3.138519	0.621952	-1.141891
19	6	0	3.904856	-1.093757	0.424771
20	6	0	4.437095	1.084359	-1.254362
21	1	0	2.320110	1.098218	-1.690865
22	6	0	5.196739	-0.614999	0.296323
23	1	0	3.680336	-1.939007	1.081514
24	6	0	5.473566	0.471603	-0.540779

S51

25	1	0	4.652170	1.938254	-1.903116
26	1	0	6.006178	-1.089758	0.858191
27	1	0	6.497577	0.843483	-0.634904
28	6	0	-2.560808	1.211977	-0.455592
29	6	0	-2.373467	3.389379	0.467024
30	1	0	-3.088698	4.118390	0.875886
31	1	0	-1.578709	3.238746	1.220320
32	1	0	-3.310111	0.458024	-0.725280
33	1	0	-1.168722	0.626275	-1.954729
34	1	0	-2.596344	4.057461	-1.555131
35	6	0	-0.407297	-0.222585	1.277145
36	6	0	-0.203988	-0.917937	2.560547
37	7	0	-0.066060	-1.487202	3.560808
38	6	0	0.173573	1.117186	1.375646
39	7	0	0.673908	2.158400	1.463766
40	1	0	-2.623721	-0.017822	1.675195
41	6	0	-0.843935	2.792517	-1.405850
42	8	0	-3.111034	2.181943	0.306525
43	1	0	-0.588840	3.008604	-2.458433
44	1	0	0.120093	2.808848	-0.857770

^TInt2_{HF-cis} E(opt)= -1070.275993 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.197664	2.468626	1.119831
2	6	0	-3.097776	1.658932	-0.012198

S52

3	6	0	-1.879585	1.051983	-0.304278
4	6	0	-0.761367	1.304574	0.502386
5	6	0	-0.862040	2.095571	1.644457
6	6	0	-2.092890	2.668063	1.953015
7	1	0	0.022055	2.273839	2.264723
8	1	0	-2.190718	3.301560	2.839096
9	6	0	-1.549663	0.041016	-1.368387
10	6	0	-1.147051	-1.880652	0.263514
11	6	0	-3.042175	-1.585689	1.647629
12	1	0	-3.240192	-0.493991	1.663914
13	1	0	-3.966469	1.514681	-0.662888
14	6	0	0.434818	0.681210	-0.074262
15	6	0	1.650982	0.558559	0.398031
16	6	0	2.974972	0.178754	0.544168
17	6	0	3.299539	-1.118966	1.033834
18	6	0	4.039321	1.069040	0.226735
19	6	0	4.621141	-1.497498	1.185749
20	1	0	2.483625	-1.807243	1.274782
21	6	0	5.354313	0.669350	0.387296
22	1	0	3.796112	2.065625	-0.152705
23	6	0	5.655588	-0.610330	0.866749
24	1	0	4.856673	-2.500142	1.553803
25	1	0	6.163249	1.360182	0.132828
26	1	0	6.697846	-0.917873	0.989050
27	6	0	-1.893491	-1.429276	-0.945000
28	6	0	-3.805739	-2.247927	0.523366
29	1	0	-3.568633	-3.327667	0.532293
30	1	0	-4.890137	-2.158915	0.699336
31	8	0	-1.651466	-1.817895	1.513568

32	6	0	-3.421229	-1.626870	-0.812637
33	1	0	-3.793316	-2.245272	-1.645121
34	1	0	-3.936033	-0.656203	-0.909611
35	1	0	-1.524226	-2.054696	-1.778801
36	1	0	-0.173100	-2.373589	0.211315
37	1	0	-3.326640	-1.985681	2.633110
38	6	0	-0.003298	0.238987	-1.508679
39	6	0	0.255407	1.360418	-2.423146
40	7	0	0.445987	2.258246	-3.130110
41	6	0	0.733893	-0.938433	-1.968794
42	7	0	1.326312	-1.874888	-2.306184
43	1	0	-2.052588	0.251571	-2.329826
44	1	0	-4.147901	2.956806	1.353941

^TInt2_{HH-trans} E(opt)= -1070.279219 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.046880	2.759458	-0.431314
2	6	0	2.938980	1.654488	0.411253
3	6	0	1.719164	0.988581	0.492396
4	6	0	0.615648	1.449434	-0.234139
5	6	0	0.722866	2.549692	-1.084064
6	6	0	1.950205	3.197681	-1.181776
7	1	0	-0.151366	2.892839	-1.646569
8	1	0	2.055720	4.066501	-1.837581
9	6	0	1.405511	-0.277312	1.242602

S54

10	6	0	3.506495	-1.570821	0.816321
11	6	0	4.036159	-1.534083	-1.476902
12	1	0	4.180830	-2.629434	-1.584845
13	1	0	3.803350	1.304459	0.983078
14	6	0	-0.570715	0.639751	0.055956
15	6	0	-1.773313	0.650666	-0.465933
16	6	0	-3.109721	0.283588	-0.576950
17	6	0	-3.522154	-0.733833	-1.480253
18	6	0	-4.097225	0.933212	0.214678
19	6	0	-4.858282	-1.080454	-1.575968
20	1	0	-2.763112	-1.244202	-2.080729
21	6	0	-5.428565	0.571434	0.102671
22	1	0	-3.780322	1.708344	0.919159
23	6	0	-5.818133	-0.431292	-0.791442
24	1	0	-5.163200	-1.872103	-2.266149
25	1	0	-6.177991	1.070563	0.723442
26	1	0	-6.871874	-0.711945	-0.873338
27	6	0	2.025679	-1.561212	0.619134
28	6	0	2.614577	-1.165003	-1.830459
29	1	0	2.507780	-0.066484	-1.826519
30	1	0	2.396322	-1.498027	-2.858825
31	8	0	4.362225	-1.163023	-0.148761
32	6	0	1.653493	-1.820207	-0.848417
33	1	0	0.613194	-1.517520	-1.057105
34	1	0	1.679790	-2.913612	-1.009081
35	1	0	1.614391	-2.392053	1.226019
36	1	0	3.931036	-1.469570	1.821906
37	1	0	4.770043	-1.030991	-2.124099
38	6	0	-0.168531	-0.271313	1.262405

39	6	0	-0.640866	0.402570	2.478409
40	7	0	-1.006482	0.964379	3.423696
41	6	0	-0.789171	-1.594678	1.177703
42	7	0	-1.288498	-2.635302	1.080036
43	1	0	1.768895	-0.229349	2.285210
44	1	0	3.999673	3.291150	-0.505468

[†]Int2_{HF-cis} E(opt)= -1070.280389 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.855271	-3.549542	-0.676484
2	6	0	-2.982936	-2.389597	0.086532
3	6	0	-1.869007	-1.577040	0.267078
4	6	0	-0.643809	-1.921760	-0.307374
5	6	0	-0.512703	-3.078121	-1.074926
6	6	0	-1.628506	-3.888911	-1.255941
7	1	0	-3.721356	-4.201496	-0.821277
8	1	0	0.456264	-3.333208	-1.516028
9	1	0	-1.545551	-4.803207	-1.850356
10	6	0	-1.806511	-0.256204	0.984862
11	6	0	-2.601275	2.127461	0.987546
12	6	0	-2.151973	3.353597	-1.134967
13	1	0	-2.509999	4.190014	-1.757551
14	1	0	-3.945263	-2.124348	0.537615
15	6	0	0.384647	-0.937395	0.032781
16	6	0	1.631021	-0.830808	-0.355161

17	6	0	2.925303	-0.331704	-0.404650
18	6	0	3.304411	0.635329	-1.376712
19	6	0	3.907889	-0.791411	0.516694
20	6	0	4.601961	1.113702	-1.414267
21	1	0	2.547550	1.000549	-2.076870
22	6	0	5.200328	-0.299634	0.460572
23	1	0	3.615605	-1.525603	1.273707
24	6	0	5.557330	0.650085	-0.502710
25	1	0	4.879420	1.864511	-2.159651
26	1	0	5.944466	-0.653831	1.179668
27	1	0	6.580620	1.034071	-0.539796
28	6	0	-2.567893	0.839160	0.240461
29	6	0	-2.486185	2.030736	-1.789958
30	1	0	-2.036764	1.943777	-2.791193
31	1	0	-3.588152	1.922703	-1.910680
32	1	0	-3.617932	0.453690	0.120661
33	1	0	-2.788428	2.080121	2.067436
34	1	0	-1.054218	3.441555	-1.063017
35	6	0	-0.262332	0.016724	1.092402
36	6	0	0.217215	-0.418164	2.411273
37	7	0	0.590945	-0.794030	3.441743
38	6	0	0.173933	1.401307	0.876188
39	7	0	0.617746	2.457281	0.699702
40	1	0	-2.239505	-0.320064	1.999549
41	6	0	-2.762811	3.414191	0.262059
42	8	0	-1.987524	0.952115	-1.032587
43	1	0	-2.327577	4.241403	0.850158
44	1	0	-3.846786	3.657681	0.176404

¹Int2_{HF-trans} E(opt)= -1070.277859 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.824880	-3.504423	-0.992924
2	6	0	-3.023751	-2.346826	-0.240933
3	6	0	-1.920615	-1.575174	0.109415
4	6	0	-0.635908	-1.958587	-0.289231
5	6	0	-0.434000	-3.111162	-1.046872
6	6	0	-1.539645	-3.881444	-1.394926
7	1	0	-3.681716	-4.125634	-1.268490
8	1	0	0.578827	-3.396540	-1.348883
9	1	0	-1.402740	-4.794057	-1.981845
10	6	0	-1.909223	-0.260676	0.835338
11	6	0	-1.657884	1.161548	-1.236365
12	6	0	-2.634186	3.419297	-1.117181
13	1	0	-2.520220	4.472800	-1.419363
14	1	0	-4.030855	-2.051912	0.072186
15	6	0	0.357309	-0.986894	0.182080
16	6	0	1.619422	-0.844914	-0.135846
17	6	0	2.902592	-0.344243	-0.266789
18	6	0	3.173251	0.694896	-1.203578
19	6	0	3.981376	-0.856779	0.508134
20	6	0	4.456663	1.189230	-1.345772
21	1	0	2.342538	1.100778	-1.789401
22	6	0	5.257615	-0.346859	0.348457
23	1	0	3.778551	-1.650232	1.232993

24	6	0	5.506242	0.673552	-0.576430
25	1	0	4.649145	1.994019	-2.060943
26	1	0	6.076815	-0.744164	0.954573
27	1	0	6.518157	1.070894	-0.694400
28	6	0	-2.464990	0.889918	-0.015439
29	6	0	-2.464248	3.306266	0.380488
30	1	0	-3.209980	3.918896	0.914826
31	1	0	-1.460148	3.681993	0.665591
32	1	0	-3.485595	0.545181	-0.328283
33	1	0	-1.294715	0.301988	-1.811222
34	1	0	-3.658764	3.114396	-1.401815
35	6	0	-0.397117	-0.073841	1.205275
36	6	0	-0.158350	-0.620933	2.547354
37	7	0	0.019487	-1.086607	3.593116
38	6	0	0.114040	1.299240	1.143255
39	7	0	0.610388	2.344601	1.077757
40	1	0	-2.516878	-0.275714	1.756396
41	6	0	-1.613186	2.530313	-1.811571
42	8	0	-2.607967	1.981618	0.859372
43	1	0	-1.772322	2.504157	-2.905348
44	1	0	-0.598649	2.965232	-1.673286

^TTS3_{HH-cis} E(opt)= -1070.250967 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.418796	2.442732	-0.815976

S59

2	6	0	3.118961	1.613104	0.263031
3	6	0	1.865229	1.012851	0.358958
4	6	0	0.885504	1.302648	-0.606117
5	6	0	1.194485	2.121800	-1.698239
6	6	0	2.463339	2.680535	-1.804689
7	1	0	0.423326	2.329474	-2.445082
8	1	0	2.701637	3.329674	-2.651706
9	6	0	1.465239	0.010907	1.408527
10	6	0	1.148619	-1.901126	-0.252398
11	6	0	3.136014	-1.640221	-1.507020
12	1	0	3.358716	-0.552703	-1.500846
13	1	0	3.865684	1.442899	1.045666
14	6	0	-0.436147	0.770888	-0.390777
15	6	0	-1.629683	0.564124	-0.687589
16	6	0	-2.988793	0.200512	-0.708952
17	6	0	-3.394067	-1.036115	-1.256641
18	6	0	-3.958357	1.055955	-0.141507
19	6	0	-4.732092	-1.398429	-1.237759
20	1	0	-2.635496	-1.700118	-1.681415
21	6	0	-5.293041	0.678694	-0.127156
22	1	0	-3.634365	2.005253	0.295595
23	6	0	-5.683780	-0.544366	-0.675999
24	1	0	-5.040146	-2.359708	-1.657994
25	1	0	-6.039148	1.340919	0.320567
26	1	0	-6.737466	-0.837042	-0.660971
27	6	0	1.821774	-1.462972	1.003145
28	6	0	3.807643	-2.323652	-0.338141
29	1	0	3.542949	-3.396672	-0.364080
30	1	0	4.903186	-2.262551	-0.442049

31	8	0	1.734888	-1.840877	-1.465875
32	6	0	3.350824	-1.688317	0.967448
33	1	0	3.659335	-2.306389	1.825763
34	1	0	3.877276	-0.726843	1.088061
35	1	0	1.391232	-2.085332	1.809546
36	1	0	0.143660	-2.328944	-0.274238
37	1	0	3.475731	-2.039972	-2.474918
38	6	0	-0.033319	0.172967	1.620229
39	6	0	-0.462084	1.372238	2.268934
40	7	0	-0.806038	2.365547	2.767419
41	6	0	-0.873368	-0.957154	1.836722
42	7	0	-1.576946	-1.874892	1.968408
43	1	0	1.992364	0.240307	2.357709
44	1	0	4.403124	2.914550	-0.881597

^TTS3_{HH-trans} E(opt)= -1070.249982 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.944298	3.520851	-0.604767
2	6	0	2.962871	2.341832	0.134688
3	6	0	1.811919	1.564788	0.244434
4	6	0	0.629309	1.981889	-0.381380
5	6	0	0.614609	3.167688	-1.129644
6	6	0	1.769891	3.930907	-1.239390
7	1	0	-0.315507	3.479646	-1.613122
8	1	0	1.754897	4.859614	-1.816387

S61

9	6	0	1.772389	0.251804	0.991532
10	6	0	1.961547	-1.096490	-1.084025
11	6	0	3.044159	-3.183186	-1.159550
12	1	0	4.115037	-2.889950	-1.163703
13	1	0	3.881403	2.021304	0.639717
14	6	0	-0.545032	1.158401	-0.228555
15	6	0	-1.735284	0.866219	-0.464795
16	6	0	-3.031115	0.317113	-0.478020
17	6	0	-3.384458	-0.689102	-1.403391
18	6	0	-3.988986	0.752944	0.464413
19	6	0	-4.659234	-1.234046	-1.384638
20	1	0	-2.633493	-1.038539	-2.117451
21	6	0	-5.259499	0.196671	0.472214
22	1	0	-3.705497	1.521041	1.190065
23	6	0	-5.600245	-0.793457	-0.451417
24	1	0	-4.923895	-2.017759	-2.099868
25	1	0	-5.993725	0.533912	1.209137
26	1	0	-6.603310	-1.229223	-0.440016
27	6	0	2.558866	-0.842949	0.249767
28	6	0	2.549227	-3.396452	0.249435
29	1	0	1.475096	-3.648249	0.201957
30	1	0	3.064547	-4.257892	0.703060
31	8	0	2.289750	-2.168955	-1.809716
32	6	0	2.758395	-2.135249	1.079906
33	1	0	2.075675	-2.145051	1.945938
34	1	0	3.778475	-2.124268	1.501558
35	1	0	3.571070	-0.395191	0.101186
36	1	0	1.468231	-0.315919	-1.670686
37	1	0	2.942753	-4.083082	-1.783226

38	6	0	0.315896	-0.109530	1.247865
39	6	0	-0.288479	0.513940	2.383552
40	7	0	-0.772024	1.052162	3.294885
41	6	0	-0.215289	-1.393735	0.926626
42	7	0	-0.700265	-2.422446	0.675437
43	1	0	2.272314	0.398563	1.971070
44	1	0	3.849422	4.129571	-0.682916

^TTS3_{HT-cis} E(opt)= -1070.255044 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.418285	-3.136493	-0.669498
2	6	0	-3.292833	-1.993452	0.116057
3	6	0	-2.060388	-1.357004	0.229858
4	6	0	-0.943767	-1.874076	-0.439478
5	6	0	-1.072978	-3.021528	-1.232475
6	6	0	-2.308908	-3.646717	-1.345661
7	1	0	-4.386984	-3.637168	-0.752131
8	1	0	-0.193520	-3.415436	-1.749477
9	1	0	-2.408300	-4.546044	-1.959688
10	6	0	-1.858357	-0.074002	0.993278
11	6	0	-2.293310	2.388654	1.011505
12	6	0	-1.487623	3.574100	-1.028369
13	1	0	-1.653867	4.477537	-1.637896
14	1	0	-4.160870	-1.591629	0.650670
15	6	0	0.315416	-1.197316	-0.268675

16	6	0	1.526681	-0.995750	-0.479284
17	6	0	2.870810	-0.576712	-0.477987
18	6	0	3.311694	0.432725	-1.360599
19	6	0	3.785935	-1.143928	0.435361
20	6	0	4.631969	0.854250	-1.329092
21	1	0	2.591711	0.881778	-2.050377
22	6	0	5.103903	-0.711743	0.456044
23	1	0	3.433470	-1.913801	1.128208
24	6	0	5.530765	0.283602	-0.425114
25	1	0	4.967005	1.641385	-2.010095
26	1	0	5.807277	-1.149827	1.169508
27	1	0	6.570617	0.621933	-0.403171
28	6	0	-2.410886	1.129224	0.224419
29	6	0	-2.006067	2.348802	-1.749772
30	1	0	-1.520586	2.213724	-2.728695
31	1	0	-3.101410	2.438102	-1.932661
32	1	0	-3.495788	0.906693	0.032014
33	1	0	-2.570586	2.344990	2.072055
34	1	0	-0.398144	3.463891	-0.889172
35	6	0	-0.377971	0.070651	1.321213
36	6	0	0.109608	-0.720053	2.405937
37	7	0	0.501626	-1.392520	3.270836
38	6	0	0.347813	1.278879	1.093294
39	7	0	1.023726	2.204666	0.891045
40	1	0	-2.426706	-0.122254	1.943535
41	6	0	-2.166405	3.703547	0.332090
42	8	0	-1.743433	1.180383	-1.008769
43	1	0	-1.625214	4.415901	0.980157
44	1	0	-3.179000	4.148172	0.195885

^TTS3_{HT-trans} E(opt)= -1070.252336 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.066706	3.474362	-0.568632
2	6	0	3.041261	2.289496	0.162066
3	6	0	1.868360	1.542281	0.242249
4	6	0	0.709222	1.995344	-0.404913
5	6	0	0.739104	3.186940	-1.142579
6	6	0	1.916652	3.919885	-1.222913
7	1	0	3.988667	4.059723	-0.624516
8	1	0	-0.172281	3.529154	-1.640801
9	1	0	1.937596	4.853062	-1.792400
10	6	0	1.781899	0.219787	0.954722
11	6	0	1.916066	-1.165071	-1.152335
12	6	0	2.952307	-3.388044	-0.921801
13	1	0	2.927585	-4.434632	-1.265520
14	1	0	3.939841	1.941384	0.683137
15	6	0	-0.486738	1.202721	-0.276174
16	6	0	-1.679367	0.915910	-0.498547
17	6	0	-2.984794	0.387793	-0.483021
18	6	0	-3.392982	-0.576057	-1.429363
19	6	0	-3.891250	0.802225	0.517596
20	6	0	-4.674911	-1.101577	-1.375152
21	1	0	-2.678987	-0.909155	-2.187731
22	6	0	-5.170236	0.267211	0.559496

23	1	0	-3.560020	1.533927	1.260485
24	6	0	-5.566322	-0.680938	-0.385587
25	1	0	-4.984575	-1.853353	-2.106256
26	1	0	-5.866077	0.586352	1.340214
27	1	0	-6.575346	-1.101111	-0.346893
28	6	0	2.508533	-0.894975	0.184390
29	6	0	2.490482	-3.315087	0.515736
30	1	0	3.110452	-3.949442	1.170962
31	1	0	1.447094	-3.686760	0.582782
32	1	0	3.554163	-0.514916	0.045033
33	1	0	1.529063	-0.318246	-1.730004
34	1	0	4.004597	-3.053733	-0.990738
35	6	0	0.322007	-0.113914	1.216800
36	6	0	-0.288698	0.514335	2.344320
37	7	0	-0.792271	1.062553	3.238521
38	6	0	-0.233807	-1.377974	0.857526
39	7	0	-0.757982	-2.368727	0.543022
40	1	0	2.298952	0.290116	1.931525
41	6	0	2.059241	-2.503061	-1.778203
42	8	0	2.554809	-2.005327	1.048997
43	1	0	2.438895	-2.419545	-2.814230
44	1	0	1.057266	-2.976542	-1.871906

^sInt3_{HH-cis} E(opt)= -1070.273872 hartree

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

1	6	0	4.123120	0.059292	1.967252
2	6	0	3.687188	-0.086958	0.652019
3	6	0	2.330519	-0.140881	0.337012
4	6	0	1.395314	-0.057925	1.389006
5	6	0	1.837153	0.112474	2.711055
6	6	0	3.194926	0.168643	2.999621
7	1	0	1.092917	0.181695	3.509667
8	1	0	3.528452	0.284571	4.034315
9	6	0	1.900852	-0.311109	-1.104154
10	6	0	-0.407029	0.894631	-1.203957
11	6	0	-0.386991	3.201420	-0.648465
12	1	0	-0.071316	3.131271	0.407897
13	1	0	4.418198	-0.181324	-0.158280
14	6	0	-0.006115	-0.149210	1.136521
15	6	0	-1.221737	-0.269705	1.048614
16	6	0	-2.633241	-0.375859	0.897516
17	6	0	-3.484231	0.300735	1.790721
18	6	0	-3.185845	-1.138208	-0.149464
19	6	0	-4.861944	0.212652	1.642851
20	1	0	-3.045523	0.889119	2.601995
21	6	0	-4.567312	-1.209856	-0.289706
22	1	0	-2.527405	-1.659319	-0.857421
23	6	0	-5.405021	-0.541179	0.601713
24	1	0	-5.519246	0.736036	2.342829
25	1	0	-4.992159	-1.799854	-1.106216
26	1	0	-6.490689	-0.607275	0.485666
27	6	0	1.023108	0.877410	-1.582867
28	6	0	0.777310	3.389665	-1.581220
29	1	0	0.402929	3.462020	-2.618798

30	1	0	1.272105	4.347349	-1.356181
31	8	0	-1.068495	1.955778	-0.949130
32	6	0	1.730307	2.220684	-1.416131
33	1	0	2.564331	2.273834	-2.133911
34	1	0	2.188174	2.265322	-0.411497
35	1	0	0.871074	0.664895	-2.671979
36	1	0	-1.030192	0.020860	-1.453461
37	1	0	-1.166327	3.968747	-0.735393
38	6	0	1.314241	-1.684207	-1.360314
39	6	0	2.080196	-2.782930	-0.926521
40	7	0	2.768115	-3.646363	-0.540439
41	6	0	0.119746	-1.850956	-2.048513
42	7	0	-0.925006	-1.863323	-2.594686
43	1	0	2.829476	-0.170490	-1.701315
44	1	0	5.194319	0.082374	2.185475

^TInt3_{HF-cis} E(opt)= -1070.26461 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.418796	2.442732	-0.815976
2	6	0	3.118961	1.613104	0.263031
3	6	0	1.865229	1.012851	0.358958
4	6	0	0.885504	1.302648	-0.606117
5	6	0	1.194485	2.121800	-1.698239
6	6	0	2.463339	2.680535	-1.804689
7	1	0	0.423326	2.329474	-2.445082

S68

8	1	0	2.701637	3.329674	-2.651706
9	6	0	1.465239	0.010907	1.408527
10	6	0	1.148619	-1.901126	-0.252398
11	6	0	3.136014	-1.640221	-1.507020
12	1	0	3.358716	-0.552703	-1.500846
13	1	0	3.865684	1.442899	1.045666
14	6	0	-0.436147	0.770888	-0.390777
15	6	0	-1.629683	0.564124	-0.687589
16	6	0	-2.988793	0.200512	-0.708952
17	6	0	-3.394067	-1.036115	-1.256641
18	6	0	-3.958357	1.055955	-0.141507
19	6	0	-4.732092	-1.398429	-1.237759
20	1	0	-2.635496	-1.700118	-1.681415
21	6	0	-5.293041	0.678694	-0.127156
22	1	0	-3.634365	2.005253	0.295595
23	6	0	-5.683780	-0.544366	-0.675999
24	1	0	-5.040146	-2.359708	-1.657994
25	1	0	-6.039148	1.340919	0.320567
26	1	0	-6.737466	-0.837042	-0.660971
27	6	0	1.821774	-1.462972	1.003145
28	6	0	3.807643	-2.323652	-0.338141
29	1	0	3.542949	-3.396672	-0.364080
30	1	0	4.903186	-2.262551	-0.442049
31	8	0	1.734888	-1.840877	-1.465875
32	6	0	3.350824	-1.688317	0.967448
33	1	0	3.659335	-2.306389	1.825763
34	1	0	3.877276	-0.726843	1.088061
35	1	0	1.391232	-2.085332	1.809546
36	1	0	0.143660	-2.328944	-0.274238

37	1	0	3.475731	-2.039972	-2.474918
38	6	0	-0.033319	0.172967	1.620229
39	6	0	-0.462084	1.372238	2.268934
40	7	0	-0.806038	2.365547	2.767419
41	6	0	-0.873368	-0.957154	1.836722
42	7	0	-1.576946	-1.874892	1.968408
43	1	0	1.992364	0.240307	2.357709
44	1	0	4.403124	2.914550	-0.881597

^sTS4_{HH-cis} E(opt)= -1070.272697 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.389111	-1.508601	-0.709884
2	6	0	-3.810262	-0.420964	-0.059909
3	6	0	-2.426314	-0.272927	0.038947
4	6	0	-1.607967	-1.271518	-0.538072
5	6	0	-2.197628	-2.361243	-1.198480
6	6	0	-3.578411	-2.482284	-1.284978
7	1	0	-1.543199	-3.121821	-1.633372
8	1	0	-4.020524	-3.342527	-1.794681
9	6	0	-1.879948	0.941551	0.754373
10	6	0	0.418314	1.699689	0.046063
11	6	0	0.897703	1.768536	-2.284282
12	1	0	0.778334	0.705993	-2.564524
13	1	0	-4.452893	0.339176	0.396550
14	6	0	-0.184312	-1.205501	-0.475032

15	6	0	1.033335	-1.211380	-0.416882
16	6	0	2.443921	-1.127642	-0.233412
17	6	0	3.333746	-1.251223	-1.312968
18	6	0	2.950693	-0.877939	1.054402
19	6	0	4.702709	-1.123235	-1.107201
20	1	0	2.935648	-1.453990	-2.312373
21	6	0	4.320513	-0.751053	1.249620
22	1	0	2.250782	-0.794768	1.892456
23	6	0	5.197894	-0.871329	0.171802
24	1	0	5.391155	-1.222920	-1.951231
25	1	0	4.708092	-0.558201	2.253712
26	1	0	6.275403	-0.771278	0.330390
27	6	0	-1.045650	1.875060	-0.159365
28	6	0	-0.370305	2.556470	-2.476204
29	1	0	-0.190232	3.612130	-2.200673
30	1	0	-0.639956	2.549709	-3.544036
31	8	0	1.288164	1.770575	-0.887141
32	6	0	-1.466275	1.939010	-1.624739
33	1	0	-2.413308	2.496113	-1.708543
34	1	0	-1.676249	0.923456	-2.001662
35	1	0	-1.158108	2.899989	0.275376
36	1	0	0.855936	1.760745	1.049725
37	1	0	1.768515	2.179830	-2.810811
38	6	0	-1.062303	0.579671	1.995114
39	6	0	-1.159716	-0.691983	2.590364
40	7	0	-1.215673	-1.767488	3.044812
41	6	0	-0.514400	1.658937	2.694624
42	7	0	-0.007093	2.646836	3.076926
43	1	0	-2.774757	1.532079	1.046731

44 1 0 -5.477933 -1.594373 -0.761482

^s3aa E(opt)= -1070.337302 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.493291	-3.523779	-0.490508
2	6	0	-2.452695	-2.229390	0.022086
3	6	0	-1.249890	-1.531732	0.139399
4	6	0	-0.052790	-2.178954	-0.248268
5	6	0	-0.106515	-3.482798	-0.766877
6	6	0	-1.317523	-4.150169	-0.893568
7	1	0	0.829390	-3.963273	-1.065455
8	1	0	-1.342549	-5.164303	-1.301228
9	6	0	-1.193865	-0.162286	0.746169
10	6	0	-1.492087	1.960309	0.722308
11	6	0	-1.765763	3.198328	-1.322598
12	1	0	-1.797337	4.274854	-1.549030
13	1	0	-3.388452	-1.763552	0.344404
14	6	0	1.216159	-1.544100	-0.099514
15	6	0	2.305357	-1.011706	0.017647
16	6	0	3.566384	-0.357154	0.145743
17	6	0	3.679594	1.020684	-0.109189
18	6	0	4.712263	-1.075506	0.526562
19	6	0	4.906741	1.660583	0.017830
20	1	0	2.791013	1.582230	-0.415667
21	6	0	5.935932	-0.428627	0.651135

22	1	0	4.624732	-2.147415	0.724952
23	6	0	6.037384	0.939011	0.398509
24	1	0	4.982740	2.732729	-0.184008
25	1	0	6.821261	-0.997227	0.949464
26	1	0	7.002080	1.444464	0.497846
27	6	0	-0.446785	1.024834	0.094314
28	6	0	-0.498924	2.555845	-1.842602
29	1	0	-0.465004	2.662130	-2.938937
30	1	0	0.381749	3.093560	-1.440712
31	8	0	-1.883698	3.111352	0.094123
32	6	0	-0.449416	1.094022	-1.426669
33	1	0	-1.321428	0.562064	-1.850645
34	1	0	0.442271	0.581999	-1.824722
35	1	0	0.575329	1.190276	0.473156
36	1	0	-1.209260	2.222122	1.757366
37	1	0	-2.647646	2.735798	-1.804594
38	6	0	-2.486724	0.721009	0.853797
39	6	0	-3.411281	0.638991	-0.272183
40	7	0	-4.152440	0.598970	-1.162046
41	6	0	-3.217061	0.613117	2.109771
42	7	0	-3.746185	0.523653	3.136964
43	1	0	-0.817536	-0.257504	1.783363
44	1	0	-3.452617	-4.041321	-0.572744

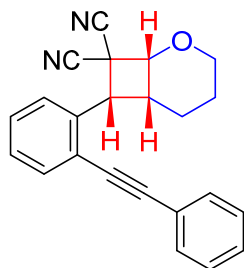
^s3(aa)' E(opt)= -1070.33925 hartree

Center	Atomic	Atomic	Coordinates (Angstroms)		
Number	Number	Type	X	Y	Z

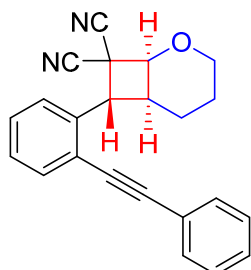
1	6	0	-2.186758	3.913558	-0.303266
2	6	0	-2.308874	2.533529	-0.453096
3	6	0	-1.187215	1.706250	-0.462988
4	6	0	0.093108	2.290786	-0.306458
5	6	0	0.204292	3.681531	-0.158657
6	6	0	-0.926961	4.487661	-0.157698
7	1	0	-3.082750	4.540023	-0.298457
8	1	0	1.199829	4.116859	-0.037540
9	1	0	-0.824708	5.569535	-0.037444
10	6	0	-1.269571	0.216355	-0.591840
11	6	0	-2.793147	-0.775879	0.588658
12	6	0	-3.356706	-3.062933	0.140759
13	1	0	-4.129629	-3.748507	0.519291
14	1	0	-3.307314	2.099917	-0.564561
15	6	0	1.261613	1.475386	-0.280317
16	6	0	2.257987	0.773647	-0.248887
17	6	0	3.446513	-0.014002	-0.216963
18	6	0	3.380180	-1.416682	-0.157727
19	6	0	4.705108	0.612370	-0.244272
20	6	0	4.548946	-2.168409	-0.127270
21	1	0	2.405183	-1.911735	-0.122654
22	6	0	5.867281	-0.148298	-0.214814
23	1	0	4.753883	1.704187	-0.287879
24	6	0	5.792871	-1.539833	-0.157009
25	1	0	4.485702	-3.258974	-0.076711
26	1	0	6.841472	0.348498	-0.236016
27	1	0	6.709348	-2.136443	-0.132853
28	6	0	-1.237545	-0.548267	0.810092

29	6	0	-2.621997	-0.450426	-0.902308
30	6	0	-3.592343	-2.698597	-1.308860
31	1	0	-3.571071	-3.614467	-1.921414
32	1	0	-4.601727	-2.259374	-1.420752
33	8	0	-3.406483	-1.930534	0.999108
34	6	0	-2.532763	-1.707172	-1.762308
35	1	0	-1.537615	-2.178981	-1.659474
36	1	0	-2.639769	-1.445234	-2.827575
37	1	0	-2.381668	-3.577472	0.245709
38	1	0	-0.445905	-0.137992	-1.234054
39	6	0	-0.897352	0.234012	1.989412
40	6	0	-0.429188	-1.756009	0.744892
41	7	0	-0.679399	0.889023	2.919908
42	7	0	0.217062	-2.713508	0.647954
43	1	0	-3.407413	0.211036	-1.304619
44	1	0	-3.282495	0.063324	1.114670

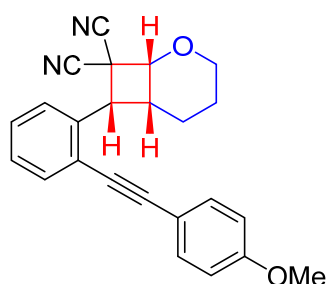
8. Characterization data for the products



(±)-**(1*R*,6*R*,7*R*)-7-(2-(Phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3aa)**: White solid. m.p. 143.8–144.6 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.64–7.60 (m, 2H), 7.493–7.489 (m, 2H), 7.45–7.43 (m, 1H), 7.39–7.34 (m, 4H), 4.86 (d, *J* = 7.8 Hz, 1H), 4.45 (t, *J* = 12.0 Hz, 1H), 4.16 (d, *J* = 7.8 Hz, 1H), 3.89–3.87 (m, 1H), 3.54–3.48 (m, 1H), 2.18–2.15 (m, 1H), 1.87–1.81 (m, 1H), 1.70–1.68 (m, 1H), 1.61–1.55 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 134.9, 133.6, 131.3, 128.9, 128.7, 128.6, 127.9, 127.0, 122.6, 122.2, 115.3, 114.8, 94.2, 87.2, 73.7, 64.6, 44.0, 40.1, 36.7, 22.1, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₃H₁₈N₂NaO]⁺: 361.1311, Found: 361.1315.

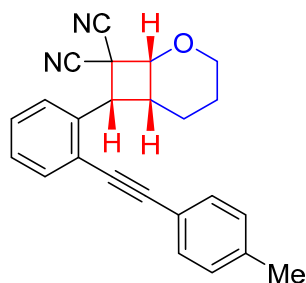


(±)-**(1*S*,6*S*,7*R*)-7-(2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile [3(aa)']**: White solid. m.p. 145.1–145.6 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.67–7.65 (m, 3H), 7.44–7.42 (m, 2H), 7.40–7.36 (m, 4H), 5.10 (d, *J* = 11.4 Hz, 1H), 4.59 (t, *J* = 5.4 Hz, 1H), 4.15–4.13 (m, 1H), 3.46 (td, *J*₁ = 1.8 Hz, *J*₂ = 12.0 Hz, 1H), 3.21–3.17 (m, 1H), 2.00–1.92 (m, 1H), 1.82–1.76 (m, 1H), 1.72–1.69 (m, 1H), 1.62–1.58 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 134.9, 133.2, 131.9, 128.9, 128.72, 128.70, 128.4, 126.9, 124.4, 122.7, 113.0, 112.4, 95.5, 86.3, 73.1, 65.3, 47.0, 38.2, 34.2, 21.0, 20.3. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₃H₁₈N₂NaO]⁺: 361.1311, Found: 361.1315.

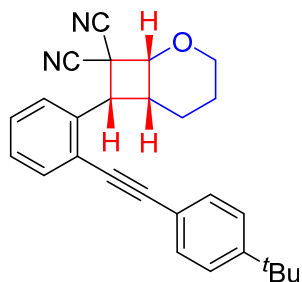


(±)-**(1*R*,6*R*,7*R*)-7-(2-((4-Methoxyphenyl)ethynyl)phenyl)-2-**

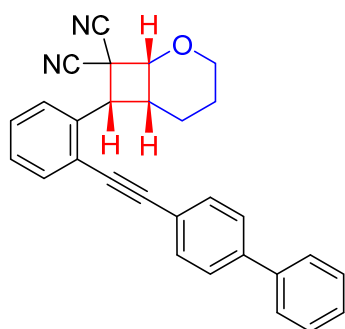
oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ba): White solid. m.p. 142.7–143.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.57 (m, 2H), 7.45–7.39 (m, 3H), 7.36–7.32 (m, 1H), 6.93–6.89 (m, 2H), 4.86 (d, *J* = 7.6 Hz, 1H), 4.45 (td, *J*₁ = 3.2 Hz, *J*₂ = 11.6 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.90–3.86 (m, 1H), 3.84 (s, 3H), 3.54–3.45 (m, 1H), 2.19–2.13 (m, 1H), 1.89–1.78 (m, 1H), 1.72–1.67 (m, 1H), 1.64–1.52 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 160.0, 134.7, 133.4, 132.8, 128.3, 127.8, 126.9, 122.5, 115.4, 114.9, 114.6, 114.2, 94.4, 86.0, 73.7, 64.6, 55.3, 44.0, 40.1, 36.7, 22.1, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₀N₂NaO₂]⁺: 391.1417, Found: 391.1417.



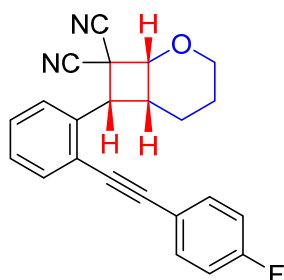
(±)-**(1*R*,6*R*,7*R*)-7-(2-(*p*-Tolyethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-**
dicarbonitrile (3ca): White solid. m.p. 123.8–125.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63–7.57 (m, 2H), 7.44–7.32 (m, 4H), 7.20–7.18 (m, 2H), 4.85 (d, *J* = 7.6 Hz, 1H), 4.44 (td, *J*₁ = 2.8 Hz, *J*₂ = 11.6 Hz, 1H), 4.14 (d, *J* = 8.0 Hz, 1H), 3.89–3.85 (m, 1H), 3.55–3.46 (m, 1H), 2.38 (s, 3H), 2.18–2.12 (m, 1H), 1.88–1.77 (m, 1H), 1.71–1.66 (m, 1H), 1.62–1.51 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.2, 134.9, 133.4, 131.2, 129.3, 128.5, 127.8, 126.9, 122.4, 119.5, 115.3, 114.8, 94.5, 86.6, 73.7, 64.6, 44.0, 40.1, 36.7, 22.1, 21.5, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₀N₂NaO]⁺: 375.1468, Found: 375.1473.



(±)-**(1R,6R,7R)-7-(2-((4-(*tert*-Butyl)phenyl)ethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3da)**: White solid. m.p. 143.6–144.8 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.64–7.62 (m, 1H), 7.60–7.58 (m, 1H), 7.44–7.40 (m, 5H), 7.36–7.33 (m, 1H), 4.86 (d, $J = 7.8$ Hz, 1H), 4.45 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.15 (d, $J = 7.8$ Hz, 1H), 3.89–3.87 (m, 1H), 3.55–3.49 (m, 1H), 2.18–2.14 (m, 1H), 1.87–1.79 (m, 1H), 1.70–1.67 (m, 1H), 1.62–1.54 (m, 1H), 1.34 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 152.3, 134.9, 133.5, 131.0, 128.5, 127.8, 126.9, 125.6, 122.4, 119.5, 115.3, 114.9, 94.4, 86.6, 73.7, 64.6, 44.0, 40.1, 36.7, 34.8, 22.1, 19.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{27}\text{H}_{26}\text{N}_2\text{NaO}]^+$: 417.1937, Found: 417.1939.

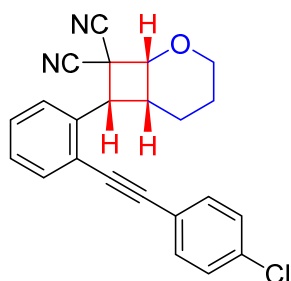


(±)-**(1R,6R,7R)-7-(2-([1,1'-Biphenyl]-4-ylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ea)**: White solid. m.p. 144.4–145.3 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.64–7.60 (m, 6H), 7.57–7.55 (m, 2H), 7.47–7.42 (m, 3H), 7.39–7.34 (m, 2H), 4.88 (d, $J = 7.8$ Hz, 1H), 4.45 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.17 (d, $J = 7.8$ Hz, 1H), 3.89–3.87 (m, 1H), 3.56–3.50 (m, 1H), 2.19–2.15 (m, 1H), 1.88–1.81 (m, 1H), 1.71–1.68 (m, 1H), 1.63–1.55 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 141.6, 140.0, 134.9, 133.6, 131.7, 128.9, 128.7, 127.85, 127.81, 127.2, 127.0, 122.2, 121.4, 115.3, 114.8, 94.2, 87.9, 73.6, 64.6, 44.0, 40.1, 36.7, 22.1, 19.8. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{29}\text{H}_{22}\text{N}_2\text{NaO}]^+$: 437.1624, Found: 437.1624.



(±)-(1*R*,6*R*,7*R*)-7-(2-((4-Fluorophenyl)ethynyl)phenyl)-2-

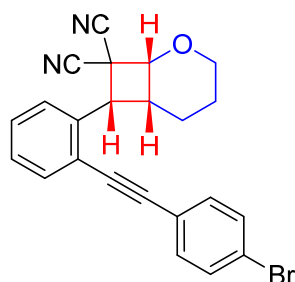
oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3fa): White solid. m.p. 144.6–145.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62–7.58 (m, 2H), 7.50–7.41 (m, 3H), 7.37–7.33 (m, 1H), 7.10–7.05 (m, 2H), 4.86 (d, *J* = 7.6 Hz, 1H), 4.44 (td, *J*₁ = 2.8 Hz, *J*₂ = 11.6 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.90–3.86 (m, 1H), 3.51–3.42 (m, 1H), 2.17–2.12 (m, 1H), 1.90–1.79 (m, 1H), 1.72–1.68 (m, 1H), 1.62–1.52 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ –109.6; ¹³C NMR (100 MHz, CDCl₃) δ 162.7 (d, *J* = 249.4 Hz), 134.8, 133.6, 133.3 (d, *J* = 8.5 Hz), 128.7, 127.8, 127.0, 122.0, 118.6 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 22.1 Hz), 115.3, 114.8, 93.2, 86.9, 73.6, 64.6, 43.9, 40.0, 36.8, 22.1, 19.8. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₃H₁₇FN₂NaO]⁺: 379.1217, Found: 379.1218.



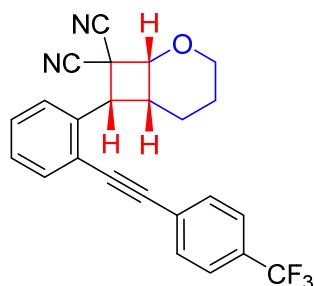
(±)-(1*R*,6*R*,7*R*)-7-(2-((4-Chlorophenyl)ethynyl)phenyl)-2-

oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ga): White solid. m.p. 147.8–148.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.63–7.59 (m, 2H), 7.47–7.42 (m, 3H), 7.37–7.34 (m, 3H), 4.86 (d, *J* = 7.6 Hz, 1H), 4.44 (td, *J*₁ = 2.8 Hz, *J*₂ = 11.6 Hz, 1H), 4.15 (d, *J* = 8.0 Hz, 1H), 3.90–3.86 (m, 1H), 3.50–3.41 (m, 1H), 2.17–2.11 (m, 1H), 1.90–1.79 (m, 1H), 1.73–1.68 (m, 1H), 1.63–1.52 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 134.93, 134.91, 133.6, 132.5, 128.90, 128.87, 127.9, 127.1, 121.9, 121.0, 115.3, 114.7, 93.2, 88.2, 73.6, 64.5, 43.9, 40.0, 36.8, 22.1,

19.8. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{23}H_{17}ClN_2NaO]^+$: 395.0922, Found: 395.0924.

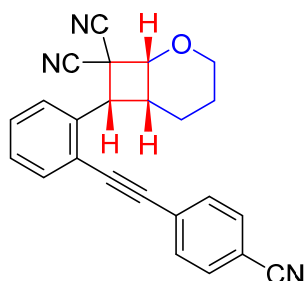


(±)-(1*R*,6*R*,7*R*)-7-(2-((4-Bromophenyl)ethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (**3ha**): White solid. m.p. 147.1–147.4 °C. 1H NMR (600 MHz, $CDCl_3$) δ 7.63–7.59 (m, 2H), 7.53–7.52 (m, 2H), 7.47–7.44 (m, 1H), 7.36–7.35 (m, 3H), 4.87 (d, $J = 7.8$ Hz, 1H), 4.45 (t, $J = 12.0$ Hz, 1H), 4.15 (d, $J = 7.8$ Hz, 1H), 3.90–3.88 (m, 1H), 3.48–3.42 (m, 1H), 2.15–2.14 (m, 1H), 1.88–1.82 (m, 1H), 1.72–1.70 (m, 1H), 1.61–1.59 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.0, 133.7, 132.7, 131.9, 129.0, 128.0, 127.2, 123.3, 121.9, 121.5, 115.3, 114.8, 93.2, 88.4, 73.7, 64.6, 44.0, 40.1, 36.9, 22.2, 19.9. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{23}H_{17}^{79}BrN_2NaO]^+$: 417.0597, Found: 417.0599.



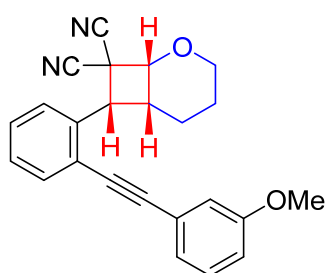
(±)-(1*R*,6*R*,7*R*)-7-(2-((4-(Trifluoromethyl)phenyl)ethynyl)phenyl)-2-oxabicyclo[4.2.0] octane-8,8-dicarbonitrile (**3ia**): White solid. m.p. 134.8–146.4 °C. 1H NMR (600 MHz, $CDCl_3$) δ 7.65–7.60 (m, 6H), 7.49–7.46 (m, 1H), 7.40–7.37 (m, 1H), 4.87 (d, $J = 7.8$ Hz, 1H), 4.45 (t, $J = 11.4$ Hz, 1H), 4.17 (d, $J = 7.8$ Hz, 1H), 3.90–3.88 (m, 1H), 3.49–3.43 (m, 1H), 2.17–2.13 (m, 1H), 1.90–1.83 (m, 1H), 1.72–1.70 (m, 1H), 1.62–1.55 (m, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.9; ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.1, 133.9, 132.1, 131.6,

130.5 (q, $J = 32.6$ Hz), 129.3, 127.2, 125.52 (q, $J = 3.3$ Hz), 125.46 (q, $J = 249.8$ Hz), 121.5, 115.3, 114.7, 92.8, 89.5, 73.6, 64.6, 43.9, 40.0, 37.0, 22.1, 19.9. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{24}H_{17}F_3N_2NaO]^+$: 429.1185, Found: 429.1183.



(±)-(1*R*,6*R*,7*R*)-7-(2-((4-Cyanophenyl)ethynyl)phenyl)-2-

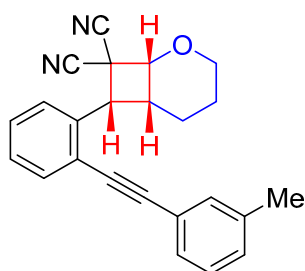
oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (**3ja**): White solid. m.p. 138.3–138.8 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.69–7.67 (m, 2H), 7.64–7.59 (m, 4H), 7.51–7.47 (m, 1H), 7.41–7.37 (m, 1H), 4.87 (d, $J = 7.6$ Hz, 1H), 4.45 (td, $J_1 = 2.8$ Hz, $J_2 = 11.6$ Hz, 1H), 4.16 (d, $J = 8.0$ Hz, 1H), 3.91–3.88 (m, 1H), 3.48–3.39 (m, 1H), 2.16–2.11 (m, 1H), 1.92–1.82 (m, 1H), 1.74–1.70 (m, 1H), 1.65–1.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.2, 134.1, 132.2, 131.9, 129.6, 128.1, 127.4, 121.3, 118.2, 115.3, 114.7, 112.2, 92.6, 91.5, 73.7, 64.6, 43.9, 40.0, 37.1, 22.1, 20.0. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{24}H_{17}N_3NaO]^+$: 386.1264, Found: 386.1269.



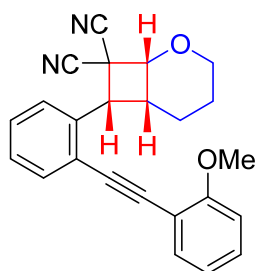
(±)-(1*R*,6*R*,7*R*)-7-(2-((3-Methoxyphenyl)ethynyl)phenyl)-2-

oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (**3ka**): White solid. m.p. 152.7–152.9 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.59 (m, 2H), 7.44–7.41 (m, 1H), 7.36–7.27 (m, 2H), 7.09–7.07 (m, 1H), 7.02 (s, 1H), 6.95–6.92 (m, 1H), 4.85 (d, $J = 7.6$ Hz, 1H), 4.43 (td, $J_1 = 2.8$ Hz, $J_2 = 11.6$ Hz, 1H), 4.14 (d, $J = 8.0$ Hz, 1H), 3.88–3.86 (m, 1H), 3.82 (s, 3H), 3.54–3.45 (m, 1H), 2.18–2.13 (m, 1H),

1.88–1.77 (m, 1H), 1.70–1.66 (m, 1H), 1.63–1.51 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.4, 134.9, 133.5, 129.6, 128.7, 127.8, 126.9, 123.7, 123.5, 122.0, 116.4, 115.3, 115.0, 114.8, 94.1, 87.0, 73.6, 64.5, 55.2, 43.9, 40.0, 36.7, 22.1, 19.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}_2]^+$: 391.1417, Found: 391.1422.

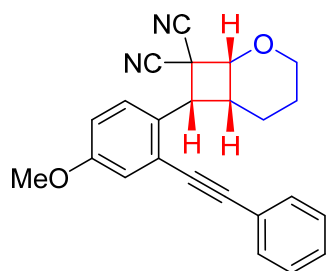


(±)-(1R,6R,7R)-7-(2-(*m*-Tolylolethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3la): White solid. m.p. 131.5–132.1 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.65–7.63 (m, 1H), 7.60–7.59 (m, 1H), 7.45–7.42 (m, 1H), 7.37–7.34 (m, 1H), 7.31–7.26 (m, 3H), 7.21–7.20 (m, 1H), 4.87 (d, $J = 7.8$ Hz, 1H), 4.45 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.15 (d, $J = 8.4$ Hz, 1H), 3.90–3.87 (m, 1H), 3.55–3.49 (m, 1H), 2.38 (s, 3H), 2.18–2.14 (m, 1H), 1.87–1.80 (m, 1H), 1.71–1.68 (m, 1H), 1.63–1.55 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.4, 134.9, 133.5, 131.8, 129.8, 128.7, 128.5, 128.4, 127.9, 127.0, 122.4, 122.3, 115.3, 114.9, 94.4, 86.9, 73.7, 64.7, 44.0, 40.1, 36.7, 22.2, 21.3, 19.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}]^+$: 375.1468, Found: 375.1469.

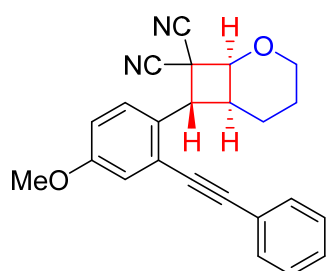


(±)-(1R,6R,7R)-7-(2-((2-Methoxyphenyl)ethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ma): White solid. m.p. 156.4–157.8 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.70–7.69 (m, 1H), 7.61–7.59 (m, 1H), 7.46–7.41 (m, 2H), 7.37–7.33 (m, 2H), 6.98–6.96 (m, 1H), 6.94–6.92 (m, 1H), 4.85 (d, $J = 7.8$ Hz, 1H), 4.46 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.22 (d, $J =$

8.4 Hz, 1H), 3.92 (s, 3H), 3.89–3.87 (m, 1H), 3.76–3.70 (m, 1H), 2.15–2.11 (m, 1H), 1.83–1.75 (m, 1H), 1.70–1.66 (m, 1H), 1.59–1.52 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 160.0, 135.0, 133.22, 133.19, 130.3, 128.5, 127.7, 126.7, 122.6, 120.7, 115.4, 115.0, 111.8, 110.7, 91.1, 90.9, 73.9, 64.7, 55.7, 43.9, 39.6, 36.4, 22.2, 19.5. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}_2]^+$: 391.1417, Found: 391.1422.

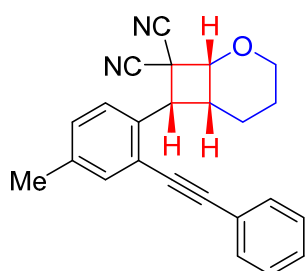


(±)-(1*R*,6*R*,7*R*)-7-(4-Methoxy-2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3na): White solid. m.p. 145.1–145.6 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.63–7.61 (m, 1H), 7.58–7.57 (m, 1H), 7.44–7.40 (m, 3H), 7.36–7.33 (m, 1H), 6.92–6.90 (m, 2H), 4.86 (d, $J=7.8$ Hz, 1H), 4.45 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.15 (d, $J = 7.8$ Hz, 1H), 3.90–3.87 (m, 1H), 3.84 (s, 3H), 3.53–3.47 (m, 1H), 2.17–2.14 (m, 1H), 1.88–1.80 (m, 1H), 1.71–1.68 (m, 1H), 1.62–1.54 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 160.1, 134.7, 133.4, 132.8, 128.4, 127.8, 126.9, 122.6, 115.4, 114.9, 114.6, 114.3, 94.4, 86.0, 73.7, 64.6, 55.4, 44.0, 40.1, 36.8, 22.2, 19.8. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. For $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}_2]^+$: 391.1417, Found: 391.1417.



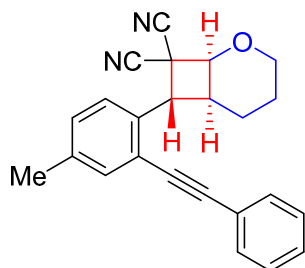
(±)-(1*S*,6*S*,7*R*)-7-(4-Methoxy-2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile [3(na)']: White solid. m.p. 144.3–145.6 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.67–7.65 (m, 2H), 7.38–7.34 (m, 4H), 7.16 (s, 1H),

6.97–6.96 (m, 1H), 5.05 (d, $J = 11.4$ Hz, 1H), 4.57–4.56 (m, 1H), 4.12 (d, $J = 11.4$ Hz, 1H), 3.84 (s, 3H), 3.44 (t, $J = 12.0$ Hz, 1H), 3.14–3.12 (m, 1H), 1.98–1.91 (m, 1H), 1.79–1.73 (m, 1H), 1.69–1.66 (m, 1H), 1.60–1.57 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.6, 131.9, 128.7, 128.4, 128.3, 128.1, 127.1, 125.5, 122.5, 117.8, 115.0, 113.1, 112.4, 95.0, 86.3, 72.9, 65.3, 55.4, 46.8, 38.4, 34.5, 20.9, 20.3. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. For $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}_2]^+$: 391.1417, Found: 391.1418.



(±)-(1*R*,6*R*,7*R*)-7-(4-Methyl-2-(phenylethynyl)phenyl)-2-

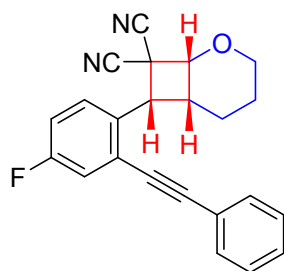
oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (30a): White solid. m.p. 143.9–144.4 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.51–7.47 (m, 3H), 7.42 (s, 1H), 7.38–7.37 (m, 3H), 7.24–7.22 (m, 1H), 4.84 (d, $J = 7.6$ Hz, 1H), 4.43 (td, $J_1 = 2.8$ Hz, $J_2 = 11.6$ Hz, 1H), 4.12 (d, $J = 8.0$ Hz, 1H), 3.88–3.85 (m, 1H), 3.51–3.42 (m, 1H), 2.36 (s, 3H), 2.17–2.12 (m, 1H), 1.89–1.78 (m, 1H), 1.70–1.66 (m, 1H), 1.62–1.51 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.7, 134.0, 131.9, 131.2, 129.5, 128.7, 128.5, 126.9, 122.6, 121.9, 115.4, 114.9, 93.7, 87.4, 73.6, 64.6, 43.7, 40.0, 36.8, 22.1, 20.7, 19.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}]^+$: 375.1468, Found: 375.1469.



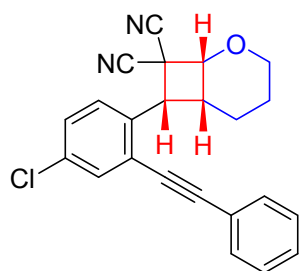
(±)-(1*S*,6*S*,7*R*)-7-(4-Methyl-2-(phenylethynyl)phenyl)-2-oxabicyclo

[4.2.0]octane-8,8-dicarbonitrile [3(0a)']: White solid. m.p. 175.8–176.2 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.66–7.64 (m, 2H), 7.48 (s, 1H), 7.37–7.34 (m, 3H),

7.32–7.31 (m, 1H), 7.24–7.23 (m, 1H), 5.06 (d, $J = 11.4$ Hz, 1H), 4.58–4.57 (m, 1H), 4.13 (d, $J = 11.4$ Hz, 1H), 3.45 (t, $J = 12.0$ Hz, 1H), 3.17–3.15 (m, 1H), 2.37 (s, 3H), 1.99–1.92 (m, 1H), 1.81–1.75 (m, 1H), 1.70–1.68 (m, 1H), 1.60–1.57 (m, 1H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.9, 133.8, 132.0, 131.9, 129.6, 128.6, 128.3, 126.8, 124.2, 122.8, 113.1, 112.4, 95.0, 86.5, 73.0, 65.3, 46.9, 38.3, 34.3, 21.0, 20.9, 20.3. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{24}\text{H}_{20}\text{N}_2\text{NaO}]^+$: 375.1468, Found: 375.1467.

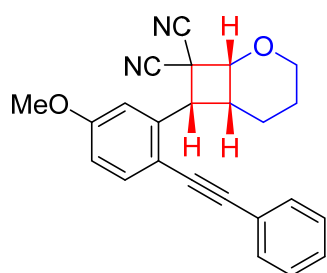


(±)-(1*R*,6*R*,7*R*)-7-(4-Fluoro-2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3pa): White solid. m.p. 148.8–150.6 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.60 (m, 1H), 7.51–7.49 (m, 2H), 7.41–7.39 (m, 3H), 7.33–7.30 (m, 1H), 7.17–7.13 (m, 1H), 4.86 (d, $J = 7.6$ Hz, 1H), 4.44 (td, $J_1 = 2.8$ Hz, $J_2 = 11.6$ Hz, 1H), 4.13 (d, $J = 8.0$ Hz, 1H), 3.90–3.87 (m, 1H), 3.52–3.43 (m, 1H), 2.16–2.10 (m, 1H), 1.89–1.79 (m, 1H), 1.74–1.69 (m, 1H), 1.64–1.53 (m, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -113.7; ^{13}C NMR (100 MHz, CDCl_3) δ 161.7 (d, $J = 247.3$ Hz), 131.4, 130.9 (d, $J = 3.3$ Hz), 129.3, 128.8, 128.7, 124.3 (d, $J = 9.4$ Hz), 122.0, 120.3 (d, $J = 22.9$ Hz), 116.0 (d, $J = 21.5$ Hz), 115.2, 114.7, 95.2, 86.0 (d, $J = 2.9$ Hz), 73.7, 64.6, 43.5, 40.0, 36.9, 22.1, 19.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{23}\text{H}_{18}\text{FN}_2\text{NaO}]^+$: 357.1398, Found: 357.1399.



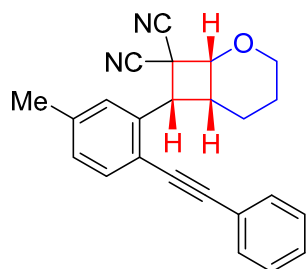
(±)-(1*R*,6*R*,7*R*)-7-(4-Chloro-2-(phenylethynyl)phenyl)-2-

oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3qa): White solid. m.p. 149.3–149.5 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.60–7.56 (m, 2H), 7.51–7.48 (m, 2H), 7.42–7.38 (m, 4H), 4.86 (d, *J* = 7.6 Hz, 1H), 4.44 (td, *J*₁ = 2.8 Hz, *J*₂ = 11.6 Hz, 1H), 4.12 (d, *J* = 8.0 Hz, 1H), 3.90–3.87 (m, 1H), 3.53–3.44 (m, 1H), 2.16–2.11 (m, 1H), 1.88–1.77 (m, 1H), 1.73–1.69 (m, 1H), 1.64–1.52 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 133.9, 133.4, 133.2, 131.4, 129.3, 128.8, 128.7, 128.3, 124.0, 122.0, 115.1, 114.6, 95.5, 85.9, 73.7, 64.6, 43.6, 40.0, 36.8, 22.1, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₃H₁₇ClN₂NaO]⁺: 395.0922, Found: 395.0926.



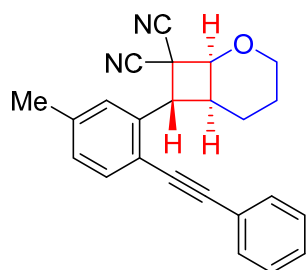
(±)-(1*R*,6*R*,7*R*)-7-(5-Methoxy-2-(phenylethynyl)phenyl)-2-

oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ra): White solid. m.p. 130.8–132.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.52–7.51 (m, 1H), 7.47–7.46 (m, 2H), 7.39–7.35 (m, 3H), 7.19–7.18 (m, 1H), 6.88–6.86 (m, 1H), 4.86 (d, *J* = 7.8 Hz, 1H), 4.45 (td, *J*₁ = 3.0 Hz, *J*₂ = 12.0 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.90–3.87 (m, 4H), 3.54–3.48 (m, 1H), 2.17–2.13 (m, 1H), 1.87–1.80 (m, 1H), 1.71–1.68 (m, 1H), 1.62–1.54 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 159.8, 136.6, 134.9, 131.1, 128.54, 128.52, 122.9, 115.3, 114.9, 114.0, 113.5, 113.1, 92.7, 87.2, 73.6, 64.7, 55.5, 44.0, 40.0, 36.7, 22.1, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₀N₂NaO₂]⁺: 391.1417, Found: 391.1422.



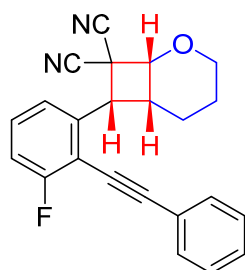
(±)-(1*R*,6*R*,7*R*)-7-(5-Methyl-2-(phenylethynyl)phenyl)-2-

oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3sa): White solid. m.p. 139.2–140.6 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.50–7.45 (m, 3H), 7.40–7.36 (m, 4H), 7.17–7.15 (m, 1H), 4.86 (d, *J* = 7.6 Hz, 1H), 4.45 (td, *J*₁ = 3.2 Hz, *J*₂ = 11.6 Hz, 1H), 4.11 (d, *J* = 8.0 Hz, 1H), 3.91–3.87 (m, 1H), 3.55–3.46 (m, 1H), 2.44 (s, 3H), 2.20–2.15 (m, 1H), 1.89–1.78 (m, 1H), 1.72–1.67 (m, 1H), 1.64–1.56 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 139.2, 134.8, 133.5, 131.2, 128.7, 128.62, 128.57, 127.7, 122.8, 119.0, 115.4, 114.9, 93.4, 87.4, 73.6, 64.6, 43.9, 40.1, 36.7, 22.2, 21.6, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₀N₂NaO]⁺: 375.1468, Found: 375.1473.



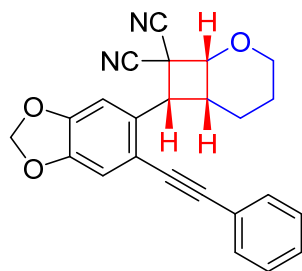
(±)-(1*S*,6*S*,7*R*)-7-(5-Methyl-2-(phenylethynyl)phenyl)-2-oxabicyclo

[4.2.0]octane-8,8-dicarbonitrile [3(sa)']: White solid. m.p. 144.4–145.5 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.65–7.63 (m, 2H), 7.54–7.53 (m, 1H), 7.38–7.34 (m, 3H), 7.21–7.19 (m, 2H), 5.07 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 4.8 Hz, 1H), 4.15–4.13 (m, 1H), 3.46 (td, *J*₁ = 1.8 Hz, *J*₂ = 12.0 Hz, 1H), 3.20–3.16 (m, 1H), 2.42 (s, 3H), 1.99–1.91 (m, 1H), 1.83–1.76 (m, 1H), 1.73–1.68 (m, 1H), 1.62–1.58 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 139.0, 134.7, 133.1, 131.8, 129.7, 128.5, 128.3, 127.6, 122.9, 121.4, 113.0, 112.4, 94.7, 86.5, 73.1, 65.3, 47.0, 38.2, 34.1, 21.7, 21.1, 20.3. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₀N₂NaO]⁺: 375.1468, Found: 375.1469.



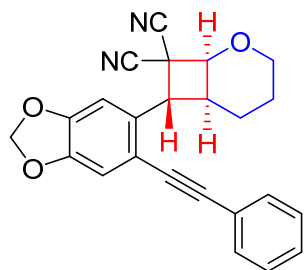
(±)-(1*R*,6*R*,7*R*)-7-(3-Fluoro-2-(phenylethynyl)phenyl)-2-

oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ta): White solid. m.p. 158.7–158.8 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.53–7.51 (m, 2H), 7.45–7.39 (m, 5H), 7.16–7.13 (m, 1H), 4.87 (d, *J* = 7.8 Hz, 1H), 4.45 (td, *J*₁ = 3.0 Hz, *J*₂ = 12.0 Hz, 1H), 4.13 (d, *J* = 8.4 Hz, 1H), 3.91–3.88 (m, 1H), 3.55–3.49 (m, 1H), 2.19–2.15 (m, 1H), 1.88–1.80 (m, 1H), 1.73–1.69 (m, 1H), 1.63–1.55 (m, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ –107.2; ¹³C NMR (150 MHz, CDCl₃) δ 163.4 (d, *J* = 251.4 Hz), 137.3, 131.4, 129.9 (d, *J* = 8.7 Hz), 129.2, 128.6, 122.6 (d, *J* = 3.3 Hz), 122.2, 115.2 (d, *J* = 15.0 Hz), 115.1, 114.7, 111.1, 111.0, 99.6 (d, *J* = 3.8 Hz), 80.3, 73.6, 64.6, 43.7 (d, *J* = 2.7 Hz), 40.1, 36.9, 22.1, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₃H₁₇FN₂NaO]⁺: 379.1217, Found: 379.1216.

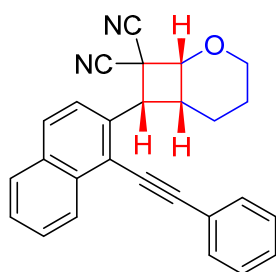


(±)-(1*R*,6*R*,7*R*)-7-(6-(Phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)-2-

oxabicyclo[4.2.0] octane-8,8-dicarbonitrile (3ua): White solid. m.p. 178.2–178.8 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.47–7.45 (m, 2H), 7.38–7.36 (m, 3H), 7.16 (s, 1H), 7.02 (s, 1H), 6.04 (s, 2H), 4.82 (d, *J* = 7.8 Hz, 1H), 4.44 (td, *J*₁ = 3.0 Hz, *J*₂ = 12.0 Hz, 1H), 4.14 (d, *J* = 8.4 Hz, 1H), 3.89–3.87 (m, 1H), 3.47–3.41 (m, 1H), 2.16–2.12 (m, 1H), 1.94–1.87 (m, 1H), 1.74–1.70 (m, 1H), 1.61–1.54 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 148.4, 147.1, 131.2, 129.7, 128.7, 128.6, 122.7, 115.7, 115.3, 114.8, 112.9, 107.7, 102.0, 93.1, 87.2, 73.7, 64.6, 43.8, 40.1, 37.0, 22.1, 19.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₁₈N₂NaO₃]⁺: 405.1210, Found: 405.1212.

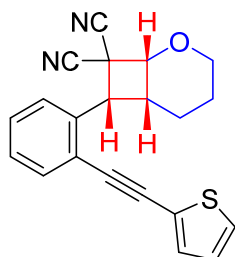


(±)-(1*S*,6*S*,7*R*)-7-(6-(Phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)-2-oxabicyclo[4.2.0] octane-8,8-dicarbonitrile [3(ua)']: White solid. m.p. 182.8–183.0 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.63–7.61 (m, 2H), 7.38–7.34 (m, 3H), 7.07 (s, 1H), 6.91 (s, 1H), 6.05–6.04 (s, 2H), 5.09 (d, *J* = 11.4 Hz, 1H), 4.58–4.57 (m, 1H), 4.13 (d, *J* = 11.4 Hz, 1H), 3.45 (td, *J*₁ = 1.8 Hz, *J*₂ = 12.0 Hz, 1H), 3.07–3.03 (m, 1H), 1.99–1.91 (m, 1H), 1.80–1.74 (m, 1H), 1.70–1.67 (m, 1H), 1.62–1.58 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 148.5, 147.9, 131.8, 129.8, 128.5, 128.4, 122.8, 118.1, 113.1, 112.5, 112.3, 107.3, 102.0, 94.0, 86.3, 72.9, 65.3, 47.1, 38.3, 34.9, 21.0, 20.3. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₁₈N₂NaO₃]⁺: 405.1210, Found: 405.1212.

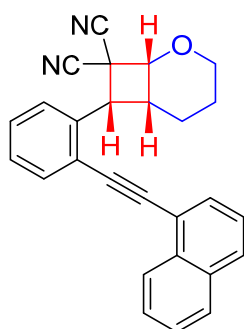


(±)-(1*R*,6*R*,7*R*)-7-(1-(Phenylethynyl)naphthalen-2-yl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3va): White solid. m.p. 132.6–133.2 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.46–8.44 (m, 1H), 7.95–7.89 (m, 2H), 7.74–7.72 (m, 1H), 7.65–7.56 (m, 4H), 7.47–7.44 (m, 3H), 4.92 (d, *J* = 7.6 Hz, 1H), 4.45 (td, *J*₁ = 2.0 Hz, *J*₂ = 11.6 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 3.91–3.88 (m, 1H), 3.68–3.59 (m, 1H), 2.27–2.21 (m, 1H), 1.94–1.84 (m, 1H), 1.71–1.68 (m, 1H), 1.65–1.55 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 133.8, 133.7, 132.3, 131.4, 129.1, 129.0, 128.7, 128.3, 127.6, 127.0, 126.0, 124.0, 122.7,

119.6, 115.5, 115.0, 100.3, 85.4, 73.8, 64.6, 44.8, 40.5, 37.1, 22.2, 20.0. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{27}H_{20}N_2NaO]^+$: 411.1468, Found: 411.1467.

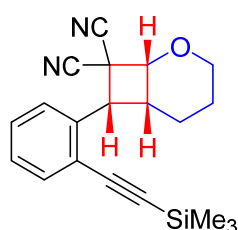


(±)-(1*R*,6*R*,7*R*)-7-(2-(Thiophen-2-ylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3wa): White solid. m.p. 113.8–115.0 °C. 1H NMR (600 MHz, $CDCl_3$) δ 7.62–7.58 (m, 2H), 7.46–7.44 (m, 1H), 7.37–7.36 (m, 2H), 7.29–7.28 (m, 1H), 7.06–7.05 (m, 1H), 4.87 (d, $J = 7.8$ Hz, 1H), 4.45 (td, $J_1 = 1.8$ Hz, $J_2 = 12.0$ Hz, 1H), 4.12 (d, $J = 7.8$ Hz, 1H), 3.90–3.89 (m, 1H), 3.52–3.46 (m, 1H), 2.18–2.15 (m, 1H), 1.87–1.80 (m, 1H), 1.72–1.69 (m, 1H), 1.64–1.59 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 135.0, 133.3, 132.1, 128.9, 128.0, 127.9, 127.4, 127.1, 122.5, 121.8, 115.3, 114.9, 91.0, 87.6, 73.6, 64.7, 44.0, 40.2, 36.8, 22.2, 19.8. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{21}H_{16}N_2NaOS]^+$: 367.0876, Found: 367.0878.

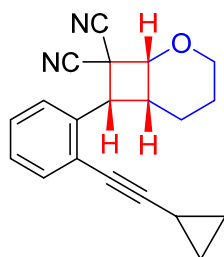


(±)-(1*R*,6*R*,7*R*)-7-(2-(Naphthalen-1-ylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3xa): White solid. m.p. 129.2–130.8 °C. 1H NMR (400 MHz, $CDCl_3$) δ 8.34–8.32 (m, 1H), 7.89–7.87 (m, 2H), 7.73–7.69 (m, 3H), 7.63–7.53 (m, 2H), 7.49–7.44 (m, 2H), 7.41–7.37 (m, 1H), 4.84 (d, $J = 7.6$ Hz, 1H), 4.43 (td, $J_1 = 2.8$ Hz, $J_2 = 11.6$ Hz, 1H), 4.24 (d, $J = 8.0$

Hz, 1H), 3.86–3.83 (m, 1H), 3.58–3.49 (m, 1H), 2.20–2.15 (m, 1H), 1.91–1.80 (m, 1H), 1.68–1.64 (m, 1H), 1.57–1.46 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.9, 133.6, 133.2, 133.0, 130.3, 129.4, 128.8, 128.5, 127.9, 127.1, 127.0, 126.6, 125.6, 125.2, 122.3, 120.1, 115.3, 114.8, 92.5, 91.8, 73.7, 64.6, 44.0, 40.0, 36.7, 22.0, 19.7. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{27}\text{H}_{20}\text{N}_2\text{NaO}]^+$: 411.1468, Found: 411.1469.

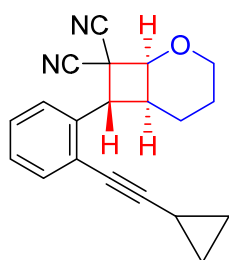


(±)-(1*R*,6*R*,7*R*)-7-(2-((Trimethylsilyl)ethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ya): White solid. m.p. 126.9–128.0 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.57–7.52 (m, 2H), 7.43–7.40 (m, 1H), 7.32–7.29 (m, 1H), 4.84 (d, $J = 7.8$ Hz, 1H), 4.44 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.09 (d, $J = 8.4$ Hz, 1H), 3.90–3.88 (m, 1H), 3.48–3.42 (m, 1H), 2.15–2.12 (m, 1H), 1.82–1.75 (m, 1H), 1.71–1.68 (m, 1H), 1.58–1.52 (m, 1H), 0.26 (s, 9H); ^{13}C NMR (150 MHz, CDCl_3) δ 135.5, 133.9, 128.9, 127.7, 126.9, 122.0, 115.3, 114.8, 102.9, 99.8, 73.6, 64.6, 43.9, 40.1, 36.7, 22.1, 19.6, -0.3. HRMS (ESI) $[\text{M}+\text{H}]^+$ Calcd. for $[\text{C}_{20}\text{H}_{23}\text{N}_2\text{OSi}]^+$: 335.1574, Found: 335.1579.



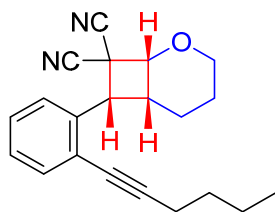
(±)-(1*R*,6*R*,7*R*)-7-(2-(Cyclopropylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3za): White solid. m.p. 127.5–128.8 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.52–7.51 (m, 1H), 7.44–7.43 (m, 1H),

7.35–7.32 (m, 1H), 7.28–7.25 (m, 1H), 4.84 (d, $J = 7.8$ Hz, 1H), 4.43 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.05 (d, $J = 8.4$ Hz, 1H), 3.90–3.87 (m, 1H), 3.40–3.34 (m, 1H), 2.09–2.05 (m, 1H), 1.83–1.76 (m, 1H), 1.72–1.67 (m, 1H), 1.63–1.55 (m, 1H), 1.51–1.46 (m, 1H), 0.93–0.91 (m, 2H), 0.83–0.77 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 134.9, 133.6, 127.7, 127.6, 126.8, 123.0, 115.5, 114.9, 99.0, 73.8, 73.7, 64.6, 43.9, 39.9, 36.9, 22.1, 19.8, 8.54, 8.49, 0.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{20}\text{H}_{18}\text{N}_2\text{NaO}]^+$: 325.1311, Found: 325.1314.

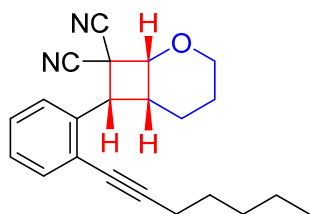


(±)-(1*S*,6*S*,7*R*)-7-(2-(Cyclopropylethynyl)phenyl)-2-oxabicyclo

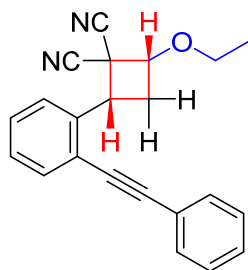
[4.2.0]octane-8,8-dicarbonitrile [3(za)']: White solid. m.p. 172.5–173.5 °C. ^1H NMR (600 MHz, CDCl_3) δ 7.47–7.46 (m, 1H), 7.35–7.33 (m, 1H), 7.31–7.28 (m, 1H), 4.93 (d, $J = 11.4$ Hz, 1H), 4.57–4.56 (m, 1H), 4.16 (d, $J = 11.4$ Hz, 1H), 3.47 (t, $J = 12.0$ Hz, 1H), 3.16–3.12 (m, 1H), 2.00–1.92 (m, 1H), 1.83–1.76 (m, 1H), 1.71–1.69 (m, 1H), 1.64–1.60 (m, 1H), 1.59–1.56 (m, 1H), 0.97–0.89 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 135.2, 133.0, 128.6, 127.8, 126.5, 125.0, 113.0, 112.5, 100.7, 73.12, 73.06, 65.3, 47.2, 38.0, 33.8, 21.0, 20.4, 8.8, 8.4, 0.6. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{20}\text{H}_{18}\text{N}_2\text{NaO}]^+$: 325.1311, Found: 325.1313.



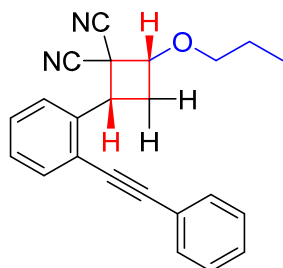
(±)-(1*R*,6*R*,7*R*)-7-(2-(Hex-1-yn-1-yl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (**3z'a**): Light yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.54–7.52 (m, 1H), 7.48–7.45 (m, 1H), 7.37–7.32 (m, 1H), 7.30–7.26 (m, 1H), 4.83 (d, *J* = 7.6 Hz, 1H), 4.43 (td, *J*₁ = 2.8 Hz, *J*₂ = 11.6 Hz, 1H), 4.07 (d, *J* = 8.0 Hz, 1H), 3.90–3.86 (m, 1H), 3.43–3.34 (m, 1H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.11–2.06 (m, 1H), 1.86–1.76 (m, 1H), 1.72–1.67 (m, 1H), 1.64–1.60 (m, 2H), 1.58–1.55 (m, 1H), 1.52–1.43 (m, 2H), 0.96 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 134.6, 133.6, 127.8, 127.7, 126.9, 123.2, 115.5, 114.9, 96.3, 78.7, 73.8, 64.6, 43.9, 39.7, 37.0, 30.5, 22.15, 22.10, 19.9, 13.6. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₁H₂₂N₂NaO]⁺: 341.1624, Found: 341.1619.



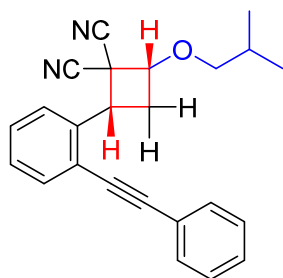
(±)-(1*R*,6*R*,7*R*)-7-(2-(Hept-1-yn-1-yl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (**3z''a**): Light yellow oil. ¹H NMR (600 MHz, CDCl₃) δ: 7.54–7.53 (m, 1H), 7.47–7.46 (m, 1H), 7.36–7.33 (m, 1H), 7.29–7.27 (m, 1H), 4.83 (d, *J* = 7.8 Hz, 1H), 4.44 (td, *J*₁ = 3.0 Hz, *J*₂ = 12.0 Hz, 1H), 4.07 (d, *J* = 8.4 Hz, 1H), 3.90–3.86 (m, 1H), 3.42–3.36 (m, 1H), 2.44 (t, *J* = 7.2 Hz, 2H), 2.10–2.07 (m, 1H), 1.85–1.77 (m, 1H), 1.72–1.67 (m, 1H), 1.64–1.60 (m, 2H), 1.59–1.56 (m, 1H), 1.46–1.41 (m, 2H), 1.40–1.34 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ: 134.7, 133.6, 127.8, 127.7, 126.9, 123.2, 115.5, 114.9, 96.4, 78.7, 73.8, 64.6, 43.9, 39.7, 36.9, 31.2, 28.1, 22.18, 22.15, 19.9, 19.7, 14.0. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₂H₂₄N₂NaO]⁺: 355.1781, Found: 355.1777.



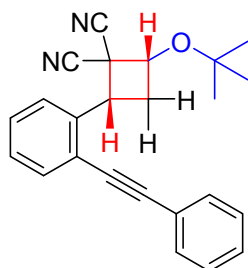
(±)-(2*R*,4*R*)-2-Ethoxy-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (**3ab**): White solid. m.p. 171.5–176.7 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64–7.61 (m, 3H), 7.45–7.44 (m, 2H), 7.39–7.36 (m, 4H), 4.49–4.39 (m, 2H), 3.85–3.77 (m, 1H), 3.72–3.65 (m, 1H), 2.86–2.71 (m, 2H), 1.34 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 134.9, 133.2, 131.8, 131.6, 128.8, 128.7, 128.3, 127.3, 123.8, 122.6, 115.2, 111.2, 95.2, 86.4, 76.7, 66.2, 42.1, 38.4, 32.0, 14.9. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₂H₁₈N₂NaO]⁺: 349.1311, Found: 349.1310.



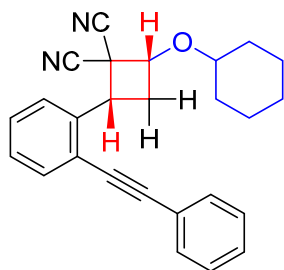
(±)-(2*R*,4*R*)-2-(2-(Phenylethynyl)phenyl)-4-propoxycyclobutane-1,1-dicarbonitrile (**3ac**): White solid. m.p. 133.8–134.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.63–7.62 (m, 3H), 7.444–7.437 (m, 2H), 7.38–7.36 (m, 4H), 4.47–4.44 (m, 1H), 4.42–4.38 (m, 1H), 3.73–3.69 (m, 1H), 3.58–3.54 (m, 1H), 2.85–2.79 (m, 1H), 2.76–2.71 (m, 1H), 1.75–1.69 (m, 2H), 1.00 (t, *J* = 4.8 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 134.9, 133.1, 131.8, 128.74, 128.72, 128.3, 127.3, 123.8, 122.6, 115.2, 111.1, 95.2, 86.4, 76.8, 72.3, 42.0, 38.4, 31.9, 22.7, 10.4. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₃H₂₀N₂NaO]⁺: 363.1468, Found: 363.1471.



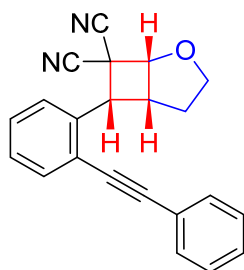
(±)-(2*R*,4*R*)-2-(*iso*-Butoxy)-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (**3ad**): White solid. m.p. 125.8–126.4 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.64–7.61 (m, 3H), 7.44–7.43 (m, 2H), 7.38–7.35 (m, 4H), 4.44–4.36 (m, 2H), 3.54–3.50 (m, 1H), 3.37–3.33 (m, 1H), 2.88–2.67 (m, 2H), 2.05–1.92 (m, 1H), 0.98 (t, *J* = 6.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 134.9, 133.1, 131.7, 128.69, 128.67, 128.3, 127.3, 123.8, 122.6, 115.2, 111.1, 95.2, 86.4, 77.1, 76.9, 41.8, 38.4, 31.8, 28.4, 19.14, 19.08. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₂N₂NaO]⁺: 377.1624, Found: 377.1629.



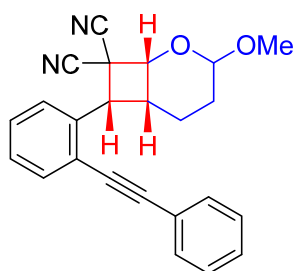
(±)-(2*R*,4*R*)-2-(*tert*-Butoxy)-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (**3ae**): White solid. m.p. 137.6–138.9 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.64–7.62 (m, 3H), 7.48–7.43 (m, 2H), 7.38–7.36 (m, 4H), 4.64 (t, *J* = 8.4 Hz, 1H), 4.43 (dd, *J*₁ = 8.4 Hz, *J*₂ = 12.0 Hz, 1H), 2.86–2.81 (m, 1H), 2.74–2.69 (m, 1H), 1.35 (s, 9H); ¹³C NMR (150 MHz, CDCl₃) δ 135.3, 133.1, 131.8, 128.8, 128.7, 128.6, 128.3, 127.4, 123.9, 122.7, 115.3, 111.7, 95.1, 86.5, 76.5, 70.6, 45.4, 38.7, 34.1, 28.2. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₂N₂NaO]⁺: 377.1624, Found: 377.1625.



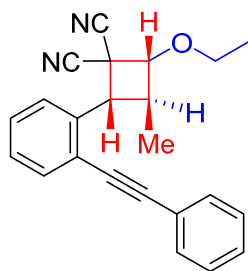
(±)-(2*R*,4*R*)-2-(Cyclohexyloxy)-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (3af): White solid. m.p. 122.6–124.4 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.63–7.62 (m, 3H), 7.46–7.43 (m, 2H), 7.38–7.36 (m, 4H), 4.59 (t, *J* = 8.4 Hz, 1H), 4.39 (dd, *J*₁ = 8.4 Hz, *J*₂ = 12.0 Hz, 1H), 3.59–3.55 (m, 1H), 2.86–2.81 (m, 1H), 2.75–2.71 (m, 1H), 2.03–1.97 (m, 2H), 1.81–1.77 (m, 2H), 1.55–1.53 (m, 1H), 1.51–1.47 (m, 1H), 1.45–1.39 (m, 1H), 1.36–1.28 (m, 2H), 1.26–1.21 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 135.1, 133.1, 131.8, 128.75, 128.71, 128.7, 128.3, 127.4, 123.8, 122.6, 115.3, 111.5, 95.1, 86.5, 78.9, 74.9, 43.4, 38.5, 33.0, 32.8, 31.5, 25.3, 23.84, 23.81. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₆H₂₄N₂NaO]⁺: 403.1781, Found: 403.1786.



(±)-(1*R*,5*R*,6*R*)-6-(2-(Phenylethynyl)phenyl)-2-oxabicyclo[3.2.0]heptane-7,7-dicarbonitrile (3ag): Lightless oil. ¹H NMR (600 MHz, CDCl₃) δ 7.64–7.62 (m, 1H), 7.53–7.50 (m, 3H), 7.44–7.42 (m, 1H), 7.39–7.35 (m, 4H), 5.06 (d, *J* = 6.6 Hz, 1H), 4.47 (d, *J* = 8.4 Hz, 1H), 4.44–4.41 (m, 1H), 4.11 (q, *J* = 8.4 Hz, 1H), 3.98–3.93 (m, 1H), 2.37–2.31 (m, 1H), 2.16–2.09 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 135.3, 134.0, 131.4, 128.9, 128.64, 128.56, 128.0, 127.2, 122.5, 115.3, 112.0, 95.5, 87.3, 82.1, 73.0, 45.5, 43.3, 38.5, 26.9. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₂H₁₆N₂NaO]⁺: 347.1155, Found: 347.1159.

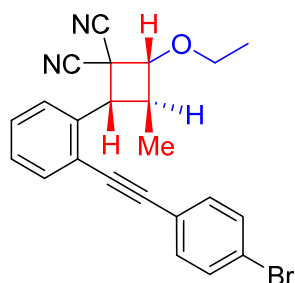


(±)-**(1*R*,6*R*,7*R*)-3-Methoxy-7-(2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8,8-dicarbonitrile (3ah)**: White solid. m.p. 149.4–150.3 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.62–7.60 (m, 1H), 7.54–7.52 (m, 1H), 7.43–7.42 (m, 2H), 7.38–7.35 (m, 1H), 7.31–7.27 (m, 4H), 5.07–5.05 (m, 1H), 4.85 (d, *J* = 7.2 Hz, 1H), 4.36 (d, *J* = 8.4 Hz, 1H), 3.41 (s, 3H), 3.34–3.28 (m, 1H), 2.01–1.97 (m, 1H), 1.94–1.89 (m, 1H), 1.75–1.68 (m, 1H), 1.33–1.27 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 134.8, 133.5, 131.4, 128.9, 128.7, 128.6, 128.0, 127.1, 122.5, 115.1, 113.5, 99.8, 94.6, 87.0, 71.8, 56.2, 44.6, 38.8, 37.4, 27.2, 17.5. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₄H₂₀N₂NaO₂]⁺: 391.1417, Found: 391.1422.

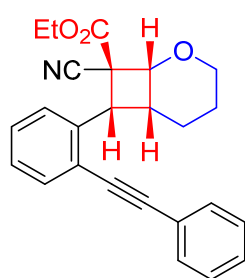


(±)-**(2*R*,3*S*,4*R*)-2-Ethoxy-3-methyl-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (3ai)**: White solid. m.p. 139.6–140.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.72–7.70 (m, 1H), 7.59–7.57 (m, 1H), 7.50–7.48 (m, 2H), 7.44–7.39 (m, 1H), 7.37–7.31 (m, 4H), 4.56 (d, *J* = 7.6 Hz, 1H), 4.21 (d, *J* = 8.8 Hz, 1H), 3.89–3.81 (m, 1H), 3.74–3.66 (m, 1H), 3.61–3.48 (m, 1H), 1.35 (t, *J* = 6.8 Hz, 3H), 1.20 (d, *J* = 7.6 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 134.7, 133.1, 131.3, 128.7, 128.6, 128.4, 127.7, 126.9, 122.6, 122.5, 115.5,

113.2, 94.2, 87.0, 78.4, 66.3, 42.8, 40.5, 37.3, 14.8, 9.1. HRMS (ESI) $[M+Na]^+$
Calcd. for $[C_{23}H_{20}N_2NaO]^+$: 363.1468, Found: 363.1472.

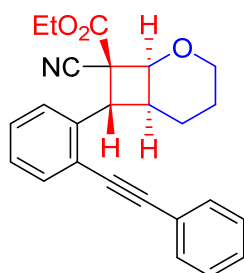


(±)-(2*R*,3*S*,4*R*)-2-((4-Bromophenyl)ethynyl)phenyl)-4-ethoxy-3-methylcyclobutane-1,1-dicarbonitrile (3hi): White solid. m.p. 142.4–143.1 °C. 1H NMR (600 MHz, $CDCl_3$) δ 7.64–7.63 (m, 1H), 7.53–7.51 (m, 2H), 7.47–7.44 (m, 2H), 7.42–7.41 (m, 2H), 7.39–7.36 (m, 1H), 4.82 (d, $J = 10.8$ Hz, 1H), 4.41 (d, $J = 9.0$ Hz, 1H), 3.88–3.83 (m, 1H), 3.74–3.69 (m, 1H), 3.37–3.31 (m, 1H), 1.37 (t, $J = 7.2$ Hz, 3H), 1.03 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 134.4, 133.3, 133.0, 128.6, 128.4, 128.0, 124.7, 123.2, 121.4, 113.9, 113.5, 94.3, 87.5, 84.3, 66.6, 44.4, 40.6, 37.5, 15.0, 13.5. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{23}H_{19}^{79}BrN_2NaO]^+$: 441.0573, Found: 441.0577; for $[C_{23}H_{19}^{81}BrN_2NaO]^+$: 443.0553, Found: 443.0558.

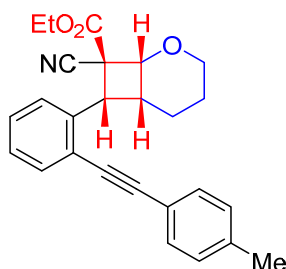


(±)-Ethyl (1*R*,6*R*,7*R*,8*S*)-8-cyano-7-(2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0] octane-8-carboxylate (5aa): White solid. m.p. 141.7–142.7 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.63–7.61 (m, 1H), 7.57–7.55 (m, 1H), 7.52–7.48 (m, 2H), 7.41–7.36 (m, 4H), 7.31–7.27 (m, 1H), 4.76 (d, $J = 7.6$ Hz, 1H), 4.51 (td, $J_1 = 3.2$ Hz, $J_2 = 11.6$ Hz, 1H), 4.33–4.20 (m, 2H), 4.16 (d, $J = 8.0$ Hz,

1H), 3.85–3.81 (m, 1H), 3.48–3.39 (m, 1H), 2.18–2.12 (m, 1H), 1.96–1.85 (m, 1H), 1.71–1.63 (m, 1H), 1.61–1.52 (m, 1H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 137.1, 133.2, 131.3, 128.6, 128.5, 128.4, 127.4, 127.0, 122.9, 122.1, 118.6, 93.5, 87.8, 71.8, 64.2, 63.2, 51.4, 41.7, 38.6, 22.5, 20.1, 14.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{25}\text{H}_{23}\text{NNaO}_3]^+$: 408.1570, Found: 408.1574.

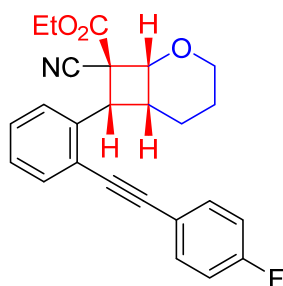


(±)-Ethyl **(1*S*,6*S*,7*R*,8*S*)-8-cyano-7-(2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8-carboxylate [5(aa)']**: White solid. m.p. 142.8–143.2 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.65–7.62 (m, 2H), 7.60–7.57 (m, 2H), 7.42–7.34 (m, 4H), 7.33–7.28 (m, 1H), 5.19 (d, $J = 11.6$ Hz, 1H), 4.69 (d, $J = 5.6$ Hz, 1H), 4.17–4.00 (m, 2H), 3.95–3.92 (m, 1H), 3.34 (td, $J_1 = 3.2$ Hz, $J_2 = 11.6$ Hz, 1H), 3.06–3.00 (m, 1H), 2.01–1.90 (m, 1H), 1.79–1.68 (m, 2H), 1.55–1.50 (m, 1H), 1.18 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.6, 138.1, 133.1, 131.8, 128.6, 128.4, 128.3, 127.8, 127.3, 123.9, 123.3, 117.1, 94.3, 87.8, 74.9, 65.1, 62.5, 50.9, 41.9, 35.4, 21.8, 20.8, 14.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{25}\text{H}_{23}\text{NNaO}_3]^+$: 408.1570, Found: 408.1574.

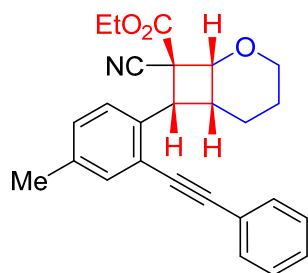


(±)-Ethyl **(1*R*,6*R*,7*R*,8*S*)-8-cyano-7-(2-(p-tolyethynyl)phenyl)-2-oxabicyclo[4.2.0]octane-8-carboxylate (5ba)**: White solid. m.p. 122.3–123.0

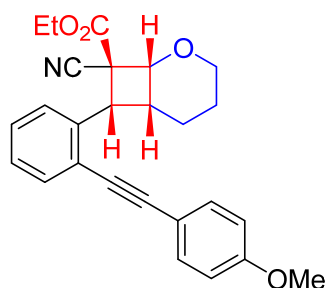
°C. ^1H NMR (600 MHz, CDCl_3) δ 7.61–7.60 (m, 1H), 7.56–7.54 (m, 1H), 7.40–7.36 (m, 3H), 7.29–7.27 (m, 1H), 7.19–7.18 (m, 2H), 4.76 (d, $J = 7.8$ Hz, 1H), 4.50 (td, $J_1 = 3.0$ Hz, $J_2 = 12.0$ Hz, 1H), 4.32–4.23 (m, 2H), 4.15 (d, $J = 7.8$ Hz, 1H), 3.84–3.82 (m, 1H), 3.46–3.40 (m, 1H), 2.39 (s, 3H), 2.16–2.13 (m, 1H), 1.93–1.86 (m, 1H), 1.69–1.65 (m, 1H), 1.61–1.53 (m, 1H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 167.6, 138.9, 137.1, 133.1, 131.2, 129.3, 128.3, 127.3, 127.0, 122.4, 119.9, 118.6, 93.8, 87.2, 71.8, 64.3, 63.2, 51.4, 41.8, 38.7, 22.6, 21.5, 20.1, 14.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{26}\text{H}_{25}\text{NNaO}_3]^+$: 422.1727, Found: 422.1731.



(±)-Ethyl (1*R*,6*R*,7*R*,8*S*)-8-cyano-7-(2-((4-fluorophenyl)ethynyl)phenyl)-2-oxabicyclo [4.2.0]octane-8-carboxylate (**5ca**): White solid. m.p. 142.8–142.3 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.63–7.61 (m, 1H), 7.56–7.54 (m, 1H), 7.51–7.46 (m, 2H), 7.41–7.37 (m, 1H), 7.31–7.27 (m, 1H), 7.11–7.05 (m, 2H), 4.75 (d, $J = 7.6$ Hz, 1H), 4.51 (td, $J_1 = 3.2$ Hz, $J_2 = 11.6$ Hz, 1H), 4.33–4.20 (m, 2H), 4.16 (d, $J = 8.0$ Hz, 1H), 3.85–3.81 (m, 1H), 3.43–3.34 (m, 1H), 2.16–2.10 (m, 1H), 1.94–1.86 (m, 1H), 1.70–1.68 (m, 1H), 1.63–1.52 (m, 1H), 1.34 (t, $J = 7.2$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -110.1; ^{13}C NMR (100 MHz, CDCl_3) δ 167.5, 162.6 (d, $J = 248.9$ Hz), 137.1, 133.2 (d, $J = 7.1$ Hz), 128.5, 127.4, 127.1, 122.0, 119.0 (d, $J = 3.5$ Hz), 118.5, 115.8 (d, $J = 22.2$ Hz), 92.5, 87.5, 71.8, 64.2, 63.2, 51.5, 41.6, 38.6, 22.5, 20.1, 14.0. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{25}\text{H}_{22}\text{FNNaO}_3]^+$: 426.1476, Found: 426.1481.

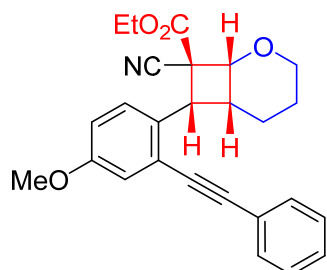


(±)-Ethyl (1*R*,6*R*,7*R*,8*S*)-8-cyano-7-(4-methyl-2-(phenylethynyl)phenyl)-2-oxabicyclo [4.2.0]octane-8-carboxylate (**5da**): White solid. m.p. 142.5–143.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.51–7.48 (m, 3H), 7.39–7.36 (m, 4H), 7.20–7.19 (m, 1H), 4.75 (d, *J* = 7.8 Hz, 1H), 4.50 (td, *J*₁ = 3.0 Hz, *J*₂ = 12.0 Hz, 1H), 4.31–4.21 (m, 2H), 4.12 (d, *J* = 7.8 Hz, 1H), 3.84–3.81 (m, 1H), 3.43–3.37 (m, 1H), 2.34 (s, 3H), 2.16–2.12 (m, 1H), 1.95–1.88 (m, 1H), 1.69–1.66 (m, 1H), 1.60–1.54 (m, 1H), 1.33 (t, *J* = 7.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 167.6, 136.8, 134.1, 133.7, 131.3, 129.3, 128.53, 128.49, 127.3, 123.0, 121.9, 118.7, 93.1, 88.0, 71.8, 64.2, 63.2, 51.5, 41.5, 38.6, 22.6, 20.7, 20.3, 20.1, 14.0. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₆H₂₅NNaO₃]⁺: 422.1727, Found: 422.1730.

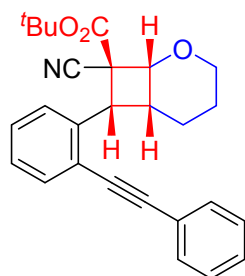


(±)-Ethyl (1*R*,6*R*,7*R*,8*S*)-8-cyano-7-(2-((4-methoxyphenyl)ethynyl)phenyl)-2-oxabicyclo[4.2.0] octane-8-carboxylate (**5ea**): White solid. m.p. 141.4–142.5 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.61–7.60 (m, 1H), 7.55–7.52 (m, 1H), 7.45–7.42 (m, 2H), 7.38–7.35 (m, 1H), 7.29–7.27 (m, 1H), 6.92–6.89 (m, 2H), 4.76 (d, *J* = 7.8 Hz, 1H), 4.51 (td, *J*₁ = 3.0 Hz, *J*₂ = 12.0 Hz, 1H), 4.32–4.22 (m, 2H), 4.15 (d, *J* = 7.8 Hz, 1H), 3.85 (s, 3H), 3.83–3.82 (m, 1H), 3.45–3.39 (m, 1H), 2.16–2.13 (m, 1H), 1.94–1.87 (m, 1H), 1.72–1.66 (m, 1H), 1.62–1.58 (m, 1H), 1.34 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 167.6, 159.9,

137.0, 133.1, 132.8, 128.1, 127.3, 127.0, 122.5, 118.7, 115.1, 114.2, 93.6, 86.6, 71.8, 64.3, 63.3, 55.4, 51.5, 41.8, 38.7, 22.6, 20.1, 14.0. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{26}H_{25}NNaO_4]^+$: 438.1676, Found: 438.1680.

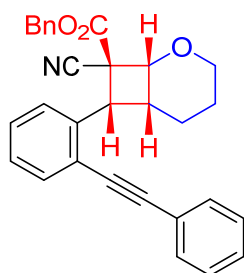


(±)-Ethyl (*1R,6R,7R,8S*)-8-cyano-7-(4-methoxy-2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0] octane-8-carboxylate (**5fa**): White solid. m.p. 143.5–144.3 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.56–7.53 (m, 1H), 7.51–7.48 (m, 2H), 7.39–7.37 (m, 3H), 7.10–7.09 (m, 1H), 6.95–6.92 (m, 1H), 4.74 (d, $J = 7.6$ Hz, 1H), 4.49 (td, $J_1 = 2.8$ Hz, $J_2 = 11.6$ Hz, 1H), 4.32–4.19 (m, 2H), 4.14–4.11 (m, 1H), 3.83 (s, 3H), 3.81–3.79 (m, 1H), 3.42–3.32 (m, 1H), 2.15–2.09 (m, 1H), 1.99–1.88 (m, 1H), 1.74–1.62 (m, 1H), 1.59–1.54 (m, 1H), 1.33 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 158.3, 131.3, 129.3, 128.7, 128.55, 128.52, 123.3, 122.8, 118.7, 118.2, 114.6, 93.3, 87.8, 71.8, 64.2, 63.2, 55.4, 51.6, 41.2, 38.6, 22.6, 20.0, 14.0. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{26}H_{25}NNaO_4]^+$: 438.1676, Found: 438.1680.

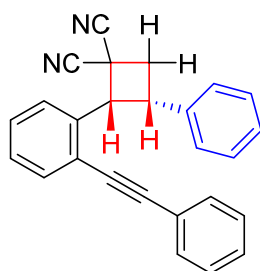


(±)-*tert*-Butyl (*1R,6R,7R,8S*)-8-cyano-7-(2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0] octane-8-carboxylate (**5ga**): White solid. m.p. 139.2–140.5 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.68–7.66 (m, 1H), 7.57–7.55 (m, 1H), 7.50–

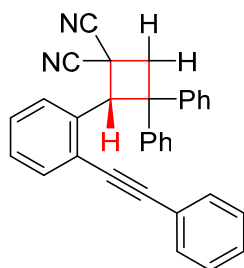
7.48 (m, 2H), 7.41–7.36 (m, 4H), 7.31–7.27 (m, 1H), 4.74 (d, $J = 7.6$ Hz, 1H), 4.49 (td, $J_1 = 3.2$ Hz, $J_2 = 11.6$ Hz, 1H), 4.08 (d, $J = 8.0$ Hz, 1H), 3.83–3.80 (m, 1H), 3.47–3.38 (m, 1H), 2.15–2.10 (m, 1H), 1.92–1.81 (m, 1H), 1.68–1.63 (m, 1H), 1.62–1.57 (m, 1H), 1.53 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.4, 137.4, 133.1, 131.2, 128.6, 128.50, 128.46, 127.3, 126.9, 123.0, 122.1, 118.8, 93.4, 87.9, 84.3, 71.2, 64.1, 52.1, 41.9, 38.5, 27.8, 22.6, 19.9. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{27}\text{H}_{27}\text{NNaO}_3]^+$: 436.1883, Found: 436.1886.



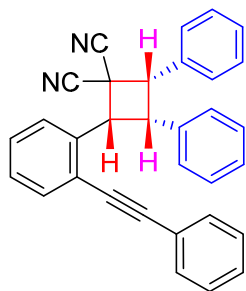
(±)-Benzyl (1*R*,6*R*,7*R*,8*S*)-8-cyano-7-(2-(phenylethynyl)phenyl)-2-oxabicyclo[4.2.0] octane-8-carboxylate (**5ha**): White solid. m.p. 150.3–150.9 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.54–7.52 (m, 1H), 7.48–7.46 (m, 4H), 7.43–7.39 (m, 2H), 7.37–7.32 (m, 5H), 7.27–7.23 (m, 2H), 5.57 (s, 1H), 5.31–5.25 (m, 2H), 4.69 (d, $J = 6.0$ Hz, 1H), 3.75–3.66 (m, 2H), 2.45–2.42 (m, 1H), 1.61–1.54 (m, 1H), 1.50–1.46 (m, 1H), 1.17–1.06 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 164.8, 138.9, 135.5, 132.6, 131.4, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 127.2, 122.9, 122.6, 118.3, 101.0, 94.0, 86.9, 70.1, 63.1, 62.0, 39.5, 35.4, 24.2, 18.5. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{30}\text{H}_{25}\text{NNaO}_3]^+$: 470.1727, Found: 470.1726.



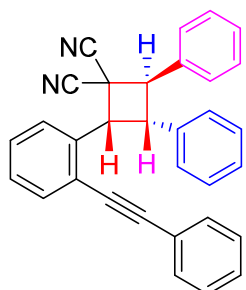
(±)-(2*R*,3*S*)-3-Phenyl-2-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (7aa): White solid. m.p. 169.6–170.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.66–7.63 (m, 2H), 7.60–7.57 (m, 1H), 7.43–7.38 (m, 3H), 7.28–7.18 (m, 4H), 7.06–7.02 (m, 1H), 6.99–6.97 (m, 2H), 6.88–6.86 (m, 1H), 5.43 (dd, *J*₁ = 2.8 Hz, *J*₂ = 9.6 Hz, 1H), 4.75 (q, *J* = 9.6 Hz, 1H), 3.44–3.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 136.9, 134.3, 132.8, 131.7, 128.8, 128.6, 128.5, 128.3, 128.2, 127.9, 127.1, 126.5, 124.9, 122.5, 116.9, 113.5, 95.9, 86.4, 52.2, 39.3, 35.7, 29.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₂₆H₁₈N₂Na]⁺: 381.1362, Found: 381.1366.



(±)-(S)-3,3-Diphenyl-2-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (7ab): White solid. m.p. 194.9–196.1 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.67–7.65 (m, 1H), 7.62–7.60 (m, 2H), 7.42–7.41 (m, 2H), 7.39–7.38 (m, 3H), 7.29–7.26 (m, 3H), 7.21–7.15 (m, 4H), 7.05–7.01 (m, 3H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.12 (s, 1H), 4.12 (d, *J* = 13.2 Hz, 1H), 3.52 (d, *J* = 13.2 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 148.7, 139.7, 134.1, 132.6, 131.7, 130.3, 128.95, 128.88, 128.7, 128.5, 128.3, 128.0, 127.8, 127.2, 126.9, 125.6, 124.7, 122.5, 116.0, 114.3, 95.6, 86.9, 55.0, 54.4, 41.0, 29.7. HRMS (ESI) [M+Na]⁺ Calcd. for [C₃₂H₂₂N₂Na]⁺: 457.1675, Found: 457.1672.

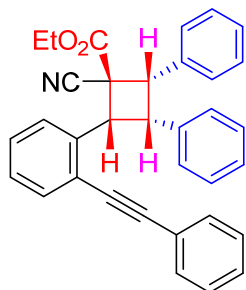


(±)-**(2*S*,3*S*,4*R*)-2,3-Diphenyl-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (7ac)**: White solid. m.p. 183.6–184.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.53–7.50 (m, 3H), 7.39–7.35 (m, 3H), 7.30–7.26 (m, 4H), 7.23–7.22 (m, 2H), 7.20–7.15 (m, 1H), 7.13–7.09 (m, 2H), 7.04–6.97 (m, 4H), 5.31 (d, *J* = 9.2 Hz, 1H), 4.94–4.84 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 134.6, 133.6, 133.1, 132.6, 131.5, 130.7, 128.8, 128.49, 128.46, 128.43, 128.2, 128.02, 127.97, 127.4, 127.1, 123.2, 122.7, 116.1, 114.0, 94.9, 87.1, 49.9, 49.8, 47.7, 37.8. HRMS (ESI) [M+Na]⁺ Calcd. for [C₃₂H₂₂N₂Na]⁺: 457.1675, Found: 457.1677.

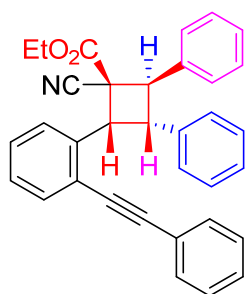


(±)-**(2*S*,3*R*,4*R*)-2,3-Diphenyl-4-(2-(phenylethynyl)phenyl)cyclobutane-1,1-dicarbonitrile (7ad)**: White solid. m.p. 195.3–197.2 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.67–7.63 (m, 3H), 7.50–7.46 (m, 4H), 7.45–7.42 (m, 1H), 7.40–7.35 (m, 3H), 7.25–7.18 (m, 4H), 7.10–7.07 (m, 1H), 7.01–6.99 (m, 3H), 5.40 (d, *J* = 9.6 Hz, 1H), 5.10–5.06 (m, 1H), 4.86 (d, *J* = 12.6 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 136.7, 134.7, 134.3, 133.0, 131.7, 129.32, 129.25, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.2, 127.1, 126.5, 125.5, 122.4, 114.8, 113.3, 96.4, 86.4,

51.6, 49.6, 42.3, 37.9. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{32}H_{22}N_2Na]^+$: 457.1675, Found: 457.1678.

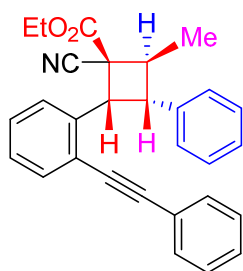


(±)-Ethyl **(1*S*,2*S*,3*S*,4*R*)-1-cyano-2,3-diphenyl-4-(2-phenylethynyl)phenylcyclobutane-1-carboxylate (7bc)**: White solid. m.p. 179.6–179.9 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.47–7.45 (m, 1H), 7.40–7.35 (m, 3H), 7.30–7.27 (m, 1H), 7.22–7.20 (m, 3H), 7.18–7.11 (m, 3H), 7.09–7.04 (m, 3H), 7.01–6.99 (m, 2H), 5.28–5.22 (m, 1H), 4.91–4.81 (m, 2H), 4.36–4.23 (m, 2H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 136.6, 135.2, 134.7, 132.6, 131.5, 131.0, 128.5, 128.4, 128.2, 128.1, 128.0, 127.7, 127.24, 127.15, 126.7, 123.1, 123.0, 117.7, 94.2, 87.8, 63.5, 52.4, 48.8, 46.6, 45.8, 14.0. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{34}H_{27}NNaO_2]^+$: 504.1934, Found: 504.1935.

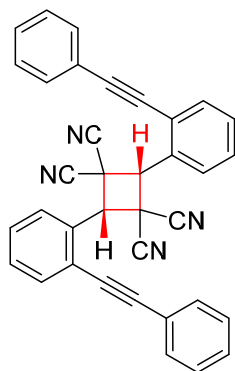


(±)-Ethyl **(1*S*,2*R*,3*S*,4*R*)-1-cyano-2,3-diphenyl-4-(2-phenylethynyl)phenylcyclobutane-1-carboxylate (7bd)**: White solid. m.p. 185.2–185.9 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.58–7.55 (m, 3H), 7.42–7.40

(m, 2H), 7.39–7.32 (m, 6H), 7.21–7.14 (m, 4H), 7.09–7.03 (m, 2H), 7.00–6.98 (m, 2H), 5.51 (d, $J = 10.0$ Hz, 1H), 5.17 (t, $J = 11.2$ Hz, 1H), 4.92 (d, $J = 12.0$ Hz, 1H), 3.88–3.75 (m, 2H), 0.77 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 138.3, 137.2, 135.7, 132.3, 131.5, 128.6, 128.44, 128.36, 128.30, 128.27, 127.9, 127.4, 127.3, 126.6, 124.9, 122.9, 117.4, 95.1, 87.4, 62.6, 51.8, 50.2, 45.3, 41.0, 13.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{34}\text{H}_{27}\text{NNaO}_2]^+$: 504.1934, Found: 504.1938.

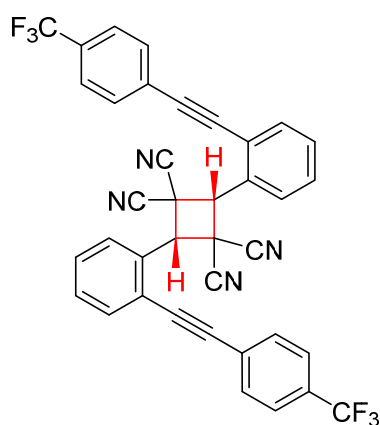


(±)-Ethyl **(1*S*,2*R*,3*R*,4*R*)-1-cyano-2-methyl-3-phenyl-4-(2-phenylethynyl)phenylcyclobutane-1-carboxylate (7be)**: White solid. m.p. 173.5–184.2 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.59–7.57 (m, 2H), 7.51–7.49 (m, 1H), 7.40–7.32 (m, 3H), 7.22–7.18 (m, 2H), 7.14–7.10 (m, 2H), 7.04–6.98 (m, 4H), 5.45 (d, $J = 10.0$ Hz, 1H), 4.40–4.32 (m, 1H), 4.31–4.19 (m, 2H), 3.83–3.75 (m, 1H), 1.40 (d, $J = 6.8$ Hz, 3H), 1.29 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.4, 138.4, 137.2, 132.1, 128.5, 128.4, 128.30, 128.28, 127.7, 127.1, 126.4, 126.3, 124.6, 123.0, 117.4, 94.7, 87.4, 62.8, 47.9, 45.7, 43.3, 16.3, 14.1. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{29}\text{H}_{25}\text{NNaO}_2]^+$: 442.1778, Found: 442.1777.



(±)-(2*S*,4*S*)-2,4-Bis(2-(phenylethynyl)phenyl)cyclobutane-1,1,3,3-

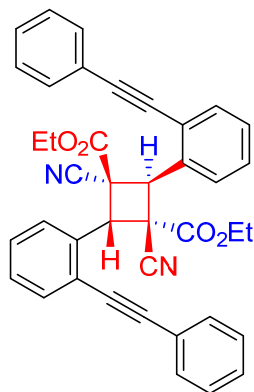
tetracarbonitrile (8aa): White solid. m.p. 212.5–212.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.21–8.19 (m, 2H), 7.79–7.75 (m, 2H), 7.60–7.57 (m, 8H), 7.40–7.36 (m, 2H), 7.34–7.30 (m, 4H), 5.64 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 134.0, 131.8, 130.9, 129.28, 129.26, 128.7, 128.5, 127.6, 124.9, 121.8, 113.2, 110.4, 97.5, 85.3, 50.9, 38.8. HRMS (ESI) [M+Na]⁺ Calcd. for [C₃₆H₂₀N₄Na]⁺: 531.1580, Found: 531.1585.



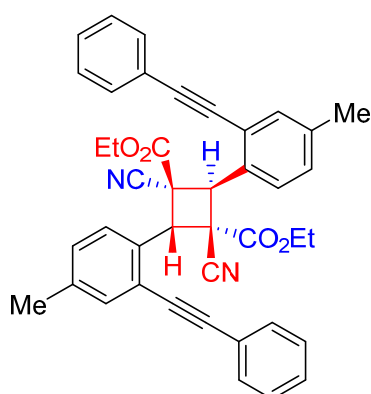
(±)-(2*S*,4*S*)-2,4-Bis(2-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)

cyclobutane-1,1,3,3-tetracarbonitrile (8ii): White solid. m.p. 203.6–204.9 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.13–8.11 (m, 2H), 7.83–7.81 (m, 2H), 7.76–7.74 (m, 4H), 7.70–7.68 (m, 4H), 7.65–7.55 (m, 4H), 5.82 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ –63.0; ¹³C NMR (100 MHz, CDCl₃) δ 134.4, 133.9, 132.14, 132.11, 131.3, 129.9, 129.8, 129.3 (q, *J* = 112.6 Hz), 125.6 (q, *J* = 3.7

Hz), 124.6 (q, $J = 145.5$ Hz), 124.4, 111.8, 96.0, 87.0, 52.0, 37.1. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{38}H_{18}F_6N_4Na]^+$: 667.1328, Found: 667.1328.



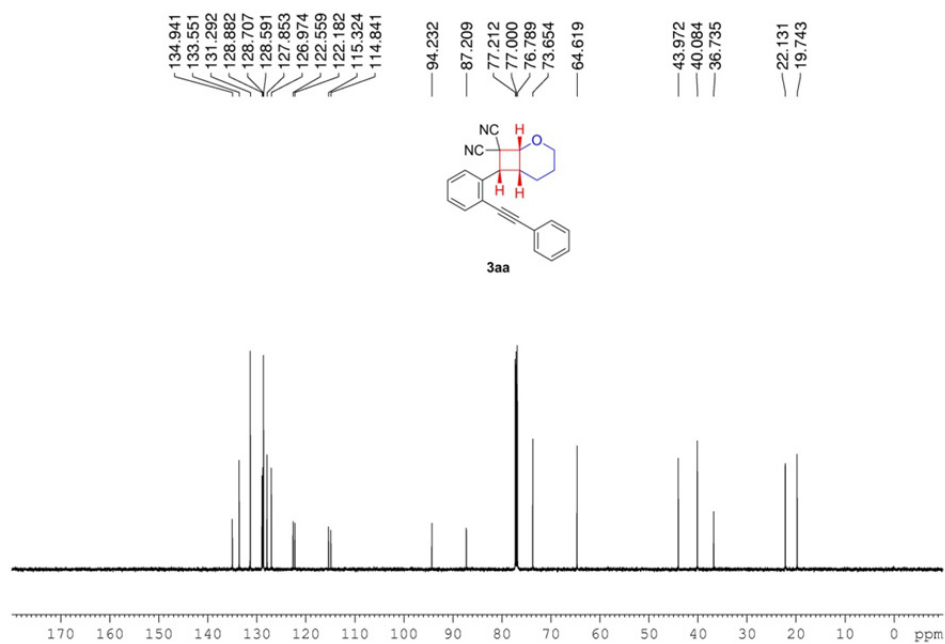
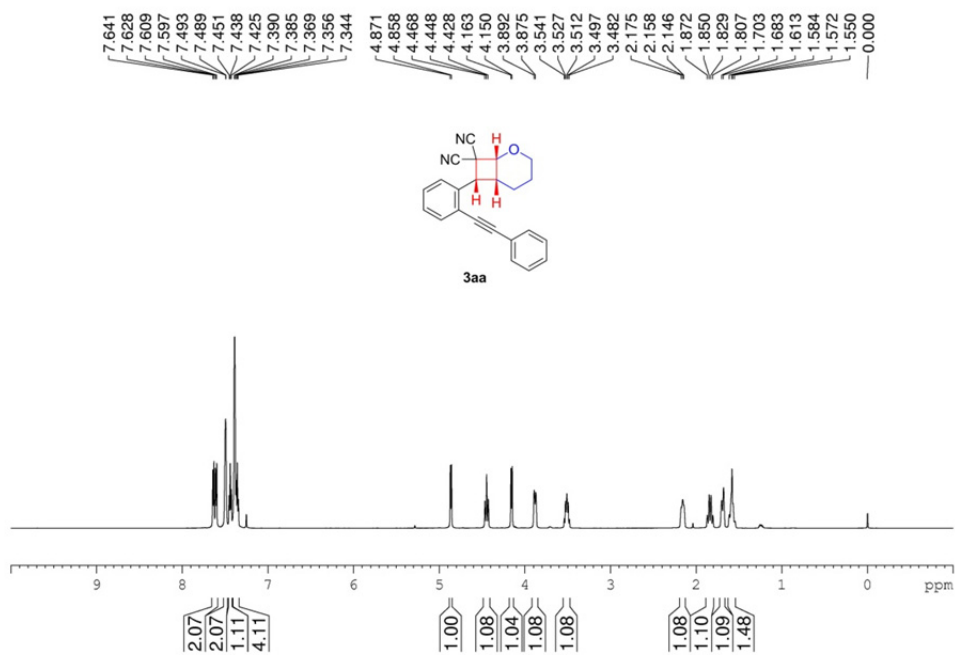
(±)-Diethyl **(1*R*,2*R*,3*S*,4*S*)-1,3-dicyano-2,4-bis(2-(phenylethynyl)phenyl)cyclobutane-1,3-dicarboxylate (9aa)**: White solid. m.p. 191.4–192.8 °C. 1H NMR (600 MHz, $CDCl_3$) δ 7.88–7.87 (m, 2H), 7.76–7.75 (m, 4H), 7.66–7.65 (m, 2H), 7.44–7.37 (m, 10H), 6.31 (s, 2H), 4.00–3.91 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.1, 133.3, 132.6, 131.9, 129.2, 128.8, 128.5, 128.3, 127.6, 125.4, 122.7, 116.6, 95.9, 86.3, 63.7, 49.1, 47.5, 13.4. HRMS (ESI) $[M+Na]^+$ Calcd. for $[C_{40}H_{30}N_2NaO_4]^+$: 625.2098, Found: 625.2100.

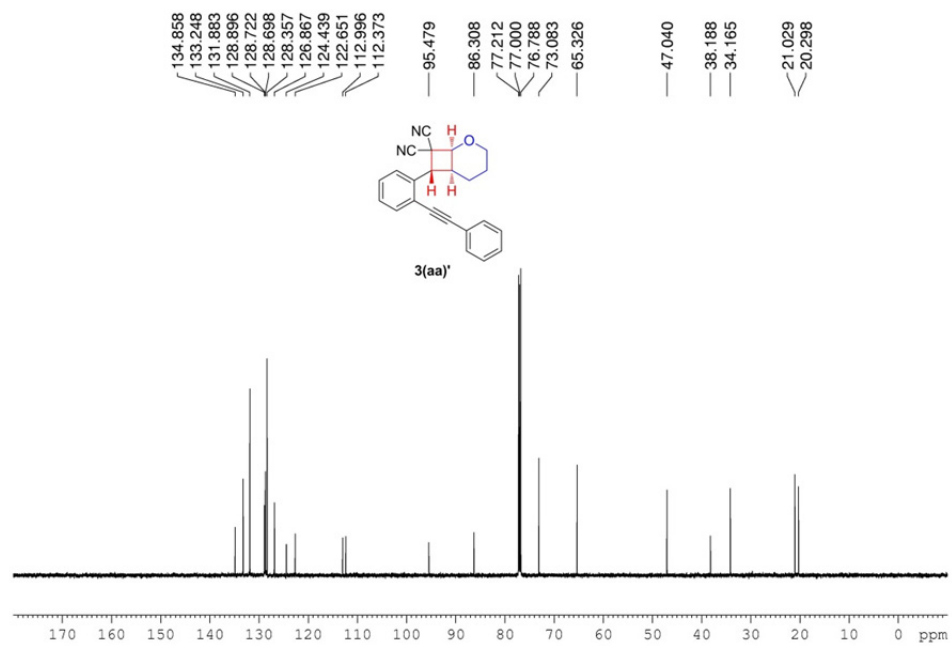
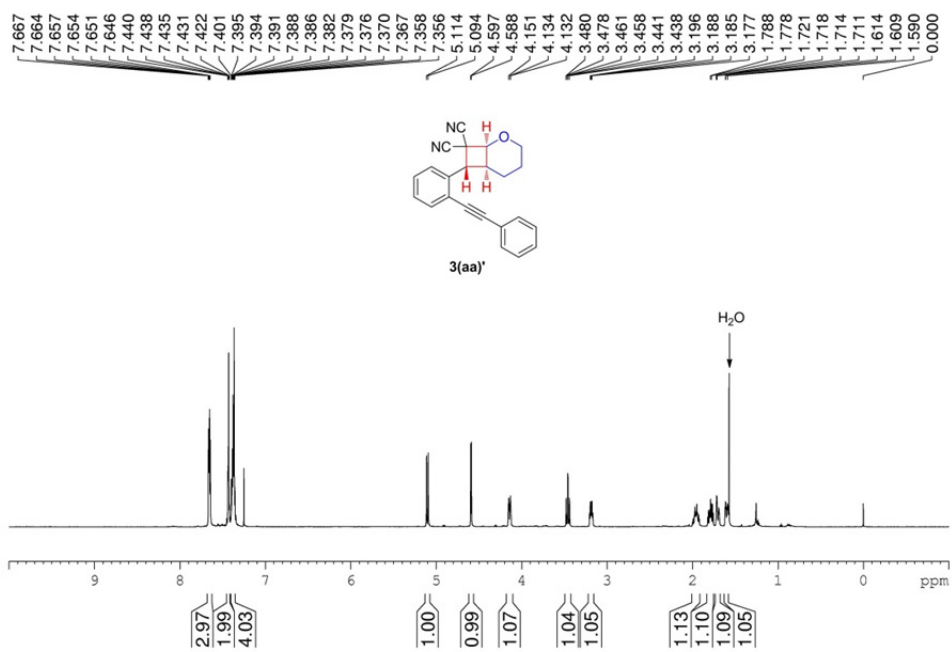


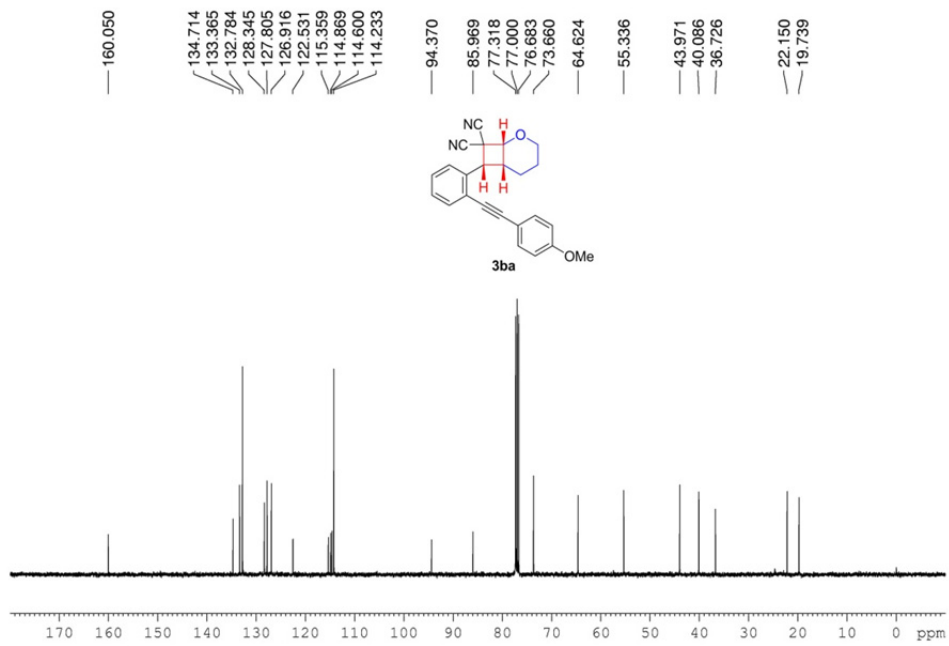
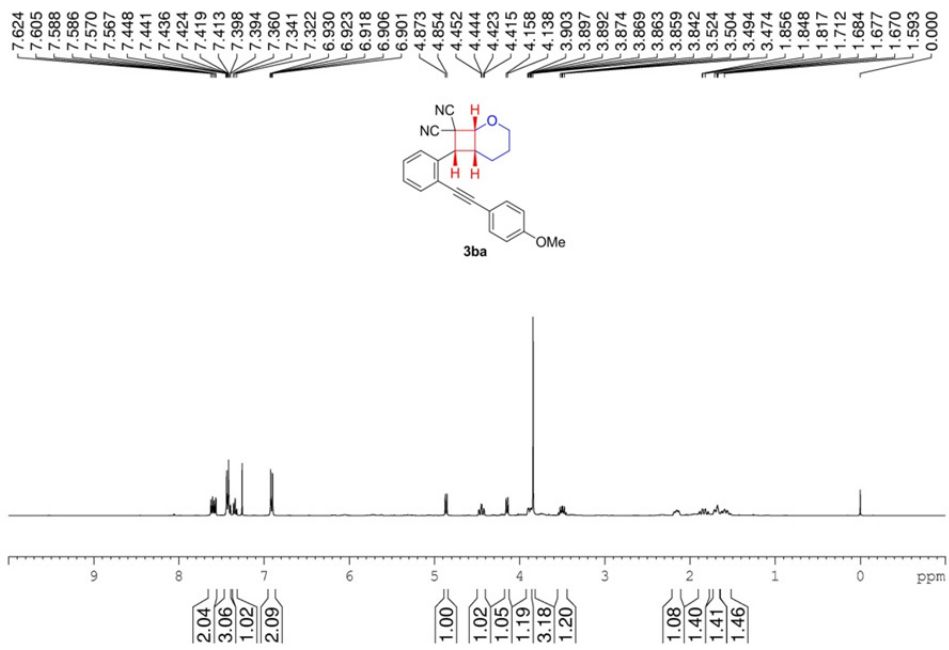
(±)-Diethyl **(1*R*,2*R*,3*S*,4*S*)-1,3-dicyano-2,4-bis(4-methyl-2-(phenylethynyl)phenyl)cyclobutane-1,3-dicarboxylate (9dd)**: White solid. m.p. 191.8–192.3 °C. 1H NMR (400 MHz, $CDCl_3$) δ 7.75–7.73 (m, 6H), 7.472–

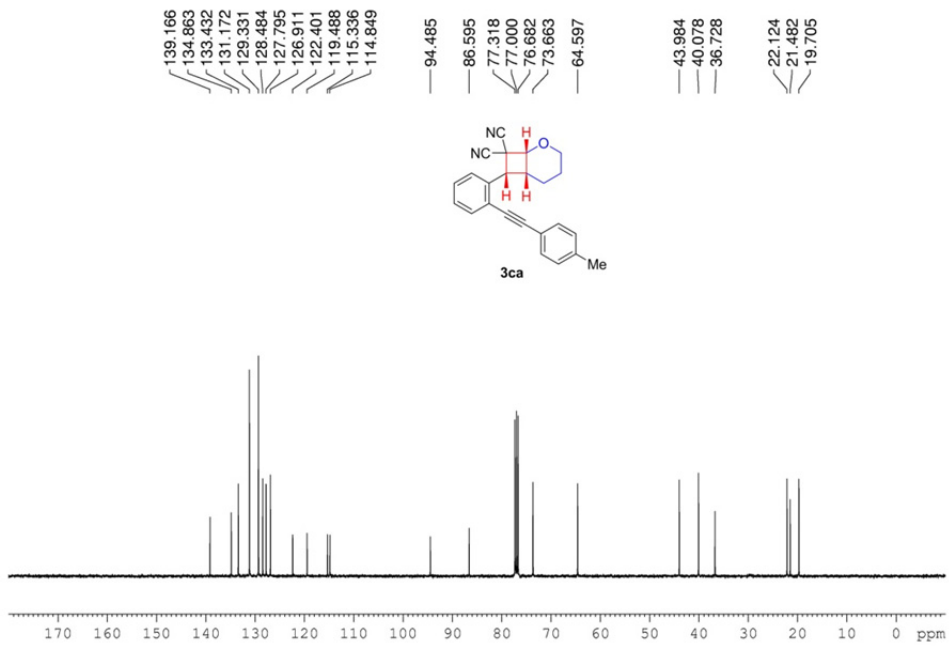
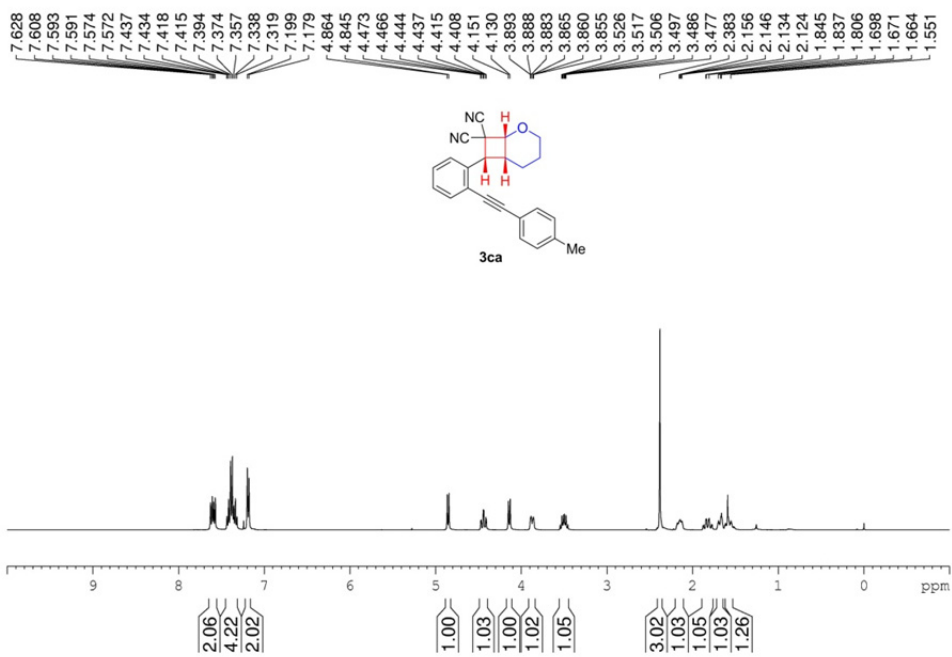
7.469 (m, 2H), 7.44–7.38 (m, 6H), 7.20–7.17 (m, 2H), 6.23 (s, 2H), 4.01–3.92 (m, 4H), 2.36 (s, 6H), 0.90 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.2, 139.3, 133.0, 131.9, 130.4, 129.2, 128.7, 128.5, 127.5, 125.2, 122.8, 116.8, 95.3, 86.5, 63.6, 49.3, 47.3, 21.0, 13.4. HRMS (ESI) $[\text{M}+\text{Na}]^+$ Calcd. for $[\text{C}_{42}\text{H}_{34}\text{N}_2\text{NaO}_4]^+$: 653.2411, Found: 653.2412.

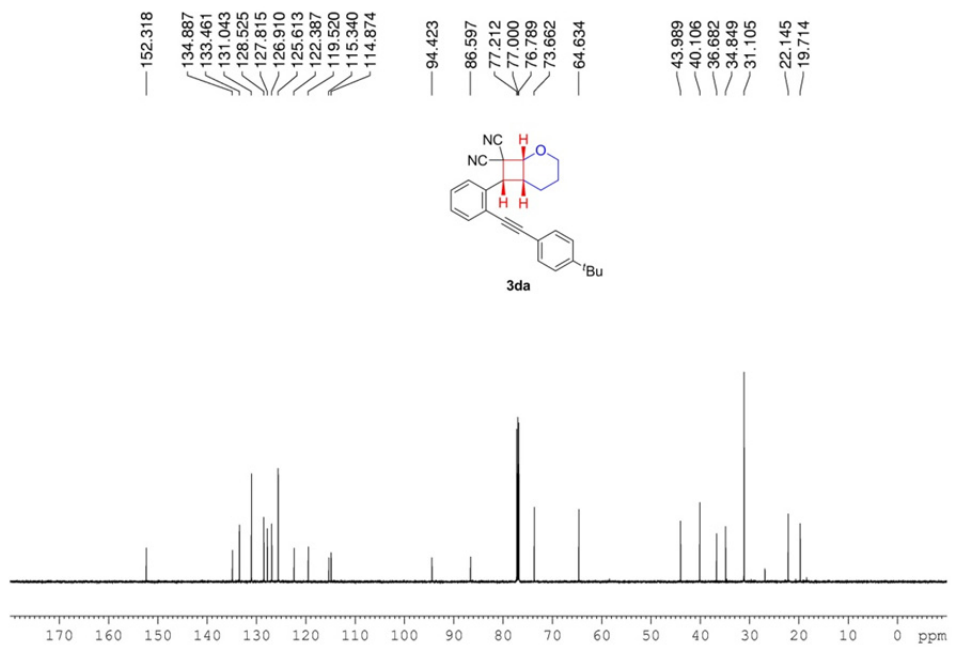
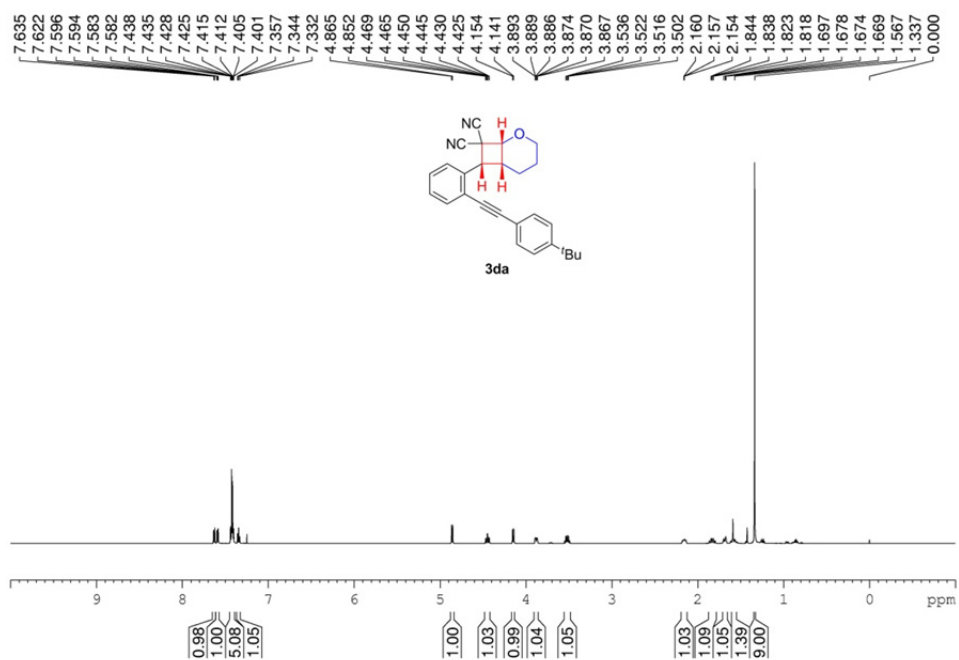
9. ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra of the products

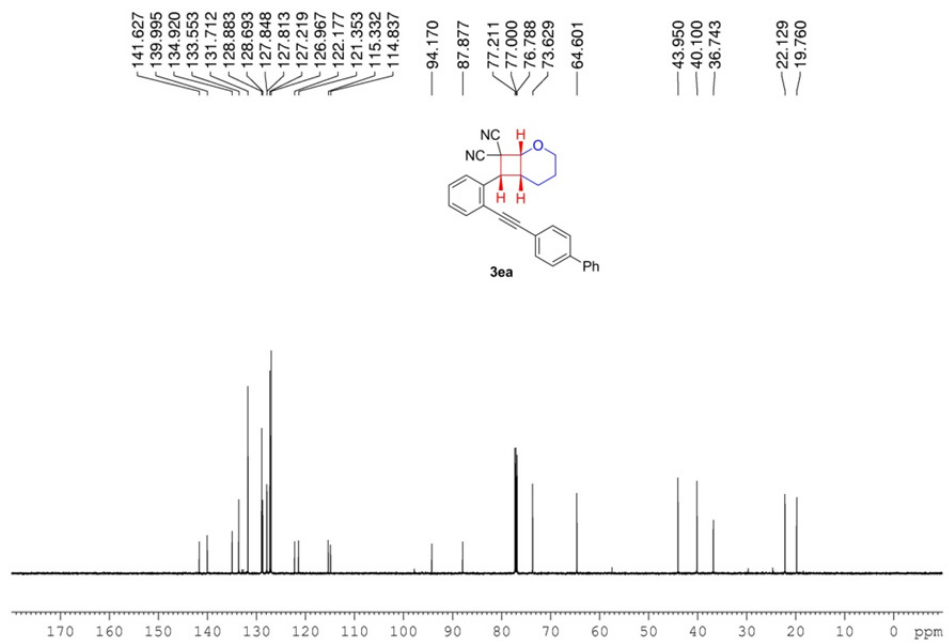
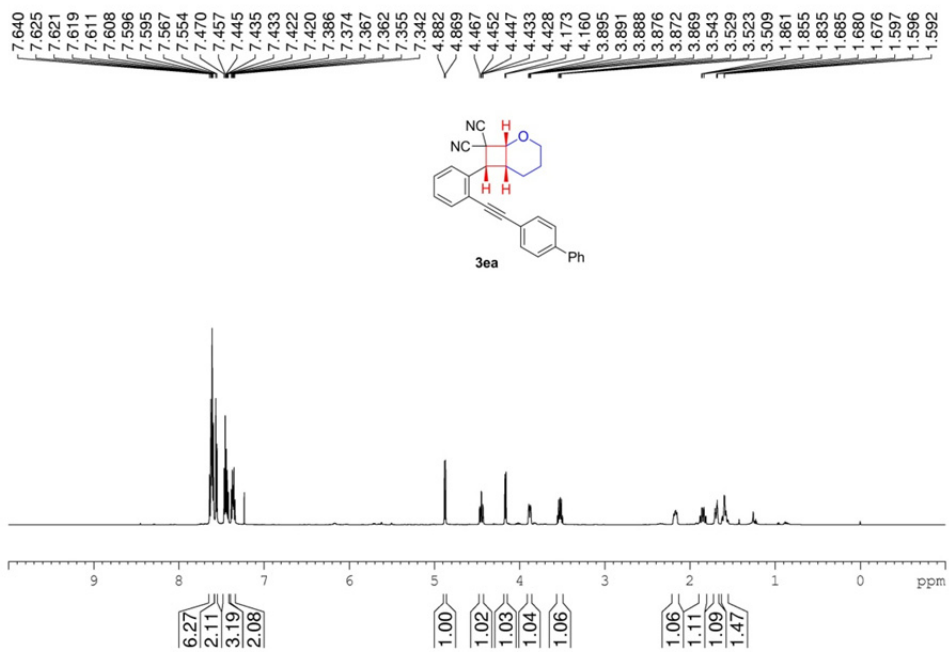


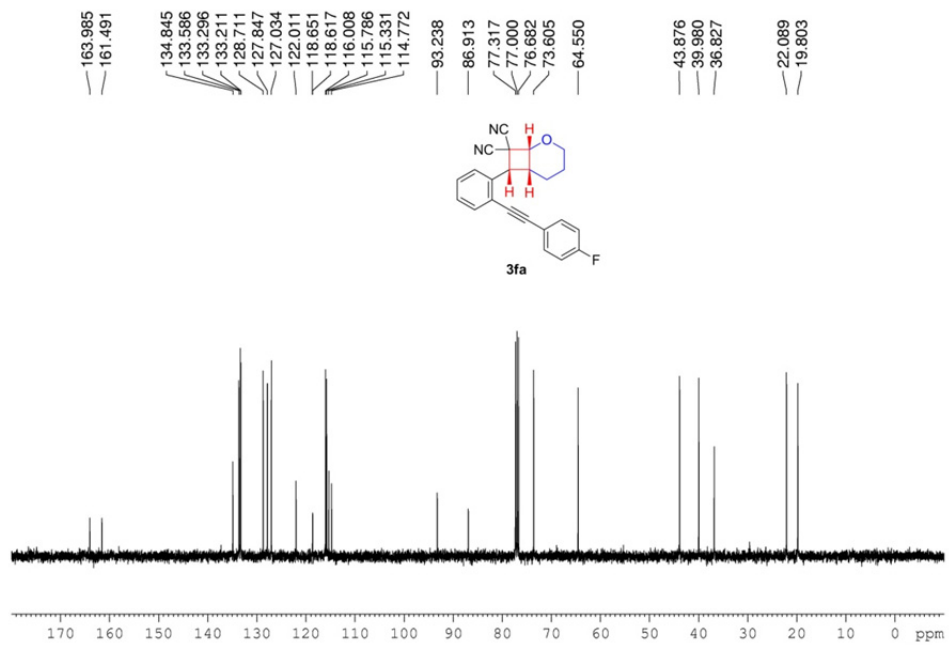
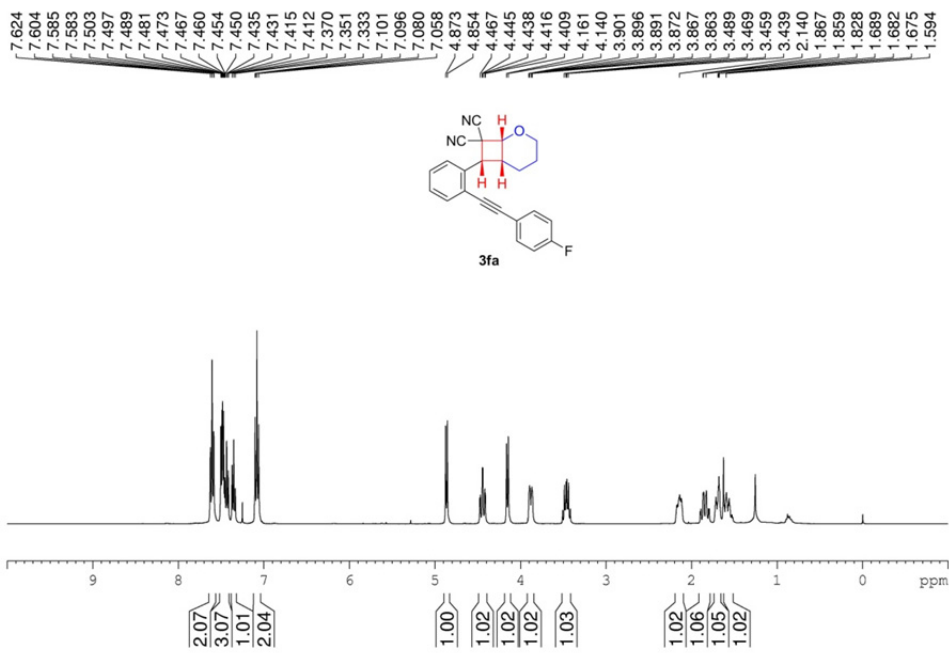


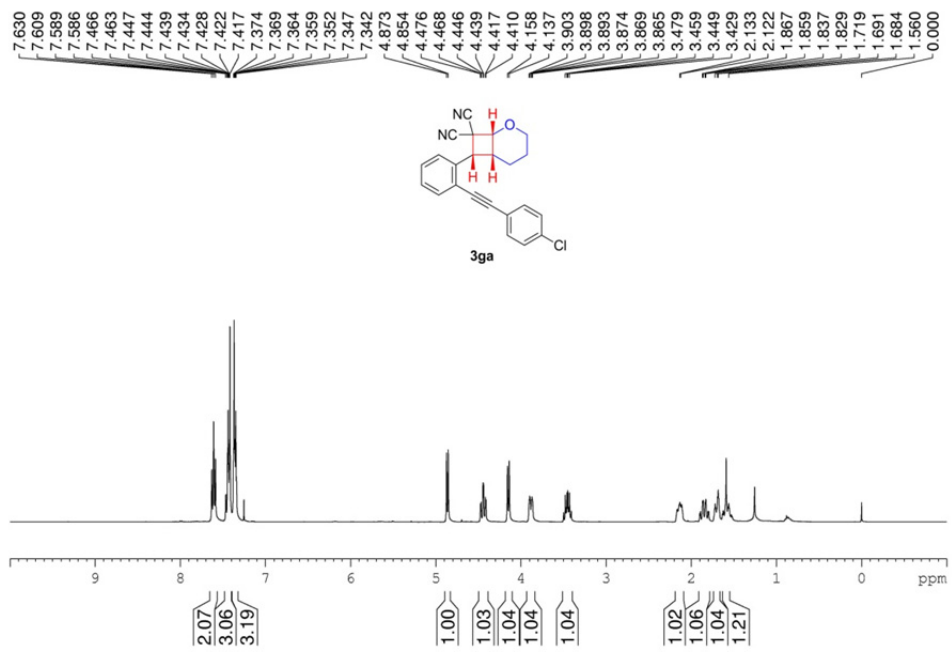
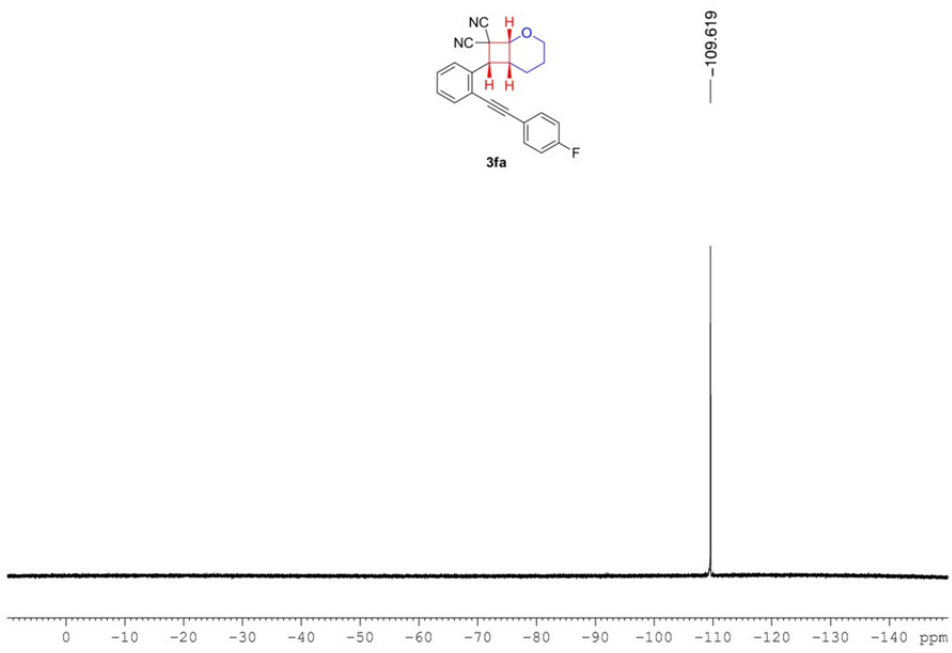


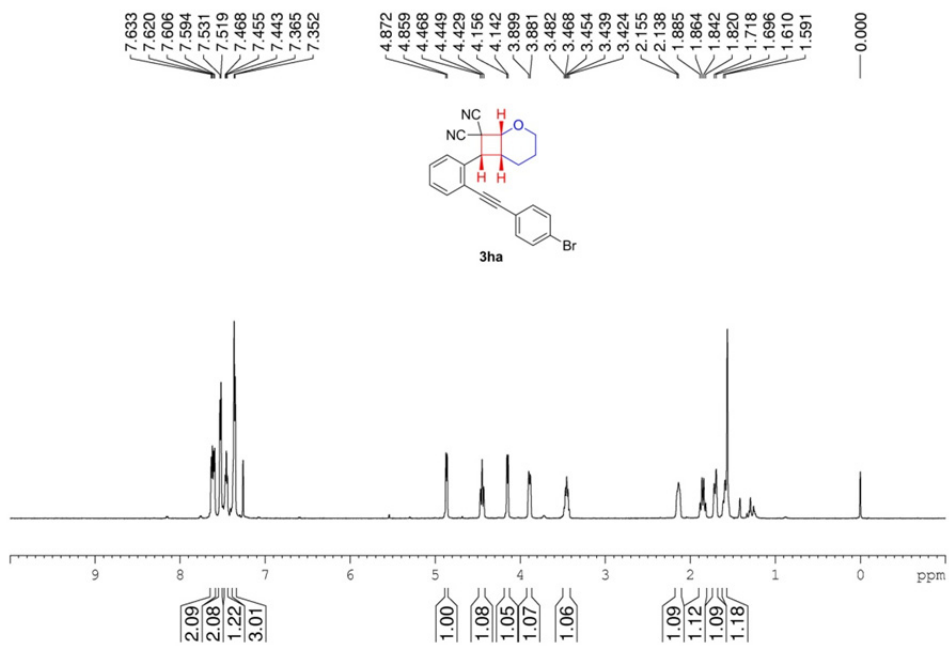
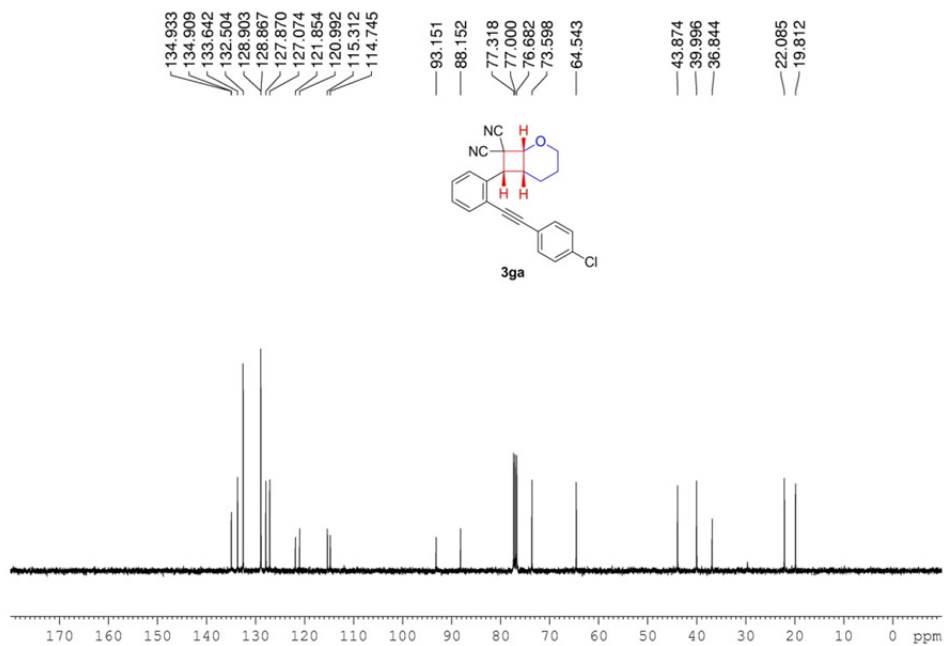


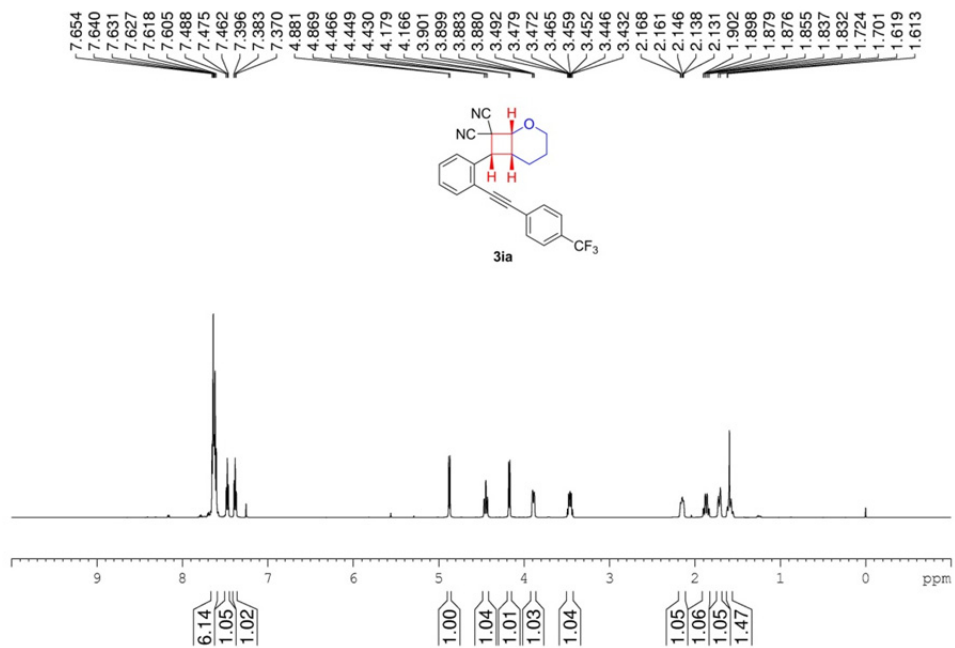
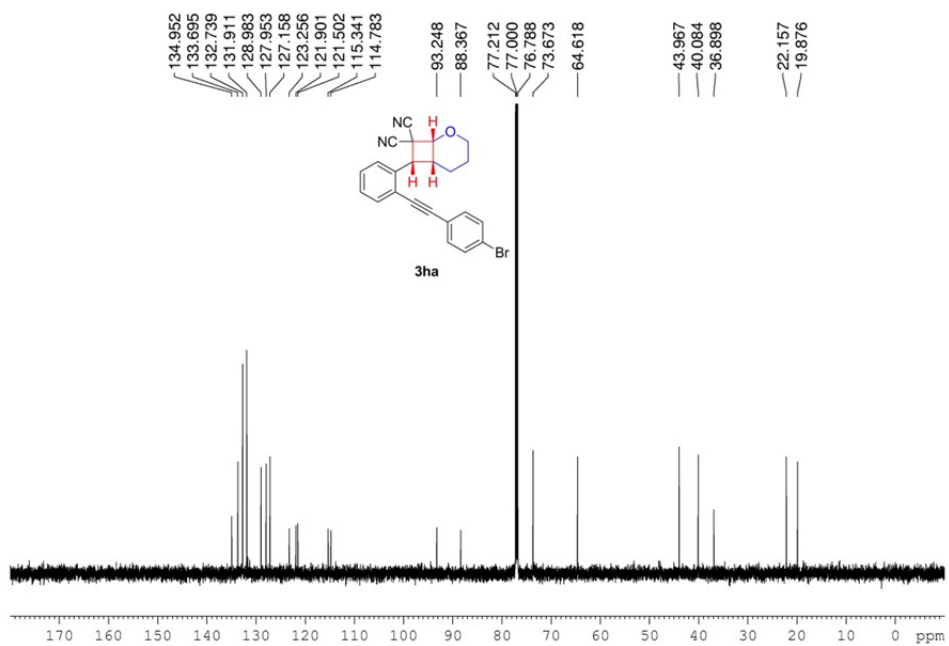


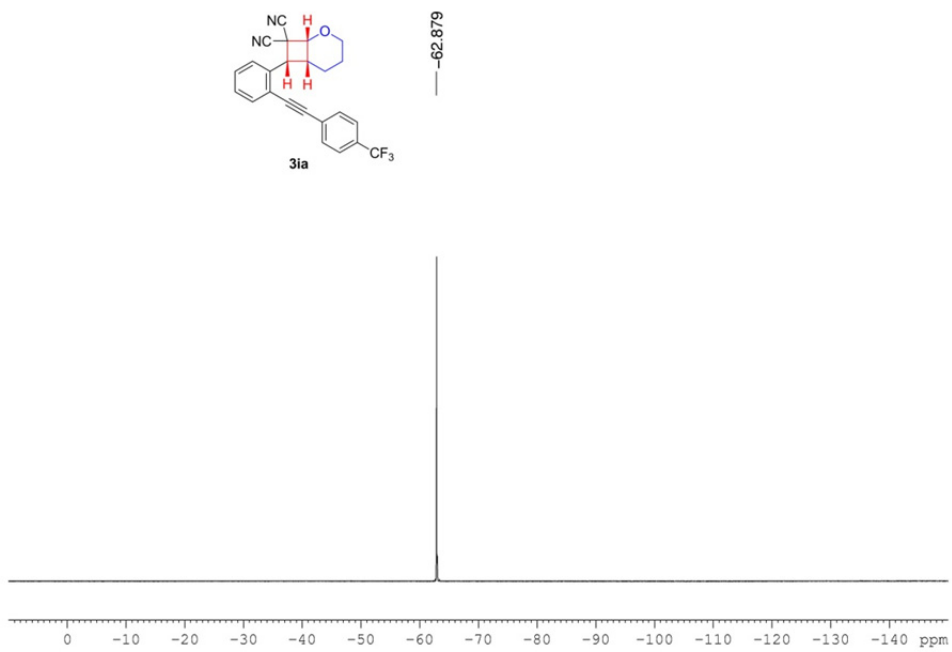
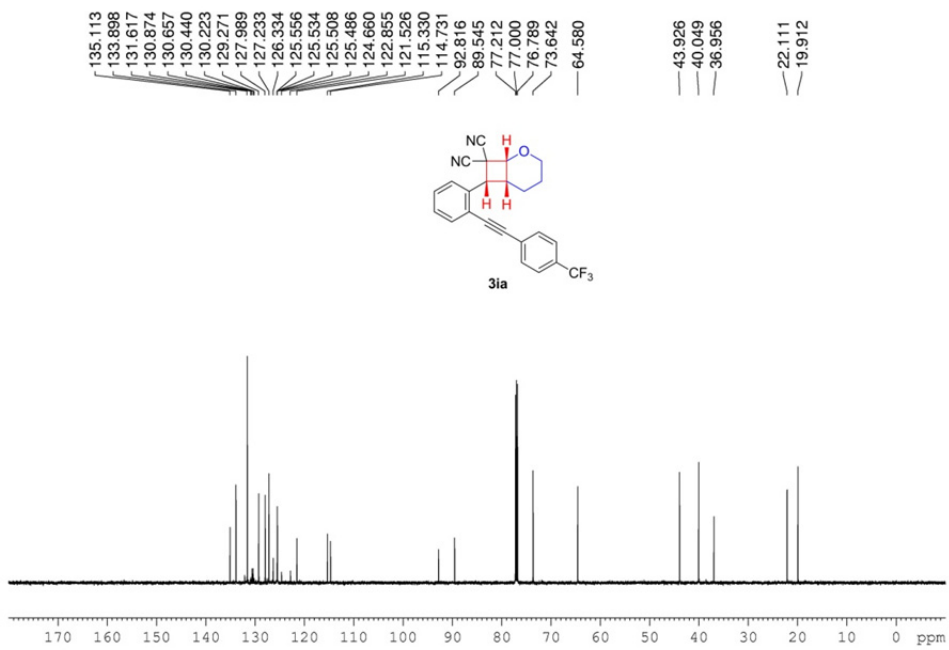


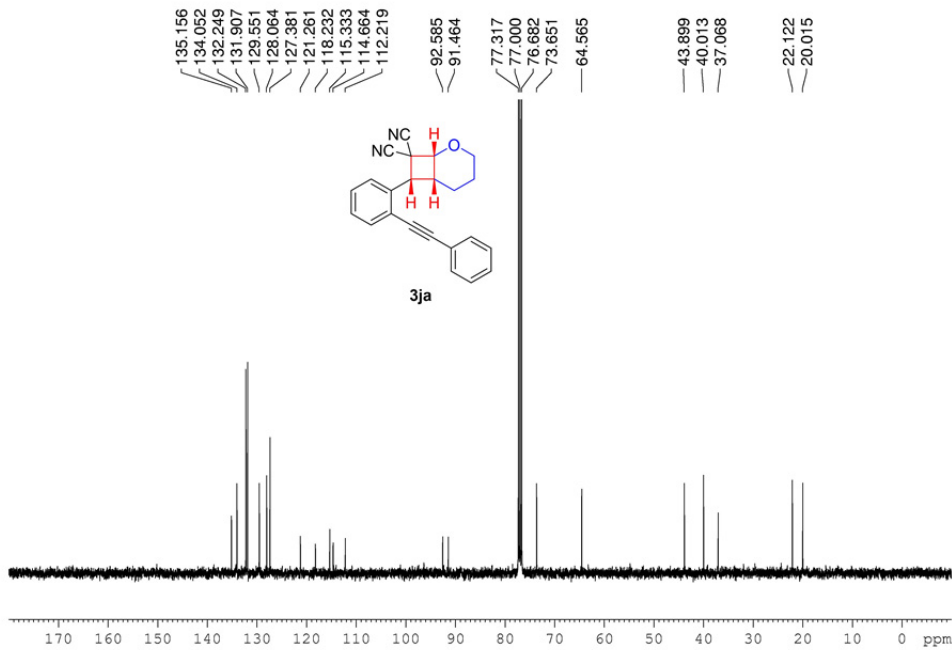
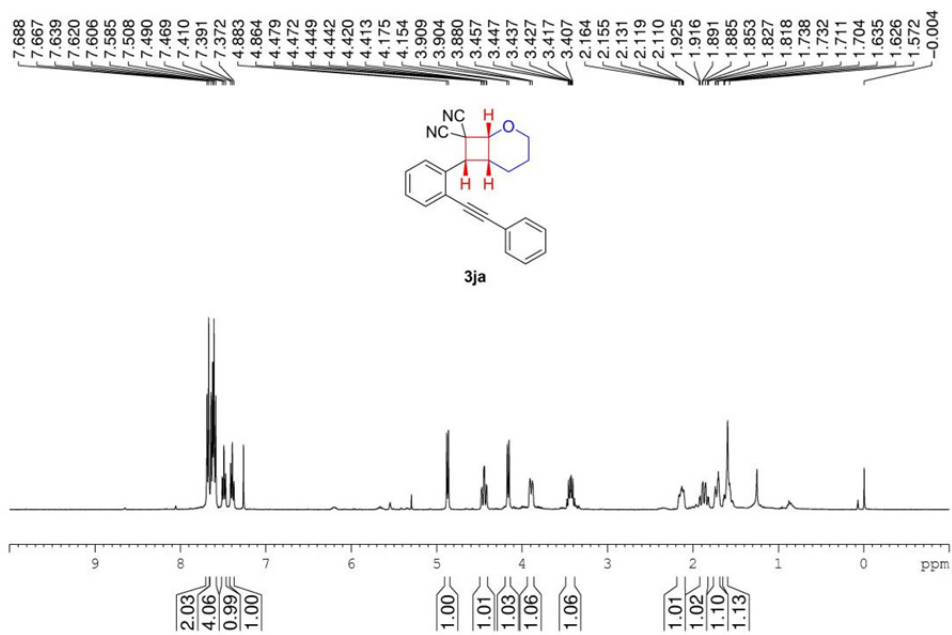


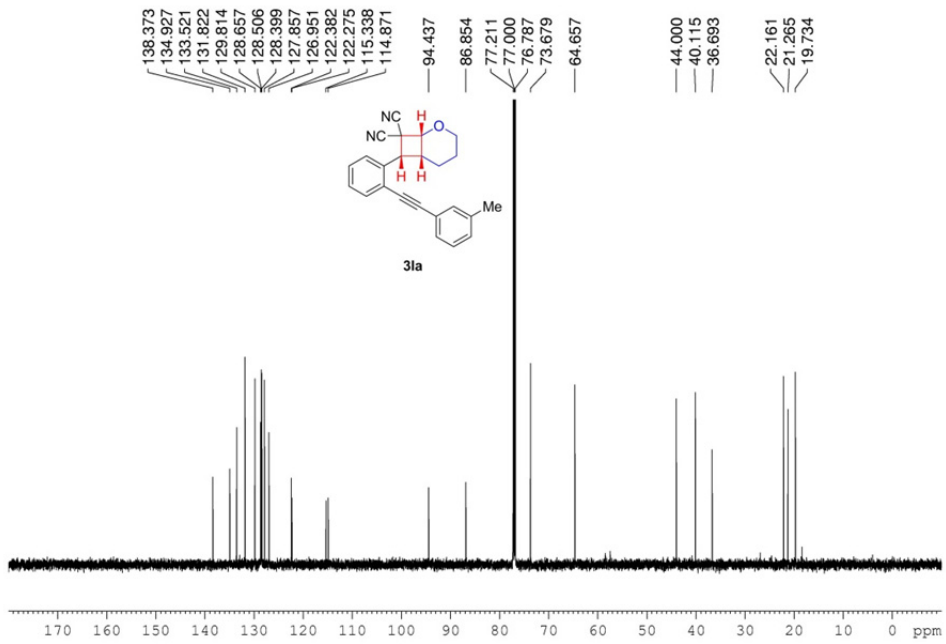
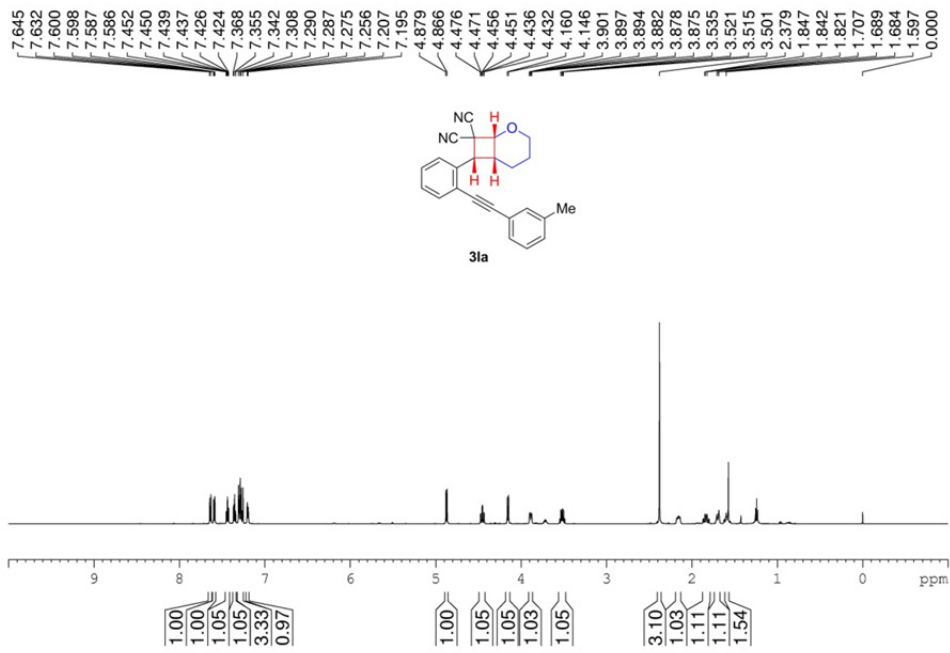


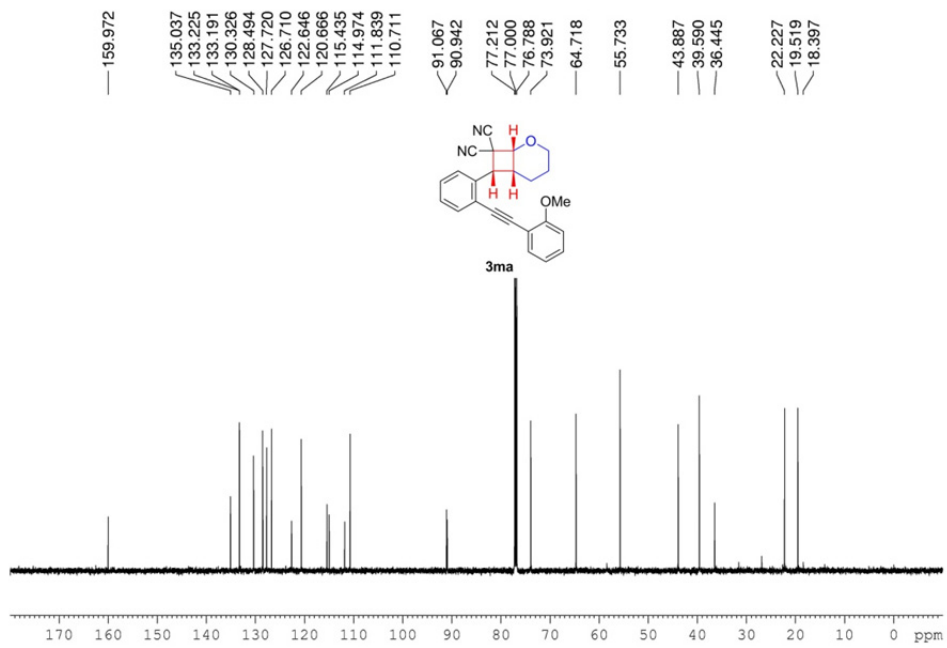
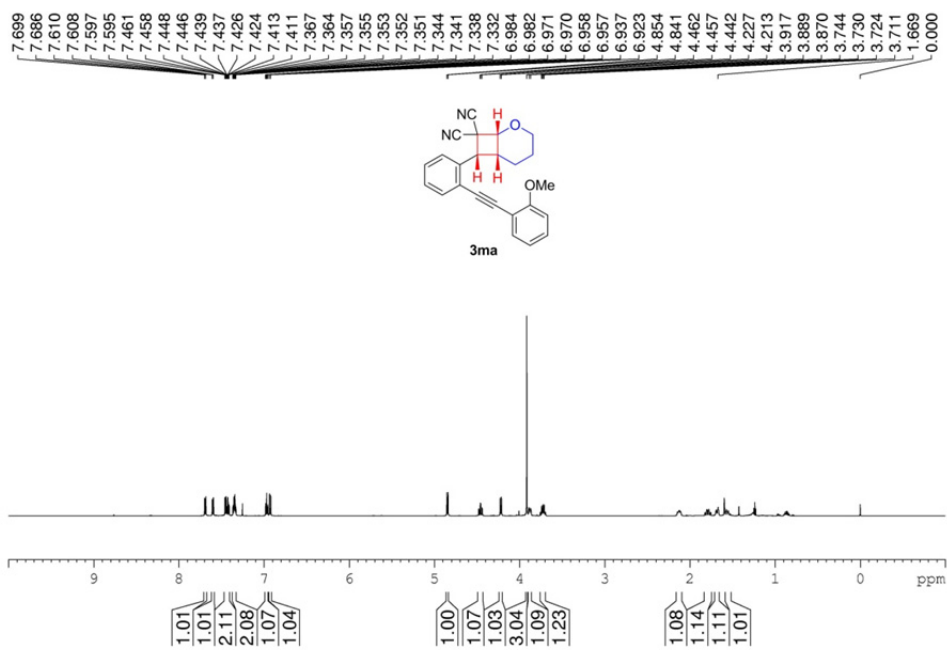


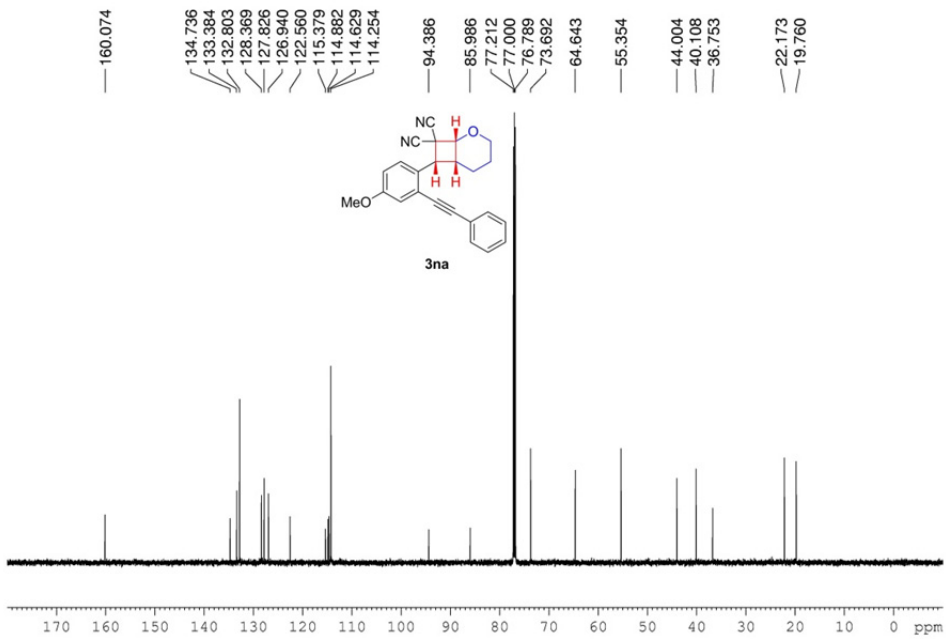
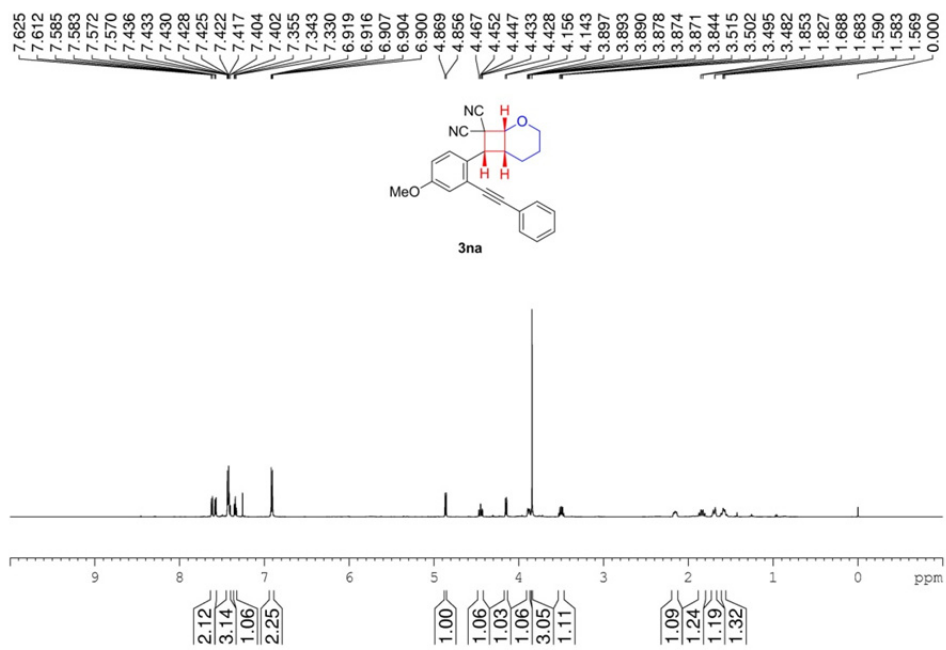


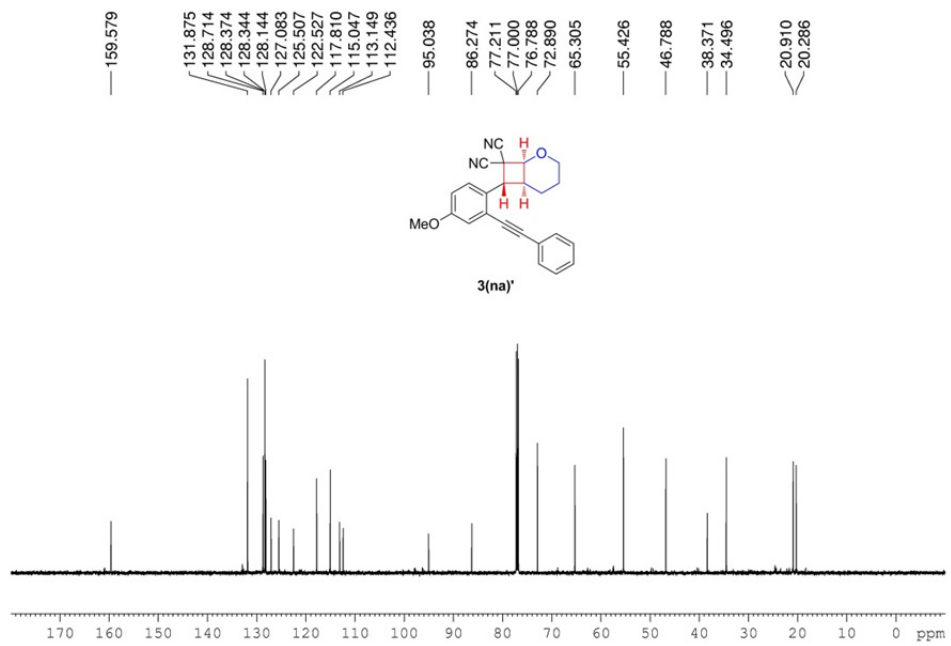
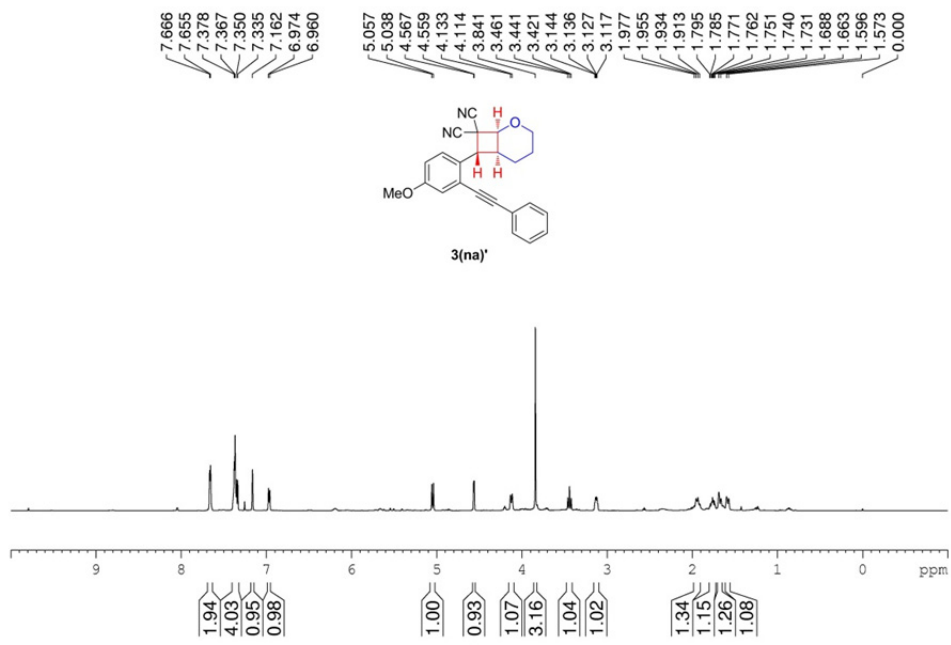


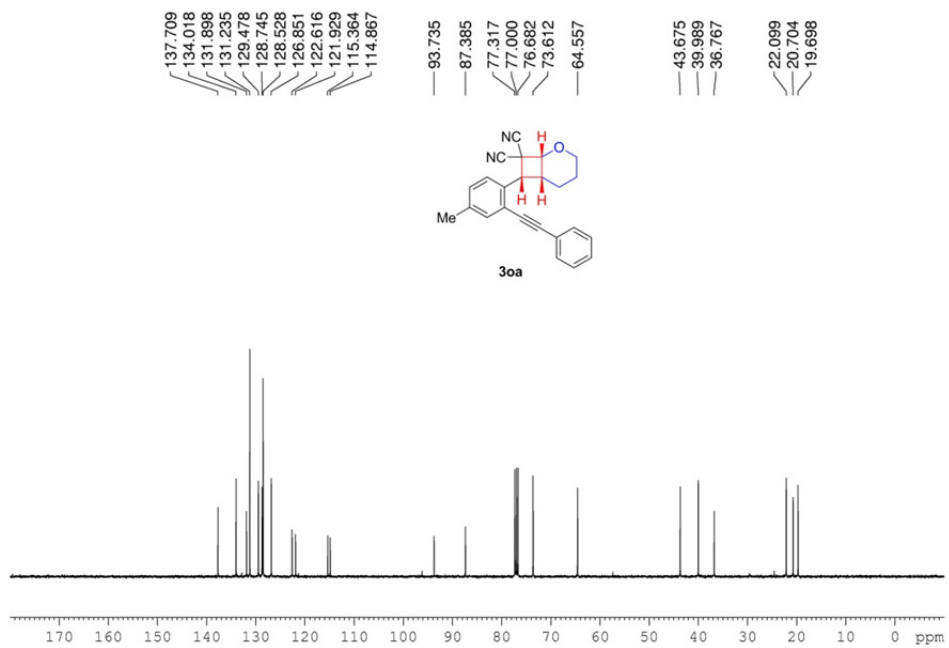
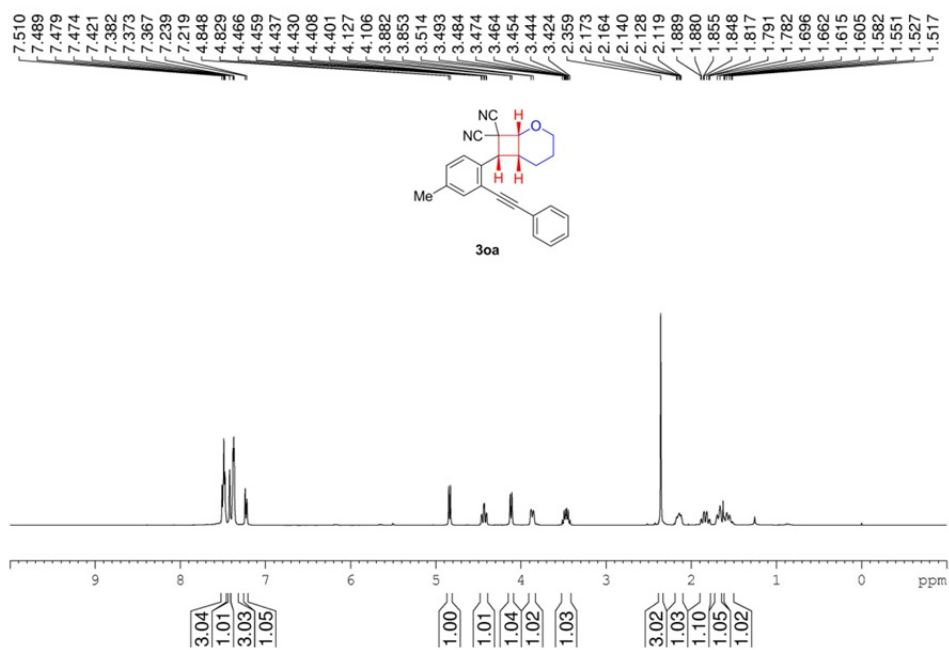


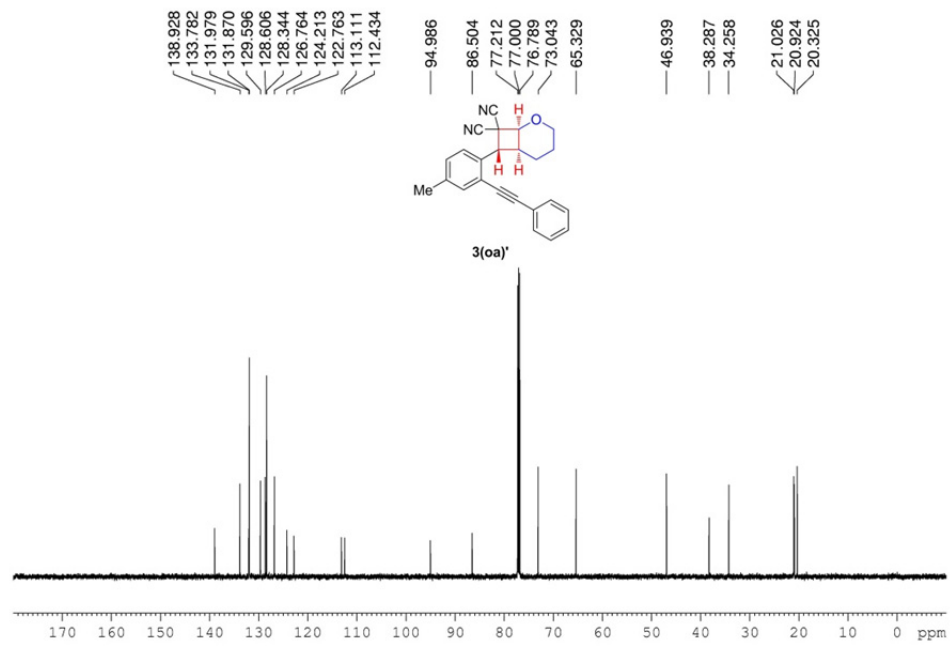
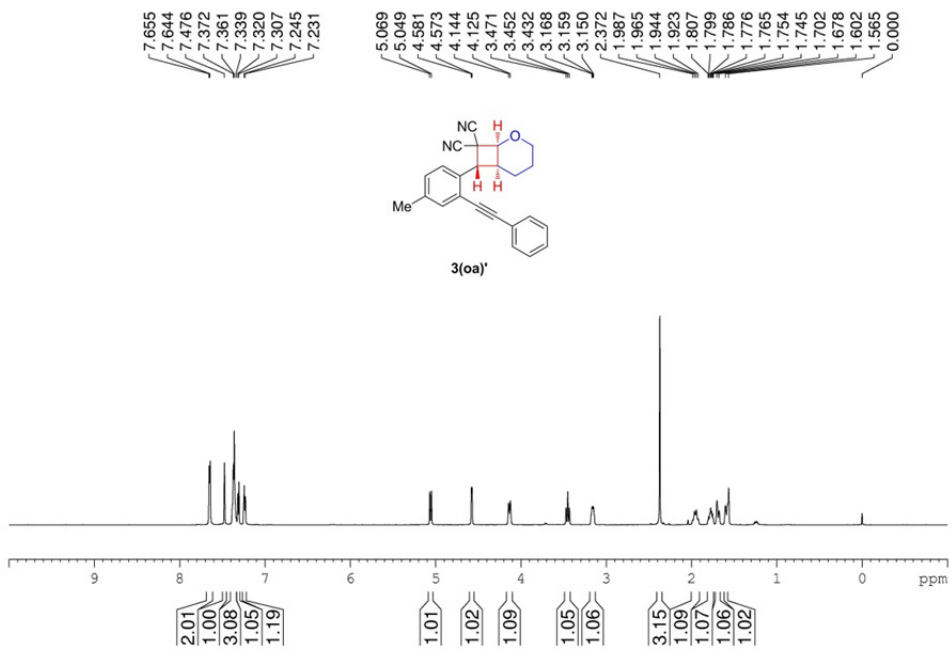


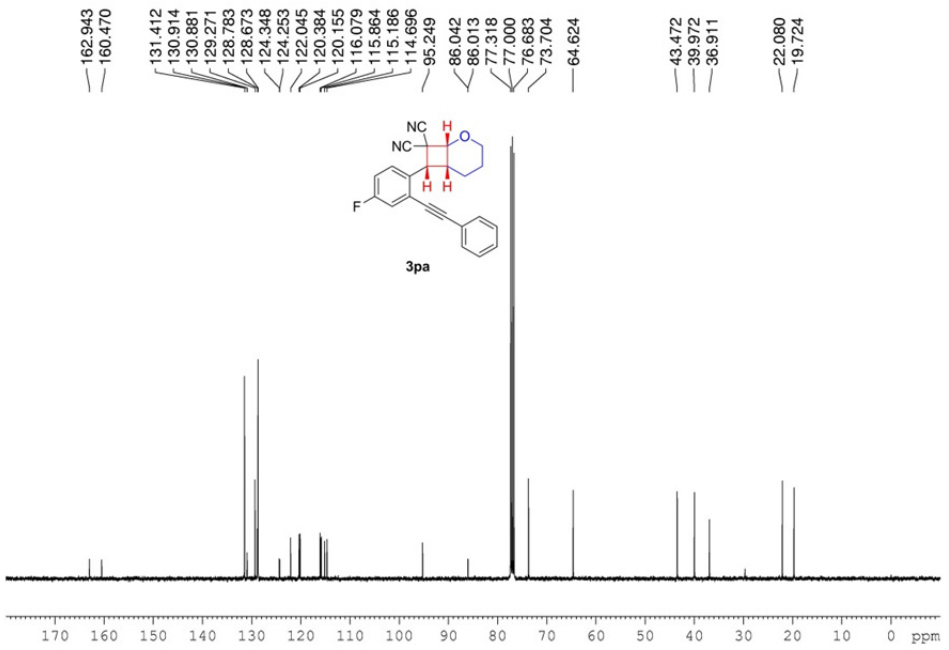
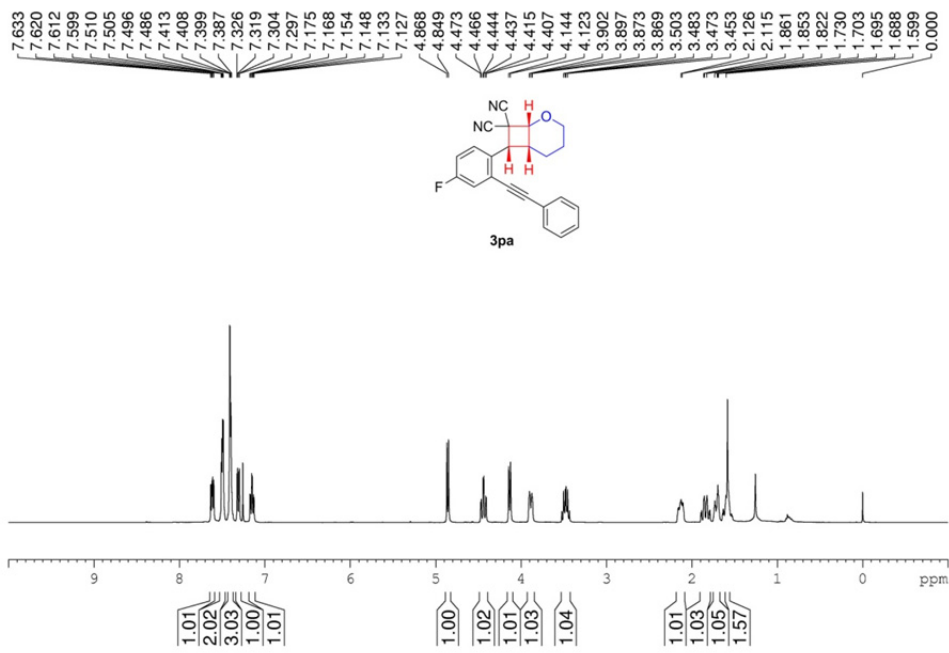


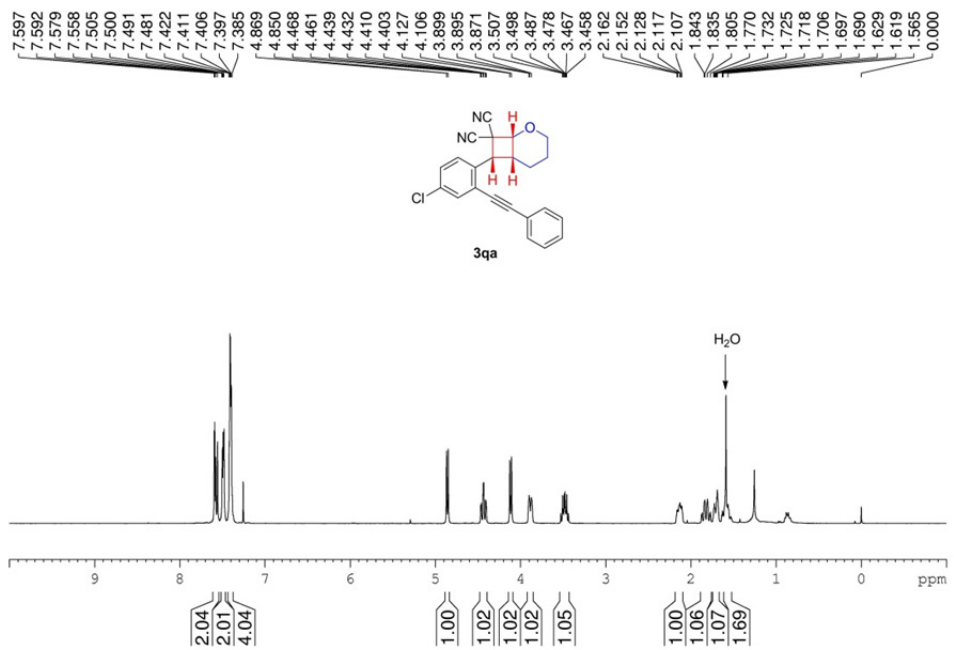
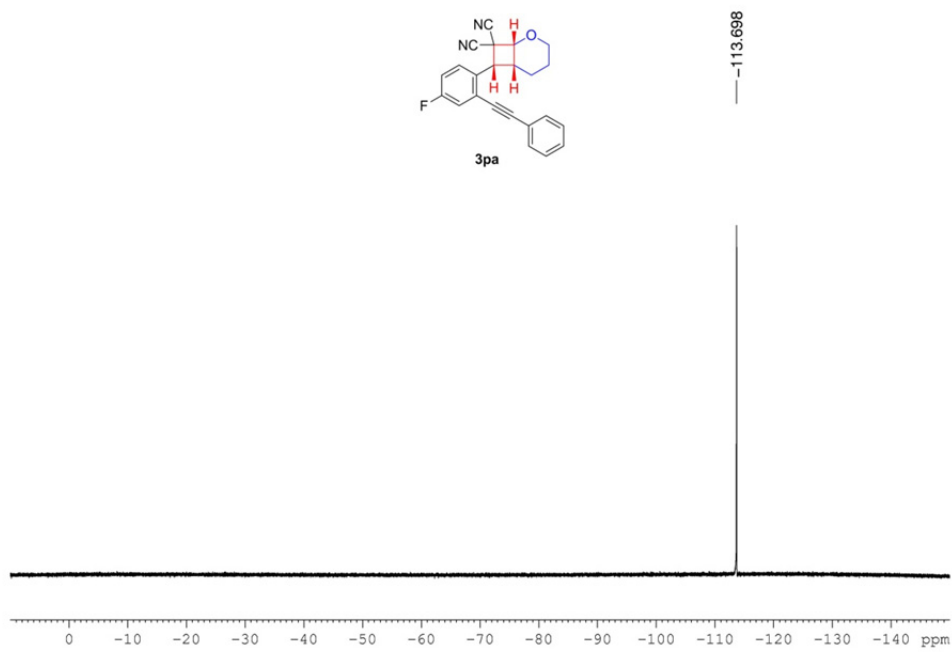


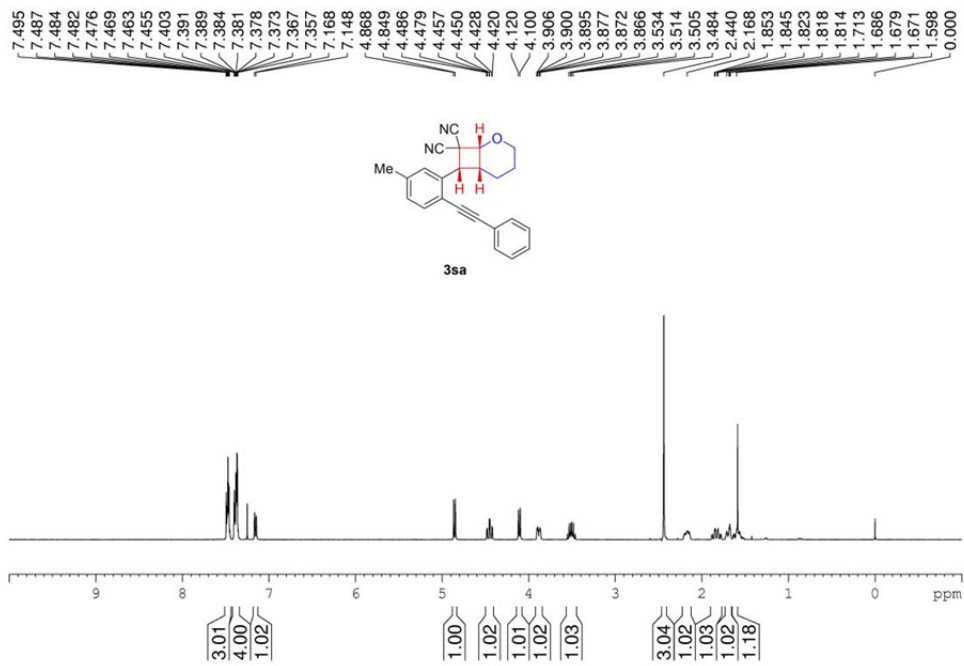
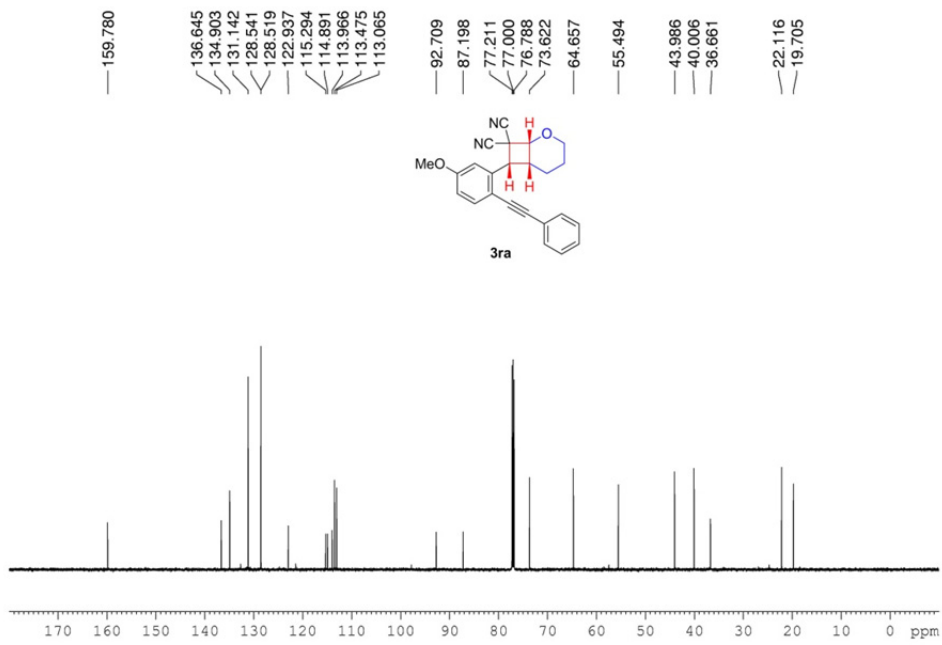


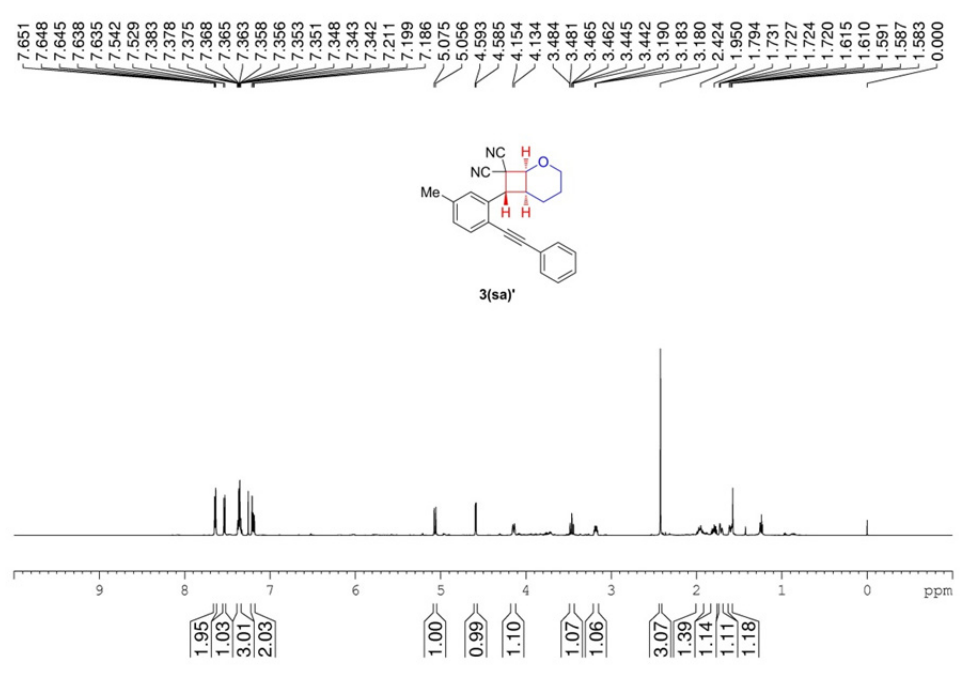
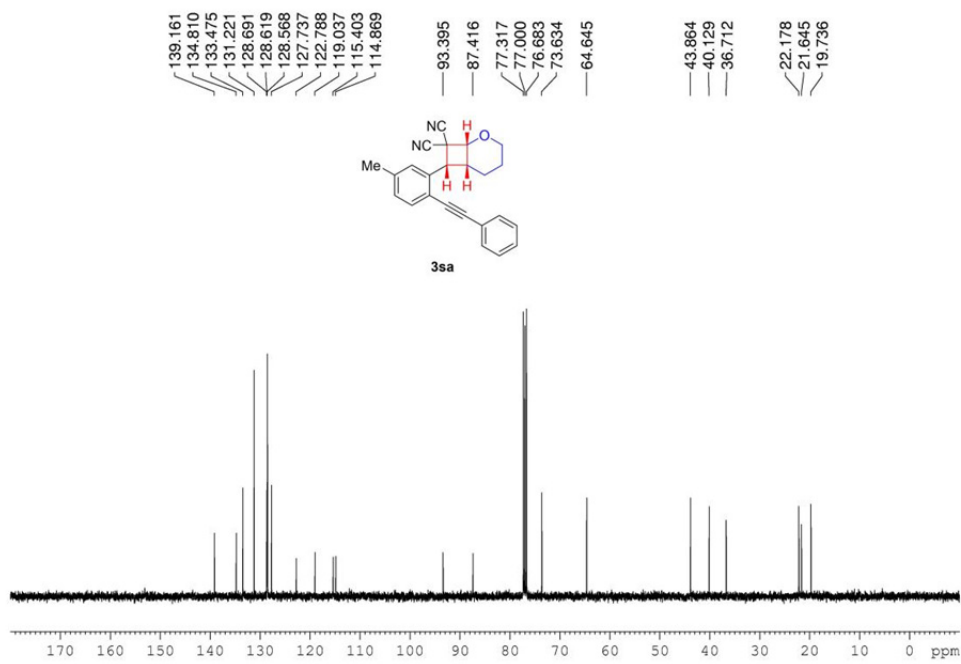


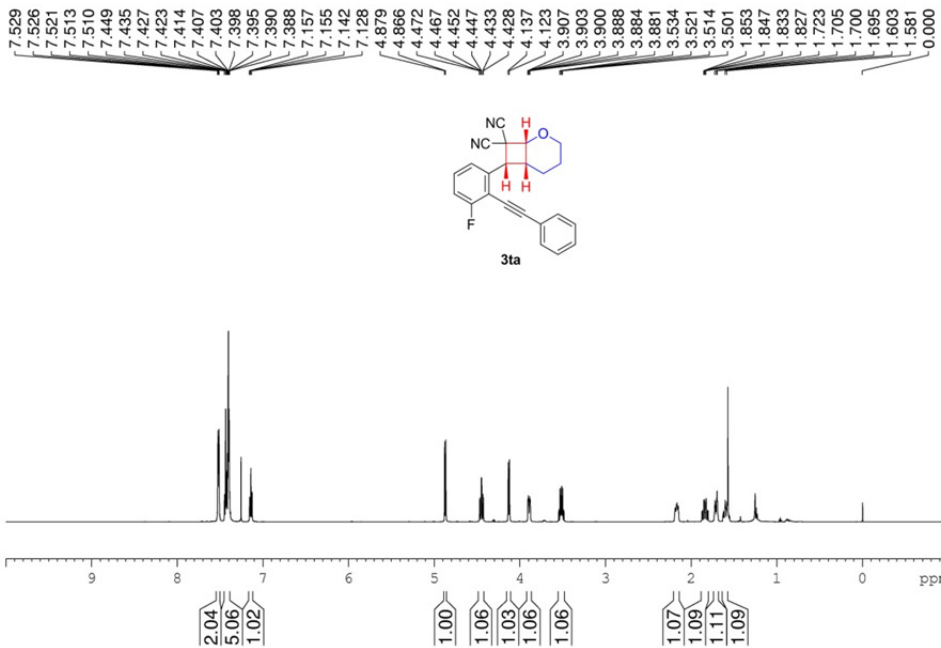
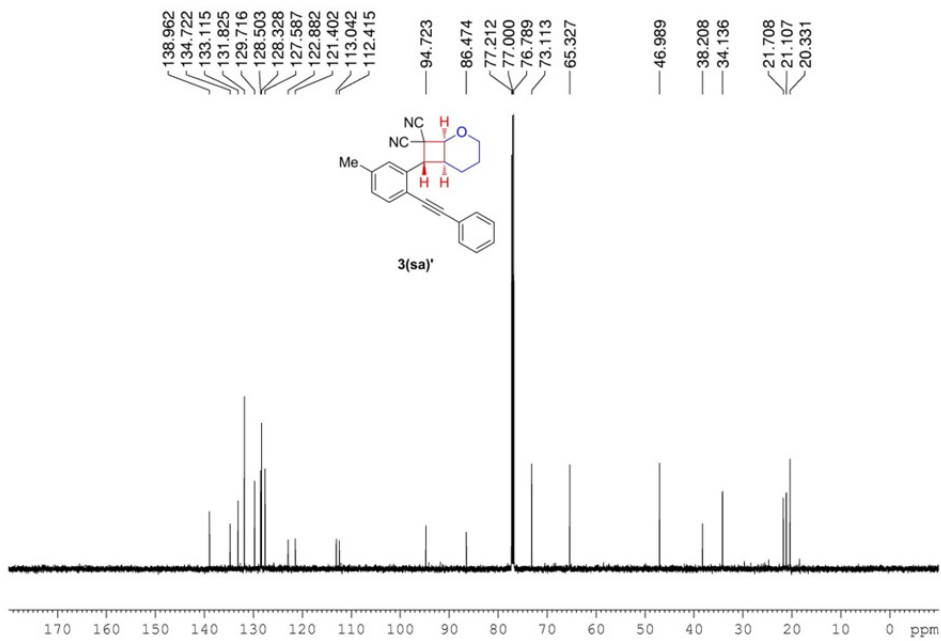


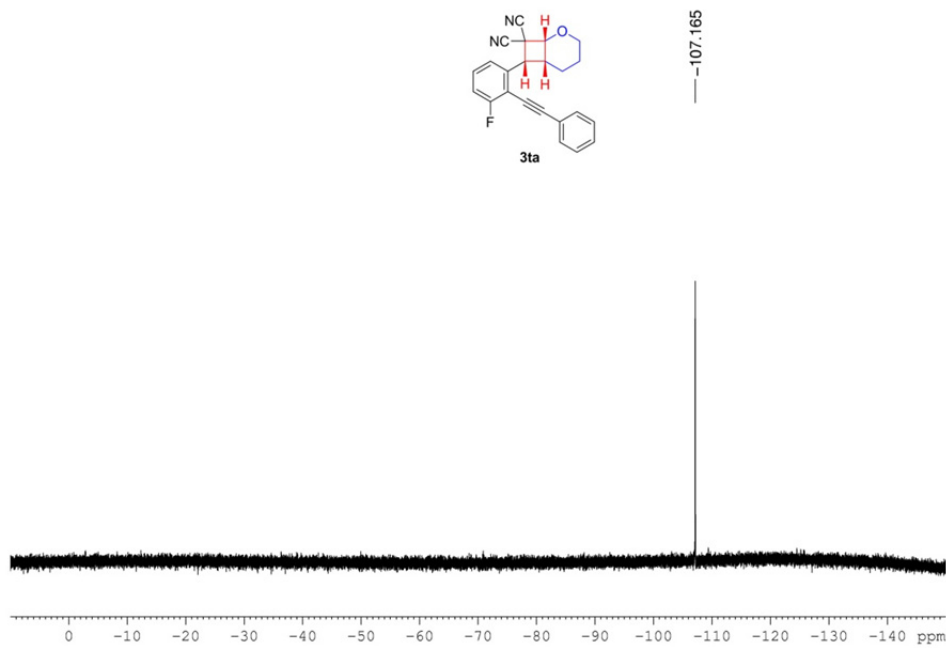
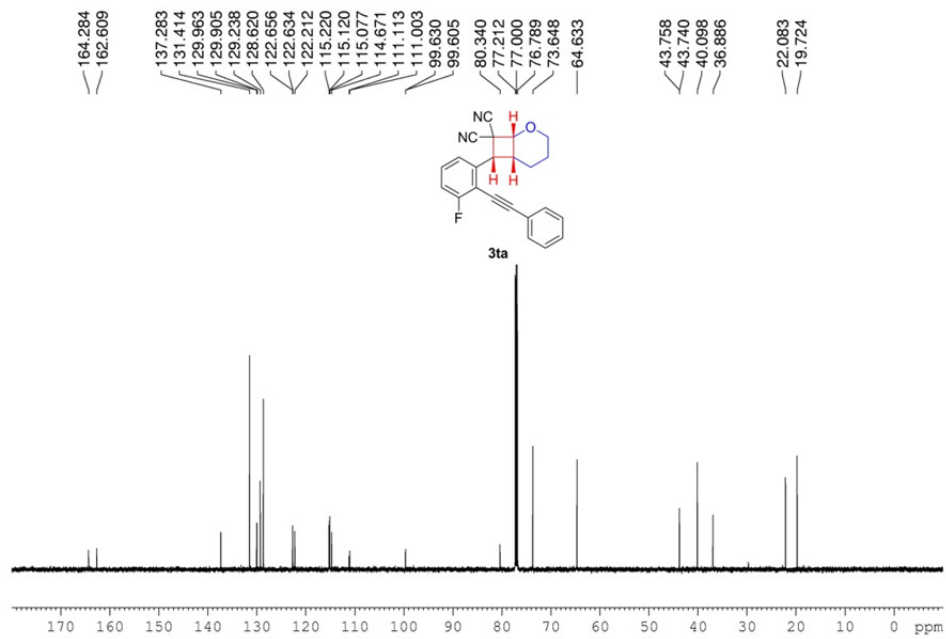


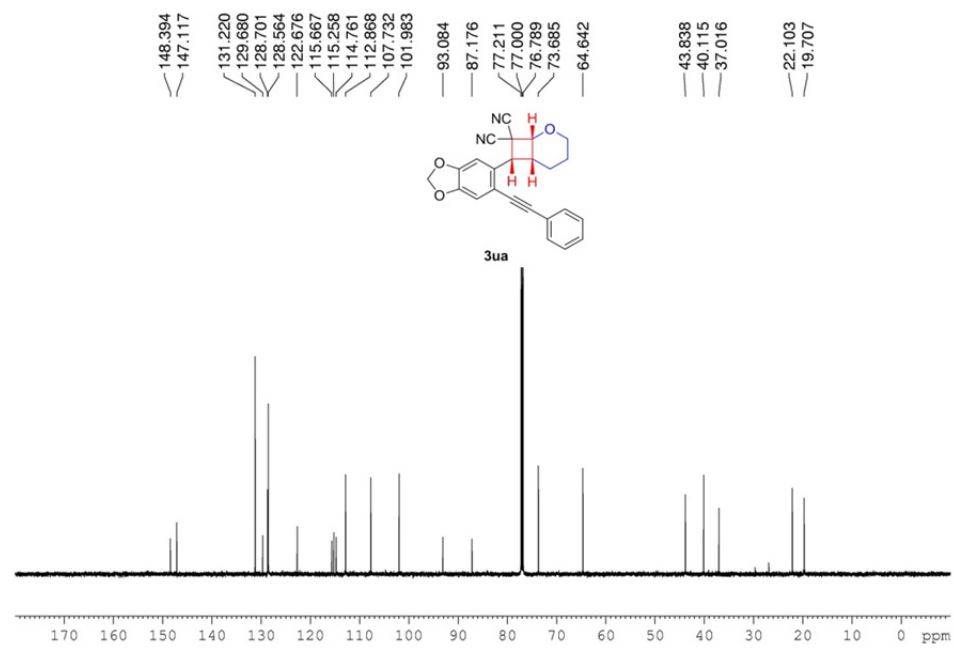
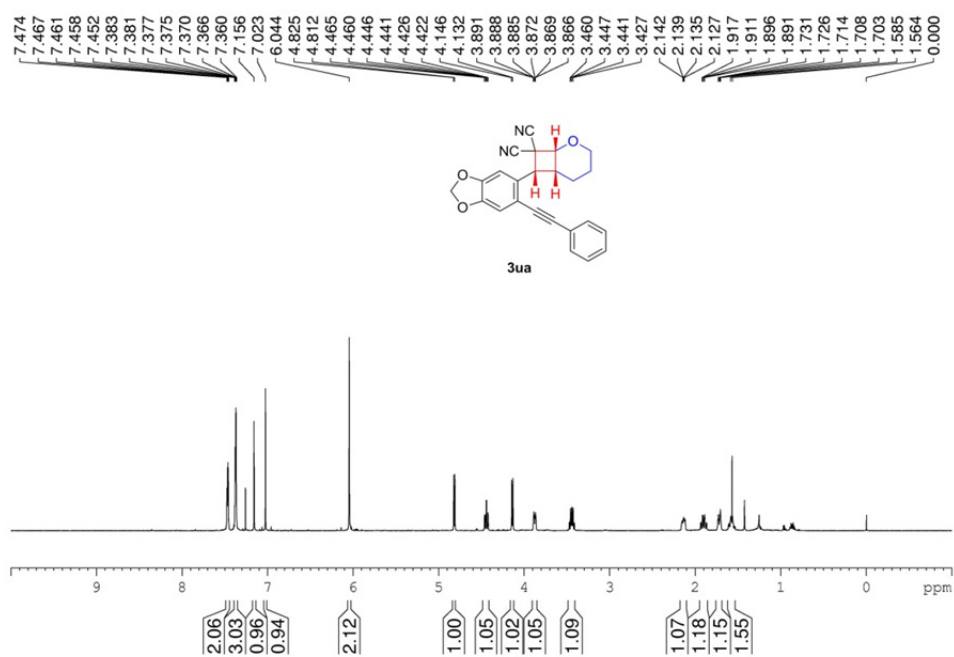


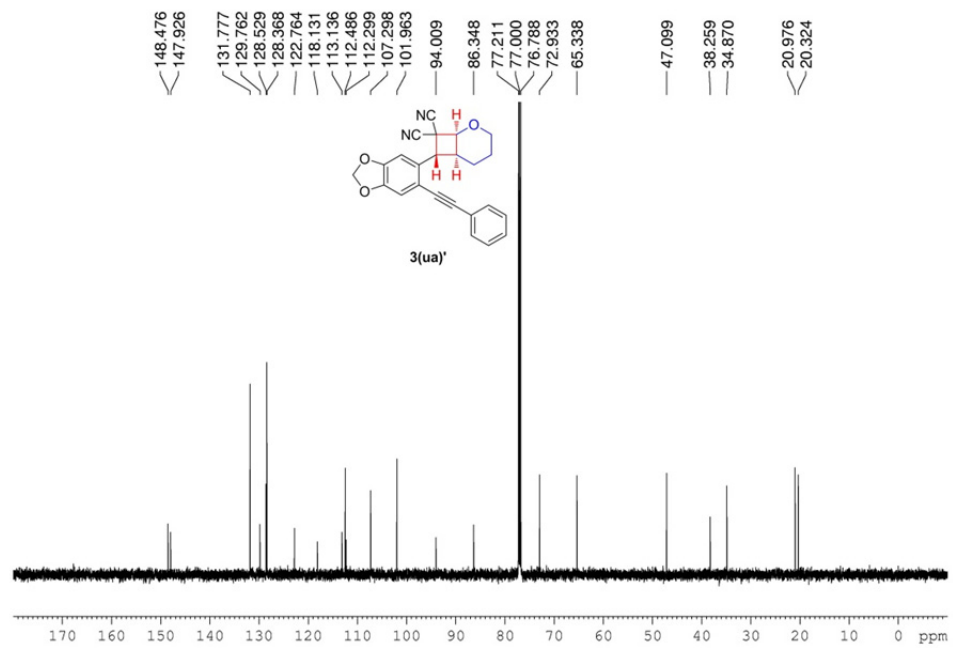
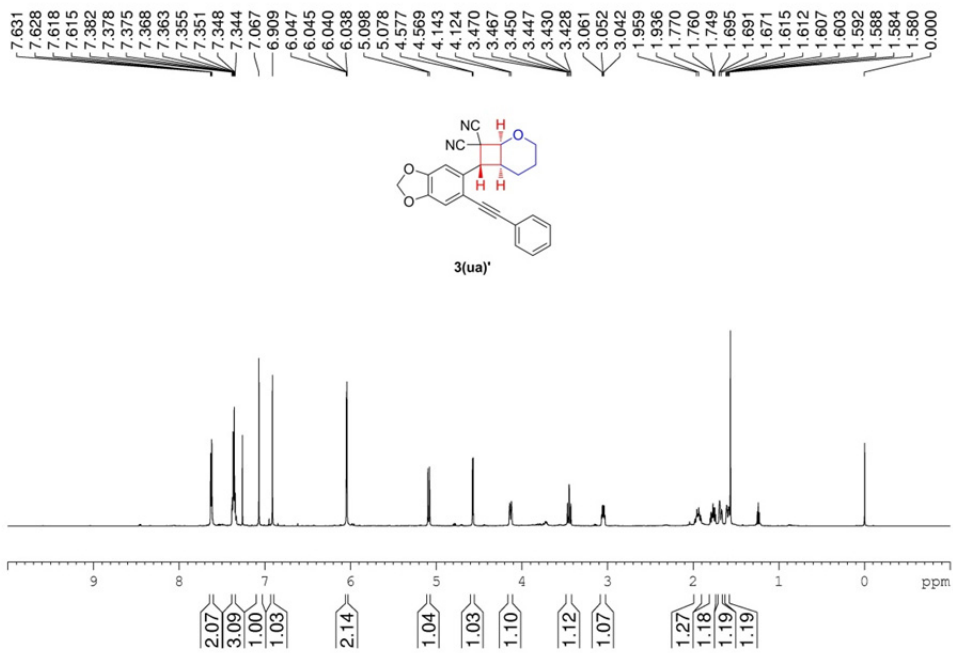


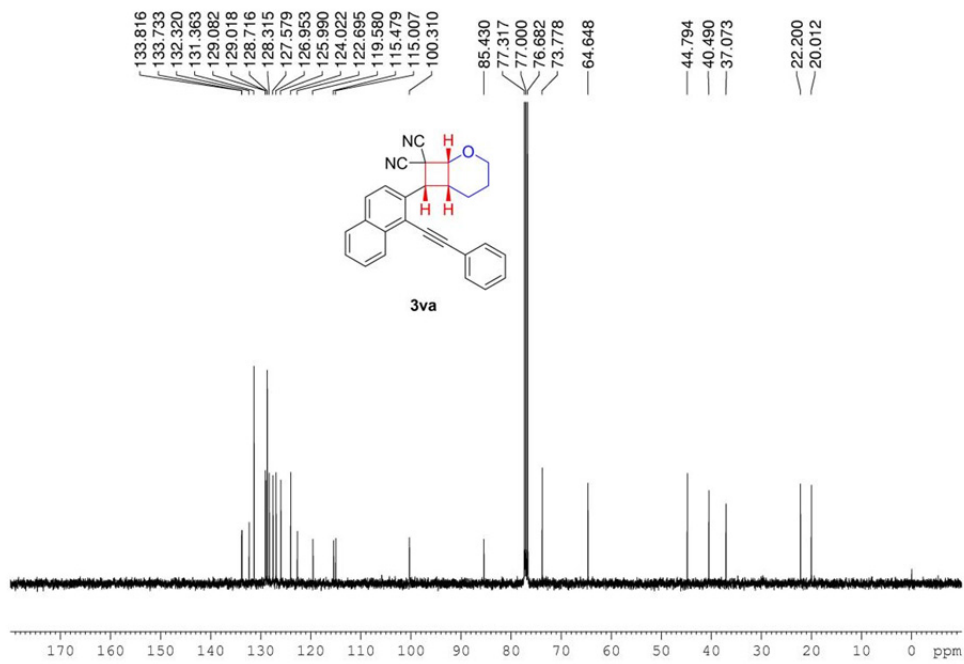
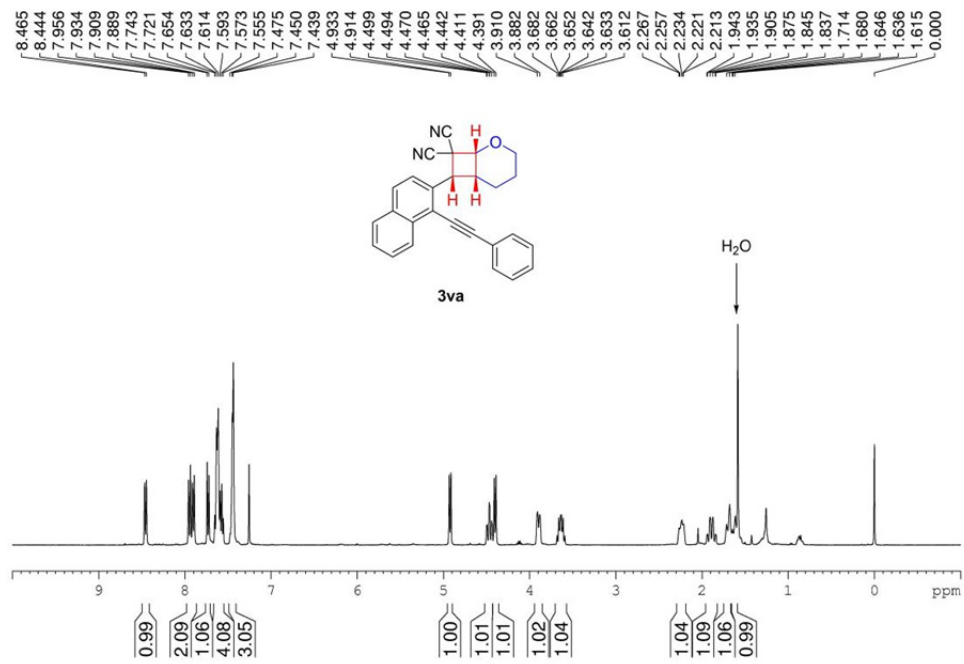


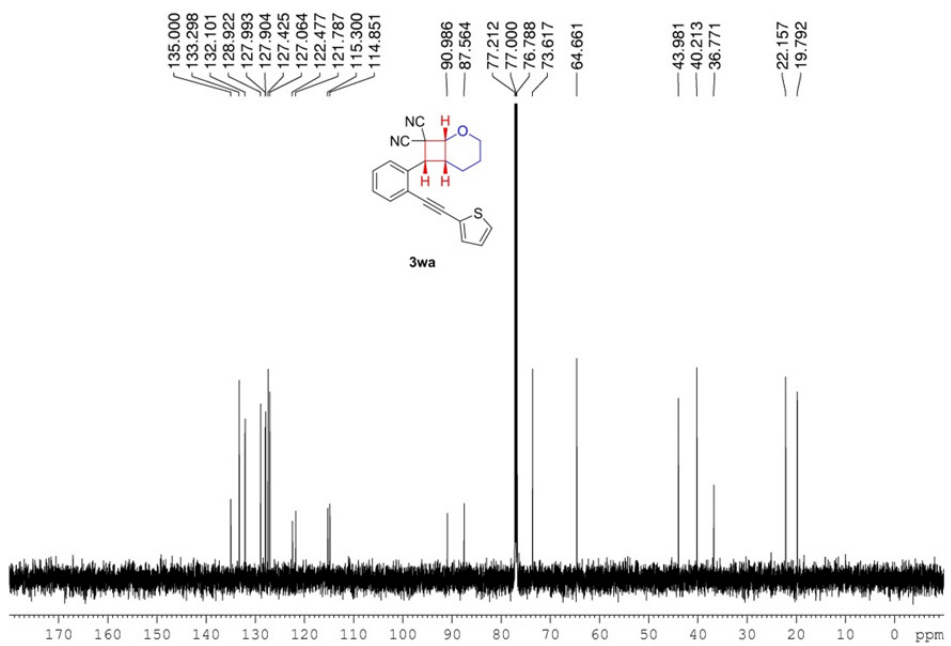
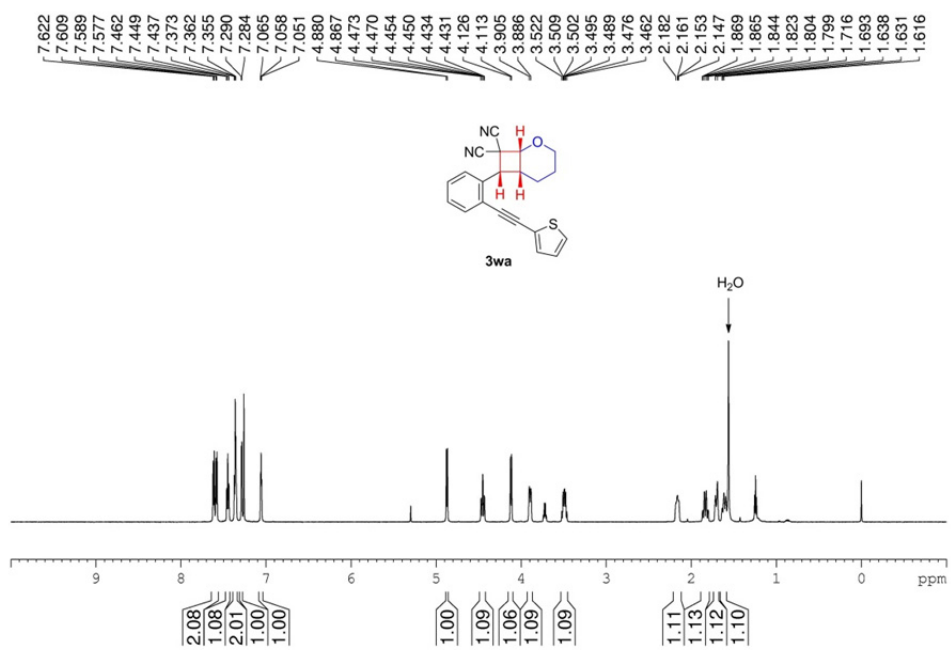


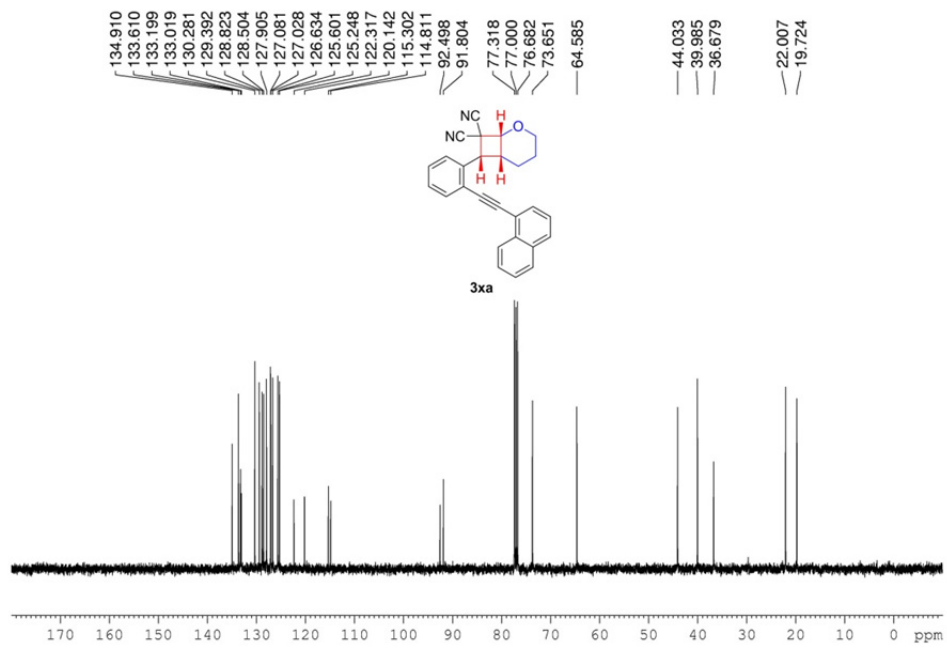
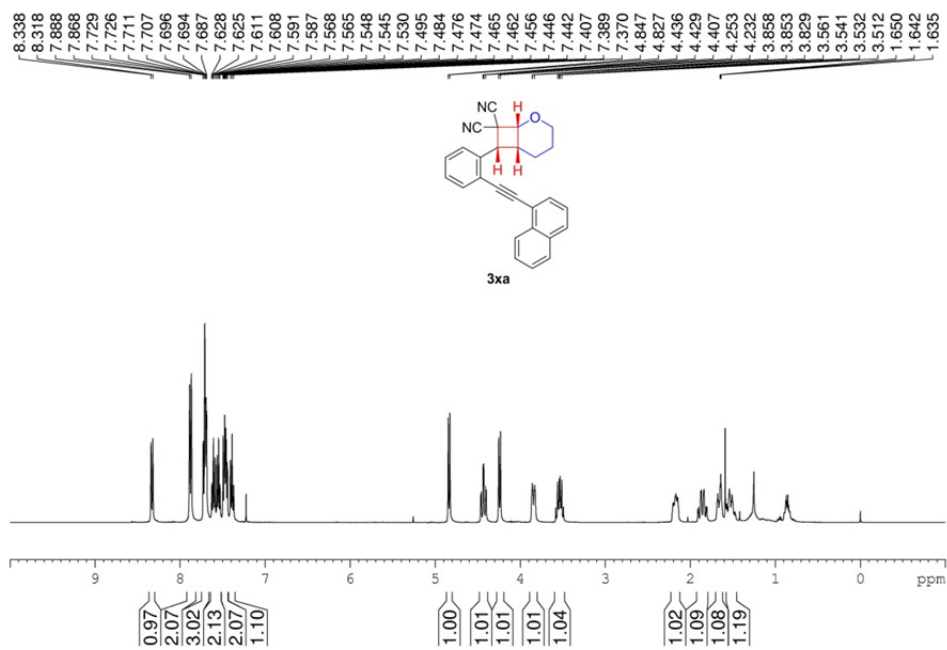


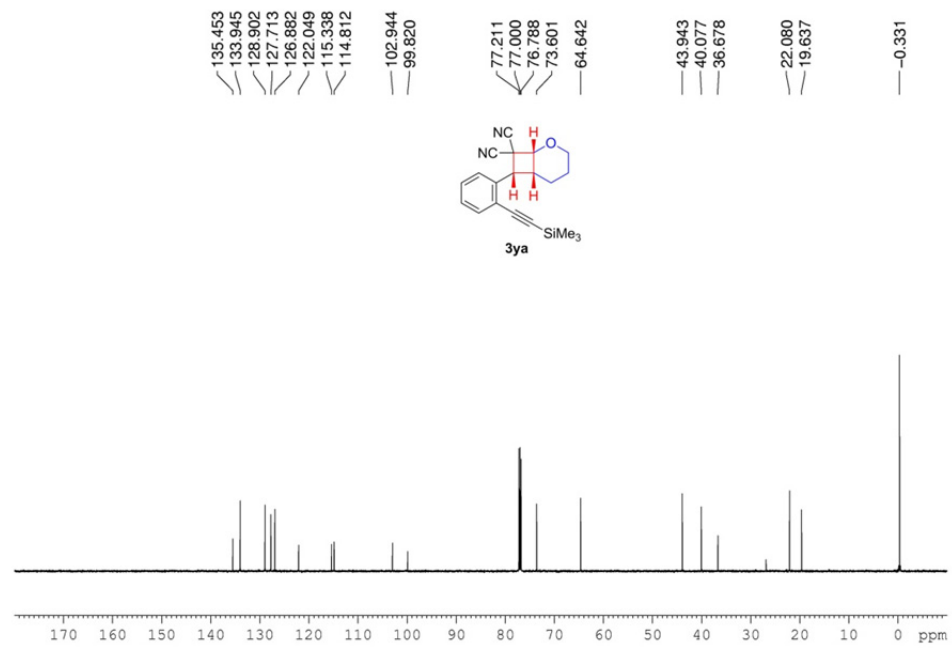
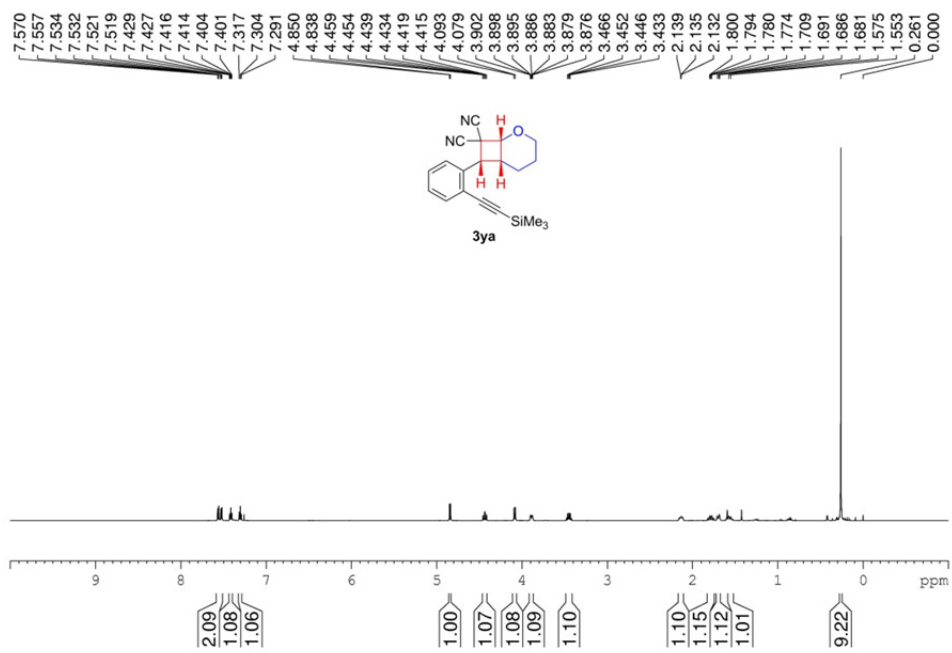


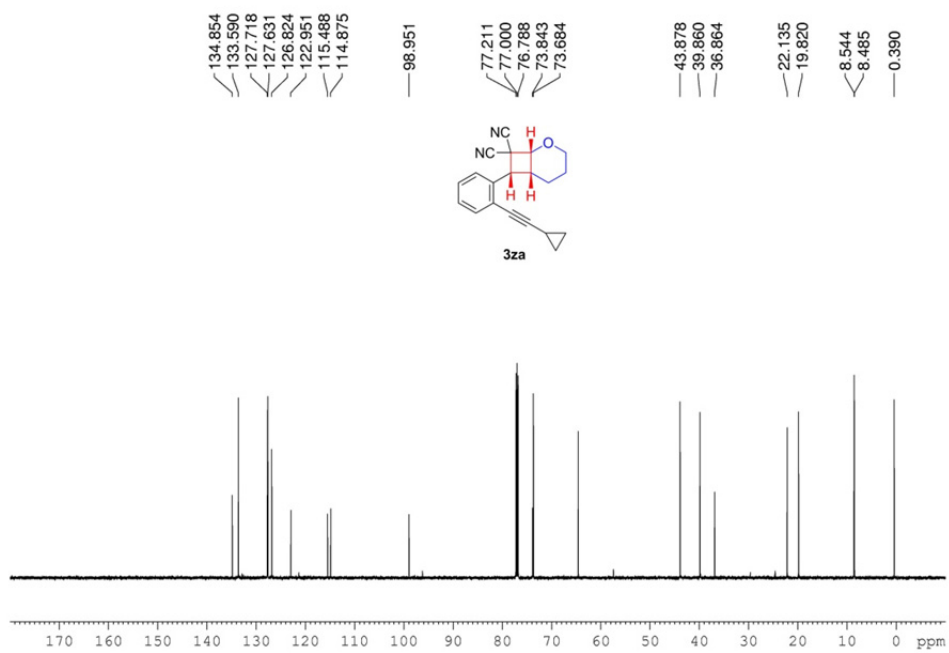
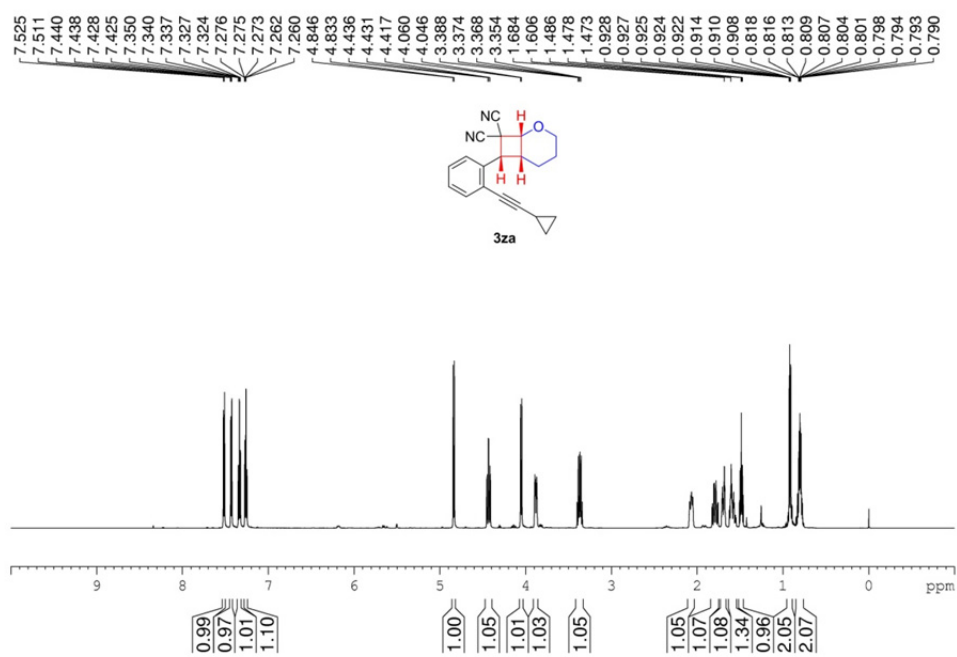


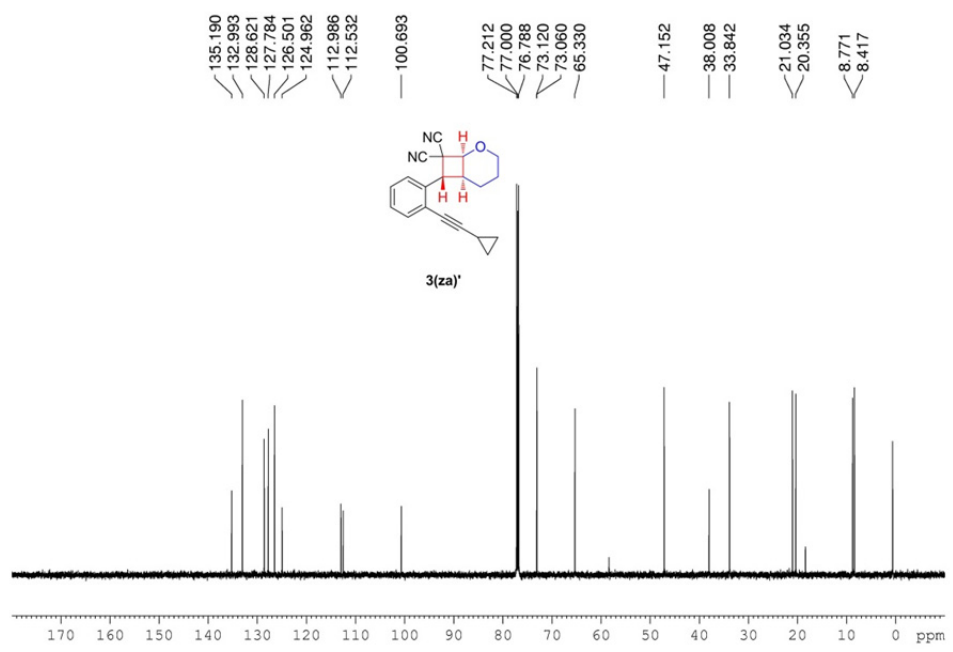
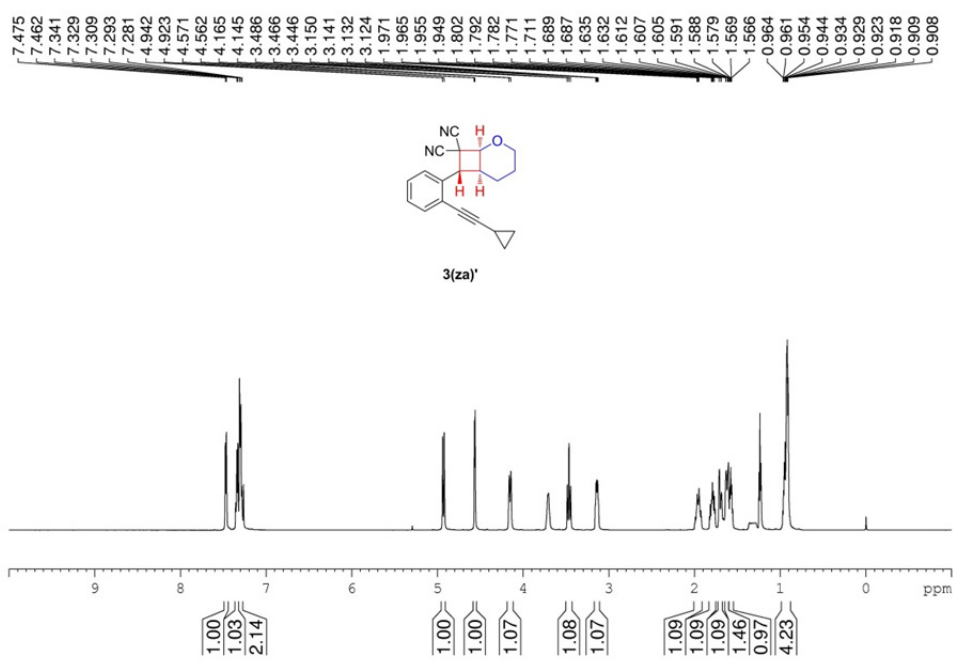


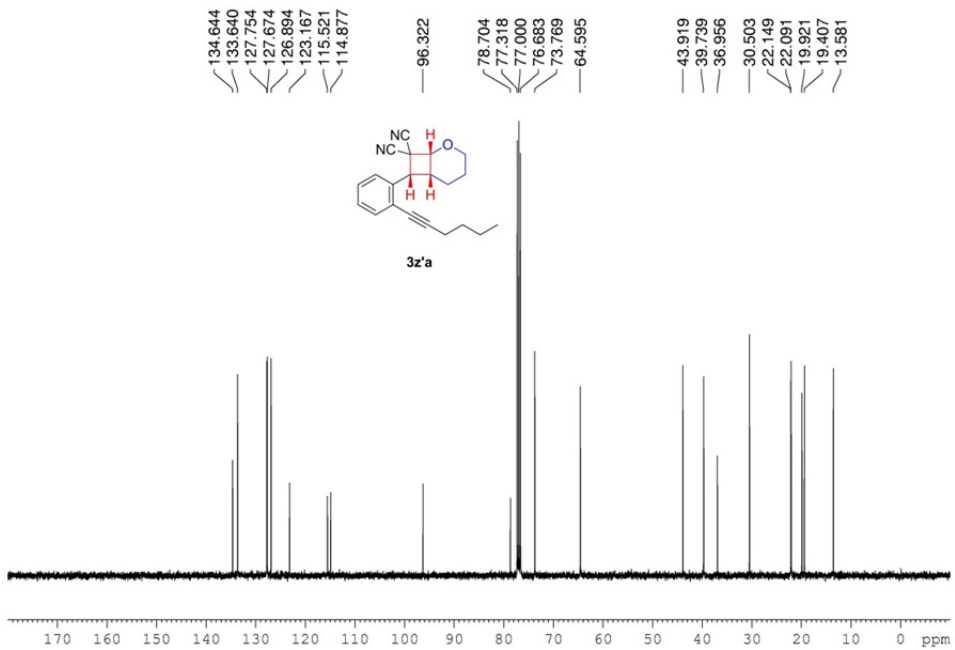
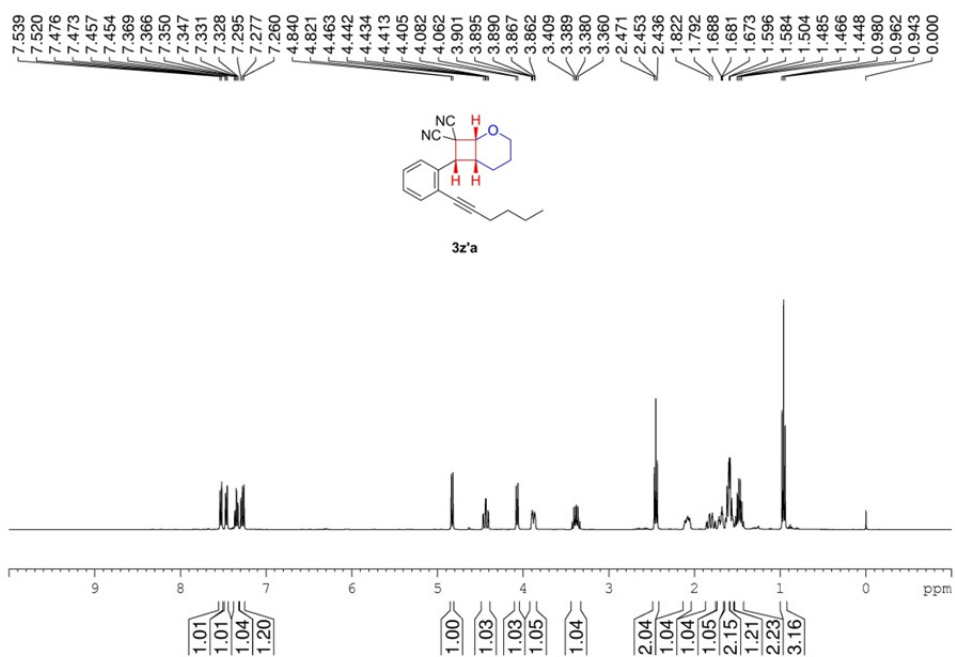


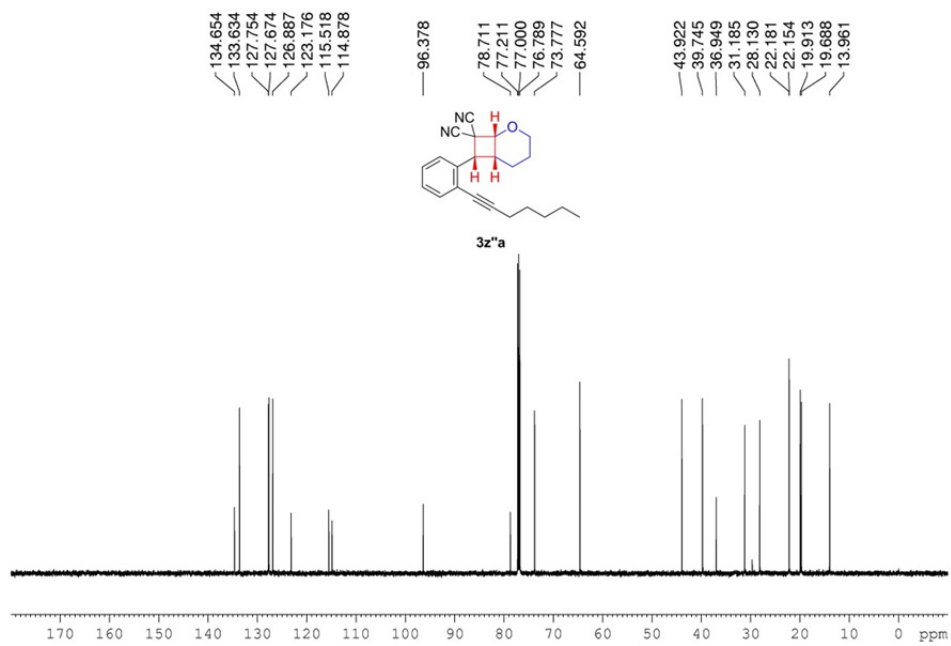
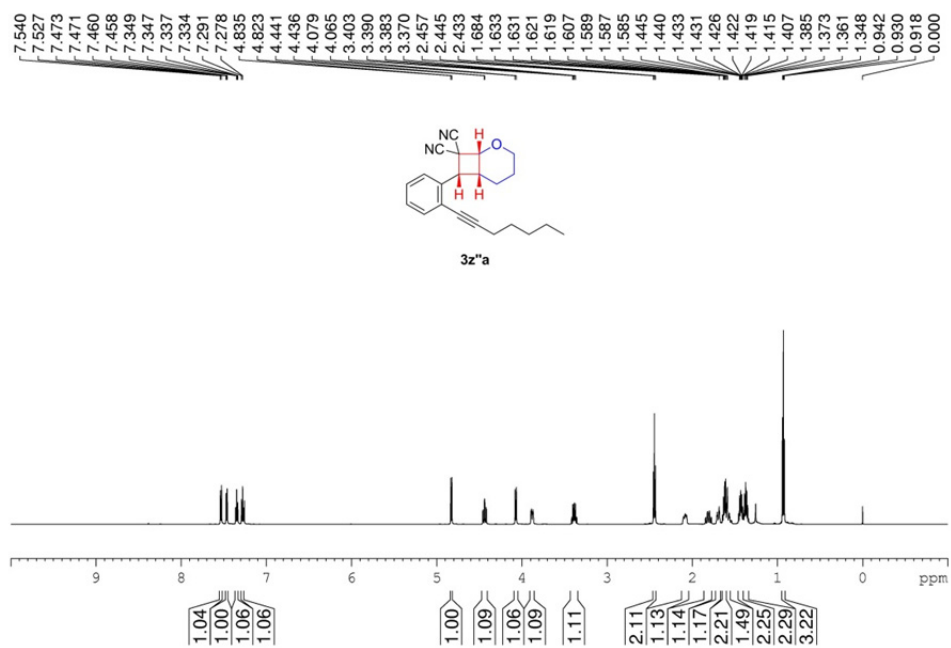


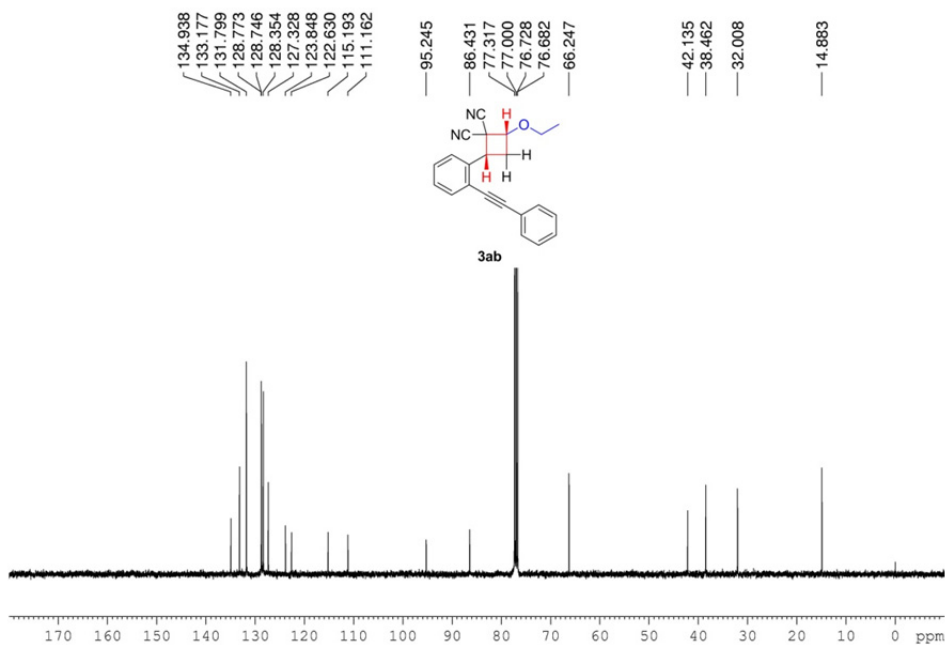
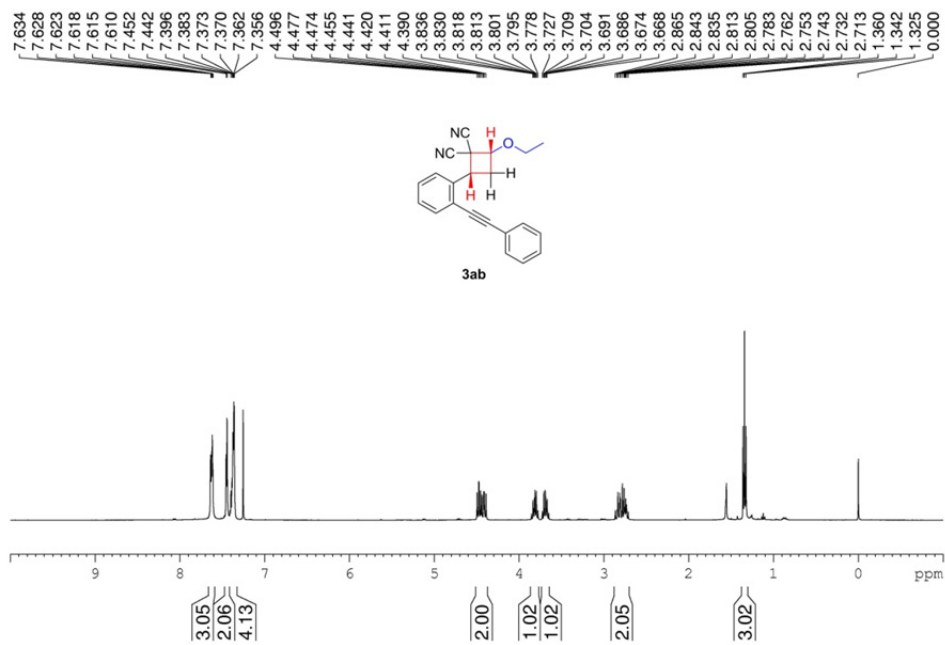


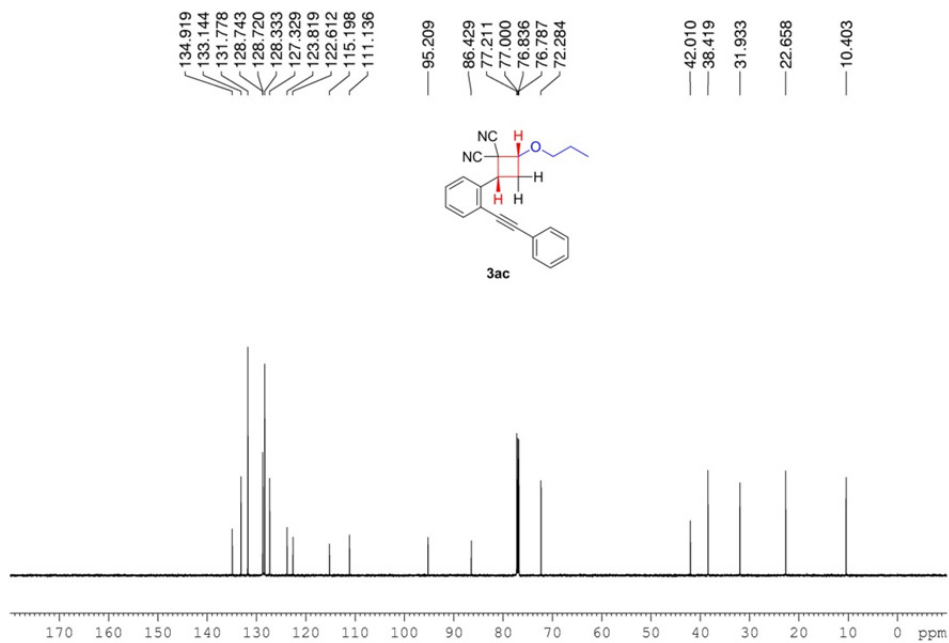
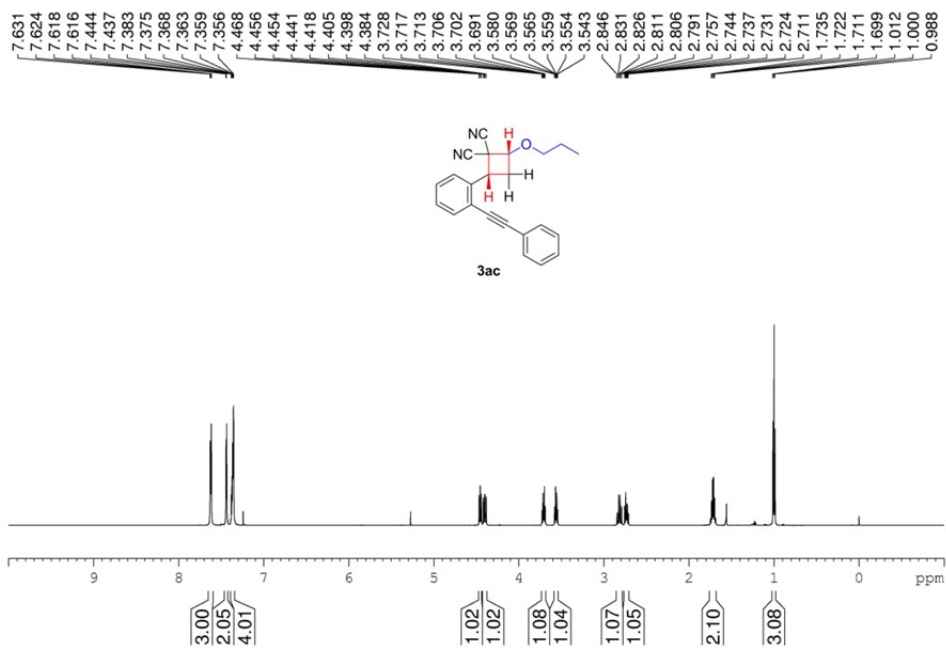


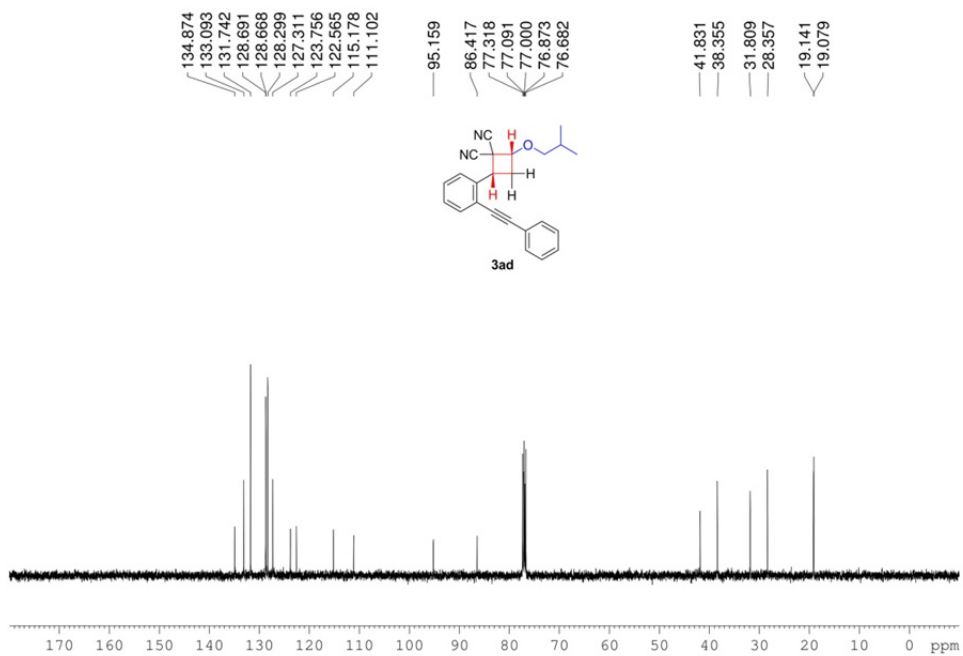
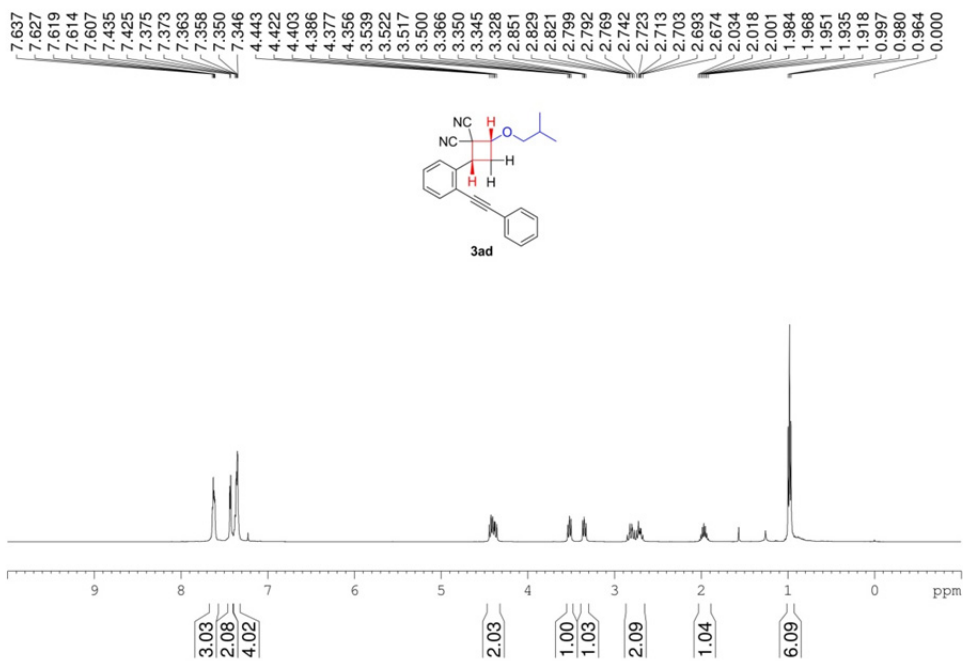


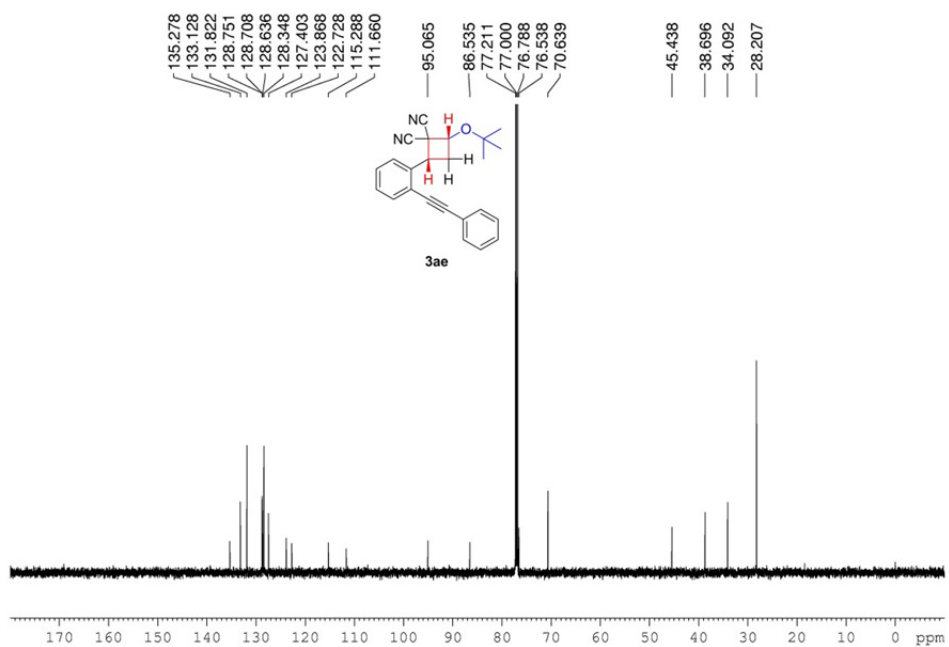
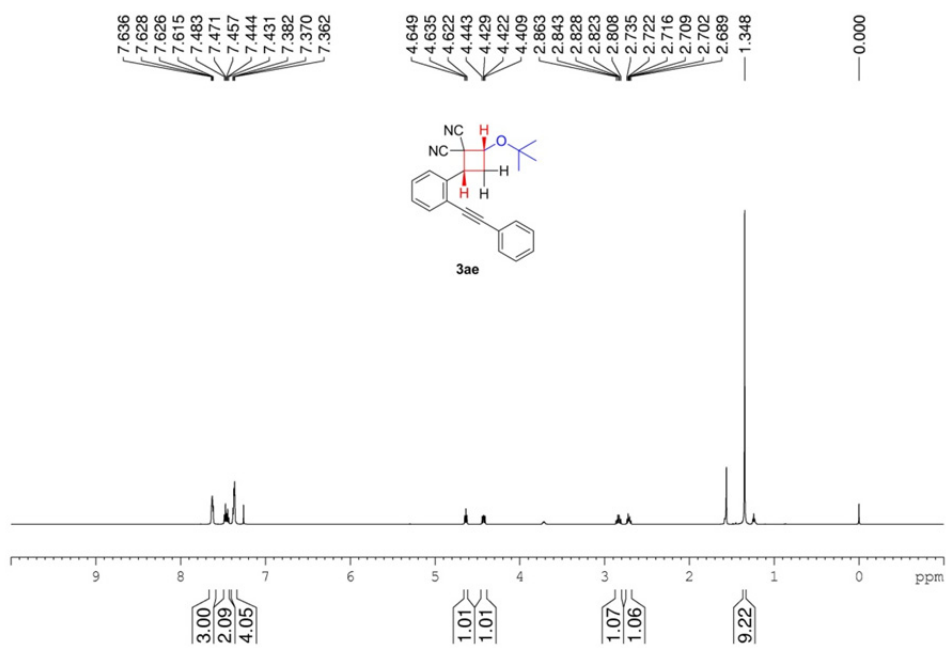


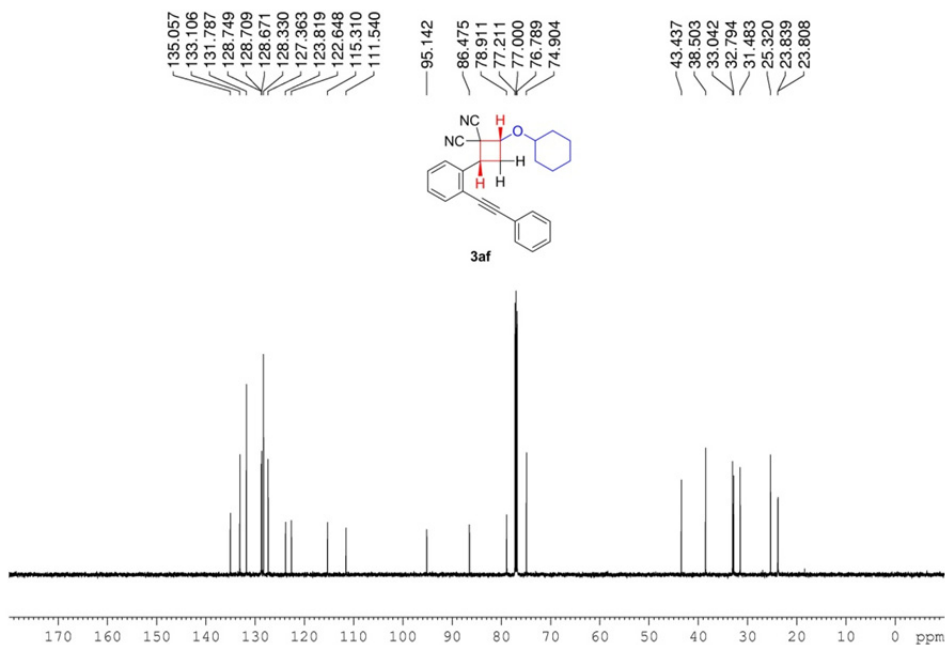
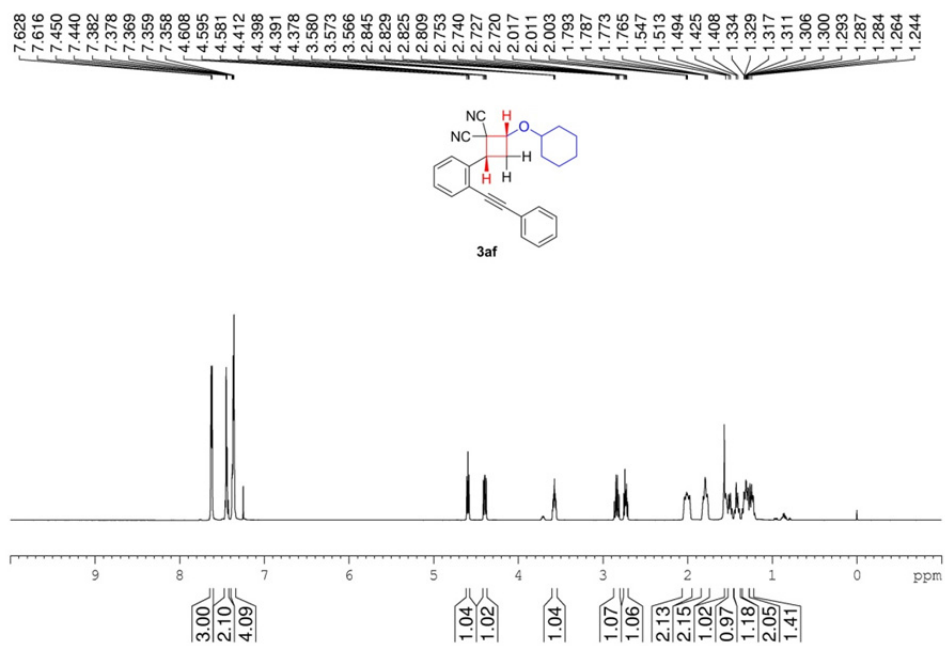


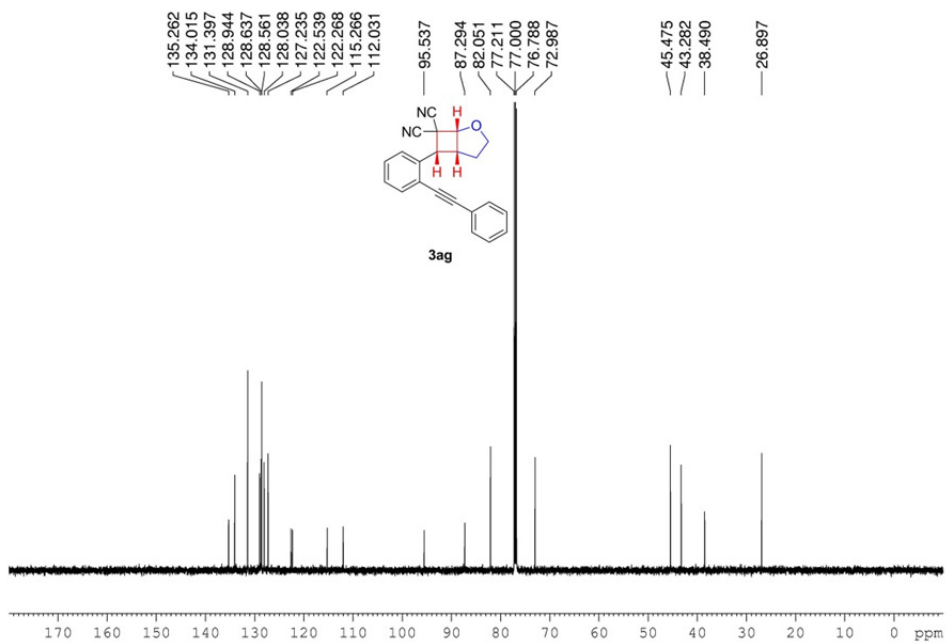
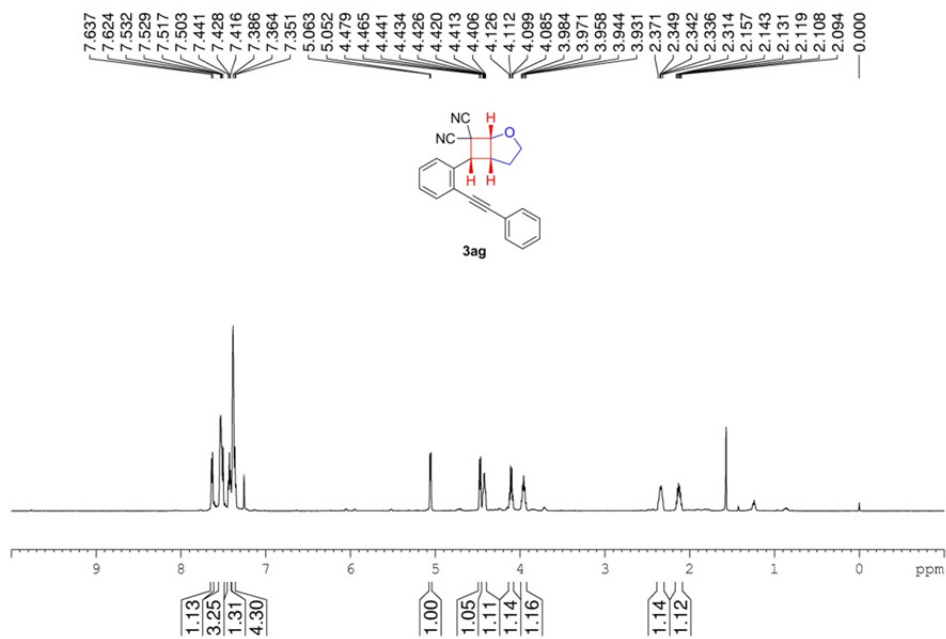


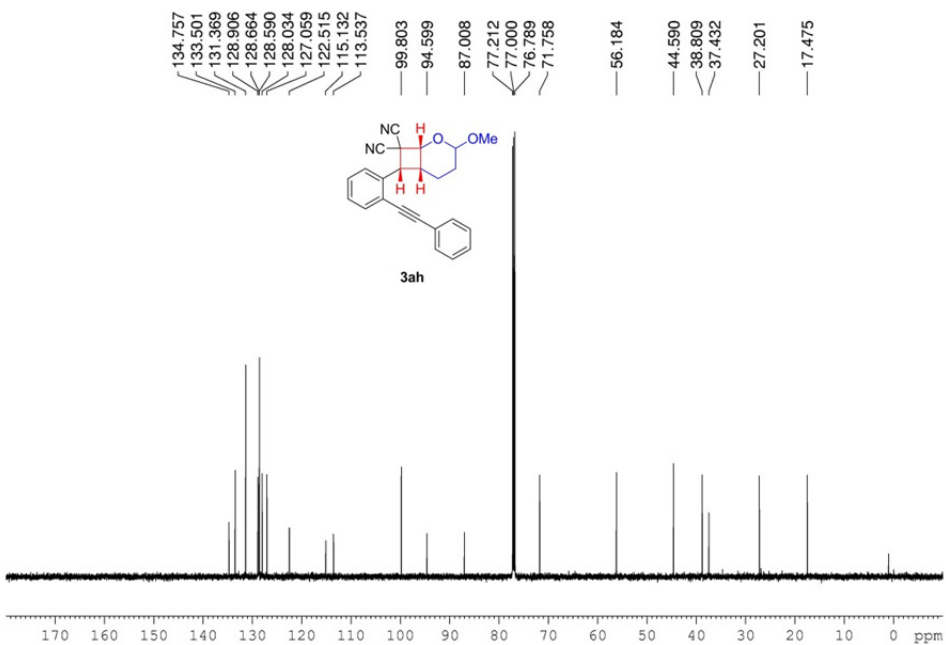
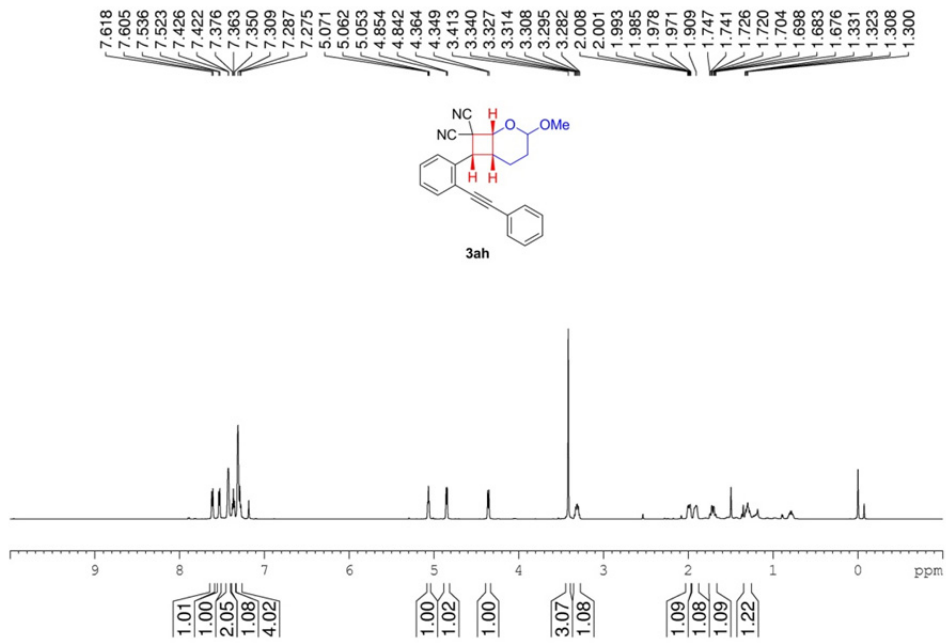


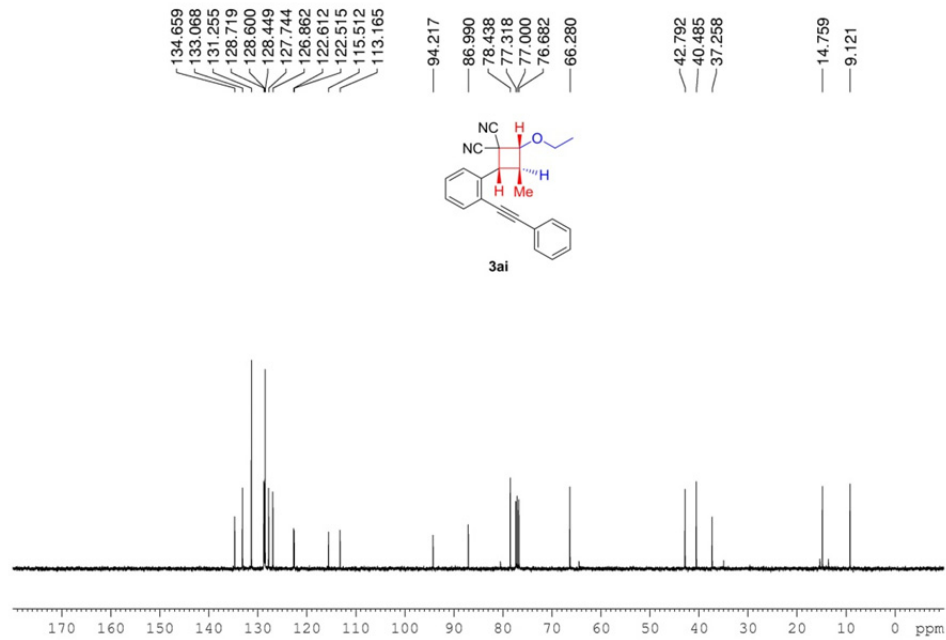
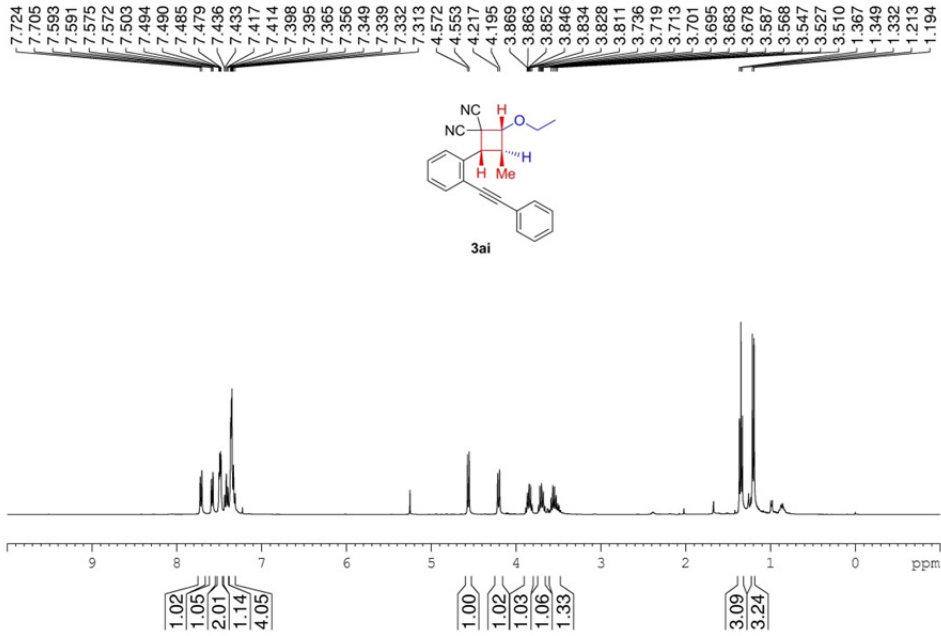


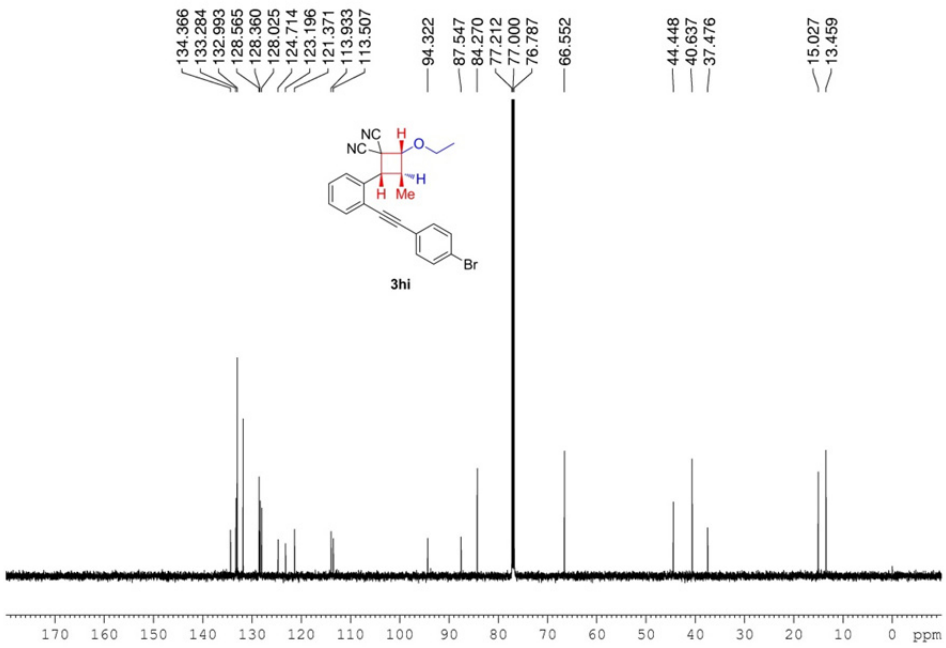
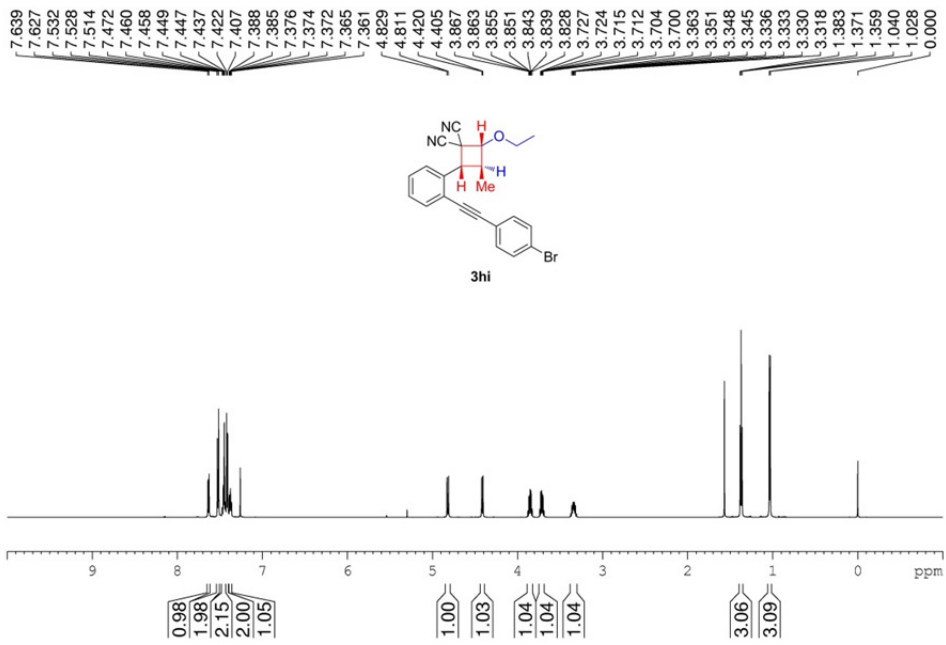


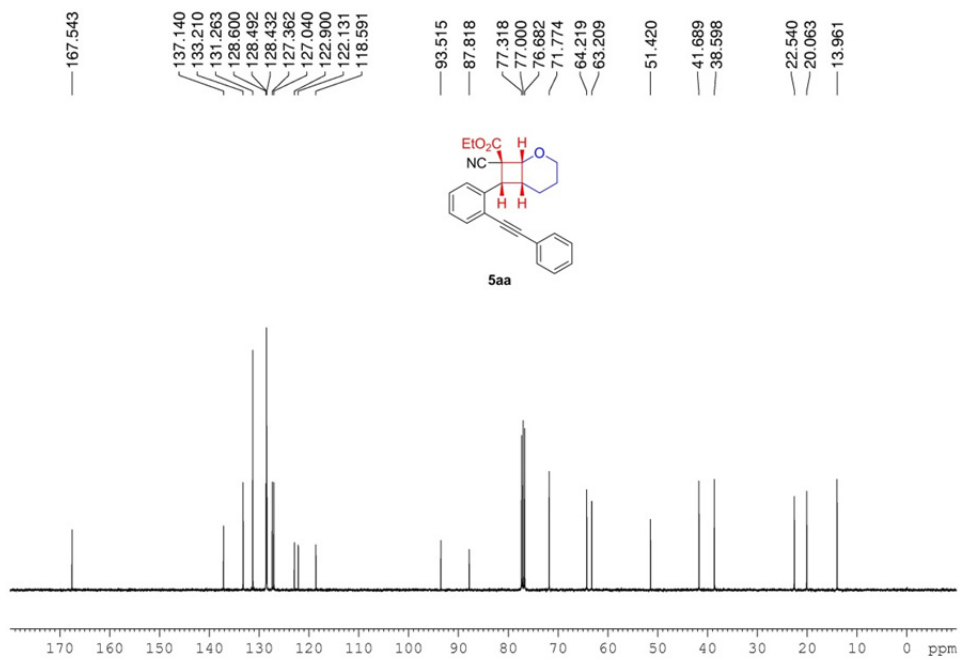
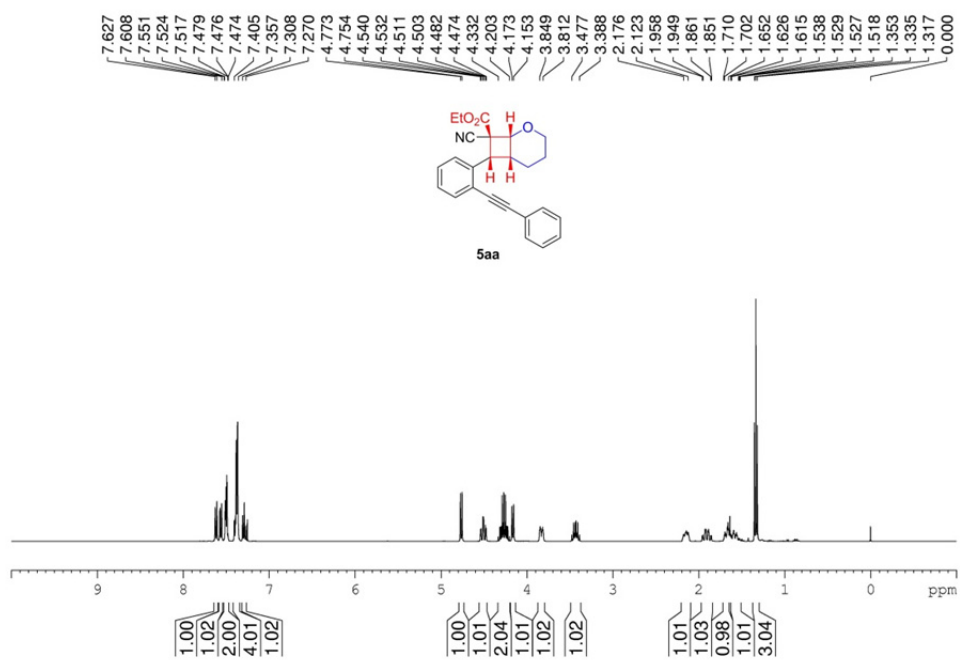


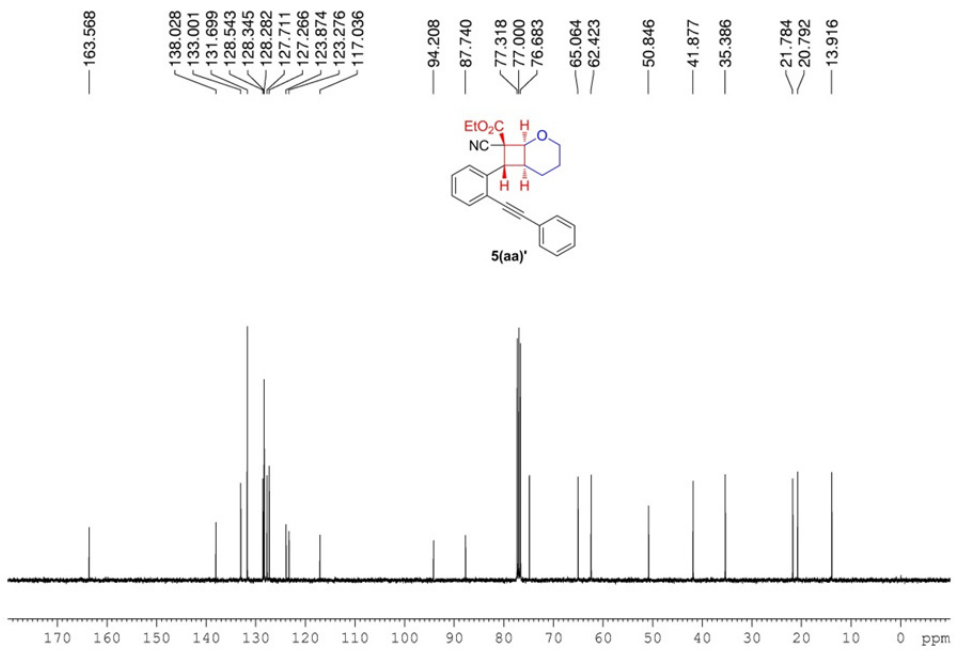
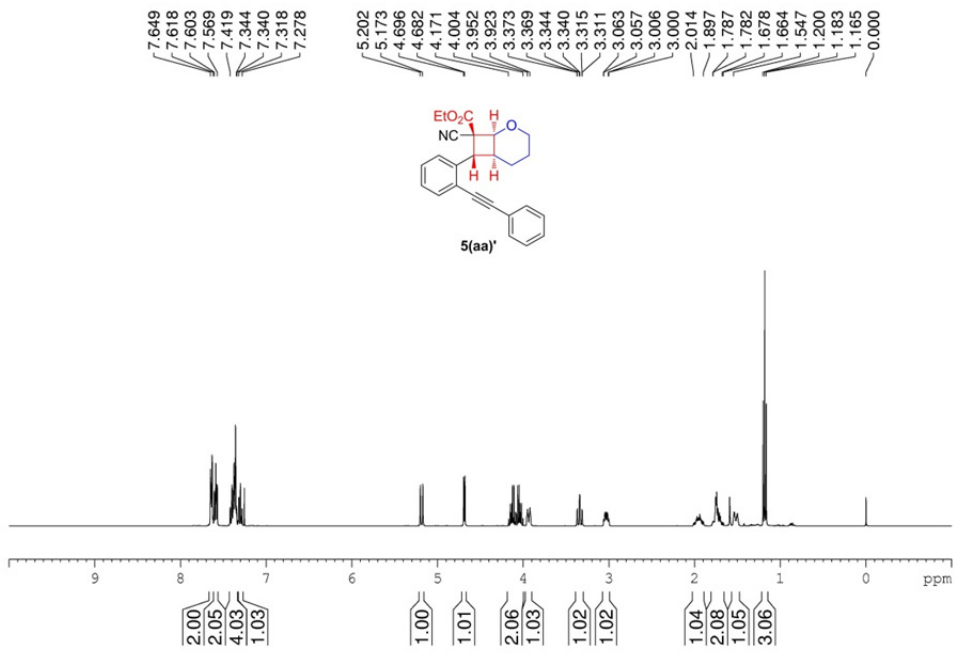


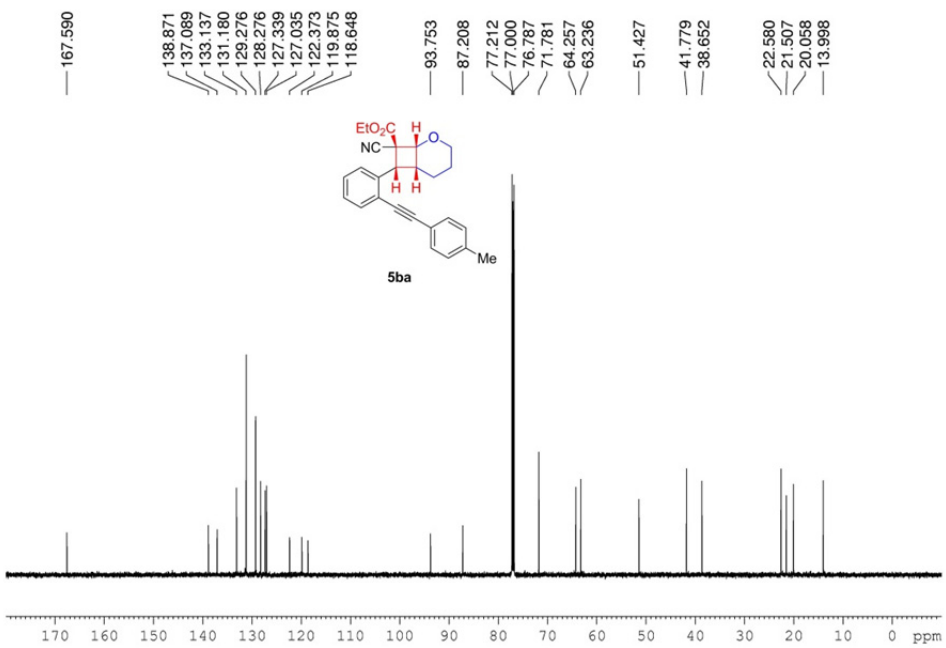
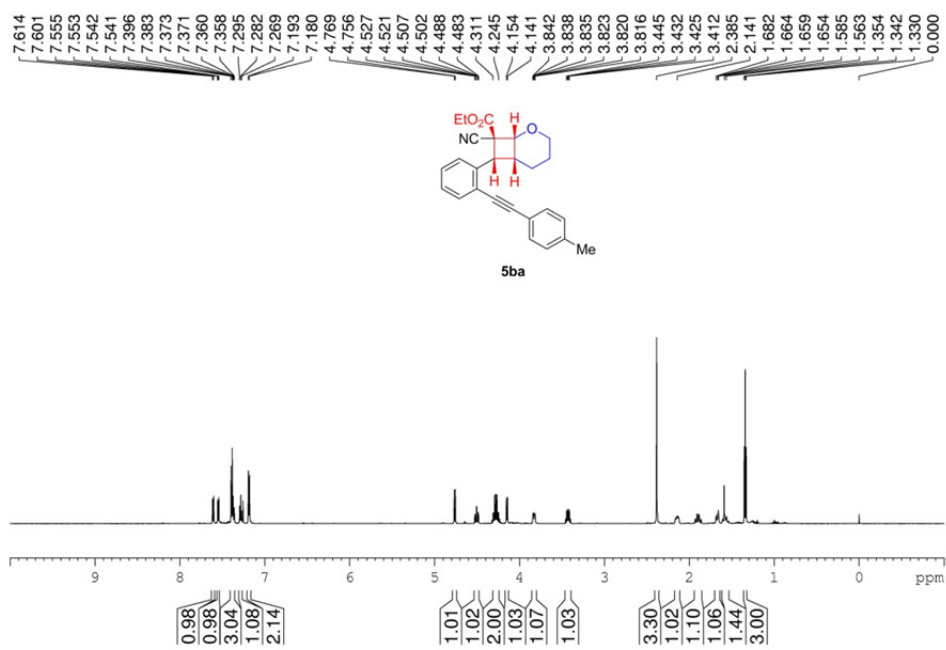


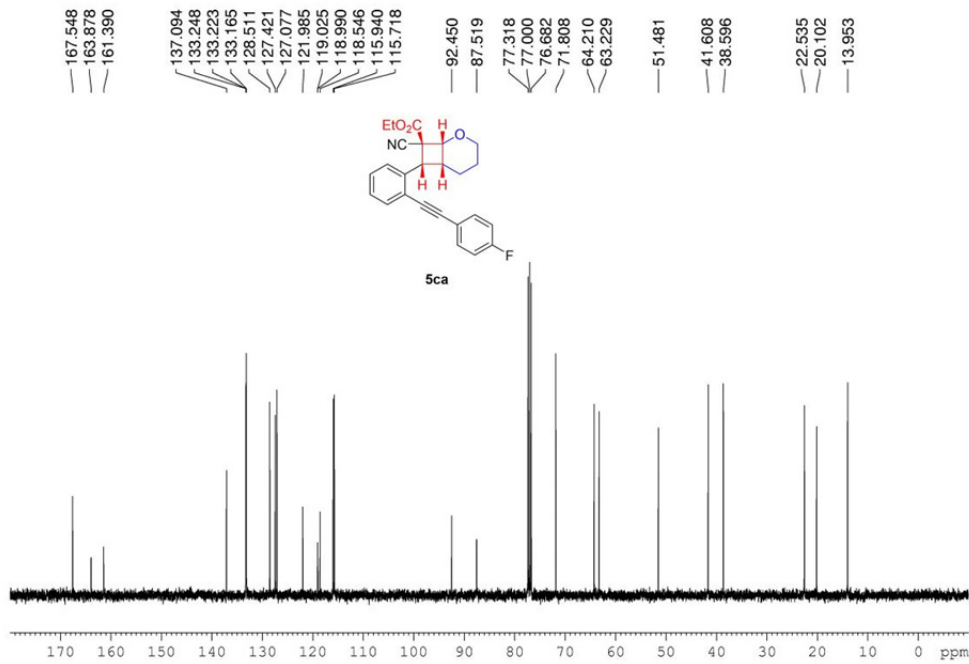
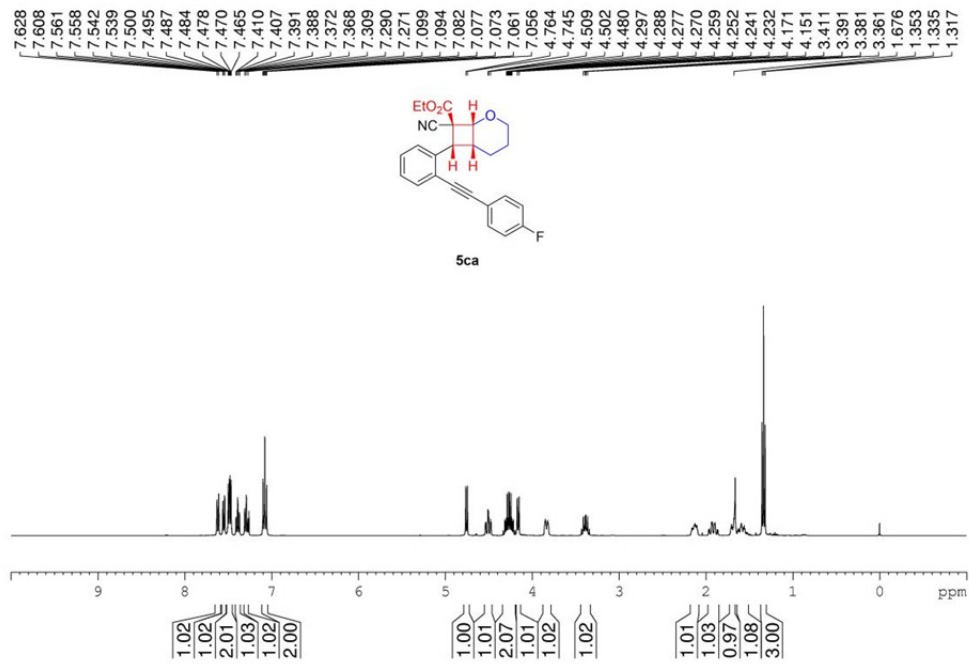


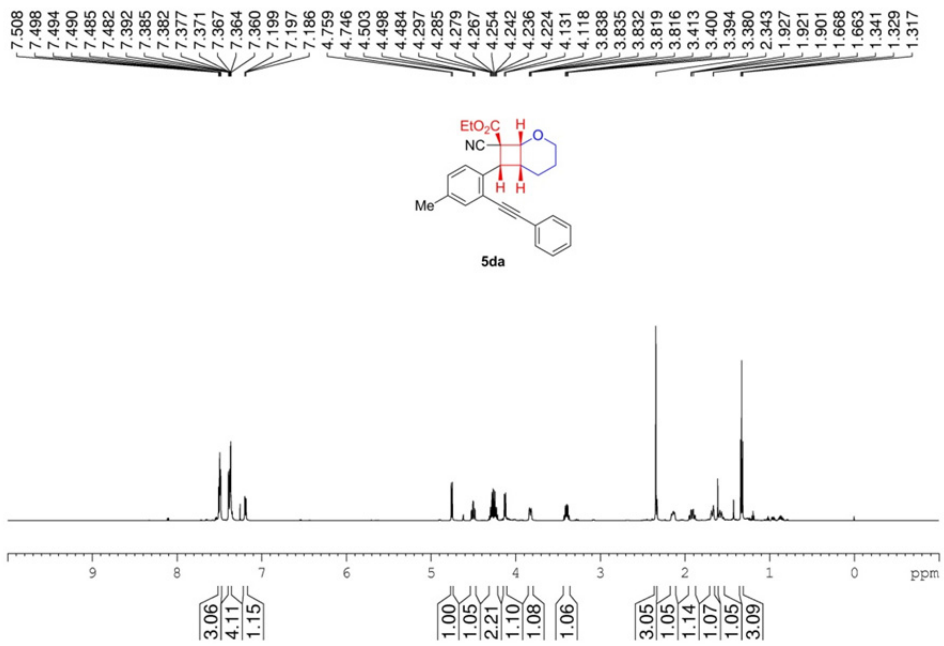
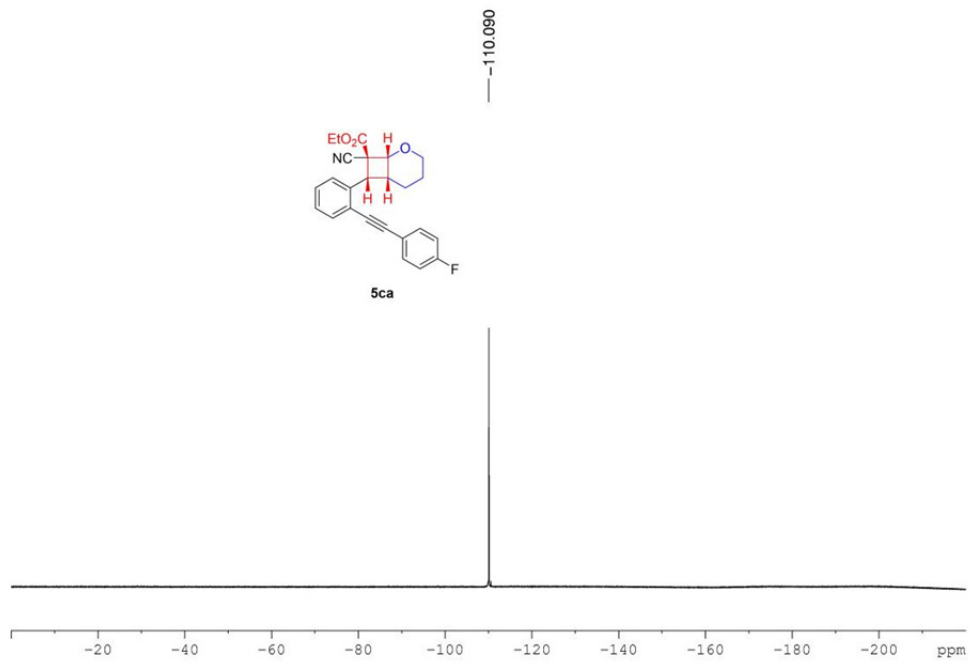


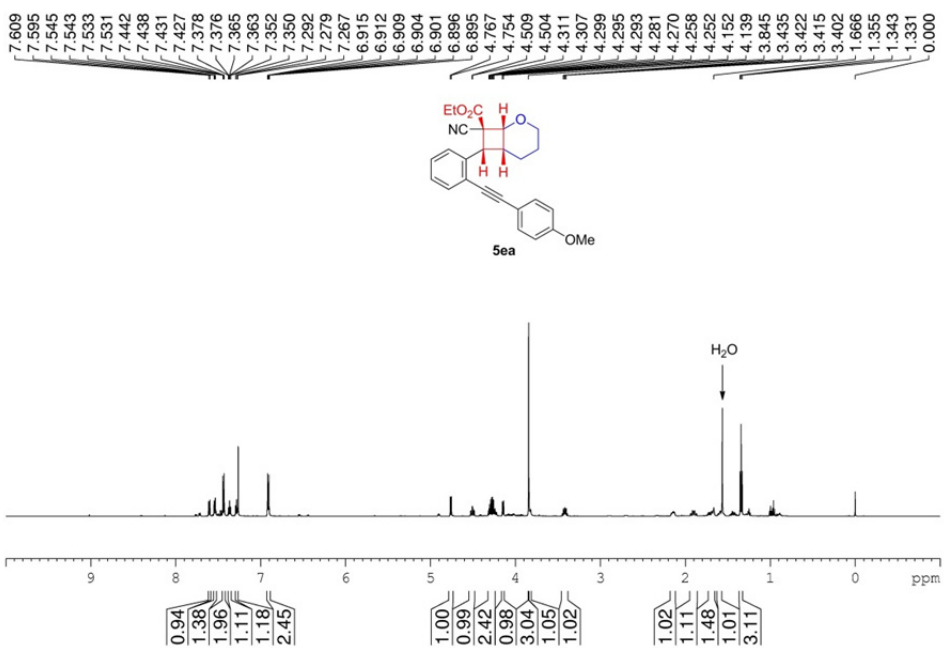
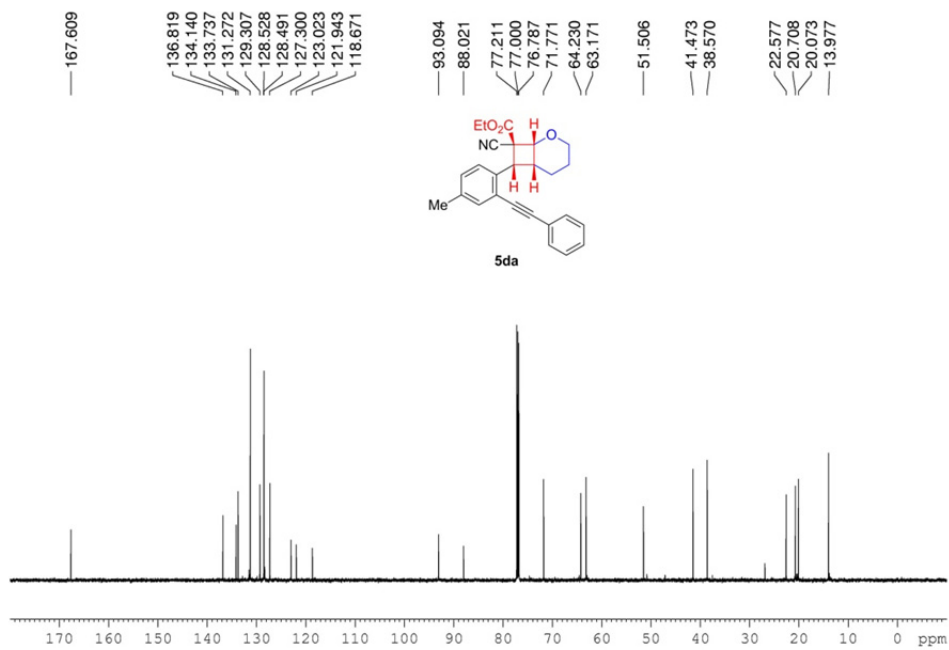


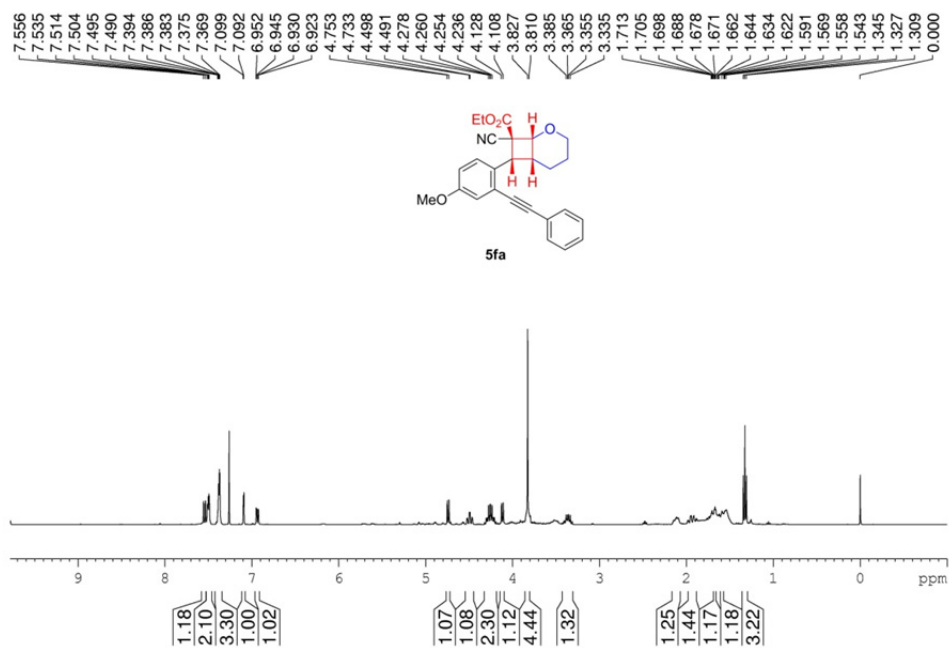
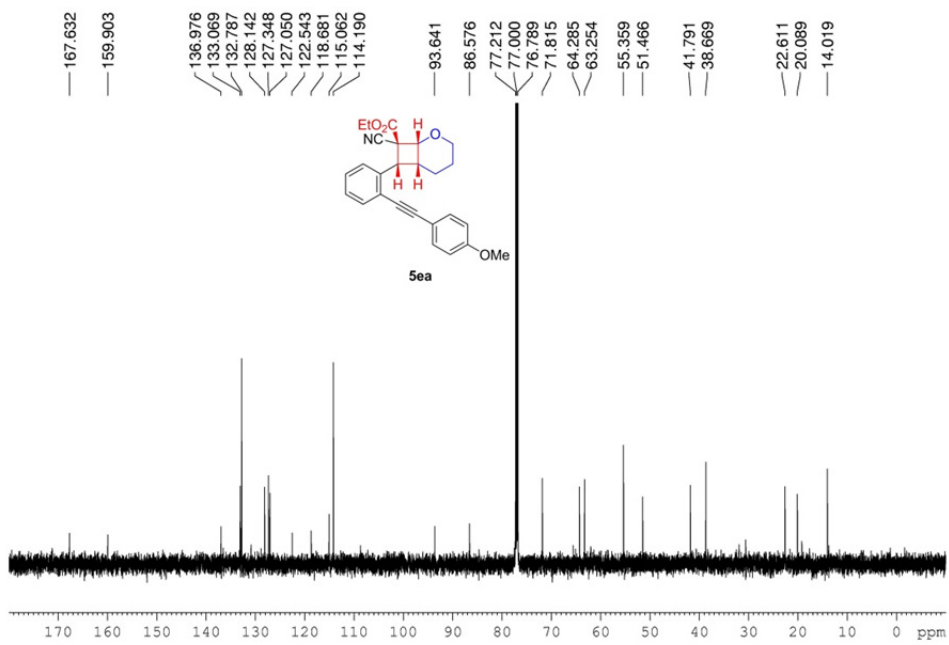


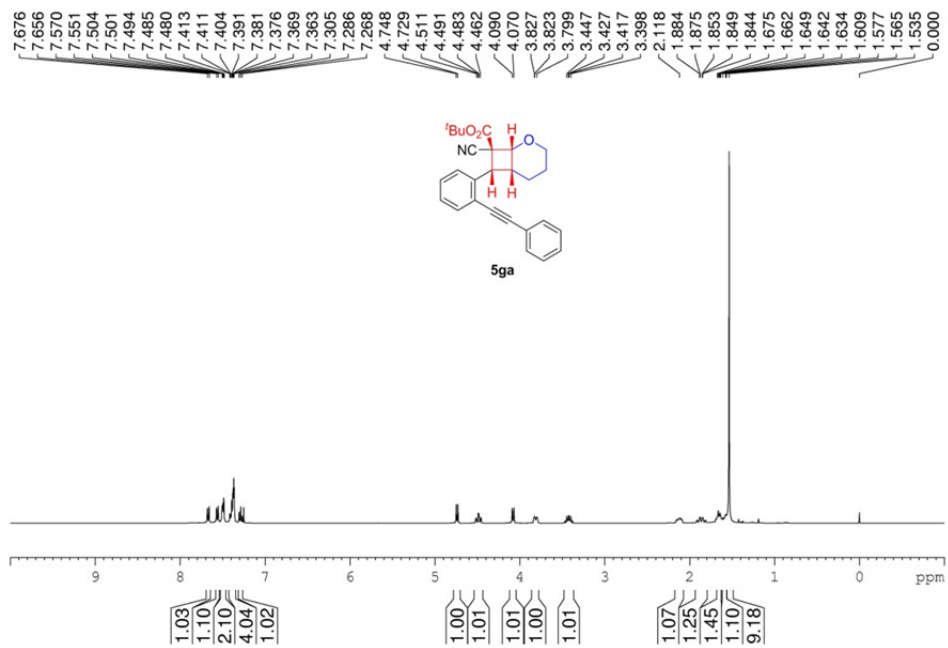
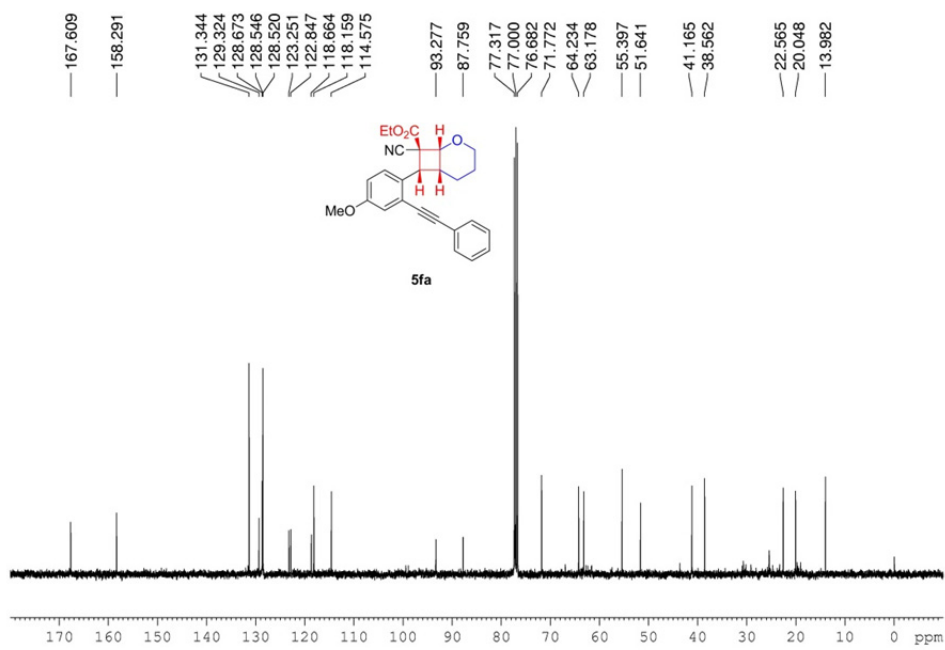


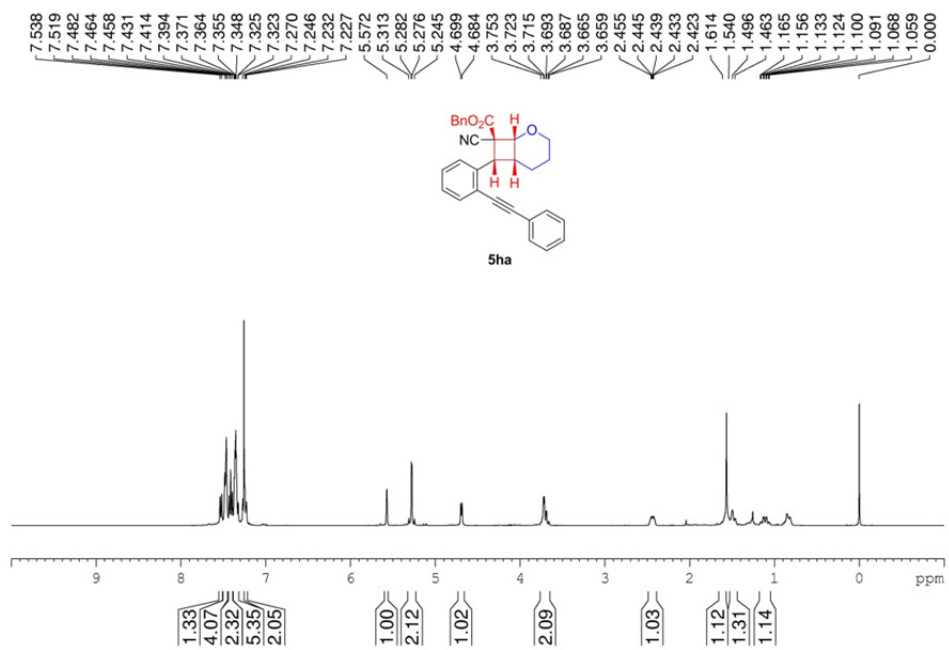
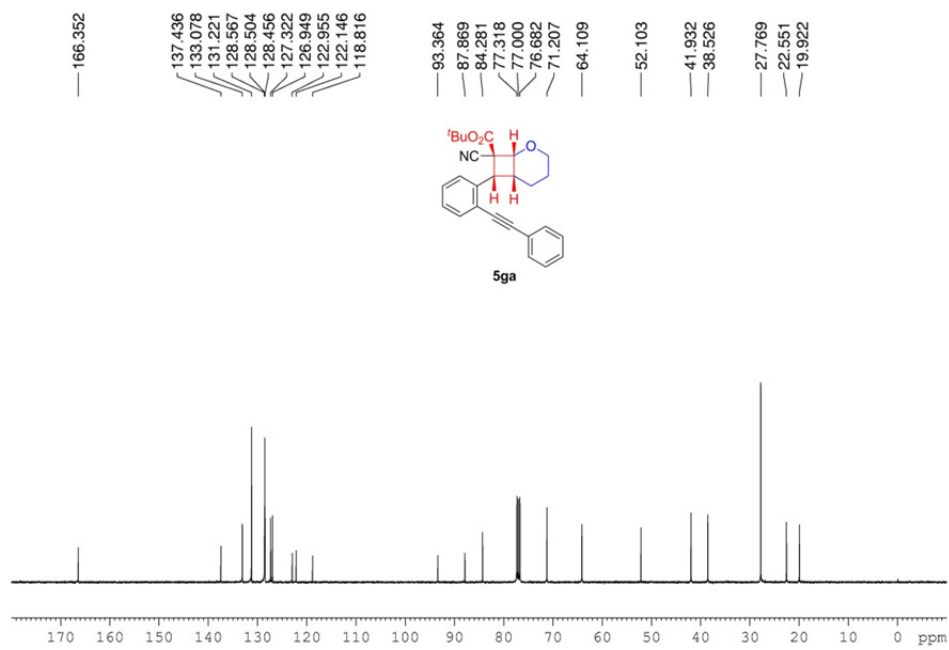


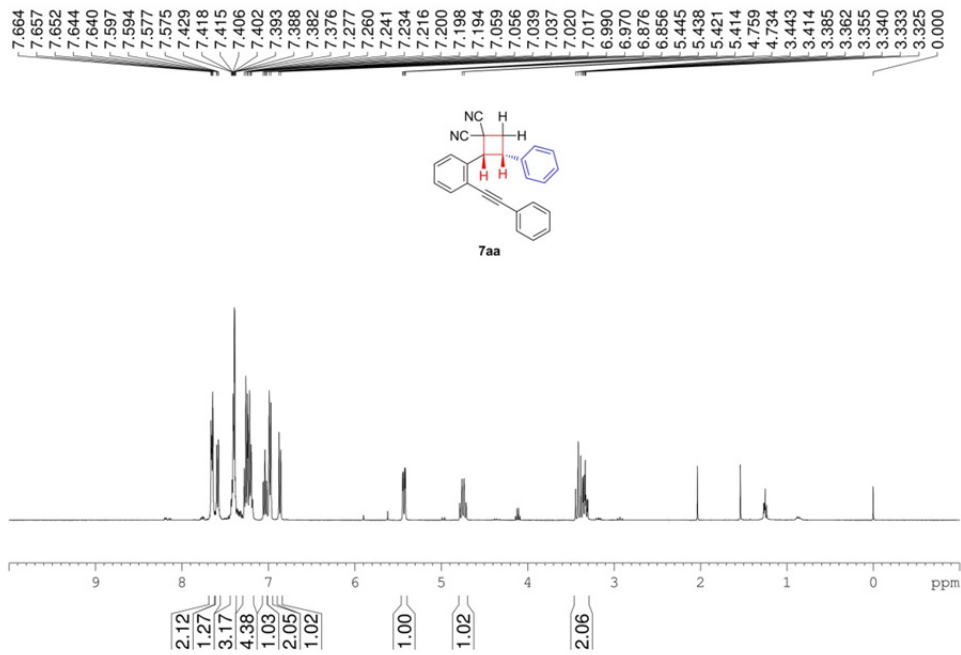
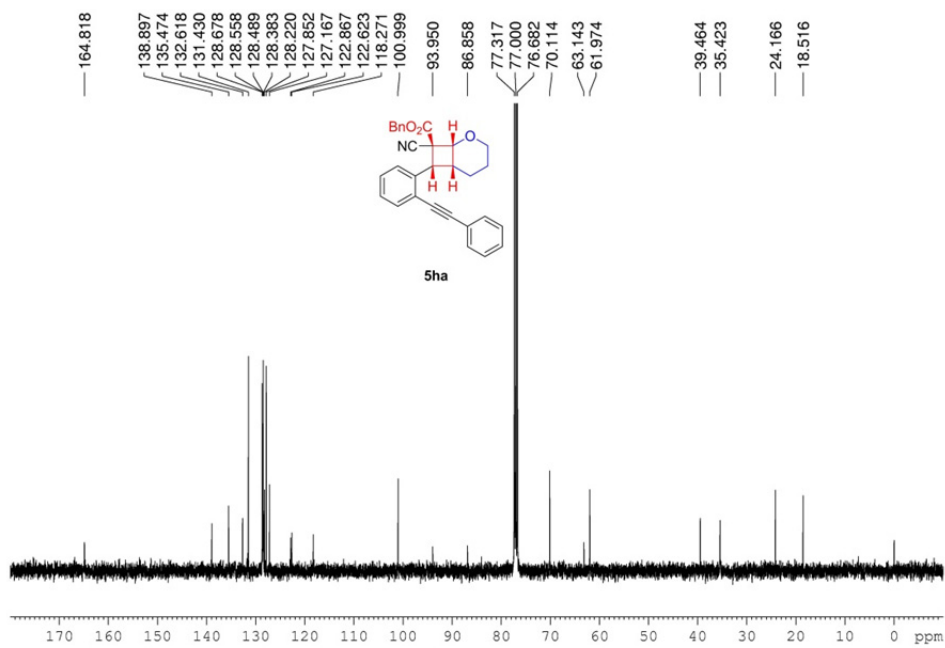


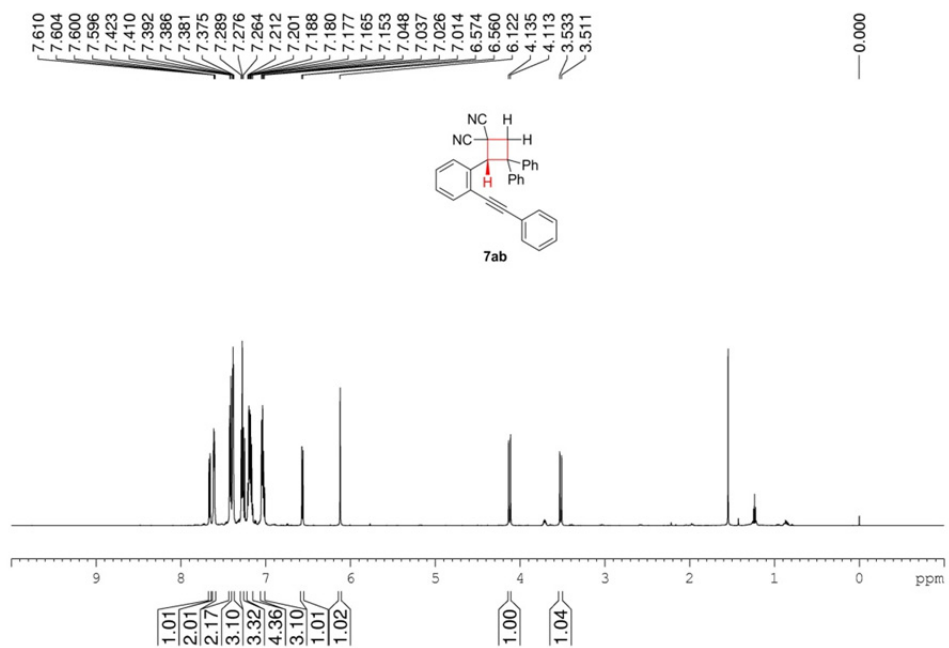
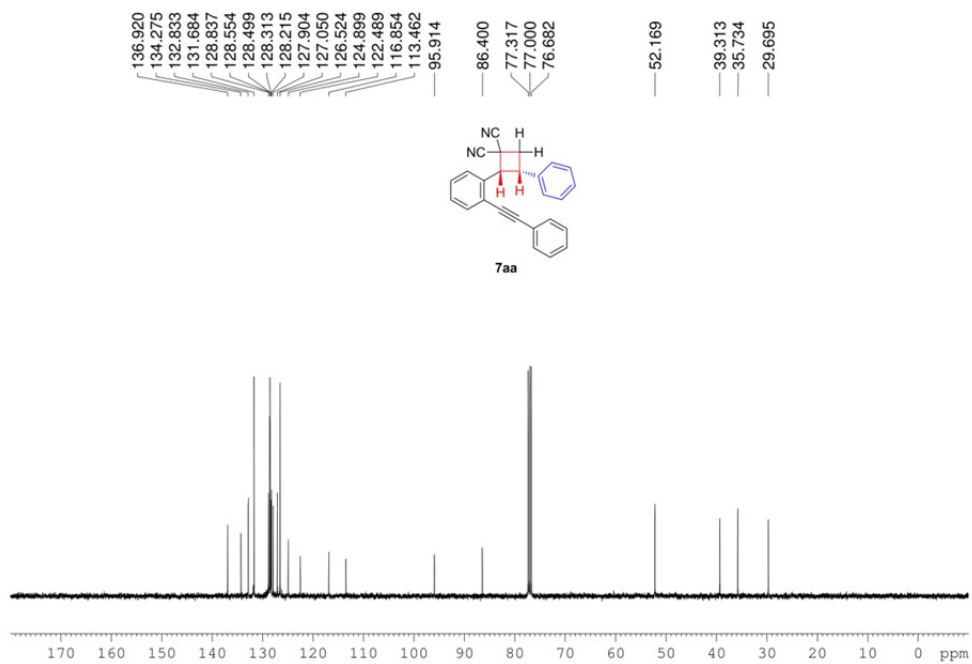


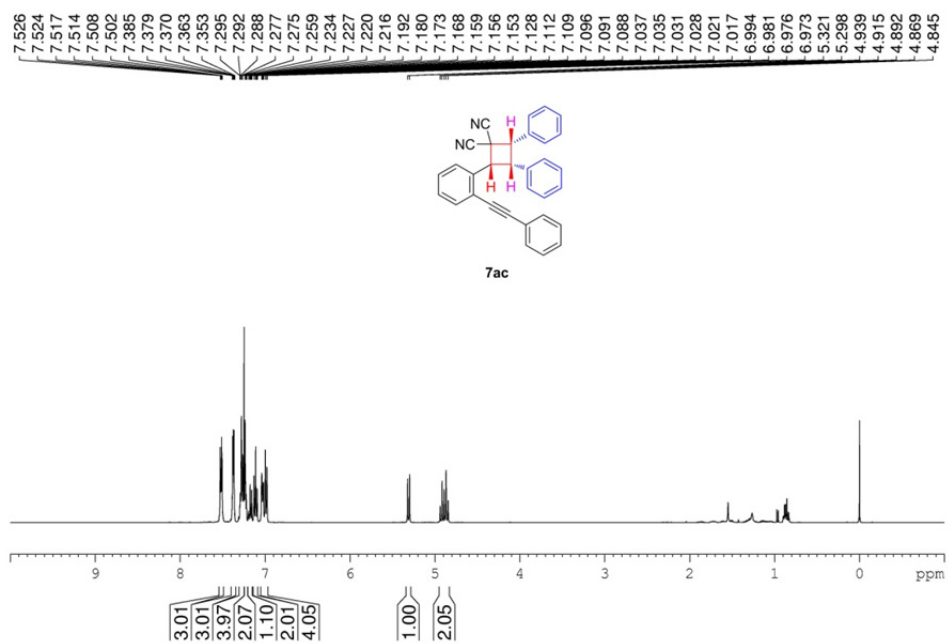
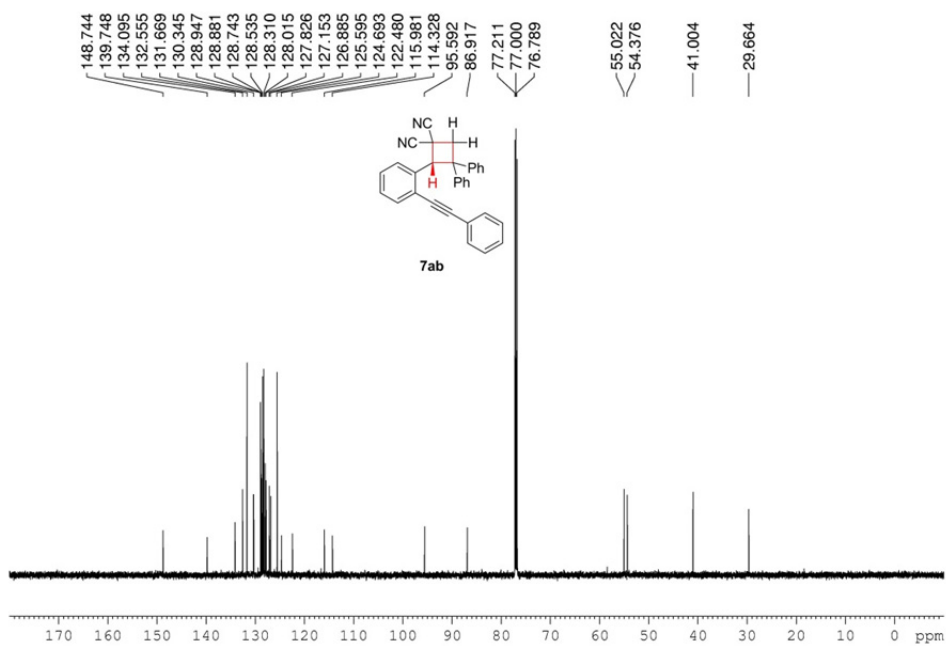


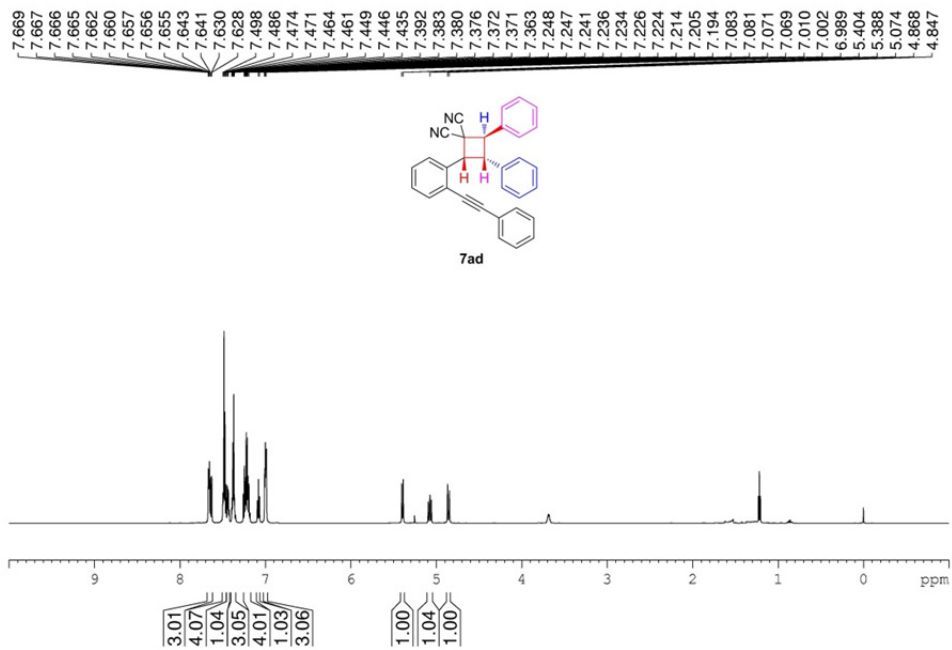
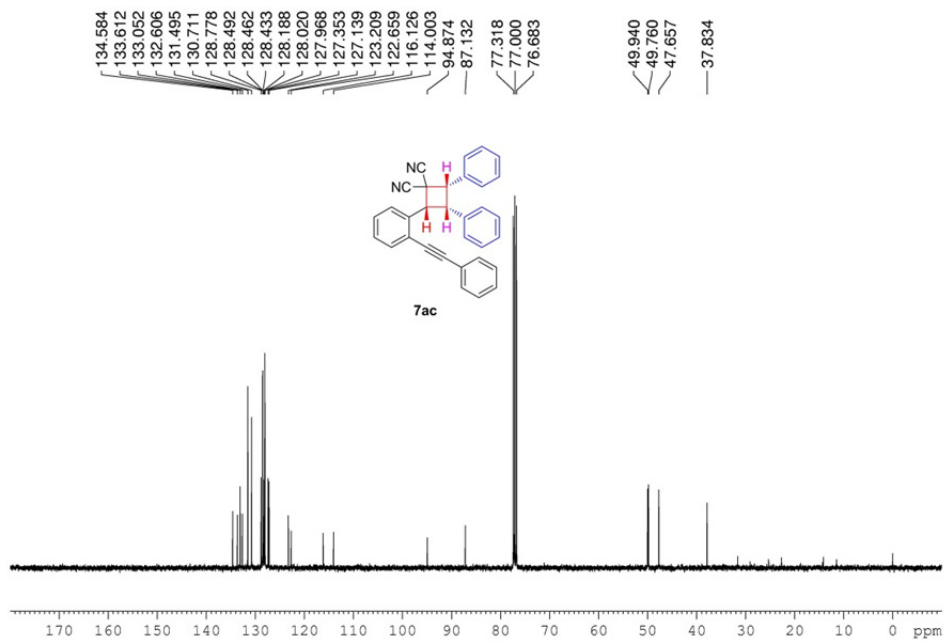


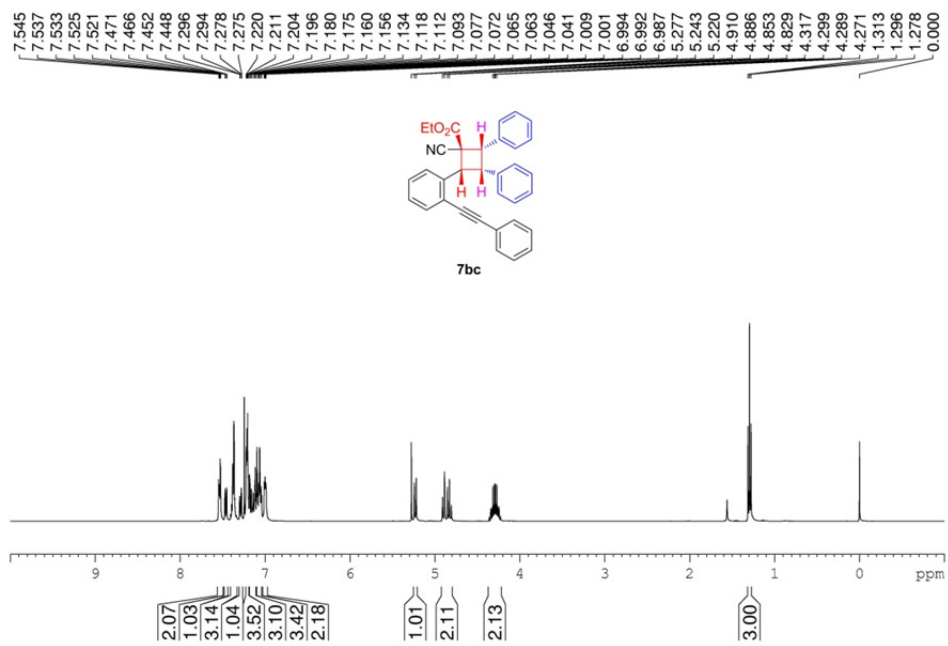
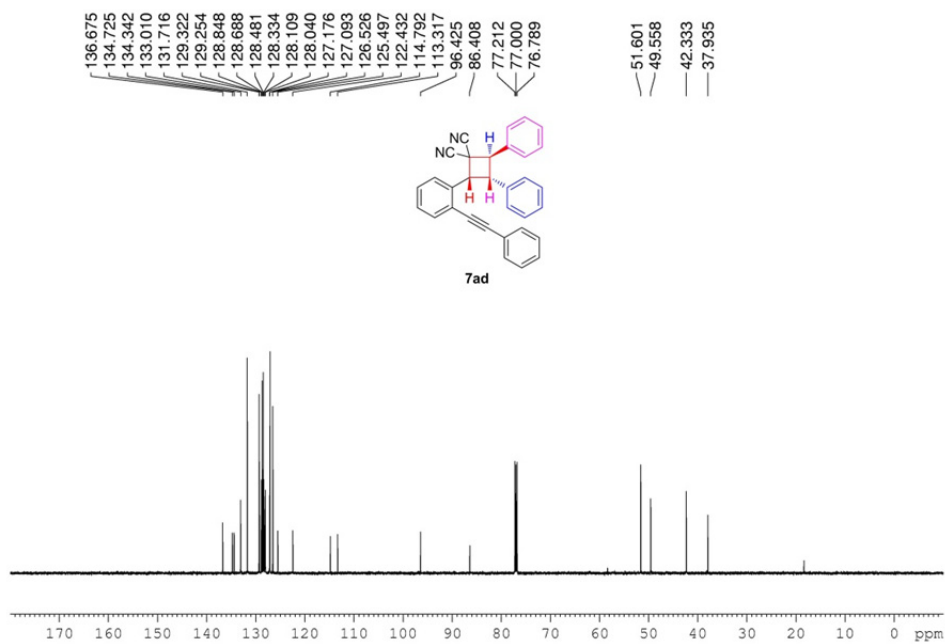


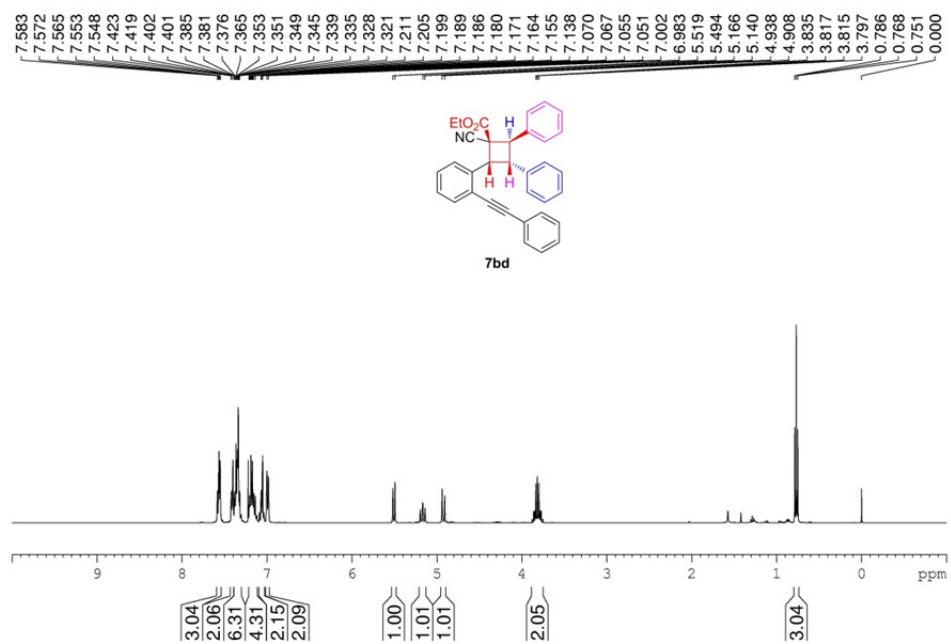
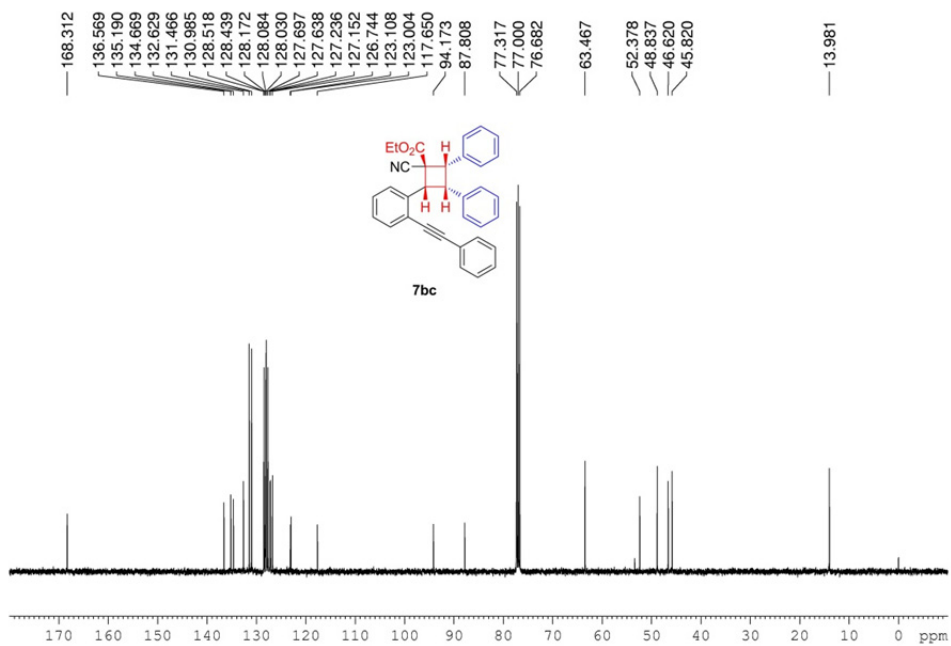


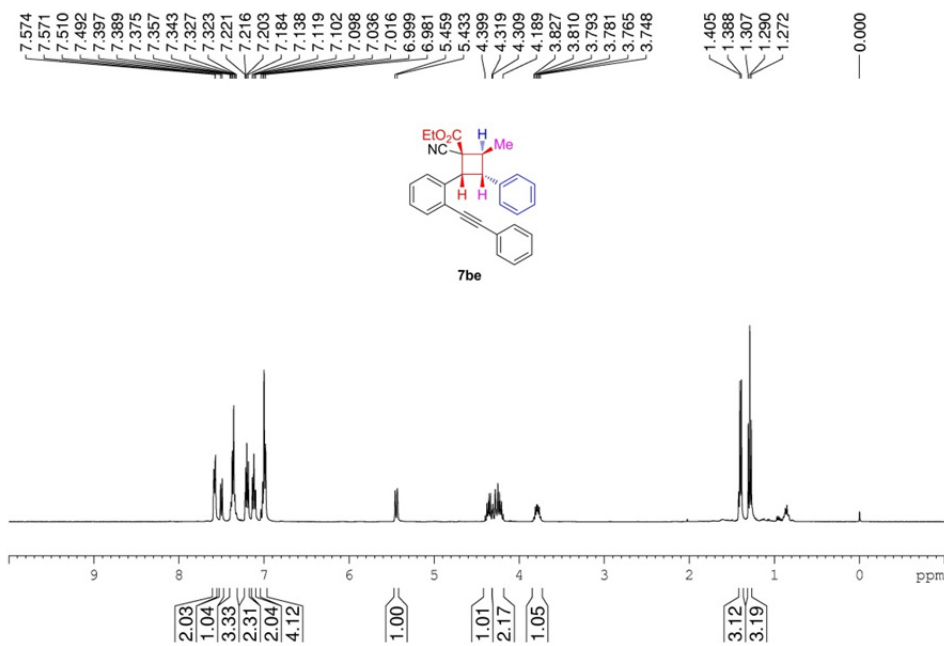
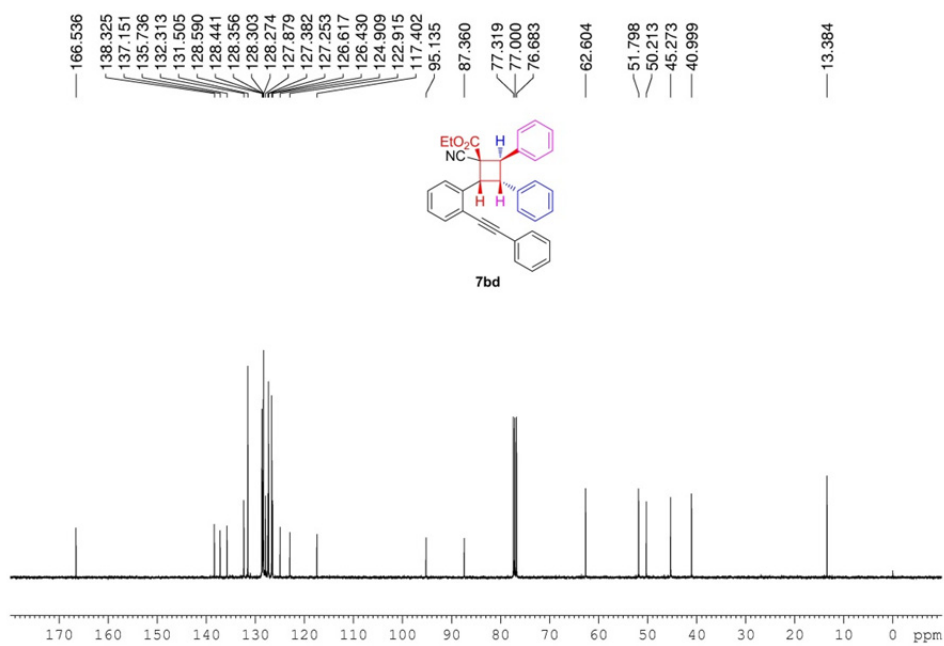


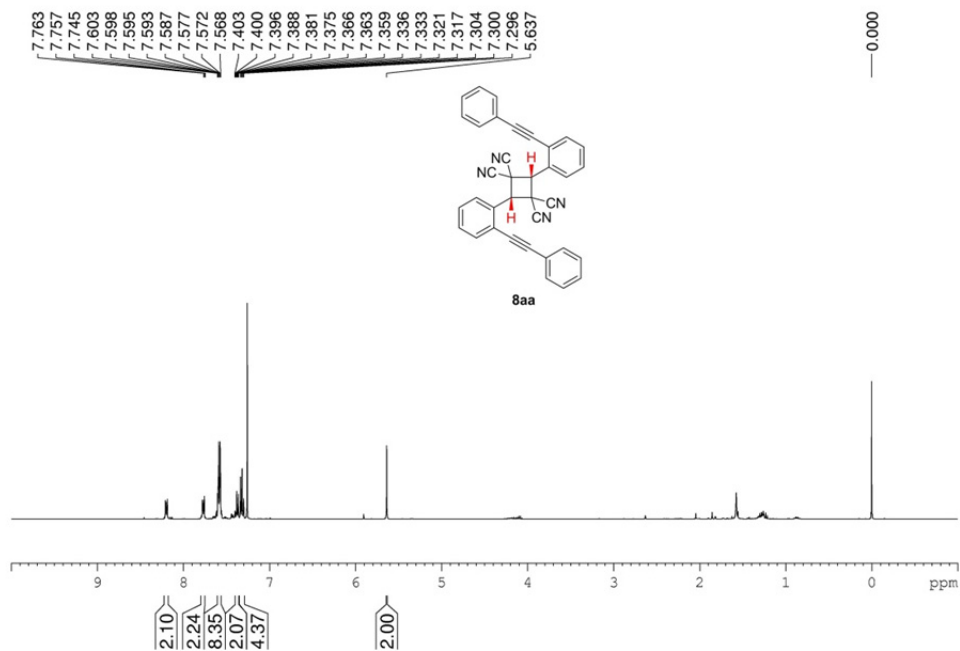
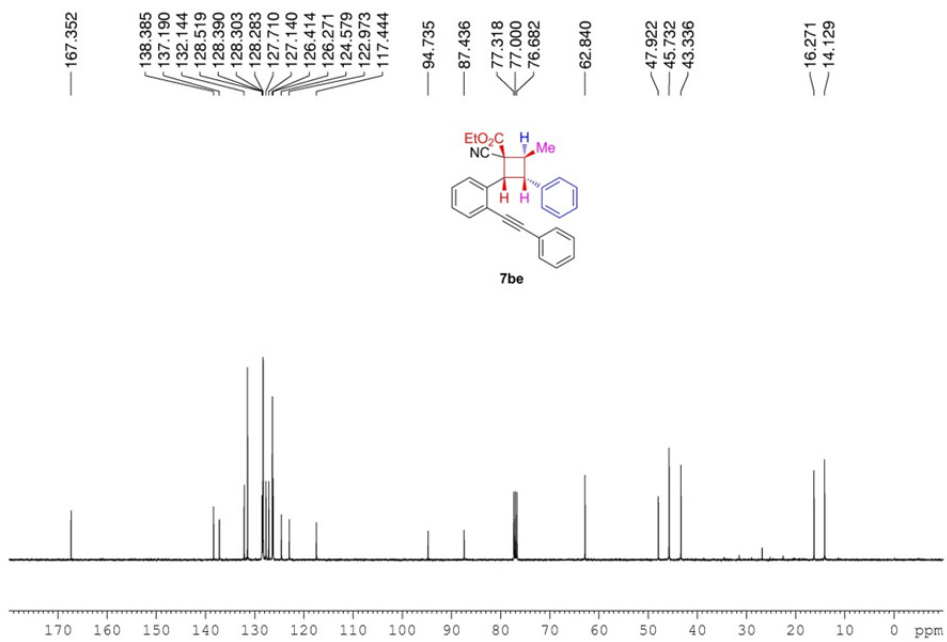


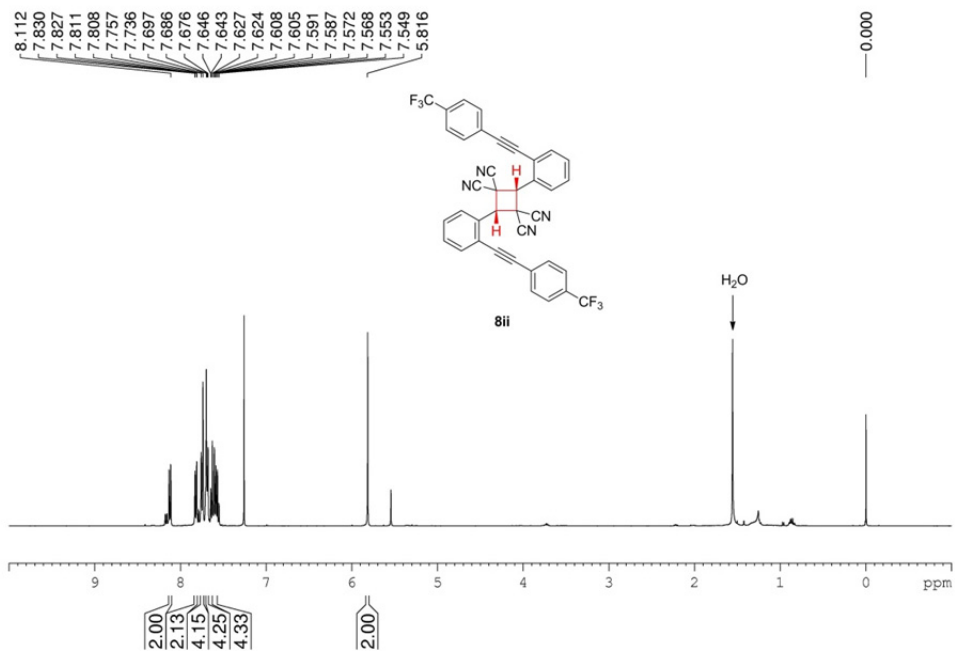
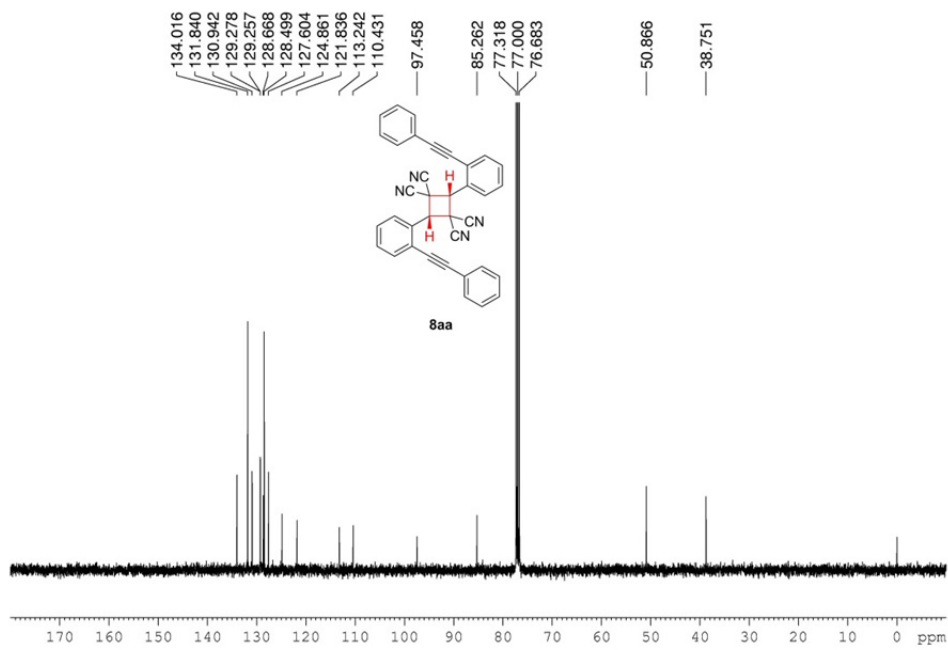


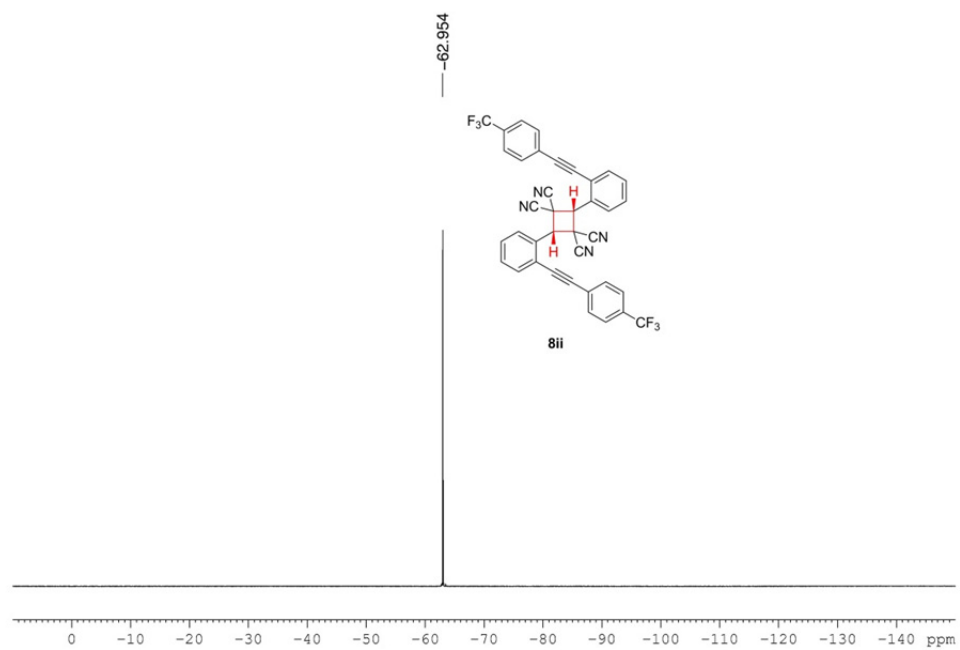
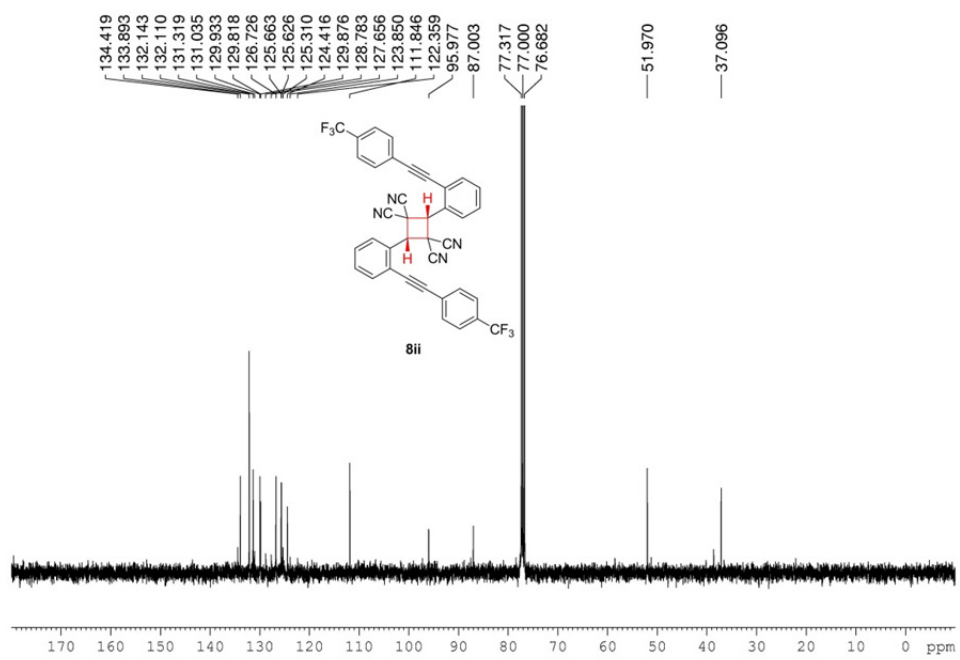


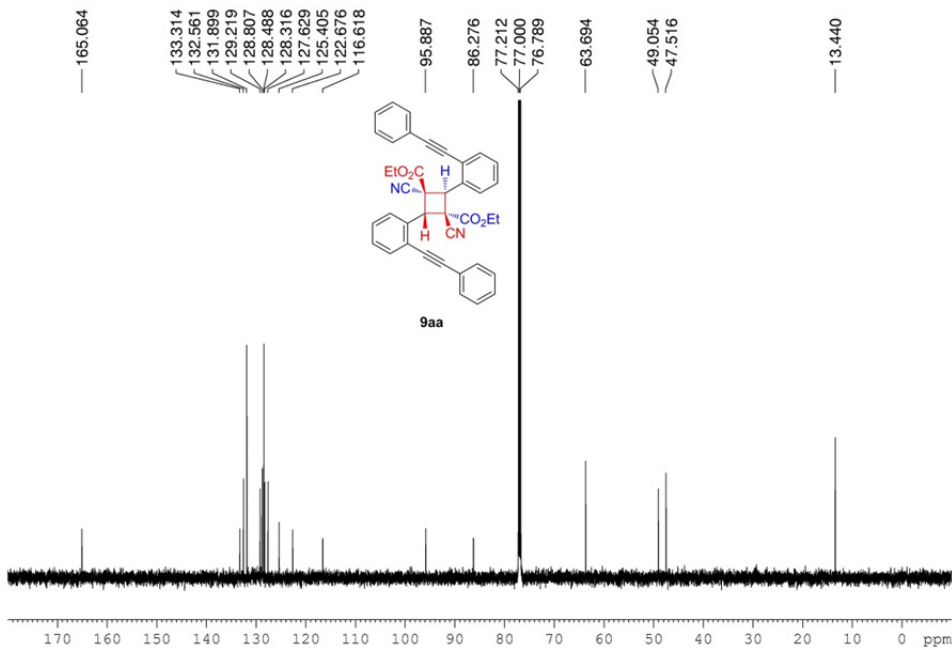
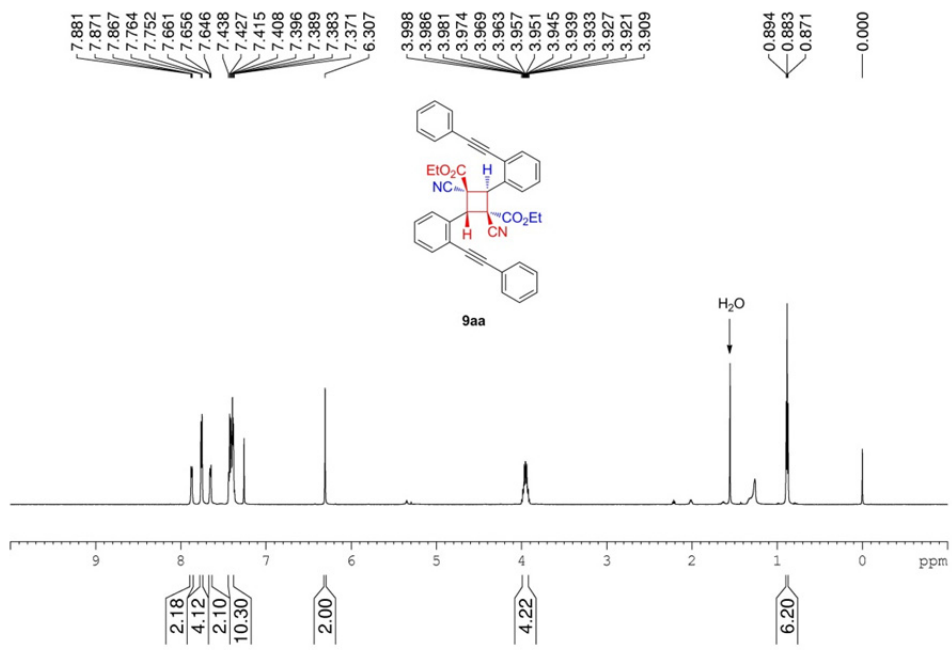


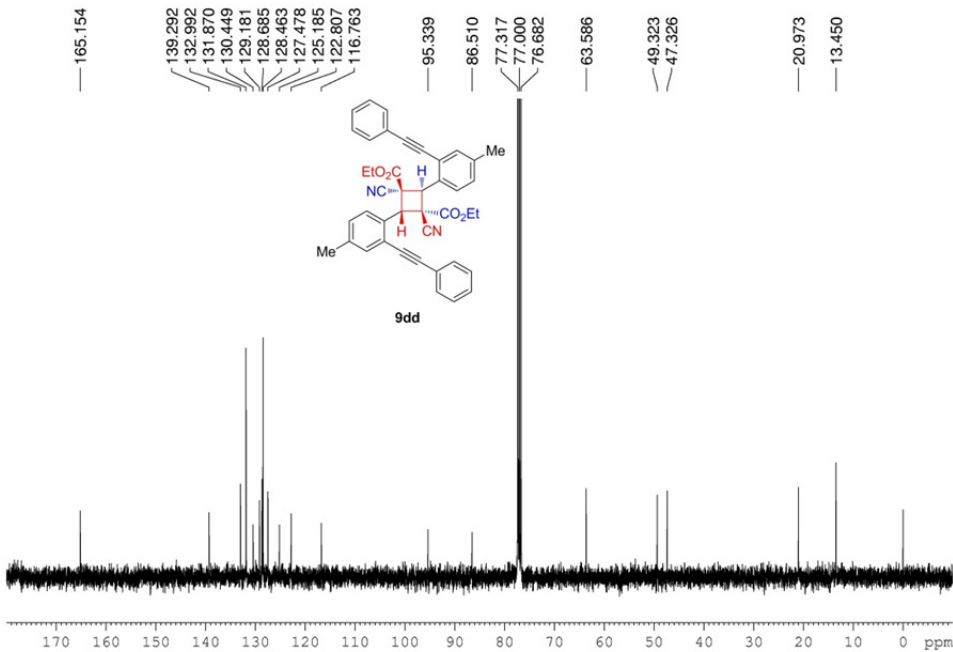
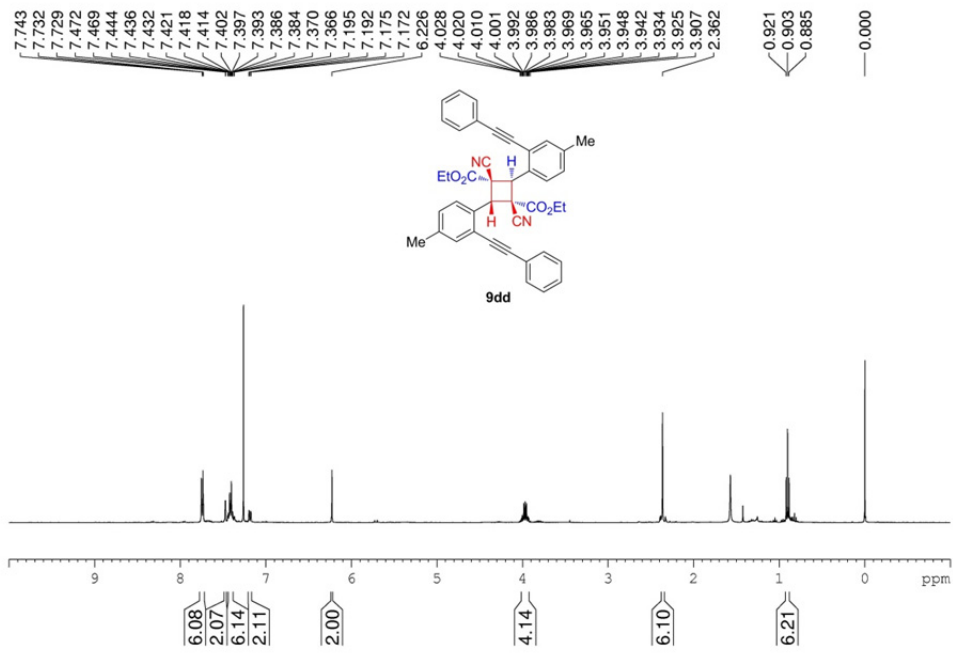




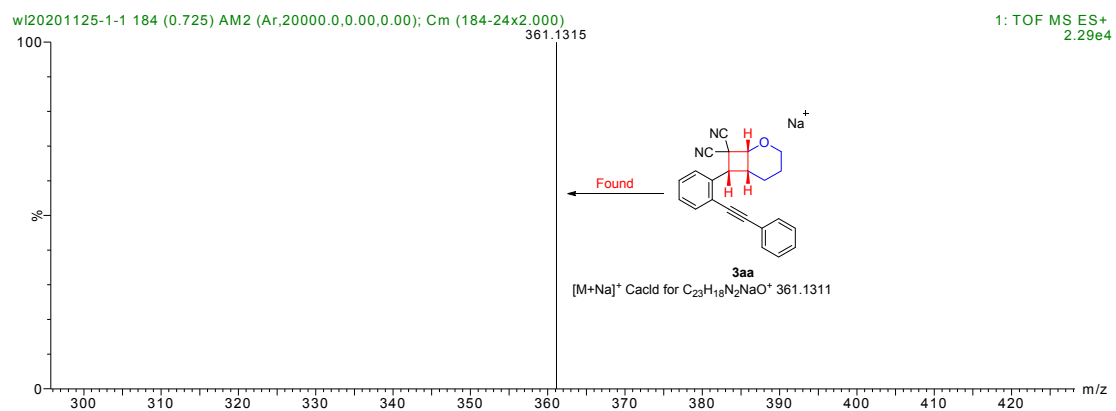
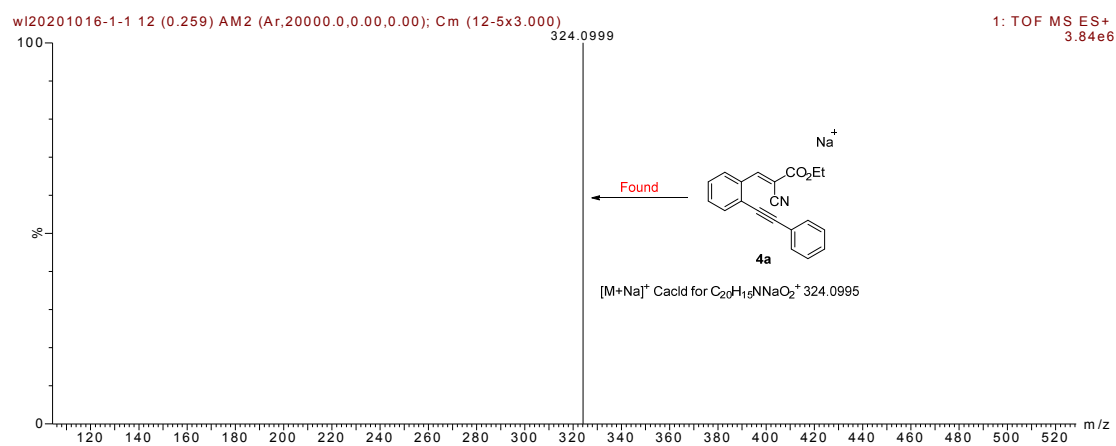
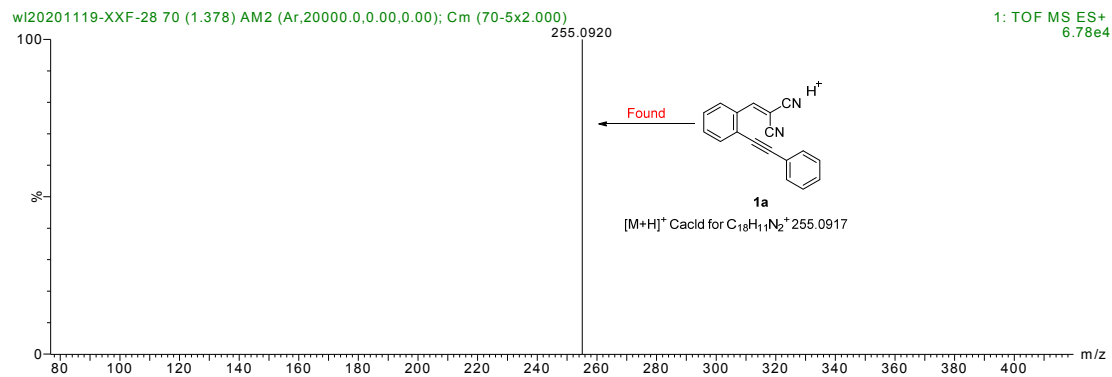


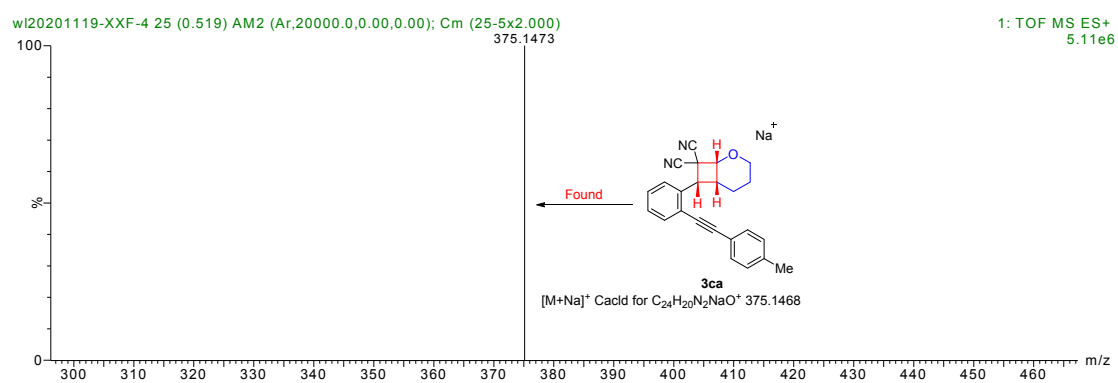
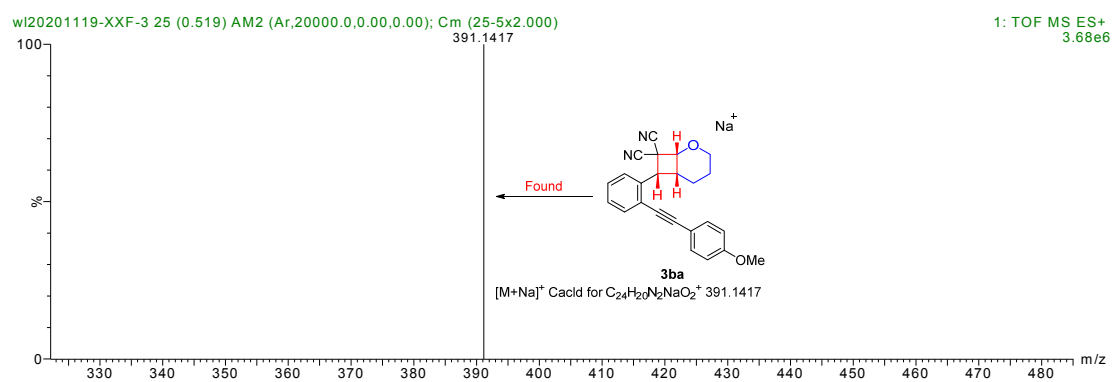
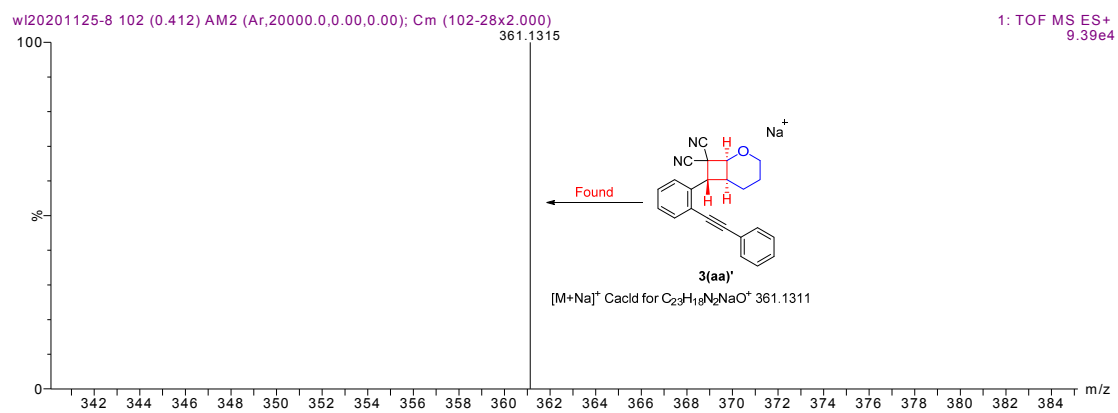


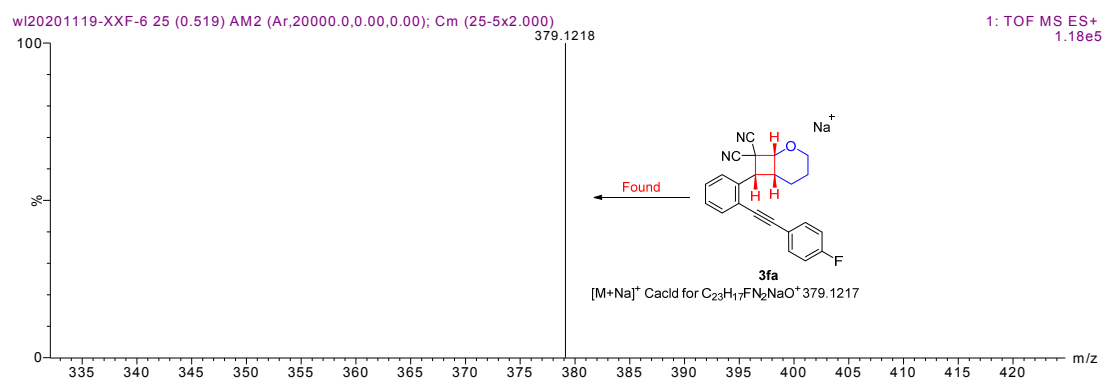
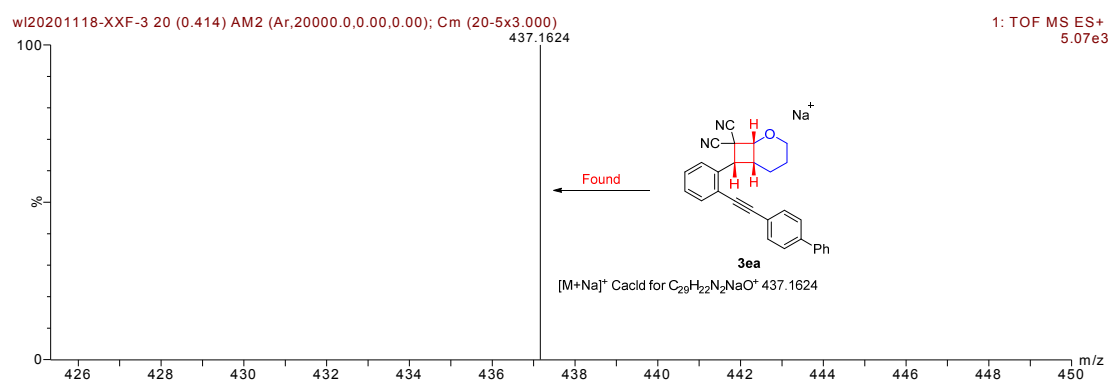
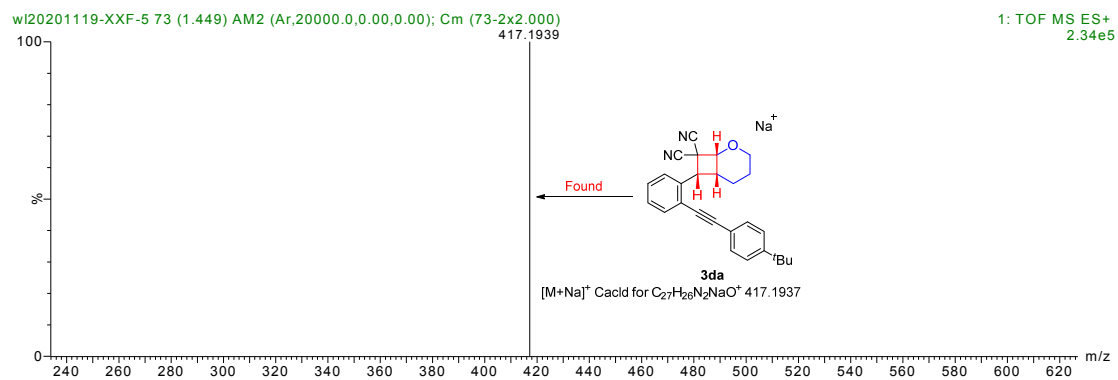


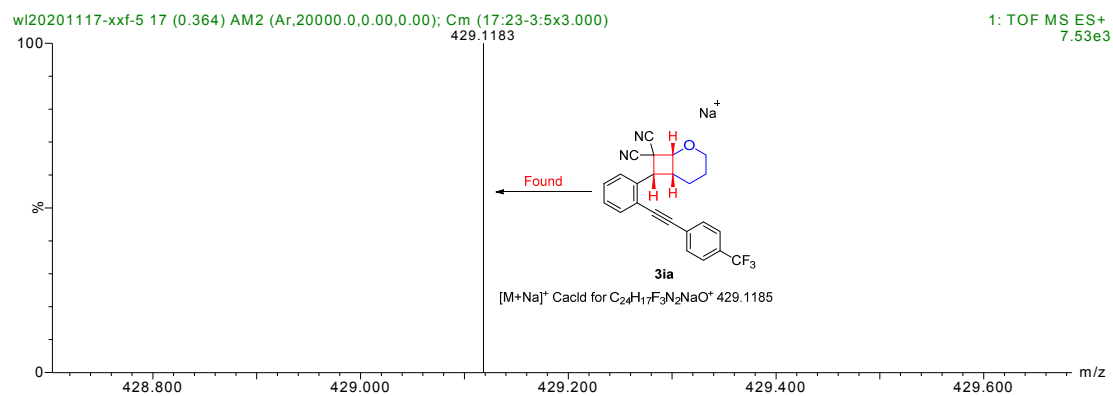
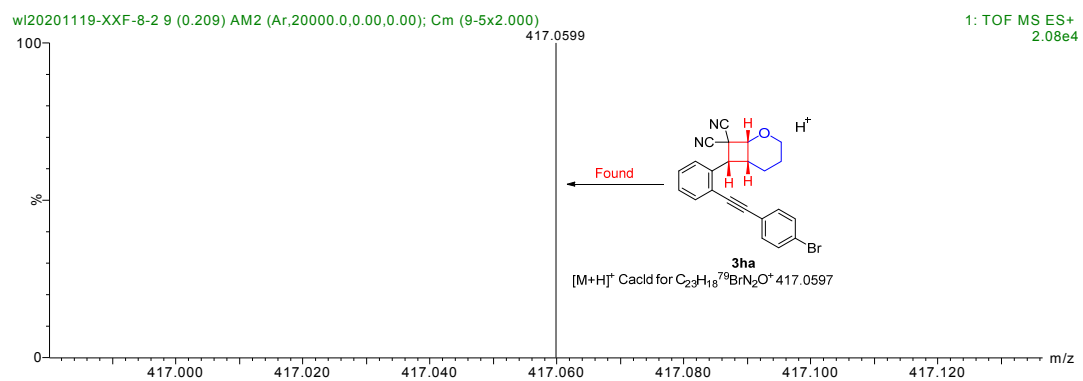
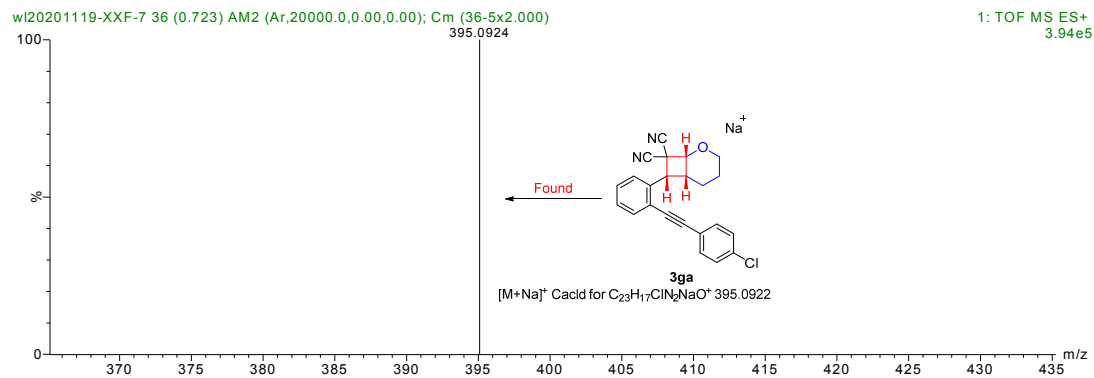


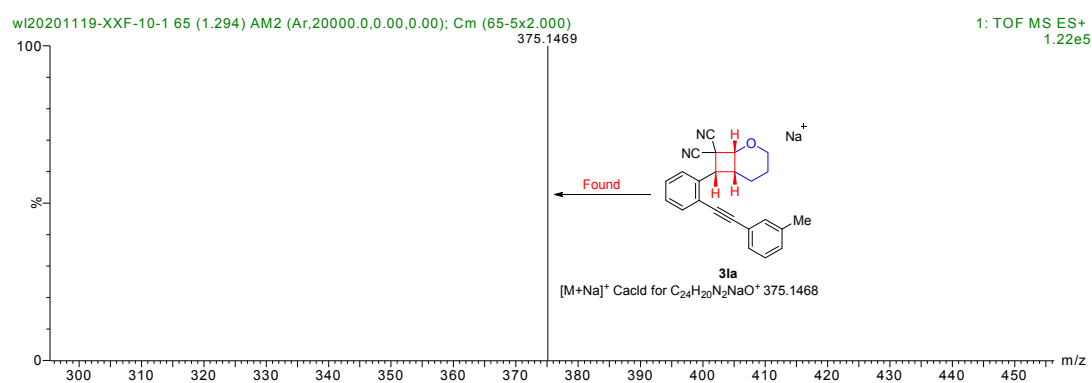
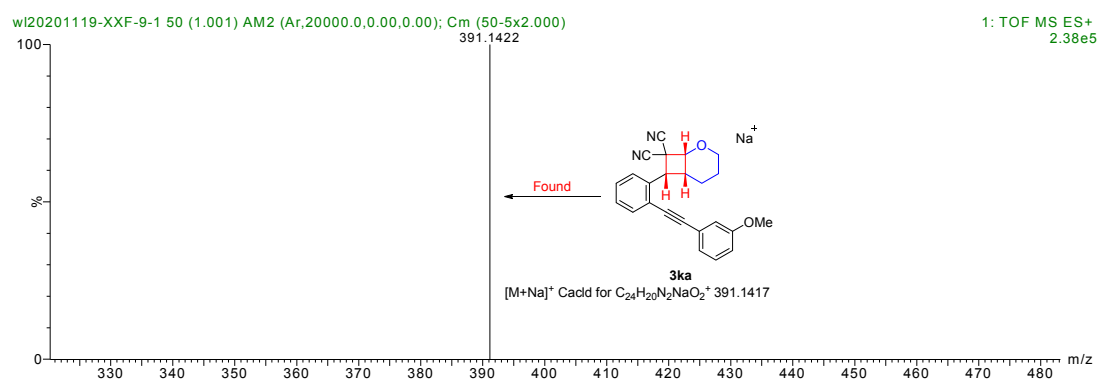
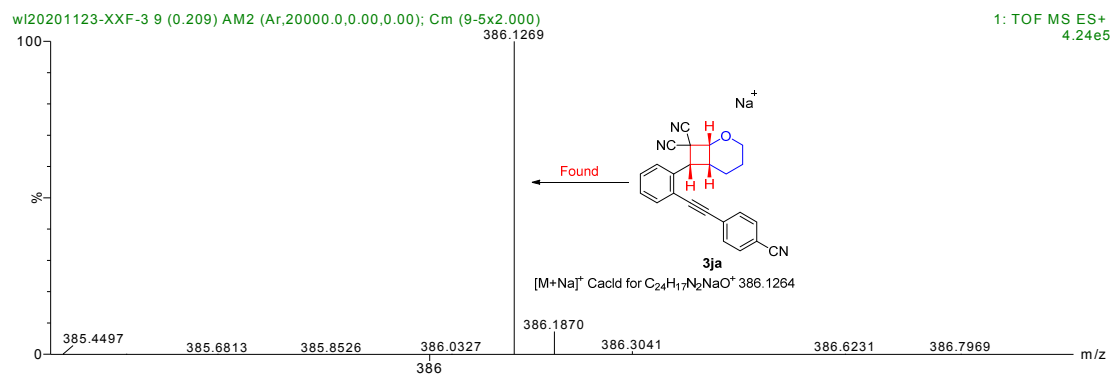
10. HRMS spectra for the products

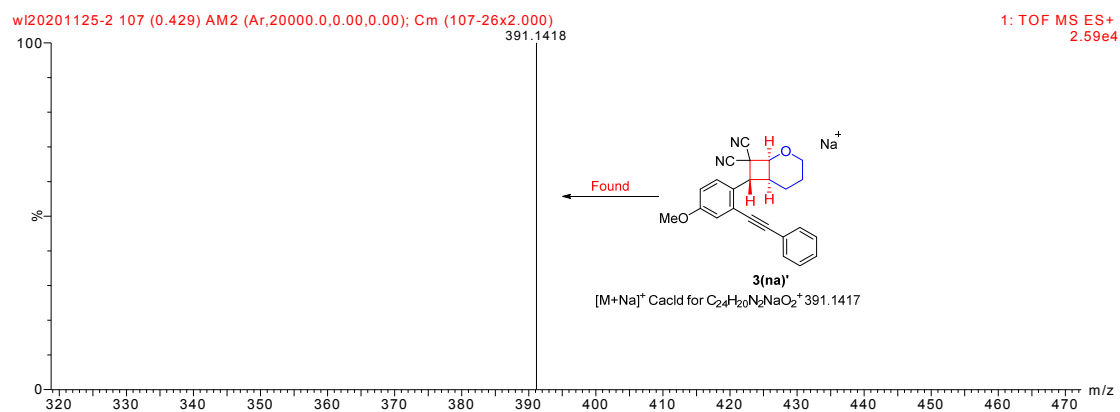
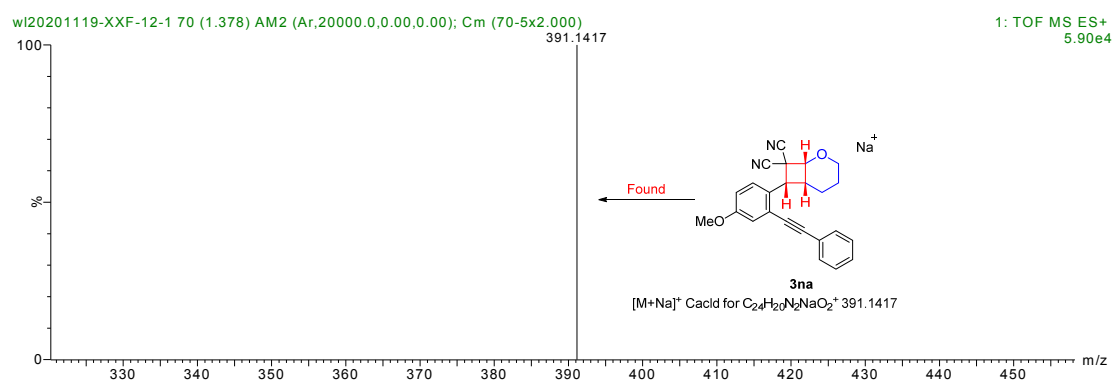
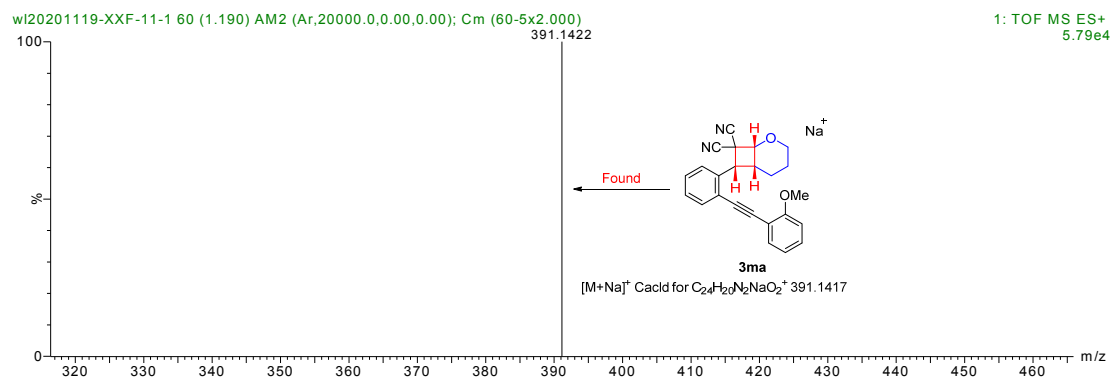


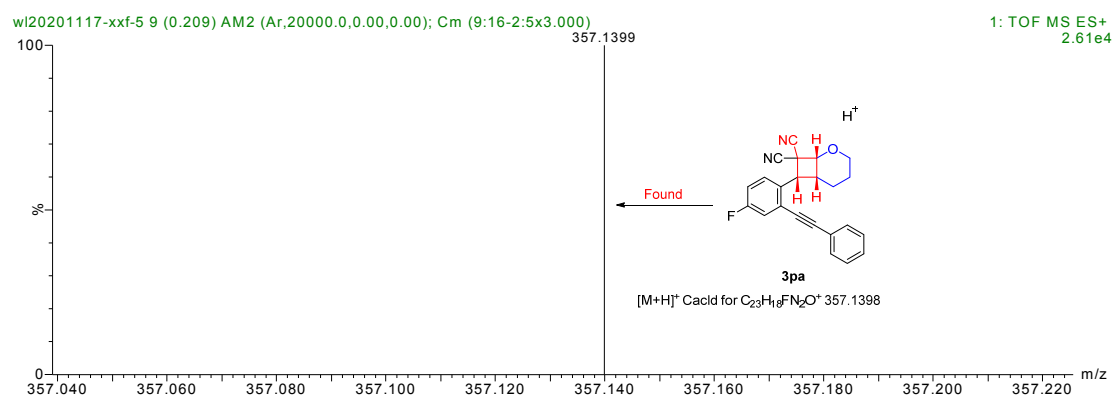
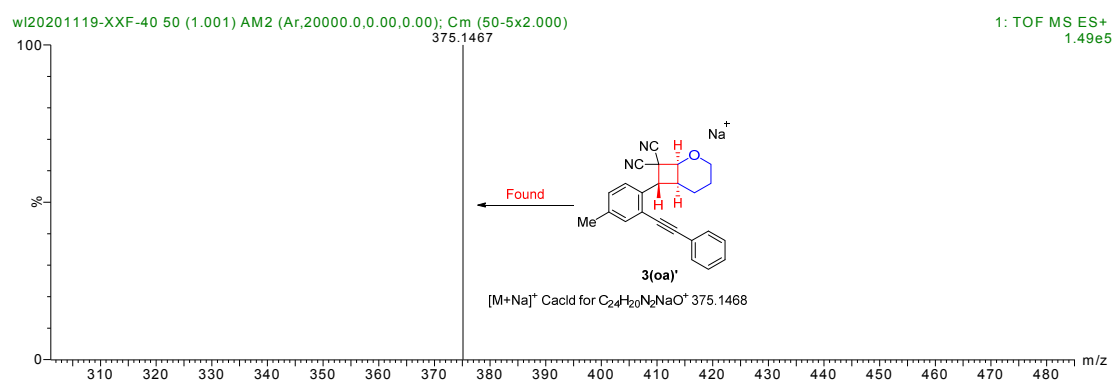
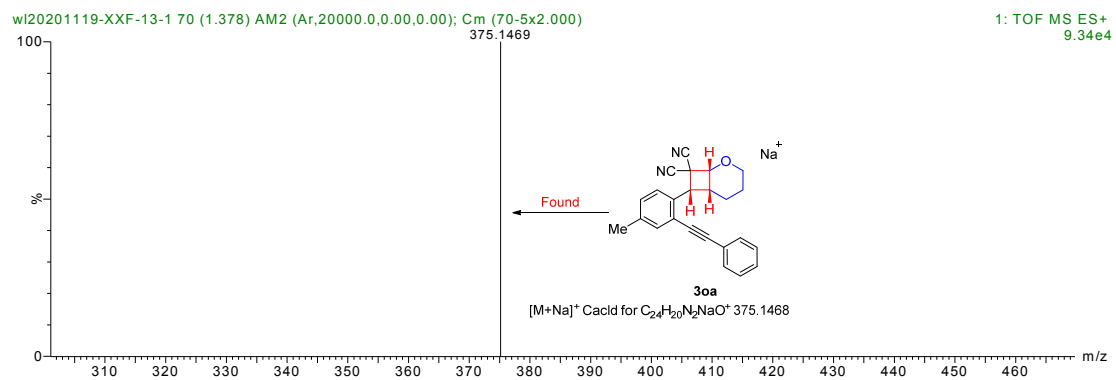


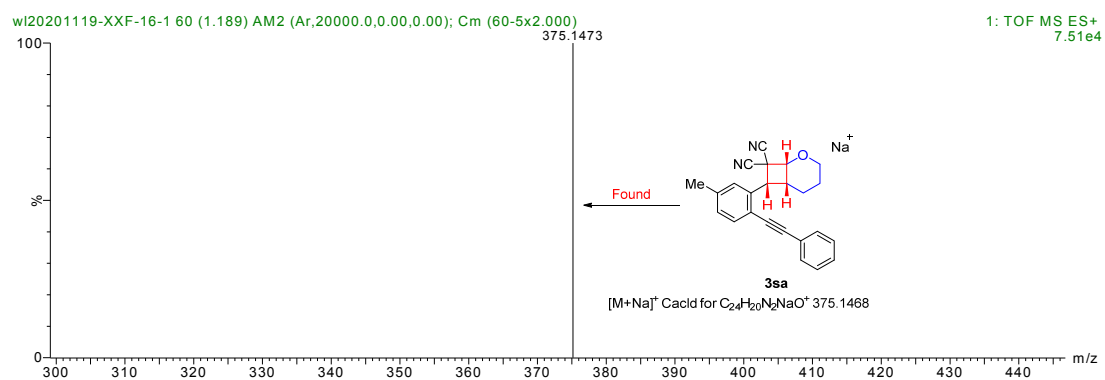
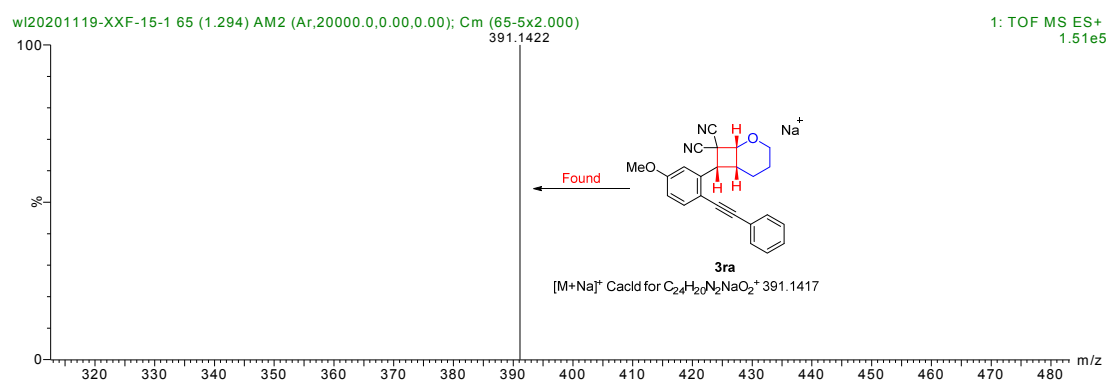
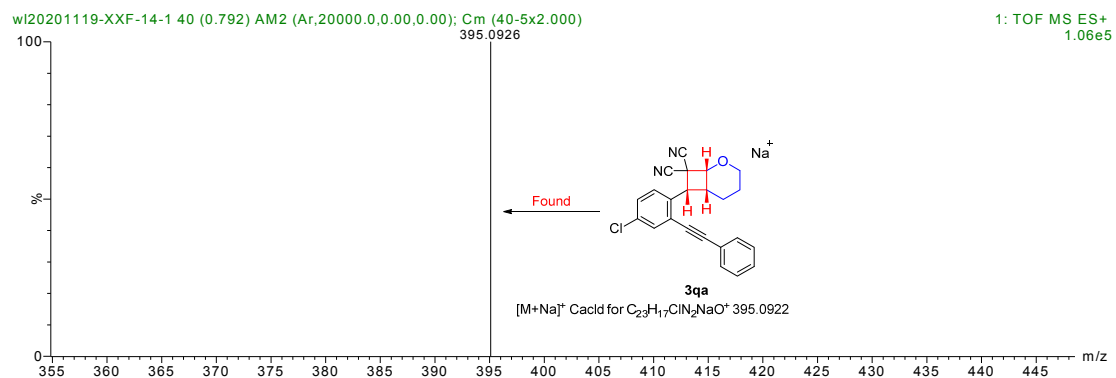


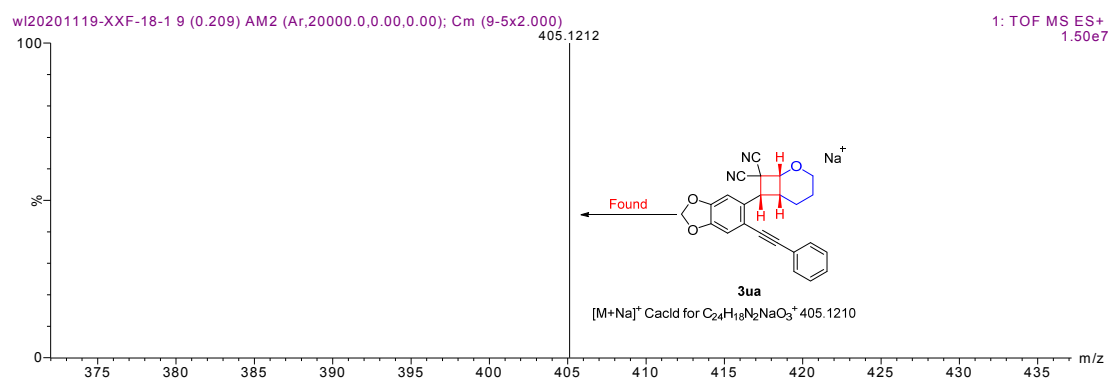
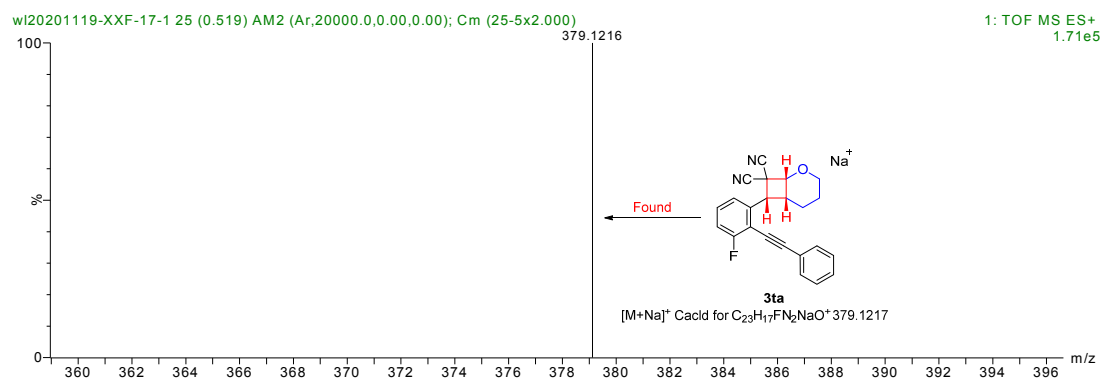
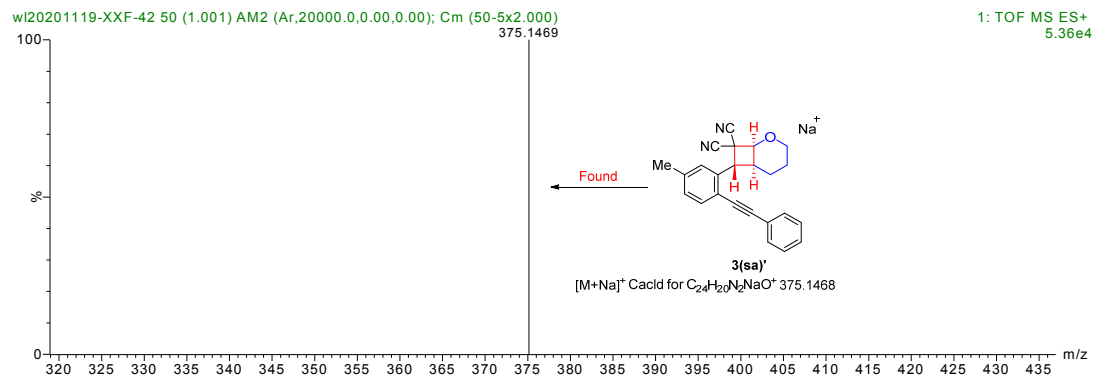


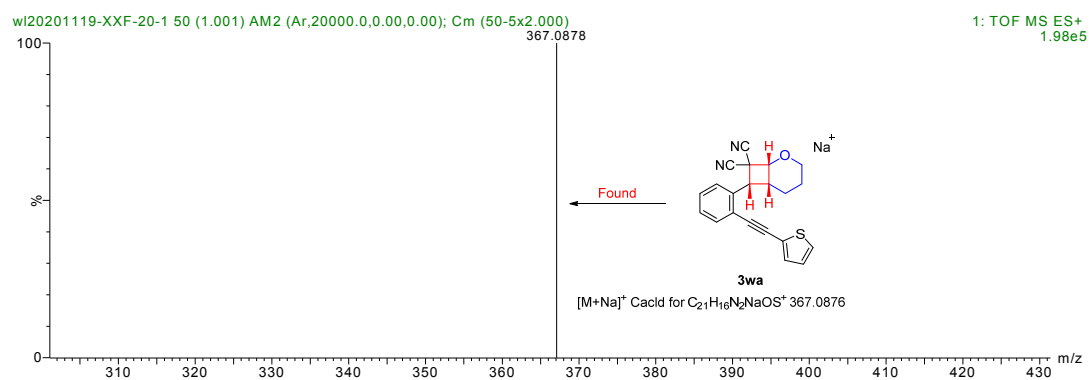
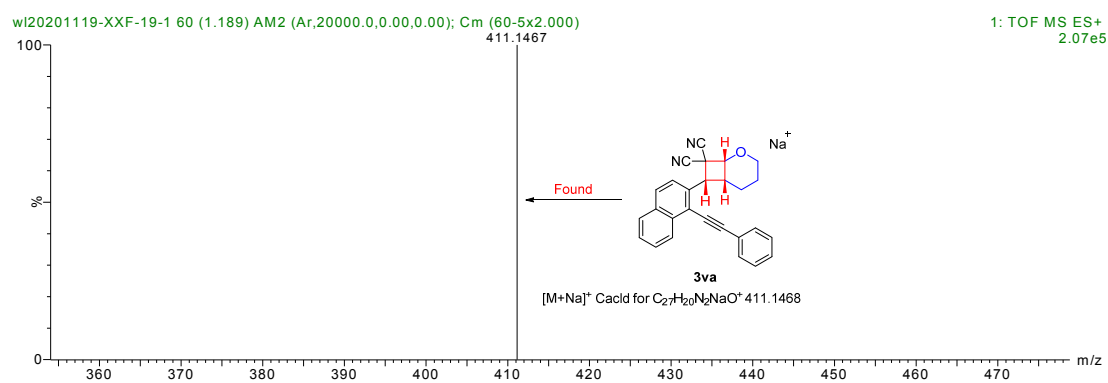
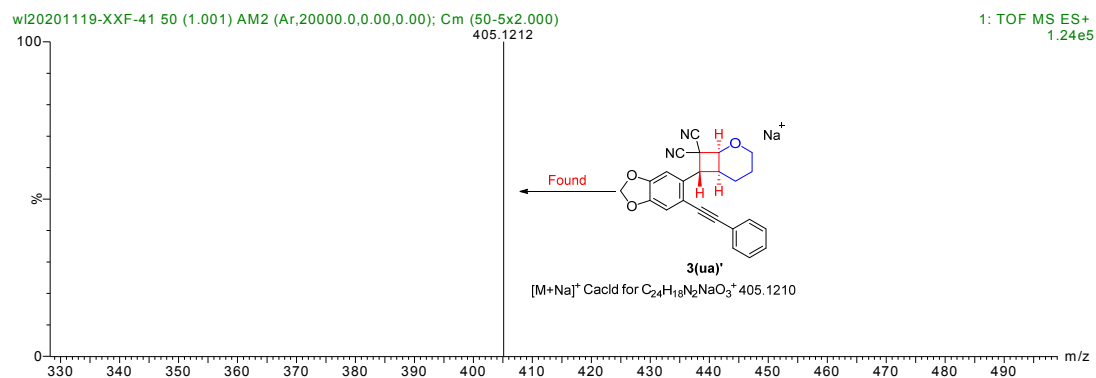


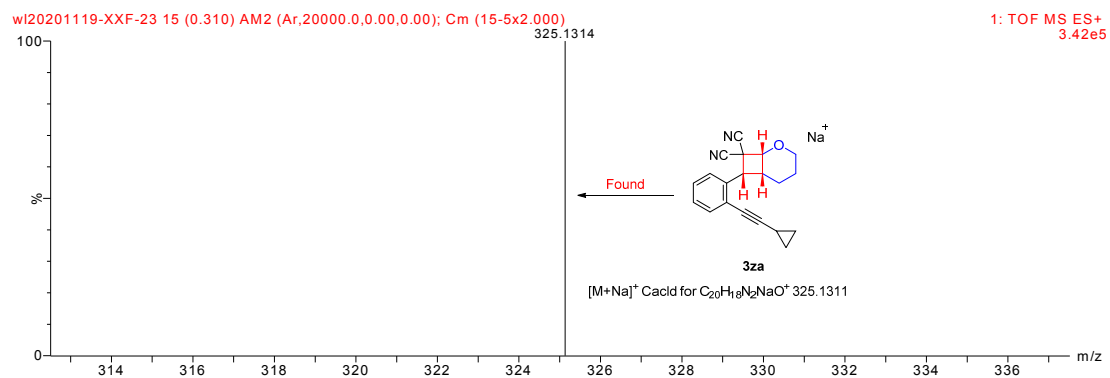
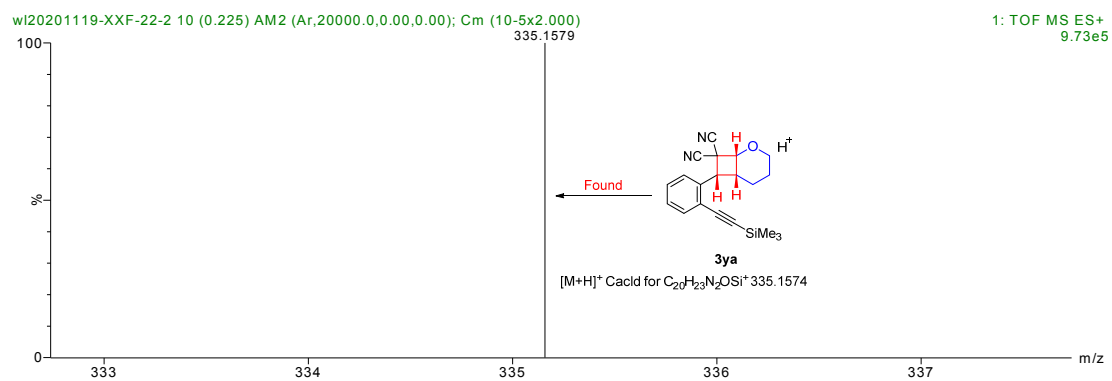
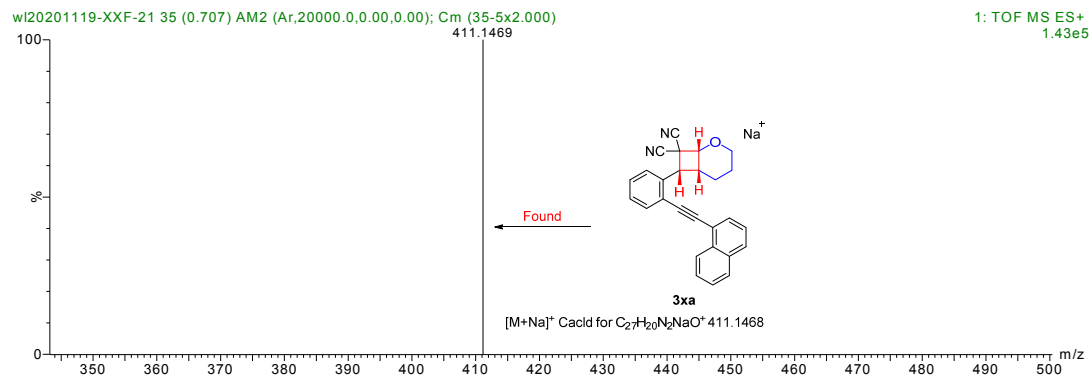


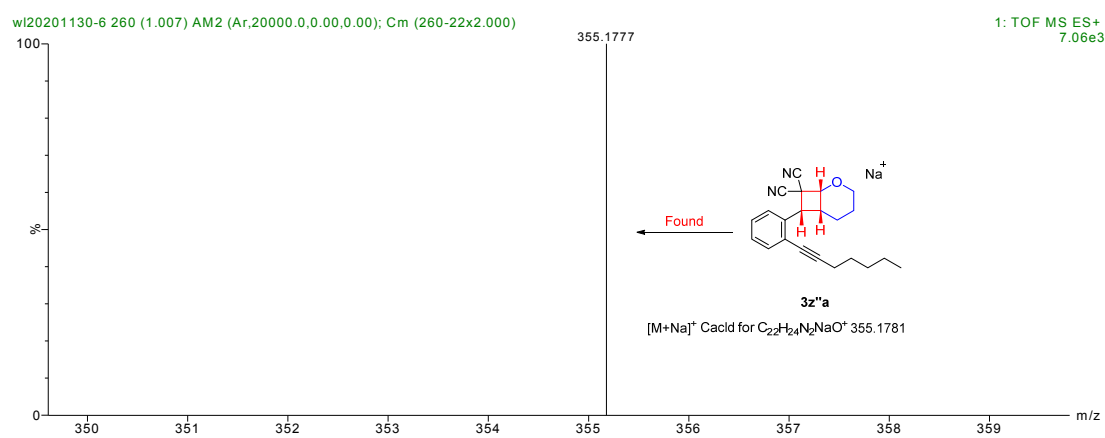
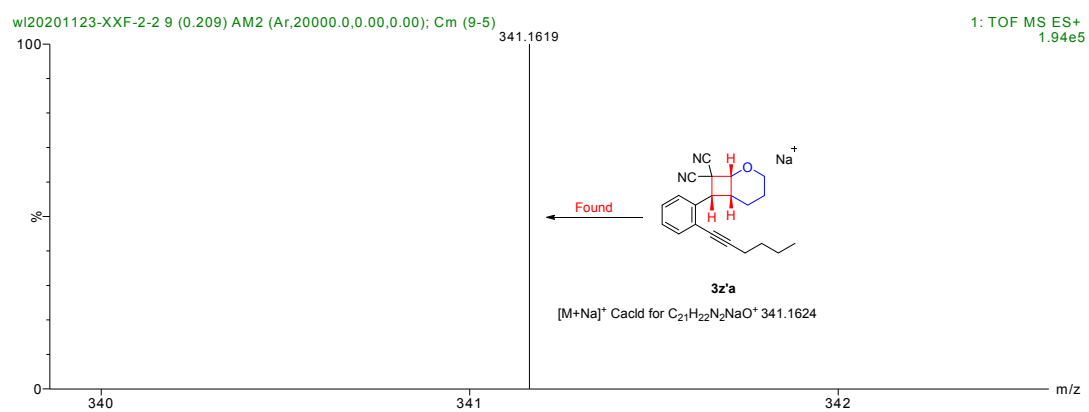
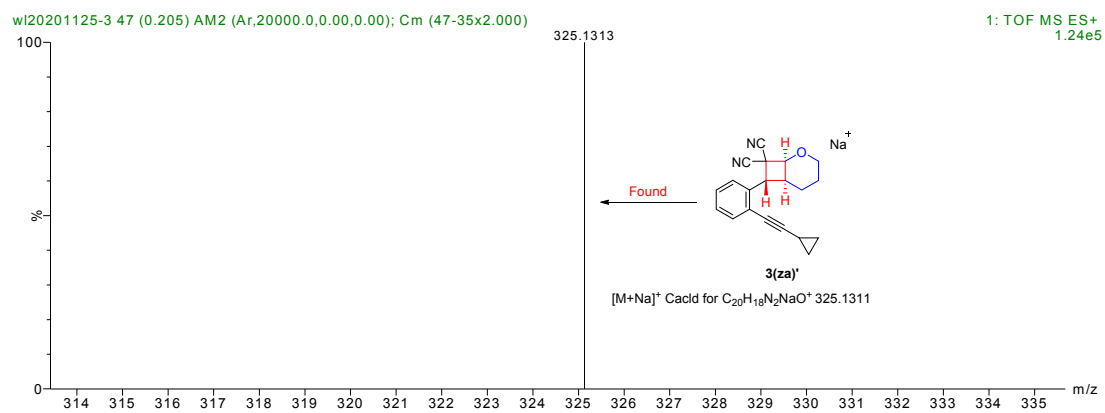


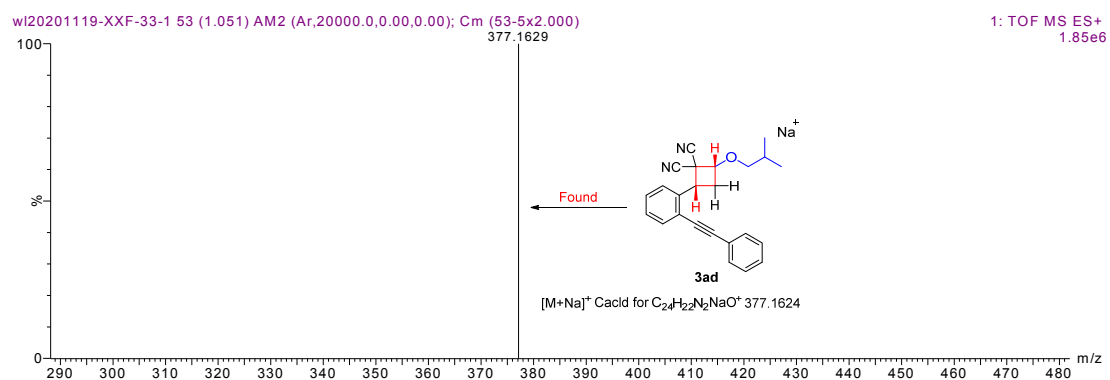
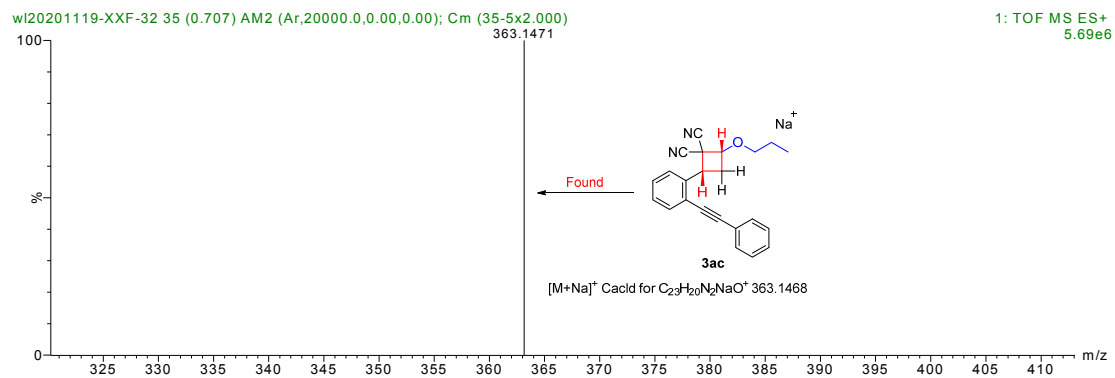
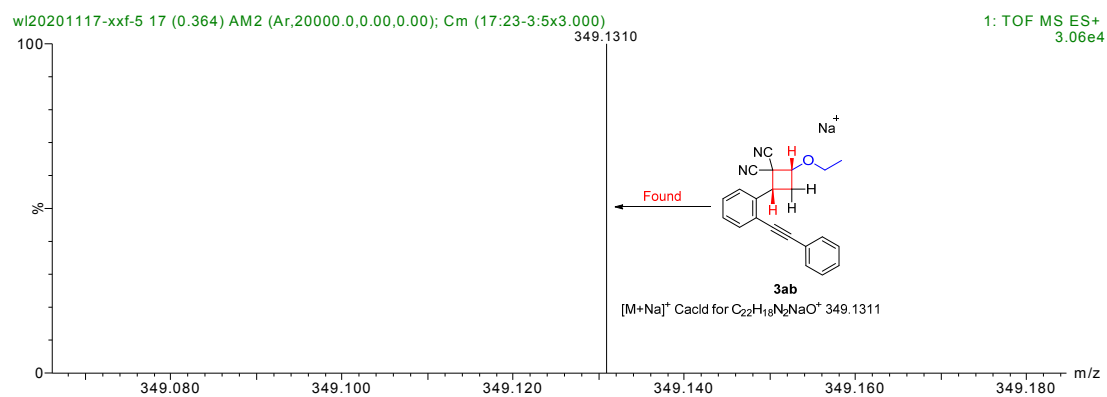


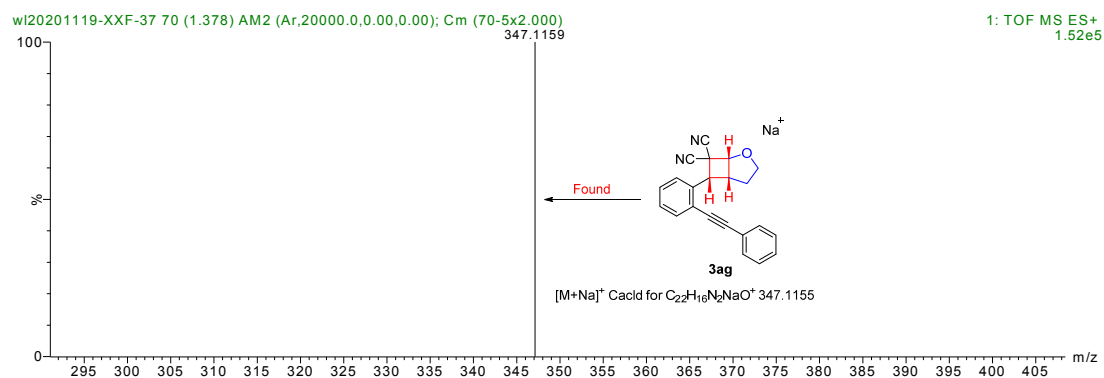
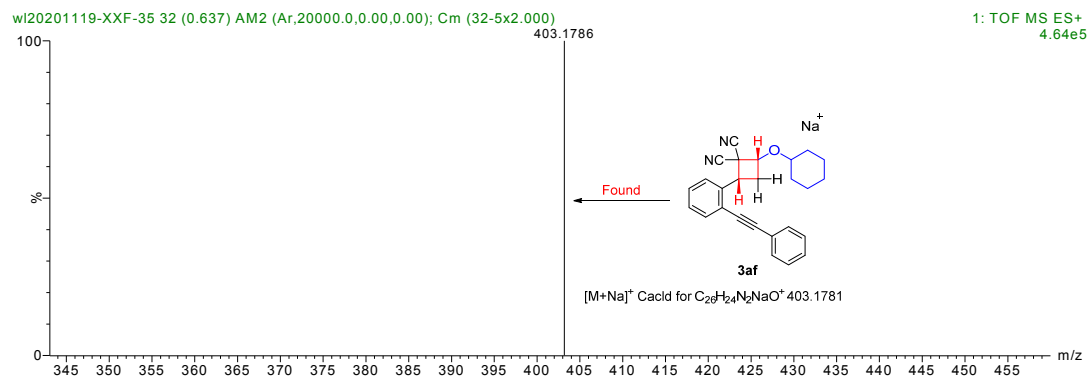
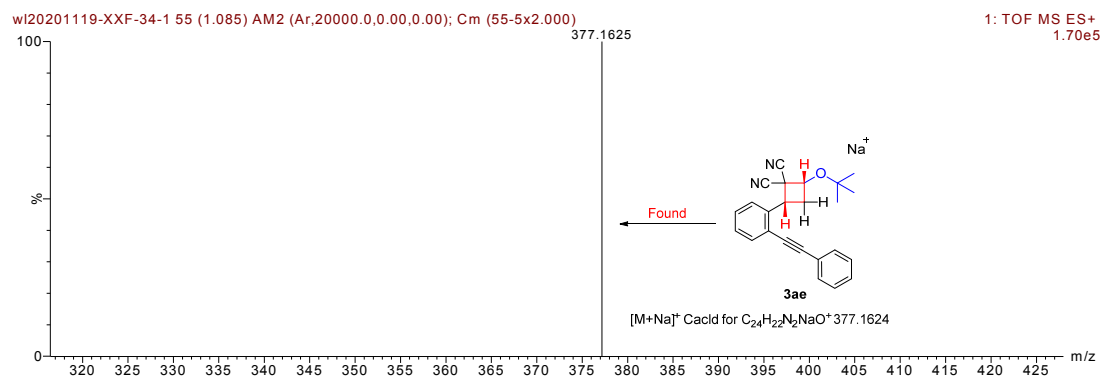


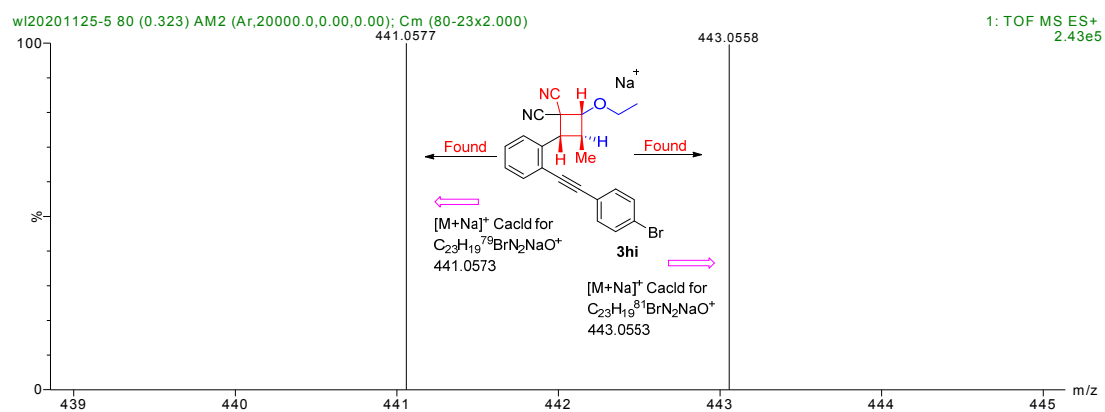
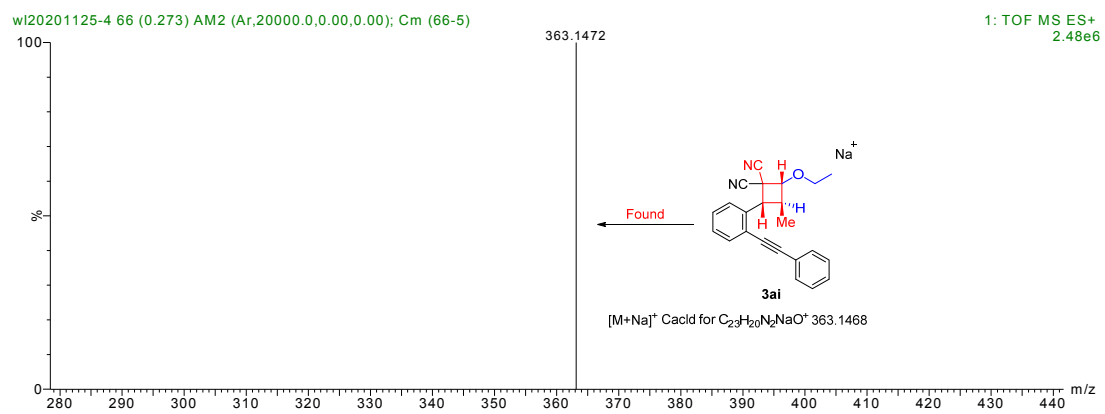
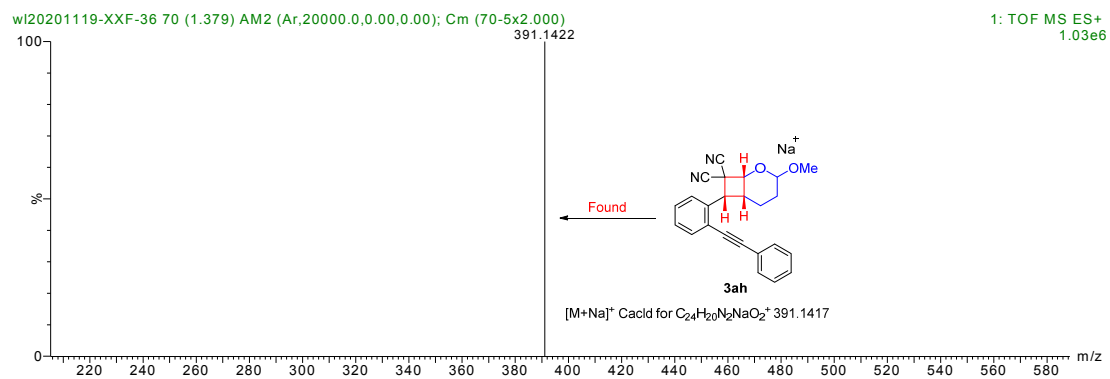


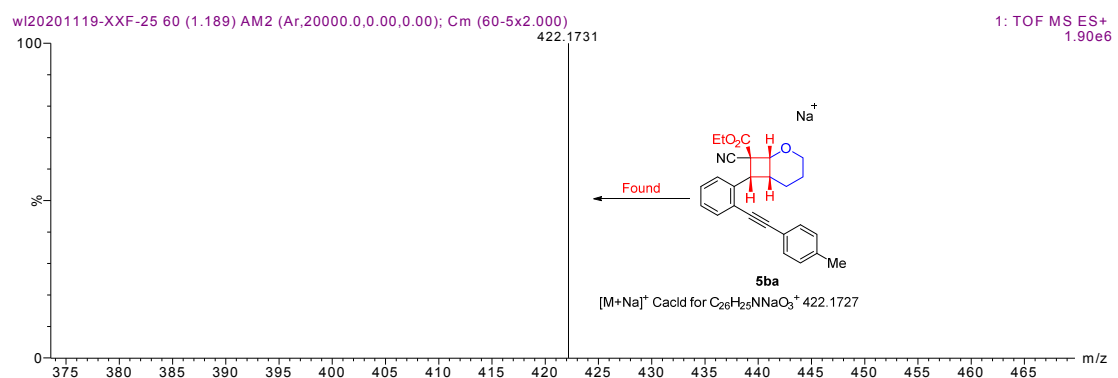
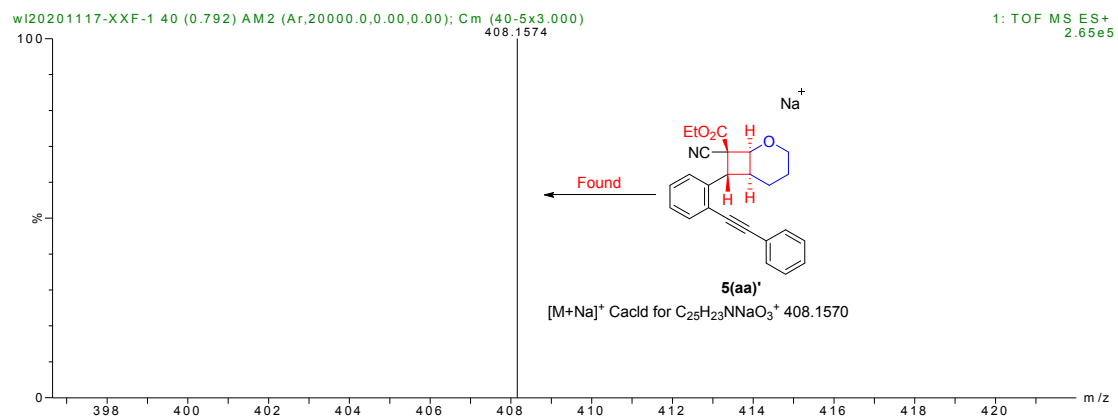
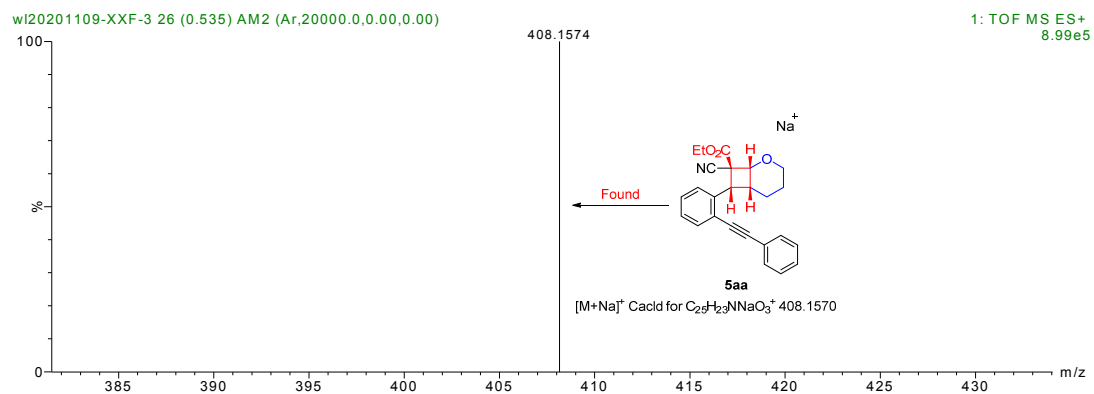


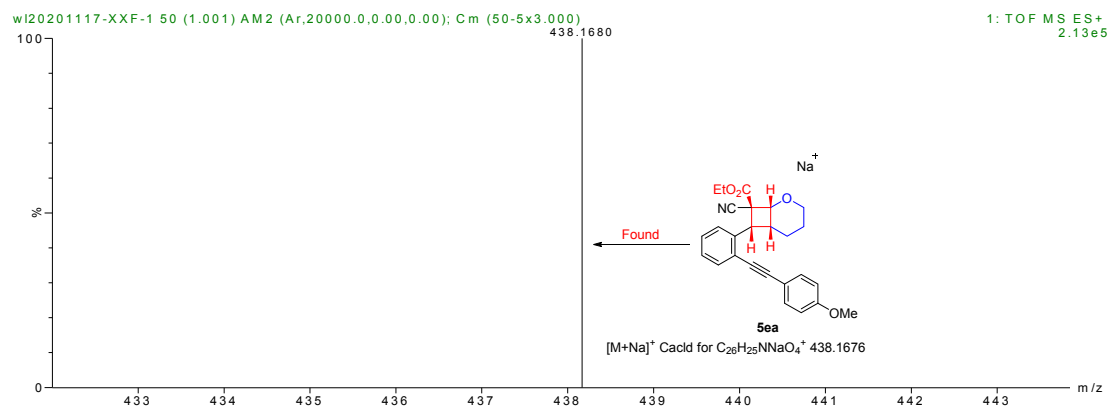
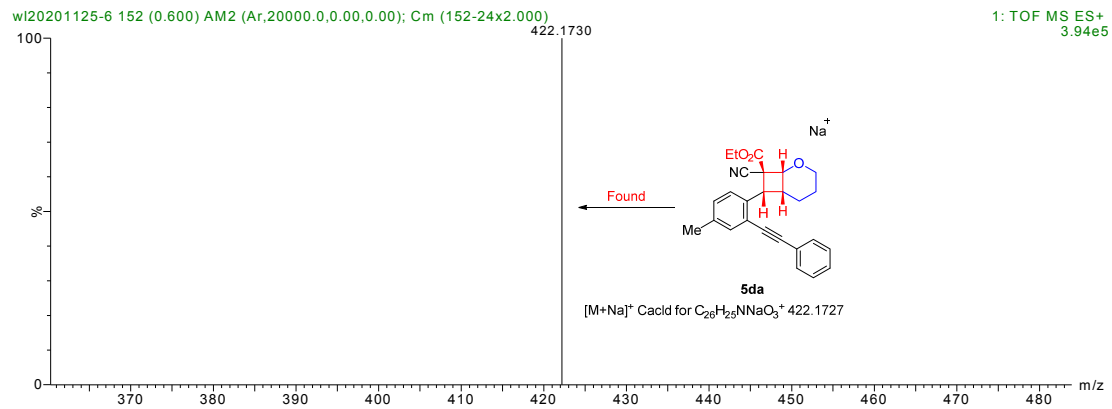
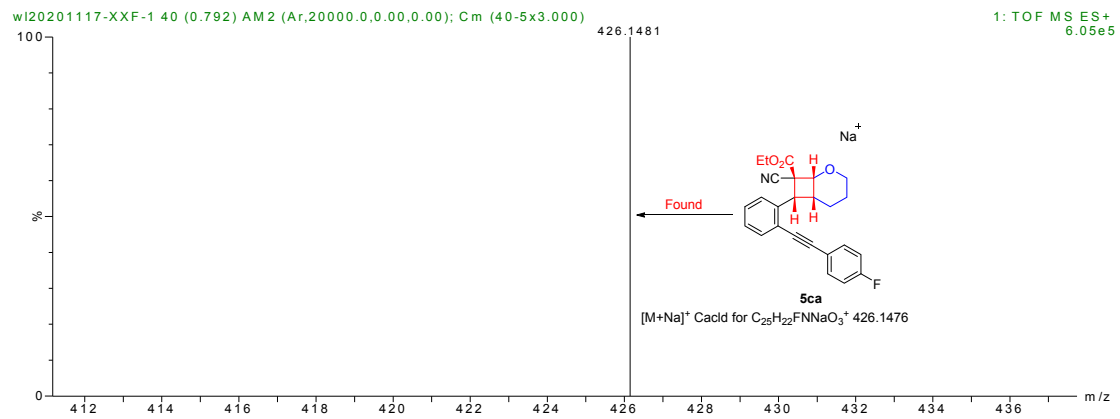


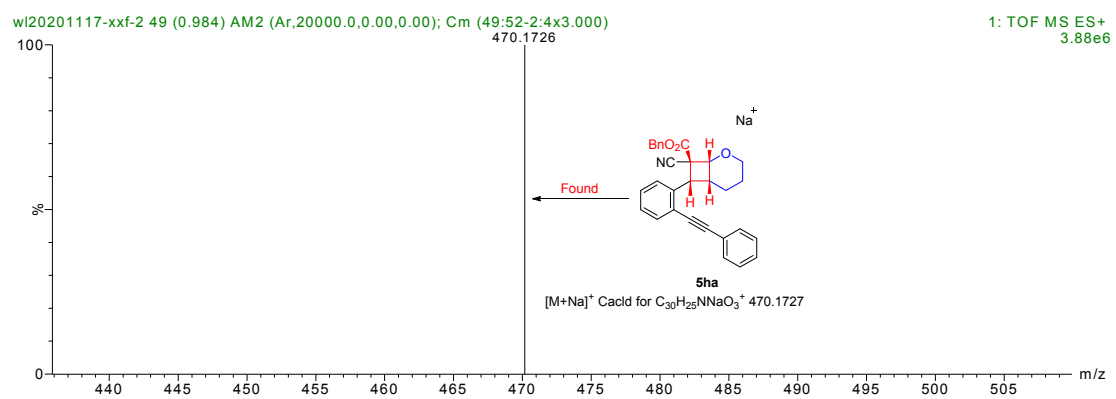
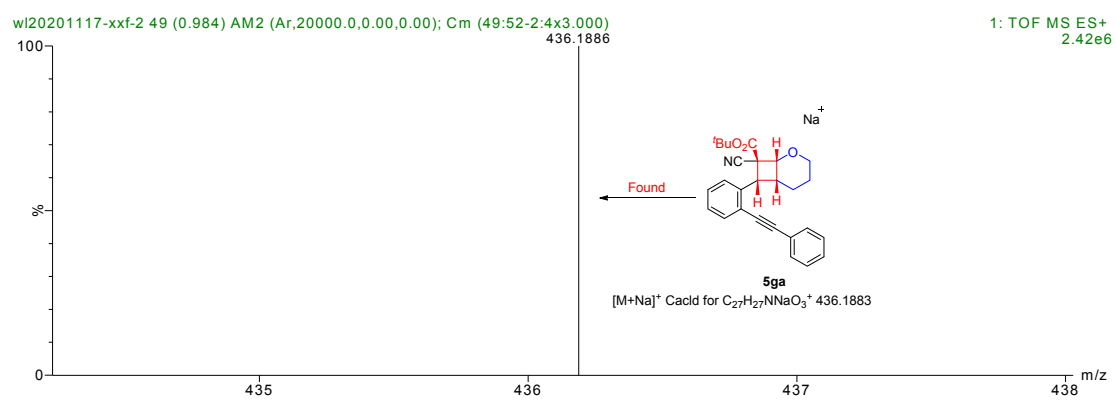
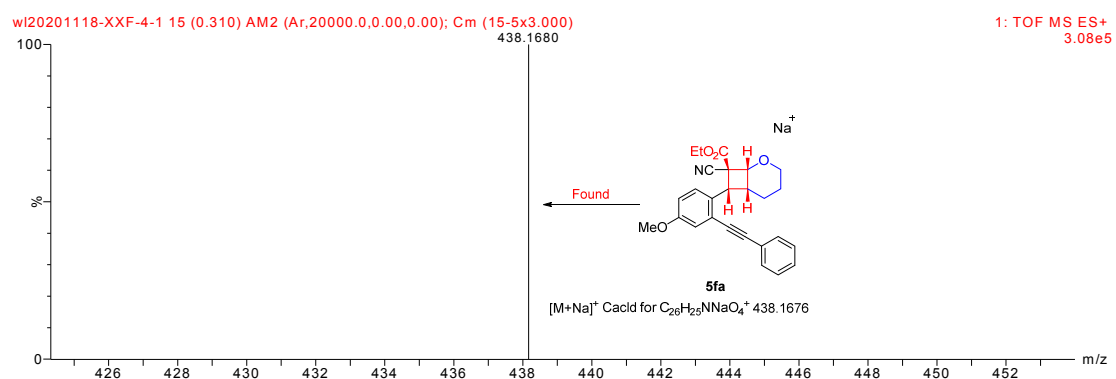






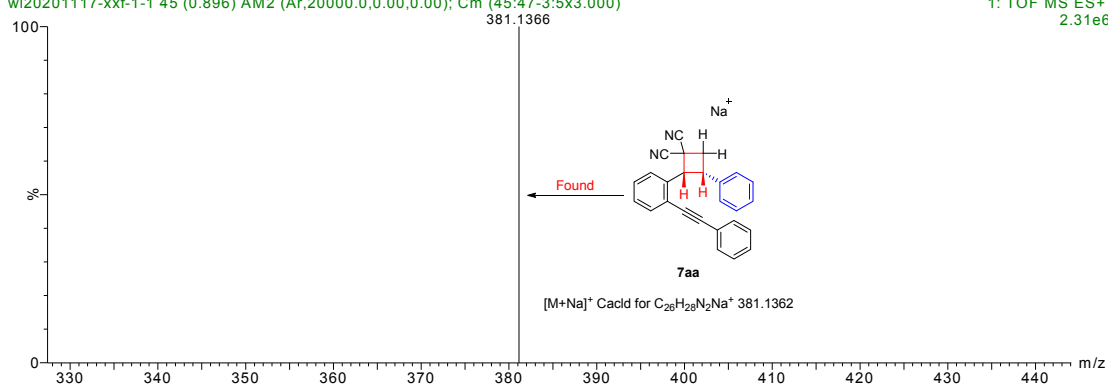






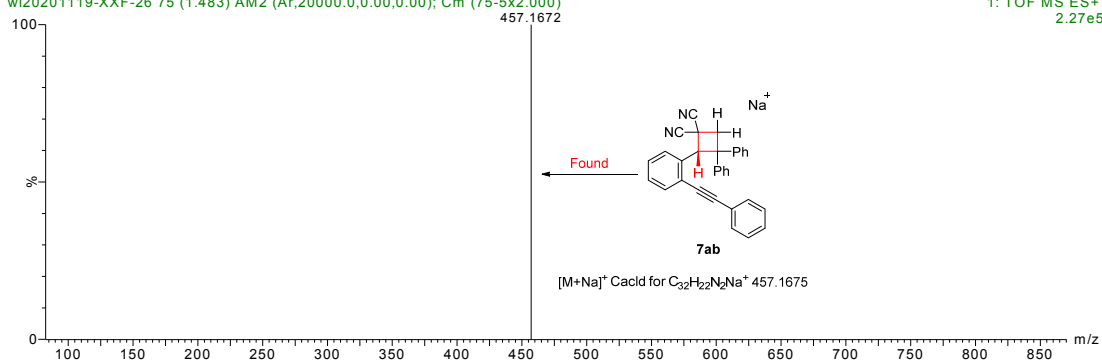
wI20201117-xxf-1-1 45 (0.896) AM2 (Ar,20000.0,0.00,0.00); Cm (45:47-3:5x3.000)

1: TOF MS ES+
2.31e6



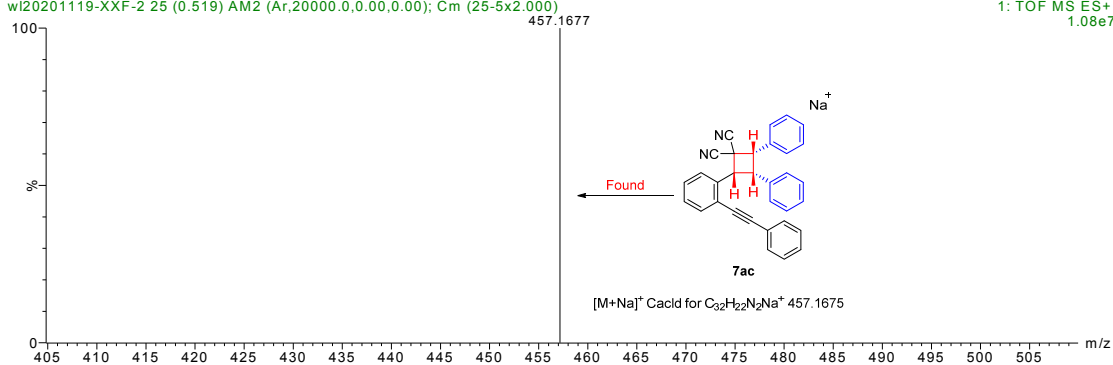
wI20201119-XXF-26 75 (1.483) AM2 (Ar,20000.0,0.00,0.00); Cm (75-5x2.000)

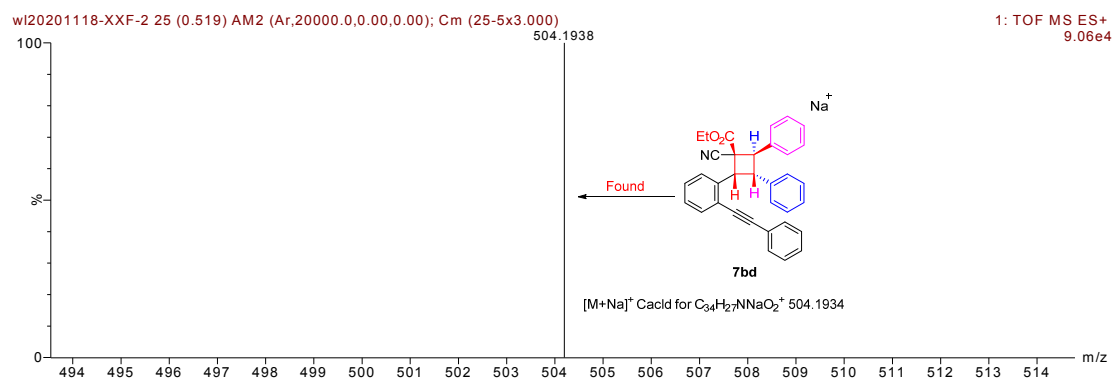
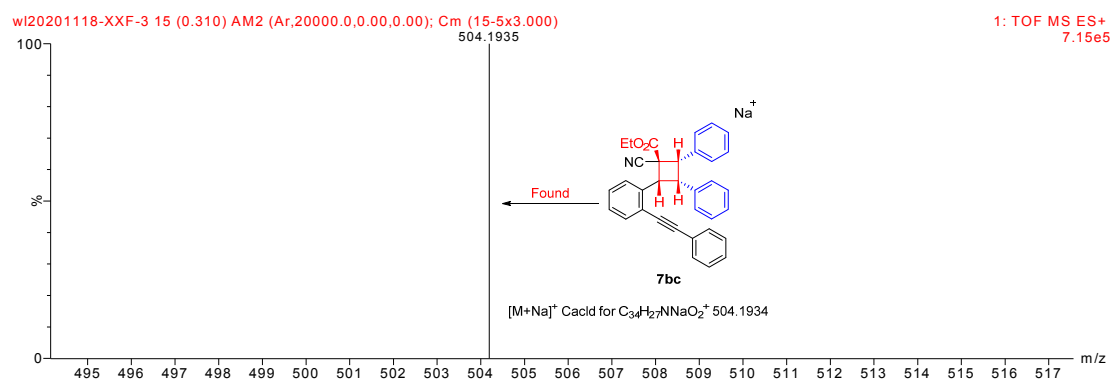
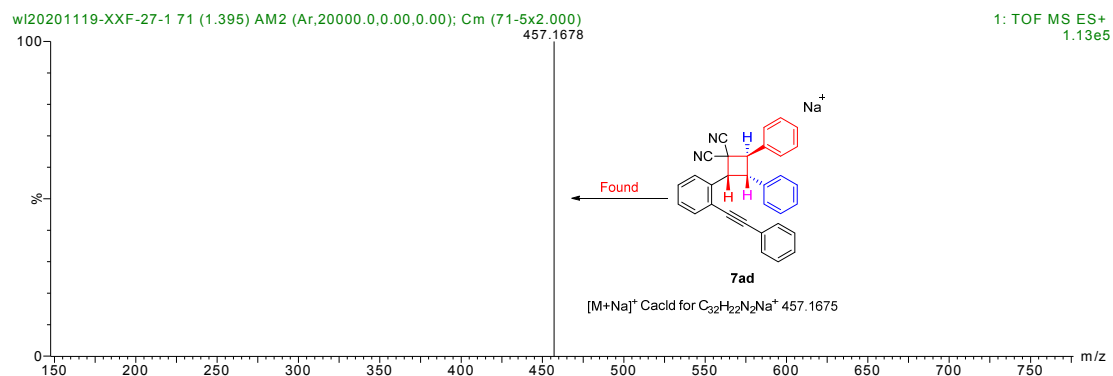
1: TOF MS ES+
2.27e5

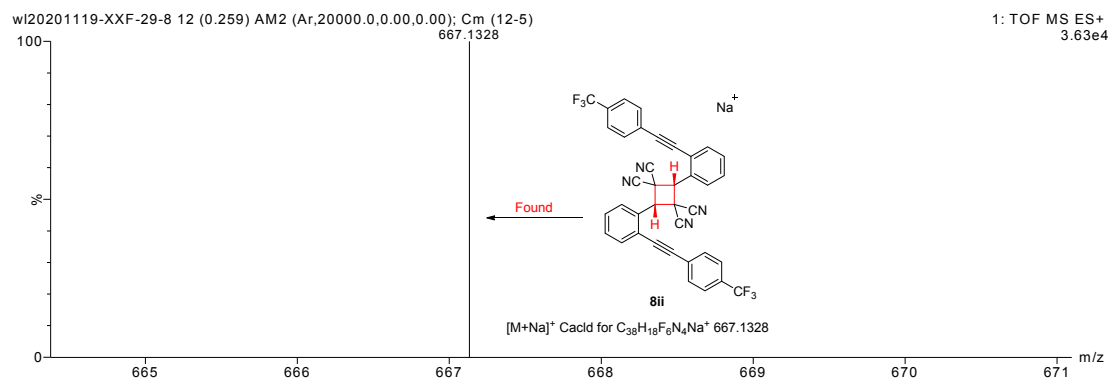
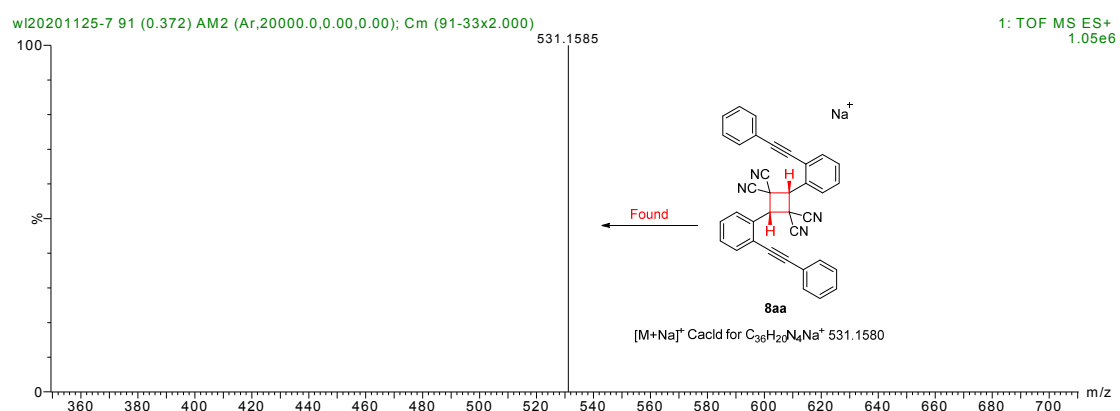
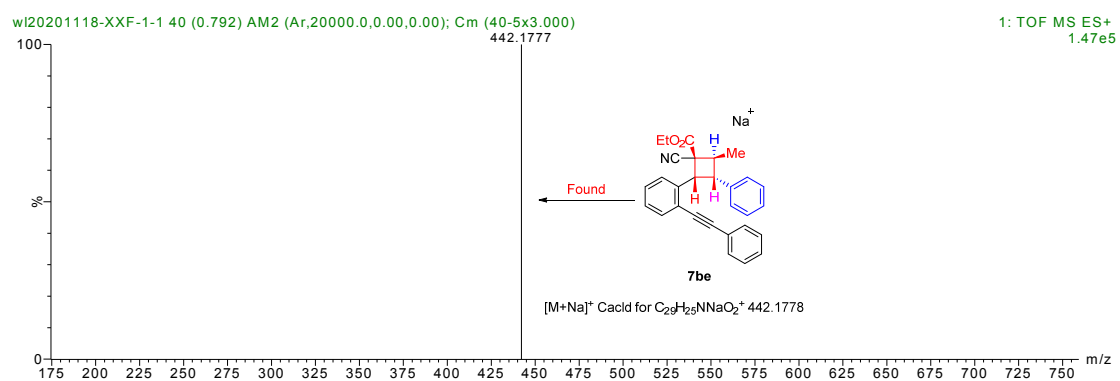


wI20201119-XXF-2 25 (0.519) AM2 (Ar,20000.0,0.00,0.00); Cm (25-5x2.000)

1: TOF MS ES+
1.08e7

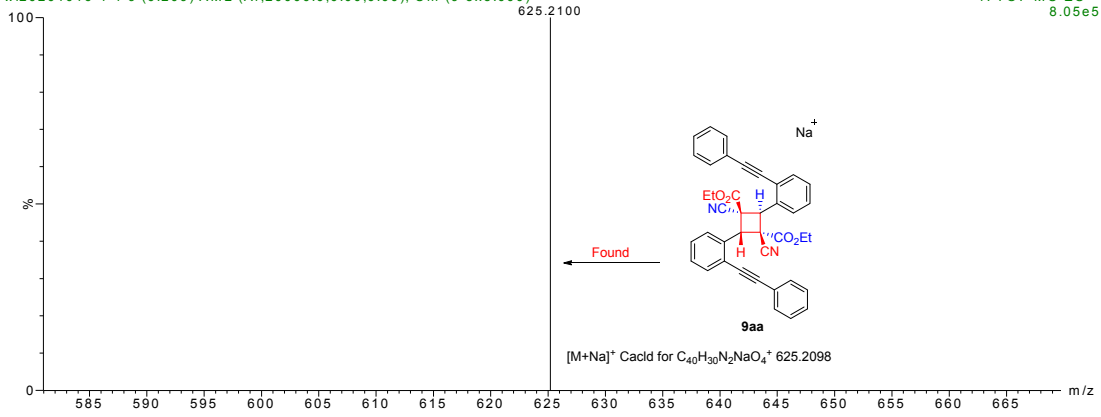






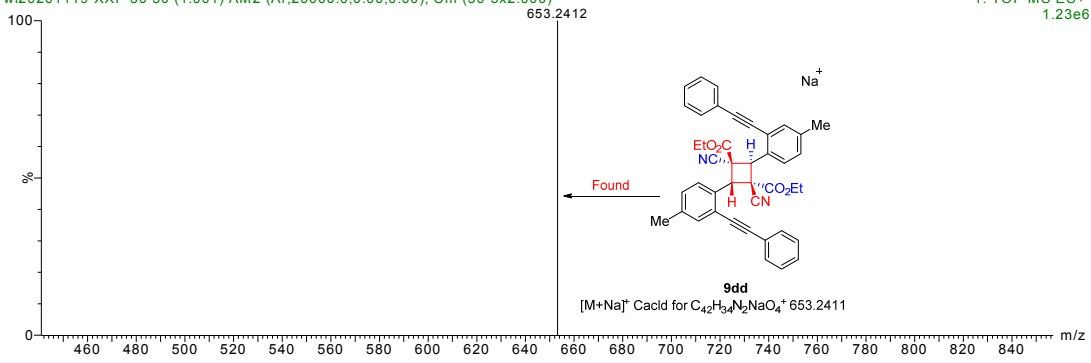
wi20201016-1-1 9 (0.209) AM2 (Ar,20000.0,0.00,0.00); Cm (9-5x3.000)

1: TOF MS ES+
8.05e5



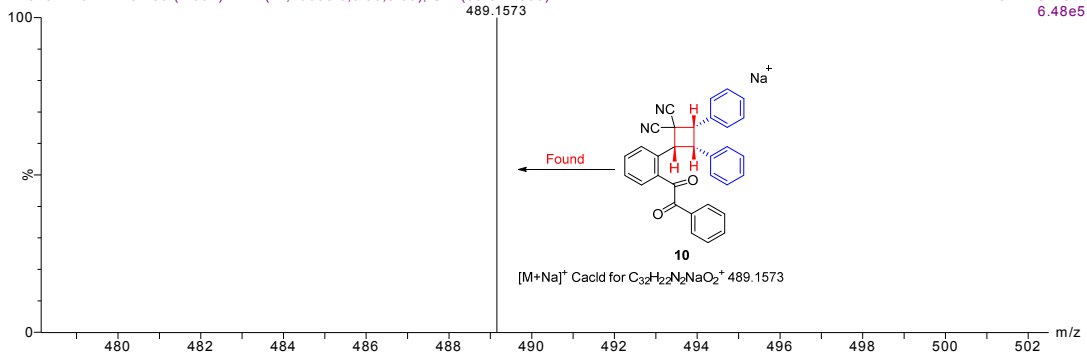
wi20201119-XXF-30 50 (1.001) AM2 (Ar,20000.0,0.00,0.00); Cm (50-5x2.000)

1: TOF MS ES+
1.23e6



wi20201119-XXF-31 50 (1.001) AM2 (Ar,20000.0,0.00,0.00); Cm (50-5x2.000)

1: TOF MS ES+
6.48e5



wi20200814-2 50 (1.001) AM2 (Ar,20000.0,0.00,0.00); Cm (50-5x2.000)

1: TOF MS ES+
1.66e6

