Supporting Information for

Photo-accelerated "Click" Reaction between Diarylsydnone and Ring-strained Alkyne for Bioorthogonal Ligation

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Supplemental Figures and Tables

General Information

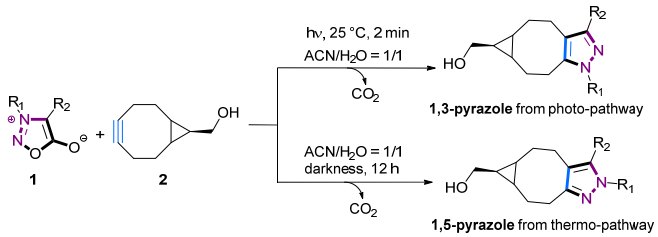
Unless otherwise indicated, all solvents and starting materials were purchased from commercial sources and used directly without further purification. BCN[1] (*endo*-bicyclo[6.1.0]nonyne, single stereoisomer were used) and TMTH[2] were synthesized according to literature procedures. EdU[3] was purchased from commercial source. C-H activation cross-coupling reactions[4] were carried out under nitrogen atmosphere in Schlenk tubes. Anhydrous solvents, purchased from Acros Organics (DMF and THF), Commercially available chemicals were obtained from Adamas, Acros Organics, Aldrich Chemical Co., Alfa, Aesar and TCI. Light sources: hand-held lamp (311 nm, 10.8 mW/cm^2) and LED assay (373 nm, 38.5 mW/cm^2 or 405 nm, 33.6 mW/cm^2) were purchased from commercial sources. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Brüker Advance spectrometer (^{1}H: 400 or 800 MHz, ^{13}C: 101 MHz, ^{19}F: 376 MHz). Chemical shifts (δ) for ^{1}H and ^{13}C NMR spectra are given in ppm relative to TMS, The residual solvent signals were used as references for ^{1}H and ^{13}C NMR spectra and the chemical shifts converted to the TMS scale ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; methanol-d_4 3.31 ppm for ^{1}H NMR and 49.05 ppm for ^{13}C NMR; DMSO-d_6, 2.50 ppm for ^{1}H NMR and 39.50 ppm for ^{13}C NMR; D_2O, 4.80 ppm for ^{1}H NMR). Shifts Multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

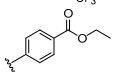
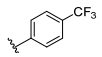
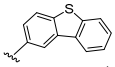
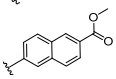
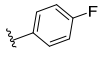
UV-Vis absorption spectra were recorded using 1 cm quartz cuvettes on a Thermo NANODROP 2000C Spectrophotometer. Spectroscopic data for kinetic[4-5] was recorded using 1 cm quartz cuvettes on a HORIBA Fluoromax-4 Spectrofluorometer at 25 ºC. Exactly ESI mass spectra were recorded on a SHIMADZU LCMS-IT-TOF. ESI-MS were obtained on a Thermo LTQ-XL mass spectrometer.

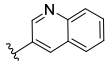
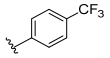
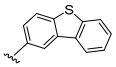
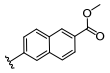
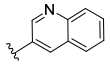
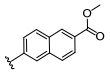
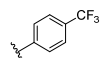
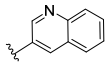
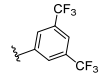
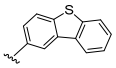
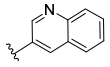
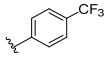
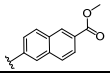
Western Blot was performed by semi-dry transfer using a PVDF membrane which was the same size of SDS-PAGE. Transfer buffer: 200 mL methanol, 2.9 g glycine, 5.8 g TRIS, adjusted to pH = 8.3; Blocking buffer, TBS: 4.4 g NaCl, 10 mL 1.5 M Tris-HCl (pH = 8.0), adjusted to pH = 7.5, to a volume of 500 mL; Washing buffer, TBST: 4.4 g NaCl, 10 mL 1.5 M Tris-HCl (pH = 8.0), 0.5 mL Tween-20, adjusted pH = 7.5, to a volume of 500 mL; Blocking solution (5% BSA): 5 g BSA, 100 mL TBS; commercially available HRP-Avidin as a Western Blot antibody conjugate; ECL luminescent solution: using commercially available Moon A and Moon B luminescent solution from Beyotime (Shanghai, China).

A549 cells were ordered from Cell bank of Chinese Academy of Sciences (Shanghai, China). Cell imaging experiments were carried out on an Olympus IX83 live cell fluorescence microscope, cells were stained with commercially available (Beyotime) NucBlue ™ Live Ready Probe ™ Reagent and DIO (3,3'-Dioctadecyloxacarbocyanine) dyes for cell nuclear and cell membrane imaging and identification.

Table S1. The reaction between DASyds (**1a-5c**) and BCN used the corresponding light sources or placed in dark for 12 h, determined by HPLC-MS[a].



Entry		Terminal		Yield		311 nm	373 nm	405 nm laser	Dark (12h)
		R_1	R_2	hν[g]	dark[h]				
1	1a			82.1%	79.2%	99%[c]	99%[b]	23.2%[d]	31.8%[d]
2	1b			73.8%	90.7%	91.1%[c]	99%[c]	34.2%[d]	19.2%[e]
3	1c			86.1%	68.4%	99%[b]	99%[b]	30.1%[d]	19.0%[e]
4	1d			73.4%	63.3%	89.0%[c]	99%[b]	23.0%[e]	3.90%[e]
5	1e			--	--	91.8%[b]	99%[b]	34.8%[d]	<1%[e]
6	1f			--	--	98.8%[c]	99%[b]	96.6%[c]	23.1%[e]
7	1g			80.6%	67.0%	89.0%[b]	99%[b]	90.8%[c]	13.6%[e]
8	1h			--	--	99%[c]	99%[c]	10.6%[e]	14.5%[e]
9	1i			83.1%	77.8%	99%[d]	99%[d]	10.4%[e]	10.1%[e]
10	1j			88.3%	88.2%	99%[c]	99%[c]	16.5%[e]	5.10%[e]
11	1k			75.3%	90.7%	99%[b]	99%[b]	8.01%[e]	>5.0%[f]
12	1l			77.2%	50.0%	92.3%[f]	94.0%[f]	16.5%[f]	4.90%[e]
13	1m			42.0%	79.4%	13.0%[d]	15.3%[d]	8.82%[d]	11.9%[e]

14	**1n**			81.0%	98.9%	40%[f]	99%[c]	99%[c]	10.0%[e]
15	**2a**			--	--	72.0%[d]	83.0%[d]	8.9%[f]	20.7%[d]
16	**2b**			--	--	91.4%[c]	99%[c]	88.9%	33.0%[d]
17	**2c**			--	--	76.9%[d]	99%[d]	40.2%[d]	0.40%[e]
18	**2d**			70.7%	73.3%	61.6%[d]	99%[c]	93.4%[f]	26.7%[d]
19	**3a**			--	--	85.3%[c]	92.6%[c]	11.6%[e]	3.40%[e]
20	**3b**			--	--	98.3%[c]	99%[c]	55.0%[d]	32.0%[d]
21	**3c**			76.0%	89.2%	72.7%[d]	99%[b]	90.7%[c]	14.7%[e]
22	**4a**			--	--	59.8%[d]	41.6%[d]	15.8%[d]	28.2%[d]
23	**4b**			--	--	--[f]	--[f]	9.8%[f]	32.1%[d]
24	**4c**			--	--	98.0%[d]	99%[d]	99%[d]	99%[b]
25	**4d**			--	--	60.5%[d]	99%[c]	78.3%[d]	36.7%[d]
26	**5a**			--	--	94.6%[c]	99%[c]	49.7%[d]	39.3%[d]
27	**5b**			71.2%	96.0%	99%[b]	99%[b]	15.6%[e]	39.5%[d]
28	**5c**			75.3%	90.7%	88.4%[c]	99%[c]	81.0%[d]	19.8%[e]

[a]A solution of 100 μM DASyd and 500 μM BCN in ACN/H_2O = 1/1 was irradiated with the corresponding light sources for 120 s or was placed in dark for 12 h. Determined by HPLC-MS. Note: hand-held lamp (311 nm, 10.8 mW/cm^2) and LED assay (373 nm, 38.5 mW/cm^2 or 405 nm, 33.6 mW/cm^2). [b]Exclusive desired reaction conversion >85%, no by-products were observed. [c]Conversion > 80%, having a small amount of hydrolysate. [d]The conversion was between 20% and 80% with small amount of non photo-induced adduct or the DASyd had been completely transformed with small amount of by-products generated. [e]The conversion was less than 25%. [f]Messy reaction or DASyd peak and product peak were overlapping on HPLC. [g]The photo-reaction yield for 30 mg DASyd and 1.2 eq. BCN in 200 mL EA was irradiated with 311 nm light source. [h]The non photo-induced reaction yield for 30 mg DASyd and 1.2 eq. BCN in 10 mL EA was placed in dark for 15 days at room temperature.

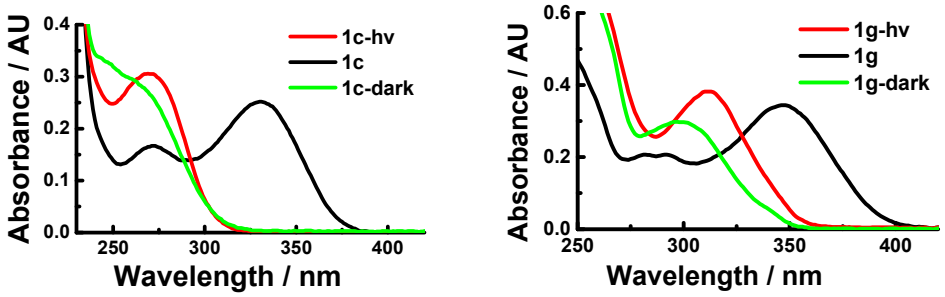


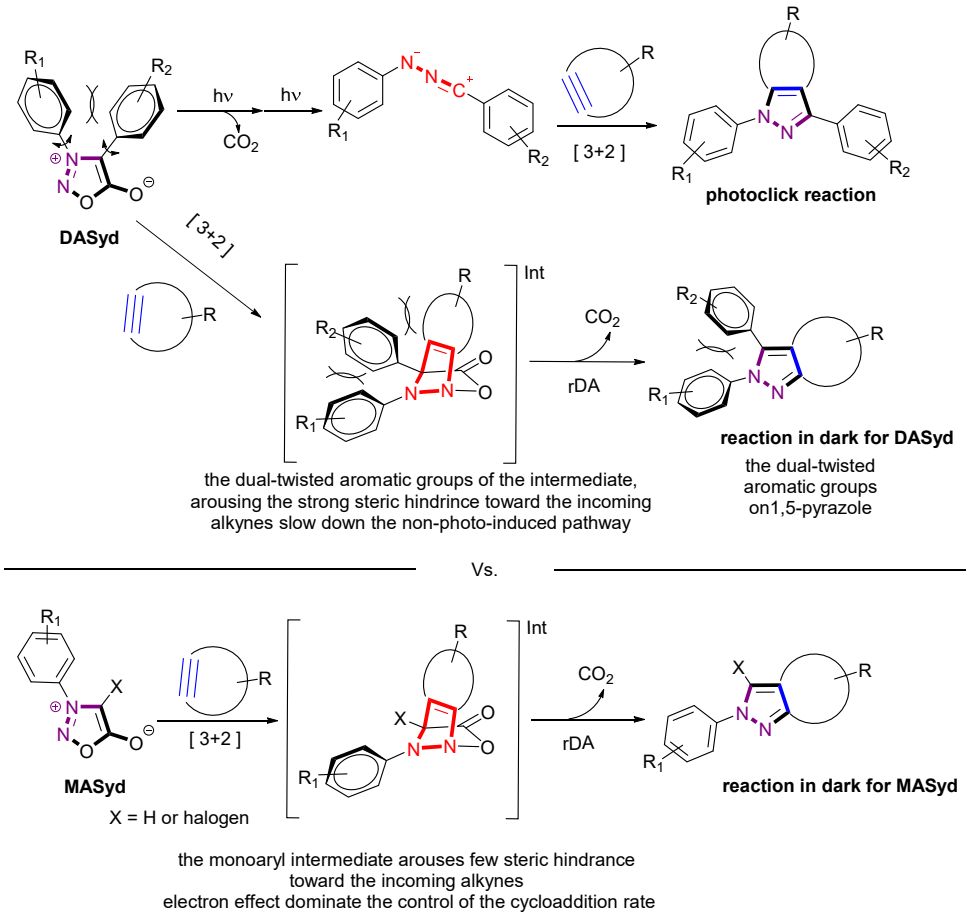
Figure S2. UV-Vis absorption spectra (the products for DASyds **1g** and **1c** with BCN under the condition of photo-activation or in dark. the cycloadduct and DASyds were dissolved DMSO to derive concentrations of 30 μM in (ACN/H_2O = 1/1, v/v).

Obvious kinetic study of photo-induced[4] or non-photo-induced reaction[5] for 1,3-dipolar cycloaddition of DASyds 1g and 1c with BCN.

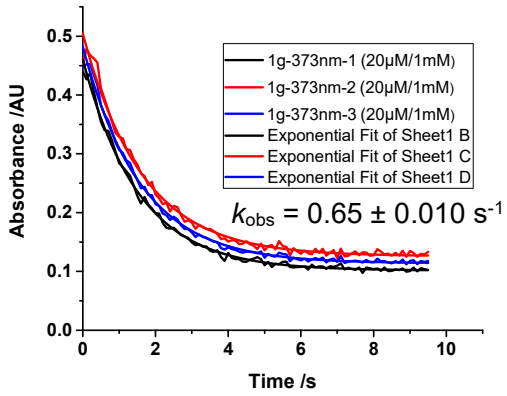
Rate constants *k* for the different DASyds (**1g** or **1c**) were measured under *pseudo*-first-order conditions with 10- to 100-fold excess of BCN in ACN/H_2O = 1/1 upon a 373 nm LED array irradiation (38.5 mW/cm^2) by time-dependent analysis. The LED light irradiation was sat in front of a quartz lens to converge the divergent light ray from the LED emitting surface of the chip, while the whole cuvette was exposed to the irradiation spot as evenly as possible. Mixing appropriate volume of the prepared stock solutions to derive the desired final concentration in sample vials, and the mixture was transferred into 1 cm optical path quartz optical cuvette. Signals were read out by monitoring the disappearance of absorption peak signal of raw material at 350 nm for **1g** or 335 nm for **1c** using a modified **HORIBA Fluoromax-4 Spectrofluorometer**. Kinetic runs were recorded using the following instrumental parameters: 10 data points per second over the recorded time range. Stock solutions of the reactants were prepared for DASyds (10 mM in DMSO) and BCN (10 mM in ACN/H_2O = 1/1, v/v). The non photo-induced reaction were monitored via the disappearance of absorption peak signal at 350 nm for **1g** or 335 nm for **1c** using **Thermo NANODROP 2000C Spectrophotometer**, which were measured under *pseudo*-first-order conditions with 30, 50, 75, 100-fold excess of BCN in ACN/H_2O = 1/1.

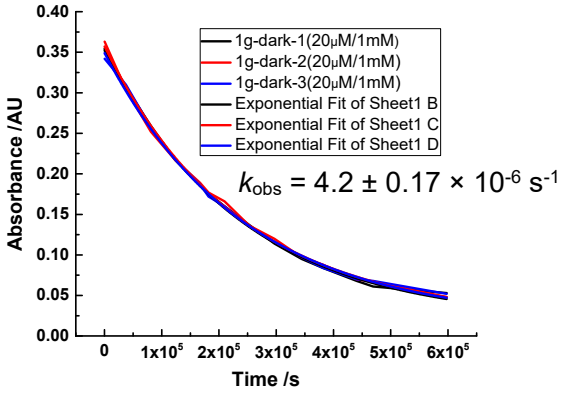
The data sets, averaged out of at least three replicates, were recorded and analyzed with the commercial software Graphpad prism 7. All data processing was performed using Origin pro software.

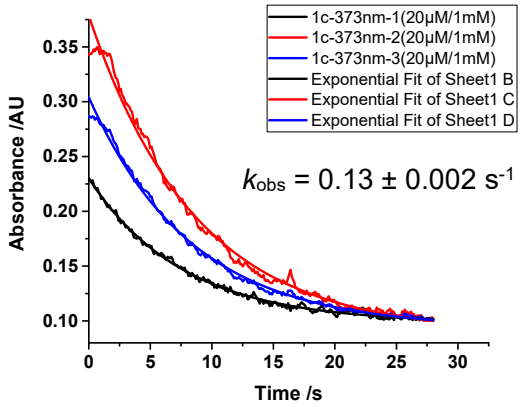
a)

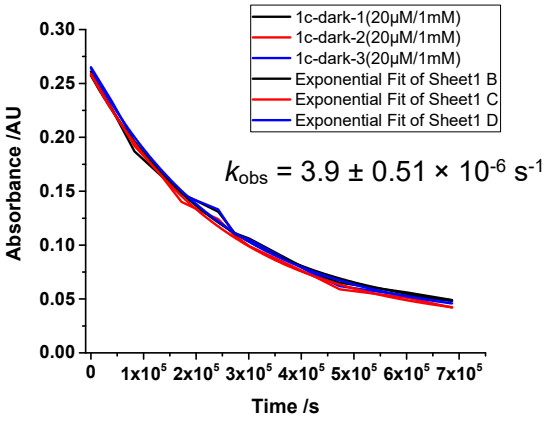


b)









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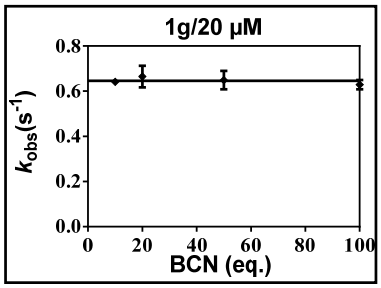
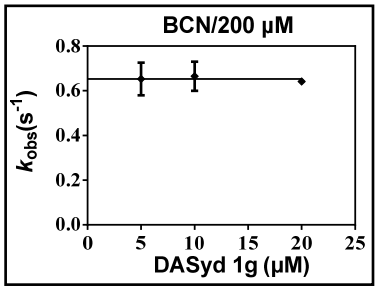
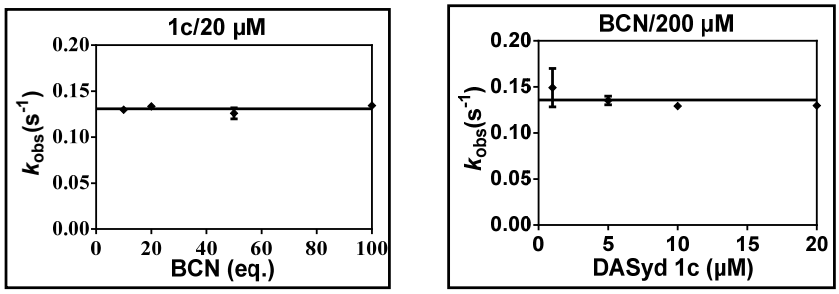


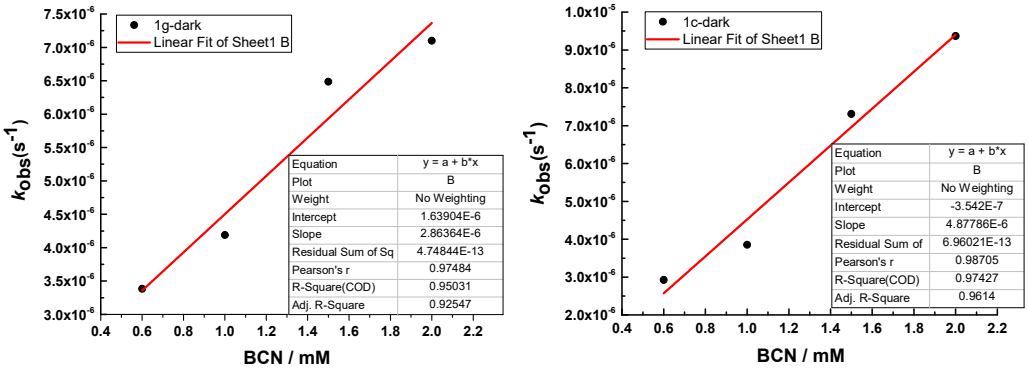


Test	k_{obs} (s^{-1})
1g (20 μM)	0.6462 ± 0.009189
BCN (200 μM)	0.6532 ± 0.016850



Test	k_{obs} (s^{-1})
1c (20 μM)	0.1308 ± 0.001328
BCN (200 μM)	0.1358 ± 0.003589

d)



DASyds	$y = a + bX$	
	a	**b (k_2, $M^{-1}s^{-1}$)**
1g	1.63904E-06	2.86364E-03
1c	-3.542E-07	4.87786E-03

Figure S3. a) The mechanism of light-accelerated reaction versus non-photo-induced reaction. The illustration of the steric effect of dual-twisted aryl group versus mono aryl group on the formation rate of the intermediate for the cycloadditions in dark. b) Representative time-dependent kinetic plots for the reaction of DASyds with BCN under the condition of photo-acceleration (DASyds/BCN = 20 μM/1 mM). c) Plots of rate constants, k_{obs}, various alkyne concentrations be measured at 25 °C or fixed the concentration of BCN at 200 μM then reduced

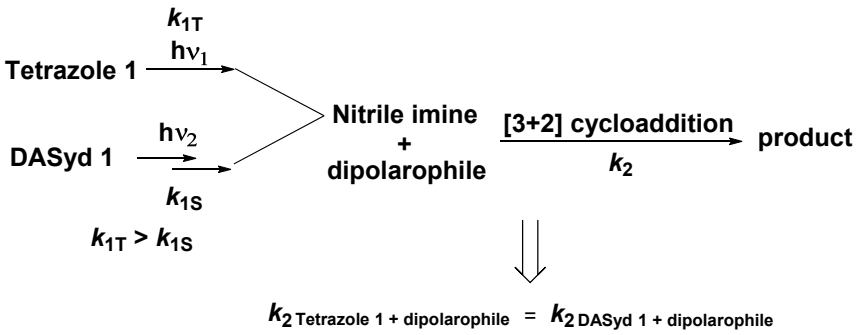
the concentration of DASyds under the condition of photo-acceleration. d) Kinetic test for non-photo-induced reaction, k_{obs}, the concentration of DASyd was fixed at 20 μM, and the concentration of BCN was 30 eq., 50 eq., 75 eq. and 100 eq. compared with DASyd under the condition in dark.

Determination of the second-order kinetic constant k_2 for DASyds 1c with BCN

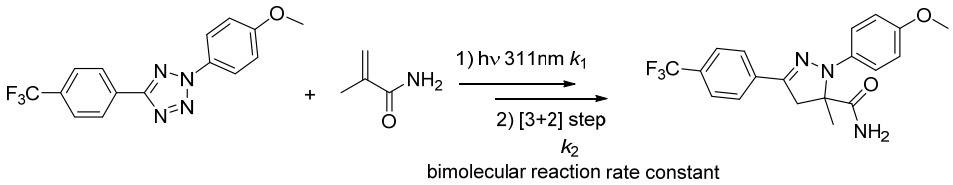
Based on the above study, we were unable to obtain k_2 by changing the alkyne concentration or increasing the light intensity, because the photo-induced conversion step is the rate-limiting step (k_{1S}) before the [3+2] cycloaddition between **NI** and BCN. In order to obtain the k_2 for the reaction of DASyds with BCN, we used an indirect method: it is known that the reaction of the nitrile imine produced by DASyds with BCN is the same as the tetrazole with BCN. Therefore, the second-order rate constant of the **NI** toward alkyne (BCN) in the [3+2] cycloaddition step would be the same, the k_2 of the DASyds with BCN is the same as that of the tetrazole, because both reagents produce the identical nitrile imine intermediate. In addition, due to the failure of ultrafast [3+2] cycloaddition for directly determining the k_2 for tetrazole with BCN, we prefer to choose methacrylamide (MAA) as the dipolarophile for **Tetrazole 1**, which had a relatively slow k_2 to make sure the [3+2] cycloaddition becoming the rate-limiting step rather that the photo-conversion step (k_{1T}). Secondly, under the pseudo first-order reaction conditions, the photo-competition experiments were carried out to determine the relative ratio of desired cycloadduct between methacrylamide (MAA) and the BCN (based on the integrated peak area in HPLC traces) for DASyds, and then the k_2 of the BCN with DASyds could be obtained. The rate constants k_2 for **Tetrazole 1** with MAA was measured under pseudo-first-order conditions with variation of MAA concentration from 0.25 to 1.0 mM (50-fold to200-fold excess) in H_2O/ACN = 1:1, v/v, upon the 311 nm LED array irradiation by time-dependent analysis. Signals were read out by monitoring the fluorescence signal appearance of the cycloaddition product, pyrazoline (**Pyr**) at the λ_{em} = 530 nm. 10 data points per second over the recorded time range. The final reactant solutions **tetrazole 1** were prepared at 5 μM in H_2O/ACN = 1:1 (v/v).

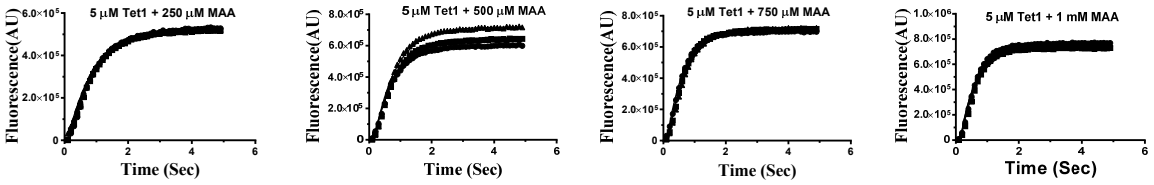
The data sets, averaged out of at least three replicates, were recorded and analyzed with the commercial software Graphpad prism 7. All data processing was performed using Origin pro software.

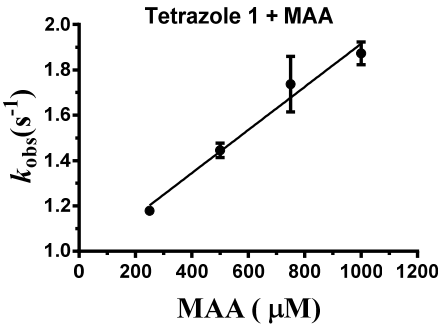
a)



b)

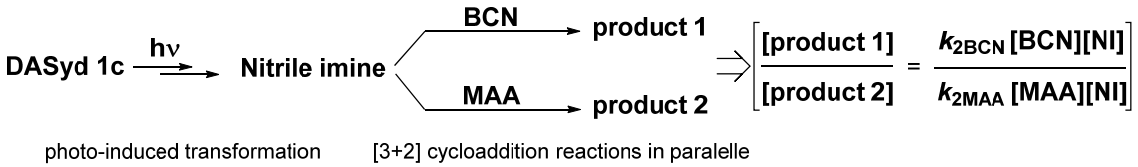




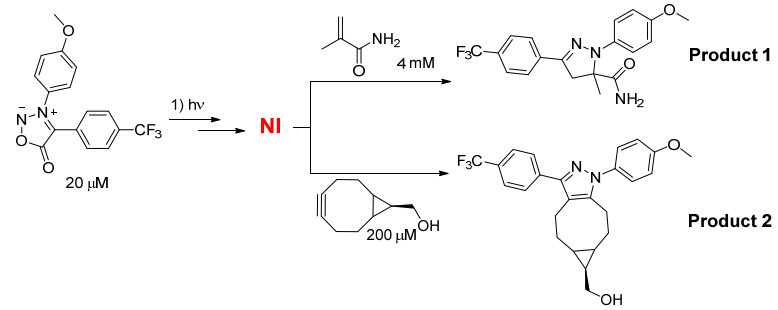


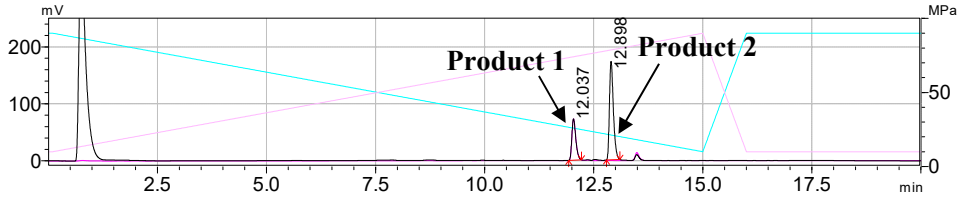
Reactant	k_2 / $M^{-1}s^{-1}$
Tetrazole 1+MAA	$9.5 \pm 0.765 \times 10^2$

c)



The competitive reaction was performed at DASyds **1c** (20 μM) with an excess of **MAA** (200 eq.) and **BCN** (10 eq.). The reaction mixture was irradiated with the 373 nm (38.5 mW/cm^2) LED lamp and analyzed by HPLC-MS. Product concentration were derived via the calibration curve of corresponding cycloadducts, analysis based on absorption at 254 nm, HPLC peak assignments were based on mass-to-charge ratio in mass spectra.





Peak No.	Time	Area	Height	%Area
1	12.037	456029	72196	29.599
2	12.898	1084657	172647	70.401

$$\left[\frac{[\text{product 1}]}{[\text{product 2}]} = \frac{k_{2MAA}\,[MAA]}{k_{2BCN}\,[BCN]}\right] \Longrightarrow \frac{[\text{product 1}] = 7.27\ \mu M}{[\text{product 2}] = 12.72\ \mu M} = \frac{k_{2MAA}\,[MAA]}{k_{2BCN}\,[BCN]} = \frac{7.27}{12.72}$$

k_{2MAA} / $M^{-1}s^{-1}$	k_{2BCN} / $M^{-1}s^{-1}$
$9.5 \pm 0.765 \times 10^2$	$3.32 \pm 0.0026 \times 10^4$

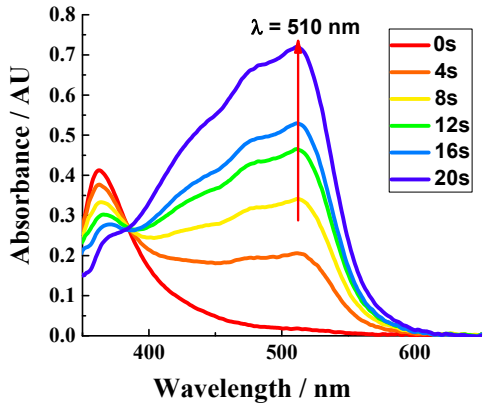
Figure S4. (a) The scheme to illustrate that the photo-induced transformation step is prior to the [3+2] cycloaddition step in both the tetrazole and DASyd photo-click reaction. (b) The determination of the rate constants k_2 for **Tetrazole 1** with MAA via time-dependent analysis of the appearance of the fluorescence of the desired pyrazoline (530 nm). (c) The determination of the relative rate constants k_{2BCN} for DASyd **1c** with BCN through competitive reaction via HPLC analysis. The cycloadduct calibration curve was used to determine the concentration of the corresponding product in the competitive reaction mixture.

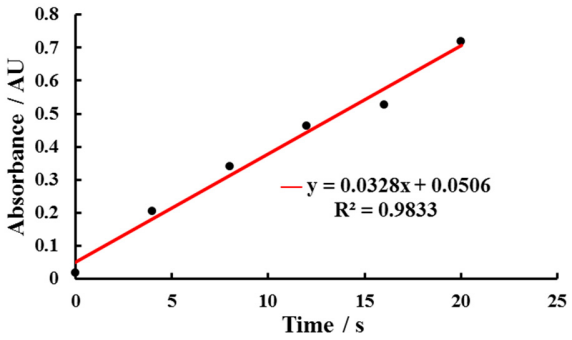
Table S5. Spectroscopic data of **1a-5c**. Compounds were dissolved in (ACN/H_2O = 1/1, v/v) to derive concentration for 30 μM, Repeated three times for each sample.

Entry	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	ε_{405} ($M^{-1}cm^{-1}$)	Entry	λ_{max} (nm)	ε_{max} ($M^{-1}cm^{-1}$)	ε_{405} ($M^{-1}cm^{-1}$)
1a	332	12,533	10	**2a**	331	11,467	90
1b	338	16,767	210	**2b**	337	13,667	757
1c	332	13,357	190	**2c**	296	12,010	310
1d	295	12,390	123	**2d**	345	18,090	1023
1e	344	10466	1733	**3a**	281	12,157	290
1f	337	14,443	667	**3b**	344	13,667	243
1g	346	20,767	767	**3c**	345	19,443	1010
1h	327	9733	30	**4a**	332	10,800	143
1i	300	9820	166	**4b**	345	13,867	323
1j	316	10033	330	**4c**	333	12,577	57
1k	274	9666	166	**4d**	338	13,677	823
1l	344	11267	5	**5a**	344	15,877	167
1m	343	11167	930	**5b**	331	11,243	90
1n	344	13827	283	**5c**	346	19,657	710

Determination of quantum yields of the photo-click reaction of DASyds 1g and 1c toward BCN.

The quantum yields of DASyds **1g** or **1c** were determined using potassium ferrioxalate-based chemical actinometer.[6] In brief, a 250 μL fresh solution of 6 mM potassium ferrioxalate in 0.1 M H_2SO_4 was irradiated with 373 nm LED in a quartz tube for specified times before quenching by addition of 4.75 mL of NaOAc/HOAc buffer (pH = 4.3) and 5 mL of 0.1% 1,10- phenanthroline solution in water. The mixture was stirred for 30 min before UV-Vis measurement. All the work was carried out in the dark and the samples were protected from light with aluminum foil during handling. The quantum yield for a test compound was calculated based on the following equation:[4] $\Phi_t = [(\varepsilon_c/\varepsilon_t)(k_t/k_c)(c_c/c_t)]/(\varepsilon_{test}/\varepsilon_{510}) \times \Phi_c$, where ε_c and ε_t were extinction coefficients of the standard material and DASyds **1g** and **1c** at 373 nm, respectively; k_t and k_c were slopes for the test compound and the standard (absorbance versus time), respectively; c_c and c_t were concentrations of the standard or the test compounds, respectively; and ε_{510} are extinction coefficients of the Fe^{2+}-(1,10-phenanthroline)$_3$ complex at 510 nm for the actinometer; the ε_{test} for **1g** at 350 nm and **1c** at 335 nm, respectively.





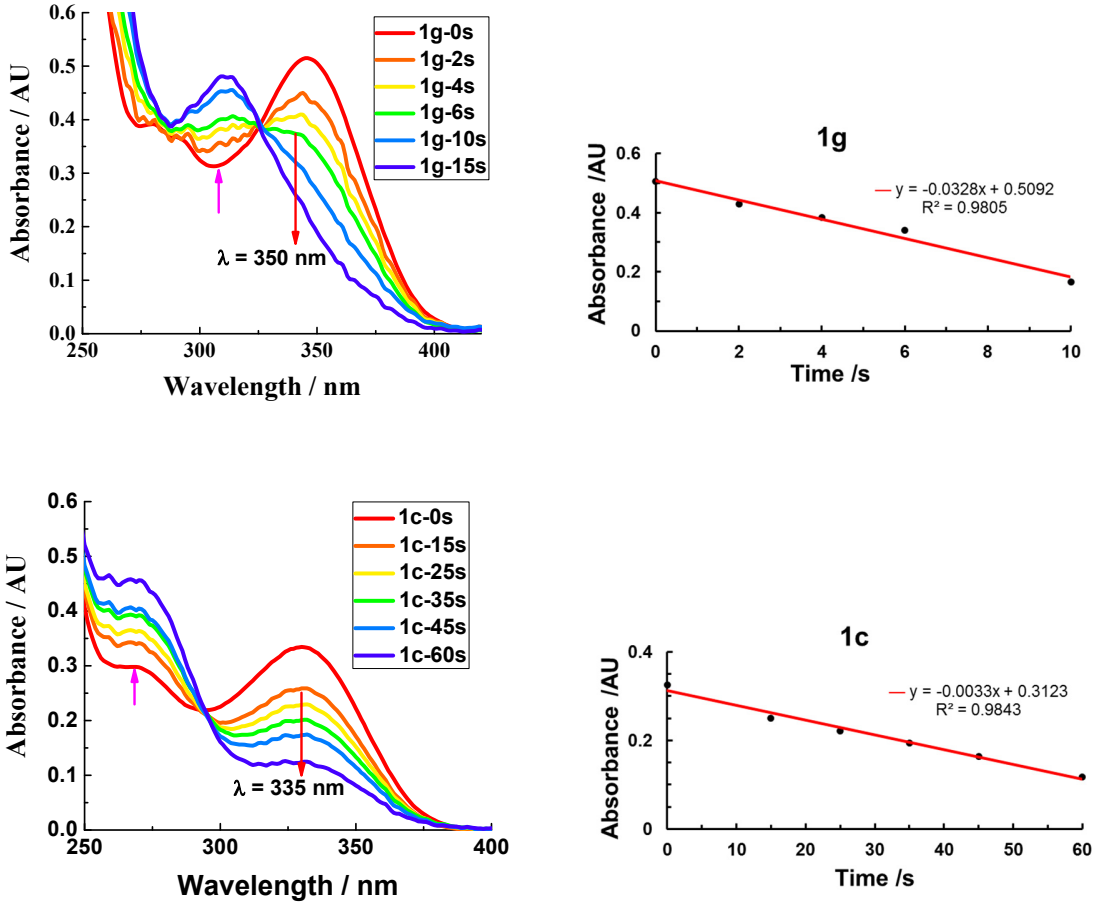
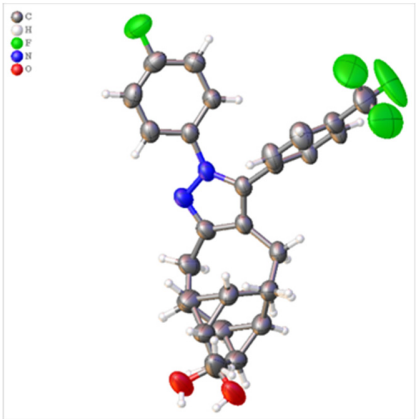


Figure S6. The quantum yields of 373 nm light-induced transformation for DASyds **1g** and **1c** in ACN/H_2O = 1/1 was determined to be 0.24, 0.21, respectively.

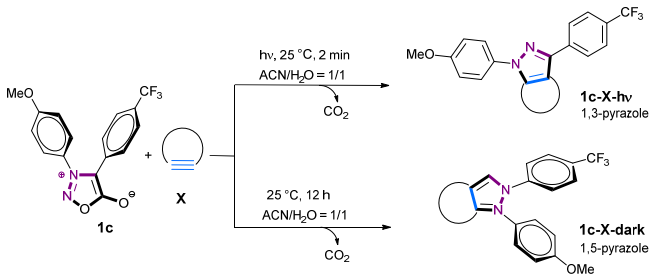
Table S7. Crystal data and structure refinement for **5bd-dark**.

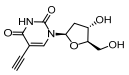
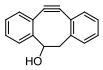
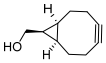


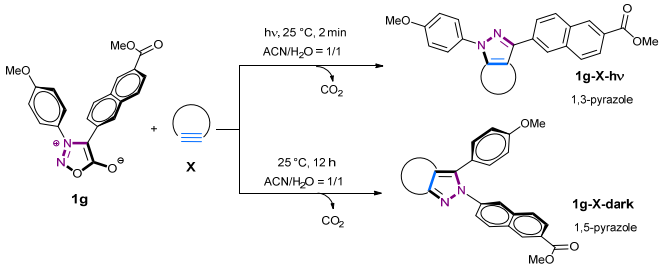
Identification code	180921_s1_zxc	
Empirical formula	$C_{24}H_{22}F_4N_2O$	
Formula weight	430.43	
Temperature	293.15	
Crystal system	triclinic	
Space group	P-1	
Unit cell dimensions	*a* = 5.7422(4) Å	α=93.263(4) °
	b = 8.6225(4) Å	β=95.198(5) °
	c = 22.5087(13) Å	γ = 106.430(5) °
Volume	1060.56(11) $Å^3$	
Z	2	
Density (calculated)	1.348 mg/m^3	
Absorption coefficient	0.107 mm^{-1}	
F (000)	448.0	
Crystal size	0.35 x 0.3 x 0.25 mm^3	
Radiation	MoKα (λ = 0.71073)	
2Θ range for data collection	6.394 to 52.744°	
Index ranges	-7≤h≤7, -10≤k≤10, -28≤l≤28	
Reflections collected	9014	
Independent reflections	4338 [R_{int} = 0.0225, Rsigma = 0.0478]	
Data / restraints / parameters	4338/0/295	
Goodness-of-fit on F^2	1.041	
Final *R* indices [*I*>2 sigma (*I*)]	*R*1 = 0.0656, *wR*2 = 0.1707	
Final *R* indices (all data)	*R*1 = 0.1160, *wR*2 = 0.1993	
Largest diff. peak and hole	0.33/-0.28 e. $Å^{-3}$	

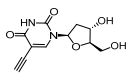
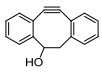
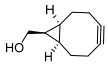
Single crystal of **5bd-dark** [$C_{24}H_{22}F_4N_2O$] was obtained by recrystallization in $CHCl_3$. CCDC-1904446 (CIF) contains the supplementary crystallographic data which can be obtained free of charge from Cambridge Crystallographic Data Center *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S8. 1,3-Dipolar cycloaddition of **1c** with various alkyne dipolarophiles under the condition of photo-activation or in dark[a]



Entry	Alkyne	311 nm	373 nm	405 nm	Dark 12 h	$Iso_{(hv)}$ [e]	$Iso_{(dark)}$ [f]
a		trace	trace	N.D.[c]	N.D.[c]	--	--
b		trace	trace	N.D.[c]	N.D.[c]	--	--
c		57.5[c]	97.1	<1[c]	<1[c]	80.9	76.5
d		98.6	>99	29.8[c,d]	18.2[c]	86.1	68.4
e		74.2	82.1	1.32[c,d]	92.6	73.0	87.6

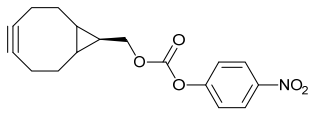


Entry	Alkyne	$Iso_{(hv)}$ [e]	$Iso_{(dark)}$ [f]
a		--	--
b		--	--
c		38.5	38.5
d		80.6	67.0
e		79.4	84.2

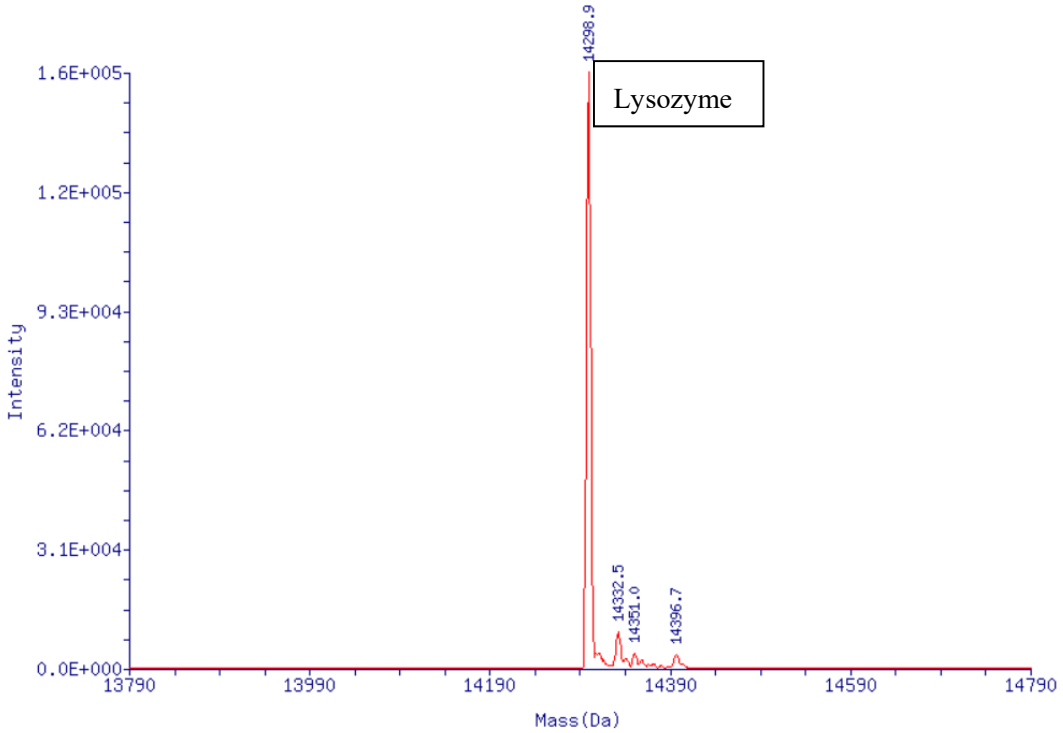
[a]A solution of 100 μM DASyd **1c** and **1g** and 500 μM alkynes in ACN/H_2O = 1/1 was irradiated with corresponding light sources for 120 s. Yields (%) were determined based on calibration curve via HPLC-MS analysis. See Figures S17-S18 in SI for details. [b]N.D. = not detected. [c]Incomplete transformation of DASyd. [d]The non photo-induced reaction product was formed. [e]The light reaction yield for 30 mg **1c** and 1.2 eq. corresponding alkyne in 200 mL EA was irradiated with 311 nm light source. [f]The non-photo-induced cycloaddition reaction yield for 30 mg **1c** and 1.2 eq. corresponding alkyne in 10 mL EtOAc was placed at room temperature for 15 days.

Chemical Modification of Lyso (chicken lysozyme) by BCN-OCOO-PNP

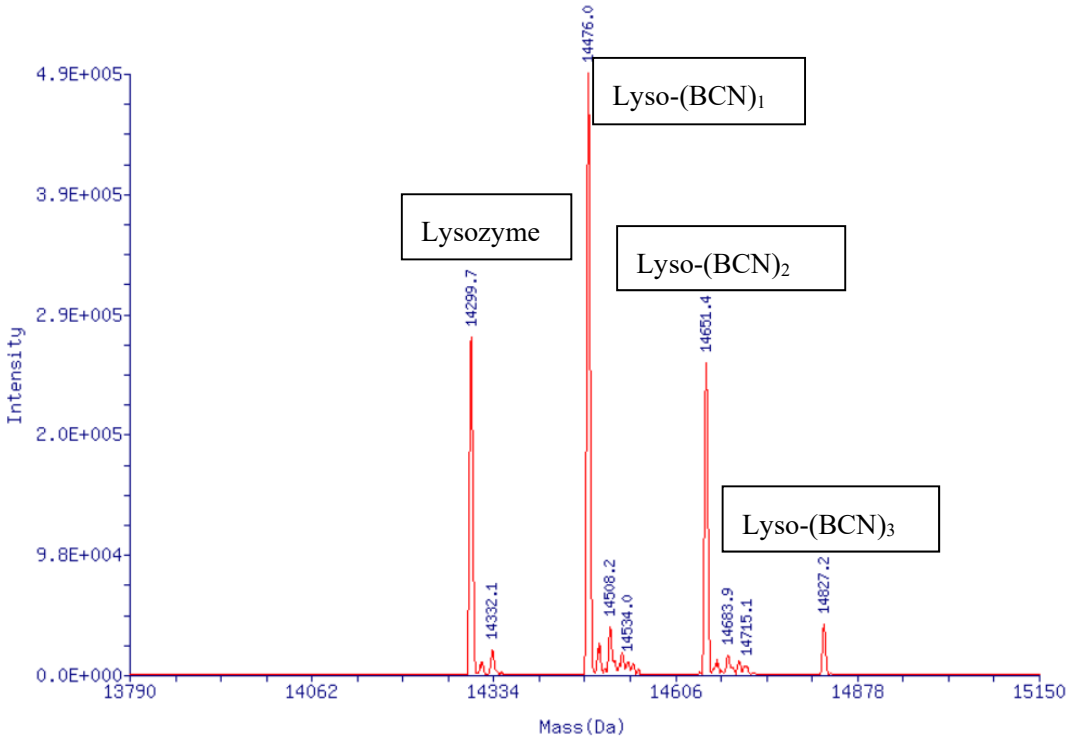
To 0.485 mL solution of lysozyme (100 μM in 100 mM NaH_2PO_4, 25 mM NaOAc, pH = 8.5) was added BCN-OCOO-PNP (10 μL, 10 mM in DMF; final concentration = 200 μM). The resulting solution was incubated on a rotating shaker at room temperature for 8 h. The tagging reaction was quenched by 0.25 M $NH_3 \cdot H_2O$ solution. And excess amount of small molecules was removed from the lysozyme through a 10 kDa spin columns using PB buffer (pH = 6.0) as eluent.



BCN-OCOO-PNP



Mass (Da)	+- Std. Dev.	Intensity	Score	Delta Mass	%Relative	%Total
14298.9	0.2	1.56E+005	10.49	0.0	100.00	90.34
14332.5	0.4	9.41E+003	8.26	33.6	6.05	5.47
14351.0	1.0	3.79E+003	7.73	52.1	2.44	2.20



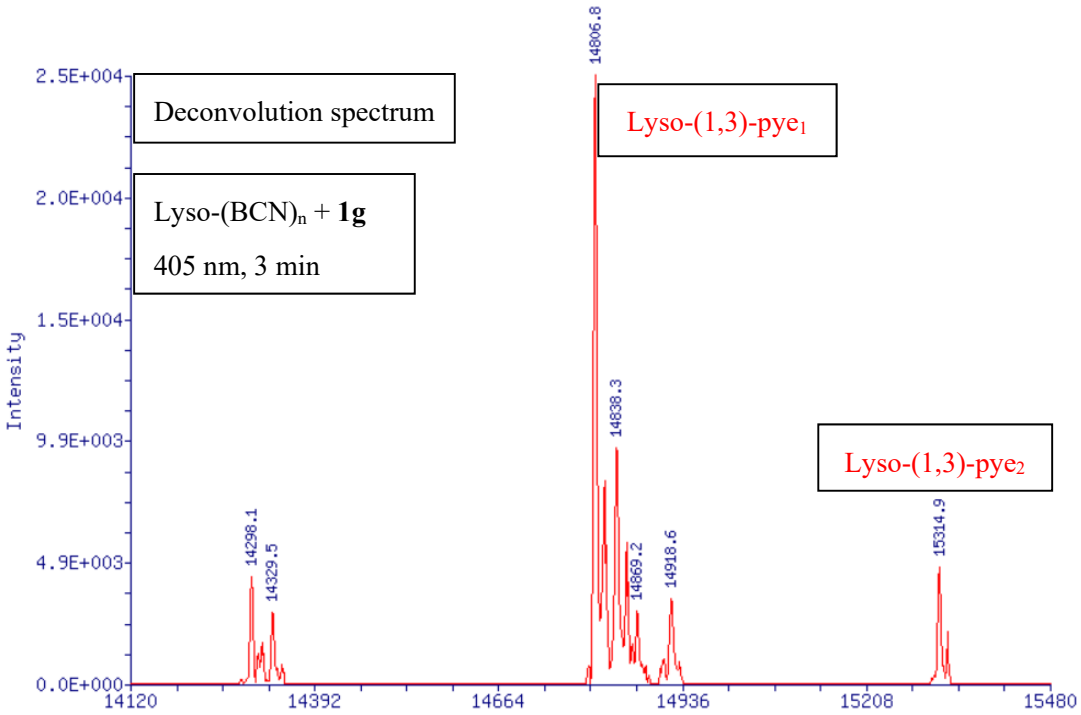
Mass (Da)	+- Std. Dev.	Intensity	Score	Delta Mass	%Relative	%Total
14476.0-(BCN)$_1$	0.3	4.66E+005	10.87	0.0	100.00	39.49
14299.7	0.3	2.83E+005	7.55	-176.4	60.70	23.97
14651.4-(BCN)$_2$	0.2	2.63E+005	9.87	175.3	56.36	22.26
14827.2-(BCN)$_3$	0.3	4.12E+004	4.45	351.1	8.84	3.49

Figure S9. HPLC-MS spectra of the chicken lysozyme (Lyso) and BCN-modified Lyso. The alkyne-modified lysozyme was characterized by LC-ESI/MS: Lyso, calcd. 14302 Da, found 14298.9 ± 0.2 Da, Lyso-(BCN)$_1$, found 14476.0 ± 0.3 Da, Lyso-(BCN)$_2$, found 14651.4 ± 0.2 Da, Lyso-(BCN)$_3$, found 14827.2 ± 0.3 Da.

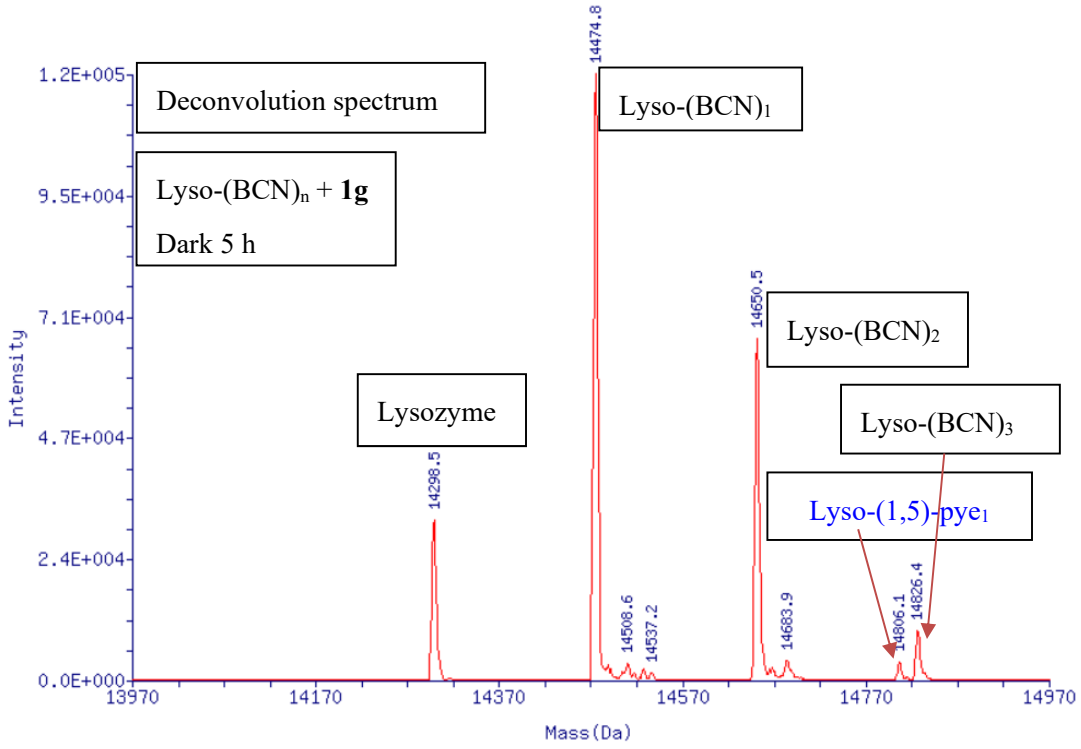
Comparison of photo-activation strategy versus non photo-induced reaction between Lyso-(BCN)$_n$ and DASyd 1g for protein labeling

To 20 µL samples of 5 µM Lyso-(BCN)$_n$ in PB (phosphate buffer, pH = 6.0) were added 4 µL of DASyd **1g** (250 µM in ACN/H_2O = 1/1, v/v; final concentration = 50 µM). Irradiation with 405 nm LED (33.6 mW/cm^2) for 3 min. As for the non-photo-induced reaction, the concentration was

the same as the above, protected with alumina foil, and the samples were placed for 5 h. All samples analyzed by HPLC-ESI/MS.



Mass (Da)	+- Std. Dev.	Intensity	Score	Delta Mass	%Relative	%Total
14806.8-pye1	0.4	3.64E+004	8.10	0.0	100.00	49.65
14838.3	0.6	1.22E+004	7.12	32.2	33.59	16.68
14298.1	0.7	5.07E+003	4.23	-508.2	13.92	6.91
15314.9-pye2	0.5	3.35E+003	2.92	508.4	9.21	4.58



Mass (Da)	+- Std. Dev.	Intensity	Score	Delta Mass	%Relative	%Total
14474.8-(BCN)$_1$	0.2	1.18E+005	10.27	0.0	100.00	49.33
14650.5-(BCN)$_2$	0.3	6.65E+004	9.34	175.7	56.25	27.75
14298.5-(BCN)$_3$	0.2	3.12E+004	6.04	-176.3	26.40	13.02
14806.1-(pye)$_1$	0.8	3.33E+003	2.93	331.3	2.82	1.39

Figure S10. LC/ESI-MS analysis of Lyso-BCN$_n$ with DASyd **1g** after the conditions of photo-accelerated reaction at 405 nm LED irradiation for 3 min or in dark for 5 h. Lyso-(1,3)-pye$_1$ found 14806.8 ± 0.4 Da, Lyso-(1,3)-pye$_2$ found 15314.9 ± 0.5 Da, Lyso-(1,5)-pye$_1$ found 14806.1 ± 0.8 Da. No non-specific reaction was detected (starting material Lyso adding the nitrile imine derived from DASyd **1g**).

SDS-PAGE analysis and Western Blot for the Lyso-(BCN)$_n$ and Biotin-sulfo-Cy3-DASyd (6a) in PB buffer.

To 20 µL samples of 5 µM Lyso-(BCN)$_n$ in PB (phosphate buffer, pH = 6.0) were added 4 µL of bifunctional DASyds **6a** (250 µM in ACN/H_2O; final concentration = 50 µM). Irradiation with

405 nm LED (33.6 mW/cm^2) for 3 min. As for the non photo-induced reaction, the concentration was the same as the above, and the samples were wrapped with alumina foil for 1 h before subsequent process.

A 15% SDS polyacrylamide gel electrophoresis separation gel solution was used, and a semi-dry transfer method was used after electrophoresis. The PVDF film was incubated for 4 h in a blocking solution, then, incubated with a 1/2000 (HRP-Avidin/TBS) antibody dilution for 2 h. And then the PVDF membrane was washed four times with TBST for 10 min each time. The Moon A and B solution were mixed in equal volume and sprayed on the PVDF membrane for imaging.

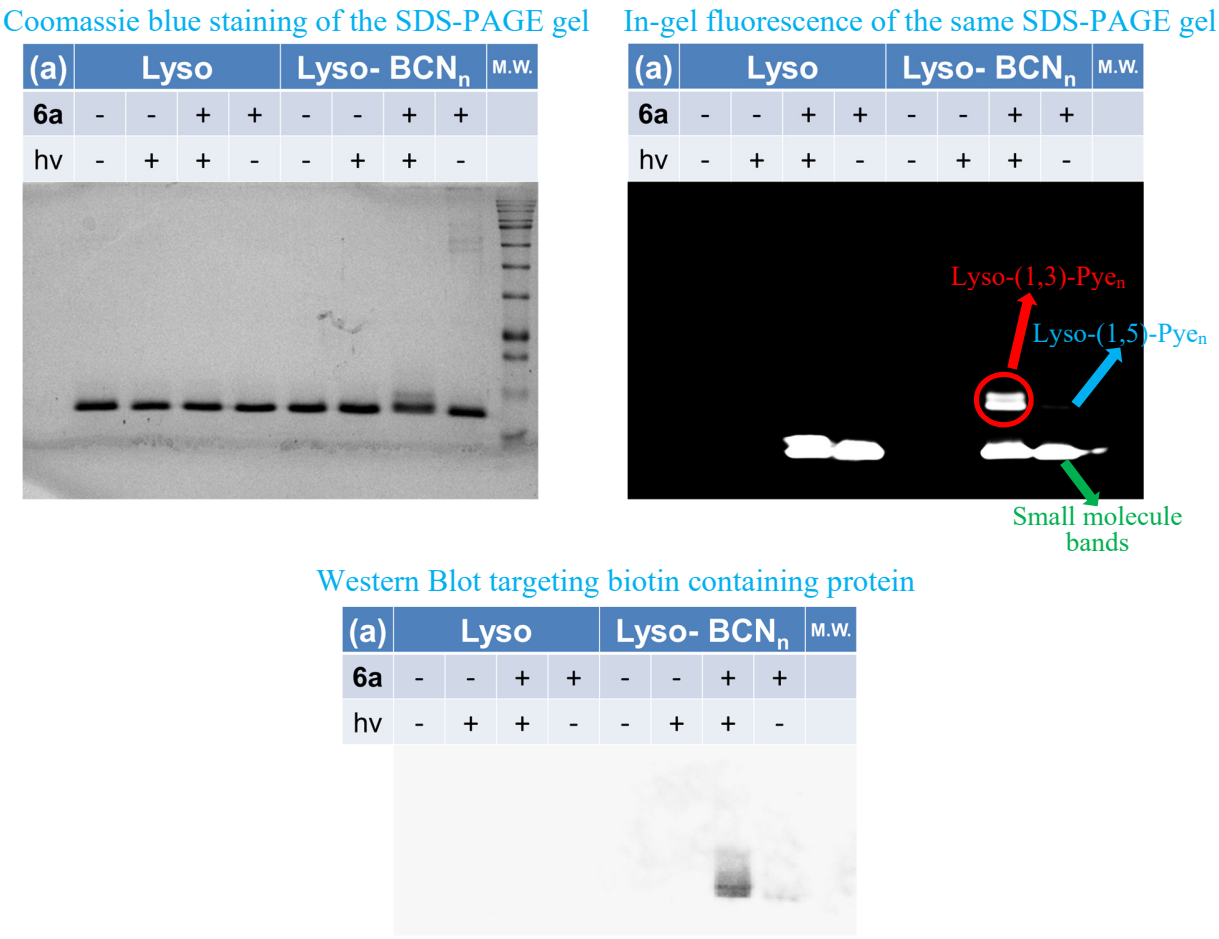


Figure S11. The mixture was denatured at 80 ºC for 5 min in loading buffer, resolved by SDS-PAGE and developed via Western Blot assay, the SDS-PAGE gel of the repeated experiment was imaged via in-gel fluorescence imager, followed by staining with Coomassie blue to confirm

the sizes and equal loading of the proteins. There are two bands in fluorescence imaging channel and Coomassie blue staining in the SDS-PAGE gel, due to the formation of Lyso-pye$_1$ and Lyso-pye$_2$ products which was about 14 and 16 kDa mass more than that of the starting Lyso-(BCN)$_n$ (14.3 kDa), respectively.

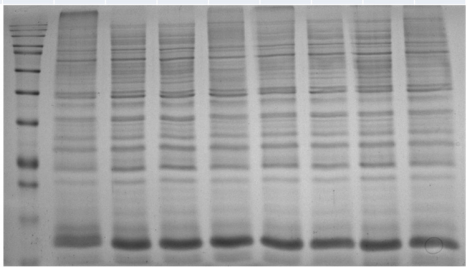
SDS-PAGE analysis and Western Blot for the Lyso-BCN$_n$ and Biotin-sulfo-Cy3-DASyd (6a) in *E. coli* lysate.

To 20 μL samples of 5 μM Lyso-(BCN)$_n$ and *E. coli* lysate in PB (phosphate buffer, pH = 6.0) were added 4 μL of different DASyd **6a** (250 μM in ACN/H_2O; final concentration = 50 μM). Irradiation with 405 nm LED (33.6 mW/cm^2) for 3 min. As for the non photo-induced reaction, the concentration was the same as the above, and the samples were wrapped with alumina foil for 1 h before subsequent process.

A 15% SDS polyacrylamide gel electrophoresis separation gel solution was used, and a semi-dry transfer method was used after electrophoresis. The PVDF film was incubated for 4 h in a blocking solution, then, incubated with a 1/2000 (HRP-Avidin/TBS) antibody dilution for 2 h. And then the PVDF membrane was washed four times with TBST for 10 min each time. The Moon A and B solution were mixed in equal volume and sprayed on the PVDF film for imaging.

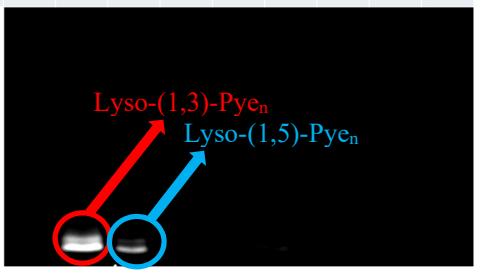
Coomassie blue staining of the SDS-PAGE gel

(a)	M.W.	Lyso - BCN$_n$				Lyso			
6a		+	+	-	-	+	+	-	-
hv		+	-	+	-	+	-	+	-



In-gel fluorescence of the same SDS-PAGE gel

(a)	M.W.	Lyso - BCN$_n$				Lyso			
6a		+	+	-	-	+	+	-	-
hv		+	-	+	-	+	-	+	-



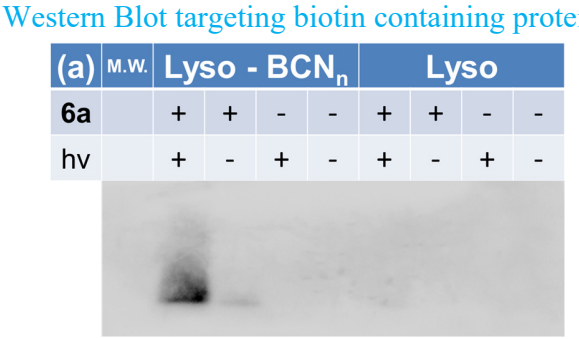


Figure S12.The mixture was denatured at 80 ºC for 5 min in loading buffer, resolved by SDS-PAGE and developed via Western Blot assay, the SDS-PAGE gel of the repeated experiment was imaged via in-gel fluorescence imager, followed by staining with Coomassie blue to confirm the sizes and equal loading of the proteins. There are two bands in fluorescence imaging channel and Coomassie blue staining in the SDS-PAGE gel, due to the formation of Lyso-pye$_1$ and Lyso-pye$_2$ products which was about 14 and 16 kDa mass more than that of the starting Lyso-(BCN)$_n$ (14.3 kDa), respectively.

Living cell imaging

1×10^5 A549 cells were seeded in 35-mm glass bottom tissue culture dishes. When reaching 80% confluency, A549 cells were incubated with Cetuximab-BCN (50 μg/mL) for 1 h at 37 ºC and then washed with PBS for three times. A mixture of 2 mL DASyds **6a** (50 μM) in PBS (pH = 7.4) was added into 35-mm cell culture dish. And then the glass bottom tissue culture dishes was irradiated with the 405 nm LED array for 20 s and further washed with PBS for three times. After that, the A549 cells were incubated with NucBlue™ Live Ready Probe™ Reagent at 37 °C for 15 min to stain the nucleus, then, washed with PBS for three times, and stained with membrane-embedding dye 3,3'-Dioctadecyloxacarbocyanine (DIO). After 10 min, A549 cells were then imaged immediately under an Olympus IX83 live cell fluorescence microscope with corresponding excitation and filter cubes.

Labeling of Cetuximab with BCN-OCOO-PNP

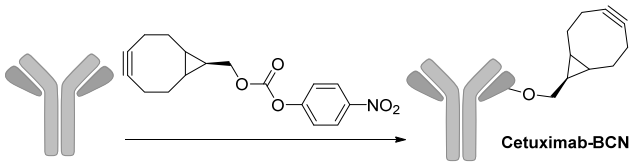


Figure S13. A solution of Cetuximab (2 mg/mL) in PBS (pH = 7.4) was mixed with 100 eq. BCN at room temperature and incubated for 2 h. Then, the reaction mixture was purified using ultracentrifuge filter (molecular weight cutoff 10 kDa, 15,000 g), through 3 times exchanged with PBS to get rid of small molecules. Finally, Cetuximab labeled with BCN was collected and stored at 4 ℃. The concentration of Cetuximab-BCN was quantified with BCA protein assay kit (Pierce).

Time-tracking of the non photo-induced reactions in cell labeling experiments

A549 cells were incubated with Cetuximab-BCN (50 μg/mL) for 1 h at room temperature and then washed with PBS for three times. A mixture of 2 mL DASyds **6a** (50 μM) in PBS (pH = 7.4) was added into 35-mm cell culture dishes. And then the glass bottom tissue culture dishes were incubated for different times (0 min, 30 min, 60 min, 150 min) and further washed with PBS for three times. After that, the A549 cells were incubated with NucBlue^{TM} Live Ready Probe^{TM} Reagent at 37 °C for 15 min to stain the nucleus, then, washed with PBS for three times. Then the glass bottom tissue culture dishes were imaged immediately under an Olympus IX83 live cell fluorescence microscope with corresponding filters.

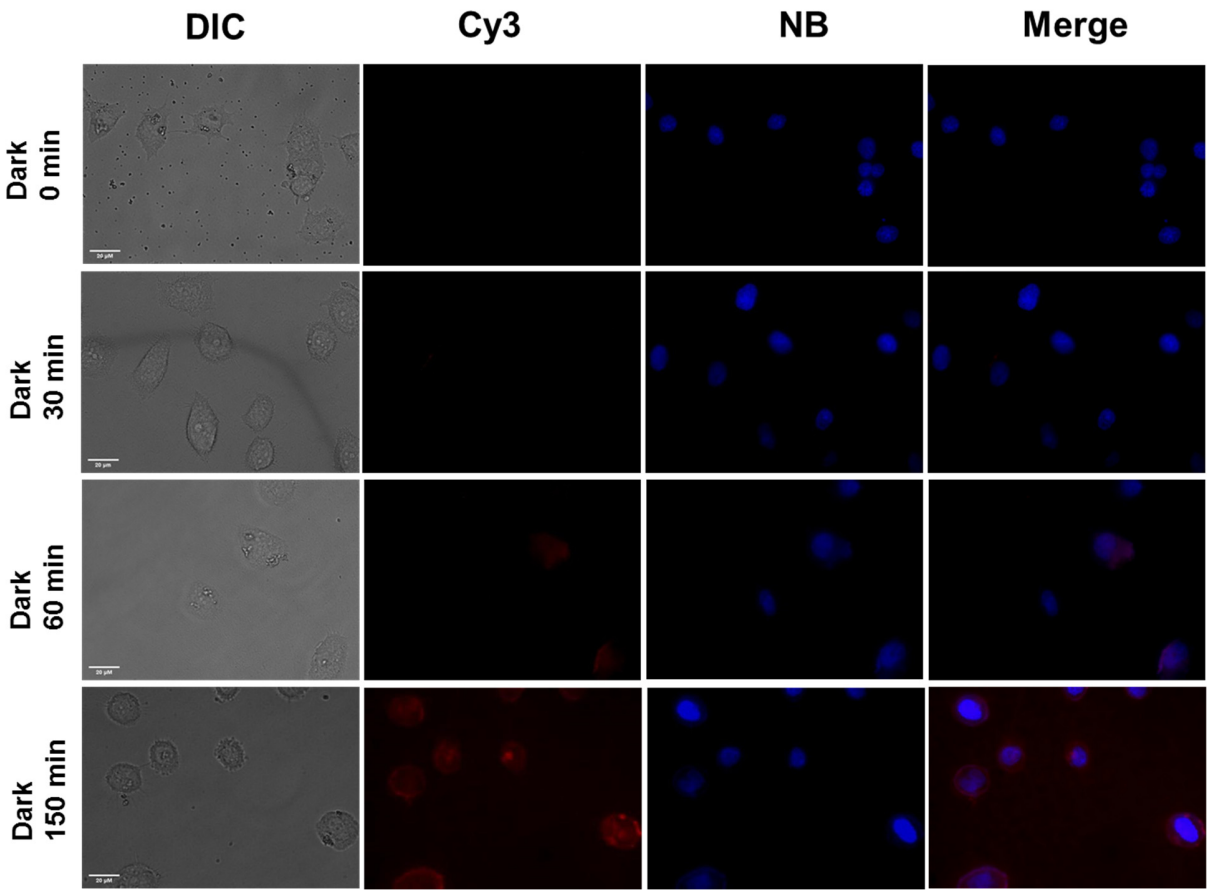


Figure S14. The time trace of the non photo-induced reaction indicates that the non photo-induced reaction was very slow. and after a 60 min incubation, a little red spot appeared. Exposure time: 2 s, Scale bar: 20 μm.

Time tracking of control reaction in cell labeling experiments

A549 cells were incubated with Cetuximab (50 μg/mL) for 1 h at room temperature and then washed with PBS for three times. A mixture of 2 mL DASyd **6a** (50 μM) in PBS (pH = 7.4) was added into 35-mm cell culture dishes. And then the glass bottom tissue culture dishes were incubated for different times (0 min, 30 min, 60 min, 150 min) and further washed with PBS for three times. After that, the A549 cells were incubated with NucBlue^{TM} Live Ready Probe^{TM} Reagent at 37 °C for 15 min to stain the nucleus, then, washed with PBS for three times. Then

the glass bottom tissue culture dishes were imaged immediately under an Olympus IX83 live cell fluorescence microscope with corresponding filters.

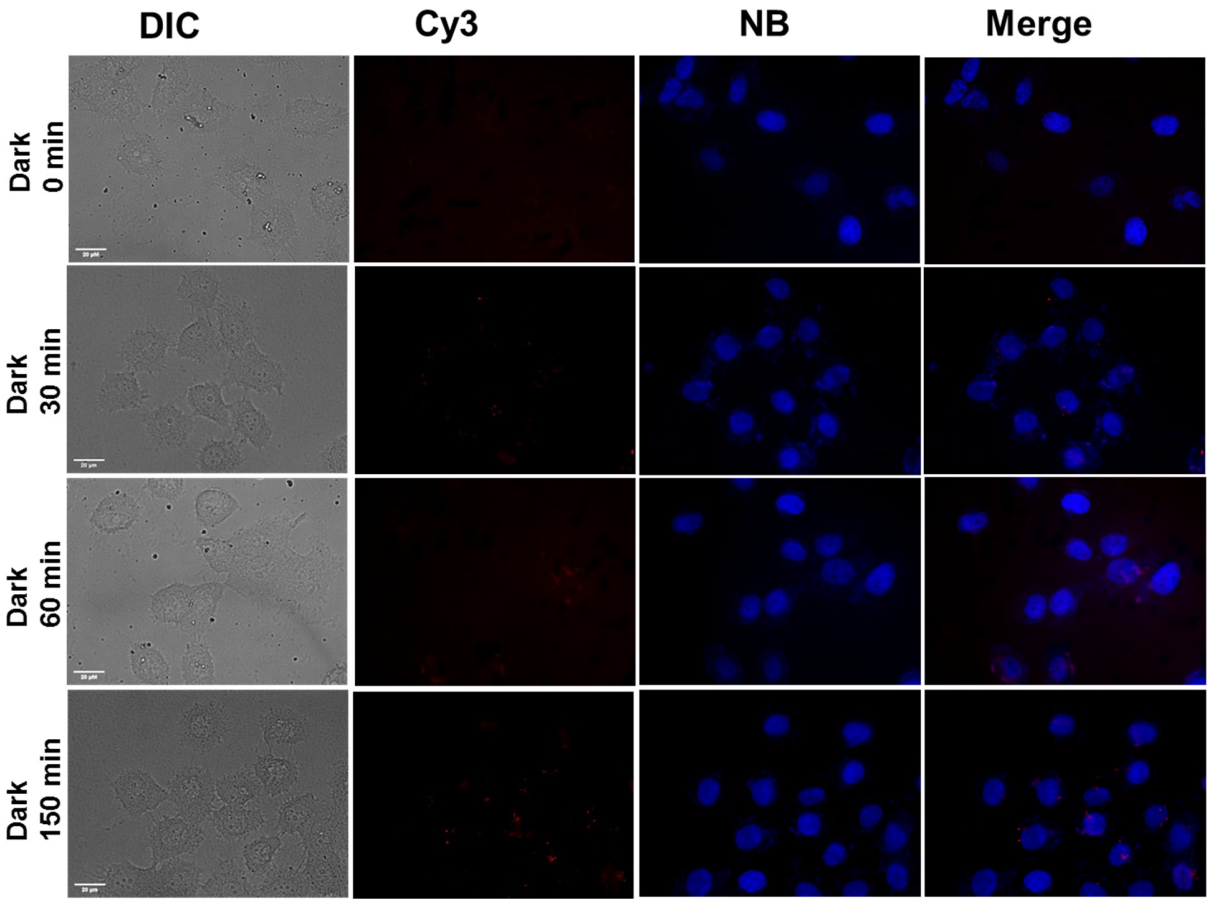


Figure S15. The time trace of the control reaction indicated that non-specific bioconjugation to Cetuximab has never been found, even after incubation with **6a** for 2.5 h. Exposure time: 2 s, Scale bar: 20 μm.

Spatiotemporal controllability tracking for photo-accelerated reaction in cell labeling experiments

A549 cells were incubated with Cetuximab-BCN (50 μg/mL) for 1 h at room temperature and then washed with PBS for three times. A mixture of 2 mL DASyds **6a** (50 μM) in PBS (pH = 7.4) was added into 35-mm cell culture dishes. And the petri dish was wrapped in aluminum foil with a pinhole, And then the glass bottom tissue culture dishes were illuminated with a 405 nm LED

array for 20 s and further washed with PBS for three times. After that, the A549 cells were incubated with NucBlue™ Live Ready Probe™ Reagent at 37 °C for 15 min to stain the nucleus, then, washed with PBS for three times. Then the glass bottom tissue culture dishes were imaged immediately under an Olympus IX83 live cell fluorescence microscope with corresponding filters.

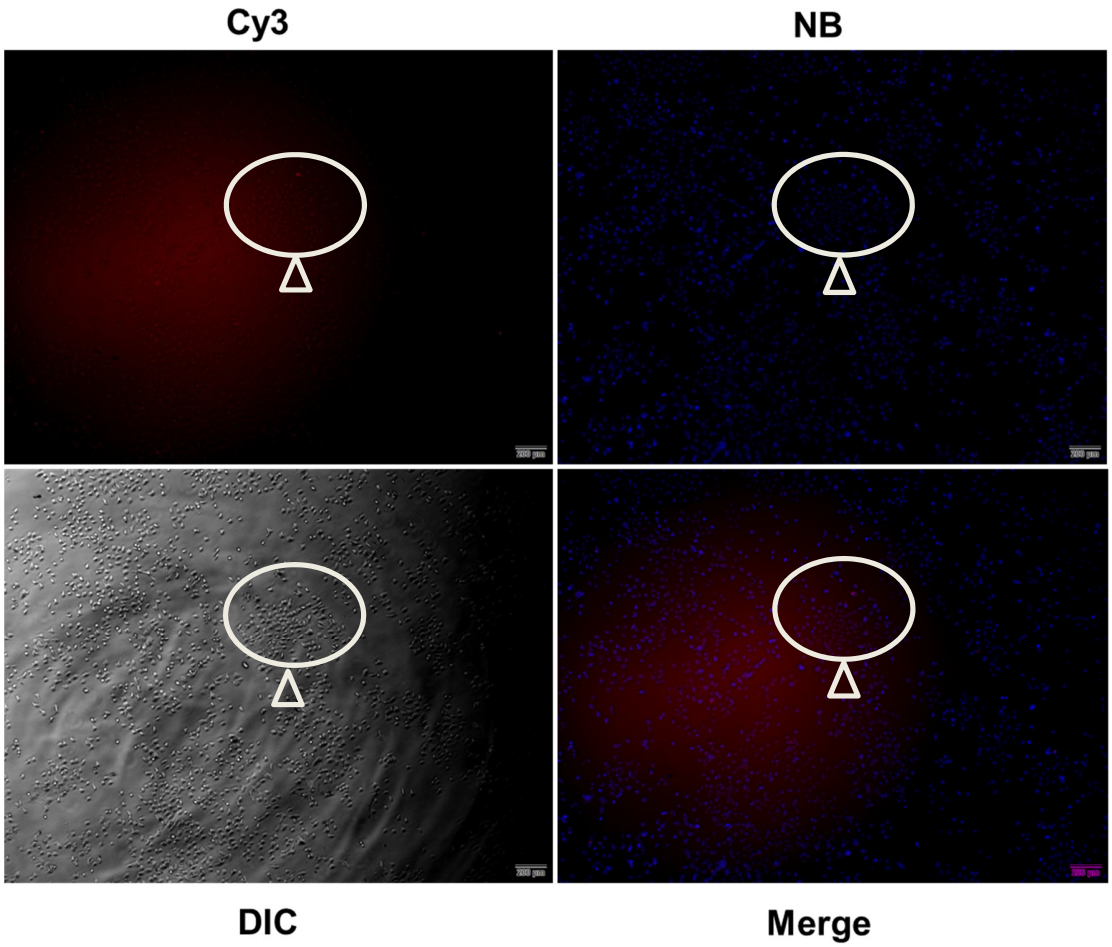
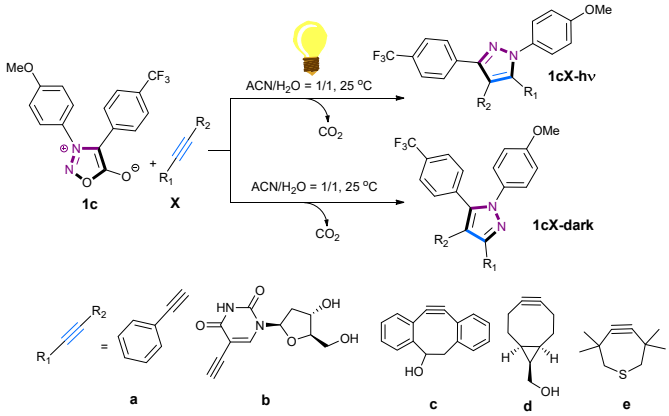
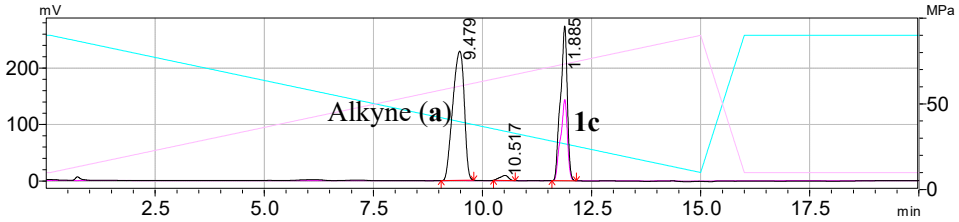


Figure S16. Spatiotemporal controllability tracking for photo-accelerated reaction in cell labeling experiments demonstrated the advantages of light responsive ligation. Exposure time: 8 s, Scale bar: 200 μm.

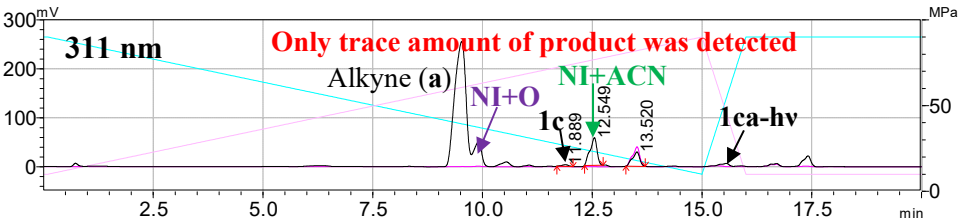
HPLC-MS analysis for the conversion of 1c into pyrazoles with a range of alkynes (1c:Alkyne = 1:5,1c = 100 µM) in ACN/H_2O = 1/1 using corresponding light sources or placing 12 h in dark. HPLC peak assignments based on mass-to-charge ratio in mass spectrum: [**NI**] = corresponding nitrile imine or active intermediate with the same mass-to-charge ratio; [**NI+H_2O**] = hydrolysis product of corresponding **NI**; [**NI+ACN**] = Adducts of corresponding **NI** with acetonitrile (from solvent); [**NI+O**] = corresponding NI with an oxygen atom.



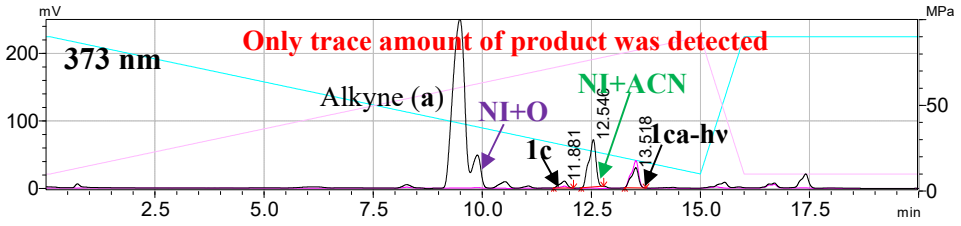
DASyd (**1c**) - Alkyne (**a**)



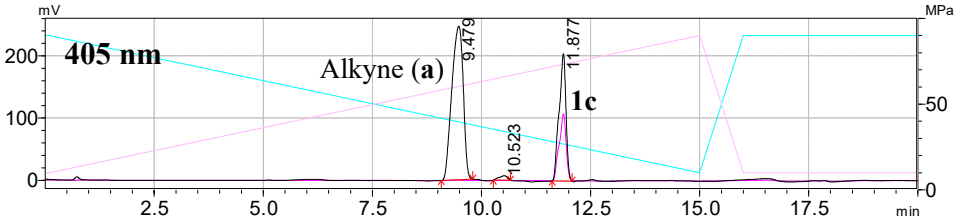
Peak No.	Time	Area	Height	%Area
1	11.867	1956725	263713	100



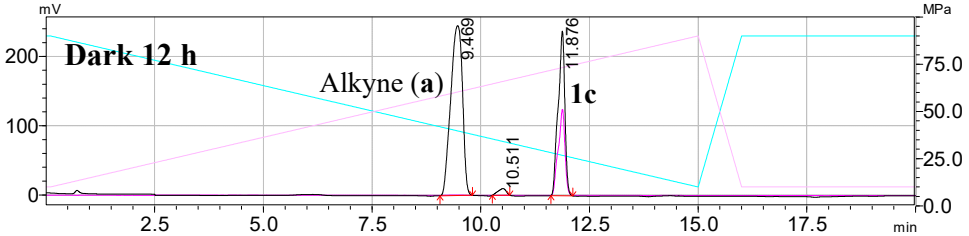
Peak No.	Time	Area	Height	%Area
1	11.889	36384	3418	3.651



Peak No.	Time	Area	Height	%Area
1	11.881	120205	10225	9.477

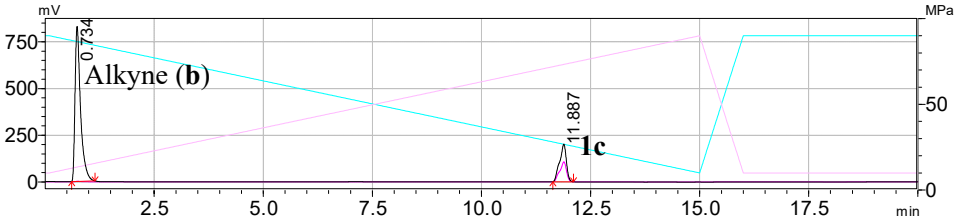


Peak No.	Time	Area	Height	%Area
1	11.877	2254807	204505	100

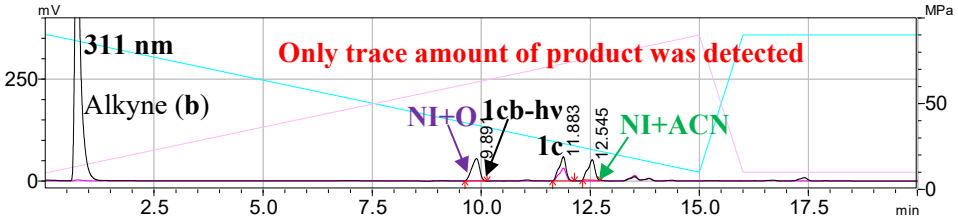


Peak No.	Time	Area	Height	%Area
1	11.876	2557274	237296	100

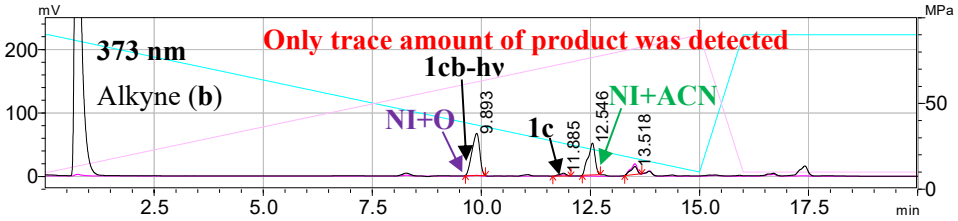
DASyd (**1c**) - Alkyne (**b**)

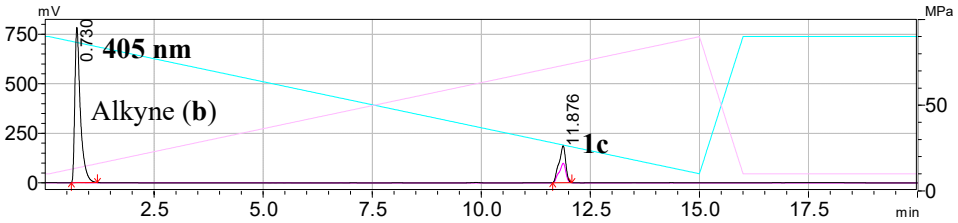


Peak No.	Time	Area	Height	%Area
1	11.887	2169941	201032	23.001

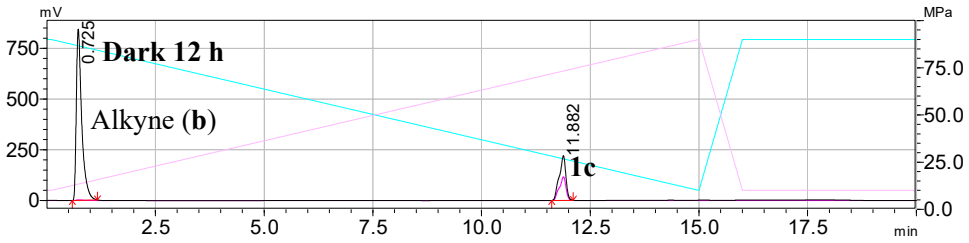


Peak No.	Time	Area	Height	%Area
1	11.883	655171	58989	34.708



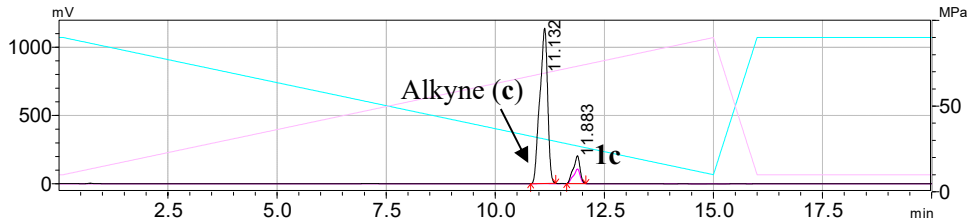


Peak No.	Time	Area	Height	%Area
1	11.876	1999708	185624	100

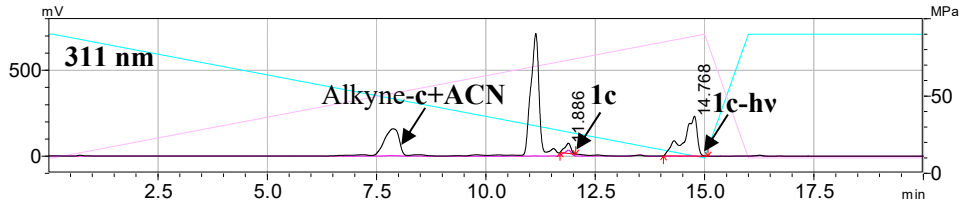


Peak No.	Time	Area	Height	%Area
1	11.882	2326943	219684	24.085

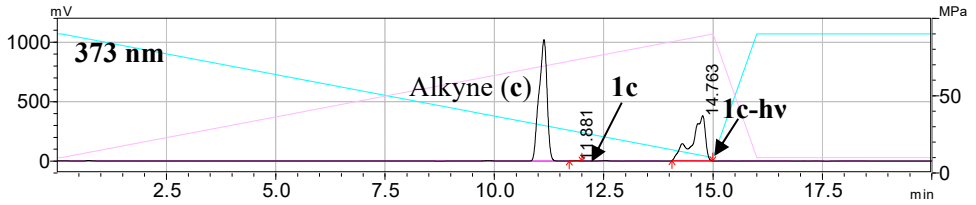
DASyd (**1c**) - Alkyne (**c**)



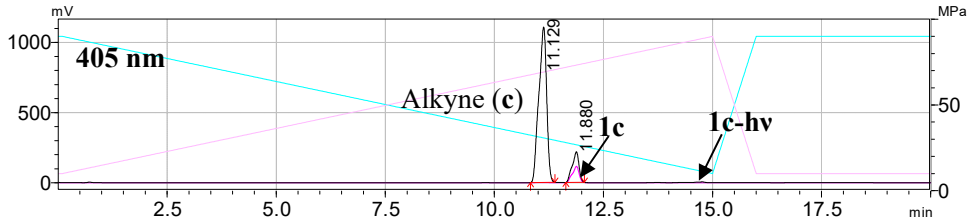
Peak No.	Time	Area	Height	%Area
1	11.883	2179378	202504	100



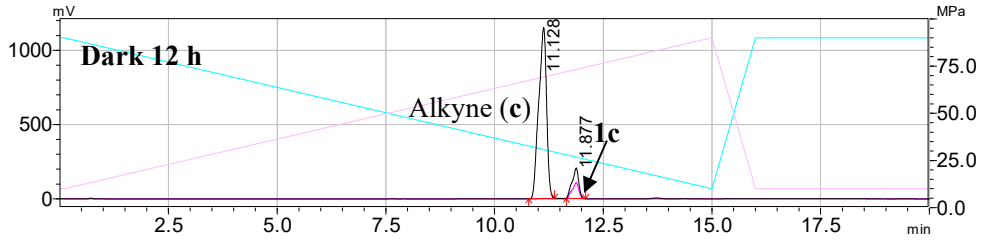
Peak No.	Time	Area	Height	%Area
1	11.886	588019	59687	10.546
2	14.768	4987524	231366	89.454



Peak No.	Time	Area	Height	%Area
1	11.881	25235	2752	0.307
2	14.763	8200283	379349	99.693

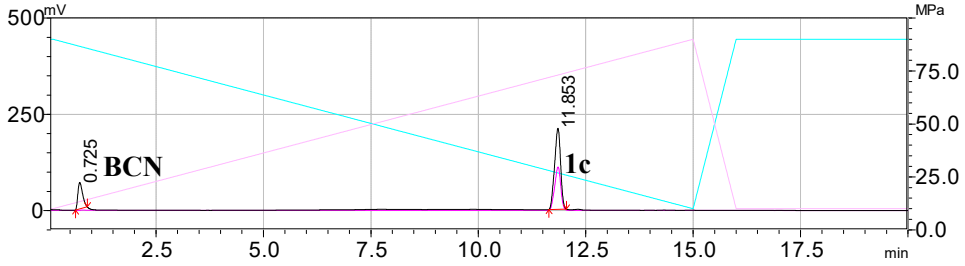


Peak No.	Time	Area	Height	%Area
1	11.880	2339316	217132	14.475

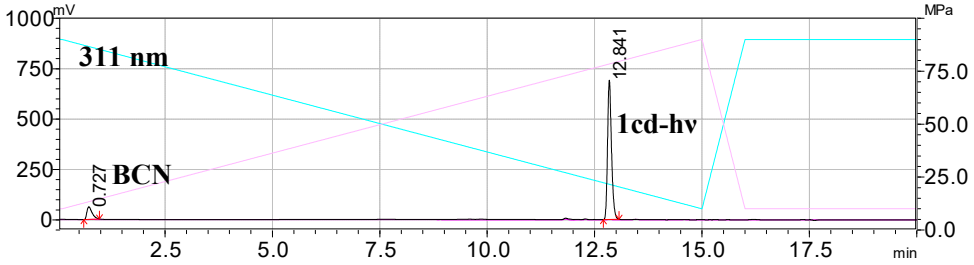


Peak No.	Time	Area	Height	%Area
1	11.877	2159511	203838	13.014

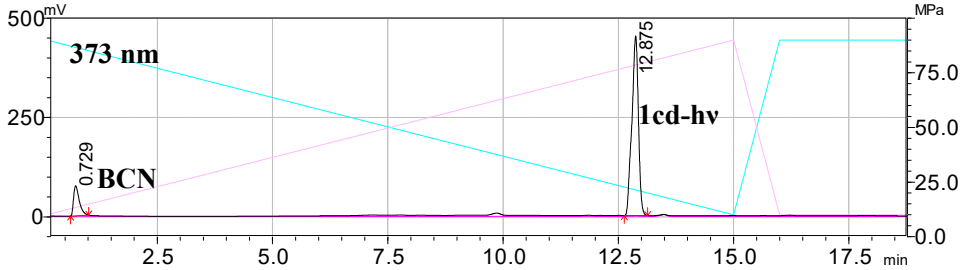
DASyd (**1c**) - Alkyne (**d**)



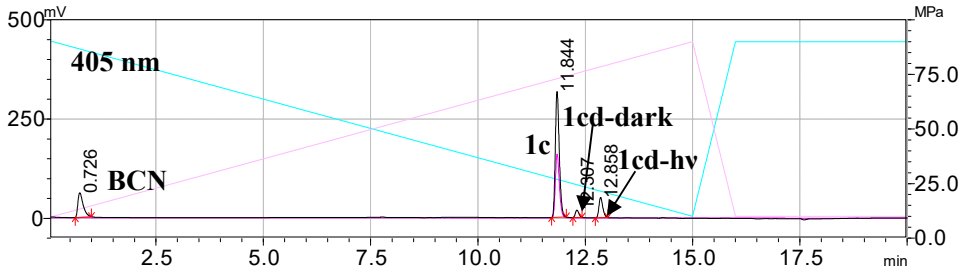
Peak No.	Time	Area	Height	%Area
1	11.853	2049348	209798	79.856



Peak No.	Time	Area	Height	%Area
1	12.841	4203465	689046	89.328

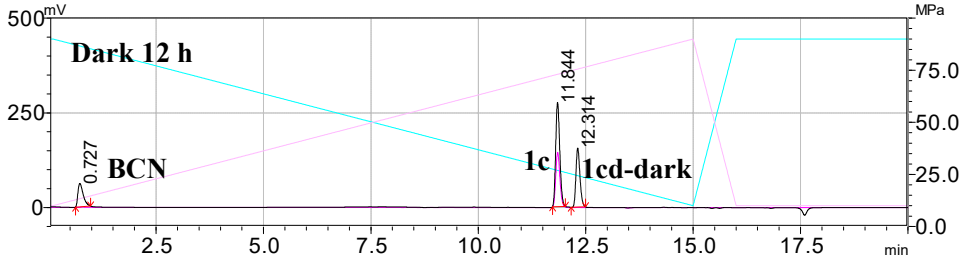


Peak No.	Time	Area	Height	%Area
1	12.875	4264034	451440	87.313



Peak No.	Time	Area	Height	%Area
1	11.844	1948079	315172	82.968

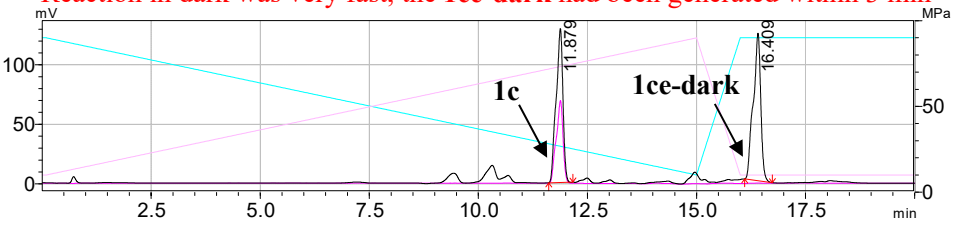
2	12.307	103987	18601	4.213
3	12.858	316443	50824	12.819



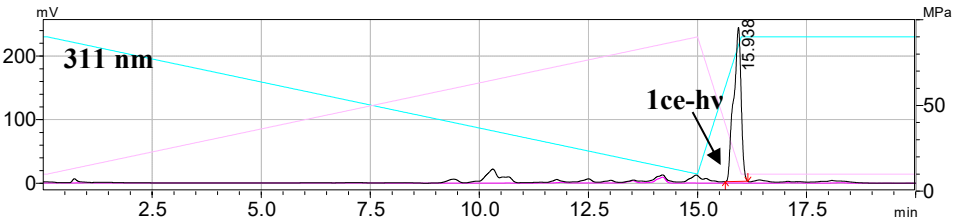
Peak No.	Time	Area	Height	%Area
1	11.844	1826901	273552	54.449
2	12.314	1002895	155230	29.890

DASyd (**1c**) - Alkyne (**e**)

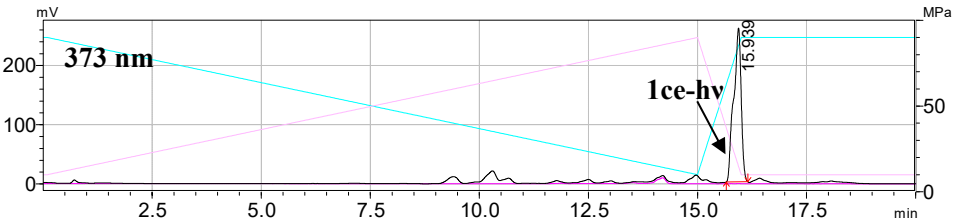
Reaction in dark was very fast, the **1ce-dark** had been generated within 3 min



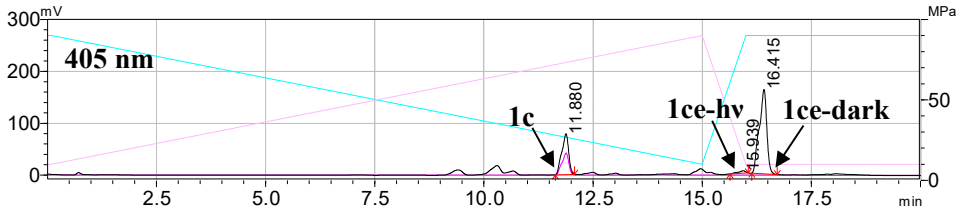
Peak No.	Time	Area	Height	%Area
1	11.879	1405674	129202	48.621
2	16.409	1485434	123853	51.379



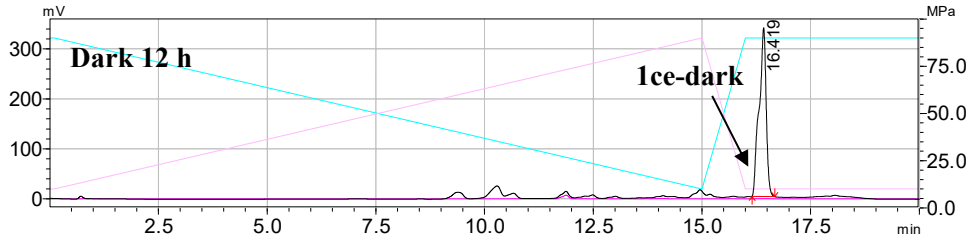
Peak No.	Time	Area	Height	%Area
1	15.938	3076587	241450	100.000



Peak No.	Time	Area	Height	%Area
1	15.939	3402433	259245	100.000



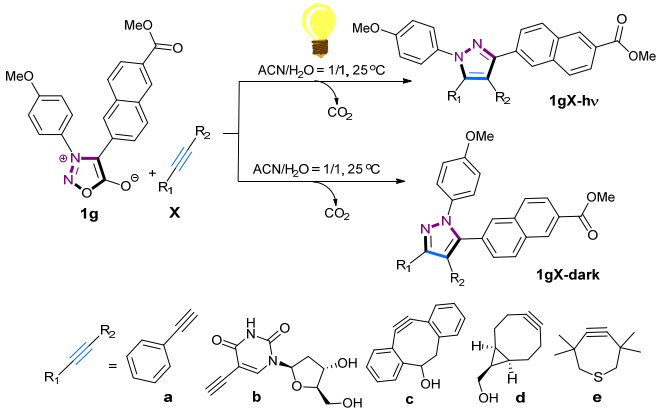
Peak No.	Time	Area	Height	%Area
1	11.880	861257	78479	30.009
2	15.939	54693	4590	1.906
3	16.415	1954071	162686	68.086



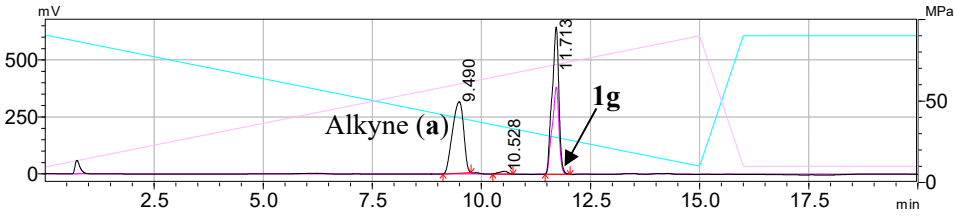
Peak No.	Time	Area	Height	%Area
1	16.419	3824190	336935	100.000

Figure S17. HPLC-MS analysis for the reactions of **1c** converting into pyrazoles with a range of alkynes with various light sources *vs.* in dark for 12 h. Alkyne, TMTH (**e**), showed significant reactivity under dark condition.

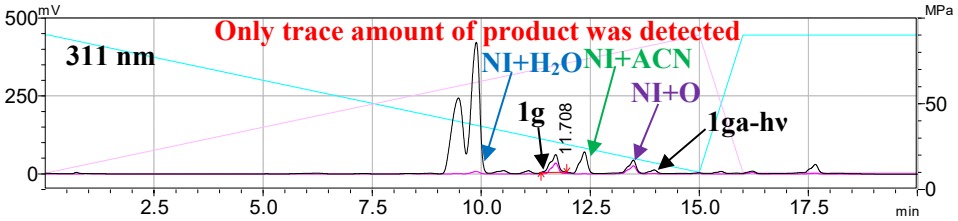
HPLC-MS analysis for the conversion of 1g into pyrazoles with a range of alkynes (1g:Alkyne = 1:5,1g = 100 μM)in ACN/H_2O = 1/1 using corresponding light sources or placing 12 h or 2 min in dark. HPLC peak assignments based on mass-to-charge ratio in mass spectrum: [**NI**] = corresponding nitrile imine or active intermediate with the same mass-to-charge ratio; [**NI+H_2O**] = hydrolysis product of corresponding **NI**; [**NI+ACN**] = Adducts of corresponding **NI** with acetonitrile (from solvent); [**NI+O**] = corresponding NI with an oxygen atom.



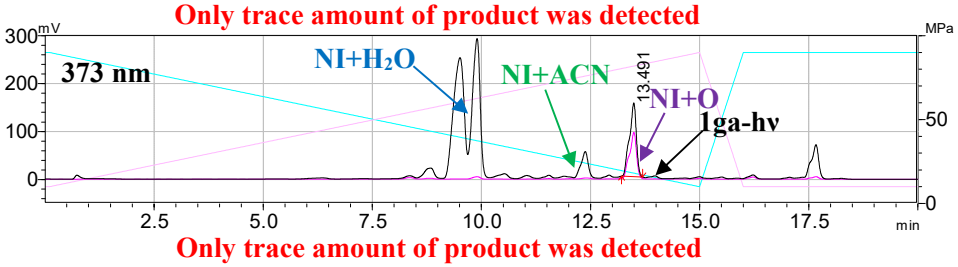
DASyd (**1g**) - Alkyne (**a**) = 1:5

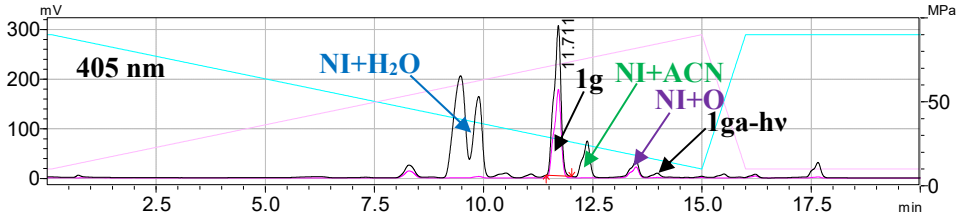


Peak No.	Time	Area	Height	%Area
1	11.713	7004415	646130	100.000

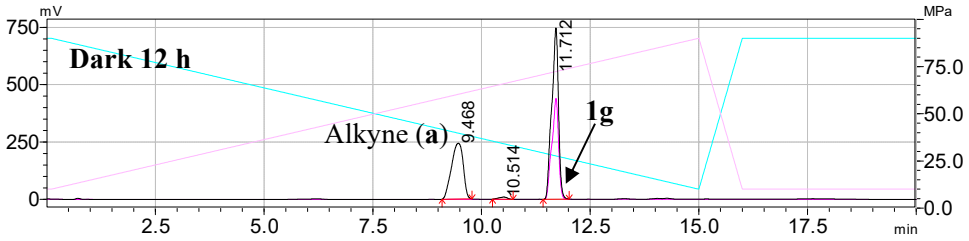


Peak No.	Time	Area	Height	%Area
1	11.708	712887	57155	100.000

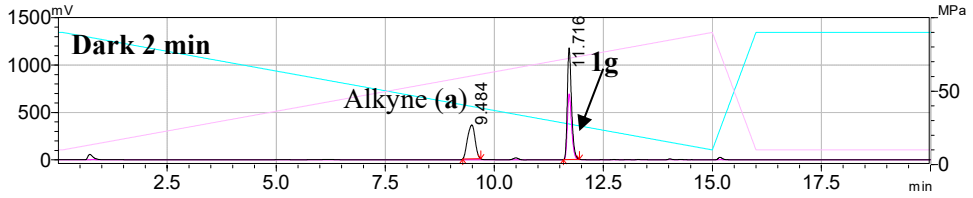




Peak No.	Time	Area	Height	%Area
1	11.711	3413864	301703	100.000

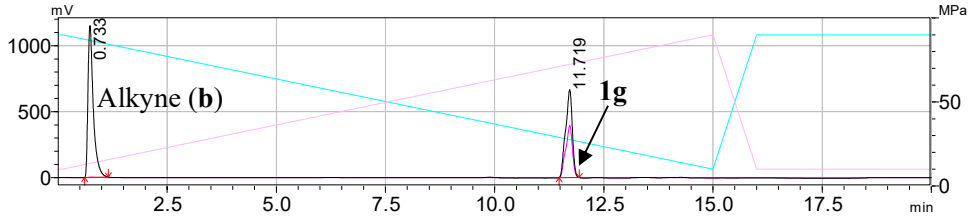


Peak No.	Time	Area	Height	%Area
1	11.712	7076293	745210	100

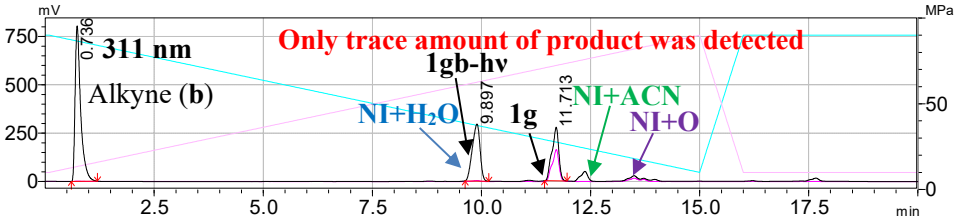


Peak No.	Time	Area	Height	%Area
1	11.716	7872335	1174760	100.000

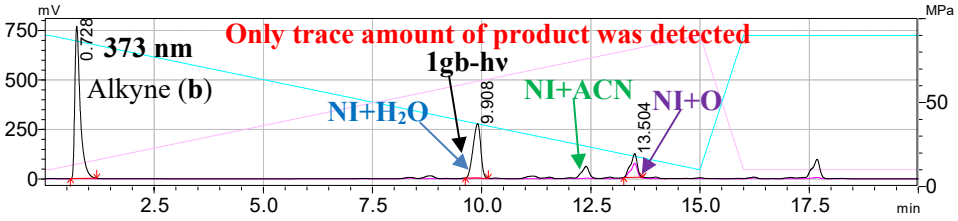
DASyd (**1g**) - Alkyne (**b**) = 1:5

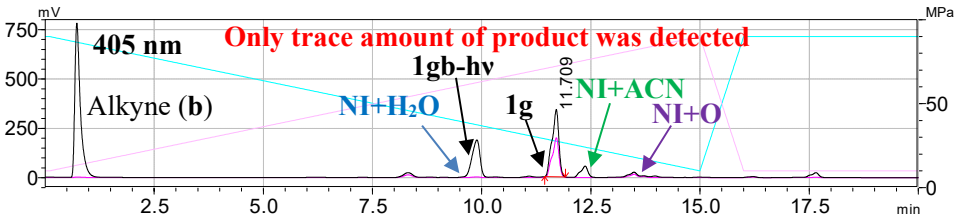


Peak No.	Time	Area	Height	%Area
1	11.719	7120885	664383	100.000

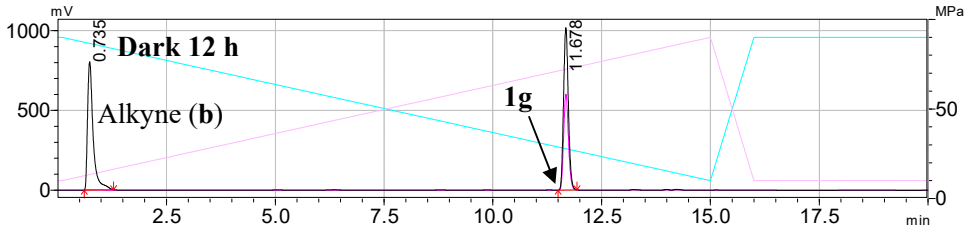


Peak No.	Time	Area	Height	%Area
1	11.713	3026849	276778	22.027

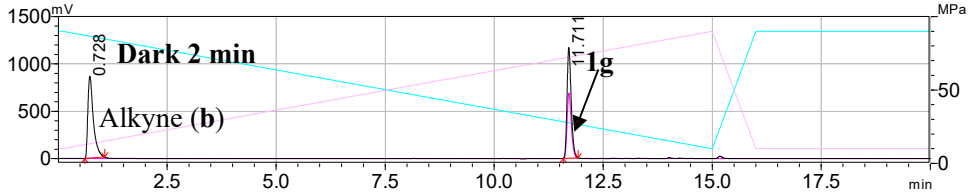




Peak No.	Time	Area	Height	%Area
1	11.709	3731921	339892	89.000

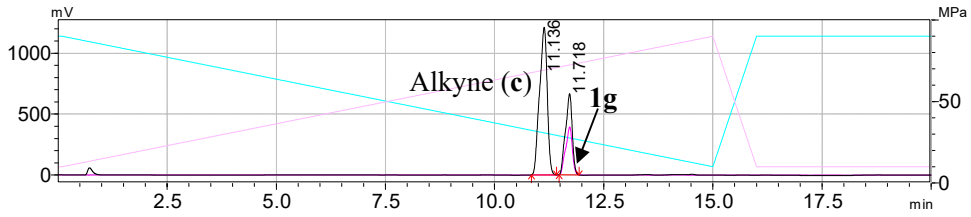


Peak No.	Time	Area	Height	%Area
1	11.678	7835718	1014022	100.00

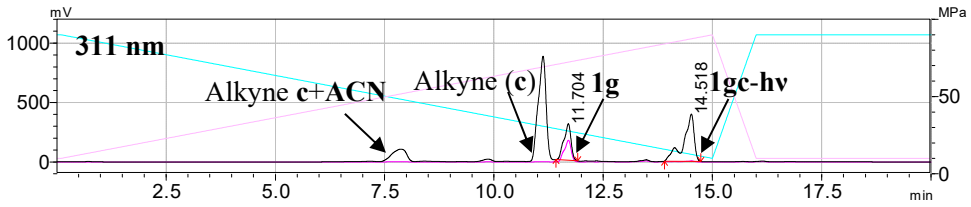


Peak No.	Time	Area	Height	%Area
1	11.711	7785865	1164161	100.000

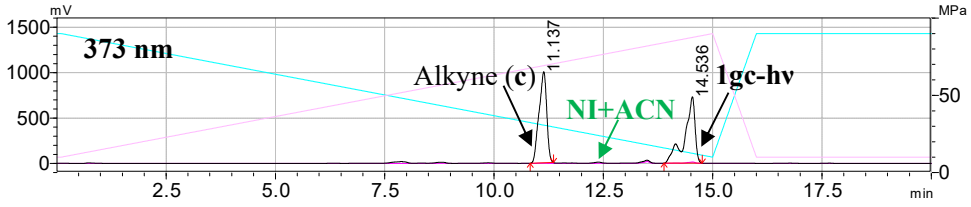
DASyd (**1g**) - Alkyne (**c**) = 1:5



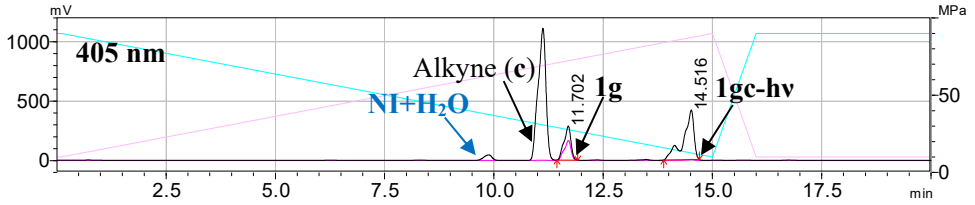
Peak No.	Time	Area	Height	%Area
1	11.718	7109641	664333	100.000



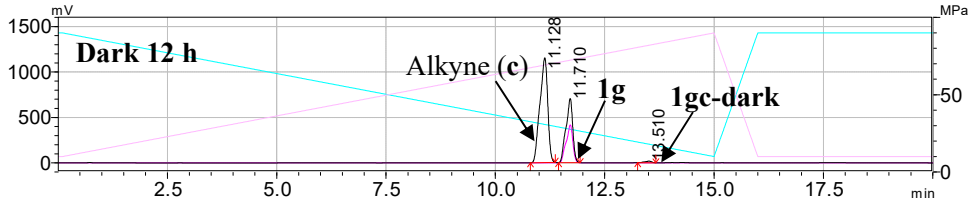
Peak No.	Time	Area	Height	%Area
1	11.704	3491808	306916	34.531
2	14.518	6620155	398282	65.469



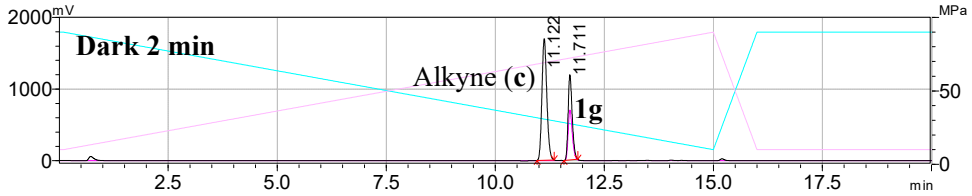
Peak No.	Time	Area	Height	%Area
1	14.536	11929410	728134	49.374



Peak No.	Time	Area	Height	%Area
1	11.702	3158759	286275	31.422
2	14.516	6893884	417286	68.578

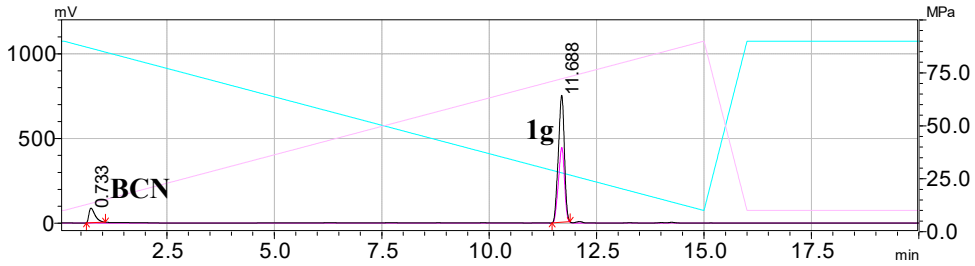


Peak No.	Time	Area	Height	%Area
1	11.710	7593761	704069	34.270
2	13.510	193311	17627	0.872

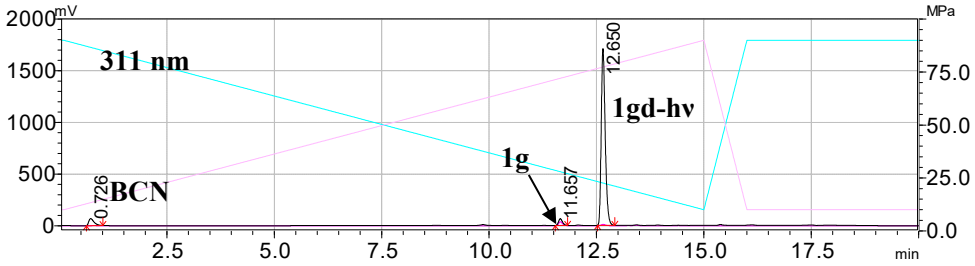


Peak No.	Time	Area	Height	%Area
1	11.711	7748661	1181240	100.000

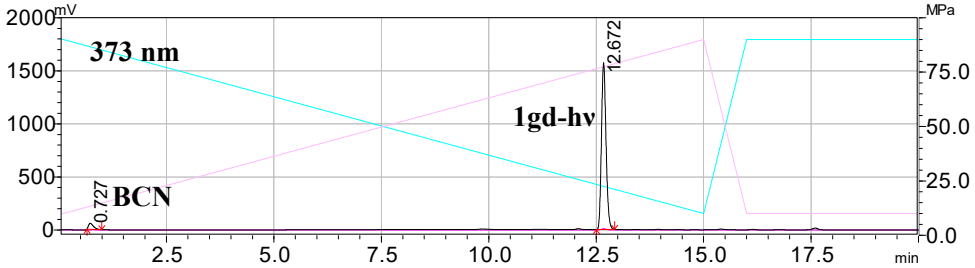
DASyd (**1g**) - Alkyne (**d**) = 1:5



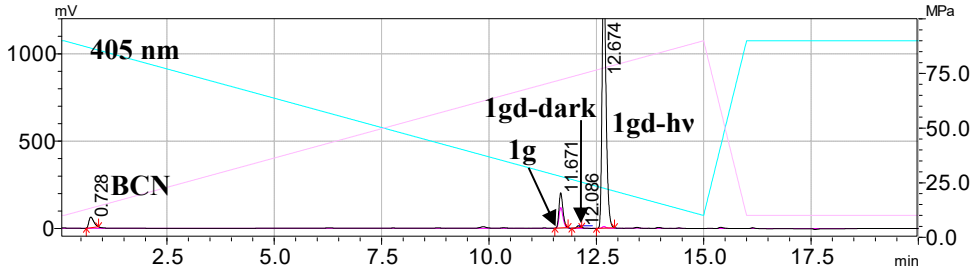
Peak No.	Time	Area	Height	%Area
1	11.688	7339357	748376	89.490



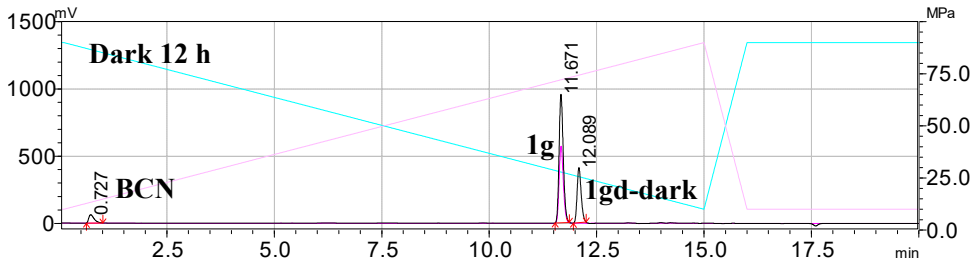
Peak No.	Time	Area	Height	%Area
1	11.657	402066	65813	3.513
2	12.650	9008663	1703485	91.634



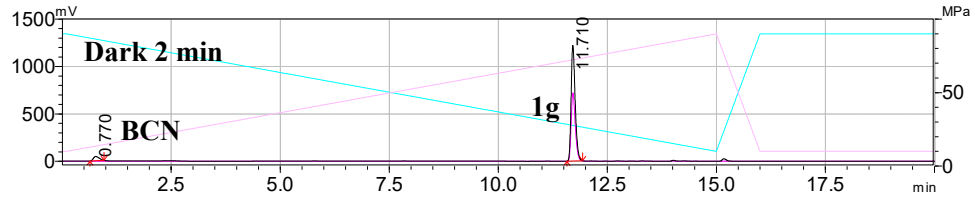
Peak No.	Time	Area	Height	%Area
1	12.672	10059981	1566724	96.346



Peak No.	Time	Area	Height	%Area
1	11.671	1288373	200022	11.815
2	12.086	47255	10794	0.433
3	12.674	9569184	1487683	87.752



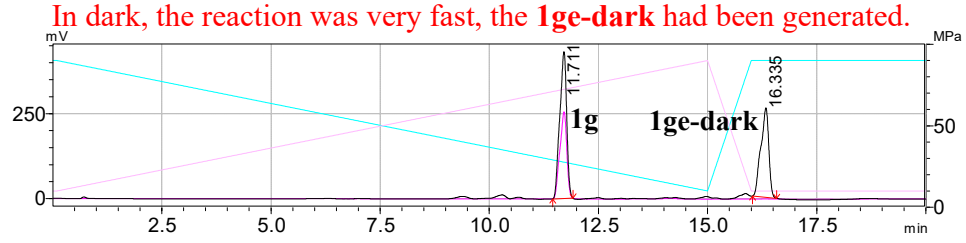
Peak No.	Time	Area	Height	%Area
1	11.671	6490731	953335	66.806
2	12.089	2482558	408068	27.610



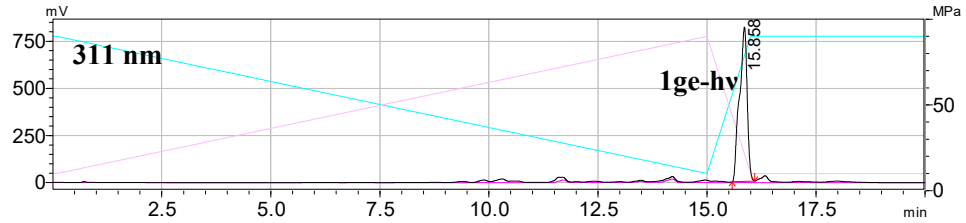
Peak No.	Time	Area	Height	%Area
1	11.710	7975287	1214444	100.000

DASyd (**1g**) - Alkyne (**e**) = 1:5

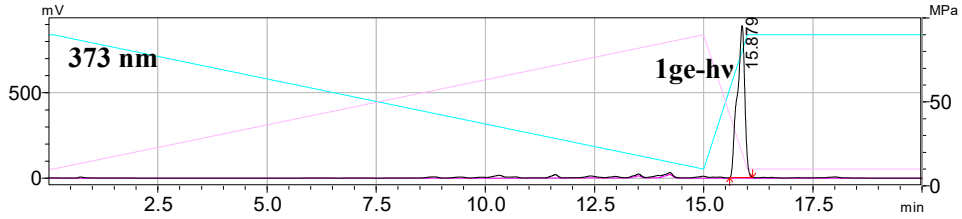
In dark, the reaction was very fast, the **1ge-dark** had been generated.



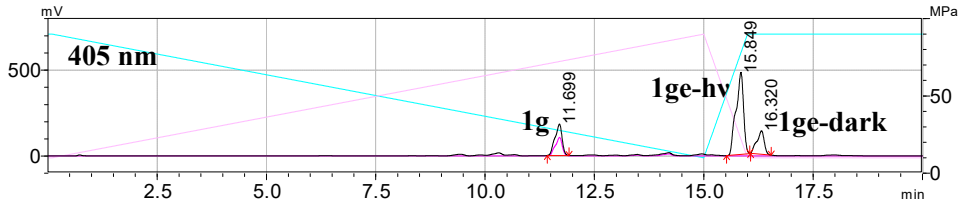
Peak No.	Time	Area	Height	%Area
1	11.711	4763654	430936	58.872
2	16.335	3327870	262570	41.128



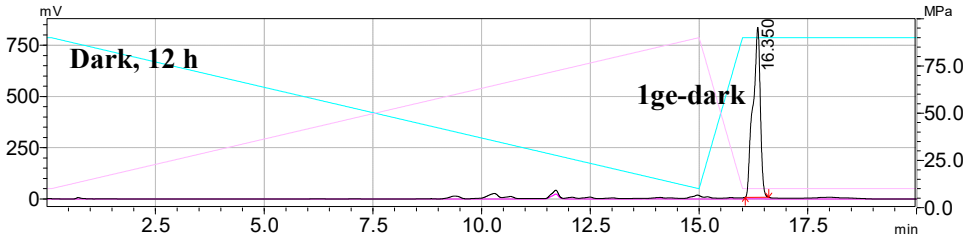
Peak No.	Time	Area	Height	%Area
1	15.858	9024182	818108	100.000



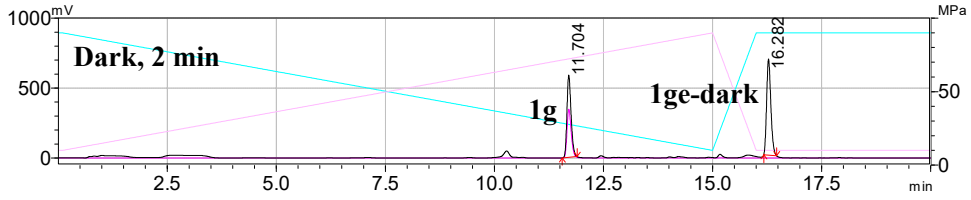
Peak No.	Time	Area	Height	%Area
1	15.879	9663019	886964	100.000



Peak No.	Time	Area	Height	%Area
1	11.699	2068618	182917	21.978
2	15.849	5730712	476451	60.886
3	16.320	1612888	137121	17.136



Peak No.	Time	Area	Height	%Area
1	16.350	9798280	828543	100.000



Peak No.	Time	Area	Height	%Area
1	11.704	3864553	585445	45.623
2	16.282	4606029	685482	54.377

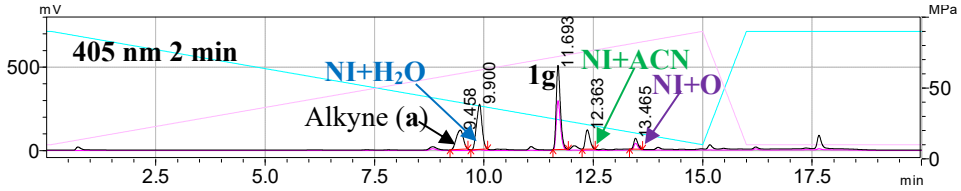
Figure S18. HPLC-MS analysis for the reactions of **1g** converting into pyrazoles with a range of alkynes with various light sources *vs.* in dark for 12 h. Alkyne, TMTH (**e**), showed significant

reactivity under dark condition; Alkyne, BCN (**d**), showed the best reactivity under 405 nm light irradiation.

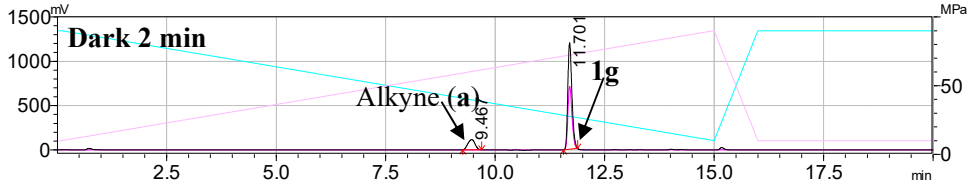
HPLC-MS analysis for the conversion of 1g into pyrazoles with a range of alkynes (1g:Alkyne = 1:1; 1g = 100 μM, stoichiometric amount) in ACN/H_2O = 1/1 using corresponding light sources or placing 2 min in dark. HPLC peak assignments based on mass-to-charge ratio in mass spectrum: [**NI**] = corresponding nitrile imine or active intermediate with the same mass-to-charge ratio; [**NI+H_2O**] = hydrolysis product of corresponding **NI**; [**NI+ACN**] = Adducts of corresponding **NI** with acetonitrile (from solvent); [**NI+O**] = corresponding NI with an oxygen atom.

Alkyne	**1g**/ Alkyne = 1/1 (**1g**, 100 μM) In dark, 2 min	**1g**/ Alkyne = 1/1 (**1g**, 100 μM) 405 nm irradiation, 2 min
a	N.D.	N.D.
b	N.D.	N.D.
c	N.D.	65.1%
d	N.D.	16.7%
e	3.32%	(hν = 32.4%，dark = 1.30%)

DASyd (**1g**) - Alkyne (**a**) = 1:1

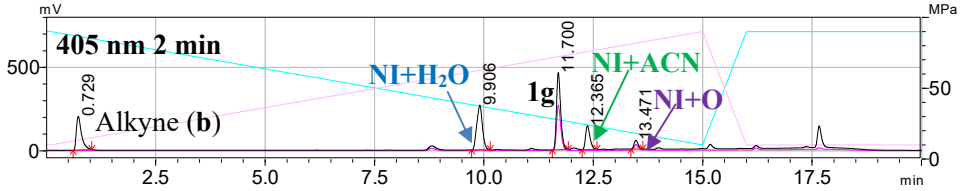


Peak No.	Time	Area	Height	%Area
1	11.693	3349234	502160	100.000

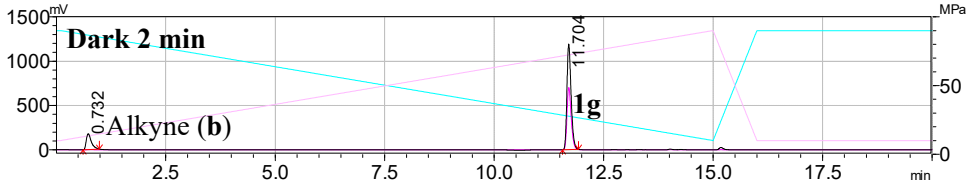


Peak No.	Time	Area	Height	%Area
1	11.701	7821312	1197191	100.000

DASyd (**1g**) - Alkyne (**b**) = 1:1

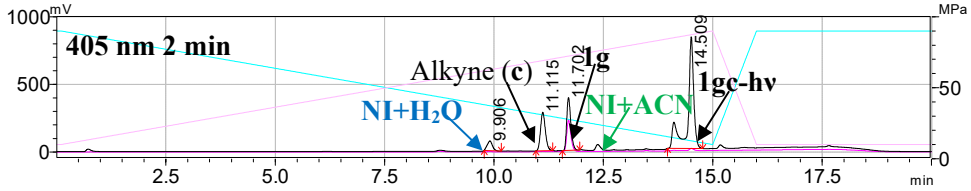


Peak No.	Time	Area	Height	%Area
1	11.700	3071277	460479	100.000

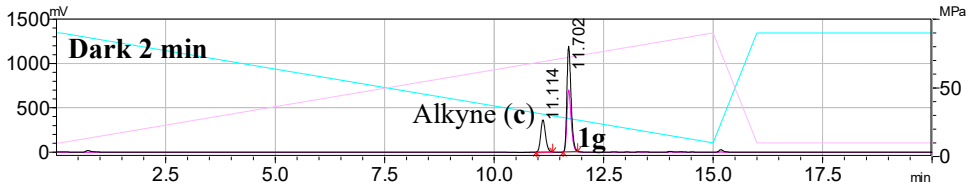


Peak No.	Time	Area	Height	%Area
1	11.704	7897881	1183540	100.000

DASyd (**1g**) - Alkyne (**c**) = 1:1

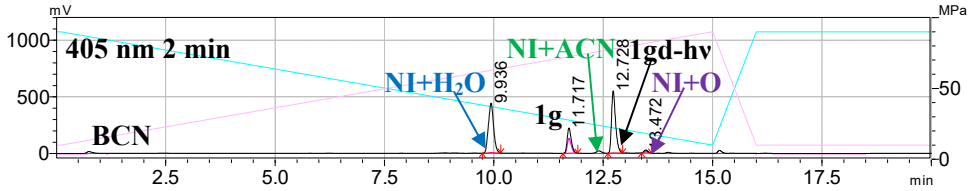


Peak No.	Time	Area	Height	%Area
1	11.702	2572286	388052	24.291
2	14.509	8017167	824370	75.709

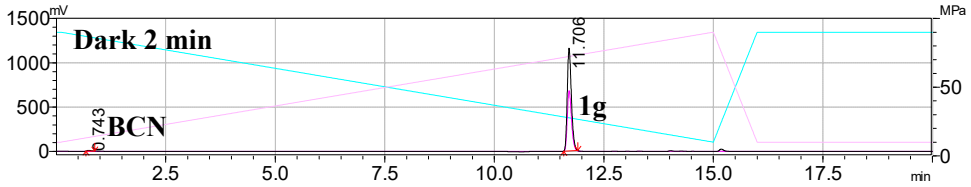


Peak No.	Time	Area	Height	%Area
1	11.702	7869310	1183694	100.000

DASyd (**1g**) - Alkyne (**d**) = 1:1

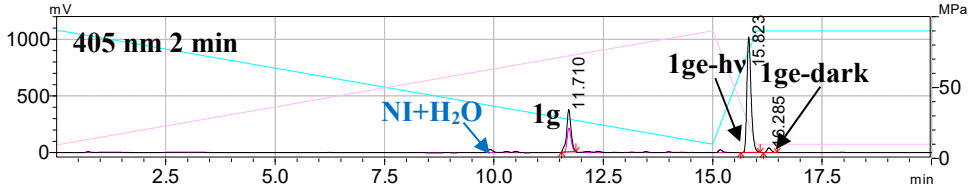


Peak No.	Time	Area	Height	%Area
1	11.717	1441964	221583	29.108
2	12.728	3511926	543883	70.892

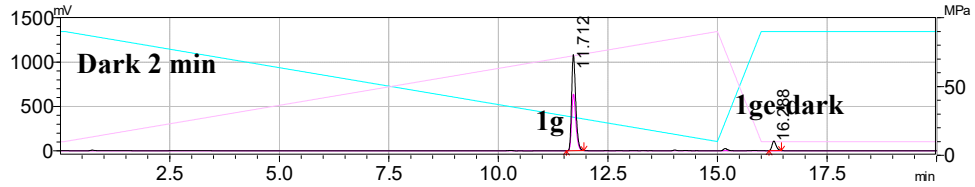


Peak No.	Time	Area	Height	%Area
1	11.706	7643654	1156545	100.000

DASyd (**1g**) - Alkyne (**e**) = 1:1



Peak No.	Time	Area	Height	%Area
1	11.710	2618852	369261	27.182
2	15.823	6745363	1018201	70.012
3	16.285	270310	40925	2.806



Peak No.	Time	Area	Height	%Area
1	11.712	7132889	1076801	91.051
2	16.288	701082	107215	8.949

Figure S19. HPLC-MS analysis for the reactions of **1g** converting into pyrazoles with a range of alkynes with various light sources *vs.* in dark for 2 min. Even under the stoichiometric amounts of DASyd and dipolarophile (**1g** : Alkyne = 1:1; **1g** = 100 μM). Interestingly, the results show that TMTH (**e**) displayed significant reactivity with the yield up to 3.32% under dark condition in 2 min; but for other alkynes, there were no backgroud reaction products detected. On the other hand, under the condition with 405 nm irradiation, the yield of corresponding 1,3-pyrazole product, **1g**-BCN(**d**), was reduced to 16.7%, accompanied with increase in the hydrolyzate and the acetonitrile adduct; for the photo-reaction of **1g**-TMTH(**e**), the desired yield reached 32.4% while the 1,5-pyrazole product was up to 1.30% in 2 min time scale. Lastly, the photo-reaction yield of **1g**-DIBO(**c**) is even better than that with 5 eq. of DIBO, giving the target 1,3-pyraole in 65.1% yield, and accompany with a small amount of the hydrolyzate. The results clearly indicate that, comparing with the dipolarophile concentration in 5 eq. excess, the photo-click reaction yield was dropped significantly toward stoichiometric amout for other alkyne, except the DIBO which leads to slight elevation in desired adduct yield. This might be caused by the π-π interaction between the aromatics on DIBO and the diaryl moieties on DASyd, maintaining the yield under more striengent ligation condition.

Compound characterization of the cycloadducts for DASyds 1c and 1g with different alkynes both photo-irradiation and non-photo-induced reaction

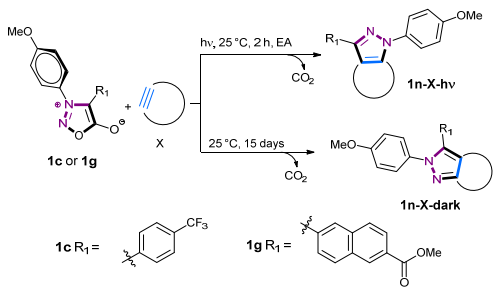
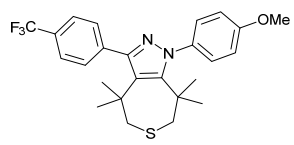
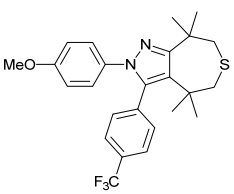


Photo-click reaction: A solution of DASyd with corresponding alkyne (1.2 eq.) in 200 mL EtOAc was vigorously stirred and irradiated simultaneously with a 311 nm UV lamp (10.8 mW/cm^2) in quartz flask at room temperature for 2 h. The solvent was then evaporated, and the residue was purified by silica gel flash chromatography to give the corresponding cycloaddition products.

Non photo-induced reaction: A solution of DASyd with corresponding alkyne (1.2 eq.) in 10 mL EtOAc was placed in dark for 15 days, The solvent was then evaporated, and the residue was purified by silica gel flash chromatography to give the corresponding cycloaddition products.

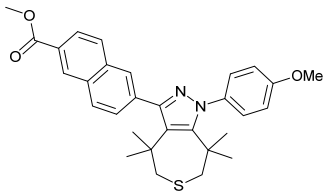


Pyrazole 1ce-hv: Sydnone **1c** (30.0 mg, 0.089 mmol) and TMTH (18.0 mg, 0.107 mmol) in 200 mL EtOAc were subjected to the general condition affording **1ce-hv** as a white solid (32.5 mg, 73.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.99-6.91 (m, 2H), 6.71-6.64 (m, 2H), 3.72 (s, 3H), 2.79 (s, 2H), 2.71 (s, 2H), 1.57 (s, 6H), 1.16 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 156.2, 139.6, 138.6, 133.2, 132.0, 130.5 (q, J = 33.3 Hz), 127.1, 125.9, 125.0 (q, J = 3.1 Hz), 124.0 (q, J = 273.7 Hz), 113.8, 55.5, 49.1, 45.7, 41.7, 37.6, 31.9, 30.8. HRMS (ESI) calcd. for $C_{25}H_{28}F_3N_2OS^+$ 461.1869 [M+H$^+$], found 461.1862.

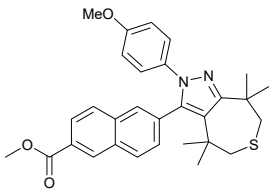


Pyrazole 1ce-dark: Sydnone **1c** (30.0 mg, 0.089 mmol) and TMTH (18.0 mg, 0.107 mmol) in 10 mL EtOAc were subjected to the general condition affording **1ce-dark** as a white solid (35.9 mg, 87.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.33-7.28 (m,

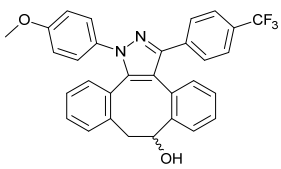
2H), 6.96-6.89 (m, 2H), 3.85 (s, 3H), 2.82 (s, 2H), 2.73 (s, 2H), 1.32 (d, J = 3.0 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 150.1, 148.1, 142.1, 136.5, 130.6, 129.8 (q, J = 33.3 Hz), 129.2, 125.9, 125.0, 124.4 (q, J = 273.7 Hz), 114.1, 55.7, 44.7, 44.5, 38.6, 36.9, 31.9, 30.3. HRMS (ESI) calcd. for $C_{25}H_{28}F_3N_2OS^+$ 461.1869 [M+H$^+$], found 461.1866.



Pyrazole 1ge-hv: Sydnone **1g** (30.0 mg, 0.080 mmol) and TMTH (16.1 mg, 0.096 mmol) in 200 mL EtOAc were subjected to the general condition affording **1ge-hv** as a light yellow solid (31.8 mg, 79.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 8.06 (dd, J = 8.6, 1.7 Hz, 1H), 7.95 (d, J = 8.9 Hz, 2H), 7.86 (d, J = 8.6 Hz, 1H), 7.65 (dd, J = 8.4, 1.7 Hz, 1H), 7.37-7.30 (m, 2H), 6.97-6.88 (m, 2H), 3.98 (s, 3H), 3.84 (s, 3H), 2.85 (s, 2H), 2.74 (s, 2H), 1.35 (d, J = 2.6 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 159.8, 150.1, 148.0, 138.3, 136.6, 135.3, 131.9, 130.9, 129.3, 128.9, 128.5, 127.6, 126.0, 125.6, 114.0, 55.7, 52.4, 52.3, 44.7, 44.5, 38.6, 36.9, 31.9, 30.3. HRMS (ESI) calcd. for $C_{30}H_{33}N_2O_3S^+$ 501.2206 [M+H$^+$], found 501.2208.



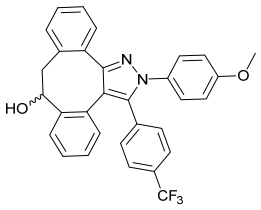
Pyrazole 1ge-dark: Sydnone **1g** (30.0 mg, 0.080 mmol) and **TMTH** (16.1 mg, 0.096 mmol) in 10 mL EtOAc were subjected to the general conditions affording **1ge-dark** as a white solid (33.7 mg, 84.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 1.7 Hz, 1H), 8.07 (dd, J = 8.6, 1.7 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.80 (d, J = 8.6 Hz, 1H), 7.75 (d, J = 1.6 Hz, 1H), 7.38 (dd, J = 8.4, 1.6 Hz, 1H), 7.00 (d, J = 8.9 Hz, 2H), 6.64-6.55 (m, 2H), 3.98 (s, 3H), 3.64 (s, 3H), 2.82 (s, 2H), 2.78-2.66 (m, 2H), 1.60 (d, J = 7.2 Hz, 6H), 1.23 (s, 3H), 1.13 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.3, 156.2, 140.4, 134.8, 134.6, 133.4, 131.9, 130.9, 130.8, 129.9, 129.1, 128.5, 128.3, 126.9, 126.0, 125.9, 113.7, 55.4, 52.5, 49.1, 45.8, 41.7, 37.7, 32.0, 31.8, 30.9, 30.7. HRMS (ESI) calcd. for $C_{30}H_{33}N_2O_3S^+$ 501.2206 [M+H$^+$], found 501.2219.



Pyrazole 1cc-hv: Sydnone **1c** (30.0 mg, 0.089 mmol) and DIBO (23.5 mg, 0.107 mmol) in 200 mL EtOAc were subjected to the general condition affording **1cc-hv** as a white solid (36.9 mg, 80.9%). **Pyrazole 1cc-hv (upper spot):** ^{1}H NMR (400 MHz, $CDCl_3$) δ7.80-7.67 (m, 4H), 7.54 (dd, J = 8.3, 4.3 Hz, 3H), 7.50-7.45 (m, 2H), 7.41 (d, J = 7.6 Hz, 1H), 7.36-7.28 (m, 1H), 7.27 (d, J = 1.8 Hz, 1H), 7.25-7.23 (m, 1H), 7.23-7.19 (m, 1H), 7.18-7.12 (m, 1H), 7.11-7.05 (m, 2H), 7.05-6.97 (m, 2H), 6.90-6.78 (m, 5H), 5.58 (t, J = 8.0 Hz, 0.5H), 5.22 (t, J = 9.2 Hz, 1H), 3.89 (dd, J = 15.4, 6.9 Hz, 0.5H), 3.78 (s, 4.5H), 3.45 (d, J = 9.2

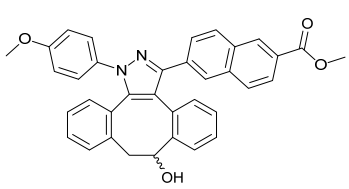
Hz, 2H), 3.12 (dd, J = 15.4, 6.9 Hz, 0.5H). HRMS (ESI) calcd. for $C_{31}H_{24}F_3N_2O_2^+$ 513.1784 [M+H$^+$], found 513.1785. There were at least four isomers, and the ratio of each isomer shown in the ^{1}H NMR was Isomer 1: Isomer 2 = 1:2.

Pyrazole 1cc-hv (**mixture of products**)**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.76 (m, 4H), 7.72 (dd, J = 12.0, 8.2 Hz, 4H), 7.56-7.51 (m, 6H), 7.50-7.46 (m, 1H), 7.42-7.38 (m, 2H), 7.35-7.28 (m, 5H), 7.25-7.21 (m, 4H), 7.20-7.16 (m, 3H), 7.15-7.10 (m, 3H), 7.08-7.06 (m, 3H), 7.04-6.98 (m, 4H), 6.94-6.88 (m, 3H), 6.87-6.78 (m, 8H), 6.73 (dd, J = 7.7, 1.3 Hz, 1H), 5.68-5.62 (m, 1H), 5.58-5.54 (m, 0.4H), 5.24-5.15 (m, 1.8H), 3.95-3.84 (m, 1.4H), 3.79 (s, 3H), 3.78 (s, 3H), 3.77 (s, 1H), 3.77 (s, 2H), 3.52-3.40 (m, 3.6H), 3.18-3.08 (m, 1.4H). HRMS (ESI) calcd. for $C_{31}H_{24}F_3N_2O_2^+$ 513.1784 [M+H$^+$], found 513.1785. There were at least four isomers, and the ratio of each isomer shown in the ^{1}H NMR was Isomer 1: Isomer 2: Isomer 3 = 3:1:5.



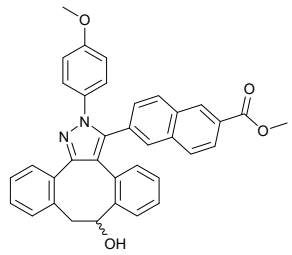
Pyrazole 1cc-dark: Sydnone **1c** (30.0 mg, 0.089 mmol) and DIBO (23.5 mg, 0.107 mmol) in 10 mL EtOAc were subjected to the general condition affording **1cc-dark** as a white solid (34.9 mg, 76.5%). **Pyrazole 1cc-dark (upper spot):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74(d, J = 8.0 Hz, 1H) 7.54 (dd, J = 7.3, 1.6 Hz, 1H), 7.53-7.44 (m, 5H), 7.38-7.36 (m, 1H), 7.32-7.28 (m, 9H), 7.25-7.14 (m, 5H), 7.12-7.08 (m, 1H), 7.01-6.98 (m, 1H), 6.97-6.93 (m, 1H), 6.90-6.86 (m, 4H), 6.70-6.68 (m, 1H), 6.58-6.56 (m, 1H), 5.72-5.66 (m, 1H), 5.24-5.19 (m, 1H), 3.90-3.84 (m, 1H), 3.83 (s, 6H), 3.50-3.44 (m, 1H), 3.38-3.33 (m, 1H), 3.24-3.18 (m, 1H). HRMS (ESI) calcd. for $C_{31}H_{24}F_3N_2O_2^+$ 513.1784 [M+H$^+$], found 513.1787. There were at least four isomers, and the ratio of each isomer shown in the ^{1}H NMR was Isomer 1: Isomer 2 = 1:1.

Pyrazole 1cc-dark (mixture of products): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.61-7.57 (m, 1.5H), 7.52-7.46 (m, 6H), 7.42-7.36 (m, 4H), 7.34-7.28 (m, 8H), 7.25-7.14 (m, 8H), 7.07 (t, J = 7.4 Hz, 1H), 7.00-6.94 (m, 2H), 6.90-6.84 (m, 6H), 6.76-6.72 (m, 1.5H), 6.57 (d, J = 7.8 Hz, 1H), 5.54-5.50 (m, 1H), 5.18-5.12 (m, 1.5H), 3.83 (s, 7.3H), 3.50-3.36 (m, 3.5H), 3.22-3.14 (m, 1H). HRMS (ESI) calcd. for $C_{31}H_{24}F_3N_2O_2^+$ 513.1784 [M+H$^+$], found 513.1787. There were at least four isomers, and the ratio of each isomer shown in the ^{1}H NMR was Isomer 1: Isomer 2 = 2:3.



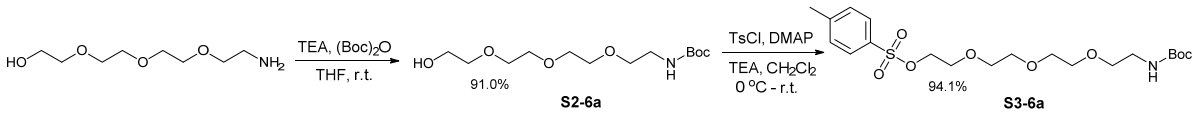
Pyrazole 1gc-hv (**mixture of products**)**:** Sydnone **1g** (30.0 mg, 0.080 mmol) and DIBO (21.1 mg, 0.096 mmol) in 200 mL EtOAc were subjected to the general condition affording **1gc-hv** as a white solid (17.0 mg, 38.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 9.49 (s, 0.5H), 8.91 (s, 1H), 8.67 (s, 0.5H), 8.46 (d, J =

5.5 Hz, 3H), 8.10-8.08 (m, 2H), 8.06-8.02 (m, 4H), 7.94-7.90 (m, 5H), 7.78-7.73 (m, 6H), 7.72-7.68 (m, 4H), 7.58-7.54 (m, 2H), 7.45-7.39 (m, 4H), 7.36-7.32 (m, 2H), 7.29-7.26 (m, 3H), 7.24-7.20 (m, 4H), 7.17-7.15 (m, 2H), 7.11-7.07 (m, 3H), 7.04-7.01 (m, 3H), 6.99-6.92 (m, 6H), 6.88-6.83 (m, 4H), 6.80-6.73 (m, 8H), 6.61-6.57 (m, 2H), 5.66-5.62 (m, 0.8H), 5.58-5.54 (m, 0.8H), 5.20-5.12 (m, 2H), 4.08-4.02 (m, 2H), 3.93 (s, 6H), 3.91 (s, 3H), 3.88 (s, 3H), 3.74-3.67 (m, 12H), 3.46-3.40 (m, 3.5H), 3.14-3.05 (m, 2H). HRMS (ESI) calcd. for $C_{36}H_{29}N_2O_4^+$ 553.2122 [M+H$^+$], found 553.2121. There were at least four isomers, and the ratio of each isomer shown in the ^{1}H NMR was Isomer 1: Isomer 2: Isomer 3 = 1:1:2.4.

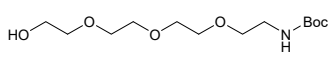


Pyrazole 1gc-dark (**mixture of products**)**:** Sydnone **1g** (30.0 mg, 0.080 mmol) and DIBO (21.1 mg, 0.096 mmol) in 10 mL EtOAc were subjected to the general condition affording **1gc-dark** as a yellow solid (17.0 mg, 38.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46-8.39 (m, 3H), 7.92-7.88 (m, 3H), 7.72-7.63 (m, 6H), 7.59-7.46 (m, 8H), 7.44-7.40 (m, 1H), 7.35-7.20 (m, 14H), 7.18-7.04 (m, 10H), 6.98-6.88 (m, 2H), 6.82-6.70 (m, 10H), 6.68-6.60 (m, 2H), 6.52-6.48 (m, 1H), 5.64 (s, 1H), 5.48 (s, 0.5H), 5.14-5.06 (m, 1.8H), 3.87 (s, 10H), 3.86-3.78 (m, 1.5H), 3.68 (s, 10H), 3.50-3.42 (m, 1.8H), 3.36-3.25 (m, 2H), 3.16-3.08 (m, 1.5H). HRMS (ESI) calcd. for $C_{25}H_{28}F_3N_2OS^+$ 461.1869 [M+H$^+$], found 461.1862. HRMS (ESI) calcd. for $C_{36}H_{29}N_2O_4^+$ 553.2122 [M+H$^+$], found 553.2128. There were at least four isomers, and the ratio of each isomer shown in the ^{1}H NMR was Isomer 1: Isomer 2: Isomer 3 = 2:1:4.

The synthesis of Biotin-sulfo-Cy3-DASyd (6a) and compound characterization

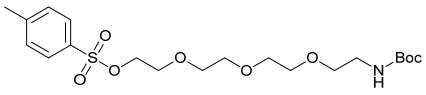


***tert*-Butyl(2-(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)ethyl)carbamate (S2-6a):**

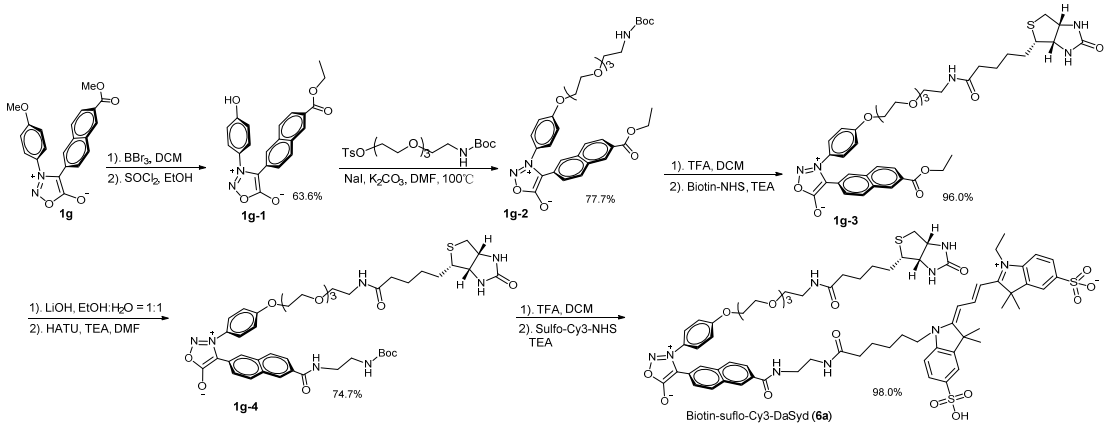


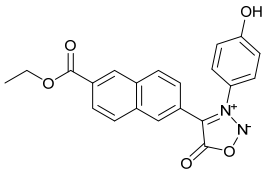
$(Boc)_2O$ (1.76 g, 8.05 mmol) was added to a solution of 2-(2-(2-(2-aminoethoxy)ethoxy)ethoxy)ethan-1-ol (600 mg, 3.10 mmol) in a 9:1 (v/v) mixture of 20 mL methanol/TEA. The reaction was left stirring under reflux and upon completion. The solvent was removed under reduced pressure and the residue extracted with DCM. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to yield **S2-6a** (835mg, 2.85mmol), yield 92%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.76-3.68

(m, 4H), 3.67-3.60 (m, 8H), 3.53 (t, *J* = 5.0 Hz, 2H), 3.31 (t, *J* = 5.0 Hz, 2H), 1.44 (s, 9H). HRMS (ESI) calcd. for $C_{13}H_{28}NO_6^+$ 294.1911 [M+H$^+$], found 294.1904.



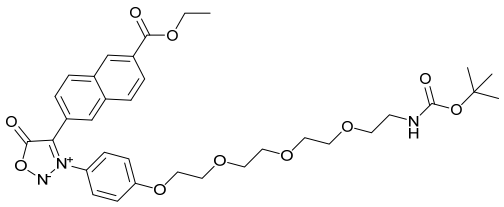
2,2-Dimethyl-4-oxo-3,8,11,14-tetraoxa-5-azahexadecan-16-yl 4-methylbenzenesulfonate (S3-6a): To a solution of compound **S2-6a** (300 mg, 1.02 mmol) in DCM 30 mL was added triethylamine (213 µL, 1.53 mmol), *p*-toluenesulfonyl chloride (234 mg, 1.23 mmol) and a catalytic amount of DMAP (6.30 mg, 0.051 mmol). The reaction mixture was stirred at room temperature for 16 h, then 0.1 M HCl (30 mL) was added. And the aqueous layer was extracted with DCM. The organic layer was combined, washed with brine, dried over $MgSO_4$, filtered and concentrated. The crude was purified by silica gel flash chromatography (DCM/MeOH = 95/5, R*f* = 0.45) affording product as a pale-yellow oil (430 mg, 0.962 mmol), yield 94.1%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 4.18-4.14 (m, 2H), 3.70 (q, *J* = 5.9, 4.8 Hz, 3H), 3.68-3.64 (m, 2H), 3.63-3.60 (m, 6H), 3.53 (t, *J* = 5.1 Hz, 2H), 3.33-3.28 (m, 2H), 2.05 (s, 3H), 1.44 (d, *J* = 3.5 Hz, 9H). HRMS (ESI) calcd. for $C_{20}H_{34}NO_8S^+$ 448.2000 [M+H$^+$], found 448.2002.



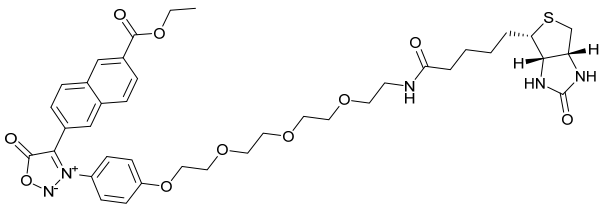


1g-1: To a solution of the compound **1g** (300 mg, 0.798 mmol) in DCM (25 mL) was added 1M BBr_3 solution in DCM (12.0 mL, 11.97 mmol) at -78 °C, then the mixture was vigorously stirred for 8 h at room temperature. The mixture was added 10 ml H_2O under ice bath, then NaOH aqueous to adjust the pH until the solid of mixture dissolves. Then 3 M HCl was added

until the solid was precipitated, vacuum filtered, washed with water and EtOAc. Vacuum drying to afford compound **1g-1** as a yellow solid (218 mg, 0.626 mmol), yield 78.5%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54-8.48 (m, 1H), 8.10-8.02 (m, 2H), 7.79 (dd, J = 8.7, 2.6 Hz, 2H), 7.42-7.33 (m, 2H), 7.24 (dd, J = 8.7, 1.8 Hz, 1H), 7.05-6.97 (m, 2H), 6.43 (s, 1H), 4.44 (q, J = 7.1 Hz, 2H), 1.44 (t, J = 7.1 Hz, 3H). HRMS (ESI) calcd. for $C_{21}H_{17}N_2O_5^+$ 377.1132 [M+H$^+$], found 377.1131.

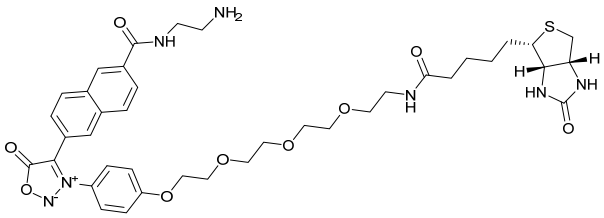


1g-2: To a solution of the compound **S3-6a** (0.274 g, 122.5 mmol) in DMF (10 mL) was added K_2CO_3 (103 mg, 0.747 mmol), NaI (3.73 mg, 0.0249 mmol) and **1g-1** (90 mg, 0.249 mmol). The reaction mixture was stirred at 100 °C for 8 h, The crude reaction mixture was then diluted with 1M HCl (50 mL) and extracted with EtOAc (3 × 200 mL). The organic layers were combined, washed with 1M HCl (50 mL) and brine (50 mL) then dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel flash chromatography (DCM/EtOAc = 9/1 to 6/4; Rf = 0.3 in DCM/EtOAc = 6/4) affording compound **1g-2** as an orange oil (123 mg, 0.189 mmol), yield 75.9%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 1.5 Hz, 1H), 8.08-8.01 (m, 2H), 7.78 (dd, J = 8.7, 2.6 Hz, 2H), 7.45-7.38 (m, 2H), 7.19 (dd, J = 8.7, 1.8 Hz, 1H), 7.09-7.02 (m, 2H), 4.42 (q, J = 7.1 Hz, 2H), 4.21 (t, J = 4.6 Hz, 2H), 3.90 (t, J = 4.6 Hz, 2H), 3.76-3.72 (m, 2H), 3.71-3.66 (m, 2H), 3.66-3.58 (m, 4H), 3.52 (t, J = 5.2 Hz, 2H), 3.32-3.26 (m, 2H), 1.44-1.40 (m, 12H). HRMS (ESI) calcd. for $C_{34}H_{42}N_3O_{10}^+$ 652.2865 [M+H$^+$], found 652.2862.

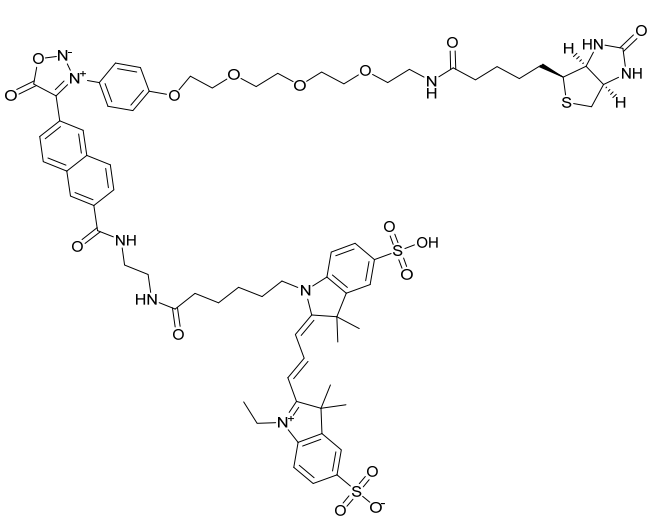


1g-3: Compound **1g-2** (90.0 mg, 0.138 mmol) was dissolved in TFA/DCM (0.25/0.5 mL) at 0 °C, then stirred at room temperature for 1 h. The reaction mixture was concentrated. Without any purification, the residue was dissolved in DCM. TEA (1.00 mL, 6.99 mol) and Biotin-NHS (57.0 mg, 0.166 mmol) was added. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was purified by HPLC preparation with a **C18** column (A: HCOOH/H_2O 0.1%; B: HCOOH/ACN 0.1%) affording **1g-3** as a milky white solid (103 mg, 96.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, J = 1.6 Hz, 1H), 8.10-8.01 (m, 2H), 7.78 (dd, J = 8.7, 2.6 Hz, 2H), 7.47-7.39 (m, 2H), 7.19 (dd, J =

8.6, 1.8 Hz, 1H), 7.10-7.03 (m, 2H), 6.84 (t, *J* = 5.5 Hz, 1H), 6.59 (s, 1H), 5.67 (s, 1H), 4.48-4.38 (m, 3H), 4.26-4.18 (m, 3H), 3.89 (t, *J* = 4.5 Hz, 2H), 3.76-3.70 (m, 2H), 3.70-3.66 (m, 2H), 3.64-3.58 (m, 4H), 3.54 (t, *J* = 5.0 Hz, 2H), 3.44-3.34 (m, 2H), 3.14-3.04 (m, 1H), 2.86-2.82 (m, 1H), 2.70 (d, *J* = 12.8 Hz, 1H), 2.19 (t, *J* = 7.4 Hz, 2H), 1.68-1.58 (m, 4H), 1.44-1.34 (m, 5H). HRMS (ESI) calcd. for $C_{39}H_{48}N_5O_{10}S^+$ 778.3116 [M+H$^+$], found 778.3108.

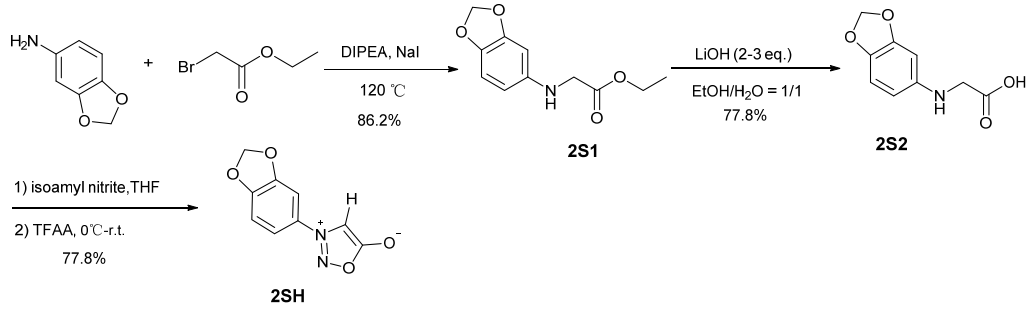


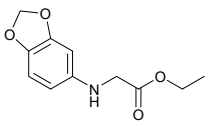
1g-4: A mixture of **1g-3** (103 mg, 0.133 mmol) and LiOH·H_2O (10.6 mg, 0.266 mmol) in a solution of H_2O/EtOH = 1/1 (30 mL), It was stirred vigorously at room temperature 2 h and was traced with TLC till the conversion was completed. The residue was purified by silica gel flash chromatography (MeOH/EtOAc = 9/1; R*f* = 0.2 in MeOH/EtOAc = 9/1) affording product as an orange solid. The **orange solid** (80.0 mg，0.117 mmol), HATU 1.2 eq. (53.6 mg, 0.141 mmol) and 3 mL TEA (23.7 mg, 0.234 mmol) were dissolved by a solution of DMF. Then the mixture was added dropwise into a mixture of *tert*-Butyl (2-aminoethyl)carbamate in 2 mL DCM. It was stirred vigorously at room temperature 1 h and was traced by HPLC, till the conversion was completed. Without any purification, the mixture was dissolved in TFA/DCM (0.25/0.5 mL) at 0 °C then stirred at room temperature for 1 h. The reaction mixture was then concentrated and was purified by HPLC preparation with a **C18** column (A: HCOOH/H_2O 0.1%; B: HCOOH/ACN 0.1%) affording product as a yellow oil (25.0 mg, 0.032 mmol), yield 45.0%. ^{1}H NMR (400 MHz, Methanol-*d*$_4$) δ 8.37 (d, *J* = 1.7 Hz, 1H), 8.23 (s, 2H), 8.02 (d, *J* = 1.7 Hz, 1H), 7.95-7.84 (m, 3H), 7.60-7.53 (m, 2H), 7.32 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.21-7.12 (m, 2H), 4.27-4.20 (m, 3H), 3.91-3.85 (m, 2H), 3.76-3.55 (m, 10H), 3.51 (t, *J* = 5.4 Hz, 2H), 3.33 (d, *J* = 5.4 Hz, 2H), 3.20 (t, *J* = 5.9 Hz, 2H), 3.16-3.11 (m, 1H), 2.91-2.84 (m, 2H), 2.66 (d, *J* = 12.7 Hz, 1H), 2.16 (t, *J* = 7.4 Hz, 2H), 1.70-1.50 (m, 4H), 1.42-1.32 (m, 2H). HRMS (ESI) calcd. for $C_{39}H_{50}N_7O_9S^+$ 792.3385 [M+H$^+$], found 792.3379.



Biotin-suflo-Cy3-DASyd (6a): Compound **1g-4** (2.00 mg, 0.003 mmol) was dissolved in 1 mL DMF and Suflo-Cy3-NHS (2.10 mg, 0.003 mmol) was added. The reaction mixture was stirred at room temperature for 10 h. The reaction mixture was purified by HPLC preparation with a **C18** column (A: HCOOH/H_2O 0.1%; B: HCOOH/ACN 0.1%) affording **1g-3** as a red solid (3.20 mg, 90.0%). ^{1}H NMR (800 MHz, D_2O) δ 8.17 (s, 1H), 8.04 (s, 1H), 7.81-7.70 (m, 4H), 7.60 (s, 1H), 7.40 (d, J = 42.3 Hz, 2H), 7.10 (d, J = 59.2 Hz, 4H), 6.81 (s, 3H), 6.17 (d, J = 115.1 Hz, 2H), 4.39 (s, 1H), 4.17 (s, 1H), 3.95 (d, J = 75.3 Hz, 3H), 3.73 (s, 2H), 3.64-3.36 (m, 18H), 3.22 (s, 2H), 2.92 (s, 1H), 2.65 (d, J = 11.0 Hz, 1H), 2.47 (d, J = 12.7 Hz, 1H), 2.15 (s, 2H), 1.99 (q, J = 6.7, 5.7 Hz, 2H), 1.70 (s, 1H), 1.46-1.32 (m, 22H), 1.30-1.04 (m, 9H). HRMS (ESI) calcd. for $C_{70}H_{85}N_9O_{16}S_3$. 1403.5276 $[M]^+$, found 1403.5236.

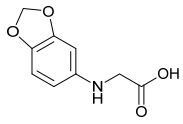
Synthetic experimental procedures and characterization data for 4-H-Monoarylsydnone for 2n, 3n, 4n, 5n



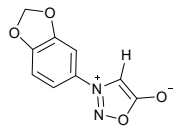


Ethyl benzo[*d*][1,3]dioxol-5-ylglycinate (2S1): To a solution of Benzo[*d*][1,3]dioxol-5-amine (1.70 g, 12.2 mmol) was dissolved in 20 mL of anhydrous DMF, DIPEA (7.40 mL, 42.6 mmol) and sodium iodide (2.00 g, 13.4 mmol) was added under argon; then, Ethyl-2-bromoacetate (1.85 g , 11.1 mmol) was added.

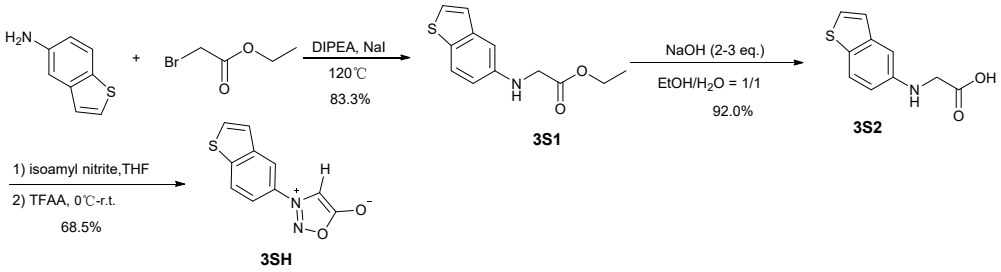
This reaction was traced by TLC till the conversion was completed. This mixture was extracted with EtOAc, then the organic layer was subsequently washed with water, saturated brine and dried over $MgSO_4$ before the volatiles were removed in vacuum. The residue was then purified through flash chromatography (hexanes/EtOAc = 10/1) to give the desired product as a brown solid (2.13 g, 86.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.66 (d, J = 8.3 Hz, 1H), 6.28 (d, J = 2.2 Hz, 1H), 6.06 (dd, J = 8.3, 2.3 Hz, 1H), 5.86 (s, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.84 (s, 2H), 1.29 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 148.6, 142.5, 140.6, 108.8, 105.1, 100.9, 96.7, 61.5, 47.1, 14.3. HRMS (ESI) calcd. for $C_{11}H_{14}NO_4^+$ 224.0917 [M+H$^+$], found 224.0912.

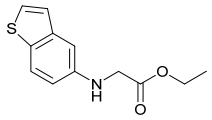


Benzo[*d*][1,3]dioxol-5-ylglycine (2S2): A mixture of **2S1** (2.10 g, 9.41 mmol) and LiOH·H_2O (0.800 g, 18.9 mmol) in a solution of H_2O/EtOH = 1/1 (30 mL), It was stirred vigorously at room temperature over 30 min and was traced with TLC till the conversion was completed. The mixture was then evaporated to remove organic solution in vacuum and was acidified with 3 M aq. HCl to adjust the pH till the solid precipitate out. The resulting mixture then was vacuum filtered to collect the off-white precipitate, then washed with hexanes/EtOAc = 5/1 then H_2O. Subsequently, dried over vacuum to give desired product as an off-white solid (1.43 g, 77.8%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.01 (s, 1H), 6.65 (d, J = 8.3 Hz, 1H), 6.29 (d, J = 2.2 Hz, 1H), 5.95 (dd, J = 8.3, 2.3 Hz, 1H), 5.83 (s, 2H), 3.72 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.7, 147.7, 144.1, 138.3, 108.4, 103.2, 100.0, 95.3, 45.5. HRMS (ESI) calcd. For $C_9H_8NO_4^-$ 194.0459 [M-H$^-$], found 194.0452.

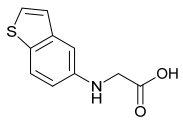


3-(Benzo[*d*][1,3]dioxol-5-yl)-4H-sydnone (2SH): To a solution of **2S2** (1.30 g, 6.66 mmol) was dissolved in 30 mL of anhydrous THF under argon at 0 °C and isoamyl nitrite (1.34 mL, 10.0 mmol) was added dropwise. The solution was stirred vigorously over 2 h at 0 °C and was traced with TLC till the conversion was completed before the introduction of TFAA (1.85 mL, 13.3 mmol) and stirred at room temperature for 1 h. The reaction was quenched with H_2O and the aqueous layer was extracted with EtOAc. The organic layers were combined and washed with water, saturated brine before being dried over $MgSO_4$ and evaporated. The crude was purified by column to give **2SH** as an orange solid (1.07 g, 77.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.55 (d, J = 2.3 Hz, 1H), 7.46 (dd, J = 8.5, 2.3 Hz, 1H), 7.19 (d, J = 8.4 Hz, 1H), 6.22 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 150.3, 148.4, 128.4, 116.0, 108.7, 102.9, 102.7, 94.8. HRMS (ESI) calcd. for $C_9H_7N_2O_4^+$ 207.0400 [M+H$^+$], found 207.0412.

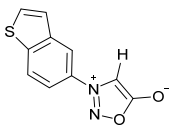




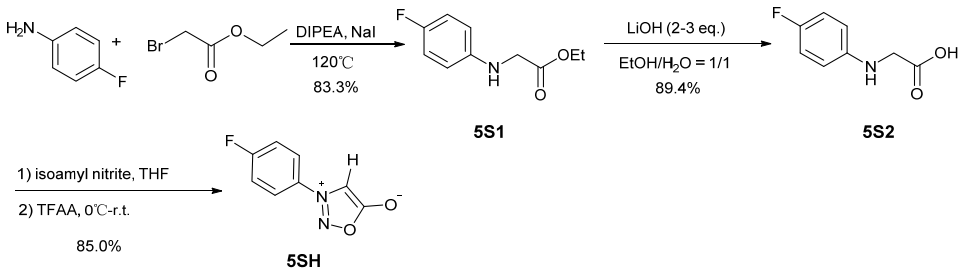
Ethyl benzo[*b*]thiophen-5-ylglycinate (3S1): To a solution of Benzo[*b*]thiophen-5-amine (2.00 g, 13.4 mmol) was dissolved in 20 mL of anhydrous DMF, DIPEA (7.43 mL, 42.7 mmol) and sodium iodide (2.00 g, 13.4 mmol) was added under argon, then, Ethyl 2-bromoacetate (1.35 mL, 12.2 mmol) was then added. This reaction was traced by TLC till the conversion was completed. This mixture was extracted with EtOAc, then the organic layer was subsequently washed with water, saturated brine and dried over $MgSO_4$ before the volatiles were removed in vacuum. The residue was then purified through flash chromatography (hexanes/EA = 8/1) to give the desired product as a brown solid (2.38 g, 83.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.6 Hz, 1H), 7.38 (d, J = 5.4 Hz, 1H), 7.18 (d, J = 5.4 Hz, 1H), 6.95 (d, J = 2.3 Hz, 1H), 6.78 (dd, J = 8.6, 2.4 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.96 (s, 2H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 144.7, 141.0, 130.2, 127.2, 123.5, 123.1, 114.2, 105.3, 61.5, 46.5, 14.4. HRMS (ESI) calcd. for $C_{12}H_{14}NO_2S^+$ 236.0740 [M+H$^+$], found 236.0735.

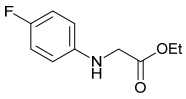


Benzo[*b*]thiophen-5-ylglycine (3S2): A mixture of **3S1** (2.38 g, 10.1 mmol) and NaOH (0.680 g, 17.0 mmol) in a solution of H_2O/EtOH = 1/1 (30 mL) was stirred vigorously at room temperature over 30 min and was traced with TLC till the conversion was completed. The mixture was then evaporated to remove organic solution in vacuum and was acidified with 3 M aq. HCl to adjust the pH till the white solid precipitate out. The resulting mixture then was vacuum filtered to collect the white precipitate, washing with hexanes:EtOAc = 5:1 then H_2O. Subsequently, a white solid was dried over vacuum to give desired product. (1.90 g, 92.0%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.64 (d, J = 8.7 Hz, 1H), 7.58 (d, J = 5.4 Hz, 1H), 7.21 (d, J = 5.4 Hz, 1H), 6.87 (d, J = 2.3 Hz, 1H), 6.80 (dd, J = 8.7, 2.3 Hz, 1H), 3.84 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.8, 145.9, 140.7, 127.6, 127.2, 123.5, 122.5, 113.9, 103.7, 45.0, 40.2, 39.9, 39.7, 39.5, 39.3, 39.1, 38.9. HRMS (ESI) calcd. For $C_{10}H_8NO_2S^-$ 206.0281 [M-H$^-$], found 206.0279.

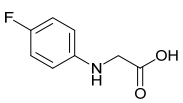


3-(Benzo[*b*]thiophen)sydnone (3SH): To a solution of **3S2** (1.80 g, 8.69 mmol) was dissolved in 40 mL of anhydrous THF under argon at 0 °C and isoamyl nitrite (1.75 mL, 13.1 mmol) was added dropwise. The solution was stirred vigorously over 2 h at 0 °C and was traced with TLC till the conversion was completed before the introduction of TFAA (2.42 mL, 17.4 mmol) and stirred at room temperature for 1 h. The reaction was quenched with H_2O and the aqueous layer was extracted with EtOAc. The organic layers were combined and washed with saturated brine before being dried over $MgSO_4$ and evaporated. The crude was purified by flash chromatography (hexanes/ EtOAc = 1/1) to give **3SH** as an orange solid (1.23 g, 68.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 2.2 Hz, 1H), 8.36 (d, J = 8.7 Hz, 1H), 8.06 (d, J = 5.4 Hz, 1H), 7.88 (dd, J = 8.7, 2.2 Hz, 1H), 7.85 (s, 1H), 7.66 (d, J = 5.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 142.4, 139.7, 131.6, 131.5, 124.4, 124.3, 116.9, 116.8, 95.2. HRMS (ESI) calcd. for $C_{10}H_7N_2O_2S^+$ 219.0223 [M+H$^+$], found 219.0225.



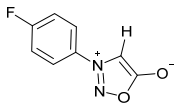


Ethyl (4-fluorophenyl)glycinate (5S1): To a solution of 4-Fluoroaniline (2.00 g, 18.0 mmol) was dissolved in 20 mL of anhydrous DMF, DIPEA (10.0 mL, 148 mmol) and sodium iodide (2.70 g, 18.0 mmol) was added under argon, then, Ethyl 2-bromoacetate (1.82 mL , 16.4 mmol) was added. This reaction was traced by TLC till the conversion was completed. This mixture was extracted with EtOAc, then the organic layer was subsequently washed with water, saturated brine and dried over $MgSO_4$ before the volatiles were removed in vacuum. The residue was then purified through flash chromatography (hexanes/EtOAc = 6/1) to give the desired product as a yellow solid (2.96 g, 83.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93-6.86 (m, 2H), 6.58-6.51 (m, 2H), 4.24 (q, J = 7.2 Hz, 2H), 3.86 (s, 2H), 1.29 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 156.4 (d, J = 236.5 Hz), 143.5 (d, J = 1.9 Hz), 115.9 (d, J = 22.5 Hz), 114.0 (d, J = 7.6 Hz), 61.5, 46.6, 14.3. HRMS (ESI) calcd. for $C_{10}H_{13}FNO_2^+$ 198.0925 [M+H$^+$], found 198.0920.



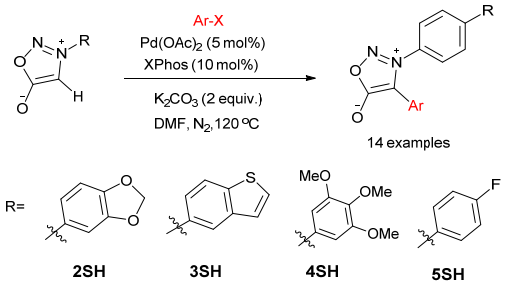
(4-Fluorophenyl)glycine (5S2): A mixture of **5S1** (2.50 g, 12.7 mmol) and NaOH (0.760 g, 19.0 mmol) in a solution of H_2O/EtOH = 1/1 (30 mL), It was

stirred vigorously at room temperature over 30 min and was traced with TLC till the conversion was completed. The mixture was then evaporated to remove organic solution in vacuum and was acidified with 3 M aq. HCl to adjust the pH till the off-white solid precipitate out. The resulting mixture then was vacuum filtered to collect the white precipitate, washing with hexanes/EtOAc = 5/1 then H_2O. Subsequently, white solid dried over vacuum to give desired product (1.92 g, 89.4%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 6.95-6.87 (m, 2H), 6.57-6.50 (m, 2H), 3.76 (s, 2H); ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 172.6, 154.5 (d, J = 231.9 Hz), 144.9 (d, J = 1.2 Hz), 115.2 (d, J = 22.1 Hz), 112.9 (d, J = 7.4 Hz), 45.1. HRMS (ESI) calcd. For $C_8H_7FNO_2^-$ 168.0466 [M-H$^-$], found 168.0463.

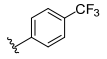
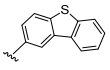
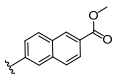
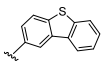
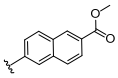
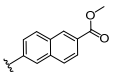


3-(4-Fluorophenyl)-5-H-sydnone (5SH): To a solution of **5S2** (1.90 g, 11.2 mmol) was dissolved in 50 mL of anhydrous THF under argon at 0 °C and isoamyl nitrite (2.26 mL, 16.8 mmol) was added dropwise. The solution was stirred vigorously over 2 h at 0 °C and was traced with TLC till the conversion was completed before the introduction of TFAA (3.10 mL, 22.4 mmol) and stirred at room temperature for 1 h. The reaction was quenched with H_2O and the aqueous layer was extracted with EtOAc. The organic layers were combined and washed with saturated brine before being dried over $MgSO_4$ and evaporated. The crude was purified by flash chromatography (hexanes/EtOAc = 1/1) to give **5SH** as a yellow solid (1.71 g, 85.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 8.9, 4.5 Hz, 2H), 7.32 (t, J = 8.3 Hz, 2H), 6.75 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 164.6 (d, J = 255.8 Hz), 131.0, 123.7(d, J = 9.2 Hz), 117.7(d, J = 23.7 Hz), 94.0. HRMS (ESI) calcd. for $C_8H_6FN_2O_2^+$ 181.0408 [M+H$^+$], found 181.0412.

Table S20: General procedure for palladium (II) -XPhos complex catalyzed C-H activation cross-coupling for the Direct Arylation of corresponding N^3-Aryl-Sydnones[4,7].

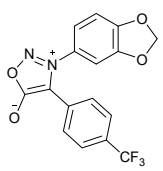


Entry	N^3-term	C^4-term	Yield	Entry	N^3-term	C^4-term	Yield

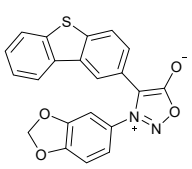
2a			70.7%	**4a**			72.5%
2b			72.7%	**4b**			48.5%
2c			79.5%	**4c**			64.6%
2d			40.2%	**4d**			51.6%
3a			51.8%	**5a**			97.8%
3b			89.1%	**5b**			86.4%
3c			29.3%	**5c**			62.2%

[a]Using corresponding 4-H-Sydnone as starting material

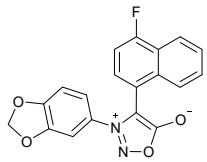
A flask equipped with a reflux condenser was charged with a mixture of 4-H-Sydnone **1SH** (**2SH, 3SH, 4SH, 5SH**) (1.0 eq.), aryl halide (1.2 eq.), palladium acetate (5 mol %), XPhos (10 mol%) and potassium carbonate (2-3 eq.) in DMF under an atmosphere of nitrogen and heated at 100 - 120 °C for 3 h. The reaction was allowed to cool to ambient temperature, then water was added. The resulting mixture was extracted with EtOAc and the combined organic layers dried over $MgSO_4$ and concentrated in vacuo. Flash silica chromatography (eluting solvent 20%-100% EtOAc in hexanes) afforded the target DASyds. The compounds could be further purified by recrystallization from ethanol or EtOAc/hexanes.



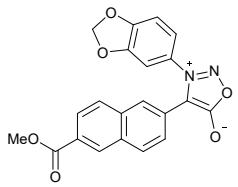
3-(Benzo[*d*][1,3]dioxol-5-yl)-4-(4-(trifluoromethyl)phenyl)sydnone (2a): Sydnone **2SH** (100 mg, 0.485 mmol) and 1-Bromo-4-(trifluoromethyl)benzene (174 mg, 0.777 mmol) were subjected to the general condition affording **2a** as a white solid (120 mg, 70.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.3 Hz, 2H), 7.03-6.93 (m, 2H), 6.90 (d, J = 2.1 Hz, 1H), 6.16 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 151.1, 149.2, 130.2 (q, J = 32.9 Hz), 128.2, 127.9, 127.1, 125.8 (q, J = 1.9 Hz), 123.8 (q, J = 273.2 Hz), 119.4, 109.2, 106.4, 105.7, 103.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.94. HRMS (ESI) calcd. for $C_{16}H_{10}F_3N_2O_4^+$ 351.0587 [M+H$^+$], found 351.0588.



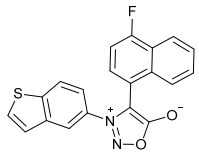
3-(Benzo[*d*][1,3]dioxol-5-yl)-4-(dibenzo[*b*,*d*]thiophen-2-yl)sydnone (2b): Sydnone **2SH** (100 mg, 0.485 mmol) and 2-Bromodibenzo[*b*,*d*]thiophene (204 mg, 0.777 mmol) were subjected to the general condition affording **2b** as a yellow solid (137 mg, 72.7%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 (d, J = 1.7 Hz, 1H), 8.14-8.04 (m, 2H), 8.03 (d, J = 8.7 Hz, 1H), 7.57-7.50 (m, 2H), 7.39 (d, J = 2.1 Hz, 1H), 7.34-7.29 (m, 2H), 7.17 (d, J = 8.3 Hz, 1H), 6.19 (s, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.4, 150.2, 148.1, 139.0, 138.9, 134.9, 134.3, 127.8, 127.6, 126.0, 125.2, 123.4, 123.3, 121.6, 121.2, 120.8, 120.3, 108.9, 108.4, 106.5, 102.9. HRMS (ESI) calcd. for $C_{21}H_{13}N_2O_4S^+$ 389.0591 [M+H$^+$], found 389.0580.



3-(Benzo[*d*][1,3]dioxol-5-yl)-4-(4-fluoronaphthalen-1-yl)sydnone(2c): Sydnone **2SH** (100 mg, 0.485 mmol) and 1-Bromo-4-fluoronaphthalene (175 mg, 0.777 mmol) were subjected to the general condition affording **2c** as a yellow solid (135 mg, 79.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.10 (m, 1H), 7.78-7.72 (m, 1H), 7.61-7.54 (m, 2H), 7.21 (dd, J = 8.0, 5.2 Hz, 1H), 7.08 (dd, J = 9.9, 8.0 Hz, 1H), 6.83 (dd, J = 8.4, 2.2 Hz, 1H), 6.77 (d, J = 2.2 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 5.99 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 160.0 (d, J = 258.6 Hz), 150.5, 148.6, 133.3 (d, J = 6.06 Hz), 130.5 (d, J = 9.09 Hz), 128.5, 128.0, 127.2 (d, J = 2.02 Hz), 124.8 (d, J = 2.02 Hz), 124.2 (d, J = 17.2 Hz), 121.4 (d, J = 6.06 Hz), 118.6, 117.7 (d, J = 5.05 Hz), 109.5 (d, J = 21.2 Hz), 108.7, 106.4, 104.9, 102.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -118.17. HRMS (ESI) calcd. for $C_{19}H_{12}FN_2O_4^+$ 351.0776 [M+H$^+$], found 351.0781.

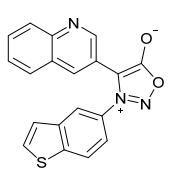


3-(Benzo[*d*][1,3]dioxol-5-yl)-4-(6-(methoxycarbonyl)naphthalen-2-yl)sydnone (2d): Sydnone **2SH** (100 mg, 0.485 mmol) and Methyl 6-bromo-2-naphthoate (155 mg, 0.583 mmol) were subjected to the general condition affording **2d** as a yellow solid (76.0 mg, 40.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (s, 1H), 8.10 (s, 1H), 8.05 (dd, J = 8.6, 1.7 Hz, 1H), 7.81 (dd, J = 8.7, 4.9 Hz, 2H), 7.24 (dd, J = 8.7, 1.8 Hz, 1H), 7.03 (dd, J = 8.3, 2.1 Hz, 1H), 6.94 (d, J = 0.9 Hz, 1H), 6.93 (d, J = 5.0 Hz, 1H), 6.15 (s, 2H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 167.0, 150.9, 149.1, 135.2, 131.8, 130.7, 129.8, 128.8, 128.5, 128.2, 126.8, 126.3, 124.6, 124.3, 119.4, 109.1, 107.5, 105.8, 103.0, 52.5. HRMS (ESI) calcd. for $C_{21}H_{15}N_2O_6^+$ 391.0925 [M+H$^+$], found 391.0926.

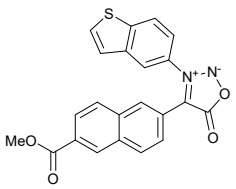


3-(Benzo[*b*]thiophen-5-yl)-4-(4-fluoronaphthalen-1-yl) sydnone (3a): Sydnone **3SH** (100 mg, 0.460 mmol) and 1-Bromo-4-fluoronaphthalene (165 mg, 0.734 mmol) were subjected to the general condition affording **3a** as a

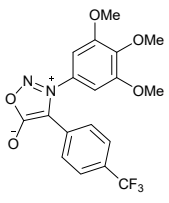
yellow solid (86.0 mg, 51.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16-8.10 (m, 1H), 7.91 (d, J = 2.0 Hz, 1H), 7.90-7.85 (m, 1H), 7.78 (d, J = 8.7 Hz, 1H), 7.62-7.53 (m, 3H), 7.30 (d, J = 5.5 Hz, 1H), 7.19-7.12 (m, 2H), 7.00 (dd, J = 9.9, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.6, 160.0 (d, J = 258.6 Hz), 142.7, 139.8, 133.3 (d, J = 6.06 Hz), 131.2, 130.6 (d, J = 9.09 Hz), 130.2, 128.5, 127.2 (d, J = 2.02 Hz), 124.9 (d, J = 3.03 Hz), 124.3, 124.1, 124.0 (d, J = 15.2 Hz), 121.4 (d, J = 6.06 Hz), 119.3, 119.1, 117.8 (d, J = 4.04 Hz),109.5 (d, J = 21.2 Hz), 106.8; ^{19}F NMR (376MHz, $CDCl_3$) δ -118.21. HRMS (ESI) calcd. for $C_{20}H_{12}FN_2O_2S^+$ 363.0598 [M+H$^+$], found 363.0597.



3-(Benzo[*b*]thiophen-5-yl)-4-(quinolin-3-yl)sydnone (3b): Sydnone **3SH** (100 mg, 0.460 mmol) and 3-Bromoquinoline (152 mg, 0.734 mmol) were subjected to the general condition affording **3b** as a brown solid (141 mg, 89.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 2.2 Hz, 1H), 8.36 (d, J = 2.3 Hz, 1H), 8.06-8.01 (m, 2H), 7.93 (d, J = 8.4 Hz, 1H), 7.77 (d, J = 8.2 Hz, 1H), 7.70-7.65 (m, 2H), 7.53 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 5.5 Hz, 1H), 7.38 (dd, J = 8.6, 2.2 Hz, 1H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.1, 147.4, 146.9, 143.4, 140.2, 134.2, 131.1, 130.8, 130.6, 129.2, 128.3, 127.7, 127.4, 124.7, 124.1, 119.9, 119.6, 118.4. HRMS (ESI) calcd. for $C_{19}H_{12}N_3O_2S^+$ 346.0645 [M+H$^+$], found 346.0642.

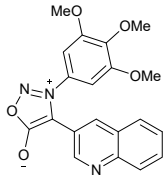


. **3-(Benzo[*b*]thiophen-5-yl)-4-(6-(methoxycarbonyl)naphthalen-2-yl) sydnone (3c):** Sydnone **3SH** (150 mg, 0.688 mmol) and Methyl 6-bromo-2-naphthoate (219 mg, 0.826 mmol) were subjected to the general condition affording **3c** as a yellow solid (195 mg, 48.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.48 (m, 1H), 8.15-8.13 (m, 1H), 8.08-8.04 (m, 2H), 8.04-8.02 (m, 1H), 7.76 (dd, J = 17.6, 8.7 Hz, 2H), 7.72 (d, J = 5.5 Hz, 1H), 7.45 (d, J = 5.5 Hz, 1H), 7.40 (dd, J = 8.6, 2.1 Hz, 1H), 7.18 (dd, J = 8.7, 1.8 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 167.2, 166.9, 143.2, 140.1, 135.2, 131.8, 131.4, 130.7, 130.6, 129.8, 128.7, 128.5, 126.8, 126.2, 124.6, 124.4, 124.3, 124.2, 120.1, 119.9, 107.8, 52.5. HRMS (ESI) calcd. for $C_{22}H_{15}N_2O_4S^+$ 403.0747 [M+H$^+$], found 403.0745.

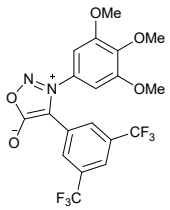


4-(4-(Trifluoromethyl)phenyl)-3-(3,4,5-trimethoxyphenyl)sydnone (4a): Sydnone **4SH** (100 mg, 0.397 mmol) and 1-Bromo-4-(trifluoromethyl)benzene (142 mg, 0.635 mmol) were subjected to the general condition affording **4a** as a white solid (114 mg, 72.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.4 Hz, 2H), 7.50 (d, J = 8.3 Hz, 2H), 6.67 (s, 2H), 3.95 (s, 3H), 3.80 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 154.3, 141.0, 130.1(q, J = 33.3 Hz), 129.5, 128.2, 126.9, 125.6 (q, J

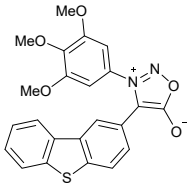
= 3.03 Hz), 122.2 (q, J = 273.7 Hz), 106.3, 102.4, 61.2, 56.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.93. HRMS (ESI) calcd. for $C_{18}H_{16}F_3N_2O_5^+$ 397.1006 [M+H$^+$], found 397.1001.



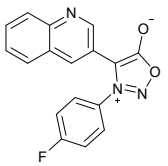
4-(quinolin-3-yl)-3-(3,4,5-trimethoxyphenyl)sydnone (4b): Sydnone **4SH** (100 mg, 0.397 mmol) and 3-Bromoquinoline (131 mg, 0.635 mmol) were subjected to the general condition affording **4b** as a white solid (73.0 mg, 48.5%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59-8.51 (m, 2H), 8.01 (d, J = 8.4 Hz, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.76-7.70 (m, 1H), 7.60-7.54 (m, 1H), 6.74 (s, 2H), 3.94 (s, 3H), 3.77 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 154.5, 147.3, 147.0, 141.3, 133.9, 130.7, 129.7, 129.3, 128.4, 127.8, 127.3, 118.5, 105.5, 102.3, 61.3, 56.7. HRMS (ESI) calcd. for $C_{20}H_{18}N_3O_5^+$ 380.1241 [M+H$^+$], found 380.1235.



4-(3,5-Bis(trifluoromethyl)phenyl)-3-(3,4,5-trimethoxyphenyl)sydnone (4c): Sydnone **4SH** (100 mg, 0.397 mmol) and 1-Bromo-3,5-bis(trifluoromethyl)benzene (186 mg, 0.635 mmol) were subjected to the general condition affording **4c** as a white solid (119 mg, 64.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.75 (s, 1H), 6.69 (s, 2H), 3.94 (s, 3H), 3.83 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 154.8, 141.9, 132.2 (q, J = 33.3 Hz), 129.0, 127.0, 125.9, 124.3, 121.6 (q, J = 3.03 Hz), 105.0, 102.7, 61.4, 56.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.29. HRMS (ESI) calcd. for $C_{19}H_{15}F_6N_2O_5^+$ 465.0880 [M+H$^+$], found 465.0877.

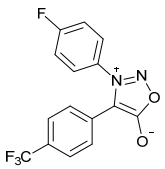


4-(Dibenzo[*b*,*d*]thiophen-2-yl)-3-(3,4,5-trimethoxyphenyl)sydnone (4d): Sydnone **4SH** (100 mg, 0.397 mmol) and 2-Bromodibenzo[*b*,*d*]thiophene (167 mg, 0.635 mmol) were subjected to the general condition affording **4d** as a yellow solid (89.0 mg, 51.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 1.7 Hz, 1H), 8.03 (dd, J = 7.0, 2.3 Hz, 1H), 7.85 (dd, J = 6.5, 1.5 Hz, 1H), 7.76 (d, J = 8.5 Hz, 1H), 7.51-7.44 (m, 2H), 7.28 (d, J = 1.8 Hz, 1H), 6.74 (s, 2H), 3.94 (s, 3H), 3.76 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 154.2, 140.8, 139.9, 139.7, 135.8, 134.9, 129.9, 127.4, 125.1, 124.8, 123.0, 122.9, 121.8, 120.8, 120.3, 107.9, 102.6, 61.3, 56.7. HRMS (ESI) calcd. for $C_{23}H_{19}N_2O_5S^+$ 435.1009 [M+H$^+$], found 435.1001.

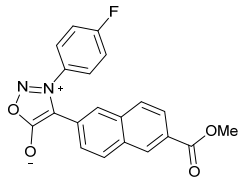


3-(4-Fluorophenyl)-4-(quinolin-3-yl)sydnone (5a): Sydnone **5SH** (100 mg, 0.556 mmol) and 3-Bromoquinoline (184 mg, 0.890 mmol) were subjected to the general condition affording **5a** as a brown solid (167 mg, 97.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, J = 13.5 Hz, 2H), 7.96 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.56-7.51 (m, 3H), 7.30-7.21 (m, 2H); ^{13}C NMR (101 MHz,

$CDCl_3$) δ 166.9, 164.7 (d, J = 257.6 Hz), 147.3, 147.0, 134.6, 130.9, 130.5, 129.3, 128.4, 127.9, 127.4, 127.1 (q, J = 9.1 Hz), 118.2, 118.1 (q, J = 23.2 Hz), 105.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -104.57. HRMS (ESI) calcd. for $C_{17}H_{11}FN_3O_2^+$ 308.0830 [M+H$^+$], found 308.0829.

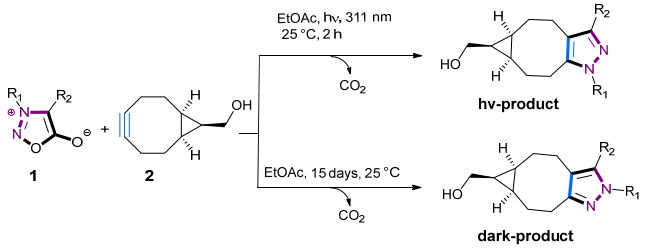


3-(4-Fluorophenyl)-4-(4-(trifluoromethyl)phenyl)sydnone (5b): Sydnone **5SH** (100 mg, 0.556 mmol) and 1-Bromo-4-(trifluoromethyl)benzene (199 mg, 0.890 mmol) were subjected to the general condition affording **5b** as a brown solid (140 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59-7.50 (m, 4H), 7.42 (d, J = 8.2 Hz, 2H), 7.35-7.29 (m, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99, -104.72. HRMS (ESI) calcd. for $C_{15}H_9F_4N_2O_2^+$ 325.0595 [M+H$^+$], found 325.0595.



3-(4-Fluorophenyl)-4-(6-(methoxycarbonyl)naphthalen-2-yl)sydnone (5c): Sydnone **5SH** (100 mg, 0.556 mmol) and Methyl 6-bromo-2-naphthoate (200 mg, 0.890 mmol) were subjected to the general condition affording **5c** as a yellow solid (126 mg, 62.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (s, 1H), 8.09-8.01 (m, 2H), 7.80 (dd, J = 8.7, 3.3 Hz, 2H), 7.59-7.53 (m, 2H), 7.33-7.26 (m, 2H), 7.19 (dd, J = 8.7, 1.9 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 164.7 (d, J = 256.5 Hz), 135.2, 131.9, 130.8, 130.7, 130.0, 128.8, 128.7, 127.2 (d, J = 9.1 Hz), 127.0, 126.5, 124.6, 124.0, 117.9 (q, J = 23.2 Hz), 107.8, 100.1, 52.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.10. HRMS (ESI) calcd. for $C_{20}H_{14}N_2O_4^+$ 365.0932 [M+H$^+$], found 365.0933.

Compound characterization for the 1,3-dipolar cycloadducts of DASyds 1a-5c with BCN both photo-irradiation and non photo-induced reaction

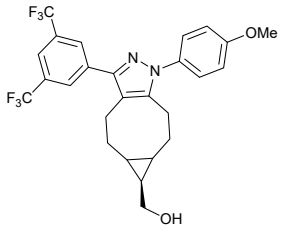


General Conditions:

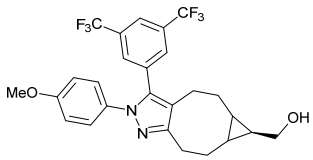
Photo-click reaction: A solution of DASyd and BCN (1.2 eq.) in 200 mL EtOAc was vigorously stirred and irradiated simultaneously with 311 nm UV lamp (10.8 mW/cm^2) in quartz

flask at room temperature for 2 h. The solvent was then evaporated, and the residue was purified by silica gel flash chromatography to give the **photo-click** products.

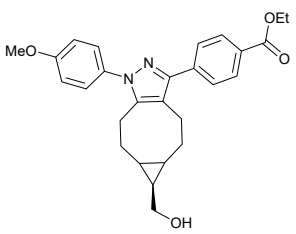
Non photo-induced reaction: A solution of DASyd and BCN (1.2 eq.) in 10 mL EtOAc was vigorously stirred at room temperature for 15 days. The solvent was then evaporated, and the residue was purified by silica gel flash chromatography to give the **non photo-induced** products.



Pyrazole 1ad-hv: Sydnone **1a** (30.0 mg, 0.074 mmol) and BCN (13.4 mg, 0.089 mmol) in 200 mL EtOAc were performed for the general photo-click condition to affording **1ad-hv** as a white solid (31.0 mg, 82.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.04 (m, 2H), 7.84 (s, 1H), 7.37-7.31 (m, 2H), 7.04-6.97 (m, 2H), 3.87 (s, 3H), 3.71-3.82 (m, 2H), 2.94-3.01 (m, 2H), 2.65-2.72 (m, 2H), 2.29-2.35 (m, 1H), 2.20-2.25 (m, 1H), 1.59-1.68 (m, 2H), 1.18-1.26 (m, 1H), 1.04-1.12 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.70, 148.12, 143.26, 136.36, 132.61, 131.73 (q, J =33.3 Hz) 128.49, 127.47, 121.08, 123.6 (q, J = 273.8 Hz) 117.44, 114.51, 60.01, 55.73, 24.83, 24.45, 23.45, 22.93, 21.87, 20.01, 19.90; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.78 (s). HRMS (ESI) calcd. for $C_{26}H_{25}F_6N_2O_2^+$ 511.1815 [M+H$^+$], found 511.1827.

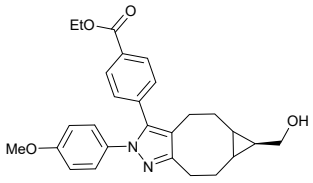


Pyrazole 1ad-dark: Sydnone **1a** (30.0 mg, 0.074 mmol) and BCN (13.4 mg, 0.089 mmol) in 10 mL EtOAc were subjected to the general dark condition affording **1ad-dark** as a white solid (29.9 mg, 79.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.57-7.53 (m, 2H), 7.07-7.02 (m, 2H), 6.83-6.77 (m, 2H), 3.77 (s, 3H), 3.80-3.71 (m, 2H), 3.17-3.11 (m, 1H), 2.84-2.70 (m, 2H), 2.53-2.46 (m, 1H), 2.38-2.21 (m, 2H), 1.53-1.40 (m, 2H), 1.25-1.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.9, 153.6, 137.7, 133.1, 132.5, 131.9 (q, J = 33.3 Hz), 130.2, 126.5, 123.1 (q, J = 273.7 Hz), 121.6 (q, J = 3.1 Hz), 120.5, 114.4, 60.1, 55.7, 27.4, 24.9, 23.7, 22.9, 22.1, 21.1, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.02. HRMS (ESI) calcd. for $C_{26}H_{25}F_6N_2O_2^+$ 511.1815 [M+H$^+$], found 511.1827.

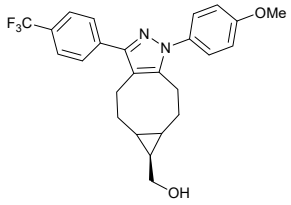


Pyrazole 1bd-hv: Sydnone **1b** (30.0 mg, 0.091 mmol) and BCN (16.4 mg, 0.110 mmol) in 200 mL EtOAc were subjected to the general photo-click condition affording **1bd-hv** as a white solid (30.0 mg, 73.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11-8.08 (m, 2H), 7.71-7.68 (m, 2H), 7.36-7.32 (m, 2H), 7.01-6.97 (m, 2H), 4.39 (q, J = 8.0 Hz, 2H),

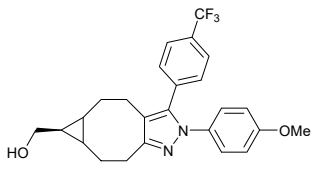
3.86 (s, 3H), 3.81-3.71 (m, 2H), 3.03-2.94 (m, 2H), 2.73-2.64 (m, 2H), 2.34-2.19 (m, 2H), 1.68-1.58 (m, 2H) 1.41 (t, J = 8.0 Hz, 3H), 1.25-1.15 (m, 1H), 1.13-1.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 159.5, 149.8, 142.9, 138.7, 132.9, 129.7, 129.3, 128.4, 127.5, 117.6, 114.4, 61.1, 60.0, 55.7, 24.9, 24.7, 23.6, 23.0, 21.9, 20.2, 20.1, 14.5. HRMS (ESI) calcd. for $C_{27}H_{31}N_2O_4^+$ 447.2278 [M+H$^+$], found 447.2288.



Pyrazole 1bd-dark: Sydnone **1b** (30.0 mg, 0.091 mmol) and BCN (16.4 mg, 0.11 mmol) in 10 mL EtOAc were subjected to the general dark condition affording **1bd-dark** as a white solid (37.0 mg, 90.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.21-7.16 (m, 2H), 7.09-7.02 (m, 2H), 6.78-6.72 (m, 2H), 4.37 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 3.79-3.69 (m, 2H), 3.16-3.10 (m, 1H), 2.82-2.71 (m, 2H), 2.49-2.42(m, 1H), 2.36-2.18 (m, 2H), 1.55-1.41 (m, 2H), 1.38 (t, J = 7.1 Hz, 3H), 1.23-1.11 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 158.3, 153.5, 139.7, 135.5, 133.2, 130.2, 130.0, 129.6, 126.2, 120.1, 114.0, 61.2, 60.0, 55.5, 55.5, 27.4, 25.0, 23.8, 22.8, 22.1, 21.1, 14.41. HRMS (ESI) calcd. for $C_{27}H_{31}N_2O_4^+$ 447.2278 [M+H$^+$], found 447.2288.

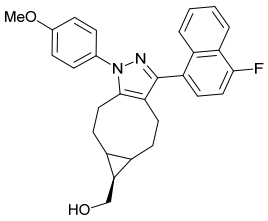


Pyrazole 1cd-hv: Sydnone **1c** (30.0 mg, 0.089 mmol) and BCN (16.2 mg, 0.107 mmol) in 200 mL EtOAc were subjected to the general photo-click condition affording **1cd-hv** as a white solid (34.0 mg, 86.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.0 Hz, 2H), 7.36-7.32 (m, 2H), 7.01-6.97 (m, 2H), 3.86 (s, 3H), 3.80-3.71 (m, 2H), 3.02-2.94 (m, 2H), 2.72-2.65 (m, 2H), 2.35-2.18 (m, 2H), 1.68-1.57 (m, 2H), 1.23-1.14 (m, 1H), 1.11-1.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 149.5, 142.9, 137.8, 132.9, 129.42 (q, J = 30.3 Hz) 128.8, 127.5, 125.4 (q, J = 4.04 Hz), 124.5 (q, J = 262.6 Hz), 117.5, 114.4, 60.1, 55.7, 24.9, 24.7, 23.6, 23.0, 21.9, 20.2, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.39 (s). HRMS (ESI) calcd. for $C_{25}H_{26}F_3N_2O_2^+$ 443.1941 [M+H$^+$], found 443.1938.

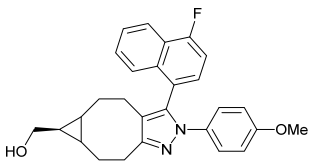


Pyrazole 1cd-dark: Sydnone **1c** (30.0 mg, 0.089 mmol) and BCN (16.2 mg, 0.107 mmol) in 10 mL EtOAc were subjected to the general condition affording **1cd-dark** as a white solid (27.0 mg, 68.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.0 Hz 2H), 7.24 (d, J = 8.0 Hz 2H), 7.08-7.05 (m, 2H), 6.80-6.76 (m, 2H), 3.78 (s, 3H), 3.81-3.71 (m, 2H), 3.18-3.11 (m, 1H) 2.83-2.71 (m, 2H), 2.50-2.43 (m, 1H), 2.38-2.20 (m, 2H), 1.53-1.41 (m, 2H), 1.26-1.14 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.5, 153.5, 139.4, 134.6, 133.0, 130.6, 130.1 (q, J = 32.3 Hz), 126.3, 125.5(q, J = 4.04 Hz), 124.1(q, J = 272.7 Hz) 120.2, 114.2, 60.2, 55.6, 27.4,

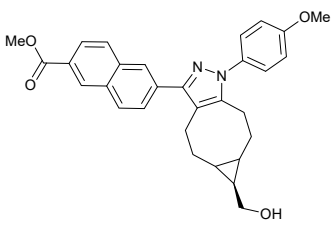
25.0, 23.8, 22.8, 22.1, 21.2, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.63 (s). HRMS (ESI) calcd. for $C_{25}H_{26}F_3N_2O_2^+$ 443.1941 [M+H$^+$], found 443.1938.



Pyrazole 1dd-hv: Sydnone **1d** (30.0 mg, 0.089 mmol) and BCN (16.1 mg, 0.107 mmol) in 200 mL EtOAc were subjected to the general condition affording **1dd-hv** as a white solid (29.0 mg, 73.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, J = 7.7 Hz, 1H), 7.98-7.92 (m, 1H), 7.56-7.48 (m, 2H), 7.46-7.43 (m, 1H), 7.42-7.36 (m, 2H), 7.19 (dd, J = 10.4, 7.9 Hz, 1H), 7.02-6.95 (m, 2H), 3.86 (s, 3H), 3.78-3.68 (m, 2H), 3.10-3.03 (m, 1H), 2.78-2.71 (m, 1H), 2.67-2.60 (m, 1H), 2.44-2.37 (m, 1H), 2.30-2.22 (m, 1H), 2.12-2.05 (m, 1H), 1.69-1.61 (m, 1H), 1.51-1.42 (m, 1H), 1.28-1.21 (m, 1H), 1.16-1.06 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 158.8 (d, J = 253.5 Hz), 149.7, 141.7, 134.2 (d, J = 5.05 Hz), 133.1, 128.1 (d, J = 8.08 Hz), 127.8 (d, J = 5.05 Hz), 127.3, 127.0, 126.6 (d, J = 3.03 Hz), 126.1 (d, J = 2.02 Hz), 123.9 (d, J = 17.2 Hz), 120.6 (d, J = 6.06 Hz), 119.3, 114.2, 109.0 (d, J = 20.2 Hz), 59.9, 55.7, 25.1, 24.7, 23.6, 23.1, 21.9, 20.5, 20.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -122.87. HRMS (ESI) calcd. for $C_{28}H_{28}FN_2O_2^+$ 443.2129 [M+H$^+$], found 443.2132.

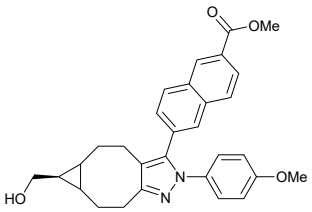


Pyrazole 1dd-dark: Sydnone **1d** (30.0 mg, 0.089 mmol) and BCN (16.1 mg, 0.107 mmol) in 10 mL EtOAc were subjected to the general condition affording **1dd-dark** as a white solid (23.0 mg, 63.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.3 Hz, 1H), 7.63-7.44 (m, 3H), 7.24-7.08 (m, 2H), 7.04-6.97 (m, 2H), 6.63-6.57 (m, 2H), 3.80-3.70 (m, 2H), 3.66 (s, 3H), 3.24-3.17 (m, 1H), 2.90-2.82 (m, 1H), 2.45-2.25 (m, 3H), 2.07-1.98 (m, 1H), 1.62-1.52 (m, 1H), 1.43-1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2 (d, J = 254.5 Hz), 158.0, 152.9, 138.5 (d, J = 3.03 Hz), 134.1 (d, J = 5.05 Hz), 133.5 (d, J = 2.02 Hz), 129.5 (d, J = 9.09 Hz), 127.7, 126.6, 125.7 (d, J = 3.03 Hz), 125.1, 125.0 (d, J = 5.05 Hz), 123.8 (d, J = 16.2 Hz), 121.4, 121.1 (d, J = 3.03 Hz), 113.9, 109.2, 60.3, 55.4, 27.7, 24.6, 23.7, 23.1, 22.0, 21.2, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -120.98. HRMS (ESI) calcd. for $C_{28}H_{28}FN_2O_2^+$ 443.2129 [M+H$^+$], found 443.2132.

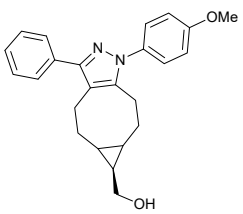


Pyrazole 1gd-hv: Sydnone **1g** (30.0 mg, 0.080 mmol) and BCN (14.4 mg, 0.096 mmol) in 200 mL EtOAc were subjected to the general condition affording **1gd-hv** as a yellow solid (31.0 mg, 80.6%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.10 (s, 1H), 8.06 (dd, J = 8.6, 1.7 Hz, 1H), 8.00 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.85 (dd, J = 8.5, 1.6 Hz, 1H), 7.40-7.34 (m, 2H), 7.03-

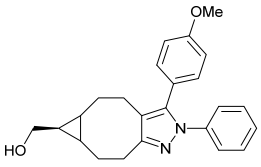
6.97 (m, 2H), 3.99 (s, 3H), 3.87 (s, 3H), 3.81-3.73 (m, 2H), 3.12-2.96 (m, 2H), 2.80-2.66 (m, 2H), 2.40-2.20 (m, 1H), 1.72-1.40 (m, 2H), 1.28-1.18 (m, 1H), 1.16-1.07 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 159.4, 150.3, 142.8, 135.7, 134.1, 132.9, 131.8, 131.0, 129.4, 128.5, 127.7, 127.5, 127.3, 127.0, 125.5, 117.8, 114.4, 60.0, 55.7, 52.4, 24.9, 24.7, 23.6, 23.1, 21.9, 20.2, 20.1. HRMS (ESI) calcd. for $C_{30}H_{31}N_2O_4^+$ 483.2278 [M+H$^+$], found 483.2285.



Pyrazole 1gd-dark: Sydnone **1g** (30.0 mg, 0.080 mmol) and BCN (14.4 mg, 0.096 mmol) in 10 mL EtOAc were subjected to the general condition affording **1gd-dark** as a yellow solid (25.0 mg, 67.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.08 (dd, J = 8.6, 1.7 Hz, 1H), 7.85 (t, J = 8.6 Hz, 2H), 7.70 (s, 1H), 7.22 (dd, J = 8.4, 1.6 Hz, 1H), 7.13-7.08 (m, 2H), 6.76-6.69 (m, 2H), 3.98 (s, 3H), 3.82-3.70 (m, 2H), 3.73 (s, 3H), 3.20-3.12 (m, 1H), 2.86-2.78 (m, 2H), 2.54-2.46 (m, 1H), 2.40-2.20 (m, 2H), 1.57-1.44 (m, 2H), 1.28-1.15 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.2, 153.5, 140.2, 135.2, 133.3, 131.8, 130.9, 130.9, 129.5, 129.2, 128.6, 128.5, 128.1, 126.1, 125.9, 120.2, 114.0, 60.1, 55.5, 52.5, 27.5, 25.1, 23.8, 22.9, 22.1, 21.2, 21.1. HRMS (ESI) calcd. for $C_{30}H_{31}N_2O_4^+$ 483.2278 [M+H$^+$], found 483.2285.

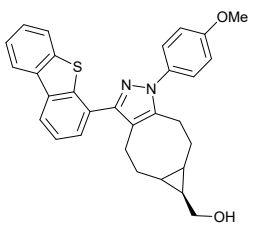


Pyrazole 1id-hv: Sydnone **1i** (25.0 mg, 0.093 mmol) and BCN (16.8 mg, 0.112 mmol) in 200 mL EtOAc were subjected to the general condition affording **1id-hv** as a white solid (29.0 mg, 83.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.57 (m, 2H), 7.42 (t, J = 7.5 Hz, 2H), 7.37-7.31 (m, 3H), 7.01-6.95 (m, 2H), 3.86 (s, 3H), 3.80-3.70 (m, 2H), 3.03-2.94 (m, 2H), 2.71-2.64 (m, 2H), 2.33-2.18 (m, 2H), 1.67-1.53 (m, 2H), 1.24-1.16 (m, 1H), 1.14-1.05 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 151.0, 142.5, 134.1, 133.1, 128.7, 128.4, 127.5, 127.4, 117.2, 114.3, 60.0, 55.7, 24.9, 24.8, 23.7, 22.9, 21.9, 20.3, 20.2. HRMS (ESI) calcd. for $C_{24}H_{27}N_2O_2^+$ 375.2067 [M+H$^+$], found 375.2064.

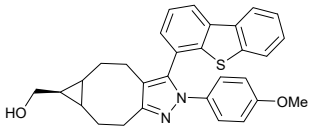


Pyrazole 1id-dark: Sydnone **1i** (35.0 mg, 0.131 mmol) and BCN (20.2 mg, 0.202 mmol) in 10 mL EtOAc were subjected to the general condition affording **1id-dark** as a white solid (38.0 mg, 77.8%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.30 (m, 3H), 7.14-7.11 (m, 2H), 7.09-7.06 (m, 2H), 6.77-6.73 (m, 2H), 3.75 (s, 5H), 3.78-3.69 (m, 2H), 3.17-3.10 (m, 1H), 2.82-2.72 (m, 2H), 2.48-2.41(m, 1H), 2.35-2.17 (m, 2H), 1.55-1.37 (m, 3H), 1.22-1.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.1, 153.2, 140.8, 133.6, 131.0, 130.3, 128.5, 128.0, 126.1, 119.6, 113.9, 60.2, 55.5,

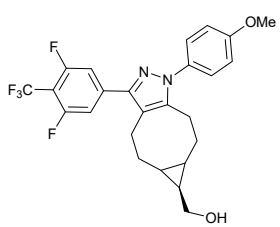
27.6, 25.1, 23.8, 22.9, 22.1, 21.2. HRMS (ESI) calcd. for $C_{24}H_{27}N_2O_2^+$ 375.2067 [M+H$^+$], found 375.2076.



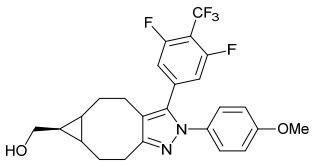
Pyrazole 1jd-hv: Sydnone **1j** (30.0 mg, 0.080 mmol) and BCN (14.5 mg, 0.096 mmol) in 200 mL EtOAc were subjected to the general condition affording **1jd-hv** as a yellow solid (34.0 mg, 88.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.13 (m, 2H), 7.85-7.82 (m, 1H), 7.58-7.50 (m, 2H), 7.47-7.40 (m, 4H), 7.05-6.98 (m, 2H), 3.87 (s, 3H), 3.79-3.70 (m, 2H), 3.08-2.92 (m, 2H), 2.80-2.63 (m, 2H), 2.30-2.23(m, 2H), 1.68-1.55 (m, 2H),1.26-1.09 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 149.5, 142.5, 140.7, 139.9, 136.3, 135.7, 133.1, 129.2, 127.3, 127.2, 126.6, 124.4, 124.2, 122.7, 121.6, 120.7, 118.1, 114.3, 60.0, 55.7, 25.0, 24.8, 23.7, 23.0, 21.9, 20.4, 20.3. HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_2S^+$ 481.1944 [M+H$^+$], found 481.1964.



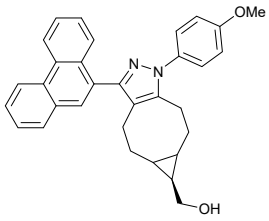
Pyrazole 1jd-dark: Sydnone **1j** (30.0 mg, 0.080 mmol) and BCN (14.5 mg, 0.096 mmol) in 10 mL EtOAc were subjected to the general condition affording **1jd-dark** as a yellow solid (33.9 mg, 88.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21-8.11 (m, 2H), 7.87-7.78 (m, 1H), 7.50-7.44 (m, 2H), 7.44-7.38 (m, 1H), 7.17 (dd, J = 20.3, 7.4 Hz, 1H), 7.11 (dd, J = 8.8, 5.2 Hz, 2H), 6.67-6.61 (m, 2H), 3.82-3.68 (m, 2H), 3.66 (s, 3H), 3.26-3.17 (m, 1H), 2.92-2.80 (m, 1H), 2.68-2.43 (m, 2H), 2.38-2.32 (m, 1H), 2.17-2.07 (m, 1H), 1.66-1.48 (m, 2H), 1.24-1.06 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.2, 153.2, 141.3, 139.7, 139.1, 135.9, 135.7, 133.3, 129.3, 127.1, 126.4, 125.2, 124.8, 124.7, 123.0, 121.9, 121.8, 120.9, 113.9, 60.2, 55.4, 27.7, 24.7, 23.6, 23.2, 22.1, 21.3, 21.0. HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_2S^+$ 481.1944 [M+H$^+$], found 481.1964.



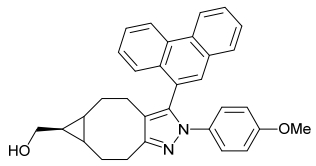
Pyrazole 1kd-hv: Sydnone **1k** (30.0 mg, 0.081 mmol) and BCN (14.5 mg, 0.097 mmol) in 200 mL EtOAc were subjected to the general photo-click condition affording **1kd-hv** as a white solid (29.0 mg, 75.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.27 (m, 4H), 7.03-6.96 (m, 2H), 3.87 (s, 3H), 3.80-3.68 (m, 2H), 3.03-2.93 (m, 2H), 2.74-2.63 (m, 2H), 2.33-2.19 (m, 2H), 1.67-1.59 (m, 2H), 1.26-1.19 (m, 1H), 1.09-1.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.73, 147.13, 143.41, 127.38, 117.65, 114.49, 112.21, 112.18, 111.97, 60.0, 55.8, 24.7, 24.3, 23.4, 23.0, 21.8, 19.9, 19.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.1 (t, J = 22.56 Hz), -111.2 (t, J = 22.56 Hz).HRMS (ESI) calcd. for $C_{25}H_{24}F_5N_2O_2^+$ 479.1752 [M+H$^+$], found 479.1758.



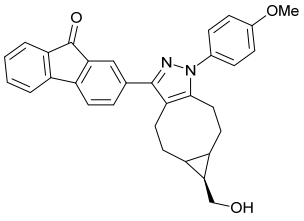
Pyrazole 1kd-dark: Sydnone **1k** (30.0 mg, 0.081 mmol) and BCN (14.5 mg, 0.097 mmol) in 10 mL EtOAc were subjected to the general condition affording **1kd-dark** as a white solid (35.0 mg, 90.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.05 (m, 2H), 6.88-6.81 (m, 2H), 6.76 (d, J = 10.1 Hz, 2H), 3.81 (s, 3H), 3.79-3.70 (m, 2H), 3.16-3.09 (m, 1H), 2.82-2.72 (m, 2H), 2.52-2.45 (m, 1H), 2.37-2.23 (m, 2H), 1.49-1.39 (m, 2H), 1.27-1.16 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.0, 158.9, 153.7, 137.5, 137.0, 126.3, 120.8, 114.5, 114.4, 114.2, 60.1, 55.6, 27.3, 24.9, 23.7, 22.8, 22.1, 21.1, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -56.3 (t, J = 22.56 Hz), -109.7 (t, J = 22.56 Hz). HRMS (ESI) calcd. for $C_{25}H_{24}F_5N_2O_2^+$ 479.1752 [M+H$^+$], found 479.1758.



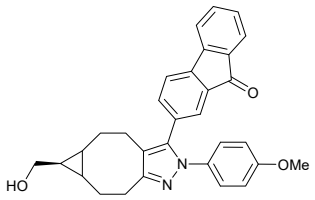
Pyrazole 1ld-hv: Sydnone **1l** (30.0 mg, 0.082 mmol) and BCN (14.7 mg, 0.098 mmol) in 200 mL EtOAc were subjected to the general condition affording **1ld-hv** as a yellow solid (30.0 mg, 77.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (dd, J = 12.5, 8.2 Hz, 2H), 8.00 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 7.6 Hz, 1H), 7.83 (s, 1H), 7.71-7.63 (m, 2H), 7.63-7.53 (m, 2H), 7.46-7.40 (m, 2H), 7.03-6.96 (m, 2H), 3.86 (s, 3H), 3.78-3.68 (m, 2H), 3.11-3.05 (m, 1H), 2.80-2.73 (m, 1H), 2.70-2.63 (m, 1H), 2.47-2.40 (m, 1H), 2.30-2.24 (m, 1H), 2.08-2.02 (m, 1H), 1.68-1.63 (m, 1H), 1.52-1.43 (m, 1H), 1.20-1.11(m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.2, 150.4, 141.6, 133.1, 131.9, 131.6, 130.5, 130.5, 130.4, 129.2, 128.9, 127.3, 127.3, 126.8, 126.7, 126.6, 126.5, 122.8, 122.6, 119.4, 114.2, 59.9, 55.7, 25.2, 24.5, 23.6, 23.2, 21.8, 20.5, 20.2. HRMS (ESI) calcd. for $C_{32}H_{31}N_2O_2^+$ 475.2380 [M+H$^+$], found 475.2389.



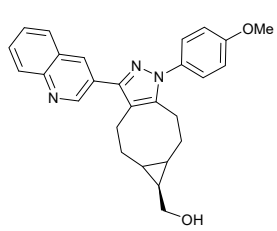
Pyrazole 1ld-dark: Sydnone **1l** (30.0 mg, 0.082 mmol) and BCN (14.7 mg, 0.0980 mmol) in 10 mL EtOAc were subjected to the general condition affording **1ld-dark** as a yellow solid (19.4 mg, 50.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (t, J = 7.2 Hz, 2H), 7.82 (t, J = 7.8 Hz, 1H), 7.71-7.57 (m, 5H), 7.55-7.46 (m, 1H), 7.15-7.08 (m, 2H), 6.58-6,52 (m, 2H), 3.82-3.69 (m, , 2H), 3.59 (s, 3H), 3.27-3.20 (m, 1H), 2.94-2.86 (m, 1H), 2.54-2.46 (m, 1H), 2.42-2.30 (m, 3H), 2.06-1.98 (m, 1H), 1.66-1.56 (m, 1H), 1.44-1.36 (m, 1H), 1.20-1.09 (m, 2H), 0.92-0.87 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.9, 153.0, 139.2, 133.7, 131.4, 131.2, 130.6, 130.5, 129.1, 127.9, 127.5, 127.1, 127.0, 126.5, 124.9, 123.0, 122.7, 121.5, 113.9, 60.2, 55.3, 27.7, 24.6, 23.7, 23.1, 22.0, 21.2, 21.0. HRMS (ESI) calcd. for $C_{32}H_{31}N_2O_2^+$ 475.2380 [M+H$^+$], found 475.2389.



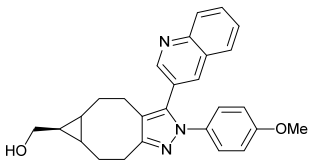
Pyrazole 1md-hv: Sydnone **1m** (50.0 mg, 0.135 mmol) and BCN (24.0 mg, 0.162 mmol) in 200 mL EtOAc were subjected to the general condition affording **1md-hv** as a yellow solid (27.0 mg, 42.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.4 Hz, 1H), 7.54-7.41 (m, 4H), 7.32-7.30 (m, 1H), 7.18 (dd, J = 7.6, 1.7 Hz, 1H), 7.14-7.08 (m, 2H), 6.82-6.72 (m, 2H), 3.74 (s, 3H), 3.79-3.70 (m, 2H), 3.16-3.09 (m, 1H), 2.82-2.71 (m, 2H), 2.50-2.44 (m, 1H), 2.35-2.19 (m, 2H), 1.50-1.38 (m, 2H), 1.24-1.12 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 158.4, 153.4, 144.0, 143.9, 139.7, 136.6, 135.0, 134.5, 134.4, 133.2, 132.0, 129.5, 126.3, 125.8, 124.6, 120.7, 120.5, 120.0, 114.1, 60.2, 55.5, 27.5, 25.03, 23.8, 23.0, 22.1, 21.2, 21.1. HRMS (ESI) calcd. for $C_{31}H_{29}N_2O_3^+$ 477.2173 [M+H$^+$], found 477.2173.



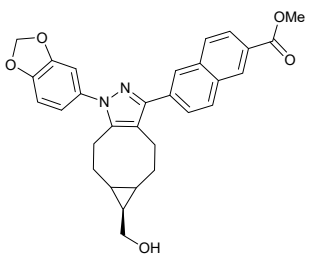
Pyrazole 1md-dark: Sydnone **1m** (30.0 mg, 0.082 mmol) and BCN (14.6 mg, 0.097 mmol) in 10 mL EtOAc were subjected to the general condition affording **1md-dark** as a yellow solid (31.0 mg, 79.4%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.3 Hz, 1H), 7.53-7.44 (m, 4H), 7.33-7.29 (m, 1H), 7.19 (dd, J = 7.6, 1.6 Hz, 1H), 7.15-7.09 (m, 2H), 6.81-6.74 (m, 2H), 3.75 (s, 3H), 3.80-3.71 (m, 2H), 3.17-3.11 (m, 1H), 2.83-2.72 (m, 2H), 2.51-2.44 (m, 1H), 2.36-2.21 (m, 2H), 1.54-1.39 (m, 2H), 1.25-1.12 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.4, 158.3, 153.4, 144.0, 143.9, 139.6, 136.6, 135.0, 134.4, 134.3, 133.2, 132.0, 129.5, 126.2, 125.8, 124.6, 120.6, 120.5, 120.0, 114.1, 60.1, 55.5, 27.5, 25.0, 23.7, 23.0, 22.1, 21.2, 21.1. HRMS (ESI) calcd. for $C_{31}H_{29}N_2O_3^+$ 477.2173 [M+H$^+$], found 477.2188.



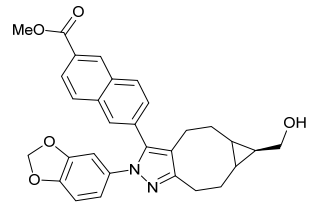
Pyrazole 1nd-hv: Sydnone **1n** (25.0 mg, 0.078 mmol) and BCN (14.1 mg, 0.094 mmol) in 200 mL EtOAc were subjected to the general photo-click condition affording **1nd-hv** as a yellow solid (27.0 mg, 81.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.38 (s, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.74-7.68 (m, 1H), 7.60-7.51 (m, 1H), 7.39-7.31 (m, 2H), 7.04-6.95 (m, 2H), 3.86 (s, 3H), 3.80-3.70 (m, 2H), 3.08-2.94 (m, 2H), 2.78-2.66 (m, 2H), 2.36-2.18 (m, 2H), 1.70-1.57 (m, 2H), 1.23-1.17 (m, 1H), 1.12-1.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.5, 150.8, 147.8, 147.2, 143.0, 135.0, 132.8, 129.5, 129.2, 128.2, 128.1, 127.5, 127.0, 117.8, 114.4, 60.0, 55.7, 24.9, 24.7, 23.6, 23.1, 21.9, 20.2, 20.1. HRMS (ESI) calcd. for $C_{27}H_{28}N_3O_2^+$ 426.2176 [M+H$^+$], found 426,2179.



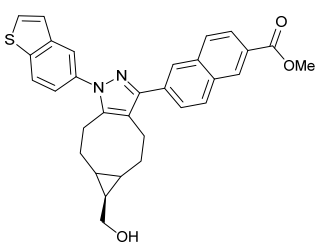
Pyrazole 1nd-dark: Sydnone **1n** (22.0 mg, 0.069 mmol) and BCN (12.4 mg, 0.083 mmol) in 10 mL EtOAc were subjected to the general dark condition affording **1nd-dark** as a yellow solid (29.0 mg, 98.9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 2.2 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 2.1 Hz, 1H), 7.81-7.72 (m, 2H), 7.58 (t, J = 7.3 Hz, 1H), 7.14-7.08 (m, 2H), 6.78-6.72 (m, 2H), 3.82-3.72 (m, 2H), 3.73 (s, 3H), 3.22-3.14 (m, 1H), 2.88-2.76 (m, 2H), 2.58-2.48 (m, 1H), 2.39-2.21 (m, 2H), 1.54-1.40 (m, 2H), 1.26-1.18 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 153.6, 151.3, 147.1, 137.5, 136.9, 133.0, 130.3, 129.4, 128.1, 127.5, 127.3, 126.4, 124.4, 120.8, 114.3, 60.1, 55.5, 27.5, 25.1, 23.8, 23.0, 22.2, 21.2, 21.1; HRMS (ESI) calcd. for $C_{27}H_{28}N_3O_2^+$ 426.2176 [M+H$^+$], found 426.2192.



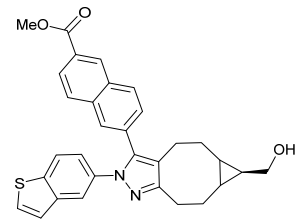
Pyrazole 2dd-hv: Sydnone **2d** (30.0 mg, 0.077 mmol) and BCN (13.8 mg, 0.092 mmol) in 200 mL EtOAc were subjected to the general condition affording **2dd-hv** as a yellow solid (27.0 mg, 70.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.09 (s, 1H), 8.06 (dd, J = 8.6, 1.7 Hz, 1H), 7.99 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.6 Hz, 1H), 7.84 (dd, J = 8.5, 1.6 Hz, 1H), 6.95 (s, 1H), 6.91-6.87 (m, 2H), 6.05 (s, 2H), 3.98 (s, 3H), 3.82-3.71 (m, 2H), 3.10-2.98 (m, 2H), 2.80-2.68 (m, 2H), 2.40-2.21 (m, 2H), 1.67-1.62 (m, 2H), 1.25-1.19 (m, 1H), 1.18-1.03 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 150.4, 148.2, 147.7, 142.9, 135.7, 134.0, 133.9, 131.9, 131.0, 129.5, 128.5, 127.7, 127.4, 127.1, 125.6, 119.9, 117.7, 108.2, 107.8, 102.0, 60.1, 52.4, 24.9, 24.7, 23.6, 23.1, 22.0, 20.2, 20.1. HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_5^+$ 497.2071 [M+H$^+$], found 497.2041.



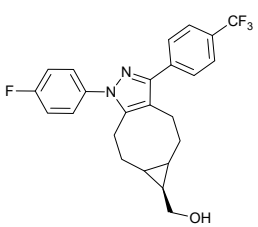
Pyrazole 2dd-dark: Sydnone **2d** (30.0 mg, 0.077 mmol) and BCN (13.8 mg, 0.092 mmol) in 10 mL EtOAc were subjected to the general condition affording **2dd-dark** as a yellow solid (28.0 mg, 73.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.08 (d, J = 8.5 Hz, 1H), 7.86 (dd, J = 11.8, 8.6 Hz, 2H), 7.70 (s, 1H), 7.23 (d, J = 8.4 Hz, 1H), 6.76 (s, 1H), 6.59 (s, 2H), 5.90 (s, 2H), 3.98 (s, 3H), 3.80-3.70 (m, 2H), 3.18-3.12 (m, 1H), 2.85-2.77 (m, 2H), 2.52-2.45 (m, 1H), 2.38-2.18 (m, 2H), 1.55-1.41 (m, 2H), 1.25-1.16(m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 153.5, 147.8, 146.5, 140.3, 135.2, 134.3, 131.9, 130.9, 130.7, 129.6, 129.1, 128.5, 128.5, 128.2, 126.0, 120.4, 118.6, 107.9, 106.6, 101.6, 60.1, 52.5, 27.5, 25.0, 23.7, 22.9, 22.1, 21.2, 21.1. HRMS (ESI) calcd. for $C_{30}H_{29}N_2O_5^+$ 497.2071 [M+H$^+$], found 497.2065.



Pyrazole 3cd-hv: Sydnone **3c** (30.0 mg, 0.075 mmol) and BCN (13.4 mg, 0.090 mmol) in 200 mL EtOAc were subjected to the general condition affording **3cd-hv** as a yellow solid (28.0 mg, 76.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.12 (s, 1H), 8.07 (dd, J = 8.6, 1.7 Hz, 1H), 7.99 (dd, J = 15.1, 8.5 Hz, 2H), 7.92 (d, J = 9.0 Hz, 2H), 7.87 (dd, J = 8.5, 1.6 Hz, 1H), 7.56 (d, J = 5.4 Hz, 1H), 7.44 (dd, J = 8.5, 2.0 Hz, 1H), 7.39 (d, J = 5.4 Hz, 1H), 3.98 (s, 3H), 3.81-3.71 (m, 2H), 3.14-3.03 (m, 2H), 2.83-2.70 (m, 2H), 2.41-2.19 (m, 2H), 1.69-1.61 (m, 2H), 1.27-1.05 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 150.7, 142.9, 140.1, 139.4, 136.7, 135.7, 134.1, 131.9, 131.0, 129.5, 128.6, 128.5, 127.7, 127.4, 127.1, 125.6, 124.1, 123.1, 122.6, 121.0, 118.0, 60.0, 52.4, 25.0, 24.7, 23.7, 23.1, 21.9, 20.2, 20.1. HRMS (ESI) calcd. for $C_{31}H_{29}N_2O_3S^+$ 509.1893 [M+H$^+$], found 509.1889.

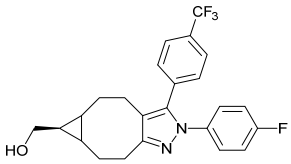


Pyrazole 3cd-dark: Sydnone **3c** (30.0 mg, 0.075 mmol) and BCN (13.4 mg, 0.090 mmol) in 10 mL EtOAc were subjected to the general condition affording **3cd-dark** as a yellow solid (34.0 mg, 89.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.07 (dd, J = 8.6, 1.6 Hz, 1H), 7.83 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 1.8 Hz, 2H), 7.63 (d, J = 8.6 Hz, 1H), 7.41 (d, J = 5.4 Hz, 1H), 7.23 (dd, J = 8.4, 1.6 Hz, 1H), 7.17 (d, J = 5.4 Hz, 1H), 7.10 (dd, J = 8.6, 2.0 Hz, 1H), 3.98 (s, 3H), 3.81-3.72 (m, 2H), 3.23-3.16 (m, 1H), 2.89-2.81 (m, 2H), 2.56-2.50 (m, 1H), 2.41-2.20 (m, 2H), 1.58-1.43 (m, 2H), 1.25-1.16 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 153.9, 140.4, 140.0, 138.0, 137.1, 135.3, 131.9, 131.0, 130.9, 129.6, 129.2, 128.6, 128.5, 128.2, 128.0, 126.0, 124.1, 122.6, 121.5, 120.7, 119.5, 60.2, 52.5, 27.5, 25.0, 23.8, 22.9, 22.2, 21.2, 21.1. HRMS (ESI) calcd. for $C_{31}H_{29}N_2O_3S^+$ 509.1893 [M$^+$H$^+$], found 509.1894.

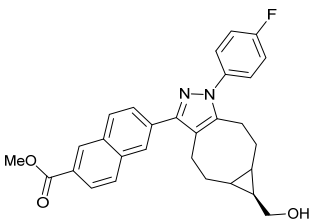


Pyrazole 5bd-hv: Sydnone **5b** (30.0 mg, 0.093 mmol) and BCN (16.8 mg, 0.112 mmol) in 200 mL EtOAc were subjected to the general condition affording **5bd-hv** as a white solid (31.0 mg, 71.2%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (q, J = 8.3 Hz, 4H), 7.44-7.38 (m, 2H), 7.20-7.13 (m, 2H), 3.80-3.67 (m, 2H), 3.01-2.94 (m, 2H), 2.72-2.64 (m, 2H), 2.35-2.17 (m, 2H), 1.66-1.58 (m, 2H), 1.25-1.16 (m, 1H), 1.14-1.02 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3 (d, J = 249.5 Hz), 150.1, 142.7, 137.6, 136.0, 129.6 (d, J = 33.3 Hz), 128.8, 127.9 (d, J = 8.08 Hz), 125.5 (q, J = 4.04 Hz), 125.4 (q, J = 272.7 Hz), 118.0, 116.2 (d, J

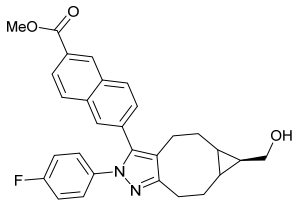
= 23.2 Hz), 60.0, 24.9, 24.6, 23.6, 22.9, 21.9, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.43, -113.09. HRMS (ESI) calcd. for $C_{24}H_{23}F_4N_2O^+$ 431.1741 [M+H$^+$], found 431.1743.



Pyrazole 5bd-dark: Sydnone **5b** (30.0 mg, 0.093mmol) and BCN (16.8 mg, 0.112 mmol) in 10 mL EtOAc were subjected to the general condition affording **5bd-dark** as a white solid (42.0 mg, 96.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 8.8, 4.8 Hz, 2H), 6.95 (t, J = 8.4 Hz, 2H), 3.78-3.68 (m, 2H), 3.16-3.10 (m, 1H), 2.83-2.69 (m, 2H), 2.48-2.42 (m, 1H), 2.39-2.18 (m, 2H), 1.53-1.36 (m, 2H), 1.22-1.09 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.3 (d, J = 247.5 Hz), 154.0, 139.4, 136.0 (d, J = 4.04 Hz), 134.4, 130.5, 130.3 (q, J = 32.3 Hz), 126.5 (d, J = 8.08 Hz), 125.6 (d, J = 4.04 Hz), 124.0 (q, J = 273.7 Hz), 120.8, 115.9 (d, J = 23.2 Hz), 60.1, 27.4, 24.9, 23.7, 22.8, 22.1, 21.1, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67, -114.66. HRMS (ESI) calcd. for $C_{24}H_{23}F_4N_2O^+$ 431.1741 [M+H$^+$], found 431.1769.



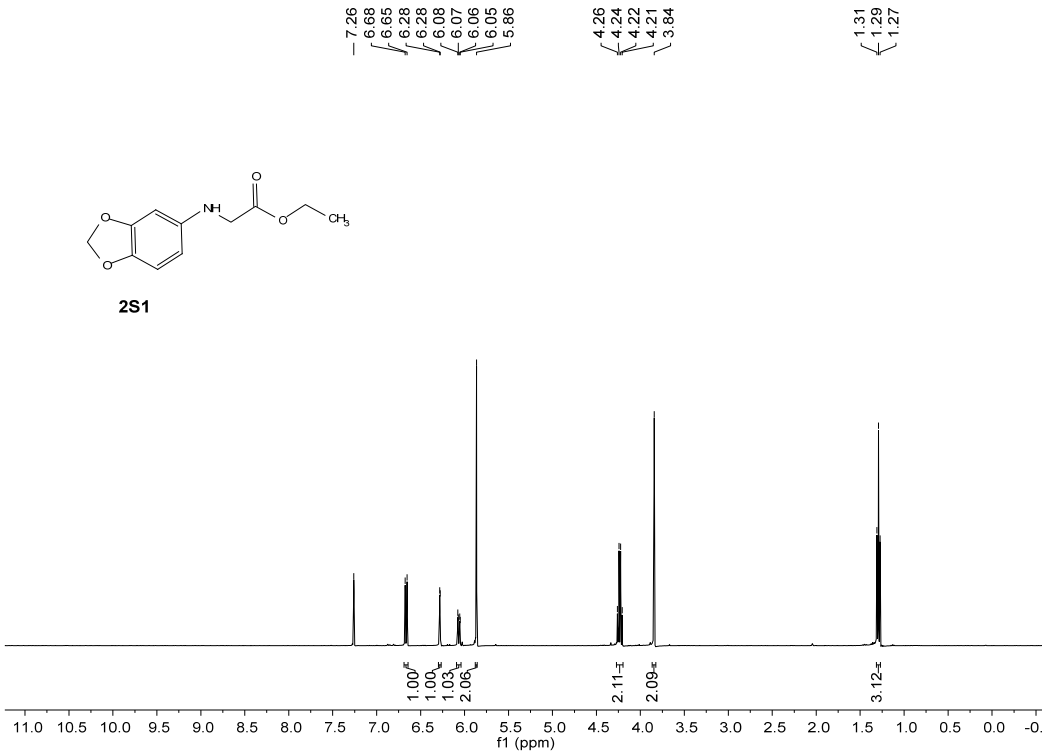
Pyrazole 5cd-hv: Sydnone **5c** (30.0 mg, 0.082mmol) and BCN (14.9 mg, 0.099 mmol) in 200 mL EtOAc were subjected to the general condition affording **5cd-hv** as a yellow solid (27.0 mg, 75.3%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 1H), 8.11-8.03 (m, 2H), 8.00 (d, J = 8.5 Hz, 1H), 7.91 (d, J = 8.7 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.47-7.39 (m, 2H), 7.18 (t, J = 8.6 Hz, 2H), 3.98 (s, 3H), 3.81-3.72 (m, 2H), 3.12-2.95 (m, 2H), 2.80-2.68 (m, 2H), 2.42-2.17 (m, 2H), 1.72-1.64 (m, 2H), 1.24-1.04 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 162.2 (d, J = 248.5 Hz), 150.9, 142.8, 136.0, 135.7, 133.9, 131.0, 129.5, 128.5, 127.9 (d, J = 9.09 Hz), 127.6, 127.5, 127.1, 125.7, 118.1, 116.2 (d, J = 23.2 Hz), 60.1, 52.4, 25.0, 24.7, 23.7, 23.1, 22.0, 20.2, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.05. HRMS (ESI) calcd. for $C_{29}H_{27}FN_2O_3^+$ 471.2078 [M+H$^+$], found 471.2081.

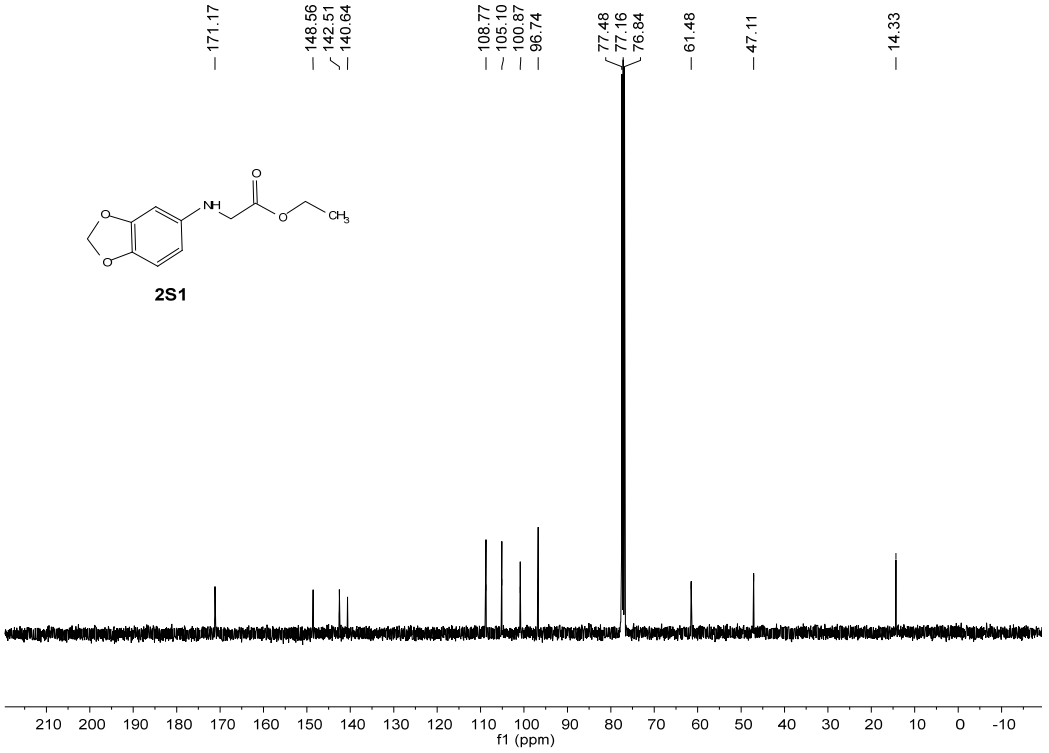


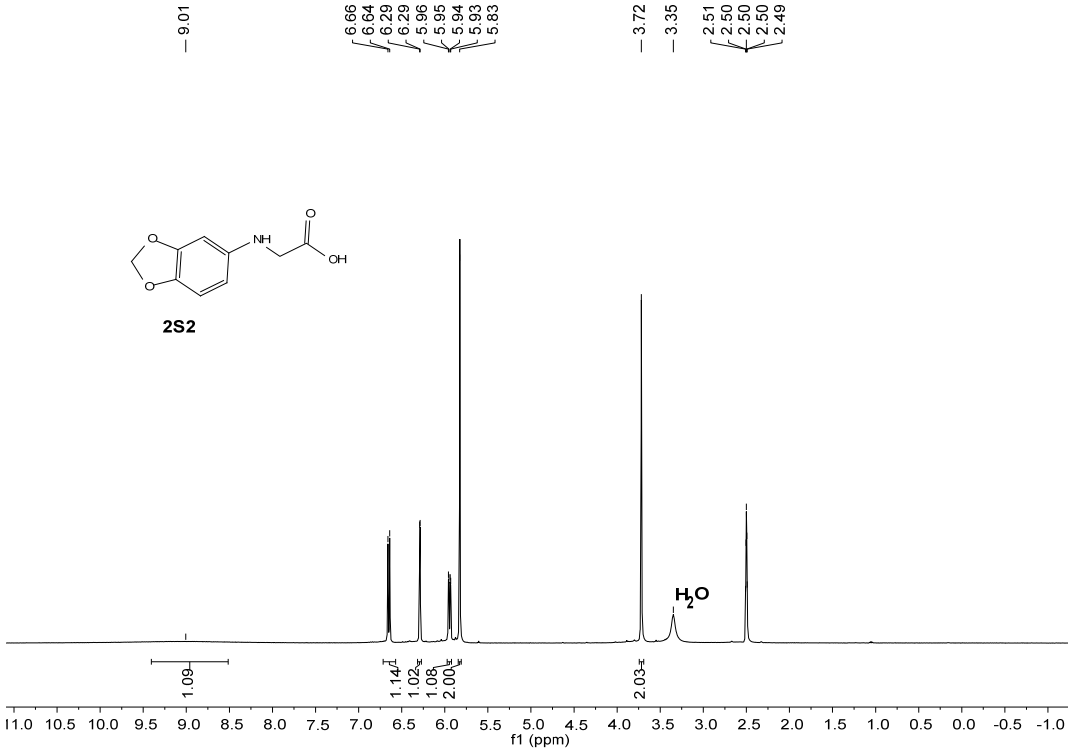
Pyrazole 5cd-dark: Sydnone **5c** (30.0 mg, 0.082mmol) and BCN (14.9 mg, 0.099 mmol) in 10 mL EtOAc were subjected to the general condition affording **5cd-dark** as a yellow solid (32.5 mg, 90.7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H), 8.09 (dd, J = 8.6, 1.7 Hz, 1H), 7.86 (dd, J = 17.0, 8.6 Hz, 2H), 7.70 (s, 1H), 7.21 (dd, J = 8.4, 1.7 Hz, 1H), 7.18-7.13 (m, 2H), 6.92-6.86 (m, 2H), 3.98 (s, 3H), 3.80-3.71 (m, 2H), 3.19-3.12 (m, 1H), 2.86-2.78 (m, 2H), 2.53-2.46 (m, 1H), 2.40-2.18 (m, 2H), 1.57-1.42 (m, 2H),1.23-1.14 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 161.1 (d, J = 247.5 Hz), 154.0, 140.3, 136.3 (d, J = 4.04 Hz), 135.2, 131.9, 130.9, 130.7, 129.7, 129.2, 128.5, 128.3, 126.3, 126.2, 126.1,

120.8, 115.7 (d, J = 23.2 Hz), 60.1, 52.5, 27.5, 25.0, 23.7, 22.9, 22.1, 21.2, 21.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.72, -114.70. HRMS (ESI) calcd. for $C_{29}H_{27}FN_2O_3^+$ 471.2078 [M+H$^+$], found 471.2075.

^{1}H, ^{19}F and ^{13}C NMR Spectra



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5.94
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2.50
2.50
2.50
2.49
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OH
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O
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H2O
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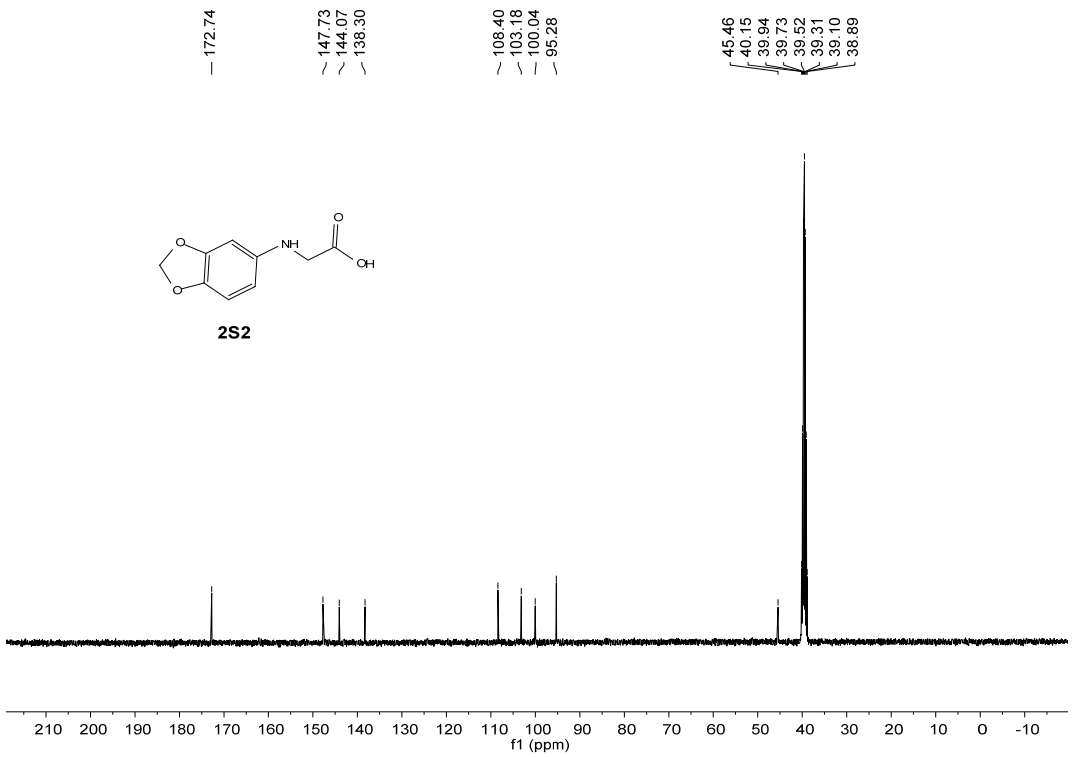
1.14
1.02
1.08
2.00
2.03
f1 (ppm)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39.10
38.89
NH
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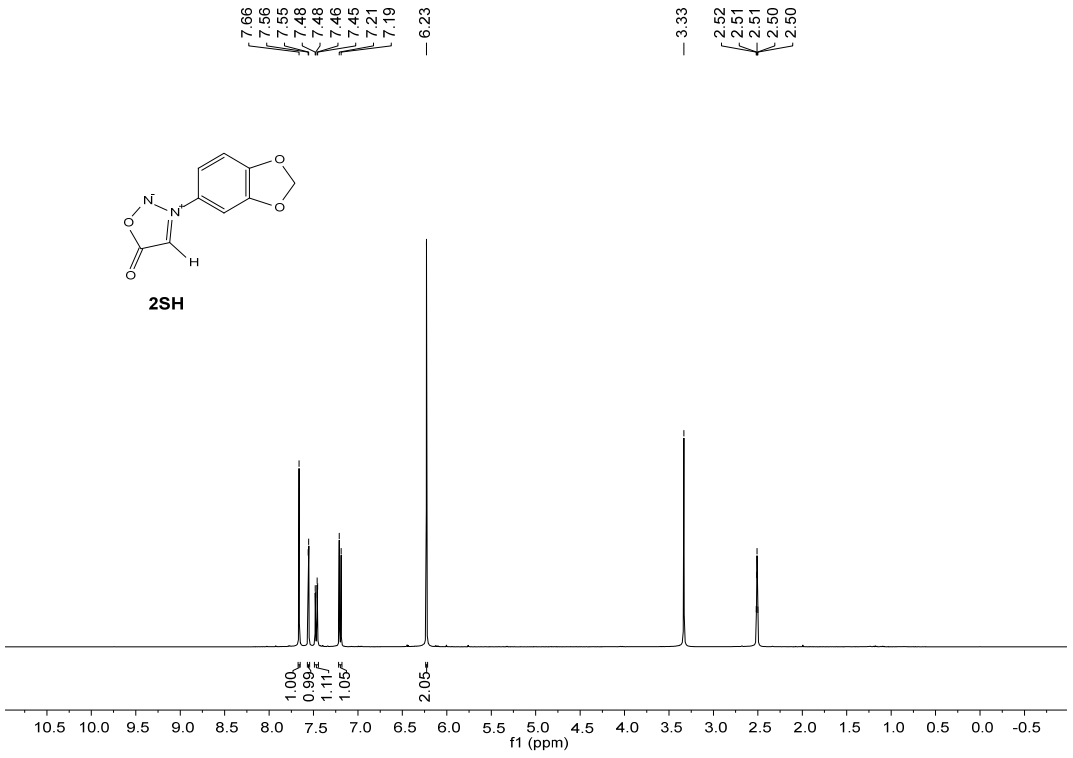
OH
O
O
2S2
f1 (ppm)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7.21
7.19
6.23
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2.50
2.50
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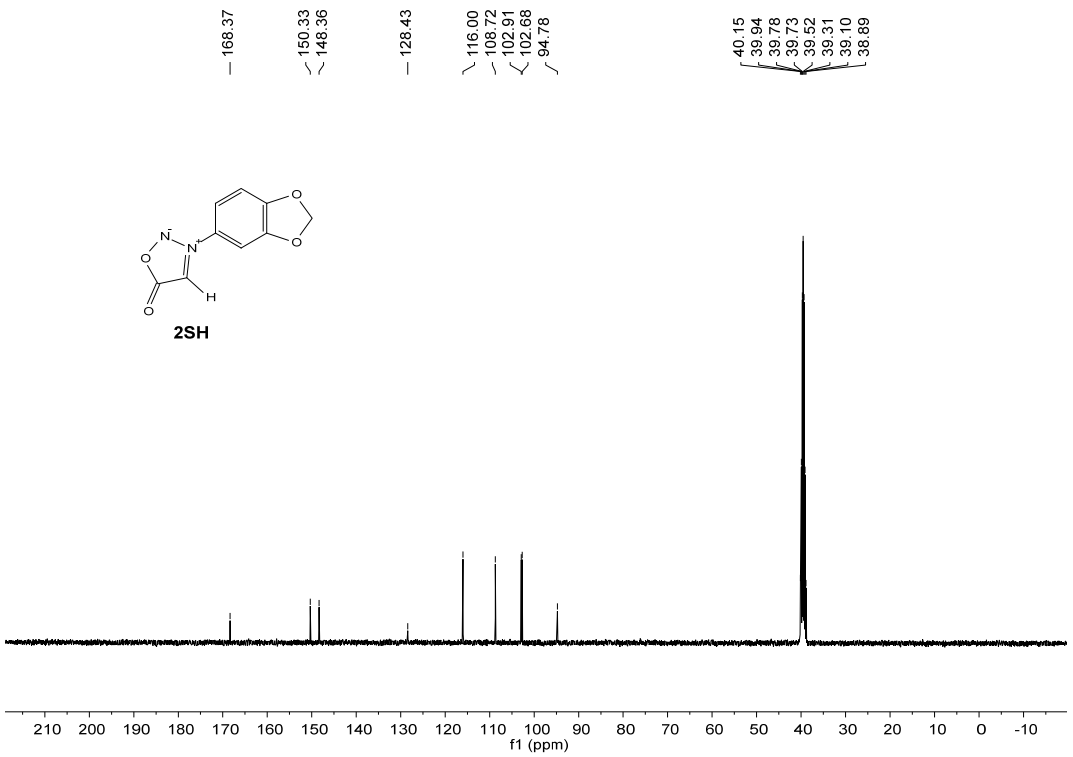
1.11
1.05
2.05
f1 (ppm)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102.68
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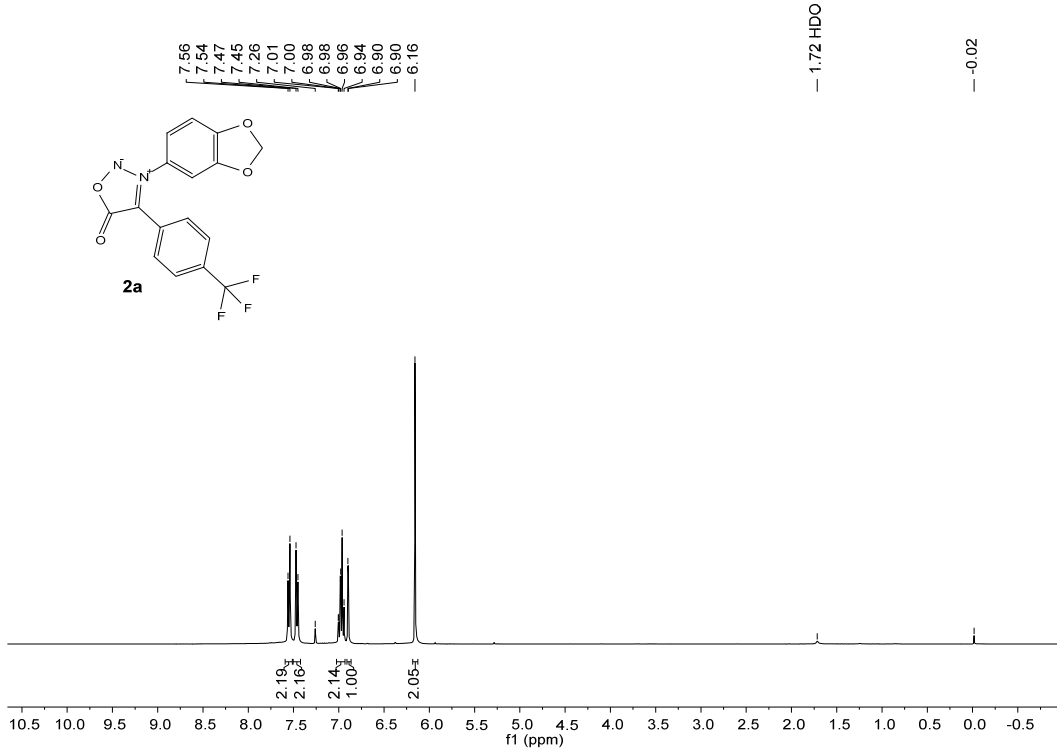
39.31
39.10
38.89
2SH
f1 (ppm)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7.00
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6.98
6.96
6.94
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6.90
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2a
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2.14
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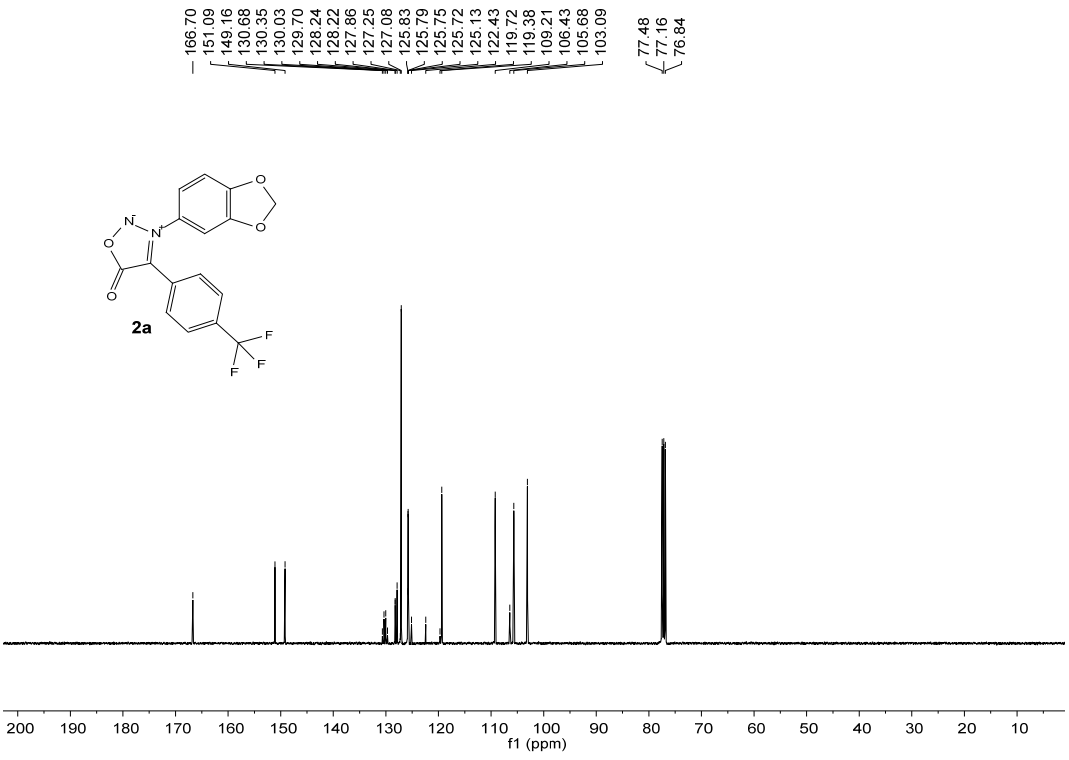
2.05
f1 (ppm)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125.13
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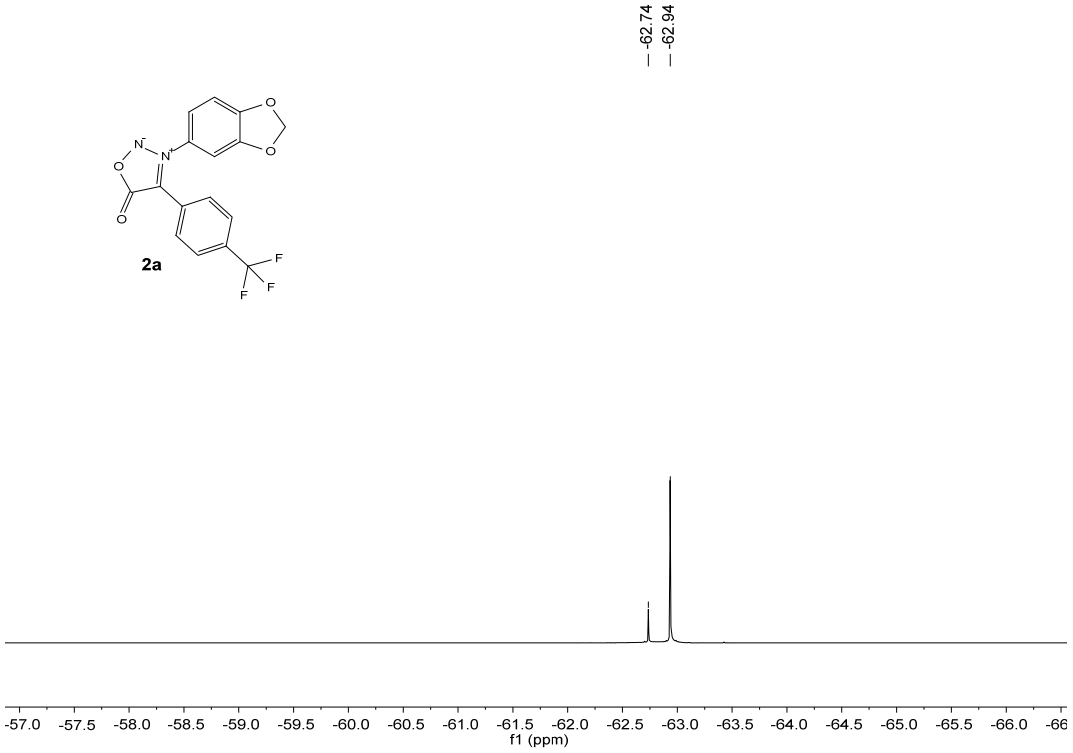
f1 (ppm)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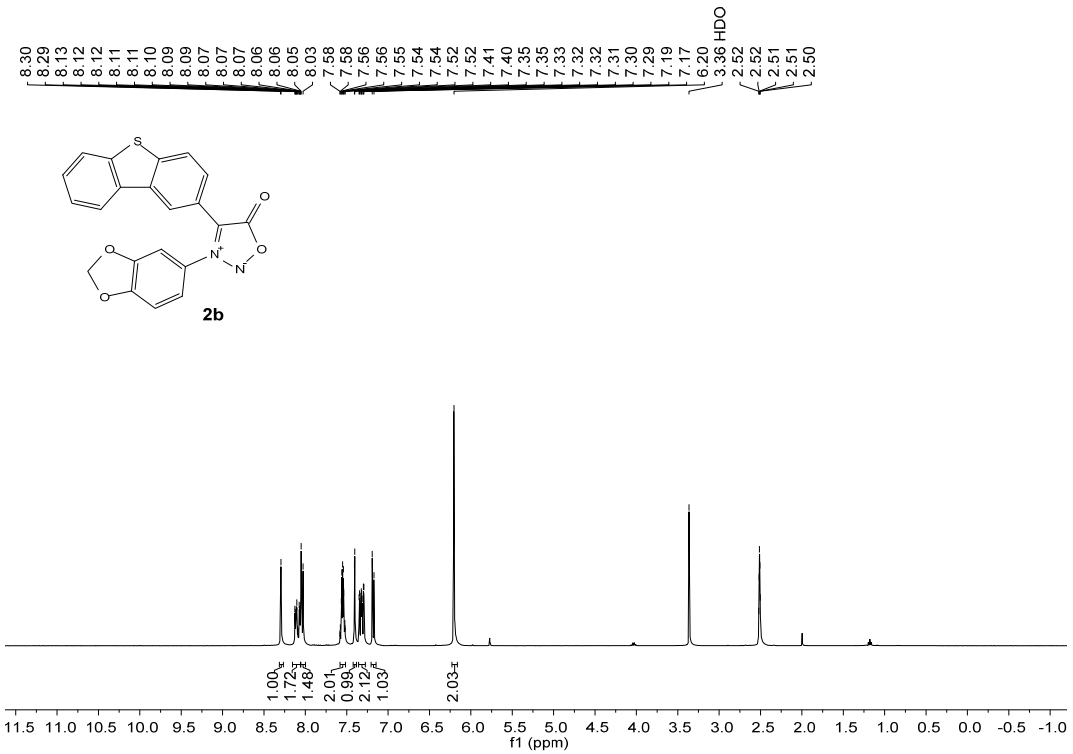
f1 (ppm)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7.32
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7.19
7.17
6.20
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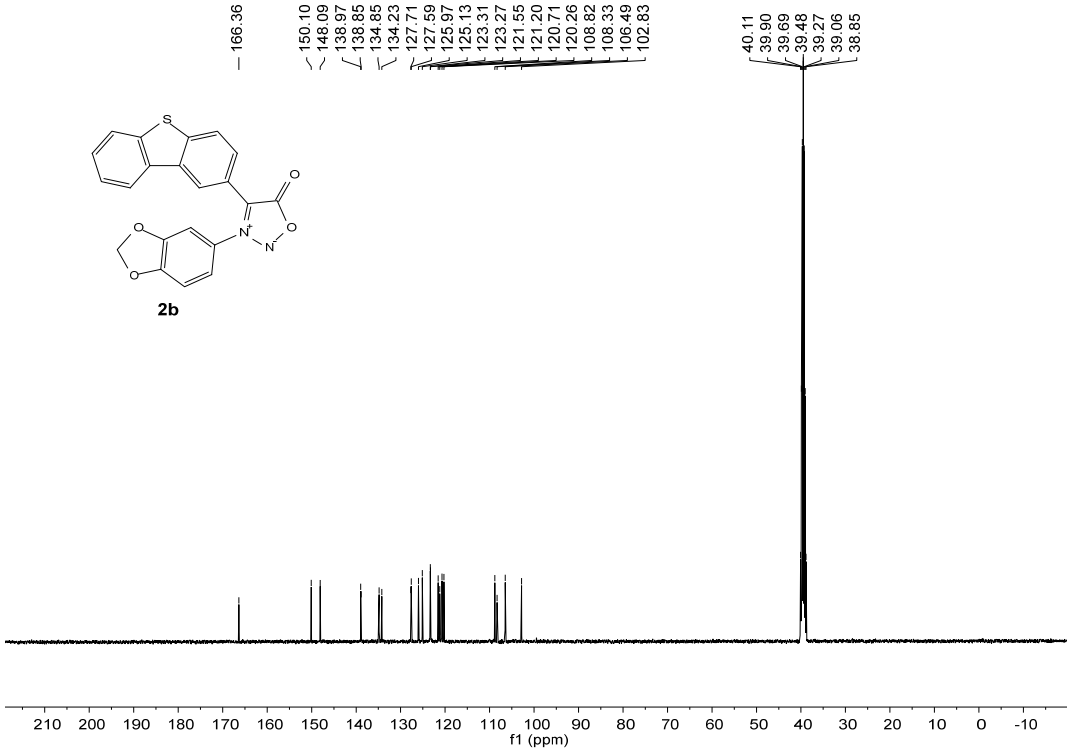
f1 (ppm)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120.71
120.26
108.82
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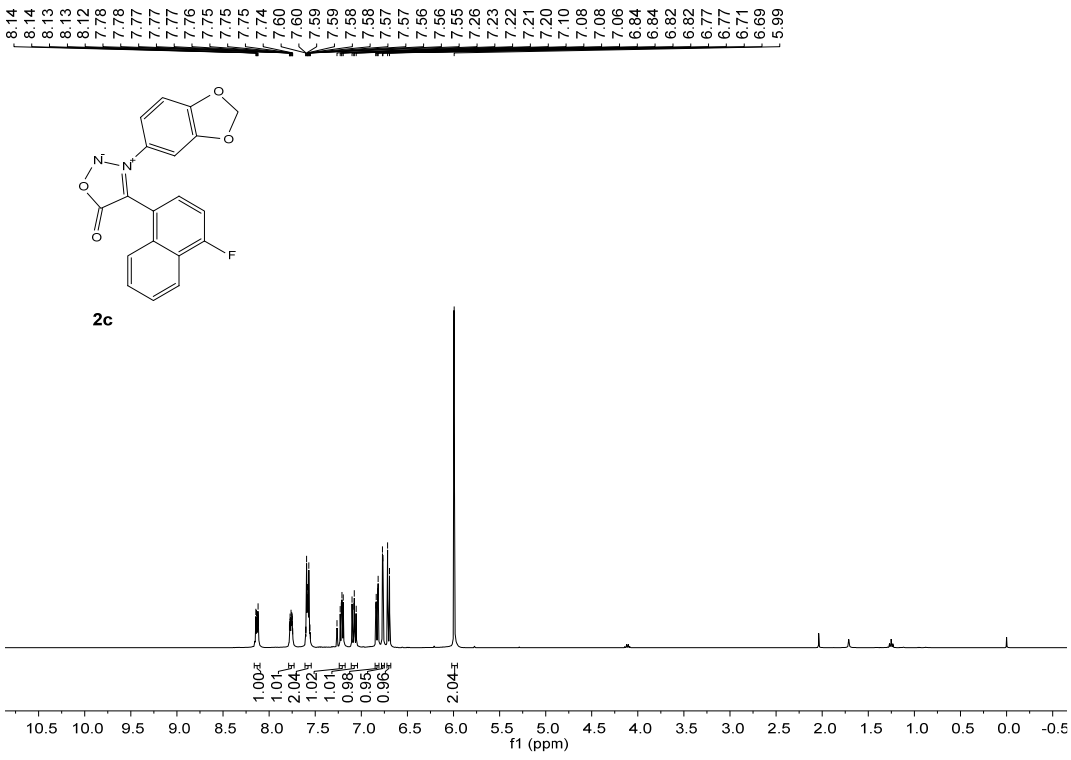
39.69
39.48
39.27
39.06
38.85
2b
f1 (ppm)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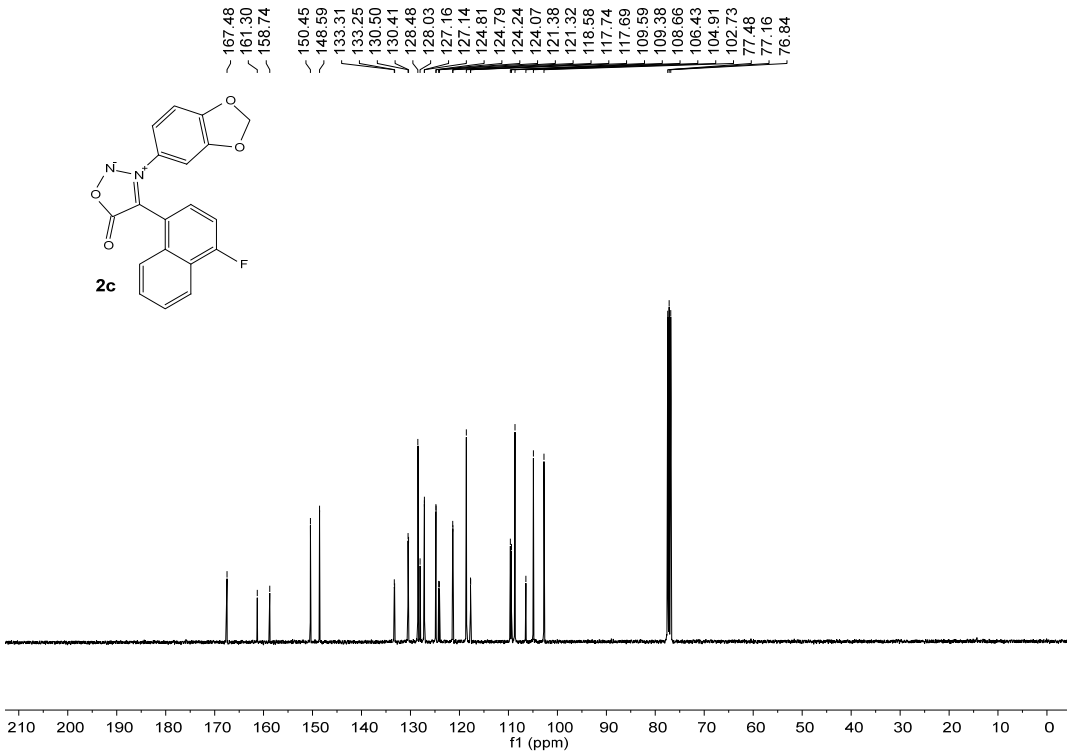
f1 (ppm)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121.32
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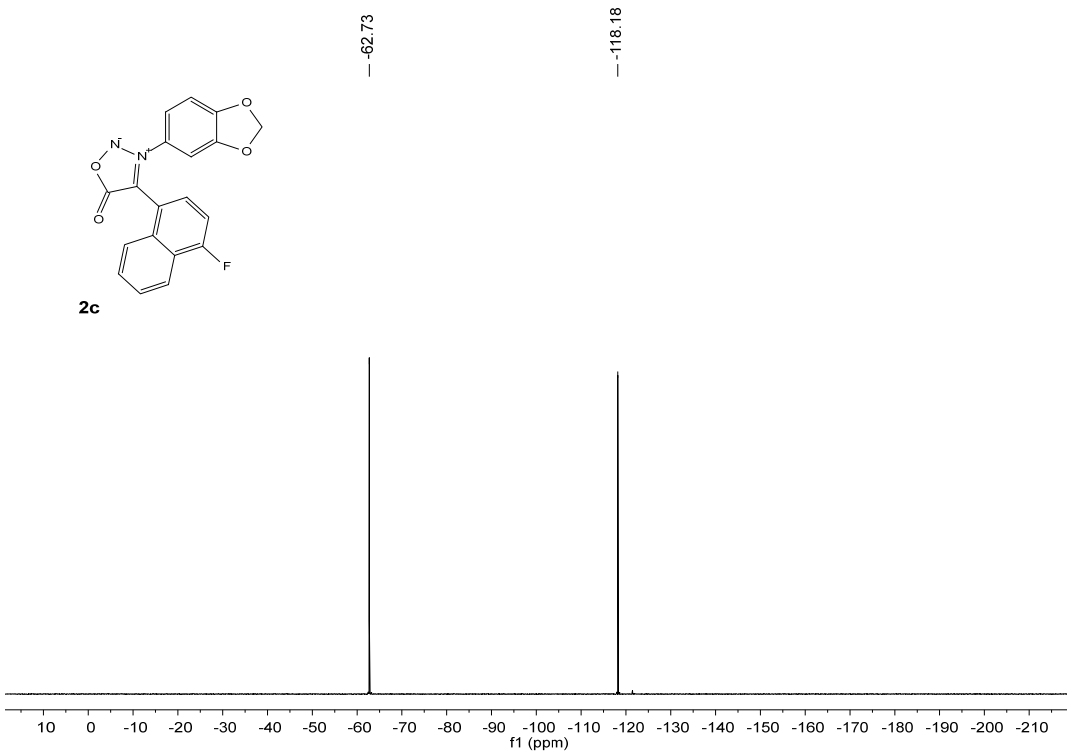
f1 (ppm)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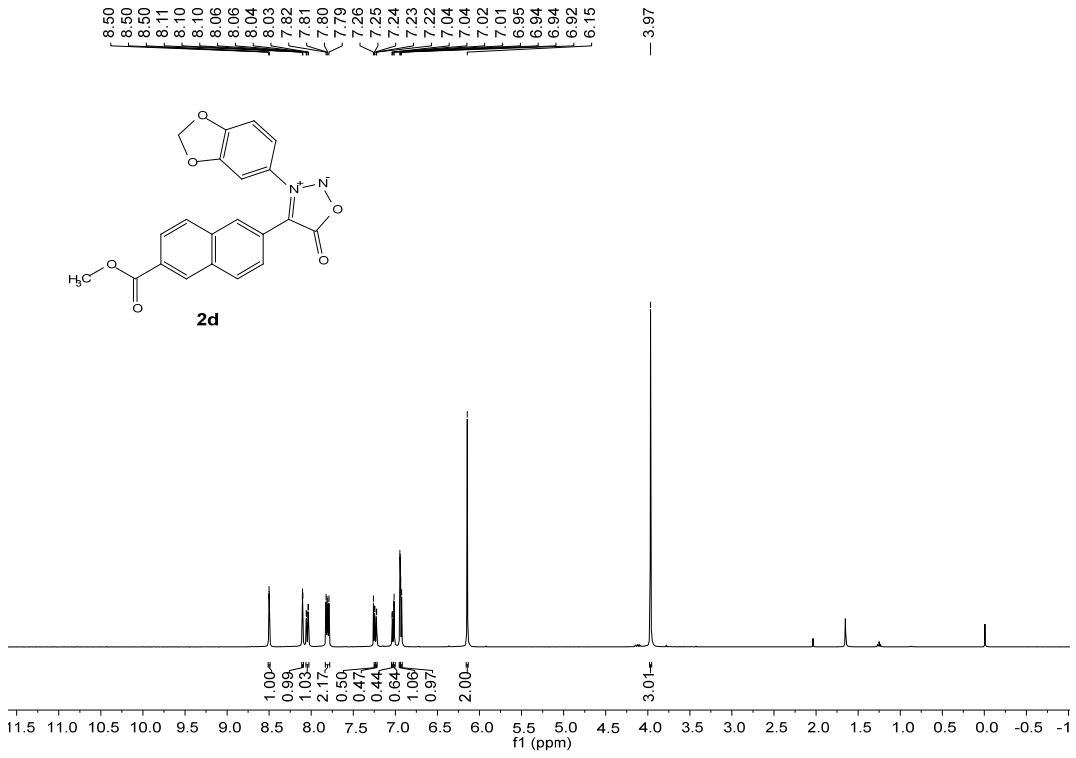
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7.04
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7.02
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6.94
6.94
6.92
6.15
3.97
2d
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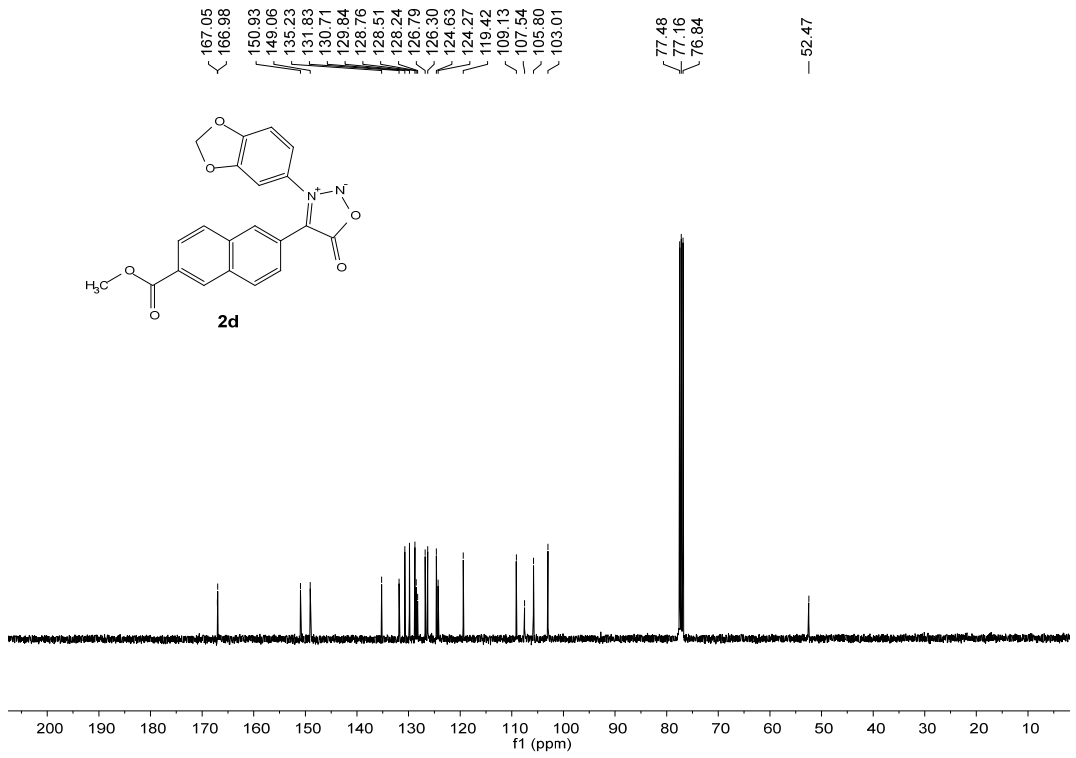
f1 (ppm)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77.16
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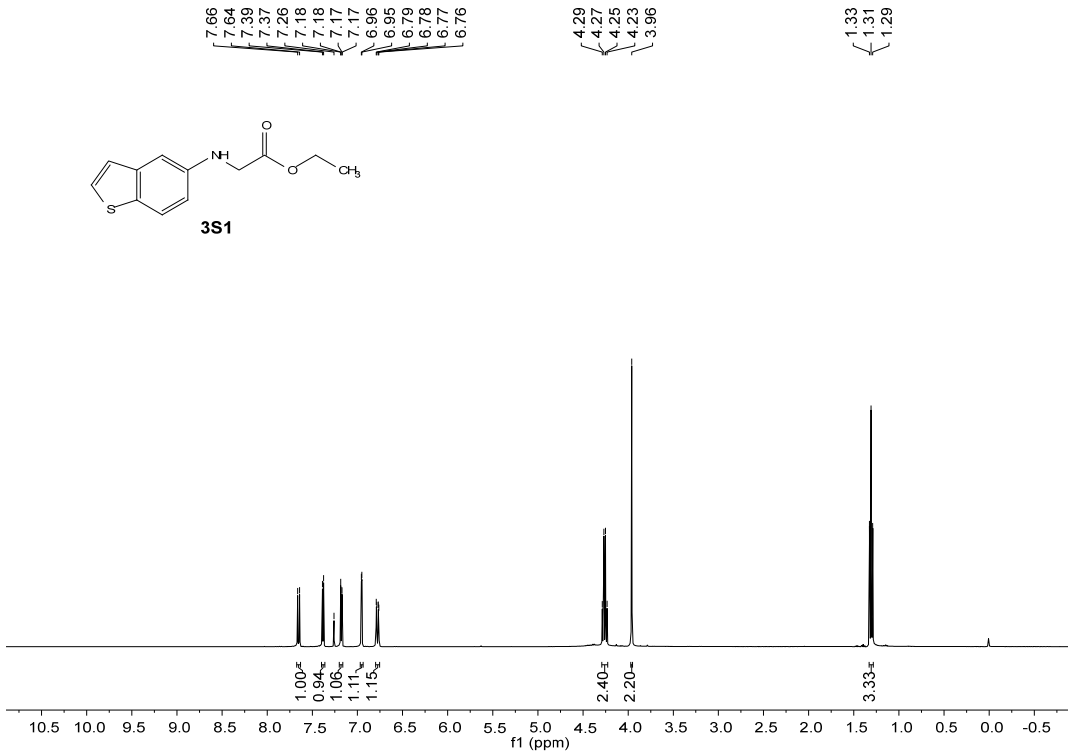
f1 (ppm)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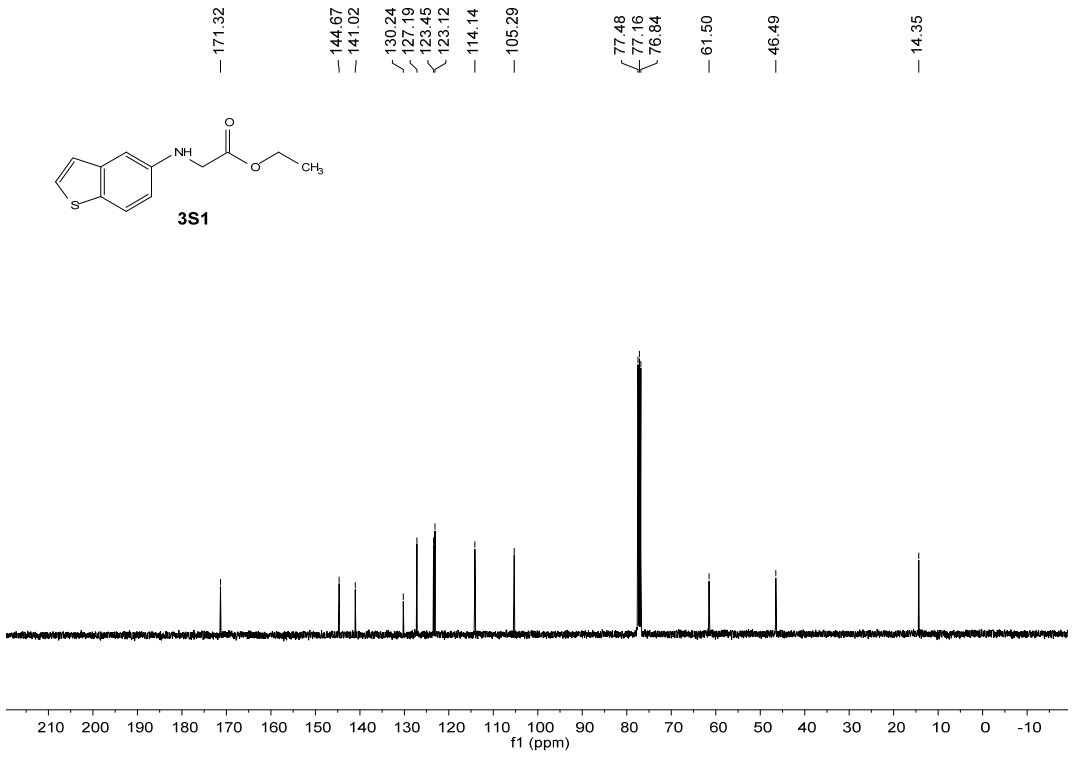
4.27
4.25
4.23
3.96
1.33
1.31
1.29
NH
O
O
CH3
S
3S1
1.00
0.94
1.06
1.11
1.15
2.40
2.20
3.33
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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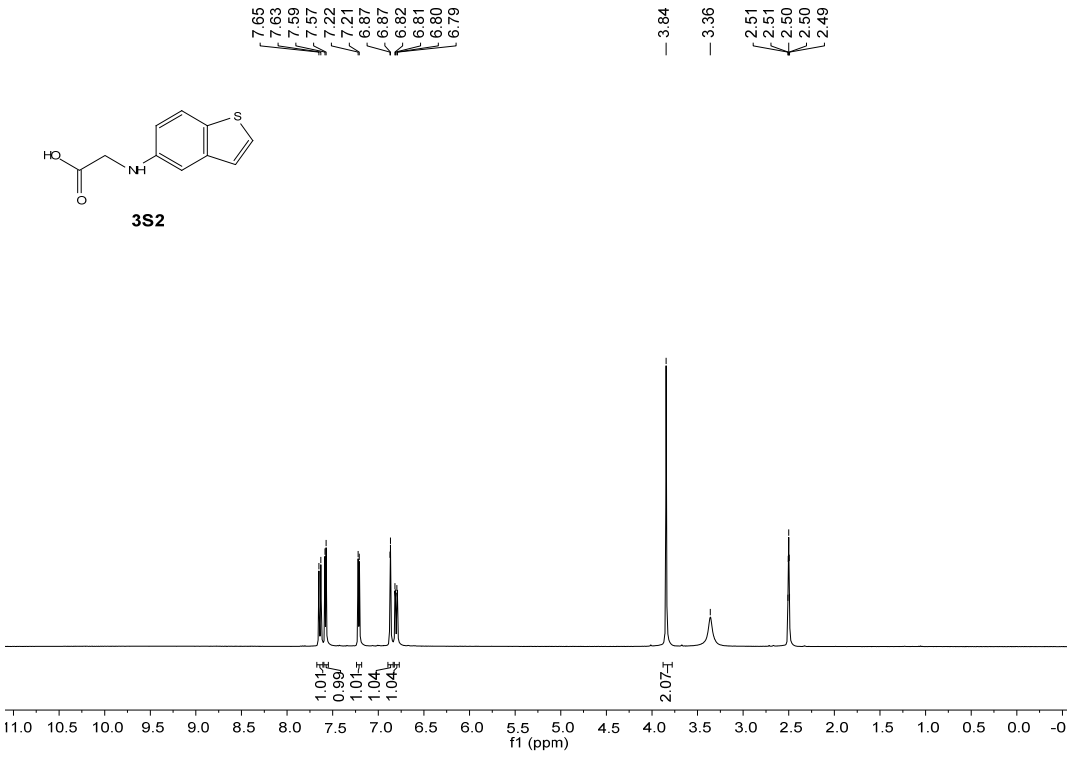
141.02
130.24
127.19
123.45
123.12
114.14
105.29
77.48
77.16
76.84
61.50
46.49
14.35
NH
O
O
CH3
S
3S1
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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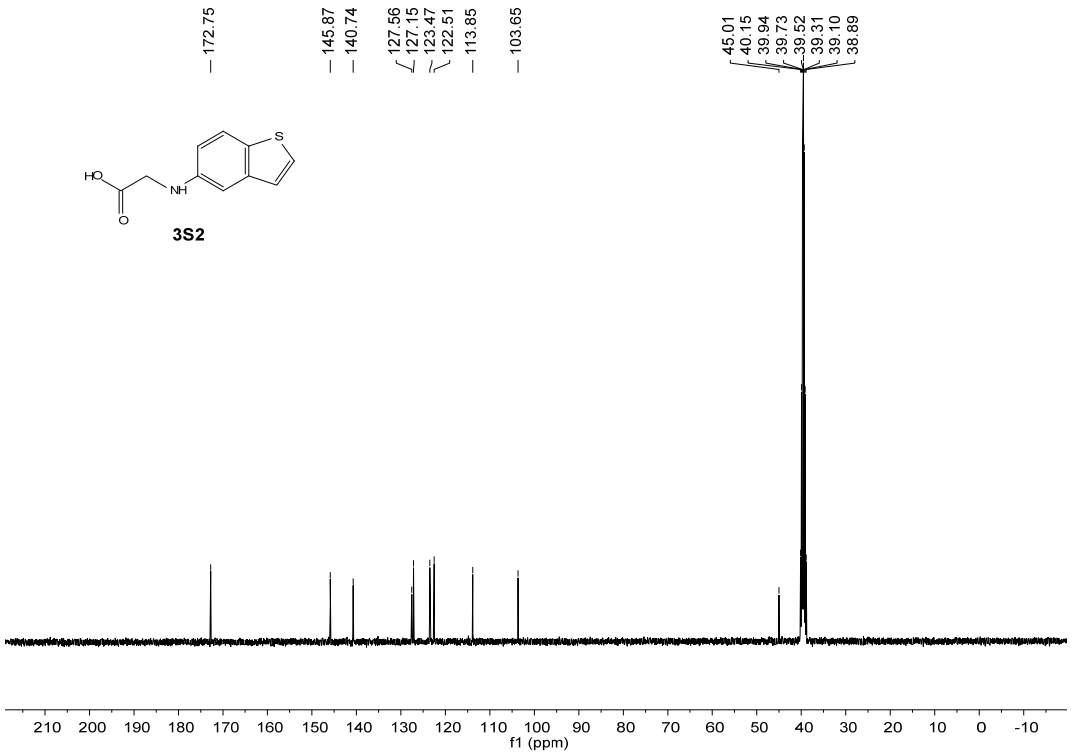
7.63
7.59
7.57
7.22
7.21
6.87
6.87
6.82
6.81
6.80
6.79
3.84
3.36
2.51
2.51
2.50
2.50
2.49
HO
O
NH
S
3S2
1.01
0.99
1.01
1.04
1.04
2.07
f1 (ppm)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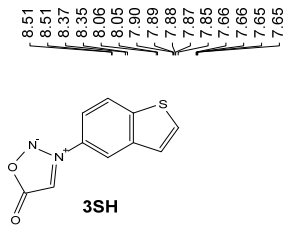
145.87
140.74
127.56
127.15
123.47
122.51
113.85
103.65
45.01
40.15
39.94
39.73
39.52
39.31
39.10
38.89
HO
O
NH
S
3S2
f1 (ppm)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8.51
8.37
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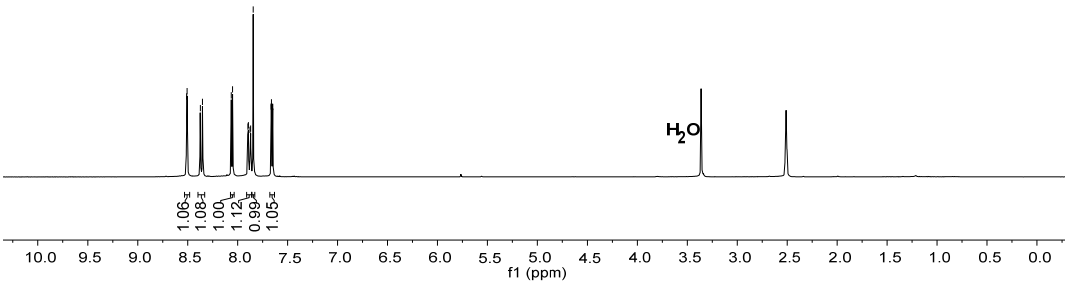
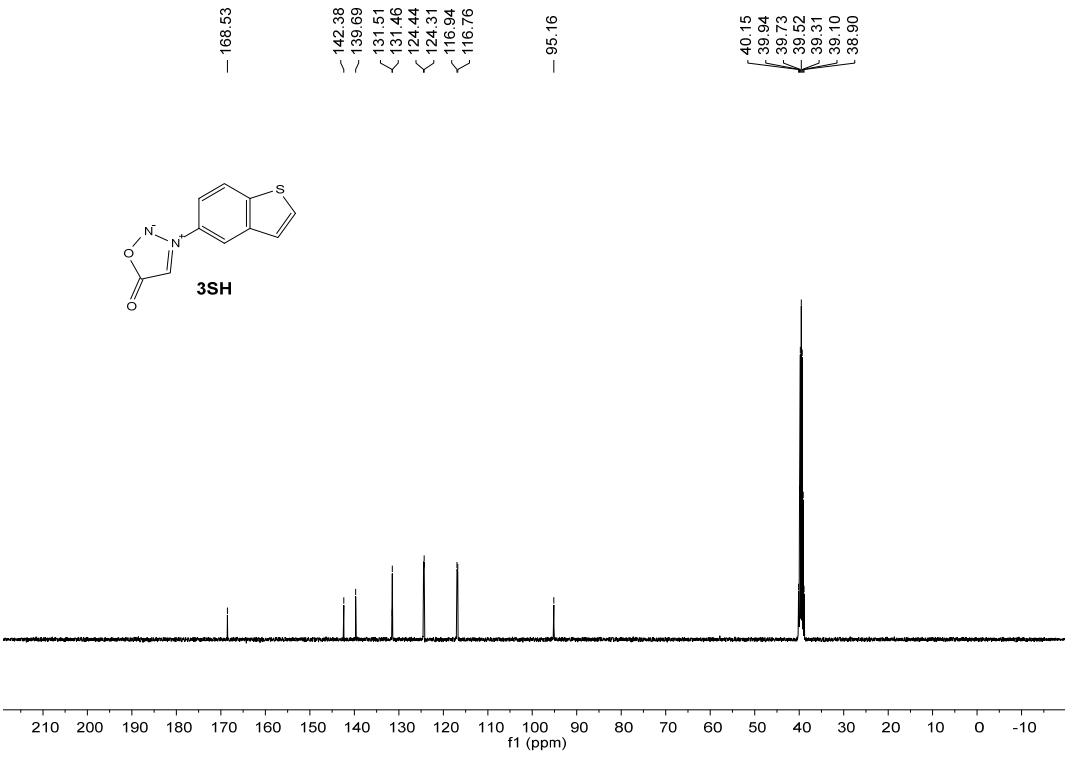
8.05
7.90
7.89
7.88
7.87
7.85
7.66
7.66
7.65
7.65
S
N
N
O
O
3SH


H2O
1.06
1.08
1.00
1.12
0.99
1.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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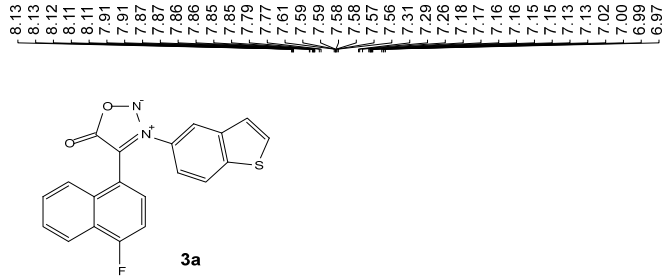
142.38
139.69
131.51
131.46
124.44
124.31
116.94
116.76
95.16
40.15
39.94
39.73
39.52
39.31
39.10
38.90
S
N
N
O
O
3SH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.13
8.12
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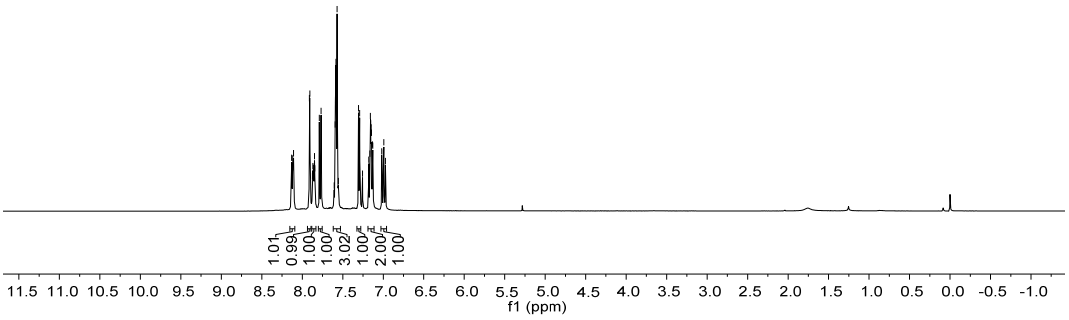
7.91
7.87
7.87
7.86
7.86
7.85
7.85
7.79
7.77
7.61
7.59
7.59
7.58
7.58
7.57
7.56
7.31
7.29
7.26
7.18
7.17
7.16
7.16
7.15
7.15
7.13
7.13
7.02
7.00
6.99
6.97
O
N
N
S
F
3a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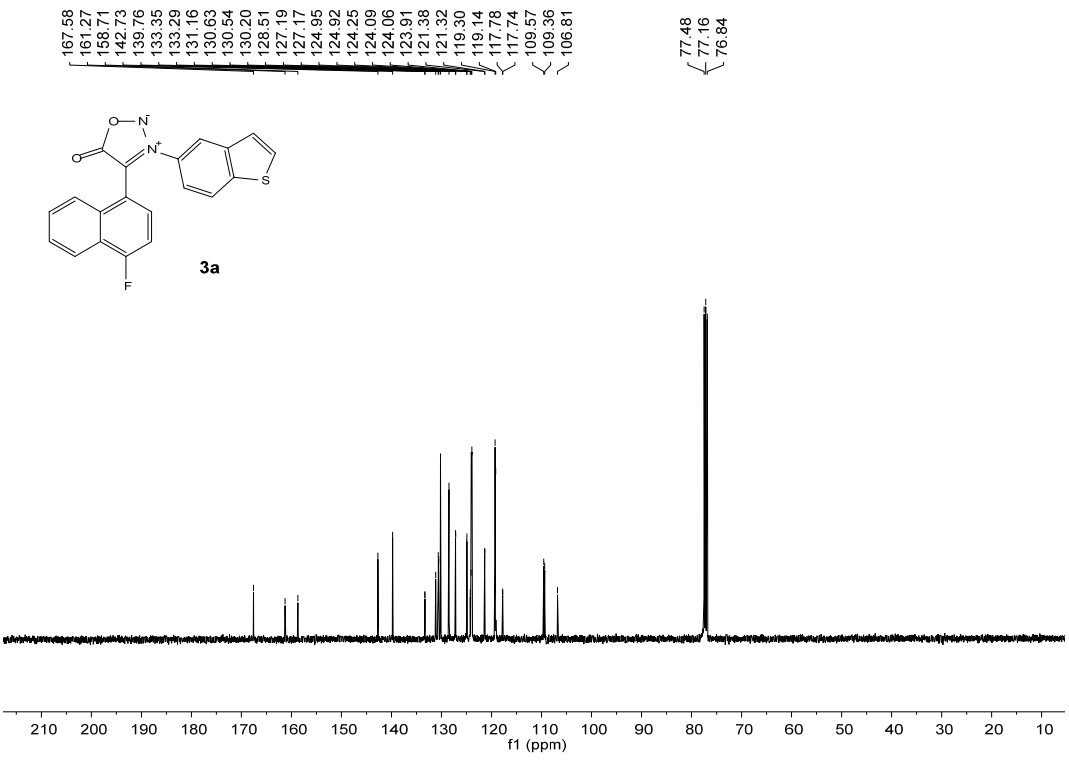
0.99
1.00
1.00
3.02
1.00
2.00
1.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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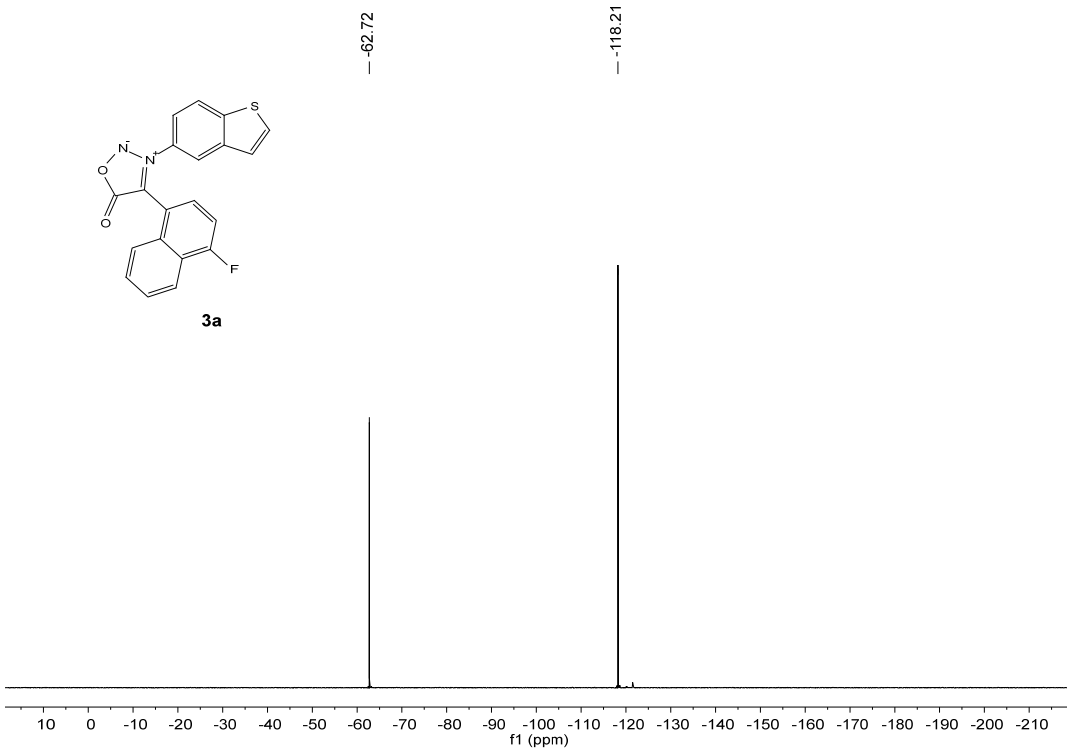
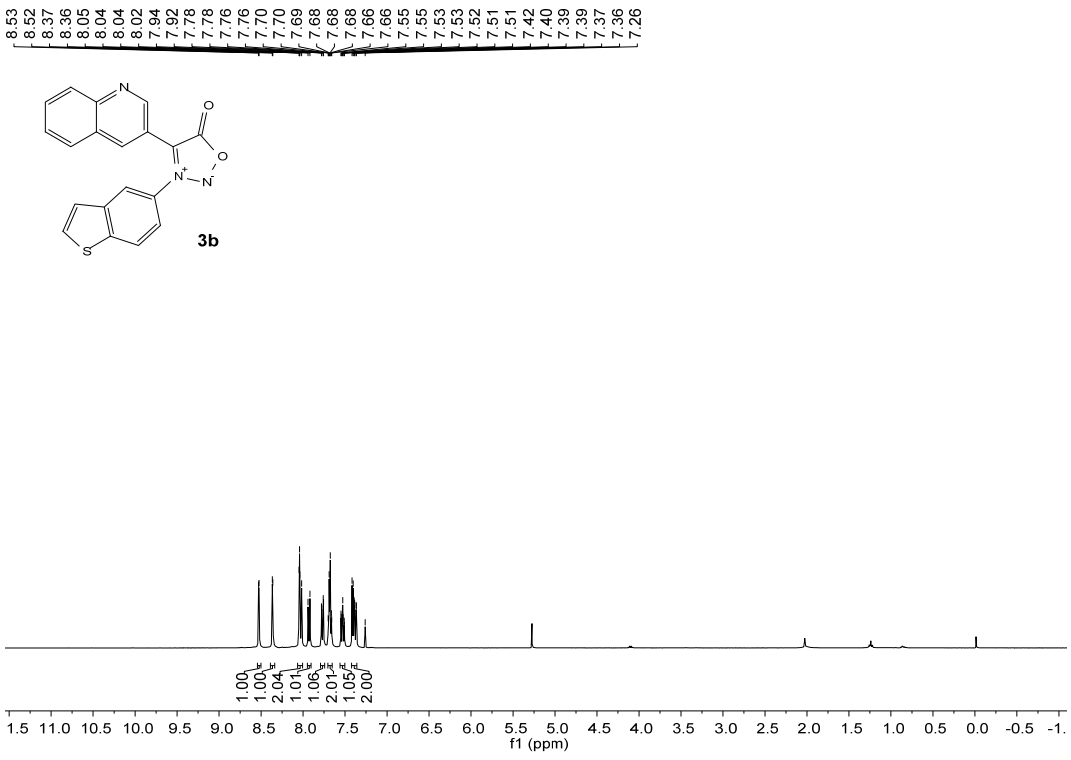
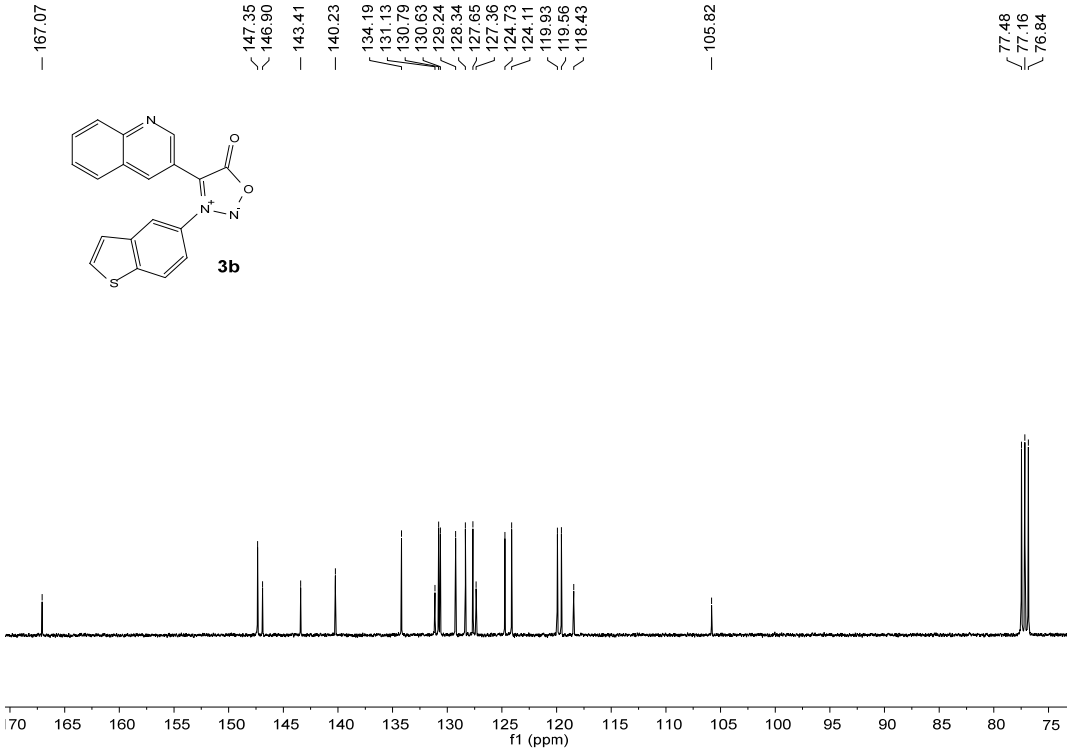
161.27
158.71
142.73
139.76
133.35
133.29
131.16
130.63
130.54
130.20
128.51
127.19
127.17
124.95
124.92
124.25
124.09
124.06
123.91
121.38
121.32
119.30
119.14
117.78
117.74
109.57
109.36
106.81
77.48
77.16
76.84
O
N
N
S
F
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-62.72
-118.21
S
N
N
O
O
F
3a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.53 8.52 8.37 8.36 8.05 8.04 8.04 8.02 7.94 7.92 7.78 7.78 7.76 7.76 7.70 7.70 7.69 7.68 7.68 7.68 7.66 7.66 7.55 7.55 7.53 7.53 7.52 7.51 7.51 7.42 7.40 7.39 7.39 7.37 7.36 7.26
N
O
O
N
N
S
3b
1.00 1.00 2.04 1.01 1.06 2.01 1.05 2.00
1.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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147.35
146.90
143.41
140.23
134.19
131.13
130.79
130.63
129.24
128.34
127.65
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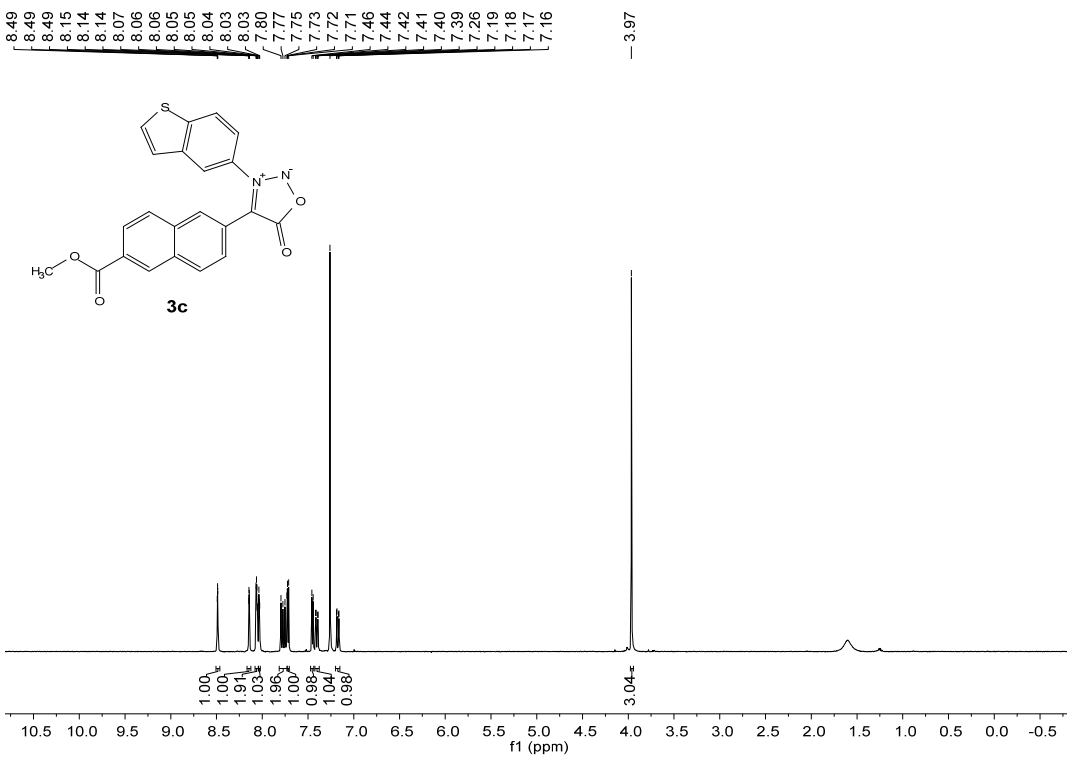
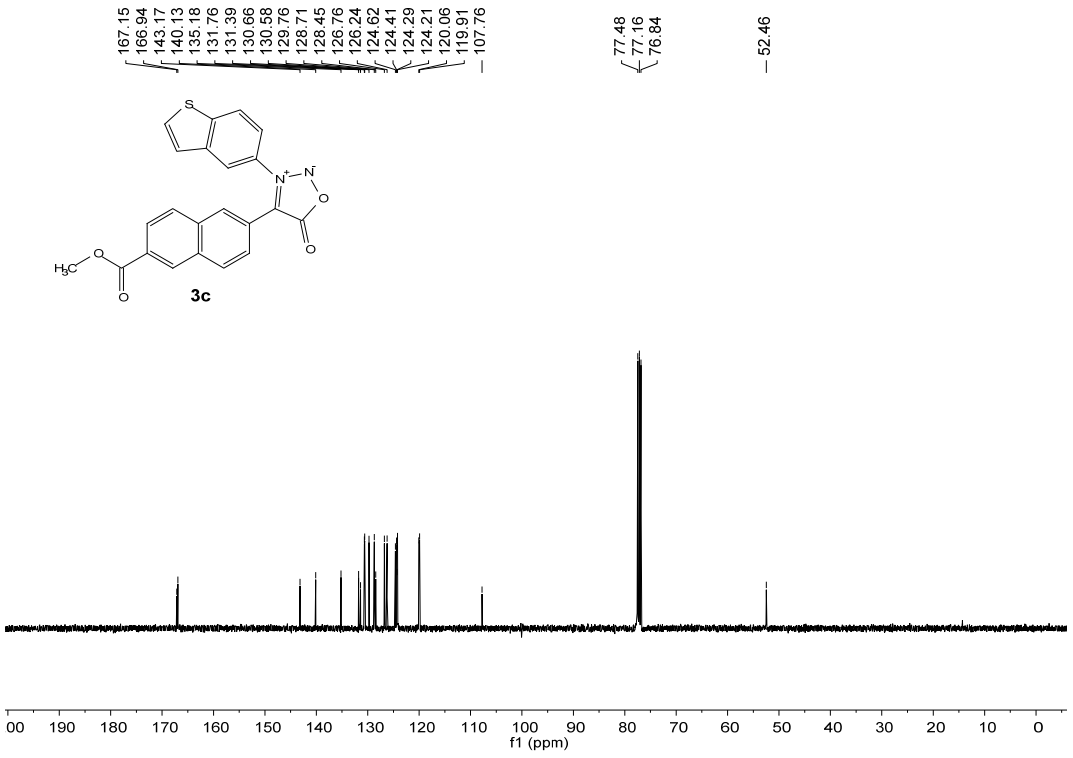
124.73
124.11
119.93
119.56
118.43
105.82
77.48
77.16
76.84
3b
f1 (ppm)


8.49
8.49
8.49
8.15
8.14
8.14
8.07
8.06
8.06
8.05
8.05
8.04
8.03
8.03
7.80
7.77
7.75
7.73
7.72
7.71
7.46
7.44
7.42
7.41
7.40
7.39
7.26
7.19
7.18
7.17
7.16
3.97
3c
1.00
1.00
1.91
1.03
1.96
1.00
0.98
1.04
0.98
3.04
f1 (ppm)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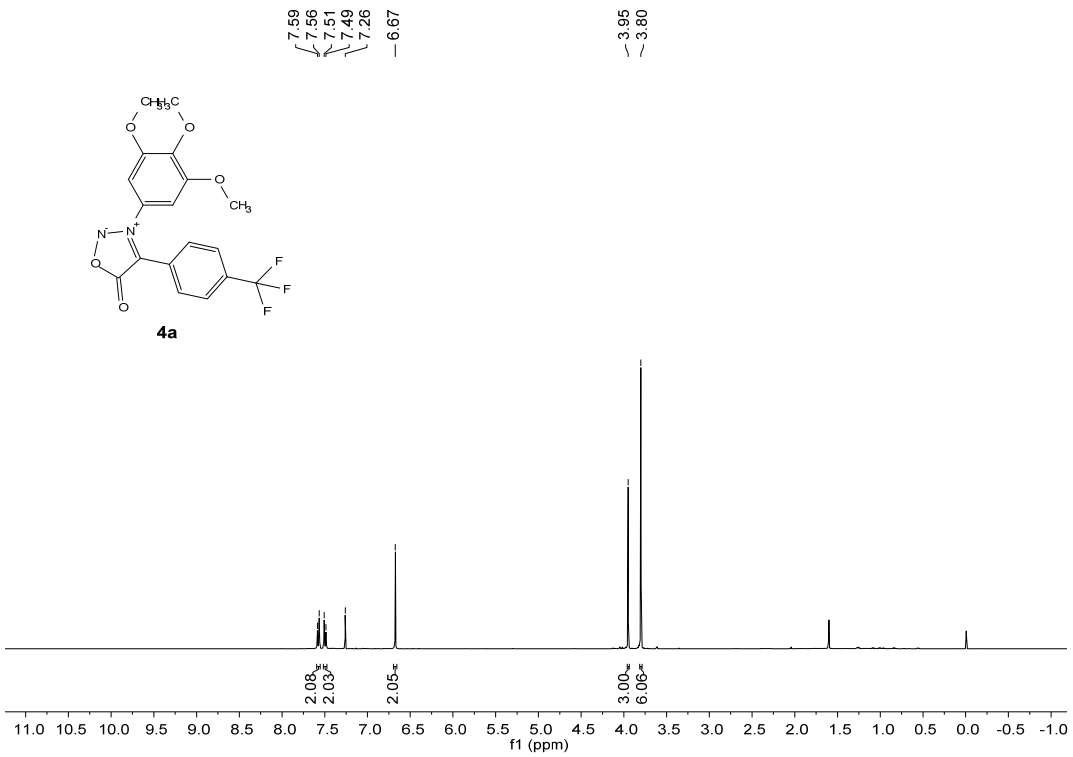
166.94
143.17
140.13
135.18
131.76
131.39
130.66
130.58
129.76
128.71
128.45
126.76
126.24
124.62
124.41
124.29
124.21
120.06
119.91
107.76
77.48
77.16
76.84
52.46
3c
f1 (ppm)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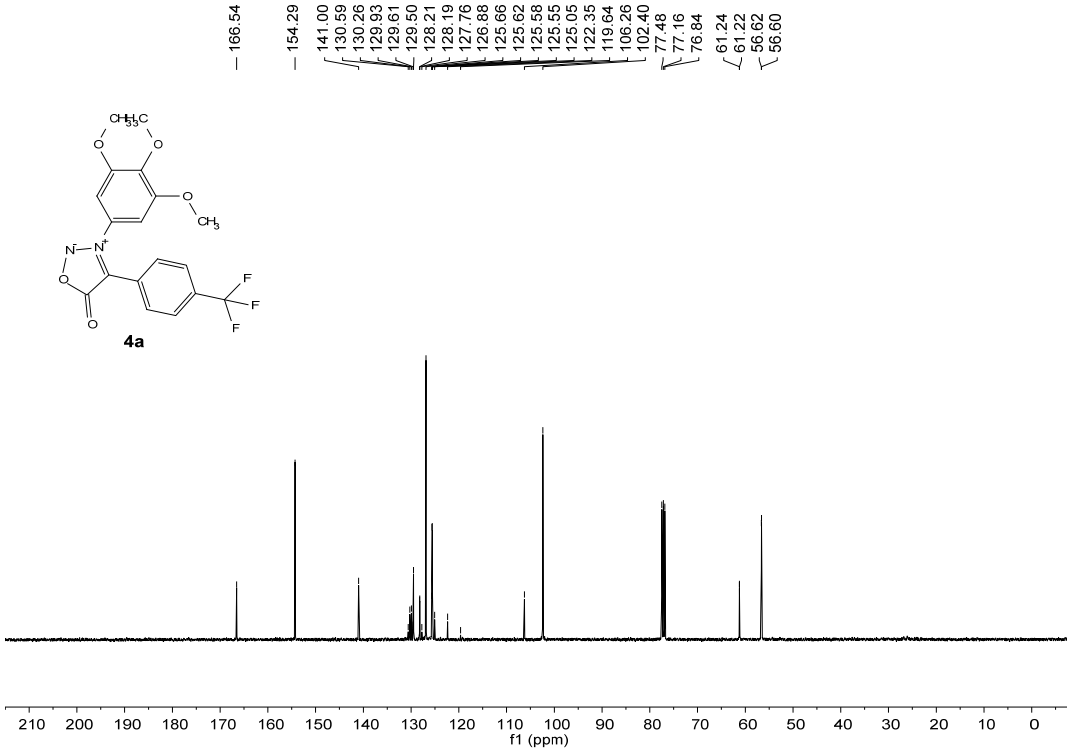
7.56
7.51
7.49
7.26
6.67
3.95
3.80
4a
2.08
2.03
2.05
3.00
6.06
f1 (ppm)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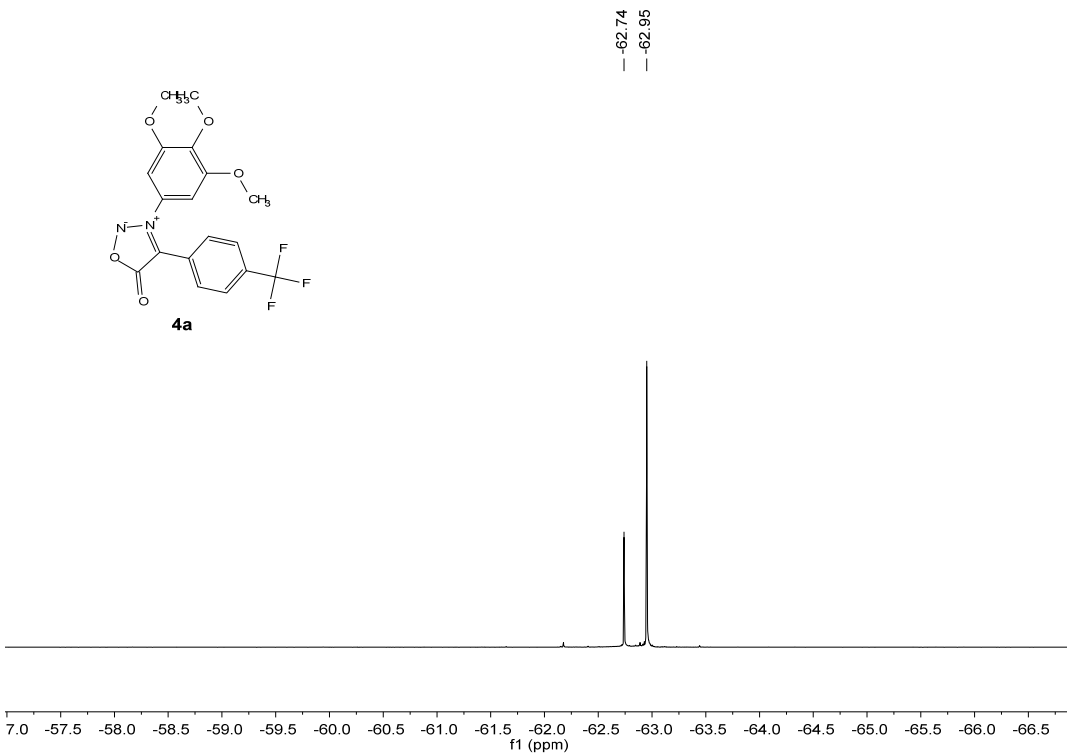
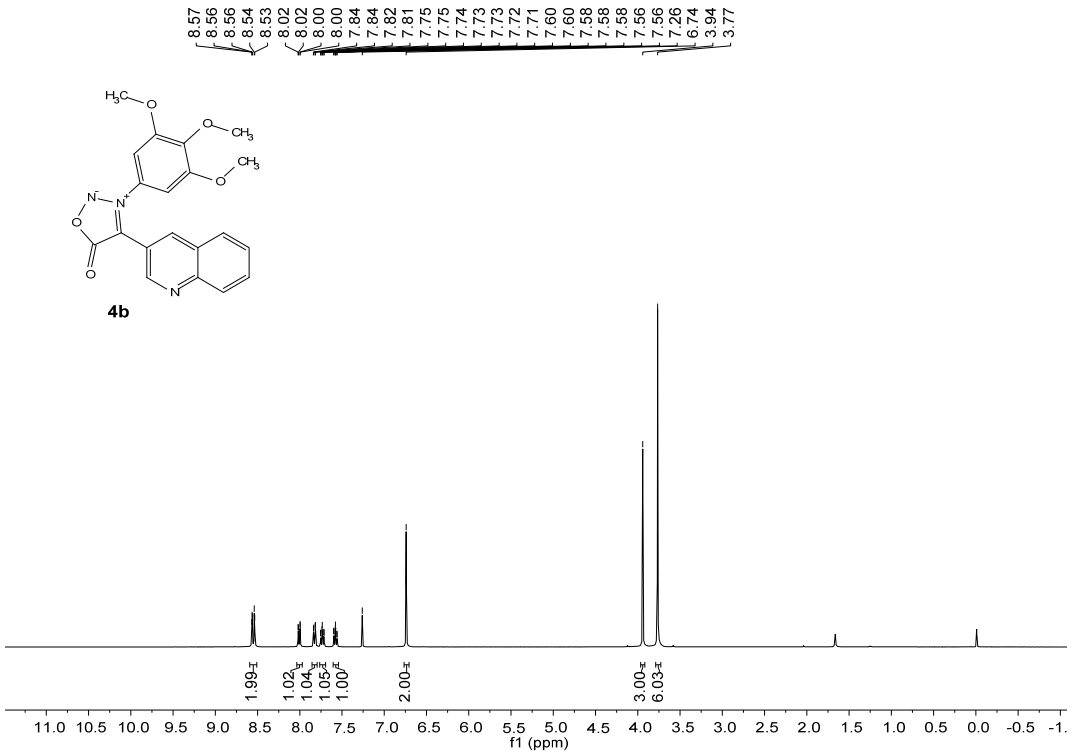
128.19
127.76
126.88
125.66
125.62
125.58
125.55
125.05
122.35
119.64
106.26
102.40
77.48
77.16
76.84
61.24
61.22
56.62
56.60
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.74
-62.95
4a
7.0 -57.5 -58.0 -58.5 -59.0 -59.5 -60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5
f1 (ppm)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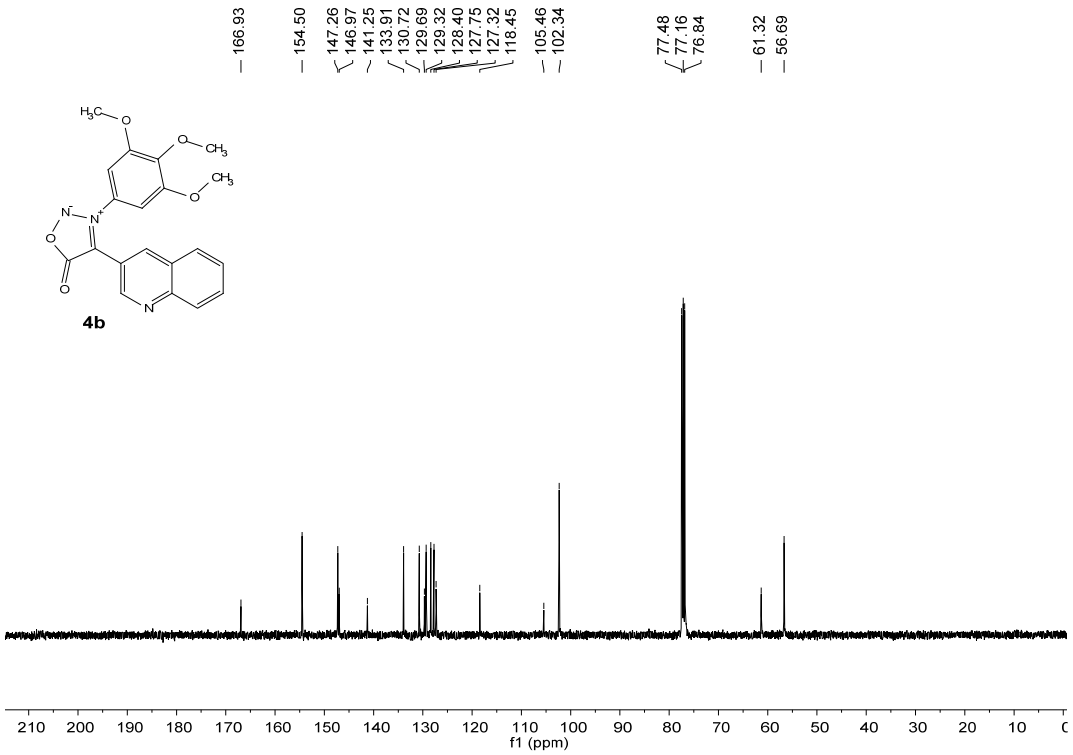
8.56
8.56
8.54
8.53
8.02
8.02
8.00
8.00
7.84
7.84
7.82
7.81
7.75
7.75
7.74
7.73
7.73
7.72
7.71
7.60
7.60
7.58
7.58
7.58
7.56
7.56
7.26
6.74
3.94
3.77
4b
1.99
1.02
1.04
1.05
1.00
2.00
3.00
6.03
f1 (ppm)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128.40
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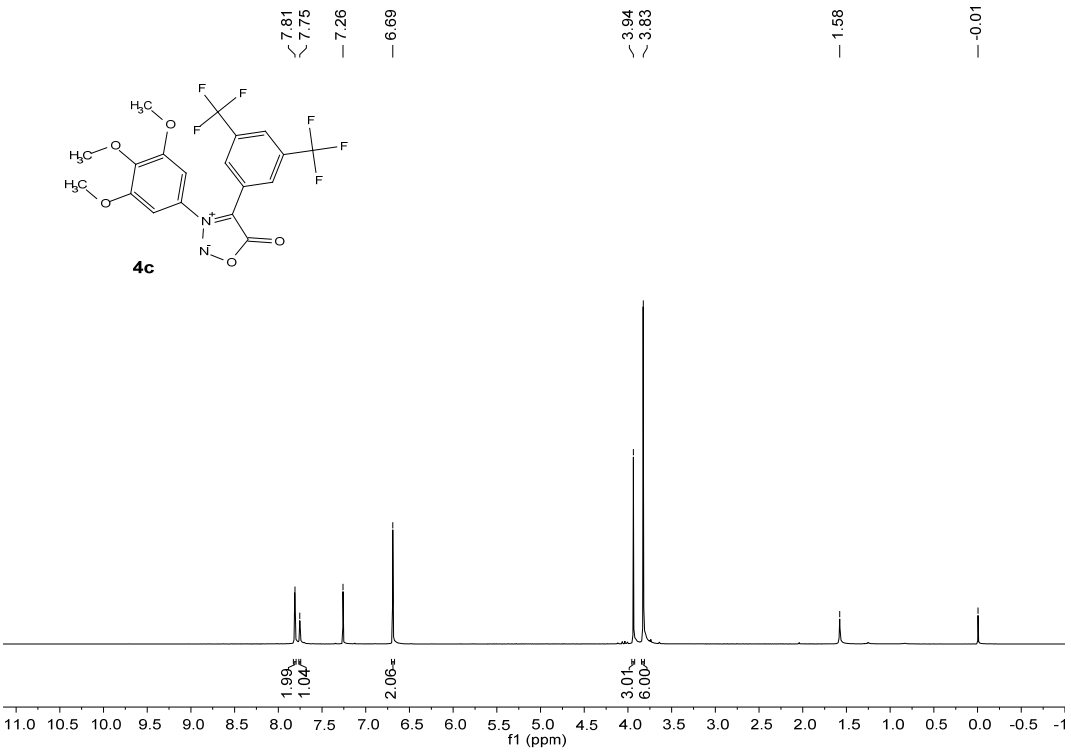
76.84
61.32
56.69
4b
f1 (ppm)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7.75
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1.58
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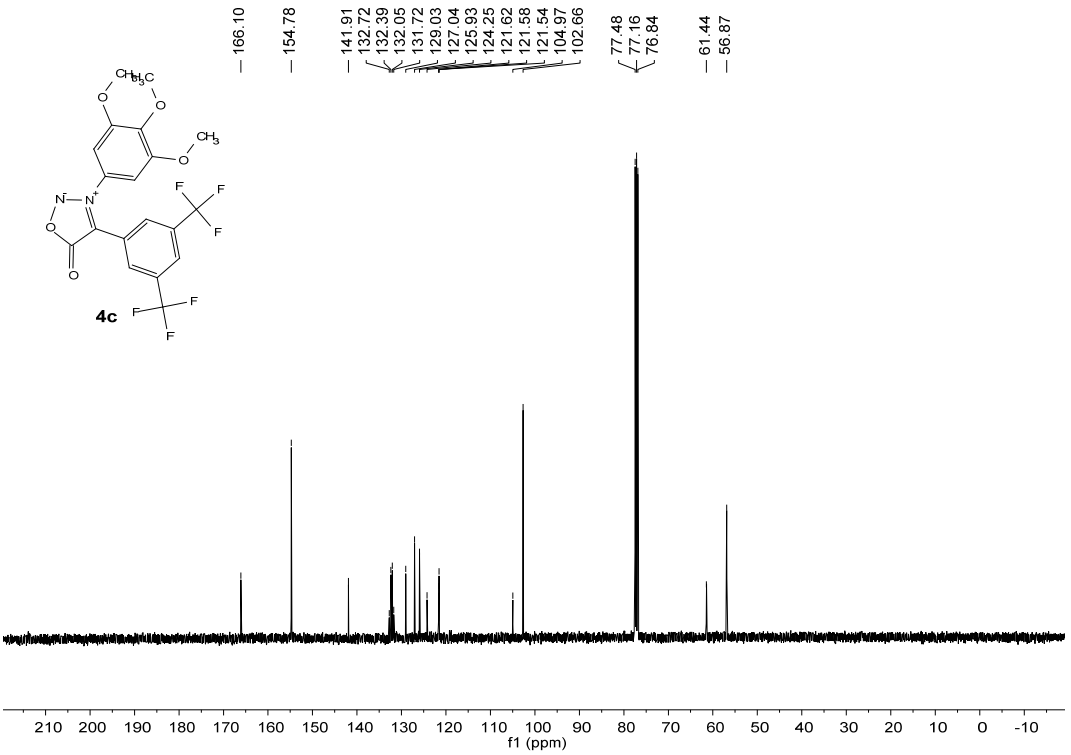
4c
1.99
1.04
2.06
3.01
6.00
f1 (ppm)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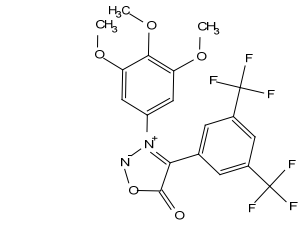
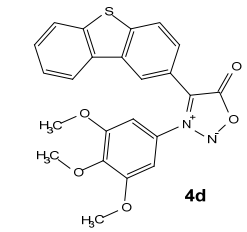
141.91
132.72
132.39
132.05
131.72
129.03
127.04
125.93
124.25
121.62
121.58
121.54
104.97
102.66
77.48
77.16
76.84
61.44
56.87
4c
f1 (ppm)



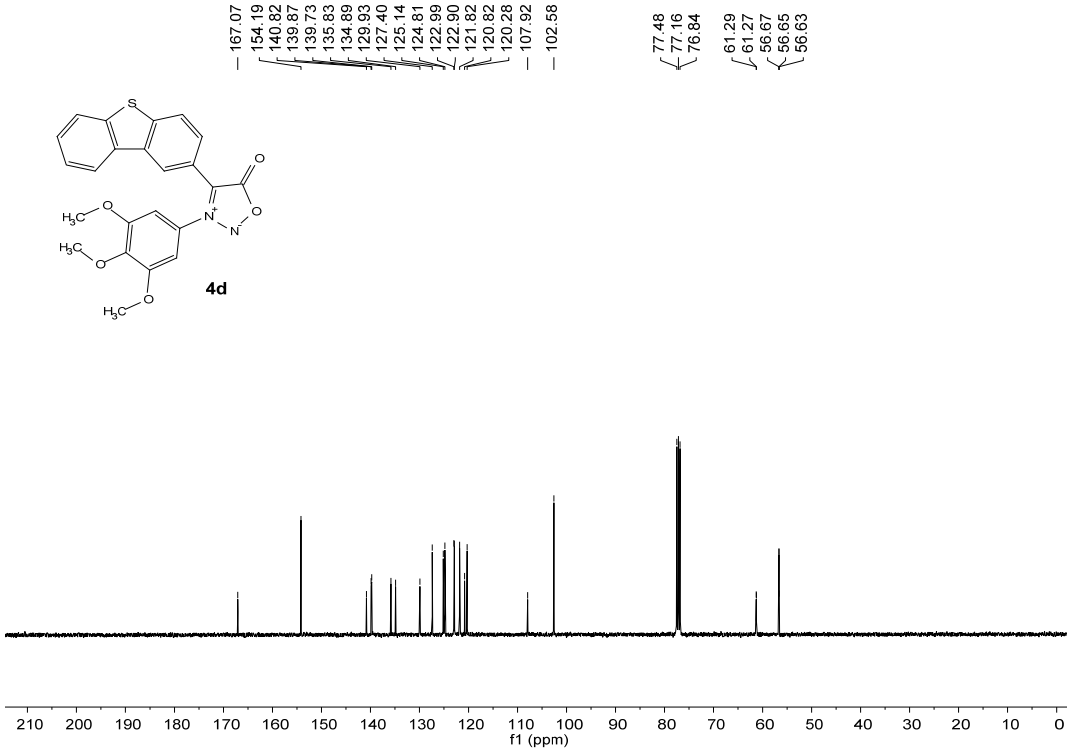
4c

-62.74
-63.32
0
-5
-10
-15
-20
-25
-30
-35
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
f1 (ppm)



4d

8.33
8.33
8.04
8.03
7.86
7.86
7.84
7.84
7.77
7.75
7.49
7.49
7.48
7.47
7.47
7.47
7.46
7.29
7.28
3.94
3.77
1.09
1.06
1.07
1.02
2.27
0.95
1.92
3.04
5.94
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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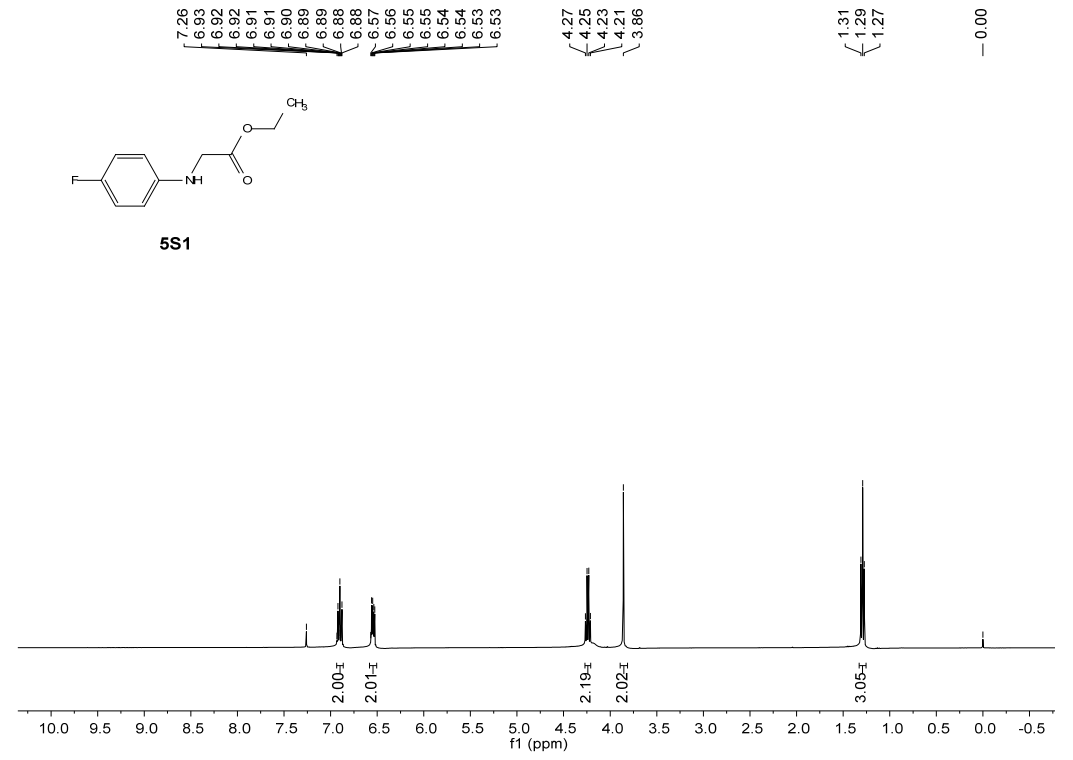
129.93
127.40
125.14
124.81
122.99
122.90
121.82
120.82
120.28
107.92
102.58
77.48
77.16
76.84
61.29
61.27
56.67
56.65
56.63
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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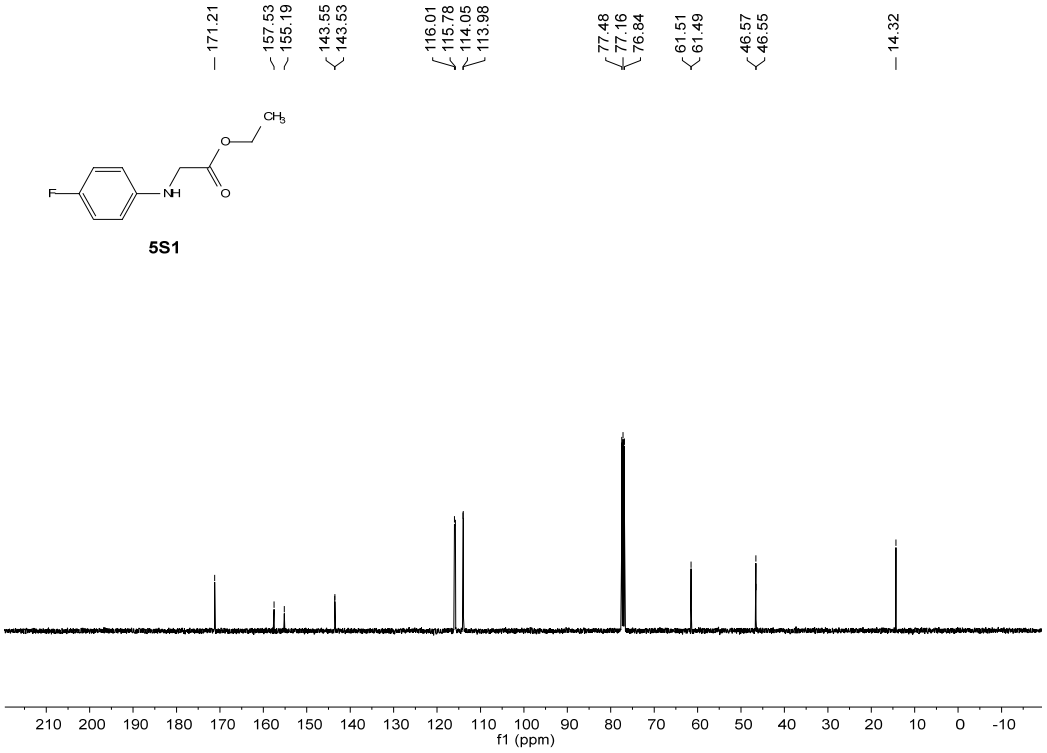
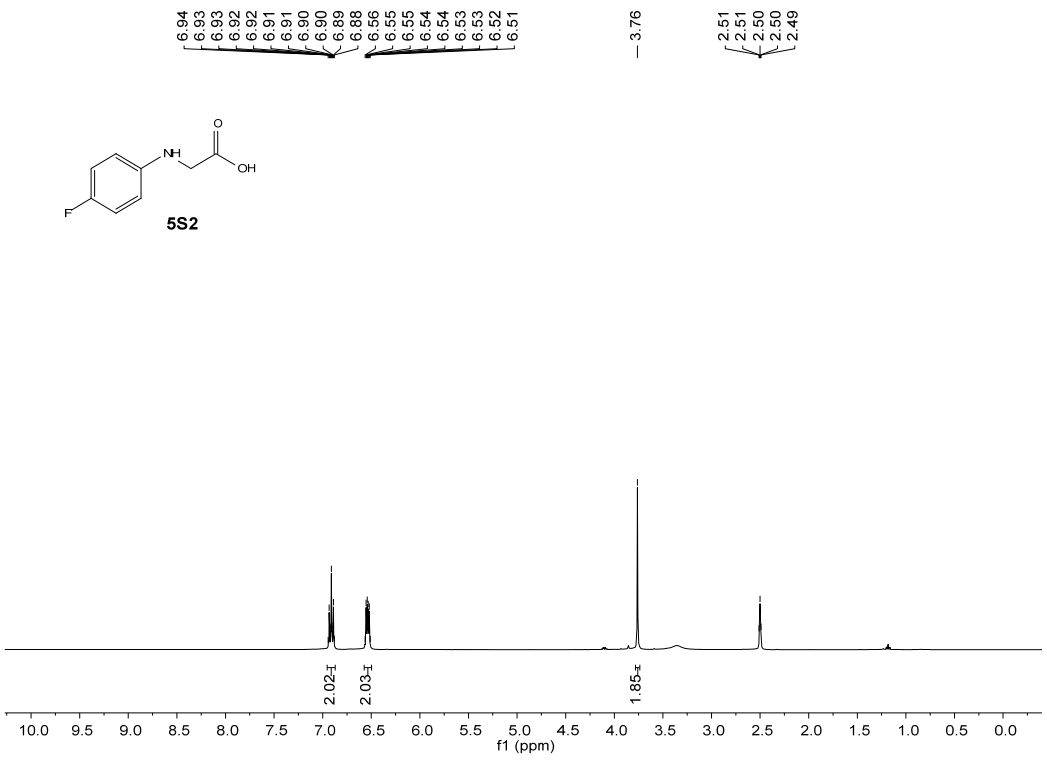
6.92
6.92
6.91
6.91
6.90
6.89
6.89
6.88
6.88
6.57
6.56
6.55
6.55
6.54
6.54
6.53
6.53
4.27
4.25
4.23
4.21
3.86
1.31
1.29
1.27
0.00
5S1
2.00
2.01
2.19
2.02
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.21
157.53
155.19
143.55
143.53
116.01
115.78
114.05
113.98
77.48
77.16
76.84
61.51
61.49
46.57
46.55
14.32
CH3
O
O
F
NH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

5S1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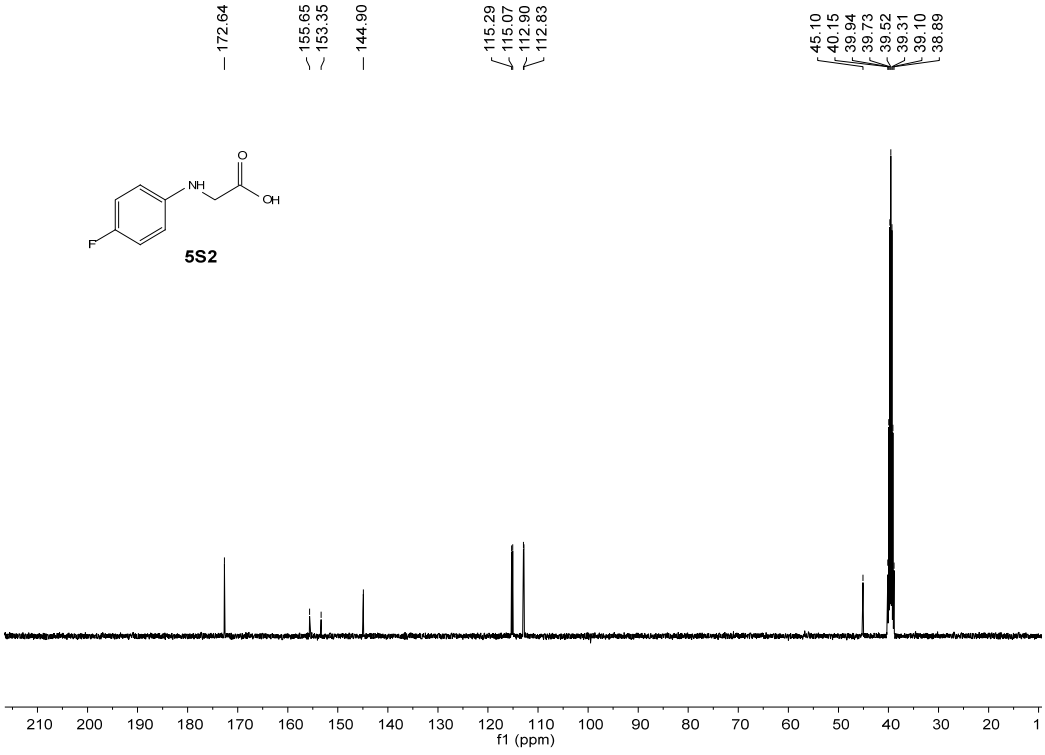
6.93
6.93
6.92
6.92
6.91
6.91
6.90
6.90
6.89
6.88
6.56
6.55
6.55
6.54
6.54
6.53
6.53
6.52
6.51
3.76
2.51
2.51
2.50
2.50
2.49
O
NH
OH
F
2.02
2.03
1.85
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

5S2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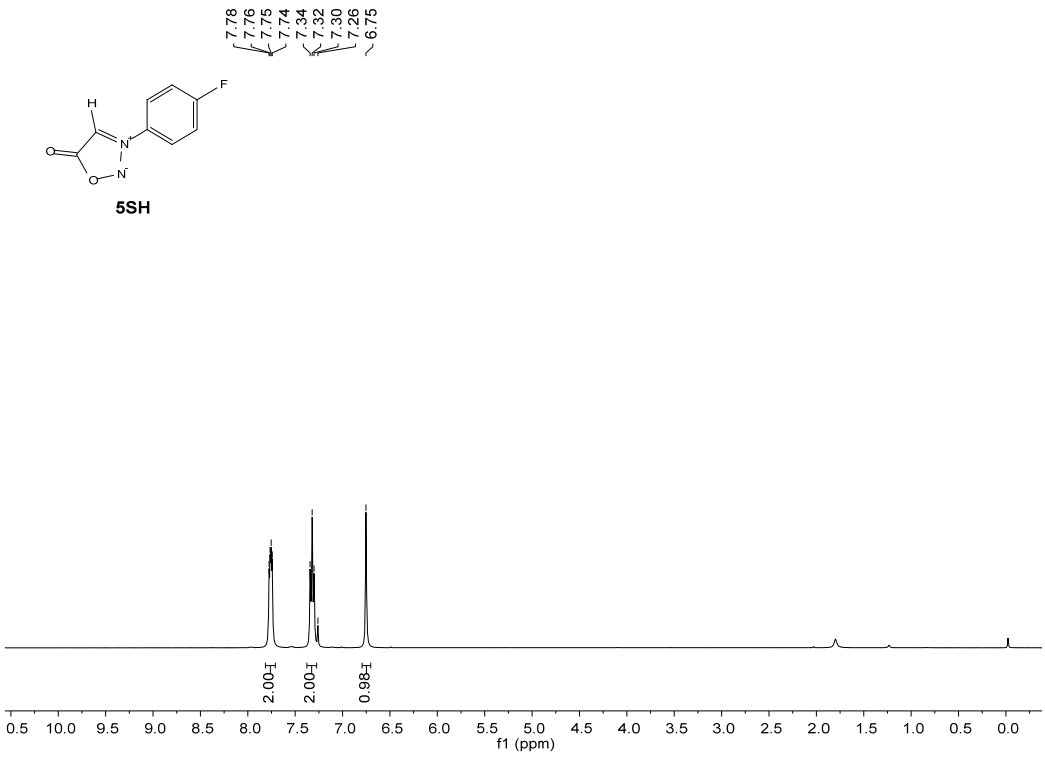
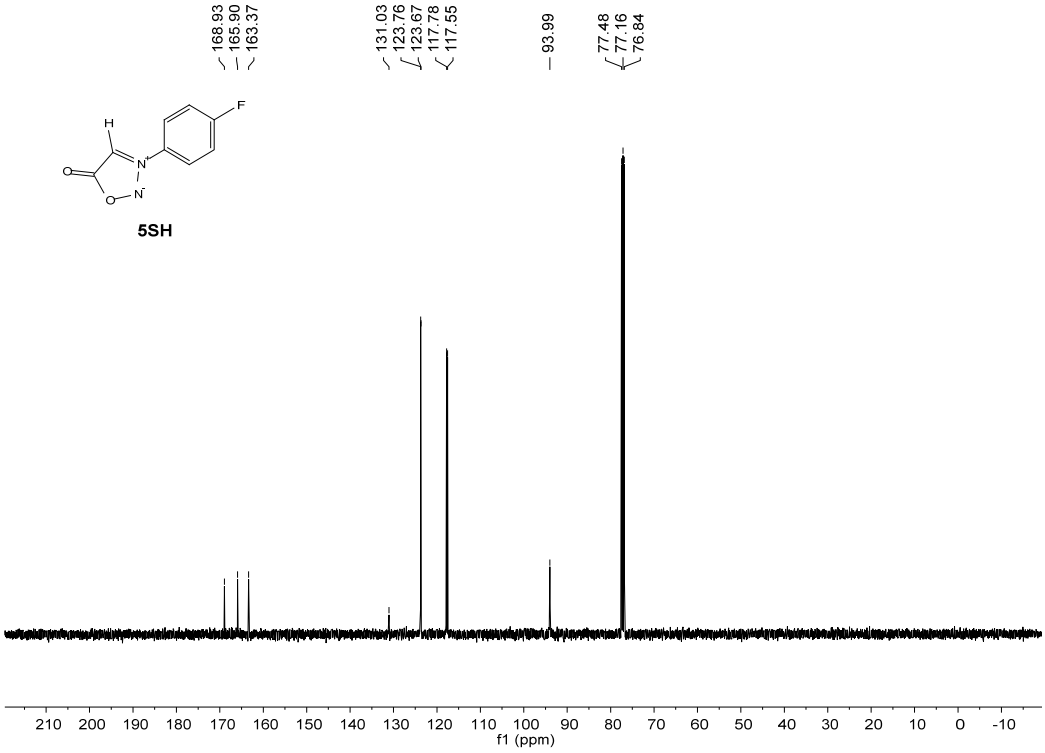
153.35
144.90
115.29
115.07
112.90
112.83
45.10
40.15
39.94
39.73
39.52
39.31
39.10
38.89
NH
O
OH
F
5S2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 1
f1 (ppm)


7.78
7.76
7.75
7.74
7.34
7.32
7.30
7.26
6.75
H
F
O
N
O
N
5SH
2.00
2.00
0.98
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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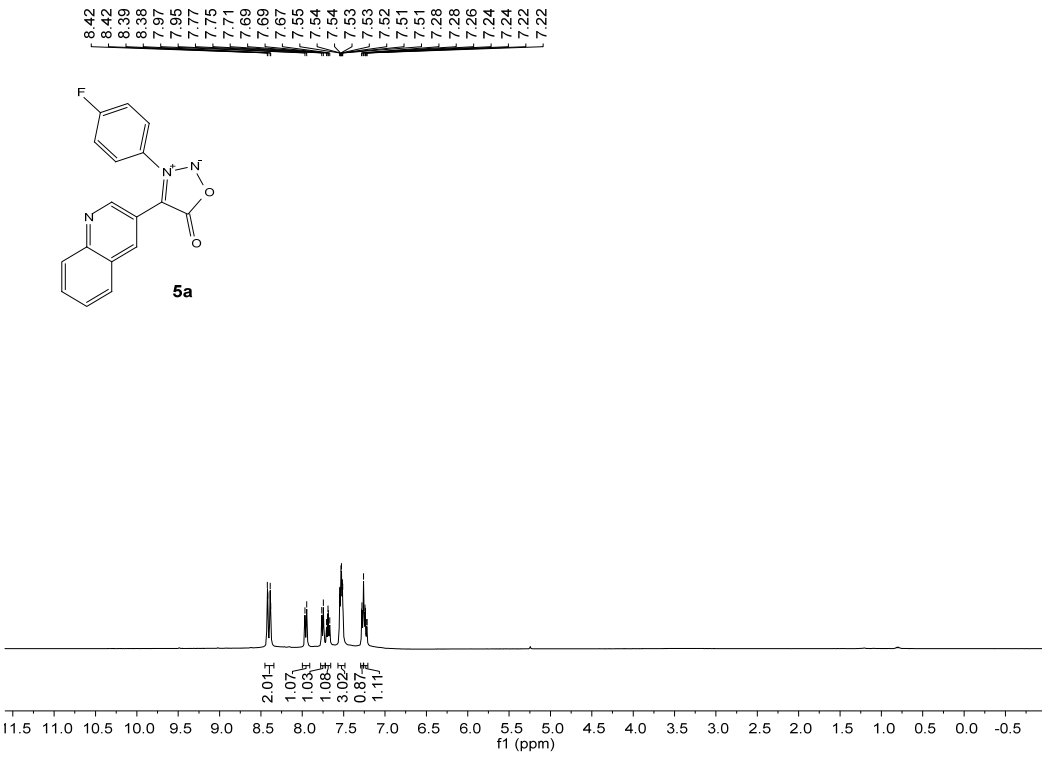
165.90
163.37
131.03
123.76
123.67
117.78
117.55
93.99
77.48
77.16
76.84
F
H
O
N+
N-
O
5SH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.75
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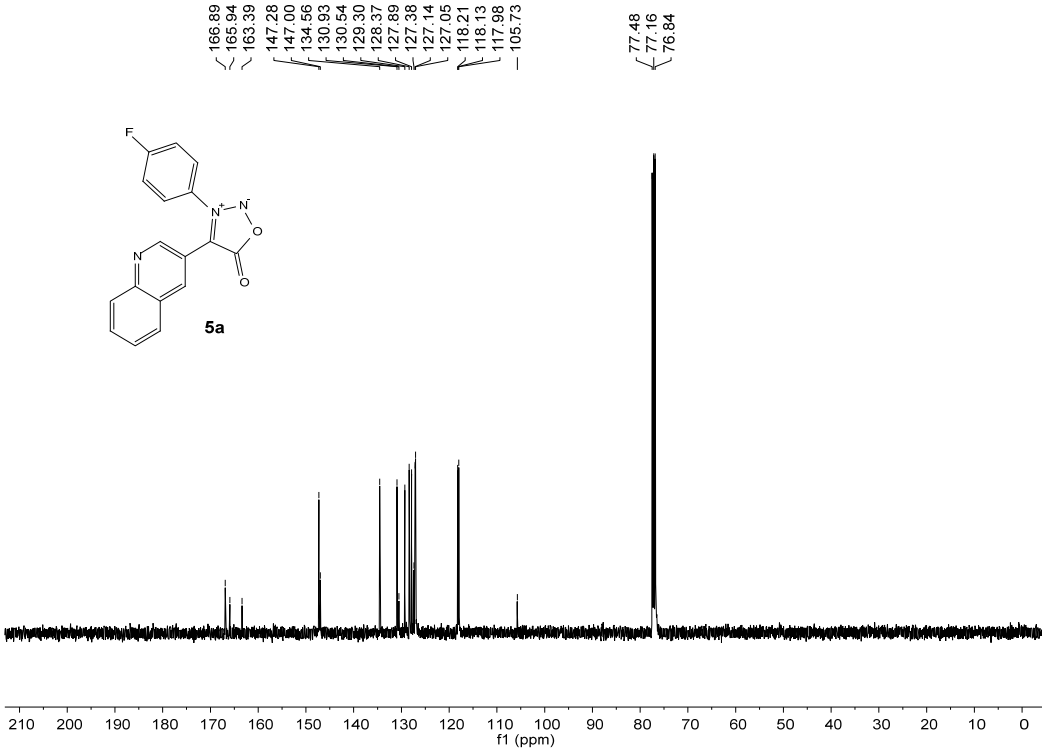
7.69
7.67
7.55
7.54
7.54
7.53
7.53
7.52
7.51
7.51
7.28
7.28
7.26
7.24
7.24
7.22
7.22
F
N+
N-
O
N
O
5a
2.01
1.07
1.03
1.08
3.02
0.87
1.11
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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130.54
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127.89
127.38
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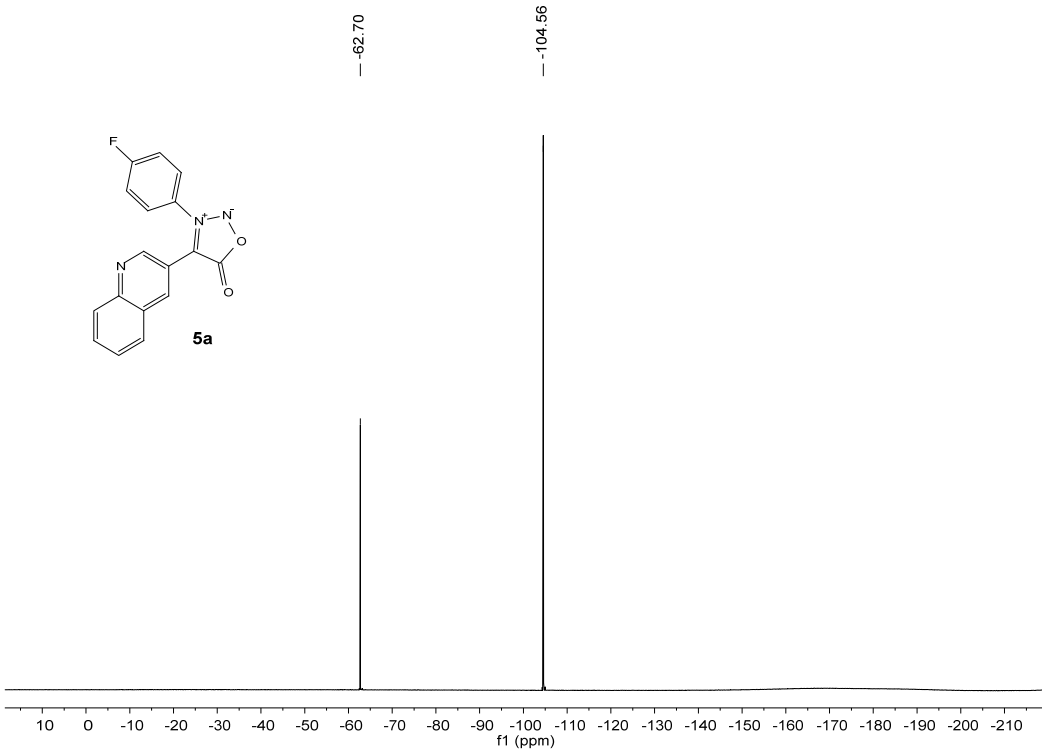
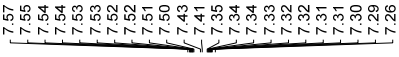
118.13
117.98
105.73
77.48
77.16
76.84
F
N
O
O
5a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-62.70
-104.56
F
N
O
O
5a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.51
7.50
7.43
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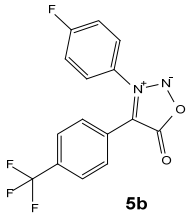
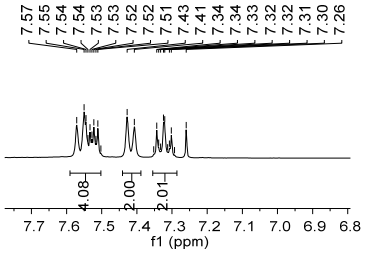
7.32
7.31
7.31
7.30
7.29
7.26


F
N
N
O
O
F
F
F

5b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7.52
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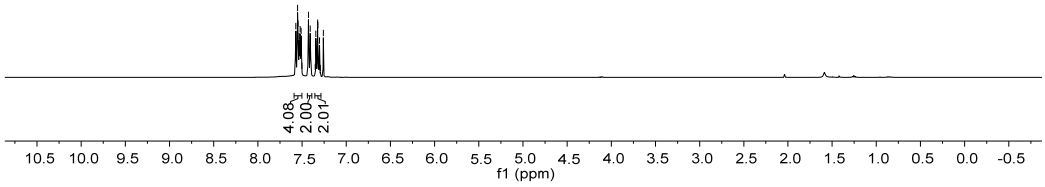
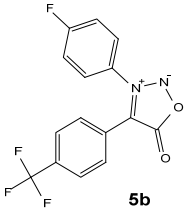
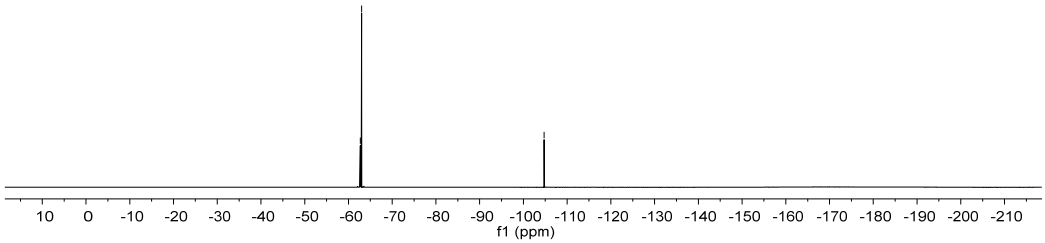
7.43
7.41
7.34
7.34
7.33
7.32
7.32
7.31
7.30
7.26
4.08
2.00
2.01
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8
f1 (ppm)

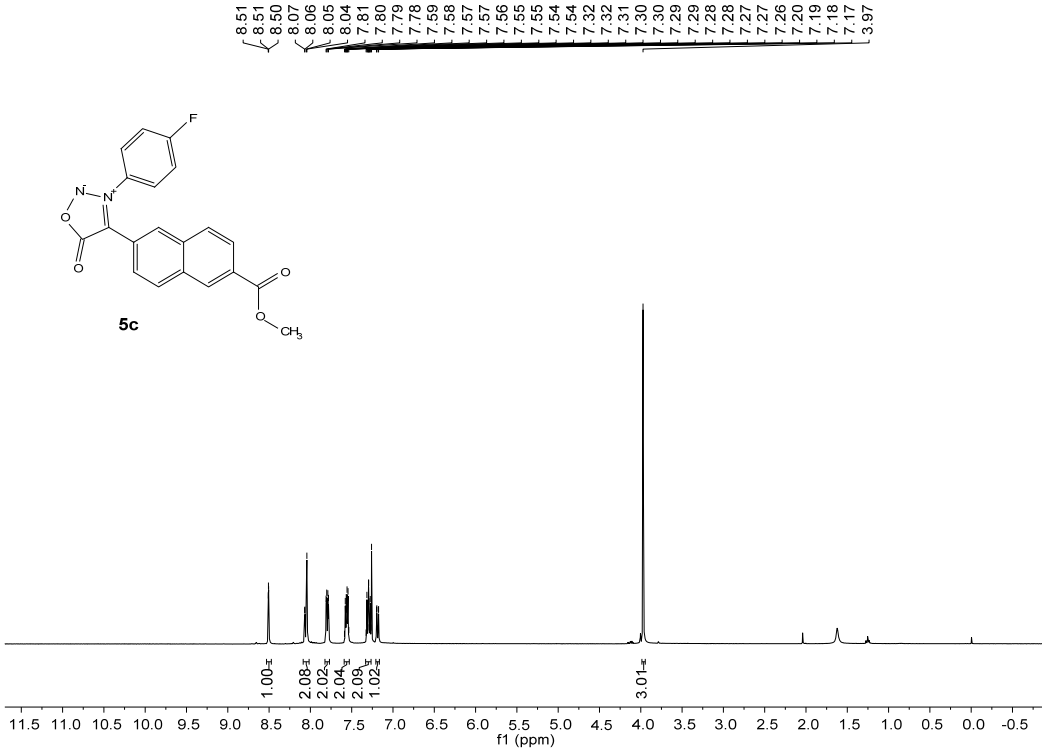

4.08
2.00
2.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


-62.73
-62.99
-104.73


F
N
N
O
O
F
F
F

5b


10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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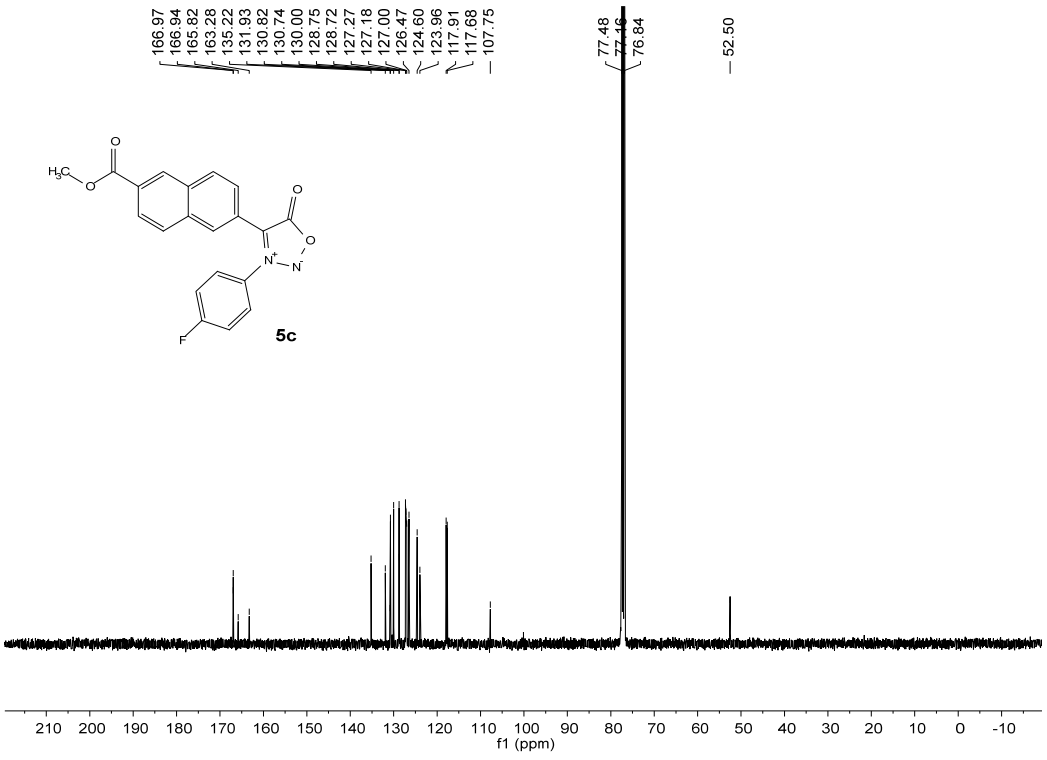
8.51
8.50
8.07
8.06
8.05
8.04
7.81
7.80
7.79
7.78
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.54
7.54
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.20
7.19
7.18
7.17
3.97
F
O
O
N
N
O
O
O
CH3
5c
1.00
2.08
2.02
2.04
2.09
1.02
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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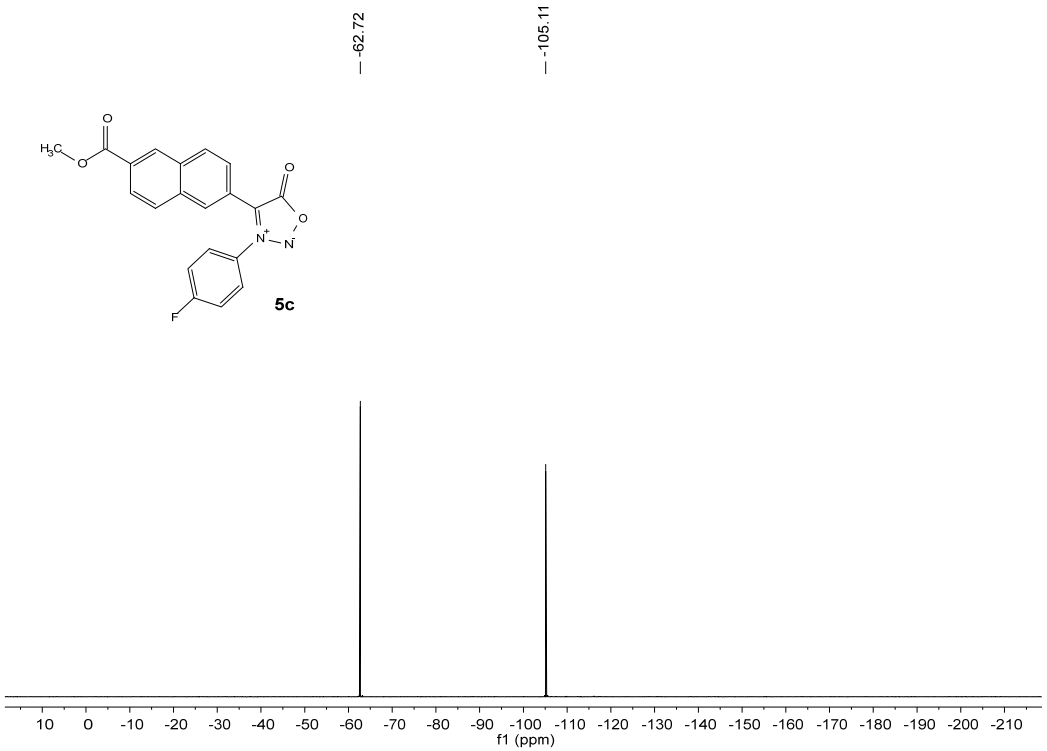
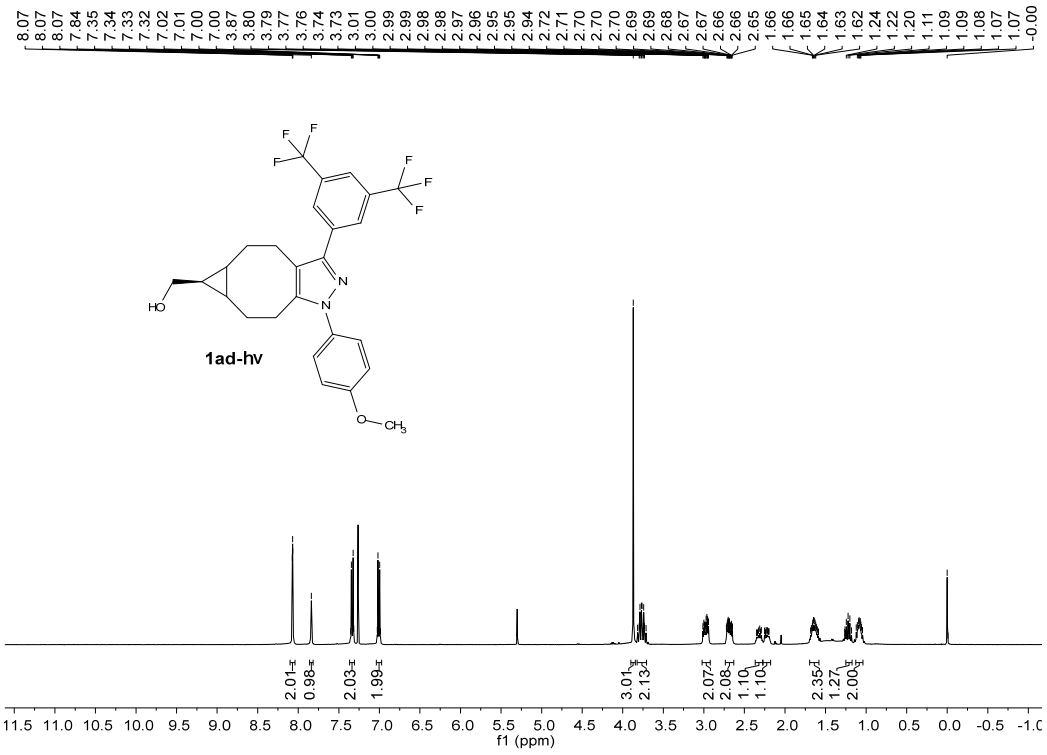
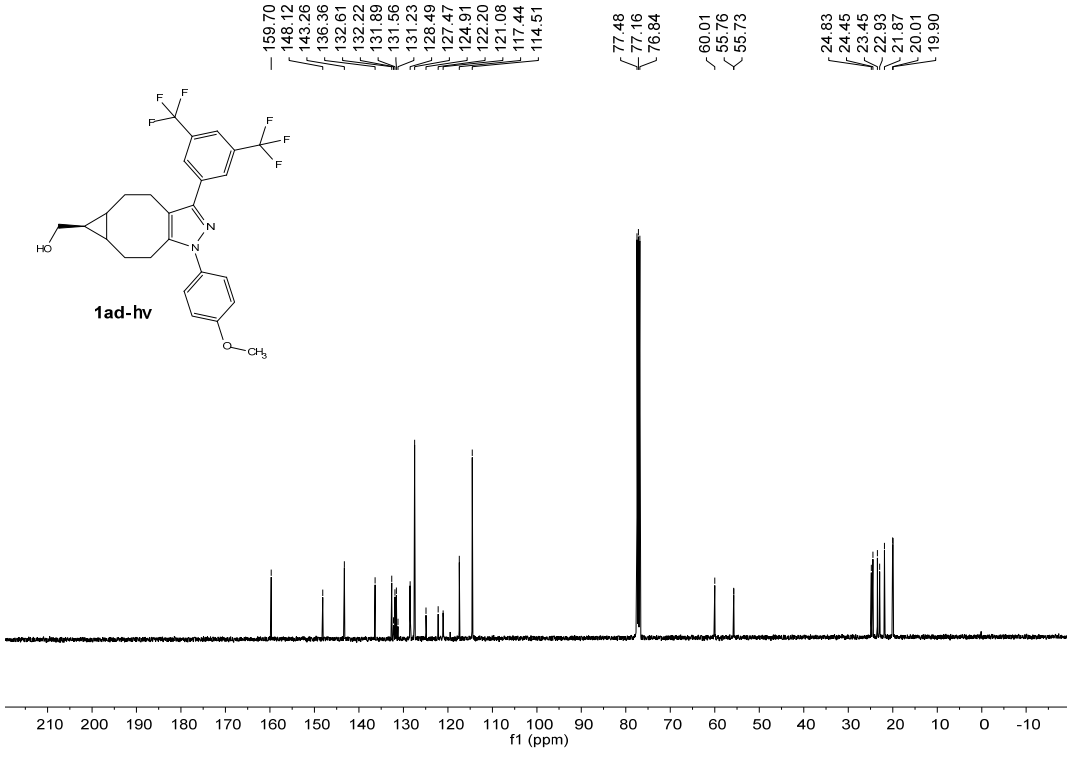
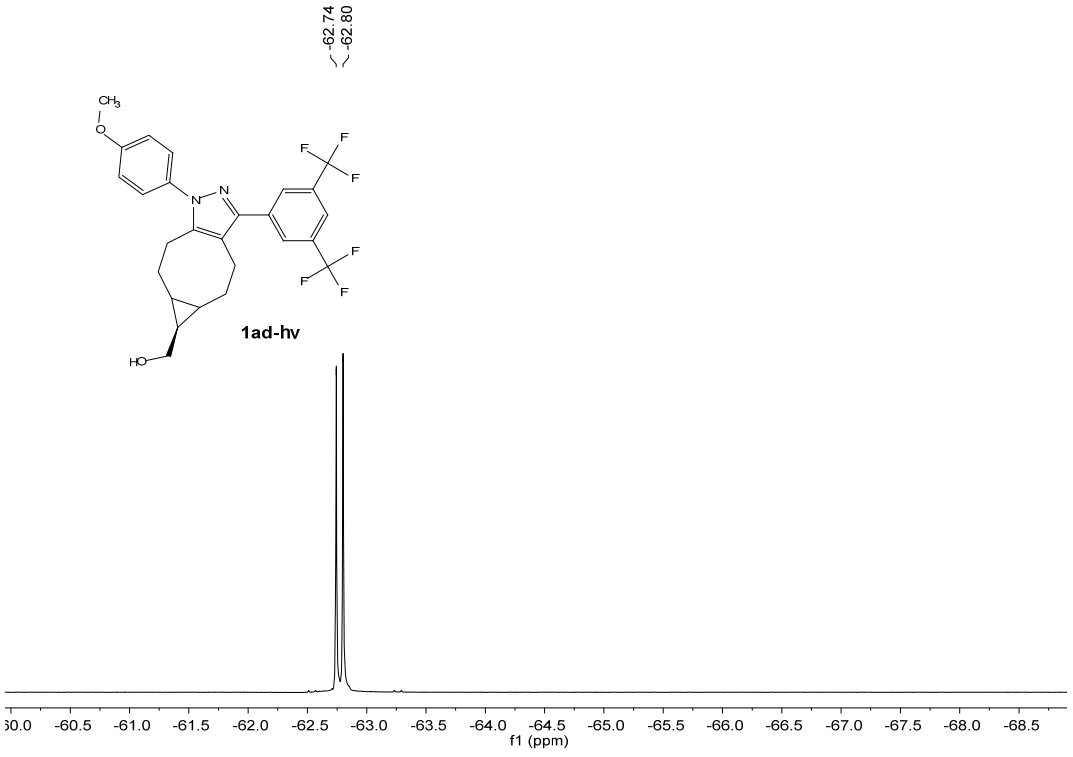
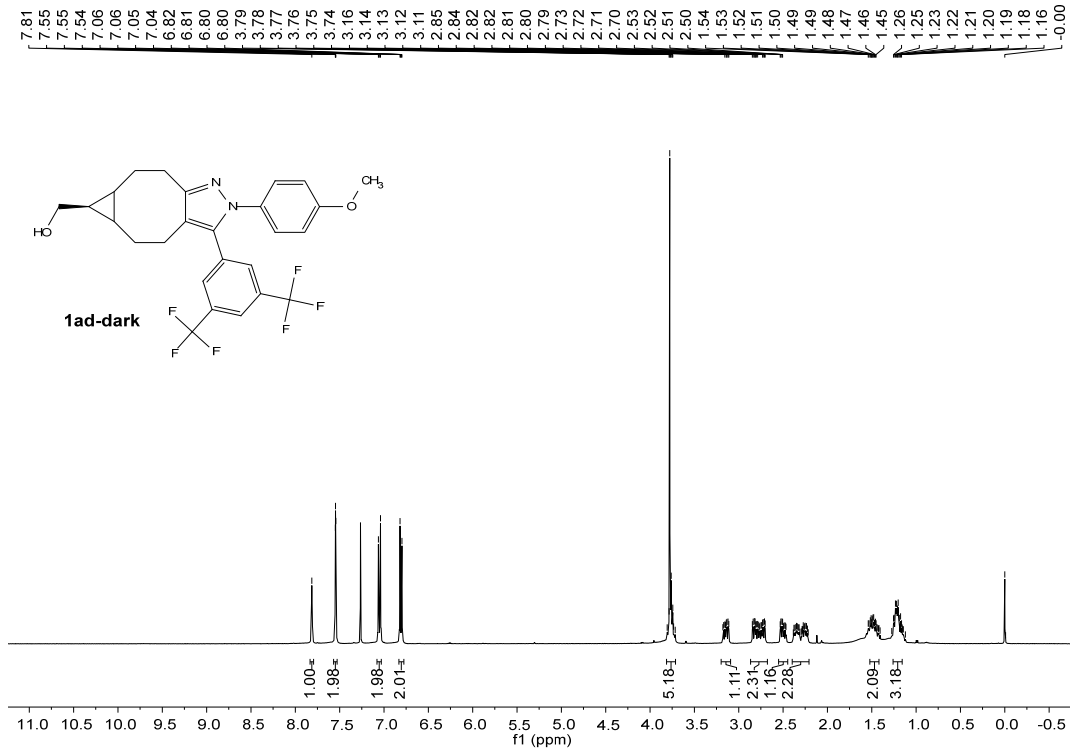
166.94
165.82
163.28
135.22
131.93
130.82
130.74
130.00
128.75
128.72
127.27
127.18
127.00
126.47
124.60
123.96
117.91
117.68
107.75
77.48
77.16
76.84
52.50
H3C
O
O
O
O
N
N
F
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

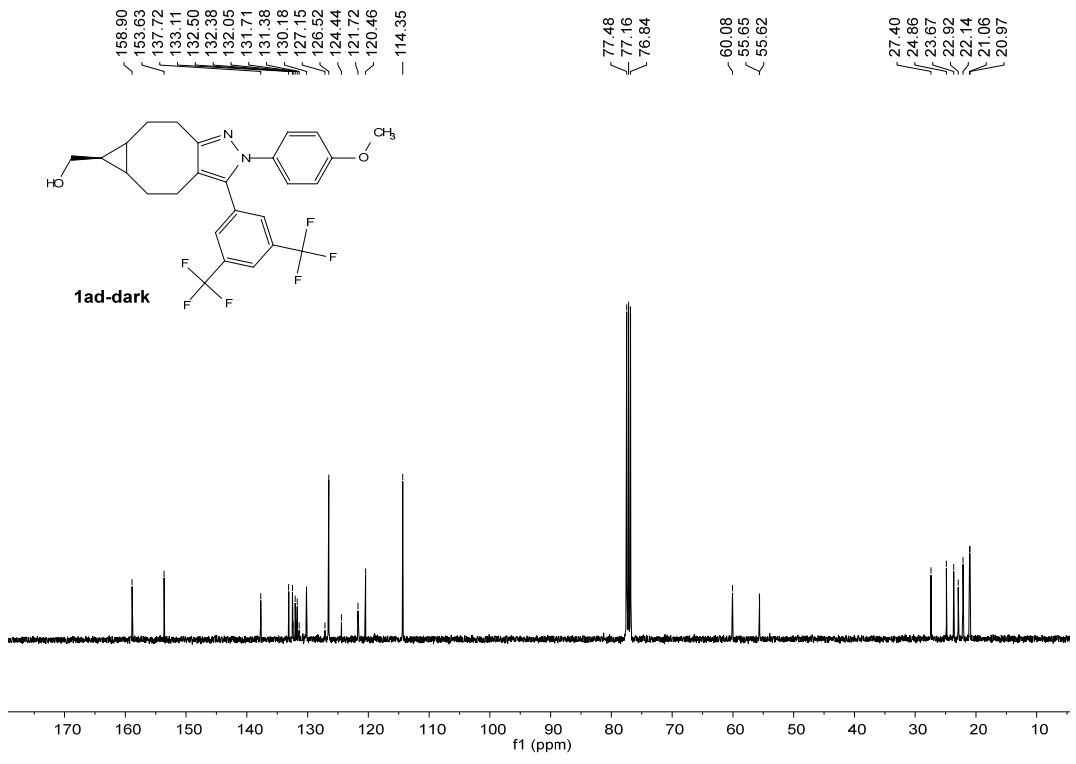

-62.72
-105.11
5c
f1 (ppm)

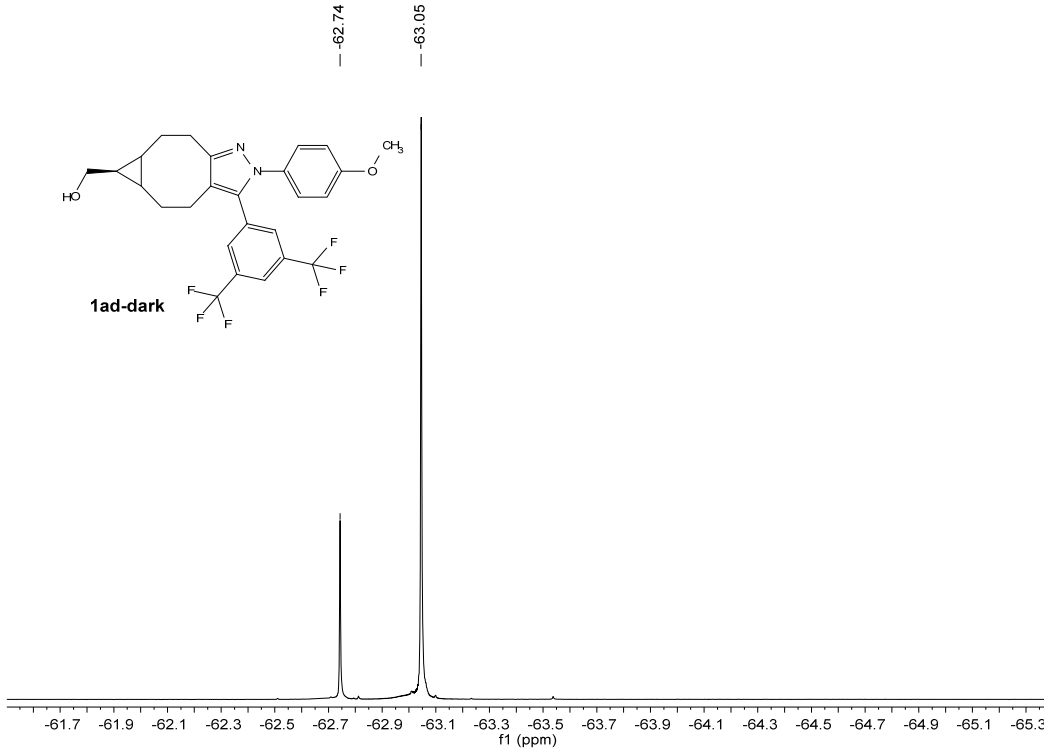

1ad-hv
2.01
0.98
2.03
1.99
3.01
2.13
2.07
2.08
1.10
1.10
2.35
1.27
2.00
f1 (ppm)

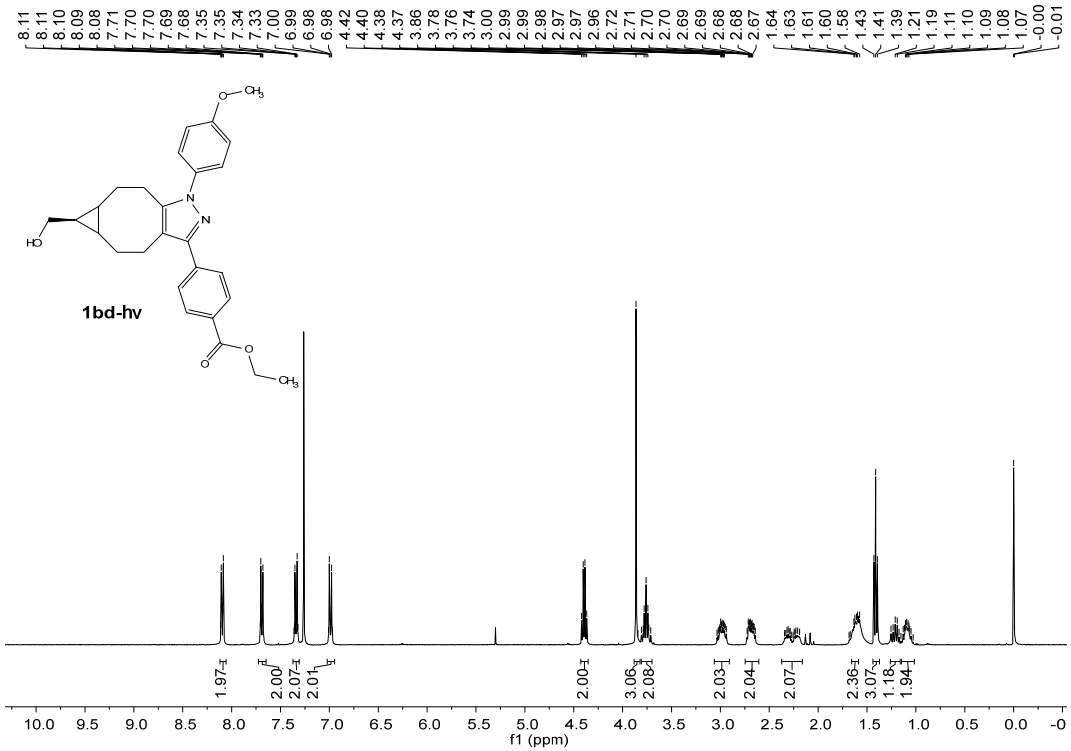

159.70
148.12
143.26
136.36
132.61
132.22
131.89
131.56
131.23
128.49
127.47
124.91
122.20
121.08
117.44
114.51
77.48
77.16
76.84
60.01
55.76
55.73
24.83
24.45
23.45
22.93
21.87
20.01
19.90
1ad-hv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

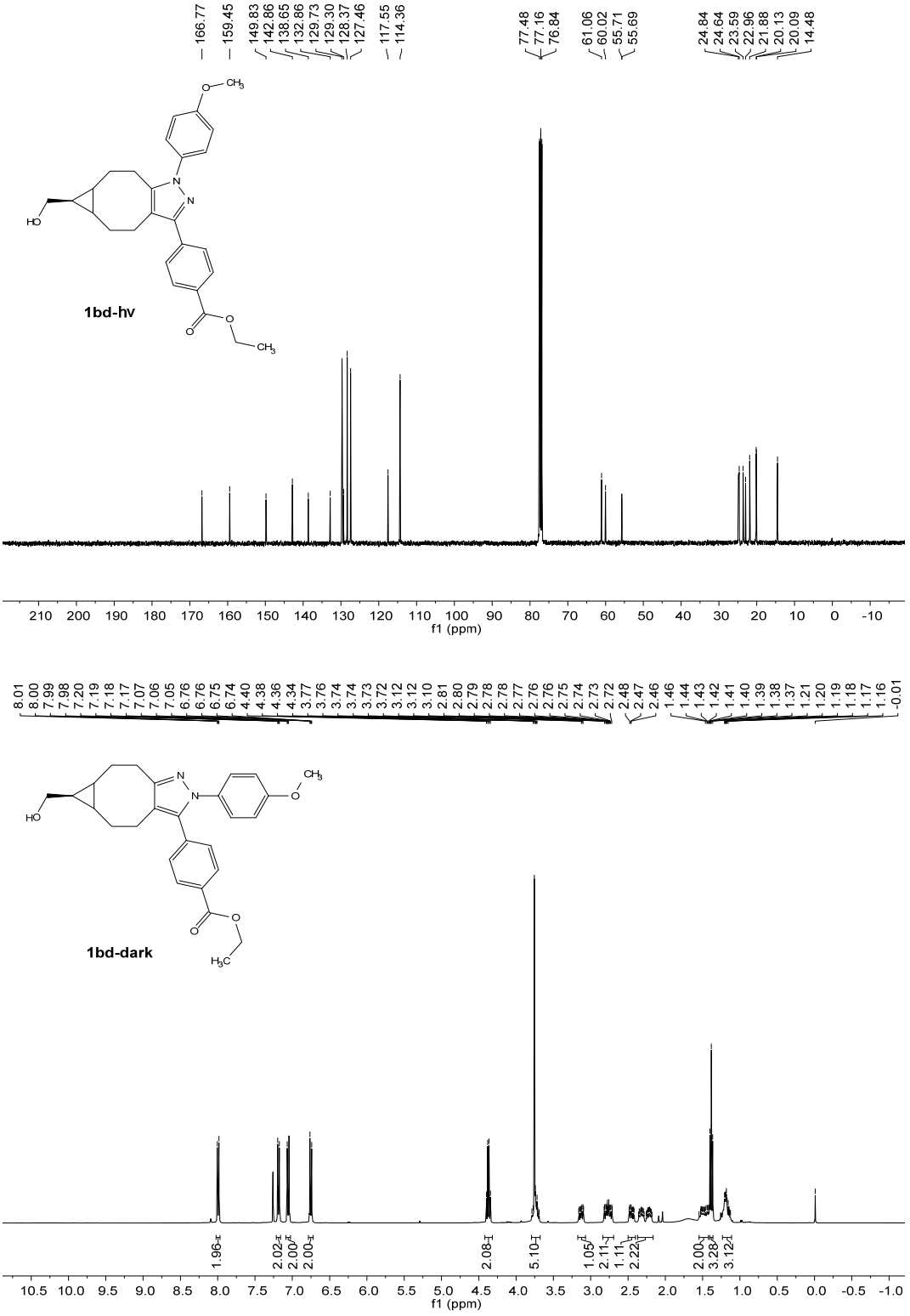

-62.74
-62.80
1ad-hv
-60.0 -60.5 -61.0 -61.5 -62.0 -62.5 -63.0 -63.5 -64.0 -64.5 -65.0 -65.5 -66.0 -66.5 -67.0 -67.5 -68.0 -68.5
f1 (ppm)


7.81 7.55 7.55 7.54 7.06 7.06 7.05 7.04 6.82 6.81 6.80 6.80 3.79 3.78 3.77 3.76 3.75 3.74 3.16 3.14 3.13 3.12 3.11 2.85 2.84 2.82 2.82 2.81 2.80 2.79 2.73 2.72 2.71 2.70 2.53 2.52 2.51 2.50 1.54 1.53 1.52 1.51 1.50 1.49 1.49 1.48 1.47 1.46 1.45 1.26 1.25 1.23 1.22 1.21 1.20 1.19 1.18 1.16 -0.00
1ad-dark
1.00 1.98 1.98 2.01 5.18 1.11 2.31 1.16 2.28 2.09 3.18
f1 (ppm)


158.90 153.63 137.72 133.11 132.50 132.38 132.05 131.71 131.38 130.18 127.15 126.52 124.44 121.72 120.46 114.35
77.48 77.16 76.84
60.08 55.65 55.62
27.40 24.86 23.67 22.92 22.14 21.06 20.97
1ad-dark
f1 (ppm)


-62.74
-63.05
1ad-dark
-61.7 -61.9 -62.1 -62.3 -62.5 -62.7 -62.9 -63.1 -63.3 -63.5 -63.7 -63.9 -64.1 -64.3 -64.5 -64.7 -64.9 -65.1 -65.3
f1 (ppm)


1bd-hv
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)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132.86
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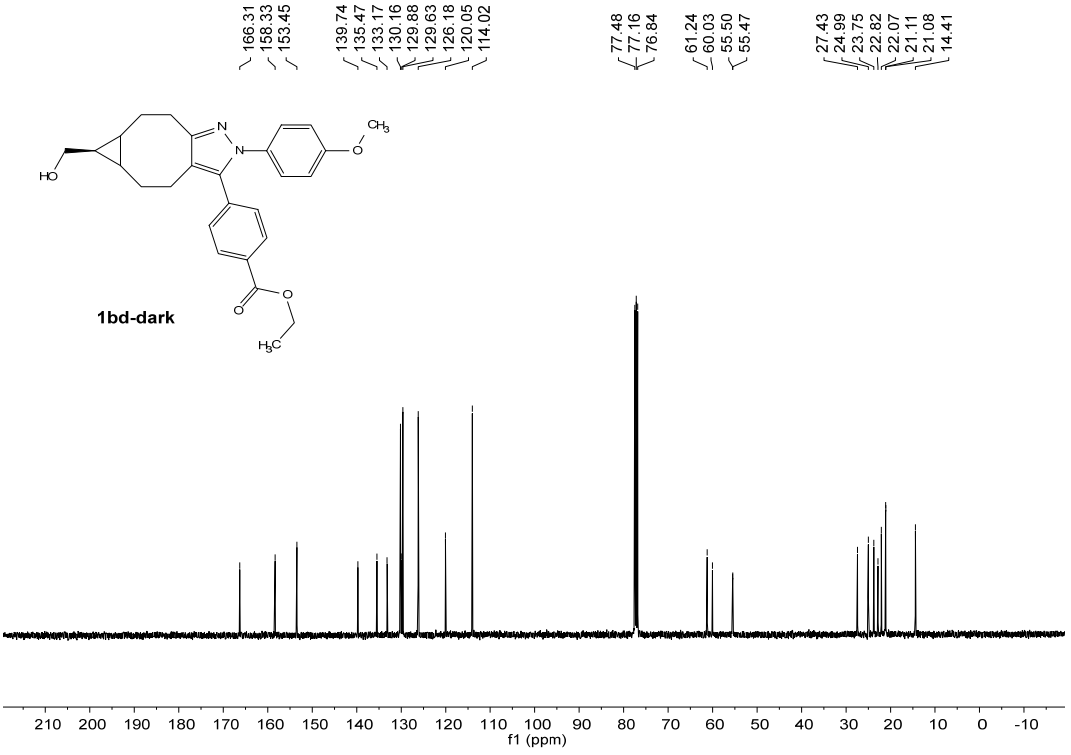
129.30
128.37
127.46
117.55
114.36
77.48
77.16
76.84
61.06
60.02
55.71
55.69
24.84
24.64
23.59
22.96
21.88
20.13
20.09
14.48
1bd-hv
f1 (ppm)
8.01
8.00
7.99
7.98
7.20
7.19
7.18
7.17
7.07
7.06
7.05
6.76
6.76
6.75
6.74
4.40
4.38
4.36
4.34
3.77
3.76
3.74
3.74
3.73
3.72
3.12
3.12
3.10
2.81
2.80
2.79
2.78
2.78
2.77
2.76
2.76
2.75
2.74
2.73
2.72
2.48
2.47
2.46
1.46
1.44
1.43
1.42
1.41
1.40
1.39
1.38
1.37
1.21
1.20
1.19
1.18
1.17
1.16
-0.01
1bd-dark
1.96
2.02
2.00
2.00
2.08
5.10
1.05
2.11
1.11
2.22
2.00
3.28
3.12
f1 (ppm)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133.17
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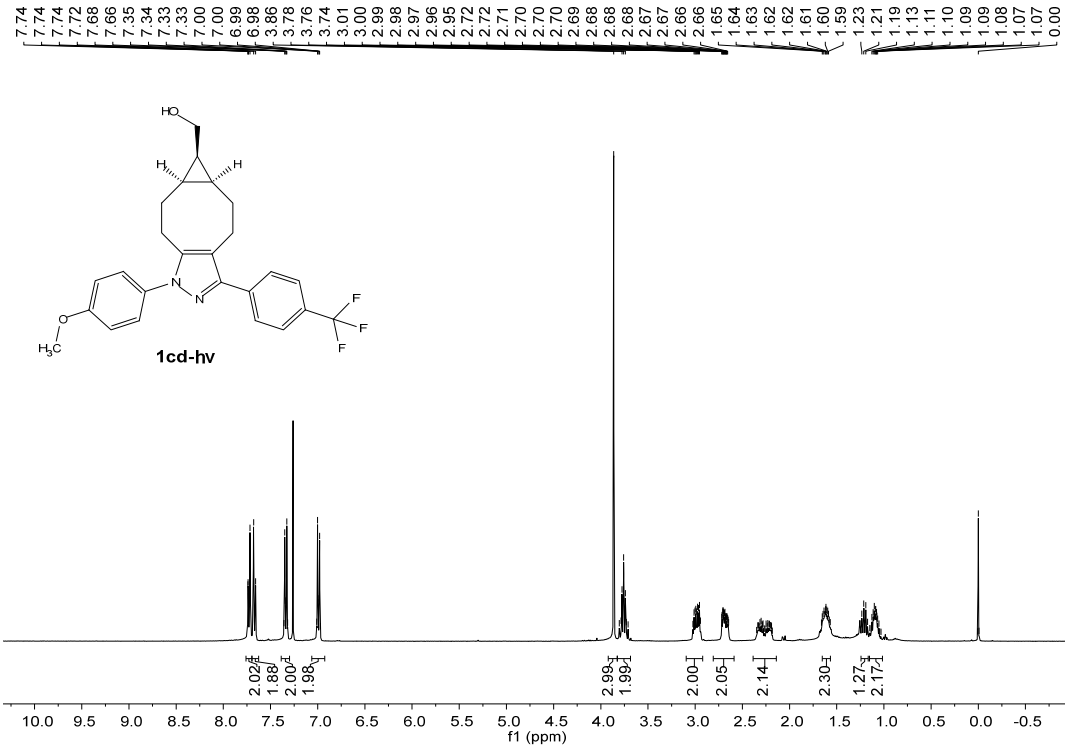
129.88
129.63
126.18
120.05
114.02
77.48
77.16
76.84
61.24
60.03
55.50
55.47
27.43
24.99
23.75
22.82
22.07
21.11
21.08
14.41
1bd-dark
f1 (ppm)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7.00
6.99
6.98
3.86
3.78
3.76
3.74
3.01
3.00
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2.67
2.67
2.66
2.66
1.65
1.64
1.63
1.62
1.62
1.61
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1.59
1.23
1.21
1.19
1.13
1.11
1.10
1.09
1.09
1.08
1.07
1.07
0.00
1cd-hv
2.02
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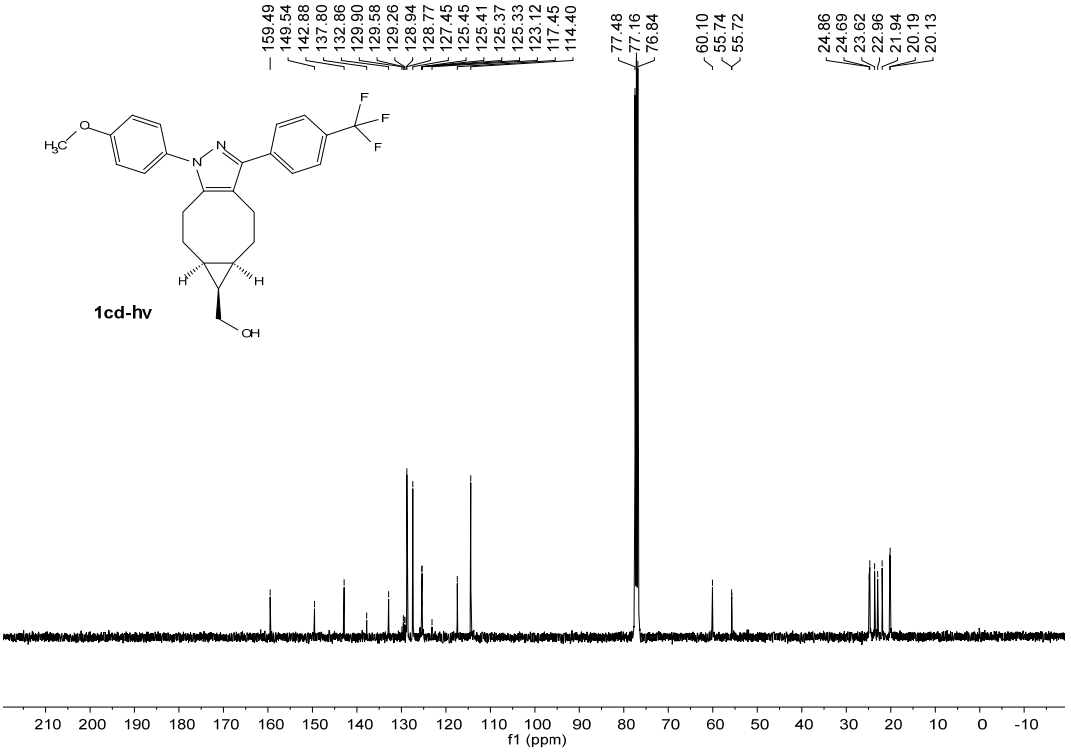
2.99
1.99
2.00
2.05
2.14
2.30
1.27
2.17
f1 (ppm)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132.86
129.90
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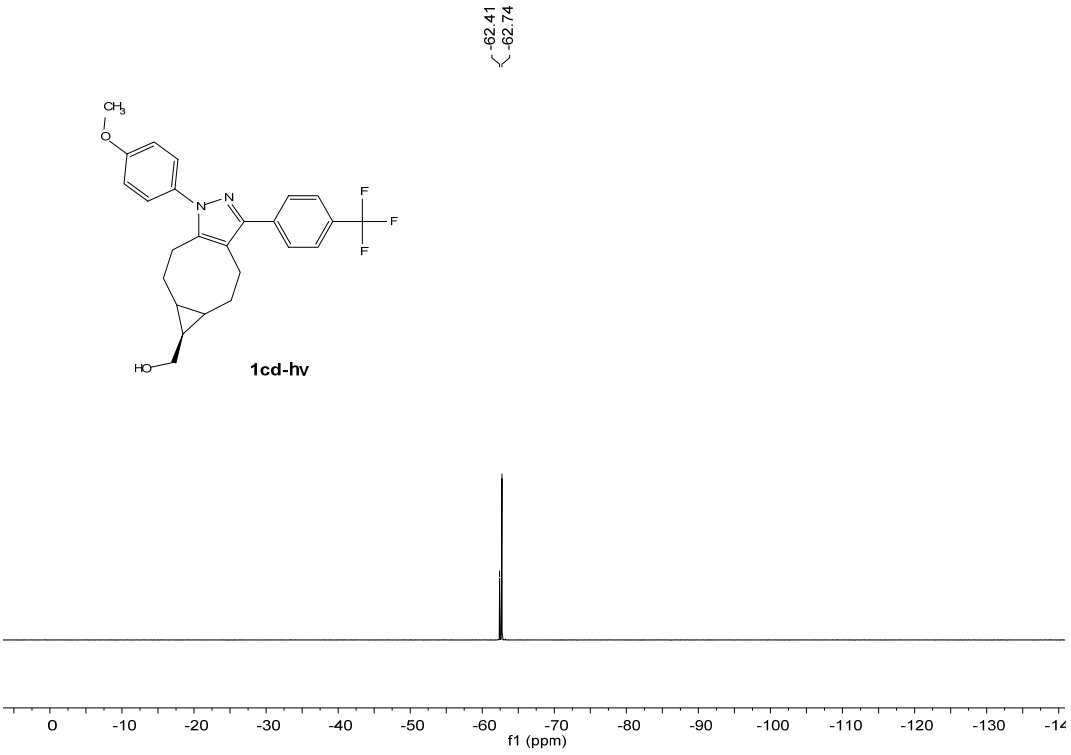
129.26
128.94
128.77
127.45
125.45
125.41
125.37
125.33
123.12
117.45
114.40
77.48
77.16
76.84
60.10
55.74
55.72
24.86
24.69
23.62
22.96
21.94
20.19
20.13
1cd-hv
f1 (ppm)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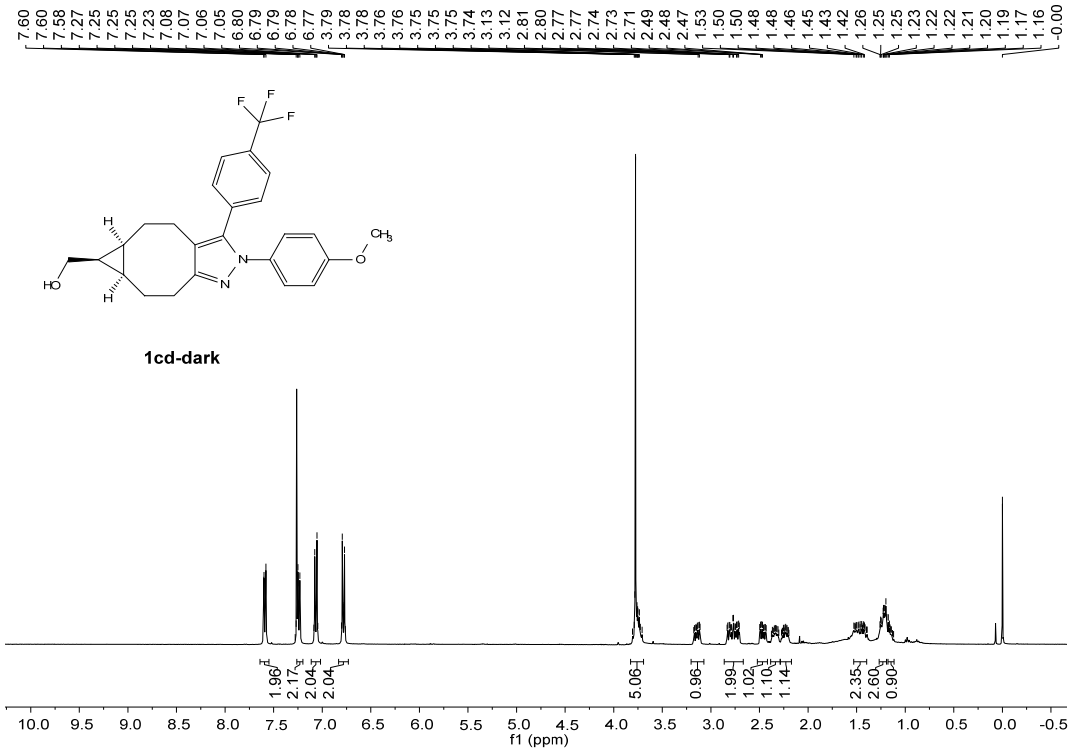
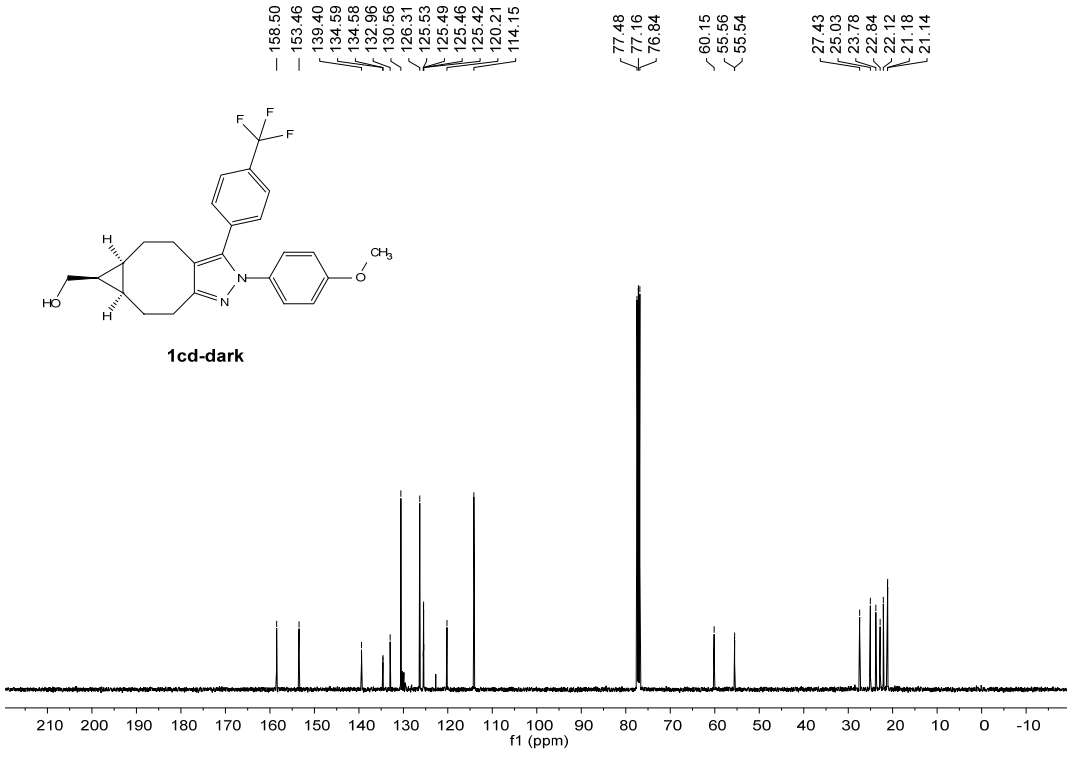
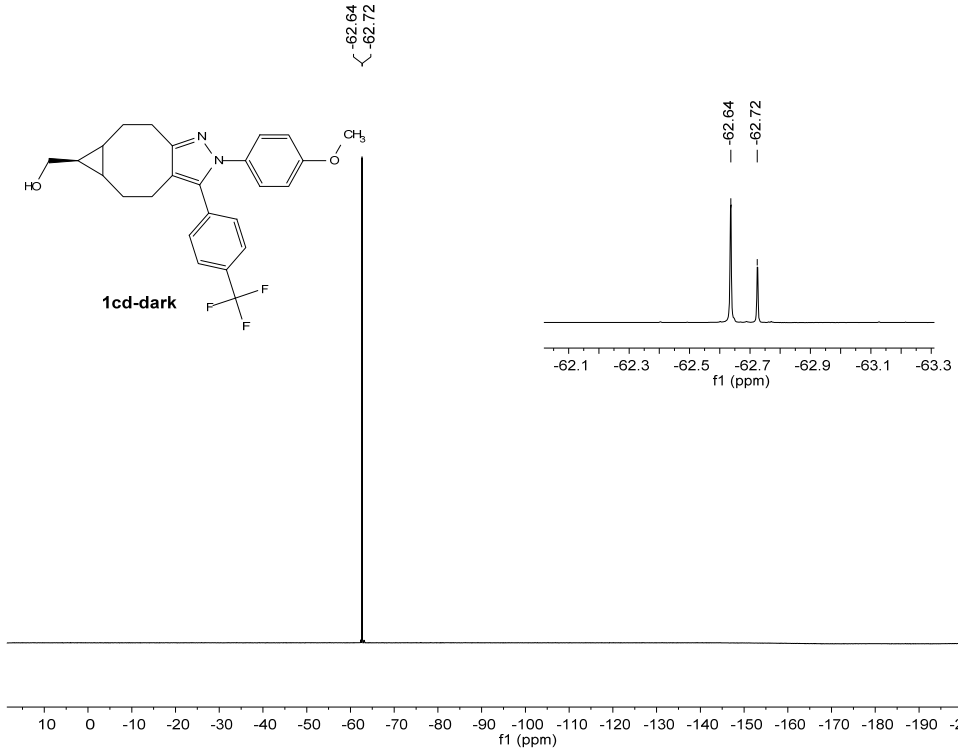
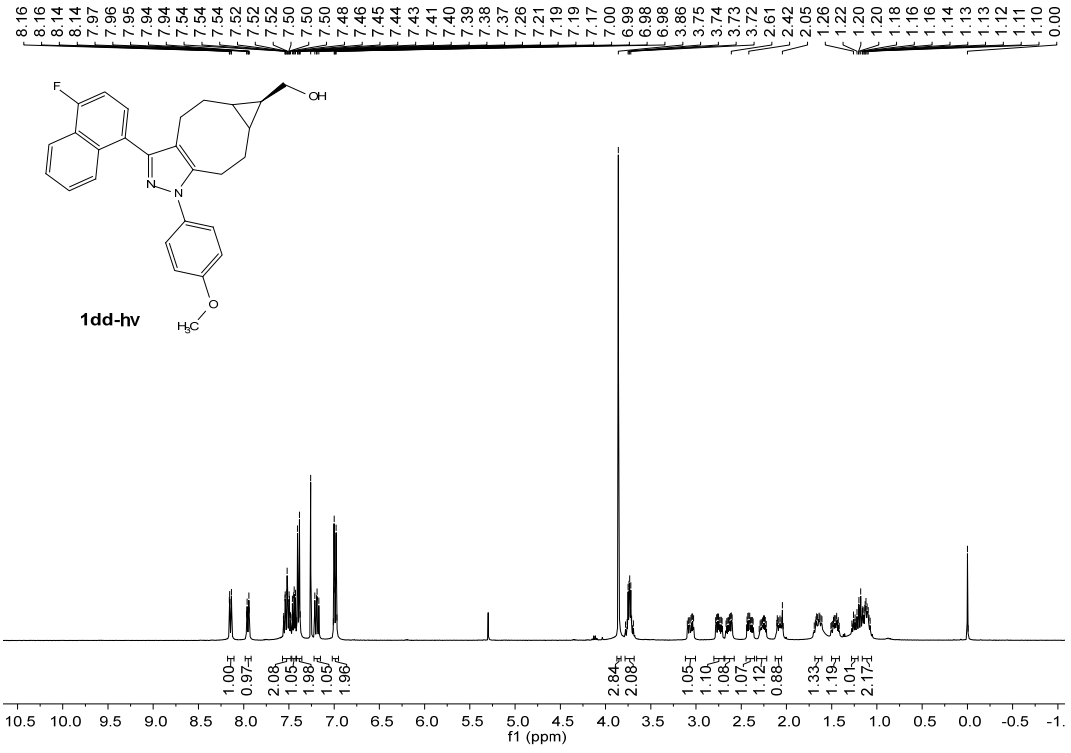
-62.74
1cd-hv
f1 (ppm)


1cd-dark
f1 (ppm)


1cd-dark
f1 (ppm)


-62.64
-62.72
HO
N
N
O
CH3
F
F
F
1cd-dark
-62.64
-62.72
-62.1
-62.3
-62.5
-62.7
-62.9
-63.1
-63.3
f1 (ppm)
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)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7.21
7.19
7.19
7.17
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6.99
6.98
6.98
3.86
3.75
3.74
3.73
3.72
2.61
2.42
2.05
1.26
1.22
1.20
1.20
1.18
1.16
1.16
1.14
1.13
1.12
1.11
1.10
0.00
F
OH
N
N
O
H3C
1dd-hv
1.00
0.97
2.08
1.05
1.98
1.05
1.96
2.84
2.08
1.05
1.10
1.08
1.07
1.12
0.88
1.33
1.19
1.01
2.17
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
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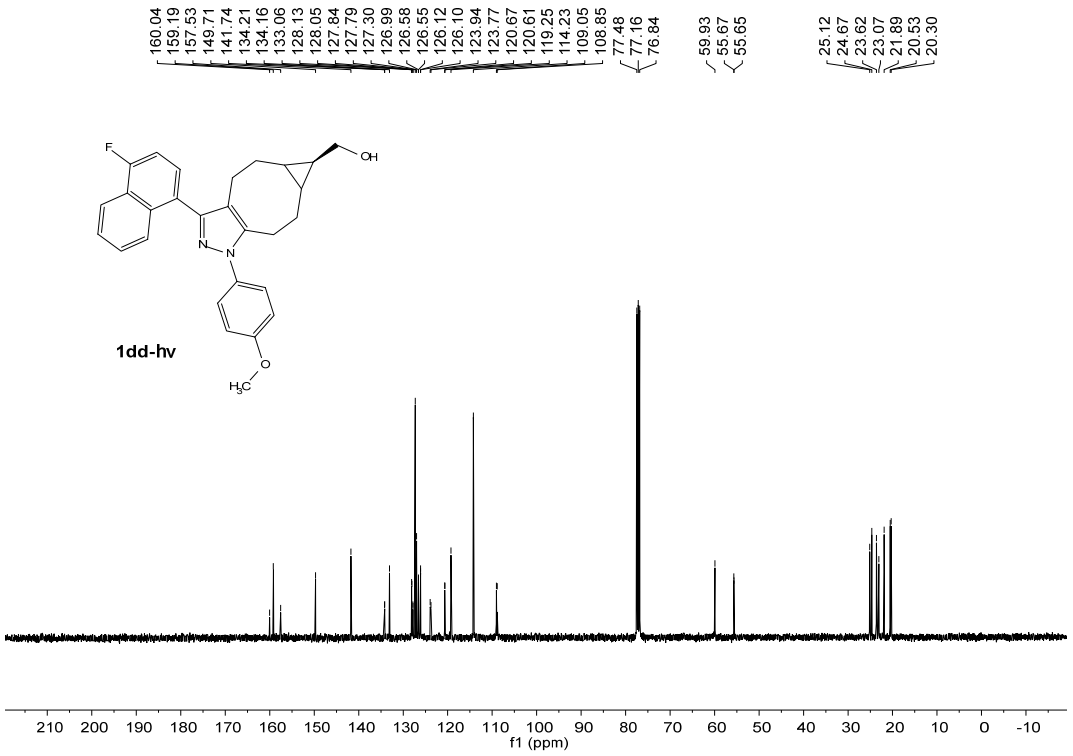
f1 (ppm)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126.58
126.55
126.12
126.10
123.94
123.77
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119.25
114.23
109.05
108.85
77.48
77.16
76.84
59.93
55.67
55.65
25.12
24.67
23.62
23.07
21.89
20.53
20.30
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OH
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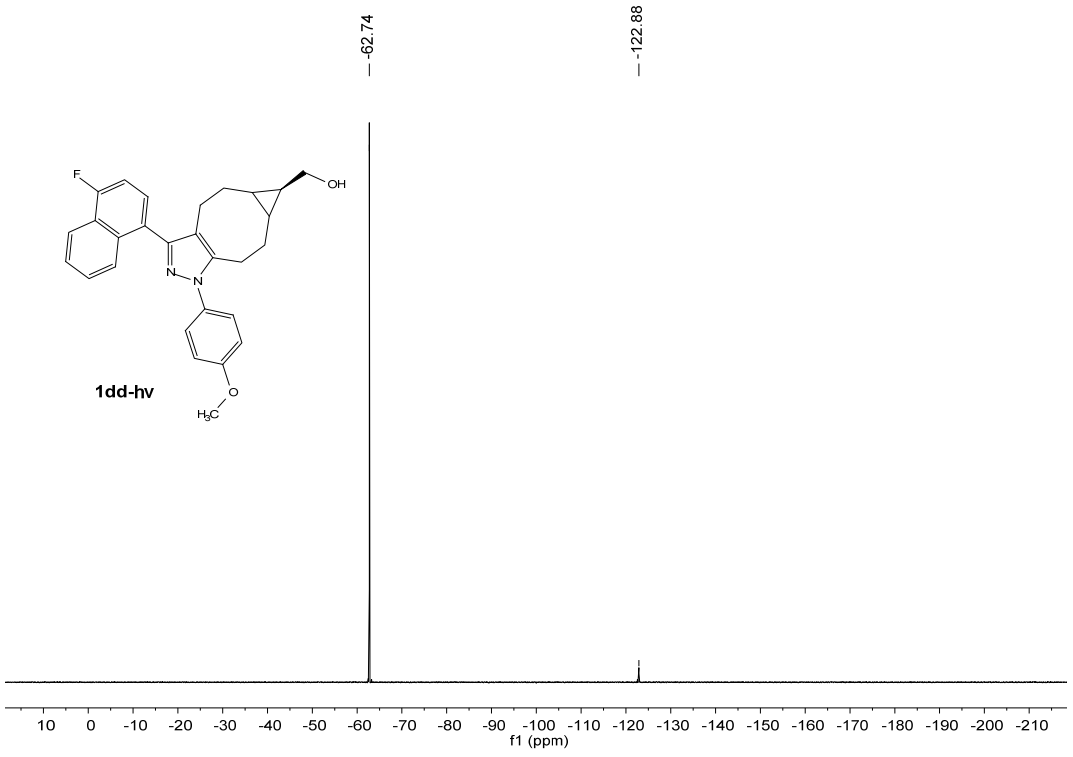
N
O
H3C
1dd-hv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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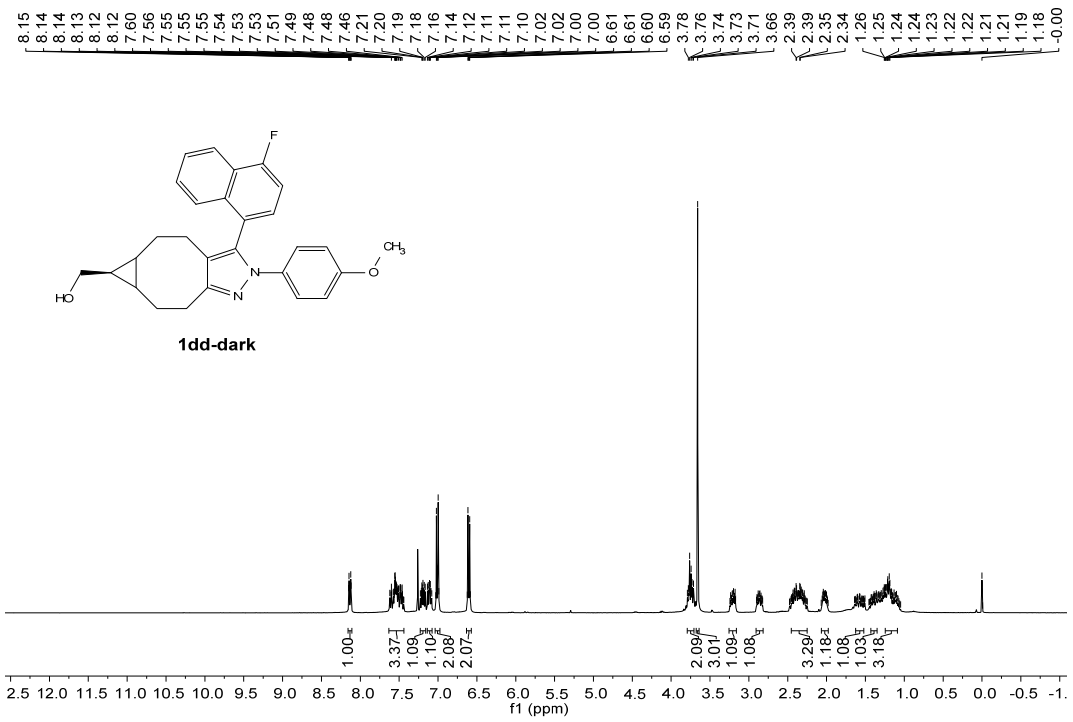
-122.88
F
OH
N
N
O
H3C
1dd-hv
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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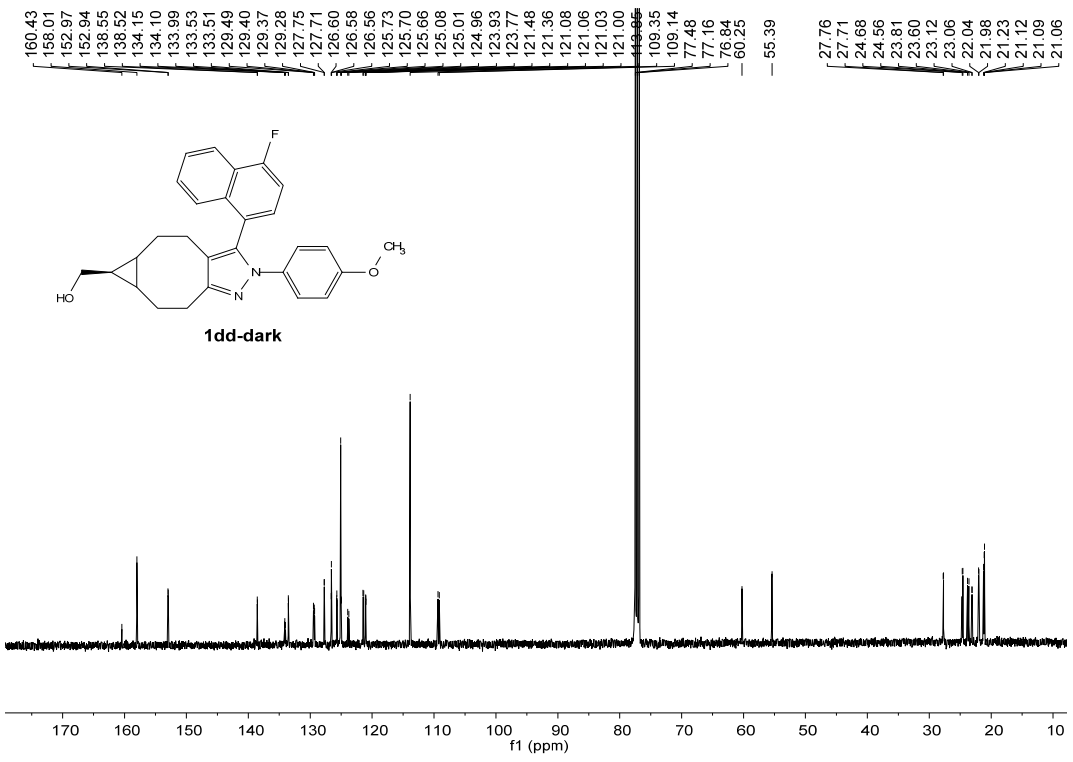
F
CH3
O
N
N
HO
1dd-dark
1.00 3.37 1.09 1.10 2.08 2.07 2.09 3.01 1.09 1.08 3.29 1.18 1.08 1.03 3.18 1
2.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)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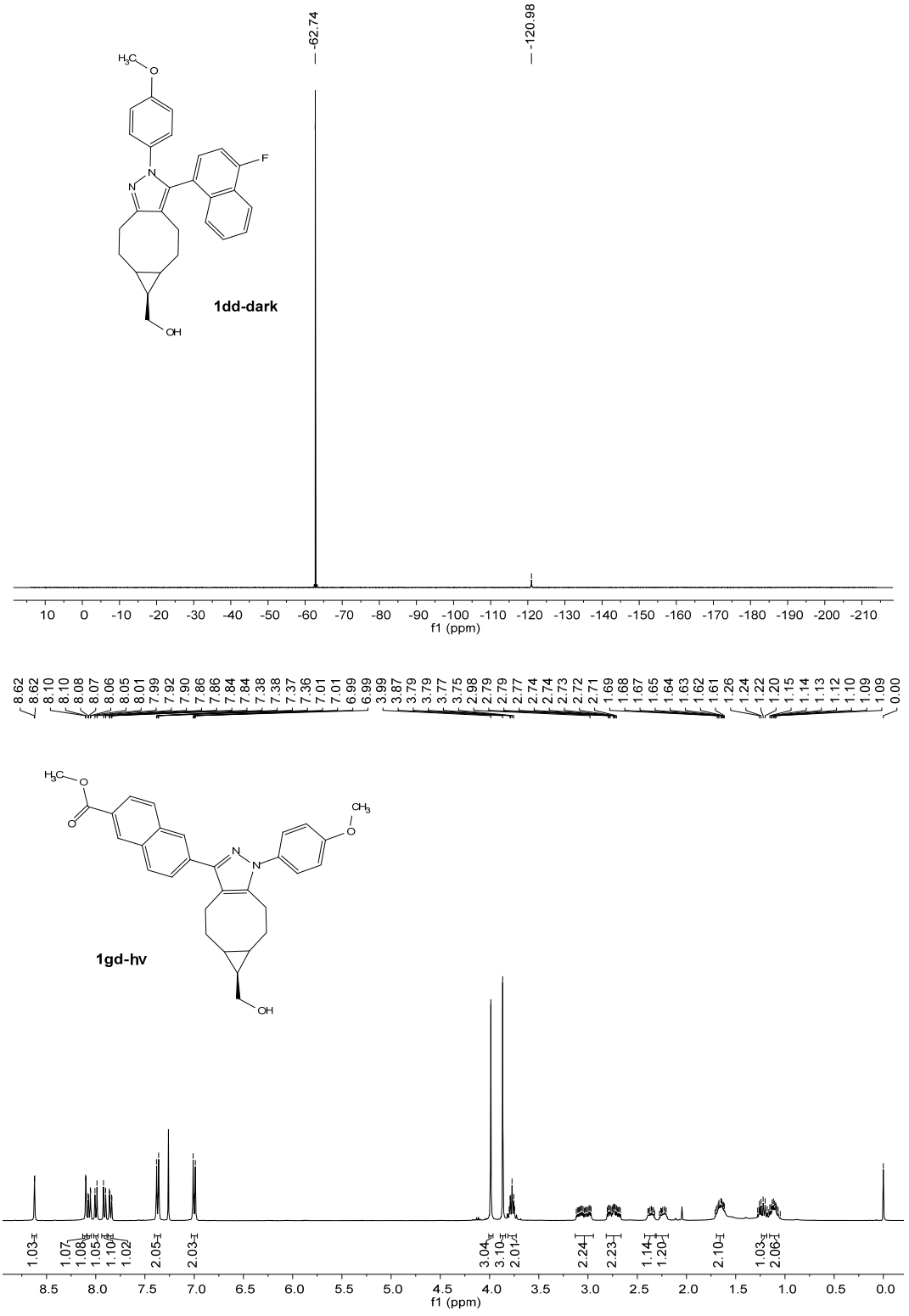
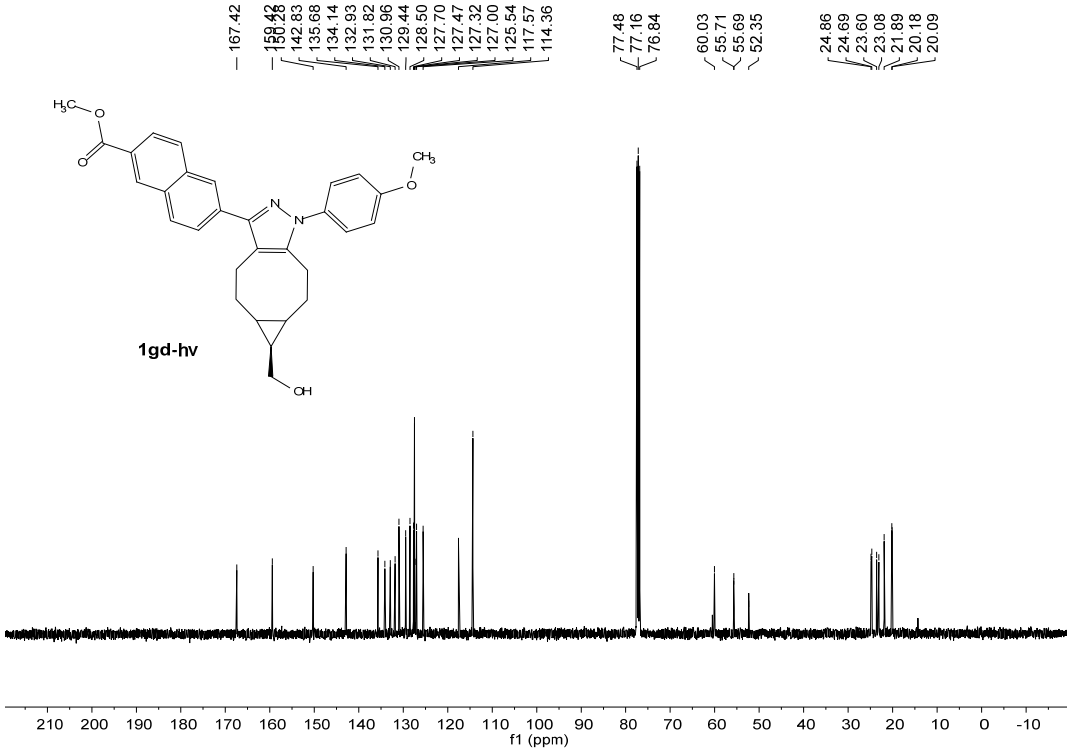
F
CH3
O
N
N
HO
1dd-dark
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-62.74
-120.98
1dd-dark
f1 (ppm)
1gd-hv
f1 (ppm)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127.47
127.32
127.00
125.54
117.57
114.36
77.48
77.16
76.84
60.03
55.71
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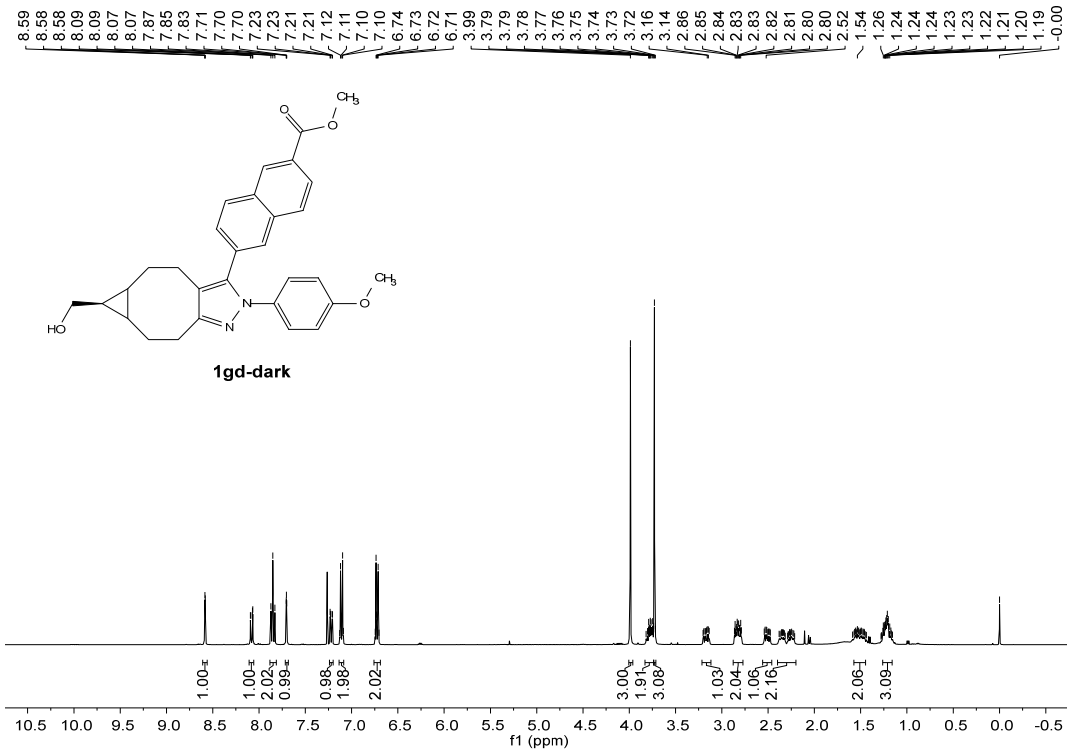
20.18
20.09
1gd-hv
f1 (ppm)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7.70
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7.23
7.21
7.21
7.12
7.11
7.10
7.10
6.74
6.73
6.72
6.71
3.99
3.79
3.79
3.78
3.77
3.76
3.75
3.74
3.73
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3.14
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2.83
2.82
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2.80
2.80
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1.54
1.26
1.24
1.24
1.24
1.23
1.23
1.22
1.21
1.20
1.19
-0.00
1.00
1.00
2.02
0.99
0.98
1.98
2.02
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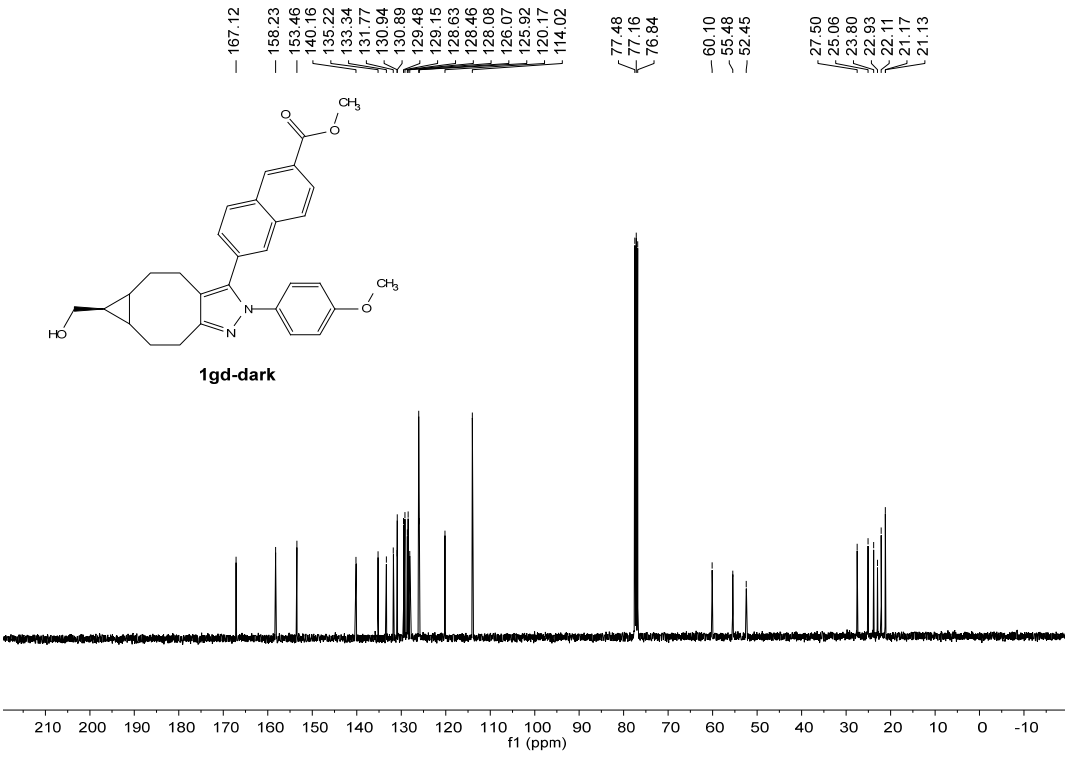
3.08
1.03
2.04
1.06
2.16
2.06
3.09
1gd-dark
f1 (ppm)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128.08
126.07
125.92
120.17
114.02
77.48
77.16
76.84
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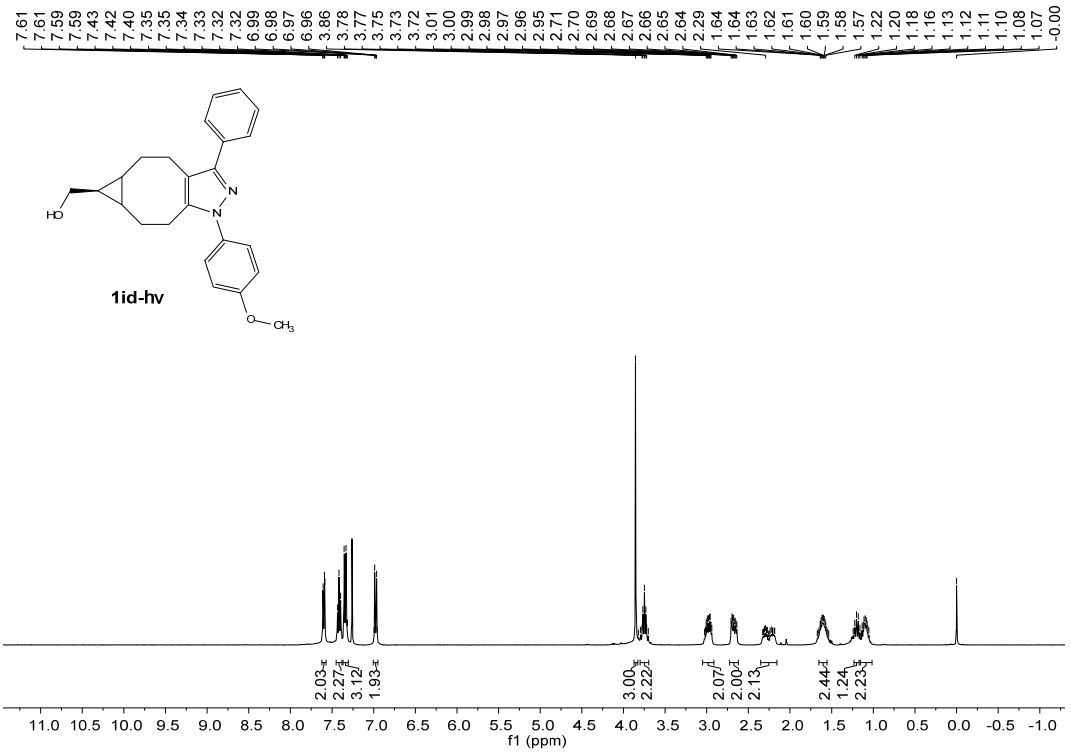
23.80
22.93
22.11
21.17
21.13
1gd-dark
f1 (ppm)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2.64
2.29
1.64
1.64
1.63
1.62
1.61
1.60
1.59
1.58
1.57
1.22
1.20
1.18
1.16
1.13
1.12
1.11
1.10
1.08
1.07
-0.00
1id-hv
2.03
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3.12
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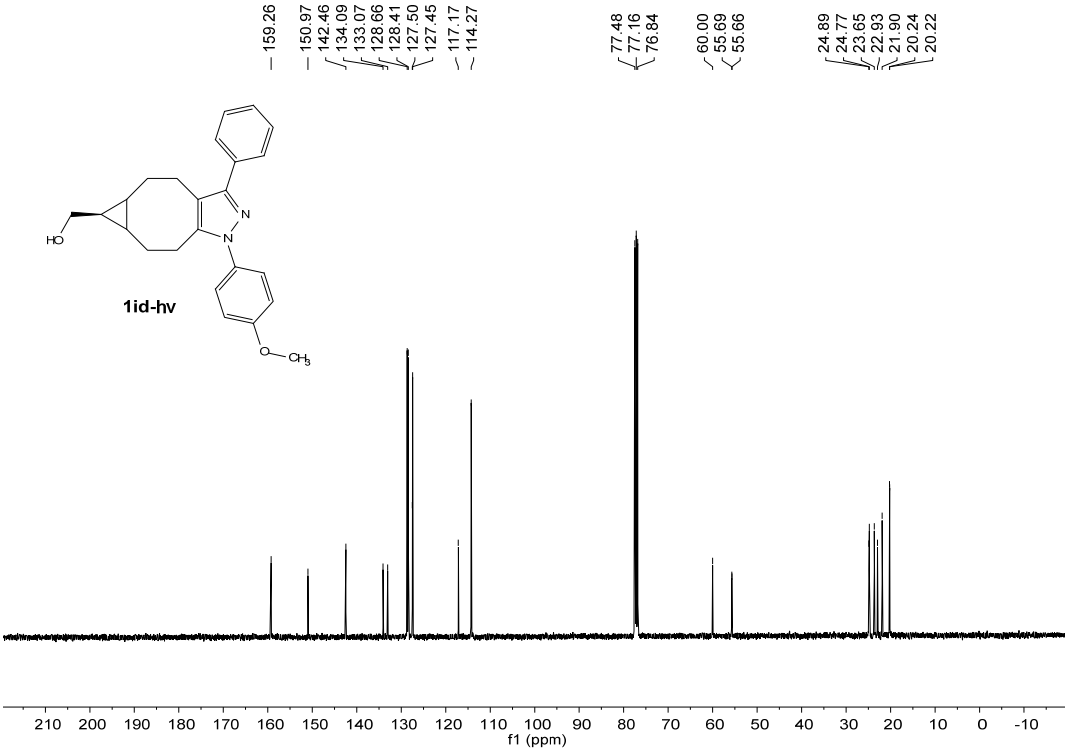
2.07
2.00
2.13
2.44
1.24
2.23
f1 (ppm)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117.17
114.27
77.48
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76.84
60.00
55.69
55.66
24.89
24.77
23.65
22.93
21.90
20.24
20.22
HO
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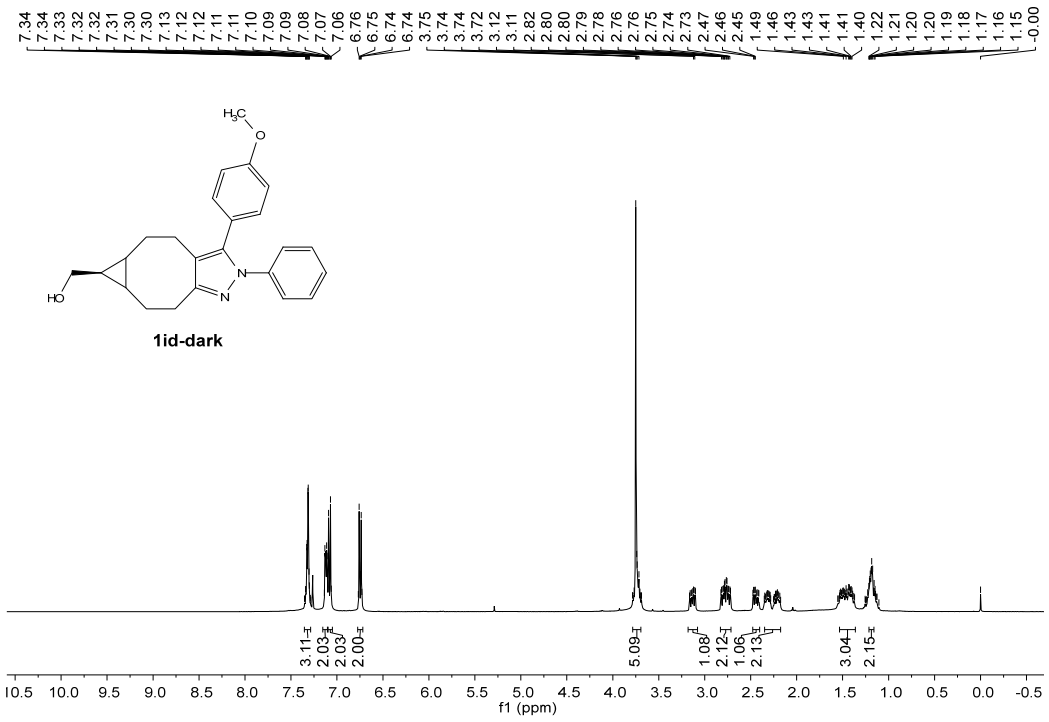
N
O
CH3
1id-hv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.74
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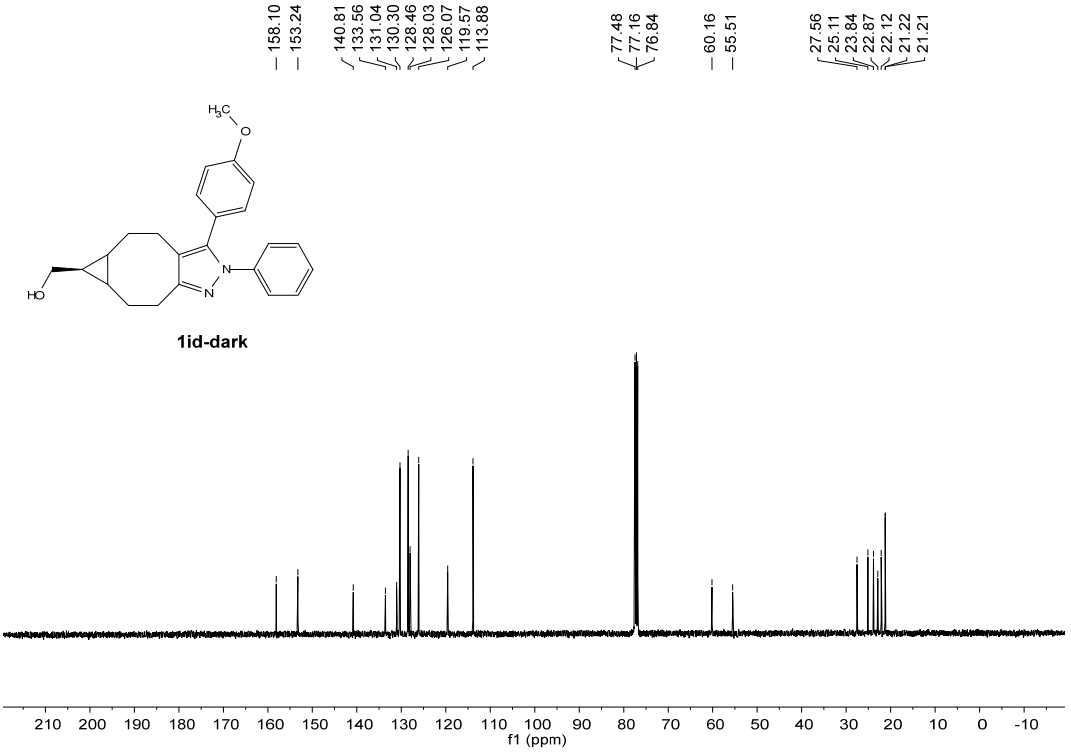
1.46
1.43
1.43
1.41
1.41
1.40
1.22
1.21
1.20
1.20
1.19
1.18
1.17
1.16
1.15
-0.00
H3C
O
HO
N
N
1id-dark
3.11
2.03
2.03
2.00
5.09
1.08
2.12
1.06
2.13
3.04
2.15
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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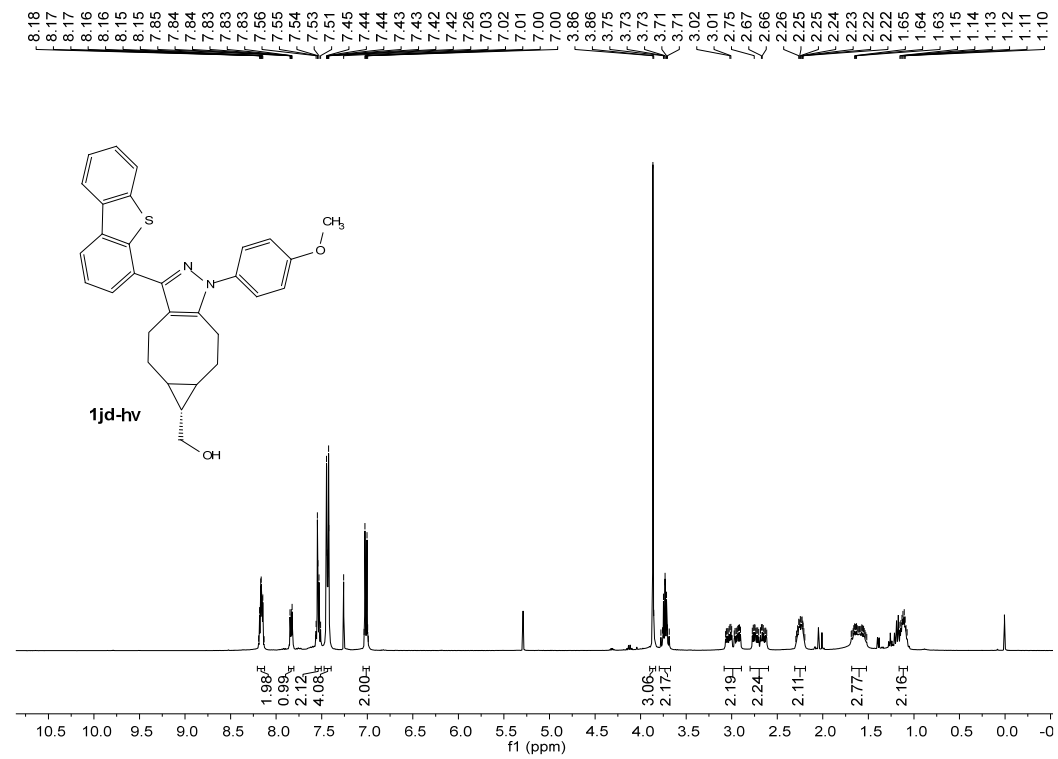
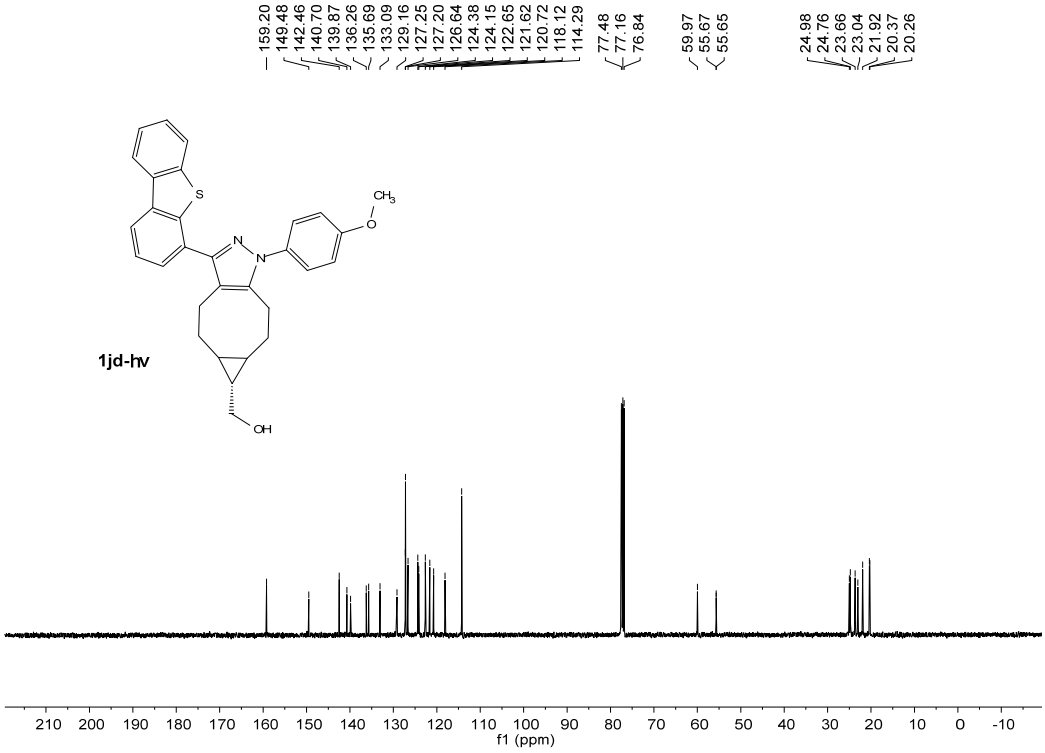
23.84
22.87
22.12
21.22
21.21
1id-dark
f1 (ppm)


1jd-hv
f1 (ppm)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77.16
76.84
59.97
55.67
55.65
24.98
24.76
23.66
23.04
21.92
20.37
20.26
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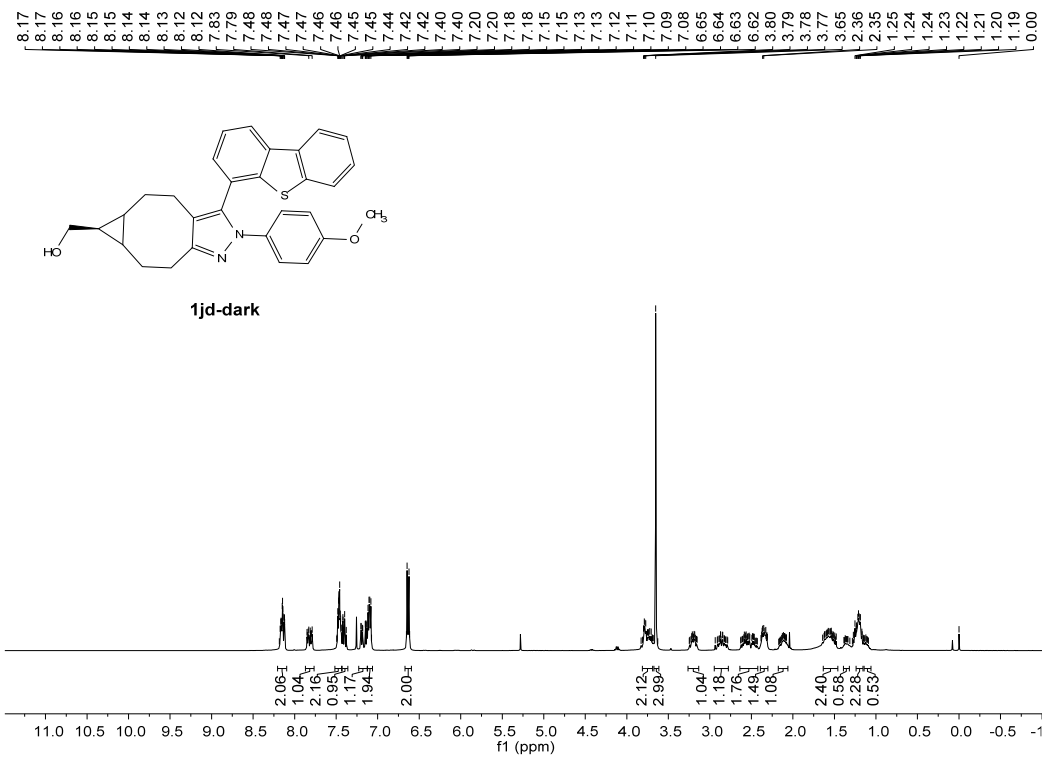
O
CH3
OH
1jd-hv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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7.18
7.15
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3.77
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2.35
1.25
1.24
1.24
1.23
1.22
1.21
1.20
1.19
0.00
S
N
N
O
CH3
HO
1jd-dark
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1.94
2.00
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1.04
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1.49
1.08
2.40
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2.28
0.53
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
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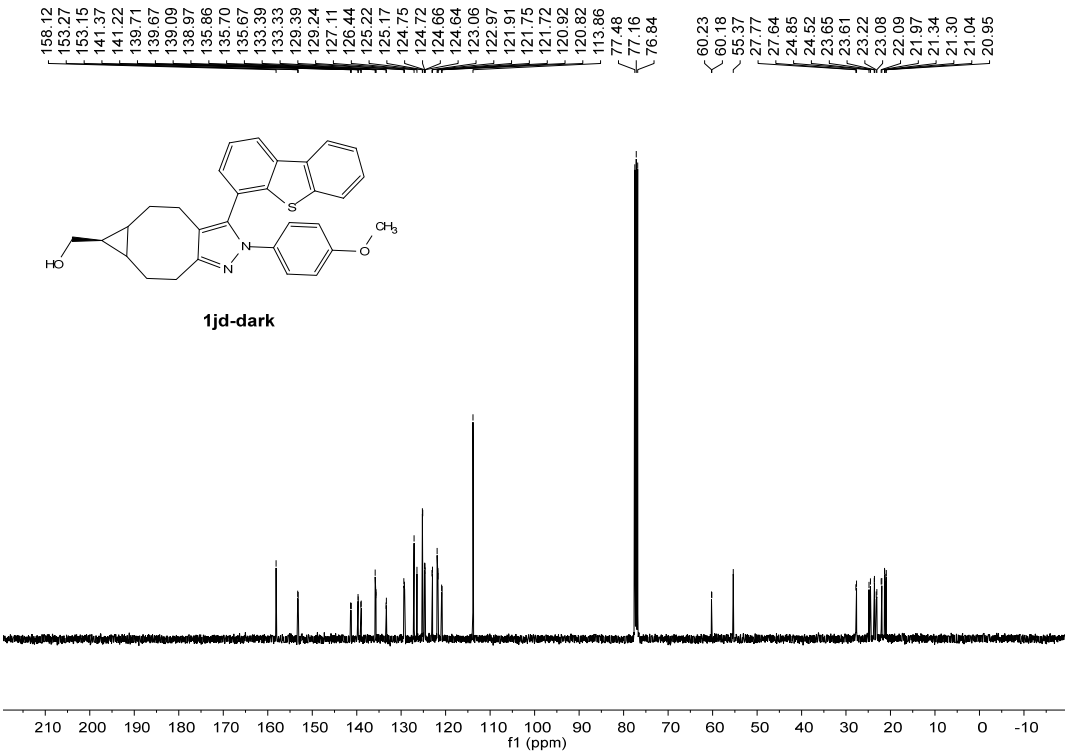
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123.06
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120.82
113.86
77.48
77.16
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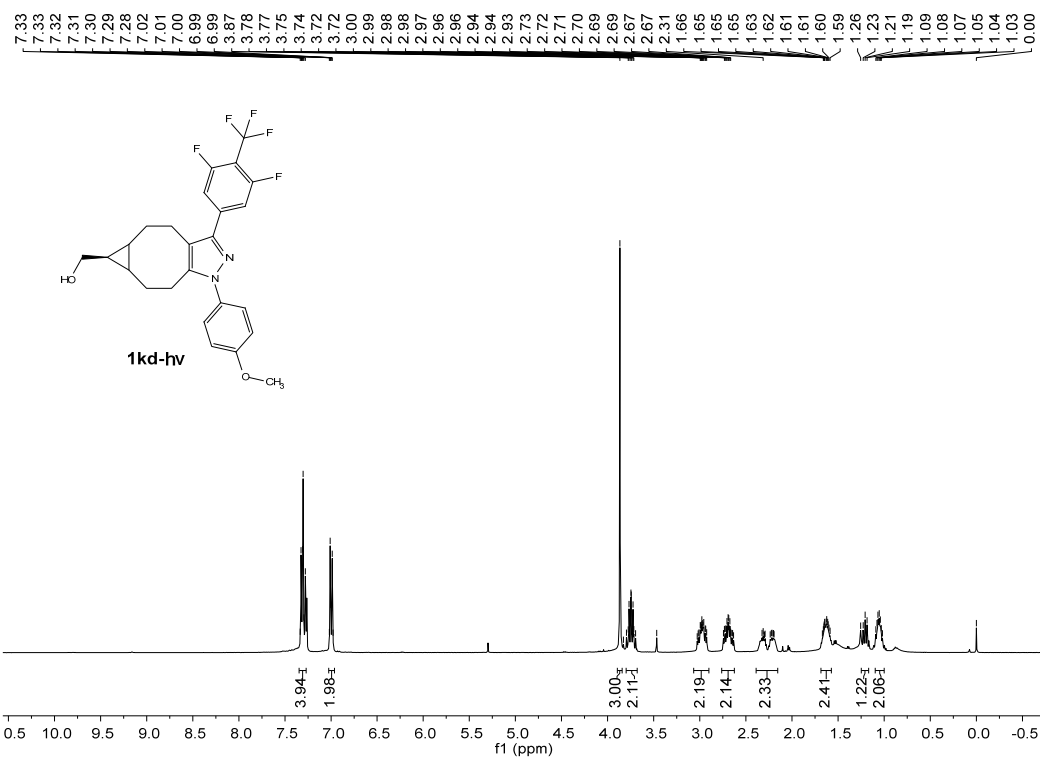
23.65
23.61
23.22
23.08
22.09
21.97
21.34
21.30
21.04
20.95
HO
S
N
N
O
CH3
1jd-dark
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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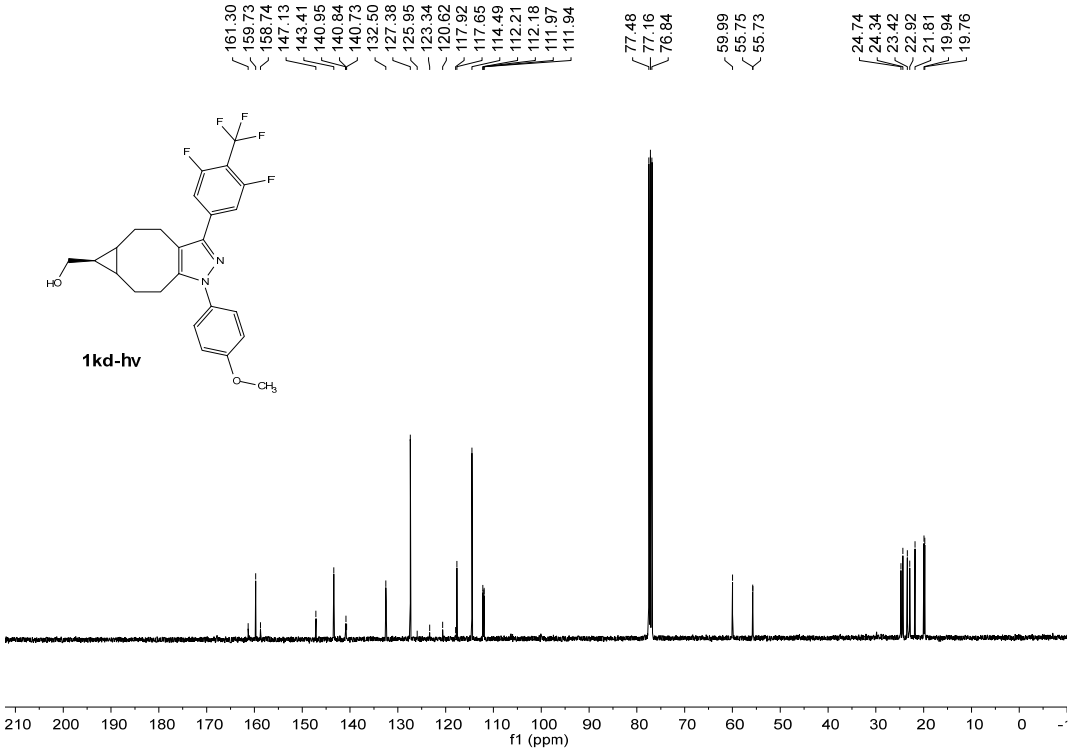
1.26
1.23
1.21
1.19
1.09
1.08
1.07
1.05
1.04
1.03
0.00
F
F
F
F
F
HO
N
N
O
CH3
1kd-hv
3.94
1.98
3.00
2.11
2.19
2.14
2.33
2.41
1.22
2.06
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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123.34
120.62
117.92
117.65
114.49
112.21
112.18
111.97
111.94
77.48
77.16
76.84
59.99
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24.34
23.42
22.92
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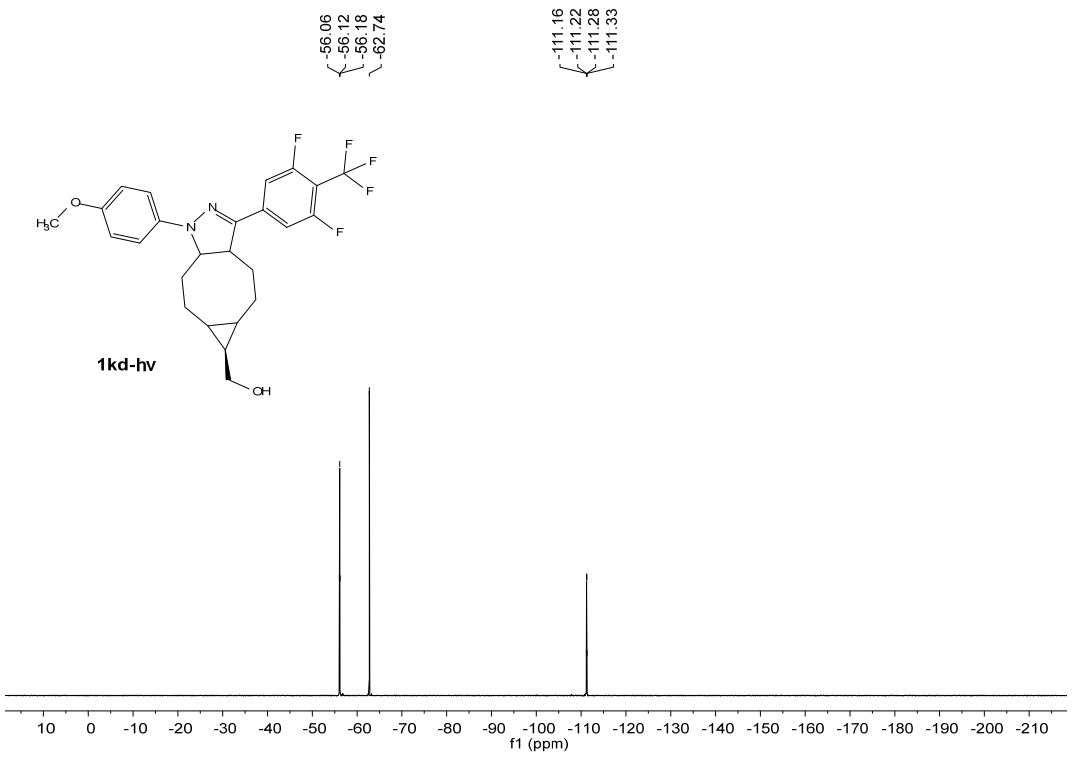
19.94
19.76
1kd-hv
f1 (ppm)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-111.16
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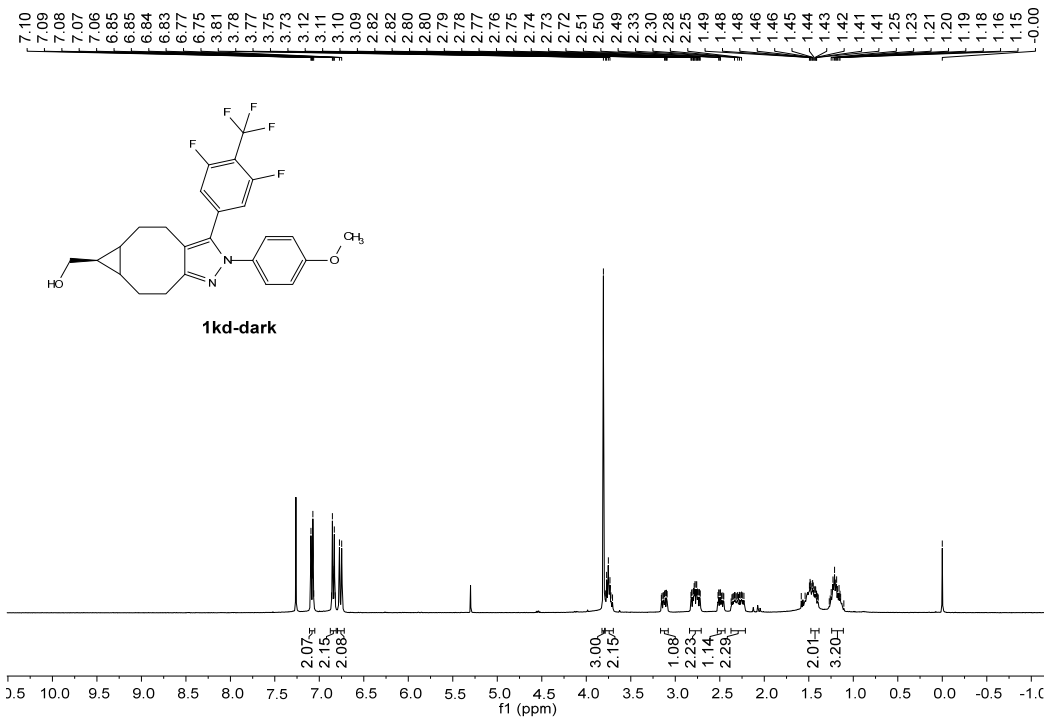
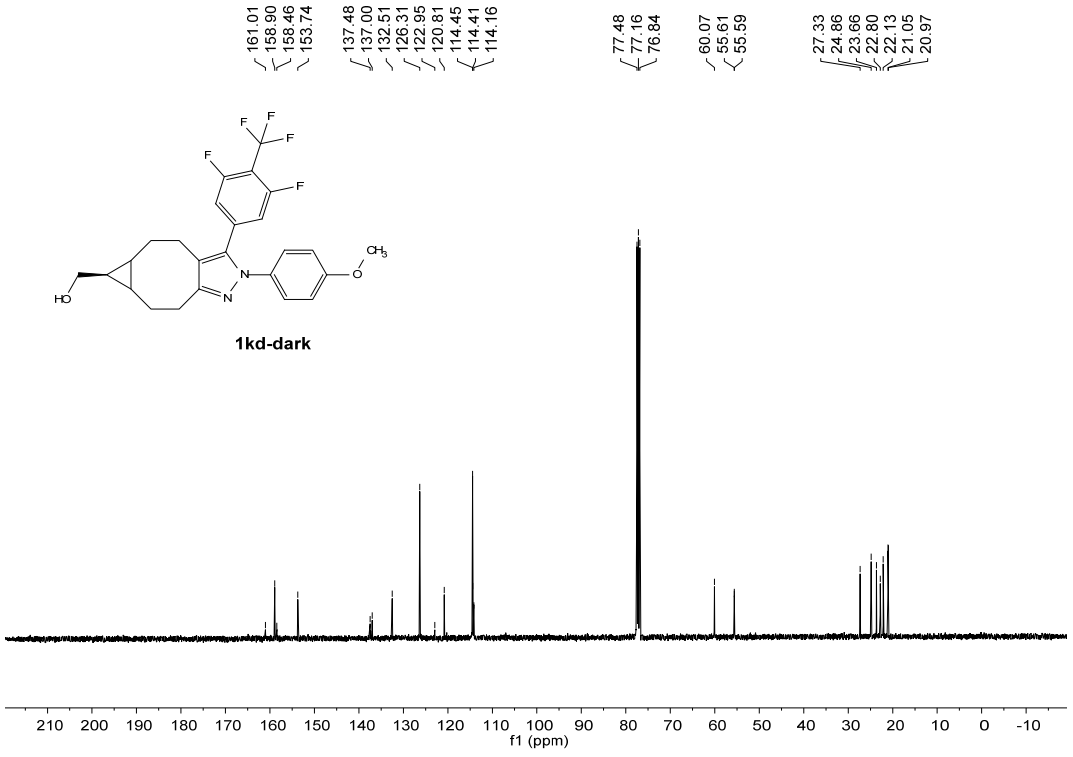
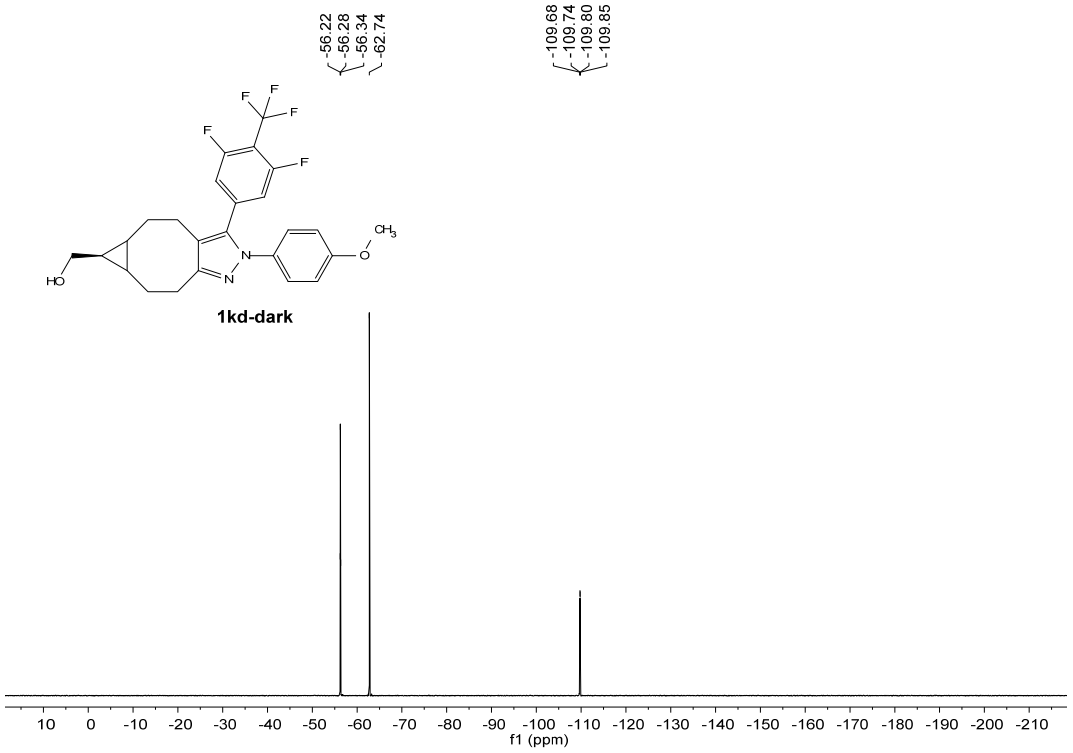
-111.28
-111.33
1kd-hv
f1 (ppm)


1kd-dark
f1 (ppm)


1kd-dark
f1 (ppm)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-109.68
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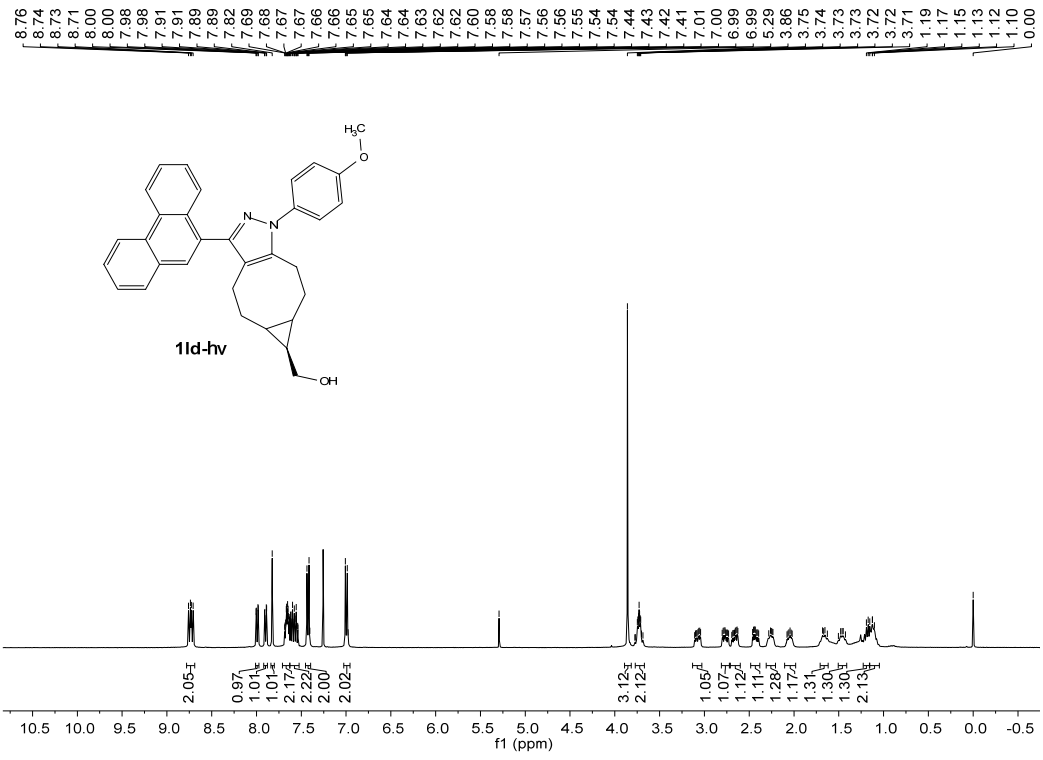
-109.80
-109.85
F
F
F
F
F
CH3
O
N
N
HO
1kd-dark
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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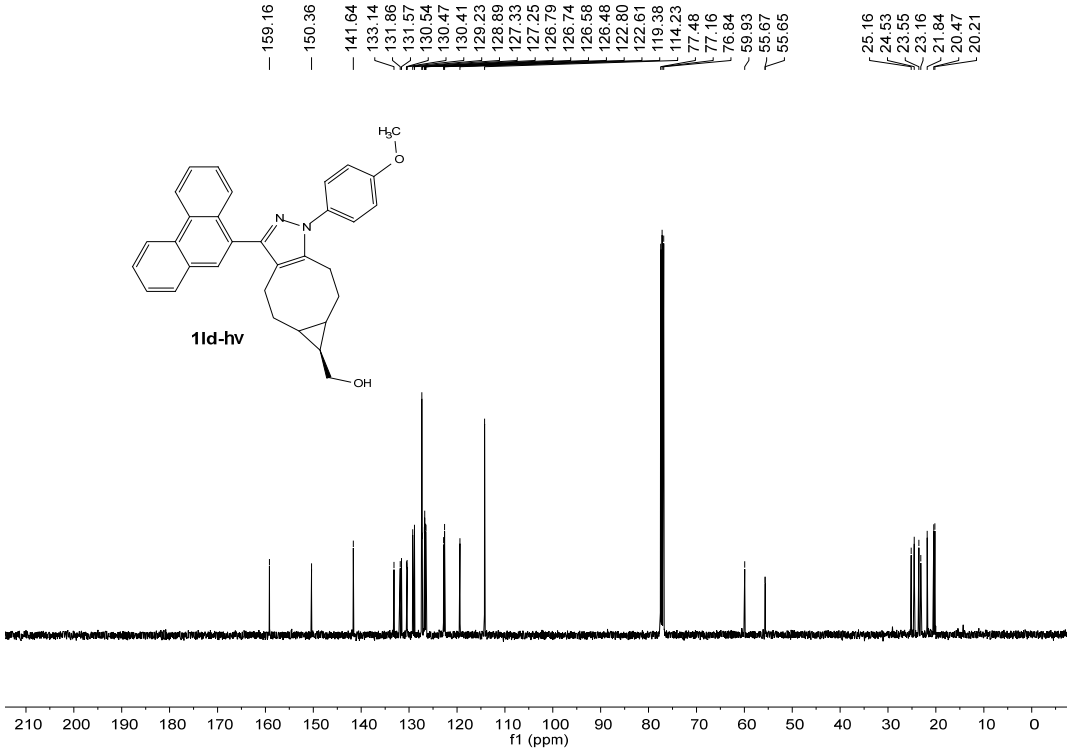
H3C
O
N
N
OH
1ld-hv
2.05 0.97 1.01 1.01 2.17 2.22 2.00 2.02 3.12 2.12 1.05 1.07 1.12 1.11 1.28 1.17 1.31 1.30 1.30 2.13
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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122.80
122.61
119.38
114.23
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77.16
76.84
59.93
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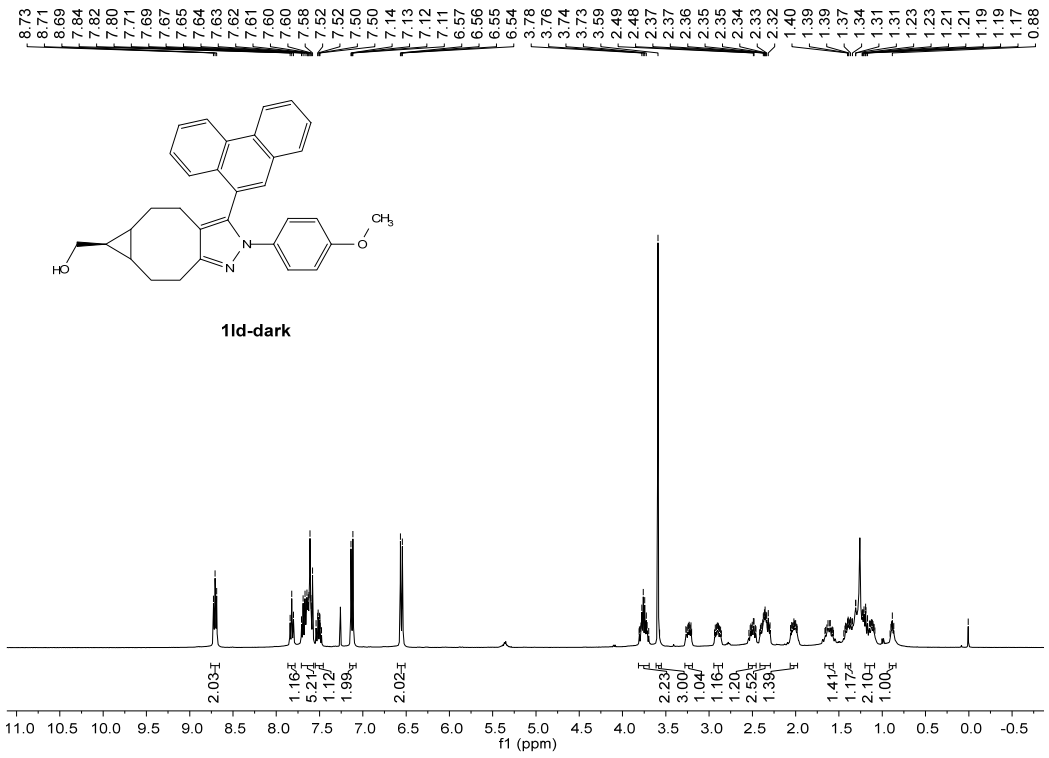
23.16
21.84
20.47
20.21
1ld-hv
f1 (ppm)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7.58
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7.52
7.50
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7.13
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6.55
6.54
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3.76
3.74
3.73
3.59
2.49
2.48
2.37
2.37
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2.35
2.34
2.33
2.32
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1.39
1.39
1.37
1.34
1.31
1.31
1.23
1.23
1.21
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1.19
1.19
1.17
0.88
1ld-dark
2.03
1.16
5.21
1.12
1.99
2.02
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1.16
1.20
2.52
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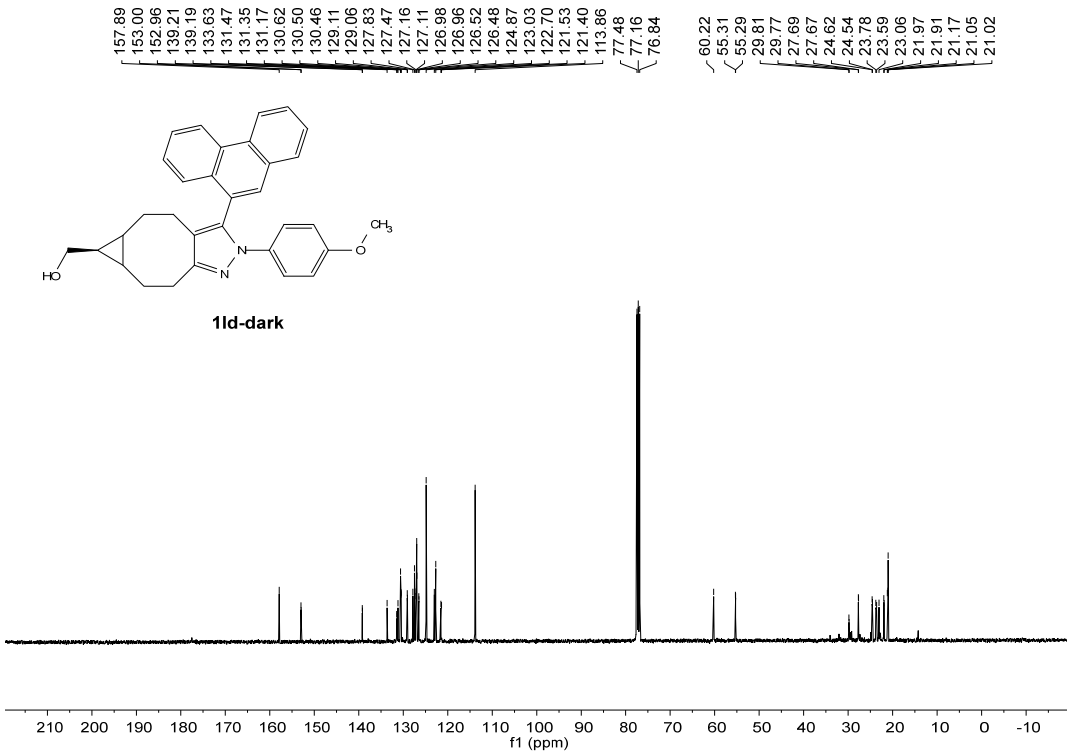
1.41
1.17
2.10
1.00
f1 (ppm)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127.47
127.16
127.11
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126.48
124.87
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122.70
121.53
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77.16
76.84
60.22
55.31
55.29
29.81
29.77
27.69
27.67
24.62
24.54
23.78
23.59
23.06
21.97
21.91
21.17
21.05
21.02
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N
O
CH3
1ld-dark
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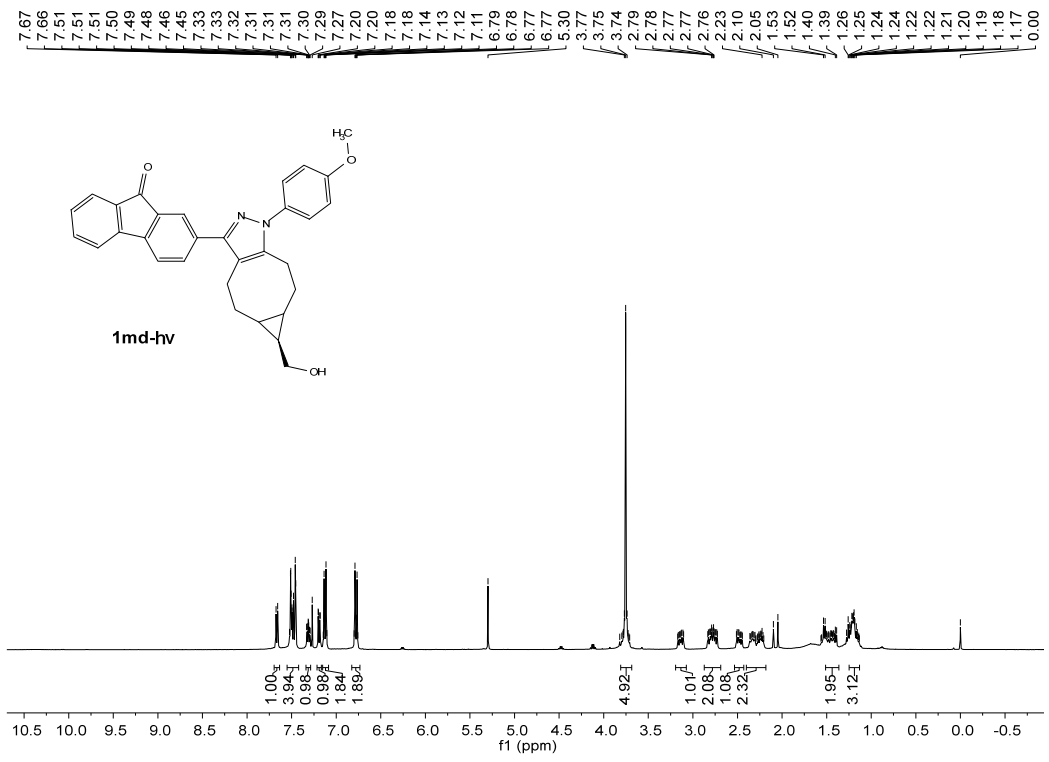
f1 (ppm)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2.77
2.77
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1.25
1.24
1.24
1.22
1.22
1.21
1.20
1.19
1.18
1.17
0.00
H3C
O
O
N
N
OH
1md-hv
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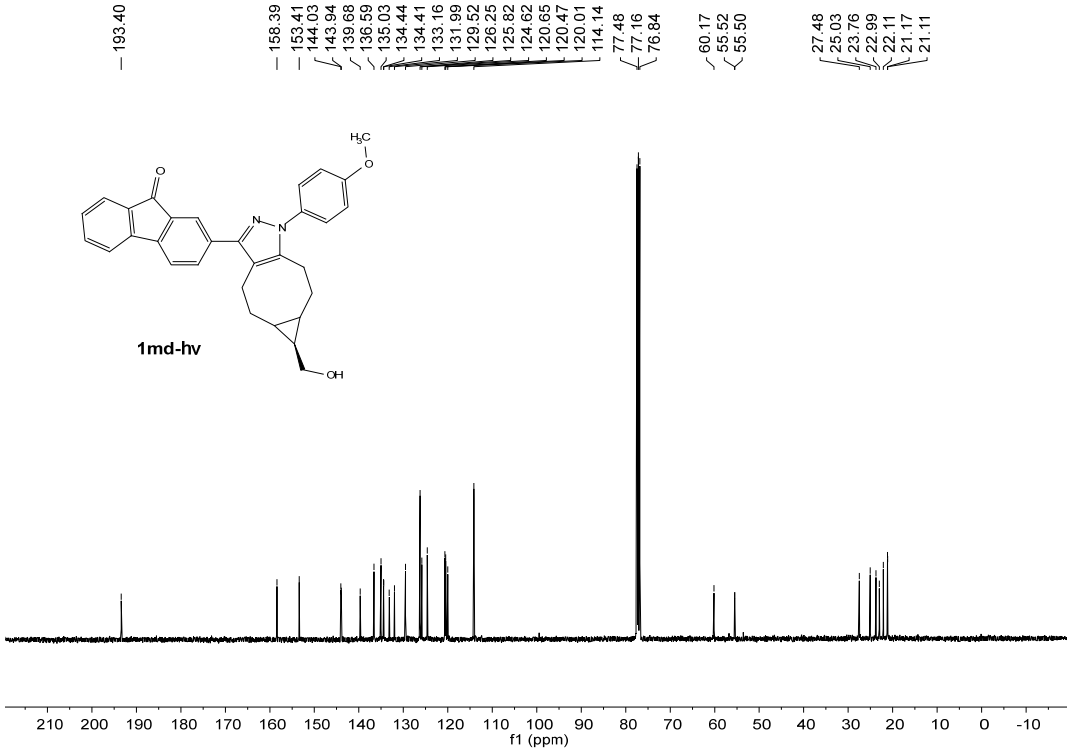
3.94
0.98
0.98
1.84
1.89
4.92
1.01
2.08
1.08
2.32
1.95
3.12
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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126.25
125.82
124.62
120.65
120.47
120.01
114.14
77.48
77.16
76.84
60.17
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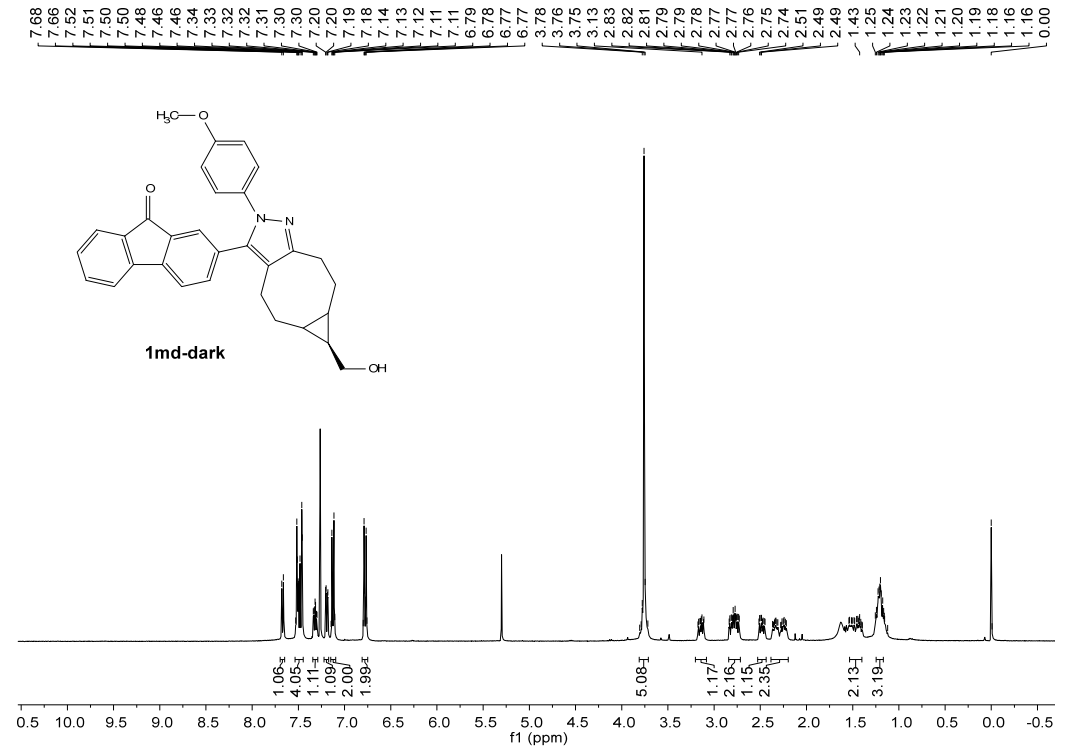
27.48
25.03
23.76
22.99
22.11
21.17
21.11
1md-hv
f1 (ppm)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7.20
7.19
7.18
7.14
7.13
7.12
7.11
7.11
6.79
6.78
6.77
6.77
3.78
3.76
3.75
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2.76
2.75
2.74
2.51
2.49
2.49
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1.25
1.24
1.23
1.22
1.21
1.20
1.19
1.18
1.16
1.16
0.00
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4.05
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1.09
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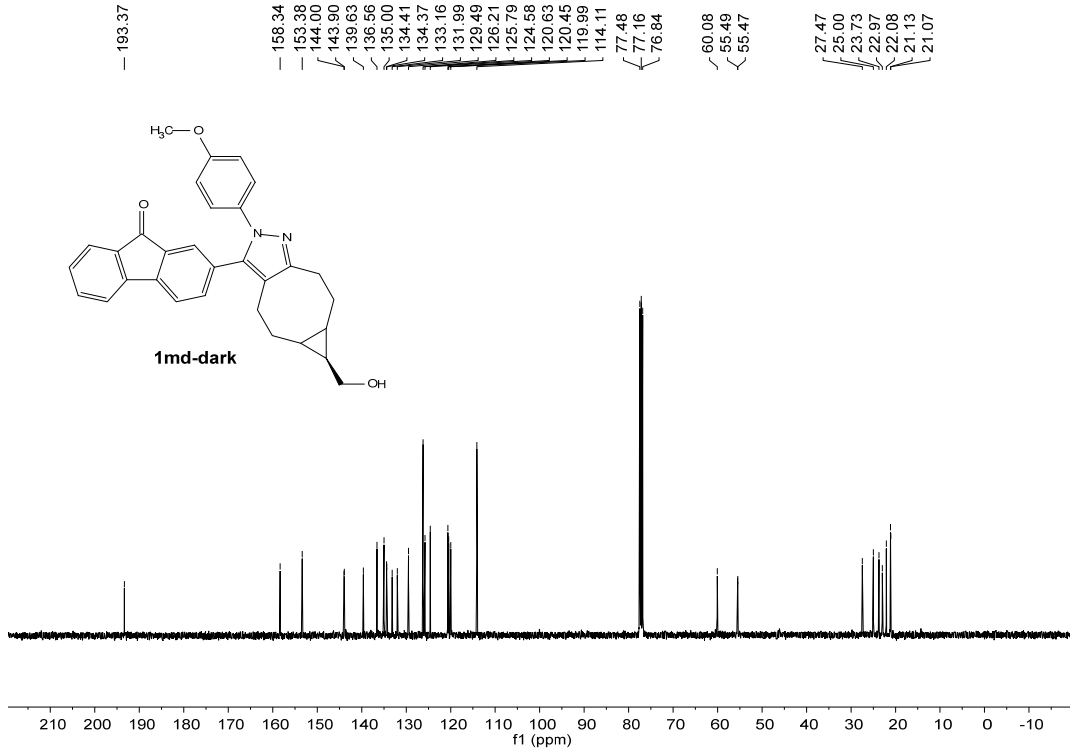
1.99
5.08
1.17
2.16
1.15
2.35
2.13
3.19
f1 (ppm)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125.79
124.58
120.63
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119.99
114.11
77.48
77.16
76.84
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27.47
25.00
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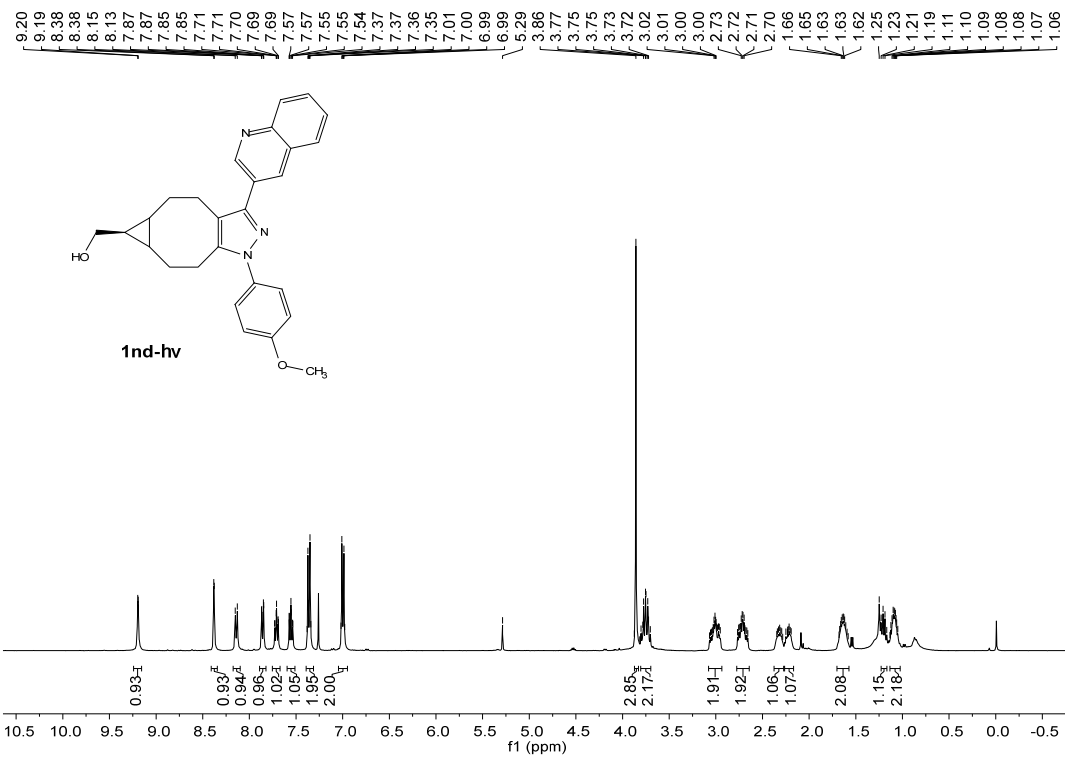
22.97
22.08
21.13
21.07
1md-dark
f1 (ppm)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7.69
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7.55
7.55
7.54
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7.37
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7.35
7.01
7.00
6.99
6.99
5.29
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1.06
1nd-hv
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0.93
0.94
0.96
1.02
1.05
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2.00
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1.06
1.07
2.08
1.15
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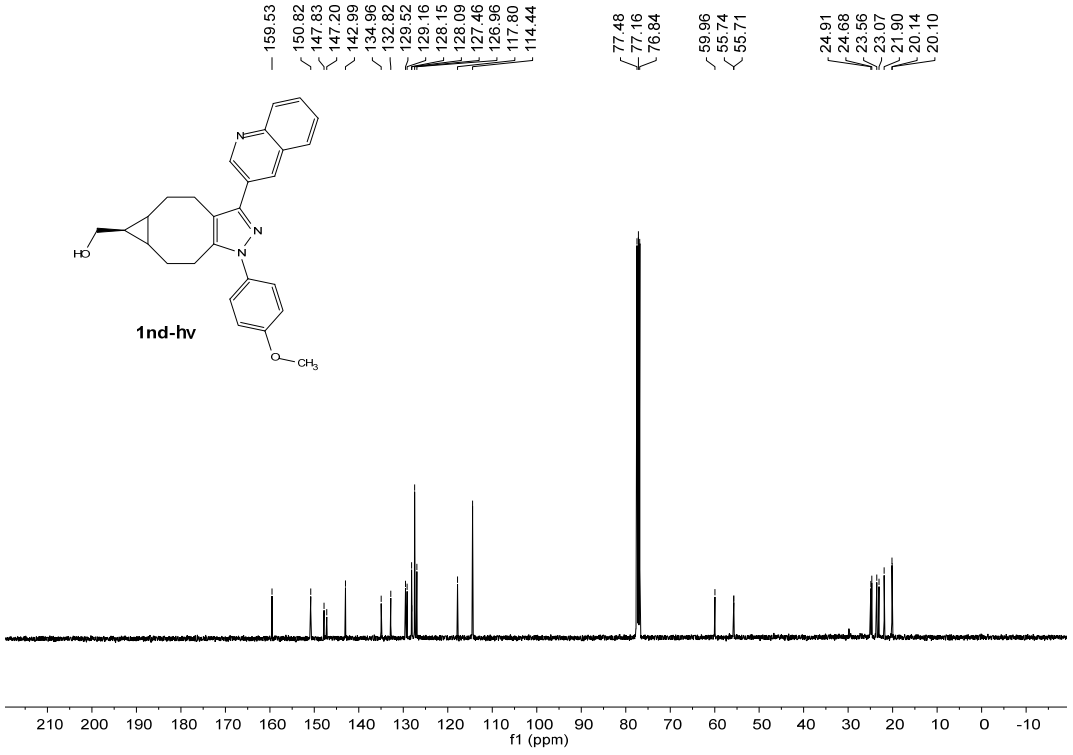
f1 (ppm)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128.09
127.46
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77.48
77.16
76.84
59.96
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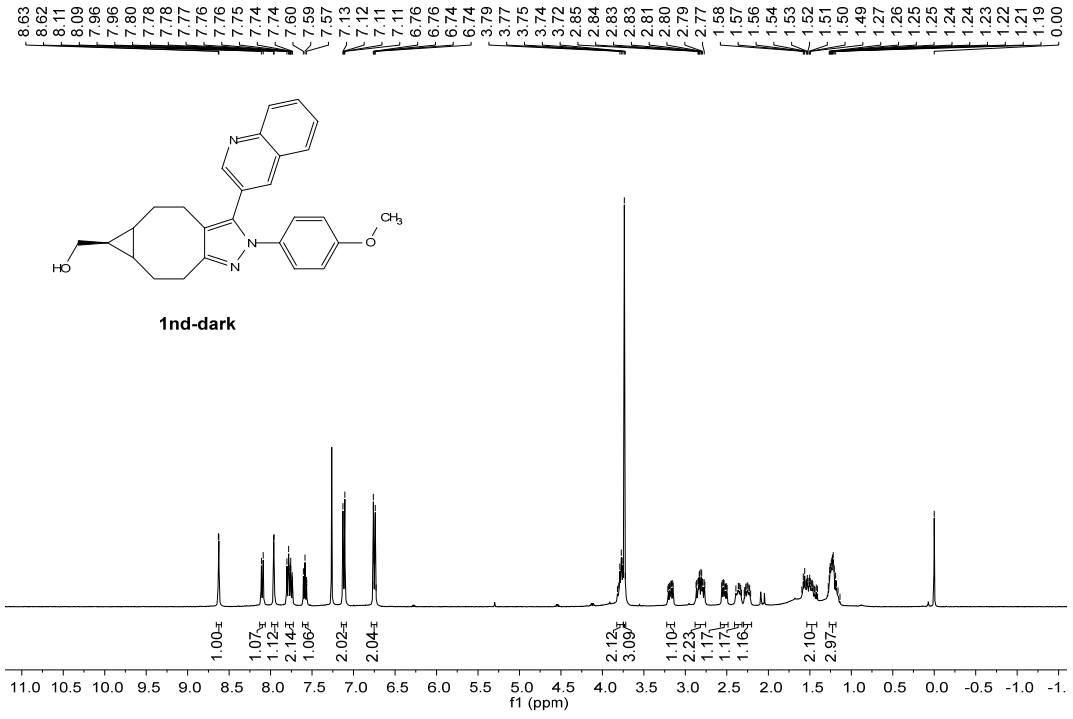
24.68
23.56
23.07
21.90
20.14
20.10
1nd-hv
f1 (ppm)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7.76
7.75
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7.74
7.60
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7.57
7.13
7.12
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3.77
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3.74
3.72
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2.83
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2.79
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1.24
1.23
1.22
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1nd-dark
1.00
1.07
1.12
2.14
1.06
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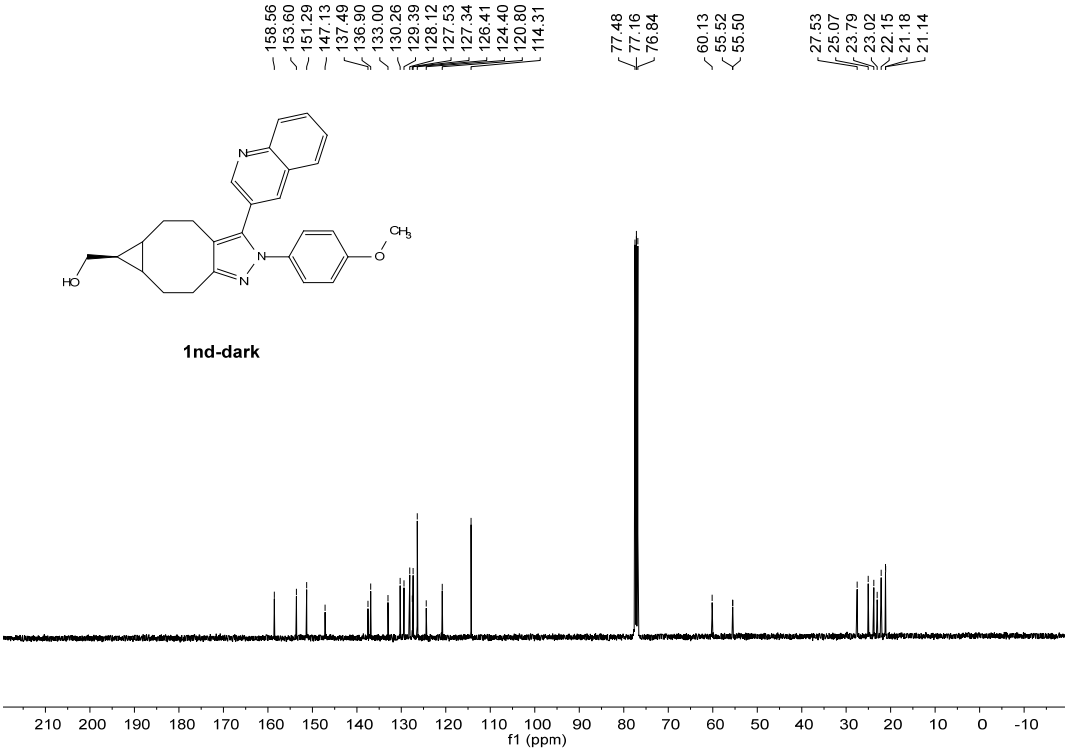
1.10
2.23
1.17
1.17
1.16
2.10
2.97
f1 (ppm)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127.34
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120.80
114.31
77.48
77.16
76.84
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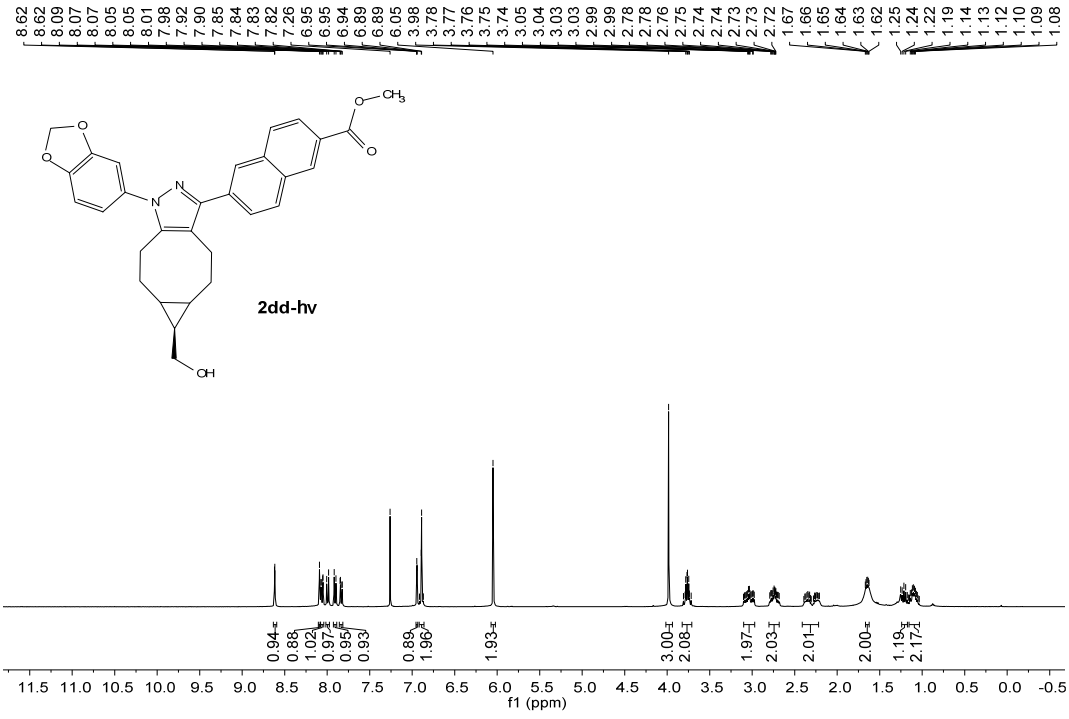
27.53
25.07
23.79
23.02
22.15
21.18
21.14
1nd-dark
f1 (ppm)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8.01
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7.85
7.84
7.83
7.82
7.26
6.95
6.95
6.94
6.89
6.89
6.05
3.98
3.78
3.77
3.76
3.75
3.74
3.05
3.04
3.03
3.03
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2.99
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2.76
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1.19
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1.13
1.12
1.10
1.09
1.08
2dd-hv
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0.88
1.02
0.97
0.95
0.93
0.89
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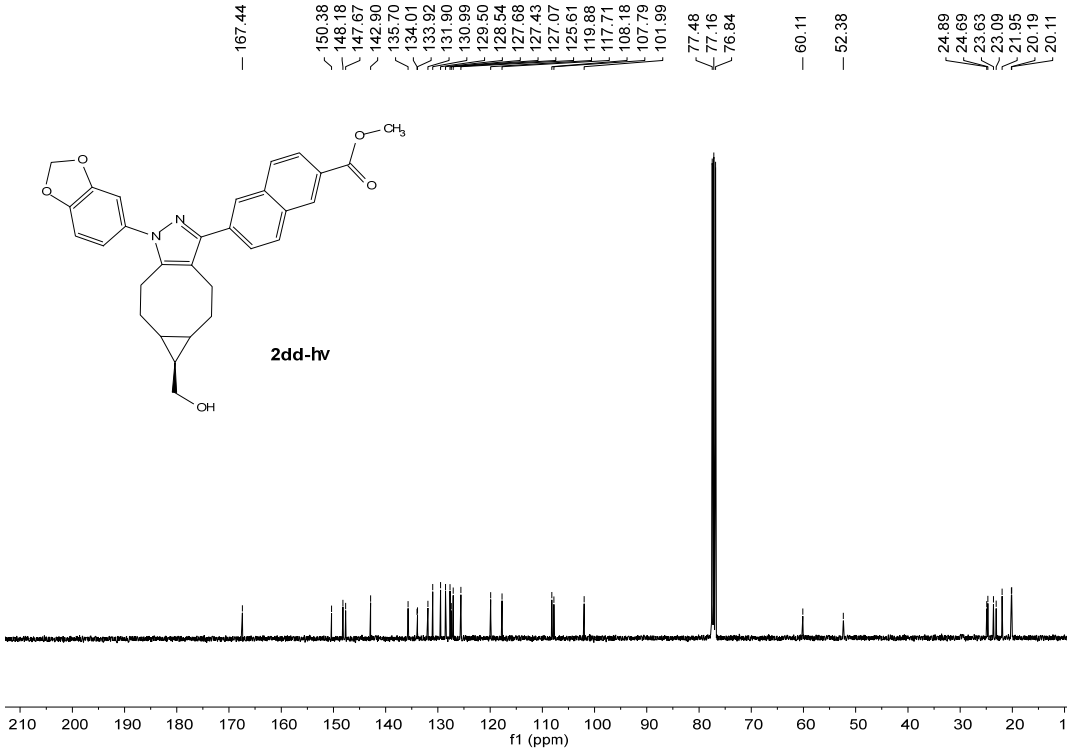
2.08
1.97
2.03
2.01
2.00
1.19
2.17
f1 (ppm)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101.99
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77.16
76.84
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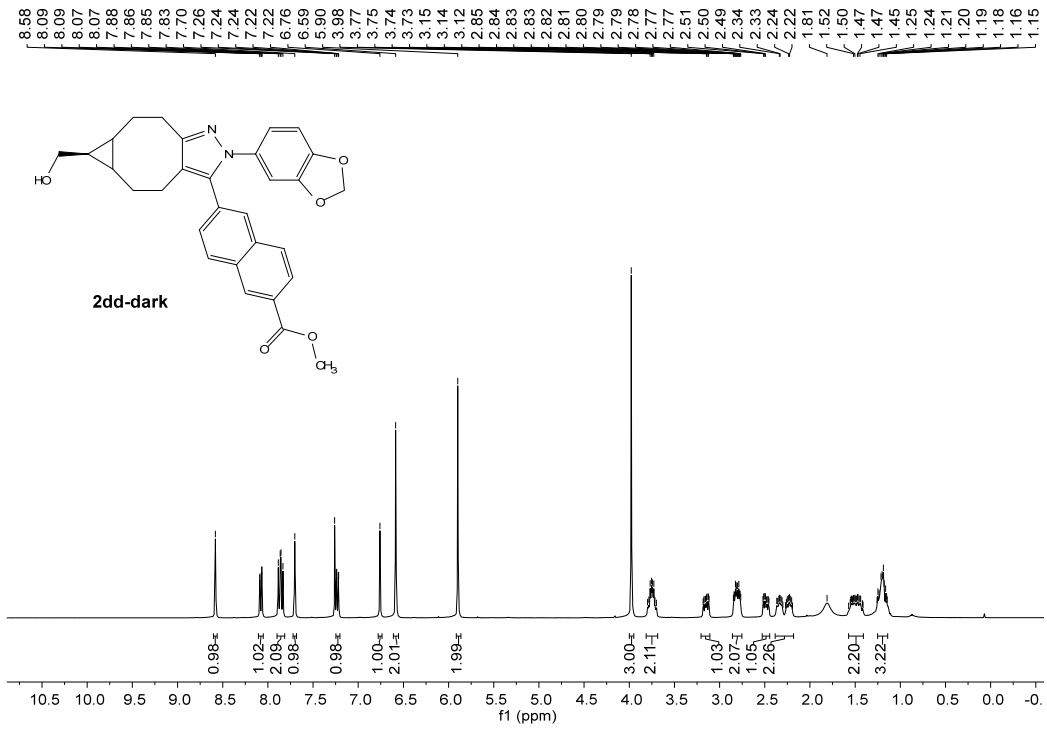
21.95
20.19
20.11
2dd-hv
f1 (ppm)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5.90
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3.73
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2.82
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2.80
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1.47
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1.24
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1.20
1.19
1.18
1.16
1.15
2dd-dark
0.98
1.02
2.09
0.98
0.98
1.00
2.01
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3.00
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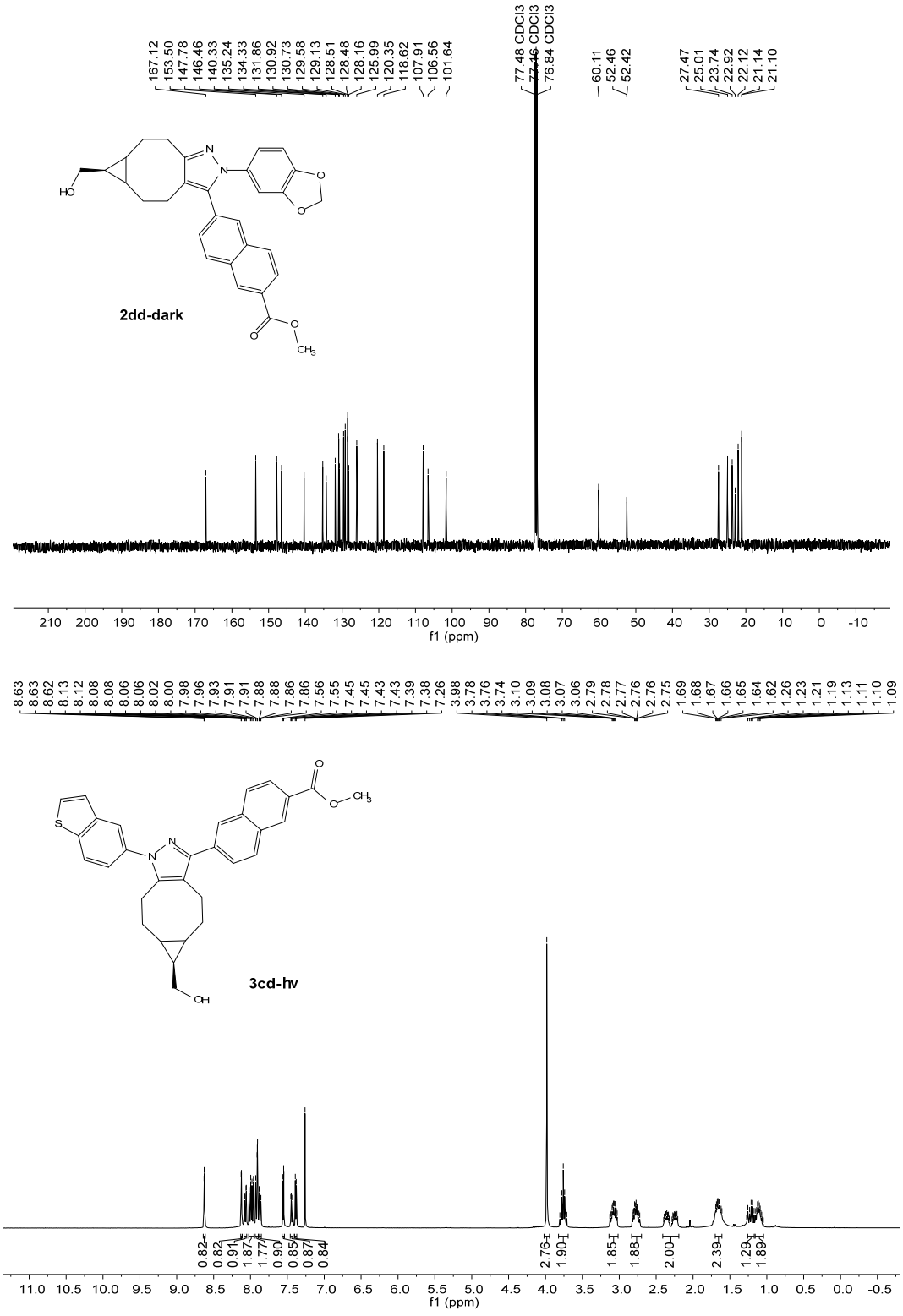
1.03
2.07
1.05
2.26
2.20
3.22
f1 (ppm)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128.48
128.16
125.99
120.35
118.62
107.91
106.56
101.64
77.48 CDCl3
77.46 CDCl3
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60.11
52.46
52.42
27.47
25.01
23.74
22.92
22.12
21.14
21.10
HO
N
N
O
O
O
O
CH3
2dd-dark
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
8.63
8.63
8.62
8.13
8.12
8.08
8.08
8.06
8.06
8.02
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3.09
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3.07
3.06
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1.65
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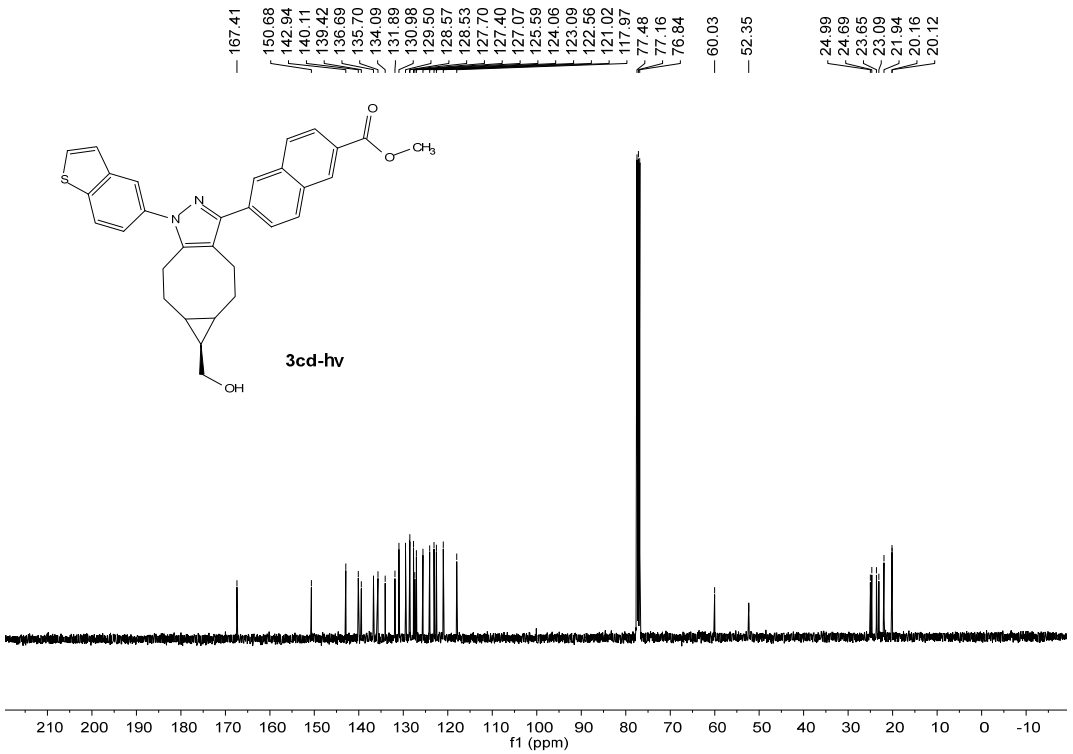
1.21
1.19
1.13
1.11
1.10
1.09
O
O
CH3
S
N
N
OH
3cd-hv
0.82
0.82
0.91
1.87
1.77
0.90
0.85
0.87
0.84
2.76
1.90
1.85
1.88
2.00
2.39
1.29
1.89
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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127.40
127.07
125.59
124.06
123.09
122.56
121.02
117.97
77.48
77.16
76.84
60.03
52.35
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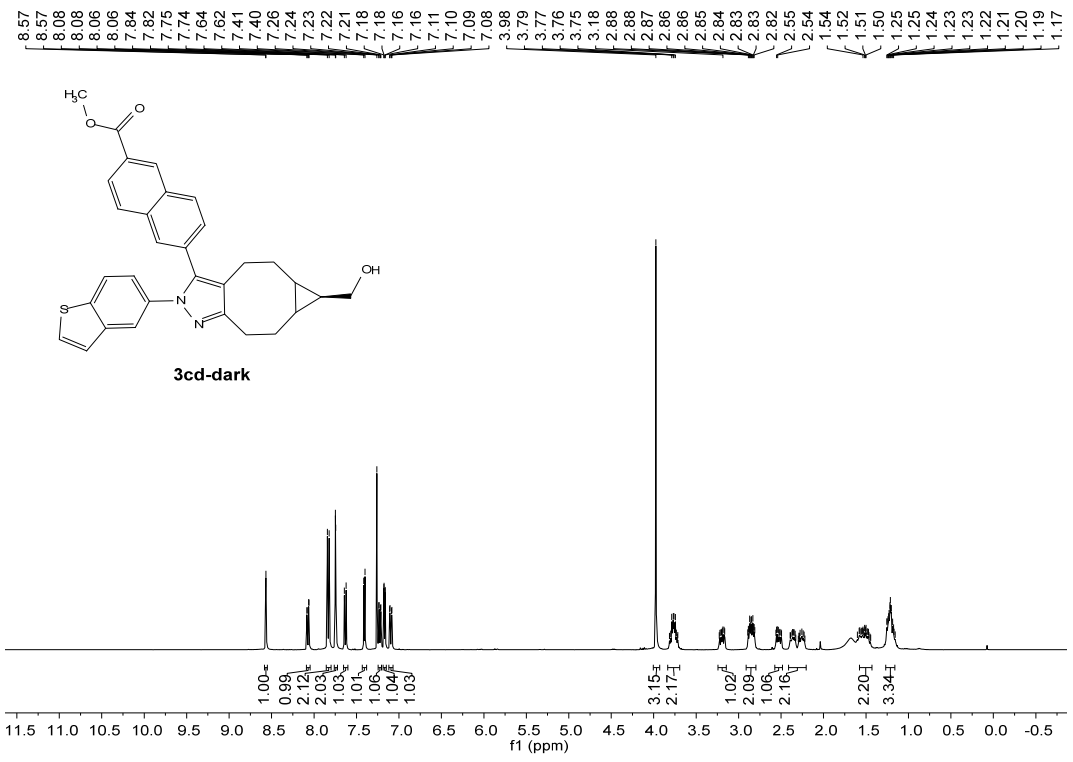
24.69
23.65
23.09
21.94
20.16
20.12
O
O
CH3
S
N
N
OH
3cd-hv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.08
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8.06
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7.41
7.40
7.26
7.24
7.23
7.22
7.21
7.18
7.16
7.16
7.11
7.10
7.09
7.08
3.98
3.79
3.77
3.76
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2.83
2.83
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1.52
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1.25
1.24
1.23
1.23
1.22
1.21
1.20
1.19
1.17
H3C
O
O
O
OH
S
N
N
3cd-dark
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0.99
2.12
2.03
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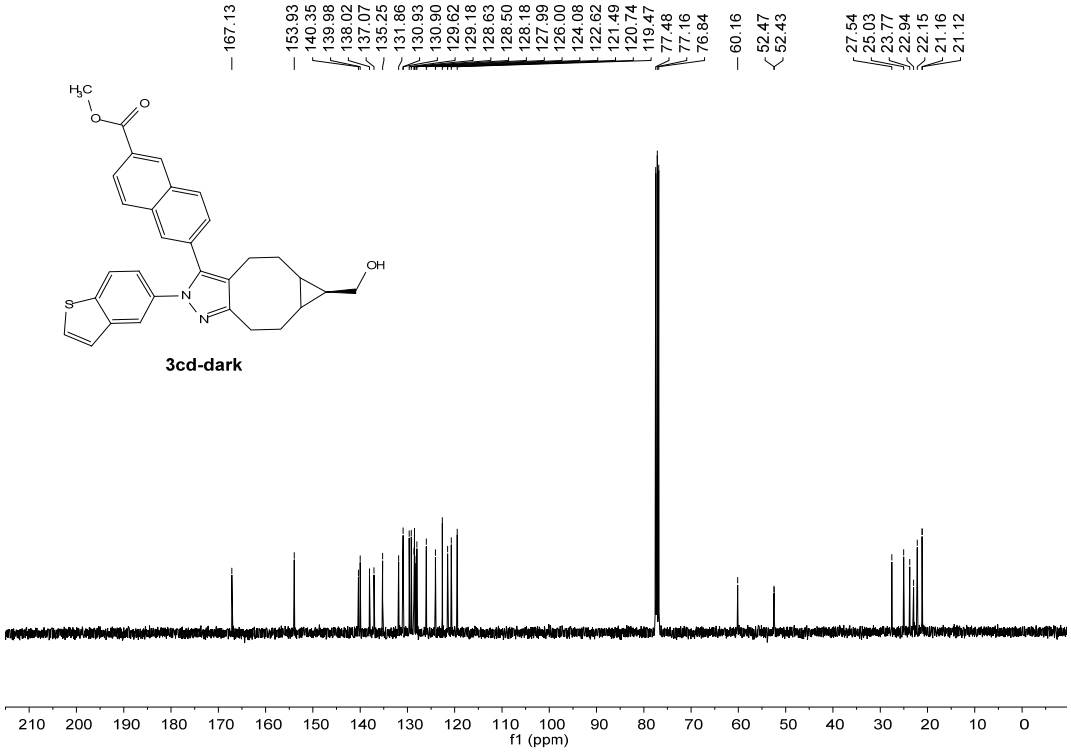
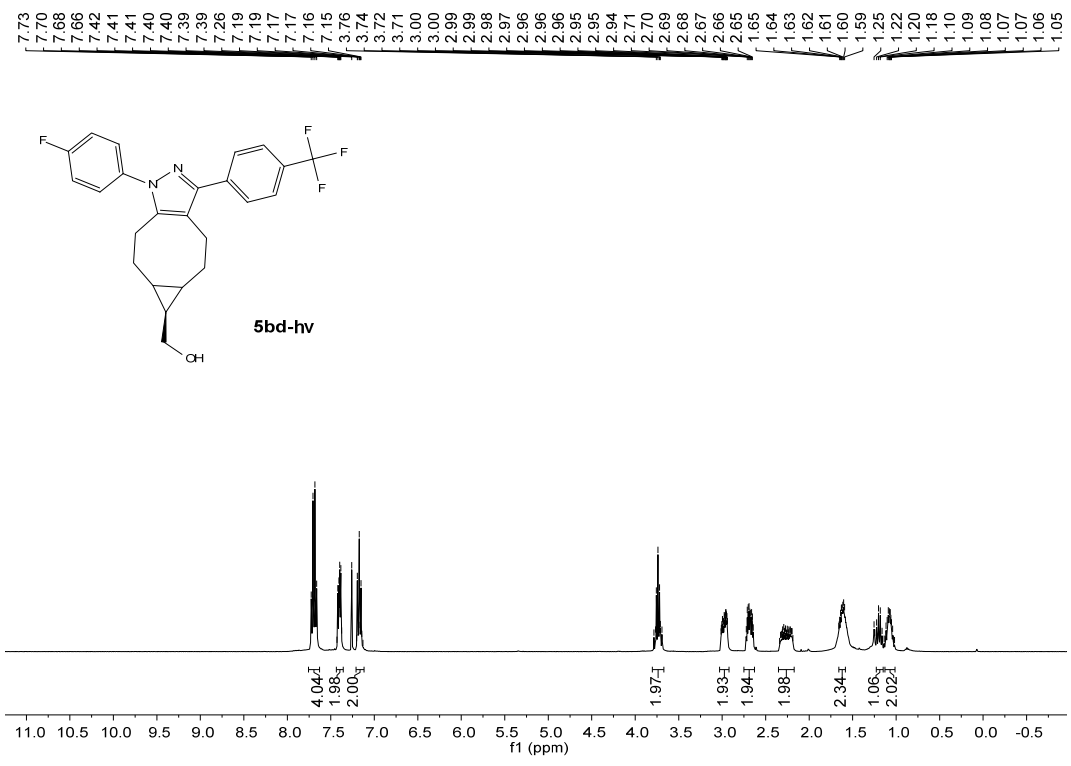
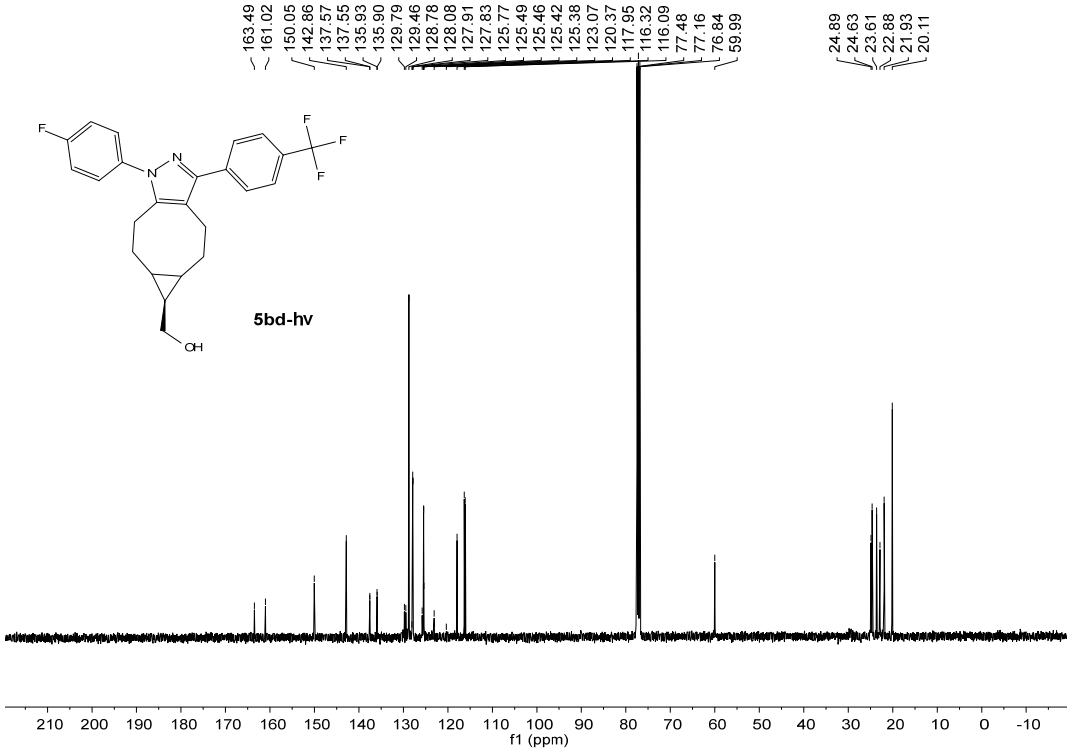
1.01
1.06
1.04
1.03
3.15
2.17
1.02
2.09
1.06
2.16
2.20
3.34
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.13
153.93
140.35
139.98
138.02
137.07
135.25
131.86
130.93
130.90
129.62
129.18
128.63
128.50
128.18
127.99
126.00
124.08
122.62
121.49
120.74
119.47
77.48
77.16
76.84
60.16
52.47
52.43
27.54
25.03
23.77
22.94
22.15
21.16
21.12
3cd-dark
f1 (ppm)


7.73
7.70
7.68
7.66
7.42
7.41
7.41
7.40
7.40
7.39
7.26
7.19
7.19
7.17
7.17
7.16
7.15
3.76
3.74
3.72
3.71
3.00
3.00
2.99
2.99
2.98
2.97
2.96
2.96
2.96
2.95
2.95
2.94
2.71
2.70
2.69
2.68
2.67
2.66
2.65
1.65
1.64
1.63
1.62
1.61
1.60
1.59
1.25
1.22
1.20
1.18
1.10
1.09
1.08
1.07
1.07
1.06
1.05
5bd-hv
4.04
1.98
2.00
1.97
1.93
1.94
1.98
2.34
1.06
2.02
f1 (ppm)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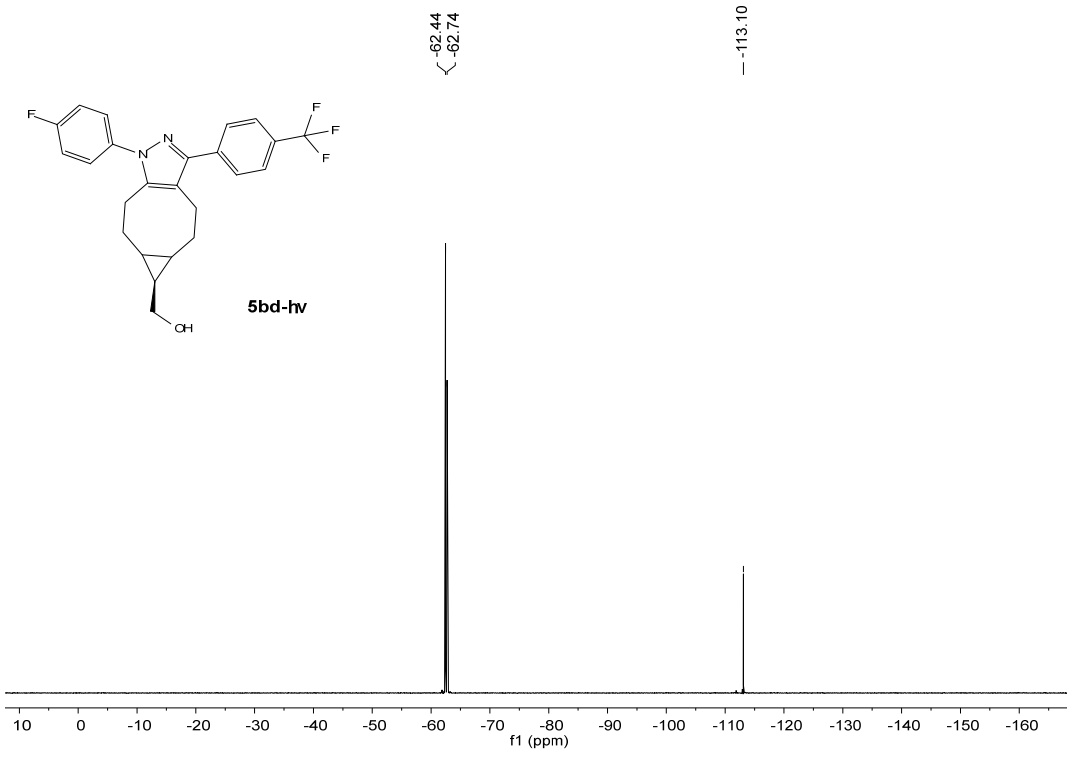
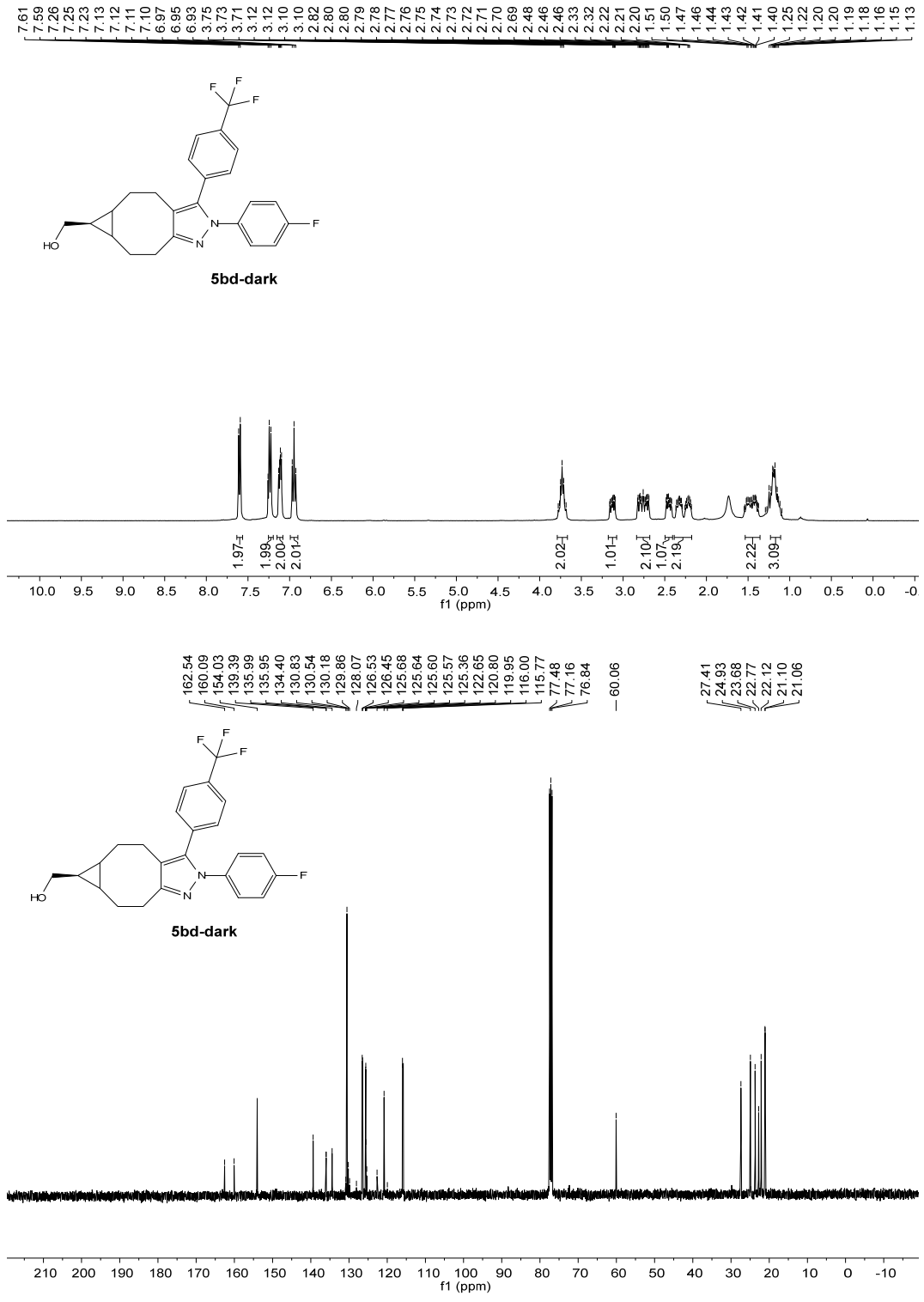
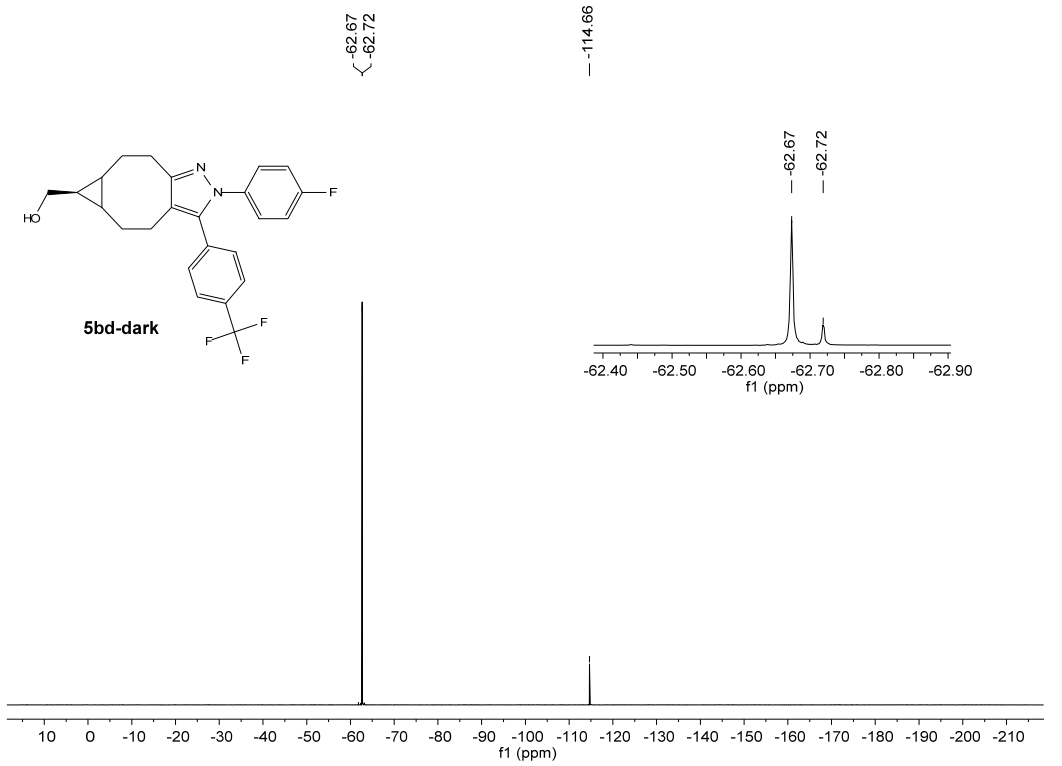
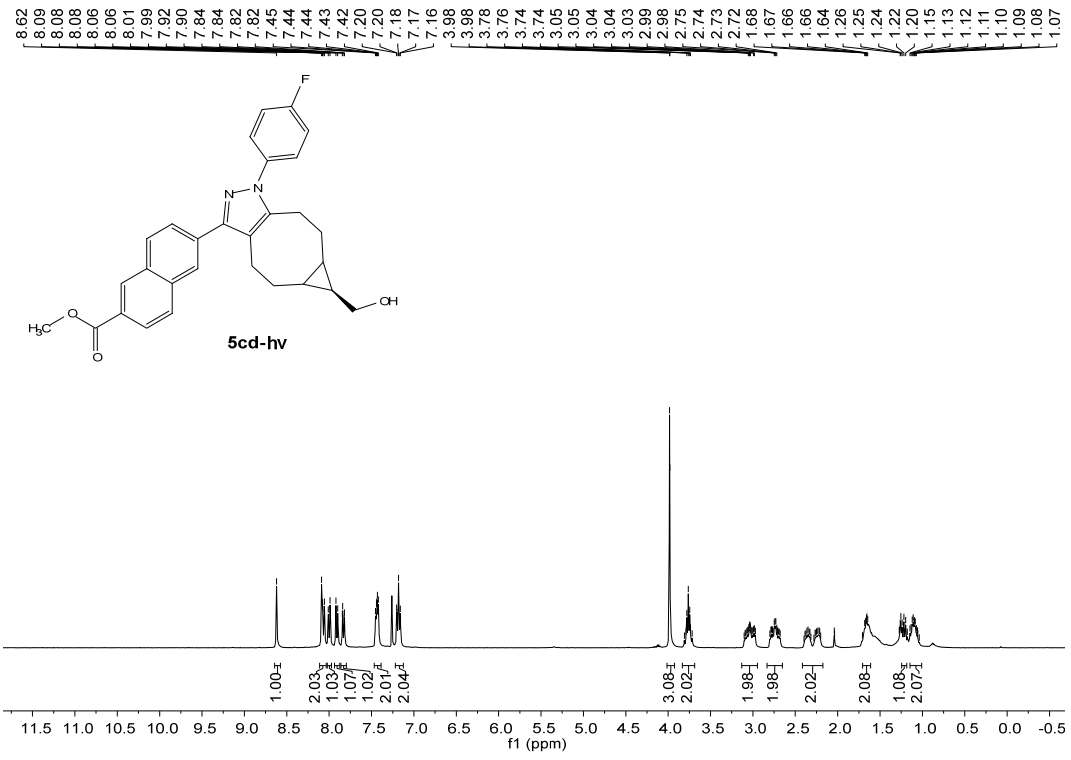
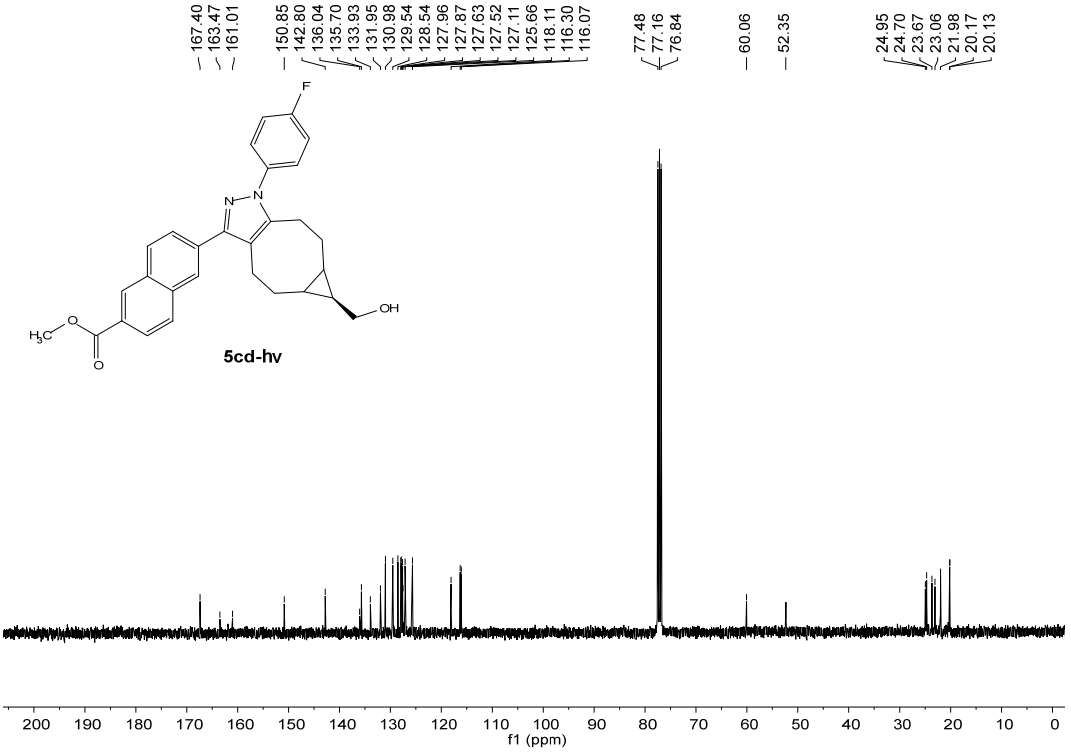
161.02
150.05
142.86
137.57
137.55
135.93
135.90
129.79
129.46
128.78
128.08
127.91
127.83
125.77
125.49
125.46
125.42
125.38
123.07
120.37
117.95
116.32
116.09
77.48
77.16
76.84
59.99
24.89
24.63
23.61
22.88
21.93
20.11
F
N
N
F
F
F
OH
5bd-hv
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

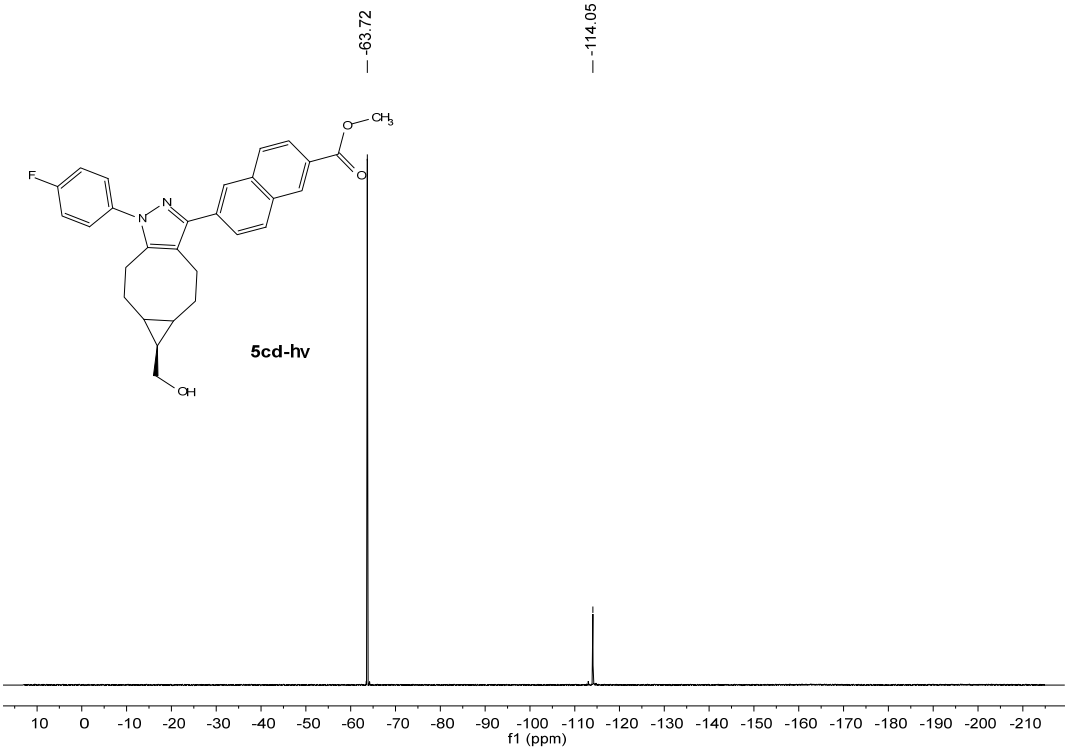

-62.44
-62.74
-113.10
F
N
N
F
F
F
OH
5bd-hv
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

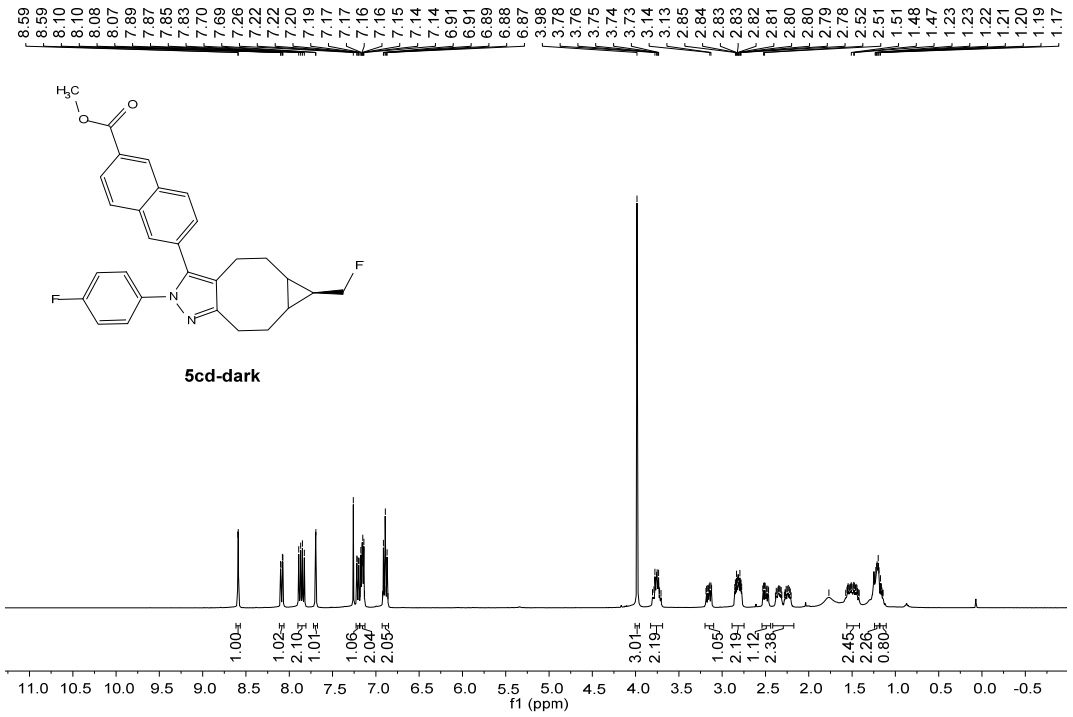

7.61 7.59 7.26 7.25 7.23 7.13 7.12 7.11 7.10 6.97 6.95 6.93 3.75 3.73 3.71 3.12 3.12 3.10 3.10 2.82 2.80 2.80 2.79 2.78 2.77 2.76 2.75 2.74 2.73 2.72 2.71 2.70 2.69 2.48 2.46 2.46 2.33 2.32 2.22 2.21 2.20 1.51 1.50 1.47 1.46 1.44 1.43 1.42 1.41 1.40 1.25 1.22 1.20 1.20 1.19 1.18 1.16 1.15 1.13
F
F
F
N
N
F
HO
5bd-dark
1.97
1.99
2.00
2.01
2.02
1.01
2.10
1.07
2.19
2.22
3.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
162.54 160.09 154.03 139.39 135.99 135.95 134.40 130.83 130.54 130.18 129.86 128.07 126.53 126.45 125.68 125.64 125.60 125.57 125.36 122.65 120.80 119.95 116.00 115.77 77.48 77.16 76.84 60.06 27.41 24.93 23.68 22.77 22.12 21.10 21.06
F
F
F
N
N
F
HO
5bd-dark
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

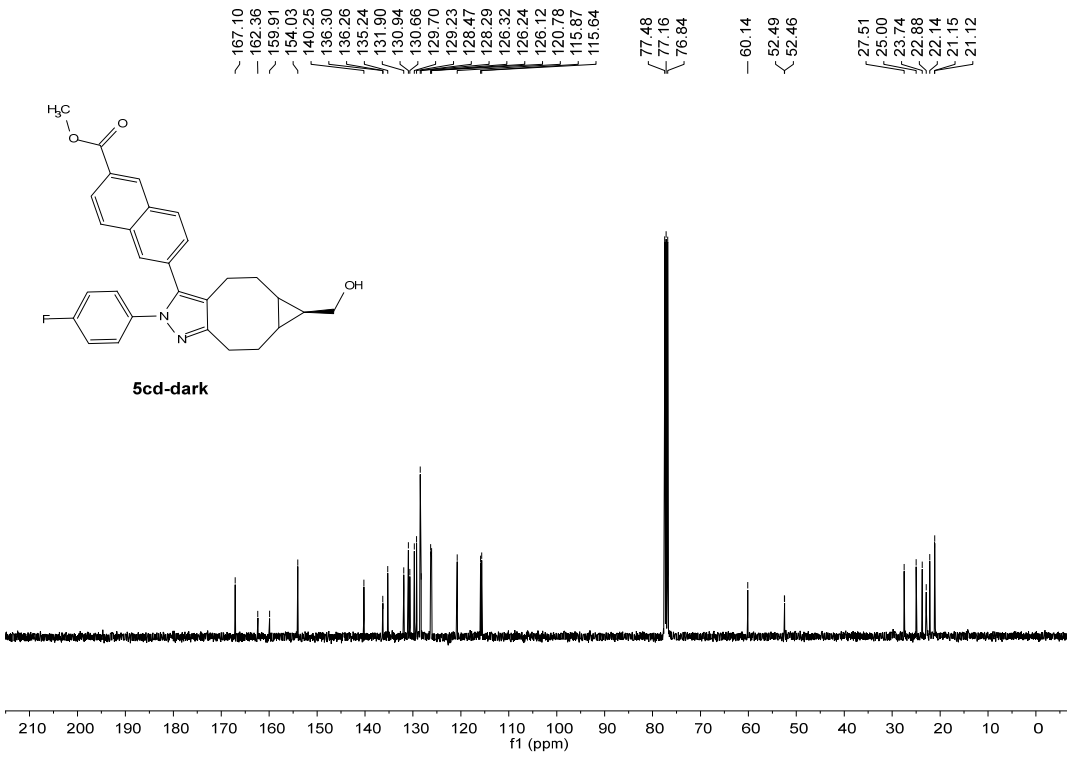

-62.67
-62.72
-114.66
5bd-dark
-62.67
-62.72
-62.40 -62.50 -62.60 -62.70 -62.80 -62.90
f1 (ppm)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

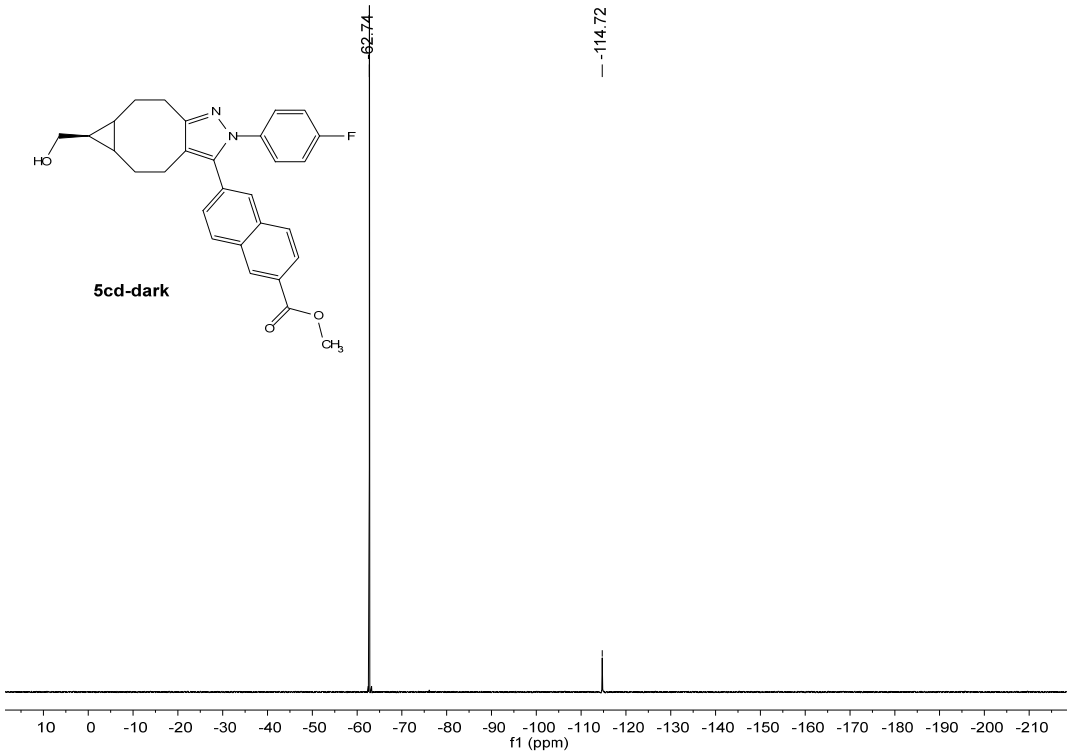

8.62 8.09 8.08 8.08 8.06 8.06 8.01 7.99 7.92 7.90 7.84 7.84 7.82 7.82 7.45 7.44 7.44 7.43 7.42 7.20 7.20 7.18 7.17 7.16
3.98 3.98 3.78 3.76 3.74 3.74 3.05 3.05 3.04 3.04 3.03 2.99 2.98 2.75 2.74 2.73 2.72 1.68 1.67 1.66 1.66 1.64 1.26 1.25 1.24 1.22 1.20 1.15 1.13 1.12 1.11 1.10 1.09 1.08 1.07
5cd-hv
1.00 2.03 1.03 1.07 1.02 2.01 2.04 3.08 2.02 1.98 1.98 2.02 2.08 1.08 2.07
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

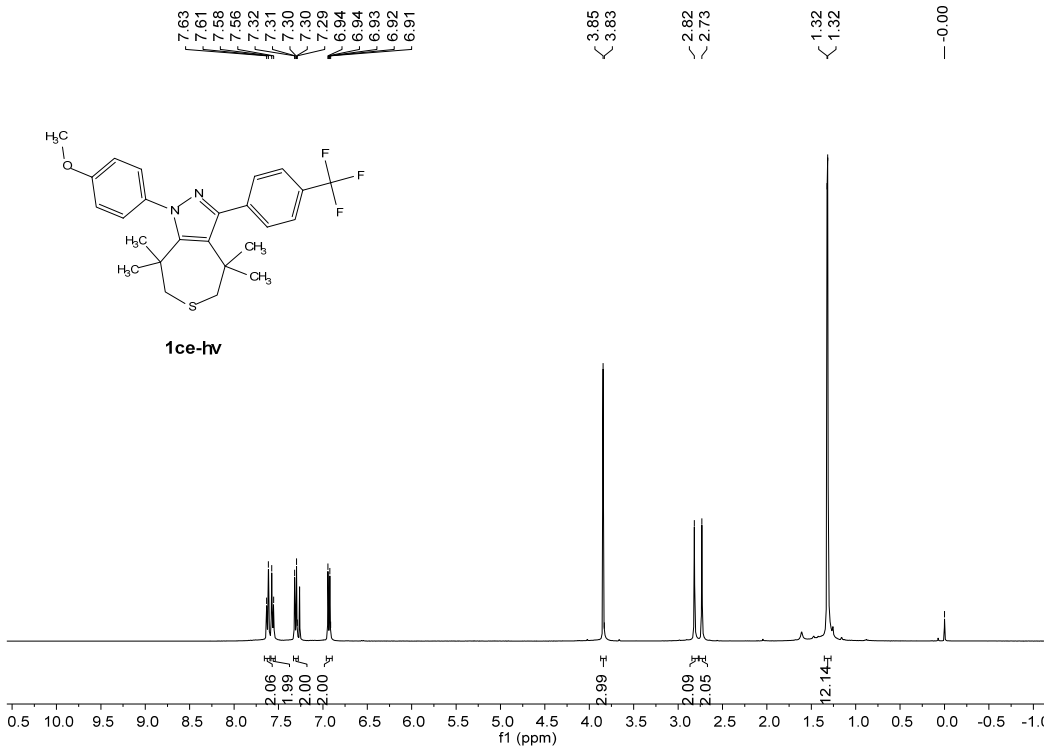

167.40
163.47
161.01
150.85
142.80
136.04
135.70
133.93
131.95
130.98
129.54
128.54
127.96
127.87
127.63
127.52
127.11
125.66
118.11
116.30
116.07
77.48
77.16
76.84
60.06
52.35
24.95
24.70
23.67
23.06
21.98
20.17
20.13
F
N
N
O
O
H3C
OH
5cd-hv
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-63.72
-114.05
F
N
N
O
O
CH3
OH
5cd-hv
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.59 8.59 8.10 8.10 8.08 8.07 7.89 7.87 7.85 7.83 7.70 7.69 7.26 7.22 7.22 7.20 7.19 7.17 7.17 7.16 7.16 7.15 7.14 7.14 6.91 6.91 6.89 6.88 6.87 3.98 3.78 3.76 3.75 3.74 3.73 3.14 3.13 2.85 2.84 2.83 2.83 2.82 2.81 2.80 2.80 2.79 2.78 2.52 2.51 1.51 1.48 1.47 1.23 1.23 1.22 1.21 1.20 1.19 1.17
5cd-dark
1.00 1.02 2.10 1.01 1.06 2.04 2.05 3.01 2.19 1.05 2.19 1.12 2.38 2.45 2.26 0.80
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


167.10 162.36 159.91 154.03 140.25 136.30 136.26 135.24 131.90 130.94 130.66 129.70 129.23 128.47 128.29 126.32 126.24 126.12 120.78 115.87 115.64
77.48 77.16 76.84
60.14
52.49 52.46
27.51 25.00 23.74 22.88 22.14 21.15 21.12
5cd-dark
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


62.74
-114.72
5cd-dark
f1 (ppm)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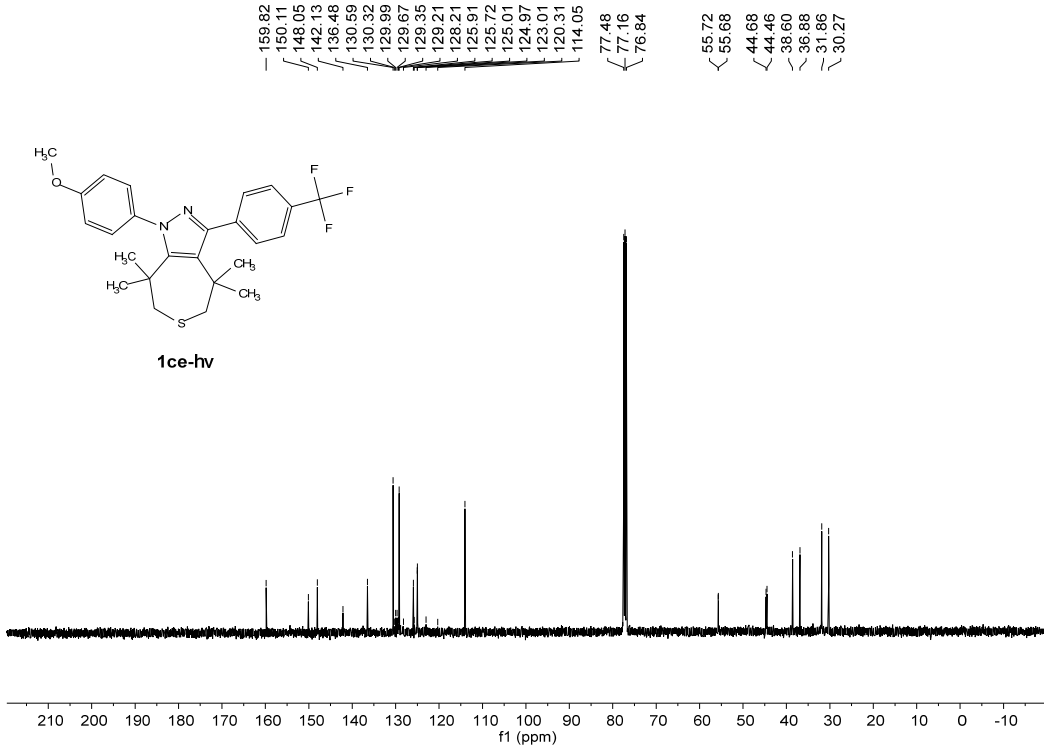
7.61
7.58
7.56
7.32
7.31
7.30
7.30
7.29
6.94
6.94
6.93
6.92
6.91
3.85
3.83
2.82
2.73
1.32
1.32
0.00
1ce-hv
2.06
1.99
2.00
2.00
2.99
2.09
2.05
12.14
f1 (ppm)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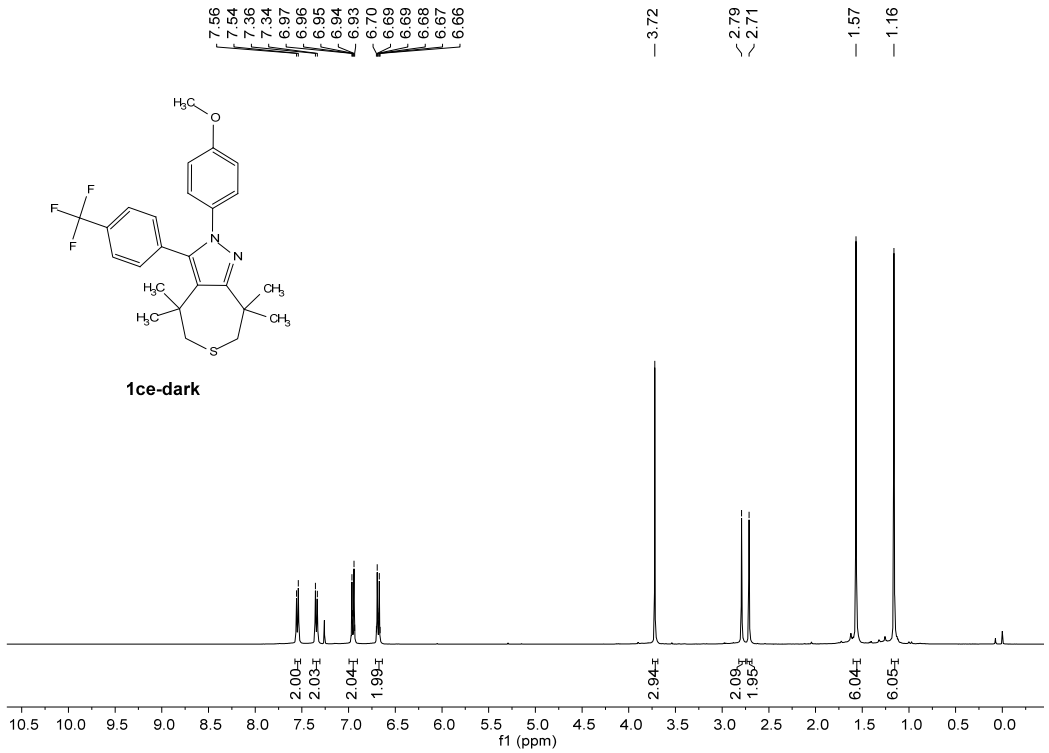
150.11
148.05
142.13
136.48
130.59
130.32
129.99
129.67
129.35
129.21
128.21
125.91
125.72
125.01
124.97
123.01
120.31
114.05
77.48
77.16
76.84
55.72
55.68
44.68
44.46
38.60
36.88
31.86
30.27
1ce-hv
f1 (ppm)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7.54
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7.34
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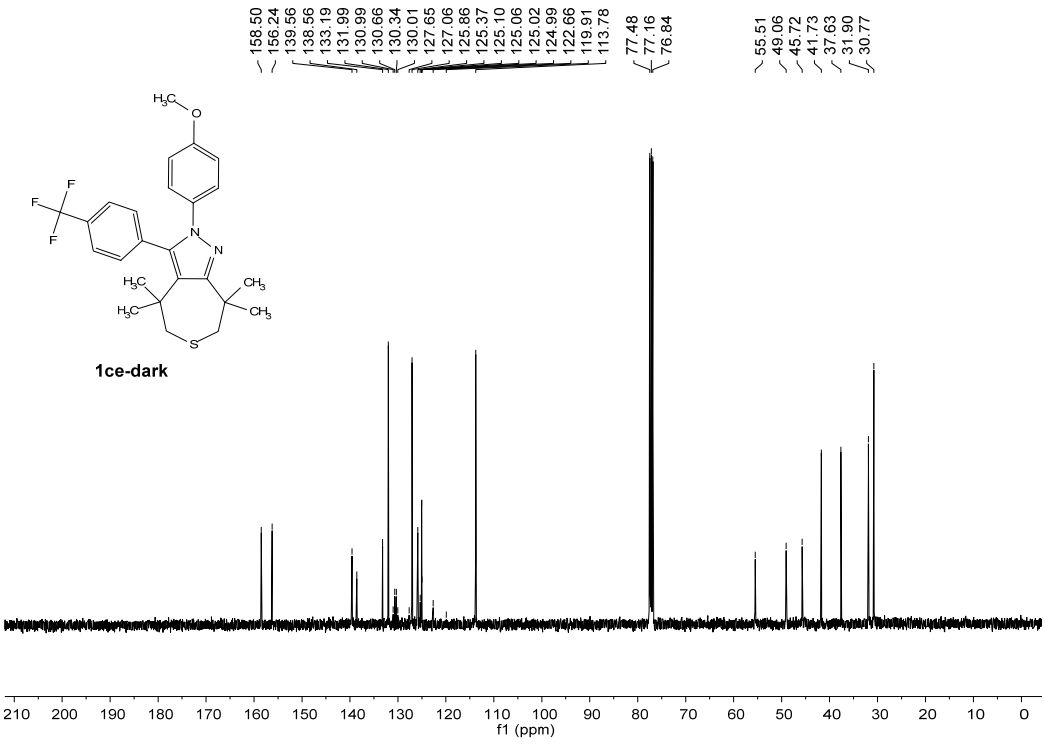
6.96
6.95
6.94
6.93
6.70
6.69
6.69
6.68
6.67
6.66
3.72
2.79
2.71
1.57
1.16
1ce-dark
2.00
2.03
2.04
1.99
2.94
2.09
1.95
6.04
6.05
f1 (ppm)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156.24
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130.99
130.66
130.34
130.01
127.65
127.06
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125.37
125.10
125.06
125.02
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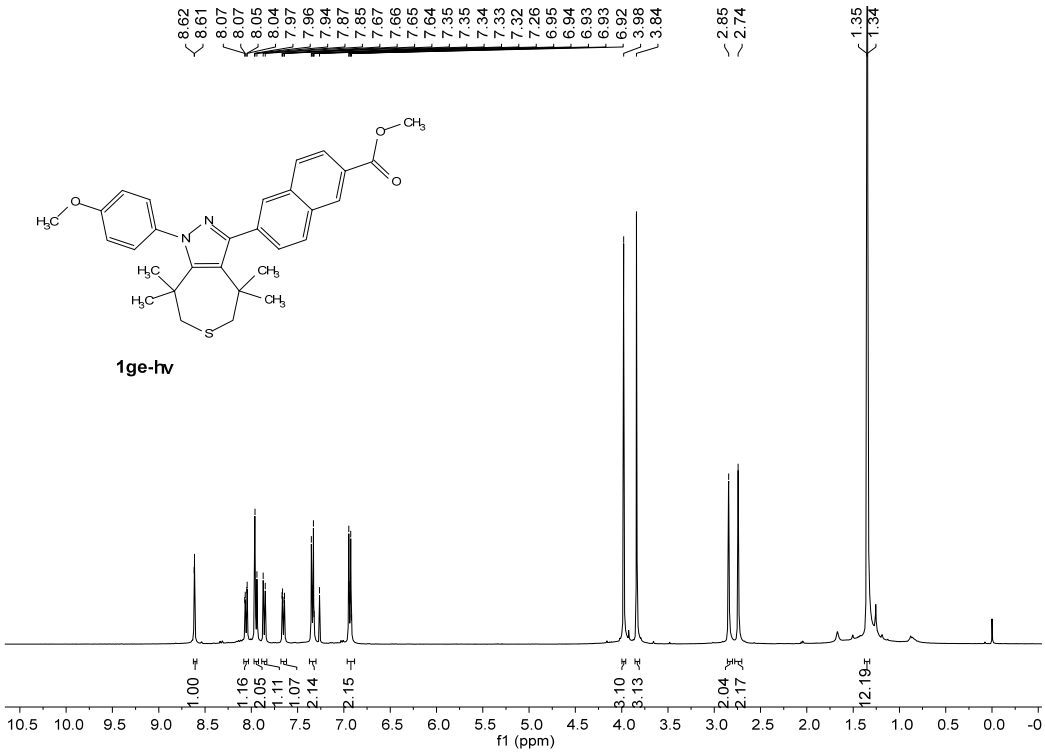
122.66
119.91
113.78
77.48
77.16
76.84
55.51
49.06
45.72
41.73
37.63
31.90
30.77
1ce-dark
f1 (ppm)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7.94
7.87
7.85
7.67
7.66
7.65
7.64
7.35
7.35
7.34
7.33
7.32
7.26
6.95
6.94
6.93
6.93
6.92
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2.74
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1.34
1.00
1.16
2.05
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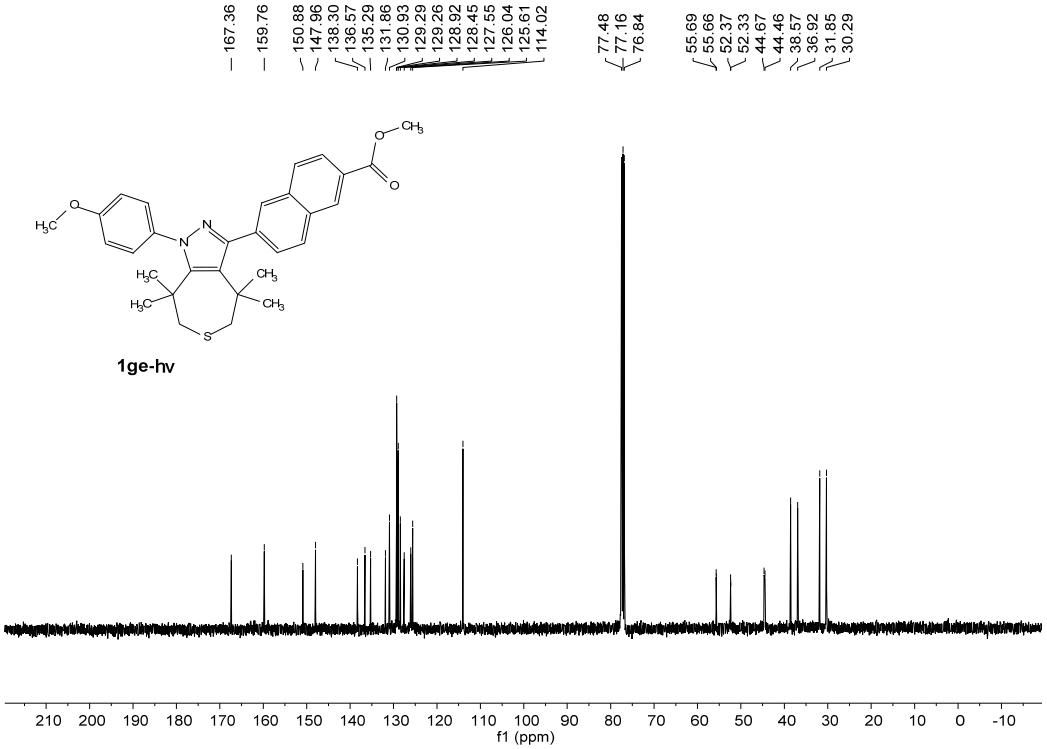
1.07
2.14
2.15
3.10
3.13
2.04
2.17
12.19
1ge-hv
f1 (ppm)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147.96
138.30
136.57
135.29
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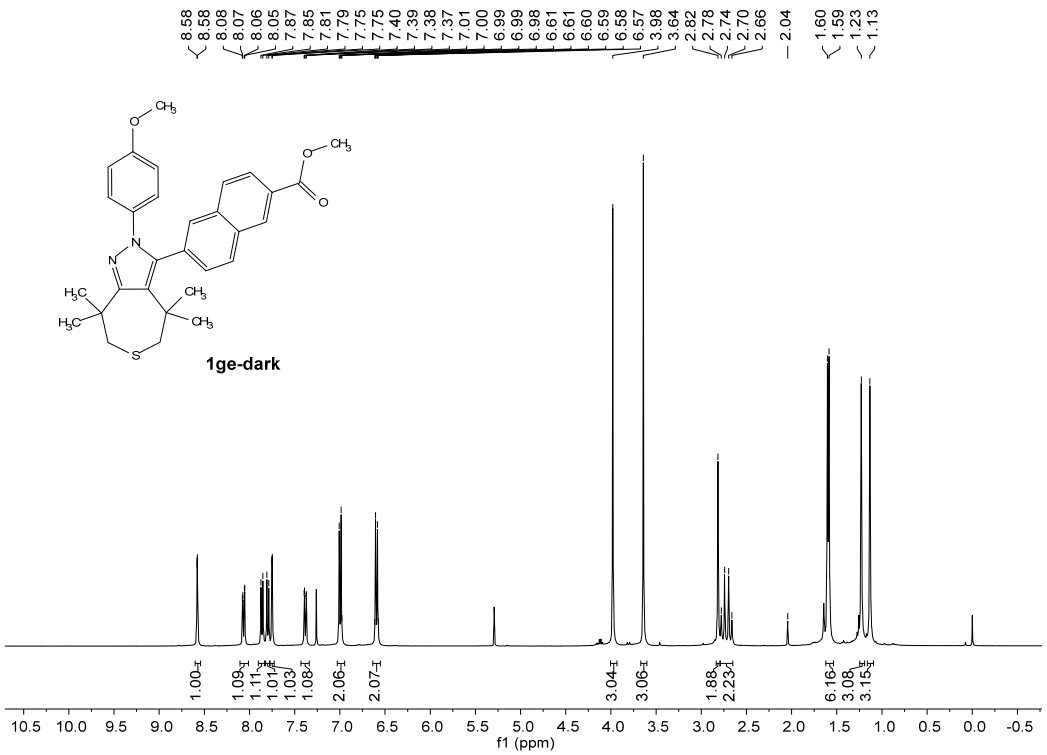
130.93
129.29
129.26
128.92
128.45
127.55
126.04
125.61
114.02
77.48
77.16
76.84
55.69
55.66
52.37
52.33
44.67
44.46
38.57
36.92
31.85
30.29
1ge-hv
f1 (ppm)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8.58
8.08
8.07
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8.05
7.87
7.85
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7.75
7.75
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7.00
6.99
6.99
6.98
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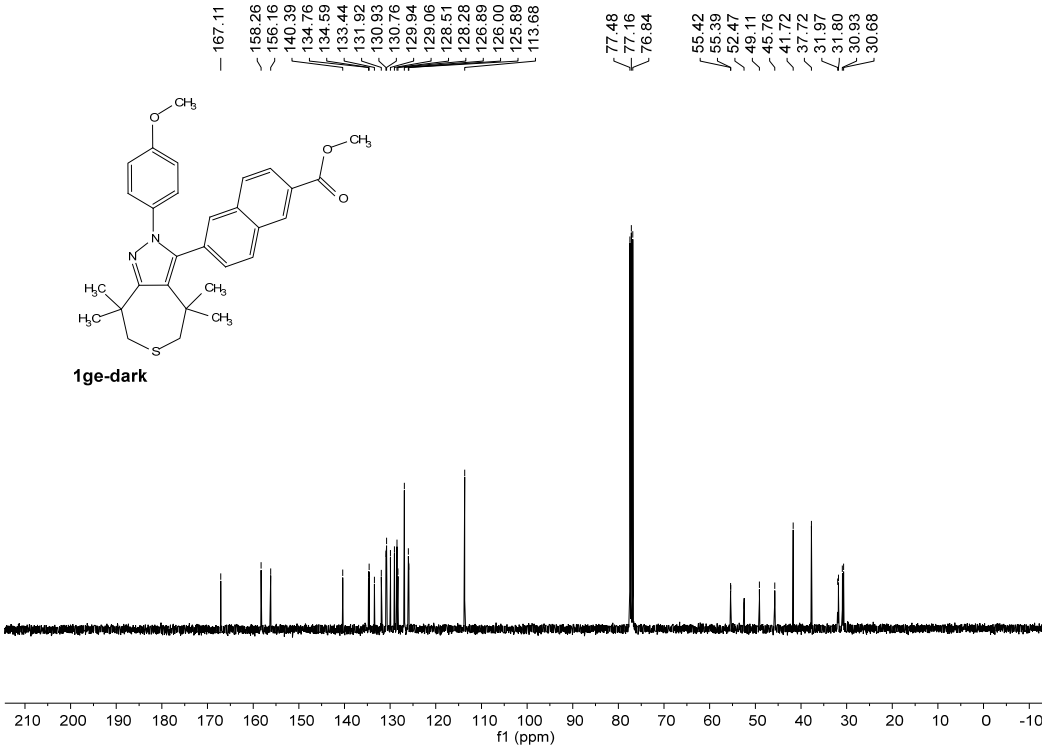
6.59
6.58
6.57
3.98
3.64
2.82
2.78
2.74
2.70
2.66
2.04
1.60
1.59
1.23
1.13
1.00
1.09
1.11
1.01
1.03
1.08
2.06
2.07
3.04
3.06
1.88
2.23
6.16
3.08
3.15
1ge-dark
f1 (ppm)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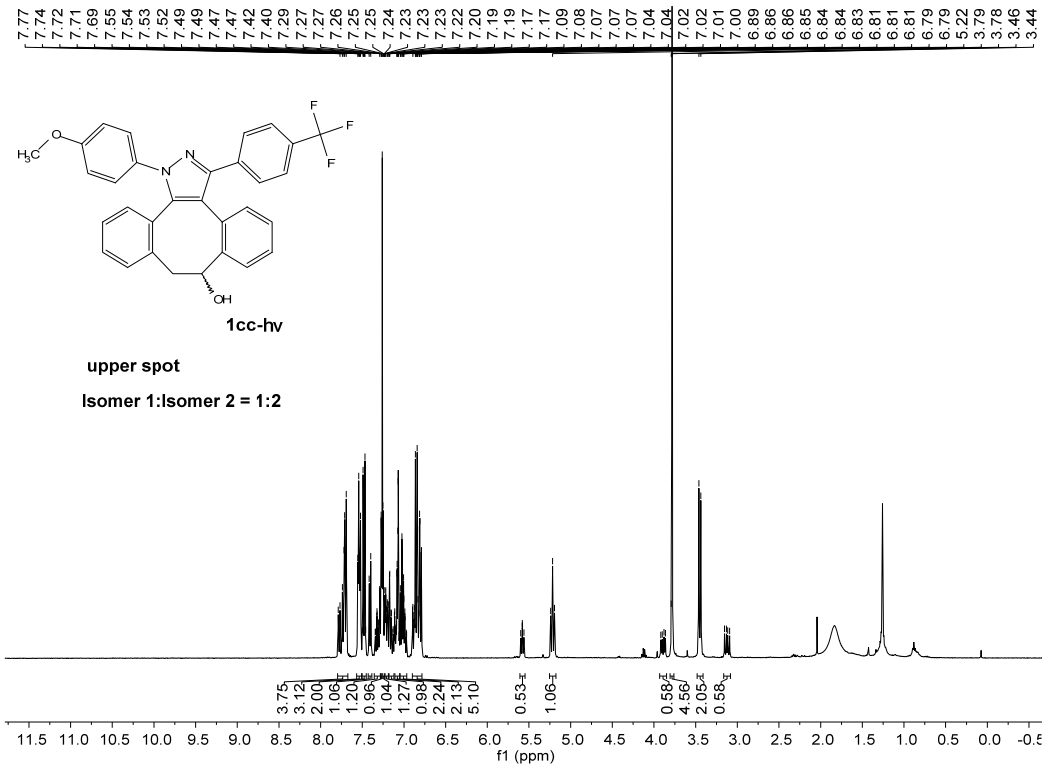
134.59
133.44
131.92
130.93
130.76
129.94
129.06
128.51
128.28
126.89
126.00
125.89
113.68
77.48
77.16
76.84
55.42
55.39
52.47
49.11
45.76
41.72
37.72
31.97
31.80
30.93
30.68
1ge-dark
f1 (ppm)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7.71
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7.53
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7.47
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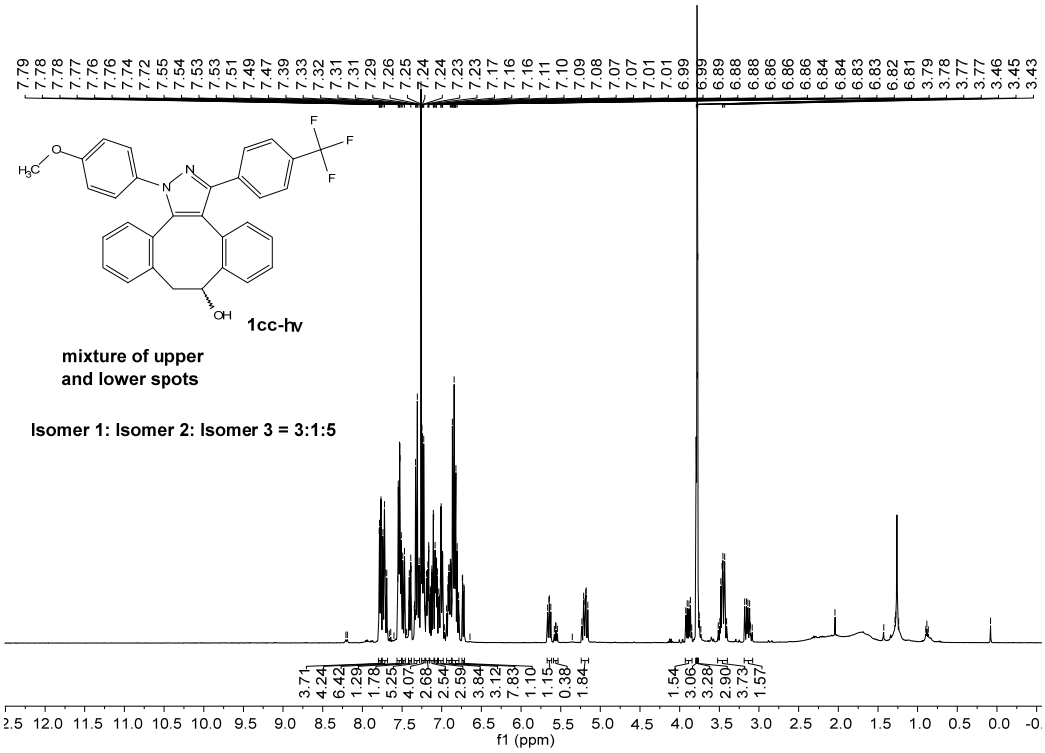
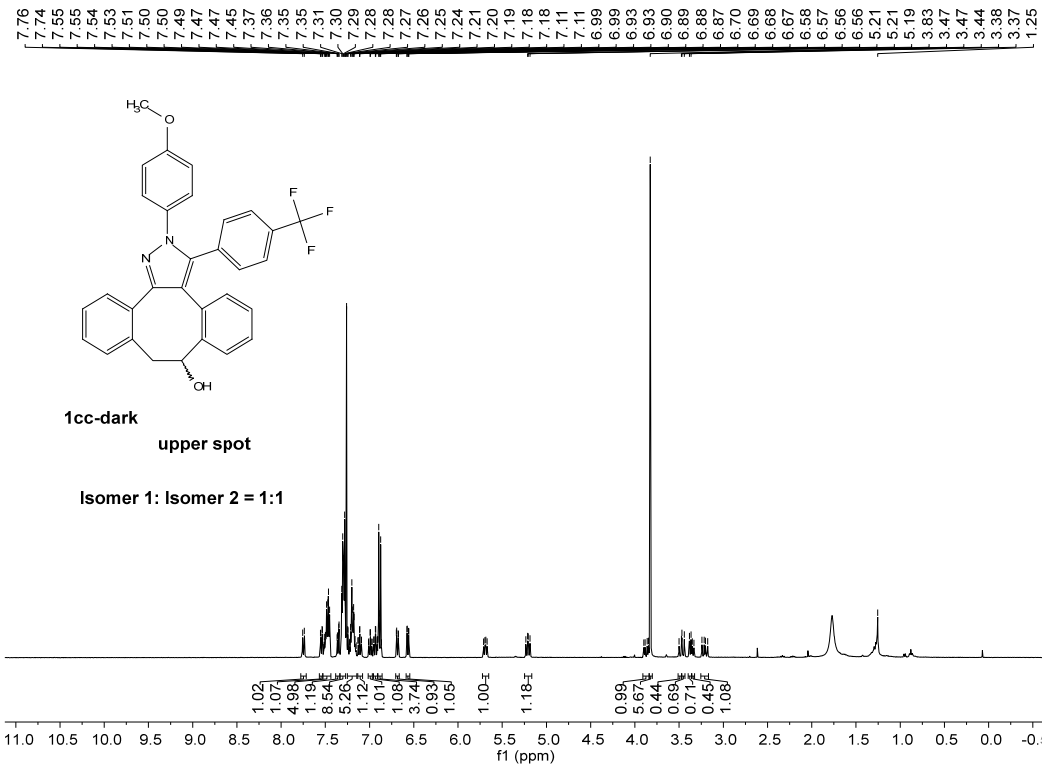
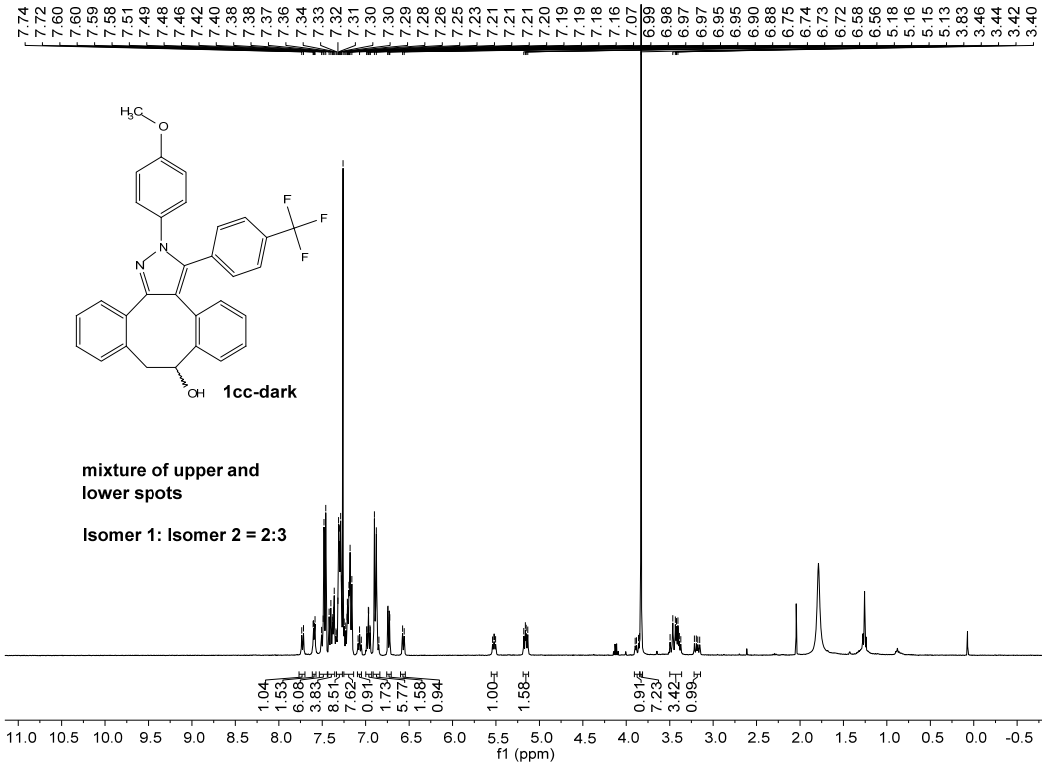
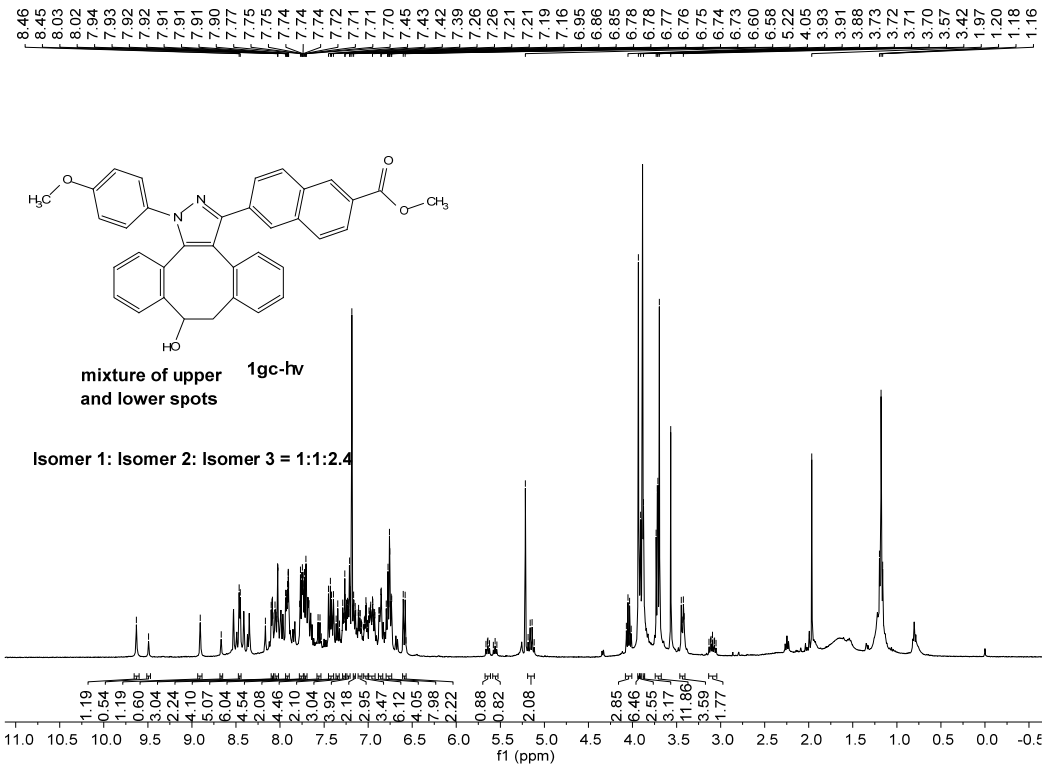
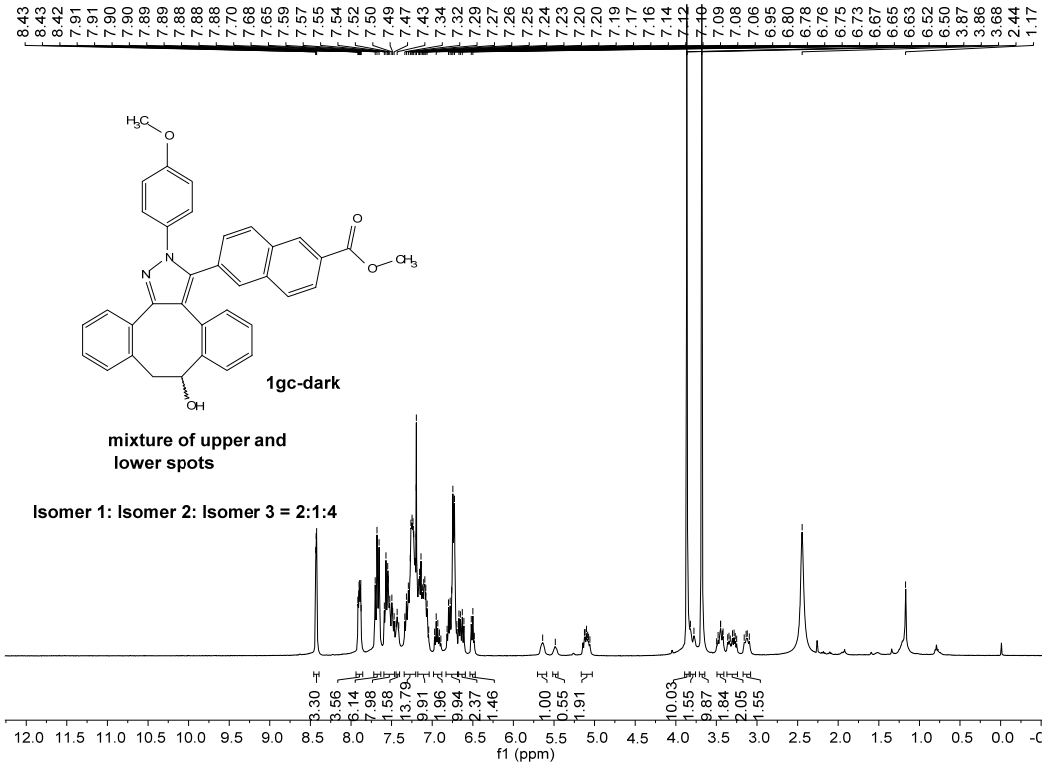
7.42
7.40
7.29
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.23
7.23
7.22
7.20
7.19
7.19
7.17
7.17
7.09
7.08
7.07
7.07
7.07
7.04
7.04
7.02
7.02
7.01
7.00
6.89
6.86
6.86
6.85
6.84
6.84
6.83
6.81
6.81
6.79
6.79
5.22
3.79
3.78
3.46
3.44
1cc-hv
upper spot
Isomer 1:Isomer 2 = 1:2
3.75
3.12
2.00
1.06
1.20
0.96
1.04
1.27
0.98
2.24
2.13
5.10
0.53
1.06
0.58
4.56
2.05
0.58
f1 (ppm)

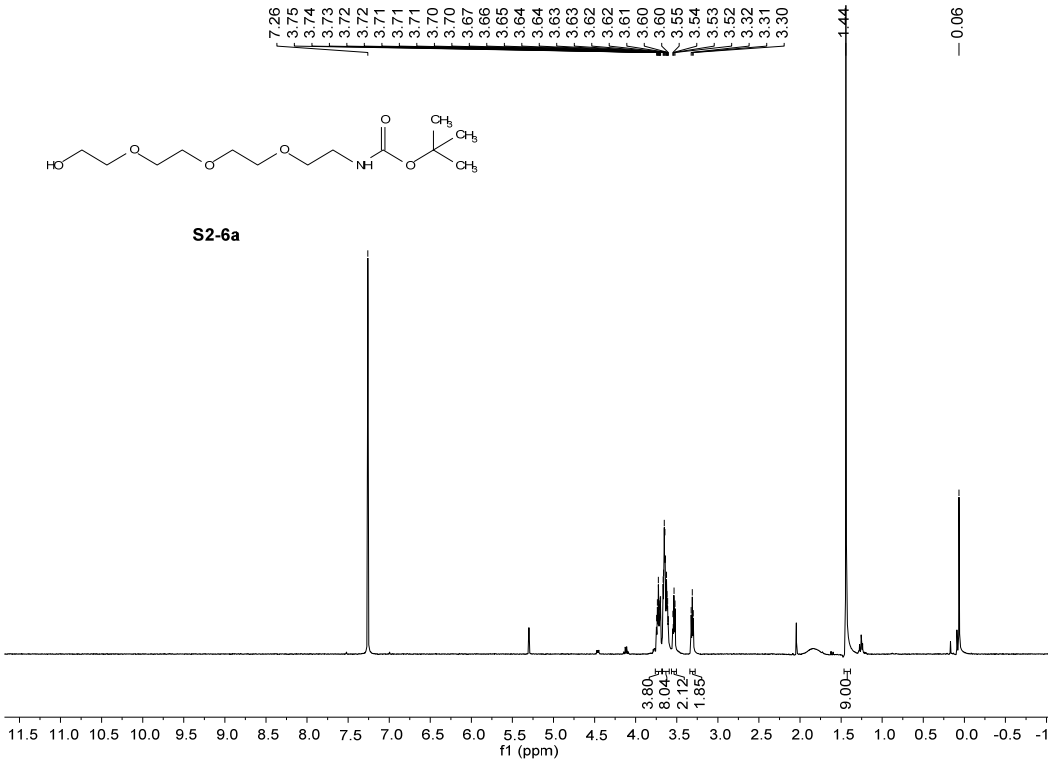

1cc-hv
mixture of upper
and lower spots
Isomer 1: Isomer 2: Isomer 3 = 3:1:5
f1 (ppm)

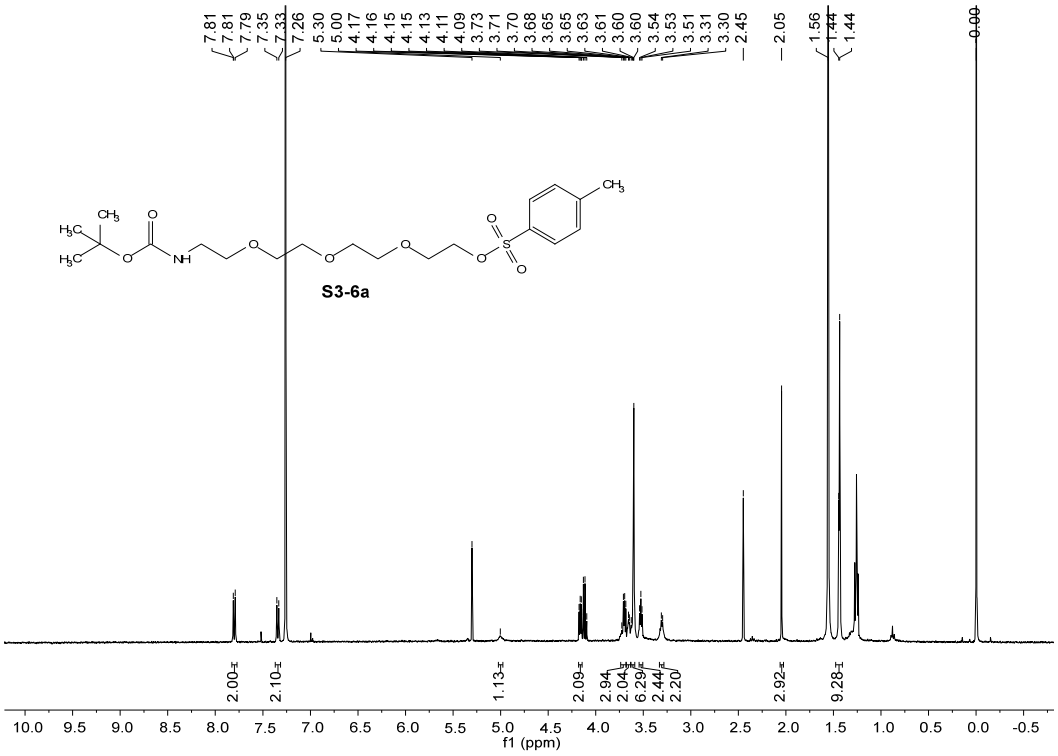

1cc-dark
upper spot
Isomer 1: Isomer 2 = 1:1
f1 (ppm)

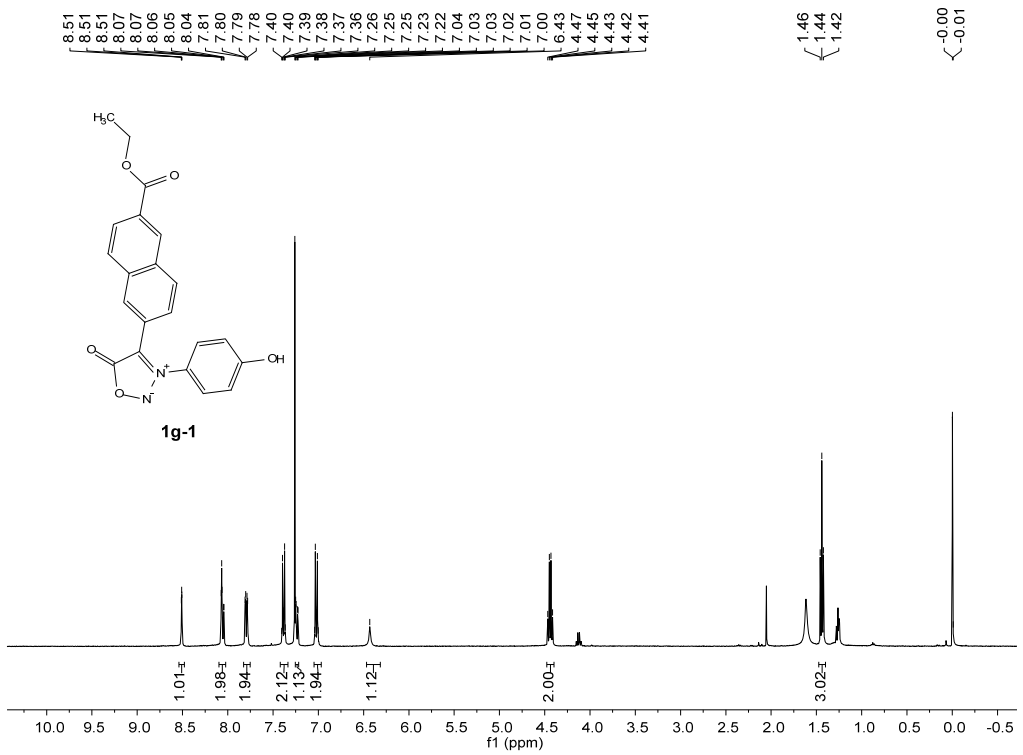

1cc-dark
mixture of upper and lower spots
Isomer 1: Isomer 2 = 2:3
f1 (ppm)

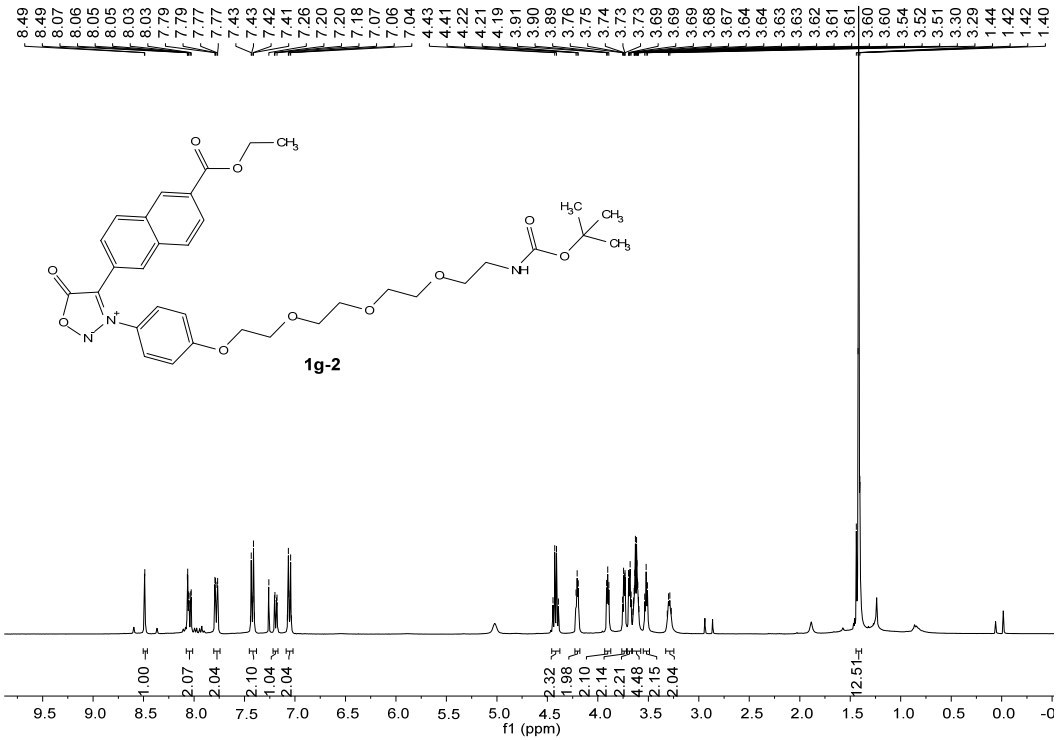

1gc-hv
mixture of upper and lower spots
Isomer 1: Isomer 2: Isomer 3 = 1:1:2.4
f1 (ppm)

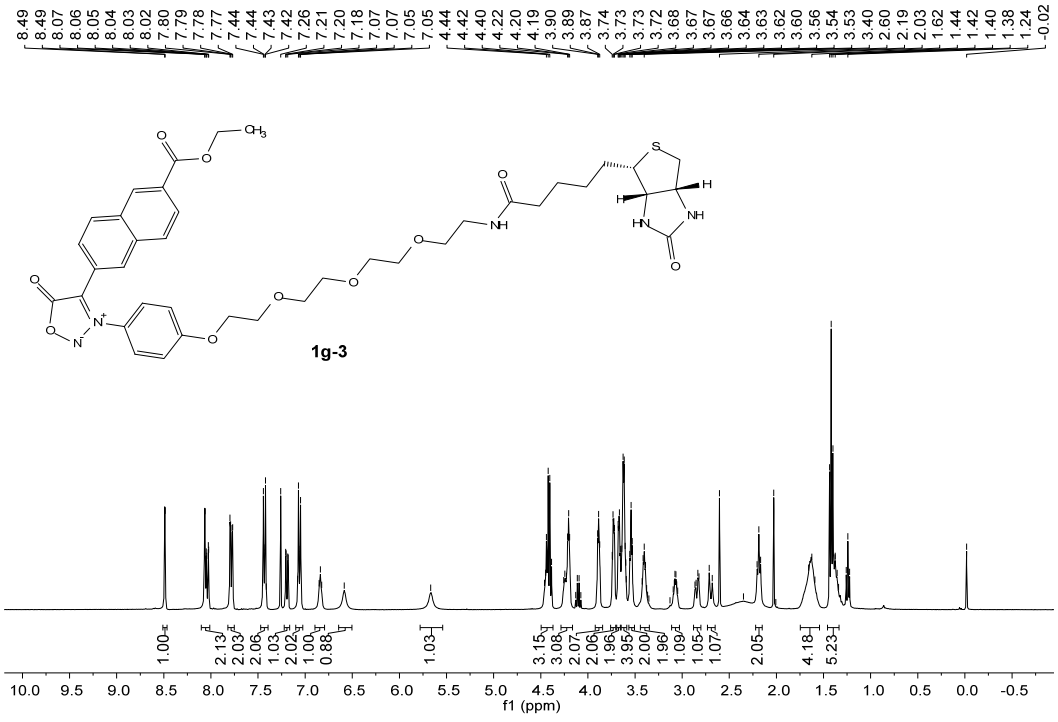

1gc-dark
mixture of upper and lower spots
Isomer 1: Isomer 2: Isomer 3 = 2:1:4
f1 (ppm)

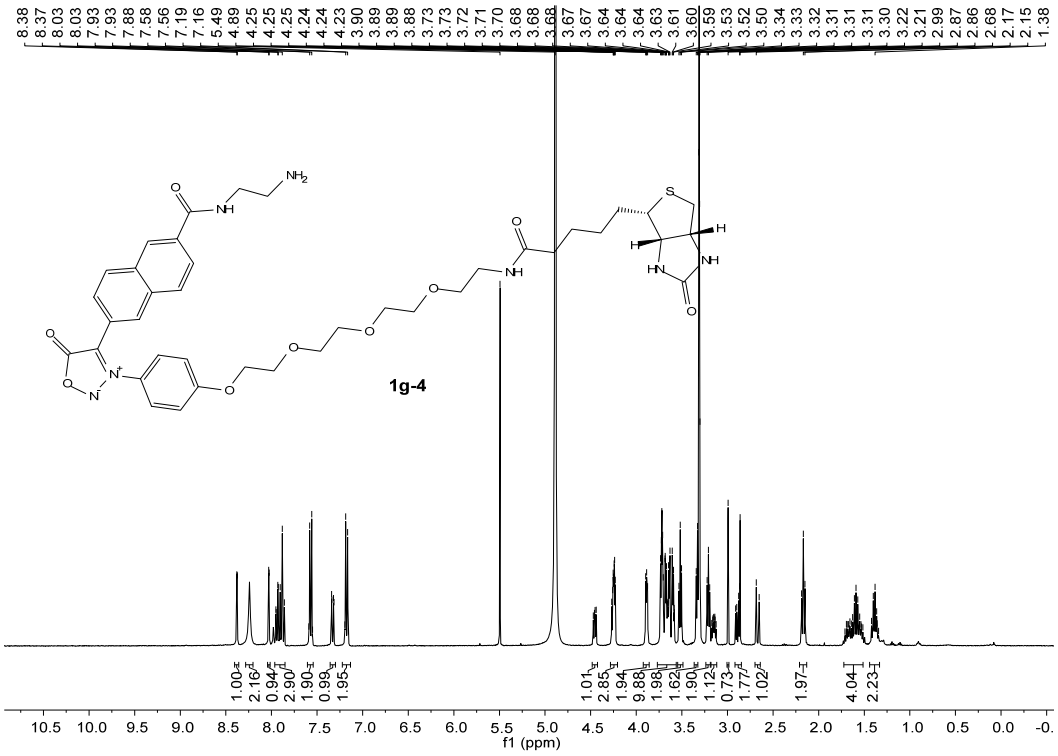

S2-6a
f1 (ppm)

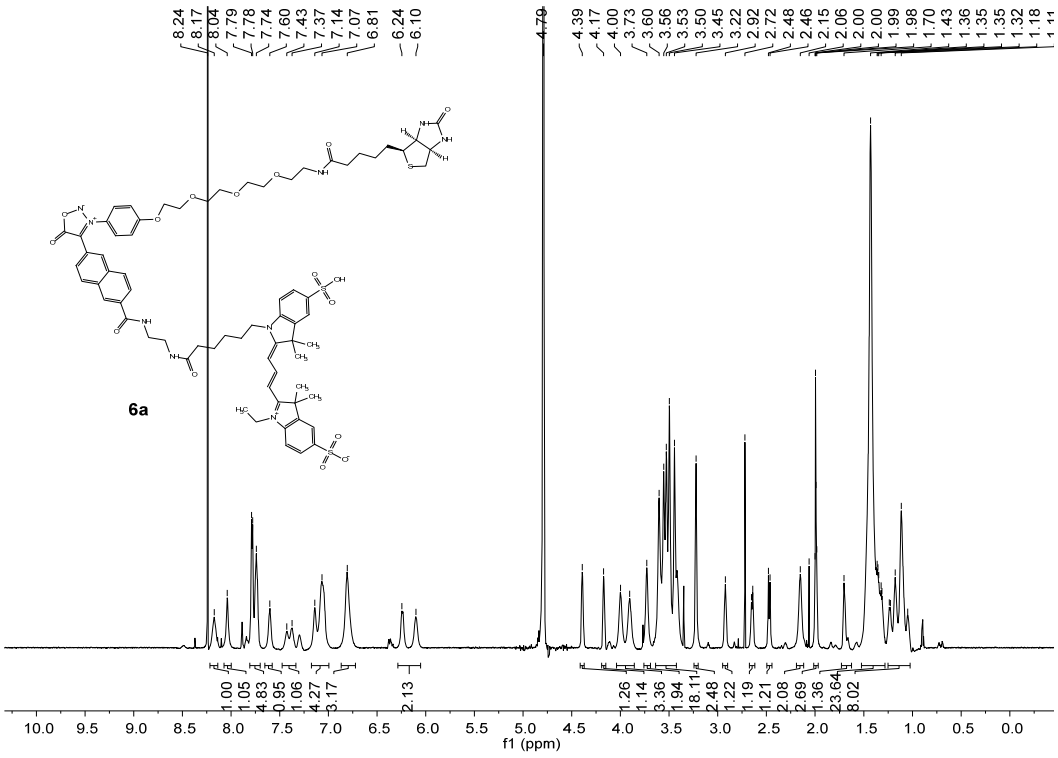

S3-6a
f1 (ppm)


1g-1
f1 (ppm)


1g-2
f1 (ppm)


1g-3
f1 (ppm)


1g-4
f1 (ppm)


6a
f1 (ppm)

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