Supplementary Material

Photoswitchable hydrazones with pyridine-based rotors and halogen substituents

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NMR = Nuclear magnetic res	sonance
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COSY = Correlation spectroscopy

HSQC = Heteronuclear single-quantum correlation spectroscopy

HMBC = Heteronuclear multiple-bond correlation spectroscopy

UV-VIS = Ultraviolet-visible spectroscopy

MS = Mass spectrometry

Figure S2. 13 C NMR of compound 1, CDCl ₃ , 125 MHz, 298 K.5Figure S3. 14 NMR spectrum of 2-F, CDCl ₃ , 500 MHz, 298 K.6Figure S4. 19 F NMR spectrum of 2-F, CDCl ₃ , 470 MHz, 298 K, ref. CF ₃ COOH δ = -78.50 ppm.7Figure S6. 13 C- 11 H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.9Figure S6. 13 C- 11 H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.9Figure S7. 13 C- 11 H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.10Figure S9. 14 NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K.12Figure S10. 14 C- 14 H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz-500 MHz, 298 K.13Figure S11. 16 C- 14 H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz-500 MHz, 298 K.14Figure S12. 16 C- 14 H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz-500 MHz, 298 K.15Figure S13. 15 C NMR spectrum of 2-B, CDCl ₃ , 500 MHz, 298 K.16Figure S14.H NMR spectrum of 2-B, CDCl ₃ , 500 MHz, 298 K.17Figure S15. 16 C- 14 H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.19Figure S14. 16 C- 14 H MMB correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.19Figure S15. 16 C- 14 H MSQc correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.20Figure S14. 16 C- 14 H MSQc correlation chart of 2-1, CDCl ₃ , 125 MHz-500 MHz, 298 K.21Figure S21. 16 C- 14 H MSQc correlation chart of 2-1, CDCl ₃ , 125 MHz-500 MHz,	Figure S1. ¹ H NMR of compound 1, CDCl ₃ , 500 MHz, 298 K 4
Figure S3. ¹ H NMR spectrum of 2-F, CDCl ₃ , 500 MHz, 298 K.6Figure S4. ¹⁹ F NMR spectrum of 2-F, CDCl ₃ , 470 MHz, 298 K, ref. CF ₃ COOH δ = -78.50 ppm.7Figure S6. ¹³ C ¹ H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.8Figure S7. ¹³ C ¹ H HSQC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.10Figure S9. ¹³ C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K.11Figure S10. ¹ H- ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 125 MHz, 298 K.12Figure S11. ¹³ C ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz, 500 MHz, 298 K.13Figure S11. ¹⁴ C ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz, 500 MHz, 298 K.14Figure S13. ¹³ C ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz, 500 MHz, 298 K.15Figure S13. ¹³ C ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz, 298 K.16Figure S13. ¹³ C ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz, 298 K.17Figure S14. ¹⁴ H NR spectrum of 2-Br, CDCl ₃ , 120 MHz, 298 K.18Figure S15. ¹ H- ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.19Figure S15. ¹¹ ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.20Figure S15. ¹¹ ¹ H MBC correlation chart of 2-Br, CDCl ₃ , 125 MHz, 298 K.21Figure S14. ¹⁴ D-WR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K.21Figure S14. ¹⁴ D-WR spectrum of 2-I, CDCl ₃ , 125 MHz, 500 MHz, 298 K.22Figure S20. ¹⁴ - ¹ H MMSC correlation chart of 2-I, CDCl ₃ , 125 MHz, 500 MHz, 298 K.22Figure S21. ¹³ C-WR spectrum of 2-I, CDCl ₃ , 100 MHz, 298 K.23 </td <td>Figure S2. ¹³C NMR of compound 1, CDCl₃, 125 MHz, 298 K</td>	Figure S2. ¹³ C NMR of compound 1 , CDCl ₃ , 125 MHz, 298 K
Figure S4. ¹⁹ F NMR spectrum of 2-F, CDCl ₃ , 470 MHz, 298 K, ref. CF ₃ COOH δ = -78.50 ppm.7Figure S6. ¹³ C- ¹ H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.9Figure S7. ¹³ C- ¹ H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.10Figure S8. ¹³ C- ¹ H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz-500 MHz, 298 K.11Figure S10. ¹ H - ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K.12Figure S10. ¹ H- ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 125 MHz-500 MHz, 298 K.13Figure S11. ¹³ C- ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz-500 MHz, 298 K.14Figure S11. ¹³ C- ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz-500 MHz, 298 K.15Figure S13. ¹³ C - ¹ H HSQC correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K.17Figure S15. ¹⁴ - ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.19Figure S15. ¹⁴ - ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.19Figure S15. ¹⁴ - ¹⁴ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz, 298 K.19Figure S16. ¹³ C- ¹⁴ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.20Figure S16. ¹³ C- ¹⁴ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz-500 MHz, 298 K.20Figure S20. ¹⁴ - ¹⁴ HMBC correlation chart of 2-1, CDCl ₃ , 125 MHz-500 MHz, 298 K	Figure S3. ¹ H NMR spectrum of 2-F , CDCl ₃ , 500 MHz, 298 K
Figure S5. 1 H ¹ H COSY correlation chart of 2-F, CDCl ₃ , 500 MHz, 298 K.8Figure S6. 13 C- ¹ H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz–500 MHz, 298 K.9Figure S7. 12 C- ¹ H HSQC correlation chart of 2-F, CDCl ₃ , 125 MHz–500 MHz, 298 K.10Figure S9. 14 NMR spectrum of 2-Cl, CDCl ₃ , 500 MHz, 298 K.11Figure S10. 11 H- ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K.13Figure S11. 13 C- ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K.14Figure S11. 13 C- ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K.15Figure S11. 13 C- ¹ H HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K.16Figure S13. 13 C-NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K.16Figure S14. 14 H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K.17Figure S15. 11 C- ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.19Figure S10. 13 C- ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.20Figure S19. 14 C-NMR spectrum of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.21Figure S19. 14 H-MR Spectrum of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.21Figure S20. 14 H-1 COSY correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.23Figure S21. 13 C- ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.24Figure S21. 13 C- ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.22Figure S21. 13 C- ¹ H MBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.23Figure S21. 13 C-	Figure S4. ¹⁹ F NMR spectrum of 2-F , CDCl ₃ , 470 MHz, 298 K, ref. CF ₃ COOH δ = -78.50 ppm 7
Figure S6. 13 C- 14 HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz–500 MHz, 298 K. 9 Figure S7. 13 C- 14 HSQC correlation chart of 2-F, CDCl ₃ , 125 MHz–500 MHz, 298 K. 10 Figure S8. 13 C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 12 Figure S10. 11 H- 14 COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K. 12 Figure S11. 13 C- 14 HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 13 Figure S12. 13 C- 14 HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 14 Figure S13. 13 C- 14 HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 16 Figure S14. 14 HNR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. 14 H-1 COSY correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S16. 13 C- 14 HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S16. 13 C- 14 HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 21 Figure S17. 13 C- 14 HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S14. 14 NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S15. 11 -1 HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K. 22 Figure S16. 13 C-1 H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K.	Figure S5. ¹ H– ¹ H COSY correlation chart of 2-F, CDCl ₃ , 500 MHz, 298 K
Figure S7. 13 C- 14 HSQC correlation chart of 2-F, CDCl ₃ , 125 MHz, 298 K. 10 Figure S8. 13 C NMR spectrum of 2-F, CDCl ₃ , 125 MHz, 298 K. 11 Figure S10. 14 H- 14 COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K. 13 Figure S10. 14 H- 14 COSY correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 14 Figure S11. 13 C- 14 HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 14 Figure S12. 13 C- 14 HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 15 Figure S13. 13 C NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 16 Figure S15. 14 H-IMCSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. 14 C- ¹⁴ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S15. 11 C- 14 HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S14. 13 C- 14 HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 21 Figure S20. 14 C- 14 HMBC correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S21. 13 C- 14 HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 23 Figure S21. 13 C- 14 HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 23 Figure S21. 13 C- 14 HMBC correlation chart of 2-I, CDCl ₃ , 12	Figure S6. ¹³ C– ¹ H HMBC correlation chart of 2-F, CDCl ₃ , 125 MHz–500 MHz, 298 K
Figure S8. ¹³ C NMR spectrum of 2-F, CDCl ₃ , 125 MHz, 298 K. 11 Figure S9. ¹ H NMR spectrum of 2-Cl, CDCl ₃ , 500 MHz, 298 K. 12 Figure S10. ¹ H ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K. 13 Figure S11. ¹³ C ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 14 Figure S12. ¹³ C ¹ H HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 15 Figure S13. ¹³ C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 16 Figure S14. ¹ H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. ¹ H ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 100 MHz, 298 K. 18 Figure S16. ¹³ C ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S17. ¹³ C ¹ H HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. ¹³ C NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 21 Figure S19. ¹⁴ H HMSC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 22 Figure S10. ¹⁴ H-I COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 21 Figure S20. ¹ H ¹ H COSY correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 23 Figure S21. ¹³ C ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K. 24 Figure S21. ¹³ C ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz,	Figure S7. ¹³ C– ¹ H HSQC correlation chart of 2-F , CDCl ₃ , 125 MHz–500 MHz, 298 K 10
Figure S9. ¹ H NMR spectrum of 2-Cl, CDCl ₃ , 500 MHz, 298 K. 12 Figure S10. ¹ H– ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K. 13 Figure S11. ¹³ C– ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 14 Figure S12. ¹³ C– ¹ H HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 15 Figure S13. ¹³ C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 16 Figure S15. ¹ H– ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S16. ¹³ C– ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 18 Figure S16. ¹³ C– ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S16. ¹³ C– ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S11. ¹³ C– ¹ H HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 21 Figure S11. ¹³ C– ¹ H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K. 22 Figure S20. ¹ H– ¹ H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K. 24 Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K. 23 Figure S21. ¹³ C– ¹ H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz, 298 K. 24 Figure S21. ¹³ C– ¹ H HSQC correl	Figure S8. ¹³ C NMR spectrum of 2-F, CDCl ₃ , 125 MHz, 298 K 11
Figure S10. $^{1}H-^{1}H$ COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K.13Figure S11. $^{13}C-^{1}H$ HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K.14Figure S13. ^{13}C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K.16Figure S13. ^{13}C NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K.16Figure S15. $^{1}H-^{1}H$ COSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K.17Figure S16. $^{13}C-^{1}H$ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.19Figure S17. $^{13}C-^{1}H$ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.20Figure S19. ^{14}H NR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K.21Figure S10. ^{14}H HMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K.22Figure S10. $^{14}H-^{1}H$ COSY correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.20Figure S10. ^{14}H NR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K.21Figure S20. $^{14}H-^{1}H$ COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K.23Figure S21. $^{13}C-^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.24Figure S21. $^{13}C-^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.25Figure S21. $^{13}C-^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.26Figure S23. ^{13}C NMR spectrum of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.26Figure S23. ^{13}C NMR spectrum of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. </td <td>Figure S9. ¹H NMR spectrum of 2-Cl, CDCl₃, 500 MHz, 298 K 12</td>	Figure S9. ¹ H NMR spectrum of 2-Cl , CDCl ₃ , 500 MHz, 298 K 12
Figure S11. $^{13}C^{-1}H$ HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 14 Figure S12. $^{13}C^{-1}H$ HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K. 15 Figure S13. ^{13}C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 16 Figure S14. ^{1}H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. $^{1}H^{-1}H$ COSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 18 Figure S16. $^{13}C^{-1}H$ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S17. $^{13}C^{-1}H$ HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. ^{13}C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 21 Figure S19. ^{1}H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. $^{1}H^{-1}H$ COSY correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 23 Figure S21. $^{13}C^{-1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. $^{13}C^{-1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. $^{13}C^{-1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S21. $^{13}C^{-1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 26 Figure S23. ^{13}C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K. 25	Figure S10. ¹ H– ¹ H COSY correlation chart of 2-Cl, CDCl ₃ , 500 MHz, 298 K 13
Figure S12. 13 C– 14 HSQC correlation chart of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 15 Figure S13. 13 C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 16 Figure S14. 14 H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. 14 H– 14 COSY correlation chart of 2-Br, CDCl ₃ , 100 MHz, 298 K. 18 Figure S16. 13 C– 14 HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S17. 13 C– 14 HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. 13 C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S19. 14 H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. 14 H– 14 COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. 13 C– 14 HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. 13 C– 14 HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. 13 C– 14 HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S23. 13 C– 14 HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 26 Figure S23. MS spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K. 26 Figure S24. MS spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 27 <	Figure S11. ¹³ C– ¹ H HMBC correlation chart of 2-Cl, CDCl ₃ , 125 MHz–500 MHz, 298 K 14
Figure S13. ¹³ C NMR spectrum of 2-Cl, CDCl ₃ , 125 MHz, 298 K. 16 Figure S14. ¹ H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. ¹ H– ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 18 Figure S16. ¹³ C– ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S17. ¹³ C– ¹ H HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. ¹³ C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S19. ¹ H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. ¹ H– ¹ H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S22. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S23. ¹³ C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K. 26 Figure S24. MS spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K. 26 Figure S25. MS spectrum of 2-Cl in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 27 Figure S26. MS spectrum of 2-Br in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum (bottom). 29 Figure S27. MS spectrum of 2-I in MeO	Figure S12. ¹³ C– ¹ H HSQC correlation chart of 2-Cl , CDCl ₃ , 125 MHz–500 MHz, 298 K 15
Figure S14. ¹ H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K. 17 Figure S15. ¹ H– ¹ H COSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 18 Figure S16. ¹³ C– ¹ H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S17. ¹³ C– ¹ H HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. ¹³ C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S19. ¹ H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. ¹ H– ¹ H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S22. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S23. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S23. ¹³ C NMR spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 27 Figure S25. MS spectrum of 2-CI in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Cl+Na] ⁺ ion, top) and simulated spectrum (bottom). 28 Figure S26. MS spectrum of 2-Br in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Cl+Na] ⁺ ion, top) and simulated spectrum (bottom). 29 Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion, top) and simulated spectrum (bottom). 30 Figure S28. Top – MS spectrum of mixture of c	Figure S13. ¹³ C NMR spectrum of 2-Cl , CDCl ₃ , 125 MHz, 298 K 16
Figure S15. 1 H– 1 H COSY correlation chart of 2-Br, CDCl ₃ , 500 MHz, 298 K. 18 Figure S16. 13 C– 1 H HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S17. 13 C– 1 H HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. 13 C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S19. 1 H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. 1 H– 1 H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. 13 C– 1 H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. 13 C– 1 H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S23. 13 C– 1 H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S23. 13 C– 1 H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 26 Figure S24. MS spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 27 Figure S25. MS spectrum of 2-CI in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum (bottom). 28 Figure S26. MS spectrum of 2-Br in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum (bottom). 29 Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion, top) and simulated spectrum (bottom). 30	Figure S14. ¹ H NMR spectrum of 2-Br, CDCl ₃ , 500 MHz, 298 K 17
Figure S16. ${}^{13}C-{}^{1}H$ HMBC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 19 Figure S17. ${}^{13}C-{}^{1}H$ HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K. 20 Figure S18. ${}^{13}C$ NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S19. ${}^{1}H$ NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. ${}^{1}H-{}^{1}H$ COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. ${}^{13}C-{}^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S22. ${}^{13}C-{}^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 24 Figure S21. ${}^{13}C-{}^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K. 25 Figure S23. ${}^{13}C$ NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K. 26 Figure S24. MS spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 27 Figure S25. MS spectrum of 2-Cl in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Cl+Na] ⁺ ion, top) and simulated spectrum (bottom). 28 Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum (bottom). 29 Figure S28. Top – MS spectrum of mixture of compounds 2-I ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion) and 2-I_azo ([C ₁₈ H ₁₃ N ₅ I ₂ +Na] ⁺ ion) in MeOH. Bottom – simulated spectrum for 2-I azo. 31	Figure S15. ¹ H– ¹ H COSY correlation chart of 2-Br , CDCl ₃ , 500 MHz, 298 K 18
Figure S17. $^{13}C-^{1}H$ HSQC correlation chart of 2-Br, CDCl ₃ , 125 MHz–500 MHz, 298 K.20Figure S18. ^{13}C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K.21Figure S19. ^{1}H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K.22Figure S20. $^{1}H-^{1}H$ COSY correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.23Figure S21. $^{13}C-^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.24Figure S22. $^{13}C-^{1}H$ HMSC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.25Figure S23. ^{13}C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K.26Figure S24. MS spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom).27Figure S25. MS spectrum of 2-CI in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Cl+Na] ⁺ ion, top) and simulated spectrum (bottom).28Figure S26. MS spectrum of 2-Br in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum (bottom).29Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion, top) and simulated spectrum (bottom).30Figure S28. Top – MS spectrum of mixture of compounds 2-I ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion) and 2-I_azo ([C ₁₈ H ₁₃ N ₅ I ₂ +Na] ⁺ ion) in MeOH. Bottom – simulated spectrum for 2-I azo.31	Figure S16. ¹³ C– ¹ H HMBC correlation chart of 2-Br , CDCl ₃ , 125 MHz–500 MHz, 298 K 19
Figure S18. ¹³ C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K. 21 Figure S19. ¹ H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K. 22 Figure S20. ¹ H- ¹ H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K. 23 Figure S21. ¹³ C- ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz-500 MHz, 298 K. 24 Figure S22. ¹³ C- ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz-500 MHz, 298 K. 25 Figure S23. ¹³ C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K. 26 Figure S24. MS spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 27 Figure S25. MS spectrum of 2-Cl in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum (bottom). 28 Figure S26. MS spectrum of 2-Br in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum (bottom). 29 Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion, top) and simulated spectrum (bottom). 29 Figure S28. Top – MS spectrum of mixture of compounds 2-I ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion) and 2-I_azo ([C ₁₈ H ₁₃ N ₅ I ₂ +Na] ⁺ ion) in MeOH. Bottom – simulated spectrum for 2-I azo. 31	Figure S17. ¹³ C– ¹ H HSQC correlation chart of 2-Br , CDCl ₃ , 125 MHz–500 MHz, 298 K 20
Figure S19. ¹ H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K.22Figure S20. ¹ H– ¹ H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K.23Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.24Figure S22. ¹³ C– ¹ H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.25Figure S23. ¹³ C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K.26Figure S24. MS spectrum of 2-F in MeOH ($[C_{15}H_{14}N_{3}O_{2}F+Na]^{+}$ ion, top) and simulated spectrum27Figure S25. MS spectrum of 2-CI in MeOH ($[C_{15}H_{14}N_{3}O_{2}CI+Na]^{+}$ ion, top) and simulated spectrum28Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_{3}O_{2}Br+Na]^{+}$ ion, top) and simulated spectrum29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_{3}O_{2}Br+Na]^{+}$ ion, top) and simulated spectrum30Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_{3}O_{2}I+Na]^{+}$ ion) and 2-I azo31	Figure S18. ¹³ C NMR spectrum of 2-Br, CDCl ₃ , 125 MHz, 298 K 21
Figure S20. 1 H– 1 H COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K.23Figure S21. 13 C– 1 H HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.24Figure S22. 13 C– 1 H HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.25Figure S23. 13 C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K.26Figure S24. MS spectrum of 2-F in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ F+Na] ⁺ ion, top) and simulated spectrum27Figure S25. MS spectrum of 2-Cl in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Cl+Na] ⁺ ion, top) and simulated spectrum28Figure S26. MS spectrum of 2-Br in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ Br+Na] ⁺ ion, top) and simulated spectrum29Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion, top) and simulated spectrum20fottom).29Figure S27. MS spectrum of 2-I in MeOH ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion, top) and simulated spectrum30Figure S28. Top – MS spectrum of mixture of compounds 2-I ([C ₁₅ H ₁₄ N ₃ O ₂ I+Na] ⁺ ion) and 2-I_azo31	Figure S19. ¹ H NMR spectrum of 2-I, CDCl ₃ , 500 MHz, 298 K 22
Figure S21. ${}^{13}C-{}^{1}H$ HMBC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.24Figure S22. ${}^{13}C-{}^{1}H$ HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.25Figure S23. ${}^{13}C$ NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K.26Figure S24. MS spectrum of 2-F in MeOH ($[C_{15}H_{14}N_3O_2F+Na]^+$ ion, top) and simulated spectrum27Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum28Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum30Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo31	Figure S20. $^{1}H-^{1}H$ COSY correlation chart of 2-I, CDCl ₃ , 500 MHz, 298 K 23
Figure S22. ${}^{13}C-{}^{1}H$ HSQC correlation chart of 2-I, CDCl ₃ , 125 MHz–500 MHz, 298 K.25Figure S23. ${}^{13}C$ NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K.26Figure S24. MS spectrum of 2-F in MeOH ($[C_{15}H_{14}N_3O_2F+Na]^+$ ion, top) and simulated spectrum (bottom).27Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum (bottom).28Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum (bottom).29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum (bottom).29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion, top) and simulated spectrum (bottom).30Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo ($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I azo.31	Figure S21. ¹³ C– ¹ H HMBC correlation chart of 2-I , CDCl ₃ , 125 MHz–500 MHz, 298 K 24
Figure S23. 13 C NMR spectrum of 2-I, CDCl ₃ , 125 MHz, 298 K.26Figure S24. MS spectrum of 2-F in MeOH ($[C_{15}H_{14}N_3O_2F+Na]^+$ ion, top) and simulated spectrum27(bottom).27Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum28Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum30Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo31	Figure S22. ¹³ C– ¹ H HSQC correlation chart of 2-I , CDCl ₃ , 125 MHz–500 MHz, 298 K 25
Figure S24. MS spectrum of 2-F in MeOH ($[C_{15}H_{14}N_3O_2F+Na]^+$ ion, top) and simulated spectrum(bottom).27Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum(bottom).28Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum(bottom).29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion, top) and simulated spectrum(bottom).29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion, top) and simulated spectrum(bottom).30Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I azo.31	Figure S23. ¹³ C NMR spectrum of 2-I , CDCl ₃ , 125 MHz, 298 K
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Figure S24. MS spectrum of 2-F in MeOH ($[C_{15}H_{14}N_3O_2F+Na]^+$ ion, top) and simulated spectrum
Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum(bottom).28Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum(bottom).29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion, top) and simulated spectrum(bottom).29Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion, top) and simulated spectrum(bottom).30Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I azo.31	(bottom)
(bottom)	Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum
Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum (bottom). Figure S27. MS spectrum of 2-I in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion, top) and simulated spectrum (bottom). Solution S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo ($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I azo	(bottom)
(bottom)	Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^{\top}$ ion, top) and simulated spectrum
Figure S27. MS spectrum of 2-1 in MeOH ($[C_{15}H_{14}N_{3}O_{2}I+Na]^{+}$ ion, top) and simulated spectrum (bottom)	(bottom).
Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo ($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I azo	Figure S27. MS spectrum of 2-1 in MeOH ($[C_{15}H_{14}N_3O_2I+Na]^2$ ion, top) and simulated spectrum
($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I azo	(bollom)
$([C_1811]_{31})_{512}$ $([n]_{101})$ in [vicO11. Douoni – sinulated spectrum for 2-1 alo	Figure S26. 10p – MS spectrum of mixture of compounds 2-1 ($[C_{15}T_{14}N_3O_2]^+$ Na] 10n) and 2-1_azo ($[C_{15}T_{14}N_3O_2]^+$ ion) in MeOH Bottom simulated spectrum for 2 L azo
Figure S29 Comparison of N-H shift (npm) of 2-F ¹ H NMR spectrum of obtained 2-F in blue ¹ H	Figure S29 Comparison of N-H shift (nnm) of $2-F$ ⁻¹ H NMR spectrum of obtained $2-F$ in blue ¹ H
NMR spectrum after 420 nm/30 min. ¹ H NMR spectrum after 460 nm/30 min. in green CDCl ₂ 500	NMR spectrum after 420 nm/30 min. ¹ H NMR spectrum after 460 nm/30 min. in green CDCl ₂ 500
MHz, 298 K	MHz, 298 K

Figure S30. Comparison of C–F shift (ppm) of 2-F . ¹⁹ F NMR spectrum of obtained 2-F (blue). ¹⁹ F NMR spectrum after 420 nm/30 min (red). ¹⁹ F NMR spectrum after 460 nm/30 min. (green). CDCl ₃ ,
470 MHz, 298 K, ref. CF ₃ COOH $δ$ = -78.50 ppm
Figure S31. Comparison of N–H shift (ppm) of 2-Cl. ¹ H NMR spectrum of obtained 2-Cl (blue). ¹ H NMR spectrum after 420 nm/30 min (red). ¹ H NMR spectrum after 460 nm/30 min. (green). CDCl ₃ , 500 MHz, 298 K
Figure S32 . Comparison of N–H shift (ppm) of 2-Br . ¹ H NMR spectrum of obtained 2-Br in blue. ¹ H NMR spectrum after 420 nm/30 min. ¹ H NMR spectrum after 460 nm/30 min. in green. CDCl ₃ , 500 MHz, 298 K
Figure S33. Comparison of N–H shift (ppm) of 2-I . ¹ H NMR spectrum of obtained 2-I in blue. ¹ H NMR spectrum after 420 nm/30 min. ¹ H NMR spectrum after 460 nm/30 min. in green. CDCl ₃ , 500 MHz 298 K
Figure S34. UV-VIS spectrum of compound 2-F before (black line) and after irradiation at 420 nm (2-F - <i>E</i> , red line) and 460 nm (2-F - <i>Z</i> , blue line) for 30 minutes $(2.73 \times 10^{-5} \text{ M}, \text{CHCl}_3)$
 GHCl₃)
toluene)
Figure S39. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 3 min (top red dots). The absorbances at 370 nm are plotted $(2.73 \times 10^{-5} \text{ M}, \text{CHCl}_3)$
Figure S40. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 371 nm are plotted (2.73×10 ⁻⁵ M, CHCl ₃).
Figure S41. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 370 nm are plotted $(2.05 \times 10^{-5} \text{ M}, \text{toluene})$.
Figure S42. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 367 nm are plotted (2.78×10 ⁻⁵ M, acetonitrile)
Figure S43. Isomerization cycles of 2-Br upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 1 min (top red dots). The absorbances at 371 nm are plotted $(2.73 \times 10^{-5} \text{ M}, \text{CHCl}_3)$.
Figure S44. Isomerization cycles of 2-Br upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 371 nm are plotted (2.73×10 ⁻⁵ M, CHCl ₃).
Figure S45. Isomerization cycles of 2-I upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 3 min (top red dots). The absorbances at 370 nm are plotted $(1.36 \times 10^{-5} \text{ M}, \text{CHCl})$
Figure S46. ¹ H NMR spectrum of 2-Br ($c = 0.02$ M) recorded after exposition on 460 nm over 3 hours, CDCl ₃ , 500 MHz, 298 K
Figure S47. Positive ion mode MS spectrum of 2-Br (in MeOH) after exposition to 460 nm irradiation for 3 hours at 0.02 M concentration

Figure S48. Negative ion mode MS spectrum of 2-Br (in MeOH) after exposition to 460 nm
irradiation for 3 hours at 0.02 M concentration
Figure S49. ¹ H NMR spectrum of 2-Br ($c = 0.1$ M) recorded after exposition on 460 nm over 3 hours,
CDCl ₃ , 500 MHz, 298 K
Figure S50. $^{15}N-^{1}H$ HSQC correlation chart of 2-Br (c = 0.1 M), CDCl ₃ , 50 MHz–500 MHz, 298 K,
ref. $NH_{3(liq.)} \delta = 380.20 \text{ ppm}.$
Figure S51. ¹⁵ N– ¹ H HMBC correlation chart of 2-Br ($c = 0.1$ M), CDCl ₃ , 50 MHz–500 MHz, 298 K,
ref. $NH_{3(liq.)} \delta = 380.20 \text{ ppm}.$
Figure S52. The minimal energy pathway for Z-E isomerization for 2-F calculated with CAM-
B3LYP+D4/def2-TZVP/C-CPCM(CHCl ₃): relative energies, enthalpies, and Gibbs energies
Figure S53. The minimal energy pathway for Z-E isomerization for 2-Br calculated with CAM-
B3LYP+D4/def2-TZVP/C-CPCM(CHCl ₃): relative energies, enthalpies, and Gibbs energies
Figure S54. The minimal energy pathway for Z-E isomerization for 2-I calculated with CAM-
B3LYP+D4/def2-TZVP/C-CPCM(CHCl ₃): relative energies, enthalpies, and Gibbs energies
Figure S55. The graphically marked fragments of 2-Cl-Z (left) and 2-Cl-E* (right) used for ICFT
analysis of TD-DFT spectra
Figure S56. Depiction of the Laplacian of calculated electron density $\nabla 2\rho(\mathbf{r})$ for the optimized
geometries (implicit solvation model C-PCM) of studied hydrazone switches in the Z-configuration.
The (3, -1) bond critical points (brown dots) and bond paths (black solid and dashed lines) are
depicted
Figure S57. Depiction of the Laplacian of calculated electron density $V2\rho(\mathbf{r})$ for the optimized
geometries (implicit solvation model C-PCM) of studied hydrazone switches in the <i>E</i> -configuration.
deniated
Eigenvalue 559 . Condition the contract of the continuing dependence of the continuing dependence $(z = 0.42 \text{ cm})$ for the continuing dependence (in the contract of the continuing dependence).
Figure S56. Oradient isosurfaces ($s = 0.42$ au) for the optimized geometries (implicit solvation model C PCM) of studied hydrozone switches in the Z configuration. The surfaces are colored on a blue
green-red scale according to values of sign(λ_2)r ranging from -0.04 to 0.04 au Blue indicates strong
attractive interactions and red indicates strong nonbonded overlap 78
Figure S59 Gradient isosurfaces ($s = 0.42$ au) for the optimized geometries (implicit solvation model
C-PCM) of studied hydrazone switches in the <i>E</i> -configuration. The surfaces are colored on a blue-
green-red scale according to values of sign(λ_2) r , ranging from -0.04 to 0.04 au. Blue indicates strong
attractive interactions, and red indicates strong nonbonded overlap



Figure S1. ¹H NMR of compound 1, CDCl₃, 500 MHz, 298 K.











Figure S4. ¹⁹F NMR spectrum of 2-F, CDCl₃, 470 MHz, 298 K, ref. CF₃COOH δ = -78.50 ppm.



Figure S5. ¹H–¹H COSY correlation chart of **2-F**, CDCl₃, 500 MHz, 298 K.



Figure S6. ¹³C–¹H HMBC correlation chart of 2-F, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S7. ¹³C–¹H HSQC correlation chart of 2-F, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S8. ¹³C NMR spectrum of 2-F, CDCl₃, 125 MHz, 298 K.



Figure S9. ¹H NMR spectrum of 2-Cl, CDCl₃, 500 MHz, 298 K.



Figure S10. ¹H–¹H COSY correlation chart of 2-Cl, CDCl₃, 500 MHz, 298 K.



Figure S11. ¹³C–¹H HMBC correlation chart of 2-Cl, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S12. ¹³C–¹H HSQC correlation chart of 2-Cl, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S13. ¹³C NMR spectrum of 2-Cl, CDCl₃, 125 MHz, 298 K.



Figure S14. ¹H NMR spectrum of 2-Br, CDCl₃, 500 MHz, 298 K.



Figure S15. ¹H–¹H COSY correlation chart of **2-Br**, CDCl₃, 500 MHz, 298 K.



Figure S16. ¹³C–¹H HMBC correlation chart of 2-Br, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S17. ¹³C–¹H HSQC correlation chart of **2-Br**, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S18. ¹³C NMR spectrum of 2-Br, CDCl₃, 125 MHz, 298 K.



Figure S19. ¹H NMR spectrum of **2-I**, CDCl₃, 500 MHz, 298 K.



Figure S20. ¹H–¹H COSY correlation chart of 2-I, CDCl₃, 500 MHz, 298 K.



Figure S21. ¹³C–¹H HMBC correlation chart of 2-I, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S22. ¹³C–¹H HSQC correlation chart of 2-I, CDCl₃, 125 MHz–500 MHz, 298 K.



Figure S23. ¹³C NMR spectrum of **2-I**, CDCl₃, 125 MHz, 298 K.



Figure S24. MS spectrum of **2-F** in MeOH ($[C_{15}H_{14}N_3O_2F+Na]^+$ ion, top) and simulated spectrum (bottom).



Figure S25. MS spectrum of 2-Cl in MeOH ($[C_{15}H_{14}N_3O_2Cl+Na]^+$ ion, top) and simulated spectrum (bottom).



Figure S26. MS spectrum of 2-Br in MeOH ($[C_{15}H_{14}N_3O_2Br+Na]^+$ ion, top) and simulated spectrum (bottom).



Figure S27. MS spectrum of 2-I in MeOH ([C₁₅H₁₄N₃O₂I+Na]⁺ ion, top) and simulated spectrum (bottom).



Figure S28. Top – MS spectrum of mixture of compounds 2-I ($[C_{15}H_{14}N_3O_2I+Na]^+$ ion) and 2-I_azo ($[C_{18}H_{13}N_5I_2+Na]^+$ ion) in MeOH. Bottom – simulated spectrum for 2-I_azo.



Figure S29. Comparison of N–*H* shift (ppm) of 2-F. ¹H NMR spectrum of obtained 2-F in blue. ¹H NMR spectrum after 420 nm/30 min. ¹H NMR spectrum after 460 nm/30 min. in green. CDCl₃, 500 MHz, 298 K.



Figure S30. Comparison of C–F shift (ppm) of 2-F. ¹⁹F NMR spectrum of obtained 2-F (blue). ¹⁹F NMR spectrum after 420 nm/30 min (red). ¹⁹F NMR spectrum after 460 nm/30 min. (green). CDCl₃, 470 MHz, 298 K, ref. CF₃COOH δ = -78.50 ppm.



Figure S31. Comparison of N–*H* shift (ppm) of 2-Cl. ¹H NMR spectrum of obtained 2-Cl (blue). ¹H NMR spectrum after 420 nm/30 min (red). ¹H NMR spectrum after 460 nm/30 min. (green). CDCl₃, 500 MHz, 298 K.



Figure S32. Comparison of N–*H* shift (ppm) of 2-Br. ¹H NMR spectrum of obtained 2-Br in blue. ¹H NMR spectrum after 420 nm/30 min. ¹H NMR spectrum after 460 nm/30 min. in green. CDCl₃, 500 MHz, 298 K.



Figure S33. Comparison of N–H shift (ppm) of 2-I. ¹H NMR spectrum of obtained 2-I in blue. ¹H NMR spectrum after 420 nm/30 min. ¹H NMR spectrum after 460 nm/30 min. in green. CDCl₃, 500 MHz, 298 K.


Figure S34. UV-VIS spectrum of compound 2-F before (black line) and after irradiation at 420 nm (2-F-*E*, red line) and 460 nm (2-F-*Z*, blue line) for 30 minutes (2.73×10⁻⁵ M, CHCl₃).



Figure S35. UV-VIS spectrum of compound 2-I before (black line) and after irradiation at 420 nm (2-I-*E*, red line) and 460 nm (2-I-*Z*, blue line) for 30 minutes (1.36×10⁻⁵ M, CHCl₃).

Photoswitching efficiency

All compounds were irradiated for 1 minute at 420 nm ($Z \rightarrow E$) and for 3 minutes at 460 nm ($E \rightarrow Z$) in chloroform. The optimalization of irradiation conditions was performed for **2-Cl** and **2-Br**: 20 seconds at 420 nm ($Z \rightarrow E$) and 20 seconds at 365 nm ($E \rightarrow Z$). Compounds **2-F** and **2-Cl** were also photoswitched in toluene and acetonitrile.



Figure S36. Isomerization cycles of 2-F upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 3 min (top red dots). The absorbances at 370 nm are plotted (2.73×10⁻⁵ M, CHCl₃).



Figure S37. Isomerization cycles of 2-F upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 365 nm are plotted (2.41×10⁻⁵ M, toluene).



Figure S38. Isomerization cycles of 2-F upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 365 nm are plotted (1.92×10⁻⁵ M, acetonitrile).



Figure S39. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 3 min (top red dots). The absorbances at 370 nm are plotted (2.73×10⁻⁵ M, CHCl₃).



Figure S40. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 371 nm are plotted (2.73×10⁻⁵ M, CHCl₃).



Figure S41. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 370 nm are plotted (2.05×10⁻⁵ M, toluene).



Figure S42. Isomerization cycles of 2-Cl upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 367 nm are plotted (2.78×10⁻⁵ M, acetonitrile).



Figure S43. Isomerization cycles of 2-Br upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 1 min (top red dots). The absorbances at 371 nm are plotted (2.73×10⁻⁵ M, CHCl₃).



Figure S44. Isomerization cycles of 2-Br upon alternating irradiation at 420 nm for 20 s (bottom red dots) and 365 nm for 20 s (top red dots). The absorbances at 371 nm are plotted (2.73×10⁻⁵ M, CHCl₃).



Figure S45. Isomerization cycles of 2-I upon alternating irradiation at 420 nm for 1 min (bottom red dots) and 460 nm for 3 min (top red dots). The absorbances at 370 nm are plotted (1.36×10⁻⁵ M, CHCl₃).



Figure S46. ¹H NMR spectrum of 2-Br (c = 0.02 M) recorded after exposition on 460 nm over 3 hours, CDCl₃, 500 MHz, 298 K.



Figure S47. Positive ion mode MS spectrum of 2-Br (in MeOH) after exposition to 460 nm irradiation for 3 hours at 0.02 M concentration.



Figure S48. Negative ion mode MS spectrum of 2-Br (in MeOH) after exposition to 460 nm irradiation for 3 hours at 0.02 M concentration.



Figure S49. ¹H NMR spectrum of 2-Br (c = 0.1 M) recorded after exposition on 460 nm over 3 hours, CDCl₃, 500 MHz, 298 K.



Figure S50. ¹⁵N–¹H HSQC correlation chart of 2-Br (c = 0.1 M), CDCl₃, 50 MHz–500 MHz, 298 K, ref. NH_{3(liq.)} δ = 380.20 ppm.



Figure S51. ¹⁵N–¹H HMBC correlation chart of 2-Br (c = 0.1 M), CDCl₃, 50 MHz–500 MHz, 298 K, ref. NH_{3(liq.)} δ = 380.20 ppm.



Figure S52. The minimal energy pathway for Z-E isomerization for 2-F calculated with CAM-B3LYP+D4/def2-TZVP/C-CPCM(CHCl₃): relative energies, enthalpies, and Gibbs energies.



Figure S53. The minimal energy pathway for Z-E isomerization for 2-Br calculated with CAM-B3LYP+D4/def2-TZVP/C-CPCM(CHCl₃): relative energies, enthalpies, and Gibbs energies.



Figure S54. The minimal energy pathway for Z-E isomerization for 2-I calculated with CAM-B3LYP+D4/def2-TZVP/C-CPCM(CHCl₃): relative energies, enthalpies, and Gibbs energies.

	2-Br	2-I
Formula	$C_{15}H_{14}BrN_3O_2$	$C_{15}H_{14}IN_3O_2$
M _r	348.201	395.202
Crystal system	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_{1}/c$
T/K	150.00(10)	100.00(10)
<i>a</i> (Å)	4.7716(1)	4.6839(2)
<i>b</i> (Å)	18.2538(5)	18.5687(8)
<i>c</i> (Å)	16.7147(4)	16.9966(6)
α (°)	90	90
β(°)	97.171(2)	95.506(4)
γ (°)	90	90
$V(Å^3)$	1444.46(6)	1471.44(10)
Ζ	4	4
λ (Å), Cu K α	1.54184	1.54184
$D_{\text{calc}} \left(\mathbf{g} \cdot \mathbf{cm}^{-3} \right)$	1.601	1.784
$\mu (\mathrm{mm}^{-1})$	3.956	17.179
F (000)	703.4	779.0
Reflections collected	10145	7046
$R_{\rm int}, R_{ m sigma}$	0.0414, 0.0353	0.0441, 0.0390
Data/restraints/parameters	2653/0/191	2730/0/191
Goodness-of-fit on F^2	1.033	1.040
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0336$	$R_1 = 0.0550$
	$wR_2 = 0.0918$	$wR_2 = 0.1458$
Final R indices (all data)	$R_1 = 0.0370$	$R_1 = 0.0583$
	$wR_2 = 0.0945$	$wR_2 = 0.1492$
Larg. d. peak/hole / e Å ⁻³	0.75/-0.60	1.22/-2.12
CCDC no.	2335394	2335397

Table S1. Crystal data and structure refinement for 2-Br and 2-I.

Table S2. The CAM-B3LYP calculated values of $\Delta H_{iso}^{E \rightarrow Z}$ for **2-X**.

	kcal/mol	kcal/mol	kJ/mol kJ/	mol
X=	H(E)-H(Z)	H(E*)-H(Z*)	H(E*)-H(Z*) G(E	E)-G(Z)
F	4.52	1.30	18.90	5.43
Cl	4.45	1.47	18.61	6.16
Br	4.42	1.54	18.50	6.44
Ι	4.37	1.64	18.27	6.87

Table S3. The CAM-B3LYP calculated values of $\Delta G^{\ddagger E \rightarrow Z}$ for **2-X**.

	kcal/mol	kcal/mol		kJ/mol	kJ/mol	
X=	G(TS)-G(E)	G(TS*)-G(I	E*)	G(TS)-G(E)	G(TS*)-G(E*)	
F	23.38	25.98		97.84	108.71	
Cl	28.08	30.49		117.50	127.59	
Br	21.07	25.67		88.14	107.41	
I	33.02	35.51		138.14	148.57	

<u>ermir 80</u>	DII/I		. • • • • • • • •	
Ζ	Atom	shift[p	pm]	30
	rel.int	ensity		29 31
	2	15.65	1.00	32
	12	8.43	1.00	27 26
	14	7.72	1.00	
	16	7.70	1.00	6 1 2
	18	7.78	1.00	13
	20	9.16	1.00	6 22
	24	7.47	1.00	7 3 23
	27	4.38	1.00	
	28	4.30	1.00	9 15
	30	1.47	1.00	10 2 16
	31	1.72	1.00	4 0
	32	1.64	1.00	33 - 21
	33	8.39	1.00	17 19
	34	8.71	1.00	20
				18
Z-a	2	20.32	1.00	18
	12	8.60	1.00	20
	14	7.68	1.00	19
	16	7.72	1.00	33 21
	18	7.58	1.00	
	20	8.47	1.00	10 16
	24	7.61	1.00	84 9 15
	27	4.31	1.00	6
	28	4.28	1.00	3 23 24
	30	1.45	1.00	0 2 11 13
	31	1.67	1.00	12
	32	1.65	1.00	6 (4
	33	8.54	1.00	28.00
	34	9.81	1.00	27 26
				29 31
				2
				30

Table S4. The isomer shifts of ¹H NMR relative to TMS together with atom numbering scheme, calculated with CAM-B3LYP/PCSSEG-2/C-PCM(CHCl₃), for **2-F**.

<i>E-</i> b	2	12.47	1.00	30
	12	8.37	1.00	
	14	7.76	1.00	29 31
	16	7.68	1.00	27 26 32
	18	7.21	1.00	
	20	8.24	1.00	
	24	7.60	1.00	6
	27	4.27	1.00	22 12
	28	4.27	1.00	A A A
	30	1.39	1.00	34 7 13
	31	1.69	1.00	
	32	1.62	1.00	10 8
	33	8.36	1.00	9 24
	34	9.50	1.00	4 2 15
				17
				19 16
				18 20
E-c	11	7.83	1.00	19
	13	7.63	1.00	17
	15	7.68	1.00	16 18 13
	17	7.15	1.00	3 34 11 12 23
	19	8.14	1.00	20 10 22
	23	7.66	1.00	7 14
	26	5.10	1.00	9 2 5 15
	27	3.93	1.00	
	29	1.12	1.00	
	30	1.47	1.00	21
	31	1.63	1.00	4 29
	32	8.29	1.00	
	33	9.15	1.00	25 97
	34	12.38	1.00	
				31 28
				29
F	11	8 30	1 00	
	12	0.30 7 70	1.00	13
	15	7.70	1.00	17 18 12
	17	7.07 7.72	1.00	
	19	9.11	1.00	3
	23	7 4 5	1.00	32 20
	26	5 23	1.00	9 2 5 14
	27	4.37	1.00	
	29	1.26	1.00	
	30	1.43	1.00	21 0
	31	1.64	1.00	
	32	8.23	1.00	
	33	8.02	1.00	
	34	11.66	1.00	26 27
				31 28 30
				I
				29

Z*	2	15.05	1.00	18
	12	8.40	1.00	20
	14	7.70	1.00	17
	16	7.67	1.00	19
	18	7.78	1.00	33 21
	20	9.18	1.00	
	24	7.43	1.00	
	27	4.46	1.00	10 8 2 16
	28	4.31	1.00	34 9
	30	1.38	1.00	1 15
	31	1.40	1.00	
	32	1.52	1.00	62 23
	33	8.37	1.00	25 22 11 24
	34	8.18	1.00	31)9
				26 6 6
				30 14
				28
Z*-a	2	20.76	1.00	18
	12	8.66	1.00	
	14	7.69	1.00	17 20
	16	7.70	1.00	33 19
	18	7.53	1.00	21
	20	8.48	1.00	
	24	7.61	1.00	
	27	4.48	1.00	8
	28	4.36	1.00	34 9
	30	1.49	1.00	1 15
	31	1.64	1.00	7 6
	32	1.71	1.00	32
	33	8.48	1.00	31 22 11 24
	34	9.08	1.00	29 13
				30 20 27 5 12
				14
- * 1		10.04	4.00	
<i>E*</i> -b	2	12.34	1.00	18
	12	8.36	1.00	20
	14	1.75	1.00	1/ 19
	10	7.00 7.10	1.00	33
	20	7.12	1.00	21
	20	8.19	1.00	4 2 (16)
	24	/.59	1.00	10 0
	2/	4.51	1.00	8 15
	20	4.22	1.00	84
	3U 21	1.44 1 FF	1.00	7 3 23 24
	31 22	1.55	1.00	6
	2∠ 22	1.05 7 Q	1.00	
	55 24	0.21 0 07	1.00	32 31 22 11 3
	54	0.02	1.00	29 14
				27 28
L				~

- *				
<i>E*-</i> C	11	7.84	1.00	17 19
	13	7.60	1.00	
	15	7.65	1.00	16 18
	17	7.04	1.00	
	19	8.07	1.00	32 20 3 34 13
	23	7.65	1.00	11 12
	26	5.14	1.00	10 23
	27	3.95	1.00	9 7 22
	29	1.21	1.00	33 2 5
	30	1.43	1.00	6 14
	31	1.67	1.00	8 15
	32	8.17	1.00	21
	33	8.52	1.00	24
	34	12.08	1.00	
				2825
				27
				29 26
E*	11	8.31	1.00	19
E*	11 13	8.31 7.68	1.00 1.00	19
E*	11 13 15	8.31 7.68 7.67	1.00 1.00 1.00	19 17 18
E*	11 13 15 17	8.31 7.68 7.67 7.72	1.00 1.00 1.00 1.00	19 17 16 18 13
E*	11 13 15 17 19	8.31 7.68 7.67 7.72 9.11	1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23	8.31 7.68 7.67 7.72 9.11 7.46	1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26	8.31 7.68 7.67 7.72 9.11 7.46 5.04	1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$	
E*	11 13 15 17 19 23 26 27 29 30	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$	
E*	11 13 15 17 19 23 26 27 29 30 31	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48 1.78	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$	$\begin{array}{c} 19 \\ 17 \\ 16 \\ 18 \\ 32 \\ 20 \\ 9 \\ 7 \\ 6 \\ 2 \\ 1 \\ 34 \\ 15 \\ 10 \\ 12 \\ 22 \\ 23 \\ 14 \\ 15 \\ 15 \\ 14 \\ 15 \\ 15 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 15 \\ 10 \\ 10$
E*	11 13 15 17 19 23 26 27 29 30 31 32	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48 1.78 8.24	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48 1.78 8.24 8.02	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$	17 19 13 13 13 12 22 23 9 7 6 2 5 14 15 21 34 0 0
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48 1.78 8.24 8.02 13.34	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ \end{array}$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48 1.78 8.24 8.02 13.34	$\begin{array}{c} 1.00\\$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.31 7.68 7.67 7.72 9.11 7.46 5.04 3.95 1.26 1.48 1.78 8.24 8.02 13.34	$\begin{array}{c} 1.00\\$	$ \begin{array}{c} 17 \\ 16 \\ 18 \\ 32 \\ 20 \\ 9 \\ 7 \\ 6 \\ 21 \\ 34 \\ 0 \end{array} $ $ \begin{array}{c} 13 \\ 10 \\ 12 \\ 22 \\ 34 \\ 0 \end{array} $

 Table S5. The isomer shifts of ¹H NMR relative to TMS together with atom numbering scheme, calculated with CAM-B3LYP/PCSSEG-2/C-PCM(CHCl₃), for 2-Cl.

Ζ	Atom	shift[p	pm]	30
	rel.int	ensity		31
	2	15.81	1.00	83 82
	12	8.46	1.00	28 26 14
	14	7.83	1.00	12 13
	16	7.94	1.00	
	18	7.79	1.00	
	20	9.21	1.00	
	24	7.46	1.00	
	27	4.38	1.00	
	28	4.31	1.00	34 8 2
	30	1.48	1.00	
	31	1.72	1.00	
	32	1.65	1.00	33 21 10
	33	8.40	1.00	17 19 00
	34	8.71	1.00	
				18
Z-a	2	20.48	1.00	18
	12	8.59	1.00	17
	14	7.80	1.00	33 (19)
	16	8.00	1.00	
	18	7.61	1.00	
	20	8.56	1.00	
	24	7.58	1.00	
	27	4.32	1.00	
	28	4.29	1.00	6 15
	30	1.45	1.00	22
	31	1.65	1.00	11 23
	32	1.66	1.00	12 13 24
	33 24	8.57	1.00	27 28
	54	9.83	1.00	6
				29 31
				60

<i>F-</i> h	2	12 61	1 00	18 00	
2.0	12	7 20	1.00		
	1/	7.05	1.00	17 19	
	14	7.01	1.00		
	10	7.94	1.00	33 21 4 2 16	
	18	7.21	1.00		
	20	8.13	1.00	10 8 9 23	
	24	7.56	1.00		
	27	4.26	1.00	6 13	
	28	4.24	1.00		
	30	1.34	1.00		
	31	1.49	1.00	<u>6</u> 22 12	
	32	1.60	1.00		
	33	8.37	1.00	<u> </u>	
	34	9.60	1.00	28 (26)	
	0.	5.00	2.00	27 31	
				29 32	
				30	
E-C	11	7 74	2.00	10	
20	15	7.06	1.00	47 (13	
	17	7.50	1.00	18 23	
	10	7.17	1.00	16 12 22	
	19	8.15	1.00	3 34 11 10	
	23	7.60	1.00	20 14	
	26	5.13	1.00	32 20 7 5 1	5
	27	3.96	1.00	9 2 8	
	29	1.13	1.00	6 1	
	30	1.53	1.00	83	
	31	1.63	1.00	0	
	32	8.31	1.00		
	33	9.18	1.00		
	34	12.43	1.00		
				26 25 27	
				31 28 30	
				29	
Ε	11	8.34	1.00	13	
	13	7.83	1.00	19	
	15	7.92	1.00	12 23	
	17	7.72	1.00	17 18 10 22	
	19	9.11	1.00	16 3	
	22	7 44	1.00		
	26	5 20	1 00	e20 7 2 5 15	
	20	1 20	1.00		
	21	1)7	1.00	33	
	29	1.2/	1.00	34	
	30	1.50	1.00	21	
	31	1.63	1.00	4	
	32	8.23	1.00		
	33	7.99	1.00	25 67	
	34	11.92	1.00	26 30	
				28	
				1	
				29	

Z*	2	15.18	1.00	18
	12	8.44	1.00	20
	14	7.82	1.00	17
	16	7.92	1.00	19
	18	7.79	1.00	33 21
	20	9.22	1.00	
	24	7.42	1.00	
	27	4.47	1.00	
	28	4.31	1.00	34
	30	1.38	1.00	
	31	1.40	1.00	7 15
	32	1.52	1.00	
	33	8.39	1.00	25 22
	34	8.19	1.00	31.9 11 24
				26 5 12 13
				28 14
<i>Z*</i> -a	2	20.88	1.00	18
	12	8.68	1.00	
	14	7.81	1.00	17 20
	16	7.99	1.00	33 19
	18	7.56	1.00	21
	20	8.58	1.00	
	24	7.57	1.00	
	27	4.49	1.00	34 8
	28	4.36	1.00	16
	30	1.49	1.00	
	31	1.63	1.00	6 15
	32	1.72	1.00	81 J 63
	33	8.50	1.00	29 22 23
	34	9.07	1.00	30 2627 11 24
				28
C* b	2	10.70	1.00	
Е*-D	2	12.76	1.00	18
	14	7.95	1.00	20
	14	7.82	1.00	17 19
	10	7.95	1.00	33
	20	7.10	1.00	21
	20	0.14	1.00	4 2
	24	1.37	1.00	10 16
	27	4.29	1.00	8
	20	4.23 1 17	1.00	34 9 15
	21	1.47	1.00	7 3 22 24
	22	1 67	1.00	6
	22	2.04 2.21	1.00	81 25 27 1
	33	9.34 9.7	1.00	32 00 11 13
		5.07	1.00	26
				30 12
				27
L	1			

-			
<i>E*</i> -c	11	7.70 1.00	17 19
	13	7.72 1.00	
	15	7.93 1.00	16 18
	17	7.05 1.00	13
	19	8.07 1.00	3 34
	23	7.60 1.00	32 20 11 12 23
	26	5.15 1.00	10 22
	27	3.96 1.00	9 0
	29	1.22 1.00	6 2 5 14
	30	1.43 1.00	
	31	1.68 1.00	
	32	8.19 1.00	21
	33	8.53 1.00	
	34	12.10 1.00	30 31
			28 25
			27
			29 20
E*	11	8.35 1.00	19
E*	11 13	8.35 1.00 7.79 1.00	19 13
E*	11 13 15	8.35 1.00 7.79 1.00 7.92 1.00	19 17 18 18
E*	11 13 15 17	8.351.007.791.007.921.007.731.00	17 16 18 11 12 73
E*	11 13 15 17 19	8.351.007.791.007.921.007.731.009.111.00	17 16 18 3 11 10 22 23
E*	11 13 15 17 19 23	8.351.007.791.007.921.007.731.009.111.007.451.00	19 17 16 18 3 11 10 22 32 20 7
E*	11 13 15 17 19 23 26	8.351.007.791.007.921.007.731.009.111.007.451.005.051.00	17 16 18 3 11 12 23 32 9 7 2 5 10 22 3 10 22 3 10 10 10 10 10 10 10 10 10 10
E*	11 13 15 17 19 23 26 27	8.35 1.00 7.79 1.00 7.92 1.00 7.73 1.00 9.11 1.00 7.45 1.00 5.05 1.00 3.97 1.00	$\begin{array}{c} 19 \\ 17 \\ 16 \\ 3 \\ 32 \\ 20 \\ 9 \\ 7 \\ 6 \\ 1 \\ 10 \\ 22 \\ 33 \\ 22 \\ 9 \\ 7 \\ 6 \\ 1 \\ 10 \\ 22 \\ 33 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14 \\ 14$
E*	11 13 15 17 19 23 26 27 29	8.35 1.00 7.79 1.00 7.92 1.00 7.73 1.00 9.11 1.00 7.45 1.00 5.05 1.00 3.97 1.00 1.27 1.00	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
E*	11 13 15 17 19 23 26 27 29 30	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{c} 19 \\ 17 \\ 16 \\ 33 \\ 32 \\ 9 \\ 33 \\ 6 \\ 1 \\ 34 \\ 15 \\ 34 \\ 15 \\ 14 \\ 15 \\ 15 \\ 14 \\ 15 \\ 15 \\ 1$
E*	11 13 15 17 19 23 26 27 29 30 31	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
E*	11 13 15 17 19 23 26 27 29 30 31 32 22	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c} 19 \\ 17 \\ 16 \\ 18 \\ 3 \\ 11 \\ $
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 24	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	

Ζ	Atom	shift[p	pm]	18
	rel.in	tensity		
	2	15.85	1.00	· 17
	12	8.49	1.00	21 19 20
	14	7.88	1.00	
	16	8.01	1.00	
	18	7.79	1.00	34 8
	20	9.23	1.00	
	24	7.44	1.00	
	27	4.39	1.00	
	28	4.31	1.00	
	30	1.48	1.00	15
	31	1.72	1.00	27 00
	32	1.65	1.00	20 12 23
	33	8.40	1.00	13 24
	34	8.71	1.00	29 31
				30 22 14
<i>Z</i> -a	2	20.29	1.00	18
	12	8.62	1.00	33 47
	14	7.84	1.00	21
	16	8.08	1.00	19 20
	18	7.62	1.00	10
	20	8.61	1.00	34 4
	24	7.56	1.00	8 2
	27	4.32	1.00	T P
	28	4.29	1.00	
	30	1.46	1.00	
	31	1.65	1.00	6 9 46
	32	1.67	1.00	
	33	8.58	1.00	27 26 11
	34	9.84	1.00	12 23
				13 24
				30 32 At
				U

Table S6. The isomer shifts of ¹H NMR relative to TMS together with atom numbering scheme, calculated with CAM-B3LYP/PCSSEG-2/C-PCM(CHCl₃), for **2-Br**.

<i>E-</i> b	2	12.62	1.00	18
	12	7.86	1.00	20
	14	7.85	1.00	17 19
	16	8.02	1.00	
	18	7.21	1.00	······································
	20	8.13	1.00	
	24	7.56	1.00	
	27	4.26	1.00	34 9 3
	28	4.25	1.00	7 3 23
	30	1.33	1.00	
	31	1.48	1.00	6 22 11 13
	32	1.59	1.00	14
	33	8.37	1.00	12
	34	9.59	1.00	28 26
				27 01
				29 32
				80
E-c	11	7.77	1.00	19 13
	13	7.79	1.00	
	15	8.07	1.00	17 18 22
	17	7.18	1.00	16 34 11 10
	19	8.16	1.00	3 14 15
	23	7.58	1.00	5 8
	26	5.13	1.00	20 7 2
	27	3.97	1.00	9 6
	29	1.13	1.00	
	30	1.58	1.00	33
	31	1.62	1.00	21 21
	32	8.31	1.00	
	33	9.18	1.00	25. 27
	34	12.44	1.00	26 30
				31 28
E	11	8.37	1.00	13
	13	7.87	1.00	12 23
	15	7.98	1.00	19 11 22
	1/	1.12	1.00	10
	19	9.11	1.00	14 16 14
	23	7.42	1.00	6 6
	26	5.31	1.00	20 7 2 0
	27	4.40	1.00	9 6
	29	1.27	1.00	33 34
	30	1.54	1.00	
	31	1.63	1.00	
	32	8.24	1.00	
	33	8.00	1.00	25 27
	34	11.97	1.00	26 30
				31 20
				29

7*	2	15 22	1.00	60
2	12	13.23	1.00	
	12	0.40	1.00	17 20
	14	7.87	1.00	23 40
	16	7.98	1.00	21
	18	7.80	1.00	Ť
	20	9.24	1.00	
	24	7.40	1.00	
	27	4.48	1.00	34 8
	28	4.32	1.00	e e
	30	1.39	1.00	
	31	1.41	1.00	
	32	1 5 3	1 00	
	22	8 30	1.00	30 26
	24	0.35	1.00	5 11 23
	54	8.20	1.00	28 12 24
Z*-a	2	20.64	1.00	18
	12	8.71	1.00	
	14	7.85	1.00	33 17 20
	16	8.06	1.00	21 19
	18	7.56	1.00	T T
	20	8.63	1.00	
	24	7.55	1.00	
	27	4.49	1.00	34 8 2
	28	4 36	1 00	
	20	4.50	1.00	32
	21	1.49	1.00	31 9 16
	31	1.03	1.00	29 3 6 15
	32	1.72	1.00	30 26
	33	8.51	1.00	
	34	9.05	1.00	28 12 23
	_			
<i>E*</i> -b	2	12.81	1.00	18
	12	7.90	1.00	
	14	7.85	1.00	17 20
	16	8.02	1.00	19
	18	7.18	1.00	33 21
	20	8.14	1.00	
	24	7.56	1.00	4
	27	4.27	1.00	10 0
	28	4.26	1.00	8 16
	30	1 47	1 00	
	21	1. ,	1 00	7 9 15
	27	1 6/	1.00	
	22	1.04 0.25	1.00	
	22	0.33	1.00	32 29
	54	9.09	1.00	26 28
				27 12 14

<i>E*</i> -c	11	7.73	1.00	19
	13	7.77	1.00	17
	15	8.04	1.00	18
	17	7.06	1.00	16 12 23
	19	8.07	1.00	3 34 11 40 22
	23	7.57	1.00	20
	26	5.15	1.00	32 14
	27	3.96	1.00	9 2 5 8 15
	29	1.22	1.00	6 1 0
	30	1.44	1.00	33
	31	1.69	1.00	
	32	8.19	1.00	21 0
	33	8.50	1.00	24 4
	34	12.09	1.00	30, 31
				28 25
				27 26
				23
E*	11	8.39	1.00	19 13
E*	11 13	8.39 7.84	1.00 1.00	19
E*	11 13 15	8.39 7.84 7.99	1.00 1.00 1.00	19 17 18 11 12 23
E*	11 13 15 17	8.39 7.84 7.99 7.73	1.00 1.00 1.00 1.00	19 17 18 11 10 22 23
E*	11 13 15 17 19	8.39 7.84 7.99 7.73 9.12	1.00 1.00 1.00 1.00 1.00	19 17 18 10 10 22 10 10 22
E*	11 13 15 17 19 23	8.39 7.84 7.99 7.73 9.12 7.44	1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26	8.39 7.84 7.99 7.73 9.12 7.44 5.05	1.00 1.00 1.00 1.00 1.00 1.00 1.00	19 17 18 3 11 10 22 5 14 15
E*	11 13 15 17 19 23 26 27	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29 30	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29 30 31	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50 1.81	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29 30 31 32	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50 1.81 8.25	$ \begin{array}{c} 1.00\\ 1.00$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50 1.81 8.25 8.02	$ \begin{array}{c} 1.00\\ 1.00$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50 1.81 8.25 8.02 13.50	$\begin{array}{c} 1.00\\$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50 1.81 8.25 8.02 13.50	$ \begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00 \end{array} $	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.39 7.84 7.99 7.73 9.12 7.44 5.05 3.97 1.27 1.50 1.81 8.25 8.02 13.50	$ \begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00 \end{array} $	

			· · · · · · · · · · · · · · · · · · ·	-//
Ζ	Atom	shift[p	pm]	18
	rel.in	tensity		33
	2	15.82	1.00	21 17
	12	8.51	1.00	19 20
	14	7.90	1.00	10
	16	8.09	1.00	84 4
	18	7.80	1.00	8
	20	9.28	1.00	
	24	7.40	1.00	
	27	4.39	1.00	
	28	4.31	1.00	
	30	1.48	1.00	
	31	1.72	1.00	15 10
	32	1.65	1.00	12
	33	8.41	1.00	30 32 31 13 23
	34	8.71	1.00	24
				14
Z-a	2	19.93	1.00	18
	12	8.63	1.00	33
	14	7.87	1.00	21
	16	8.17	1.00	19 20
	18	7.61	1.00	34 10
	20	8.71	1.00	4
	24	7.52	1.00	2
	27	4.31	1.00	
	28	4.29	1.00	
	30	1.46	1.00	
	31	1.66	1.00	6 9
	32	1.67	1.00	27 26 16
	33	8.58	1.00	15 10
	34	9.85	1.00	12
				30 32 13 23
				24
				14

 Table S7. The isomer shifts of ¹H NMR relative to TMS together with atom numbering scheme, calculated with CAM-B3LYP/PCSSEG-2/C-PCM(CHCl₃), for 2-I.

<i>E</i> -b	2	12.47	1.00	18
	12	7.78	1.00	20
	14	7.86	1.00	
	16	8.10	1.00	33
	18	7.21	1.00	21
	20	8.11	1.00	4 2
	24	7.54	1.00	10
	27	4.27	1.00	64 16
	28	4.24	1.00	9 15
	30	1.32	1.00	23 24
	31	1.46	1.00	6 22 1 6
	32	1.57	1.00	11 13
	33	8.36	1.00	
	34	9.55	1.00	28 12 14
				27 31
				29
				30 32
E-c	11	7.78	1.00	13 23
	13	7.82	1.00	19 12 00
	15	8.18	1.00	
	17	7.19	1.00	17 18 11 10 14 17
	19	8.17	1.00	
	23	7.55	1.00	5 6
	26	5.13	1.00	
	27	4.00	1.00	20 7 1
	29	1.12	1.00	
	30	1.70	1.00	
	31	1.63	1.00	⁶³ 21
	32	8.32	1.00	
	33	9.25	1.00	25 27
	34	12.47	1.00	26 30
				31 28
				20
F	11	0 20	1.00	
E	12	0.39 7 00	1.00	23
	15	2 05	1.00	12 02
	17	8.05 7.72	1.00	11
	19	9 1 1	1.00	14
	23	7.39	1.00	17 18
	26	5.32	1.00	16 3 5 8
	27	4.45	1.00	
	29	1.27	1.00	
	30	1.61	1.00	
	31	1.64	1.00	01
	32	8.24	1.00	
	33	7.99	1.00	
	34	11.86	1.00	25 27 30
				²⁶ 31 28
				-]
				29
Z*	2	15.15	1.00	18
--------------	----	-------	------	------------------
	12	8.50	1.00	
	14	7.88	1.00	17 20
	16	8.07	1.00	21 19
	18	7.80	1.00	Ť
	20	9.29	1.00	40 4
	24	7.37	1.00	34 9 0
	27	4.48	1.00	
	28	4.31	1.00	
	30	1.38	1.00	
	31	1.41	1.00	30 22 3 9 16
	32	1.52	1.00	26 6 15
	33	8.39	1.00	6
	34	8.20	1.00	20 II 03
				12 13 04
				14
Z*-a	2	20.17	1.00	18
	12	8.71	1.00	
	14	7.87	1.00	33 17 20
	16	8.15	1.00	21 19
	18	7.55	1.00	
	20	8.73	1.00	10 4
	24	7.51	1.00	34 8 2 0
	27	4.50	1.00	
	28	4.35	1.00	31 22
	30	1.48	1.00	29 29 10 1
	31	1.62	1.00	30 26 22 3 6 9
	32	1.71	1.00	27 15
	33	8.50	1.00	28 6
	34	9.04	1.00	12 11 23
				13 24
- * 1		40.5-	4.00	
<i>L*</i> -b	2	12.35	1.00	18
	12	7.76	1.00	20
	14	7.84	1.00	07
	16	8.09	1.00	³³ 21
	18	7.10	1.00	
	20	8.06	1.00	
	24	7.52	1.00	
	27	4.25	1.00	34 8
	28	4.32	1.00	6
	30	1.44	1.00	7 3 9 15
	31	1.63	1.00	
	32	1.55	1.00	
	33	8.26	1.00	
	34	8.76	1.00	27 11 13
				12 14
L				• • •

<i>E*</i> -c	11	7.68	1.00	19
	13	7.79	1.00	13
	15	8.14	1.00	17 18 12 23
	17	7.06	1.00	16 24 11 22
	19	8.07	1.00	3
	23	7.54	1.00	14 15
	26	5.16	1.00	20 5 8
	27	3.96	1.00	
	29	1.22	1.00	6
	30	1.43	1.00	83
	31	1.69	1.00	
	32	8.20	1.00	
	33	8.53	1.00	24
	34	12.08	1.00	31
				28 25
				26
				2
E*	11	8.40	1.00	19 13
E*	11 13	8.40 7.86	1.00 1.00	19 13 23
E*	11 13 15	8.40 7.86 8.07	1.00 1.00 1.00	
E*	11 13 15 17	8.40 7.86 8.07 7.73	1.00 1.00 1.00 1.00	
E*	11 13 15 17 19	8.40 7.86 8.07 7.73 9.12	1.00 1.00 1.00 1.00 1.00	19 17 16 3 11 10 22 23 14 15
E*	11 13 15 17 19 23	8.40 7.86 8.07 7.73 9.12 7.40	1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26	8.40 7.86 8.07 7.73 9.12 7.40 5.06	1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	17 18 3 11 10 22 3 4 11 10 22 18 3 11 10 22 23 14 15 8 15 8 15 15 15 15 15 15 15 15 15 15
E*	11 13 15 17 19 23 26 27 29	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	17 16 3 11 10 22 23 17 16 3 11 10 22 23 20 9 6 2 1 6 4 15 20 9 6 33 21 0
E*	11 13 15 17 19 23 26 27 29 30	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$
E*	11 13 15 17 19 23 26 27 29 30 31	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50 1.82	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	$\begin{array}{c} 19 \\ 17 \\ 16 \\ 20 \\ 9 \\ 32 \\ 9 \\ 33 \\ 24 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ 4 \\ $
E*	11 13 15 17 19 23 26 27 29 30 31 32	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50 1.82 8.25	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50 1.82 8.25 8.02	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50 1.82 8.25 8.02 13.38	1.00 1.00 1.00 1.00 1.00 1.00 1.00 1.00	$ \begin{array}{c} $
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50 1.82 8.25 8.02 13.38	$\begin{array}{c} 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00\\ 1.00 \end{array}$	
E*	11 13 15 17 19 23 26 27 29 30 31 32 33 34	8.40 7.86 8.07 7.73 9.12 7.40 5.06 3.97 1.27 1.50 1.82 8.25 8.02 13.38	1.00 1.00	



Figure S55. The graphically marked fragments of 2-Cl-Z (left) and 2-Cl-E* (right) used for ICFT analysis of TD-DFT spectra.



Figure S56. Depiction of the Laplacian of calculated electron density $\nabla^2 \rho(\mathbf{r})$ for the optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches in the *Z*-configuration. The (3, -1) bond critical points (brown dots) and bond paths (black solid and dashed lines) are depicted.



Figure S57. Depiction of the Laplacian of calculated electron density $\nabla^2 \rho(\mathbf{r})$ for the optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches in the *E*-configuration. The (3, -1) bond critical points (brown dots) and bond paths (black solid and dashed lines) are depicted.



Figure S58. Gradient isosurfaces (s = 0.42 au) for the optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches in the *Z*-configuration. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)r, ranging from -0.04 to 0.04 au. Blue indicates strong attractive interactions, and red indicates strong nonbonded overlap.



Figure S59. Gradient isosurfaces (s = 0.42 au) for the optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches in the *E*-configuration. The surfaces are colored on a blue-green-red scale according to values of sign(λ_2)r, ranging from -0.04 to 0.04 au. Blue indicates strong attractive interactions, and red indicates strong nonbonded overlap.

Table S8. Topological and energetic properties of $\rho(\mathbf{r})$ calculated at the selected (3, -1) critical points optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches in the Z-configuration. All values are provided in atomic units (a. u.) unless stated otherwise.

	$ abla^2 ho(\mathbf{r})$	<i>h</i> _e (<i>r</i>)	G(r)	<i>V</i> (r)	<i>V</i> (r) / <i>G</i> (r)	3	E _{int} /kcal.mol ⁻¹
2-F N-H…N	0.12198	-0.000819	0.0313	-0.03213	1.03	0.005	10.1
N-H···F	_	_	_	_	_	_	_
2-CI N-H···N	0.12356	-0.000891	0.031779	-0.032669	1.03	0.00603	10.3
N–H…Cl	0.06519	0.00199	0.01431	-0.01231	0.86	1.1195	3.9
2-Br N−H…N	0.123537	-0.000899	0.03177	-0.032662	1.03	0.00671	10.2
N–H…Br	0.05507	0.001252	0.012515	-0.01126	0.90	0.6856	3.5
2-I N–H…N	0.12335	-0.000852	0.03169	-0.03254	1.03	0.008143	10.2
N–H…I	0.04736	0.000937	0.0109025	-0.009966	0.91	0.529034	3.1

Table S9. Topological and energetic properties of $\rho(\mathbf{r})$ calculated at the selected (3, -1) critical points optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches in the *E*-configuration. All values are provided in atomic units (a. u.) unless stated otherwise.

	$ abla^2 ho(\mathbf{r})$	<i>h</i> _e (<i>r</i>)	G(r)	<i>V</i> (r)	<i>V</i> (r) / <i>G</i> (r)	3	E _{int} /kcal.mol ⁻¹
2-F N−H…O	0.12360	+0.00078	0.03012	-0.02934	0.97	0.0166	9.2
N-H…F	_	_	_	_	_	_	_
2-CI N−H…O	0.12538	+0.00076	0.03058	-0.02982	0.98	0.01979	9.4
N–H…Cl	0.06427	+0.00185	0.01422	-0.01237	0.87	0.8039	3.9
2-Br N−H…O	0.12498	+0.00079	0.03046	-0.02967	0.97	0.02222	9.3
N–H…Br	0.05464	+0.00112	0.01254	-0.01143	0.91	0.5115	3.6
2-I N–H…O	0.12448	+0.00086	0.03026	-0.02940	0.97	0.02512	9.2
N-H···I	0.04691	+0.00081	0.01092	-0.01012	0.93	0.39755	3.2

Table S10. The values of sign $(\lambda_2)\rho$ calculated at (3, -1) critical points of the N–H…X for optimized geometries (implicit solvation model C-PCM) of studied hydrazone switches.

	Cl	Br	I
Z-configuration	+0.026878	+0.023961	-0.022858
E- configuration	+0.026700	-0.024296	-0.02323