**Supporting Information**

# Furan-Containing Chiral Spiro-Fused Polycyclic Aromatic Compounds: Synthesis and Photophysical Properties

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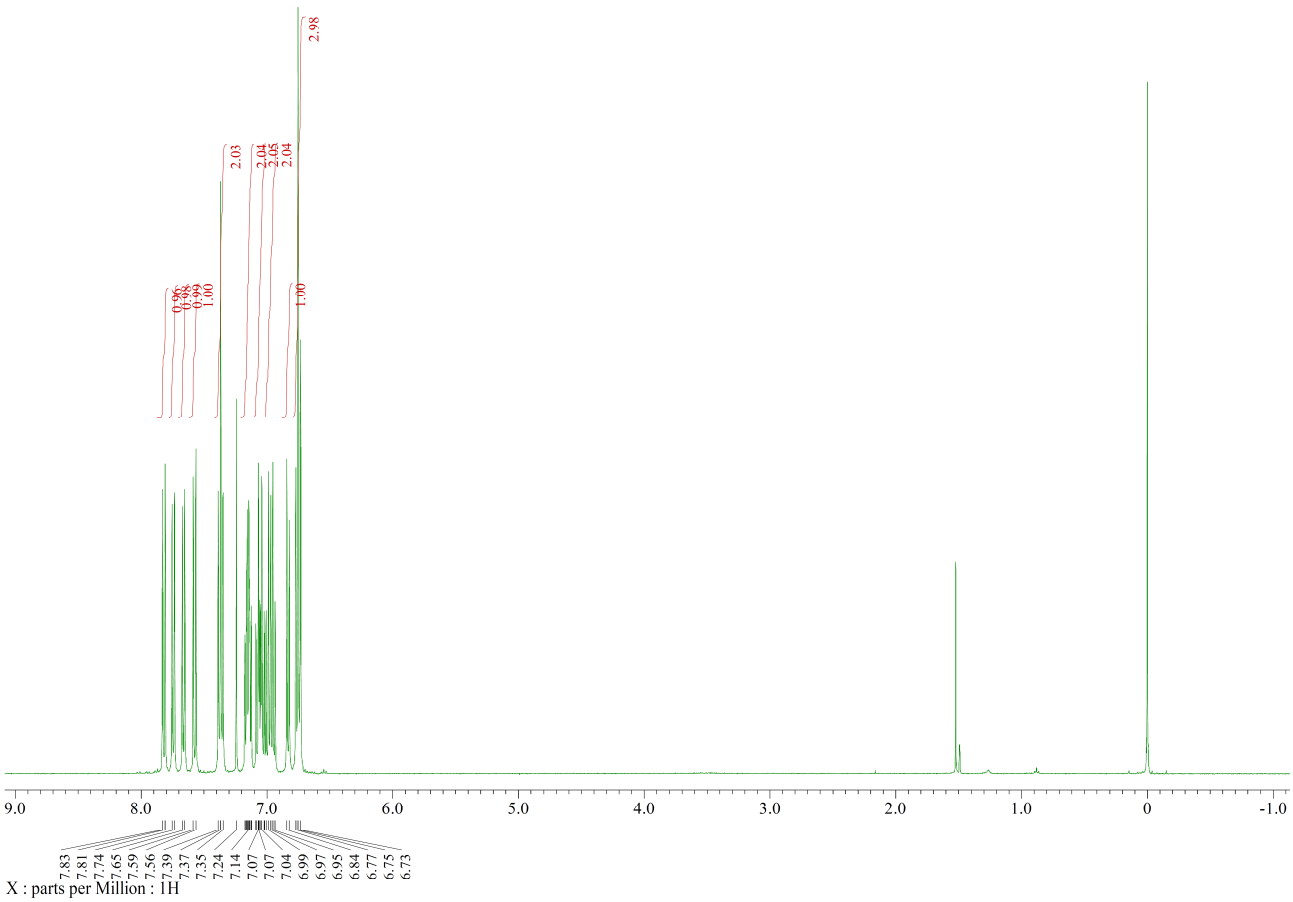


**Figure S1.** $^{1}$H NMR spectrum of *rac*-**1** (400 MHz, $CDCl_3$).

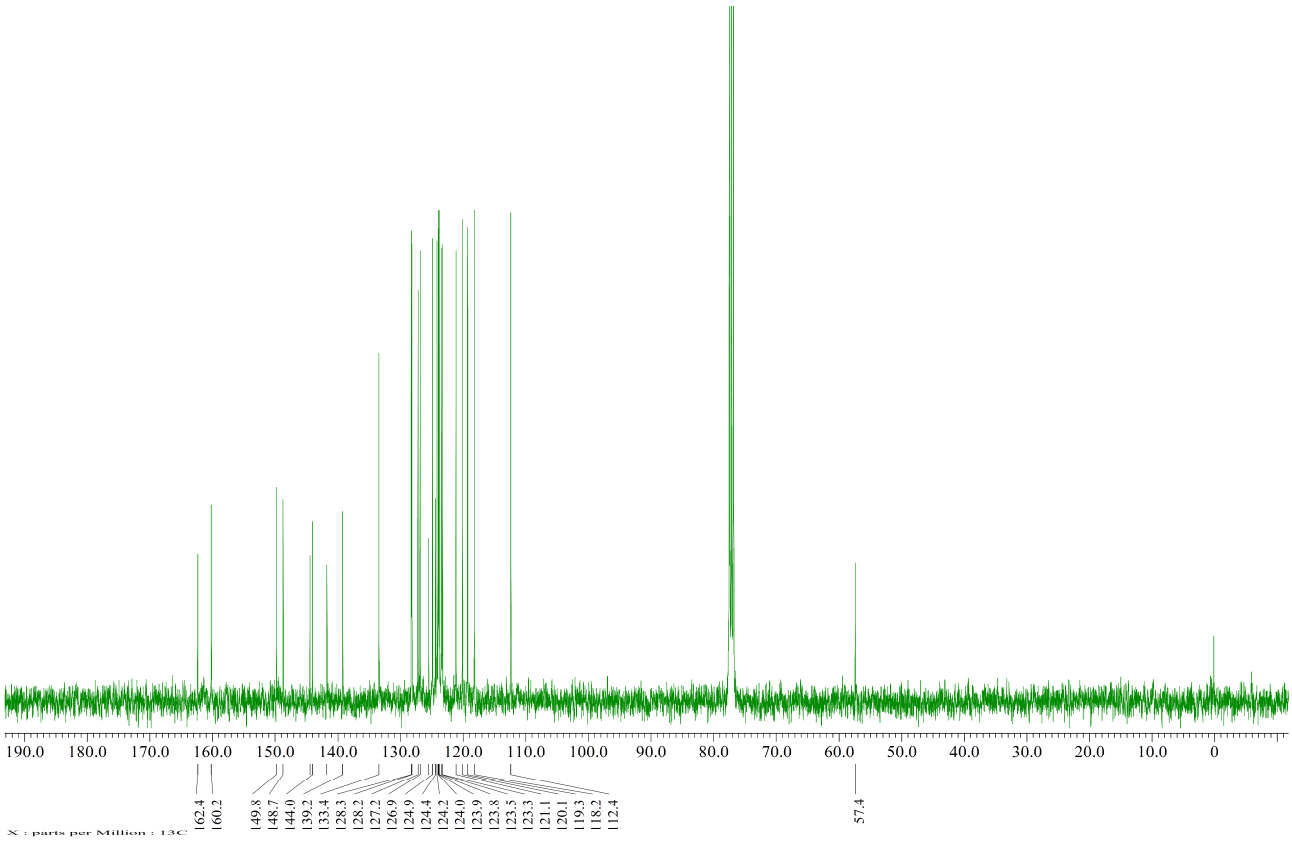


**Figure S2.** $^{13}$C NMR spectrum of *rac*-**1** (101 MHz, $CDCl_3$).

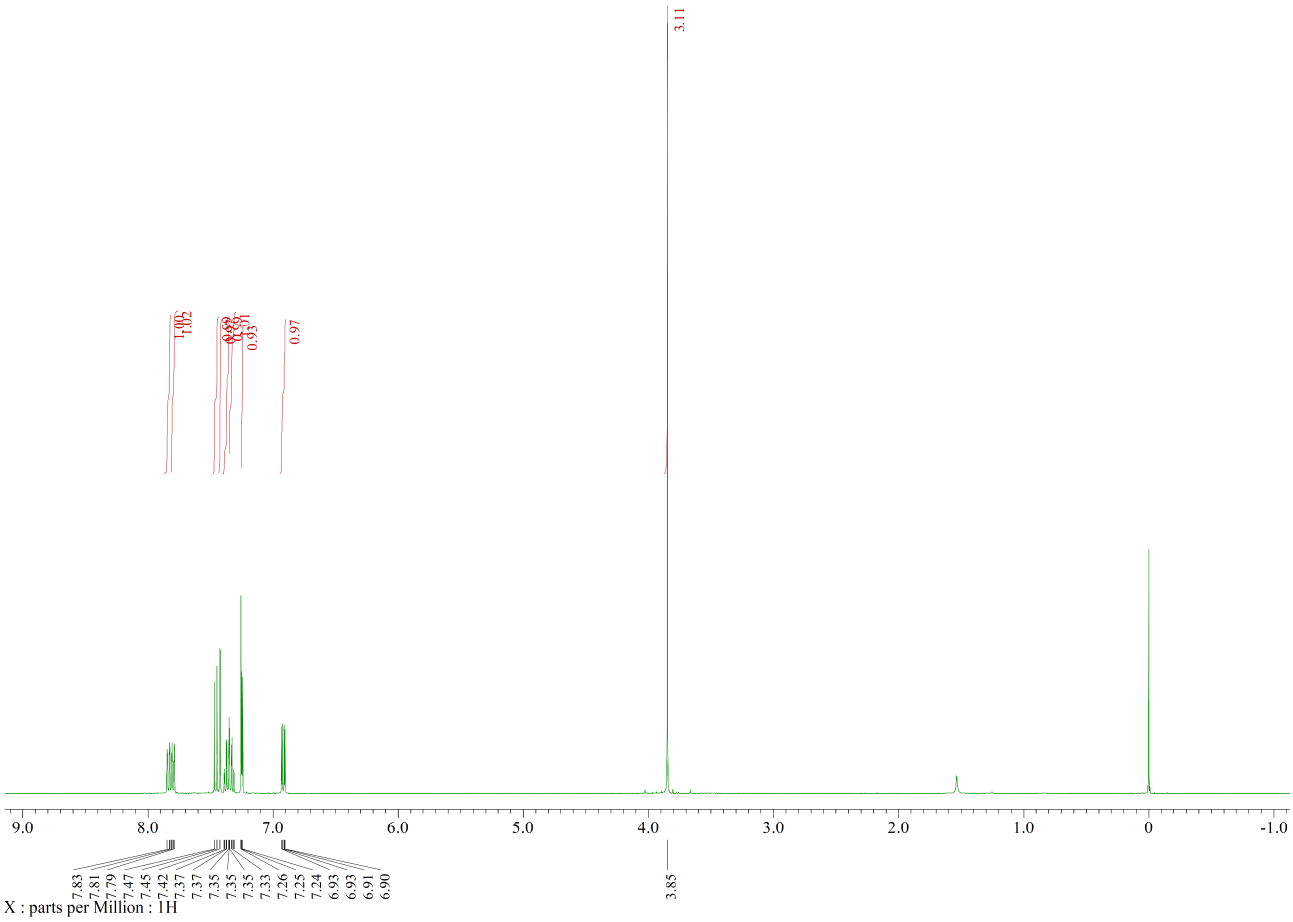


**Figure S3.** $^{1}$H NMR spectrum of **7** (400 MHz, $CDCl_3$).

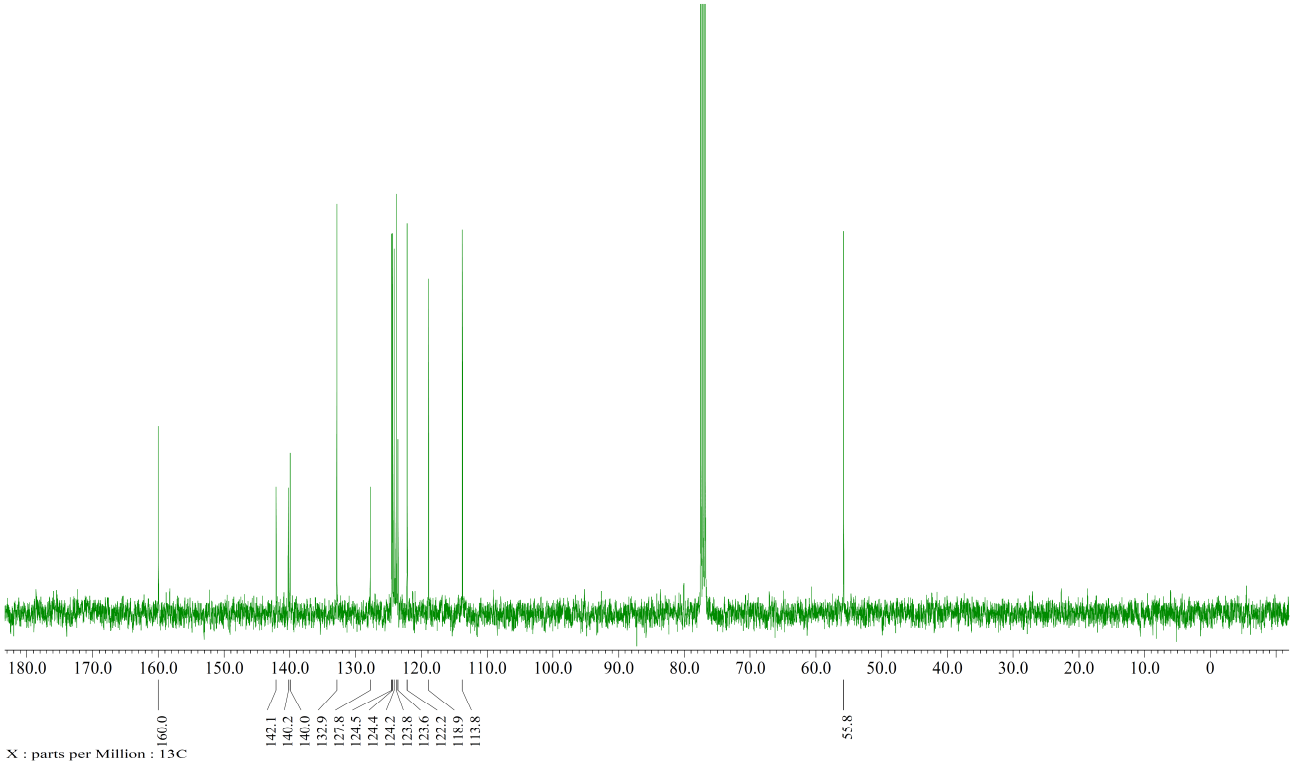


**Figure S4.** $^{13}$C NMR spectrum of **7** (101 MHz, $CDCl_3$).

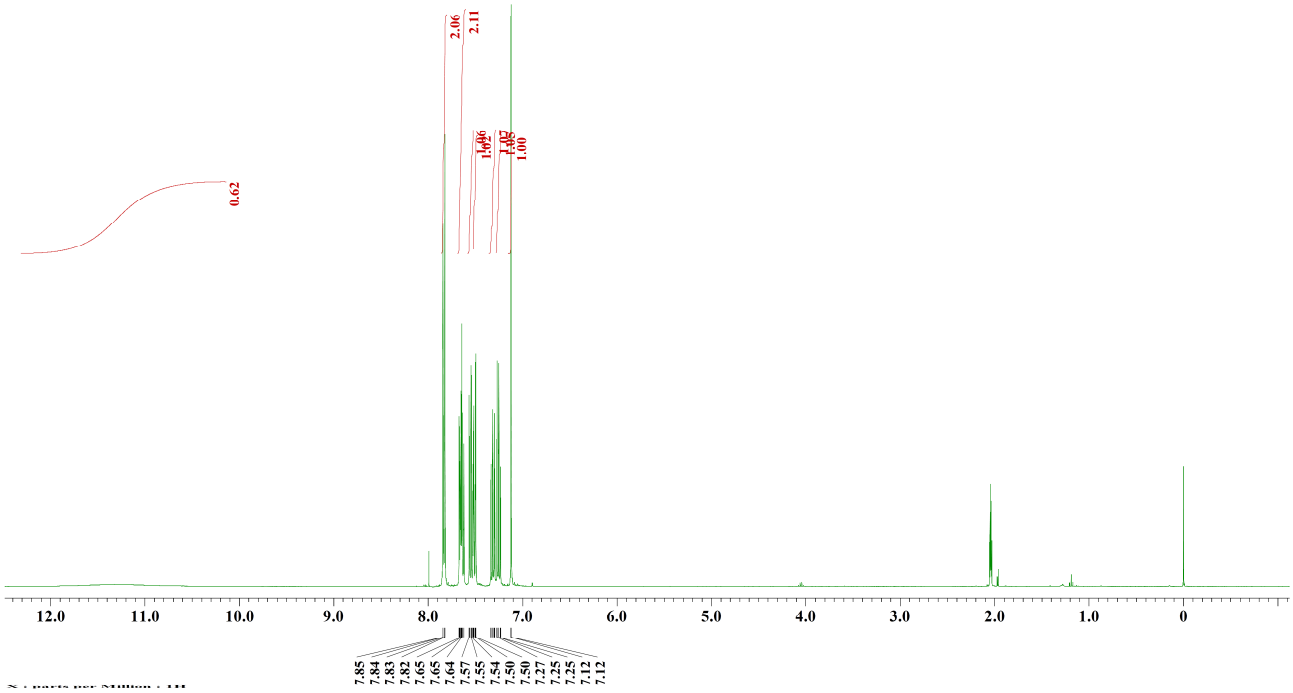

**Figure S5.** $^{1}$H NMR spectrum of **13** (400 MHz, acetone-$d_6$).

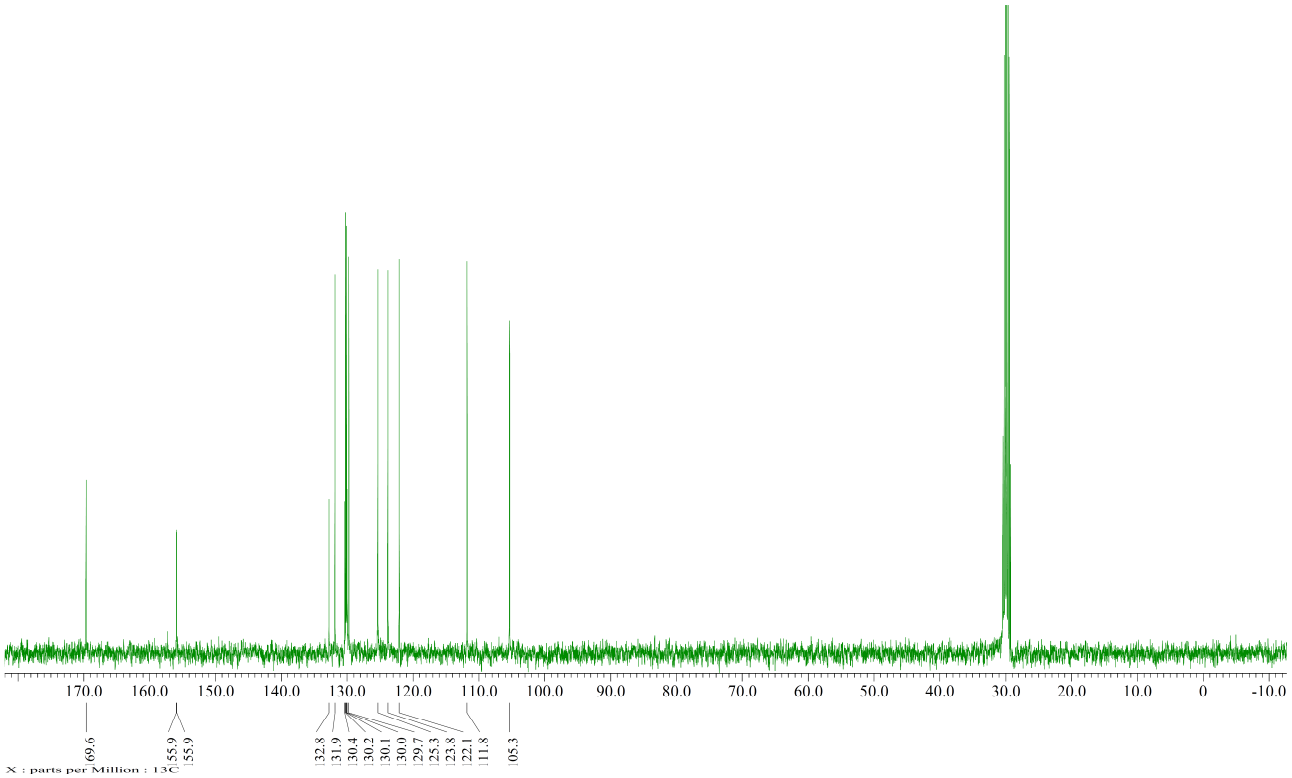

**Figure S6.** $^{13}$C NMR spectrum of **13** (101 MHz, acetone-$d_6$).

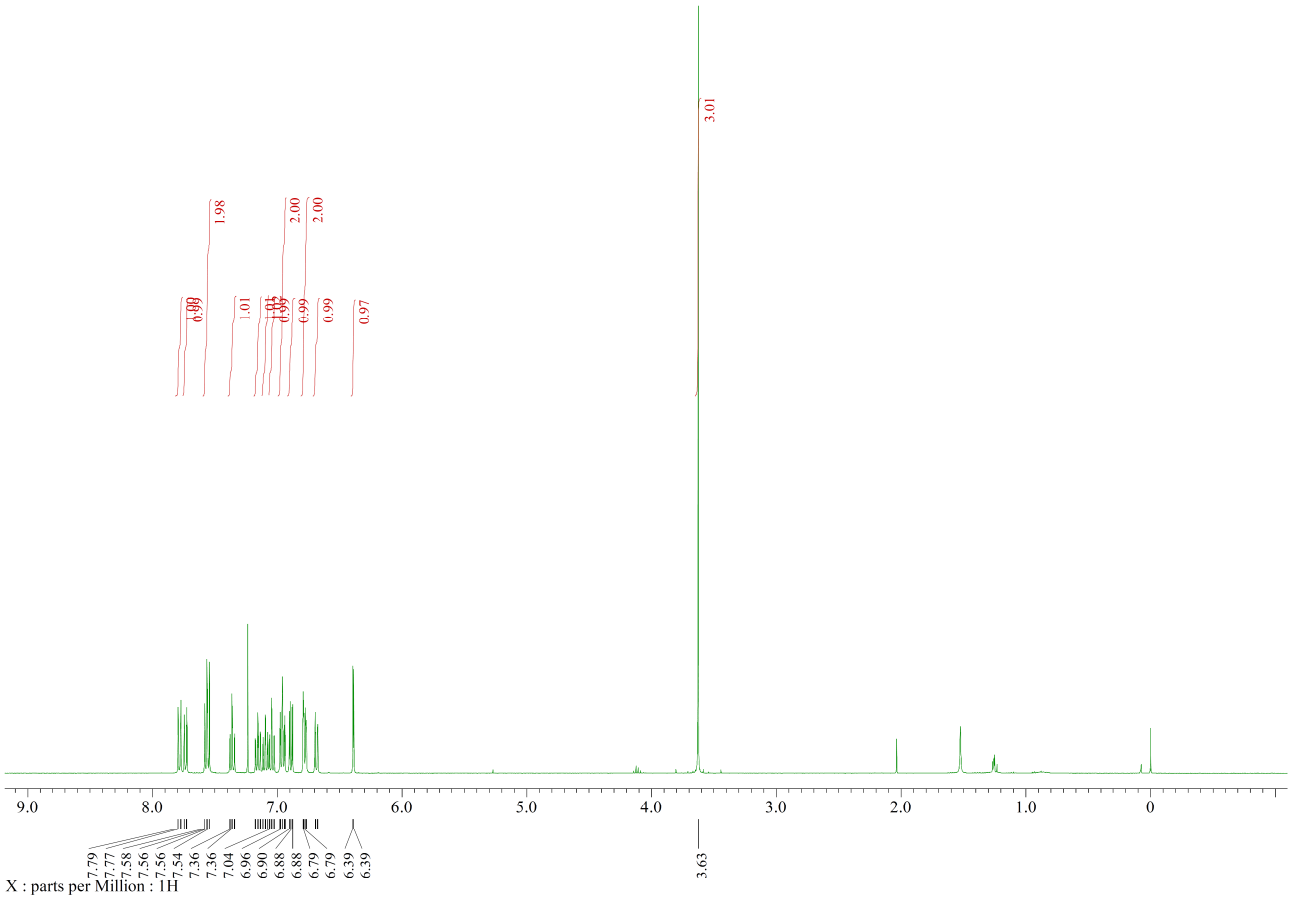


**Figure S7.** $^{1}$H NMR spectrum of *rac*-**10** (400 MHz, $CDCl_3$).

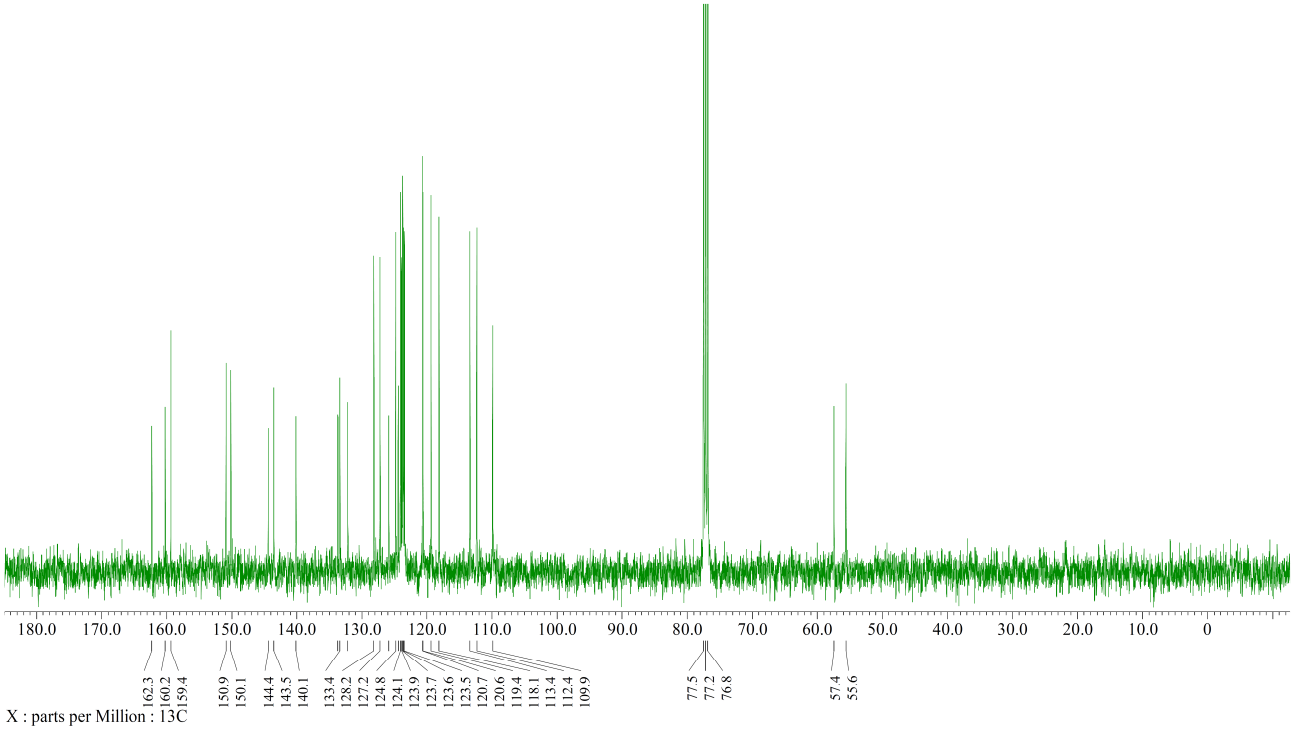


**Figure S8.** $^{13}$C NMR spectrum of *rac*-**10** (101 MHz, $CDCl_3$).

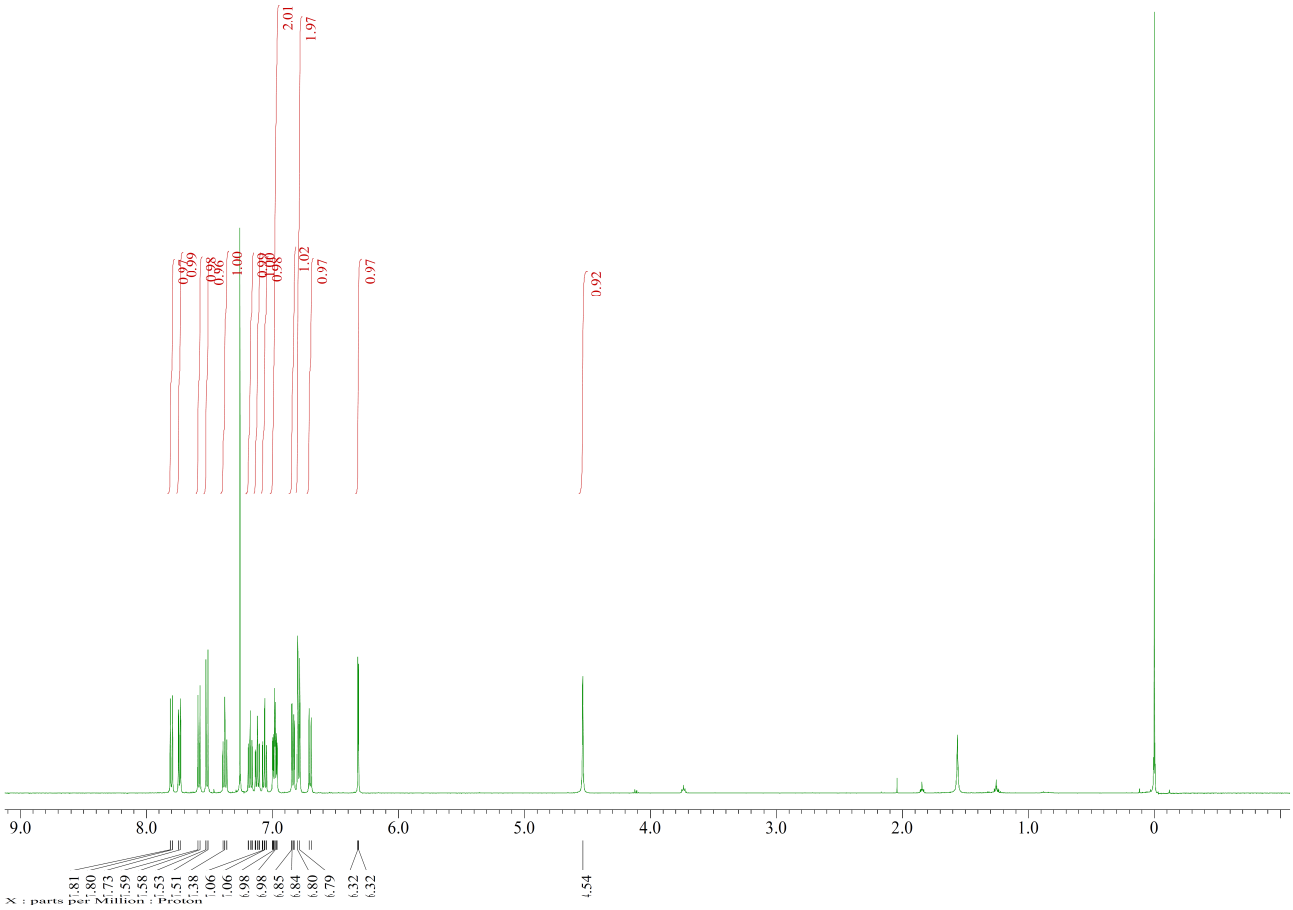

**Figure S9.** $^{1}$H NMR spectrum of *rac*-**11** (500 MHz, $CDCl_3$).

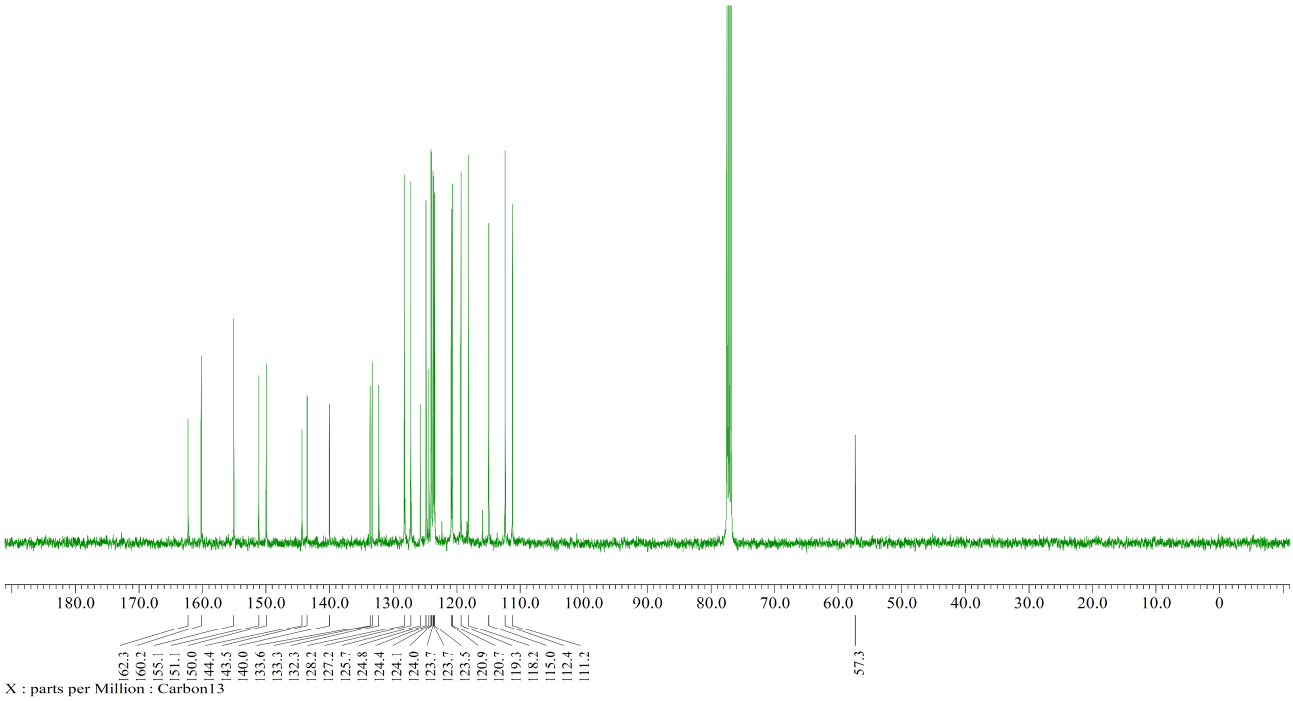

**Figure S10.** $^{13}$C NMR spectrum of *rac*-**11** (101 MHz, $CDCl_3$).

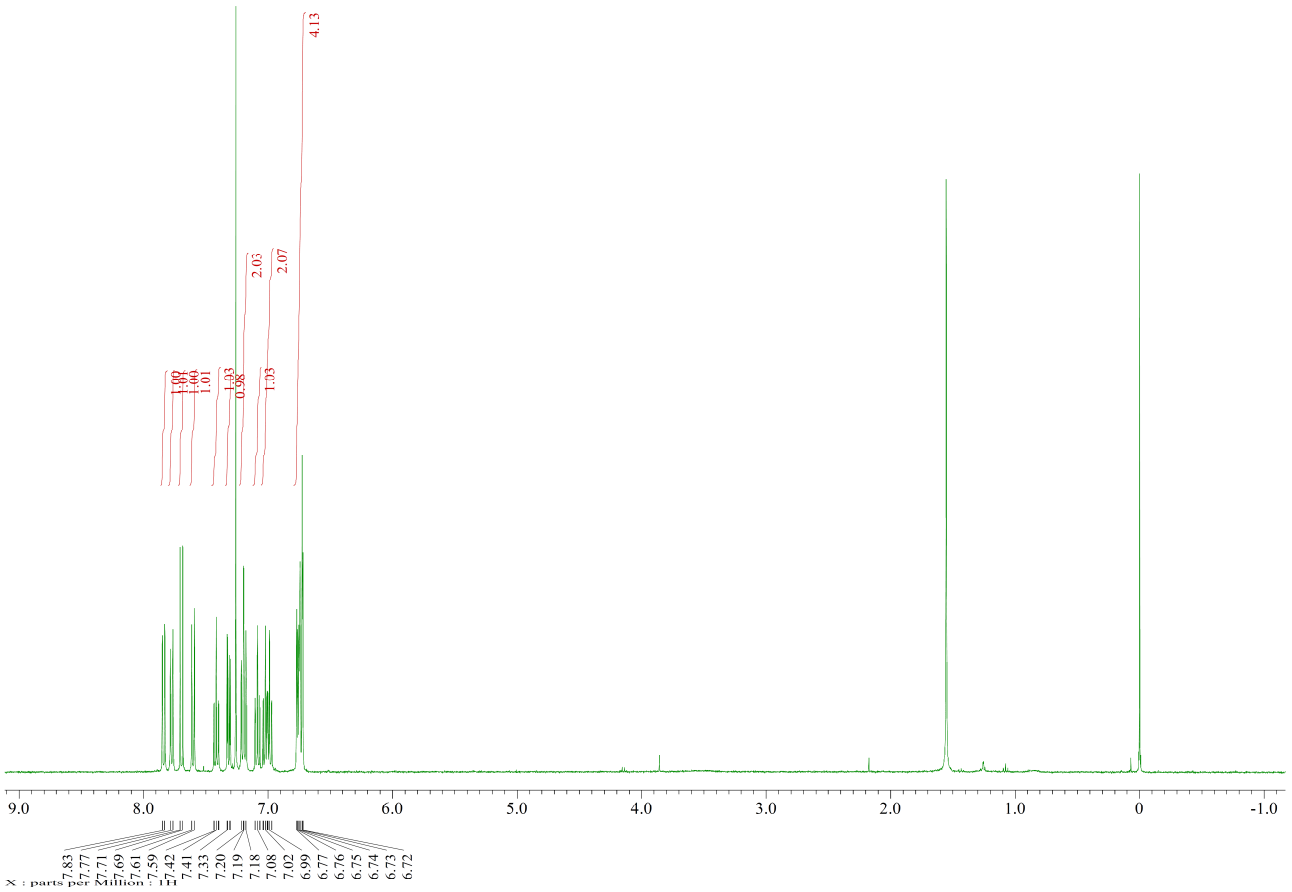

**Figure S11.** $^{1}$H NMR spectrum of *rac*-**12** (400 MHz, $CDCl_3$).

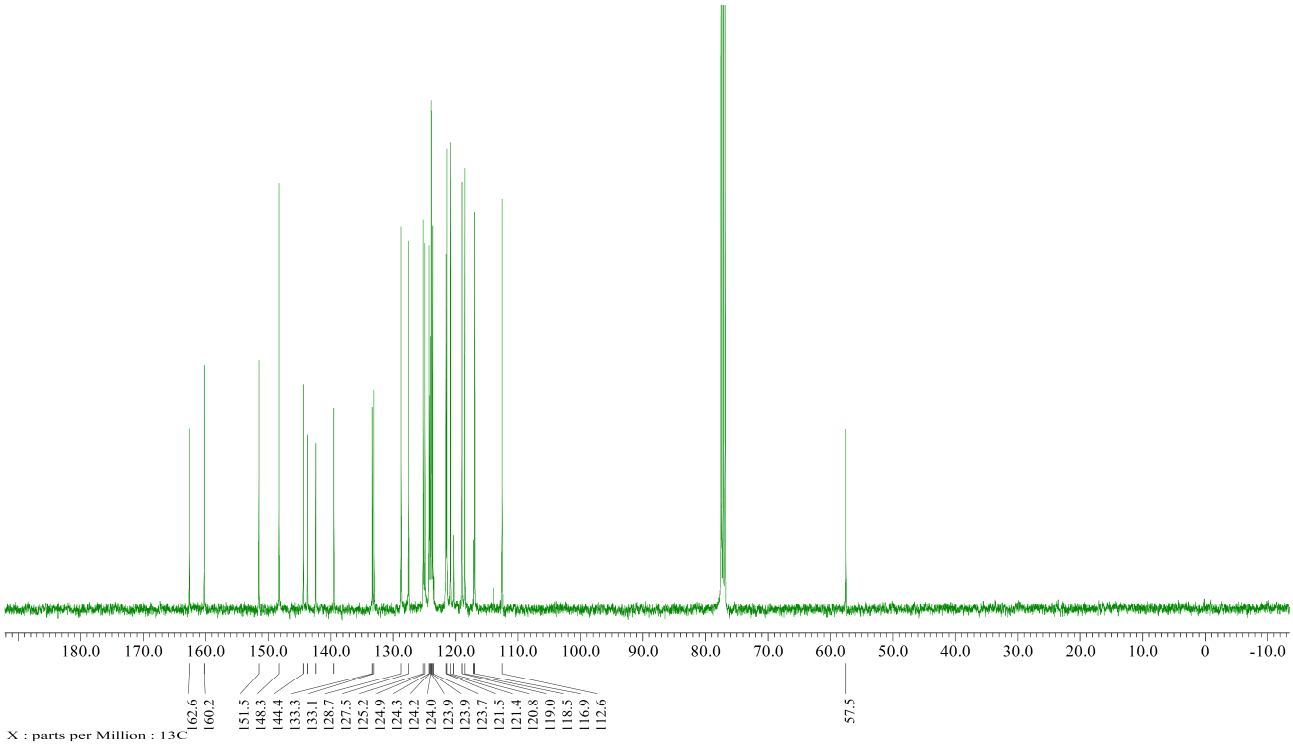

**Figure S12.** $^{13}$C NMR spectrum of *rac*-**12** (101 MHz, $CDCl_3$).

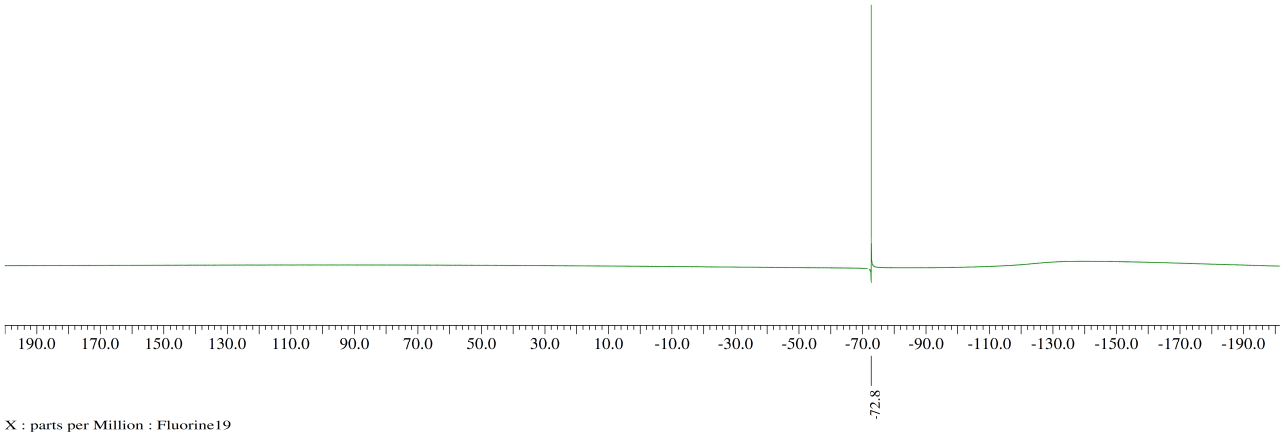


**Figure S13.** $^{19}F$ NMR spectrum of *rac*-**12** (376 MHz, $CDCl_3$).

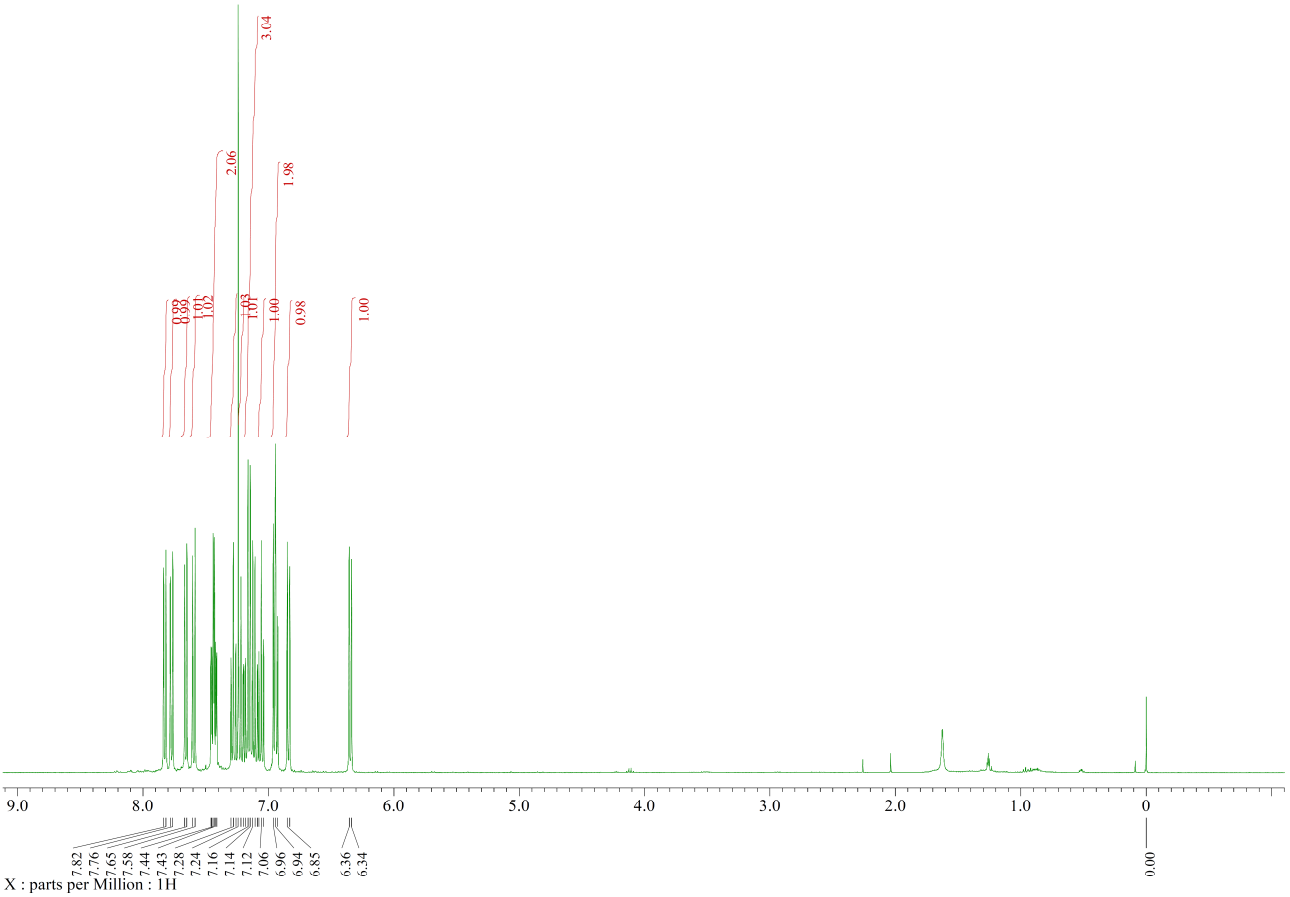


**Figure S14.** $^{1}$H NMR spectrum of *rac*-**2** (400 MHz, $CDCl_3$).

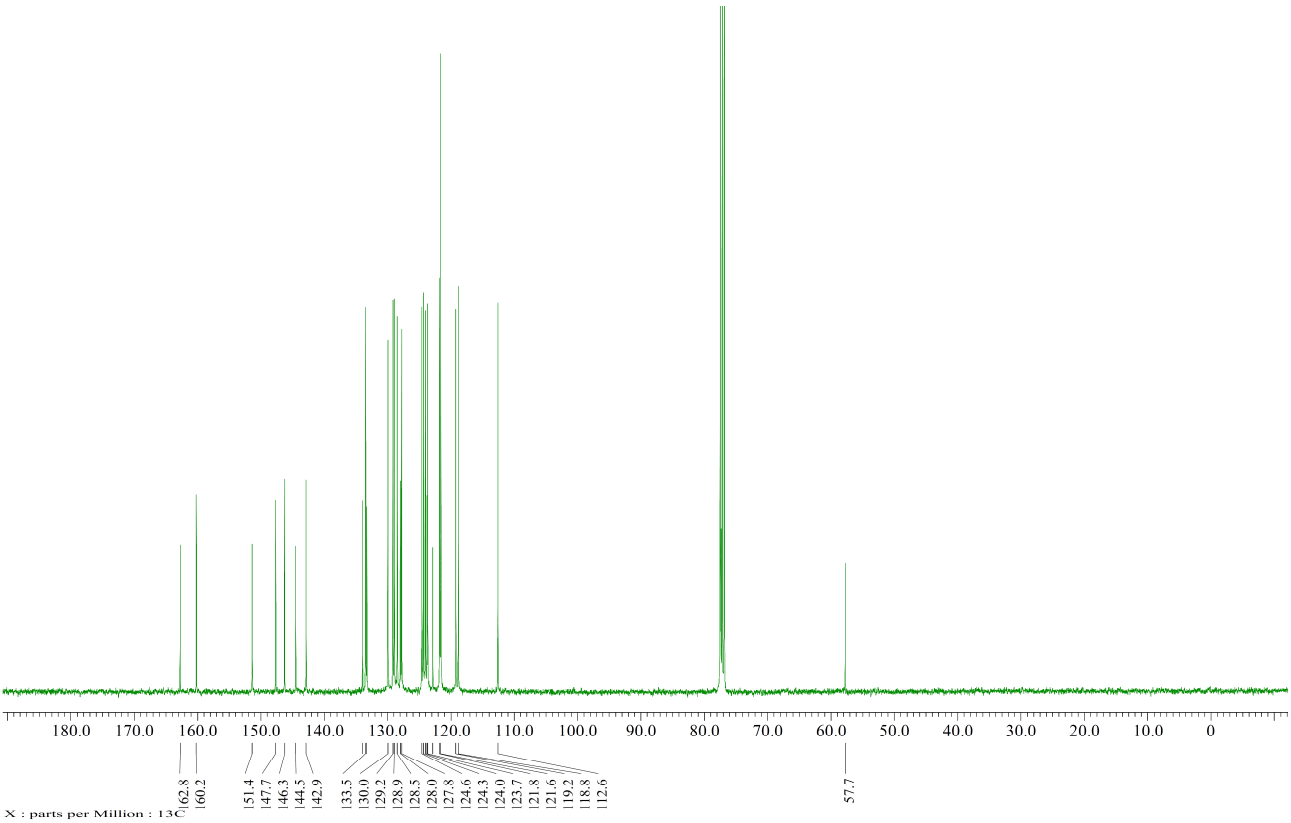


**Figure S15.** $^{13}$C NMR spectrum of *rac*-**2** (101 MHz, $CDCl_3$).

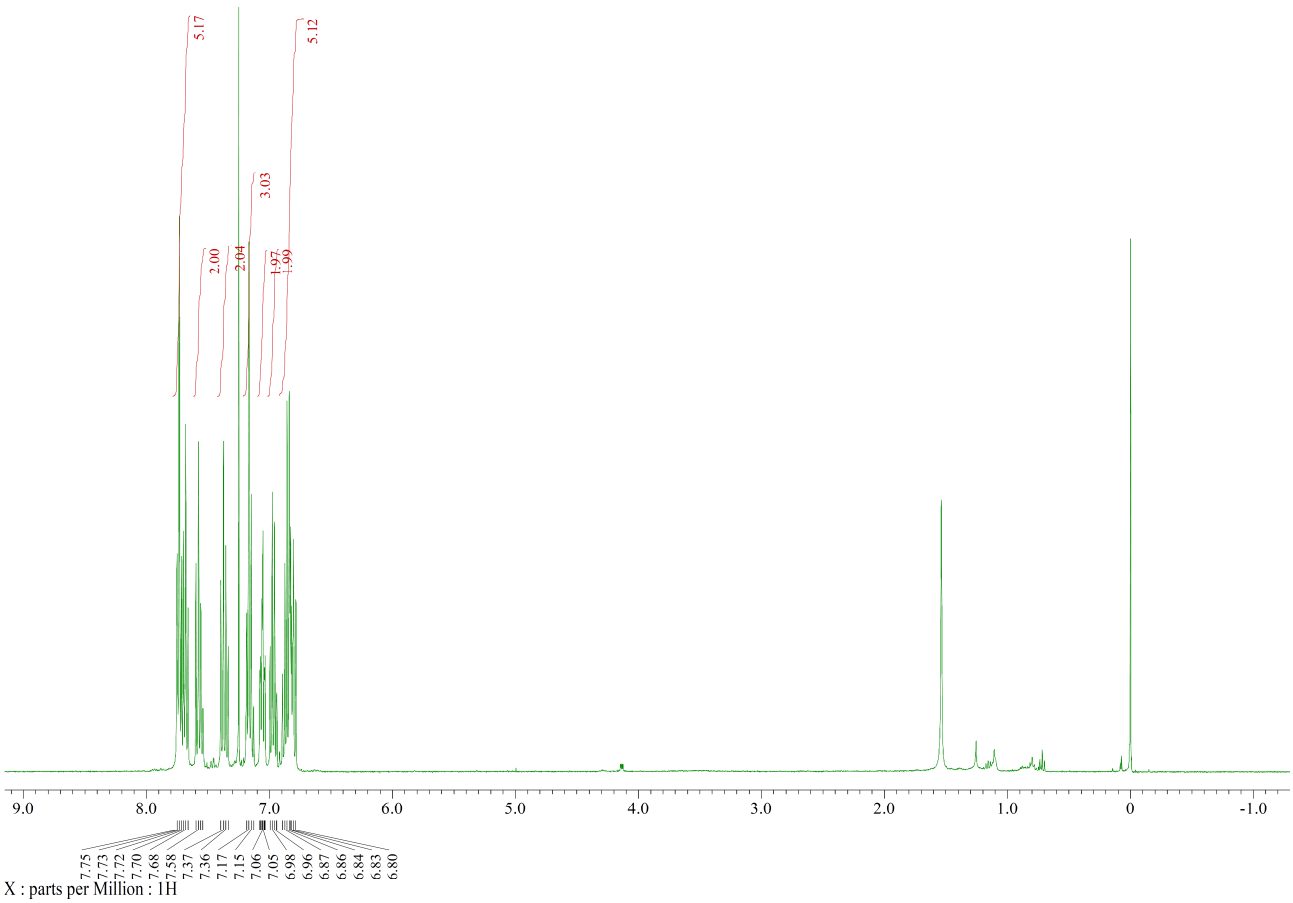


**Figure S16.** $^{1}$H NMR spectrum of *rac*-**3** (400 MHz, $CDCl_3$).

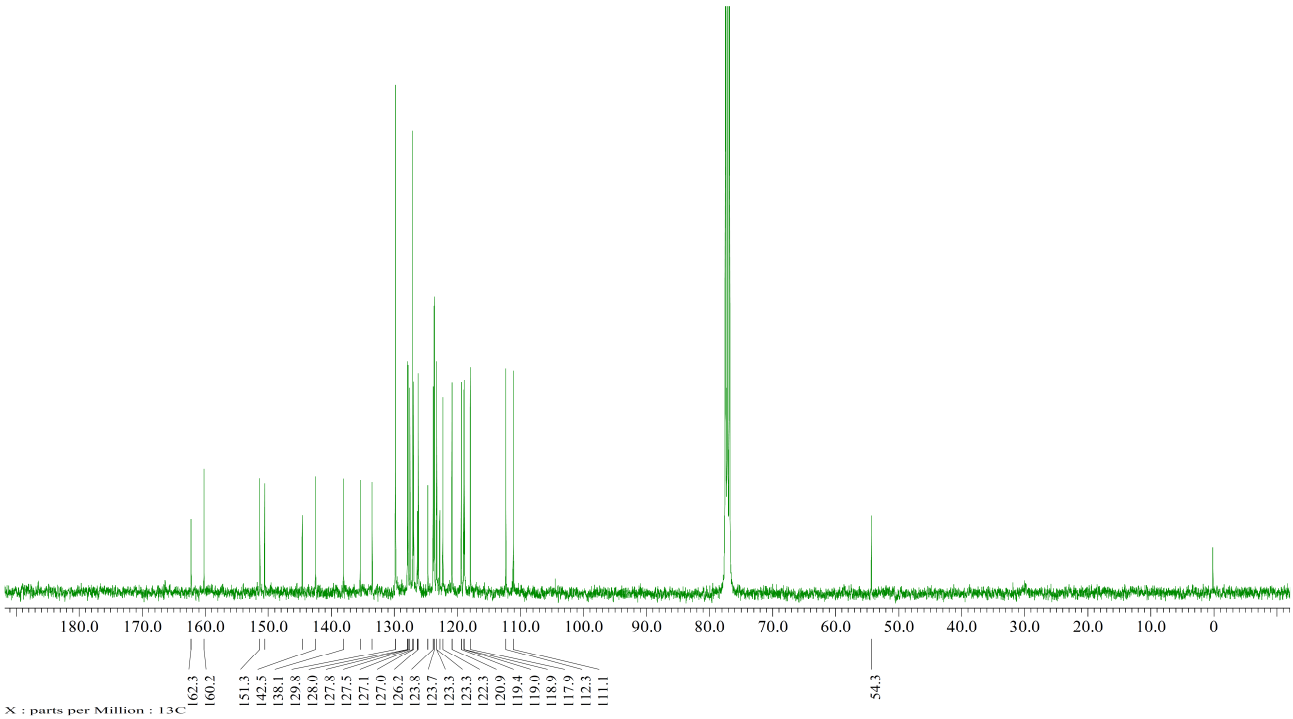


**Figure S17.** $^{13}$C NMR spectrum of *rac*-**3** (101 MHz, $CDCl_3$).

**Table S1.** Crystallographic data and structure refinement details for *rac*-**1**

| | | |
|---|---|---|
| Formula | $C_{29}H_{16}OS$ | |
| Formula weight | 412.48 | |
| Temperature | 193(2) K | |
| Wavelength | 1.54187 Å | |
| Crystal system | monoclinic | |
| Space group | $P2_1/n$ | |
| Unit cell dimensions | $a$ = 14.2753(3) Å | $\alpha$ = 90° |
| | $b$ = 9.8401(2) Å | $\beta$ = 114.4630(10)° |
| | $c$ = 15.7643(3) Å | $\gamma$ = 90° |
| Volume | 2015.63(7) Å$^3$ | |
| $Z$ | 4 | |
| Density (calculated) | 1.359 g/cm$^3$ | |
| Absorption coefficient | 1.566 mm$^{-1}$ | |
| $F$(000) | 856 | |
| Crystal size | 0.50 × 0.40 × 0.30 mm$^3$ | |
| Theta range for data collection | 3.519 to 68.226° | |
| Index ranges | –17<=h<=17, –11<=k<=11, –18<=l<=18 | |
| Reflections collected | 34993 | |
| Independent reflections | 3684 [$R_{int}$ = 0.0448] | |
| Completeness to theta | 100.0% | |
| Max. and min. transmission | 0.625 and 0.492 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3684 / 0 / 280 | |
| Goodness-of-fit on $F^2$ | 1.046 | |
| Final $R$ indices [$I$>2sigma($I$)] | $R_1$ = 0.0688, w$R_2$ = 0.1992 | |
| $R$ indices (all data) | $R_1$ = 0.0729, w$R_2$ = 0.2028 | |
| Largest diff. peak and hole | 1.219 and –0.486 e/Å$^3$ | |

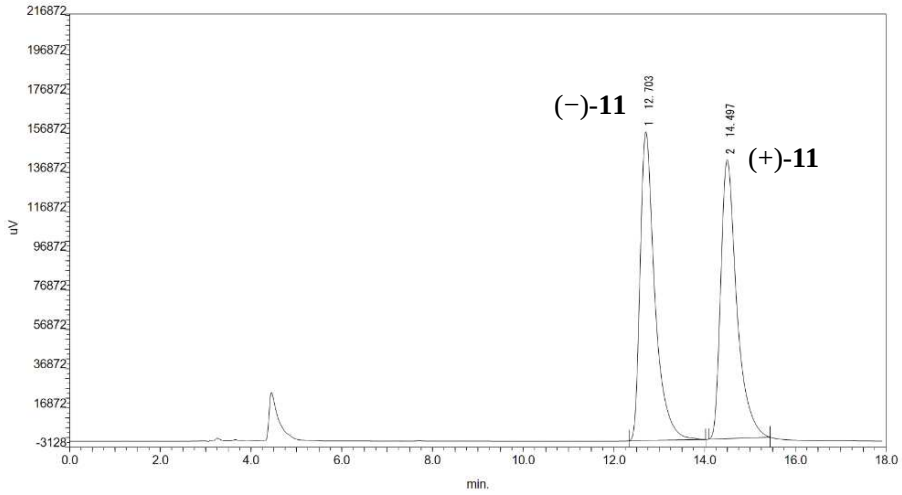


**Figure S18.** HPLC chart of *rac*-**11** with a DAICEL CHIEAPAK® IA-3 column (flow rate: 1.0 mL/min; eluent: hexane/$CHCl_3$ =50/50)].

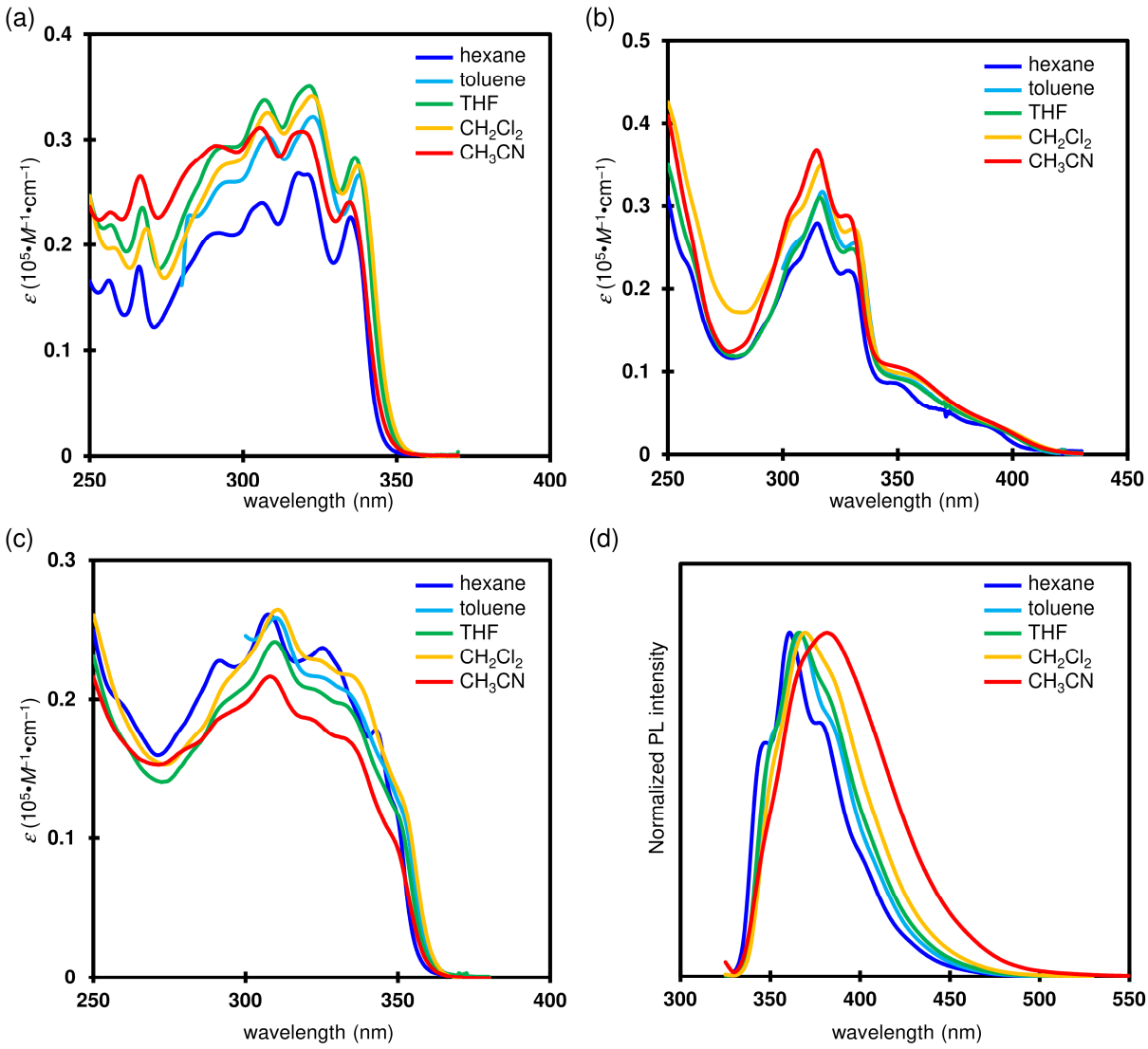


**Figure S19.** UV–vis absorption of (a) *rac*-**1**, (b) *rac*-**2**, and (c) *rac*-**3** and (d) PL spectra of *rac*-**1** in varioussolvents.

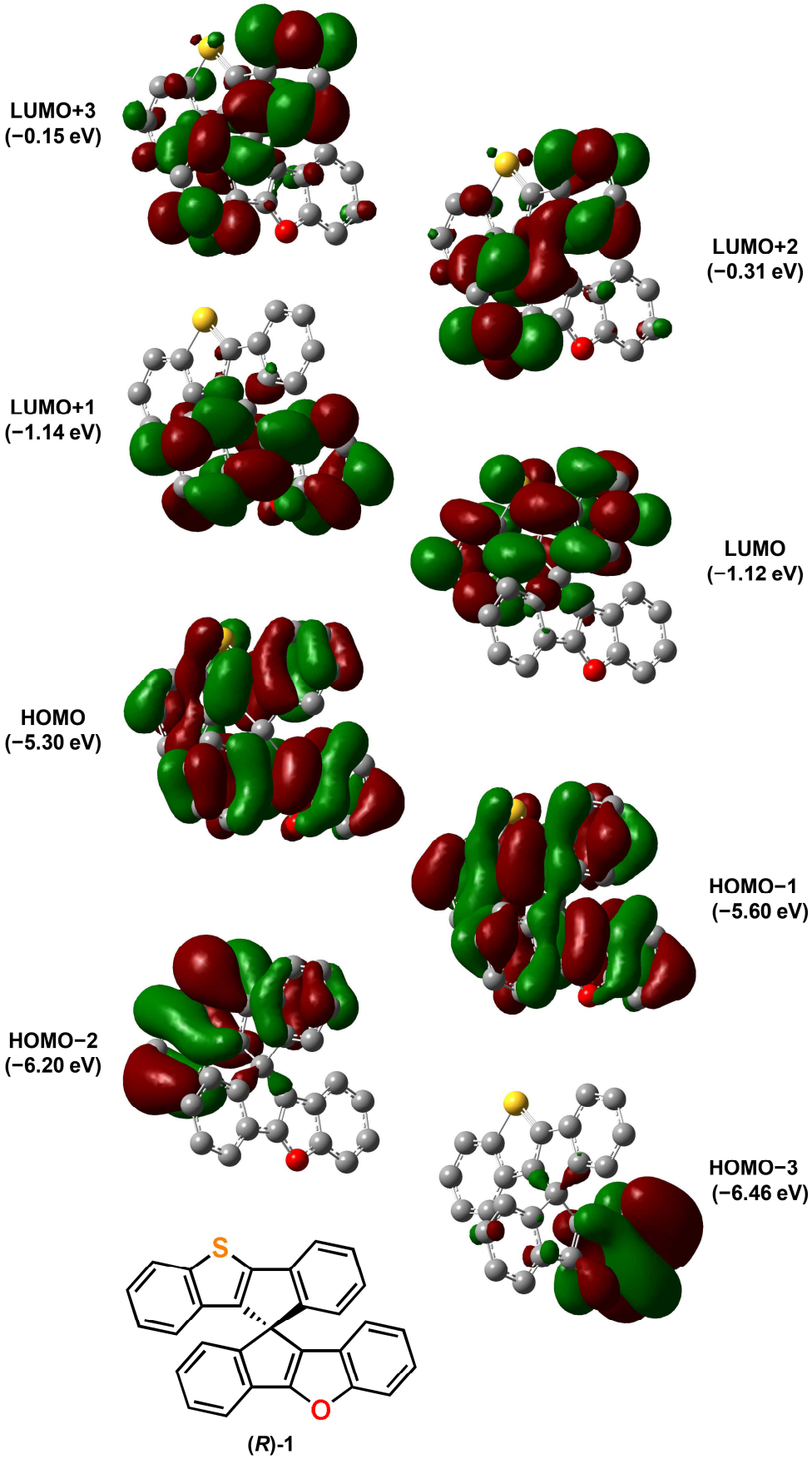


**Figure S20**. Molecular orbitals of (*R*)-**1** calculated by DFT method at the B3LYP/6-31G(d) level of theory.

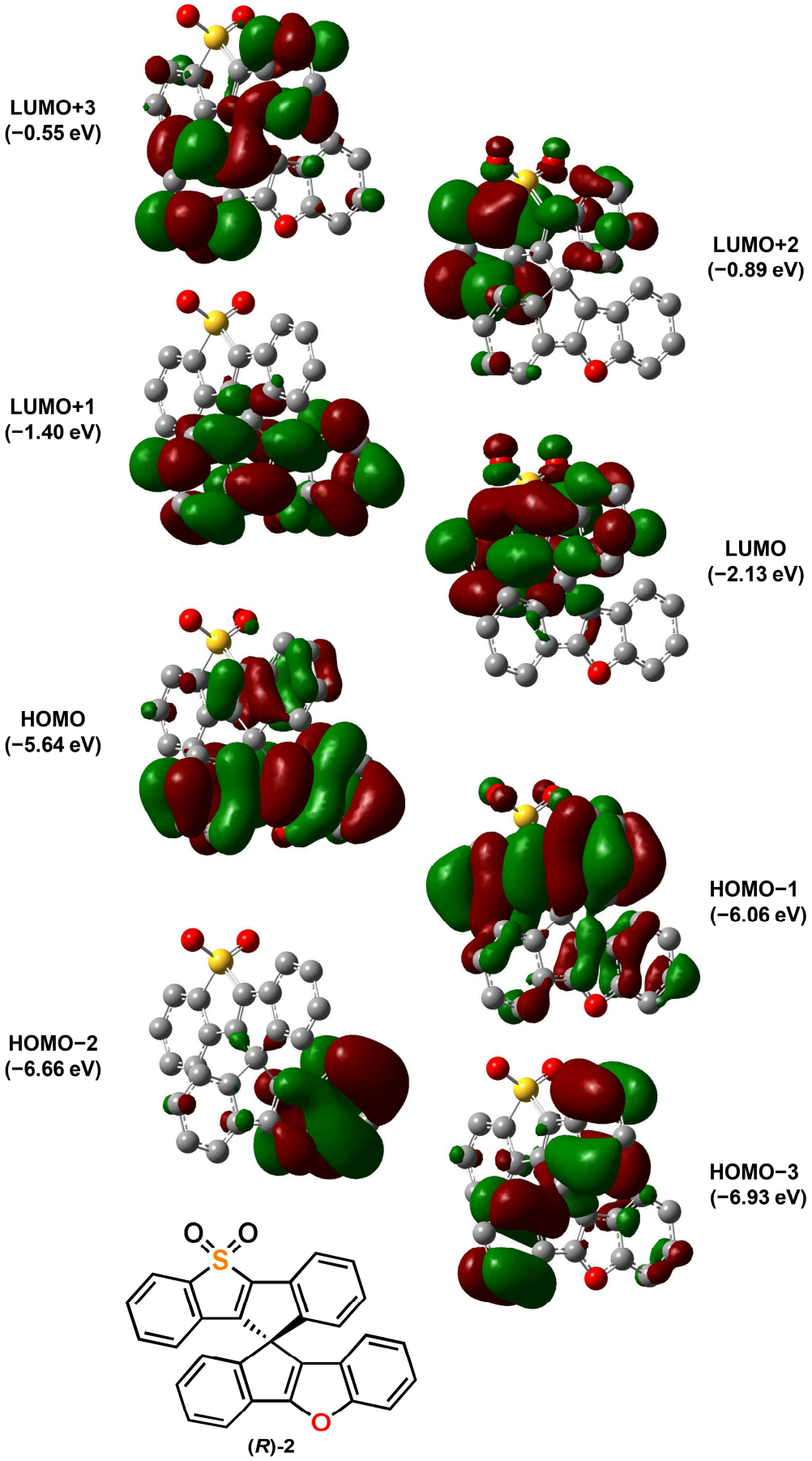


**Figure S21**. Molecular orbitals of (*R*)-**2** calculated by DFT method at the B3LYP/6-31G(d) level of theory.

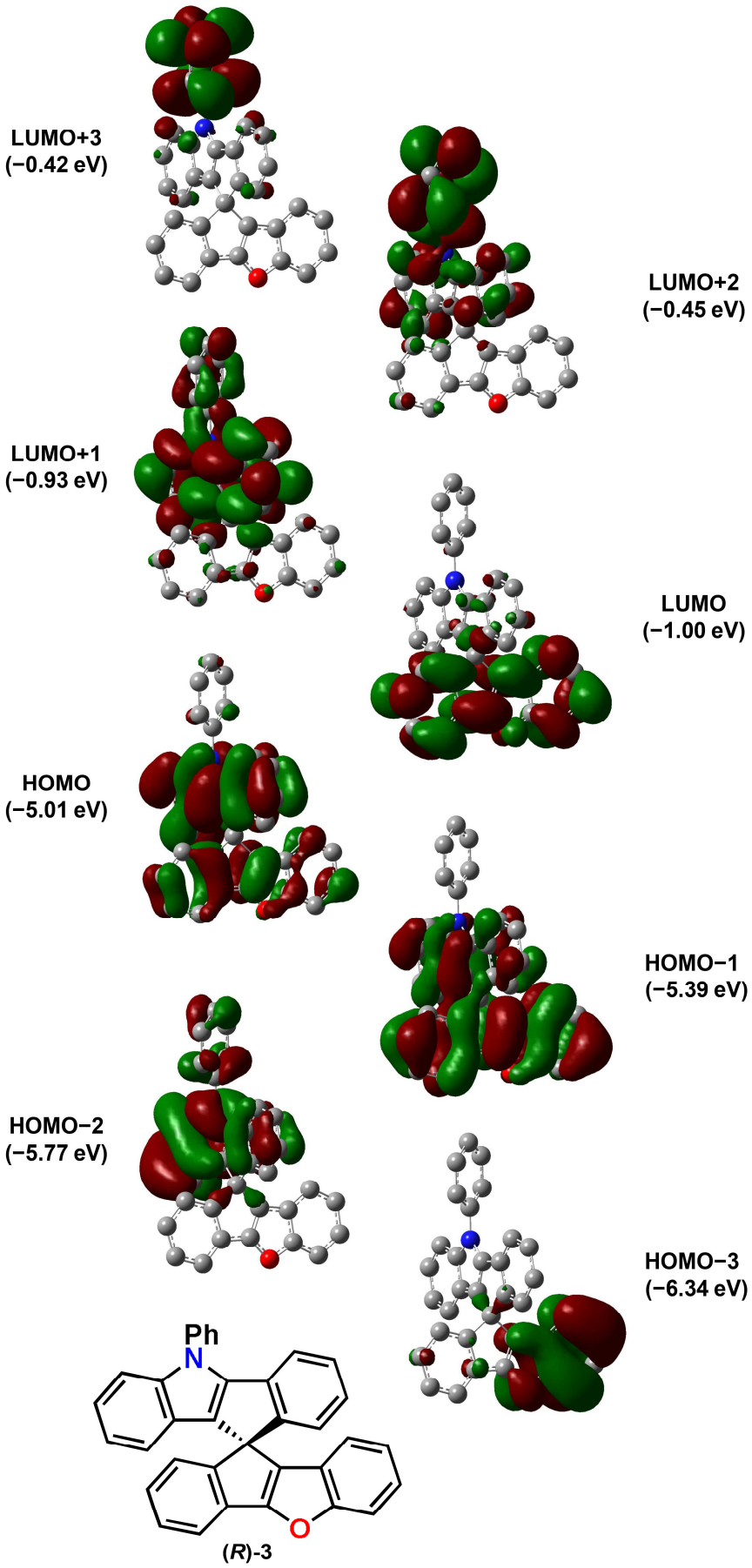


**Figure S22**. Molecular orbitals of (*R*)-**3** calculated by DFT method at the B3LYP/6-31G(d) level of theory.

**Table S2**. Coordinates (Å) and absolute energy of the optimized structure for (*R*)-**1**[a]

| atom | x | y | z | atom | x | y | z |
|---|---|---|---|---|---|---|---|
| C | -1.952556 | 0.713568 | -0.980512 | C | 0.908700 | 1.079226 | 4.474445 |
| C | -1.218143 | -0.066353 | -0.130187 | C | 1.443432 | 0.319601 | 2.264482 |
| C | -1.839531 | -1.319636 | 0.184752 | C | -0.632506 | 1.523600 | 2.642659 |
| C | -3.090107 | -1.441756 | -0.483274 | C | -0.286602 | 1.624666 | 3.998632 |
| C | -1.274387 | 1.969390 | -1.268473 | C | 1.789044 | 0.418749 | 3.611005 |
| C | 0.488915 | 4.113317 | -1.427488 | H | -1.563855 | 1.948774 | 2.278381 |
| C | -1.608536 | 3.063616 | -2.066023 | H | -0.957772 | 2.132506 | 4.685612 |
| C | -0.057493 | 1.947510 | -0.547451 | H | 2.717980 | -0.006735 | 3.978901 |
| C | 0.824751 | 3.013453 | -0.625482 | H | 1.158335 | 1.167717 | 5.528240 |
| C | -0.714295 | 4.136363 | -2.138087 | C | 1.351249 | -0.134100 | -0.033818 |
| H | -2.542224 | 3.083868 | -2.621634 | C | 2.107253 | -0.770625 | -1.075829 |
| H | 1.761881 | 2.998158 | -0.075379 | C | 4.119451 | -2.159510 | -2.436201 |
| H | -0.958553 | 4.996642 | -2.755308 | C | 3.267895 | -1.257354 | -0.419542 |
| H | 1.172467 | 4.954901 | -1.497209 | C | 1.972016 | -0.997547 | -2.454161 |
| C | -3.439973 | -3.603759 | 0.486482 | C | 2.981736 | -1.690256 | -3.116919 |
| H | -4.049561 | -4.494158 | 0.612259 | C | 4.280988 | -1.948368 | -1.065557 |
| C | -3.890638 | -2.575737 | -0.337352 | H | 1.097902 | -0.639923 | -2.989466 |
| H | -4.843128 | -2.655337 | -0.853564 | H | 2.890242 | -1.873593 | -4.183872 |
| C | -2.207916 | -3.501219 | 1.155503 | H | 5.152311 | -2.303533 | -0.525078 |
| H | -1.876364 | -4.315491 | 1.793788 | H | 4.887809 | -2.696505 | -2.984852 |
| C | -1.409765 | -2.374312 | 1.011911 | C | 2.078038 | -0.277245 | 1.107931 |
| H | -0.459360 | -2.299134 | 1.531127 | O | 3.248710 | -0.951781 | 0.931479 |
| C | 0.077066 | 0.637554 | 0.252558 | S | -3.460954 | -0.017354 | -1.471410 |
| C | 0.231493 | 0.872791 | 1.777457 | | | | |

absolute energy E (B3LYP): −1588.14244225 au

[a]Calculated by DFT method [B3LYP/6-31G(d)]

**Table S3**. Coordinates (Å) and absolute energy of the optimized structure for (*R*)-**2**[a]

| atom | x | y | z | atom | x | y | z |
|---|---|---|---|---|---|---|---|
| C | 1.803199 | 0.692254 | 0.542259 | C | -2.073923 | 0.318492 | -2.070142 |
| C | 0.928803 | -0.073780 | -0.148048 | C | -0.070306 | 1.476036 | -2.817100 |
| C | 1.423834 | -1.387385 | -0.561583 | C | -0.634024 | 1.549792 | -4.099974 |
| C | 2.751328 | -1.593741 | -0.137523 | C | -2.634676 | 0.391531 | -3.343785 |
| C | 1.229610 | 1.973213 | 0.920810 | H | 0.913323 | 1.895287 | -2.623287 |
| C | -0.410213 | 4.171761 | 1.335144 | H | -0.078539 | 2.029310 | -4.900817 |
| C | 1.734381 | 3.063068 | 1.628716 | H | -3.617652 | -0.024736 | -3.542759 |
| C | -0.092537 | 1.979189 | 0.417426 | H | -2.317822 | 1.082541 | -5.357443 |
| C | -0.915745 | 3.074830 | 0.623374 | C | -1.610965 | -0.082624 | 0.193679 |
| C | 0.897525 | 4.164603 | 1.829906 | C | -2.193594 | -0.676471 | 1.364610 |
| H | 2.749352 | 3.055500 | 2.014039 | C | -3.976340 | -1.988755 | 3.073718 |
| H | -1.933554 | 3.085811 | 0.243045 | C | -3.453977 | -1.154790 | 0.921238 |
| H | 1.269115 | 5.025010 | 2.379146 | C | -1.835666 | -0.872148 | 2.707546 |
| H | -1.044451 | 5.037346 | 1.504549 | C | -2.734211 | -1.527183 | 3.545282 |
| C | 2.794100 | -3.763552 | -1.124431 | C | -4.358478 | -1.808396 | 1.743200 |
| H | 3.315376 | -4.689527 | -1.348216 | H | -0.879256 | -0.521188 | 3.082666 |
| C | 3.450557 | -2.755675 | -0.401810 | H | -2.471106 | -1.686439 | 4.587108 |
| H | 4.473647 | -2.884787 | -0.061889 | H | -5.312764 | -2.158117 | 1.363305 |
| C | 1.478938 | -3.581220 | -1.555602 | H | -4.652468 | -2.495656 | 3.755959 |
| H | 0.983853 | -4.370160 | -2.114560 | C | -2.517837 | -0.238893 | -0.809655 |
| C | 0.783654 | -2.397645 | -1.280618 | O | -3.652699 | -0.883206 | -0.423648 |
| H | -0.238017 | -2.266189 | -1.621193 | S | 3.365616 | -0.148013 | 0.769709 |
| C | -0.393850 | 0.662541 | -0.319712 | O | 4.436725 | 0.521147 | 0.016621 |
| C | -0.790564 | 0.861879 | -1.805782 | O | 3.579763 | -0.474882 | 2.187276 |
| C | -1.898890 | 1.014691 | -4.357308 | | | | |

absolute energy E (B3LYP): -1738.49812445 au

[a]Calculated by DFT method [B3LYP/6-31G(d)]

**Table S4**. Coordinates (Å) and absolute energy of the optimized structure for (*R*)-**3**[a]

| atom | x | y | z | atom | x | y | z |
|---|---|---|---|---|---|---|---|
| H | 3.819280 | -1.969443 | -2.299164 | H | 2.837248 | 1.461118 | 2.427472 |
| C | 2.746894 | -1.843217 | -2.408289 | H | -2.078842 | 2.310088 | 2.135841 |
| C | -0.061901 | -1.492334 | -2.727400 | H | 1.695152 | 2.833057 | 4.148215 |
| C | 2.012611 | -1.070374 | -1.505228 | H | -0.739722 | 3.263371 | 4.007949 |
| C | 2.057457 | -2.442814 | -3.458377 | C | 0.219568 | -0.005684 | -0.588616 |
| C | 0.667638 | -2.273532 | -3.613661 | C | -1.003873 | 0.664490 | 0.000880 |
| C | 0.604643 | -0.870800 | -1.656896 | C | -1.708381 | 1.659332 | -0.958435 |
| H | 2.605235 | -3.051408 | -4.172580 | C | -3.351858 | 3.205899 | -2.598364 |
| H | 0.161649 | -2.759000 | -4.443657 | C | -1.165936 | 2.741031 | -1.632324 |
| H | -1.131470 | -1.355773 | -2.856841 | C | -3.083343 | 1.346524 | -1.109227 |
| N | 2.452128 | -0.352827 | -0.380998 | C | -3.911316 | 2.114256 | -1.926097 |
| C | 3.799214 | -0.247609 | 0.064449 | C | -1.996817 | 3.516070 | -2.455301 |
| C | 6.450753 | -0.040720 | 0.930474 | H | -0.112042 | 2.984358 | -1.527340 |
| C | 4.526897 | -1.402527 | 0.375331 | H | -4.963337 | 1.869052 | -2.038098 |
| C | 4.401514 | 1.010632 | 0.184376 | H | -1.579928 | 4.365937 | -2.988695 |
| C | 5.720458 | 1.110244 | 0.627301 | H | -3.979056 | 3.817758 | -3.241034 |
| C | 5.851665 | -1.294961 | 0.798554 | C | -2.166515 | -0.247885 | 0.344053 |
| H | 4.047052 | -2.372857 | 0.295496 | C | -2.540320 | -1.407670 | 1.104213 |
| H | 3.835101 | 1.899316 | -0.076479 | C | -4.042273 | -3.485300 | 2.227288 |
| H | 6.181280 | 2.089724 | 0.721109 | C | -3.924395 | -1.573064 | 0.835548 |
| H | 6.411453 | -2.194702 | 1.038615 | C | -1.911891 | -2.321577 | 1.964148 |
| H | 7.480450 | 0.039393 | 1.267115 | C | -2.672345 | -3.349764 | 2.514993 |
| C | 1.341736 | 0.286365 | 0.148832 | C | -4.694258 | -2.591056 | 1.375887 |
| C | 1.020925 | 1.121928 | 1.300195 | H | -0.854925 | -2.226129 | 2.192645 |
| C | -0.251858 | 2.662355 | 3.245562 | H | -2.198455 | -4.064527 | 3.182170 |
| C | 1.771085 | 1.647946 | 2.354079 | H | -5.750322 | -2.680813 | 1.143025 |
| C | -0.375279 | 1.362514 | 1.228196 | H | -4.605273 | -4.299646 | 2.674185 |
| C | -1.008687 | 2.129165 | 2.192377 | C | -3.295528 | 0.173445 | -0.287777 |
| C | 1.120858 | 2.419827 | 3.323259 | O | -4.391034 | -0.594486 | -0.025874 |

absolute energy E (B3LYP): −1476.35246608 au

[a]Calculated by DFT method [B3LYP/6-31G(d)]

**Table S5.** The Selected Absorption of (*P*)-**1**–**3** Calculated by TD–DFT Method at the B3LYP/6-31G(d) Level of Theory

| | excited state | transition energy (eV) | wavelength (nm) | main transition configuration (CI expansion coefficient) | oscillator strength *f* | Rotatory Strength ($10^{-40}$ erg·esu·cm/gauss) | | transition electric dipole moments (a.u.) | | | transition magnetic dipole moments (a.u.) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | $R_{velocity}$ | $R_{length}$ | x | y | z | x | y | z |
| (*R*)-**1** | 1 | 3.5246 | 352 | HOMO → LUMO (0.66852) | 0.0402 | −28.0408 | −27.9770 | 0.1674 | 0.6420 | −0.1595 | −0.2803 | 0.4060 | 0.5962 |
| | 2 | 3.6405 | 341 | HOMO → LUMO+1 (0.64566) | 0.0702 | −0.0310 | 1.1379 | 0.3880 | −0.3638 | −0.7103 | −0.3981 | −0.8916 | 0.2459 |
| | 3 | 3.9846 | 311 | HOMO−1 → LUMO (0.65536) | 0.3077 | 44.7448 | 46.0587 | −0.4951 | −1.5800 | 0.6405 | 0.4860 | −0.5350 | −1.2491 |
| | 4 | 4.0486 | 306 | HOMO−1 →LUMO+1 (0.62751) | 0.3357 | −48.7745 | −47.2841 | 0.7241 | −0.7894 | −1.4956 | −0.5213 | −1.5154 | 0.4134 |
| | 5 | 4.3139 | 287 | HOMO−2 → LUMO (0.46858)<br>HOMO → LUMO+2 (0.42326) | 0.0621 | −29.3488 | −30.6337 | −0.3486 | −0.2343 | −0.6412 | 0.1461 | −0.2047 | −0.2073 |
| | 6 | 4.3596 | 284 | HOMO → LUMO+2 (0.47078)<br>HOMO−2 → LUMO (−0.36831) | 0.0303 | 52.5987 | 53.2310 | 0.6404 | 0.2591 | −0.7063 | 0.0016 | −0.1231 | 0.2761 |
| (*R*)-**2** | 1 | 2.8963 | 428 | HOMO → LUMO (0.70392) | 0.0110 | −9.3543 | −8.9640 | 0.0463 | 0.3637 | 0.1423 | 0.0297 | 0.1548 | −0.1380 |
| | 2 | 3.4462 | 360 | HOMO−1 → LUMO (0.69430) | 0.2207 | −4.7145 | −2.1271 | −0.4761 | 1.4650 | 0.4905 | −0.1184 | 0.0185 | −0.1517 |
| | 3 | 3.8275 | 324 | HOMO → LUMO+1 (0.64303) | 0.2119 | 1.1459 | 3.2585 | −0.4315 | −0.5325 | 1.3377 | 0.4585 | −1.5043 | −0.4612 |
| | 4 | 4.0079 | 309 | HOMO−2 → LUMO (0.70213) | 0.0003 | 0.3028 | 0.3081 | −0.0007 | 0.0348 | 0.0458 | −0.0187 | −0.0589 | 0.0160 |
| | 5 | 4.1177 | 301 | HOMO−1 → LUMO+1 (0.61428) | 0.1646 | 42.0854 | 46.3874 | 0.3768 | 0.3608 | −1.1662 | −0.2803 | 1.1407 | 0.4311 |
| | 6 | 4.1398 | 300 | HOMO−3 → LUMO (0.65245) | 0.0098 | 8.4063 | 8.7941 | 0.2188 | 0.2190 | 0.0334 | −0.2234 | −0.0112 | 0.4204 |
| (*R*)-**3** | 1 | 3.4366 | 361 | HOMO → LUMO (0.68501) | 0.0330 | −31.5369 | −31.2033 | 0.1402 | 0.5524 | −0.2589 | −0.1432 | 0.6092 | 0.7108 |
| | 2 | 3.6098 | 343 | HOMO → LUMO+1 (0.65694) | 0.1078 | −1.1846 | −0.7116 | −0.1112 | −0.5955 | −0.9227 | −0.0758 | −0.7913 | 0.5165 |
| | 3 | 3.9377 | 315 | HOMO → LUMO+2 (0.47770)<br>HOMO−1 → LUMO+1 (0.44947) | 0.0767 | 3.6022 | 4.9026 | −0.5520 | −0.3286 | −0.6180 | 0.1269 | −0.1278 | −0.0117 |
| | 4 | 3.9791 | 312 | HOMO → LUMO+2 (0.46482)<br>HOMO−1 → LUMO+1 (−0.34814)<br>HOMO−1 → LUMO (0.24808) | 0.0882 | 166.7527 | 168.7944 | −0.3028 | 0.0875 | 0.8975 | 0.1065 | 0.3798 | −0.7989 |
| | 5 | 4.0281 | 308 | HOMO → LUMO+3 (0.53651)<br>HOMO−1 → LUMO (−0.40656) | 0.1286 | 192.2917 | 198.3647 | 0.1567 | 0.6460 | −0.9283 | −0.1526 | 0.6956 | 1.3648 |
| | 6 | 4.0481 | 306 | HOMO−1 → LUMO (0.44502)<br>HOMO → LUMO+3 (0.36395)<br>HOMO−1 → LUMO+1 (0.32045) | 0.2607 | −376.3605 | −387.3010 | −0.0165 | −1.5624 | 0.4331 | 0.0647 | −1.3542 | −1.0889 |