

1 **Supplementary Material:**

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4 **An Azobenzene based photothermal energy storage system for co-harvest photon**
5 **energy and low-grade ambient heat by photoinduced crystal-to-liquid transition**

6

7 **Liqi Dong^{1,2}, Fei Zhai¹, Hui Wang^{1,2}, Cong Peng¹, Yiyu Feng¹, Wei Feng^{*1,3}**

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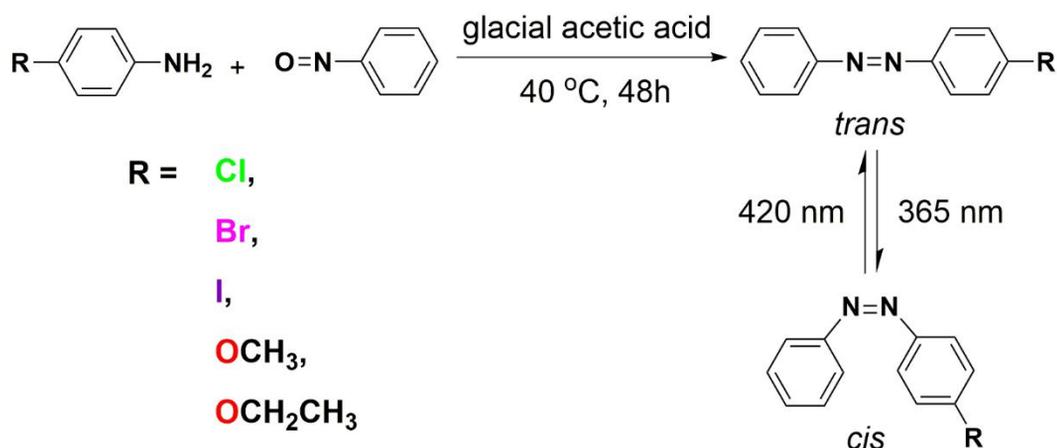
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22 **1. Synthetic route of Azo compounds**

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24 **Scheme S1.** Synthetic route of azobenzene derivatives

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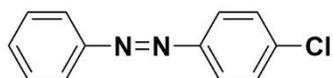
26 **2. General procedure**

27 To a stirred solution of nitrosobenzene (2.14 g, 20 mmol) in glacial acetic acid
28 (100~120 mL) was added *para*-substituted aniline (24 mmol). The resulting solution
29 was stirred at 40 °C for 48 h. Afterward the mixture was diluted with H₂O (500 mL)
30 and extracted with CH₂Cl₂ (5×500 mL). The organic layer was washed with brine
31 (2×500 mL). dried over Na₂SO₄, and filtered, and the solvent was removed in vacuum.
32 The resulting crude product was purified by silica gel column chromatography
33 (hexane/ethyl acetate, 200:1) to give the pure product.

34

3. ¹H and ¹³C NMR, HRMS and FT-IR of Azo compounds

3.1 Compound (E)-1-(4-chlorophenyl)-2-phenyldiazene (Azo-Cl)

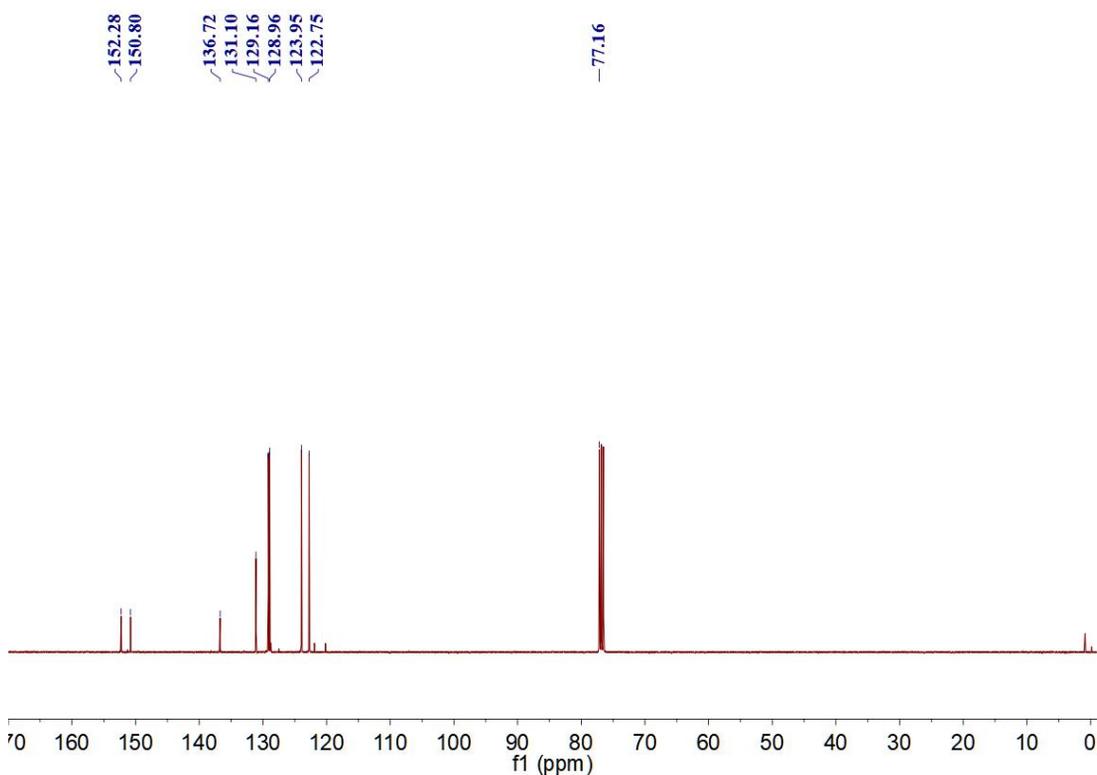


¹H NMR: (400 MHz, Chloroform-*d*) δ : 7.94-7.89 (m, 2H), 7.89-7.84 (m, 2H), 7.55-7.51 (m, 2H), 7.50-7.47 (m, 3H)

¹³C NMR: (100 MHz, Chloroform-*d*) δ : 152.28, 150.80, 136.72, 131.10, 129.16, 128.96, 123.95, 122.75, 77.16.

HRMS (ESI): m/z calculated for C₁₂H₉N₂Cl [M+H]⁺ 217.6701, found 217.95952

¹³C NMR spectrum

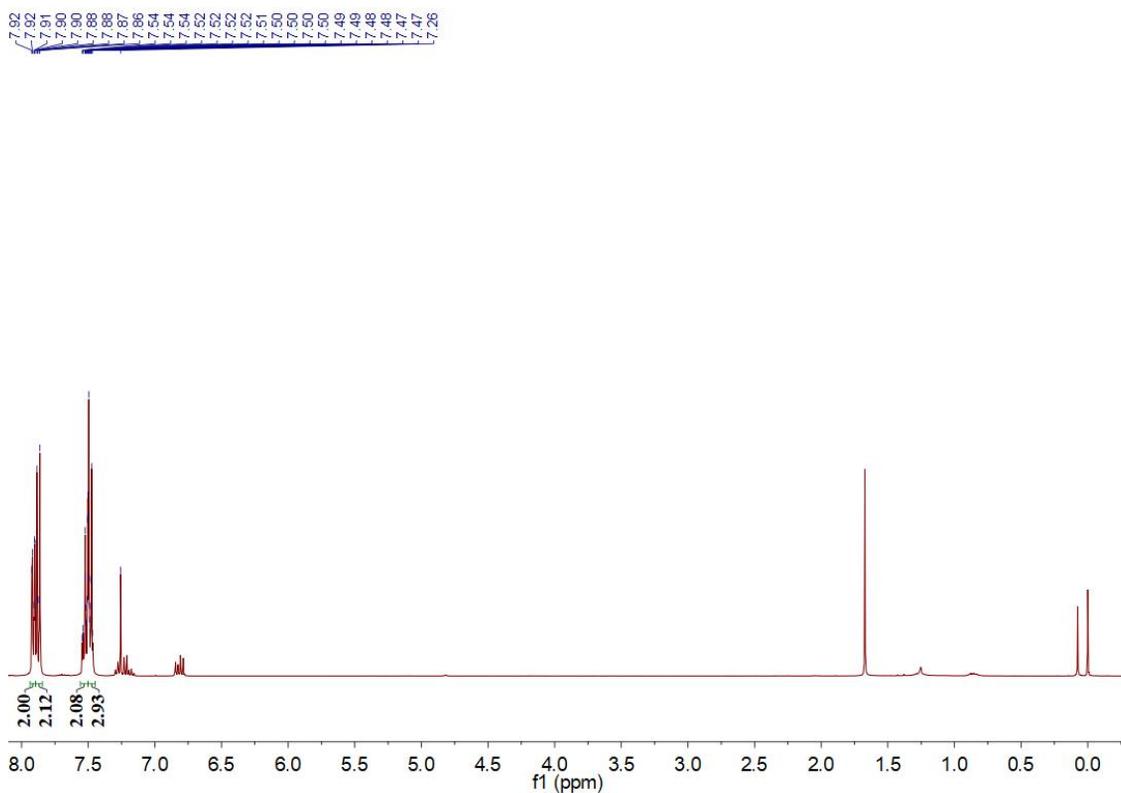


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¹H NMR spectrum of *trans* isomer



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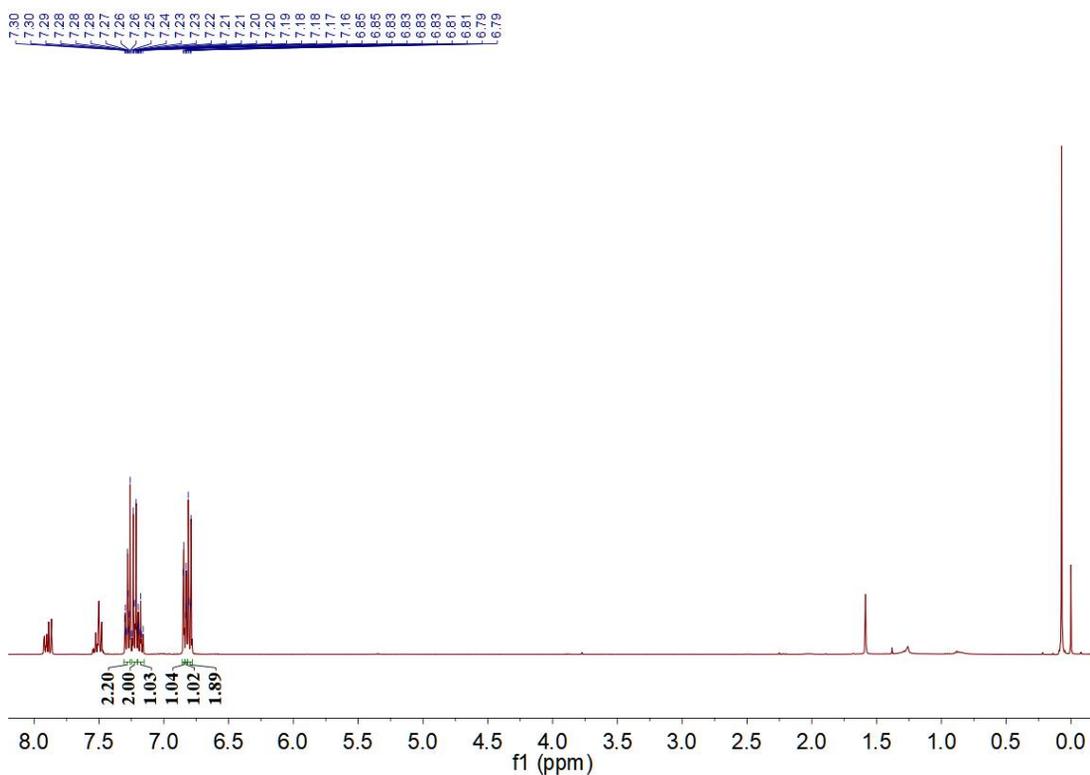
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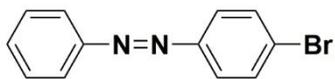
¹H NMR spectrum of *cis* isomer



60

61 3.2 Compound (E)-1-(4-bromophenyl)-2-phenyldiazene (Azo-Br)

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64

65

66 **¹H NMR:** (400 MHz, Chloroform-*d*) δ : 7.95-7.89 (m, 2H), 7.83-7.78 (m, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.56-7.46 (m, 3H).

67

68 **¹³C NMR:** (101 MHz, Chloroform-*d*) δ : 152.59, 151.47, 132.46, 131.46, 129.28, 125.50, 124.49, 123.08, 77.16.

69

70 **HRMS (ESI):** m/z calculated for C₁₂H₉N₂Br [M+H]⁺ 261.002187, found 261.002906

71

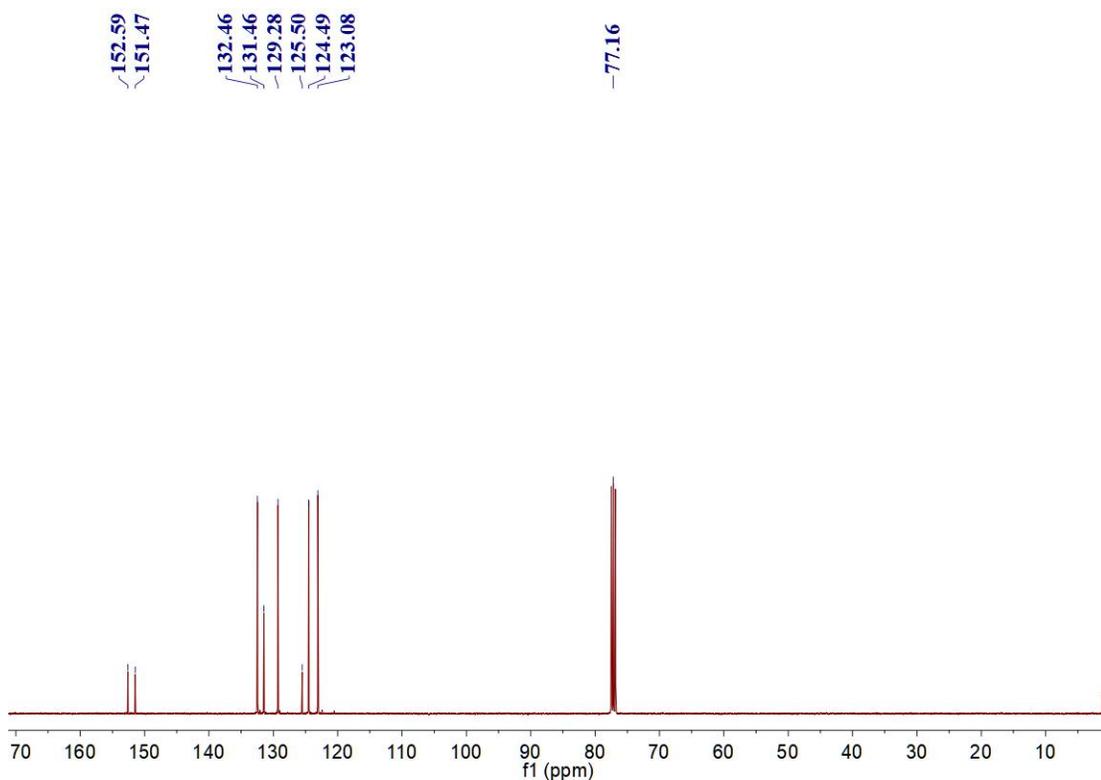
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¹³C NMR spectrum

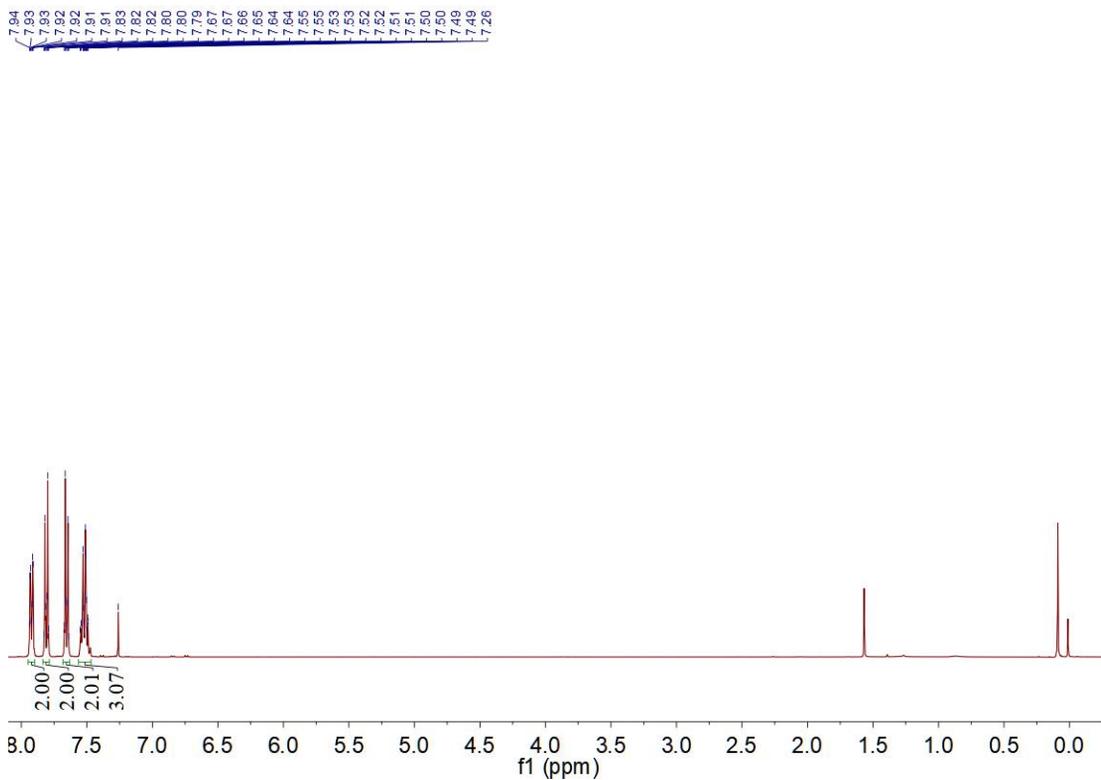
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^1H NMR spectrum of *trans* isomer



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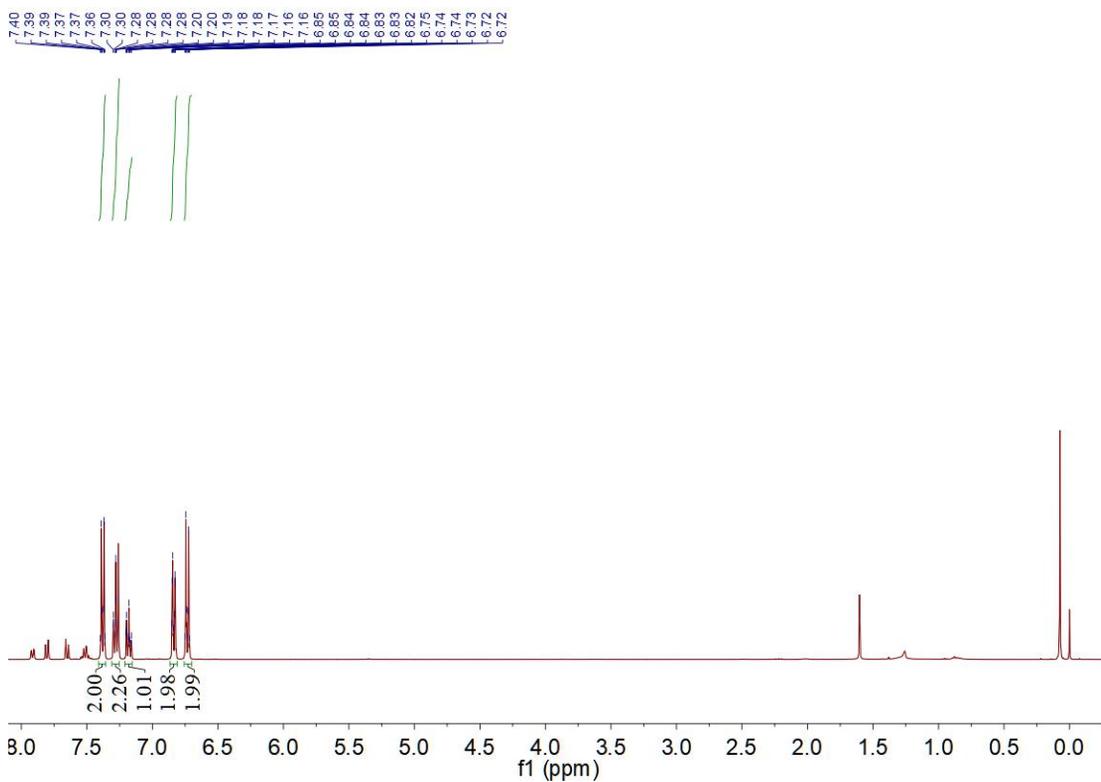
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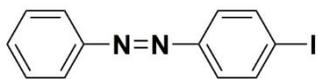
^1H NMR spectrum of *cis* isomer



86

87 3.3 Compound (E)-1-(4-iodophenyl)-2-phenyldiazene (Azo-I)

88



90

91 **¹H NMR:** (400 MHz, Chloroform-*d*) δ : 7.94-7.89 (m, 2H), 7.89-7.84 (m, 2H),
92 7.68-7.63 (m, 2H), 7.55-7.47 (m, 3H).

93

94 **¹³C NMR:** (101 MHz, Chloroform-*d*) δ : 152.26, 151.75, 138.17, 131.17, 128.97,
95 124.29, 122.78, 97.46.

96

97 **HRMS (ESI):** m/z calculated for C₁₂H₉N₂I [M+H]⁺ 308.988318, found 308.988900

98

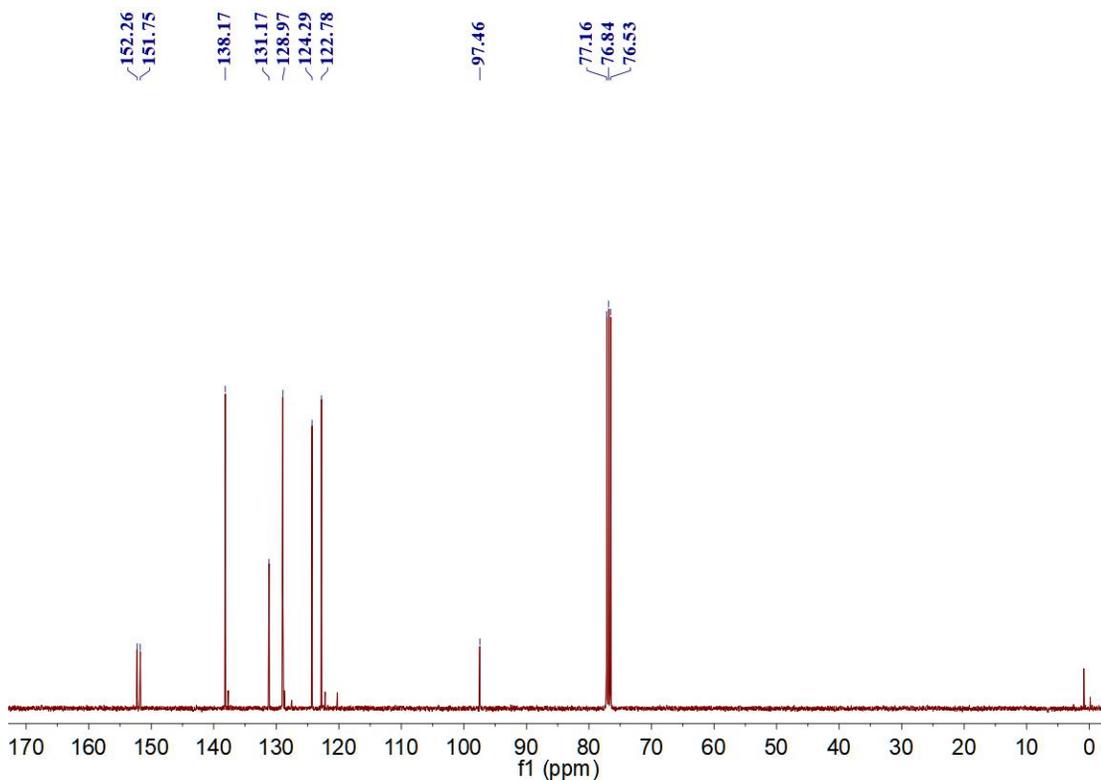
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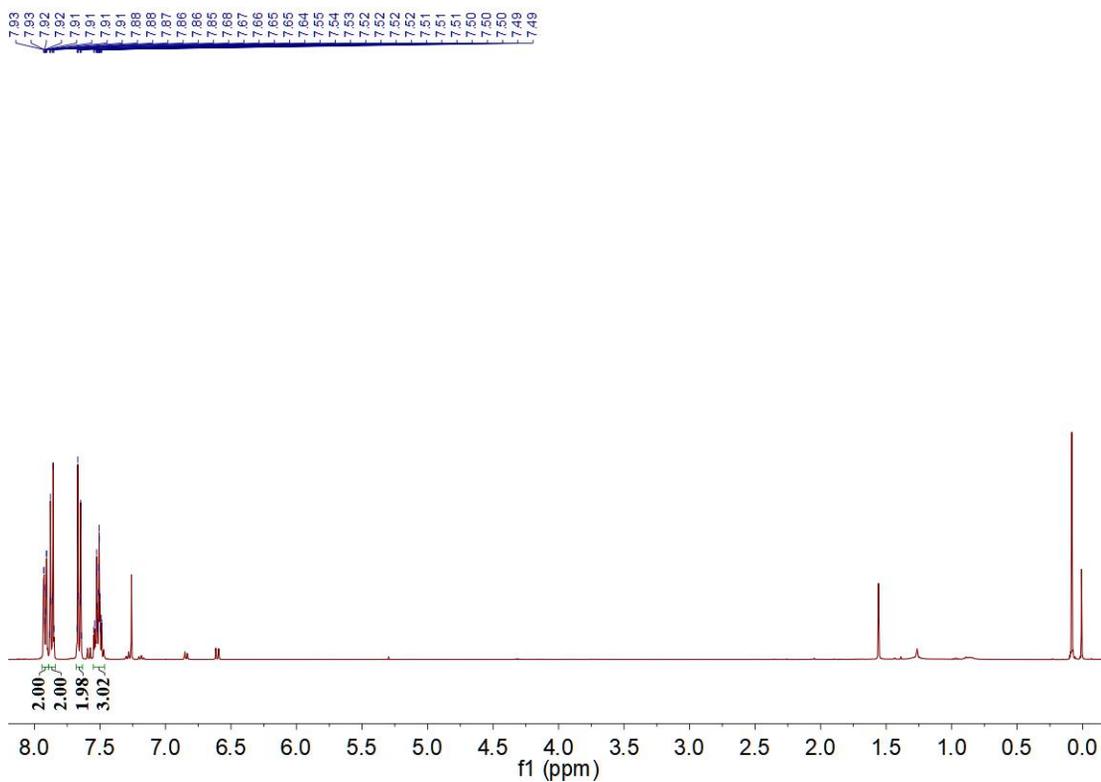
¹³C NMR spectrum

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^1H NMR spectrum of *trans* isomer



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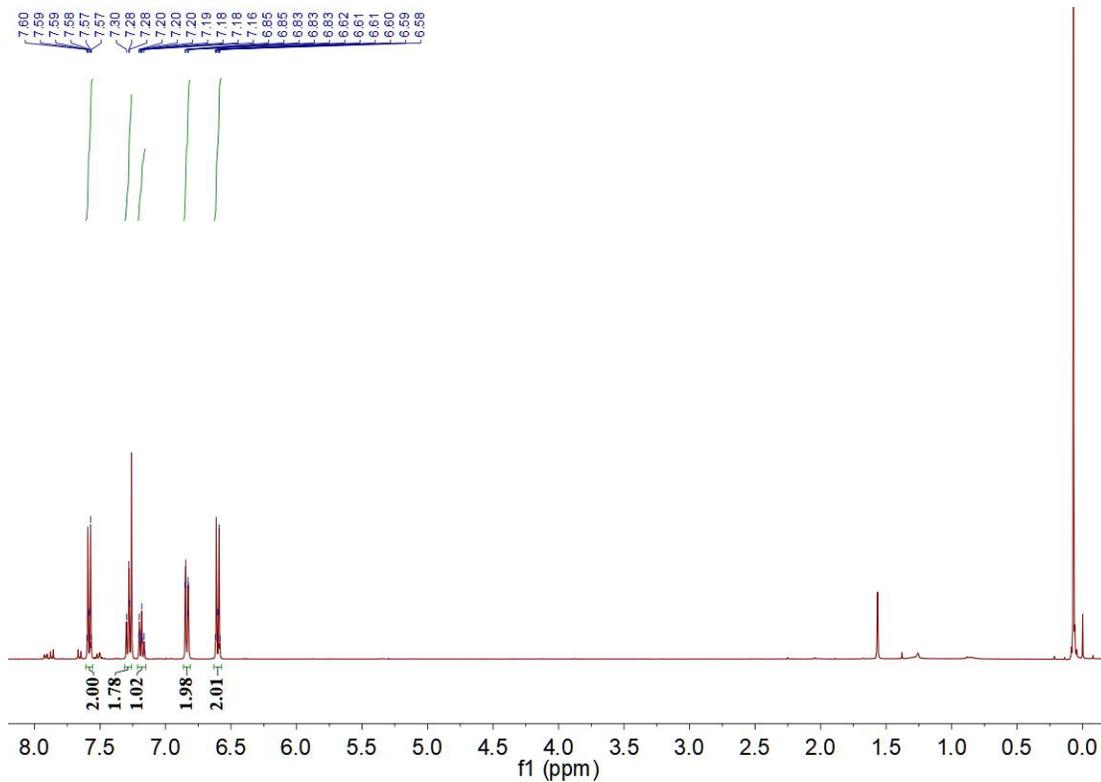
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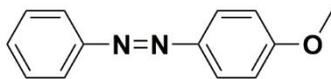
^1H NMR spectrum of *cis* isomer



112

113 3.4 Compound (E)-1-(4-methoxyphenyl)-2-phenyldiazene (Azo-OMe)

114



116

117

117 **¹H NMR:** (400 MHz, Chloroform-*d*) δ: 7.97–7.91 (m, 2H), 7.91–7.86 (m, 2H),
118 7.55–7.48 (m, 2H), 7.48–7.42 (m, 1H), 7.05–6.99 (m, 2H), 3.90 (s, 3H).

119

120 **¹³C NMR:** (101 MHz, Chloroform-*d*) δ: 161.01, 151.73, 145.98, 129.31, 127.98,
121 123.71, 121.51, 113.17, 54.54.

122

123 **HRMS (ESI):** m/z calculated for C₁₂H₉N₂Cl [M+H]⁺ 213.102239, found 213.102333

124

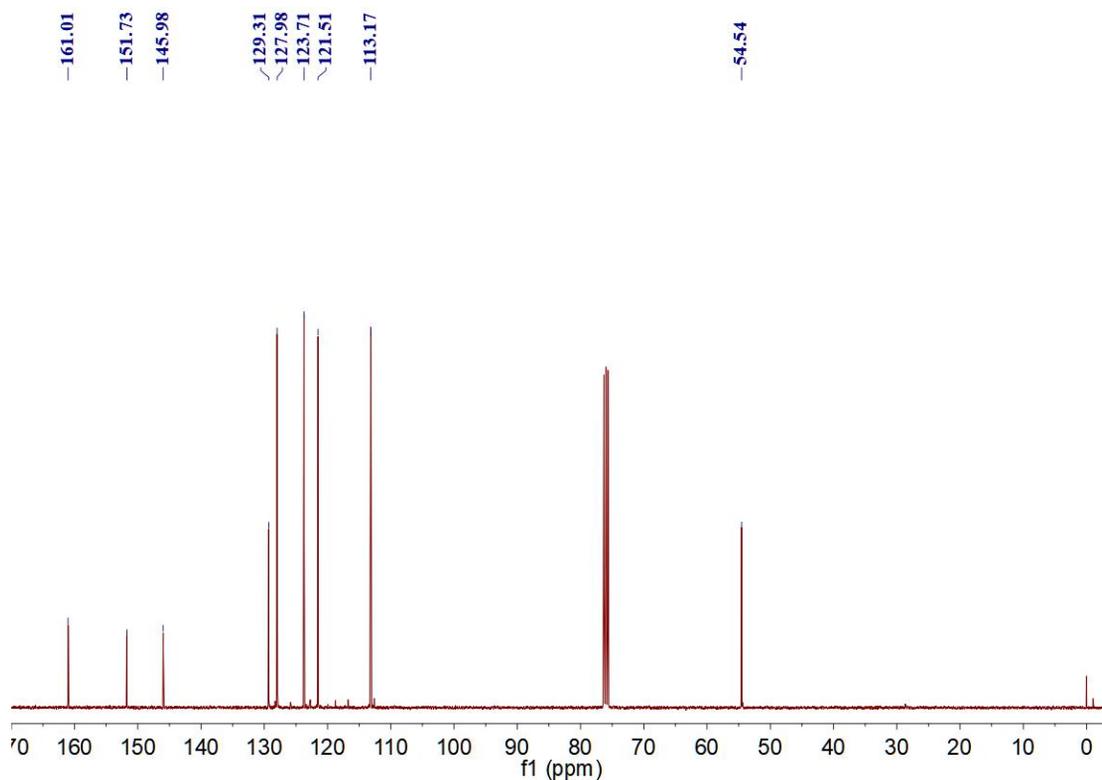
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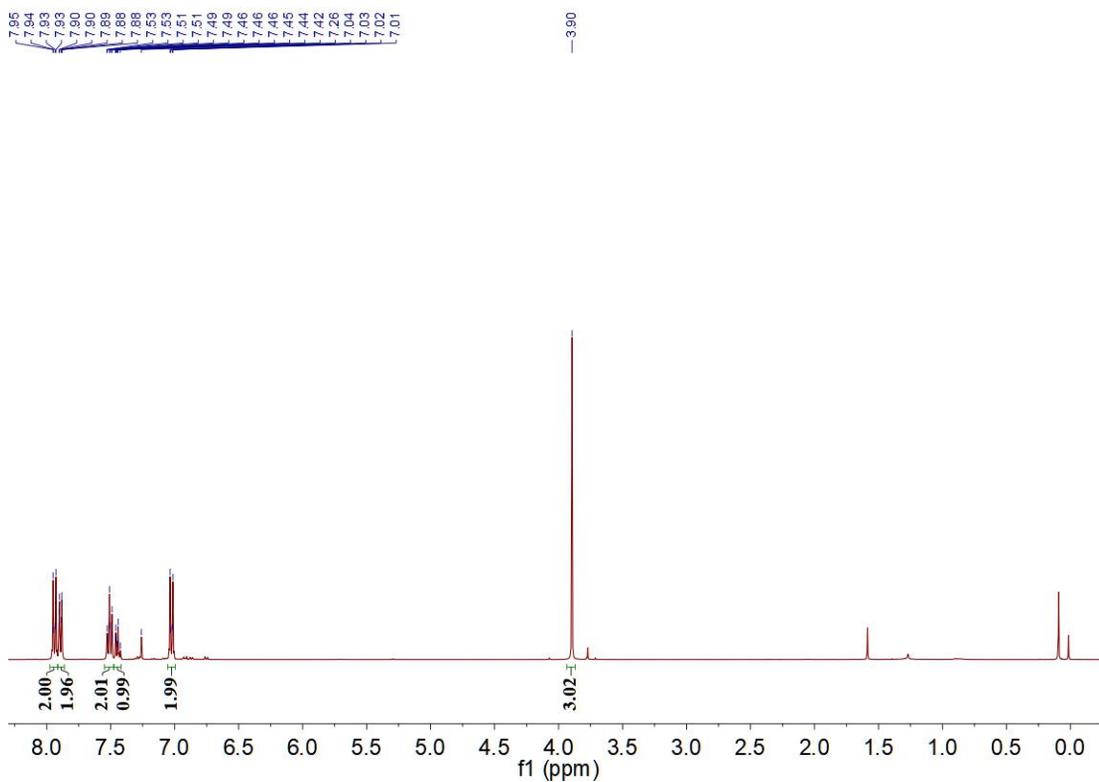
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¹³C NMR spectrum

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 ^1H NMR spectrum of *trans* isomer

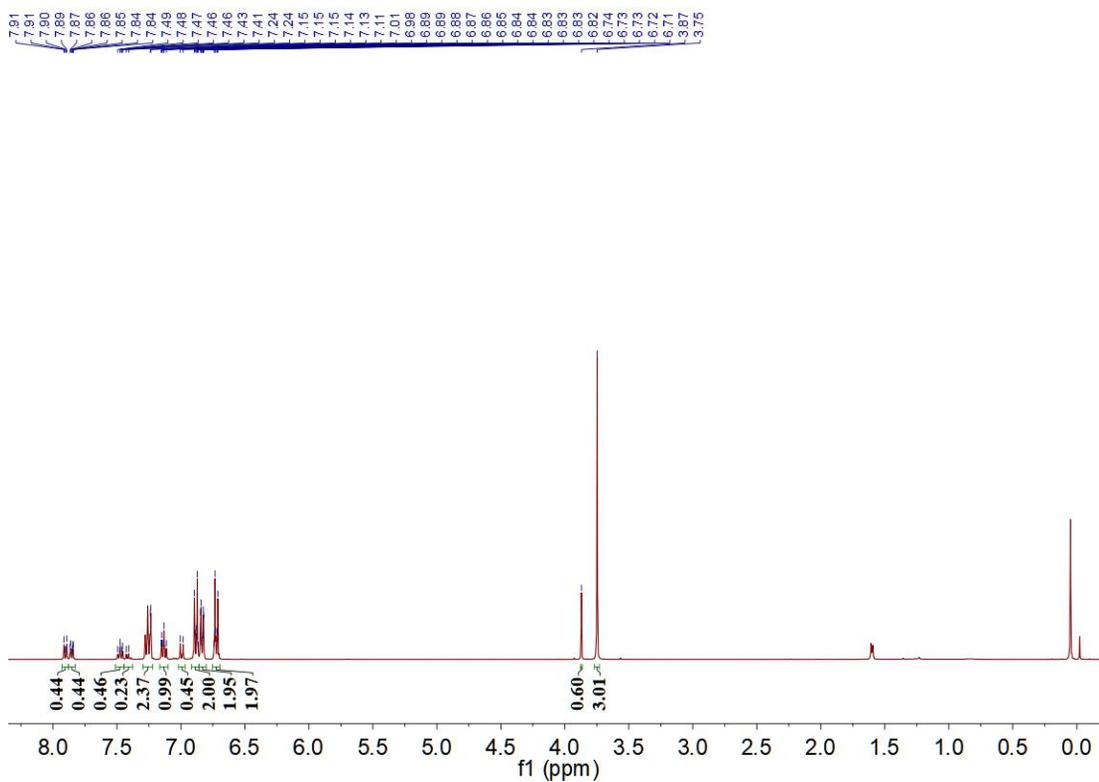
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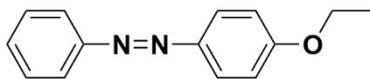
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 ^1H NMR spectrum of *cis* isomer

138

139 3.5 Compound (E)-1-(4-ethoxyphenyl)-2-phenyldiazene (Azo-OEt)

140



142

143

143 **¹H NMR:** (400 MHz, Chloroform-*d*) δ : 7.95-7.90 (m, 2H), 7.90-7.86 (m, 2H),
144 7.53-7.47 (m, 2H), 7.47-7.41 (m, 1H), 7.04-6.98 (m, 2H), 4.12 (q, $J = 7.0$ Hz, 2H),
145 1.46 (t, $J = 7.0$ Hz, 3H).

146

147 **¹³C NMR:** (101 MHz, Chloroform-*d*) δ : 161.39, 152.69, 146.79, 130.20, 128.92,
148 124.65, 122.44, 114.58, 63.73, 14.68.

149

150 **HRMS (ESI):** m/z calculated for $C_{12}H_9N_2Cl$ $[M+H]^+$ 227.117890, found 227.117913

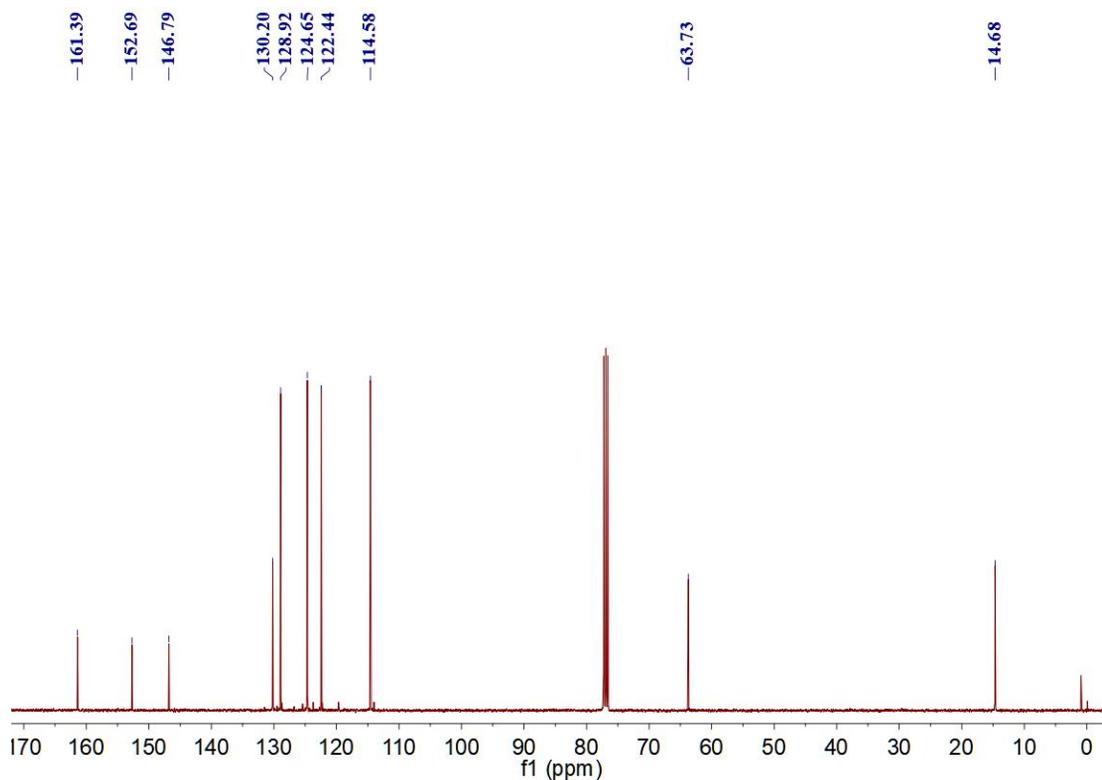
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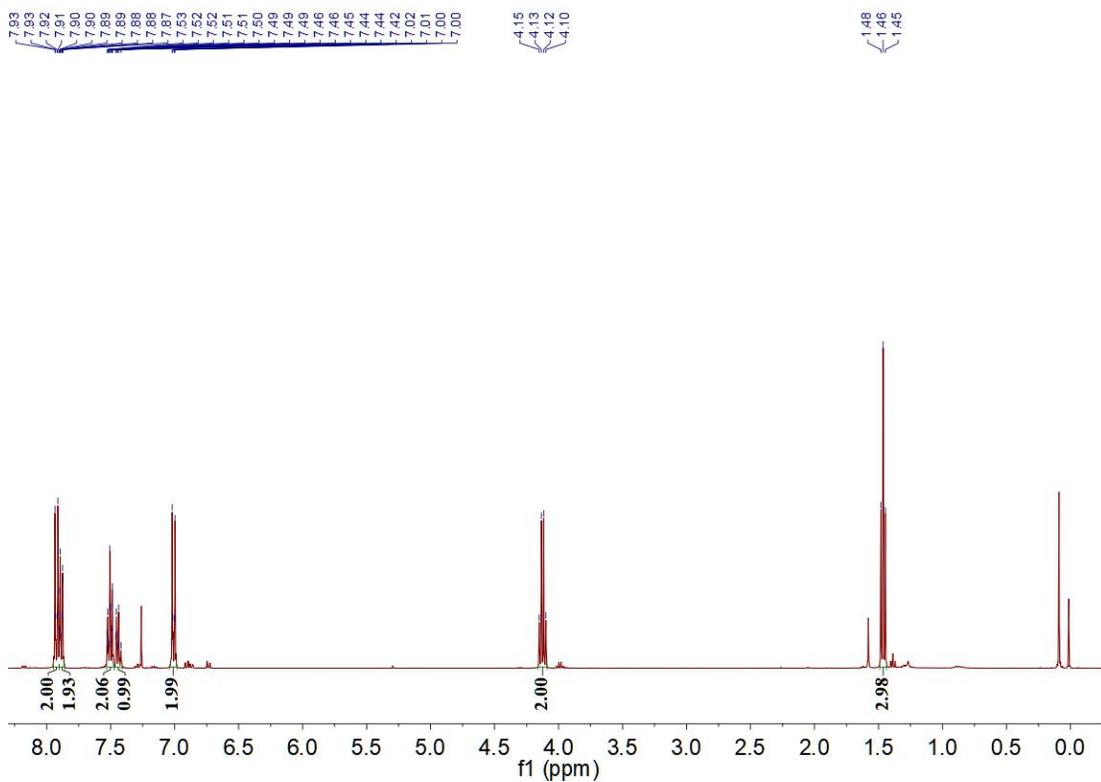
¹³C NMR spectrum

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¹H NMR spectrum of *trans* isomer



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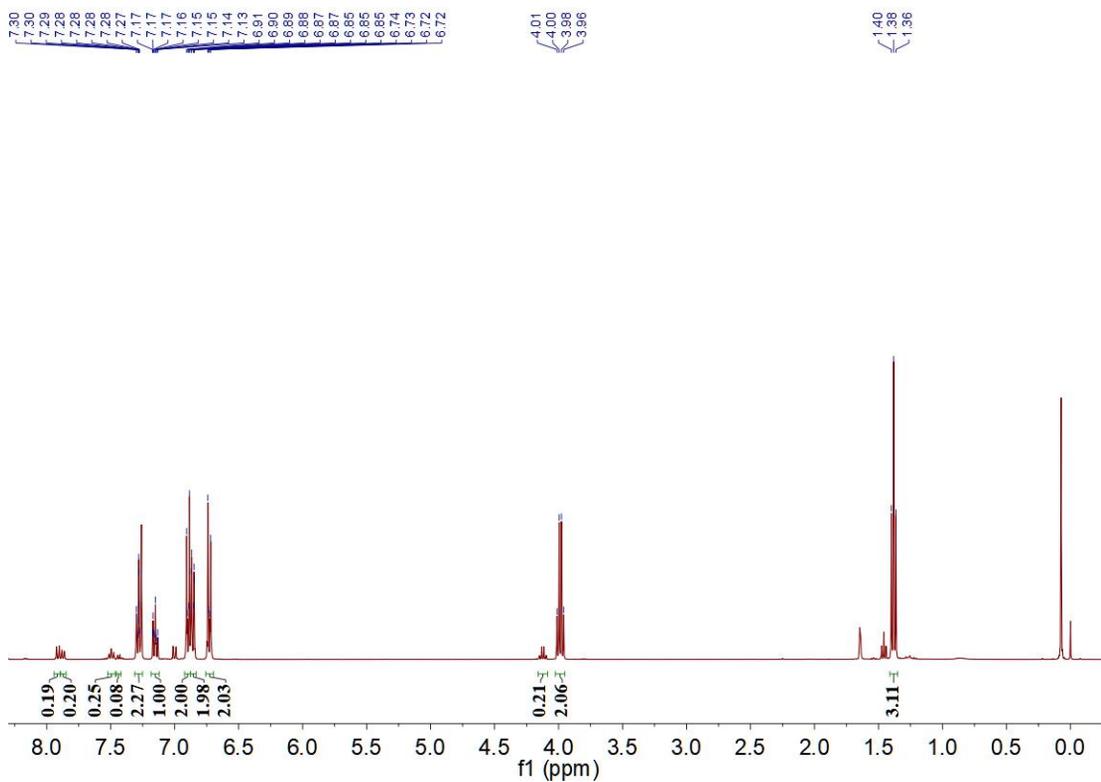
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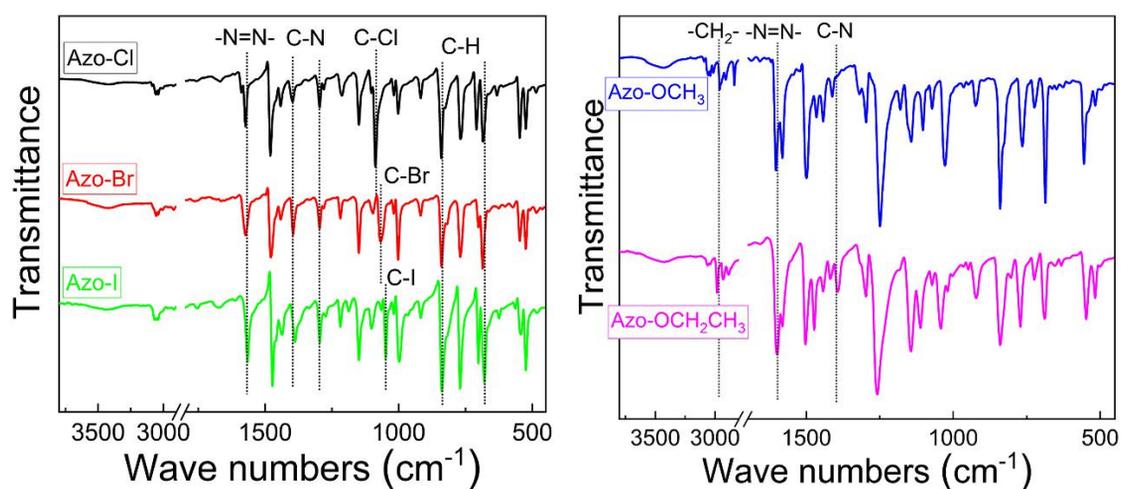
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¹H NMR spectrum of *cis* isomer



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165 3.6 FT-IR spectra



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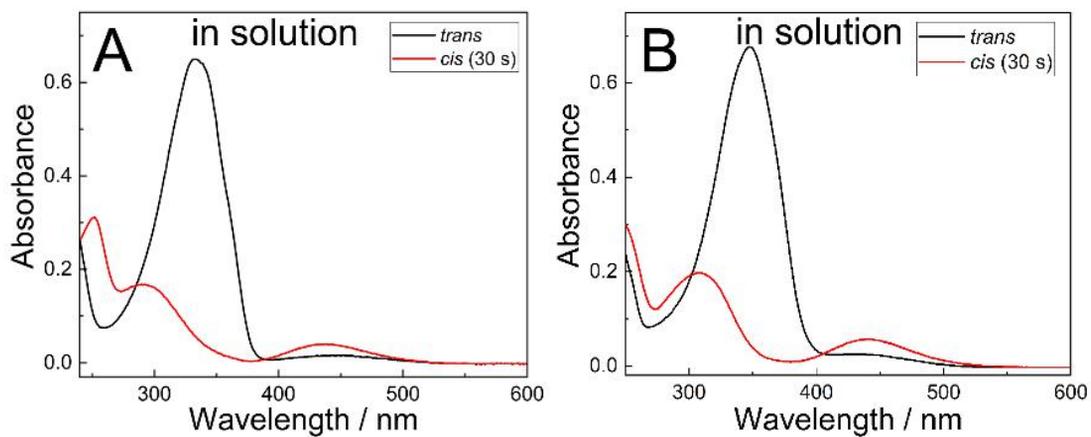
168

169 **Supplementary Table S1.** Assignment of FT-IR spectra for Azo compounds

Band (cm ⁻¹)					Assignment
Azo-Cl	Azo-Br	Azo-I	Azo-OMe	Azo-OEt	
3058	3058	3068			Weak, C-H (v)
			2961, 2838	2983	-CH ₃ (v)
				2930, 2881	-CH ₂ - (v)
1573	1573	1566	1604, 1580	1600	-N=N- (v)
1480	1472	1478	1502	1502	=C-H and ring C=C (v)
1397, 1295	1388, 1295	1395, 1295	1298	1296	C-N (v)
			1250, 1241	1258, 1242	C-O-C (v)
			1103	1110	C-H (v) of -CH ₃
1087					C-Cl
	1068				C-Br
		1049			C-I
840, 770, 684	840, 770, 686	839, 770, 679	924	923	=C-H of benzene ring (γ)
548, 524	547, 524	544, 523	555	547	=C-X (γ)

170

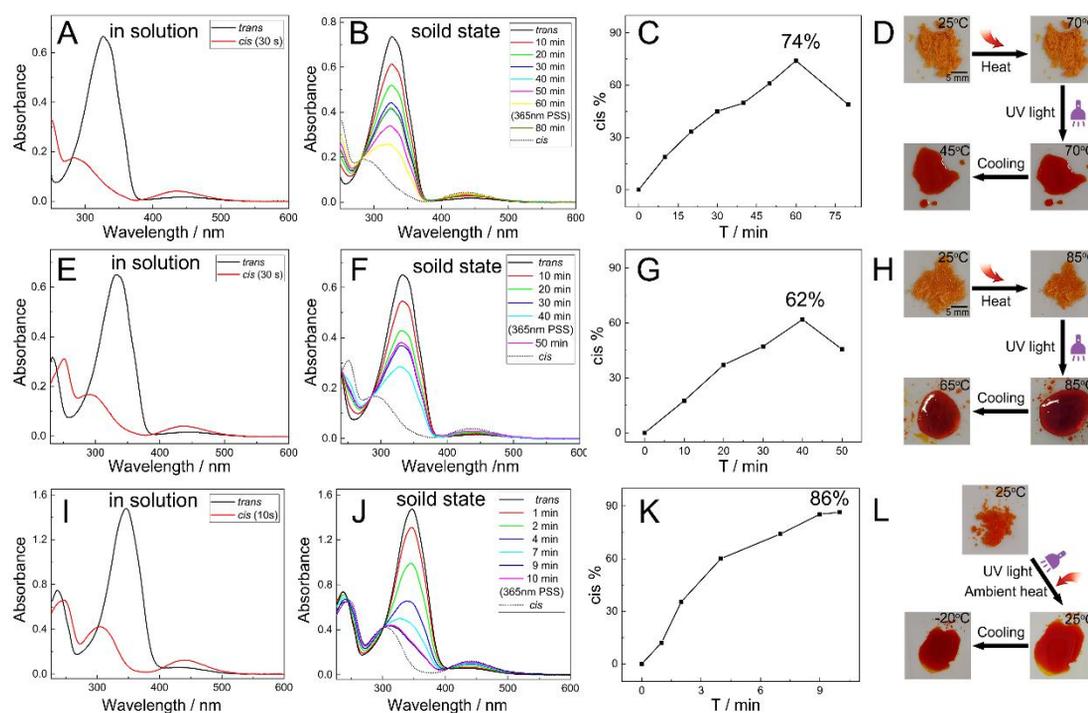
171 **4. UV-Vis absorption spectra**



172

173 **Figure S1.** Time-evolved UV-Vis absorption spectra of Azo-Cl (A) and Azo-OEt (B)174 samples irradiated with UV light of 365-nm in DCM solution (1×10^{-4} mol L⁻¹).

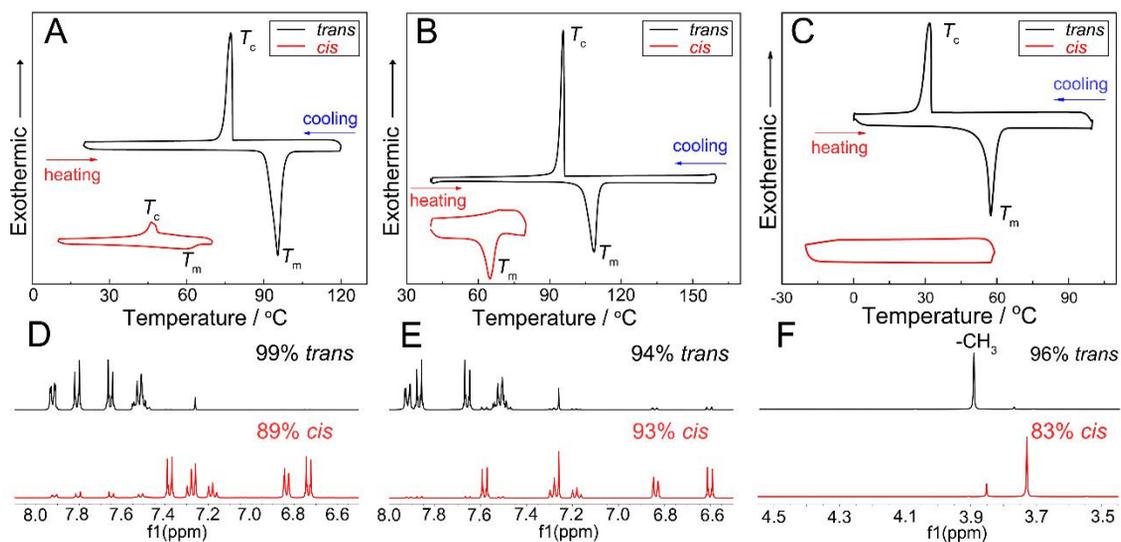
175

176 **5. The energy charging process: *trans*-crystal to *cis*-liquid transition**

177

178 **Figure S2.** Co-harvesting of photon energy and ambient T heat, i.e., the energy charging
 179 process. First column: time-evolved UV-Vis absorption spectra of the Azo-Br (A),
 180 Azo-I (E), and Azo-OMe (I) samples irradiated with UV light of 365-nm in DCM
 181 solution (1×10^{-4} mol L⁻¹). Second column: time-evolved UV-Vis absorption spectra of
 182 *trans*-crystals form for the Azo-Br (B), Azo-I (F), and Azo-OMe (J) samples irradiated
 183 with UV light of 365-nm. Samples were taken during irradiation and dissolved in DCM,
 184 and the spectra had been normalized with respect to the isosbestic point at 281-nm for
 185 Azo-Br, 285-nm for Azo-I, and 301-nm for Azo-OMe, respectively. Third column: the
 186 *cis* isomer content of Azo-Br (C), Azo-I (G), and Azo-OMe (K) vs. irradiation time.
 187 Fourth column: images of the Azo-Br (D), Azo-I (H), and Azo-OMe (L) samples on
 188 glass slides. As indicated by the arrows, the *trans*-crystals before irradiation, *cis*-liquid
 189 after 365-nm light irradiation, and *cis*-liquid after cooling.

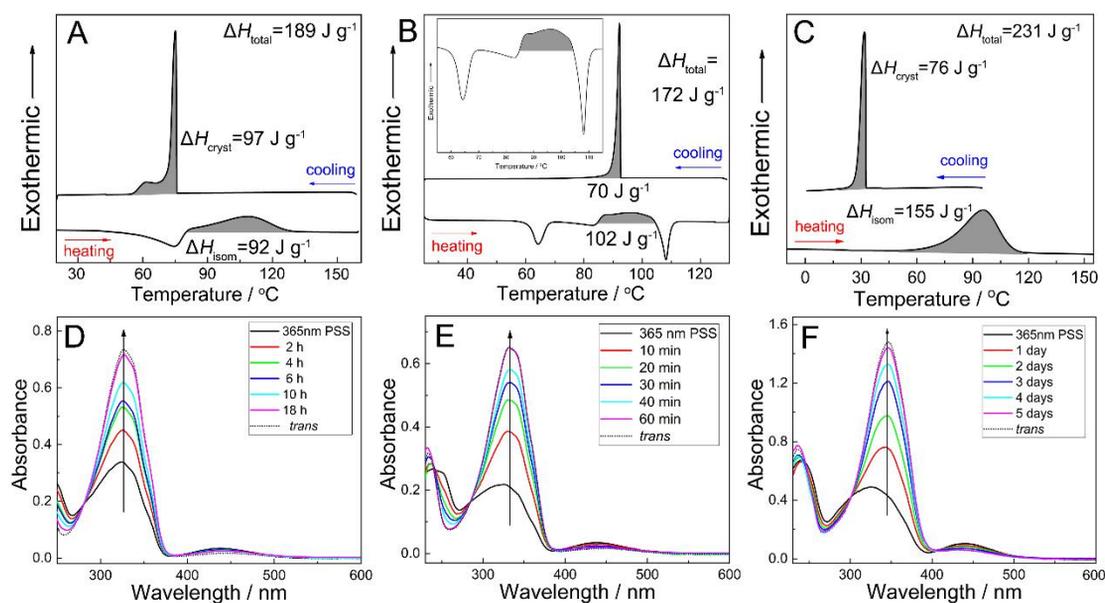
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191 **6. Phase transition properties of isomers**

192

193 **Figure S3.** Phase transition of isomers. First row: DSC plots of trans (top curve) and
194 cis (bottom curve) isomers upon heating and cooling for Azo-Br (A), Azo-I (B), and
195 Azo-OME (C). T_m represents the melting temperature, and T_c represents the
196 crystallization temperature. Second row: the ^1H NMR spectra of the Azo-Br (D), Azo-I
197 (E), and Azo-OME (F) isomers for DSC tests.

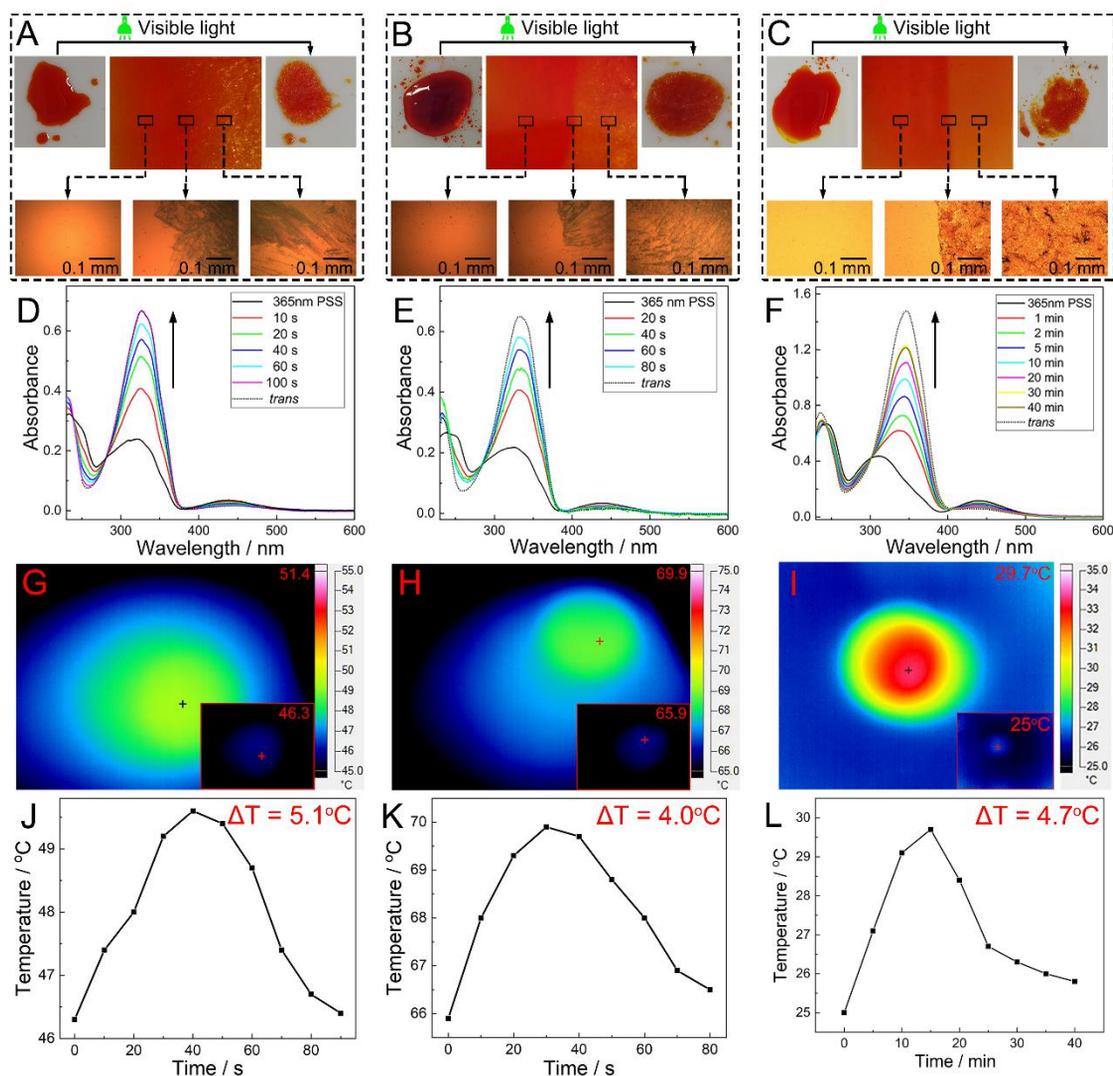
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199 **7. Energy storage properties of the *cis* isomer**

200

201 **Figure S4.** Energy storage properties. First row: DSC curves of typical *cis*-liquid Azos
 202 for Azo-Br (A), Azo-I (B), and Azo-OMe (C). For clarity, the heating and cooling
 203 curves are not shown with the same scale of the Y-axis. Second row: time-evolved
 204 UV-Vis absorption spectra of the *cis*-liquid form of Azo-Br (D), Azo-I (E), and
 205 Azo-OMe (F) reversion in darkness (the spectra had been normalized with respect
 206 to their corresponding isosbestic point). The arrows indicate the test order.

207

208 **8. The energy discharging process: *cis*-liquid to *trans*-crystal transition**

209

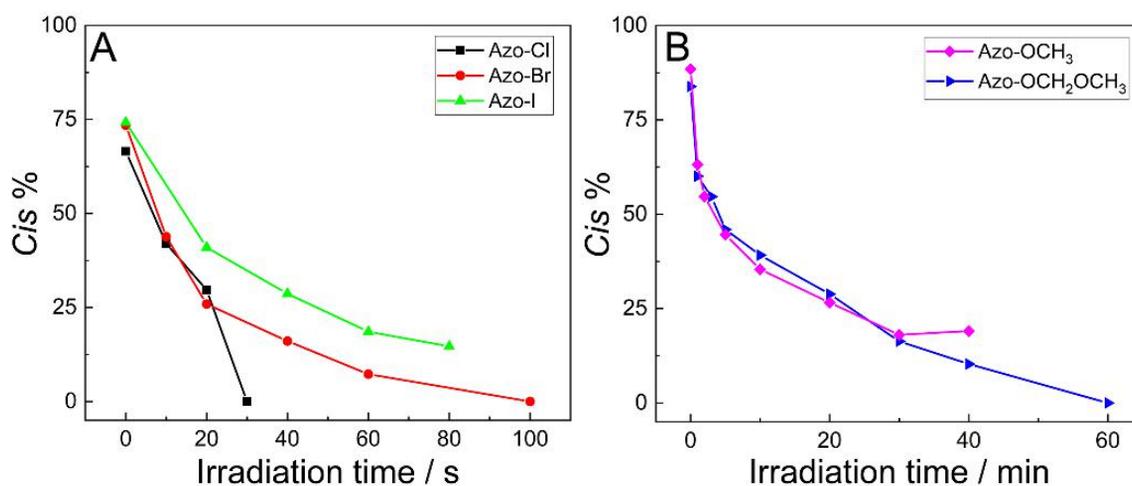
210 **Figure S5.** Experimental demonstration of the selective photo-induced crystallization
 211 process of the liquid sample and the photoinduced heat release monitoring. (A-C) The
 212 selective photoinduced crystallization process of Azo-Br (A), Azo-I (B), and Azo-OMe
 213 (C), which are irradiated with visible light (420-nm) at the ambient temperature of
 214 45 °C, 65 °C and -20 °C, respectively. The left side of the liquid film is covered with
 215 cardboard to preserve the *cis* isomers in their stable liquid state. Optical microscope
 216 images of the left side, right side, and center of the film showing liquid phase, solid
 217 phase, and the boundary between liquid and crystalline solid, respectively. The images
 218 on the top corners show *cis*-liquid samples before (left) and after (right) 420-nm light
 219 irradiation. (D-F) Normalized UV-Vis spectra of the uncovered parts for Azo-Br (D),
 220 Azo-I (E), and Azo-OMe (F) during the 420-nm light irradiation. The arrows indicate
 221 the test order. (G-I) IR thermal images of Azo-Br (G), Azo-I (H) and Azo-OMe (I)

222 under 420-nm light irradiation. The insets show the samples before the light irradiation.
223 The number in the upper right corner of each figure indicates the highest temperature of
224 the materials. (J-L) Temperature-time curves of Azo-Br (J), Azo-I (K), and Azo-OMe
225 (L) during heat release. ΔT represent temperatures difference before and after the heat
226 release.

227

228

229 9. Decrease of *cis* content upon 420 nm light irradiation



230

231 **Figure S6.** The *cis* isomer content of Azo compounds vs. irradiation time during the
232 420-nm light irradiation.

233

234 **10. Tables**

235 **Table S2.** The heat temperature and the final temperature to maintain the liquid state of
 236 each Azo compounds

Samples	Heat temperature T_1 (°C)	Final temperature T_2 (°C)
Azo-Cl	60	35
Azo-Br	70	45
Azo-I	85	65
Azo-OMe	25	-20
Azo-OEt	25	-20

237

238 **Table S3.** T_m and T_c of *trans* and *cis* Azo compounds and the corresponding ΔT

Azo compounds	T_m (°C)			T_c (°C)		
	<i>Trans</i> isomer	<i>Cis</i> isomer	ΔT_m	<i>Trans</i> isomer	<i>Cis</i> isomer	ΔT_c
Azo-Cl	92	47	45	67	9	58
Azo-Br	95	60	35	77	46	31
Azo-I	108	64	44	95	No data	
Azo-OMe	57	< -20	> 77	32	No data	
Azo-OEt	78	< -20	> 98	33	No data	

239