Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences.

SUPPORTING INFORMATION

Solid State and Surface Effects in Thin-Film Molecular Switches

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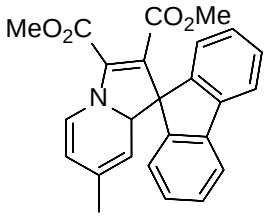
General Experimental Methods:

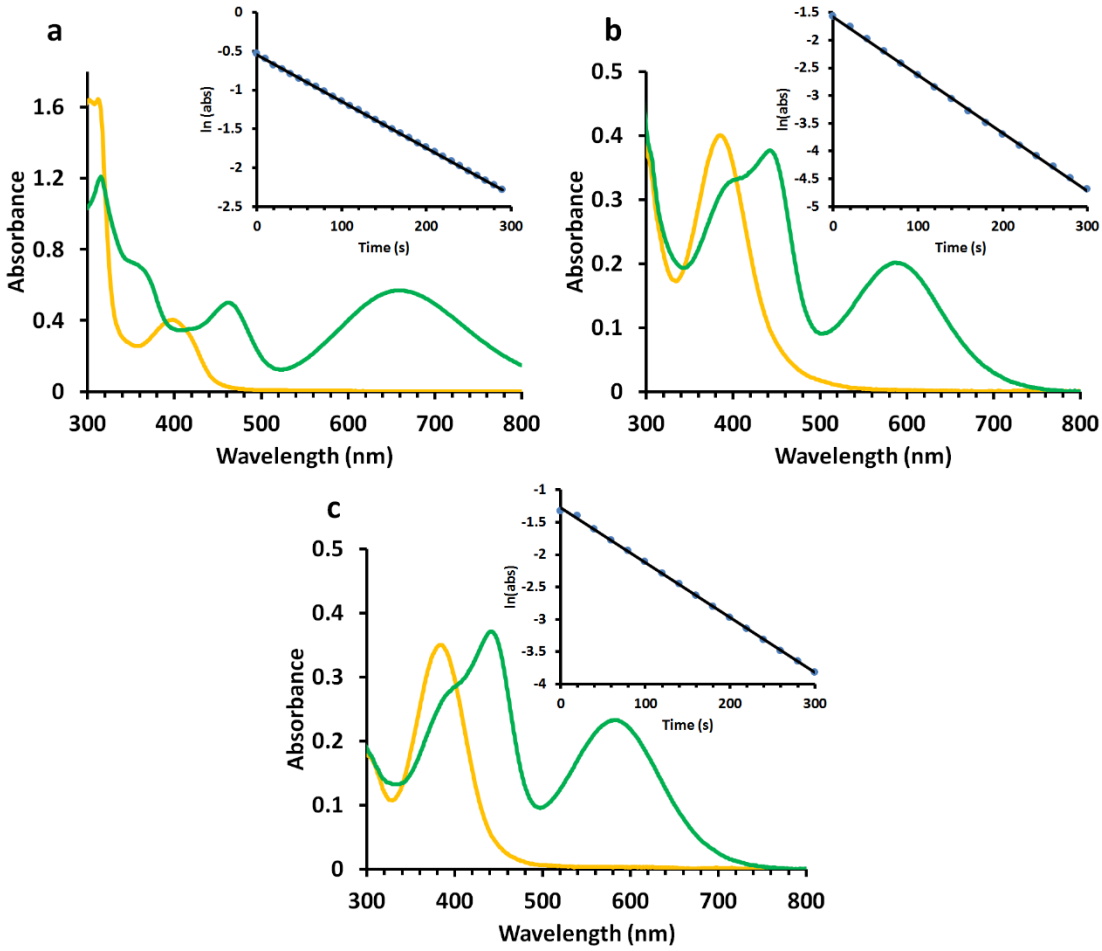
All reactions were run under a nitrogen atmosphere unless otherwise stated. All column chromatography separations were performed on silica gel 60 (40-63 μm from BDH). Thin layer chromatography was carried out on silica gel (F_{254}) with glass support. All NMR spectra were taken on a Varian 500 MHz spectrometer. All ^{1}H and ^{13}C chemical shifts (δ) were referenced to trimethylsilane in $CDCl_3$. IR spectra were acquired on a Shimadzu IRAffinity-1S FTIR with a Pike Technologies MIRacle single reflection horizontal ATR accessory. Mass spectra were acquired on a Shimadzu ESI-TOF. Dimethyl spiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate was prepared following a previous procedure.[1]

Synthesis of DHI-9:



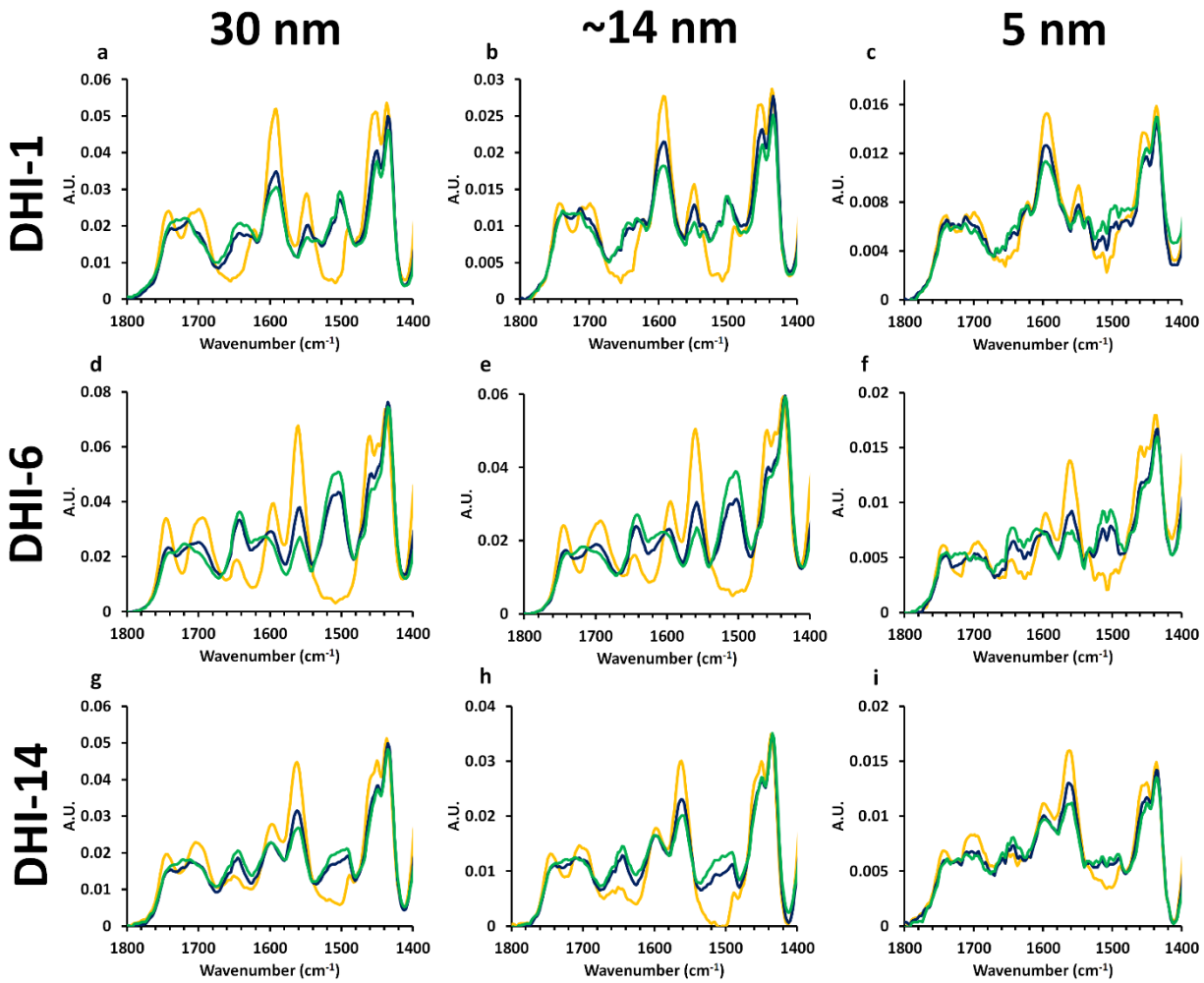
7′-Methyl-8a′*H*-spiro[fluorine-9,1′-indolizine]-2′,3′-dicarboxilate (DHI-9): 4-Methylpyridine (0.010 g, 0.11 mmol) and dimethyl spiro[cycloprop[2]ene-1,9′-fluorene]-2,3-dicarboxylate (0.037 g, 0.12 mmol) were added to a round bottomed flask. The flask was evacuated and filled with nitrogen (×3). Dichloromethane (2 mL) was added and the flask and the solution was stirred in the dark for 4 h. The product (0.028 g, 0.069 mmol) was purified via column chromatography (100% DCM, R_f = 0.38) and collected as a green oil at a 65% yield. ^{1}H NMR (500 MHz) δ 7.72 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.40-7.29 (m, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 7.3 Hz, 1H), 5.43 (s, 1H), 5.06 (dd, *J* = 7.5, 1.1 Hz, 1H), 4.19 (s, 1H), 3.99 (s, 3H), 3.26 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (125 MHz) δ 163.6, 162.1, 147.3, 146.5, 142.5, 141.5, 140.1, 131.5, 128.0, 127.8, 127.3, 126.8, 124.6, 123.7, 123.3, 119.7, 119.4, 112.5, 108.6, 108.2, 69.9, 64.2, 53.1, 50.9, 20.6. IR (ATR, cm^{-1}): 2949, 2789, 1742, 1694, 1649, 1593, 1557, 1460, 1435, 1393, 1308, 1263, 1225, 1182, 1130, 1084, 731. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}NO_4H$ 400.1504; Found 400.1525.

Figure S1: Solution UV-vis of **DHI-1**, **6**, and **14** half-life data



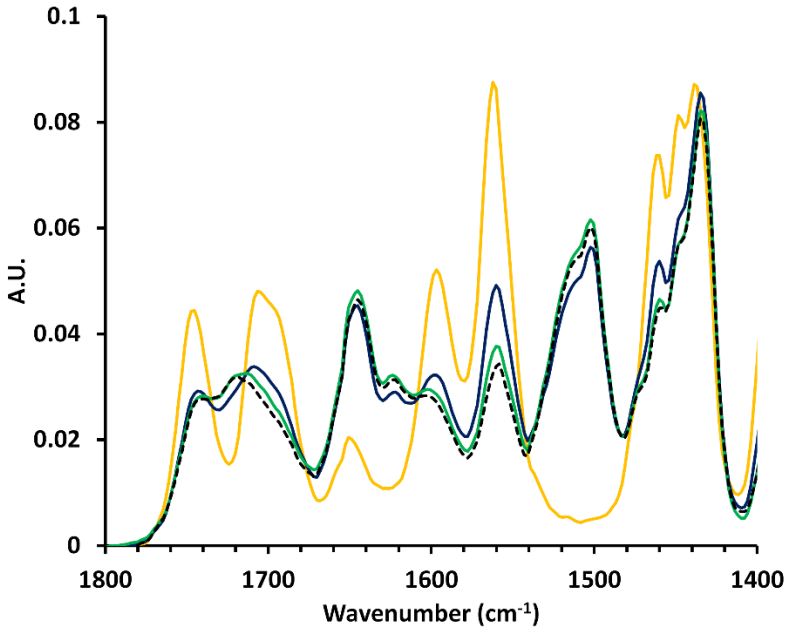
Optical of properties of (a) **DHI-1** (7.0×10^{-5} M), (b) **6** (6.9×10^{-5} M), and (c) **14** (7.0×10^{-5} M) were studied via solution (dichloromethane) UV-vis. In the spiro form (yellow), the typical π-π* transition can be observed at 397, 385, and 386 nm respectively. Upon irradiation with 400 nm light for 2 minutes (green), the presumed charge transfer band is observed at 657, 586, and 602 nm respectively. Half-lives (insets) were found to be 115, 66, and 47 seconds respectively and followed predicted first order rate.

Figure S2: PM-IRRAS spectra for DHI thin-films

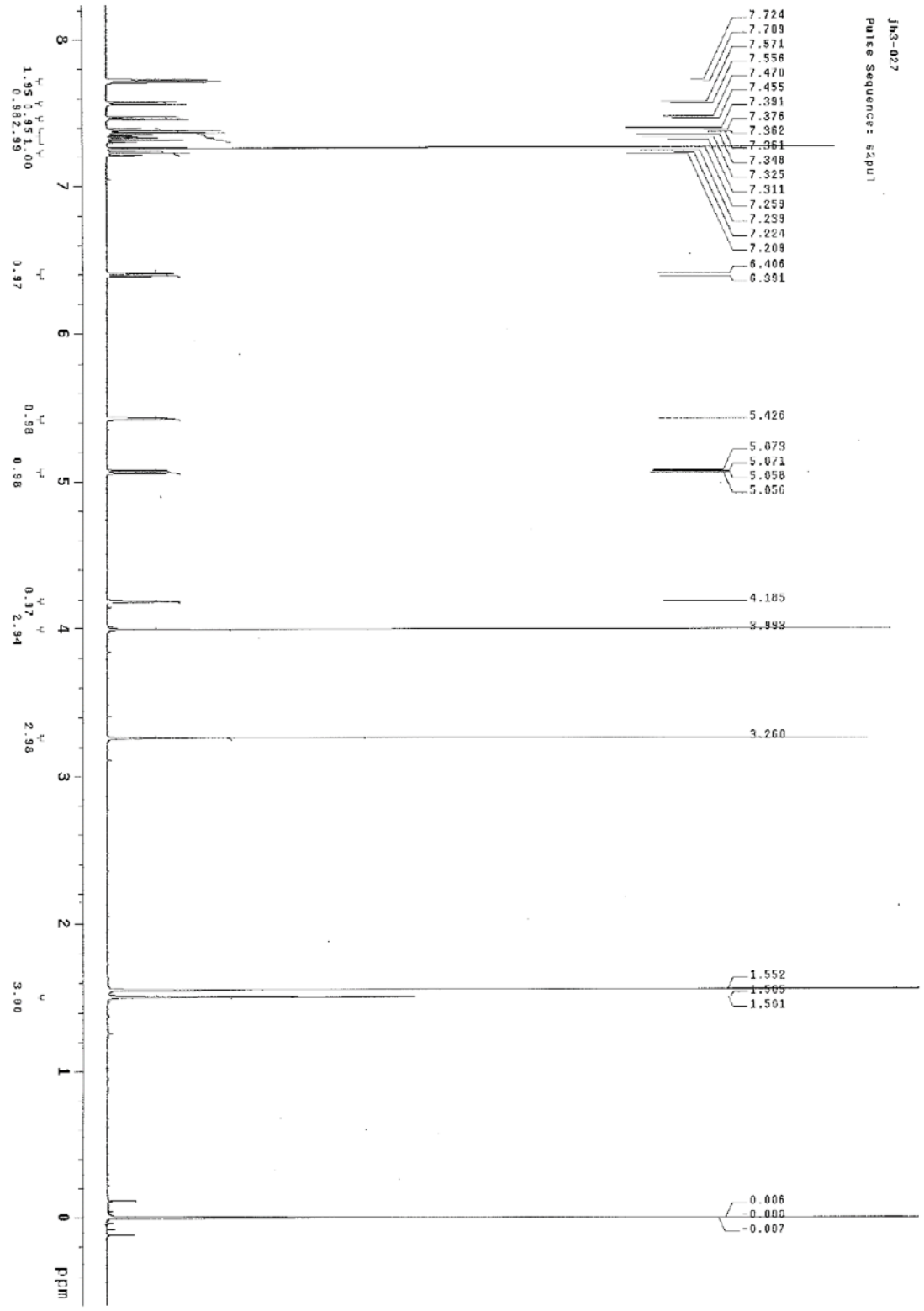


DHI-1 (**a-c**), **6** (**d-f**), and **14** (**g-i**) spiro (yellow) thin-films were irradiated with 400 nm light for 2 (blue) and 8 minutes (green). Consumption of the stretch at 1560 cm^{-1} along with the growth of the stretch at 1500 cm^{-1} indicates successful photoconversion.

Figure S3: PM-IRRAS spectra of **DHI-9**



Representative spectra for **DHI-9** thin-films. The spiro (yellow) film was irradiated with 400 nm light for 2 (blue), 8 (green), and 13 (black dotted) minutes. The consumption of the stretch at 1560 cm^{-1} along with the growth of the stretch at 1500 cm^{-1}, indicates successful photoconversion.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7.455
7.391
7.376
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7.325
7.311
7.259
7.239
7.224
7.209
6.406
6.391
5.426
5.079
5.071
5.058
5.050
4.185
3.993
3.260
1.552
1.565
1.561
0.006
0.000
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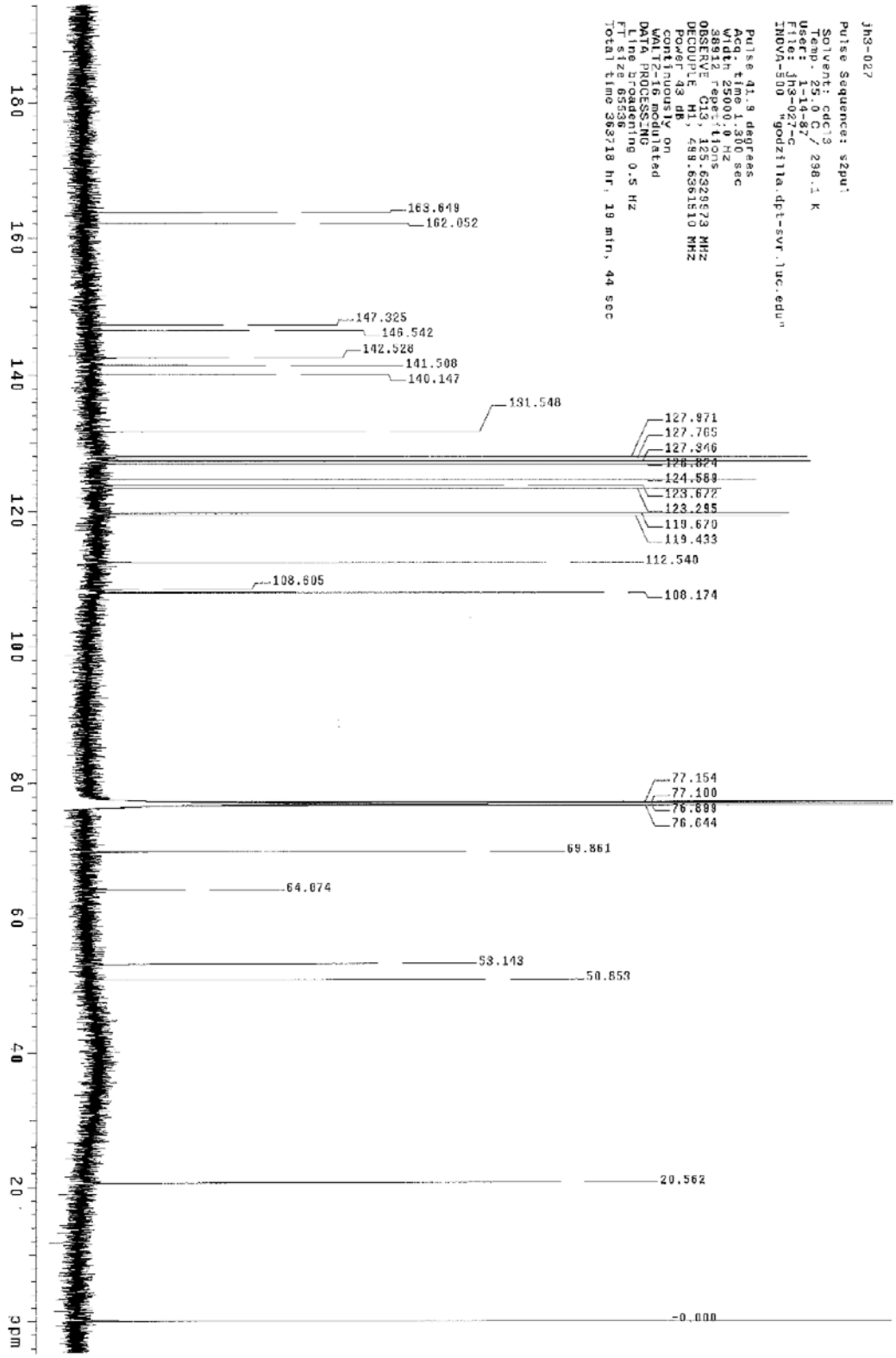
0.97
0.98
0.97 2.94
2.98
3.00
ppm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Solvent: cdcl3
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User: 1-14-87
File: jh3-027-c
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DECOUPLE H1, 499.8361510 MHZ
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESS-NG
Line broadening 0.5 Hz
FT size 65536
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77.154
77.100
76.899
76.644
69.861
64.074
53.143
50.853
20.562
-0.000
ppm

References

(1) Bartucci, M. A.; Wierzbiki, P. M.; Gwengo, C.; Shajan, S.; Hussain, S. H.; Ciszek, J. W. Synthesis of dihydroindolizines for potential photoinduced work function alteration. *Tetrahedron Lett.* **2010**, *51*, 6839-6842