Synthesis of New Spiropyrans With a Polyaromatic or Heteroaromatic Pendant and Their Photochromic Behaviors

PANG, Mei-Li(庞美丽)   **NIE, Yun-Tong**(聂云橦)   **WANG, Yong-Mei**(王永梅)
MENG, Ji-Ben*(孟继本)   **WANG, Ji-Tao**(王积涛)
Department of Chemistry, Nankai University, Tianjin 300071, China

A series of spiropyrans with a polyaromatic or heteroaromatic pendant was synthesized conveniently. Their photochromic behaviors were investigated with the aid of absorption spectral measurements. The results indicated that the compounds with the same parent spiropyran but different aromatic pendant show significantly different photochromic properties. This may be due to the π-π orbital interaction between the polyaromatic pendant and the open photomerocyanine form of spiropyran. The results obtained are very useful in the molecule design area.

Keywords   spiropyran, photochromism, UV-absorption spectrum

Introduction

Discovery of the photochromic reactions of spiropyrans by Fischer and Hirshberg[1] in 1952 and Hirshberg's idea of using the phenomenon for a "photochemical erasable memory"[2] initiated active research on photochromism. Numerous other applications based on reversible color and other changes in physical and chemical properties were suggested and examined for photochromic spiropyrans: self-developing photography, actinometry, displays, filters, and lenses of variable optical density, including eye-protective glasses, etc.[3] Typical cause of the photochromic reactions of spiropyrans is the reversible photochemical cleavage and closure of the C—O bond in the spiropyran ring (Scheme 1).

Merocyanines have a characteristic absorption band in the visible wavelength region due to the extended con-

Scheme 1

SP

PMC
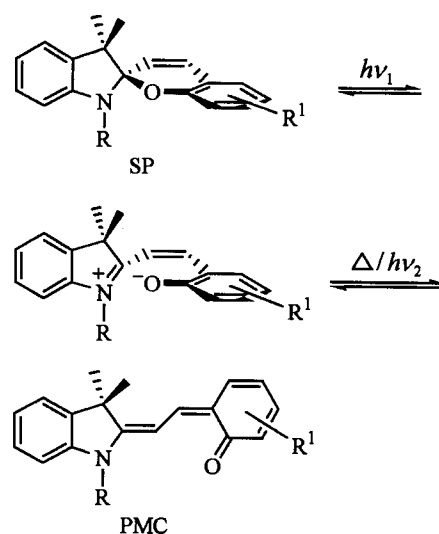
jugation of the π-electron system as compared to that of the spiro form with an orthogonal geometry. Thus, the profound change of light-induced absorption makes it easy to analyze the primary photochromic processes by ultra-violet spectroscopy. As we know, the photochromic behaviors of spiropyrans are affected by their structures and the media. Different substituents and different media might change the microenviroment of the spiropyrans, thus, affect their photochromic behaviors, such as the rate of color change, the λ_{max} of the colored form, the aggregation of the compounds, especially the stability of the open form.[4] We are interested to see how different molecular size of the aromatic groups linked as a pendant to a

spiropyran through a number of σ bonds could affect its photochromic behavior.

With this in mind, we report here the synthesis of a series of new spiropyrans bearing a polyaromatic or heteroaromatic residues and their photochromic behavior in solution with the aid of UV-absorption spectroscopy.

Result and discussion

Synthesis

The following method was used to obtain our title compounds. In the first step, various 3-arylacyl propionic acids (4a—4k) were synthesized through the succinoyla-

tion of the corresponding aromatic hydrocarbons. Second, the condensation of 1-(2-hydroxyethyl)-2,3,3-trimethyl-indoleninium iodide (2) with 5-nitrosalicylaldehyde gave 3 containing a hydroxy group (Scheme 2). Finally, considering the fragile structure of the spiropyran substituted alcohol, the linking reaction should be performed in mild condition. We chose the methodology of synthesizing peptide, using dicyclohexylcarbodiimide (DCC) as the condensation reagent of the acid and the alcohol to obtain 5a—5k (Scheme 3). Using this method, a series of new spiropyrans (5a—5k) containing an aromatic or heteroaromatic pendant were synthesized with 53%—97% isolated yield, providing an effective method for preparing the spiro-photochromic compounds containing various pendants.

Scheme 2
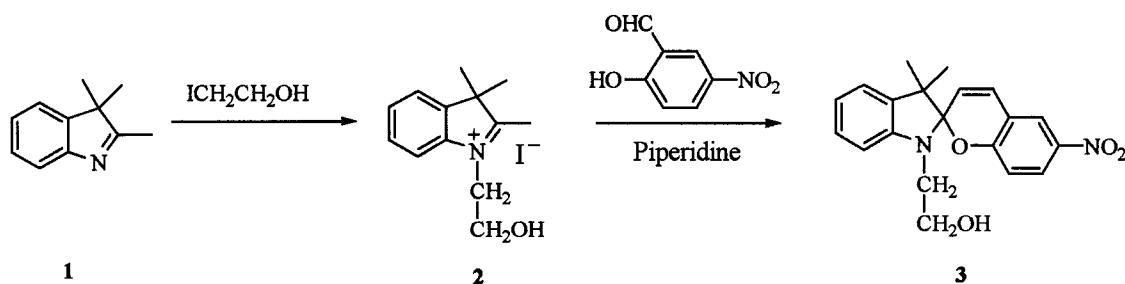
Scheme 3
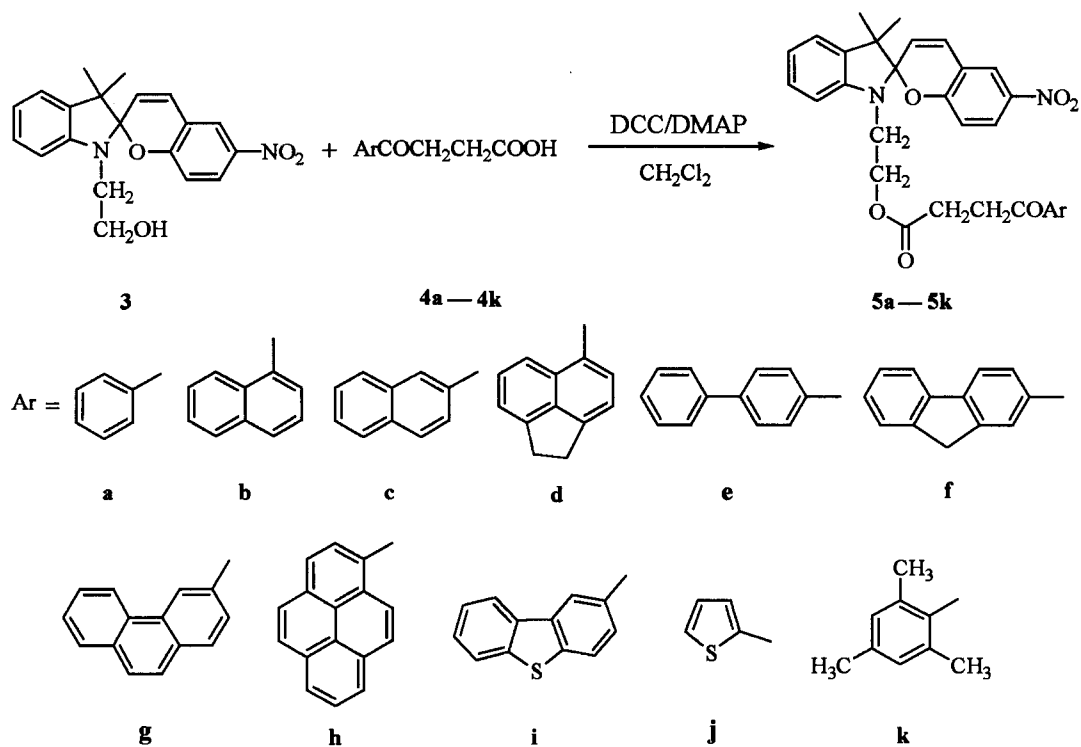
Photochromism

The photochromism behaviors of the compounds were investigated with the aid of absorption spectral measurements, giving several features on the photochromism of these spiropyran derivatives. Table 1 shows the UV spectral data for these spiropyrans **5a—5k** presumably in the closed spiro form in various solvents. The absorption maxima of the open colored form (PMC form of Scheme 1) of the irradiation of **5a—5k** in various solvents with sunlight are listed in Table 2. It was observed that the solvent polarity effect on the absorption maximum position depends on the types of aromatic groups. The opening isomers so far synthesized have absorption maxima ranging of 540—608 nm.

A semi-quantitative study on the decoloration process of the open colored form of the spiropyran derivatives was carried out in various solvent. Typical examples are given in Figs. 1 and 2, which illustrate the change of absorption spectra for the decoloration process in the dark of the open form of spiropyrans **5i** and **5h** respectively, taken at 5.0×10^{-4} mol/L concentration in cyclohexane.

As we compare the different absorption of compounds **5i** and **5h** in Figs. 1 and 2 respectively, it can be seen that the λ_{max} shifts hypsochromically for about 20 nm during the decoloration process. We presume that the less extent of open dipolar form (PMC) takes less energy dissipation due to the collision of the open form, because the ionic interaction should be stronger than that of the closed form. Thus, the less energy dissipation resulted in higher emission energy, thus bringing the λ_{max} shifted hypsochromically.

In order to compare the decoloration rate of compounds **5i** and **5h**, the absorption value at λ_{max} was chosen to make a curve vs. time shown at Fig. 3, showing

Table 1   Absorption maximum (λ_{max}) data of the spiro-photochromic compounds in closed spiro form in various solvents

Compd	Solvent ($E_{value}{}^a$)				
	Methanol (55.5)	Acetonitrile (37.5)	Acetone (20.7)	Chloroform (–)	Cyclohexane (2.02)
5a	248.8, 284, 2, 342	300, 322, 356.8	340	281.6, 342	236, 263.2, 322.4
5b	220.8, 266, 295.2	295.6	335.2	248, 260, 299.2	217.6, 260.8, 299.2
5c	244, 268, 334	292.8, 328, 341.6	339.2	253.6, 270.4, 340.4	242.4, 263.2, 324.8
5d	243.2, 330.4	328, 338	341.6	256, 337.6	236, 324.8
5e	220.8, 243.2, 272.8	295.2, 338	336.8	284.8, 340	223.2, 268.8
5f	204.8, 312	301.6	332.8	288.8	220, 264.8, 315.6
5g	249.6, 304	291.2, 304	327.2	264.0, 311.2	251.2, 257.6, 303.2
5h	239.2, 274, 349.6	287.6, 349.2	354	276, 328, 355.2	340, 272, 344
5i	240, 264, 304	288	328	283.2	240, 264.8, 289.6
5j	243.6, 268, 334.4	292, 339.2	340.4	284.8, 327.6, 344.8	245.6, 256.8, 320.8
5k	267.2, 327.6, 346.4	292, 339.6	336.4	268, 344	232.8, 265.6, 321.2

[a] Dimroth's solvent polarity parameter E, was taken from Murov, S. L. Handbook of Photochemistry, Dekker, M. New York, 1973.

Table 2   Absorption maximum (λ_{max}) data of the photochromic compounds in various solvents after sunlight irradiation

Compd	Solvent ($E_{value}{}^a$)				
	Methanol (55.5)	Acetonitrile (37.5)	Acetone (20.7)	Chloroform (–)	Cyclohexane (2.02)
5a	540	566	574	586	596
5b	540	568	576	588	603.2
5c	540	568	574.4	588	588
5d	540	568	572	588	600
5e	540	564	568	578	598
5f	538.4	567.2	573.6	590	576.8
5g	540.8	567.2	572	588	580
5h	540.8	568.8	575.2	588.8	593.6
5i	540	568	573.8	586	607.2
5j	539.6	568.4	574.6	591.2	580
5k	540	568.8	575.2	590	599.2

[a] Dimroth's solvent polarity parameter E, was taken from Murov, S. L. Handbook of Photochemistry, Dekker, M. New York, 1973.

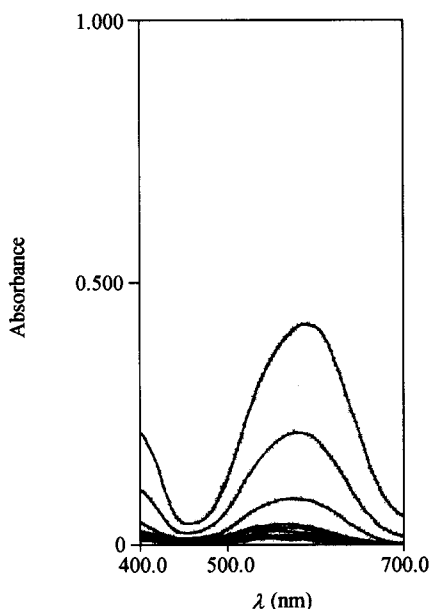that the decoloration rate of **5i** was evidently faster than that of **5h**.

Fig. 1 Spectral change for the decoloration process of compound **5i** in cyclohexane solution ($c = 5.0 \times 10^{-4}$ mol/L) in the dark after irradiation with sunlight sufficiently. Time interval of measurement, 1.25 min (from top to bottom).

Fig. 2 Spectral change for the decoloration process of compound **5h** in cyclohexane solution ($c = 5.0 \times 10^{-4}$ mol/L) in the dark after irradiation with sunlight sufficiently. Time interval of measurement, 1.25 min (from top to bottom).
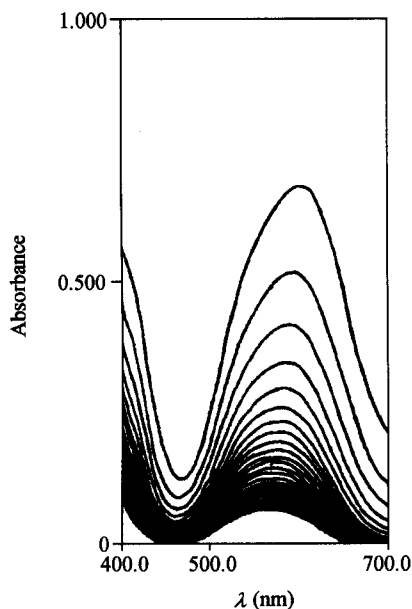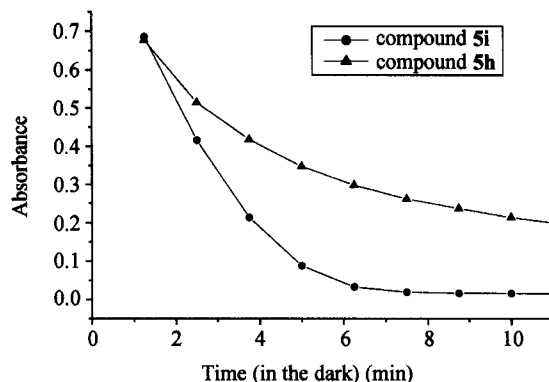

Fig. 3 Absorbance value vs. time for the decoloration process of compounds **5i** and **5h**.

For the other spiropyran derivatives, we observed that the decoloration rate is also quite different due to different aromatic pendant. In the polar solvent, $e.g.$ CH_3OH, with the increasing size of the conjugated ring, the decoloration rate of the compound was dramatically increasing; while in nonpolar solvent, the order is reversed. During the experiment, it was observed that **5a**, **5j** and **5k** possess the similar photochromic properties. Similarly, **5b**, **5c**, **5d**, **5e** and **5f** are analogical, so do **5g** and **5i**. This implies that there must exist some interaction between the PMC form and the aromatic part. It is presumed that in the nonpolar solvent, the flexibility of the long carbon chain provide sterial possibility for the aromatic pendant to approach the conjugated merocyanine part, thus, giving a π-π overlapping interaction with the open form of spiropyran. More extent overlapping should provide an additional stabilization effect on the merocyanine form, thus increasing the activated energy of the decoloration reaction, and then, decreasing the decoloration rate of the open form of merocyanine. In the polar solvent, maybe the solvent stabilization effect gives a major influence. When the pendant size is bulky, the hydrophobility of compounds becomes large, thus decreasing the polarity of the open dipolar ion form of spiropyran. According to the solution theory, the polar compound should be more stable in polar solvent, so the increment of pendant size should make compound less stable in polar solvent, thus bringing the observed result.

Experimental

All melting points were uncorrected. The spectral and microanalytical data were recorded with the following instruments: IR spectra, a Bio-Rad FTS135 spectrophotometer (with KBr pellets); ^{1}H NMR spectra, a Bruker AC-P200 spectrometer; UV spectra, a Shimadzu UV-

160A UV-vis spectrophotometer; mass spectra, a 7070E-HE spectrometer, and elemental analysis, a YANACO CHN CORDER MT-3 analyzer.

Compounds **4a—4k** were prepared according to the reported methods using corresponding aromatic hydrocarbon and succinic anhydride as the starting materials.[5-13] Compound **3** was prepared according to the reported methods with the condensation of 1-(2-hydroxyeuhyl)-2,3,3-trimethylindoleninium iodide (**2**) and 5-nitrosalicylaldehyde.[14,15] The compounds were confirmed by the melting point and IR spectral data.

General procedure of synthesis of compounds **5a—5k**

A mixture solution of 0.176 g (0.5 mmol) of compounds **3**, 0.5 mmol of compounds **4a—4k**, 6 mg (0.05 mmol) DMAP and 0.122 g (0.6 mmol) of DCC in 10 mL of dry dichloromethane was stirred in the dark at r.t. for 24 h. The solid was removed by filtration. The solution was successively washed by a saturated aqueous Na_2CO_3 solution and water to remove the unreacted acid, dried with anhydrous Na_2SO_4. After removing the solvent, the residue was submitted to silica gel chromatography using ethylacetate and petroleum ($V/V = 1/3$) as the eluent. Crystallines **5a—5k** were obtained. The structure assigned to products **5a—5k** are based on elemental analyses, ^{1}H NMR, IR and MS spectra (Tables 3 and 4).

Determination of the photochromism of the synthesized compounds

The solutions of spiropyrans in different solvents (methanol, acetonitrile, acetone, chloroform and cyclohexane) with the concentration of 1×10^{-5}—1×10^{-4} mol/L were prepared respectively. The UV spectrum of each solution before and after irradiation with sunlight was recorded on a Schimadzu UV-160A UV-vis spectrophotometer, and the λ_{max} of the compounds were listed in Tables 3 and 4 respectively.

Table 3 Physical properties and elemental analyses of compounds **5a—5k**

Compd	Yield (%)	M.p. (℃)	Molecular formula	Crystal	Elemental analyses cacld (found, %)		
					C	H	N
5a	76.6	98—99	$C_{30}H_{28}O_6N_2$	yellow crystal	70.30 (70.29)	5.51 (5.49)	5.49 (5.48)
5b	64.8	103—104	$C_{34}H_{30}O_6N_2$	light yellow crystal	72.58 (72.62)	5.38 (5.41)	4.98 (4.93)
5c	61.2	155—156	$C_{34}H_{30}O_6N_2$	light yellow crystal	72.58 (72.56)	5.38 (5.38)	4.98 (4.95)
5d	65.3	86—87	$C_{36}H_{32}O_6N_2$	light yellow crystal	73.45 (73.41)	5.48 (5.49)	4.76 (4.75)
5e	94.6	154—155	$C_{36}H_{32}O_6N_2$	light green crystal	73.45 (73.42)	5.48 (5.49)	4.76 (4.73)
5f	90.7	162—163	$C_{37}H_{32}O_6N_2$	light yellow crystal	73.98 (73.92)	5.37 (5.40)	4.66 (4.63)
5g	53.6	159—160	$C_{38}H_{32}O_6N_2$	pale red crystal	74.49 (74.43)	5.27 (5.29)	4.57 (4.55)
5h	62.9	172—173	$C_{40}H_{32}O_6N_2$	light yellow crystal	75.45 (75.43)	5.07 (5.06)	4.40 (4.41)
5i	97.1	185—186	$C_{36}H_{30}O_6N_2$	slight yellow crystal	69.88 (69.86)	4.89 (4.85)	4.53 (4.52)
5j	76.4	100—101	$C_{28}H_{26}O_6N_2$	slight yellow crystal	64.85 (64.83)	5.05 (5.09)	5.40 (5.39)
5k	97.5	90—91	$C_{33}H_{34}O_6N_2$	light green crystal	71.46 (71.40)	6.18 (6.20)	5.05 (5.06)

Table 4 IR, mass and ^{1}H NMR spectral data of compounds **5a—5k**

Compd	IR (KBr) ν (cm^{-1})	MS m/z (%)	^{1}H NMR
5a	1736, 1512, 1480, 1338, 1274, 1172, 1092, 956	512 (M$^+$, 10), 335 (31), 307 (13), 158 (70), 130 (11), 105 (100), 91 (8), 77 (65)	1.20 (s, 3H, CH$_3$), 1.27 (s, 3H, CH$_3$), 2.70 (t, 2H, CH$_2$), 3.24 (t, 2H, CH$_2$), 3.42—3.54 (m, 2H, CH$_2$), 4.24 (t, $J = 6.4$ Hz, 2H, CH$_2$), 5.91 (d, $J = 9.6$ Hz, 1H), 6.68—8.00 (m, 13H, ArH)
5b	1736, 1512, 1480, 1336, 1274, 1172, 1092, 956	562 (M$^+$, 3), 351 (4), 335 (34), 211 (15), 158 (84), 127 (100), 115 (10), 99 (14), 77 (12)	1.22 (bs, 6H, 2CH$_3$), 2.76 (t, $J = 6.5$ Hz, 2H, CH$_2$), 3.30 (t, $J = 6.5$ Hz, 2H, CH$_2$), 3.41—3.55 (m, 2H, CH$_2$), 4.26 (t, $J = 6.5$ Hz, 2H, CH$_2$), 5.91 (d, $J = 9.6$ Hz, 1H), 6.70—8.01 (m, 15H, ArH)

Continued

Compd	IR (KBr) ν (cm^{-1})	MS m/z (%)	^{1}H NMR
5c	1730, 1508, 1480, 1336, 1274, 1158, 1090, 958	562 (M$^+$, 3), 351 (2), 335 (13), 211 (13), 155 (67), 144 (17), 127 (100), 101 (7), 77 (12)	1.20 (bs, 6H, 2CH$_3$), 2.75 (t, J = 6.5 Hz, 2H, CH$_2$), 3.31—3.47 (m, 4H, 2CH$_2$), 4.25 (t, J = 6.5 Hz, 2H, CH$_2$), 5.92 (d, J = 9.6 Hz, 1H), 6.86—8.44 (m, 15H, ArH)
5d	1732, 1518, 1482, 1336, 1272, 1158, 1090, 956	588 (M$^+$, 8), 335 (29), 307 (32), 237 (48), 181 (100), 158 (97), 130 (17), 99 (28), 55 (23)	1.23 (bs, 6H, 2CH$_3$), 2.74 (t, J = 6.4 Hz, 2H, CH$_2$), 3.25—3.47 (m, 8H, 4CH$_2$), 4.25 (t, J = 6.4 Hz, 2H, CH$_2$), 5.90 (d, J = 9.2 Hz, 1H), 6.69—8.05 (m, 13H, ArH)
5e	1732, 1512, 1482, 1336, 1272, 1168, 1090, 956	588 (M$^+$, 8), 335 (36), 307 (18), 237 (30), 181 (100), 158 (86), 130 (17), 115 (14), 91 (14), 77 (13)	1.15 (s, 3H, CH$_3$), 1.26 (s, 3H, CH$_3$), 2.72 (t, J = 6.6 Hz, 2H, CH$_2$), 3.28 (t, J = 6.6 Hz, 2H, CH$_2$), 3.43—3.52 (m, 2H, CH$_2$), 4.25 (t, J = 6.6 Hz, 2H, CH$_2$), 5.90 (d, J = 10.4 Hz, 1H), 6.66—8.01 (m, 17H, ArH)
5f	1718, 1518, 1478, 1340, 1272, 1164, 1090, 956	600 (M$^+$, 10), 352 (2), 335 (20), 307 (13), 249 (21), 165 (100), 144 (24), 99 (11), 55 (21)	1.16 (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 2.72 (t, J = 6.4 Hz, 2H, CH$_2$), 3.30 (t, J = 6.4 Hz, 2H, CH$_2$), 3.41—3.57 (m, 2H, CH$_2$), 3.93 (s, 2H, CH$_2$), 4.28 (t, J = 6.0 Hz, 2H, CH$_2$), 5.92 (d, J = 9.2 Hz, 1H), 6.87—8.10 (m, 15H, ArH)
5g	1736, 1514, 1480, 1338, 1276, 1162, 1092, 956	612 (M$^+$, 5), 333 (5), 307 (9), 272 (3), 246 (5), 158 (16), 127 (7), 101 (4), 71 (4), 44 (100)	1.22 (bs, 6H, 2CH$_3$), 2.84 (t, J = 6.5 Hz, 2H, CH$_2$), 3.39—3.51 (m, 4H, 2CH$_2$), 4.30 (t, J = 6.5 Hz, 2H, CH$_2$), 5.88 (d, J = 10.4 Hz, 1H), 6.71—8.16 (m, 17H, ArH)
5h	1734, 1512, 1480, 1338, 1276, 1160, 1092, 954	636 (M$^+$, 1), 333 (17), 307 (16), 285 (13), 158 (34), 144 (11), 130 (7), 99 (6), 55 (5)	1.19 (bs, 6H, 2CH$_3$), 2.85 (t, J = 6.5 Hz, 2H, CH$_2$), 3.42—3.54 (m, 4H, 2CH$_2$), 4.29 (t, J = 6.5 Hz, 2H, CH$_2$), 5.92 (d, J = 9.2 Hz, 1H), 6.74—8.87 (m, 17H, ArH)
5i	1732, 1514, 1480, 1336, 1276, 1162, 1092, 956	618 (M$^+$, 3), 351 (6), 333 (33), 307 (23), 267 (35), 158 (100), 130 (19), 99 (14), 77 (7)	1.21 (bs, 6H, 2CH$_3$), 2.76 (t, J = 6.5 Hz, 2H, CH$_2$), 3.30—3.50 (m, 4H, 2CH$_2$), 4.26 (t, J = 6.5 Hz, 2H, CH$_2$), 5.92 (d, J = 9.6 Hz, 1H), 6.70—8.72 (m, 15H, ArH)
5j	1728, 1514, 1480, 1336, 1274, 1166, 1090, 956	518 (M$^+$, 10), 333 (39), 307 (21), 171 (16), 158 (97), 144 (25), 130 (15), 111 (100), 99 (15), 77 (5)	1.15 (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 2.70 (t, J = 6.7 Hz, 2H, CH$_2$), 3.19 (t, J = 6.7 Hz, 2H, CH$_2$), 3.41—3.59 (m, 2H, CH$_2$), 4.18—4.28 (m, 2H, CH$_2$), 5.88 (d, J = 10.2 Hz, 1H), 6.67—8.00 (m, 11H, ArH)
5k	1736, 1514, 1480, 1336, 1274, 1170, 1090, 956	554 (M$^+$, 21), 353 (3), 333 (34), 307 (18), 203 (14), 158 (100), 99 (53), 55 (56)	1.15 (s, 3H, CH$_3$), 1.24 (s, 3H, CH$_3$), 2.03 (s, 3H, CH$_3$), 2.16 (s, 3H, CH$_3$), 2.26 (s, 3H, CH$_3$), 2.65 (t, J = 6.5 Hz, 2H, CH$_2$), 2.96 (t, J = 6.5 Hz, 2H, CH$_2$), 3.43—3.53 (m, 2H, CH$_2$), 4.18—4.26 (m, 2H, CH$_2$), 5.91 (d, J = 9.6 Hz, 1H), 6.61—7.97 (m, 10H, ArH)

References

1   Fischer, E.; Hirshberg, Y. *J. Chem. Soc.* **1952**, 4522.

2   Hirshberg, Y. *J. Am. Chem. Soc.* **1956**, 78, 2304.

3   Berkovic, G.; Krongauz, V.; Weiss, V. *Chem. Rev.* **2000**, 100, 1741.

4　Fissi, A.; Pieroi, O.; Ruggeri, G.; Ciardelli, F. *Macro-molecules* **1995**, *28*, 302.

5　Somerville, L. F.; Allen, C. F. H. *Org. Synth.* **1943**, Coll. *Vol. 2*, 81.

6　Fieser, L. F. *Org. Synth.* **1940**, *20*, 1.

7　Haworth, R, D. *J. Chem. Soc.* **1932**, 1125.

8　Hey, D. H.; Wilkinson, R. *J. Chem. Soc.* **1940**, 1030.

9　Barnett, B.; Goodway, N. F.; Watson, J. W. *Ber.* **1933**, *66*, 1876.

10　Bachmann, W. E.; Bradbury, J. T. *J. Org. Chem.* **1937—1938**, *2*, 175.

11　Fieser, L. F.; Fieser, M. *J. Am. Chem. Soc.* **1935**, *57*, 782.

12　Gilman, H.; Jacoby, A. L. *J. Org. Chem.* **1938**, *3*, 108.

13　Fieser, L. F.; Kenelly, R. G. *J. Am. Chem. Soc.* **1935**, *57*, 1611.

14　Sacconi, L.; Ciampolini, M.; Maggio, F.; Cavasino, F. P. *J. Am. Chem. Soc.* **1962**, *84*, 3246.

15　Liu, R. L.; Wang, D. Q.; Zhao, F. Z.; Deng, F. X.; Yang, H. T. *Chin. J. Org. Chem.* **1987**, *2*, 124.