

Supporting Information

A visible-light-induced “on-off” one-pot synthesis of 3-arylacetylene coumarins with AIE properties

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1. General information

All reactions were performed using quartz tube. Solvents were dried by standard methods before they were used. Aryl alkynoates were synthesized according to the literature.¹ Commercial grade reagents were used without further purification. Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. All reactions were carried out with photoreactor (Serial No: PEA12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro+ and Digital Single Channel Adjustable Automatic Electronic Pipette Micropipette dPetee+ were purchased from Dragon Laboratory Instruments Limited. ¹H NMR and ¹³C NMR spectra were recorded on 400 and 100 MHz NMR instruments using CDCl₃ as the solvent and TMS as the internal standard. ¹⁹F NMR spectra was recorded at 376.5 MHz on Bruker DPX-400, the chemical shifts δ are reported relative to CFC₃ ($\delta = 0$ ppm) as internal standard. The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet. High resolution mass spectra (HRMS) was obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV/Vis absorption spectra was recorded on a Perkin Elmer Lambda 35 Spectrometer, and the fluorescence emission was recorded using a F-4500 FL spectrophotometer, the solid fluorescence quantum yield spectra was recorded on a C13534 UV-NIR absolute PL Quantum Yield Spectrometer.

2. UV/Vis absorption spectra, fluorescence emission spectra, measurement and calculation of fluorescence quantum yield

1) UV/Vis absorption spectra

The UV/Vis absorption spectra was recorded in MeCN of a 0.05 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

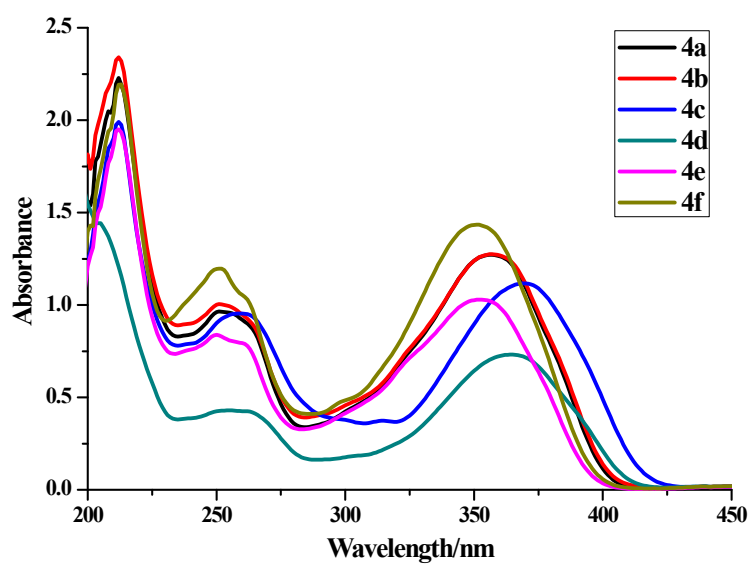


Figure S1. Absorption spectra of 4a-f in MeCN

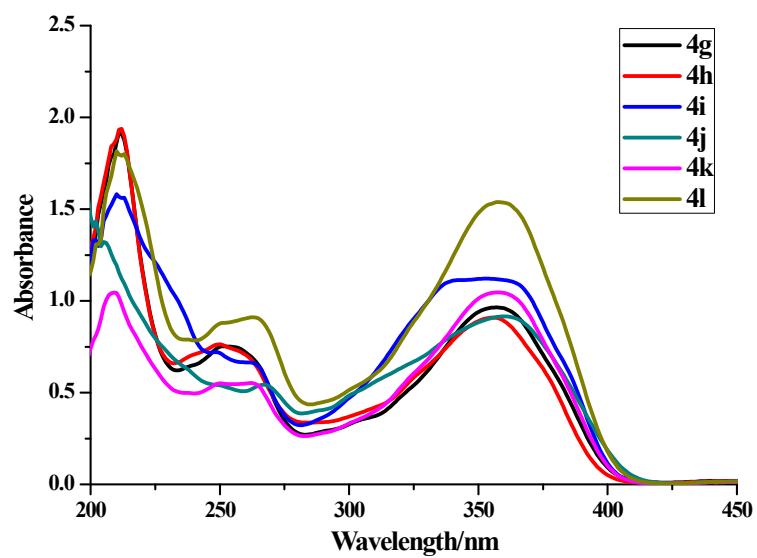


Figure S2. Absorption spectra of 4g-l in MeCN

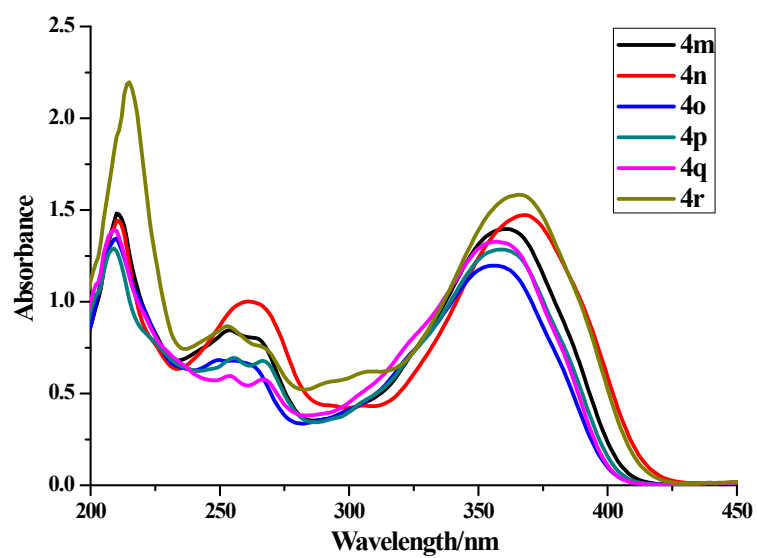


Figure S3. Absorption spectra of **4m-r** in MeCN

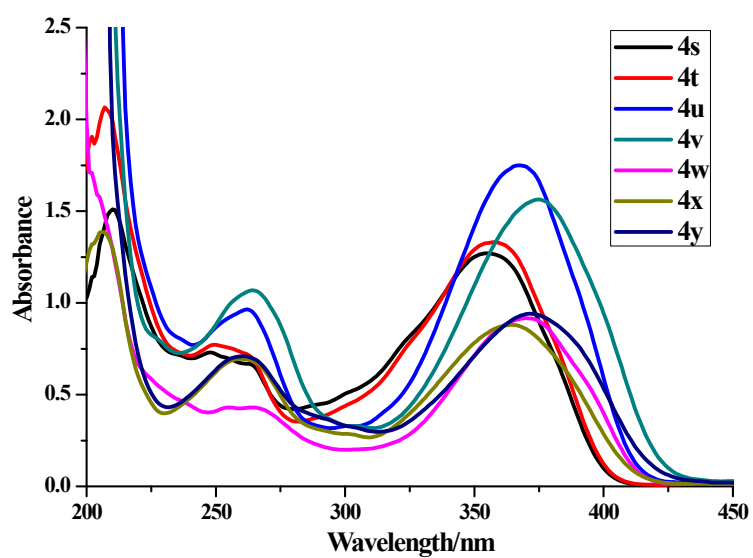


Figure S4. Absorption spectra of **4s-y** in MeCN

2) Fluorescence emission spectra were recorded using a F-4500 FL spectrophotometer in MeCN.

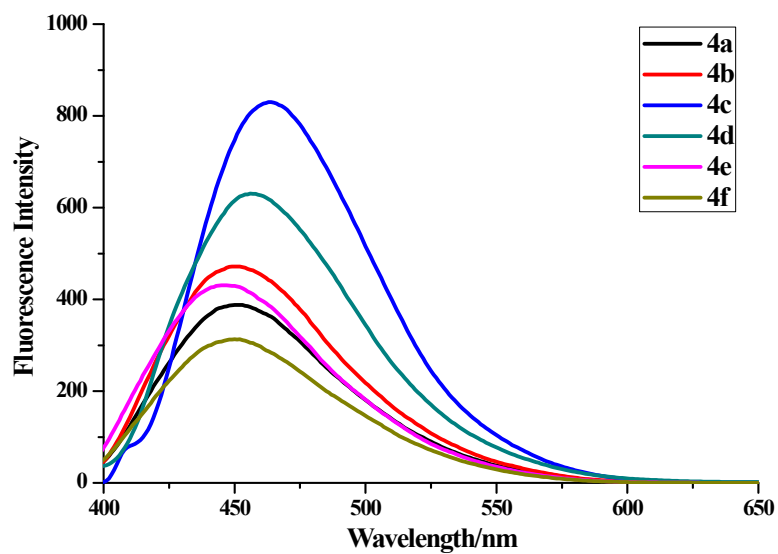


Figure S5. Fluorescence emission spectra of 4a-f in MeCN

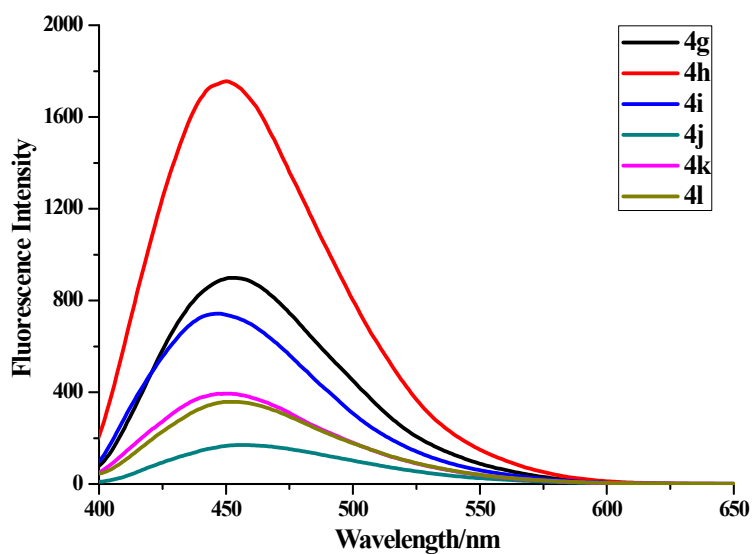


Figure S6. Fluorescence emission spectra of 4g-l in MeCN

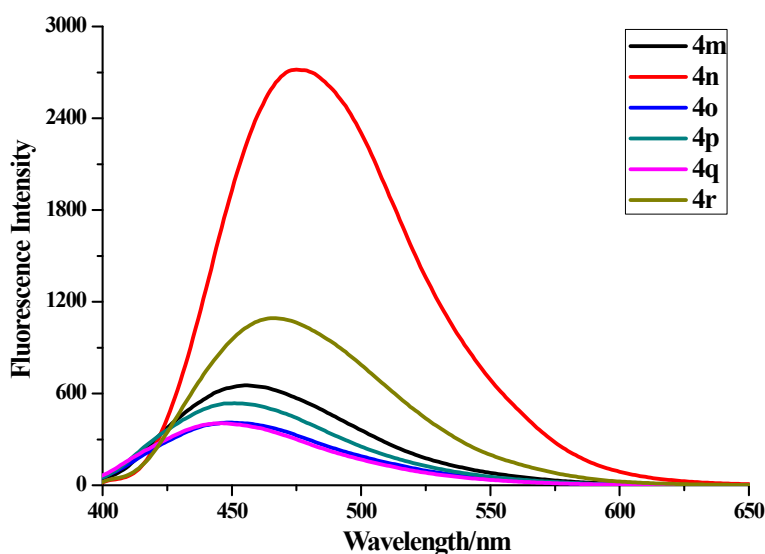


Figure S7. Fluorescence emission spectra of **4m-r** in MeCN

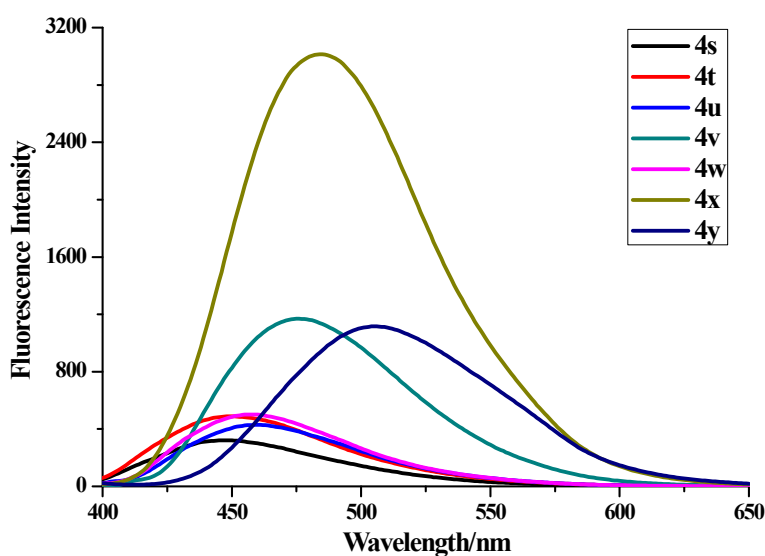


Figure S8. Fluorescence emission spectra of **4s-y** in MeCN

3) Measurement and calculation of fluorescence quantum yield

The quantum yields of the different samples were calculated using quinine sulfate (QY = 0.55) as the standard (in 0.1 M H₂SO₄).² Emission spectra of solutions were recorded from 300 to 650 nm, and 360 nm as the excitation wavelength as reference for calculation of quantum yield. Absorption and emission data of each samples were measured in 1 μM at 360 nm. And absorbance (optical density, OD) of all the samples was recorded at 360 nm. Fluorescence quantum yields were calculated according to equation (1),³ in which

Φ_{std} is the quantum yield of the standard, F_x and F_{std} are the areas under the emission spectra of the sample and the reference, respectively, A_{std} and A_x are the absorbance of the standard and the sample; η_x^2 and η_{std}^2 are the refractive indices of the standard and the sample in solution.

$$\Phi_x = \Phi_{\text{std}} \times \frac{F_x}{F_{\text{std}}} \times \frac{A_{\text{std}}}{A_x} \times \frac{\eta_x^2}{\eta_{\text{std}}^2} \quad (1)$$

Table S1. Absorption, emission maxima and fluorescence quantum yield in acetonitrile solutions.

coumarins	λ_{abs} (nm)	λ_{em} (nm)	Φ_F
4a	356	451	0.014
4b	361	450	0.017
4c	371	464	0.014
4d	365	456	0.014
4e	352	445	0.011
4f	352	450	0.009
4g	357	452	0.031
4h	356	450	0.066
4i	354	446	0.026
4j	360	455	0.010
4k	358	450	0.015
4l	358	454	0.012
4m	361	456	0.021
4n	368	475	0.080
4o	356	449	0.017
4p	358	451	0.020
4q	357	446	0.012
4r	366	467	0.035
4s	354	449	0.008
4t	358	450	0.019
4u	375	476	0.028
4v	369	460	0.012

4w	370	458	0.013
4x	365	484	0.115
4y	371	506	0.047

3. Photophysical properties of compounds **4a**, **4e**, **4h**, **4n** and **4x** in different solvents

1) Normalized UV and FL spectra of compounds **4a**, **4e**, **4h**, **4n** and **4x** in different solvents

All luminescence spectra data were measured at 0.05 mM solution in different solvents, UV is ultraviolet absorption, FL is fluorescence intensity. The UV absorption spectra was measured in quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer, and fluorescence emission spectra were measured by a F-4500 FL spectrophotometer.

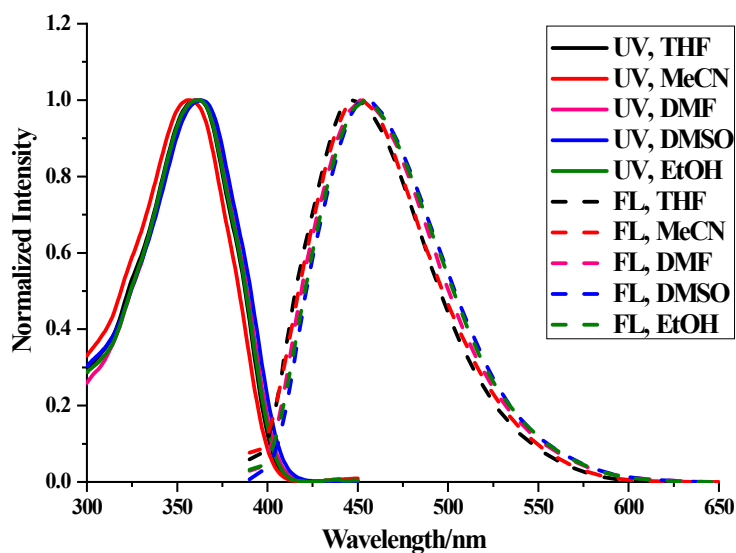


Figure S9. Normalized UV and FL spectra of compound **4a** in different solvents

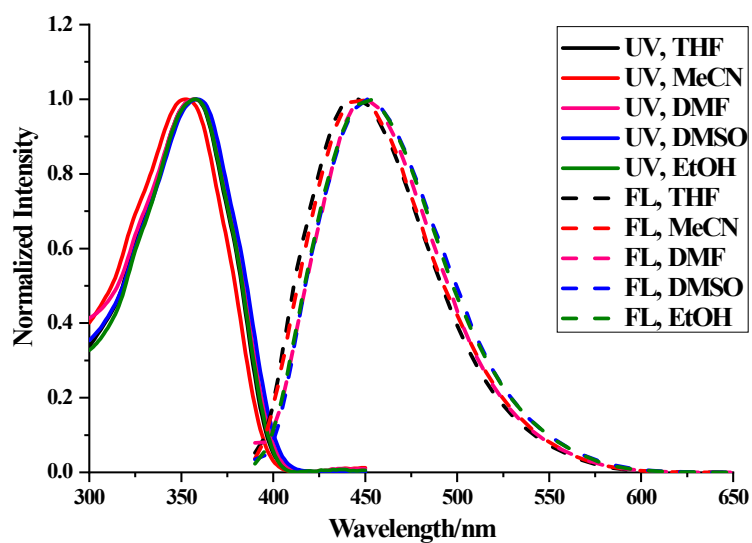


Figure S10. Normalized UV and FL spectra of compound **4e** in different solvents

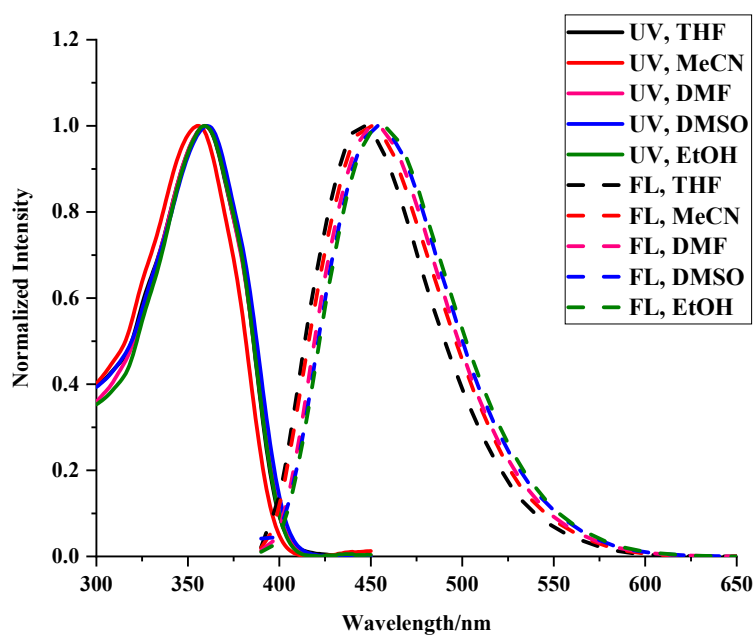


Figure S11. Normalized UV and FL spectra of compound **4h** in different solvents

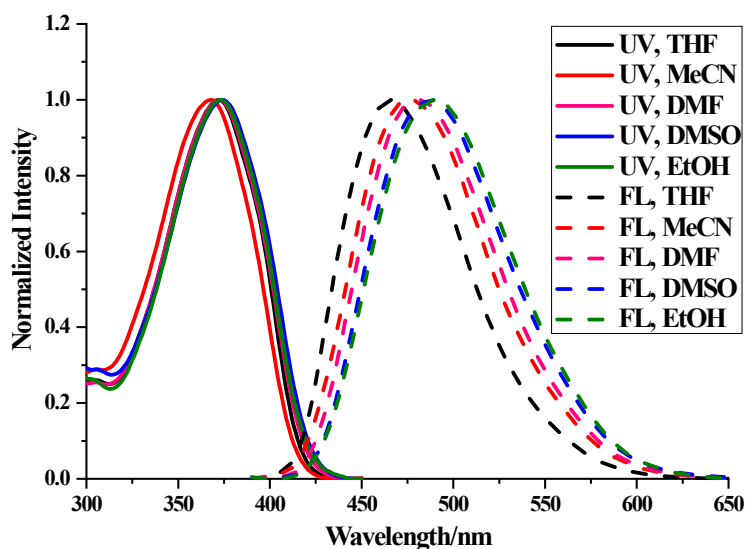


Figure S12. Normalized UV and FL spectra of compound **4n** in different solvents

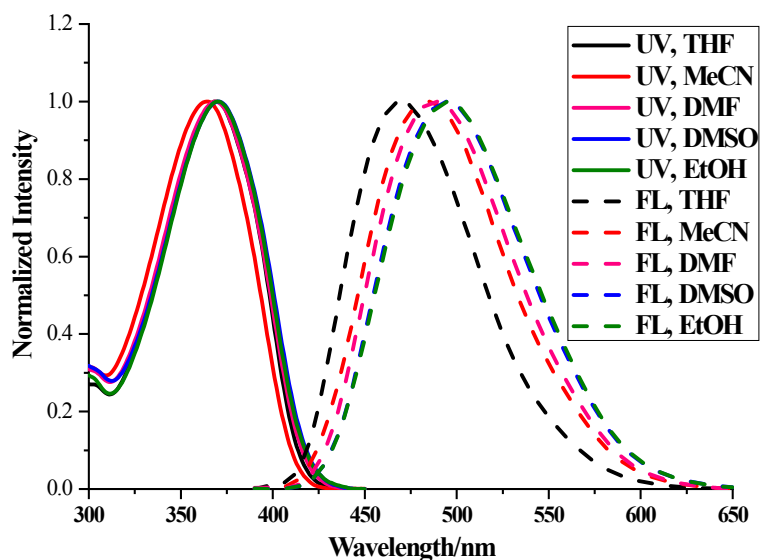


Figure S13. Normalized UV and FL spectra of compound **4x** in different solvents

2) UV spectra data, FL spectra data and calculation of fluorescence quantum yield of compounds **4a**, **4e**, **4h**, **4n** and **4x** in different solvents

UV and FL spectra data were measured at 0.05 mM solution in different solvents, data of fluorescence quantum yield were measured at 1 μ M solution in different solvents. UV is ultraviolet absorption, FL is fluorescence emission intensity, λ_{St} is Stokes shift, Φ_F is fluorescence quantum yield. The UV absorption spectra was measured in quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer, and fluorescence

emission spectra were measured by a F-4500 FL spectrophotometer.

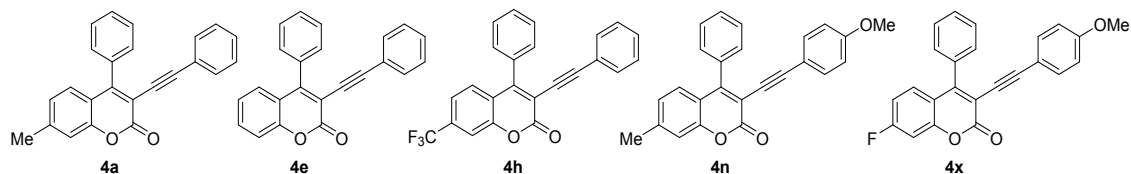


Table S2. UV, FL and fluorescence quantum yield in different solutions.^{a,b}

Solvent	4a			4e			4h			4n			4x		
	λ_{abs}	λ_{em}	Φ_{F}	λ_{abs}	λ_{em}	Φ_{F}	λ_{abs}	λ_{em}	Φ_{F}	λ_{abs}	λ_{em}	Φ_{F}	λ_{abs}	λ_{em}	Φ_{F}
	(nm)	(nm)		(nm)	(nm)		(nm)	(nm)		(nm)	(nm)		(nm)	(nm)	
THF	361	447	0.047	357	446	0.061	359	446	0.136	372	466	0.143	370	470	0.209
MeCN	357	451	0.014	352	445	0.011	356	450	0.066	368	475	0.080	365	484	0.115
DMF	362	452	0.047	358	450	0.033	360	453	0.136	372	479	0.155	368	489	0.172
DMSO	363	454	0.034	359	451	0.106	360	454	0.055	374	488	0.160	370	494	0.137
EtOH	362	454	0.022	358	451	0.020	359	455	0.061	373	489	0.121	370	495	0.128
<i>Solid</i>	441	490	0.486	446	476	0.168	435	486	-	458	514	-	472	512	0.439

^a UV and FL spectra data were measured at 0.05 mM solution in different solvents. ^b The quantum yield was calculated using quinine sulfspecate as the standard (in 0.1 M H₂SO₄) at 360 nm in different solvents.

4. References

- 1 C. E. Song, D. Jung, S. Y. Choung, E. J. Roh and S. Lee, *Angew. Chem. Int. Ed.*, 2004, **43**, 6183-6185.
- 2 W. H. Melhuish, *J. Phys. Chem.*, 1961, **65**, 229-235.

5. NMR spectra of intermediate 5a and all products

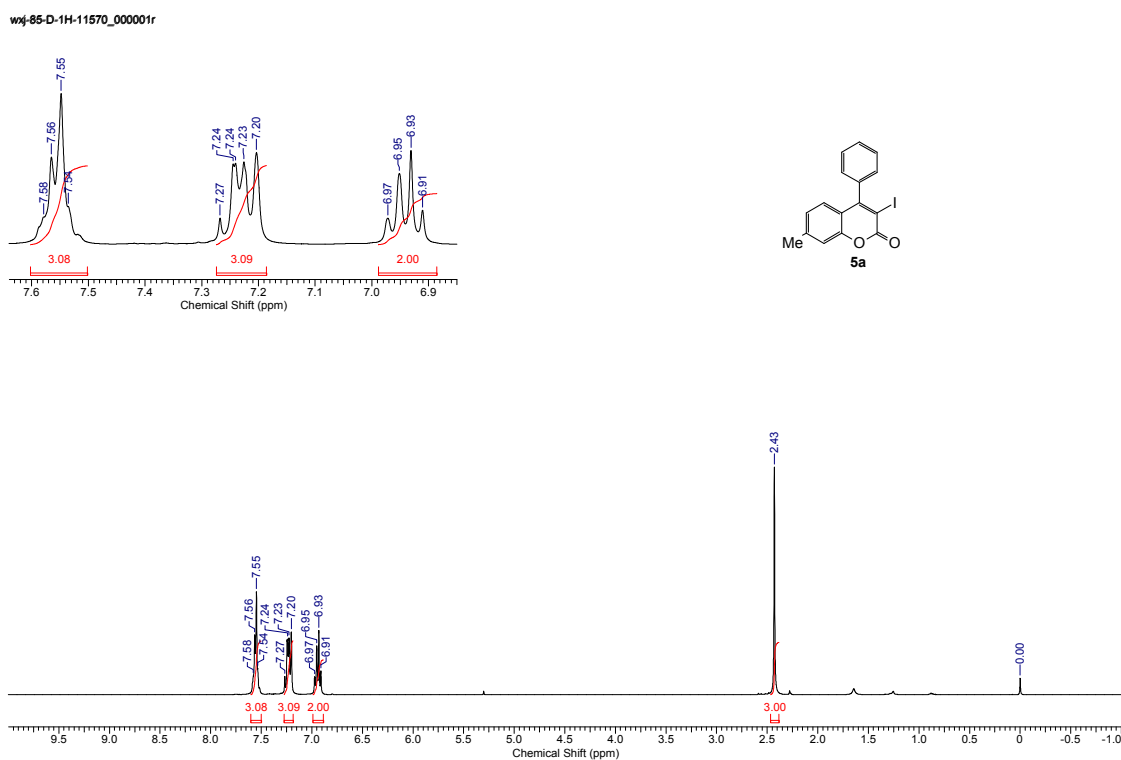


Figure S14. ¹H NMR spectrum of compound **5a**

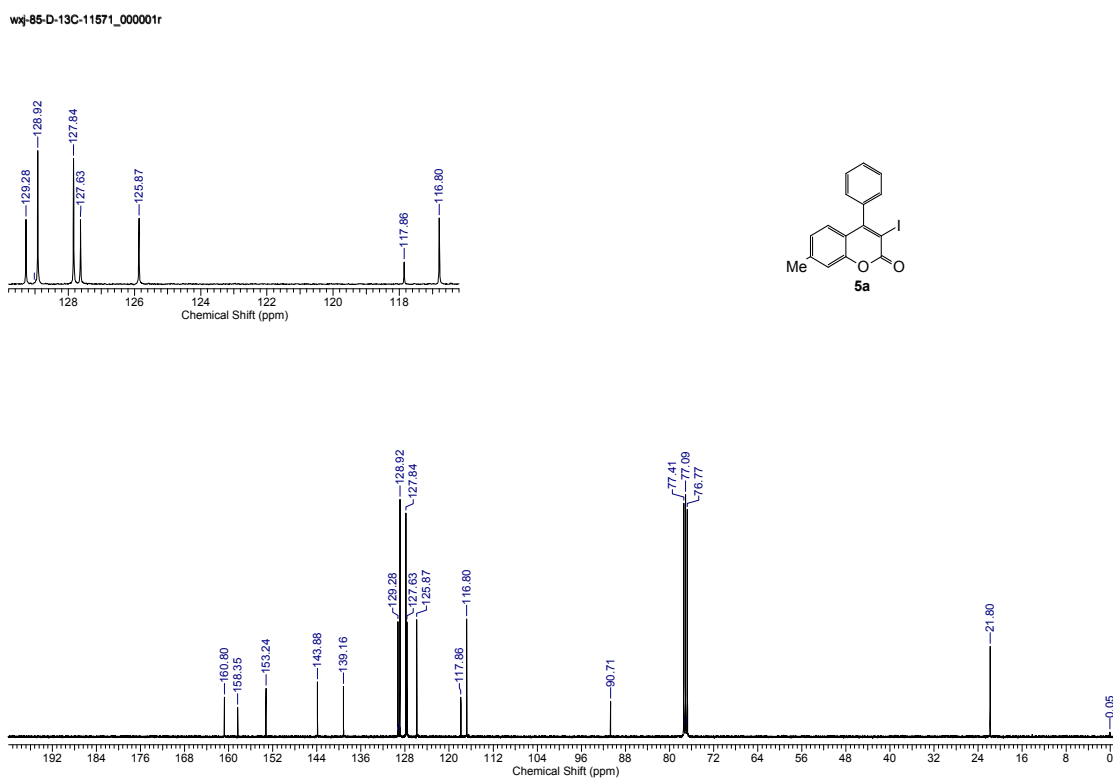


Figure S15. ¹³C NMR spectrum of compound **5a**

WXJ-79-1H,11140_000001r

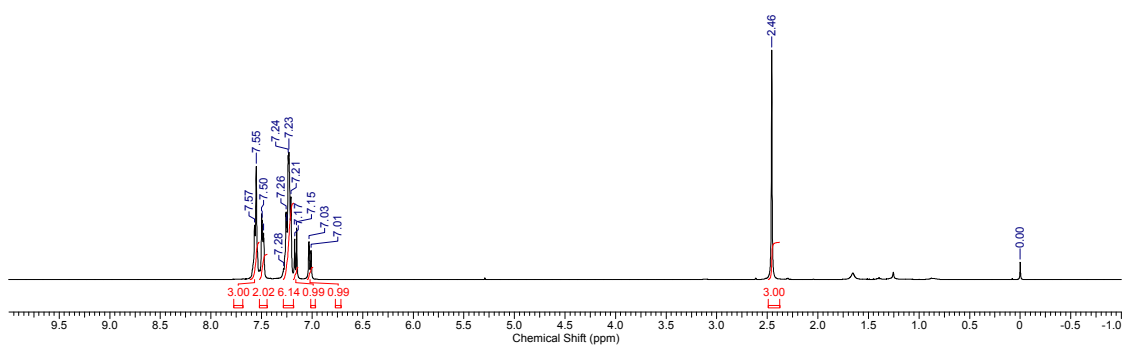
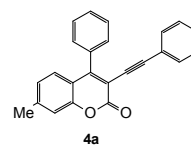
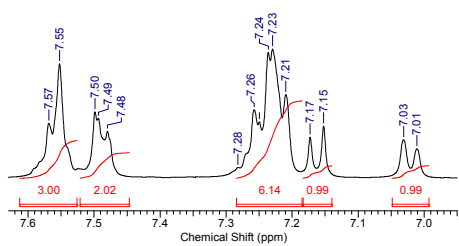


Figure S16. ¹H NMR spectrum of compound 4a

WXJ-80-13C,11451_000001r

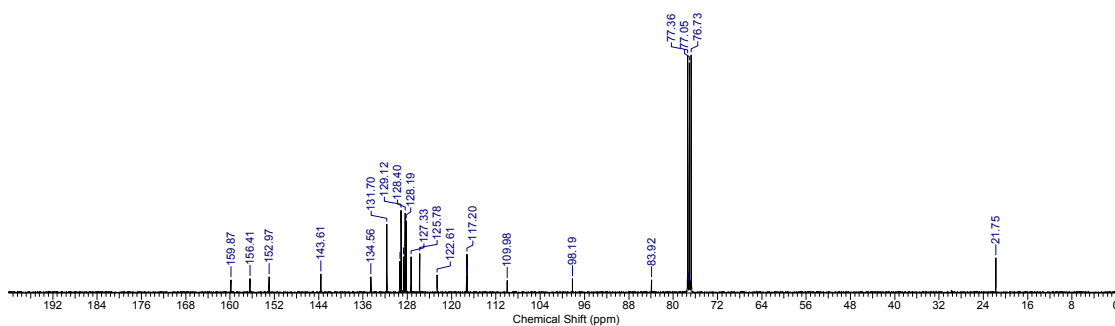
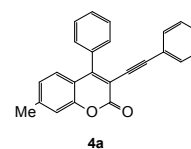
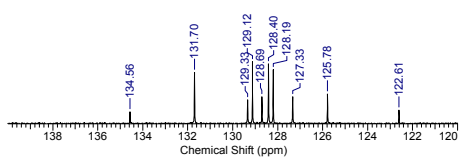


Figure S17. ¹³C NMR spectrum of compound 4a

WXJ-139-1H,2160_000001r

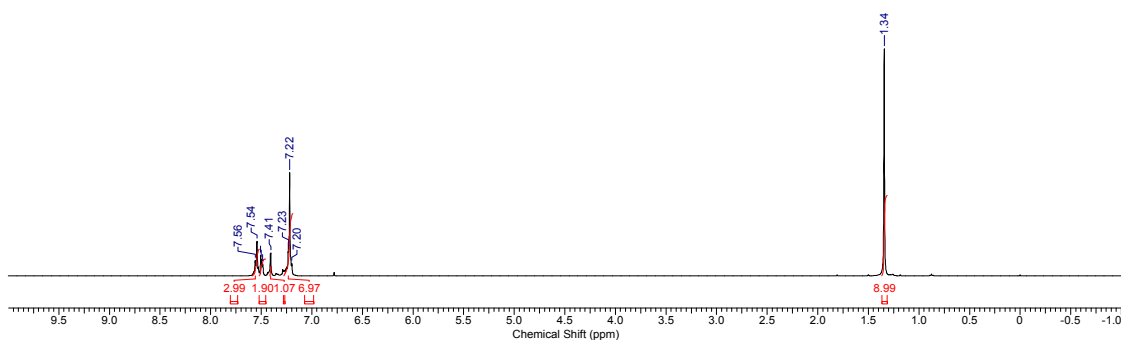
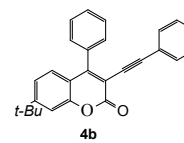
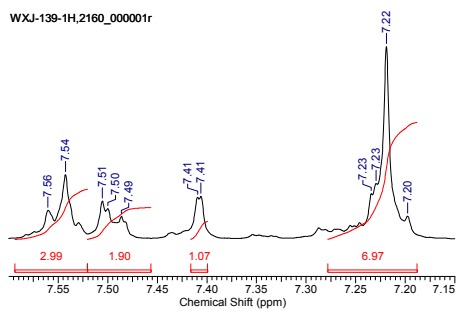


Figure S18. ¹H NMR spectrum of compound **4b**

WXJ-139-13C,1801_000001r

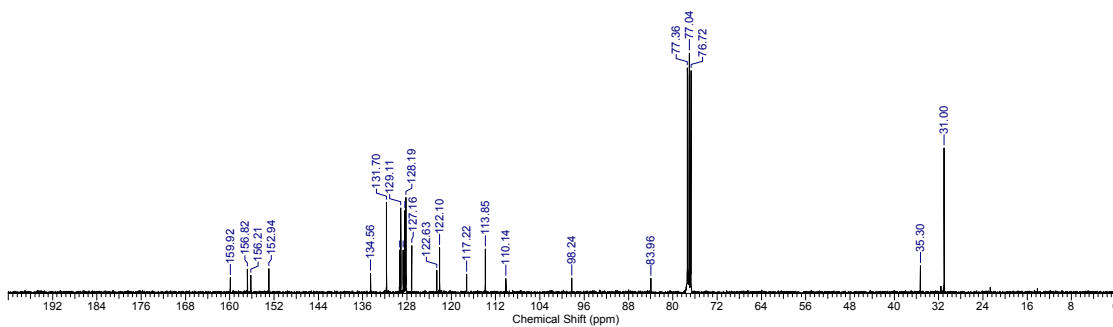
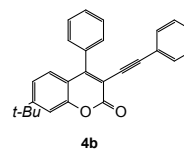
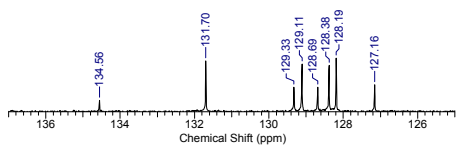


Figure S19. ¹³C NMR spectrum of compound **4b**

WXJ-138-1H,1430_000001r

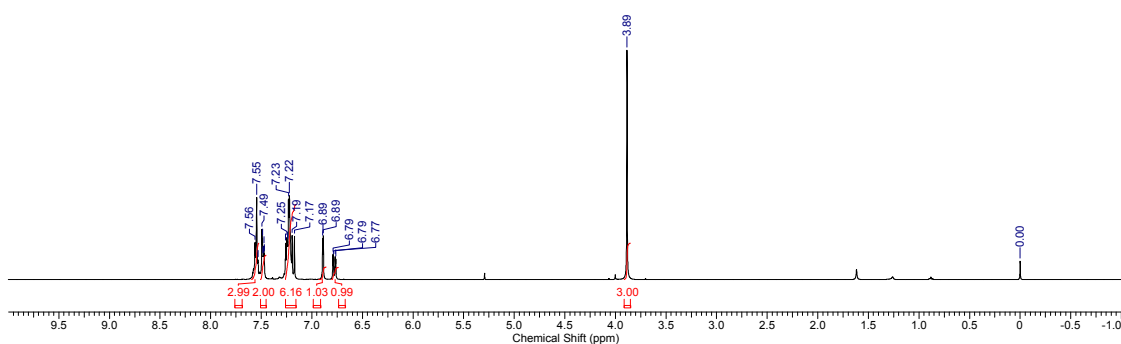
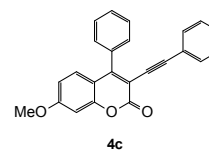
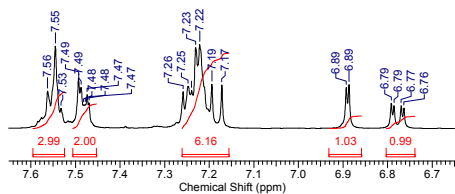


Figure S20. ¹H NMR spectrum of compound **4c**

WXJ-138-13C,1431_000001r

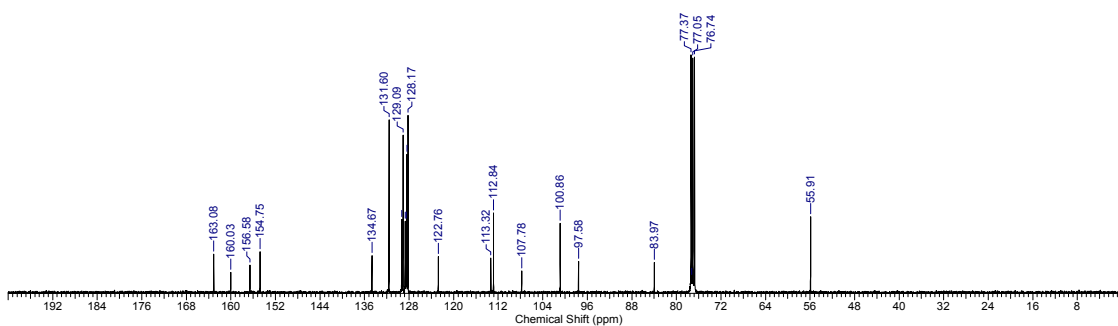
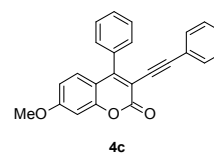
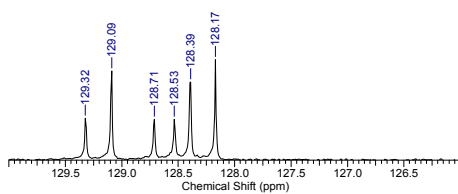


Figure S21. ¹³C NMR spectrum of compound **4c**

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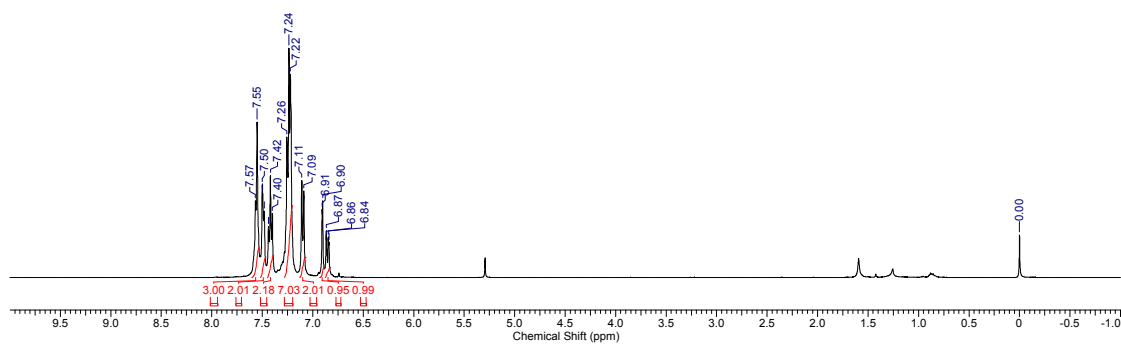
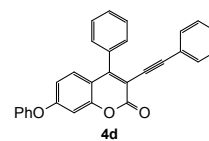
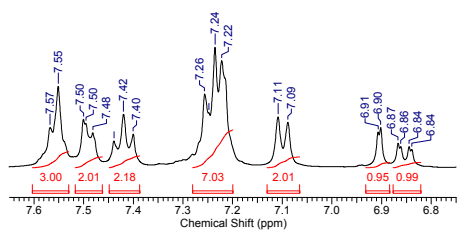


Figure S22. ^1H NMR spectrum of compound **4d**

WXJ-202-13C,3051_000001r

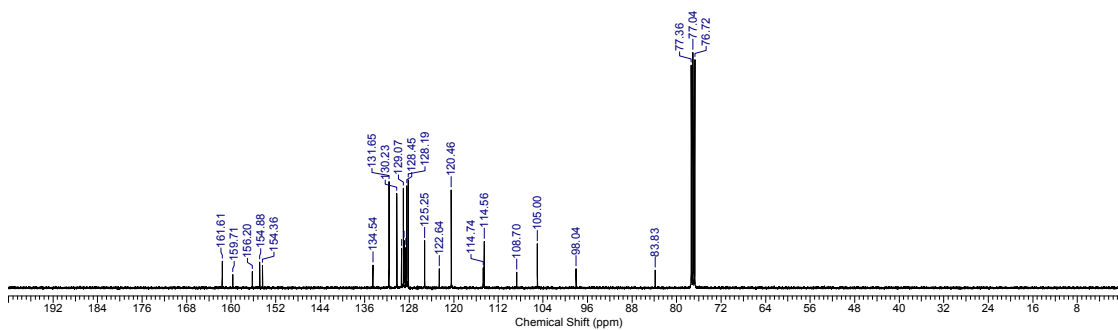
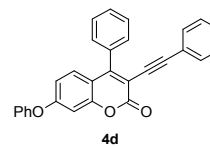
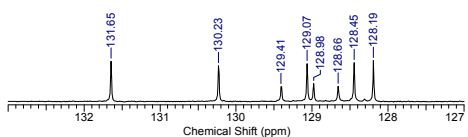


Figure S23. ^{13}C NMR spectrum of compound **4d**

WXJ-203-1H,3060_000001r

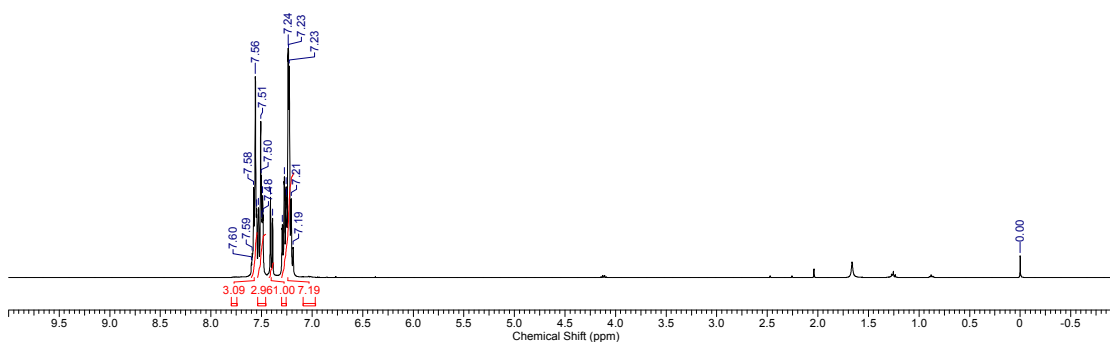
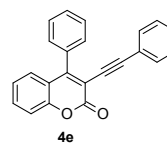
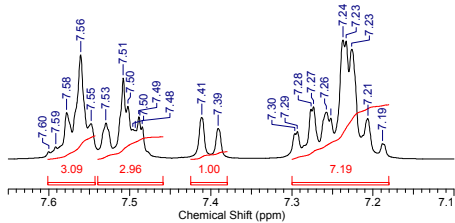


Figure S24. ¹H NMR spectrum of compound 4e

WXJ-203-13C,3061_000001r

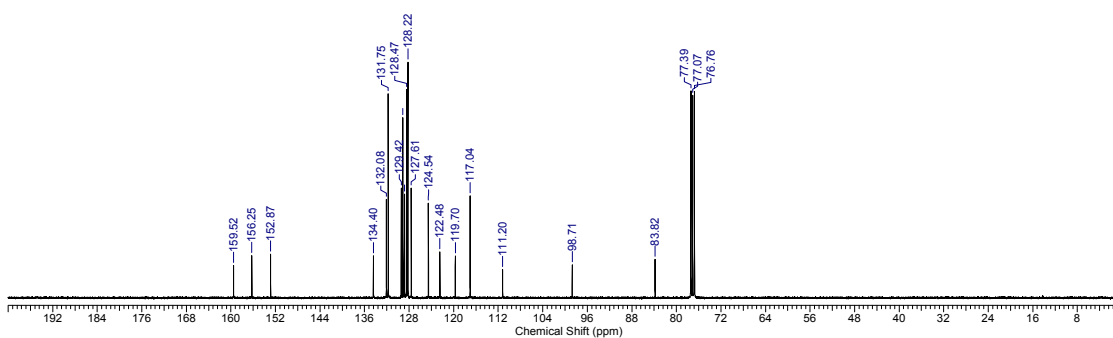
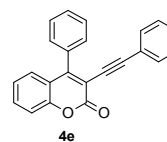
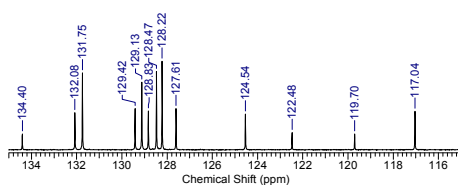


Figure S25. ¹³C NMR spectrum of compound 4e

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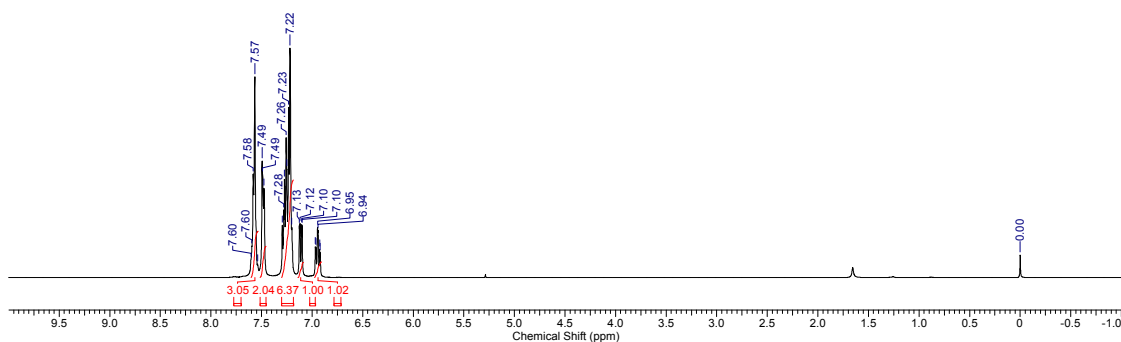
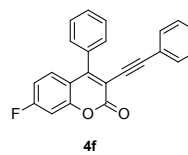
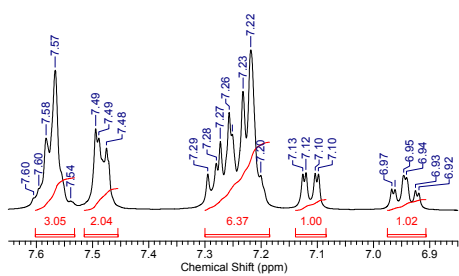


Figure S26. ¹H NMR spectrum of compound 4f

WXJ-200-13C,2931_000001r

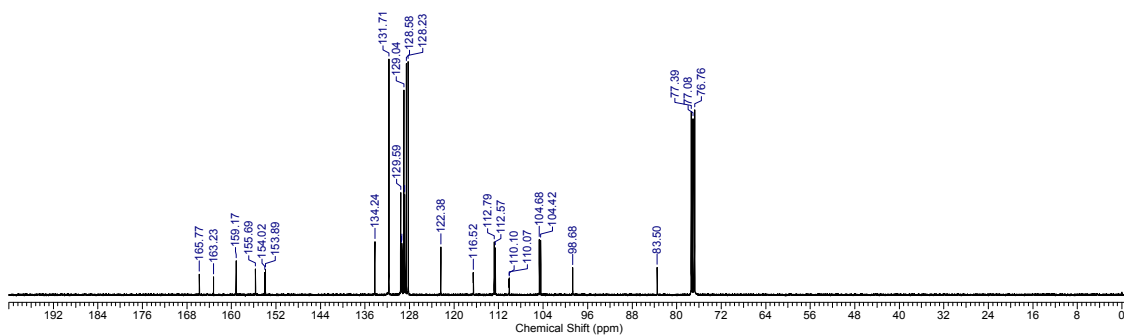
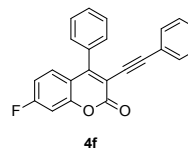
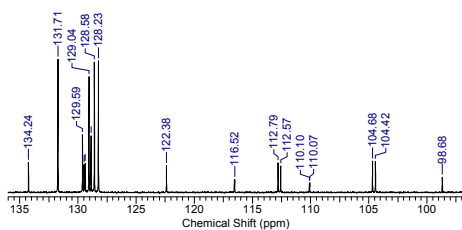
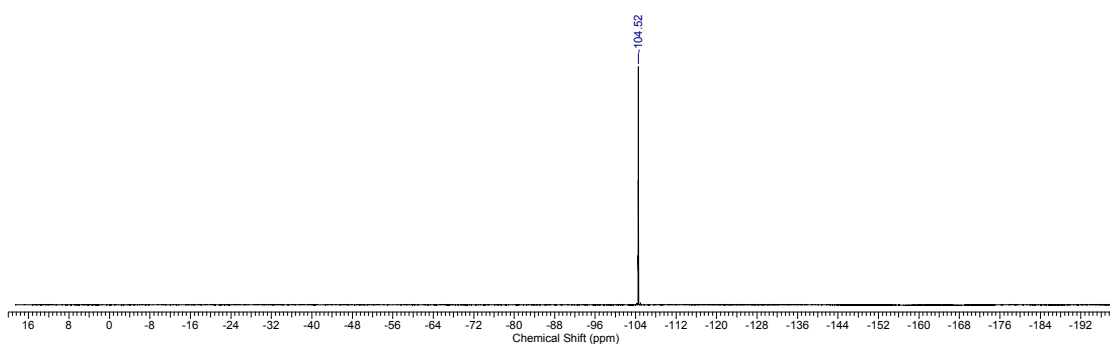
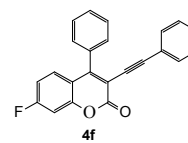
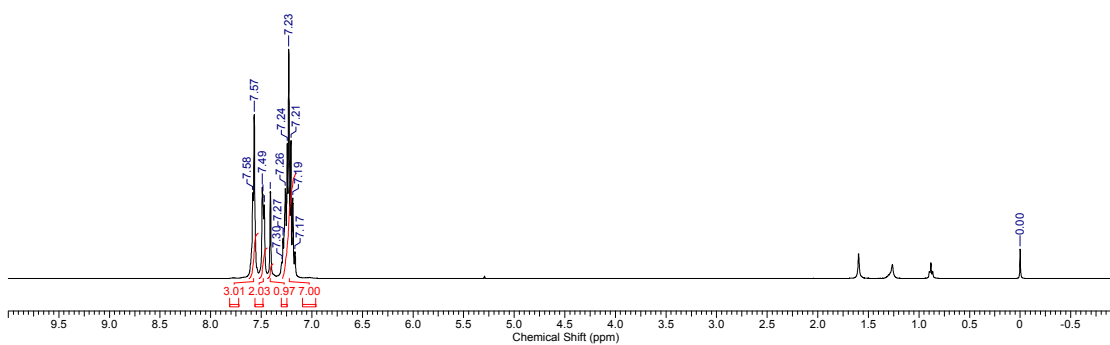
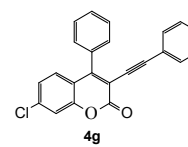
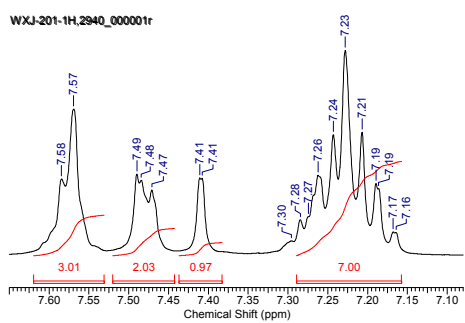


Figure S27. ¹³C NMR spectrum of compound 4f

Figure S28. ^{19}F NMR spectrum of compound 4fFigure S29. ^1H NMR spectrum of compound 4g

WXJ-201-13C.2941_000001r

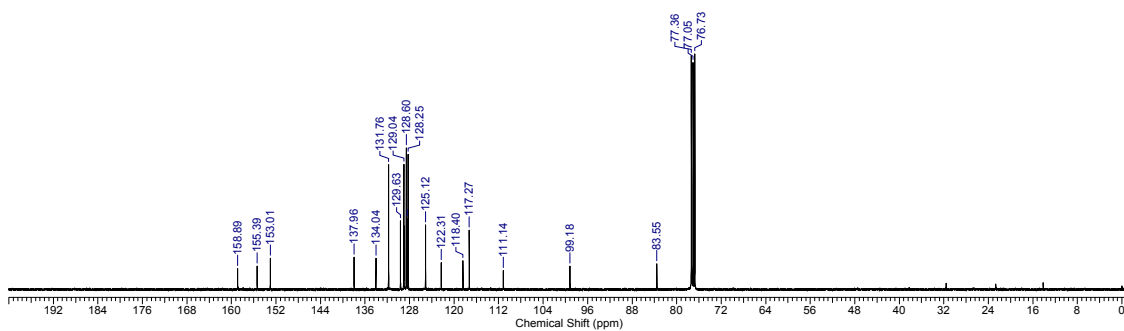
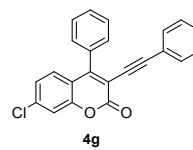
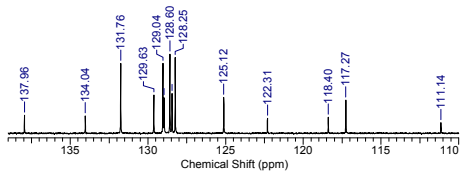


Figure S30. ¹³C NMR spectrum of compound 4g

WXJ-237-1H.6160_000001r

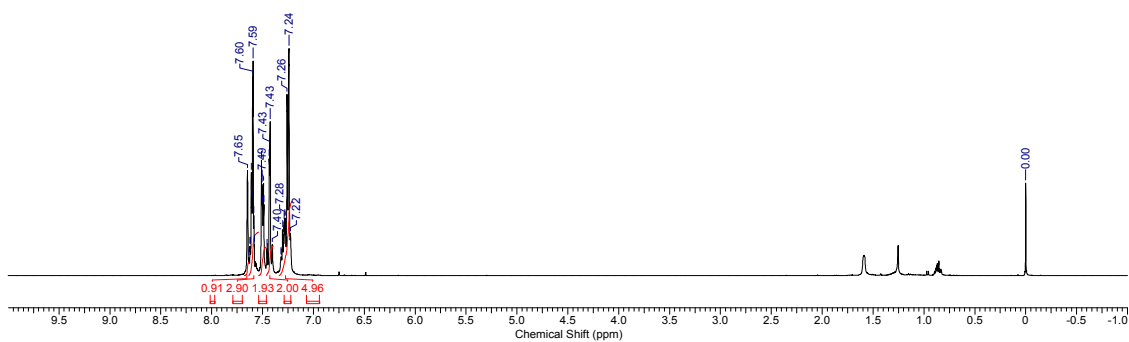
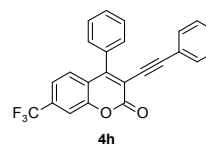
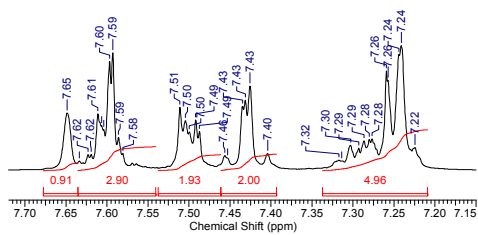


Figure S31. ¹H NMR spectrum of compound 4h

WXJ-237-13C_4931_000001r

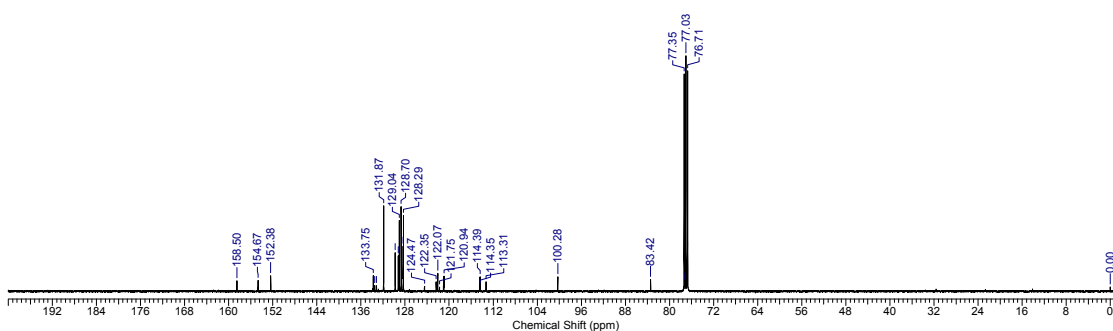
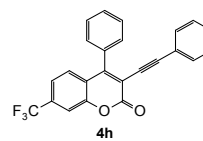
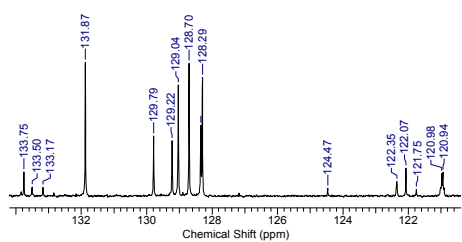


Figure S32. ¹³C NMR spectrum of compound 4h

WXJ-237-19F_4932_000001r

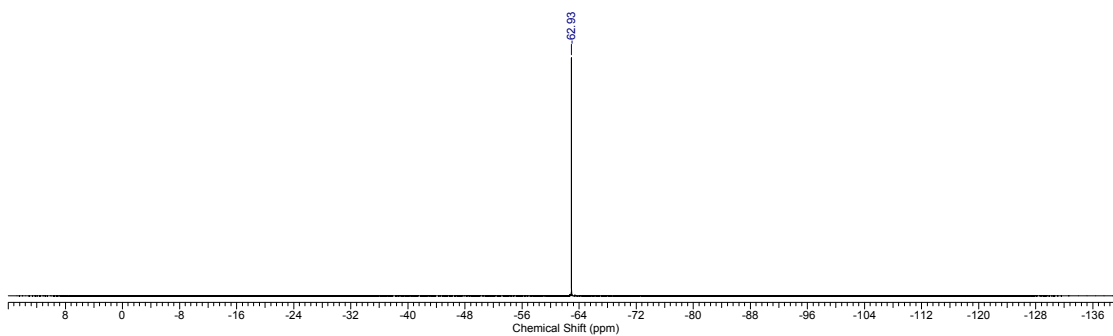
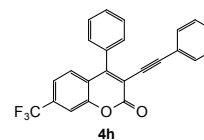


Figure S33. ¹⁹F NMR spectrum of compound 4h

WXJ-146-1H_520_000001r

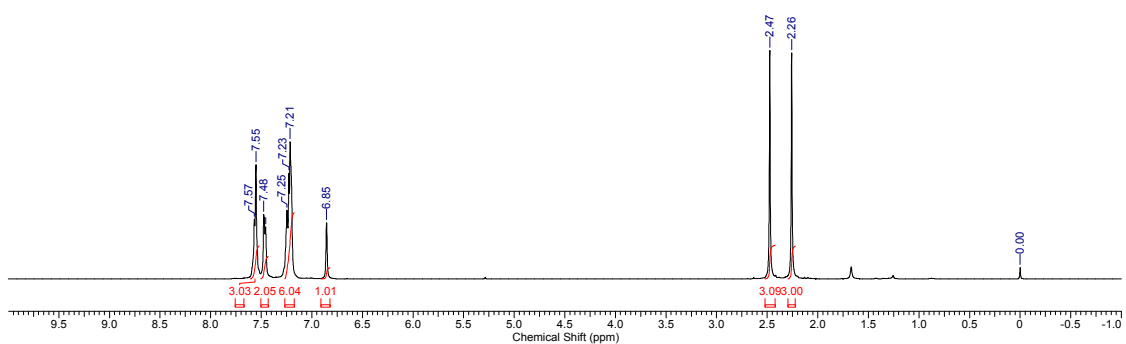
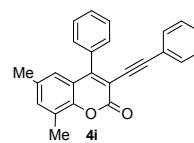
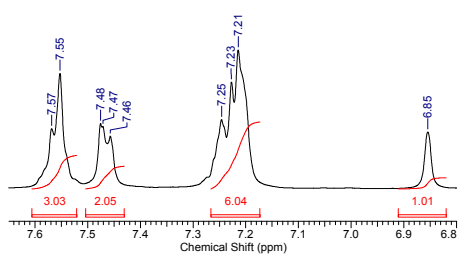


Figure S34. ¹H NMR spectrum of compound **4i**

WXJ-146-13C_521_000001r

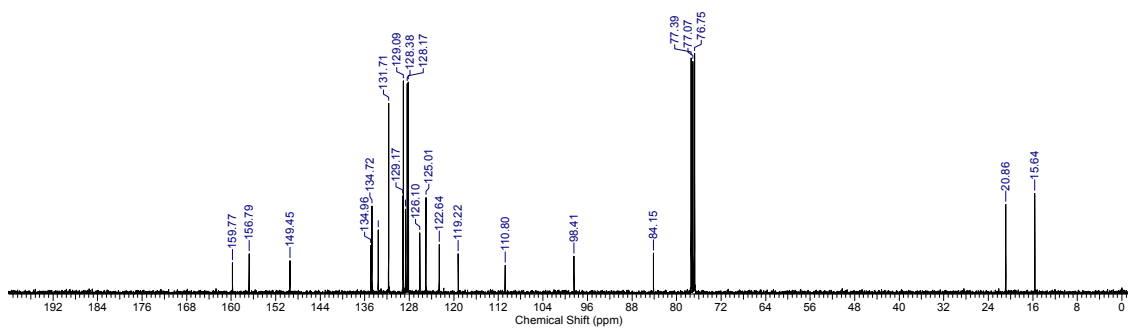
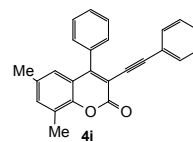
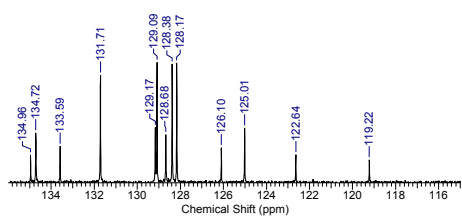


Figure S35. ¹³C NMR spectrum of compound **4i**

WXJ-254-1H,14170_000001r

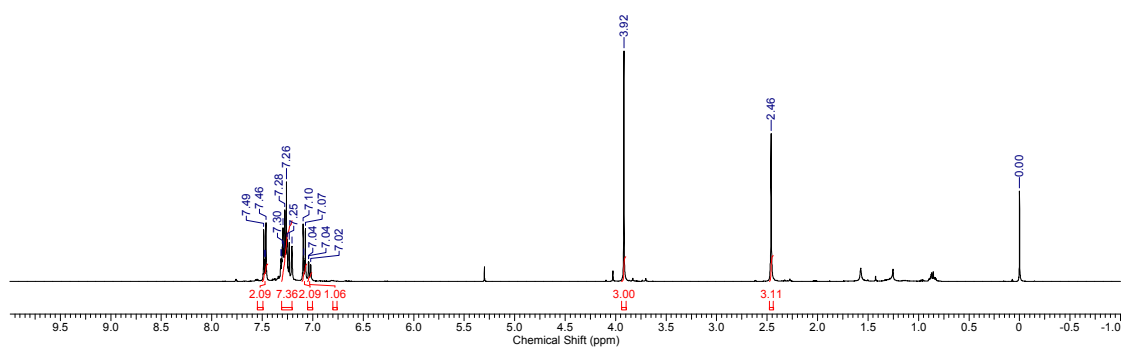
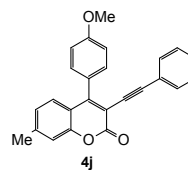
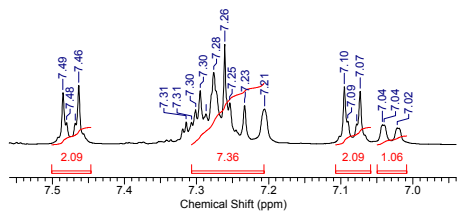


Figure S36. ¹H NMR spectrum of compound 4j

WXJ-254-13C,6331_000001r

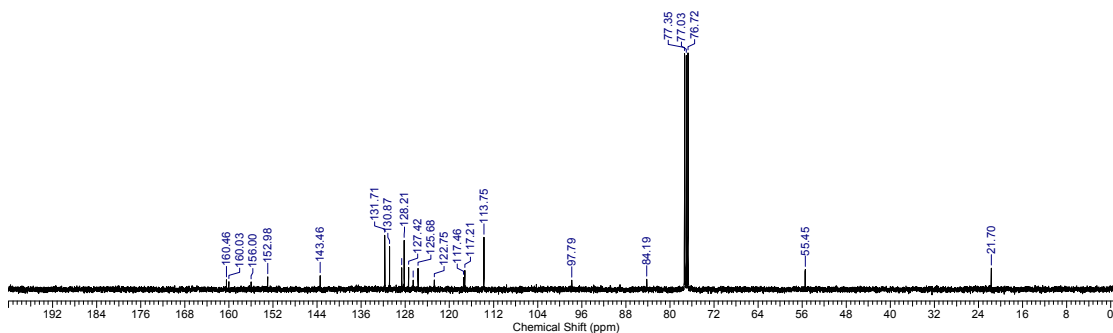
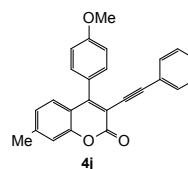
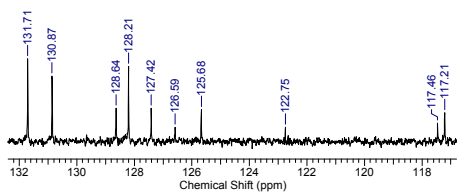


Figure S37. ¹³C NMR spectrum of compound 4j

WXJ-246-1H,5700_000001r

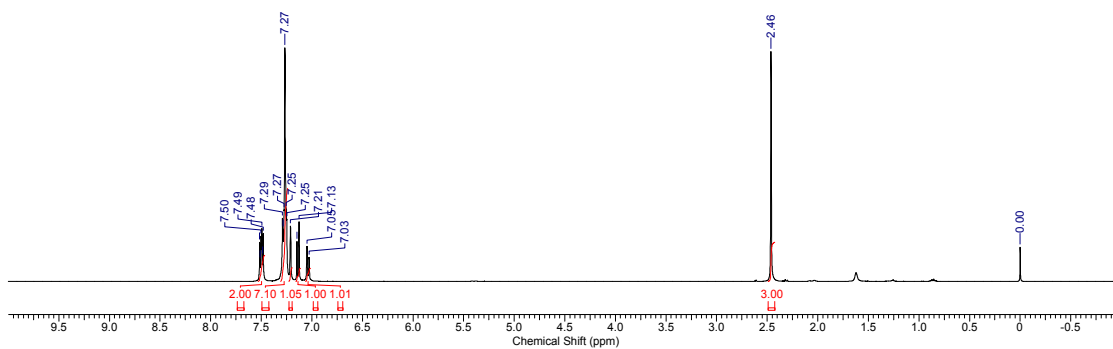
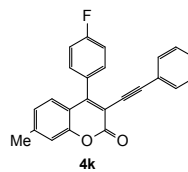
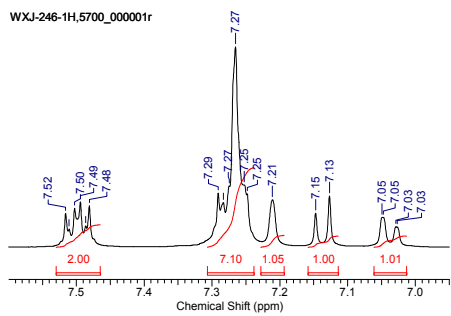


Figure S38. ^1H NMR spectrum of compound **4k**

WXJ-246-13C,5701_000001r

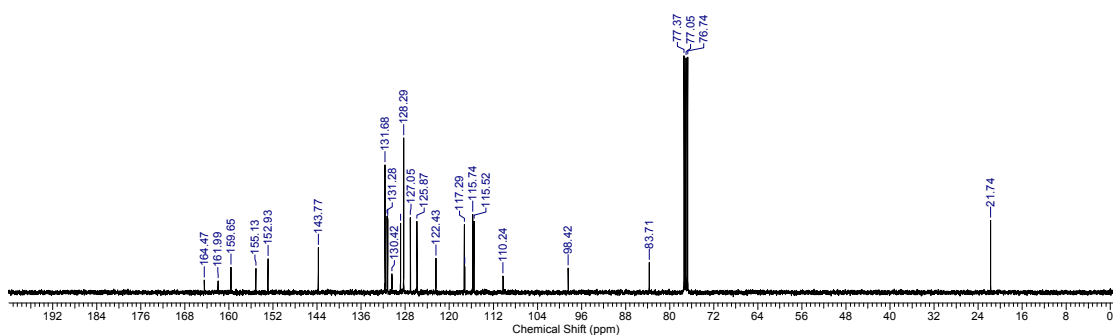
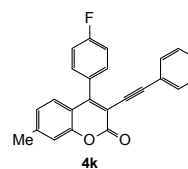
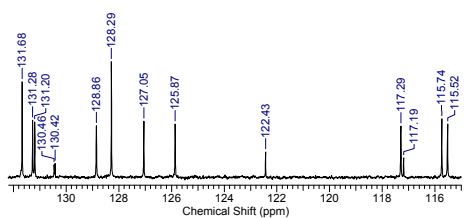
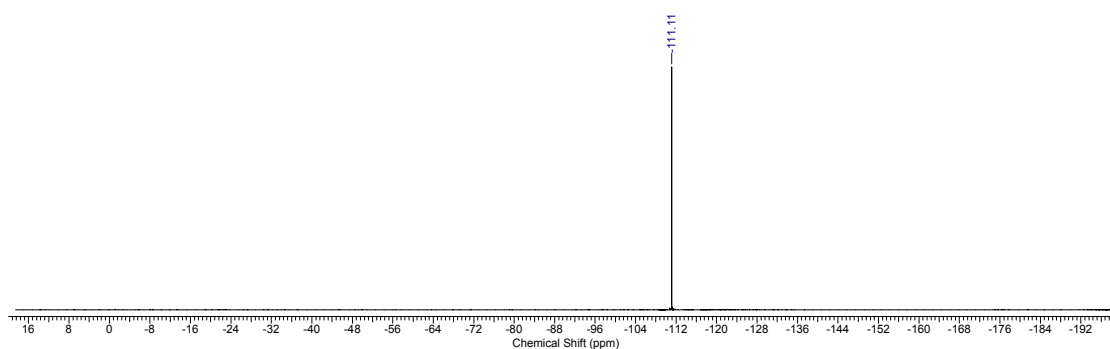
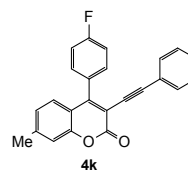
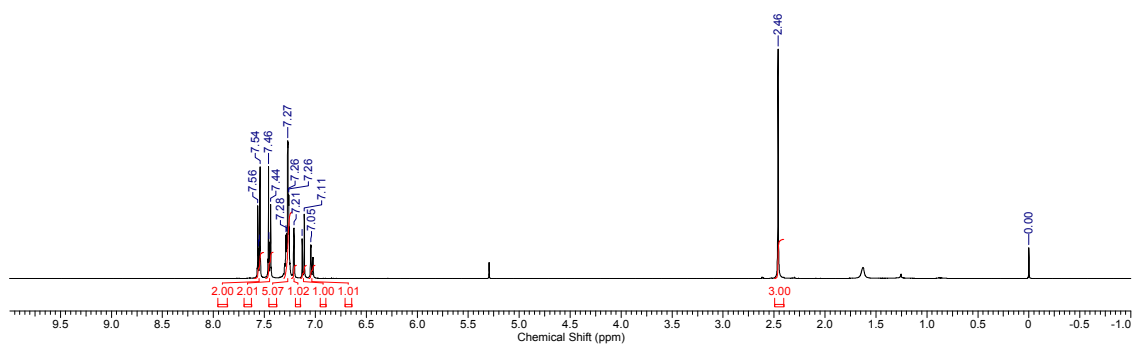
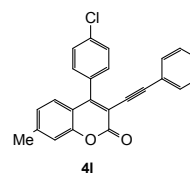
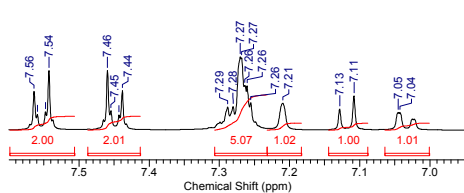


Figure S39. ^{13}C NMR spectrum of compound **4k**

Figure S40. ^{19}F NMR spectrum of compound 4kFigure S41. ^1H NMR spectrum of compound 4l

WXJ-245-13C,5691_000001r

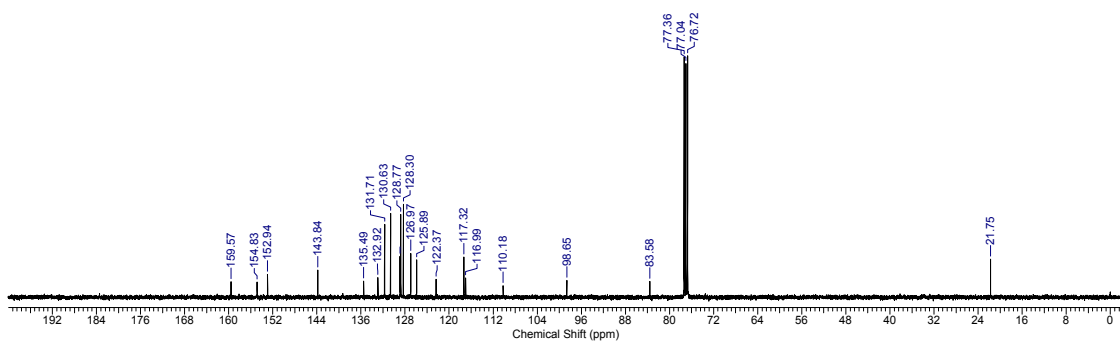
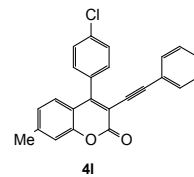
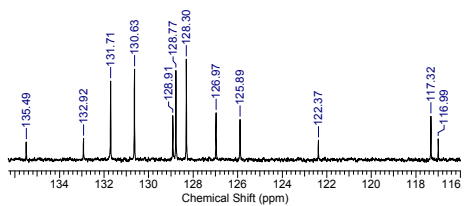


Figure S42. ¹³C NMR spectrum of compound 41

WXJ-159-1H,1640_000001r

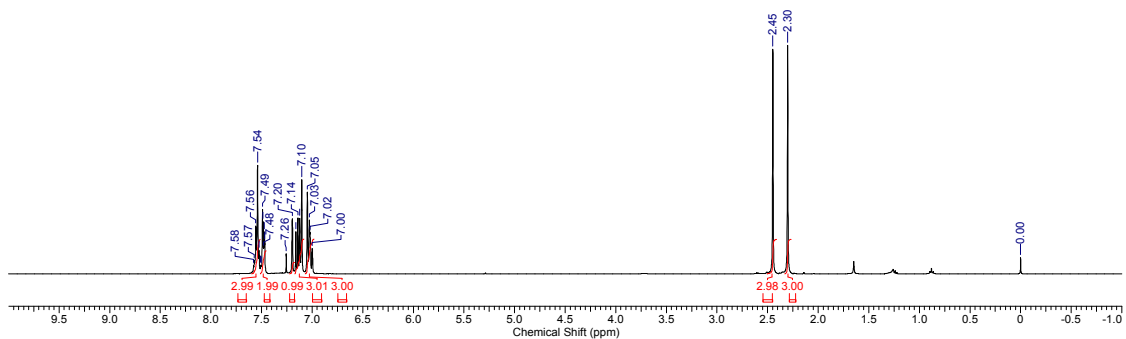
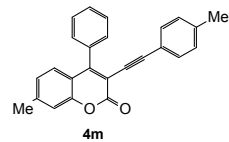
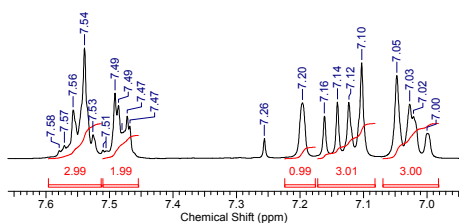


Figure S43. ¹H NMR spectrum of compound 4m

WXJ-159-13C,1641_000001r

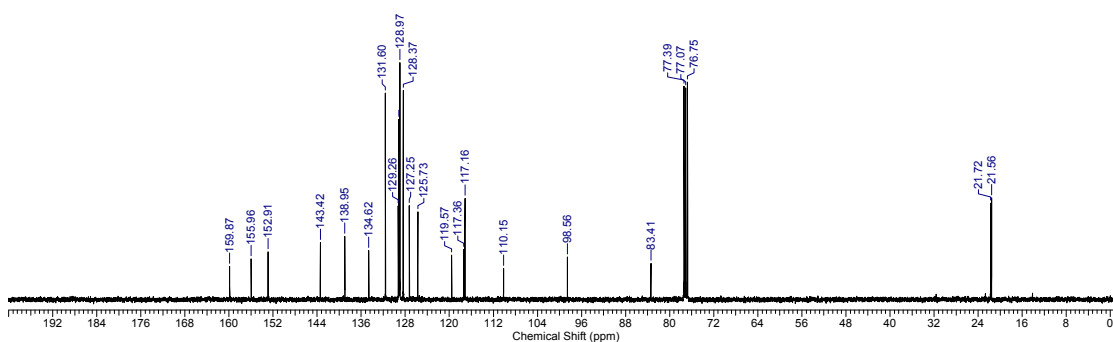
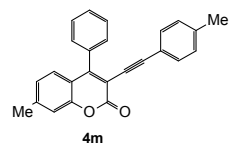
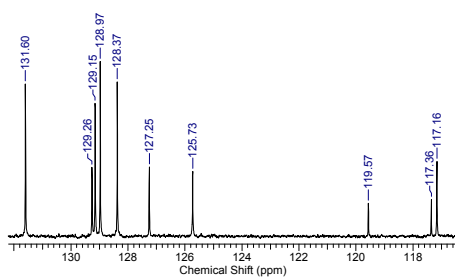


Figure S44. ¹³C NMR spectrum of compound 4m

WXJ-232-1H,4910_000001r

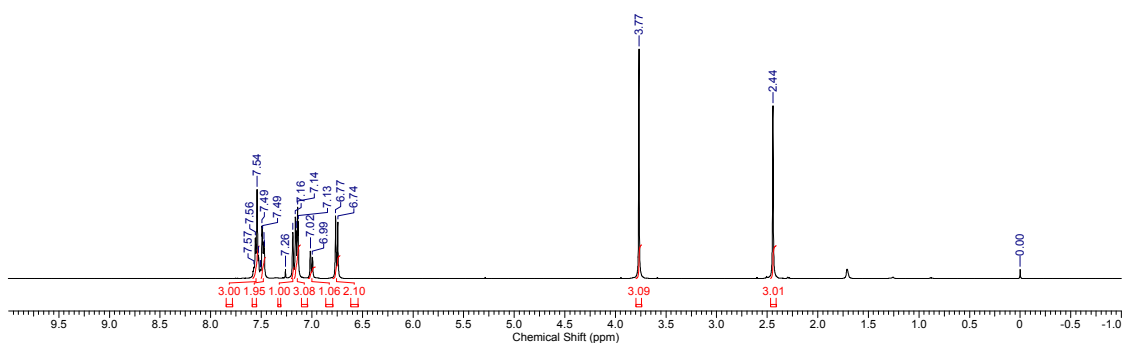
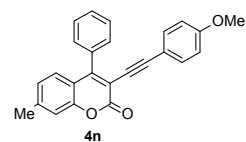
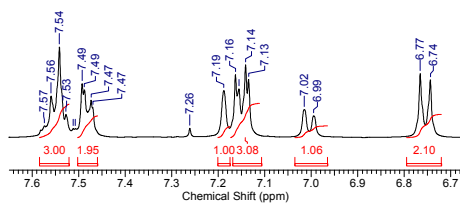


Figure S45. ¹H NMR spectrum of compound 4n

WXJ-232-13C_4911_000001r

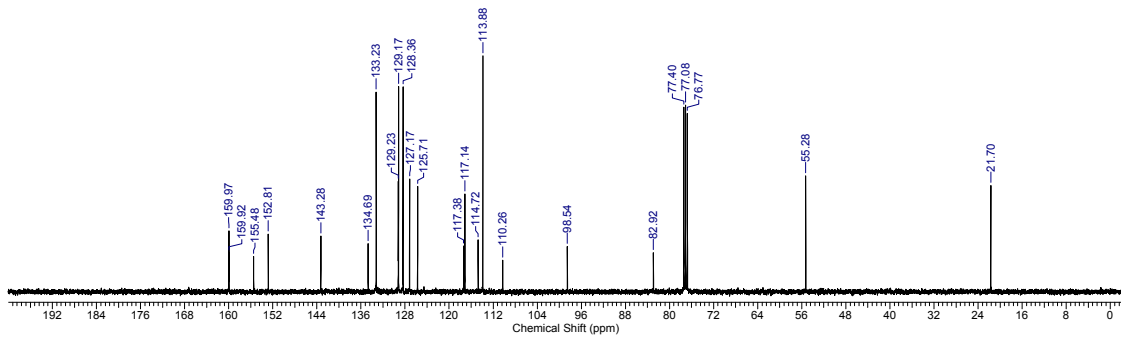
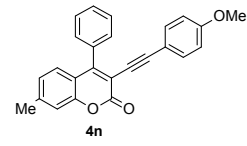
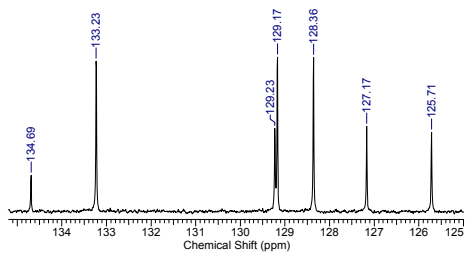


Figure S46. ¹³C NMR spectrum of compound 4n

WXJ-154-1H_510_000001r

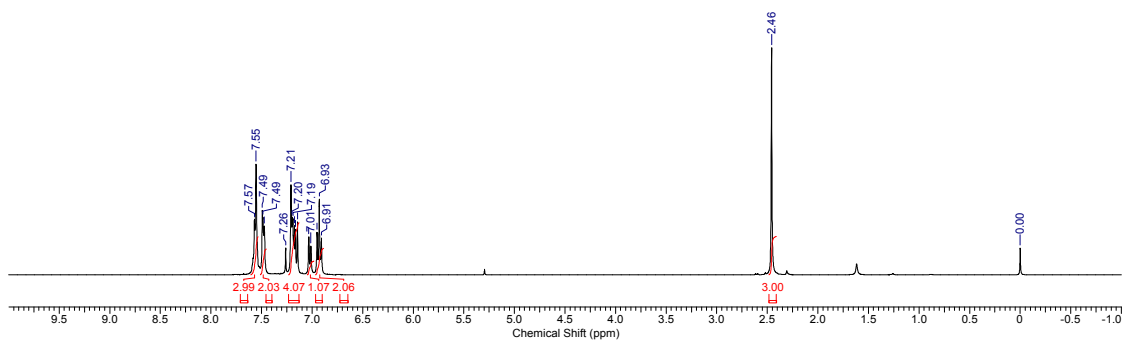
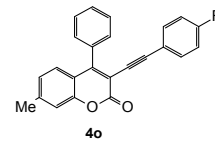
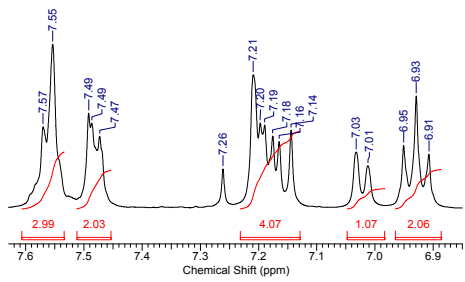


Figure S47. ¹H NMR spectrum of compound 4o

WXJ-154-13C,1221_000001r

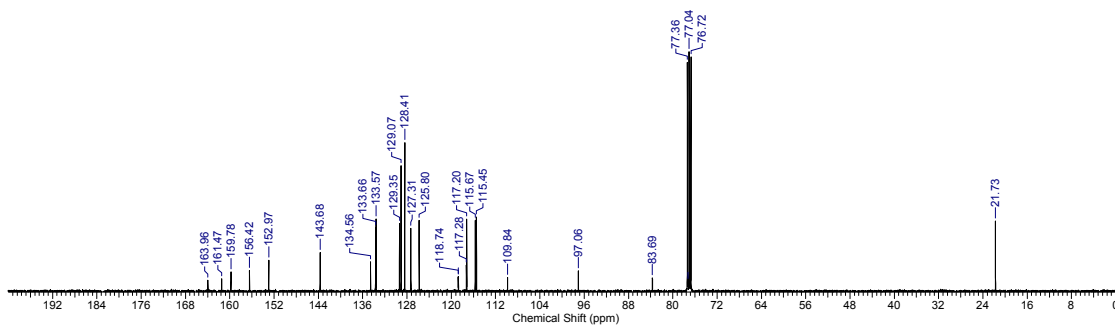
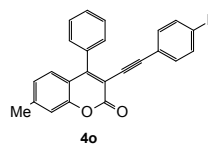
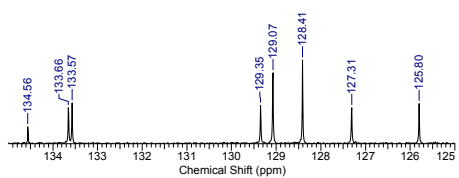


Figure S48. ¹³C NMR spectrum of compound **4o**

WXJ-154-19F,1222_000001r

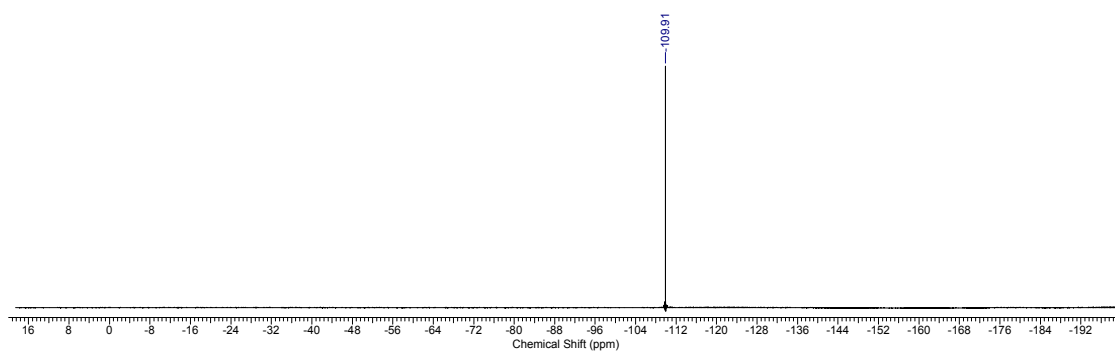
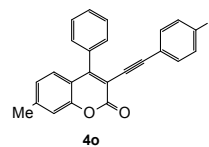


Figure S49. ¹⁹F NMR spectrum of compound **4o**

WXJ-160-1H,1660_000001r

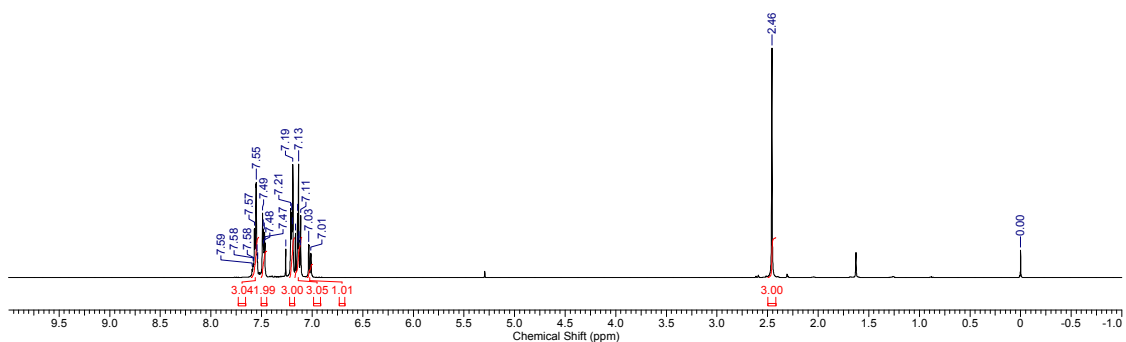
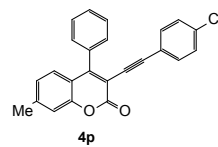
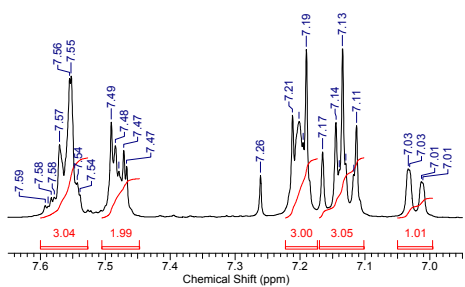


Figure S50. ¹H NMR spectrum of compound 4p

WXJ-160-13C,1661_000001r

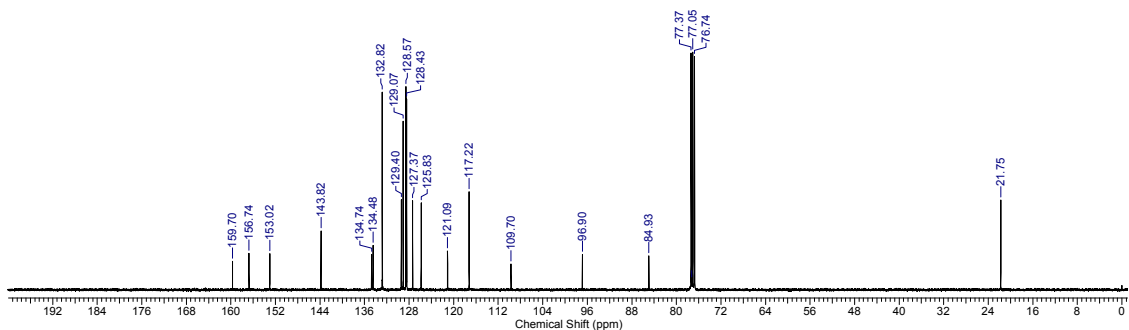
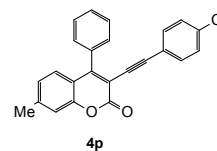
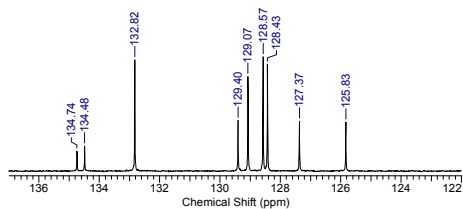


Figure S51. ¹³C NMR spectrum of compound 4p

WXJ-255-1H,6300_000001r

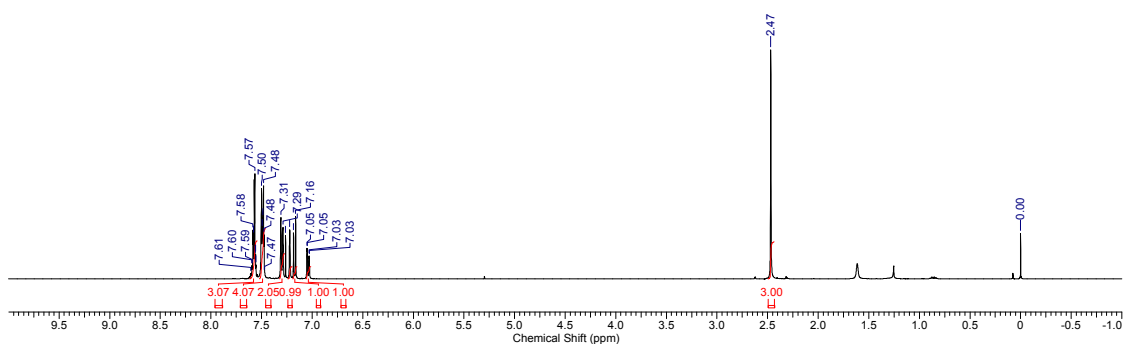
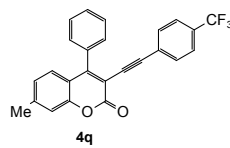
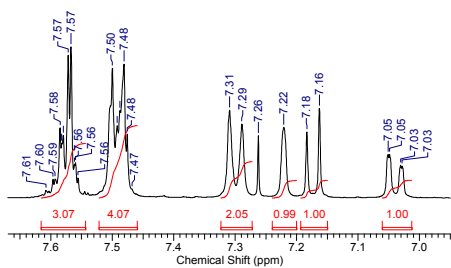


Figure S52. ^1H NMR spectrum of compound **4q**

WXJ-255-13C,6121_000001r

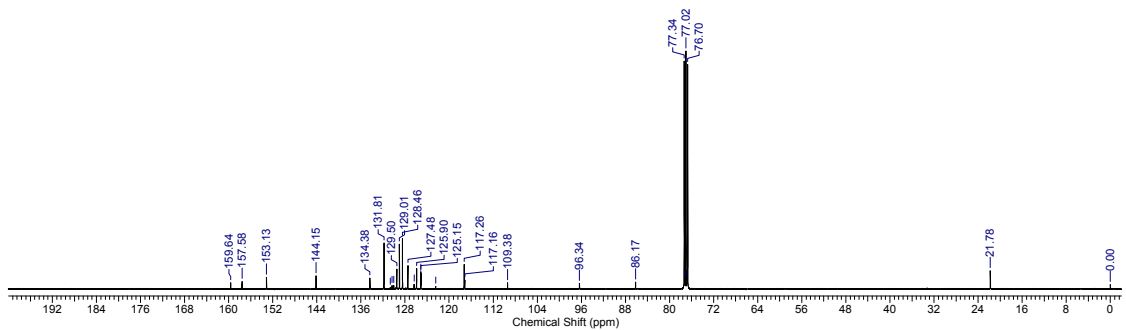
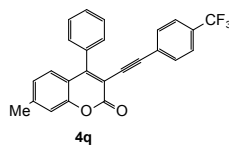
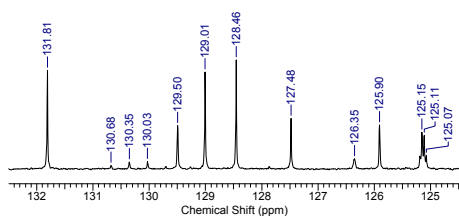
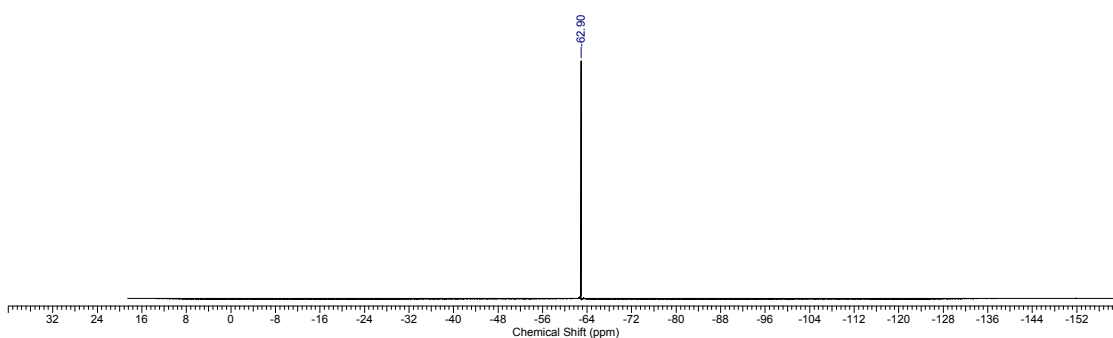
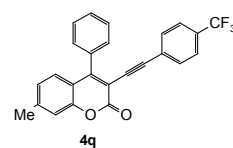
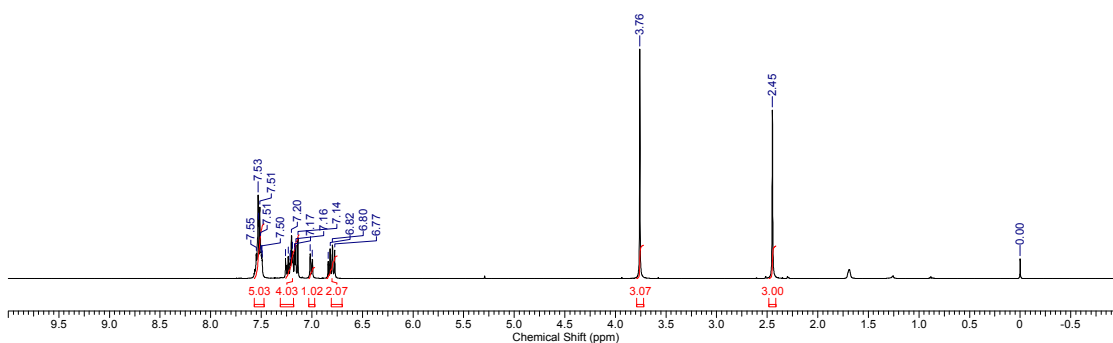
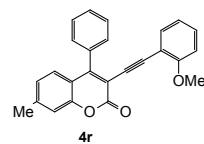
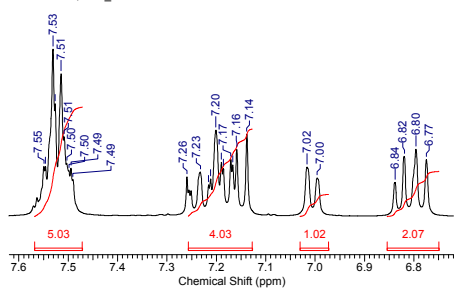


Figure S53. ^{13}C NMR spectrum of compound **4q**

Figure S54. ^{19}F NMR spectrum of compound **4q**Figure S55. ^1H NMR spectrum of compound **4r**

WXJ-233-13C_4921_000001r

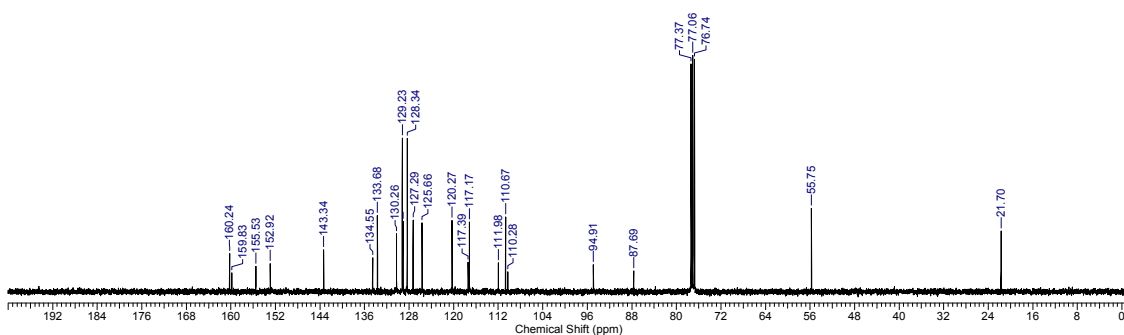
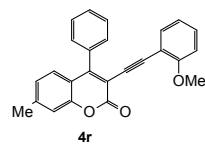
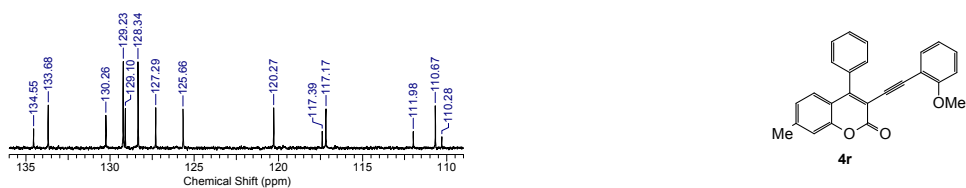


Figure S56. ¹³C NMR spectrum of compound 4r

WXJ-161-1H_2080_000001r

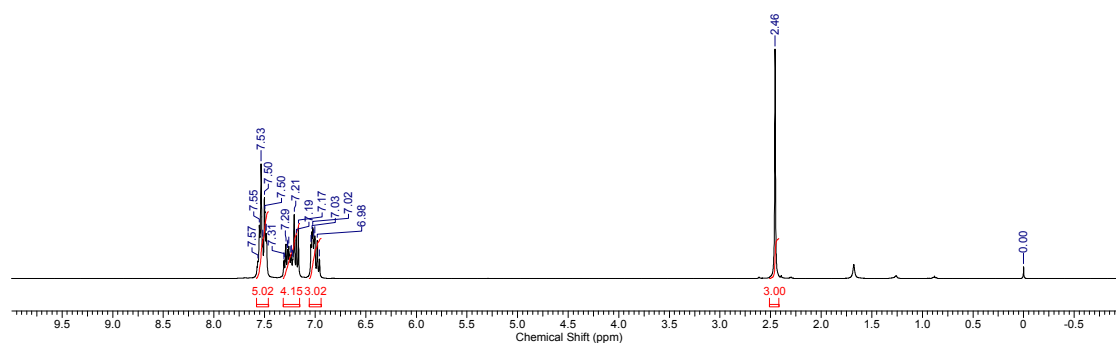
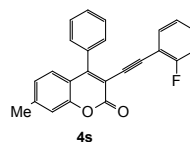
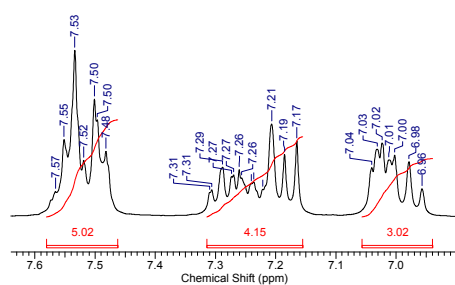


Figure S57. ¹H NMR spectrum of compound 4s

WXJ-161-19G,1671_000001r

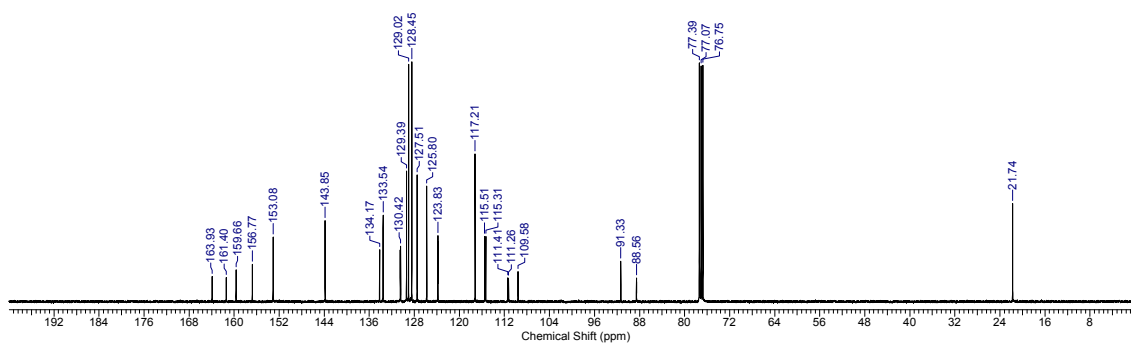
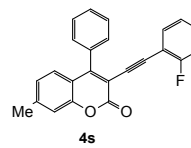
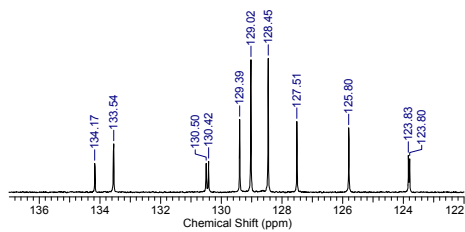


Figure S58. ¹³C NMR spectrum of compound 4s

WXJ-161-19F,1672_000001r

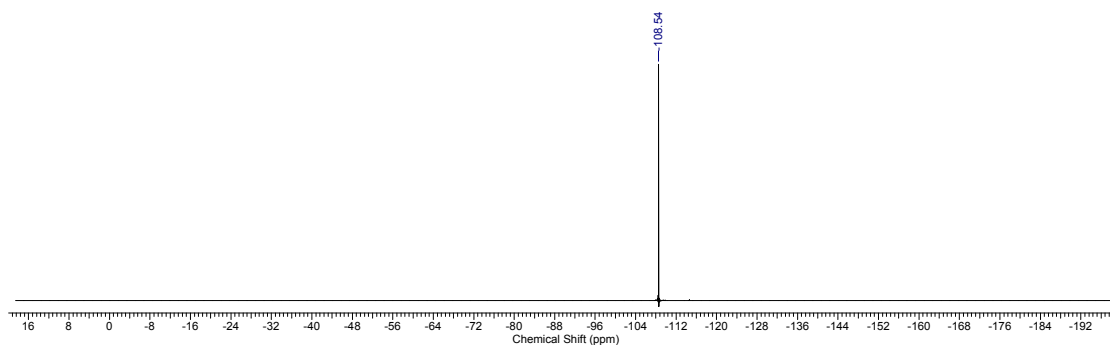
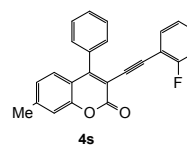


Figure S59. ¹⁹F NMR spectrum of compound 4s

WXJ-263-1H,6760_000001r

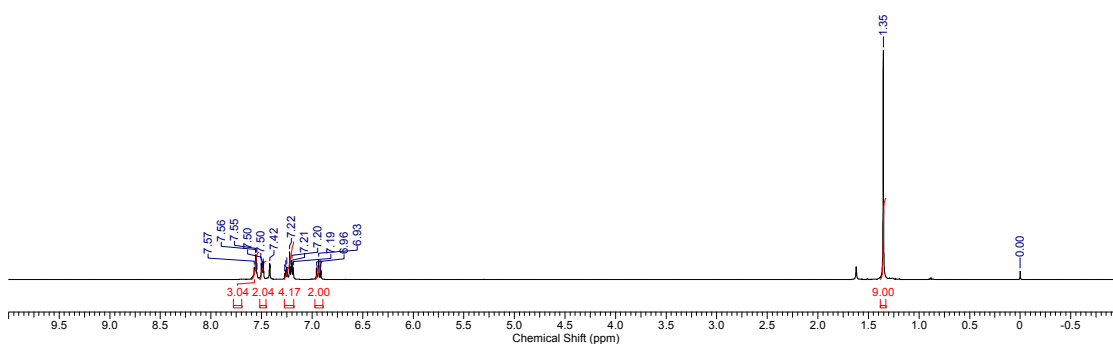
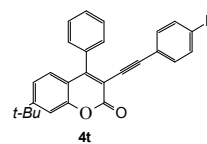
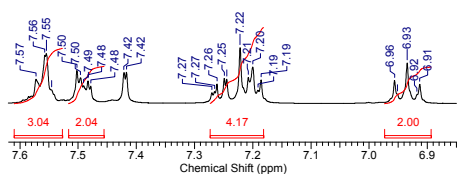


Figure S60. ^1H NMR spectrum of compound **4t**

WXJ-263-13C,6751_000001r

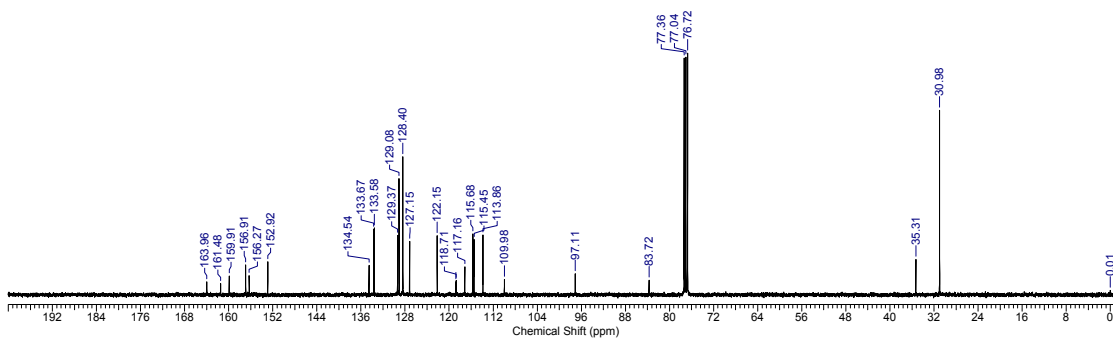
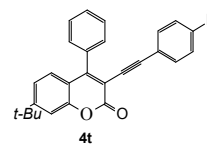
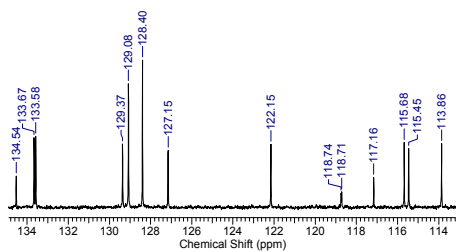
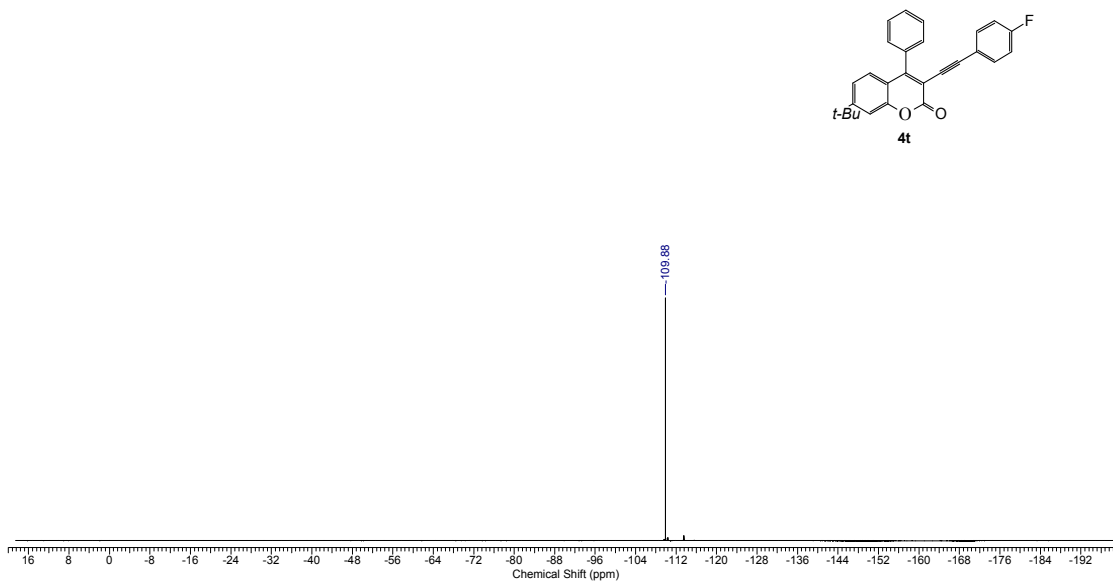
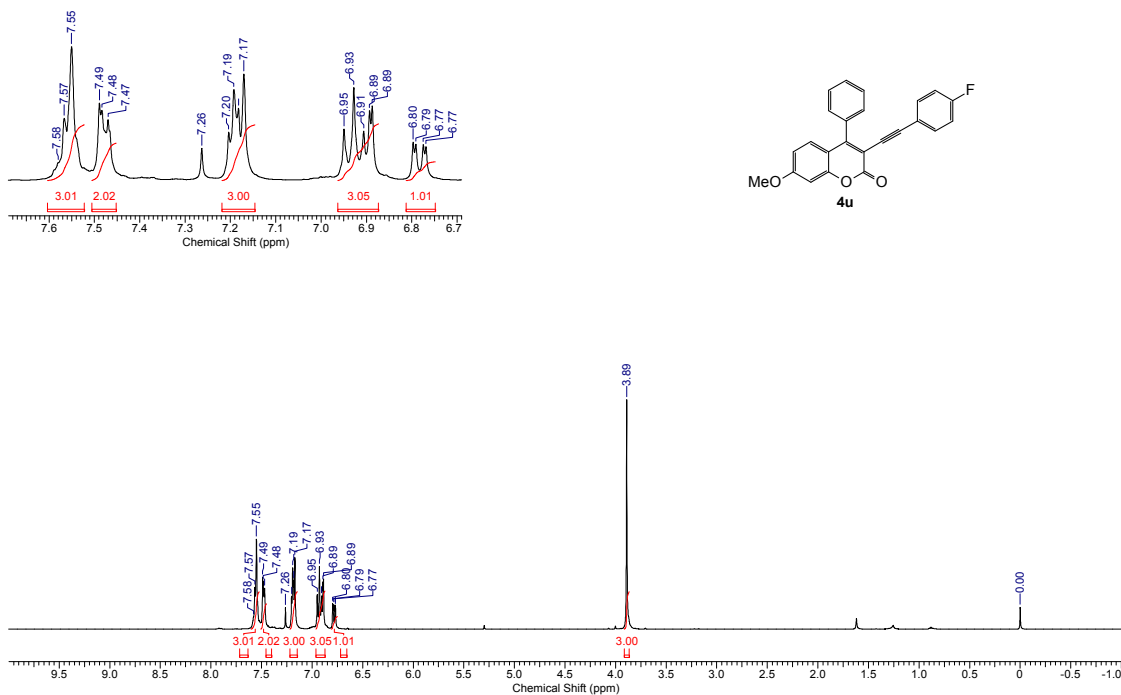


Figure S61. ^{13}C NMR spectrum of compound **4t**

Figure S62. ¹⁹F NMR spectrum of compound **4t**Figure S63. ¹H NMR spectrum of compound **4u**

WXJ-259-13C,6611_000001r

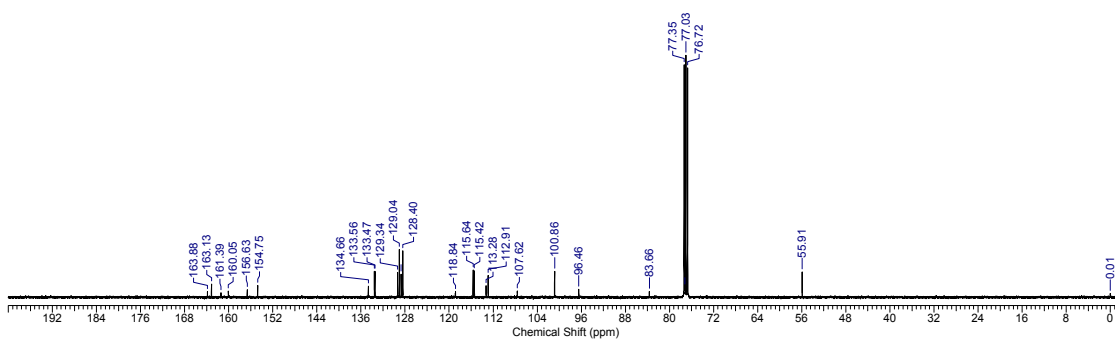
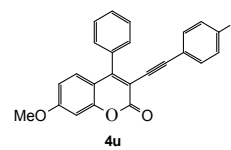
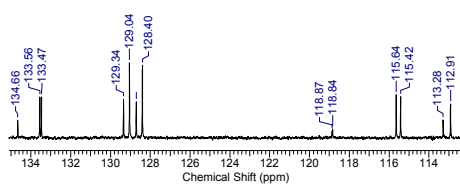


Figure S64. ^{13}C NMR spectrum of compound **4u**

WXJ-259-19F,6612_000001r

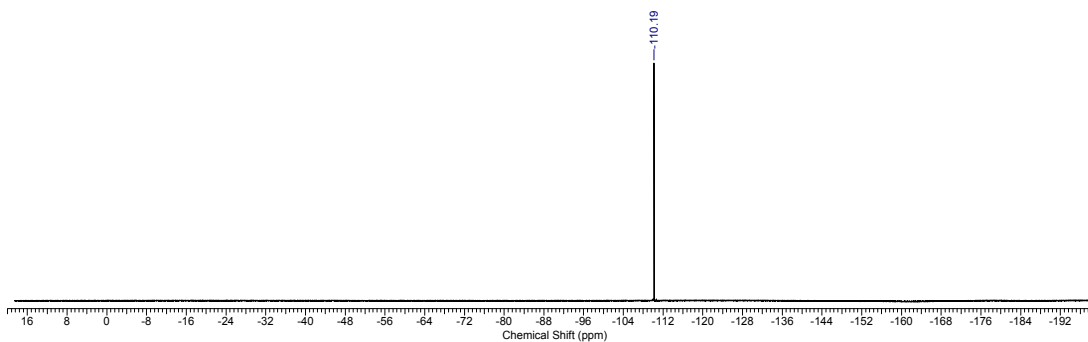
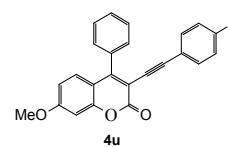


Figure S65. ^{19}F NMR spectrum of compound **4u**

WXJ-258-1H,14520_000001r

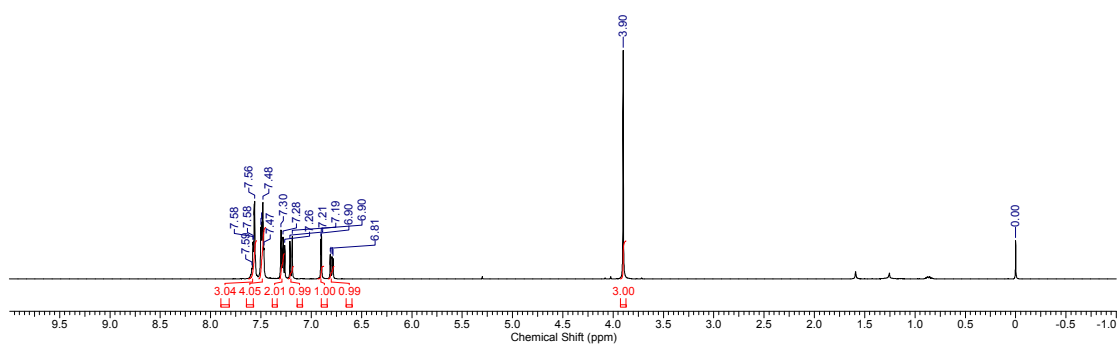
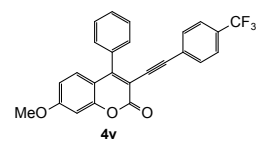
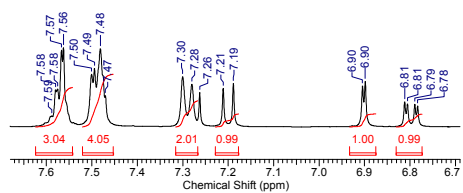


Figure S66. ¹H NMR spectrum of compound **4v**

WXJ-258-13C,6601_000001r

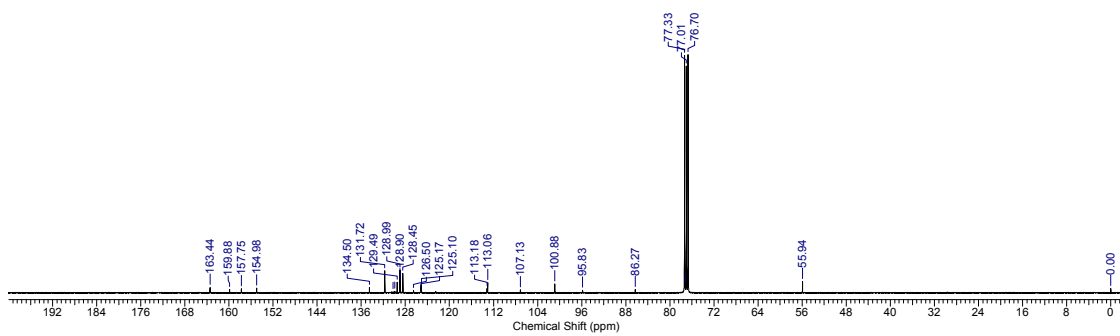
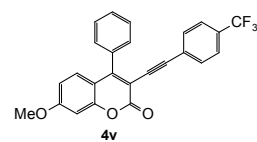
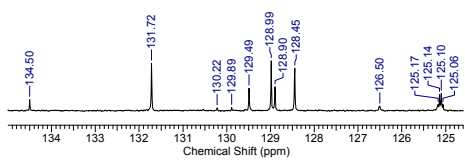
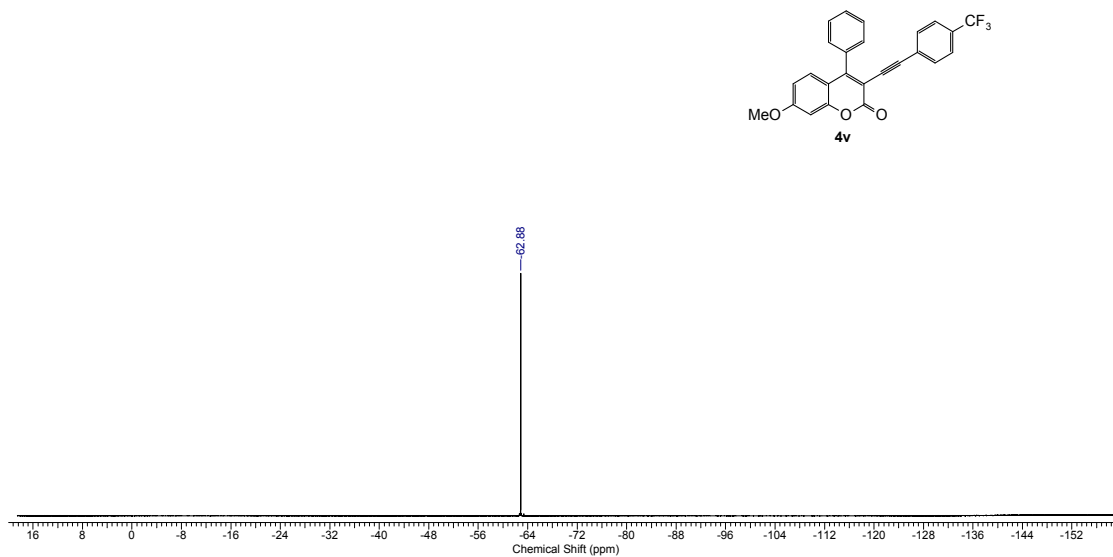
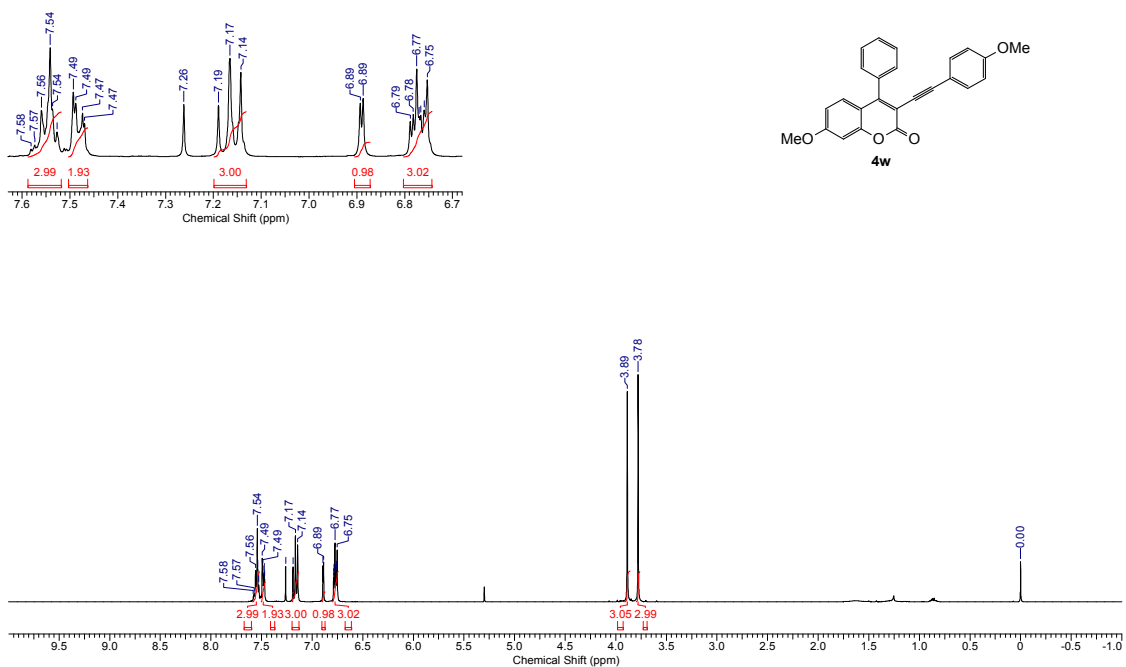


Figure S67. ¹³C NMR spectrum of compound **4v**

Figure S68. ¹⁹F NMR spectrum of compound **4v**Figure S69. ¹H NMR spectrum of compound **4w**

WXJ-260-13C,6621_000001r

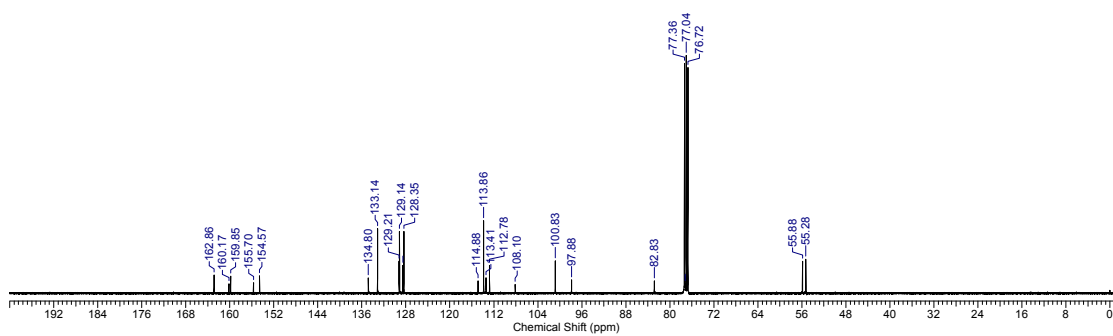
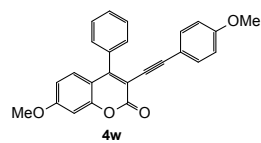
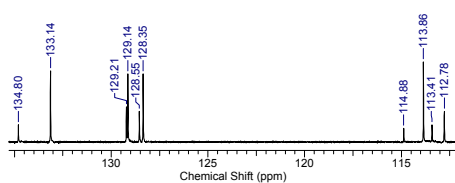


Figure S70. ¹³C NMR spectrum of compound **4w**

WXJ-262-1H,6740_000001r

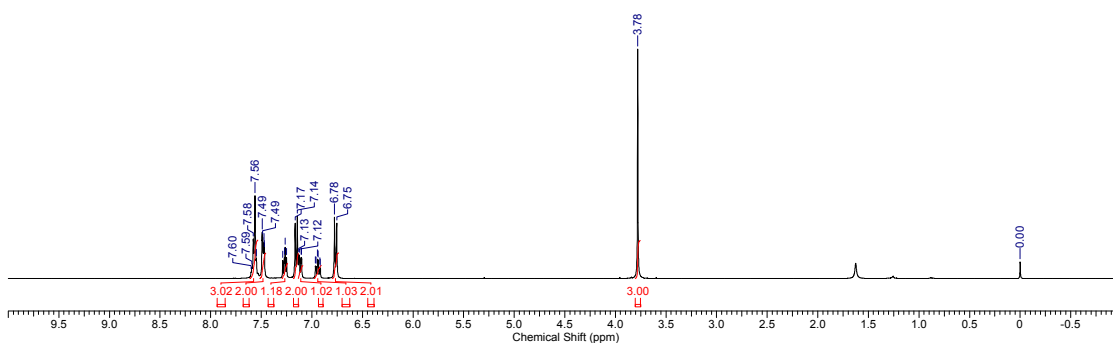
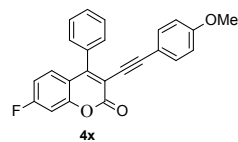
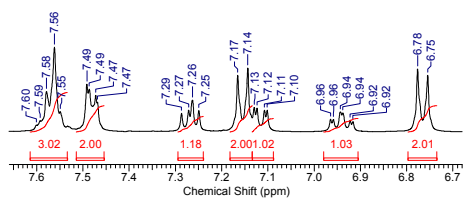


Figure S71. ¹H NMR spectrum of compound **4x**

WXJ-262-13C,6742_000001r

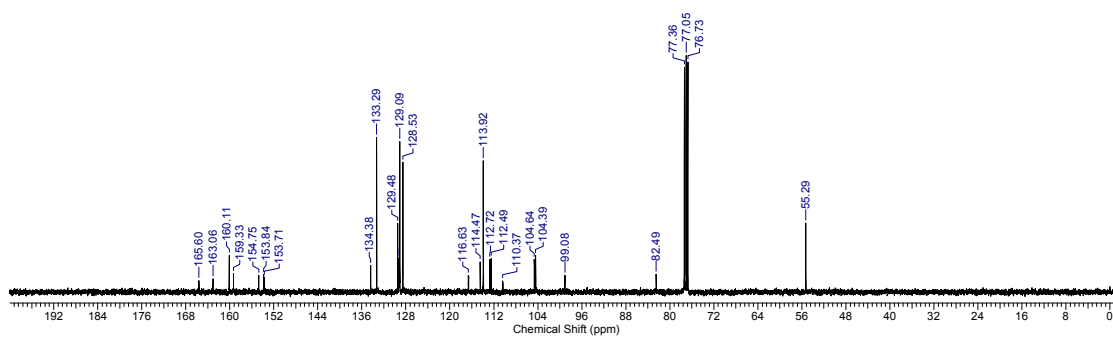
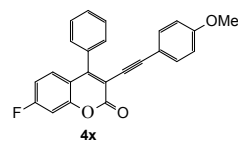
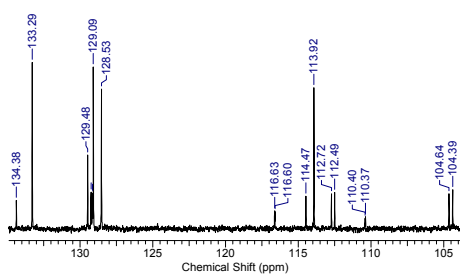


Figure S72. ¹³C NMR spectrum of compound 4x

WXJ-262-19F,6741_000001r

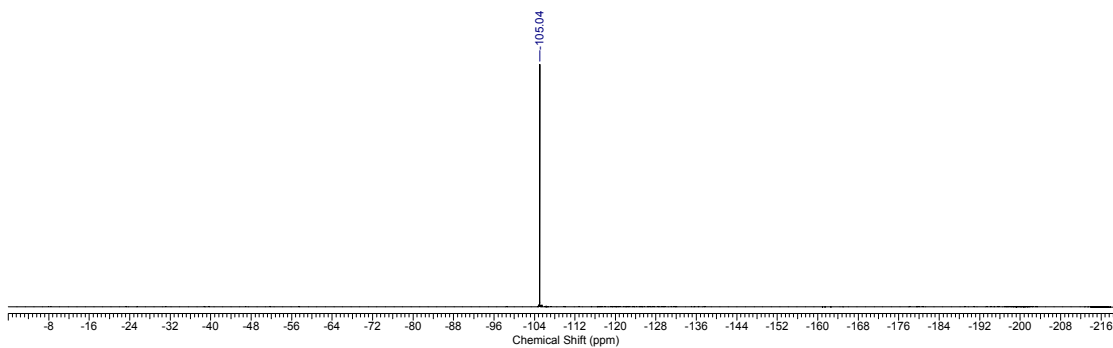
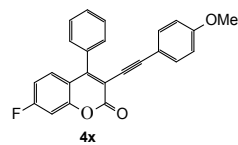


Figure S73. ¹⁹F NMR spectrum of compound 4x

WXJ-261-1H,6730_000001r

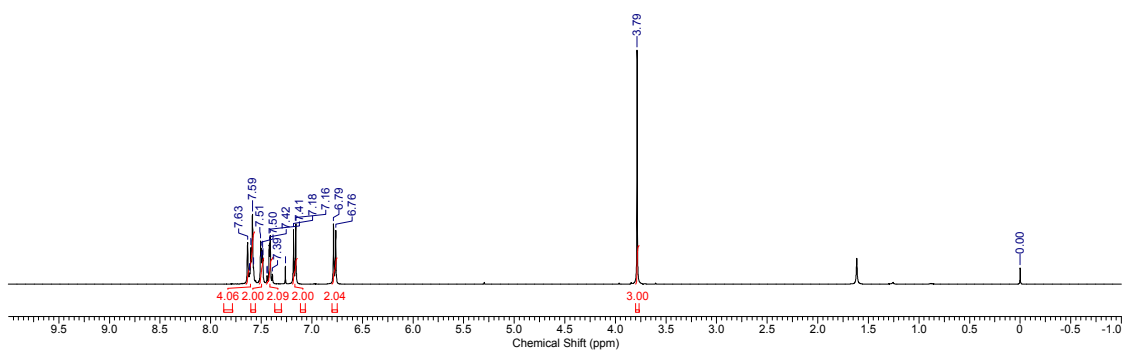
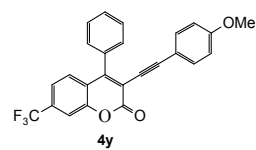
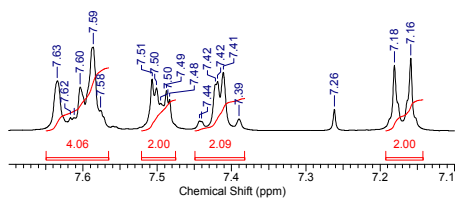


Figure S74. ¹H NMR spectrum of compound **4y**

WXJ-261-13C,6731_000001r

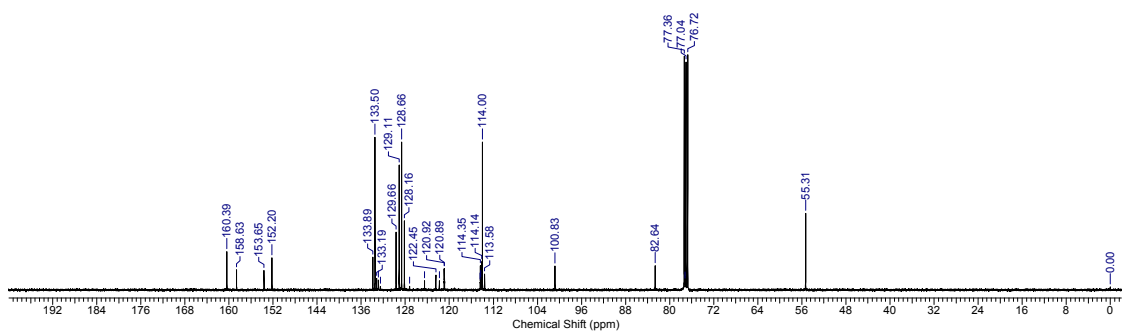
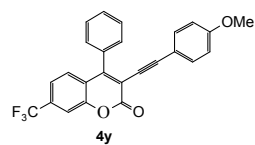
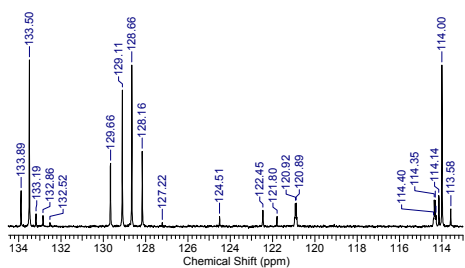


Figure S75. ¹³C NMR spectrum of compound **4y**

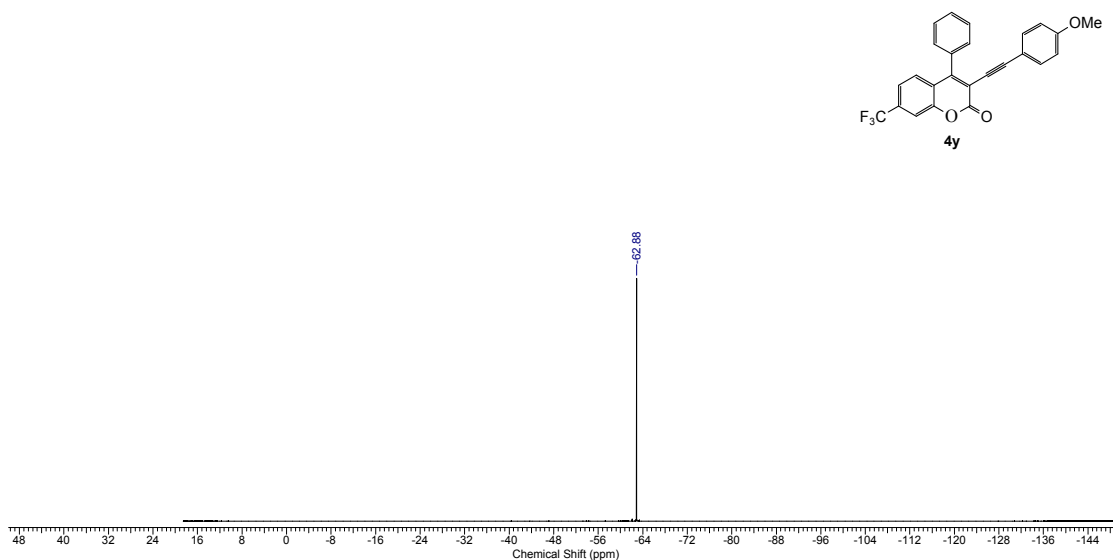


Figure S76. ^{19}F NMR spectrum of compound **4y**

6. X-ray data

1) Structure determination of **4a**

The structure of **4a** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (V/V = 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1881743.

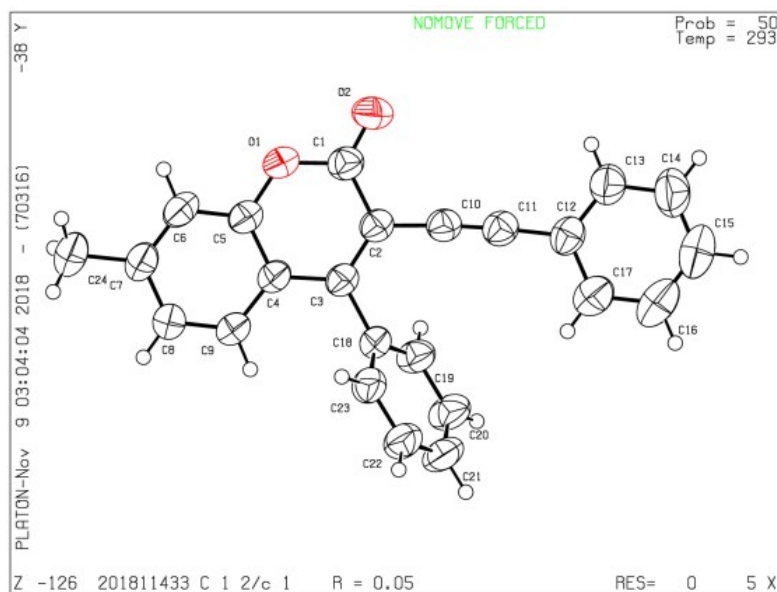


Table S3. Crystal data and structure refinement for 4a.

Identification code	201811433
Empirical formula	C ₂₄ H ₁₆ O ₂
Formula weight	336.37
Temperature/K	293(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	29.831(4)
b/Å	11.1480(6)
c/Å	14.9443(19)
α/°	90
β/°	133.61(2)
γ/°	90
Volume/Å ³	3598.1(11)
Z	8
ρ _{calc} /cm ³	1.242
μ/mm ⁻¹	0.617
F(000)	1408.0
Crystal size/mm ³	0.2 × 0.16 × 0.14
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.188 to 134.124
Index ranges	-35 ≤ h ≤ 27, -8 ≤ k ≤ 13, -16 ≤ l ≤ 17
Reflections collected	6687
Independent reflections	3221 [R _{int} = 0.0226, R _{sigma} = 0.0294]
Data/restraints/parameters	3221/0/237
Goodness-of-fit on F ²	1.036
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0480, wR ₂ = 0.1334
Final R indexes [all data]	R ₁ = 0.0656, wR ₂ = 0.1501
Largest diff. peak/hole / e Å ⁻³	0.19/-0.19

2) Structure determination of 4e

The structure of **4e** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (V/V = 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1966836.

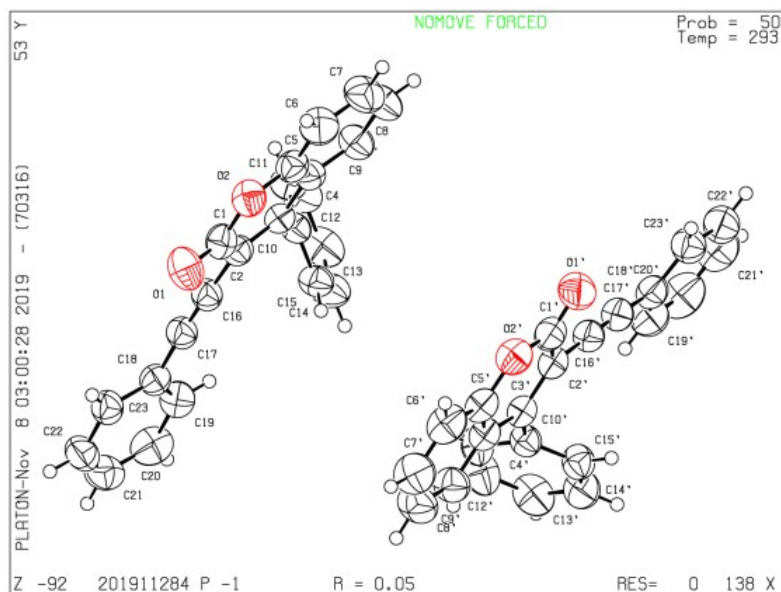


Table S4. Crystal data and structure refinement for 4e.

Identification code	201911284
Empirical formula	C ₂₃ H ₁₄ O ₂
Formula weight	322.34
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	10.9195(8)
b/Å	11.7513(7)
c/Å	14.2060(6)
α/°	87.690(5)
β/°	77.763(5)
γ/°	71.943(6)
Volume/Å ³	1693.11(19)
Z	4
ρ _{calc} /cm ³	1.265
μ/mm ⁻¹	0.634
F(000)	672.0
Crystal size/mm ³	0.16 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.916 to 134.158
Index ranges	-13 ≤ h ≤ 13, -14 ≤ k ≤ 13, -12 ≤ l ≤ 16
Reflections collected	11792
Independent reflections	5950 [R _{int} = 0.0230, R _{sigma} = 0.0328]
Data/restraints/parameters	5950/0/452
Goodness-of-fit on F ²	1.018
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0473, wR ₂ = 0.1252

Final R indexes [all data]	$R_1 = 0.0637$, $wR_2 = 0.1428$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.20/-0.16

3) Structure determination of **4h**

The structure of **4h** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (V/V = 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1966837.

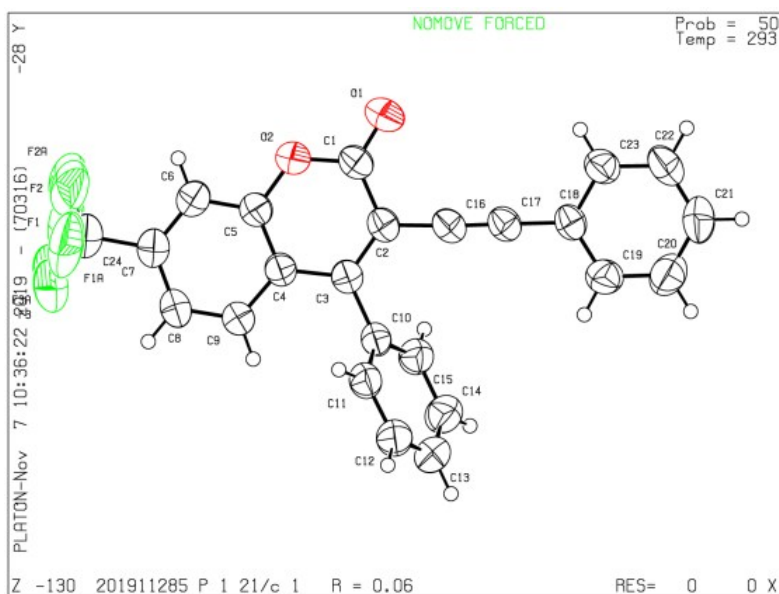


Table S5. Crystal data and structure refinement for **4h.**

Identification code	201911285
Empirical formula	$C_{24}H_{13}F_3O_2$
Formula weight	390.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	11.8769(8)
$b/\text{\AA}$	11.8650(6)
$c/\text{\AA}$	14.2912(11)
$\alpha/^\circ$	90
$\beta/^\circ$	110.026(8)
$\gamma/^\circ$	90
Volume/ \AA^3	1892.2(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.370
μ/mm^{-1}	0.902
F(000)	800.0
Crystal size/ mm^3	$0.12 \times 0.11 \times 0.1$

Radiation	CuK α ($\lambda = 1.54184$)
2 θ range for data collection/ $^\circ$	7.924 to 134.126
Index ranges	$-14 \leq h \leq 13$, $-14 \leq k \leq 10$, $-17 \leq l \leq 16$
Reflections collected	7164
Independent reflections	3371 [$R_{\text{int}} = 0.0234$, $R_{\text{sigma}} = 0.0304$]
Data/restraints/parameters	3371/67/273
Goodness-of-fit on F^2	1.040
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0605$, $wR_2 = 0.1653$
Final R indexes [all data]	$R_1 = 0.0800$, $wR_2 = 0.1862$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.33/-0.44

4) Structure determination of **4n**

The structure of **4n** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane ($V/V = 1/1$). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1966838.

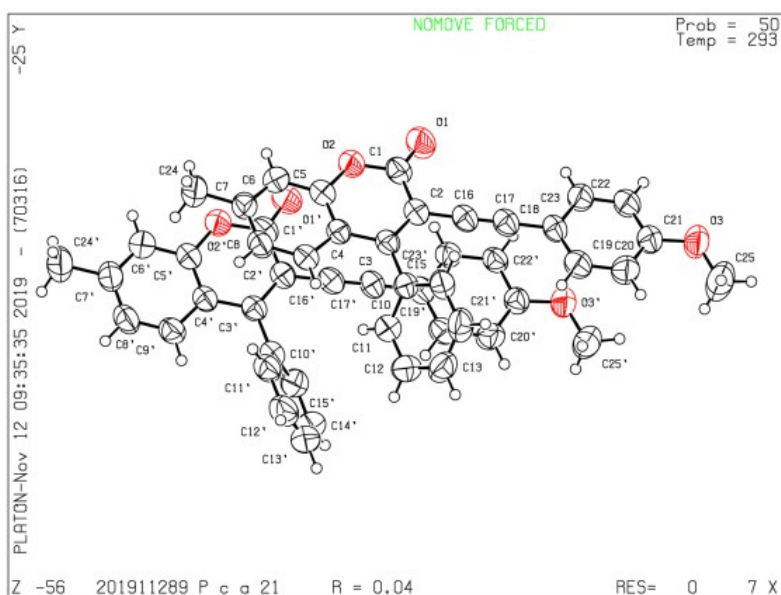


Table S6. Crystal data and structure refinement for **4n.**

Identification code	201911289
Empirical formula	$C_{25}H_{18}O_3$
Formula weight	366.39
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$Pca2_1$
$a/\text{\AA}$	21.9993(4)
$b/\text{\AA}$	12.5762(3)
$c/\text{\AA}$	13.8028(3)
$\alpha/^\circ$	90

$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/ \AA^3	3818.78(14)
Z	8
$\rho_{\text{calc}}/\text{cm}^3$	1.275
μ/mm^{-1}	0.664
F(000)	1536.0
Crystal size/ mm^3	$0.1 \times 0.09 \times 0.08$
Radiation	CuK α ($\lambda = 1.54184$)
2Θ range for data collection/ $^\circ$	8.038 to 134.152
Index ranges	$-17 \leq h \leq 26, -15 \leq k \leq 14, -14 \leq l \leq 16$
Reflections collected	15382
Independent reflections	6179 [$R_{\text{int}} = 0.0275, R_{\text{sigma}} = 0.0319$]
Data/restraints/parameters	6179/1/510
Goodness-of-fit on F^2	1.022
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0422, wR_2 = 0.1094$
Final R indexes [all data]	$R_1 = 0.0521, wR_2 = 0.1193$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	0.18/-0.13
Flack parameter	0.2(3)

5) Structure determination of **4x**

The structure of **4x** was determined by the X-ray diffraction. Recrystallized from EtOH/dichloromethane (V/V = 1/1). Further information can be found in the CIF file. This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1966843.

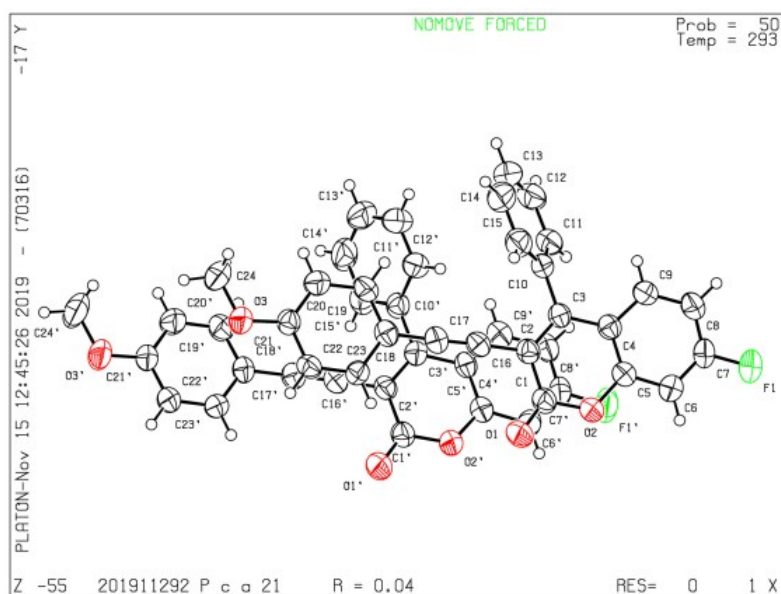


Table S7. Crystal data and structure refinement for **4x.**

Identification code	201911292
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Empirical formula	C ₂₄ H ₁₅ FO ₃
Formula weight	370.36
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Pca2 ₁
a/Å	21.9897(6)
b/Å	12.2777(3)
c/Å	13.5508(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3658.47(17)
Z	8
ρ _{calc} /cm ³	1.345
μ/mm ⁻¹	0.782
F(000)	1536.0
Crystal size/mm ³	0.16 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	7.2 to 134.674
Index ranges	-26 ≤ h ≤ 26, -13 ≤ k ≤ 14, -16 ≤ l ≤ 11
Reflections collected	13127
Independent reflections	4929 [R _{int} = 0.0319, R _{sigma} = 0.0371]
Data/restraints/parameters	4929/1/508
Goodness-of-fit on F ²	1.021
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0421, wR ₂ = 0.1018
Final R indexes [all data]	R ₁ = 0.0573, wR ₂ = 0.1161
Largest diff. peak/hole / e Å ⁻³	0.16/-0.15
Flack parameter	-0.15(18)
